The Unique Character of Copper

in Photoredox Catalysis

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Für meine Familie

„Die Sonne lehrt alle Lebewesen die Sehnsucht nach dem Licht. Doch es ist die Nacht, die uns alle zu den Sternen erhebt.“

Khalil Gibran

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List of Abbreviations

A	absorbance
Ac	acetyl
AIBN	2,2'-azobis(isobutyronitrile)
anh.	anhydrous
APCI	atmospheric pressure chemical ionization
aq.	aqueous
Ar	aryl
ATRA	atom transfer radical addition
BAM	bis(amidine)
BDMA	*N*-benzyl dimethyl amine
BINAP	2,2'-bis(diphenyl-phosphonio)-1,1'-binapthyl
binc	bis(2-isocyanophenyl)-phenyl phosphonate
BINOL	1,1'-bi-2-naphthol
Bn	benzyl
Boc	*tert*-butyloxycarbonyl
bpy	2,2'-bipyridine
brsm	based on recovered starting material
bs	broad singulet (spectra)
BSA	bis(trimethylsilyl)acetamide
Bu/^{n}Bu	*n*-butyl (unbranched)
^{s}Bu	*sec*-butyl
^{t}Bu	*tert*-butyl
°C	degree celsius
c	concentration; centi (10^{-2})
c	speed of light
CCDC	Cambridge Crystallographic Data Centre
CFL	compact fluorescence lamp
cm	centi (10^{-2}) meter
cod	1,5-cyclooctadiene
conc.	concentrated
*m*CPBA	*meta*-chloroperoxybenzoic acid
crm	complex reaction mixture
4-CzIPN	1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene
d	doublet (spectra); day(s)
ΔT	heat (thermal activation)
δ	chemical shift
dap	2,9-bis(*para*-anisyl)-1,10-phenanthroline
dba	dibenzylideneacetone
DBU	1,8-diazabicyclo-[5.4.0]undec-7-ene
DCC	dicyclohexylcarbodiimide
DCM	dichloromethane
DE	diethyl ether
dF(CF_3)ppy	2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine
DIPEA	*N*,*N*-diisopropylethylamine
dipp	2,6-diisopropylphenyl
DMA	*N*,*N*-dimethylacetamide
DMAP	4-dimethylaminopyridine
DMC	dimethyl carbonate
DMF	*N*,*N*-dimethylformamide
dmp	2,9-dimethyl-1,10-phenanthroline
DMSO	dimethyl sulfoxide
DNs	di-nosyl (2,4-dinitro benzenesulfonyl)
dpa	dipyridylamine
dpp	2,9-diphenyl-1,10-phenanthroline
dq	2,2'-biquinoline
d.r.	diastereomeric ratio
dtbbpy	4,4'-di-*tert*-butyl-2,2'-bipyridine

$E/E_{1/2}/E_{red}$	standard reduction potential
ε	extinction coefficient
EDG	electron-donating group
e.g.	exempli gratia (*Latin*: for example)
EI	electron ionization
EPR	electron paramagnetic resonance
equiv	equivalents
ESI	electrospray ionization
Et	ethyl
et al.	et alia (*Latin*: and others)
EtOAc	ethyl acetate
EWG	electron-withdrawing group
f	correction factor
fac	facial
fs	femto (10^{-15}) seconds
FTIR	Fourier-transform infrared spectroscopy
G	gauss
g	gram
gem	geminal
glyme	1,2-dimethoxyethane
GP	general procedure
h	hour(s)
h	Planck constant
HAT	hydrogen atom transfer
HE	Hantzsch ester
hept	heptet (spectra)
HetAr	hetero aryl
^{n}Hex	*n*-hexyl (unbranched)
HMDS	1,1,1,3,3,3-hexamethyl disilazane
HPLC	high pressure liquid chromatography
HRMS	high resolution mass spectroscopy
Hz	Hertz
I_{max}	maximal current
IR	infrared
ISC	intersystem crossing
J	coupling constant
Js	Joule-second
K	Kelvin
kcal	kilo (10^{3}) calorie
L	ligand; Liter
λ	wavelength
λ_{ex}	excitation wavelength
$\lambda_{dom}/\lambda_{max}$	dominating wavelength/ wavelength of maxima
λ_{vis}	wavelength of visible light
LDA	lithium diisopropylamide
LED	light emitting diode
LMCT	ligand-to-metal charge transfer
lum	lumen
M	molar; mega (10^{6}); metal
m	meter; milli (10^{-3}); multiplet (spectra)
m	*meta*
mA	milli (10^{-3}) ampere
Me	methyl
MeCN	acetonitrile
MeOH	methanol
mg	milli (10^{-3}) gram
MHz	mega (10^{6}) hertz
min	minute(s)
µJ	micro (10^{-6}) joule
mL	milli (10^{-3}) liter
µL	micro (10^{-6}) liter
MLCT	metal-to-ligand charge transfer
mm	milli (10^{-3}) meter
mM	milli (10^{-3}) molar
mmol	milli (10^{-3}) mole

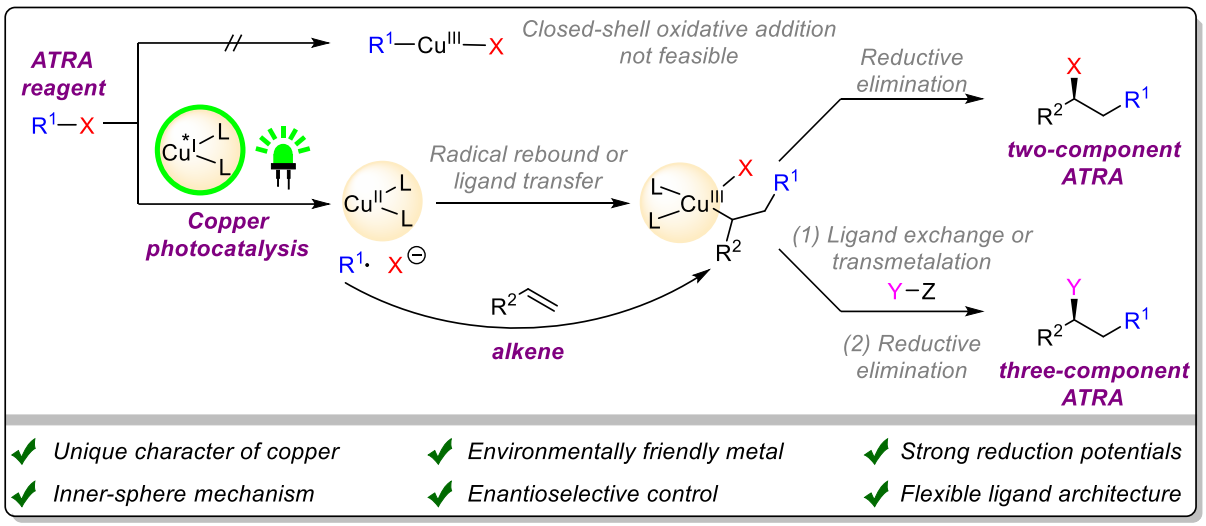
µmol	micro (10^{-6}) mole
mOD	optical density in 10^{-3}
mol	mole
mol%	mole percent
mp	melting point
µs	micro (10^{-6}) seconds
mW	milli (10^{-3}) Watt
m/z	mass-to-charge ratio
N_A	Avogadro constant
$N_{ph,abs}$	number of absorbed photons
$N_{product}$	number of created molecules
$n_{product}$	molar amount of product
ν	frequency
NFSI	*N*-fluorobenzenesulfonimide
NIS	*N*-iodosuccinimide
nm	nano (10^{-9}) meter
NMR	nuclear magnetic resonance
nr	no reaction
Ns	nosyl (= 4-nitrobenzene sulfonyl)
ns	nano (10^{-9}) seconds
Nu	nucleophile
o	*ortho*
OD	optical density
p	pentet (spectra)
p	*para*
P_{abs}	absorbed radiant power
P_{ref}	radiant power of reference
P_{sample}	radiant power of sample
PBN	*C*-phenyl-*N*-*tert*-butylnitrone
PC	photocatalyst
PG	protecting group
Ph	phenyl
pH	power of hydrogen
phen	phenanthroline
phth	phthalimide
pin	pinacolato
ppm	parts per million
ppy	2-phenylpyridine
^{i}Pr	*iso*-propyl
ps	pico (10^{-12}) seconds
PTH	10-phenylphenothiazine
q	quartet (spectra)
Φ	quantum yield
Q-TOF	quadrupole time-of-flight
R	arbitrary rest; reflection coefficient
R_f	perfluorinated carbon chain
R_f	retardation factor
rac	racemic
redox	reduction-oxidation
ref.	reference
rt	room temperature (25 °C)
RuPhos	2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl
s	second(s); singulet (spectra)
sat.	saturated
SCE	standard calomel electrode
SET	single electron transfer
sex	sextet (spectra)
SPhos	2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl
T	temperature
t	time; triplet (spectra)
$\tau_{excited\ state}$	excited state lifetime
TBAB	tetra-*n*-butylammonium bromide
TBAF	tetra-*n*-butylammonium fluoride
TBS	*tert*-butyldimethylsilyl

TD-DFT	time-dependent density functional theory
TEMPO	(2,2,6,6-tetramethyl-piperidin-1-yl)oxyl
Tf	triflyl (= trifluoromethane-sulfonyl)
THF	tetrahydrofuran
TLC	thin layer chromatography
tmp	3,4,7,8-tetramethyl-1,10-phenanthroline
TMS	trimethylsilyl
Tol	*para*-tolyl
TPMA	tris(2-pyridylmethyl)amine
TREN	tris(2-aminoethyl)amine
Ts	tosyl (= toluenesulfonyl)
UV	ultraviolet
vis	visible light
UFTA	ultrafast transient absorption spectroscopy
V	Volt
V-70	2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)
VLIH	visible-light-induced homolysis
vs.	versus (*Latin*: against)
W	Watt
wt%	weight percent
X	arbitrary halogen
Xantphos	4,5-bis(diphenylphosphino) 9,9-dimethylxanthene
XRD	X-ray diffraction
	relative stereochemistry
	absolute stereochemistry

Chapter 1

Introduction – The Unique Character of Copper in Photo-ATRA Reactions

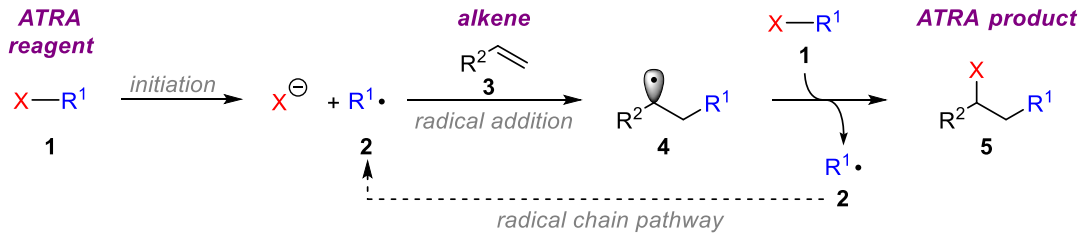
1.1 Abstract



Atom Transfer Radical Addition (ATRA) reactions are linchpin transformations in synthetic chemistry enabling the atom-economic difunctionalization of alkenes. Thereby a rich chemical space can be accessed through clever combinations of simple starting materials. However, usually these reactions required toxic and hazardous radical initiators or harsh thermal activation and thus, the recent resurgence and dramatic evolution of photocatalysis appeared as an appealing complement to catalyze such transformations in a mild and energy-efficient manner. Initially this technique relied primarily on complexes of precious metals, such as ruthenium or iridium to absorb the visible light. Hence, copper photocatalysis rapidly developed into a powerful alternative, not just from an economic point of view. Copper complexes excel through their flexible ligand architecture and multiple accessible oxidation states, empowering them to capture incipient radicals in their inner-coordination sphere, thus stabilizing and controlling reaction intermediates. This unique character of copper offers the possibility to access heretofore elusive two-component, but also three-component ATRA reactions even under enantioselective control, not feasible with ruthenium or iridium catalysts. In this regard, the idea of using Cu(I)-substrates assemblies as active photocatalysts is an upcoming field reflected by an increasing number of reports, which will be also covered in this review.

1.2 History and Recent Resurgence of ATRA Reactions

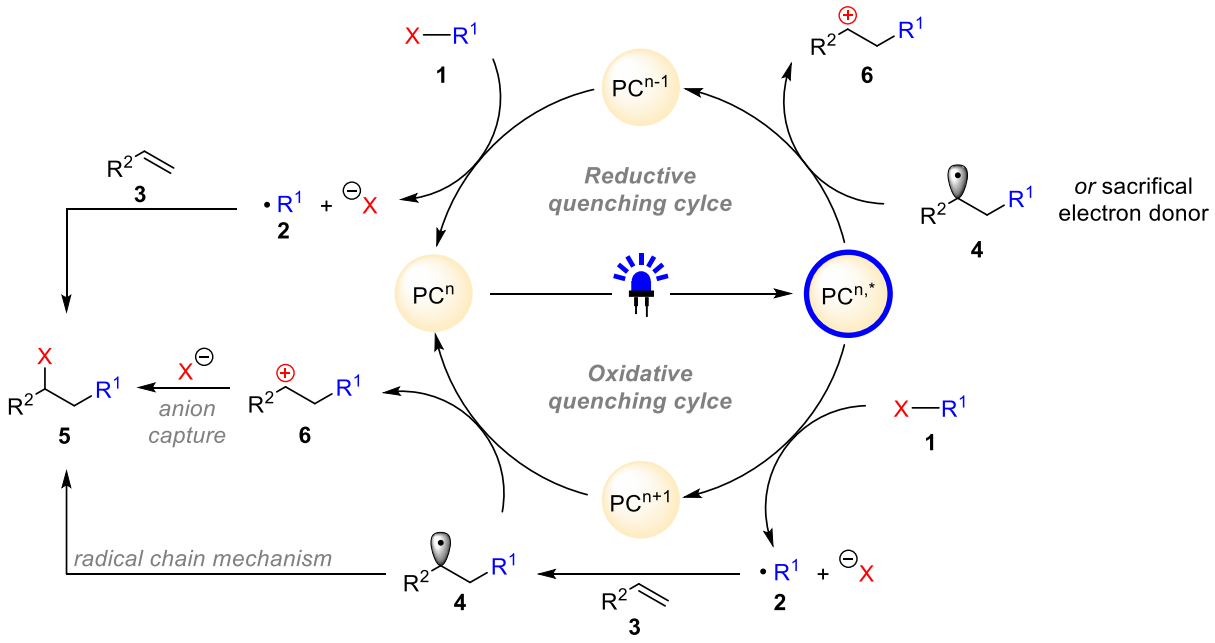
The mono- and difunctionalization of olefins is a critical paradigm in organic chemistry, whose pervasiveness has encouraged a revitalized interest in synthetic methodologies involving clever strategies to rapidly build up molecular complexity through straightforward operations. As olefins display one of the most fundamental functional groups in organic chemistry – being often derived from simple chemical feedstock – their difunctionalization emerged as a powerful procedure to access a rich chemical space through clever combinations of simple starting materials. Pioneered by Kharasch[1] in the mid-1900s, Atom Transfer Radical Addition (ATRA) reactions onto alkenes has had a tremendous impact on these fields and hence, have found wide applications in industry and academic research laboratories. ATRA reactions are linchpin transformations outstanding through their perfect atom- as well as step-economic manner to incorporate two functional groups into unsaturated C-C bonds in a single operation. Formally, ATRA is the transposition of a pre-existing σ-bond of an ATRA reagent **1** across a π-bond of an alkene **3** (or alkyne), via free radical intermediates simultaneously constructing two new σ-bonds, a C-X and a C-C bond (Scheme 1).



Scheme 1. General pathway for free radical initiated ATRA reactions.

However, ATRA reactions initially required the use of stochiometric quantities of harmful oxidants,[1] organotin reagents,[2] or organoboron reagents[3] as radical initiators and were limited to substrates that are not prone to subsequently undergo radical polymerization reactions. Later, it was found that transition metal complexes are capable to act as halogen atom transfer reagents to efficiently catalyze such ATRA-type processes within a reversible redox pathway.[4] However, these protocols still relied on either harsh thermal reaction conditions and/or toxic reagents. In this context, the recent resurgence and dramatic evolution of visible-light mediated photoredox catalysis has mandated a paradigm shift in radical chemistry by enabling a broad range of carbon-carbon and carbon-heteroatom bond formations under ecologically benign reaction conditions in an energy-efficient manner.[5] Thus, it was a nature of choice that photoredox catalysis successfully conquered the area of ATRA reactions obviating the aforementioned

shortcomings. Following seminal work by Barton[6] and Stephenson,[7] the most commonly employed photoredox catalysts for ATRA processes are displayed by ruthenium(II)- or iridium(III)-polypyridyl complexes owing to their high photostability, long-lived excited state lifetimes and favorable photoredox potentials.[8] In principle, this class of photoredox catalysts involve the activation of the ATRA reagent **1** by single-electron transfer (SET) either through a reductive or oxidative quenching cycle of the excited catalyst (Scheme 2). The so-formed radical **2** may now add to the alkene **3** generating the key radical intermediate **4**, which subsequently gets oxidized by the catalyst to the corresponding carbocation **6**. The latter is then captured by the generated anion to deliver the desired product **5** in an outer-sphere process.[8] Although the class of ruthenium(II)- and iridium(III)-based photocatalysts enjoyed signal success over the last years, the high costs and adverse environmental impact of these compounds call for more economic and green alternatives.

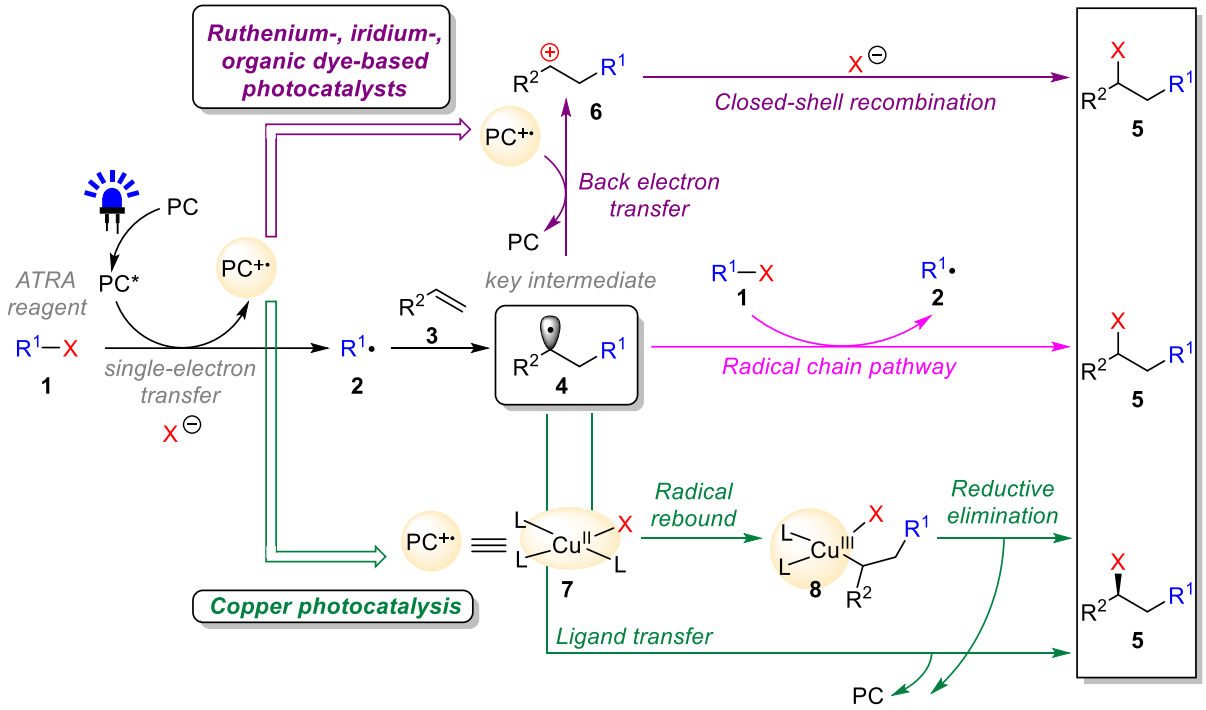


Scheme 2. Typical mechanistic picture for photo-ATRA reactions promoted by ruthenium(II)- or iridium(III)-based photocatalysts.

1.3 Spotlight on Copper – The Basics of Its Success in Photo-ATRA Reactions

Copper(I) photoredox catalysis gained tremendous impact in this field and emerged as an appealing complement.[9] Besides the economic benefits, copper photocatalysts excel through their flexible ligand architecture and multiple accessible oxidation states, empowering them to rapidly capture incipient radicals or anionic species in a rebound process, stabilizing and

controlling reaction intermediates. In this regard, copper photocatalysts most likely undergo different mechanistic pathways in such ATRA processes and as such offer the unique possibility to access heretofore elusive reaction pathways, not feasible via anouter-sphere mechanism typically promoted by ruthenium(II)- or iridium(III)-based photocatalysts (Scheme 3).

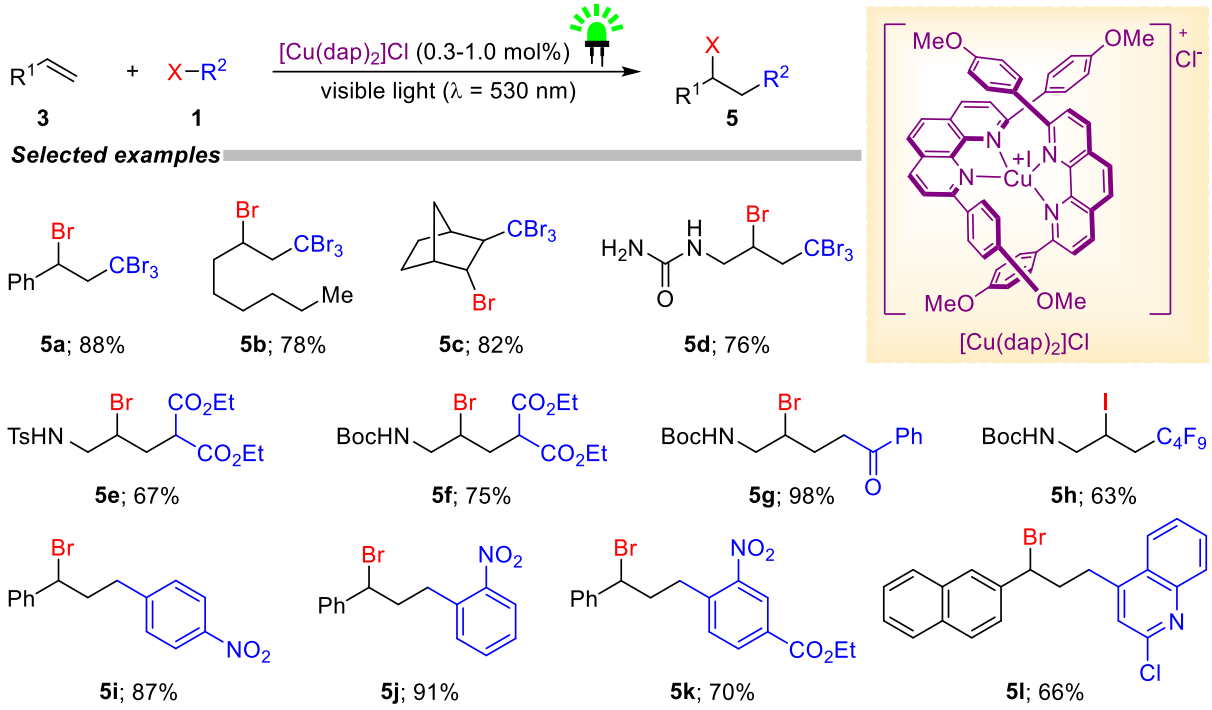


Scheme 3. Unique character of copper catalysts in photo-ATRA reactions.

As already discussed before, the ATRA reagent **1** is activated by single-electron transfer from the excited photocatalyst to deliver the corresponding radical **2**, which immediately adds to an alkene **3** generating the key radical intermediate **4**. Ruthenium(II)- or iridium(III)-catalyzed photoredox ATRA reactions now rely on a back-electron transfer from **4** to the previously oxidized catalyst $PC^{+\bullet}$ to yield carbocation **6** closing the catalytic cycle. The final ATRA product **5** is then formed upon closed-shell recombination of carbocation **6** with the corresponding anion X^-, previously generated from the ATRA reagent **1**. In contrast, the oxidized form of the catalyst in the case of copper(I) photocatalysis represents a copper(II) complex like **7**. The later can undergo a ligand transfer cycle with **4** to yield the desired ATRA product **5** and revert to the initial catalyst. Alternatively, the intermediary radical **4** can rebind to the copper(II)-species **7**, being in fact a persistent radical itself, to generate the copper(III)-intermediate **8**. The final product **5** is then released upon reductive elimination, recreating the initial catalyst and closing the rebound cycle. The fact, that the final coupling to the product takes place in the inner-coordination sphere of the catalyst offers the unique opportunity to create stereoselective control in product formation through an asymmetric ligand environment.

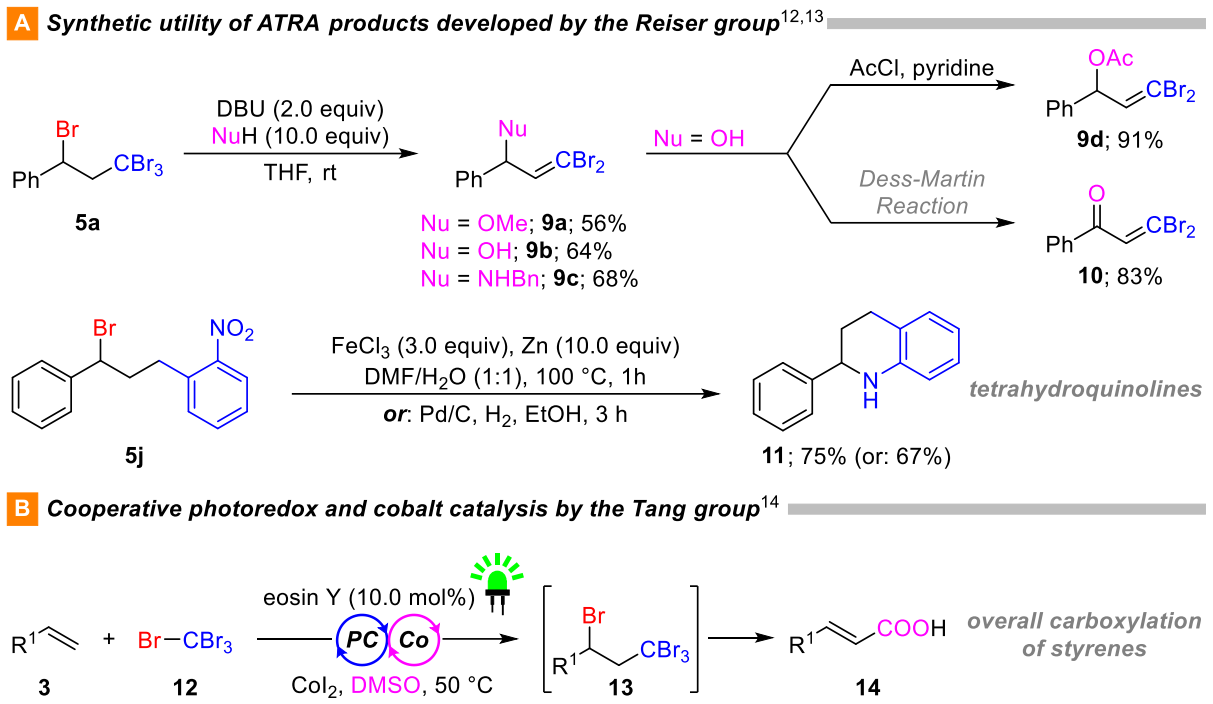
1.4 Throwback: Copper Sees the Light of Day in Photo-ATRA Reactions

In 1977, McMillin and co-workers for the first time demonstrated the complex $[Cu(dmp)_2]BF_4$ as a capable photocatalyst being able to reduce Co(III) in K[*cis*-Co(iminodiacetato)$_2$]·1.5 H_2O to the corresponding Co(II) species after excitation at 454 nm.[10] Ten years later, in 1987, Sauvage pioneered the complex $[Cu(dap)_2]Cl$ as active photocatalyst to promote reductive coupling of nitrobenzyl bromide to the corresponding bibenzylic product under irradiation at 350 nm.[11] The additional ligand architecture of the dap ligand effectively rigidified the coordination geometry and thus perceptible extended the excited state lifetime. Pioneered by this work, it took several decades till this complex stepped out of hibernation and was demonstrated for the first time in 2012, and in following studies in 2013, to sufficiently trigger visible-light mediated ATRA reactions (Scheme 4).[12,13]



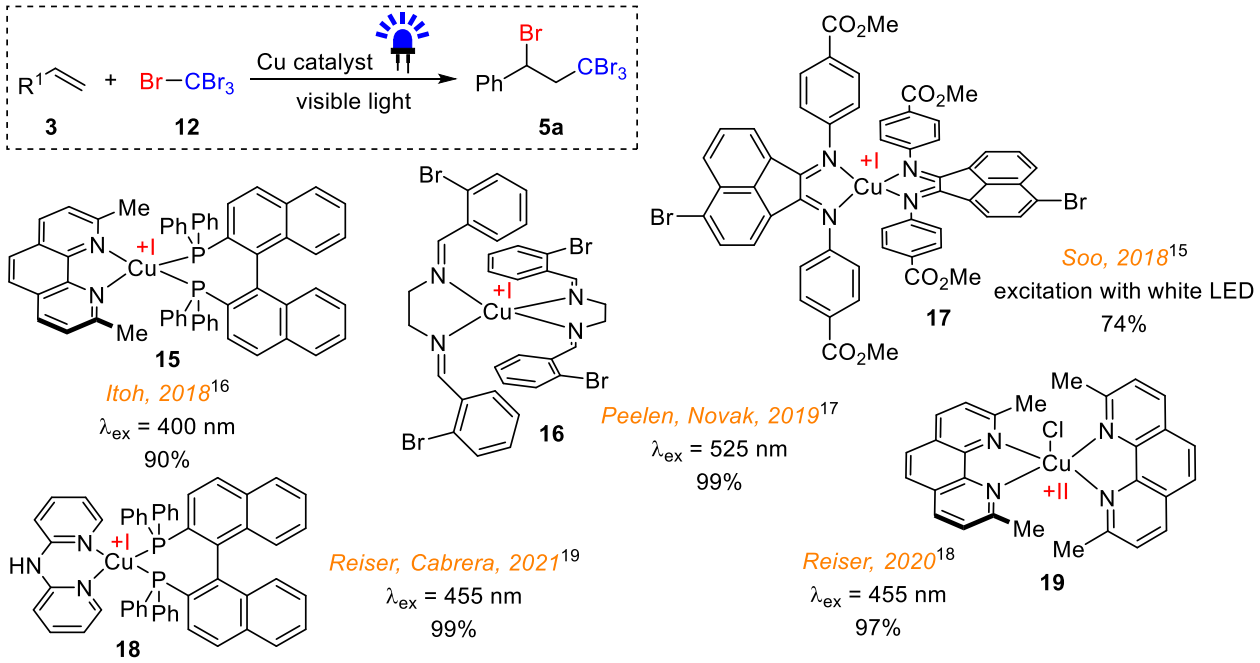
Scheme 4. First examples of visible-light mediated $[Cu(dap)_2]Cl$-catalyzed ATRA reactions between organohalides **1** and alkenes **3**.[12,13]

The synthetic utility of such highly brominated products **5** was demonstrated on the one hand by the Reiser group (Scheme 5, A),[12,13] but also impressively highlighted in a study by Chen and Tang et al. in 2017, who successfully applied these class of compounds in an overall carboxylation of styrenes using cooperative photoredox and cobalt catalysis (Scheme 5, B).[14]



Scheme 5. Synthetic utility of CBr_4-ATRA product **5a**/**13** and ATRA product **5j**.

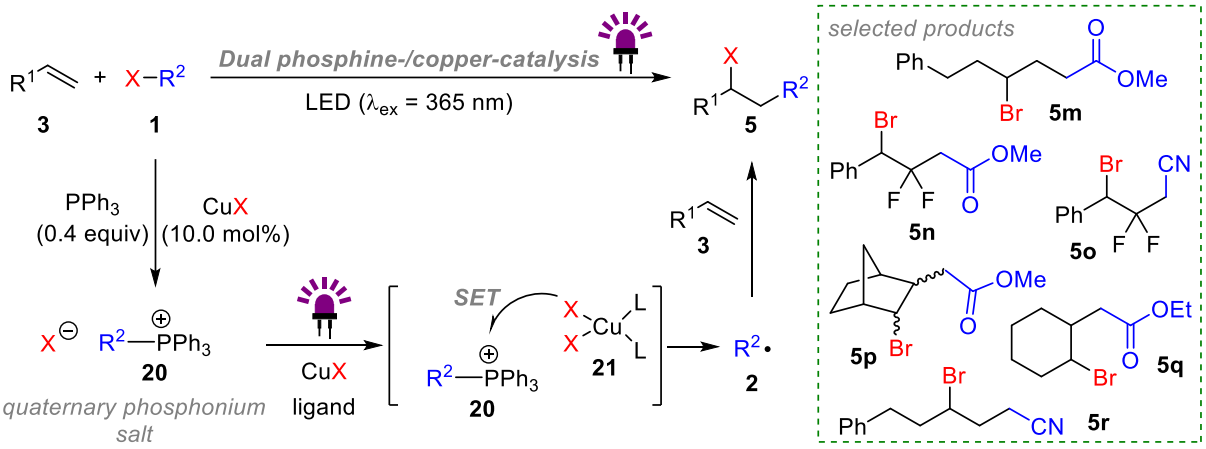
Based on these reports, a whole series of publications started to further explore different copper photocatalysts accessing this class of ATRA products under environmentally friendly and energy-efficient manners (Scheme 6).



Scheme 6. Selected copper catalysts promoting ATRA reactions with CBr_4 (**12**).

In 2019 Dilman and co-workers impressively demonstrated the use of triphenylphosphine in such ATRA reactions, which can effectively activate the ATRA reagent **1** through the formation

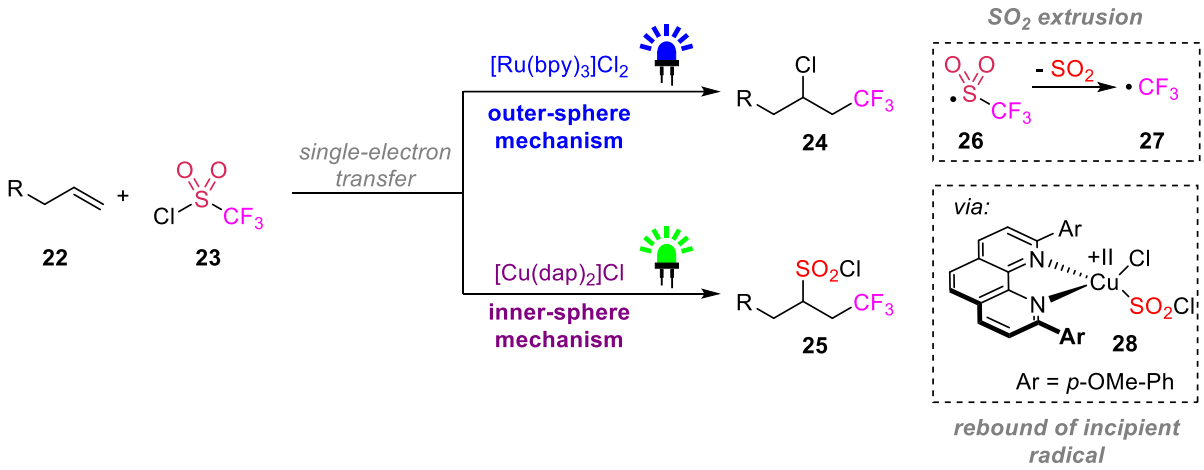
of a quaternary phosphonium salt **20** being much easier to reduce by the copper catalyst **21** compared to the unactivated reagent **1**. This concept allowed the successful activation of esters of bromo- and iodoacetic acids and subsequent addition to *gem*-difluorinated styrenes, for which ATRA reactions are usually challenging and rare processes (Scheme 7).[20]



Scheme 7. Light-mediated dual phosphine-/copper-catalyzed ATRA reactions developed by Dilman and co-workers.[20]

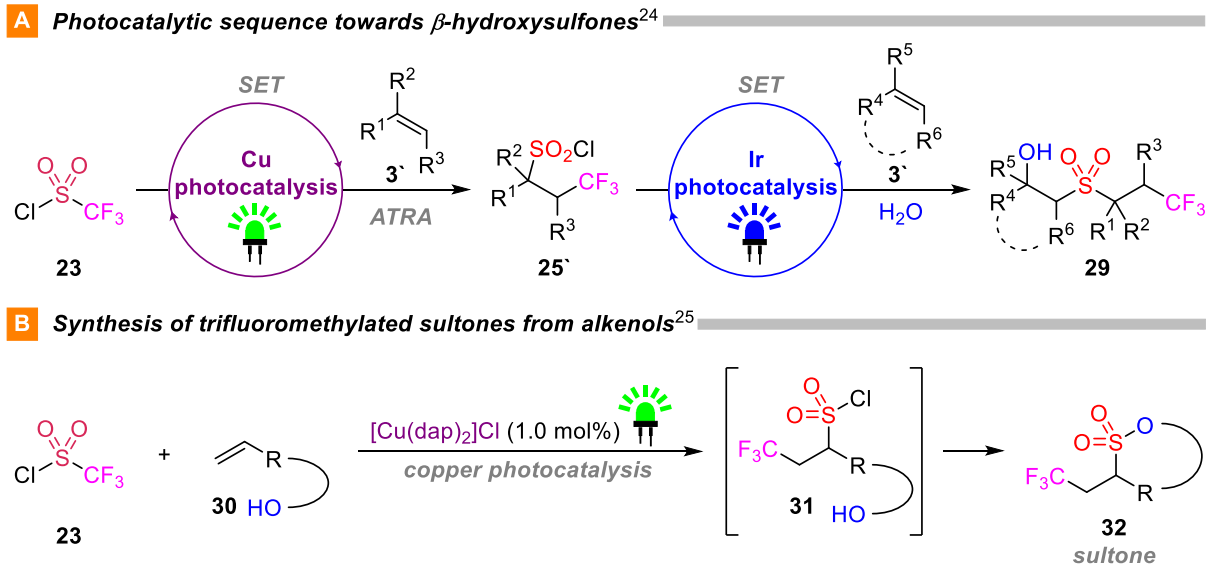
1.5 Copper Makes the Difference – First Evidence for Its Unique Character

While in aforementioned ATRA reactions the copper photocatalyst only serve as a photo-reductant, thus representing an economic alternative to ruthenium(II)- or iridium(III)-based complexes, the first example pointing towards the unique feature of copper photocatalysts in such transformations was demonstrated in 2015 with the development of a vicinal chlorotrifluoromethylation/chlorosulfonylation of unactivated olefins **22** (Scheme 8).[21]



Scheme 8. Photocatalyzed chlorotrifluoromethylation and trifluoromethylchlorosulfonylation of unactivated alkenes **22**. $[Ru(bpy)_3]Cl_2$ catalysis: Han et al.;[22] $[Cu(dap)_2]Cl$ catalysis: Reiser et al.[21]

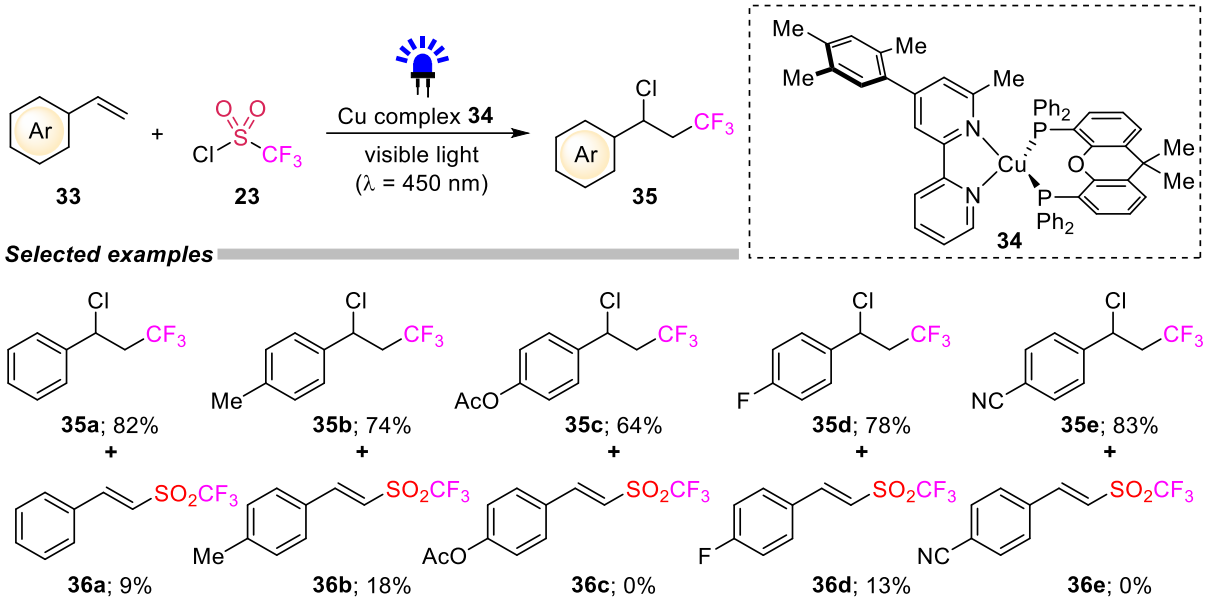
When electron-neutral unactivated olefins **22** were subjected to triflyl chloride (**23**) in the presence of $[Cu(dap)_2]Cl$ as the photocatalysts, the corresponding trifluoromethyl-chlorosulfonylated products **25** were observed in high yields, contrasting the reaction promoted by $[Ru(bpy)_3]Cl_2$ as photocatalyst, which exclusively gave rise to chlorotrifluoromethylated products **24**. The unique reaction pathway of $[Cu(dap)_2]Cl$ was attributed to an inner-sphere capture of the chlorosulfonyl anion by copper (see species **28**), which is generated upon single-electron reduction from triflyl chloride (**23**). At the same time, Tang and Dolbier demonstrated that fluorinated sulfonyl chlorides also undergo SO_2 extrusion and hence deliver the corresponding chlorotrifluoromethylated products **24**, when electron deficient alkenes are used as coupling partners.[23] One year later, the exclusive formation of the chlorosulfonylated products **25`** by copper photocatalysis could be further explored in the rapid synthesis of *β*-hydroxysulfones **29** in a photocatalytic sequence (Scheme 9, A)[24] or in the construction of trifluoromethylated sultones **32** starting from alkenols **30** (Scheme 9, B).[25]



Scheme 9. (A) Photocatalytic sequence towards *β*-hydroxysulfones **29**.[24] (B) Synthesis of trifluoromethylated sultones **32** from alkenols **30** using copper photocatalysis.[25]

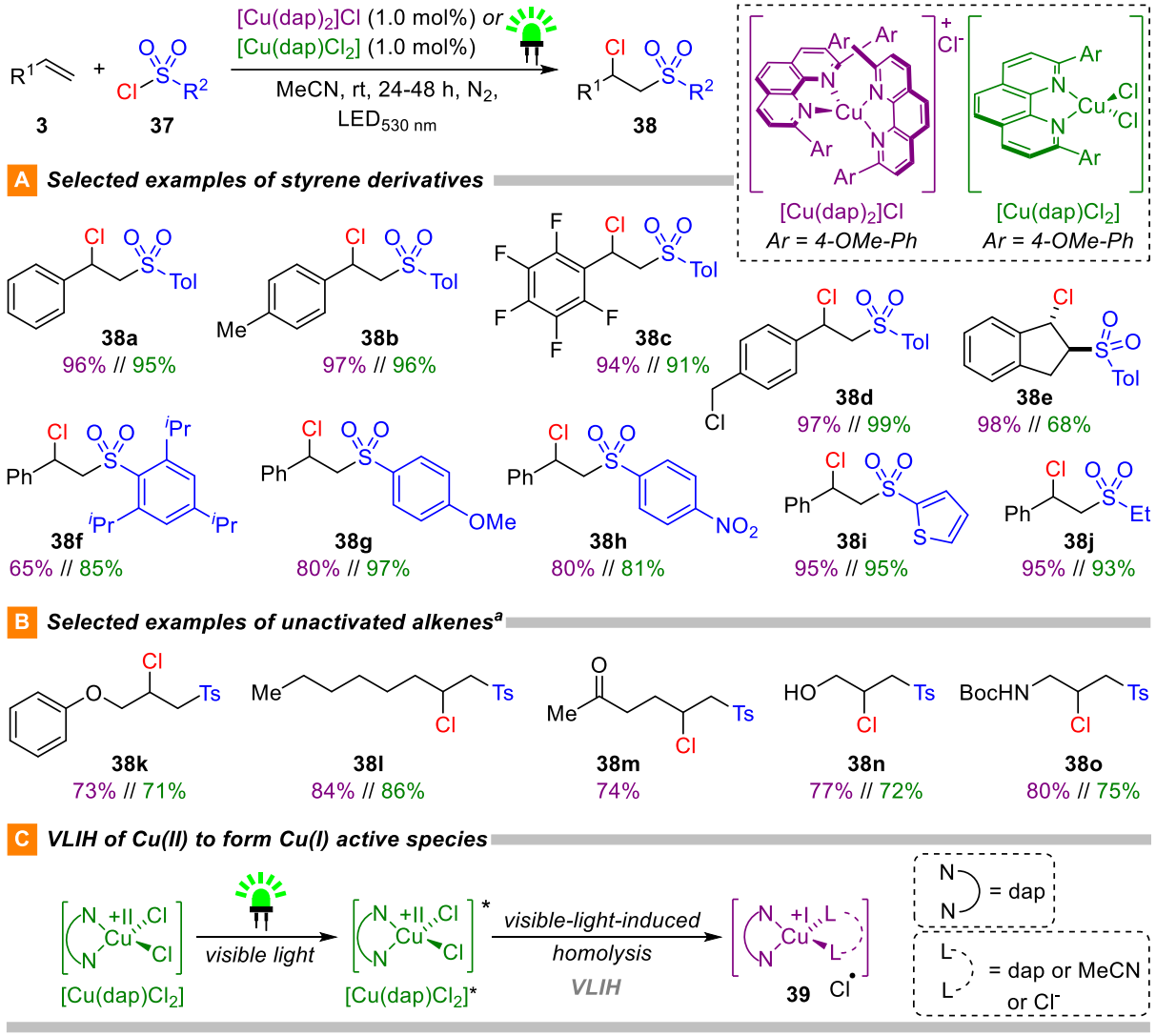
A limitation in these protocols seemed to be found in the use of styrene derivatives as coupling partners for the copper-catalyzed ATRA reaction with triflyl chloride (**23**), except *p*-nitrostyrene, which selectively underwent chlorotrifluoromethylation. Nevertheless, in 2018 Hu and co-workers reported the heteroleptic copper complex **34** as an efficient photocatalyst for broadly applicable chlorotrifluoromethylation of styrene derivatives **33** (Scheme 10).[26] As a by-product small amounts of chlorotrifluorosulfonylation with subsequent HCl elimination **36** is observed. The complex **34**, which is based a new 4,6-disubstituted 2,2'-bipyridine ligand,

excels through longer excited state lifetimes ($\tau_{excited\ state}$ = 720 ns) and more positive Cu(I)/Cu(II) redox couples compared to [Cu(dap)$_2$]Cl.



Scheme 10. Copper photoredox catalyst supported by a 4,6-disubstituted 2,2'-bipyridine ligand and its application in chlorotrifluoromethylation of styrenes **33** developed by Hu and co-workers.[26]

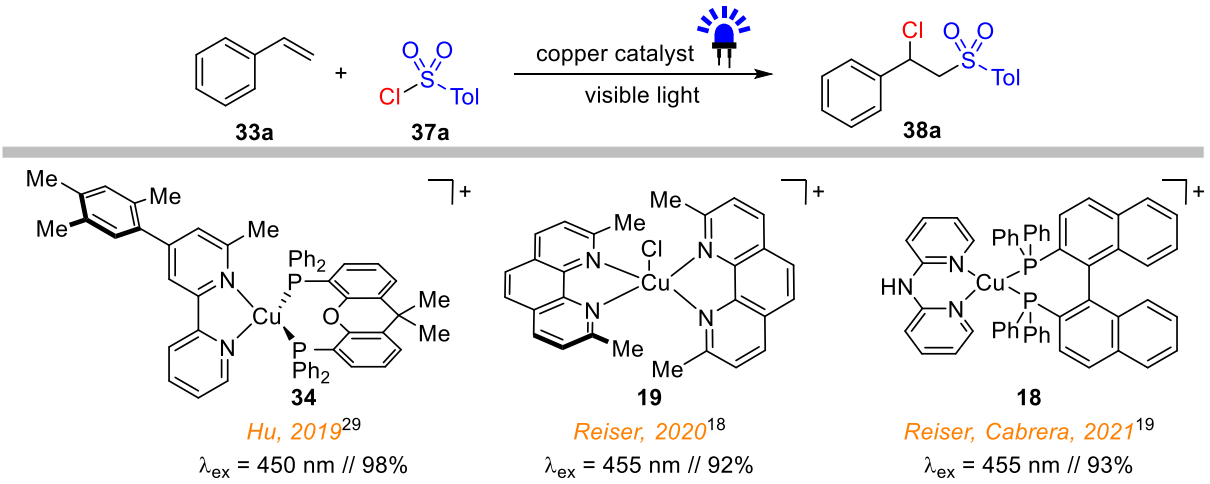
Based on this studies, the Reiser group questioned in 2019 the use of other sulfonyl chlorides **37** as ATRA reagents in copper photoredox catalysis (see ***Chapter 2*** of this work).[27] Indeed, [Cu(dap)$_2$]Cl proved to be a highly effective catalyst to convert a large number of olefins **3** together with electronically and structurally variegated sulfonyl chlorides **37** into their desired chlorosulfonylated products **38** (Scheme 11). Besides the aforementioned Cu(I)-complex, the corresponding Cu(II) complex [Cu(dap)Cl$_2$] appeared to be often even more efficient in the title transformation, being advantageous from an economic point of view but also opening up new avenues for photoredox catalysis. The activation of the latter most likely proceeds through visible-light induced homolysis (VLIH)[28] (Scheme 11, C): After photo-excitation of [Cu(dap)Cl$_2$] homolytic cleavage of the Cu(II)-chloride bond leads to in-situ formation of the catalytically active Cu(I)-complex **39** along with catalytical amounts of chlorine radicals. Both copper catalysts presented in this study clearly outperformed commonly used ruthenium(II)- or iridium(III)-photocatalysts owing to their ability to interact with incipient radicals in their inner-coordination sphere. Besides styrene derivatives as coupling partners, the use of stochiometric amounts of Na_2CO_3 in combination with the copper catalyst was found to be essential to transform unactivated olefins to the corresponding products, which is attributed to the prevention of catalyst poisoning through traces of HCl being formed during the reaction once the sulfonyl radical is not being rapidly trapped by the alkene (Scheme 11, B).



Scheme 11. Visible-light mediated chlorosulfonylation of alkenes catalyzed either by $[Cu(dap)_2]Cl$ or $[Cu(dap)Cl_2]$. [a]2.0 equiv of alkene **3** and 1.0 equiv of Na_2CO_3 as an additive.[27]

Subsequently, the chlorosulfonylation reaction developed into a popular model reaction to probe the catalytic efficiency of various copper complexes (Scheme 12). Hu and co-workers reported their copper complex **34** supported by a 4,6-disubstituted 2,2'-bipyridine ligand to be also a suitable choice in the visible-light mediated chlorosulfonylation of activated alkenes.[29] In 2020, the Cu(II)-complex $[Cu(dmp)_2Cl]Cl$ (**19**) being readily prepared from commercially available and low-cost $CuCl_2$ and two equivalents dmp, was demonstrated as an economic alternative in copper photocatalysis not just for the chlorosulfonylation but also for many other ATRA-type processes, decarboxylative couplings and Appel reactions (see ***Chapter 3*** of this work).[18] Recently, Reiser and Cabrera evaluated a series of heteroleptic copper complexes based on dipyridylamine (dpa) and various phosphine ligands in photoredox catalysis. Thereby, $[Cu(dpa)(S\text{-BINAP})]BF_4$ (**18**) revealed to be the most active complex in several photocatalytic

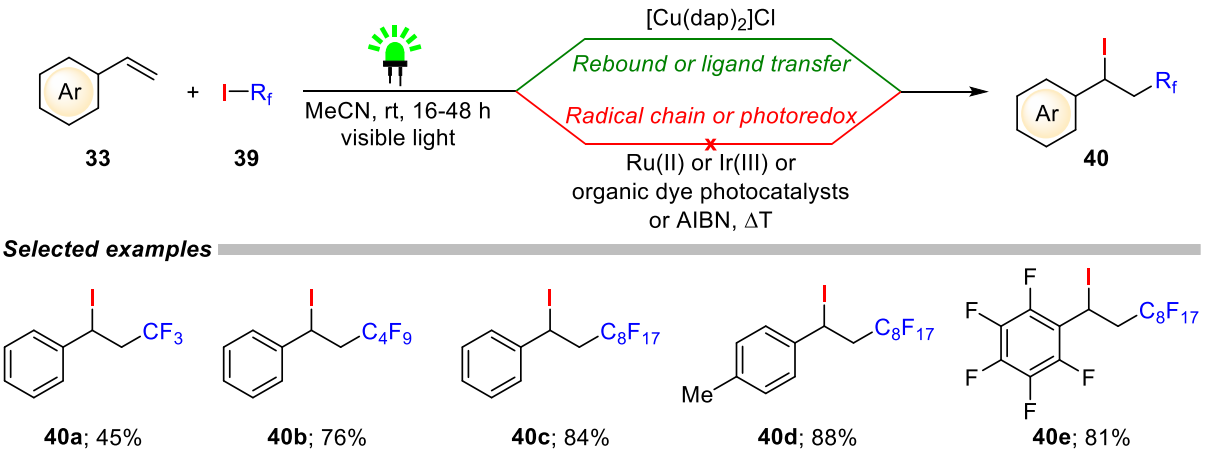
test reactions providing a high excited state reduction potential (E_{red} = -1.39 V vs. SCE) and sufficient excited state lifetime ($\tau_{excited\ state}$ = 20.8 µs).[19]



Scheme 12. Visible-light mediated chlorosulfonylation of styrene (**33a**) as a prominent model reaction for copper photocatalysis.

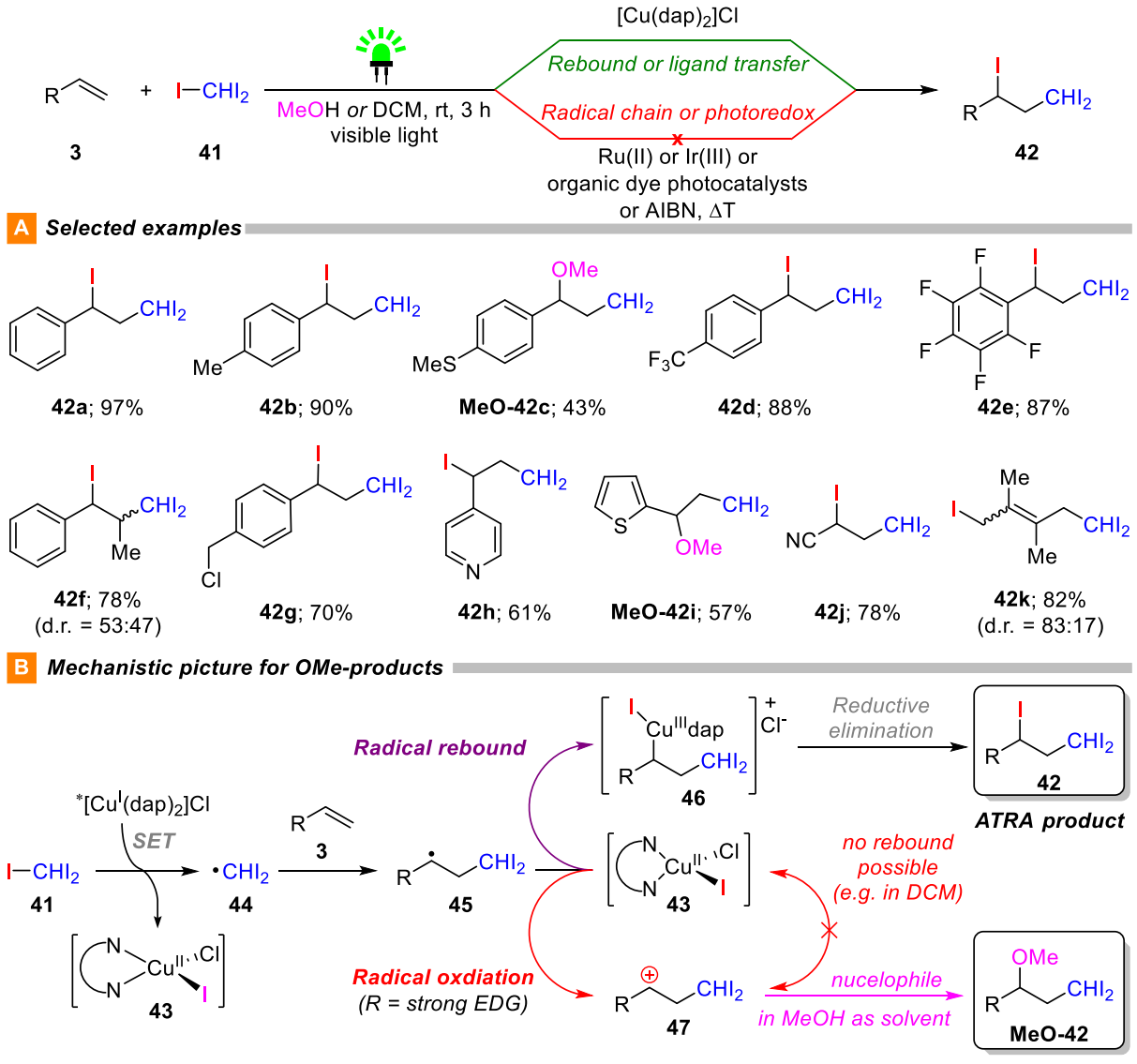
1.6 More Two-Component Copper Photo-ATRA Reactions

Another interesting difunctionalization of alkenes, showcasing the additional role of copper catalysts beyond photoinduced electron transfer, is represented by the iodoperfluoroalkylation reaction being known for many years. While a variety of protocols are reported for the iodoperfluoroalkylation of unactivated alkenes including ruthenium-, eosin Y-, other metal-free based photoredox strategies, or also thermal approaches, the conversion of styrene derivatives **33** still emerged as a major limitation. Thus, it was a nature of choice applying copper photocatalysis to this kind of transformation. Indeed, $[Cu(dap)_2]Cl$ revealed to be capable to convert miscellaneous styrene derivatives **33** to the desired perfluoroalkyl tagged ethylbenzenes **40** in high yields (Scheme 13).[30]



Scheme 13. Visible-light mediated copper-catalyzed iodoperfluoroalkylation of styrenes **33**.[30]

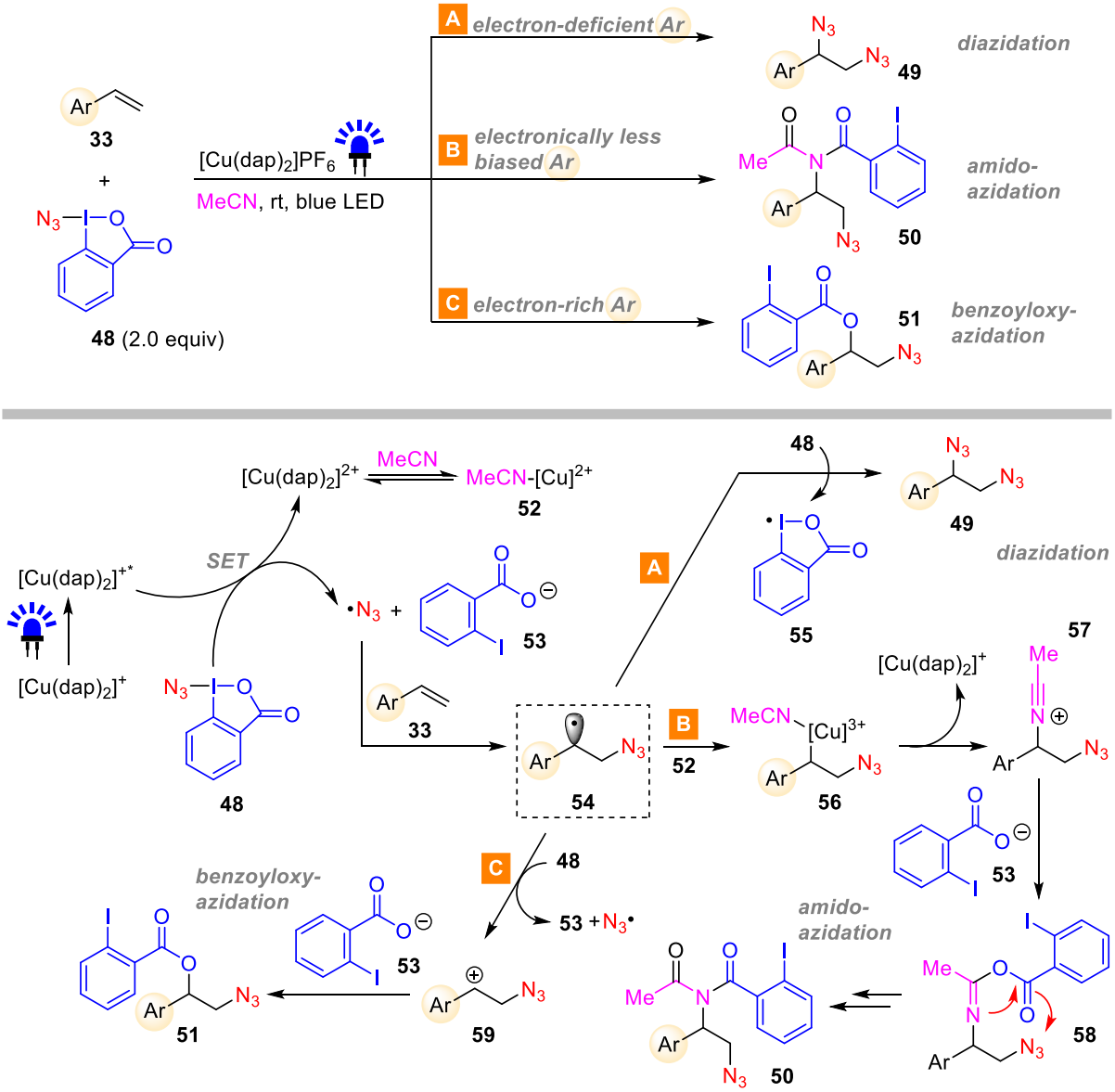
Along the same lines of reasoning, the ATRA reaction of iodoform (**41**) – representing long time an elusive transformation – revealed to be accessible by copper photocatalysis. While seminal attempts back in the 1940s failed initiating the desired process under thermal activation or UV-light irradiation, employment of milder reaction conditions with several ruthenium(II)-, iridium(III)- or organic dye-based photocatalysts under visible-light excitation proved to be incompatible in the same way. However, irradiating iodoform (**41**) together with activated alkenes **3** in the presence of [Cu(dap)$_2$]Cl with visible light (green LED) gave rise to the desired ATRA products **42** in good to excellent yields (see ***Chapter 4*** of this work) (Scheme 14, A).[31]



Scheme 14. Visible-light mediated copper-catalyzed ATRA reactions with iodoform (**41**).[31]

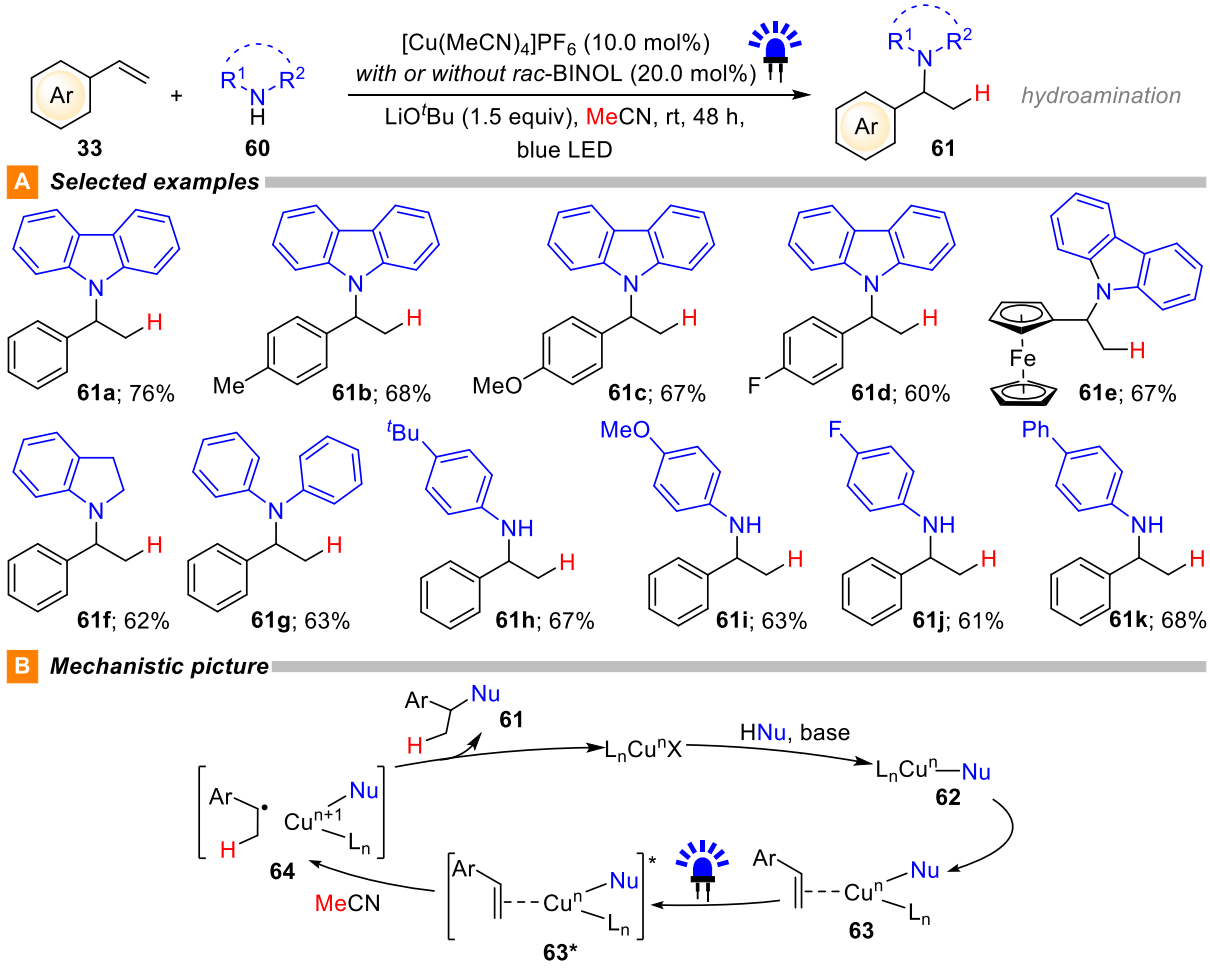
Interestingly, the electronic nature of the alkene **3** greatly influences the mechanistic pathway and thus the resulting product formation (Scheme 14, B). After photoexcitation of the catalyst and subsequent reduction of iodoform (**41**), the corresponding carbon-centered radical **44** adds

to the alkene **3** forming the benzylic radical **45** as the key intermediate. For most of the substrates the latter likely binds back to the Cu(II)-species **43** leading to Cu(III)-species **46**, which will release the desired iodinated product **42** upon reductive elimination. In contrast, when the carbon-centered radical **44** adds to highly electron-rich alkenes **3**, fast oxidation of the resulting benzylic radical **45** to the corresponding benzylic carbocation **47** might be favored. The latter is not able to couple with iodide[31] and also no longer able to rebind to the Cu(II)-intermediate **43**, but instead is stable enough to be nucleophilic attacked by the solvent, thus forming the observed MeOH-substituted products **MeO-42**. Similar observations were made by Yu and co-workers in their visible-light driven copper-catalyzed azidation of vinyl arenes **33** with azidobenziodoxole (**48**) as the azidation agent (Scheme 15).[32]



Scheme 15. Visible-light mediated copper-catalyzed azidation/difunctionalization of vinyl arenes **33** by Yu and co-workers.[32]

The reaction generates three different types of difunctionalization products depending on the electronic nature of the aryl group attached to the olefin **33**. When the aryl group was electron-rich, the reaction exclusively delivered benzoyloxy-azidation products **51**, contrasting electron-deficient vinyl arenes yielding diazidation products **49**. When the electronics were either moderately electron-rich or electron-poor, a three-component coupling involving the solvent acetonitrile was observed giving rise to amido-azidation products **50**. In 2019, Zhang and co-workers impressively demonstrated the formal ATRA reaction of commercially available primary and secondary amines **60** yielding in an overall intermolecular Markovnikov hydroamination approach of alkenes **33** (Scheme 16).[33]

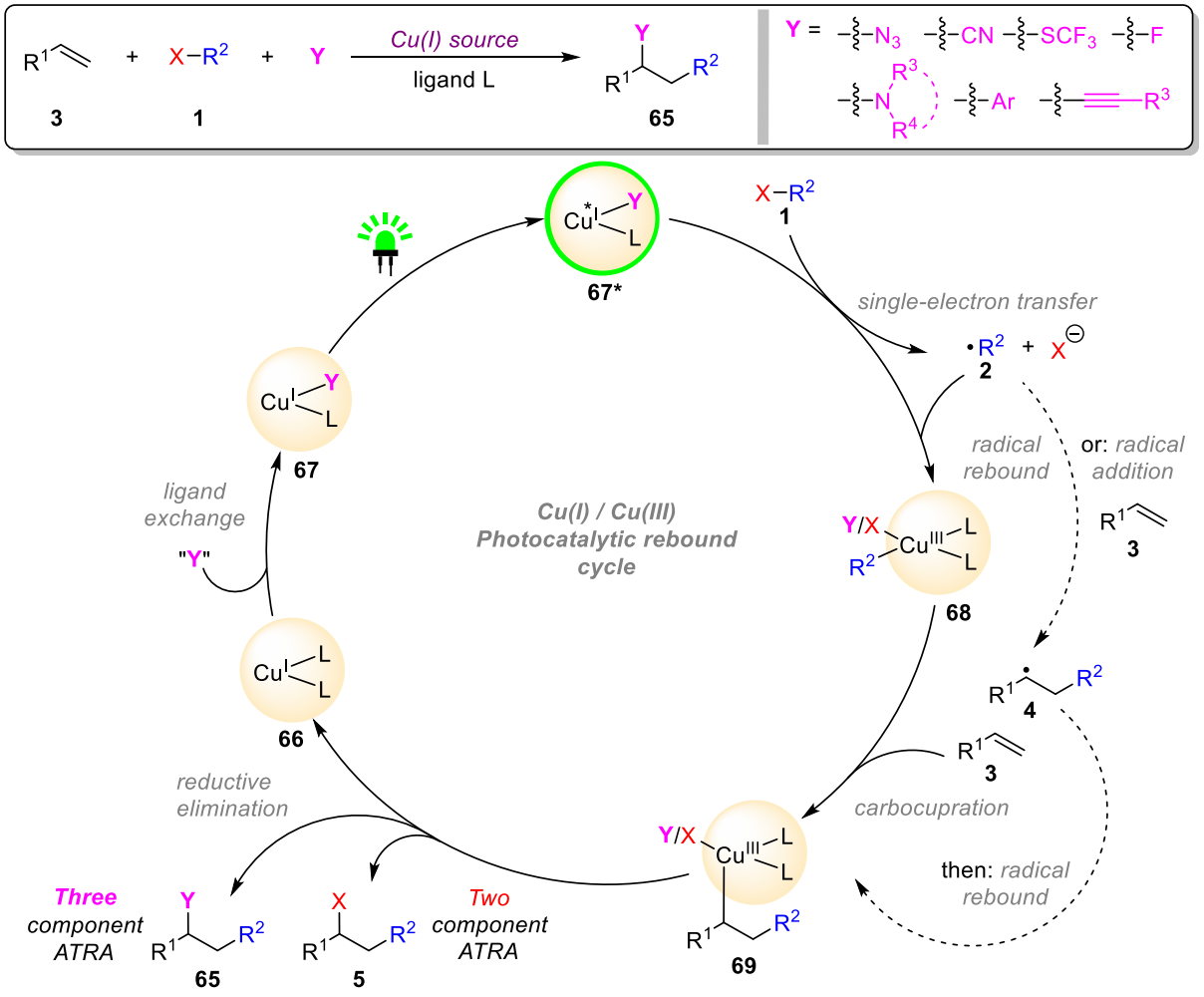


Scheme 16. Copper-catalyzed intermolecular Markovnikov photo-hydroamination of alkenes **33**.[33]

Mechanistic investigations revealed that the hydrogen atom in the final product molecule **61** is originated from the solvent. After excitation of copper complex **63** (Scheme 16, B), single-electron transfer (SET) from the copper center to the alkene and subsequent hydrogen atom abstraction from the solvent leads to complex **64**, which can be also understood as a Cu(III)-intermediate, releasing the final coupling product **61** after reductive elimination.

1.7 A New Concept Arising: Three-Component Copper Photo-ATRA Reactions

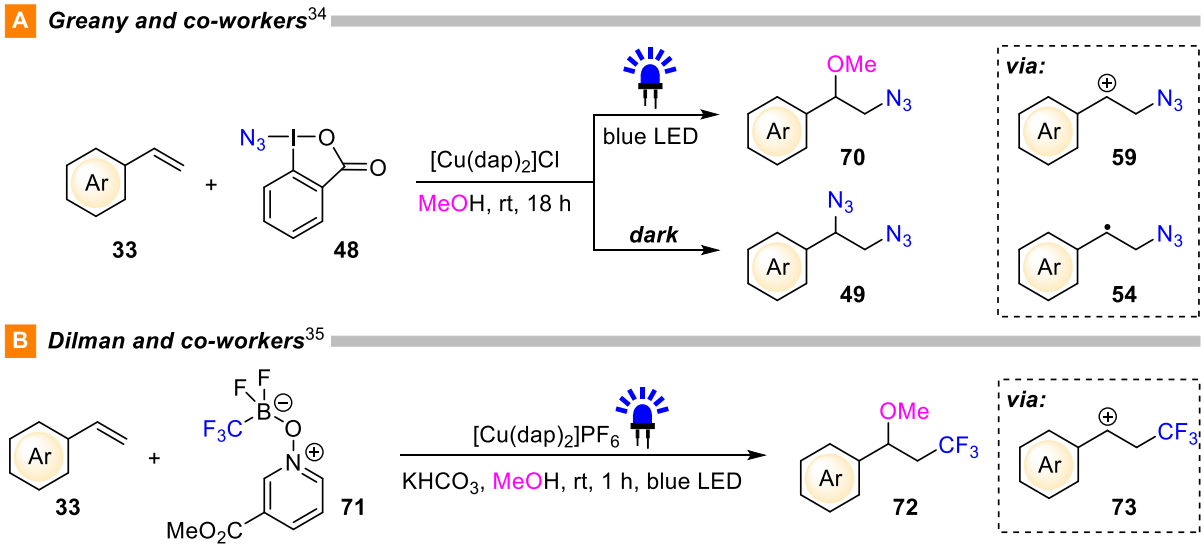
Besides well-established two-component ATRA processes discussed in previous chapters, copper photocatalysts conjointly offer the possibility to introduce a third component in ATRA-type transformations owing to their flexible ligand architecture and thus, their ability to directly interact with substrates in the inner-coordination sphere. The fact that the desired coupling step takes place in the coordination sphere of the copper catalyst offers the unique possibility to render such transformations in a chiral fashion, contrasting three-component ATRA reactions catalyzed by ruthenium(II)- or iridium(III)-based photocatalysts, which go through outer-sphere mechanisms. This chapter aims to give an overview of the recent developments made in this field, which currently is evolving into a rapidly increasing area in copper photocatalysis. The general concept of three-component copper-catalyzed photo-ATRA reactions is depicted in Scheme 17.



Scheme 17. General concept of copper-catalyzed three-component photo-ATRA reactions.

Starting from a Cu(I)-complex **66**, ligand exchange with the third component **Y** affords the corresponding Cu(I)-complex **67**, which now can be irradiated by light. Subsequent single-electron transfer (SET) from the excited Cu(I)-complex **67*** to the ATRA reagent **1** gives rise to the corresponding radical **2**, which might be either trapped by the alkene **3** or by the concurrently formed Cu(II)-species ultimately leading to a Cu(III)-intermediate **68**. In the first case, radical addition product **4** binds back to the previously formed Cu(II)-intermediate to yield Cu(III)-species **69**, while in the second case the latter is formed via carbocupration with alkene **3**. Lastly, reductive elimination releases either the final two- or three-component ATRA product **5** or **65** with concurrent recreation of the catalyst **66** (Scheme 17).

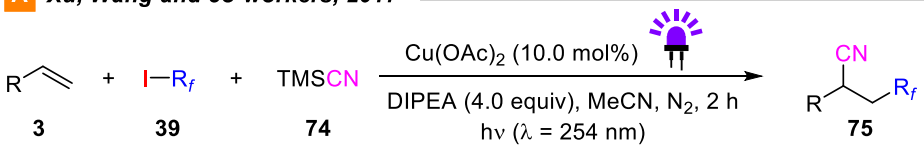
However, in the beginning of this field, Greany[34] and Dilman[35] presented three-component copper-catalyzed ATRA reactions being driven through an outer-sphere mechanism similarly to ruthenium(II)- or iridium(III)-based photocatalysis (Scheme 18). In both studies, the third component is displayed by the solvent methanol, which acts as a nucleophile trapping the intermediary carbocation **59** or **73** being formed after oxidation of the corresponding radical intermediate. Interestingly, in the study of Greany (Scheme 18, A), this oxidation step is only feasible under visible-light conditions, while performing the reaction in the dark yields the corresponding double azidination product **49**.



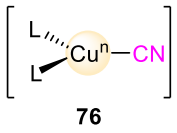
Scheme 18. Copper-catalyzed three-component photo-ATRA reactions via outer-sphere pathways.

Mechanistically more unique and hence auspicious to access heretofore elusive reaction pathways appears to be light-mediated three-component ATRA reactions occurring in the inner-coordination sphere of the copper catalyst (Scheme 19).

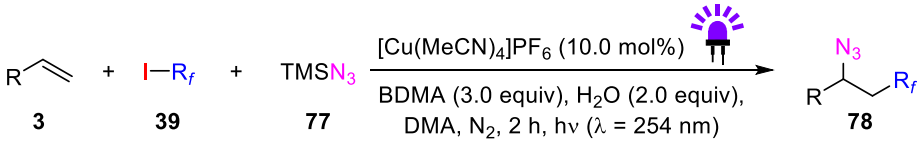
A ***Xu, Wang and co-workers, 2017***[36]

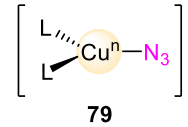


Key species

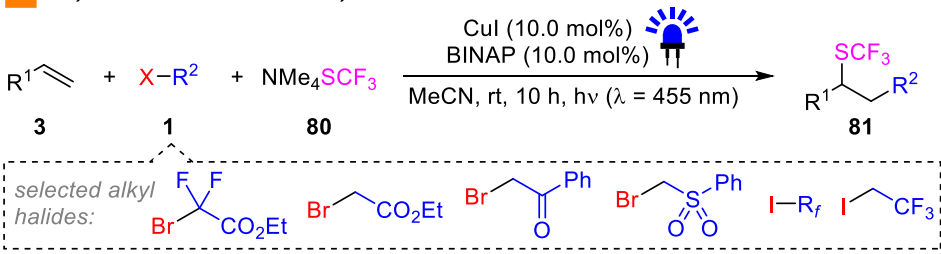


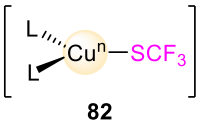
B ***Chen, Xu and co-workers, 2018***[37]



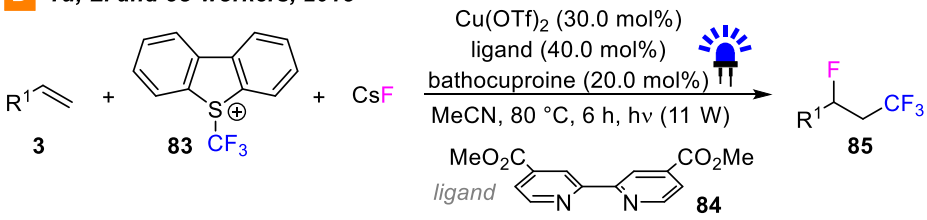


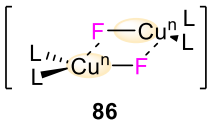
C ***Fu, Peters and co-workers, 2018***[38]



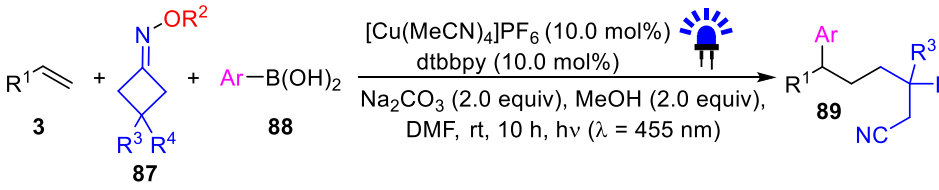


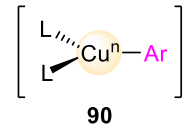
D ***Yu, Li and co-workers, 2018***[39]



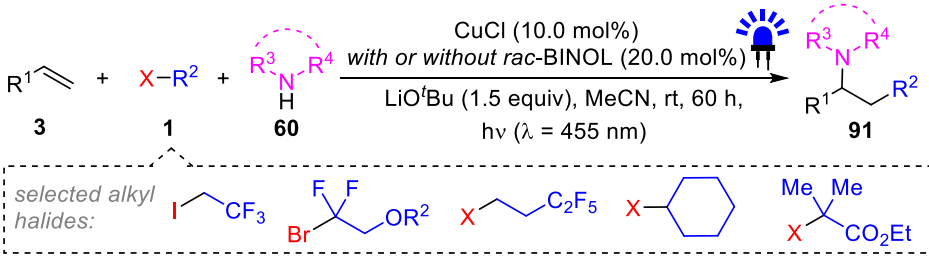


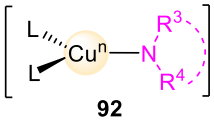
E ***Chen, Xiao and co-workers, 2018***[40]



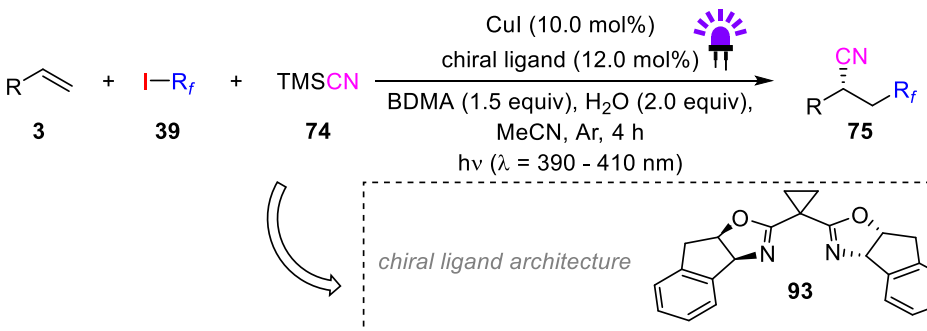


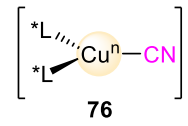
F ***Zhang and co-workers, 2019***[41]

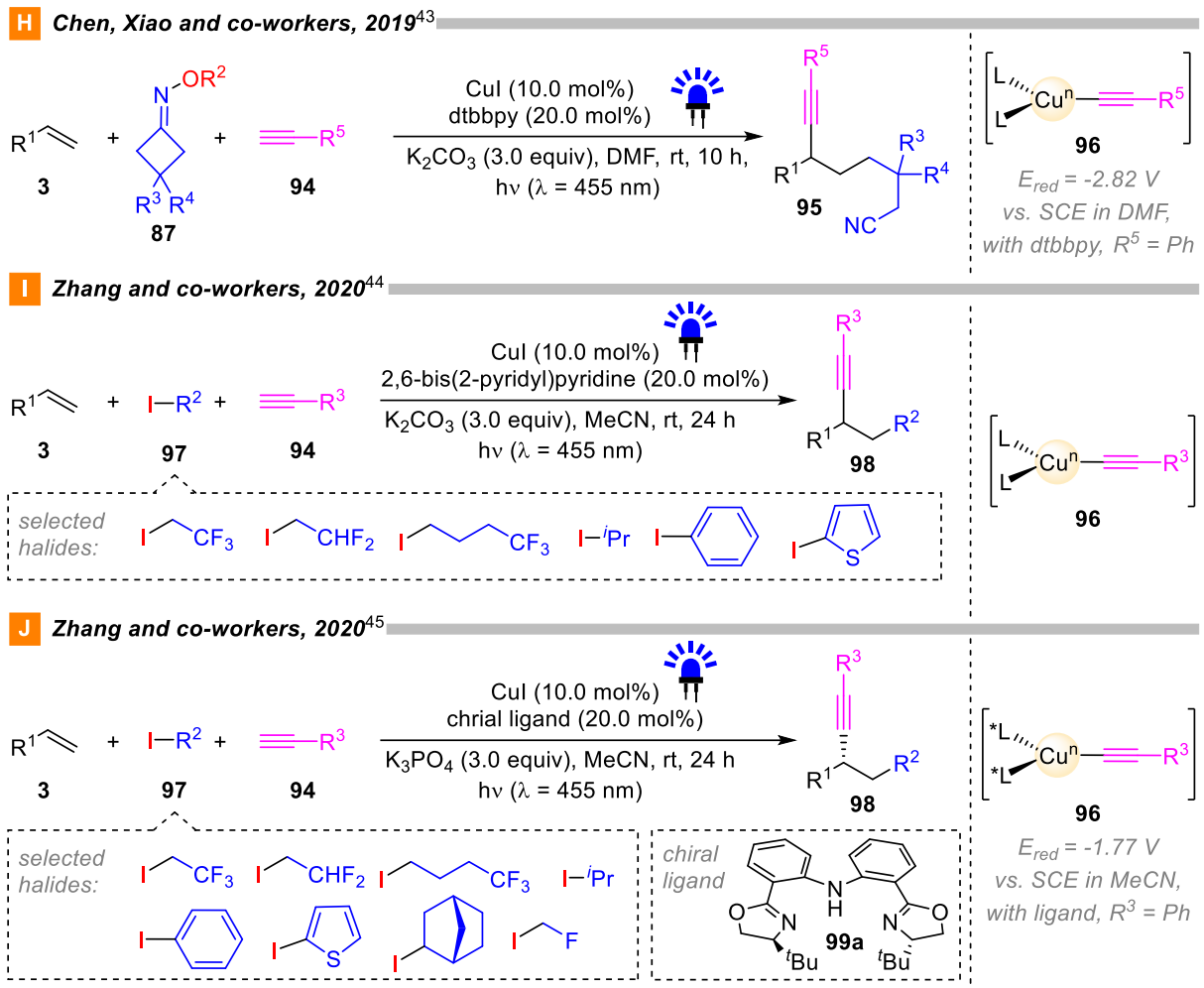




G ***Wang, Xu and co-workers, 2019***[42]



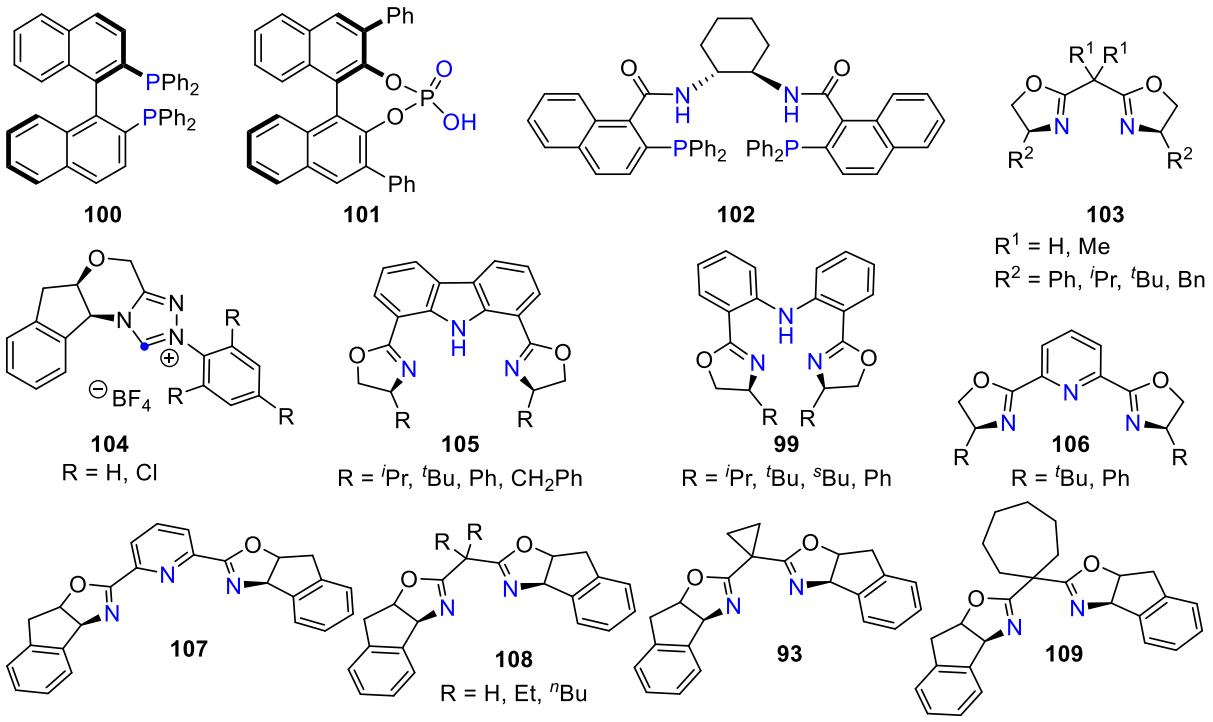




Scheme 19. Overview on light-mediated copper-catalyzed three-component ATRA reactions via inner-sphere mechanism.

This story started in 2017, when Xu and Wang excited a Cu(I)-substrate complex generated in-situ from $Cu(OAc)_2$ and an extraneous cyanide source **74** ultimately leading to a photoactive Cu(I)-CN species **76**. The latter is excited by UV-light empowering the complex to undergo single-electron transfer with the ATRA reagent **39**. The so-generated radical adds to the alkene **3** and subsequently gets trapped by the concurrently formed Cu(II)-intermediate. After reductive elimination the desired three-component coupling product **75** is obtained in good to excellent yields (Scheme 19, A).[36] One year later, Chen, Xu and co-workers expanded this reaction principle to a Cu(I)-azide species **79** under similar reaction conditions yielding in an overall azidofluoroalkylation of alkenes **3**, but still being driven by UV-light (Scheme 19, B).[37] However, in the same year Fu and Peters impressively demonstrated a three-component coupling reaction utilizing a variety of electronically and sterically variegated alkyl halides **1** and a SCF_3-source **80** to overall achieve for example trifluoromethylthiolation of alkenes **3** (Scheme 19, C).[38] It is noteworthy, that addition of BINAP as a ligand system for the copper

source shifts the reaction into the visible region being advantageous to previously reports in an energy-efficient manner. The protocol provided the first example for C_{sp3}-SCF_3 bond construction using photoinduced copper catalysis. While transition metal-assisted Cl- or Br-transfer radical processes are well documented, the analogous F-transfer process is quite rare. Yu and Li imposingly demonstrated, that such a process is feasible through visible-light mediated copper-catalyzed three-component coupling going through a Cu(II)-F intermediate **86** (Scheme 19, D).[39] Thus, an overall fluorotrifluoromethylation of unactivated alkenes **3** becomes accessible using the developed protocol. While so far halogen- or pseudo-halogen moieties were transferred in the coupling reactions, Chen and Xiao demonstrated in 2018 that also aryl groups are suitable ligands on the copper center (Scheme 19, E).[40] Therefore, oxime esters **87** and styrenes **3** are reacted in the presence of the copper source and an aryl boronic acid **88**, which can transfer its aryl group via transmetalation to the copper catalyst and thus paves the way to finally introduce the aryl group in the final three-component coupling product **89**. In 2019, the Zhang group discovered a visible-light induced copper-catalyzed carboamination reaction of alkenes **3**, which relies on a copper-amine complex **92** as key species (Scheme 19, F).[41] It should be noted that amines **60** having a sufficient enlarged π-system can directly act as the ligand to shift the excitation wavelength of the copper catalyst into the visible region, making it redundant to use an external ligand as an additive. However, once amines **60** with a small π-system are subjected to the reaction conditions, the use of *rac*-BINOL as a ligand for the copper source becomes to be crucial. Having now covered a vast array of possible copper-substrate assemblies for inner-sphere three-component coupling, it was a nature of choice to run this kind of reaction under stereo induction of a chiral ligand architecture on the copper center. Wang and Xu impressively presented the asymmetric cyanofluoroalkylation of alkenes **3** utilizing the copper catalyst as both the photoredox catalyst for the outer-sphere electron transfer and the asymmetric cross-coupling catalyst for the final enantioselective C-CN bond formation (Scheme 19, G).[42] Remarkably, the differences in yield and enantioselectivity when screening several chiral ligands were tremendous, underpinning the importance of the exact nature of ligand architecture on the copper catalyst. Out of a library of 13 different chiral ligands only one of them revealed to suitable yielding both a good chemical yield as well as high enantiomeric excess. Scheme 20 shows a selection of possible chiral ligand structures for copper photocatalysis.

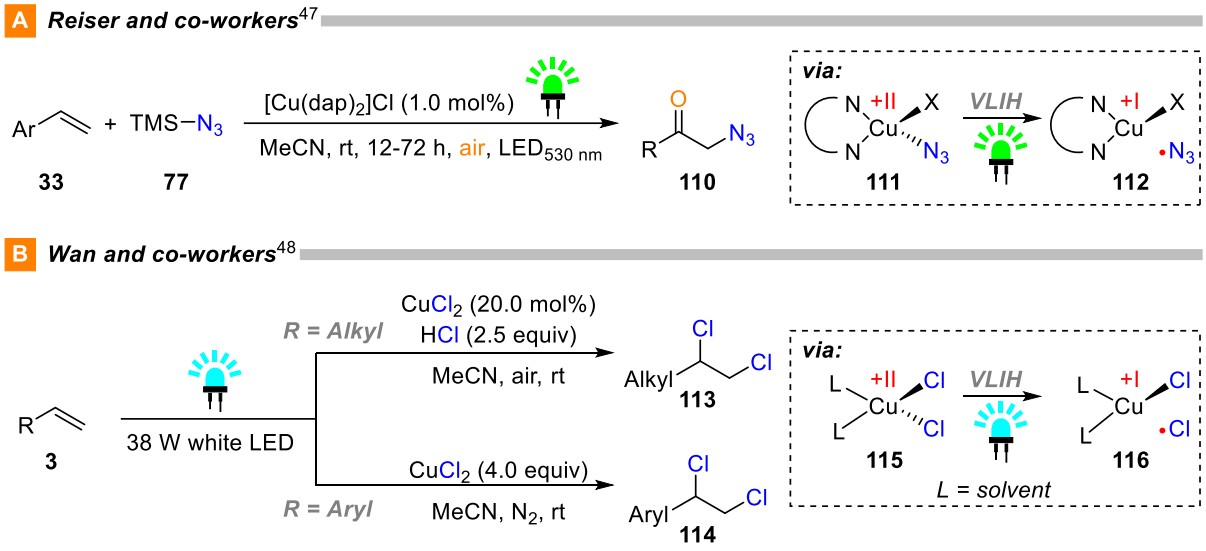


Scheme 20. Selected chiral ligands for copper photocatalysis.

Pioneered by Hwang and co-workers,[46] who demonstrated in 2015 that a Cu(I)-acetylide complex can serve as a highly effective photo-reductant (E_{red} = -2.05 V vs. SCE for Cu(I)-phenylacetylene in MeCN), Chen and Xiao could further apply this principle to a three-component ATRA reaction of alkenes **3** with oxime esters **87** (Scheme 19, H).[43] Remarkably, their study revealed that Cu(I)-phenylacetylene in DMF (E_{red} = -0.89 V vs. SCE) is by far not feasible to undergo SET with oxime ester **87** (E_{red} = -2.18 V vs. SCE in DMF). However, upon addition of the dtbbpy ligand the reduction power of the Cu(I)-phenylacetylene complex **96** drastically increases (E_{red} = -2.82 V vs. SCE), thus making SET reduction of the oxime ester **87** thermodynamically feasible. These observations once more underly the fact that the nature of the ligand environment tremendously impacts the reactivity of the overall active copper photocatalyst. While Chen and Xiao were limited to oxime esters **87** as ATRA reagents, in 2020 Zhang and co-workers expanded this idea to the use of several alkyl- and aryl iodides **97** (Scheme 19, I).[44] Few month later, they further optimized their protocol utilizing a chiral ligand to gain enantioselective control in the desired transformation (Scheme 19, J).[45] Interestingly, the excited state reduction potential of the Cu(I)-phenylacetylene complex in MeCN **96** in the presence of the chiral ligand is determined to be -1.77 V vs. SCE and thus significantly differing from aforementioned complexes. Nevertheless, the reduction power is still sufficient to reduce for instance trifluoroethyl iodide (E_{red} = -1.61 V vs. SCE in MeCN).

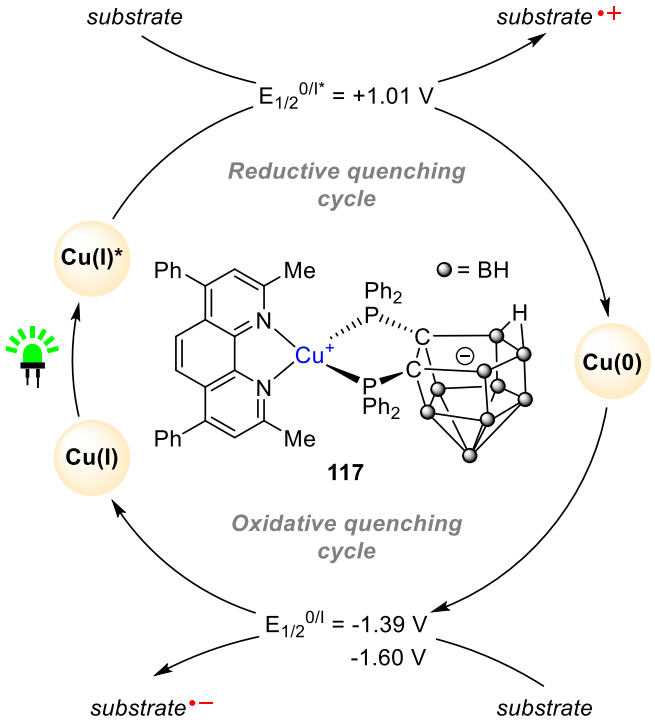
1.8 Future Perspective for Copper Alkene Functionalization

While all reactions previously discussed dominantly rely on single-electron reduction from photoexcited states involving the transition from Cu(I)* to Cu(II), there has been tangible success now that exploit a Cu(II)-substrate complex for excitation do trigger visible-light induced homolysis (VLIH) to Cu(I) and the corresponding substrate radical. While the activation of a Cu(II)-Cl precatalyst with visible-light to form a photoactive Cu(I)-species was discussed before in the example of $[Cu(dap)Cl_2]$[27] and $[Cu(dmp)_2Cl]Cl$,[18] the strategy to activate stochiometric substrates for follow-up reaction pathways via a Cu(II)-substrate complex is an upcoming field reflected by an increasing number of reports in the last years.[28] This synthetic plan can be also applied to difunctionalization of alkenes being discussed in this review. In 2018, Reiser and co-workers demonstrated a visible-light accelerated oxo-azidation of alkenes **33** with trimethylsilylazide (**77**) and molecular oxygen as stochiometric oxidant (Scheme 21, A).[47] As a key intermediate a Cu(II)-azide complex **111** is proposed which will undergo light-accelerated homolysis to form Cu(I) **112** and azide radicals. In 2020, Wan and co-workers[48] capitalized on Kochi`s discovery[49] back in 1962 and developed a visible-light-induced vicinal dichlorination of olefins **3** by directly exciting $CuCl_2$ in MeCN as a coordinating solvent without any exogeneous ligand (Scheme 21, B). While a combination of 20.0 mol% $CuCl_2$ and 2.5 equiv hydrochloric acid as the stochiometric chlorine source were sufficient for the dichlorination of unactivated alkenes, 4.0 equiv $CuCl_2$ alone were adequate to promote the same process for activated alkenes. This activation principle may open up new avenues for visible-light mediated copper-catalyzed photocatalysis for alkene difunctionalization.



Scheme 21. Alkene difunctionalization through visible-light-induced homolysis (VLIH) of copper(II)-substrate complexes.

Another possible transition in copper photocatalysis is displayed by Cu(I)* to Cu(0). In general, the low stability of a Cu(0)-species makes such a process really challenging. Nevertheless, there have been tangible success exploiting the potential of this transition.[50] Chen and co-workers introduced the photostable zwitterionic copper-based photocatalyst **117** which is capable to run through the reductive quenching cycle involving a Cu(0)-intermediate (Scheme 22).[50a]



Scheme 22. Photostable zwitterionic copper-based photocatalyst **117** developed by the Chen group.[50a]

1.9 Conclusion

Over the last decade, light mediated ATRA reactions utilizing homoleptic or heteroleptic copper complexes have gained a significant growth. Copper photocatalysts proved to be a powerful choice in these kinds of transformations not just from an economic point of view but also due to their ability to interact and stabilize radical intermediates in their inner-coordination sphere, thus empowering them to access heretofore elusive reaction pathways. The flexible architecture in the coordination sphere and ligand binding modes offers the possibility to further develop more sophisticated catalytic systems. For instance, the idea of using certain Cu(I)-substrate assemblies as photoredox active catalysts allow the effective construction of three-component couplings even in an enantioselective fashion. We do believe that in the upcoming years the field of copper photocatalysis using complexes with such augmented potential is still in its infancy and will almost certainly gain tremendous impact in organic synthesis, material science and pharmaceutical applications.

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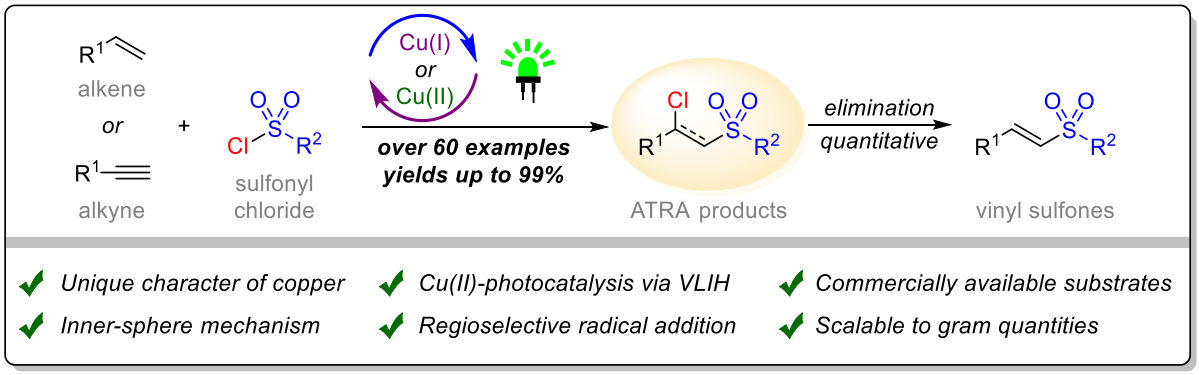
Chapter 2

Photochemical Chlorosulfonylation‡

This chapter was mostly processed during my Master Thesis[1], finished up and published during my PhD Thesis. While the complete study can be found in my Master Thesis[1], the key findings are briefly summarized in this chapter as a basis and starting point for the following work.

2.1 Abstract

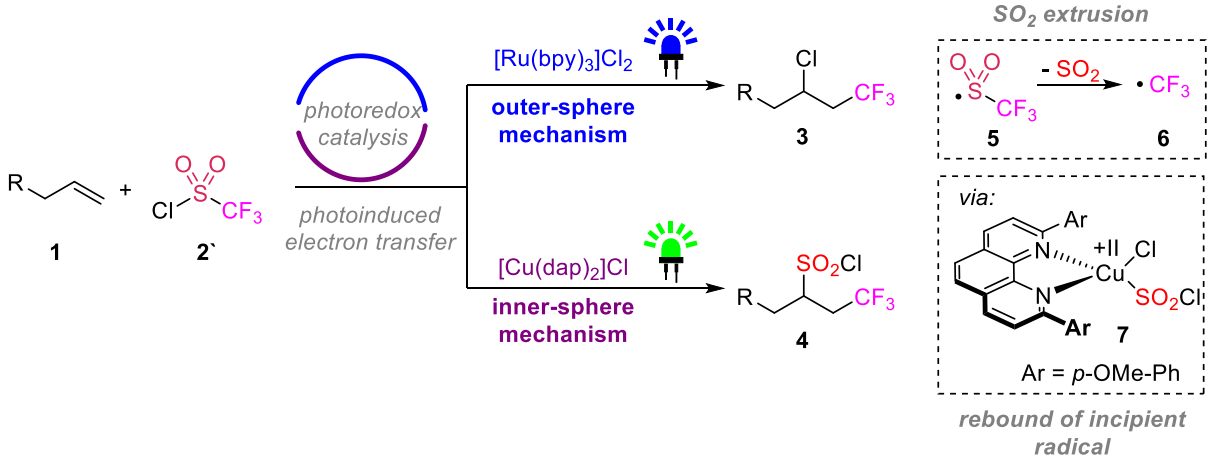


In Chapter 2, we report a visible-light mediated copper-catalyzed protocol enabling the rapid chlorosulfonylation of miscellaneous alkenes and alkynes. Besides the Cu(I)-complex $[Cu(dap)_2]Cl$, now well-established in such ATRA processes, the corresponding Cu(II)-complex $[Cu(dap)Cl_2]$ proved to be often even more efficient in the title reaction, being advantageous from an economic point of view but also opening up new avenues in copper photoredox catalysis. Moreover, those outperformed commonly used ruthenium-, iridium- or organic dye-based photocatalysts, owing to their ability to stabilize and interact with transient radical intermediates in their inner-coordination sphere. Furthermore, the protocol excels through high yields utilizing commercially available substrates and can be smoothly scaled to gram-quantities of product. The latter can be quantitatively transformed upon elimination giving rise to their corresponding vinyl sulfones, which are of great importance in several fields in synthetic organic as well as medicinal chemistry

‡ This chapter is partially based on: Hossain, A.†; Engl, S.†; Lutsker, E.†; Reiser, O. *ACS Catal.* **2019**, *9*, 1103-1109. (†Authors contributed equally). And on: Henriquez, M. A.; Engl, S.; Jaque, P.; Gonzalez, I. A.; Natali, M.; Reiser, O.; Cabrera, A. R. *Eur. J. Inorg. Chem.* **2021**, 4020-4029.

2.2 Introduction

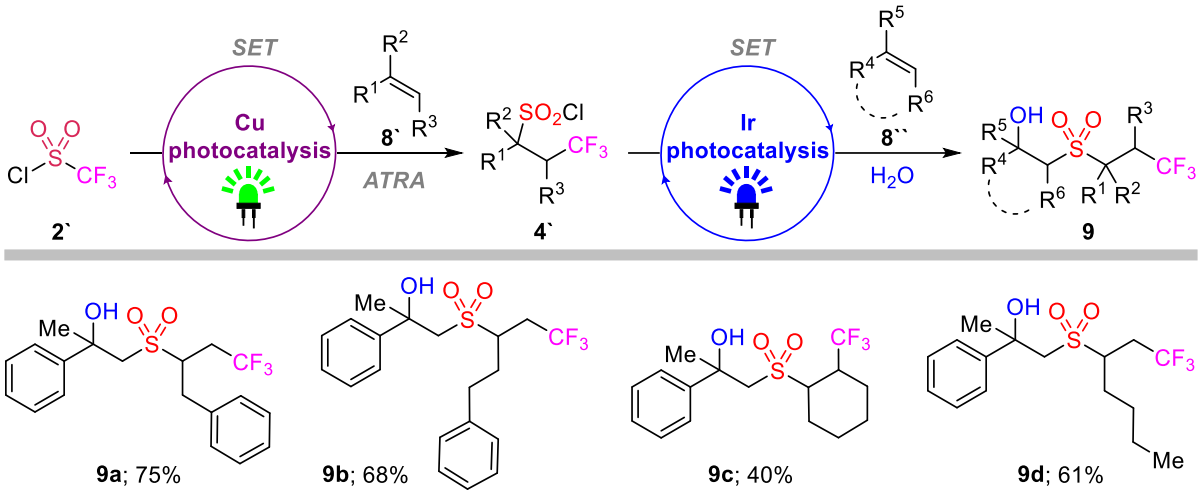
Sulfones represent a privileged class of important motifs frequently found in many natural occurring organic compounds and drug candidates with intriguing biological activities.[2] Hence, many efforts have been made by various scientific groups for the direct incorporation of a sulfone moiety, which is reflected by a broad range of publications.[3] Thereby, the development of new catalytic methodologies employing mild and ecologically benign reaction conditions is highly desirable. Photocatalysis, featuring most prominently ruthenium- or iridium-based metal complexes has developed into a powerful tool in synthetic organic chemistry for carbon-carbon and carbon-heteroatom bond formations in an energy-efficient manner.[4] Although ruthenium- and iridium-based photocatalysts excel through their high photostability, long-lived excited state lifetimes and favorable photoredox potentials, they do not meet the requirements for modern industrial manufacturing processes due to their high costs and scarcity. In this regard, copper photocatalysis gained a strong foothold in photocatalysis and emerged as an appealing complement.[5] Contrasting ruthenium- or iridium-photocatalysts, which show no or at the best very slow ligand exchange dynamics, copper photocatalysts thereon offer the unique opportunity to undergo ligand exchange mechanisms allowing them to interact with incipient radicals in their inner-coordination sphere, thus stabilizing and controlling reaction intermediates. This unique character of copper in photoredox catalysis was for the first time impressively demonstrated by Reiser and co-workers in 2015 (Scheme 1).[6]



Scheme 1. Photocatalyzed chlorotrifluoromethylation and trifluoromethylchlorosulfonylation of unactivated alkenes **1**. $[Ru(bpy)_3]Cl_2$ catalysis: Han et al.;[7] $[Cu(dap)_2]Cl$ catalysis: Reiser et al.[6]

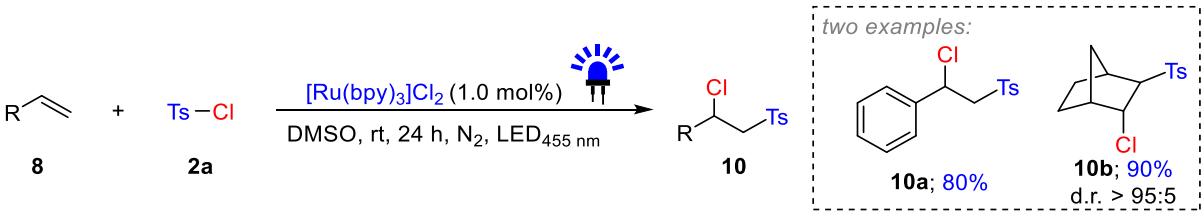
While photoredox activation of triflyl chloride (**2`**) with $[Ru(bpy)_3]Cl_2$ exclusively leads to the chlorotrifluoromethylation product **3** after SO_2 extrusion of radical intermediate **5**, employing $[Cu(dap)_2]Cl$ allows the isolation of the corresponding trifluoromethylchlorosulfonylation

products **4**. The formation of the unexpected sulfonyl chloride **4** is attributed to the interaction of the chlorosulfonyl fragment, which is generated after single-electron transfer (SET) of the excited copper catalyst and the concurrently formed Cu(II)-species. The exclusive formation of the sulfonyl chloride products **4`** in the presence of a copper photocatalyst could be further explored by the Reiser group in a sequential process activating the latter by iridium-based photocatalysis to rapidly build up *β*-hydroxysulfones **9** in a one-pot reaction (Scheme 2).[8]



Scheme 2. Photochemical synthesis of *β*-hydroxysulfones **9** utilizing a photocatalytic sequence by Reiser and co-workers.[8]

Intrigued by this unique transformation, we questioned the reactivity of other sulfonyl chlorides **2** as ATRA reagents. Single-electron transfer (SET) from the excited photocatalyst to an aryl or alkyl sulfonyl chloride may form a *S*-centered radical which then can add to alkenes ultimately forming hetero-difunctionalized products. In fact, seminal work by Stephenson and co-workers describes this basic idea in two examples utilizing $[Ru(bpy)_3]Cl_2$ as the photocatalyst (Scheme 3),[9] while pioneering work back in the 1900s reported the use of CuCl or $CuCl_2$ under thermal initiation.[10] Thus, we aimed in this chapter to develop a broadly applicable visible-light mediated photoredox chlorosulfonylation of alkenes and alkynes utilizing copper-based photocatalysts demonstrating the unique character and advantages of the latter compared to the previously established ruthenium-mediated protocol.

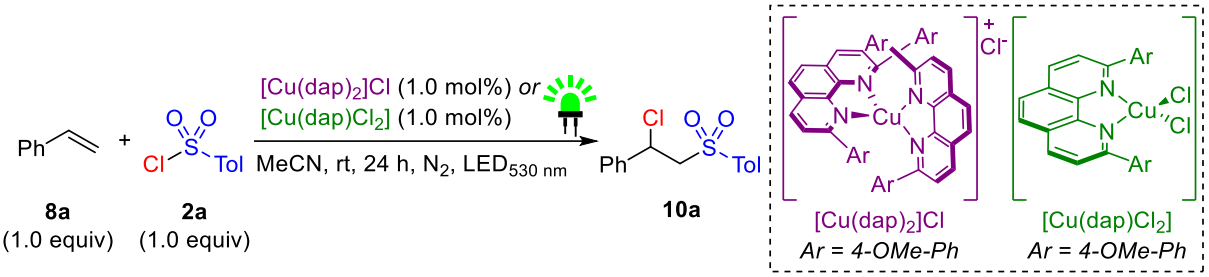


Scheme 3. Seminal work on ATRA reactions of tosyl chloride (**2a**) on two examples reported by Stephenson and co-workers.[9]

2.3 Reaction Optimization

We started our investigations using styrene (**8a**) and tosyl chloride (**2a**) as the model substrates in the presence of 1.0 mol% of $[Cu(dap)_2]Cl$ as a photocatalyst under visible-light irradiation with green LED (λ = 530 nm) (Table 1).

Table 1. Reaction optimization.

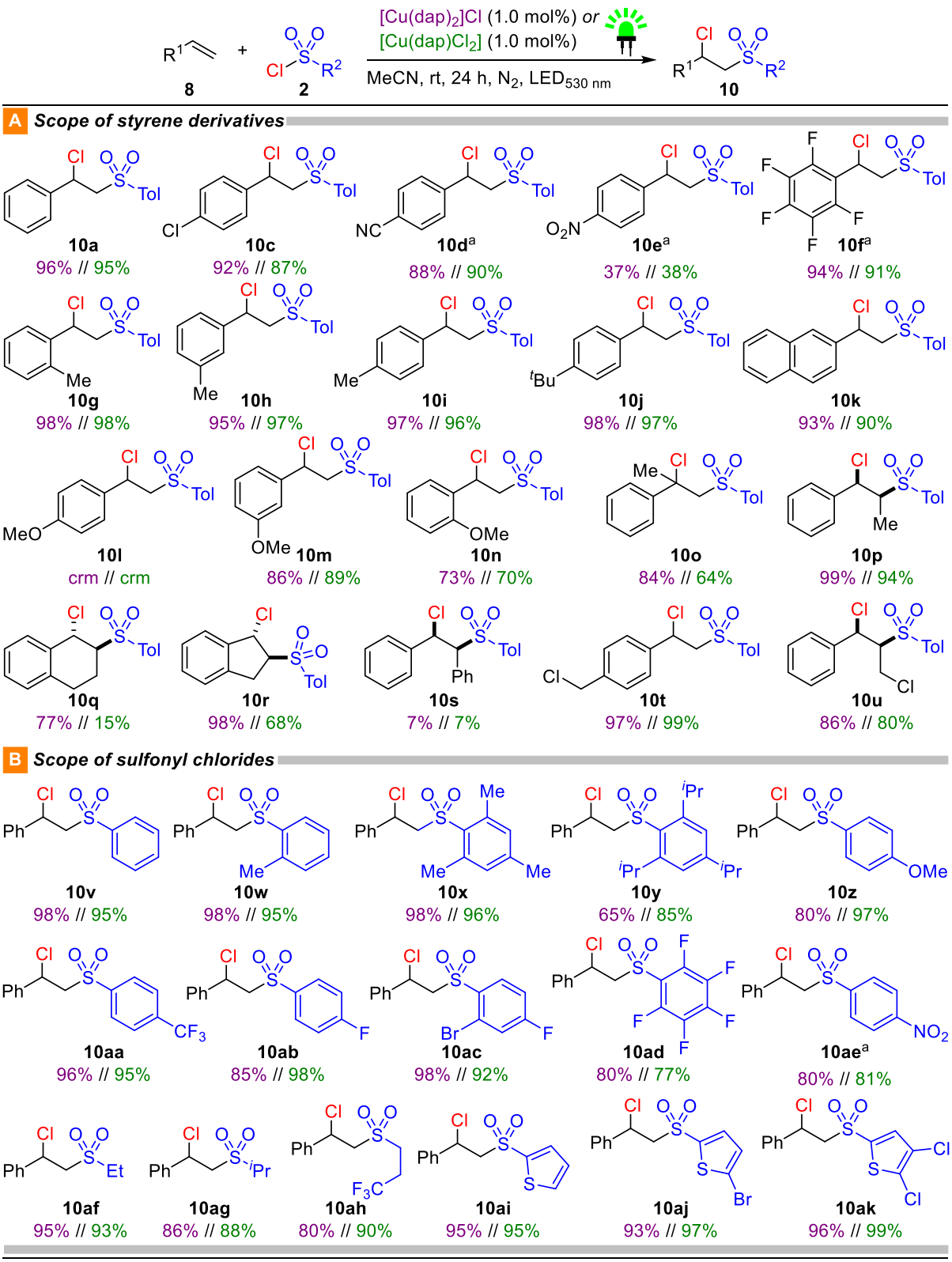


Entry	Variations from "standard"	Yield for $[Cu(dap)_2]Cl$[a]	Yield for $[Cu(dap)Cl_2]$[a]
1	---	96%[b]	95%[b]
2	DCM as a solvent	58%	55%
3	DMF as a solvent	20%	19%
4	DMSO as a solvent	18%	15%
5	0.1 mol% catalyst loading	nr	nr
6	0.5 mol% catalyst loading	52%	54%
7	0.75 mol% catalyst loading	83%	86%
8	irradiation with blue LED (λ = 455 nm)	92%	91%
9	Na_2CO_3 (1.0 equiv) as an additive	93%	93%
10[c]	$[Ru(bpy)_3]Cl_2$ (1.0 mol%)	80%	
11[c]	*fac*-$[Ir(ppy)_3]$ (1.0 mol%)	45%	
12[c]	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ (1.0 mol%)	7%	
13	eosin Y (1.0 mol%)	nr	
14	AIBN (10.0 mol%), T = 80 °C	nr	
15	no catalyst	nr	
16	no light	nr	nr
17	CuCl (10.0 mol%) or $CuCl_2$ (10.0 mol%)	nr	nr
18	only dap ligand (10.0 mol%)	nr	
19	CuCl (5.0 mol%) and phen (10.0 mol%)	nr	
20	$CuCl_2$ (5.0 mol%) and phen (10.0 mol%)	nr	

Reaction conditions: Styrene (**8a**) (0.5 mmol, 1.0 equiv), tosyl chloride (**2a**) (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]NMR yield using diphenoxymethane as an internal standard. [b]Isolated yield. [c]Irradiation at 455 nm (blue LED).

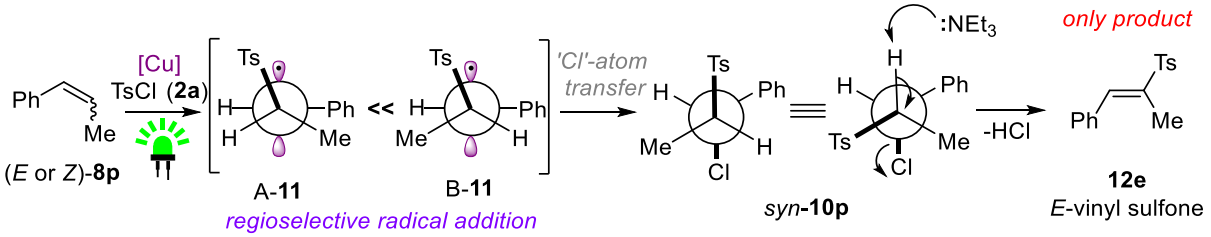
We were pleased to observe the formation of the desired product **10a** in an almost quantitative isolated yield of 96% using $[Cu(dap)_2]Cl$, while unexpectedly, the corresponding Cu(II)-complex $[Cu(dap)Cl_2]$ also catalyzed the reaction and delivered **10a** in 95% (Table 1, entry 1). Therefore, we decided to further investigate and introduce the corresponding Cu(II)-complex in visible-light mediated photoredox catalysis, as the latter offers a considerable cost advantage, given that only half the amount of dap ligand is required. Screening of solvents and catalyst loading revealed lower yields for both copper catalysts when DCM, DMF and DMSO were used as solvents or when the reaction was performed with lower catalyst loadings (Table 1, entries 2-7). As both copper catalysts show a stronger absorption band in the region of blue light (extinction coefficient ε = 10210 $L \cdot mol^{-1} \cdot cm^{-1}$ at 455 nm)[11] compared to the region of green light (extinction coefficient ε = 5353 $L \cdot mol^{-1} \cdot cm^{-1}$ at 530 nm)[11], the title reaction was performed upon blue light irradiation (λ = 455 nm) (Table 1, entry 8). Both catalysts gave the desired product **10a** in slightly lower but still excellent yields of 92% and 91%, respectively. During this study, two co-workers Dr. Asik Hossain[12] and Dr. Eugen Lutsker[13] found out that also unactivated alkenes are suitable starting materials in the titled reaction, however, it is crucial to add one equivalent of Na_2CO_3 as a base to prevent the catalyst from poisoning by traces of acid formed when the generated radicals cannot be rapidly trapped by the alkene. Hence, as a control experiment also the chlorosulfonylation of activated alkenes was carried out in the presence of one equivalent Na_2CO_3 (Table 1, entry 9). Contrasting less reactive unactivated alkenes, no effect of base was observed in the model reaction of styrene (**8a**). Next, we settled out to test the influence of the unique character of copper photocatalysts in the title reaction. While $[Cu(dap)_2]Cl$ and $[Cu(dap)Cl_2]$ provide the desired product **10a** in almost quantitative yields, for $[Ru(bpy)_3]Cl_2$, *fac*-$[Ir(ppy)_3]$, $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ or eosin Y the yield of **10a** was found to be significantly lower (Table 1, entries 10-13), which is consistent with the report of Stephenson an co-workers,[9] but surprisingly not consistent with a more recent study,[14] reporting no reaction under these conditions. Noteworthy, the reduction potential of all catalysts is sufficient to undergo SET to tosyl chloride (**2a**) generating the corresponding sulfonyl radical. In the same way, thermal initiation with AIBN was not possible, yielding in no conversion of starting materials (Table 1, entry 14). Control experiments proved the necessity of both catalyst and light (Table 1, entries 15-16) as well as the importance of dap ligand in combination with the corresponding copper salts (Table 1, entries 17-20). Thus, the conditions established in entry 1 were found to be the best for both copper complexes and subsequently applied to investigate the scope of this reaction.

2.4 Substrate Scope



Scheme 4. Substrate scope for photochemical chlorosulfonylation of alkenes **8**. *Reaction conditions*: Alkene **8** (0.5 mmol, 1.0 equiv), sulfonyl chloride **2** (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]Reaction time 48 h.

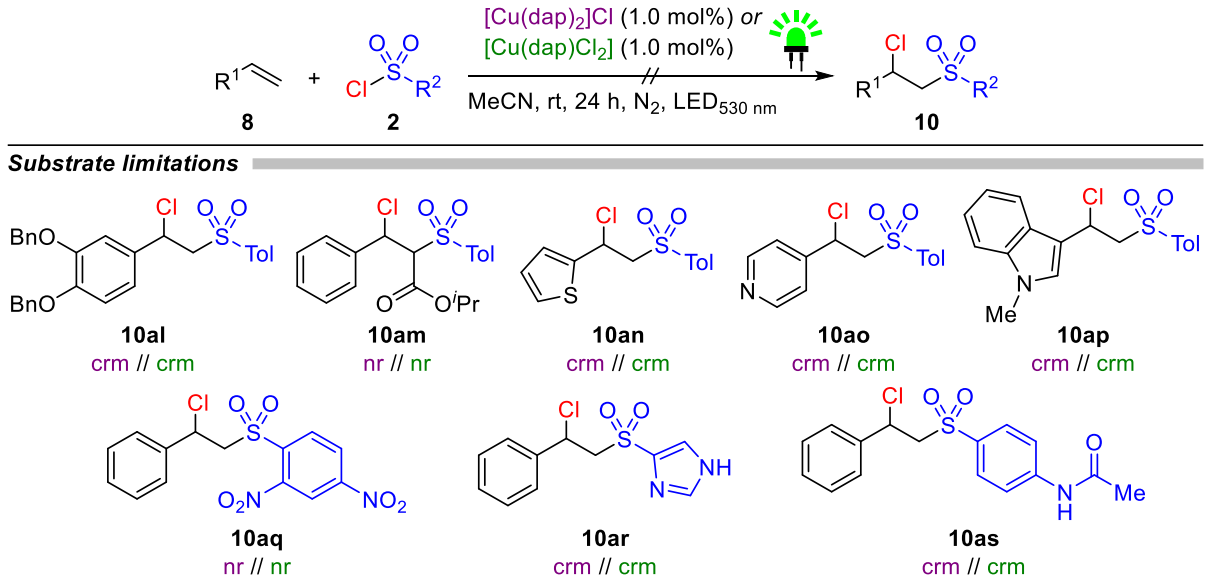
For a plethora of activated alkenes **8** both Cu(I)- and Cu(II)-dap catalysts could be successfully employed in the title reaction (Scheme 4, A). Electron-deficient styrene derivatives were suitable substrates giving rise to the corresponding products **10c**-**10f** in very high yields. Noteworthy, *p*NO_2 substitution showed significantly lower yields in this series of substrates, probably caused by the ability of the nitro-group to either act as an electron acceptor leading to amines, or to act as a triplet state quencher under such photochemical conditions.[15] Switching to electron-donating derivatives, methyl substitution was well tolerated in *ortho*, *meta* and *para* position yielding the desired products **10g**-**10i** in excellent yields for both catalysts. Sterically demanding ^{t}Bu substitution and a vinyl naphthalene derived starting material were both suitable substrates delivering products **10j** and **10k** in high yields. Increasing the electron-donating character with *p*OMe substitution led to a complex reaction mixture, probably given by the strong mesomeric effect of the oxygen lone-pairs making the radical intermediate prone to be easily oxidized or highly reactive. In line, when the methoxy group is installed in *meta* position, thus acting as an acceptor, the desired chlorosulfonylation product **10m** is obtained in 86% for the Cu(I)-dap and 89% for the Cu(II)-dap catalyst. Surprisingly, also *ortho* methoxy-substituted styrene successfully participated in the reaction although with distinctly lower yields. As the *ortho*-OMe group also acts as a strong donor, the steric proximity to the reactive center may predominate, hindering fast side-reactions of the reaction intermediate. Both *α*- and *β*-alkyl substitution on the styrene were well tolerated in this reaction (**10o**-**10r**), while stilbene showed poor reactivity giving only 7% of **10s**. Remarkably, when two new stereocenters were formed (**10p**-**10s**), only one diastereomer was observed in the title reaction. Interestingly, *trans*- as well as *cis*-*β*-methyl styrene (**8p**) provided a single diastereomer *syn*-**10p**, which upon treatment with base exclusively yielded *E*-vinyl sulfone **12e** (Scheme 5). The repulsive interaction between the phenyl- and the methyl in A-**11** and B-**11** probably results in the formation of *syn*-**10p**, being in line with a similar discussion by Stephenson and co-workers.[16]



Scheme 5. Diastereoselectivity during product formation in the photochemical chlorosulfonylation.

Remarkably, benzylic- or allylic chlorides showed no cross reactivity, giving rise to the desired products **10t** and **10u** in very good to excellent yields.

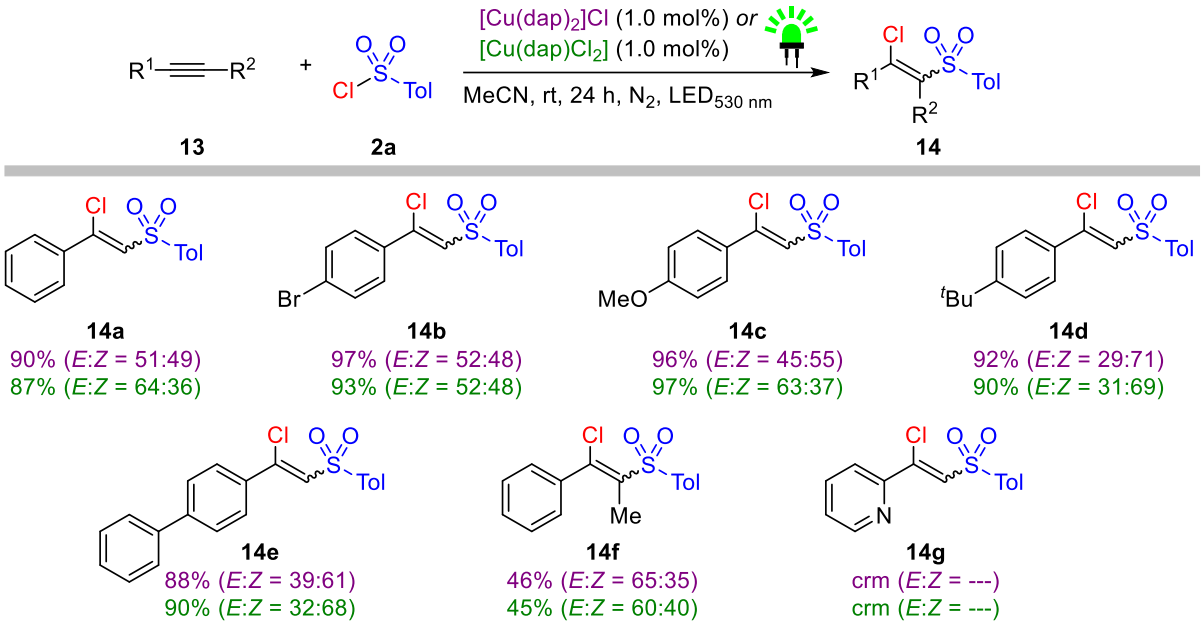
We next pursued with the construction of photoproducts derived from electronically and structurally variegated sulfonyl chlorides as radical precursors (Scheme 4, B). Increasing the steric bulk from *o*Me- to trimethyl- or even triisopropyl-substituted sulfonyl chlorides did not alter the reactivity, yielding the corresponding products **10w**-**10y** in good to excellent yields for both copper catalysts. We were pleased to observe that both strongly electron-donating and strongly electron-withdrawing substituted sulfonyl chlorides successfully participated in the desired photoreaction in very high yields (**10z**-**10ae**). Remarkably, compared to the scope of different styrene derivatives, nitro-substitution on the sulfonyl chloride is well tolerated accessing **10ae** in 80% and 81% yield, respectively. Gratifyingly, also alkyl sulfonyl chlorides underwent the desired coupling in high yields (**10af**-**10ah**). It should be noted, that alkyl sulfonyl chlorides have been proven to be incompatible for such ATRA reactions employing $[Ru(bpy)_3]Cl_2$ as the photocatalyst (see Chapter 2.5). Considering thiophene-derived substrates as potential poison for the copper photocatalyst, they nevertheless allowed the isolation of the corresponding photoproducts **10ai**-**10ak** in excellent yields. Limitations of the developed chlorosulfonylation protocol are depicted in Scheme 6.



Scheme 6. Substrate limitations in the photochemical chlorosulfonylation. *Reaction conditions*: Alkene **8** (0.5 mmol, 1.0 equiv), sulfonyl chloride **2** (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h.

Highly electron-rich substrates, *α*,*β*-unsaturated double bonds and vinyl heterocycles proved to be clear limitations on the alkene side (**10al**-**10ap**), while highly electron-poor sulfonyl chlorides as well as sulfonyl chlorides having free NH groups only led to complex reaction mixtures in the desired photoreaction (**10aq**-**10as**).

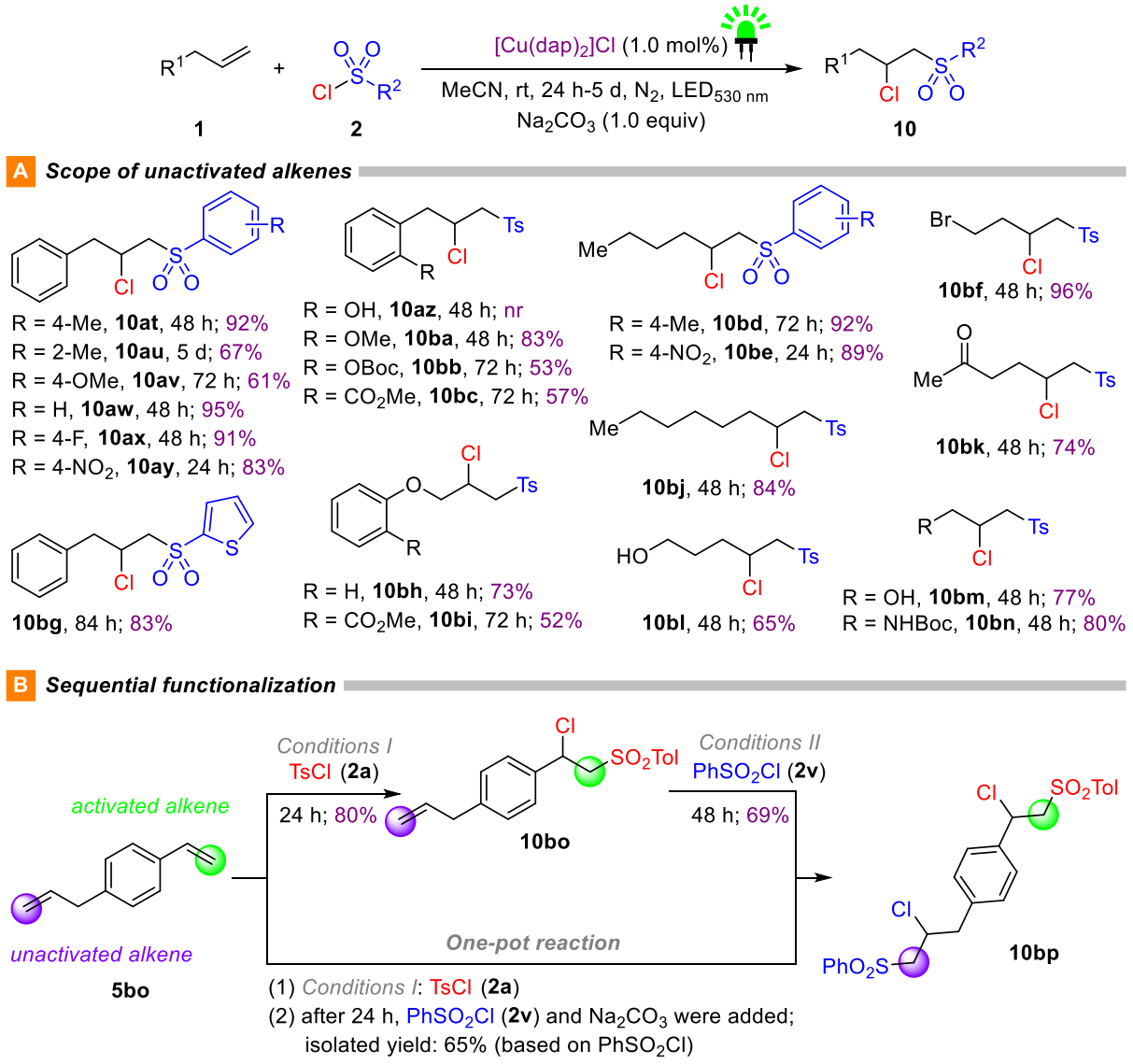
Next, we investigated the scope of different alkynes **13** for the ATRA reaction with sulfonyl chloride **2a** (Scheme 7).



Scheme 7. Substrate scope for photochemical chlorosulfonylation of alkynes **13**. *Reaction conditions*: Alkyne **13** (0.5 mmol, 1.0 equiv), tosyl chloride (**2a**) (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. Both isomers were separated by flash column chromatography. The yields are shown as overall isolated yields. *E* and *Z* ratios are based on the isolated products. Stereochemistry was assigned in analogy to literature[17] (see Experimental Part 7.4.1).

Gratifyingly, phenylacetylene-derived substrates **13** were suitable reaction partners in the same way giving access to the corresponding halovinyl sulfones **14** in high yields. The products were obtained as *E* and *Z* mixtures in almost equimolar ratios, which can be smoothly separated by flash column chromatography. Electronical variations by installing either an electron-withdrawing halogen- or an electron-donating methoxy-substituent did not alter the reactivity allowing isolation of **14b** and **14c** in almost quantitative yields. The reaction between *p*^{t}Bu- or *p*Ph-substituted phenylacetylene and tosyl chloride (**2a**) afforded the desired products **14d** and **14e** in excellent yields, this time favoring the formation of the corresponding *Z* isomer probably due to the increased steric influence of the substituents in *para* position. Disubstituted alkyne still formed the desired ATRA product **14f**, however, the yield of **14f** decreased to a moderate range (45%-46%) for both catalysts. A limitation seemed to be found in the use of heterocyclic alkynes aiming in the synthesis of **14g**, which instead lead to a complex reaction mixture. In parallel to the investigations on the chlorosulfonylation of activated alkenes and alkynes, cooperation with two co-workers Dr. Asik Hossain[12] and Dr. Eugen Lutsker[13] revealed the analogous transformation for unactivated alkenes (Scheme 8). Thereby, the use of stochiometric

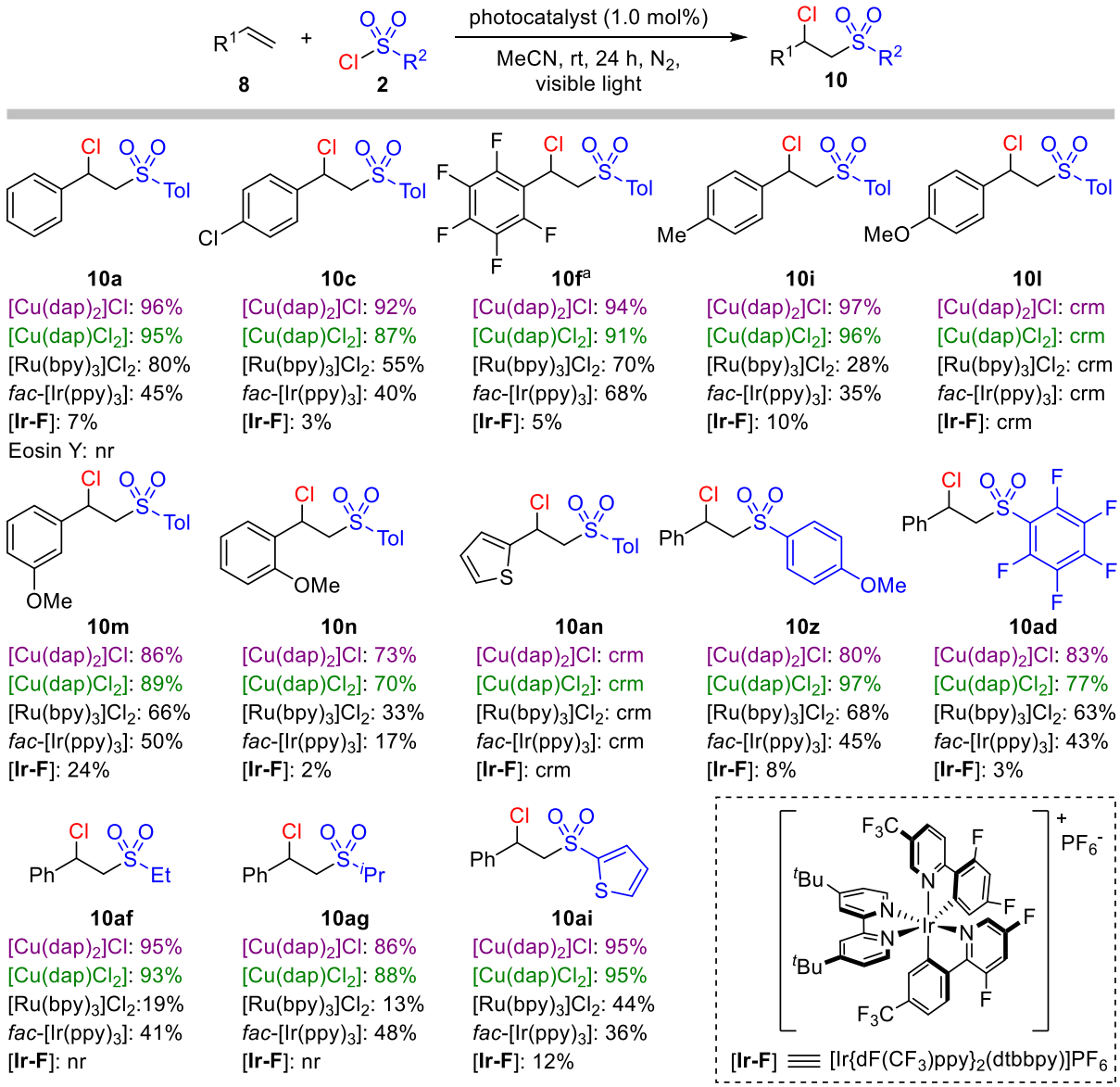
amounts of Na_2CO_3 as a base was found to be crucial to prevent the catalyst from poisoning by traces of acid formed when the generated radicals cannot be rapidly trapped by the alkene. Furthermore, contrasting activated alkenes, unactivated double bonds afforded an excess of the alkene as well as prolongation of reaction times. With these optimized conditions in hand, Dr. Asik Hossain and Dr. Eugen Lutsker were able to successfully convert 20 alkenes to their corresponding chlorosulfonylation products (Scheme 8, A).[13,12]



Scheme 8. Substrate scope of photochemical chlorosulfonylation of unactivated alkenes **1**. *Reaction conditions*: (A) Alkene **1** (1.0 mmol, 2.0 equiv), sulfonyl chloride **2** (0.5 mmol, 1.0 equiv), Na_2CO_3 (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. Reactions carried out by Dr. Asik Hossain[12] and Dr. Eugen Lutsker[13]. (B) *Conditions I*: Alkene **5bo** (0.5 mmol, 1.0 equiv), tosyl chloride (**2a**) (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. *Conditions II*: see (A). Reactions carried out by Dr. Asik Hossain.[12]

Given the fact that chlorosulfonylation of unactivated alkenes requires the use of base as an additive, we seized the opportunity to perform the sequential functionalization of **5bo** (Scheme 8, B). Indeed, **10bp** could be isolated in 80% first functionalizing the activated double bond with tosyl chloride (**2a**), followed by a second ATRA reaction on the unactivated double bond using $PhSO_2Cl$ (**2v**) in 69% yield. Running this sequence in a single-flask with 1.0 mol% $[Cu(dap)_2]Cl$ proved to be even more efficient accessing product **10bp** in 65% overall yield.

2.5 Comparison with Other Photocatalysts

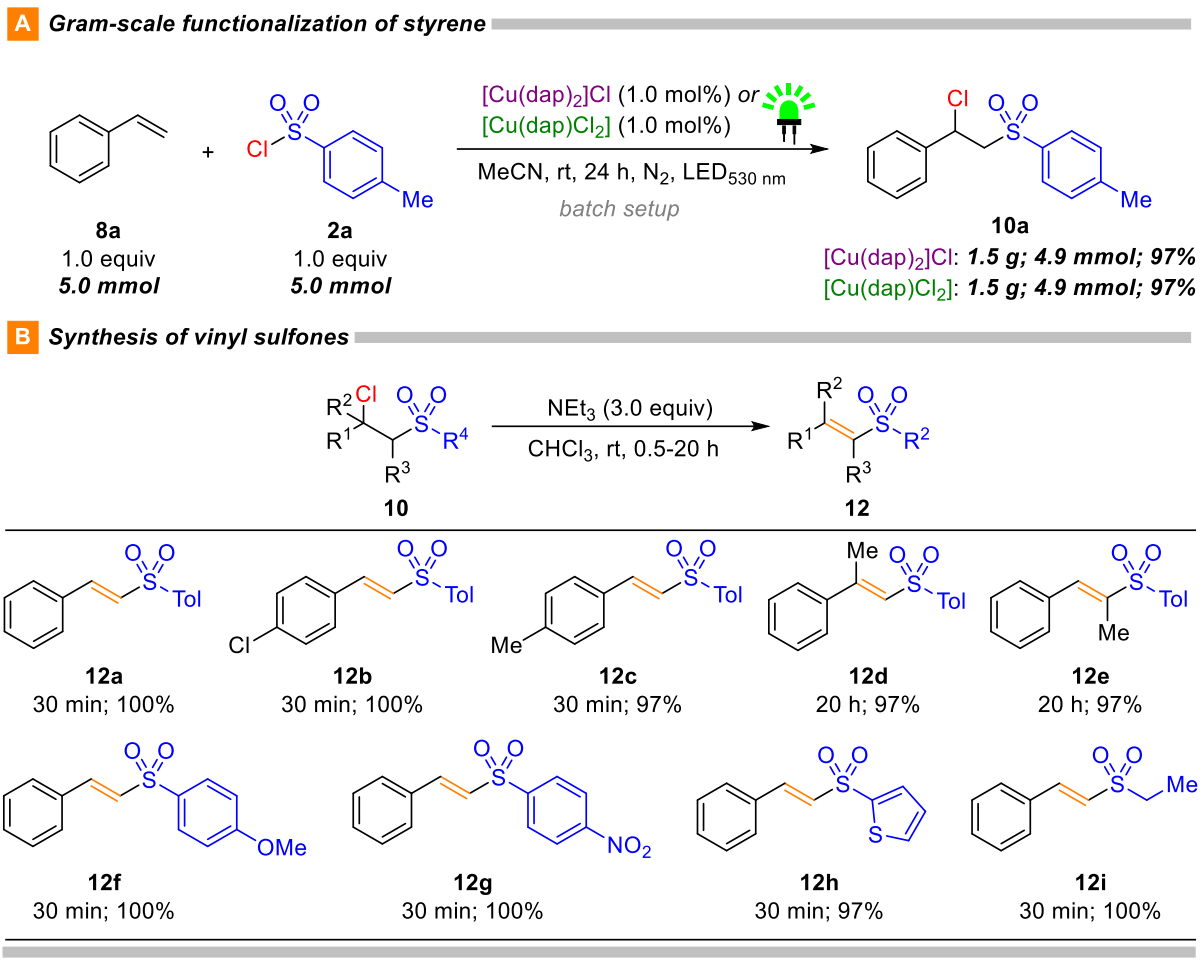


Scheme 9. Comparison of different photocatalysts for photochemical chlorosulfonylation. *Reaction conditions*: Alkene **8** (0.5 mmol, 1.0 equiv), sulfonyl chloride **2** (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) for $[Cu(dap)_2]Cl$, $[Cu(dap)Cl_2]$ and eosin Y and irradiation at 455 nm (blue LED) for $[Ru(bpy)_3]Cl_2$, *fac*-$[Ir(ppy)_3]$ and [**Ir-F**] under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]Reaction time 48 h.

To further prove the necessity of the unique character of copper photocatalyst in the title reaction, we settled out to test selective representative examples with other well-established photocatalysts (Scheme 9). As already discussed in Chapter 2.3, $[Ru(bpy)_3]Cl_2$, *fac*-$[Ir(ppy)_3]$, $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ ([**Ir-F**]) and eosin Y proved to be far less effective in the title chlorosulfonylation reaction between styrene (**8a**) and tosyl chloride (**2a**). As eosin Y already failed in the transformation of the model substrates aiming in the synthesis of **10a**, no further screening was processed on the latter. Investigations on electronically variegated alkenes and sulfonyl chlorides revealed that again the established copper catalysts $[Cu(dap)_2]Cl$ and $[Cu(dap)Cl_2]$ clearly outperform ruthenium- and iridium-based photocatalysts. Notably, especially electron-rich alkenes transpired to be clear limitations for ruthenium- and iridium-based photocatalysts yielding e.g. **10i** or **10n** in only low yields. Another limitation for the latter seemed to be found when aliphatic sulfonyl chlorides like ethane sulfonyl chloride (E_{red} = -1.39 V vs. SCE)[18] aiming in the synthesis of **10af** were subjected to the reaction conditions. While the reduction potentials of $[Ru(bpy)_3]Cl_2$ ($E_{Ru(III)/Ru(II)^*}$ = -0.81 V vs. SCE)[4b] and [**Ir-F**] ($E_{Ir(IV)/Ir(III)^*}$ = -0.89 V vs. SCE)[4b] are far out of reach for SET with the ATRA reagent and hence only very low yields are observed, the reduction potential of *fac*-$[Ir(ppy)_3]$ ($E_{Ir(IV)/Ir(III)^*}$ = -1.73 V vs. SCE)[4b] would be well in reach for SET to ethane sulfonyl chloride. However, still only a moderate yield of **10af** is observed for *fac*-$[Ir(ppy)_3]$, showcasing that not only the redox potential itself but also the ability of copper photocatalysts to interact with incipient radical intermediates in a rebound process (see Chapter 2.8) plays a key role in such photochemical ATRA processes. In a similar manner, secondary aliphatic sulfonyl chloride could not be efficiently transformed in the desired product **10ag** when ruthenium- or iridium-based photocatalysts were employed in the reaction. Lastly, contrasting $[Cu(dap)_2]Cl$ and $[Cu(dap)Cl_2]$ accessing the chlorosulfonylation of heterocyclic sulfonyl chlorides to yield **10ai** in excellent yields, ruthenium- or iridium-based photocatalysts again only gave **10ai** in moderate yields. Photoproducts **10l** and **10an** being not accessible by copper catalysts, in the same way failed to be produced with ruthenium- and iridium-based photocatalysts. In general, for all cases both copper catalysts confirmed the initial screening results in Chapter 2.3 clearly outperforming ruthenium-, iridium- and organic dye-based photocatalysts and hence demonstrated its unique character in the visible-light mediated chlorosulfonylation of alkenes.

2.6 Gram-Scale Functionalization and Synthetic Utility

Next, we set out to demonstrate the viability of the method for preparative purposes. Thereby, chlorosulfonylation product **10a** was obtained on a multigram scale in a simple batch setup with an excellent yield of 97% for both copper catalysts without the need to prolong the reaction time or to increase the catalyst loading (Scheme 10, A).

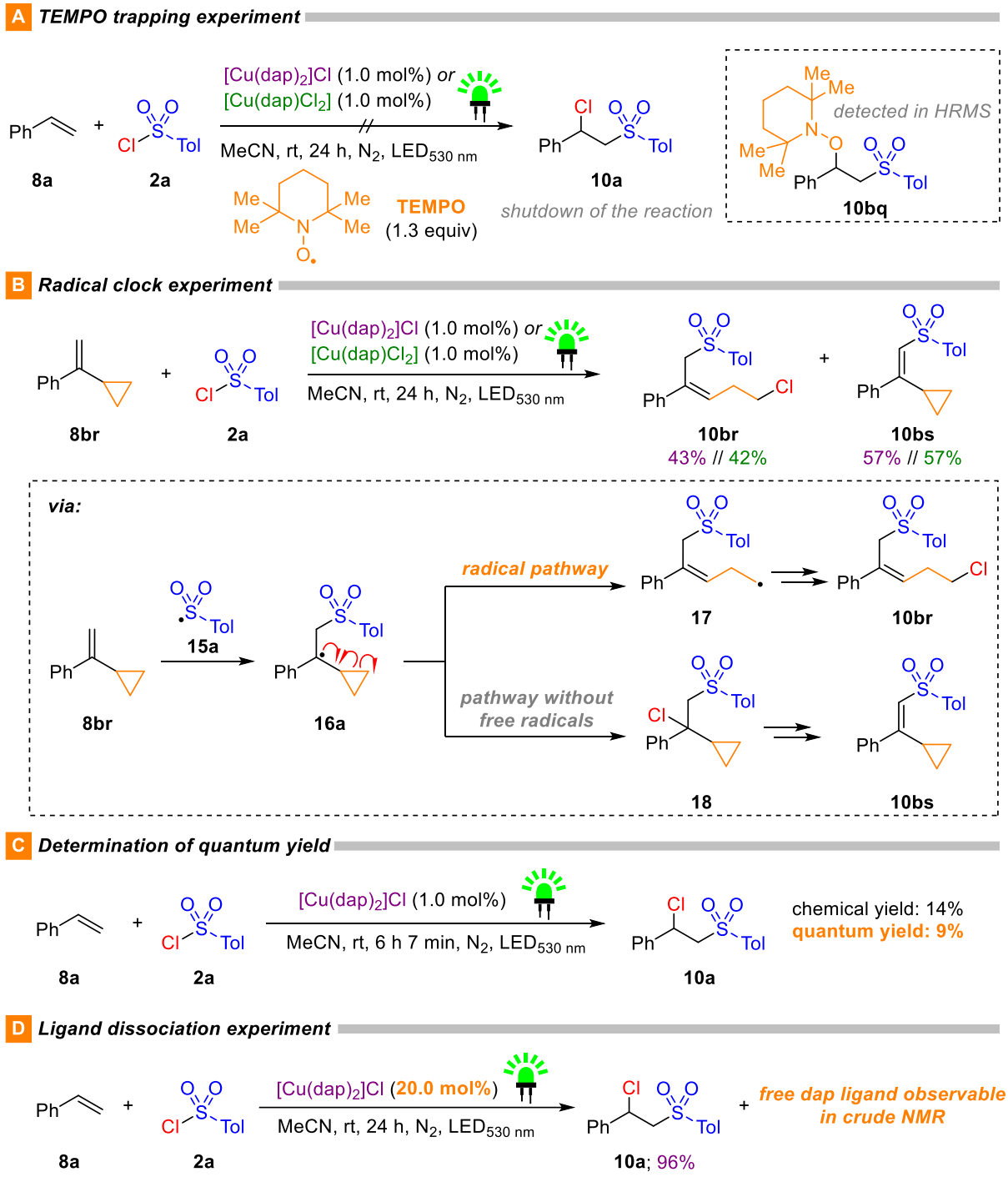


Scheme 10. Gram-scale reaction and synthetic utility of chlorosulfonilation products **10**. *Reaction Conditions*: (A) Styrene (**8a**) (5.0 mmol, 1.0 equiv), tosyl chloride (**2a**) (5.0 mmol, 1.0 equiv), catalyst (50.0 µmol, 1.0 mol%) in MeCN (anh., degassed, 20.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. (B) Chlorosulfone **10** (0.2 mmol, 1.0 equiv), NEt_3 (0.6 mmol, 3.0 equiv) in $CHCl_3$ (2.0 mL, 0.1 M) under air atmosphere at room temperature (25 °C) for indicated time. Stereochemistry was assigned by $^3J_{HH}$ coupling constants in ^{1}H-NMR spectroscopy or in analogy to literature for **12d**[19] and **12e**[20].

The obtained chlorosulfonylation products **10** can smoothly and quantitively be converted by elimination to their corresponding vinyl sulfones **12** (Scheme 10, B), representing a privileged class of synthetic synthons and a key motif frequently found in in many biologically active compounds.[21]

2.7 Mechanistic Studies

Having addressed synthetic aspects, we next aimed for deeper mechanistic insights into the underlying reaction mechanism and hence carried out several mechanistic experiments (Scheme 11).



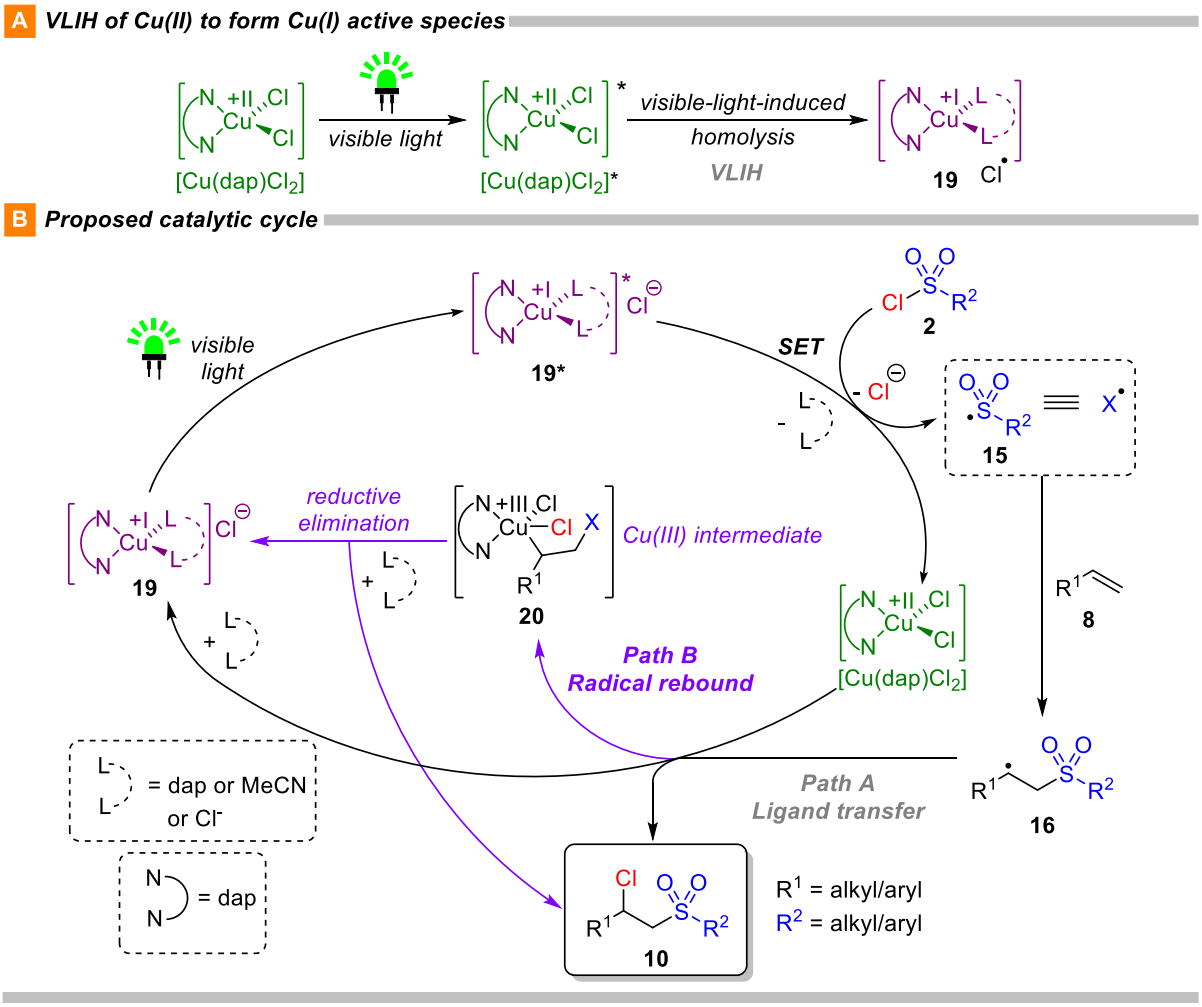
Scheme 11. Mechanistic studies on the photochemical chlorosulfonylation. *Reaction conditions:* For the detailed experiments and analysis of the obtained data, please see my Master thesis.[1]

Radical trapping experiments with TEMPO revealed a complete shutdown of the catalytic cycle with concurrent formation of the TEMPO-trapping adduct **10bq** being in line with a mechanistic pathway including radical intermediates (Scheme 11, A). Along the same lines, the reaction of radical clock substrate **8br** with tosyl chloride (**2a**) under the established reaction conditions lead to formation of **10br** for both catalysts, which is in agreement with radical intermediate **16a** rapidly undergoing radical-mediated ring-opening to **17** and finally delivering the observed product **10br** (Scheme 11, B). The quantum yield of the reaction was found to be 9% disputing a photoinitiated radical chain process, which typically shows values greater than 100% being also consistent with the results of the AIBN experiment in Chapter 2.3 (Scheme 11, C). Nevertheless, such interpretations must be made with cautions since it does not consider the participation of other photoinitiated shorter chain processes or processes not leading to product formation. Ligand dissociation experiments (Scheme 11, D) should proof whether the photoactive $[Cu(dap)_2]Cl$ catalyst can lose one dap ligand during the photoprocess and thus opening up a vacant coordination side for a possible radical rebound to the metal center. Therefore, the model reaction was carried out with a high catalyst loading of 20.0 mol% enabling the detection of reasonable amount of free dap ligand after the photoreaction by ^{1}H-NMR spectroscopy. Indeed, analysis of the crude NMR revealed the emersion of free dap ligand after the chlorosulfonylation reaction undergirding the aforementioned mechanistic pathway. Control experiments proved the photostability of $[Cu(dap)_2]Cl$ in the absence of the substrates.

2.8 Proposed Reaction Mechanism

Taking the preceding mechanistic investigations into consideration, we propose a rebound (Scheme 12, Path B) or ligand transfer mechanism (Scheme 12, Path A), showcasing the unique character of copper photocatalysts to access heretofore elusive reaction pathways (Scheme 12). When the reaction was performed with the corresponding Cu(II)-complex $[Cu(dap)Cl_2]$ we nevertheless assume an in-situ reduction of $[Cu(dap)Cl_2]$ to a catalytically active Cu(I)-species **19** through visible-light-induced homolysis of the Cu(II)-Cl bond in $[Cu(dap)Cl_2]^*$ (VLIH) (Scheme 12, A).[22] Intermediate **19** might be coordinated either by another dap ligand with chloride as a counteranion (corresponds to the used Cu(I)-complex) or by the solvent. After excitation of the latter by visible light, single-electron transfer (SET) to sulfonyl chloride **2** generates the corresponding sulfonyl radical **15** upon oxidation of the catalyst forming the Cu(II)-species $[Cu(dap)Cl_2]$, which has been independently synthesized in this study and found to be a capable photocatalyst for the title transformation as well. Sulfonyl radical **15** adds to

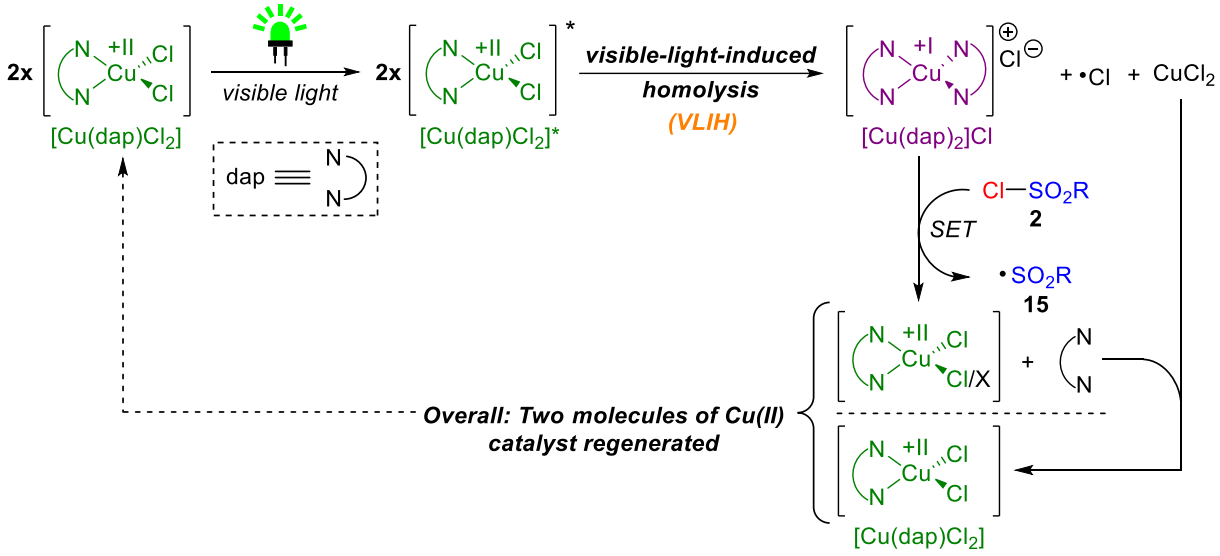
alkene **8** leading to the *C*-centered radical intermediate **16**, which can either take back chlorine from [Cu(dap)Cl_2] concurrent with the regeneration of the catalyst **19** (Ligand Transfer, Path A) or bind back to the Cu(II)-species [Cu(dap)Cl_2] (Radical Rebound, Path B) being a persistent radical itself. The latter leads to a Cu(III)-intermediate **20**, which can release the final product **10** upon reductive elimination regenerating the active catalyst by trapping free dap ligand.



Scheme 12. Plausible reaction mechanism for copper-catalyzed photochemical chlorosulfonylation.

The exact stoichiometry of the visible-light-induced homolysis (VLIH) to activate the Cu(II)-catalyst [Cu(dap)Cl_2] for photochemical Cu(I)-chemistry is depicted in Scheme 13. Two molecules of [Cu(dap)Cl_2] get excited by visible-light undergoing Cu(II)-Cl homolytic bond cleavage. Thereby, photoactive [Cu(dap)$_2$]Cl is formed by picking up one dap ligand under concurrent generation of $CuCl_2$. After SET of the excited Cu(I) active species [Cu(dap)$_2$]Cl to the ATRA reagent **2**, the corresponding Cu(II)-catalyst [Cu(dap)Cl_2] is regenerated upon release of dap ligand, which is rapidly coordinated to the previously generated $CuCl_2$. Hence,

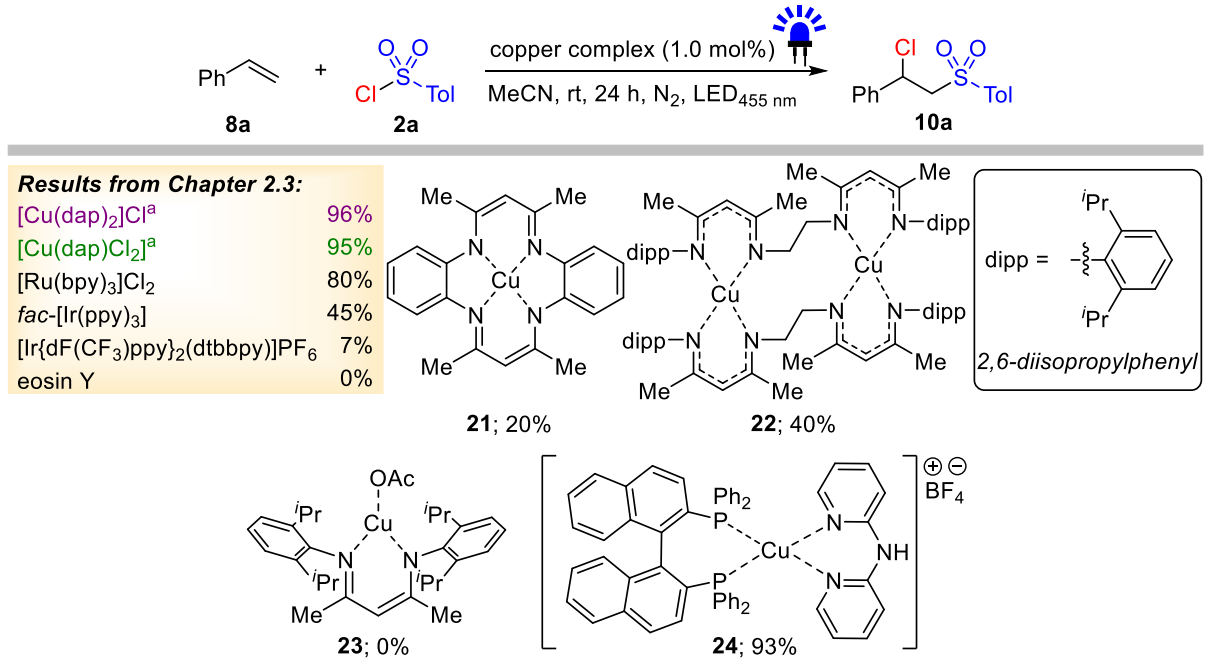
overall, two molecules of [Cu(dap)Cl_2] are regenerated representing the starting point of this mechanistic consideration.



Scheme 13. Exact stoichiometry for the activation of [Cu(dap)Cl_2] by visible-light-induced homolysis (VLIH).

2.9 Exploring New Types of Copper Complexes

Besides [Cu(dap)$_2$]Cl and [Cu(dap)Cl_2], several new type of copper complexes were tested for potential activity as photocatalysts in the title transformation (Scheme 14).



Scheme 14. Exploring new types of copper complexes in photochemical chlorosulfonylation. *Reaction conditions*: Styrene (**8a**) (0.5 mmol, 1.0 equiv), tosyl chloride (**2a**) (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]Irradiation at 530 nm (green LED).

UV-vis absorption measurements revealed that excitation in the blue region (455 nm) should be sufficient for excitation of the shown complexes.[1] While $[Cu(dap)_2]Cl$ and $[Cu(dap)Cl_2]$ showed excellent yields in the desired transformation, copper complexes **21**, **22** and **23**, previously synthesized by the inorganic department, appeared to be unsuitable to efficiently promote visible-light mediated chlorosulfonylation between styrene (**8a**) and tosyl chloride (**2a**). Prof. Alan R. Cabrera and his co-worker Marco Henriquez synthesized a series of five new heteroleptic Cu(I)-complexes of the type $[Cu(dpa)(P,P)]BF_4$ based on dipyridylamine (dpa) as *N*,*N*-ligand and commercial diphosphines as *P*,*P* ancillary ligands and examined their photophysical properties. In cooperation with our group, we also investigated the capacity of the complexes in photoredox catalysis. Indeed, the complex [Cu(dpa)(BINAP)] (**24**) proved to be effective in the desired reaction yielding photoproduct **10a** in 93% yield constituting an attractive alternative to well-established phenanthroline-based copper complexes. The detailed structural characterization (NMR, FTIR, HRMS and XRD), photophysical evaluations (cyclic voltammetry, UV-vis spectroscopy, steady-state and time-resolved luminescence and TD-DFT calculations), as well as the complete study on different photoredox catalyzed reactions can be found in our joint publication.[23]

2.10 Conclusion

In conclusion, we have developed a highly efficient, copper-catalyzed photocatalytic protocol to transform a broad scope of alkenes and alkynes to their corresponding vicinal chlorosulfonylated products. The latter can smoothly be converted in quantitative yields to the analog vinyl sulfones representing key synthons in organic synthesis and frequently occurring motifs in natural organic compounds and drug candidates with intriguing biological properties. Moreover, the oxidation- and bench-stable Cu(II)-complex $[Cu(dap)Cl_2]$ was for the first time introduced in visible-light photocatalysis being not just beneficial from an economic point of view as only half amount of dap ligand is required compared to well-established $[Cu(dap)_2]Cl$ but also opening-up new avenues for Cu(II)-catalyzed photoredox catalysis through visible-light-induced homolysis (VLIH). Moreover, both copper catalysts outperformed commonly used ruthenium-, iridium- and organic dye-based photocatalysts owing to their ability to interact with transient radical intermediates in their inner-coordination sphere. In contrast to activated olefins, in cooperation with two co-workers Dr. Asik Hossain and Dr. Eugen Lutsker, it was found that utilizing stochiometric amounts of base also can open up the substrate class of unactivated alkenes for the title reaction by preventing the active catalyst from poisoning.

2.11 References

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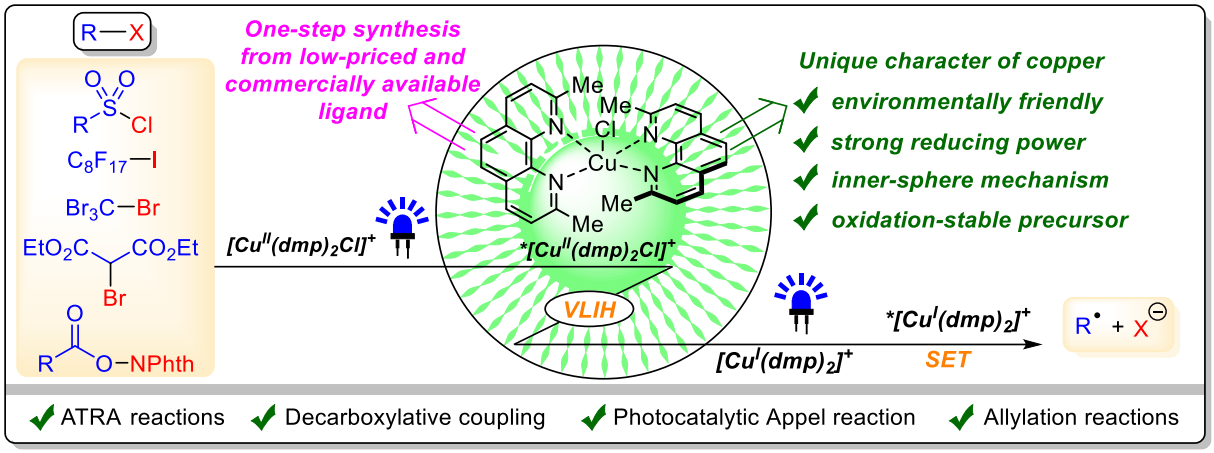
Chapter 3

Introducing [Cu(dmp)$_2$Cl]Cl to Photocatalysis‡

3.1 Abstract

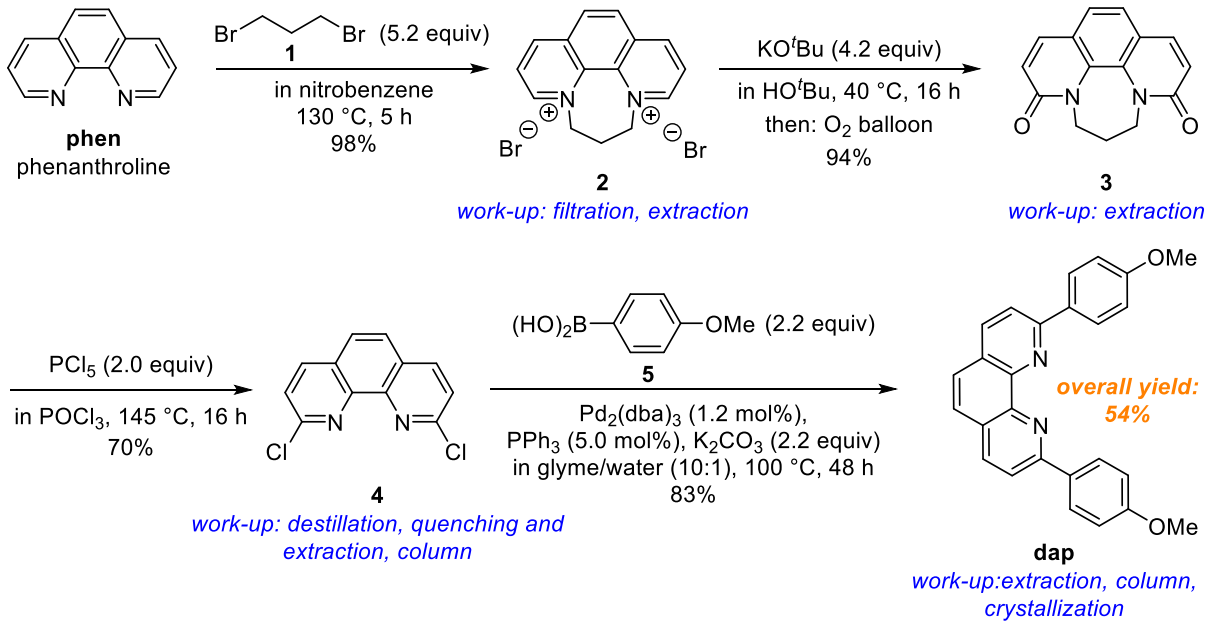


In Chapter 3, we introduce for the first time the Cu(II)-complex [Cu(dmp)$_2$Cl]Cl as an oxidation- and bench-stable photocatalyst for activation by visible-light-induced homolysis (VLIH) to undergo Cu(I)-photoredox catalysis. The complex is highly efficient and considerably more cost-effective compared to previously established Cu(I) photocatalysts as it is synthesized from commercially available starting materials in one step. Its performance and efficiency are demonstrated within a broad scope of atom transfer radical addition (ATRA) reactions, allowing rapid 1,2-difunctionalization of alkenes as well as for decarboxylative coupling, for a photocatalytic Appel reaction and for photochemical allylation reactions. Moreover, the utility of the catalyst is presented by gram-scale functionalizations of styrene, thus suggesting [Cu(dmp)$_2$Cl]Cl to be a low-priced alternative catalyst. Furthermore, this study provides UV-vis evidence on the mechanism for the VLIH activation of Cu(II)-complexes opening up novel avenues for photocatalysis. In cooperation with the Prof. Castellano group, combined results from static spectroscopy, ultrafast transient absorption and paramagnetic resonance spin trapping experiments strongly support VLIH occurring in <100 fs.

‡ This chapter is partially based on: Engl, S; Reiser, O. *Eur. J. Org. Chem.* **2020**, 1523-1533. (VIP Paper). And on: Fayad, R.; Engl, S.; Danilov, E. O.; Hauke, C. E.; Reiser, O.; Castellano, F. N. *J. Phys. Chem. Lett.* **2020**, *11*, 5345-5349.

3.2 Introduction

In recent years, visible-light mediated photoredox catalysis has mandated a paradigm shift in synthetic organic chemistry allowing carbon-carbon and carbon-heteroatom bond formations under mild an ecologically benign reaction conditions.[1] By now, the most commonly employed photocatalysts are represented by ruthenium- or iridium-based metal complexes, featuring desired aspects for photocatalysts like photostability, long excited state lifetimes, strong absorption in the visible region and high redox potentials. However, high costs, potential toxicity and the scarcity of the corresponding metal salts display major drawbacks of this class of catalysts,[2] while organic dye based photocatalysts provide low-cost and metal-free alternatives but suffer in general from lower photostability.[3] Given the imperative need to develop more alternatives, copper complexes gained great importance in the field of photoredox catalysis. Besides the economic benefits on the one hand, copper complexes also opened up unique reaction modes due to their ability to easily undergo structural redistribution and ligand exchange.[4] However, although the copper salts are low-priced and highly economic, most copper complexes suffer from time- and price-consuming ligand synthesis.[4,5] For instance, $[Cu(dap)_2]Cl$ being the leading representative among copper photocatalysts, calls for a four-step ligand synthesis including a Pd-catalyzed cross-coupling reaction (Scheme 1).[6–8]

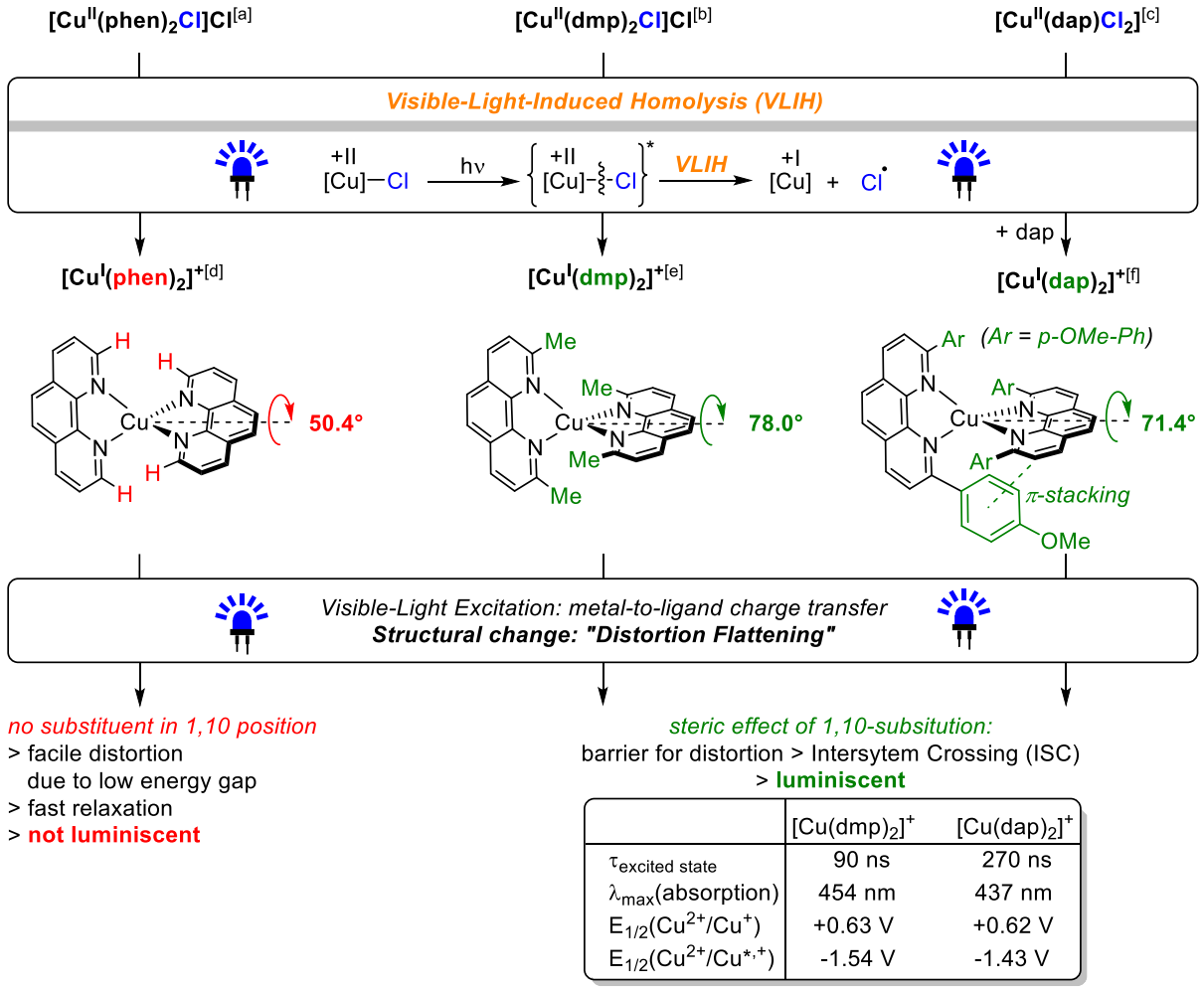


Scheme 1. Synthesis of dap ligand by Reiser and co-workers.[8]

In Chapter 2, we reported a visible-light mediated chlorosulfonylation of alkenes and alkynes utilizing besides the established Cu(I)-complex $[Cu(dap)_2]Cl$ also the corresponding Cu(II)-

complex [Cu(dap)Cl_2].[9] The latter proved to be activated by visible-light-induced homolysis (VLIH) to form a catalytically active Cu(I)-species, which showed high efficiency in the title reaction, but being at the same time considerable more cost-efficient as only half amount of the dap ligand is required compared to [Cu(dap)$_2$]Cl. Based on this study[9] in chapter 2, we now aimed in chapter 3 for the search of new Cu(II)-complexes for photoredox catalysis utilizing alternative ligands that would be commercially available or could be easily accessed. Additionally, we aimed to gain deeper mechanistic insights and proof of our previously proposed concept of VLIH.

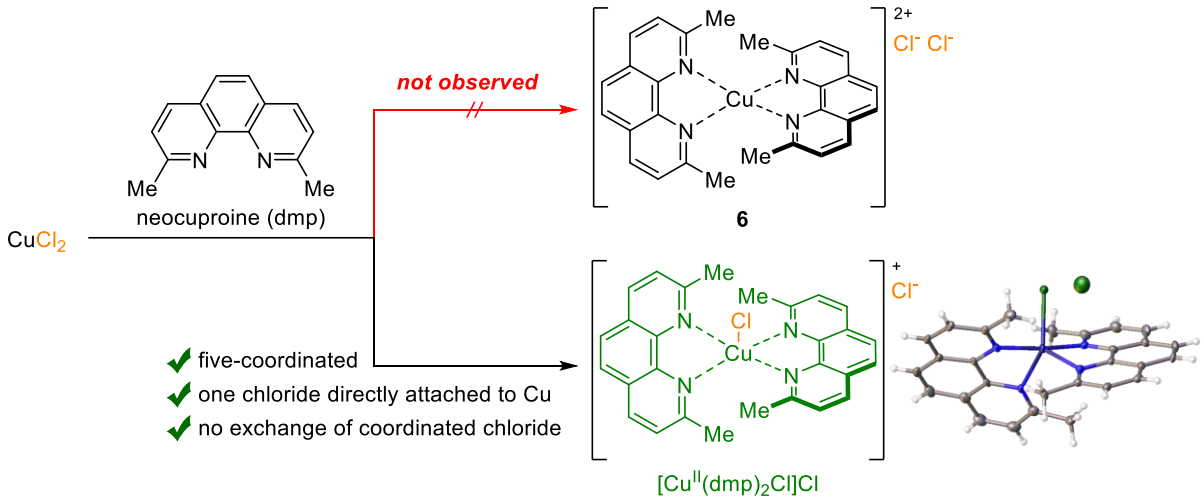
Arguably the most readily available Cu(II)-phenanthroline complex would be [Cu(phen)$_2$Cl]Cl, which can be prepared according to literature from $CuCl_2$ and 1,10-phenanthroline (phen).[10] Following the concept of VLIH of Cu(II)-complexes in photocatalysis (see Chapter 2), [Cu(phen)$_2$Cl]Cl should be in-situ reduced to the corresponding Cu(I)-complex acting as the catalytically active species in ATRA reactions studied (Scheme 2).



	[Cu(dmp)$_2$]$^+$	[Cu(dap)$_2$]$^+$
$\tau_{excited\ state}$	90 ns	270 ns
λ_{max}(absorption)	454 nm	437 nm
$E_{1/2}(Cu^{2+}/Cu^{+})$	+0.63 V	+0.62 V
$E_{1/2}(Cu^{2+}/Cu^{*,+})$	-1.54 V	-1.43 V

Scheme 2. Comparison of Cu(II)- and the corresponding Cu(I)-complexes in photocatalysis. [a]Ref.[10]; [b]Ref.[11]; [c]Ref.[12]; [d]Ref.[13]; [e]Ref.[14]; [f]Ref.[15]

Upon visible-light irradiation, the following metal-to-ligand charge transfer (MLCT) leads to a photoinduced "flattening" of the geometry in the excited state. However, due to the lack of substitution in the 1,10-position of the phen ligand, $[Cu(phen)_2]^+$ is conformationally mobile and thus prone to rapidly return to its electronical ground state. Consequently, $[Cu(phen)_2]^+$ shows no luminescence.[16] In line, no ATRA reaction between styrene (**7a**) and tosyl chloride (**8a**) was observed employing $[Cu(phen)_2Cl]Cl$ as a potential photocatalyst (Chapter 3.3, table 1, entry 1), contrasting $[Cu(dap)Cl_2]$ catalyzing the desired ATRA process in 95% yield (Chapter 3.3, table 1, entry 3). In the latter the steric influence of the aryl-substitution in the 1,10-position prevents rapid geometrical relaxation and thus quenching of the excited state allowing for intersystem crossing (ISC) to attain a stable triplet excited state, which then can act as the reductant in the following photoprocess. Aiming at rigidifying the coordination geometry and thus extending the excited state lifetime but still simplifying the ligand, we next switched to $[Cu(dmp)_2Cl]Cl$, readily prepared form $CuCl_2$ and two equivalents of dmp, following the protocol recently developed by Kloo and co-workers (Scheme 3).[11]



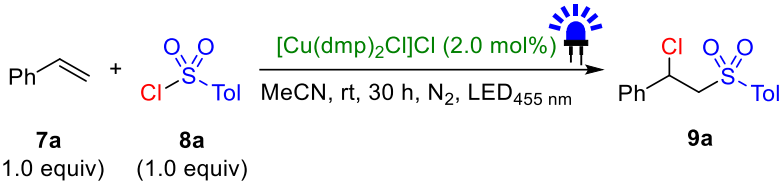
Scheme 3. Synthesis of $[Cu(dmp)_2Cl]Cl$ reported by Kloo and co-workers.[11] The shown X-ray structure of $[Cu(dmp)_2Cl]Cl$ was obtained by us. For details, please see experimental part.

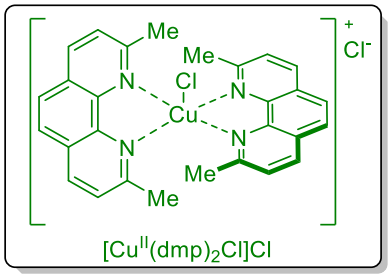
Indeed, the corresponding Cu(I)-complex $[Cu(dmp)_2]^+$ meets desired requirements like luminescence and an even higher excited state reduction potential compared to that of $[Cu(dap)_2]^+$ (Scheme 2). However, although these photochemical characteristics of $[Cu(dmp)_2]^+$ were reported,[17] there have been only few applications in synthetic organic photoredox catalysis reflected by a small number of reports utilizing $[Cu(dmp)]^+$ as part of screening efforts for reaction optimization.[13,18] Hence, we were wondering in this chapter, if $[Cu(dmp)_2Cl]Cl$ can serve as an oxidation- and bench-stable precursor for VLIH to $[Cu(dmp)_2]^+$, which then can act as Cu(I)-photoredox catalyst.

3.3 Reaction Optimization

We started the investigations with our previously reported chlorosulfonylation of alkenes **7** (Chapter 2). As already discussed in the introduction, [Cu(phen)$_2$Cl]Cl is not able to instigate the desired photoreaction as the complex does not show any luminescence under visible-light irradiation (Table 1, entry 1). Gratifyingly, [Cu(dmp)$_2$Cl]Cl proved indeed to be a capable catalyst for the title reaction between styrene (**7a**) and tosyl chloride (**8a**), delivering the desired product **9a** in up to 92% isolated yield (Table 1, entries 4-7) and thus showcasing its role as economic alternative compared to [Cu(dap)$_2$]Cl and [Cu(dap)$_2$]Cl, which showed similar yields (Table 1, entries 2-3).

Table 1. Reaction optimization.





Entry	Variations from "standard"	NMR-yield[a] of **9a**
1	[Cu(phen)$_2$Cl]Cl (1.0 mol%)	nr
2[b]	[Cu(dap)$_2$]Cl (1.0 mol%); green LED (λ = 530 nm)	96%
3[b]	[Cu(dap)Cl$_2$] (1.0 mol%); green LED (λ = 530 nm)	95%
4	1.0 mol% catalyst; green LED (λ = 530 nm)	75%
5	2.0 mol% catalyst; green LED (λ = 530 nm)	89%
6	1.0 mol% catalyst	86%
7	---	92%[c]
8	no catalyst	nr
9	no light	nr
10	AIBN (10.0 mol%); T = 80 °C	nr
11	CuCl$_2$ (10.0 mol%)	nr
12	dmp (10.0 mol%)	4%
13	CuCl$_2$ (5.0 mol%) + phen (10.0 mol%)	nr

Reaction conditions: Styrene (**7a**) (0.5 mmol, 1.0 equiv), tosyl chloride (**8a**) (0.5 mmol, 1.0 equiv), [Cu(dmp)$_2$Cl]Cl (10.0 µmol, 2.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 30 h. [a]NMR yield using diphenoxymethane as an internal standard. [b]Results from Chapter 2.[9] [c]Isolated yield.

Control experiments omitting either the catalyst or the light showed no conversion in the title reaction between styrene (**7a**) and tosyl chloride (**8a**) (Table 1, entries 8-9), while attempts for thermal initiation with AIBN under reflux temperature failed and resulted in no product formation as well (Table 1, entry 10). Utilizing $CuCl_2$ or dmp ligand as potential stand-alone catalysts nevertheless were not able to promote the desired ATRA reaction (Table 1, entries 11-12). Notably, while previously reported $[Cu(dap)_2]Cl$ or $[Cu(dap)Cl_2]$ sufficiently catalyzed the title reaction with 1.0 mol% catalyst loading (Table 1, entries 2-3), $[Cu(dmp)_2Cl]Cl$ shows slightly higher yields of 92% with a loading of 2.0 mol% (Table 1, entry 7) compared to 86% yield for 1.0 mol% catalyst loading (Table 1, entry 6). However, given the low costs and high availability of $[Cu(dmp)_2Cl]Cl$ prompted us to explore the following substrate scope with best-optimized conditions (Table 1, entry 7), while selected examples still were also tested with lower catalyst loading to probe the limit of the catalytic activity and allow a better comparison with $[Cu(dap)_2]Cl$ possible.

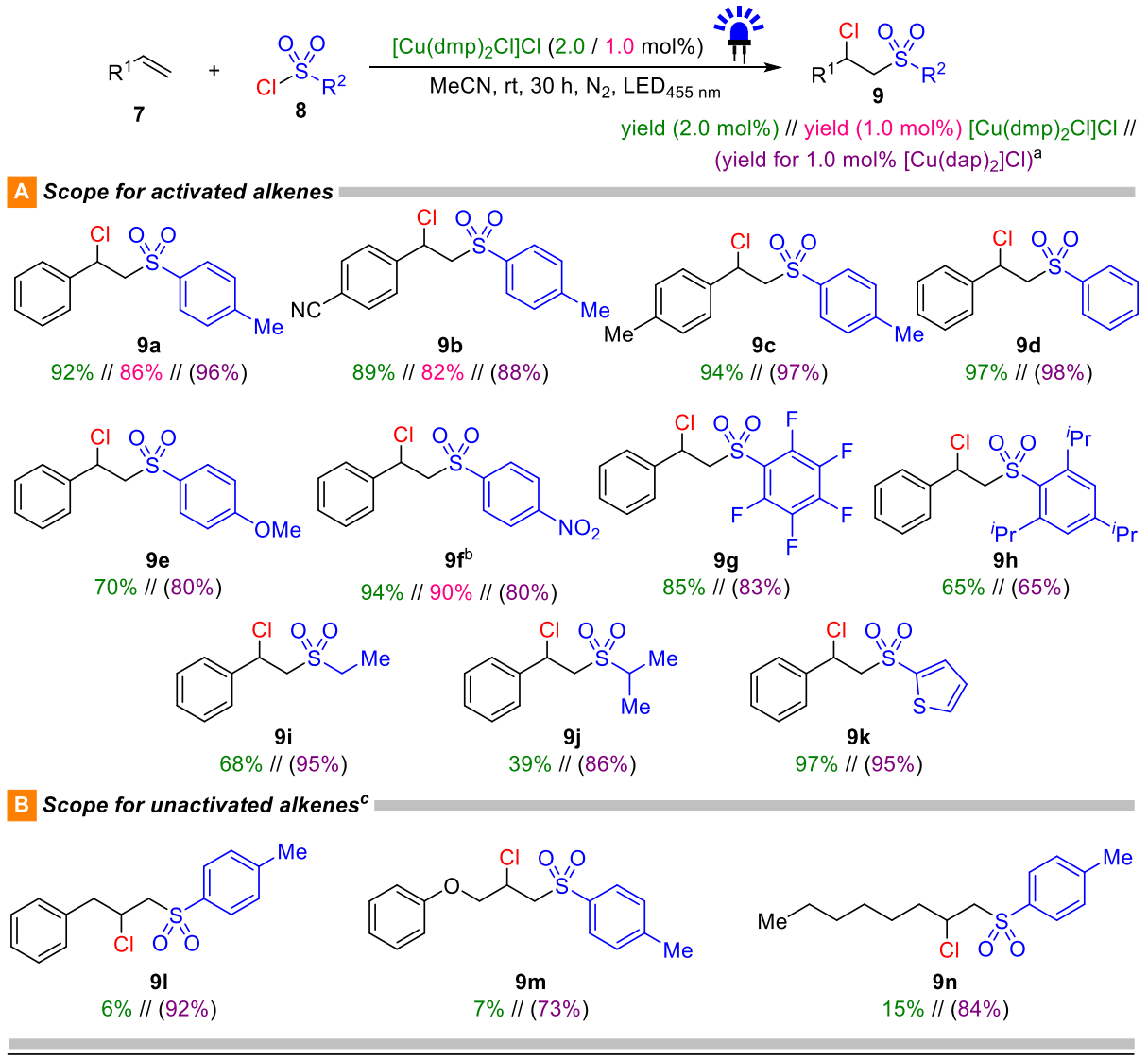
3.4 Substrate Scope

In this chapter the performance and efficiency of the Cu(II)-catalyst $[Cu(dmp)_2Cl]Cl$ is evaluated within a broad scope of different atom transfer radical addition (ATRA) reactions, allowing the rapid 1,2-difunctionalization of alkenes as well as on other photocatalytic test reactions, including decarboxylative coupling, Appel reaction and allylation reactions.

3.4.1 Photochemical Chlorosulfonylation

Hence, we started our substrate screening with the visible-light mediated chlorosulfonylation of alkenes **7** optimized in the previous chapter (Scheme 4). We were pleased to see that both electron-rich as well as electron-poor styrene derivatives worked well in the desired transformation giving rise to the corresponding products **9b** and **9c** in high yields comparable to the yield utilizing $[Cu(dap)_2]Cl$. In the same way, electronically variegated sulfonyl chlorides were well tolerated, thus accessing products **9d**-**9g** in high yields, in the case of **9f** even outperforming the established $[Cu(dap)_2]Cl$ system. Increasing the steric impact aiming in the synthesis of **9h** did not alter the reactivity allowing the isolation of the desired product **9h** in good yields. However, when utilizing alkyl-substituted sulfonyl chlorides a significant decrease in yield of **9j** was observed, while the primary ethane sulfonyl chloride still gave the desired product **9i** in synthetically useful yield of 65%. Heterocyclic sulfonyl chlorides appeared to be

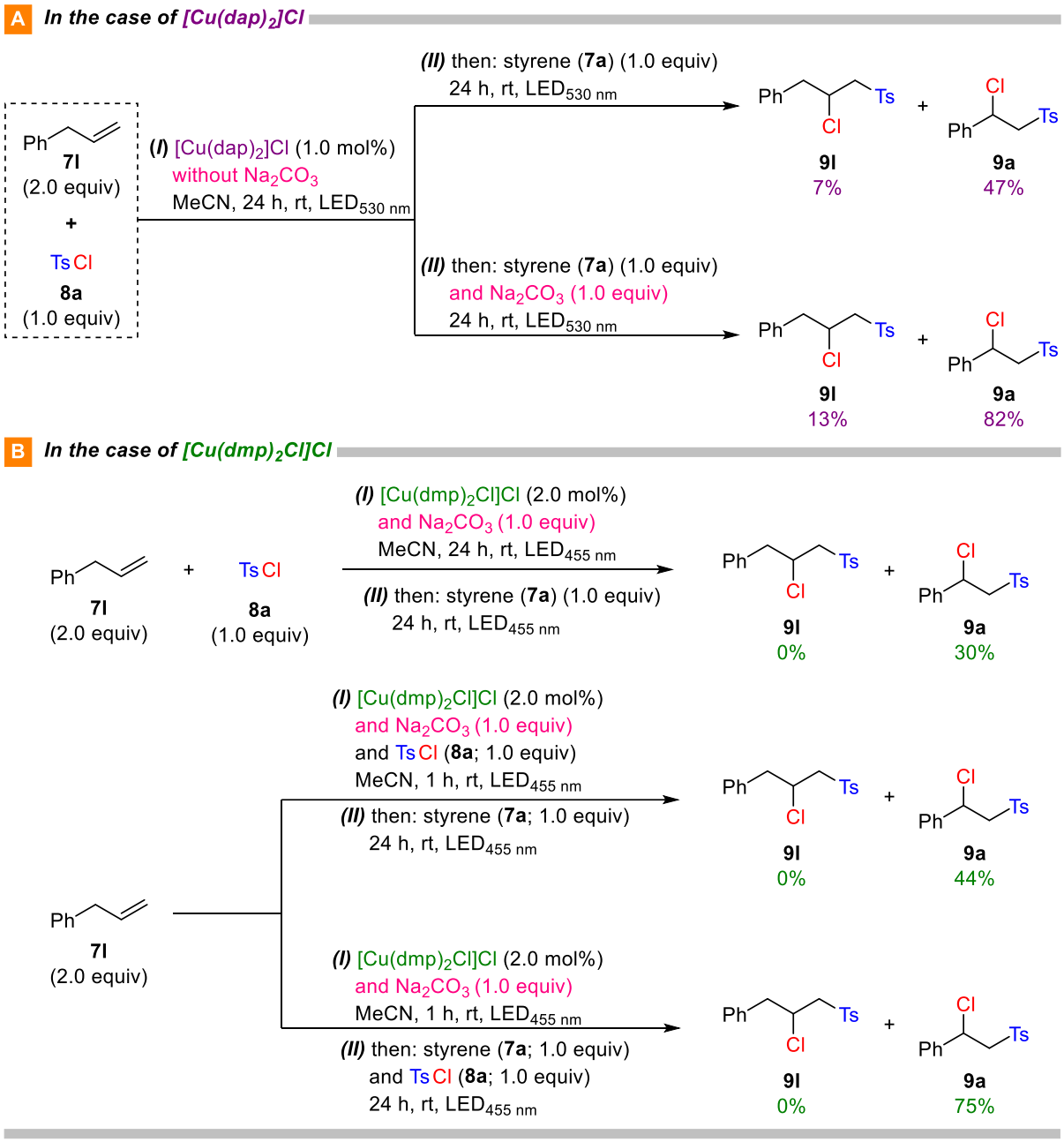
suitable reaction partners yielding the corresponding product **9k** in an almost quantitative yield. In our previous study[9] (see Chapter 2), also unactivated alkenes were accessible in the developed chlorosulfonylation protocol with [Cu(dap)$_2$]Cl adding one equivalent of Na_2CO_3 as a base to prevent the catalyst from poisoning. Nevertheless, applying this modified protocol for [Cu(dmp)$_2$Cl]Cl only low yields of the desired products **9l**-**9n** were obtained (Scheme 4, B).



Scheme 4. Substrate scope for photochemical chlorosulfonylation. *Reaction conditions*: Alkene **7** (0.5 mmol, 1.0 equiv), sulfonyl chloride **8** (0.5 mmol, 1.0 equiv), [Cu(dmp)$_2$Cl]Cl (indicated amount) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 30 h. [a]Results from Chapter 2: [Cu(dap)$_2$]Cl (1.0 mol%) under irradiation at 530 nm (green LED)[9]. [b]Reaction time 48 h. [c]Alkene **7** (1.0 mmol, 2.0 equiv), Na_2CO_3 (0.5 mmol, 1.0 equiv) as an additive, reaction time 48 h.

Catalyst stability tests (Scheme 5) concluded a significant poisoning of the catalytically active species presumably due to the formation of acidic traces originating from sulfonyl chloride or sulfonyl radicals when not being efficiently trapped by the alkene. When a mixture of **7l** and

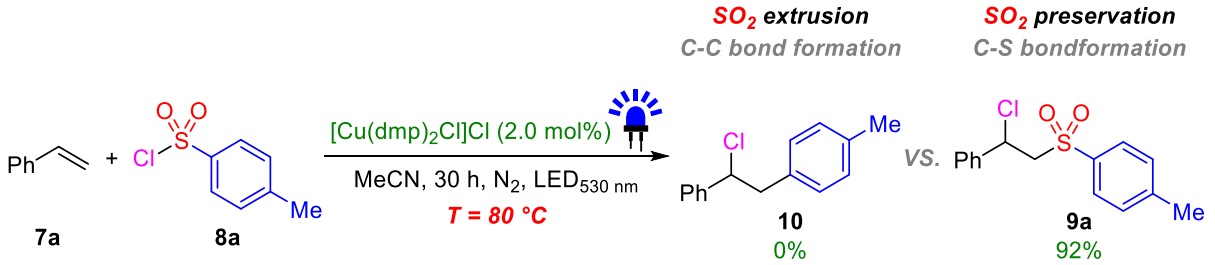
8a with Na_2CO_3 was irradiated for 24 h followed by the addition of styrene (**7a**) with continuing irradiation for another 24 h, the formation of only 30% of **9a** along with 0% of **9l** was observed (Scheme 5, B, first part), clearly contrasting the case of $[Cu(dap)_2]Cl$ where the same poisoning occurred without addition of Na_2CO_3 but could be effectively inhibited when the base was added together with styrene (**7a**) (Scheme 5, A).



Scheme 5. Catalyst stability tests in the chlorosulfonylation of unactivated alkenes **7** for $[Cu(dap)_2]Cl$ and $[Cu(dmp)_2Cl]Cl$. *Reaction conditions*: Alkene **7** (indicated amount), sulfonyl chloride **8a** (0.5 mmol, 1.0 equiv), catalyst (indicated amount) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at the indicated wavelength under N_2 atmosphere at room temperature (25 °C) for indicated time. Addition of reactants in step (II) was done under a slight nitrogen overpressure. Yields were determined from the crude ^{1}H-NMR using diphenoxymethane as an internal standard.

These results indicate the protective role of Na_2CO_3 for $[Cu(dap)_2]Cl$, while no effect of base was observed for the $[Cu(dmp)_2Cl]Cl$ catalyst. To further investigate the time scale of poisoning, the same experiment was carried out with only one hour of irradiation before styrene (**7a**) was added (Scheme 5 B, second part). However, apparent poisoning of the catalyst within only one hour of irradiation time was recognized reducing the yield of the desired ATRA product **9a** to 44%. In contrast, when the catalyst was stirred for one hour under irradiation in the absence of tosyl chloride (**8a**), followed by addition of both reactants **7a** and **8a** together, no significant decrease in yield of **9a** was observed, clearly suggesting tosyl chloride (**8a**) to be the source of catalyst poisoning. It should be noted that no poisoning is observed for activated alkenes, being much more efficient radical acceptors than unactivated alkenes and thus apparently preventing catalyst poising originating from sulfonyl radicals as well.

Assuming sulfonyl chlorides **8** being also radical precursors for carbon-centered radicals after SO_2 extrusion under elevated temperature,[19] we next investigated a possible C-C bond formation in the ATRA reaction between styrene (**7a**) and tosyl chloride (**8a**) under reflux temperature. While in the case of $[Cu(dap)_2]Cl$ or $[Cu(dap)_2Cl]$ no SO_2 extrusion under such conditions was observed in my Master thesis,[20] also $[Cu(dmp)_2Cl]Cl$ only yielded the corresponding C-S bond formation (Scheme 6).

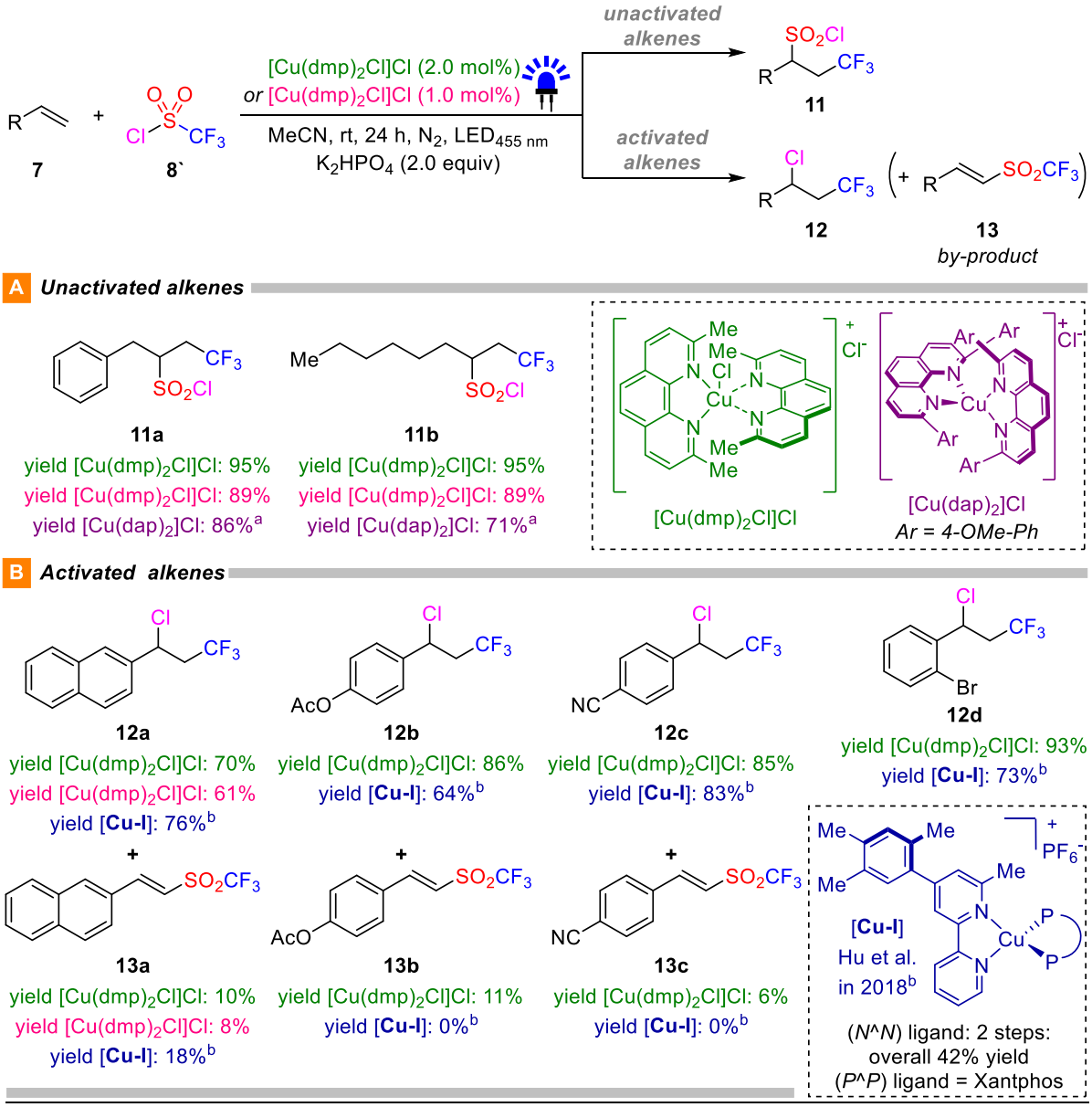


Scheme 6. High-temperature experiments for the chlorosulfonylation reaction. *Reaction conditions*: Styrene (**7a**) (0.5 mmol, 1.0 equiv), tosyl chloride (**8a**) (0.5 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (10.0 µmol, 2.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at 80 °C for 30 h. Yields were determined from the crude ^{1}H-NMR using diphenoxymethane as an internal standard.

3.4.2 Photochemical Trifluoromethylchlorosulfonylation

We next investigated the trifluoromethylchlorosulfonylation reaction of unactivated alkenes **7**, being a unique transformation for Cu(I)-photocatalysts[21,22] (Scheme 7, A). We were pleased to see that $[Cu(dmp)_2Cl]Cl$ was able to convert unactivated alkenes to the desired photoproducts **11a** and **11b** in almost quantitative yields even outperforming the established $[Cu(dap)_2]Cl$

catalyst. In both cases, lowering the catalyst loading to 1.0 mol% still furnished the desired products **11a** and **11b** in high yields of 89%, respectively.



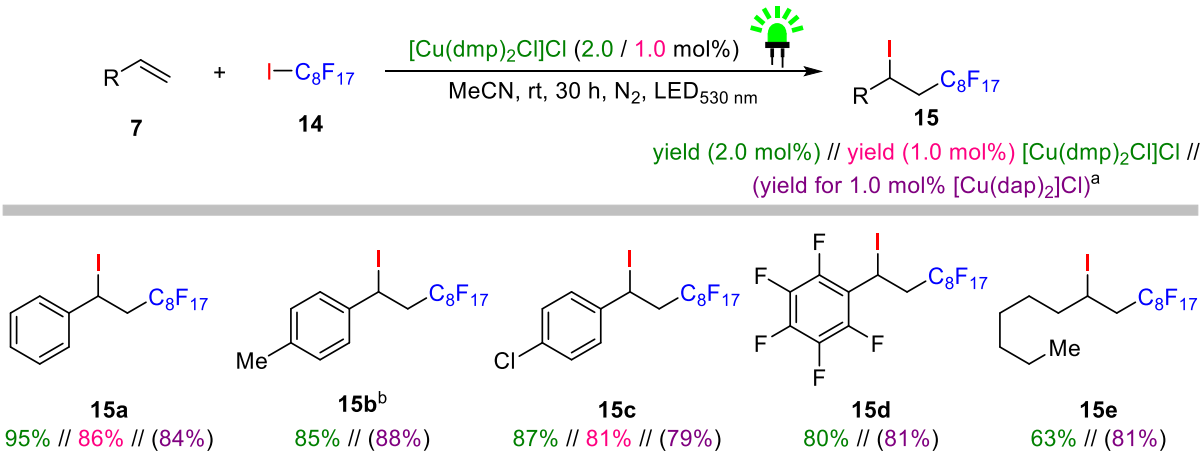
Scheme 7. Substrate scope for trifluoromethylchlorosulfonylation and chlorotrifluoromethylation reactions. *Reaction conditions*: Alkene **7** (0.5 mmol, 1.0 equiv), TfCl (**8`**) (1.0 mmol, 2.0 equiv), K_2HPO_4 (1.0 mmol, 2.0 equiv), [Cu(dmp)$_2$Cl]Cl (indicated amount) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]Results taken from a previous report[21]: [Cu(dap)$_2$]Cl (1.0 mol%) under irradiation at 530 nm (green LED). [b]Results from Hu and co-workers.[23]

Recently, Bissember et al. reported the influence of the ligand in several homoleptic 2,9-diaryl-1,10-phen Cu(I)-complexes in the trifluoromethylchlorosulfonylation reaction.[13] Surprisingly, they only report a yield of 24% of **11b** under similar reaction conditions using the corresponding Cu(I)-complex [Cu(dmp)$_2$]Cl, presumably due to the use of elevated temperature (45 °C) along

with highly volatile TfCl (**8**`) reagent. We next investigated the use of activated alkenes in the title reaction (Scheme 7, B). While [Cu(dap)$_2$]Cl appeared to be incompatible for the reaction with styrene derivatives instead leading to mixtures of various products (exception of *para*-nitrostyrene),[21] [Cu(dmp)$_2$Cl]Cl proved to be a suitable catalyst enabling the conversion of activated alkenes; however the corresponding chlorotrifluoromethylation products **12** upon SO_2 extrusion are observed. These findings are in accordance with two recent literature reports, who also observed copper-catalyzed chlorotrifluoromethylation when using various styrene derivatives.[23,24] While Xiao and co-workers[24] developed a thermal approach using $CuCl_2$ and base under 100 °C, Hu et al. reported a photoredox catalyzed protocol introducing a new copper catalyst [**Cu-I**] (for structure see Scheme 7, B).[23] However, although the phosphine ligand xantphos is commercially available, the introduced *N*,*N*-ligand suffers from a three-step synthesis with an overall yield of only 42% being clearly economically at a disadvantage compared to the [Cu(dmp)$_2$Cl]Cl system developed in this work.

3.4.3 Photochemical Iodoperfluorination

In 2018, the Reiser group successfully developed a visible-light mediated copper-catalyzed iodoperfluorination of styrenes **7** utilizing the [Cu(dap)$_2$]Cl catalyst, a reaction that fails with organic dyes, ruthenium- or iridium-based photocatalysts, showcasing the unique character of copper in photoredox catalysis.[8] Gratifyingly, also [Cu(dmp)$_2$Cl]Cl performed well in this reaction both with activated as well as with unactivated alkenes **7** (Scheme 8).



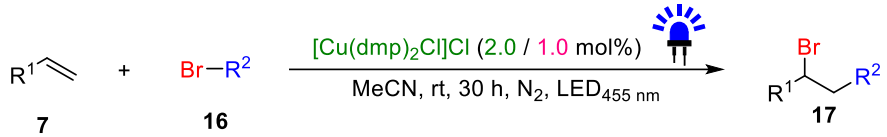
Scheme 8. Substrate scope for iodoperfluorination of alkenes **7**. *Reaction conditions*: Alkene **7** (0.5 mmol, 1.0 equiv), $C_8F_{17}I$ (**14**) (1.0 mmol, 2.0 equiv), [Cu(dmp)$_2$Cl]Cl (indicated amount) in MeCN (anh., degassed, 1.0 mL, 0.5 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 30 h. [a]Results from a previous report[8]: [Cu(dap)$_2$]Cl (1.0 mol%) under irradiation at 530 nm (green LED) for 16-20 h. [b]DCM (anh., degassed, 1.0 mL, 0.5 M) was used as a solvent.

However, starting with styrene (**7a**), $C_8F_{17}I$ (**14**) and [Cu(dmp)$_2$Cl]Cl as the photocatalyst under blue LED irradiation (λ = 455 nm) provided only 45% of the desired ATRA product **15a**. According to the previous study,[8] it was found that traces of molecular iodine formed during the photoprocess significantly absorb in the region of 400-500 nm, thus preventing the excitation of the catalyst at 455 nm with blue LED. Hence, switching to irradiation with green LED (λ = 530 nm) for this transformation increased the yield of **15a** to 95% even outperforming the previously reported [Cu(dap)$_2$]Cl catalyst. Electronically variegated styrene derivatives like *p*Me-, *p*Cl- or penta-F-substituted ones were well tolerated giving rise to the corresponding products **15b**-**15d** in high yields of 80-87% being in the same range compared to [Cu(dap)$_2$]Cl. Furthermore, also an unactivated alkene was transformed into the corresponding product **15e** in a yield of 63% being slightly lower compared to that of [Cu(dap)$_2$]Cl.

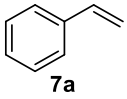
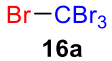
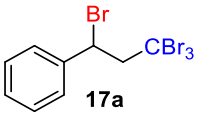
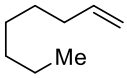
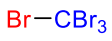
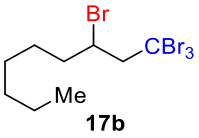
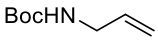
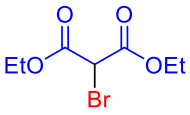
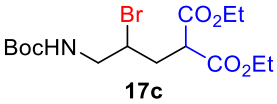
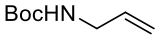
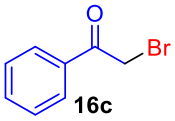
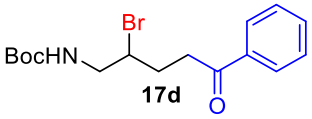
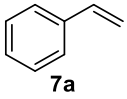
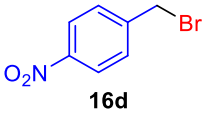
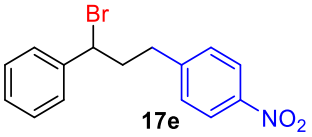
3.4.4 Photochemical ATRA Reactions with Activated Bromides

Having a broad scope of chloride- and iodide-based ATRA reagents, we next evaluated various bromine-based radical precursors **16**, that proved to be successful for [Cu(dap)$_2$]Cl (Table 2).[7,25] Perbromomethane (**16a**) addition to alkenes is a widely used test reaction for photocatalytic activity.[26] Two previous reports screened the corresponding Cu(I)-complex [Cu(dmp)$_2$]Cl in the addition of CBr_4 (**16a**) to styrene (**7a**), yielding the desired product **17a** in 12%[18a] with a catalyst loading of 0.3 mol% in combination with irradiation at 525 nm, and 60%[18c] with 2,6-lutidine (1.0 equiv) as an additive in DCM for one hour at 400 nm irradiation, respectively. However, in our hands, starting from the Cu(II)-complex [Cu(dmp)$_2$Cl]Cl and given reaction conditions, both activated alkene **7a** as well as unactivated alkene **7n** were successfully transformed into the desired products **17a** and **17b** in almost quantitative yields, thus surpassing previous results obtained with [Cu(dap)$_2$]Cl (Table 2, entries 1-2).[7,25] Next, we switched to bromomalonate **16b** as ATRA reagent affording the desired photoproduct **17c** in a synthetically useful yield of 62%, being still comparable to using [Cu(dap)$_2$]Cl (Table 2, entry 3). A limitation for [Cu(dmp)$_2$Cl]Cl seemed to be found in the photochemical activation of *α*-bromo acetophenone (**16c**) and benzyl bromide **16d**, forming the corresponding products **17d** and **17e** in significantly lower yields (12-15%) compared to [Cu(dap)$_2$]Cl (87-98%) (Table 2, entries 4-5). Considering the excited $[Cu(dmp)_2]^{*,+}$ complex being the stronger reductant compared to excited $[Cu(dap)_2]^{*,+}$, these results were surprising for us and might point towards an insufficient excited state lifetime of the former making single-electron transfer (SET) to **16c** or **16d** inefficient.

Table 2. Substrate scope of ATRA reactions with various activated bromides **16**.



yield (2.0 mol%) // yield (1.0 mol%) [Cu(dmp)$_2$Cl]Cl // (yield for 1.0 mol% [Cu(dap)$_2$]Cl)[a]

Entry	Alkene **7**	Halide **16**	Product **17**	Yield
1	 **7a**	 **16a**	 **17a**	97% // 91% (88%)[a]
2	 **7n**	 **16a**	 **17b**	92% // 88% (78%)[a]
3[b]	 **7o**	 **16b**	 **17c**	62% (75%)[a]
4[b]	 **7o**	 **16c**	 **17d**	12% (98%)[a]
5[c]	 **7a**	 **16d**	 **17e**	15% (87%)[a]

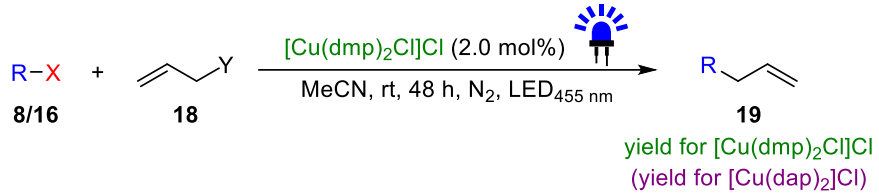
Reaction conditions: Alkene **7** (0.5 mmol, 1.0 equiv), halide **16** (0.5 mmol, 1.0 equiv), [Cu(dmp)$_2$Cl]Cl (indicated amount) in MeCN (anh., degassed, 1.0 mL, 0.5 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 30 h. [a]Results from previous reports:[7,25] [Cu(dap)$_2$]Cl (1.0 mol%) under irradiation at 530 nm (green LED) for 24 h. [b]Halide **16** (1.0 mmol, 2.0 equiv), LiBr (1.0 mmol, 2.0 equiv) as additive, solvent DMF/water (1:4, 1.0 mL, 0.5 M). [c]5.0 equiv (2.5 mmol) of styrene (**7a**).

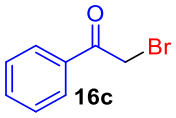
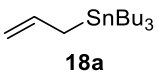
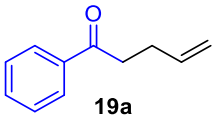
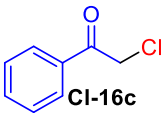
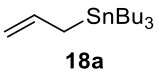
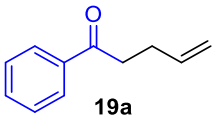
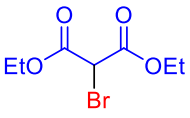
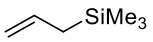
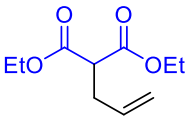
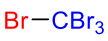
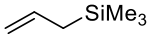
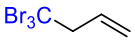
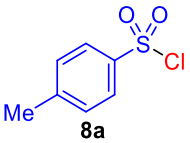
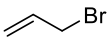
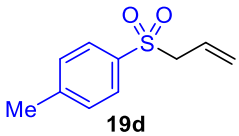
3.4.5 Photochemical Allylation Reactions

Having addressed a broad array of different ATRA reactions, we next aimed for the use of activated halides **8** or **16** in visible-light mediated photochemical allylation reactions, also being established for [Cu(dap)$_2$]Cl (Table 3).[7] Subjecting α-bromo acetophenone (**16c**) or α-chloro acetophenone (**Cl-16c**) to the photochemical allylation reaction with allyltributylstannane (**18a**) indeed yielded the desired product **19a** in synthetically useful yields of 58-60%, but significantly lower compared to the yields with [Cu(dap)$_2$]Cl (Table 3, entries 1-2). Attempts to run the photochemical allylation between bromomalonate **16b** or CBr_4 (**16a**) and allyltrimethylsilane (**18b**) gave only rise to low amounts of product **19b** and **19c** (10-12%),

contrasting [Cu(dap)$_2$]Cl who still enables such allylation reactions in good yields (60-61%) (Table 3, entries 3-4). Previously, Dr. Eugen Lutsker developed a [Cu(dap)$_2$]Cl catalyzed photochemical allylation protocol between tosyl chloride (**8a**) and allyl bromide (**18c**) giving access to allyl sulfones from non-toxic and low-priced starting materials.[27] We were pleased to see that also [Cu(dmp)$_2$Cl]Cl is capable for this reaction giving rise to allyl sulfone **19d** in high yields of 80% (Table 3, entry 5).

Table 3. Photochemical allylation reactions.

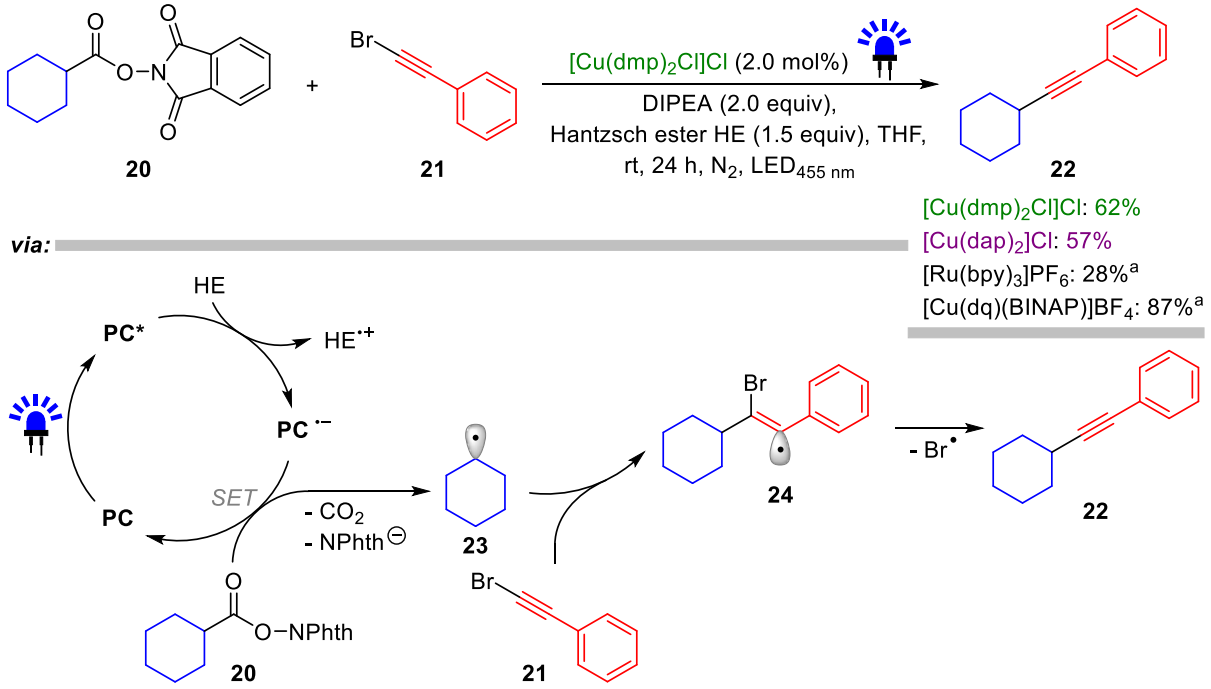


Entry	Halide **8/16**	Allyl reagent **18**	Product **19**	Yield
1	 **16c**	 **18a**	 **19a**	60% (80%)[a]
2	 **Cl-16c**	 **18a**	 **19a**	58% (85%)[a]
3	 **16b**	 **18b**	 **19b**	12% (61%)[b]
4	 **16a**	 **18b**	 **19c**	11% (60%)[a]
5[c]	 **8a**	 **18c**	 **19d**	80% (93%)[d]

Reaction conditions: Halide **8/16** (0.5 mmol, 1.0 equiv), allyl reagent **18** (0.5 mmol, 1.0 equiv), [Cu(dmp)$_2$Cl]Cl (10.0 µmol, 2.0 mol%) in MeCN (anh., degassed, 1.0 mL, 0.5 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 48 h. [a]Results taken from a previous report:[7] [Cu(dap)$_2$]Cl (1.0 mol%) under irradiation at 530 nm (green LED) for 5-24 h. [b]Results taken from a previous report:[28] [Cu(dap)$_2$]Cl (1.0 mol%). [c]6.0 equiv (3.0 mmol) of allyl reagent **18c**, Na_2CO_3 (0.5 mmol, 1.0 equiv) as additive, solvent MeCN (anh., degassed, 2.0 mL). [d]Results taken from a previous report:[27] [Cu(dap)$_2$]Cl (1.0 mol%) under irradiation at 530 nm (green LED).

3.4.6 Photochemical Decarboxylative Coupling

Next, we targeted the visible-light mediated decarboxylative fragmentation of *N*-(acyloxy)phthalimide **20** with subsequent C_{sp3}-C_{sp} coupling to bromoalkyne **21** (Scheme 9).



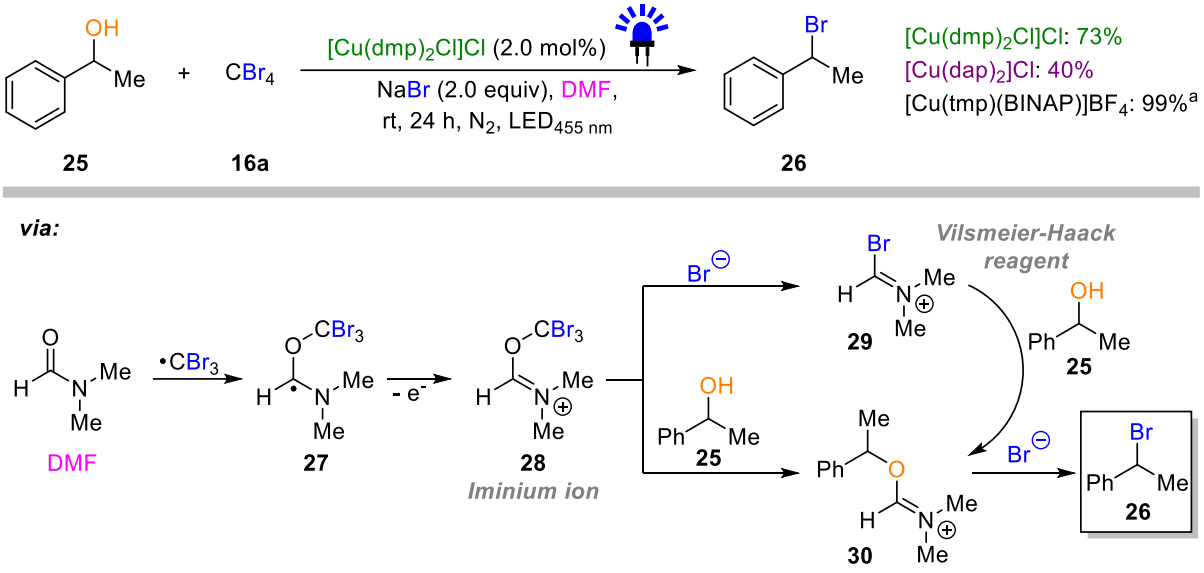
Scheme 9. Photochemical decarboxylative coupling reaction. *Reaction conditions*: Active ester **20** (0.5 mmol, 1.0 equiv), bromoalkyne **21** (0.75 mmol, 1.5 equiv), DIPEA (1.0 mmol, 2.0 equiv), Hantzsch ester (0.75 mmol, 1.5 equiv), $[Cu(dmp)_2Cl]Cl$ (10.0 µmol, 2.0 mol%) in THF (anh., degassed, 1.5 mL, 0.33 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]Results taken from a previous report.[18d]

Indeed, subjecting aforementioned starting materials to the indicated reaction conditions yielded the desired coupling product **22** in synthetically useful yields of 62%. A previously reported ruthenium catalyst only formed the product **22** in 28%,[29] whereas the heteroleptic Cu(I)-complex $[Cu(dq)(BINAP)]BF_4$ evaluated by Collins and co-workers[18d] gave rise to 87% of coupling product **22**. Considering the low costs and high availability of $[Cu(dmp)_2Cl]Cl$, these results are still appreciable from an economic point of view.

3.4.7 Photochemical Appel Reaction

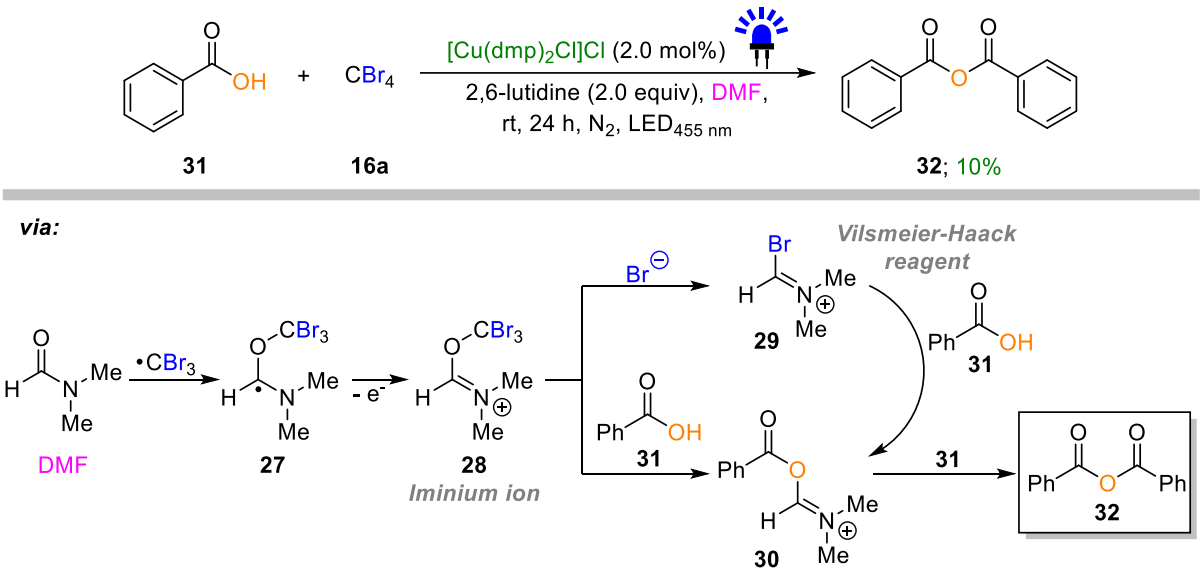
Additionally, Collins and co-workers[30] demonstrated the heteroleptic Cu(I)-complex $[Cu(tmp)(BINAP)]BF_4$ as an effective alternative in the photochemical Appel-type conversion of alcohols to the corresponding bromides developed by Stephenson et al.[31] in 2011.

Gratifyingly, also [Cu(dmp)$_2$Cl]Cl proved to be effective in the photochemical Appel reaction giving rise to the corresponding product **26** in 73% yield (Scheme 10), surprisingly being in contrast to recent results by Collins and co-workers for the corresponding Cu(I)-complex [Cu(dmp)$_2$]Cl, which failed to achieve this transformation.[30]



Scheme 10. Photochemical Appel reaction. *Reaction conditions*: Alcohol **25** (0.5 mmol, 1.0 equiv), CBr_4 (**16a**) (1.0 mmol, 2.0 equiv), NaBr (1.0 mmol, 2.0 equiv), [Cu(dmp)$_2$Cl]Cl (10.0 µmol, 2.0 mol%) in DMF (anh., degassed, 3.0 mL, 0.17 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]Results taken from a previous report.[30]

3.4.8 Photochemical Synthesis of Symmetric Anhydrides



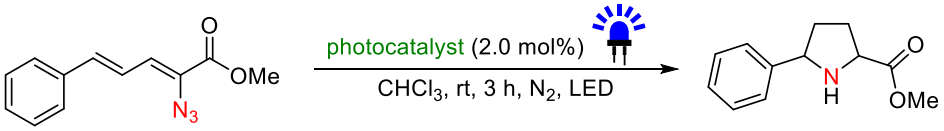
Scheme 11. Photochemical synthesis of symmetric anhydrides **32**. *Reaction conditions*: Carboxylic acid **31** (0.5 mmol, 1.0 equiv), CBr_4 (**16a**) (0.5 mmol, 1.0 equiv), 2,6-lutidine (1.0 mmol, 2.0 equiv), [Cu(dmp)$_2$Cl]Cl (10.0 µmol, 2.0 mol%) in DMF (anh., degassed, 5.0 mL, 0.1 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 24 h.

In 2012, Stephenson and co-workers impressively applied the basic mechanistic concept of the photocatalytic Appel reaction to the synthesis of symmetric anhydrides.[32] Unfortunately, $[Cu(dmp)_2Cl]Cl$ appeared to be an unsuitable catalyst to effectively promote this reaction, thus yielding anhydride **32** in only low yields of 10%.

3.4.9 Photochemical Sensitization of Vinyl Azides

As a test reaction to probe the capability of $[Cu(dmp)_2Cl]Cl$ to undergo energy-transfer processes, we employed the visible-light mediated sensitization of vinyl azides **33** as a test reaction, recently investigated by Collins and co-workers[18d] for heteroleptic Cu(I)-complexes (Table 4). Indeed, $[Cu(dmp)_2Cl]Cl$ successfully promoted the desired transformation giving rise to pyrrole **34** in excellent yields of 97% (Table 3, entry 1). In the same way $[Cu(dap)_2]Cl$ turned out to be a suitable catalyst furnishing the desired product **34** in up to 93% yield (Table 4, entries 2-3). However, when running the reaction in absence of catalyst, we still observed 82% yield of the corresponding photoproduct **34**, being surprisingly not consistent with Collins and co-workers, who report only small amounts of product (19%) under irradiation with 450 nm.[18d]

Table 4. Photochemical sensitization of vinyl azide **33**.



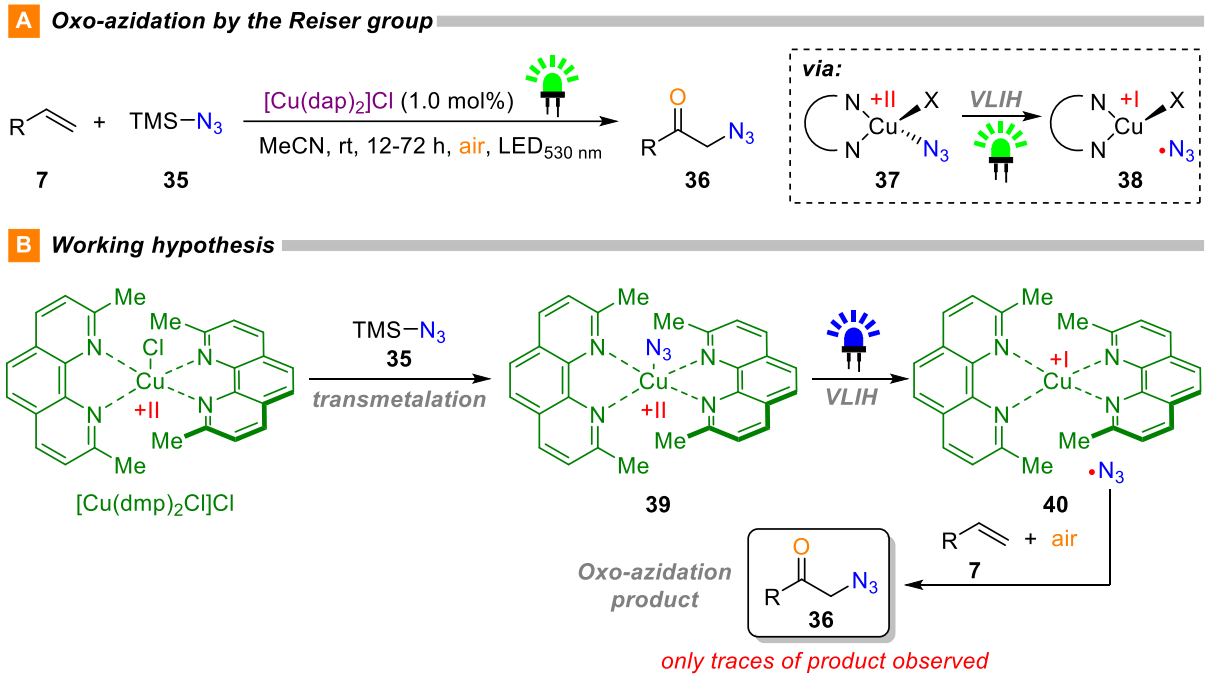
33 **34**

Entry	Photocatalyst	Yield[a]
1	$[Cu(dmp)_2Cl]Cl$; blue LED (λ = 455 nm)	97%[b]
2	$[Cu(dap)_2]Cl$; blue LED (λ = 455 nm)	93%
3	$[Cu(dap)_2]Cl$; green LED (λ = 530 nm)	80%
4	no catalyst; blue LED (λ = 455 nm)	82%

Reaction conditions: Vinyl azide **33** (0.75 mmol, 1.0 equiv), catalyst (15.0 µmol, 2.0 mol%) in $CHCl_3$ (anh., degassed, 7.5 mL, 0.1 M); Irradiation at indicated wavelength under N_2 atmosphere at room temperature (25 °C) for 3 h. [a]NMR yield using diphenoxymethane as an internal standard. [b]Isolated yield.

3.4.10 Photochemical Oxo-Azidation

In 2018, the Reiser group reported a visible-light accelerated Cu(II)-catalyzed oxo-azidation of activated alkenes **7** using trimethylsilylazide (**35**) and molecular oxygen as the stochiometric oxidant (Scheme 12, A).[12] Thereby, a Cu(II)-azide complex **37** is proposed as the catalytically active species, which upon irradiation will undergo visible-light induced homolysis to form Cu(I) **38** and azide radicals. The latter are rapidly trapped by activated alkenes **7** followed by reaction with molecular oxygen and rebound to the copper center. Elimination of the desired product **36** regenerates the catalyst and closes the catalytic cycle.

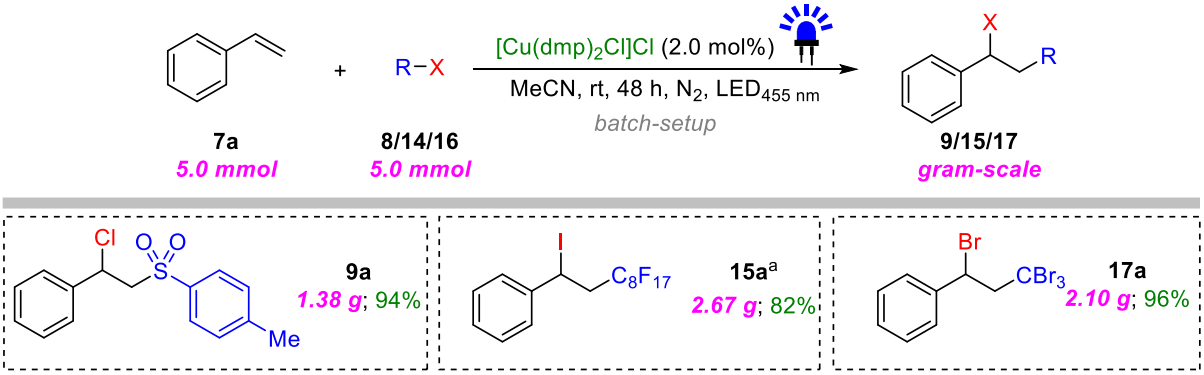


Scheme 12. Photochemical oxo-azidation of alkenes **7**. (A) Previous report by Reiser and co-workers.[12] (B) Attempts to use [Cu(dmp)$_2$Cl]Cl. *Reaction conditions*: Alkene **7** (0.5 mmol; 1.0 equiv), trimethylsilylazide (**35**) (1.0 mmol, 2.0 equiv), [Cu(dmp)$_2$Cl]Cl (10.0 µmol, 2.0 mol%) in MeCN (2.0 mL, 0.25 M); Irradiation at 455 nm (blue LED) under air at room temperature (25 °C) for 24 h.

Hence, we aimed to investigate whether [Cu(dmp)$_2$Cl]Cl sufficiently can undergo transmetalation with trimethylsilylazide (**35**) to from an azide-coordinated species **39** being subsequently excited by visible light to trigger homolysis to **40** to form azide radicals. Unfortunately, attempts to run the previously reported oxo-azidation with [Cu(dmp)$_2$Cl]Cl only led to the formation of traces of product **36**. Presumably, the much smaller π-system of the dmp ligand compared to the dap ligand makes the excitation of the corresponding Cu(II)-azide bond in **39** not feasible in the region of visible light.

3.5 Gram-Scale Functionalization

With a large variety of different copper-catalyzed photoreactions successfully established for [Cu(dmp)$_2$Cl]Cl, we moved on demonstrating the viability of the catalyst for preparative purposes. Therefore, scale-up of three different 1,2-difunctionalization reactions of styrene (**7a**) were tested on a multigram scale (Scheme 13).



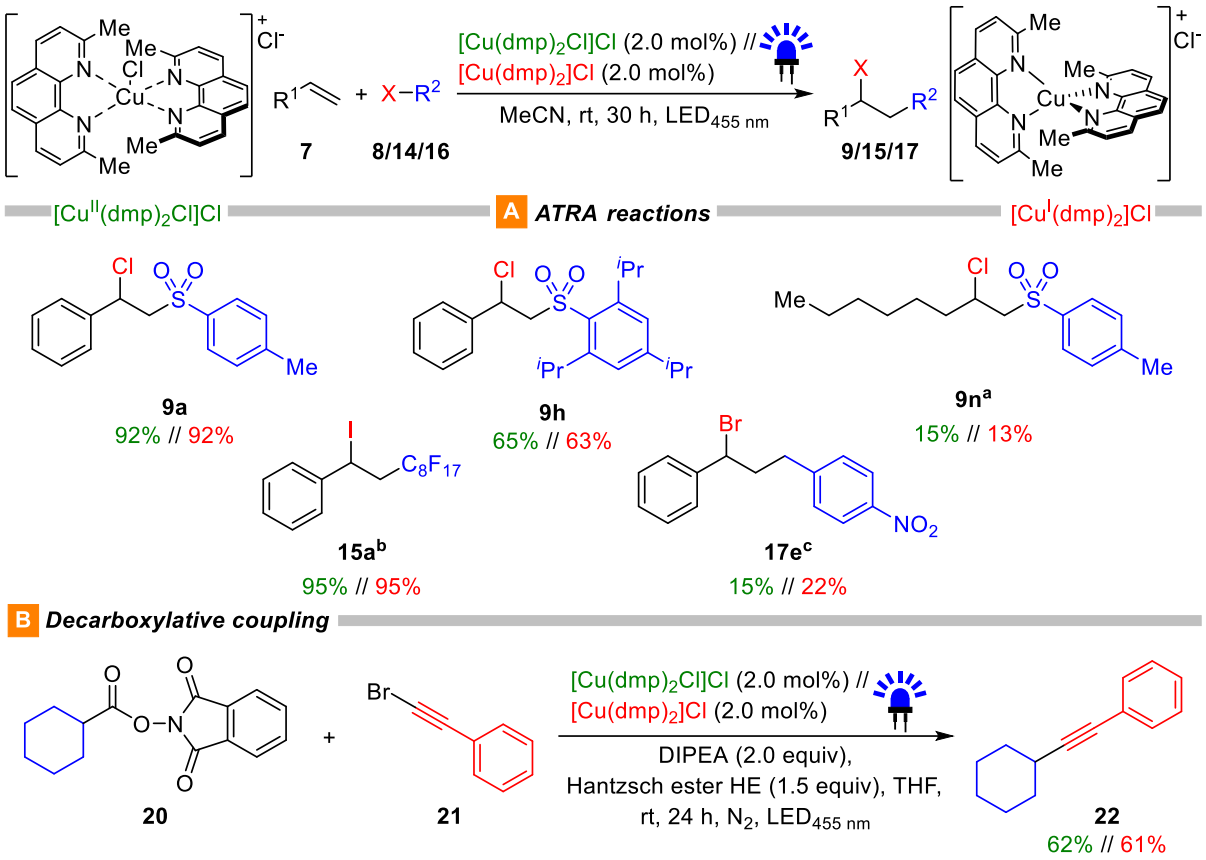
Scheme 13. Photochemical gram-scale 1,2-difunctionalizations of styrene (**7a**). *Reaction conditions*: Styrene (**7a**) (5.0 mmol, 1.0 equiv), halide **8/14/16** (5.0 mmol, 1.0 equiv), [Cu(dmp)$_2$Cl]Cl (0.1 mmol, 2.0 mol%) in MeCN (anh., degassed, 20.0 mL, 0.25 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 48 h. [a]$C_8F_{17}I$ (**14**) (10.0 mmol, 2.0 equiv) in MeCN (anh., degassed, 10.0 mL, 0.5 M); irradiation at 530 nm (green LED).

Chlorosulfonylation, iodoperfluorination as well as CBr_4-addtion were performed on a tenfold bigger scale giving rise to the desired photoproducts **9a**, **15a** and **17a** in excellent yields (82-96%) in gram quantities of 1.38-2.67 g in a simple batch-setup highlighting the possible application of [Cu(dmp)$_2$Cl]Cl in synthetic use.

3.6 Mechanistic Studies

Next, we aimed for deeper mechanistic understanding considering the activation of Cu(II)-complexes by visible-light-induced homolysis (VLIH). By now, there are only few examples in literature that consider ligand-to-metal charge transfer (LMCT) for Cu(II)-complexes[9,12,33] (*please note*: after this study appeared several groups entered the field of VLIH reflected by an increased number of reports[34]) resulting in VLIH to Cu(I) as a conceivable mechanistic proposal for photochemistry starting from Cu(II)-complexes, based on the pioneering study by Kochi investigating the photolysis of $CuCl_2$ upon UV-light irradiation.[35] However, by now there is only scarce experimental evidence present supporting this mechanistic hypothesis. In the case of [Cu(dmp)$_2$Cl]Cl, the resulting Cu(I)-species would be a Cu(I)-complex like [Cu(dmp)$_2$]Cl, which would then be the active photocatalyst being able to promote transformations as shown

above. Testing this hypothesis, we synthesized the corresponding Cu(I)-complex [Cu(dmp)$_2$]Cl and compared its efficiency in a representative selection of transformations to [Cu(dmp)$_2$Cl]Cl (Scheme 14). In all tested reactions both catalysts [Cu(dmp)$_2$Cl]Cl and [Cu(dmp)$_2$]Cl showed similar yields, clearly indicating that the latter indeed might act as the catalytically active species.



Scheme 14. Yield comparison of [Cu(dmp)$_2$Cl]Cl and [Cu(dmp)$_2$]Cl for selected photochemical reactions. *Reaction conditions*: (A) Alkene **7** (0.5 mmol, 1.0 equiv), halide **8/14/16** (0.5 mmol, 1.0 equiv), catalyst (10.0 µmol, 2.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 30 h. [a]Na_2CO_3 (0.5 mmol, 1.0 equiv) as an additive. [b]$C_8F_{17}I$ (1.0 mmol, 2.0 equiv) in MeCN (anh., degassed, 1.0 mL, 0.5 M); Irradiation at 530 nm (green LED). [c]5.0 equiv (2.5 mmol) of alkene **7**. (B) Active ester **20** (0.5 mmol, 1.0 equiv), bromoalkyne **21** (0.75 mmol, 1.5 equiv), DIPEA (1.0 mmol, 2.0 equiv), Hantzsch ester (0.75 mmol, 1.5 equiv), catalyst (10.0 µmol, 2.0 mol%) in THF (anh., degassed, 1.5 mL, 0.33 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 24 h.

Besides the similar results in the reaction yield, it was already noticed upon visual inspection that both catalysts showed a strong color change during irradiation. Thus, we started to monitor the model reaction between styrene (**7a**) and tosyl chloride (**8a**) catalyzed with both complexes by UV-vis spectroscopy (Figure 1).

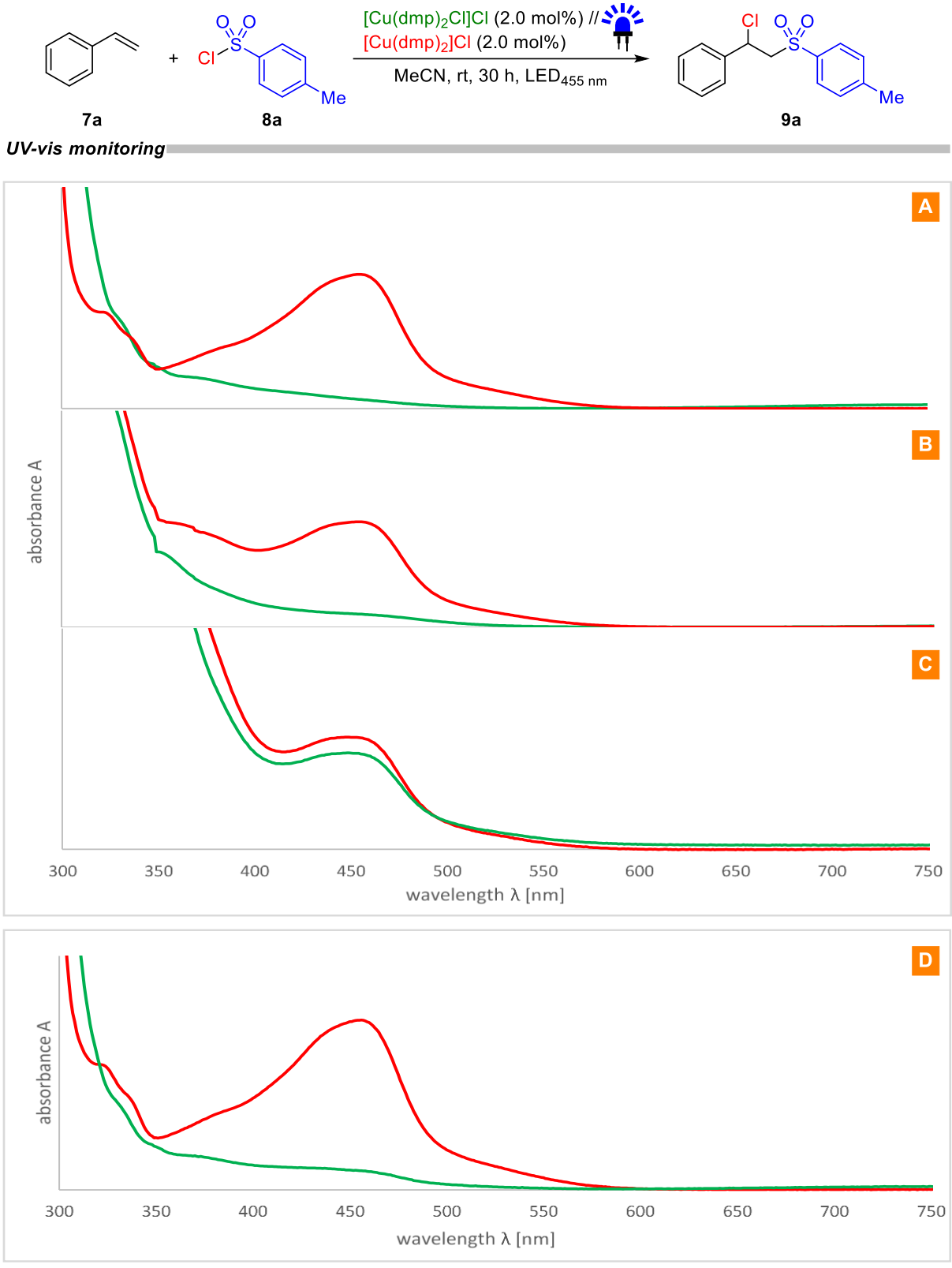


Figure 1. UV-vis monitoring of chlorosulfonylation reaction between styrene (**7a**) and tosyl chloride (**8a**) using [Cu(dmp)$_2$Cl]Cl (green line) and [Cu(dmp$_2$]Cl (red line). (A) Copper catalysts alone. (B) Reaction mixture for chlorosulfonylation: Styrene (**7a**), tosyl chloride (**8a**) and corresponding catalyst. (C) Crude reaction mixture after irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 30 h. (D) Control experiment: Corresponding catalyst together with chlorosulfonylation product **9a**. All UV-vis spectra are recorded in MeCN (anh., 0.02 mM).

Contrasting previously reported [Cu(dap)Cl_2] and [Cu(dap)$_2$]Cl for which both catalysts showed similar UV-vis spectra,[12] the corresponding UV-vis spectra of [Cu(dmp)$_2$Cl]Cl (green line) and [Cu(dmp)$_2$]Cl (red line) significant differ from each other (Figure 1, A). While the absorption measurement of [Cu(dmp)$_2$]Cl in anhydrous MeCN showed a distinct maximum in the blue region, the corresponding Cu(II)-complex is much less luminescent, thus enabling the monitoring of the different species by UV-vis spectroscopy. Addition of the starting materials styrene (**7a**) and tosyl chloride (**8a**) to the prior measurement of the respective catalyst solutions led to no change of the UV-vis spectra in the case of [Cu(dmp)$_2$Cl]Cl, whereas a slight interaction with the substrates was observed for [Cu(dmp)$_2$]Cl, still maintaining the characteristic absorption maxima in the blue region (Figure 1, B). Further UV-vis measurements revealed that in particular tosyl chloride (**8a**) is responsible for the aforementioned change in the spectra.[36] Subsequently, both reaction mixtures were irradiated for 30 h at 455 nm and the corresponding UV-vis spectra were recorded again (Figure 1, C). Remarkably, both spectra converged and, henceforth, show a high similarity regarding the absorption pattern, being characteristic for the Cu(I)-species. These results indicate that both catalysts undergo the same catalytic cycle, most likely having a Cu(I)-complex as the active species, which then can undergo photoinduced SET to the substrate following our previously reported mechanistic proposal for [Cu(dap)Cl_2] and [Cu(dap)$_2$]Cl (see Chapter 3.7). Control UV-vis experiments with the corresponding catalysts combined with product molecule **9a** ruled out a potential interaction of both influencing the spectra (Figure 1, D). Thus, this study provides experimental support for the activation of Cu(II)-complexes via VLIH.

However, as this experimental set-up relies on long-term irradiation and steady-state UV-vis spectroscopy, more detailed mechanistic investigations were carried out in cooperation with Prof. Castellano and co-workers.[37] In the following, the key findings are shortly summarized. ***Please note:*** The corresponding copper complexes were synthesized by us, whereas mechanistic experiments and calculations were carried out by the Castellano group.

Time-resolved UV-vis absorption spectra of [Cu(dmp)$_2$Cl]Cl dissolved in MeCN are depicted in Figure 2. Based on electronic structure calculations, absorbance at 650 nm predominantly corresponds to metal-localized d-d electronic transitions, while the absorption in the region of approximately 350-500 nm is attributed as ligand-to-metal charge transfer (LMCT), largely Cl to Cu(II) in character. Upon irradiation with 427 nm LED (288 mW/cm^2) into the LMCT transition, absorbance in the blue region drastically increases, indicating the in-situ formation

of [Cu(dmp)$_2$]Cl having its metal-to-ligand charge transfer (MLCT) absorption band quantitatively matched in this region (Figure 2, right). The Castellano group determined the corresponding photolysis quantum yield resulting from irradiation at 427 nm to be 2.8%.[37]

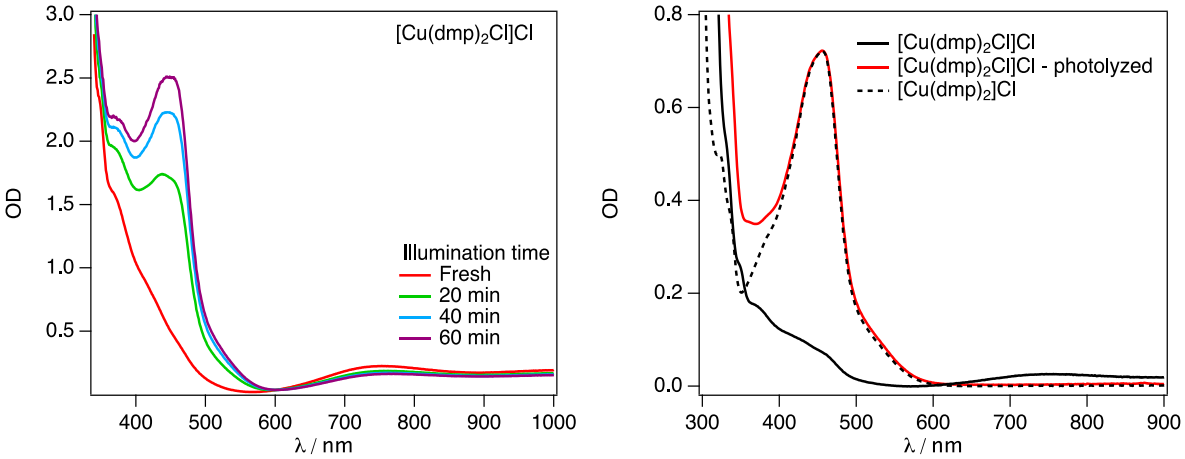


Figure 2. *Left*: Time-resolved UV-vis absorption spectra of [Cu(dmp)$_2$Cl]Cl in MeCN (anh., degassed, 1.7 mM) (red trace), irradiation with 427 nm LED for 20 min (green trace), 40 min (blue trace) and 60 min (purple trace). *Right*: UV-vis spectra of [Cu(dmp)$_2$Cl]Cl (solid black trace) in MeCN (anh., degassed, 1.7 mM) and of the same sample after irradiation at 427 nm LED for 3 h (solid red trace) clearly matching with UV-vis spectra of [Cu(dmp)$_2$]Cl (dotted black trace). Experiments were carried out by the Castellano group and the shown graphics were kindly provided by them.

This photochemical reduction is consistent with LMCT excitation leading in VLIH of the Cu-Cl bond in [Cu(dmp)$_2$Cl]Cl to generate [Cu(dmp)$_2$]Cl. Remarkably, this process was also observed under ambient lighting conditions, while samples kept in the dark completely remained intact (Figure 3).

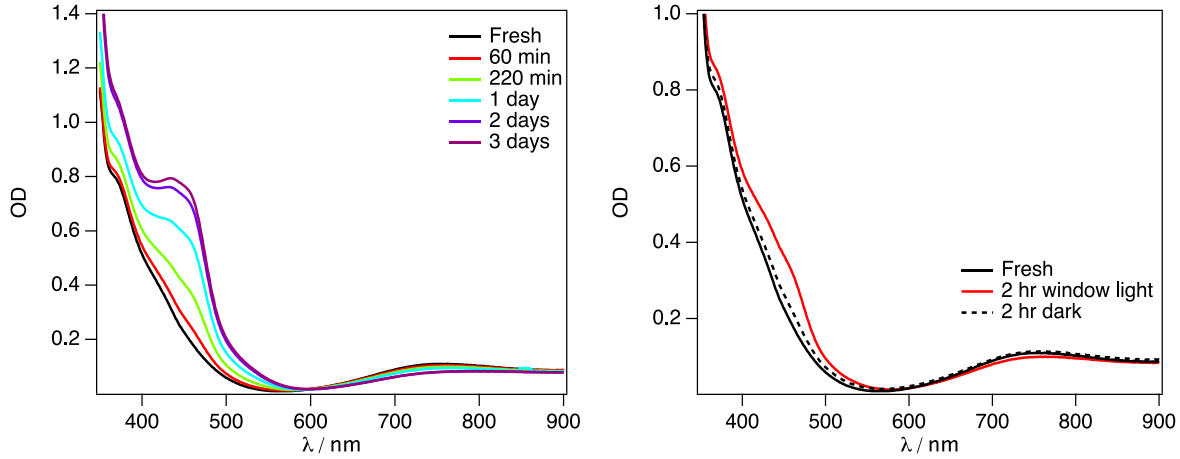


Figure 3. *Left*: Steady-state absorption of [Cu(dmp)$_2$Cl]Cl in MeCN (anh., 1.7 mM) undergoing VLIH at irradiation with window light for the times indicated in the legend. *Right*: Control experiment of freshly prepared sample (solid black trace), kept 2 h in the dark (dotted black trace), and kept 2 h under window light (solid red trace). Experiments were carried out by the Castellano group and the shown graphics were kindly provided by them.

Interestingly, excitation of [Cu(dmp)$_2$Cl]Cl into its metal-localized d-d electronic transitions in the red region with a 785 nm laser diode (P = 800 mW) resulted in no VLIH and thus in no generation of any permanent photoproduct (Figure 4).

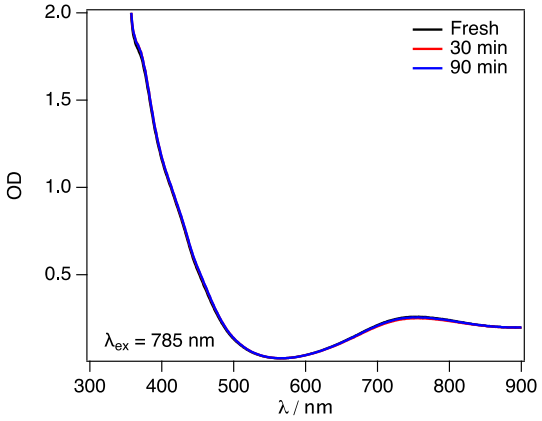


Figure 4. UV-vis absoprtion spectra of [Cu(dmp)$_2$Cl]Cl in MeCN (anh., degassed, 1.7 mM) at irradiation with a 785 nm laser diode for time indicated in the legend. Experiments were carried out by the Castellano group and the shown graphics were kindly provided by them.

Electron paramagnetic resonance (EPR) spin trapping experiments with [Cu(dmp)$_2$Cl]Cl and *C*-phenyl-*N*-*tert*-butylnitrone (PBN) in THF under irradiation at 427 nm revealed the existence of THF radicals being trapped as PBN-THF adducts **41** (Figure 5). It is believed that THF radicals might be produced following hydrogen atom abstraction by chlorine radicals generated upon VLIH of [Cu(dmp)$_2$Cl]Cl. Control experiments omitting the copper complex showed no measurable EPR signal under identical experimental conditions. Notably, same results were obtained when the sample was exposed to ambient light, thus underpinning our observations of VLIH under irradiation of room light.

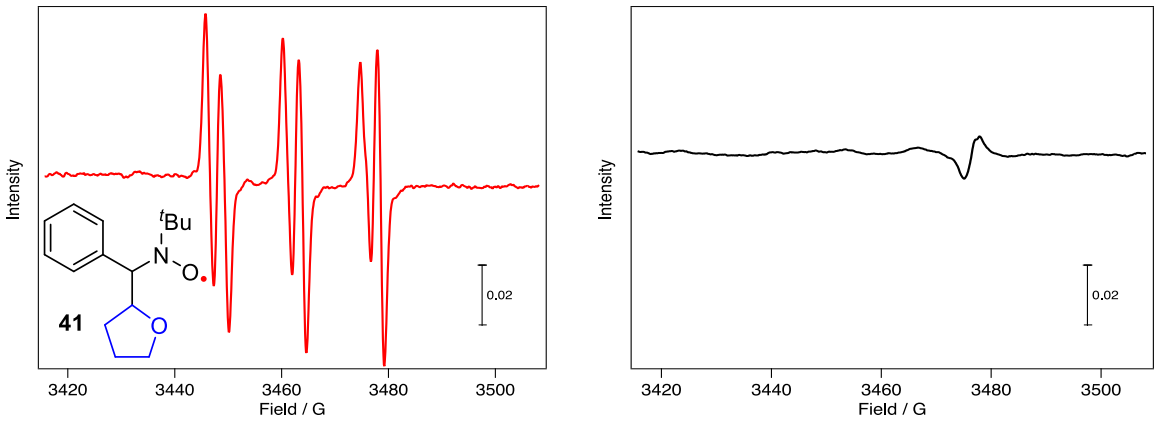


Figure 5. *Left*: EPR spectrum of the spin adduct obtained from a solution of [Cu(dmp)$_2$Cl]Cl and PBN in THF (anh., degassed, 10.0 mM) under irradiation at 427 nm directly in the EPR cavity at room temperature. *Right*: EPR control experiment: PBN in THF (anh., degassed, 10.0 mM) under irradiation at 427 nm. Experiments were carried out by the Castellano group and the shown graphics were kindly provided by them.

In an attempt to get deeper mechanistic insights into the kinetics of the VLIH in [Cu(dmp)$_2$Cl]Cl, the Castellano group performed ultrafast transient absorbance (UFTA) experiments of [Cu(dmp)$_2$Cl]Cl and [Cu(dmp)$_2$]Cl in MeCN. The samples were excited at 470 nm by a laser pulse with a pulse width of 100 fs (Figure 6).

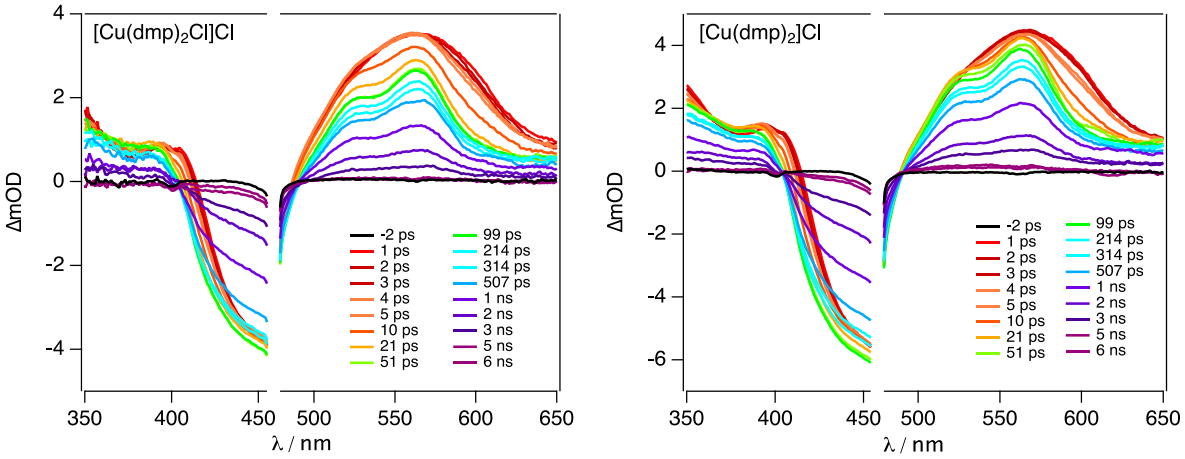


Figure 6. UFTA difference spectra of [Cu(dmp)$_2$Cl]Cl (left) and [Cu(dmp)$_2$]Cl (right) in MeCN following 470 nm pulsed laser excitation (1.2 µJ/pulse, 100 fs pulse width) with experimental delay times indicated in the legend. Experiments were carried out by the Castellano group and the shown graphics were kindly provided by them.

The UFTA spectra from [Cu(dmp)$_2$Cl]Cl shows a ground state bleach between 400-500 nm and a broad positive absorption from 500-650 nm evolving to a double top feature over the first 20 ps after the laser pulse. Notably, the different spectra recorded for [Cu(dmp)$_2$Cl]Cl appeared to be very similar to that generated for the corresponding Cu(I)-analogue (Figure 6, right). Given the differences in the extinction coefficients (33-fold),[37] the observed spectroscopic pattern emanate largely from the photoproduct [Cu(dmp)$_2$]Cl after VLIH of the corresponding Cu(II)-complex. In summary, these data are consistent with in-pulse formation of the Cu(I)-species, placing a lower limit (<100 fs) on the time constant for the ultrafast VLIH process occurring in [Cu(dmp)$_2$Cl]Cl. Notably, excitation of the latter into its metal-localized d-d electronic transitions in the red region at 800 nm exclusively resolved the Cu(II)-based transients while completely circumventing the VLIH process.[37] Furthermore, electronic structure calculations were carried out by Castellano and co-workers to further provide insight into the nature of the unpaired electron and behavior of the Cu(II)-complex under irradiation into the different absorption bands. Therefore, spin density for [Cu(dmp)$_2$Cl]Cl was calculated from the single X-ray structure geometry (see experimental part) (Figure 7). The spin density, and thus the unpaired electron, is located primarily on the chlorine and copper atoms, pointing towards a mixing between the two. TD-DFT on the optimized structure of the Cu(II)-complex

revealed three states with oscillator strength containing minimal spin contamination, serving as a basis to construct the electron density difference surfaces (Figure 7). The two lower excited states are attributed to the absorption band at 700-800 nm showing very little change in the spin density around the copper or chlorine atom. Contrasting, the higher energy state corresponding to the absorption in the blue region indicates loss of density around the chlorine-copper bond with concurrent density gain on the copper center and on the dmp ligand. These results are in line with the behavior of the complex upon VLIH.

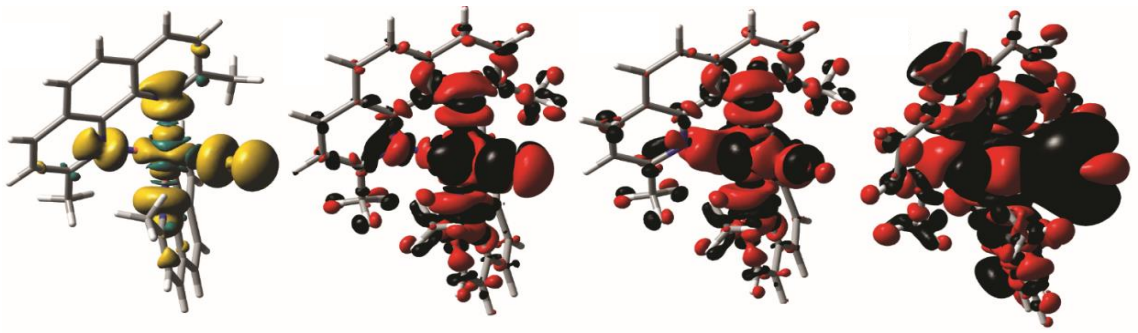
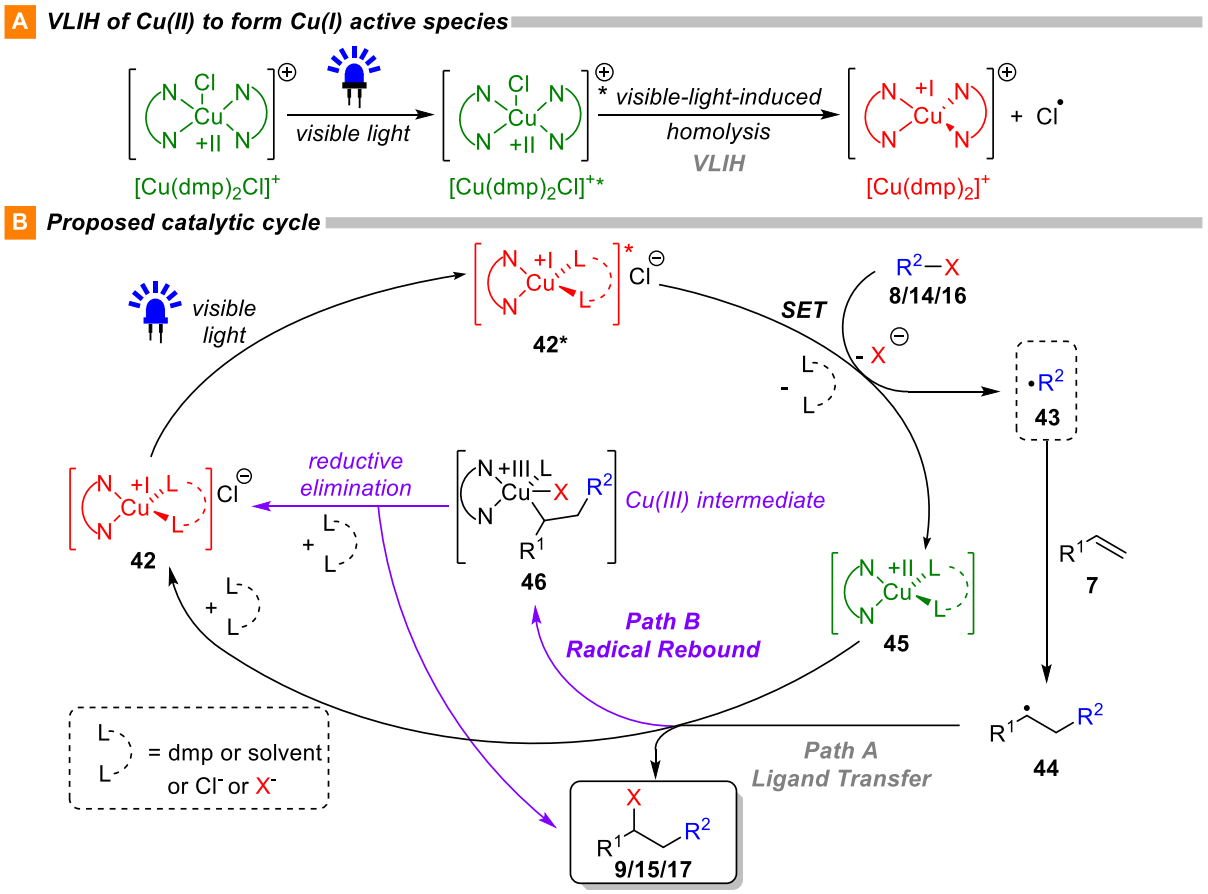


Figure 7. Electronic structure calculations. (a) Spin density of $[Cu(dmp)_2Cl]Cl$ rendered at an iso value of 0.0008. (b-d) Electronic density difference maps for the calculated 1st, 2nd and 5th excited states, respectively (red corresponds to density gain, black is density loss). Rendered at an iso value of 0.0004. Basis Set: 6-31g(d), functional (for TD-DFT): B3LYP. For details, please see publication.[37] Calculations were carried out by the Castellano group and the shown graphics were kindly provided by them.

3.7 Proposed Reaction Mechanism

Hence, we propose in accordance to our previous study on the chlorosulfonylation catalyzed by $[Cu(dap)_2]Cl$ and $[Cu(dap)Cl_2]$ (see Chapter 2) the following mechanism (Scheme 15). After irradiation at 455 nm (blue LED) the excited Cu(II)-complex $[Cu(dmp)_2Cl]Cl$ undergoes visible-light-induced homolysis (VLIH) of the Cu(II)-Cl bond forming the catalytically active Cu(I)-species $[Cu(dmp)_2]^+$ or rather Cu(I)-species **42**, which might be coordinated either by dmp ligand, solvent or halide (Scheme 15, A). After excitation of the latter by visible light, single-electron transfer (SET) to the reagent **8/14/16** generates the corresponding radical **43** under oxidation of the catalyst to the Cu(II)-species **45**. Radical **43** now can add to the present alkene **7** forming the *C*-centered radical **44**, which now may proceed by two different pathways. In pathway A, radical **44** takes back chlorine from **45** concurrent with the regeneration of the catalyst **42**. Alternatively, intermediate **44** can directly bind to the Cu(II)-species **45** (pathwayB), which is in fact a persistent radical, forming a Cu(III)-intermediate **46**. This rebound cycle is closed upon reductive elimination releasing the desired product **9/15/17** and recreating the active Cu(I)-catalyst.



Scheme 15. Plausible reaction mechanism for ATRA reactions catalyzed by [Cu(dmp)$_2$Cl]Cl.

3.8 Conclusion

In conclusion, we have evaluated the oxidation- and bench-stable Cu(II)-complex [Cu(dmp)$_2$Cl]Cl as a visible-light mediated photoredox catalyst being much more robust and economic compared to other copper photocatalysts, especially to the well-established [Cu(dap)$_2$]Cl. The present complex does not suffer from time- and price-consuming ligand synthesis, thus providing an abundant alternative in photochemistry. The catalytic activity was demonstrated within a broad scope of ATRA reactions enabling rapid 1,2-difunctionalization of alkenes, a decarboxylative coupling reaction, an Appel reaction and various allylation protocols. In some cases, [Cu(dmp)$_2$Cl]Cl even outperformed the established [Cu(dap)$_2$]Cl system. By various gram-scale 1,2-difunctionalizations of styrene, the viability of the catalyst for synthetic use was demonstrated, underpinning the role of a low-priced and economic alternative. Furthermore this study and the following cooperation with Castellano et al. provided for the first time strong mechanistic evidence for the visible-light-induced homolysis (VLIH) activation of Cu(II)-complexes for photocatalysis opening-up new avenues for radical generation using metal-substrate complexes from first row transition metals.

3.9 References

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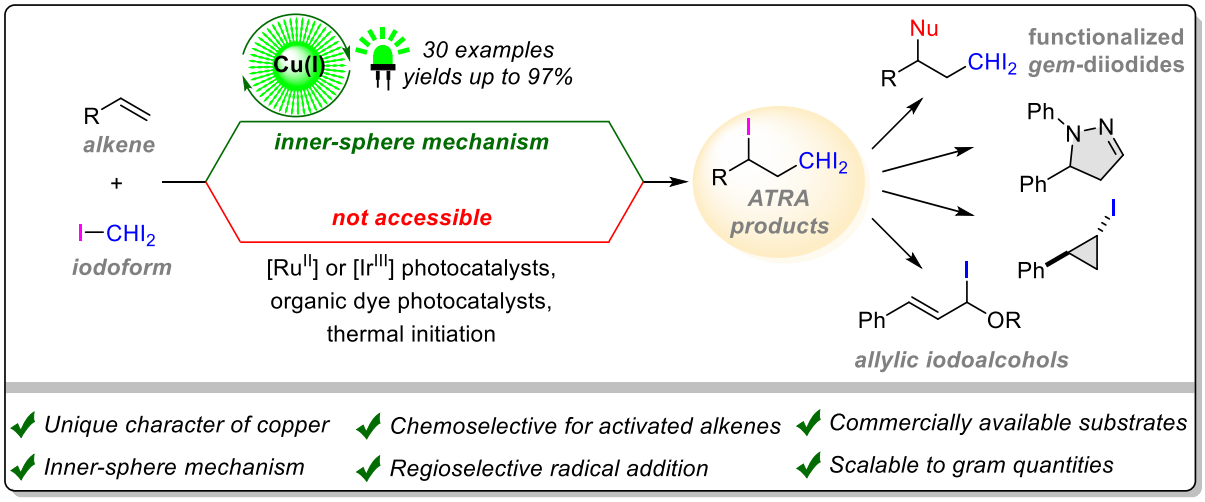
Chapter 4

Photochemical ATRA Reactions of Iodoform‡

4.1 Abstract



In Chapter 4, we report a visible-light mediated copper-catalyzed protocol enabling the highly economic 1,2-difunctionalization of olefins utilizing the readily available and low-cost bulk chemical iodoform. Although this transformation seems to be simple on paper, it turned out that the title transformation is not feasible via commonly employed ruthenium-, iridium- or organic dye-based photocatalysts, thus undergirding the unique role of copper in photoredox catalysis owing to its ability to interact and stabilize incipient radical intermediates in the inner-coordination sphere. The developed protocol is characterized by high yields under environmentally benign reaction conditions and allows for the regio- and chemoselective functionalization of activated double bonds as well as for late-stage functionalization of bioactive molecules. Furthermore, the protocol can be smoothly scaled to gram-quantities of product, which offers manifold possibilities for further transformations, including intramolecular cyclopropanation, the synthesis of heterocycles or the synthesis of functionalized *gem*-diiodides being privileged building blocks in organic synthesis but usually challenging to access.

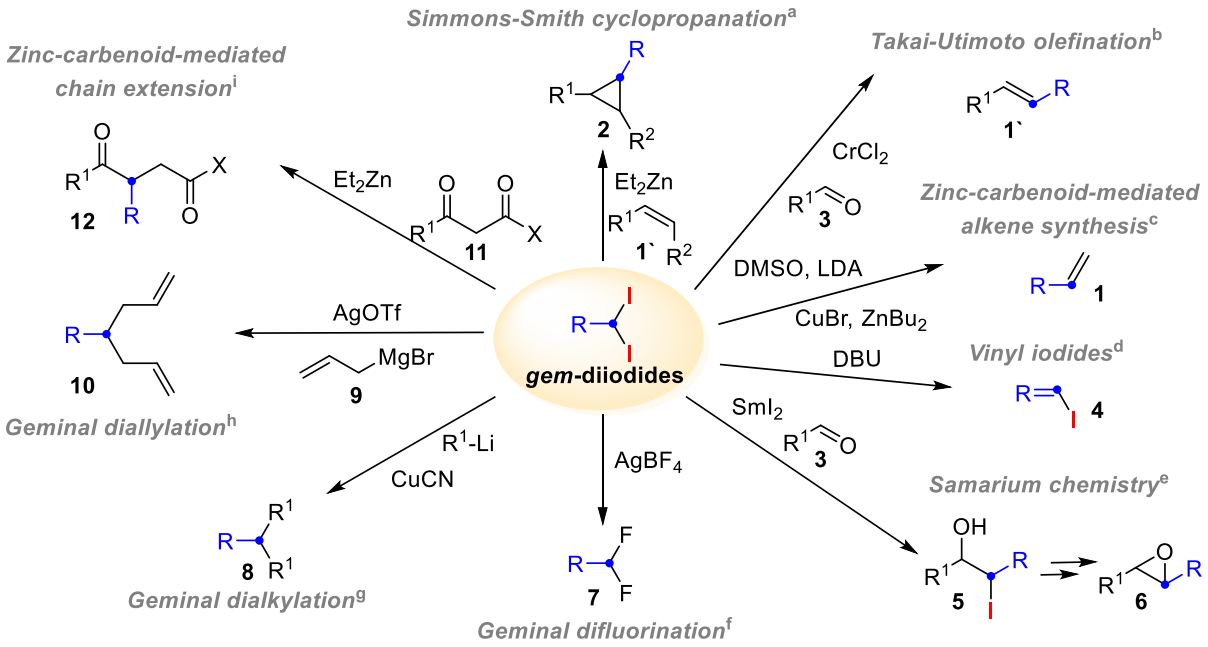
‡ This chapter is partially based on: Engl, S.; Reiser, O. *ACS Catal.* **2020**, *10*, 9899-9906.

4.2 Introduction

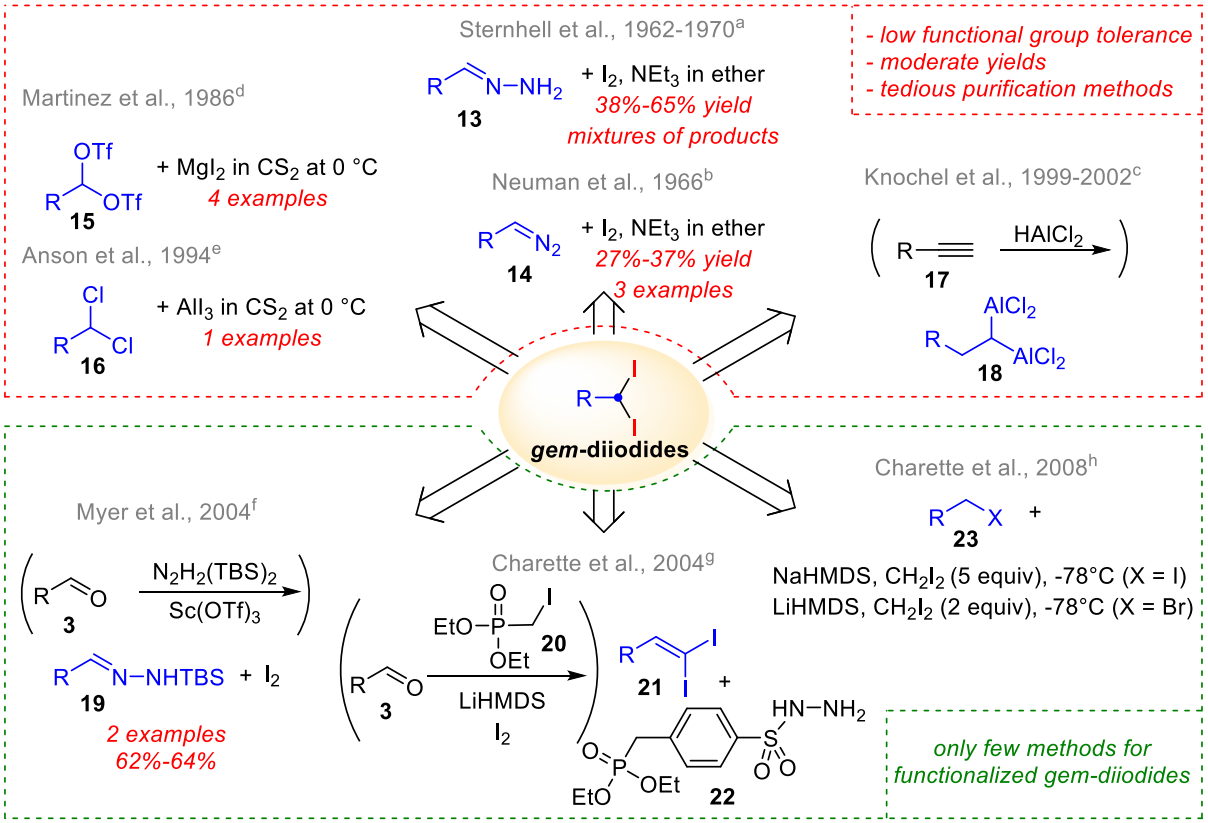
Pioneered by Karash[1] in the mid-1900s, Atom Transfer Radical Addition (ATRA) reactions have developed into a powerful and versatile tool in synthetic organic chemistry allowing rapid difunctionalization of alkenes in an atom- as well as step-economic manner. Thereby, a rich chemical space and high molecular complexity can be accessed through simple operations on unsaturated C-C bonds representing a fundamental moiety in organic chemistry often derived from simple chemical feedstock. However, usually common ATRA reactions of early days required harsh reactions conditions and toxic or hazardous reagents to initiate a radical chain process. Hence, the renaissance of visible-light photoredox catalysis[2] with its capacity to promote such radical processes under mild and ecologically benign reaction conditions appeared to be an interesting alternative for such transformations.[3] Following seminal work of Barton[4] and Stephenson[5], the most commonly employed catalysts in such ATRA processes are represented by ruthenium- and iridium-based complexes owing to their high photostability, long excited state lifetimes and favorable photoredox potentials. However, the high costs and the adverse environmental impact of these metals call for more economic and green alternatives. In this regard, copper photocatalysis successfully conquered the area and gained tremendous impact emerging as an appealing complement.[6] Thus, $[Cu(dap)_2]Cl$ – by now representing one of the most prominent copper photocatalysts – was employed in a broad array of visible-light mediated ATRA reactions.[7] Besides the economic benefits, copper photocatalysts offer high ligand exchange dynamics and multiple accessible oxidation states, thus empowering them to capture incipient radicals in their inner-coordination sphere to stabilize and control reaction intermediates. Following the same line of reasoning, copper photocatalysts open up heretofore elusive reaction avenues not accessible by other aforementioned photocatalysts.

Iodoform – a low-cost and non-toxic industrial bulk chemical – represents one of the most readily available polyiodo compounds typically produced in the so-called iodoform reaction. We questioned whether this chemical feedstock can be sufficiently employed as a radical precursor to simultaneously incorporate iodine and the CHI_2 group in aforementioned ATRA-type transformations yielding in a robust and broadly applicable protocol for the synthesis of highly iodinated compounds. The *gem*-diiodide (CHI_2) moiety represents a privileged synthon in synthetical organic chemistry offering a plethora of possibilities for further transformations, most prominently Simmons-Smith cyclopropanation or Takai-Utimoto olefination (Scheme 1). However, the use of functionalized *gem*-diiodides in such transformations still remains scarce

mostly because of the rarity of suitable methods accessing them when other functional groups are present (Scheme 2). Furthermore, these methods often require hazardous metal reagents along with only moderate isolated yields.

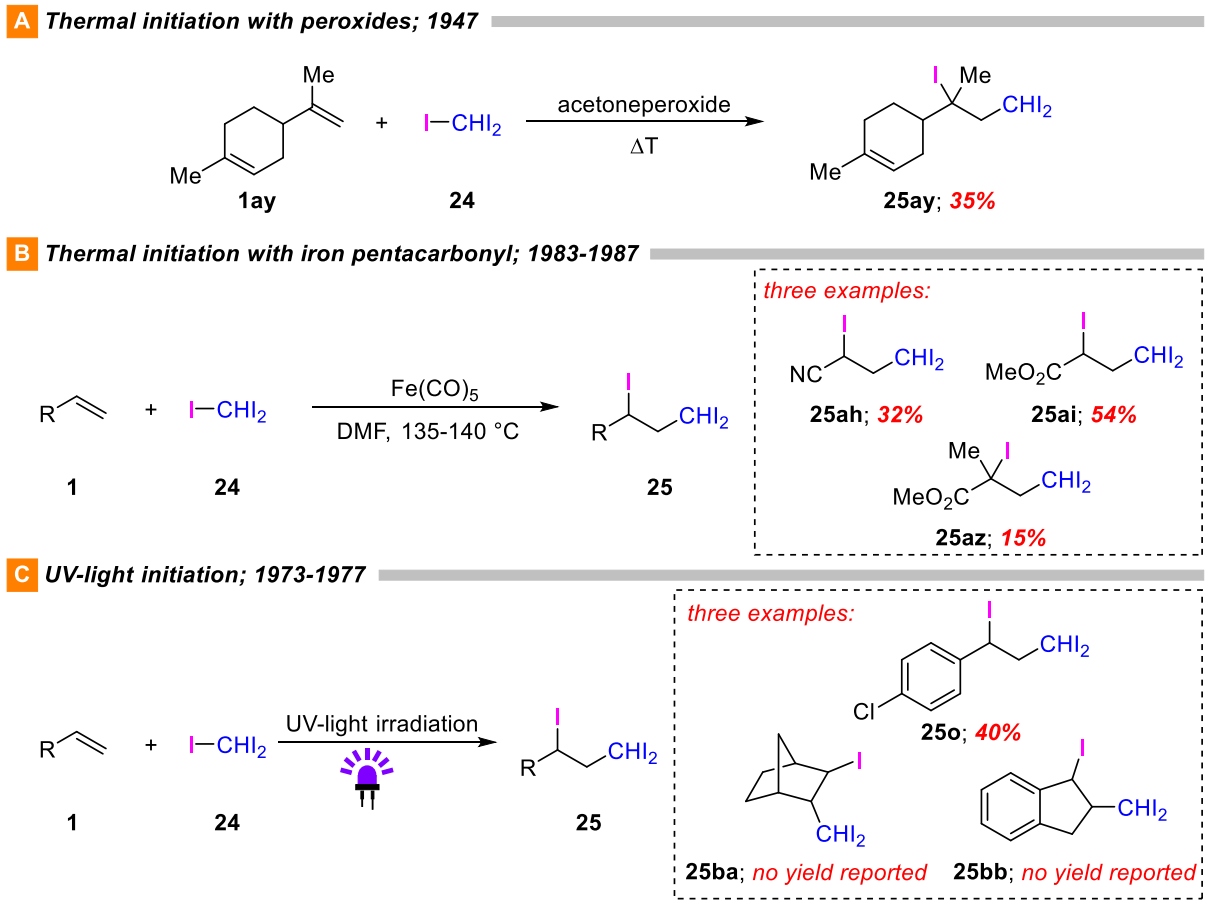


Scheme 1. Overview of representative synthetic transformations of *gem*-diiodides. [a]Ref.[8], [b]Ref.[9], [c]Ref.[10], [d]Ref.[11], [e]Ref.[12], [f]Ref.[13], [g]Ref.[14], [h]Ref.[15], [i]Ref.[16]



Scheme 2. Overview of representative examples for the synthesis of *gem*-diiodides. [a]Ref.[17], [b]Ref.[18], [c]Ref.[19], [d]Ref.[20], [e]Ref.[21], [f]Ref.[22], [g]Ref.[23], [h]Ref.[24]

Given the imperative need to develop step-economic, time-saving and high-yielding processes to access *gem*-diiodides, nevertheless, the idea of utilizing the low-cost and non-toxic bulk chemical iodoform in an ATRA-type transformation on alkenes, received only little attention in recent literature. Seminal attempts back in the 1940s to 1980s describe this basic concept (Scheme 3) but failed in developing a viable protocol for the target reaction by employing thermal initiation with peroxides[25] (Scheme 3, A), ironpentacarbonyl[26] (Scheme 3, B) or UV-light irradiation[27] (Scheme 3, C). In all cases only one to three examples in very low to moderate or even unreported yields along with difficulties in product isolation are described, showcasing that although this reaction seems to be quite straightforward on paper, much milder and more selective conditions might be needed to control the generated radical intermediates.

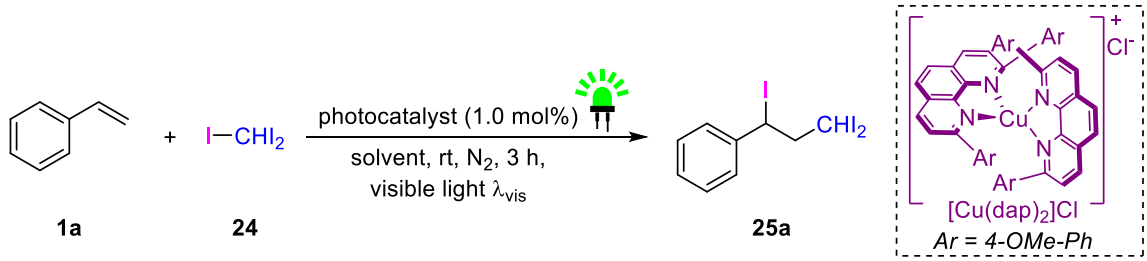


Scheme 3. Seminal attempts on ATRA reactions with iodoform (**24**). (A) Ref.[25], (B) Ref.[26], (C) Ref.[27]

Nonetheless, motivated by this literature void, we started our investigations with iodoform (**24**) and styrene (**1a**) using visible-light mediated copper-catalyzed photoredox catalysis (Chapter 4.3).

4.3 Reaction Optimization

Table 1. Reaction optimization.



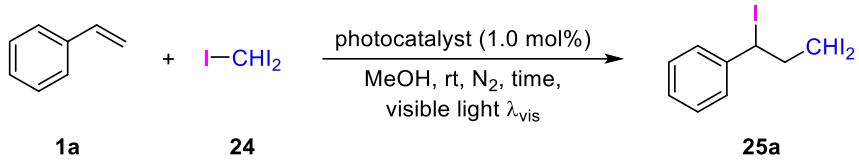
Entry	Photocatalyst	λ_{vis}	Solvent	Variations	Yield[a]
1	$[Cu(dap)_2]Cl$	530 nm	MeCN	---	24%
2	$[Cu(dap)_2]Cl$	530 nm	DMF	---	40%
3	$[Cu(dap)_2]Cl$	530 nm	DMSO	---	33%
4	$[Cu(dap)_2]Cl$	530 nm	THF	---	29%
5	$[Cu(dap)_2]Cl$	530 nm	$CHCl_3$	---	88%
6	$[Cu(dap)_2]Cl$	530 nm	DCM	---	97% (94%[b])
7	$[Cu(dap)_2]Cl$	530 nm	MeOH	---	97% (97%[b])
8	$[Cu(dap)_2]Cl$	530 nm	H_2O	---	26%
9	$[Cu(dap)_2]Cl$	530 nm	MeOH	equivalents (**1a**:**24**) = 1:1	46%
10	$[Cu(dap)_2]Cl$	530 nm	DCM	equivalents (**1a**:**24**) = 1:1	47%
11	$[Cu(dap)_2]Cl$	530 nm	MeOH	equivalents (**1a**:**24**) = 1:2	41%
12	$[Cu(dap)_2]Cl$	530 nm	MeOH	catalyst loading 0.1 mol%	53%
13	$[Cu(dap)_2]Cl$	530 nm	MeOH	catalyst loading 0.5 mol%	87%
14	$[Cu(dap)_2]Cl$	455 nm	MeOH	---	54%
15	$[Cu(dap)_2]Cl$	no	MeOH	---	nr
16	no	530 nm	MeOH	---	18%
17	no	530 nm	MeOH	12 h reaction time	20%
18	no	530 nm	DCM	12 h reaction time	< 6%
19	no	455 nm	MeOH	---	crm
20	no	no	MeOH	AIBN (10 mol%), 80°C	15%
21	CuCl	530 nm	MeOH	catalyst loading 5.0 mol%	nr
22	$[Cu(MeCN)_4]BF_4$	530 nm	MeOH	catalyst loading 5.0 mol%	nr
23	$CuCl_2$	530 nm	MeOH	catalyst loading 5.0 mol%	nr
24	dap	530 nm	MeOH	catalyst loading 10 mol%	12%
25	$[Cu(dap)_2]Cl$	530 nm	MeOH	air atmosphere	nr

Reaction conditions: Styrene (**1a**) (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at indicated wavelength λ_{vis} under N_2 atmosphere at room temperature (25 °C) for 3 h. [a]NMR yield using diphenoxymethane as an internal standard. [b]Isolated yield.

Starting the reaction screening with styrene (**1a**) and iodoform (**24**) in the presence of $[Cu(dap)_2]Cl$ under visible-light irradiation with green LED (λ = 530 nm), furnished the desired ATRA product **25a** in up to 97% yield after 3 h irradiation using DCM as the solvent (Table 1, entries 1-6). However, addressing the principles of green chemistry, it is supremely desirable to replace chlorinated solvents by more environmentally friendly and preferable alternatives. Thus, we were pleased to observe also an almost quantitative yield of **25a** using the much more sustainable solvent MeOH (Table 1, entry 7). Noteworthy, no iodine substitution by MeOH is observed in the final product **25a**. Remarkably, the title reaction also proceeded in an aqueous solution, thus paving the way for further screening of such reactions in cellular media. Unfortunately, attempts to reduce the excess amount of styrene (**1a**) to a more atom-economic equimolar ratio significantly decreased the yield in DCM or MeOH to 46-47% (Table 1, entries 9-10). Experiments using iodoform (**24**) – being the less expensive and more abundant component in this coupling – in an excess failed and delivered the desired product **25a** in only moderate yields (Table 1, entry 11). In the same way, reducing the catalyst loading to 0.1 mol% drastically decreased the yield to 53%, while a catalyst loading of 0.5% still furnished the desired product **25a** in high yield of 87% (Table 1, entries 12-13). Remarkably, switching the irradiation source from 530 nm (green LED) to 455 nm (blue LED) revealed a significant decrease in the reaction yield of **25a** to 54% (Table 1, entry 14), despite the fact that the absorption of $[Cu(dap)_2]Cl$ is substantially higher at the latter wavelength. In agreement with our previous study,[7i] this might be attributed to the formation of traces of molecular iodine during the reaction absorbing light in the region of 400-500 nm, thus preventing excitation of the catalyst with blue LED. The photocatalytic nature of the reaction was proven by observing no formation of product **25a** in the absence of light, however, omission of the catalyst still yielded **25a** in 18% after 3 h pointing towards a photoinduced radical chain background reaction (Table 1, entries 15-16). Attempts to improve the efficiency of this radical chain pathway failed, thus, prolonged irradiation time to 12 h in MeOH or DCM still yielded **25a** in only 20% (Table 1, entries 17-18), while increasing the irradiation energy gave a complex reaction mixture (Table 1, entry 19). Likewise, initiation of the radical chain pathway with AIBN under thermal conditions resulted in 15% of product **15a** along with several unidentified by-products (Table 1, entry 20). Hence, promoting the reaction via a radical chain pathway does not seem to be sufficient in the desired transformation, being in accordance to aforementioned previous literature attempts (Scheme 3).[25-27] Testing either a Cu(I)- or Cu(II)-salt as a potential stand-alone catalyst did not lead to any conversion of starting materials, apparently also shutting down

the radical chain background reaction (Table 1, entries 21-23). In contrast, employing the dap ligand as a potential catalyst yielded **25a** in 12% (Table 1, entry 24). It is noteworthy, that the reaction completely shuts down when being driven under an air atmosphere (Table 1, entry 25).

Table 2. Comparison with other photocatalysts.



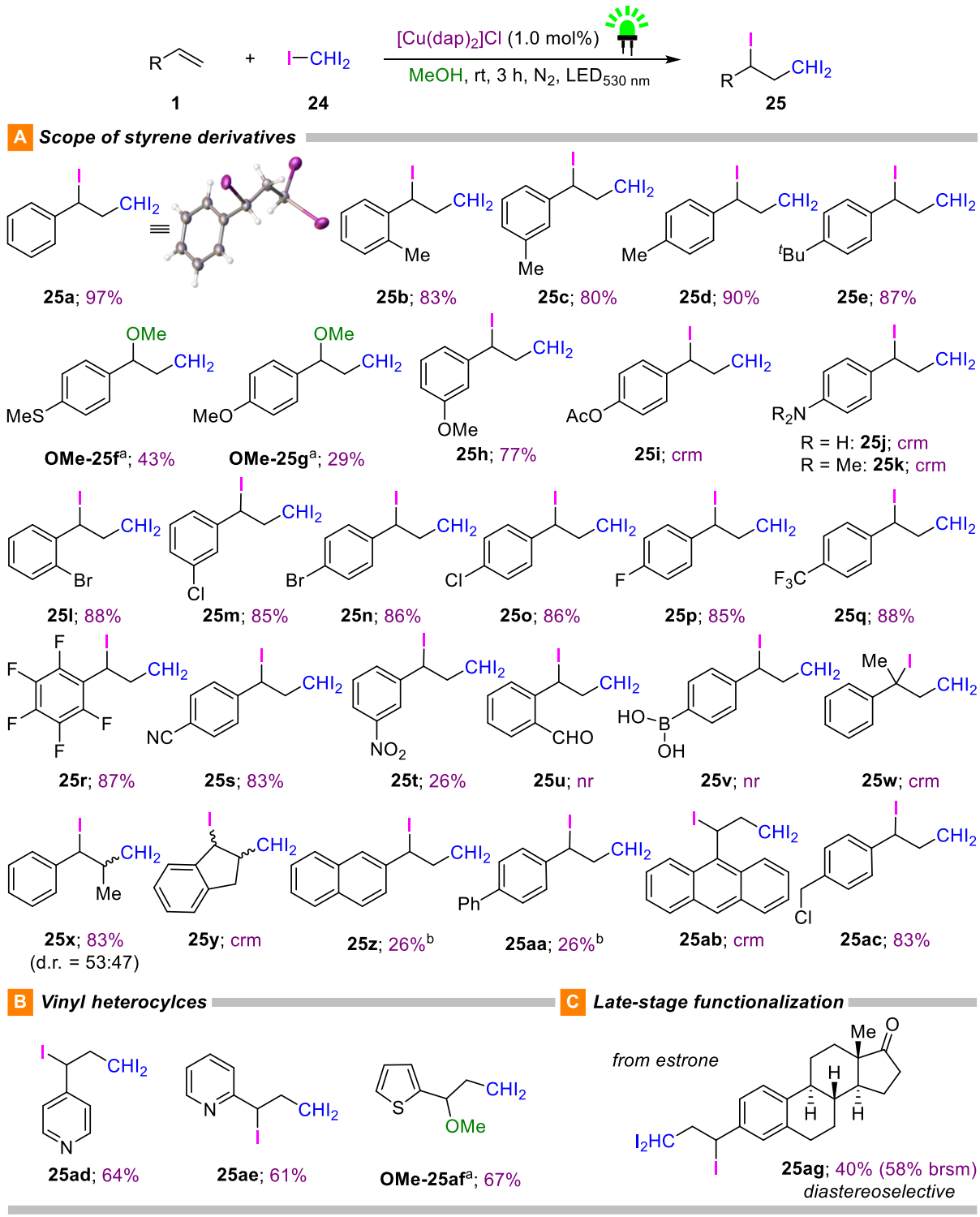
1a **24** **25a**

Entry	Photocatalyst (1.0 mol%)	λ_{vis}	Reaction time	Yield[a]
1	$[Cu(dap)_2]Cl$	530 nm	3 h	97% (97%[b])
2	$[Cu(dap)_2]Cl$	455 nm	3 h	54%
3	$[Ru(bpy)_3]Cl_2$	455 nm	3 h	15%
4	$[Ru(bpy)_3]Cl_2$	455 nm	12 h	15%
5[c]	$[Ru(bpy)_3]Cl_2$	455 nm	3 h	13%
6	$[Ru(bpy)_3]Cl_2$	530 nm	3 h	nr
7	*fac*-$[Ir(ppy)_3]$	455 nm	3 h	14%
8	*fac*-$[Ir(ppy)_3]$	455 nm	12 h	15%
9	*fac*-$[Ir(ppy)_3]$	530 nm	3 h	5%
10	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$	455 nm	3 h	17%
11	$[Ir(dtbbpy)(ppy)_2]PF_6$	455 nm	3 h	12%
12	Na_2-eosin Y	530 nm	3 h	18%
13	Na_2-eosin Y	530 nm	12 h	22%
14	Na_2-Rose Bengal	530 nm	12 h	11%
15	Rhodamine B	530 nm	12 h	16%
16	Rhodamine 6G	530 nm	12 h	3%
17	4-CzIPN	455 nm	12 h	24%
18	PTH	367 nm	12 h	8%
19	$[Cu(dap)Cl_2]$	530 nm	3 h	65%
20	$[Cu(phen)_2Cl]Cl$	530 nm	3 h	nr
21	$[Cu(dmp)_2]Cl$	530 nm	3 h	15%
22	$[Cu(dmp)_2Cl]Cl$	530 nm	3 h	13%
23	$[Cu(dpp)(binc)]BF_4$	530 nm	3 h	82%

Reaction conditions: Styrene (**1a**) (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeOH (anh., degassed, 2.0 mL, 0.25 M); Irradiation at indicated wavelength λ_{vis} under N_2 atmosphere at room temperature (25 °C) for the given reaction time. [a]NMR yield using diphenoxymethane as an internal standard. [b]Isolated yield. [c]Reductive quenching cycle using sodium ascorbate (0.175 mmol, 0.35 equiv) as sacrificial electron donor.

Finally, we checked whether this transformation is also accessible for commonly employed ruthenium-, iridium- or organic dye-based photocatalysts (Table 2). Entries 1 and 2 are taken from previous screening (Table 1) to offer a better comparison within Table 2. Attempts to access either the oxidative or reductive quenching cycle of $[Ru(bpy)_3]Cl_2$ under blue but also green light irradiation afforded the desired product **25a** in a maximum yield of 15%, even when the reaction time is prolonged from 3 h to 12 h (Table 2, entries 3-6). In the same way, screening efforts utilizing the strongly reducing photocatalyst *fac*-$[Ir(ppy)_3]$ in the title transformation with either blue or green light irradiation for up to 12 h reaction time furnished only up to 15% yield of **25a**. Other commonly employed iridium-based photocatalysts like $[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]PF_6$ or $[Ir(dtbbpy)(ppy)_2]PF_6$ appeared to be unsuitable catalysts in the same way failing to sufficiently promote the desired transformation, thus yielding **25a** in 17% and 12% yield, respectively. Considering organic dye-based photocatalysts as a low-cost alternative, several well-established representatives namely eosin Y, rose bengal, rhodamine B, rhodamine 6G, 4-CzIPN and strongly reducing PTH were tested under irradiation at various wavelengths for up to 12 h (Table 2, entries 12-18). Nevertheless, the desired product **25a** was only observed in low yields of 3-24%, which might be also attributed to the photoinduced radical chain background reaction under the given wavelengths taking place even in the absence of a photocatalyst. In Chapter 2, the corresponding Cu(II)-complex $[Cu(dap)Cl_2]$ was demonstrated to show similar efficiency compared to the Cu(I)-complex $[Cu(dap)_2]Cl$ but being considerable more cost-effective as only half amount of dap ligand is required. However, $[Cu(dap)Cl_2]$ proved to be significantly less effective in the title reaction between iodoform (**24**) and styrene (**1a**) delivering the desired product **25a** in only 65% yield (Table 2, entry 19) compared to 97% yield for the corresponding Cu(I)-complex (Table 2, entry 1). In the same way, the Cu(dmp)-system introduced in Chapter 3 failed to sufficiently promote the desired photoreaction leading to low yields in the range of 13-15% of **25a** (Table 2, entries 21-22). Only the Cu(I)-complex $[Cu(dpp)(binc)]BF_4$ demonstrated by the Reiser group as suitable catalyst for ATRA reactions[7d] produced the desired product **25a** in high yields of 82% (Table 2, entry 23) but still being outperformed by $[Cu(dap)_2]Cl$.

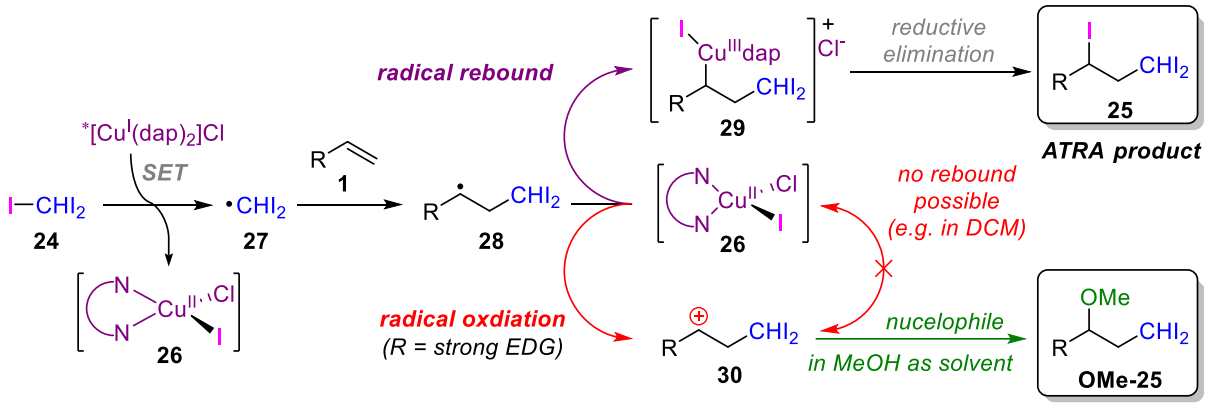
4.4 Substrate Scope



Scheme 4. Scope of different alkenes **1** in the photochemical ATRA reaction with iodoform (**24**). *Reaction conditions*: Alkene **1** (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (5.0 µmol, 1.0 mol%) in MeOH (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 3 h. [a]When the solvent DCM was used instead of MeOH, a complex reaction mixture was observed. [b]Product could not be isolated. Yield was determined by ^{1}H-NMR from the crude using diphenoxymethane as an internal standard.

Having identified the necessity of a copper photocatalyst for the desired transformation, we next set out to evaluate the scope of different alkenes **1** in the title reaction (Scheme 4). Starting with variations of styrene derivatives (Scheme 4, A), we were pleased to observe that electron-donating alkyl-substitution was well tolerated in *ortho*, *meta* and *para* position giving rise to the corresponding products **25b**-**25e** in high to excellent yields. Surprisingly, further increase of the electron-donating character by installing *p*SMe or *p*OMe moieties led to the isolation of the MeOH-substituted products **OMe-25f** and **OMe-25g** in moderate yields. Notably, performing these reactions in DCM being an equally effective solvent system for styrene (**1a**) (Chapter 4.3) gave a complex reaction mixture, pointing towards a different mechanistic pathway for highly electron-rich substrates (see later, Scheme 5). In line, when the methoxy group is placed in *meta* position, thus acting as an acceptor, rather than in *para* position, the desired iodinated product **25h** is obtained in 77% yield. Unfortunately, attempts to weaken the oxygen-substituent in *para* position by installing an electron-withdrawing acetyl-group at the oxygen aiming in the synthesis of **25i**, nevertheless failed and led to a complex reaction mixture. In the same way, strongly electron-donating nitrogen substitution was not tolerated resulting in a complex reaction mixture instead of the formation of the targeted products **25j** and **25k**. Styrene derivatives bearing electron-withdrawing halogen substitution in various positions furnished the desired products **25l**-**25p** in high yields. Further increasing the electron-withdrawing character of the styrene by either trifluoromethyl-, perfluoro-, or cyano-substitution was still well tolerated giving rise to the corresponding products **25q**-**25s** in 83%-88% yield. Notably, *m*NO_2 substitution showed a significant lower yield for **25t** in this series of substrates, probably caused by the ability of the nitro-group to either act as an electron acceptor leading to amines or as a triplet state quencher under such photochemical conditions.[28] A limitation seemed to be found in the use of aldehyde- or boronic acid-substituted styrene derivatives aiming in the synthesis of **25u** and **25v**, but instead giving no reaction of the corresponding starting materials. While α-substitution for the synthesis of **25w** appeared to be unsuitable under the present reaction conditions, β-substitution proved to be compatible in the desired transformation allowing the isolation of **25x** in 78% yield in a diastereomeric mixture of 53:47. Surprisingly, substrates showing extended π-systems led to a significant decrease in the yield (**25z**-**25ab**) along with problems in product isolation. It is believed that molecular iodine formed during the reaction might undergo stacking with these π-systems which might form species also absorbing light in the visible region and hence, shutting down the reaction efficiency. Remarkably, a benzylic chloride-containing styrene, presenting both a highly

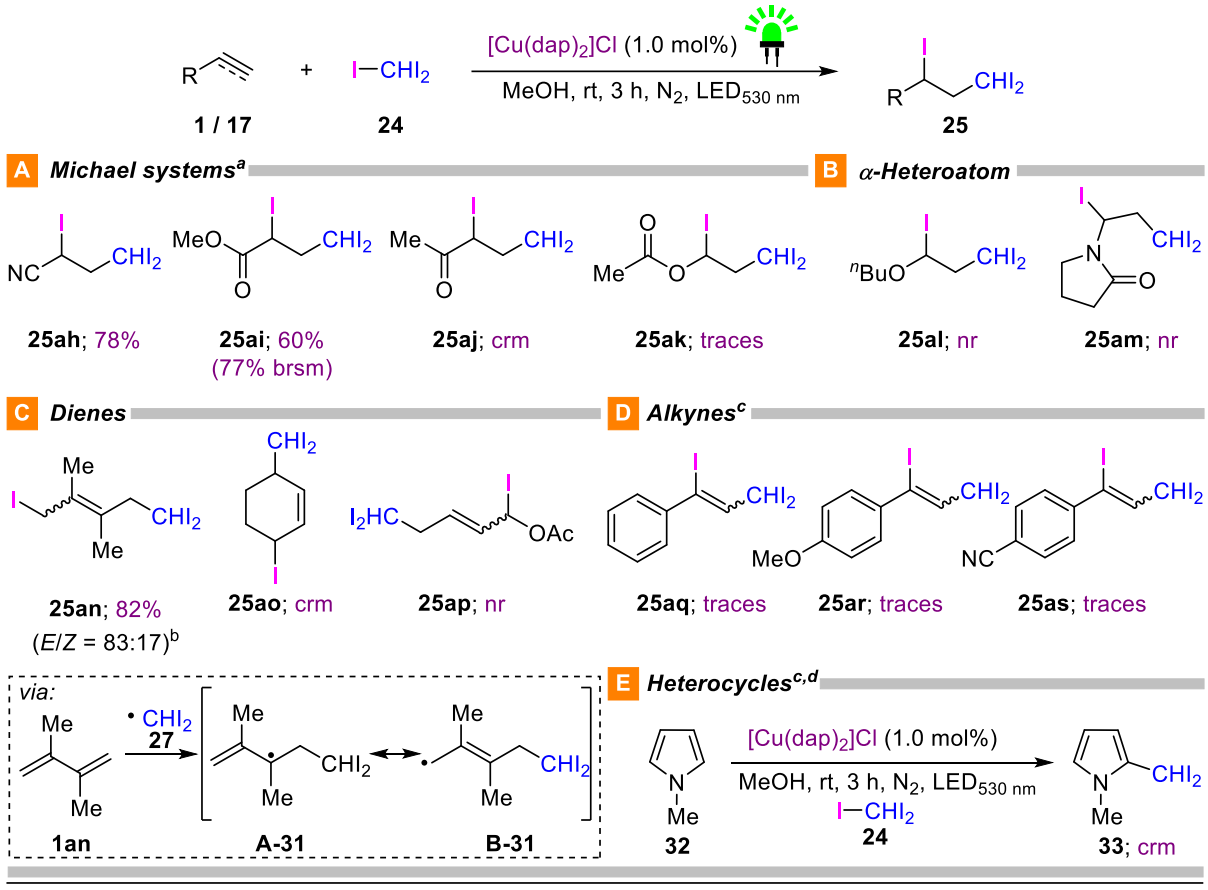
reactive C-H or C-Cl bond showed no cross-reactivity and furnished the desired product **25ac** in 83% yield. We were pleased that also vinyl heterocyclic compounds being not tolerated in the previously developed chlorosulfonylation (Chapter 2) were amenable substrates in the presented ATRA reaction with iodoform (**24**), thus giving access to the desired products **25ad-25ae** in synthetically useful yields (Scheme 4, B). Notably, a more-electron rich five-membered heterocycle again led to the formation of the MeOH-substituted product **OMe-25af**. An Estrone-derived substrate was diastereoselective transformed to the desired product **25ag** in good yields of 58% based on recovered starting material undergirding the capacity of the developed protocol for late-stage functionalization of bioactive compounds (Scheme 4, C). As already discussed before, Scheme 5 shows a plausible mechanistic explanation for the formation of the MeOH-substituted products **OMe-25f**, **OMe-25g** and **OMe-25af** during the reaction course of highly electron-rich alkenes.



Scheme 5. Plausible mechanistic proposal for the formation of the MeOH-substituted products **OMe-25f**, **OMe-25g** and **OMe-25af** when highly electron-rich alkenes **1** are used in the photochemical ATRA reaction with iodoform (**24**).

Photoexcited [Cu(dap)$_2$]Cl reduces iodoform (**24**) by single-electron transfer (SET) under oxidation to the Cu(II)-species **26** generating the corresponding carbon-centered radical **27**, which will then add to the alkene **1** leading to formation of benzylic radical **28**. The latter most likely binds back to the Cu(II)-species **26**, which can be regarded as a persistent radical itself, leading to Cu(III)-species **29** releasing the desired iodinated product **25** upon reductive elimination. However, in contrast, when the carbon-centered radical **27** adds to highly electron-rich alkenes **1**, fast oxidation of the resulting benzylic radical **28** to the corresponding benzylic carbocation **30** might be favored. The latter is not able to couple with iodide[7i] and also no longer able to rebind to the Cu(II)-intermediate **26** resulting in a complex reaction mixture when DCM is used as a solvent. Instead, when the reaction is performed in MeOH, benzylic carbocation **30**

seems to be stable enough to be attacked by the solvent acting as a nucleophile, thus forming the observed MeOH-substituted products **OMe-25**. It should be noted that this route is only feasible for highly electron-rich systems, as there is no formation of **OMe-25** observed, when the reaction is carried out with other styrene derivatives **1** using ruthenium- or iridium-based photocatalysts. However, one should also take into account, that irradiation with blue LED, being essential for ruthenium- or iridium-photocatalyst, is prevented by molecular iodine partially formed in the reaction mixture, thus shutting down the catalytic cycle of the latter. In the same way, the yield significantly decreased when $[Cu(dap)_2]Cl$ is excited with blue instead of green LED (Table 2, entries 1-2). Next, we pursued with other substrate classes for potential coupling in the desired photochemical ATRA reaction with iodoform (**24**) (Scheme 6).

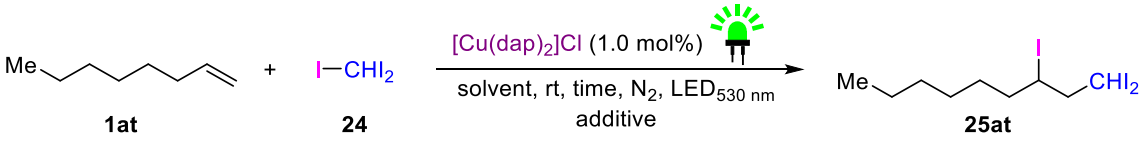


Scheme 6. Substrate scope for other substrate classes in the photochemical ATRA reaction with iodoform (**24**). *Reaction conditions*: Alkene **1** (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (5.0 µmol, 1.0 mol%) in MeOH (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 3 h. [a]3.0 equiv (1.5 mmol) of alkene **1** was used. [b]Stereochemistry was assigned in analogy to literature.[29] [c]Reaction was screened in MeOH and DCM (anh., degassed, 2.0 mL, 0.25 M). [d]Pyrrole **32** (1.0 mmol, 2.0 equiv).

Gratifyingly, also *α,β*-unsaturated substrates – being usually challenging for the addition of electrophilic radicals[30] – are tolerated in the title reaction, giving rise to the corresponding

products **25ah** and **25ai** in good yields (Scheme 6, A). Considering the increasing nucleophilicity from trifluoromethyl- to trichloromethylradical,[31] we assume the CHI_2 radical **27** to be even more nucleophilic in character, thus allowing addition to electron-poor double bonds. Moreover, this protocol could also be successfully applied to the substrate class of conjugated dienes, accessing a 1,4-radical addition pattern in product **25an** in 82% yield with a *E*/*Z* ratio[29] of 83:17 (Scheme 6, C). Unfortunately, alkenes activated by *α*-heteroatom substitution revealed to be unsuitable reaction partners resulting in no conversion of starting materials (Scheme 6, B). Another limitation of the protocol seemed to be found in the use of alkynes **17** (Scheme 6, D) or heterocycle **32** (Scheme 6, E) as radical trappers, which showed either no conversion or formation of a complex reaction mixture. We also settled out to test the use of unactivated alkene **1at** in the visible-light mediated copper-catalyzed ATRA reaction with iodoform (**24**) and therefore screened different reaction conditions (Table 3).

Table 3. Screening different reaction conditions for unactivated alkene (**1at**).



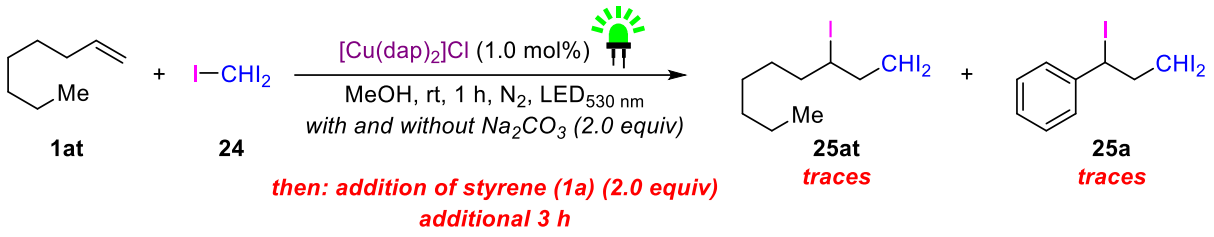
1at **24** **25at**

Entry	Solvent	Additive	Reaction time	Yield[a]
1	MeOH	no	3 h	3%
2	MeOH	no	12 h	3%
3	DCM	no	12 h	8%
4	MeOH	Na_2CO_3 (2.0 equiv)	12 h	11%
5	DCM	Na_2CO_3 (2.0 equiv)	12 h	7%
6	MeOH	$NaHCO_3$ (2.0 equiv)	12 h	6%
7	MeOH	K_2HPO_4 (2.0 equiv)	12 h	8%
8	MeOH	$KHSO_4$ (2.0 equiv)	12 h	5%

Reaction conditions: 1-Octen (**1at**) (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), additive (1.0 mmol, 2.0 equiv), $[Cu(dap)_2]Cl$ (5.0 µmol, 1.0 mol%) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at indicated wavelength 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for the given reaction time. [a]NMR yield using diphenoxymethane as an internal standard.

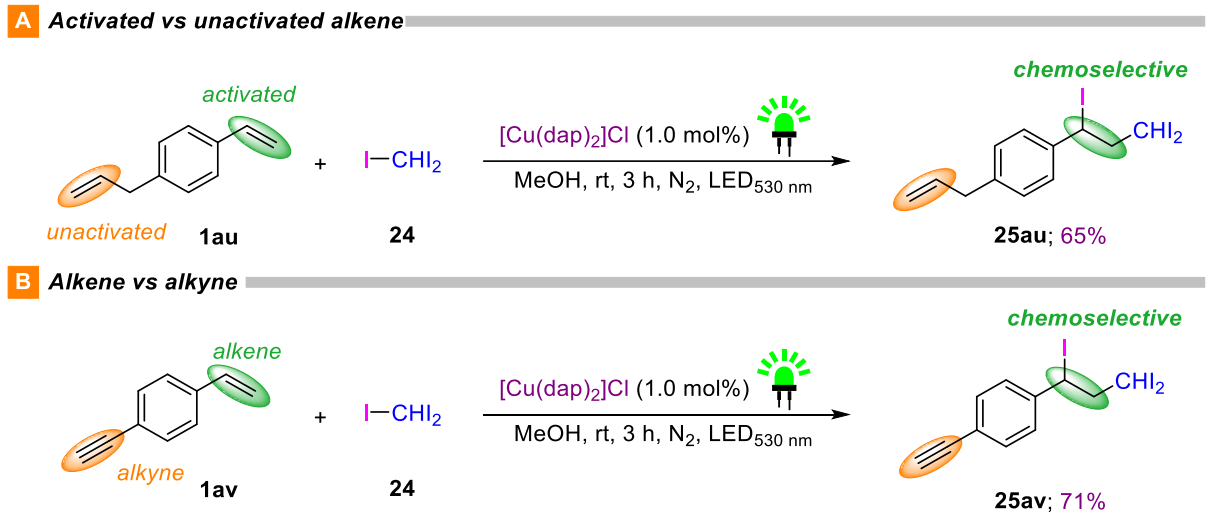
Subjecting 1-octen (**1at**) to the established reaction conditions for activated alkenes, nevertheless resulted in only low yields in the solvent DCM as well as in MeOH for up to 12 h reaction time (Table 3, entries 1-3). In accordance with our previous studies (Chapter 2 and Chapter 3) it is assumed that traces of acids, which might be generated during the reaction when the radical intermediates are not rapidly trapped by the alkene **1**, are poisoning the active catalyst and thus shutting down the catalytic cycle. Unfortunately, several attempts to prevent

catalyst poisoning by addition of base failed (Table 3, entries 4-8). Catalyst stability test proved aforementioned catalyst poisoning (Scheme 7). When a mixture of unactivated alkene **1at** and iodoform (**24**) was irradiated for 1 h followed by the addition of styrene (**1a**) with continuing the irradiation for another 3 h, formation of only traces of **25a**, being usually delivered in almost quantitative yields, are observed, thus pointing toward a significant poisoning of the catalyst.



Scheme 7. Catalyst stability test for unactivated alkene **1at**. *Reaction conditions*: 1-Octen (**1at**) (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), with and without Na_2CO_3 (1.0 mmol, 2.0 equiv), $[Cu(dap)_2]Cl$ (5.0 µmol, 1.0 mol%) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at indicated wavelength 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 1 h. Then: Addition of styrene (**1a**) (1.0 mmol, 2.0 equiv) under a slight nitrogen overpressure and continuing irradiation at 530 nm (green LED) under N_2 atmosphere for 3 h at room temperature (25 °C).

However, although substrate classes of alkynes and unactivated alkenes revealed to be not feasible in the title reaction, we seized the opportunity and exploited substrates **1au** and **1av** to test the chemoselectivity of the shown protocol (Scheme 8).



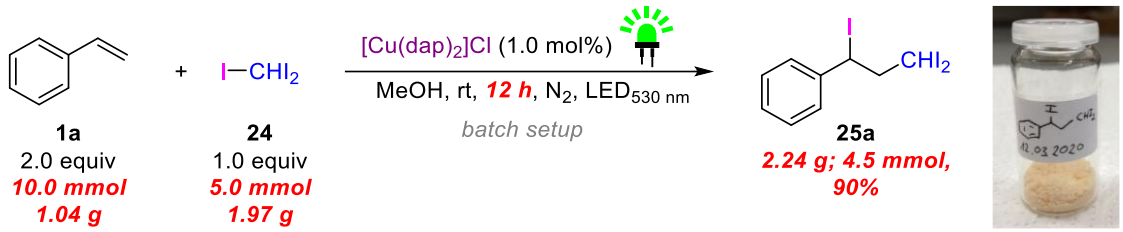
Scheme 8. Chemoselectivity of photochemical ATRA reaction with iodoform (**24**). *Reaction conditions*: alkene **1** (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (5.0 µmol, 1.0 mol%) in MeOH (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 3 h.

Offering an activated as well as an unactivated double bond in the same molecule **1au** to the established reaction conditions, only the activated double bond is selectively functionalized to

the desired product **25au**, while the unactivated one stays completely untouched (Scheme 8, A). Similarly, when at the same time a triple bond is present as seen in **1av**, again only the activated double bond is cleanly transformed to the corresponding iodo-alkylated product **25av** (Scheme 8, B).

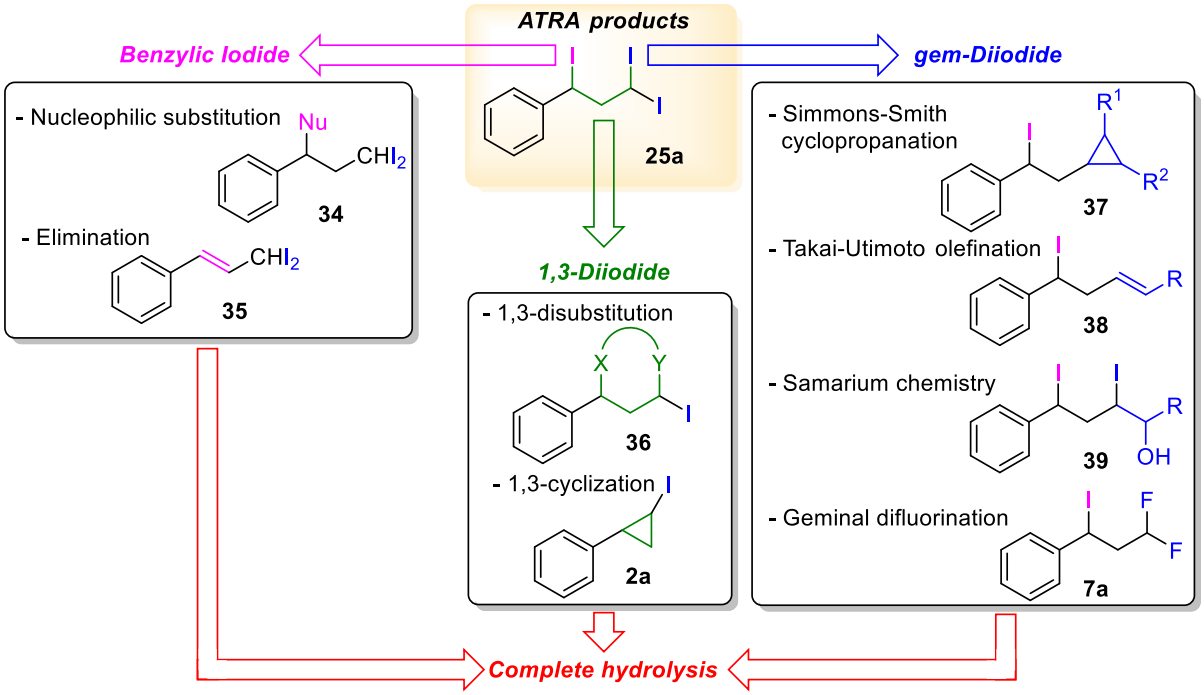
4.5 Gram-Scale Functionalization and Synthetic Utility

Next, we established the viability of the protocol for preparative purposes. Iodo-alkylated product **25a** was obtained in multi-gram amount in a simple batch-setup with an excellent yield of 90% applying a slightly prolonged reaction time of 12 h (Scheme 9).



Scheme 9. Gram-scale functionalization of styrene (**1a**) with iodoform (**24**). *Reaction conditions*: Styrene (**1a**) (10.0 mmol, 2.0 equiv), iodoform (**24**) (5.0 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (50.0 µmol, 1.0 mol%) in MeOH (anh., degassed, 20.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 12 h.

Finally, we proceeded to demonstrate the synthetic utility of the highly iodinated products **25a** for further transformations.



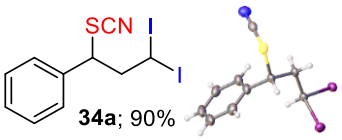
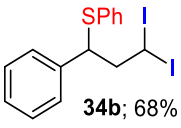
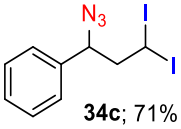
Scheme 10. Structural analysis of photoproduct **25a** for potential further transformations.

A structural analysis of the obtained photoproduct **25a** for potential further transformations is depicted in Scheme 10. In general, **25a** offers several structural motifs to target: benzylic iodide for substitution or elimination reactions (Chapter 4.4.1), vicinal diiodides for 1,3-disubstitutions or 1,3-cyclizations (Chapter 4.4.2), geminal diiodides for various known transformations already discussed in the introduction, e.g. Simmons-Smith cyclopropanation or Takai-Utimoto olefination (Chapter 4.4.3), or hydrolysis of the whole molecule (Chapter 4.4.4).

4.5.1 Nucleophilic Substitutions and Eliminations

We started our investigations with various attempts on the nucleophilic substitution of the benzylic iodide in **25a** (Table 4).

Table 4. Screening different nucleophilic substitutions on **25a**.

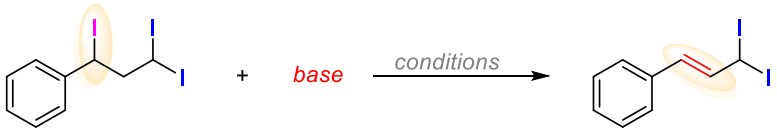
Entry	Nucleophile	Conditions	Yield
1[a]	MeOH (solvent)	*m*CPBA (1.2 equiv), MeOH/DCM (1:1), rt, N_2, 12 h	crm
2	MeOH (3.0 equiv)	Na_2CO_3 (2.5 equiv), MeCN (anh.), rt, N_2, 12 h	nr
3	PhOH (3.0 equiv)	Na_2CO_3 (2.5 equiv), MeCN (anh.), rt, N_2, 12 h	nr
4[b,c]	NaSCN (2.5 equiv)	Na_2CO_3 (2.5 equiv), MeCN (anh.), rt, N_2, 12 h	 **34a**; 90%
5	PhSH (2.5 equiv)	Na_2CO_3 (2.5 equiv), MeCN (anh.), rt, N_2, 12 h	 **34b**; 68%
6[d]	NaCN (2.5 equiv)	DMSO (anh.), rt, N_2, 12 h	crm
7	NaCN (2.5 equiv)	Na_2CO_3 (2.5 equiv), MeCN (anh.), rt, N_2, 12 h	nr
8[a]	NaN_3 (10.0 equiv)	DMF (anh.), rt, N_2, 12 h	crm
9	NaN_3 (2.5 equiv)	Na_2CO_3 (2.5 equiv), MeCN (anh.), rt, N_2, 12 h	 **34c**; 71%

Reaction conditions: Reactions were performed on a 0.2 mmol scale of **25a** (1.0 equiv) in solvent (anh., 2.0 mL, 0.1 M) under N_2 atmosphere at room temperature (25 °C) for 12 h. [a]Based on Ref.[32]. [b]Based on Ref.[33]. [c]Reaction was also performed on a 3.0 mmol scale: yield of **34a** was 85%. [d]Based on Ref.[34]

While MeOH- or PhOH-substitution was not feasible under various conditions (Table 4, entries 1-3) being in accordance with our observations performing the photoreaction in MeOH as a solvent, NaSCN, thiophenol or NaN_3 pleasingly underwent selective benzylic substitution to furnish functionalized *gem*-diiodides **34a**, **34b** and **34c** in 68%-90% yields in up to gram quantities. Thus, the obtained photoproducts **25** offer the possibility to access a family of functionalized *gem*-diiodides representing privileged precursors to manifold organometallic intermediates (see Introduction Chapter 4.2, Scheme 1) being otherwise challenging to access (see Introduction Chapter 4.2, Scheme 2).

Unfortunately, several attempts utilizing different basic systems aiming in synthesis of **35** via elimination of the benzylic iodide failed, resulting in either no conversion of starting materials or complex reaction mixtures (Table 5). Subjecting **25a** to a solution of triethylamine in $CHCl_3$, which proved to be highly efficient in the elimination of the chlorosulfonylation products (Chapter 2), yielded no conversion of the starting material **25a** (Table 5, entry 1). In the same way, applying two different conditions for the elimination of benzylic iodides as reported in literature appeared to be unsuitable for the highly iodinated product **25a**, which may be attributed to the increased sterically demand and thus effective shielding of the benzylic iodide by the *gem*-diiodide moiety (Table 5, entries 3-4).

Table 5. Several attempts towards elimination of the benzylic iodide in **25a**.



25a **35**

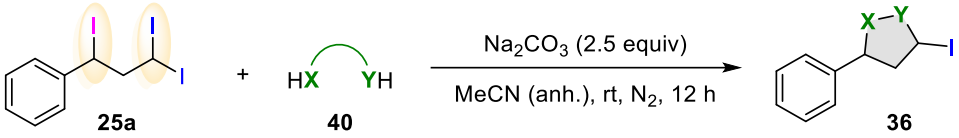
Entry	Base	Conditions	Yield
1	NEt_3 (3.0 equiv)	$CHCl_3$, rt, 2 h	nr
2[a]	DMAP (3.0 equiv)	acetone, rt, 1 h	crm
3[b]	KO^{t}Bu (1.3 equiv)	DE, 0°C, 4 h	crm
4	DIPEA (3.0 equiv)	MeCN, rt, 2h	nr

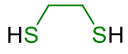
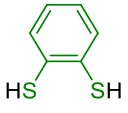
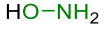
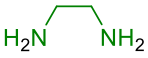
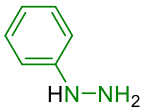
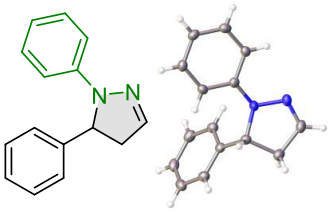
Reaction conditions: Reactions were performed on a 0.2 mmol scale of **25a** (1.0 equiv) in solvent (anh., 2.0 mL, 0.1 M) under N_2 atmosphere at indicated temperature for the indicated time. [a]Based on Ref.[33], [b]Based on Ref.[35]

4.5.2 Heterocycle Synthesis and Intramolecular 1,3-Cyclizations

Next, we set out to investigate the plausibility of applying a binucleophile for the substitution of both the benzylic iodide as well as one of the *gem*-diiodides being in a 1,3-distance. This approach might ultimately yield in the rapid construction of heterocycles (Table 6).

Table 6. Attempts on nucleophilic substitutions of **25a** with binucleophiles.



Entry	Binucleophile	Yield
1	 **40a** (2.5 equiv)	crm
2	 **40b** (2.5 equiv)	crm
3	 **40c** (2.5 equiv)	nr
4	 **40d** (2.5 equiv)	crm
5	 **40e** (2.5 equiv)	 **36a**; 60%

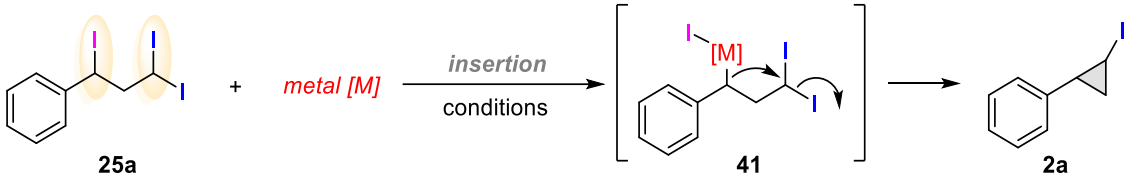
Reaction conditions: **25a** (0.2 mmol, 1.0 equiv), binucleophile **40** (0.5 mmol, 2.5 equiv), Na_2CO_3 (0.5 mmol, 2.5 equiv) in MeCN (anh., 2.0 mL, 0.1 M) under N_2 atmosphere at room temperature (25 °C) for 12 h.

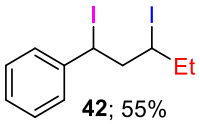
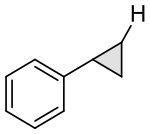
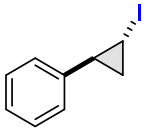
We were pleased to observe the formation of 2-pyrazoline derivative **36a** in good yields of 60% when phenylhydrazine (**40e**) was employed as the binucleophile (Table 6, entry 5). 2-Pyrazolidines represent a privileged and valuable class of azaheterocycles frequently found in many natural occurring compounds and drug candidates with intriguing biological properties like antidepressant, anti-inflammatory, anticancer, antibacterial, or antiviral activities.[36] Unfortunately, several attempts using other binucleophiles to rapidly construct various heterocycles failed, giving mostly complex reaction mixtures or no conversion of starting materials (Table 6, entries 1-4).

The 1,3-correlation of two iodides in the photoproduct **25a** might also offer the opportunity to insert a metal preferably into the benzylic carbon-iodide bond yielding intermediate **41**, which then can subsequently trigger an intramolecular 1,3-cyclization eliminating one of the iodides

in the corresponding 1,3-distance to conclusively access iodo-substituted cyclopropane **2a** (Table 7).

Table 7. Attempts to trigger intramolecular cyclopropanation in **25a**.

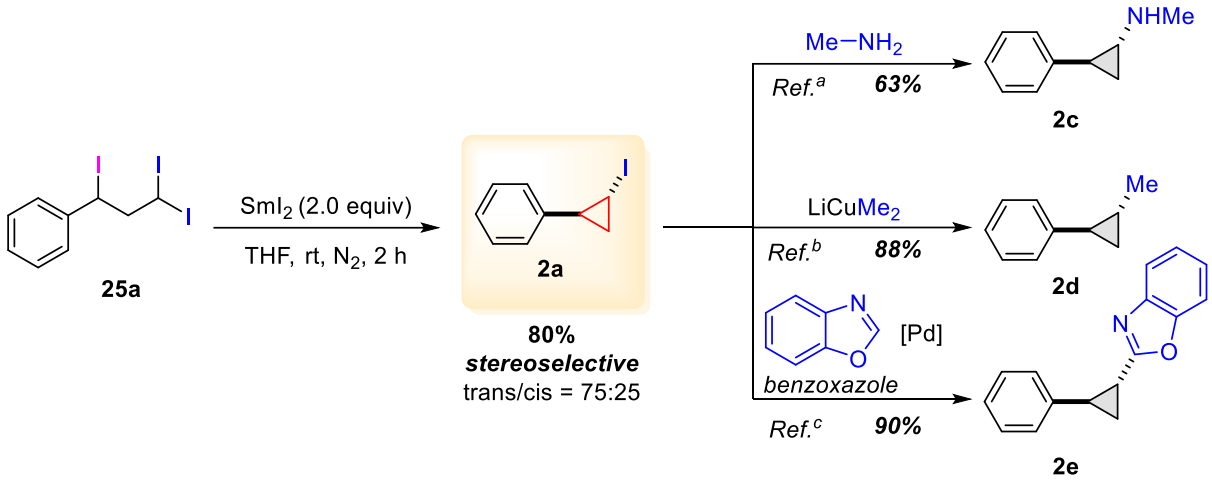


Entry	Metal [M]	Conditions	Yield
1	Et_2Zn (1.5 equiv)	DCM (anh.), 0 °C to rt, N_2, 3 h	 **42**; 55% *(only one diastereomer observed)*
2	Zn-powder (2.0 equiv)	DCM (anh.), rt, N_2, 12 h	nr
3	Zn-powder (2.0 equiv)	EtOH (anh.), reflux, N_2, 3 h	 **2b**; 33%[a]
4[b]	SmI_2 (2.0 equiv)	THF (anh.), rt, N_2, 2 h	 **2a**; 80% (trans/cis = 75:25)

Reaction conditions: **25a** (0.2 mmol, 1.0 equiv), metal (indicated amount) in solvent (anh., degassed, 2.0 mL, 0.1 M) under N_2 atmosphere at indicated temperature (room temperature corresponds to 25 °C) for the indicated time. [a]Product could not be isolated. Yield was determined by ^{1}H-NMR from the crude using diphenoxymethane as an internal standard. [b]A solution of SmI_2 in THF (0.1 M, 4.0 mL, 0.40 mmol, 2.0 equiv).

When diethylzinc is used as the metal source, no insertion in the benzylic iodide bond is observed, but instead the negatively polarized ethyl residue substituted one of the *gem*-diiodides resulting in compound **42** in 55% yield (Table 7, entry 1). This result is surprising, as nucleophilic substitution should preferably occur on the benzylic iodide as shown in chapter 4.4.1. Remarkably, NMR revealed that only one diastereomer is formed. Hence, detailed studies and exact analysis to further exploit this initial result remain to be determined and are ongoing in our laboratories. Switching from diethylzinc to zinc-powder eliminating a possible ethyl substitution led to no reaction in DCM at room temperature (Table 7, entry 2), while indeed 33% of cyclopropane **2b** were observed in the crude NMR when ethanol and reflux conditions are employed (Table 7, entry 3). The latter might be formed when another zinc metal inserts into the iodinated cyclopropane **2a** generated in the first step and then the resulting species traps

a proton from the solvent. Unfortunately, due to its volatility the final product **2b** could not be isolated. However, replacing zinc by samarium, we were really pleased to observe the desired iodocyclopropane **2a** in 80% yield with a trans/cis ratio of 75:25 (Table 7, entry 4). We assume, samarium to be less reactive compared to zinc only inserting in the more reactive benzylic iodide bond of the starting material **25a**, but not into the one of **2a** which would lead to undesired follow-up reactions. The iodinated cyclopropane **2a** proved to be a key building block in recent literature reports, e.g. palladium-catalyzed cross-coupling provides access to elegantly and rapidly link the cyclopropane building block on various heterocycles, thus building up value-added products with desired molecular complexity (Scheme 11).

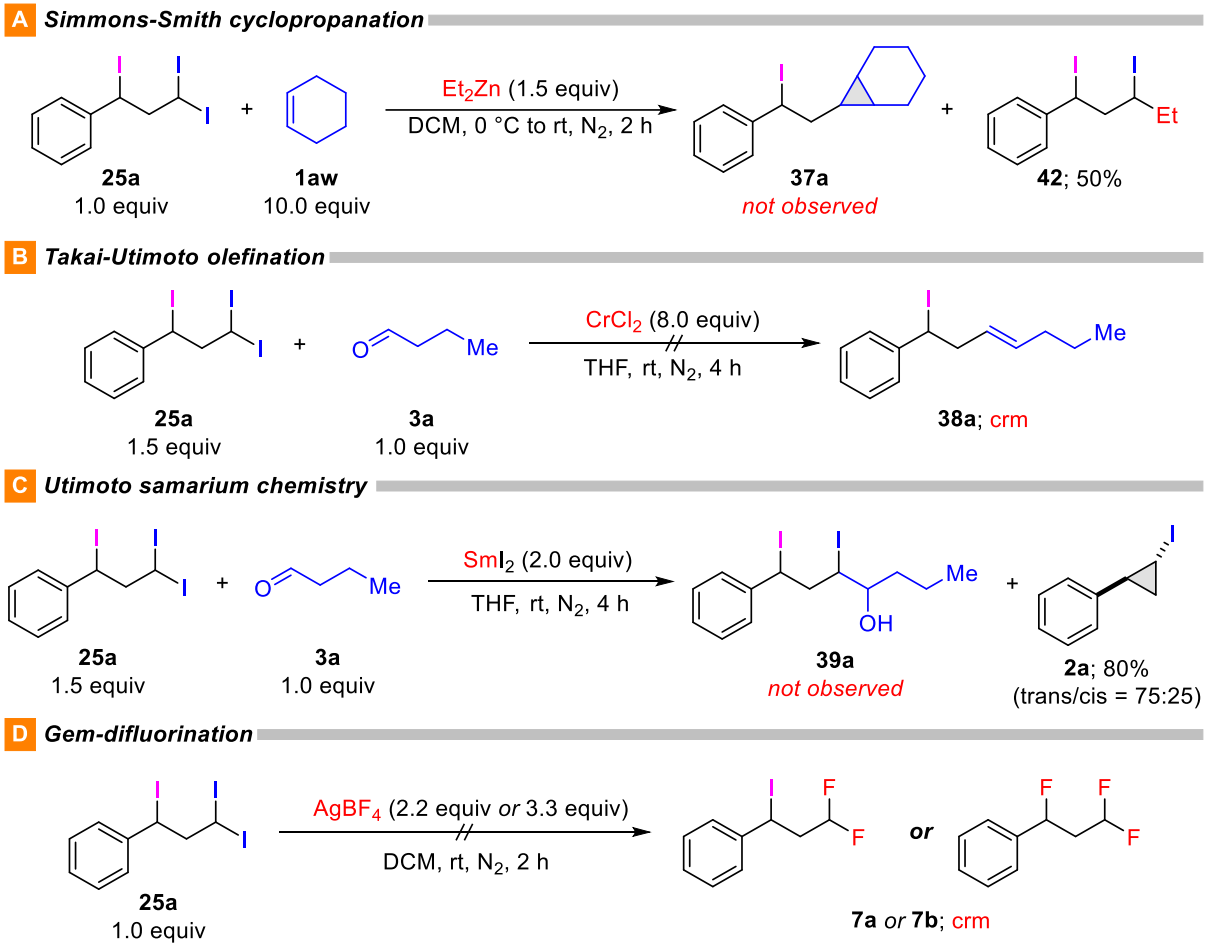


Scheme 11. Possible further transformations of iodocyclopropane **2a**. [a]Ref.[37], [b]Ref.[38], [c]Ref.[39]

4.5.3 Transformations of the Geminal Diiodide Moiety

To further broaden the scope of applications, we shifted our attention to the *gem*-diiodide moiety in the obtained photoproduct **25a** (Scheme 12). The importance of *gem*-diiodides as a valuable synthetic building block is already discussed in the introduction part (Chapter 4.2, Scheme 1). Hence, we started our investigations employing photoproduct **25a** in a Simmons-Smith cyclopropanation on cyclohexene (**1aw**) (Scheme 12, A). In line with the results obtained in the previous chapter (4.4.2), the diethylzinc reagent acts as a source for an ethyl nucleophile leading to the formation of **42** instead of the desired cyclopropanation product **37a**. Efforts on Takai-Utimoto olefination between **25a** and **3a** failed yielding a complex reaction mixture (Scheme 12, B). In the same way, employing SmI_2 in the presence of aldehyde **3a** aiming for the synthesis of **39a** (Scheme 12, C) was not feasible, instead giving rise to the corresponding intramolecular cyclopropanation to **2a** being in accordance to the observation made in chapter

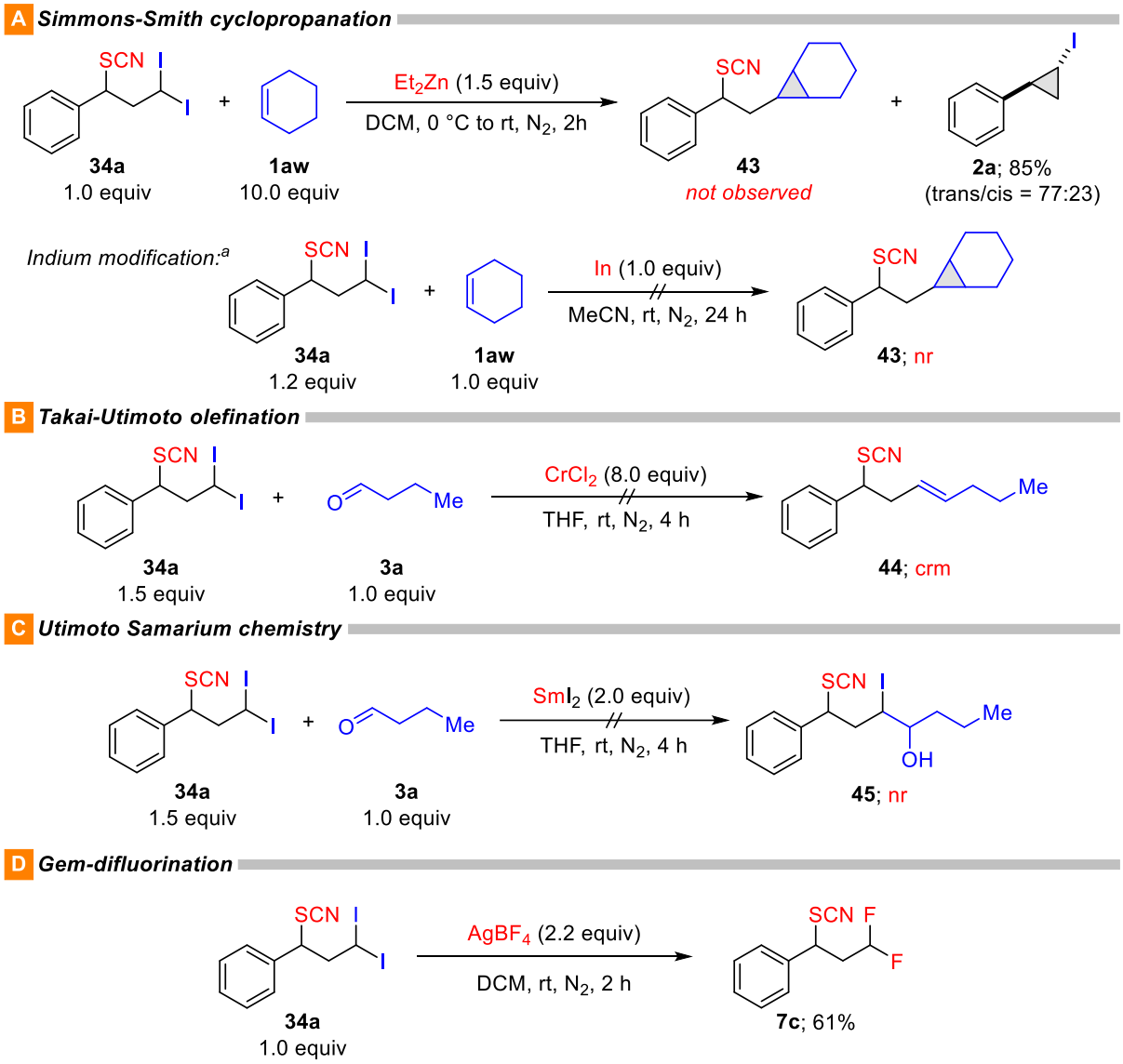
4.4.2. Attempts on the *gem*-difluorination of **25a** with $AgBF_4$ unfortunately resulted in a complex reaction mixture (Scheme 4, D).



Scheme 12. Attempts on further applications for the *gem*-diiodide moiety in **25a**. *Reaction conditions*: (A) **25a** (0.2 mmol, 1.0 equiv), alkene **1aw** (2.0 mmol, 10.0 equiv), Et_2Zn (0.3 mmol, 1.5 equiv) in DCM (anh., degassed, 2.0 mL, 0.1 M) under N_2 atmosphere at room temperature (25 °C) for 2 h. Ref.[8]; (B) **25a** (0.3 mmol, 1.5 equiv), aldehyde **3a** (0.2 mmol, 1.0 equiv), $CrCl_2$ (1.6 mmol, 8.0 equiv) in THF (anh., degassed, 8.0 mL, 0.04 M) under N_2 atmosphere at room temperature (25 °C) for 4 h. Ref.[9]; (C) **25a** (0.3 mmol, 1.5 equiv), aldehyde **3a** (0.2 mmol, 1.0 equiv), solution of SmI_2 in THF (0.1 M, 4.0 mL, 0.40 mmol, 2.0 equiv) under N_2 atmosphere at room temperature (25 °C) for 4 h. Ref.[12]; (D) **25a** (0.2 mmol, 1.0 equiv), $AgBF_4$ (0.44 mmol-0.66 mmol, 2.2-3.3 equiv) in DCM (anh., degassed, 1.5 mL, 0.13 M) under N_2 atmosphere at room temperature (25 °C) for 2 h. Ref.[13]

Overall, we assume that the coexisting and highly reactive benzylic iodide might interfere in aforementioned reactions leading to cross-reactivity and undesired reaction pathways. Hence, we set out to examine the reactivity of the *gem*-diiodide when the benzylic iodide is substituted beforehand with SCN being a much less reactive benzylic substituent (Scheme 13). Unfortunately, the Simmons-Smith cyclopropanation of **34a**, using diethylzinc and **1aw** as the alkene aiming for the synthesis of **43**, instead furnished 1,3-intramolecular cyclization product

2a in 85% yield with a trans/cis ratio of 77:23 (Scheme 13, A). Attempts on replacing diethylzinc by a milder method for Simmons-Smith cyclopropanation, reported in 2005 by Bir and co-workers utilizing indium as the metal source,[40] failed resulting in no reaction of the starting materials **34a** and **1aw**.

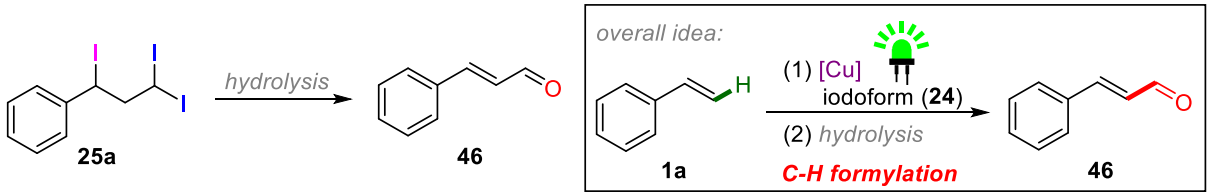


Scheme 13. Attempts on further applications for the *gem*-diiodide moiety in **34a**. *Reaction conditions*: (A) **34a** (0.2 mmol, 1.0 equiv), alkene **1aw** (2.0 mmol, 10.0 equiv), Et_2Zn (0.3 mmol, 1.5 equiv) in DCM (anh., degassed, 2.0 mL, 0.1 M) under N_2 atmosphere at room temperature (25 °C) for 2 h. Ref.[8]; [a]Indium modification: **34a** (0.24 mmol, 1.2 equiv), alkene **1aw** (0.2 mmol, 1.0 equiv), In (0.2 mmol, 1.0 equiv) in MeCN (anh., degassed, 2.0 mL, 0.1 M) under N_2 atmosphere at room temperature (25 °C) for 24 h. Ref.[40]; (B) **34a** (0.3 mmol, 1.5 equiv), aldehyde **3a** (0.2 mmol, 1.0 equiv), $CrCl_2$ (1.6 mmol, 8.0 equiv) in THF (anh., degassed, 8.0 mL, 0.04 M) under N_2 atmosphere at room temperature (25 °C) for 4 h. Ref.[9]; (C) **34a** (0.3 mmol, 1.5 equiv), aldehyde **3a** (0.2 mmol, 1.0 equiv), solution of SmI_2 in THF (0.1 M, 4.0 mL, 0.40 mmol, 2.0 equiv) under N_2 atmosphere at room temperature (25 °C) for 4 h. Ref.[12]; (D) **34a** (0.2 mmol, 1.0 equiv), $AgBF_4$ (0.44 mmol, 2.2 equiv) in DCM (anh., degassed, 1.5 mL, 0.13 M) under N_2 atmosphere at room temperature (25 °C) for 2 h. Ref.[13]

Takai-Utimoto olefination between **34a** and **3a** (Scheme 13, B) as well as the corresponding samarium-promoted coupling (Scheme 13, C) were not feasible yielding either a complex reaction mixture or in no conversion of the starting materials. However, we were pleased to observe that contrasting the *gem*-difluorination of **25a**, in the case of **34a** the reaction proceeded well accessing the desired product **7c** in a synthetical useful yield of 61% (Scheme 13, D). In general, the introduction of a difluoromethyl group into molecules is a rapidly expanding field,[41] as fluorine can productively impact metabolic pathways and pharmacological properties.[42]

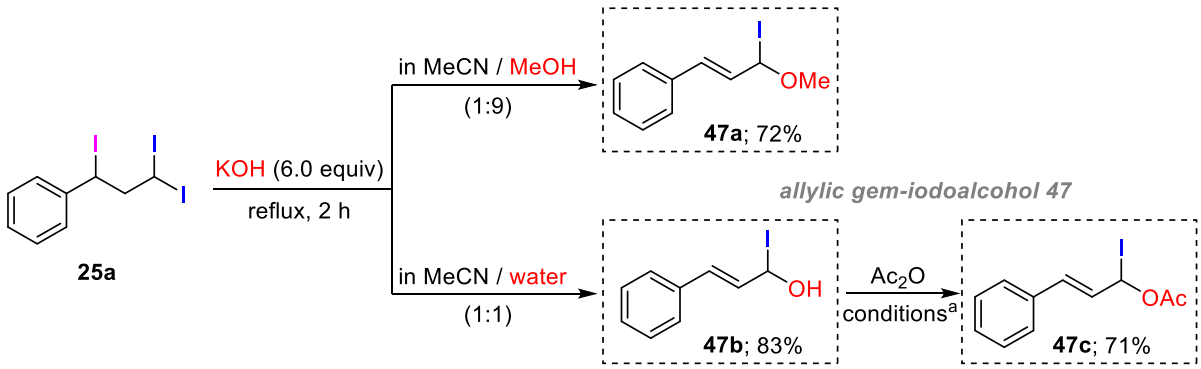
4.5.4 Hydrolysis towards Allylic Iodoalcohols and Further Studies

Lastly, we aimed for complete hydrolysis of photoproduct **25a** ultimately yielding in an overall C-H formylation protocol (Scheme 14).



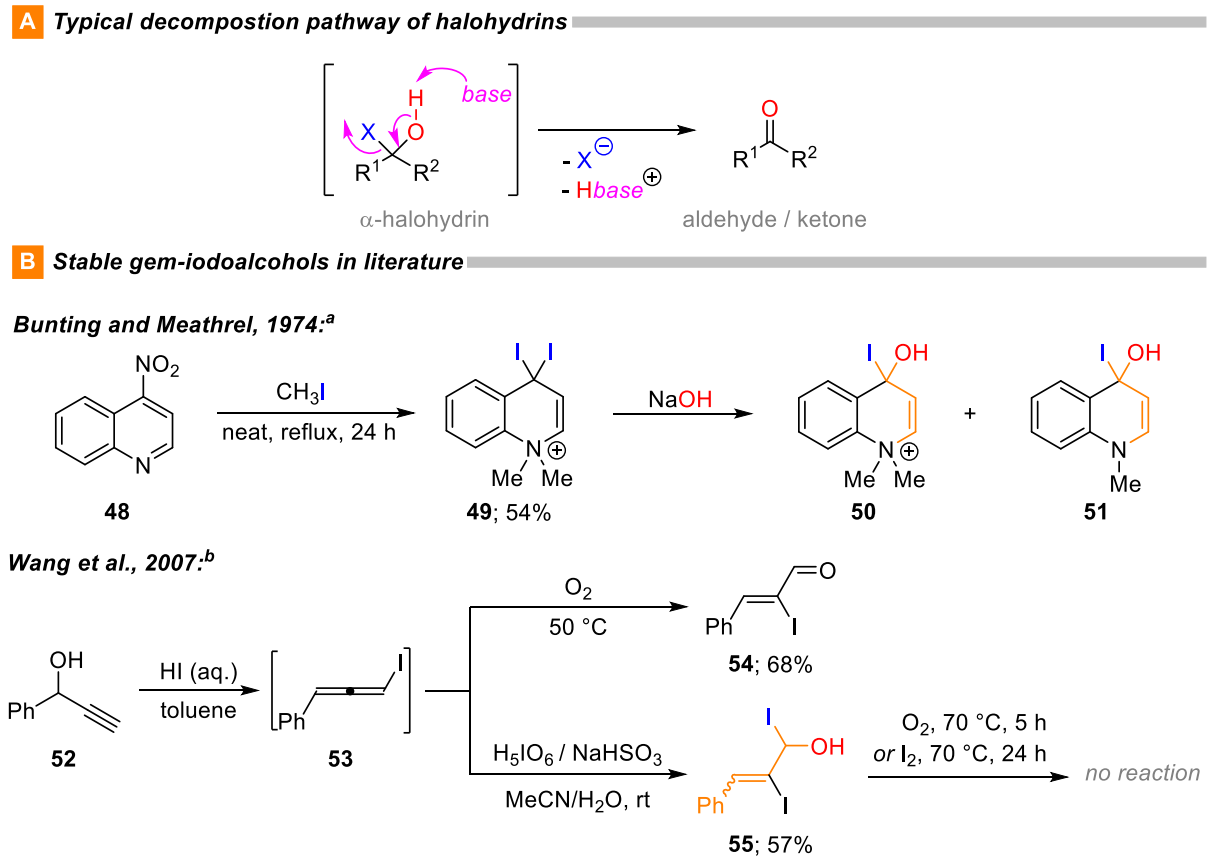
Scheme 14. Synthesis plan for hydrolysis of **25a** aiming in an overall C-H formylation protocol.

However, to our surprise, we exclusively observed formation of the methyl-protected allylic *gem*-iodoalcohol **47a** in 72% yield when the solvent system MeCN/MeOH is used, or the free alcohol moiety **47b** in 83% yield when MeCN/water is employed (Scheme 15). The latter can also be smoothly protected by an acetyl group giving rise to **47c** in 71% yield on a gram-scale.



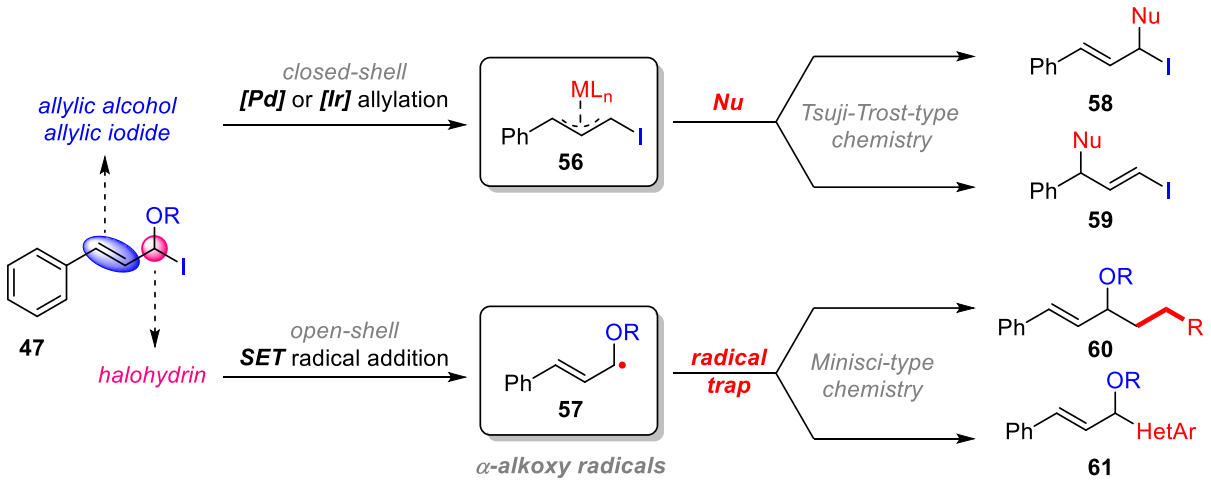
Scheme 15. Hydrolysis of **25a**. *Reaction conditions*: **25a** (0.2 mmol, 1.0 equiv), KOH (1.2 mmol, 6.0 equiv) in the indicated solvent systems (4.0 mL, 0.05 M) under reflux for 2 h. Reactions were also performed on 5.0 mmol scale to give **47a** in 72% yield and **47b** in 83% yield. [a]Crude mixture of **47b** (4.0 mmol scale), NEt_3 (8.0 mmol, 2.0 equiv), DMAP (0.4 mmol, 10.0 mol%) and Ac_2O (8.0 mmol, 2.0 equiv) in DCM (20.0 mL, 0.2 M) at 0 °C to room temperature (25 °C) for 3 h.

This class of products is synthetically challenging to access and displays a unique structural motif combining three valuable functionalities, namely, an allylic iodide, an allylic alcohol and a *gem*-iodoalcohole at the same time. In general *gem*-iodoalcohols (*α*-halohydrins) are prone to rapidly undergo facile decomposition to either aldehydes (primary halohydrin) or ketones (secondary halohydrins) (Scheme 16, A).[43] Hence studies done hitherto were usually theoretical in nature.[43] Nevertheless, there are few studies reporting stable *gem*-iodoalcohols (Scheme 16, B). While exploring reactions on quaternary nitrogen heterocycles in the 1900s, Bunting and Meathrel serendipitously revealed the formation of *gem*-diiodide **49**, which subsequently formed *gem*-iodoalcohols **50** and **51** upon treatment with NaOH.[44] More recently, Wang and co-workers demonstrated **53** as an intermediate to form allylic *gem*-iodoalcohol **55** in 57% yield, which turned out to be stable even after heating under O_2 or I_2 atmosphere (Scheme 16, B).[45]



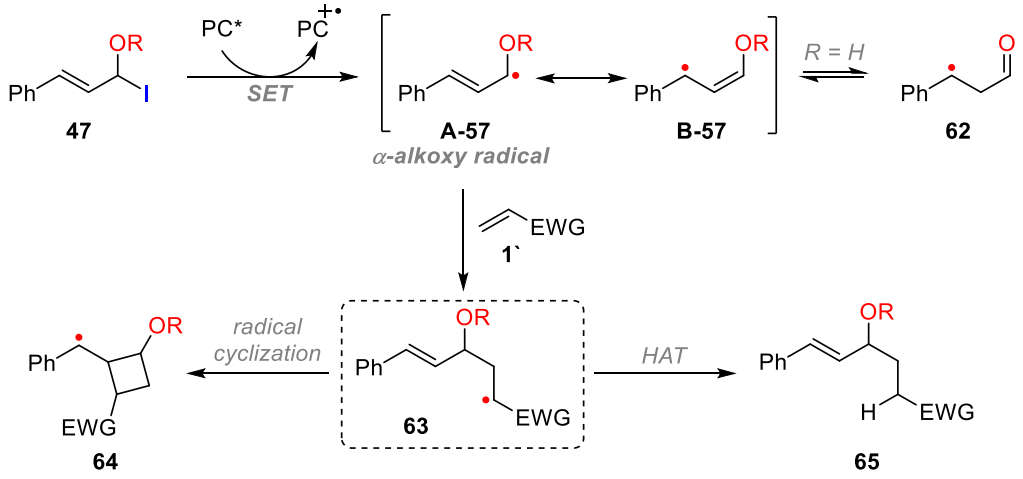
Scheme 16. (A) Typical decomposition pathway of *gem*-iodoalcohols.[43] (B) Stable *gem*-iodoalcohols from the literature. [a]Ref.[44], [b]Ref.[45]

Considering the allylic *gem*-iodoalcohol **47** as a starting point, conceptual dissection of **47** reveals closed-shell reactivity for palladium- or iridium-catalyzed Tsuji-Trost-type allylation reactions or open-shell radical chemistry generating α-alkoxy radicals for Minisci-type chemistry (Scheme 17).



Scheme 17. Conceptual dissection of allylic *gem*-iodoalcohol **47**.

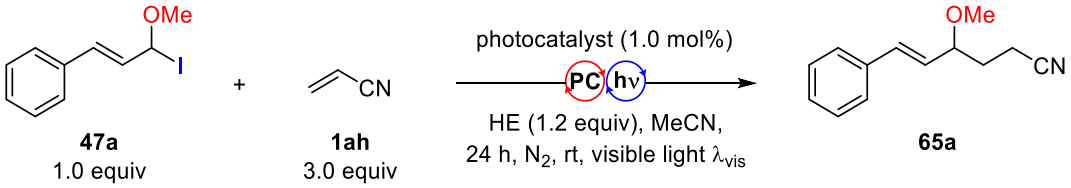
Thus, we started our investigations on this unique structural motif employing photoredox catalysis to trigger single-electron transfer (SET) reducing the carbon-iodide bond to form α-alkoxy radical **A-57**, which is stabilized through resonance to the corresponding benzylic radical **B-57** (Scheme 18). We then envisioned to trap the α-alkoxy radical **57** being electron-rich in nature with an electron-poor double bond **1`** resulting in radical intermediate **63**, which either can undergo radical cyclization to form a four-membered ring **64** or releases product **65** after hydrogen atom transfer (HAT) (Scheme 18).



Scheme 18. Plausible reaction pathways for activation of **47** by photoredox catalysis.

Thus, we started to screen the model reaction between methyl-protected allylic iodoalcohol **47a** and acrylnitrile (**1ah**) in the presence of several established photocatalysts under visible-light irradiation and Hantzsch ester as a source for hydrogen atoms (Table 8).

Table 8. Attempts on activation of **47a** by photoredox catalysis.

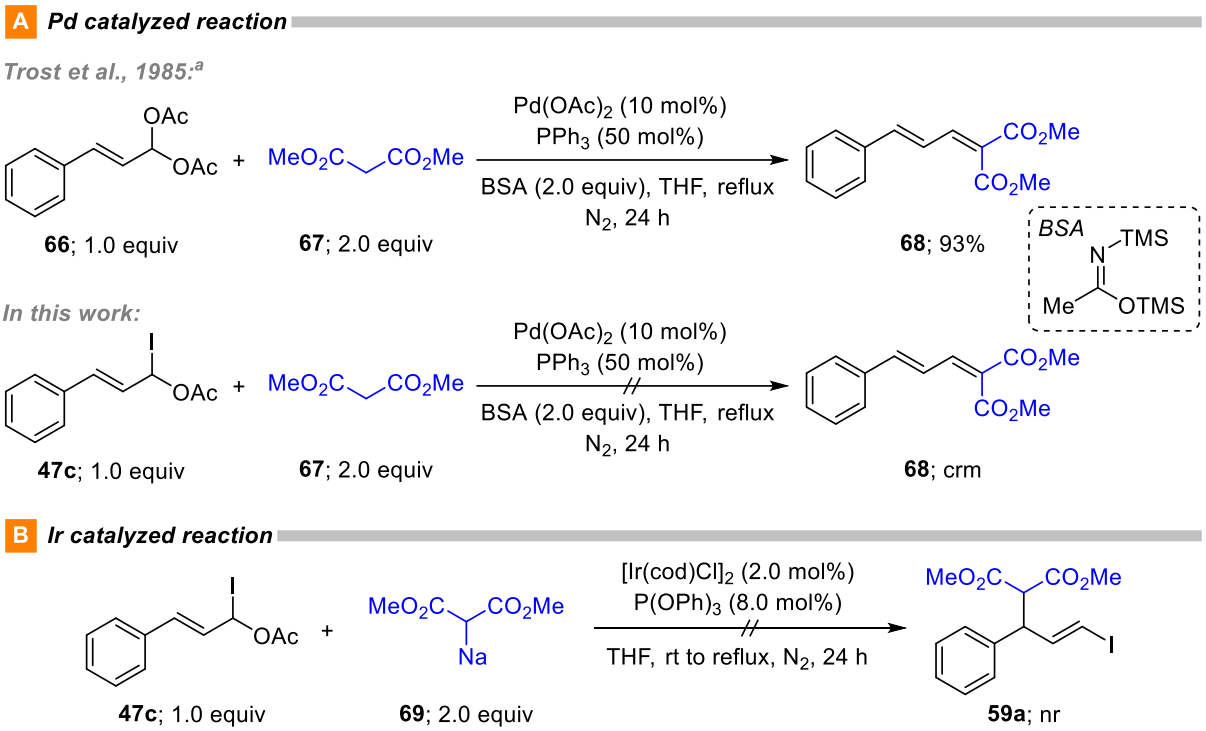


Entry	Photocatalyst	λ_{vis}	Yield
1	$[Cu(dap)_2]Cl$ (1.0 mol%)	530 nm	nr
2	$[Cu(dpp)(binc)]BF_4$ (1.0 mol%)	530 nm	nr
3	$[Cu(dpp)(binc)]BF_4$ (1.0 mol%)	455 nm	nr
4	$[Ru(bpy)_3]Cl_2$ (1.0 mol%)	455 nm	nr
5	*fac*-$[Ir(ppy)_3]$ (1.0 mol%)	455 nm	nr
6	4-CzIPN (1.0 mol%)	455 nm	nr
7	PTH (1.0 mol%)	367 nm	nr

Reaction conditions: **47a** (0.3 mmol, 1.0 equiv), acrylnitrile (**1ah**) (0.9 mmol, 3.0 equiv), Hantzsch ester HE (0.36 mmol, 1.2 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeCN (anh., degassed, 2.0 mL, 0.15 M); Irradiation at indicated wavelength λ_{vis} under N_2 atmosphere at room temperature (25 °C) for 24 h.

Unfortunately, several attempts utilizing different kind of copper-, ruthenium-, iridium- or organic dye-based photocatalysts failed and showed no conversion of the corresponding starting materials. Further screening of such a transformation remains to be determined.

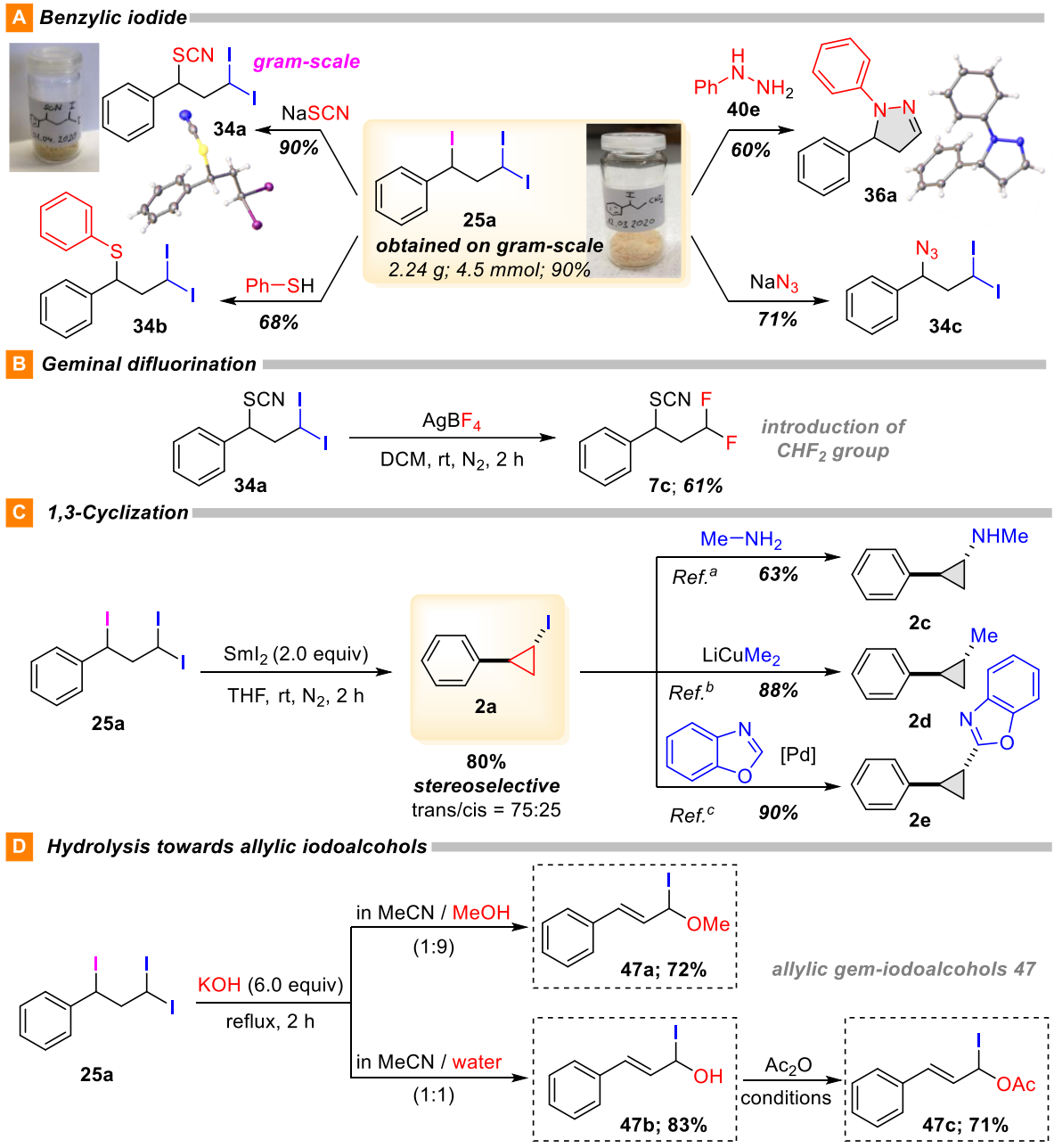
Next, we aimed using the allylic OAc-motif to trigger palladium- (Scheme 18, A) or iridium- (Scheme 18, B) catalyzed allylation reactions (Scheme 18). In 1985, Trost and co-workers reported a palladium-catalyzed substitution of an allylic geminal diacetate **66** with stabilized nucleophiles like dimethyl malonate (**67**).[46] However, employing this reaction conditions on our allylic *gem*-iodoalcohol **47c** aiming in the synthesis of **68** failed and instead yielded a complex reaction mixture. In the same way, attempts to promote such an allylation reaction with $[Ir(cod)Cl]_2$ being well established in literature,[47] resulted in no reaction of the corresponding starting materials **47c** and **69**.



Scheme 19. Attempts on utilization of allylic *gem*-iodoalcohol **47c** in transition-metal catalyzed allylation reactions. *Reaction conditions*: (A) **47c** (0.3 mmol, 1.0 equiv), dimethyl malonate (**67**) (0.6 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.03 mmol, 10.0 mol%), PPh_3 (0.15 mmol, 0.5 equiv), BSA (0.6 mmol, 2.0 equiv) in THF (anh., degassed, 2.0 mL, 0.15 M) under N_2 atmosphere at reflux conditions for 24 h. (B) **47c** (0.3 mmol, 1.0 equiv), sodium dimethyl malonate (**69**) (0.6 mmol, 2.0 equiv), $[Ir(cod)Cl]_2$ (6.0 µmol, 2.0 mol%), $P(OPh)_3$ (24.0 µmol, 8.0 mol%) in THF (anh., degassed, 2.0 mL, 0.15 M) under N_2 atmosphere at room temperature (25 °C) to reflux conditions for 24 h. [a]Ref.[46]

In conclusion, further investigations on this unique structural motif of allylic *gem*-iodoalcohol **47** as synthetic building blocks remain to be determined and are ongoing in our laboratories.

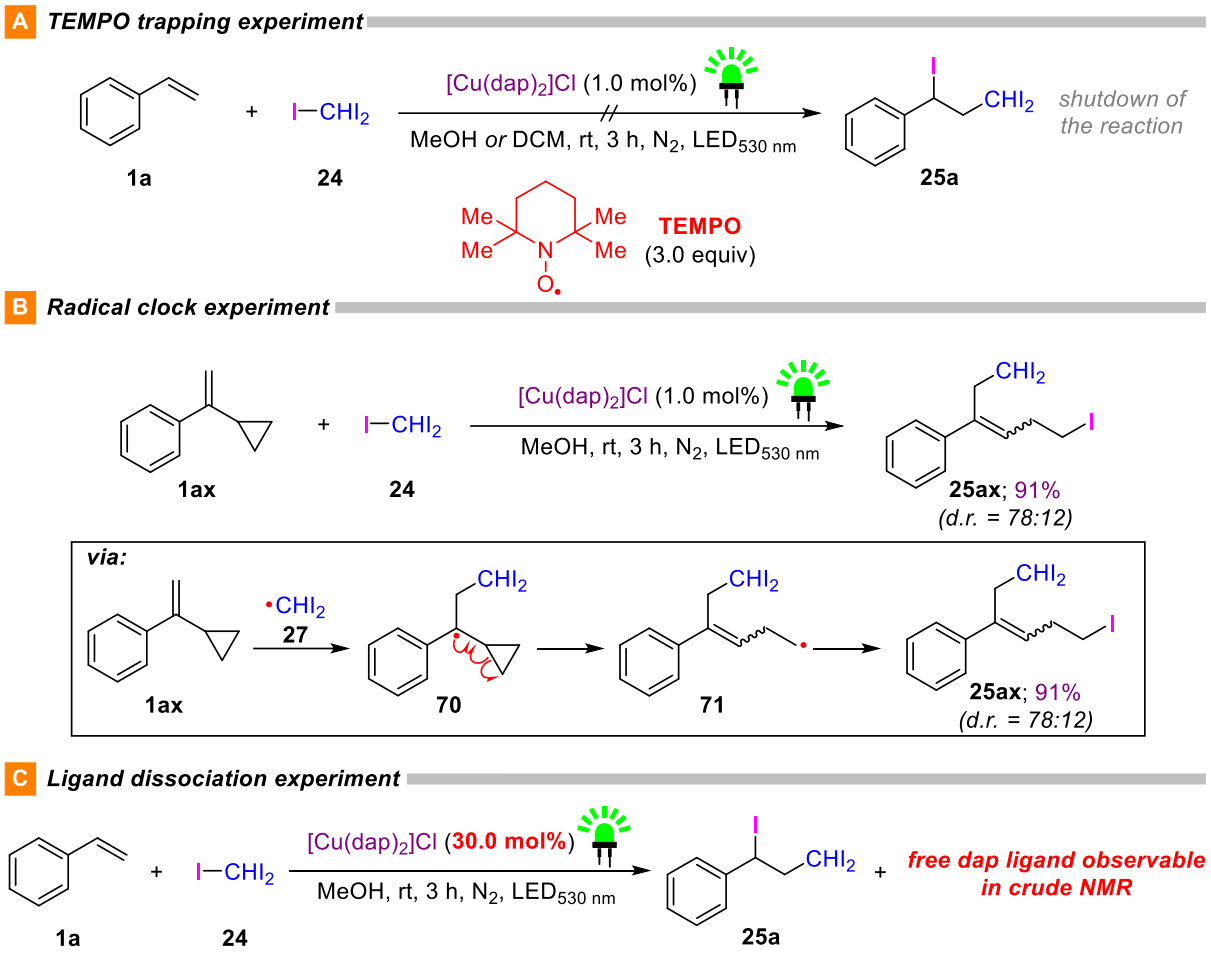
4.5.5 Overview on Successful Synthetic Transformations



Scheme 20. Overview on synthetic utility of photoproduct **25a**. *Reaction conditions*: (A) **25a** (0.2 mmol, 1.0 equiv), nucleophile (0.5 mmol, 2.5 equiv), Na_2CO_3 (0.5 mmol, 2.5 equiv) in MeCN (anh., 2.0 mL, 0.1 M) under N_2 atmosphere at room temperature (25 °C) for 12 h. Reaction towards **34a** was also performed on a 3.0 mmol scale: Yield of **34a** was 85%. (B) **34a** (0.2 mmol, 1.0 equiv), $AgBF_4$ (0.44 mmol, 2.2 equiv) in DCM (anh., degassed, 1.5 mL, 0.13 M) under N_2 atmosphere at room temperature (25 °C) for 2 h. (C) **25a** (0.2 mmol, 1.0 equiv), a solution of SmI_2 in THF (0.1 M, 4.0 mL, 0.40 mmol, 2.0 equiv) under N_2 atmosphere at room temperature (25 °C) for 2 h. (D) **25a** (0.2 mmol, 1.0 equiv), KOH (1.2 mmol, 6.0 equiv) in the indicated solvent systems (4.0 mL, 0.05 M) under reflux for 2 h. Reactions were also performed on 5.0 mmol scale to give **47a** in 72% yield and **47b** in 83% yield. Synthesis of **47c**: Crude mixture of **47b** (4.0 mmol scale), NEt_3 (8.0 mmol, 2.0 equiv), DMAP (0.4 mmol, 10.0 mol%) and Ac_2O (8.0 mmol, 2.0 equiv) in DCM (20.0 mL, 0.2 M) at 0 °C to rt for 3 h. [a]Ref.[37], [b]Ref.[38], [c]Ref.[39]

4.6 Mechanistic Studies

Having addressed synthetic aspects, we next aimed for mechanistic insights and accordingly carried out several experiments (Scheme 21).



Scheme 21. Mechanistic studies. *Reaction conditions*: (A) Styrene (**1a**) (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), TEMPO (1.5 mmol, 3.0 equiv), $[Cu(dap)_2]Cl$ (5.0 µmol, 1.0 mol%) in MeOH or DCM (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 3 h. (B) Alkene **1ax** (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (5.0 µmol, 1.0 mol%) in MeOH (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 3 h. (C) Styrene (**1a**) (0.6 mmol, 2.0 equiv), iodoform (**24**) (0.3 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (15.0 µmol, 30.0 mol%) in MeOH (anh., degassed, 3.0 mL, 0.1 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 3 h.

In line with a mechanistic pathway calling for radical intermediates, the addition of TEMPO to the standard reaction conditions revealed a complete shutdown of the catalytic cycle (Scheme 21, A). In the same way, radical clock experiment between **1ax** and iodoform (**24**) exclusively led to the formation of product **25ax** in 91% yield, being in agreement with the radical

intermediate **70**, which immediately undergoes radical-initiated ring-opening to **71** (Scheme 21, B). Both experiments clearly undergird the radical character of the reaction. However a simple radical chain process seems not to be sufficient given by the failure of previous literature attempts[25-27] (see Introduction Chapter 4.2) or aforementioned screening attempts to carry out the reaction thermally with AIBN or under photolysis with catalysts other than $[Cu(dap)_2]Cl$. To get deeper understanding of the reactivity on the copper center, a ligand-dissociation experiment should proof, whether the departure of one dap ligand from the active catalyst is feasible, thus opening up a vacant coordination side on the catalyst for a rebound mechanism with incipient radical intermediates (Scheme 21, C). Therefore, the standard model reaction was carried out in the presence of 30.0 mol% $[Cu(dap)_2]Cl$, enabling the analysis of potential free dap ligand in reasonable amount after the photoreaction by crude ^{1}H-NMR. Indeed, the corresponding crude NMR revealed the coexistence of free dap ligand after the desired photoprocess (Figure 1). A control experiment irradiating the $[Cu(dap)_2]Cl$ in the absence of any substrate pinned the photostability of the latter (Figure 2).

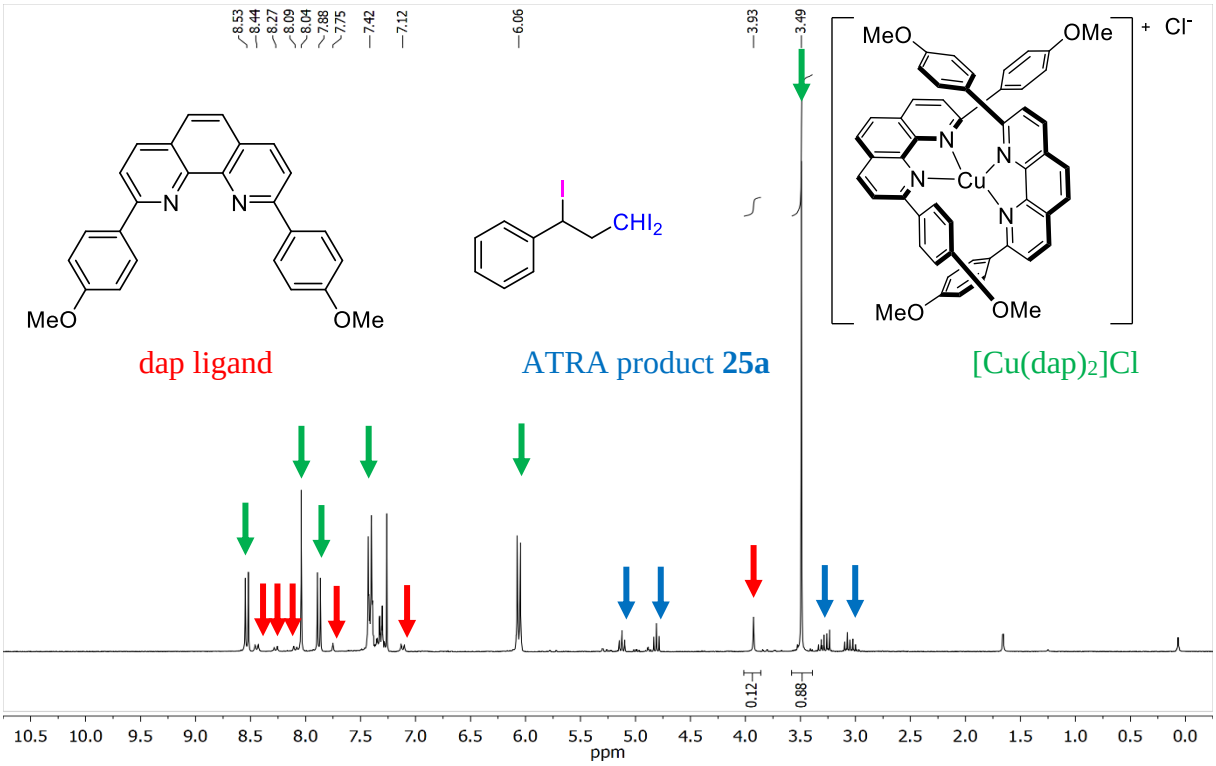


Figure 1. Crude ^{1}H-NMR in $CDCl_3$ of ligand dissociation experiment. *Reaction conditions*: Styrene (**1a**) (0.6 mmol, 2.0 equiv), iodoform (**24**) (0.3 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (15.0 µmol, 30.0 mol%) in MeOH (anh., degassed, 3.0 mL, 0.1 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 3 h.

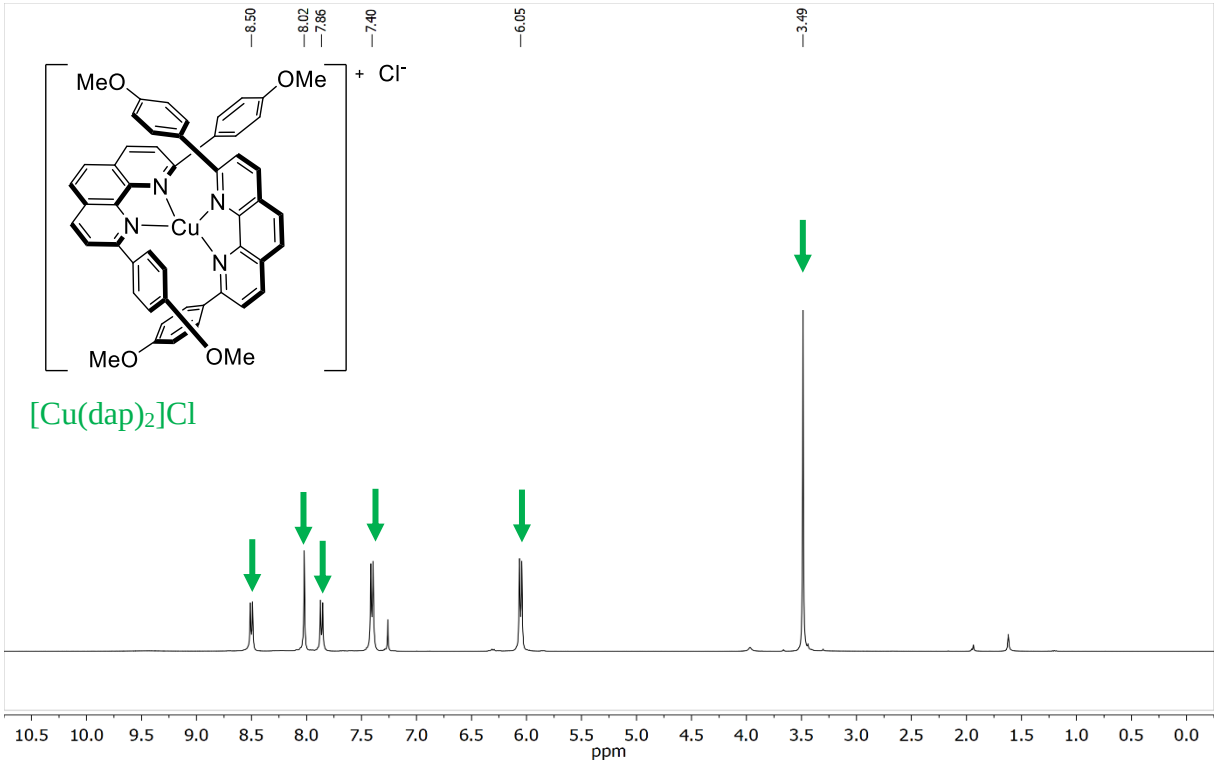
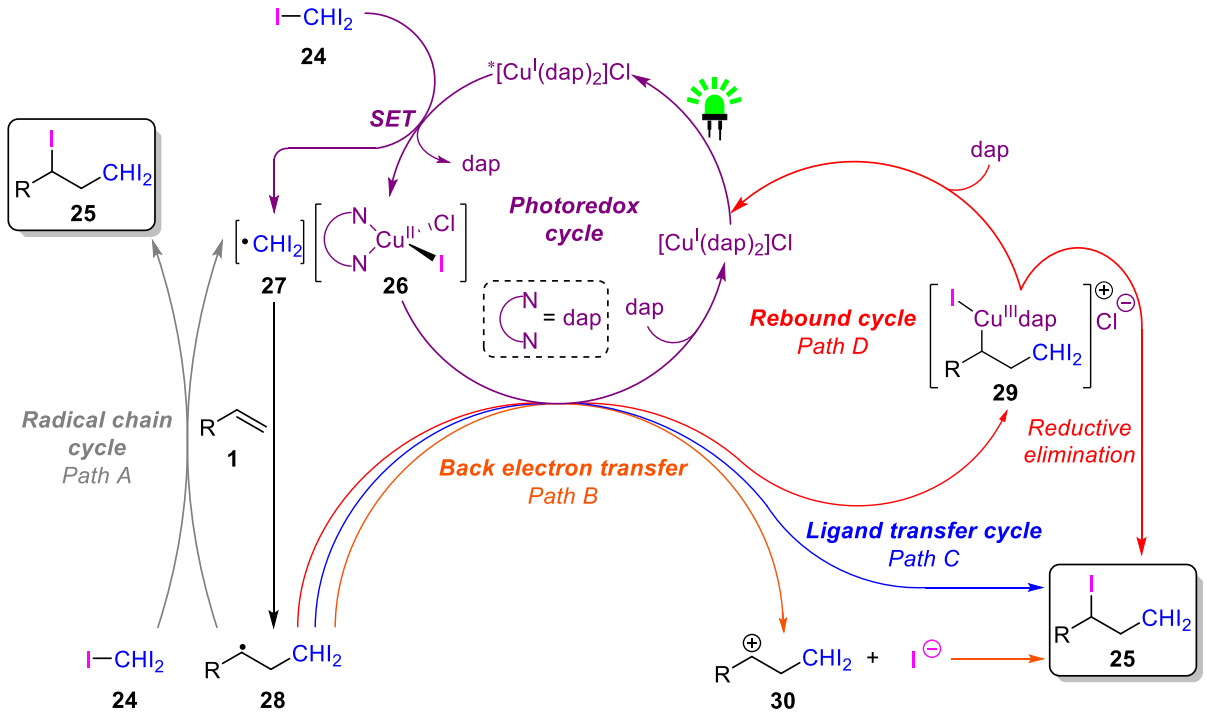


Figure 2. Crude ^{1}H-NMR in $CDCl_3$ of the control experiment pinning photostability of $[Cu(dap)_2]Cl$ in absence of any substrate. *Reaction conditions*: $[Cu(dap)_2]Cl$ (15.0 µmol, 1.0 equiv) in MeOH (anh., degassed, 3.0 mL, 5.0 mM); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 3 h.

4.7 Proposed Reaction Mechanism

Taking the preceding mechanistic experiments into account, the following mechanistic picture is proposed (Scheme 22). After excitation of $[Cu(dap)_2]Cl$ by visible light, single-electron transfer (SET) to iodoform (**24**) generates the corresponding CHI_2-radical (**27**) and iodide under oxidation to the Cu(II)-species **26**. As soon as Cu(I)*→Cu(II) transition happens, the copper center loses one dap ligand (according to the ligand dissociation experiment in chapter 4.6), thus opening up a vacant coordination side for the following inner-sphere reaction pathway. Regioselective radical addition of the CHI_2-radical (**27**) to the alkene **1** affords benzylic radical **28**, which now may proceed by four different pathways. In pathway A, the reaction could propagate by a radical chain pathway (Scheme 22, Path A) by abstracting iodine from another molecule of iodoform (**24**) to give product **25** with concurrent regeneration of CHI_2-radical (**27**). However, this pathway seems to be only sufficient up to a certain extent given by the failure of previous literature attempts[25-27] (see Chapter 4.2) or aforementioned screening attempts to carry out the reaction thermally with AIBN or under photolysis with catalysts other than $[Cu(dap)_2]Cl$. Alternatively, in pathway B benzylic radical intermediate **28** may be

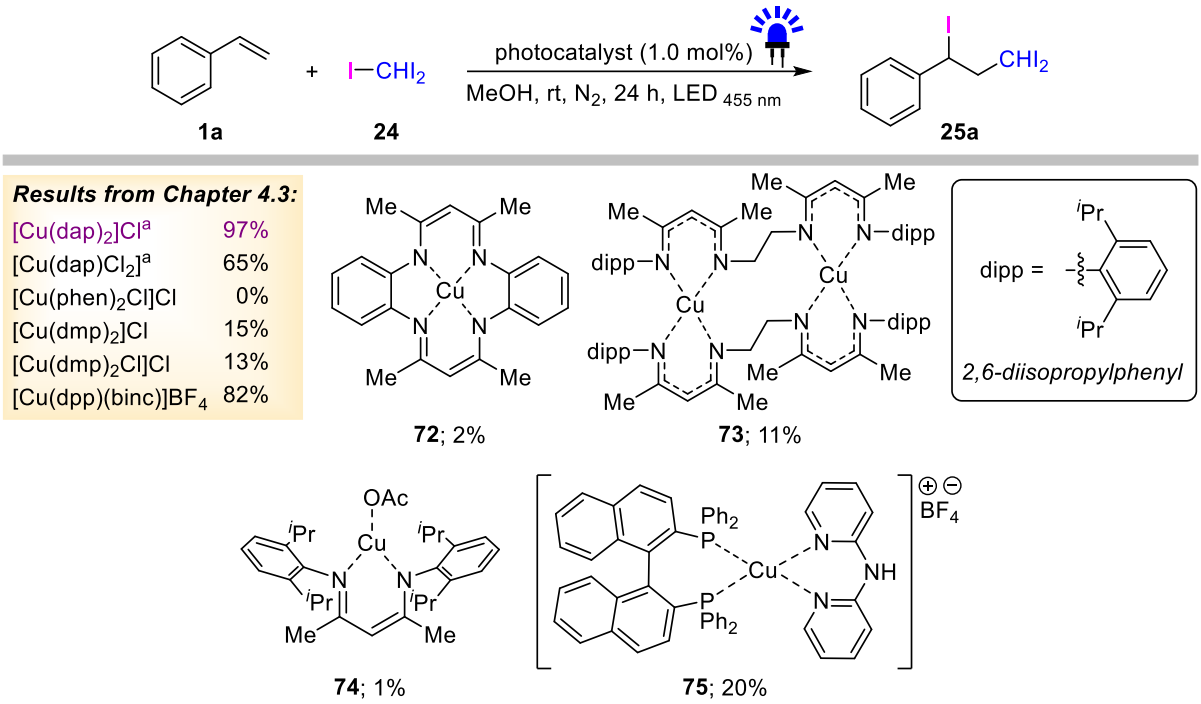
oxidized to the corresponding carbocation **30** that subsequently combines with iodide anion giving rise to the desired product **25** under regeneration of the photocatalyst (Scheme 22, Path B). Nevertheless, back electron transfer is at the best plausible for highly electron-rich alkenes **1**, which was already discussed in chapter 4.4 for the formation of the MeOH-substituted products, underpinned by the fact that the desired transformation is not feasible for ruthenium-, iridium- or organic dye-based photocatalysts being also in agreement with our previous study.[7i] It should be noted that the failure of ruthenium- or iridium-photocatalysts might be also owed to the fact (as already discussed in chapter 4.2) that partially formed traces of molecular iodine absorb visible light in the blue region, thus preventing such catalysts from excitation at 455 nm, while control experiments revealed excitation of the latter with green LED (λ = 530 nm) is not sufficient. In contrast, copper photocatalysts excel through their flexible ligand architecture and multiple accessible oxidation states opening up two further possible mechanistic pathways. In ligand transfer pathway C, radical intermediate **28** takes back iodine from the Cu(II)-species **26**, which thereby reverts to the initial catalyst by reuniting with the previously departed dap ligand (Scheme 22, Path C). Alternatively, radical intermediate **28** might also bind back to the Cu(II)-species **26** – being in fact a persistent radical itself – to generate a Cu(III)-intermediate **29**. The final product **25** is then released upon reductive elimination recreating the initial catalyst and closing the rebound cycle (Scheme 22, Path D).



Scheme 22. Proposed reaction mechanism for photochemical ATRA reactions of iodoform (**24**).

4.8 Exploring New Types of Copper Complexes

Besides the established copper photocatalysts, which have already been tested for the photochemical ATRA reaction between styrene (**1a**) and iodoform (**24**) in chapter 4.3, Scheme 23 shows several new types of copper complexes for potential use as photocatalysts in the title reaction. However, all tested complexes turned out to be insufficient in the desired transformation yielding product **25a** in only up to 20% yield. It should be noted that these complexes required irradiation with blue LED (λ = 455 nm), which might be also insulated from traces of molecular iodine being formed during the process, thus preventing the corresponding complexes from excitation (for detailed discussion see previous chapters).

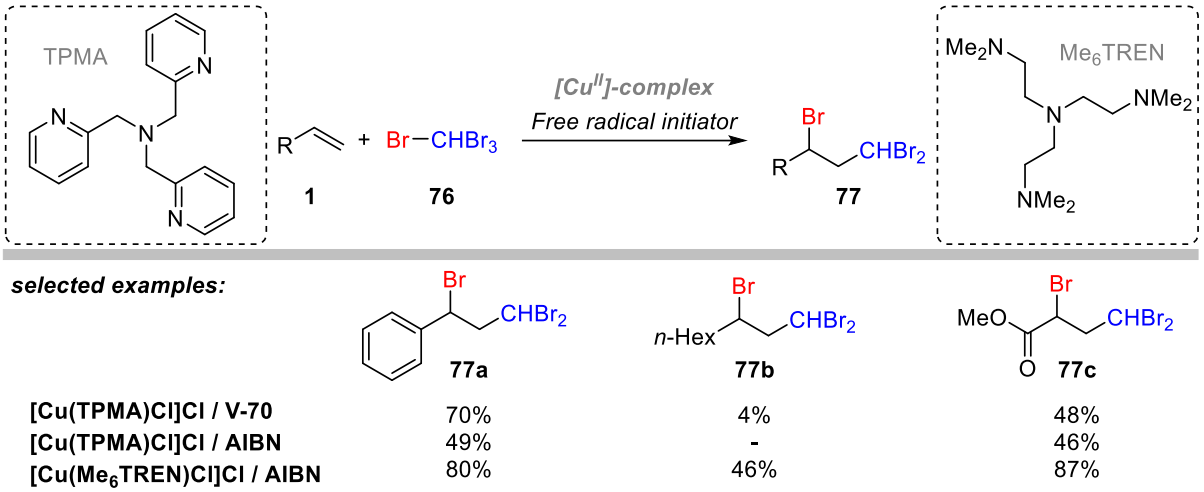


Scheme 23. Exploring new types of copper complexes for the photochemical ATRA reaction of iodoform (**24**). *Reaction conditions*: Styrene (**1a**) (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in MeOH (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]Irradiation at 530 nm (green LED).

In a similar way, the visible-light mediated chlorosulfonylation of styrene (**1a**) with tosyl chloride reported in chapter 2 and 3 failed to be efficiently promoted with the new copper complexes **72-74**.[48] However, complex **75** indeed revealed to be a suitable catalyst for the chlorosulfonylation of alkenes, which was further explored in cooperation with Prof. Alan Cabrera and his co-worker Marco Henriquez in a separate publication.[49]

4.9 Studies on Bromoform

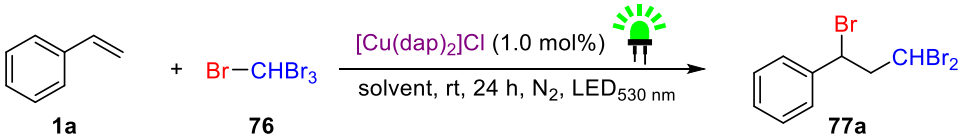
In contrast to its related higher polyhalogenated homologue iodoform (**24**), the corresponding bromo-compound bromoform (**76**) also allows for free-radical promoted ATRA-type reactions, which has been extensively studied by Pintauer and co-workers (Scheme 24).[50]



Scheme 24. Selected free-radical promoted ATRA reactions with bromoform (**76**) reported by Pintauer and co-workers.[50]

As the reports by Pintauer et al. mainly focused on mechanistic and kinetic trends and lacked a complete compound characterization of **77**, we questioned whether our developed visible-light mediated copper-catalyzed protocol might offer the opportunity for studies focusing on more synthetic aspects. Hence, we started our investigations using styrene (**1a**) and bromoform (**76**) in the presence of 1.0 mol% $[Cu(dap)_2]Cl$ under green LED (530 nm) irradiation (Table 9).

Table 9. Attempts on photochemical ATRA reactions of bromoform (**76**).



Entry	Solvent	Yield[a]
1	MeCN (anh., degassed, 0.25 M)	10%
2	DCM (anh., degassed, 0.25 M)	traces
3	MeOH (anh., degassed, 0.25 M)	traces
4	DMF (anh., degassed, 0.25 M)	nr

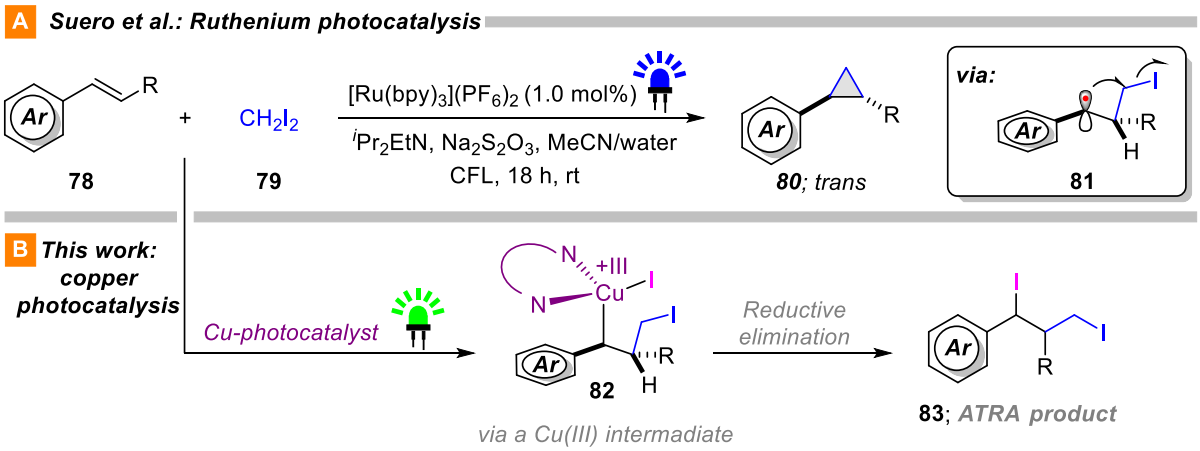
Reaction conditions: Styrene (**1a**) (1.0 mmol, 2.0 equiv), bromoform (**76**) (0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (5.0 µmol, 1.0 mol%) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at indicated wavelength 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]NMR yield using diphenoxymethane as an internal standard.

Unfortunately, screening several solvent systems, being typically used in such ATRA-processes, resulted in low yields of the desired product **77a**. Further studies remain to be determined and are ongoing in our laboratories.

4.10 Studies on Diiodomethane

Recently, Suero and co-workers impressively reported the first stereoconvergent cyclopropanation reaction by means of photoredox catalysis utilizing diiodomethane (**79**) as the methylene source (Scheme 25).[51] Thereby, photo-excited $[Ru(bpy)_3](PF_6)_2$ is reduced by $^{i}Pr_2EtN$ through SET accessing a highly reducing Ru(I)-species ($E_{Ru(II)/Ru(I)}$ = -1.33 V vs. SCE), which now is feasible to donate an electron to CH_2I_2 (**79**) (E_{red} = -1.44 V vs. SCE) generating the corresponding iodomethyl CH_2I-radical. The latter adds to the alkene **78** forming the key intermediate **81**, which can equilibrate through C-C bond rotation yielding in the corresponding anti-orientation of the product **80** upon cyclization by homolytic substitution (Scheme 25, A). It should be noted that the difference of 0.11 V in redox potentials of the Ru(I)-species and diiodomethane (**79**) only implies an energy barrier as low as 2.5 kcal/mol. Although this electron transfer is slightly enderogenic, the overall process might be driven by an exerogenic alkene radical addition and subsequent irreversible cyclopropane formation.[51]

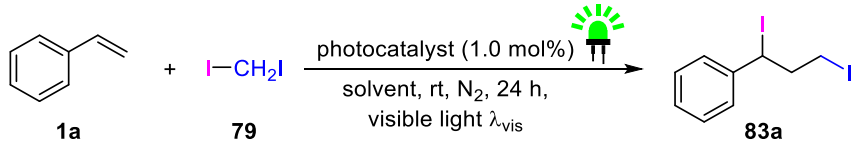
Given the fact, that copper photocatalysts are able to stabilize and interact with radical intermediates such as **81**, we were wondering if one could access a rebound mechanism on copper and thus, ultimately giving rise to the corresponding ATRA product **83** upon reductive elimination from the Cu(III)-intermediate **82** (Scheme 25, B).



Scheme 25. (A) Stereoconvergent photoredox-catalyzed cyclopropanation by Suero and co-workers.[51] (B) Synthetic plan of this work using copper photocatalysis for the synthesis of **83**.

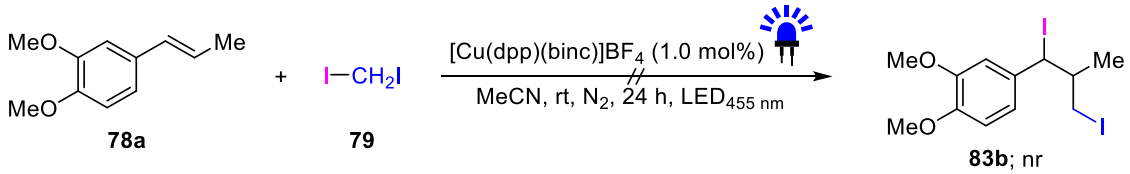
Hence, we started our investigations on this idea with the reaction between styrene (**1a**) and diiodomethane (**79**) (E_{red} = -1.44 V vs. SCE)[51] in the presence of several copper photocatalysts under visible-light irradiation (Table 10). Unfortunately, employing $[Cu(dap)_2]Cl$ ($E_{Cu(II)/Cu(I)^*}$ = -1.43 V vs. SCE)[52] in several solvents used for such ATRA processes resulted in no conversion of starting materials, although the excited-state reduction power of the latter should be sufficient to undergo SET to diiodomethane (**79**) (Table 10, entries 1-4). In the same way, copper complexes showing even higher reduction potentials like $[Cu(dmp)_2]Cl$ ($E_{Cu(II)/Cu(I)^*}$ = -1.54 V vs. SCE)[53] or $[Cu(dpp)(binc)]BF_4$ ($E_{Cu(II)/Cu(I)^*}$ = -1.88 V vs. SCE)[54] nevertheless proved to be unable to sufficiently promote the desired reaction (Table 10, entries 5-6). In case of the latter, traces of cyclopropanation were observed being in accordance to the report by Suero[51] (Table 10, entry 5). Attempts to use a more electron-rich *β*-substituted styrene derivative **78a** – being the most suitable substrate reported by Suero[51] – nevertheless showed no conversion of starting materials in the presence of $[Cu(dpp)(binc)]BF_4$ (Scheme 26).

Table 10. Attempts on photochemical ATRA reaction with diiodomethane (**79**).



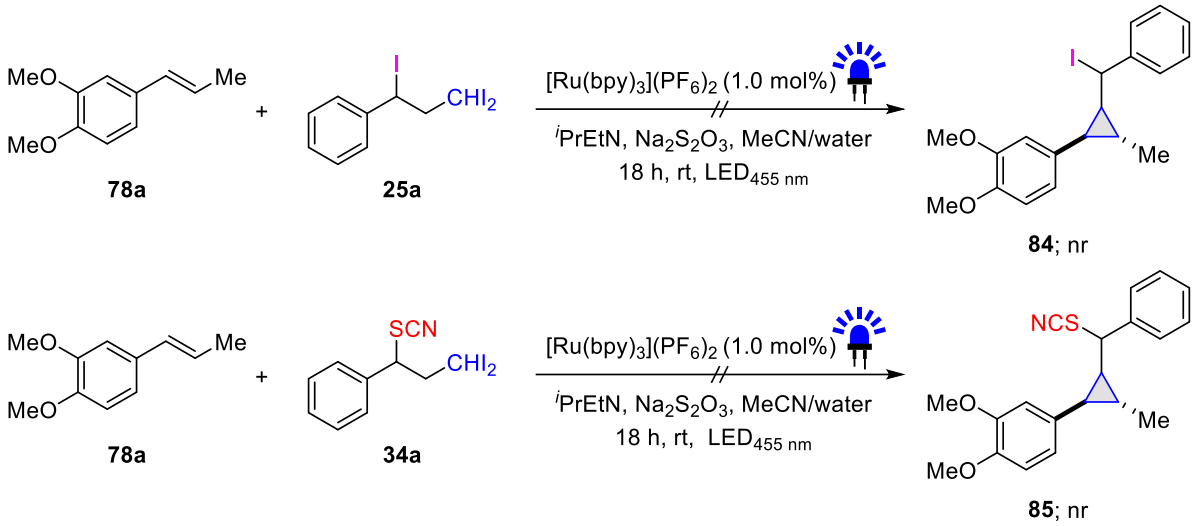
Entry	Photocatalyst (1.0 mol%)	Solvent (anh., degassed)	λ_{vis}	Yield
1	$[Cu(dap)_2]Cl$	MeOH	530 nm	nr
2	$[Cu(dap)_2]Cl$	DCM	530 nm	nr
3	$[Cu(dap)_2]Cl$	MeCN	530 nm	nr
4	$[Cu(dap)_2]Cl$	DMF	530 nm	nr
5	$[Cu(dpp)(binc)]BF_4$	MeCN	455 nm	traces of cyclopropane
6	$[Cu(dmp)_2]Cl$	MeCN	455 nm	nr

Reaction conditions: Styrene (**1a**) (1.0 mmol, 2.0 equiv), diiodomethane (**79**) (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at indicated wavelength λ_{vis} under N_2 atmosphere at room temperature (25 °C) for 24 h.



Scheme 26. Electron-rich *β*-substituted styrene derivative **78a** in a potential copper-catalyzed ATRA reaction with diiodomethane (**79**). *Reaction conditions*: **78a** (1.0 mmol, 2.0 equiv), diiodomethane (**79**) (0.5 mmol, 1.0 equiv), catalyst (5.0 µmol, 1.0 mol%) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at indicated wavelength λ_{vis} under N_2 atmosphere at room temperature (25 °C) for 24 h.

Furthermore, we questioned ourselves whether *gem*-diiodide products **25a** or **34a** obtained during this study can serve as suitable starting materials for the photochemical cyclopropanation reported by Suero and co-workers.[51] Hence, we subjected our products **25a** and **34a** to the reaction conditions presented by Suero (Scheme 27). However, in both cases, for the iodo- as well as thiocyanide-substituted *gem*-diiodides **25a** and **34a**, no conversion in the desired transformation was observed (Scheme 27).

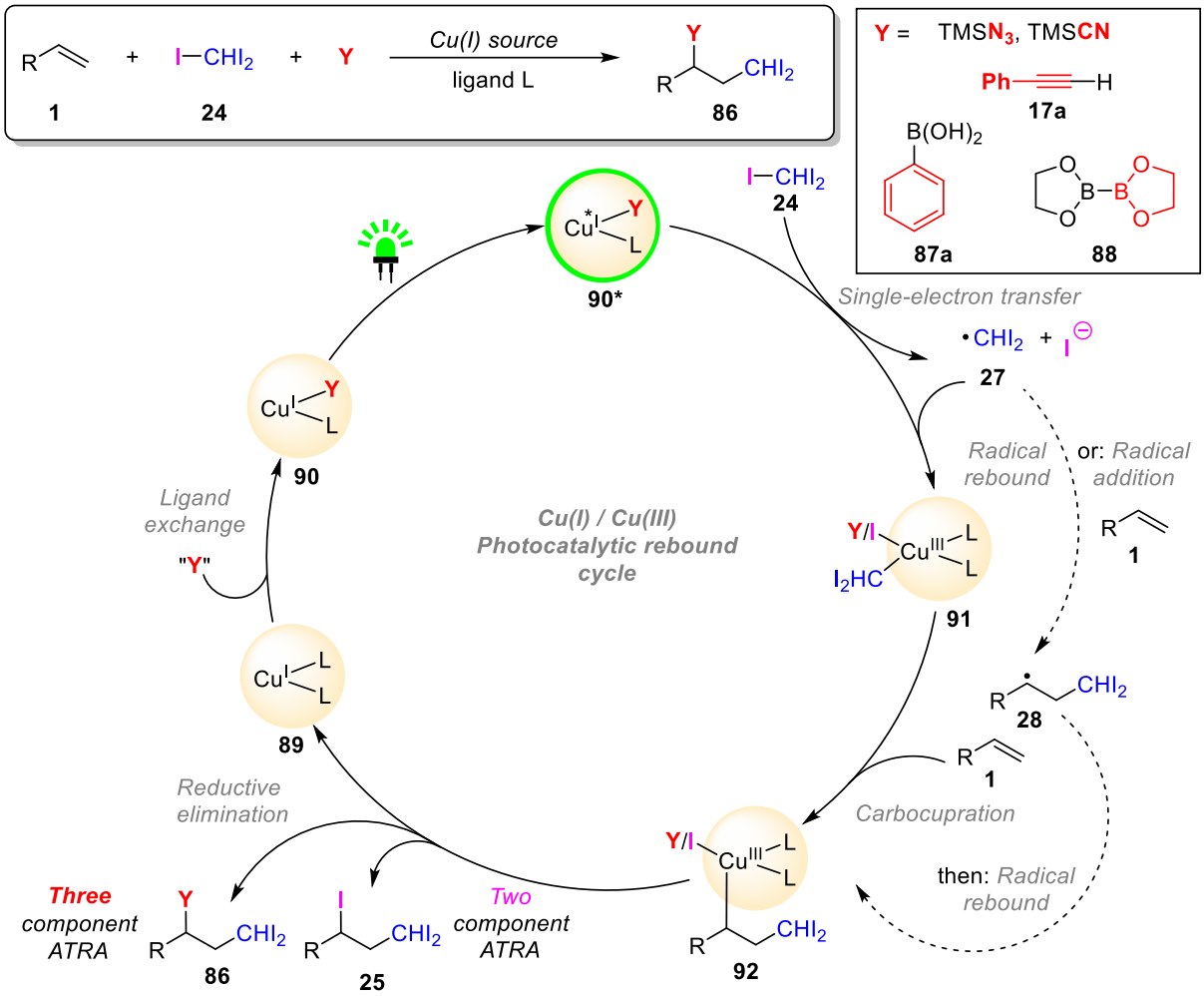


Scheme 27. Attempts on utilization of our photoproducts **25a** and **34a** in the photochemical cyclopropanation reported by Suero and co-workers.[51] *Reaction conditions*: Alkene **78a** (0.3 mmol, 1.0 equiv), **25a** or **34a** (0.6 mmol, 2.0 equiv), $^{i}Pr_2EtN$ (1.5 mmol, 5.0 equiv), $Na_2S_2O_3$ aqueous solution (1.5 mmol, 1.33 M) in MeCN (degassed, 3.0 mL, 0.1 M)); Irradiation at 455 nm (blue LED) under N_2 atmosphere at room temperature (25 °C) for 18 h.

4.11 Studies on Three-Component ATRA Processes

Besides well-established two-component ATRA processes previously discussed, copper photocatalysts conjointly offer the possibility to introduce a third component in ATRA-type transformations owing to their flexible ligand architecture and thus, their ability to directly interact with substrates in the inner-coordination sphere. In this chapter we aimed in the development of a three-component ATRA reaction utilizing iodoform (**24**) as one of the coupling partners ultimately yielding in the synthesis of a library of functionalized *gem*-diiodides **86**. A plausible mechanistic picture of such a process is depicted in Scheme 28. The Cu(I)-photocatalyst **89** can undergo ligand exchange with the third component **Y** to give a copper-substrate complex **90**, which subsequently is excited by visible-light being now able to donate one electron by SET to iodoform (**24**) to generate the CHI_2-radical (**27**). The latter has two options. Either **27** directly bind back to the concurrently formed Cu(II)-intermediate

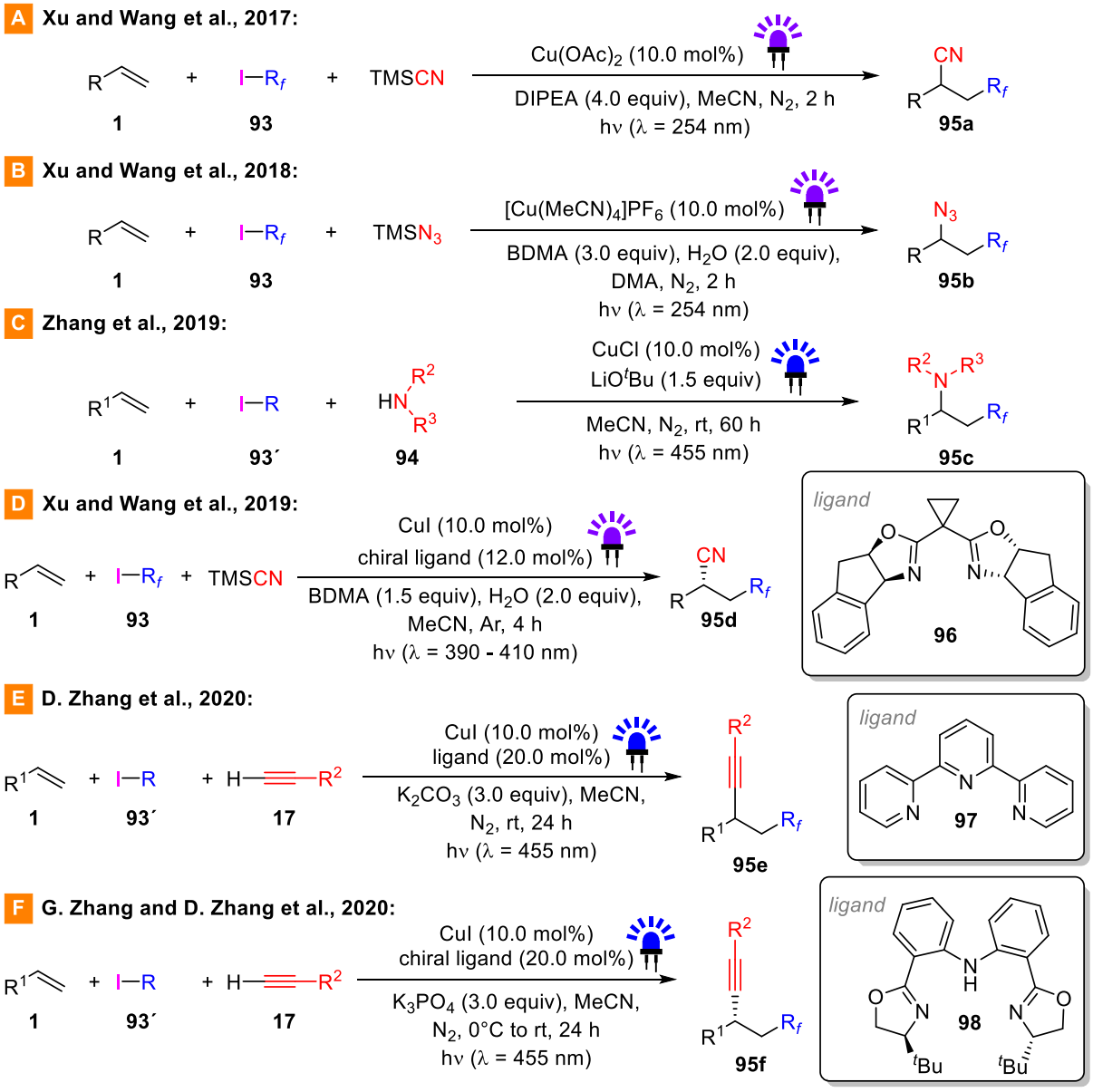
resulting in a Cu(III)-species **91** which subsequently undergoes carbocupration with alkene **1** to forge the Cu(III)-species **92**. Alternatively, CHI_2-radical (**27**) first adds to the alkene **1** forming the carbon-centered radical **28**, which then go through a rebound cycle to yield the Cu(III)-species **92**. Reductive elimination recreates the copper photocatalyst **89** under release of the corresponding two- or three-component ATRA reaction products **25** or **86** (Scheme 28). It should be noted, that ligand exchange with the third component **Y** might also take place from the Cu(II)-species formed after SET of the excited Cu(I)-species **89**.



Scheme 28. Plausible mechanistic picture for visible-light mediated copper-catalyzed three-component ATRA-type reactions.

This basic idea already gained impressive attention in recent literature (Scheme 29, *for a detailed review, please see* ***Chapter 1***). While seminal work by Xu and Wang employed UV-light irradiation for the three-component coupling between alkene **1**, activated halide **93** and either TMSCN[55] or $TMSN_3$[56], in 2019 Zhang an co-workers reported a visible-light mediated three-component ATRA reaction using secondary amides serving both as a ligand for the

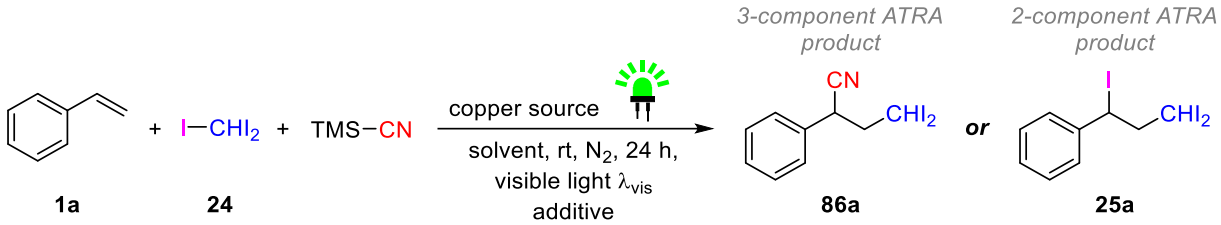
catalyst as well as the third coupling component.[57] Later that year, Xu and Wang impressively demonstrated such a three-component ATRA-reaction for the first time under enantioselective control installing a chiral ligand on the reactive copper center.[58] Very recently, Zhang et al. utilized a Cu(I)-acetylide catalyst-substrate complex, which acts upon visible-light excitation as a photo-reductant activating **93`** by SET. After addition of the corresponding radical to alkene **1** the resulting intermediate is trapped by the Cu(II)-acetylide complex releasing the desired three-component coupling product **95e** after reductive elimination.[59] Capitalizing this reaction principle, the same group further developed the corresponding reaction also in an enantioselective fashion using a chiral ligand on the copper center.[60]



Scheme 29. Selected examples of copper-catalyzed three-component ATRA-type reactions using iodo-ATRA reagents reported in literature. For a detailed review, please see Chapter 1. (A) Ref.[55], (B) Ref.[56], (C) Ref.[57], (D) Ref.[58], (E) Ref.[59], (F) Ref.[60]

Intrigued by these impressive results, we wondered whether the photochemical ATRA reaction with iodoform (**24**) presented in this chapter, could be successfully extended in a three-component fashion yielding in the synthesis of functionalized *gem*-diiodides **86**. We started our investigations with TMSCN as the corresponding third component in such a ATRA process (Table 11).

Table 11. Attempts towards three-component ATRA reaction with TMSCN.



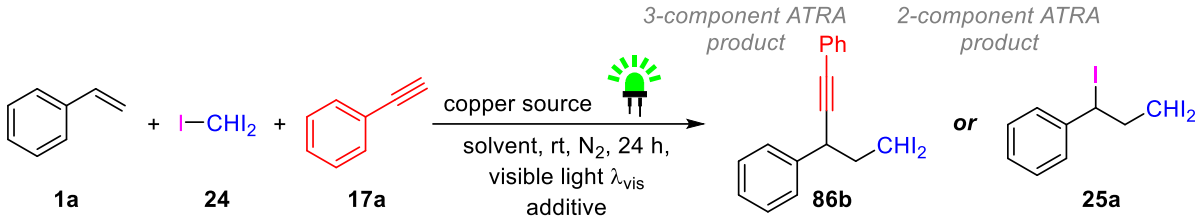
Entry	Catalyst	Solvent	Additive	λ_{vis}	Yield[a]
1	$[Cu(dap)_2]Cl$ (1.0 mol%)	DCM	---	530 nm	22% **25a**
2	$[Cu(dap)_2]Cl$ (1.0 mol%)	DCM	DIPEA (3.0 equiv)	530 nm	15% **25a**
3	$[Cu(dap)_2]Cl$ (1.0 mol%)	MeCN	DIPEA (3.0 equiv)	530 nm	crm
4[b]	$Cu(OAc)_2$ (10.0 mol%)	MeCN	DIPEA (3.0 equiv)	367 nm	12% **25a**

Reaction conditions: Styrene (**1a**) (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), TMSCN (1.0 mmol, 2.0 equiv), additive (1.5 mmol, 3.0 equiv), catalyst (indicated amount) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at indicated wavelength under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]NMR yield using diphenoxymethane as an internal standard. [b]Based on literature.[55]

Unfortunately, several attempts using our established conditions from the two-component reaction or modified conditions using different solvents or additives employed in literature, failed yielding only the two-component ATRA product **25a** in moderate yields (Table 11, entries 1-3). In the same way, conditions reported by Xu and Wang[55] proved to be unsuitable for iodoform (**24**), thus giving again the two-component product **25a** in 12% yield (Table 11, entry 4).

Next, we switched to alkyne **17a** as the third component coupling partner (Table 12). While employment of the standard reaction conditions resulted in a complete shutdown of the catalytic cycle in the presence of phenylacetylene (**17a**), replacement of MeOH by DCM quantitatively delivered the two-component product **25a** (Table 11, entries 1-2). Conducting the experiment with conditions reported by Zhang and co-workers[59] again resulted in undesired product **25a** in up to 46% under green LED irradiation (Table 11, entries 4-5).

Table 12. Attempts towards three-component ATRA reaction with phenylacetlyene (**17a**).

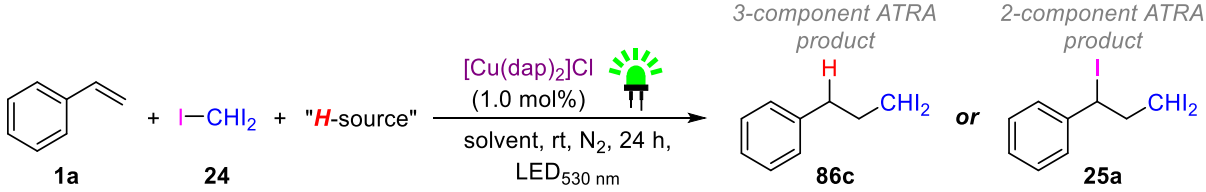


Entry	Catalyst	Solvent	Additive	λ_{vis}	Yield[a]
1	$[Cu(dap)_2]Cl$ (1.0 mol%)	MeOH	K_2CO_3 (3.0 equiv)	530 nm	nr
2	$[Cu(dap)_2]Cl$ (1.0 mol%)	DCM	K_2CO_3 (3.0 equiv)	530 nm	97% **25a**
3	$[Cu(dap)_2]Cl$ (1.0 mol%)	MeCN	K_2CO_3 (3.0 equiv)	530 nm	49% **25a**
4[b]	CuI (10.0 mol%) + terpyridine (20.0 mol%)	MeCN	K_2CO_3 (3.0 equiv)	530 nm	46% **25a**
5[b]	CuI (10.0 mol%) + terpyridine (20.0 mol%)	MeCN	K_2CO_3 (3.0 equiv)	455 nm	23% **25a**

Reaction conditions: Styrene (**1a**) (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), phenylacetylene (**17a**) (1.0 mmol, 2.0 equiv), K_2CO_3 (1.5 mmol, 3.0 equiv), catalyst (indicated amount) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at indicated wavelength under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]NMR yield using diphenoxymethane as an internal standard. [b]Based on literature.[59]

In 2016, Noël and co-workers achieved a visible-light mediated photochemical hydrotrifluoromethylation of styrenes using *fac*-$[Ir(ppy)_3]$, CF_3I and 4-hydroxythiophenol as the hydrogen source.[61] Recently, the Yajima group presented a metal-free approach for the visible-light mediated hydroperfluoroalkylation of unactivated alkenes in the presence of eosin Y as the photocatalyst.[62] Thereby, they revealed that the hydrogen source varies with the reaction conditions, thus the hydrogen can be either derived from water or from THF.

Table 13. Attempts towards three-component ATRA reaction with various hydrogen sources.



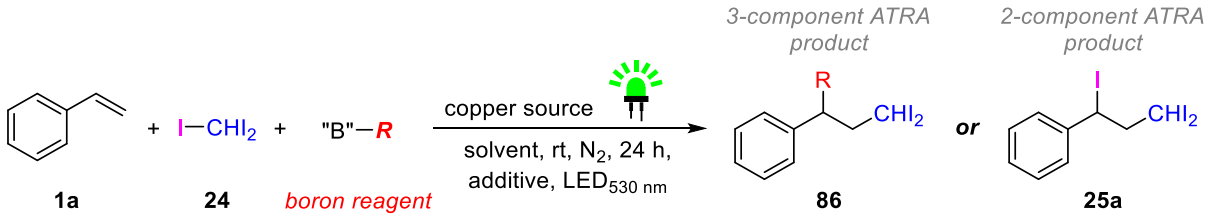
Entry	Catalyst	Solvent	"H-source"	Yield[a]
1[b]	$[Cu(dap)_2]Cl$	DCM/MeOH (9:1)	PhSH (2.0 equiv)	31% **25a**
2[c]	$[Cu(dap)_2]Cl$	MeCN/THF (1:1)	$Na_2S_2O_3$ (aq., 5.0 equiv)	nr

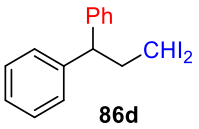
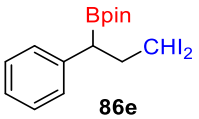
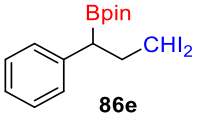
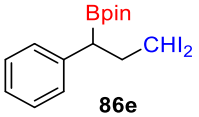
Reaction conditions: Styrene (**1a**) (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), "H-source" (indicated amount), $[Cu(dap)_2]Cl$ (5.0 µmol, 1.0 mol%) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]NMR yield using diphenoxymethane as an internal standard. [b]Based on literature.[61] [c]Based on literature.[62]

We wondered whether these reactions conditions are also applicable to our system using iodoform (**24**) (Table 13). Unfortunately, both reaction conditions turned out to be incompatible in the ATRA reaction with iodoform (**24**) giving rise to a maximum of 31% of the two-component ATRA product **25a** (Table 13, entries 1-2).

In 2019, Qing and co-workers discovered a copper-catalyzed borylfluoromethylation of alkenes. Thereby, transmetalation to a Cu-boryl species with subsequent carbocupration of the alkene revealed to be the mechanistic key step.[63] We wondered whether we could use such a Cu-species for a photochemical three-component ATRA reaction with iodoform (**24**) (Table 14). However, employing either phenylboronic acid or B_2pin_2 as the boron source under basic conditions in MeOH or DMSO as a solvent, showed at the best only traces of two-component ATRA product **25a** (Table 14, entries 1-3). In the same way, when carrying out the reaction under the same conditions reported by Qing et al.,[63] no reaction was observed (Table 14, entry 4).

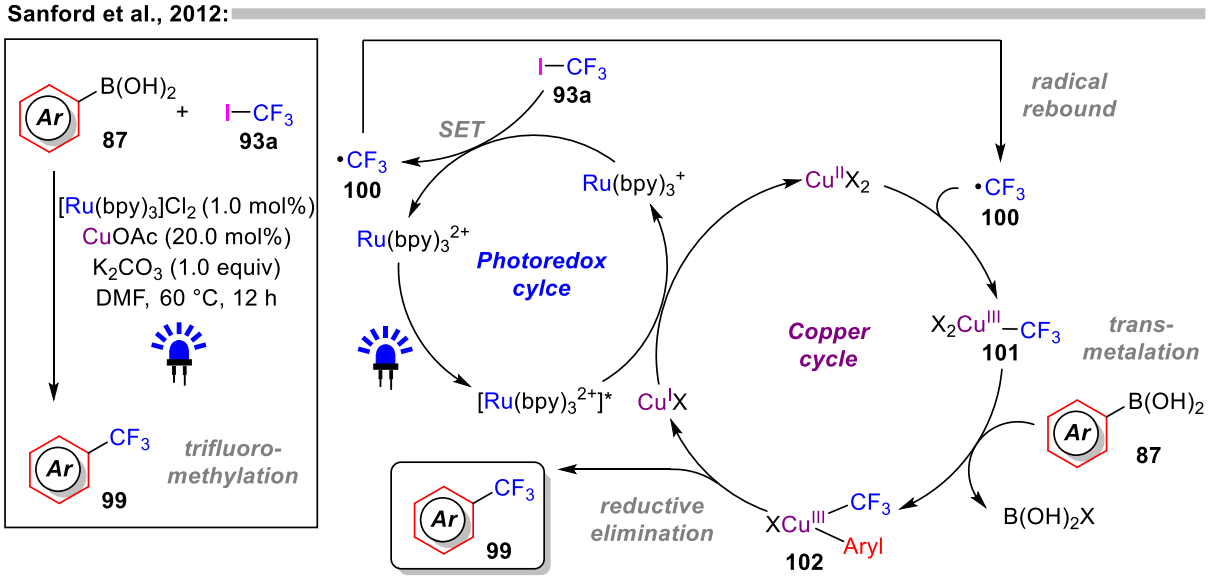
Table 14. Attempts towards three-component ATRA reactions with boron reagents.



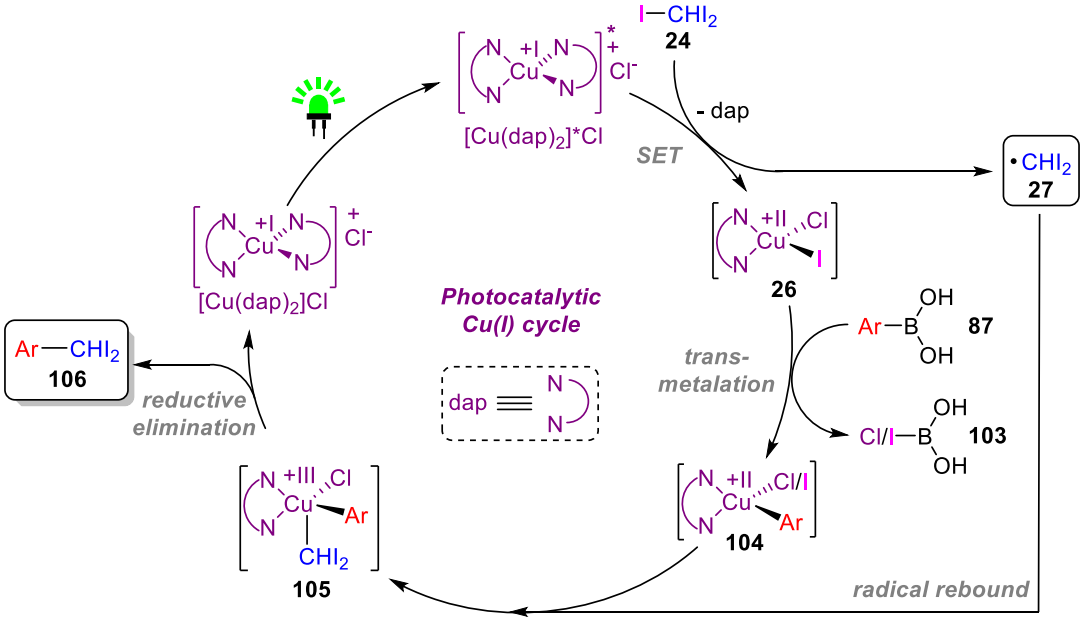
Entry	Catalyst	Boron reagent	Solvent	Additive	Product	Yield[a]
1	$[Cu(dap)_2]Cl$ (1.0 mol%)	$PhB(OH)_2$ (**87a**)	MeOH	Na_2CO_3 (2.0 equiv)	 **86d**	10% **25a**
2	$[Cu(dap)_2]Cl$ (1.0 mol%)	B_2pin_2 (**88**)	MeOH	LiO^tBu (2.0 equiv)	 **86e**	nr
3	$[Cu(dap)_2]Cl$ (1.0 mol%)	B_2pin_2 (**88**)	DMSO	LiO^tBu (2.0 equiv)	 **86e**	nr
4[b]	CuCl (10.0 mol%) IMes (12.0 mol%)	B_2pin_2 (**88**)	DMSO	LiO^tBu (2.0 equiv)	 **86e**	nr

Reaction conditions: Styrene (**1a**) (1.0 mmol, 2.0 equiv), iodoform (**24**) (0.5 mmol, 1.0 equiv), boron reagent (1.0 mmol, 2.0 equiv), additive (1.0 mmol, 2.0 equiv), catalyst (indicated amount) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h. [a]NMR yield using diphenoxymethane as an internal standard. [b]Irradiation at 455 nm (blue LED). Based on literature.[63]

In 2012, the Sanford group impressively developed a visible-light mediated photochemical trifluoromethylation of boronic acids **87** via the merger of photoredox and copper catalysis (Scheme 30).[64] The authors propose photoexcitation of $[Ru(bpy)_3]Cl_2$ followed by one-electron reduction by Cu(I) to furnish Cu(II) and $[Ru(bpy)_3]^+$. The latter is able to donate an electron to CF_3I (**93a**) generating the corresponding radical **100**, which subsequently gets trapped by the previously formed Cu(II)-species. The resulting Cu(III)-complex **101** might undergo base-promoted transmetalation to form a Cu(III)(aryl)(CF_3) species **102** releasing the final product **99** upon reductive elimination (Scheme 30).



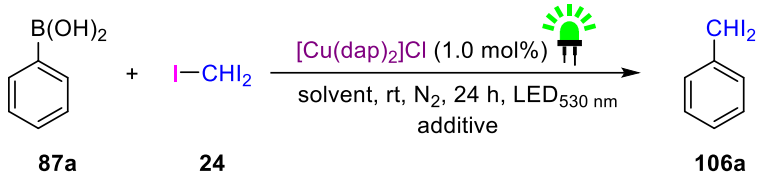
Scheme 30. Trifluoromethylation of boronic acids **87** through the merger of photoredox and copper catalysis reported by Sanford and co-workers.[64]



Scheme 31. Concept of visible-light mediated copper-catalyzed couplings with boronic acids **87**.

Along these lines, we questioned whether such transformations could be also achieved using only a copper photocatalyst acting as both the photoexcited reductant and the reactive metal center for radical rebound, transmetalation with the boronic acid **87** and subsequent reductive elimination to release the final product **106** (Scheme 31). A hypothetic mechanistic picture is depicted in Scheme 31. Preliminary studies, utilizing iodoform (**24**) as the radical source are presented in Table 15.

Table 15. Attempts on copper-catalyzed photochemical radical coupling with boronic acids.



87a **24** **106a**

Entry	Solvent	Additive	Yield
1	DMF	MeOH (4.0 equiv); Na_2CO_3 (2.0 equiv)	nr
2	DMF	Cu(OAc) (20.0 mol%); K_2CO_3 (2.0 equiv)	nr
3	DCM/MeOH (1:1)	Cu(OAc) (20.0 mol%); K_2CO_3 (2.0 equiv)	nr

Reaction conditions: Boronic acid **87a** (0.5 mmol, 1.0 equiv), iodoform (**24**) (1.0 mmol, 2.0 equiv), additive (indicated amounts), $[Cu(dap)_2]Cl$ (5.0 µmol, 1.0 mol%) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 h.

Unfortunately, initial attempts promoting the desired transformation in different solvent systems and in presence of additional copper source, failed resulting in no reaction (Table 15, entries 1-3). Nevertheless, further studies on various conditions and different radical precursors remain to be determined and are ongoing in our laboratories.

4.12 Conclusion

In conclusion, we have developed a highly efficient protocol using the low-cost and non-toxic bulk chemical iodoform for visible-light mediated copper-catalyzed ATRA reactions to various olefins. The protocol excels through high yields and environmentally benign reaction conditions, allowing regio- as well as chemoselective 1,2-difunctionalization of activated double bonds, but also late-stage functionalizations of bioactive molecules. It was found that this transformation is only accessible by copper photocatalysts owing to their ability to interact and stabilize radical intermediates in their inner-coordination sphere, which underscores once more the unique character of the latter in the field of photoredox catalysis. Furthermore, the synthetic utility of the reaction was demonstrated on gram-scale functionalization of styrene and a plethora of further transformations of the obtained products. Among them, nucleophilic

substitution provides a library of functionalized *gem*-diiodides, displaying valuable precursors to manifold organometallic reactions, but being usually synthetically challenging to access. Employing binucleophile phenylhydrazine gave rise to heterocyclic synthesis of 2-pyrazoline derivatives representing a privileged aza-heterocycle frequently found in many bioactive compounds. Intramolecular cyclopropanation reaction delivered an iodocyclopropane serving as an interesting building block for cross-coupling reactions to rapidly create molecular complexity. Finally, partial hydrolysis surprisingly furnished an allylic halohydrin – a unique structural motif, which still is under investigation in our laboratories for further transformations.

4.13 References

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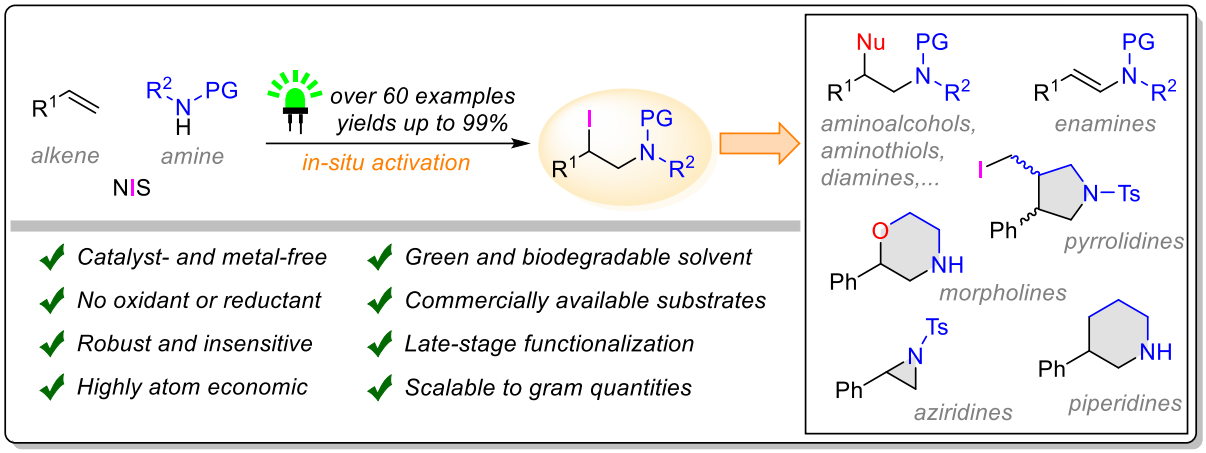
Chapter 5

Photochemical Iodoamination‡

5.1 Abstract



In Chapter 5, we report a catalyst- and metal-free visible-light mediated iodoamination of miscellaneous alkenes through in-situ activation of sulfonamides with NIS. The protocol is characterized by high yields under environmentally benign reaction conditions utilizing commercially available substrates and a green and biodegradable solvent. Furthermore, the protocol allows for late-stage functionalization of bioactive molecules and can be smoothly scaled to gram quantities of product, which offers a plethora of possibilities for further transformations including the synthesis of 1,2-functionalized amines, enamines or various heterocycles like morpholines, piperidines, pyrrolidines and aziridines.

‡ This chapter is partially based on: Engl, S.; Reiser, O. *Org. Lett.* **2021**, *23*, 5581-5586.

5.2 Introduction

Nitrogen-containing organic molecules are widely present in natural products and pharmaceutical active molecules, thus playing an irreplaceable role in synthetic organic chemistry due to their unique activities for chemical materials, dyes or agriculturals.[1] More than 90% of drug molecules contain nitrogen atoms; amines are present in over 40% of the top 200 small molecule pharmaceuticals by retail sales in 2019 (Figure 1).[1c] Henceforth, the selective construction of nitrogen-containing molecules from easily available chemical raw materials has gained tremendous impact in synthetic organic chemistry. In this regard, haloamination, also coined aminohalogenation, has developed into a powerful tool to incorporate an amine as well as a halogen group into unsaturated C-C bonds, representing one of the most fundamental moieties in organic chemistry often derived from simple chemical feedstock (Scheme 1).

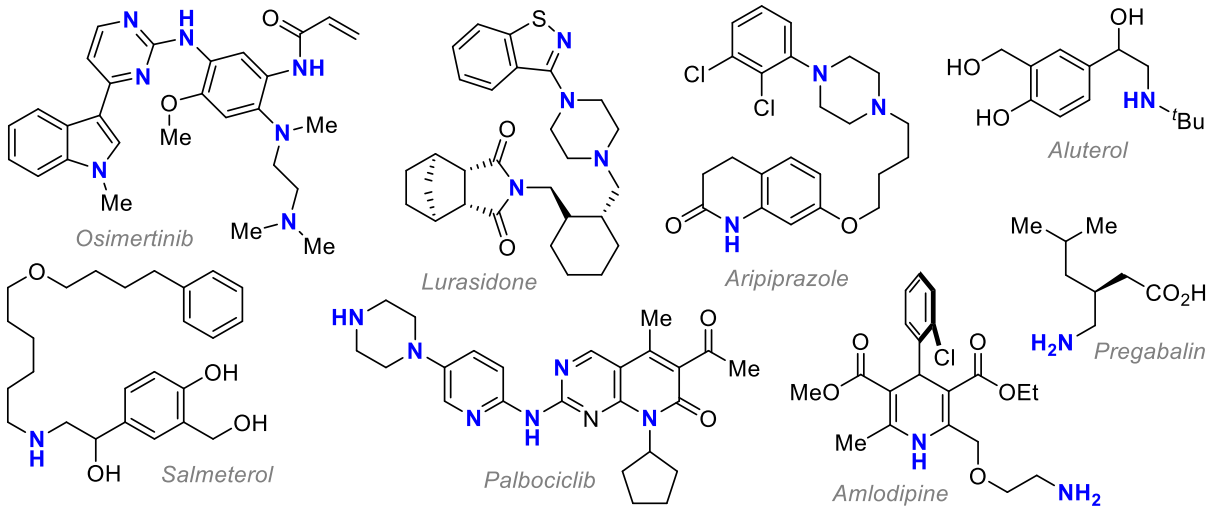
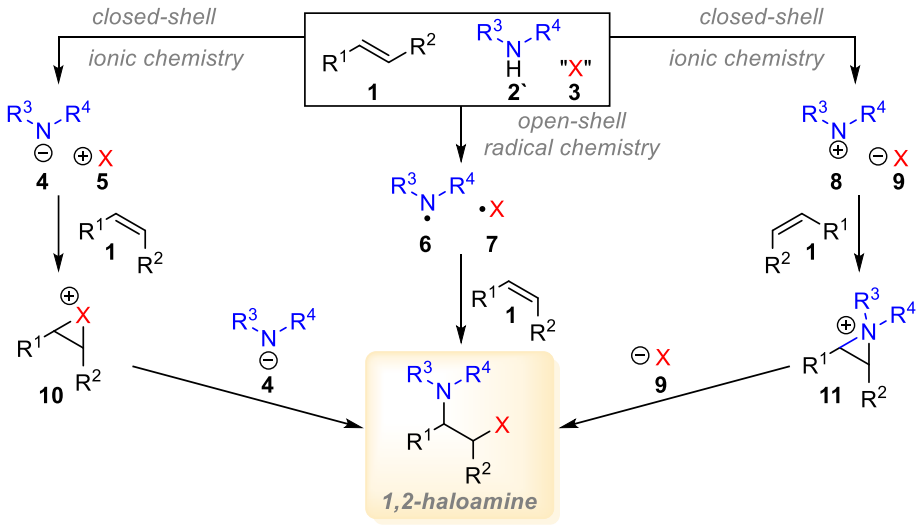
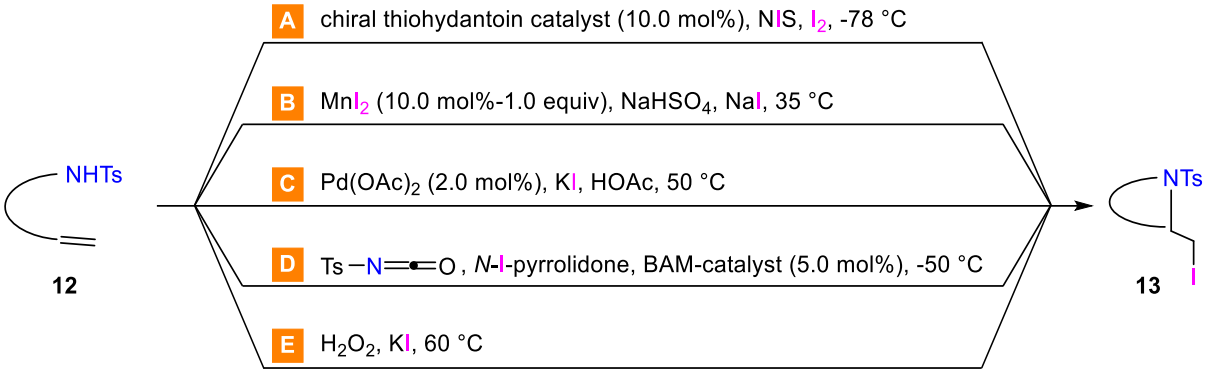


Figure 1. Amine-containing molecules among the 40% top selling 200 small molecule drugs.[1c]



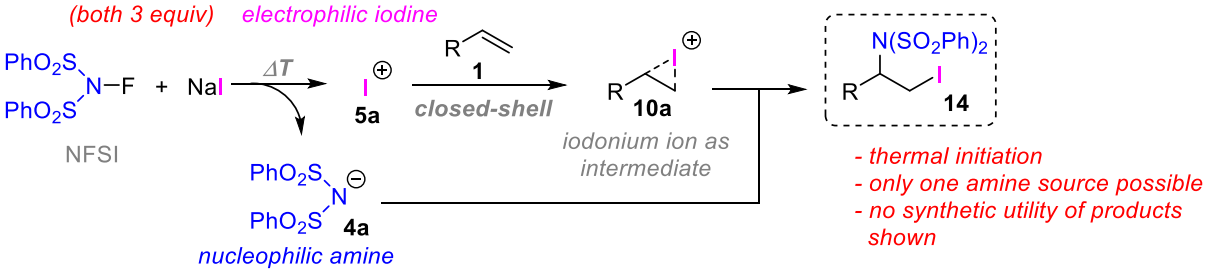
Scheme 1. Possible synthetic strategies for the formation of vicinal haloamines from alkenes **1**.

The obtained vicinal haloamine moiety displays a key motif and versatile intermediate, as the halogen can serve as a reactive functional group in substitution and cross-coupling reactions.[1] Consequently, a broad range of protocols for chloroamination[2,3] and bromoamination[4] of unfunctionalized double bonds have been disclosed. However, while impressive work has been reported on intramolecular iodoamination[5] yielding heterocyclic products **13** (Scheme 2), the analogous intermolecular ATRA-type iodoamination seems to be far less explored.



Scheme 2. Overview of intramolecular iodoaminations reported in literature. (A) Ref.[5a], (B) Ref.[5b], (C) Ref.[5c], (D) Ref.[5d], (E) Ref.[5e]

Seminal work describes this basic idea in only limited examples[6,7] and with difficulties and failures in product isolation.[8] Notably, Li and co-workers reported a thermal closed-shell approach for the iodoamination of alkenes **1** with *N*-fluorobenzenesulfonimide (NFSI) through an iodonium intermediate **10a** affording the corresponding products **14** with the iodine atom located at the terminal secondary carbon (Scheme 3).[9] However, the protocol could only employ NFSI as the nitrogen source being expensive and required in huge excess.



Scheme 3. Thermal iodoamination with NFSI reported by Li and co-workers.[9]

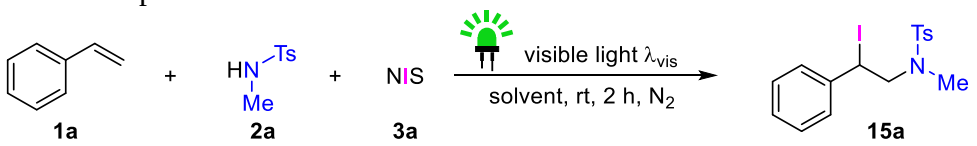
Nonetheless, especially when further synthetic utility of the corresponding halogen moiety is envisioned to rapidly build up complex amine-containing molecules, the highly reactive C-I bond might offer distinct advantages against its lighter homologues. This fact is reflected by the lack of applications for chloroamination of styrenes[2] and by the limited number of

applications in bromoamination studies.[4e,g] Motivated by this literature void, we aimed for the development of a broadly applicable protocol for the iodoamination of various alkenes, which can further serve as versatile building blocks for subsequent diversification and construction of molecular complexity through simple operations.

5.3 Reaction Optimization

On the basis of our experience in the field of photochemical ATRA reactions (previous chapters), we started our investigations using styrene (**1a**), *N*,4-dimethylbenzenesulfonamide (**2a**) and NIS (**3a**) in the presence of various metal-based photocatalysts under visible-light irradiation (Table 1, entries 1-3). The desired iodoamination product **15a** was delivered in up to 46% yield utilizing [Cu(dap)$_2$]Cl under irradiation with green LED (Table 1, entry 1).

Table 1. Reaction optimization.

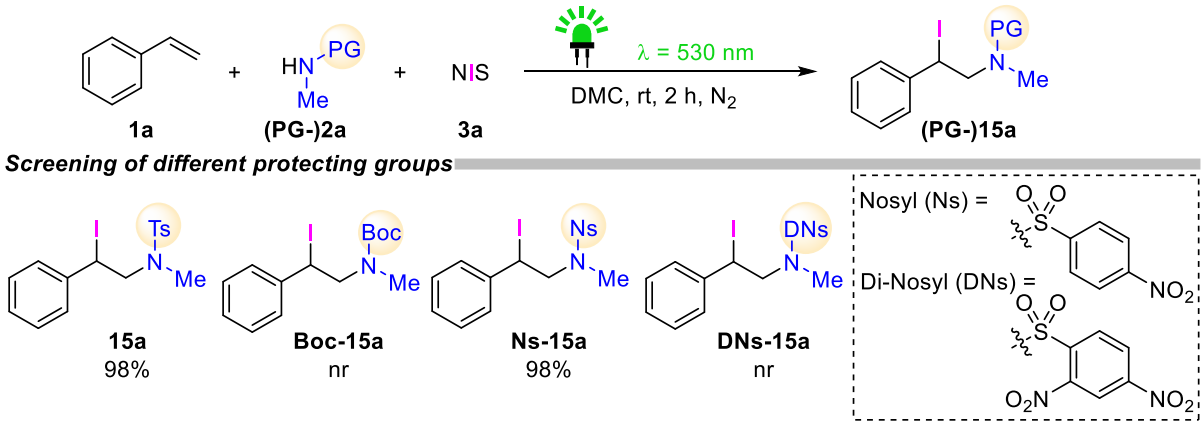


1a **2a** **3a** **15a**

Entry	Solvent	Ratio **1a**:**2a**:**3a**	Conditions	λ_{vis}	Yield[a]
1[b]	DCM	2:1:1	[Cu(dap)$_2$]Cl (1.0 mol%)	530 nm	46%
2[b]	DCM	2:1:1	[Ru(bpy)$_3$]Cl$_2$ (1.0 mol%)	455 nm	34%
3[b]	DCM	2:1:1	*fac*-[Ir(ppy)$_3$] (1.0 mol%)	455 nm	33%
4[b]	DCM	2:1:1	[Cu(dap)$_2$]Cl (1.0 mol%)	no	19%
5	DCM	2:1:1	no	530 nm	98%
6	DCM	1:1:1	no	530 nm	98%
7	DCM	1:1:1	no	455 nm	91%
8	DCM	1:1:1	no	367 nm	72%
9	DCM	1:1:1	no	white LED	98%
10	MeCN	1:1:1	no	530 nm	90%
11	MeOH	1:1:1	no	530 nm	11%
12	THF	1:1:1	no	530 nm	nr
13	DMC	1:1:1	no	530 nm	98%[c]
14[b]	DMC	1:1:1	no	no	19%
15[b]	DMC	1:1:1	T = 50 °C	no	3%
16	DMC	1:1:1	under air	530 nm	93%

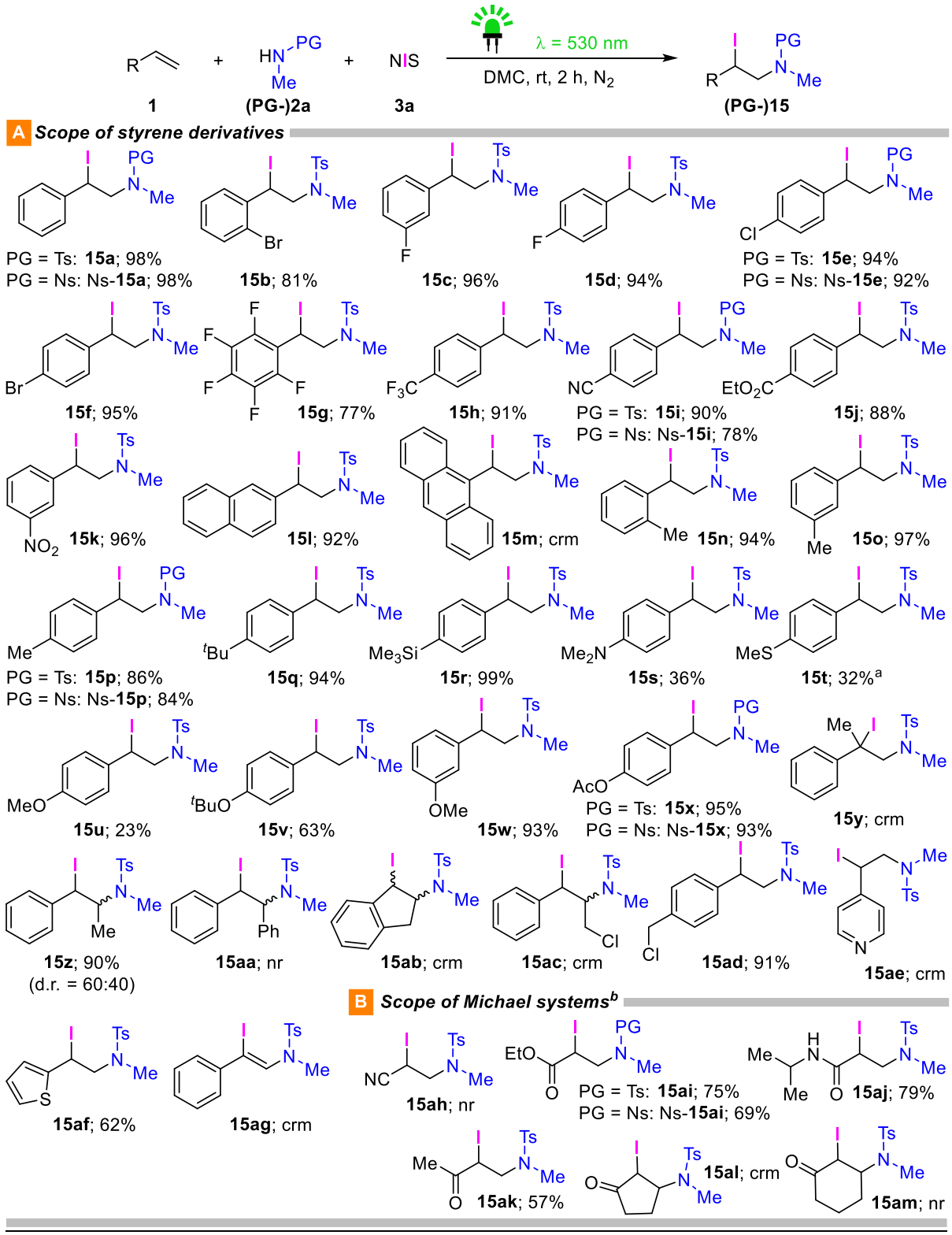
Reaction conditions: Styrene (**1a**) (indicated equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (0.5 mmol, 1.0 equiv), NIS (**3a**) (0.5 mmol, 1.0 equiv) in solvent (anh., degassed, 2.0 mL, 0.25 M); Irradiation at indicated wavelength under N_2 atmosphere at room temperature (25 °C) for 2 h. [a]NMR yield using diphenoxymethane as an internal standard. [b]Reaction time 24 h. [c]Isolated yield.

In absence of light the yield of **15a** decreased to 19%, while, surprisingly, omitting the photocatalyst increased the yield to 98%, providing a catalyst- and metal-free protocol (Table 1, entries 4-5). In accordance with our previous study[10] (Chapter 4), we assume that traces of metal might inhibit free radical chain pathways of such processes. Gratifyingly, also an almost quantitative yield of **15a** was observed, when the equivalents of the starting materials are changed to an equimolar ratio of 1:1:1 (Table 1, entry 6). Variation of different irradiation wavelengths showed no improvement in the reaction efficiency compared to green light irradiation (Table 1, entries 7-9). Following the principles of green chemistry, it is highly desirable to replace chlorinated solvents by more environmentally friendly and preferable alternatives. Thus, we were pleased to see that solvent screening revealed an excellent isolated yield of 98% utilizing dimethyl carbonate (DMC) as a green and biodegradable solvent (Table 1, entries 10-13). Control experiments omitting the light or promoting the reaction under thermal activation significantly decreased the yield of **15a** even after 24 h reaction time (Table 1, entries 14-15). Noteworthy, performing the reaction open to air did not alter the reactivity giving rise to the desired product **15a** in 93% yield, thus demonstrating the robustness and insensitivity of the title reaction system (Table 1, entry 16). Next, we aimed to explore the use of different protecting groups on the amine (Scheme 4). Unfortunately, a limitation was found when the tosyl group was replaced by a Boc group, leading to no conversion of starting materials. However, considering the nosyl group being a much milder removeable sulfonyl protecting group compared with the tosyl group,[11] we were very pleased to observe that the nosyl group was tolerated in the same way and yielded the desired product **Ns-15a** in 98%. Further increasing the electron-withdrawing character of the protecting group revealed to be incompatible, giving no reaction when the amine is protected with the di-nosyl group.



Scheme 4. Screening of protecting groups. *Reaction conditions*: Styrene (**1a**) (0.5 mmol, 1.0 equiv), amine **2** (0.5 mmol, 1.0 equiv), NIS (**3a**) (0.5 mmol, 1.0 equiv) in DMC (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h.

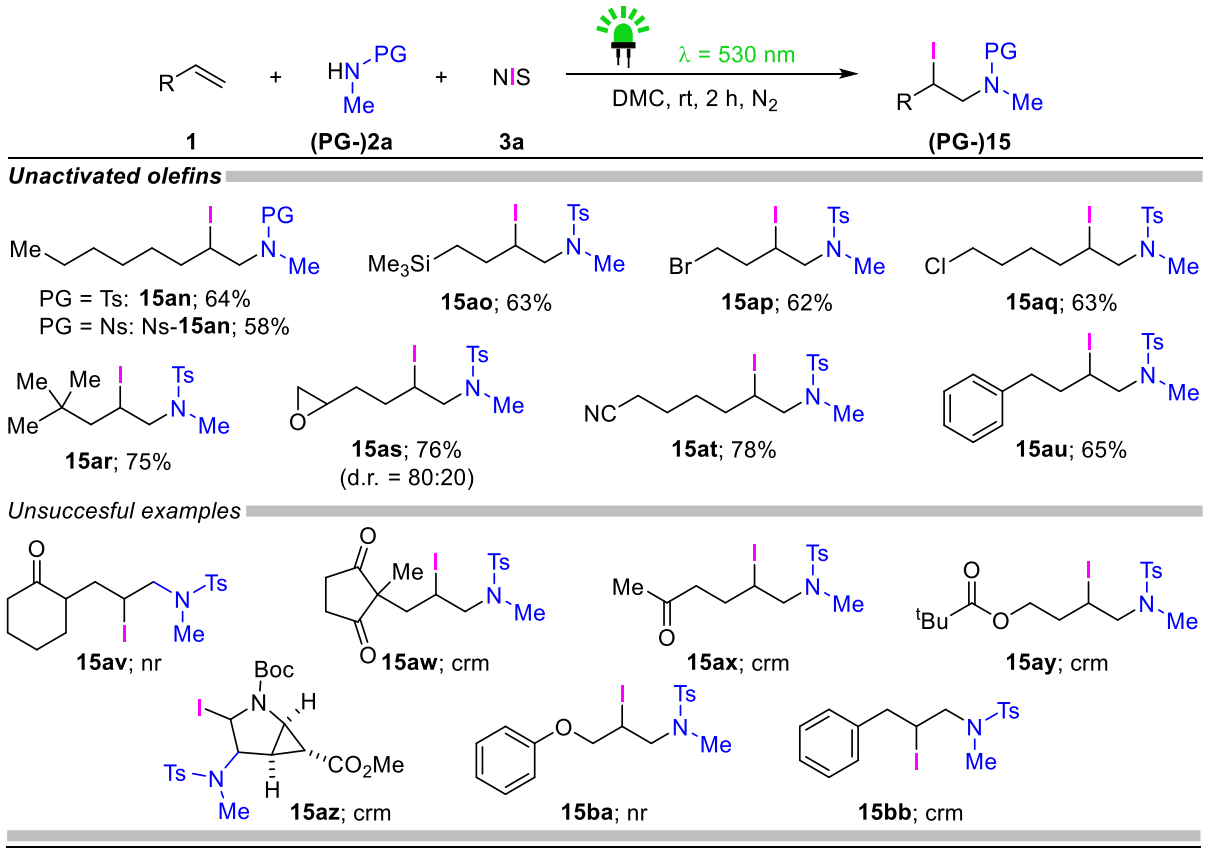
5.4 Substrate Scope



Scheme 5. Scope of activated alkenes **1** in photochemical iodoamination. *Reaction conditions*: Alkene **1** (0.5 mmol, 1.0 equiv), amine **2** (0.5 mmol, 1.0 equiv), NIS (**3a**) (0.5 mmol, 1.0 equiv) in DMC (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h. [a]Product could not be isolated. Yield was determined by ^{1}H-NMR from the crude using diphenoxymethane as an internal standard. [b]4.0 equiv (2.0 mmol) of alkene **1**.

Next, we set out to explore the scope of the title reaction (Scheme 5). Starting with various styrene derivatives (Scheme 1, A), we were pleased to see that electron-withdrawing halogen substitution was well tolerated in various positions giving rise to the corresponding products **15b**-**15f** in high to excellent yields. Further increase in the electron-withdrawing character nevertheless did not alter the reactivity and delivered the desired photoproducts **15g**-**15k** in 77%-96% yield. While vinyl naphthalene was a suitable reaction partner in the same way furnishing **15l** in 92%, a further extend in the π-system aiming in the synthesis of **15m** proved to be incompatible leading to a complex reaction mixture. In accordance with our previous study[10] (Chapter 4), it is assumed that traces of iodine formed during the reaction might undergo stacking with the extended π-system and thus creating a species that also absorbs visible light, which might lead to undesired shielding and side-reactions. Electron-donating alkyl-substitution in *ortho*, *meta* or *para*-position revealed to be well tolerated accessing the desired products **15n**-**15q** in high to excellent yields. In the same way, photoproduct **15r** bearing a silicon substitution could be isolated in almost quantitative yields. However, further increasing the electron-donating character by installing *p*N(Me)$_2$, *p*SMe or *p*OMe decreased the yield of the corresponding products **15s**-**15u** to 23%-36%. In line, when the OMe-group is placed in *meta* position, thus acting as an acceptor, the desired photoproduct **15w** could be isolated in 93% yield. In the same way, protection of the electron-donating alkoxy substituent with an electron-withdrawing acetyl group in *para* position, increased the yield of the corresponding iodoamination product **15x** to 95% yield. While *α*-substitution aiming at the synthesis of **15y** was not tolerated, *β*-substitution proved to be compatible allowing the isolation of **15z** in 90% with a diastereomeric ratio of 60:40. Unfortunately, conversion of other *β*-substituted substrates for the synthesis of **15aa**-**15ac** failed in the title reaction. Remarkably, a benzylic chloride containing substrate, presenting both a highly reactive C-H or C-Cl bond, nevertheless showed no cross-reactivity and furnished the desired product **15ad** in excellent yield of 91%. We were pleased to see that also vinyl thiophene revealed to be an amenable substrate accessing iodoamination product **15af** in synthetically useful yield of 62%. A limitation seemed to be found in the use of phenylacetylene, which instead resulted in a complex reaction mixture. In the same way, utilization of [Cu(dap)$_2$]Cl as a photocatalyst capable to control radical intermediates failed to sufficiently promote this transformation. Considering the substrate class of *α*,*β*-unsaturated Michael systems as usually challenging substrates for the addition of electrophilic radicals,[12] we were pleased to see that the developed protocol is also suitable to convert the latter to the desired products **15ah**-**15ak** in good to high yields. It should be noted,

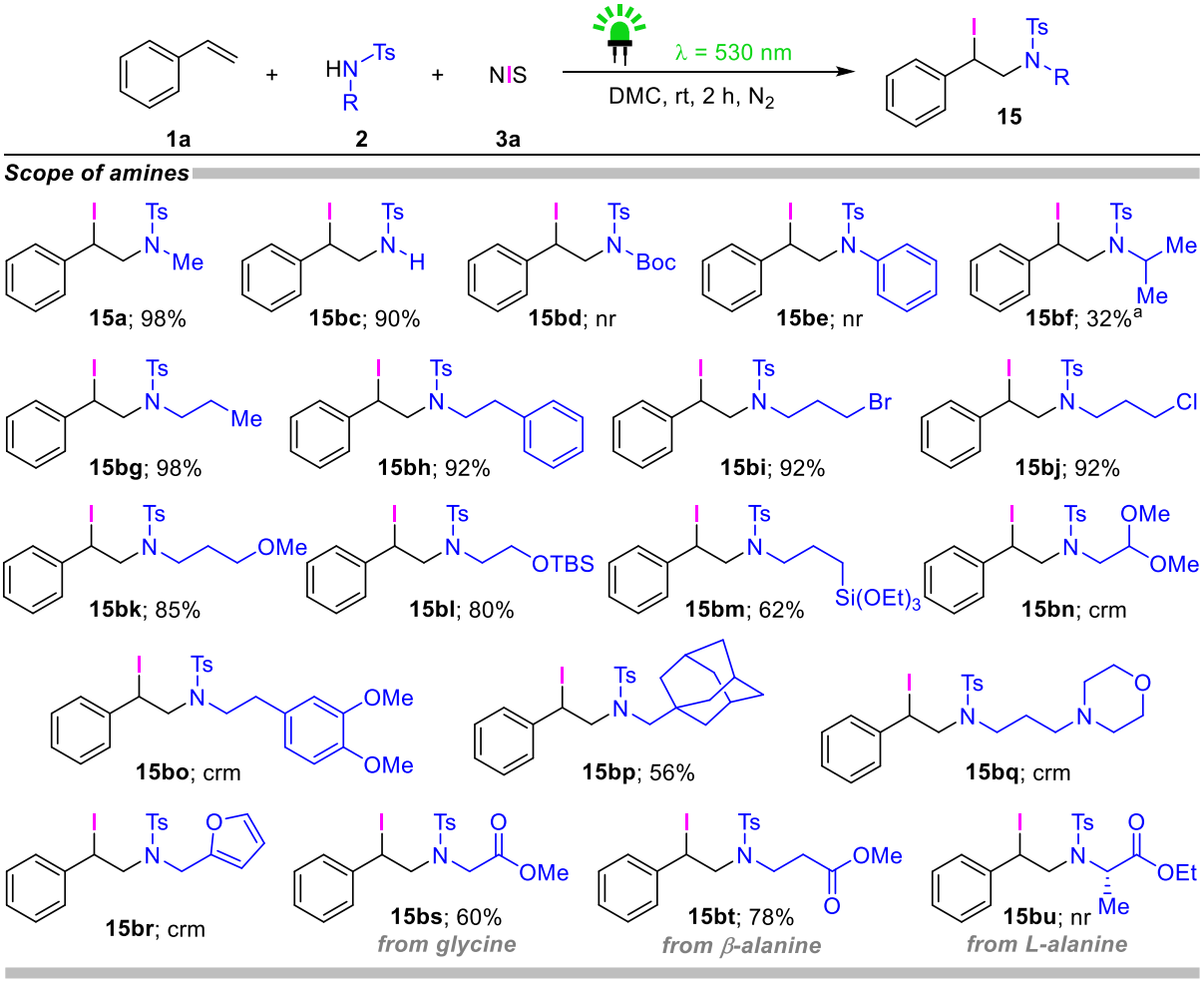
that selected representative examples were also converted with the corresponding nosyl-protected amines aiming in the synthesis of **Ns-15a**, **Ns-15e**, **Ns-15i**, **Ns-15p**, **Ns-15x** and **Ns-15ai** in similar high yields demonstrating the nosyl group to be an valuable alternative, which is much milder removable compared to the tosyl group.[11] Next, we questioned the reactivity of unactivated olefins in the developed iodoamination protocol (Scheme 6).



Scheme 6. Scope of unactivated olefins **1** in the photochemical iodoamination. *Reaction conditions*: Alkene **1** (2.0 mmol, 4.0 equiv), amine **2** (0.5 mmol, 1.0 equiv), NIS (**3a**) (0.5 mmol, 1.0 equiv) in DMC (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h.

Besides activated alkenes, unactivated alkenes were also accessible in the title transformation by adjustment of the reaction stoichiometry using 4.0 equivalents of alkene **1**. When an equimolar ratio of 1:1:1 is employed, the yield of **15an** significantly decreased to 47%. Remarkably, a broad range of different functional groups was well tolerated, giving rise to the desired photoproducts **15an-15au** in synthetically useful yields. We pursued with variation of the amine coupling partners in the developed iodoamination protocol (Scheme 7). Remarkably, a primary tosyl amide was well tolerated leading to the formation of product **15bc** in excellent yield, enabling easy access to aziridines (see chapter 5.5.2). While the Boc group proved to be incompatible in the desired reaction (chapter 5.3), the presence of both tosyl and Boc protecting

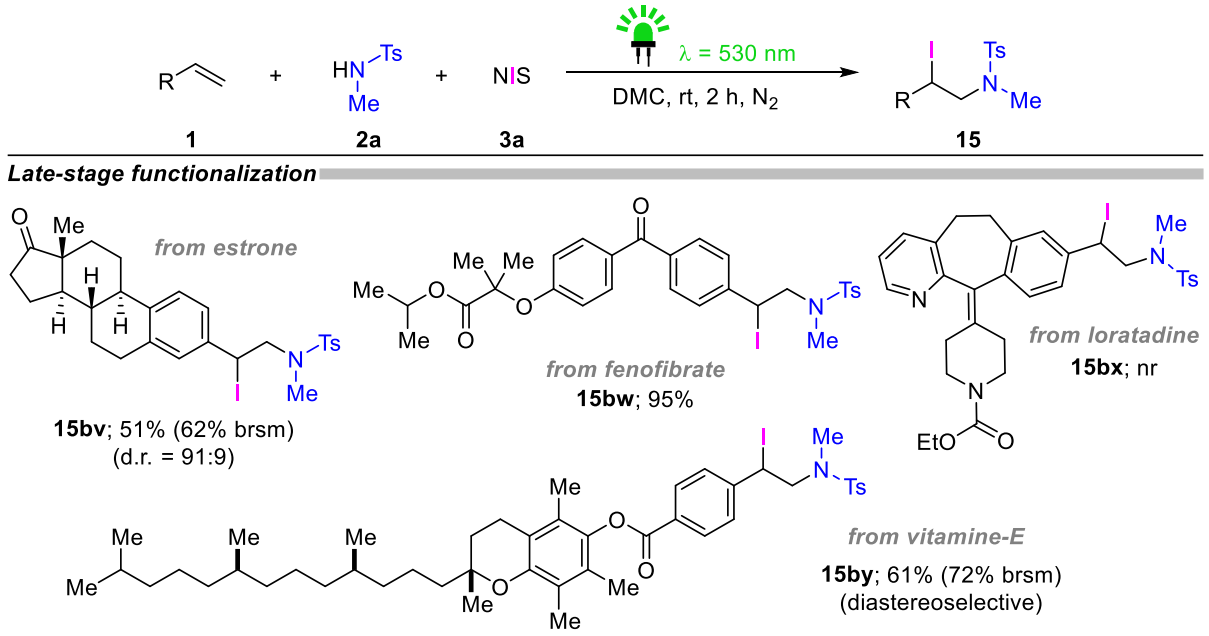
groups showed no conversion in the transformation as well probably being too electron-poor in nature. In the same way, phenyl-substituted tosyl amide aiming in the synthesis of **15be** resulted in no reaction. When an α-branched tosyl amide was subjected to the reaction, the yield of the corresponding product **15bf** dropped to 32% along with product isolation issues. We assume, that the nitrogen-centered radical generated in the reaction might undergo a hydrogen atom shift to give the more stabilized radical interfering with the planned reaction pathway. Hence, we next tested unbranched tosyl amides. Gratifyingly, a broad range of different functional groups were well tolerated, allowing rapid access to highly functionalized amine-containing moieties. The latter offer manifold possibilities to further build up molecular complexity through simple operations, which is demonstrated later in chapter 5.5. Sterically demanding adamantly substitution did not alter the reactivity yielding iodoamination product **15bp** in 56% yield.



Scheme 7. Scope of different amines **2** in the photochemical iodoamination. *Reaction conditions*: Styrene (**1a**) (0.5 mmol, 1.0 equiv), amine **2** (0.5 mmol, 1.0 equiv), NIS (**3a**) (0.5 mmol, 1.0 equiv) in DMC (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h. [a]Product could not be isolated. Yield was determined by ^{1}H-NMR from the crude using diphenoxymethane as an internal standard.

Unfortunately, heterocyclic substituted amines aiming in the synthesis of **15bq** and **15br** proved to be incompatible in the desired reaction leading to complex reaction mixtures. Subjecting amino acid derivatives to the established reaction conditions gave rise to the desired products **15bs** and **15bt** in good yields, contrasting branched *L*-alanine, which showed no reaction.

We next investigated the late-stage functionalization of more complex, biologically active molecules (Scheme 8).

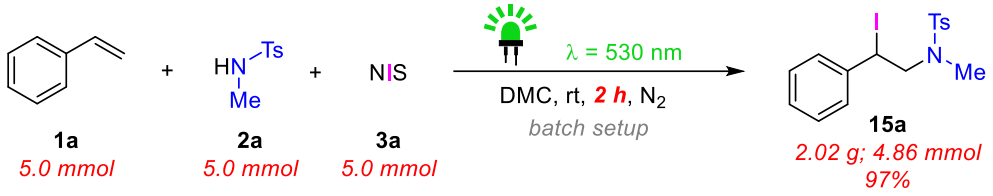


Scheme 8. Late-stage functionalization of bioactive molecules. *Reaction conditions*: Alkene **1** (0.5 mmol, 1.0 equiv), amine **2a** (0.5 mmol, 1.0 equiv), NIS (**3a**) (0.5 mmol, 1.0 equiv) in DMC (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h.

Estrone-, fenofibrate- and vitamin-E-derived substrates were successfully transformed into the desired iodoamination products **15bv**, **15bw** and **15by** in good to excellent yields showcasing the capacity of the protocol in multi-step syntheses of complex molecules.

5.5 Gram-Scale Functionalization and Synthetic Utility

Next, we set out to demonstrate the viability of the protocol for preparative purposes. When the scale was increased by the factor of ten, iodoamination product **15a** was obtained in multigram amounts in an almost quantitative yield of 97% in a simple batch setup without the necessity to prolong the reaction time (Scheme 9).

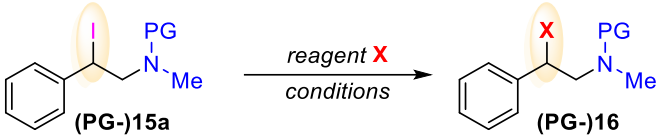


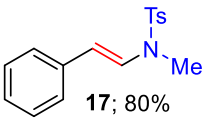
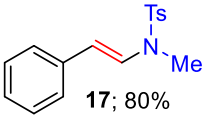
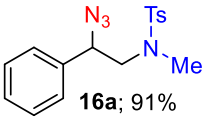
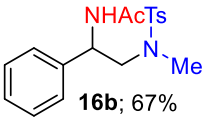
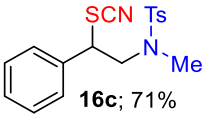
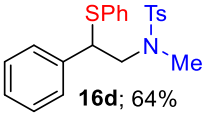
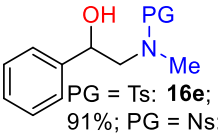
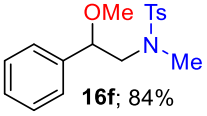
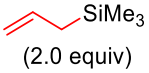
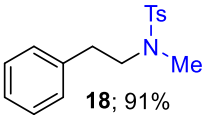
Scheme 9. Gram-scale iodoamination of styrene (**1a**). *Reaction conditions*: Styrene (**1a**) (5.0 mmol, 1.0 equiv), amine **2a** (5.0 mmol, 1.0 equiv), NIS (**3a**) (5.0 mmol, 1.0 equiv) in DMC (anh., degassed, 20.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h.

5.5.1 Nucleophilic Substitutions and Eliminations

Given the scarcity of synthetic transformations of the corresponding benzylic chloro[2]- and bromoamination compounds,[4e,g] we were pleased to find that the benzylic iodides offer manifold possibilities for further reactions (Table 2). Treatment with base provided access to the corresponding enamine **17** in high yields (Table 2, entry 1). Unfortunately, employing sodium cyanide as a carbon nucleophile also resulted in elimination (Table 2, entries 2-3). In contrast, sodium azide smoothly afforded benzylic substitution giving rise to the desired 1,2-diamine **16a** in excellent yields (Table 2, entry 4). Following a literature procedure,[13] subjecting iodoamination product **15a** to a mixture of iron(III)chloride hexahydrate in MeCN allowed isolation of the corresponding acetyl-protected diamine **16b** (Table 2, entry 6). In the same way, sulfur nucleophiles provided the desired 1,2-thioamines **16c** and **16d** in good yields (Table 2, entries 7-10), while oxygen nucleophiles delivered the 1,2-aminoalcohols **16f** but also **Ts-16e** and **Ns-16e** from the tosyl- and nosyl-protected amines, respectively (Table 2, entries 11-12). Vicinal aminoalcohols represent key structural motifs in many biologically intriguing compounds and are from major importance in coordination chemistry.[14] It should be noted, that **Ts-16e** can be smoothly converted to the corresponding α-aminoketone by a literature reported procedure in 98% yield.[15] Barton-McCombie dehalogenation gave rise to product **18** in high yields (Table 2, entry 14).

Table 2. Attempts on benzylic substitutions and eliminations in **15a**.

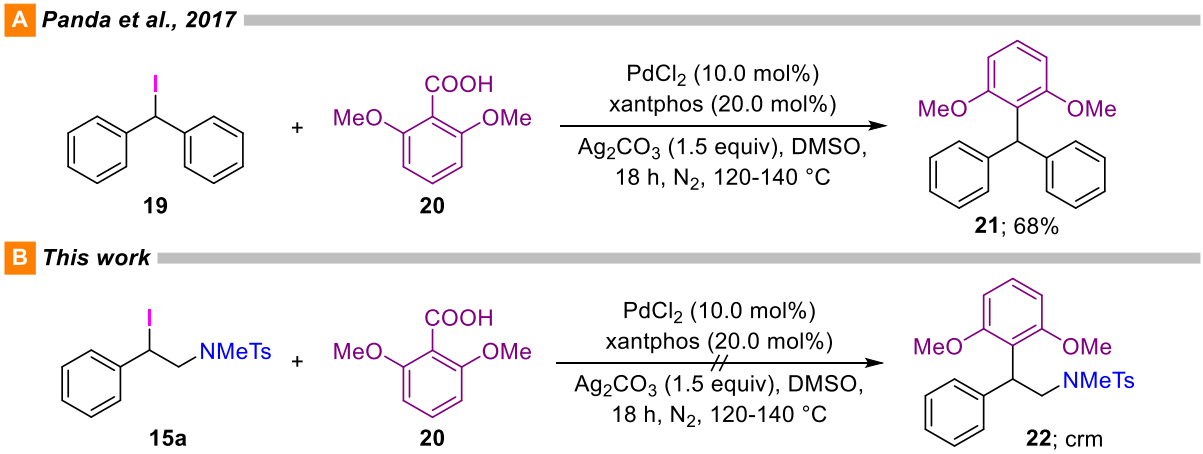


Entry	Reagent X	Conditions	Yield
1[a]	NaOAc (10.0 equiv)	DMF, rt, 5 h	 **17**; 80%
2[b]	NaCN (2.5 equiv)	DMSO, rt, 12 h	 **17**; 80%
3	NaCN (2.5 equiv)	Na_2CO_3 (2.0 equiv), MeCN, reflux, 12 h	nr
4[c]	NaN_3 (5.0 equiv)	DMF, rt, 12 h	 **16a**; 91%
5[a]	$PhCH_2NH$ (5.0 equiv)	Na_2CO_3 (2.0 equiv), MeCN, rt, 12 h	nr
6[d]	MeCN (solvent)	$FeCl_3 \cdot 6\ H_2O$ (4.0 equiv), rt, 12 h	 **16b**; 67%
7[e]	NaSCN (2.5 equiv)	Na_2CO_3 (2.0 equiv), MeCN, rt, 12 h	nr
8	NaSCN (2.5 equiv)	DMF, rt, 12 h	 **16c**; 71%
9	PhSH (10.0 equiv)	DMF, rt, 12 h	nr
10[e]	PhSH (10.0 equiv)	Na_2CO_3 (2.0 equiv), MeCN, rt, 12 h	 **16d**; 64%
11	H_2O (solvent)	H_2O / acetone (1:1), 100 °C, 12 h	 PG = Ts: **16e**; 91%; PG = Ns: **Ns-16e**; 91%
12	MeOH (solvent)	MeOH / acetone (1:1), 65 °C, 12 h	 **16f**; 84%
13[f]	 (2.0 equiv)	$FeCl_3$ (5.0 mol%), DCM, rt	nr
14	Bu_3SnH (3.0 equiv)	AIBN (10.0 mol%), benzene, 80 °C	 **18**; 91%
15	PhCHO (2.0 equiv)	Mg (2.0 equiv), THF, N_2, reflux, 2h	β-hetero elimination

Reaction conditions: Reactions were performed on a 0.3 mmol scale of **15a** (1.0 equiv) in solvent (anh., 2.0 mL, 0.1 M) under N_2 atmosphere at room temperature (25 °C) for 12 h. [a]Based on Ref.[6], [b]Based on Ref.[16], [c]Based on Ref.[17], [d]Based on Ref.[13], [e]Based on Chapter 4 / Ref.[10], [f]Based on Ref.[18]

Unfortunately, attempts to insert magnesium into the benzylic iodide to trigger Grignard-type reactivity with an aldehyde, instead led to *β*-hetero elimination giving styrene (**1a**) and the amine **2a** (Table 2, entry 15).

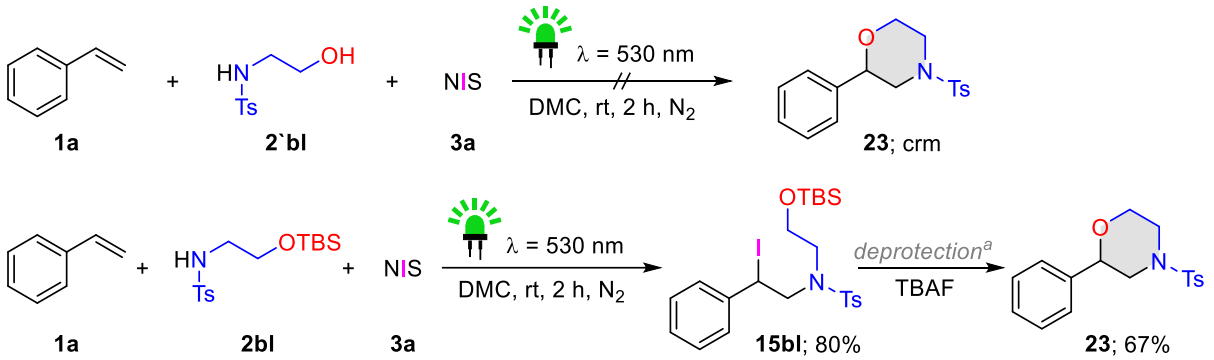
In 2017, Panda and co-workers reported a palladium-catalyzed decarboxylative cross-coupling utilizing diaryl methyl iodides **19** and aromatic carboxylic acids **20** (Scheme 10, A).[19] Hence, we questioned ourselves, whether iodoamination product **15a** might also serve as a suitable starting material for such a process and hence carried out the corresponding experiment under the literature established conditions (Scheme 10, B). Unfortunately, our system revealed to be incompatible in the desired reaction leading to a complex reaction mixture.



Scheme 10. (A) Palladium-catalyzed decarboxylative cross-coupling reported by Panda and co-workers.[19] (B) This work: Palladium-catalyzed decarboxylative coupling of **15a**. *Reaction conditions*: **15a** (0.3 mmol, 1.0 equiv), carboxylic acid **20** (0.3 mmol, 1.0 equiv), $PdCl_2$ (30.0 µmol, 10.0 mol%), xantphos (60.0 µmol, 20.0 mol%), Ag_2CO_3 (0.45 mmol, 1.5 equiv) in DMSO (anh., degassed, 2.0 mL, 0.15 M) under N_2 atmosphere at 120-140 °C for 18 h.

5.5.2 Manifold Heterocycle Syntheses

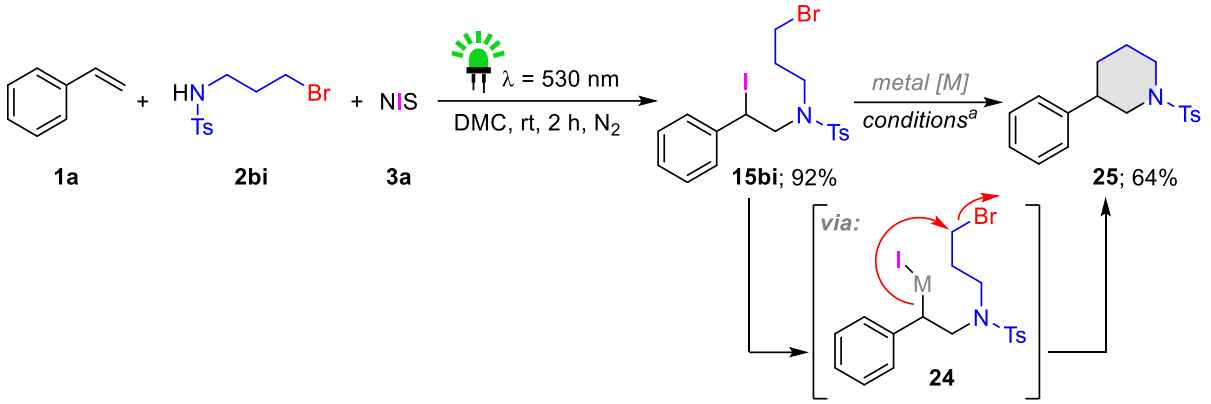
Next, we set out to employ functionalized iodoamination products to trigger intramolecular cyclization reactions accessing a variety of valuable heterocycles. While the photoreaction between styrene (**1a**) and aminoalcohol **2`bl** led to a complex reaction mixture, the corresponding TBS-protected aminoalcohol **2bl** showed no cross-reactivity allowing the isolation of **15bl** in high yields of 80% (Scheme 11). Deprotection of the alcohol moiety in **15bl** promoted rapid intramolecular cyclization giving rise to the substrate class of morpholines **23**, which are representing a ubiquitous pharmacophore in bioorganic and medicinal chemistry.[20]



Scheme 11. Morpholine synthesis based on photochemical iodoamination. *Reaction conditions*: Styrene (**1a**) (0.5 mmol, 1.0 equiv), amine **2** (0.5 mmol, 1.0 equiv), NIS (**3a**) (0.5 mmol, 1.0 equiv) in DMC (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h. [a]Deprotection: **15bl** (0.3 mmol, 1.0 equiv), TBAF (0.36 mmol, 1.2 equiv) in THF (1.0 mL, 0.3 M) at room temperature (25 °C) for 1 h.

Taking iodoamination of styrene (**1a**) with functionalized amine **2bi** as a basis, we wondered if the corresponding product **15bi** might serve as a starting material to insert a metal into the benzylic carbon-iodide bond to subsequently trigger intramolecular cyclization via substitution on the primary bromide motif (Table 3). First attempts using a zinc metal under reflux conditions (Table 3, entry 1) again led to *β*-hetero elimination, which has also been observed for magnesium aiming in formation of a Grignard-type reactivity (Table 2, entry 15). However, carrying out the reaction under milder room temperature conditions revealed no conversion of the starting materials (Table 3, entry 2). In 2014, Qian and Gong reported a nickel-catalyzed reductive cyclization of alkyl dihalides under mild room temperature.[21] Hence, applying this protocol to **15bi** gratifyingly afforded the desired piperidine **25** in synthetically useful yield of 64% (Table 3, entry 3). The substrate class of 3-aryl piperidines has been investigated since the early 1980s in view of their dopaminergic activities and usually require harsh reaction conditions for their synthesis.[22]

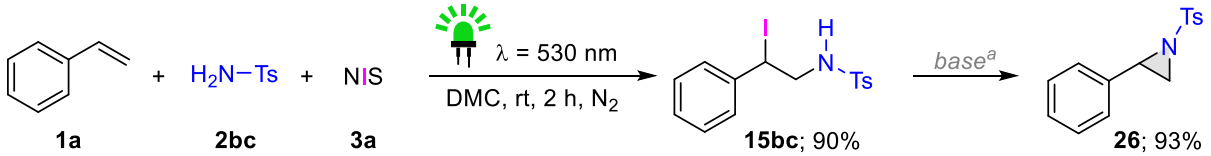
Table 3. Piperidine synthesis based on the photochemical iodoamination.



Entry	Metal [M]	Conditions	Yield
1	Zn-powder (2.0 equiv)	EtOH, reflux, 2 h, N_2	*β*-hetero elimination
2	Zn-powder (2.0 equiv)	DCM, rt, 24 h, N_2	nr
3[b]	NiI_2 (10.0 mol%); Zn-powder (3.0 equiv)	2,2'-bipyridine (10.0 mol%), DMA, rt, 16 h, N_2	64% of **25**

Reaction conditions: Styrene (**1a**) (0.5 mmol, 1.0 equiv), amine **2bi** (0.5 mmol, 1.0 equiv), NIS (**3a**) (0.5 mmol, 1.0 equiv) in DMC (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h. [a]Cyclization attempts: Reactions were performed on a 0.3 mmol scale of **15bi** (1.0 equiv) in solvent (anh., 2.0 mL, 0.1 M) under N_2 atmosphere at indicated temperature for indicated time. [b]Based on Ref.[21]

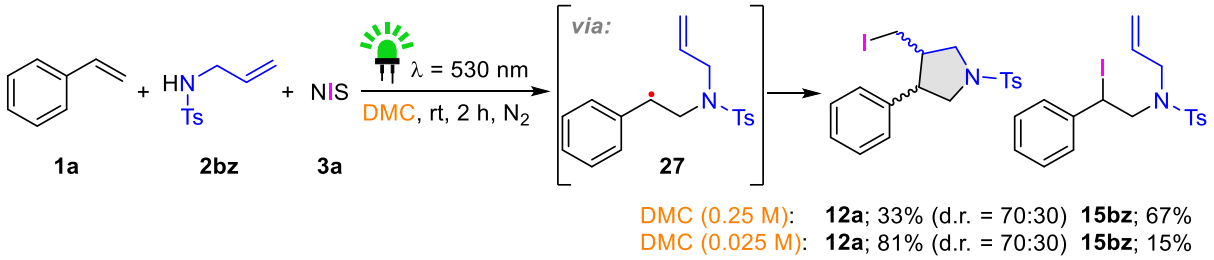
Aziridines represent a privileged class of structural motifs frequently found in many natural occurring compounds with intriguing biological activities but they also serve as valuable building blocks for further synthetic applications.[23] Thus, we envisioned the iodoamination between styrene (**1a**) and tosyl amine (**2bc**) to deliver a suitable starting material **15bc** for base-promoted intramolecular cyclization to the corresponding aziridine **26**. Indeed, we were pleased to observe formation of **26** in 93% upon treatment of **15bc** with triethylamine under mild room temperature conditions (Scheme 12).



Scheme 12. Synthesis of aziridines based on the photochemical iodoamination. *Reaction conditions*: Styrene (**1a**) (0.5 mmol, 1.0 equiv), tosyl amine (**2bc**) (0.5 mmol, 1.0 equiv), NIS (**3a**) (0.5 mmol, 1.0 equiv) in DMC (anh., degassed, 2.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h. [a]Cyclization: **15bc** (0.3 mmol, 1.0 equiv), NEt_3 (0.9 mmol, 3.0 equiv) in DCM (2.0 mL, 0.15 M) at room temperature (25 °C) for 3 h.

Lastly, we questioned the reactivity of allyl amine **2bz** in the developed iodoamination protocol. After radical addition of the corresponding amino-radical to styrene (**1a**) the resulting benzylic

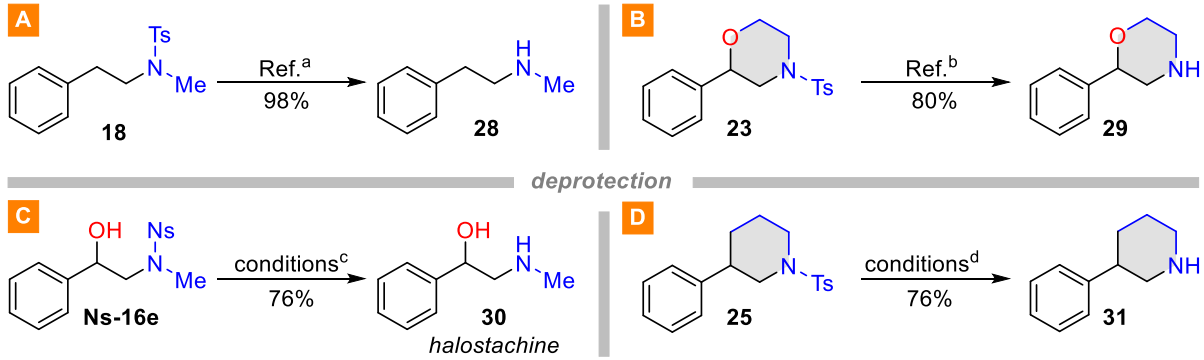
radical **27** might either be trapped by an iodine radical to yield **15bz** or might undergo 5-*exo*-trig radical cyclization to form pyrrolidine **12a** (Scheme 13). While running the reaction in a 0.25 M concentration afforded a separable mixture of 33% of the desired pyrrolidine **12a** and 67% of uncyclized **15bz**, dilution by the factor of ten increased the yield of pyrrolidine **12a** to 81%. Thus, the protocol allows for easy access to pyrrolidines in a single step from commercially available starting materials under mild reaction conditions. Notably, the analogous intramolecular chloroamination requires either harsh thermal conditions[24] or the use of expensive Ir-based photocatalysts.[25]



Scheme 13. Synthesis of pyrrolidines based on the iodoamination. *Reaction conditions*: Styrene (**1a**) (0.5 mmol, 1.0 equiv), allyl amine **2bz** (0.5 mmol, 1.0 equiv), NIS (**3a**) (0.5 mmol, 1.0 equiv) in DMC (anh., degassed, indicated concentration); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h.

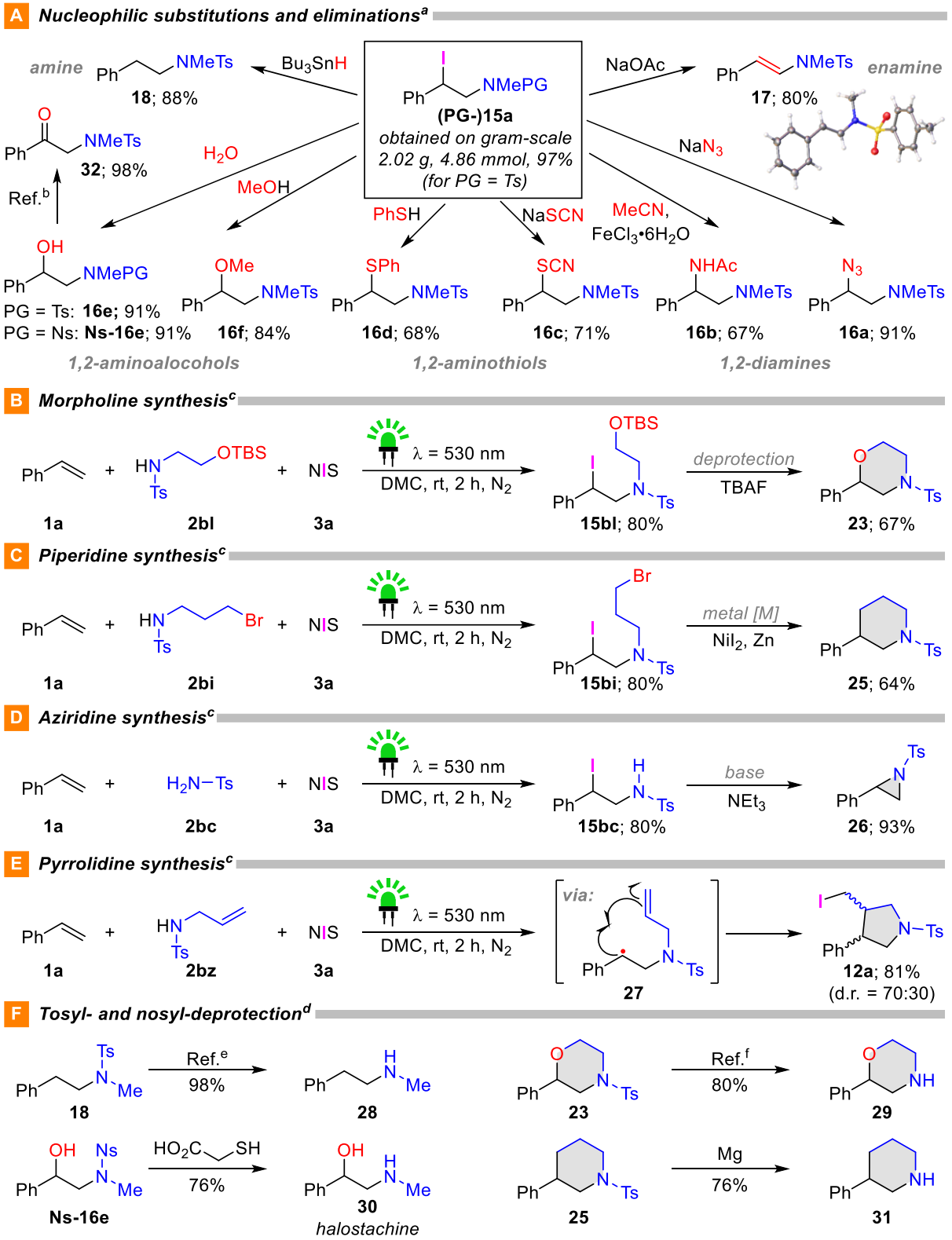
5.5.3 Tosyl- and Nosyl-Deprotection

Finally, we aimed for tosyl- and nosyl deprotection of representative examples (Scheme 14). While amine **18**, morpholine **23** and piperidine **25** can smoothly be tosyl-deprotected under mild reductive conditions, the introduced nosyl group offers the possibility to deprotect more functionalized molecules like **Ns-16e** under much milder redox-neutral conditions, giving halostachine (**30**) in good yields.



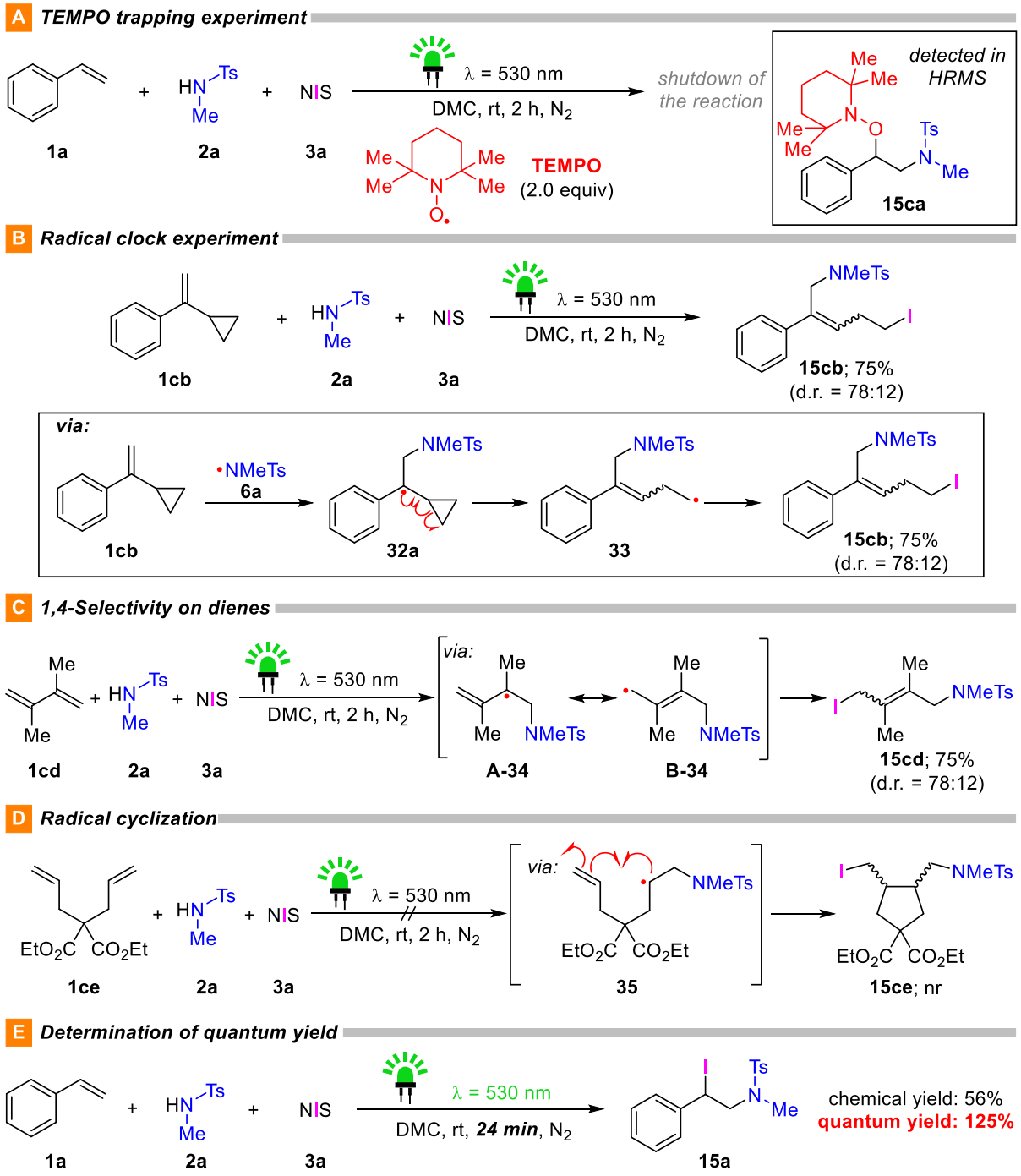
Scheme 14. Tosyl- and nosyl-deprotection of representative examples. (A) Ref.[26], (B) Ref.[27], *Reaction conditions*: (C) **Ns-16e** (0.2 mmol, 1.0 equiv), 2-mercaptoacetic acid (1.2 mmol, 6.0 equiv), DBU (1.2 mmol, 6.0 equiv) in DMF (3.0 mL, 0.07 M) at room temperature (25 °C) for 12 h. (D) **25** (0.2 mmol, 1.0 equiv), Mg (2.0 mmol, 10.0 equiv) in MeOH (1.0 mL, 2.0 M) at room temperature (25 °C) for 3 h.

5.5.4 Overview on Successful Synthetic Transformations



Scheme 15. Overview on successful synthetic utility. *Reaction conditions*: [a]For details, please see chapter 5.5.1, [b]Ref.[15], [c]For details, please see chapter 5.5.2, [d]For details, please see chapter 5.5.3, [e]Ref.[26], [f]Ref.[27]

5.6 Mechanistic Studies

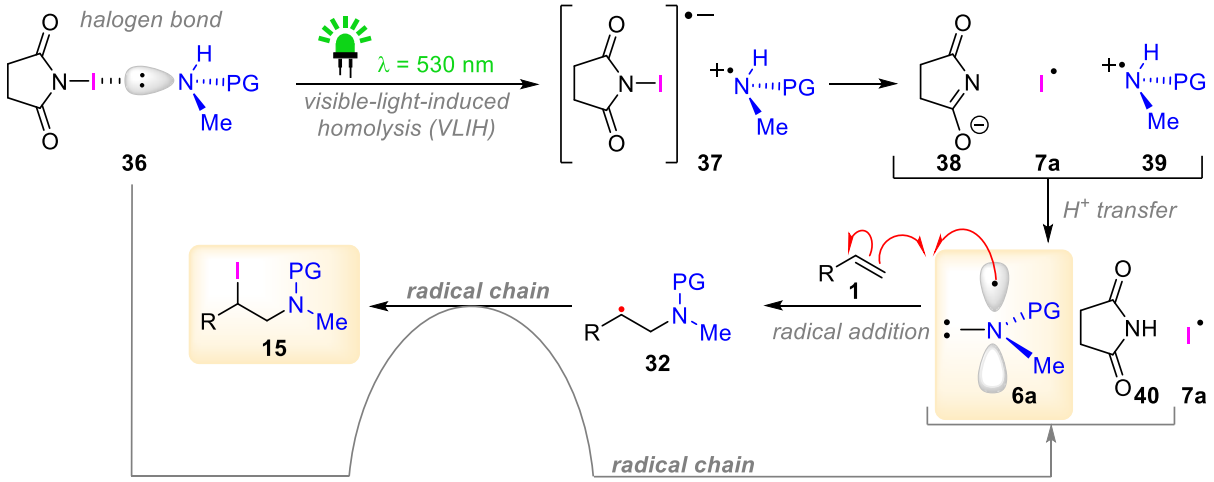


Scheme 16. Mechanistic studies. *Reaction conditions*: (A) Styrene (**1a**) (0.5 mmol, 1.0 equiv), amine **2a** (0.5 mmol, 1.0 equiv), NIS (**3a**) (5.0 mmol, 1.0 equiv), TEMPO (1.0 mmol, 2.0 equiv) in DMC (anh., degassed, 20.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h. (B-D) Alkene **1** (0.5 mmol, 1.0 equiv), amine **2a** (0.5 mmol, 1.0 equiv), NIS (**3a**) (5.0 mmol, 1.0 equiv) in DMC (anh., degassed, 20.0 mL, 0.25 M); Irradiation at 530 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 2 h. (E) Styrene (**1a**) (0.5 mmol, 1.0 equiv), amine **2a** (0.5 mmol, 1.0 equiv), NIS (**3a**) (5.0 mmol, 1.0 equiv) in DMC (anh., degassed, 20.0 mL, 0.25 M); Irradiation at 528 nm (green LED) under N_2 atmosphere at room temperature (25 °C) for 24 min. For more details, please see Experimental Part.

Having explored synthetic aspects of the photochemical iodoamination, we next aimed for deeper mechanistic understanding (Scheme 16). Along a mechanistic pathway calling for radical intermediates, the addition of TEMPO to the standard reaction conditions proved to completely shut down the reaction, while TEMPO trapping adduct **15ca** was observed in HRMS (Scheme 16, A). In the same way, radical clock experiment subjecting **1cb** to the established reaction conditions exclusively gave rise to product **15cb** being in agreement with radical intermediate **32a**, which rapidly undergoes radical-initiated ring opening to yield **33** (Scheme 16, B). Performing the developed iodoamination reaction on diene **1cd** led to formation of product **15cd** with exclusive 1,4-selectivity caused by resonance of radical intermediate **34** resulting at the higher substituted double bond (Scheme 16, C). Unfortunately, attempts using alkene **1ce** as a starting point for intramolecular radical cyclization to **15ce** failed and thus no conversion was observed (Scheme 16, D). The quantum yield of the title reaction was determined to be 125%, clearly pointing toward a radical chain mechanism (Scheme 16, E).

5.7 Proposed Reaction Mechanism

Hence, in agreement with aforementioned mechanistic experiments and a very recent study on the halogen-bond induced C-H amination initiated by 4-methylbenzenesulfonamide and **NIS** (3a),[8] we propose the following mechanism (Scheme 17).



Scheme 17. Proposed reaction mechanism for the photochemical iodoamination.

First, the halogen bonding complex **36** absorbs visible light, thus leading to visible-light induced homolysis (VLIH) and generation of complex **37**. Extensive mechanistic studies of the aforementioned literature report revealed this activation mode of such substrates, e.g. by UV-vis absorption studies and a downfield shift for the nitrogen signal in ^{15}N-NMR of complex **36** by

around one ppm.[8] After charge- and proton transfer, the iodine radical **7a** and the nitrogen-centered radical **6a** get extruded. The latter preferentially adds to the alkene **1** forming the benzylic radical intermediate **32**, which now can abstract iodine form the starting complex **36** or from NIS (**3a**) to deliver the final product **15** with concurrent regeneration of nitrogen-centered radical **6a**.

5.8 Conclusion

In conclusion, we have developed a highly efficient, catalyst- and metal-free protocol for visible-light mediated iodoamination of miscellaneous olefins. The reaction relies on in-situ activation of simple and abundant sulfonamides with NIS without necessity for further oxidants or reductants in the desired transformation. The protocol is robust and insensitive to air, is driven in a green and biodegradable solvent and also allows for late-stage functionalizations of bioactive molecules. For preparative purpose the protocol can be smoothly scaled to gram quantities of products, which serve as versatile building blocks in synthetic chemistry allowing a plethora of further transformations. Thus, nucleophilic substitution with manifold nucleophiles provides a library of 1,2-functionalized amines, including aminoalcohols, aminothiols and diamines. Furthermore, several classes of valuable and biologically important heterocycles can be rapidly accessed using the iodoamination products as starting points, e.g. morpholines, piperidines, aziridines and pyrrolidines.

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Chapter 6

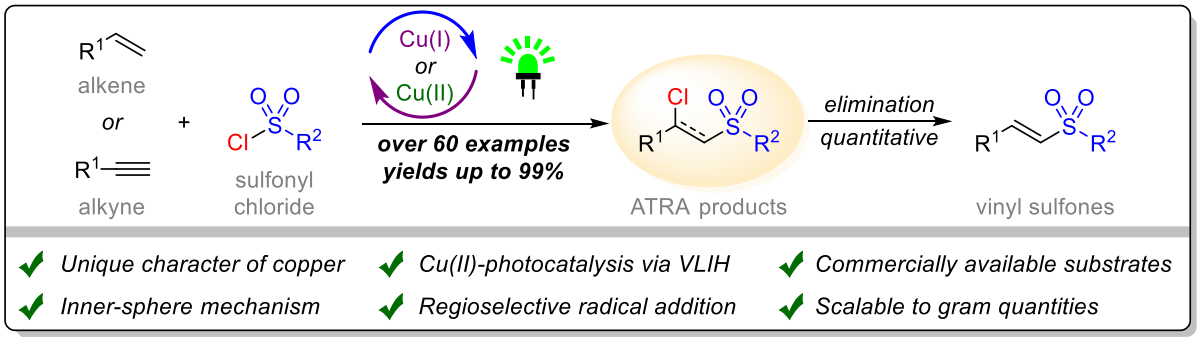
Summary / Zusammenfassung

6.1 Summary and Outlook

Photochemical Chlorosulfonylation

This chapter is based on: Hossain, A.†; Engl, S.†; Lutsker, E.†; Reiser, O. *ACS Catal.* **2019**, *9*, 1103-1109. (†Authors contributed equally). ***And on***: Henriquez, M. A.; Engl, S.; Jaque, P.; Gonzalez, I. A.; Natali, M.; Reiser, O.; Cabrera, A. R. *Eur. J. Inorg. Chem.* **2021**, 4020-4029.

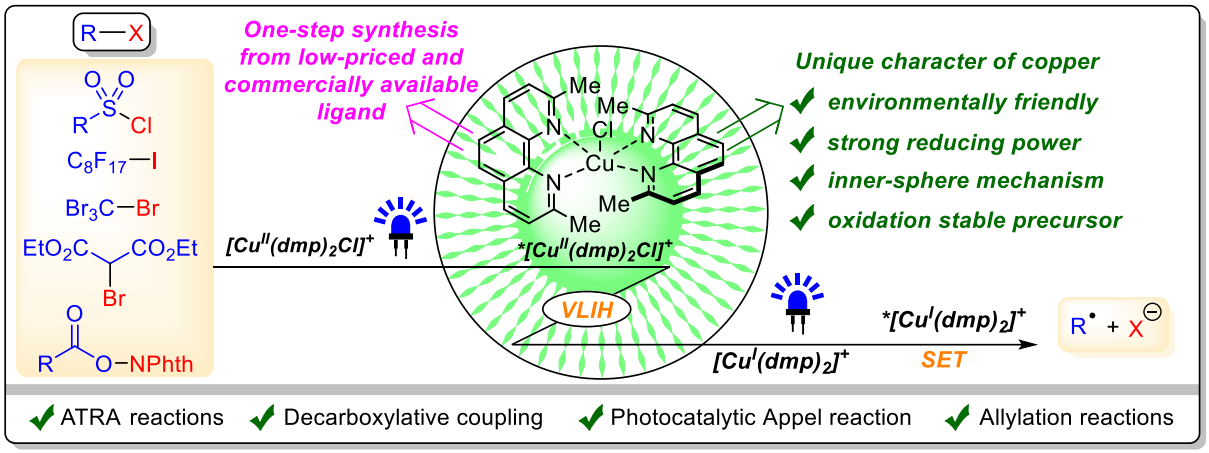
We report a visible-light mediated copper-catalyzed protocol enabling the rapid chlorosulfonylation of miscellaneous alkenes and alkynes. Besides the Cu(I)-complex $[Cu(dap)_2]Cl$, now well-established in such ATRA processes, the corresponding Cu(II)-complex $[Cu(dap)Cl_2]$ proved to be often even more efficient in the title reaction, being advantageous from an economic point of view but also opening up new avenues in copper photoredox catalysis. Moreover, those outperformed commonly used ruthenium-, iridium- or organic dye-based photocatalysts, owing to their ability to stabilize and interact with transient radical intermediates in their inner-coordination sphere. Furthermore, the protocol excels through high yields utilizing commercially available substrates and can be smoothly scaled to gram-quantities of product. The latter can be quantitatively transformed upon elimination giving rise to their corresponding vinyl sulfones, which are of great importance in several fields in synthetic organic as well as medicinal chemistry.



Introducing Chlorobis(dmp)copper(II) to Photocatalysis

This chapter is based on: Engl, S; Reiser, O. *Eur. J. Org. Chem.* **2020**, 1523-1533. (VIP Paper). ***And on:*** Fayad, R.; Engl, S.; Danilov, E. O.; Hauke, C. E.; Reiser, O.; Castellano, F. N. *J. Phys. Chem. Lett.* **2020**, *11*, 5345-5349.

This chapter introduces for the first time the Cu(II)-complex [Cu(dmp)$_2$Cl]Cl as an oxidation- and bench-stable photocatalyst for activation by visible-light-induced homolysis (VLIH) to undergo Cu(I)-photoredox catalysis. The complex is highly efficient and considerably more cost-effective compared to previously established Cu(I) photocatalysts as it is synthesized from commercially available starting materials in one step. Its performance and efficiency are demonstrated within a broad scope of atom transfer radical addition (ATRA) reactions, allowing rapid 1,2-difunctionalization of alkenes, as well as for decarboxylative coupling, for a photocatalytic Appel reaction and for photochemical allylation reactions. Moreover, the utility of the catalyst is presented by gram-scale functionalizations of styrene, thus suggesting [Cu(dmp)$_2$Cl]Cl to be a low-priced alternative catalyst. Furthermore, this study provides UV-vis evidence on the mechanism for the VLIH activation of Cu(II)-complexes opening up novel avenues for photocatalysis. In cooperation with the Prof. Castellano group, combined results from static spectroscopy, ultrafast transient absorption and paramagnetic resonance spin trapping experiments strongly support VLIH occurring in <100 fs.

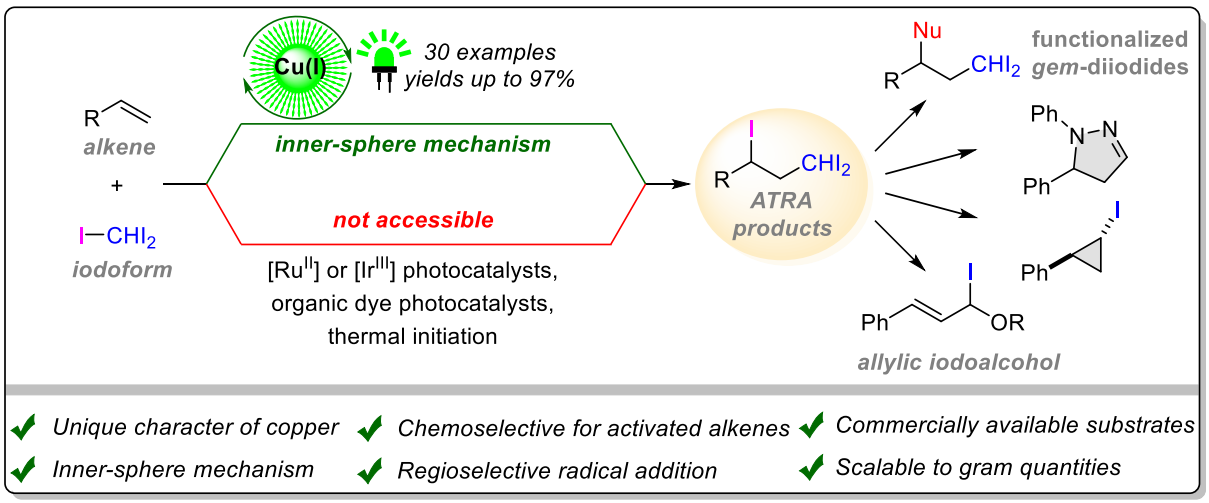


Photochemical ATRA Reactions of Iodoform

This chapter is based on: Engl, S.; Reiser, O. *ACS Catal.* **2020**, *10*, 9899-9906.

In this chapter, we report a visible-light mediated copper-catalyzed protocol enabling the highly economic 1,2-difunctionalization of olefins utilizing the readily available and low-cost bulk chemical iodoform. Although this reaction seems to be simple on paper, it turned out that the title transformation is not feasible via commonly employed ruthenium-, iridium- or organic dye-based photocatalysts, thus undergirding the unique role of copper in photoredox catalysis owing to its ability to interact and stabilize incipient radical intermediates in the inner-coordination sphere. The developed protocol is characterized by high yields under environmentally benign reaction conditions and allows for the regio- and chemoselective

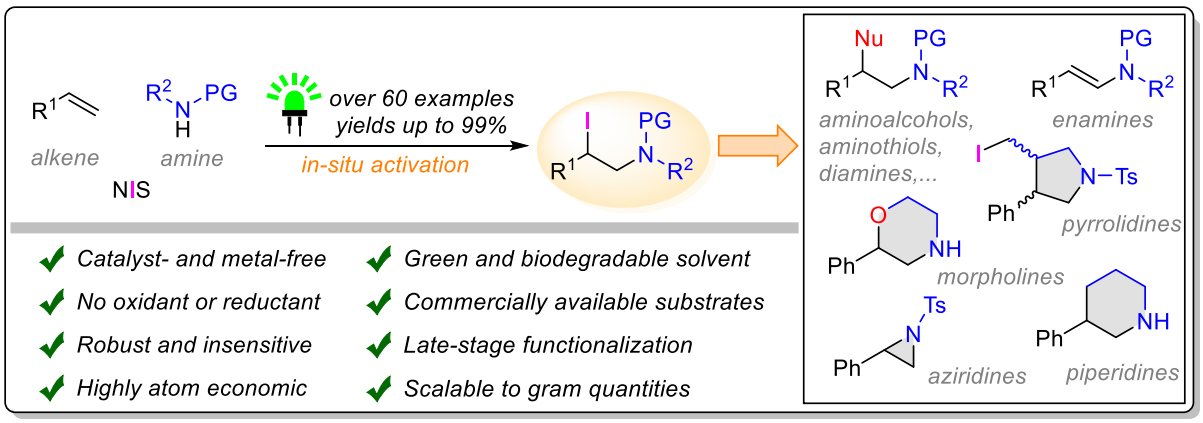
functionalization of activated double bonds as well as for late-stage functionalization of bioactive molecules. Furthermore, the protocol can be smoothly scaled to gram-quantities of product, which offers manifold possibilities for further transformations, including heterocycle synthesis, intramolecular cyclopropanation or the synthesis of functionalized *gem*-diiodides being privileged building blocks in organic synthesis but usually challenging to access.



Photochemical Iodoamination

This chapter is based on: Engl, S.; Reiser, O. *Org. Lett.* **2021**, *23*, 5581-5586.

This chapter describes a catalyst- and metal-free visible-light mediated iodoamination of miscellaneous alkenes through in-situ activation of sulfonamides with NIS. The protocol is characterized by high yields under environmentally benign reaction conditions utilizing commercially available substrates and a green and biodegradable solvent. Furthermore, the protocol allows for late-stage functionalization of bioactive molecules and can be smoothly scaled to gram quantities of product, which offers a plethora of possibilities for further transformations including the synthesis of 1,2-functionalized amines, enamines or various heterocycles like morpholines, piperidines, pyrrolidines and aziridines.

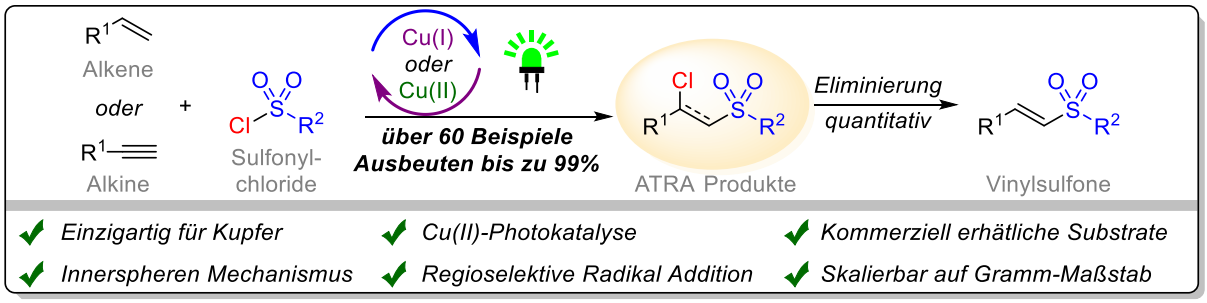


6.2 Zusammenfassung und Ausblick

Photochemical Chlorosulfonylation

Dieses Kapitel basiert auf: Hossain, A.†; Engl, S.†; Lutsker, E.†; Reiser, O. *ACS Catal.* **2019**, *9*, 1103-1109. (†Autoren trugen zu gleichen Teilen zur Arbeit bei). ***Und auf:*** Henriquez, M. A.; Engl, S.; Jaque, P.; Gonzalez, I. A.; Natali, M.; Reiser, O.; Cabrera, A. R. *Eur. J. Inorg. Chem.* **2021**, 4020-4029.

Dieses Kapitel beschreibt eine durch sichtbares Licht und Kupferkatalysatoren induzierte Chlorosulfonylierung von zahlreichen Alkenen und Alkinen. Neben dem Cu(I)-Komplex $[Cu(dap)_2]Cl$, der in solchen Prozessen bereits etabliert ist, wird hier zum ersten Mal der entsprechende Cu(II)-Komplex $[Cu(dap)Cl_2]$ eingeführt. Dieses neuartige Verfahren von Cu(II)-Komplexen in der Photochemie eröffnet nicht nur komplett neue Möglichkeiten der Reaktionsführung, sondern bietet zudem auch noch wirtschaftliche Vorteile, da zur Synthese von $[Cu(dap)Cl_2]$ nur die Hälfte an Liganden benötigt wird. Generell zeigte sich in der Studie, dass Kupferkatalysatoren die üblicherweise verwendeten Ruthenium- oder Iridium-basierten Katalysatoren weit übertreffen, was an ihrer einzigartigen Fähigkeit liegt, mit radikalischen Reaktionsintermediaten zu interagieren. Das entwickelte Protokoll zeichnet sich durch hohe Ausbeuten bei Verwendung kostengünstiger und kommerziell erhältlicher Substrate aus, und kann problemlos auf Gramm-Maßstab skaliert werden. Die so erhaltenen Produkte können quantitativ in die entsprechenden Vinylsulfone umgewandelt werden, welche auf zahlreichen Gebieten der synthetischen sowie der medizinischen Chemie von großer Bedeutung sind.

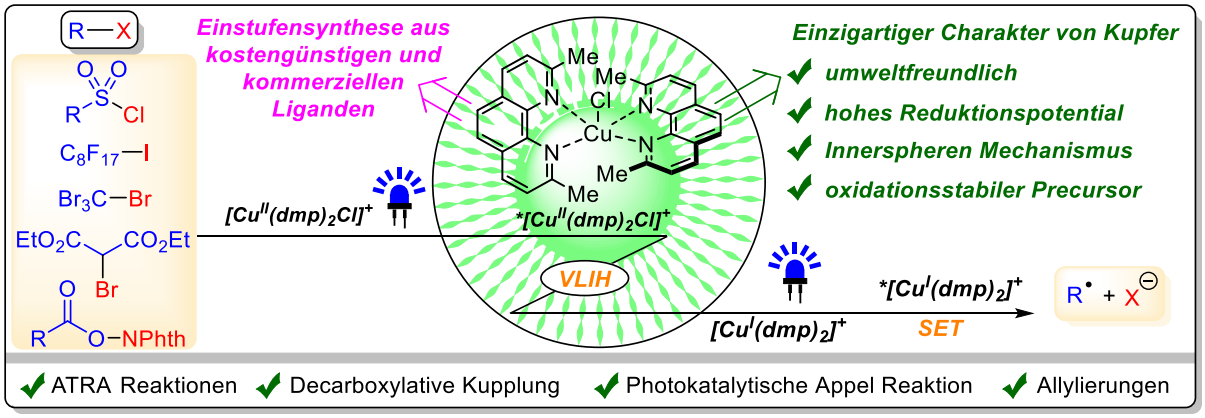


Introducing Chlorobis(dmp)copper(II) to Photocatalysis

Dieses Kapitel basiert auf: Engl, S; Reiser, O. *Eur. J. Org. Chem.* **2020**, 1523-1533. (VIP Paper). ***Und auf:*** Fayad, R.; Engl, S.; Danilov, E. O.; Hauke, C. E.; Reiser, O.; Castellano, F. N. *J. Phys. Chem. Lett.* **2020**, *11*, 5345-5349.

Dieses Kapitel führt erstmals den Cu(II)-Komplex $[Cu(dmp)_2Cl]Cl$ als oxidationsstabilen Katalysator in die Photochemie ein und etabliert so das neuartige Aktivierungsprinzip von Cu(II)-Komplexen durch sichtbares Licht-induzierte Homolyse (VLIH). Der Komplex ist dabei

hocheffizient und deutlich kostengünstiger, verglichen mit bisherig verwendeten Cu(I)-Katalysatoren, da er über kommerzielle Ausgangsmaterialien in nur einer Stufe zugänglich ist. Seine Leistungsfähigkeit wurde anhand einer Reihe von photochemischen ATRA Reaktionen evaluiert, die eine rapide Funktionalisierung von Alkenen ermöglichen. Desweiteren konnte sich der Katalysator auch in einer decarboxylativen Kupplung, einer photokatalytischen Appel-Reaktion, sowie wie für photochemische Allylierungen als effiziente Alternative beweisen. Der synthetische Nutzen konnte durch verschiedene Funktionalisierungen im Multigramm-Maßstab demonstriert werden, was einmal mehr seine Rolle als kostengünstige Alternative in der Photochemie unterstreicht. Darüber hinaus konnten in dieser Studie erstmals mechanistische Hinweise zur VLIH angetragen werden, die in einer Kooperation mit der Gruppe von Prof. Castellano aus den Vereinigten Staaten von Amerika in einer separaten Publikation nochmals enorm aus spektroskopischer und physikalischer Sicht vertieft wurden. So zeigten zum Beispiel statische Spektroskopie, Ultrakurzzeit Spektroskopie und paramagnetische Spinresonanz Experimente, dass diese Aktivierung auf einer Zeitskala von unter 100 fs stattfindet.

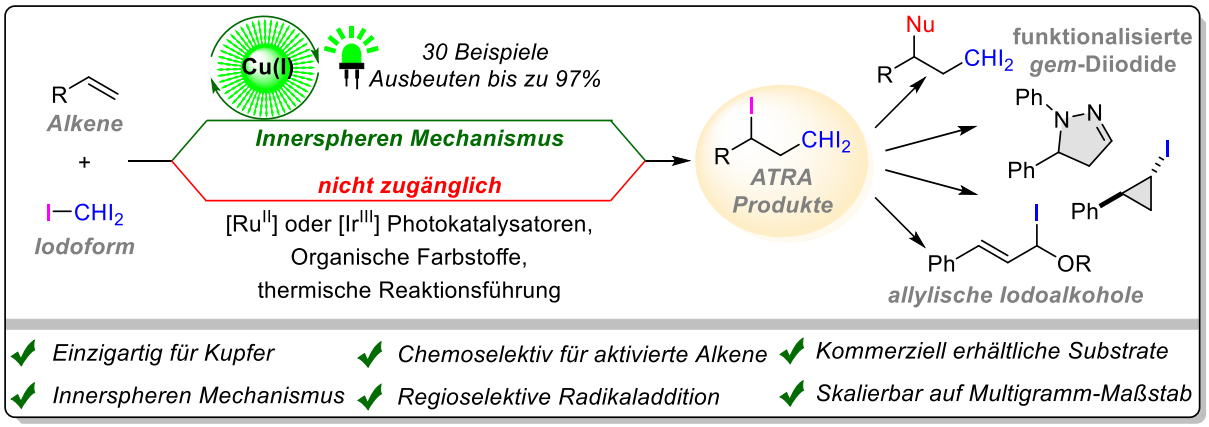


Photochemical ATRA Reactions of Iodoform

Dieses Kapitel basiert auf: Engl, S.; Reiser, O. *ACS Catal.* **2020**, *10*, 9899-9906.

Dieses Kapitel beschreibt ein durch sichtbares Licht und Kupferkatalysator induziertes Verfahren für die ökonomische Funktionalisierung von Alkenen unter Verwendung der kostengünstigen Bulkchemikalie Iodoform. Obwohl der Grundgedanke dieser Transformation leicht umsetzbar zu sein scheint, stellte sich während dieser Studie heraus, dass die üblicherweise verwendeten Photokatalysatoren basierend auf Ruthenium, Iridium oder organischen Farbstoffen nicht in der Lage sind, die gewünschten Produkte zu erzeugen, was einmal mehr den einzigartigen Charakter von Kupfer-Katalysatoren unterstreicht. Letztere ermöglichen durch ihre flexible Liganden Architektur eine Wechselwirkung mit intermediären Radikalen und können so bisher unerreichte Reaktionswege zugänglich machen. Die hier

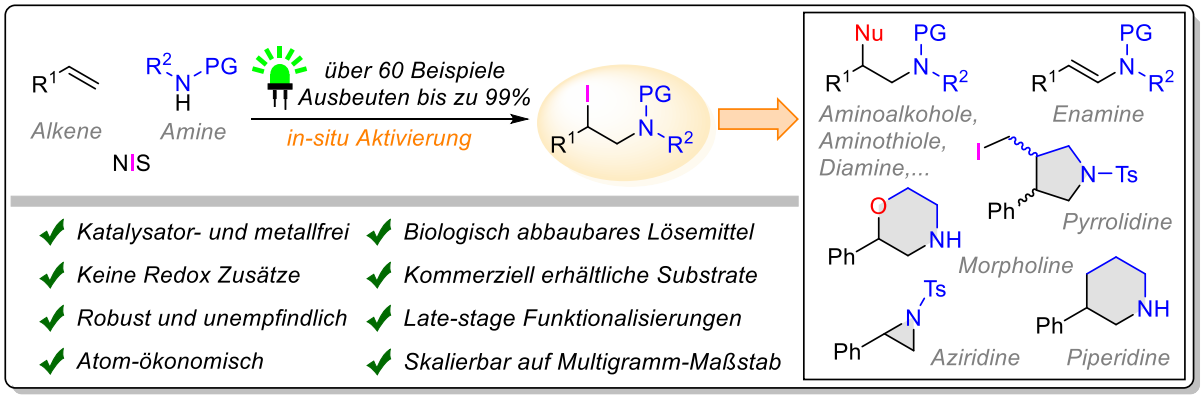
entwickelte Reaktion besticht durch hohe Ausbeuten unter umweltschonenden Bedingungen und ermöglicht die Funktionalisierung aktivierter Doppelbindungen, sowie komplexer bioaktiver Substanzen. Darüber hinaus kann das Protokoll problemlos auf Multigramm-Maßstab skaliert werden. Die so erhaltenen Produkte bieten vielfältige Anwendungen in der synthetischen Chemie. So dienen sie als Ausgangspunkt für die Synthese funktionalisierter *gem*-Diiodide, sowie die Synthese wichtiger Heterocyclen oder Cyclopropanierungsreaktionen.



Photochemical Iodoamination

Dieses Kapitel basiert auf: Engl, S.; Reiser, O. *Org. Lett.* **2021**, *23*, 5581-5586.

Kapitel 5 berichtet über die Entwicklung eines durch sichtbares Licht induzierten Verfahrens zur Iodoaminierung verschiedenster Alkene. Das Protokoll ist frei von jeglichen Katalysatoren oder Metallen und zeichnet sich durch hohe Ausbeuten unter umweltschonenden Reaktionsbedingungen in einem biologisch-abbaubaren Lösemittel aus. Darüber hinaus ermöglicht die entwickelte Reaktion die Funktionalisierung von komplexen biologisch aktiven Substanzen und kann problemlos auf Multigramm-Maßstab skaliert werden. Die so erhaltenen Produkte bieten eine Fülle an weiteren Reaktionsmöglichkeiten, wie zum Beispiel die Synthese 1,2-funktionalisierter Amine, Enamine sowie die Konstruktion verschiedener biologisch und medizinisch wichtiger Heterocylcen, wie Morpholine, Piperidine, Pyrrolidine oder Aziridine.



Chapter 7

Experimental Part

7.1 General Aspects

Commercially available chemical materials were purchased in high quality and were used without further purification. Thereby, weight was calculated based on purity mentioned on the container. All reactions were carried out in oven-dried glassware under atmospheric conditions unless otherwise stated. Reactions with moisture or oxygen sensitive reagents were performed in flame-dried glassware under an atmosphere of pre-dried nitrogen. All photochemical reactions were carried out in flame-dried glassware applying three consecutive freeze-pump-thaw cycles. Reactions were monitored by thin layer chromatography (TLC). Anhydrous solvents were prepared by established laboratory procedures.[1] DCM, EtOAc, *n*-pentane and hexanes (40-60 °C) for chromatography were distilled prior to use. The reported yields are referred to isolated compounds unless otherwise stated. NMR yields were determined using diphenoxymethane (for synthesis see chapter 7.3), 1,1,2,2-tetrachloroethane or 1,3,5-trimethoxybenzene as an internal standard.

Chromatography

Thin layer chromatography (TLC) was performed with TLC precoated aluminum sheets (Merck) Silica gel 60 F_{254}, 0.2 mm layer thickness and visualized by a dual short (λ = 254 nm) / long (λ = 366 nm) wavelength UV lamp. Staining was done with Seebach`s Magic Stain (2.5 g phosphomolybdic acid, 1.0 g cerium(IV) sulfate tetrahydrate, 94.0 mL distilled water and 6.0 mL conc. sulfuric acid), vanillin (6.0 g vanillin, 100.0 mL ethanol (95%) and 1.0 mL conc. sulfuric acid), ninhydrin (300.0 mg ninhydrin, 3.0 mL conc. acetic acid, 100.0 mL ethanol) or potassium permanganate (1.0 g $KMnO_4$, 2.0 g Na_2CO_3 and 100.0 mL distilled water) followed by heating. Column chromatography was performed with silica gel (Merck, 0.063-0.200 mm particle size) and flash silica gel (Merck, 0.040-0.063 mm particle size). Purification using a flash system was performed with flash silica gel (Merck, 0.040-0.063 mm particle size) on a Reveleris® X2 Flash System (Büchi).

NMR-Spectroscopy

^{1}H-NMR spectra were recorded on Bruker Avance 300 (300 MHz), Bruker Avance 400 (400 MHz) or Bruker Avance III 400 "Nanobay" (400 MHz) Spectrometer. Spectra were evaluated in first order and coupling constants *J* are reported in Hertz (Hz). Splitting patterns for the spin multiplicity of the signals in the spectra are given as the following: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, hept = heptet, m = multiplet and combinations thereof. Chemical shifts for ^{1}H-NMR were reported as δ, parts per million (ppm), relative to the signal of $CHCl_3$ at 7.26 ppm, H_2O at 4.79 ppm or relative to the center line signal of the DMSO quintet at 2.50 ppm.

^{13}C-NMR spectra were recorded on Bruker Avance 300 (75 MHz), Bruker Avance 400 (101 MHz) or Bruker Avance III 400 "Nanobay" (101 MHz) Spectrometer. Chemical shifts for ^{13}C-NMR were reported as δ, parts per million (ppm), relative to the center line signal of the $CDCl_3$ triplet at 77.2 ppm or relative to the center line signal of the DMSO-d_6 septet at 39.5 ppm.

^{19}F-NMR spectra were recorded on Bruker Avance 300 (282 MHz), Bruker Avance 400 (376 MHz) or Bruker Avance III 400 "Nanobay" (376 MHz) Spectrometer.

IR-Spectroscopy

FTIR spectroscopy was carried out on a Cary 630 FTIR Spectrometer with ZnSe windows and diamond single reflection accessory. Solid and liquid compounds were measured neatly and the wave numbers are reported as cm^{-1}.

Mass Spectrometry

Mass spectra were recorded by the Central Analytic Department of the University of Regensburg using Jeol AccuTOF GCX and Agilent Q-TOF 6540 UHD Spectrometer. High-resolution mass spectra were measured using atmospheric pressure chemical ionization (APCI), electron ionization (EI) or electrospray ionization (ESI) with a quadrupole time-of-flight (Q-TOF) detector.

X-Ray Crystallography

X-ray crystallographic analysis was performed by the Central Analytic Department of the University of Regensburg using an Agilent Technologies SuperNova, an Agilent Technologies Gemini R Ultra, an Agilent GV 50 or a Rigaku GV 50 diffractometer. Suitable crystals were mounted on a Lindemann tube oil and kept at a steady temperature of T = 293 K during data

collection. The structures were solved with the SheIXT (Scheldrick 2015) structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface. The model was refined with SheIXL using Least Squares minimization.

Photochemical setup

All photochemical reactions were performed in flame-dried Schlenk tubes (10.0 mL size; Figure 1, D) equipped with a magnetic stirring bar (Figure 1, E) using monochromatic light emitting diodes (LED; Figure 1, A) as irradiation source. The LED is placed on a glass rod (8.0 mm diameter; borosilicate glass Schott Borofloat® 33; Figure 1, B) acting as a light conductor, which is directly immersed into the reaction mixture through a Teflon sealed inlet (Figure 1, C).

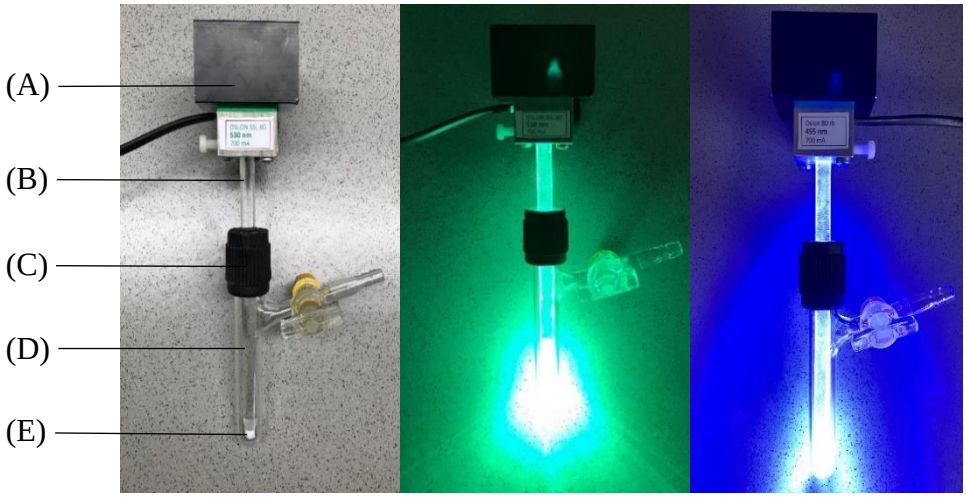


Figure 1. Irradiation setup for photochemical reactions: (A) LED; (B) glass rod (used as a light conductor); (C) Teflon adapter; (D) Schlenk tube (10.0 mL size); (E) Teflon-coated magnetic stirring bar.

Light Source

For all photochemical reactions monochromatic light emitting diodes (LED) were used as irradiation source. All relevant data are taken from the official data sheets provided by Osram, which are available free of charge via the internet at the Osram web page:

- Blue light irradiation was performed using an Osram OSLON® SSL deep blue (3 W, 700 mA, dominant wavelength λ_{dom} = 455 nm, spectral bandwidth at 50% I_{max} = 20 nm, radiant power at 25 °C and 700 mA ~ 900 mW).
- Green light irradiation was performed using an Osram OSLON® SSL 80 green (3 W, 700 mA, dominant wavelength λ_{dom} = 530 nm, spectral bandwidth at 50% I_{max} = 30 nm, luminous flux at 25 °C and 700 mA ~ 250 lum).

Melting Point Measurement

The measurement of melting point (mp) was carried out on a SRS MPA 100 – Automated melting point system by OptiMelt using a ramp rate of 1 K/min.

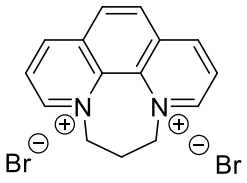
Polarimetry

Determination of optical rotation was carried out on a MCP 500 Modular Circular Polarimeter by Anton Paar at 589 nm (Na-D-line).

7.2 Synthesis and Characterization of Catalysts

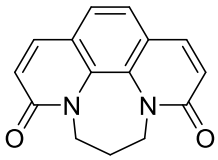
Synthesis of $[Cu(dap)_2]Cl$ and $[Cu(dap)Cl_2]$

6,7-dihydro-5*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-4,8-diium bromide (2)



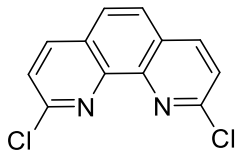
A three-neck flask equipped with a magnetic stirring bar, dropping funnel and a reflux condenser was charged with 1,10-phenanthroline (phen) (5.3 g, 29.4 mmol, 1.0 equiv) and dissolved in nitrobenzene (40 mL, 0.74 M). After gradually adding 1,3-dibromopropane (15.5 mL, 152.9 mmol, 5.2 equiv) the reaction mixture was stirred at 130 °C for 5 h. During the reaction, product formation was observed as precipitation out of the reaction mixture. Afterwards, the mixture was allowed to cool to room temperature (25 °C) and the precipitate was collected by filtration, washed with hexanes and dried over anhydrous $CaCl_2$ in a desiccator overnight (16 h) to yield 11.3 g (28.8 mmol, 98%) of the title compound as a yellowish solid. **^{1}H-NMR** (400 MHz, D_2O) δ = 9.70 (dd, *J* = 5.8, 1.3 Hz, 2H), 9.49 (dd, *J* = 8.4, 1.3 Hz, 2H), 8.63 (s, 2H), 8.58 (dd, *J* = 8.4, 5.7 Hz, 2H), 5.19 (t, *J* = 7.0 Hz, 4H), 3.47 (p, *J* = 7.0 Hz, 2H). **^{13}C-NMR** (101 MHz, D_2O) δ = 150.9, 147.4, 134.2, 133.5, 130.3, 127.4, 60.5, 31.0.

6,7-dihydro-5*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9-dione (3)



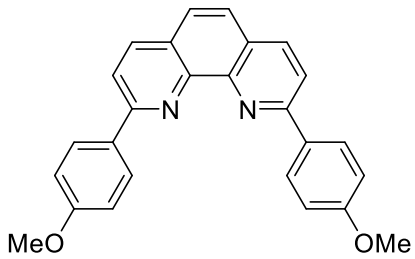
A round-bottom flask equipped with a magnetic stirring bar was charged with a mixture of 6,7-dihydro-5*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10] phenanthroline-4,8-diium bromide (**2**) (10.0 g, 26.2 mmol, 1.0 equiv) and KO^{t}Bu (12.3 g, 109.9 mmol, 4.2 equiv) in *tert*-butyl alcohol (150 mL, 0.17 M) was stirred at 40 °C for 16 h in an open flask. After oxygen gas was bubbled through the solution by a balloon, the reaction mixture was diluted with water (30 mL) and $CHCl_3$ (30 mL) and extracted five times with $CHCl_3$. The combined organic layers were washed twice with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to yield 6.2 g (24.6 mmol, 94%) of the title compound as a brownish solid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 9.5 Hz, 2H), 7.35 (s, 2H), 6.78 (d, *J* = 9.5 Hz, 2H), 4.30 (t, *J* = 6.6 Hz, 4H), 2.44 (p, *J* = 6.6 Hz, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 162.8, 138.9, 132.2, 123.2, 122.9, 122.9, 45.8, 25.8.

2,9-dichloro-1,10-phenanthroline (4)



A flame-dried three-neck flask equipped with a magnetic stirring bar and a reflux condenser was charged with 6,7-dihydro-5*H*-[1,4]diazepino [1,2,3,4-*lmn*][1,10]phenanthroline-3,9-dione (**3**) (3.8 g, 15.1 mmol, 1.0 equiv) and PCl_5 (6.3 g, 30.2 mmol, 2.0 equiv) under nitrogen atmosphere. Afterwards, $POCl_3$ (60 mL, 0.25 M) was added to the reaction and the resulting mixture was stirred for 16 h at 145 °C. After the excess of $POCl_3$ was removed by distillation, the brownish residue was cooled to 0 °C and quenched carefully by gradually adding ice followed by aqueous NH_3 (1.0 M) until neutral pH. Subsequently, the dark solution was extracted four times with DCM and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (DCM) to yield 2.6 g (10.4 mmol, 70%) of the title compound as a yellowish solid. $\mathbf{R_f}$ (DCM) = 0.55, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.19 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 2H), 7.61 (d, *J* = 8.4 Hz, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 152.0, 145.0, 138.9, 127.8, 126.3, 125.0.

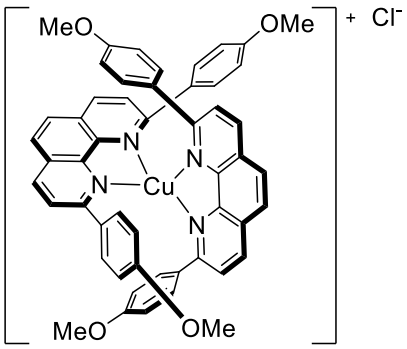
2,9-bis(4-methoxyphenyl)-1,10-phenanthroline (dap)



A three-neck round-bottom flask equipped with a reflux condenser and a magnetic stirring bar was charged with 2,9-dichloro-1,10-phenanthroline (**4**) (2.0 g, 8.0 mmol, 1.0 equiv), (4-methoxyphenyl)boronic acid (2.7 g, 17.7 mmol, 2.2 equiv), triphenylphosphane (105.3 mg, 401.5 mmol, 5.0 mol%), $Pd_2(dba)_3$ (88.2 mg, 96.4 mmol, 1.2 mol%) and dissolved in freshly distilled glyme (80 mL, 0.10 M) under a nitrogen atmosphere. The reaction mixture was degassed by three freeze-pump-thaw cycles. Afterwards, a solution of K_2CO_3 (2.4 g, 17.7 mmol, 2.2 equiv) in 8.0 mL water was added and the mixture was degassed again by one freeze-pump-thaw cycle. The resulting solution was stirred for 48 h at 100 °C. Then, the mixture was allowed to cool to room temperature (25 °C) and extracted four times with DCM. The combined organic layers were washed four times with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (DCM, followed by DCM / MeOH 98:2) followed by recrystallization from hot toluene to yield 2.6 g (6.7 mmol, 83%) of the title compound as a white to yellowish solid. $\mathbf{R_f}$ (DCM / MeOH 9:1) = 0.80, Staining: UV, $KMnO_4$. **^{1}H-NMR**

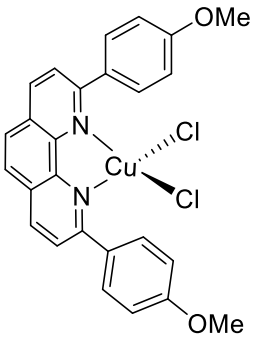
(400 MHz, $CDCl_3$) δ = 8.49 – 8.39 (m, 4H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.71 (s, 2H), 7.15 – 7.05 (m, 4H), 3.92 (s, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 161.0, 156.5, 146.1, 136.9, 132.3, 129.1, 128.3, 127.6, 125.7, 119.4, 114.3, 55.5.

[Cu(dap)$_2$]Cl



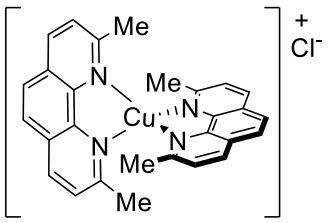
A 100 mL round-bottom flask equipped with a magnetic stirring bar was charged with 2,9-bis(4-methoxyphenyl)-1,10-phenanthroline (dap) (1.0 g, 2.6 mmol, 2.0 equiv), dissolved in $CHCl_3$ (25 mL, 0.10 M) and stirred at room temperature (25 °C) for 30 min. CuCl (126.0 mg, 1.3 mmol, 1.0 equiv) was added slowly and the resulting mixture was stirred for 30 min at room temperature (25 °C). The violet solution was stirred for another 30 min at 60 °C. Afterwards, the reaction mixture was concentrated in vacuo to yield 1.1 g (1.3 mmol, >99%) of the title compound as a violet-black solid. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.51 (d, *J* = 8.3 Hz, 1H), 8.03 (s, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.03 (d, *J* = 8.4 Hz, 2H), 3.47 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 160.1, 156.3, 143.4, 137.2, 131.1, 129.2, 127.8, 126.2, 124.5, 112.5, 55.3.

[Cu(dap)Cl$_2$]



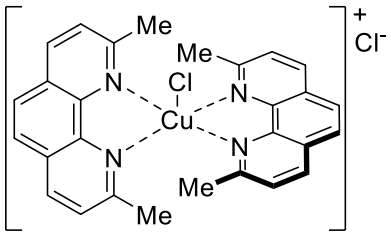
In a round-bottom flask equipped with a magnetic stirring bar $CuCl_2$ (500.0 mg, 1.3 mmol, 1.0 equiv) was suspended in $CHCl_3$ (4.0 mL, 0.33 M) and sonicated at room temperature for 3 min. To the stirred solution a suspension of 2,9-bis(4-methoxyphenyl)-1,10-phenanthroline (171.3 mg, 1.3 mmol, 1.0 equiv) in 4.0 mL of $CHCl_3$ was added. The reaction mixture was sonicated again at room temperature for 3 min and then stirred for another 60 min at room temperature followed by precipitation in DE to yield 401.3 mg (761 µmol, 60%) of the title compound as a brownish green solid.

[Cu(dmp)$_2$]Cl



A 100 mL round-bottom flask equipped with a magnetic stirring bar was charged with 2,9-dimethyl-1,10-phenanthroline (833.1 mg, 4.0 mmol, 2.0 equiv), dissolved in $CHCl_3$ (40 mL, 0.10 M) and stirred at room temperature for 30 min. CuCl (198.0 mg, 2.0 mmol, 1.0 equiv) was added slowly and the resulting mixture was stirred for 2 h at room temperature followed by precipitation in DE. Afterwards, the red precipitate was collected by vacuum filtration using a fritted funnel. The solid was washed with cold DE and dried under vacuum to yield 734.6 mg (1.4 mmol, 71%) of the title compound as a red solid. Suitable crystals for X-ray analysis were obtained by slow evaporation of a MeCN solution containing [Cu(dmp)$_2$]Cl. The crystals obtained were red and plate-shaped. These data are in accordance to literature (see ***Chapter 8.6***; crystallographic data: CCDC 1581109).[2] **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.53 (d, *J* = 8.2 Hz, 4H), 8.04 (s, 4H), 7.78 (d, *J* = 8.2 Hz, 4H), 2.41 (s, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 157.6, 143.1, 137.5, 127.7, 126.2, 125.7, 26.0.

[Cu(dmp)$_2$Cl]Cl[3]

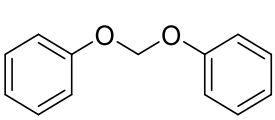


Based on a literature procedure[3], a round-bottom flask equipped with a magnetic stirring bar was charged with $CuCl_2$ (268.9 mg, 2.0 mmol, 1.0 equiv) and dissolved in ethanol (120 mL, 0.02 M). After complete dissolution, 2,9-dimethyl-1,10-phenanthroline (916.4 mg, 4.4 mmol, 2.2 equiv) was added to the stirred reaction mixture resulting in a green precipitate after a few minutes. The suspension was left to fully react by stirring at room temperature for another 2 h. Afterwards, the green precipitate was collected by vacuum filtration using a fritted funnel. The solid was washed with cold ethanol, cold DE and dried under vacuum to yield 840.7 mg (1.5 mmol, 76%) of the title compound as a bright green solid. The X-ray structure of [Cu(dmp)$_2$Cl]PF_6 complex[3] (crystallographic data: CCDC 1819088) and [Cu(dmp)$_2$Cl]Cl·MeOH (crystallographic data: CCDC 1861809) have been reported. Since we evaluated [Cu(dmp)$_2$Cl]Cl and its catalytic performance in MeCN in this study, a X-ray structure of this complex crystallized from MeCN was obtained by us. Therefore suitable crystals for X-ray analysis were accessed by slow evaporation of a MeCN solution containing [Cu(dmp)$_2$Cl]Cl. The crystals obtained were green and needle-shaped. CCDC 1922265 contain the supplementary crystallographic data for this work (for X-ray structure and data, please see ***Chapter 8.6***).

7.3 Synthesis of Literature Known Compounds

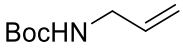
The following compounds were synthesised according to the reported literature procedures. The spectral data are in agreement with the data reported and the specific reference is given directly at the compound name. *Please note*, that compounds might have two different numbers according to the respective chapters they can be found.

diphenoxymethane[4] *(used as an internal NMR standard)*



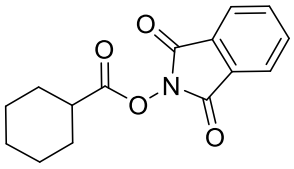
Based on a literature procedure,[4] a 500 mL round-bottom flask equipped with a magnetic stirring bar was charged with KOH (33.1 g, 590.0 mmol, 8.0 equiv) and water (100 mL). The reaction mixture was cooled to 0 °C and after complete dissolution, phenol (7.0 g, 74.4 mmol, 1.0 equiv), DCM (69.9 mL, 93.0 g, 1.1 mol, 15.0 equiv) and TBAB (2.9 g, 8.9 mmol, 0.1 equiv) were added. The resulting reaction mixture was stirred for 30 h at 50 °C and transferred to a separatory funnel. The organic layer was washed five times with sat. aqueous $NaHCO_3$ and five times with brine, dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure to yield 6.0 g (37.2 mmol, 81%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[4] **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.37 – 7.29 (m, 4H), 7.18 – 7.10 (m, 4H), 7.09 – 7.00 (m, 2H), 5.75 (s, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 157.1, 129.7, 122.6, 116.6, 91.3.

***tert*-butyl allylcarbamate (1bn//7o)[5]**



Based on a lliterature procedure,[5] a round-bottom flask equipped with a magnetic stirring bar was charged with allylamine (5.0 g, 87.7 mmol, 1.0 equiv), freshly distilled triethylamine (26.8 mL, 192.9 mmol, 2.2 equiv) and anhydrous DCM (100 mL, 0.88 M). Afterwards, the solution was cooled to 0 °C and Boc_2O (21.1 g, 96.5 mmol, 1.1 equiv) was added in two portions. The resulting reaction mixture was allowed to warm up to room temperature and stirred for 16 h. The reaction was monitored by TLC. Finally, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 5:1) to yield 12.7 g (80.8 mmol, 92%) of the title compound as a white solid. Spectral data are in accordance to literature.[5] **R_f** (hexanes / EtOAc 5:1) = 0.53, Staining: Ninhydrin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 5.82 (ddt, *J* = 17.2, 10.5, 5.5 Hz, 1H), 5.23 – 5.04 (m, 2H), 4.61 (bs, 1H), 3.77 – 3.67 (m, 2H), 1.44 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 155.9, 135.1, 115.8, 79.5, 43.2, 28.5.

1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate (20)[6]

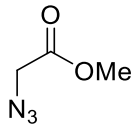


Based on a literature procedure,[6] a round-bottom flask equipped with a magnetic stirring bar was charged with cyclohexanecarboxylic acid (1.0 g, 7.8 mmol, 1.0 equiv), *N*-hydroxyphthalimide (1.4 g, 8.6 mmol, 1.1 equiv) and DCM (40 mL, 0.20 M). The resulting solution was cooled to 0 °C. Afterwards, *N*,*N´*-dicyclohexylcarbodiimide (1.8 g, 8.6 mmol, 1.1 equiv) was added and the resulting reaction mixture was stirred at 0 °C for 30 min followed by continuous stirring at 25 °C for 16 h. The reaction was monitored by TLC. Finally, the reaction mixture was filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 20:1 to 3:1) to yield 1.5 g (5.5 mmol, 70%) of the title compound as a white solid. Spectral data are in accordance to literature.[7] $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.53, Staining: Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.77 (dd, *J* = 5.5, 3.1 Hz, 2H), 2.73 (tt, *J* = 10.9, 3.7 Hz, 1H), 2.17 – 2.05 (m, 2H), 1.89 – 1.78 (m, 2H), 1.66 (tt, *J* = 14.1, 7.5 Hz, 3H), 1.45 – 1.28 (m, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 171.9, 162.2, 134.8, 129.1, 124.0, 40.6, 28.9, 25.6, 25.2.

(bromoethynyl)benzene (21)[6]

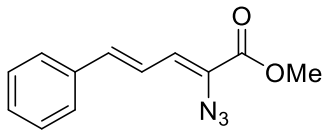
Based on a literature procedure,[6] a round-bottom flask equipped with a magnetic stirring bar was charged with ethynylbenzene (1.08 mL, 1.0 g, 9.79 mmol, 1.0 equiv), *N*-bromosuccinimide (2.1 g, 11.77 mmol, 1.2 equiv), $AgNO_3$ (332.6 mg, 1.96 mmol, 20 mol%) and acetone (65 mL, 0.15 M) at room temperature. The resulting reaction mixture was heated to 40 °C and stirred for 15 min upon complete conversion of starting material judged by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes) to yield 1.6 g (8.95 mmol, 92%) of the title compound as yellowish oil. Spectral data are in accordance to literature.[8] $\mathbf{R_f}$ (hexanes) = 0.63, Staining: Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.52 – 7.41 (m, 2H), 7.38 – 7.27 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 132.1, 128.8, 128.5, 122.8, 80.2, 49.9.

methyl 2-azidoacetate[9]



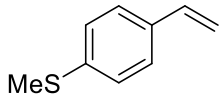
Based on a literature procedure,[9] a round-bottom flask equipped with a magnetic stirring bar was charged with methyl chloroformate (8.0 mL, 10.0 g, 92.0 mmol, 1.0 equiv), NaN_3 (6.0 g, 92.0 mmol, 1.0 equiv) and DMF (10 mL, 9.2 M) and stirred at room temperature for three days. Afterwards, the reaction mixture was quenched with water and extracted three times with DE. The combined organic layers were washed three times with water, dried over anhydrous Na_2SO_4 and concentrated in vacuo without the use of any heating bath to yield 6.1 g (53.0 mmol, 58%) of the title compound as a colorless oil. Spectral data are in accordance to literature.[9] **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 3.89 (s, 2H), 3.80 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 168.9, 52.8, 50.4.

methyl (2*Z*,4*E*)-2-azido-5-phenylpenta-2,4-dienoate (33)[10]



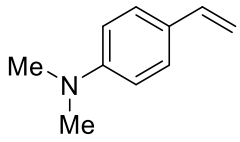
Based on a literature procedure,[10] a flame-dried three-neck round-bottom flask equipped with a reflux condenser and a magnetic stirring bar was charged with anhydrous MeOH (4.0 mL). Under a slight nitrogen overpressure sodium metal (277.5 mg, 12.1 mmol, 1.52 equiv) was added in portions under vigorous stirring until complete dissolution and the reflux condenser was replaced by a septum. After cooling of the reaction mixture to -22 °C, cinnamon aldehyde (1.0 mL, 1.0 g, 7.9 mmol, 1.0 equiv) and methyl 2-azidoacetate (3.7 g, 31.8 mmol, 4.0 equiv) were added dropwise via syringe over 30 min. The resulting mixture was allowed to warm to -10 °C and stirred for 4 h until complete consumption of cinnamon aldehyde judged by TLC. Afterwards, the heterogenous mixture was diluted with water (20 mL) and EtOAc (20 mL). The phases were separated, and the resulting aqueous phase was reextracted twice with EtOAc. The combined organic layers were washed twice with water and brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting crude residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 20:1 to 10:1) to yield 1.3 g (5.7 mmol, 71%) of the title compound as a bright yellow solid. Spectral data are in accordance to literature.[10] **R_f** (hexanes / EtOAc 9:1) = 0.53, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.51 – 7.46 (m, 2H), 7.39 – 7.28 (m, 3H), 7.17 (dd, *J* = 15.7, 11.2 Hz, 1H), 6.85 – 6.72 (m, 2H), 3.88 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 163.7, 139.2, 136.5, 129.1, 128.9, 127.4, 127.3, 125.6, 122.3, 52.8.

methyl(4-vinylphenyl)sulfane (1f//1t)[11]



Based on a literature procedure,[11] a flame-dried round-bottom flask equipped with a magnetic stirring bar was charged with methyltriphenylphosphonium bromide (1.71 g, 4.8 mmol, 1.2 equiv) and anhydrous THF (30.0 mL, 0.13 M). The resulting solution was cooled to 0 °C and *n*-butyllithium (3.0 mL, 1.6 M in hexanes, 4.8 mmol, 1.2 equiv) was added dropwise. The reaction was magnetically stirred for 40 min at 0 °C. Afterwards, 4-(methylthio)benzaldehyde (0.53 mL, 608.8 mg, 4.0 mmol, 1.0 equiv) in anhydrous THF (10.0 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature (25 °C) and stirred for 12 h. After being quenched with sat. aqueous NH_4Cl, the mixture was extracted three times with DE. The combined organic layers were washed three times with water, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes to hexanes / EtOAc 15:1) to yield 404.4 mg (2.69 mmol, 67%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[12] $\mathbf{R_f}$ (hexanes / EtOAc 9:1 on silica) = 0.60, Staining: UV, Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 8.2 Hz, 1H), 7.22 (s, 2H), 6.67 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.22 (dd, *J* = 10.9, 0.9 Hz, 1H), 2.49 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 138.1, 136.3, 134.7, 126.7, 126.7, 113.3, 16.0.

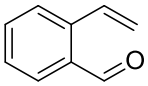
***N*,*N*-dimethyl-4-vinylaniline (1k//1s)[13]**



Based on a literature procedure,[13] a flame-dried round-bottom flask equipped with a magnetic stirring bar was charged with methyltriphenylphosphonium bromide (1.71 g, 4.8 mmol, 1.2 equiv) and anhydrous THF (30.0 mL, 0.13 M). The resulting solution was cooled to 0 °C and *n*-butyllithium (3.0 mL, 1.6 M in hexanes, 4.8 mmol, 1.2 equiv) was added dropwise. The reaction was magnetically stirred for 40 min at 0 °C. Afterwards, 4-(dimethylamino)benzaldehyde (596.8 mg, 4.0 mmol, 1.0 equiv) in anhydrous THF (10.0 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature (25 °C) and stirred for 12 h. After being quenched with sat. aqueous NH_4Cl, the mixture was extracted three times with DE. The combined organic layers were washed three times with water, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes to hexanes / EtOAc 10:1) to yield 530.4 mg (3.6 mmol, 90%) of the title compound as a colorless oil. Spectral data are in agreement with those reported

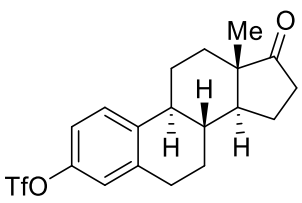
in literature.[13] **R_f** (hexanes / EtOAc 3:1 on silica) =0.70, Staining: UV, Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.40 – 7.29 (m, 2H), 6.75 – 6.61 (m, 3H), 5.58 (dd, *J* = 17.6, 1.1 Hz, 1H), 5.06 (dd, *J* = 10.9, 1.1 Hz, 1H), 2.99 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 150.3, 136.7, 127.3, 126.3, 112.5, 109.5, 40.7.

2-vinylbenzaldehyde (1u)[14]



Based on a literature procedure,[14] a flame-dried round-bottom flask equipped with a magnetic stirring bar was charged with 2-bromostyrene (1.25 mL, 1.83 g, 10.0 mmol, 1.0 equiv) and anhydrous THF (18.0 mL, 0.56 M). The resulting solution was cooled to -78 °C and *n*-butyllithium (7.5 mL, 1.6 M in hexanes, 12.0 mmol, 1.2 equiv) was added dropwise. The reaction was magnetically stirred for 1 h at -78 °C. Afterwards, a solution of DMF (1.16 mL, 1.10 g, 15.0 mmol, 1.5 equiv) in THF (1.2 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature (25 °C) and stirred for 16 h. After being quenched with sat. aqueous NH_4Cl, the mixture was extracted three times with DE. The combined organic layers were washed three times with water, dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes to hexanes / EtOAc 10:1) to yield 937.2 mg (7.09 mmol, 71%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[15] **R_f** (hexanes / EtOAc 9:1 on silica) = 0.58, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 10.30 (s, 1H), 7.83 (dt, *J* = 7.6, 1.0 Hz, 1H), 7.62 – 7.48 (m, 3H), 7.48 – 7.38 (m, 1H), 5.70 (dd, *J* = 17.3, 1.2 Hz, 1H), 5.52 (dd, *J* = 11.0, 1.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 192.6, 140.7, 133.9, 133.5, 133.0, 131.4, 128.1, 127.6, 119.6.

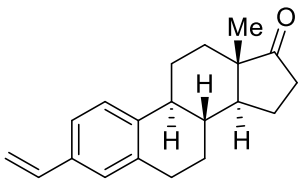
(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate[16]



Based on a literature procedure,[16] a flame-dried three-neck round-bottom flask equipped with a magnetic stirring bar was charged with estrone (2.70 g, 10.0 mmol, 1.0 equiv), pyridine (1.62 mL, 1.58 g, 20.0 mmol, 2.0 equiv) and anhydrous DCM (30 mL, 0.3 M). The resulting reaction mixture was cooled to 0 °C and triflic anhydride (2.02 mL, 3.39 g, 12.0 mmol, 1.2 equiv) was added dropwise. The reaction was allowed to warm to room temperature (25 °C) and stirred for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was diluted with H_2O (20 mL) and extracted three times with DCM. The

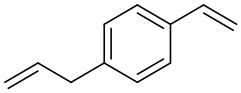
combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes / EtOAc 10:1 to 5:1) to yield 3.82 g (9.5 mmol, 95%) of the title compound as a white solid. Spectral data are in agreement with those reported in literature.[16] **R_f** (hexanes / EtOAc 5:1 on silica) = 0.49, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 8.7 Hz, 1H), 7.03 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.99 (d, *J* = 2.7 Hz, 1H), 2.94 (dd, *J* = 9.0, 4.4 Hz, 2H), 2.52 (dd, *J* = 19.0, 8.6 Hz, 1H), 2.45 – 2.37 (m, 1H), 2.30 (td, *J* = 10.7, 4.3 Hz, 1H), 2.23 – 2.09 (m, 1H), 2.10 – 1.94 (m, 3H), 1.67 – 1.45 (m, 6H), 0.92 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 220.5, 147.7, 140.4, 139.4, 127.3, 121.4, 118.9 (q, *J* = 320.8 Hz), 118.5, 50.5, 48.0, 44.2, 37.9, 36.0, 31.6, 29.5, 26.2, 25.8, 21.7, 13.9. **^{19}F-NMR** (377 MHz, $CDCl_3$) δ = -73.49 (s, 3F).

(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (1ag//1bv)[16]



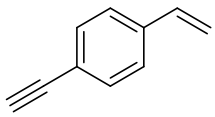
Based on a literature procedure,[16] a flame-dried three-neck round-bottom flask equipped with a magnetic stirring bar was charged with (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-deca hydro-6*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethane sulfonate (2.01 g, 5.0 mmol, 1.0 equiv), potassium vinyltrifluoroborate (739.9 mg, 5.0 mmol, 1.0 equiv), Cs_2CO_3 (4.89 g, 15.0 mmol, 3.0 equiv), $PdCl_2$ (17.7 mg, 0.1 mmol, 2 mol%), PPh_3 (78.7 mg, 0.3 mmol, 60 mol%) and THF / water (9:1, 10 mL, 0.50 M) and stirred under reflux conditions for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was diluted with H_2O (50 mL) and extracted three times with DCM. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes / EtOAc 10:1 to 5:1) to yield 757.1 mg (2.7 mmol, 54%) of the title compound as a white solid. Spectral data are in agreement with those reported in literature.[16] **R_f** (hexanes / EtOAc 5:1 on silica) = 0.46, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.31 – 7.20 (m, 2H), 7.15 (d, *J* = 1.8 Hz, 1H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.20 (dd, *J* = 10.8, 1.0 Hz, 1H), 2.93 (dd, *J* = 9.0, 4.3 Hz, 2H), 2.52 (dd, *J* = 18.9, 8.5 Hz, 1H), 2.47 – 2.39 (m, 1H), 2.31 (td, *J* = 10.7, 4.5 Hz, 1H), 2.21 – 1.95 (m, 4H), 1.71 – 1.39 (m, 6H), 0.92 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 223.0, 139.7, 136.7, 135.3, 127.0, 125.7, 123.7, 113.3, 50.6, 48.1, 44.6, 38.3, 36.0, 31.7, 29.5, 26.6, 25.9, 21.7, 14.0.

1-allyl-4-vinylbenzene (1au)[17]



Based on a modified literature procedure,[17] a flame-dried Schlenk flask equipped with a magnetic stirring bar was charged with [$Pd(dba)_2$] (138.0 mg, 0.24 mmol, 3.0 mol%), tricyclohexylphosphonium tetrafluoroborate (176.8 mg, 0.48 mmol, 0.06 equiv), CsF (2.67 g, 17.6 mmol, 2.2 equiv) and dissolved in anhydrous dioxane (8.0 mL, 1.0 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, 4-bromostyrene (1.05 mL, 1.46 g, 8.0 mmol, 1.0 equiv) and allyltributyltin (2.6 mL, 2.78 g, 8.4 mmol, 1.05 equiv) were added under a slight nitrogen overpressure. The resulting solution was magnetically stirred in an oil bath at 101 °C for 72 h. The reaction was monitored by TLC. Next, the reaction mixture was allowed to cool to room temperature (25 °C), quenched with sat. aqueous NH_4Cl and extracted three times with DE. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes) to yield 727.6 mg (5.05 mmol, 63%) of the title compound as a clear colorless liquid. Spectral data are in agreement with those reported in literature.[17] $\mathbf{R_f}$ (hexanes on silica) = 0.58, Staining: Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.09 – 5.89 (m, 1H), 5.75 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.24 (dd, *J* = 10.9, 1.0 Hz, 1H), 5.16 – 5.11 (m, 1H), 5.09 (t, *J* = 1.5 Hz, 1H), 3.41 (d, *J* = 6.7 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 139.9, 137.4, 136.8, 135.6, 128.9, 126.4, 116.0, 113.3, 40.1.

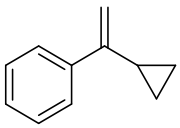
1-ethynyl-4-vinylbenzene (1av)[18]



Based on a literature procedure,[18] a flame-dried Schlenk flask equipped with a magnetic stirring bar was charged with [$PdCl_2(PPh_3)_2$] (278.8 mg, 0.4 mmol, 4.0 mol%), dissolved in anhydrous triethylamine (40.0 mL, 0.25 M) and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, 4-bromostyrene (1.31 mL, 1.83 g, 10.0 mmol, 1.0 equiv) and ethynyltrimethylsilane (3.19 mL, 2.26 g, 23.0 mmol, 2.3 equiv) were added under a slight nitrogen overpressure. The reaction mixture was magnetically stirred in an oil bath at 50 °C for 10 min, then CuI (57.1 mg, 0.3 mmol, 3.0 mol%) was added under a slight nitrogen overpressure and the resulting reaction mixture was magnetically stirred for another 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was allowed to cool to room temperature (25 °C), quenched with sat. aqueous NH_4Cl and extracted three times with DE. The combined organic phase was

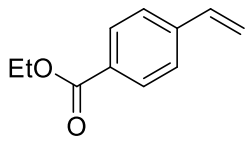
washed with water and brine, dried over Na_2SO_4, filtered and concentrated in vacuo to afford trimethyl((4-vinylphenyl)ethynyl)silane as crude product, which was directly used without further purification for the next step. A mixture of above crude product was dissolved in methanol (20.0 mL, 0.25 M) and K_2CO_3 (2.76 g, 20.0 mmol, 2.0 equiv) was added. The reaction mixture was magnetically stirred at room temperature (25 °C) for 24 h. Afterwards, the reaction mixture was quenched with sat. aqueous NH_4Cl and extracted three times with DE. The combined organic phase was washed with water and brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes) to yield 883.1 mg (6.9 mmol, 69%) of the title compound as a clear colorless liquid. Spectral data are in agreement with those reported in literature.[18] **R_f** (hexanes on silica) = 0.49, Staining: Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.71 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.78 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.31 (dd, *J* = 10.9, 0.7 Hz, 1H), 3.12 (s, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.1, 136.3, 132.4, 126.2, 121.5, 115.2, 83.8, 77.9.

(1-cyclopropylvinyl)benzene (1ax//1cb)[19]



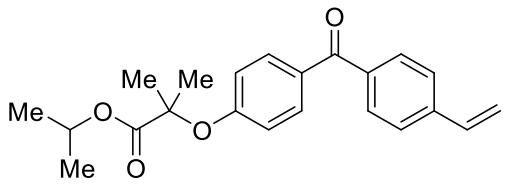
Based on a literature procedure,[19] a flame-dried round-bottom flask equipped with a magnetic stirring bar was charged with methyltriphenylphosphonium bromide (7.1 g, 20.0 mmol, 2.0 equiv) and anhydrous THF (60.0 mL, 0.17 M). The resulting solution was cooled to 0 °C and *n*-butyllithium (12.5 mL, 1.6 M in hexanes, 20.0 mmol, 2.0 equiv) was added dropwise. The reaction was allowed to warm up to room temperature (25 °C) and stirred for an additional hour. Cyclopropyl(phenyl)methanone (1.4 mL, 1.5 g, 10.0 mmol, 1.0 equiv) in anhydrous THF (6.0 mL) was added dropwise, and the reaction was stirred for 12 h at 40 °C. After being quenched with brine, the mixture was extracted three times with hexanes. The combined organic layers were washed three times with water, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes) to yield 1.31 g (9.1 mmol, 91%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[19] **R_f** (hexanes on silica) = 0.78, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.69 – 7.58 (m, 2H), 7.43 – 7.27 (m, 3H), 5.31 (d, *J* = 1.1 Hz, 1H), 4.96 (t, *J* = 1.2 Hz, 1H), 1.68 (ttd, *J* = 8.3, 5.4, 1.2 Hz, 1H), 0.92 – 0.82 (m, 2H), 0.67 – 0.58 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 149.5, 141.8, 128.3, 127.6, 126.3, 109.1, 15.8, 6.8.

ethyl 4-vinylbenzoate (1j)[20]



Based on a literature procedure,[20] a round-bottom flask equipped with a magnetic stirring bar was charged with 4-vinylbenzoic acid (829.7 mg, 5.6 mmol, 1.0 equiv), DCC (1.33 g, 6.44 mmol, 1.15 equiv), DMAP (68.4 mg, 0.56 mmol, 0.1 equiv) and DCM (40 mL, 0.14 M). Afterwards, EtOH (3.3 mL, 2.58 g, 56.0 mmol, 10.0 equiv) was added and the resulting reaction mixture was stirred at room temperature (25 °C) for 12 h. The reaction was monitored by TLC. The reaction mixture was concentrated in vacuo and the residue purified by flash column chromatography on silica gel (hexanes / EtOAc 8:1) to yield 838.8 mg (4.76 mmol, 85%) of the title compound as a colorless sticky oil. Spectral data are in agreement with those reported in literature.[20] **R_f** (hexanes / EtOAc 4:1 on silica) = 0.75, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.86 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.38 (dd, *J* = 10.8, 0.7 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 166.5, 141.9, 136.2, 130.0, 129.8, 126.2, 116.5, 61.1, 14.5.

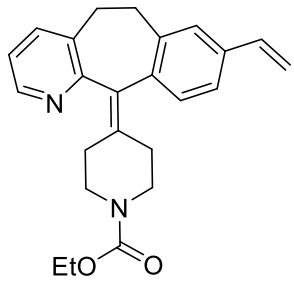
isopropyl 2-methyl-2-(4-(4-vinylbenzoyl)phenoxy)propanoate (1bw)[21]



Based on a literature procedure,[21] a flame-dried round-bottom flask equipped with a magnetic stirring bar was charged with Fenofibrate (3.25 g, 9.0 mmol, 1.0 equiv), potassium vinyltrifluoroborate (2.11 g, 15.75 mmol, 1.75 equiv), Cs_2CO_3 (8.8 g, 27.0 mmol, 3.0 equiv), $PdCl_2$ (79.79 mg, 0.45 mmol, 5.0 mol%), RuPhos (420.0 mg, 0.9 mmol, 10.0 mol%) and THF / water (7:1, 24 mL, 0.38 M) and stirred at 85 °C for 48 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was diluted with H_2O (50 mL) and extracted three times with DE. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes / EtOAc 15:1 to 9:1) to yield 2.92 g (8.3 mmol, 92%) of the title compound as a white solid. Spectral data are in agreement with those reported in literature.[21] **R_f** (hexanes / EtOAc 9:1 on silica) = 0.43, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.79 – 7.68 (m, 4H), 7.49 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.77 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.87 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.38 (dd, *J* = 10.9, 0.7 Hz, 1H), 5.08 (hept, *J* = 6.3 Hz, 1H), 1.66 (s, 6H), 1.20 (d, *J* = 6.3 Hz, 6H). **^{13}C-**

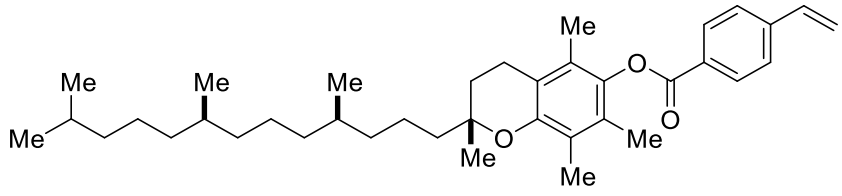
NMR (101 MHz, $CDCl_3$) δ = 195.1, 173.3, 159.6, 141.2, 137.4, 136.2, 132.1, 130.9, 130.4, 126.1, 117.3, 116.4, 79.5, 69.4, 25.5, 21.7.

ethyl 4-(8-vinyl-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (1bx)[22]



Based on a literature procedure,[22] a flame-dried round-bottom flask equipped with a magnetic stirring bar was charged with Loratadine (2.68 g, 7.0 mmol, 1.0 equiv), potassium vinyltrifluoroborate (1.41 g, 10.5 mmol, 1.5 equiv), K_2CO_3 (2.9 g, 21.0 mmol, 3.0 equiv), $Pd(OAc)_2$ (78.6 mg, 0.05 mmol, 5.0 mol%), SPhos (287.4 mg, 0.1 mmol, 10.0 mol%) and dioxane / water (6:1, 35 mL, 0.20 M) and stirred at 90 °C for 48 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was allowed to cool to room temperature and then passed through a pad of celite and rinsed with EtOAc. The filtrate was partitioned between H_2O and EtOAc. The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes / EtOAc 1:3) to yield 2.11 g (5.63 mmol, 80%) of the title compound as a yellowish solid. Spectral data are in agreement with those reported in literature.[22] $\mathbf{R_f}$ (hexanes / EtOAc 1:3 on silica) = 0.28, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.39 (dd, *J* = 4.8, 1.7 Hz, 1H), 7.43 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.24 – 7.14 (m, 3H), 7.08 (dd, *J* = 7.7, 4.8 Hz, 1H), 6.65 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.71 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.20 (dd, *J* = 10.8, 0.9 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.88 – 3.75 (m, 2H), 3.38 (dtt, *J* = 13.9, 9.3, 5.1 Hz, 2H), 3.19 – 3.06 (m, 2H), 2.84 (qt, *J* = 13.3, 9.0, 5.7 Hz, 2H), 2.54 – 2.26 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 157.5, 155.6, 146.6, 138.8, 137.9, 137.6, 137.1, 136.8, 136.5, 135.0, 133.8, 129.7, 127.1, 124.0, 122.2, 113.8, 61.4, 45.0, 44.9, 32.0, 31.8, 30.9, 30.7, 14.8.

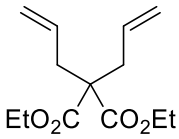
2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-vinylbenzoate (1by)[23]



Based on a literature procedure,[23] a flame-dried three-neck round-bottom flask equipped with a magnetic stirring bar was charged with 4-vinylbenzoic acid (889.0 mg, 6.0 mmol, 1.0 equiv),

racemic vitamine-E (2.58 g, 6.0 mmol, 1.0 equiv), DCC (1.49 g, 7.2 mmol, 1.2 equiv), DMAP (879.6 mg, 7.2 mmol, 1.2 equiv) and anhydrous DCM (60 mL, 0.1 M) and stirred at room temperature (25 °C) for 44 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue purified by flash column chromatography on silica gel (hexanes / EtOAc 8:1 to 6:1) to yield 2.79 g (5.0 mmol, 83%) of the title compound as an orange sticky oil. Spectral data are in agreement with those reported in literature.[23] $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.75, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.24 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 6.82 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.93 (d, *J* = 17.6 Hz, 1H), 5.45 (d, *J* = 10.9 Hz, 1H), 2.66 (t, *J* = 6.8 Hz, 2H), 2.17 (s, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 1.93 – 1.77 (m, 2H), 1.64 – 1.12 (m, 24H), 0.94 – 0.87 (m, 12H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 165.0, 149.6, 142.6, 140.8, 136.1, 130.6, 128.9, 127.0, 126.4, 125.2, 123.2, 117.6, 116.9, 75.2, 39.5, 37.7, 37.6, 37.5, 37.4, 32.9, 32.9, 32.8, 28.1, 25.0, 25.0, 24.6, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 19.8, 13.2, 12.3, 12.0.

diethyl 2,2-diallylmalonate (1ce)[24]

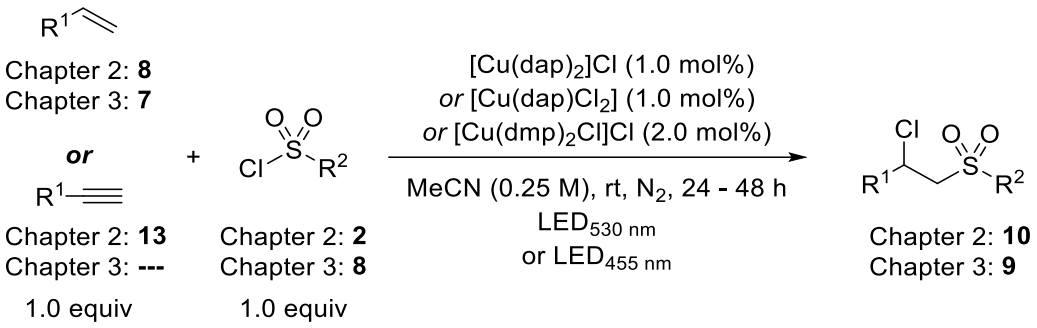


Based on a literature procedure,[24] a flame-dried bottom flask equipped with a magnetic stirring bar was charged with NaH (1.0 g, 25.0 mmol, 2.5 equiv, 60% wt% dispersion in oil) and anhydrous THF (50 mL, 0.20 M) at 0 °C. Diethyl malonate (1.52 mL, 1.6 g, 10.0 mmol, 1.0 equiv) in anhydrous THF (12 mL) was added dropwise under a N_2 atmosphere. The resulting reaction mixture was allowed to warm to room temperature (25 °C) and stirred for 15 min. Afterwards, allyl bromide (1.73 mL, 2.42 g, 20.0 mmol, 2.0 equiv) was added and the resulting reaction mixture was heated to reflux and stirred for 16 h. The reaction was monitored by TLC. Next, the reaction mixture was quenched with NH_4Cl and extracted three times with DE. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo and the residue purified by flash column chromatography on silica gel (hexanes / EtOAc 7:1) to yield 2.38 g (9.9 mmol, 99%) of the title compound as a colorless liquid. Spectral data are in agreement with those reported in literature.[24] $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.68, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.65 (ddt, *J* = 16.6, 10.6, 7.4 Hz, 2H), 5.14 – 5.09 (m, 2H), 5.07 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 4H), 2.63 (dt, *J* = 7.4, 1.2 Hz, 4H), 1.24 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 170.9, 132.4, 119.3, 61.4, 57.4, 36.9, 14.3.

7.4 Experimental Part for Chapter 2 and Chapter 3

7.4.1 Compound Characterization of Chlorosulfonylation Products

General procedure for photochemical chlorosulfonylation of activated alkenes and alkynes (Chapter 2 and Chapter 3) (*GP-I*)



A flame-dried Schlenk tube (10.0 mL size; Figure 2, D) equipped with a magnetic stirring bar (Figure 2, E) was charged with sulfonyl chloride (0.5 mmol, 1.0 equiv), the corresponding photocatalyst (5.0-10.0 µmol, 1.0-2.0 mol%) and dissolved in anhydrous MeCN (2.0 mL, 0.25 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, alkene or alkyne (0.5 mmol, 1.0 equiv) was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet (Figure 2, C) for a glass rod (Figure 2, B), through which irradiation with a 530 nm high power LED for $[Cu(dap)_2]Cl$ and $[Cu(dap)Cl_2]$ and a 455 nm high power LED for $[Cu(dmp)_2Cl]Cl$ (Figure 2, A) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for the indicated time. The reaction was monitored by TLC. Finally, the reaction mixture was concentrated in vacuo and the residue purified by flash column chromatography on silica gel. *Please note*, that chlorosulfonylation products can be found in chapter 2 and chapter 3, and therefore are marked with two different molecule numbers according to the respective chapters.

General procedure for photochemical chlorosulfonylation of unactivated alkenes (Chapter 2 and Chapter 3) (*GP-II*)

A flame-dried Schlenk tube (10.0 mL size Figure 2, D) equipped with a magnetic stirring bar (Figure 2, E) was charged with sulfonyl chloride (0.5 mmol, 1.0 equiv), Na_2CO_3 (53.0 mg, 0.5 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and dissolved in anhydrous MeCN (2.0 mL, 0.25 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, the alkene (1.0 mmol, 2.0 equiv) was

added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet (Figure 2, C) for a glass rod (Figure 2, B), through which irradiation with a 455 nm high power LED (blue LED) (Figure 2, A) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 48 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was saturated by addition of brine solution and the aqueous phase was washed three times with EtOAc. The combined organic fractions were dried over anhydrous Na_2SO_4, concentrated in vacuo and the crude residue was purified by flash column chromatography on silica gel. *Please note*, that chlorosulfonylation products can be found in chapter 2 and chapter 3, and therefore are marked with two different molecule numbers according to the respective chapters.

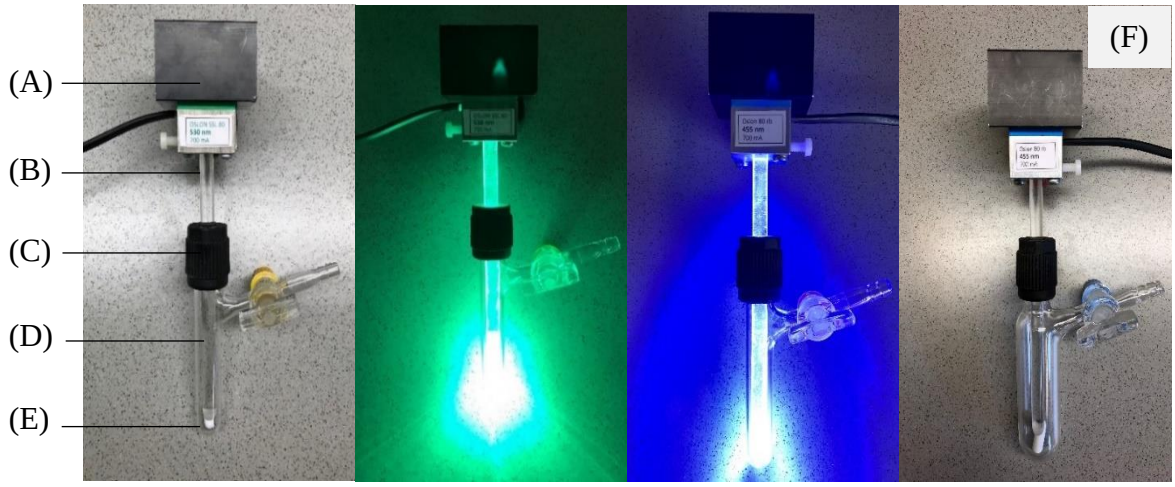
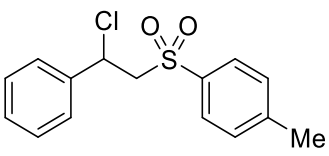


Figure 2. Irradiation setup for photochemical chlorosulfonylation. (A) LED; (B) glass rod (used as a light conductor); (C) Teflon adapter; (D) Schlenk tube (10.0 mL size); (E) Teflon-coated magnetic stirring bar; (F) Schlenk tube (30.0 mL size) for upscaling experiments.

***Please note**, that the values for [Cu(dap)$_2$]Cl and [Cu(dap)Cl$_2$] were obtained during my master thesis[25] and published during the PhD[26] and are therefore marked directly at procedure with the corresponding references.*

1-((2-chloro-2-phenylethyl)sulfonyl)-4-methylbenzene (10a//9a)



Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 10:1 to 6:1).

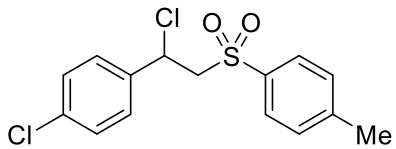
$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	141.2 mg (479 µmol, 96%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	139.8 mg (474 µmol, 95%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	30 h	135.6 mg (460 µmol, 92%)

Gram-Scale: This procedure can be also scaled-up to gram-quantities following ***GP-I*** in a flame-dried Schlenk tube (30.0 mL size, Figure 2, F) using styrene (0.57 mL, 520.8 mg, 5.0 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (953.2 mg, 5.0 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) anhydrous MeCN (20.0 mL, 0.25 M) at room temperature (25 °C) for the indicated time to yield the given amount of the title compound as a white solid after analogous work-up.

$[Cu(dap)_2]Cl$[25,26]	(44.2 mg, 50.0 µmol, 1.0 mol%)	24 h	1.39 g (4.72 mmol, 94%)
$[Cu(dap)Cl_2]$[25,26]	(26.3 mg, 50.0 µmol, 1.0 mol%)	24 h	1.36 g (4.61 mmol, 92%)
$[Cu(dmp)_2Cl]Cl$	(55.1 mg, 0.1 mmol, 2.0 mol%)	48 h	1.38 g (4.68 mmol, 94%)

mp: 82 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.30, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.22 (m, 7H), 5.33 (t, *J* = 6.9 Hz, 1H), 3.94 (dd, *J* = 14.8, 6.9 Hz, 1H), 3.85 (dd, *J* = 14.8, 6.9 Hz, 1H), 2.41 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.0, 138.7, 136.3, 129.9, 129.2, 129.0, 128.3, 127.2, 64.2, 55.2, 21.8. **IR** (neat): 3034, 2986, 2930, 2807, 1595, 1484, 1450, 1409, 1383, 1305, 1280, 1200, 1183, 1139, 1081, 1010, 1006, 917, 801, 757, 693 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{15}ClNaO_2S$ ($[M+Na]^+$) 317.0373, found 317.0372.

1-chloro-4-(1-chloro-2-tosylethyl)benzene (10c)



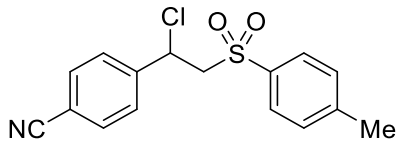
Following general procedure ***GP-I*** using 1-chloro-4-vinylbenzene (60.0 µL, 69.3 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 10:1 to 6:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	151.6 mg (460 µmol, 92%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	143.5 mg (436 µmol, 87%)

mp: 116 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.35, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.15 (m, 6H), 5.29 (dd, *J* = 7.9, 6.3 Hz, 1H), 3.91 (dd, *J* = 14.7, 6.3 Hz, 1H), 3.84 (dd, *J* = 14.7, 7.9 Hz, 1H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.2, 136.9, 136.1, 135.2, 129.9, 129.1, 128.7, 128.2, 63.9, 54.4, 21.7. **IR** (neat):

3064, 2986, 2922, 1595, 1491, 1481, 1413, 1410, 1353, 1290, 1210, 1200, 1139, 1130, 1085, 1044, 1014, 902, 820, 813, 772, 705, 690 cm^{-1}. **HRMS** (APCI) m/z calculated for $C_{15}H_{18}Cl_2NO_2S$ ($[M+NH_4]^+$) 346.0430, found 346.0434.

4-(1-chloro-2-tosylethyl)benzonitrile (10d//9b)

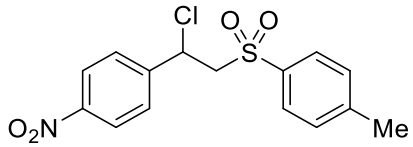


Following general procedure ***GP-I*** using 4-vinylbenzonitrile (64.6 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 1:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	48 h	140.7 mg (440 µmol, 88%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	48 h	143.8 mg (450 µmol, 90%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	48 h	143.0 mg (447 µmol, 89%)

mp: 109 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.18, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.58 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.32 (dd, *J* = 7.7, 6.4 Hz, 1H), 3.90 (dd, *J* = 14.7, 6.4 Hz, 1H), 3.85 (dd, *J* = 14.7, 7.7 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.3, 143.2, 135.8, 132.5, 129.9, 128.1, 128.0, 118.0, 112.7, 63.3, 53.9, 21.6. **IR** (neat): 3042, 2978, 2933, 2236, 1595, 1510, 1448, 1410, 1405, 1327, 1271, 1208, 1163, 1137, 1085, 1040, 1021, 921, 878, 842, 805, 775, 693 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{15}ClNO_2S$ ($[M+H]^+$) 320.0507, found 320.0511.

1-((2-chloro-2-(4-nitrophenyl)ethyl)sulfonyl)-4-methylbenzene (10e)



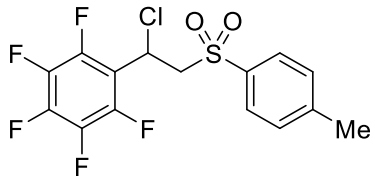
Following general procedure ***GP-I*** using 1-nitro-4-vinylbenzene (64.1 µL, 74.6 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a yellowish solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	48 h	62.1 mg (183 µmol, 37%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	48 h	63.9 mg (188 µmol, 38%)

mp: 122 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.25, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.25

(d, *J* = 8.3 Hz, 2H), 5.40 (dd, *J* = 8.0, 6.2 Hz, 1H), 3.93 (dd, *J* = 14.6, 6.2 Hz, 1H), 3.86 (dd, *J* = 14.6, 8.0 Hz, 1H), 2.41 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 148.1, 145.6, 145.2, 136.0, 130.0, 128.6, 128.2, 124.2, 63.6, 53.6, 21.7. **IR** (neat): 3116, 3090, 2993, 2926, 2859, 1595, 1521, 1405, 1346, 1312, 1275, 1208, 1163, 1137, 1090, 1073, 1020, 1000, 960, 913, 857, 800, 787, 710, 696 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{14}ClKNO_4S$ ($[M+K]^+$) 377.9964, found 377.9965.

1-(1-chloro-2-tosylethyl)-2,3,4,5,6-pentafluorobenzene (10f)

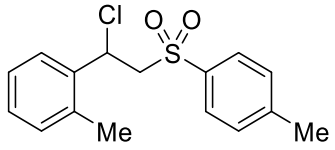


Following general procedure ***GP-I*** using 1,2,3,4,5-pentafluoro-6-vinylbenzene (69.0 µL, 97.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	48 h	180.1 mg (468 µmol, 94%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	48 h	174.9 mg (455 µmol, 91%)

mp: 97 °C. **R_f** (hexanes / EtOAc 5:1) = 0.52, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.29 (m, 2H), 5.58 (dd, *J* = 10.5, 4.8, 1H), 4.17 (dd, *J* = 14.6, 10.5 Hz, 1H), 3.88 (dd, *J* = 14.6, 4.8 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 146.4 – 146.0 (m), 145.9, 143.8 – 143.3 (m), 141.0 –140.6 (m), 139.3 – 138.7 (m), 136.8 – 136.1 (m), 135.4, 130.1, 128.1, 112.4 (td, *J* = 14.1, 4.0 Hz), 60.5 (t, *J* = 3.1 Hz), 42.9, 21.7. **^{19}F-NMR** (376 MHz, $CDCl_3$) δ = -140.70 (s, 2F), -152.00 (tt, *J* = 21.0, 3.7 Hz, 1F), -161.17 (td, *J* = 22.3, 8.7 Hz, 2F). **IR** (neat): 2980, 2930, 1655, 1599, 1506, 1416, 1380, 1319, 1301, 1218, 1189, 1141, 1085, 1050, 999, 951, 876, 808, 802, 764, 700, 693 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{10}ClF_5NaO_2S$ ($[M+Na]^+$) 406.9902, found 406.9910.

1-(1-chloro-2-tosylethyl)-2-methylbenzene (10g)

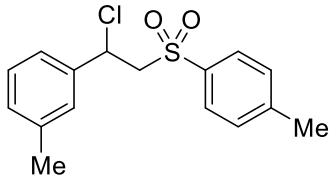


Following general procedure ***GP-I*** using 1-methyl-2-vinylbenzene (64.5 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	152.0 mg (492 µmol, 98%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	151.5 mg (491 µmol, 98%)

R_f (hexanes / EtOAc 5:1) = 0.40, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.01 (m, 6H), 5.62 (t, *J* = 6.8 Hz, 1H), 3.96 (dd, *J* = 14.8, 6.8 Hz, 1H), 3.88 (dd, *J* = 14.8, 6.8 Hz, 1H), 2.41 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.0, 136.7, 136.2, 135.6, 131.0, 129.9, 129.0, 128.2, 126.8, 126.8, 63.5, 51.4, 21.7, 19.2. **IR** (neat): 3030, 3027, 2978, 2928, 1595, 1491, 1461, 1402, 1320, 1291, 1270, 1204, 1137, 1085, 1036, 1030, 900, 895, 842, 813, 760, 721, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{21}ClNO_2S$ ($[M+NH_4]^+$) 326.0976, found 326.0974.

1-(1-chloro-2-tosylethyl)-3-methylbenzene (10h)

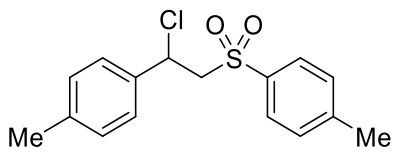


Following general procedure ***GP-I*** using 1-methyl-3-vinylbenzene (65.7 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	146.4 mg (474 µmol, 95%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	150.0 mg (486 µmol, 97%)

R_f (hexanes / EtOAc 5:1) = 0.38, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.18 – 7.12 (m, 1H), 7.10 – 6.99 (m, 4H), 5.29 (t, *J* = 7.0 Hz, 1H), 3.94 (dd, *J* = 14.8, 7.0 Hz, 1H), 3.84 (dd, *J* = 14.8, 7.0 Hz, 1H), 2.40 (s, 3H), 2.25 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.9, 138.8, 138.4, 136.3, 129.9, 129.8, 128.9, 128.3, 127.8, 124.4, 64.1, 55.3, 21.7, 21.4. **IR** (neat): 3030, 2922, 1691, 1685, 1595, 1491, 1450, 1402, 1360, 1320, 1250, 1215, 1161, 1137, 1085, 1040, 934, 928, 887, 875, 798, 768, 728, 701, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{17}ClNaO_2S$ ($[M+Na]^+$) 331.0530, found 331.0535.

1-((2-chloro-2-(*p*-tolyl)ethyl)sulfonyl)-4-methylbenzene (10i//9c)



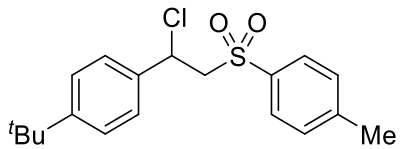
Following general procedure ***GP-I*** using 1-methyl-4-vinylbenzene (72.0 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature

(25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 8:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	149.7 mg (485 µmol, 97%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	148.4 mg (481 µmol, 96%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	30 h	145.3 mg (471 µmol, 94%)

mp: 83 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.45, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 5.30 (t, *J* = 6.9 Hz, 1H), 3.93 (dd, *J* = 14.7, 6.9 Hz, 1H), 3.85 (dd, *J* = 14.7, 6.9 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.9, 139.2, 136.3, 135.7, 129.8, 129.6, 128.3, 127.1, 64.2, 55.2, 21.7, 21.3. **IR** (neat): 3027, 2986, 2937, 2866, 1595, 1517, 1492, 1450, 1413, 1410, 1316, 1271, 1208, 1200, 1159, 1130, 1085, 1036, 1008, 913, 798, 772, 692 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{17}ClNaO_2S$ ($[M+Na]^+$) 331.0530, found 331.0532.

1-(*tert*-butyl)-4-(1-chloro-2-tosylethyl)benzene (10j)

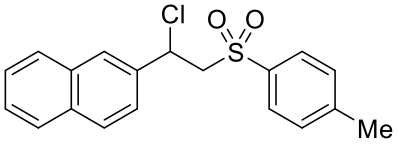


Following general procedure ***GP-I*** using 1-(*tert*-butyl)-4-vinylbenzene (90.6 µL, 80.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	172.8 mg (492 µmol, 98%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	172.4 mg (491 µmol, 98%)

mp: 127 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.45, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.14 (m, 6H), 5.33 (t, *J* = 6.9 Hz, 1H), 3.95 (dd, *J* = 14.8, 6.9 Hz, 1H), 3.90 (dd, *J* = 14.8, 6.9 Hz, 1H), 2.38 (s, 3H), 1.28 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 152.4, 144.7, 136.3, 135.4, 129.8, 128.2, 127.0, 125.9, 64.1, 55.2, 34.7, 31.4, 21.8. **IR** (neat): 3053, 2967, 2926, 2870, 1595, 1513, 1509, 1465, 1416, 1383, 1307, 1286, 1193, 1159, 1141, 1088, 1040, 1030, 891, 824, 813, 768, 733, 705, 681 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{19}H_{27}ClNO_2S$ ($[M+NH_4]^+$) 368.1446, found 368.1442.

2-(1-chloro-2-tosylethyl)naphthalene (10k)

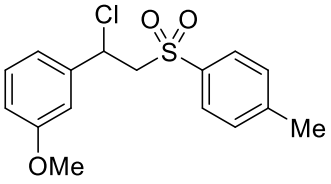


Following general procedure ***GP-I*** using 2-vinylnaphthalene (77.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	160.8 mg (466 µmol, 93%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	155.8 mg (452 µmol, 90%)

mp: 146 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.30, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.79 – 7.71 (m, 2H), 7.70 – 7.64 (m, 2H), 7.54 – 7.47 (m, 4H), 7.30 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 2H), 5.49 (t, *J* = 6.5 Hz, 1H), 4.07 – 3.95 (m, 2H), 2.21 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.9, 135.9, 135.3, 133.4, 132.8, 129.6, 129.1, 128.2, 128.1, 127.7, 127.0, 126.8, 124.1, 63.9, 55.6, 21.5. **IR** (neat): 3058, 2982, 2922, 1595, 1510, 1500, 1443, 1387, 1311, 1297, 1252, 1226, 1156, 1120, 1081, 1044, 1029, 975, 966, 899, 869, 825, 816, 793, 757, 742, 691 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{19}H_{21}ClNO_2S$ ($[M+NH_4]^+$) 362.0976, found 362.0978.

1-(1-chloro-2-tosylethyl)-3-methoxybenzene (10m)



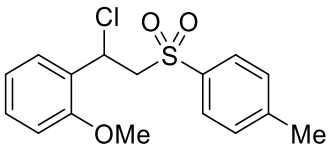
Following general procedure ***GP-I*** using 1-methoxy-3-vinylbenzene (69.4 µL, 67.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	139.7 mg (430 µmol, 86%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	144.5 mg (445 µmol, 89%)

mp: 55 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.23, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.86 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.79 (ddd, *J* = 8.3, 2.1, 1.2 Hz, 1H), 6.74 (t, *J* = 2.1 Hz, 1H), 5.28 (t, *J* = 6.9 Hz, 1H), 3.92 (dd, *J* = 14.8, 6.9 Hz, 1H), 3.83 (dd, *J* = 14.8, 6.9 Hz, 1H), 3.74 (s, 3H), 2.40 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 159.9, 145.0, 140.0, 136.2, 130.1, 129.8, 128.3, 119.5, 114.7, 112.6, 64.1, 55.3, 55.2, 21.7. **IR** (neat): 3001, 2971, 2932, 2837, 1588, 1491,

1457, 1420, 1402, 1312, 1291, 1276, 1241, 1156, 1128, 1085, 1044, 939, 897, 867, 801, 788, 710, 699, 690, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{21}ClNO_3S$ ($[M+NH_4]^+$) 342.0925, found 342.0925.

1-(1-chloro-2-tosylethyl)-2-methoxybenzene (10n)

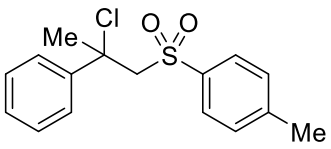


Following general procedure ***GP-I*** using 1-methoxy-2-vinylbenzene (67.2 µL, 67.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	118.6 mg (365 µmol, 73%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	113.3 mg (349 µmol, 70%)

$\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.20, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.21 (m, 4H), 6.87 (td, *J* = 7.5, 1.1 Hz, 1H), 6.72 (dd, *J* = 7.5, 1.1 Hz, 1H), 5.62 (t, *J* = 6.9 Hz, 1H), 4.05 (dd, *J* = 14.8, 6.8 Hz, 1H), 3.88 (dd, *J* = 14.8, 6.8 Hz, 1H), 3.75 (s, 3H), 2.40 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 156.4, 144.7, 136.3, 130.5, 129.6, 128.9, 128.4, 126.3, 120.9, 111.1, 62.7, 55.5, 51.2, 21.7. **IR** (neat): 3012, 2941, 2840, 1599, 1491, 1461, 1425, 1402, 1320, 1290, 1249, 1141, 1100, 1088, 1021, 907, 895, 842, 814, 791, 753, 657 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{17}ClNaO_3S$ ($[M+Na]^+$) 347.0479, found 347.0483.

1-((2-chloro-2-phenylpropyl)sulfonyl)-4-methylbenzene (10o)



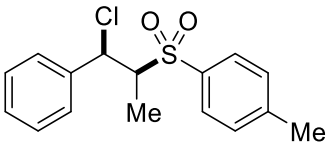
Following general procedure ***GP-I*** using prop-1-en-2-ylbenzene (65.0 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	130.2 mg (422 µmol, 84%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	98.5 mg (319 µmol, 64%)

mp: 125 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.50, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.45 – 7.35 (m, 3H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.16 (d, *J* = 14.7 Hz, 1H), 3.98 (d,

J = 14.7 Hz, 1H), 2.37 (s, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.5, 141.3, 137.1, 129.7, 128.4, 128.3, 127.9, 126.6, 69.7, 67.8, 29.8, 21.7. **IR** (neat): 3060, 2982, 2926, 1595, 1495, 1446, 1400, 1390, 1316, 1271, 1185, 1153, 1137, 1085, 1047, 915, 900, 872, 813, 764, 713, 693, 670 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{17}ClNaO_2S$ ($[M+Na]^+$) 331.0530, found 331.0528.

***syn*-1-((1-chloro-1-phenylpropan-2-yl)sulfonyl)-4-methylbenzene (10p)**

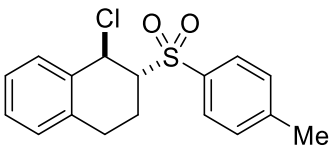


Following general procedure ***GP-I*** using (*E*)-prop-1-en-1-ylbenzene (69.4 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound diastereoselective as a colorless oil after flash column chromatography (hexanes / EtOAc 5:1). For the explanation and determination of the stereochemistry please see Main Part Chapter 2.

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	153.0 mg (495 µmol, 99%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	145.4 mg (471 µmol, 94%)

Note: Using the corresponding *Z*-alkene (*Z*)-prop-1-en-1-ylbenzene (59.1 mg, 0.5 mmol, 1.0 equiv) afforded **10p** as a colorless oil in 152.0 mg (492 µmol, 98%) for $[Cu(dap)_2]Cl$ and 144.2 mg (467 µmol, 93%) for $[Cu(dap)Cl_2]$. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.35, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.27 (m, 7H), 5.69 (d, *J* = 3.2 Hz, 1H), 3.46 (qd, *J* = 6.9, 3.2 Hz, 1H), 2.44 (s, 3H), 1.42 (d, *J* = 6.9 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.1, 138.7, 134.6, 129.8, 129.4, 128.8, 128.6, 127.2, 66.9, 59.8, 21.8, 9.1. **IR** (neat): 3064, 3030, 2986, 2941, 1737, 1595, 1495, 1454, 1402, 1390, 1307, 1301, 1234, 1144, 1088, 1060, 1013, 1000, 883, 850, 816, 768, 723, 696, 670 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{17}ClNaO_2S$ ($[M+Na]^+$) 331.0530, found 331.0532.

***trans*-1-chloro-2-tosyl-1,2,3,4-tetrahydronaphthalene (10q)**



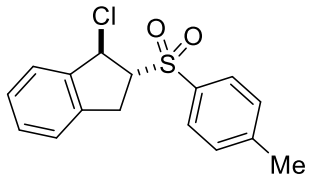
Following general procedure ***GP-I*** using 1,2-dihydronaphthalene (65.3 µL, 65.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound diastereoselective as an orange oil after flash column

chromatography (hexanes / EtOAc 5:1). Stereochemistry was assigned according to coupling constants in ^{1}H-NMR.

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	122.8 mg (383 µmol, 77%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	24.8 mg (77 µmol, 15%)

R_f (hexanes / EtOAc 5:1) = 0.48, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.32 (m, 3H), 7.25 – 7.18 (m, 2H), 7.12 – 7.04 (m, 1H), 5.57 (d, *J* = 3.5 Hz, 1H), 3.84 (ddd, *J* = 6.4, 5.1, 3.5 Hz, 1H), 3.08 (ddd, *J* = 17.0, 8.8, 5.1 Hz, 1H), 2.89 (dt, *J* = 17.0, 6.4 Hz, 1H), 2.63 – 2.50 (m, 1H), 2.46 (s, 3H), 2.24 (dqd, *J* = 14.4, 6.1, 0.9 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.4, 136.0, 135.0, 133.6, 130.2, 130.1, 128.9, 128.9, 128.9, 126.9, 67.4, 54.1, 25.6, 21.8, 19.9. **IR** (neat): 3065, 3027, 2930, 1595, 1491, 1454, 1402, 1316, 1264, 1210, 1186, 1141, 1085, 1037, 1009, 981, 951, 917, 880, 816, 738, 710, 690, 659 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{21}ClNO_2S$ ($[M+NH_4]^+$) 338.0976, found 338.0978.

***trans*-1-chloro-2-tosyl-2,3-dihydro-1*H*-indene (10r)**

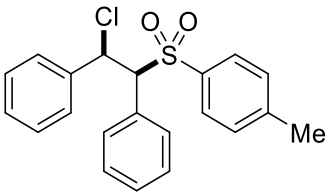


Following general procedure ***GP-I*** using 1*H*-indene (58.3 µL, 58.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound diastereoselective as a yellowish solid after flash column chromatography (hexanes / EtOAc 5:1). Stereochemistry was assigned according to coupling constants in ^{1}H-NMR.

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	118.6 mg (365 µmol, 73%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	113.3 mg (349 µmol, 70%)

mp: 81 °C. **R_f** (hexanes / EtOAc 5:1) = 0.40, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.29 – 7.26 (m, 2H), 7.22 – 7.16 (m, 1H), 5.70 (d, *J* = 4.9 Hz, 1H), 4.17 (ddd, *J* = 8.9, 6.2, 4.9 Hz, 1H), 3.55 (dd, *J* = 17.0, 6.2 Hz, 1H), 3.45 (dd, *J* = 17.0, 8.9 Hz, 1H), 2.46 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.5, 140.4, 139.0, 134.8, 130.2, 129.7, 128.9, 128.1, 125.3, 124.7, 72.7, 60.7, 32.0, 21.8. **IR** (neat): 3049, 2930, 2863, 1923, 1595, 1476, 1447, 1419, 1402, 1307, 1300, 1282, 1220, 1205, 1185, 1179, 1144, 1085, 1036, 1002, 992, 951, 913, 865, 842, 803, 790, 771, 742, 698, 667 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{15}ClNaO_2S$ ($[M+Na]^+$) 329.0373, found 329.0373.

syn-(1-chloro-2-tosylethane-1,2-diyl)dibenzene (10s)

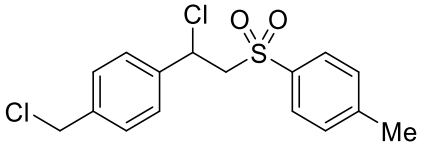


Following general procedure ***GP-I*** using (*E*)-1,2-diphenylethene (90.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound diastereoselective as a white solid after flash column chromatography (hexanes / EtOAc 5:1). For the explanation and determination of the stereochemistry please see Main Part Chapter 2.

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	12.9 mg (35 µmol, 7%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	12.8 mg (35 µmol, 7%)

mp: 183 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.30, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.37 – 7.26 (m, 12H), 7.04 (d, *J* = 8.2 Hz, 2H), 5.86 (d, *J* = 8.3 Hz, 1H), 4.63 (d, *J* = 8.3 Hz, 1H), 2.32 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.4, 138.5, 135.8, 131.2, 130.7, 129.3, 129.3, 129.1, 128.7, 128.6, 128.5, 128.1, 77.0, 60.4, 21.7. **IR** (neat): 3064, 3034, 2922, 2855, 1599, 1491, 1454, 1402, 1301, 1219, 1185, 1137, 1081, 1033, 917, 869, 804, 794, 770, 731, 693, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{21}H_{23}ClNO_2S$ ($[M+NH_4]^+$) 388.1133, found 388.1130.

1-((2-chloro-2-(4-(chloromethyl)phenyl)ethyl)sulfonyl)-4-methylbenzene (10t)



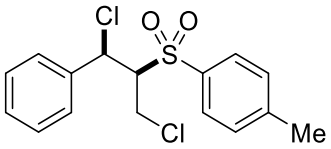
Following general procedure ***GP-I*** using 1-(chloromethyl)-4-vinylbenzene (70.5 µL, 76.3 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	166.4 mg (485 µmol, 97%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	168.1 mg (490 µmol, 98%)

mp: 122 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.35, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.19 (m, 6H), 5.32 (t, *J* = 6.8 Hz, 1H), 4.51 (s, 2H), 3.94 (dd, *J* = 14.8, 6.8 Hz, 1H), 3.87 (dd, *J* = 14.7, 6.8 Hz, 1H), 2.39 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 145.0, 138.6, 138.5, 136.1, 129.9, 129.1, 128.1, 127.7, 64.0, 54.8, 45.5, 21.7. **IR** (neat): 2989, 2937, 1916, 1797, 1595, 1500, 1494, 1436, 1428, 1400, 1391, 1316, 1271, 1208, 1189, 1137, 1101, 1085, 1050, 1022, 924, 846, 809, 798, 763, 737, 706, 700,

678 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{16}Cl_2NaO_2S$ ($[M+Na]^+$) 365.0140, found 365.0142.

***syn*-1-((1,3-dichloro-1-phenylpropan-2-yl)sulfonyl)-4-methylbenzene (10u)**

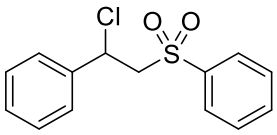


Following general procedure ***GP-I*** using (*E*)-(3-chloroprop-1-en-1-yl)benzene (63.2 µL, 76.3 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.1 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound diastereoselective as a white solid after flash column chromatography (hexanes / EtOAc 5:1). For the explanation and determination of the stereochemistry please see Main Part Chapter 2.

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	147.6 mg (430 µmol, 86%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	137.2 mg (400 µmol, 80%)

mp: 154 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.33, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 8.2 Hz, 2H), 7.29 (dd, *J* = 8.2, 1.6 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 5.71 (d, *J* = 7.5 Hz, 1H), 4.33 – 4.23 (m, 2H), 3.95 (ddd, *J* = 7.5, 4.6, 3.4 Hz, 1H), 2.40 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 145.0, 137.4, 136.2, 129.8, 129.1, 128.8, 128.5, 128.1, 71.5, 58.7, 39.7, 21.8. **IR** (neat): 3034, 2982, 2933, 1595, 1495, 1457, 1423, 1290, 1249, 1215, 1190, 1141, 1081, 1033, 984, 902, 839, 813, 738, 700, 682 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{16}Cl_2NaO_2S$ ($[M+Na]^+$) 365.0140, found 365.0139.

(1-chloro-2-(phenylsulfonyl)ethyl)benzene (10v//9d)



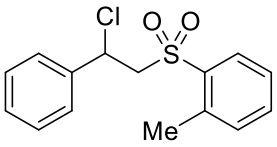
Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), benzenesulfonyl chloride (88.3 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	137.1 mg (488 µmol, 98%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	133.4 mg (475 µmol, 95%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	30 h	136.3 mg (485 µmol, 97%)

mp: 88 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.38, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.73 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.59 – 7.49 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.20 (m, 5H), 5.35 (t, *J* = 7.0 Hz, 1H), 3.98 (dd, *J* = 14.8, 6.9 Hz, 1H), 3.88 (dd, *J* = 14.8,

6.9 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 139.0, 138.3, 133.8, 129.1, 129.1, 128.8, 128.0, 127.1, 63.8, 55.1. **IR** (neat): 3071, 3034, 2989, 2930, 2789, 1595, 1495, 1479, 1446, 1409, 1320, 1305, 1290, 1200, 1141, 1081, 1070, 1059, 1000, 910, 850, 794, 788, 746, 708, 686 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_{13}ClNaO_2S$ ($[M+Na]^+$) 303.0217, found 303.0216.

1-((2-chloro-2-phenylethyl)sulfonyl)-2-methylbenzene (10w)

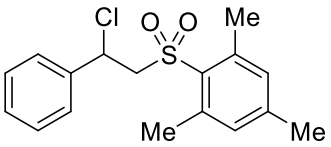


Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 2-methylbenzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	143.0 mg (485 µmol, 97%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	140.3 mg (476 µmol, 95%)

mp: 117 °C. **R_f** (hexanes / EtOAc 5:1) = 0.43, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.78 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.43 (td, *J* = 7.5, 1.4 Hz, 1H), 7.29 – 7.22 (m, 7H), 5.34 (t, *J* = 6.8 Hz, 1H), 3.99 (dd, *J* = 14.8, 6.8 Hz, 1H), 3.89 (dd, *J* = 14.8, 6.8 Hz, 1H), 2.66 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.6, 137.8, 137.3, 133.9, 132.7, 130.4, 129.3, 129.0, 127.1, 126.7, 63.2, 55.2, 20.5. **IR** (neat): 3064, 2997, 2937, 1595, 1520, 1495, 1480, 1451, 1400, 1370, 1312, 1264, 1208, 1163, 1126, 1081, 1047, 910, 794, 749, 693, 670 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{15}ClKO_2S$ ($[M+K]^+$) 333.0113, found 333.0111.

2-((2-chloro-2-phenylethyl)sulfonyl)-1,3,5-trimethylbenzene (10x)



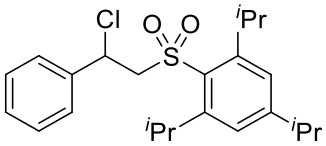
Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 2,4,6-trimethylbenzenesulfonyl chloride (109.4 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	158.2 mg (490 µmol, 98%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	154.8 mg (479 µmol, 96%)

mp: 97 °C. **R_f** (hexanes / EtOAc 5:1) = 0.53, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.35 – 7.27 (m, 5H), 6.89 (s, 2H), 5.41 (dd, *J* = 7.2, 6.3 Hz, 1H), 3.95 (dd, *J* = 14.7, 7.2 Hz, 1H), 3.84 (dd, *J* = 14.7, 6.3 Hz, 1H), 2.61 (s, 6H), 2.28 (s, 3H). **^{13}C-NMR** (75 MHz,

$CDCl_3$) δ = 143.7, 140.0, 139.0, 133.3, 132.4, 129.1, 129.0, 127.0, 64.2, 55.3, 23.0, 21.1. **IR** (neat): 3068, 2993, 2948, 1737, 1599, 1562, 1495, 1457, 1402, 1312, 1260, 1200, 1163, 1133, 1044, 910, 857, 774, 753, 707, 697 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{19}ClNaO_2S$ ($[M+Na]^+$) 345.0686, found 342.0690.

2-((2-chloro-2-phenylethyl)sulfonyl)-1,3,5-triisopropylbenzene (10y//9h)

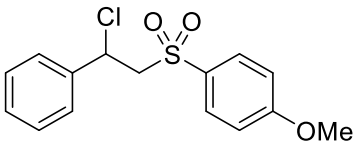


Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 2,4,6-triisopropylbenzenesulfonyl chloride (151.4 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	132.3 mg (325 µmol, 65%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	172.4 mg (424 µmol, 85%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	30 h	132.3 mg (325 µmol, 65%)

mp: 119 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.73, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.38 – 7.28 (m, 5H), 7.16 (s, 2H), 5.50 (dd, *J* = 7.5, 5.7 Hz, 1H), 4.11 (hept, *J* = 6.8 Hz, 2H), 4.02 (dd, *J* = 14.6, 7.5 Hz, 1H), 3.87 (dd, *J* = 14.6, 5.7 Hz, 1H), 2.90 (hept, *J* = 6.9 Hz, 1H), 1.31 – 1.23 (m, 18H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 154.1, 151.1, 139.3, 132.8, 129.2, 129.1, 127.0, 124.2, 66.1, 55.2, 34.4, 29.8, 25.2, 25.0, 23.7, 23.7. **IR** (neat): 3067, 2960, 2930, 2870, 1603, 1566, 1494, 1457, 1424, 1390, 1364, 1316, 1297, 1258, 1203, 1144, 1098, 1080, 1069, 1021, 1008, 921, 910, 883, 846, 790, 771, 738, 720, 699, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{35}ClNO_2S$ ($[M+NH_4]^+$) 424.2072, found 424.2074.

1-((2-chloro-2-phenylethyl)sulfonyl)-4-methoxybenzene (10z//9e)

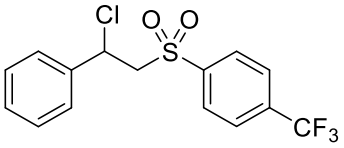


Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 4-methoxybenzenesulfonyl chloride (103.3 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 7:1 to 4:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	123.5 mg (397 µmol, 80%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	150.1 mg (483 µmol, 97%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	30 h	108.9 mg (350 µmol, 70%)

mp: 79 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.25, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 9.0 Hz, 2H), 7.26 (s, 5H), 6.88 (d, *J* = 9.0 Hz, 2H), 5.32 (t, *J* = 6.9 Hz, 1H), 3.94 (dd, *J* = 14.8, 6.9 Hz, 1H), 3.83 (s, 3H), 3.83 (dd, *J* = 14.8, 6.9 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 163.9, 138.7, 130.6, 130.4, 129.2, 129.0, 127.2, 114.4, 64.3, 55.8, 55.3. **IR** (neat): 3071, 2982, 2930, 2844, 1595, 1587, 1495, 1457, 1413, 1297, 1260, 1197, 1154, 1133, 1085, 1051, 1021, 910, 831, 760, 701 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{15}ClNaO_3S$ ($[M+Na]^+$) 333.0323, found 333.0320.

1-((2-chloro-2-phenylethyl)sulfonyl)-4-(trifluoromethyl)benzene (10aa)

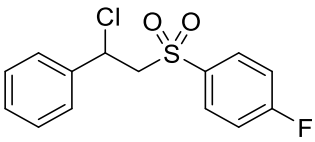


Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 4-(trifluoromethyl)benzene-sulfonyl chloride (122.3 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	166.8 mg (478 µmol, 96%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	165.9 mg (476 µmol, 95%)

mp: 128 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.53, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.18 (m, 5H), 5.36 (dd, *J* = 7.6, 6.6 Hz, 1H), 4.02 (dd, *J* = 14.9, 6.6 Hz, 1H), 3.93 (dd, *J* = 14.9, 7.6 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.6, 137.9, 135.3 (q, *J* = 33.2 Hz), 129.5, 129.1, 128.8, 127.3, 126.24 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 273.1 Hz), 63.9, 55.0. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -63.83 (s, 3F). **IR** (neat): 2990, 2933, 1741, 1498, 1457, 1405, 1323, 1271, 1211, 1167, 1137, 1100, 1088, 1078, 1014, 913, 835, 801, 759, 721, 703, 698 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{12}ClF_3NaO_2S$ ($[M+Na]^+$) 371.0091, found 371.0093.

1-((2-chloro-2-phenylethyl)sulfonyl)-4-fluorobenzene (10ab)

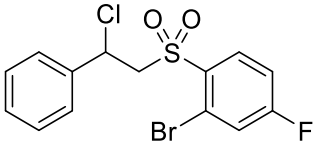


Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 4-fluorobenzenesulfonyl chloride (97.3 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1 to 4:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	127.5 mg (427 µmol, 85%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	146.0 mg (489 µmol, 98%)

mp: 87 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.48, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.73 (dd, *J* = 8.8, 5.0 Hz, 1H), 7.31 – 7.24 (m, 5H), 7.09 (t, *J* = 8.8 Hz, 2H), 5.34 (t, *J* = 6.9 Hz, 1H), 3.98 (dd, *J* = 14.8, 6.9 Hz, 1H), 3.87 (dd, *J* = 14.9, 6.9 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 165.9 (d, *J* = 256.9 Hz), 138.3, 135.3 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 9.8 Hz), 129.4, 129.1, 127.3, 116.5 (d, *J* = 22.6 Hz), 64.3, 55.2. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -103.47 (s, 3F). **IR** (neat): 2993, 2941, 1592, 1491, 1457, 1405, 1387, 1323, 1275, 1193, 1137, 1085, 1061, 1049, 1010, 913, 835, 800, 760, 710, 700 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_{12}ClFNaO_2S$ ($[M+Na]^+$) 321.0123, found 321.0124.

2-bromo-1-((2-chloro-2-phenylethyl)sulfonyl)-4-fluorobenzene (10ac)

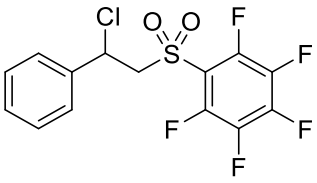


Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 2-bromo-4-fluorobenzenesulfonyl chloride (136.8 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	185.6 mg (491 µmol, 98%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	173.5 mg (459 µmol, 92%)

mp: 117 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.60, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.82 (dd, *J* = 8.9, 5.7 Hz, 1H), 7.37 (dd, *J* = 7.8, 2.5 Hz, 1H), 7.28 – 7.20 (m, 5H), 6.98 (ddd, *J* = 9.1, 7.8, 2.5 Hz, 1H), 5.32 (t, *J* = 7.1 Hz, 1H), 4.31 (dd, *J* = 15.1, 7.5 Hz, 1H), 4.22 (dd, *J* = 15.1, 6.7 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 164.9 (d, *J* = 261.0 Hz), 137.9, 134.6 (d, *J* = 3.5 Hz), 134.5 (d, *J* = 9.9 Hz), 129.4, 129.0, 127.3, 122.7 (d, *J* = 25.3 Hz), 122.2 (d, *J* = 10.4 Hz), 115.2 (d, *J* = 21.6 Hz), 61.3, 55.3. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -102.55 (s, 3F). **IR** (neat): 3109, 3087, 3034, 2990, 2937, 1577, 1485, 1461, 1400, 1379, 1323, 1258, 1204, 1156, 1130, 1095, 1080, 1030, 1025, 910, 861, 820, 798, 768, 757, 712, 695, 670 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_{15}BrClFNO_2S$ ($[M+NH_4]^+$) 393.9674, found 393.9678.

1-((2-chloro-2-phenylethyl)sulfonyl)-2,3,4,5,6-pentafluorobenzene (10ad//9g)

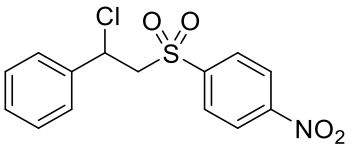


Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 2,3,4,5,6-pentafluorobenzenesulfonyl chloride (133.3 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	153.8 mg (415 µmol, 83%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	142.6 mg (383 µmol, 77%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	30 h	157.7 mg (425 µmol, 85%)

mp: 128 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.65, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.37 – 7.24 (m, 5H), 5.41 (t, *J* = 7.3 Hz, 1H), 4.13 – 4.05 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 148.1 – 145.8 (m), 143.8 – 142.5 (m), 140.3 – 138.6 (m), 137.4, 136.7 – 135.4 (m), 129.8, 129.5 – 129.2 (m), 129.1, 127.3, 115.1 – 114.7 (m), 64.9, 55.0. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -135.14 – -135.74 (m, 2F), -143.41 (tt, *J* = 21.0, 7.9 Hz, 1F), -158.45 – -158.85 (m, 2F). **IR** (neat): 2997, 2937, 1648, 1521, 1491, 1479, 1402, 1346, 1301, 1275, 1211, 1170, 1143, 1096, 1025, 1009, 988, 928, 850, 801, 793, 746, 702, 693 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_8ClF_5NaO_2S$ ($[M+Na]^+$) 392.9746, found 392.9748.

1-((2-chloro-2-phenylethyl)sulfonyl)-4-nitrobenzene (10ae//9f)



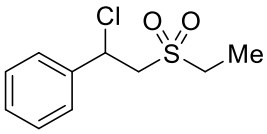
Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 4-nitrobenzenesulfonyl chloride (110.8 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	48 h	130.2 mg (400 µmol, 80%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	48 h	132.3 mg (406 µmol, 81%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	48 h	152.8 mg (469 µmol, 94%)

mp: 129 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.38, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.9 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 2H), 7.28 – 7.21 (m, 5H), 5.37 (t, *J* = 7.1 Hz, 1H), 4.05 (dd, *J* = 15.1, 7.1 Hz, 1H), 3.94 (dd, *J* = 15.1, 7.1 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 150.7, 144.8, 137.9, 129.8, 129.6, 129.2, 127.4, 124.2, 64.2, 55.0. **IR** (neat): 3109, 3071, 3038, 2982, 2937, 2866, 1607, 1525, 1495, 1457, 1401, 1349, 1320, 1305,

1290, 1208, 1151, 1140, 1100, 1085, 1040, 1000, 913, 858, 801, 768, 742, 710, 698, 690 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_{16}ClN_2O_4S$ ($[M+NH_4]^+$) 343.0514, found 343.0516.

(1-chloro-2-(ethylsulfonyl)ethyl)benzene (10af//9i)

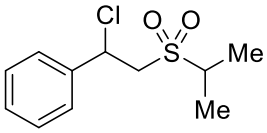


Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), ethanesulfonyl chloride (64.3 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a yellowish solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	110.5 mg (475 µmol, 95%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	108.3 mg (465 µmol, 93%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	30 h	79.2 mg (340 µmol, 68%)

mp: 67 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.18, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.46 – 7.36 (m, 5H), 5.39 (dd, *J* = 7.7, 5.9 Hz, 1H), 3.81 (dd, *J* = 15.1, 7.7 Hz, 1H), 3.59 (dd, *J* = 15.1, 5.9 Hz, 1H), 2.93 – 2.74 (m, 2H), 1.32 (t, *J* = 7.5 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.9, 129.6, 129.3, 127.2, 60.7, 55.6, 49.0, 6.6. **IR** (neat): 3068, 3038, 2986, 2937, 2878, 1498, 1457, 1409, 1375, 1297, 1252, 1238, 1137, 1089, 1040, 1025, 977, 931, 895, 822, 775, 757, 716, 698, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{10}H_{17}ClNO_2S$ ($[M+NH_4]^+$) 250.0663, found 250.0664.

(1-chloro-2-(isopropylsulfonyl)ethyl)benzene (10ag//9j)



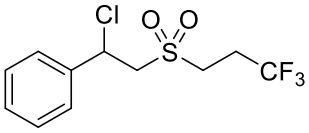
Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), propane-2-sulfonyl chloride (71.3 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	106.6 mg (432 µmol, 86%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	108.4 mg (439 µmol, 88%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	30 h	48.3 mg (196 µmol, 39%)

$\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.25, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.47 – 7.36 (m, 5H), 5.42 (dd, *J* = 7.6, 5.9 Hz, 1H), 3.83 (dd, *J* = 15.0, 7.6 Hz, 1H), 3.57 (dd, *J* = 15.0, 5.9 Hz, 1H), 2.98 (hept, *J* = 6.8 Hz, 1H), 1.33 (dd, *J* = 13.4, 6.8 Hz, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 139.1, 129.5, 129.2, 127.2, 58.3, 55.5, 54.1, 15.4, 14.8. **IR** (neat): 3050, 3017, 2982, 2941, 1495, 1457, 1394, 1357, 1301, 1260, 1200, 1170, 1118, 1077, 1058, 1030,

891, 842, 775, 697, 661 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{11}H_{15}ClNaO_2S$ ($[M+Na]^+$) 269.0373, found 269.0373.

(1-chloro-2-((3,3,3-trifluoropropyl)sulfonyl)ethyl)benzene (10ah)

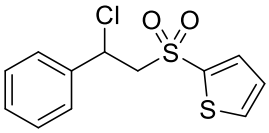


Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 3,3,3-trifluoropropane-1-sulfonyl chloride (98.3 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	120.3 mg (400 µmol, 80%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	135.1 mg (449 µmol, 90%)

mp: 50 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.48, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.48 – 7.38 (m, 5H), 5.39 (dd, *J* = 7.7, 6.0 Hz, 1H), 3.87 (dd, *J* = 15.3, 7.7 Hz, 1H), 3.66 (dd, *J* = 15.3, 6.0 Hz, 1H), 3.15 – 2.88 (m, 2H), 2.68 – 2.49 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 138.3, 129.9, 129.5, 127.2, 62.4, 55.3, 47.7, 47.7, 27.0 (q, *J* = 31.7 Hz). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -66.48 (s, 3F). **IR** (neat): 3042, 3004, 2952, 2926, 1498, 1443, 1379, 1327, 1282, 1249, 1207, 1126, 1088, 1025, 982, 891, 854, 772, 731, 690, 644 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{11}H_{12}ClF_3NaO_2S$ ($[M+Na]^+$) 323.0091, found 323.0091.

2-((2-chloro-2-phenylethyl)sulfonyl)thiophene (10ai//9k)



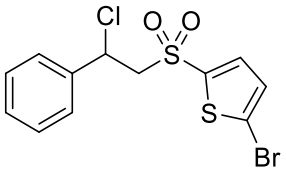
Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), thiophene-2-sulfonyl chloride (91.3 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a yellowish solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	136.7 mg (477 µmol, 95%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	136.0 mg (474 µmol, 95%)
$[Cu(dmp)_2Cl]Cl$	(5.5 mg, 10.0 µmol, 2.0 mol%)	30 h	139.4 mg (486 µmol, 97%)

mp: 93 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.33, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.65 (dd, *J* = 4.9, 1.4 Hz, 1H), 7.47 (dd, *J* = 3.8, 1.4 Hz, 1H), 7.34 – 7.27 (m, 5H), 7.01 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.37 (t, *J* = 6.9 Hz, 1H), 4.06 (dd, *J* = 14.8, 6.9 Hz, 1H), 3.97 (dd, *J* = 14.8, 6.9 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.0, 138.5, 135.0, 134.7, 129.3,

129.1, 128.0, 127.2, 65.3, 55.2. **IR** (neat): 3094, 3064, 3038, 2974, 4502, 1457, 1402, 1308, 1281, 1223, 1170, 1126, 1088, 1047, 1014, 917, 858, 801, 777, 753, 723, 693, 662 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{12}H_{11}ClNaO_2S_2$ ($[M+Na]^+$) 308.9781, found 308.9780.

2-bromo-5-((2-chloro-2-phenylethyl)sulfonyl)thiophene (10aj)

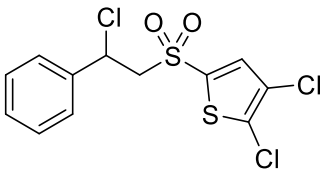


Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 5-bromothiophene-2-sulfonyl chloride (130.8 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as an orange solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	169.5 mg (464 µmol, 93%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	176.5 mg (483 µmol, 97%)

mp: 77 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.50, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.31 (s, 5H), 7.19 (d, *J* = 4.1 Hz, 1H), 6.96 (d, *J* = 4.1 Hz, 1H), 5.35 (t, *J* = 7.0 Hz, 1H), 4.04 (dd, *J* = 14.9, 7.0 Hz, 1H), 3.95 (dd, *J* = 14.9, 7.0 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.7, 138.3, 135.2, 131.0, 129.4, 129.1, 127.3, 123.1, 65.3, 55.1. **IR** (neat): 3105, 3075, 2980, 2937, 1495, 1457, 1384, 1320, 1271, 1211, 1189, 1129, 1090, 1025, 977, 921, 861, 798, 753, 708, 698, 657 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{12}H_{10}BrClNaO_2S_2$ ($[M+Na]^+$) 386.8886, found 386.8888.

2,3-dichloro-5-((2-chloro-2-phenylethyl)sulfonyl)thiophene (10ak)



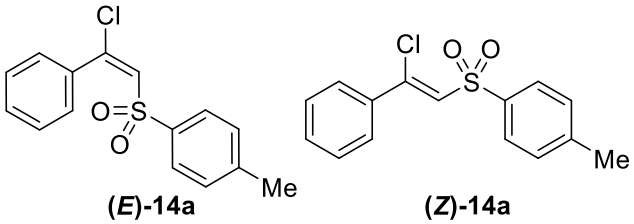
Following general procedure ***GP-I*** using styrene (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 4,5-dichlorothiophene-2-sulfonyl chloride (125.8 mg, 0.5 mmol, 1.0 equiv), the corresponding [Cu]-photocatalyst (indicated amount) at room temperature (25 °C) for the indicated time yielded the given amount of the title compound as a yellowish solid after flash column chromatography (hexanes / EtOAc 5:1).

$[Cu(dap)_2]Cl$[25,26]	(4.4 mg, 5.0 µmol, 1.0 mol%)	24 h	171.0 mg (481 µmol, 96%)
$[Cu(dap)Cl_2]$[25,26]	(2.6 mg, 5.0 µmol, 1.0 mol%)	24 h	176.6 mg (497 µmol, 99%)

mp: 115 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.60, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.37 – 7.28 (m, 5H), 7.04 (s, 1H), 5.34 (dd, *J* = 7.8, 6.5 Hz, 1H), 4.10 – 3.95 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 137.9, 136.0, 134.4, 134.0, 129.7, 129.1, 127.4, 125.6,

65.2, 55.0. **IR** (neat): 3101, 2977, 2908, 1498, 1457, 1398, 1320, 1271, 1219, 1167, 1149, 1121, 1029, 913, 880, 849, 794, 781, 763, 690 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{12}H_{13}Cl_3NO_2S_2$ ($[M+NH_4]^+$) 371.9448, found 371.9454.

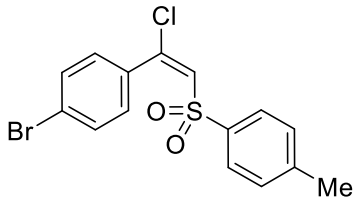
1-((2-chloro-2-phenylvinyl)sulfonyl)-4-methylbenzene (14a)



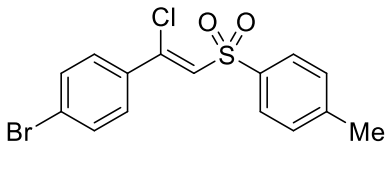
Following general procedure ***GP-I*** using ethynylbenzene (54.9 µL, 51.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzene-sulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 67.0 mg (229 µmol, 46%) of the title compound (*E*)-**14a** as a yellowish solid and 64.4 mg (220 µmol, 44%) of the title compound (*Z*)-**14a** as a yellowish solid after flash column chromatography (hexanes / EtOAc 20:1 to 10:1) (Overall: Yield = 90%, d.r. (*E*:*Z*) = 51:49).[25,26] Following general procedure ***GP-I*** using ethynylbenzene (54.9 µL, 51.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)Cl_2]$ (2.6 mg, 5.0 µmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 81.9 mg (280 µmol, 56%) of the title compound (*E*)-**14a** as a yellowish solid and 46.1 mg (157 µmol, 31%) of the title compound (*Z*)-**14a** as a yellowish solid after flash column chromatography (hexanes / EtOAc 20:1 to 10:1) (Overall: Yield = 90%, d.r. (*E*:*Z*) = 51:49).[25,26] Stereochemistry was assigned in analogy to literature.[27] **mp** ((*E*)-**14a**): 102 °C. **mp** ((*Z*)-**14a**): 119 °C. $\mathbf{R_f}$ ((*E*)-**14a**, hexanes / EtOAc 5:1) = 0.48, Staining: UV, Vanillin. $\mathbf{R_f}$ ((*Z*)-**14a**, hexanes / EtOAc 5:1) = 0.38, Staining: UV, Vanillin. **^{1}H-NMR** ((*E*)-**14a**, 300 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 8.7 Hz, 2H), 7.46 – 7.33 (m, 5H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.93 (s, 1H), 2.39 (s, 3H). **^{13}C-NMR** ((*E*)-**14a**, 75 MHz, $CDCl_3$) δ = 148.0, 144.7, 137.6, 134.4, 131.1, 130.7, 129.7, 128.9, 128.1, 127.8, 21.7. **^{1}H-NMR** ((*Z*)-**14a**, 300 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 8.3 Hz, 2H), 7.67 – 7.54 (m, 2H), 7.50 – 7.31 (m, 5H), 7.13 (s, 1H), 2.44 (s, 3H). **^{13}C-NMR** ((*Z*)-**14a**, 75 MHz, $CDCl_3$) δ = 146.0, 144.9, 137.9, 135.2, 131.7, 129.8, 128.9, 128.3, 128.0, 127.3, 21.8. **IR** ((*E*)-**14a**, neat): 3042, 1592, 1580, 1491, 1443, 1402, 1323, 1297, 1148, 1081, 1033, 1027, 928, 898, 801, 795, 768, 723, 690, 650 cm^{-1}. **IR** ((*Z*)-**14a**, neat): 3060, 2922, 1592, 1561, 1491, 1443, 1391, 1312, 1287, 1238, 1207, 1182, 1141, 1081, 1009, 933, 917, 813, 789, 746, 707, 678 cm^{-1}. **HRMS** (ESI) m/z calculated for (*E*)-**14a** $C_{15}H_{14}ClO_2S$ ($[M+H]^+$) 293.0398, found

293.0399. **HRMS** (ESI) m/z calculated for (*Z*)-**14a** $C_{15}H_{13}ClNaO_2S$ ($[M+Na]^+$) 315.0217, found 315.0219.

1-bromo-4-(1-chloro-2-tosylvinyl)benzene (14b)



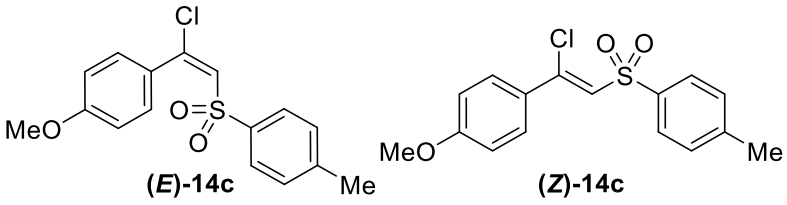
(*E*)-14b



(*Z*)-14b

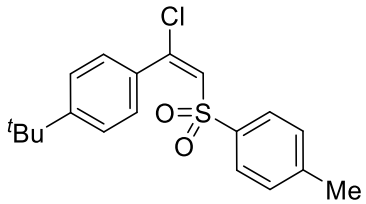
Following general procedure ***GP-I*** using 1-bromo-4-ethynylbenzene (90.5 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 μmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 93.8 mg (252 μmol, 50%) of the title compound (*E*)-**14b** as a white solid and 86.5 mg (233 μmol, 47%) of the title compound (*Z*)-**14b** as a white solid after flash column chromatography (hexanes / EtOAc 20:1 to 10:1) (Overall: Yield = 97%, d.r. (*E*:*Z*) = 52:48).[25,26] Following general procedure ***GP-I*** using 1-bromo-4-ethynylbenzene (90.5 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)Cl_2]$ (2.6 mg, 5.0 μmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 89.9 mg (242 μmol, 48%) of the title compound (*E*)-**14b** as a white solid and 82.9 mg (223 μmol, 45%) of the title compound (*Z*)-**14b** as a white solid after flash column chromatography (hexanes / EtOAc 20:1 to 10:1) (Overall: Yield = 93%, d.r. (*E*:*Z*) = 52:48).[25,26] Stereochemistry was assigned in analogy to literature.[28] **mp** ((*E*)-**14b**): 101 °C. **mp** ((*Z*)-**14b**): 143 °C. $\mathbf{R_f}$ ((*E*)-**14b**, hexanes / EtOAc 5:1) = 0.53, Staining: UV, Vanillin. $\mathbf{R_f}$ ((*Z*)-**14b**, hexanes / EtOAc 5:1) = 0.45, Staining: UV, Vanillin. **^{1}H-NMR** ((*E*)-**14b**, 300 MHz, $CDCl_3$) δ = 7.56 – 7.48 (m, 4H), 7.30 – 7.24 (m, 4H), 6.91 (s, 1H), 2.42 (s, 3H). **^{13}C-NMR** ((*E*)-**14b**, 75 MHz, $CDCl_3$) δ = 146.4, 145.1, 137.5, 133.3, 131.5, 131.4, 130.5, 129.9, 127.9, 125.5, 21.8. **^{1}H-NMR** ((*Z*)-**14b**, 300 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.07 (s, 1H), 2.40 (s, 3H). **^{13}C-NMR** ((*Z*)-**14b**, 75 MHz, $CDCl_3$) δ = 145.1, 144.7, 137.7, 134.2, 132.2, 129.9, 128.7, 128.5, 128.4, 126.4, 21.8. **IR** ((*E*)-**14b**, neat): 3049, 2922, 1621, 1600, 1595, 1483, 1460, 1394, 1320, 12920, 1193, 1144, 1085, 1070, 1014, 967, 902, 827, 812, 795, 746, 700, 661 cm^{-1}. **IR** ((*Z*)-**14b**, neat): 3086, 3047, 2926, 1580, 1554, 1487, 1394, 1316, 1294, 1220, 1215, 1141, 1081, 1010, 958, 924, 805, 775, 702, 691 cm^{-1}. **HRMS** (ESI) m/z calculated for (*E*)-**14b** $C_{15}H_{16}BrClNO_2S$ ($[M+NH_4]^+$) 387.9768, found 387.9769. **HRMS** (ESI) m/z calculated for (*Z*)-**14b** $C_{15}H_{13}BrClO_2S$ ($[M+H]^+$) 370.9503, found 370.9505.

1-((2-chloro-2-(4-methoxyphenyl)vinyl)sulfonyl)-4-methylbenzene (14c)

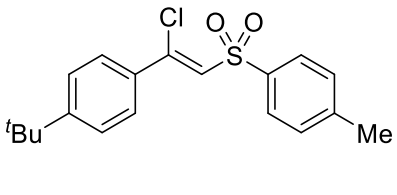


Following general procedure ***GP-I*** using 1-ethynyl-4-methoxybenzene (66.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 70.1 mg (217 µmol, 43%) of the title compound (*E*)-**14c** as a yellowish solid and 85.6 mg (265 µmol, 53%) of the title compound (*Z*)-**14c** as a yellowish solid after flash column chromatography (hexanes / EtOAc 20:1 to 7:1) (Overall: Yield = 96%, d.r. (*E*:*Z*) = 45:55).[25,26] Following general procedure ***GP-I*** using 1-ethynyl-4-methoxybenzene (66.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)Cl_2]$ (2.6 mg, 5.0 µmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 98.2 mg (304 µmol, 61%) of the title compound (*E*)-**14c** as a yellowish solid and 57.7 mg (179 µmol, 36%) of the title compound (*Z*)-**14c** as a yellowish solid after flash column chromatography (hexanes / EtOAc 20:1 to 7:1) (Overall: Yield = 97%, d.r. (*E*:*Z*) = 63:37).[25,26] Stereochemistry was assigned in analogy to literature.[27] **mp** ((*E*)-**14c**): 77 °C. **mp** ((*Z*)-**14c**): 71 °C. $\mathbf{R_f}$ ((*E*)-**14c**, hexanes / EtOAc 5:1) = 0.30, Staining: UV, Vanillin. $\mathbf{R_f}$ ((*Z*)-**14c**, hexanes / EtOAc 5:1) = 0.15, Staining: UV, Vanillin. **^{1}H-NMR** ((*E*)-**14c**, 400 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.69 (s, 1H), 3.70 (s, 3H), 2.26 (s, 3H). **^{13}C-NMR** ((*E*)-**14c**, 101 MHz, $CDCl_3$) δ = 161.8, 148.1, 144.6, 138.0, 131.1, 129.8, 129.7, 127.8, 126.6, 113.5, 55.5, 21.7. **^{1}H-NMR** ((*Z*)-**14c**, 400 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.04 (s, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 2.43 (s, 3H). **^{13}C-NMR** ((*Z*)-**14c**, 101 MHz, $CDCl_3$) δ = 162.5, 145.9, 144.7, 138.3, 129.8, 129.0, 128.3, 127.3, 125.6, 114.3, 55.6, 21.8. **IR** ((*E*)-**14c**, neat): 3042, 2967, 2937, 2840, 1599, 1506, 1461, 1443, 1297, 1249, 1178, 1141, 1085, 1021, 924, 898, 819, 809, 797, 783, 700, 678, 650 cm^{-1}. **IR** ((*Z*)-**14c**, neat): 3049, 2977, 2933, 2844, 1599, 1587, 1560, 1506, 1450, 1421, 1301, 1289, 1260, 1178, 1131, 1081, 1029, 950, 928, 828, 807, 760, 719, 702, 675, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for (*E*)-**14c** $C_{16}H_{15}ClNaO_3S$ ($[M+Na]^+$) 345.0323, found 345.0323. **HRMS** (ESI) m/z calculated for (*Z*)-**14c** $C_{16}H_{15}ClNaO_3S$ ($[M+Na]^+$) 345.0323, found 345.0326.

1-(*tert*-butyl)-4-(1-chloro-2-tosylvinyl)benzene (14d)



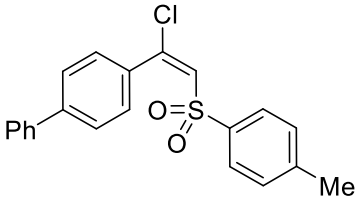
(*E*)-14d



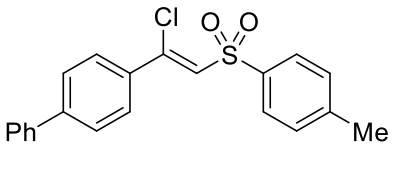
(*Z*)-14d

Following general procedure ***GP-I*** using 1-(*tert*-butyl)-4-ethynylbenzene (79.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), [Cu(dap)$_2$]Cl (4.4 mg, 5.0 µmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 46.6 mg (133 µmol, 27%) of the title compound (*E*)-**14d** as a yellowish oil and 113.5 mg (325 µmol, 65%) of the title compound (*Z*)-**14d** as a yellowish solid after flash column chromatography (hexanes / EtOAc 20:1 to 10:1) (Overall: Yield = 92%, d.r. (*E*:*Z*) = 29:71).[25,26] Following general procedure ***GP-I*** using 1-(*tert*-butyl)-4-ethynylbenzene (79.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), [Cu(dap)Cl$_2$] (2.6 mg, 5.0 µmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 49.1 mg (141 µmol, 28%) of the title compound (*E*)-**14d** as a yellowish oil and 109.3 mg (313 µmol, 62%) of the title compound (*Z*)-**14d** as a yellowish solid after flash column chromatography (hexanes / EtOAc 20:1 to 10:1) (Overall: Yield = 90%, d.r. (*E*:*Z*) = 31:69). Stereochemistry was assigned in analogy to other substrates. **mp** ((*Z*)-**14d**): 153 °C. **R$_f$** ((*E*)-**14d**, hexanes / EtOAc 5:1) = 0.53, Staining: UV, Vanillin. **R$_f$** ((*Z*)-**14d**, hexanes / EtOAc 5:1) = 0.43, Staining: UV, Vanillin. **^{1}H-NMR** ((*E*)-**14d**, 300 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.15 (d, *J* = 8.3 Hz, 1H), 6.92 (s, 1H), 2.37 (s, 4H), 1.33 (s, 9H). **^{13}C-NMR** ((*E*)-**14d**, 75 MHz, $CDCl_3$) δ = 154.3, 148.3, 144.5, 137.6, 131.4, 130.9, 129.6, 128.9, 127.9, 125.0, 35.0, 31.3, 21.7. **^{1}H-NMR** ((*Z*)-**14d**, 300 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.12 (s, 1H), 2.44 (s, 3H), 1.30 (s, 9H). **^{13}C-NMR** ((*Z*)-**14d**, 75 MHz, $CDCl_3$) δ = 155.5, 146.1, 144.8, 138.1, 132.3, 129.8, 128.3, 127.1, 127.0, 125.9, 35.0, 31.2, 21.8. **IR** ((*E*)-**14d**, neat): 3042, 2960, 2919, 2870, 1595, 1506, 1461, 1402, 1377, 1320, 1293, 1200, 1173, 1167, 1141, 1100, 1085, 1018, 954, 910, 835, 805, 757, 720, 650 cm^{-1}. **IR** ((*Z*)-**14d**, neat): 3045, 2967, 2870, 1580, 1551, 1510, 1480, 1405, 1367, 1312, 1290, 1374, 1238, 1201, 1144, 1081, 1021, 932, 842, 807, 790, 738, 710, 662 cm^{-1}. **HRMS** (ESI) m/z calculated for (*E*)-**14d** $C_{19}H_{21}ClNaO_2S$ ([M+Na]$^+$) 371.0843, found 371.0849. **HRMS** (ESI) m/z calculated for (*Z*)-**14d** $C_{19}H_{22}ClO_2S$ ([M+H]$^+$) 366.1289, found 366.1295.

4-(1-chloro-2-tosylvinyl)-1,1'-biphenyl (14e)



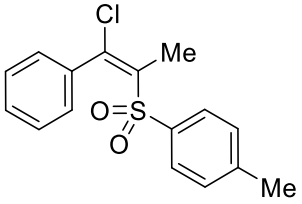
(*E*)-**14e**



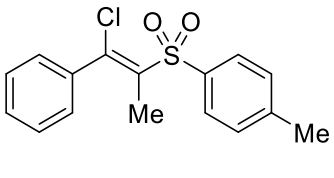
(*Z*)-**14e**

Following general procedure ***GP-I*** using 4-ethynyl-1,1'-biphenyl (89.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzene-sulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), [Cu(dap)$_2$]Cl (4.4 mg, 5.0 μmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 63.3 mg (172 μmol, 34%) of the title compound (*E*)-**14e** as a yellowish solid and 99.0 mg (268 μmol, 54%) of the title compound (*Z*)-**14e** as a yellowish solid after flash column chromatography (hexanes / EtOAc 20:1 to 10:1) (Overall: Yield = 88%, d.r. (*E*:*Z*) = 39:61).[25,26] Following general procedure ***GP-I*** using 4-ethynyl-1,1'-biphenyl (89.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), [Cu(dap)Cl$_2$] (2.6 mg, 5.0 μmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 52.8 mg (143 μmol, 29%) of the title compound (*E*)-**14e** as a yellowish solid and 112.3 mg (305 μmol, 61%) of the title compound (*Z*)-**14e** as a yellowish solid after flash column chromatography (hexanes / EtOAc 20:1 to 10:1) (Overall: Yield = 90%, d.r. (*E*:*Z*) = 32:68).[25,26] Stereochemistry was assigned in analogy to other substrates. **mp** ((*E*)-**14e**): 121 °C. **mp** ((*Z*)-**14e**): 185 °C. **R$_f$** ((*E*)-**14e**, hexanes / EtOAc 5:1) = 0.45, Staining: UV, Vanillin. **R$_f$** ((*Z*)-**14e**, hexanes / EtOAc 5:1) = 0.33, Staining: UV, Vanillin. **^{1}H-NMR** ((*E*)-**14e**, 300 MHz, $CDCl_3$) δ = 7.63 – 7.54 (m, 6H), 7.51 – 7.40 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.95 (s, 1H), 2.40 (s, 3H). **^{13}C-NMR** ((*E*)-**14e**, 75 MHz, $CDCl_3$) δ = 147.8, 144.8, 143.7, 140.1, 137.7, 133.2, 131.0, 129.8, 129.6, 129.1, 128.2, 128.0, 127.3, 126.8, 21.8. **^{1}H-NMR** ((*Z*)-**14e**, 300 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.3 Hz, 2H), 7.70 – 7.57 (m, 6H), 7.50 – 7.35 (m, 5H), 7.20 (s, 1H), 2.46 (s, 3H). **^{13}C-NMR** ((*Z*)-**14e**, 75 MHz, $CDCl_3$) δ = 145.7, 144.9, 144.5, 139.5, 138.0, 133.9, 129.8, 129.1, 128.4, 128.4, 127.8, 127.6, 127.5, 127.2, 21.8. **IR** ((*E*)-**14e**, neat): 3068, 2922, 1599, 1484, 1446, 1402, 1323, 1293, 1211, 1193, 1144, 1081, 1018, 1001, 951, 895, 842, 820, 790, 753, 723, 690, 650 cm^{-1}. **IR** ((*Z*)-**14e**, neat): 3049, 1599, 1573, 1550, 1484, 1446, 1402, 1316, 1298, 1241, 1204, 1141, 1081, 1018, 991, 924, 846, 813, 757, 690, 681, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for (*E*)-**14e** $C_{21}H_{18}ClO_2S$ ($[M+H]^+$) 369.0711, found 369.0712. **HRMS** (ESI) m/z calculated for (*Z*)-**14e** $C_{21}H_{17}ClNaO_2S$ ($[M+Na]^+$) 391.0530, found 391.0530.

1-((1-chloro-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene (14f)



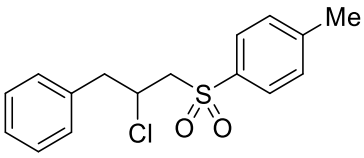
(*E*)-14f



(*Z*)-14f

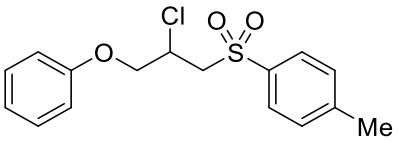
Following general procedure ***GP-I*** using prop-1-yn-1-ylbenzene (62.6 µL, 58.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzene sulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 45.9 mg (150 µmol, 30%) of the title compound (*E*)-**14f** as a white solid and 24.7 mg (81 µmol, 16%) of the title compound (*Z*)-**14f** as a white solid after flash column chromatography (hexanes / EtOAc 20:1 to 10:1) (Overall: Yield = 46%, d.r. (*E*:*Z*) = 65:35).[25,26] Following general procedure ***GP-I*** using prop-1-yn-1-ylbenzene (62.6 µL, 58.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)Cl_2]$ (2.6 mg, 5.0 µmol, 1.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 24 h yielded 41.5 mg (135 µmol, 27%) of the title compound (*E*)-**14f** as a white solid and 27.6 mg (90 µmol, 18%) of the title compound (*Z*)-**14f** as a white solid after flash column chromatography (hexanes / EtOAc 20:1 to 10:1) (Overall: Yield = 45%, d.r. (*E*:*Z*) = 60:40).[25,26] Stereochemistry was assigned in analogy to literature.[28] **mp** ((*E*)-**14f**): 103 °C. **mp** ((*Z*)-**14f**): 49 °C. $\mathbf{R_f}$ ((*E*)-**14f**, hexanes / EtOAc 5:1) = 0.48, Staining: UV, Vanillin. $\mathbf{R_f}$ ((*Z*)-**14f**, hexanes / EtOAc 5:1) = 0.38, Staining: UV, Vanillin. **^{1}H-NMR** ((*E*)-**14f**, 300 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.24 – 7.14 (m, 4H), 2.39 (s, 3H), 2.35 (s, 3H). **^{13}C-NMR** ((*E*)-**14f**, 75 MHz, $CDCl_3$) δ = 144.3, 144.1, 137.9, 137.4, 137.1, 129.6, 129.5, 128.9, 128.0, 21.7, 18.2. **^{1}H-NMR** ((*Z*)-**14f**, 300 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.34 (m, 6H), 7.32 – 7.26 (m, 2H), 2.47 (s, 3H), 2.18 (s, 3H). **^{13}C-NMR** ((*Z*)-**14f**, 75 MHz, $CDCl_3$) δ = 144.7, 139.0, 137.9, 137.7, 137.5, 129.9, 129.7, 128.7, 128.3, 128.2, 21.8, 19.1. **IR** ((*E*)-**14f**, neat): 3058, 3021, 2926, 2855, 1633, 1595, 1487, 1443, 1402, 1312, 1291, 1223, 1156, 1120, 1087, 1007, 913, 883, 839, 809, 772, 743, 697, 671, 650 cm^{-1}. **IR** ((*Z*)-**14f**, neat): 3060, 2963, 2926, 1595, 1491, 1443, 1400, 1397, 1316, 1230, 1197, 1156, 1118, 1077, 1006, 924, 902, 842, 813, 775, 746, 697, 667 cm^{-1}. **HRMS** (ESI) m/z calculated for (*E*)-**14f** $C_{16}H_{19}ClNO_2S$ ($[M+NH_4]^+$) 324.0820, found 324.0822. **HRMS** (ESI) m/z calculated for (*Z*)-**14f** $C_{16}H_{15}ClNaO_2S$ ($[M+Na]^+$) 329.0373, found 329.0379.

1-((2-chloro-3-phenylpropyl)sulfonyl)-4-methylbenzene (10at//9l)



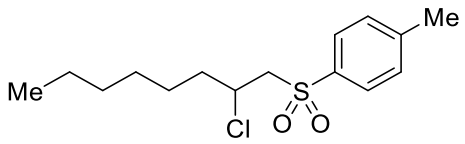
Following general procedure ***GP-II*** using allylbenzene (132.4 µL, 118.2 mg, 1.0 mmol, 2.0 equiv), 4-methylbenzene-sulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), Na_2CO_3 (53.0 mg, 0.5 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (2.0 mL, 0.25 M) at room temperature (25 °C) for 48 h yielded 9.9 mg (32 µmol, 6%) of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 9:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1) = 0.22, Staining: UV, $KMnO_4$. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 8.3 Hz, 2H), 7.40 – 7.19 (m, 7H), 4.50 (dq, *J* = 7.7, 6.3 Hz, 1H), 3.53 (d, *J* = 6.3 Hz, 2H), 3.29 (dd, *J* = 14.3, 5.5 Hz, 1H), 3.10 (dd, *J* = 14.3, 7.7 Hz, 1H), 2.45 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.3, 136.4, 135.9, 130.1, 129.7, 128.6, 128.2, 127.4, 62.4, 54.5, 43.9, 21.8. **IR** (neat): 3042, 2989, 2911, 1595, 1495, 1454, 1390, 1342, 1297, 1185, 1137, 1088, 895, 820, 768, 701 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{21}ClNO_2S$ ($[M+NH_4]^+$) 326.0976, found 326.0980.

1-((2-chloro-3-phenoxypropyl)sulfonyl)-4-methylbenzene (10bh//9m)



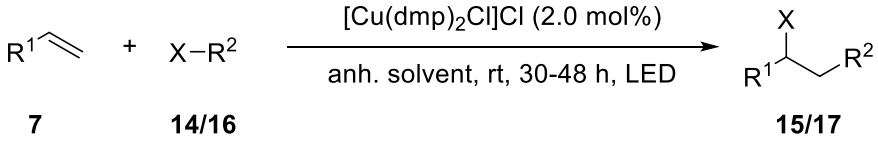
Following general procedure ***GP-II*** using (allyloxy)benzene (137.2 µL, 134.2 mg, 1.0 mmol, 2.0 equiv), 4-methyl-benzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), Na_2CO_3 (53.0 mg, 0.5 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (2.0 mL, 0.25 M) at room temperature (25 °C) for 48 h yielded 11.5 mg (35 µmol, 7%) of the title compound as colorless oil after flash column chromatography (hexanes / EtOAc 9:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1) = 0.41, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.08 – 6.92 (m, 1H), 6.85 (dd, *J* = 8.8, 1.1 Hz, 2H), 4.60 (ddd, *J* = 11.3, 6.6, 5.5 Hz, 1H), 4.25 (dd, *J* = 10.3, 4.8 Hz, 1H), 4.19 (dd, *J* = 10.3, 5.4 Hz, 1H), 3.88 (dd, *J* = 14.8, 6.0 Hz, 1H), 3.58 (dd, *J* = 14.8, 6.7 Hz, 1H), 2.43 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 157.8, 145.5, 136.4, 130.2, 129.7, 128.3, 121.9, 114.9, 70.2, 60.1, 51.3, 21.8. **IR** (neat): 3042, 2930, 1599, 1495, 1461, 1398, 1290, 1238, 1141, 1085, 1044, 928, 842, 816, 753, 690 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{16}H_{17}ClO_3S$ ($[M]^{\bullet+}$) 324.0581, found 324.0588.

1-((2-chlorooctyl)sulfonyl)-4-methylbenzene (10bj//9n)



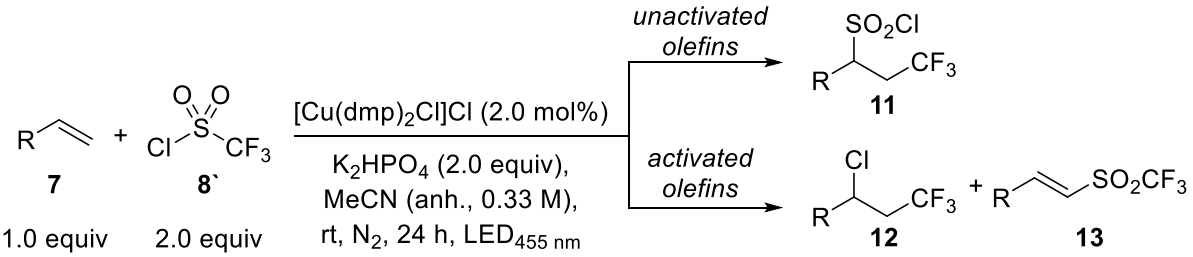
Following general procedure ***GP-II*** using oct-1-en (157.0 µL, 112.2 mg, 1.0 mmol, 2.0 equiv), 4-methyl-benzenesulfonyl chloride (95.3 mg, 0.5 mmol, 1.0 equiv), Na_2CO_3 (53.0 mg, 0.5 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (2.0 mL, 0.25 M) at room temperature (25 °C) for 48 h yielded 22.9 mg (76 µmol, 15%) of the title compound as colorless oil after flash column chromatography (hexanes / EtOAc 9:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1) = 0.68, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.80 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 4.30 (dtd, *J* = 8.9, 6.3, 3.8 Hz, 1H), 3.56 (dd, *J* = 14.6, 6.2 Hz, 1H), 3.45 (dd, *J* = 14.6, 6.5 Hz, 1H), 2.46 (s, 3H), 1.97 (dddd, *J* = 14.1, 9.9, 5.8, 3.9 Hz, 1H), 1.81 – 1.69 (m, 1H), 1.54 – 1.36 (m, 2H), 1.34 – 1.22 (m, 6H), 0.92 – 0.84 (m, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 145.3, 136.7, 130.1, 128.3, 63.7, 54.8, 38.1, 31.7, 28.6, 25.9, 22.7, 21.8, 14.2. **IR** (neat): 2930, 2859, 1595, 1495, 1461, 1402, 1305, 1141, 1088, 1040, 924, 891, 842, 816, 757, 693 cm^{-1}. **HRMS** (APCI) m/z calculated for $C_{15}H_{27}ClNO_2S$ ($[M+NH_4]^+$) 320.1446, found 320.1450.

General procedure for photochemical "standard ATRA reaction" (Chapter 3) (*GP-III*)



A flame-dried Schlenk tube (10.0 mL size, Figure 3, D) equipped with a magnetic stirring bar (Figure 3, E) was charged with halide **14/16**, $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and dissolved in anhydrous solvent, sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, alkene **7** was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet (Figure 3, C) for a glass rod (Figure 3, B), through which irradiation with LED (Figure 3, A) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 30-48 h. The reaction was monitored by TLC. Finally, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (eluent hexanes / EtOAc).

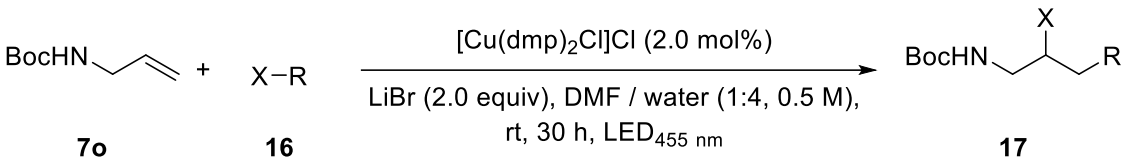
General procedure for photochemical trifluoromethylchlorosulfonylation of unactivated alkenes and chlorotrifluoromethylation of activated alkenes (Chapter 3) (*GP-IV*)



A flame-dried Schlenk tube (10.0 mL size, Figure 3, D) equipped with a magnetic stirring bar (Figure 3, E) was charged with K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and dissolved in anhydrous MeCN (1.5 mL, 0.33 M) sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, alkene **7** (0.5 mmol, 1.0 equiv) and trifyl chloride (**8`**) (106.5 µL, 168.5 mg, 1.0 mmol, 2.0 equiv) were added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet (Figure 3, C) for a glass rod (Figure 3, B), through which irradiation with a 455 nm high power LED (Figure 3, A) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water and the crude mixture was extracted three times with DCM. The combined organic

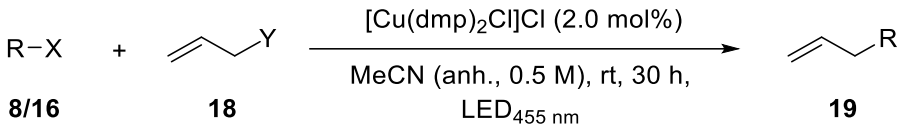
layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (eluent hexanes / EtOAc).

General procedure for photo-ATRA reactions with *N*-Boc allylamine (Chapter 3) (*GP-V*)



A Schlenk tube (10.0 mL size, Figure 3, D) equipped with a magnetic stirring bar (Figure 3, E) was charged with *N*-Boc allylamine (**7o**) (78.6 mg, 0.5 mmol, 1.0 equiv), halide **16** (1.0 mmol, 2.0 equiv), LiBr (86.6 mg, 1.0 mmol, 2.0 equiv), [Cu(dmp)$_2$Cl]Cl (5.5 mg, 10.0 µmol, 2.0 mol%) and dissolved in a DMF (0.2 mL)/water (0.8 mL) mixture (1:4, 1.0 mL, 0.5 M) sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. The screw-cap was replaced with a Teflon sealed inlet (Figure 3, C) for a glass rod (Figure 3, B), through which irradiation with a 455 nm high power LED (Figure 3, A) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 30 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was saturated by addition of brine solution and the aqueous phase was extracted three times with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo and the crude residue was purified by flash column chromatography on silica gel (eluent hexanes / EtOAc).

General procedure for photochemical allylation reactions (Chapter 3) (*GP-VI*)



A flame-dried Schlenk tube (10.0 mL size, Figure 3, D) equipped with a magnetic stirring bar (Figure 3, E) was charged with halide **8/16**, [Cu(dmp)$_2$Cl]Cl (5.5 mg, 10.0 µmol, 2.0 mol%) and dissolved in anhydrous MeCN (2.0 mL, 0.5 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, allyl reagent **18** was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet (Figure 3, C) for a glass rod (Figure 3, B), through which irradiation with a 455 nm power LED (Figure 3, A) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 30 h. The reaction was monitored by

TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (eluent hexanes / EtOAc).

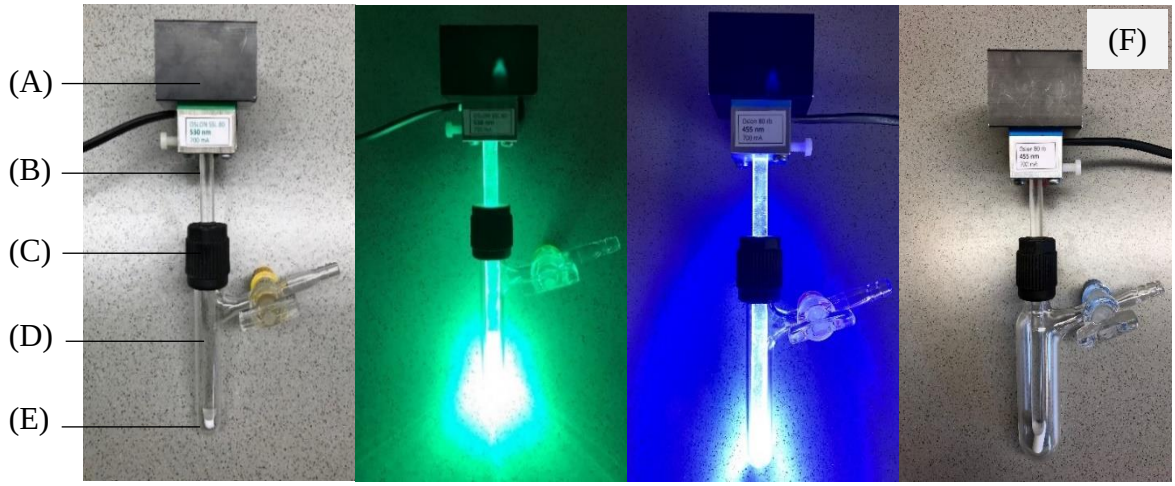
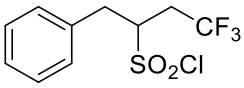


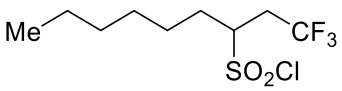
Figure 3. Irradiation setup for **GP-III** to **GP-VI**. (A) LED; (B) glass rod (used as a light conductor); (C) Teflon adapter; (D) Schlenk tube (10.0 mL size); (E) Teflon-coated magnetic stirring bar. (F) Schlenk tube (30.0 mL size) for upscaling experiments.

4,4,4-trifluoro-1-phenylbutane-2-sulfonyl chloride (11a)[29]



Following general procedure ***GP-IV*** using allylbenzene (**7l**) (66.2 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), trifyl chloride (**8`**) (106.5 µL, 168.5 mg, 1.0 mmol, 2.0 equiv), K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.5 mL, 0.33 M) at room temperature (25 °C) for 24 h yielded 136.8 mg (477 µmol, 95%) of the title compound as colorless oil after flash column chromatography (hexanes / EtOAc 9:1). Spectral data are in agreement with those reported in literature.[29] $\mathbf{R_f}$ (hexanes / EtOAc 9:1) = 0.73, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.32 (m, 3H), 7.30 – 7.22 (m, 2H), 4.07 (qt, *J* = 9.6, 4.7 Hz, 1H), 3.58 (dd, *J* = 14.9, 5.6 Hz, 1H), 3.27 (dd, *J* = 14.9, 6.9 Hz, 1H), 3.14 – 2.96 (m, 1H), 2.76 – 2.58 (m, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 133.9, 129.5, 129.2, 128.1, 124.8 (q, *J* = 278.0 Hz), 71.0 (q, *J* = 2.4 Hz), 36.2, 34.0 (q, *J* = 31.1 Hz). **^{19}F-NMR** (376 MHz, $CDCl_3$) δ = -63.95 (s, 3F).

1,1,1-trifluorononane-3-sulfonyl chloride (11b)[29]

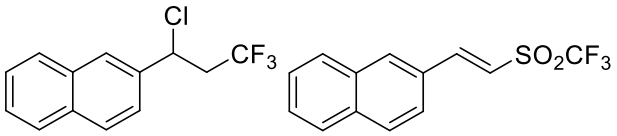


Following general procedure ***GP-IV*** using oct-1-en (**7n**) (66.2 µL, 56.1 mg, 0.5 mmol, 1.0 equiv), trifyl chloride (**8`**) (106.5 µL, 168.5 mg, 1.0 mmol, 2.0 equiv), K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$

(5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.5 mL, 0.33 M) at room temperature (25 °C) for 24 h yielded 133.4 mg (475 µmol, 95%) of the title compound as colorless oil after flash column chromatography (hexanes / EtOAc 9:1). Spectral data are in agreement with those reported in literature.[29] **R_f** (hexanes / EtOAc 9:1) = 0.34, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 3.76 (dtd, *J* = 8.6, 5.7, 2.8 Hz, 1H), 3.07 (dqd, *J* = 15.6, 10.6, 2.8 Hz, 1H), 2.59 (ddt, *J* = 18.3, 15.6, 9.7 Hz, 1H), 2.20 (ddt, *J* = 15.8, 10.2, 6.1 Hz, 1H), 2.09 – 1.94 (m, 1H), 1.57 (dddd, *J* = 12.1, 10.2, 6.8, 5.0 Hz, 2H), 1.41 – 1.27 (m, 6H), 0.93 – 0.86 (m, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 24.92 (d, *J* = 277.9 Hz), 69.98 (q, *J* = 2.6 Hz), 34.66 (q, *J* = 30.8 Hz), 31.24, 30.42, 28.78, 25.92, 22.44, 13.95. **^{19}F-NMR** (376 MHz, $CDCl_3$) δ = -64.26 (s, 3F).

2-(1-chloro-3,3,3-trifluoropropyl)naphthalene (12a)[31,30]

(*E*)-2-(2-((trifluoromethyl)sulfonyl)vinyl)naphthalene (13a)[30]

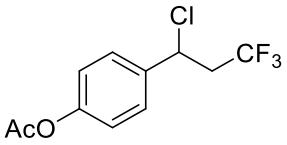


12a **13a**

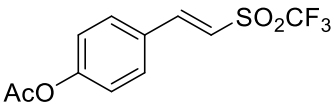
Following general procedure ***GP-IV*** using 2-vinylnaphthalene (77.1 mg, 0.5 mmol, 1.0 equiv), trifyl chloride (**8`**) (106.5 µL, 168.5 mg, 1.0 mmol, 2.0 equiv), K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.5 mL, 0.33 M) at room temperature (25 °C) for 24 h yielded 90.7 mg (351 µmol, 70%) of the title compound **12a** as colorless oil and 14.1 mg (49 µmol, 10%) of the title compound **13a** as white solid after flash column chromatography (hexanes / EtOAc 12:1 to 9:1). Spectral data for **12a**[31,30] and **13a**[30] are in agreement with those reported in literature. **R_f** (**12a**, hexanes / EtOAc 9:1) = 0.60, Staining: UV, $KMnO_4$. **^{1}H-NMR** (**12a**, 300 MHz, $CDCl_3$) δ = 8.08 – 7.77 (m, 4H), 7.75 – 7.44 (m, 3H), 5.32 (t, *J* = 7.1 Hz, 1H), 3.24 – 2.89 (m, 2H). **^{13}C-NMR** (**12a**, 75 MHz, $CDCl_3$) δ = 136.9, 133.5, 133.1, 129.3, 128.3, 127.9, 127.0, 126.9, 126.8 (q, *J* = 277.9, 277.5 Hz), 126.3, 124.0, 55.3 (q, *J* = 3.4 Hz), 43.8 (q, *J* = 28.3 Hz). **^{19}F-NMR** (**12a**, 282 MHz, $CDCl_3$) δ = -64.40 (s, 3F). **R_f** (**13a**, hexanes / EtOAc 9:1) = 0.35, Staining: UV, $KMnO_4$; **^{1}H-NMR** (**13a**, 300 MHz, $CDCl_3$) δ = 8.09 – 8.01 (m, 2H), 7.96 – 7.86 (m, 3H), 7.70 – 7.54 (m, 3H), 6.92 (dd, *J* = 15.5, 0.9 Hz, 1H). **^{13}C-NMR** (**13a**, 75 MHz, $CDCl_3$) δ = 154.0, 135.5, 133.4, 133.0, 129.6, 129.3, 129.1, 128.7, 128.1, 127.6, 123.3, 122.0 (q, *J* = 324.9 Hz), 116.4. **^{19}F-NMR** (**13a**, 282 MHz, $CDCl_3$) δ = -79.20 (s, 3F).

4-(1-chloro-3,3,3-trifluoropropyl)phenyl acetate (12b)[31,32,30]

(*E*)-4-(2-((trifluoromethyl)sulfonyl)vinyl)phenyl acetate (13b)



12b

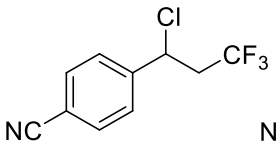


13b

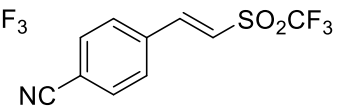
Following general procedure ***GP-IV*** using 4-vinylphenyl acetate (76.5 µL, 81.1 mg, 0.5 mmol, 1.0 equiv), trifyl chloride (**8`**) (106.5 µL, 168.5 mg, 1.0 mmol, 2.0 equiv), K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.5 mL, 0.33 M) at room temperature (25 °C) for 24 h yielded 114.7 mg (430 µmol, 86%) of the title compound **12b** as white solid and 16.8 mg (57 µmol, 11%) of the title compound **13b** as white solid after flash column chromatography (hexanes / EtOAc 12:1 to 9:1). Spectral data for **12b**[31,32,30] are in agreement with those reported in literature. $\mathbf{R_f}$ (**12b**, hexanes / EtOAc 9:1) = 0.53, Staining: UV, $KMnO_4$. **^{1}H-NMR** (**12b**, 400 MHz, $CDCl_3$) δ = 7.41 (d, *J* = 8.6 Hz, 2H), 7.12 (d, *J* = 8.6 Hz, 2H), 5.11 (t, *J* = 6.4 Hz, 1H), 3.06 – 2.78 (m, 2H), 2.30 (s, 3H). **^{13}C-NMR** (**12b**, 101 MHz, $CDCl_3$) δ = 169.3, 151.1, 137.4, 128.1, 126.2 (q, *J* = 277.9 Hz), 122.3, 54.2 (q, *J* = 3.4 Hz), 44.0 (q, *J* = 28.5 Hz), 21.2. **^{19}F-NMR** (**12b**, 376 MHz, $CDCl_3$) δ = -64.55 (s, 3F). **mp** (**13b**): 105 °C. $\mathbf{R_f}$ (**13b**, hexanes / EtOAc 9:1) = 0.33, Staining: UV, $KMnO_4$. **^{1}H-NMR** (**13b**, 400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 15.5 Hz, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 15.4 Hz, 1H), 2.33 (s, 3H). **^{13}C-NMR** (**13b**, 75 MHz, $CDCl_3$) δ = 168.9, 154.5, 152.7, 131.0, 128.9, 123.0, 121.4 (q, *J* = 321.3 Hz), 116.8, 21.3. **^{19}F-NMR** (**13b**, 376 MHz, $CDCl_3$) δ = -79.23 (s, 3F). **IR** (**13b**, neat): 3064, 1744, 1603, 1591, 1510, 1425, 1361, 1328, 1185, 1115, 1047, 1021, 988, 970, 921, 869, 823, 801, 793, 712. **HRMS** (**13b**, ESI) m/z calculated for $C_{11}H_{10}F_3O_4S$ ($[M+H]^+$) 295.0246, found 295.0247.

4-(1-chloro-3,3,3-trifluoropropyl)benzonitrile (12c) [31,32,30]

(*E*)-4-(2-((trifluoromethyl)sulfonyl)vinyl)benzonitrile (13c)



12c

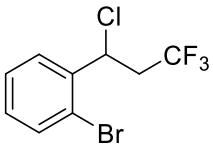


13c

Following general procedure ***GP-IV*** using 4-vinylbenzonitrile (64.6 mg, 0.5 mmol, 1.0 equiv), trifyl chloride (**8`**) (106.5 µL, 168.5 mg, 1.0 mmol, 2.0 equiv), K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.5 mL, 0.33 M) at room temperature (25 °C) for 24 h yielded 99.8 mg (427 µmol, 85%) of the title compound **12c** as colorless oil and 7.7 mg (29 µmol, 6%) of the title compound **13c** as white solid after flash column chromatography (hexanes / EtOAc 12:1 to 9:1). Spectral data for

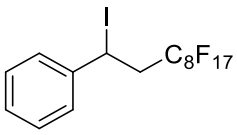
12c[31,32,30] are in agreement with those reported in literature. $\mathbf{R_f}$ (**12c**, hexanes / EtOAc 9:1) = 0.43, Staining: UV, $KMnO_4$. **^{1}H-NMR** (**12c**, 400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 5.12 (t, *J* = 7.1 Hz, 1H), 3.08 – 2.79 (m, 2H). **^{13}C-NMR** (**12c**, 101 MHz, $CDCl_3$) δ = 144.5, 132.9, 127.9, 125.9 (q, *J* = 278.5 Hz), 118.2, 113.2, 53.7 (q, *J* = 3.4 Hz), 43.6 (q, *J* = 28.7 Hz). **^{19}F-NMR** (**12c**, 376 MHz, $CDCl_3$) δ = -64.37 (s, 3F). **mp** (**13c**): 169 °C. $\mathbf{R_f}$ (**13c**, hexanes / EtOAc 9:1) = 0.20, Staining: UV, $KMnO_4$. **^{1}H-NMR** (**13c**, 400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 15.5 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 15.6 Hz, 1H). **^{13}C-NMR** (**13c**, 101 MHz, $CDCl_3$) δ = 151.0, 135.1, 133.2, 129.9, 121.3 (q, *J* = 324.4 Hz), 120.9, 117.7, 116.4. **^{19}F-NMR** (**13c**, 376 MHz, $CDCl_3$) δ = -78.79 (s, 3F). **IR** (**13c**, neat): 3101, 3090, 2233, 1610, 1588, 1510, 1416, 1357, 1319, 1301, 1189, 1107, 984, 865, 820, 798, 716. **HRMS** (**13c**, ESI) m/z calculated for $C_{10}H_7F_3NO_2S$ ($[M+H]^+$) 262.0144, found 262.0143.

1-bromo-2-(1-chloro-3,3,3-trifluoropropyl)benzene (12d)[31,32,30]



Following general procedure ***GP-IV*** using 1-bromo-2-vinylbenzene (62.7 µL, 91.5 mg, 0.5 mmol, 1.0 equiv), trifyl chloride (**8`**) (106.5 µL, 168.5 mg, 1.0 mmol, 2.0 equiv), K_2HPO_4 (174.2 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.5 mL, 0.33 M) at room temperature (25 °C) for 24 h yielded 134.4 mg (467 µmol, 93%) of the title compound as colorless oil after flash column chromatography (hexanes / EtOAc 9:1). Spectral data are in agreement with those reported in literature.[31,32,30] $\mathbf{R_f}$ (hexanes / EtOAc 9:1) = 0.33, Staining: UV, $KMnO_4$; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.60 (ddd, *J* = 8.2, 7.3, 1.5 Hz, 2H), 7.40 (td, *J* = 7.6, 1.3 Hz, 1H), 7.21 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 5.68 (dd, *J* = 7.8, 5.9 Hz, 1H), 2.98 – 2.81 (m, 2H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 152.2, 138.8, 133.4, 130.5, 128.6 (d, *J* = 32.9 Hz), 124.8 (q, *J* = 278.1 Hz), 122.6 , 53.4 (q, *J* = 3.6 Hz), 43.0 (q, *J* = 28.9 Hz); **^{19}F-NMR** (376 MHz, $CDCl_3$) δ = -64.54 (s, 3F).

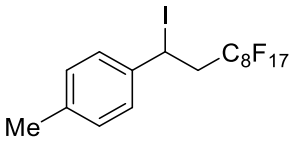
(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-iododecyl)benzene (15a)[33]



Following general procedure ***GP-III*** using styrene (**7a**) (57.3 µL, 54.1 mg, 0.5 mmol, 1.0 equiv), perfluorooctyl iodide (**14**) (264.1 µL, 546.0 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) and irradiation with green LED (λ_{max} = 530 nm) for 30 h yielded 308.3 mg (474 µmol, 95%) of the title compound as a white solid after

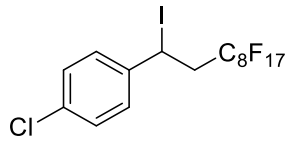
flash column chromatography (hexanes). Spectral data are in agreement with those reported in literature.[33] ***Gram-Scale***: This procedure can be also scaled-up to gram-quantities following ***GP-III*** in a flame-dried Schlenk tube (30.0 mL size, Figure 3, F) using styrene (**7a**) (0.57 mL, 520.8 mg, 5.0 mmol, 1.0 equiv), perfluorooctyl iodide (**14**) (2.64 mL, 5.46 g, 10.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (55.1 mg, 0.1 mmol, 2.0 mol%) and MeCN (20.0 mL, 0.25 M) at room temperature (25 °C) and irradiation with green LED (λ_{max} = 530 nm) for 48 h yielded 2.67 g (4.11 mmol, 82%) of the title compound as a white solid after analogous work-up. Spectral data are in agreement with those reported in literature.[33] $\mathbf{R_f}$ (hexanes) = 0.51, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.46 – 7.41 (m, 2H), 7.35 – 7.27 (m, 3H), 5.45 (dd, *J* = 9.7, 5.2 Hz, 1H), 3.39 – 3.08 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 142.9, 129.1, 128.7, 126.9, 122.9 – 107.0 (m), 42.7 (t, *J* = 20.8 Hz), 16.7. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -81.23 (t, *J* = 9.9 Hz, 3F), -111.68 – -113.69 (m, 1F), -111.33 – -115.83 (m, 1F), -121.68 – -122.65 (m, 6F), -123.21 (s, 2F), -123.77 – -124.31 (m, 2F), -126.24 – -126.99 (m, 2F).

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-iododecyl)-4-methylbenzene (15b)[33]



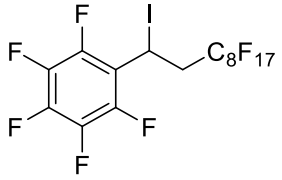
Following general procedure ***GP-III*** using 1-methyl-4-vinylbenzene (72.0 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), perfluorooctyl iodide (**14**) (264.1 µL, 546.0 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) and irradiation with green LED (λ_{max} = 530 nm) for 30 h yielded 282.4 mg (425 µmol, 85%) of the title compound as a white solid after flash column chromatography (hexanes). Spectral data are in agreement with those reported in literature.[33] $\mathbf{R_f}$ (hexanes) = 0.59, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.46 (dd, *J* = 9.8, 5.1 Hz, 1H), 3.38 – 3.08 (m, 2H), 2.32 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 140.0, 138.8, 129.7, 129.6 – 127.3 (m), 126.7, 42.7 (t, *J* = 20.6 Hz), 21.4, 17.2. **^{19}F-NMR** (376 MHz, $CDCl_3$) δ = -81.30 (t, *J* = 10.0 Hz, 3F), -112.18 – -113.42 (m, 1F), -112.05 – -115.96 (m, 1F), -114.58 – -115.78 (m, 6F), -121.93 – -122.88 (m, 2F), -123.24, -124.03 (s, 2F), -126.63 (s, 2F).

1-chloro-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-iododecyl)benzene (15c)[33]



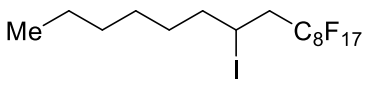
Following general procedure ***GP-III*** using 1-chloro-4-vinylbenzene (60.0 µL, 69.3 mg, 0.5 mmol, 1.0 equiv), perfluorooctyl iodide (**14**) (264.1 µL, 546.0 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) and irradiation with green LED (λ_{max} = 530 nm) for 30 h yielded 298.4 mg (436 µmol, 87%) of the title compound as a white solid after flash column chromatography (hexanes). Spectral data are in agreement with those reported in literature.[33] $\mathbf{R_f}$ (hexanes) = 0.54, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 5.41 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.34 – 3.07 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 141.4, 134.4, 129.3, 128.2, 121.0 – 107.4 (m), 42.7 (t, *J* = 20.4 Hz), 15.3. **^{19}F-NMR** (376 MHz, $CDCl_3$) δ = -81.23 (t, *J* = 9.9 Hz, 3F), -111.62 – -113.20 (m, 1F), -114.25 – -116.01 (m, 1F), -121.83 – -122.64 (m, 6F), -123.22 (s, 2F), -123.76 – -124.13 (m, 2F), -126.47 – -126.90 (m, 2F).

1,2,3,4,5-pentafluoro-6-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-iododecyl)benzene (15d)[33]



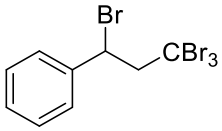
Following general procedure ***GP-III*** using 1,2,3,4,5-pentafluoro-6-vinylbenzene (69.0 µL, 97.1 mg, 0.5 mmol, 1.0 equiv), perfluorooctyl iodide (**14**) (264.1 µL, 546.0 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) and irradiation with green LED (λ_{max} = 530) for 30 h yielded 297.7 mg (402 µmol, 80%) of the title compound as a colorless oil after flash column chromatography (hexanes). Spectral data are in agreement with those reported in literature.[33] $\mathbf{R_f}$ (hexanes) = 0.90, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 5.66 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.56 – 3.36 (m, 1H), 3.19 – 2.99 (m, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.1 – 136.1 (m), 118.8 – 108.2 (m), 40.4 (t, *J* = 20.7 Hz), -3.9. **^{19}F-NMR** (376 MHz, $CDCl_3$) δ = -81.32 (t, *J* = 9.8 Hz, 3F), -113.67 – -114.19 (m, 1F), -115.79 – -116.61 (m, 1F), -122.00 – -122.53 (m, 6F), -123.25 (s, 2F), -123.98 (s, 2F), -126.65 (s, 2F), -139.69 (bs, 1F), -143.52 (bs, 1F), -153.26 (t, J = 9.8 Hz, 1F), -161.21 (td, *J* = 21.5, 7.9 Hz, 2F).

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodohexadecane (15e)[33]



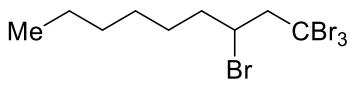
Following general procedure ***GP-III*** using oct-1-ene (**7n**) (78.5 µL, 56.1 mg, 0.5 mmol, 1.0 equiv), perfluorooctyl iodide (**14**) (264.1 µL, 546.0 mg, 1.0 mmol, 2.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) and irradiation with green LED (λ_{max} = 530 nm) for 30 h yielded 297.7 mg (402 µmol, 80%) of the title compound as a colorless oil after flash column chromatography (hexanes). Spectral data are in agreement with those reported in literature.[33] $\mathbf{R_f}$ (hexanes) = 0.80, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.34 (tdd, *J* = 8.3, 5.6, 4.3 Hz, 1H), 3.01 – 2.68 (m, 2H), 1.80 (dddd, *J* = 21.6, 14.7, 9.7, 4.6 Hz, 2H), 1.53 (q, *J* = 5.9, 5.2 Hz, 1H), 1.46 – 1.26 (m, 7H), 0.90 (t, *J* = 6.3 Hz, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 118.8 – 113.5 (m), 41.9 (t, *J* = 20.8 Hz), 40.5 (d, *J* = 2.1 Hz), 31.7, 29.7, 28.3, 22.7, 21.0, 14.2. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -81.25 (t, *J* = 10.0 Hz, 3F), -111.47 – -112.92 (m, 1F), -114.40 – -115.89 (m, 1F), -121.80 – -122.61 (m, 6F), -123.22 (s, 2F), -123.91 – -124.32 (m, 2F), -126.46 – -126.81 (m, 2F).

(1,3,3,3-tetrabromopropyl)benzene (17a)[34]



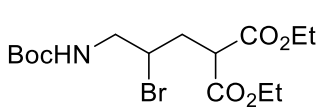
Following general procedure ***GP-III*** using styrene (**7a**) (57.3 µL, 54.1 mg, 0.5 mmol, 1.0 equiv), perbromomethane (**16a**) (165.8 mg, 0.5 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) and irradiation with blue LED (λ_{max} = 455 nm) for 30 h yielded 211.4 mg (485 µmol, 97%) of the title compound as a yellowish oil after flash column chromatography (hexanes). Spectral data are in agreement with those reported in literature.[34] ***Gram-Scale***: This procedure can be also scaled-up to gram-quantities following ***GP-III*** in a flame-dried Schlenk tube (30.0 mL size, Figure 3, F) using styrene (**7a**) (0.57 mL, 520.8 mg, 5.0 mmol, 1.0 equiv), perbromomethane (**16a**) (1.66 g, 5.0 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (55.1 mg, 0.1 mmol, 2.0 mol%) and MeCN (20.0 mL, 0.25 M) at room temperature (25 °C) and irradiation with blue LED (λ_{max} = 455 nm) for 48 h yielded 2.10 g (4.82 mmol, 96%) of the title compound as a yellowish oil after analogous work-up. Spectral data are in agreement with those reported in literature.[34] $\mathbf{R_f}$ (hexanes) = 0.48, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.54 – 7.46 (m, 2H), 7.42 – 7.28 (m, 3H), 5.34 (dd, *J* = 7.5, 4.3 Hz, 1H), 4.19 – 4.01 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 140.9, 129.1, 129.0, 128.3, 66.6, 50.2, 35.2.

1,1,1,3-tetrabromononane (17b)[34]



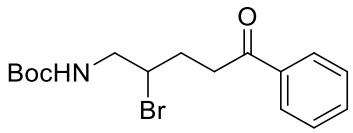
Following general procedure ***GP-III*** using oct-1-ene (**7n**) (78.5 µL, 56.1 mg, 0.5 mmol, 1.0 equiv), perbromomethane (**16a**) (165.8 mg, 0.5 mmol, 1.0 equiv), [Cu(dmp)$_2$Cl]Cl (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) and irradiation with blue LED (λ_{max} = 455 nm) for 30 h yielded 203.1 mg (458 µmol, 92%) of the title compound as a colorless oil after flash column chromatography (hexanes). Spectral data are in agreement with those reported in literature.[34] **R$_f$** (hexanes) = 0.72, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.20 (dq, *J* = 9.0, 4.5 Hz, 1H), 3.83 (dd, *J* = 16.2, 4.5 Hz, 1H), 3.54 (dd, *J* = 16.2, 4.9 Hz, 1H), 2.08 (dddd, *J* = 14.2, 10.1, 6.1, 4.2 Hz, 1H), 1.97 (dtd, *J* = 14.3, 9.3, 4.8 Hz, 1H), 1.66 – 1.46 (m, 2H), 1.42 – 1.26 (m, 6H), 0.93 – 0.84 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 67.1, 52.2, 39.9, 36.5, 31.8, 28.6, 27.5, 22.7, 14.2.

diethyl 2-(2-bromo-3-((*tert*-butoxycarbonyl)amino)propyl)malonate (17c)[34]



Following general procedure ***GP-V*** using *N*-Boc allylamine (**7o**) (78.6 mg, 0.5 mmol, 1.0 equiv), diethyl 2-bromomalonate (**16b**) (170.5 µL, 239.1 mg, 1.0 mmol, 2.0 equiv), LiBr (86.6 mg, 1.0 mmol, 2.0 equiv), [Cu(dmp)$_2$Cl]Cl (5.5 mg, 10.0 µmol, 2.0 mol%) and a DMF (0.2 mL)/water (0.8 mL) mixture (1:4, 1.0 mL, 0.5 M) at room temperature (25 °C) for 30 h yielded 122.0 mg (308 µmol, 62%) of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 10:1 to 5:1). Spectral data are in agreement with those reported in literature.[34] **R$_f$** (hexanes) = 0.30, Staining: Ninhydrin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 4.98 (bs, 1H), 4.26 – 4.15 (m, 4H), 4.14 – 4.08 (m, 1H), 3.73 (dd, *J* = 9.5, 5.0 Hz, 1H), 3.50 (p, *J* = 7.9, 6.6 Hz, 2H), 2.46 (ddd, *J* = 14.9, 9.5, 3.7 Hz, 1H), 2.25 (ddd, *J* = 15.0, 10.1, 5.0 Hz, 1H), 1.43 (s, 9H), 1.26 (td, *J* = 7.1, 2.2 Hz, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 169.0, 168.6, 155.7, 80.0, 61.9, 61.9, 53.3, 50.3, 47.2, 34.8, 28.4, 14.2, 14.1.

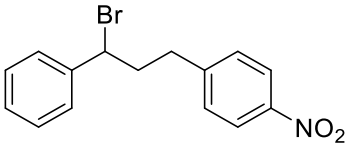
***tert*-butyl (2-bromo-5-oxo-5-phenylpentyl)carbamate (17d)[34]**



Following general procedure ***GP-V*** using *N*-Boc allylamine (**7o**) (78.6 mg, 0.5 mmol, 1.0 equiv), 2-bromo-1-phenylethan-1-one (**16c**) (199.1 mg, 1.0 mmol, 2.0 equiv), LiBr (86.6 mg, 1.0 mmol, 2.0 equiv), [Cu(dmp)$_2$Cl]Cl (5.5 mg, 10.0 µmol, 2.0 mol%) and a DMF (0.2 mL)/water (0.8 mL) mixture (1:4, 1.0 mL, 0.5 M) at room temperature (25 °C) for 30 h yielded 21.7 mg

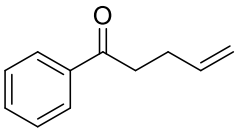
(61 µmol, 12%) of the title compound as a white solid after flash column chromatography (hexanes / EtOAc 9:1 to 4:1). Spectral data are in agreement with those reported in literature.[34] **R_f** (hexanes) = 0.43, Staining: UV, vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.00 – 7.94 (m, 2H), 7.60 – 7.53 (m, 1H), 7.46 (dd, *J* = 8.4, 7.0 Hz, 2H), 5.05 (bfs, 1H), 4.23 (dq, *J* = 12.4, 4.2 Hz, 1H), 3.61 (dt, *J* = 14.9, 5.7 Hz, 1H), 3.48 (ddd, *J* = 14.5, 7.2, 5.9 Hz, 1H), 3.23 (qdd, *J* = 17.9, 8.2, 6.0 Hz, 2H), 2.36 (dddd, *J* = 14.9, 8.2, 6.6, 3.9 Hz, 1H), 2.17 (ddd, *J* = 14.6, 10.0, 5.7 Hz, 1H), 1.45 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 198.8, 155.8, 136.8, 133.4, 128.8, 128.2, 79.9, 56.3, 47.5, 36.4, 30.2, 28.5

1-(3-bromo-3-phenylpropyl)-4-nitrobenzene (17e)[35]



Following general procedure ***GP-III*** using styrene (**7a**) (572.9 µL, 260.4 mg, 2.5 mmol, 5.0 equiv), 1-(bromomethyl)-4-nitrobenzene (**16d**) (108.0 mg, 0.5 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) and irradiation with blue LED (λ_{max} = 455 nm) for 30 h yielded 24.3 mg (76 µmol, 15%) of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 12:1 to 9:1). Spectral data are in agreement with those reported in literature.[35] **R_f** (hexanes / EtOAc 9:1) = 0.45, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.7 Hz, 2H), 7.41 – 7.28 (m, 7H), 4.88 (dd, *J* = 8.7, 6.1 Hz, 1H), 2.95 (ddd, *J* = 14.4, 9.1, 5.6 Hz, 1H), 2.82 (ddd, *J* = 13.9, 8.9, 6.6 Hz, 1H), 2.63 (dtd, *J* = 14.4, 8.8, 5.7 Hz, 1H), 2.45 (ddt, *J* = 14.3, 9.1, 6.4 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 148.4, 146.8, 141.5, 129.5, 129.0, 128.8, 127.3, 123.9, 54.1, 40.9, 34.3.

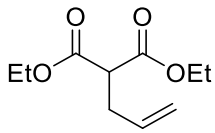
1-phenylpent-4-en-1-one (19a)[34]



Following general procedure ***GP-VI*** using 2-bromo-1-phenylethan-1-one (**16c**) (99.5 mg, 0.5 mmol, 1.0 equiv), allyltributylstannane (**18a**) (155.0 µL, 165.6 mg, 0.5 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 48 h yielded 48.4 mg (302 µmol, 60%) of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 15:1 to 9:1). ***Or***: Following general procedure ***GP-VI*** using 2-chloro-1-phenylethan-1-one (**Cl-16c**) (77.3 mg, 0.5 mmol, 1.0 equiv), allyltributylstannane (**18a**) (155.0 µL, 165.6 mg, 0.5 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 48 h yielded 46.7 mg

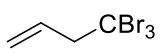
(291 µmol, 58%) of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 15:1 to 9:1). Spectral data are in agreement with those reported in literature.[34] **R_f** (hexanes / EtOAc 9:1) = 0.60, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.05 – 7.90 (m, 2H), 7.62 – 7.53 (m, 1H), 7.47 (dd, *J* = 8.2, 6.9 Hz, 2H), 5.91 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.14 – 4.99 (m, 2H), 3.08 (t, *J* = 7.4 Hz, 2H), 2.56 – 2.45 (m, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 199.6, 137.5, 137.1, 133.2, 128.7, 128.2, 115.4, 37.9, 28.3.

diethyl 2-allylmalonate (19b)[36]



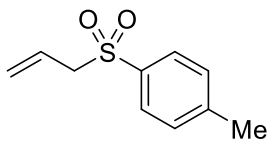
Following general procedure ***GP-VI*** using diethyl 2-bromomalonate (**16b**) (170.5 µL, 119.5 mg, 0.5 mmol, 1.0 equiv), allyltrimethylsilane (**18b**) (238.4 µL, 171.4 mg, 1.5 mmol, 3.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 48 h yielded 12.3 mg (61 µmol, 12%) of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 8:1 to 5:1). Spectral data are in agreement with those reported in literature.[36] **R_f** (hexanes / EtOAc 4:1) = 0.51, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 5.76 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.16 – 4.98 (m, 2H), 4.18 (qd, *J* = 7.1, 1.7 Hz, 4H), 3.40 (t, *J* = 7.5 Hz, 1H), 2.62 (t, *J* = 7.2 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 169.0, 134.2, 117.6, 61.5, 51.8, 32.9, 14.2.

4,4,4-tribromobut-1-ene (19c)[34]



Following general procedure ***GP-VI*** using perbromomethane (**16a**) (165.8 mg, 0.5 mmol, 1.0 equiv), allyltrimethylsilane (**18b**) (79.5 µL, 57.1 mg, 0.5 mmol, 1.0 equiv), $[Cu(dmp)_2Cl]Cl$ (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (1.0 mL, 0.5 M) at room temperature (25 °C) for 48 h yielded 14.0 mg (48 µmol, 10%) of the title compound as a colorless oil after flash column chromatography (hexanes). Spectral data are in agreement with those reported in literature.[34] **R_f** (hexanes) = 0.86, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 6.05 – 5.87 (m, 1H), 5.51 – 5.27 (m, 2H), 3.72 (dt, *J* = 6.7, 1.2 Hz, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 133.1, 121.7, 63.3, 40.6.

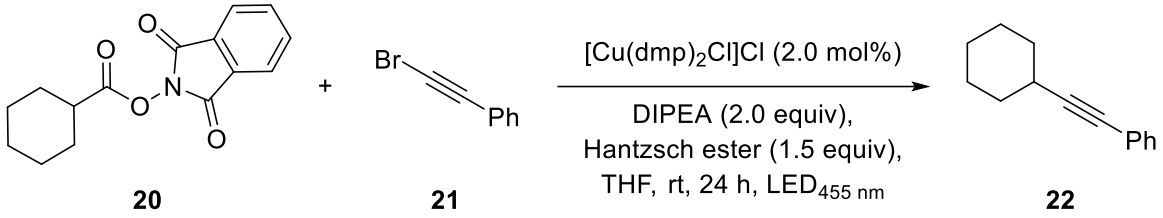
1-(allylsulfonyl)-4-methylbenzene (19d)[37]



Following general procedure ***GP-VI*** using 4-methylbenzenesulfonyl chloride (**8a**) (95.3 mg, 0.5 mmol, 1.0 equiv), Na_2CO_3 (53.0 mg, 0.5 mmol, 1.0 equiv), 3-bromoprop-1-ene (**18c**) (259.6 µL, 363.0 mg,

3.0 mmol, 6.0 equiv), [Cu(dmp)$_2$Cl]Cl (5.5 mg, 10.0 µmol, 2.0 mol%) and MeCN (2.0 mL, 0.25 M) at room temperature (25 °C) for 48 h yielded 78.9 mg (402 µmol, 80%) of the title compound as a colorless oil after flash column chromatography (hexanes / EtOAc 9:1 to 4:1). Spectral data are in agreement with those reported in literature.[37] **R$_f$** (hexanes / EtOAc 4:1) = 0.38, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.28 (m, 2H), 5.76 (ddt, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.35 – 5.25 (m, 1H), 5.13 (dq, *J* = 17.0, 1.2 Hz, 1H), 3.77 (dt, *J* = 7.4, 1.0 Hz, 2H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.8, 135.4, 129.7, 128.5, 124.8, 124.6, 61.0, 21.7.

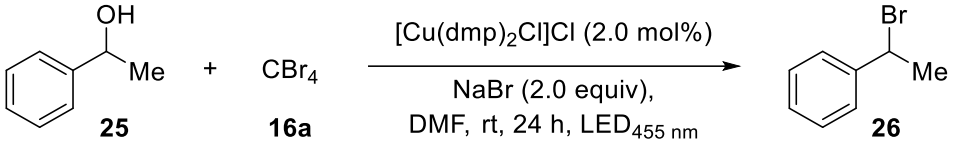
Photochemical decarboxylative coupling for the synthesis of 22



20 **21** **22**

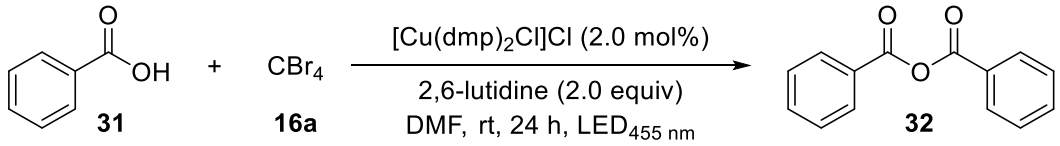
A flame-dried Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with 1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate (**20**) (136.6 mg, 0.5 mmol, 1.0 equiv), (bromoethynyl)benzene (**21**) (135.8 mg, 0.75 mmol, 1.5 equiv), Hantzsch ester (190.0 mg, 0.75 mmol, 1.5 equiv), [Cu(dmp)$_2$Cl]Cl (5.5 mg, 10.0 µmol, 2.0 mol%) and dissolved in anhydrous THF (1.5 mL, 0.33 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, diisopropylethylamine (DIPEA) (174.2 µL, 129.3 mg, 1.0 mmol, 2.0 equiv) was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with blue LED (λ_{max} = 455 nm) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes) to yield 57.1 mg (310 µmol, 62%) of (cyclohexylethynyl)benzene (**22**) as a slightly yellow oil. Spectral data are in accordance to literature.[8,6] **R$_f$** (hexanes) = 0.50, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.44 – 7.38 (m, 2H), 7.32 – 7.24 (m, 3H), 2.60 (tt, *J* = 9.2, 3.8 Hz, 1H), 1.89 (ddt, *J* = 12.6, 5.8, 3.4 Hz, 2H), 1.77 (qq, *J* = 6.5, 2.1 Hz, 2H), 1.55 (ddt, *J* = 13.7, 9.7, 4.9 Hz, 3H), 1.44 – 1.30 (m, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 131.7, 128.3, 127.5, 124.3, 94.6, 80.7, 32.9, 29.8, 26.1, 25.1.

Photochemical Appel reaction for the synthesis of 26



A flame-dried Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with perbromomethane (**16a**) (331.6 mg, 1.0 mmol, 2.0 equiv), sodium bromide (102.9 mg, 1.0 mmol, 2.0 equiv), [Cu(dmp)$_2$Cl]Cl (5.5 mg, 10.0 µmol, 2.0 mol%) and dissolved in anhydrous DMF (3.0 mL, 0.17 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, 1-phenylethan-1-ol (**25**) (61.1 mg, 0.5 mmol, 1.0 equiv) was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with blue LED (λ_{max} = 455 nm) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched by addition of water and DE. The layers were separated, and the aqueous phase was extracted three times with DE. The combined organic layers were washed with sat. aqueous $Na_2S_2O_3$ solution, brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes) to yield 67.6 mg (365 µmol, 73%) of (1-bromoethyl)benzene (**26**) as a colorless oil. Spectral data are in accordance to literature.[38] $\mathbf{R_f}$ (hexanes) = 0.58, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.49 – 7.41 (m, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.26 (m, 1H), 5.23 (q, *J* = 6.9 Hz, 1H), 2.06 (d, *J* = 6.9 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.4, 128.8, 128.5, 126.9, 49.7, 27.0.

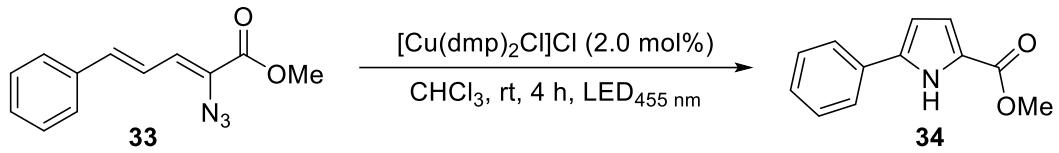
Photochemical coupling for the synthesis of 32



A flame-dried Schlenk tube (10.0 mL size) equipped with a magnetic stirring bar was charged with benzoic acid (**31**) (61.1 mg, 0.5 mmol, 1.0 equiv), perbromomethane (**16a**) (165.8 mg, 0.5 mmol, 1.0 equiv), [Cu(dmp)$_2$Cl]Cl (5.5 mg, 10.0 µmol, 2.0 mol%) and dissolved in anhydrous DMF (5.0 mL, 0.1 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Then, 2,6-lutidine (116.5 µL, 107.2 mg, 1.0 mmol, 2.0 equiv) was added under a slight nitrogen overpressure and the screw-cap was replaced with

a Teflon sealed inlet for a glass rod, through which irradiation with blue LED (λ_{max} = 455 nm) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched by addition of water and DE. The layers were separated, and the aqueous phase was extracted three times with DE. The combined organic layers were washed with sat. aqueous $NaHCO_3$ solution, water and brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 10:1) to yield 5.8 mg (26 µmol, 10%) of benzoic anhydride (**32**) as a white solid. Spectral data are in accordance to literature.[39] **R_f** (hexanes / EtOAc 7:1) = 0.45, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.23 – 8.14 (m, 4H), 7.72 – 7.65 (m, 2H), 7.53 (t, *J* = 7.8 Hz, 4H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ =162.5, 134.7, 130.7, 129.0, 129.0.

Photochemical sensitization for the synthesis of 34

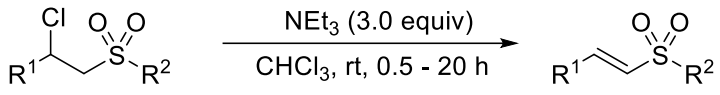


33 **34**

A flame-dried Schlenk tube (25.0 mL size) equipped with a magnetic stirring bar was charged with methyl (2*Z*,4*E*)-2-azido-5-phenylpenta-2,4-dienoate (**33**) (171.9 mg, 0.75 mmol, 1.0 equiv), [Cu(dmp)$_2$Cl]Cl (15.0 µmol, 2.0 mol%) and $CHCl_3$ (7.5 mL, 0.1 M). Therefore HPLC grade $CHCl_3$ was washed three times with NaOH (1.0 M) and three times with deionized water, passed through a column of activated, basic Al_2O_3 and fractionally distilled from K_2CO_3 prior to use. The resulting reaction mixture was sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. The screw-cap was replaced with a Teflon sealed inlet for a glass rod, through which irradiation with blue LED (λ_{max} = 455 nm) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 4 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 9:1 to 5:1) to yield 146.8 mg (730.0 mmol, 97%) of methyl 5-phenyl-1*H*-pyrrole-2-carboxylate (**34**) as a white solid. Spectral data are in accordance to literature. **R_f** (hexanes / EtOAc 5:1) = 0.43, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 9.82 (bs, 1H), 7.66 – 7.59 (m, 2H), 7.44 – 7.38 (m, 2H), 7.34 – 7.27 (m, 1H), 6.98 (dd, *J* = 3.9, 2.4 Hz, 1H), 6.55 (dd, *J* = 3.9, 2.7 Hz, 1H), 3.88 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 162.0, 137.3, 131.5, 129.1, 127.8, 125.0, 123.1, 117.1, 108.2, 51.8.

7.4.2 Compound Characterization for Further Transformations

General procedure for the synthesis of vinyl sulfones 12 (Chapter 2) (*GP-VII*)

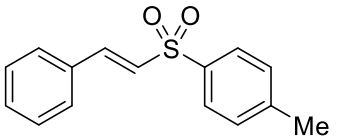


10 **12**

A mixture of chlorosulfonylation product **10** (0.2 mmol, 1.0 equiv) and triethylamine (83.6 µL, 60.7 mg, 0.6 mmol, 3.0 equiv) in $CHCl_3$ (2.0 mL, 0.1 M) was stirred at room temperature (25 °C) for 0.5-20 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was filtered through a plug of silica gel and the solvent as well as triethylamine residues were removed in vacuo to yield vinyl sulfone **12**. No further purification by column chromatography was necessary.

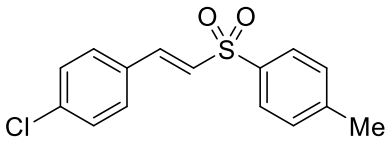
*Please note, that vinyl sulfone products **12** were obtained during my Master Thesis.*[25]

(*E*)-1-methyl-4-(styrylsulfonyl)benzene (12a)[25]



Following general procedure ***GP-VII*** using 1-((2-chloro-2-phenylethyl)sulfonyl)-4-methylbenzene (**10a**) (59.0 mg, 0.2 mmol, 1.0 equiv) yielded 51.6 mg (0.2 mmol, 100%) of the title compound as a white solid after a reaction time of 30 min. **mp**: 120 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.31, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 15.4 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.43 – 7.36 (m, 3H), 7.37 – 7.32 (m, 2H), 6.85 (d, *J* = 15.4 Hz, 1H), 2.43 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.5, 142.0, 137.8, 132.5, 131.2, 130.1, 129.2, 128.6, 127.8, 127.7, 21.7. **IR** (neat): 3045, 2926, 2110, 1605, 1595, 1577, 1495, 1450, 1402, 1390, 1301, 1288, 1200, 1141, 1085, 1017, 1000, 973, 857, 805, 746, 693, 661 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{18}NO_2S$ ($[M+NH_4]^+$) 276.1053, found 276.1054.

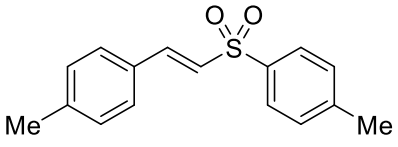
(*E*)-1-chloro-4-(2-tosylvinyl)benzene (12b)[25]



Following general procedure ***GP-VII*** using 1-chloro-4-(1-chloro-2-tosylethyl)benzene (**10c**) (65.9 mg, 0.2 mmol, 1.0 equiv) yielded 58.6 mg (0.2 mmol, 100%) of the title compound as a white solid after a reaction time of 30 min. **mp**: 152 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.34, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.3 Hz, 2H),

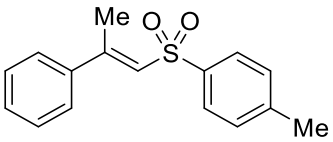
7.59 (d, *J* = 15.4 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.30 (m, 4H), 6.84 (d, *J* = 15.4 Hz, 1H), 2.42 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.7, 140.5, 137.6, 137.2, 131.0, 130.1, 129.8, 129.4, 128.4, 127.8, 21.7. **IR** (neat):3058, 2956, 2922, 1614, 1598, 1577, 1487, 1450, 1402, 1394, 1310, 1290, 1189, 1174, 1141, 1081, 1014, 969, 941, 861, 813, 783, 704, 686, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{13}ClNaO_2S$ ($[M+Na]^+$) 315.0217, found 315.0217.

(*E*)-1-methyl-4-((4-methylstyryl)sulfonyl)benzene (12c)[25]



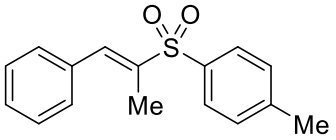
Following general procedure ***GP-VII*** using 1-((2-chloro-2-(*p*-tolyl)ethyl)sulfonyl)-4-methylbenzene (**10i**) (52.0 mg, 0.2 mmol, 1.0 equiv) yielded 52.8 mg (194 µmol, 97%) of the title compound as a white solid after a reaction time of 30 min. **mp**: 150 °C. **R_f** (hexanes / EtOAc 5:1) = 0.36, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 15.4 Hz, 1H), 7.42 – 7.29 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 15.4 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.4, 142.1, 141.8, 138.1, 130.0, 129.9, 129.8, 128.6, 127.7, 126.5, 21.7, 21.6. **IR** (neat): 3049, 2952, 2922, 2859, 2107, 1920, 1804, 1595, 1588, 1513, 1491, 1446, 1412, 1390, 1301, 1291, 1211, 1181, 1141, 1085, 1030, 1021, 977, 865, 817, 802, 794, 760, 705, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{16}O_2S$ ($[M+Na]^+$) 295.0763, found 295.0763.

(*E*)-1-methyl-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene (12d)[25]



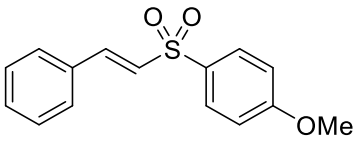
Following general procedure ***GP-VII*** using 1-((2-chloro-2-phenylpropyl)sulfonyl)-4-methylbenzene (**10o**) (61.8 mg, 0.2 mmol, 1.0 equiv) yielded 52.8 mg (194 µmol, 97%) of the title compound as a white solid after a reaction time of 20 h. Stereochemistry was assigned in analogy to literature.[40] **mp**: 93 °C. **R_f** (hexanes / EtOAc 5:1) = 0.48, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.32 (m, 7H), 6.60 (q, *J* = 1.3 Hz, 1H), 2.52 (d, *J* = 1.3 Hz, 3H), 2.44 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 153.1, 144.3, 140.3, 139.4, 130.0, 129.9, 128.8, 127.9, 127.4, 126.4, 21.7, 17.3. **IR** (neat): 3058, 2922, 1595, 1569, 1491, 1443, 1391, 1290, 1220, 1137, 1081, 1018, 980, 924, 819, 809, 797, 753, 693, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{17}O_2S$ ($[M+H]^+$) 273.0944, found 273.0949.

(*E*)-1-methyl-4-((1-phenylprop-1-en-2-yl)sulfonyl)benzene (12e)[25]



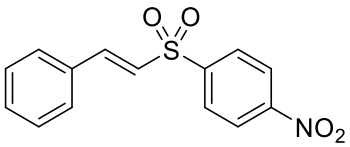
Following general procedure ***GP-VII*** using 1-((1-chloro-1-phenylpropan-2-yl)sulfonyl)-4-methylbenzene (**10p**) (61.8 mg, 0.2 mmol, 1.0 equiv) yielded 52.8 mg (194 µmol, 97%) of the title compound as a white solid after a reaction time of 20 h. Stereochemistry was assigned in analogy to literature.[41] **mp**: 115 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.45, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.86 – 7.74 (m, 3H), 7.43 – 7.30 (m, 7H), 2.43 (s, 3H), 2.10 (d, *J* = 1.4 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.4, 137.7, 137.1, 136.2, 134.0, 129.9, 129.7, 129.3, 128.8, 128.3, 21.7, 13.3. **IR** (neat): 2963, 2922, 2855, 1625, 1595, 1491, 1443, 1383, 1290, 1211, 1148, 1103, 1070, 969, 910, 816, 784, 738, 693, 652 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{16}NaO_2S$ ($[M+Na]^+$) 295.0763, found 295.0769.

(*E*)-1-methoxy-4-(styrylsulfonyl)benzene (12f)[25]



Following general procedure ***GP-VII*** using 1-((2-chloro-2-phenylethyl)sulfonyl)-4-methoxybenzene (**10z**) (62.2 mg, 0.2 mmol, 1.0 equiv) yielded 54.9 mg (0.2 mmol, 100%) of the title compound as a white solid after a reaction time of 30 min. **mp**: 85 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.23, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 9.0 Hz, 1H), 7.63 (d, *J* = 15.4 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.42 – 7.33 (m, 3H), 7.00 (d, *J* = 9.0 Hz, 1H), 6.85 (d, *J* = 15.5 Hz, 1H), 3.86 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 163.7, 141.5, 132.6, 132.2, 131.1, 130.0, 129.1, 128.6, 128.0, 114.7, 55.8. **IR** (neat): 3068, 3042, 2997, 2952, 2848, 1592, 1577, 1498, 1446, 1405, 1300, 1297, 1260, 1193, 1133, 1081, 1002, 973, 857, 828, 800, 742, 690, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{18}NO_3S$ ($[M+NH_4]^+$) 292.1002, found 292.1004.

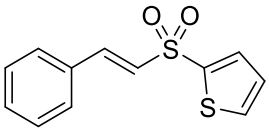
(*E*)-1-nitro-4-(styrylsulfonyl)benzene (12g)[25]



Following general procedure ***GP-VII*** using 1-((2-chloro-2-phenylethyl)sulfonyl)-4-nitrobenzene (**10ae**) (65.2 mg, 0.2 mmol, 1.0 equiv) yielded 57.9 mg (0.2 mmol, 100%) of the title compound as a white solid after a reaction time of 30 min. **mp**: 150 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.33, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.39 (d, *J* = 8.9 Hz, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 7.77 (d, *J* = 15.4 Hz, 1H), 7.56 – 7.36 (m, 5H), 6.86 (d, *J* = 15.4 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 150.6, 146.7, 145.1, 132.0, 131.9,

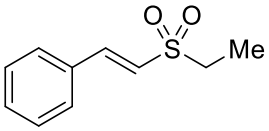
129.4, 129.2, 129.0, 125.8, 124.7. **IR** (neat): 3105, 3049, 1603, 1595, 1528, 1450, 1408, 1346, 1320, 1301, 1200, 1184, 1144, 1110, 1081, 984, 854, 813, 746, 678 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_{15}NO_4S$ ($[M+NH_4]^+$) 307.0747, found 307.0747.

(*E*)-2-(styrylsulfonyl)thiophene (12h)[25]



Following general procedure ***GP-VII*** using 2-((2-chloro-2-phenylethyl)sulfonyl)thiophene (**10ai**) (57.4 mg, 0.2 mmol, 1.0 equiv) yielded 48.6 mg (194 µmol, 97%) of the title compound as a white solid after a reaction time of 30 min. **mp**: 101 °C. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.26, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.77 – 7.62 (m, 3H), 7.54 – 7.46 (m, 2H), 7.45 – 7.33 (m, 3H), 7.13 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.97 (d, *J* = 15.3 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 142.3, 134.1, 133.6, 132.3, 131.4, 129.2, 128.7, 128.1, 128.0. **IR** (neat): 3101, 3050, 1610, 1577, 1498, 1450, 1402, 1320, 1301, 1226, 1198, 1178, 1129, 1096, 1087, 1014, 969, 857, 813, 734, 698, 661 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{12}H_{14}NO_2S_2$ ($[M+NH_4]^+$) 268.0460, found 268.0463.

(*E*)-(2-(ethylsulfonyl)vinyl)benzene (12i)[25]

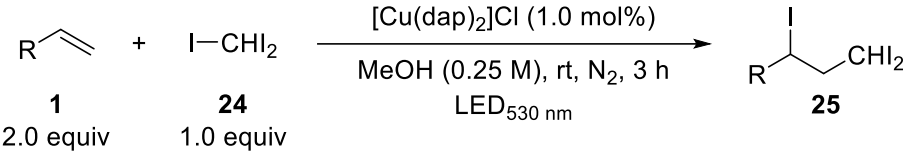


Following general procedure ***GP-VII*** using (1-chloro-2-(ethylsulfonyl)ethyl)benzene (**10af**) (46.5 mg, 0.2 mmol, 1.0 equiv) yielded 39.3 mg (0.2 mmol, 100%) of the title compound as a colorless oil after a reaction time of 30 min. $\mathbf{R_f}$ (hexanes / EtOAc 5:1) = 0.13, Staining: UV, Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 15.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.45 – 7.37 (m, 3H), 6.82 (d, *J* = 15.5 Hz, 1H), 3.09 (q, *J* = 7.5 Hz, 2H), 1.38 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 145.3, 132.3, 131.5, 129.3, 128.7, 124.1, 49.5, 7.4. **IR** (neat): 3053, 2982, 2941, 2881, 1618, 1577, 1495, 1450, 1409, 1301, 1283, 1230, 1186, 1178, 1122, 1044, 977, 857, 820, 746, 716, 681 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{10}H_{16}NO_2S$ ($[M+NH_4]^+$) 214.0896, found 214.0897.

7.5 Experimental Part for Chapter 4

7.5.1 Compound Characterization of ATRA Products using Iodoform

General procedure for photochemical ATRA reactions using iodoform (*GP-I*)



A flame-dried Schlenk tube (10.0 mL size; Figure 4, D) equipped with a magnetic stirring bar (Figure 4, E) was charged with iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and dissolved in anhydrous MeOH (2.0 mL, 0.25 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, alkene **1** (1.0 mmol, 2.0 equiv) was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet (Figure 4, C) for a glass rod (Figure 4, B), through which irradiation with a 530 nm high power LED (Figure 4, A) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 3 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo (water bath temperature of rotary evaporator should not exceed 40 °C) and the residue purified by flash column chromatography on silica gel.

Please note: *Products are sensitive to heat. Also, slow decomposition is noticeable in solution if oxygen or acid is present. Column chromatography should be performed immediately, and the solvent evaporated as soon as possible. Isolated compounds can be stored neatly in the dark at 4-8 °C (fridge).*

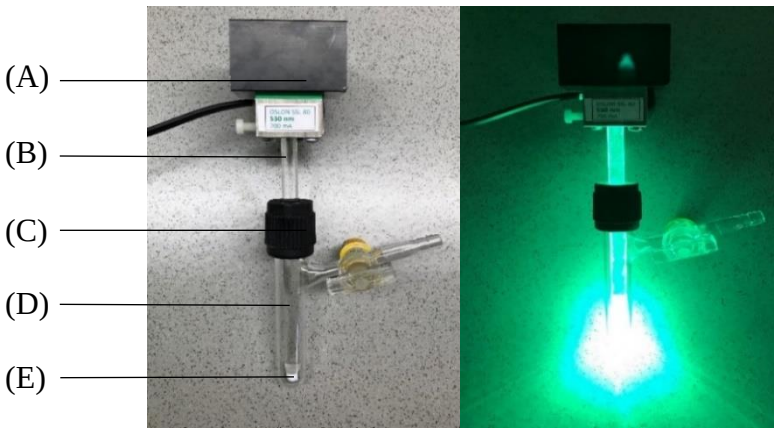
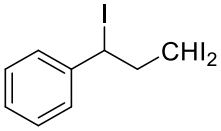
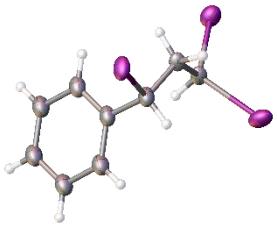


Figure 4. Irradiation setup for photochemical ATRA reaction using iodoform. (A) LED; (B) glass rod (used as a light conductor); (C) Teflon adapter; (D) Schlenk tube (10.0 mL size); (E) Teflon-coated magnetic stirring bar.

(1,3,3-triiodopropyl)benzene (25a)

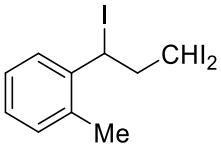


Following general procedure ***GP-I*** using styrene (**1a**) (114.6 µL, 104.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 242.3 mg (486.7 µmol, 97%) of the title compound as a brownish solid after flash column chromatography on neutral aluminum oxide (hexanes). Further purification was done by crystallization using vapor diffusion method with DCM and *n*-pentane as solvent system. The crystals obtained were white to yellowish and prism-shaped. CCDC 2013498 contain the supplementary crystallographic data for this work. The isolated product **25a** can be stored neatly in the dark at 4-8 °C (fridge).



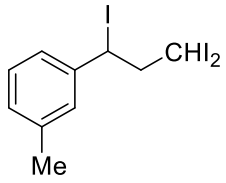
mp: 79 °C. $\mathbf{R_f}$ (hexanes on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.44 – 7.38 (m, 2H), 7.37 – 7.28 (m, 3H), 5.13 (t, *J* = 7.5 Hz, 1H), 4.82 (t, *J* = 7.3 Hz, 1H), 3.29 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.06 (dt, *J* = 15.1, 7.2 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 141.0, 129.3, 128.8, 127.6, 57.5, 31.7, -29.8. **IR** (neat): 3060, 3030, 2982, 2480, 2374, 1882, 1804, 1752, 1678, 1608, 1491, 1449, 1431, 1353, 1320, 1238, 1201, 1148, 1121, 1085, 1029, 917, 768, 693, 680 cm^{-1}. **HRMS** (EI) m/z calculated for $C_9H_9I_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 370.87881, found 370.87918.

1-methyl-2-(1,3,3-triiodopropyl)benzene (25b)



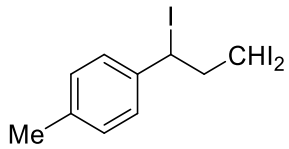
Following general procedure ***GP-I*** using 1-methyl-2-vinylbenzene (**1b**) (129.0 µL, 118.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 211.8 mg (431.7 µmol, 83%) of the title compound as a reddish oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.38, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.43 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.25 – 7.08 (m, 3H), 5.35 (t, *J* = 7.4 Hz, 1H), 4.97 (t, *J* = 7.3 Hz, 1H), 3.37 (dt, *J* = 15.3, 7.6 Hz, 1H), 3.17 (dt, *J* = 15.3, 7.1 Hz, 1H), 2.40 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 138.7, 135.3, 131.4, 128.6, 127.3, 126.7, 56.5, 28.7, 19.5, -29.5. **IR** (neat): 3064, 3019, 2974, 2855, 2371, 2322, 2110, 1603, 1487, 1455, 1435, 1380, 1286, 1238, 1186, 1081, 906, 821, 757, 723, 675 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{10}H_{11}I_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 384.89446, found 384.89365.

1-methyl-3-(1,3,3-triiodopropyl)benzene (25c)



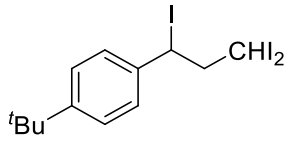
Following general procedure ***GP-I*** using 1-methyl-3-vinylbenzene (**1c**) (131.3 µL, 118.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 204.9 mg (400.3 µmol, 80%) of the title compound as a reddish oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.43, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.25 – 7.16 (m, 3H), 7.15 – 7.05 (m, 1H), 5.10 (t, *J* = 7.5 Hz, 1H), 4.83 (t, *J* = 7.3 Hz, 1H), 3.29 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.04 (dt, *J* = 15.2, 7.2 Hz, 1H), 2.36 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.8, 139.0, 129.6, 129.1, 128.2, 124.6, 57.4, 32.2, 21.6, -29.3. **IR** (neat): 3019, 2982, 2945, 2915, 2728, 2458, 2728, 2371, 2240, 1938, 1871, 1774, 1677, 1603, 1525, 1487, 1424, 1379, 1342, 1312, 1252, 1170, 1122, 1081, 999, 906, 872, 783, 731, 697 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{10}H_{11}I_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 384.89446, found 384.89460.

1-methyl-4-(1,3,3-triiodopropyl)benzene (25d)



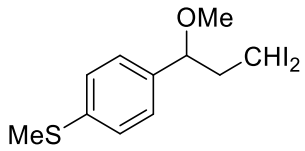
Following general procedure ***GP-I*** using 1-methyl-4-vinylbenzene (**1d**) (132.0 µL, 118.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 224.6 mg (448.5 µmol, 90%) of the title compound as a brownish solid after flash column chromatography on silica (hexanes). **mp**: 74 °C. R_f (hexanes on silica) = 0.50, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 5.14 (t, *J* = 7.5 Hz, 1H), 4.80 (t, *J* = 7.3 Hz, 1H), 3.29 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.07 (dt, *J* = 14.8, 7.2 Hz, 1H), 2.33 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 138.8, 138.0, 130.0, 127.4, 57.5, 32.0, 21.4, -29.5. **IR** (neat): 3023, 2989, 2915, 2845, 2732, 2459, 2380, 1908, 1796, 1655, 1609, 1510, 1428, 1391, 1342, 1316, 1234, 1207, 1126, 1085, 1003, 913, 844, 820, 760, 723, 671 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{10}H_{11}I_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 384.89446, found 384.89371.

1-(*tert*-butyl)-4-(1,3,3-triiodopropyl)benzene (25e)



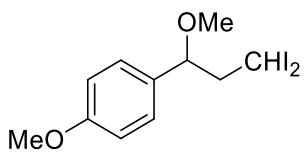
Following general procedure ***GP-I*** using 1-(*tert*-butyl)-4-vinylbenzene (**1e**) (181.3 µL, 160.3 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 227.3 mg (435.5 µmol, 87%) of the title compound as a slightly reddish oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.50, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.33 (s, 4H), 5.14 (t, *J* = 7.4 Hz, 1H), 4.83 (t, *J* = 7.3 Hz, 1H), 3.29 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.06 (dt, *J* = 15.2, 7.2 Hz, 2H), 1.32 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 152.0, 137.9, 127.2, 126.2, 57.6, 34.9, 32.2, 31.4, -29.2. **IR** (neat): 2960, 2904, 2866, 2379, 2322, 1677, 1607, 1510, 1461, 1409, 1364, 1316, 1267, 1238, 1204, 1163, 1107, 1018, 906, 831, 731, 682 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{13}H_{17}I_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 426.94141, found 426.94216.

(4-(3,3-diiodo-1-methoxypropyl)phenyl)(methyl)sulfane (OMe-25f)



Following general procedure ***GP-I*** using methyl(4-vinylphenyl)sulfane (**1f**) (150.3 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 97.0 mg (216.5 µmol, 43%) of the title compound as a colorless oil after flash column chromatography on silica (hexanes to hexanes / EtOAc 70:1). $\mathbf{R_f}$ (hexanes / EtOAc 9:1 on silica) = 0.65, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.30 – 7.15 (m, 5H), 5.12 (dd, *J* = 10.2, 4.6 Hz, 1H), 4.11 (dd, *J* = 9.1, 3.9 Hz, 1H), 3.22 (s, 3H), 2.74 (ddd, *J* = 14.9, 9.1, 4.6 Hz, 1H), 2.55 (ddd, 14.8, 10.2, 3.9 Hz, 1H), 2.50 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 138.7, 136.5, 127.4, 126.9, 83.8, 57.0, 56.4, 15.9, -30.6. **IR** (neat): 3075, 2982, 2922, 2870, 2822, 2110, 1595, 1491, 1435, 1405, 1342, 1238, 1211, 1088, 1014, 985, 872, 816, 753, 731 cm^{-1}. **HRMS** (APCI) m/z calculated for $C_{11}H_{14}I_2OS$ ($[M]^+$) 447.8849, found 447.8849.

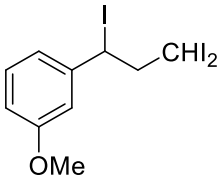
1-(3,3-diiodo-1-methoxypropyl)-4-methoxybenzene (OMe-25g)



Following general procedure ***GP-I*** using 1-methoxy-4-vinylbenzene (**1g**) (133.0 µL, 134.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol,

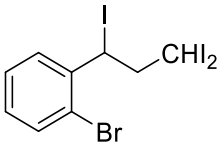
1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 61.9 mg (143.3 µmol, 29%) of the title compound as a colorless oil after flash column chromatography on silica (hexanes / EtOAc 20:1). $\mathbf{R_f}$ (hexanes / EtOAc 7:1 on silica) = 0.68, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.27 – 7.21 (m, 2H), 6.93 – 6.87 (m, 2H), 5.11 (dd, *J* = 10.1, 4.8 Hz, 1H), 4.10 (dd, *J* = 9.0, 4.0 Hz, 1H), 3.82 (s, 3H), 3.21 (s, 3H), 2.77 (ddd, *J* = 14.9, 9.0, 4.8 Hz, 1H), 2.55 (ddd, *J* = 14.8, 10.1, 4.0 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 159.6, 131.5, 128.1, 114.2, 83.7, 56.8, 56.5, 55.4, -30.1. **IR** (neat): 2997, 2933, 2904, 2833, 1610, 1600, 1510, 1461, 1423, 1342, 1305, 1245, 1174, 1096, 1033, 906, 892, 828, 768, 731 cm^{-1}. **HRMS** (APCI) m/z calculated for $C_{11}H_{14}I_2O_2$ ($[M]^+$) 431.9083, found 431.9079.

1-methoxy-3-(1,3,3-triiodopropyl)benzene (25h)



Following general procedure ***GP-I*** using 1-methoxy-3-vinylbenzene (**1h**) (138.8 µL, 134.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 204.3 mg (387.0 µmol, 77%) of the title compound as a reddish sticky oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes / EtOAc 9:1 on silica) = 0.53, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.24 (t, *J* = 7.9 Hz, 1H), 7.00 (ddd, *J* = 7.7, 1.8, 0.9 Hz, 1H), 6.93 (t, *J* = 2.1 Hz, 1H), 6.83 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 5.09 (t, *J* = 7.5 Hz, 1H), 4.81 (dd, *J* = 7.6, 7.0 Hz, 1H), 3.82 (s, 3H), 3.27 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.05 (dt, *J* = 15.1, 7.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 160.0, 142.3, 130.3, 119.8, 114.1, 113.4, 57.4, 55.5, 31.4, -29.8. **IR** (neat): 2997, 2937, 2832, 2345, 2240, 2080, 1923, 1834, 1580, 1487, 1454, 1320, 1300, 1260, 1242, 1156, 1081, 1040, 992, 906, 869, 779, 752, 727 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{10}H_{11}OI_3$ ($[M^{+\bullet}]$) 527.79385, found 527.79432.

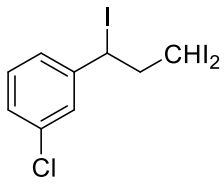
1-bromo-2-(1,3,3-triiodopropyl)benzene (25l)



Following general procedure ***GP-I*** using 1-bromo-2-vinylbenzene (**1l**) (125.4 µL, 183.1 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 254.7 mg (441.6 µmol, 88%) of the title compound as a reddish sticky oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.45, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz,

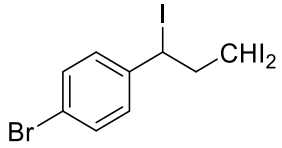
$CDCl_3$) δ = 7.53 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 2H), 7.33 (td, *J* = 7.6, 1.3 Hz, 1H), 7.15 (ddd, *J* = 8.1, 7.4, 1.7 Hz, 1H), 5.57 (dd, *J* = 8.5, 6.3 Hz, 1H), 5.00 (dd, *J* = 8.0, 6.6 Hz, 1H), 3.32 (ddd, *J* = 15.1, 8.5, 6.5 Hz, 1H), 3.06 (ddd, *J* = 15.3, 8.0, 6.3 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ =139.8, 133.9, 130.0, 129.0, 128.7, 123.2, 56.2, 30.7, -30.6. **IR** (neat): 3056, 2982, 2926, 2371, 2110, 1920, 1797, 1685, 1566, 1469, 1435, 1279, 1234, 1200, 1163, 1381, 1021, 947, 902, 753, 727, 675 cm^{-1}. **HRMS** (EI) m/z calculated for $C_9H_8BrI_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 448.78933, found 448.78845.

1-chloro-3-(1,3,3-triiodopropyl)benzene (25m)



Following general procedure ***GP-I*** using 1-chloro-3-vinylbenzene (**1m**) (127.2 µL, 138.6 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 227.3 mg (427.0 µmol, 85%) of the title compound as a reddish sticky oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.45, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.42 – 7.37 (m, 1H), 7.32 – 7.23 (m, 3H), 5.05 (dd, *J* = 8.0, 6.9 Hz, 1H), 4.83 (t, *J* = 7.3 Hz, 1H), 3.25 (ddd, *J* = 15.2, 8.0, 7.2 Hz, 1H), 2.98 (dt, *J* = 15.2, 7.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 142.9, 134.9, 130.5, 129.0, 127.8, 125.8, 57.0, 30.1, -30.2. **IR** (neat): 3056, 2982, 2110, 1752, 1600, 1589, 1476, 1431, 1342, 1234, 1197, 1163, 1077, 999, 902, 876, 828, 783, 731, 711, 692 cm^{-1}. **HRMS** (EI) m/z calculated for $C_9H_8ClI_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 404.83984, found 404.83907.

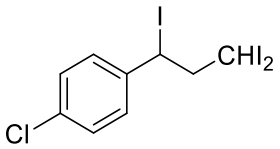
1-bromo-4-(1,3,3-triiodopropyl)benzene (25n)



Following general procedure ***GP-I*** using 1-bromo-4-vinylbenzene (**1n**) (130.8 µL, 183.1 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 247.6 mg (429.3 µmol, 86%) of the title compound as a slightly reddish solid after flash column chromatography on silica (hexanes). **mp**: 90 °C. $\mathbf{R_f}$ (hexanes on silica) = 0.55, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.07 (t, *J* = 7.5 Hz, 1H), 4.79 (t, *J* = 7.3 Hz, 1H), 3.26 (dt, *J* = 15.3, 7.6 Hz, 1H), 3.01 (dt, *J* = 15.1, 7.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.0, 132.4, 129.2, 122.6, 57.1, 30.2, -30.3. **IR** (neat): 2982, 2113, 1894, 1774, 1685, 1588, 1484, 1421, 1405, 1312, 1282, 1215, 1172, 1074, 1006,

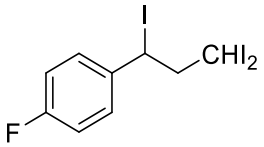
913, 900, 871, 753, 671 cm^{-1}. **HRMS** (EI) m/z calculated for $C_9H_8BrI_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 448.78933, found 448.78991.

1-chloro-4-(1,3,3-triiodopropyl)benzene (25o)



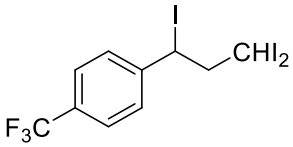
Following general procedure ***GP-I*** using 1-chloro-4-vinylbenzene (**1o**) (120.0 µL, 138.6 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 230.1 mg (423.3 µmol, 86%) of the title compound as a reddish sticky oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.45, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.38 – 7.28 (m, 4H), 5.09 (t, *J* = 7.5 Hz, 1H), 4.79 (t, *J* = 7.3 Hz, 1H), 3.26 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.01 (dt, *J* = 15.2, 7.2 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 139.5, 134.4, 129.5, 128.9, 57.2, 30.3, -30.3. **IR** (neat): 3002, 2948, 1905, 1778, 1685, 1655, 1592, 1487, 1421, 1409, 1342, 1316, 1275, 1238, 1201, 1173, 1110, 1085, 1010, 913, 831, 789, 723, 675 cm^{-1}. **HRMS** (EI) m/z calculated for $C_9H_8ClI_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 404.83984, found 404.83990.

1-fluoro-4-(1,3,3-triiodopropyl)benzene (25p)



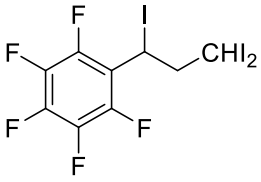
Following general procedure ***GP-I*** using 1-fluoro-4-vinylbenzene (**1p**) (119.3 µL, 122.1 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 218.2 mg (423.0 µmol, 85%) of the title compound as a brownish sticky oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.43, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.46 – 7.34 (m, 2H), 7.10 – 6.94 (m, 2H), 5.11 (t, *J* = 7.5 Hz, 1H), 4.80 (t, *J* = 7.3 Hz, 1H), 3.27 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.01 (dt, *J* = 15.2, 7.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 162.5 (d, *J* = 249.1 Hz), 136.9 (d, *J* = 3.4 Hz), 129.4 (d, *J* = 8.4 Hz), 116.3 (d, *J* = 21.8 Hz), 57.5, 30.6, -30.1. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -112.53 (s, 3F). **IR** (neat): 3041, 2982, 2630, 2570, 2453, 2080, 1885, 1800, 1599, 1506, 1416, 1353, 1297, 1226, 1159, 1122, 1081, 1032, 917, 901, 831, 779, 731, 671 cm^{-1}. **HRMS** (EI) m/z calculated for $C_9H_8FI_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 388.86939, found 388.86830.

1-(trifluoromethyl)-4-(1,3,3-triiodopropyl)benzene (25q)



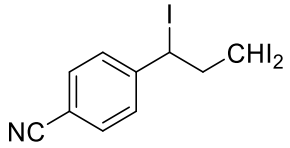
Following general procedure ***GP-I*** using 1-(trifluoromethyl)-4-vinylbenzene (**1q**) (147.8 µL, 172.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 248.2 mg (438.6 µmol, 88%) of the title compound as a reddish sticky oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.50, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.64 – 7.50 (m, 4H), 5.12 (dd, *J* = 7.9, 7.1 Hz, 1H), 4.81 (t, *J* = 7.3 Hz, 1H), 3.29 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.02 (dt, *J* = 15.2, 7.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.9, 130.8 (q, *J* = 32.7 Hz), 128.0, 126.3 (q, *J* = 3.7 Hz), 123.8 (q, J = 271.9 Hz), 56.9, 29.6, -30.7. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -63.20 (s, 3F). **IR** (neat): 2982, 1931, 1807, 1618, 1416, 1320, 1238, 1163, 1110, 1107, 1080, 1007, 840, 835, 734, 664 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{10}H_8F_3I_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 438.86620, found 438.86532.

1,2,3,4,5-pentafluoro-6-(1,3,3-triiodopropyl)benzene (25r)



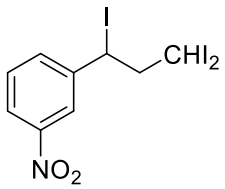
Following general procedure ***GP-I*** using 1,2,3,4,5-pentafluoro-6-vinylbenzene (**1r**) (138.1 µL, 194.1 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 256.7 mg (436.7 µmol, 87%) of the title compound as a reddish sticky oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.55, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 5.38 (dd, *J* = 8.5, 6.7 Hz, 1H), 4.91 (dd, *J* = 7.8, 6.7 Hz, 1H), 3.41 – 3.28 (m, 1H), 3.01 (ddd, *J* = 15.0, 7.9, 6.6 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ =143.3 – 142.6 (m), 140.5 – 139.9 (m), 139.6 – 138.9 (m), 137.0 – 136.5 (m), 115.6 – 114.6 (m), 54.23 (t, *J* = 3.4 Hz), 12.37, -32.72. **^{19}F-NMR** (377 MHz, $CDCl_3$) δ = -137.63 – -141.27 (m, 2F), -153.06 (tt, *J* = 21.1, 2.2 Hz, 1F), -160.71 (td, *J* = 21.4, 7.5 Hz, 2F). **IR** (neat): 2982, 2646, 2441, 2072, 1651, 1521, 1500, 1420, 1364, 1305, 1238, 1174, 1129, 1081, 1014, 984, 947, 880, 749, 686 cm^{-1}. **HRMS** (EI) m/z calculated for $C_9H_4F_5I_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 460.83170, found 460.83122.

4-(1,3,3-triiodopropyl)benzonitrile (25s)



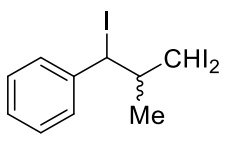
Following general procedure ***GP-I*** using 4-vinylbenzonitrile (**1s**) (129.2 µL, 129.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 216.6 mg (414.2 µmol, 83%) of the title compound as a brownish sticky oil after flash column chromatography on silica (hexanes to hexanes / EtOAc 20:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.63, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.68 – 7.57 (m, 2H), 7.55 – 7.47 (m, 2H), 5.09 (dd, *J* = 8.1, 6.8 Hz, 1H), 4.81 (t, *J* = 7.3 Hz, 1H), 3.26 (ddd, *J* = 15.2, 8.1, 7.1 Hz, 1H), 2.98 (ddd, *J* = 15.2, 7.6, 6.8 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 146.1, 133.1, 128.4, 118.3, 112.5, 56.5, 29.2, -31.3. **IR** (neat): 3084, 2982, 2374, 2229, 1912, 1758, 1685, 1603, 1502, 1413, 1342, 1286, 1238, 1200, 1163, 1081, 1018, 906, 835, 727 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{10}H_8NI_2$ ($[M^{+\bullet}-I^{\bullet}]^+$) 395.87406, found 395.87498.

1-nitro-3-(1,3,3-triiodopropyl)benzene (25t)



Following general procedure ***GP-I*** using 1-nitro-3-vinylbenzene (**1t**) (139.4 µL, 129.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 69.3 mg (127.7 µmol, 26%) of the title compound as a reddish oil after flash column chromatography on silica (hexanes to hexanes / EtOAc 50:1). $\mathbf{R_f}$ (hexanes / EtOAc 15:1 on silica) = 0.40, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.28 (t, *J* = 2.1 Hz, 1H), 8.17 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 7.75 (ddd, *J* = 7.7, 1.9, 1.0 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 5.16 (dd, *J* = 8.5, 6.5 Hz, 1H), 4.87 (dd, *J* = 7.9, 6.7 Hz, 1H), 3.31 (ddd, *J* = 15.2, 8.5, 6.7 Hz, 1H), 2.98 (ddd, *J* = 15.3, 7.9, 6.5 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 148.6, 143.3, 133.7, 130.4, 123.6, 122.6, 56.6, 29.0, -31.2. **IR** (neat): 3083, 3004, 2870, 1692, 1614, 1525, 1497, 1439, 1346, 1241, 1204, 1167, 1081, 1023, 1010, 932, 902, 805, 731, 675 cm^{-1}. **HRMS** (EI) m/z calculated for $C_9H_8NO_2I_2$ ($[M^{+\bullet}-I^{\bullet}]^+$) 415.86389, found 415.86388.

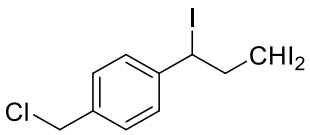
(1,3,3-triiodo-2-methylpropyl)benzene (d.r. = 53:47) (25x)



Following general procedure ***GP-I*** using (*E*)-prop-1-en-1-ylbenzene (**1x**) (129.7 µL, 118.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and

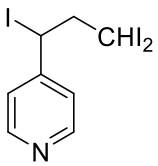
MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 200.3 mg (391.3 µmol, 78%) of the title compound as an inseparable mixture of two diastereomers (d.r. = 53:47) as a reddish oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.40, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.45 – 7.27 (m, 10H, both diastereomers), 6.15 (dd, *J* = 2.2, 0.7 Hz, 1H, minor diastereomer), 4.89 (dd, *J* = 2.3, 0.8 Hz, 1H, major diastereomer), 4.80 (d, *J* = 10.4 Hz, 1H, major diastereomer), 4.71 (d, *J* = 10.6 Hz, 1H, minor diastereomer), 2.30 – 2.21 (m, 1H, major diastereomer), 2.19 – 2.09 (m, 1H, minor diastereomer), 1.66 (dd, *J* = 6.3, 0.6 Hz, 3H, major diastereomer), 1.04 (dd, *J* = 6.3, 0.7 Hz, 3H, minor diastereomer). **^{13}C-NMR** (75 MHz, $CDCl_3$, both diastereomers) δ = 142.1, 141.7, 129.4, 129.1, 128.8, 128.5, 127.9, 127.5, 51.3, 51.2, 40.0, 35.8, 23.1, 17.5, -7.8, -19.7. **IR** (neat): 3060, 3027, 2974, 2930, 2736, 2371, 2110, 1677, 1580, 1500, 1446, 1375, 1346, 1308, 1260, 1208, 1167, 1074, 1025, 910, 828, 746, 697 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{10}H_{11}I_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 384.89446, found 384.89481.

1-(chloromethyl)-4-(1,3,3-triiodopropyl)benzene (25ac)



Following general procedure ***GP-I*** using freshly distilled 1-(chloromethyl)-4-vinylbenzene (**1ac**) (140.9 µL, 152.6 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 191.7 mg (350.9 µmol, 70%) of the title compound as a reddish oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.23, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.43 – 7.33 (m, 4H), 5.12 (t, *J* = 7.5 Hz, 1H), 4.80 (t, *J* = 7.3 Hz, 1H), 4.56 (s, 2H), 3.28 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.04 (dt, *J* = 15.1, 7.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 141.1, 138.0, 129.5, 128.0, 57.2, 45.7, 30.9, -30.0. **IR** (neat): 3124, 3027, 2982, 2952, 2822, 2706, 2654, 2624, 2520, 2453, 2374, 2341, 2244, 1908, 1793, 1689, 1607, 1562, 1509, 1420, 1349, 1316, 1264, 1222, 1200, 1163, 1081, 1021, 1001, 906, 828, 783, 727, 678 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{10}H_{10}ClI_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 418.85549, found 418.85533.

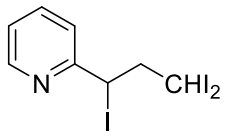
4-(1,3,3-triiodopropyl)pyridine (25ad)



Following general procedure ***GP-I*** using freshly distilled 4-vinylpyridine (**1ad**) (107.8 µL, 105.1 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL,

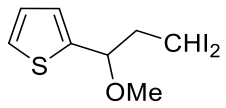
0.25 M) at room temperature (25 °C) for 3 h yielded 151.3 mg (303.3 µmol, 61%) of the title compound as an orange sticky oil after flash column chromatography on silica (hexanes to hexanes / EtOAc 5:1 to 1:1). $\mathbf{R_f}$ (hexanes / EtOAc 1:1 on silica) = 0.63, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.61 – 8.55 (m, 2H), 7.33 – 7.27 (m, 2H), 4.98 (dd, *J* = 8.2, 6.7 Hz, 1H), 4.83 (dd, *J* = 7.7, 7.0 Hz, 1H), 3.23 (ddd, *J* = 15.2, 8.2, 7.0 Hz, 1H), 2.95 (ddd, *J* = 15.2, 7.7, 6.7 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 150.6, 149.8, 122.4, 56.1, 28.1, -31.3. **IR** (neat): 2960, 2870, 1595, 1543, 1495, 1481, 1416, 1364, 1320, 1293, 1223, 1163, 1081, 995, 906, 816, 727, 707 cm^{-1}. **HRMS** (EI) m/z calculated for $C_8H_8NI_3$ ([$M^{+\bullet}$]) 498.77853, found 498.77735.

2-(1,3,3-triiodopropyl)pyridine (25ae)



Following general procedure ***GP-I*** using freshly distilled 2-vinylpyridine (**1ae**) (105.3 µL, 105.1 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), [Cu(dap)$_2$]Cl (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 158.7 mg (318.1 µmol, 64%) of the title compound as a reddish sticky oil after flash column chromatography on silica (hexanes to hexanes / EtOAc 7:1 to 3:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.63, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.59 (ddd, *J* = 4.9, 1.9, 0.9 Hz, 1H), 7.66 (td, *J* = 7.7, 1.8 Hz, 1H), 7.36 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.21 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 5.23 (t, *J* = 7.3 Hz, 1H), 4.92 (t, *J* = 7.3 Hz, 1H), 3.38 (dt, *J* = 15.0, 7.4 Hz, 1H), 3.25 (dt, *J* = 15.1, 7.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 159.0, 150.1, 137.4, 123.3, 122.5, 54.8, 32.0, -29.2. **IR** (neat): 2967, 2919, 2658, 2113, 1703, 1607, 1583, 1528, 1461, 1387, 1346, 1290, 1230, 1159, 1073, 1044, 992, 982, 850, 764, 723, 678 cm^{-1}. **HRMS** (EI) m/z calculated for $C_8H_8NI_2$ ([$M^{+\bullet}$]) 371.87406, found 371.87483.

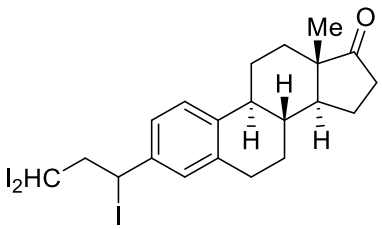
2-(3,3-diiodo-1-methoxypropyl)thiophene (OMe-25af)



Following general procedure ***GP-I*** using a freshly distilled 2-vinylthiophene (**1af**) (105.5 µL, 110.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), [Cu(dap)$_2$]Cl (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 116.6 mg (285.8 µmol, 57%) of the title compound as a reddish oil after flash column chromatography on silica (hexanes to hexanes / EtOAc 10:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.78, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.33 (ddd, *J* = 5.0, 1.3,

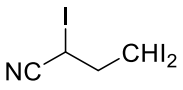
0.6 Hz, 1H), 7.06 (ddd, *J* = 3.5, 1.3, 0.5 Hz, 1H), 7.00 (dd, *J* = 5.0, 3.5 Hz, 1H), 5.10 (dd, *J* = 9.8, 5.1 Hz, 1H), 4.45 (dd, *J* = 8.9, 4.3 Hz, 1H), 3.29 (s, 3H), 2.91 (ddd, *J* = 14.8, 8.9, 5.1 Hz, 1H), 2.68 (ddd, *J* = 14.8, 9.8, 4.4 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.0, 126.8, 126.2, 125.9, 79.7, 56.9, 56.2, -31.5. **IR** (neat): 3101, 3068, 2967, 2928, 2866, 2821, 2113, 2076, 1439, 1372, 1320, 1230, 1208, 1096, 962, 906, 828, 805, 757, 693 cm^{-1}. **HRMS** (APCI) m/z calculated for $C_8H_{11}I_2OS$ ($[M]^+$) 407.8542, found 407.8542.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(1,3,3-triiodopropyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (25ag)



Following general procedure ***GP-I*** using (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**1ag**) (280.4 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and DCM (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 135.9 mg (201.6 µmol, 40% / 58% based on recovered starting material) of the title compound diastereoselective as a reddish oil after flash column chromatography on silica (hexanes to hexanes / EtOAc 9:1). **R_f** (hexanes / EtOAc 4:1 on silica) = 0.63, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.20 – 7.06 (m, 3H), 5.05 (t, *J* = 7.5 Hz, 1H), 4.77 (t, *J* = 7.3 Hz, 1H), 3.23 (dt, *J* = 15.2, 7.6 Hz, 1H), 2.99 (dtd, *J* = 15.3, 7.2, 1.1 Hz, 1H), 2.86 (dd, *J* = 9.2, 4.4 Hz, 2H), 2.47 (dd, *J* = 18.3, 8.4 Hz, 1H), 2.42 – 2.32 (m, 1H), 2.25 – 2.13 (m, 1H), 2.08 – 1.83 (m, 4H), 1.61 – 1.42 (m, 6H), 0.87 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 220.8, 140.7, 138.3, 137.5, 127.9, 126.3, 124.9, 57.4, 50.6, 48.1, 44.6, 38.1, 38.0, 36.0, 32.2, 29.5, 26.5, 25.7, 21.7, 14.0, -29.3. **IR** (neat): 2926, 2855, 1733, 1662, 1498, 1454, 1424, 1372, 1342, 1290, 1256, 1215, 1167, 1081, 1006, 921, 887, 820, 749, 691 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{21}H_{25}OI_3$ ($[M^{+\bullet}]$) 673.9093, found 673.9090.

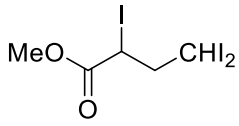
4-(1,3,3-triiodopropyl)benzonitrile (25ah)



Following general procedure ***GP-I*** using acrylonitrile (**1ah**) (98.8 µL, 79.6 mg, 1.5 mmol, 3.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 174.0 mg (389.4 µmol, 78%) of the title compound as a reddish oil after flash column chromatography on silica (hexanes to hexanes / EtOAc 10:1). **R_f** (hexanes / EtOAc 7:1 on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz,

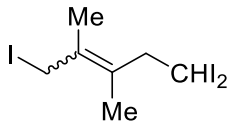
$CDCl_3$) δ = 5.03 (t, *J* = 7.4 Hz, 1H), 4.32 (t, *J* = 7.7 Hz, 1H), 3.00 (td, *J* = 7.6, 1.3 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 117.1, 52.9, -3.9, -35.6. **IR** (neat): 3002, 2945, 2236, 2113, 1420, 1338, 1311, 1299, 1230, 1174, 1100, 1081, 992, 936, 891, 835, 805, 731, 707 cm^{-1}. **HRMS** (EI) m/z calculated for $C_4H_4NI_3$ ([$M^{+\bullet}$]) 446.74723, found 446.74650.

methyl 2,4,4-triiodobutanoate (25ai)



Following general procedure ***GP-I*** using methyl acrylate (**1ai**) (135.9 µL, 129.1 mg, 1.5 mmol, 3.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), [Cu(dap)$_2$]Cl (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 144.7 mg (301.6 µmol, 60% / 77% based on recovered starting material) of the title compound as a reddish oil after flash column chromatography on silica (hexanes to hexanes / EtOAc 10:1). **R_f** (hexanes / EtOAc 7:1 on silica) = 0.65, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.02 (dd, *J* = 7.9, 6.7 Hz, 1H), 4.44 (dd, *J* = 7.8, 6.8 Hz, 1H), 3.78 (s, 3H), 2.96 (ddd, *J* = 7.9, 6.8, 4.9 Hz, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 170.2, 53.5, 52.1, 20.1, -31.8. **IR** (neat): 2982, 2948, 1722, 1431, 1343, 1301, 1260, 1200, 1148, 1091, 1081, 1021, 1000, 987, 883, 821, 753, 723, 690 cm^{-1}. **HRMS** (EI) m/z calculated for $C_5H_7O_2I_3$ ([$M^{+\bullet}$]) 479.75746, found 479.75826.

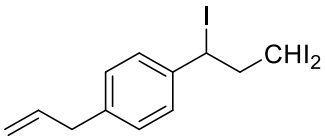
1,5,5-triiodo-2,3-dimethylpent-2-ene (*E*/*Z* = 83:17) (25an)



Following general procedure ***GP-I*** using 2,3-dimethylbuta-1,3-diene (**1an**) (113.2 µL, 82.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), [Cu(dap)$_2$]Cl (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 195.2 mg (410.2 µmol, 82%) of the title compound as an inseparable mixture of two diastereomers (*E*/*Z* = 83:17) as a reddish oil after flash column chromatography on silica (hexanes). Stereochemistry was assigned in analogy to literature.[42] **R_f** (hexanes on silica) = 0.53, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 5.15 (t, *J* = 7.7 Hz, 1H, minor diastereomer), 5.10 (t, *J* = 7.8 Hz, 1H, major diastereomer), 3.99 (s, 2H, minor diastereomer), 3.90 (s, 2H, major diastereomer), 3.25 (two overlapping d, 4H, both diastereomers), 1.84 (q, *J* = 1.5 Hz, 3H, major diastereomer), 1.77 (q, *J* = 0.9 Hz, 3H, minor diastereomer), 1.66 (two overlapping q, 6H, both diastereomers). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 133.4 (major diastereomer), 132.9 (minor diastereomer), 131.4 (major diastereomer), 131.3 (minor diastereomer), 53.5 (major

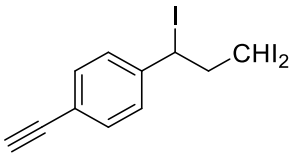
diastereomer), 53.1 (minor diastereomer), 18.9 (minor diastereomer), 18.7 (minor diastereomer), 18.3 (major diastereomer), 17.7 (major diastereomer), 11.0 (major diastereomer), 10.6 (minor diastereomer), -29.7 (major diastereomer), -30.2 (minor diastereomer). **IR** (neat): 2974, 2911, 2855, 2374, 2113, 1894, 1737, 1580, 1525, 1431, 1372, 1312, 1238, 1189, 1144, 1081, 880, 820, 738 cm^{-1}. **HRMS** (EI) m/z calculated for $C_7H_{11}I_3$ ($[M^{+\bullet}]$) 475.79893, found 475.79998.

1-allyl-4-(1,3,3-triiodopropyl)benzene (25au)



Following general procedure ***GP-I*** using 1-allyl-4-vinylbenzene (**1au**) (157.8 µL, 144.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 175.8 mg (326.8 µmol, 65%) of the title compound as a reddish oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.40, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.04 – 5.86 (m, 1H), 5.19 – 5.06 (m, 3H), 4.80 (dd, *J* = 7.7, 7.0 Hz, 1H), 3.37 (d, *J* = 6.9 Hz, 2H), 3.29 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.06 (dt, *J* = 15.1, 7.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 140.9, 138.7, 136.8, 129.4, 127.6, 116.5, 57.4, 40.1, 31.9, -29.5. **IR** (neat): 3079, 2978, 2900, 2371, 1677, 1640, 1607, 1510, 1424, 1342, 1286, 1237, 1200, 1181, 1081, 992, 906, 820, 727, 678 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{12}H_{13}I_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 410.91011, found 410.90978.

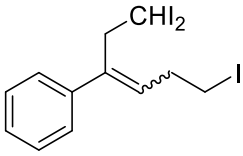
1-ethynyl-4-(1,3,3-triiodopropyl)benzene (25av)



Following general procedure ***GP-I*** using 1-ethynyl-4-vinylbenzene (**1av**) (128.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 184.4 mg (353.3 µmol, 71%) of the title compound as an orange sticky oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.43, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 5.11 (t, *J* = 7.5 Hz, 1H), 4.80 (t, *J* = 7.3 Hz, 1H), 3.27 (dt, *J* = 15.2, 7.6 Hz, 1H), 3.13 (s, 1H), 3.02 (dt, *J* = 15.2, 7.2 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 141.6, 133.0, 127.6, 122.6, 83.1, 78.5, 57.0, 30.7, -30.4. **IR** (neat): 3288, 3112, 3030, 2982, 2244, 2106, 1908, 1785, 1685, 1603,

1582, 1502, 1413, 1282, 1238, 1081, 999, 906, 831, 731, 690 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{11}H_9I_2$ ($[M^{+\bullet}\text{-}I^{\bullet}]^+$) 394.87881, found 394.87862.

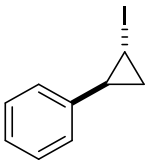
(1,1,6-triiodohex-3-en-3-yl)benzene (d.r. = 78:12) (25ax)



Following general procedure ***GP-I*** using (1-cyclopropylvinyl)benzene (**1ax**) (144.2 mg, 1.0 mmol, 2.0 equiv), iodoform (**24**) (196.9 mg, 0.5 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (4.4 mg, 5.0 µmol, 1.0 mol%) and MeOH (2.0 mL, 0.25 M) at room temperature (25 °C) for 3 h yielded 243.8 mg (453.2 µmol, 91%) of the title compound as an inseparable mixture of two diastereomers (d.r. = 78:12) as a slightly reddish oil after flash column chromatography on silica (hexanes). $\mathbf{R_f}$ (hexanes on silica) = 0.30, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.40 – 7.27 (m, 8H, both diastereomers), 7.18 – 7.13 (m, 2H, minor diastereomer), 5.82 (t, *J* = 7.2 Hz, 1H, major diastereomer), 5.61 (t, *J* = 7.2 Hz, 1H, minor diastereomer), 4.71 (t, *J* = 7.6 Hz, 1H, major diastereomer), 4.63 (t, *J* = 7.6 Hz, 1H, minor diastereomer), 3.73 (d, *J* = 7.6 Hz, 2H, major diastereomer), 3.48 (d, *J* = 7.6 Hz, 2H, minor diastereomer), 3.29 (t, *J* = 7.1 Hz, 2H, major diastereomer), 3.13 (t, *J* = 7.1 Hz, 2H, minor diastereomer), 2.86 (q, *J* = 7.2 Hz, 2H, major diastereomer), 2.49 (q, *J* = 7.1 Hz, 2H, minor diastereomer). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 141.4 (minor diastereomer), 140.9 (major diastereomer), 139.9 (major diastereomer), 131.2 (major diastereomer), 131.0 (minor diastereomer), 128.9 (major diastereomer), 128.8 (minor diastereomer), 128.5 (minor diastereomer), 128.0 (minor diastereomer), 127.9 (major diastereomer), 126.9 (major diastereomer), 90.1 (minor diastereomer), 57.9 (minor diastereomer), 48.8 (major diastereomer), 32.9 (major diastereomer), 32.9 (minor diastereomer), 4.8 (minor diastereomer), 4.6 (major diastereomer), -26.0 (minor diastereomer), -28.3 (major diastereomer). **IR** (neat): 3053, 3023, 2956, 2345, 1804, 1737, 1595, 1491, 1443, 1297, 1230, 1170, 1104, 1081, 1025, 910, 857, 764, 731, 697 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{12}H_{13}I_3$ ($[M^{+\bullet}]$) 537.81458, found 537.81322.

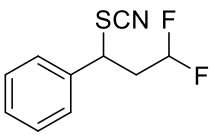
7.5.2 Compound Characterization for Further Transformations

***trans*-2-iodocyclopropyl)benzene (2a)**



A flame-dried Schlenk flask equipped with a magnetic stirring bar was charged with (1,3,3-triiodopropyl)benzene (**25a**) (99.6 mg, 0.2 mmol, 1.0 equiv). Under a slight nitrogen overpressure, a solution of SmI_2 in THF (0.1 M, 4.0 mL, 0.4 mmol, 2.0 equiv) was added and the resulting reaction mixture was magnetically stirred at room temperature (25 °C) for 2 h. The reaction was monitored by TLC. Afterwards, the crude mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes) to yield 29.5 mg (120.8 µmol, 60%) of the title compound as a colorless oil. The corresponding *cis*-diastereomer was not isolated. The trans/cis ratio (75 / 25) and overall NMR-yield (80%) was determined from the crude NMR using 1,1,2,2-tetrachloroethane as internal standard. Spectral data are in accordance with those reported in literature.[43] $\mathbf{R_f}$ (hexanes on silica) = 0.50, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.40 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.12 – 7.01 (m, 2H), 2.56 (ddd, *J* = 7.9, 5.0, 4.0 Hz, 1H), 2.33 (ddd, *J* = 9.8, 6.1, 4.0 Hz, 1H), 1.49 (dt, *J* = 7.9, 6.3 Hz, 1H), 1.41 (ddd, *J* = 9.4, 6.5, 5.0 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 140.4, 128.7, 126.6, 125.9, 27.9, 20.0, -13.1. **HRMS** (EI) m/z calculated for C_9H_9I ([$M^{+\bullet}$]) 243.97434, found 243.97377.

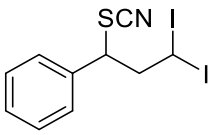
(3,3-difluoro-1-thiocyanatopropyl)benzene (7c)



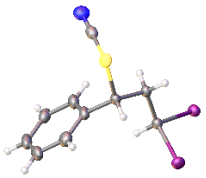
Based on a literature procedure,[44] a flame-dried Schlenk flask equipped with a magnetic stirring bar was charged with (3,3-diiodo-1-thiocyanatopropyl)-benzene (**34a**) (99.6 mg, 0.2 mmol, 1.0 equiv) and dissolved in anhydrous DCM (1.5 mL, 0.13 M) and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, $AgBF_4$ (85.7 mg, 0.44 mmol, 2.2 equiv) was added under a slight nitrogen overpressure and the resulting reaction mixture was magnetically stirred at room temperature (25 °C) for 2 h. The reaction was monitored by TLC. Finally, the crude mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes to hexanes / EtOAc 20:1 to 10:1) to yield 25.9 mg (121.5 µmol, 61%) of the title compound as a slightly yellowish oil. $\mathbf{R_f}$ (hexanes / EtOAc 9:1 on silica) = 0.55, Staining: Vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.46 – 7.38 (m, 3H), 7.36 – 7.32 (m, 2H), 5.91 (tdd, *J* = 55.8, 5.9, 3.7 Hz, 1H), 5.01 – 4.95 (m, 1H), 2.61 – 2.41 (m, 1H), 2.41 – 2.24 (m, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 137.8, 129.4, 129.1, 126.2, 125.9, 114.7 (t, *J* = 240.2 Hz), 56.5

(t, *J* = 6.7 Hz), 42.8 (t, *J* = 22.2 Hz). **^{19}F-NMR** (377 MHz, $CDCl_3$) δ = -118.36 (s, 2F). **IR** (neat): 3064, 3034, 2926, 2855, 2058, 1805, 1733, 1495, 1454, 1405, 1346, 1226, 1193, 1118, 1055, 991, 977, 913, 883, 828, 757, 697 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{15}H_{14}N_2$ ($[M^{+\bullet}]$) 213.04183, found 213.04207.

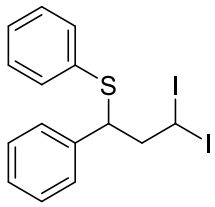
(3,3-diiodo-1-thiocyanatopropyl)benzene (34a)



Based on a modified literature procedure,[45] a flame-dried Schlenk flask equipped with a magnetic stirring bar was charged with (1,3,3-triiodopropyl)benzene (**25a**) (99.6 mg, 0.2 mmol, 1.0 equiv), NaSCN (40.5 mg, 0.5 mmol, 2.5 equiv), Na_2CO_3 (53.0 mg, 0.5 mmol, 2.5 equiv), dissolved in anhydrous MeCN (2.0 mL, 0.1 M) and magnetically stirred at room temperature (25 °C) for 12 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes to hexanes / EtOAc 10:1) to yield 77.0 mg (179.5 µmol, 90%) of the title compound as a yellowish solid. ***Gram-Scale:*** This procedure can be also scaled-up to gram-quantities using (1,3,3-triiodopropyl)benzene (**25a**) (1.49 g, 3.0 mmol, 1.0 equiv), NaSCN (608.0 mg, 7.5 mmol, 2.5 equiv), Na_2CO_3 (794.9 mg, 7.5 mmol, 2.5 equiv) and anhydrous MeCN (30.0 mL, 0.1 M) at room temperature (25 °C) for 24 h to yield 1.1 g (2.5 mmol, 85%) of the title compound as a yellowish solid after analogous work-up. Suitable crystals for X-ray analysis were obtained by crystallization using vapor diffusion method with DCM and *n*-pentane as solvent system. The crystals obtained were clear light yellow and prism-shaped. CCDC 2013499 contain the supplementary crystallographic data for this work. **mp**: 95 °C. **R_f** (hexanes / EtOAc 9:1 on silica) = 0.43, Staining: Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.47 – 7.33 (m, 5H), 4.63 (dd, *J* = 9.0, 5.8 Hz, 1H), 4.43 (dd, *J* = 8.7, 6.4 Hz, 1H), 3.30 – 3.08 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 135.2, 129.9, 129.8, 127.7, 110.5, 53.7, 52.2, -35.0. **IR** (neat): 3030, 2982, 2922, 2151, 2102, 1886, 1804, 1580, 1491, 1477, 1323, 1241, 1211, 1193, 1150, 1088, 1051, 1014, 772, 708 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{10}H_9NSI_2$ ($[M^{+\bullet}]$) 428.85396, found 428.85330.

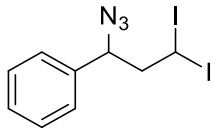


(3,3-diiodo-1-phenylpropyl)(phenyl)sulfane (34b)



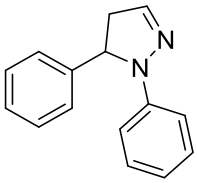
Based on a modified literature procedure,[45] a flame-dried Schlenk flask equipped with a magnetic stirring bar was charged with (1,3,3-triiodopropyl)benzene (**25a**) (99.6 mg, 0.2 mmol, 1.0 equiv), benzenethiol (51.0 µL, 55.1 mg, 0.5 mmol, 2.5 equiv), Na_2CO_3 (53.0 mg, 0.5 mmol, 2.5 equiv), dissolved in anhydrous MeCN (2.0 mL, 0.1 M) and magnetically stirred at room temperature (25 °C) for 12 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes to hexanes / EtOAc 10:1) to yield 64.9 mg (135.2 µmol, 68%) of the title compound as a yellowish oil. $\mathbf{R_f}$ (hexanes / EtOAc 9:1 on silica) = 0.75, Staining: Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.33 – 7.24 (m, 10H), 4.81 (dd, *J* = 7.9, 6.9 Hz, 1H), 4.22 (t, *J* = 7.4 Hz, 1H), 2.98 – 2.90 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 139.2, 133.5, 133.0, 129.1, 129.0, 128.1, 128.0, 127.9, 54.8, 53.4, -29.9. **IR** (neat): 3058, 3027, 2922, 2851, 1946, 1871, 1797, 1739, 1580, 1476, 1450, 1439, 1234, 1197, 1074, 1025, 913, 742, 693 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{15}H_{14}SI_2$ ($[M^{+\bullet}]$) 479.89001, found 479.88875.

(1-azido-3,3-diiodopropyl)benzene (34c)

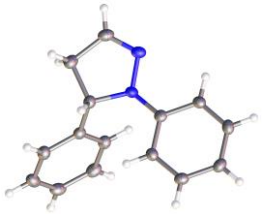


A flame-dried Schlenk flask equipped with a magnetic stirring bar was charged with (1,3,3-triiodopropyl)benzene (**25a**) (149.4 mg, 0.3 mmol, 1.0 equiv), NaN_3 (58.5 mg, 0.9 mmol, 2.5 equiv), Na_2CO_3 (79.5 mg, 0.75 mmol, 2.5 equiv), dissolved in anhydrous MeCN (3.0 mL, 0.1 M) and magnetically stirred at room temperature (25 °C) for 24 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (*n*-pentane) to yield 88.1 mg (213.3 µmol, 71%) of the title compound as a slightly yellowish oil. $\mathbf{R_f}$ (*n*-pentane on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.46 – 7.38 (m, 3H), 7.37 – 7.31 (m, 2H), 4.95 (dd, *J* = 9.1, 5.6 Hz, 1H), 4.56 (dd, *J* = 8.9, 5.3 Hz, 1H), 2.77 (ddd, *J* = 14.6, 8.9, 5.6 Hz, 1H), 2.65 (ddd, *J* = 14.7, 9.1, 5.2 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 137.2, 129.3, 129.1, 127.2, 67.4, 54.2, -32.8. **IR** (neat): 3317, 3064, 3030, 2999, 2945, 2896, 2374, 2095, 1949, 1879, 1804, 1722, 1655, 1584, 1532, 1507, 1420, 1331, 1320, 1230, 1173, 1088, 1021, 954, 869, 757, 697 cm^{-1}. **HRMS** (APCI) m/z calculated for $C_9H_{10}I_2N$ ($[(M-N_2)+H]^+$) 385.8897, found 385.8897.

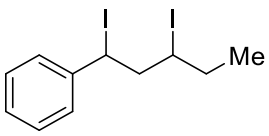
1,5-diphenyl-4,5-dihydro-*1H*-pyrazole (36a)



A flame-dried Schlenk flask equipped with a magnetic stirring bar was charged with (1,3,3-triiodopropyl)benzene (**25a**) (99.6 mg, 0.2 mmol, 1.0 equiv), phenylhydrazine (**40e**) (49.3 µL, 54.1 mg, 0.5 mmol, 2.5 equiv), Na_2CO_3 (53.0 mg, 0.5 mmol, 2.5 equiv), dissolved in anhydrous MeCN (2.0 mL, 0.1 M) and magnetically stirred at room temperature (25 °C) for 12 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes to hexanes / EtOAc 30:1) to yield 26.6 mg (119.7 µmol, 60%) of the title compound as a yellowish solid. Suitable crystals for X-ray analysis were obtained by crystallization using vapor diffusion method with DCM and *n*-pentane as solvent system. The crystals obtained were clear light yellow and needle-shaped. CCDC 2013500 contain the supplementary crystallographic data for this work. **mp**: 103 °C. $\mathbf{R_f}$ (hexanes / EtOAc 50:1 on silica) = 0.43, Staining: Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.40 – 7.27 (m, 5H), 7.22 – 7.12 (m, 2H), 7.02 – 6.91 (m, 2H), 6.85 – 6.69 (m, 2H), 5.02 (dd, *J* = 12.3, 8.0 Hz, 1H), 3.51 (ddd, *J* = 18.1, 12.3, 1.8 Hz, 1H), 2.82 (ddd, *J* = 18.0, 8.0, 1.8 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.5, 142.8, 139.0, 129.2, 129.0, 127.6, 126.0, 119.3, 113.5, 62.9, 45.3. **IR** (neat): 3064, 3027, 2922, 1737, 1677, 1595, 1581, 1491, 1454, 1349, 1267, 1241, 1156, 1103, 1025, 995, 958, 924, 857, 790, 742, 686 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{15}N_2$ ($[M+H]^+$) 223.1230, found 223.1231.



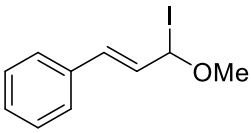
(1,3-diiodopentyl)benzene (42)



A flame-dried Schlenk flask equipped with a magnetic stirring bar was charged with anhydrous and degassed DCM (1.0 mL), cooled to 0 °C and a solution of diethylzinc in hexane (0.9 M, 15 wt%, 333.3 µL, 0.3 mmol, 1.5 equiv) was slowly added. In a separate flame-dried Schlenk flask (1,3,3-triiodopropyl)benzene (**25a**) (99.6 mg, 0.2 mmol, 1.0 equiv) was dissolved in anhydrous and degassed DCM (1.0 mL). The resulting (1,3,3-triiodopropyl)benzene (**25a**) solution was added dropwise to the previously prepared solution of diethylzinc at 0 °C and magnetically stirred at 0 °C for 20 min. The reaction mixture was allowed to warm to room temperature (25 °C) and magnetically stirred for another 2 h. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes) to yield 44.0 mg (110.0 µmol, 55%) of the title

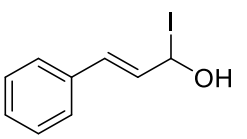
compound diastereoselective as a colorless oil. $\mathbf{R_f}$ (hexanes on silica) = 0.68, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.39 – 7.34 (m, 2H), 7.28 – 7.24 (m, 3H), 6.02 (ddd, *J* = 17.5, 9.8, 7.6 Hz, 1H), 5.13 – 5.10 (m, 1H), 5.09 – 5.06 (m, 1H), 3.21 (q, *J* = 7.5 Hz, 1H), 1.85 – 1.76 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 4H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.6, 142.4, 128.5, 127.8, 126.2, 114.2, 51.9, 28.5, 12.3. **IR** (neat): 3079, 3027, 2963, 2930, 2874, 1636, 1603, 1491, 1454, 1375, 1297, 1256, 1152, 1077, 1029, 992, 910, 842, 700, 697 cm^{-1}. **HRMS** (EI) m/z calculated for $C_{11}H_{14}I_2$ ([$M^{+\bullet}$]) 399.91794, found 399.91679.

(*E*)-(3-iodo-3-methoxyprop-1-en-1-yl)benzene (47a)



A Schlenk flask equipped with a magnetic stirring bar was charged with (1,3,3-triiodopropyl) benzene (**25a**) (99.6 mg, 0.2 mmol, 1.0 equiv), KOH (67.3 mg, 1.2 mmol, 6.0 equiv), dissolved in MeOH / water (4.0 mL, 9:1) and stirred at 100 °C for 2 h. The reaction was monitored by TLC. Afterwards, the mixture was allowed to cool to room temperature (25 °C), acidified with HCl (1.0 M), neutralized with sat. aqueous $NaHCO_3$ and extracted three times with DE. The combined organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 9:1) to yield 38.7 mg (141.2 µmol, 71%) of the title compound as a yellow oil. ***Gram-Scale:*** This procedure can be also scaled-up using (1,3,3-triiodopropyl)benzene (**25a**) (2.49 g, 5.0 mmol, 1.0 equiv), KOH (1.68 g, 30.0 mmol, 6.0 equiv) and MeOH / water (80.0 mL, 9:1) at reflux conditions for 2 h to yield 933.0 mg (3.59 mmol, 72%) of the title compound as a colorless oil after analogous work-up. $\mathbf{R_f}$ (hexanes / EtOAc 15:1 on silica) = 0.56, Staining: $KMnO_4$. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.40 – 7.28 (m, 5H), 6.64 (dd, *J* = 14.5, 6.4 Hz, 1H), 6.42 (dd, *J* = 14.5, 1.1 Hz, 1H), 4.60 (d, *J* = 6.4 Hz, 0H), 3.33 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 146.2, 139.3, 128.8, 128.2, 126.9, 85.6, 78.5, 56.7. **IR** (neat): 3060, 3027, 2982, 2926, 2855, 2822, 1879, 1808, 1603, 1491, 1454, 1312, 1267, 1204, 1103, 1092, 1029, 947, 846, 805, 768, 750, 697, 671 cm^{-1}. **HRMS** (APCI) m/z calculated for $C_{10}H_{15}INO$ ([$M+NH_4$]$^+$) 292.0193, found 292.0186.

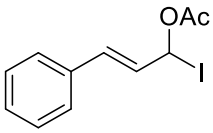
(*E*)-1-iodo-3-phenylprop-2-en-1-ol (47b)



A Schlenk flask equipped with a magnetic stirring bar was charged with (1,3,3-triiodopropyl) benzene (**25a**) (99.6 mg, 0.2 mmol, 1.0 equiv), KOH (67.3 mg, 1.2 mmol, 6.0 equiv), dissolved in MeCN / water (4.0 mL, 1:1) and stirred at 100 °C for 2 h. The reaction was monitored by TLC. Afterwards, the reaction was

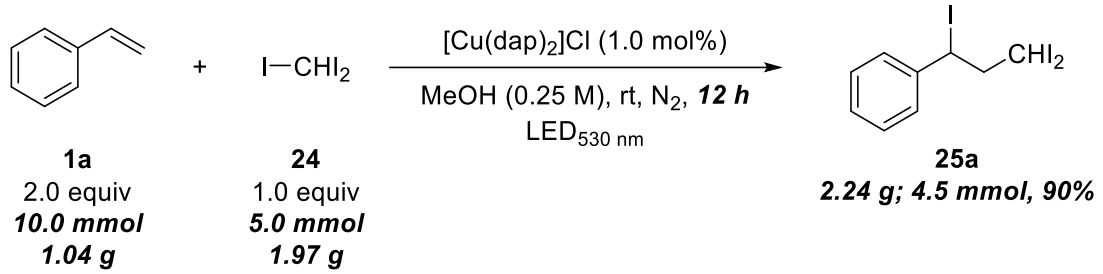
allowed to cool to room temperature (25 °C), acidified with HCl (1.0 M), neutralized with sat. aqueous $NaHCO_3$ and extracted three times with DE. The combined organic phase was dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 9:1) to yield 42.2 mg (162.3 µmol, 81%) of the title compound as a colorless oil. ***Gram-Scale**:* This procedure can be also scaled-up to gram-quantities using (1,3,3-triiodopropyl)benzene (**25a**) (2.49 g, 5.0 mmol, 1.0 equiv), KOH (1.68 g, 30.0 mmol, 6.0 equiv) and MeCN / water (80.0 mL, 1:1) at reflux conditions for 2 h to yield 1.08 g (4.15 mmol, 83%) of the title compound as a colorless oil after analogous work-up. $\mathbf{R_f}$ (hexanes / EtOAc 9:1 on silica) = 0.30, Staining: $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.41 – 7.28 (m, 5H), 6.74 (dd, *J* = 14.5, 5.9 Hz, 1H), 6.49 (dd, *J* = 14.4, 1.3 Hz, 1H), 5.17 (d, *J* = 5.8 Hz, 1H), 2.06 (s, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 147.4, 141.2, 128.9, 128.4, 126.5, 78.2, 76.8. **IR** (neat): 3302, 3060, 3030, 2863, 1665, 1607, 1562, 1491, 1454, 1390, 1267, 1191, 1163, 1062, 1006, 943, 842, 746, 697 cm^{-1}. **HRMS** (APCI) m/z calculated for $C_{19}H_{13}INO$ ($[M+NH_4]^+$) 278.0036, found 278.0031.

(*E*)-1-iodo-3-phenylallyl acetate (47c)



To the crude mixture of (*E*)-1-iodo-3-phenylprop-2-en-1-ol (**47b**) (4.0 mmol scale) was added triethylamine (1.12 mL, 809.5 mg, 8.0 mmol, 2.0 equiv), *N*,*N*-dimethylpyridin-4-amine (48.9 mg, 0.4 mmol, 10 mol%), dissolved in anhydrous DCM (20 mL, 0.2 M) and cooled to 0 °C. Afterwards, acetic anhydride (756.2 µL, 816.7 mg, 8.0 mmol, 2.0 equiv) was added and the reaction mixture was allowed to warm to room temperature (25 °C) and stirred for additional 3 h. After being quenched with brine, the mixture was extracted three times with DCM, dried over anhydrous $NaSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (hexanes to hexanes / EtOAc 18:1) to yield 851.9 mg (2.82 mmol, 71%) of the title compound as an orange oil. $\mathbf{R_f}$ (hexanes / EtOAc 9:1 on silica) = 0.55, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.41 – 7.32 (m, 5H), 6.72 (dd, *J* = 14.5, 6.3 Hz, 1H), 6.47 (dd, *J* = 14.5, 1.2 Hz, 1H), 6.20 (dd, *J* = 6.3, 1.2 Hz, 1H), 2.12 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 169.8, 143.6, 137.5, 128.9, 128.7, 127.2, 80.6, 77.1, 21.3. **IR** (neat): 3064, 2933, 1733, 1610, 1495, 1454, 1372, 1223, 1170, 1051, 1018, 943, 846, 749, 697 cm^{-1}. **HRMS** (APCI) m/z calculated for $C_{11}H_{11}O_2$ ($[M+H]^+$) 175.0754, found 175.0757.

7.5.3 Gram-Scale Functionalization



Up-scaling to gram quantities was carried out according general procedure ***GP-I*** (Chapter 7.5.1) in a flame-dried Schlenk tube (30.0 mL size, Figure 5, *A*) equipped with a magnetic stirring bar, using styrene (**1a**) (1.15 mL, 1.04 g, 10.0 mmol, 2.0 equiv), iodoform (**24**) (1.97 g, 5.0 mmol, 1.0 equiv), $[Cu(dap)_2]Cl$ (44.2 mg, 50.0 µmol, 1.0 mol%) and MeOH (20.0 mL, 0.25 M) at room temperature (25 °C) for a prolonged reaction time of 12 h to yield 2.24 g (4.50 mmol, 90%) of (1,3,3-triiodopropyl)benzene (**25a**) as a brownish to reddish solid after flash column chromatography on neutral aluminum oxide (hexanes).

Further purification was done by crystallization using vapor diffusion method with DCM and *n*-pentane as solvent system (Figure 5, *B*). The crystals obtained were white to yellowish and prism-shaped (Figure 5, *C*). The isolated product **25a** can be stored neatly in the dark at 4-8 °C (fridge).

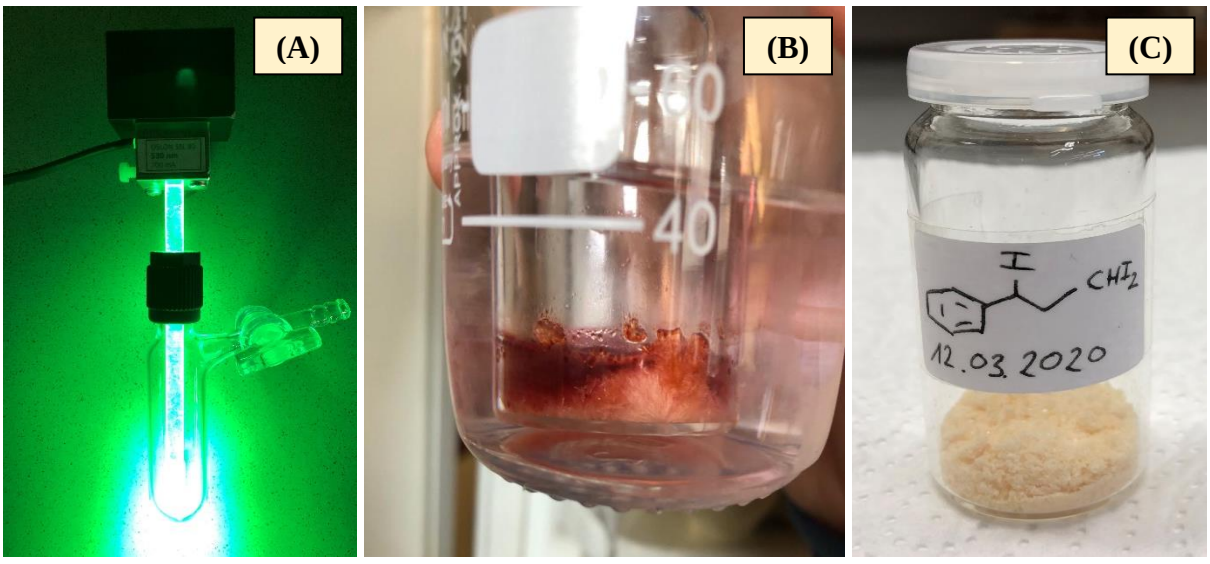
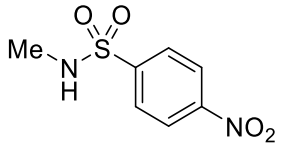


Figure 5. Reaction Upscaling: (A) Irradiation setup in a Schlenk tube (30.0 mL size); (B) Purification by crystallization using vapor diffusion method with DCM and *n*-pentane as solvent system; (C) Isolated compound **25a** after recrystallization.

7.6 Experimental Part for Chapter 5

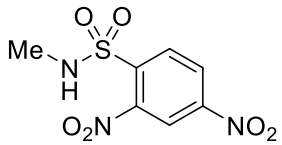
7.6.1 Compound Characterization of Protected Amines

_N_-methyl-4-nitrobenzenesulfonamide (Ns-2a)[46]



Based on a literature procedure,[46] a round-bottom flask equipped with a magnetic stirring bar was charged with 4-nitrobenzenesulfonyl chloride (2.22 g, 10.0 mmol, 1.0 equiv) and THF (10 mL, 1.0 M). Afterwards, methyl amine in THF (2.0 M, 15.0 mL, 3.0 equiv) and triethylamine (3.48 mL, 2.53 g, 25.0 mmol, 2.5 equiv) were added and the resulting mixture was stirred for 16 h at room temperature (25 °C). The reaction was monitored by TLC. Next, the reaction mixture was quenched with aqueous HCl (1.0 M) until a pH of 2 was reached and extracted three times with EtOAc. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo to yield 1.87 g (8.65 mmol, 86%) of the title compound as a white solid. Spectral data are in accordance with those reported in literature.[47] **R_f** (hexanes / EtOAc 1:1 on silica) = 0.63, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.37 (d, *J* = 8.8 Hz, 2H), 8.06 (d, *J* = 8.9 Hz, 2H), 4.93 (d, *J* = 5.3 Hz, 1H), 2.72 (d, *J* = 5.2 Hz, 4H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 150.2, 144.9, 128.6, 124.6, 29.4.

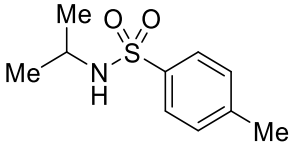
_N_-methyl-2,4-dinitrobenzenesulfonamide (DNs-2a)



A round-bottom flask equipped with a magnetic stirring bar was charged with 2,4-dinitrobenzenesulfonyl chloride (2.67 g, 10.0 mmol, 1.0 equiv) and THF (20 mL, 0.5 M). The reaction mixture was cooled to 0 °C and triethylamine (3.48 mL, 2.53 g, 25.0 mmol, 2.5 equiv) and methyl amine in THF (2.0 M, 15.0 mL, 3.0 equiv) were added sequentially in small portions. Afterwards, the resulting mixture was allowed to warm to room temperature (25 °C) and stirred for 16 h. The reaction was monitored by TLC. The reaction mixture was quenched with aqueous HCl (1.0 M) until a pH of 2 was reached and extracted three times with EtOAc. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo to yield 1.34 g (5.13 mmol, 51%) of the title compound as a yellowish solid. **mp**: 170 °C. **R_f** (hexanes / EtOAc 1:1 on silica) = 0.58, Staining: UV, $KMnO_4$. **^{1}H-NMR** (400 MHz, DMSO-d_6) δ = 8.93 – 8.85 (m, 1H), 8.82 (d, *J* = 2.8 Hz, 1H), 8.26 (ddd, *J* = 9.6, 2.8, 0.8 Hz, 1H), 7.12 (d, *J* = 9.6 Hz, 1H), 3.05 (d, *J* = 5.0 Hz, 3H). **^{13}C-NMR** (101 MHz, DMSO-d_6): δ =. 148.7,

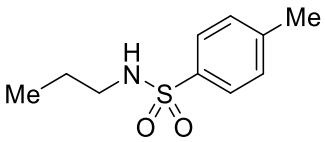
134.6, 129.9, 129.5, 123.4, 115.1, 30.3. **IR** (neat): 3355, 3097, 2930, 2419, 2363, 1618, 1584, 1521, 1500, 1409, 1334, 1308, 1274, 1230, 1182, 1136, 1107, 913, 831, 701, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_7H_8N_3O_4S$ ($[M+H]^+$) 198.0509, found 198.0509.

_N_-isopropyl-4-methylbenzenesulfonamide (2bf)[46]



Based on a literature procedure,[46] a round-bottom flask equipped with a magnetic stirring bar was charged with tosyl chloride (381.3 mg, 2.0 mmol, 1.0 equiv), THF (2.0 mL, 1.0 M) and triethylamine (696.9 µL, 506.0 mg, 5.0 mmol, 2.5 equiv). Afterwards, propan-2-amine (515.5 µL, 354.7 mg, 6.0 mmol, 3.0 equiv) was added dropwise and the resulting mixture was stirred for 4 h at room temperature (25 °C) while a precipitate formed. The reaction was monitored by TLC. Then, a solution of aqueous HCl (1.0 M) was added until a pH of 2 was reached. The solution was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield 390 mg (1.83 mmol, 91%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[46] **R_f** (hexanes / EtOAc 2:1 on silica) = 0.63, Staining: UV, Vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.77 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 1H), 4.65 (d, *J* = 7.3 Hz, 1H), 3.43 (h, *J* = 6.5 Hz, 1H), 2.42 (s, 3H), 1.06 (d, *J* = 6.5 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.3, 138.2, 129.8, 127.1, 46.2, 23.8, 21.6.

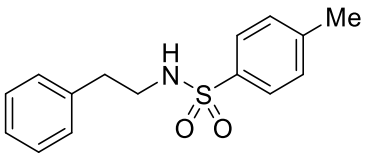
4-methyl-_N_-propylbenzenesulfonamide (2bg)[48]



Based on a literature procedure,[48] a round-bottom flask equipped with a magnetic stirring bar was charged with tosyl chloride (953.2 mg, 5.0 mmol, 1.0 equiv) and DCM (10.0 mL, 0.4 M). The resulting reaction mixture was cooled to 0 °C and propan-1-amine (619.2 µL, 443.3 mg, 7.5 mmol, 1.5 equiv) was added dropwise. The reaction was allowed to warm to room temperature (25 °C) and stirred for 30 min. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield 880.8 mg (4.13 mmol, 83%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[48] **R_f** (hexanes / EtOAc 2:1 on silica) = 0.60, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 4.81 (s, 1H), 2.88 (t, *J* = 7.1 Hz, 2H),

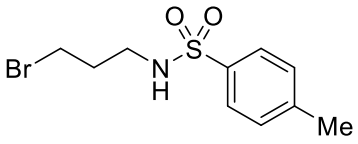
2.42 (s, 3H), 1.47 (h, *J* = 7.3 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.4, 137.1, 129.8, 127.2, 45.1, 23.0, 21.6, 11.2.

4-methyl-*N*-phenethylbenzenesulfonamide (2bh)[49]



Based on a literature procedure,[49] a round-bottom flask equipped with a magnetic stirring bar was charged with 2-phenylethan-1-amine (503.9 µL, 484.7 mg, 4.0 mmol, 1.0 equiv) and DCM (10.0 mL, 0.4 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.67 mL, 1.21 g, 12.0 mmol, 3.0 equiv) was added. Afterwards, tosyl chloride (800.7 mg, 4.2 mmol, 1.05 equiv) was added in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 6 h. The reaction was monitored by TLC. Next, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield 866.5 mg (3.15 mmol, 79%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[49] **R_f** (hexanes / EtOAc 2:1 on silica) = 0.58, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.20 (m, 5H), 7.11 – 7.04 (m, 2H), 4.56 (t, *J* = 5.7 Hz, 1H), 3.21 (q, *J* = 6.7 Hz, 2H), 2.76 (t, *J* = 7.0 Hz, 2H), 2.43 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.5, 137.8, 137.0, 129.8, 128.8, 127.2, 126.9, 44.3, 35.9, 21.7.

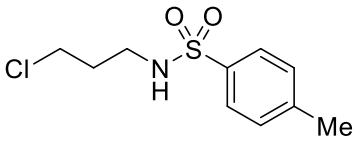
***N*-(3-bromopropyl)-4-methylbenzenesulfonamide (2bi)[50]**



Based on a literature procedure,[50] a round-bottom flask equipped with a magnetic stirring bar was charged with 3-bromopropan-1-amine hydrobromide (1.05 g, 4.8 mmol, 1.2 equiv), tosyl chloride (762.6 mg, 4.0 mmol, 1.0 equiv) and DCM (15.0 mL, 0.27 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.39 mL, 1.01 g, 10.0 mmol, 2.5 equiv) was added dropwise. The reaction was stirred for 20 min at 0 °C. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield 879.6 mg (3.01 mmol, 75%) of the title compound as a white solid. Spectral data are in agreement with those reported in literature.[50] **R_f** (hexanes / EtOAc 2:1 on silica) = 0.45, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.92 (s, 1H), 3.41 (t,

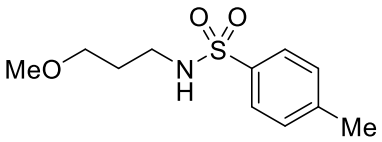
J = 6.3 Hz, 2H), 3.09 (q, *J* = 5.9 Hz, 2H), 2.43 (s, 3H), 2.02 (p, *J* = 6.4 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.8, 136.7, 129.9, 127.2, 41.5, 32.4, 30.4, 21.7.

***N*-(3-chloropropyl)-4-methylbenzenesulfonamide (2bj)**



A round-bottom flask equipped with a magnetic stirring bar was charged with 3-chloropropan-1-amine hydrochloride (624.1 mg, 4.8 mmol, 1.2 equiv), tosyl chloride (762.6 mg, 4.0 mmol, 1.0 equiv) and DCM (15.0 mL, 0.27 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.39 mL, 1.01 g, 10.0 mmol, 2.5 equiv) was added dropwise. The reaction was stirred for 20 min at 0 °C. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield 827.1 mg (3.34 mmol, 83%) of the title compound as a white solid. Spectral data are in agreement with those reported in literature.[51] **R_f** (hexanes / EtOAc 2:1 on silica) = 0.45, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 7.7 Hz, 2H), 5.04 (s, 1H), 3.55 (t, *J* = 6.2 Hz, 2H), 3.09 (q, *J* = 6.1 Hz, 2H), 2.42 (s, 3H), 1.93 (p, *J* = 6.5 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.7, 136.7, 129.9, 127.2, 42.0, 40.5, 32.3, 21.7.

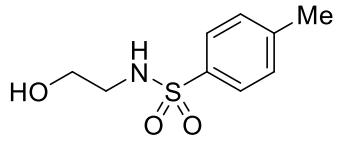
***N*-(3-methoxypropyl)-4-methylbenzenesulfonamide (2bk)[52]**



Based on a literature procedure,[52] a round-bottom flask equipped with a magnetic stirring bar was charged with 3-methoxypropan-1-amine (611.9 µL, 534.8 mg, 6.0 mmol, 1.2 equiv) and DCM (15.0 mL, 0.3 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.74 mL, 1.26 g, 12.5 mmol, 2.5 equiv) was added. Afterwards, tosyl chloride (953.2 mg, 5.0 mmol, 1.0 equiv) was added in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 20 min. The reaction was monitored by TLC. Next, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield 794.1 mg (3.26 mmol, 65%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[52] **R_f** (hexanes / EtOAc 2:1 on silica) = 0.33, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 3.39 (t, 3H), 3.27 (s, 3H), 3.10 – 2.98

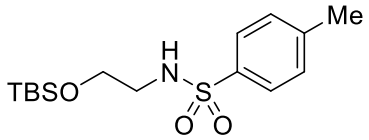
(m, 2H), 2.42 (s, 3H), 1.75 – 1.63 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.3, 137.1, 129.8, 127.2, 71.6, 58.9, 42.2, 29.0, 21.6.

***N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (2`bl)[53]**



Based on a literature procedure,[53] a round-bottom flask equipped with a magnetic stirring bar was charged with 2-aminoethan-1-ol (1.33 mL, 1.34 g, 22.0 mmol, 1.1 equiv) and DCM (40.0 mL, 0.5 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (2.66 mL, 2.02 g, 50.0 mmol, 2.5 equiv) was added. Afterwards, tosyl chloride (3.81 g, 20.0 mmol, 1.0 equiv) was subjected to the reaction mixture in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 20 min. The reaction was monitored by TLC. Next, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield 3.5 g (16.26 mmol, 81%) of the title compound as a white solid. Spectral data are in agreement with those reported in literature.[53] **R_f** (hexanes / EtOAc 1:3 on silica) = 0.33, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 1H), 3.67 (t, *J* = 5.0 Hz, 2H), 3.05 (t, *J* = 5.0 Hz, 2H), 2.41 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.7, 136.7, 129.9, 127.2, 61.4, 45.3, 21.6.

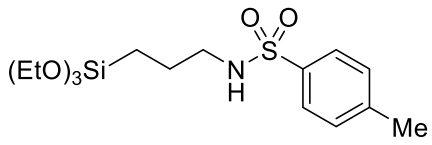
***N*-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-4-methylbenzenesulfonamide (2bl)[54]**



Based on a literature procedure,[54] a round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide (**2`bl**) (1.08 g, 5.0 mmol, 1.0 equiv), TBSCl (1.13 g, 7.5 mmol, 1.5 equiv), imidazole (680.8 mg, 10.0 mmol, 2.0 equiv) and DCM (10 mL, 0.5 M). The resulting reaction mixture was stirred for 22 h at room temperature (25 °C). Afterwards, the reaction mixture was quenched with water and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 5:1) to yield 1.39 g (4.22 mmol, 84%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[54] **R_f** (hexanes / EtOAc 3:1 on silica) = 0.58, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.81 (t, *J* = 5.8 Hz,

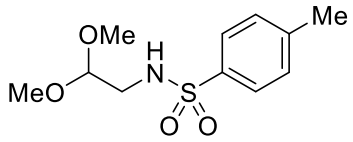
1H), 3.66 – 3.56 (m, 2H), 3.11 – 2.98 (m, 2H), 2.43 (s, 3H), 0.84 (s, 9H), 0.00 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.5, 137.0, 129.8, 127.2, 61.4, 45.3, 25.9, 21.6, 18.3, -5.4.

4-methyl-N-(3-(triethoxysilyl)propyl)benzenesulfonamide (2bm)



A round-bottom flask equipped with a magnetic stirring bar was charged with 3-(triethoxysilyl)propan-1-amine (1.41 mL, 1.33 g, 6.0 mmol, 1.2 equiv) and DCM (15.0 mL, 0.3 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.74 mL, 1.26 g, 12.5 mmol, 2.5 equiv) was added. Afterwards, tosyl chloride (953.2 mg, 5.0 mmol, 1.0 equiv) was subjected to the reaction mixture in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 20 min. The reaction was monitored by TLC. Next, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to yield 1.7 g (4.53 mmol, 91%) of the title compound as a colorless oil. **R_f** (hexanes / EtOAc 2:1 on silica) = 0.65, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 4.92 (t, *J* = 6.2 Hz, 1H), 3.77 (q, *J* = 7.0 Hz, 6H), 2.94 (q, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 1.57 (ddt, *J* = 9.2, 8.0, 6.8 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 9H), 0.61 – 0.46 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.3, 137.4, 129.7, 127.2, 58.6, 45.6, 23.1, 21.6, 18.4, 7.7. **IR** (neat): 3280, 2974, 2930, 2885, 1599, 1439, 1390, 1327, 1156, 1074, 954, 880, 813, 753, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{29}NNaO_5SSi$ ($[M+Na]^+$) 398.1428, found 398.1431.

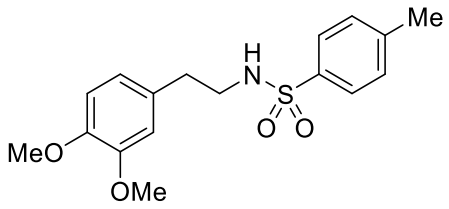
***N*-(2,2-dimethoxyethyl)-4-methylbenzenesulfonamide (2bn)[55]**



Based on a literature procedure,[55] a round-bottom flask equipped with a magnetic stirring bar was charged with 2,2-dimethoxyethan-1-amine (648.3 µL, 630.8 mg, 6.0 mmol, 1.2 equiv) and DCM (15.0 mL, 0.3 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.74 mL, 1.26 g, 12.5 mmol, 2.5 equiv) was added. Afterwards, tosyl chloride (953.2 mg, 5.0 mmol, 1.0 equiv) was added in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 20 min. The reaction was monitored by TLC. Next, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous

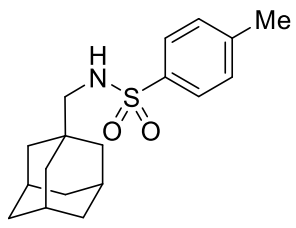
$MgSO_4$, filtered, and concentrated in vacuo to yield 1.01 g (3.89 mmol, 78%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[55] **R_f** (hexanes / EtOAc 1:3 on silica) = 0.63, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 0H), 4.72 (t, *J* = 6.2 Hz, 1H), 4.32 (t, *J* = 5.6 Hz, 1H), 3.31 (s, 6H), 3.02 (dd, *J* = 6.3, 5.6 Hz, 1H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ =143.7, 136.8, 129.9, 127.2, 102.7, 54.8, 44.7, 21.7.

***N*-(3,4-dimethoxyphenethyl)-4-methylbenzenesulfonamide (2bo)[56]**



Based on a literature procedure,[56] a round-bottom flask equipped with a magnetic stirring bar was charged with 2-(3,4-dimethoxyphenyl)ethan-1-amine (1.01 mL, 1.09 g, 6.0 mmol, 1.2 equiv) and DCM (15.0 mL, 0.3 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.74 mL, 1.26 g, 12.5 mmol, 2.5 equiv) was added. Afterwards, tosyl chloride (953.2 mg, 5.0 mmol, 1.0 equiv) was added in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 20 min. The reaction was monitored by TLC. Next, the reaction mixture was quenched with water and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 2:3) to yield 1.43 g (4.26 mmol, 85%) of the title compound as a white solid. Spectral data are in agreement with those reported in literature.[56] **R_f** (hexanes / EtOAc 2:3 on silica) = 0.58, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.62 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.56 (d, *J* = 2.0 Hz, 1H), 4.54 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.17 (t, *J* = 7.0 Hz, 2H), 2.70 (t, *J* = 6.9 Hz, 2H), 2.41 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 149.2, 148.0, 143.5, 137.0, 130.2, 129.8, 127.2, 120.8, 111.9, 111.5, 56.0, 55.9, 44.4, 35.4, 21.6.

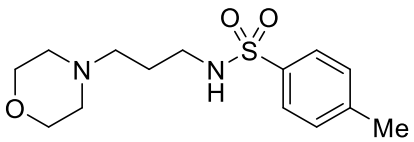
***N*-(((3*r*,5*r*,7*r*)-adamantan-1-yl)methyl)-4-methylbenzenesulfonamide (2bp)**



A round-bottom flask equipped with a magnetic stirring bar was charged with ((3*r*,5*r*,7*r*)-adamantan-1-yl)methanamine (974.3 µL, 909.0 mg, 5.5 mmol, 1.1 equiv) and DCM (15.0 mL, 0.3 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.74 mL, 1.26 g, 12.5 mmol, 2.5 equiv) was added. Afterwards, tosyl

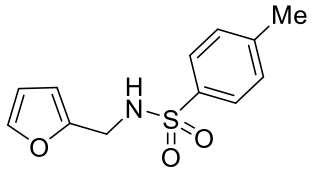
chloride (953.2 mg, 5.0 mmol, 1.0 equiv) was added in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 20 min. The reaction was monitored by TLC. Next, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to yield 875.5 mg (2.74 mmol, 55%) of the title compound as a colorless oil. **mp**: 135 °C. R_f (hexanes / EtOAc 2:1 on silica) = 0.65, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.65 (t, *J* = 6.8 Hz, 1H), 2.50 (d, *J* = 6.6 Hz, 2H), 2.37 (s, 3H), 1.90 (p, *J* = 3.0 Hz, 3H), 1.68 – 1.59 (m, 3H), 1.57 – 1.48 (m, 3H), 1.39 (d, *J* = 2.9 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ =143.3, 137.3, 129.8, 127.2, 55.0, 40.1, 36.9, 33.2, 28.2, 21.6. **IR** (neat): 3258, 2900, 2844, 1431, 1327, 1156, 1096, 1059, 917, 854, 813, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{18}H_{26}NO_2S$ ($[M+H]^+$) 320.1679, found 320.1680.

4-methyl-*N*-(3-morpholinopropyl)benzenesulfonamide (2bq)[56]



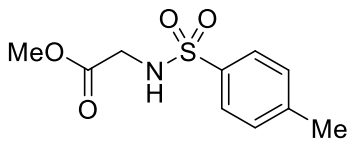
Based on a literature procedure,[56] a round-bottom flask equipped with a magnetic stirring bar was charged with 3-morpholinopropan-1-amine (876.7 µL, 865.3 mg, 6.0 mmol, 1.2 equiv) and DCM (15.0 mL, 0.3 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.74 mL, 1.26 g, 12.5 mmol, 2.5 equiv) was added. Afterwards, tosyl chloride (953.2 mg, 5.0 mmol, 1.0 equiv) was added in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 20 min. The reaction was monitored by TLC. Next, the reaction mixture was quenched with water and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel ($CHCl_3$ / MeOH 9:1) to yield 1.49 g (5.0 mmol, 100%) of the title compound as a pale-yellow oil. Spectral data are in agreement with those reported in literature.[56] **R_f** ($CHCl_3$ / MeOH 9:1 on silica) = 0.53, Staining: UV, vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 6.79 (s, 1H), 3.70 (t, *J* = 4.7 Hz, 4H), 3.04 (t, *J* = 5.9 Hz, 2H), 2.46 – 2.33 (m, 9H), 1.63 (p, *J* = 6.0 Hz, 2H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.2, 137.3, 129.7, 127.1, 66.9, 58.2, 53.6, 43.8, 24.1, 21.6.

_N_-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (2br)[57]



Based on a literature procedure,[57] a round-bottom flask equipped with a magnetic stirring bar was charged with furan-2-ylmethanamine (555.0 µL, 582.7 mg, 6.0 mmol, 1.2 equiv) and DCM (15.0 mL, 0.3 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.74 mL, 1.26 g, 12.5 mmol, 2.5 equiv) was added. Afterwards, tosyl chloride (953.2 mg, 5.0 mmol, 1.0 equiv) was added in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 20 min. The reaction was monitored by TLC. Next, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield 821.4 mg (3.27 mmol, 65%) of the title compound as a white solid. Spectral data are in agreement with those reported in literature.[57] **R_f** (hexanes / EtOAc 2:1 on silica) = 0.50, Staining: UV, vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.21 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.19 (dd, *J* = 3.3, 1.9 Hz, 1H), 6.07 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.93 (s, 1H), 4.14 (d, *J* = 3.8 Hz, 2H), 2.39 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$): δ =149.7, 143.6, 142.6, 137.0, 129.8, 127.2, 110.5, 108.3, 40.2, 21.6.

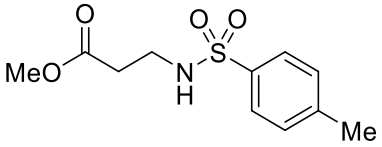
methyl tosylglycinate (2bs)[58]



Based on a literature procedure,[58] a round-bottom flask equipped with a magnetic stirring bar was charged with glycinate hydrochloride (251.1 mg, 2.0 mmol, 1.0 equiv) and DCM (10.0 mL, 5.0 M). Triethylamine (613.3 µL, 445.3 mg, 4.4 mmol, 2.2 equiv) was added and the resulting mixture was cooled to 0 °C. Afterwards, tosyl chloride (419.4 mg, 2.2 mmol, 1.1 equiv) was subjected to the reaction mixture in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 16 h. The reaction was monitored by TLC. Next, the reaction mixture was quenched with sat. aqueous NH_4Cl and extracted three times with DCM. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 1:1) to yield 405.2 mg (1.67 mmol, 83%) of the title compound as a white solid. Spectral data are in agreement with those reported in literature.[58] **R_f** (hexanes / EtOAc 1:1 on silica) = 0.68, Staining: UV, $KMnO_4$. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 5.22 (t, *J* = 5.6 Hz,

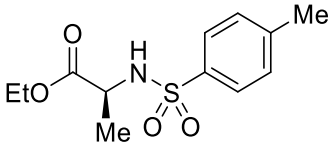
1H), 3.77 (d, *J* = 5.5 Hz, 2H), 3.62 (s, 3H), 2.41 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 169.4, 143.9, 136.2, 129.9, 127.3, 52.7, 44.1, 21.7.

methyl 3-((4-methylphenyl)sulfonamido)propanoate (2bt)



A round-bottom flask equipped with a magnetic stirring bar was charged with methyl 3-aminopropanoate hydrochloride (837.5 mg, 6.0 mmol, 1.2 equiv) and DCM (15.0 mL, 0.3 M). The resulting reaction mixture was cooled to 0 °C and triethylamine (1.74 mL, 1.26 g, 12.5 mmol, 2.5 equiv) was added. Afterwards, tosyl chloride (953.2 mg, 5.0 mmol, 1.0 equiv) was added in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 20 min. The reaction was monitored by TLC. Next, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered and concentrated in vacuo to yield 1.02 g (3.96 mmol, 80%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[59] **R_f** (hexanes / EtOAc 1:1 on silica) = 0.53, Staining: UV, vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 5.22 (t, *J* = 6.6 Hz, 1H), 3.65 (s, 3H), 3.18 (q, *J* = 6.1 Hz, 2H), 2.53 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 172.6, 143.6, 137.0, 129.9, 127.1, 52.1, 38.9, 34.0, 21.6.

ethyl tosyl-*L*-alaninate (2bu)

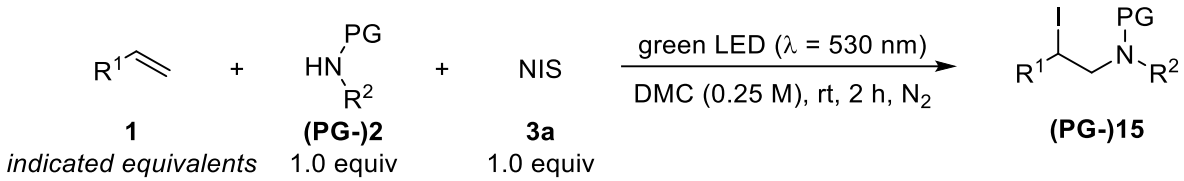


A round-bottom flask equipped with a magnetic stirring bar was charged with ethyl *L*-alaninate hydrochloride (1.11 g, 7.2 mmol, 1.2 equiv) and DCM (30.0 mL, 0.2 M). Triethylamine (2.1 mL, 1.52 g, 15.0 mmol, 2.5 equiv) was added and the resulting mixture was cooled to 0 °C. Afterwards, tosyl chloride (1.14 g, 6.0 mmol, 1.0 equiv) was added in small portions and the reaction was allowed to warm to room temperature (25 °C) and stirred for 16 h. The reaction was monitored by TLC. Next, the reaction mixture was quenched with aqueous HCl (1.0 M) and extracted three times with DCM. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield 1.12 g (4.13 mmol, 69%) of the title compound as a white solid. **Optical Rotation**: $[\alpha]_D^{25}$ = +11.2° (c = 1.0 g/mL, $CHCl_3$). **mp**: 52 °C. **R_f** (hexanes / EtOAc 1:1 on silica) = 0.70, Staining: UV, $KMnO_4$. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.72 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H),

5.38 (d, *J* = 8.5 Hz, 1H), 4.08 – 3.85 (m, 3H), 2.39 (s, 3H), 1.36 (d, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 172.3, 143.7, 136.9, 129.7, 127.3, 61.8, 51.6, 21.6, 19.9, 14.0. **IR** (neat): 3269, 3038, 2986, 1733, 1599, 1498, 1431, 1375, 1334, 1312, 1200, 1163, 1133, 1088, 1018, 895, 853, 820, 753, 690, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{12}H_{18}NO_4S$ ($[M+H]^+$) 272.0951, found 272.0956.

7.6.2 Compound Characterization of Iodoamination Products

General procedure for photochemical iodoamination of olefins (*GP-I*)



A flame-dried Schlenk tube (10.0 mL size; Figure 6, D) equipped with a magnetic stirring bar (Figure 6, E) was charged with amine **2** (0.5 mmol, 1.0 equiv), NIS (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and dissolved in DMC (2.0 mL, 0.25 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, alkene **1** (indicated equivalents) was added under a slight nitrogen overpressure and the screw-cap was replaced with a Teflon sealed inlet (Figure 6, C) for a glass rod (Figure 6, B), through which irradiation with a 530 nm high power LED (Figure 6, A) took place from above while the reaction mixture was magnetically stirred in an aluminum block at room temperature (25 °C) for 2 h. The reaction was monitored by TLC. Finally, the reaction mixture was concentrated in vacuo (water bath temperature of rotary evaporator should not exceed 40 °C) and the residue purified by flash column chromatography on silica gel.

Please note: *Products are sensitive to heat. Also, slow decomposition is noticeable in solution if oxygen or acid is present. Column chromatography should be performed immediately, and the solvent evaporated as soon as possible. Isolated compounds can be stored neatly in the dark at 4-8 °C (fridge).*

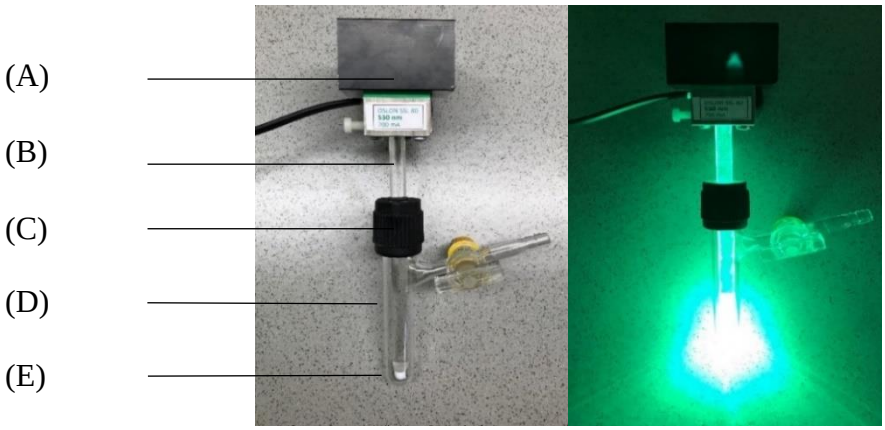
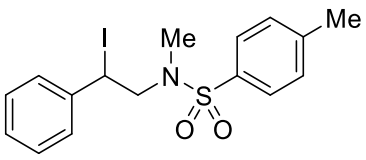


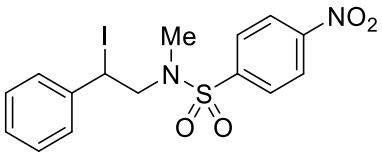
Figure 6. Irradiation setup for photochemical iodoamination reaction: (A) LED; (B) glass rod (used as a light conductor); (C) Teflon adapter; (D) Schlenk tube (10.0 mL size); (E) Teflon-coated magnetic stirring bar.

***N*-(2-iodo-2-phenylethyl)-*N*,4-dimethylbenzenesulfonamide (15a)**



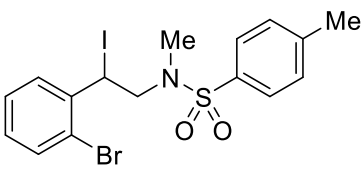
Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 204.4 mg (492.2 µmol, 98%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 5:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.50, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.35 – 7.27 (m, 5H), 5.28 (dd, *J* = 9.4, 6.5 Hz, 1H), 3.79 (dd, *J* = 14.3, 6.5 Hz, 1H), 3.59 (dd, *J* = 14.3, 9.5 Hz, 1H), 2.55 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.8, 140.7, 134.6, 129.9, 128.9, 128.6, 128.2, 127.4, 59.0, 36.5, 29.9, 21.6. **IR** (neat): 3064, 3030, 2960, 2922, 1595, 1495, 1454, 1338, 1200, 1156, 1097, 1088, 1036, 977, 924, 813, 760, 734, 693 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{19}INO_2S$ ($[M+H]^+$) 416.0176, found 416.0179.

***N*-(2-iodo-2-phenylethyl)-*N*-methyl-4-nitrobenzenesulfonamide (Ns-15a)**



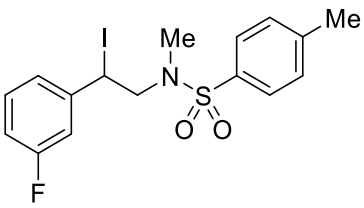
Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), *N*-methyl-4-nitrobenzenesulfonamide (**Ns-2a**) (108.1 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 219.7 mg (492.3 µmol, 98%) of the title compound as an yellowish oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.43, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.33 (d, *J* = 8.9 Hz, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.36 – 7.27 (m, 3H), 5.24 (dd, *J* = 9.5, 6.4 Hz, 1H), 3.84 (dd, *J* = 14.4, 6.4 Hz, 1H), 3.72 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.64 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 150.2, 143.8, 140.3, 129.1, 128.9, 128.6, 128.2, 124.6, 59.1, 36.3, 28.8. **IR** (neat): 3105, 3030, 2974, 2933, 2870, 1602, 1528, 1454, 1346, 1312, 1200, 1159, 1107, 1091, 1044, 977, 928, 854, 742 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{16}IN_2O_4S$ ($[M+H]^+$) 446.9870, found 446.9874.

***N*-(2-(2-bromophenyl)-2-iodoethyl)-*N*,4-dimethylbenzenesulfonamide (15b)**



Following general procedure ***GP-I*** using 1-bromo-2-vinyl-benzene (**1b**) (62.7 µL, 91.5 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 199.4 mg (403.5 µmol, 81%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.40, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.69 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.13 (ddd, *J* = 8.1, 7.3, 1.6 Hz, 1H), 5.71 (dd, *J* = 9.8, 6.4 Hz, 1H), 3.99 (dd, *J* = 13.9, 9.8 Hz, 1H), 3.55 (dd, *J* = 13.9, 6.4 Hz, 1H), 2.65 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.8, 139.2, 134.3, 133.4, 130.1, 129.9, 129.9, 128.5, 127.6, 123.4, 57.4, 35.4, 26.1, 21.7. **IR** (neat): 3027, 2967, 2922, 1595, 1439, 1342, 1211, 1156, 1088, 1051, 1021, 977, 921, 813, 738, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{18}BrINO_2S$ ($[M+H]^+$) 493.9281, found 493.9283.

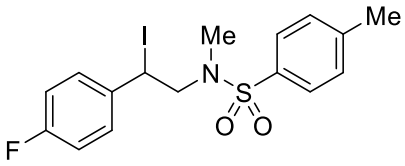
***N*-(2-(3-fluorophenyl)-2-iodoethyl)-*N*,4-dimethylbenzenesulfonamide (15c)**



Following general procedure ***GP-I*** using 1-fluoro-3-vinylbenzene (**1c**) (59.6 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 207.9 mg (479.8 µmol, 96%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.24 (m, 3H), 7.20 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.11 (ddd, *J* = 9.6, 2.5, 1.7 Hz, 1H), 6.96 (tdd, *J* = 8.3, 2.6, 1.2 Hz, 1H), 5.24 (dd, *J* = 9.4, 6.5 Hz, 1H), 3.73 (dd, *J* = 14.4, 6.4 Hz, 1H), 3.58 (dd, *J* = 14.4, 9.6 Hz, 1H), 2.58 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 164.3, 161.0, 143.9, 143.1 (d, *J* = 7.4 Hz), 134.4, 130.5 (d, *J* = 8.4 Hz), 129.9, 127.4, 123.9 (d, *J* = 2.9 Hz), 115.4 (dd, *J* = 29.9, 21.7 Hz), 59.0, 36.6, 28.1 (d, *J* = 2.0 Hz), 21.6. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -112.36 (s, 1F). IR (neat): 3027, 2967, 2922, 1588, 1491, 1450, 1338,

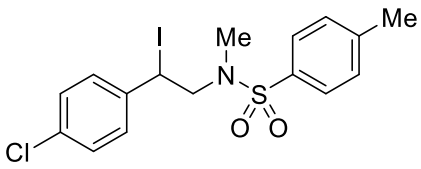
1238, 1156, 1111, 1080, 1044, 984, 932, 895, 813, 787, 749, 693, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{18}FINO_2S$ ($[M+H]^+$) 434.0081, found 434.0081.

***N*-(2-(4-fluorophenyl)-2-iodoethyl)-*N*,4-dimethylbenzenesulfonamide (15d)**



Following general procedure ***GP-I*** using 1-fluoro-4-vinylbenzene (**1d**) (59.6 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 203.2 mg (469.0 µmol, 94%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.40, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.37 (m, 2H), 7.34 – 7.28 (m, 2H), 7.03 – 6.94 (m, 2H), 5.27 (dd, *J* = 9.7, 6.4 Hz, 1H), 3.72 (dd, *J* = 14.3, 6.4 Hz, 1H), 3.61 (dd, *J* = 14.3, 9.7 Hz, 1H), 2.56 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 162.4 (d, *J* = 248.4 Hz), 143.9, 136.6 (d, *J* = 3.4 Hz), 134.4, 129.9 (d, *J* = 8.5 Hz), 129.9, 127.4, 115.9 (d, *J* = 21.7 Hz), 59.2, 36.5, 28.5, 21.6. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -113.01 (s, 1F). **IR** (neat): 3034, 2967, 2922, 1890, 1733, 1599, 1510, 1457, 1420, 1338, 1226, 1156, 1088, 1044, 980, 924, 835, 827, 734, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{18}FINO_2S$ ($[M+H]^+$) 434.0081, found 434.0084.

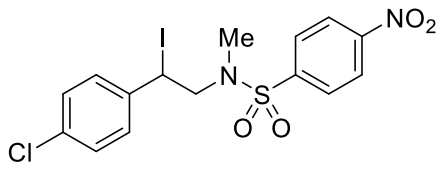
***N*-(2-(4-chlorophenyl)-2-iodoethyl)-*N*,4-dimethylbenzenesulfonamide (15e)**



Following general procedure ***GP-I*** using 1-chloro-4-vinylbenzene (**1e**) (60.0 µL, 69.3 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 210.9 mg (469.0 µmol, 94%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 5:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.26 (m, 6H), 5.24 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.71 (dd, *J* = 14.3, 6.5 Hz, 1H), 3.62 (dd, *J* = 14.3, 9.6 Hz, 1H), 2.56 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.9, 139.2, 134.4, 134.2, 129.9, 129.5, 129.1, 127.4, 59.0, 36.5, 28.2, 21.6. **IR** (neat): 3027, 2967, 2922, 1595, 1491, 1457, 1409, 1338, 1264, 1215, 1155, 1088, 1044, 1001, 977, 924, 813, 742,

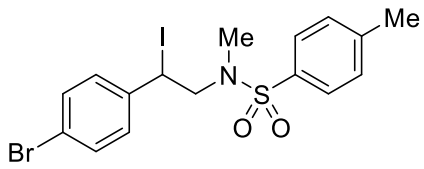
651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{18}ClINO_2S$ ($[M+H]^+$) 449.9786, found 449.9788.

***N*-(2-(4-chlorophenyl)-2-iodoethyl)-*N*-methyl-4-nitrobenzenesulfonamide (Ns-15e)**



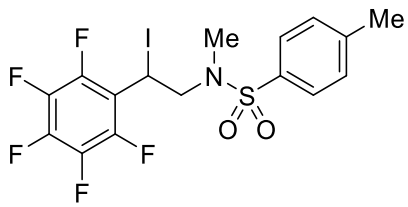
Following general procedure ***GP-I*** using 1-chloro-4-vinylbenzene (**1e**) (60.0 µL, 69.3 mg, 0.5 mmol, 1.0 equiv), *N*-methyl-4-nitrobenzenesulfonamide (**Ns-2a**) (108.1 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 221.1 mg (460.0 µmol, 92%) of the title compound as a sticky yellowish oil after flash column purification on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.38, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.34 (d, *J* = 8.8 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 5.22 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.83 – 3.63 (m, 2H), 2.65 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 150.3, 143.5, 138.8, 134.6, 129.5, 129.3, 128.6, 124.6, 59.1, 36.4, 27.2. **IR** (neat): 3105, 3034, 2970, 2933, 2870, 1603, 1528, 1500, 1461, 1402, 1346, 1312, 1267, 1200, 1163, 1088, 1047, 1001, 977, 928, 856, 760, 703, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{15}ClI_2N_2O_4S$ ($[M+H]^+$) 480.9480, found 480.9477.

***N*-(2-(4-bromophenyl)-2-iodoethyl)-*N*,4-dimethylbenzenesulfonamide (15f)**



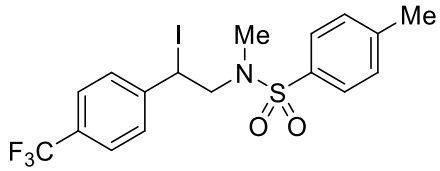
Following general procedure ***GP-I*** using 1-bromo-4-vinylbenzene (**1f**) (65.4 µL, 91.5 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 234.4 mg (474.3 µmol, 95%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 9:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.43, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.34 – 7.27 (m, 4H), 5.22 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.77 – 3.56 (m, 2H), 2.56 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.9, 139.7, 134.4, 132.1, 129.9, 129.8, 127.4, 122.4, 58.9, 36.5, 28.1, 21.7. **IR** (neat): 3027, 2922, 1595, 1487, 1454, 1405, 1338, 1264, 1208, 1156, 1088, 1010, 977, 924, 813, 738, 657 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{18}BrINO_2S$ ($[M+H]^+$) 493.9281, found 493.9275.

***N*-(2-iodo-2-(perfluorophenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (15g)**



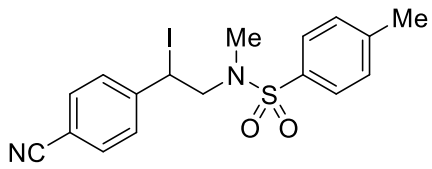
Following general procedure ***GP-I*** using 1,2,3,4,5-pentafluoro-6-vinylbenzene (**1g**) (69.0 µL, 97.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 193.4 mg (382.8 µmol, 77%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 15:1 to 9:1). $\mathbf{R_f}$ (hexanes / EtOAc 7:1 on silica) = 0.45, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 5.51 (dd, *J* = 10.5, 5.7 Hz, 1H), 3.99 (dd, *J* = 14.4, 10.6 Hz, 1H), 3.45 (dd, *J* = 14.4, 5.8 Hz, 1H), 2.76 (s, 3H), 2.43 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.1, 143.4 – 142.6 (m), 139.8 – 138.9 (m), 136.4 –135.8 (m), 133.9, 129.9, 127.4, 114.8 – 114.1 (m), 56.8 (t, *J* = 2.8 Hz), 36.6, 21.5, 8.6. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -136.42 – -143.64 (m, 2H), -153.52 (tt, *J* = 21.2, 2.5 Hz, 1H), -161.53 (td, *J* = 21.8, 7.6 Hz, 2H). **IR** (neat): 3030,2930, 1655, 1599, 1519, 1502, 1457, 1342, 1333, 1204, 1159, 1100, 1044, 1018, 972, 939, 887, 816, 739, 727, 678 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{14}F_5INO_2S$ ($[M+H]^+$) 505.9705, found 505.9715.

***N*-(2-iodo-2-(4-(trifluoromethyl)phenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (15h)**



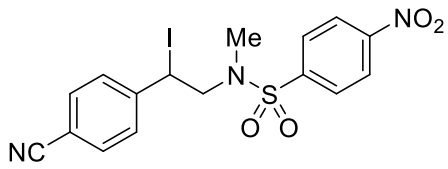
Following general procedure ***GP-I*** using 1-(trifluoromethyl)-4-vinylbenzene (**1h**) (73.9 µL, 86.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 221.0 mg (457.3 µmol, 91%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 15:1 to 9:1). $\mathbf{R_f}$ (hexanes / EtOAc 7:1 on silica) = 0.28, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.64 – 7.54 (m, 6H), 7.33 – 7.28 (m, 2H), 5.29 (t, *J* = 8.0 Hz, 1H), 3.70 (d, *J* = 8.0 Hz, 2H), 2.58 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.6, 144.6, 144.0, 134.2, 130.5 (q, *J* = 32.6 Hz), 129.9, 128.6, 127.4, 125.9 (q, *J* = 3.8 Hz), 58.7, 36.5, 27.2, 21.6. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ = -63.10 (s, 3F). **IR** (neat): 3030, 2926, 1618, 1607, 1495, 1457, 1420, 1320, 1159, 1111, 1061, 1018, 972, 924, 842, 813, 757, 719, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{18}F_3INO_2S$ ($[M+H]^+$) 484.0050, found 484.0061.

***N*-(2-(4-cyanophenyl)-2-iodoethyl)-*N*,4-dimethylbenzenesulfonamide (15i)**



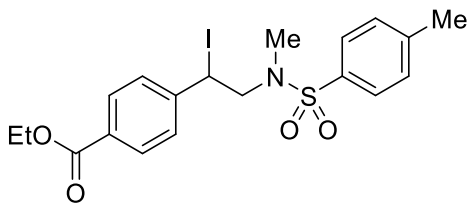
Following general procedure ***GP-I*** using 4-vinylbenzonitrile (**1i**) (64.6 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 197.5 mg (448.6 µmol, 90%) of the title compound as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 9:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.33, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.64 – 7.51 (m, 6H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.26 (dd, *J* = 9.7, 6.4 Hz, 1H), 3.72 (dd, *J* = 14.3, 9.7 Hz, 1H), 3.63 (dd, *J* = 14.3, 6.4 Hz, 1H), 2.56 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.8, 144.1, 134.0, 132.6, 130.0, 129.0, 127.4, 118.4, 112.1, 58.5, 36.5, 26.5, 21.6. **IR** (neat): 3019, 2922, 2229, 1636, 1599, 1502, 1457, 1416, 1338, 1208, 1156, 1111, 1044, 1021, 977, 924, 839, 820, 749, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{18}IN_2O_2S$ ($[M+H]^+$) 441.0128, found 441.0136.

***N*-(2-(4-cyanophenyl)-2-iodoethyl)-*N*-methyl-4-nitrobenzenesulfonamide (Ns-15i)**



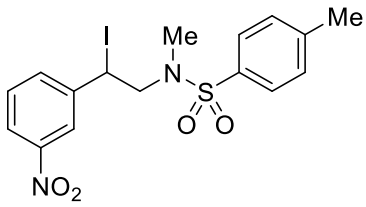
Following general procedure ***GP-I*** using 4-vinylbenzonitrile (**1i**) (60.4 µL, 64.6 mg, 0.5 mmol, 1.0 equiv), *N*-methyl-4-nitrobenzenesulfonamide (**Ns-2a**) (108.1 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 183.6 mg (389.6 µmol, 78%) of the title compound as a sticky yellowish oil after flash column purification on silica (hexanes / EtOAc 5:1 to 2:1). $\mathbf{R_f}$ (hexanes / EtOAc 2:1 on silica) = 0.45, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ =8.38 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 5.26 (dd, *J* = 8.6, 7.4 Hz, 1H), 3.79 – 3.65 (m, 2H), 2.65 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 150.4, 145.4, 143.1, 132.9, 129.1, 128.7, 124.7, 118.3, 112.6, 58.8, 36.5, 25.8. **IR** (neat):3105, 3038, 2960, 2930, 2870, 2229, 1640, 1603, 1528, 1461, 1402, 1346, 1307, 1200, 1163, 1100, 1088, 1047, 977, 928, 853, 760, 758, 731 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{15}IN_3O_4S$ ($[M+H]^+$) 471.9822, found 471.9824.

ethyl 4-(2-((*N*,4-dimethylphenyl)sulfonamido)-1-iodoethyl)benzoate (15j)



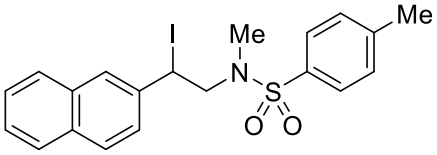
Following general procedure ***GP-I*** using ethyl 4-vinylbenzoate (**1j**) (88.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 213.6 mg (438.3 µmol, 88%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 6:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.38, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.28 (dd, *J* = 9.7, 6.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.75 (dd, *J* = 14.4, 6.2 Hz, 1H), 3.63 (dd, *J* = 14.4, 9.7 Hz, 1H), 2.54 (s, 3H), 2.41 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 166.0, 145.5, 143.9, 134.4, 130.6, 130.1, 129.9, 128.2, 127.4, 61.2, 58.8, 36.6, 28.0, 21.6, 14.4. **IR** (neat): 2982, 2930, 1711, 1607, 1448, 1416, 1342, 1275, 1159, 1103, 1021, 977, 924, 857, 817, 738, 701, 664 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{19}H_{23}INO_4S$ ($[M+H]^+$) 488.0387, found 488.0390.

***N*-(2-iodo-2-(3-nitrophenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (15k)**



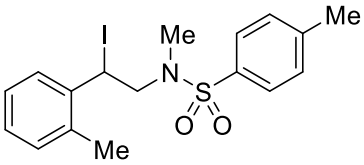
Following general procedure ***GP-I*** using 1-nitro-3-vinylbenzene (**1k**) (69.7 µL, 74.6 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 219.8 mg (477.5 µmol, 96%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.18, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.24 (t, *J* = 2.0 Hz, 1H), 8.12 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 7.79 (ddd, *J* = 7.8, 1.9, 1.1 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 2H), 5.32 (dd, *J* = 9.8, 6.4 Hz, 1H), 3.77 (dd, *J* = 14.4, 9.8 Hz, 1H), 3.66 (dd, *J* = 14.4, 6.3 Hz, 1H), 2.61 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 148.3, 144.1, 142.8, 134.3, 134.0, 130.1, 130.0, 127.4, 123.4, 123.1, 58.7, 36.6, 26.0, 21.6. **IR** (neat): 3071, 3027, 2967, 2922, 2870, 1595, 1528, 1446, 1342, 1211, 1156, 1088, 1044, 984, 928, 813, 731, 686, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{18}INO_2S$ ($[M+H]^+$) 461.0026, found 461.0031.

***N*-(2-iodo-2-(naphthalen-2-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (15l)**



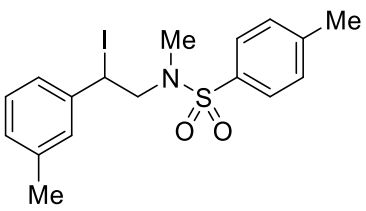
Following general procedure ***GP-I*** using 2-vinylnaphthalene (**1l**) (77.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 212.9 mg (457.5 µmol, 92%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.38, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.84 – 7.77 (m, 4H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.56 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.24 (d, *J* = 7.7 Hz, 1H), 5.48 (dd, *J* = 9.6, 6.2 Hz, 1H), 3.90 (dd, *J* = 14.4, 6.2 Hz, 1H), 3.75 (dd, *J* = 14.4, 9.7 Hz, 1H), 2.57 (s, 3H), 2.40 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.7, 137.9, 134.8, 133.2, 133.1, 129.9, 129.0, 128.1, 127.8, 127.4, 127.4, 126.8, 126.8, 125.8, 58.9, 36.6, 30.6, 21.6. **IR** (neat): 3053, 2960, 2922, 1599, 1510, 1443, 1338, 1215, 1156, 1088, 1044, 1018, 990, 924, 857, 813, 746, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{20}H_{21}INO_2S$ ($[M+H]^+$) 466.0332, found 466.0340.

***N*-(2-iodo-2-(*o*-tolyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (15n)**



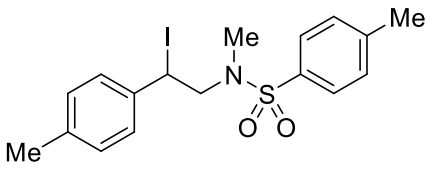
Following general procedure ***GP-I*** using 1-methyl-2-vinylbenzene (**1n**) (64.5 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 201.1 mg (468.4 µmol, 94%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.50, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.11 (m, 3H), 5.60 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.79 (dd, *J* = 14.4, 6.8 Hz, 1H), 3.67 (dd, *J* = 14.5, 8.9 Hz, 1H), 2.63 (s, 3H), 2.44 (s, 3H), 2.38 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.8, 138.8, 135.5, 134.4, 131.0, 129.9, 128.4, 128.1, 127.5, 126.9, 58.4, 36.9, 26.7, 21.6, 19.5. **IR** (neat): 3023, 2971, 2922, 2866, 1595, 1491, 1461, 1338, 1215, 1156, 1088, 1036, 977, 924, 846, 813, 723, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{21}INO_2S$ ($[M+H]^+$) 430.0332, found 430.0332.

***N*-(2-iodo-2-(*m*-tolyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (15o)**



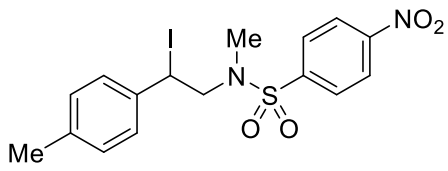
Following general procedure ***GP-I*** using 1-methyl-3-vinylbenzene (**1o**) (65.7 µL, 59.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 209.2 mg (487.3 µmol, 97%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.55, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.16 (m, 3H), 7.08 (d, *J* = 6.9 Hz, 1H), 5.25 (dd, *J* = 9.2, 6.6 Hz, 1H), 3.80 (dd, *J* = 14.4, 6.6 Hz, 1H), 3.57 (dd, *J* = 14.4, 9.3 Hz, 1H), 2.58 (s, 3H), 2.43 (s, 3H), 2.33 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.7, 140.6, 138.6, 134.7, 129.9, 129.4, 128.8, 128.7, 127.4, 125.2, 59.0 36.5, 30.3, 21.6, 21.4. **IR** (neat): 3027, 2922, 2866, 1787, 1599, 1491, 1453, 1338, 1241, 1211, 1156, 1111, 1082, 1044, 977, 928, 880, 813, 731, 701, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{21}INO_2S$ ($[M+H]^+$) 430.0332, found 430.0336.

***N*-(2-iodo-2-(*p*-tolyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (15p)**



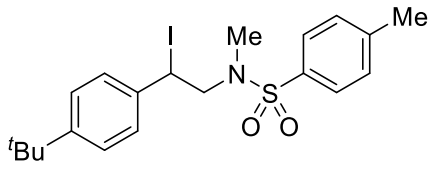
Following general procedure ***GP-I*** using 1-methyl-4-vinylbenzene (**1p**) (72.0 µL, 64.6 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 185.5 mg (432.1 µmol, 86%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 9:1 to 6:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.43, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.11 (d, *J* = 7.6 Hz, 2H), 5.27 (dd, *J* = 9.4, 6.5 Hz, 1H), 3.77 (dd, *J* = 14.3, 6.5 Hz, 1H), 3.59 (dd, *J* = 14.3, 9.5 Hz, 1H), 2.56 (s, 3H), 2.42 (s, 3H), 2.32 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ =143.7, 138.5, 137.7, 134.6, 129.9, 129.6, 128.0, 127.4, 59.0, 36.5, 30.3, 21.6, 21.4. **IR** (neat): 3027, 2922, 2863, 1595, 1513, 1450, 1338, 1208, 1156, 1111, 1087, 1040, 977, 924, 850, 813, 731, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{21}INO_2S$ ($[M+H]^+$) 430.0332, found 430.0337.

***N*-(2-iodo-2-(*p*-tolyl)ethyl)-*N*-methyl-4-nitrobenzenesulfonamide (Ns-15p)**



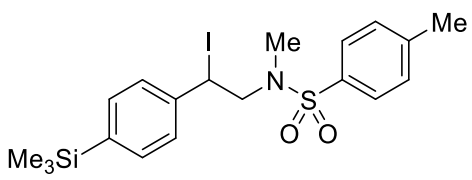
Following general procedure ***GP-I*** using 1-methyl-4-vinylbenzene (**1p**) (72.0 µL, 64.6 mg, 0.5 mmol, 1.0 equiv), *N*-methyl-4-nitrobenzenesulfonamide (**Ns-2a**) (108.1 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 194.1 mg (421.7 µmol, 84%) of the title compound as a sticky yellowish oil after flash column purification on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.43, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.32 (d, *J* = 8.9 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.24 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.83 (dd, *J* = 14.4, 6.4 Hz, 1H), 3.72 (dd, *J* = 14.3, 9.6 Hz, 1H), 2.65 (s, 3H), 2.32 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 150.2, 143.9, 138.9, 137.3, 129.8, 128.6, 128.0, 124.5, 59.1, 36.2, 29.1, 21.4. **IR** (neat): 3105, 3027, 2922, 2866, 1607, 1528, 1454, 1346, 1312, 1200, 1163, 1088, 1044, 977, 932, 854, 820, 760, 749 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{18}IN_2O_4S$ ($[M+H]^+$) 461.0026, found 461.0026.

***N*-(2-(4-(*tert*-butyl)phenyl)-2-iodoethyl)-*N*,4-dimethylbenzenesulfonamide (15q)**



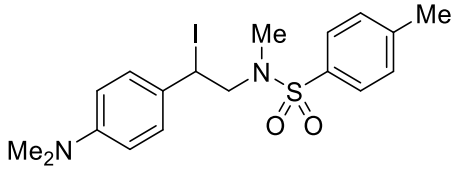
Following general procedure ***GP-I*** using 1-(*tert*-butyl)-4-vinylbenzene (**1q**) (90.6 µL, 80.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 216.2 mg (458.6 µmol, 92%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 12:1 to 10:1). $\mathbf{R_f}$ (hexanes / EtOAc 6:1 on silica) = 0.53, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.28 (m, 6H), 5.30 (dd, *J* = 9.2, 6.7 Hz, 1H), 3.77 (dd, *J* = 14.3, 6.8 Hz, 1H), 3.58 (dd, *J* = 14.3, 9.2 Hz, 1H), 2.57 (s, 3H), 2.42 (s, 3H), 1.31 (s, 9H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 151.7, 143.7, 137.6, 134.7, 129.9, 127.8, 127.5, 125.9, 58.9, 36.5, 34.8, 31.4, 30.4, 21.6. **IR** (neat): 3027, 2960, 2870, 1599, 1510, 1461, 1416, 1342, 1204, 1159, 1099, 1088, 1047, 980, 924, 835, 803, 734, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{20}H_{27}INO_2S$ ($[M+H]^+$) 472.0802, found 472.0811.

***N*-(2-iodo-2-(4-(trimethylsilyl)phenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (15r)**



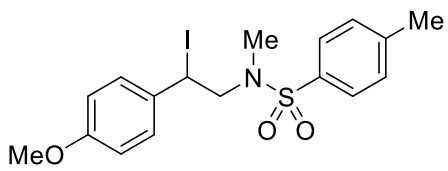
Following general procedure ***GP-I*** using trimethyl(4-vinylphenyl)silane (**1r**) (102.5 µL, 88.2 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 242.1 mg (496.6 µmol, 99%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.55, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 5.29 (dd, *J* = 9.2, 6.7 Hz, 1H), 3.76 (dd, *J* = 14.3, 6.7 Hz, 1H), 3.61 (dd, *J* = 14.3, 9.2 Hz, 1H), 2.58 (s, 3H), 2.42 (s, 3H), 0.27 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.7, 141.4, 141.0, 134.5, 133.9, 129.9, 127.5, 127.3, 58.7, 36.5, 30.1, 21.6, -1.1. **IR** (neat): 3019, 2956, 2896, 1595, 1454, 1402, 1342, 1290, 1249, 1211, 1111, 1044, 1021, 980, 924, 835, 738, 664 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{19}H_{27}INO_2SSi$ ($[M+H]^+$) 488.0571, found 488.0576.

***N*-(2-(4-(dimethylamino)phenyl)-2-iodoethyl)-*N*,4-dimethylbenzenesulfonamide (15s)**



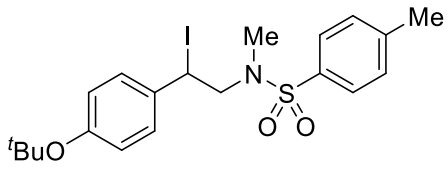
Following general procedure ***GP-I*** using *N*,*N*-dimethyl-4-vinylaniline (**1s**) (73.6 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 81.8 mg (178.5 µmol, 36%) of the title compound as a sticky greenish oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.38, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 1H), 5.24 (dd, *J* = 9.4, 6.6 Hz, 1H), 3.56 (dd, *J* = 10.3, 9.4 Hz, 1H), 3.42 (dd, *J* = 10.3, 6.6 Hz, 1H), 2.93 (s, 6H), 2.58 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 150.2, 143.3, 136.9, 129.7, 129.0, 127.4, 123.0, 112.2, 61.4, 40.5, 29.0, 21.7, 4.2. **IR** (neat): 2922, 2885, 2803, 1610, 1566, 1521, 1446, 1331, 1197, 1152, 1088, 928, 876, 813, 775, 751, 719, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{18}H_{24}IN_2O_2S$ ($[M+H]^+$) 459.0598, found 459.0596.

***N*-(2-iodo-2-(4-methoxyphenyl)ethyl)-*N*,4-dimethylbenzenesulfonamide (15u)**



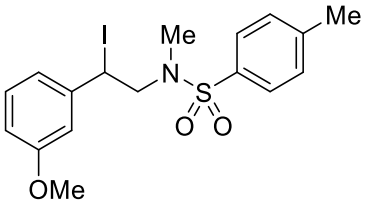
Following general procedure ***GP-I*** using 1-methoxy-4-vinylbenzene (**1u**) (66.4 µL, 67.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 51.2 mg (115.0 µmol, 23%) of the title compound as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 9:1 to 6:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 5.29 (dd, *J* = 9.4, 6.5 Hz, 1H), 3.79 (s, 3H), 3.54 (dd, *J* = 10.4, 9.4 Hz, 1H), 3.39 (dd, *J* = 10.4, 6.5 Hz, 1H), 2.59 (s, 3H), 2.43 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 159.5, 143.5, 136.7, 129.7, 129.3, 127.7, 127.3, 113.9, 61.1, 55.3, 28.9, 21.6, 3.5. **IR** (neat): 3031, 2933, 2840, 1610, 1513, 1461, 1334, 1300, 1252, 1211, 1182, 1109, 1081, 1029, 932, 880, 839, 824, 775, 727, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{21}INO_3S$ ($[M+H]^+$) 446.0281, found 446.0289.

***N*-(2-(4-(*tert*-butoxy)phenyl)-2-iodoethyl)-*N*,4-dimethylbenzenesulfonamide (15v)**



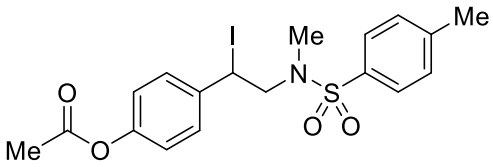
Following general procedure ***GP-I*** using 1-(*tert*-butoxy)-4-vinylbenzene (**1v**) (94.2 µL, 88.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 154.4 mg (316.8 µmol, 63%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.43, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.29 (dd, *J* = 8.7, 7.2 Hz, 1H), 3.53 (dd, *J* = 10.5, 8.7 Hz, 1H), 3.37 (dd, *J* = 10.5, 7.1 Hz, 1H), 2.62 (s, 3H), 2.40 (s, 3H), 1.32 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 155.5, 143.4, 136.7, 130.5, 129.6, 128.6, 127.3, 123.8, 78.8, 61.3, 28.9, 28.9, 21.6, 3.6. **IR** (neat): 2974, 2933, 1603, 1506, 1457, 1390, 1357, 1334, 1238, 1211, 1156, 1098, 1036, 932, 895, 857, 813, 753, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{20}H_{26}INO_3SNa$ ($[M+Na]^+$) 510.0570, found 510.0565.

_N_-(2-iodo-2-(3-methoxyphenyl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15w)



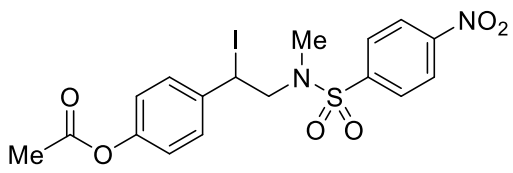
Following general procedure ***GP-I*** using 1-methoxy-3-vinylbenzene (**1w**) (69.4 µL, 67.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 206.3 mg (463.3 µmol, 93%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.43, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.19 (m, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.96 (s, 1H), 6.81 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.25 (dd, *J* = 9.4, 6.4 Hz, 1H), 3.80 (s, 3H), 3.77 (dd, *J* = 14.5, 6.6 Hz, 1H), 3.61 (dd, *J* = 14.3, 9.4 Hz, 1H), 2.58 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 159.7, 143.7, 142.1, 134.6, 129.9, 129.9, 127.4, 120.4, 114.3, 113.7, 58.9, 55.4, 36.5, 29.7, 21.6. **IR** (neat): 3004, 2922, 2837, 1599, 1491, 1454, 1338, 1260, 1211, 1156, 1110, 1040, 984, 932, 872, 816, 746, 697, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{21}INO_3S$ ($[M+H]^+$) 446.0281, found 446.0283.

4-(2-((_N_,4-dimethylphenyl)sulfonamido)-1-iodoethyl)phenyl acetate (15x)



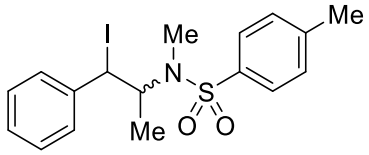
Following general procedure ***GP-I*** using ethyl 4-vinylphenyl acetate (**1x**) (76.5 µL, 81.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 223.8 mg (472.8 µmol, 95%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 9:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 5.27 (dd, *J* = 9.2, 6.7 Hz, 1H), 3.73 (dd, *J* = 14.4, 6.7 Hz, 1H), 3.55 (dd, *J* = 14.4, 9.2 Hz, 1H), 2.57 (s, 3H), 2.41 (s, 3H), 2.28 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 169.2, 150.5, 143.8, 138.2, 134.5, 129.9, 129.2, 127.5, 122.0, 59.1, 36.6, 28.9, 21.6, 21.2. **IR** (neat): 3027, 2926, 1759, 1599, 1506, 1457, 1338, 1192, 1156, 1088, 1044, 1014, 980, 910, 850, 816, 738, 664 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{18}H_{21}INO_4S$ ($[M+H]^+$) 474.0230, found 474.0230.

4-(1-iodo-2-((*N*-methyl-4-nitrophenyl)sulfonamido)ethyl)phenyl acetate (Ns-15x)



Following general procedure ***GP-I*** using ethyl 4-vinylphenyl acetate (**1x**) (76.5 µL, 81.1 mg, 0.5 mmol, 1.0 equiv *N*-methyl-4-nitrobenzene-sulfonamide (**Ns-2a**) (108.1 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 233.5 mg (463.0 µmol, 93%) of the title compound as a sticky yellowish oil after flash column purification on silica (hexanes / EtOAc 4:1 to 2:1). $\mathbf{R_f}$ (hexanes / EtOAc 2:1 on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 8.32 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.9 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 5.23 (dd, *J* = 9.2, 6.7 Hz, 1H), 3.84 – 3.64 (m, 2H), 2.66 (s, 3H), 2.30 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 169.2, 150.7, 150.2, 143.7, 137.7, 129.2, 128.6, 124.6, 122.2, 59.0, 36.2, 27.6, 21.2. **IR** (neat): 3105, 3034, 2971, 2870, 1759, 1603, 1528, 1457, 1349, 1327, 1193, 1163, 1107, 1044, 1014, 980, 910, 854, 742, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{18}IN_2O_6S$ ($[M+H]^+$) 504.9925, found 504.9922.

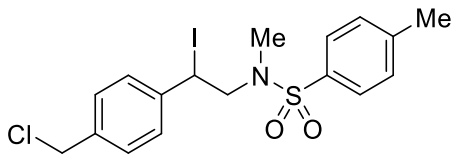
***N*-(1-iodo-1-phenylpropan-2-yl)-*N*,4-dimethylbenzenesulfonamide (d.r. = 60:40) (15z)**



Following general procedure ***GP-I*** using (*E*)-prop-1-en-1-ylbenzene (**1z**) (69.4 µL, 67.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 194.0 mg (451.9 µmol, 90%) of the title compound as an inseparable mixture of two diastereomers (d.r. = 60:40) as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 8.1 Hz, 2H, major diastereomer), 7.47 – 7.39 (m, 4H, both diastereomers), 7.37 (d, *J* = 8.1 Hz, 2H, minor diastereomer), 7.34 – 7.24 (m, 8H, both diastereomers), 7.17 (d, *J* = 8.0 Hz, 2H, minor diastereomer), 5.04 (d, *J* = 9.7 Hz, 1H, minor diastereomer), 5.00 (d, *J* = 9.9 Hz, 1H, major diastereomer), 4.76 – 4.57 (m, 2H, both diastereomers), 2.61 (s, 3H, major diastereomer), 2.50 (s, 3H, minor diastereomer), 2.42 (s, 3H, major diastereomer), 2.38 (s, 3H, minor diastereomer), 1.40 (d, *J* = 6.6 Hz, 3H, minor diastereomer), 0.88 (d, *J* = 6.8 Hz, 3H, major diastereomer). **^{13}C-NMR** (101 MHz, $CDCl_3$, both diastereomers) δ = 143.5, 143.4, 141.6, 140.9, 136.7, 136.1, 129.7, 129.7, 129.0, 128.7, 128.5,

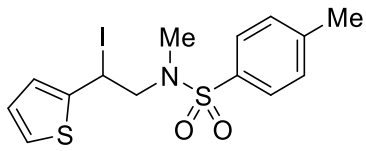
128.3, 128.3, 128.2, 127.6, 127.4, 59.0, 58.3, 36.6, 36.4, 28.5, 28.3, 21.6, 21.6, 17.4, 13.9. **IR** (neat): 3060, 3030, 2982, 2926, 1595, 1495, 1454, 1379, 1334, 1215, 1148, 1088, 999, 939, 887, 813, 764, 731, 697, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{21}INO_2S$ ($[M+H]^+$) 430.0332, found 430.0332.

***N*-(2-(4-(chloromethyl)phenyl)-2-iodoethyl)-*N*,4-dimethylbenzenesulfonamide (15ad)**



Following general procedure ***GP-I*** using 1-(chloromethyl)-4-vinylbenzene (**1ad**) (70.5 µL, 76.3 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 211.3 mg (455.6 µmol, 91%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.27 (m, 4H), 5.27 (dd, *J* = 9.4, 6.6 Hz, 1H), 4.55 (s, 2H), 3.73 (dd, *J* = 14.3, 6.6 Hz, 1H), 3.62 (dd, *J* = 14.3, 9.4 Hz, 1H), 2.56 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.8, 140.9, 137.8, 134.4, 129.9, 129.1, 128.5, 127.4, 58.8, 45.7, 36.5, 28.9, 21.6. **IR** (neat): 3027, 2960, 2922, 2870, 1595, 1495, 1446, 1338, 1267, 1215, 1156, 1111, 1087, 1044, 1011, 977, 924, 813, 727, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{20}ClINO_2S$ ($[M+H]^+$) 463.9942, found 463.9942.

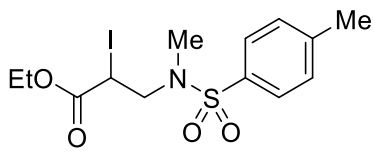
***N*-(2-iodo-2-(thiophen-2-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (15af)**



Following general procedure ***GP-I*** using 2-vinylthiophene (**1af**) (53.0 µL, 55.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 130.3 mg (309.3 µmol, 62%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 9:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.63, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.20 (m, 4H), 6.95 – 6.90 (m, 2H), 5.55 (t, *J* = 7.8 Hz, 1H), 3.59 (dd, *J* = 10.5, 7.9 Hz, 1H), 3.43 (dd, *J* = 10.5, 7.7 Hz, 1H), 2.68 (s, 3H), 2.41 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.6, 139.4, 136.4, 129.7, 127.5, 126.9, 126.8, 125.9, 57.9, 28.8, 21.7, 4.6. **IR** (neat): 3105, 3027, 2922, 1595, 1495, 1431, 1334,

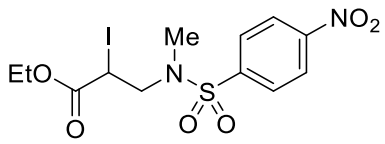
1204, 1156, 1100, 1021, 928, 835, 801, 753, 701, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_{16}INNaO_2S_2$ ($[M+Na]^+$) 443.9559, found 443.9548.

ethyl 3-((N,4-dimethylphenyl)sulfonamido)-2-iodopropanoate (15ai)



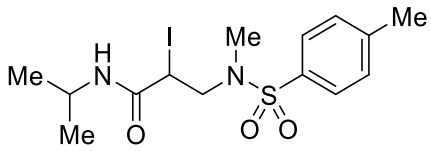
Following general procedure ***GP-I*** using ethyl acrylate (**1ai**) (213.0 µL, 200.2 mg, 2.0 mmol, 4.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 153.7 mg (373.7 µmol, 75%) of the title compound as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 1H), 4.66 (dd, *J* = 9.7, 5.8 Hz, 1H), 4.21 (qd, *J* = 7.1, 1.8 Hz, 2H), 3.52 – 3.32 (m, 2H), 2.79 (s, 3H), 2.42 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 170.7, 144.0, 133.6, 130.0, 127.6, 62.2, 55.2, 37.8, 21.6, 18.1, 13.8. **IR** (neat): 2982, 2933, 1730, 1595, 1446, 1372, 1342, 1297, 1252, 1219, 1159, 1111, 954, 887, 854, 816, 727, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{13}H_{19}INO_4S$ ($[M+H]^+$) 412.0074, found 412.0079.

ethyl 2-iodo-3-((*N*-methyl-4-nitrophenyl)sulfonamido)propanoate (Ns-15ai)



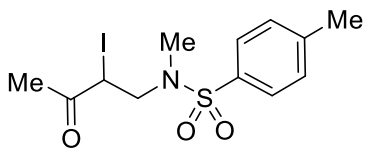
Following general procedure ***GP-I*** using ethyl acrylate (**1ai**) (213.0 µL, 200.2 mg, 2.0 mmol, 4.0 equiv), *N*-methyl-4-nitrobenzenesulfonamide (**Ns-2a**) (108.1 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 152.7 mg (345.3 µmol, 69%) of the title compound as a sticky colorless oil after flash column purification on silica (hexanes / EtOAc 5:1 to 3:1). $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.43, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.39 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 8.9 Hz, 2H), 4.65 (dd, *J* = 8.2, 7.2 Hz, 1H), 4.32 – 4.11 (m, 2H), 3.59 – 3.44 (m, 2H), 2.89 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 170.5, 150.4, 142.7, 128.8, 124.7, 62.5, 55.1, 37.7, 17.3, 13.8. **IR** (neat): 3109, 2982, 2937, 1722, 1610, 1532, 1461, 1349, 1293, 1219, 1189, 1159, 1088, 995, 879, 857, 786, 757, 712 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{12}H_{16}IN_2O_6S$ ($[M+H]^+$) 442.9768, found 442.9772.

3-((*N*,4-dimethylphenyl)sulfonamido)-2-iodo-*N*-isopropylpropanamide (15aj)



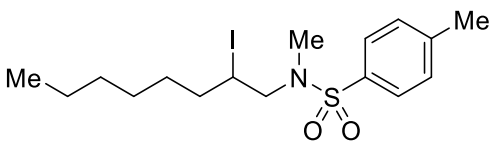
Following general procedure ***GP-I*** using *N*-isopropylacrylamide (**1aj**) (226.3 mg, 2.0 mmol, 4.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 157.0 mg (394 µmol, 79%) of the title compound as a white solid after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). **mp**: 143 °C. $\mathbf{R_f}$ (hexanes / EtOAc 2:1 on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 6.07 (d, *J* = 7.9 Hz, 1H), 4.57 (dd, *J* = 9.7, 5.7 Hz, 1H), 4.12 – 3.97 (m, 1H), 3.56 – 3.34 (m, 2H), 2.82 (s, 3H), 2.42 (s, 3H), 1.15 (dd, *J* = 13.4, 6.6 Hz, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 168.4, 144.1, 133.7, 130.0, 127.5, 55.4, 42.4, 38.0, 22.9, 22.6, 21.8, 21.7. **IR** (neat): 3258, 3086, 2967, 2933, 2874, 1691, 1640, 1583, 1566, 1491, 1379, 1346, 1307, 1249, 1156, 1088, 1062, 999, 965, 865, 842, 821, 731, 701, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_{22}IN_2O_3S$ ($[M+H]^+$) 425.0390, found 425.0394.

***N*-(2-iodo-3-oxobutyl)-*N*,4-dimethylbenzenesulfonamide (15ak)**



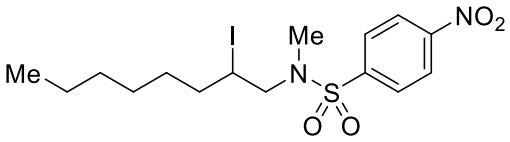
Following general procedure ***GP-I*** using but-3-en-2-one (**1ak**) (166.7 µL, 140.2 mg, 2.0 mmol, 4.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 109.2 mg (286 µmol, 57%) of the title compound as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 4.91 (dd, *J* = 9.3, 5.7 Hz, 1H), 3.49 – 3.20 (m, 2H), 2.78 (s, 3H), 2.44 (s, 3H), 2.42 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 202.2, 144.1, 133.3, 130.0, 127.6, 53.9, 38.0, 28.4, 27.3, 21.6. **IR** (neat): 2974, 2922, 1707, 1595, 1491, 1443, 1342, 1320, 1211, 1156, 1079, 992, 951, 913, 816, 731, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{12}H_{17}INO_3S$ ($[M+H]^+$) 381.9968, found 381.9967.

***N*-(2-iodooctyl)-*N*,4-dimethylbenzenesulfonamide (15an)**



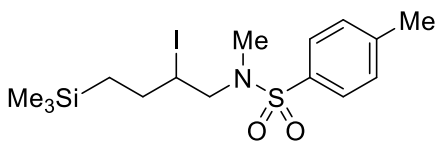
Following general procedure ***GP-I*** using oct-1-ene (**1an**) (313.9 µL, 224.4 mg, 2.0 mmol, 4.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 135.4 mg (319.8 µmol, 64%) of the title compound as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 9:1). $\mathbf{R_f}$ (hexanes / EtOAc 7:1 on silica) = 0.50, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 4.19 (tdd, *J* = 9.5, 6.1, 3.5 Hz, 1H), 3.46 (dd, *J* = 14.0, 9.0 Hz, 1H), 3.26 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.76 (s, 3H), 2.43 (s, 3H), 1.93 – 1.82 (m, 1H), 1.72 (ddt, *J* = 14.7, 9.9, 4.7 Hz, 1H), 1.60 (tq, *J* = 9.6, 5.2, 4.6 Hz, 1H), 1.40 – 1.25 (m, 7H), 0.93 – 0.85 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.8, 134.3, 129.9, 127.5, 58.9, 36.6, 36.5, 33.6, 31.8, 29.6, 28.6, 22.7, 21.6, 14.2. **IR** (neat): 2926, 2855, 1599, 1495, 1457, 1342, 1249, 1159, 1088, 1040, 965, 910, 813, 731, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{27}INO_2S$ ($[M+H]^+$) 424.0802, found 424.0811.

***N*-(2-iodooctyl)-*N*-methyl-4-nitrobenzenesulfonamide (Ns-15an)**



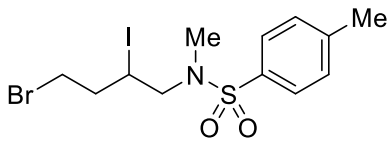
Following general procedure ***GP-I*** using oct-1-ene (**1an**) (313.9 µL, 224.4 mg, 2.0 mmol, 4.0 equiv), *N*-methyl-4-nitrobenzenesulfonamide (**Ns-2a**) (108.1 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 131.8 mg (290.1 µmol, 58%) of the title compound as a sticky colorless oil after flash column purification on silica (hexanes / EtOAc 5:1). $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.63, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.39 (d, *J* = 8.8 Hz, 2H), 7.99 (d, *J* = 8.8 Hz, 2H), 4.18 (dddd, *J* = 9.4, 8.4, 6.6, 3.8 Hz, 1H), 3.51 (dd, *J* = 14.1, 8.5 Hz, 1H), 3.35 (dd, *J* = 14.1, 6.6 Hz, 1H), 2.85 (s, 3H), 1.94 – 1.57 (m, 3H), 1.46 – 1.22 (m, 7H), 0.93 – 0.78 (m, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 150.3, 143.4, 128.7, 124.6, 58.8, 36.6, 36.3, 32.5, 31.7, 29.5, 28.5, 22.7, 14.2. **IR** (neat): 3112, 2960, 2926, 2855, 1607, 1543, 1461, 1405, 1345, 1312, 1267, 1163, 1103, 1010, 954, 924, 764, 716 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{24}IN_2O_4S$ ($[M+H]^+$) 455.0496, found 455.0499.

***N*-(2-iodo-4-(trimethylsilyl)butyl)-*N*,4-dimethylbenzenesulfonamide (15ao)**



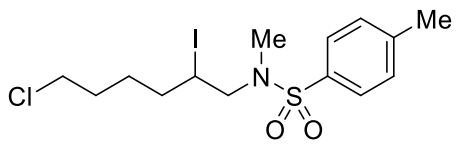
Following general procedure ***GP-I*** using but-3-en-1-yltrimethylsilane (**1ao**) (351.5 µL, 256.6 mg, 2.0 mmol, 4.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 139.2 mg (316.8 µmol, 63%) of the title compound as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.60, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 1H), 4.24 (tdd, *J* = 8.6, 6.3, 3.9 Hz, 1H), 3.48 (dd, *J* = 14.1, 8.7 Hz, 1H), 3.24 (dd, *J* = 14.1, 6.3 Hz, 1H), 2.76 (s, 3H), 2.43 (s, 3H), 1.85 (dddd, *J* = 14.9, 12.5, 4.7, 3.9 Hz, 1H), 1.69 (dddd, *J* = 14.9, 12.5, 8.2, 4.3 Hz, 1H), 0.95 – 0.74 (m, 1H), 0.54 (ddd, *J* = 14.1, 12.5, 4.7 Hz, 1H), 0.01 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.8, 134.3, 129.9, 127.6, 58.1, 38.5, 36.4, 31.4, 21.7, 16.2, -1.6. **IR** (neat): 2952, 2896, 1599, 1495, 1454, 1342, 1248, 1215, 1159, 1088, 1036, 936, 857, 831, 738, 707, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{27}INO_2SSi$ ($[M+H]^+$) 440.0571, found 440.0571.

***N*-(4-bromo-2-iodobutyl)-*N*,4-dimethylbenzenesulfonamide (15ap)**



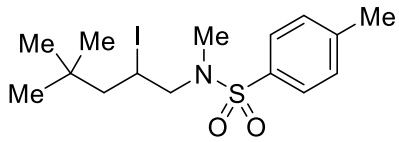
Following general procedure ***GP-I*** using 4-bromobut-1-ene (**1ap**) (203.0 µL, 218.3 mg, 2.0 mmol, 4.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 137.6 mg (308.4 µmol, 62%) of the title compound as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.50, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 4.34 (tdd, *J* = 10.2, 5.4, 3.1 Hz, 1H), 3.73 – 3.58 (m, 2H), 3.51 (td, *J* = 9.9, 5.4 Hz, 1H), 3.24 (dd, *J* = 13.8, 5.4 Hz, 1H), 2.76 (s, 3H), 2.53 – 2.39 (m, 4H), 2.24 (dddd, *J* = 15.6, 10.5, 5.4, 4.0 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.0, 134.1, 130.0, 127.5, 58.3, 39.0, 35.9, 33.2, 28.8, 21.7. **IR** (neat): 2963, 2922, 1595, 1495, 1443, 1338, 1264, 1230, 1200, 1156, 1088, 1044, 1018, 939, 813, 734, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{12}H_{18}BrINO_2S$ ($[M+H]^+$) 445.9281, found 445.9281.

***N*-(6-chloro-2-iodohexyl)-*N*,4-dimethylbenzenesulfonamide (15aq)**



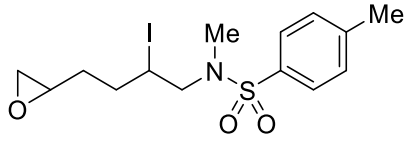
Following general procedure ***GP-I*** using 6-chlorohex-1-ene (**1aq**) (264.7 µL, 237.2 mg, 2.0 mmol, 4.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 135.9 mg (316.2 µmol, 63%) of the title compound as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 4.17 (tdd, *J* = 9.2, 5.8, 3.4 Hz, 1H), 3.63 – 3.42 (m, 3H), 3.23 (dd, *J* = 14.0, 5.8 Hz, 1H), 2.76 (s, 3H), 2.43 (s, 3H), 2.00 – 1.68 (m, 5H), 1.61 – 1.46 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.9, 134.1, 129.9, 127.5, 58.8, 44.8, 36.5, 35.7, 32.4, 31.8, 27.0, 21.7. **IR** (neat): 2926, 2866, 1595, 1495, 1454, 1338, 1211, 1111, 1097, 1036, 939, 816, 734, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_{22}ClINO_2S$ ($[M+H]^+$) 430.0099, found 430.0099.

***N*-(2-iodo-4,4-dimethylpentyl)-*N*,4-dimethylbenzenesulfonamide (15ar)**



Following general procedure ***GP-I*** using 4,4-dimethylpent-1-ene (**1ar**) (287.5 µL, 196.4 mg, 2.0 mmol, 4.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 153.8 mg (375.7 µmol, 75%) of the title compound as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.13 (dtd, *J* = 8.9, 6.2, 4.8 Hz, 1H), 3.42 (dd, *J* = 14.0, 8.8 Hz, 1H), 3.09 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.75 (s, 3H), 2.42 (s, 3H), 2.08 (d, *J* = 5.9 Hz, 1H), 0.98 (s, 9H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.8, 134.2, 129.9, 127.5, 60.4, 50.5, 36.3, 31.5, 29.8, 25.2, 21.6. **IR** (neat): 2956, 2870, 1599, 1465, 1398, 1342, 1199, 1159, 1088, 1018, 936, 813, 727, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{25}INO_2S$ ($[M+H]^+$) 410.0645, found 410.0646.

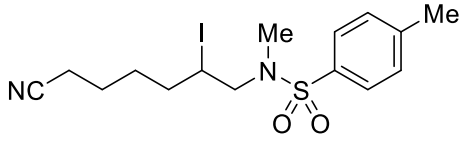
***N*-(2-iodo-4-(oxiran-2-yl)butyl)-*N*,4-dimethylbenzenesulfonamide (d.r. = 80:20) (15as)**



Following general procedure ***GP-I*** using 2-(but-3-en-1-yl)oxirane (**1as**) (225.6 µL, 196.3 mg, 2.0 mmol, 4.0 equiv),

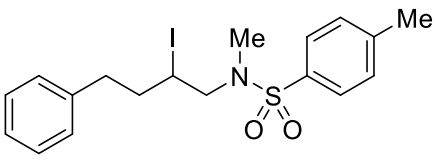
N,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 154.7 mg (378.0 µmol, 76%) of the title compound as an inseparable mixture of two diastereomers (d.r. = 80:20) as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.60, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.3 Hz, 2H, minor diastereomer), 7.64 (d, *J* = 7.3 Hz, 2H, major diastereomer), 7.35 – 7.26 (m, 4H, both diastereomers), 4.76 – 4.62 (m, 1H, minor diastereomer), 4.29 – 4.13 (m, 1H, major diastereomer), 3.46 (ddd, *J* = 19.7, 14.0, 9.2 Hz, 2H, both diastereomers), 3.22 (ddd, *J* = 15.1, 14.0, 6.0 Hz, 2H, both diastereomers), 3.00 – 2.87 (m, 2H, both diastereomers), 2.77 – 2.71 (m, 6H, both diastereomers), 2.59 (d, *J* = 5.4 Hz, 2H, both diastereomers), 2.54 – 2.45 (m, 2H, both diastereomers), 2.43 – 2.37 (m, 6H, both diastereomers), 2.27 – 1.40 (m, 8H, both diastereomers). **^{13}C-NMR** (75 MHz, $CDCl_3$, both diastereomers) δ = 143.8, 143.4, 133.9, 129.9, 129.7, 127.4, 127.4, 127.2, 58.7, 58.6, 51.7, 51.2, 47.0, 46.9, 36.5, 36.3, 33.1, 32.6, 32.4, 32.1, 31.9, 31.8, 29.4, 21.6. **IR** (neat): 2974, 2922, 1595, 1495, 1446, 1409, 1334, 1260, 1226, 1156, 1088, 1040, 917, 813, 738, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_{21}INO_3S$ ($[M+H]^+$) 410.0281, found 410.0285.

***N*-(6-cyano-2-iodohexyl)-*N*,4-dimethylbenzenesulfonamide (15at)**



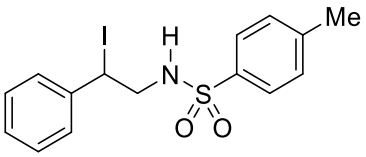
Following general procedure ***GP-I*** using hept-6-enenitrile (**1at**) (259.9 µL, 218.3 mg, 2.0 mmol, 4.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 163.8 mg (389.7 µmol, 78%) of the title compound as a sticky yellowish oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.28, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.59 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 4.12 (tdd, *J* = 9.2, 5.8, 2.9 Hz, 1H), 3.42 (dd, *J* = 14.1, 9.4 Hz, 1H), 3.16 (dd, *J* = 14.1, 5.8 Hz, 1H), 2.70 (s, 3H), 2.54 (s, 1H), 2.43 – 2.31 (m, 6H), 2.06 – 1.91 (m, 2H), 1.86 – 1.61 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.0, 133.7, 129.9, 127.4, 119.3, 58.4, 36.4, 35.0, 30.3, 29.3, 25.4, 21.6, 16.5. **IR** (neat): 2926, 2248, 1595, 1495, 1454, 1327, 1215, 1156, 1118, 1089, 1021, 947, 813, 738, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{22}IN_2O_2S$ ($[M+H]^+$) 421.0441, found 421.0441.

***N*-(2-iodo-4-phenylbutyl)-*N*,4-dimethylbenzenesulfonamide (15au)**



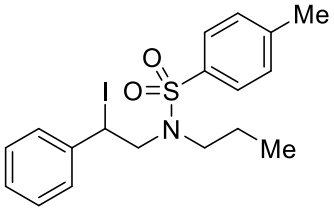
Following general procedure ***GP-I*** using but-3-en-1-ylbenzene (**1au**) (300.5 µL, 264.4 mg, 2.0 mmol, 4.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 145.1 mg (327.3 µmol, 65%) of the title compound as a sticky colorless oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 4:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.38, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.17 (m, 7H), 4.09 (tdd, *J* = 9.4, 5.7, 3.2 Hz, 1H), 3.58 (dd, *J* = 13.9, 9.6 Hz, 1H), 3.23 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.00 (ddd, *J* = 13.6, 8.9, 4.6 Hz, 1H), 2.72 (ddd, *J* = 13.7, 7.6, 1.4 Hz, 1H), 2.65 (s, 4H), 2.43 (s, 3H), 2.25 (dddd, *J* = 14.9, 9.0, 7.5, 3.2 Hz, 1H), 2.05 (dddd, *J* = 14.8, 10.0, 8.9, 4.6 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.8, 140.6, 134.2, 129.9, 128.7, 128.6, 127.5, 126.3, 58.7, 38.0, 36.0, 35.3, 31.8, 21.7. **IR** (neat): 3027, 2922, 2863, 1599, 1495, 1454, 1338, 1249, 1215, 1159, 1111, 1091, 1021, 943, 813, 734, 701, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{18}H_{23}INO_2S$ ($[M+H]^+$) 444.0489, found 444.0490.

***N*-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bc)**



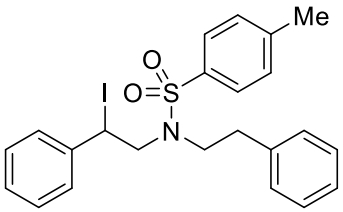
Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 4-methylbenzenesulfonamide (**2bc**) (85.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 180.7 mg (450.3 µmol, 90%) of the title compound as a yellowish solid after flash column purification on silica (hexanes / EtOAc 7:1 to 4:1). Spectral data are in accordance with those reported in literature.[60] $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.28, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.24 (m, 7H), 5.01 (dd, *J* = 8.2, 7.4 Hz, 1H), 3.78 – 3.62 (m, 1H), 3.60 – 3.44 (m, 1H), 2.45 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.0, 140.0, 137.1, 130.0, 129.2, 128.9, 127.7, 127.2, 51.4, 30.0, 21.7.

***N*-(2-iodo-2-phenylethyl)-4-methyl-*N*-propylbenzenesulfonamide (15bg)**



Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 4-methyl-*N*-propylbenzene-sulfonamide (**2bg**) (106.7 mg, 0.5 mmol, 1.0 equiv), *N*-iodo-succinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 214.9 mg (483.2 µmol, 97%) of the title compound as a yellowish oil after flash column chromatography on silica (hexanes / EtOAc 9:1). $\mathbf{R_f}$ (hexanes / EtOAc 9:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.32 – 7.23 (m, 5H), 5.34 (dd, *J* = 9.9, 5.8 Hz, 1H), 3.93 (dd, *J* = 14.8, 5.8 Hz, 1H), 3.71 (dd, *J* = 14.8, 9.9 Hz, 1H), 2.93 (ddd, *J* = 14.4, 9.7, 5.8 Hz, 1H), 2.70 (ddd, *J* = 14.5, 9.8, 5.9 Hz, 1H), 2.42 (s, 3H), 1.36 – 1.09 (m, 2H), 0.62 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.6, 140.9, 136.5, 129.8, 128.8, 128.5, 128.4, 127.3, 57.2, 51.3, 30.6, 21.6, 21.2, 11.1. **IR** (neat): 3064, 3030, 2967, 2930, 2874, 1599, 1495, 1454, 1334, 1156, 1118, 1100, 992, 939, 887, 813, 731, 697, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{18}H_{23}INO_2S$ ($[M+H]^+$) 444.0489, found 444.0492.

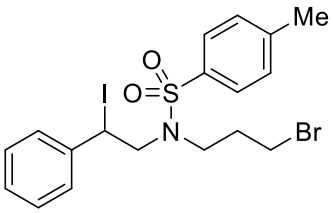
***N*-(2-iodo-2-phenylethyl)-4-methyl-*N*-phenethylbenzenesulfonamide (15bh)**



Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 4-methyl-*N*-phenethylbenzene-sulfonamide (**2bh**) (137.7 mg, 0.5 mmol, 1.0 equiv), *N*-iodo-succinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 233.4 mg (461.8 µmol, 92%) of the title compound as a yellowish oil after flash column chromatography on silica (hexanes / EtOAc 9:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.58, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 8.4 Hz, 2H), 7.43 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.37 – 7.18 (m, 8H), 7.00 – 6.91 (m, 2H), 5.33 (dd, *J* = 9.9, 5.6 Hz, 1H), 4.03 (dd, *J* = 14.9, 5.6 Hz, 1H), 3.73 (dd, *J* = 14.9, 10.0 Hz, 1H), 3.17 (ddd, *J* = 14.7, 11.0, 5.6 Hz, 1H), 2.99 (ddd, *J* = 14.7, 10.9, 5.5 Hz, 1H), 2.64 (ddd, *J* = 13.1, 10.9, 5.5 Hz, 1H), 2.44 (s, 3H), 2.32 (ddd, *J* = 13.1, 10.9, 5.5 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.8, 141.0, 138.2, 136.4, 129.9, 129.0, 128.7, 128.6, 128.6, 128.4, 127.4, 126.6, 58.0, 51.6, 35.1, 30.4, 21.6. **IR** (neat): 3064, 3027, 2926, 2870, 1599, 1495, 1454, 1334, 1219, 1156, 1088, 1033, 977, 932, 921, 835, 819,

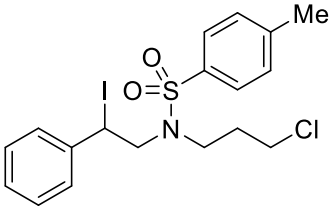
734, 697, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{25}INO_2S$ ($[M+H]^+$) 506.0645, found 506.0651.

***N*-(3-bromopropyl)-*N*-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bi)**



Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), N-(3-bromopropyl)-4-methylbenzenesulfonamide (**2bi**) (146.1 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 241.2 mg (461.9 µmol, 92%) of the title compound as an yellowish oil after flash column chromatography on silica (hexanes / EtOAc 20:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.4 Hz, 2H), 7.42 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.34 – 7.26 (m, 5H), 5.37 (dd, *J* = 9.9, 5.8 Hz, 1H), 3.93 (dd, *J* = 14.7, 5.8 Hz, 1H), 3.66 (dd, *J* = 14.7, 10.0 Hz, 1H), 3.18 – 3.04 (m, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.76 (ddtd, *J* = 32.3, 14.7, 7.3, 5.5 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.0, 140.7, 135.5, 130.0, 129.0, 128.7, 128.4, 127.5, 58.7, 48.8, 31.5, 30.6, 30.1, 21.7. **IR** (neat): 3060, 3030, 2922, 2870, 1595, 1491, 1454, 1338, 1219, 1156, 1088, 1036, 988, 933, 813, 731, 697, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{18}H_{22}BrINO_2S$ ($[M+H]^+$) 521.9594, found 521.9592.

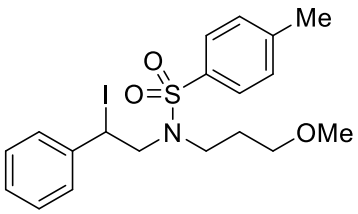
***N*-(3-chloropropyl)-*N*-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bj)**



Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), *N*-(3-chloropropyl)-4-methylbenzenesulfonamide (**2bj**) (123.9 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 220.9 mg (462.3 µmol, 92%) of the title compound as an yellowish oil after flash column chromatography on silica (hexanes / EtOAc 20:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.36 (m, 2H), 7.34 – 7.24 (m, 5H), 5.37 (dd, *J* = 10.0, 5.8 Hz, 1H), 3.93 (dd, *J* = 14.7, 5.8 Hz, 1H), 3.66 (dd, *J* = 14.7, 9.9 Hz, 1H), 3.34 – 3.15 (m, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.68 (ddtd, *J* = 30.9, 14.5, 7.2, 5.3 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.0, 140.7, 135.5, 130.0, 129.0, 128.7, 128.4, 127.5, 58.6, 47.7,

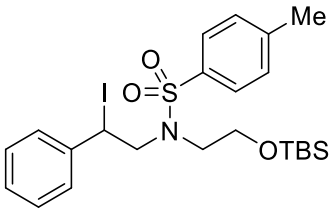
42.1, 31.3, 30.1, 21.7. **IR** (neat): 3064, 3030, 2960, 2926, 2870, 1595, 1495, 1454, 1338, 1234, 1156, 1088, 999, 932, 850, 813, 734, 697, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{18}H_{22}INO_2S$ ($[M+H]^+$) 478.0099, found 478.0100.

***N*-(2-iodo-2-phenylethyl)-*N*-(3-methoxypropyl)-4-methylbenzenesulfonamide (15bk)**



Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), *N*-(3-methoxypropyl)-4-methylbenzenesulfonamide (**2bk**) (121.7 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 201.3 mg (425.3 µmol, 85%) of the title compound as an yellowish oil after flash column chromatography on silica (hexanes / EtOAc 20:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.30, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.4 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.33 – 7.23 (m, 5H), 5.36 (dd, *J* = 9.7, 6.0 Hz, 1H), 3.92 (dd, *J* = 14.7, 6.0 Hz, 1H), 3.69 (dd, *J* = 14.7, 9.7 Hz, 1H), 3.22 (s, 3H), 3.15 – 3.09 (m, 2H), 3.04 – 2.85 (m, 2H), 2.42 (s, 3H), 1.57 – 1.44 (m, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.7, 140.9, 136.1, 129.8, 128.8, 128.5, 128.4, 127.5, 69.6, 58.6, 57.7, 47.0, 30.4, 28.5, 21.6. **IR** (neat): 3064, 3030, 2926, 2873, 2829, 1599, 1495, 1454, 1379, 1334, 1197, 1156, 1111, 1033, 992, 939, 880, 813, 731 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{19}H_{25}INO_3S$ ($[M+H]^+$) 474.0594, found 474.0592.

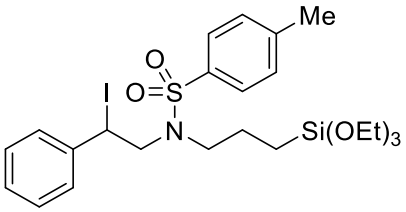
***N*-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-*N*-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bl)**



Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), *N*-(2-((*tert*-butyldimethylsilyl)-oxy)ethyl)-4-methylbenzenesulfonamide (**2bl**) (164.8 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 224.1 mg (400.5 µmol, 80%) of the title compound as an yellowish oil after flash column chromatography on silica (hexanes / EtOAc 20:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 6:1 on silica) = 0.53, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.3 Hz, 2H), 7.40 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.32 – 7.26 (m, 5H), 5.37 (dd, *J* = 9.7, 6.1 Hz, 1H), 4.06 (dd, *J* = 14.8, 6.1 Hz, 1H), 3.94 (dd, *J* = 14.8, 9.7 Hz, 1H), 3.50 (dt, *J* = 10.5, 6.3 Hz, 1H), 3.34 (dt, *J* = 10.5, 5.8 Hz, 1H), 3.16 (dt, *J* = 15.0, 5.8 Hz, 1H), 2.93

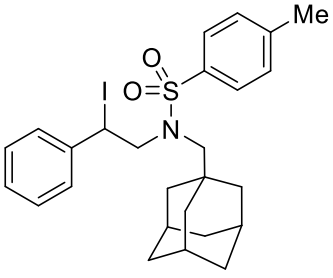
(dt, *J* = 15.0, 6.3 Hz, 1H), 2.42 (s, 3H), 0.85 (s, 9H), -0.03 (s, 3H), -0.03 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.7, 140.9, 137.0, 129.9, 128.9, 128.6, 128.5, 127.4, 62.1, 58.2, 51.2, 30.6, 26.0, 21.7, 18.3, -5.3, -5.4. **IR** (neat): 3030, 2952, 2885, 2855, 1599, 1495, 1454, 1342, 1252, 1156, 1088, 995, 932, 835, 775, 727, 697, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{23}H_{35}INO_3SSi$ ($[M+H]^+$) 560.1146, found 560.1143.

_N_-(2-iodo-2-phenylethyl)-4-methyl-_N_-(3-(triethoxysilyl)propyl)benzenesulfonamide (15bm)



Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), 4-methyl-*N*-(3-(triethoxysilyl)propyl)benzenesulfonamide (**2bm**) (187.8 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 187.2 mg (309.1 µmol, 62%) of the title compound as an yellowish oil after flash column chromatography on silica (hexanes / EtOAc 20:1 to 7:1). **R_f** (hexanes / EtOAc 4:1 on silica) = 0.58, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.35 (m, 2H), 7.30 – 7.21 (m, 5H), 5.33 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.90 (dd, *J* = 14.8, 6.0 Hz, 1H), 3.82 – 3.63 (m, 7H), 3.02 (ddd, *J* = 14.5, 10.2, 5.9 Hz, 1H), 2.73 (ddd, *J* = 14.9, 10.2, 5.5 Hz, 1H), 2.40 (s, 3H), 1.49 – 1.26 (m, 2H), 1.20 (t, *J* = 7.0 Hz, 9H), 0.31 (ddd, *J* = 9.3, 6.6, 4.6 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.5, 140.9, 136.7, 129.8, 128.8, 128.5, 128.3, 127.4, 58.5, 56.8, 51.7, 30.4, 21.6, 21.4, 18.4, 7.5. **IR** (neat): 3030, 2974, 2926, 2885, 1599, 1495, 1454, 1390, 1342, 1156, 1074, 954, 798, 738, 697, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{24}H_{37}INO_5SSi$ ($[M+H]^+$) 606.1201, found 606.1201.

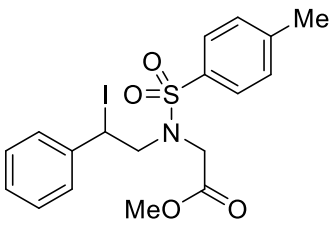
_N_-(((3_r_,5_r_,7_r_)-adamantan-1-yl)methyl)-_N_-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bp)



Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), *N*-(((3*r*,5*r*,7*r*)-adamantan-1-yl)methyl)-4-methylbenzenesulfonamide (**2bp**) (159.7 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 153.8 mg (279.9 µmol, 56%) of the title compound as an yellowish oil after flash column chromatography on silica

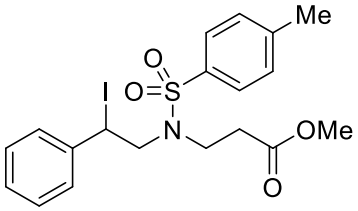
(hexanes / EtOAc 20:1 to 7:1). **R_f** (hexanes / EtOAc 7:1 on silica) = 0.50, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.19 (m, 5H), 5.31 (dd, *J* = 9.8, 5.3 Hz, 1H), 4.10 (dd, *J* = 15.3, 5.3 Hz, 1H), 3.77 (dd, *J* = 15.2, 9.8 Hz, 1H), 2.79 (d, *J* = 15.0 Hz, 1H), 2.45 (s, 3H), 1.93 – 1.85 (m, 3H), 1.63 (d, *J* = 12.4 Hz, 3H), 1.52 (d, *J* = 12.2 Hz, 3H), 1.39 (s, 6H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.7, 141.4, 137.3, 129.9, 128.8, 128.6, 128.5, 127.8, 60.8, 59.8, 41.0, 36.8, 35.3, 29.5, 28.4, 21.7. **IR** (neat): 3027, 2900, 2848, 1599, 1495, 1454, 1334, 1215, 1156, 1088, 1033, 936, 902, 813, 734, 697, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{26}H_{33}INO_2S$ ($[M+H]^+$) 550.1271, found 550.1271.

methyl *N*-(2-iodo-2-phenylethyl)-*N*-tosylglycinate (15bs)



Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), methyl tosylglycinate (**2bs**) (121.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 140.9 mg (297.7 µmol, 60%) of the title compound as an yellowish oil after flash column chromatography on silica (hexanes / EtOAc 20:1 to 7:1). **R_f** (hexanes / EtOAc 4:1 on silica) = 0.33, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.31 – 7.25 (m, 5H), 5.33 (dd, *J* = 9.5, 6.2 Hz, 1H), 4.15 – 4.03 (m, 2H), 3.84 (dd, *J* = 15.3, 9.6 Hz, 1H), 3.49 (s, 3H), 3.41 (d, *J* = 18.7 Hz, 1H), 2.42 (s, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 169.0, 143.9, 140.8, 136.2, 129.7, 129.0, 128.7, 128.1, 127.5, 57.3, 52.2, 49.5, 30.2, 21.7. IR (neat): 3030, 2952, 1744, 1599, 1495, 1439, 1338, 1211, 1156, 1088, 1018, 924, 846, 813, 753, 697, 650 cm^{-1}. HRMS (ESI) m/z calculated for $C_{18}H_{21}INO_4S$ ($[M+H]^+$) 474.0230, found 474.0230.

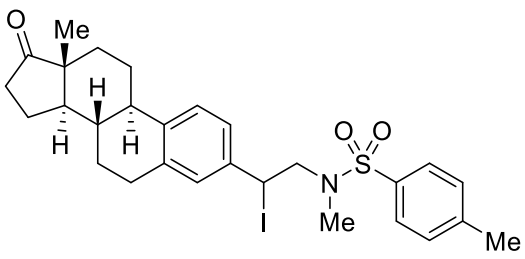
methyl 3-((*N*-(2-iodo-2-phenylethyl)-4-methylphenyl)sulfonamido)propanoate (15bt)



Following general procedure ***GP-I*** using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), methyl 3-((4-methylphenyl)-sulfonamido)propanoate (**2bt**) (128.7 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 190.0 mg (389.9 µmol, 78%) of the title compound as an yellowish oil after flash

column chromatography on silica (hexanes / EtOAc 20:1 to 7:1). $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.33, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.59 (d, *J* = 8.3 Hz, 2H), 7.37 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.29 – 7.21 (m, 5H), 5.28 (dd, *J* = 9.7, 6.1 Hz, 1H), 3.91 (dd, *J* = 14.8, 6.1 Hz, 1H), 3.68 (dd, *J* = 14.8, 9.8 Hz, 1H), 3.56 (s, 3H), 3.15 (ddd, *J* = 8.1, 6.7, 1.3 Hz, 2H), 2.46 – 2.33 (m, 4H), 2.08 (ddd, *J* = 16.7, 8.0, 6.8 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 171.8, 143.9, 140.7, 135.8, 129.9, 129.0, 128.6, 128.3, 127.4, 58.5, 51.8, 45.7, 33.7, 30.0, 21.6. **IR** (neat): 3030, 2952, 1733, 1599, 1495, 1438, 1320, 1200, 1156, 1088, 1036, 980, 936, 891, 813, 731, 697, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{19}H_{23}INO_4S$ ($[M+H]^+$) 488.0387, found 488.0383.

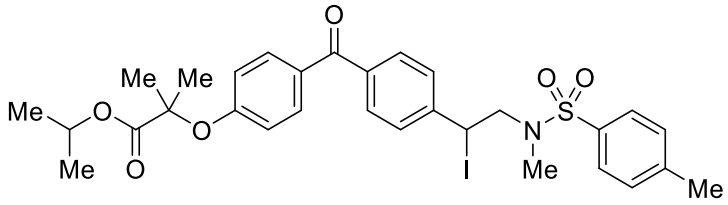
***N*-(2-iodo-2-((8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)ethyl)-*N*,4-dimethylbenzenesulfonamide (d.r. = 91:9) (15bv)**



Following general procedure ***GP-I*** using (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11, 12, 13,14,15,16-decahydro-17*H*-cyclopenta[*a*] phenanthren-17-one (**1bv**) (140.2 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DCM (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 148.5 mg (257.1 µmol, 51%/ 62% based on recovered starting material) of the title compound as an inseparable mixture of two diastereomers (d.r. = 91:9) a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 8:1 to 3:1). $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.33, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$, both diastereomers) δ = 7.73 (d, *J* = 8.3 Hz, 4H), 7.65 – 7.59 (m, 4H), 7.33 – 7.29 (m, 4H), 7.22 – 7.19 (m, 2H), 5.25 (ddd, *J* = 9.0, 6.9, 1.9 Hz, 1H, major diastereomer), 5.11 (ddd, *J* = 9.0, 6.9, 1.9 Hz, 1H, minor diastereomer), 3.72 (dd, *J* = 14.4, 6.9 Hz, 2H), 3.58 (ddd, *J* = 14.3, 9.0, 1.7 Hz, 2H), 2.93 – 2.83 (m, 4H), 2.63 – 2.58 (m, 8H), 2.55 – 2.46 (m, 2H), 2.42 – 2.41 (m, 8H), 2.16 – 1.97 (m, 8H), 1.63 – 1.44 (m, 12H), 0.90 (s, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$, both diastereomers) δ = 221.0, 221.0, 143.7, 143.5, 140.4, 140.4, 138.0, 137.1, 137.1, 136.4, 135.9, 134.5, 134.5, 129.9, 129.8, 128.5, 128.5, 127.5, 127.3, 126.0, 125.3, 125.3, 58.7, 58.7, 50.5, 50.5, 48.0, 48.0, 44.5, 44.5, 38.0, 38.0, 36.9, 36.5, 36.5, 35.9, 31.6, 30.3, 30.3, 30.3, 29.4, 29.4, 29.3, 29.3, 26.4, 25.7, 25.6, 21.7, 21.6, 21.6, 13.9, 13.9. **IR** (neat): 3019, 2926, 2863, 1733, 1599, 1498, 1454, 1375, 1331, 1260,

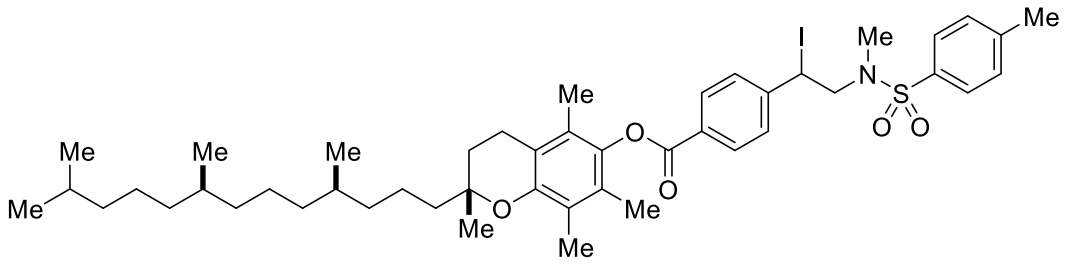
1215, 1159, 1088, 1055, 1000, 984, 924, 816, 746, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{28}H_{35}INO_3S$ ($[M+H]^+$) 592.1377, found 592.1379.

isopropyl 2-(4-(4-(2-((N,4-dimethylphenyl)sulfonamido)-1-iodoethyl)benzoyl)phenoxy)-2-methylpropanoate (15bw)



Following general procedure ***GP-I*** using isopropyl 2-methyl-2-(4-(4-vinylbenzoyl)phenoxy)propanoate (**1bw**) (176.2 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 314.3 mg (473.7 µmol, 95%) of the title compound as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 5:1 to 3:1). $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.23, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 5.32 (dd, *J* = 9.4, 6.5 Hz, 1H), 5.07 (hept, *J* = 6.3 Hz, 1H), 3.83 – 3.60 (m, 2H), 2.58 (s, 3H), 2.41 (s, 3H), 1.65 (s, 6H), 1.19 (d, *J* = 6.3 Hz, 6H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 194.7, 173.2, 159.8, 144.6, 143.9, 138.1, 134.3, 132.1, 130.3, 130.3, 129.9, 128.1, 127.4, 117.3, 79.5, 69.4, 58.8, 36.6, 28.1, 25.5, 25.4, 21.6. **IR** (neat): 2982, 2837, 1730, 1651, 1599, 1506, 1461, 1416, 1387, 1342, 1282, 1252, 1148, 1103, 1018, 973, 928, 851, 816, 746, 690, 653 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{30}H_{35}INO_6S$ ($[M+H]^+$) 664.1224, found 664.1237.

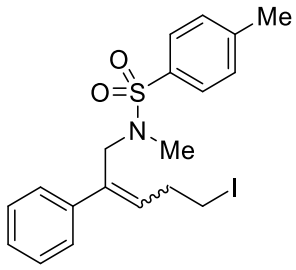
2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-(2-((N,4-dimethylphenyl)sulfonamido)-1-iodoethyl)benzoate (15by)



Following general procedure ***GP-I*** ,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-vinylbenzoate (**1by**) (280.4 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 264.7 mg

(303.6 µmol, 61% / 72% based on recovered starting material) of the title compound diastereoselective as a white solid after flash column chromatography on silica (hexanes / EtOAc 9:1 to 7:1). **mp**: 58 °C. R_f (hexanes / EtOAc 6:1 on silica) = 0.38, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.35 (t, *J* = 8.0 Hz, 1H), 3.79 – 3.68 (m, 2H), 2.67 – 2.58 (m, 5H), 2.44 (s, 3H), 2.13 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.91 – 1.76 (m, 2H), 1.60 – 1.09 (m, 24H), 0.90 – 0.84 (m, 12H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 164.6, 149.6, 146.2, 144.0, 140.6, 134.3, 130.8, 130.0, 129.7, 128.5, 127.5, 126.9, 125.2, 123.3, 117.6, 75.2, 58.8, 39.5, 37.5, 37.4, 36.7, 32.9, 32.9, 32.9, 32.8, 32.8, 28.1, 27.8, 25.0, 24.6, 22.9, 22.8, 21.7, 21.2, 20.8, 19.9, 19.8, 13.3, 12.4, 12.0. **IR** (neat): 2926, 2866, 1733, 1607, 1457, 1422, 1379, 1342, 1284, 1159, 1088, 1018, 980, 924, 857, 813, 768, 738, 701, 664 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{46}H_{67}INO_5S$ ($[M+H]^+$) 872.3779, found 872.3772.

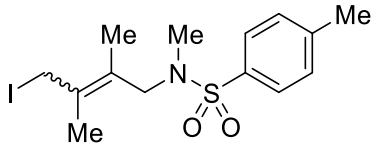
***N*-(5-iodo-2-phenylpent-2-en-1-yl)-N,4-dimethylbenzenesulfonamide (d.r. = 79:21) (15cb)**



Following general procedure ***GP-I*** using (1-cyclopropylvinyl)benzene (**1cb**) (72.1 mg, 0.5 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 2 h yielded 171.7 mg (377.1 µmol, 75%) of the title compound as an inseparable mixture of two diastereomers (d.r. = 79:21) as an orange solid after flash column chromatography on silica (hexanes / EtOAc 10:1 to 7:1). **mp**: 101 °C. R_f (hexanes / EtOAc 4:1 on silica) = 0.48, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.56 (d, *J* = 8.2 Hz, 2H, major diastereomer), 7.50 (d, *J* = 8.3 Hz, 2H, minor diastereomer), 7.38 – 7.32 (m, 2H, major diastereomer), 7.29 – 7.18 (m, 10H, both diastereomers), 7.11 – 7.07 (m, 2H, minor diastereomer), 5.79 (t, *J* = 7.2 Hz, 1H, major diastereomer), 5.54 (t, *J* = 7.2 Hz, 1H, minor diastereomer), 3.99 (s, 2H, major diastereomer), 3.81 (s, 2H, minor diastereomer), 3.16 (t, *J* = 6.8 Hz, 2H, major diastereomer), 3.04 (t, *J* = 6.9 Hz, 2H, minor diastereomer), 2.75 (q, *J* = 6.9 Hz, 2H, major diastereomer), 2.62 (s, 3H, minor diastereomer), 2.53 (q, *J* = 6.9 Hz, 2H, minor diastereomer), 2.42 (s, 3H, major diastereomer), 2.38 (s, 3H, major diastereomer), 2.35 (s, 3H, minor diastereomer). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ =143.6 (major diastereomer), 143.4 (minor diastereomer), 140.3 (major diastereomer), 137.8 (minor diastereomer), 137.7 (minor diastereomer), 136.6 (major diastereomer), 134.7 (minor diastereomer), 133.8 (major

diastereomer), 132.9 (major diastereomer), 129.8 (major diastereomer), 129.7 (minor diastereomer), 129.7 (minor diastereomer), 128.5 (minor diastereomer), 128.5 (major diastereomer), 128.5 (minor diastereomer), 127.8 (major diastereomer), 127.8 (major diastereomer), 127.7 (minor diastereomer), 127.6 (minor diastereomer), 126.8 (major diastereomer), 57.0 (minor diastereomer), 48.0 (major diastereomer), 34.5 (minor diastereomer), 34.0 (major diastereomer), 32.3 (minor diastereomer), 31.9 (major diastereomer), 21.7 (major diastereomer), 21.6 (minor diastereomer), 5.6 (minor diastereomer), 5.2 (major diastereomer). **IR** (neat): 3030, 2963, 2919, 2863, 1599, 1491, 1446, 1416, 1375, 1334, 1241, 1204, 1159, 1114, 1071, 999, 973, 924, 839, 809, 731, 697, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{19}H_{23}INO_2S$ ($[M+H]^+$) 456.0489, found 456.0491.

***N*-(4-iodo-2,3-dimethylbut-2-en-1-yl)-*N*,4-dimethylbenzenesulfonamide (d.r. = 55:45) (15cd)**

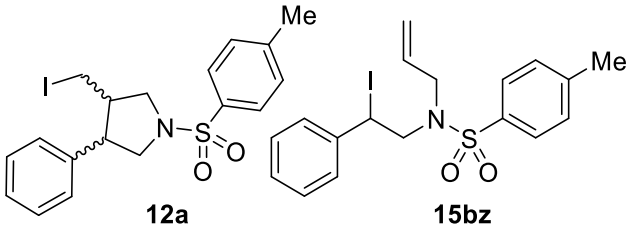


Following general procedure ***GP-I*** using 2,3-dimethylbuta-1,3-diene (**1cd**) (225.1 µL, 164.3 mg, 2.0 mmol, 4.0 equiv), *N*-allyl-4-methylbenzenesulfonamide (**2a**) (105.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DMC (2.0 mL, 0.25 M) at room temperature (25 °C) for 12 h yielded 176.3 mg (448.3 µmol, 90%) of the title compound as an inseparable mixture of two diastereomers (d.r. = 55:45) as an orange oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 5:1). $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.71 – 7.62 (m, 4H, both diastereomers), 7.38 – 7.29 (m, 4H, both diastereomers), 3.90 (s, 2H, major diastereomer), 3.88 (s, 2H, minor diastereomer), 3.53 (s, 2H, minor diastereomer), 3.49 (s, 2H, major diastereomer), 2.58 (s, 3H, minor diastereomer), 2.51 (s, 3H, major diastereomer), 2.44 (s, 3H, minor diastereomer), 2.43 (s, 3H, major diastereomer), 1.83 (q, *J* = 1.0 Hz, 3H, minor diastereomer), 1.74 (q, *J* = 1.0 Hz, 3H, major diastereomer), 1.69 – 1.65 (m, 6H, both diastereomers). **^{13}C-NMR** (75 MHz, $CDCl_3$, both diastereomers) δ = 143.6, 143.5, 134.0, 134.0, 132.3, 132.0, 129.9, 129.8, 129.0, 128.9, 127.5, 127.5, 52.4, 51.7, 34.6, 33.8, 21.7, 21.6, 18.8, 17.6, 17.1, 16.4, 10.6, 9.2. **IR** (neat): 2922, 2863, 1651, 1595, 1495, 1454, 1379, 1334, 1208, 1156, 1100, 1087, 1018, 977, 913, 815, 753, 723, 651 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{14}H_{21}INO_2S$ ($[M+H]^+$) 394.0332, found394.0335.

7.6.3 Compound Characterization for Further Transformations

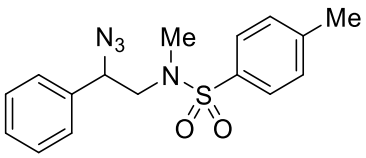
3-(iodomethyl)-4-phenyl-1-tosylpyrrolidine (d.r. = 70:30) (12a)

***N*-allyl-*N*-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bz)**



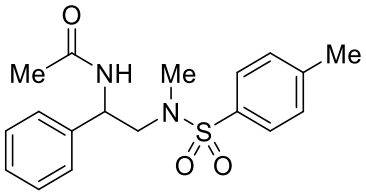
Following general procedure ***GP-I*** (Chapter 7.6.3) using styrene (**1a**) (57.3 µL, 52.1 mg, 0.5 mmol, 1.0 equiv), *N*-allyl-4-methylbenzenesulfonamide (**2bz**) (105.6 mg, 0.5 mmol, 1.0 equiv), *N*-iodo-succinimide (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and DCM (20.0 mL, 0.025 M) at room temperature (25 °C) for 2 h yielded 178.1 mg (403.6 µmol, 81%) of the title compound **12a** as an inseparable mixture of two diastereomers (d.r. = 70:30) as a colorless oil after flash column chromatography on silica (hexanes / EtOAc 20:1 to 9:1). As a by-product 32.9 mg (74.6 µmol, 15%) of the title compound **15bz** was observed as a sticky orange oil. $\mathbf{R_f}$ (**12a**; hexanes / EtOAc 7:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (**12a**; 300 MHz, $CDCl_3$) δ = 7.87 – 7.66 (m, 4H, both diastereomers), 7.44 – 7.35 (m, 4H, both diastereomers), 7.34 – 7.23 (m, 6H, both diastereomers), 7.15 – 6.99 (m, 4H, both diastereomers), 3.77 (ddd, *J* = 14.5, 10.2, 7.8 Hz, 2H, major diastereomer), 3.70 – 3.65 (m, 1H, major diastereomer), 3.44 (td, *J* = 6.6, 5.0 Hz, 1H, minor diastereomer), 3.36 (t, *J* = 9.9 Hz, 1H, major diastereomer), 3.26 (dd, *J* = 10.5, 7.7 Hz, 1H, minor diastereomer), 3.18 – 3.02 (m, 2H, major diastereomer), 2.89 (dd, *J* = 10.2, 8.1 Hz, 2H, major diastereomer), 2.74 – 2.59 (m, 2H, minor diastereomer), 2.47 (m, 8H, both diastereomers), 2.32 – 2.16 (m, 2H, minor diastereomer). **^{13}C-NMR** (**12a**; 75 MHz, $CDCl_3$, both diastereomers) δ = 143.8, 138.1, 137.6, 133.8, 133.6, 130.0, 129.9, 129.0, 128.8, 127.9, 127.7, 127.6, 127.5, 127.5, 55.0, 54.4, 52.7, 52.6, 50.3, 47.7, 46.9, 46.3, 21.7, 21.7, 6.0, 3.5. **IR** (**12a**; neat): 3060, 3030, 2948, 2881, 1595, 1495, 1467, 1402, 1342, 1156, 1092, 1014, 910, 813, 731, 701, 651 cm^{-1}. **HRMS** (**12a**; ESI) m/z calculated for $C_{18}H_{21}INO_2S$ ($[M+H]^+$) 442.0332, found 442.0330. $\mathbf{R_f}$ (**15bz**; hexanes / EtOAc 7:1 on silica) = 0.53, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (**15bz**; 300 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.4 Hz, 2H), 7.43 – 7.36 (m, 2H), 7.34 – 7.24 (m, 5H), 5.38 – 5.21 (m, 2H), 5.13 – 4.93 (m, 2H), 3.89 (ddd, *J* = 14.8, 5.9, 0.7 Hz, 1H), 3.83 – 3.67 (m, 2H), 3.24 (ddt, *J* = 15.9, 7.1, 1.2 Hz, 1H), 2.42 (s, 3H). **^{13}C-NMR** (**15bz**; 75 MHz, $CDCl_3$) δ = 143.7, 140.8, 136.6, 132.4, 129.9, 128.8, 128.6, 128.5, 127.4, 119.8, 55.4, 51.7, 30.4, 21.7. **IR** (**15bz**; neat): 3064, 3030, 2982, 2922, 1595, 1495, 1454, 1331, 1156, 1088, 992, 902, 813, 749, 697, 651 cm^{-1}. **HRMS** (**15bz**; ESI) m/z calculated for $C_{18}H_{21}INO_2S$ ($[M+H]^+$) 442.0332, found 442.0328.

***N*-(2-azido-2-phenylethyl)-*N*,4-dimethylbenzenesulfonamide (16a)**



A round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-iodo-2-phenylethyl)-*N*,4-dimethylbenzene-sulfonamide (**15a**) (124.6 mg, 0.3 mmol, 1.0 equiv), NaN_3 (97.5 mg, 1.5 mmol, 5.0 equiv) and dissolved in DMF (6.0 mL, 0.05 M). The resulting reaction mixture was stirred for 5 h at room temperature (25 °C). The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water and extracted three times with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 3:1) to yield 90.0 mg (272.4 µmol, 91%) of the title compound as a colorless oil. $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.53, Staining: UV, vanillin. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.27 (m, 7H), 4.83 (dd, *J* = 8.4, 5.6 Hz, 1H), 3.29 – 3.13 (m, 2H), 2.77 (s, 3H), 2.41 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.7, 137.1, 134.7, 129.9, 129.1, 128.9, 127.4, 127.1, 66.0, 56.0, 37.1, 21.6. **IR** (neat): 3064, 3034, 2926, 2102, 1599, 1495, 1454, 1342, 1245, 1215, 1156, 1088, 1018, 947, 872, 813, 764, 731, 701, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{19}N_4O_2S$ ($[M+H]^+$) 331.1223, found 331.1224.

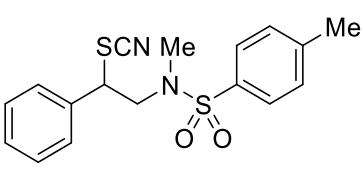
***N*-(2-((*N*,4-dimethylphenyl)sulfonamido)-1-phenylethyl)acetamide (16b)**



Based on a literature procedure,[61] a round-bottom flask equipped with a magnetic stirring bar was charged with $FeCl_3$ hexahydrate (324.3 mg, 1.2 mmol, 4.0 equiv) and dissolved in MeCN (1.0 mL). To the latter, a solution of *N*-(2-iodo-2-phenylethyl)-*N*,4-dimethylbenzenesulfonamide (**15a**) (124.6 mg, 0.3 mmol, 1.0 equiv) in MeCN (1.0 mL) was added dropwise at room temperature (25 °C). The resulting reaction mixture was stirred for 2 h at 80 °C. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water and extracted three times with EtOAc. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 1:3) to yield 70.0 mg (202.1 µmol, 67%) of the title compound as a colorless oil. Spectral data are in accordance with those reported in literature.[61] $\mathbf{R_f}$ (hexanes / EtOAc 1:3 on silica) = 0.38, Staining: UV, $KMnO_4$. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.19 (m, 7H), 6.75 (d, *J* = 7.1 Hz, 1H), 5.11 (ddd, *J* = 9.5, 7.1, 4.2 Hz, 1H), 3.44 (dd, *J* = 14.2,

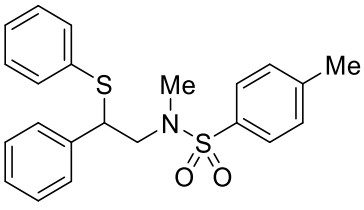
9.5 Hz, 1H), 3.00 (dd, *J* = 14.2, 4.3 Hz, 1H), 2.71 (s, 3H), 2.41 (s, 3H), 2.06 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 170.5, 143.9, 139.4, 134.6, 130.0, 128.9, 127.9, 127.3, 126.6, 55.0, 51.5, 35.9, 23.4, 21.6.

***N*,4-dimethyl-*N*-(2-phenyl-2-thiocyanatoethyl)benzenesulfonamide (16c)**



A round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-iodo-2-phenylethyl)-*N*,4-dimethylbenzene-sulfonamide (**15a**) (124.6 mg, 0.3 mmol, 1.0 equiv), NaSCN (121.6 mg, 1.5 mmol, 5.0 equiv) and dissolved in DMF (6.0 mL, 0.05 M). The resulting reaction mixture was stirred for 24 h at 70 °C. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water and extracted three times with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 3:1) to yield 67.4 mg (214.4 µmol, 71%) of the title compound as a colorless oil. $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.38, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.35 (m, 5H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.71 (t, *J* = 7.8 Hz, 1H), 3.71 (dd, *J* = 14.4, 8.0 Hz, 1H), 3.48 (dd, *J* = 14.4, 7.5 Hz, 1H), 2.70 (s, 3H), 2.43 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.2, 135.7, 133.8, 130.1, 129.6, 129.4, 128.0, 127.6, 111.1, 54.8, 52.2, 37.0, 21.7. **IR** (neat): 3034, 2974, 2926, 2154, 1599, 1495, 1454, 1338, 1204, 1156, 1100, 1044, 977, 928, 850, 816, 738, 697, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{19}N_2O_2S_2$ ($[M+H]^+$) 347.0882, found 347.0885.

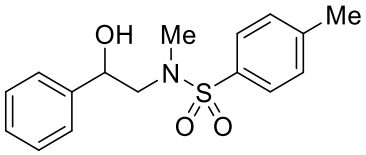
***N*,4-dimethyl-*N*-(2-phenyl-2-(phenylthio)ethyl)benzenesulfonamide (16d)**



A round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-iodo-2-phenylethyl)-*N*,4-dimethylbenzene-sulfonamide (**15a**) (124.6 mg, 0.3 mmol, 1.0 equiv), Na_2CO_3 (79.5 mg, 0.75 mmol, 2.5 equiv), thiophenol (76.5 µL, 82.6 mg, 0.75 mmol, 2.5 equiv) and dissolved in MeCN (4.0 mL, 0.075 M). The resulting reaction mixture was stirred for 24 h at room temperature (25 °C). The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water and extracted three times with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 3:1) to yield 76.0 mg (191.2 µmol, 64%) of the title compound as a colorless

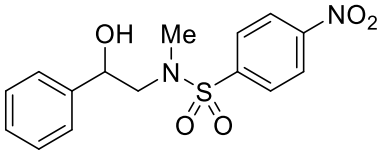
oil. $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.50, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.49 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.35 – 7.22 (m, 10H), 4.54 (dd, *J* = 9.6, 5.8 Hz, 1H), 3.57 (dd, *J* = 14.3, 5.9 Hz, 1H), 3.25 (dd, *J* = 14.2, 9.6 Hz, 1H), 2.49 (s, 3H), 2.40 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.5, 139.1, 134.6, 134.2, 132.1, 129.7, 129.0, 128.8, 128.3, 127.9, 127.5, 127.4, 55.6, 52.3, 36.9, 21.6. **IR** (neat): 3060, 3030, 2971, 2922, 1599, 1491, 1454, 1338, 1200, 1156, 1100, 1021, 980, 932, 813, 738, 693, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{22}H_{24}NO_2S_2$ ($[M+H]^+$) 398.1243, found 398.1245.

***N*-(2-hydroxy-2-phenylethyl)-*N*,4-dimethylbenzenesulfonamide (16e)**



A round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-iodo-2-phenylethyl)-*N*,4-dimethylbenzene-sulfonamide (**15a**) (124.6 mg, 0.3 mmol, 1.0 equiv) and dissolved in acetone/water (1:1, 4.0 mL, 0.075 M). The resulting reaction mixture was stirred for 12 h at 100 °C. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water and extracted three times with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 3:1) to yield 83.7 mg (274.1 µmol, 91%) of the title compound as a colorless oil. Spectral data are in accordance with those reported in literature.[62] $\mathbf{R_f}$ (hexanes / EtOAc 2:1 on silica) = 0.45, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.26 (m, 7H), 4.91 (dd, *J* = 8.9, 3.4 Hz, 1H), 3.28 (dd, *J* = 14.1, 8.9 Hz, 1H), 3.01 (dd, *J* = 14.2, 3.4 Hz, 1H), 2.92 (bs, 1H), 2.79 (s, 3H), 2.41 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.8, 141.1, 134.2, 129.9, 128.6, 128.1, 127.5, 126.1, 72.2, 58.4, 36.9, 21.6.

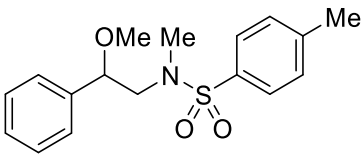
***N*-(2-hydroxy-2-phenylethyl)-*N*-methyl-4-nitrobenzenesulfonamide (Ns-16e)**



A round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-iodo-2-phenylethyl)-*N*-methyl-4-nitrobenzenesulfonamide (**15a**) (133.9 mg, 0.3 mmol, 1.0 equiv) and dissolved in acetone/water (1:1, 4.0 mL, 0.075 M). The resulting reaction mixture was stirred for 12 h at 100 °C. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water and extracted three times with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 3:1) to

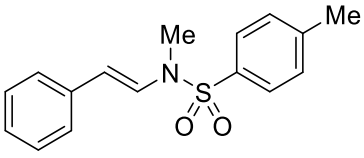
yield 92.1 mg (273.8 µmol, 91%) of the title compound as a colorless oil. $\mathbf{R_f}$ (hexanes / EtOAc 2:1 on silica) = 0.45, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 8.33 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 8.9 Hz, 2H), 7.42 – 7.27 (m, 5H), 4.94 (dd, *J* = 8.6, 3.7 Hz, 1H), 3.34 (dd, *J* = 14.3, 8.6 Hz, 1H), 3.17 (dd, *J* = 14.3, 3.7 Hz, 1H), 2.88 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 150.2, 143.7, 140.9, 128.8, 128.6, 128.4, 126.0, 124.5, 72.7, 57.9, 36.7. **IR** (neat): 3511, 3105, 3034, 2919, 2851, 1708, 1607, 1528, 1454, 1346, 1308, 1208, 1159, 1088, 1062, 962, 857, 764, 731 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{15}H_{17}N_2O_5S$ ($[M+H]^+$) 337.0853, found 337.0864.

_N_-(2-methoxy-2-phenylethyl)-_N_,4-dimethylbenzenesulfonamide (16f)



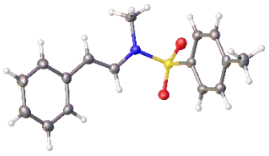
A round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-iodo-2-phenylethyl)-*N*,4-dimethylbenzene-sulfonamide (**15a**) (124.6 mg, 0.3 mmol, 1.0 equiv) and dissolved in MeOH (4.0 mL, 0.075 M). The resulting reaction mixture was stirred for 12 h at reflux temperature. The reaction was monitored by TLC. Afterwards, the reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 5:1) to yield 80.3 mg (251.4 µmol, 84%) of the title compound as a colorless oil. $\mathbf{R_f}$ (hexanes / EtOAc 2:1 on silica) = 0.68, Staining: UV, vanillin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.24 (m, 7H), 4.43 (dd, *J* = 8.2, 4.4 Hz, 1H), 3.30 – 3.19 (m, 4H), 3.12 (dd, *J* = 14.4, 8.3 Hz, 1H), 2.79 (s, 3H), 2.40 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.3, 139.4, 135.2, 129.7, 128.7, 128.2, 127.4, 126.9, 83.9, 56.9, 56.7, 37.2, 21.6. **IR** (neat): 3064, 3030, 2982, 2930, 2825, 1599, 1495, 1454, 1338, 1223, 1156, 1088, 1044, 1001, 962, 857, 816, 764, 734, 701, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{17}H_{22}NO_3S$ ($[M+H]^+$) 320.1315, found 320.1315.

(*E*)-*N*,4-dimethyl-*N*-styrylbenzenesulfonamide (17)

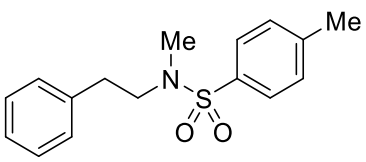


A round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-iodo-2-phenylethyl)-*N*,4-dimethylbenzene-sulfonamide (**15a**) (124.6 mg, 0.3 mmol, 1.0 equiv), NaOAc (246.1 mg, 3.0 mmol, 10.0 equiv) and dissolved in DMF (6.0 mL, 0.05 M). The resulting reaction mixture was stirred for 5 h at room temperature (25 °C). The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water and extracted three times with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered,

concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 3:1) to yield 68.9 mg (239.8 µmol, 80%) of the title compound as a white solid. Suitable crystals for X-ray analysis were obtained by crystallization from $CHCl_3$. The crystals obtained were colorless prism-shaped. **mp**: 105 °C. R_f (hexanes / EtOAc 5:1 on silica) = 0.40, Staining: UV, $KMnO_4$. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 14.4 Hz, 1H), 7.36 – 7.27 (m, 7H), 5.68 (d, *J* = 14.5 Hz, 1H), 3.00 (s, 3H), 2.41 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.1, 136.4, 134.7, 130.0, 128.8, 128.3, 127.1, 126.6, 125.6, 111.0, 32.3, 21.7. **IR** (neat): 3071, 3034, 2967, 2926, 1640, 1621, 1491, 1450, 1382, 1349, 1267, 1185, 1152, 1088, 1040, 973, 939, 809, 753, 693, 650 cm^{-1}. **HRMS** (ESI) m/z calculated for $C_{16}H_{19}NO_2S$ ($[M+H]^+$) 288.1053, found 288.1055.

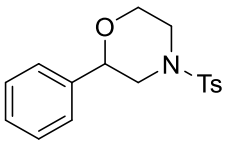


_N_,4-dimethyl-_N_-phenethylbenzenesulfonamide (18)



A round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-iodo-2-phenylethyl)-*N*,4-dimethylbenzene-sulfonamide (**15a**) (124.6 mg, 0.3 mmol, 1.0 equiv), Bu_3SnH (242.6 µL, 262.0 mg, 0.9 mmol, 3.0 equiv), AIBN (4.9 mg, 0.03 mmol, 10 mol%) and dissolved in benzene (3.0 mL, 0.1 M). The resulting reaction mixture was stirred for 12 h at reflux temperature. The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with sat. aqueous NH_4Cl and extracted three times with EtOAc. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel with 10% KF (hexanes / EtOAc 5:1) to yield 76.2 mg (263.3 µmol, 88%) of the title compound as a colorless oil. Spectral data are in accordance with those reported in literature.[63] **R_f** (hexanes / EtOAc 5:1 on silica) = 0.35, Staining: UV. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.21 (m, 5H), 7.18 (d, *J* = 7.0 Hz, 2H), 3.29 – 3.20 (m, 2H), 2.89 – 2.80 (m, 2H), 2.74 (s, 3H), 2.41 (s, 3H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 143.4, 138.4, 134.9, 129.7, 128.9, 128.7, 127.5, 126.6, 51.9, 35.3, 34.9, 21.6.

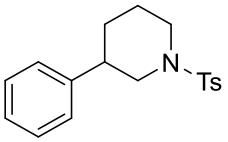
2-phenyl-4-tosylmorpholine (23)



A round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-*N*-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (**15bl**) (167.9 mg, 0.3 mmol, 1.0 equiv) and

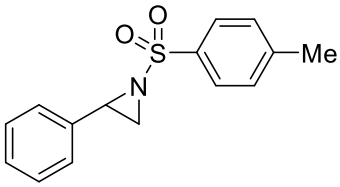
dissolved in THF (0.64 mL). A solution of TBAF in THF (1.0 M, 0.36 mL, 0.36 mmol, 1.2 equiv) was added dropwise and the resulting reaction mixture was stirred for 1 h at room temperature (25 °C). The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water and extracted three times with DCM. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 3:1) to yield 63.7 mg (200.7 µmol, 67%) of the title compound as a colorless oil. Spectral data are in agreement with those reported in literature.[64] $\mathbf{R_f}$ (hexanes / EtOAc 3:1 on silica) = 0.48, Staining: UV, $KMnO_4$. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.27 (m, 7H), 4.60 (dd, *J* = 10.3, 2.7 Hz, 1H), 4.08 (ddd, *J* = 11.6, 3.4, 1.5 Hz, 1H), 3.85 (td, *J* = 11.6, 2.7 Hz, 1H), 3.77 (dt, *J* = 11.5, 2.3 Hz, 1H), 3.63 (ddt, *J* = 11.5, 3.0, 1.6 Hz, 1H), 2.50 (td, *J* = 11.5, 3.5 Hz, 1H), 2.43 (s, 3H), 2.24 (dd, *J* = 11.5, 10.3 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 144.1, 138.8, 132.2, 129.9, 128.6, 128.4, 128.0, 126.1, 66.3, 52.1, 45.5, 21.7.

3-phenyl-1-tosylpiperidine (25)



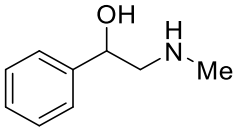
Based on a literature procedure,[65] a flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with *N*-(3-bromopropyl)-*N*-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (**15bi**) (156.7 mg, 0.3 mmol, 1.0 equiv), zinc powder (58.8 mg, 0.9 mmol, 3.0 equiv), NiI_2 (9.4 mg, 0.03 mmol, 10 mol%), 2,2'-bipyridine (4.7 mg, 0.03 mmol, 10 mol%) and dissolved in DMA (2.0 mL, 0.15 M). The reaction mixture was subsequently degassed by three consecutive freeze-pump-thaw cycles and stirred under N_2 atmosphere for 16 h at room temperature (25 °C). The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with water and extracted three times with EtOAc. The combined organic layers were washed with water, brine, dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 4:1) to yield 60.7 mg (192.4 µmol, 64%) of the title compound as a colorless oil. Spectral data are in accordance with those reported in literature.[66] $\mathbf{R_f}$ (hexanes / EtOAc 4:1 on silica) = 0.48, Staining: UV, Seebach`s Magic Stain. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.23 (m, 5H), 7.20 – 7.13 (m, 2H), 3.94 – 3.77 (m, 2H), 2.88 (tt, *J* = 11.6, 3.8 Hz, 1H), 2.43 (s, 3H), 2.33 – 2.13 (m, 2H), 2.02 – 1.89 (m, 1H), 1.89 – 1.72 (m, 2H), 1.48 – 1.34 (m, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.4, 142.6, 129.6, 128.6, 127.7, 127.2, 126.9, 125.3, 52.7, 46.4, 30.5, 25.1, 21.6.

2-phenyl-1-tosylaziridine (26)



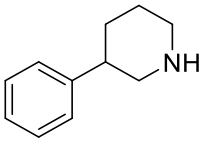
A round-bottom flask equipped with a magnetic stirring bar was charged with *N*-(2-iodo-2-phenylethyl)-4-methylbenzene-sulfonamide (**15bc**) (120.4 mg, 0.3 mmol, 1.0 equiv), triethylamine (125.5 µL, 91.1 mg, 0.9 mmol, 3.0 equiv) and DCM (2.0 mL, 0.15 M). The resulting reaction mixture was stirred at room temperature (25 °C) for 3 h. The reaction was monitored by TLC. Afterwards, the reaction was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes / EtOAc 5:1) to yield 76.4 mg (279.5 µmol, 93%) of the title compound as a white solid. Spectral data are in accordance with those reported in literature.[67] $\mathbf{R_f}$ (hexanes / EtOAc 5:1 on silica) = 0.35, Staining: Seebach`s Magic Stain. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.26 (m, 5H), 7.24 – 7.19 (m, 2H), 3.78 (dd, *J* = 7.2, 4.4 Hz, 1H), 2.98 (d, *J* = 7.2 Hz, 1H), 2.43 (s, 3H), 2.39 (d, *J* = 4.4 Hz, 1H). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ = 144.8, 135.2, 135.1, 129.9, 128.7, 128.4, 128.1, 126.7, 41.2, 36.1, 21.8.

2-(methylamino)-1-phenylethan-1-ol (30)



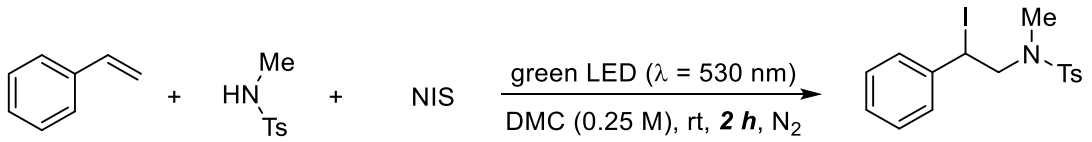
Based on a modified literature procedure,[68] a round-bottom flask equipped with a magnetic stir bar was charged with DBU (179.1 µL, 182.7 mg, 1.2 mmol, 6.0 equiv), 2-mercaptoacetic acid (83.4 µL, 110.5 mg, 1.2 mmol, 6.0 equiv) and DMF (2.0 mL). A solution of *N*-(2-hydroxy-2-phenylethyl)-*N*-methyl-4-nitrobenzenesulfonamide (**Ns-16e**) (67.3 mg, 0.2 mmol, 1.0 equiv) in DMF (1.0 mL) was added dropwise and the resulting reaction mixture was stirred for 12 h at room temperature (25 °C). The reaction was monitored by TLC. Afterwards, the reaction was directly concentrated in vacuo by addition of *p*-xylene to facilitate the removal of DMF and the residue was purified by column chromatography on silica gel ($CHCl_3$ / MeOH 9:1 to MeOH) to yield 23.1 mg (152.8 µmol, 76%) of the title compound as a white solid. Spectral data are in accordance with those reported in literature.[69] $\mathbf{R_f}$ ($CHCl_3$ / MeOH 9:1 on silica) = 0.13, Staining: ninhydrin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.42 – 7.13 (m, 5H), 4.74 (dd, *J* = 8.1, 4.8 Hz, 1H), 3.81 (bs, 2H), 2.73 – 2.54 (m, 2H), 2.30 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 143.4, 128.3, 127.4, 125.8, 71.6, 59.3, 35.8.

3-phenylpiperidine (31)



Based on a literature procedure,[70] a round-bottom flask equipped with a magnetic stirring bar was charged with 3-phenyl-1-tosylpiperidine (**25**) (63.1 mg, 0.2 mmol, 1.0 equiv), Mg (48.6 mg, 2.0 mmol, 10.0 equiv) and MeOH (1.0 mL, 0.2 M). The resulting reaction mixture was stirred for 3 h at room temperature (25 °C). The reaction was monitored by TLC. Afterwards, the reaction mixture was quenched with HCl (1.0 M) to remove excess of Mg, then NaOH was added to adjust the pH to 12. The aqueous layer was extracted three times with DCM. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (DCM / MeOH 9:1) to yield 24.5 mg (151.9 µmol, 76%) of the title compound as a colorless oil. Spectral data are in accordance with those reported in literature.[71] $\mathbf{R_f}$ (DCM / MeOH 9:1 on silica) = 0.43, Staining: UV, ninhydrin. **^{1}H-NMR** (300 MHz, $CDCl_3$) δ = 7.36 – 7.25 (m, 2H), 7.25 – 7.15 (m, 3H), 3.24 – 3.01 (m, 2H), 2.76 – 2.47 (m, 3H), 2.09 – 1.89 (m, 2H), 1.78 (ddd, *J* = 8.6, 3.7, 2.1 Hz, 1H), 1.62 (dtdd, *J* = 11.5, 6.1, 4.1, 3.0 Hz, 2H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ = 145.0, 128.4, 127.2, 126.3, 54.2, 46.7, 44.4, 32.2, 27.2.

7.6.4 Gram-Scale Functionalization



1a	**2a**	**3a**	**15a**
1.0 equiv	1.0 equiv	1.0 equiv	***2.02 g; 4.86 mmol***
5.0 mmol	***5.0 mmol***	***5.0 mmol***	***97%***

Up-scaling to gram quantities was carried out according to general procedure ***GP-I*** (Chapter 7.6.3) in a flame-dried Schlenk tube (30.0 mL size, Figure 7) equipped with a magnetic stirring bar using styrene (**1a**) (572.9 µL, 520.8 mg, 5.0 mmol, 1.0 equiv), *N*,4-dimethylbenzenesulfonamide (**2a**) (926.2 mg, 5.0 mmol, 1.0 equiv), *N*-iodosuccinimide (**3a**) (1.12 g, 5.0 mmol, 1.0 equiv) and DMC (20.0 mL, 0.25 M) at room temperature (25 °C) for 2 h to yield 2.02 g (4.86 mmol, 97%) of *N*-(2-iodo-2-phenylethyl)-*N*,4-dimethylbenzenesulfonamide (**15a**) as a sticky orange oil after flash column chromatography on silica (hexanes / EtOAc 7:1 to 5:1).

Please note: To remove remaining traces of iodine the pure compound can be dissolved in DE and extracted one time with sat. aqueous $Na_2S_2O_3$. The organic phase was dried over anhydrous Na_2SO_4 and concentrated in vacuo.

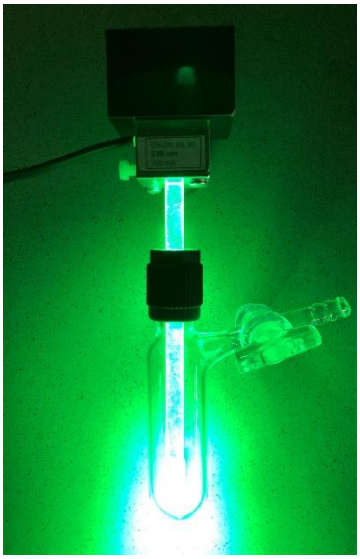


Figure 7. Irradiation setup for up-scaling in a Schlenk tube (30.0 mL size).

7.6.5 Determination of Quantum Yield

The quantum yield Φ of the visible light-mediated iodoaminiation of styrene (**1a**) with *N*,4-dimethylbenzenesulfonamide (**2a**) and NIS (**3a**) was determined using a method developed by Riedle and co-workers.[72] For irradiation, a green LED (500 mA operating current, λ_{max} = 528 nm, OSRAM LTCP7P-KXKZ) was used. The radiant power was detected with a commercial power meter (PowerMax USB – PS19Q Power Sensor from Coherent) using computer-aided read out with PowerMax software.

A flame-dried Schlenk tube was charged with *N*,4-dimethylbenzenesulfonamide (**2a**) (92.6 mg, 0.5 mmol, 1.0 equiv), NIS (**3a**) (112.5 mg, 0.5 mmol, 1.0 equiv) and dissolved in DMC (2.0 mL, 0.25 M), sealed with a screw-cap and subsequently degassed by three consecutive freeze-pump-thaw cycles. Afterwards, styrene (**1a**) (57.3µL, 52.1 mg, 0.5 mmol, 1.0 equiv) was added under a slight nitrogen overpressure. An oven-dried fluorescence cuvette equipped with a magnetic stirring bar and a septum was flushed with nitrogen. Immediately prior to the quantum yield measurement, 2.0 mL of the reaction solution was transferred to the fluorescence cuvette under nitrogen atmosphere. The whole measurement was carried out in a dark room to minimize ambient light. First of all, the radiant power of light transmitted by a fluorescence cuvette with blank solution P_{ref} was measured. Following, the fluorescence cuvette with the blank solution was exchanged by the fluorescence cuvette containing the prepared reaction mixture and the transmitted radiant power P_{sample} was determined for an irradiation time of Δt = 24 min. Finally, the reaction yield or rather the molar amount of product molecules generated $n_{product}$ was determined by ^{1}H-NMR analysis using diphenoxymethane as internal standard.

The quantum yield Φ was calculated as the following:

$$\Phi = \frac{N_{product}}{N_{ph,abs}} = \frac{n_{product} \cdot N_A \cdot h \cdot c}{P_{abs} \cdot \Delta t \cdot \lambda} = \frac{n_{product} \cdot N_A \cdot h \cdot c}{(P_{ref} - P_{sample}) \cdot \Delta t \cdot \lambda \cdot f}$$

Here, Φ is the quantum yield, $N_{product}$ is the number of created product molecules, $N_{ph,abs}$ is the number of absorbed photons, $n_{product}$ is the molar amount of product molecules generated in [mol], N_A is Avogadro's constant in [mol^{-1}], h is Planck's constant in [Js], c is the speed of light in [m/s], P_{abs} is the radiant power absorbed in [W], Δt is the irradiation time in [s], λ is the wavelength of the irradiation source in [m], P_{ref} is the radiant power transmitted by a

fluorescence cuvette with blank solution in [W], P_{sample} is the radiant power transmitted by the fluorescence cuvette containing the reaction sample in [W] and f is a correction factor depending on the reflection coefficient R of the air-glass-interface.

Neglecting second order effects, the correction factor f can be calculated from:

$$f = \frac{1 + R \cdot \frac{P_{sample}}{P_{ref}}}{1 - R}$$

The reflection coefficient R for a fused silica cuvette and an irradiation wavelength of $\lambda = 528\ \text{nm}$ is equal to $R = 0.0357$.

Having this formula in hands, the preceding data obtained from the measurement could be used to calculate the final value for the quantum yield Φ as the following:

$n_{product}$	$0.168 \cdot 10^{-3}$ mol	N_A	$6.022 \cdot 10^{23}\ \text{mol}^{-1}$
P_{sample}	$1.1 \cdot 10^{-3}$ W	h	$6.626 \cdot 10^{-34}$ Js
P_{ref}	$21.5 \cdot 10^{-3}$ W	c	$2.998 \cdot 10^{8}$ ms
Δt	1440 s	R	0.0357
λ	$528 \cdot 10^{-9}$ m		

$$f = \frac{1 + R \cdot \frac{P_{sample}}{P_{ref}}}{1 - R} = \frac{1 + 0.0357 \cdot \frac{1.1 \cdot 10^{-3}\ \text{W}}{21.5 \cdot 10^{-3}\ \text{W}}}{1 - 0.0357} = 1.039$$

$$\boldsymbol{\Phi} = \frac{n_{product} \cdot N_A \cdot h \cdot c}{(P_{ref} - P_{sample}) \cdot \Delta t \cdot \lambda \cdot f} =$$

$$= \frac{0.168 \cdot 10^{-3}\ \text{mol} \cdot 6.022 \cdot 10^{23}\ \text{mol}^{-1} \cdot 6.626 \cdot 10^{-34}\ \text{Js} \cdot 2.998 \cdot 10^{8}\ \text{ms}}{(21.5 \cdot 10^{-3}\ \text{W} - 1.1 \cdot 10^{-3}\ \text{W}) \cdot 1440\ \text{s} \cdot 528 \cdot 10^{-9}\ \text{m} \cdot 1.039}$$

$$= \mathbf{1.247} \cong \mathbf{125}\%$$

7.7 References for Experimental Part

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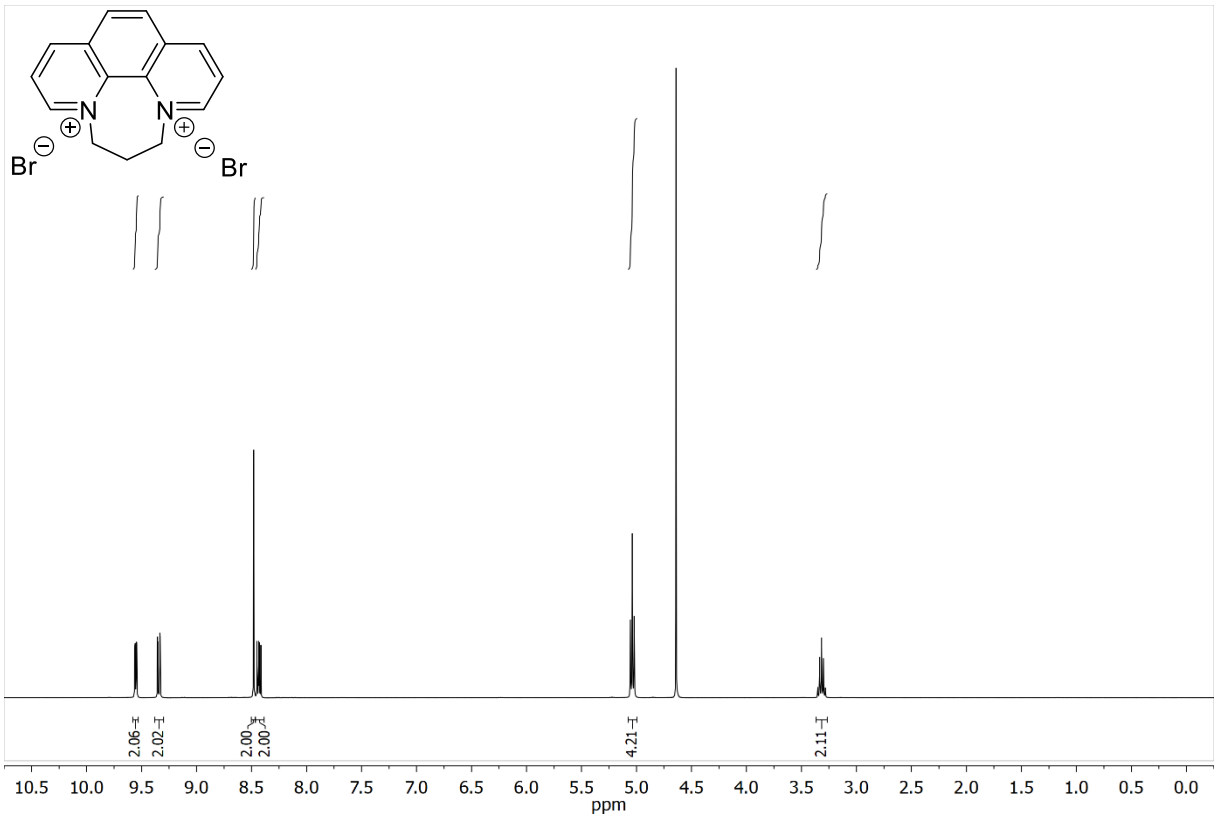
Chapter 8

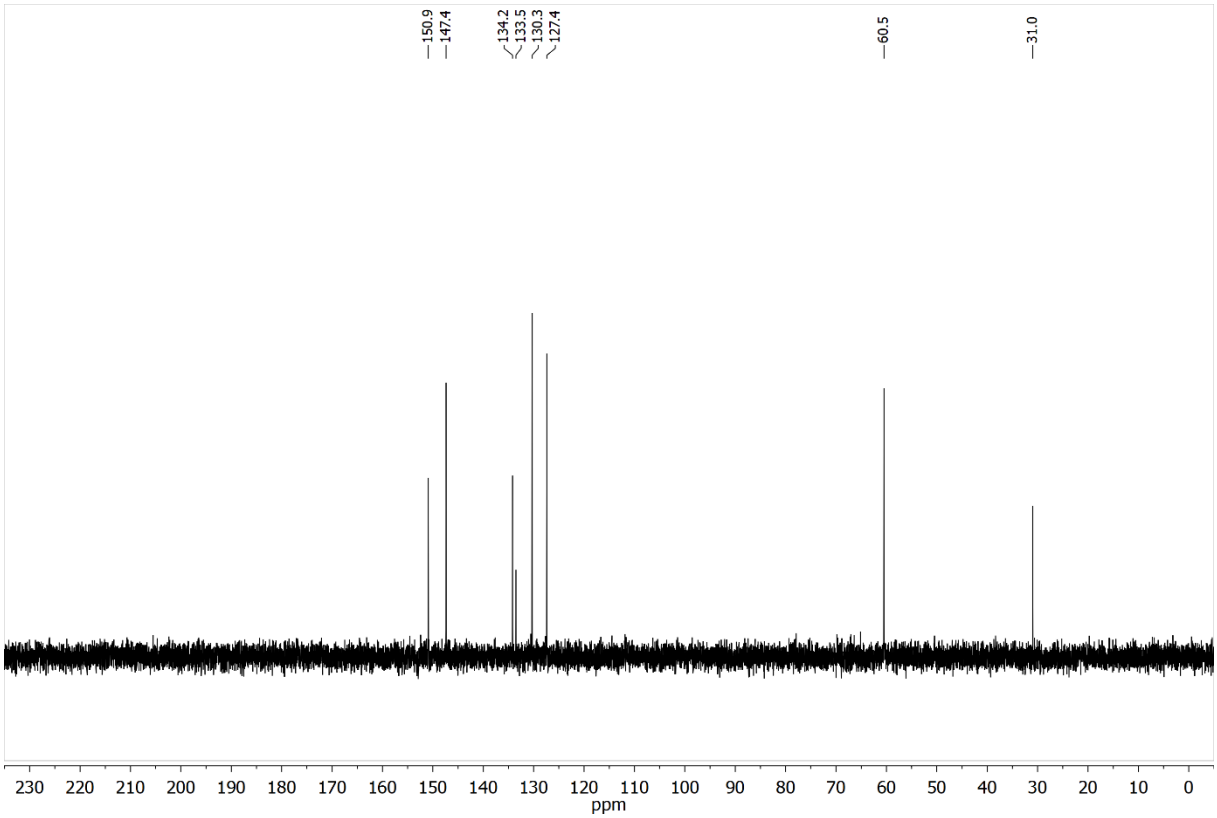
Scientific Appendix

This chapter contains copies of all NMR spectra, as well as detailed data for X-ray analysis.

8.1 NMR Spectra for Catalyst Syntheses

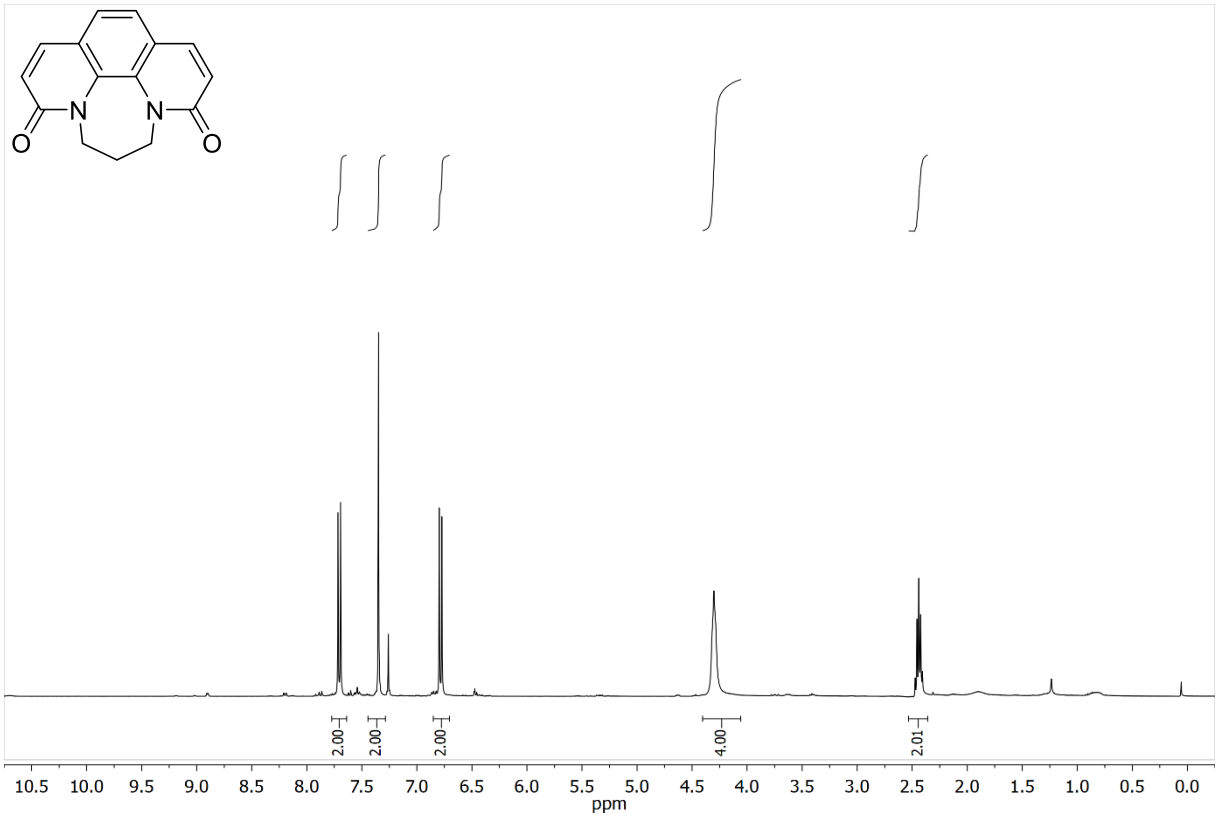
6,7-dihydro-5*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-4,8-diium bromide (2)

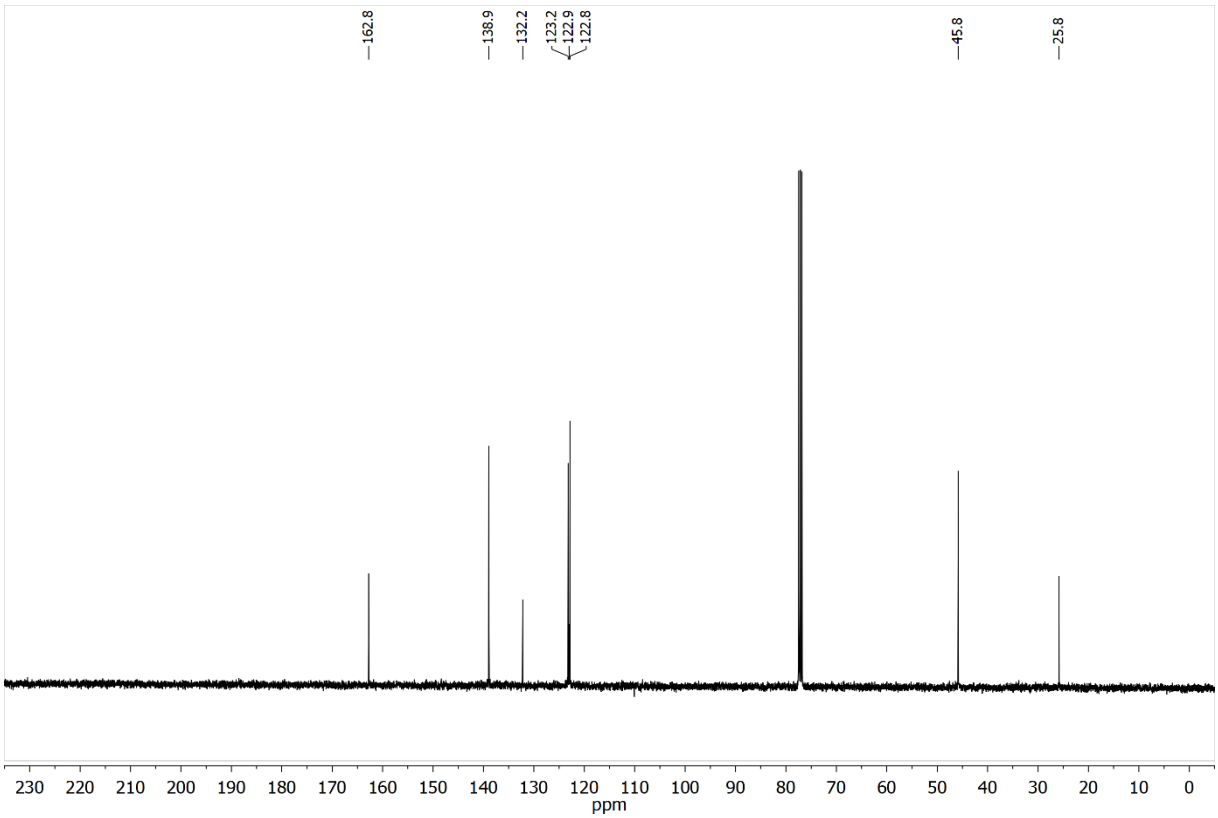




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: D_2O.

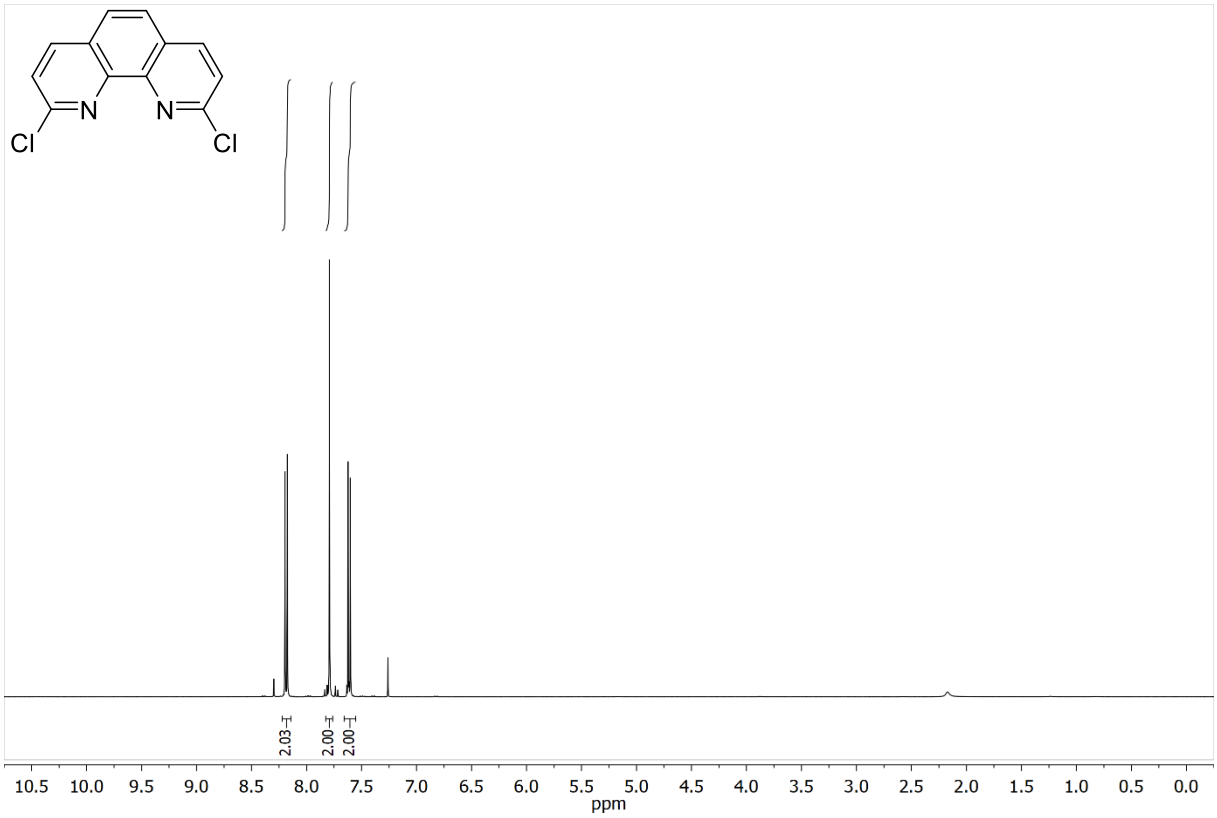
6,7-dihydro-5*H*-[1,4]diazepino[1,2,3,4-*lmn*][1,10]phenanthroline-3,9-dione (3)

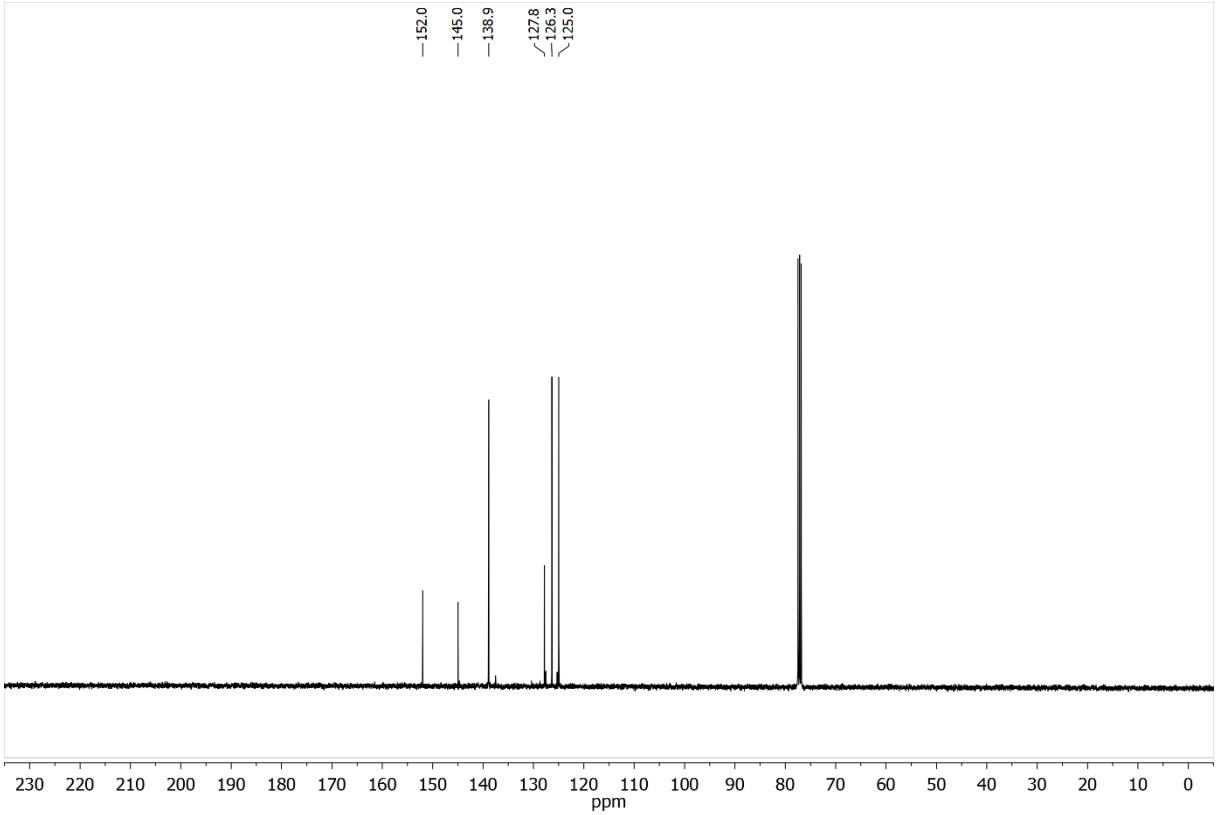




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

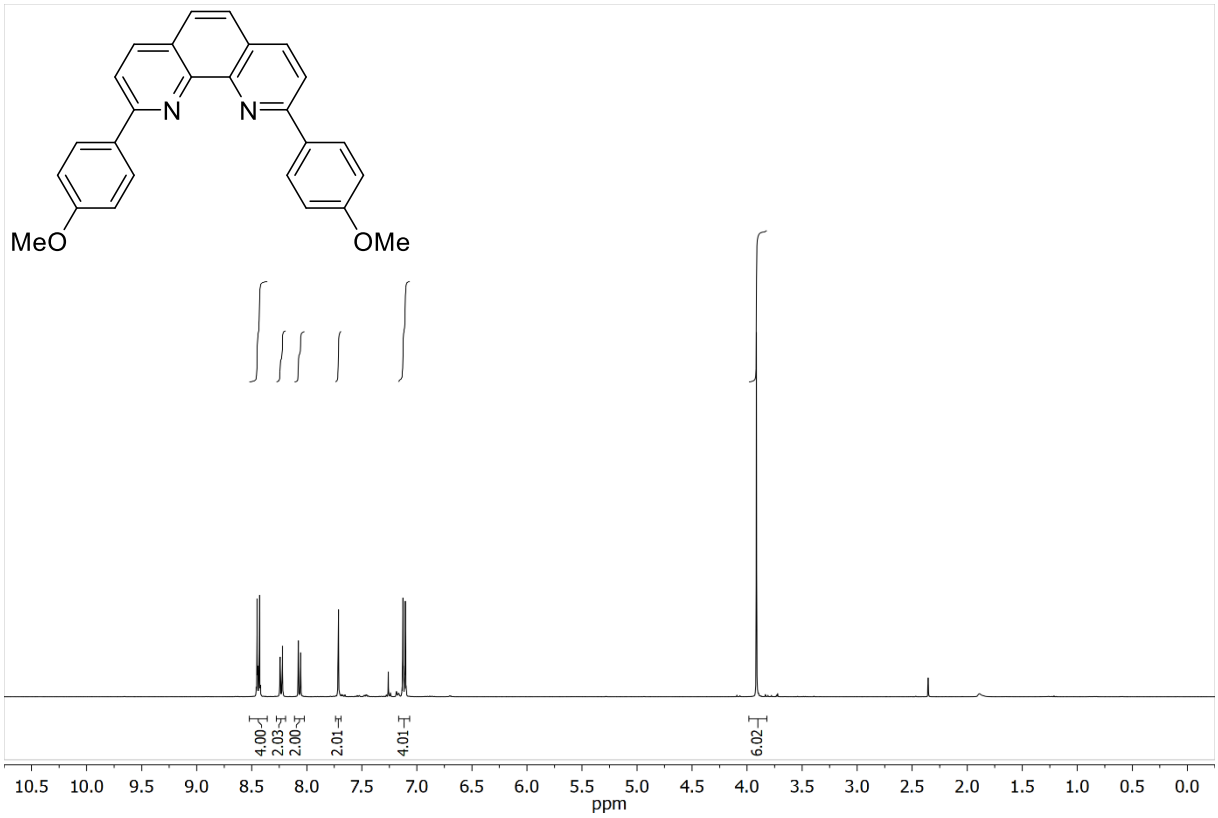
2,9-dichloro-1,10-phenanthroline (4)

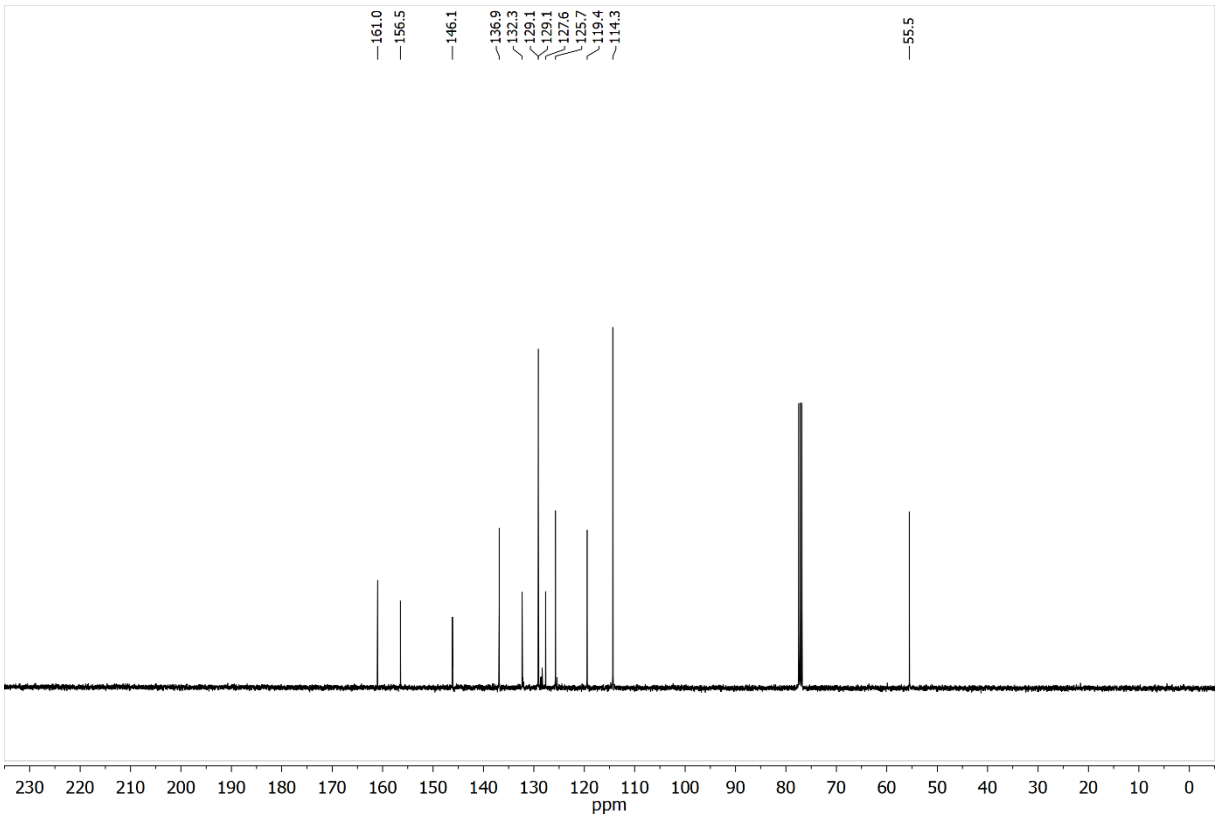




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

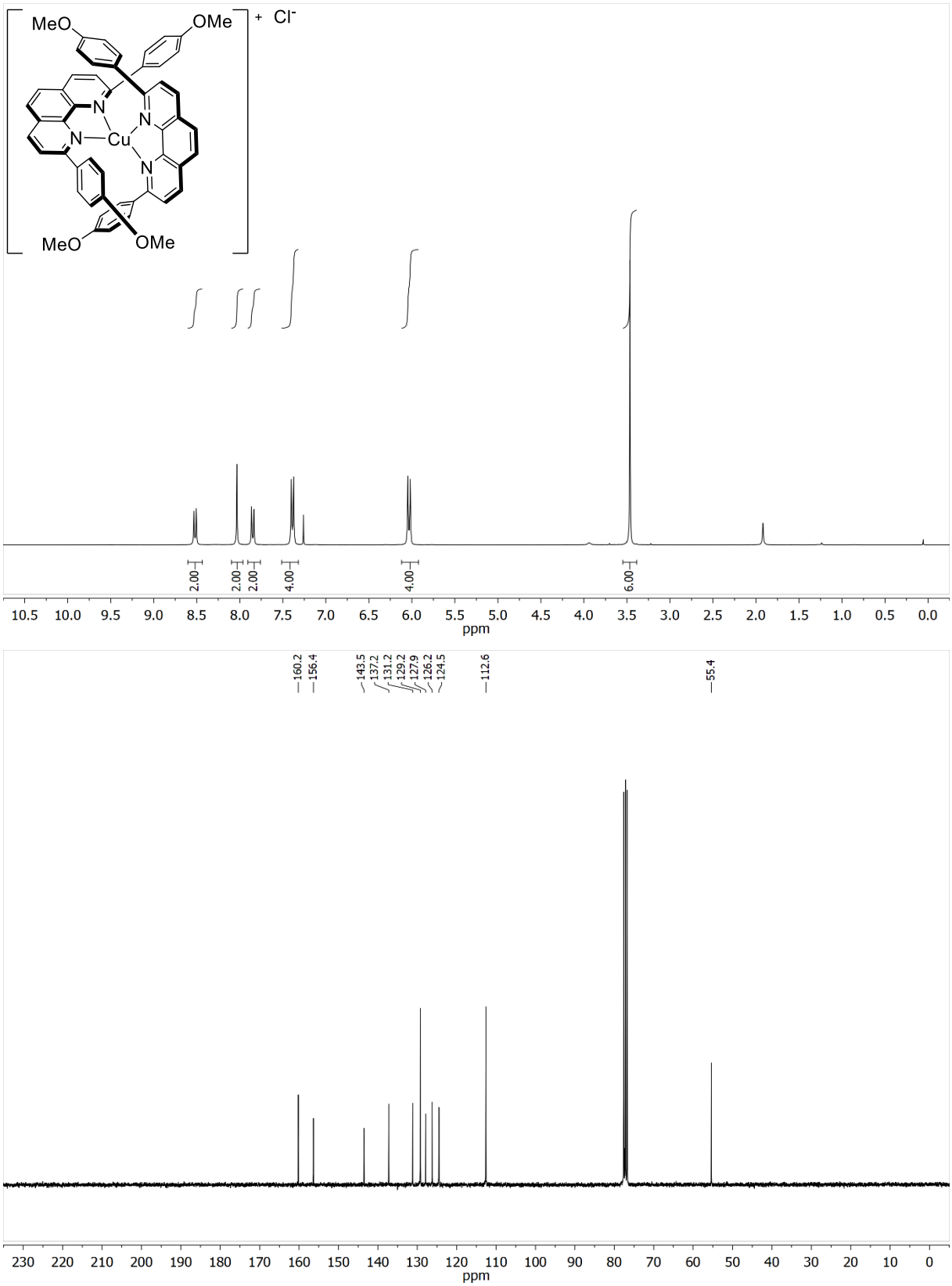
2,9-bis(4-methoxyphenyl)-1,10-phenanthroline (dap)





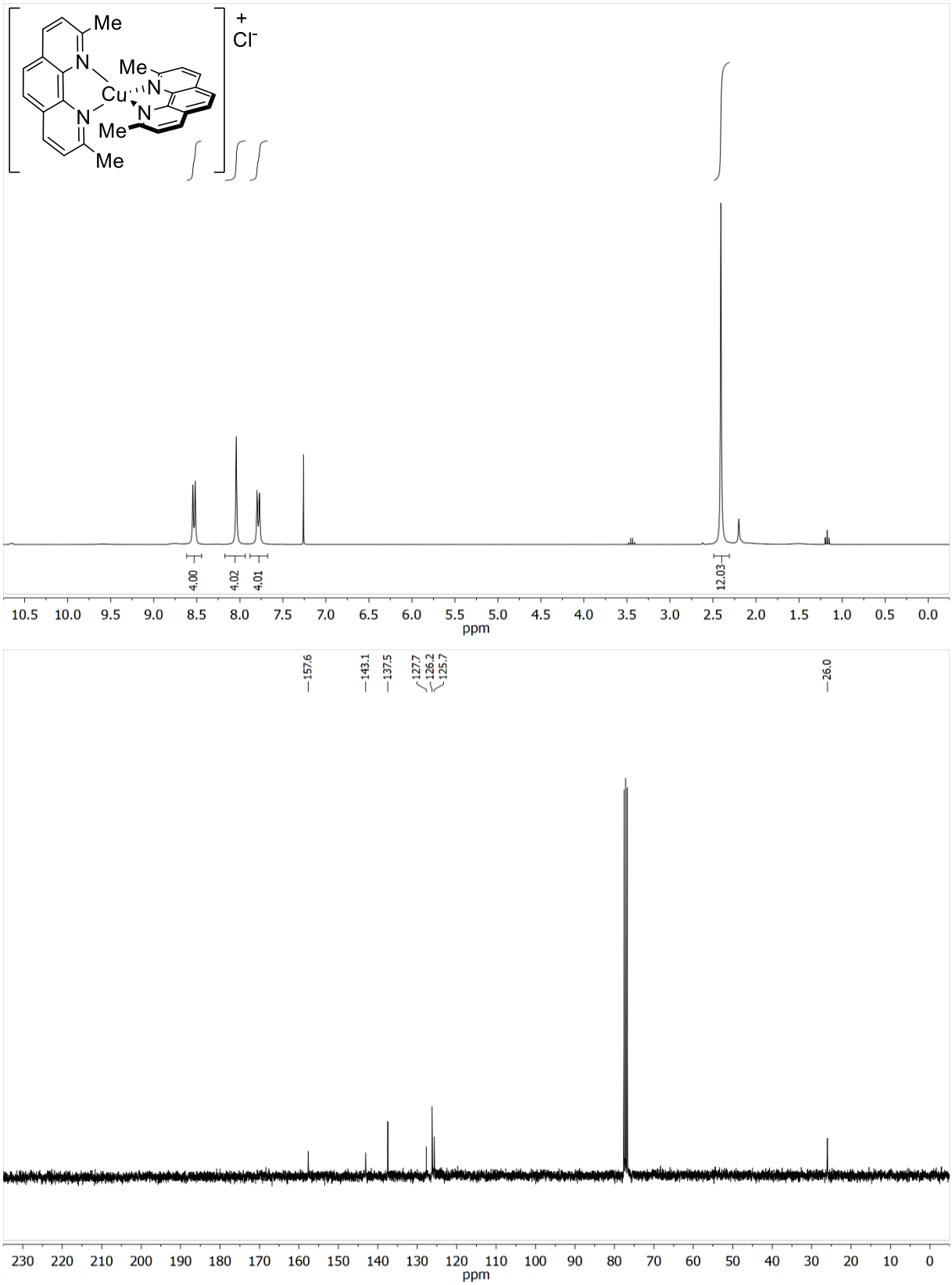
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

[Cu(dap)$_2$]Cl



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

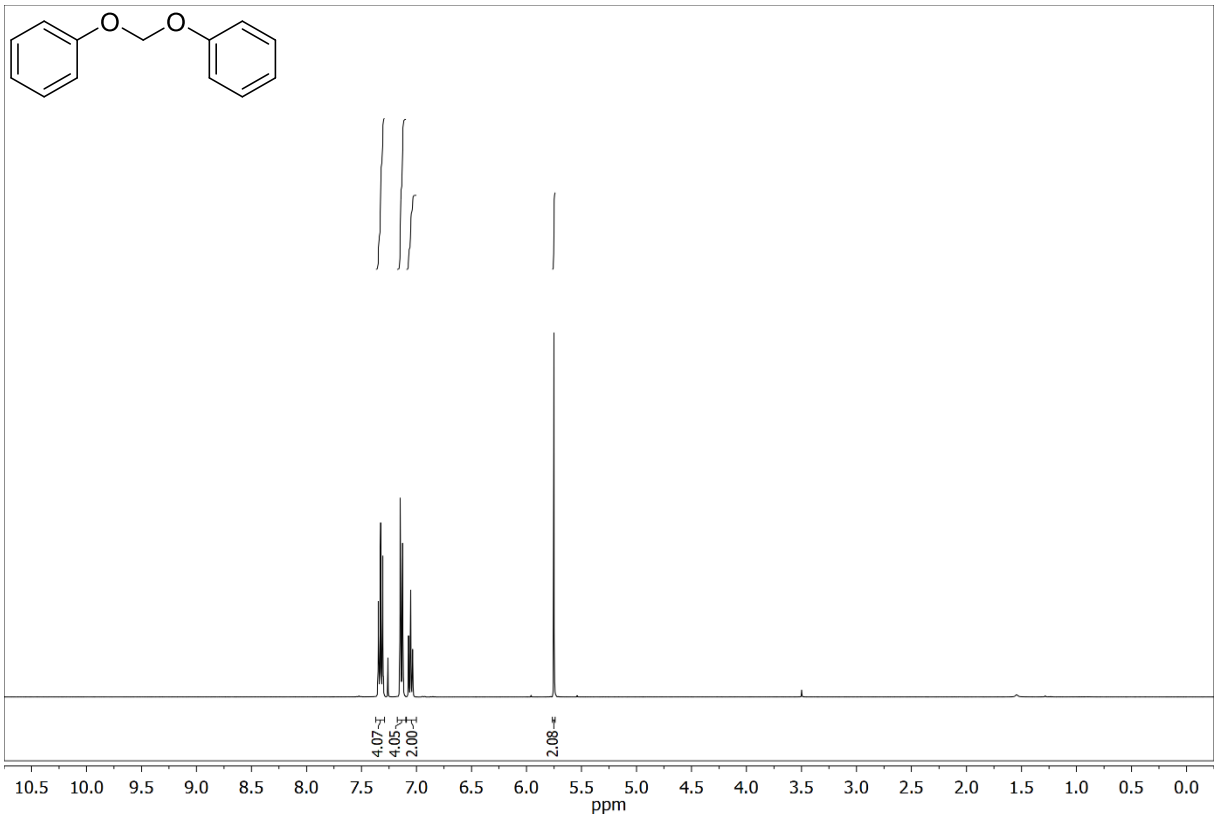
[Cu(dmp)$_2$]Cl

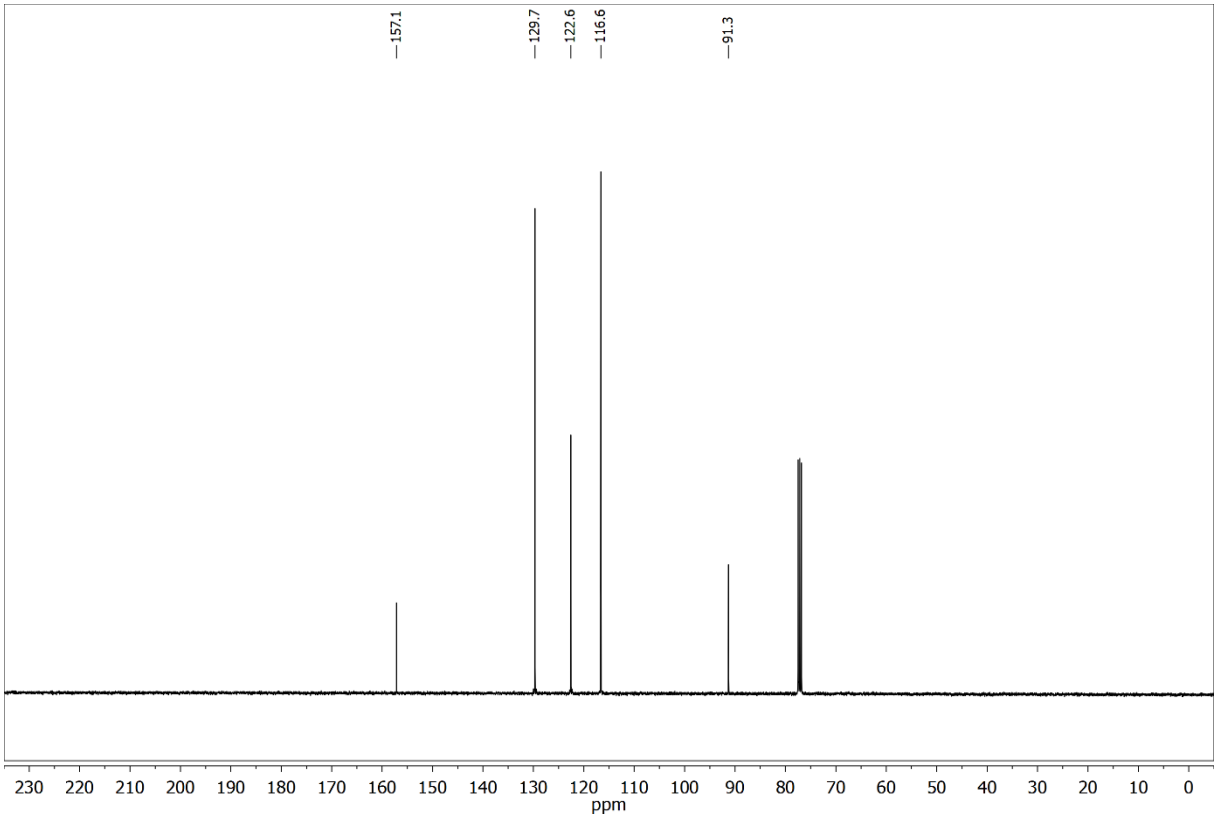


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

8.2 NMR Spectra for Literature Known Compounds

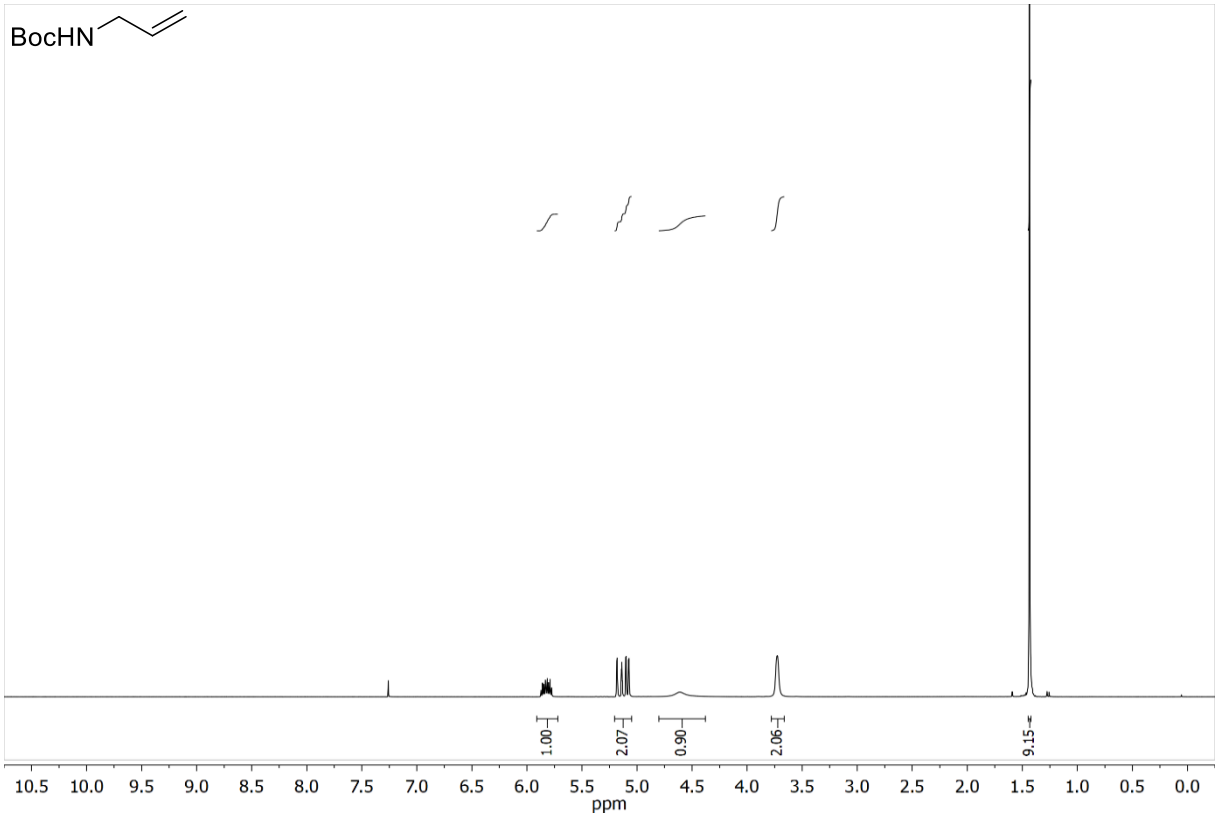
diphenoxymethane (internal NMR standard)

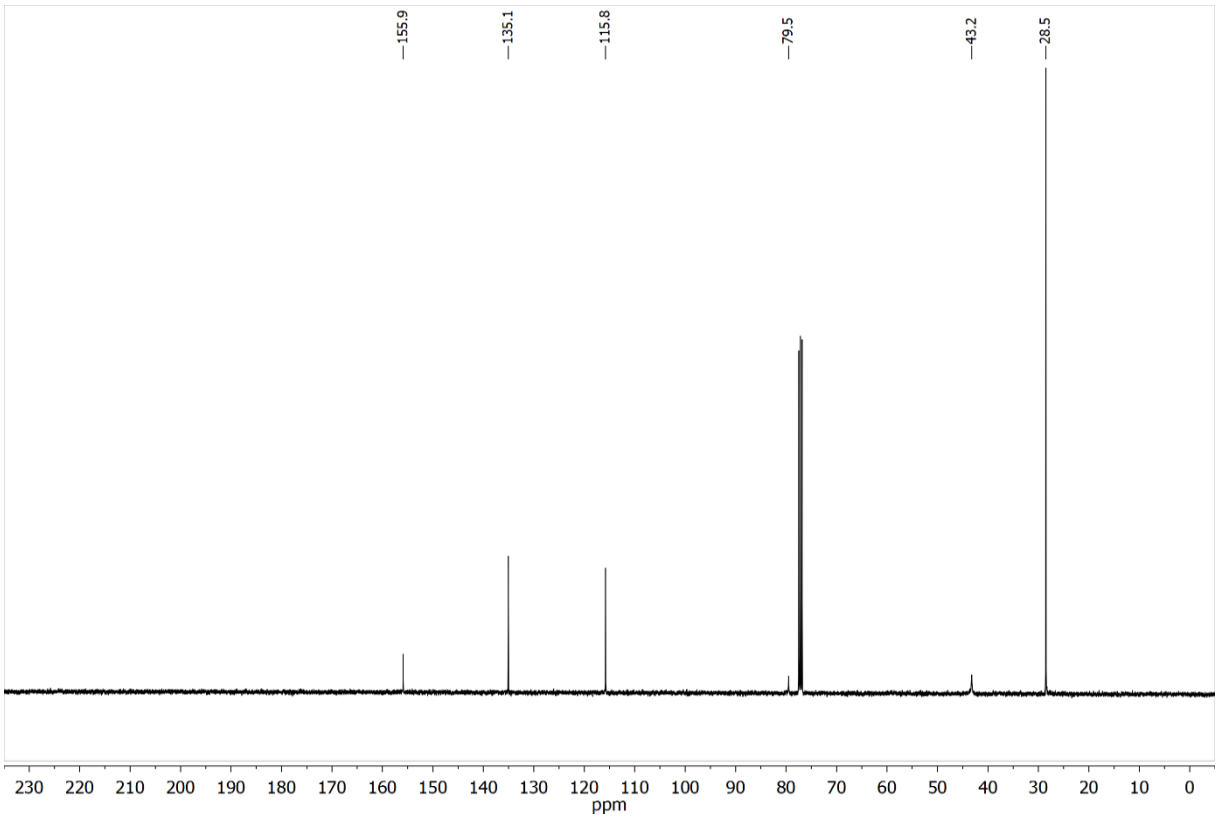




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

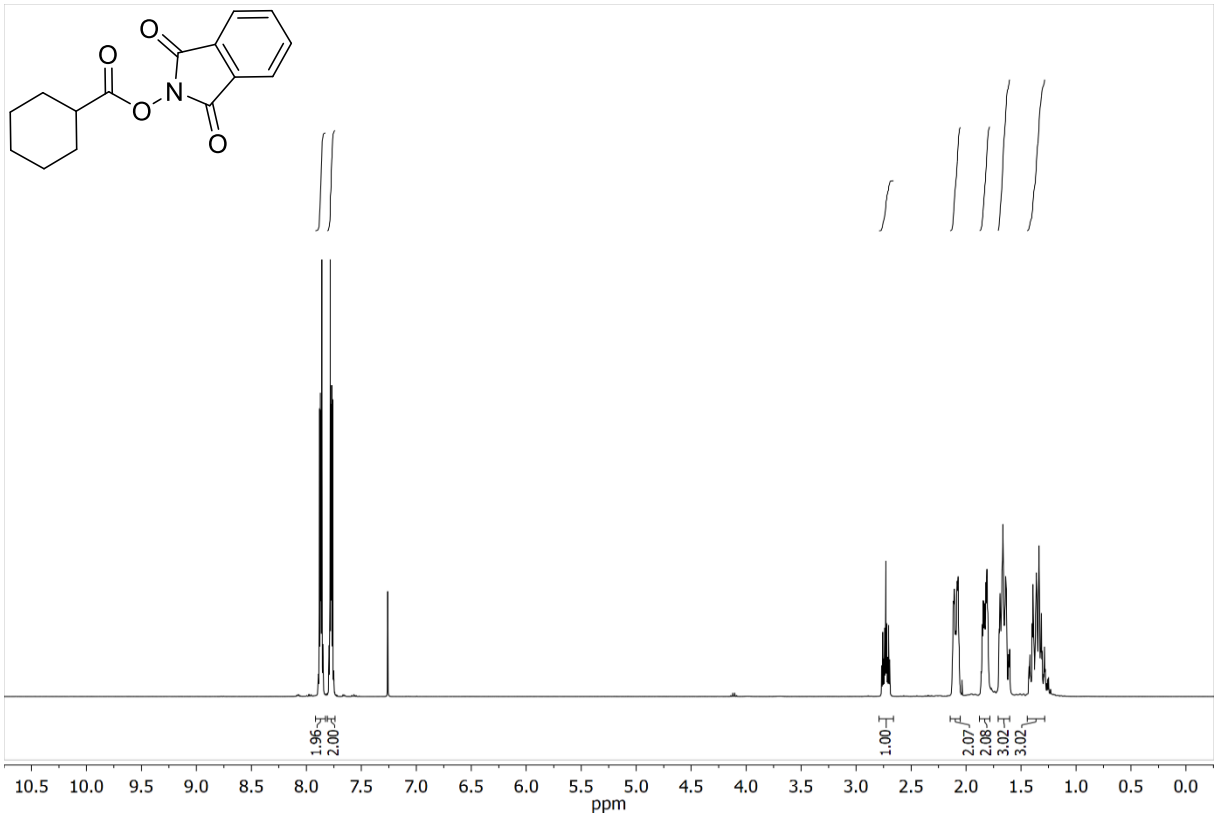
tert-butyl allylcarbamate (1bn//7o)

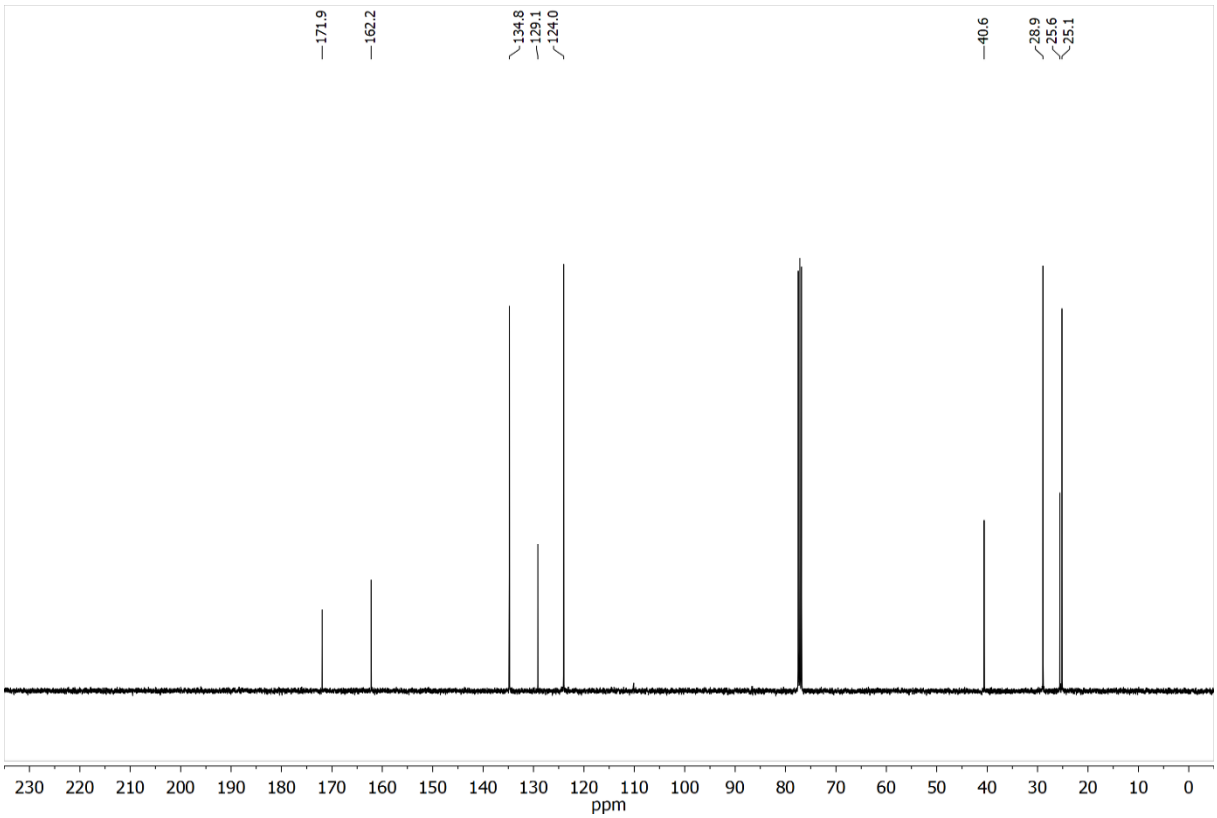




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

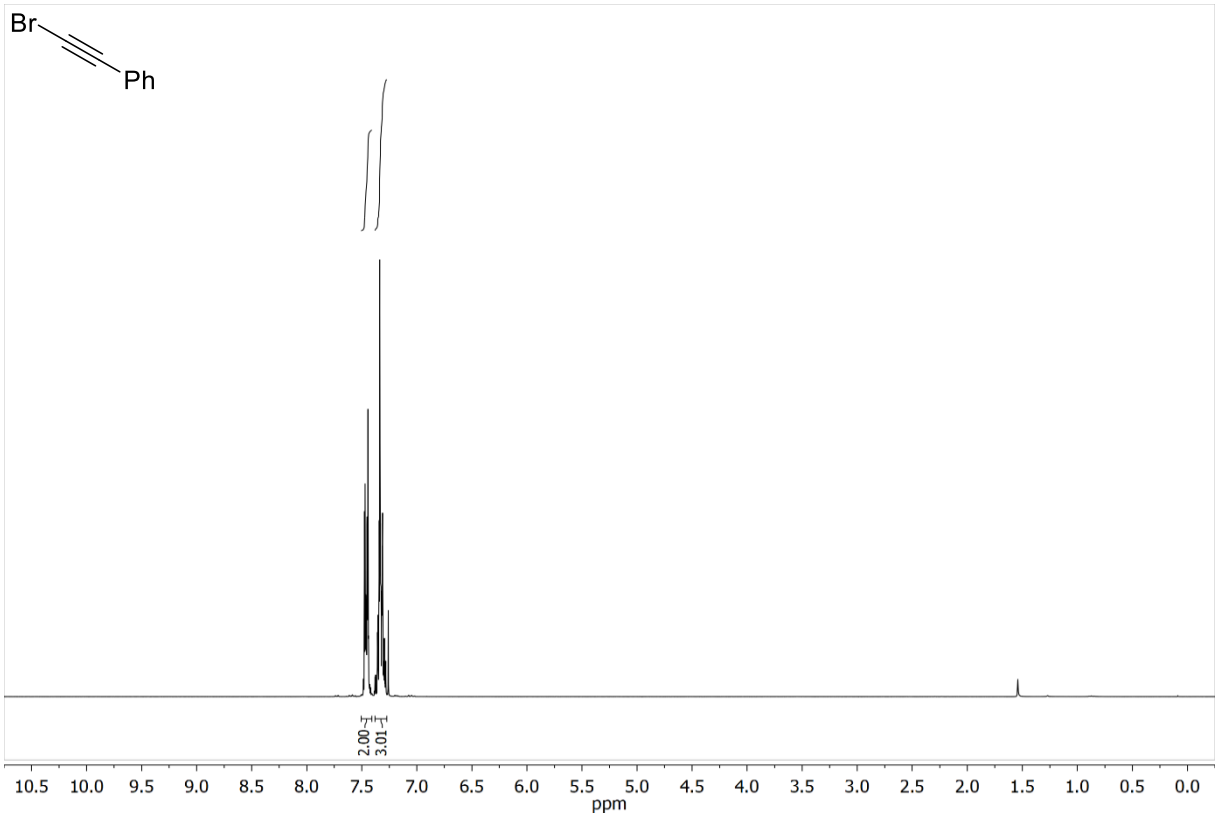
1,3-dioxoisoindolin-2-yl cyclohexanecarboxylate (20)

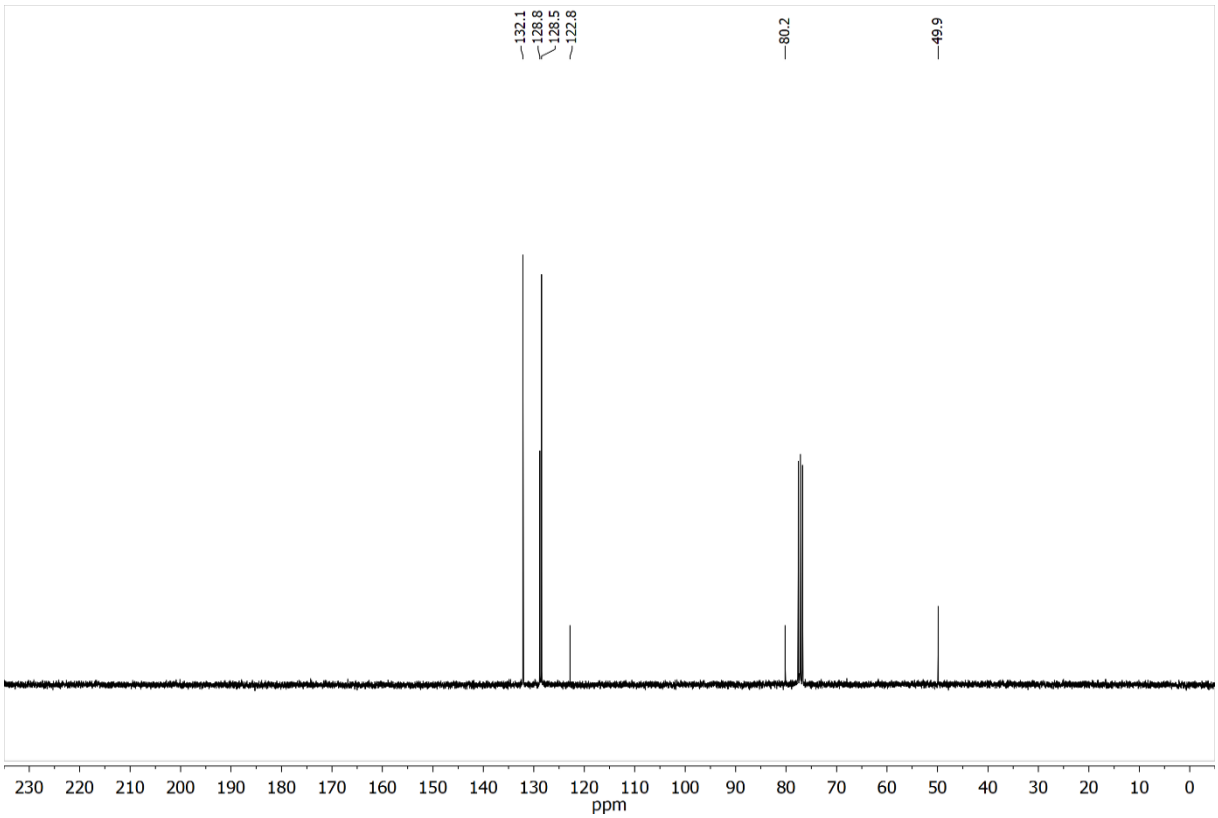




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

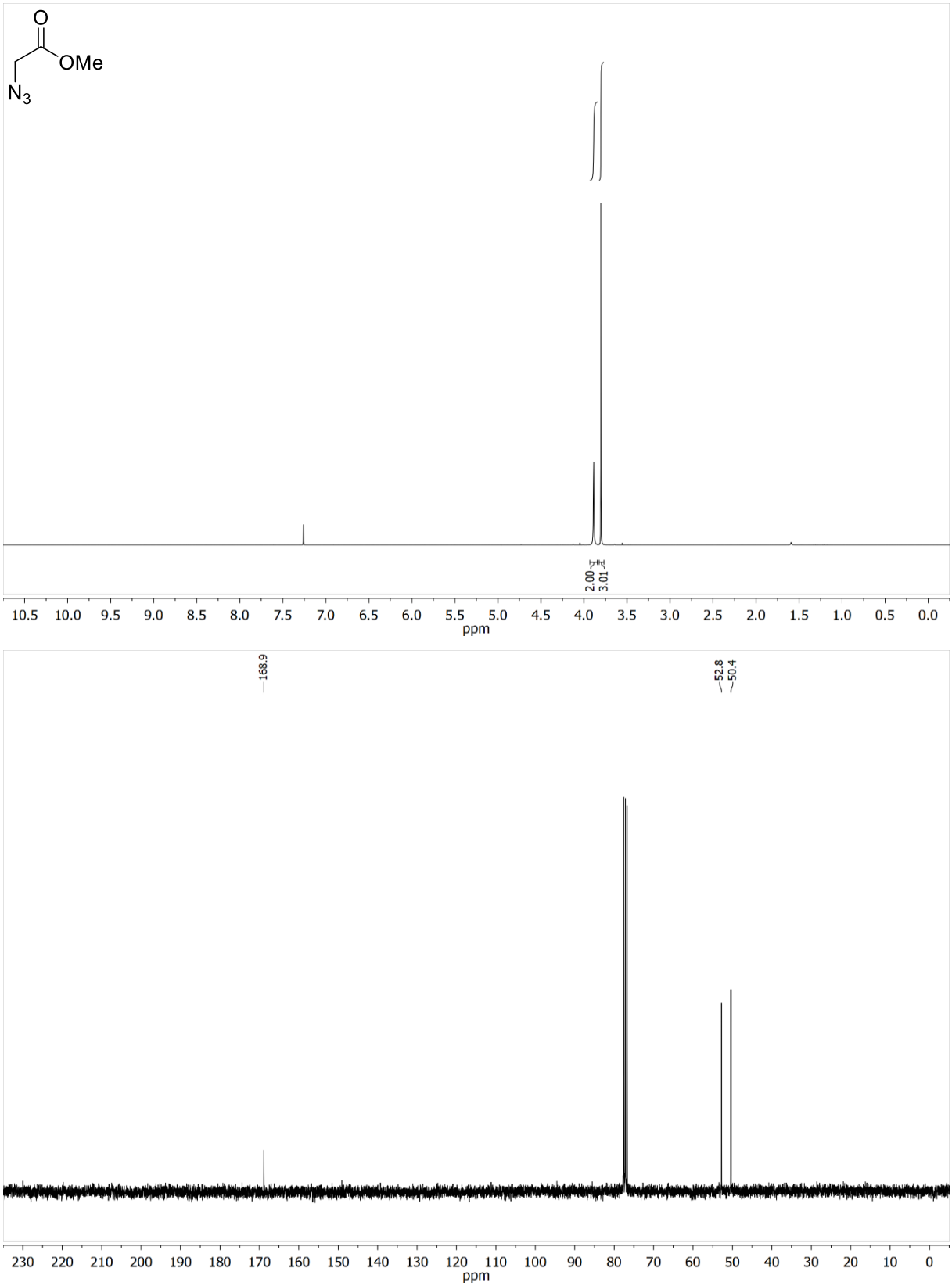
(bromoethynyl)benzene (21)





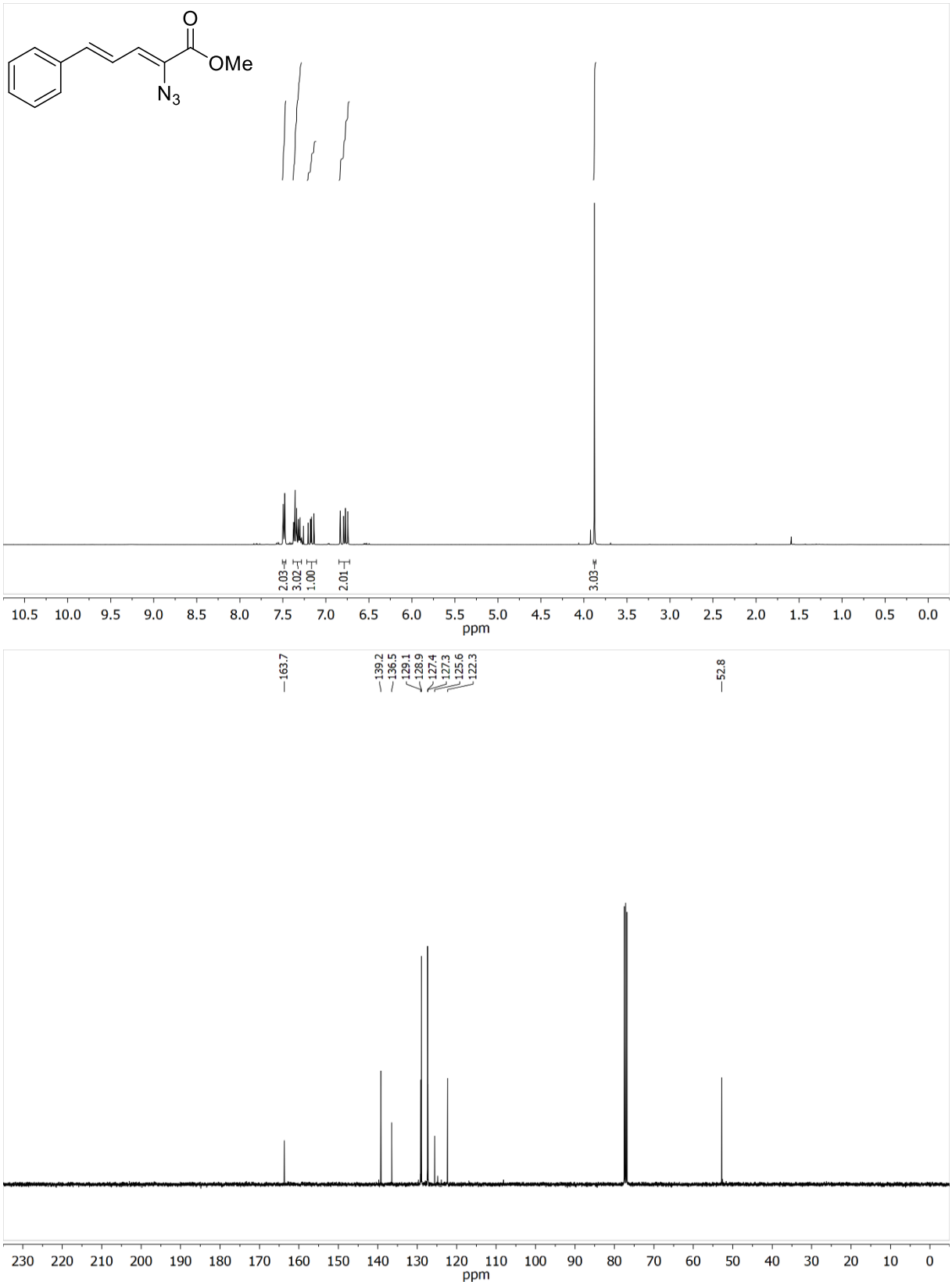
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

methyl 2-azidoacetate



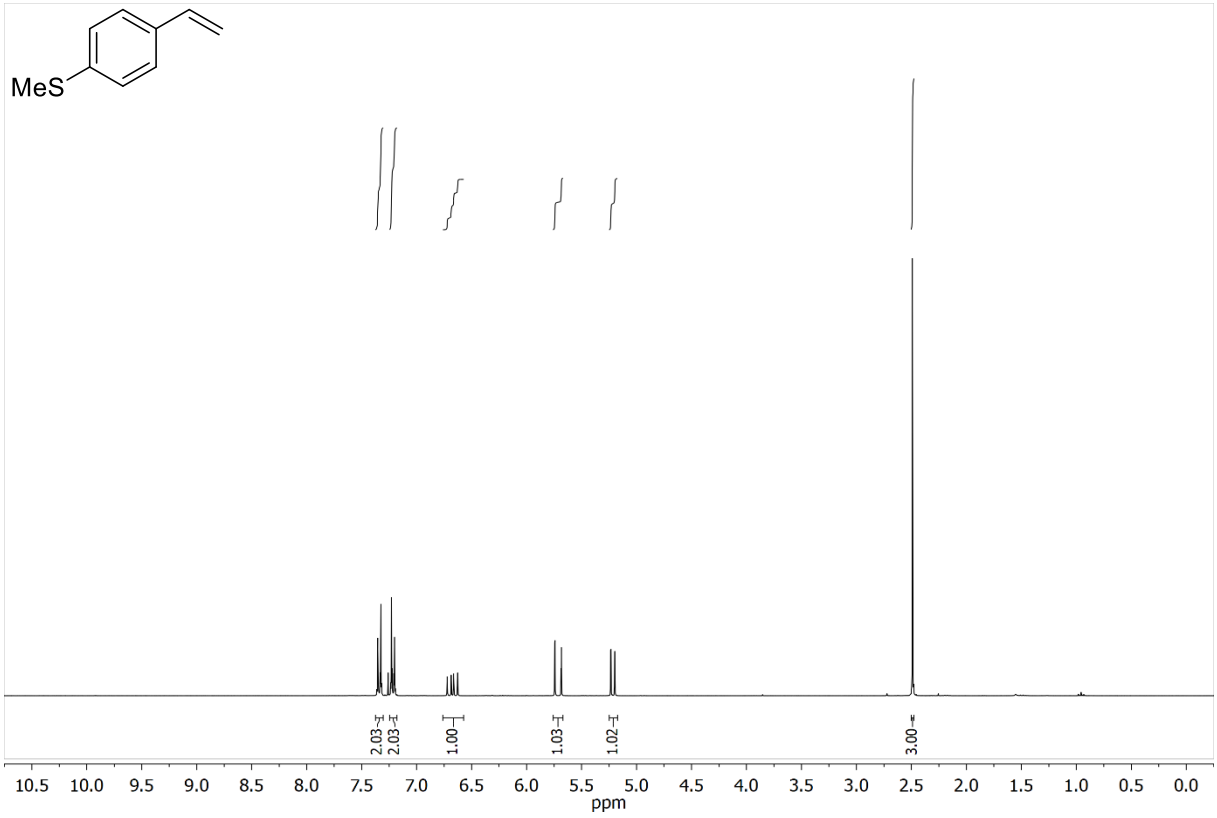
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

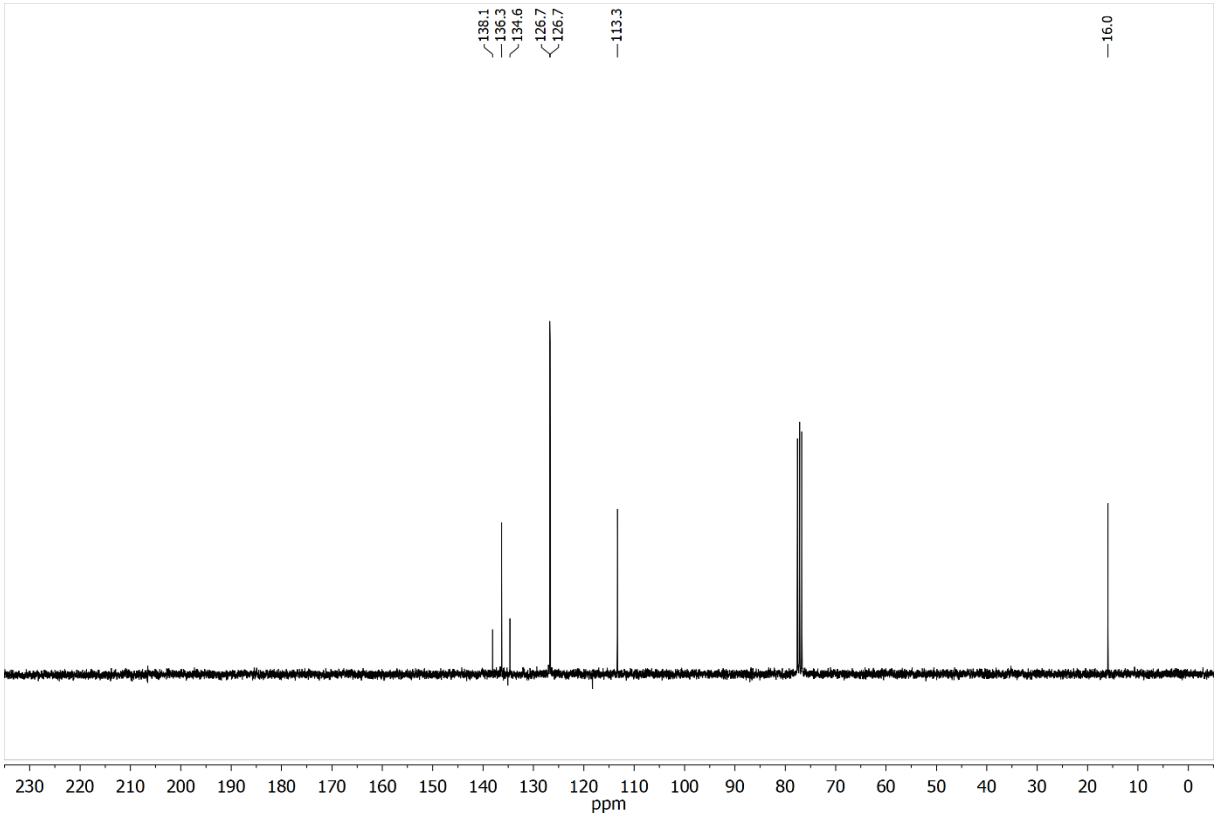
methyl (2*Z*,4*E*)-2-azido-5-phenylpenta-2,4-dienoate (33)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

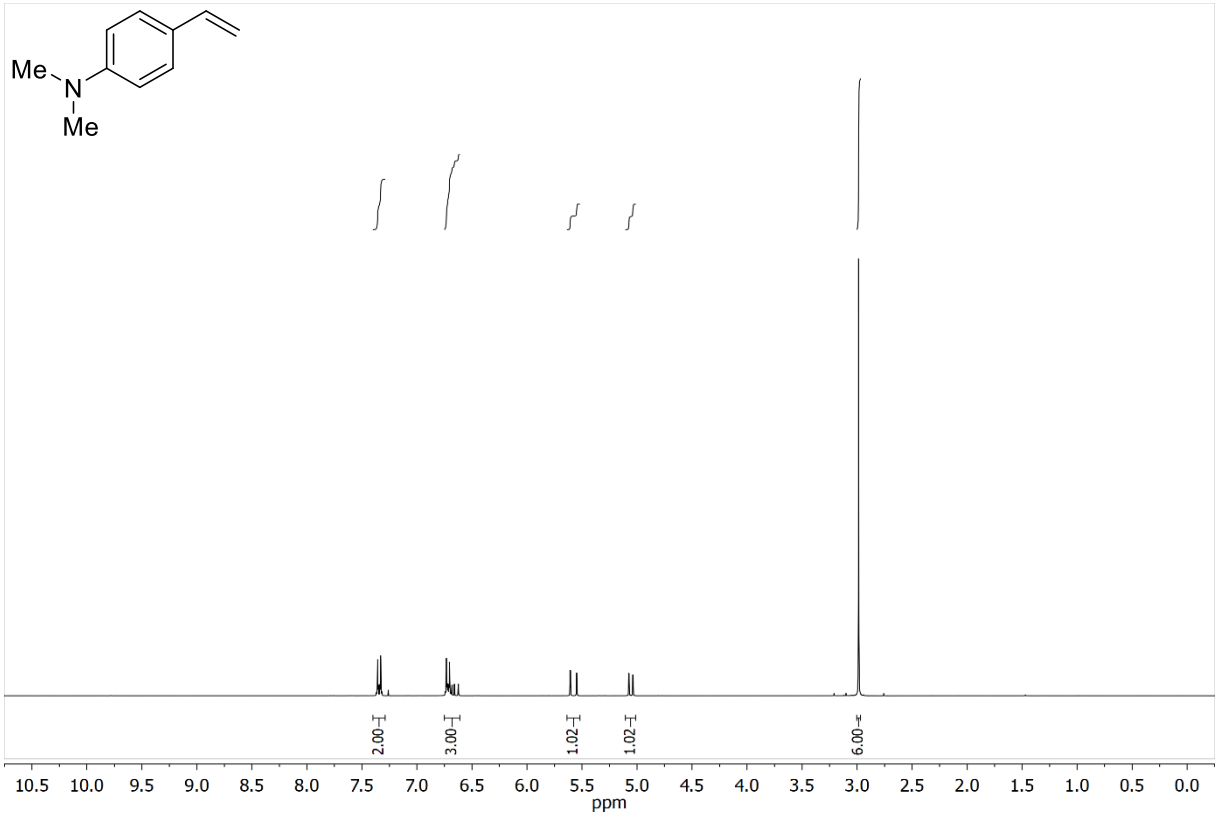
methyl(4-vinylphenyl)sulfane (1f//1t)

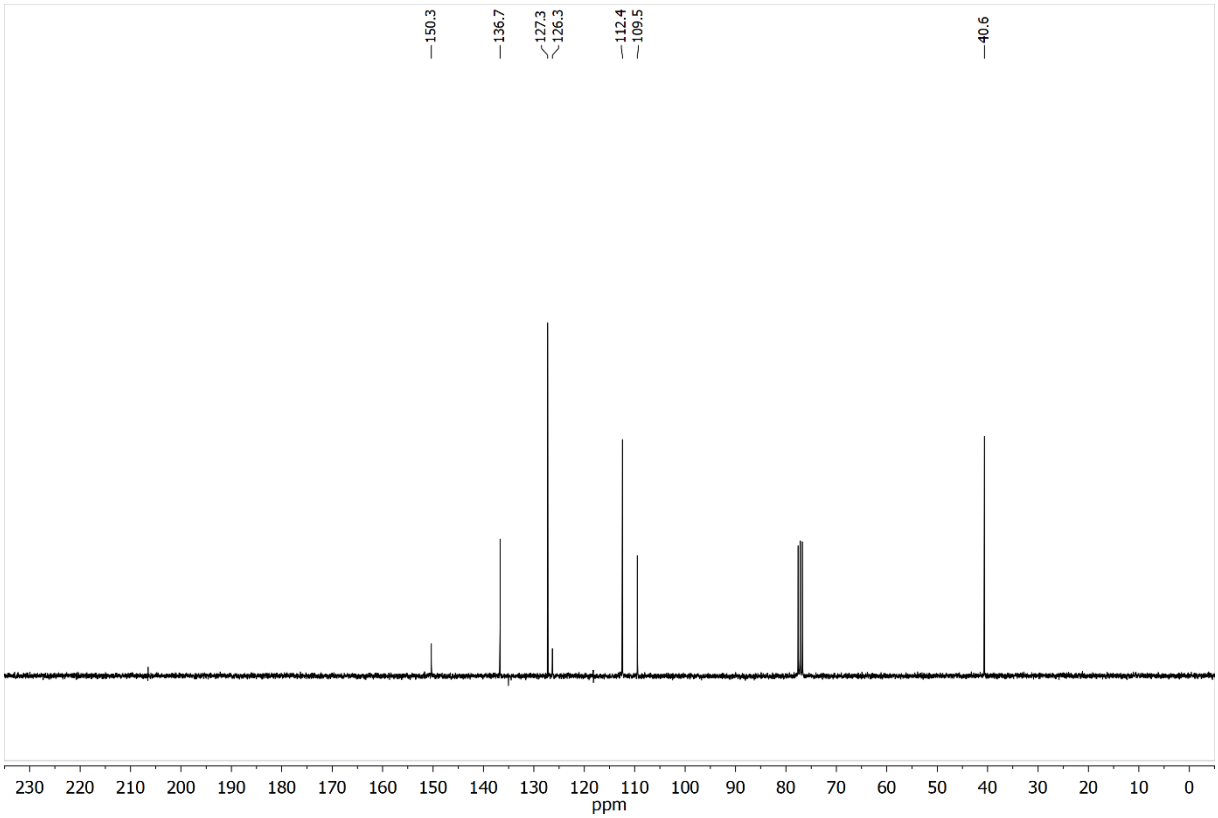




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

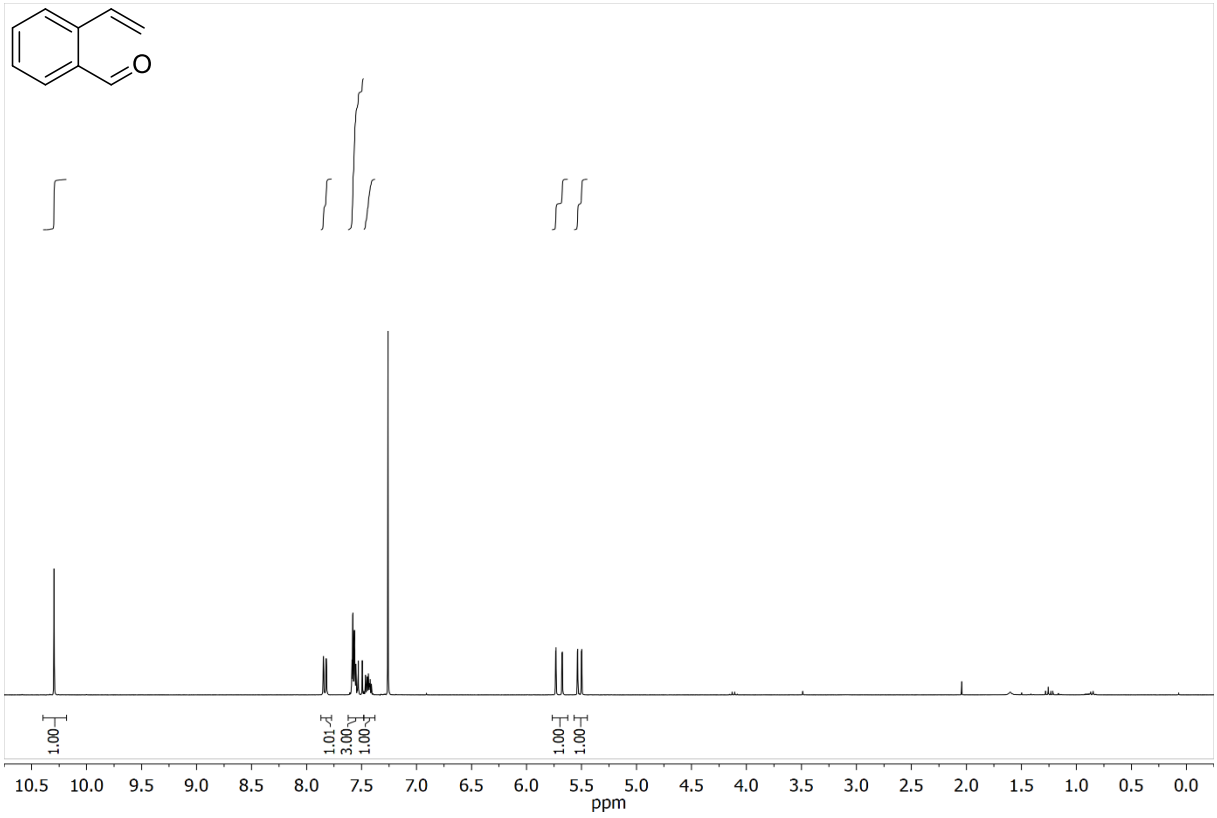
***N*,*N*-dimethyl-4-vinylaniline (1k//1s)**

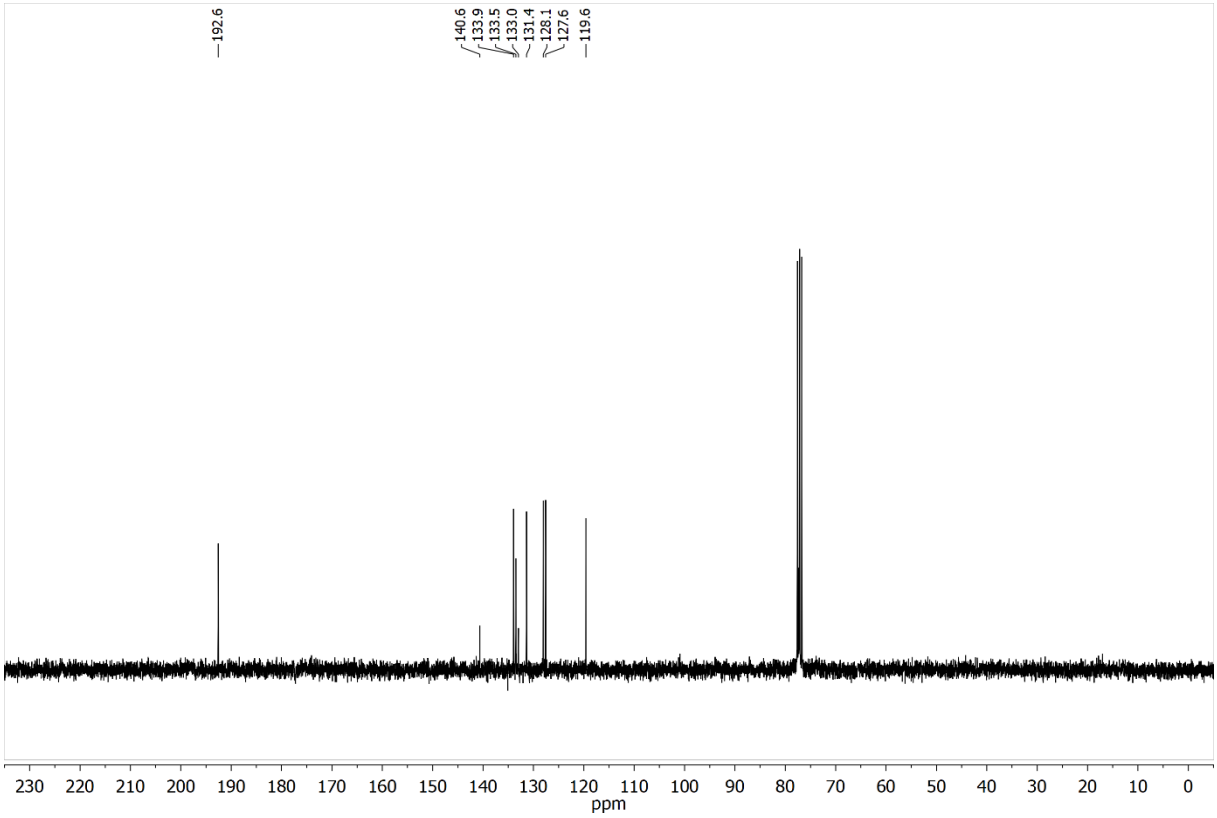




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

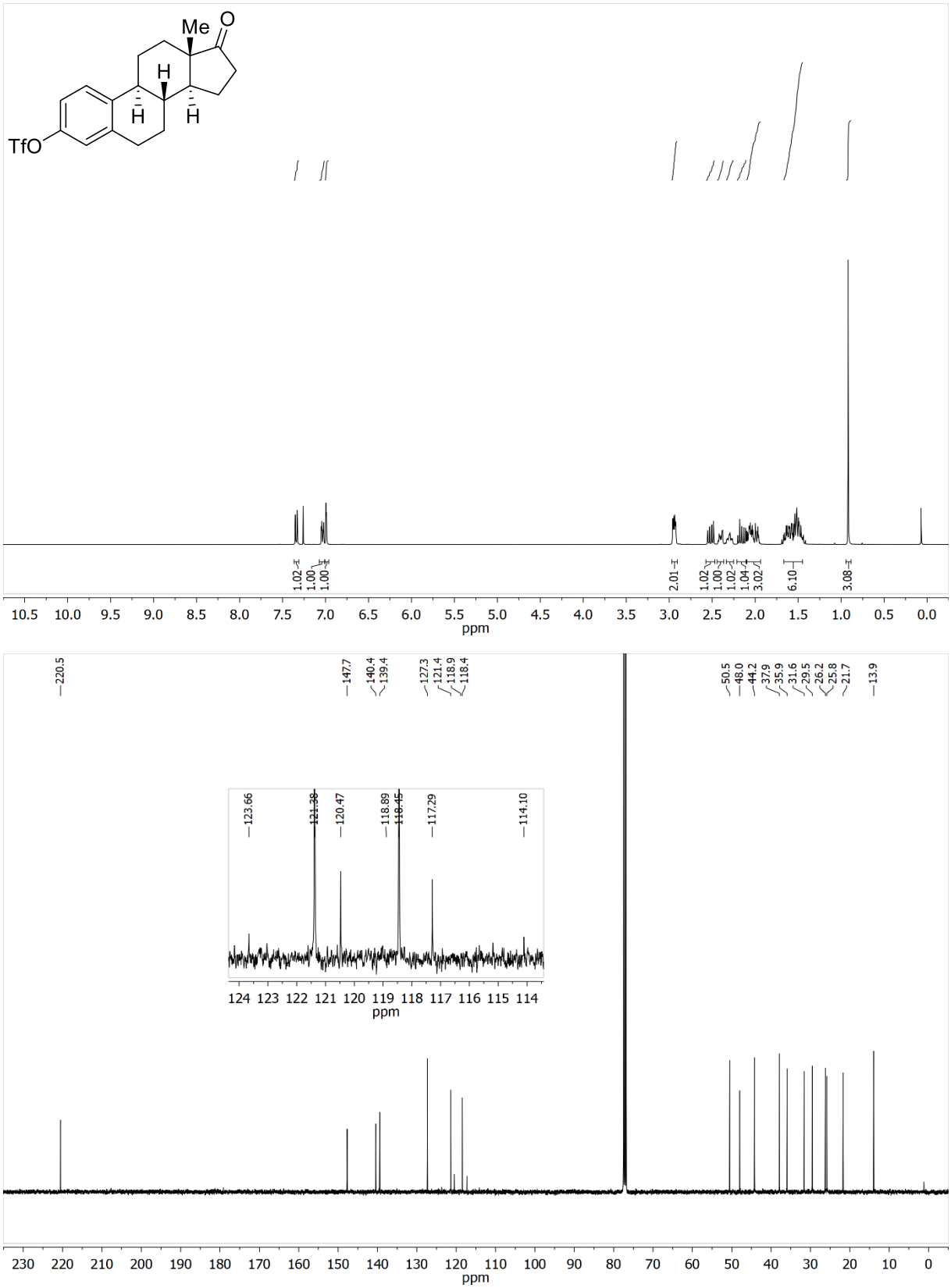
2-vinylbenzaldehyde (1u)



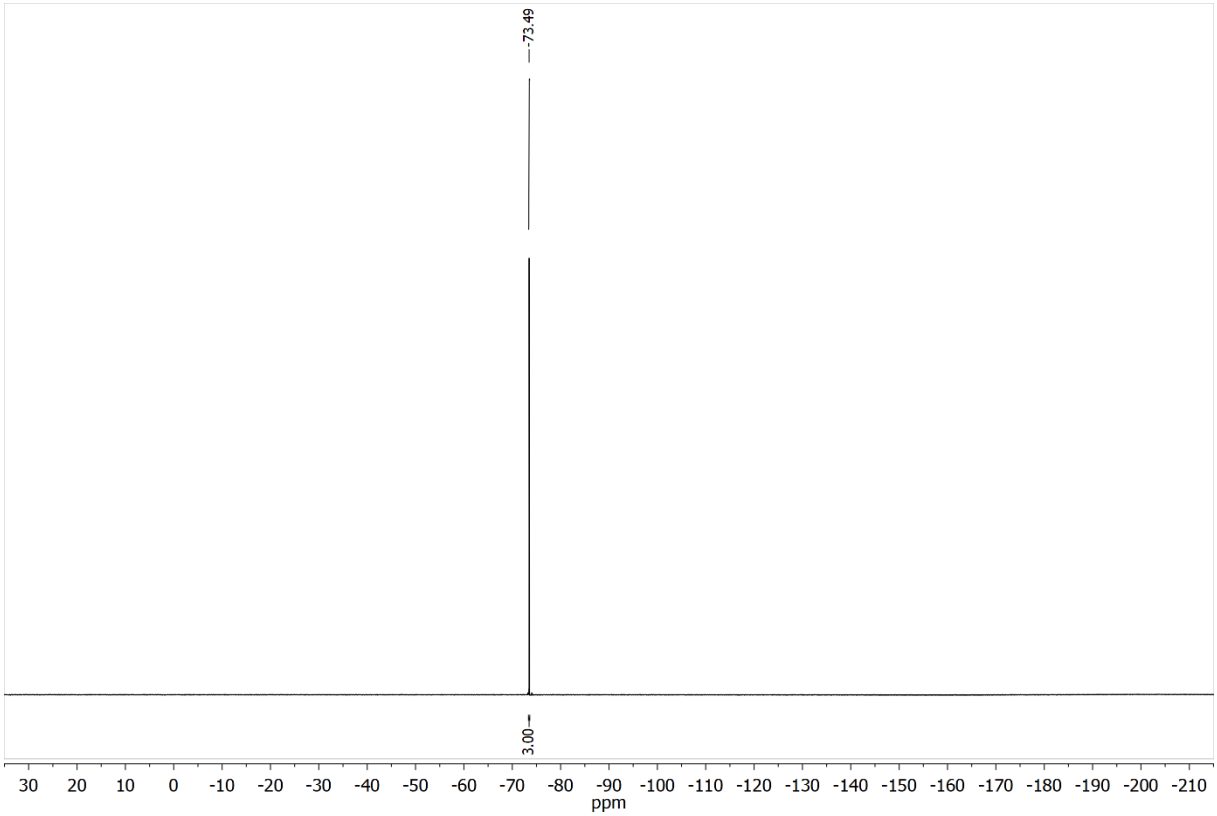


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate

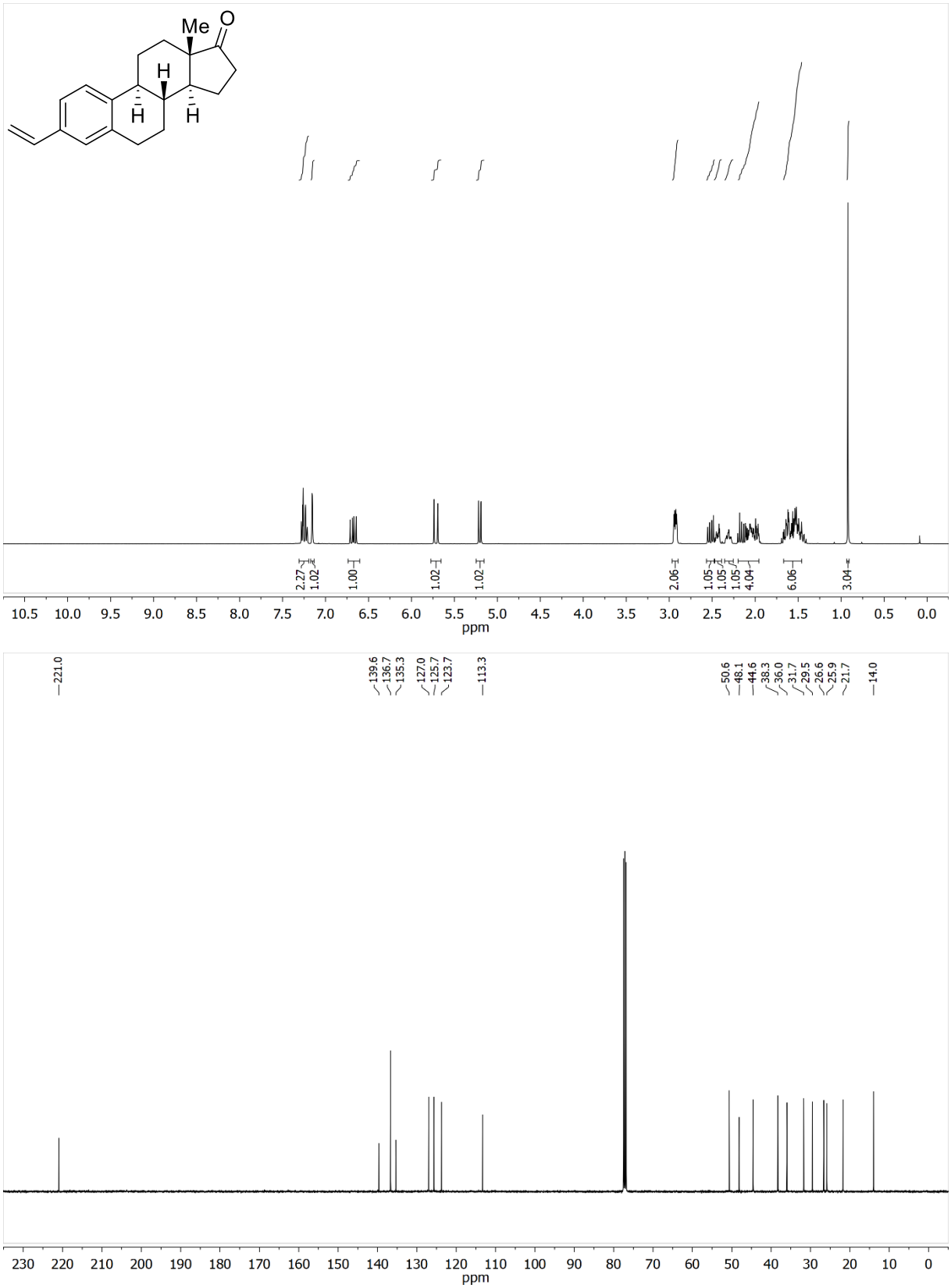


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



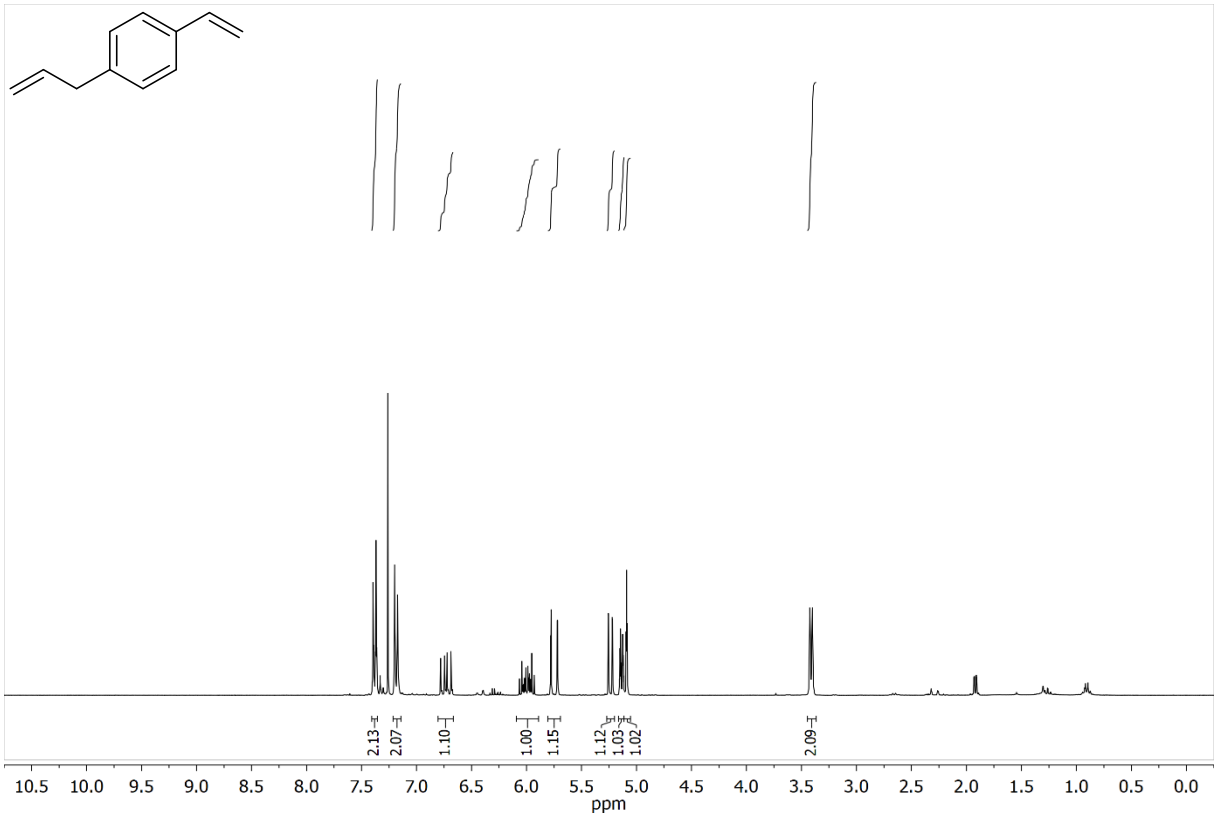
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

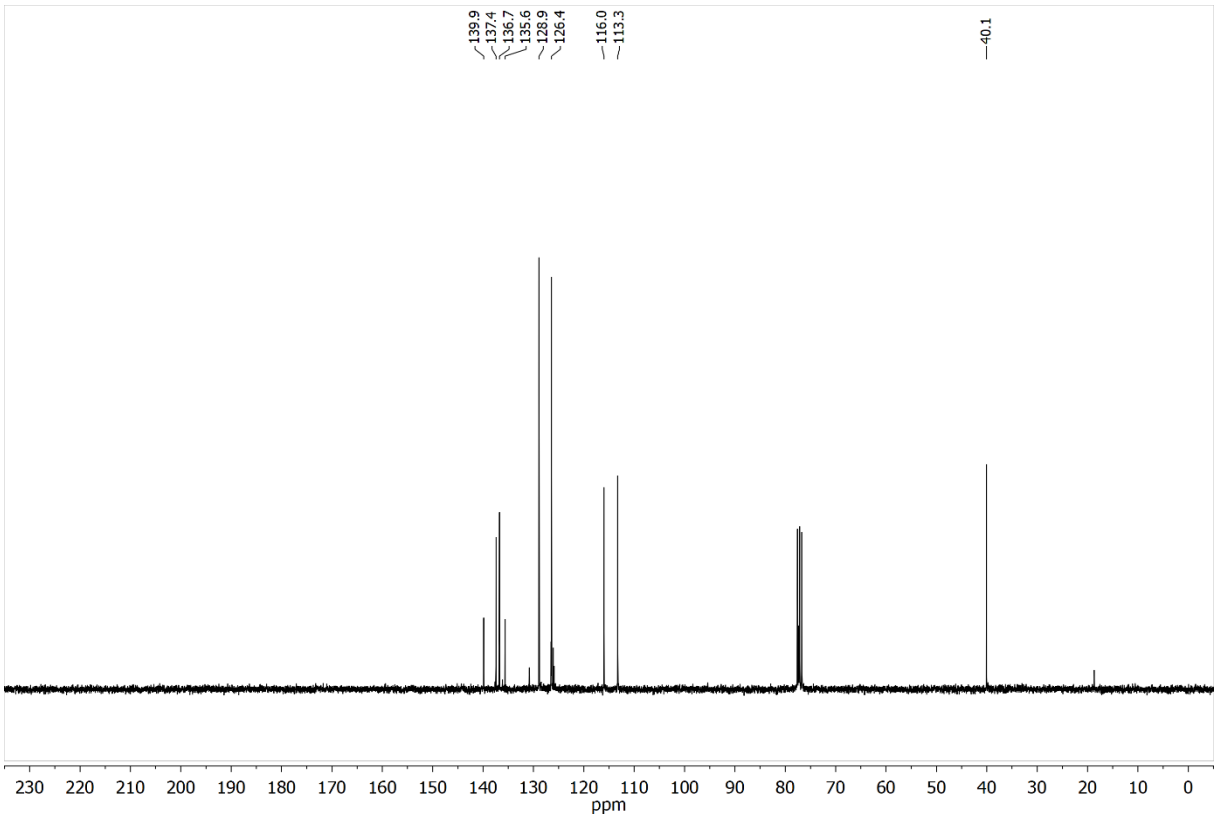
(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (1ag//1bv)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

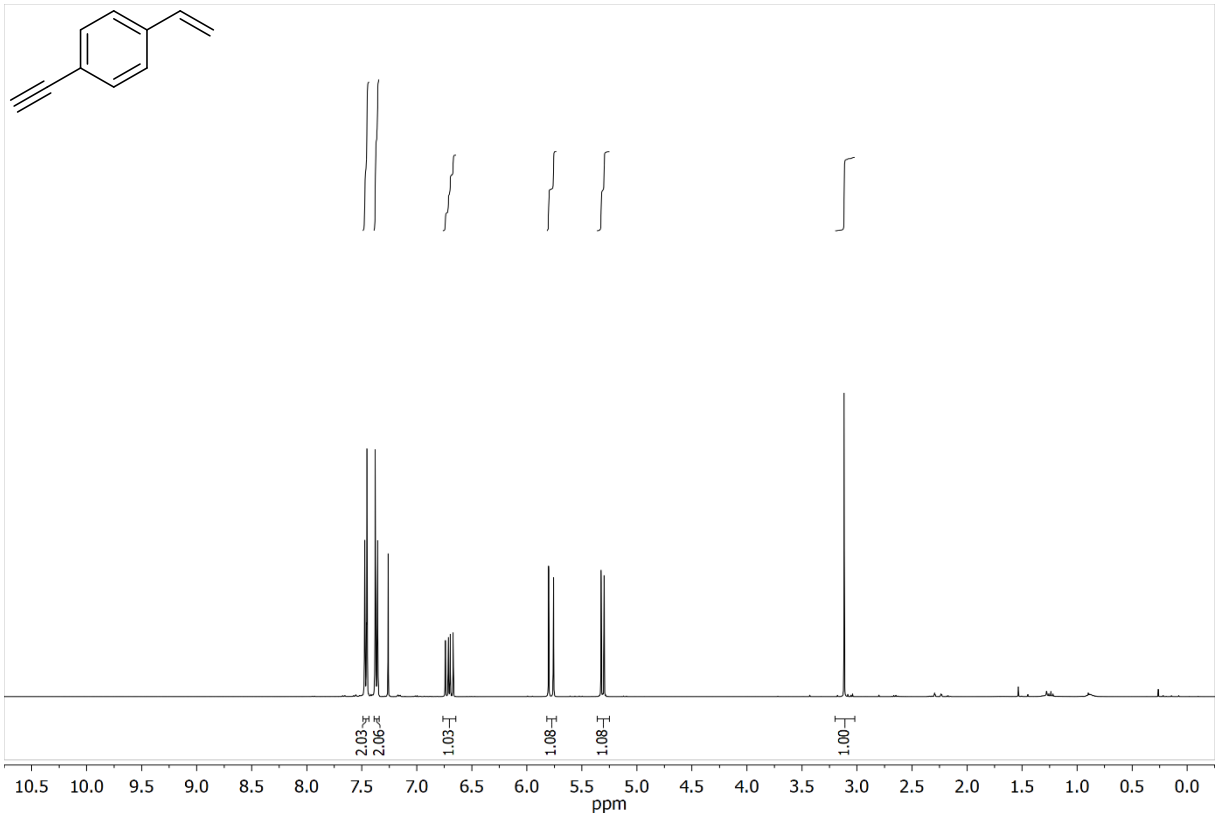
1-allyl-4-vinylbenzene (1au)

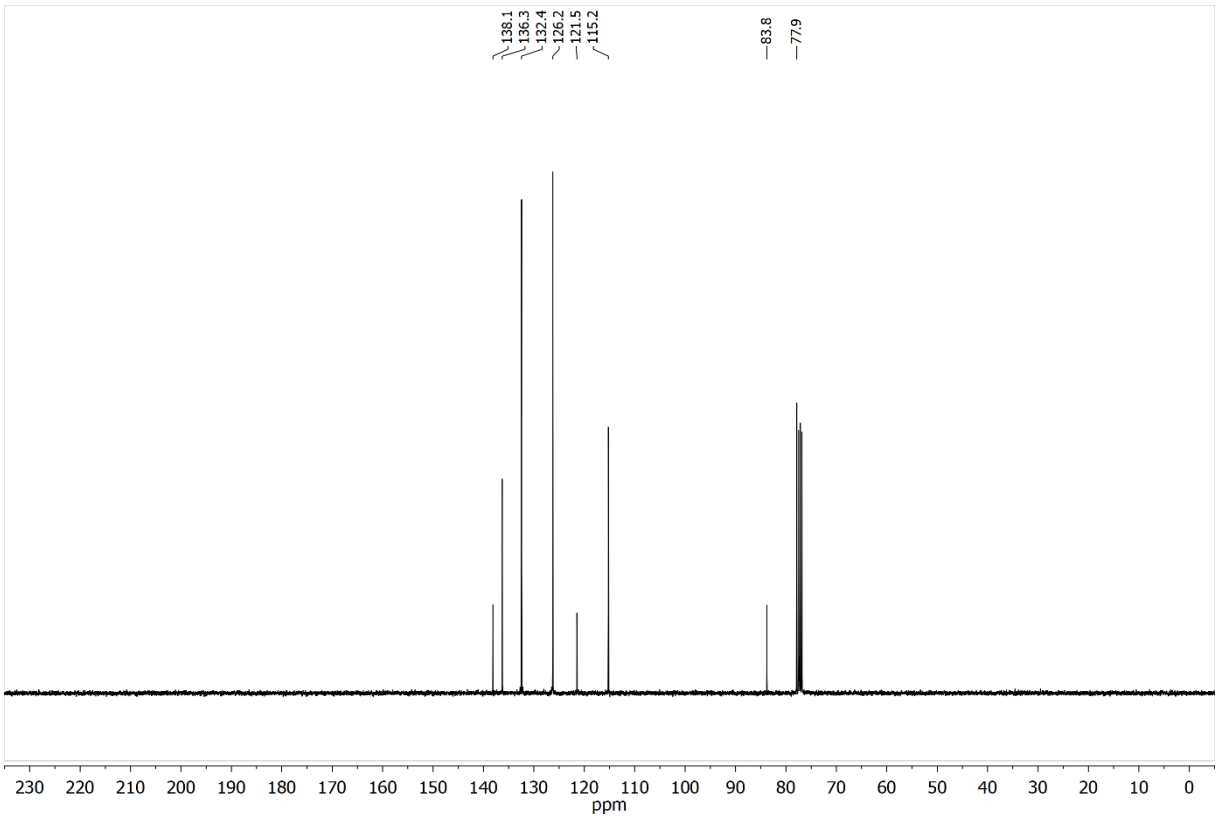




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

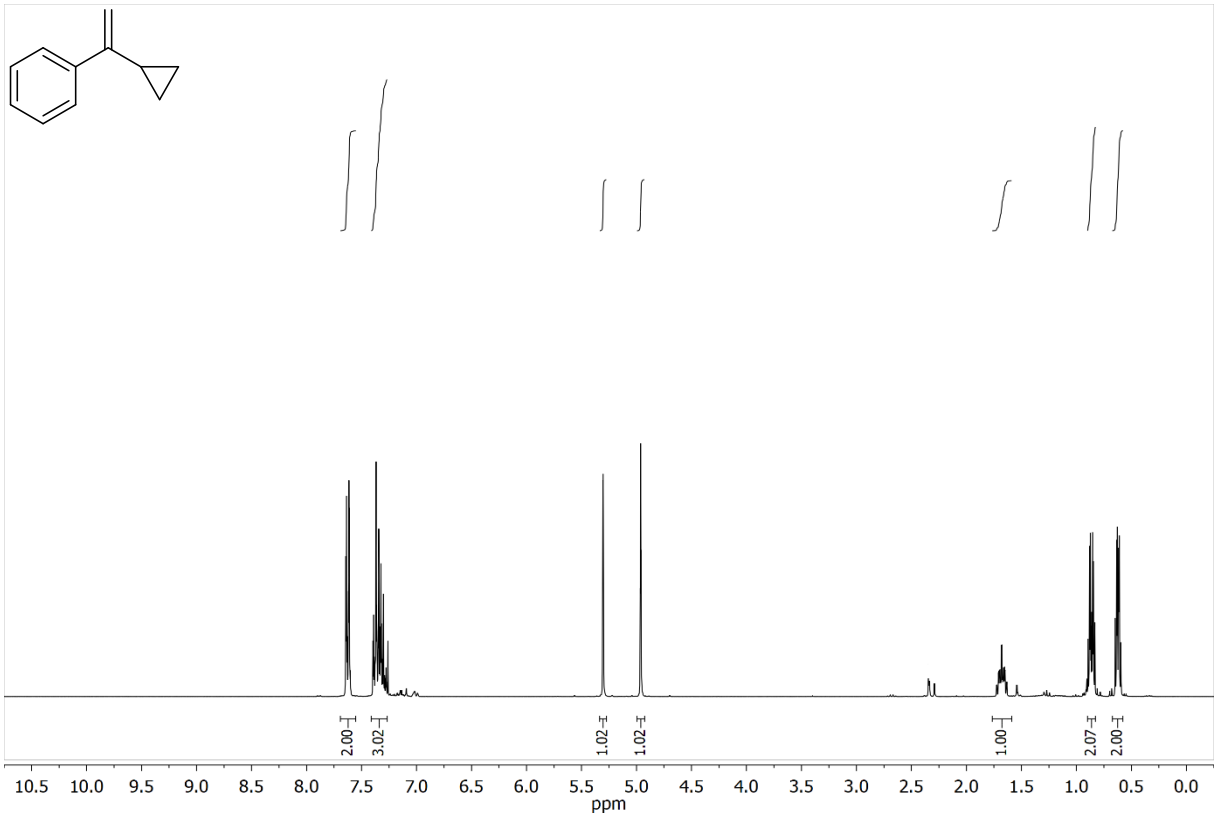
1-ethynyl-4-vinylbenzene (1av)

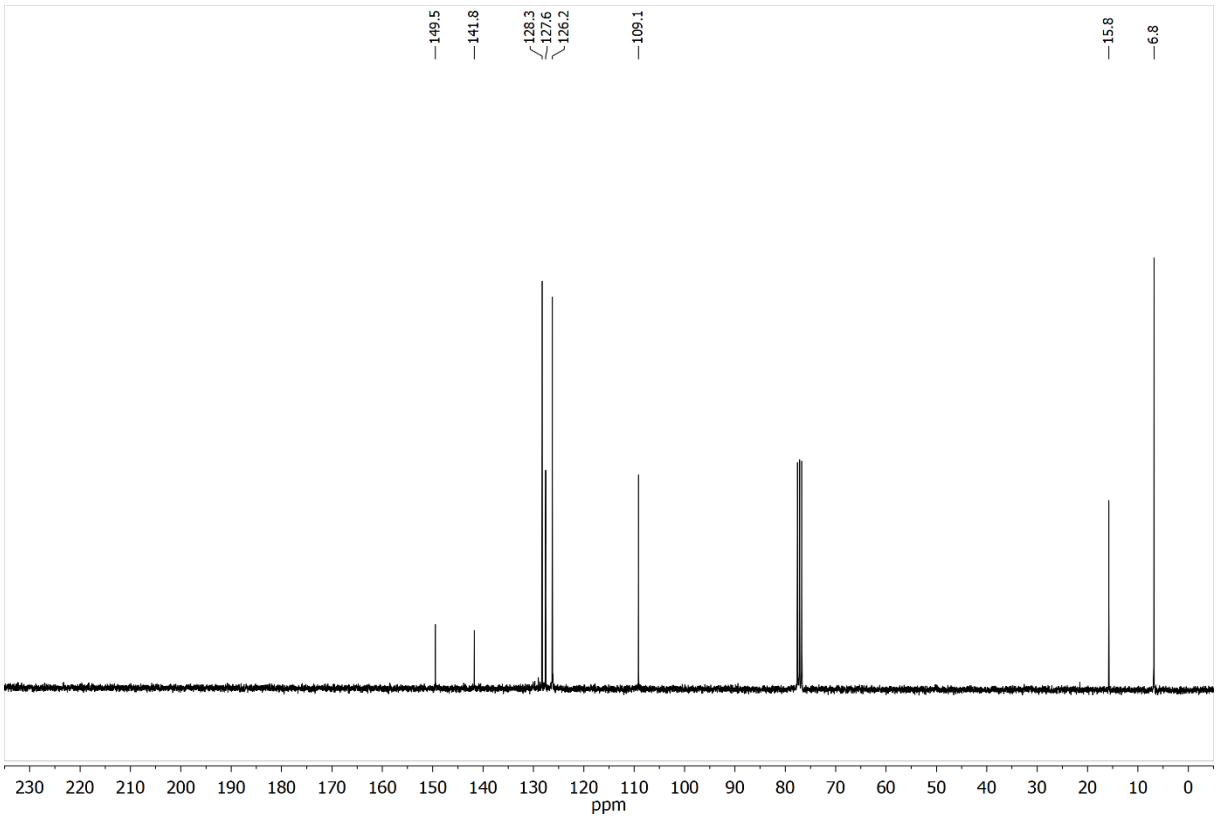




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

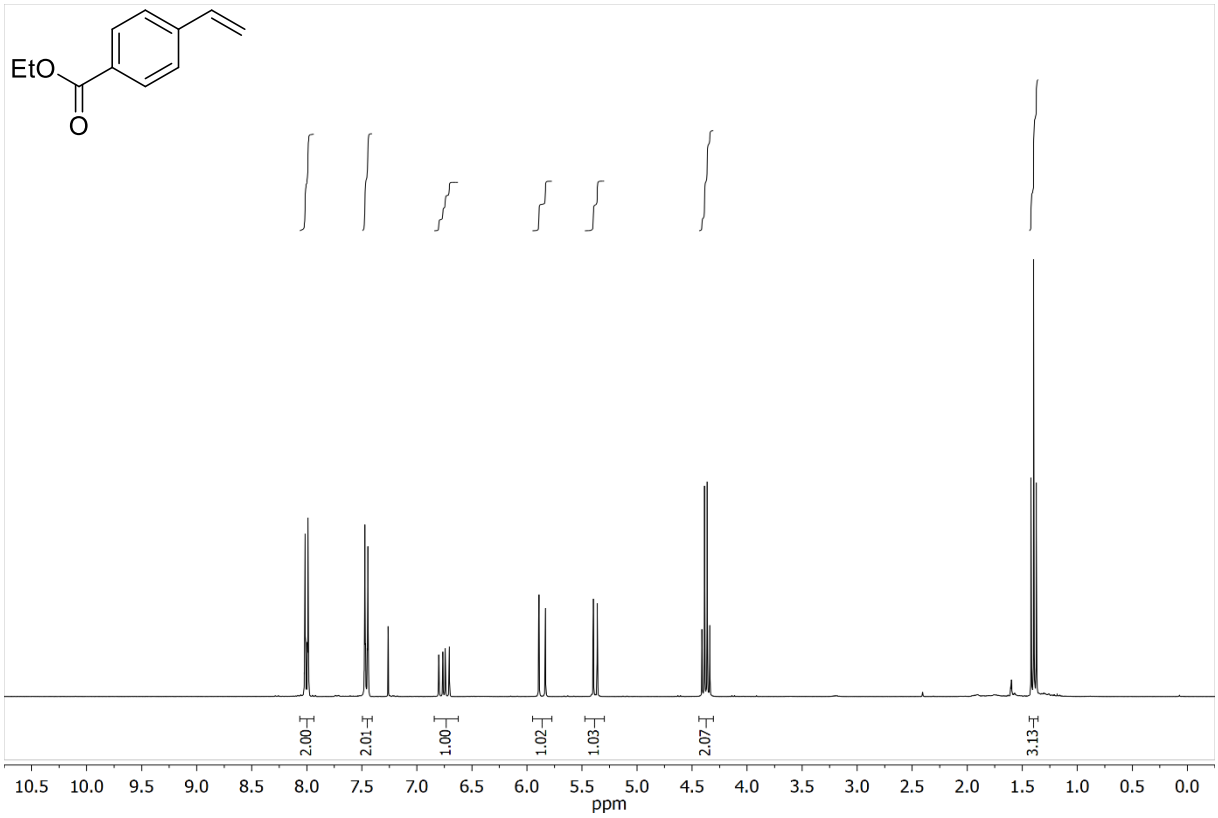
(1-cyclopropylvinyl)benzene (1ax//1cb)

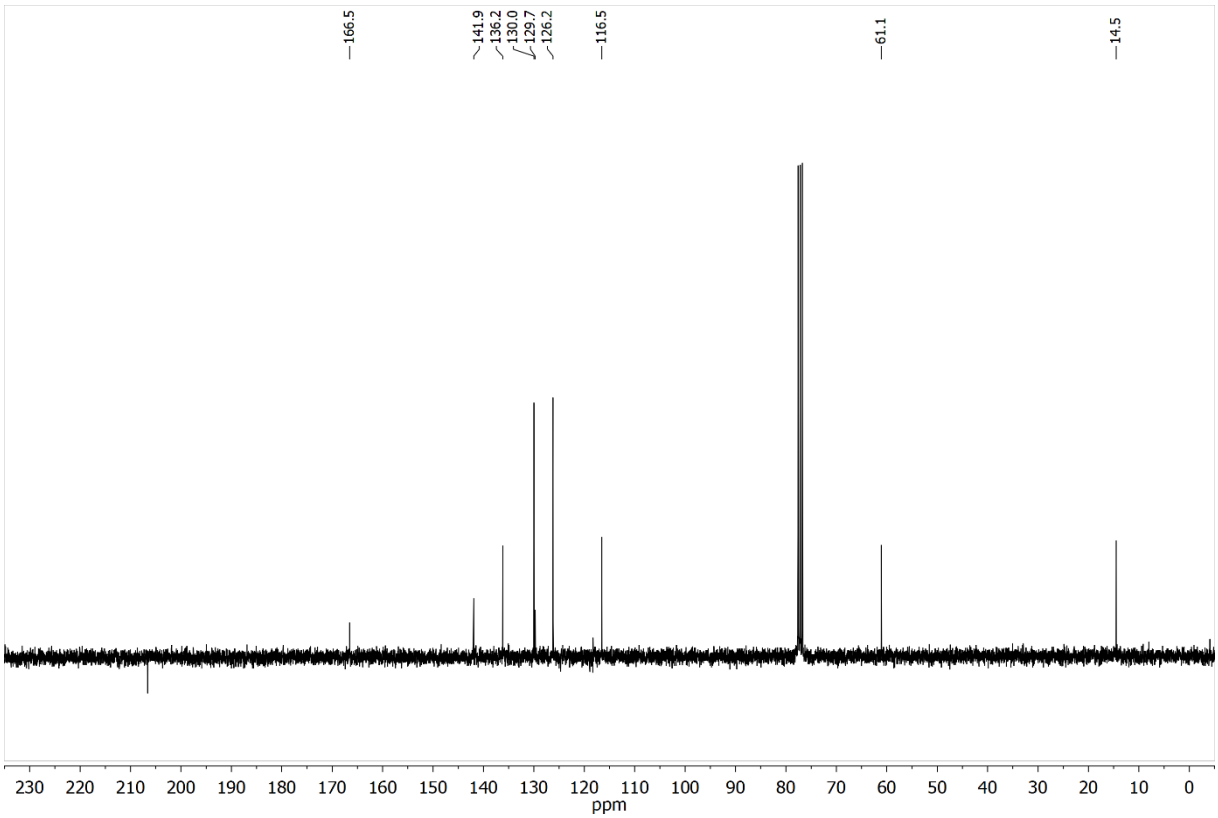




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

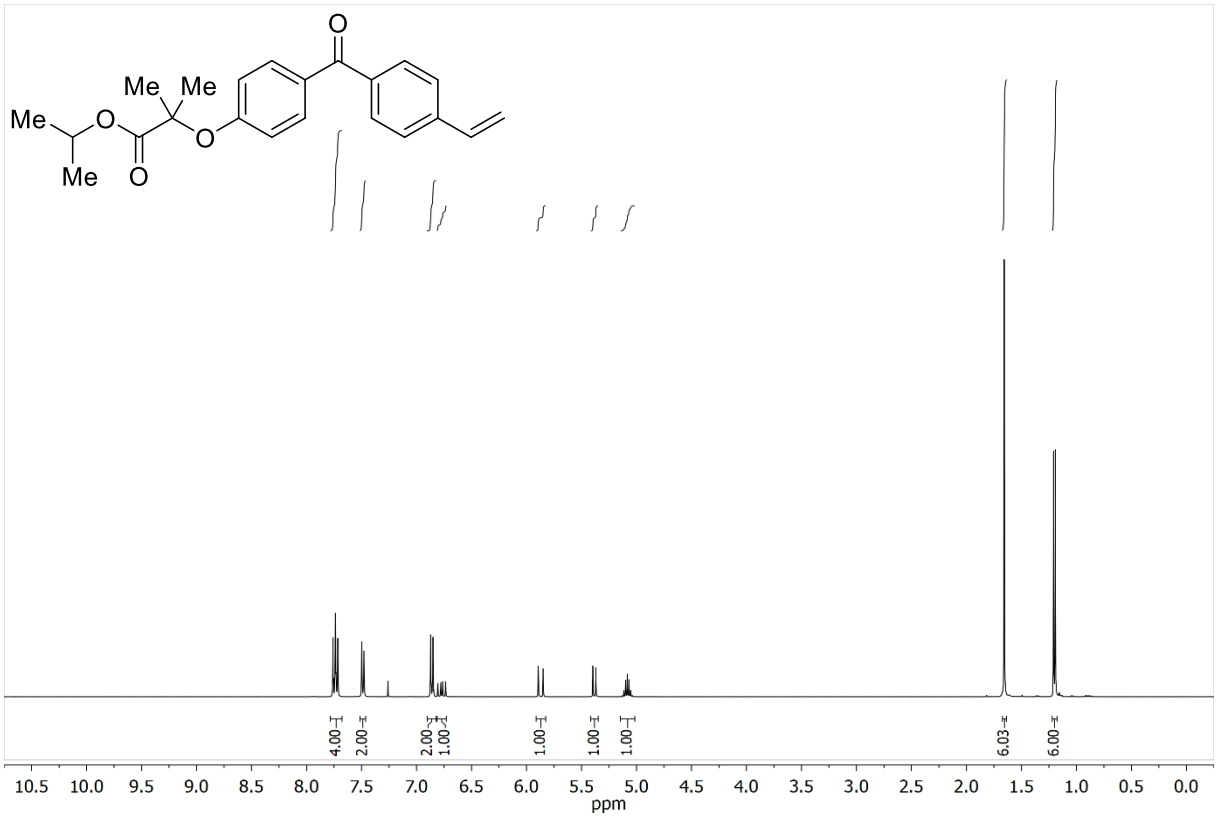
ethyl 4-vinylbenzoate (1j)

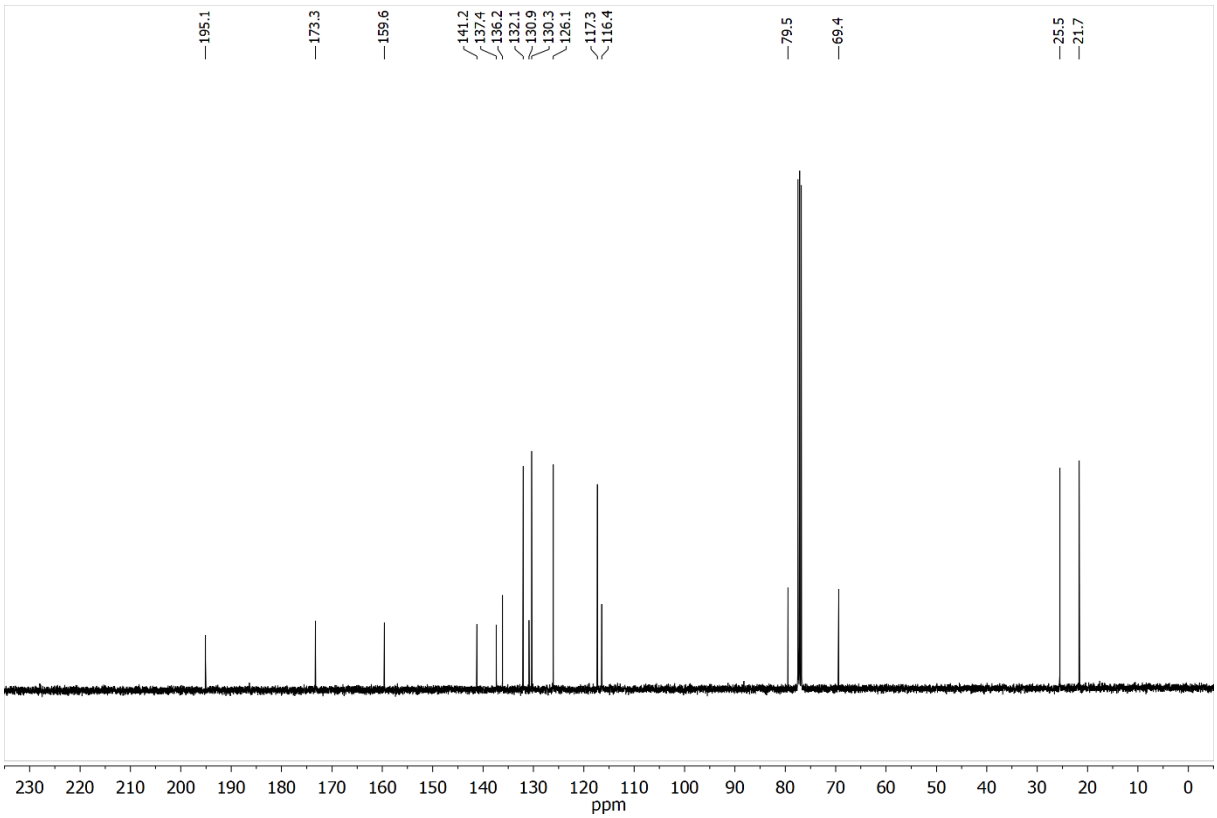




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

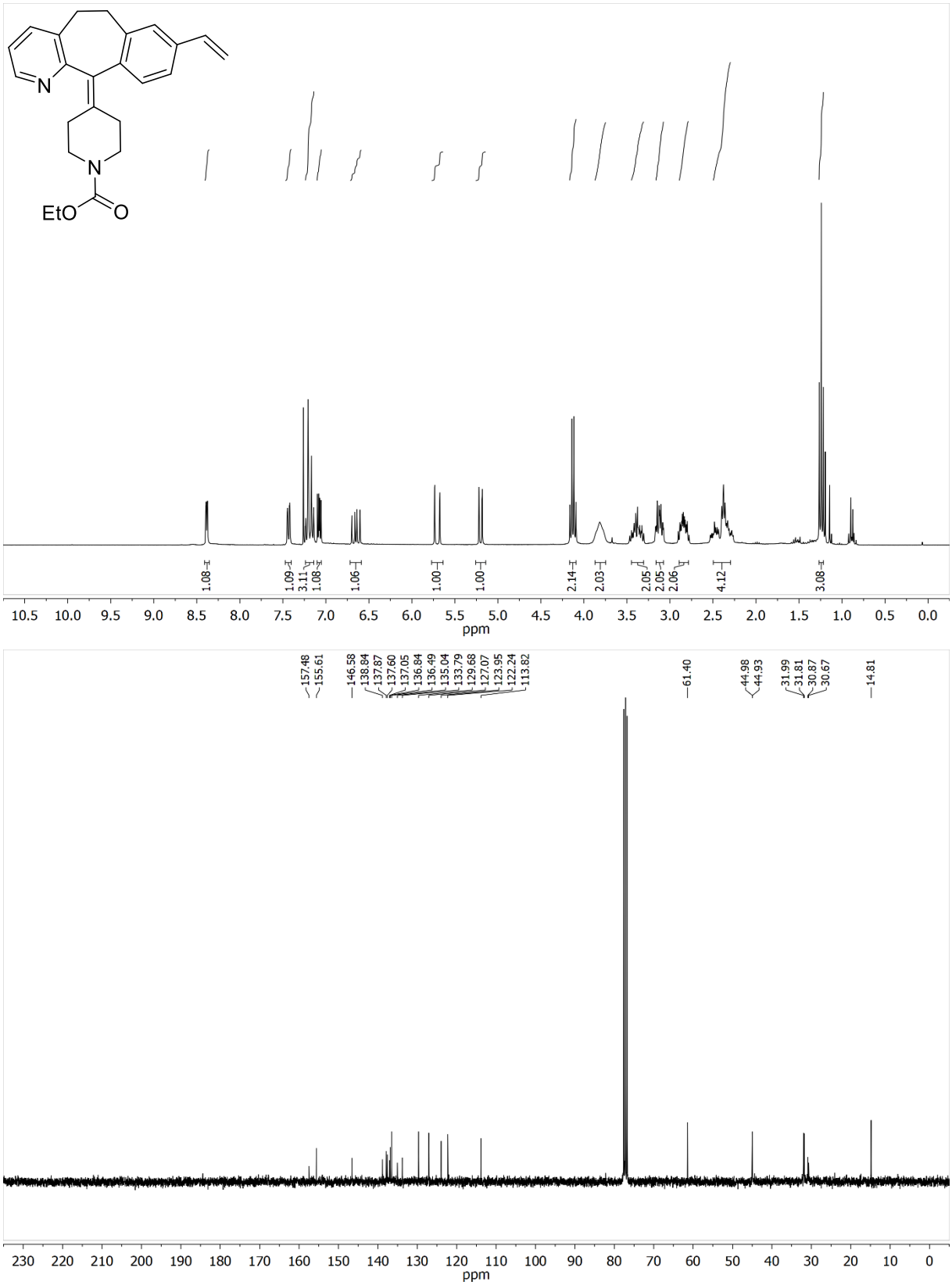
isopropyl 2-methyl-2-(4-(4-vinylbenzoyl)phenoxy)propanoate (1bw)





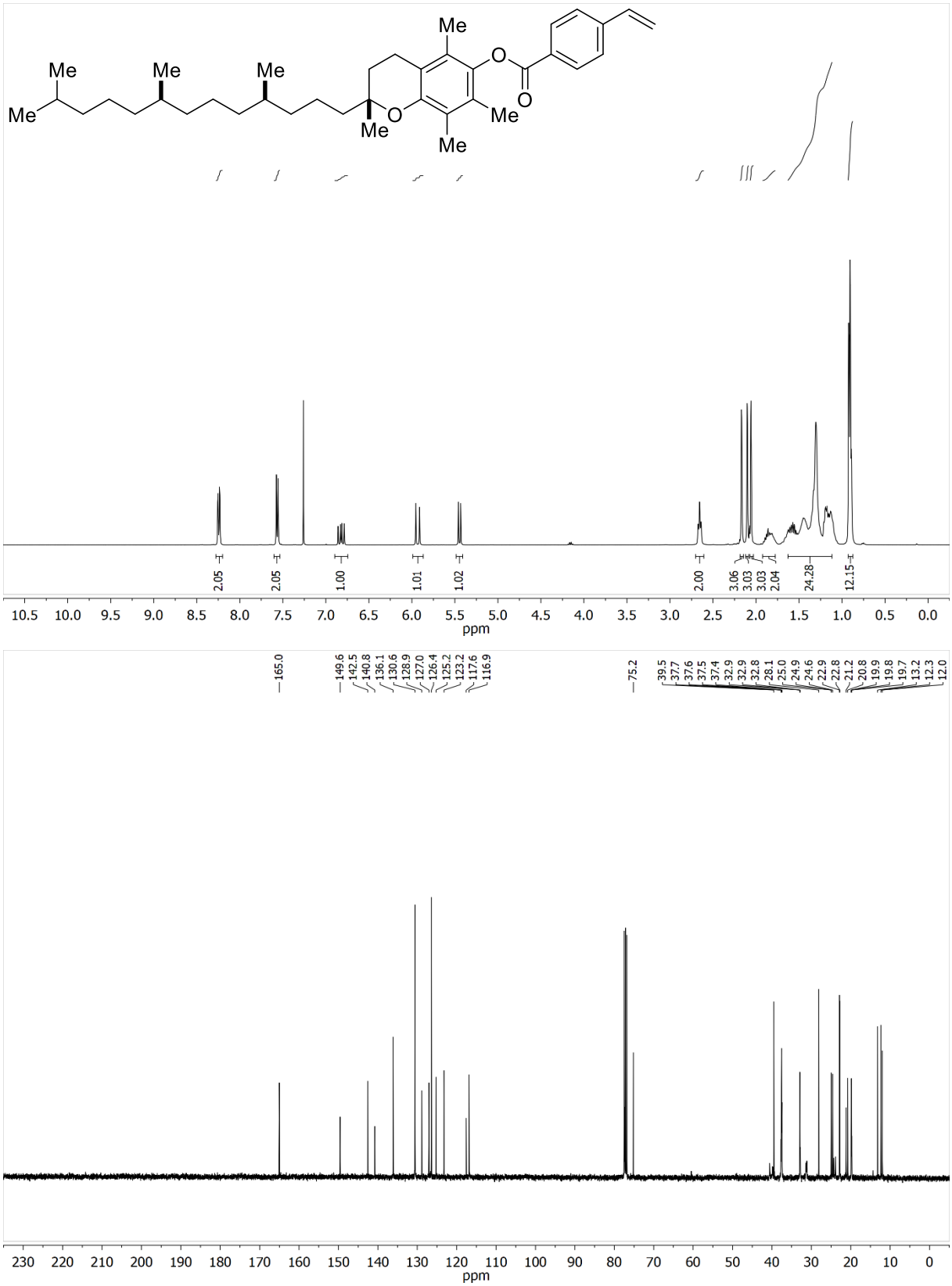
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

ethyl 4-(8-vinyl-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (1bx)



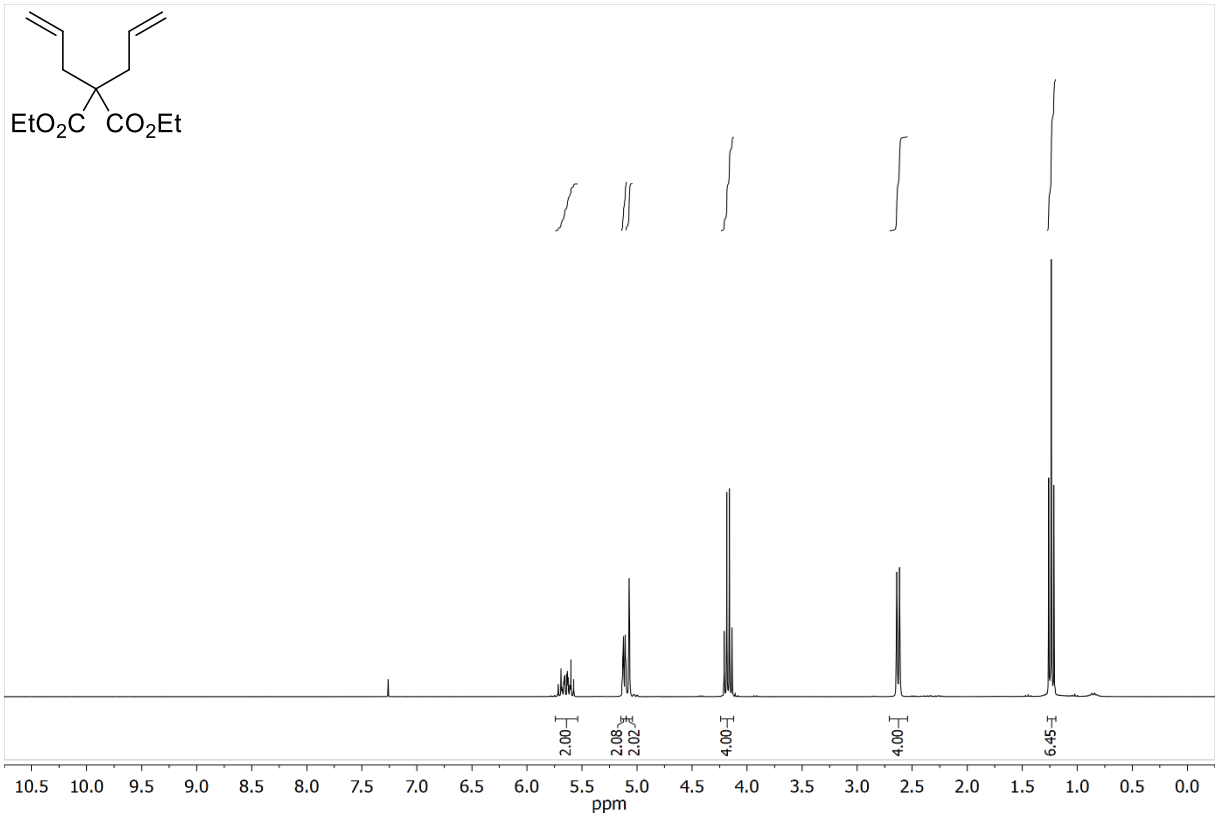
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

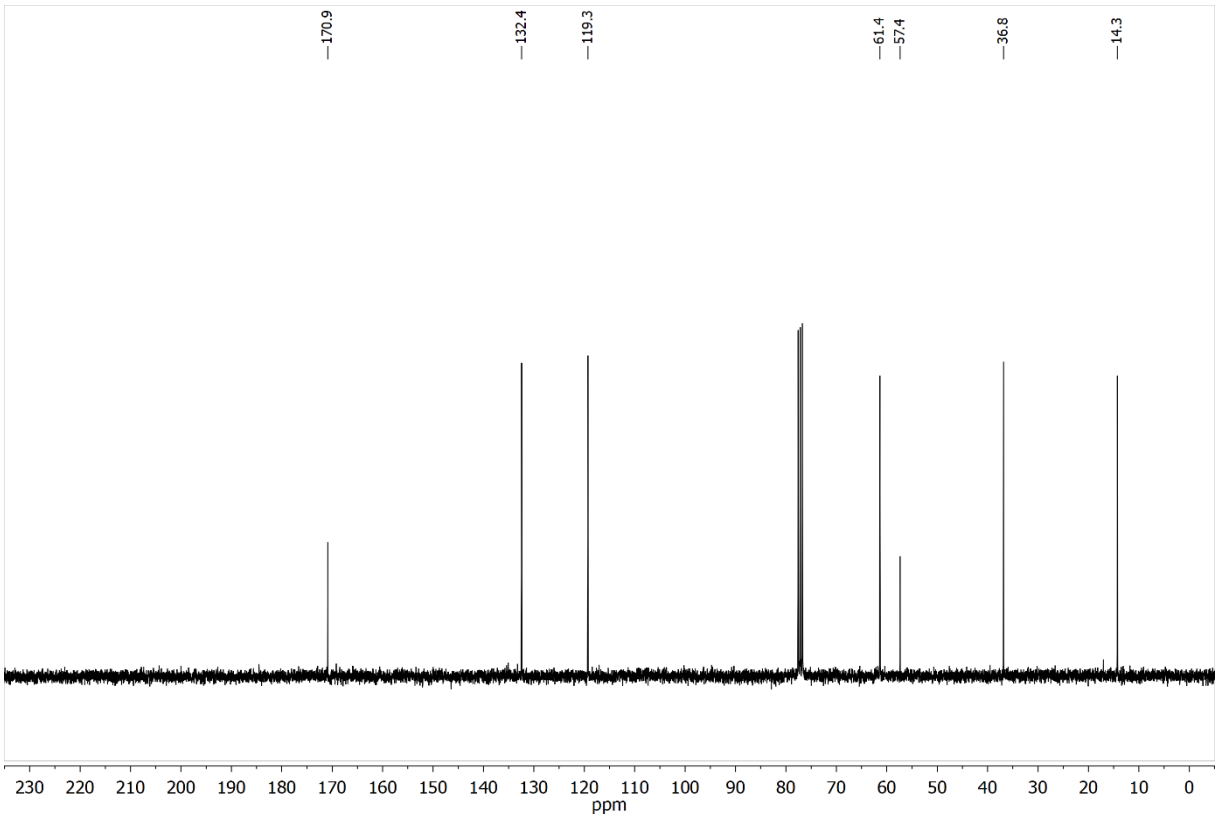
2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-vinylbenzoate (1by)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

diethyl 2,2-diallylmalonate (1ce)

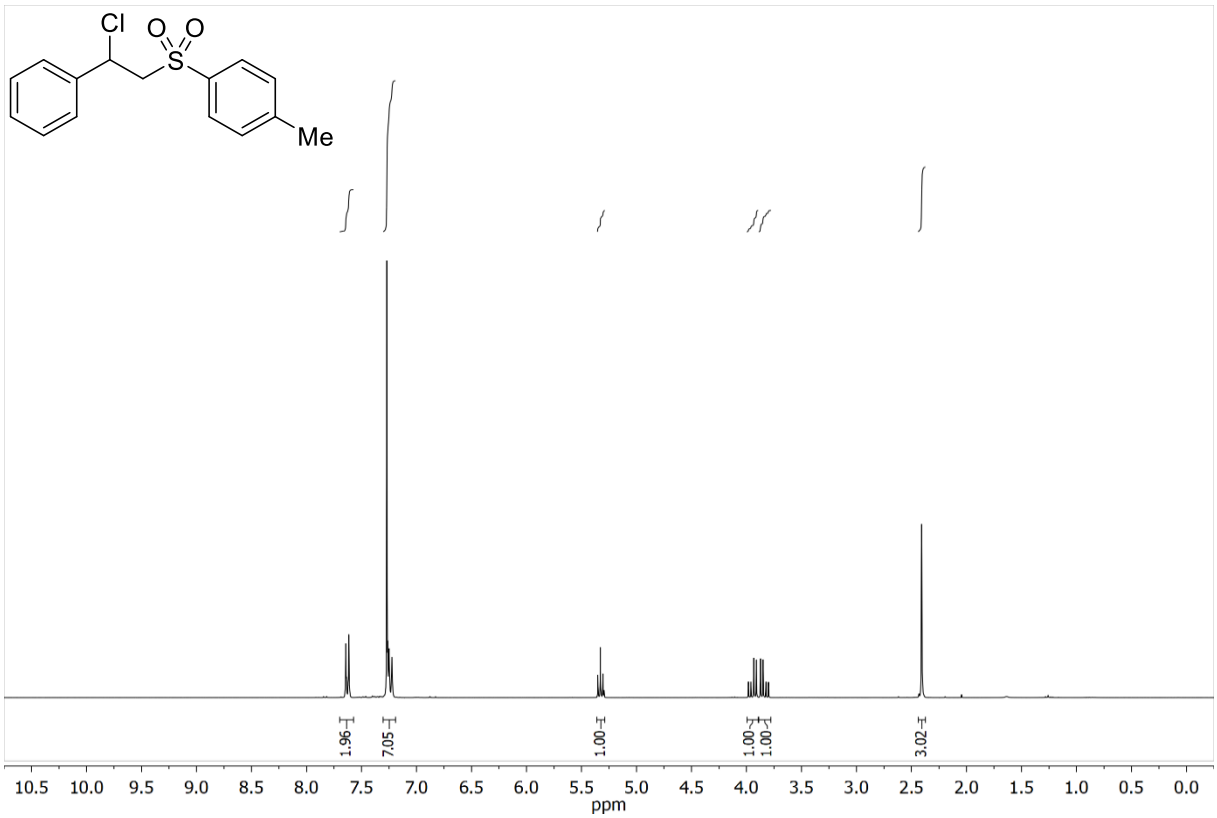


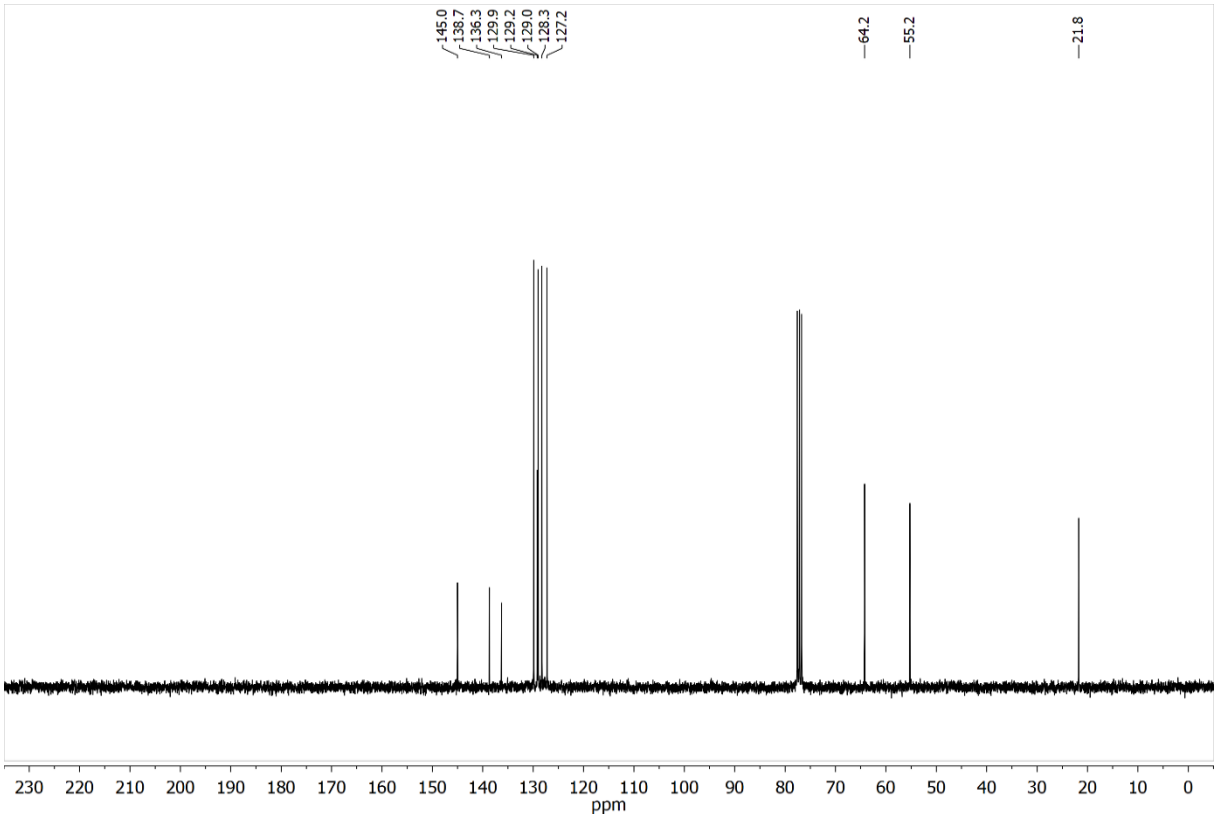


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

8.3 NMR Spectra for Chapter 2 and Chapter 3

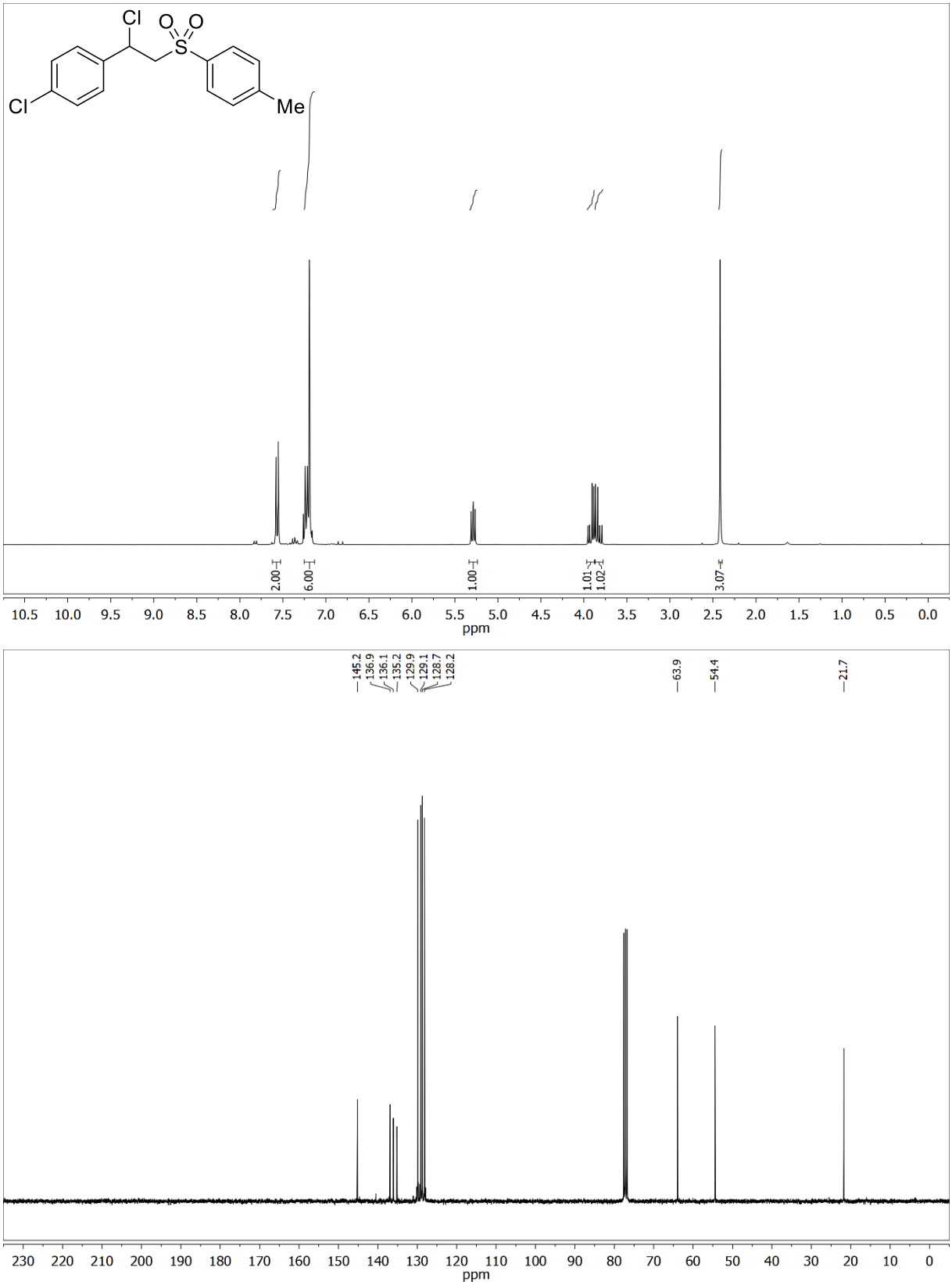
1-((2-chloro-2-phenylethyl)sulfonyl)-4-methylbenzene (10a//9a)





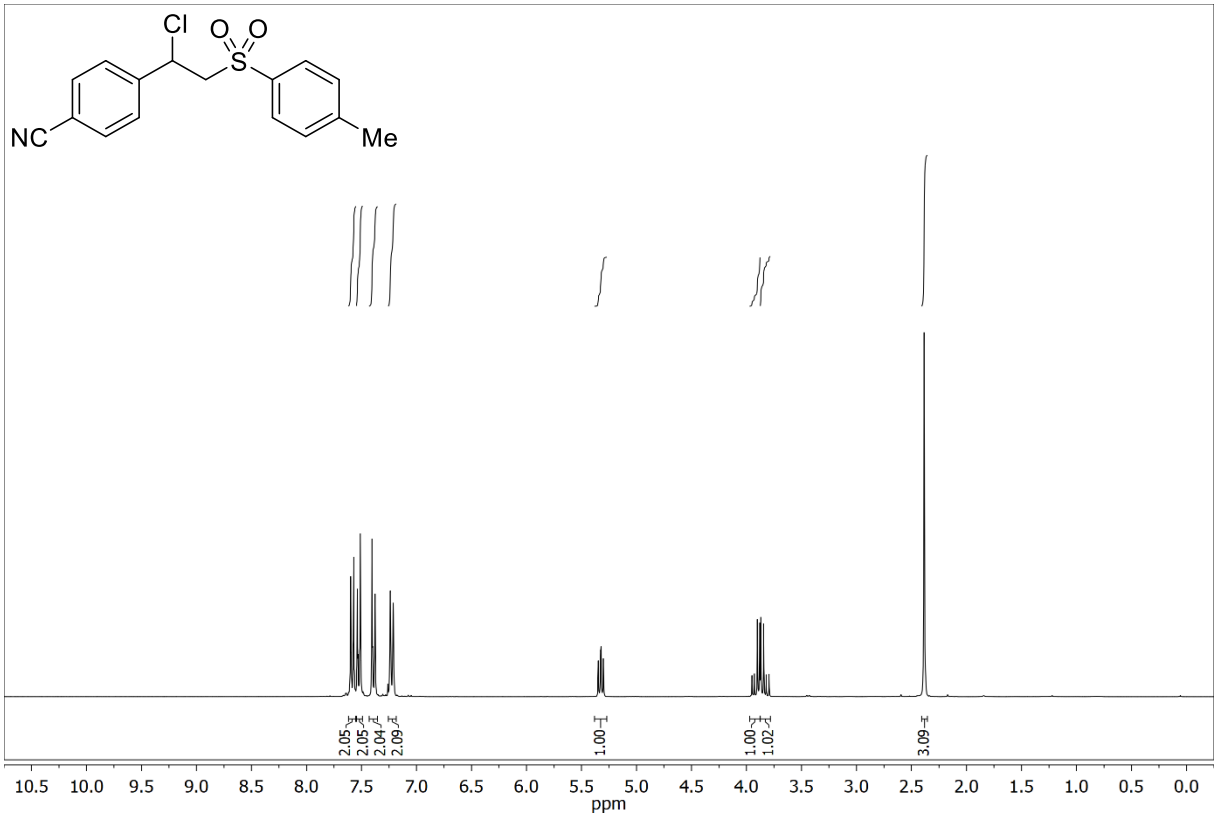
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

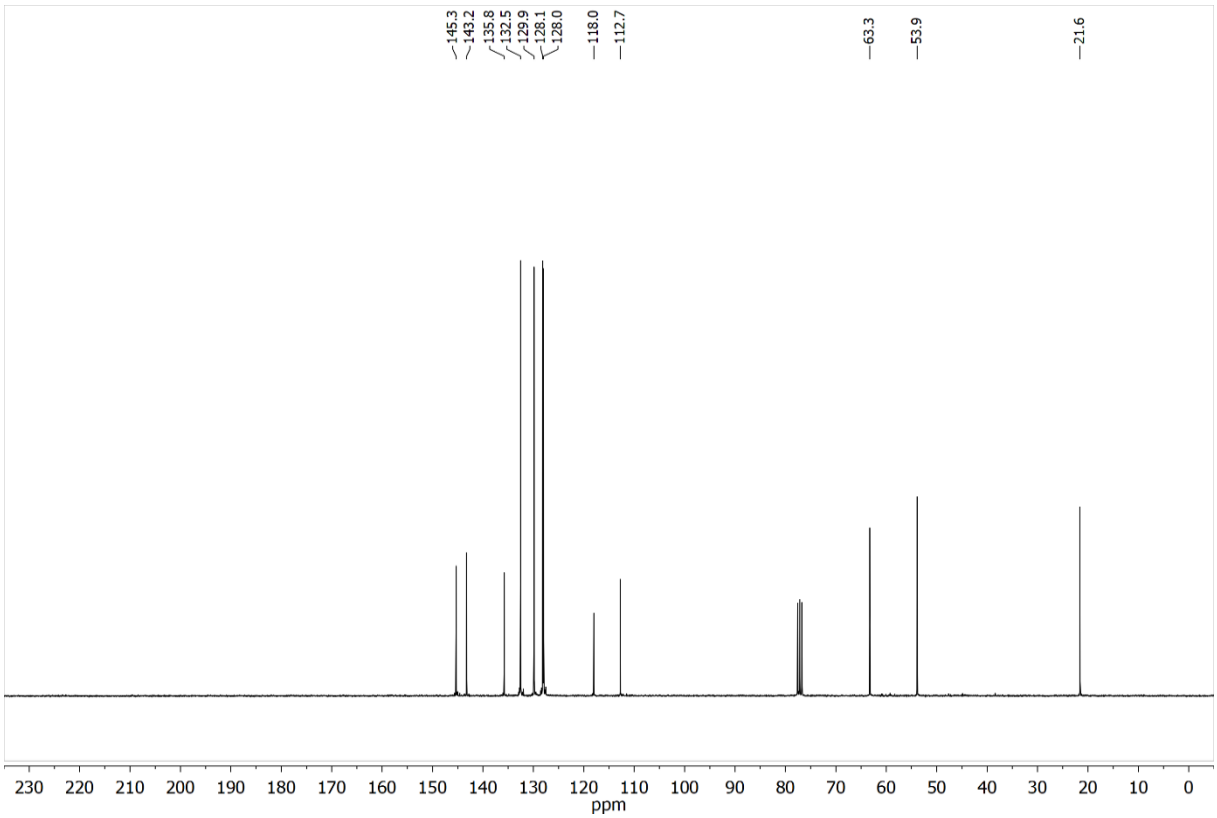
1-chloro-4-(1-chloro-2-tosylethyl)benzene (10c)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

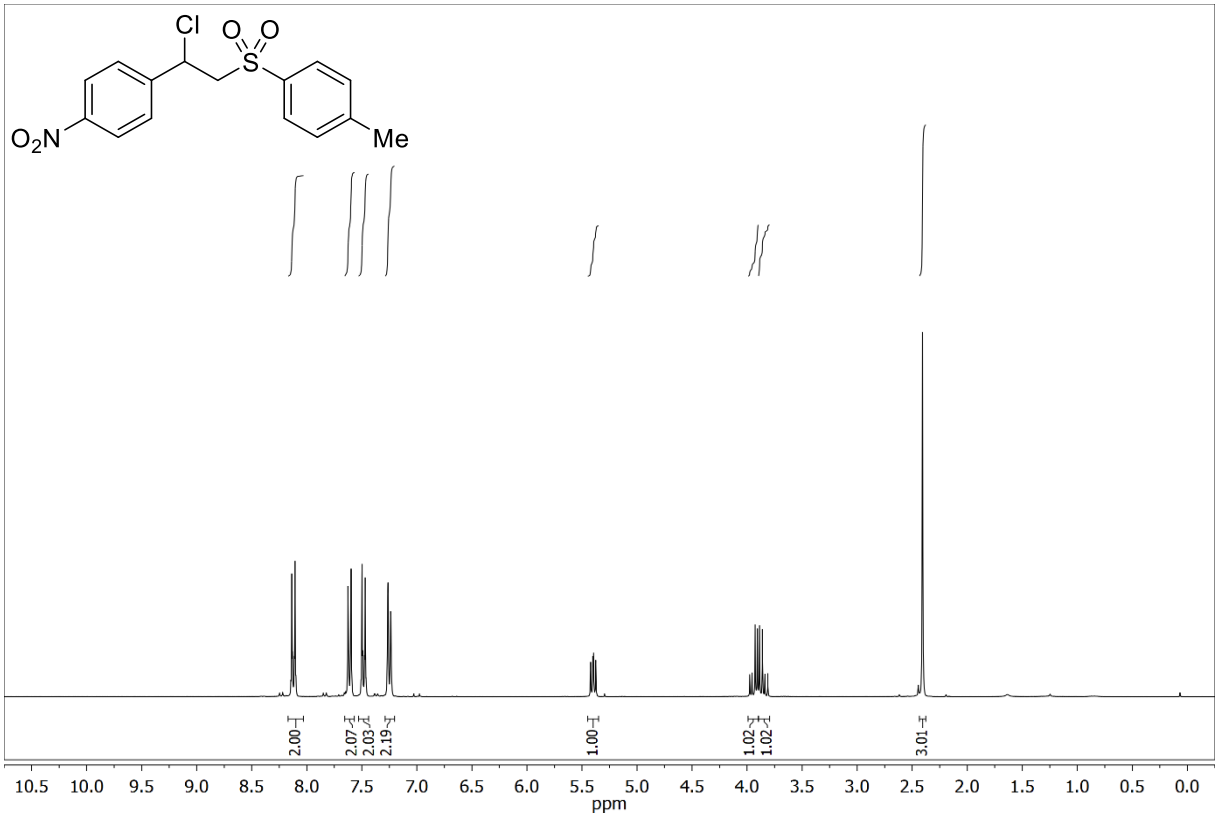
4-(1-chloro-2-tosylethyl)benzonitrile (10d//9b)

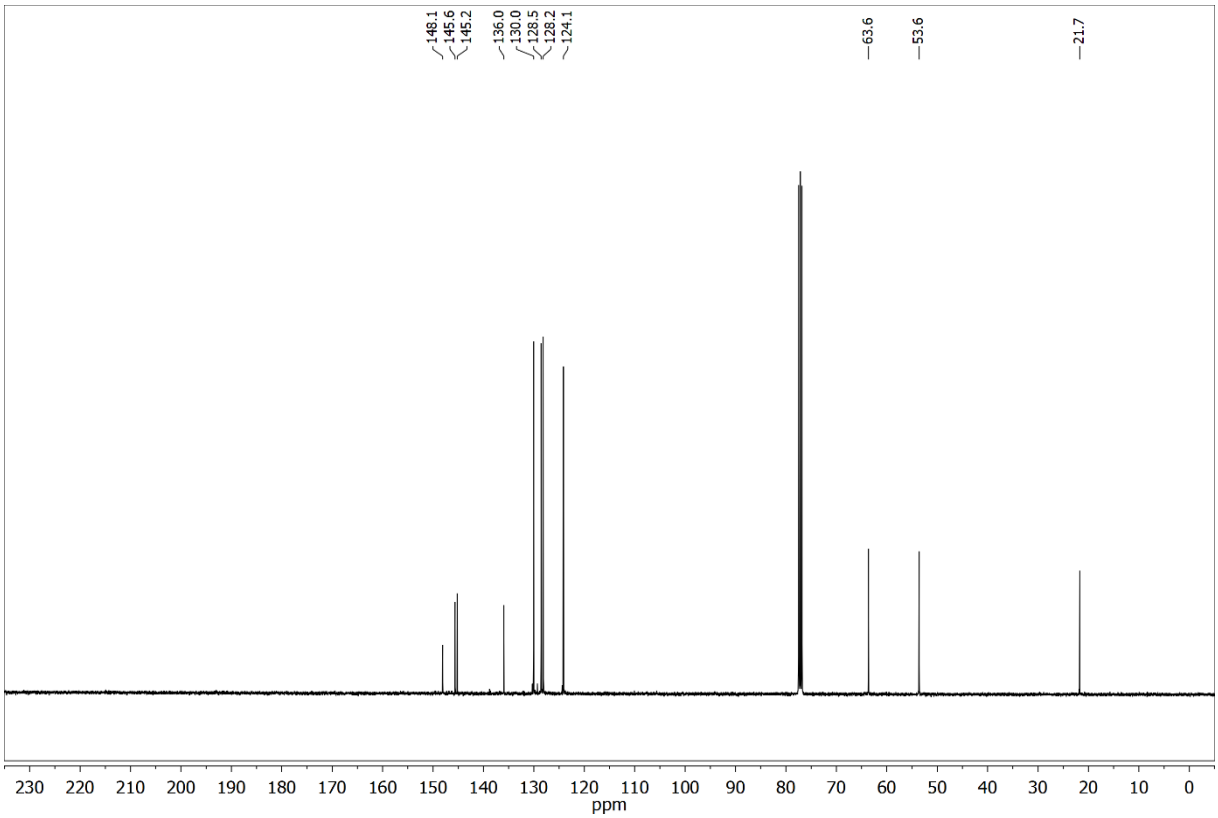




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

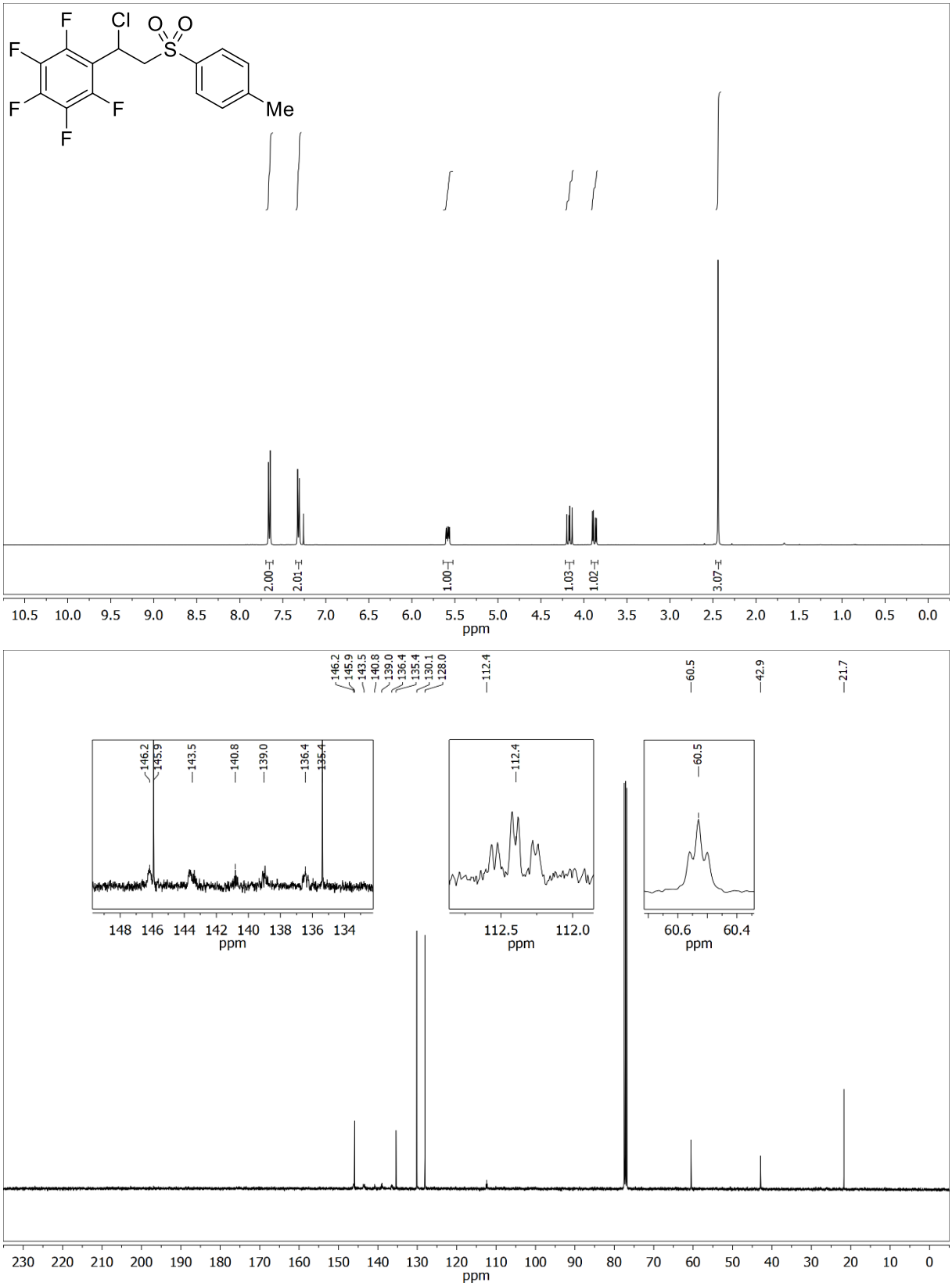
1-((2-chloro-2-(4-nitrophenyl)ethyl)sulfonyl)-4-methylbenzene (10e)



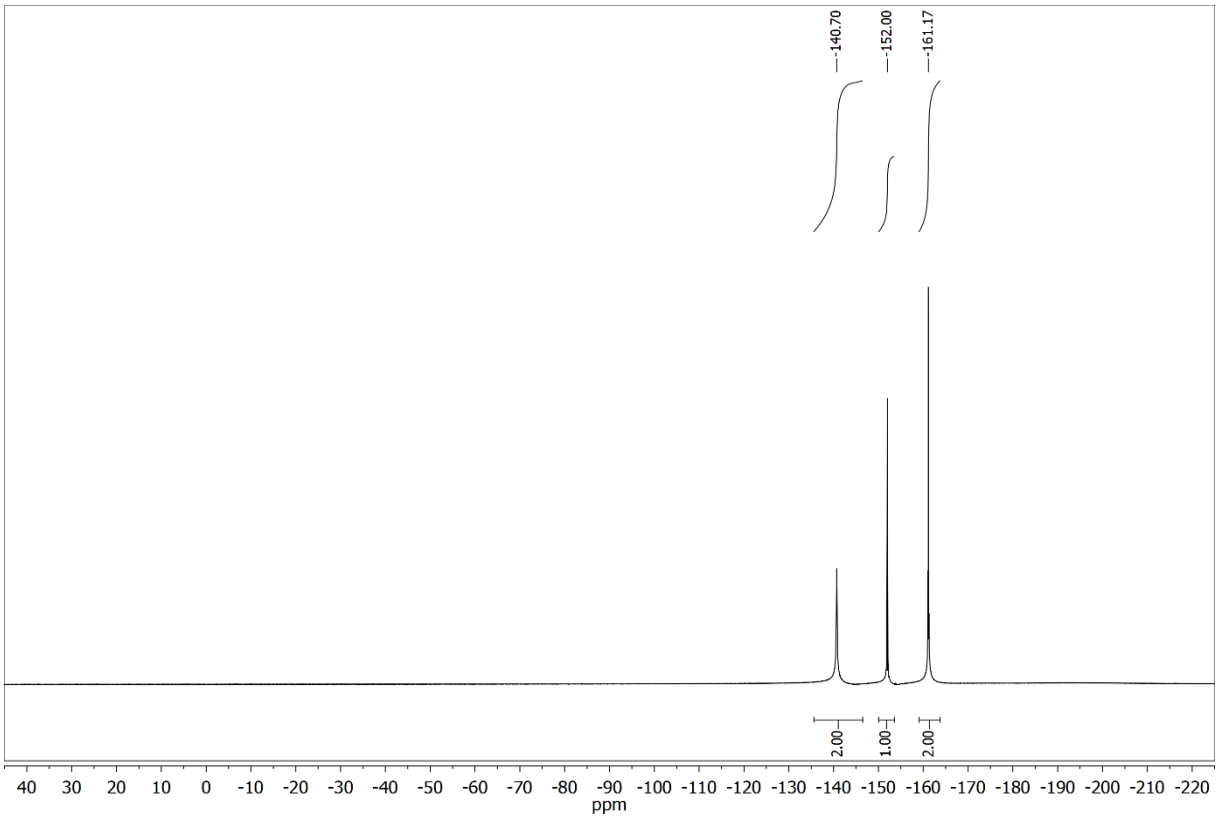


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

1-(1-chloro-2-tosylethyl)-2,3,4,5,6-pentafluorobenzene (10f)

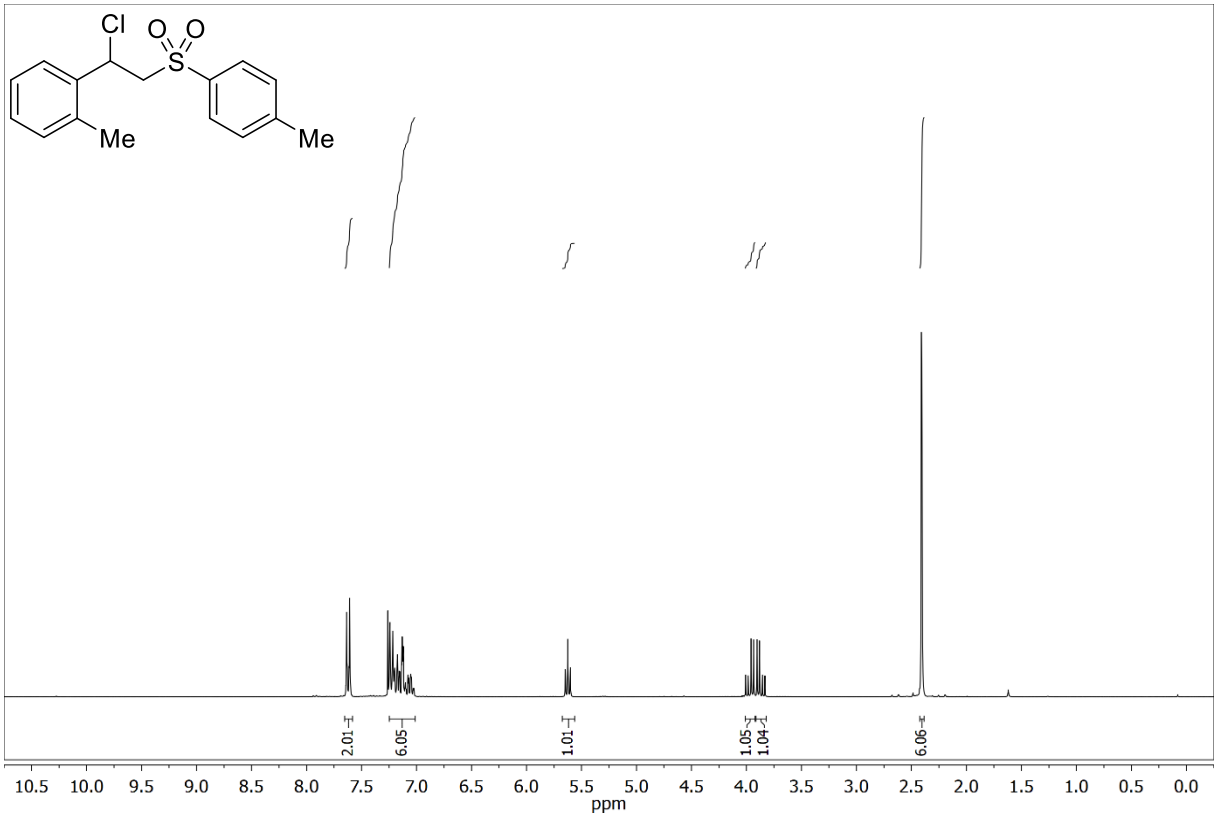


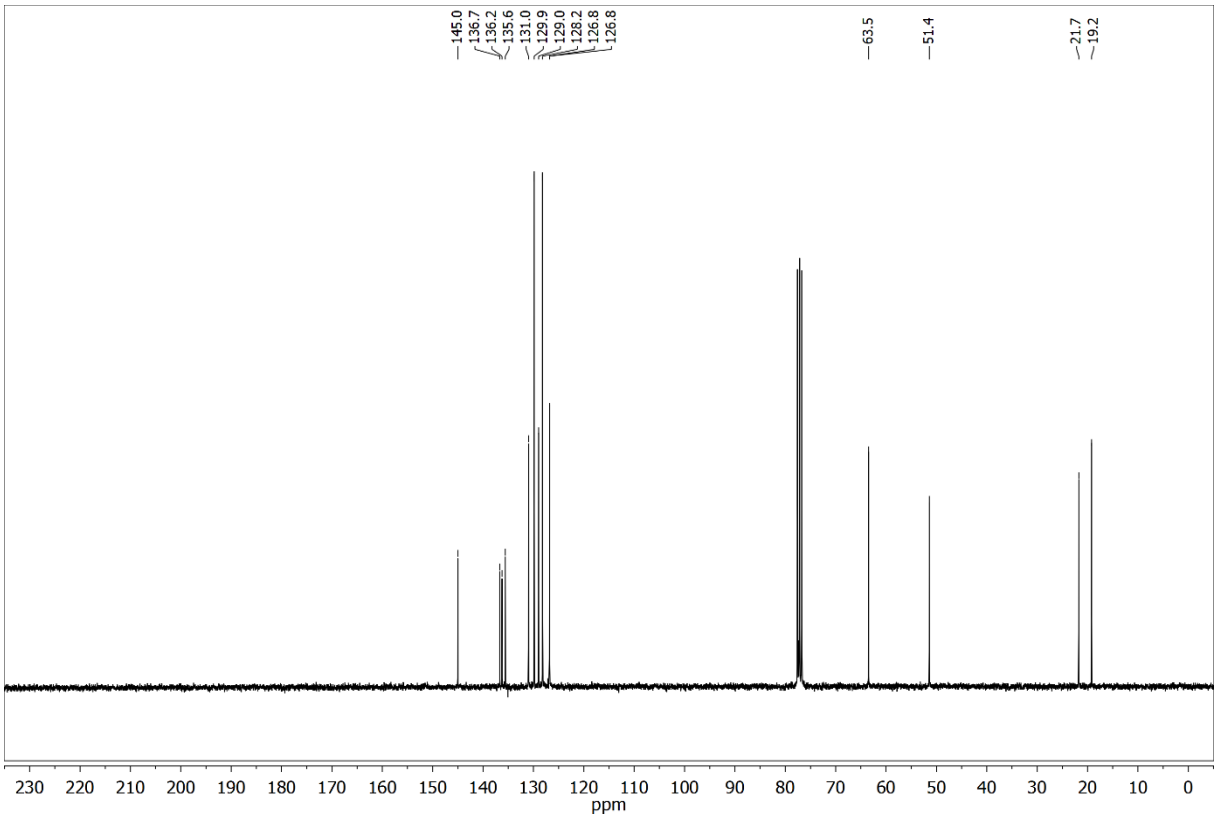
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

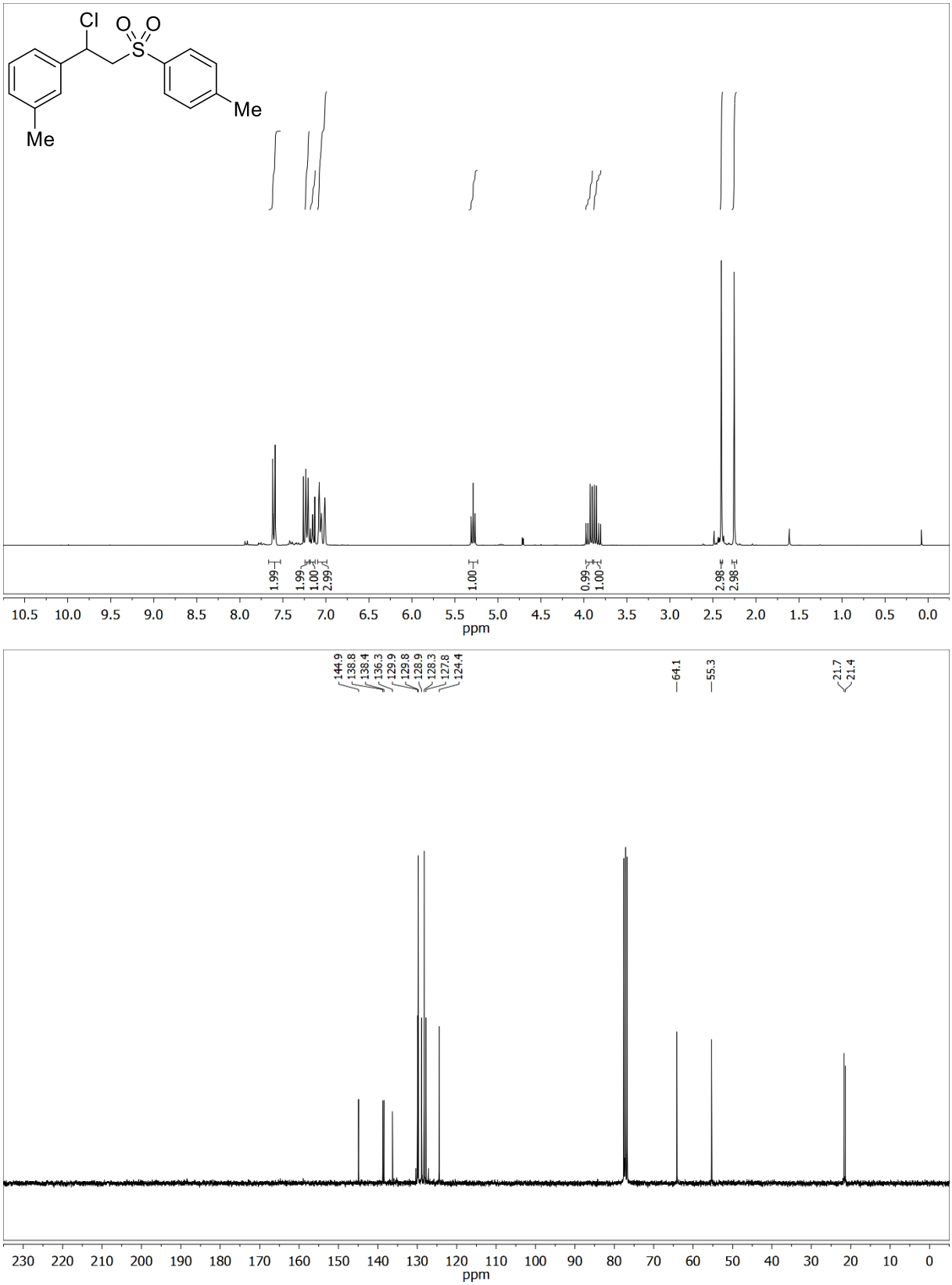
1-(1-chloro-2-tosylethyl)-2-methylbenzene (10g)





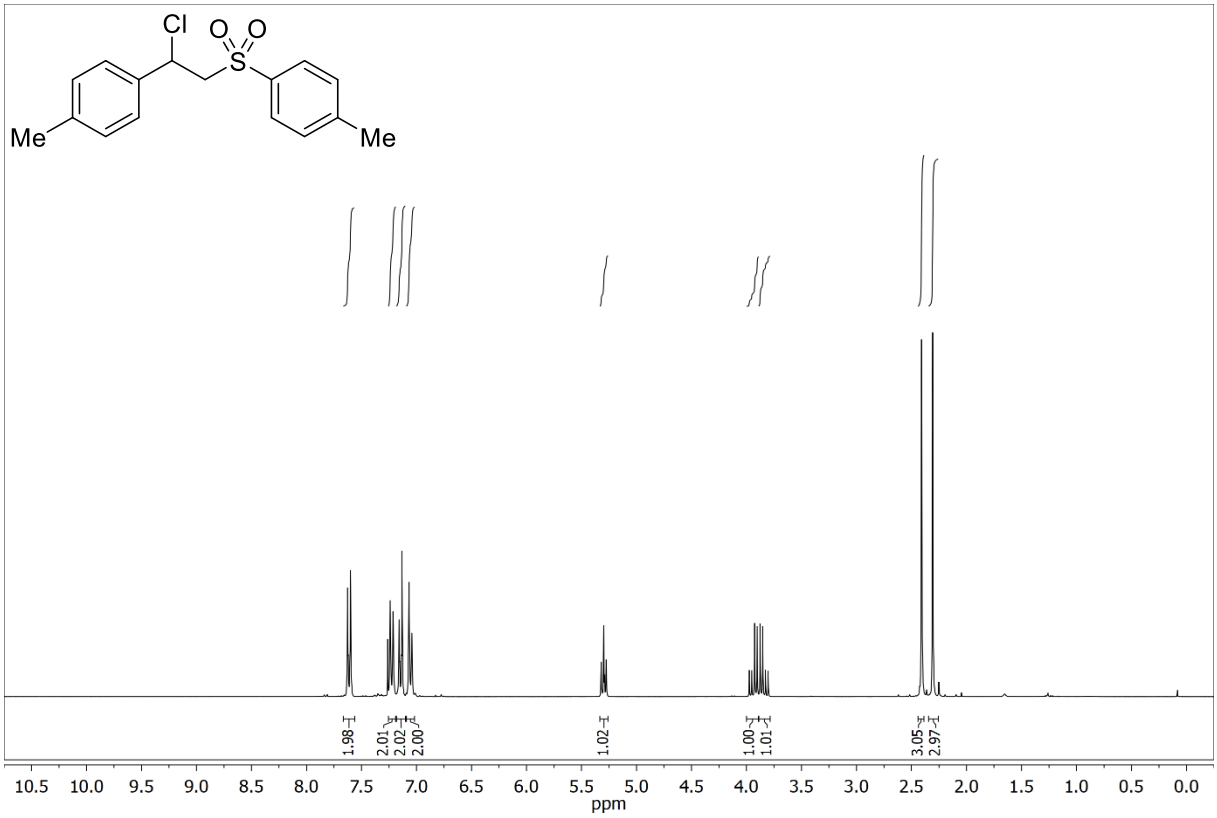
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

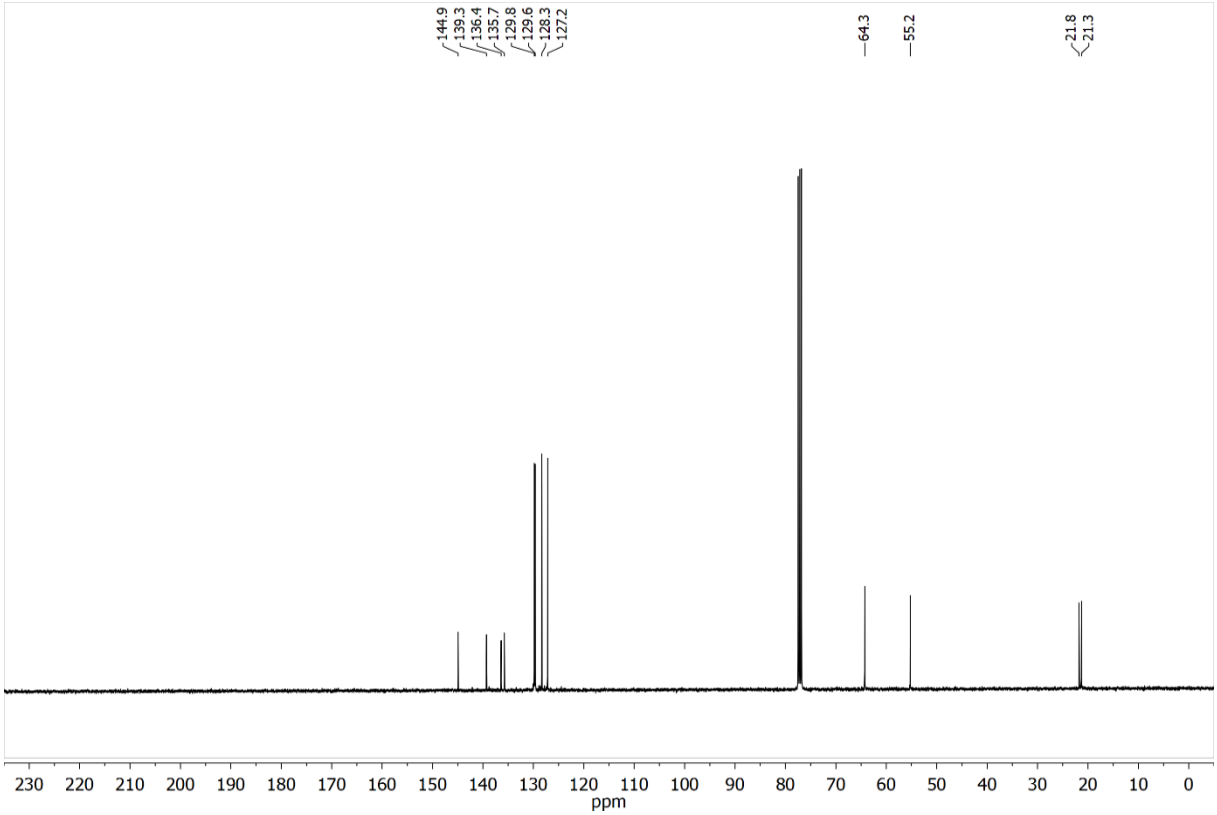
1-(1-chloro-2-tosylethyl)-3-methylbenzene (10h)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

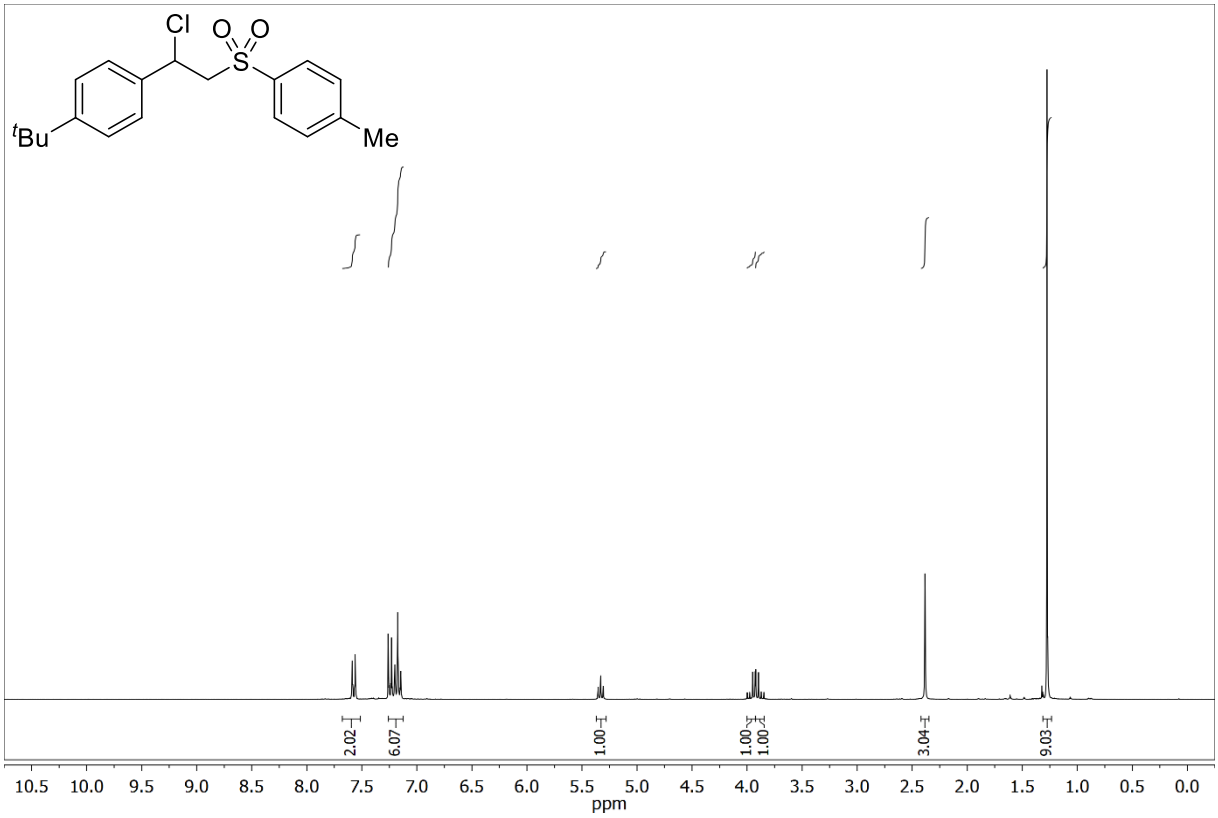
1-((2-chloro-2-(*p*-tolyl)ethyl)sulfonyl)-4-methylbenzene (10i//9c)

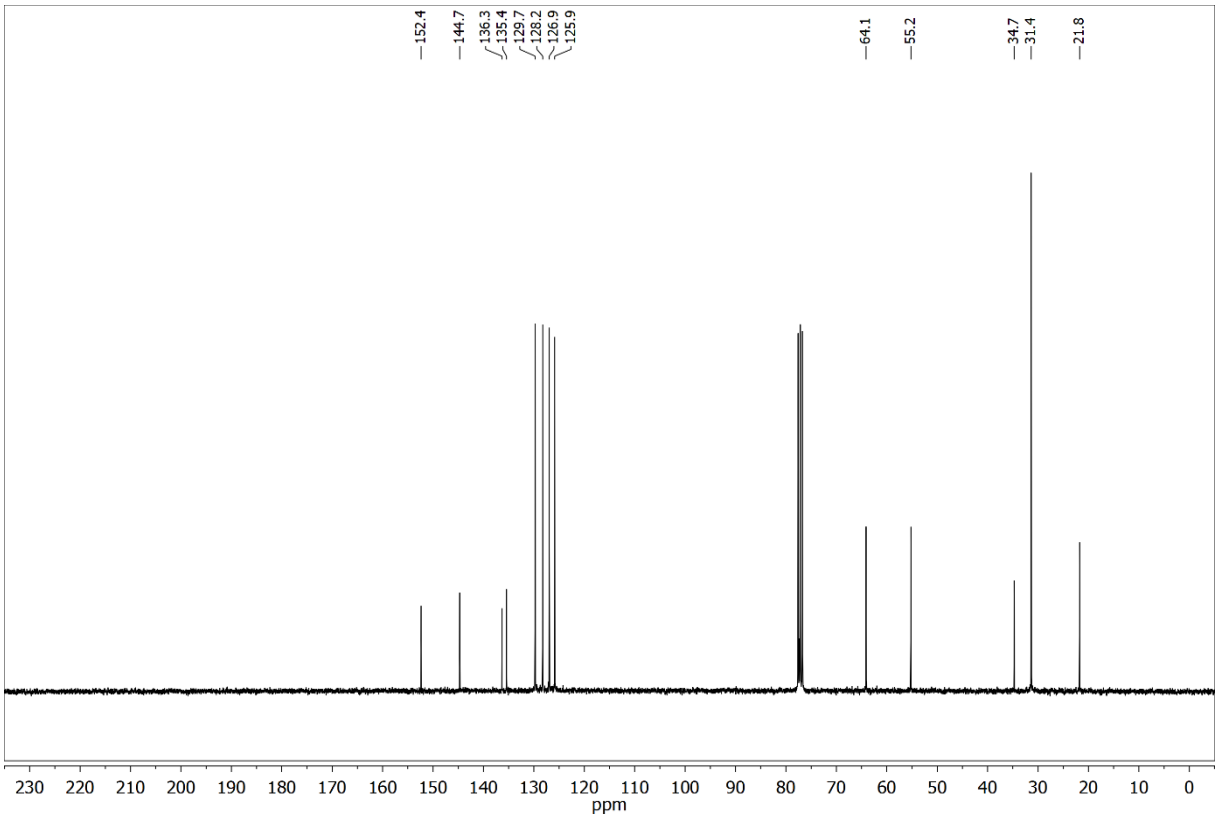




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

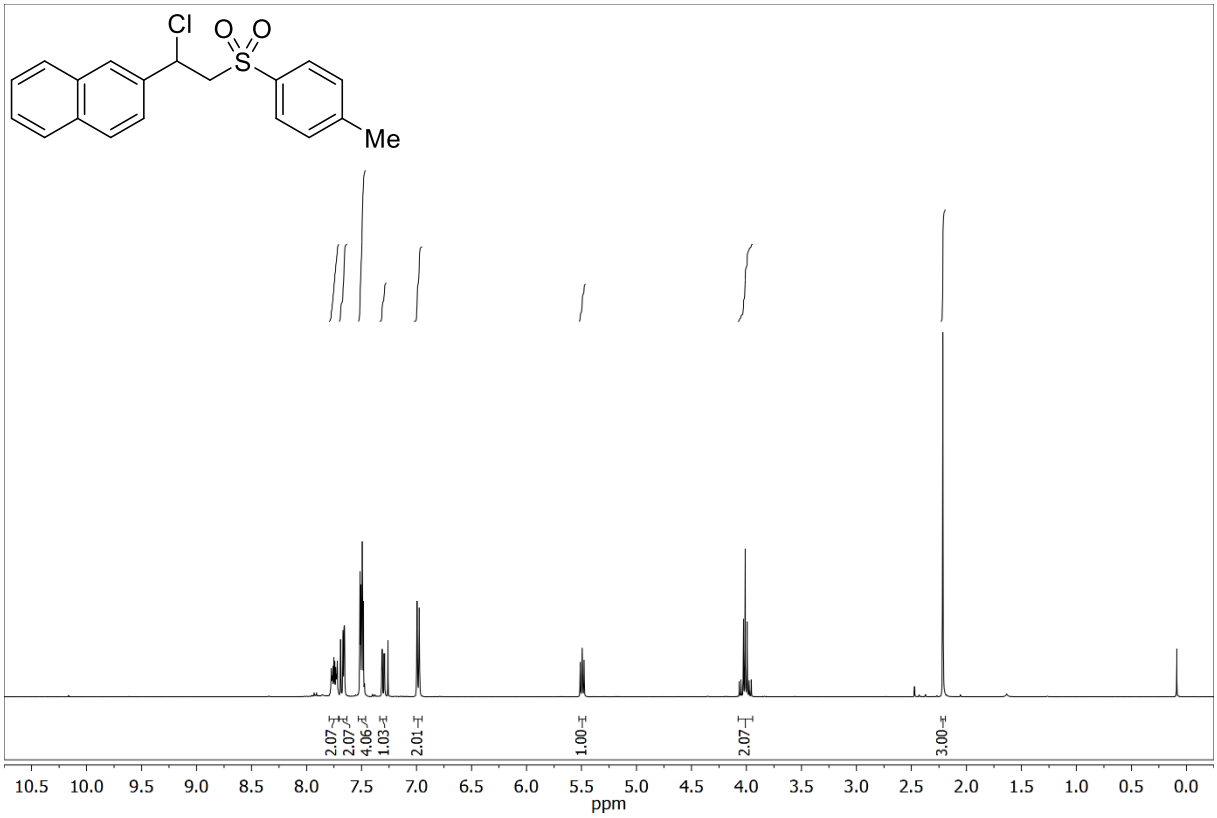
1-(*tert*-butyl)-4-(1-chloro-2-tosylethyl)benzene (10j)

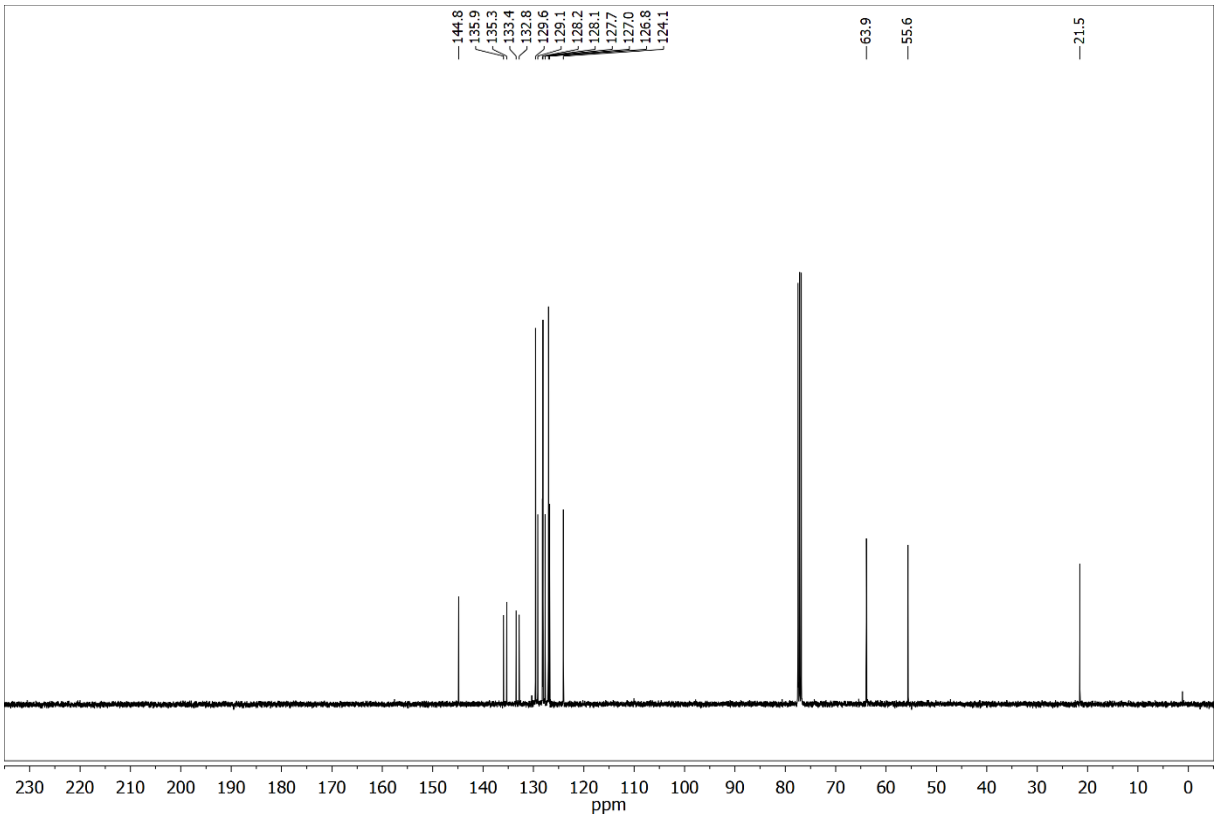




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

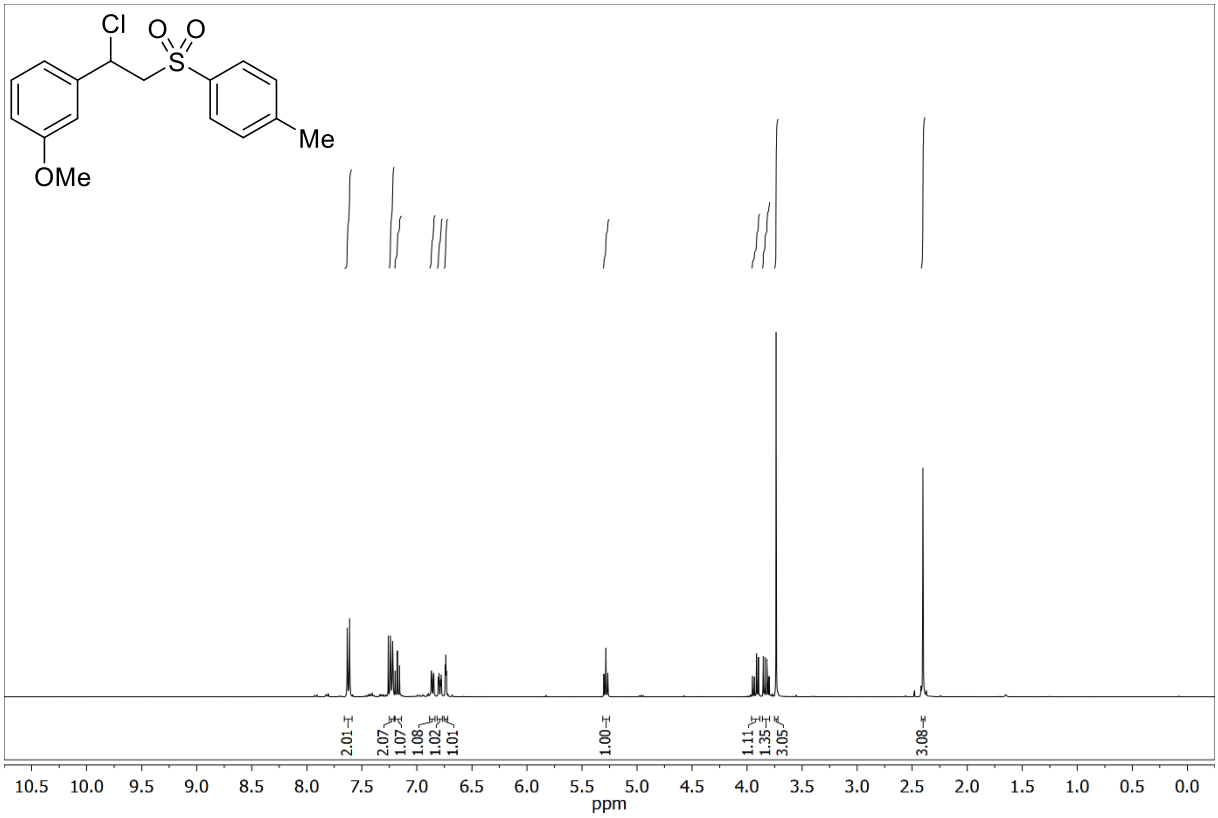
2-(1-chloro-2-tosylethyl)naphthalene (10k)

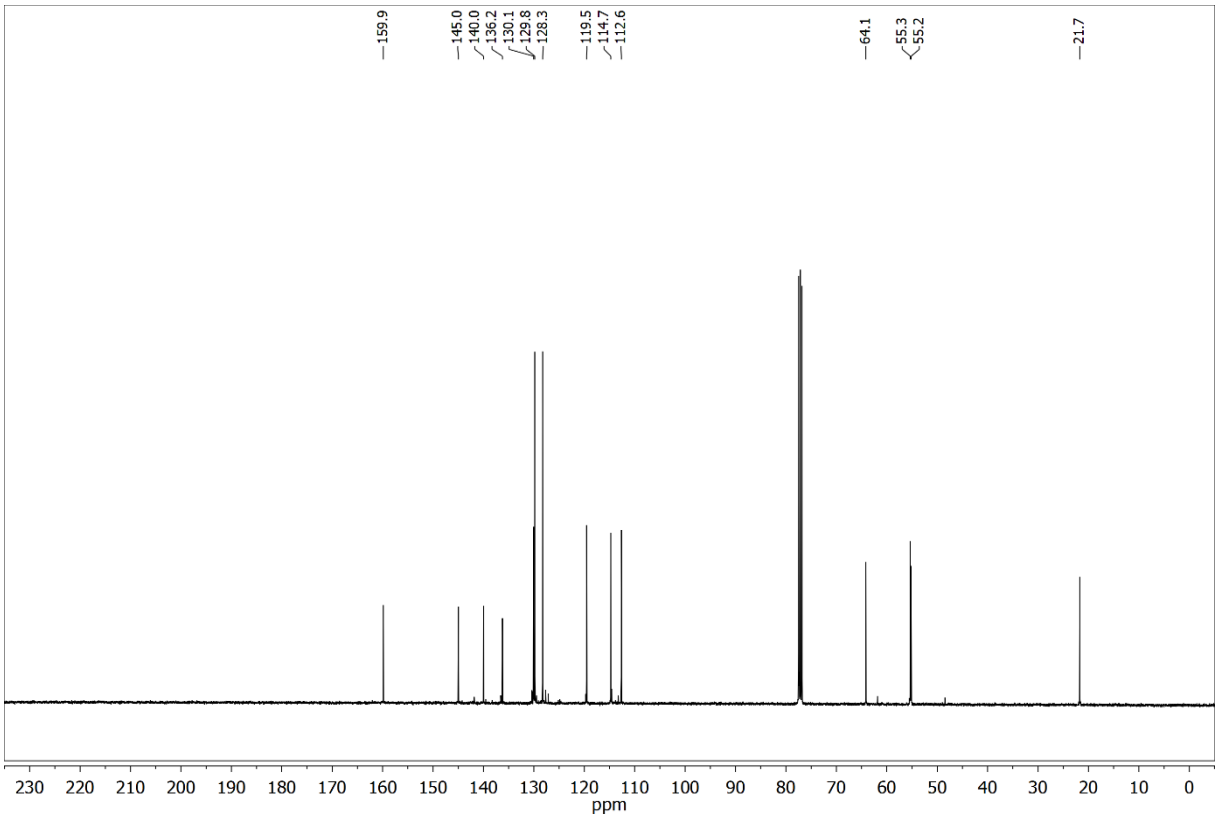




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

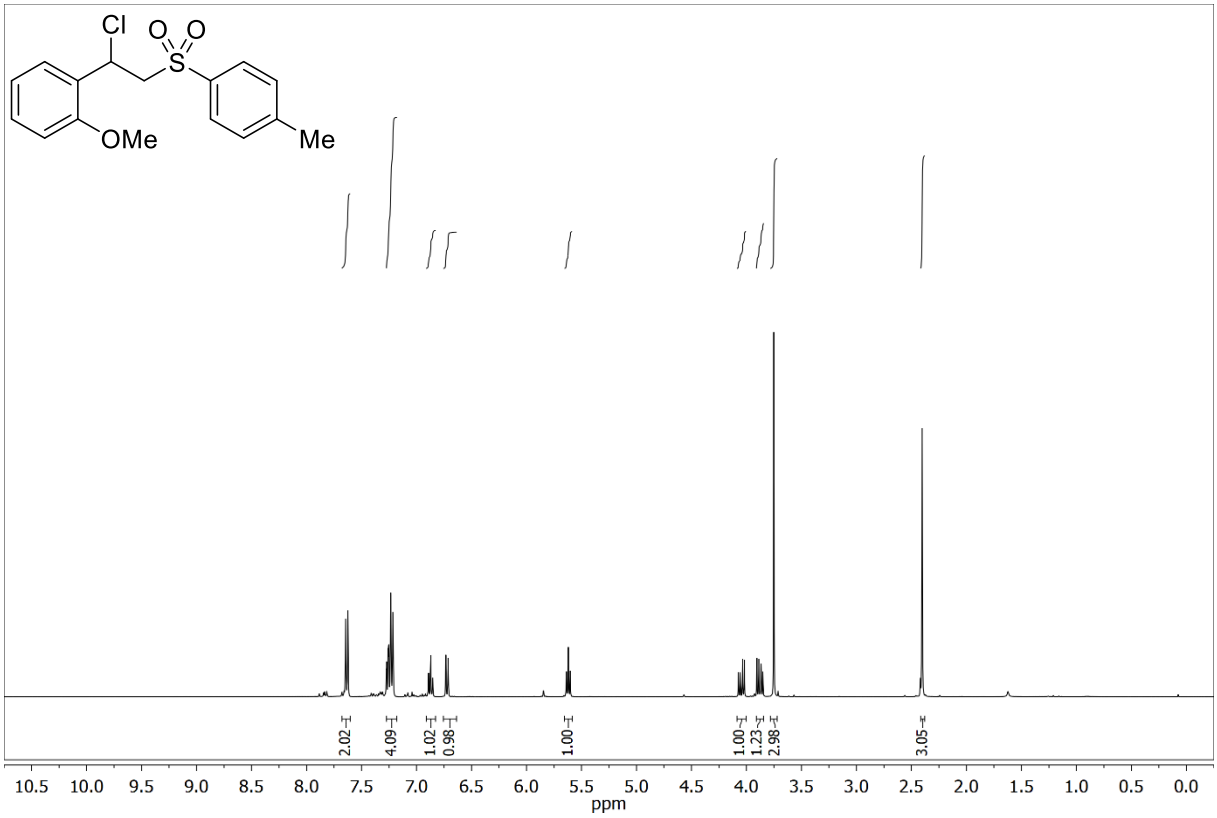
1-(1-chloro-2-tosylethyl)-3-methoxybenzene (10m)

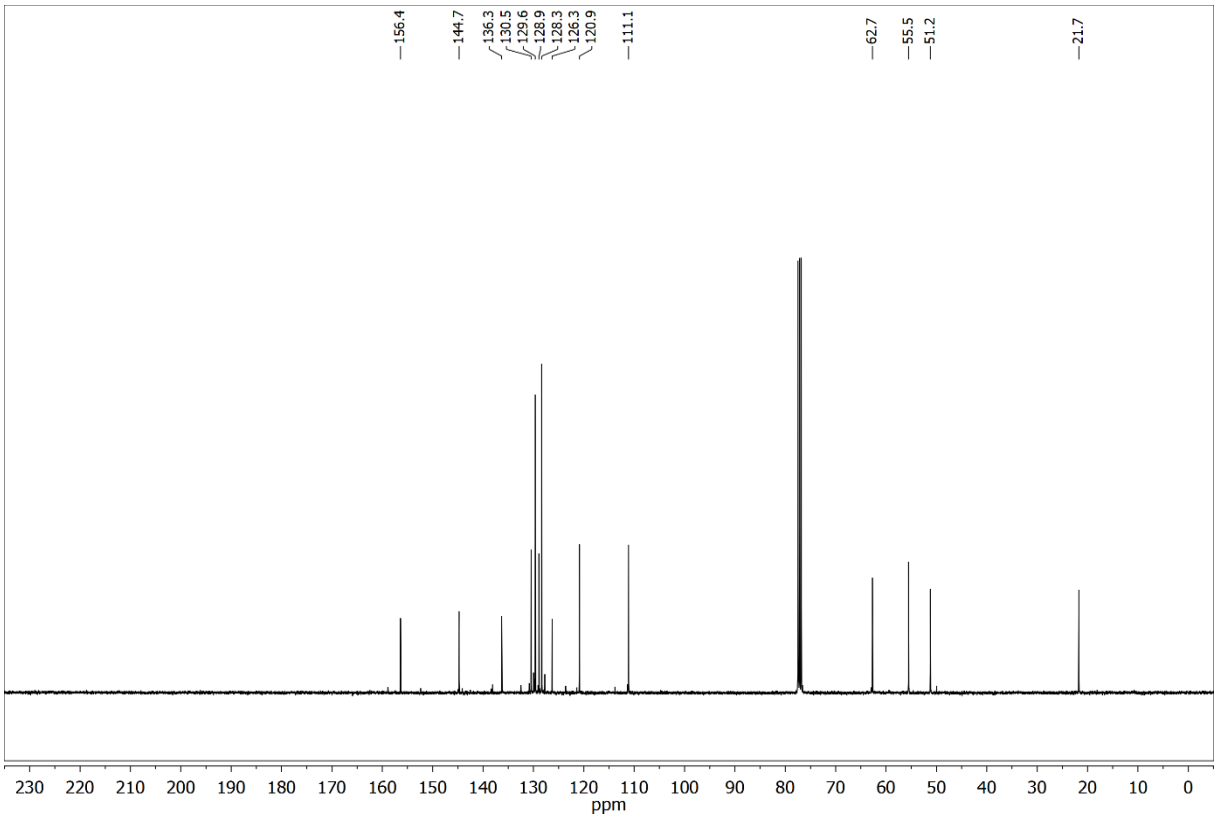




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

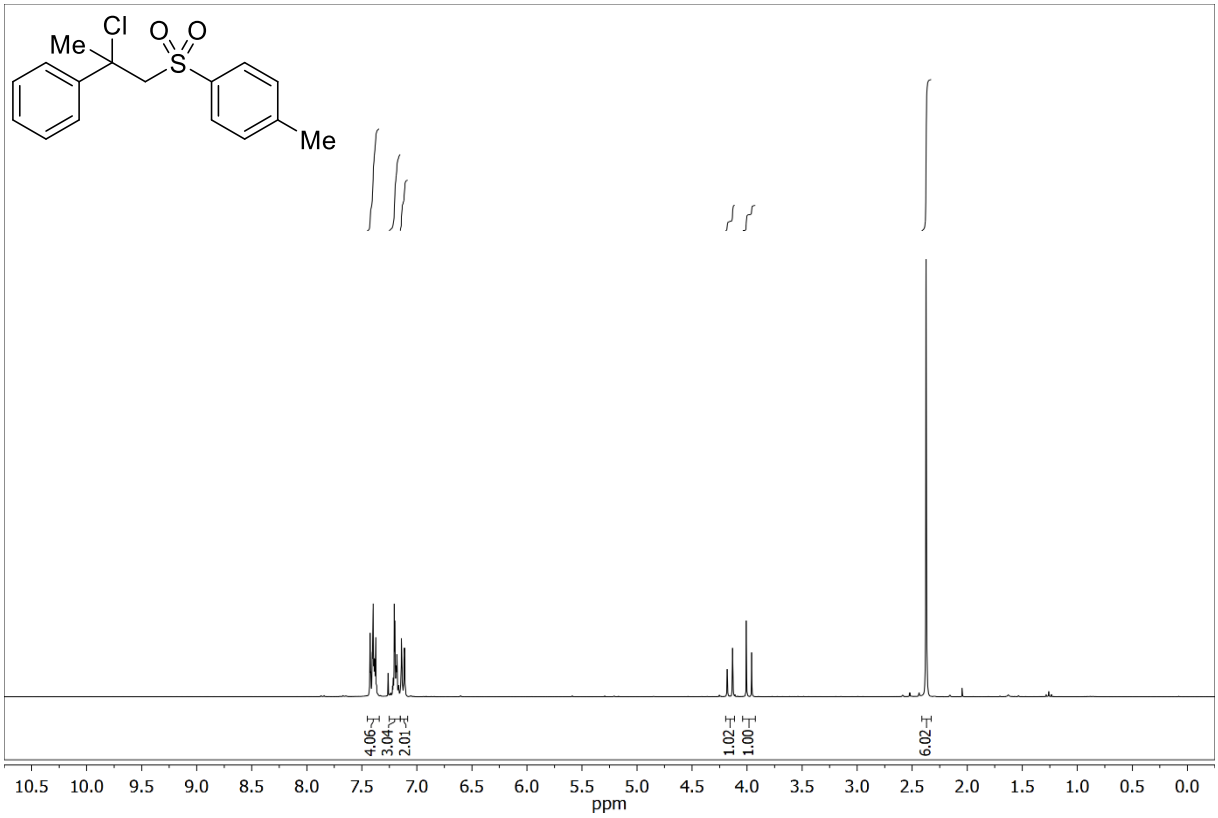
1-(1-chloro-2-tosylethyl)-2-methoxybenzene (10n)

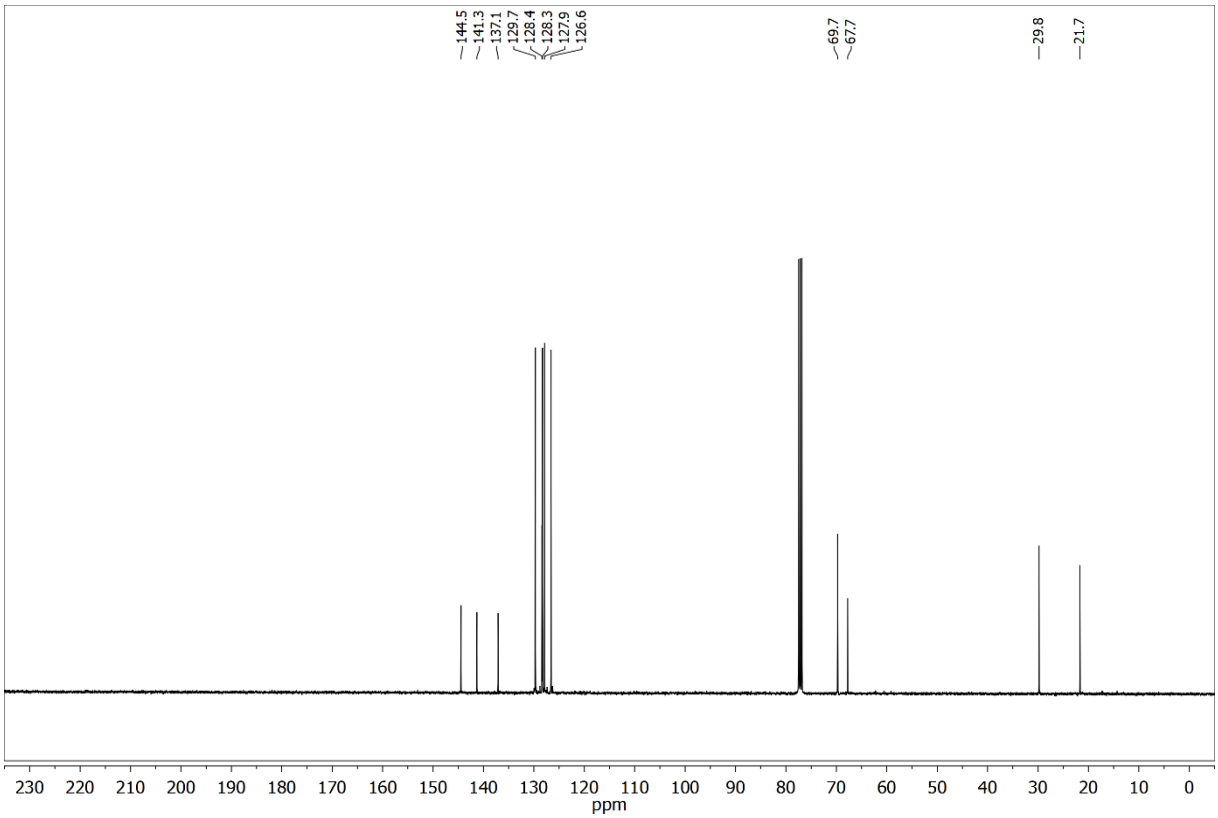




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

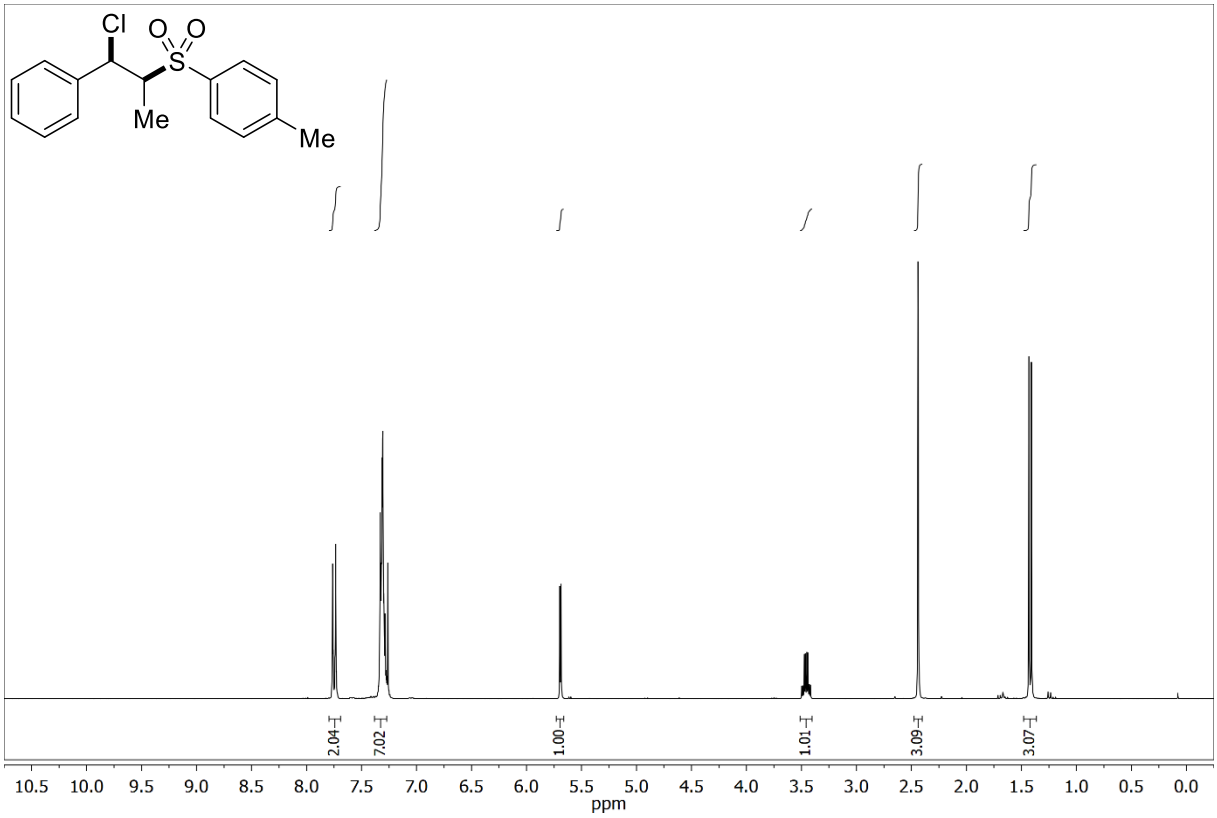
1-((2-chloro-2-phenylpropyl)sulfonyl)-4-methylbenzene (10o)

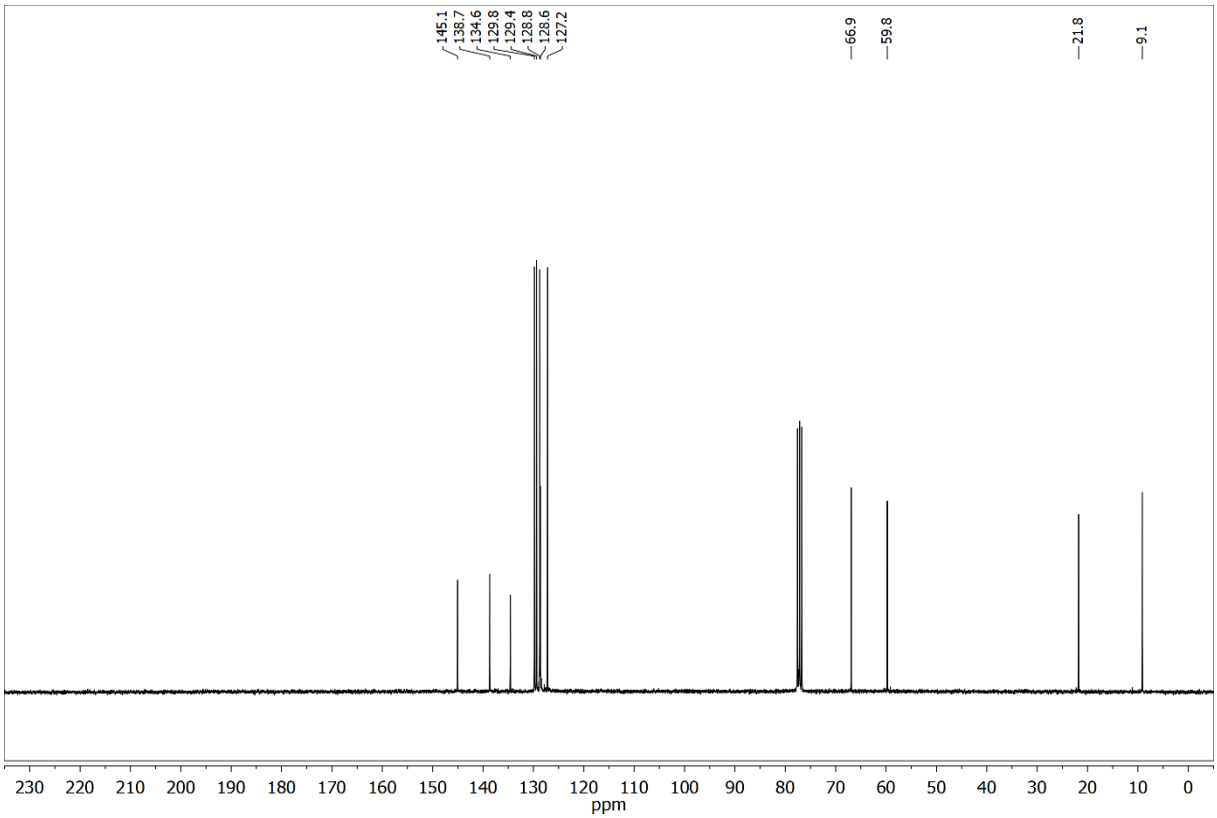




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

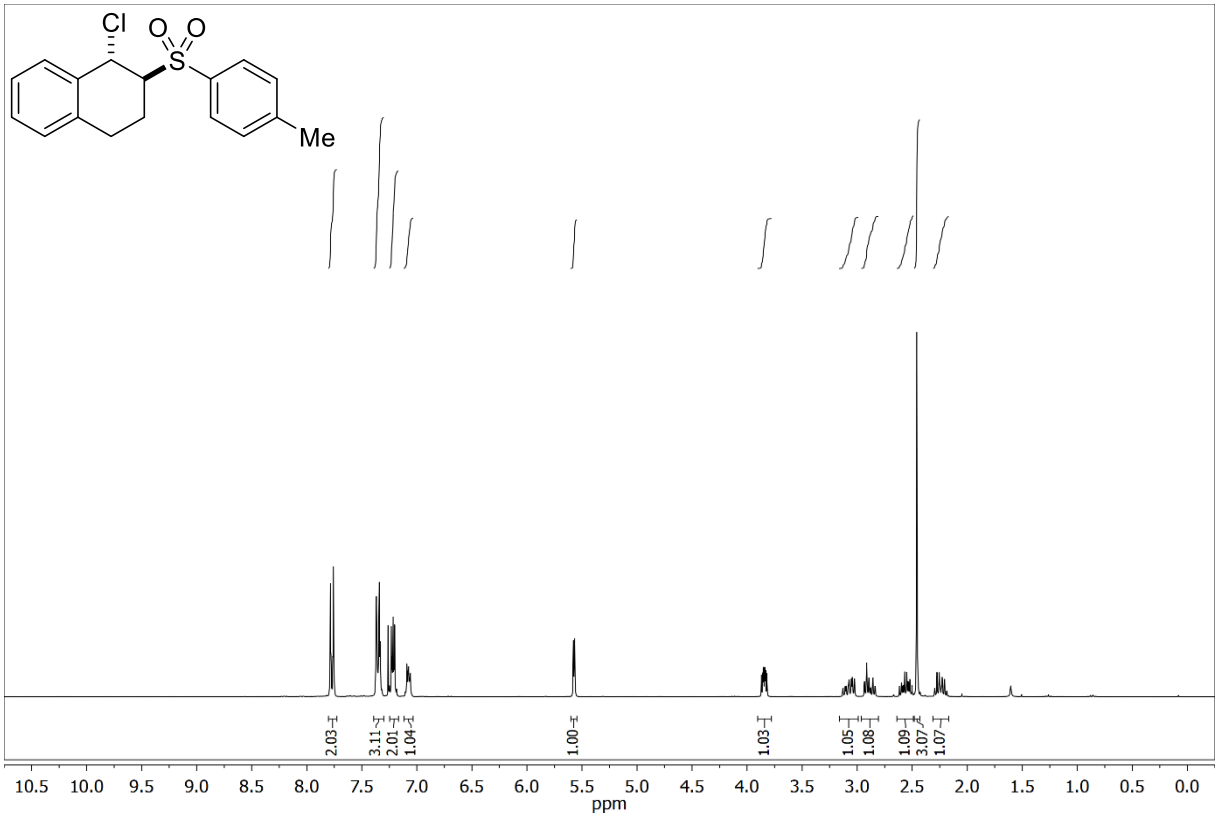
***syn*-1-((1-chloro-1-phenylpropan-2-yl)sulfonyl)-4-methylbenzene (10p)**

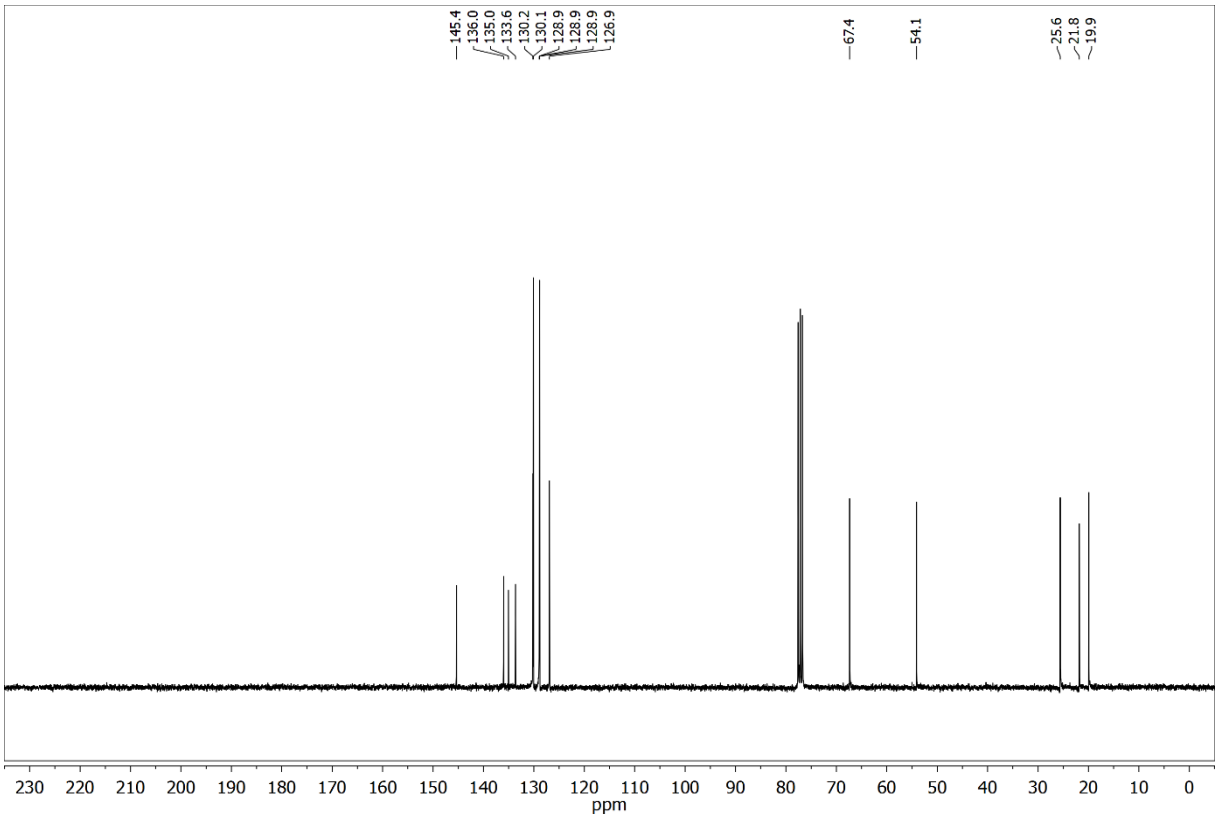




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

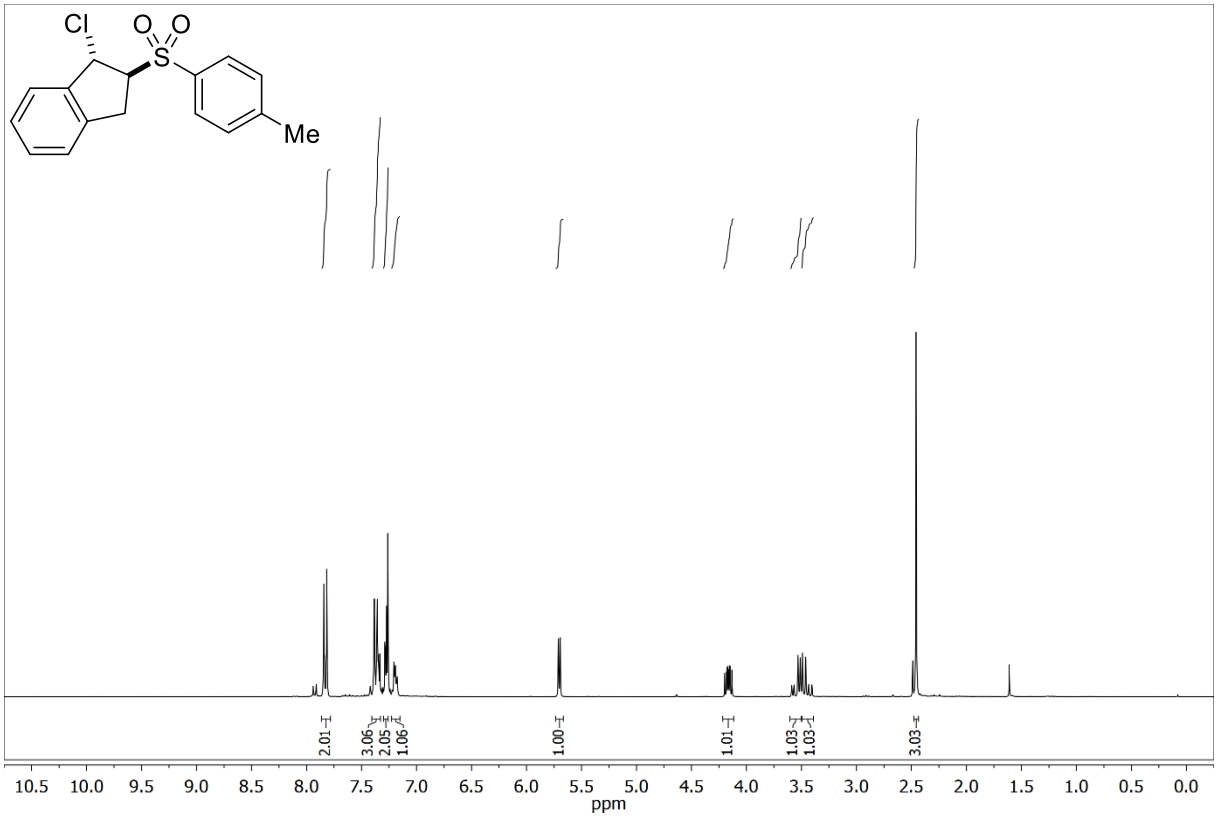
***trans*-1-chloro-2-tosyl-1,2,3,4-tetrahydronaphthalene (10q)**

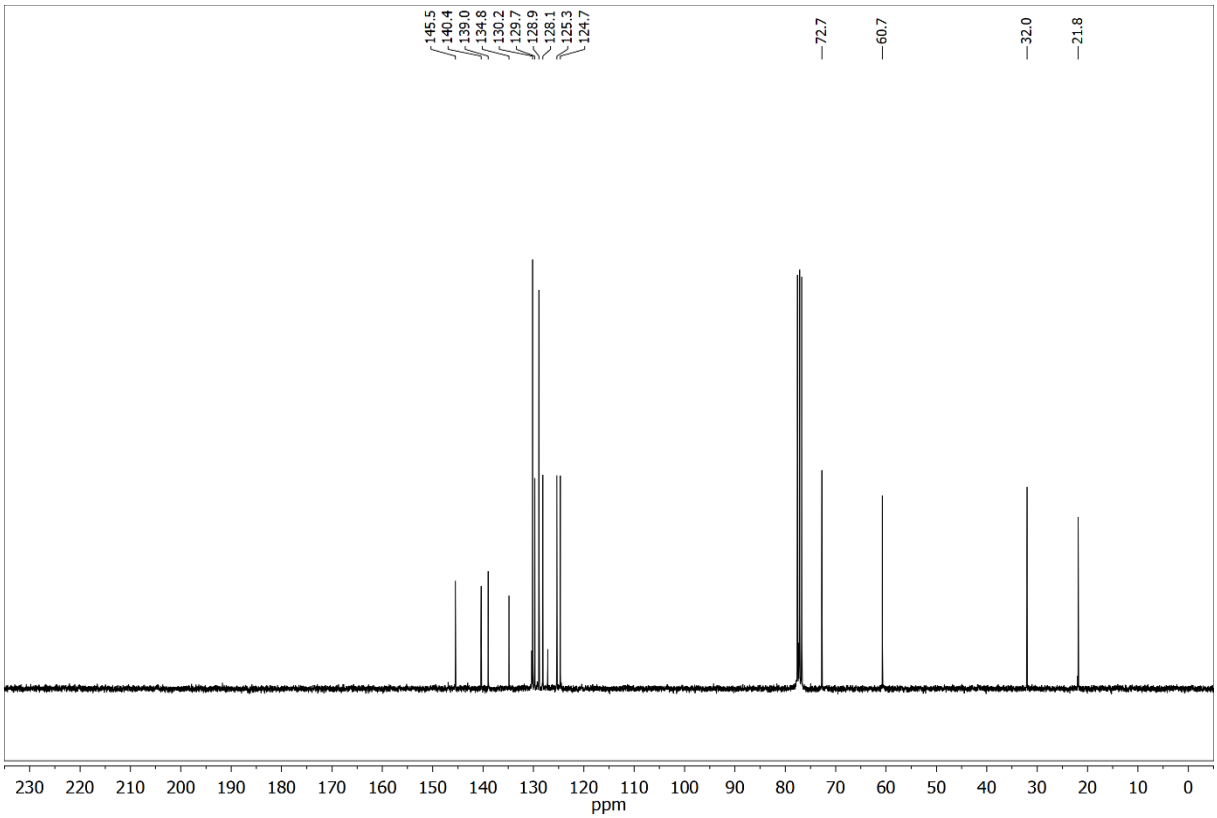




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

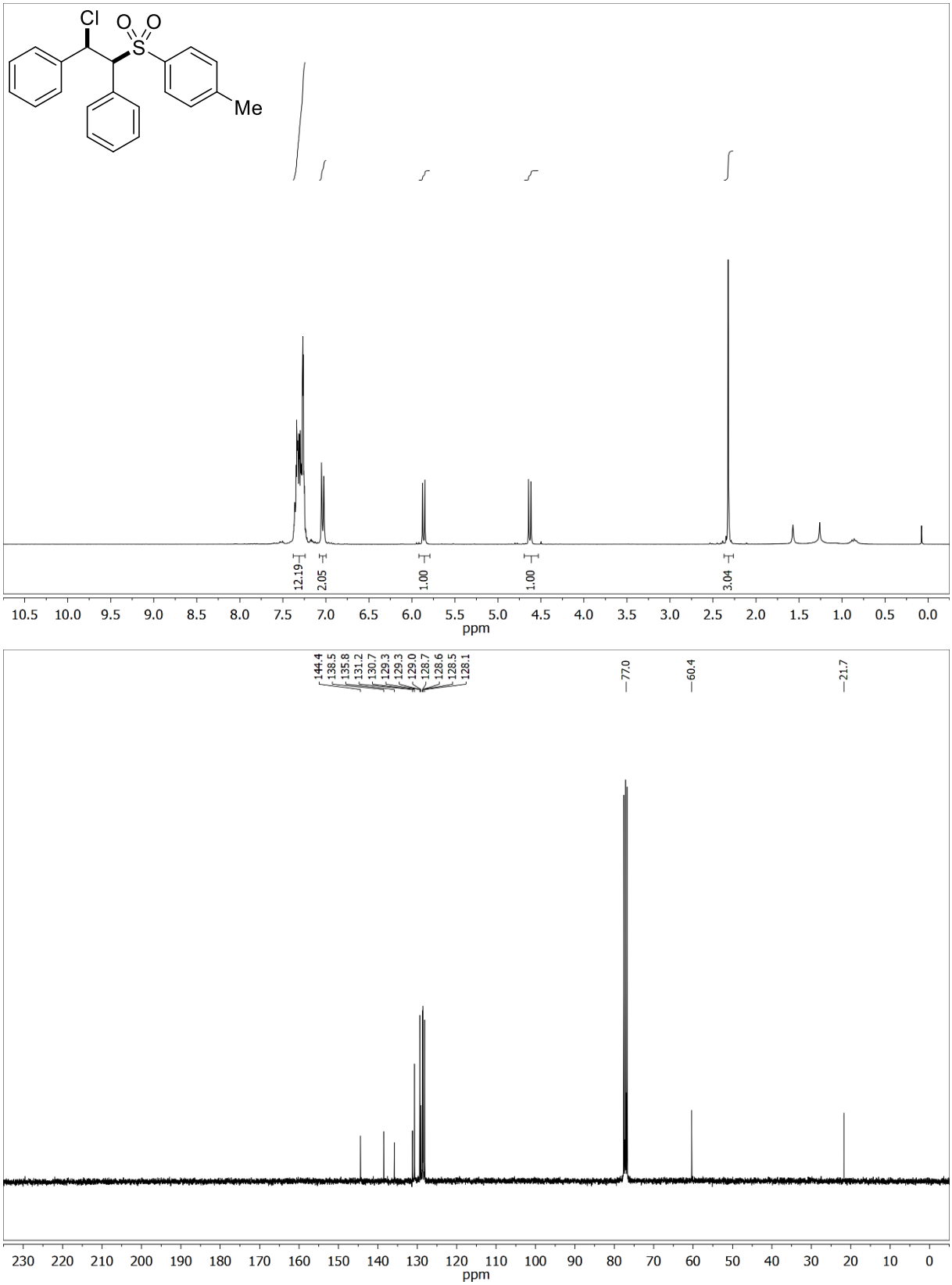
***trans*-1-chloro-2-tosyl-2,3-dihydro-1*H*-indene (10r)**





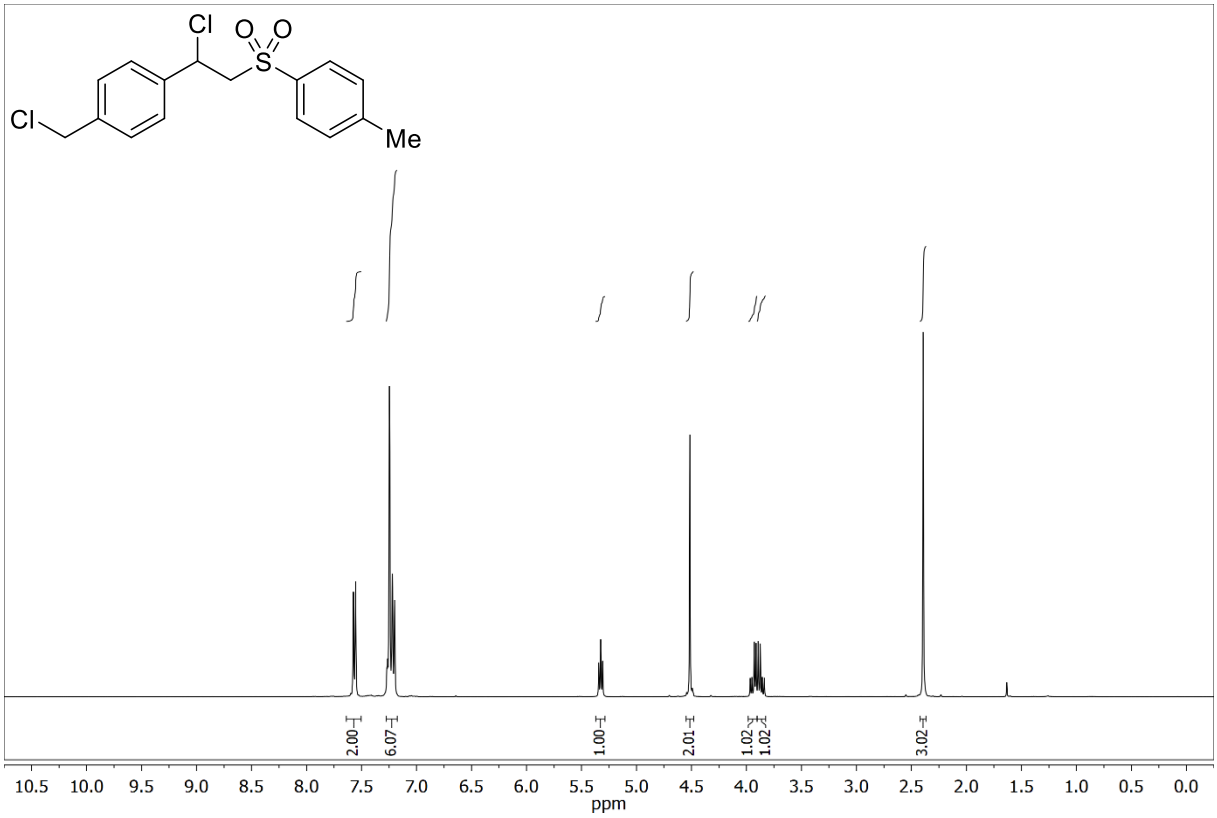
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

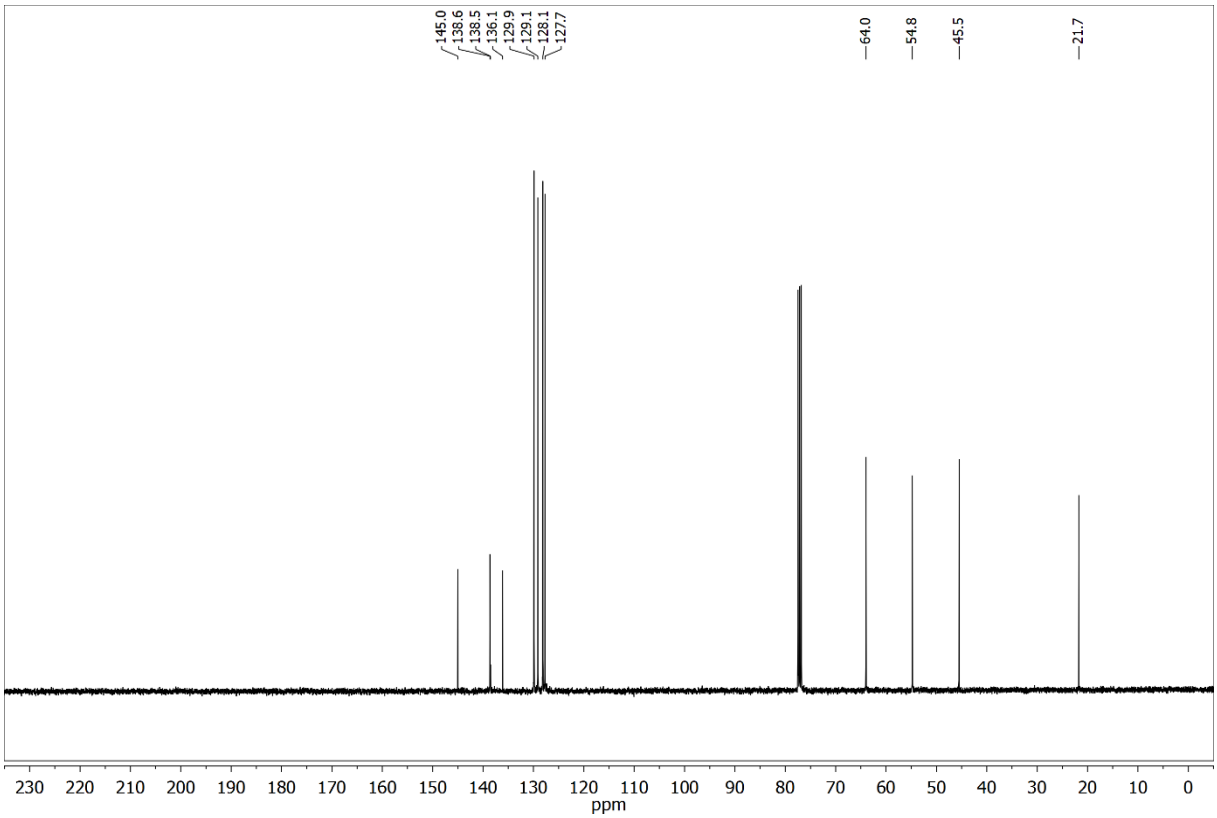
***syn*-(1-chloro-2-tosylethane-1,2-diyl)dibenzene (10s)**



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

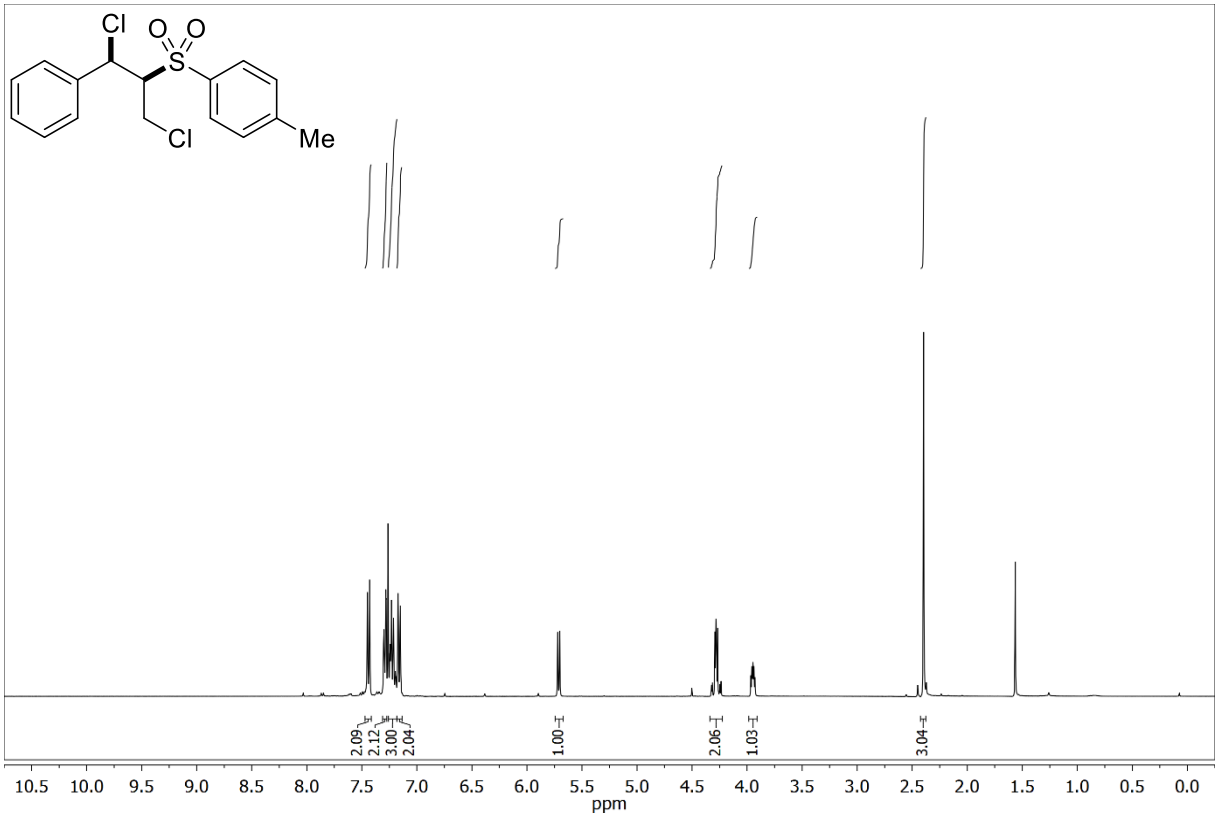
1-((2-chloro-2-(4-(chloromethyl)phenyl)ethyl)sulfonyl)-4-methylbenzene (10t)

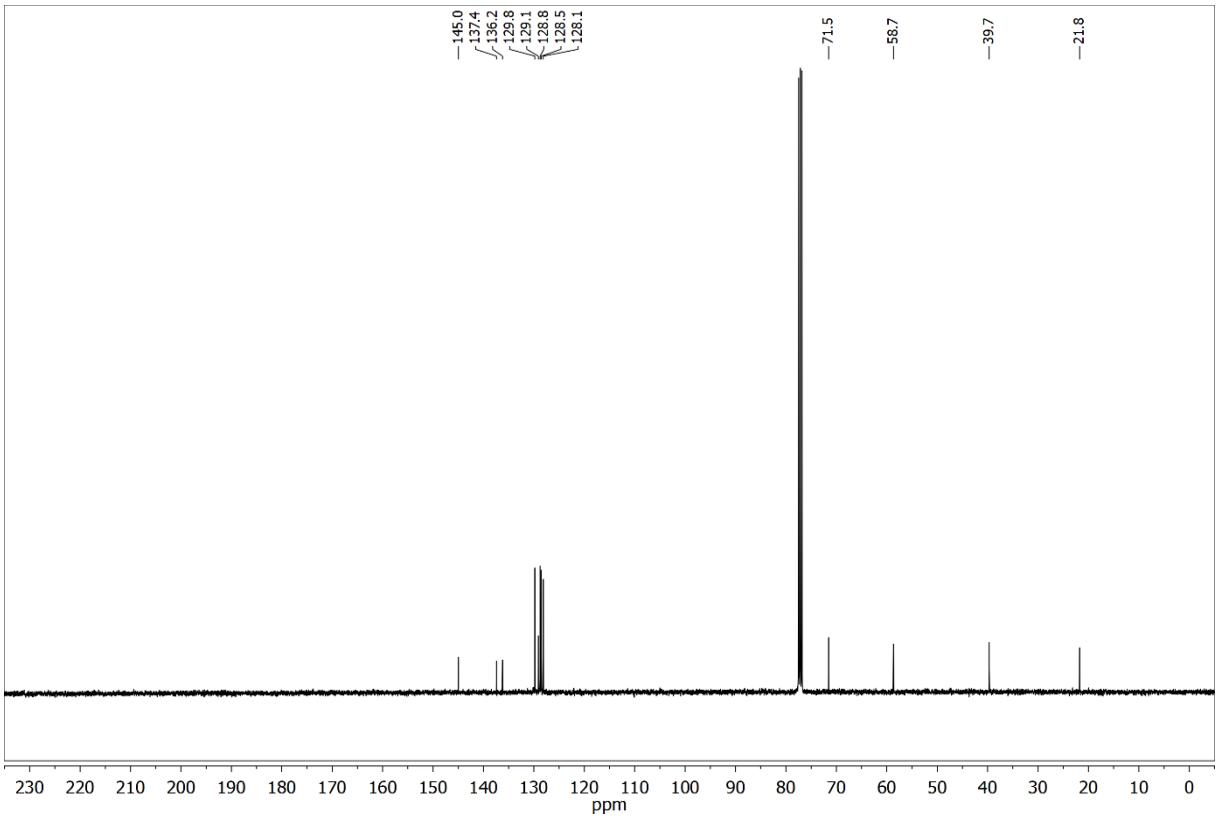




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

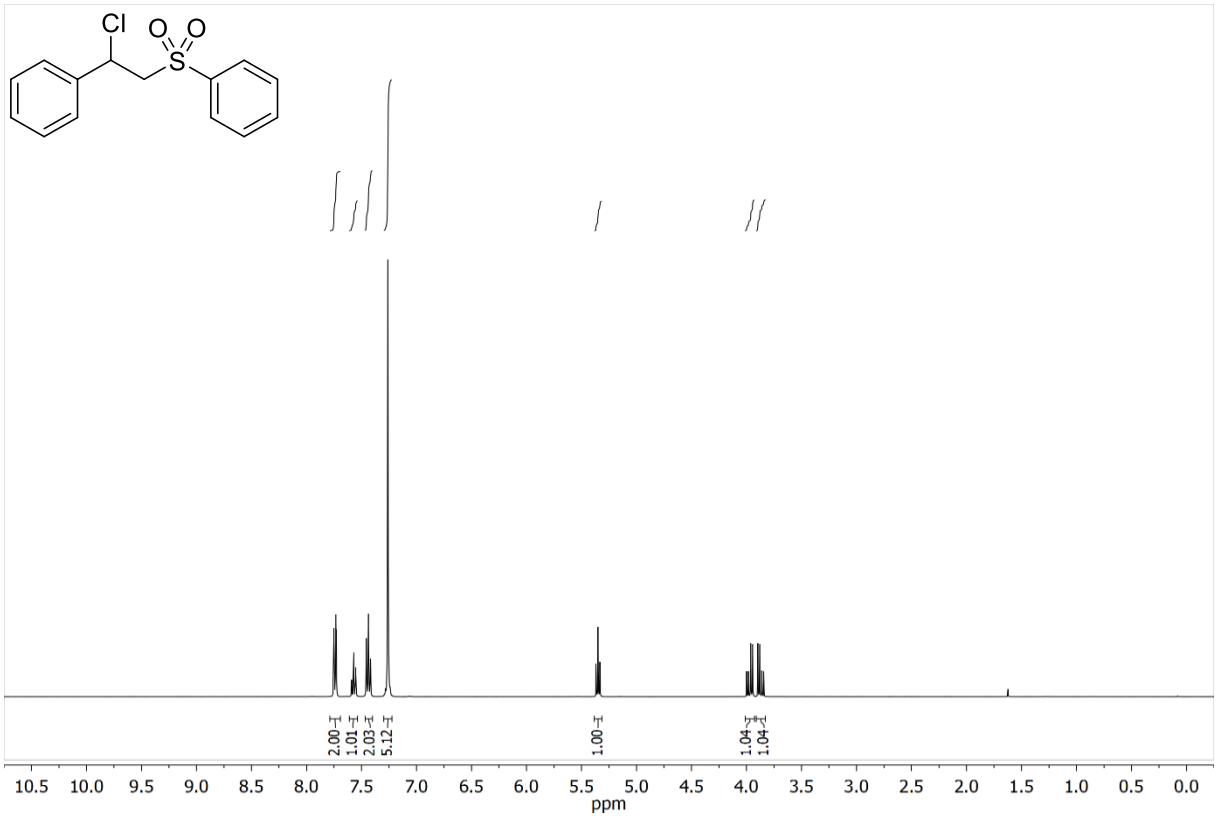
syn-1-((1,3-dichloro-1-phenylpropan-2-yl)sulfonyl)-4-methylbenzene (10u)

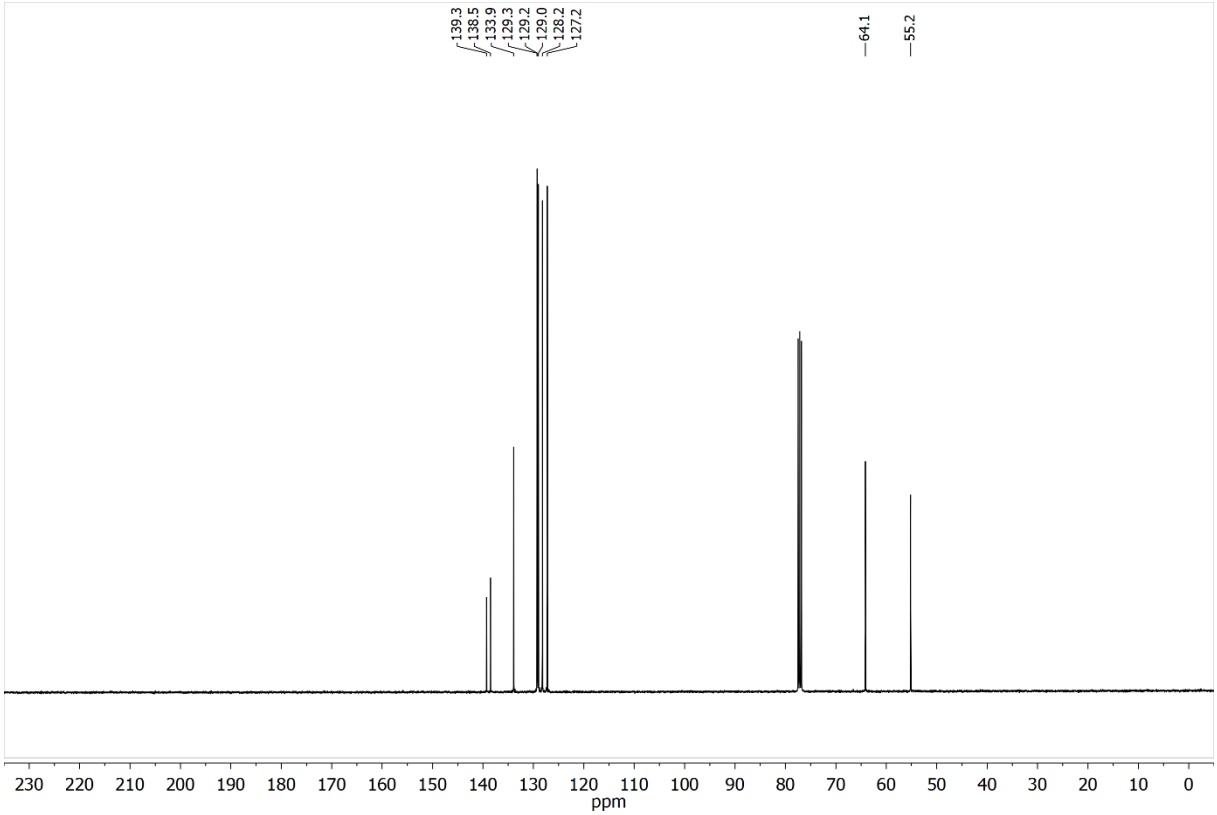




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

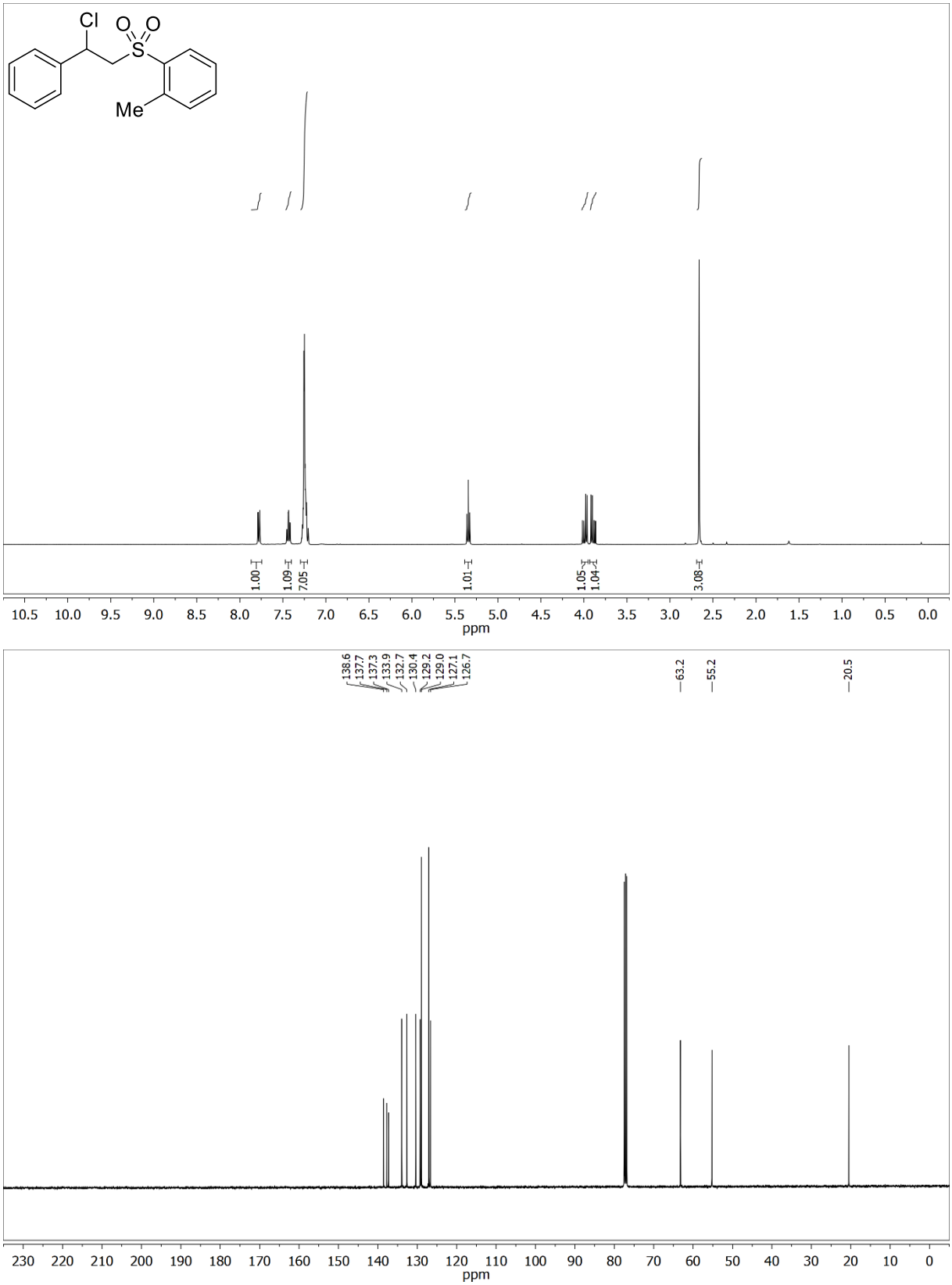
(1-chloro-2-(phenylsulfonyl)ethyl)benzene (10v//9d)





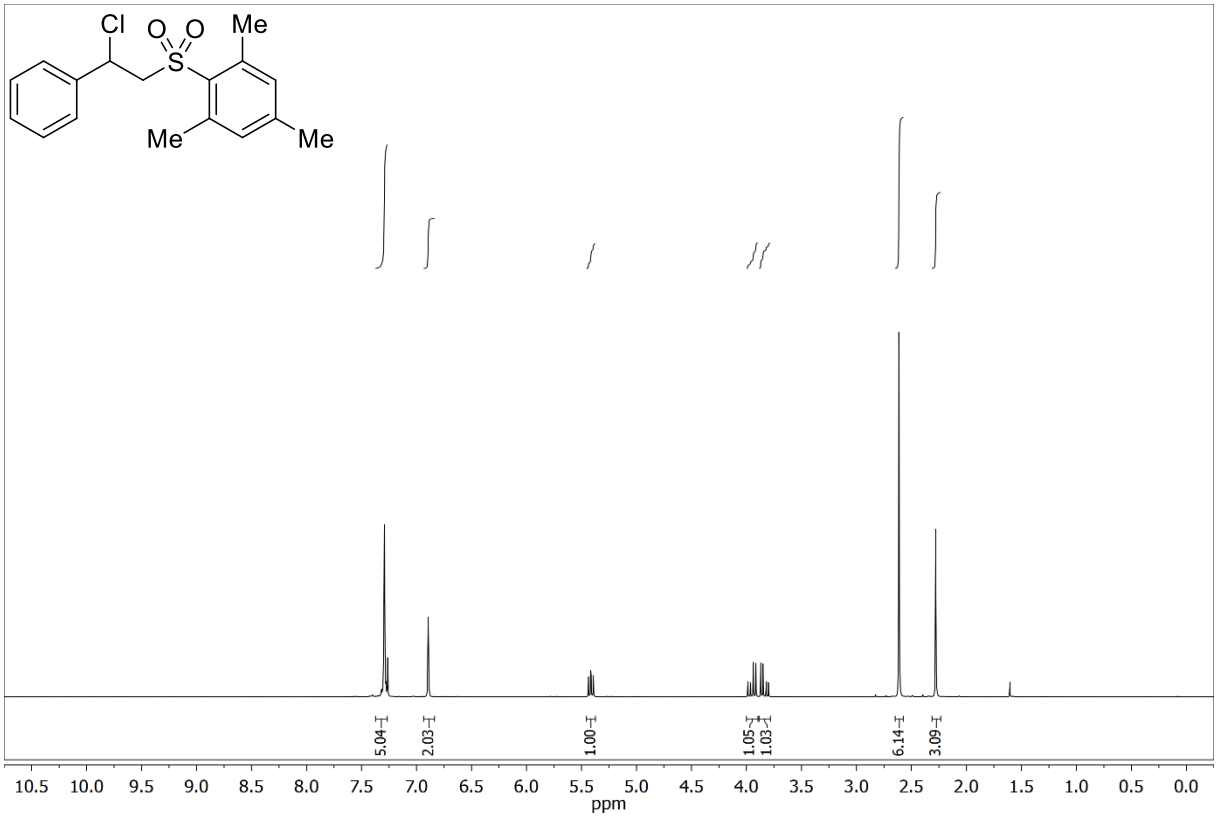
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

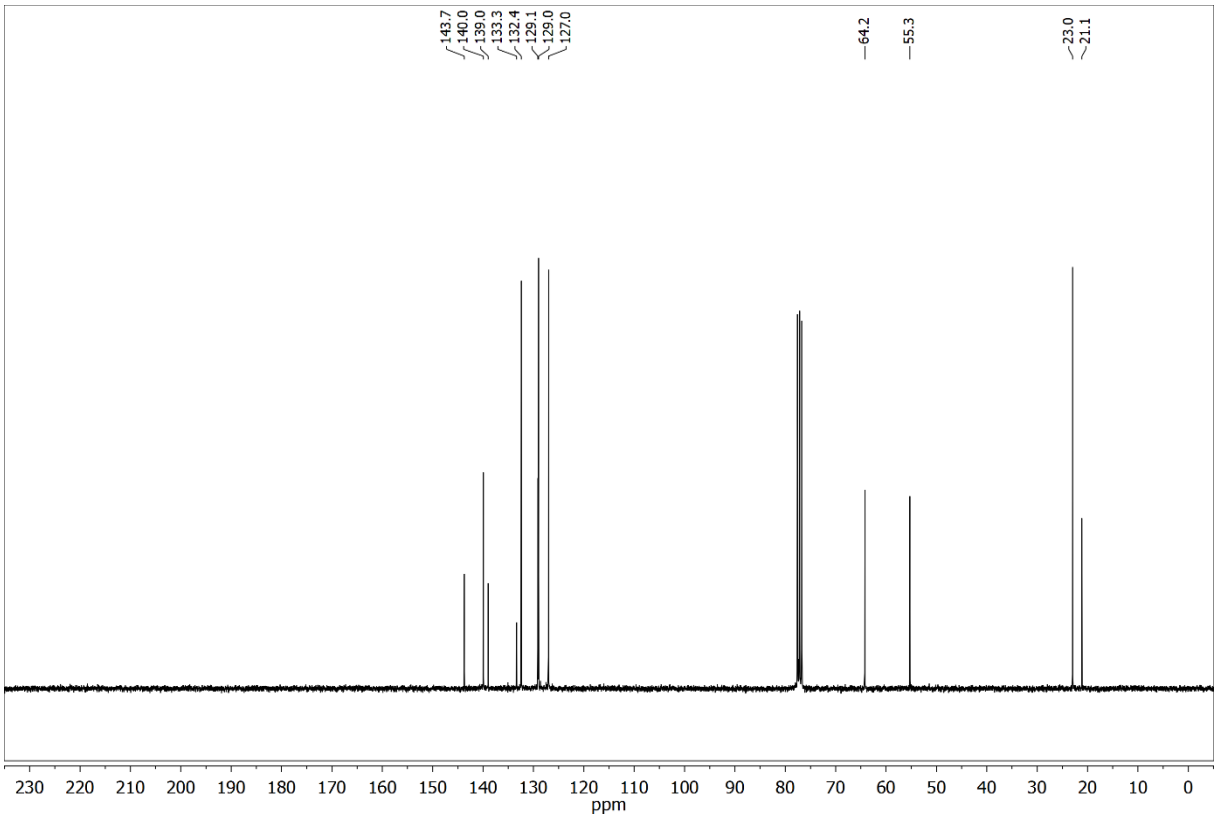
1-((2-chloro-2-phenylethyl)sulfonyl)-2-methylbenzene (10w)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

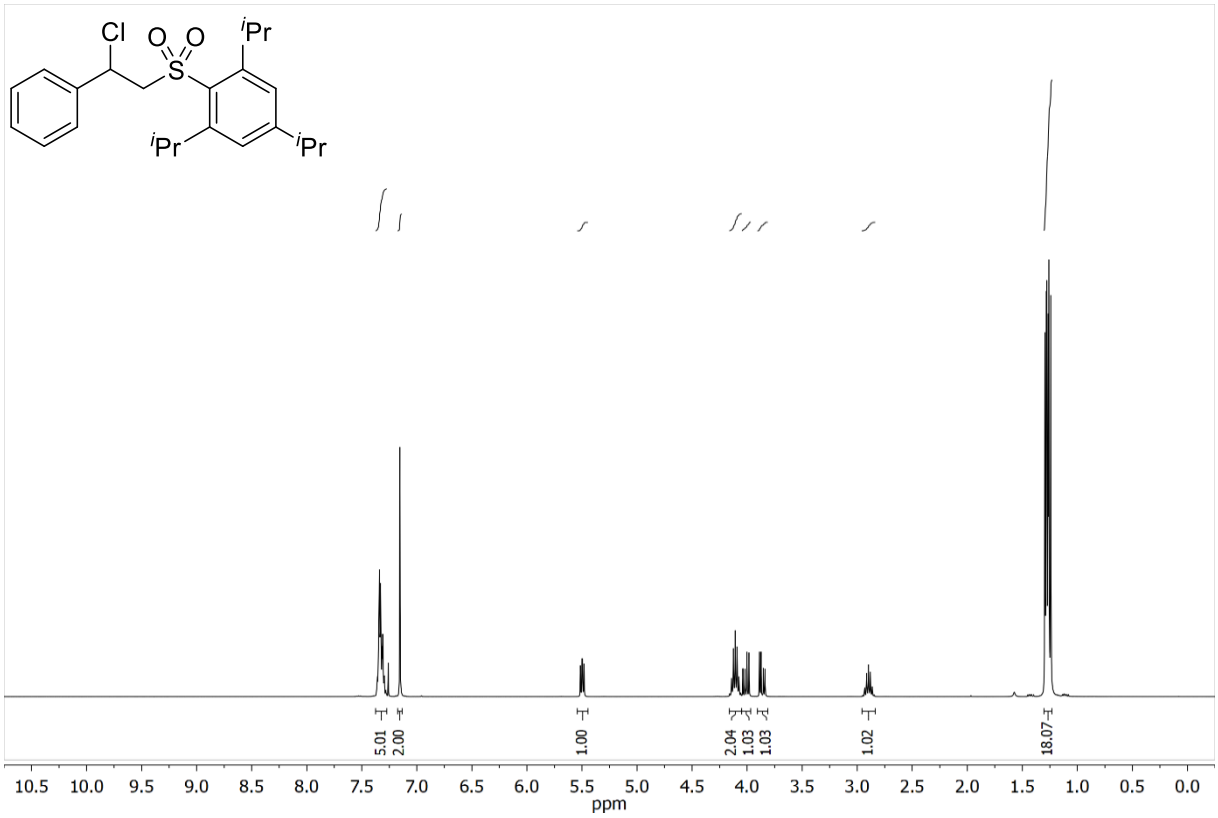
2-((2-chloro-2-phenylethyl)sulfonyl)-1,3,5-trimethylbenzene (10x)

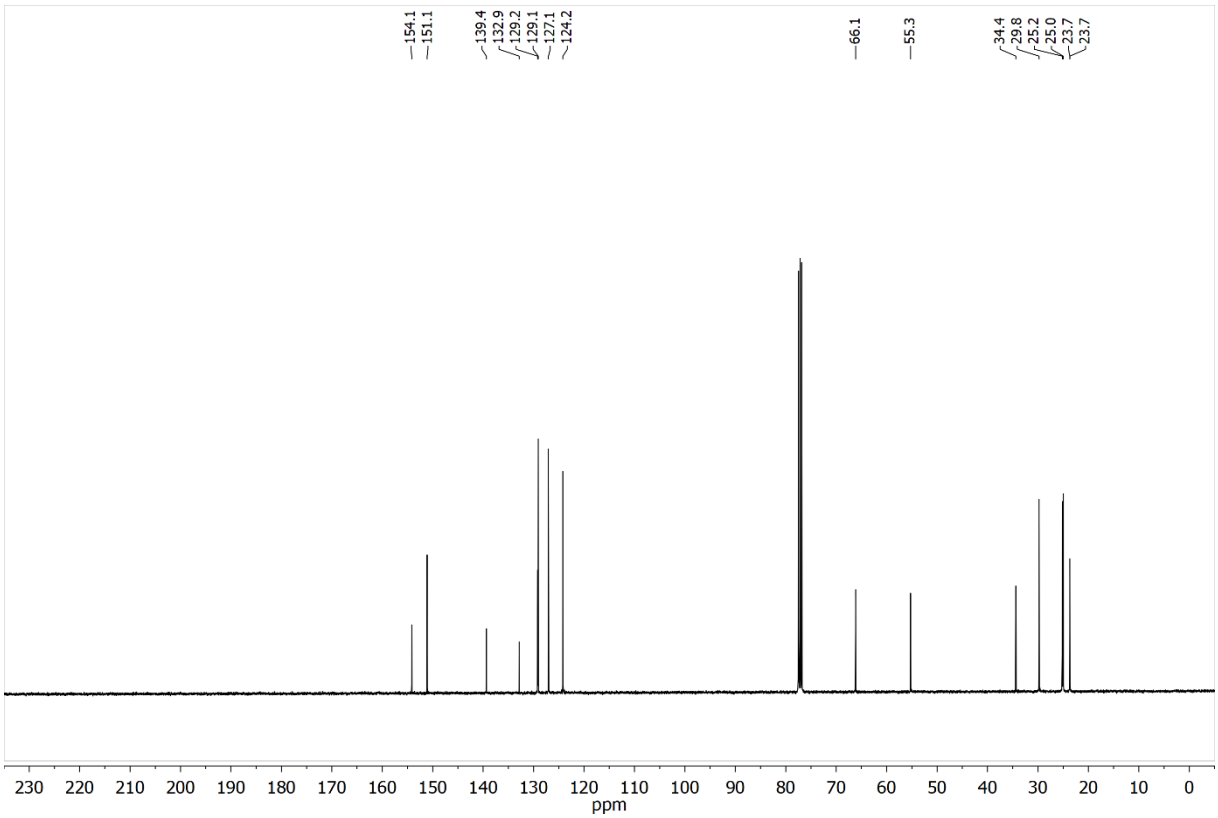




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

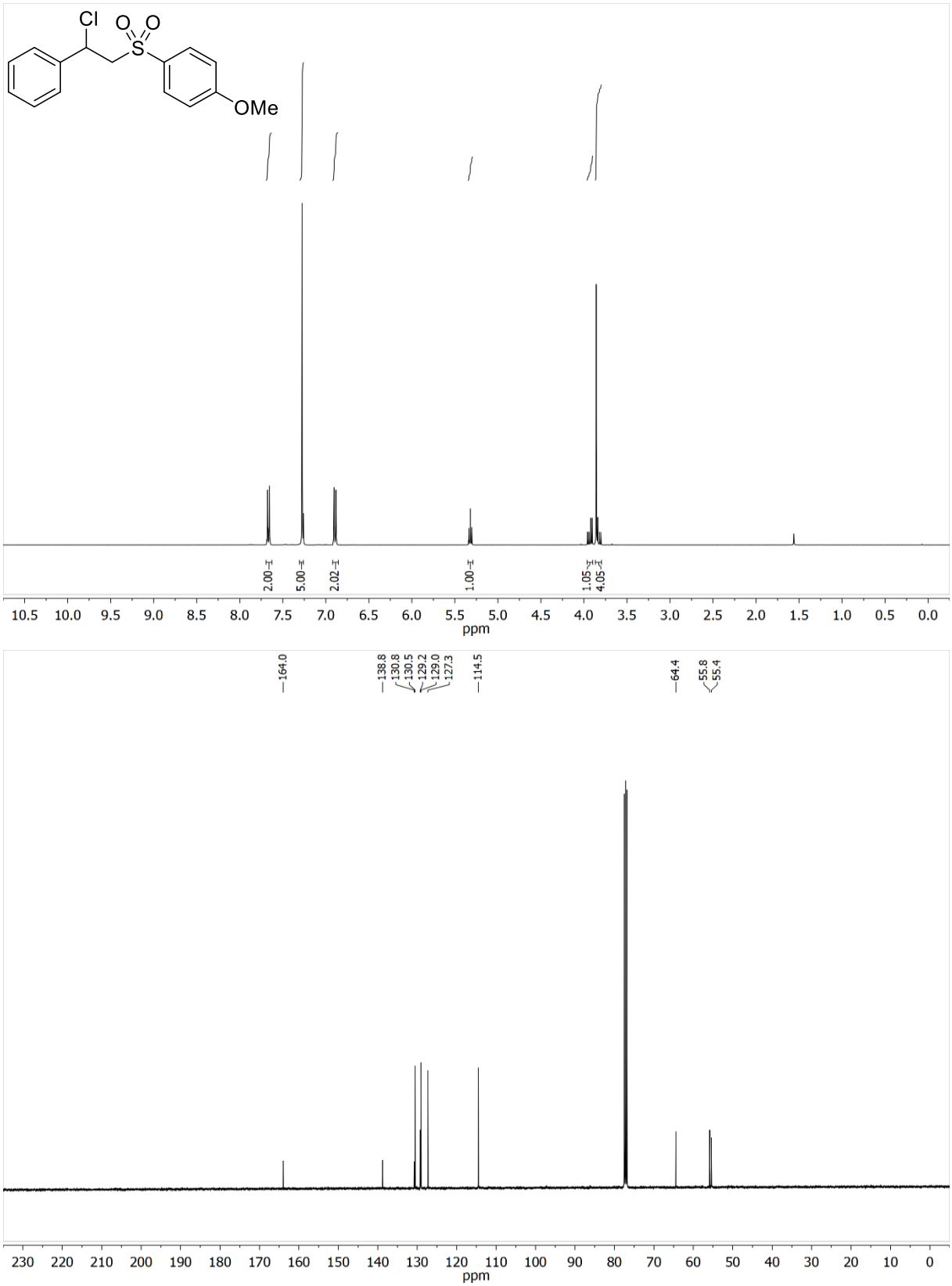
2-((2-chloro-2-phenylethyl)sulfonyl)-1,3,5-triisopropylbenzene (10y//9h)





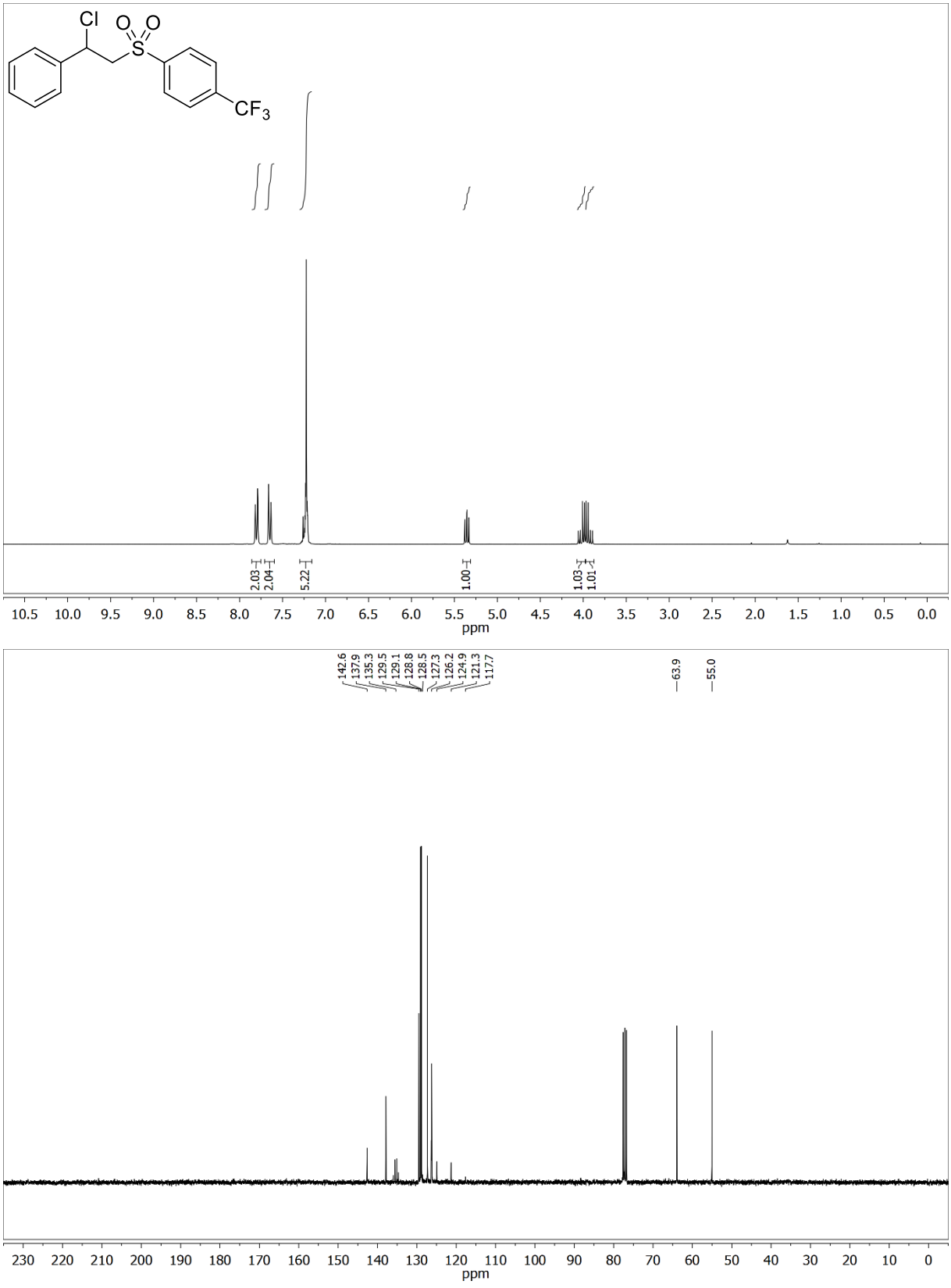
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

1-((2-chloro-2-phenylethyl)sulfonyl)-4-methoxybenzene (10z//9e)

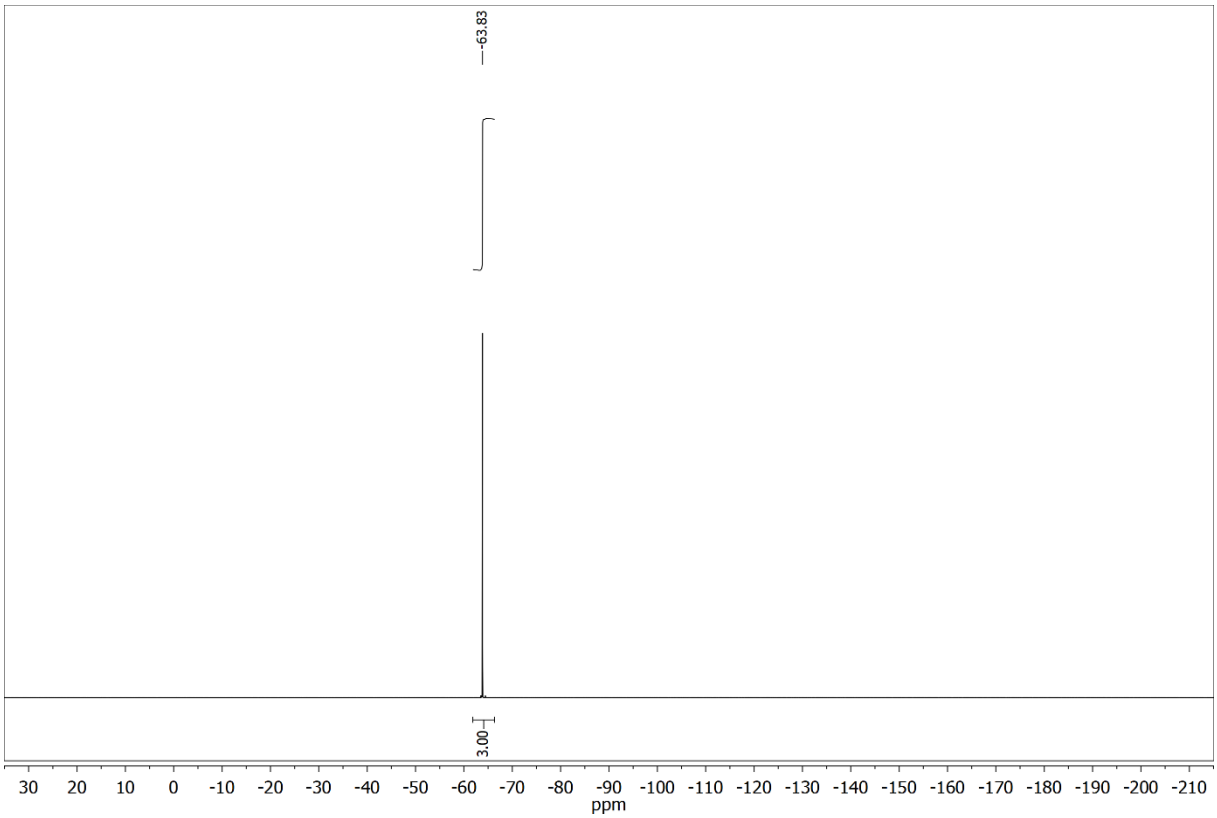


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

1-((2-chloro-2-phenylethyl)sulfonyl)-4-(trifluoromethyl)benzene (10aa)

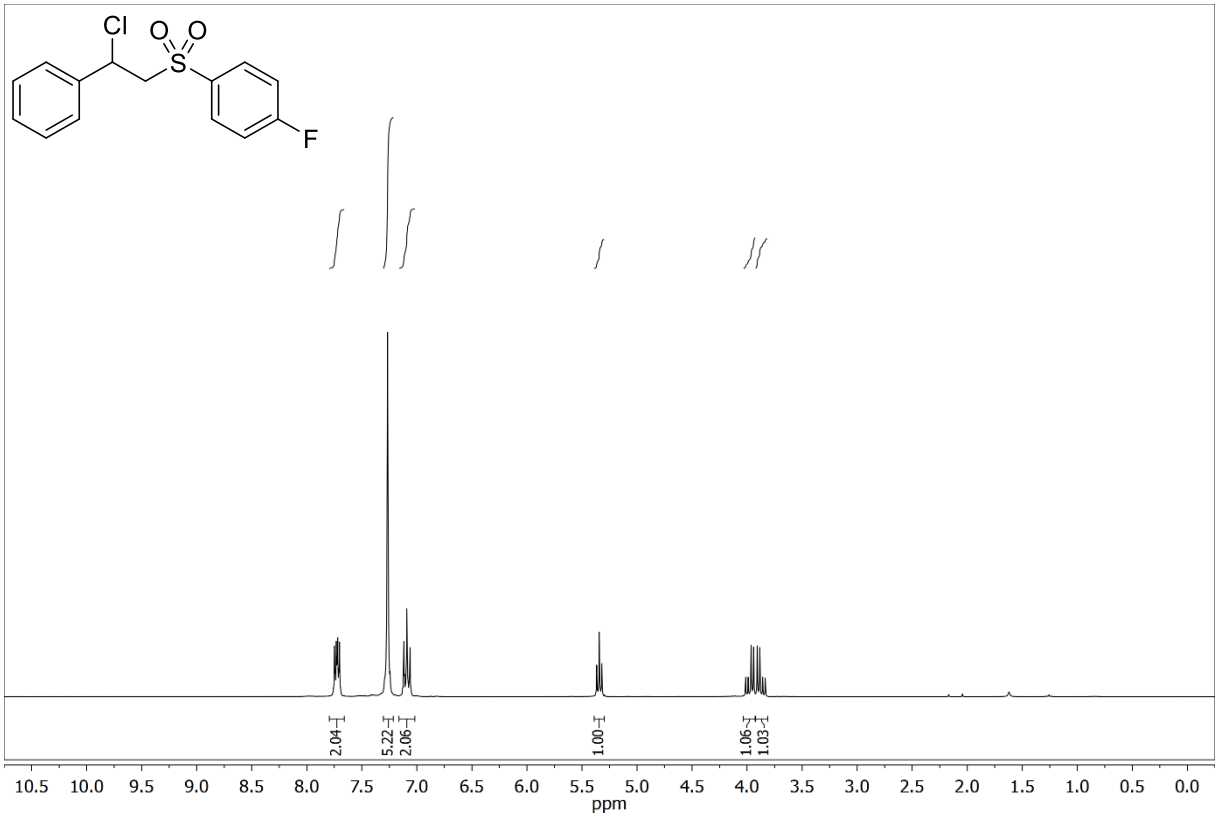


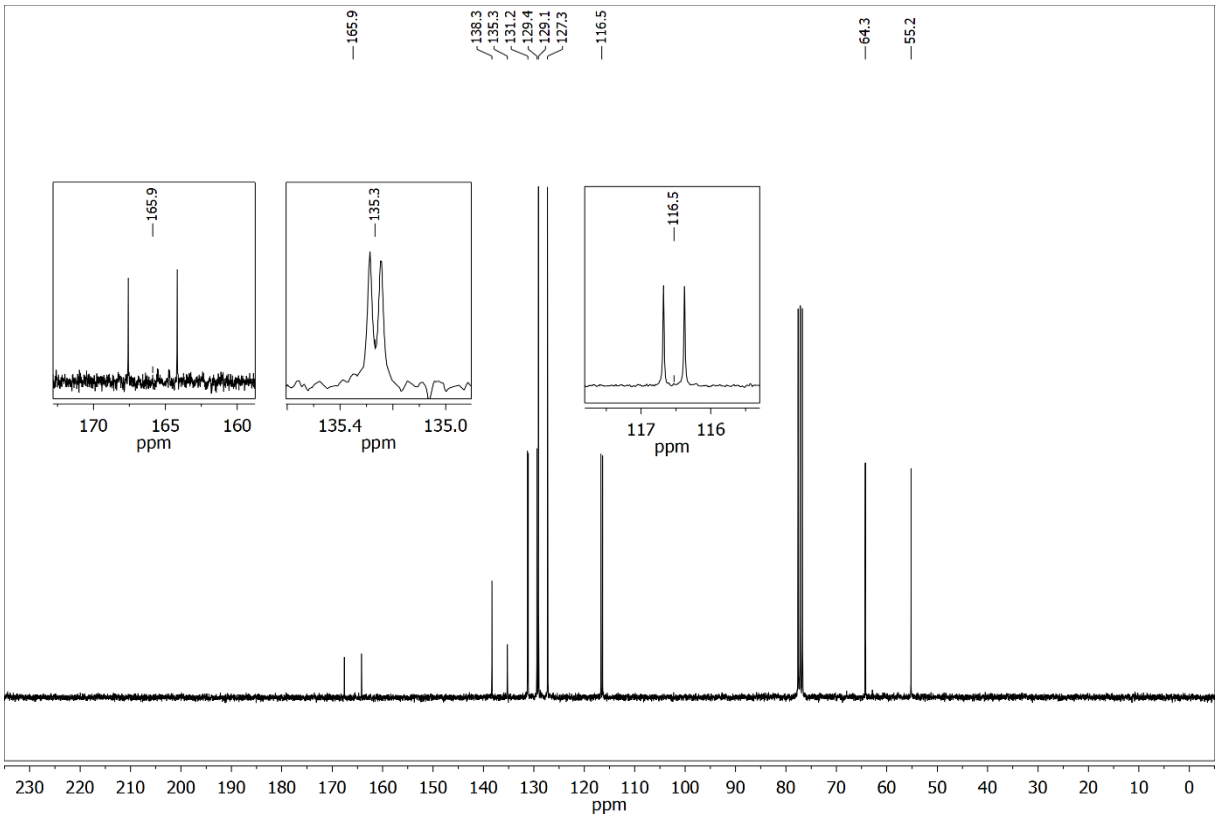
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



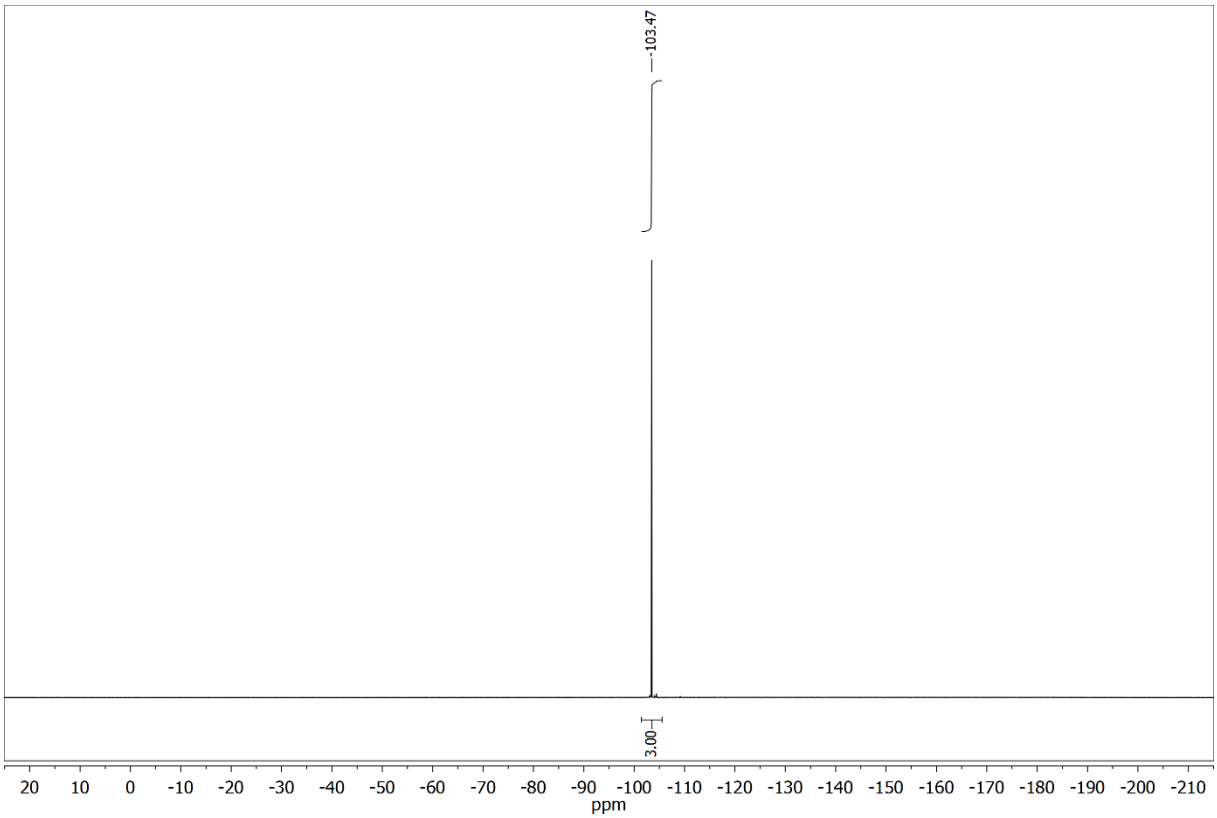
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1-((2-chloro-2-phenylethyl)sulfonyl)-4-fluorobenzene (10ab)



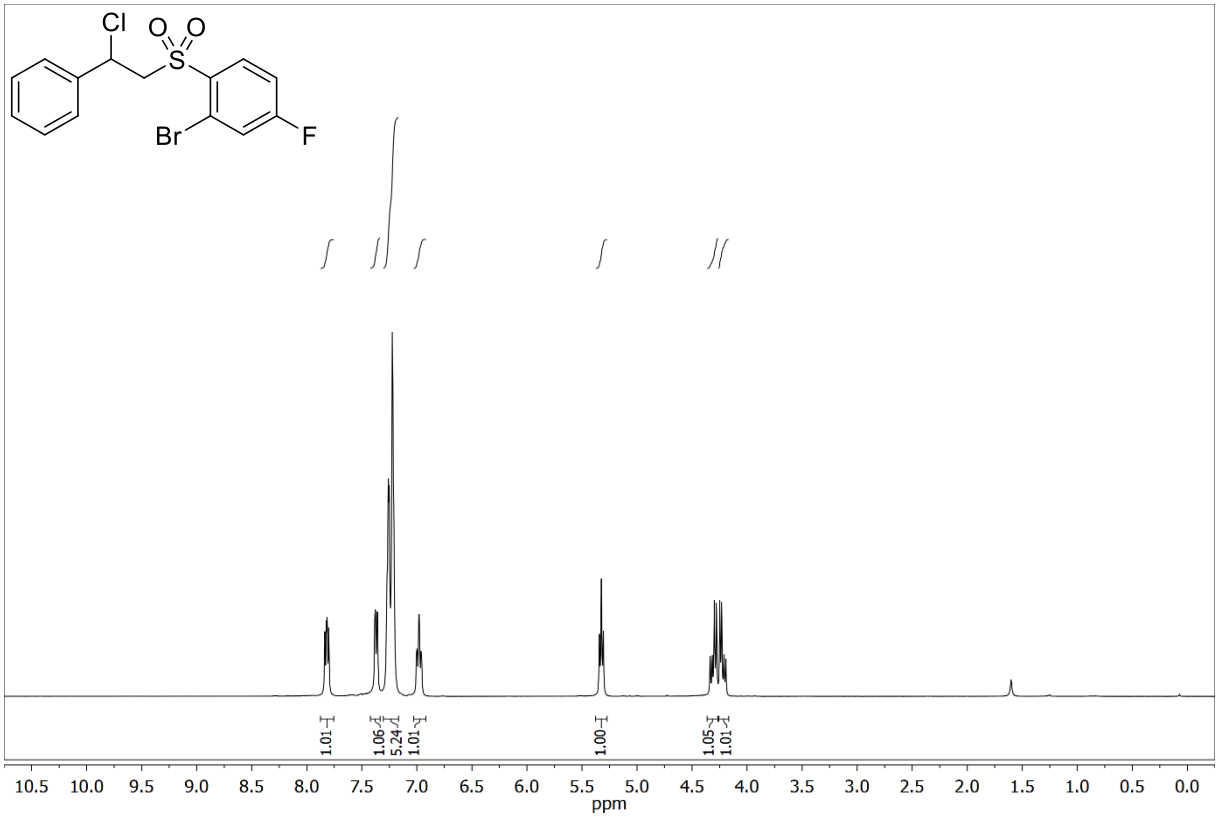


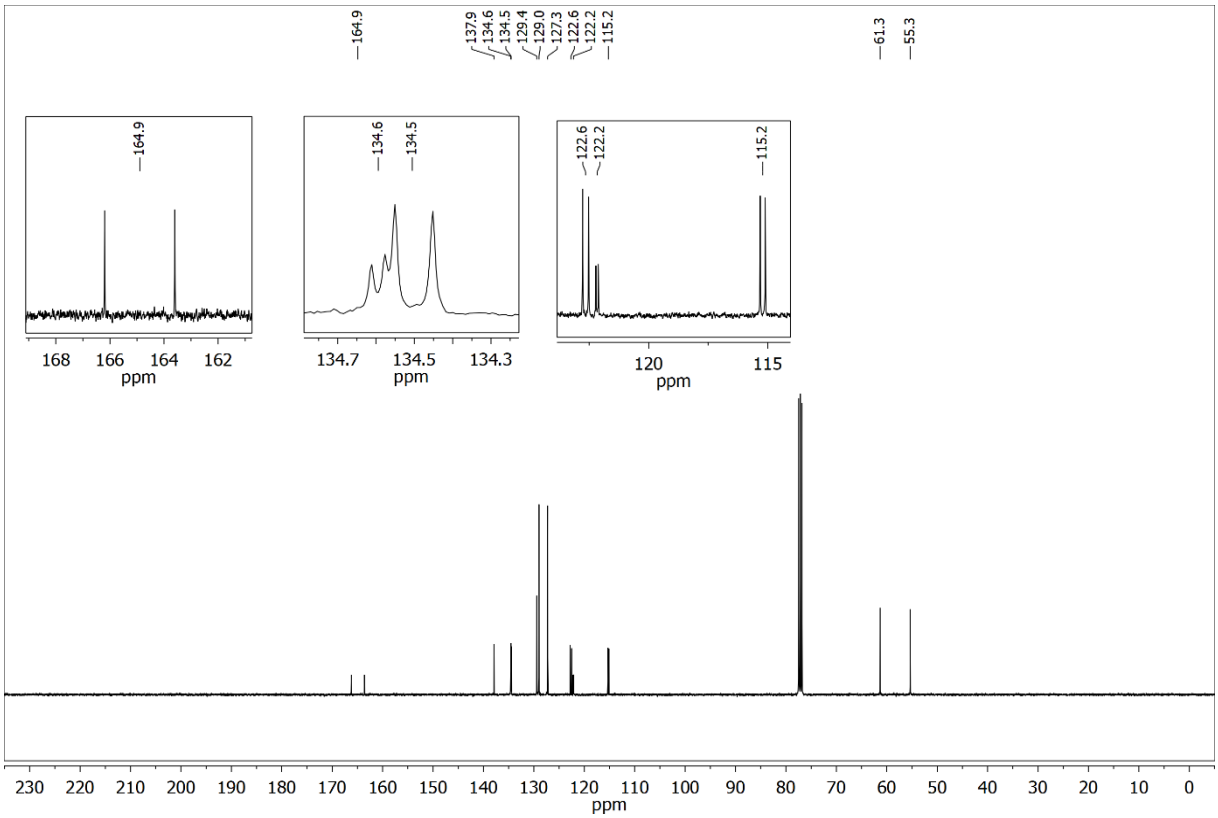
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



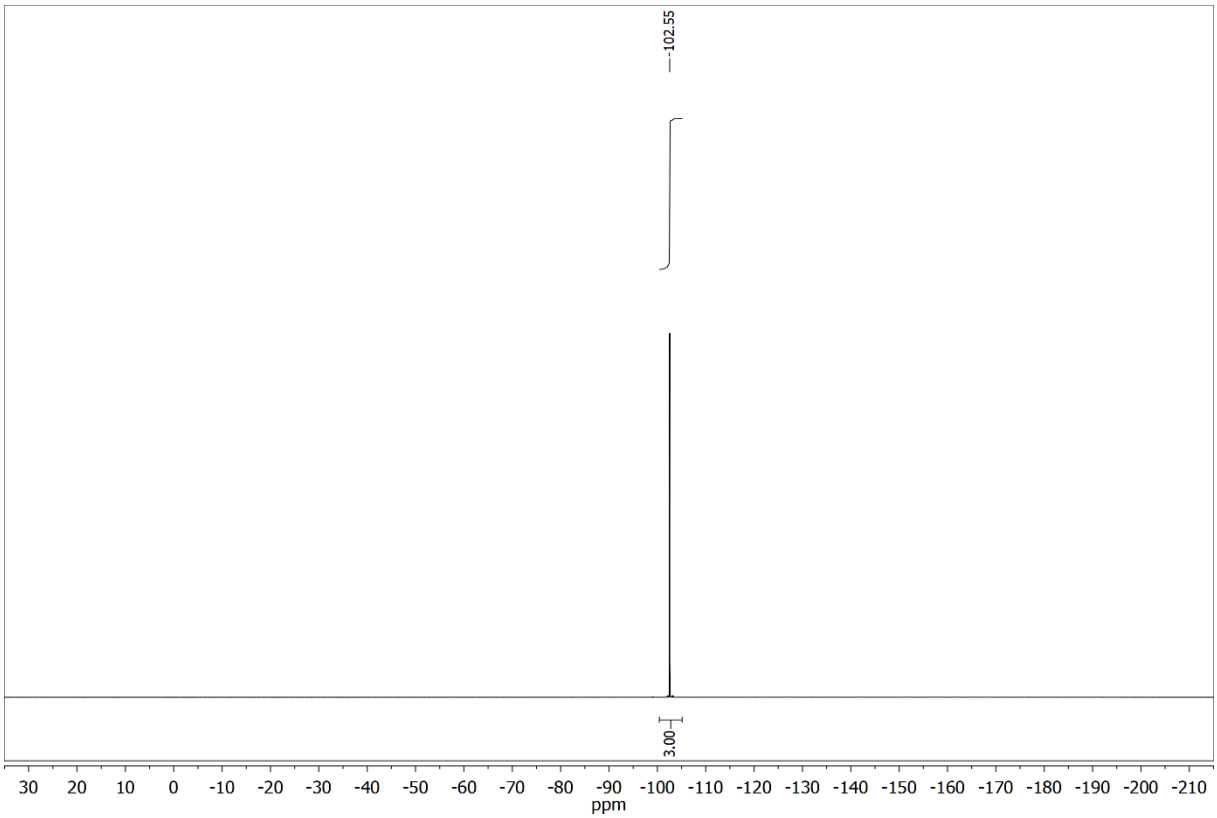
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

2-bromo-1-((2-chloro-2-phenylethyl)sulfonyl)-4-fluorobenzene (10ac)



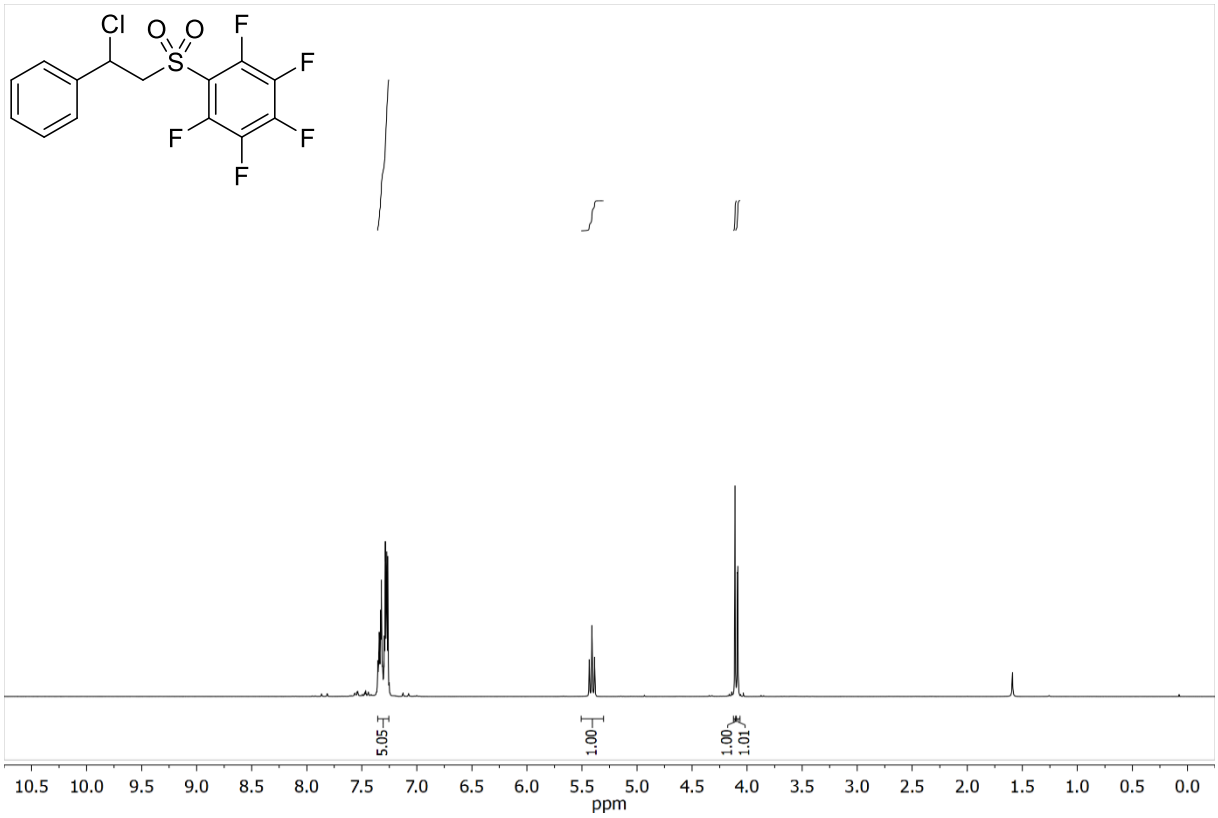


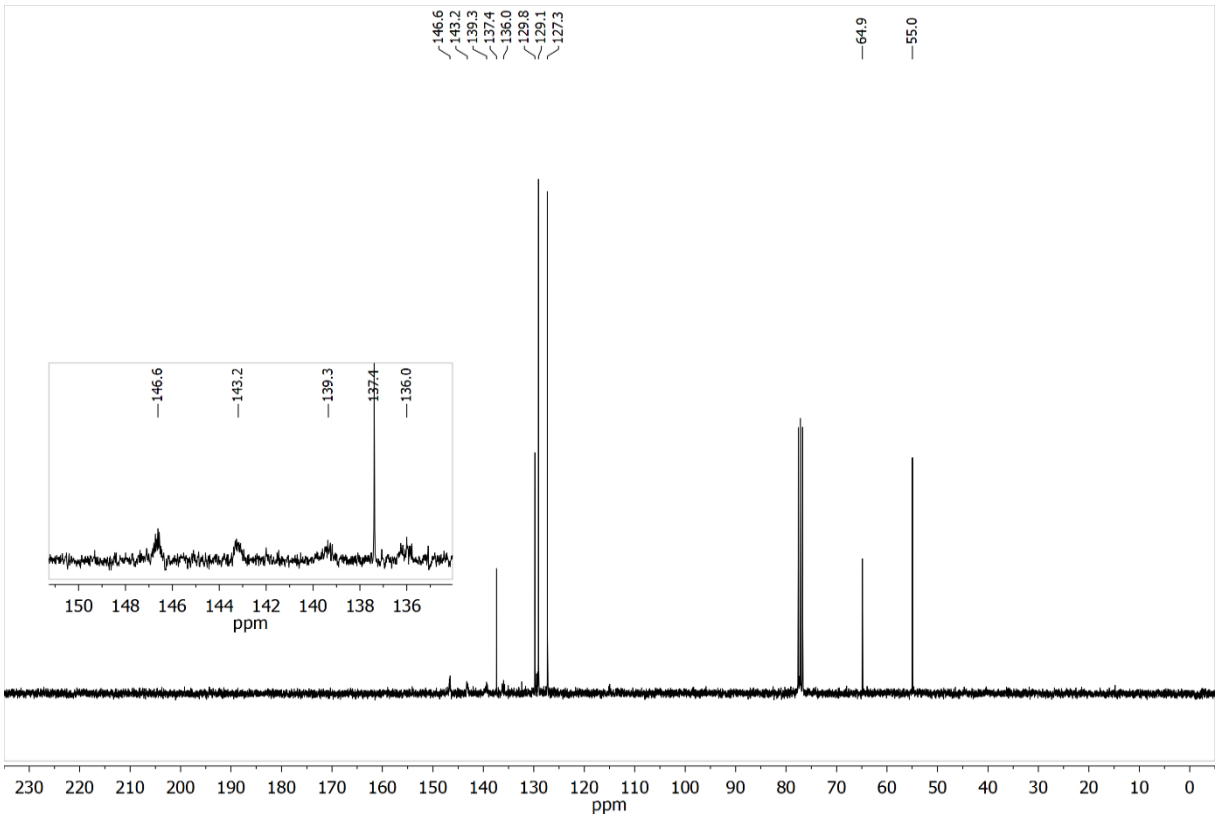
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



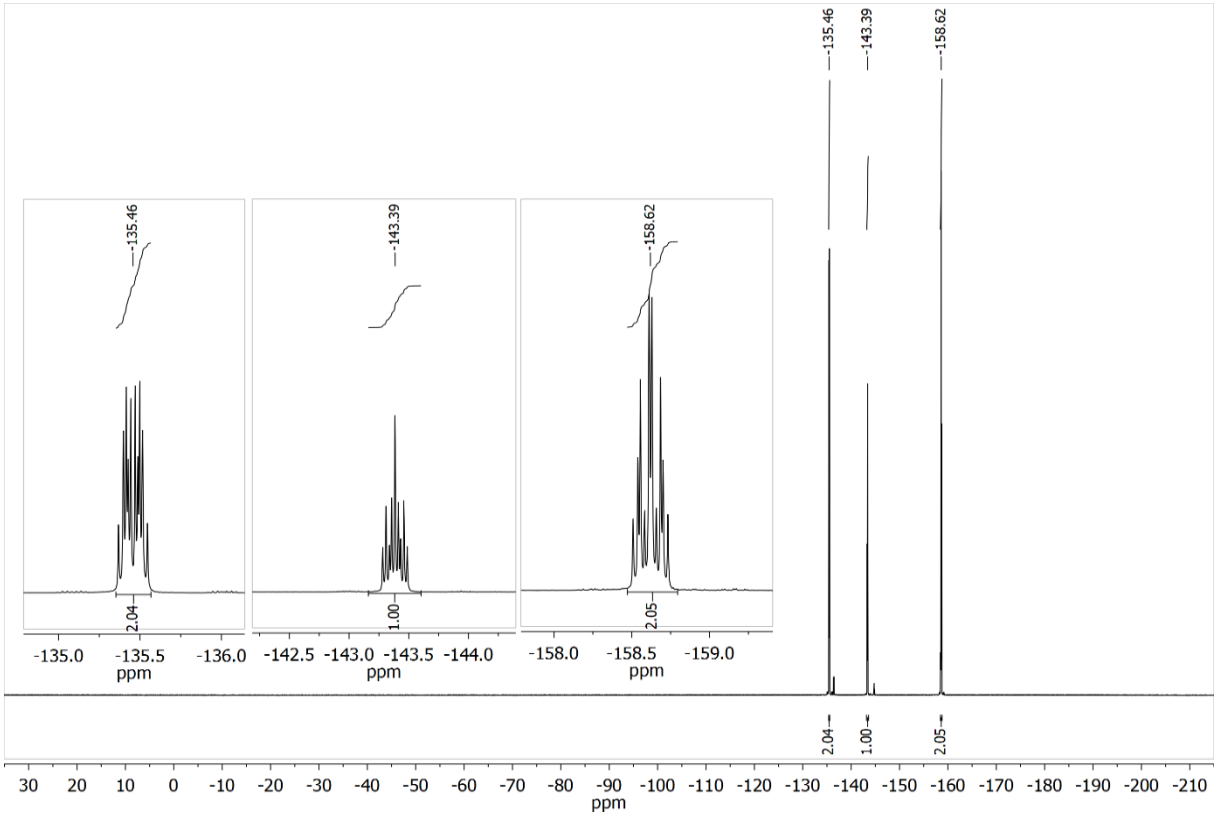
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1-((2-chloro-2-phenylethyl)sulfonyl)-2,3,4,5,6-pentafluorobenzene (10ad//9g)



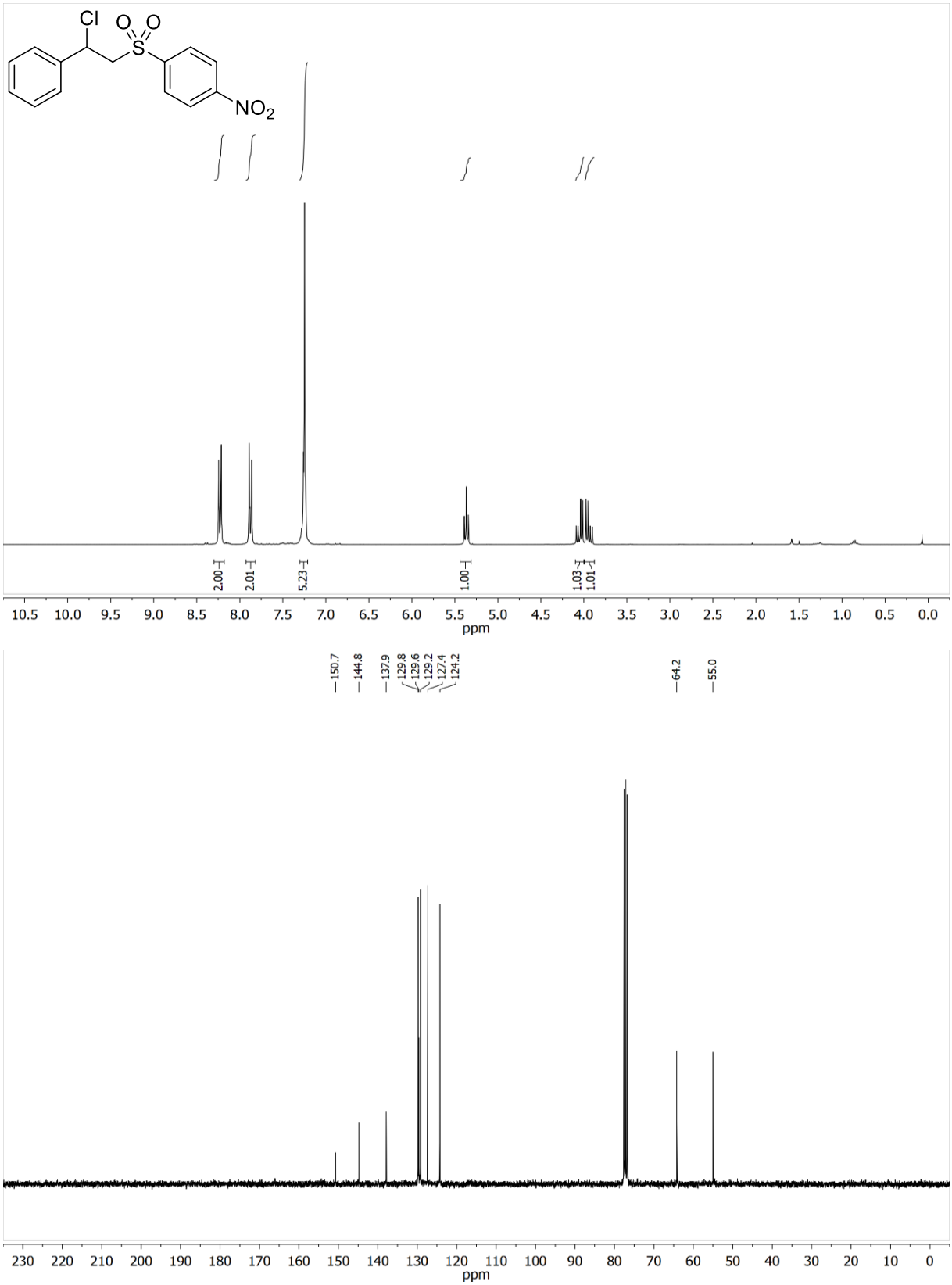


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



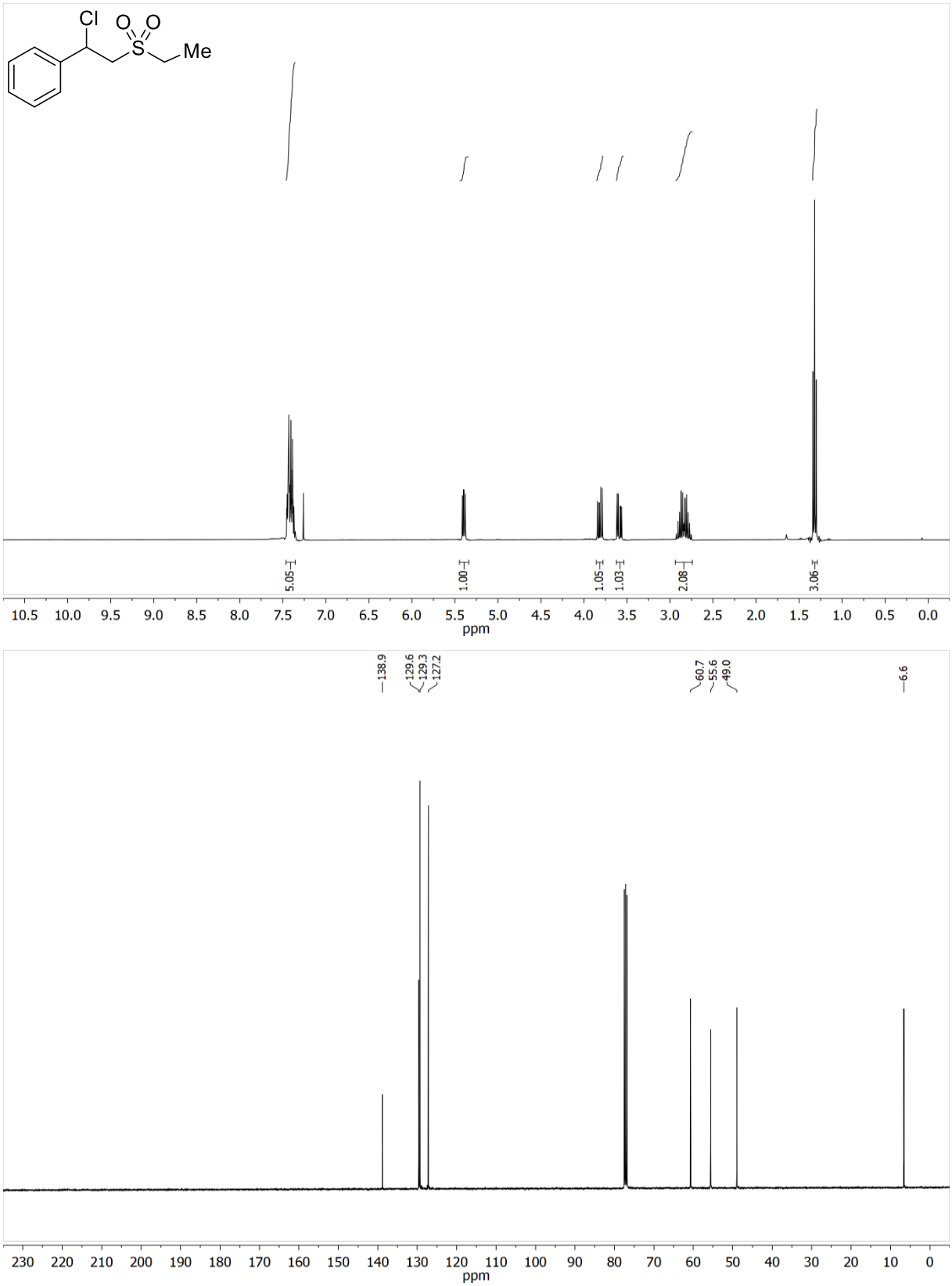
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1-((2-chloro-2-phenylethyl)sulfonyl)-4-nitrobenzene (10ae//9f)



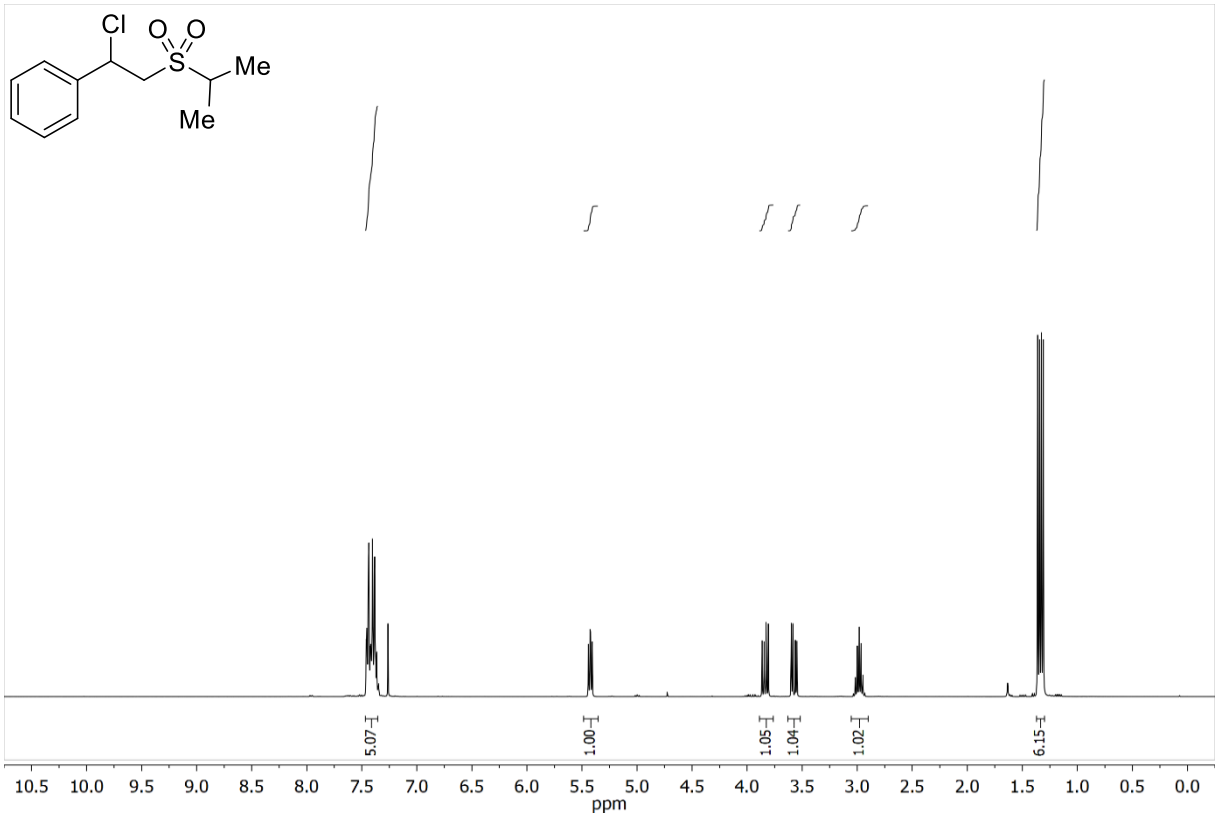
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

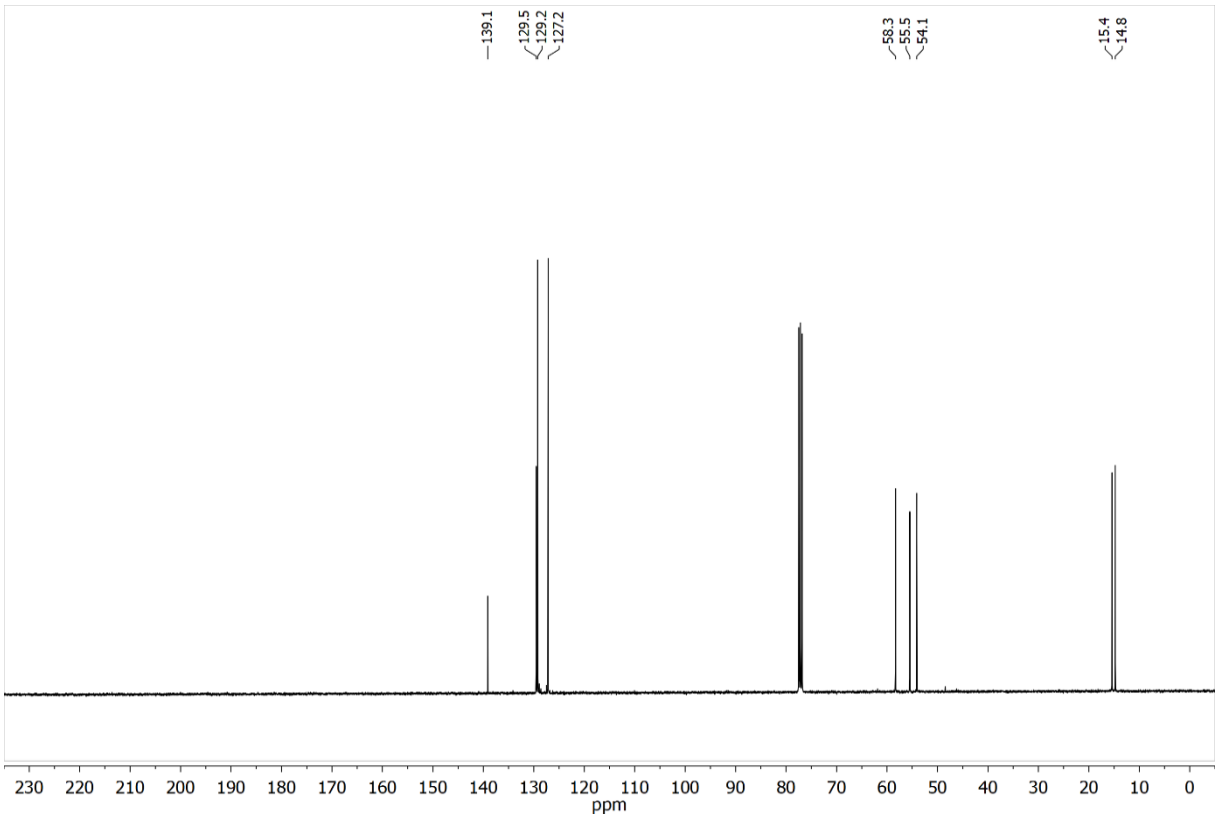
(1-chloro-2-(ethylsulfonyl)ethyl)benzene (10af((9i)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

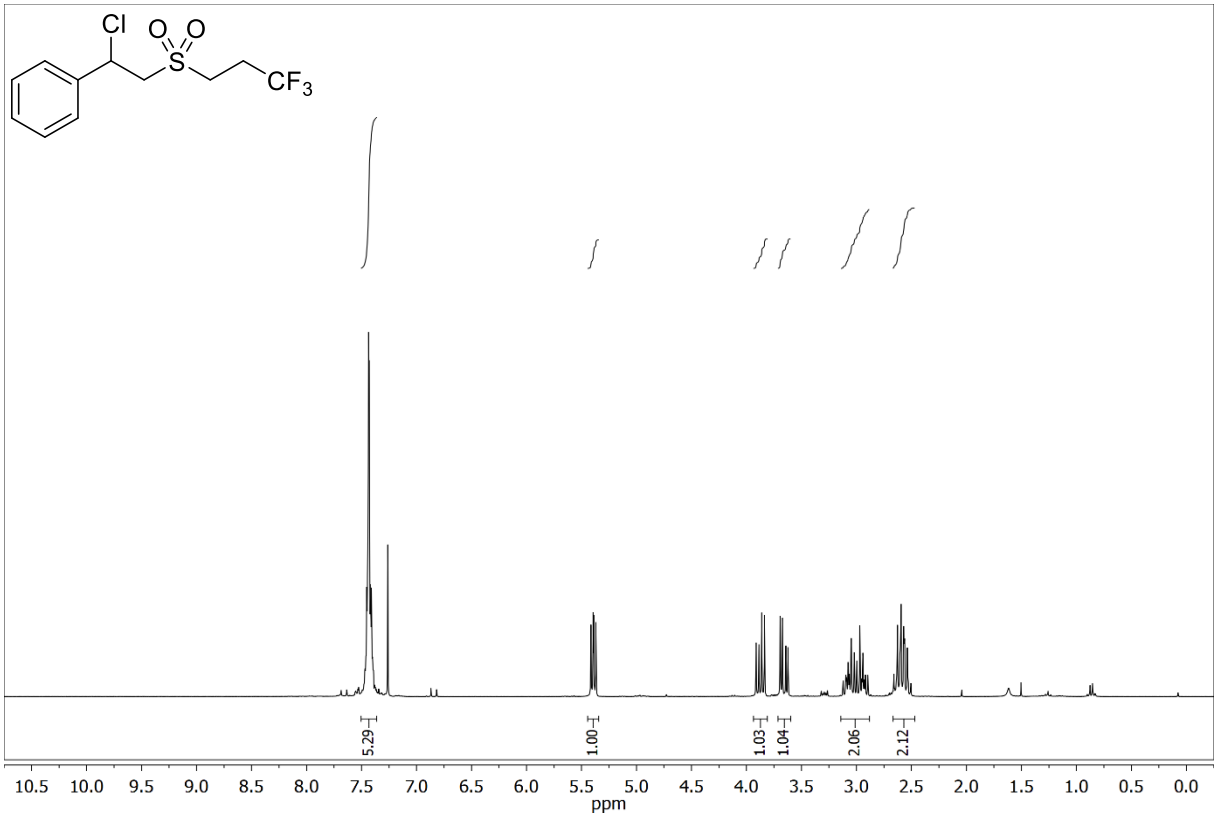
(1-chloro-2-(isopropylsulfonyl)ethyl)benzene (10ag//9j)

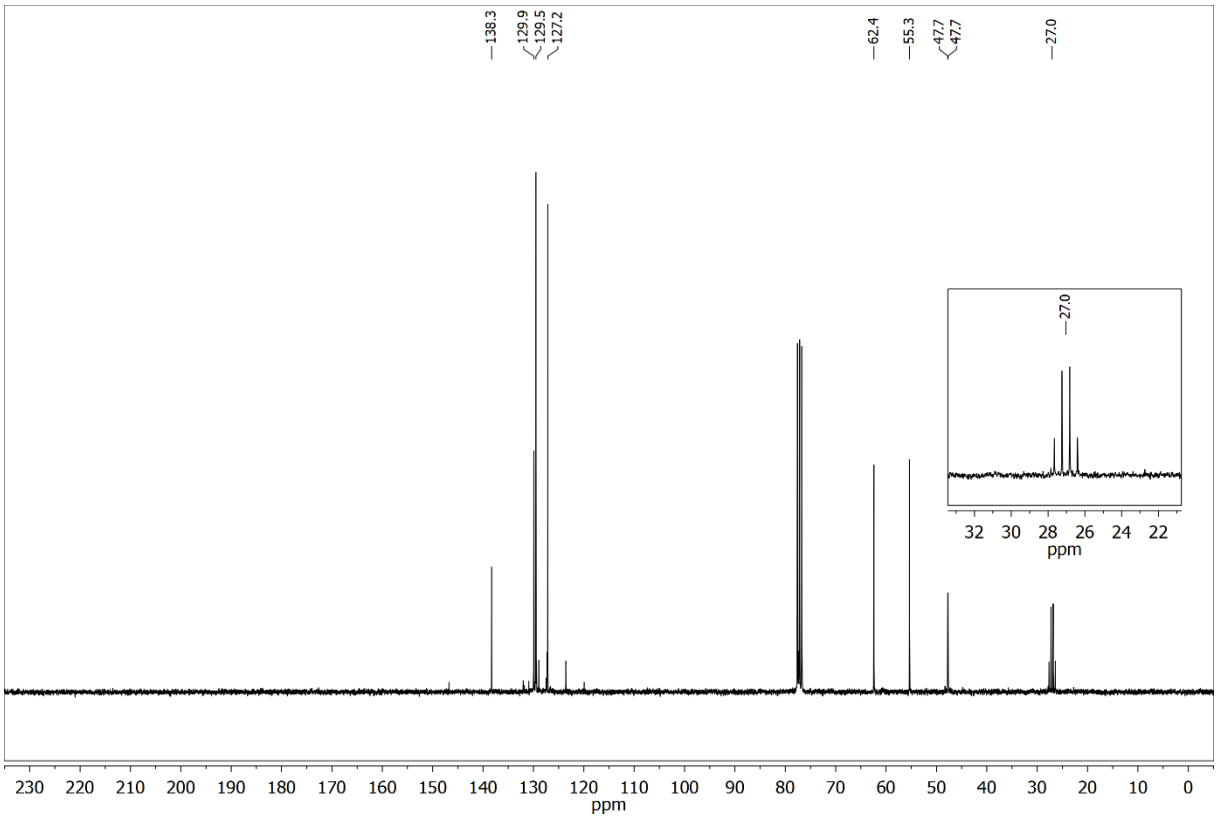




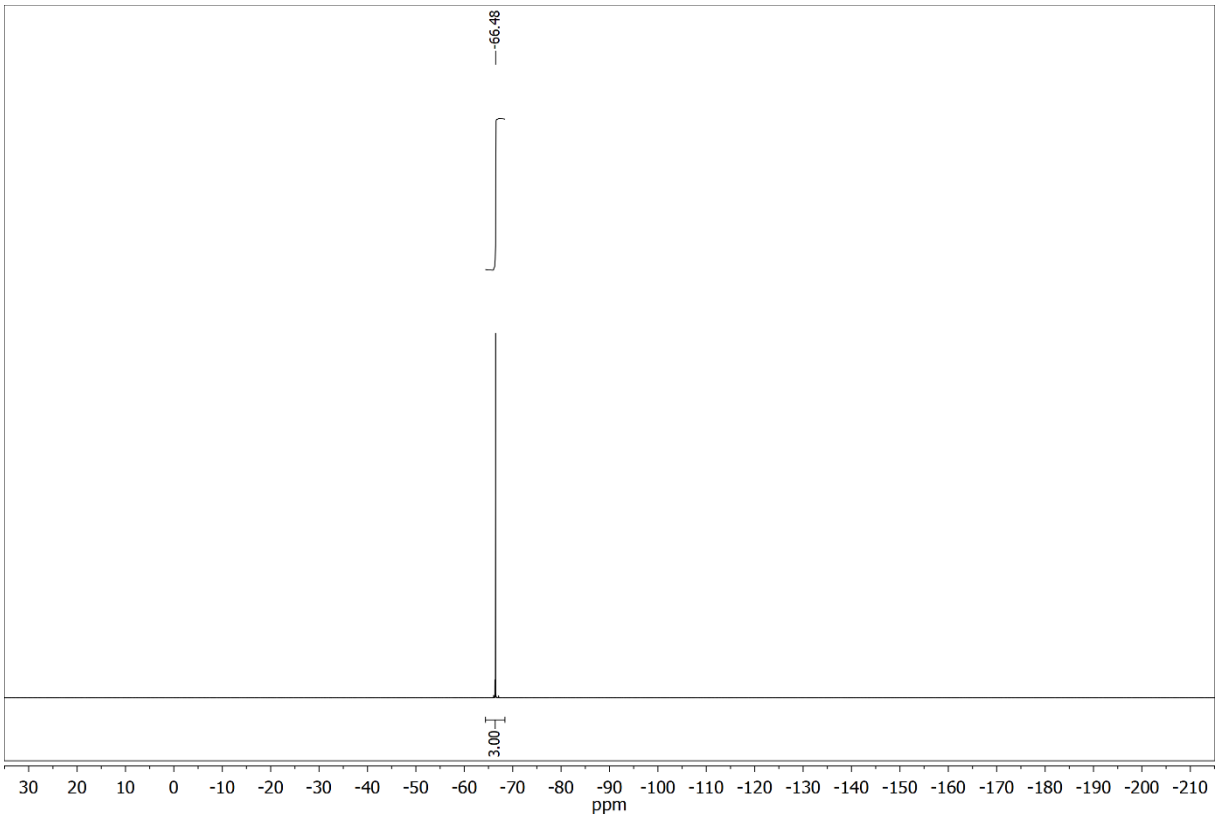
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

(1-chloro-2-((3,3,3-trifluoropropyl)sulfonyl)ethyl)benzene (10ah)



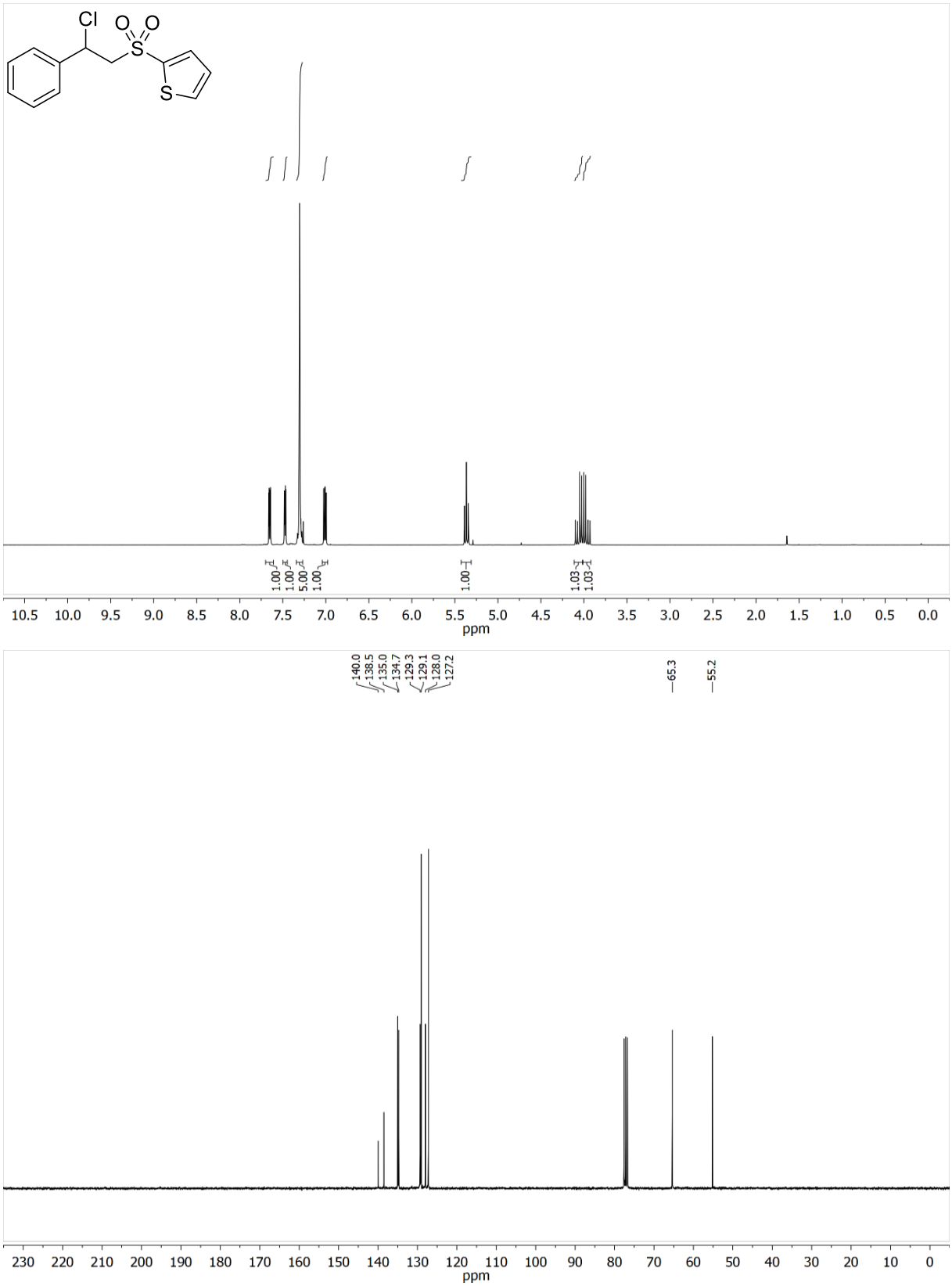


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



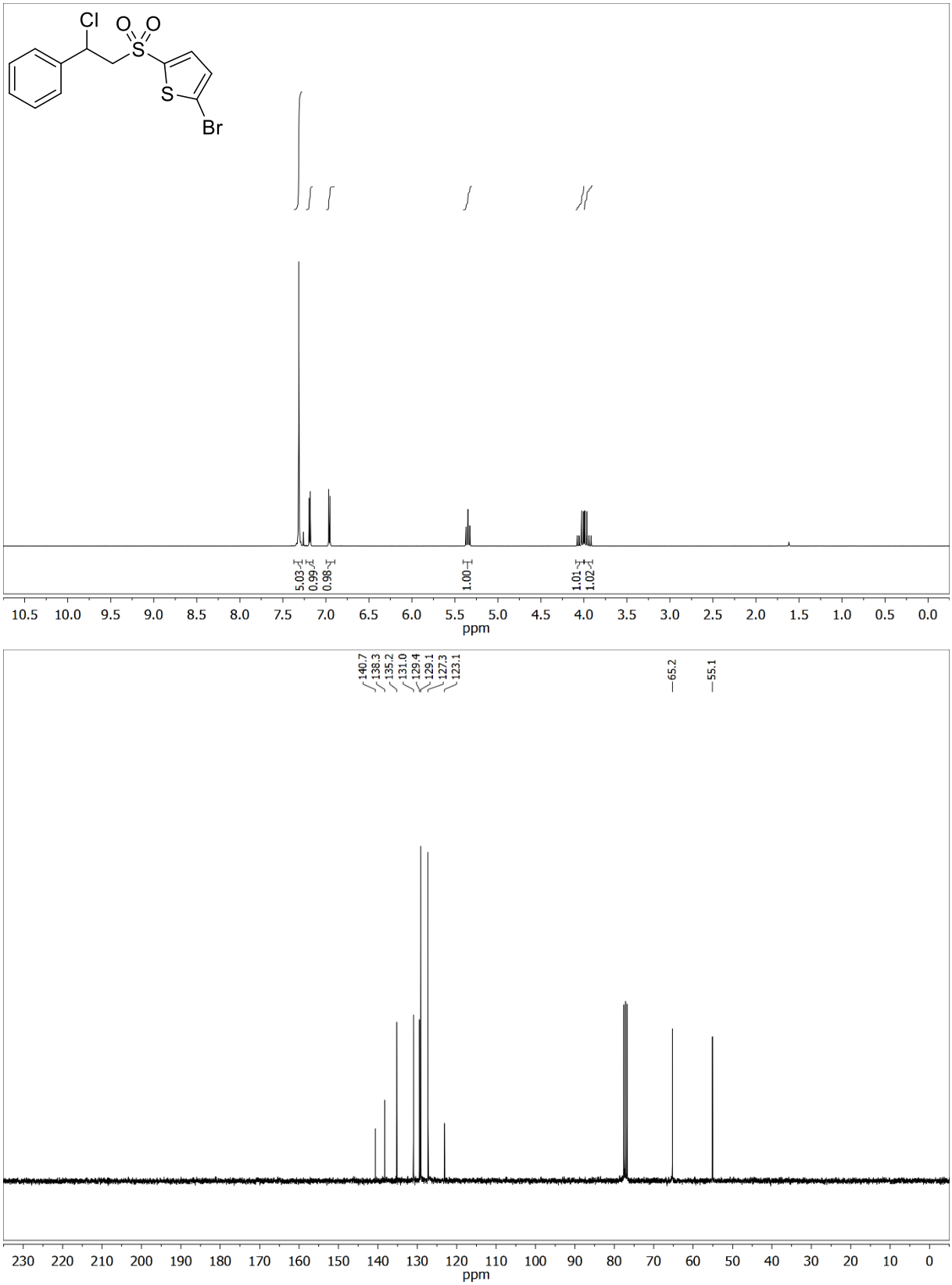
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

2-((2-chloro-2-phenylethyl)sulfonyl)thiophene (10ai//9k)



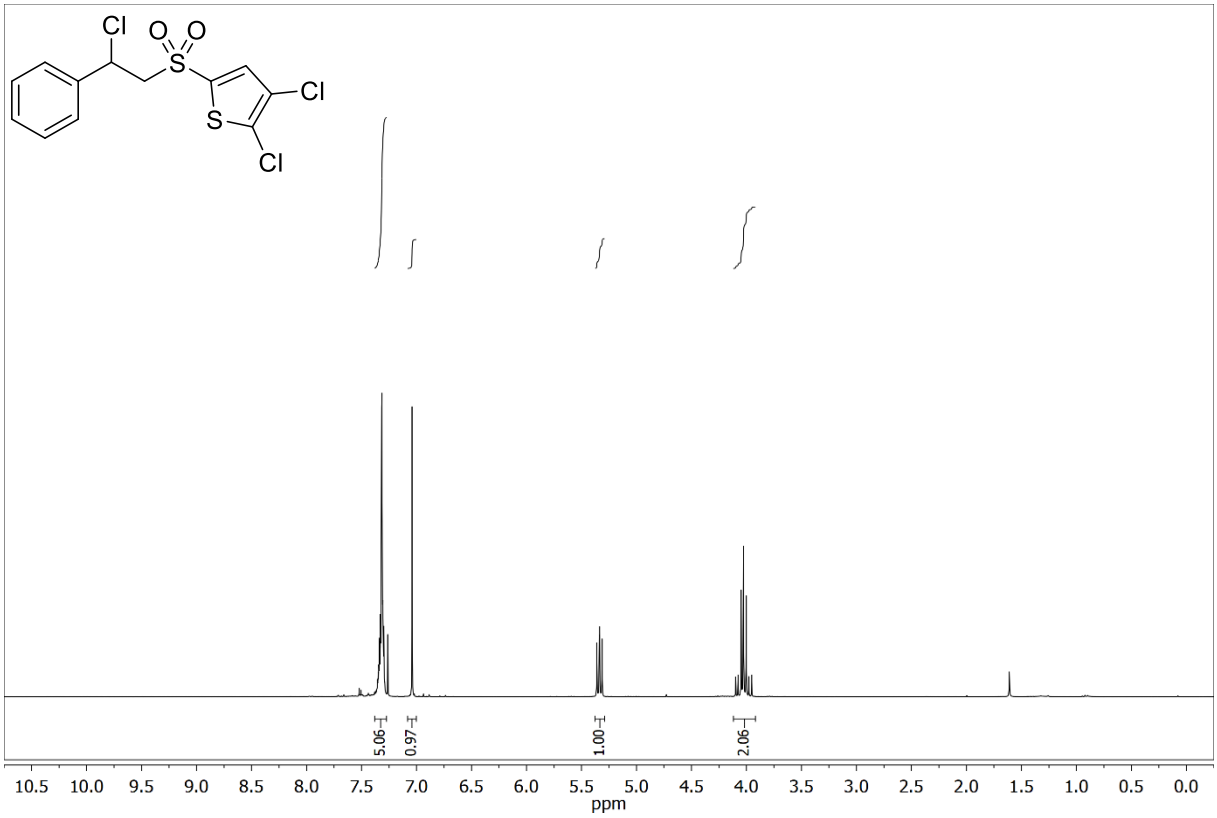
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

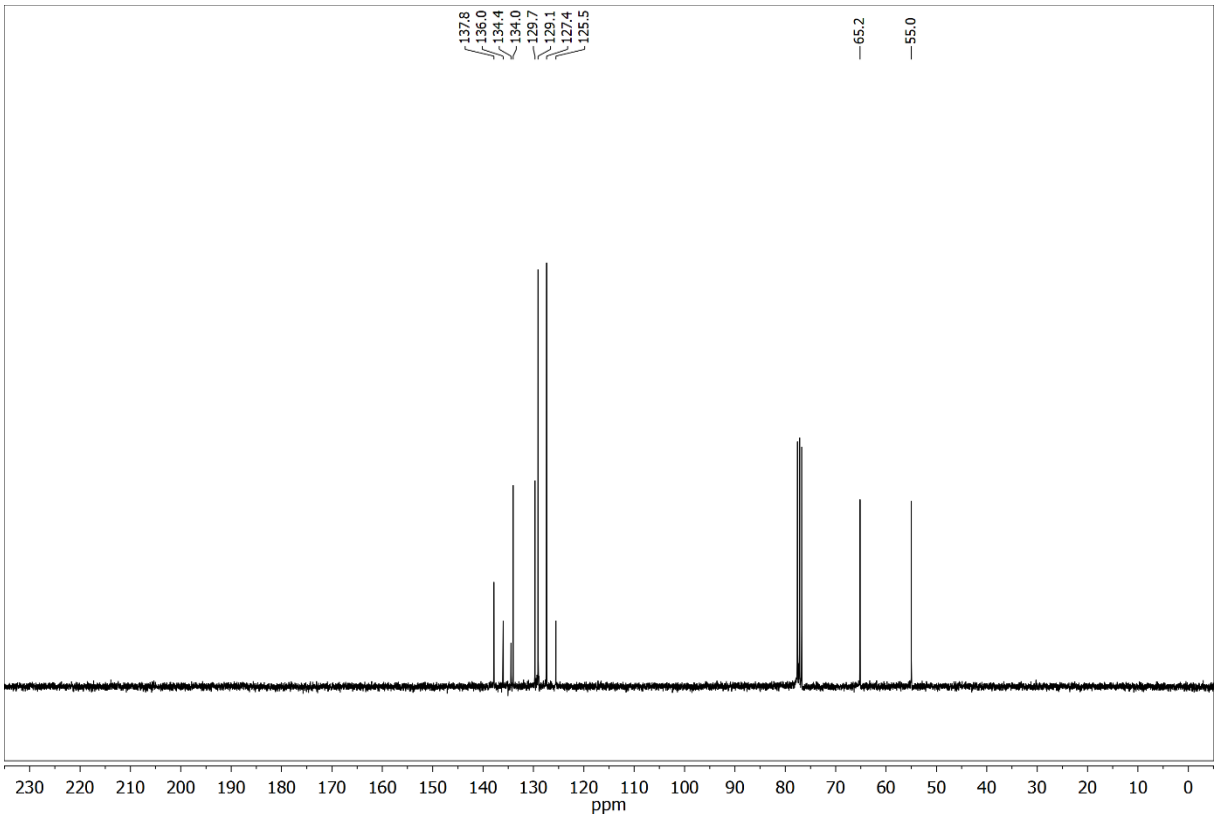
2-bromo-5-((2-chloro-2-phenylethyl)sulfonyl)thiophene (10aj)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

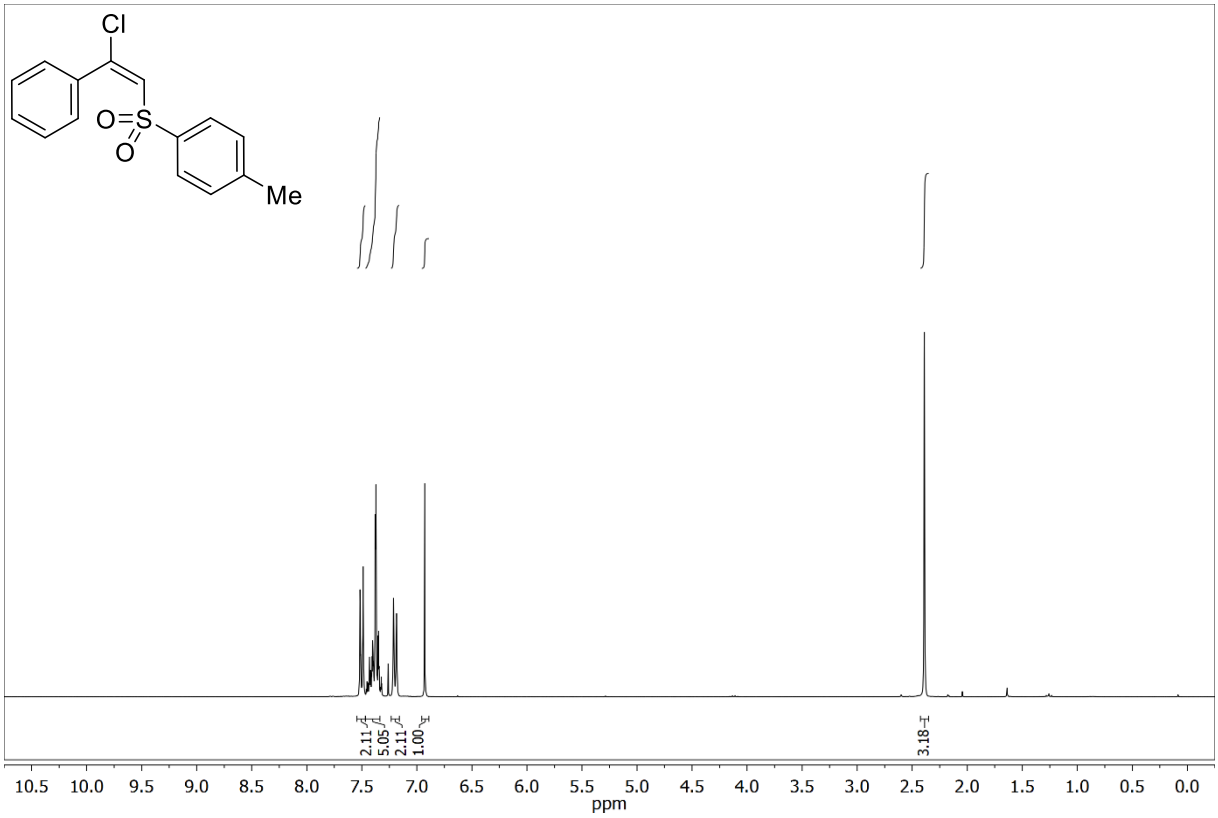
2,3-dichloro-5-((2-chloro-2-phenylethyl)sulfonyl)thiophene (10ak)

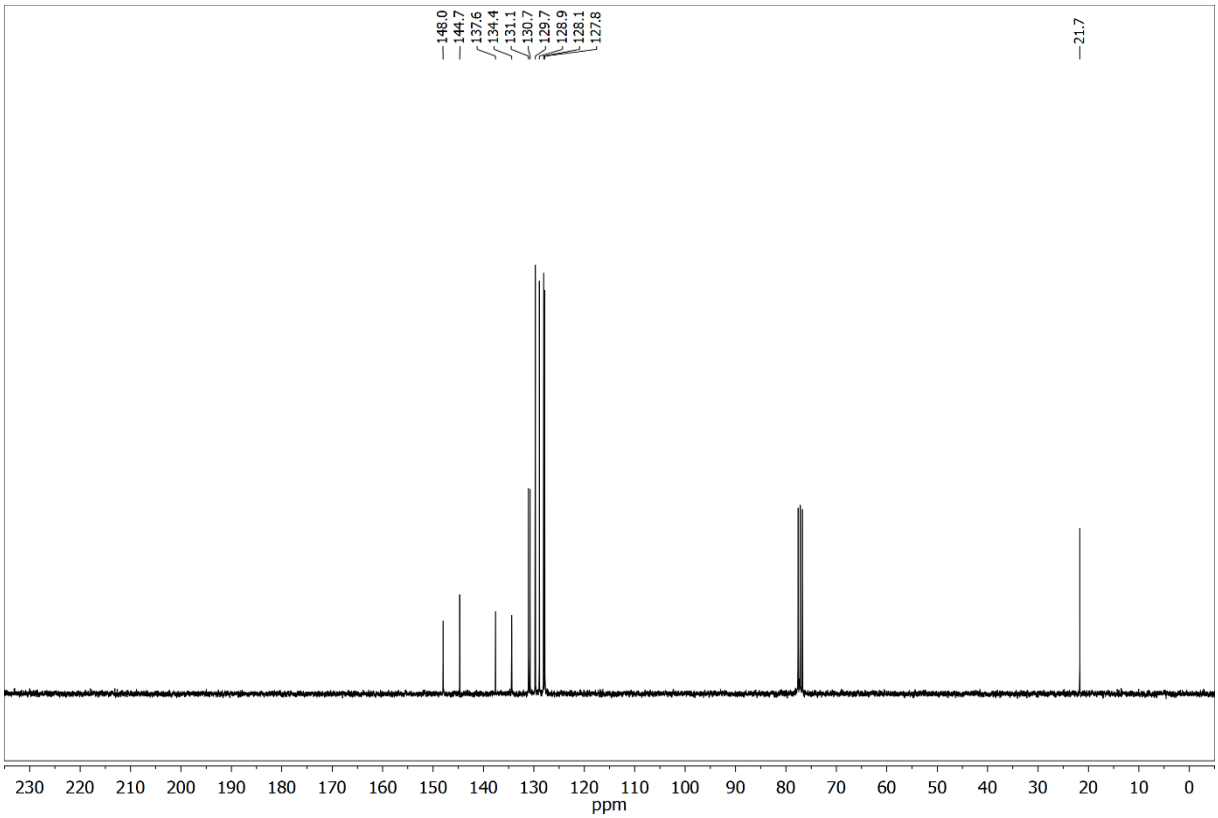




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

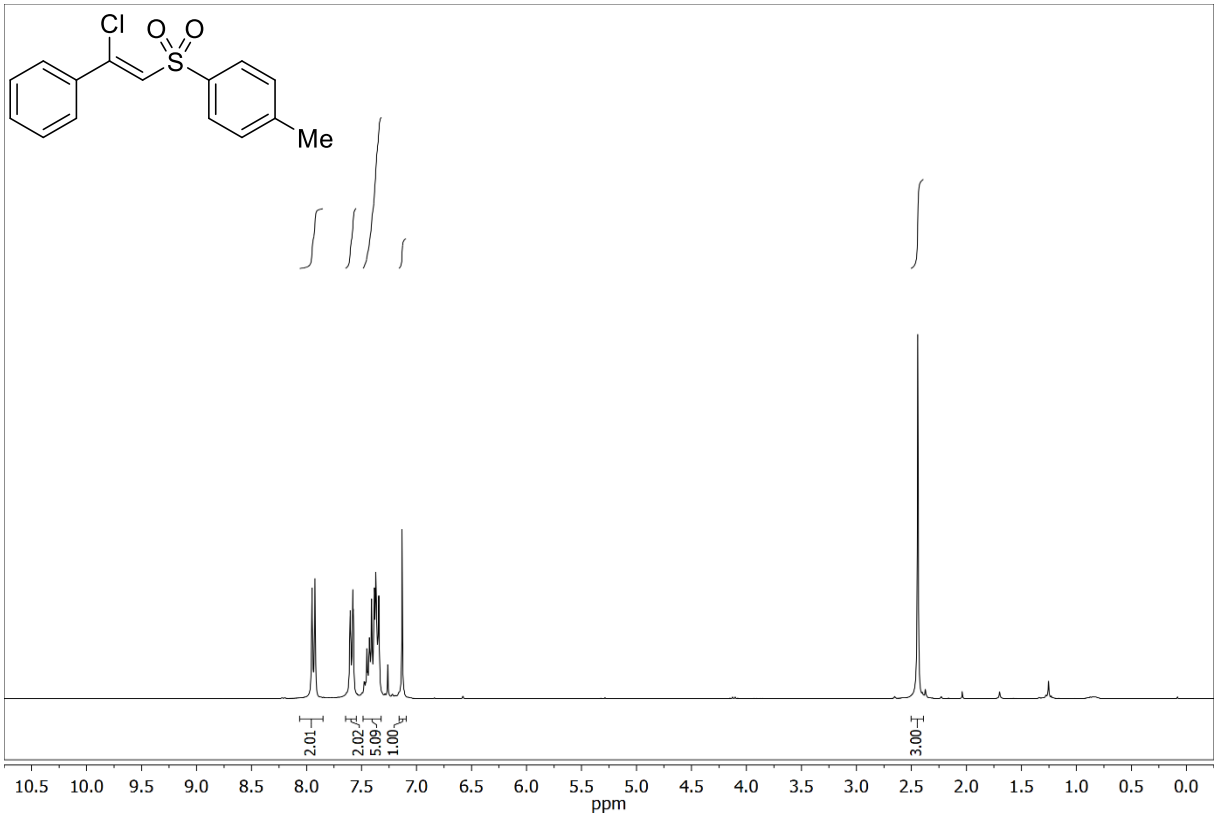
(*E*)-1-((2-chloro-2-phenylvinyl)sulfonyl)-4-methylbenzene ((*E*)-14a)

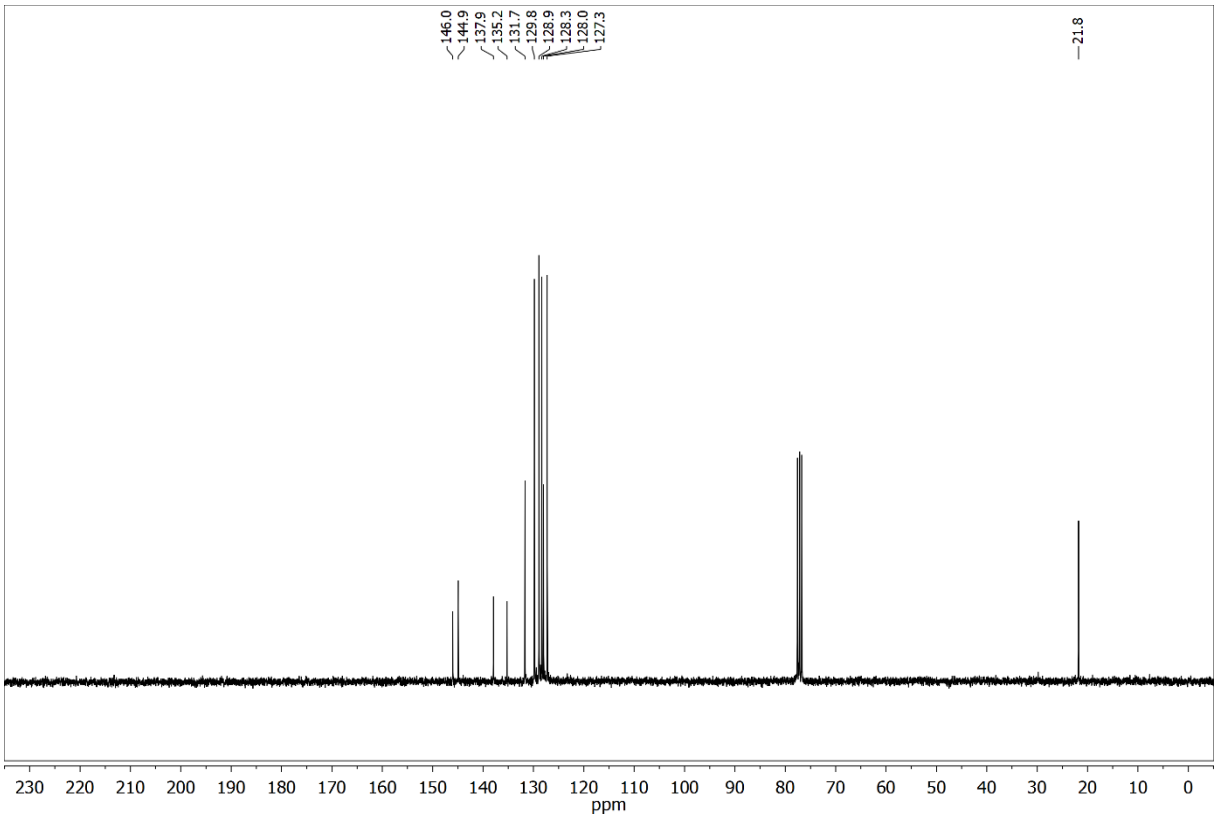




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

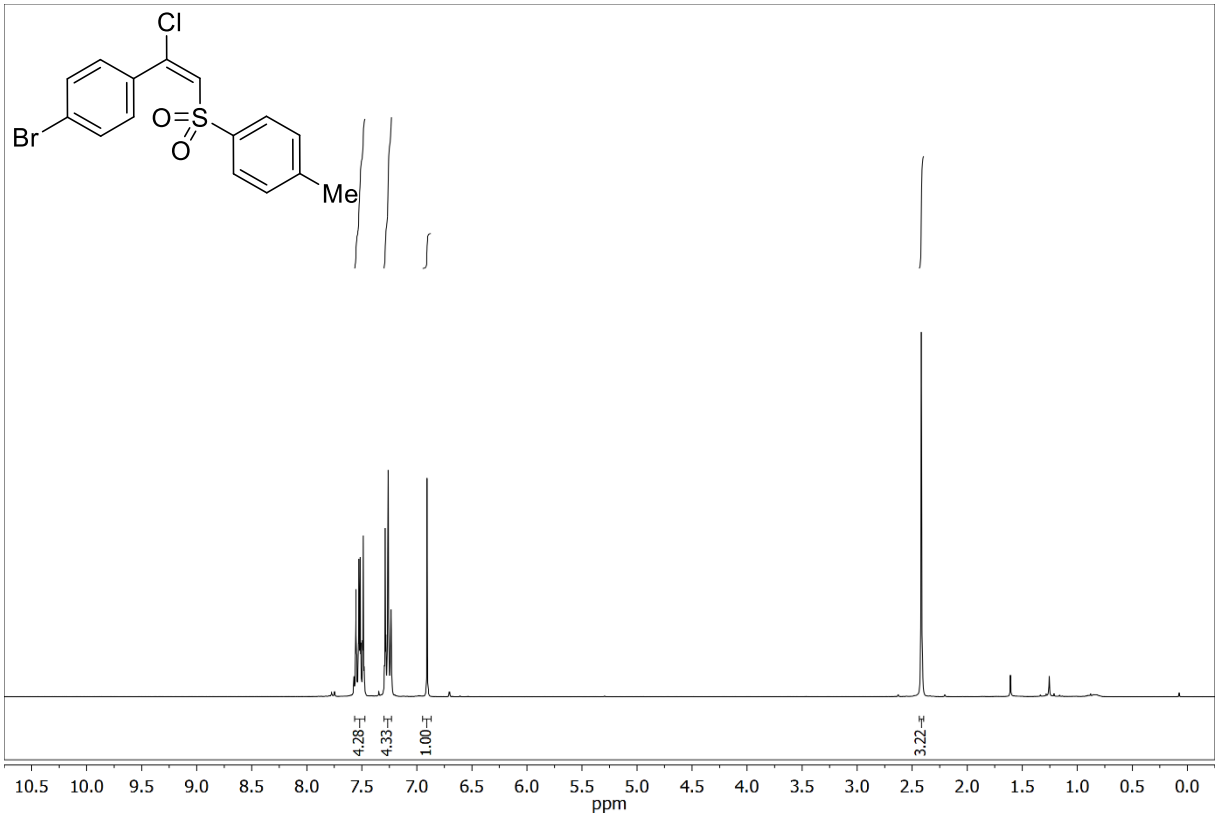
(*Z*)-1-((2-chloro-2-phenylvinyl)sulfonyl)-4-methylbenzene ((*Z*)-14a)

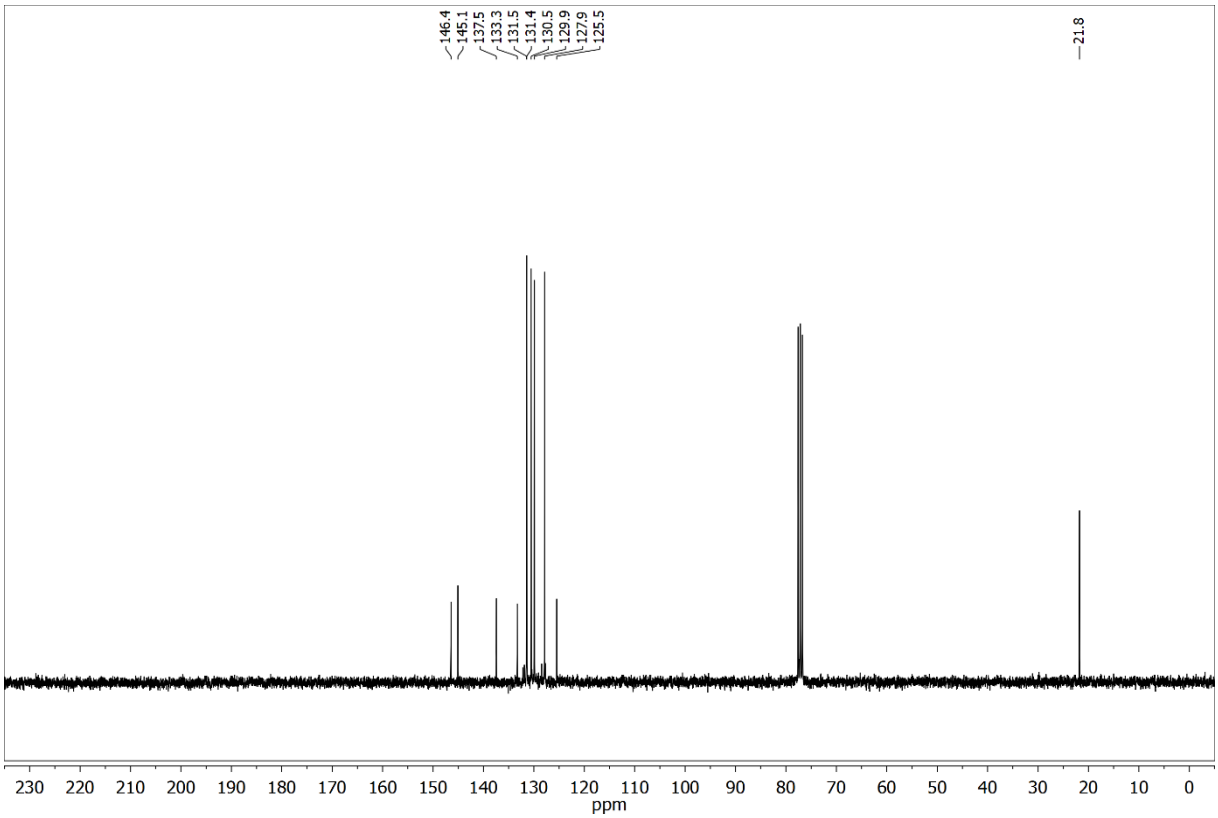




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

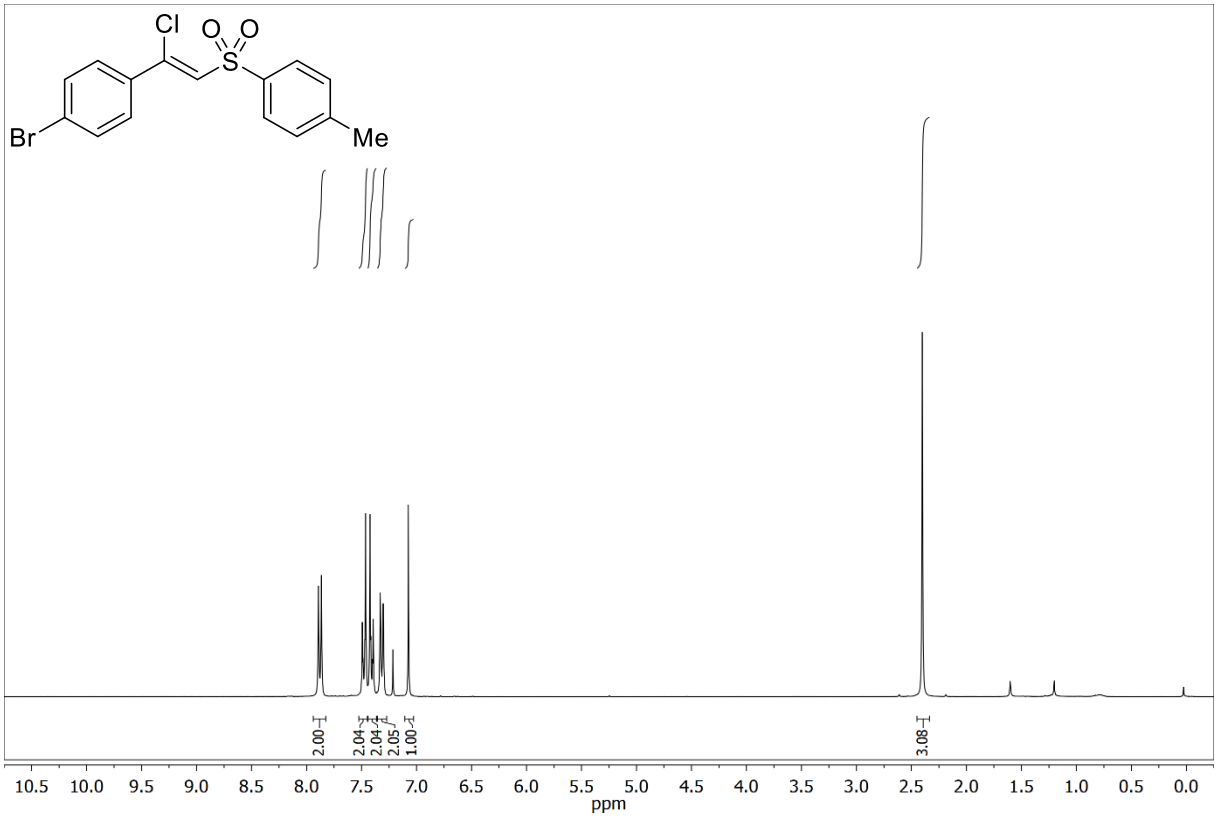
(*E*)-1-bromo-4-(1-chloro-2-tosylvinyl)benzene ((*E*)-14b)

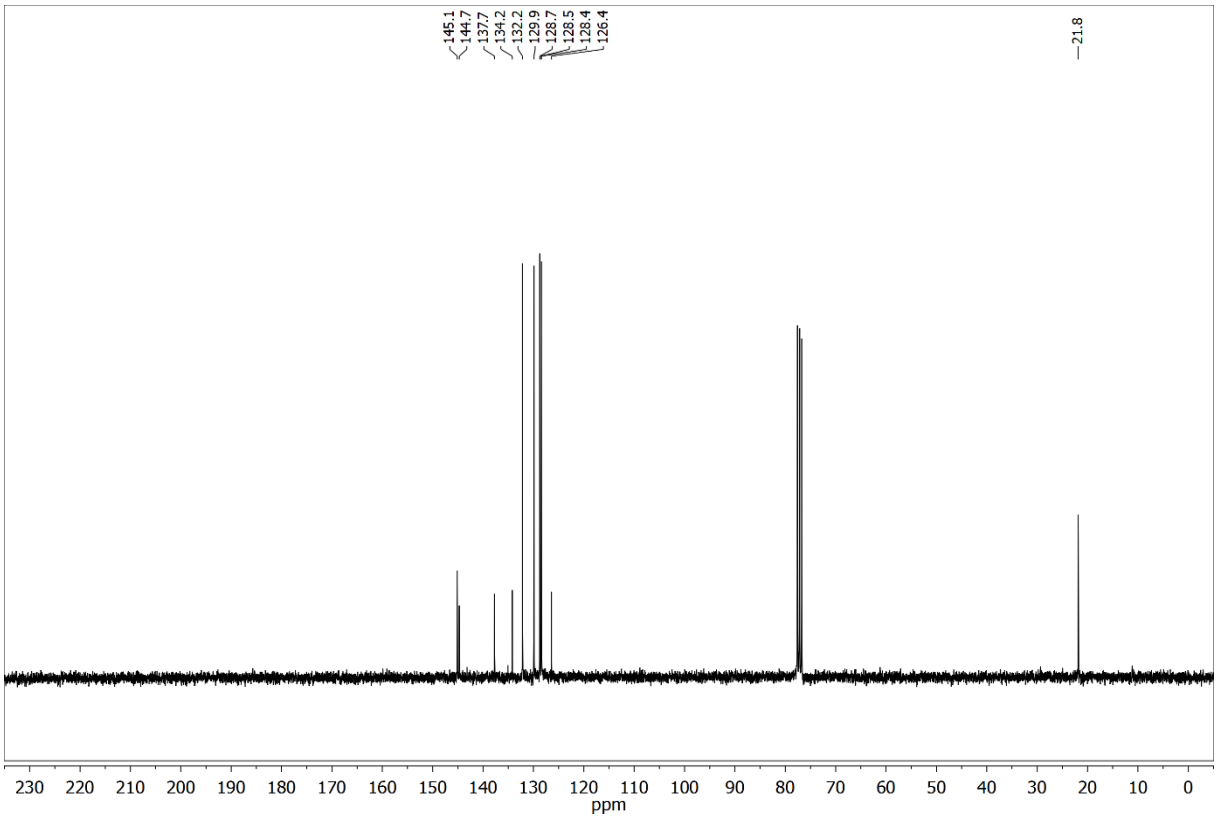




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

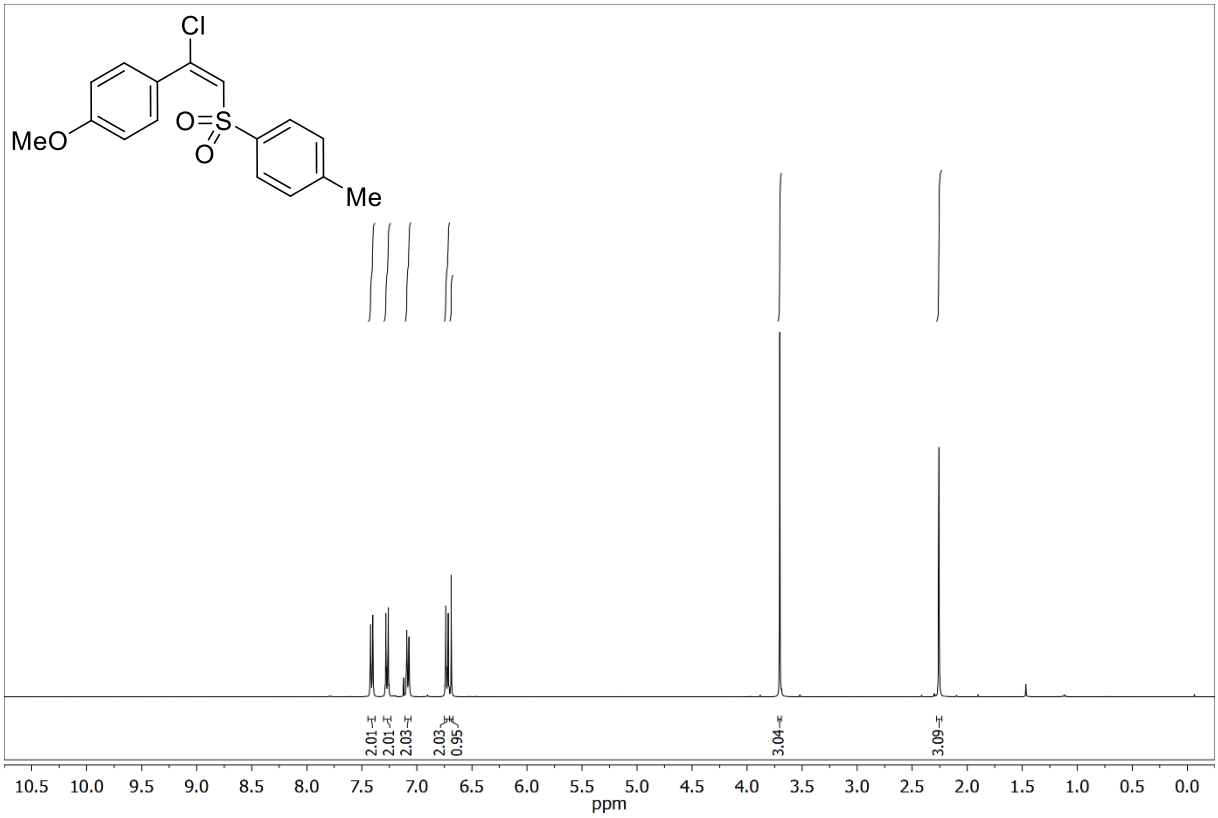
(*Z*)-1-bromo-4-(1-chloro-2-tosylvinyl)benzene ((*Z*)-14b)

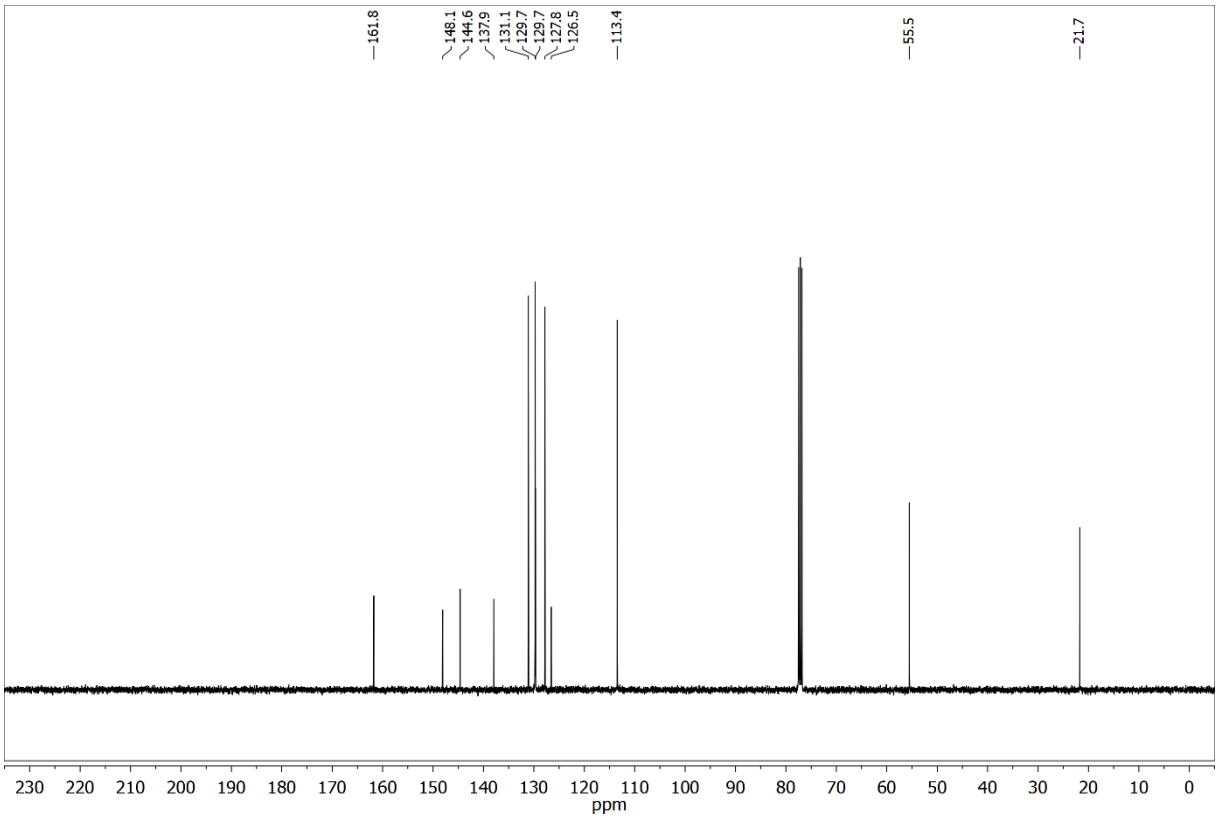




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

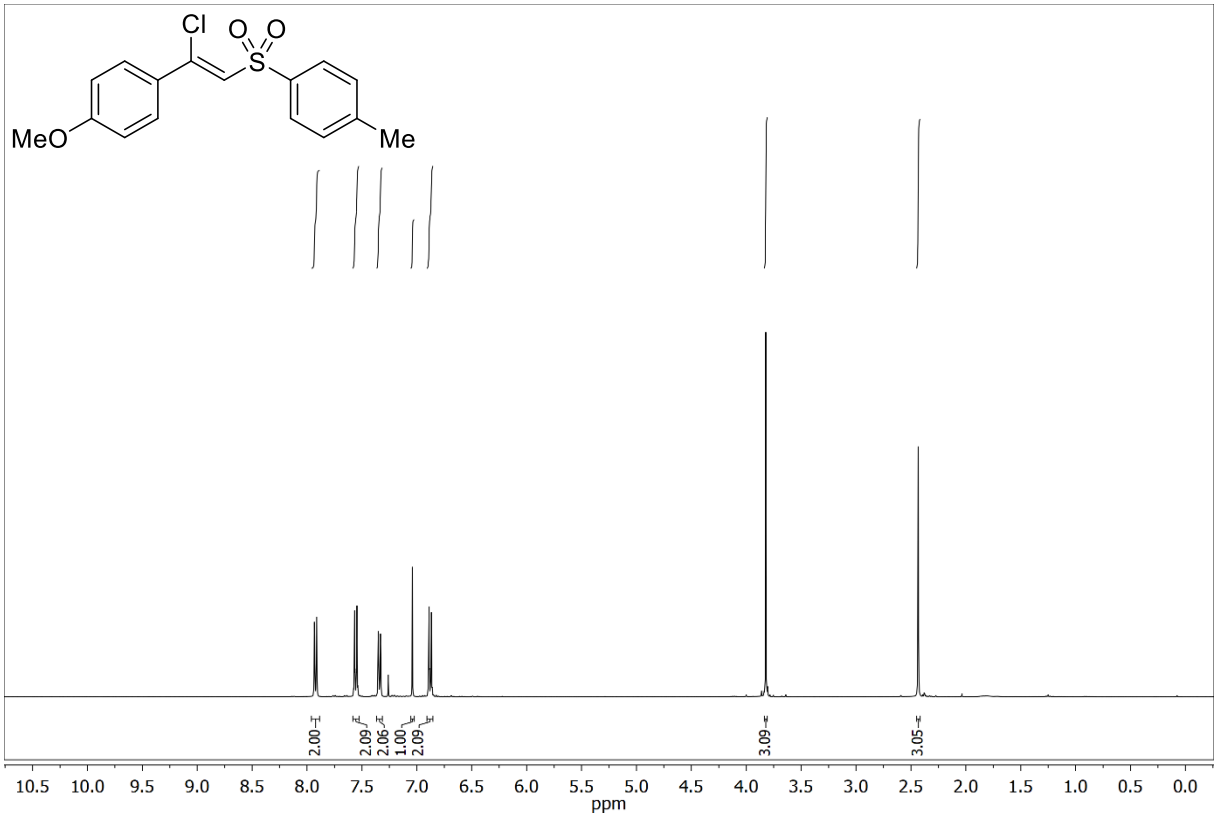
(*E*)-1-((2-chloro-2-(4-methoxyphenyl)vinyl)sulfonyl)-4-methylbenzene ((*E*)-14c)

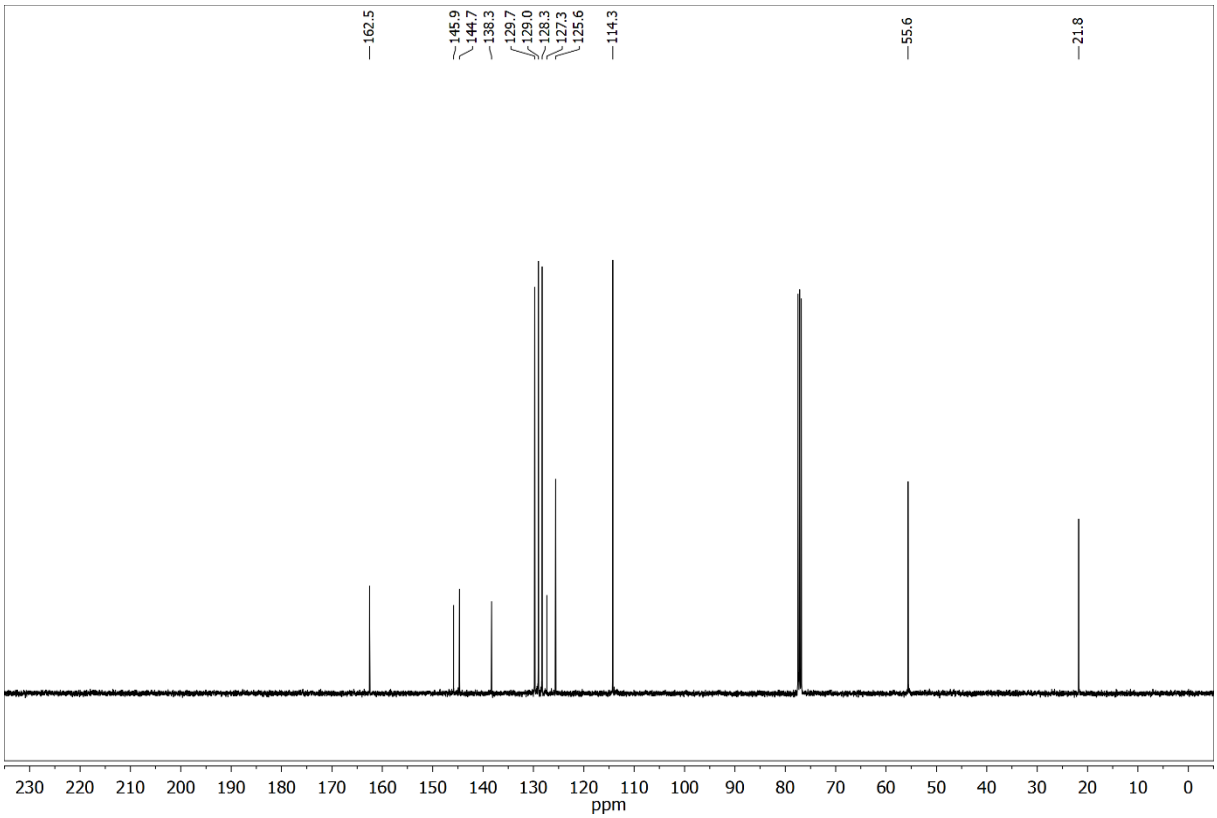




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

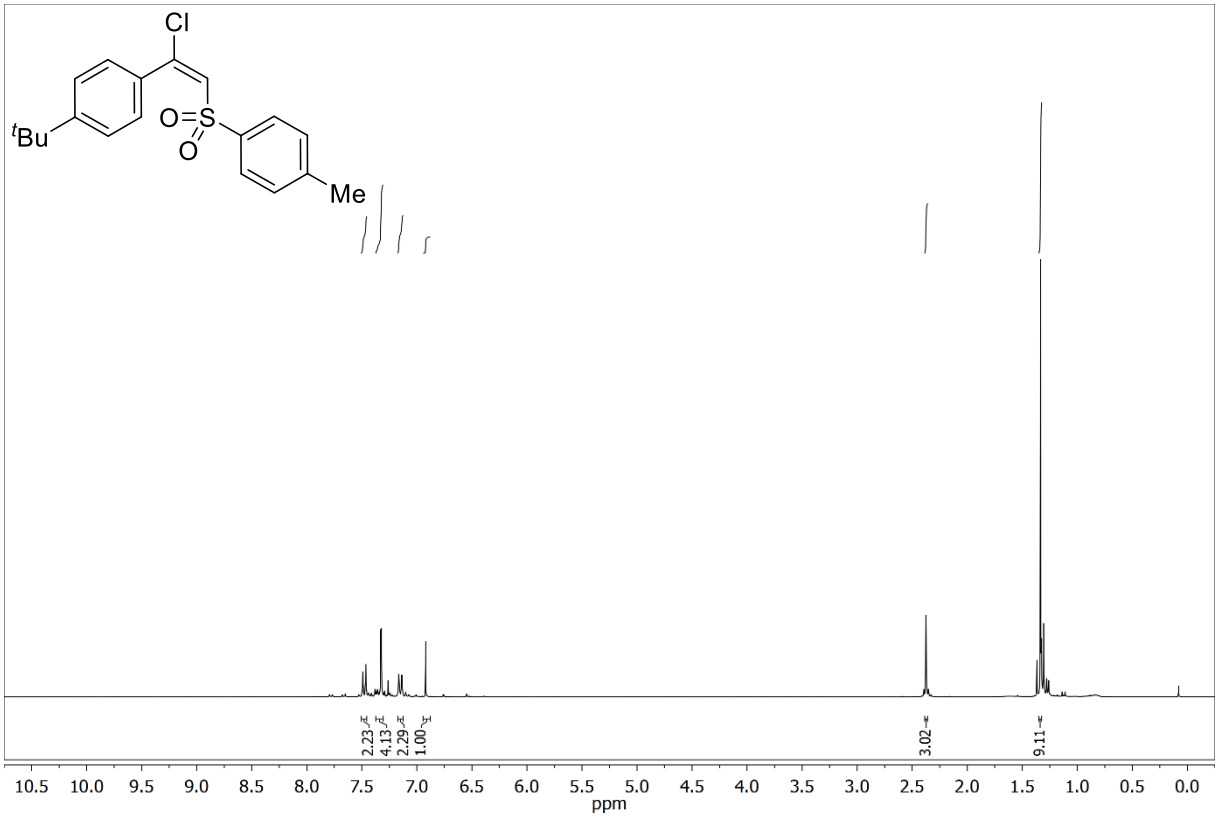
(*Z*)-1-((2-chloro-2-(4-methoxyphenyl)vinyl)sulfonyl)-4-methylbenzene ((*Z*)-14c)

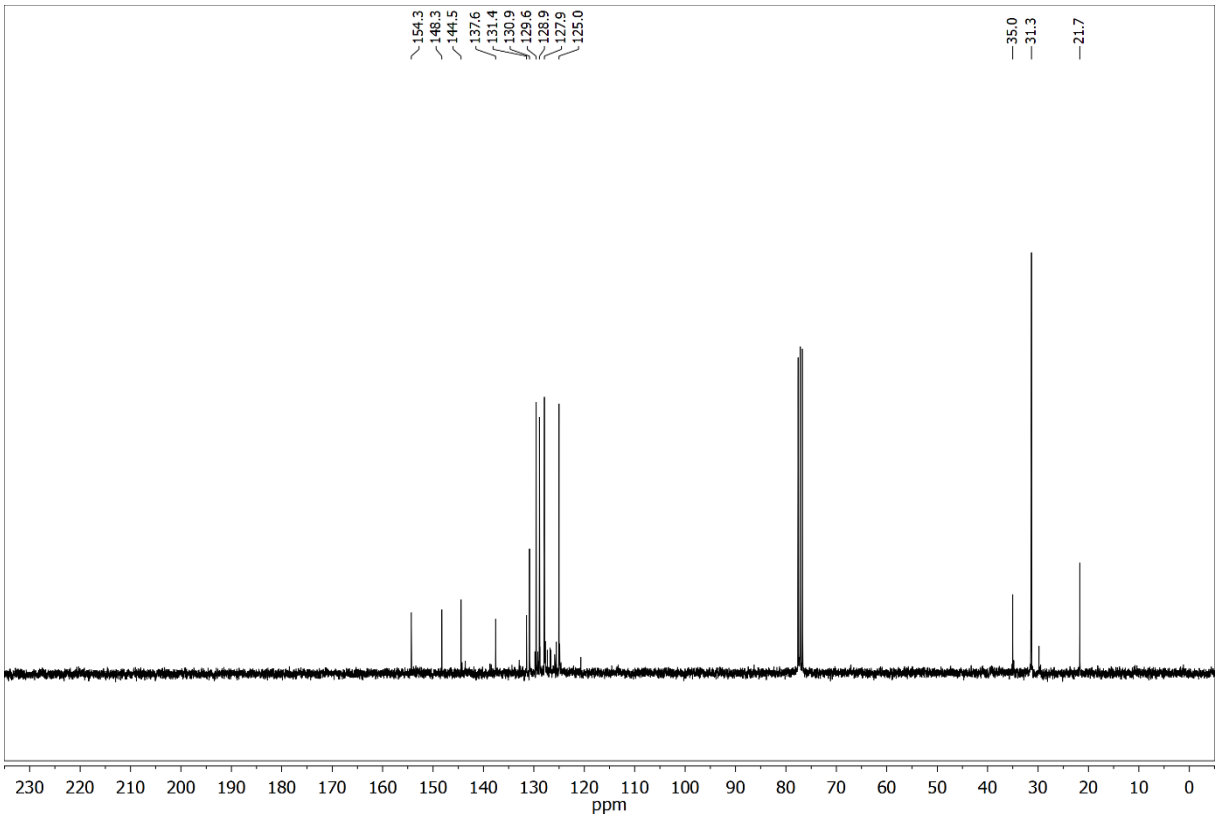




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

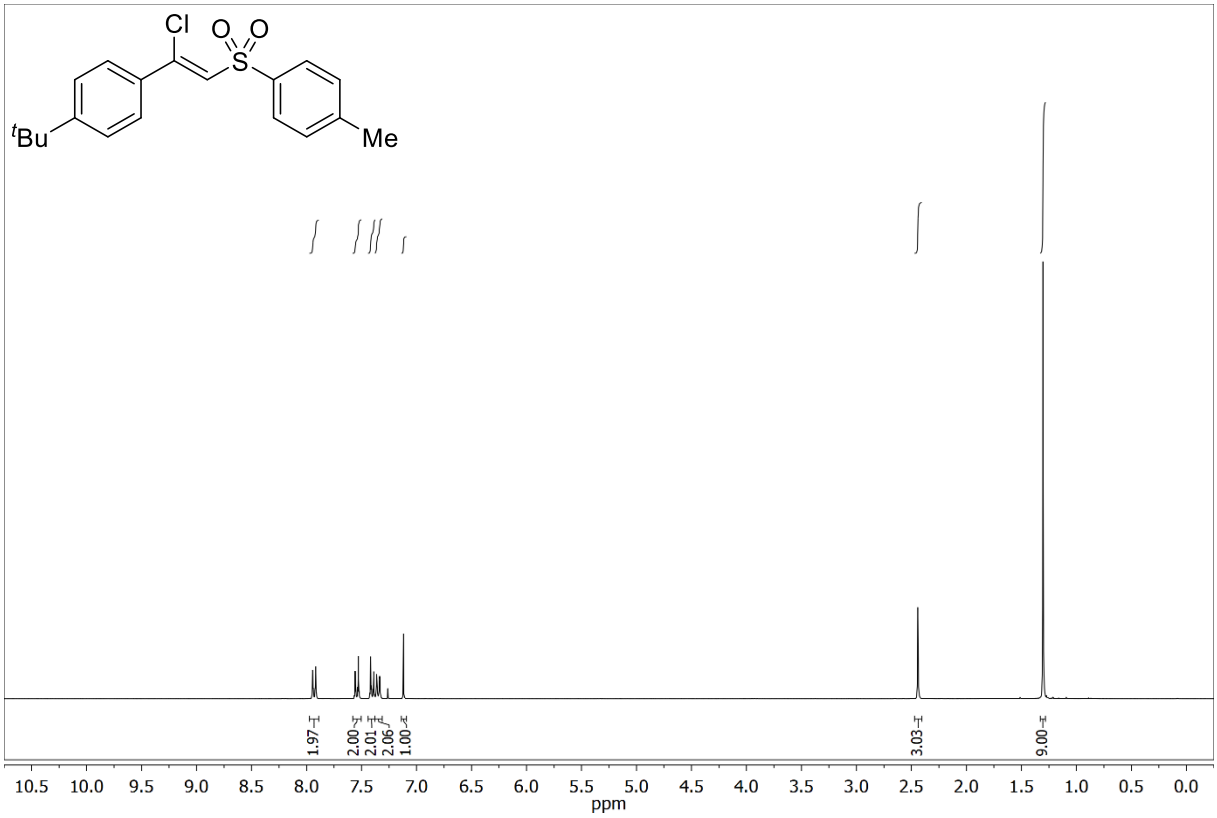
(*E*)-1-(*tert*-butyl)-4-(1-chloro-2-tosylvinyl)benzene ((*E*)-14d)

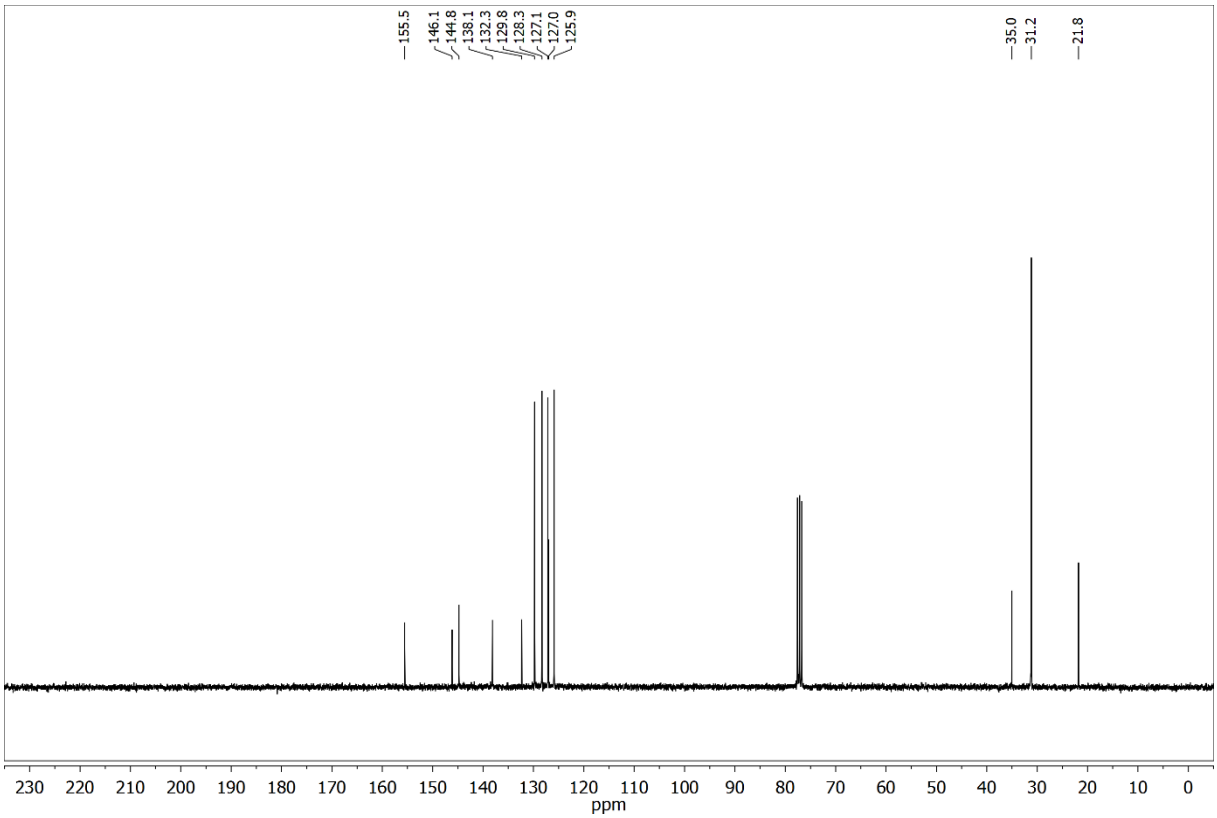




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

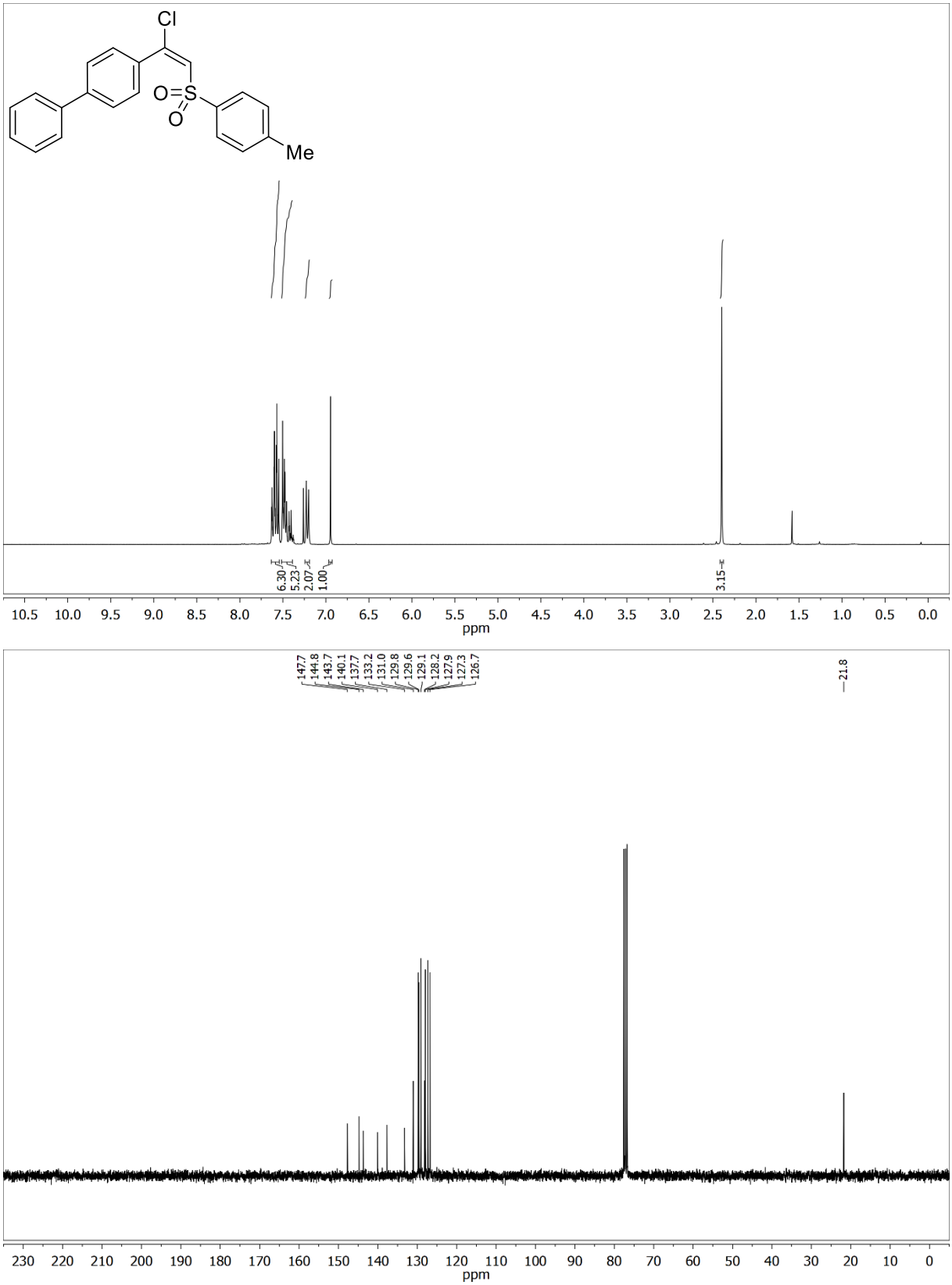
(*Z*)-1-(*tert*-butyl)-4-(1-chloro-2-tosylvinyl)benzene ((*Z*)-14d)





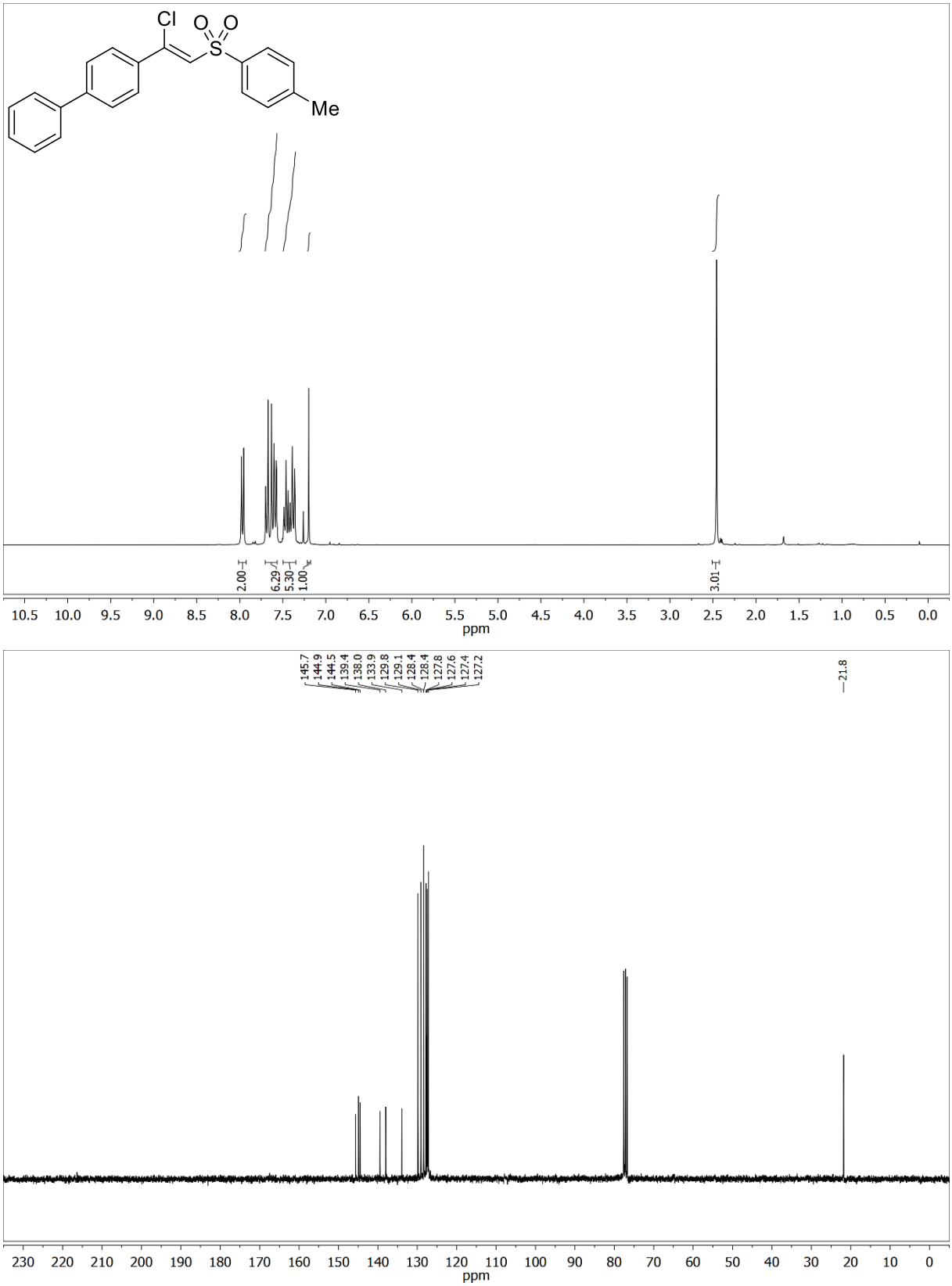
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

(*E*)-4-(1-chloro-2-tosylvinyl)-1,1'-biphenyl ((*E*)-14e)



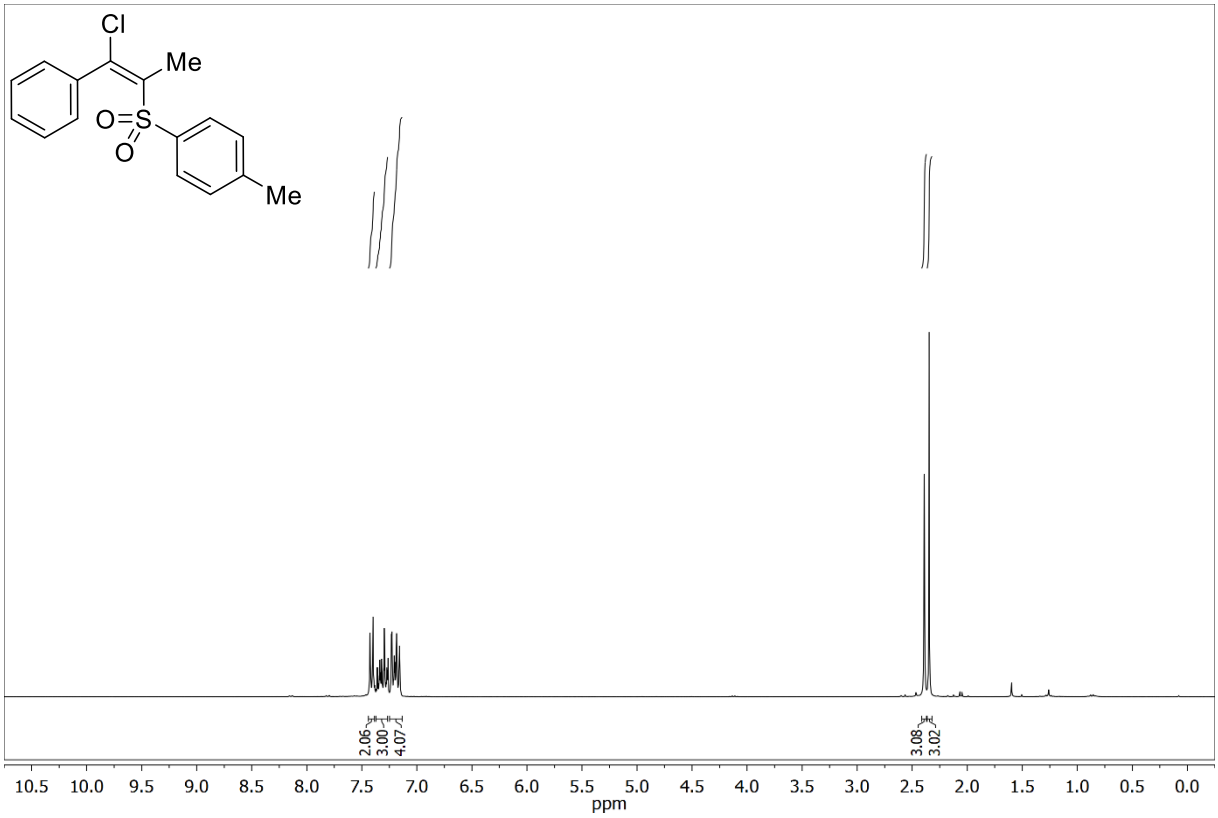
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

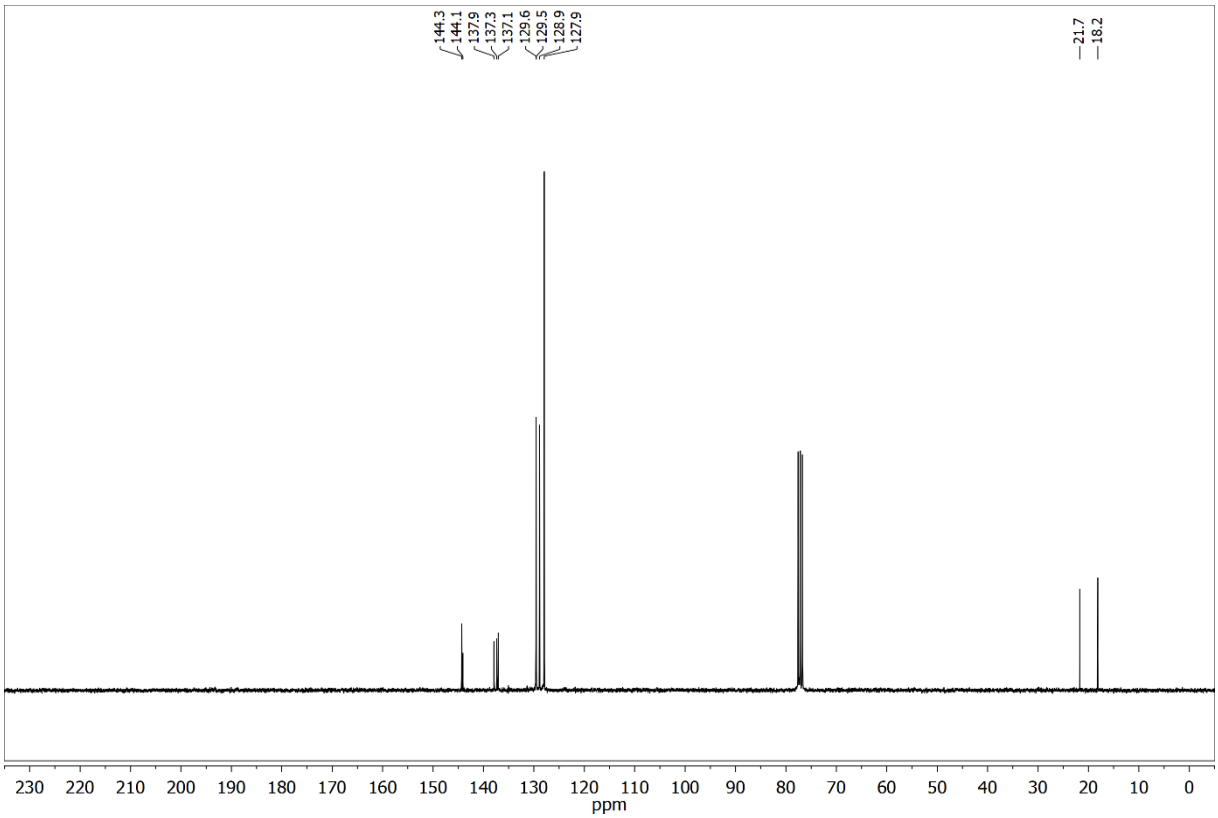
(*Z*)-4-(1-chloro-2-tosylvinyl)-1,1'-biphenyl ((*Z*)-14e)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

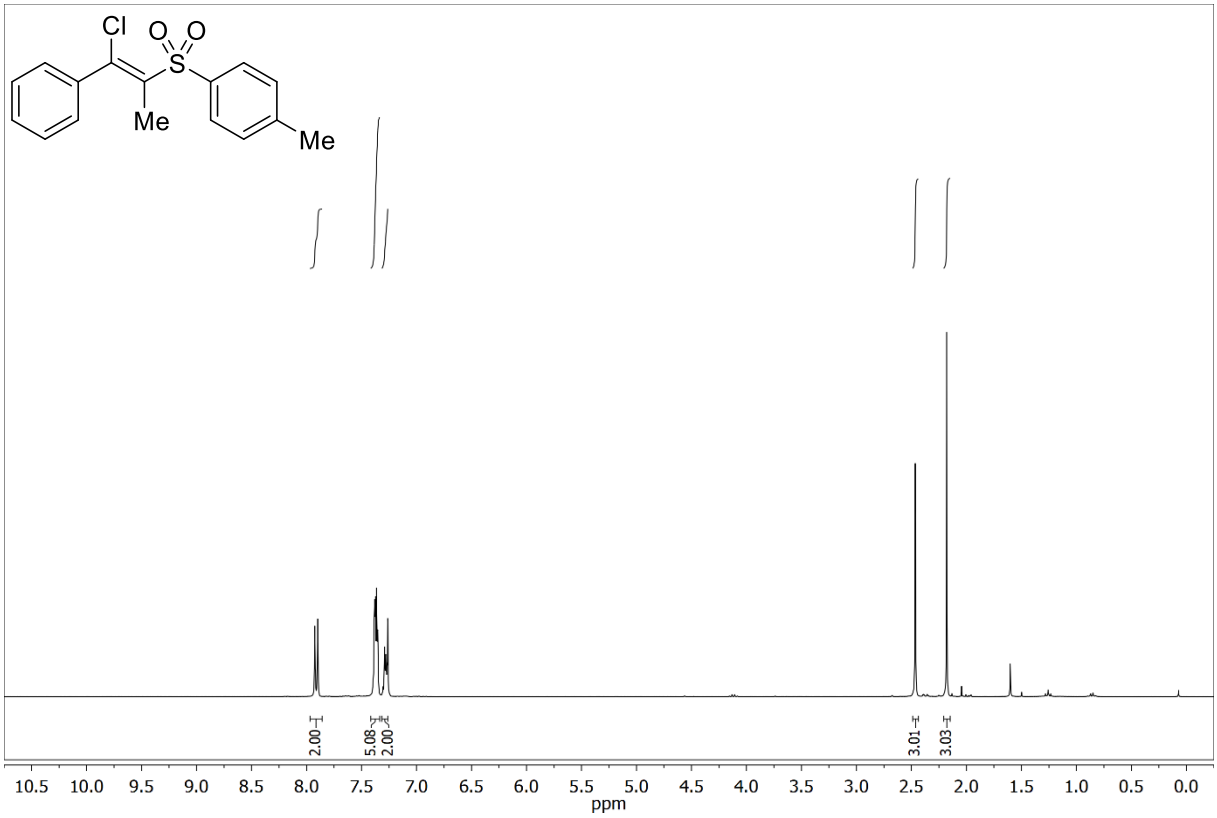
(*E*)-1-((1-chloro-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene ((*E*)-14f)

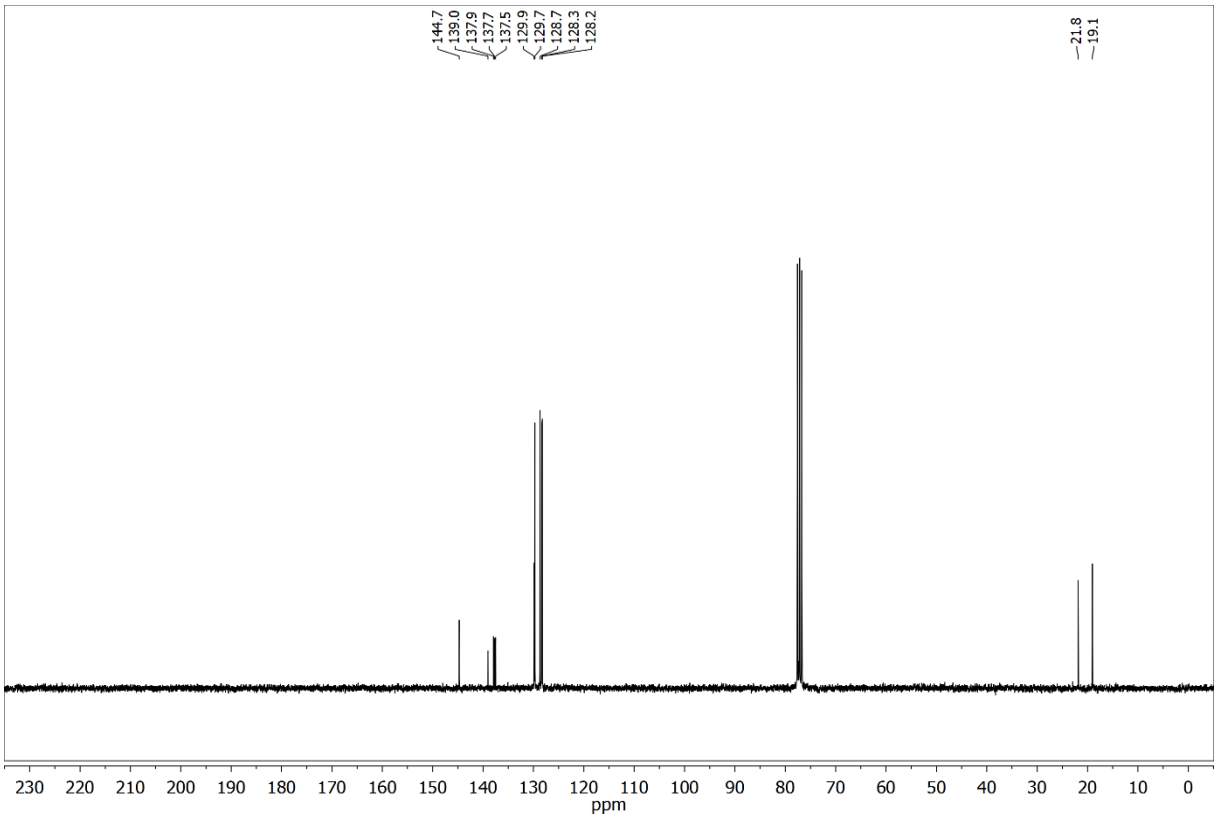




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

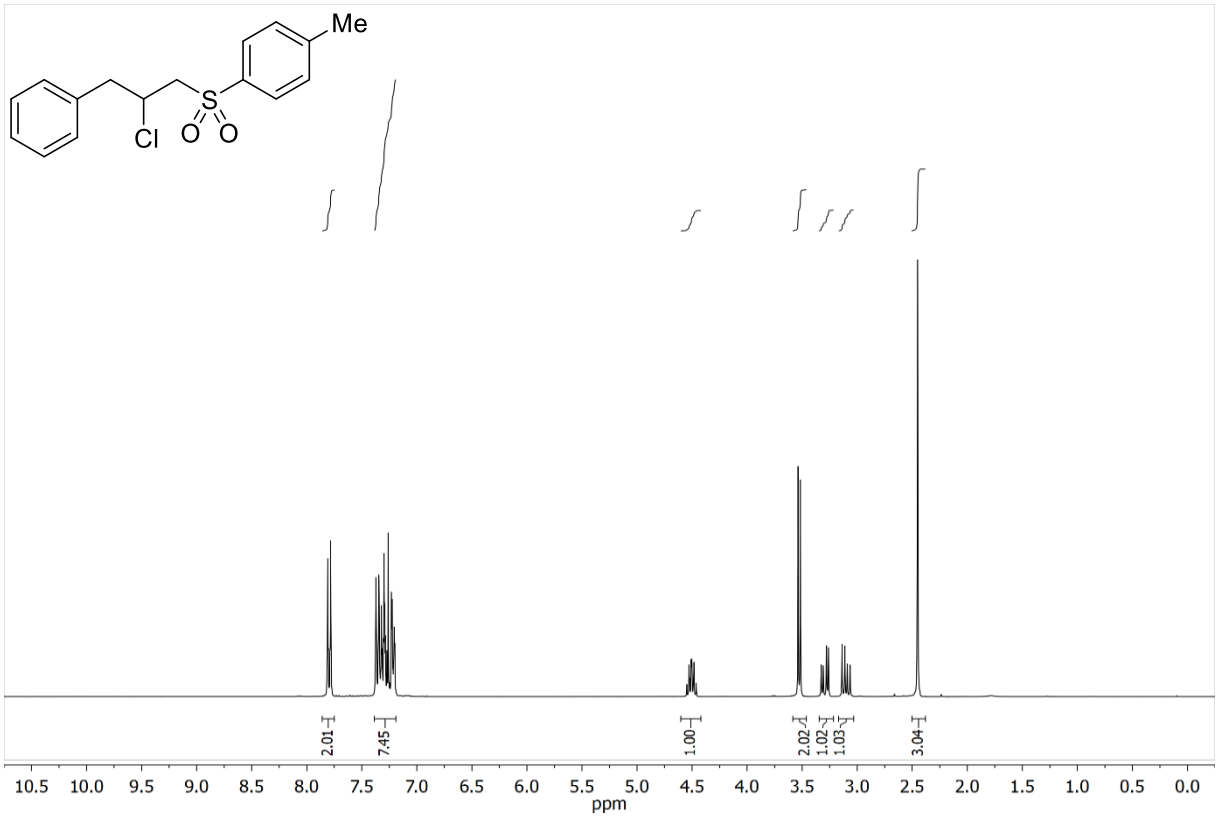
(*Z*)-1-((1-chloro-1-phenylprop-1-en-2-yl)sulfonyl)-4-methylbenzene ((*Z*)-14f)

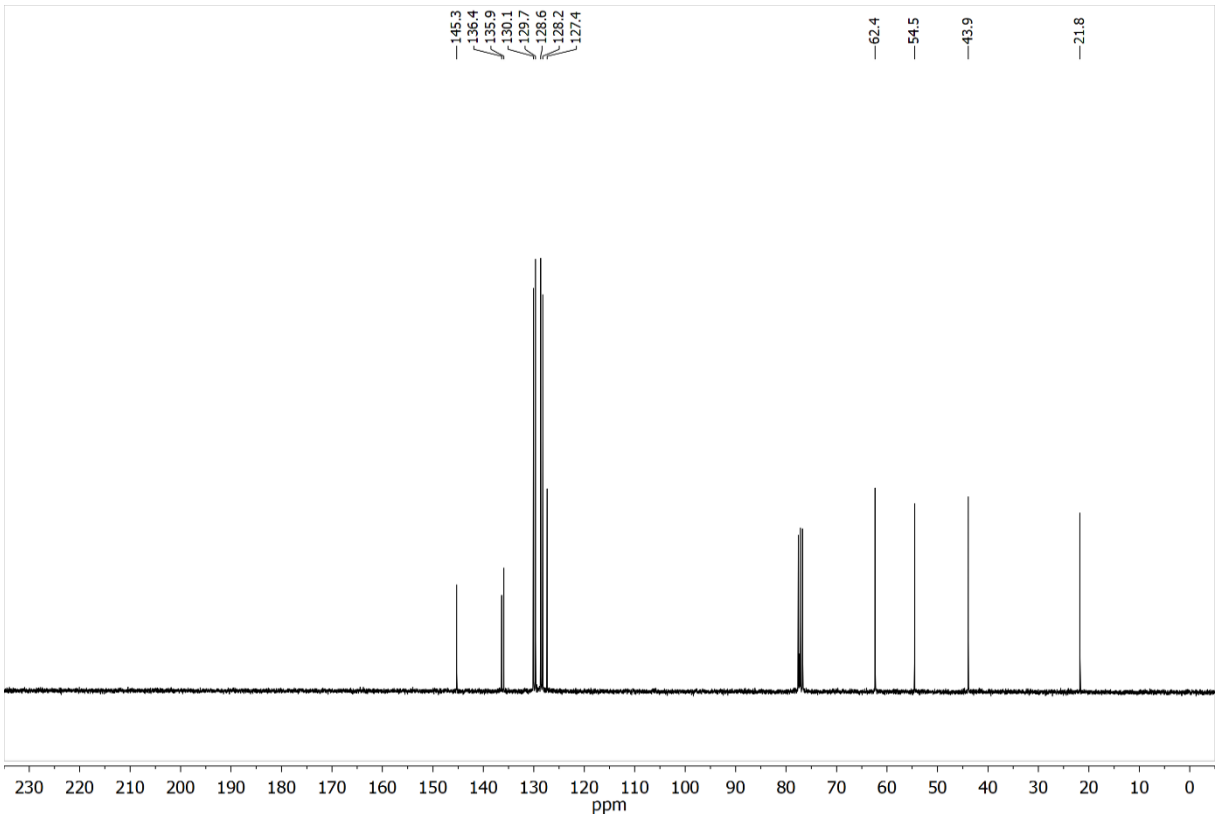




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

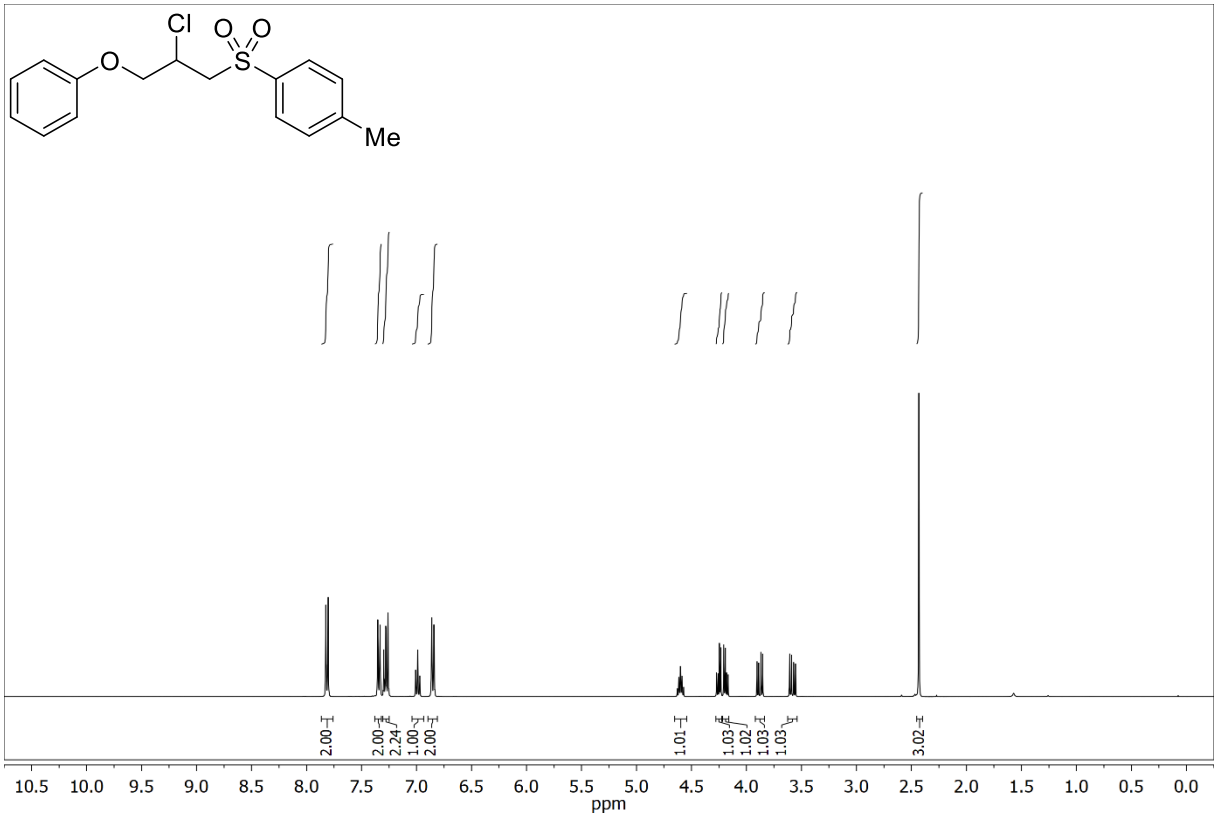
1-((2-chloro-3-phenylpropyl)sulfonyl)-4-methylbenzene (10at//9l)

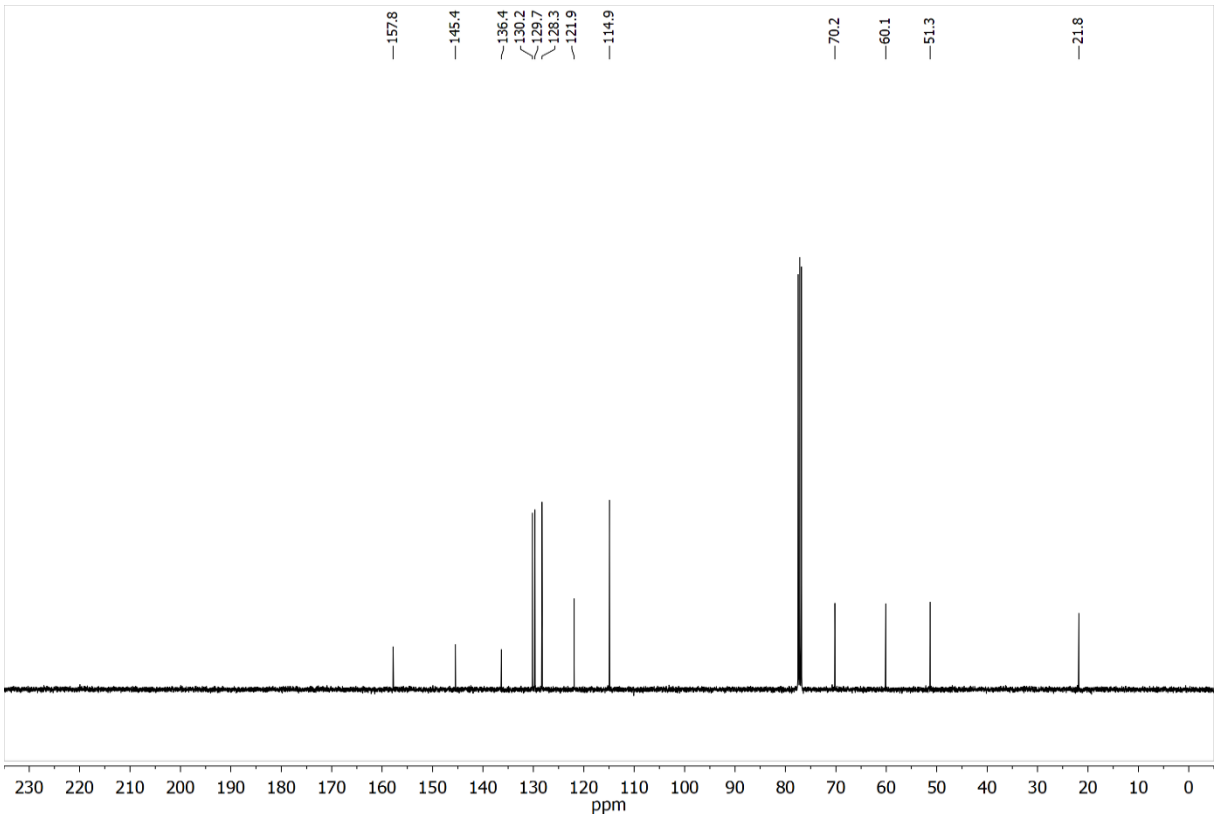




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

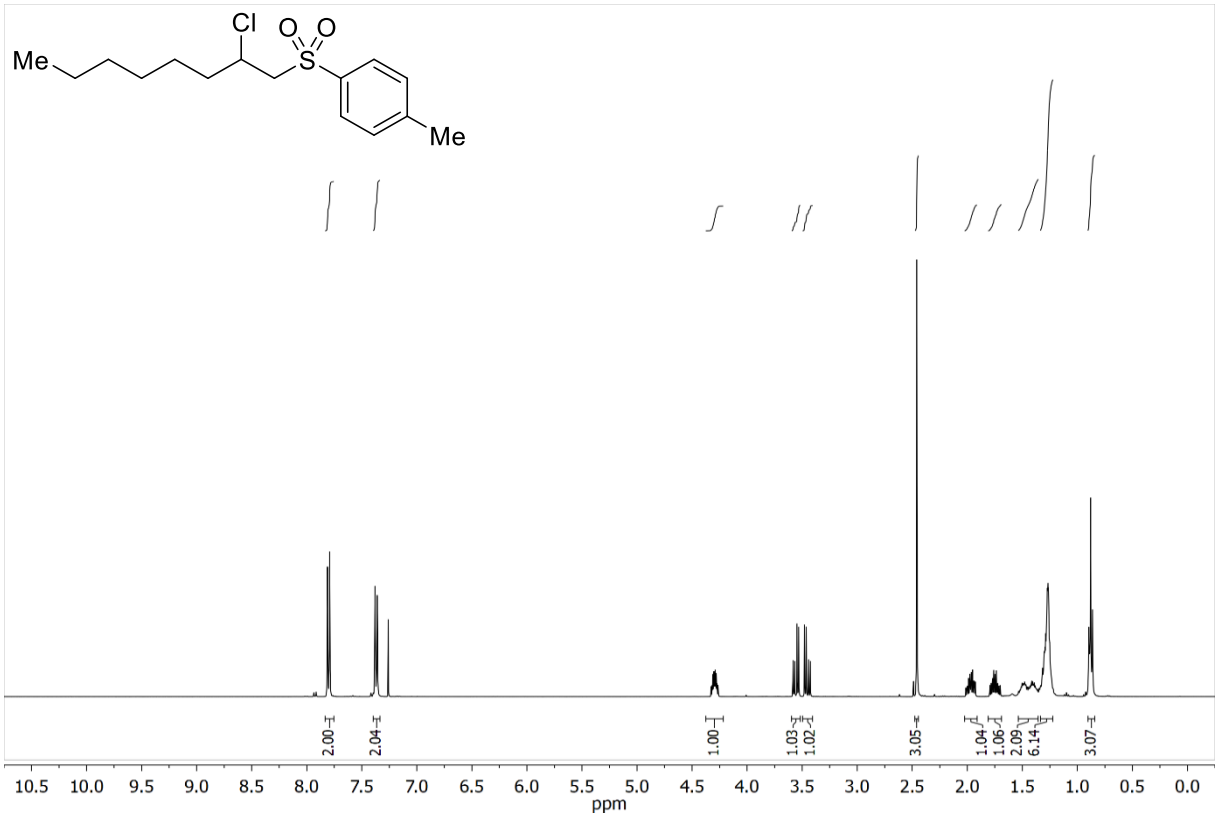
1-((2-chloro-3-phenoxypropyl)sulfonyl)-4-methylbenzene (10bh//9m)

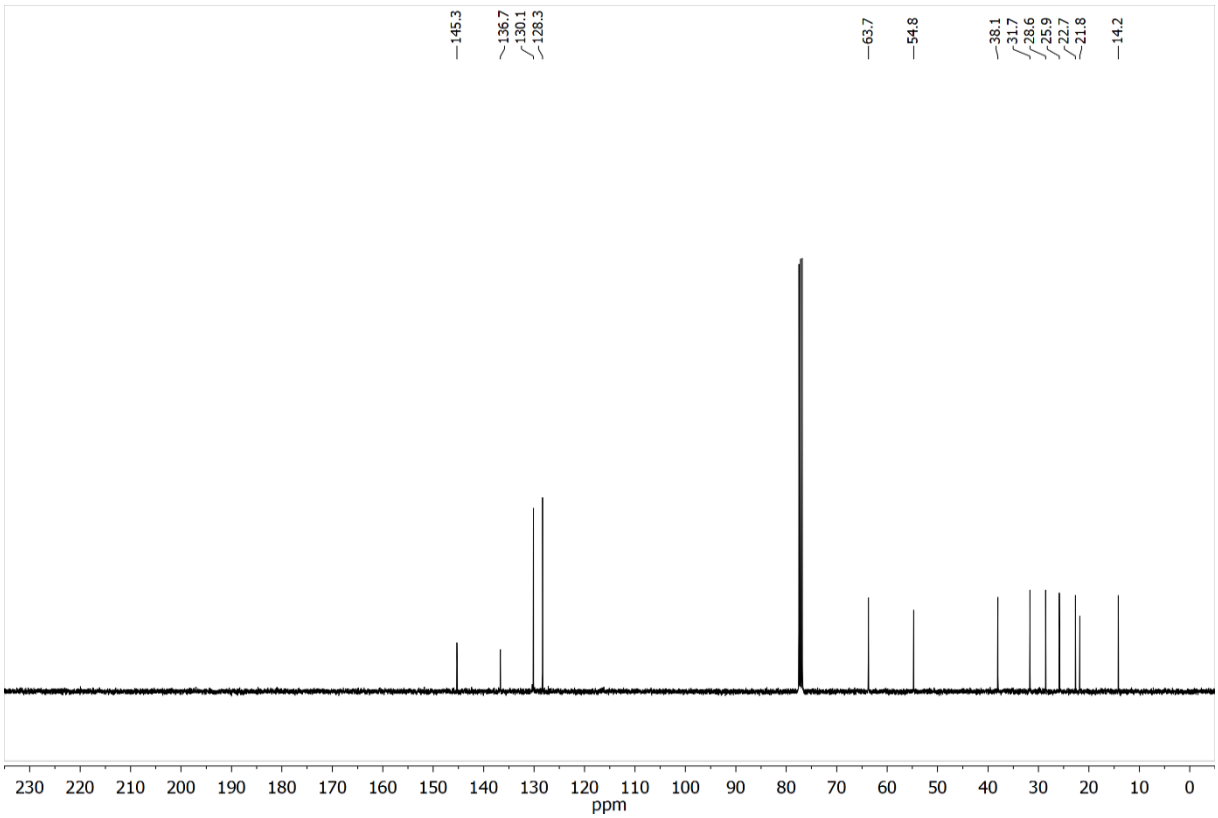




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

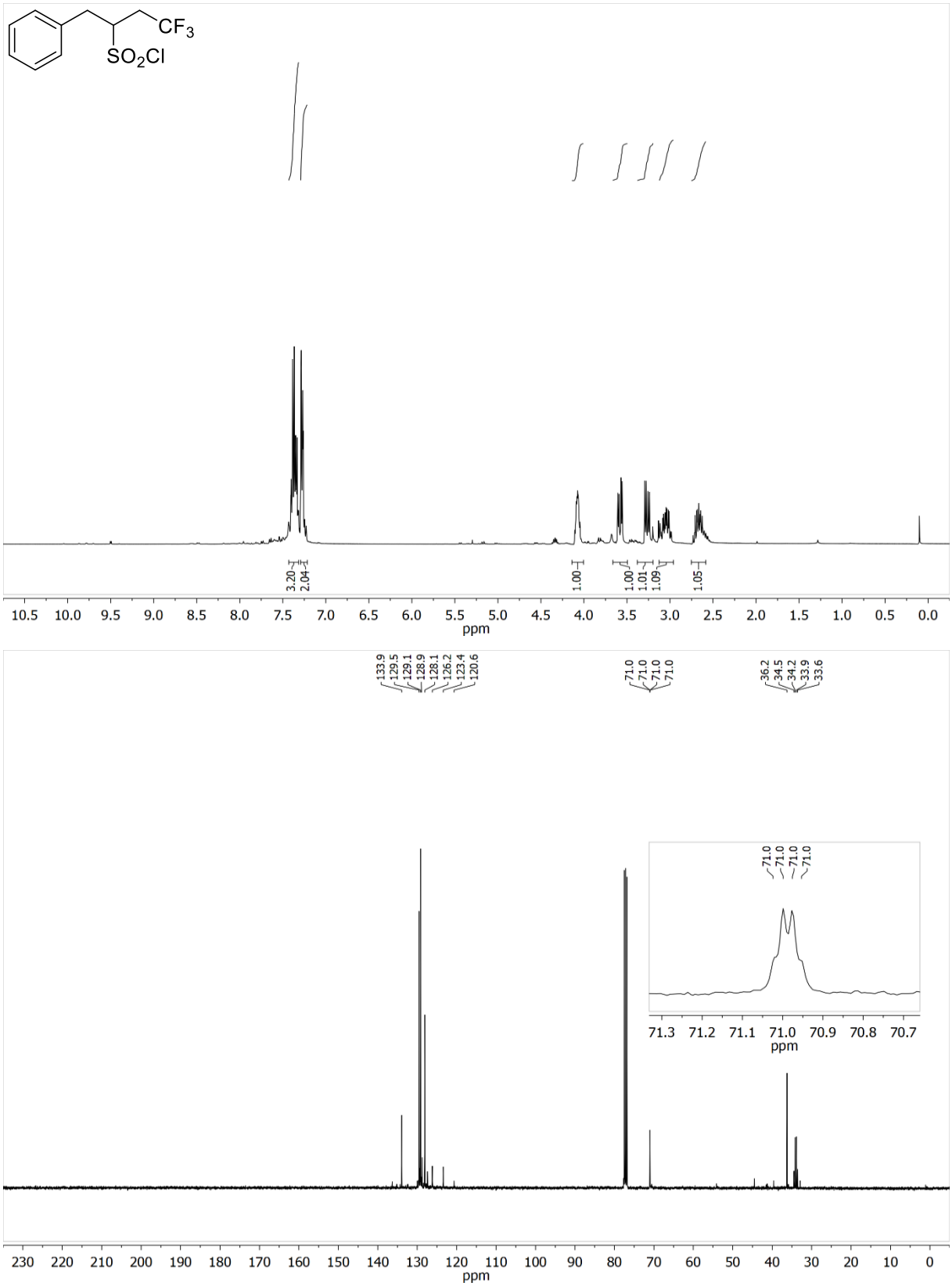
1-((2-chlorooctyl)sulfonyl)-4-methylbenzene (10bj//9n)



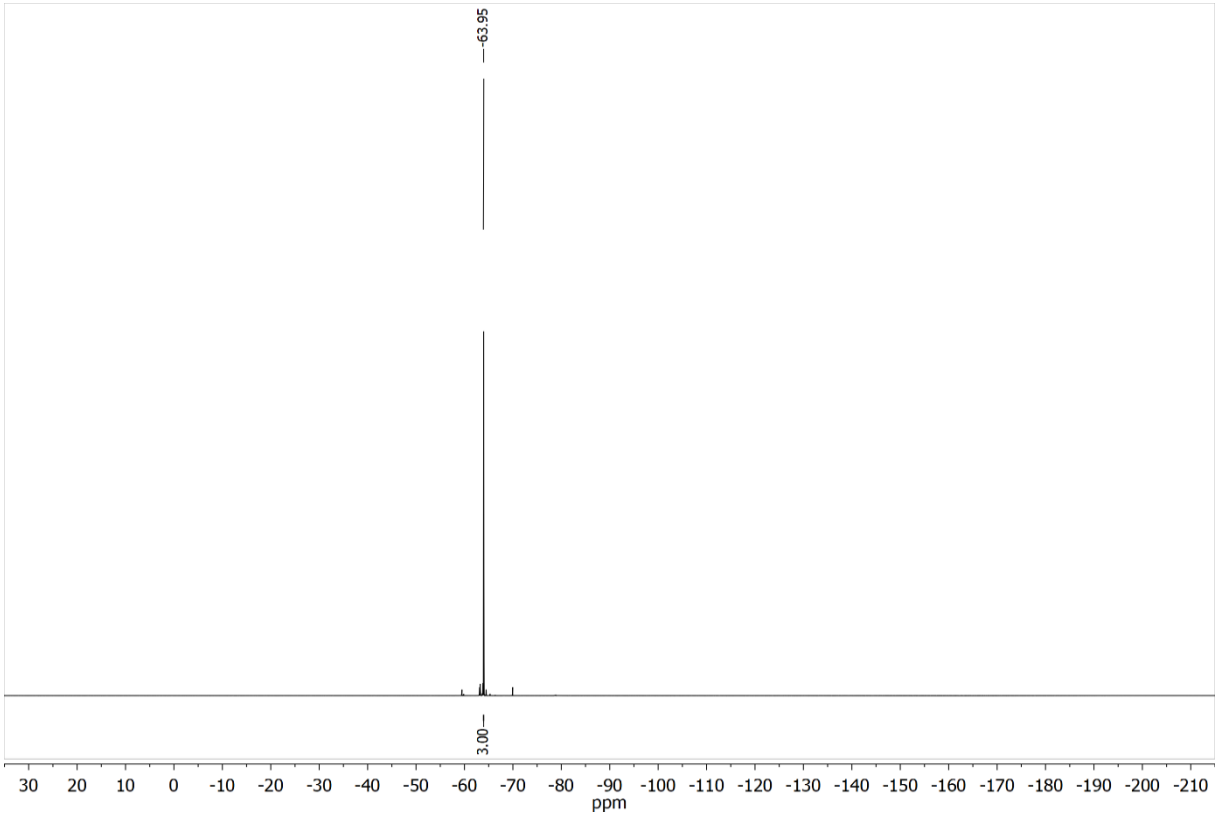


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

4,4,4-trifluoro-1-phenylbutane-2-sulfonyl chloride (11a)

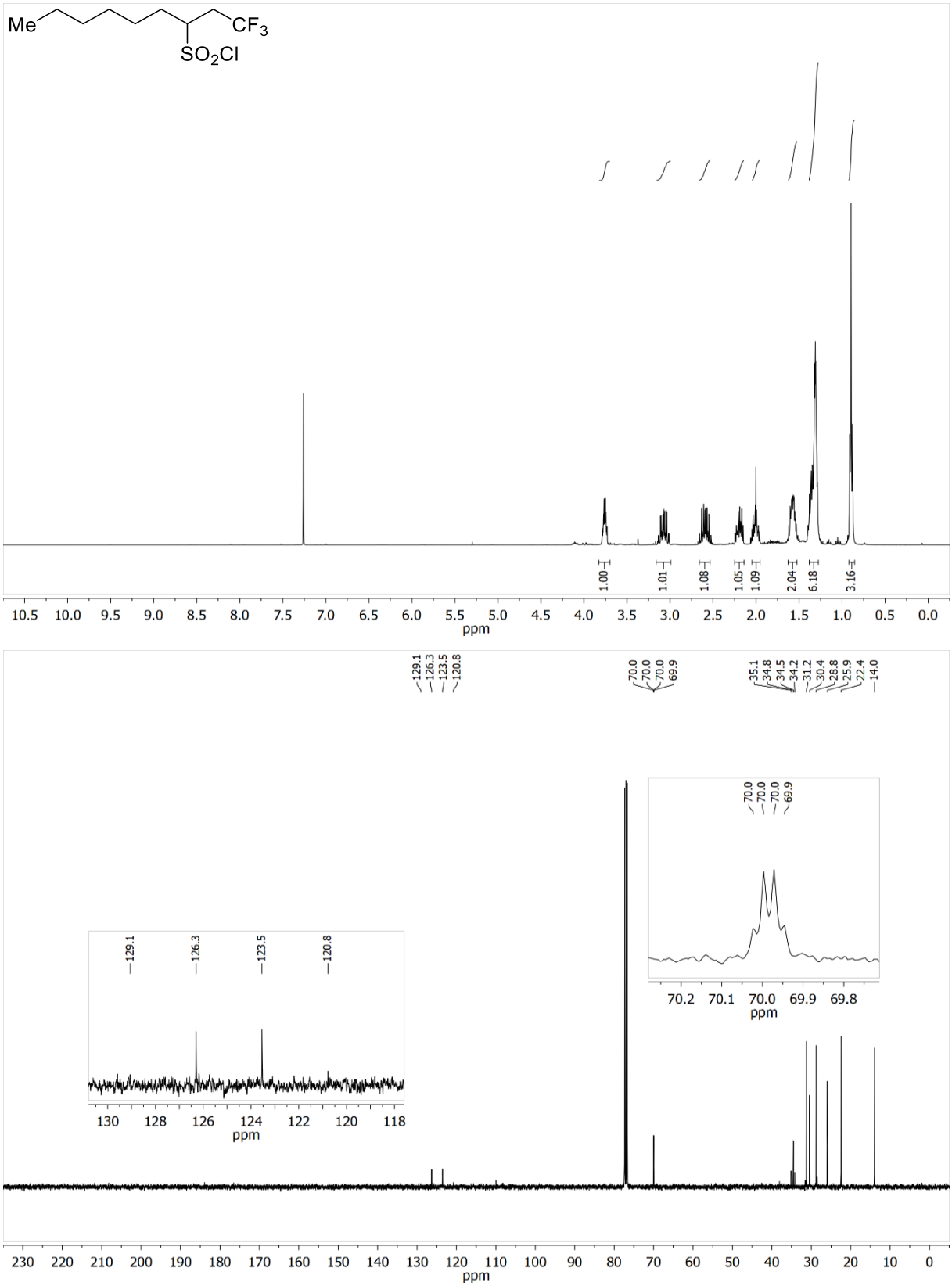


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

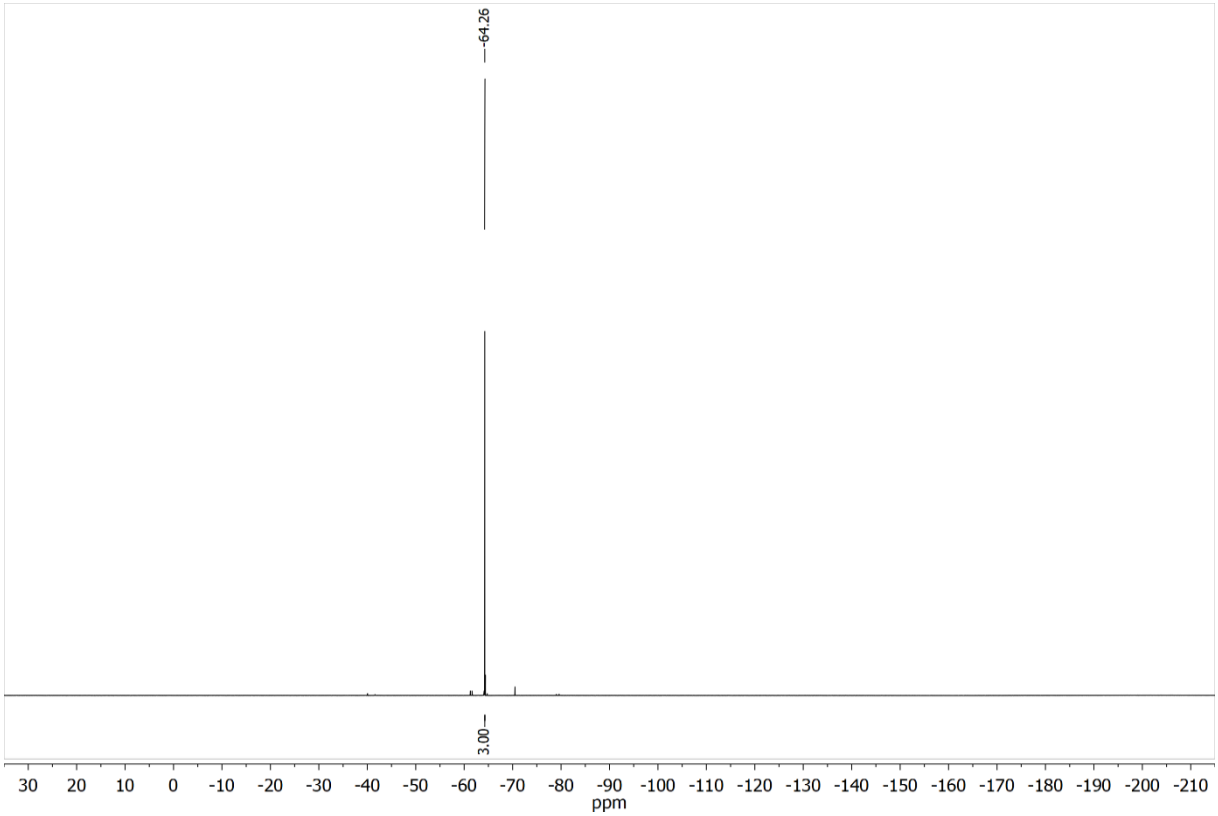


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1,1,1-trifluorononane-3-sulfonyl chloride (11b)

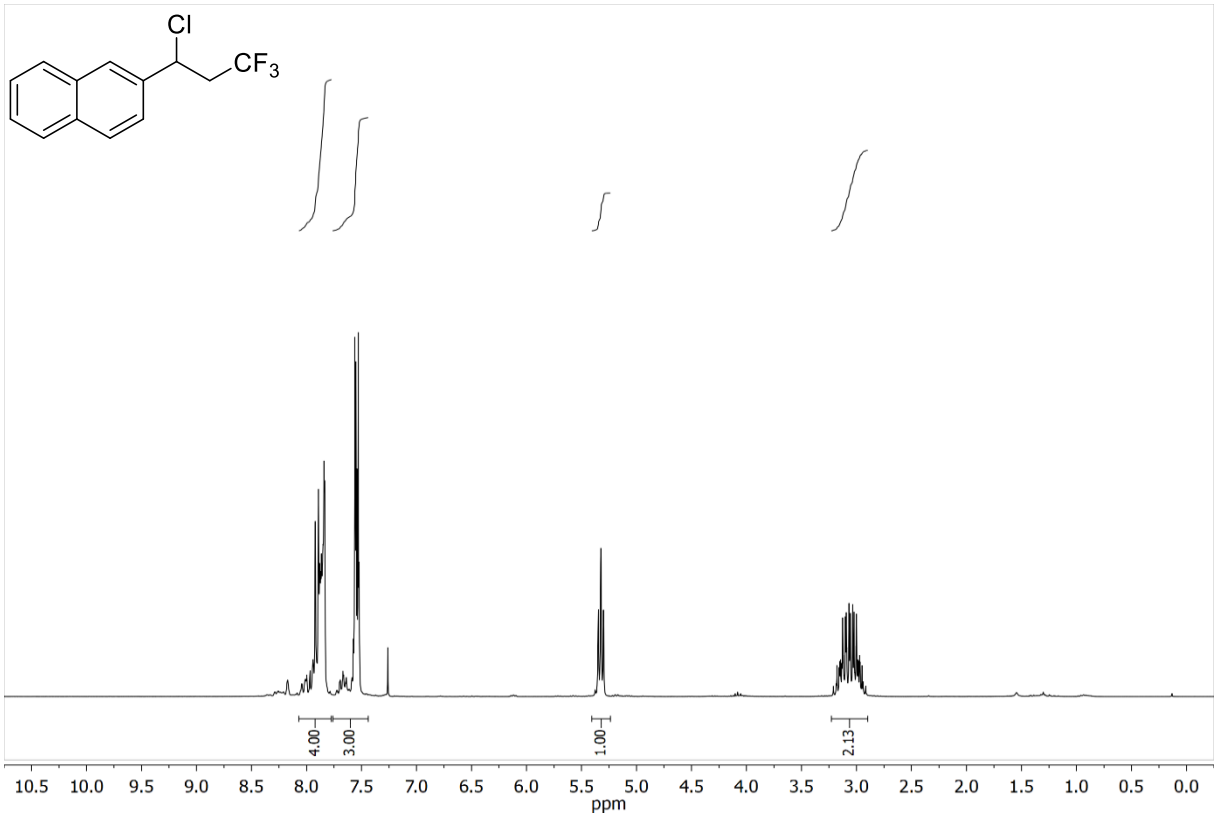


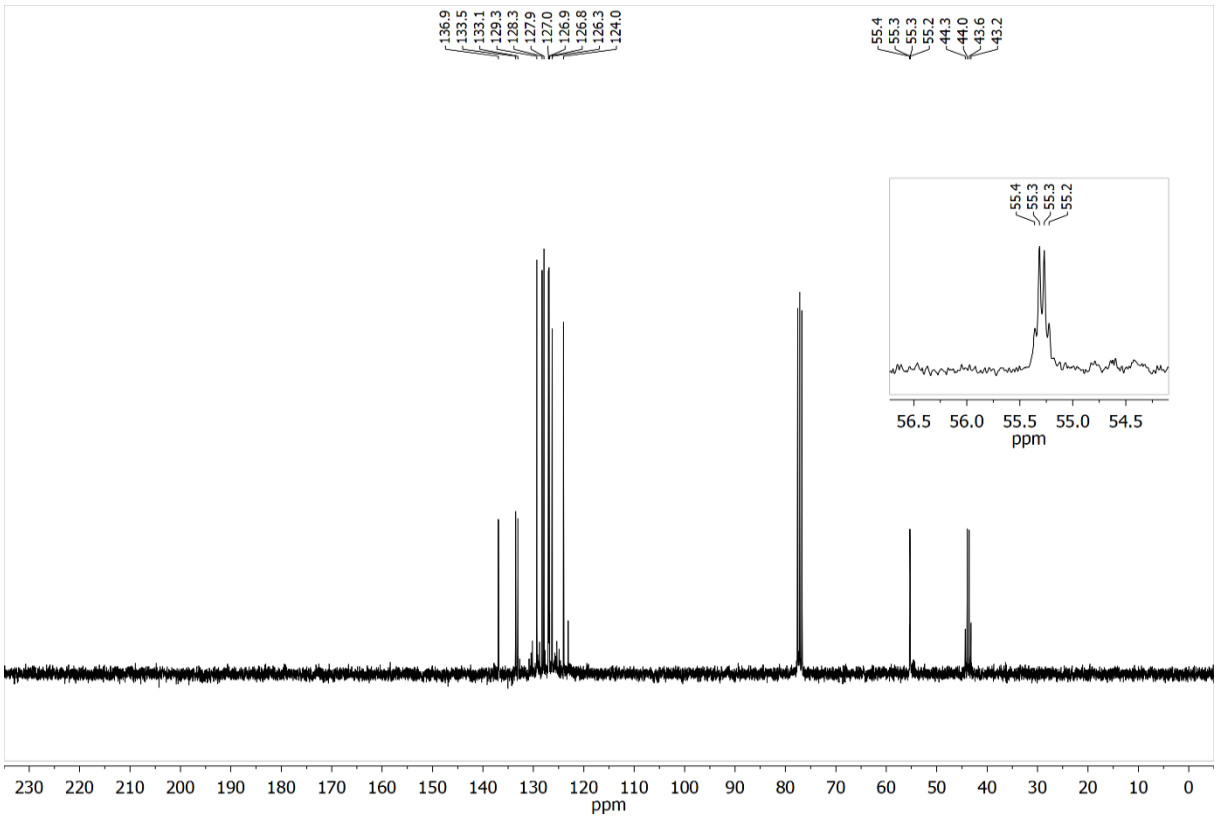
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



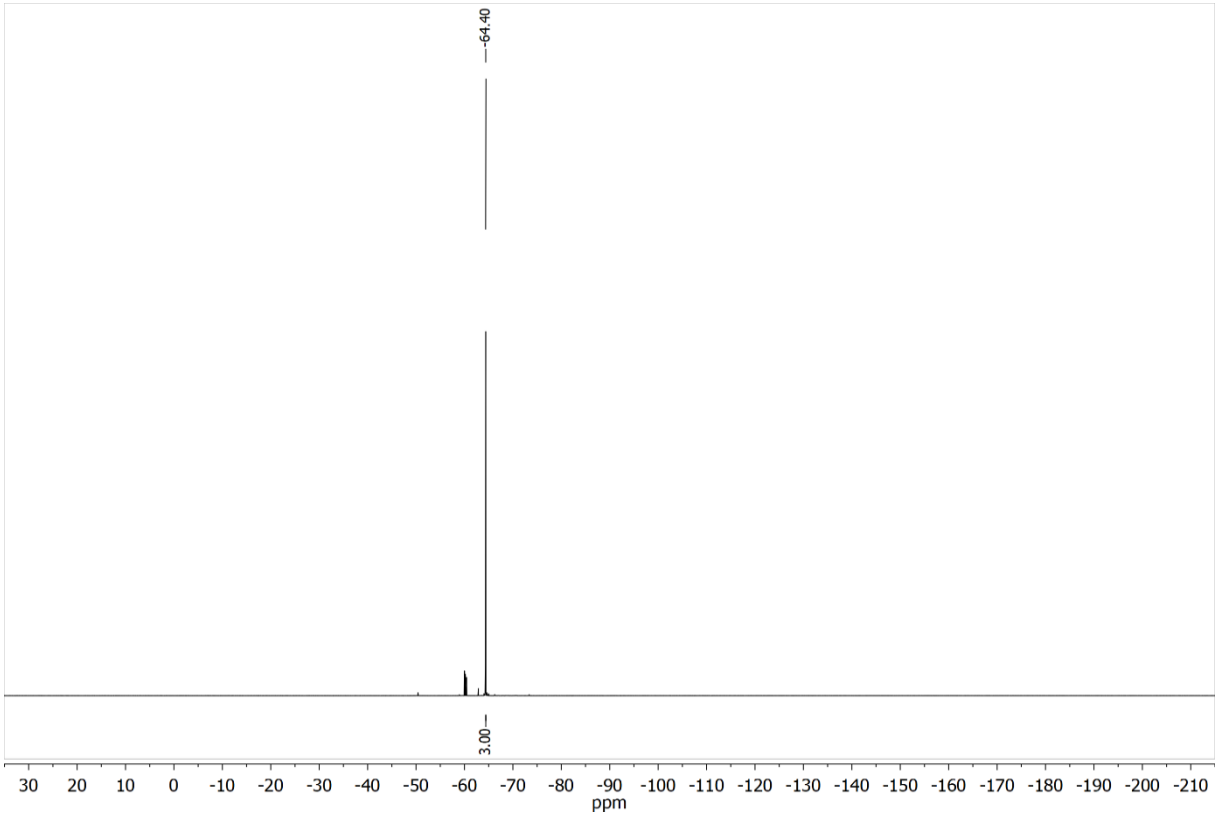
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

2-(1-chloro-3,3,3-trifluoropropyl)naphthalene (12a)



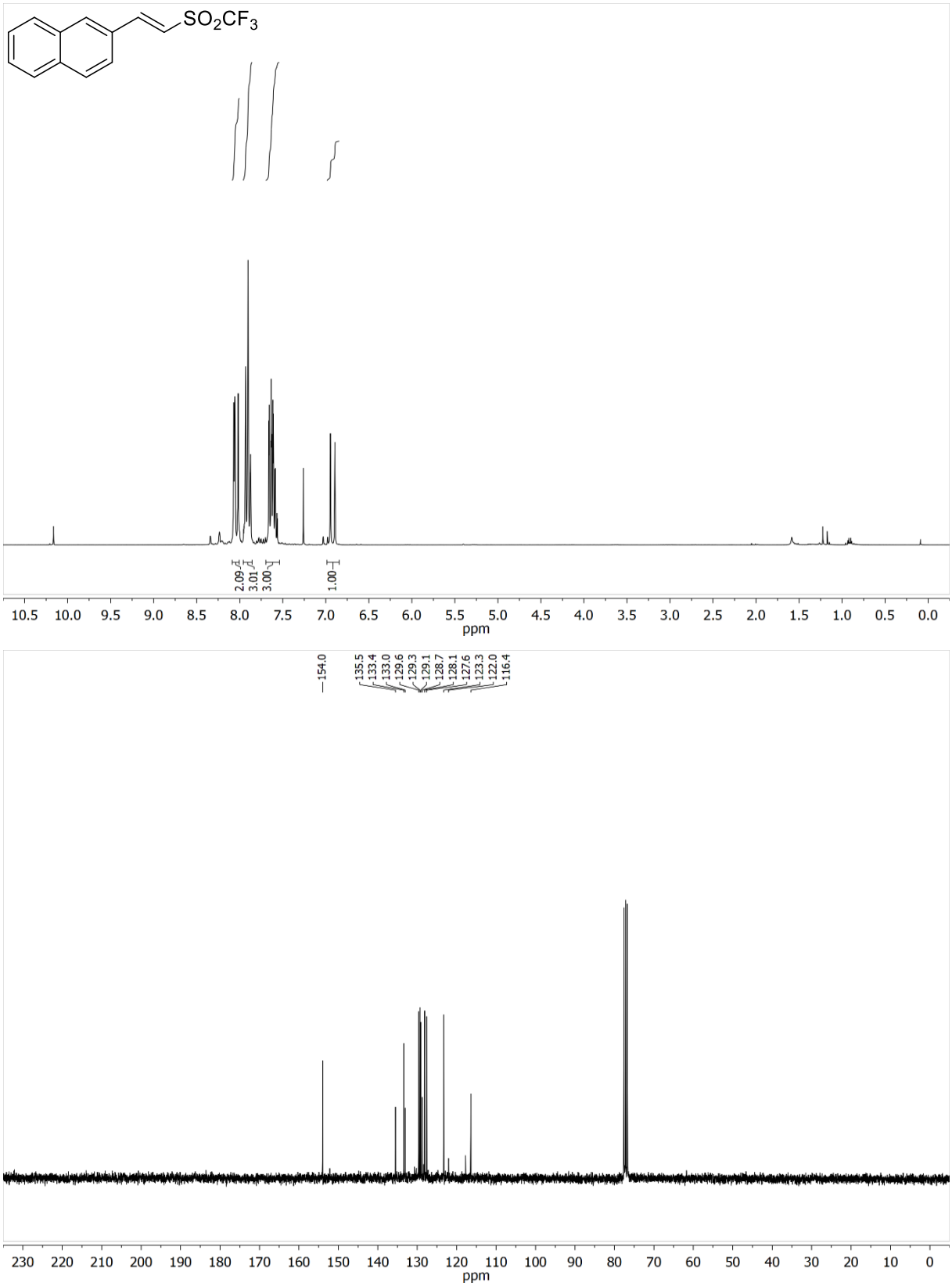


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

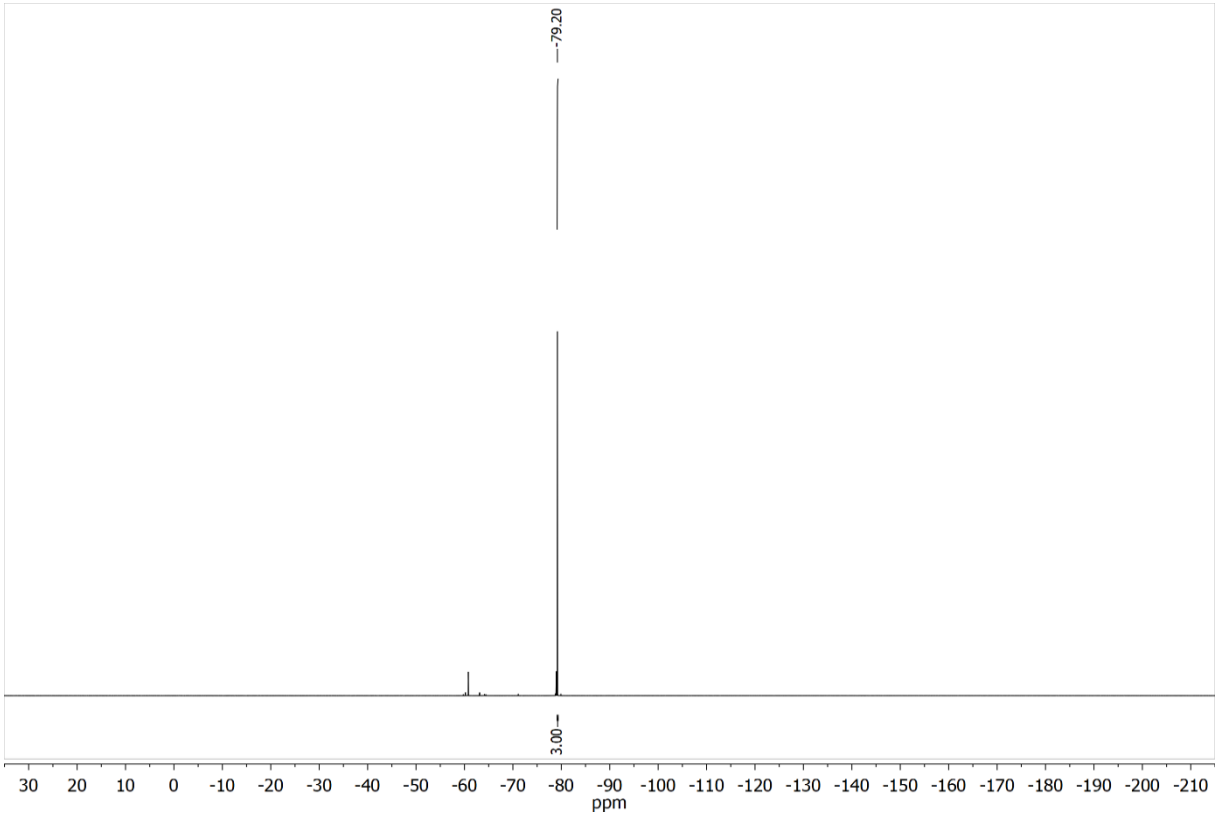


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

(*E*)-2-(2-((trifluoromethyl)sulfonyl)vinyl)naphthalene (13a)

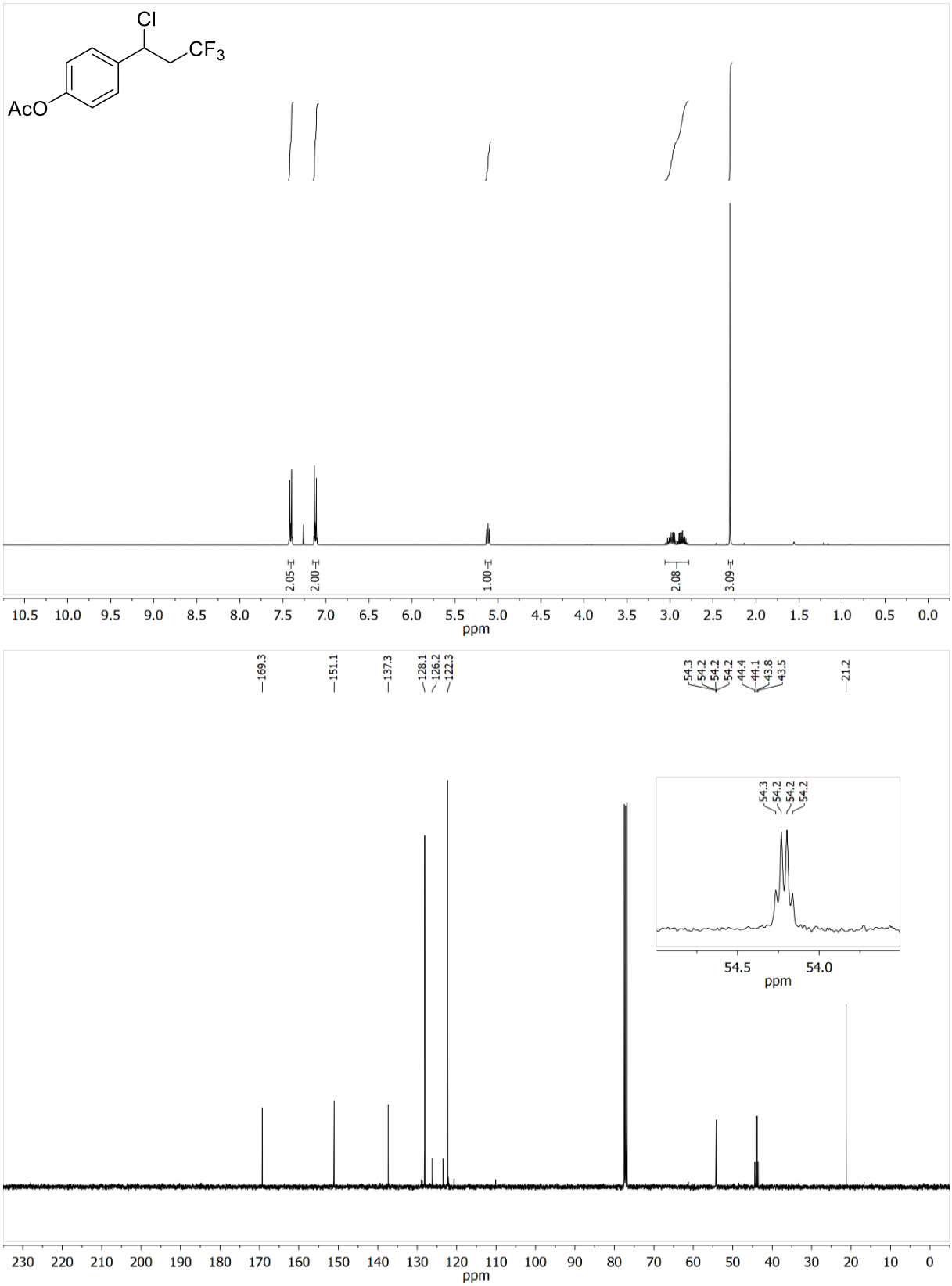


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

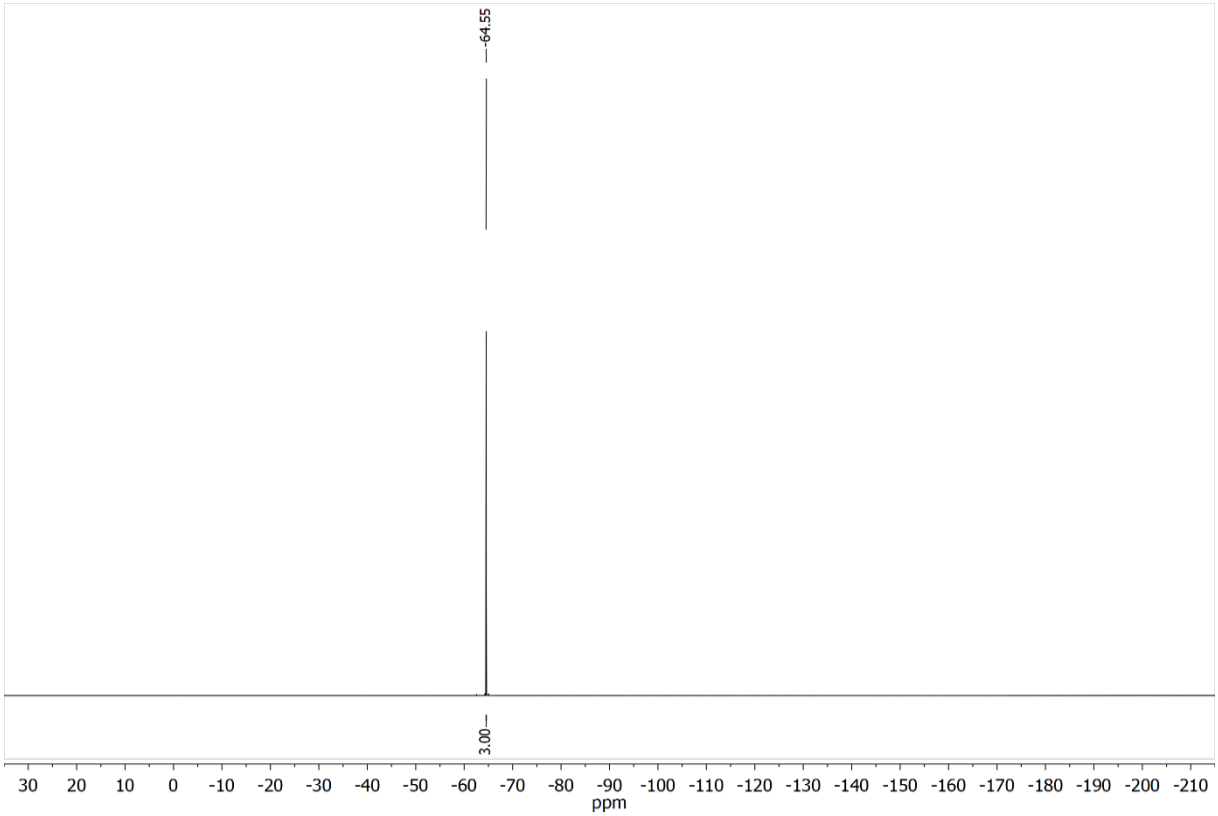


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

4-(1-chloro-3,3,3-trifluoropropyl)phenyl acetate (12b)

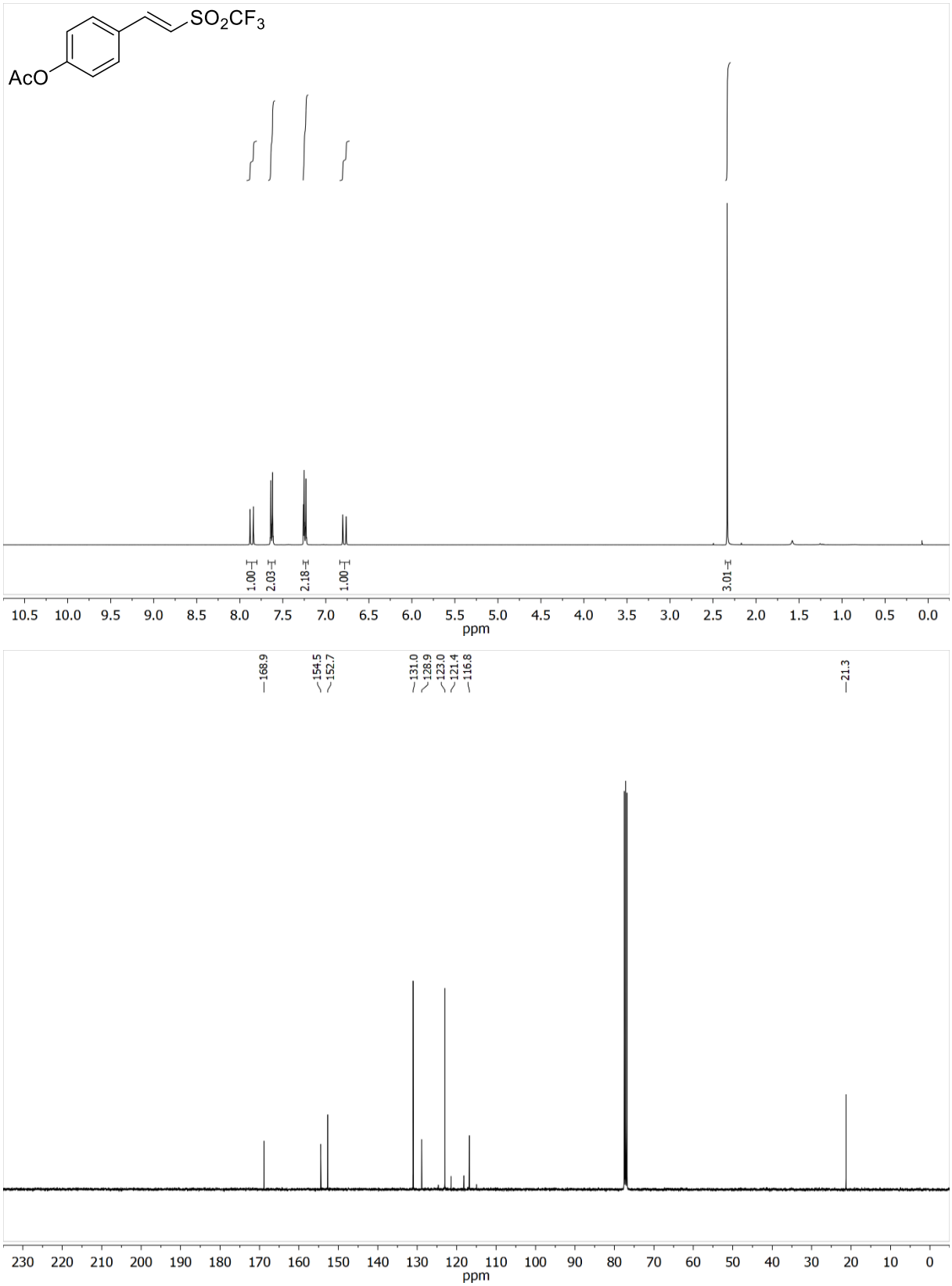


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

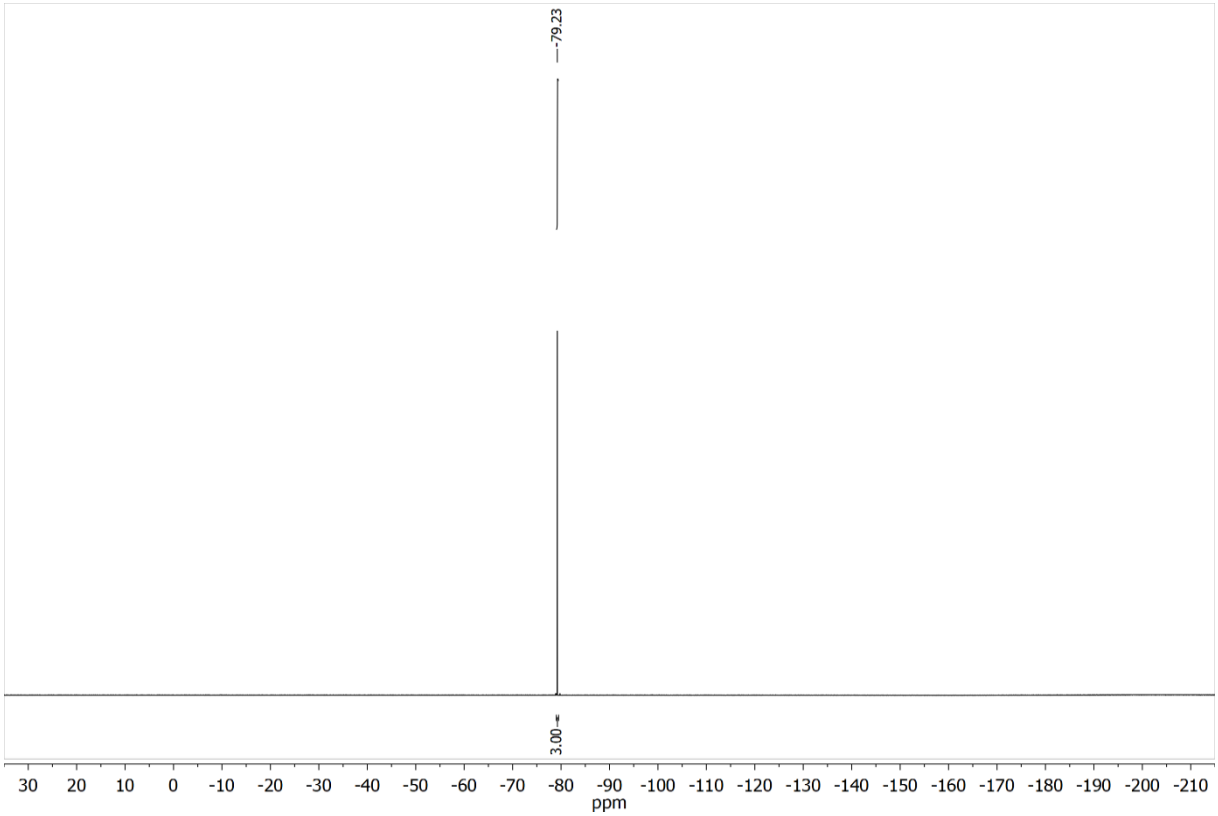


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

(*E*)-4-(2-((trifluoromethyl)sulfonyl)vinyl)phenyl acetate (13b)

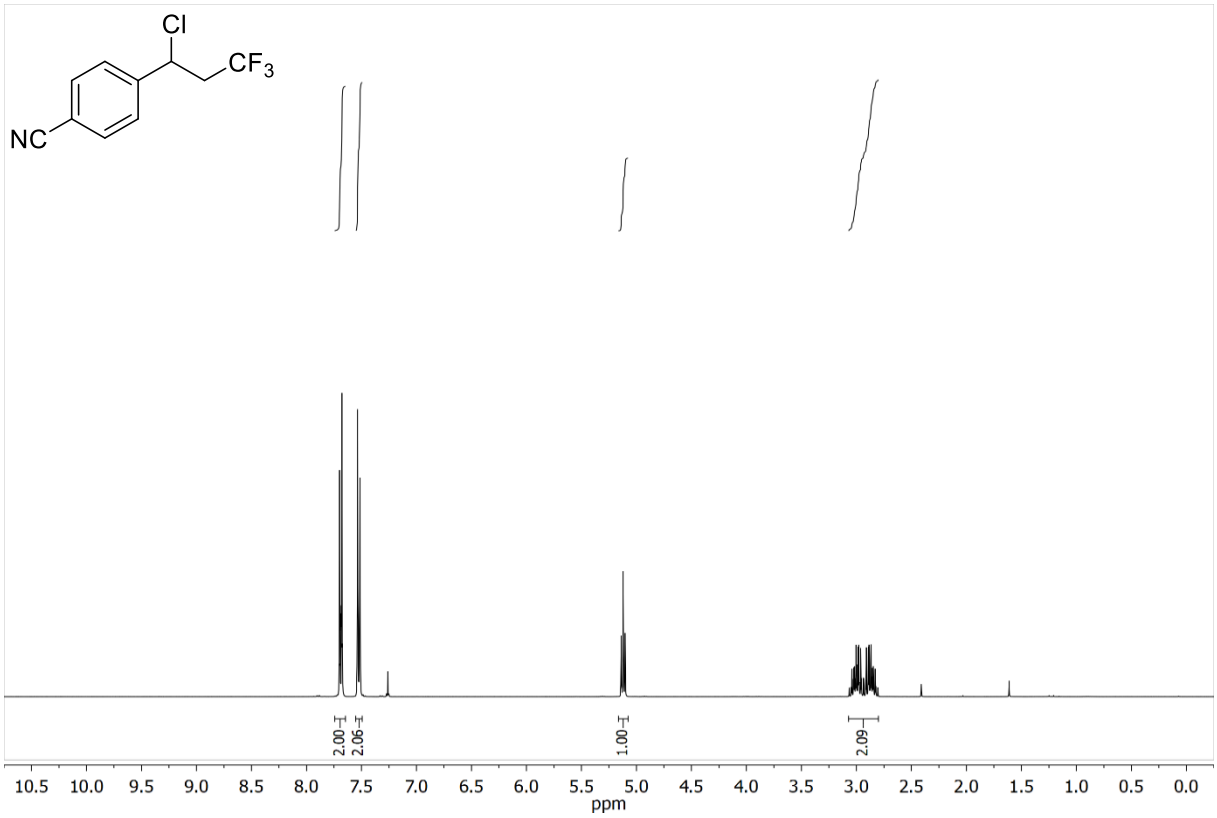


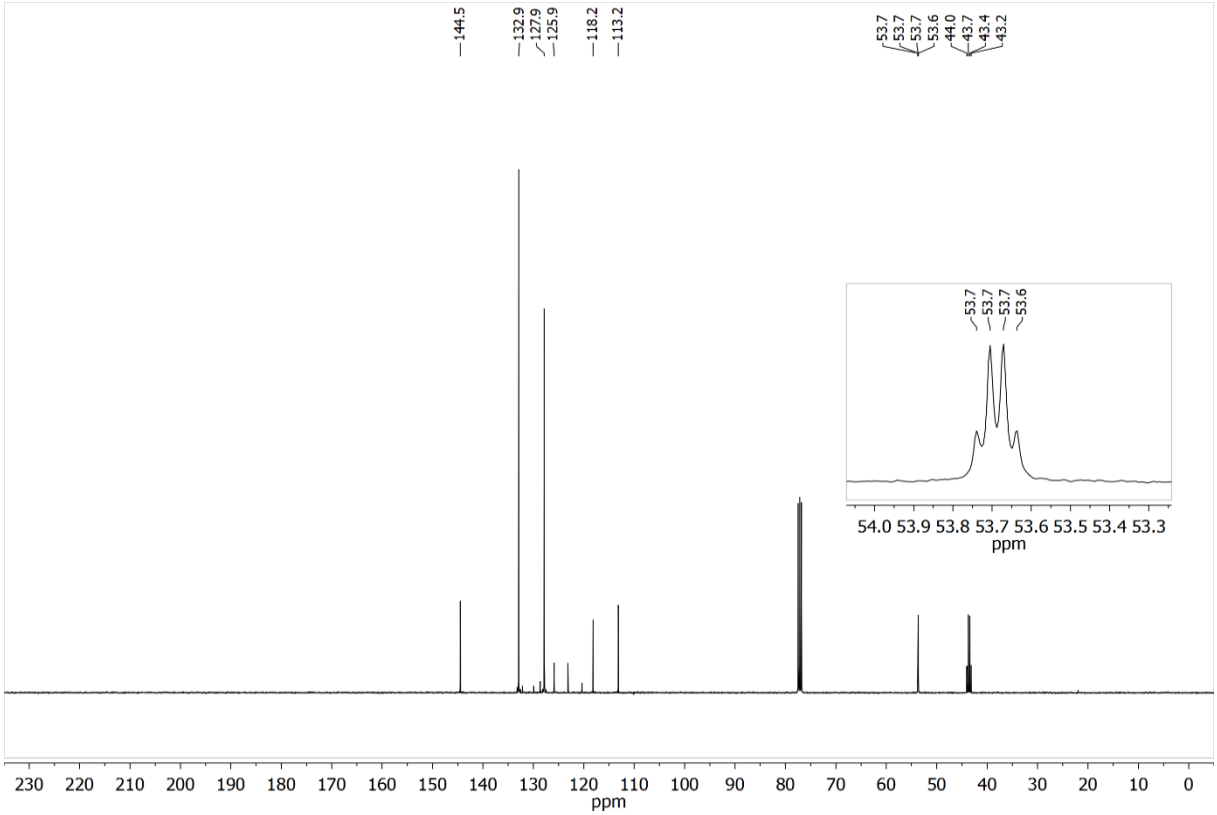
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



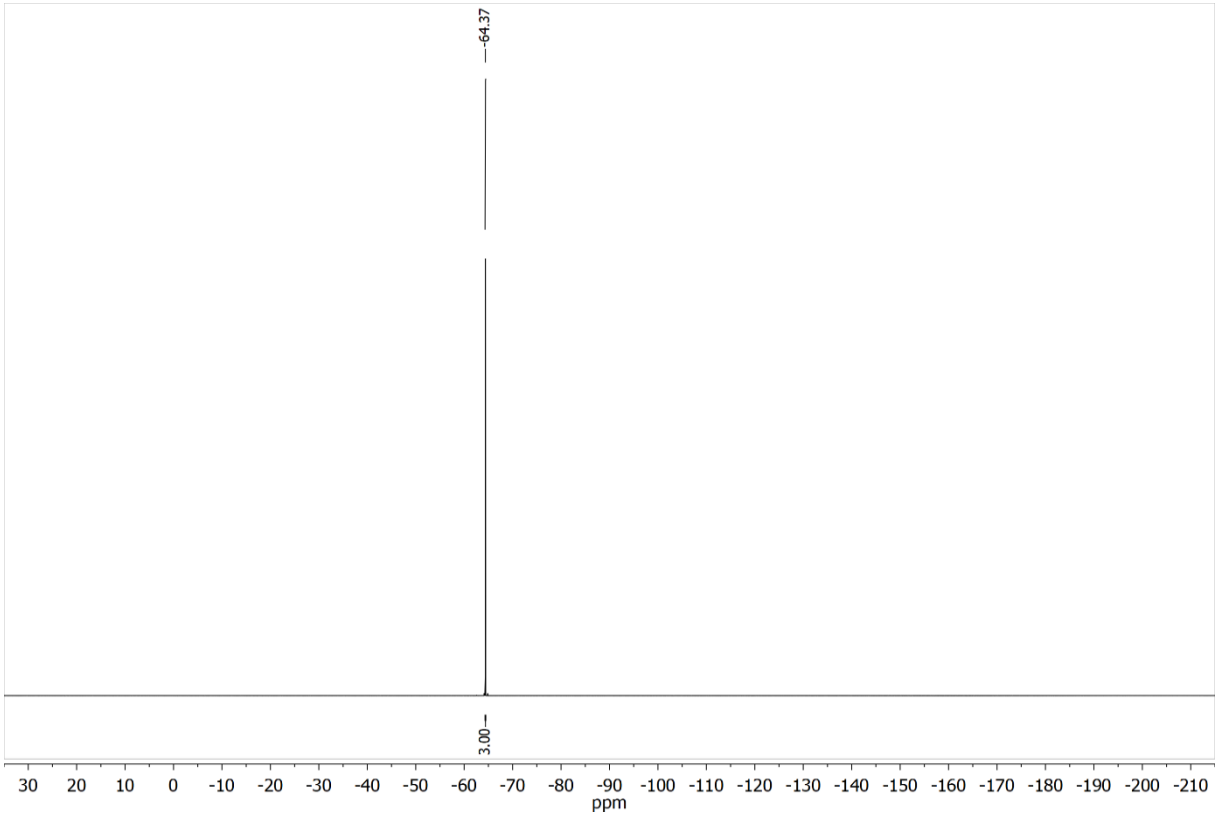
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

4-(1-chloro-3,3,3-trifluoropropyl)benzonitrile (12c)



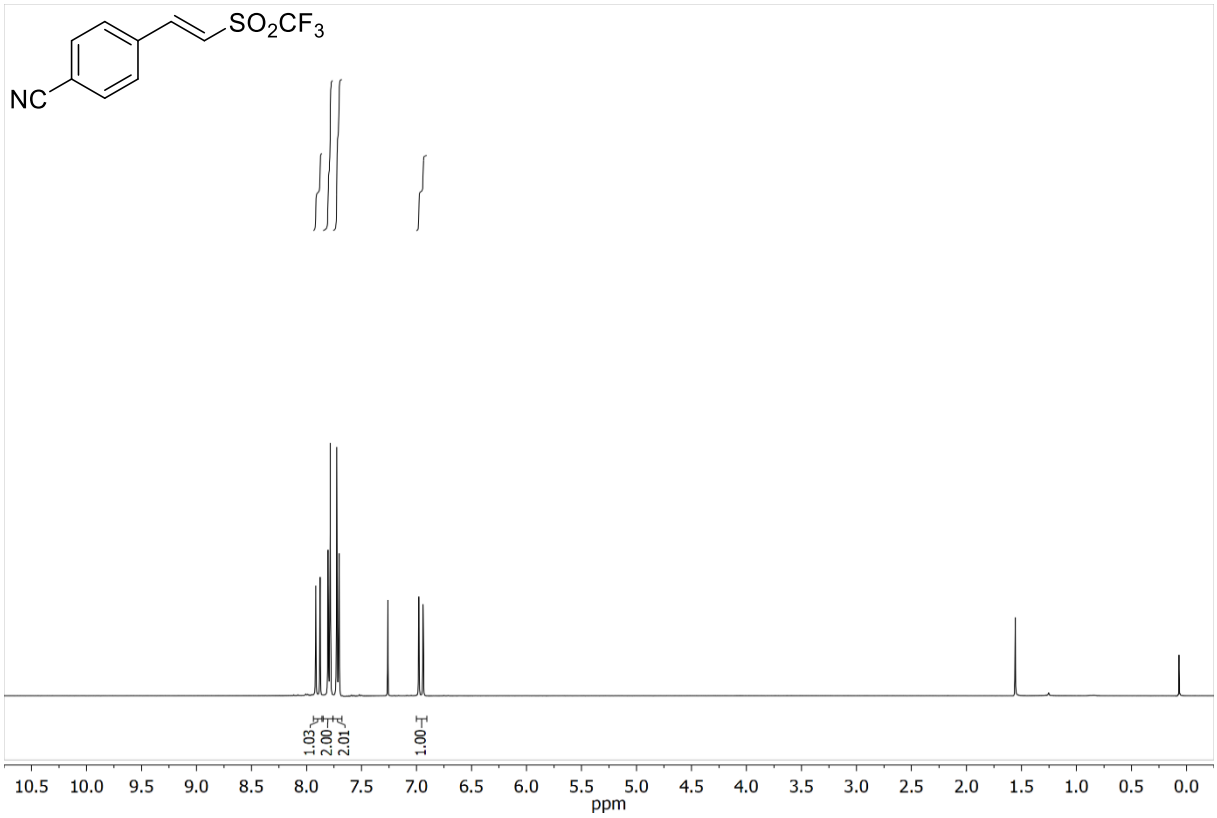


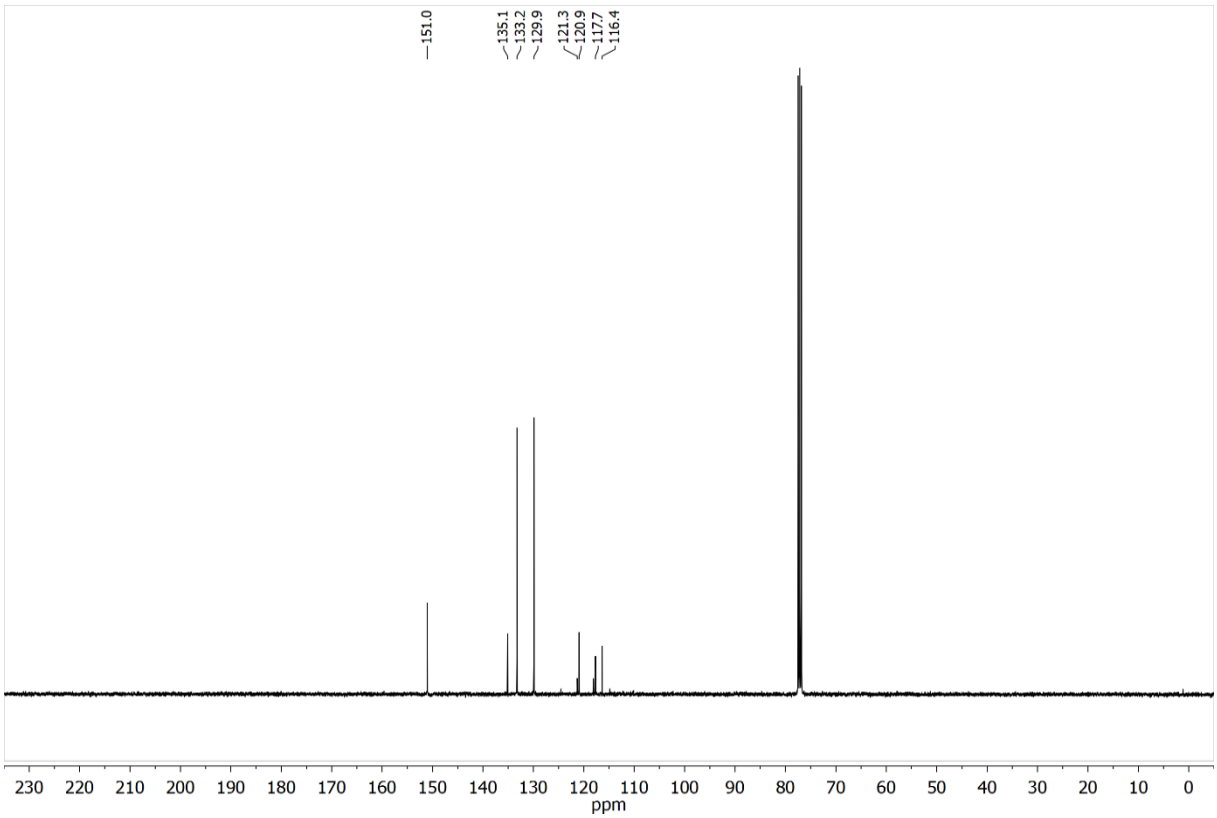
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



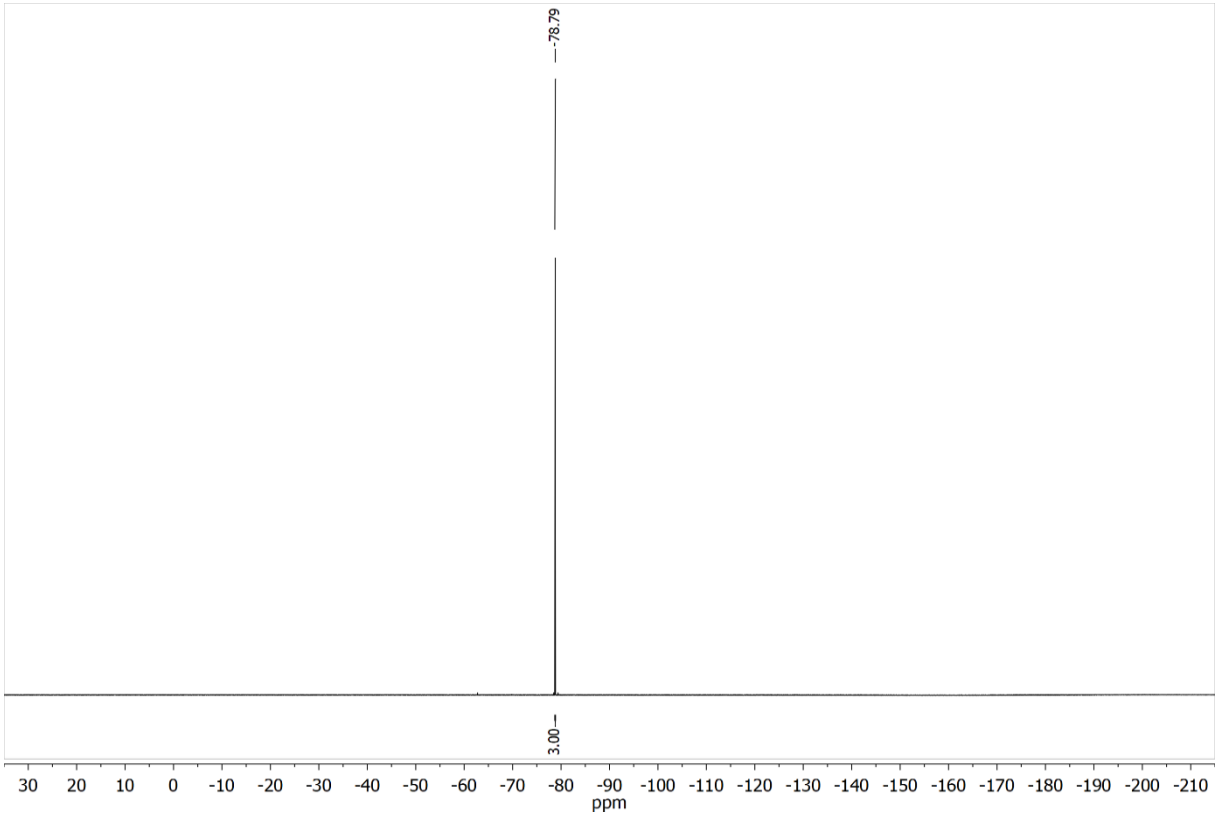
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

(*E*)-4-(2-((trifluoromethyl)sulfonyl)vinyl)benzonitrile (13c)



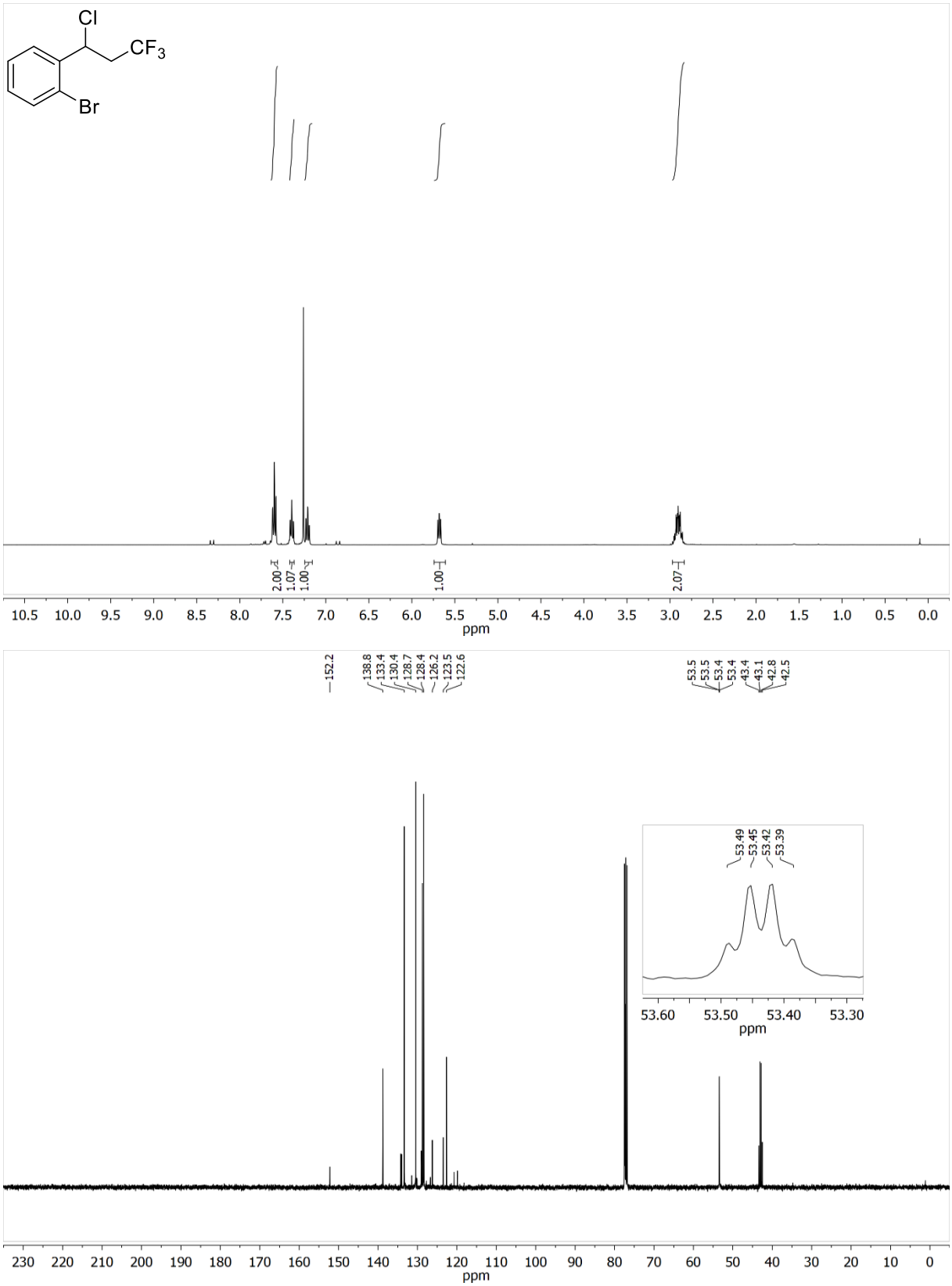


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

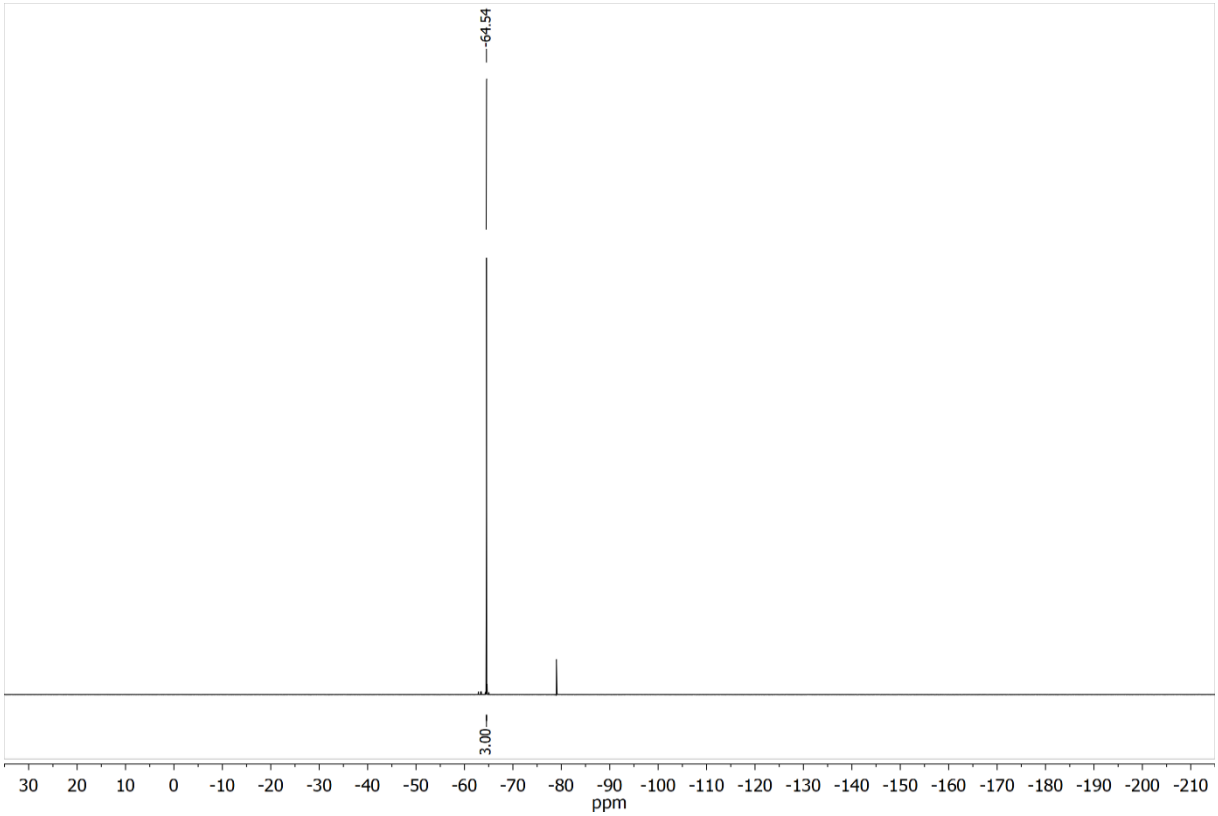


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1-bromo-2-(1-chloro-3,3,3-trifluoropropyl)benzene (12d)

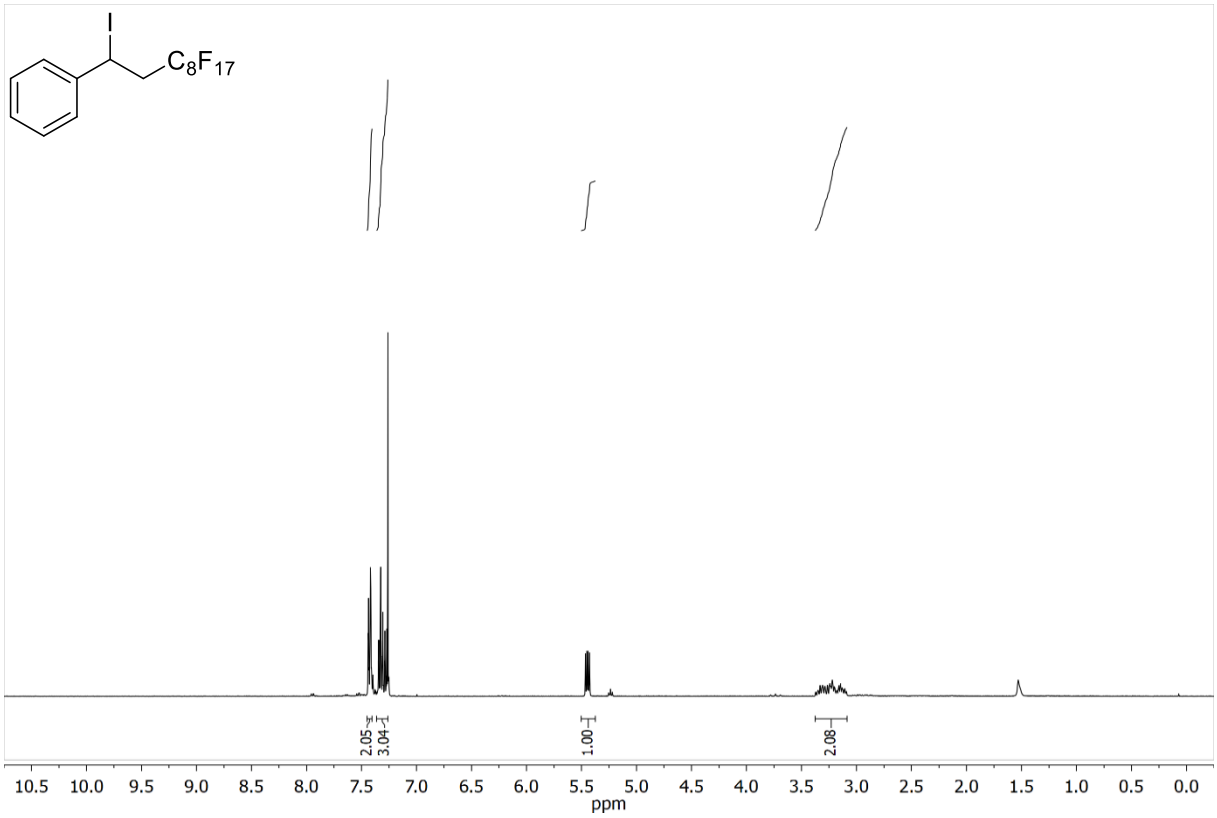


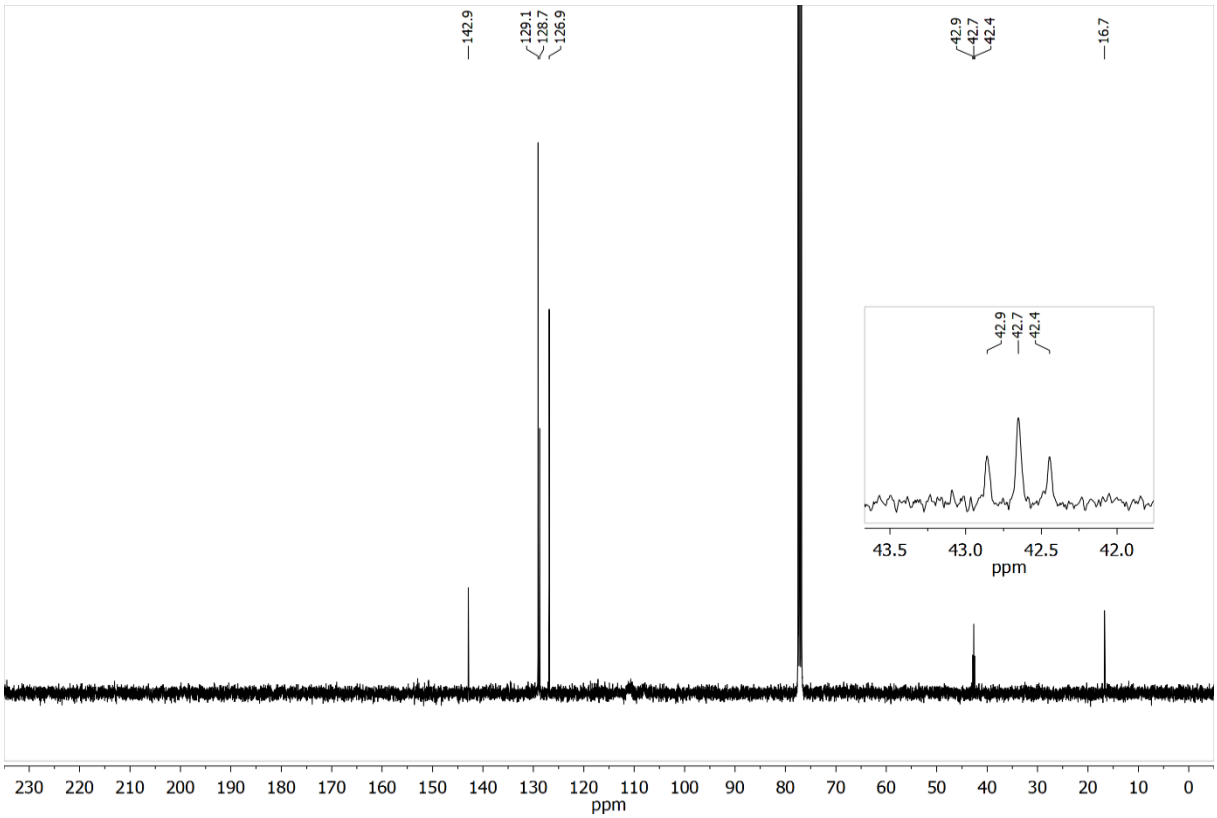
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



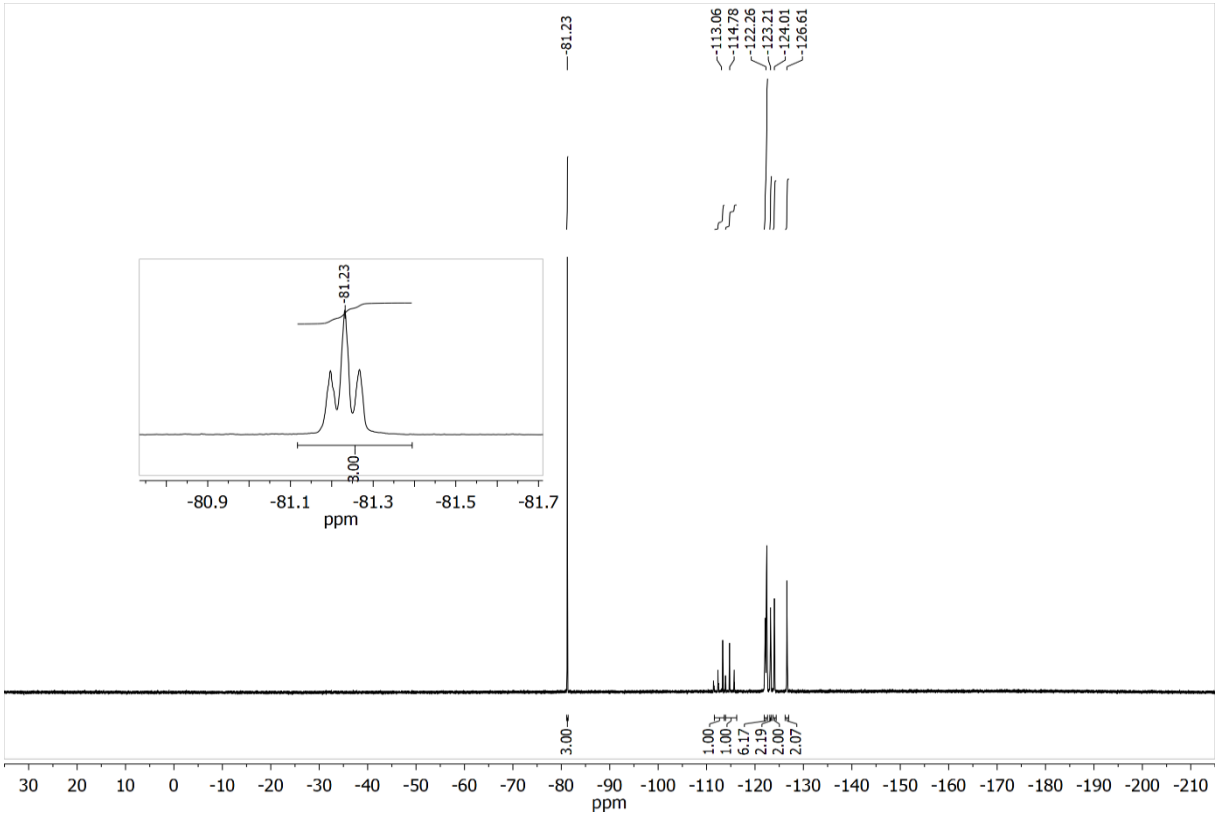
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-iododecyl)benzene (15a)



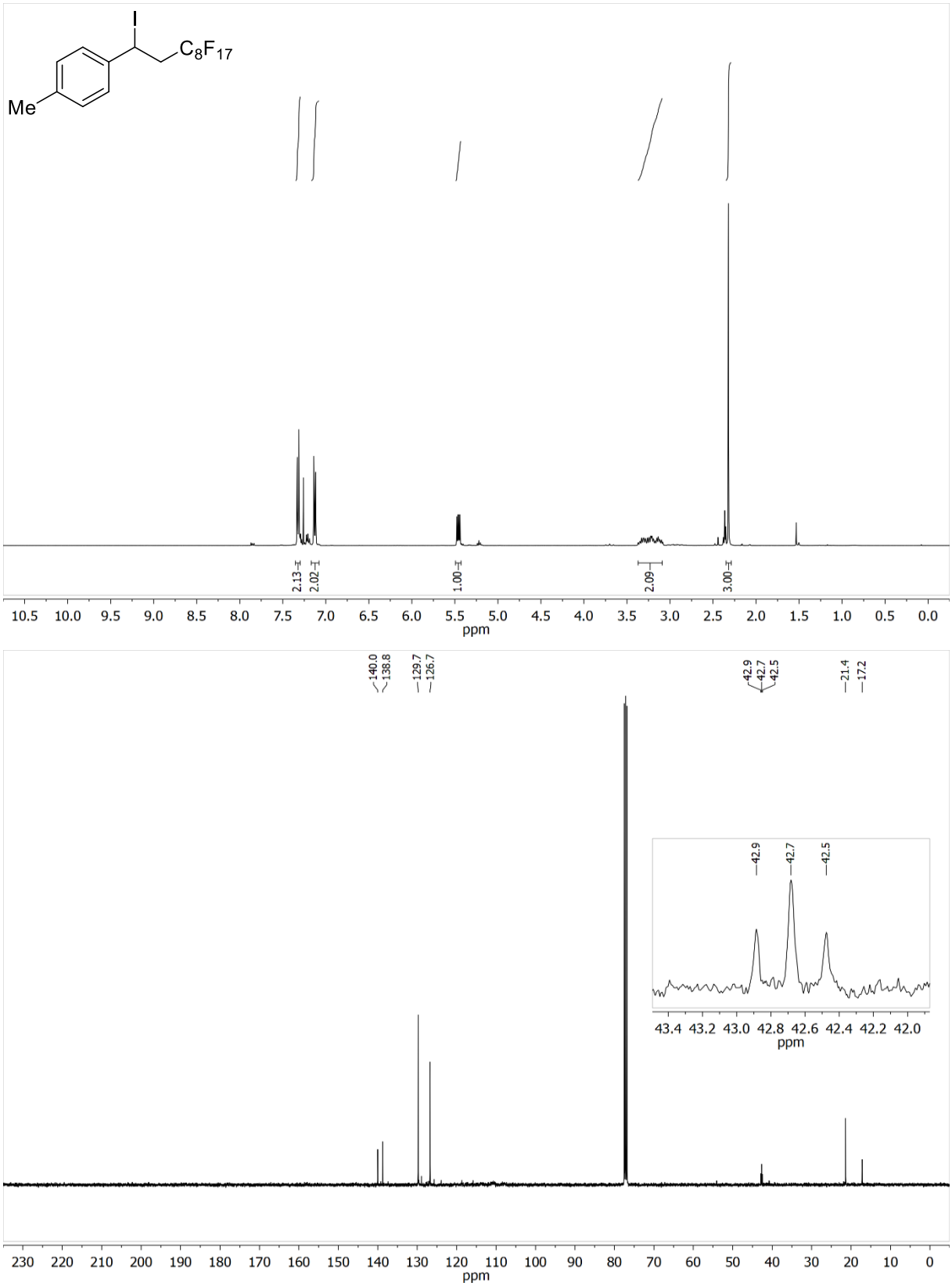


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

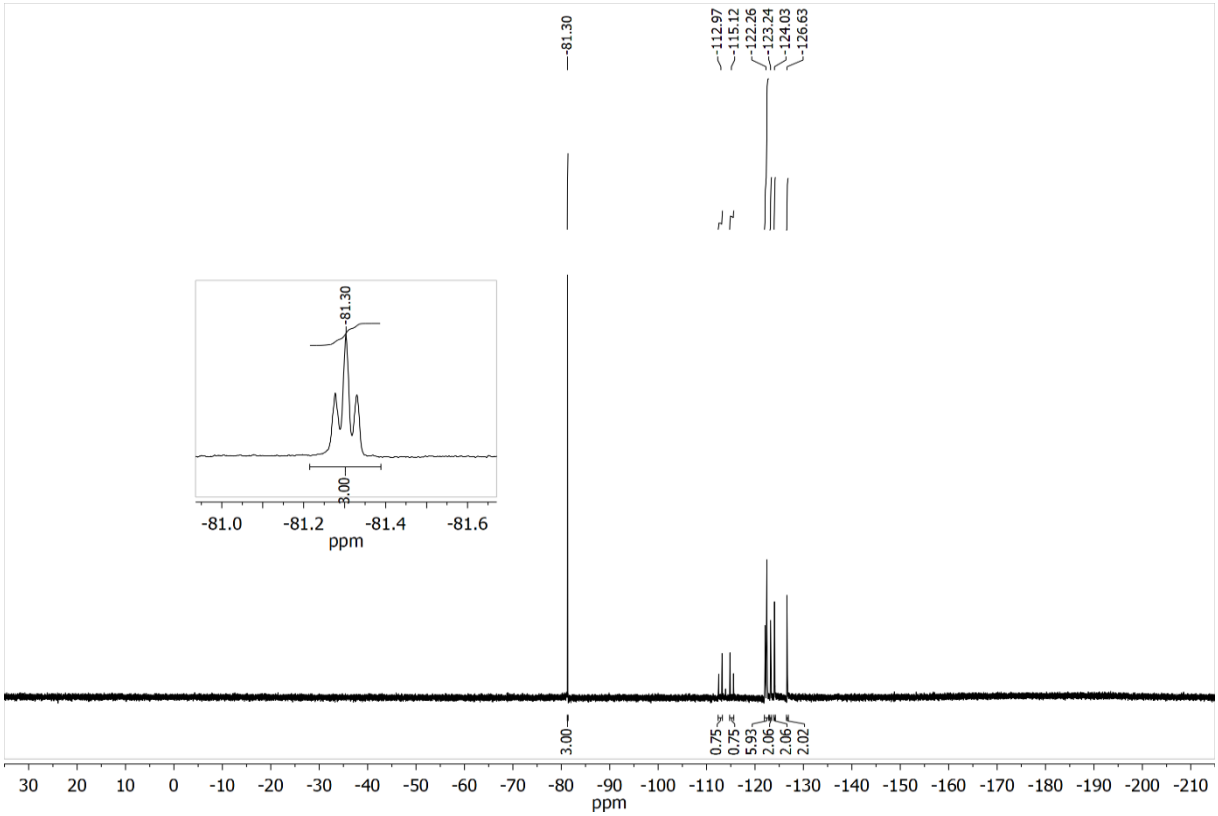


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-iododecyl)-4-methylbenzene (15b)

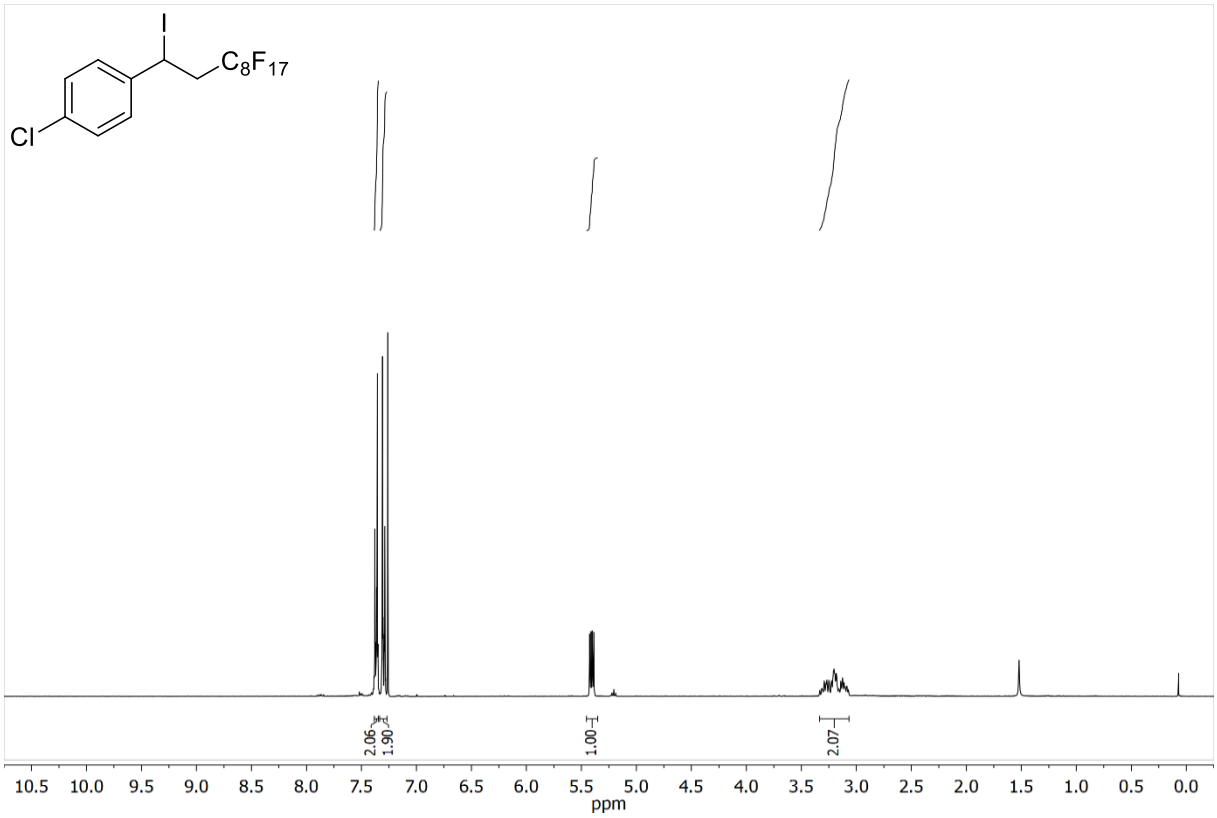


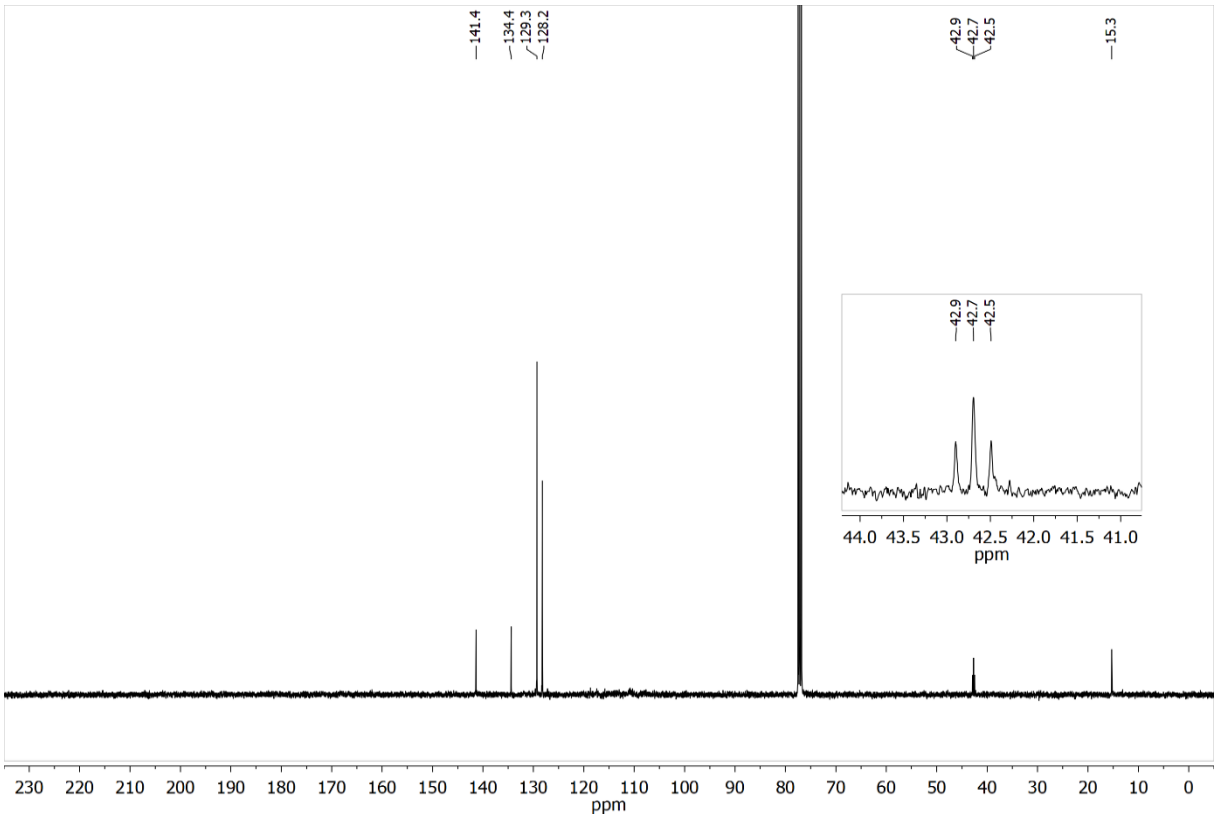
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



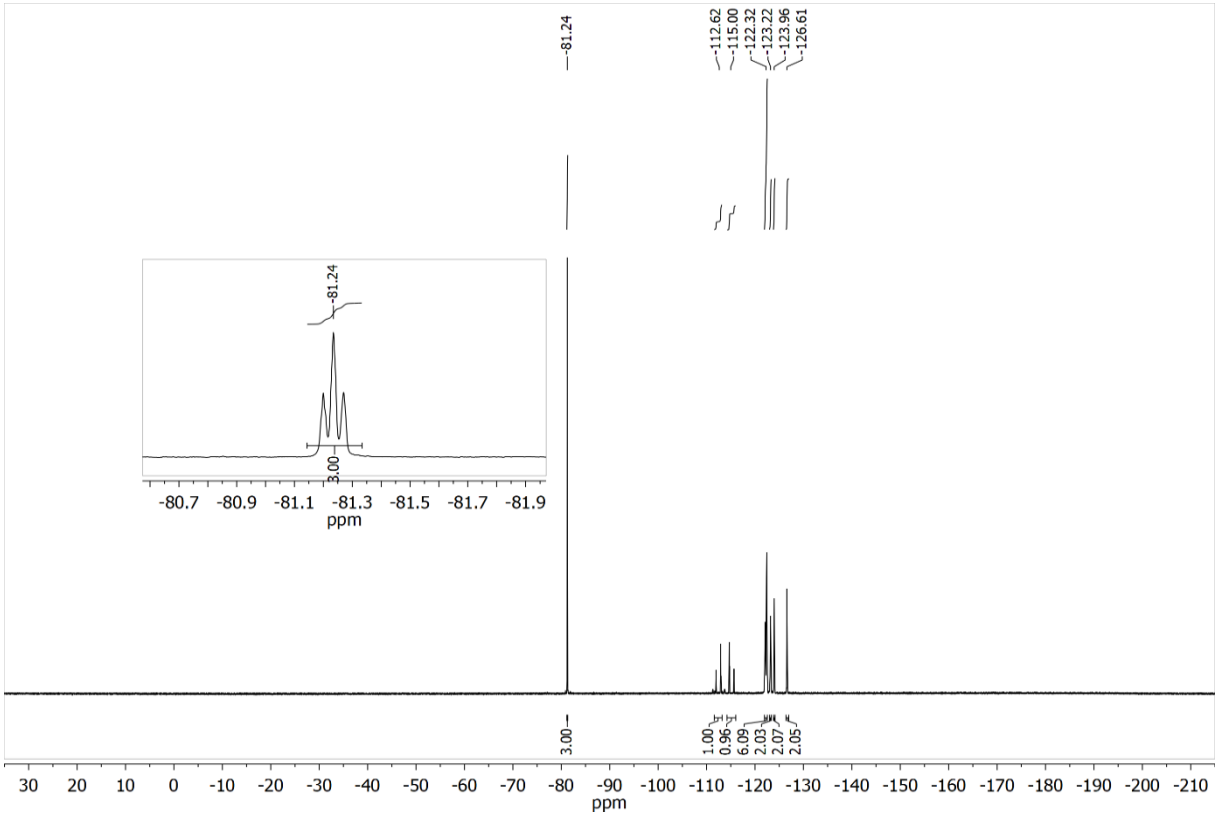
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1-chloro-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-iododecyl)benzene (15c)



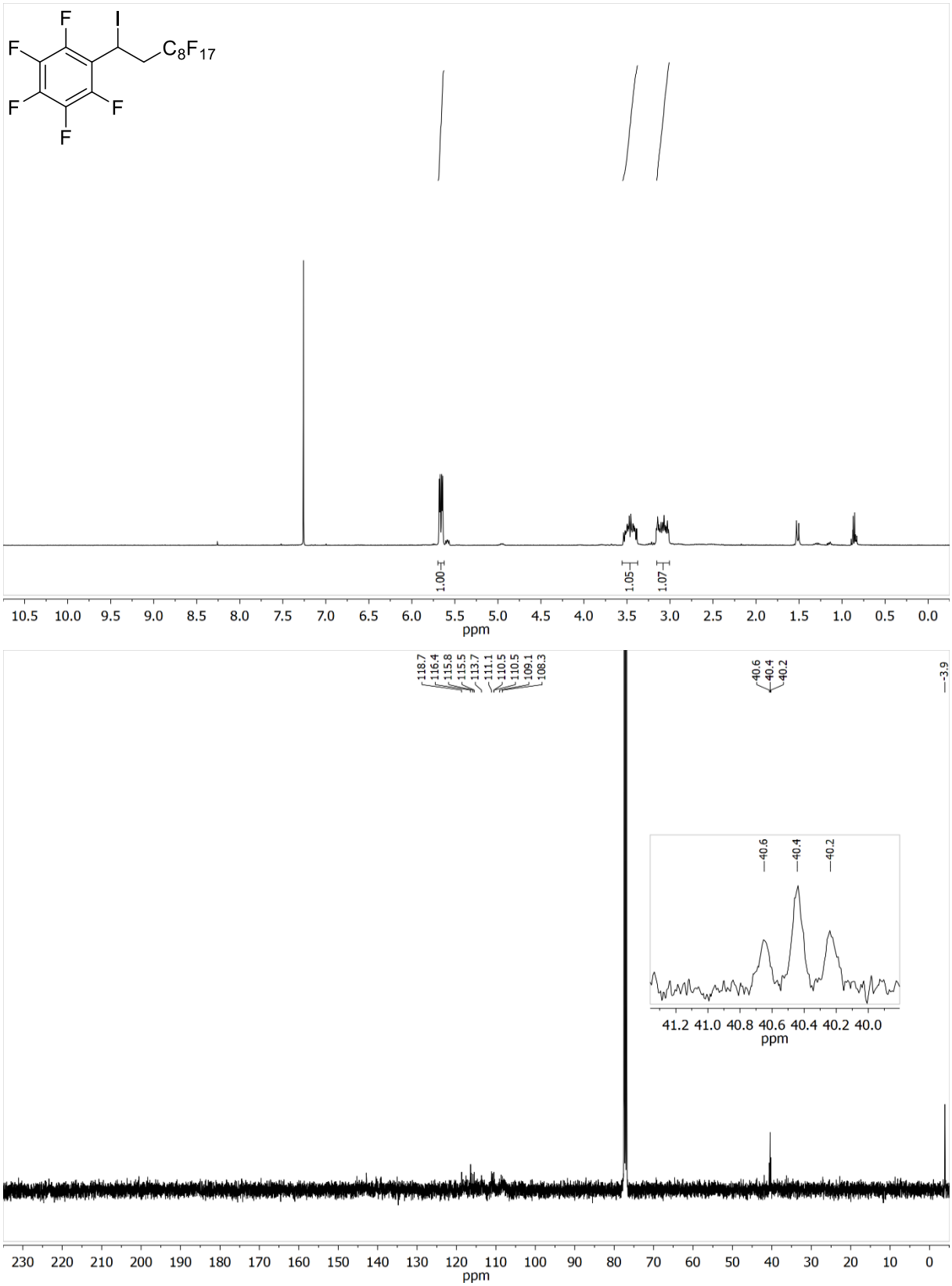


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

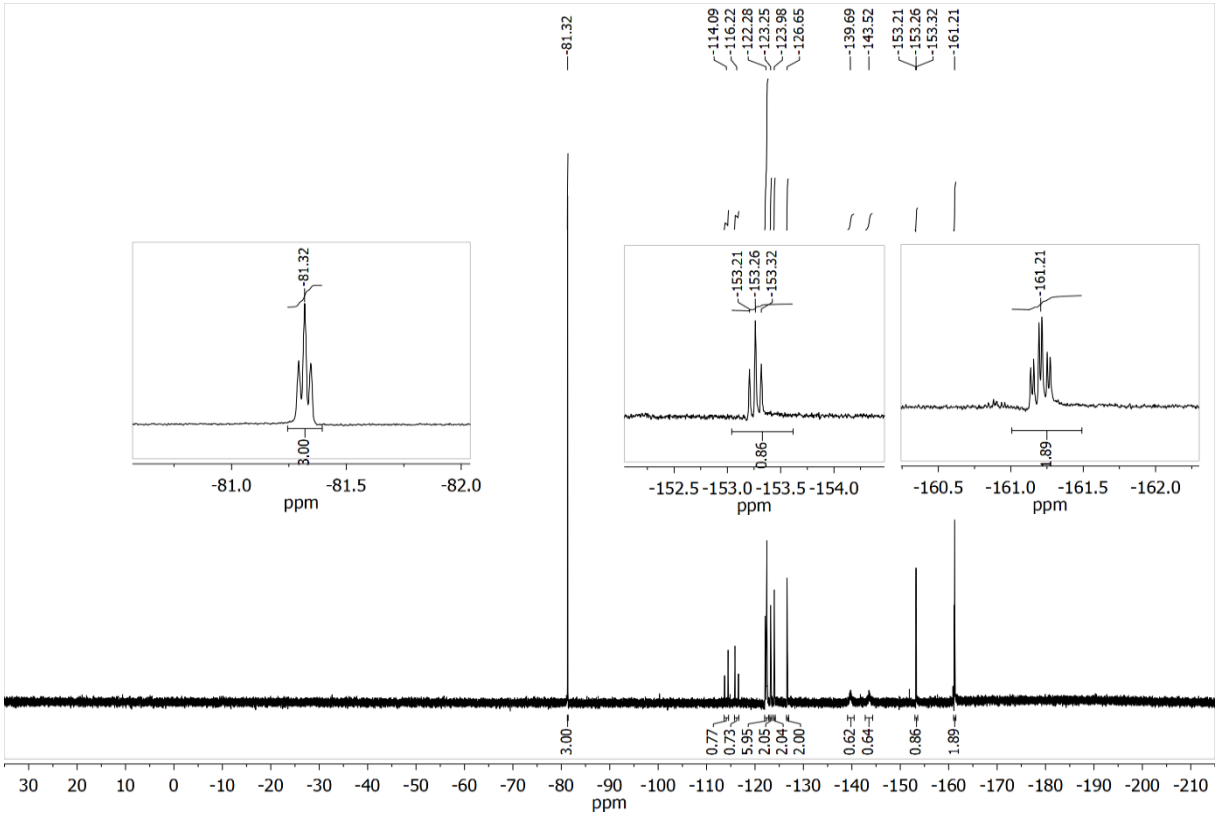


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1,2,3,4,5-pentafluoro-6-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-iododecyl)benzene (15d)

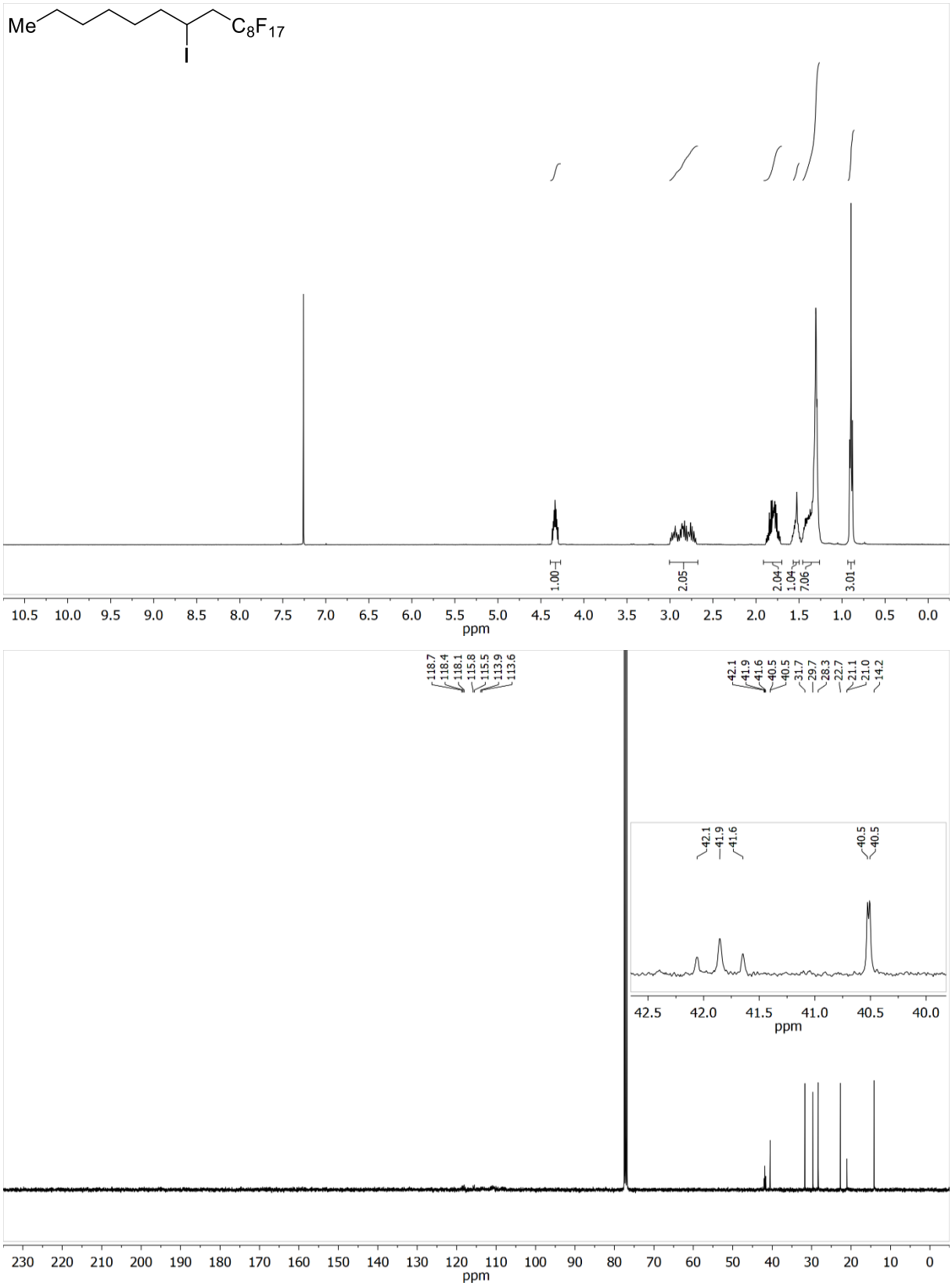


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

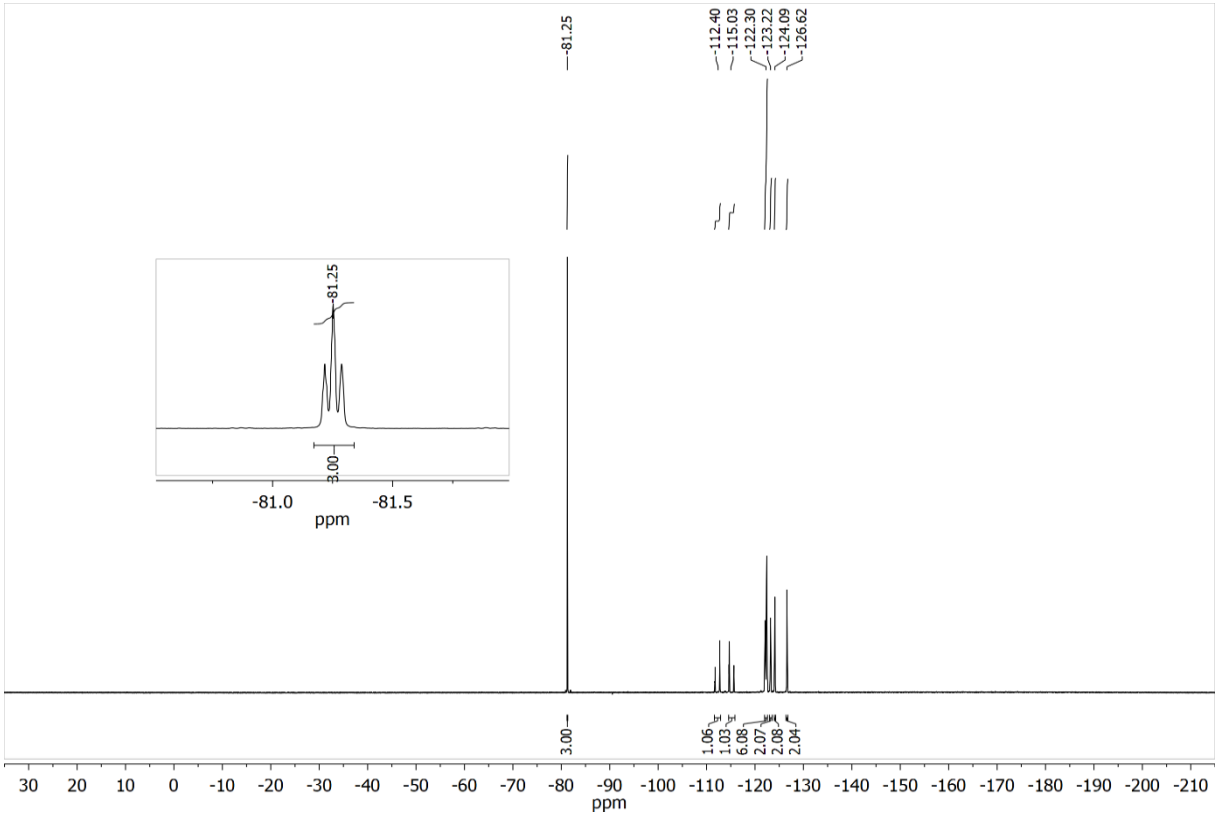


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iodohexadecane (15e)

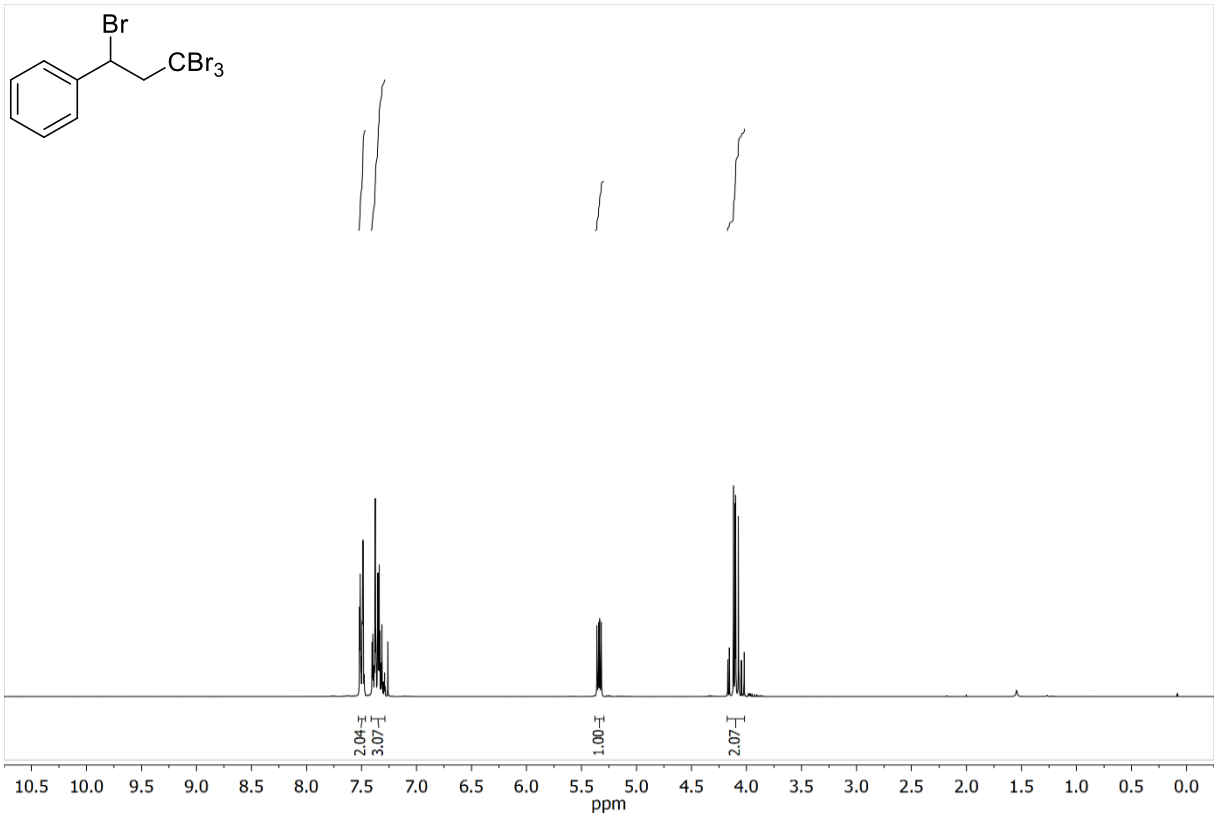


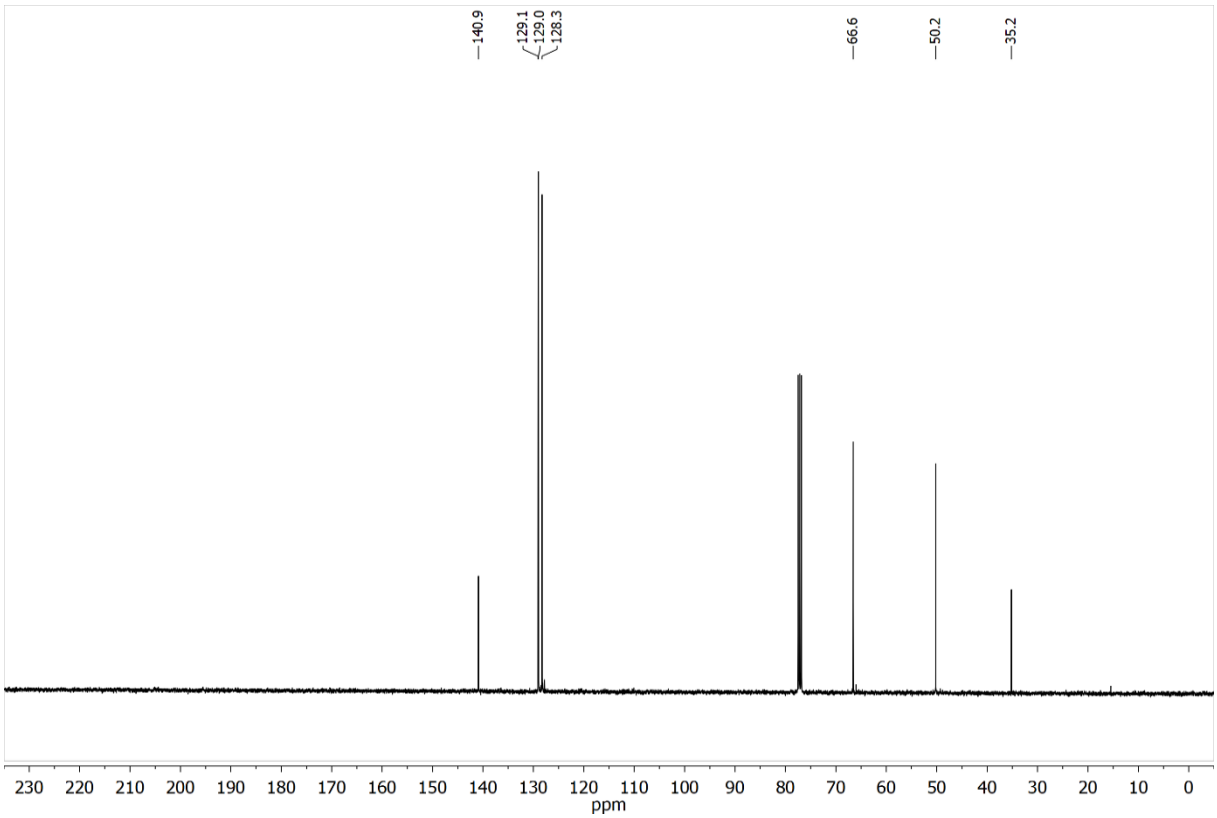
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

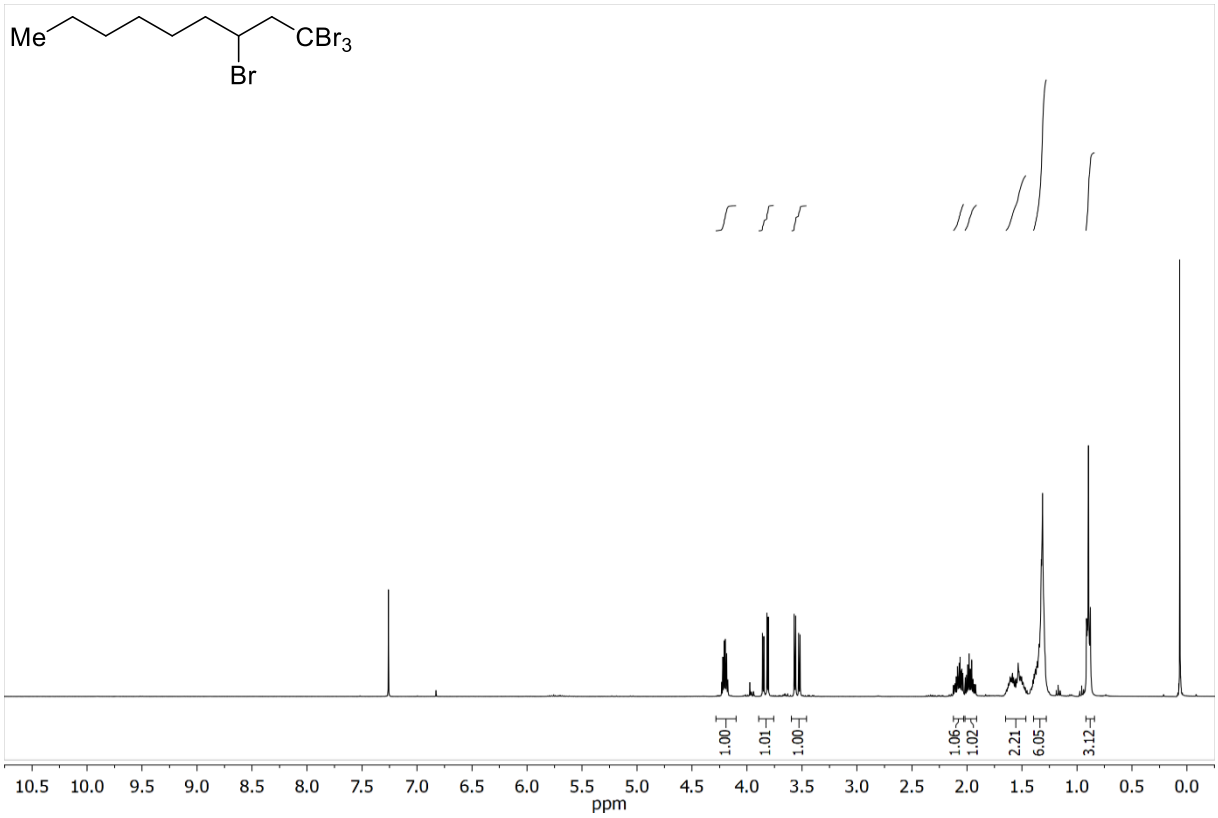
(1,3,3,3-tetrabromopropyl)benzene (17a)

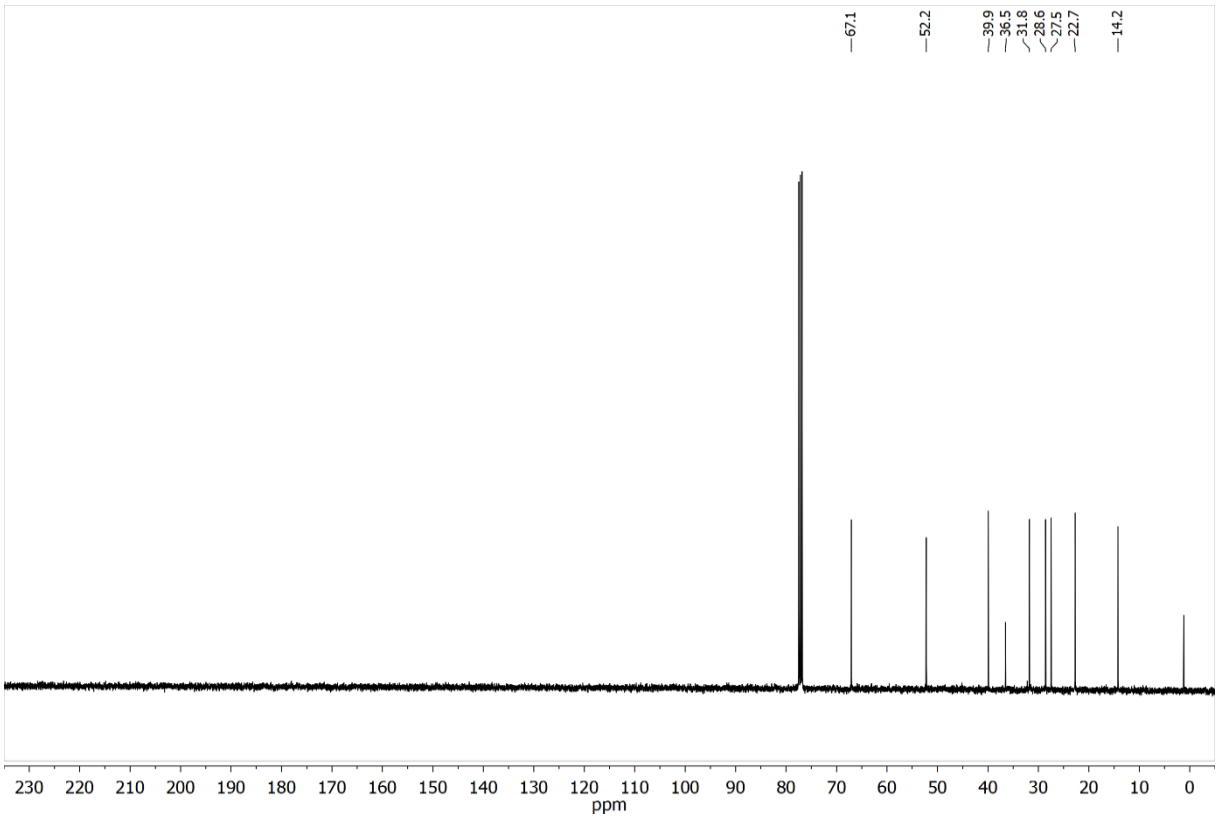




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

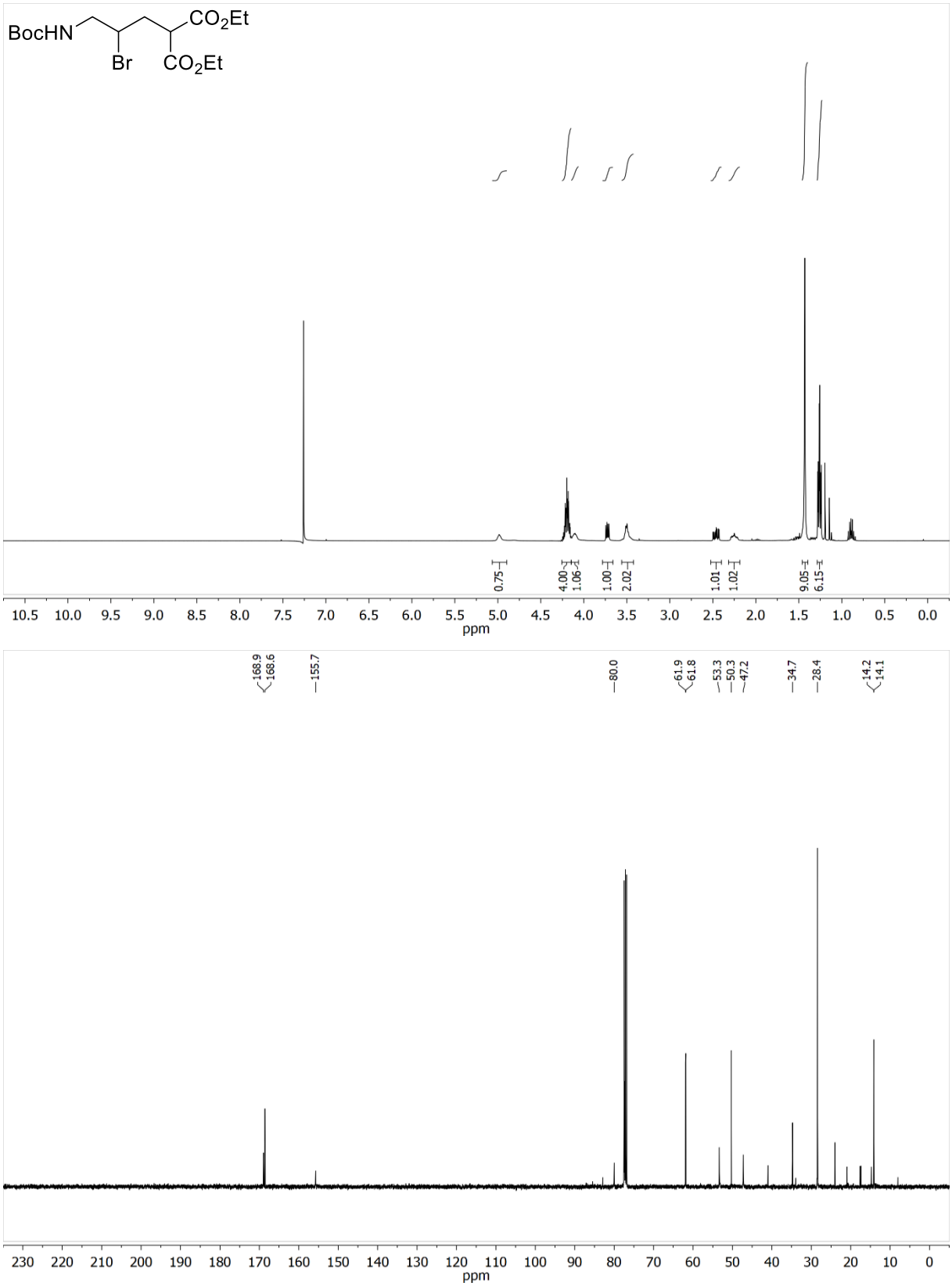
1,1,1,3-tetrabromononane (17b)





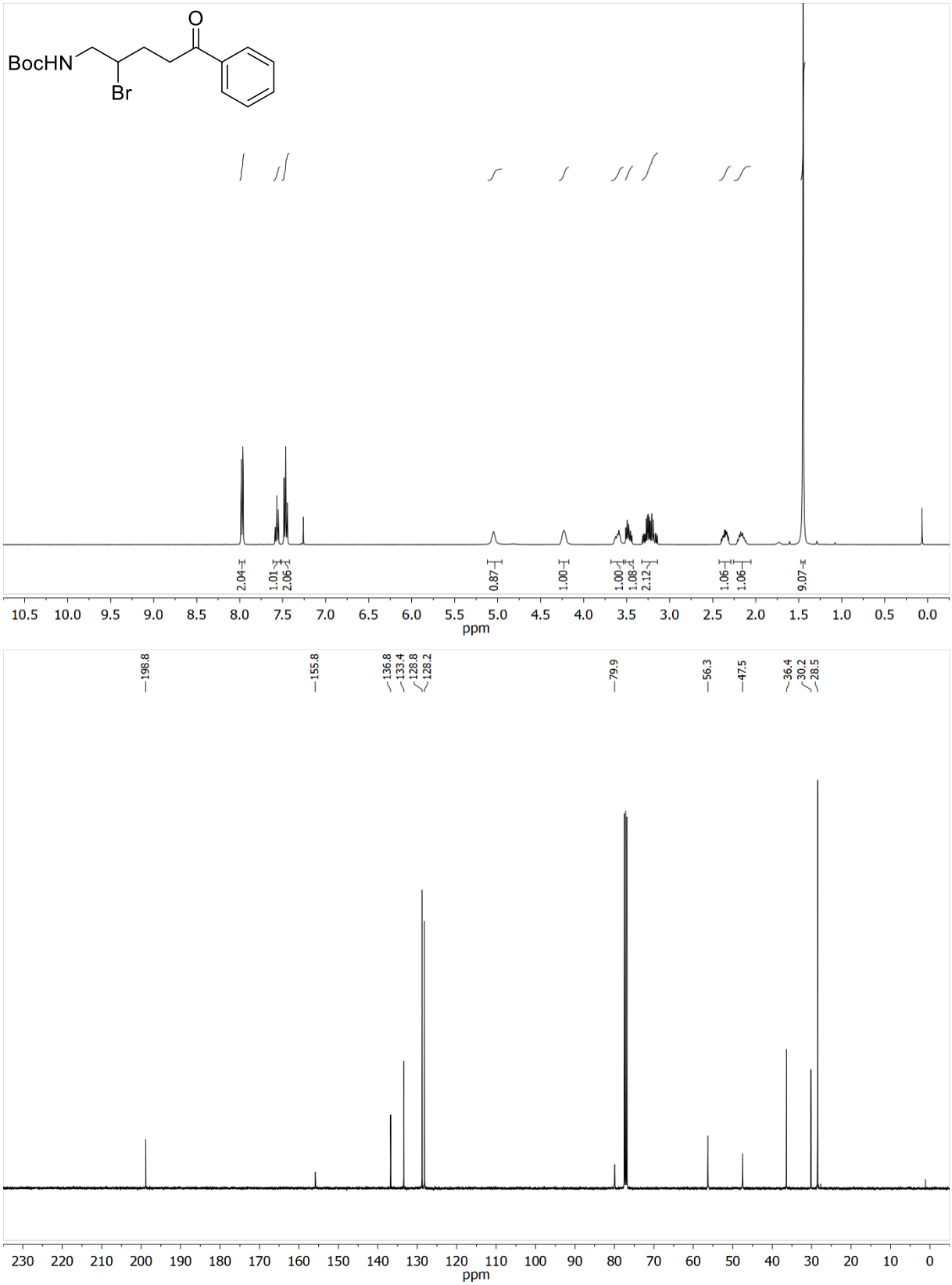
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

diethyl 2-(2-bromo-3-((*tert*-butoxycarbonyl)amino)propyl)malonate (17c)



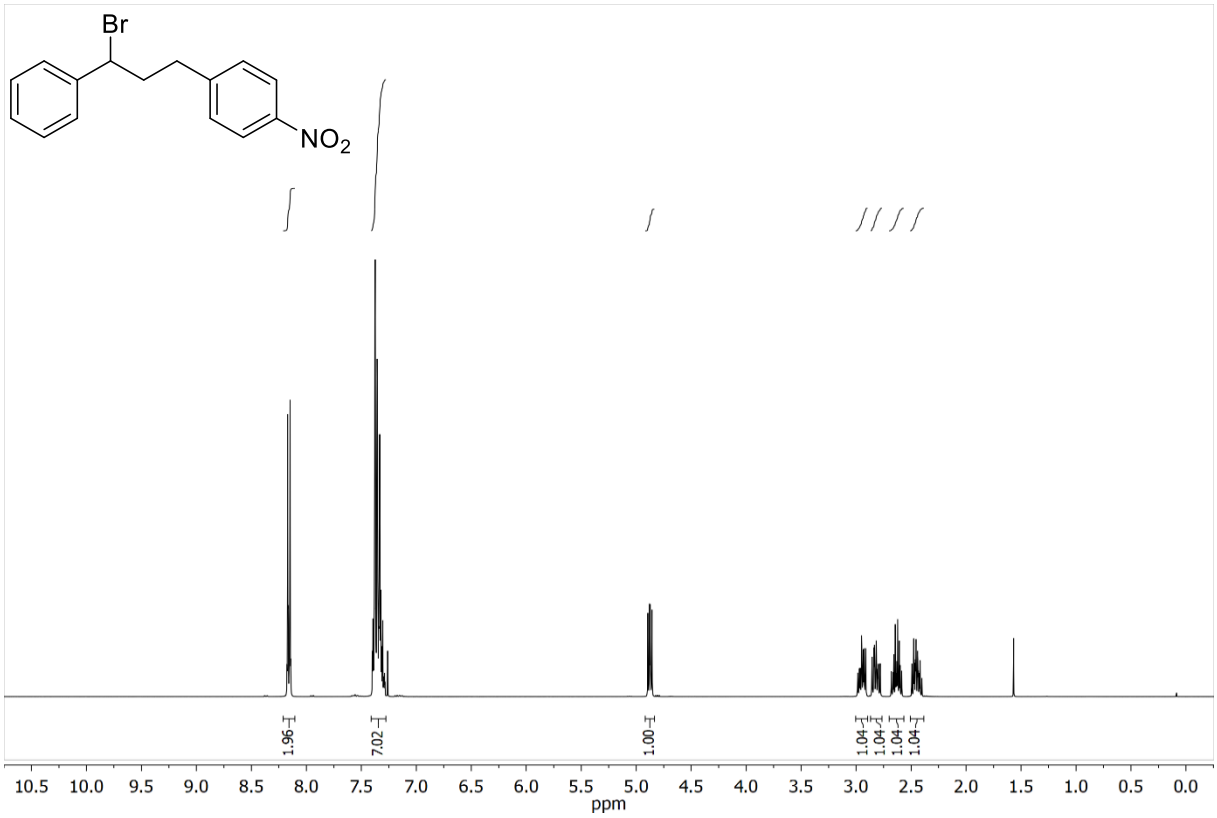
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

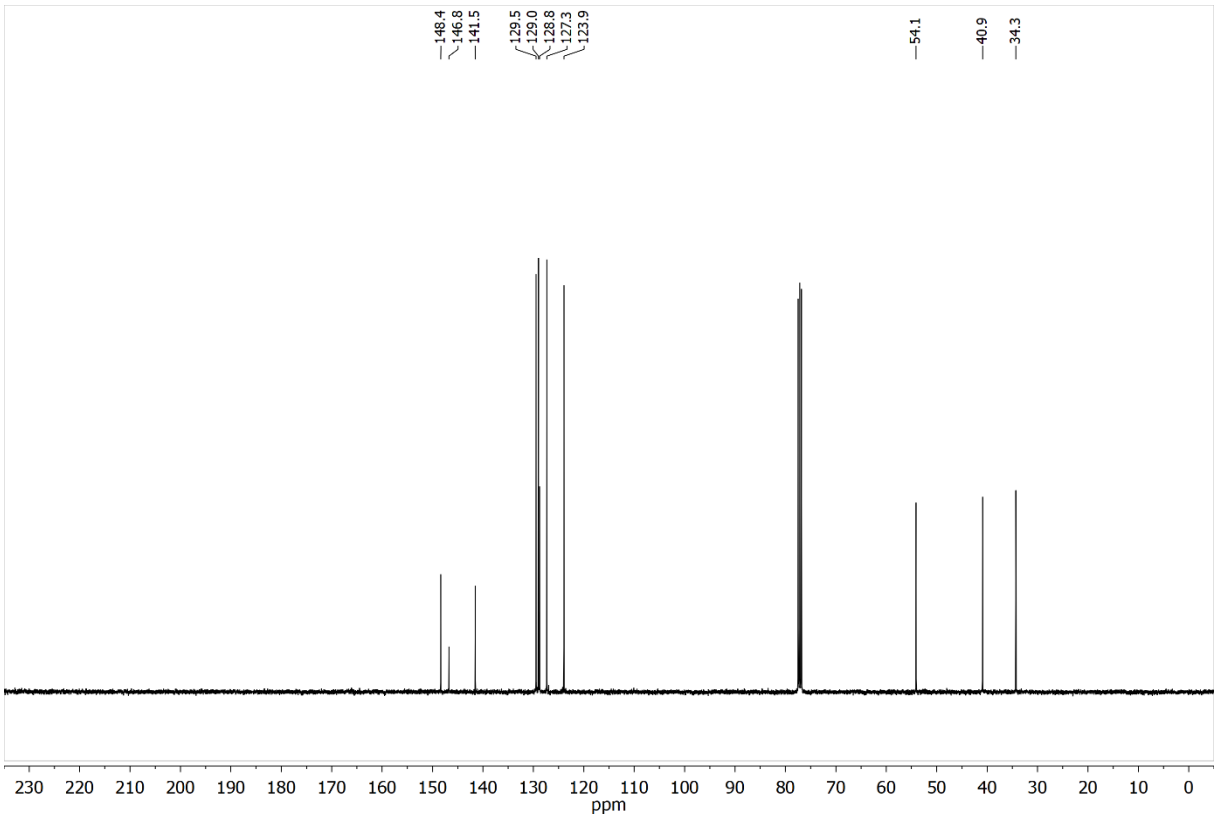
tert-butyl (2-bromo-5-oxo-5-phenylpentyl)carbamate (17d)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

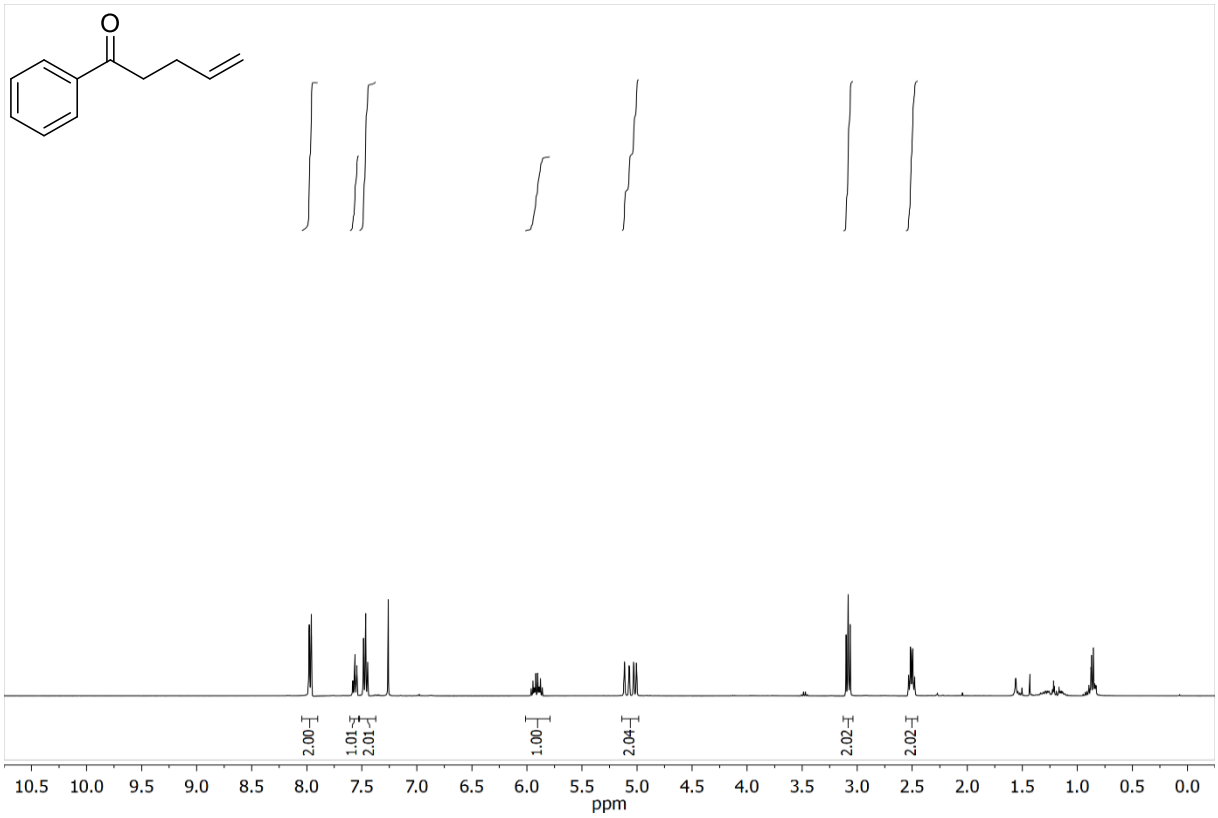
1-(3-bromo-3-phenylpropyl)-4-nitrobenzene (17e)

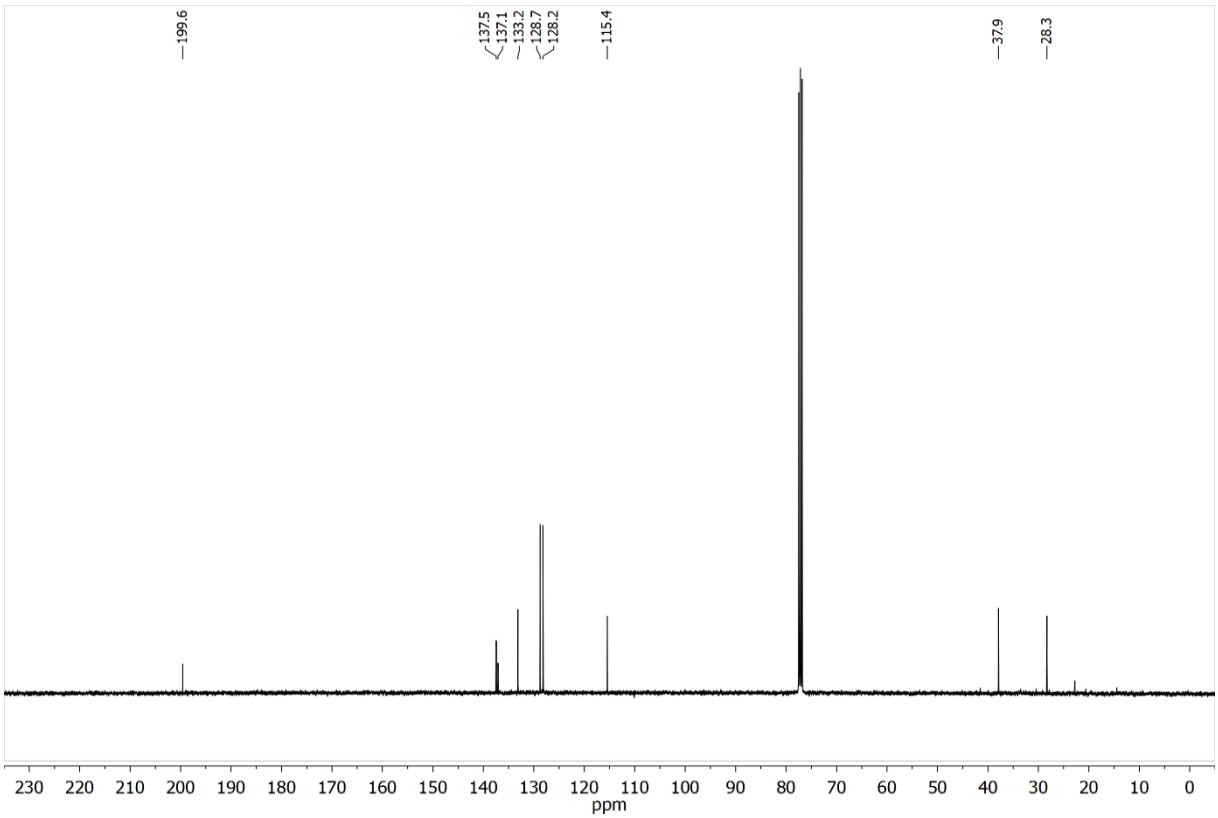




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

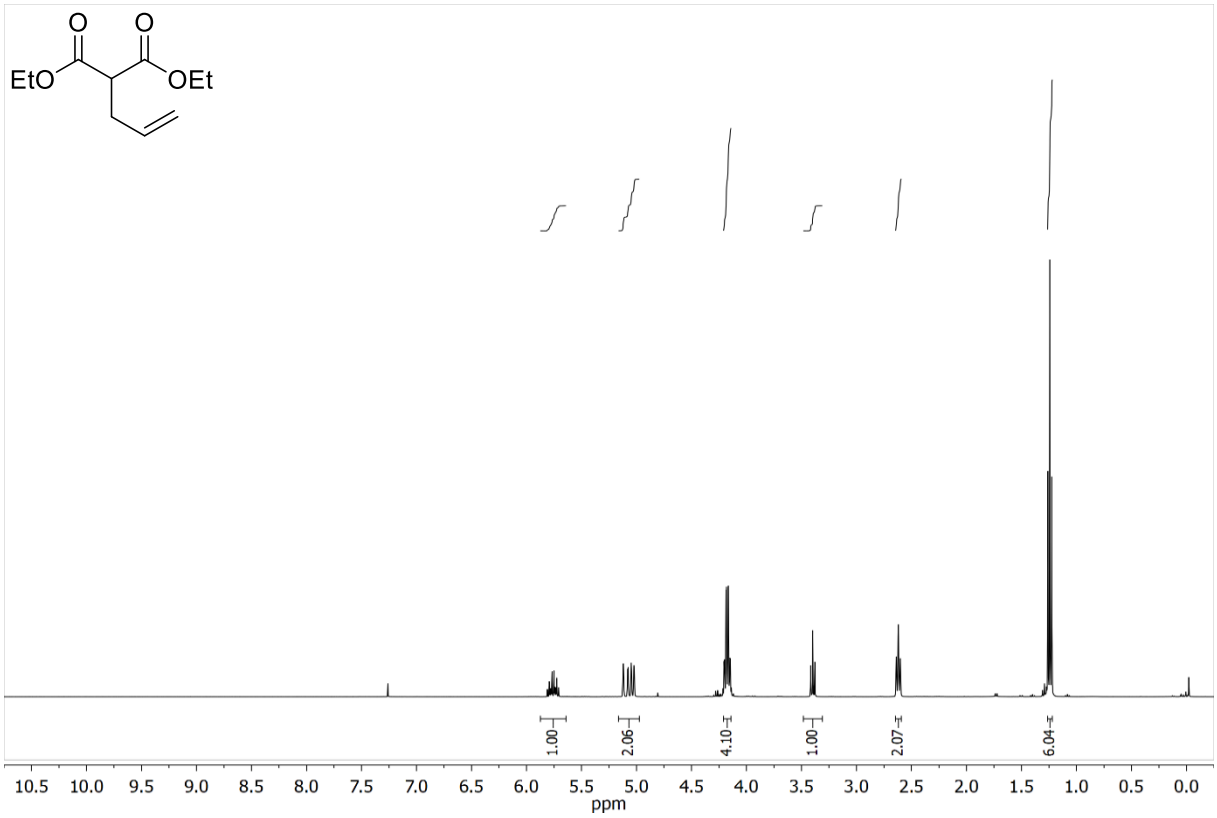
1-phenylpent-4-en-1-one (19a)

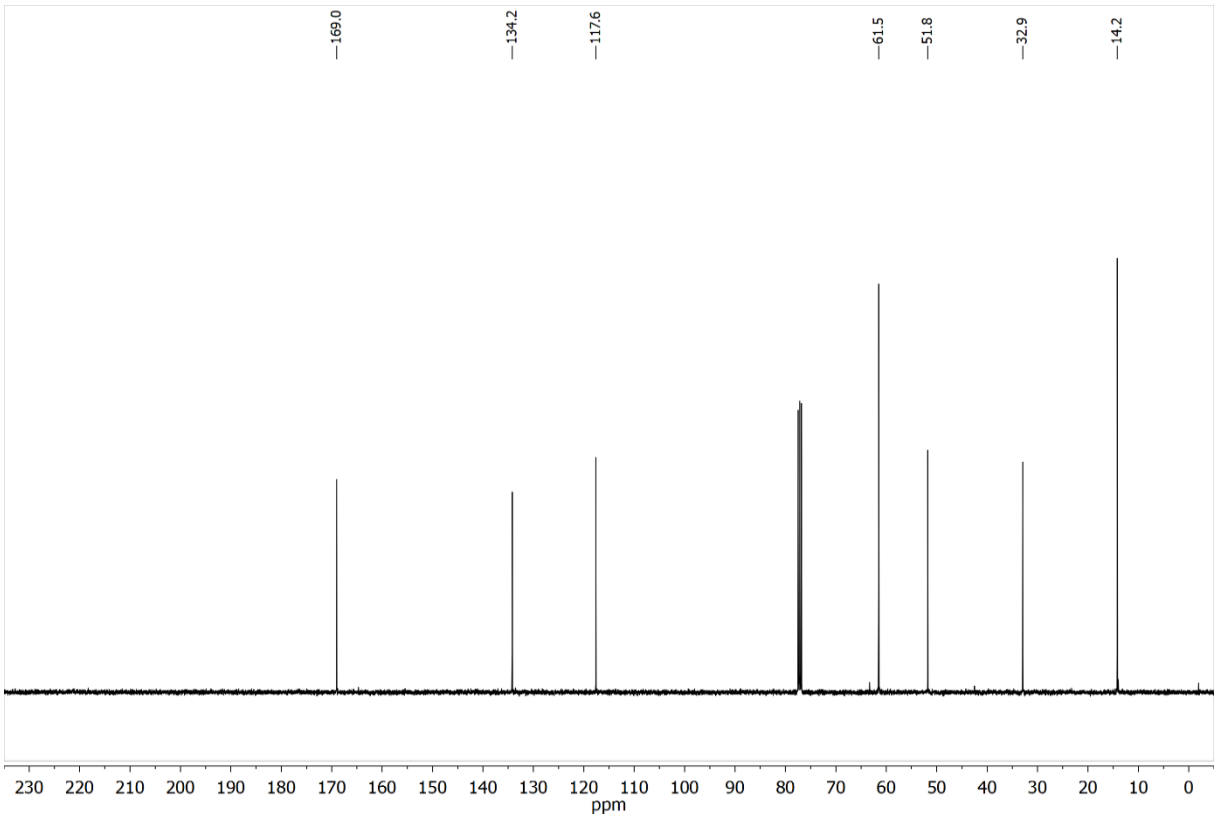




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

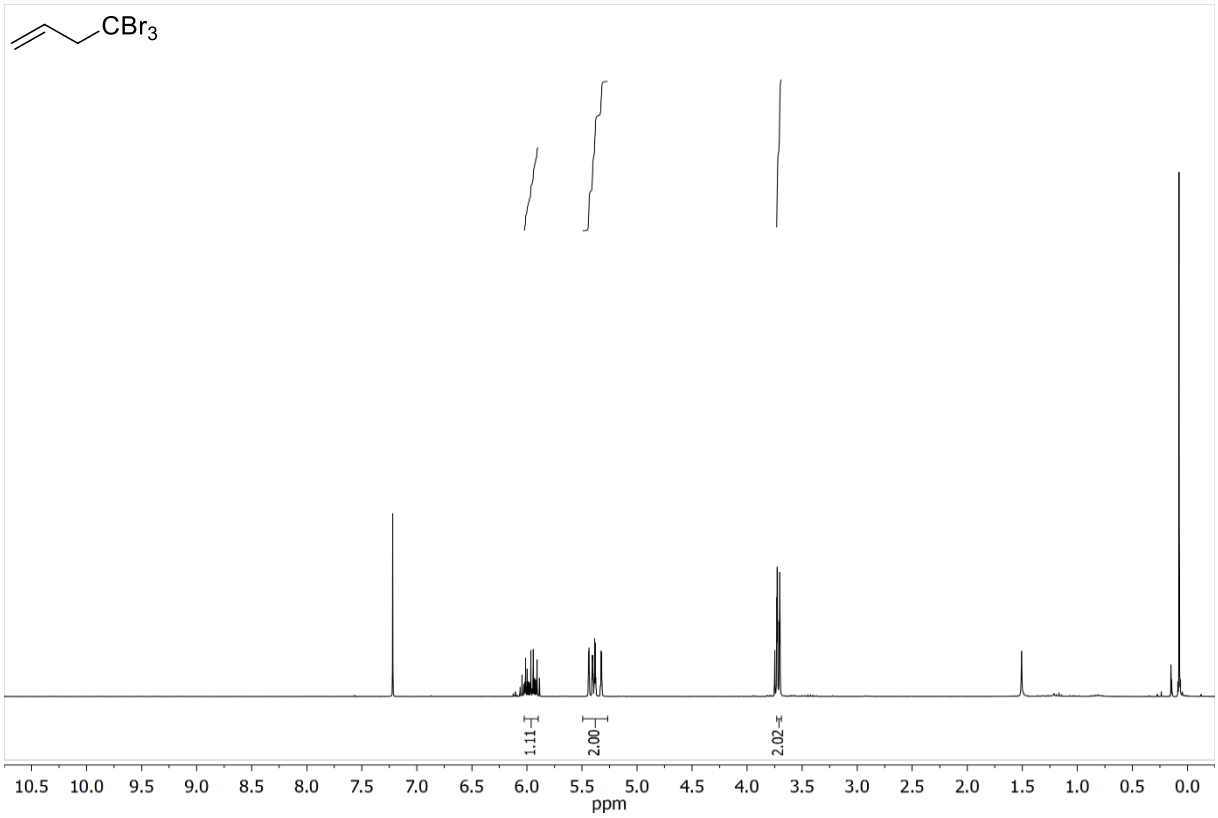
diethyl 2-allylmalonate (19b)

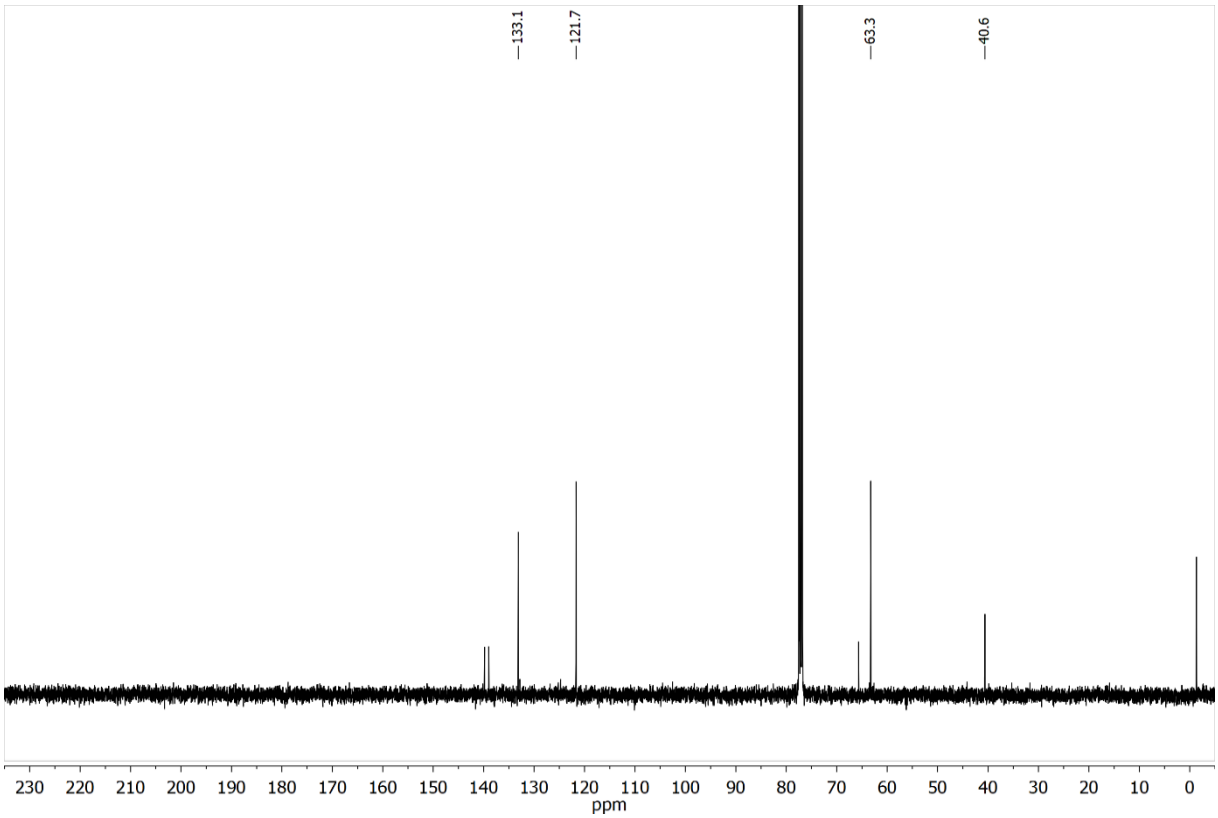




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

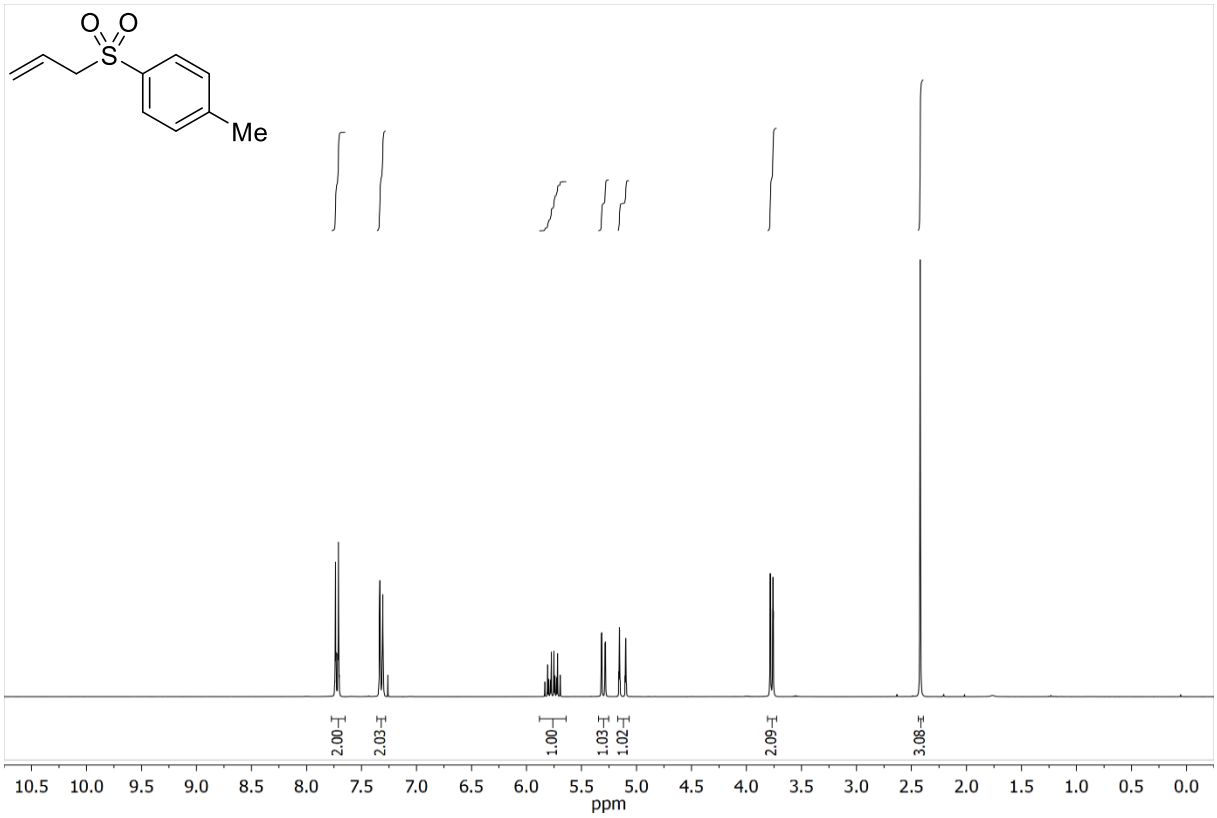
4,4,4-tribromobut-1-ene (19c)

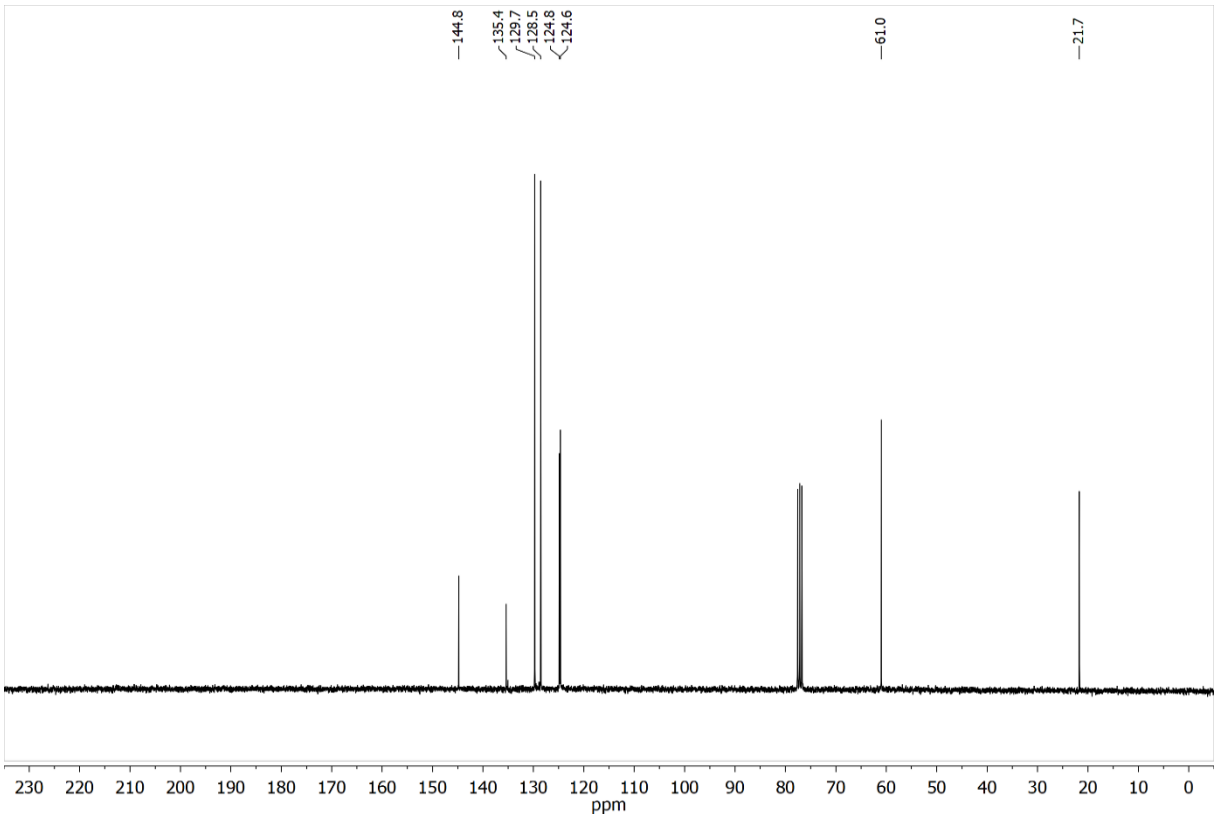




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

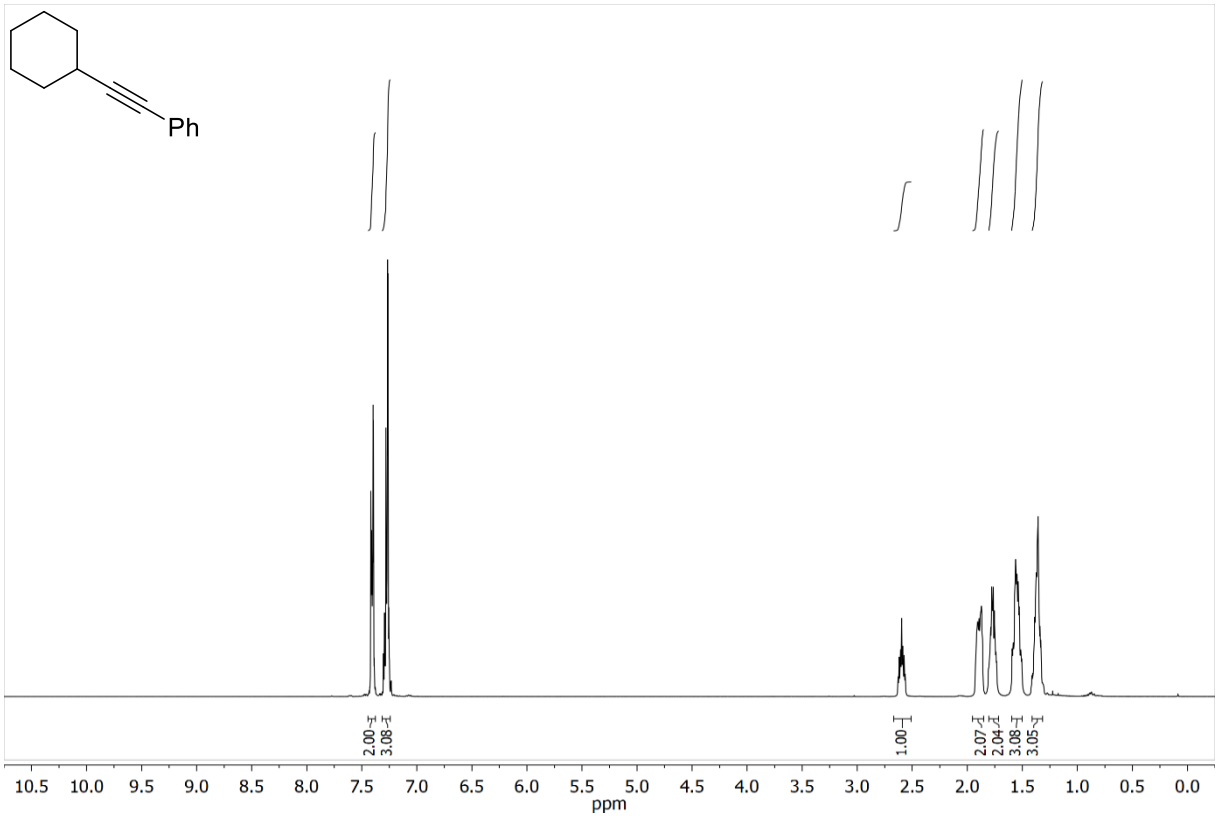
1-(allylsulfonyl)-4-methylbenzene (19d)

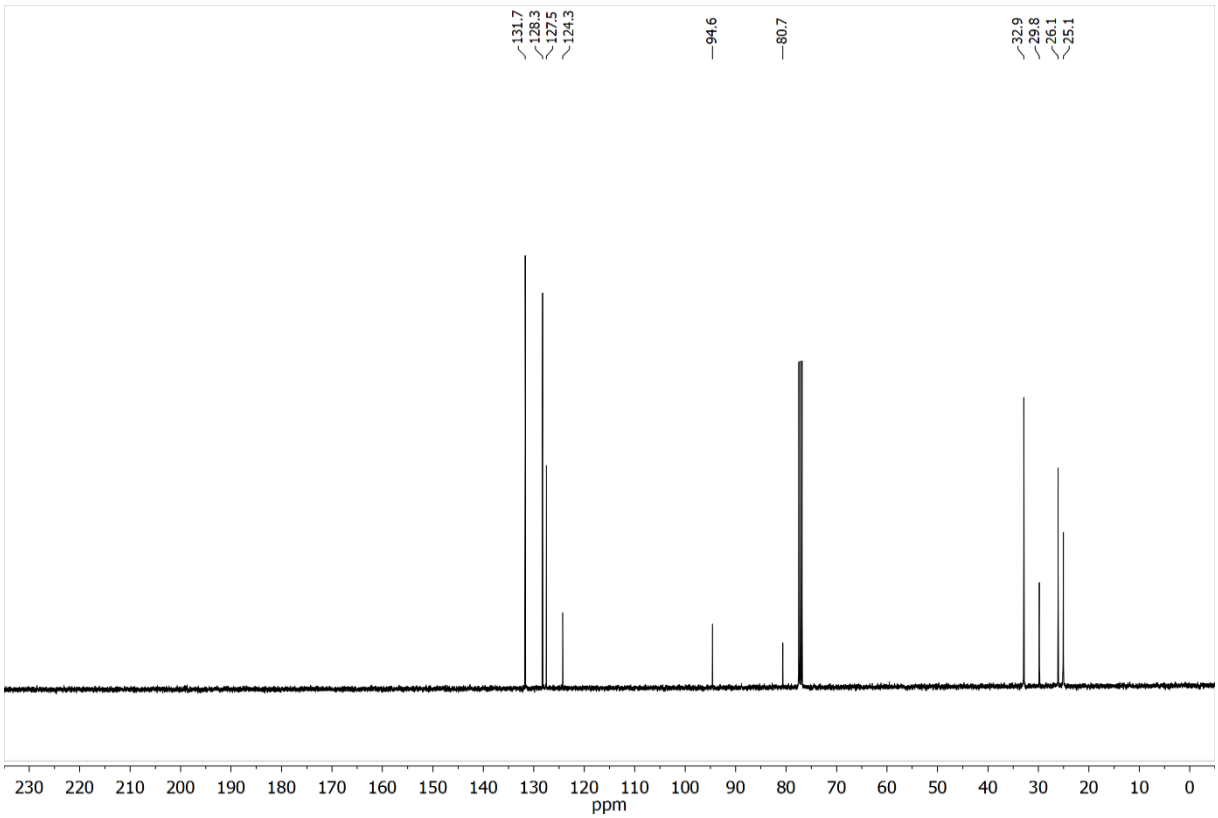




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

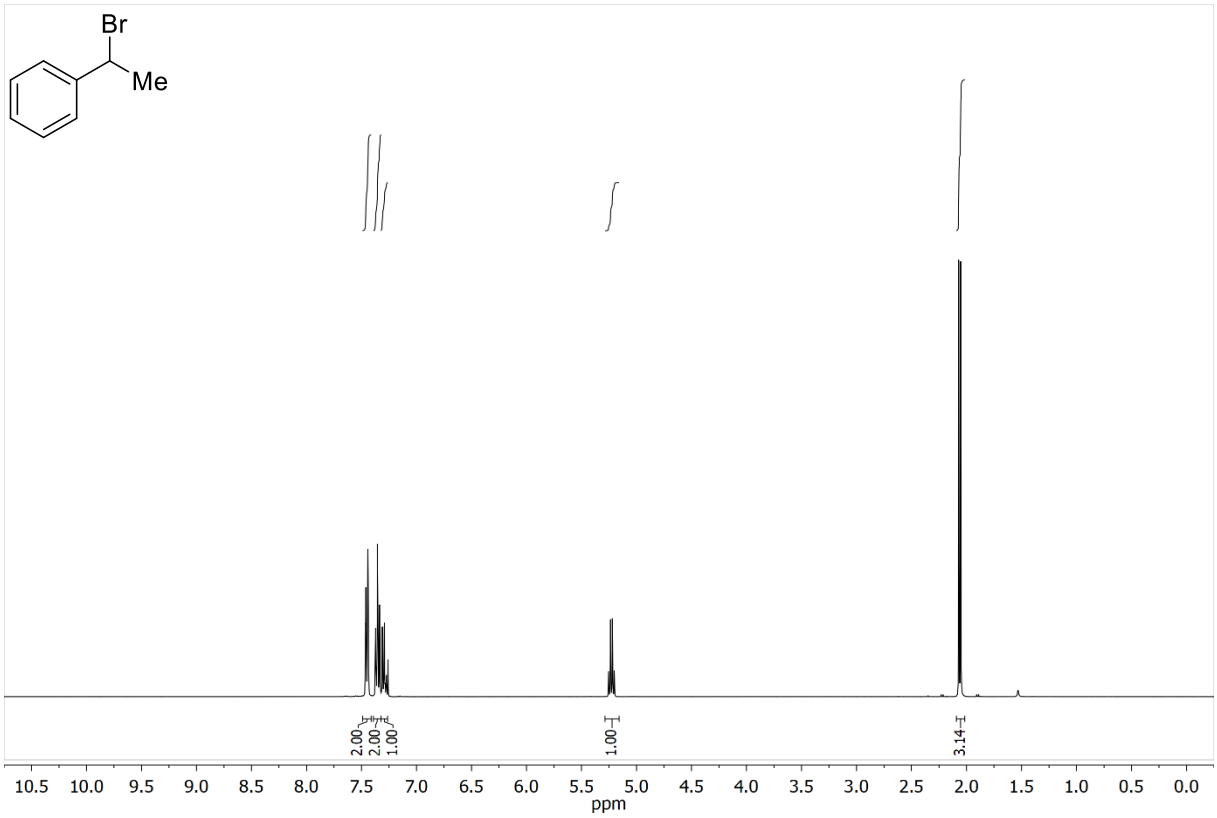
(cyclohexylethynyl)benzene (22)

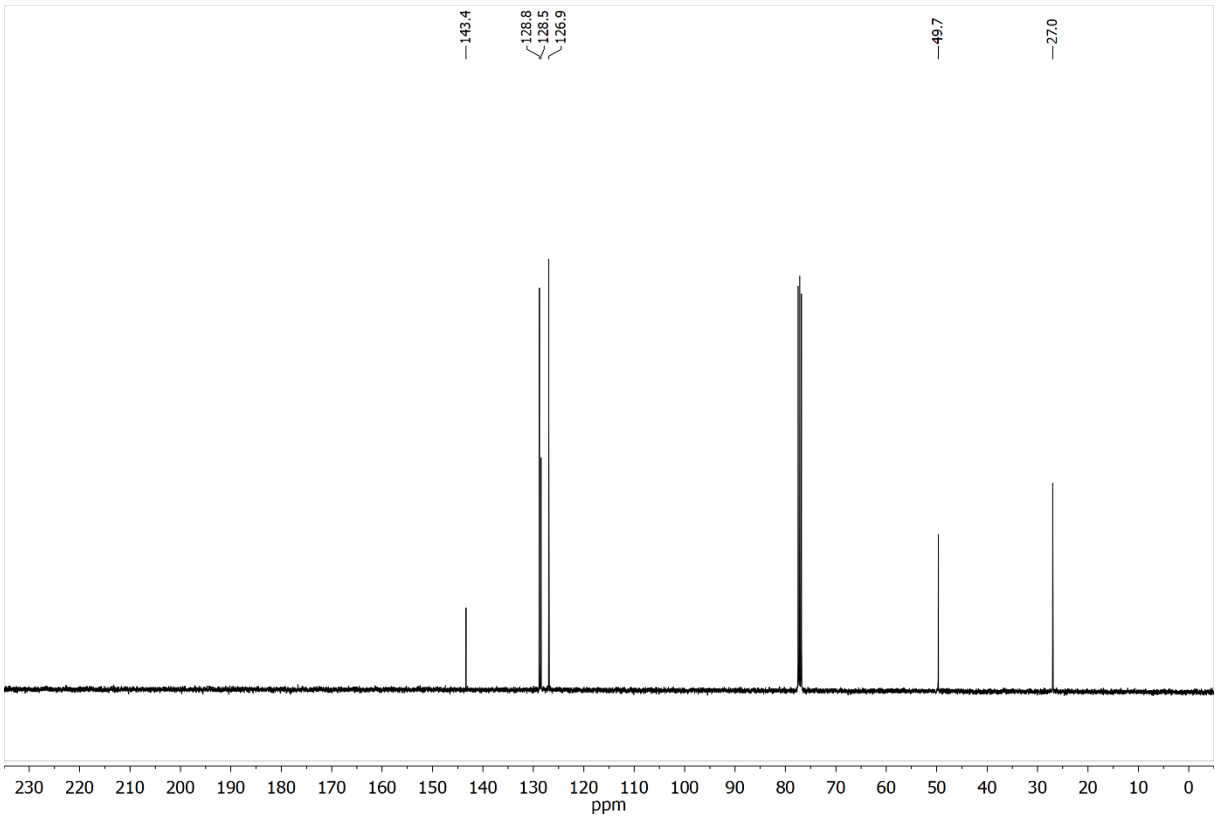




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

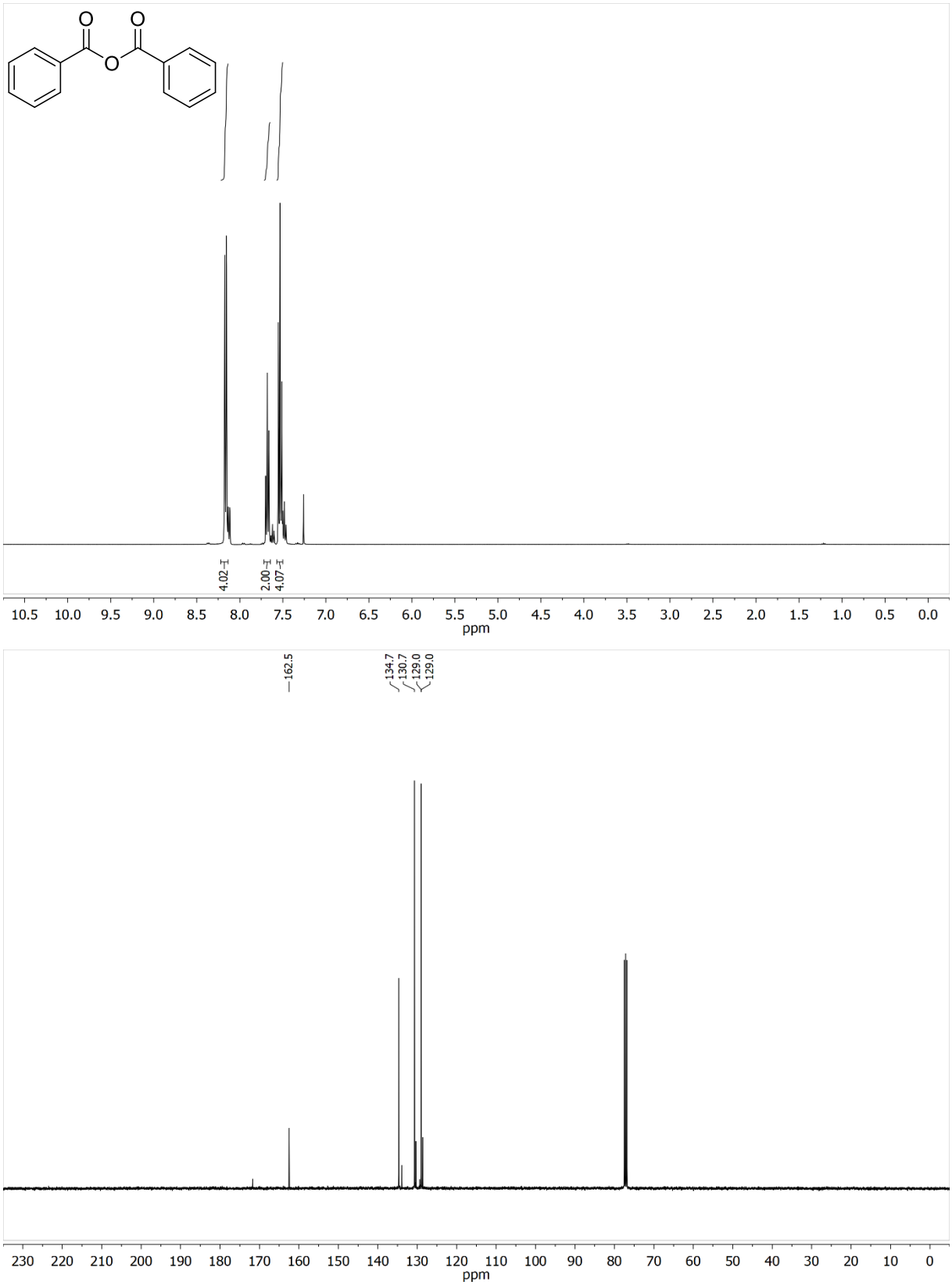
(1-bromoethyl)benzene (26)





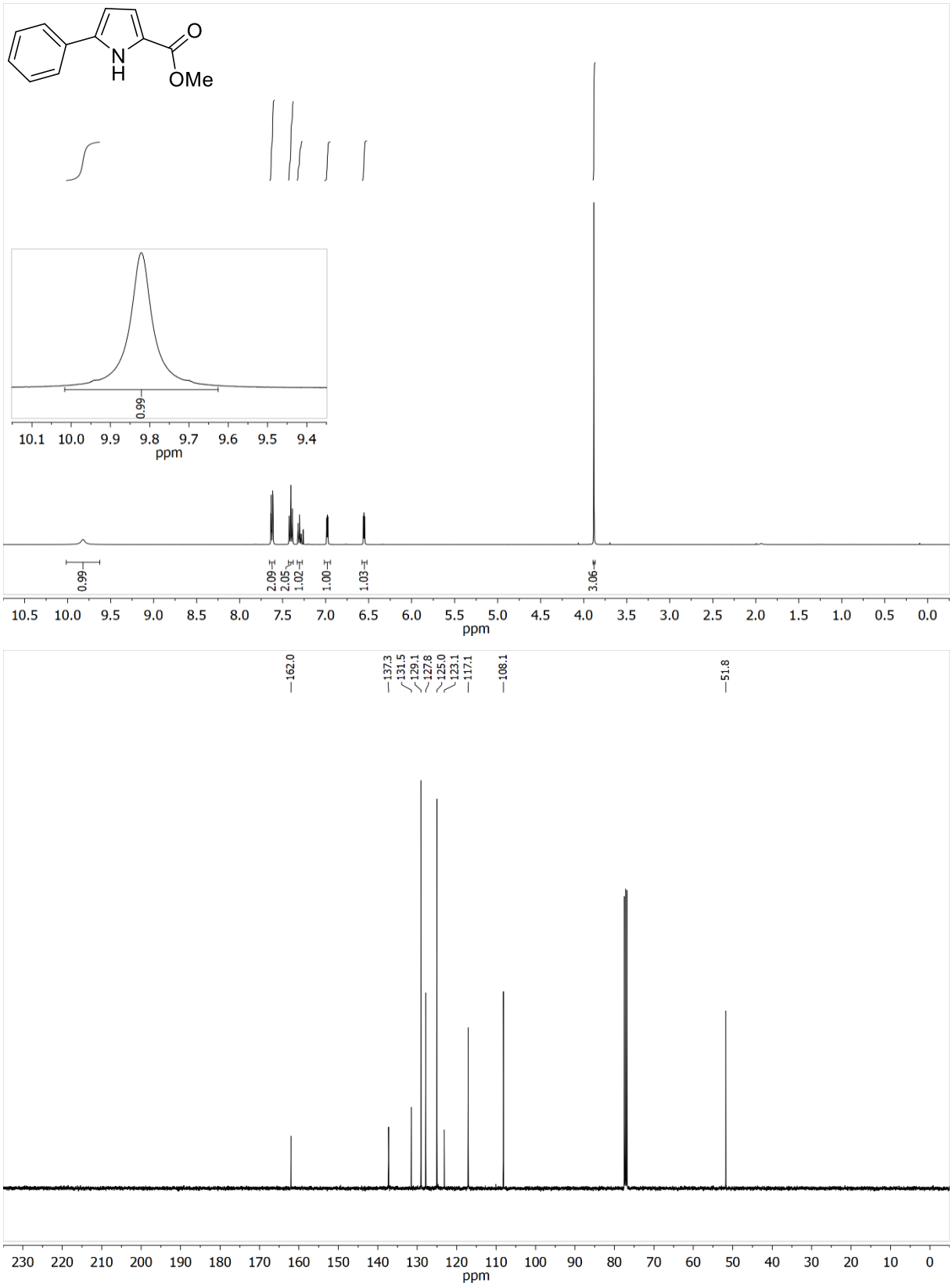
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

benzoic anhydride (32)



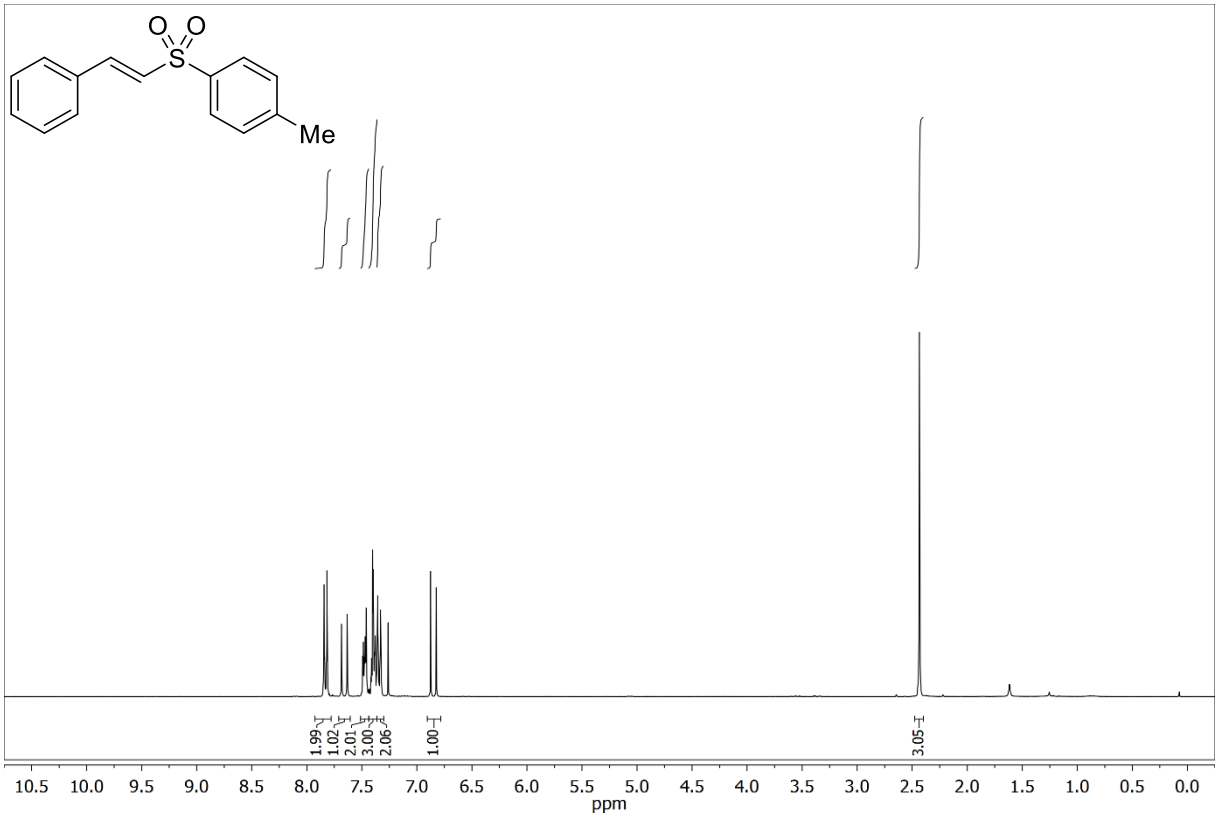
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

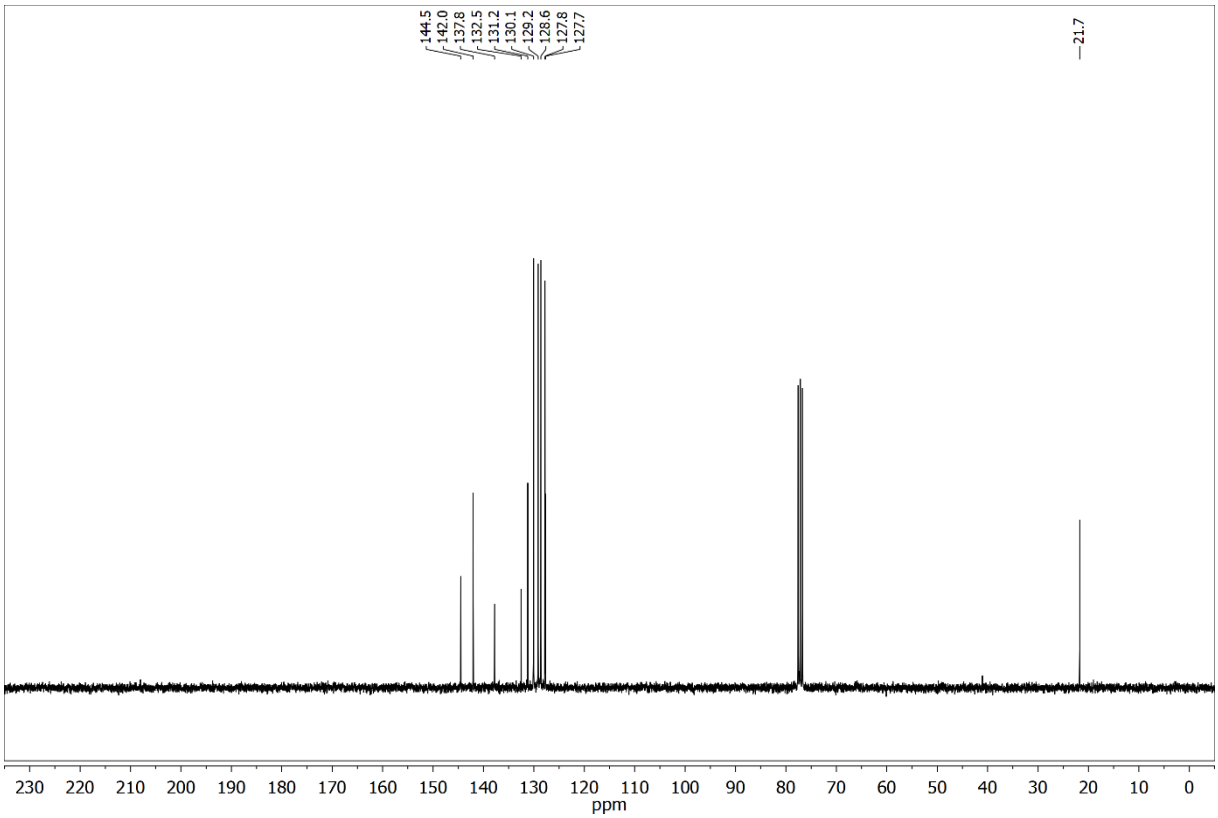
methyl 5-phenyl-1*H*-pyrrole-2-carboxylate (34)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

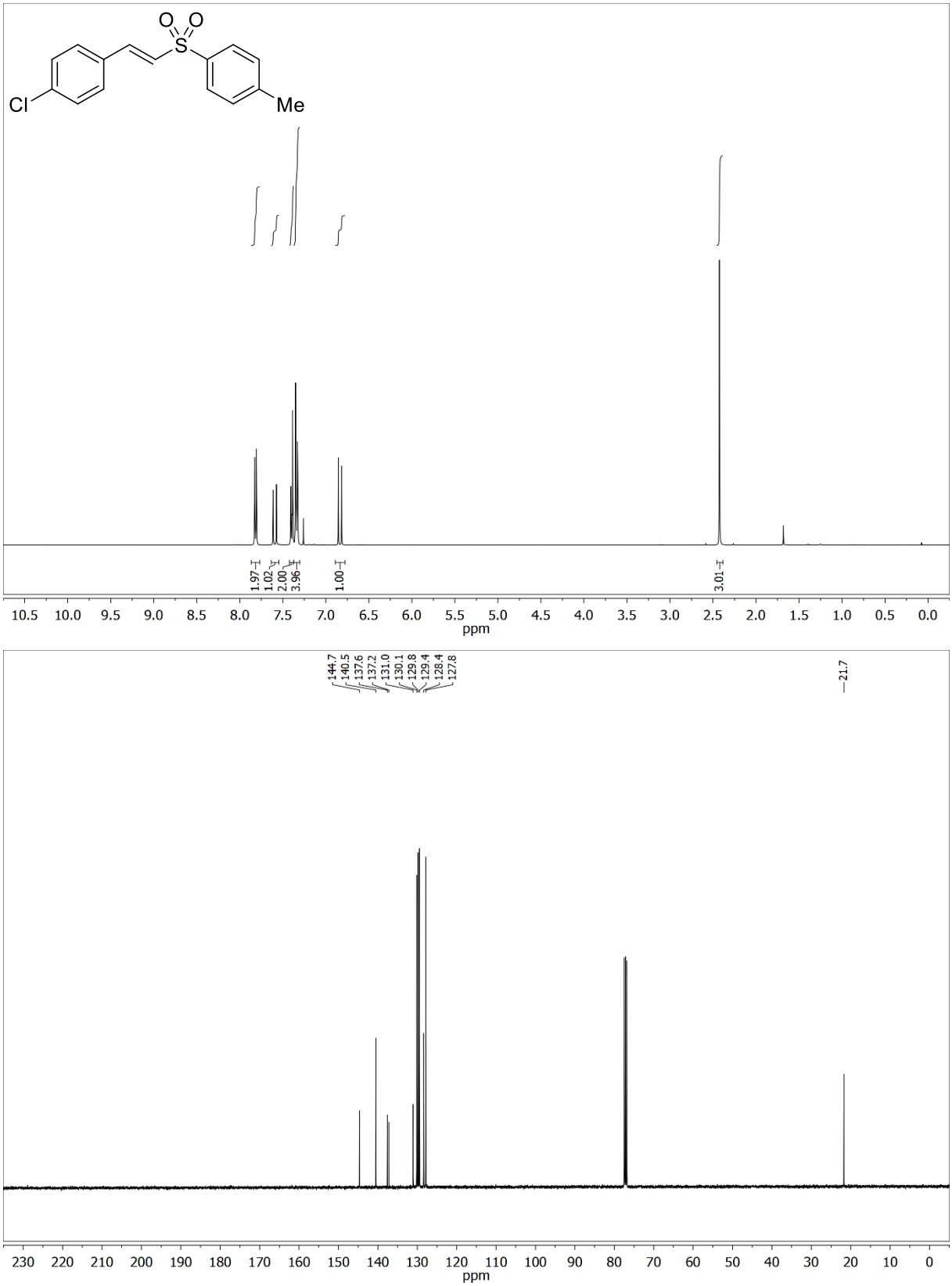
(*E*)-1-methyl-4-(styrylsulfonyl)benzene (12a)





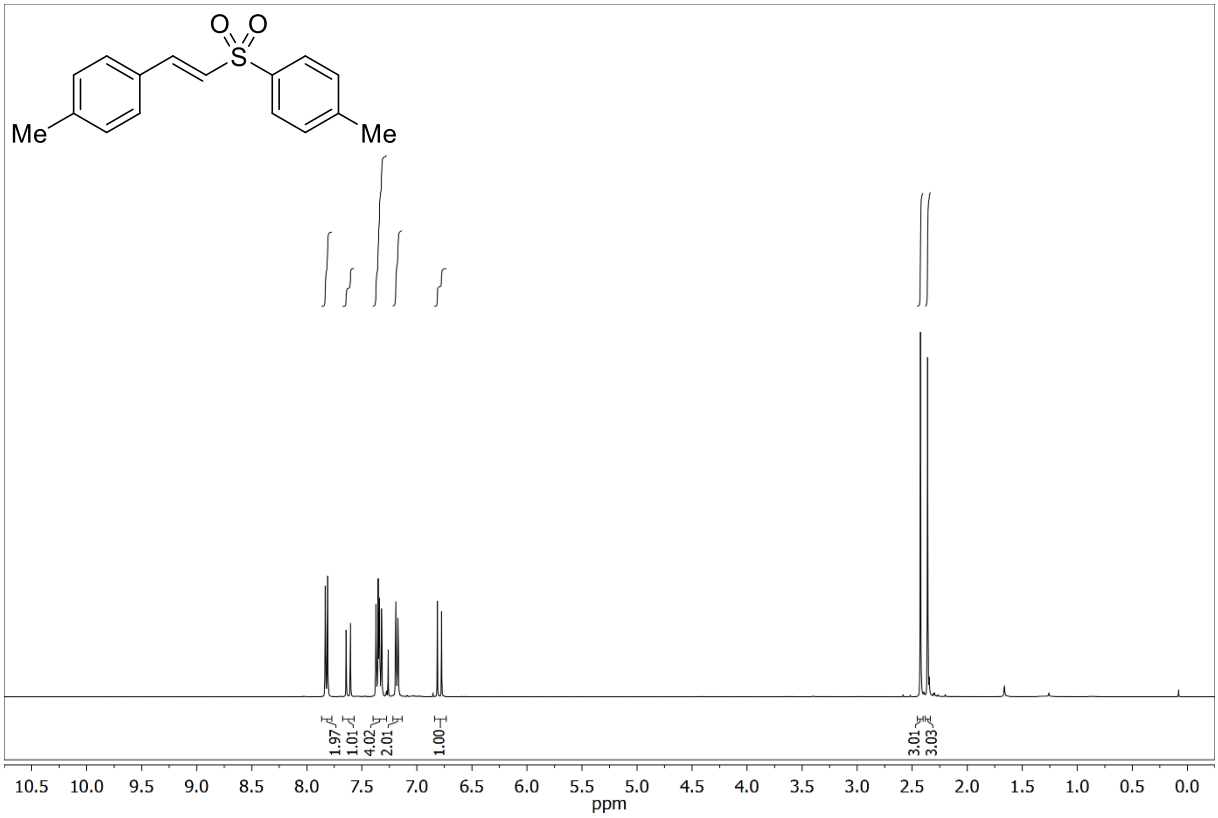
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

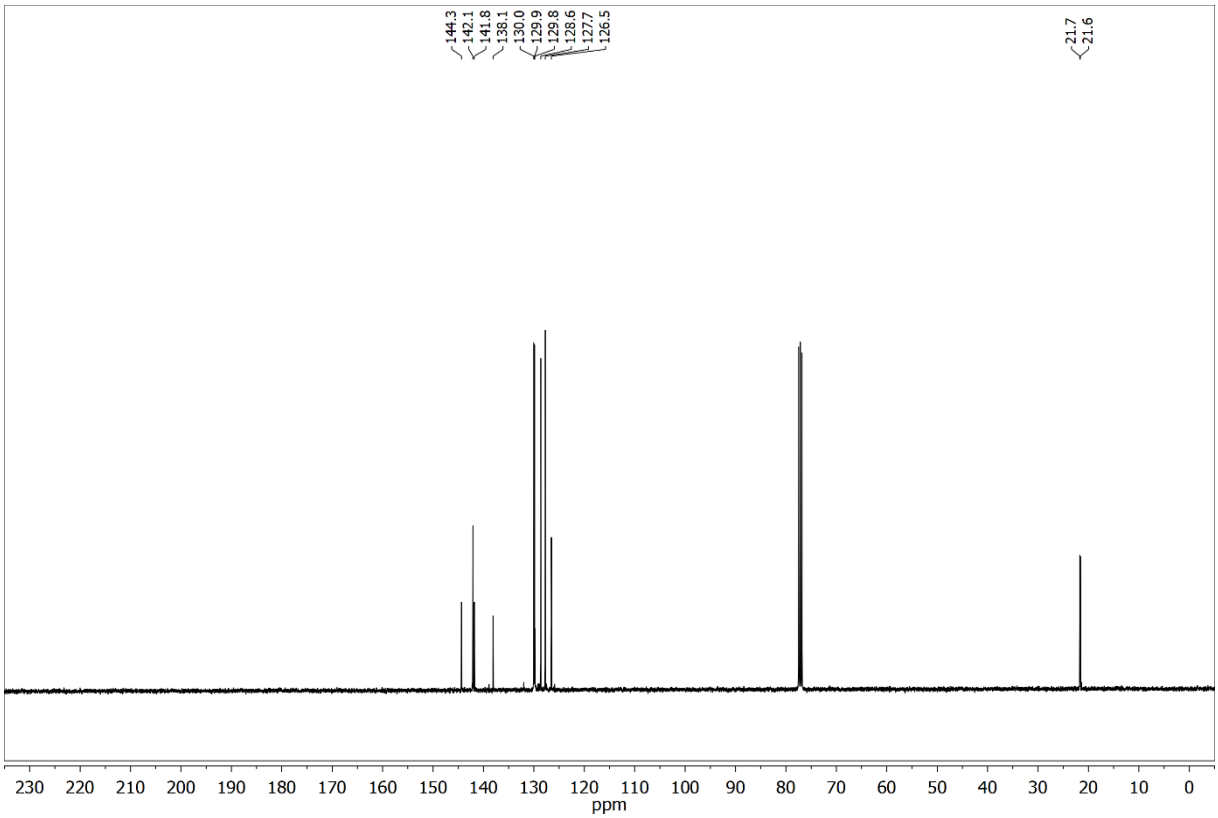
(*E*)-1-chloro-4-(2-tosylvinyl)benzene (12b)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

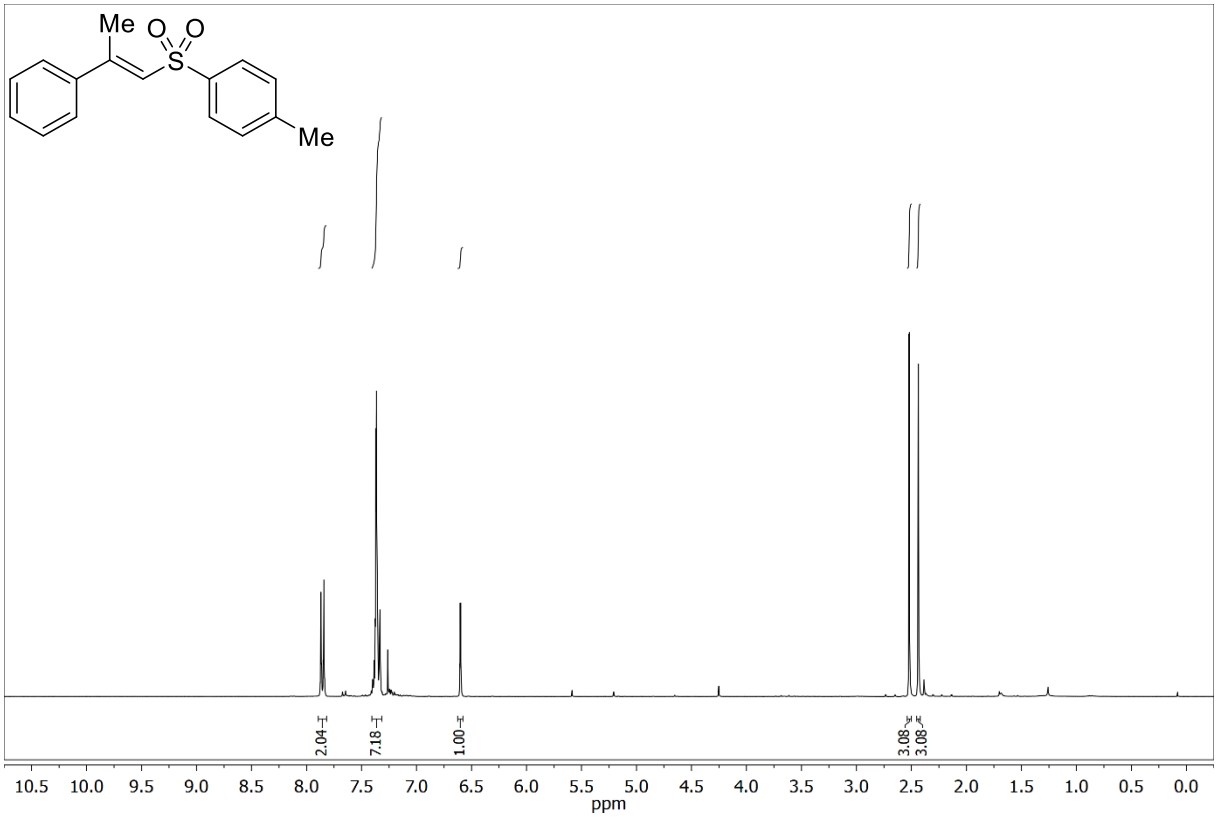
(*E*)-1-methyl-4-((4-methylstyryl)sulfonyl)benzene (12c)

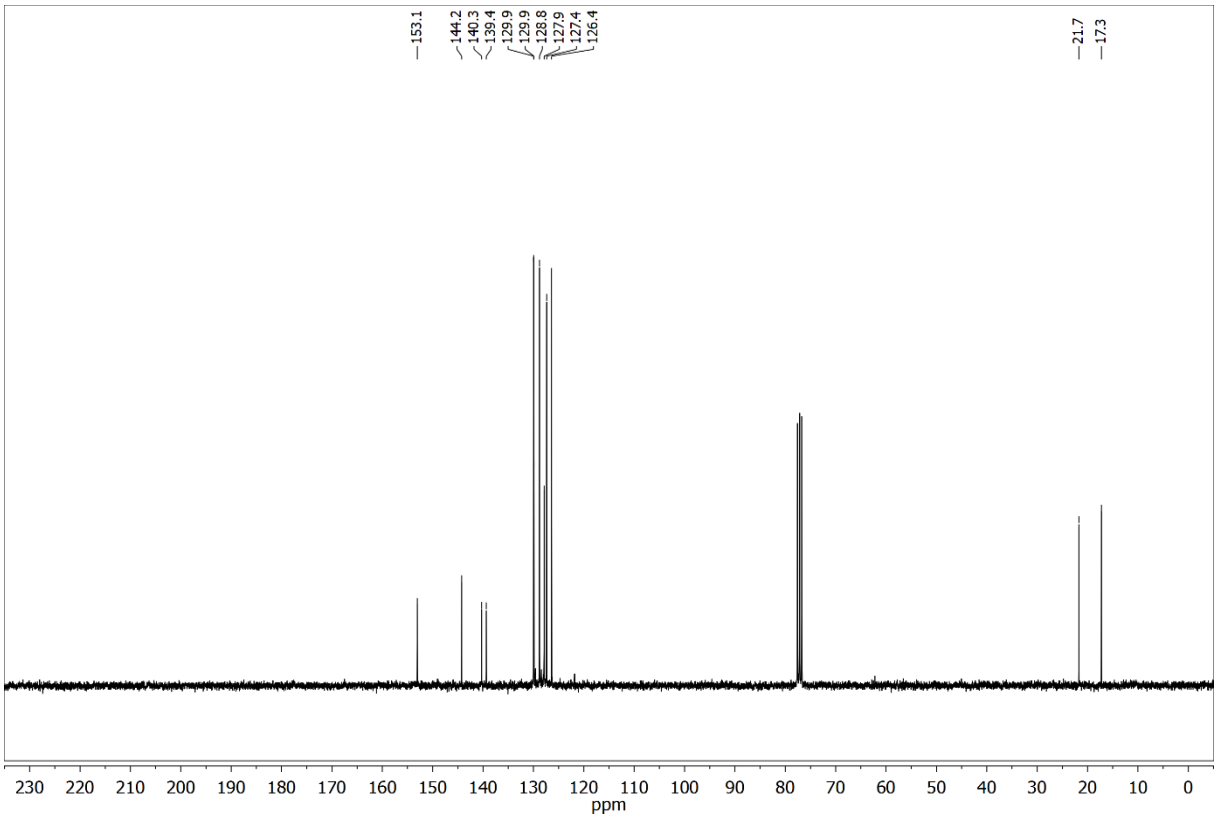




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

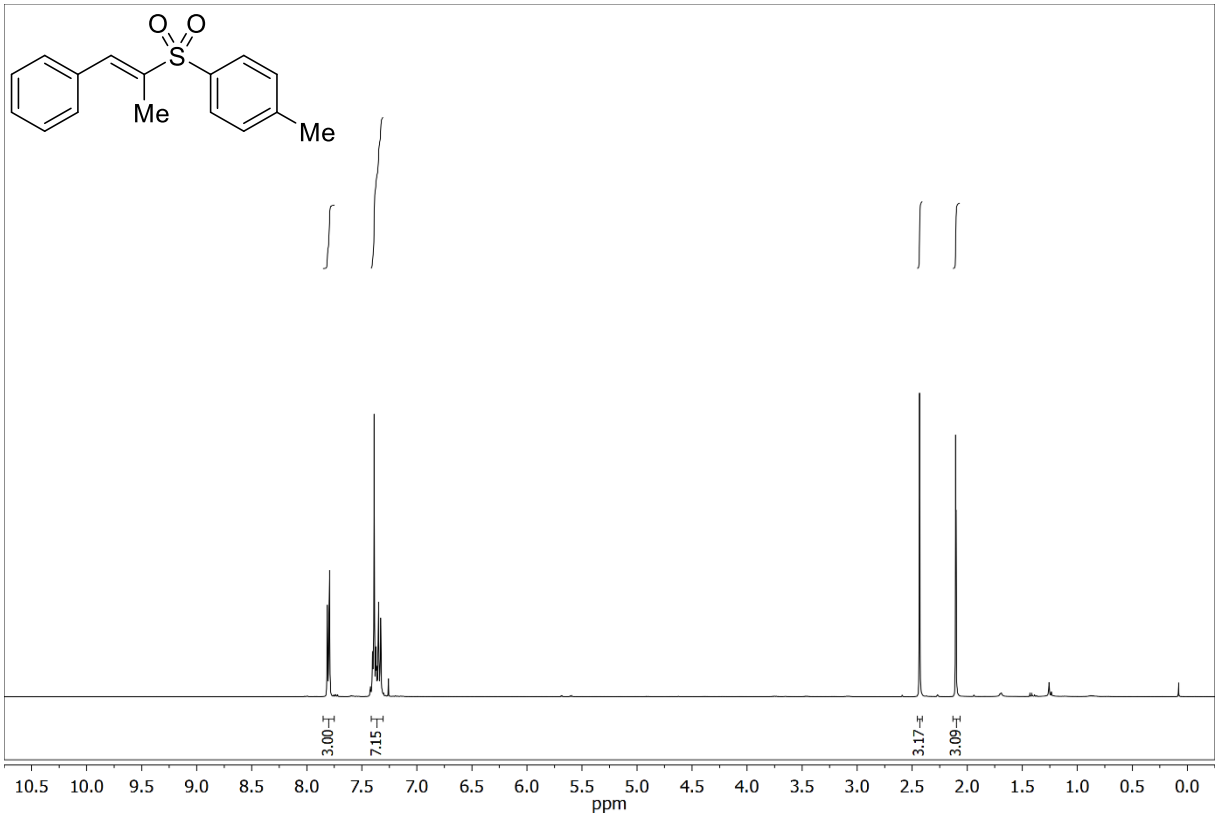
(*E*)-1-methyl-4-((2-phenylprop-1-en-1-yl)sulfonyl)benzene (12d)

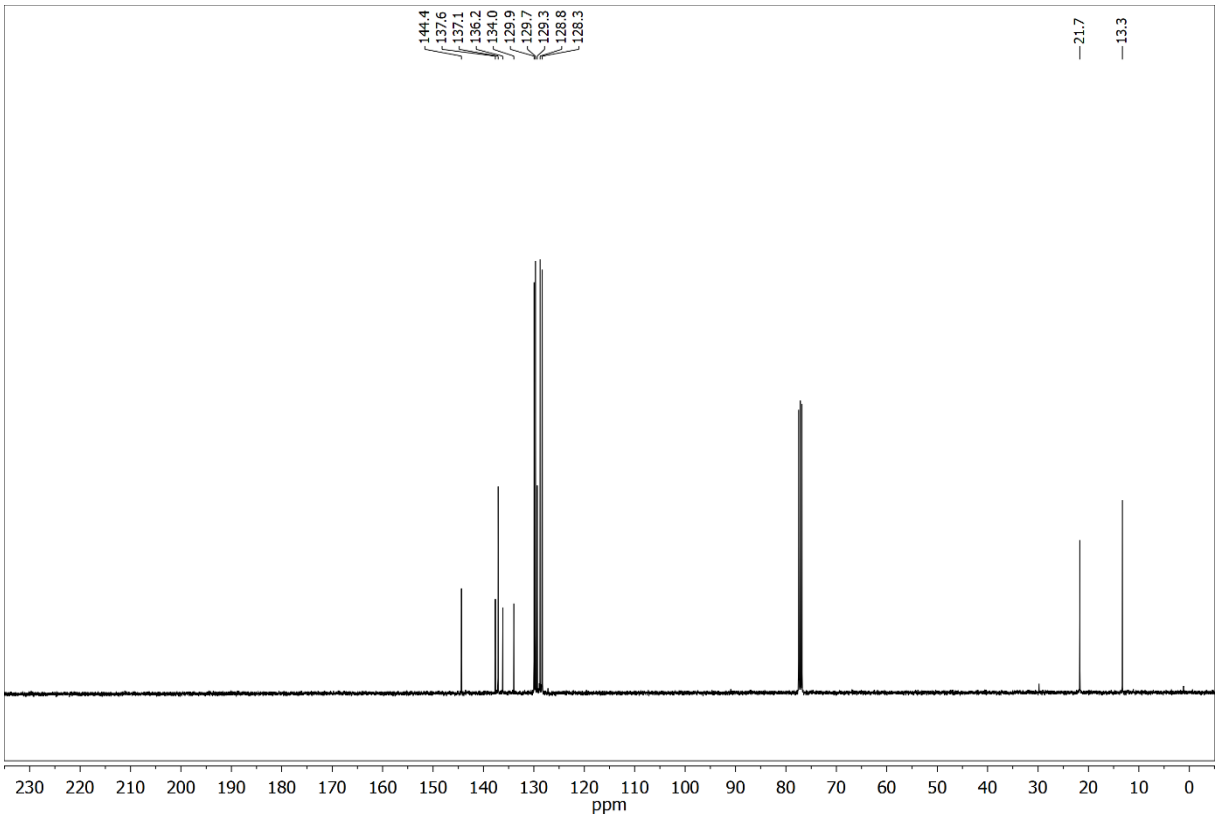




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

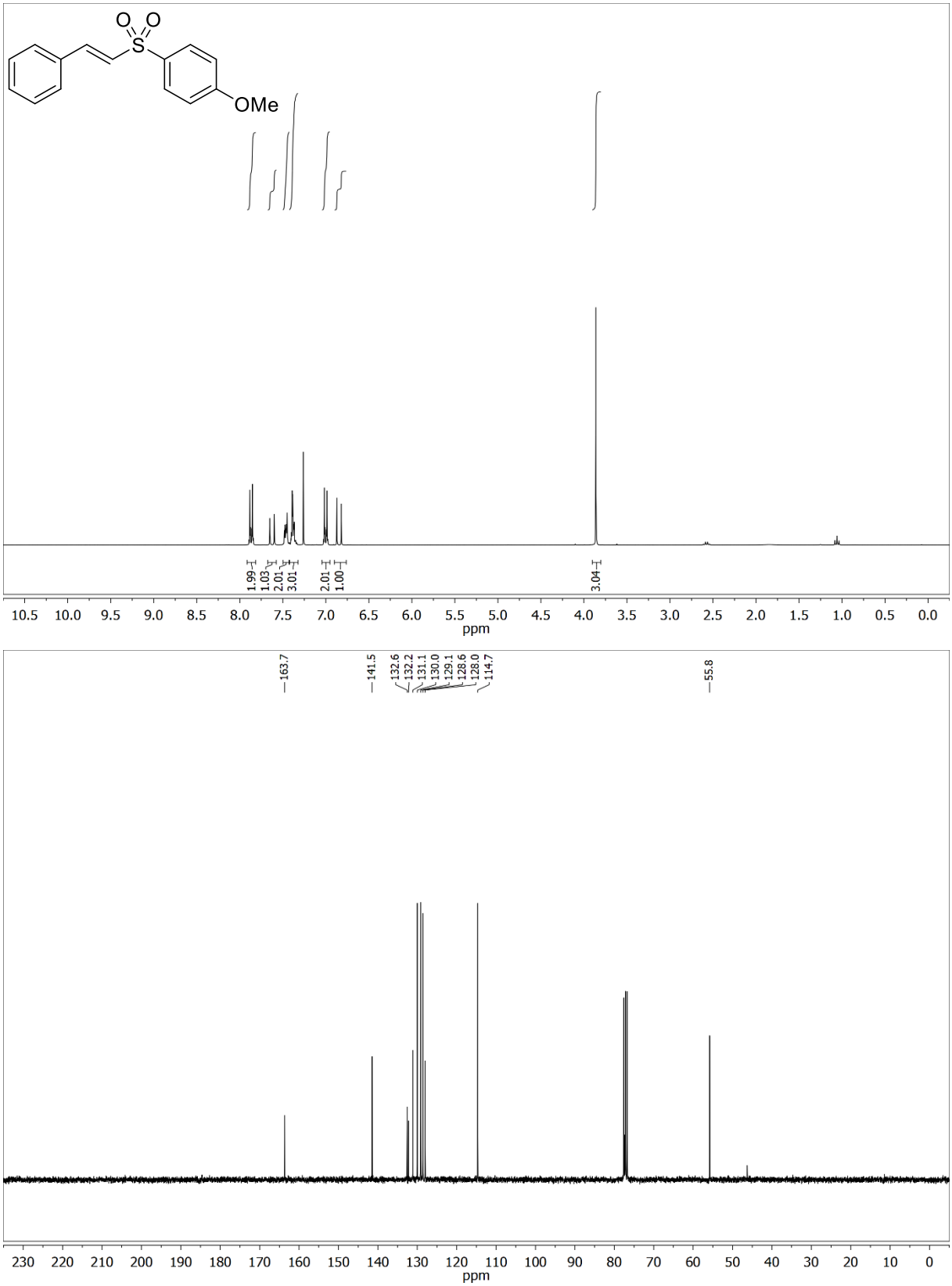
(*E*)-1-methyl-4-((1-phenylprop-1-en-2-yl)sulfonyl)benzene (12e)





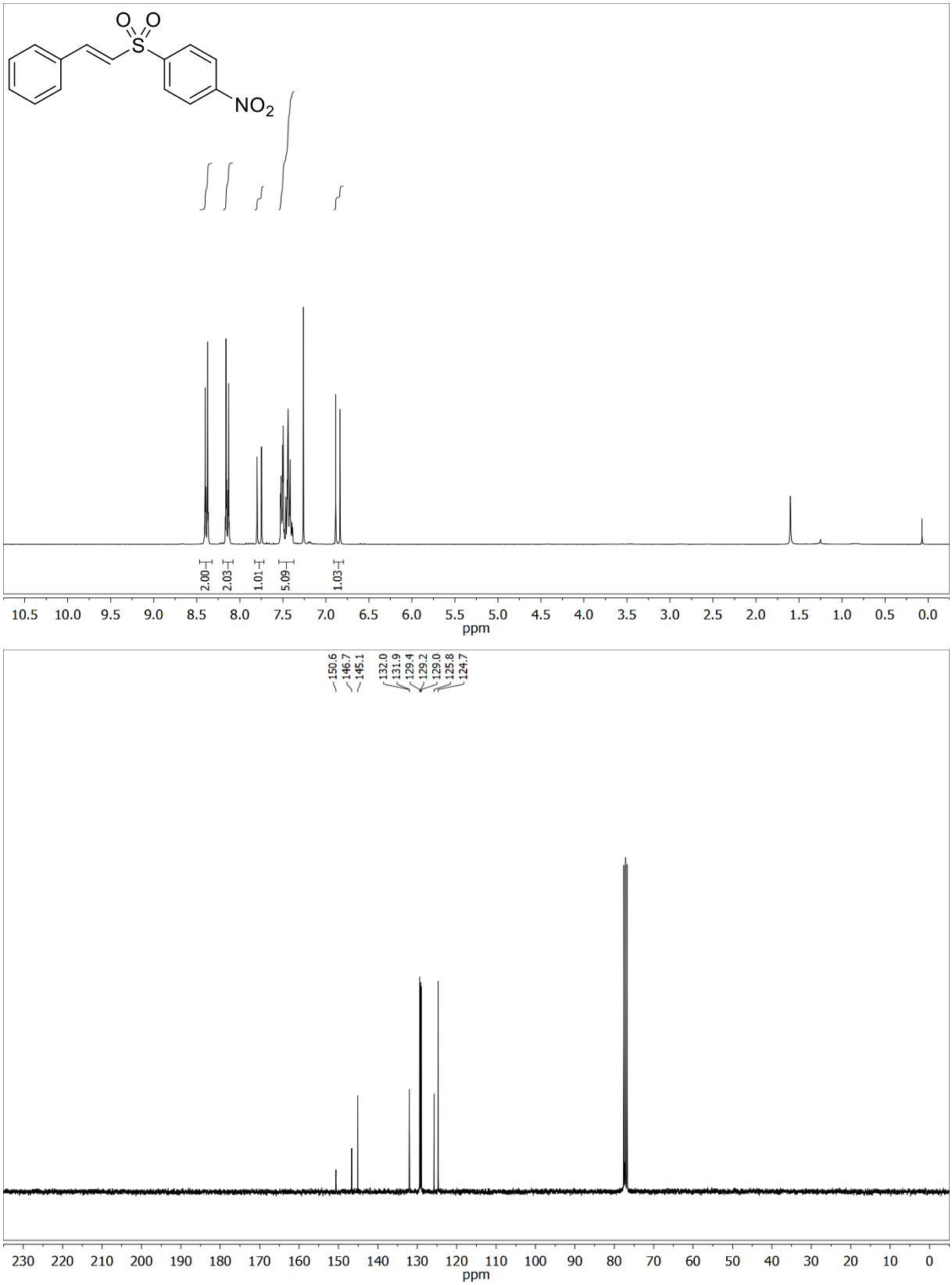
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

(*E*)-1-methoxy-4-(styrylsulfonyl)benzene (12f)



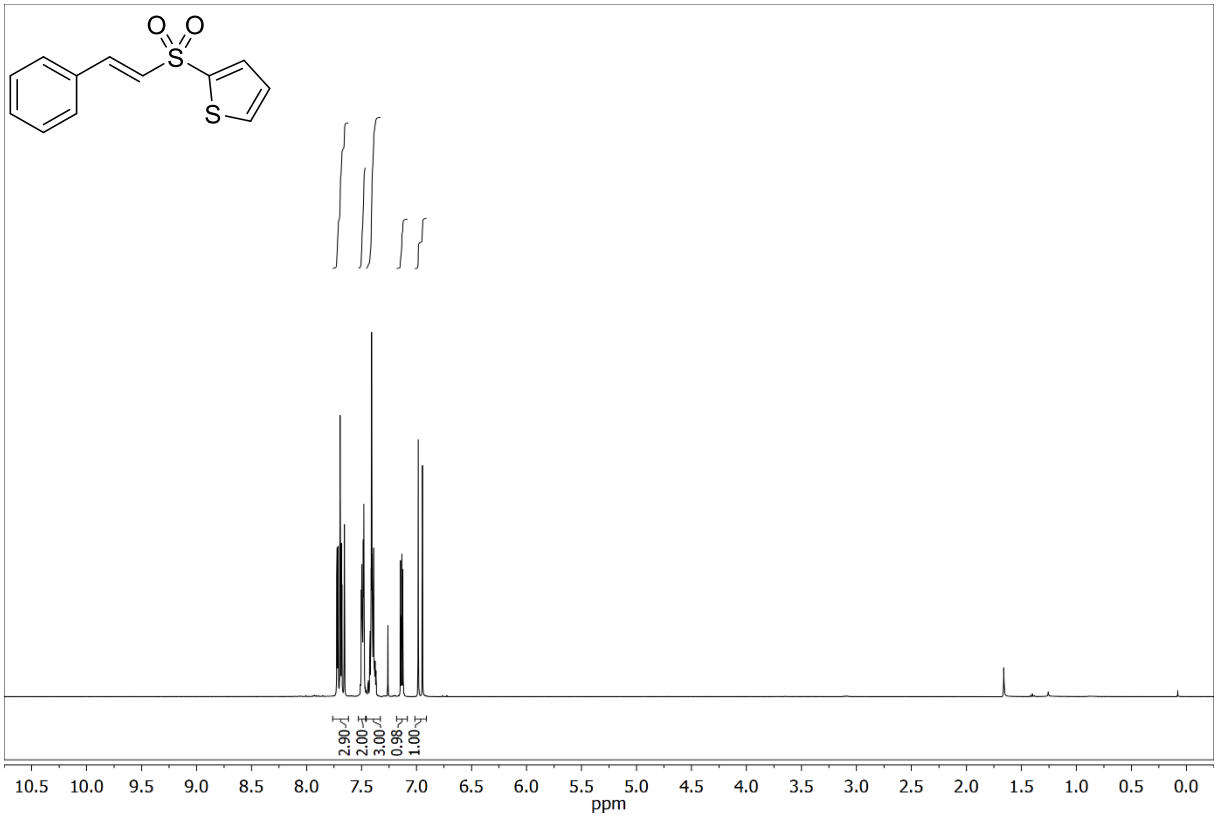
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

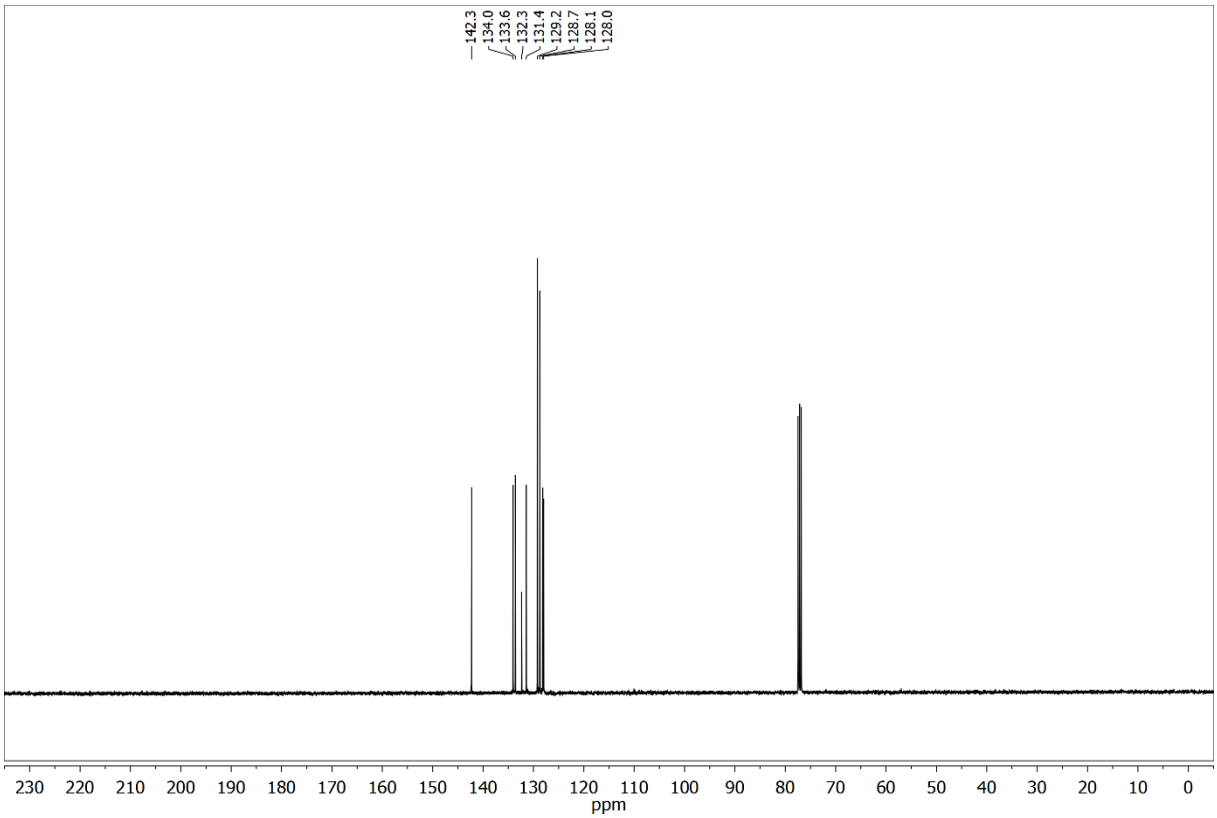
(*E*)-1-nitro-4-(styrylsulfonyl)benzene (12g)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

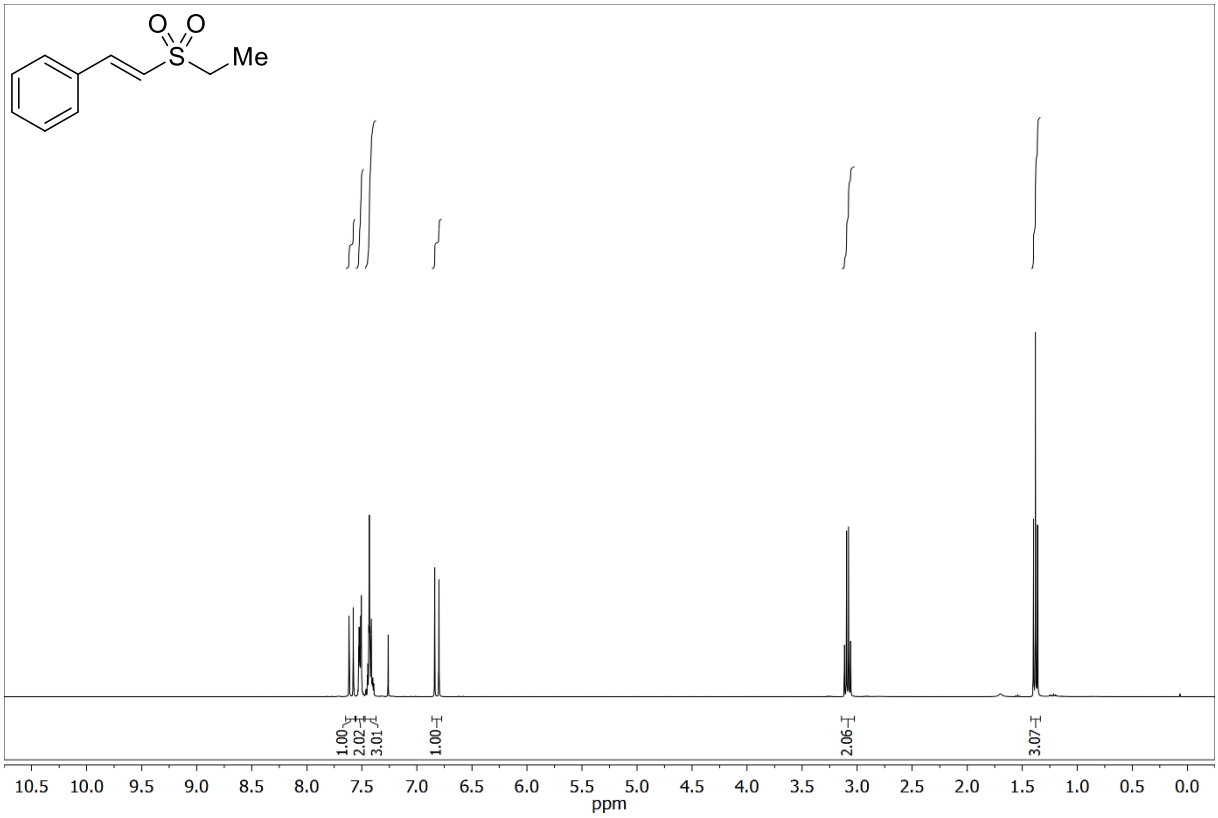
(*E*)-2-(styrylsulfonyl)thiophene (12h)

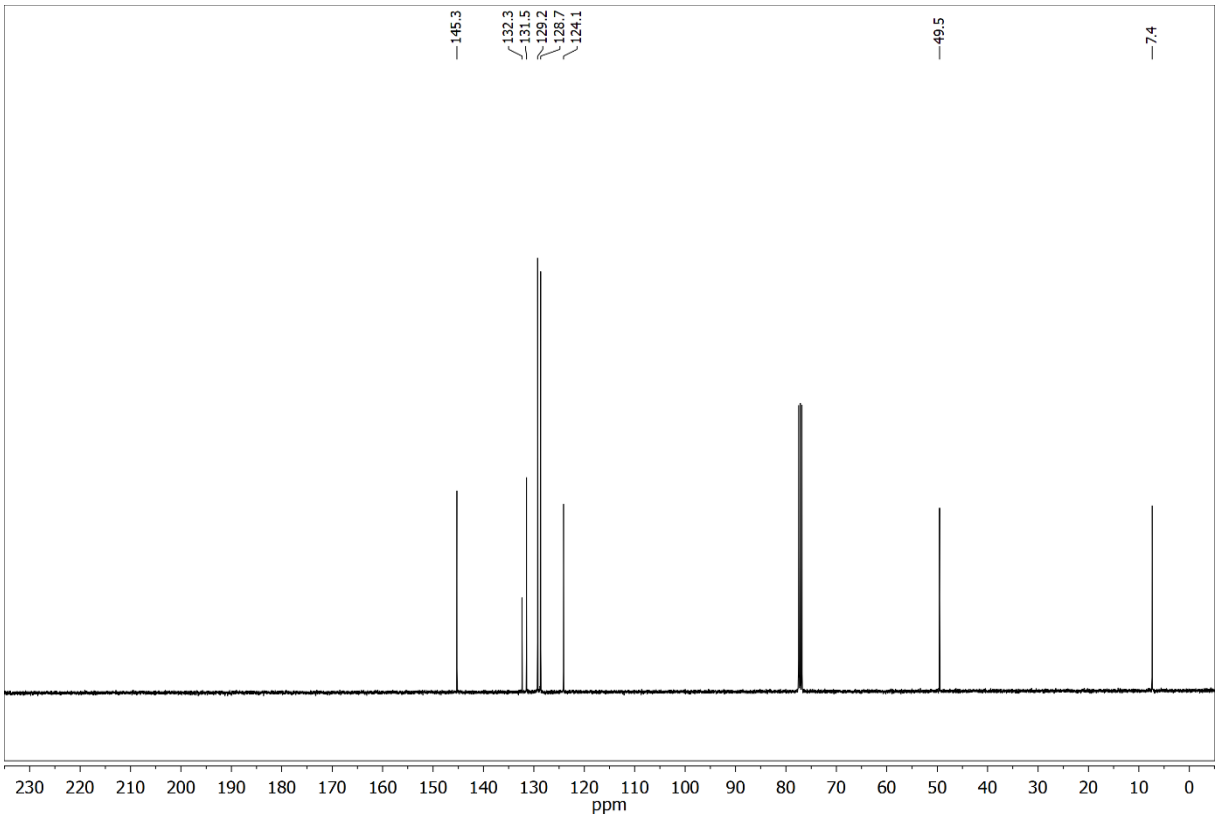




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

(*E*)-(2-(ethylsulfonyl)vinyl)benzene (12i)

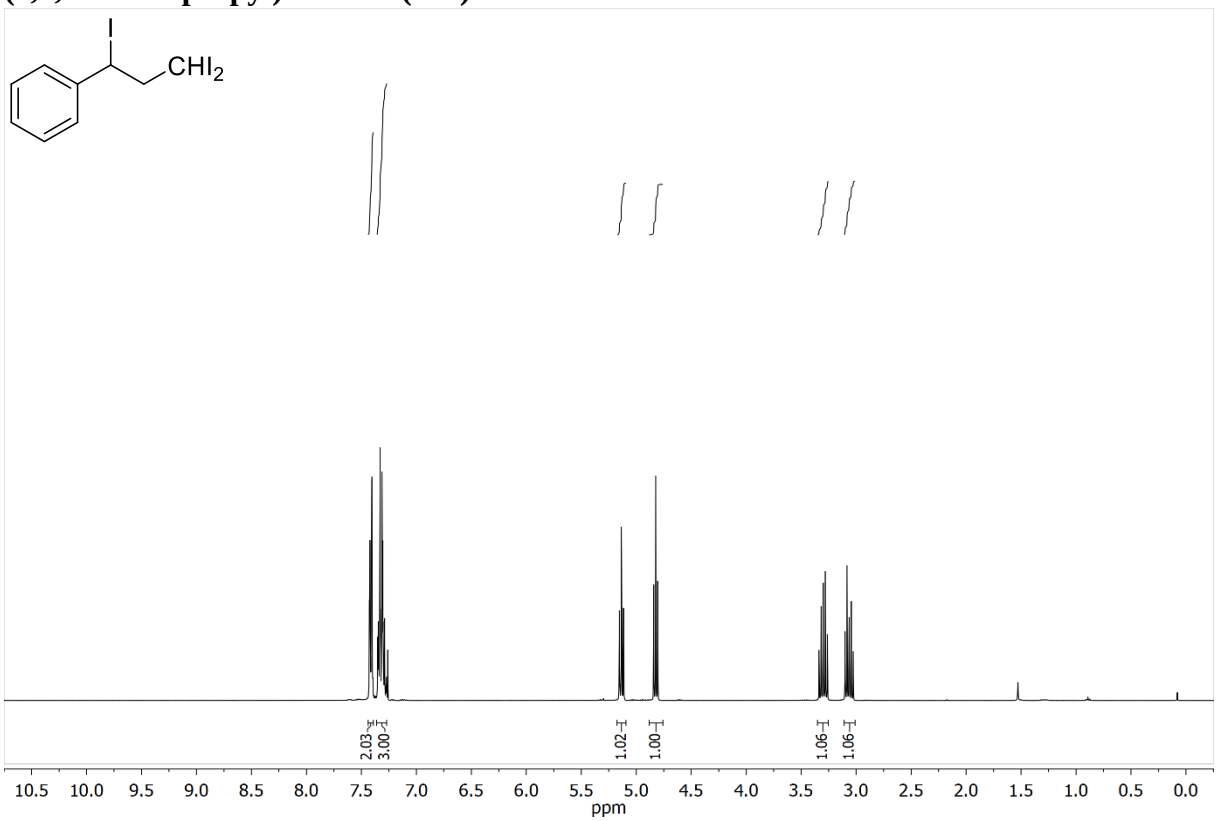


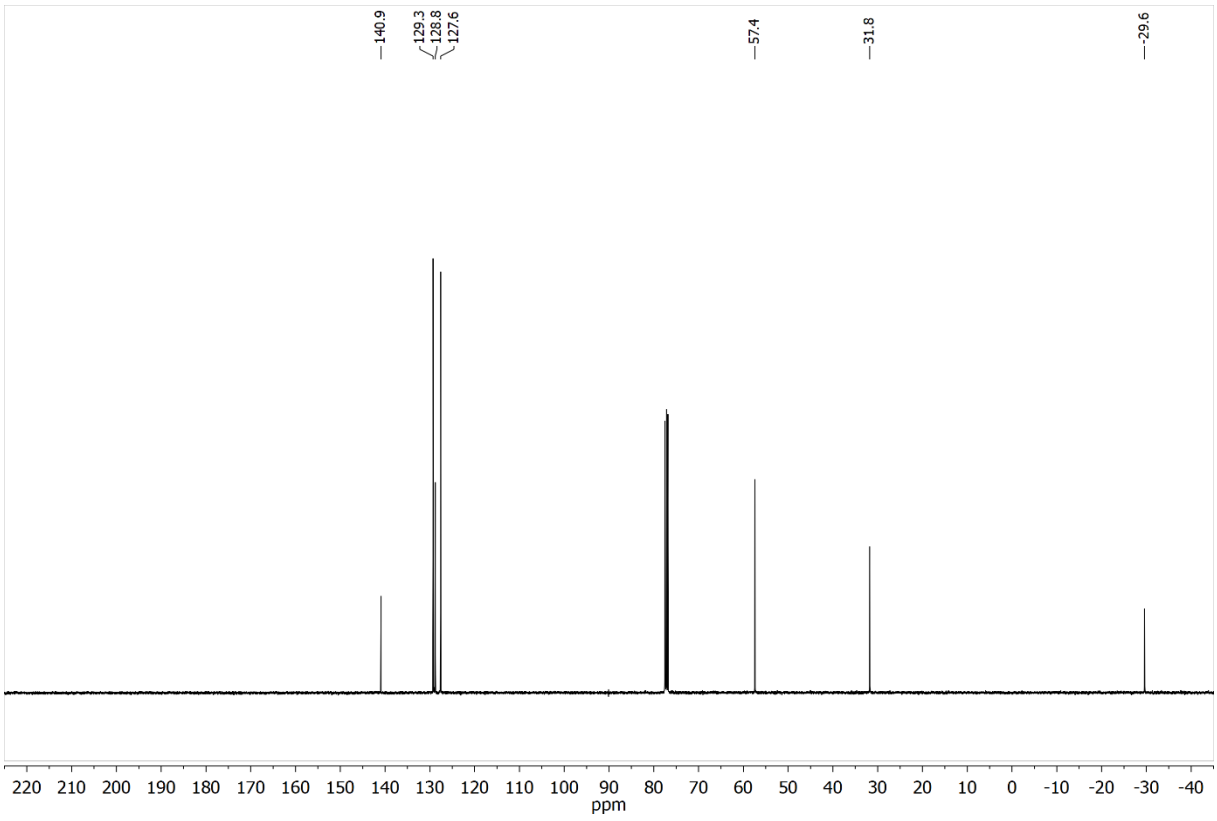


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

8.4 NMR Spectra for Chapter 4

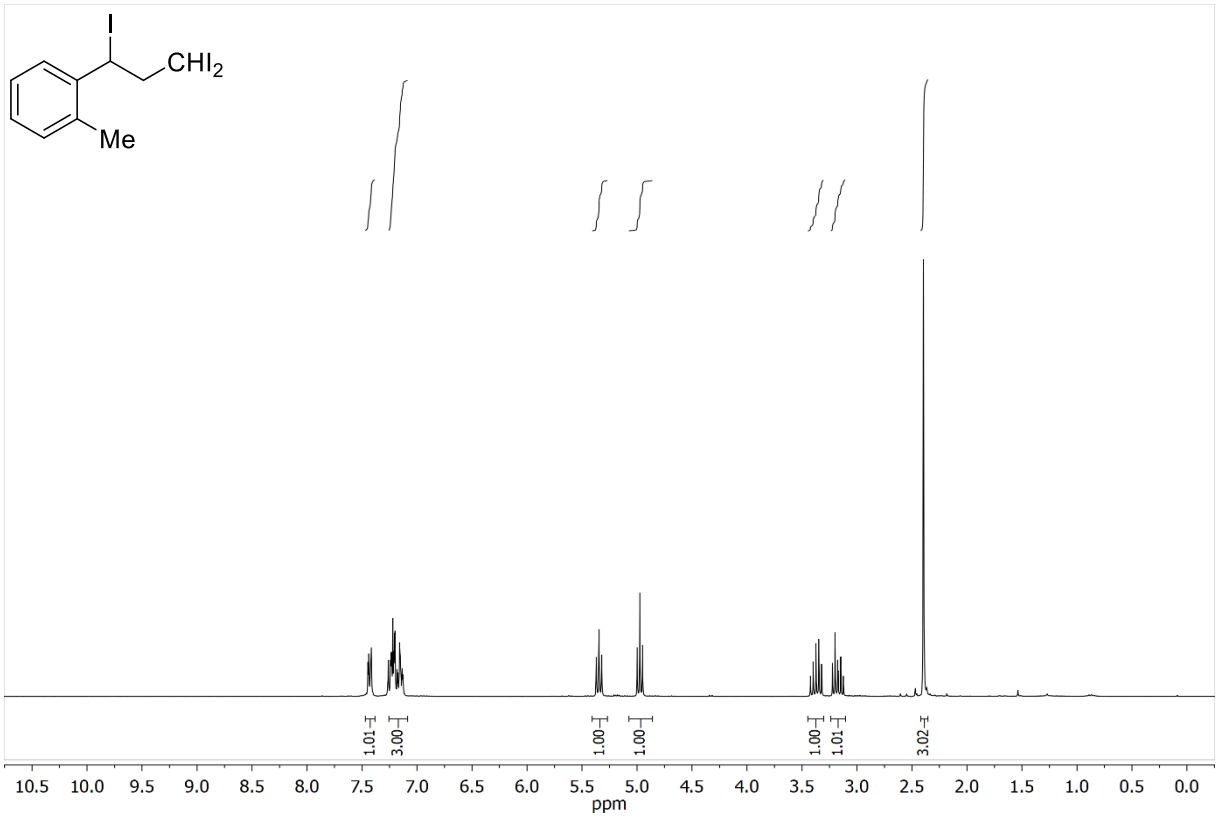
(1,3,3-triiodopropyl)benzene (25a)

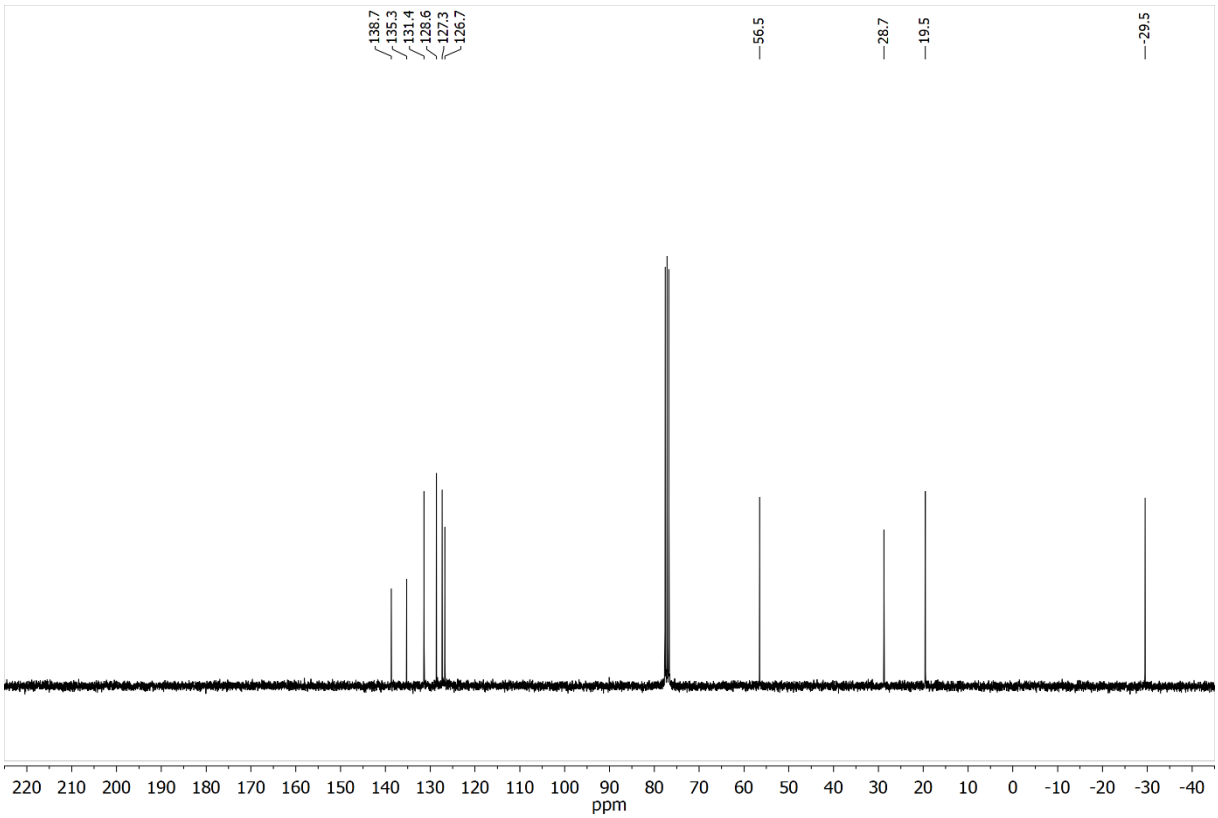




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

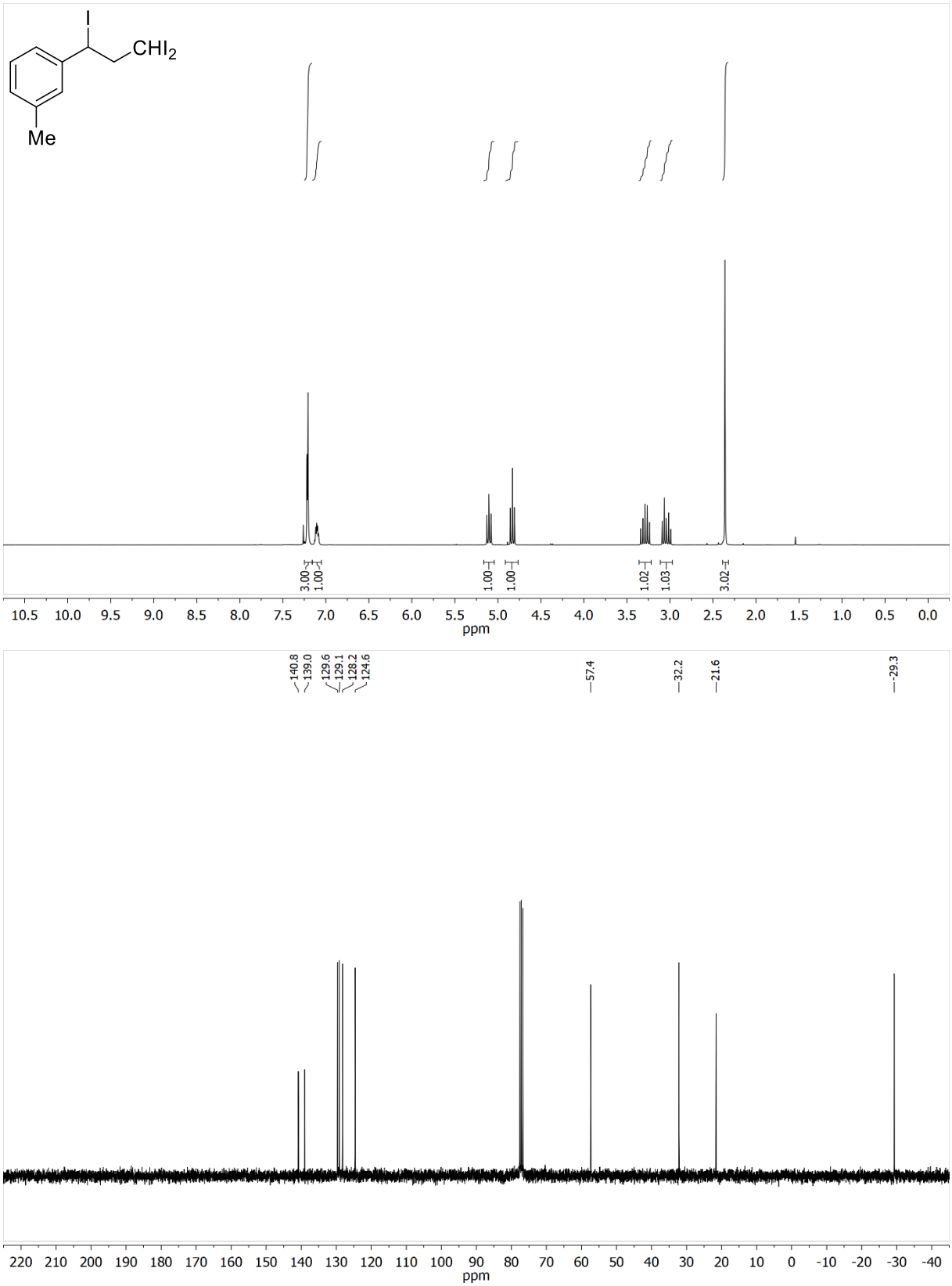
1-methyl-2-(1,3,3-triiodopropyl)benzene (25b)





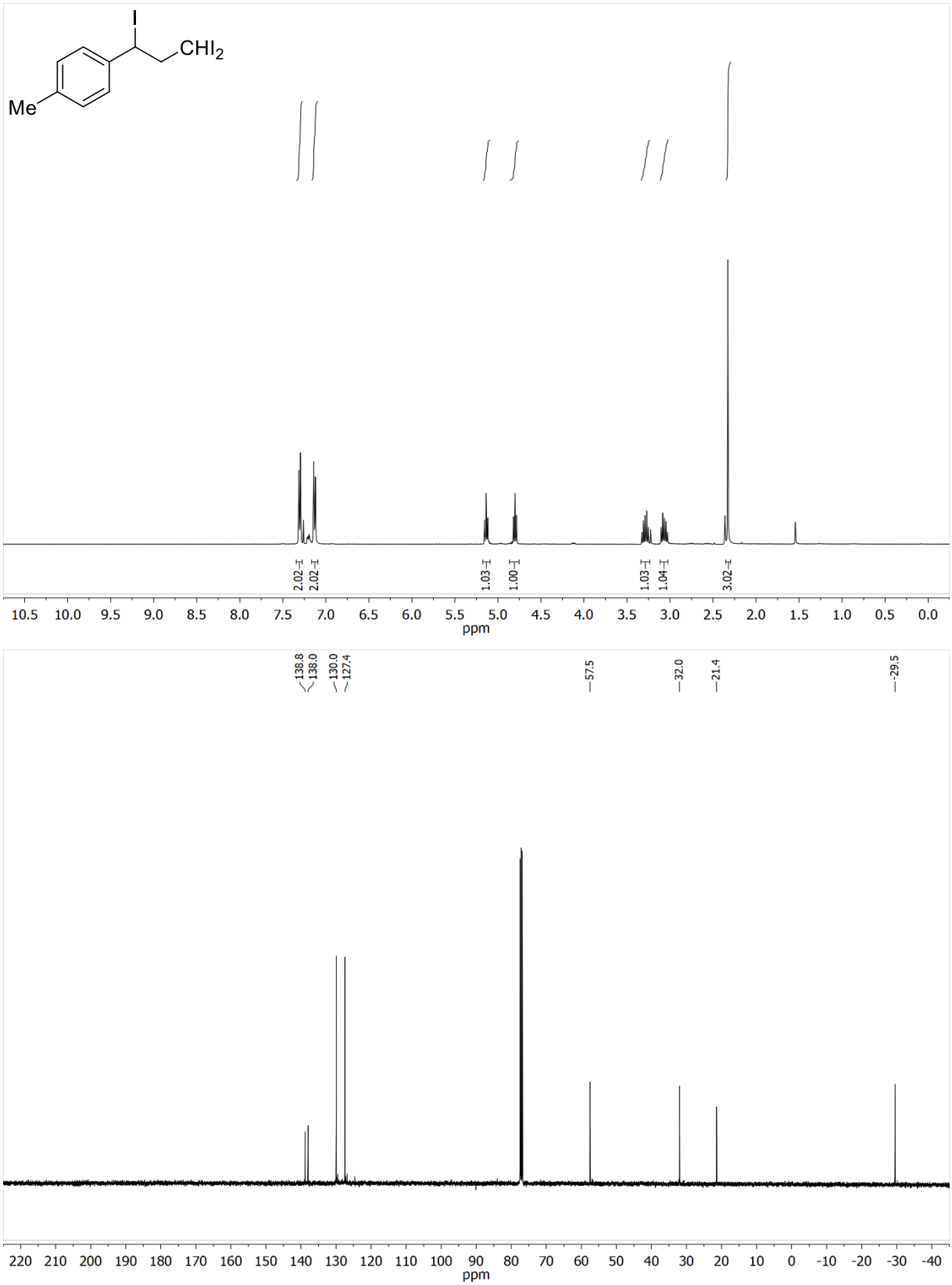
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

1-methyl-3-(1,3,3-triiodopropyl)benzene (25c)



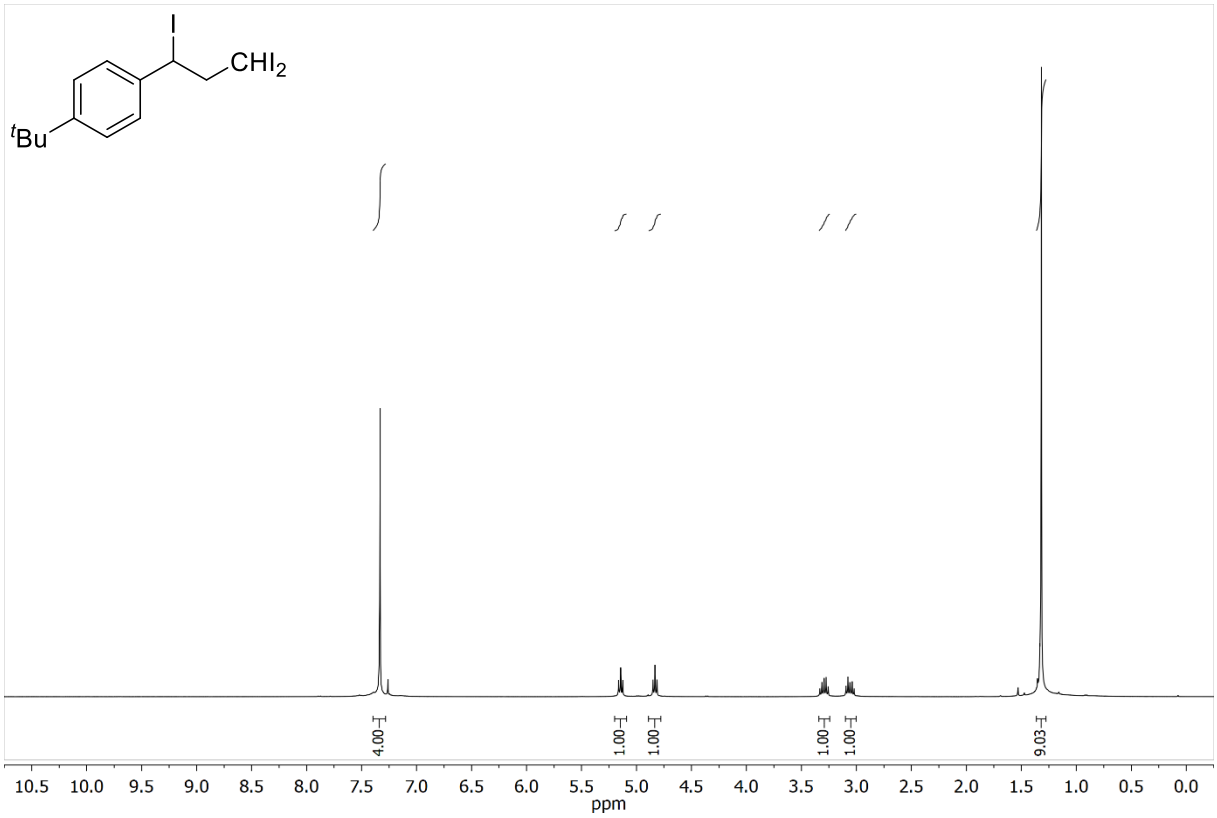
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

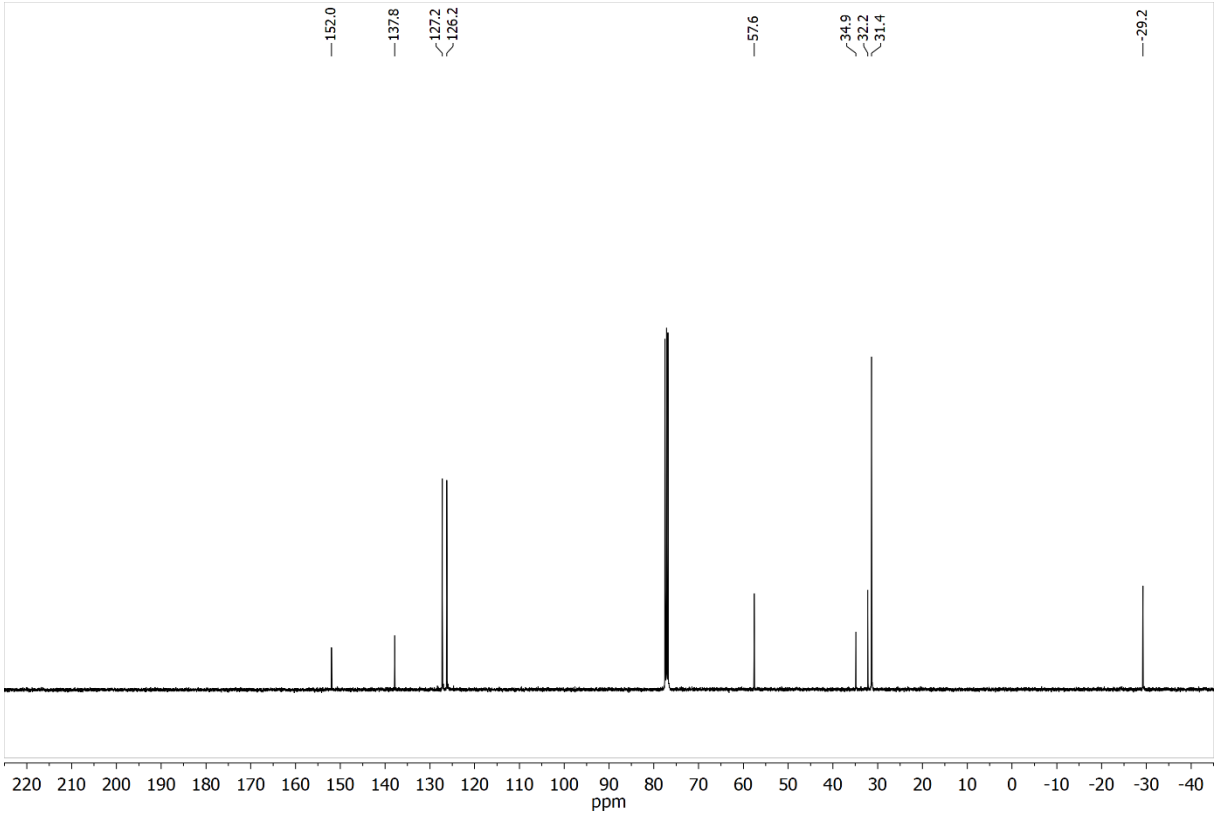
1-methyl-4-(1,3,3-triiodopropyl)benzene (25d)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

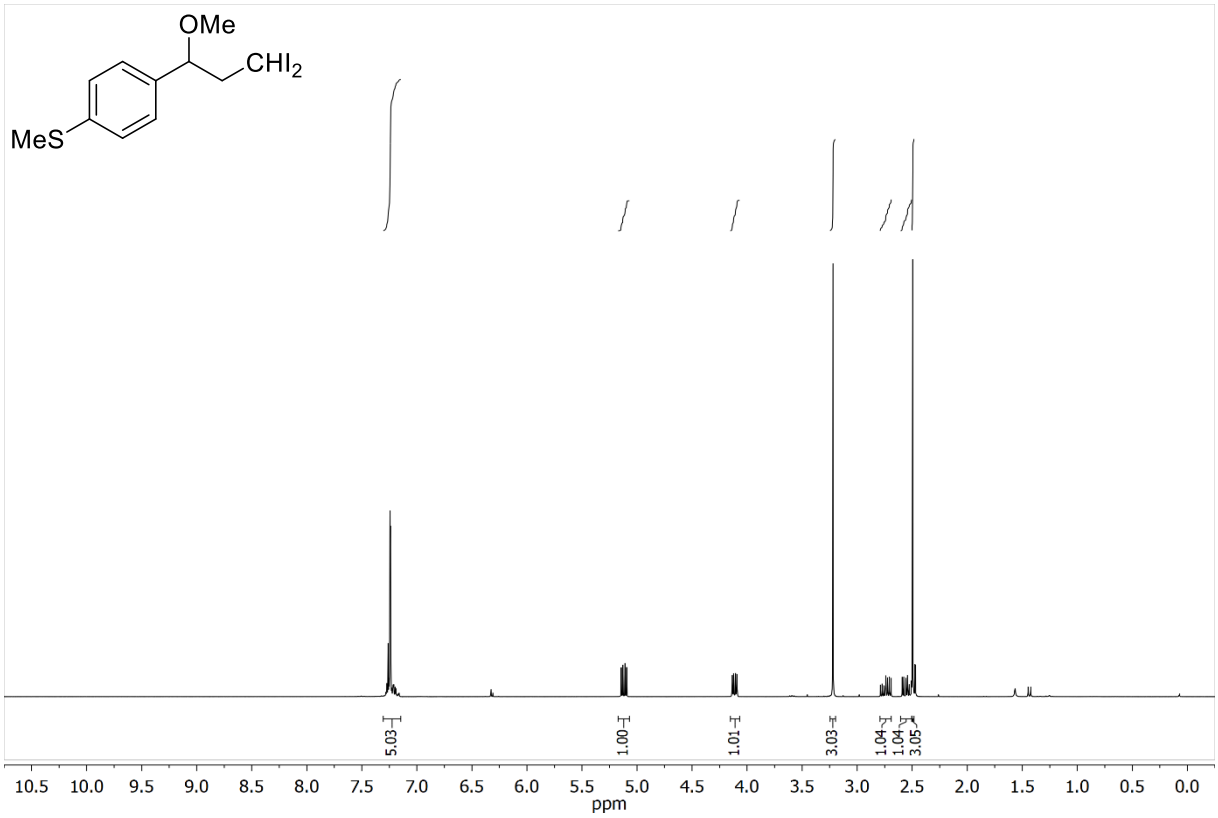
1-(*tert*-butyl)-4-(1,3,3-triiodopropyl)benzene (25e)

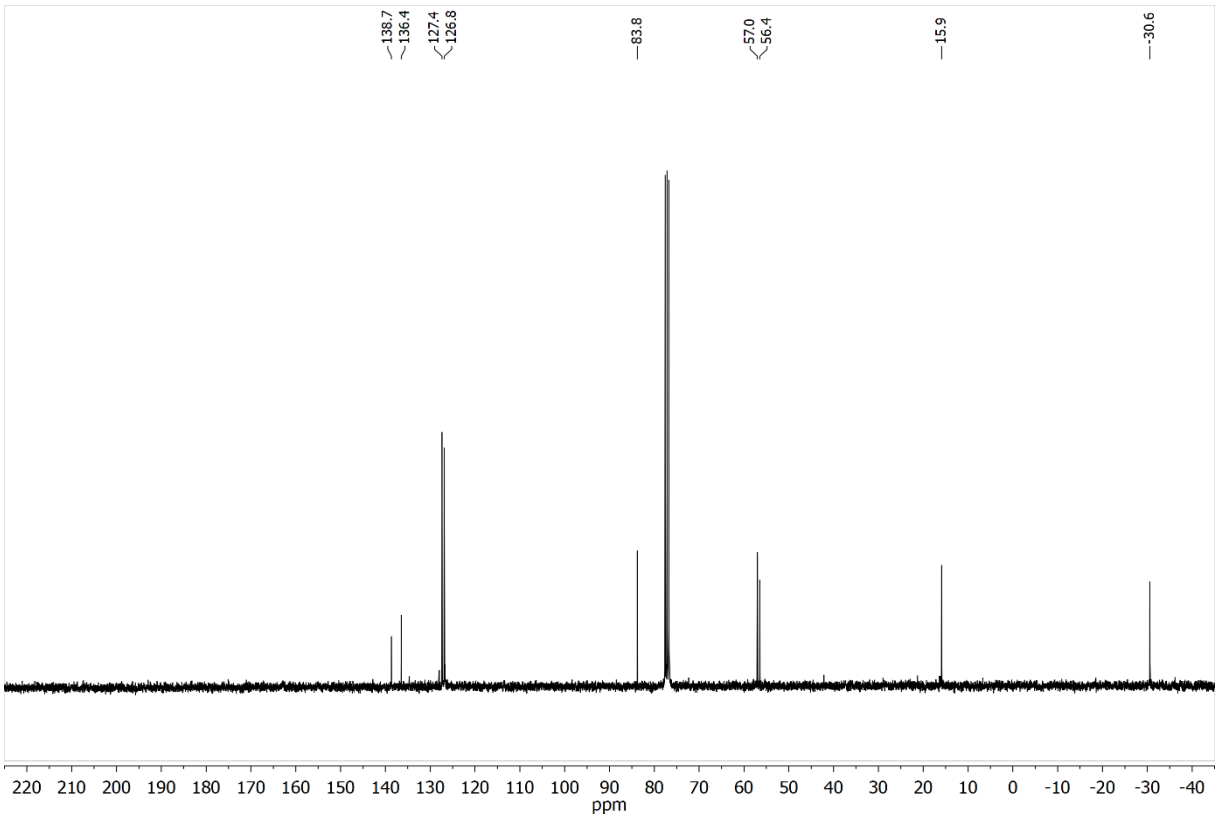




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

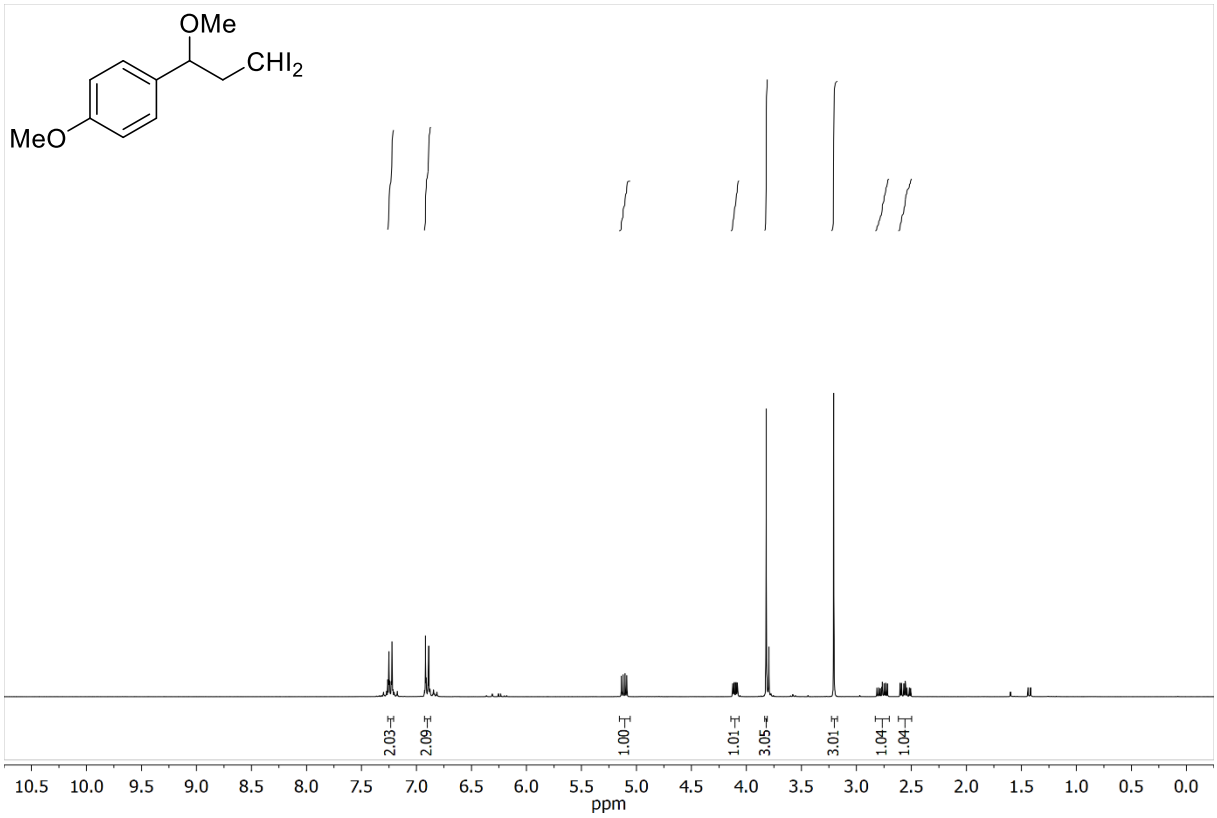
(4-(3,3-diiodo-1-methoxypropyl)phenyl)(methyl)sulfane (OMe-25f)

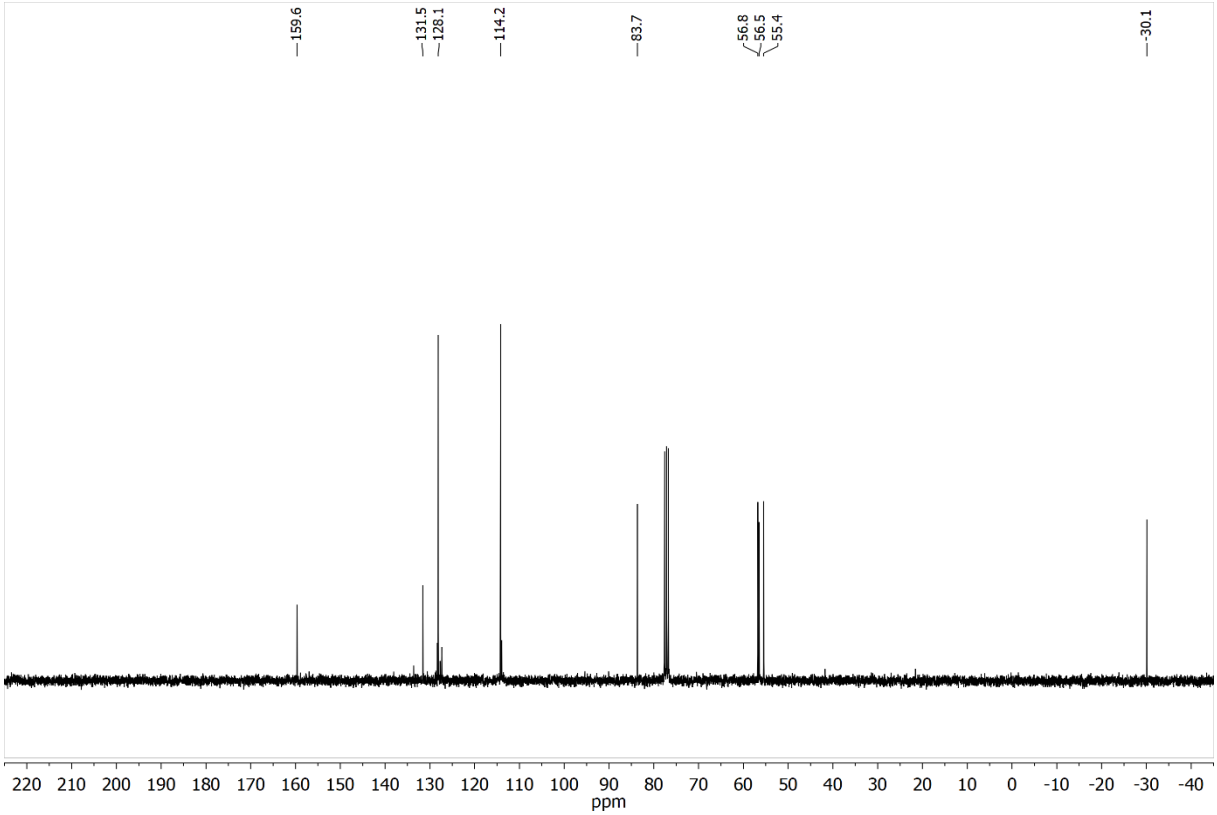




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

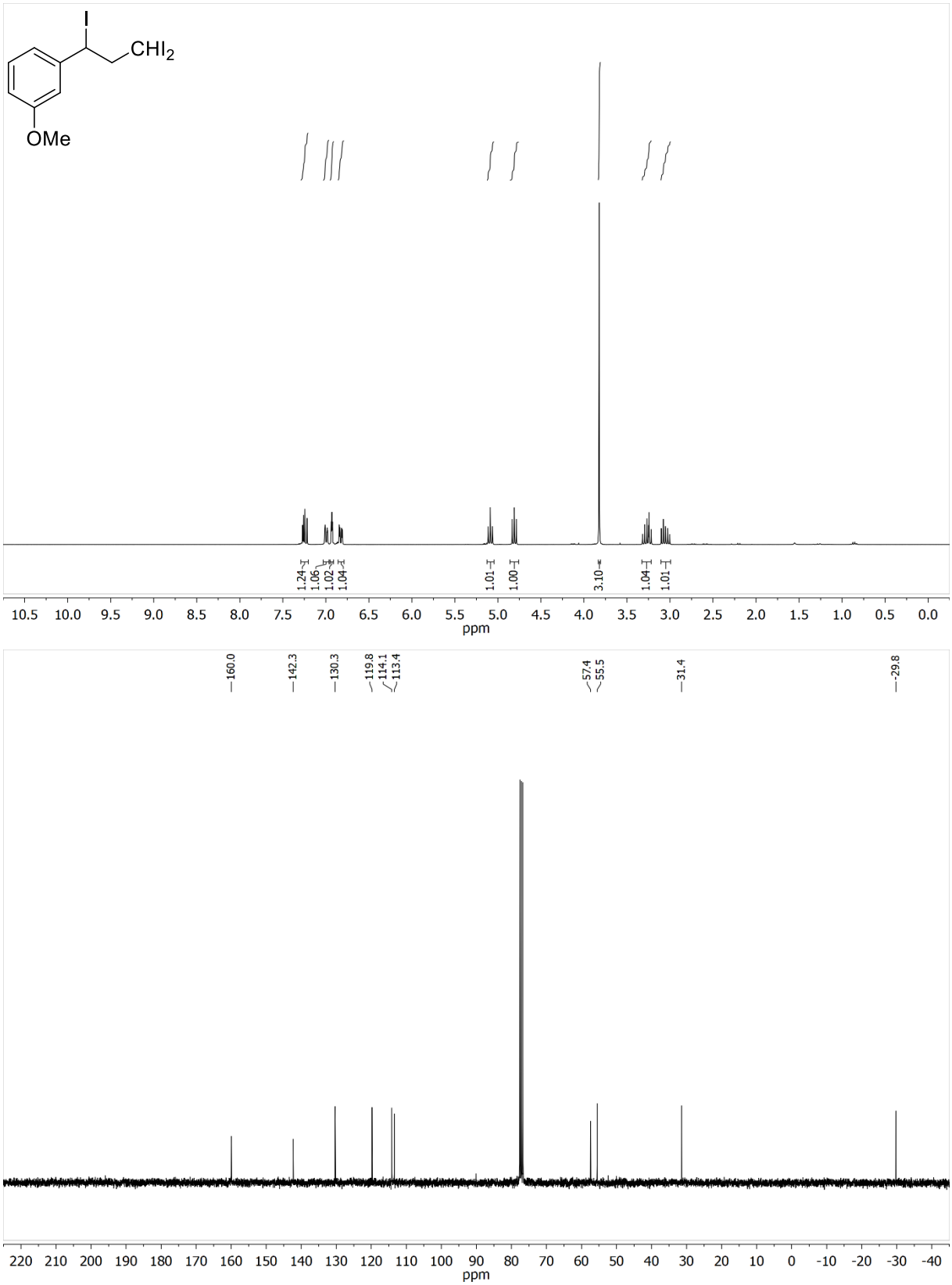
1-(3,3-diiodo-1-methoxypropyl)-4-methoxybenzene (OMe-25g)





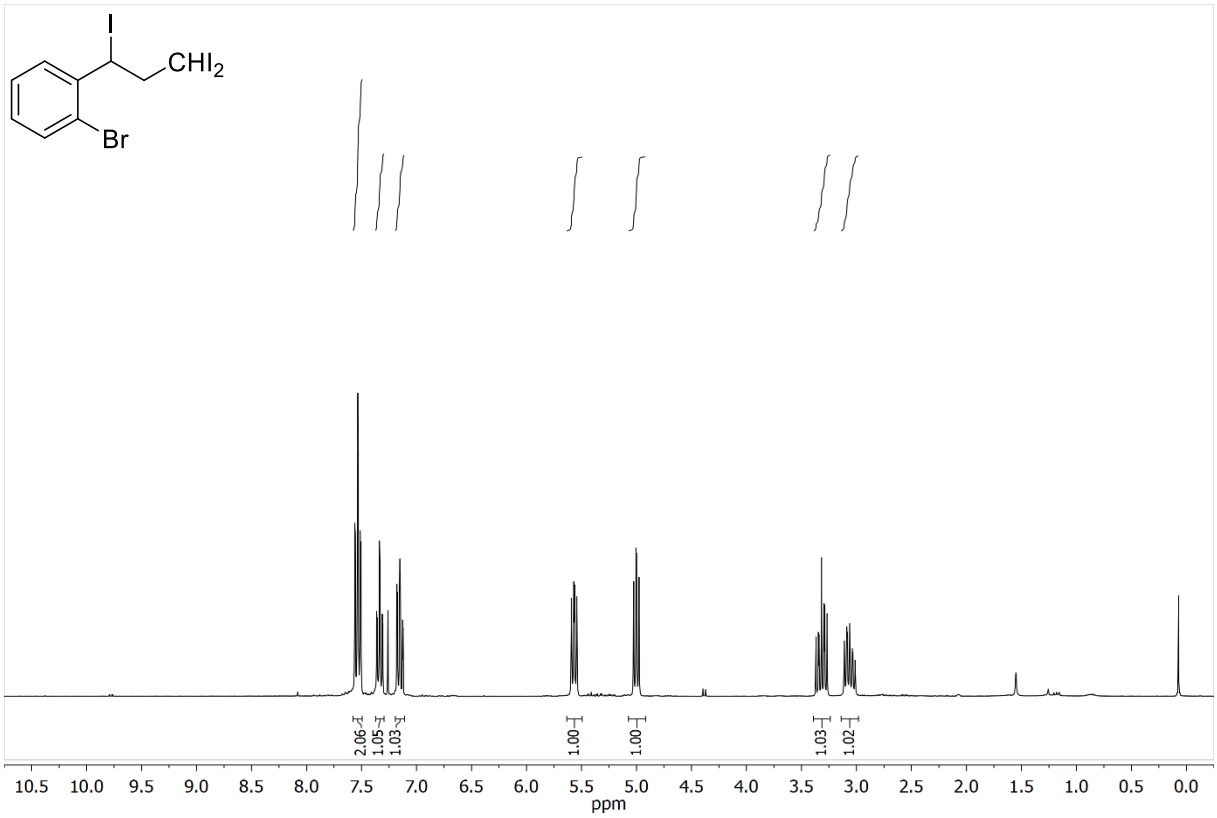
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

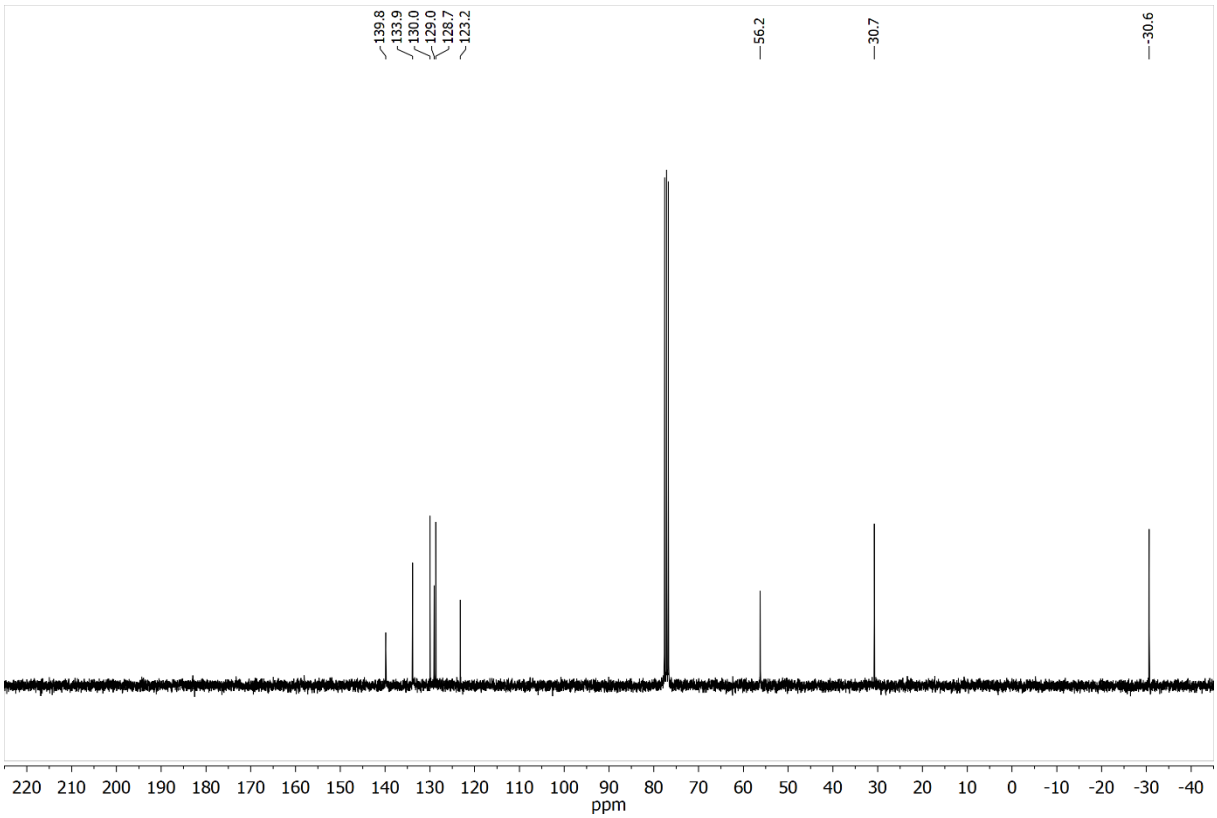
1-methoxy-3-(1,3,3-triiodopropyl)benzene (25h)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

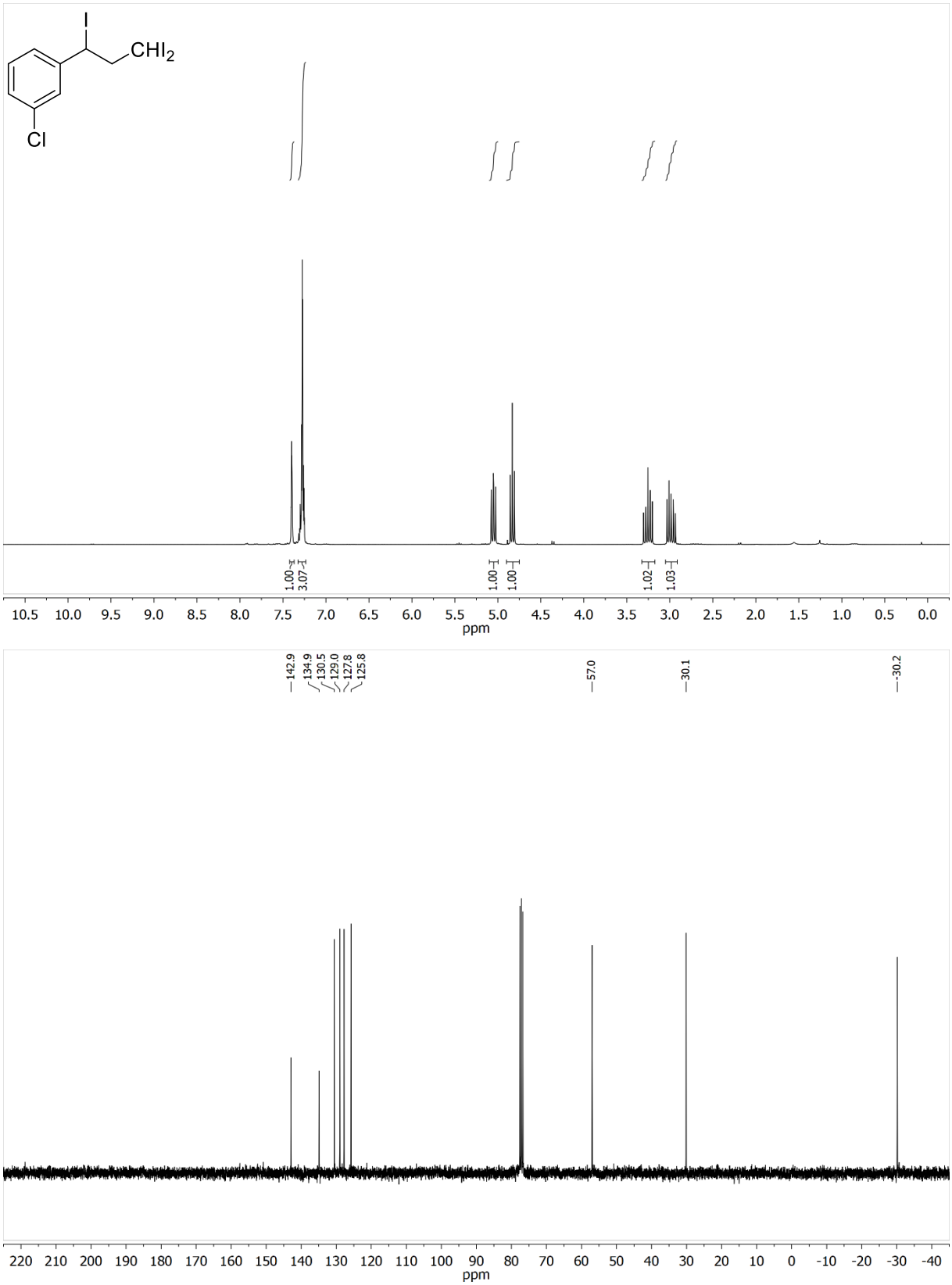
1-bromo-2-(1,3,3-triiodopropyl)benzene (25l)





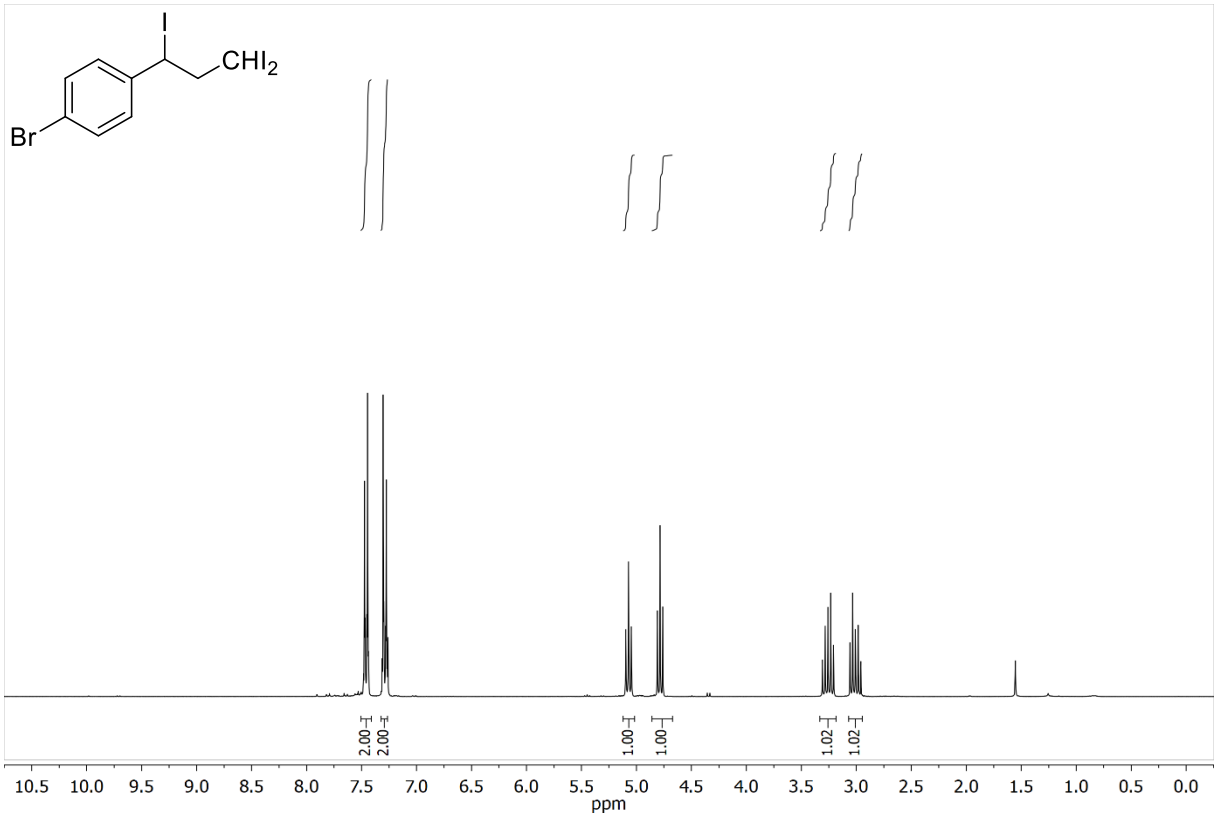
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

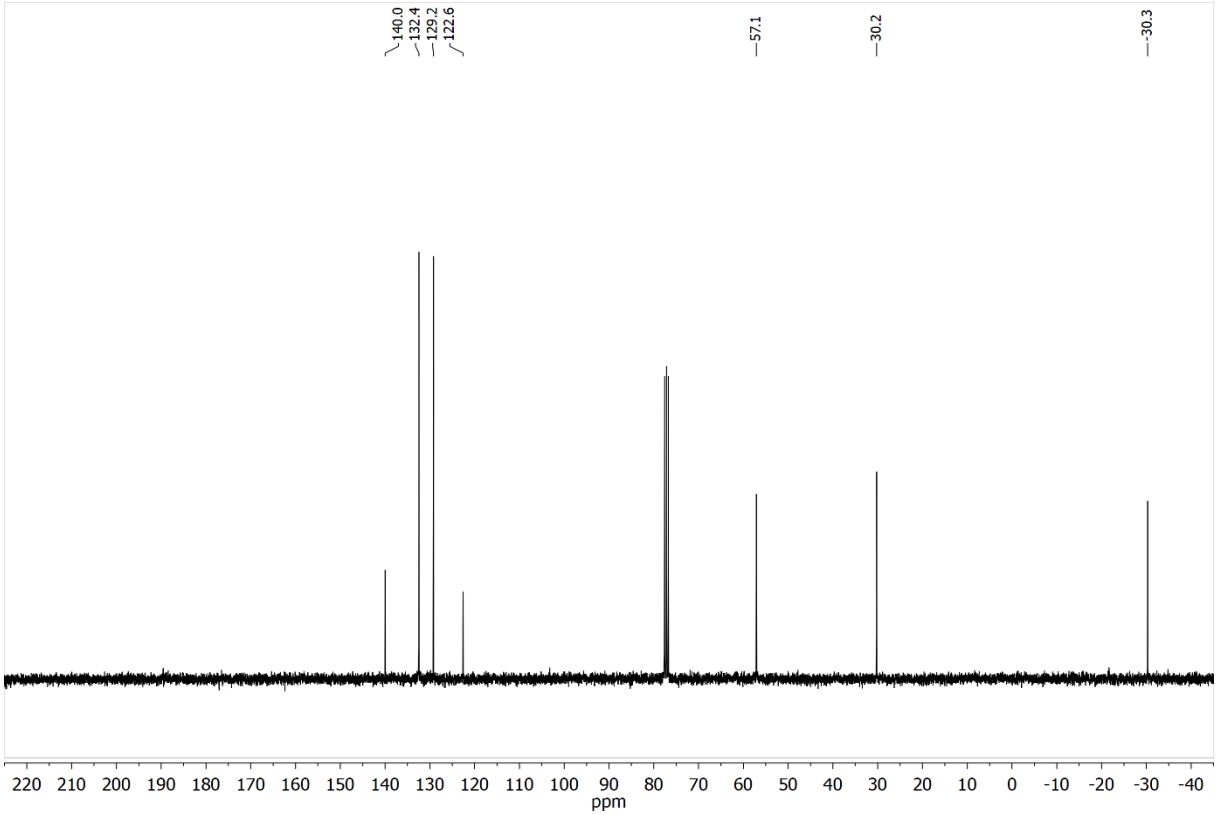
1-chloro-3-(1,3,3-triiodopropyl)benzene (25m)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

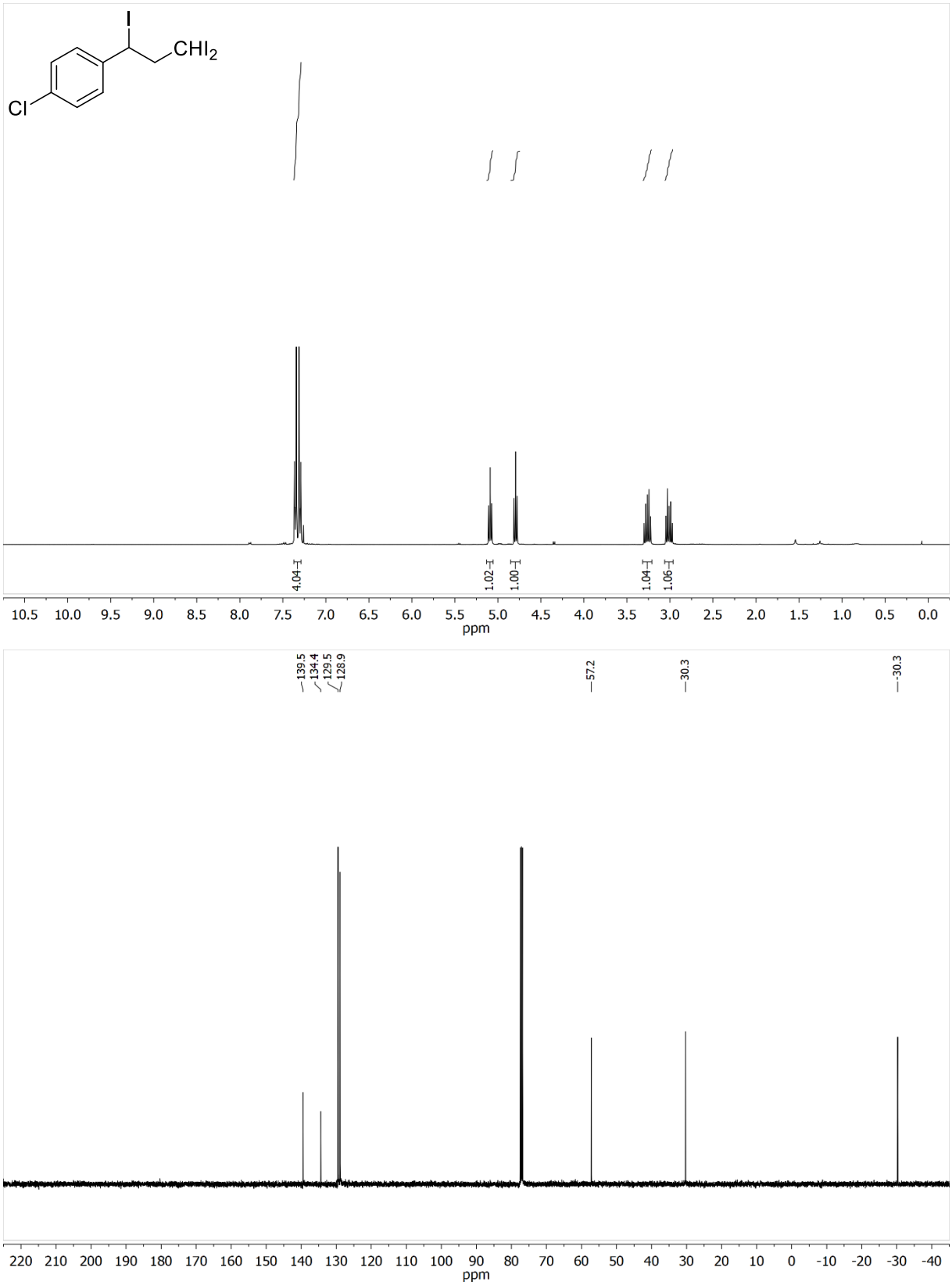
1-bromo-4-(1,3,3-triiodopropyl)benzene (25n)





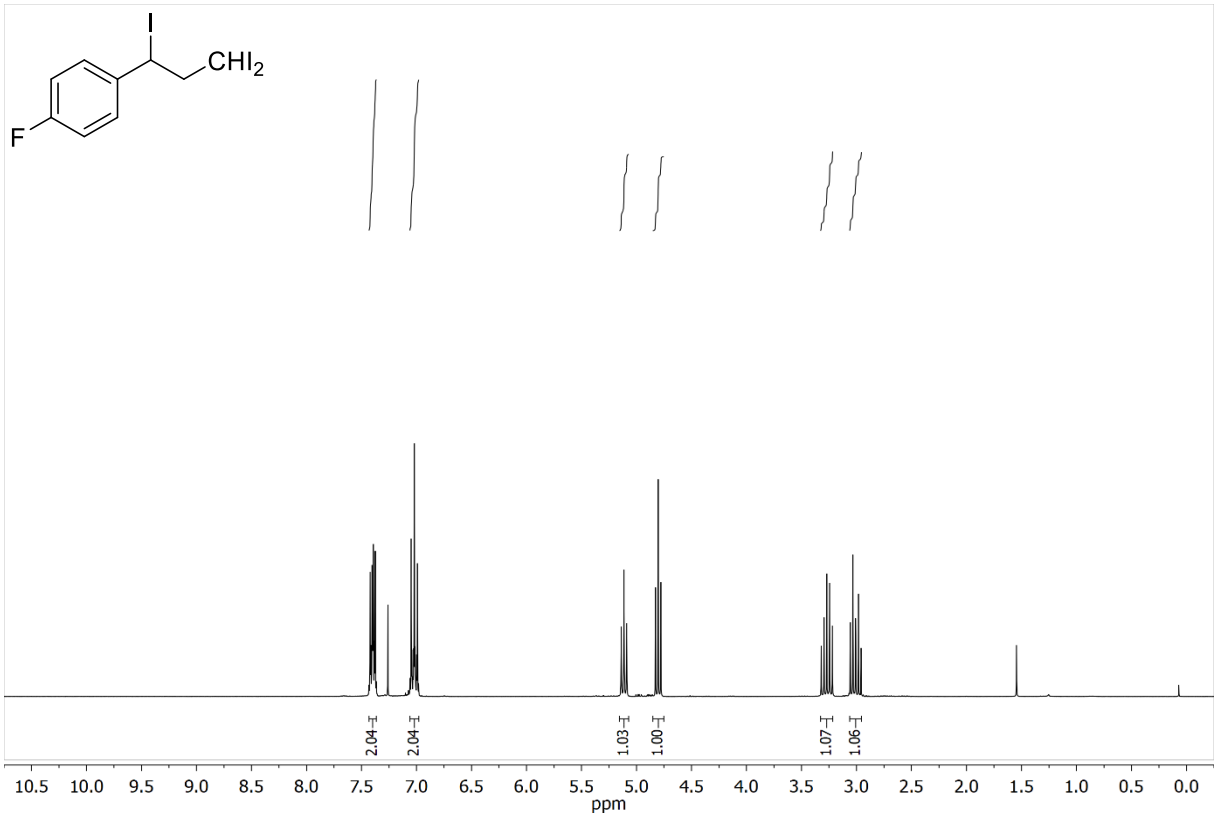
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

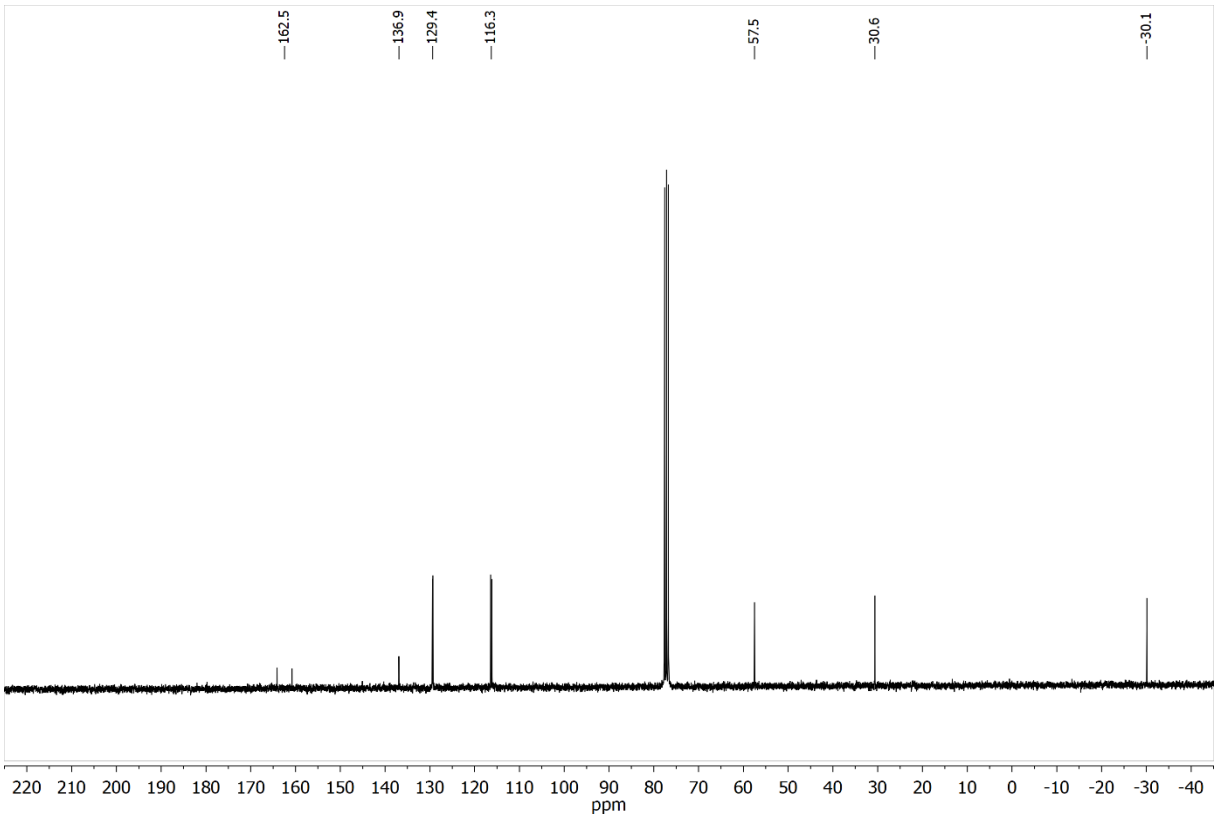
1-chloro-4-(1,3,3-triiodopropyl)benzene (25o)



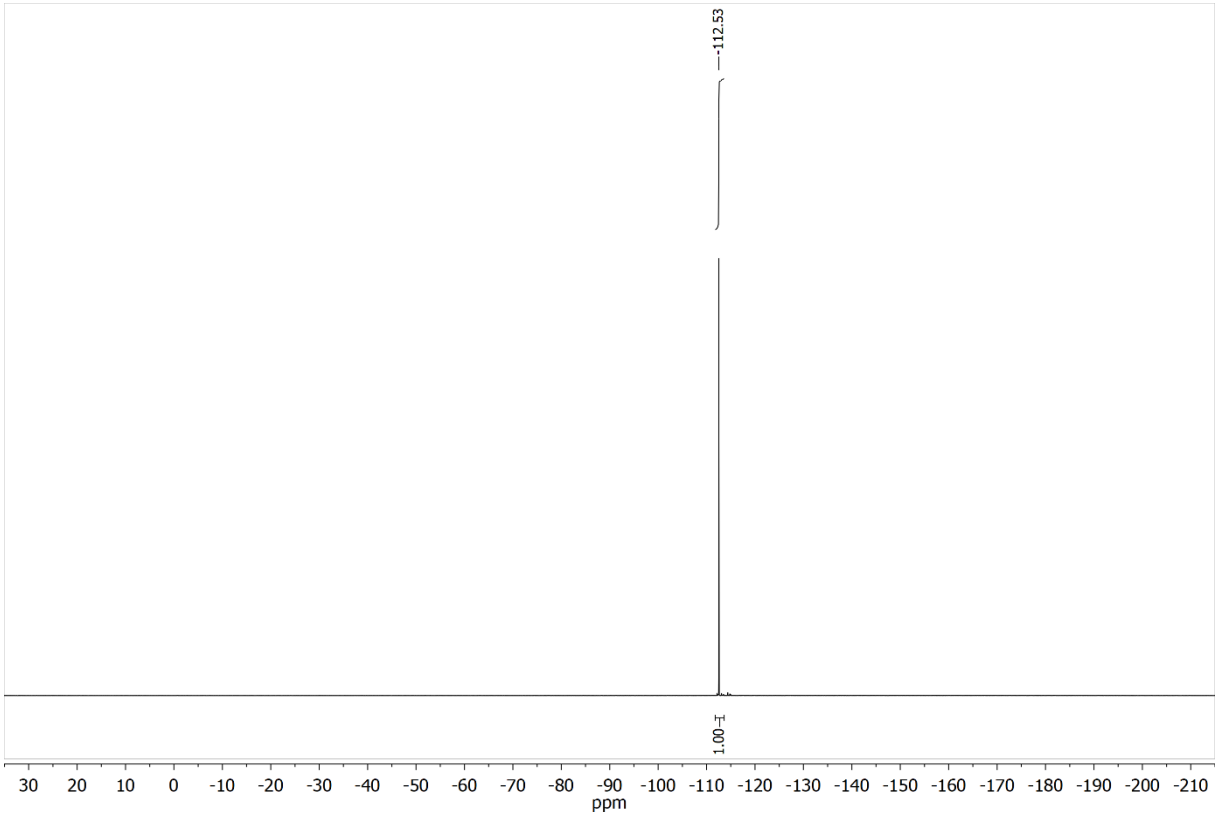
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

1-fluoro-4-(1,3,3-triiodopropyl)benzene (25p)



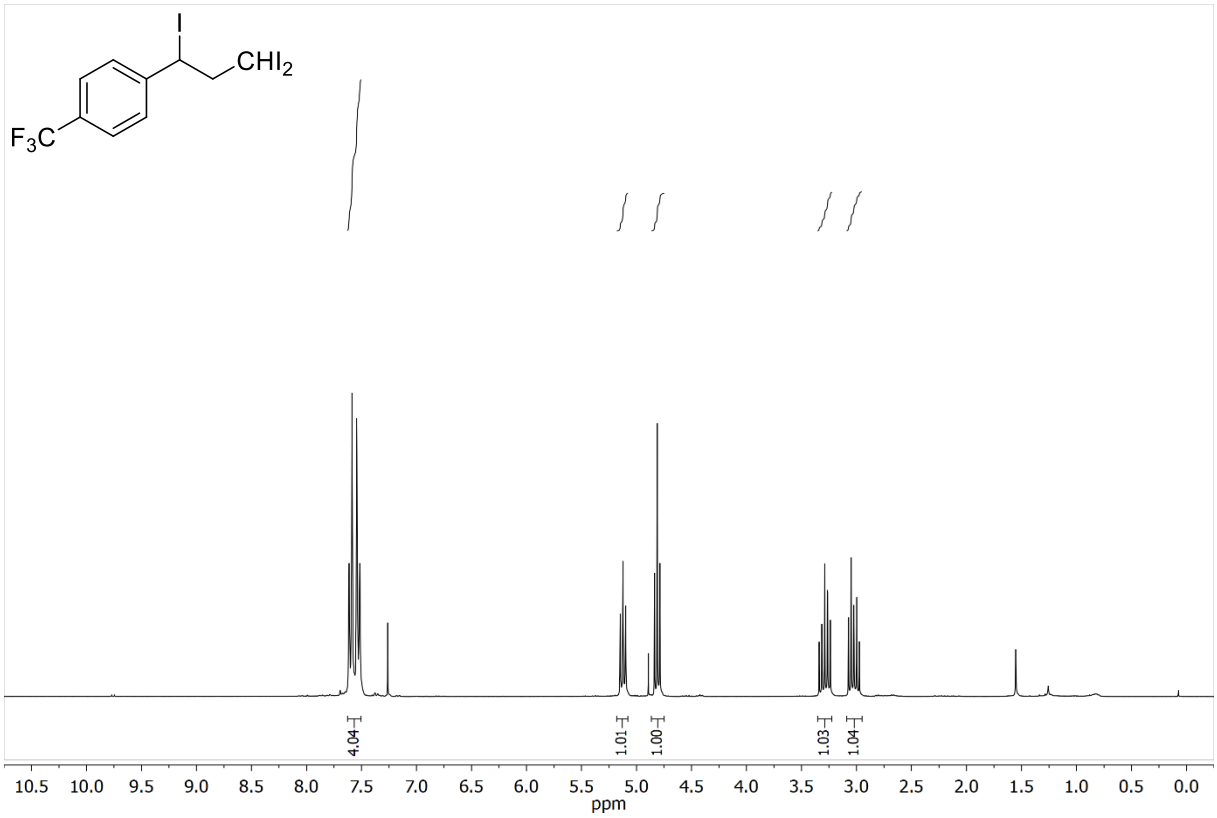


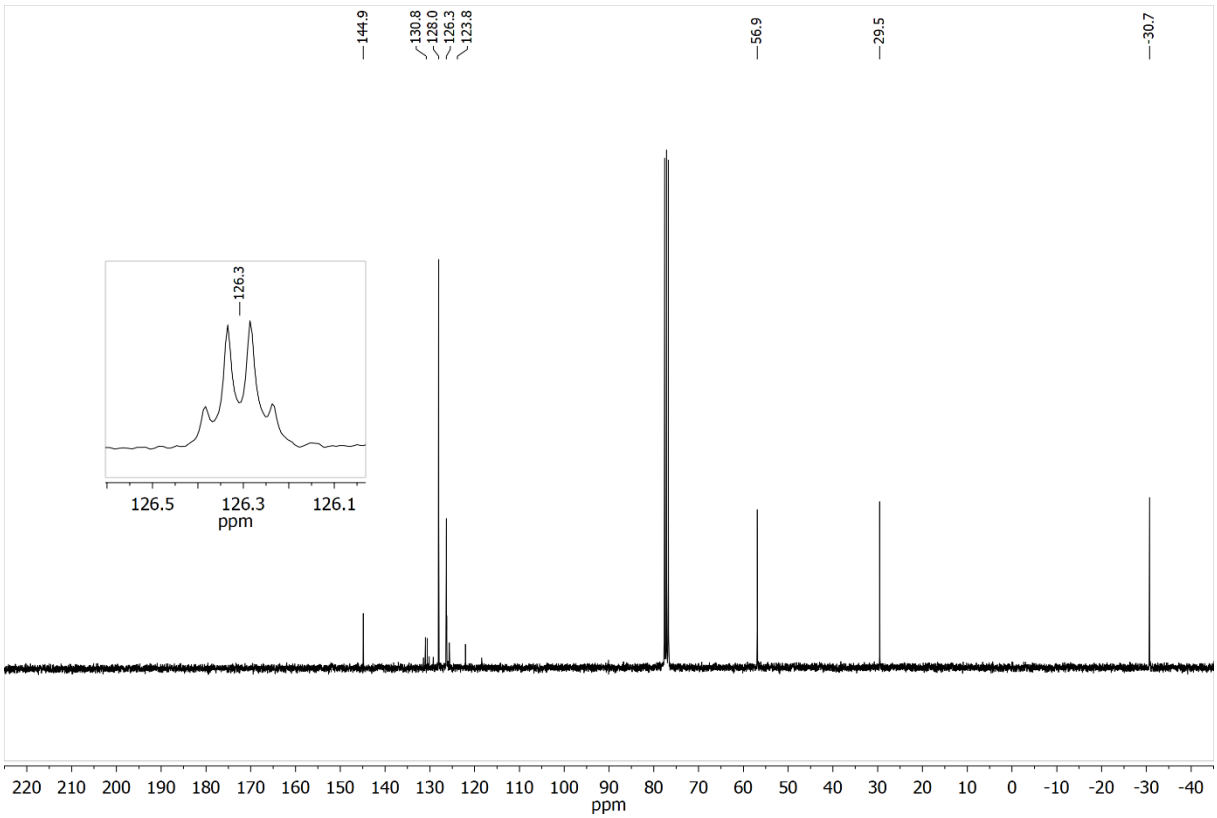
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



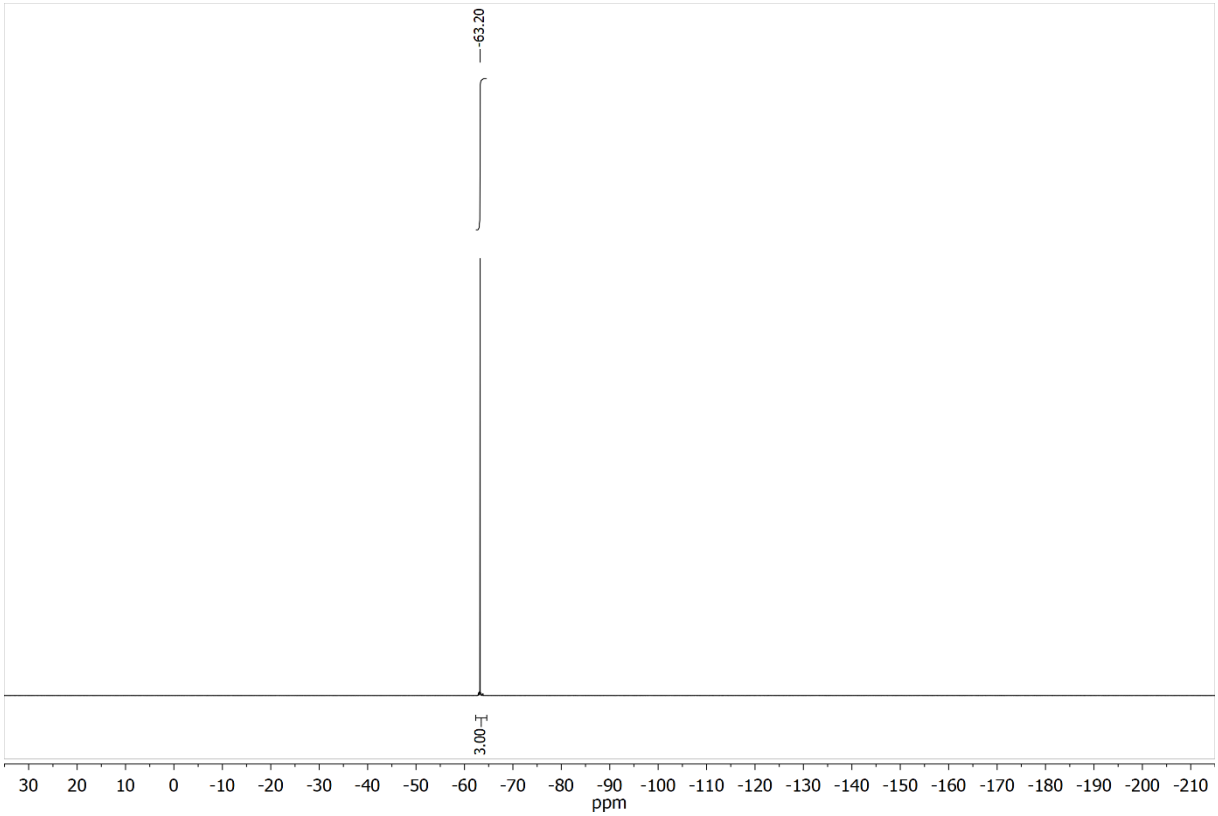
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1-(trifluoromethyl)-4-(1,3,3-triiodopropyl)benzene (25q)



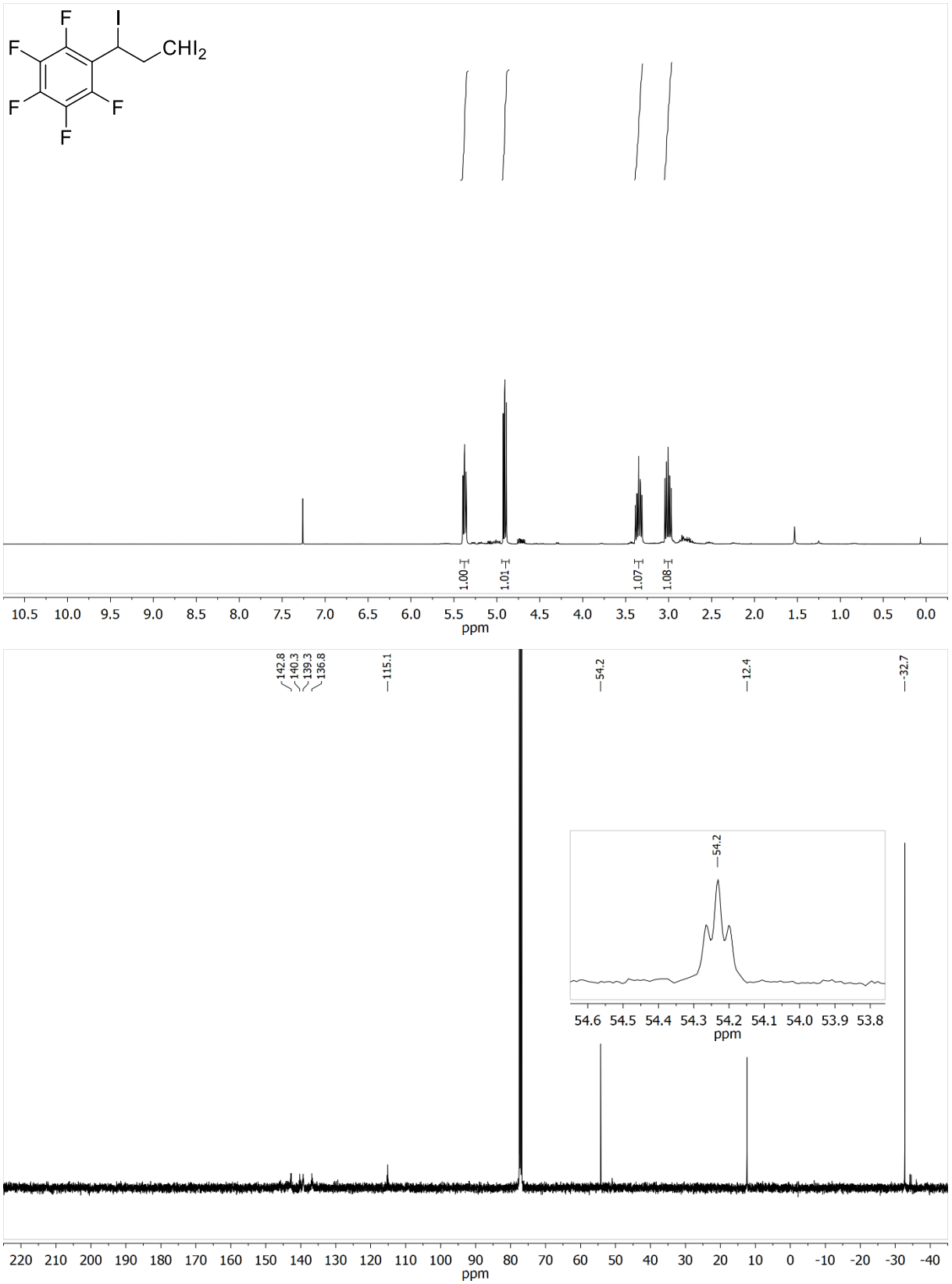


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

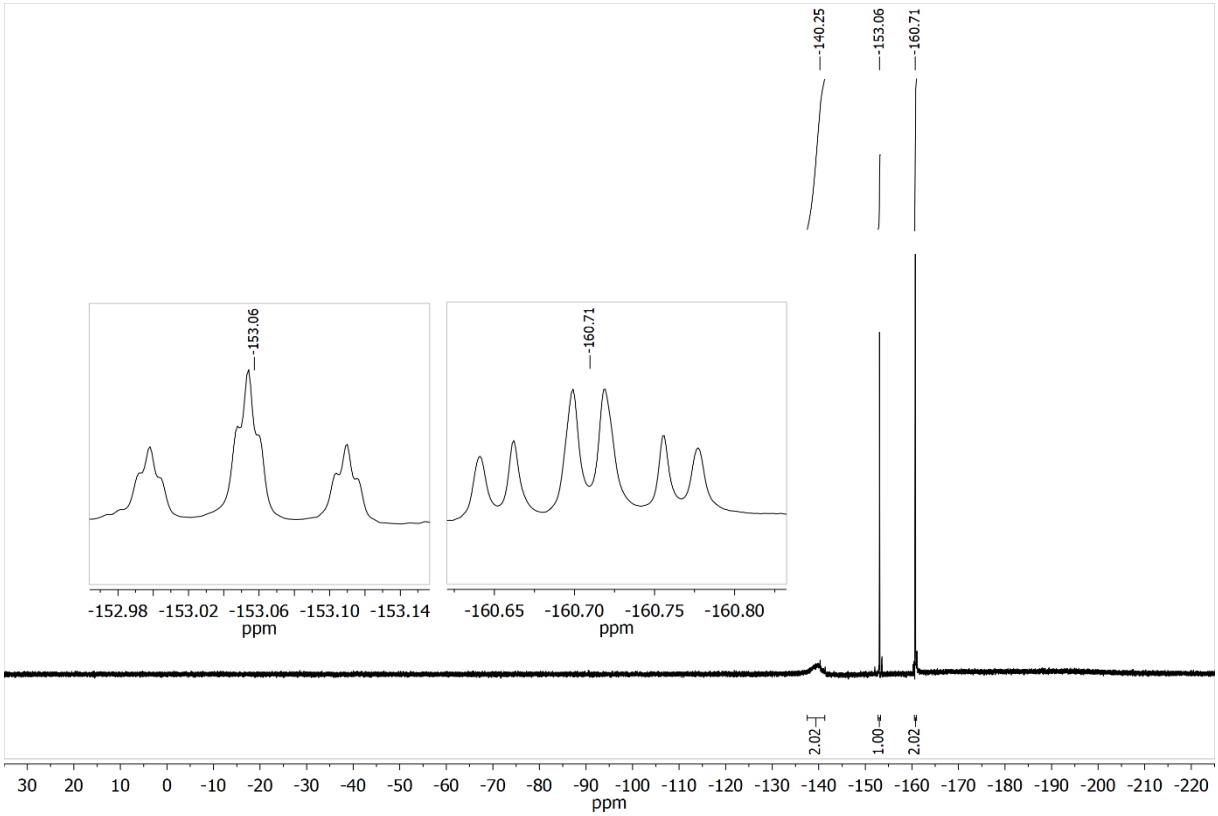


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

1,2,3,4,5-pentafluoro-6-(1,3,3-triiodopropyl)benzene (25r)

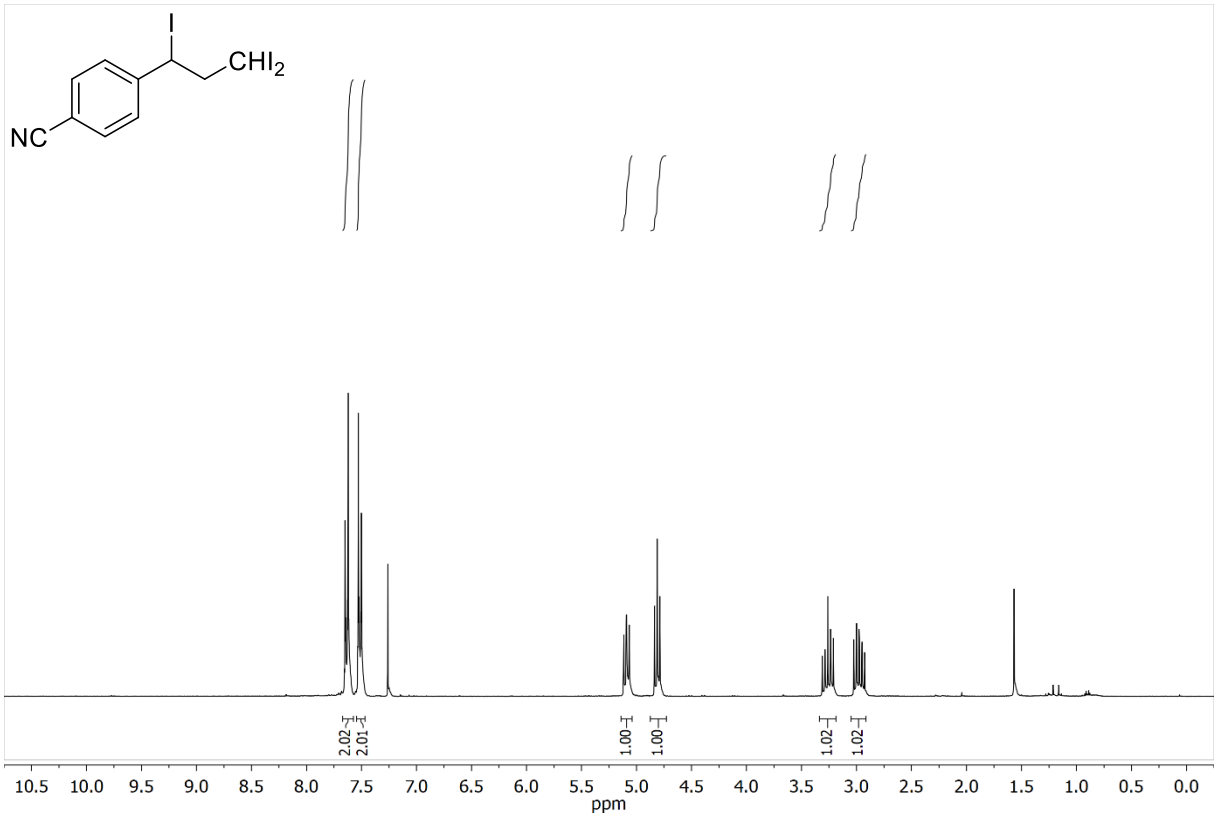


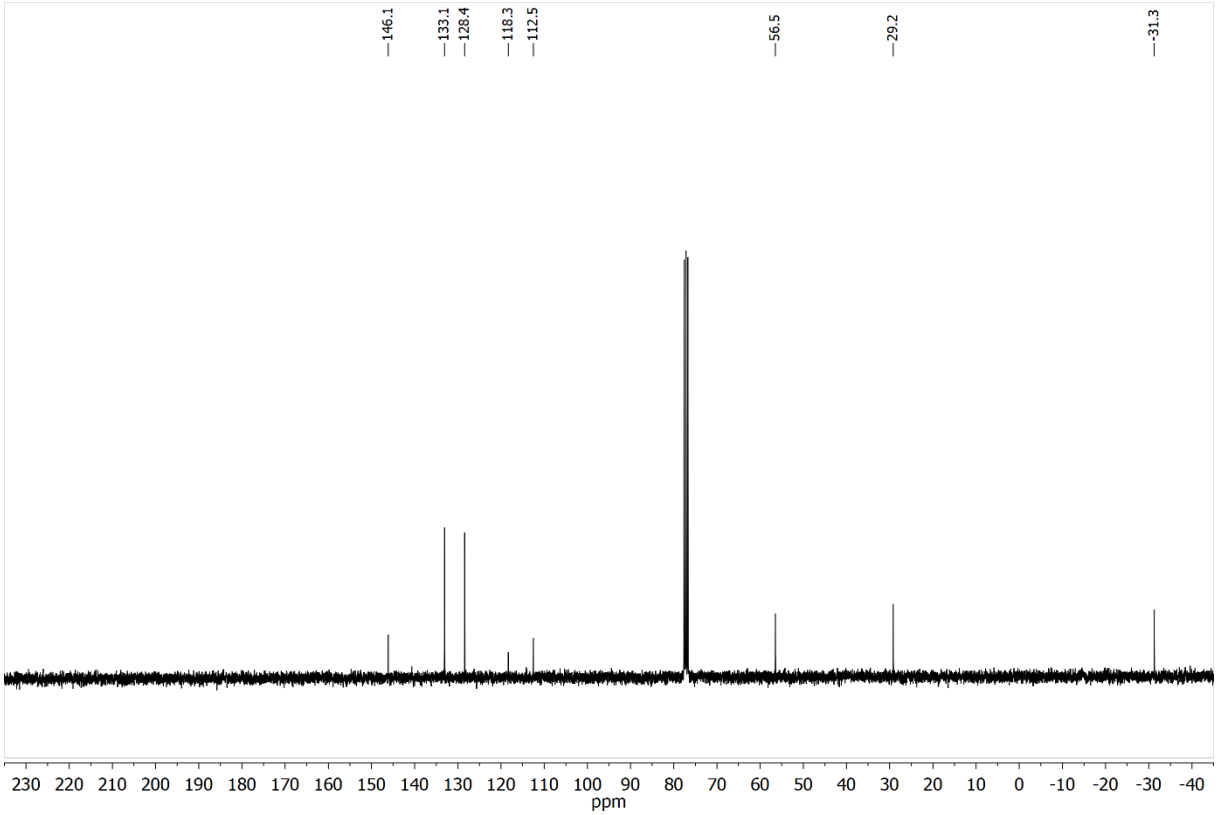
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

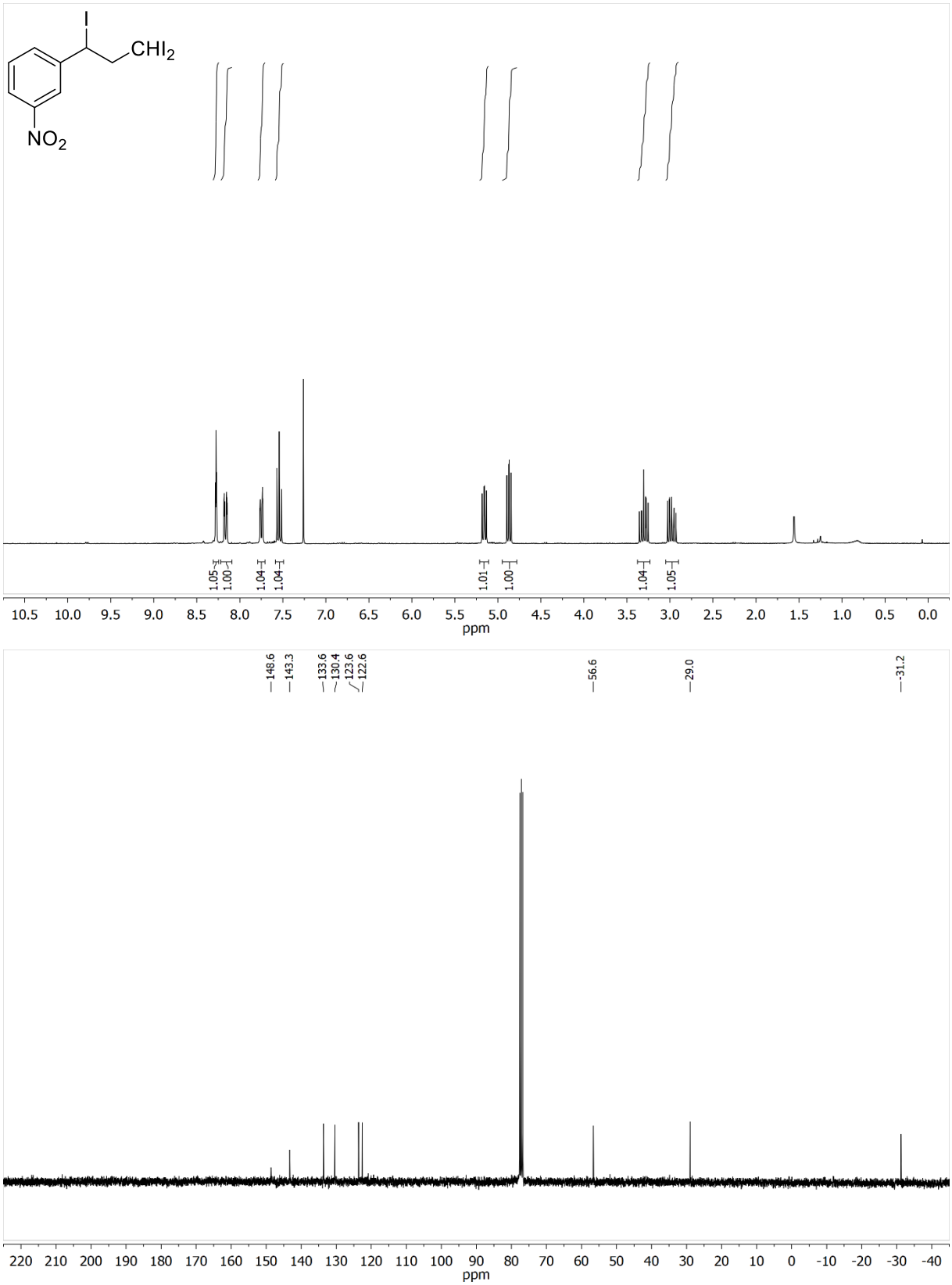
4-(1,3,3-triiodopropyl)benzonitrile (25s)





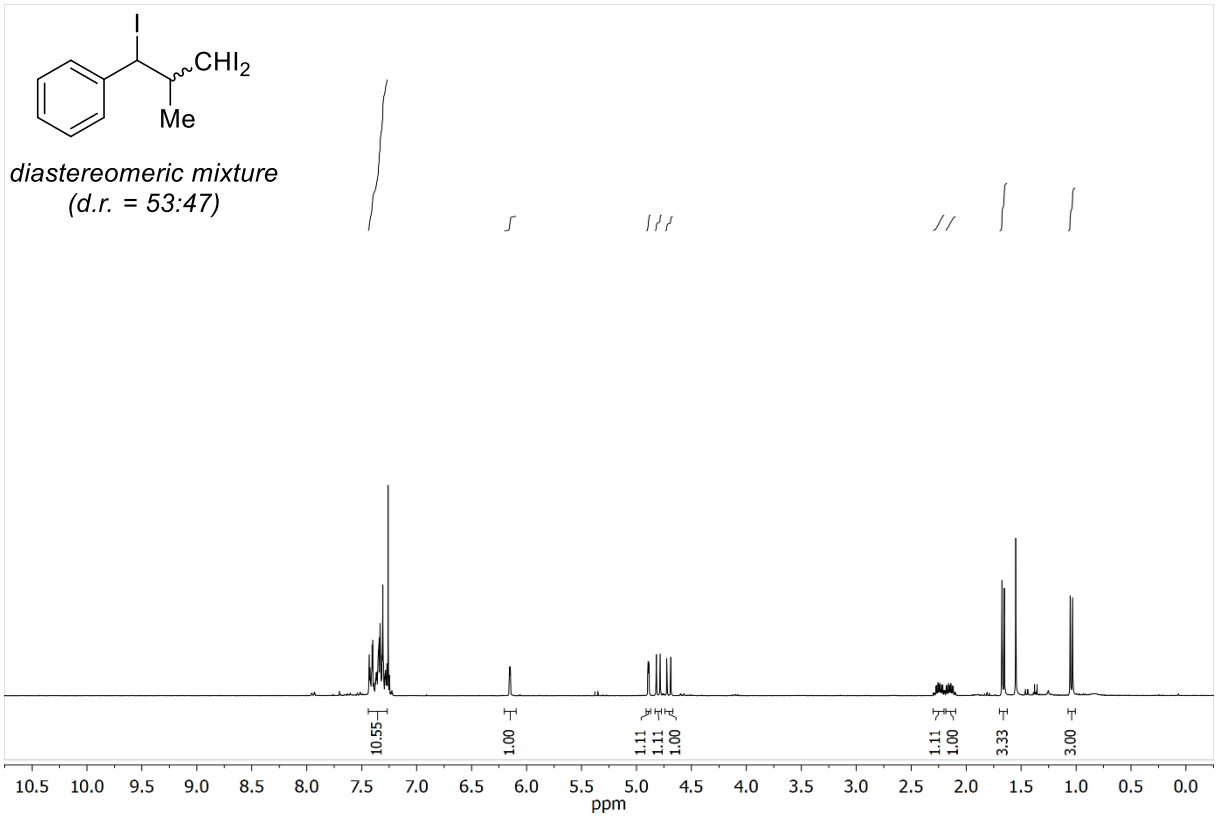
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

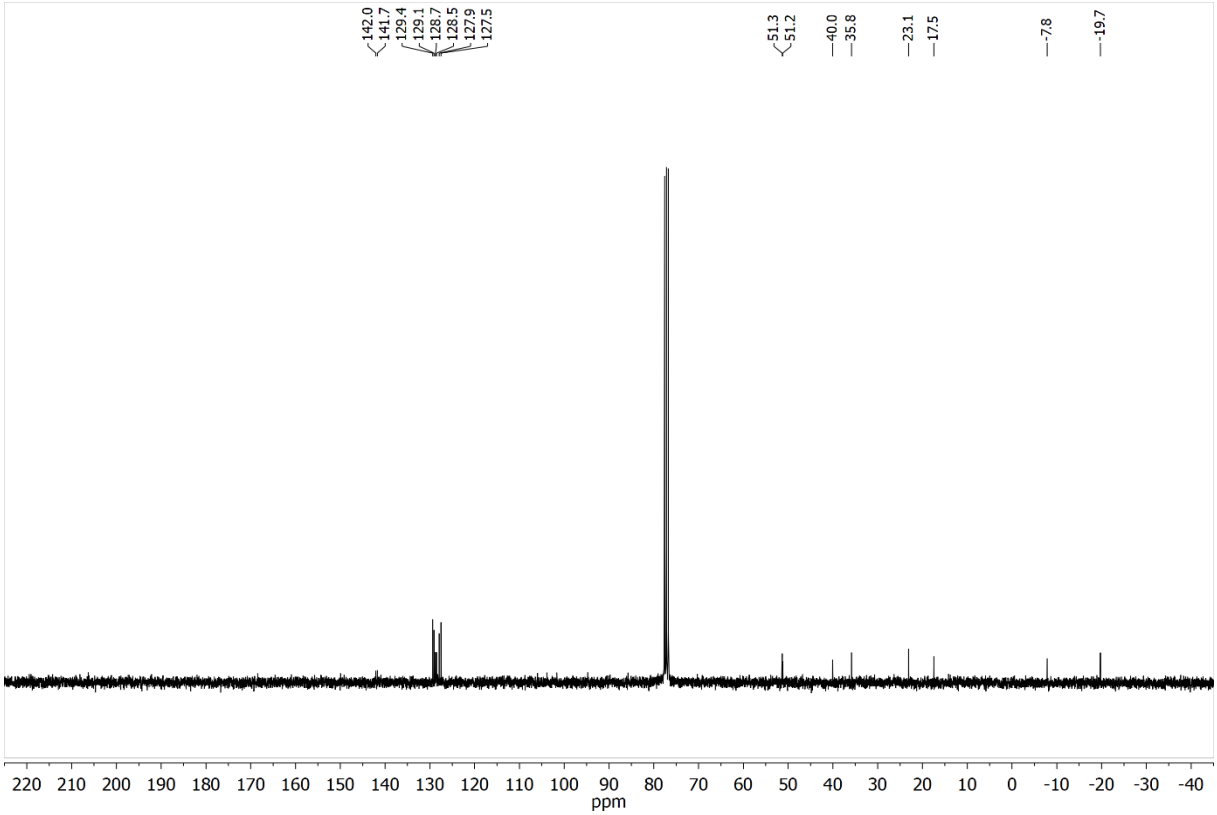
1-nitro-3-(1,3,3-triiodopropyl)benzene (25t)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

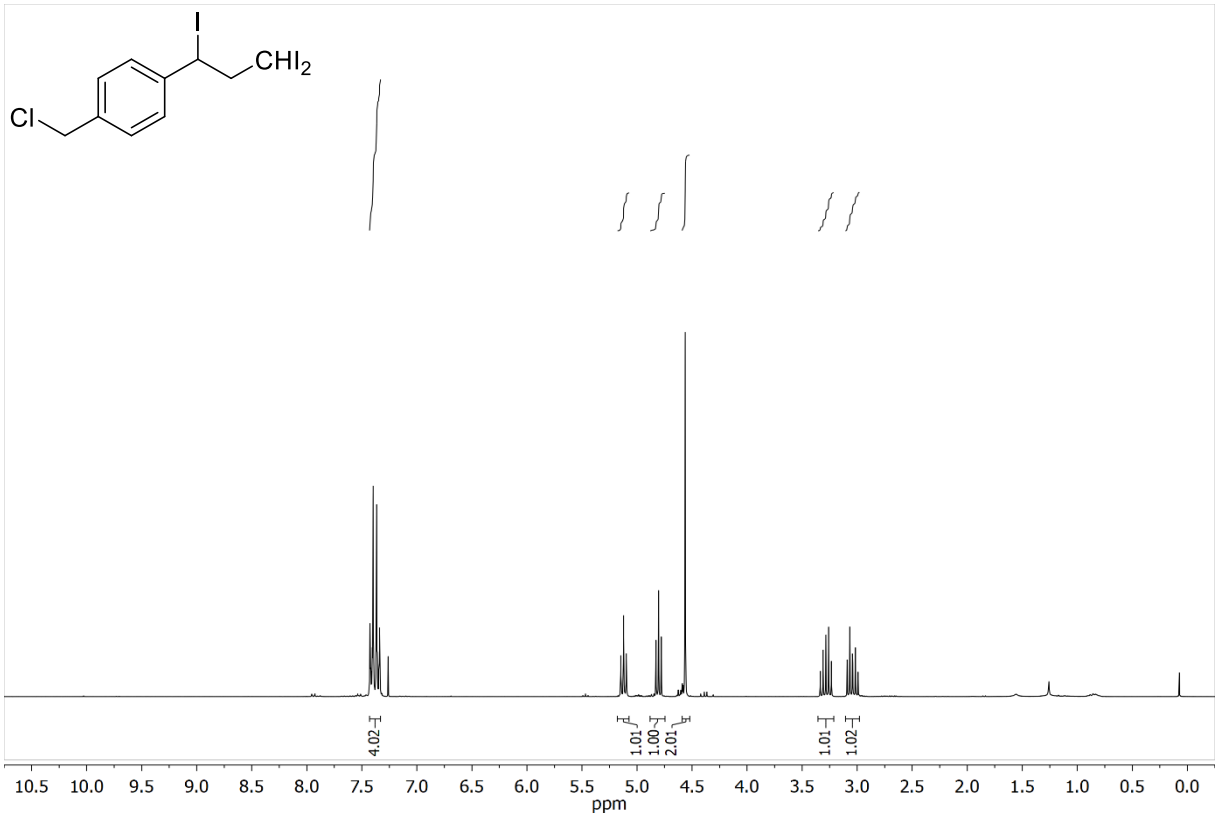
(1,3,3-triiodo-2-methylpropyl)benzene (d.r. = 53:47) (25x)

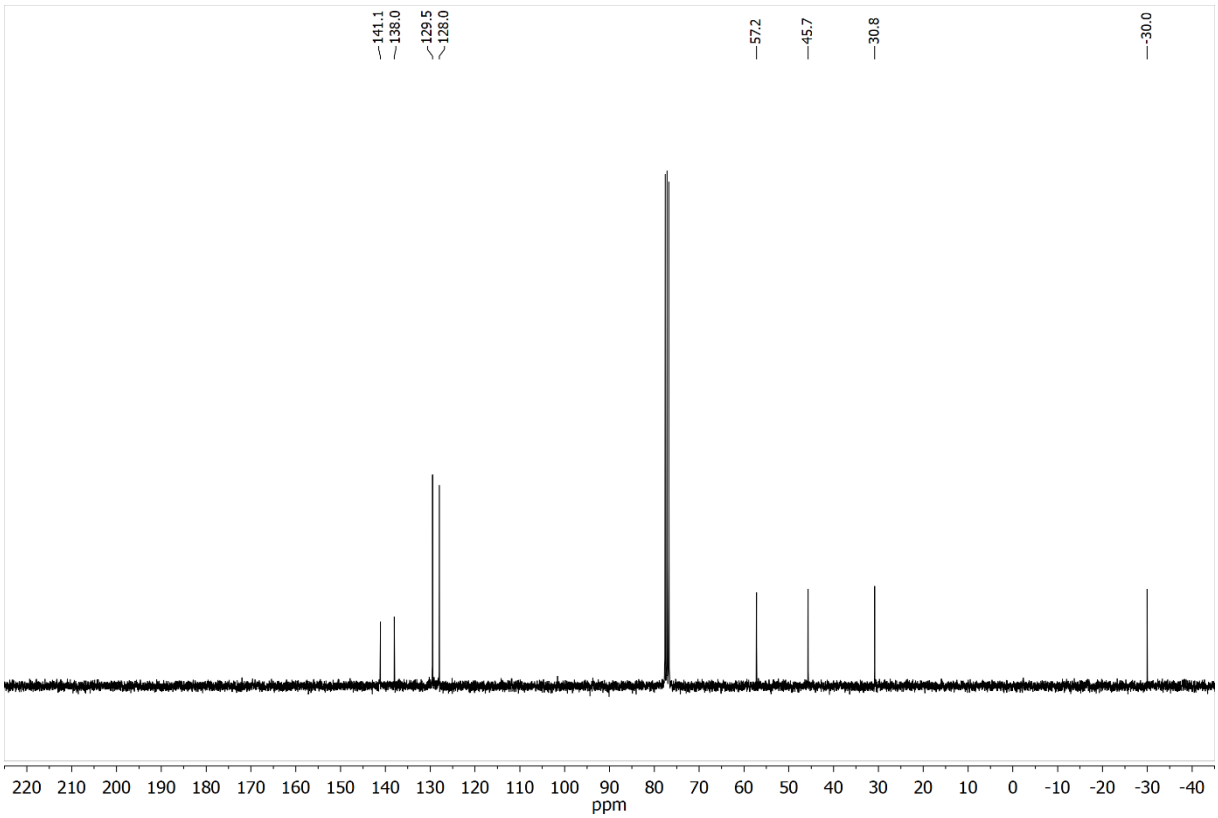




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

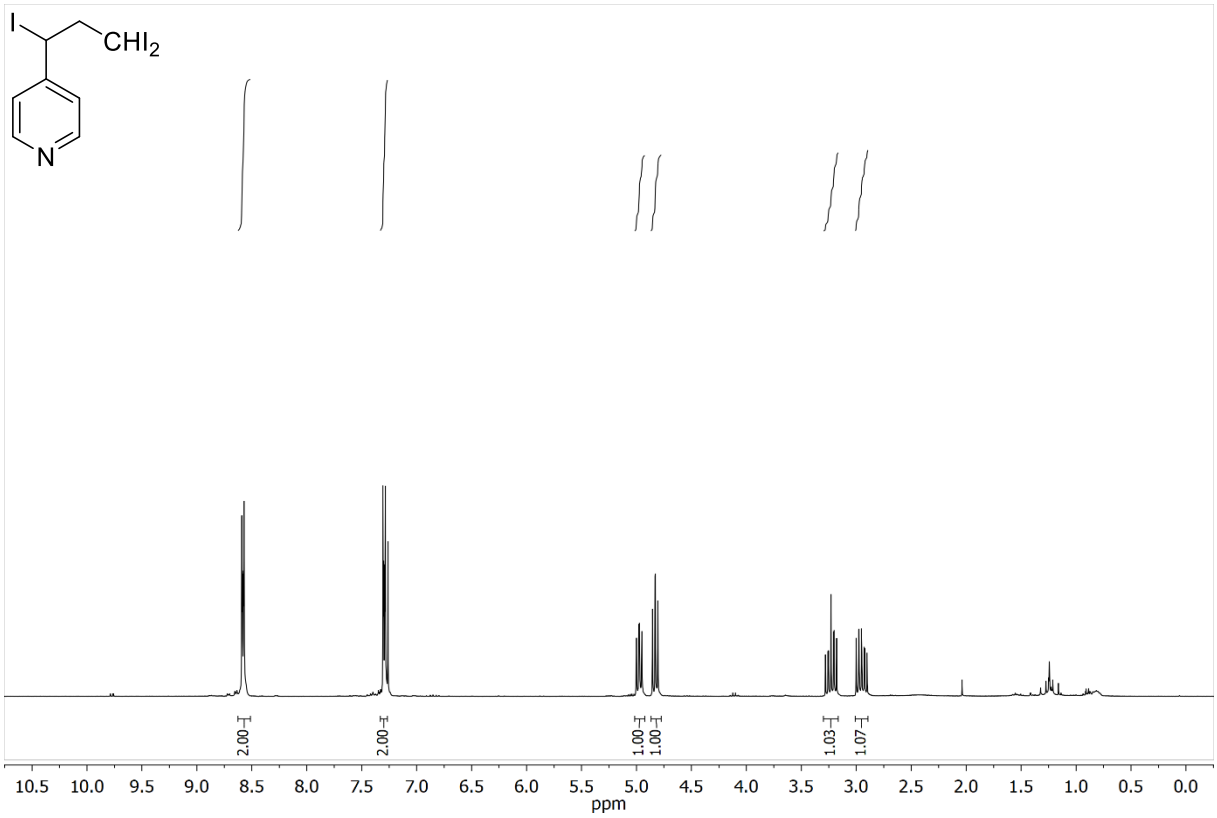
1-(chloromethyl)-4-(1,3,3-triiodopropyl)benzene (25ac)

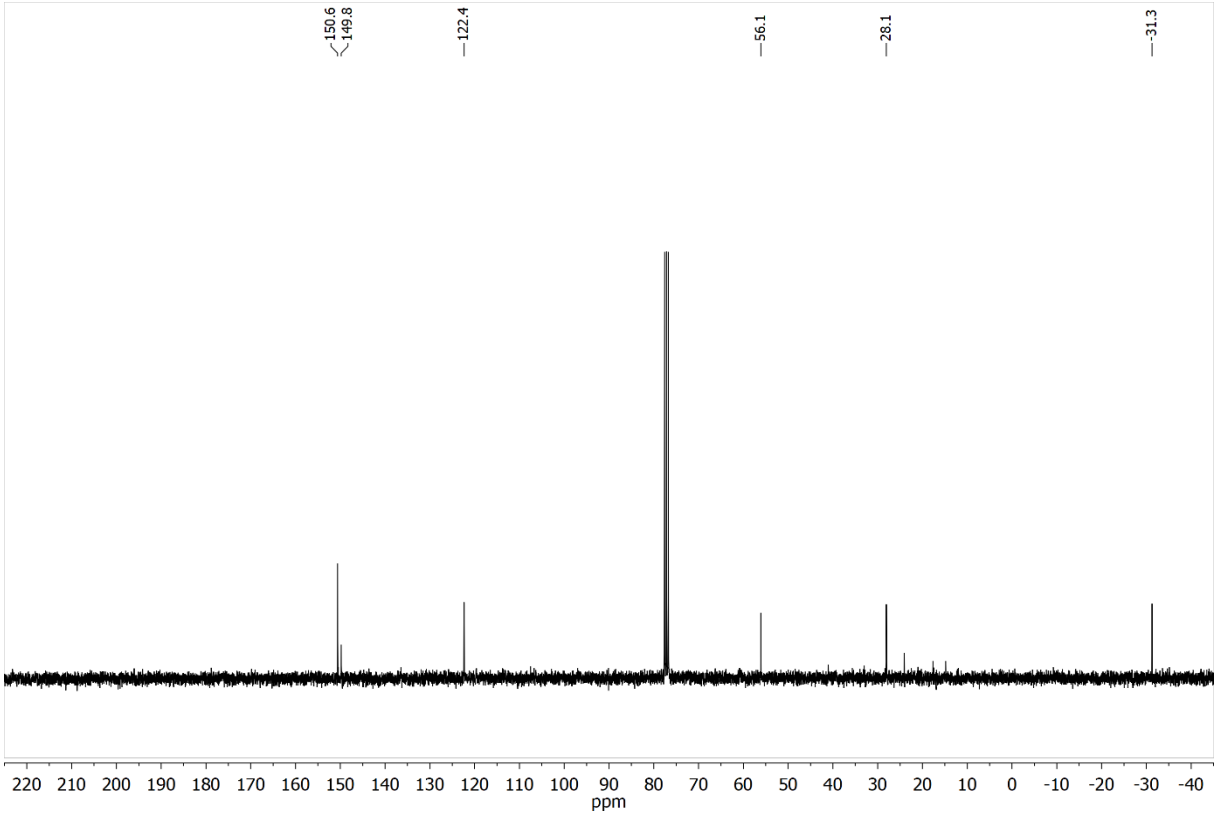




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

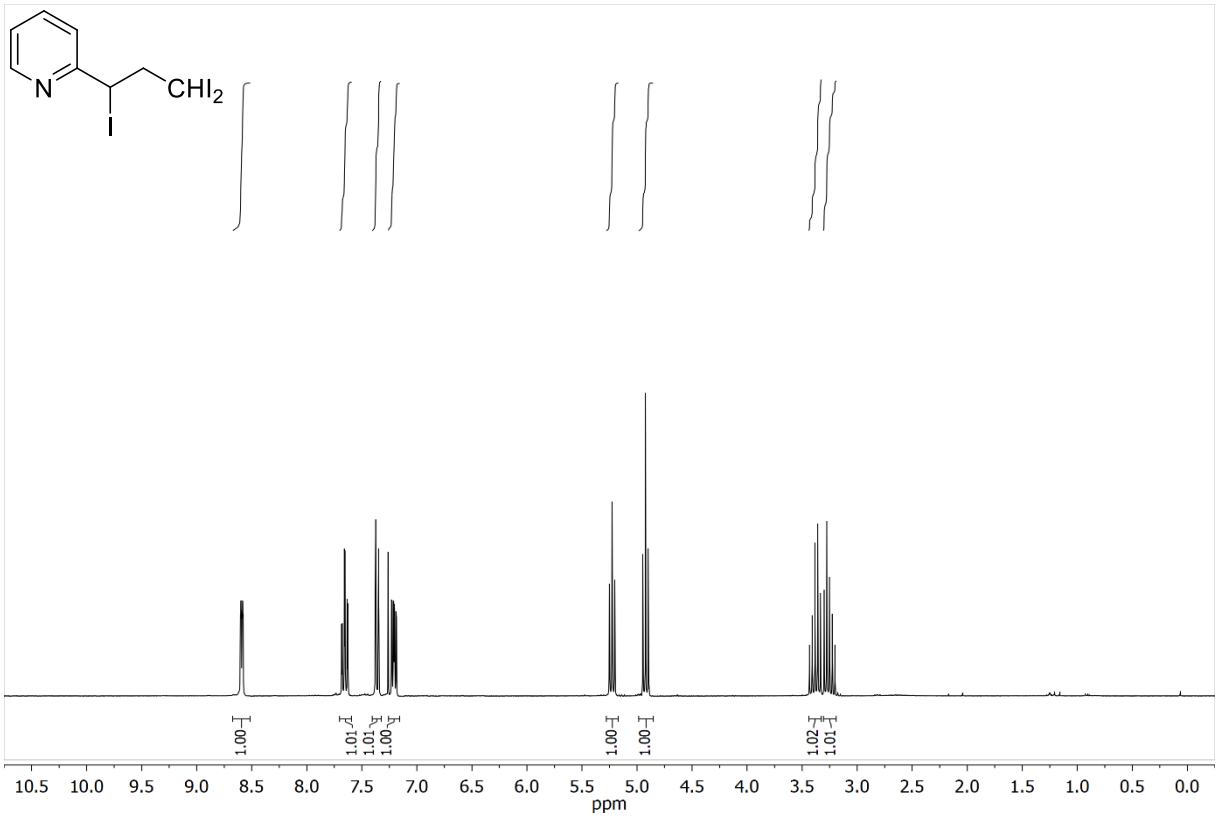
4-(1,3,3-triiodopropyl)pyridine (25ad)

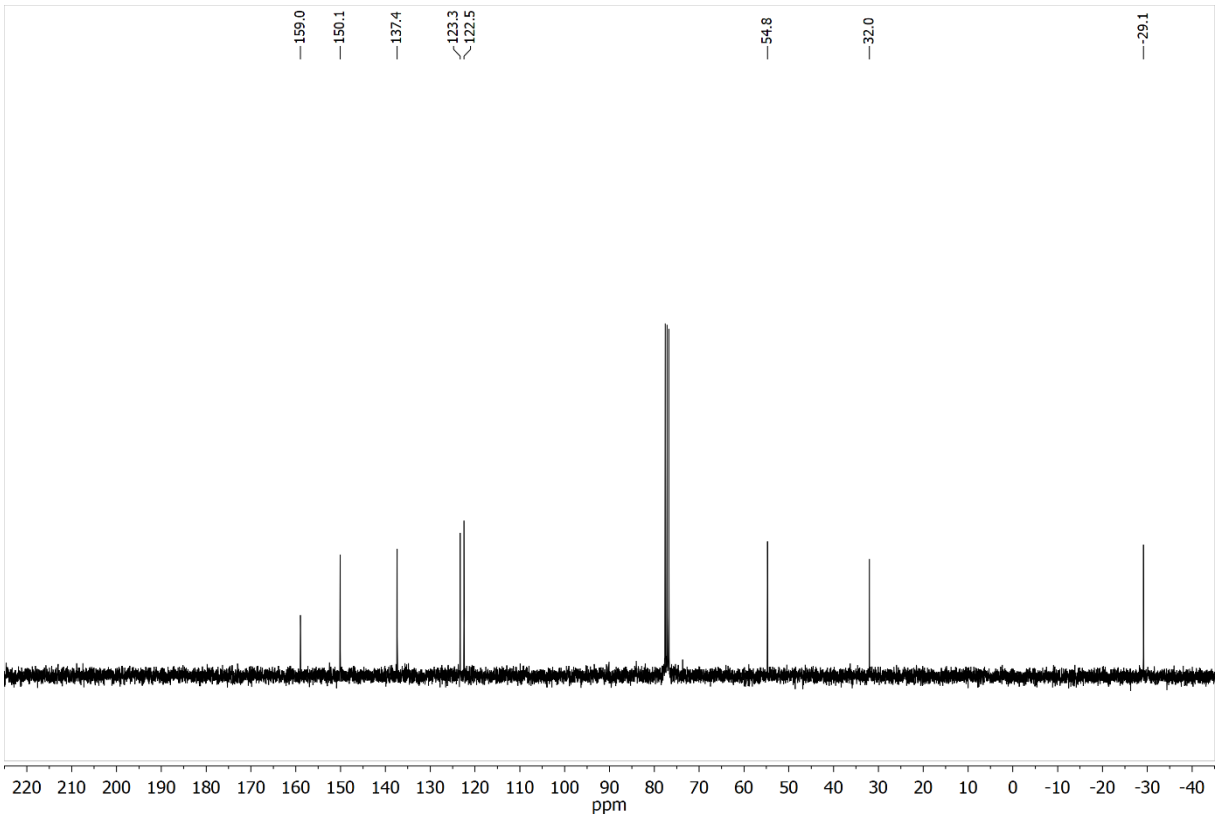




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

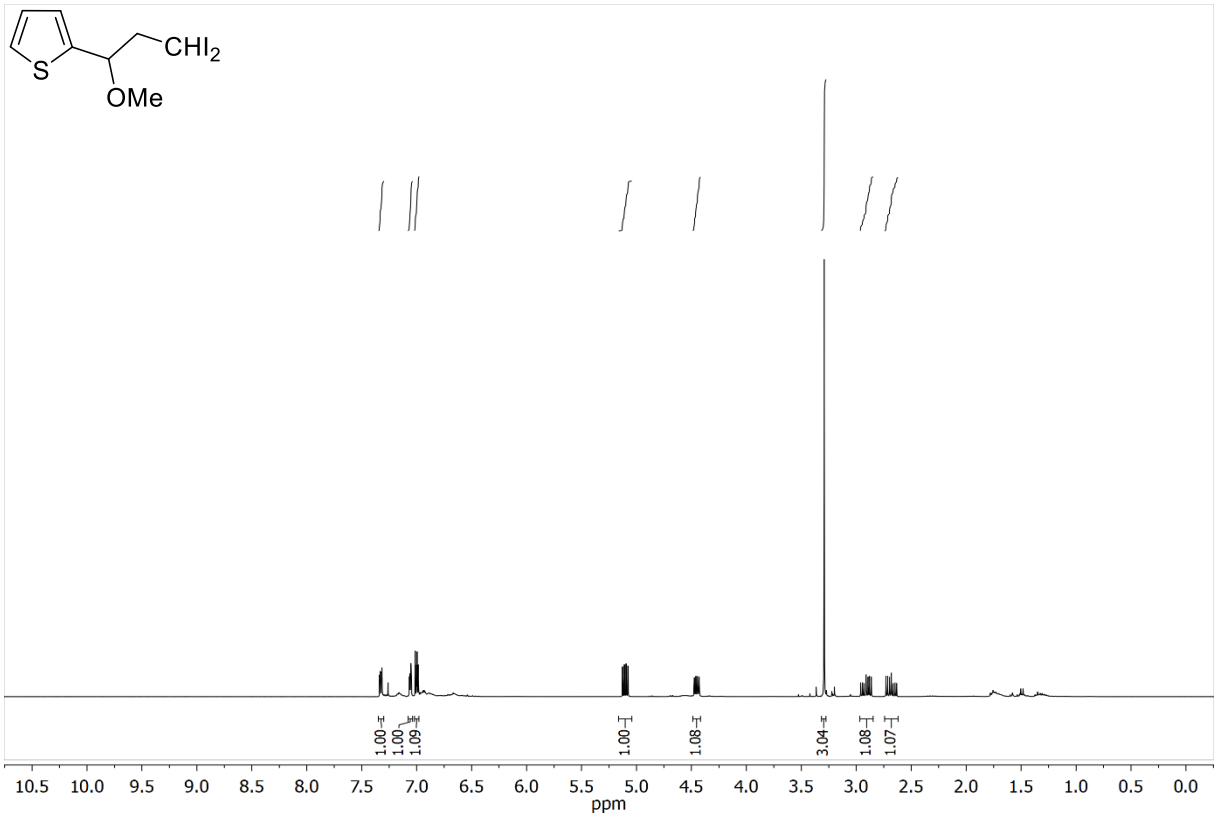
2-(1,3,3-triiodopropyl)pyridine (25ae)

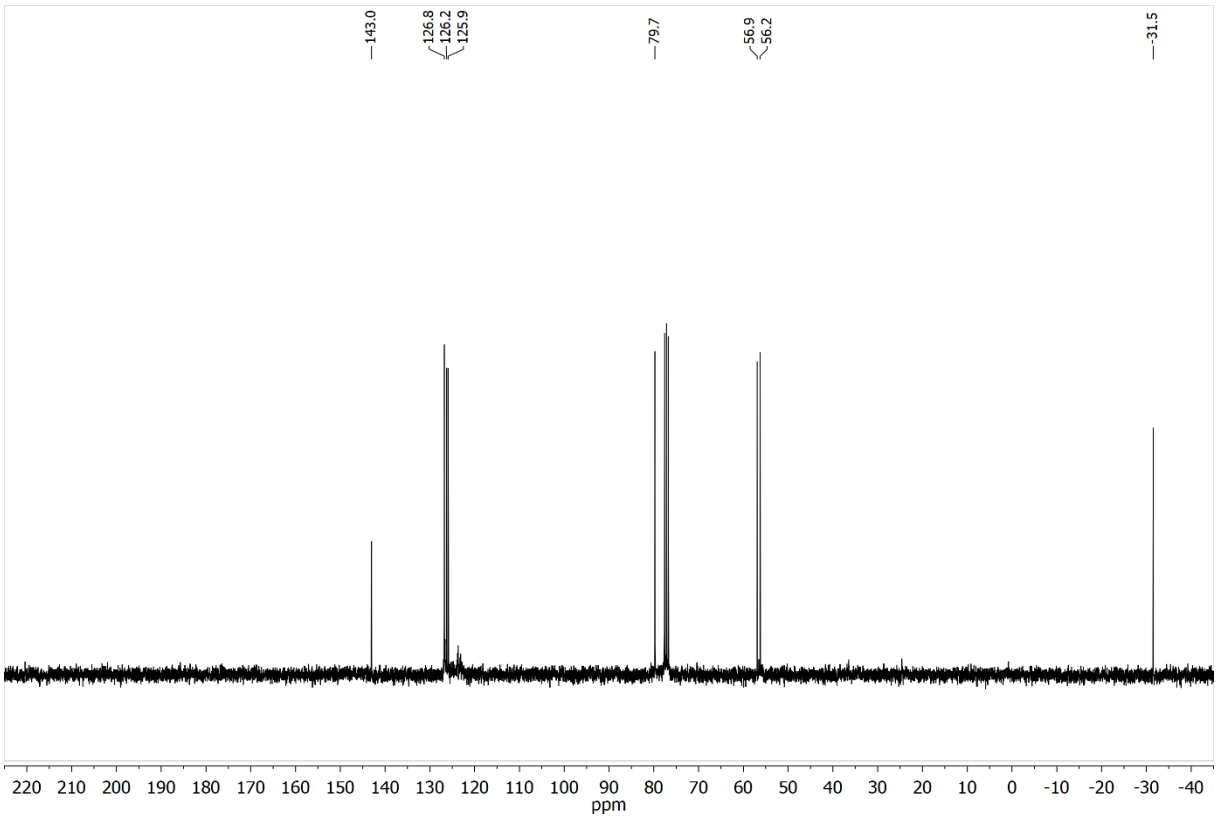




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

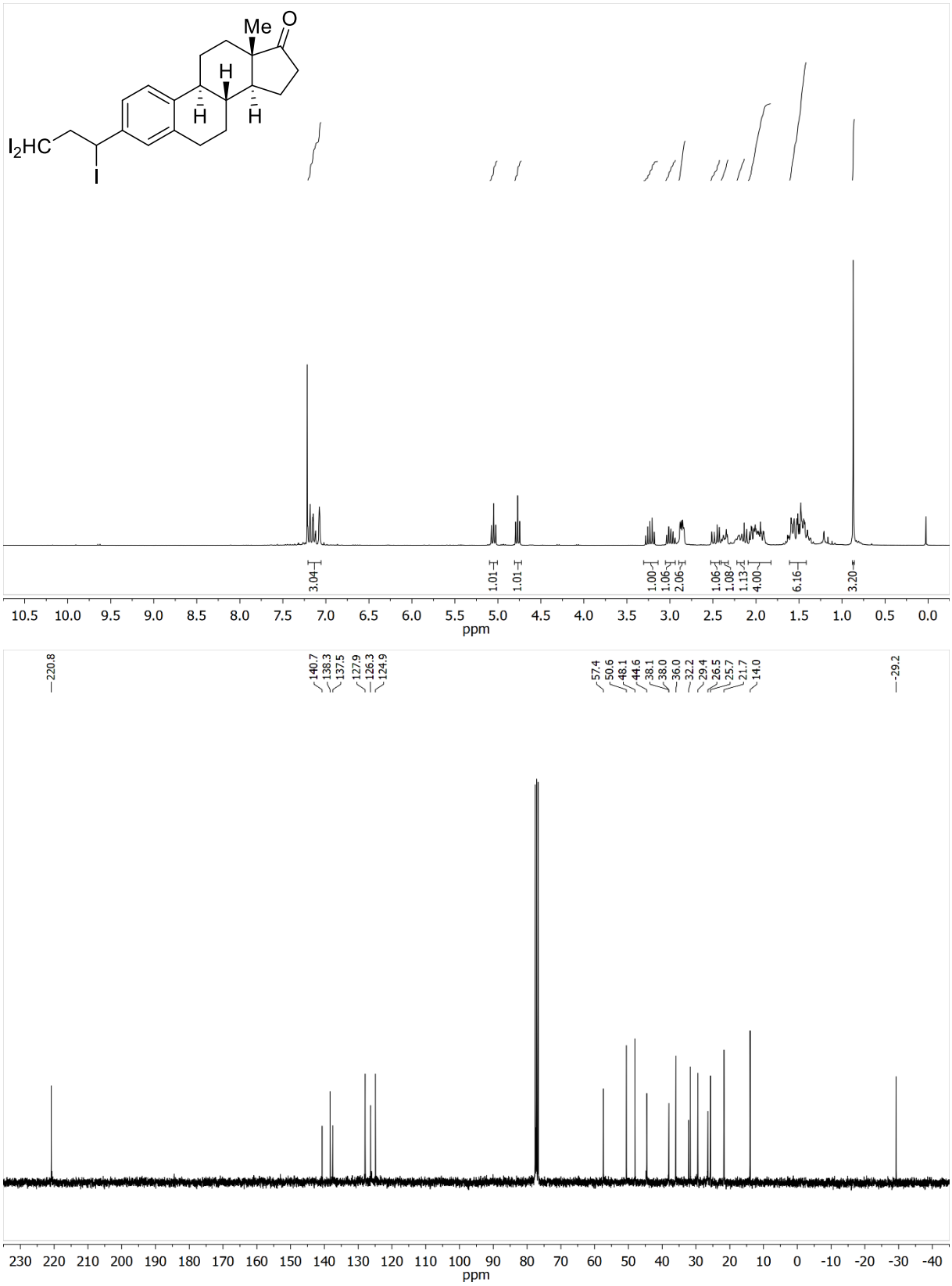
2-(3,3-diiodo-1-methoxypropyl)thiophene (OMe-25af)





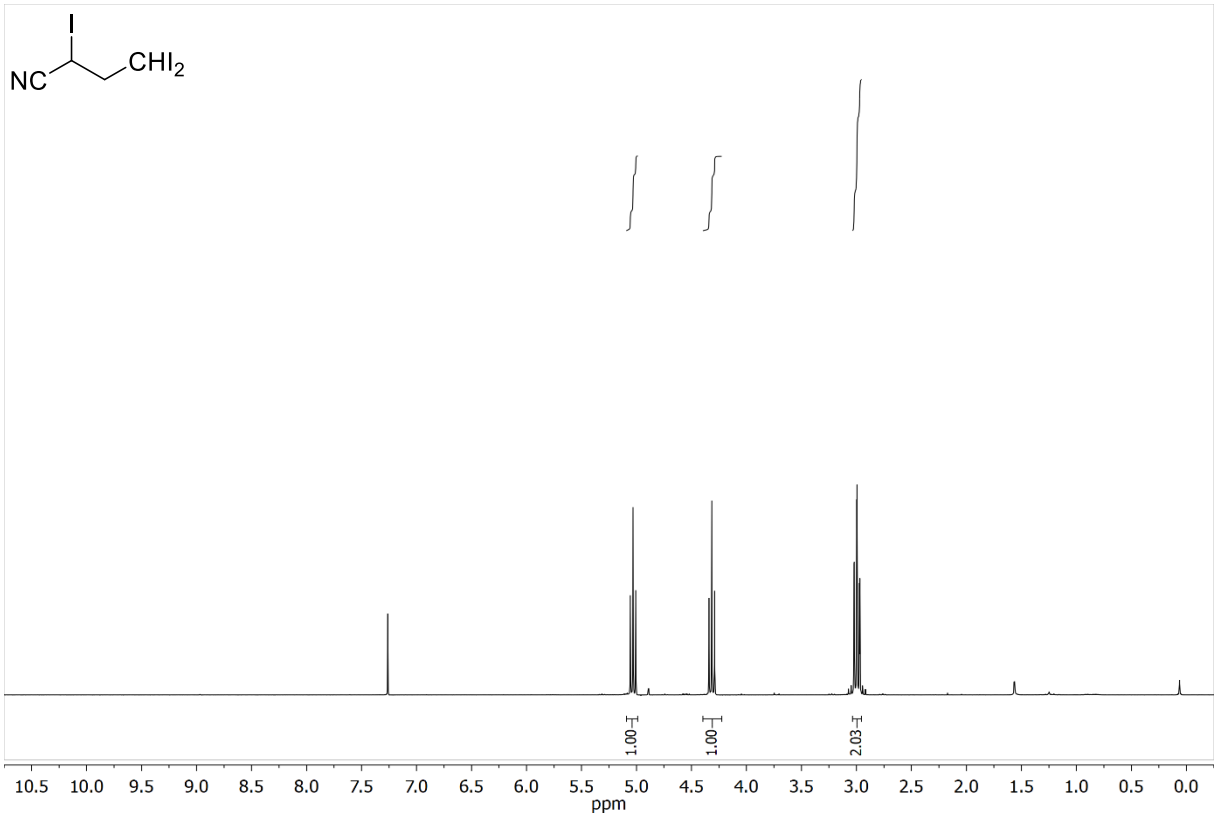
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

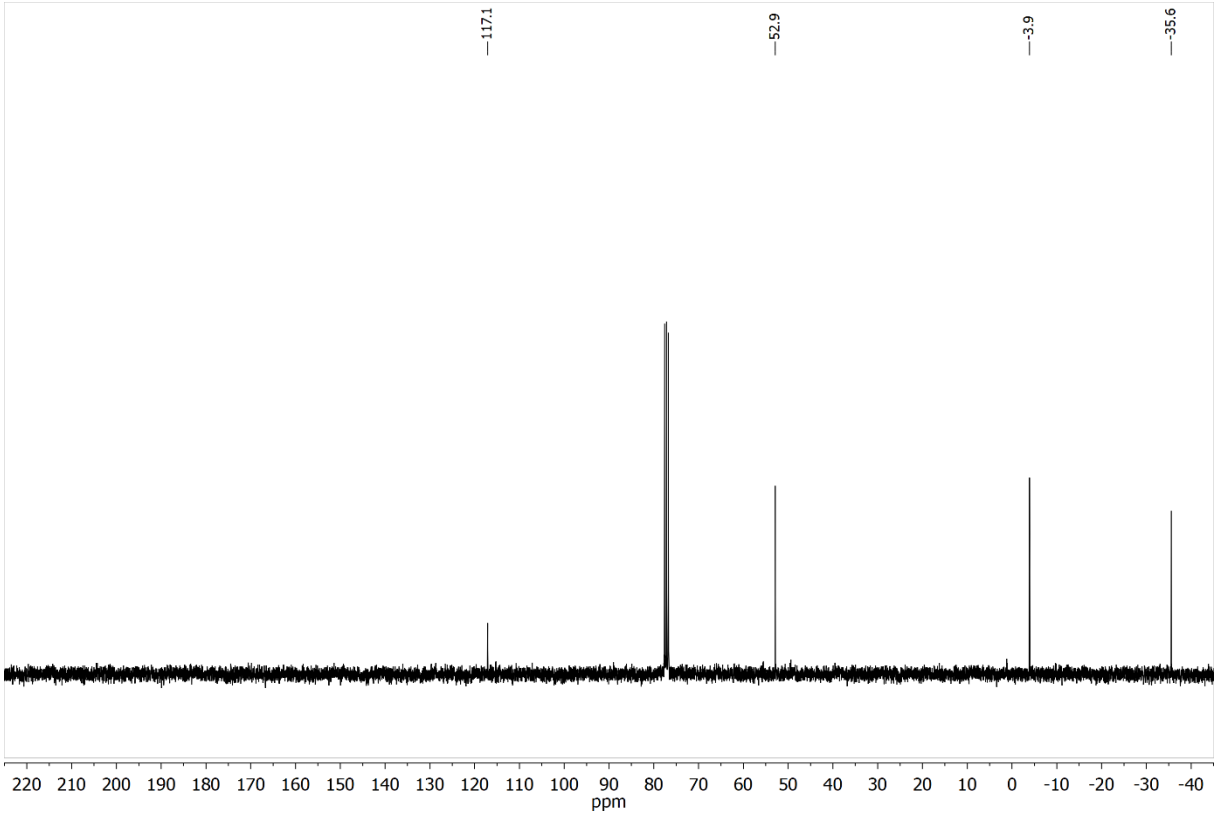
(8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(1,3,3-triiodopropyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (25ag)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

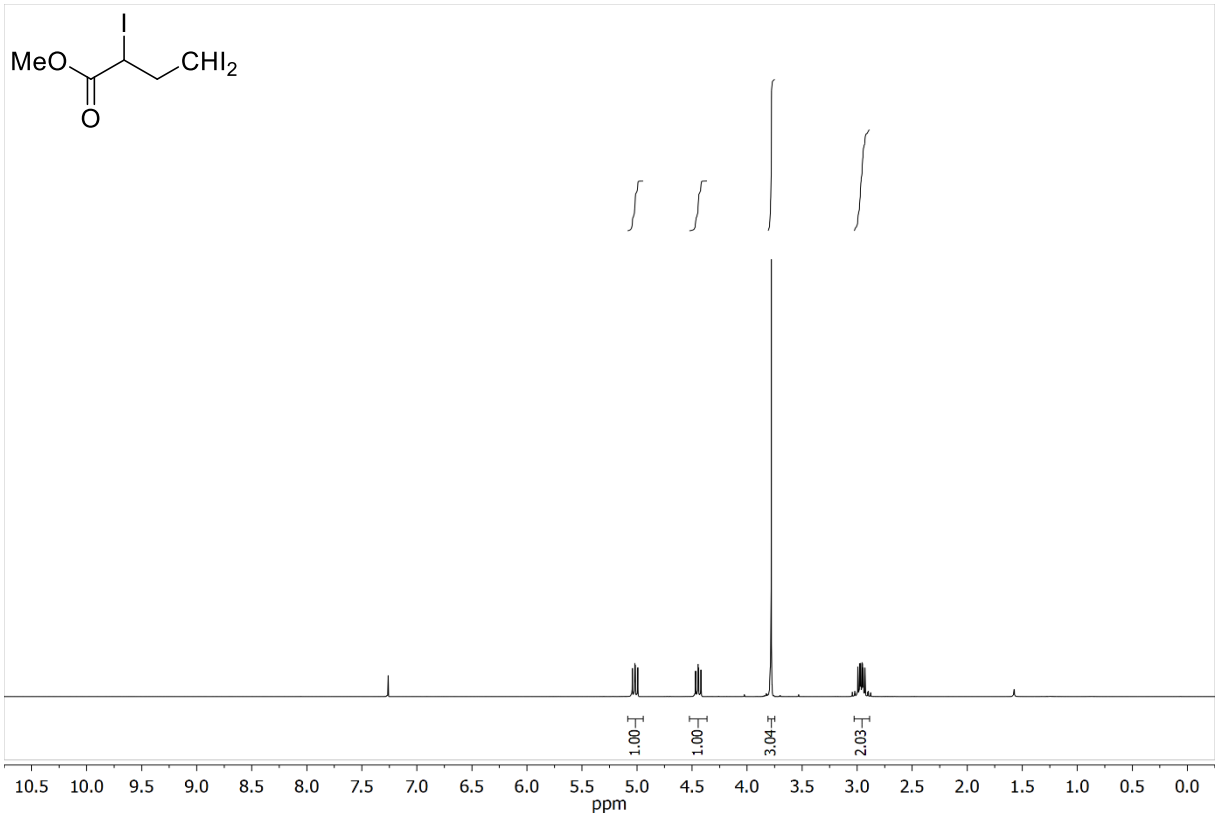
4-(1,3,3-triiodopropyl)benzonitrile (25ah)

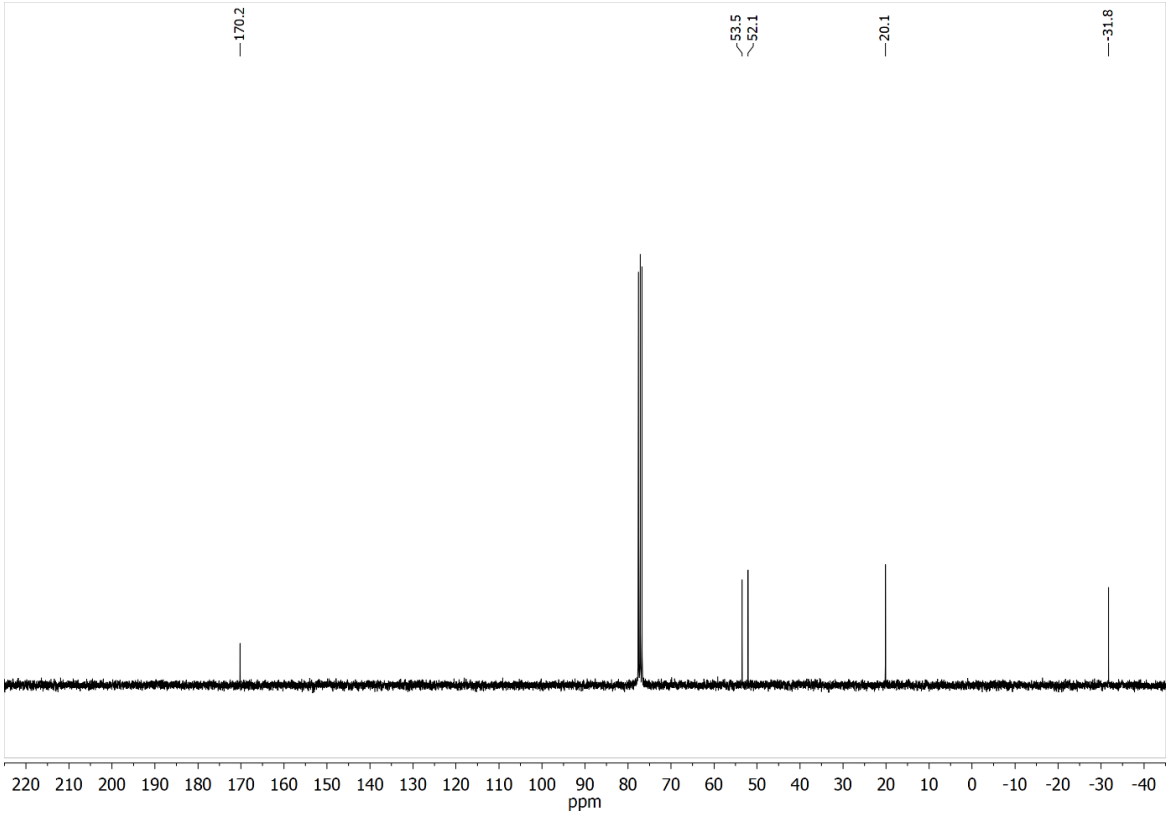




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

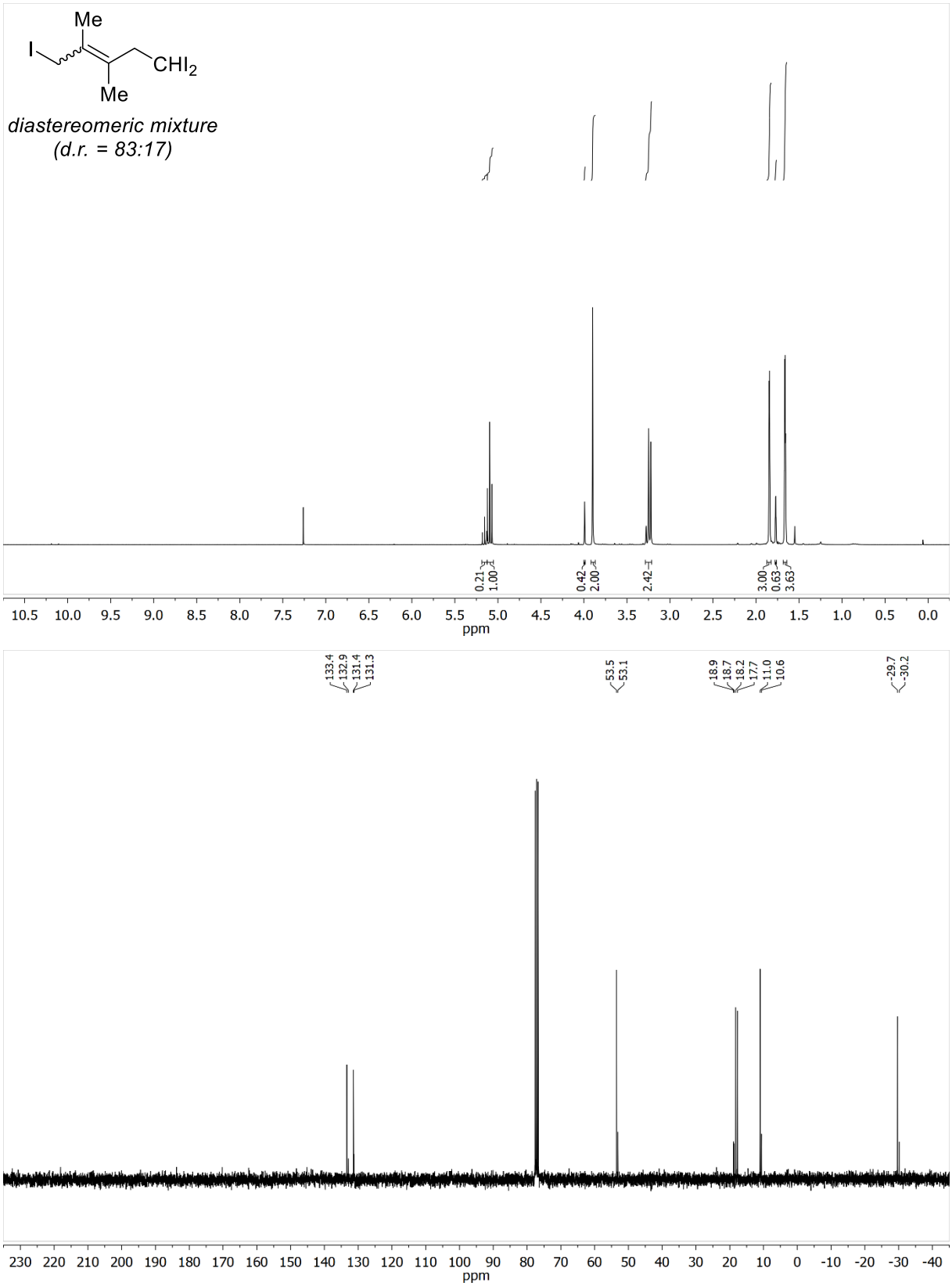
methyl 2,4,4-triiodobutanoate (25ai)





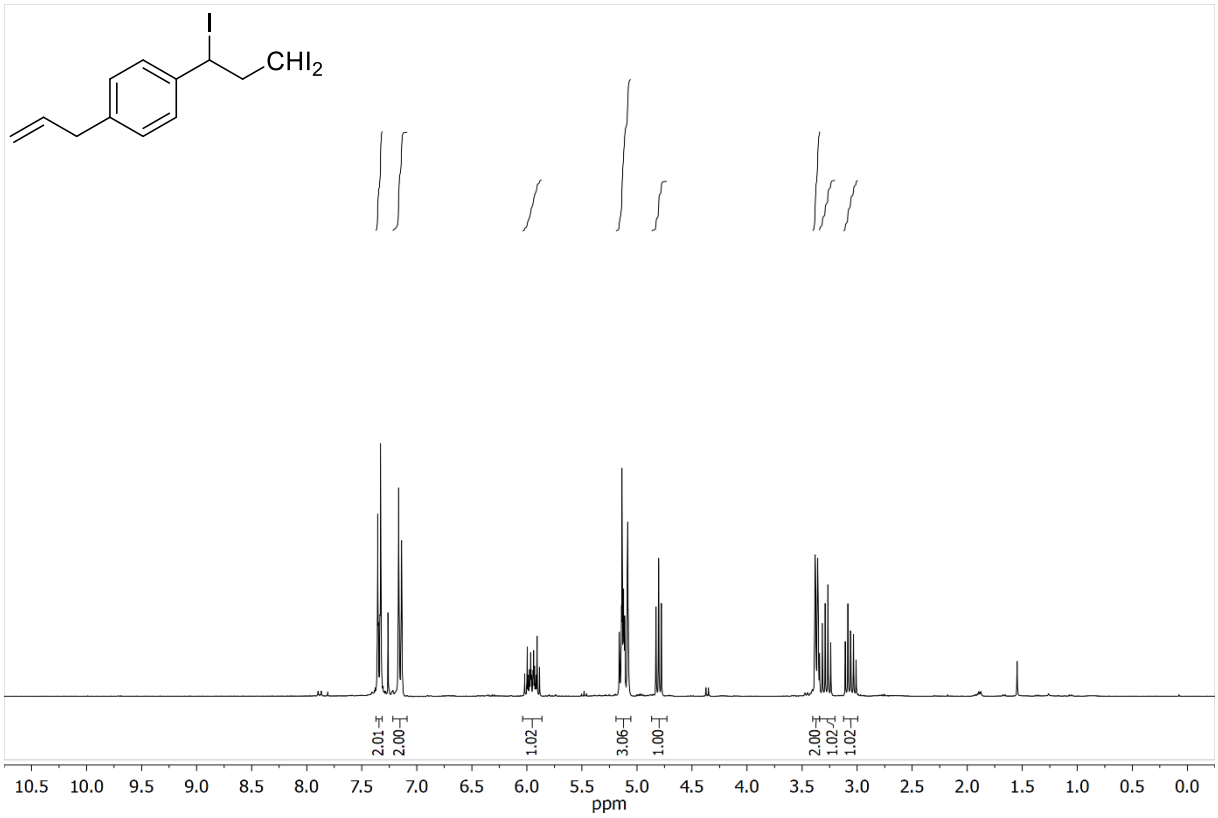
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

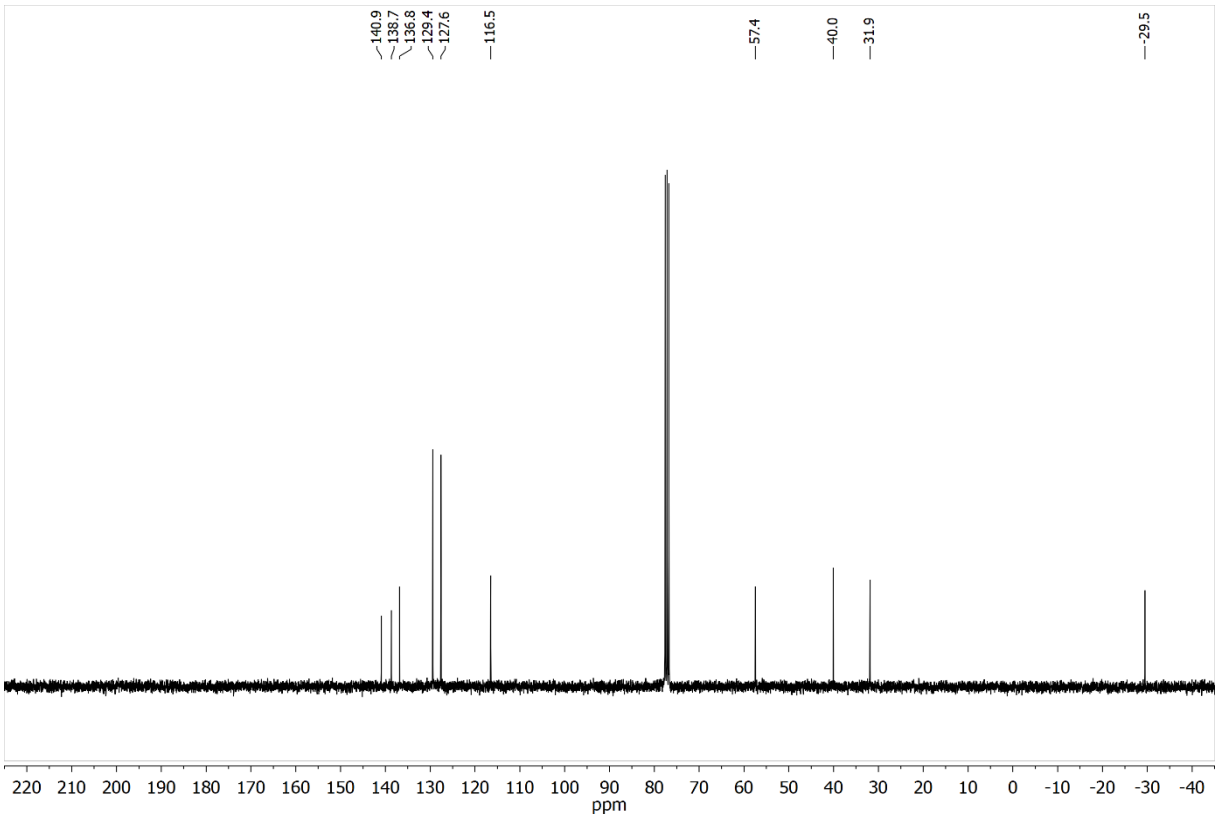
1,5,5-triiodo-2,3-dimethylpent-2-ene (d.r. = 83:17) (25an)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

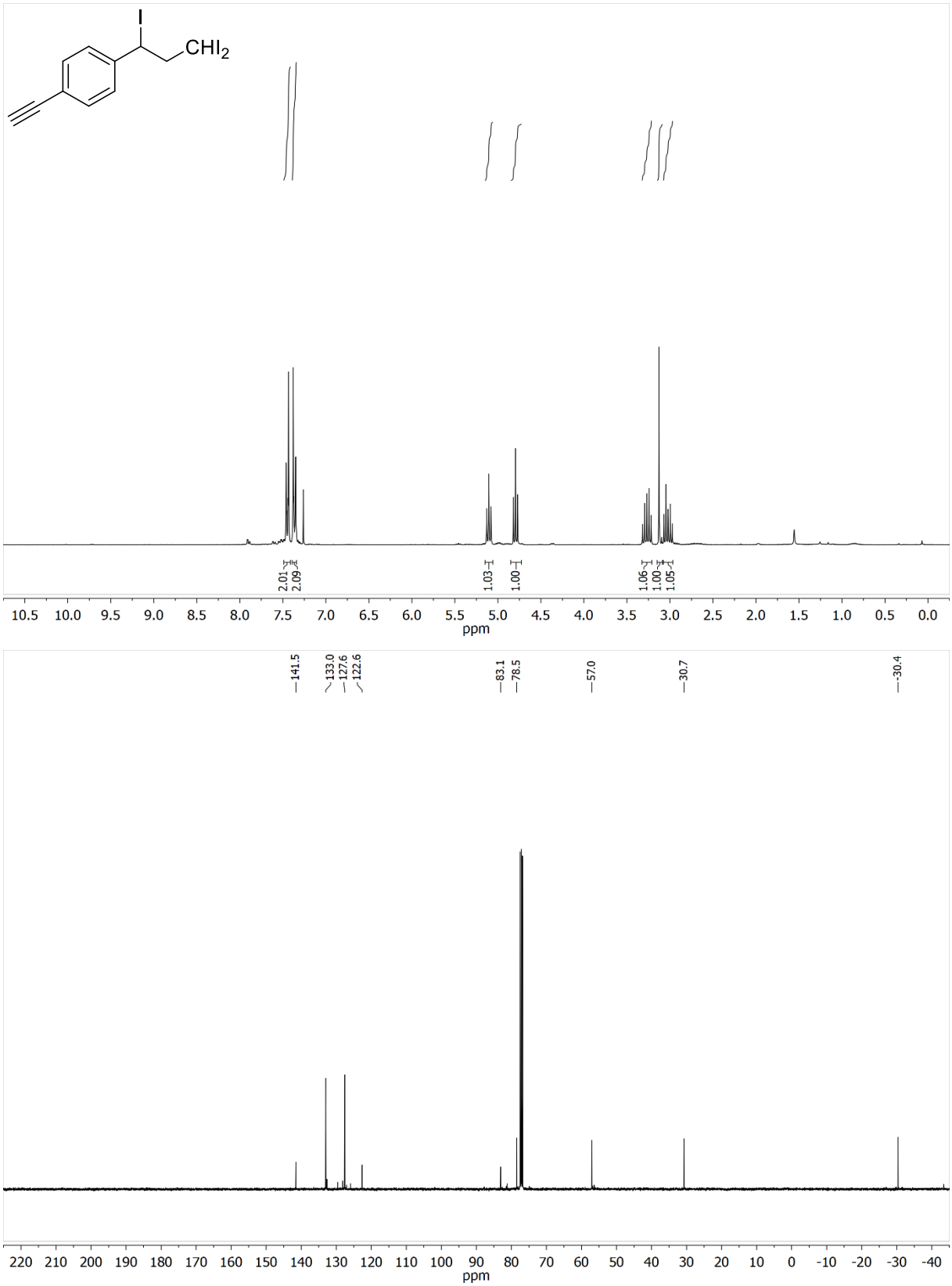
1-allyl-4-(1,3,3-triiodopropyl)benzene (25au)





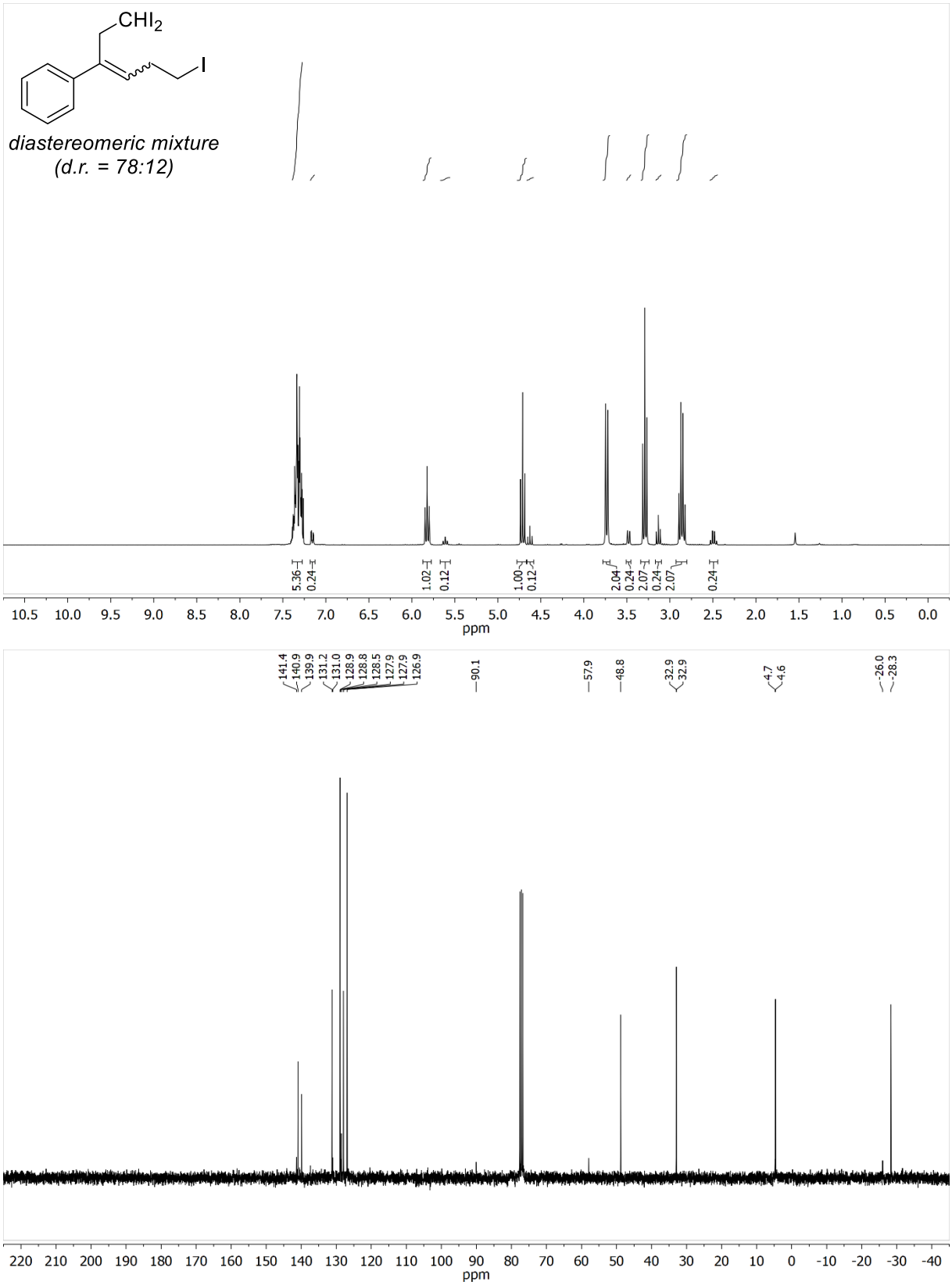
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

1-ethynyl-4-(1,3,3-triiodopropyl)benzene (25av)



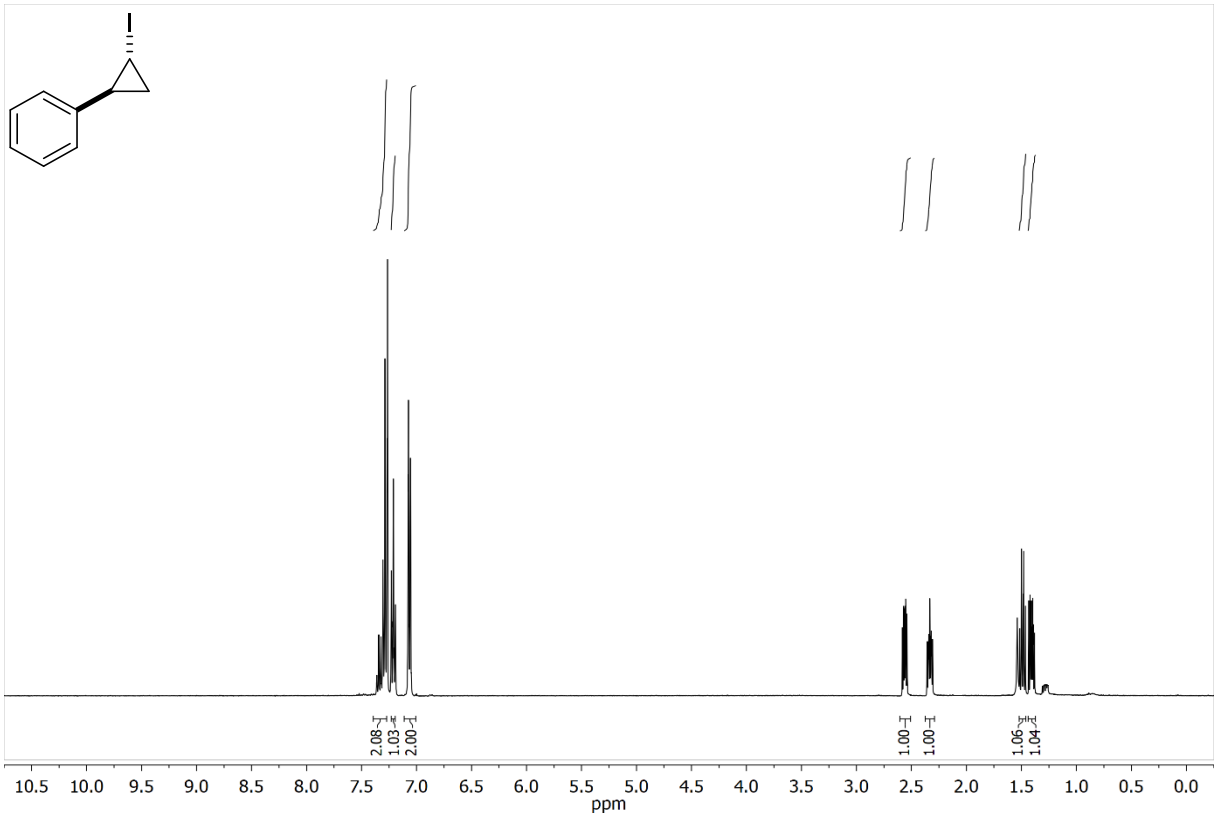
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

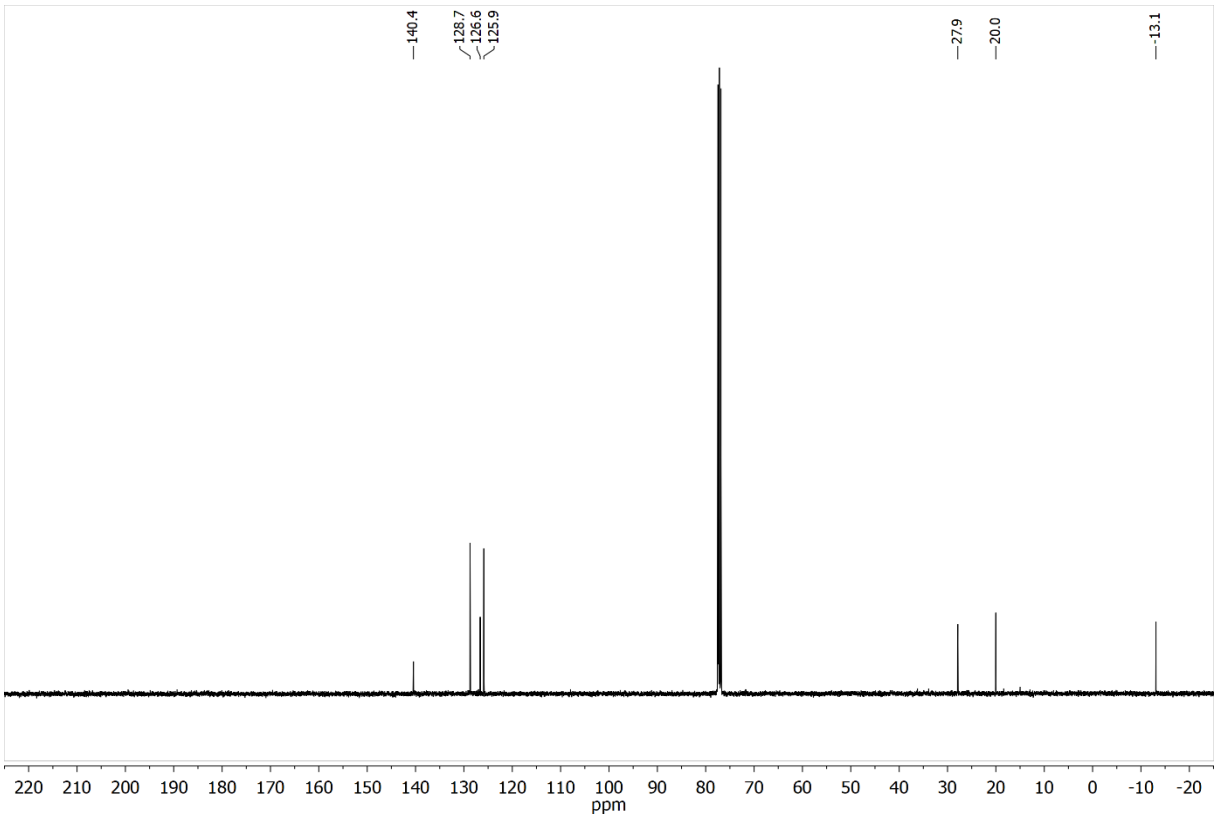
(1,1,6-triiodohex-3-en-3-yl)benzene (d.r. = 78:12) (25ax)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

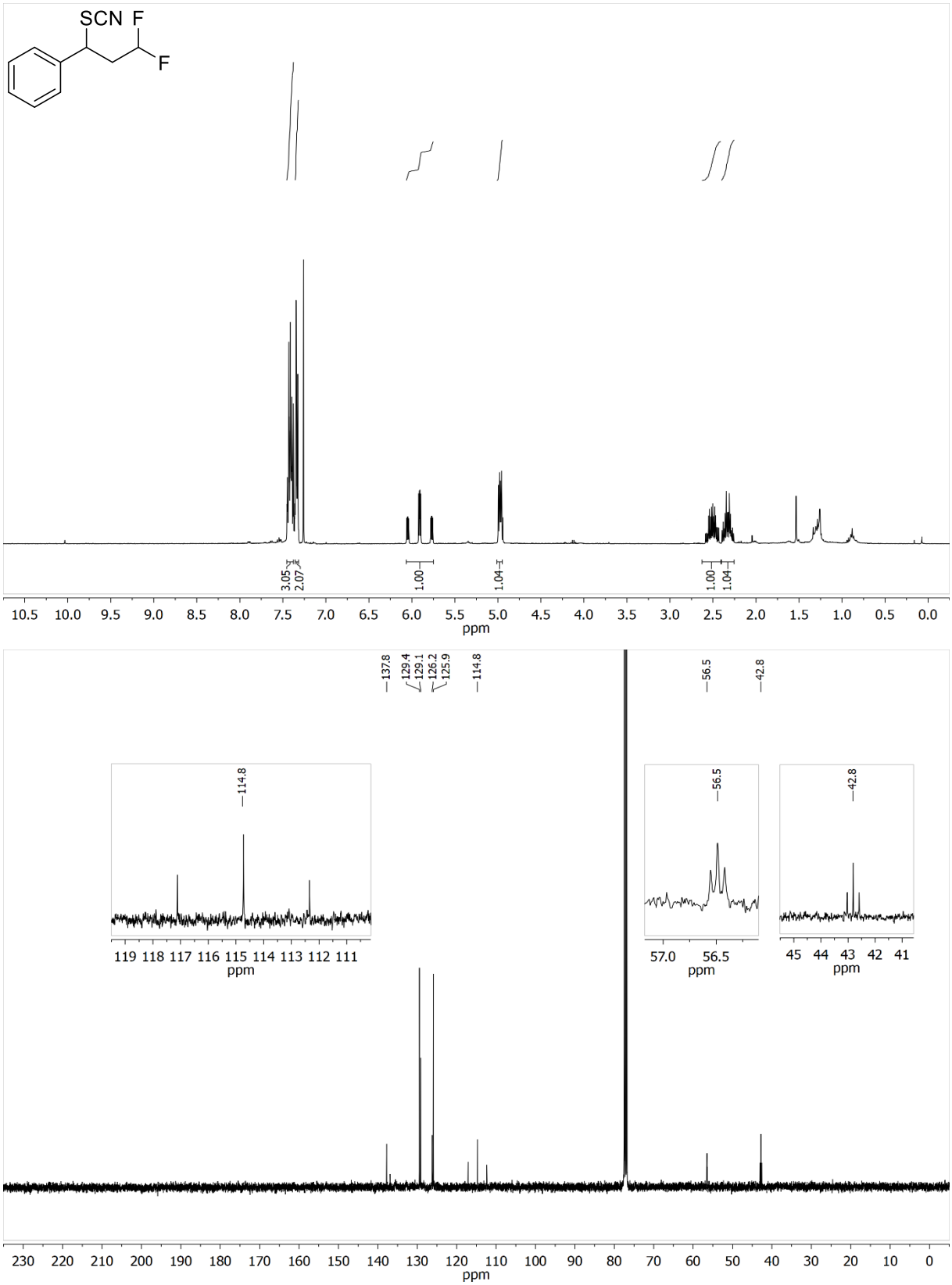
***trans*-2-iodocyclopropyl)benzene (2a)**





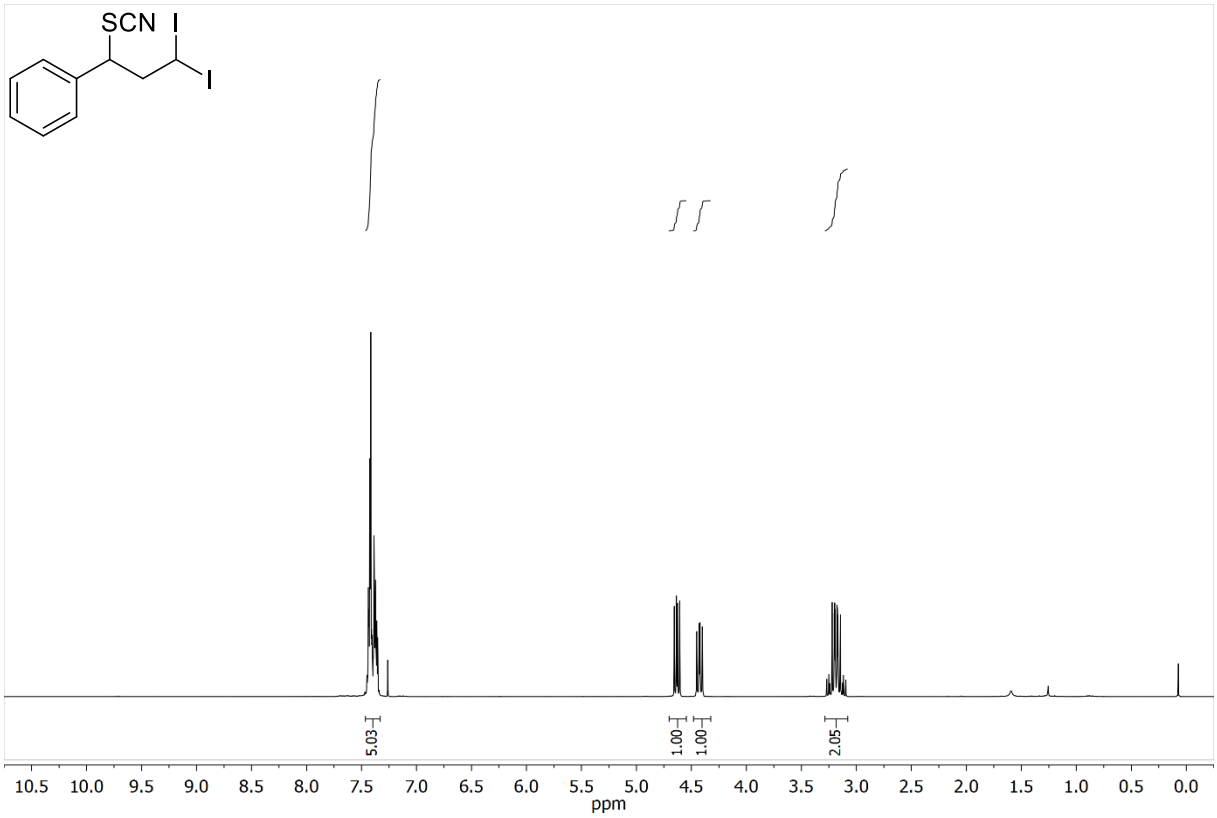
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

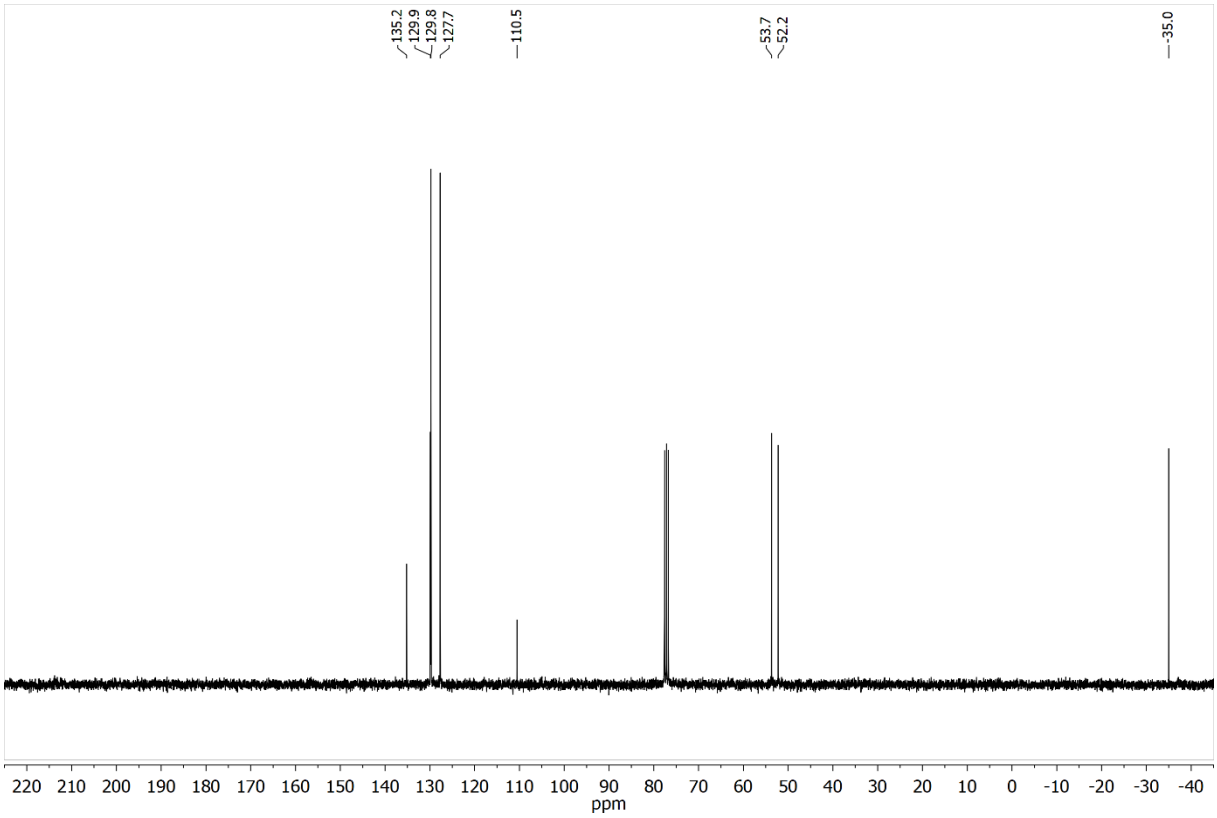
(3,3-difluoro-1-thiocyanatopropyl)benzene (7c)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

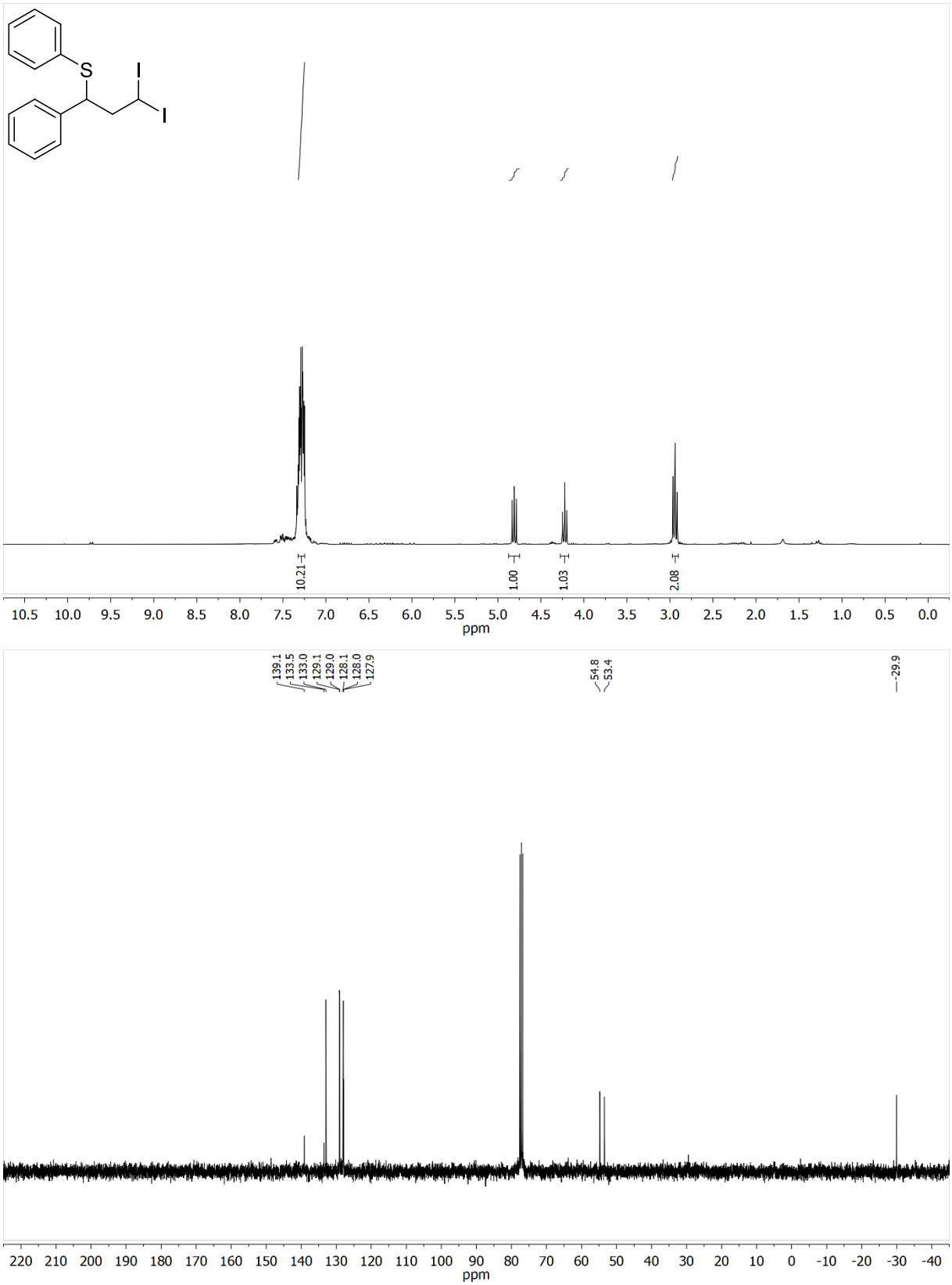
(3,3-diiodo-1-thiocyanatopropyl)benzene (34a)





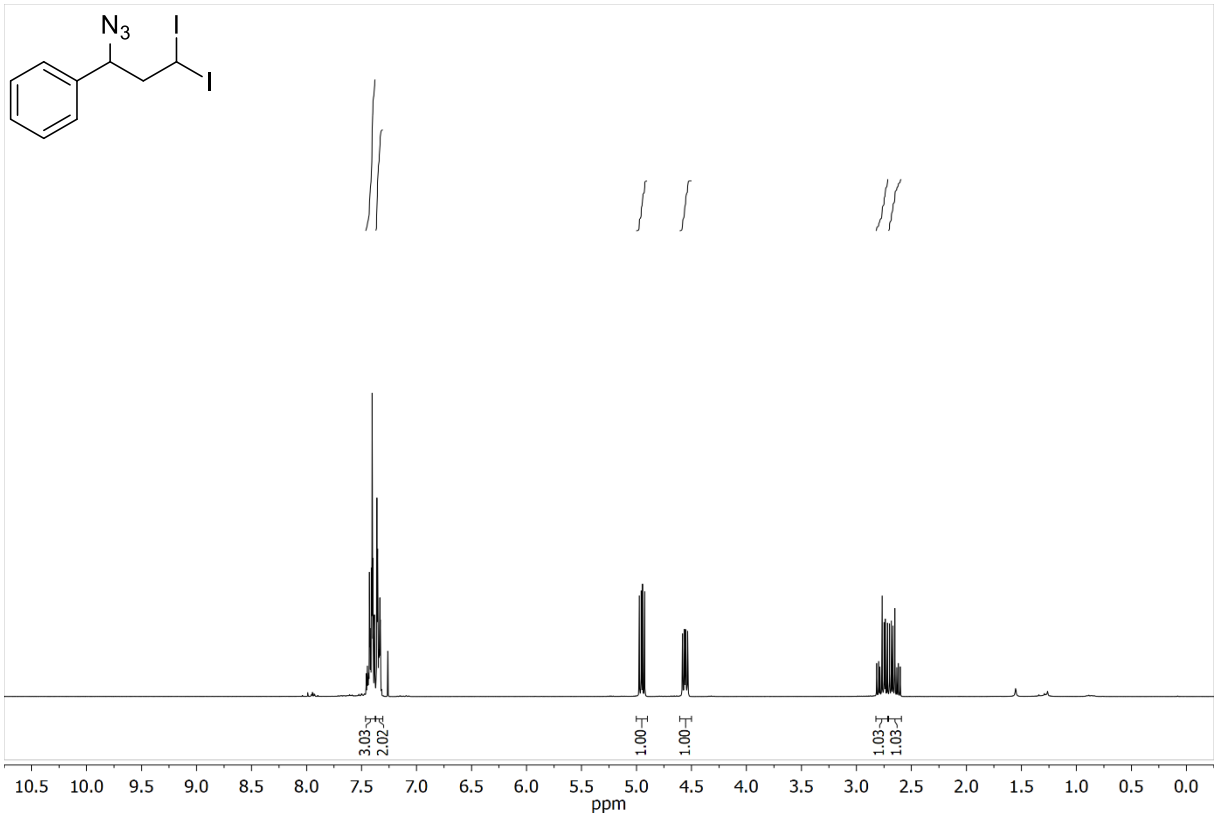
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

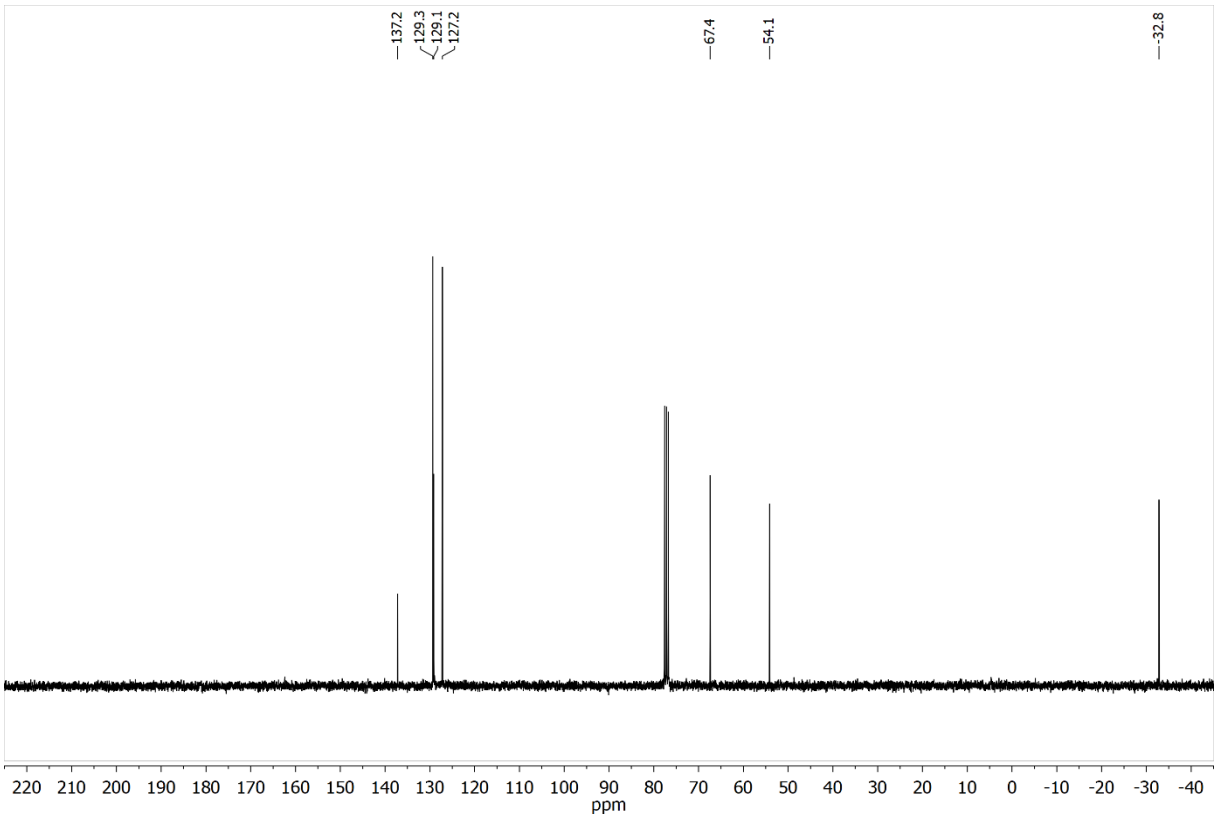
(3,3-diiodo-1-phenylpropyl)(phenyl)sulfane (34b)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

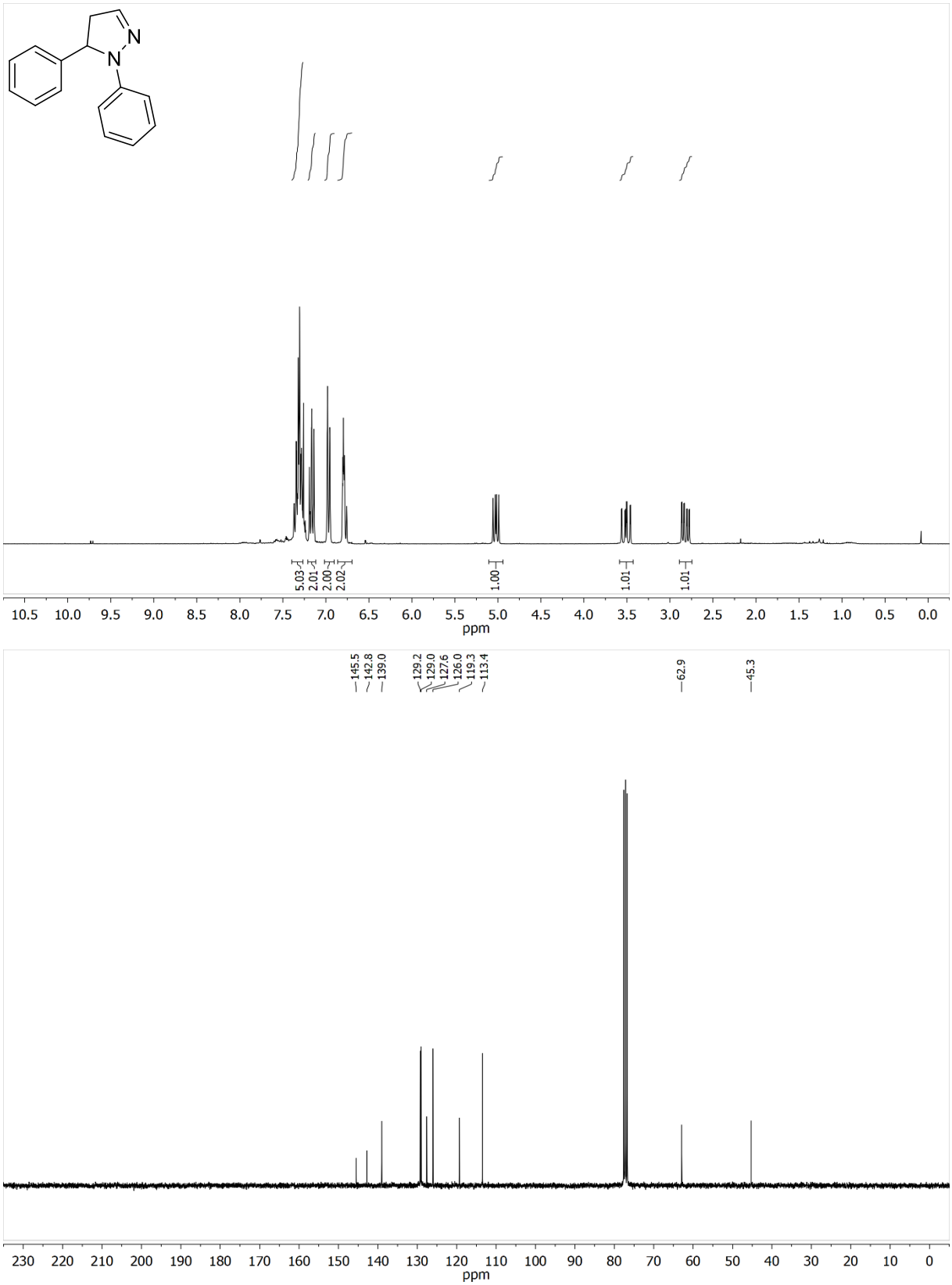
(1-azido-3,3-diiodopropyl)benzene (34c)





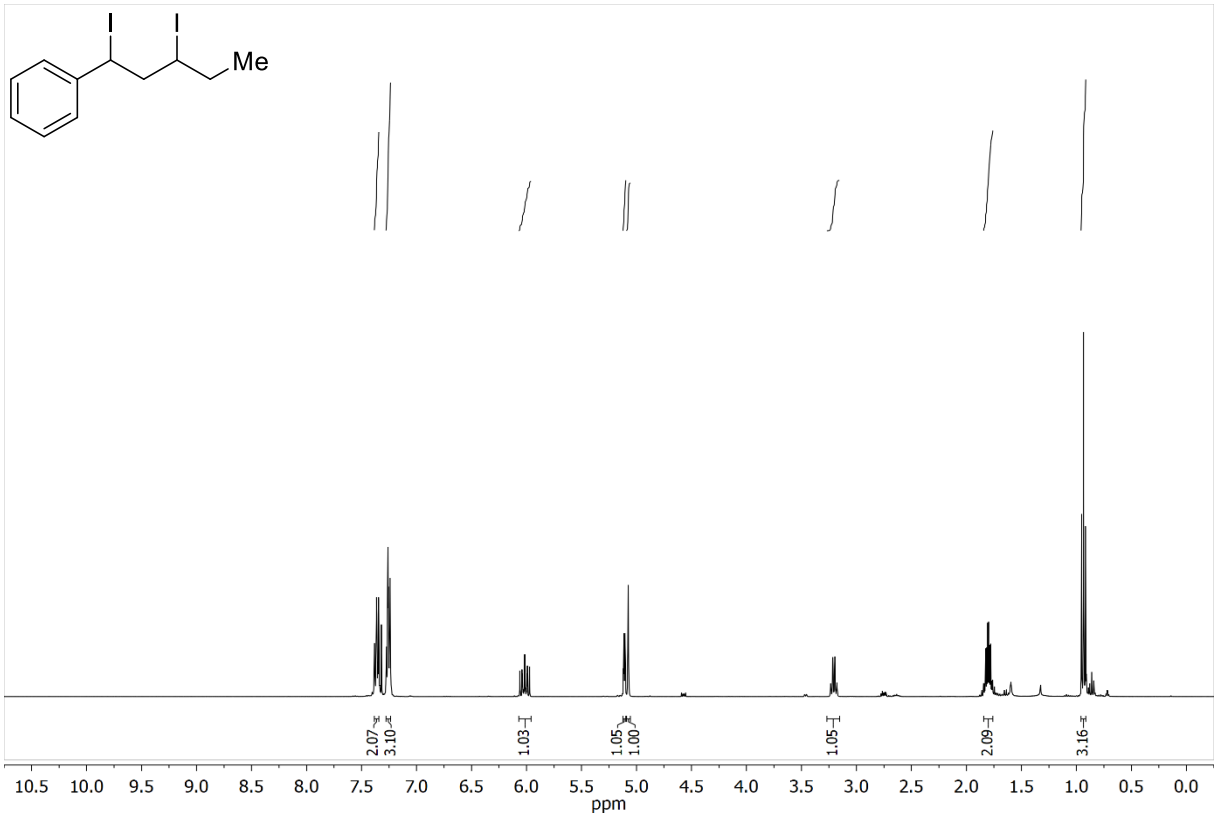
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

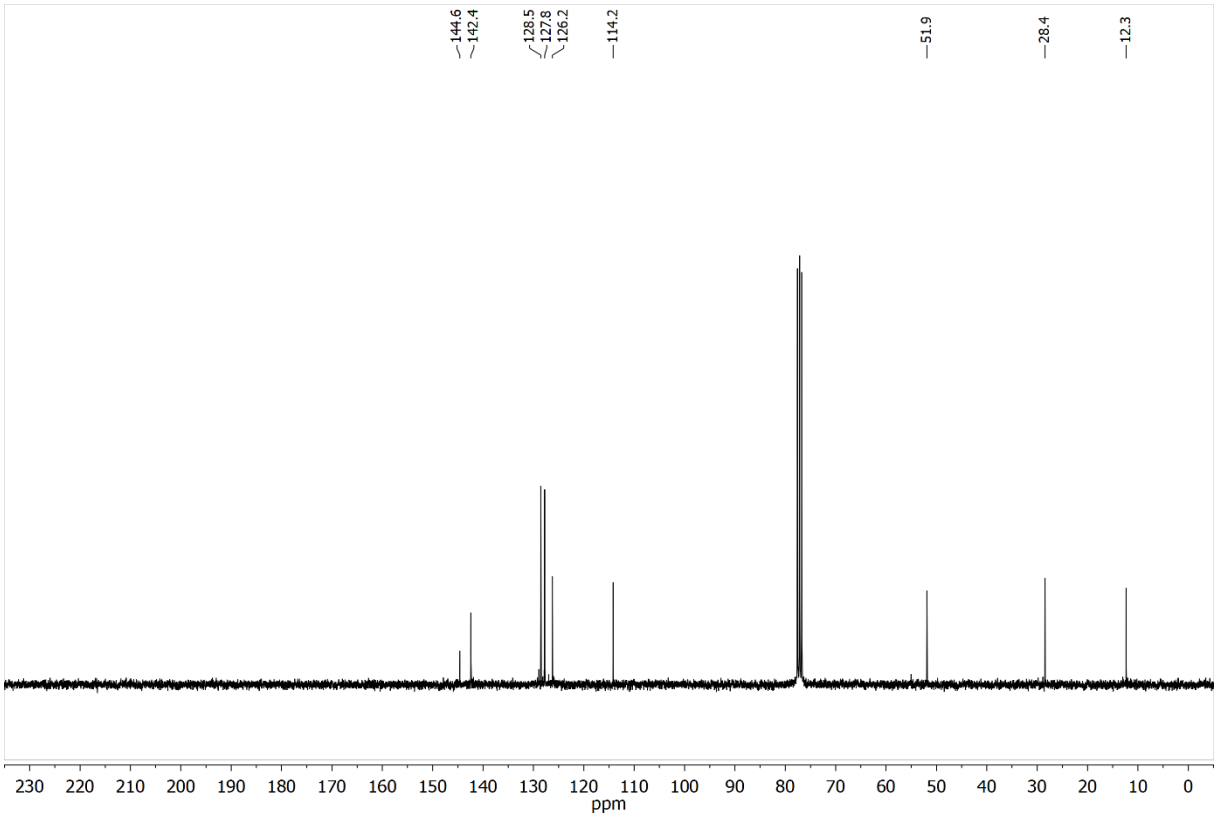
1,5-diphenyl-4,5-dihydro-*1H*-pyrazole (36a)



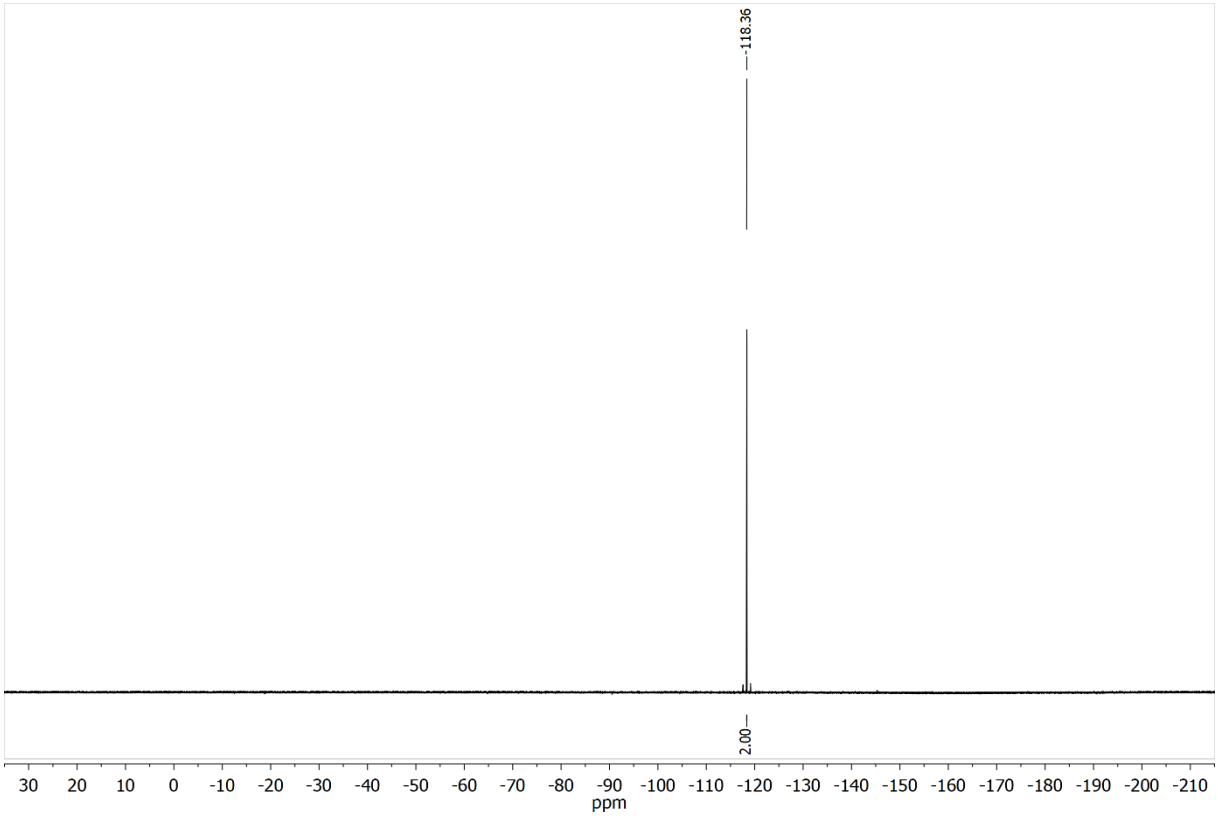
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

(1,3-diiodopentyl)benzene (42)



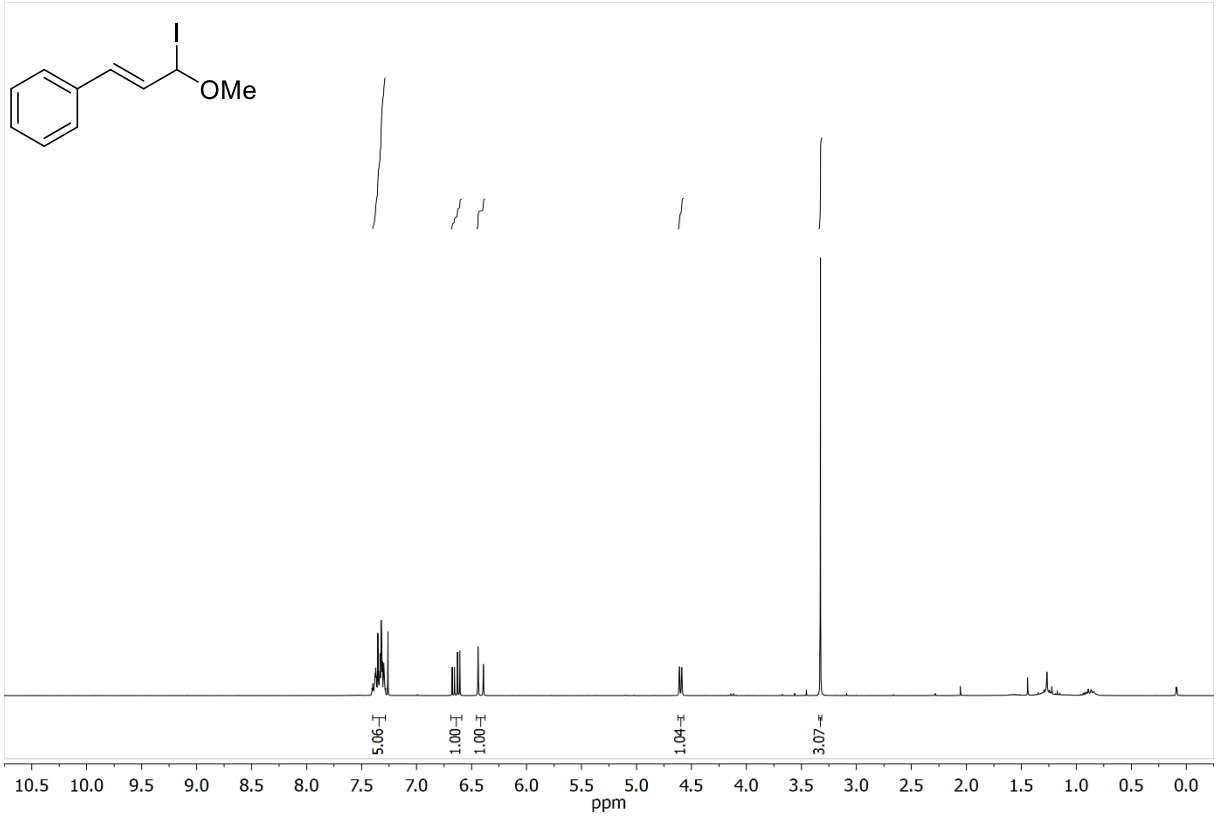


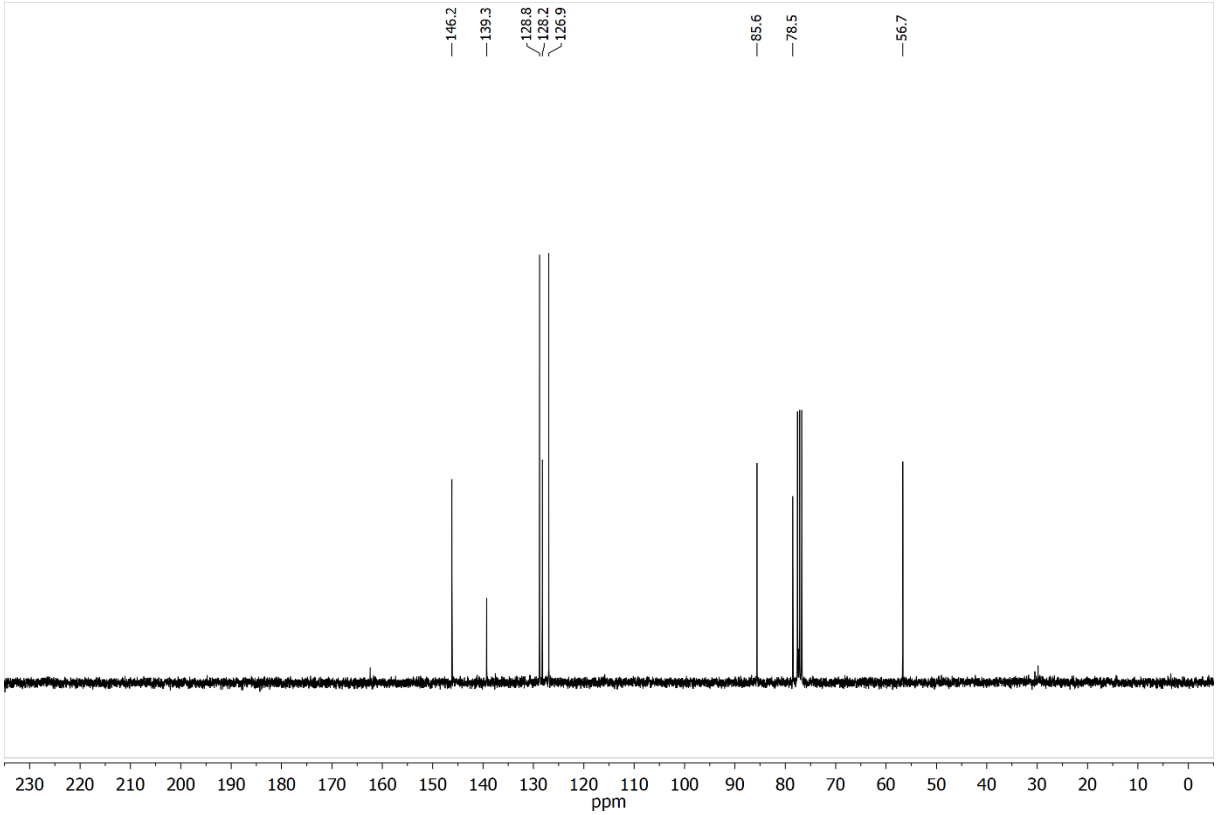
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

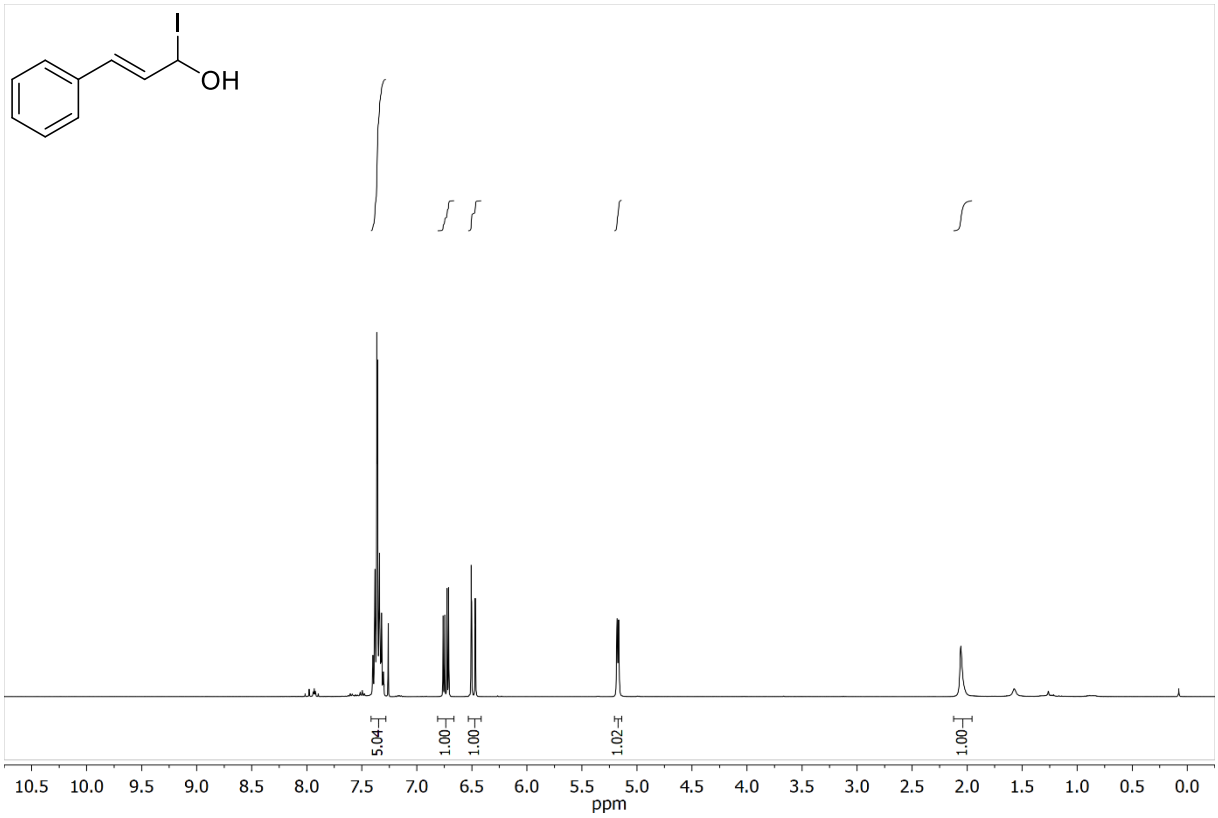
(*E*)-(3-iodo-3-methoxyprop-1-en-1-yl)benzene (47a)

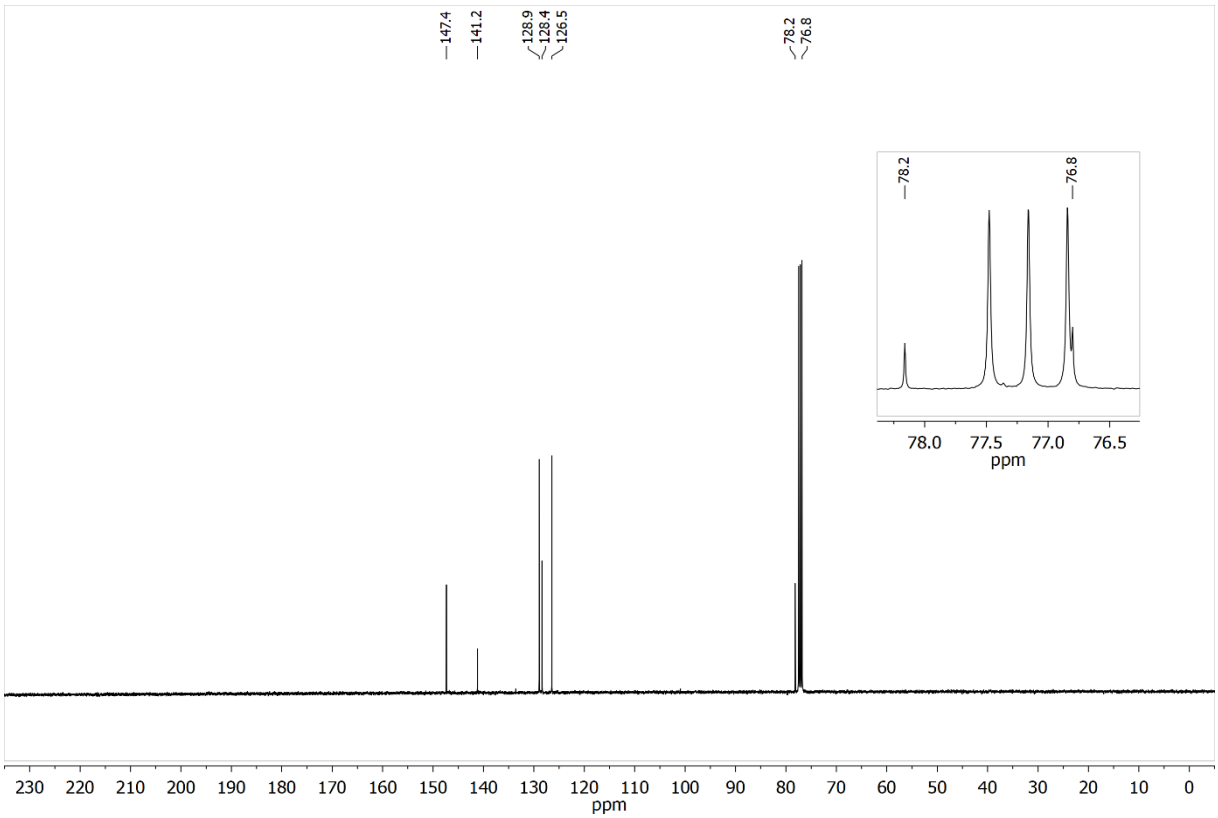




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

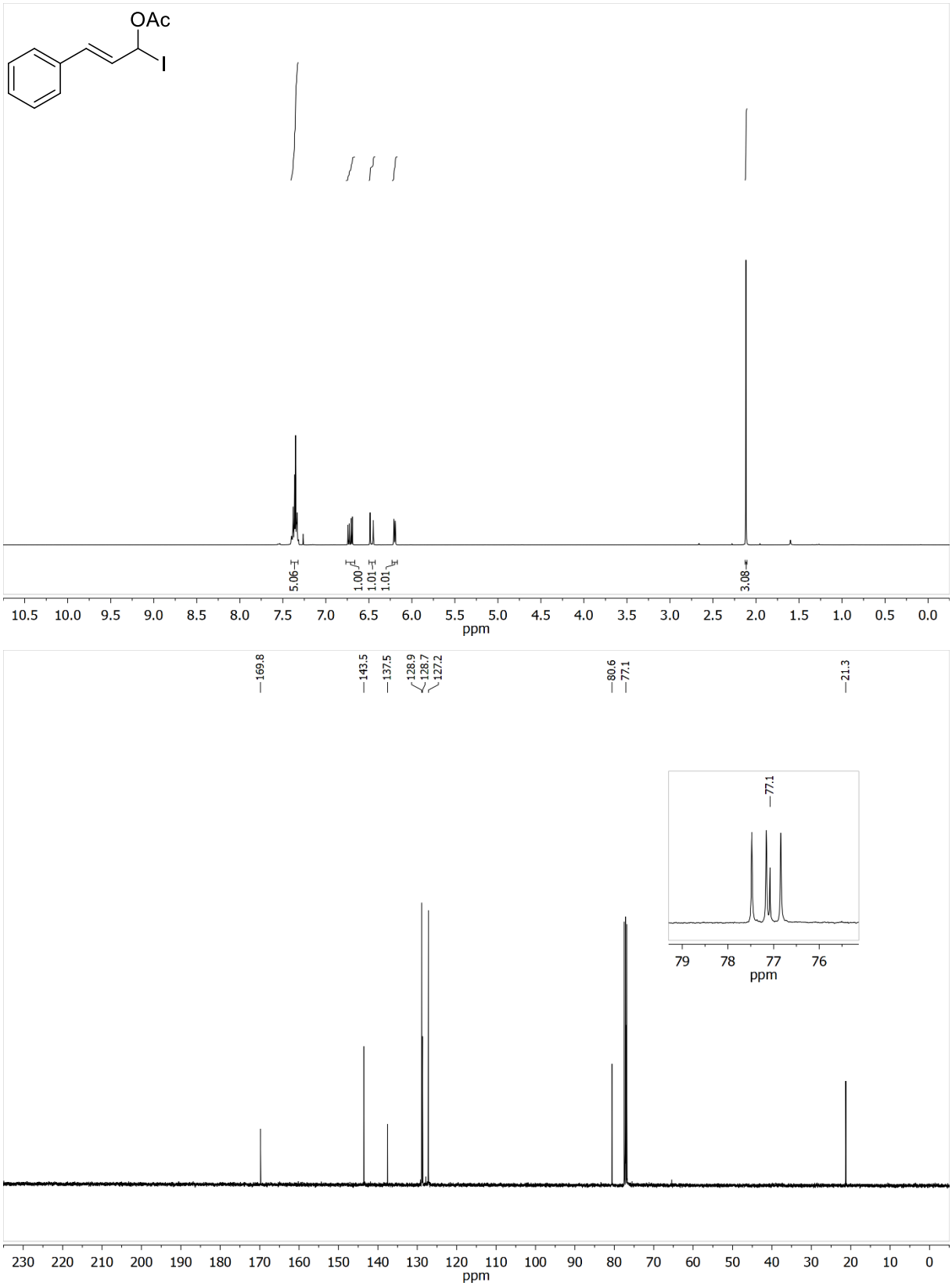
(*E*)-1-iodo-3-phenylprop-2-en-1-ol (47b)





First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

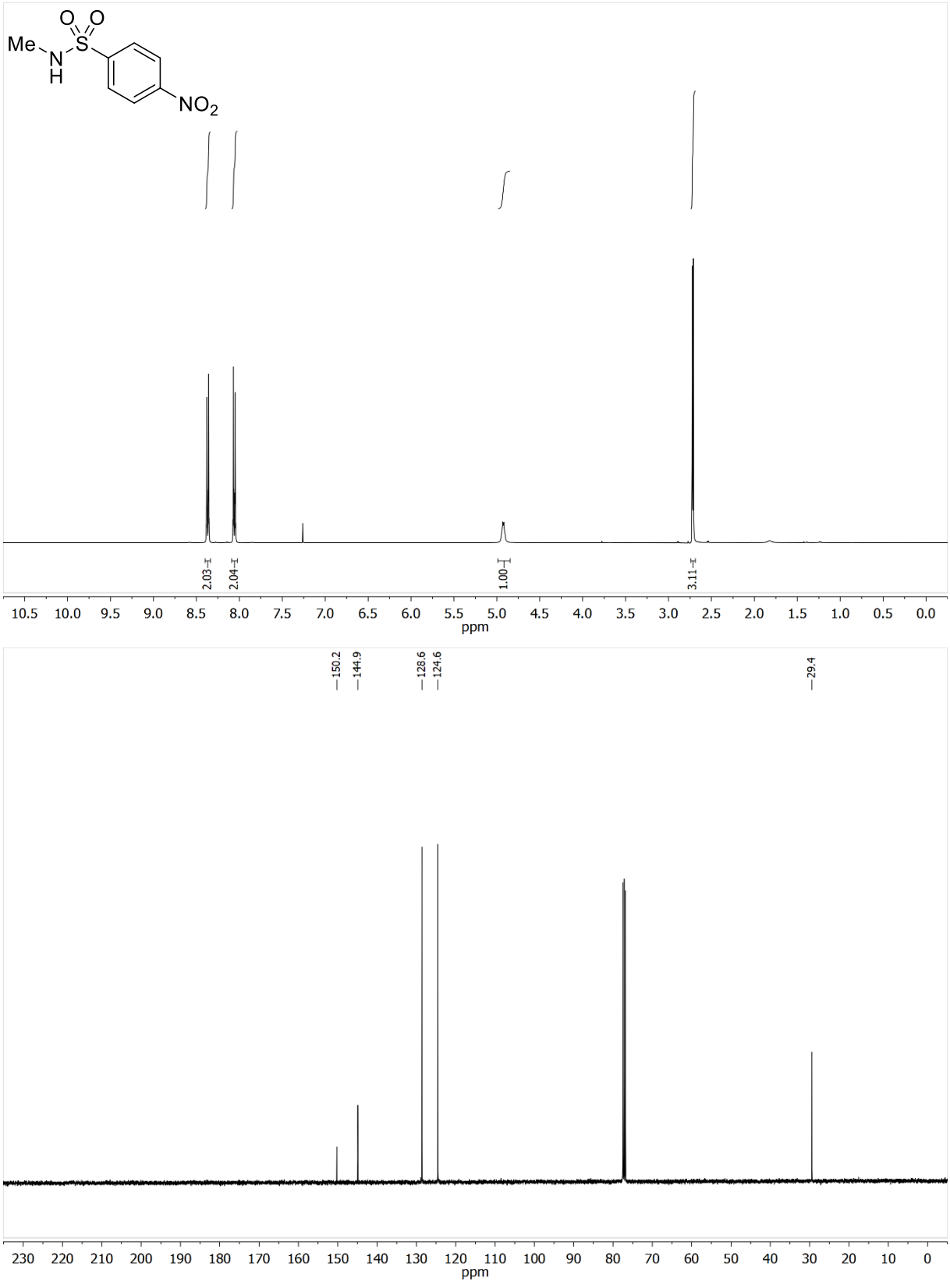
(*E*)-1-iodo-3-phenylallyl acetate (47c)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

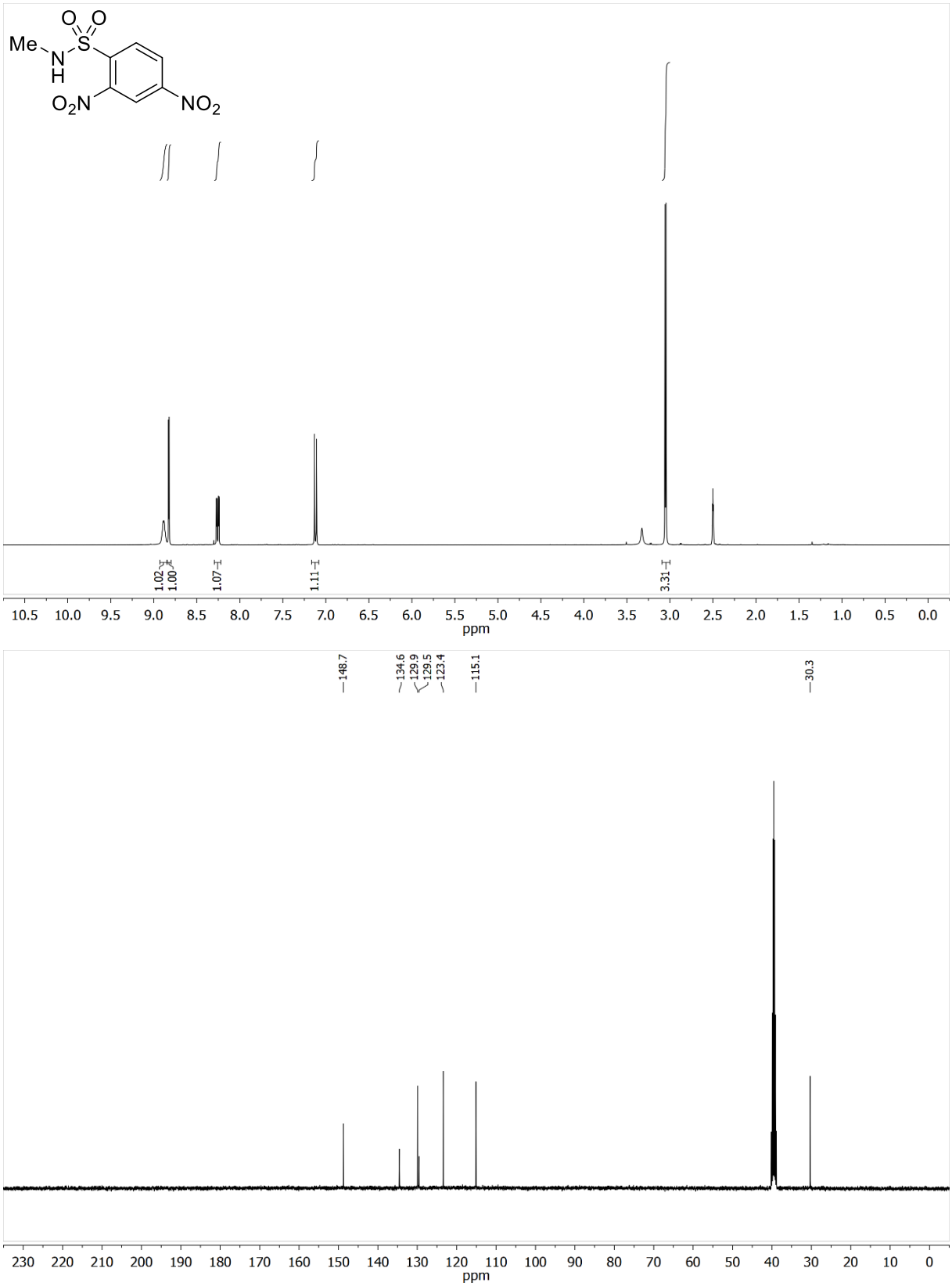
8.5 NMR Spectra for Chapter 5

_N_-methyl-4-nitrobenzenesulfonamide (Ns-2a)



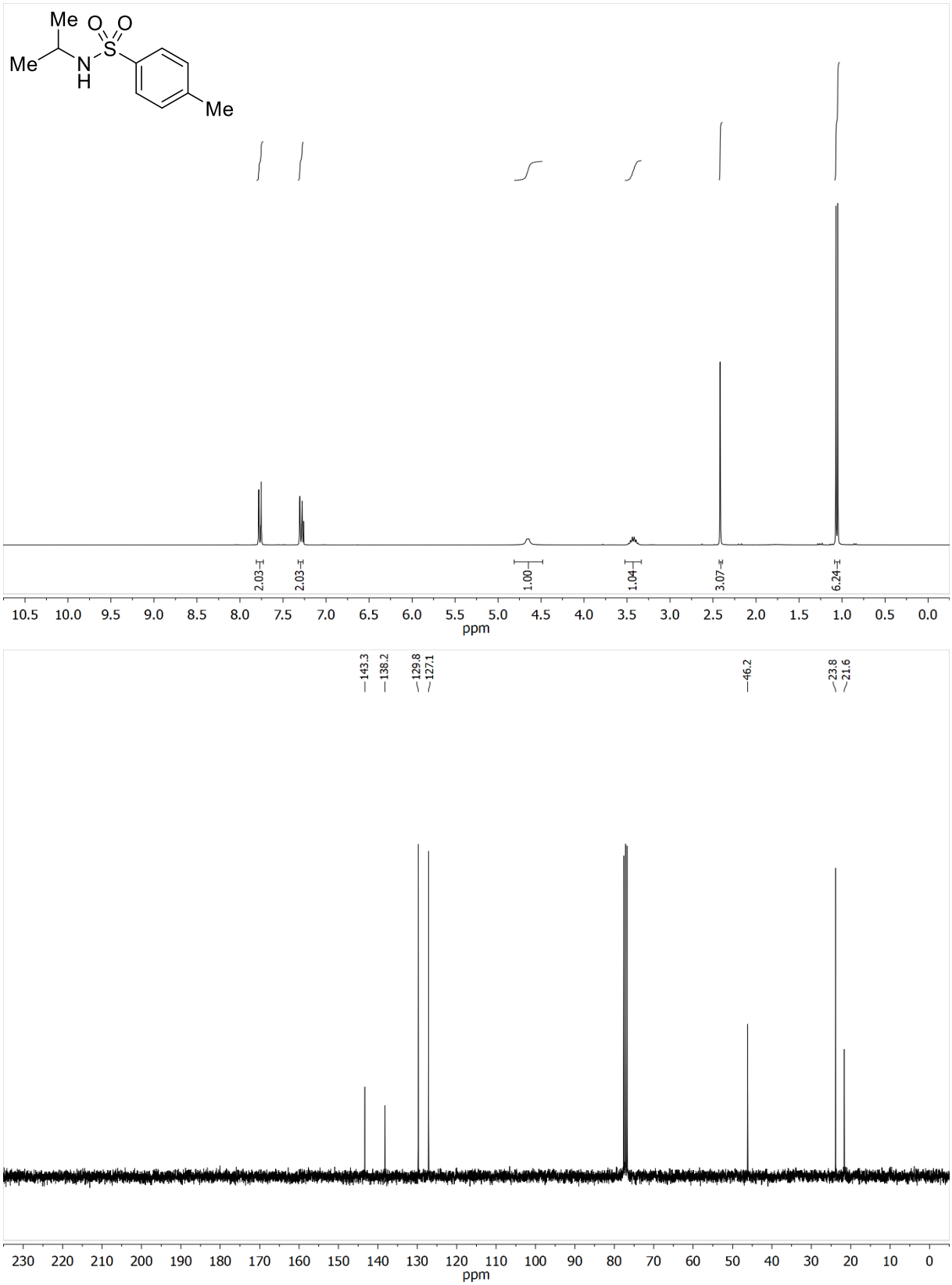
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-methyl-2,4-dinitrobenzenesulfonamide (DNs-2a)



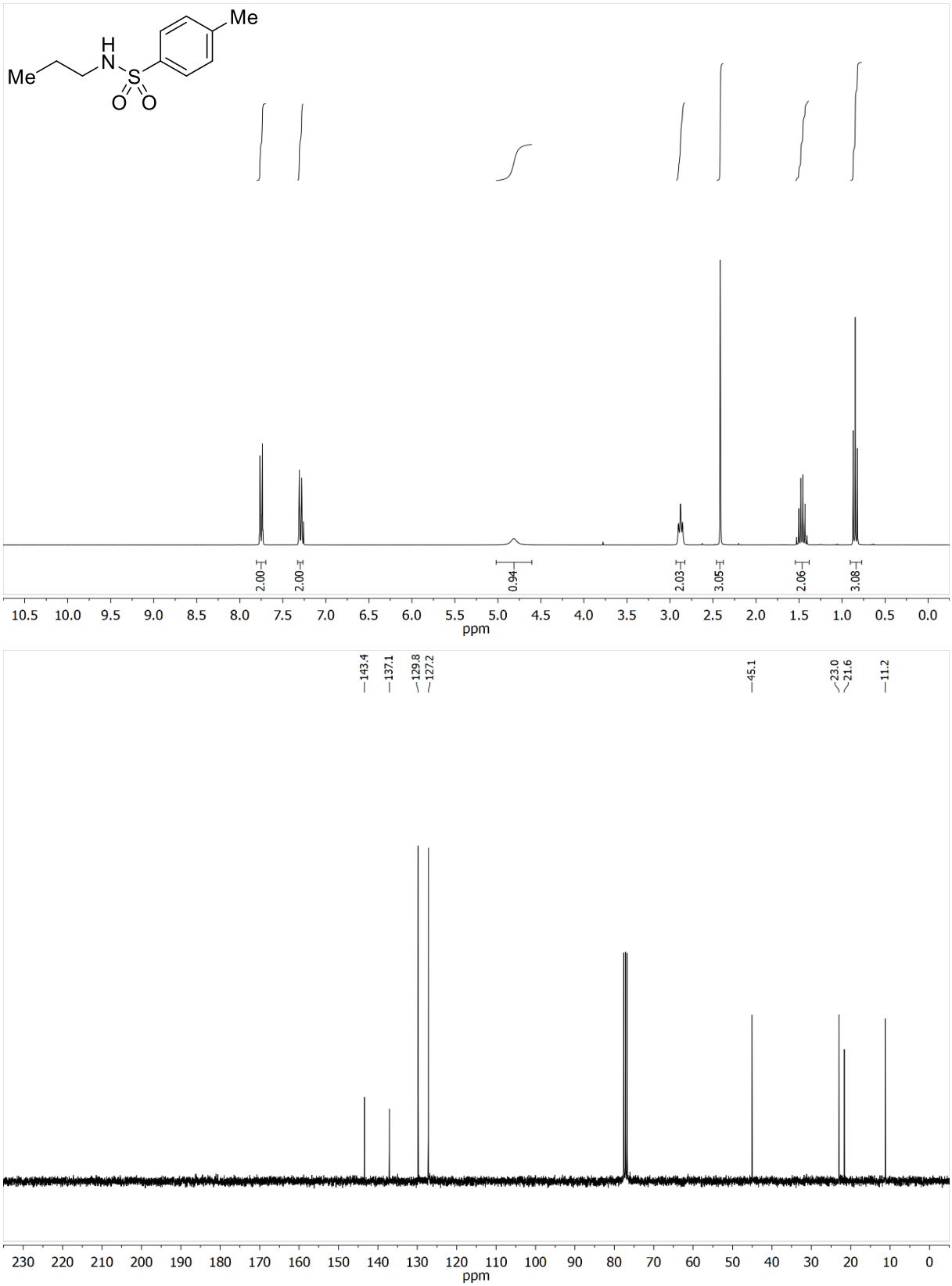
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: DMSO-d_6.

_N_-isopropyl-4-methylbenzenesulfonamide (2bf)



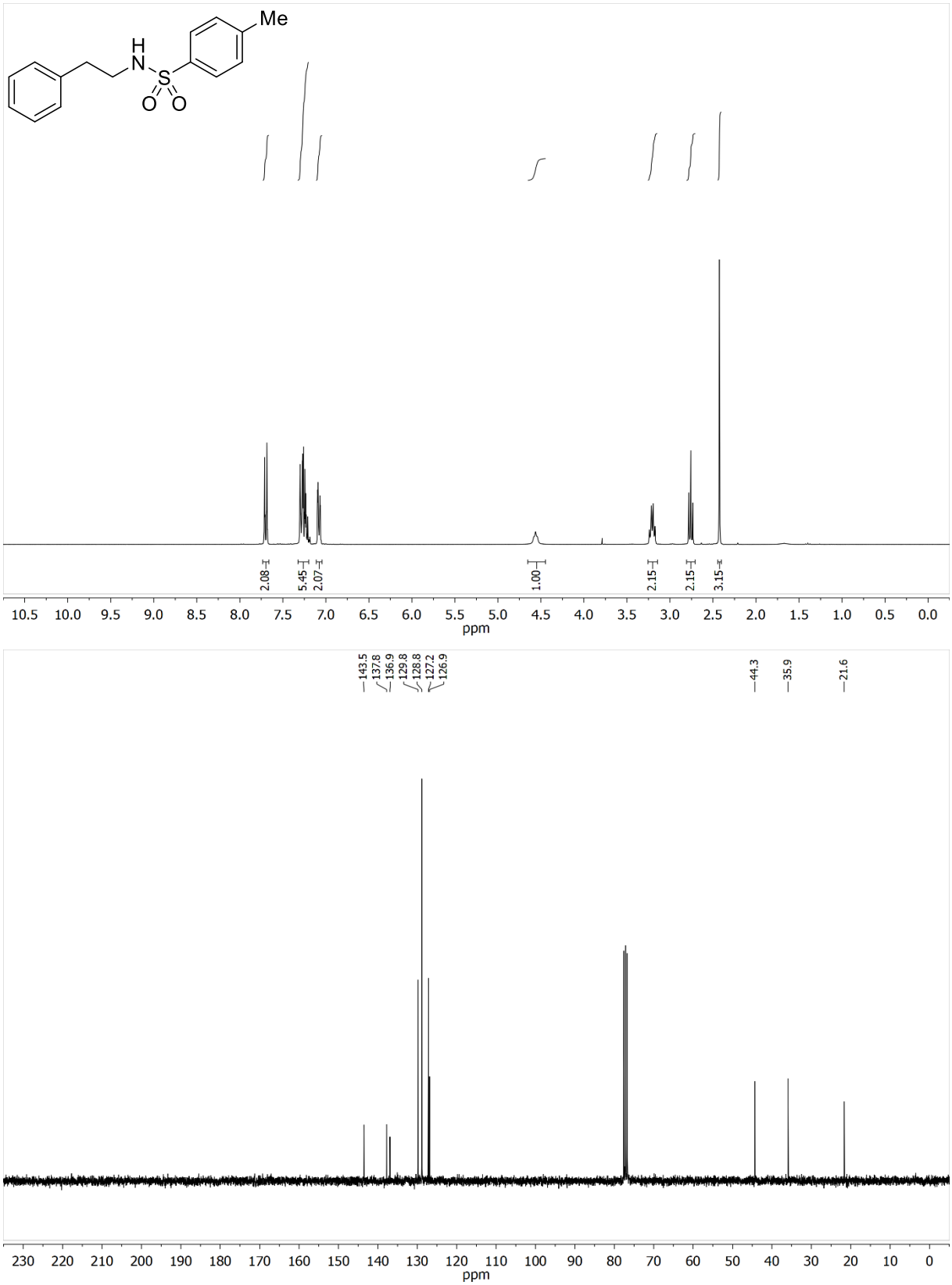
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

4-methyl-*N*-propylbenzenesulfonamide (2bg)



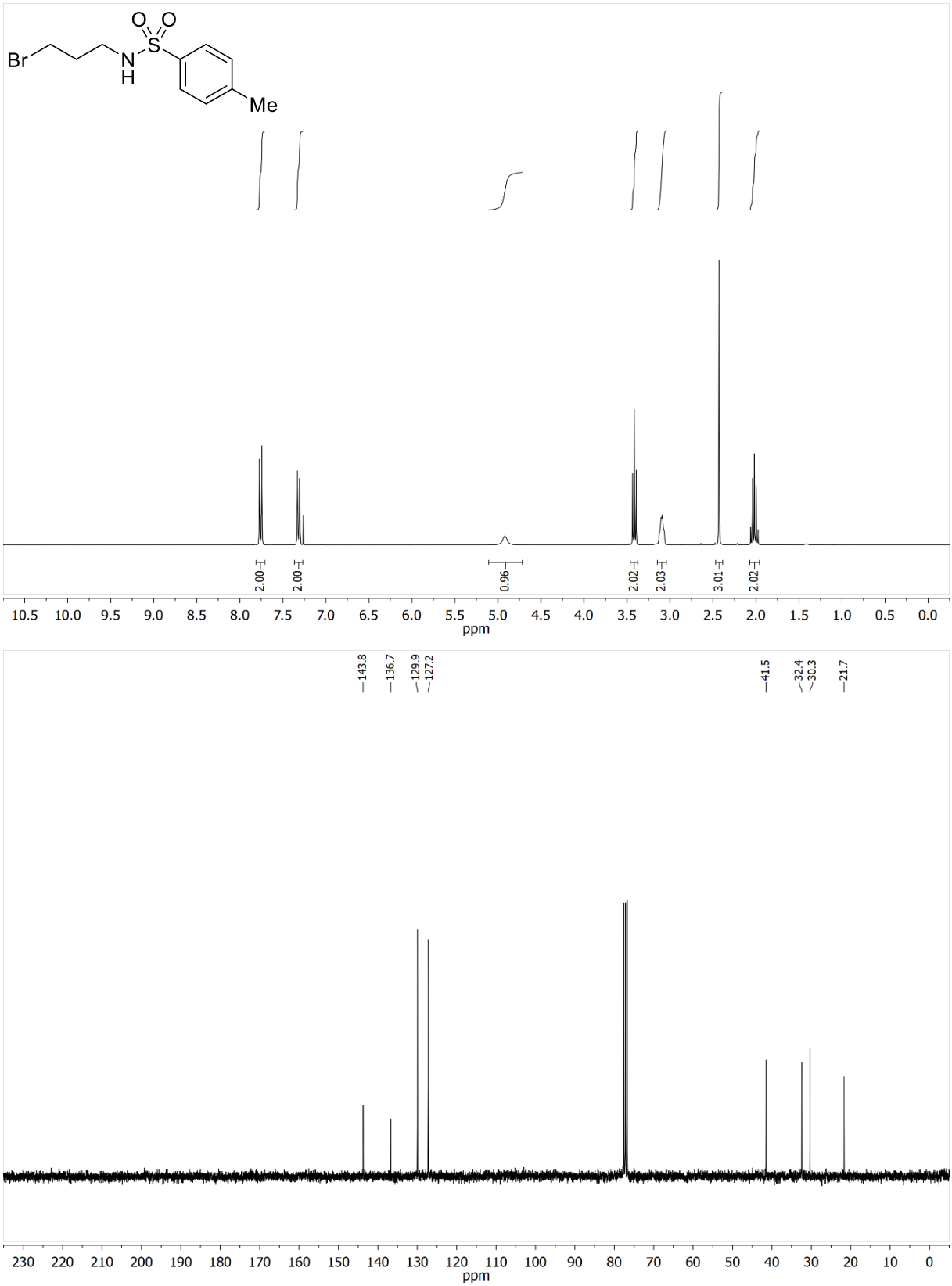
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

4-methyl-*N*-phenethylbenzenesulfonamide (2bh)



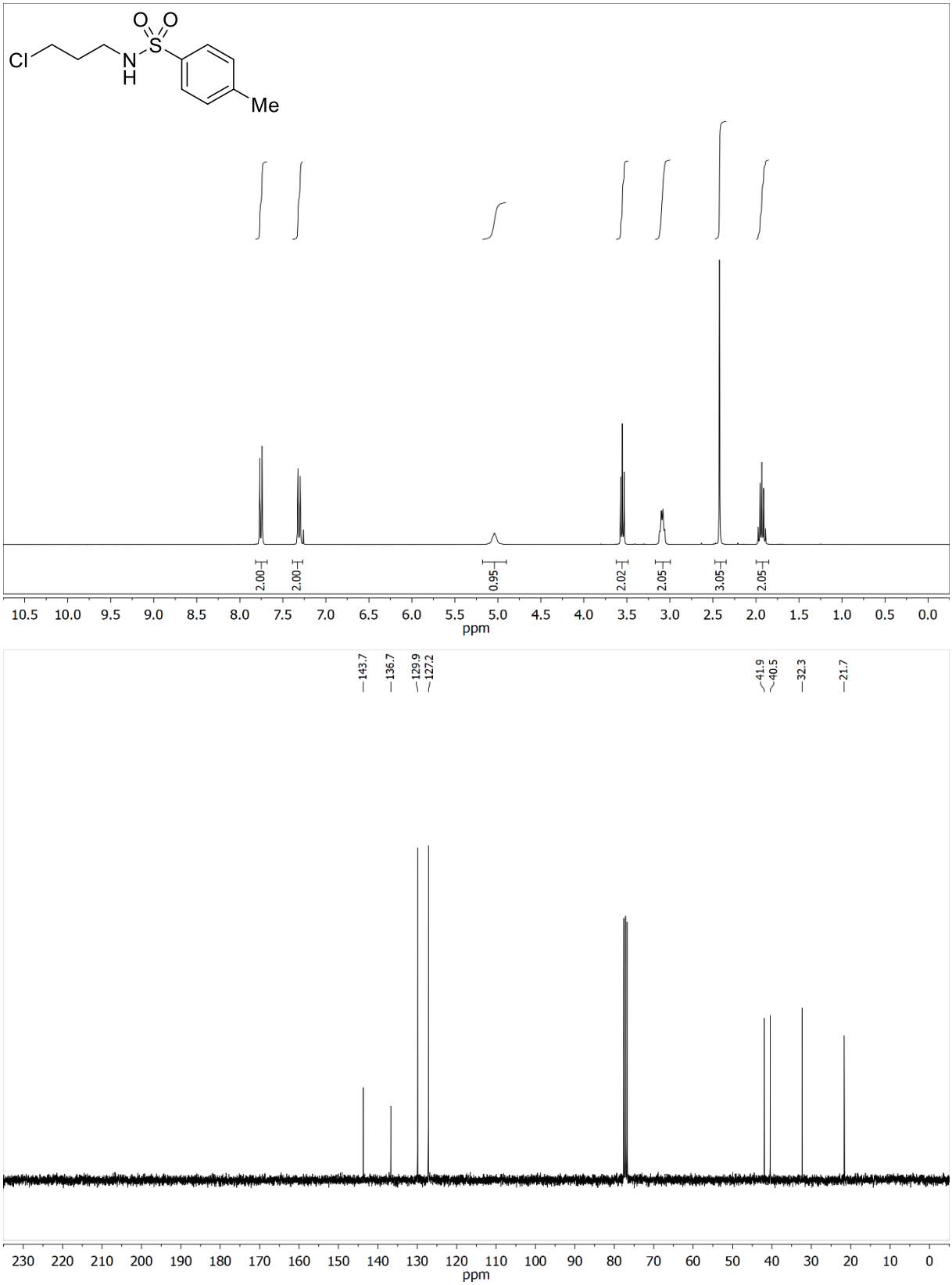
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(3-bromopropyl)-4-methylbenzenesulfonamide (2bi)



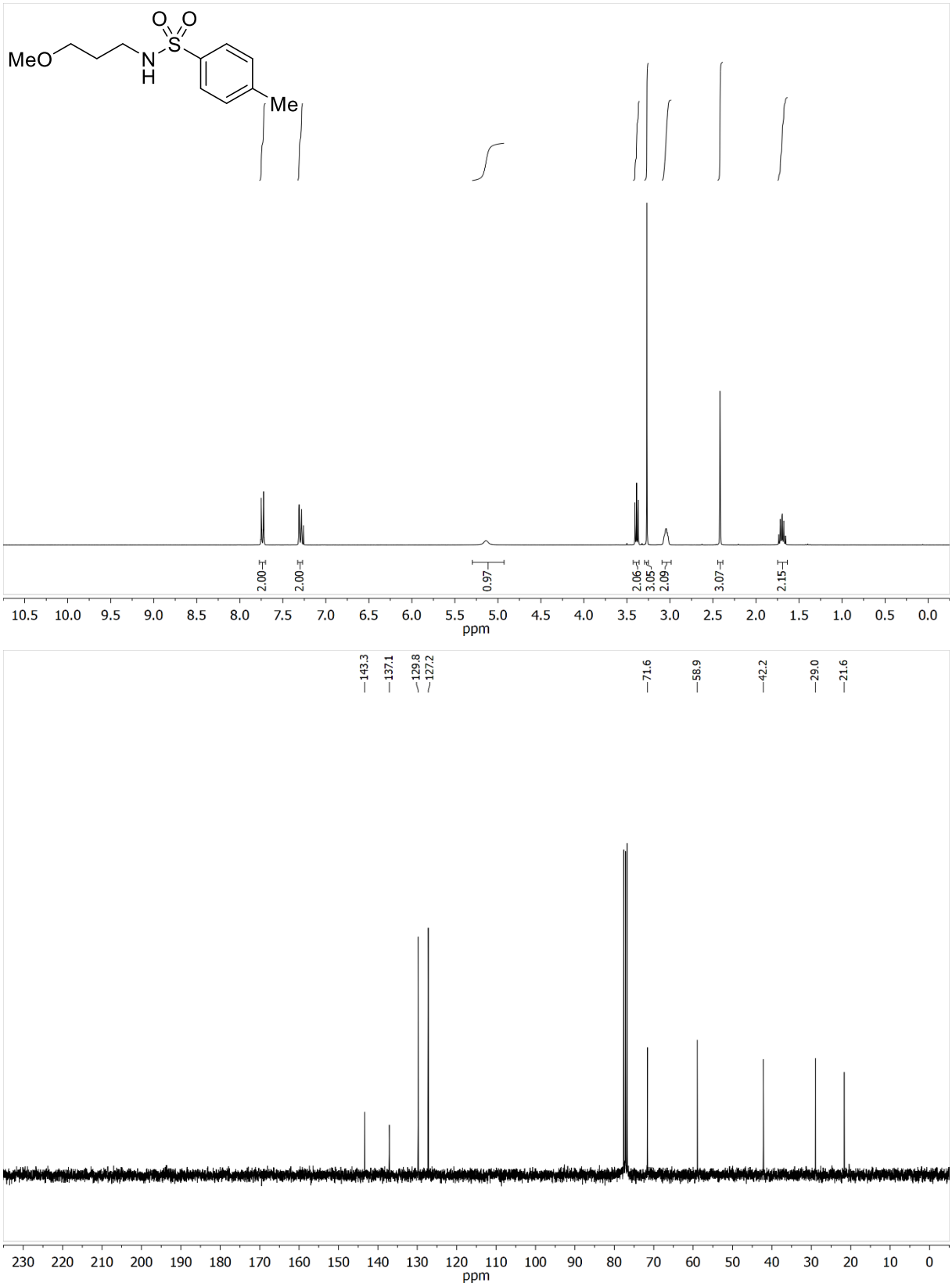
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(3-chloropropyl)-4-methylbenzenesulfonamide (2bj)



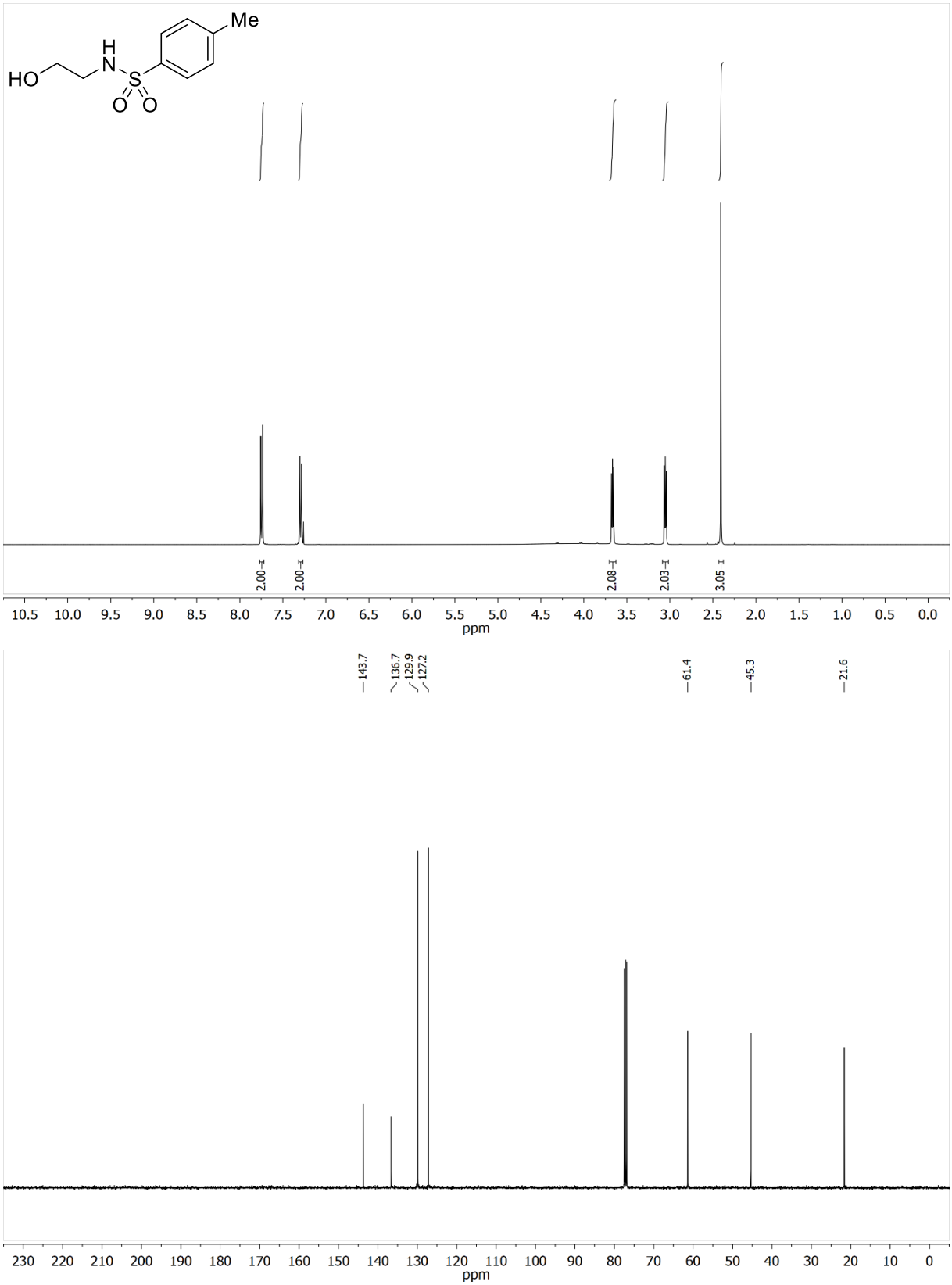
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(3-methoxypropyl)-4-methylbenzenesulfonamide (2bk)



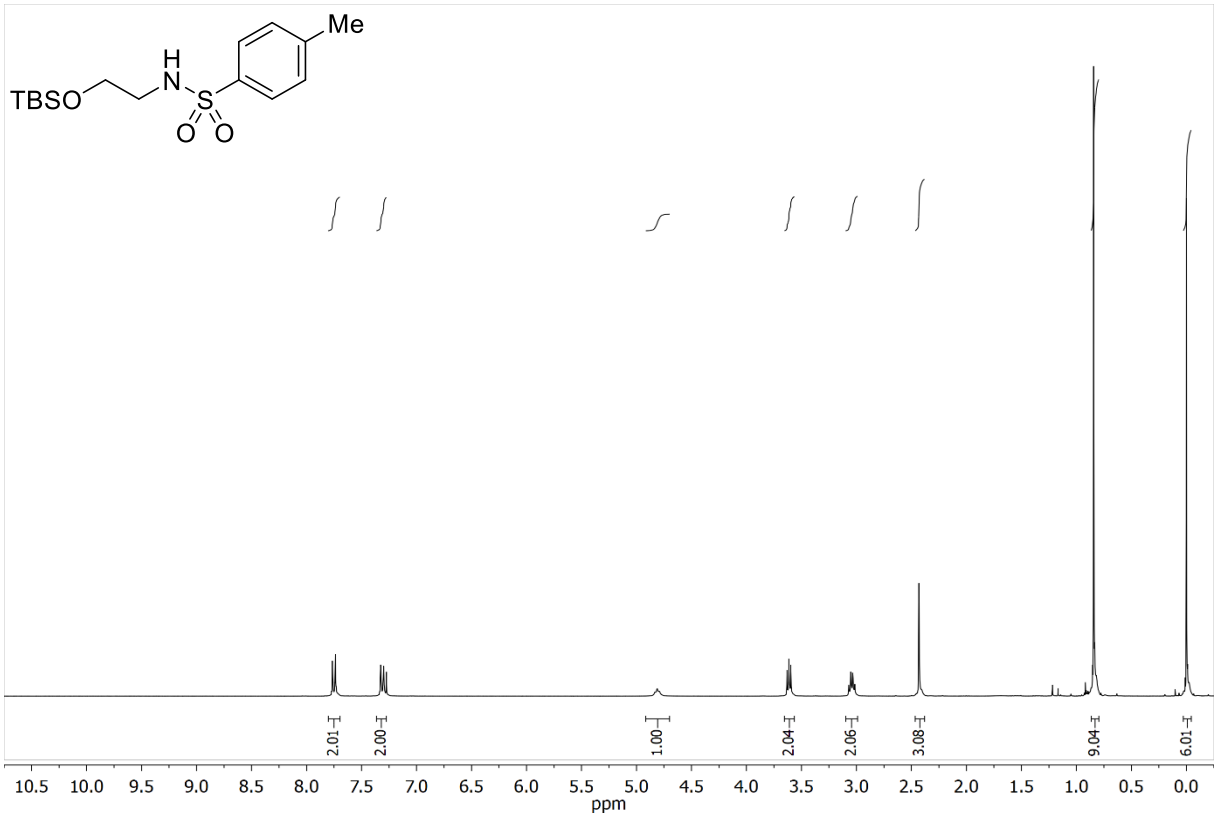
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

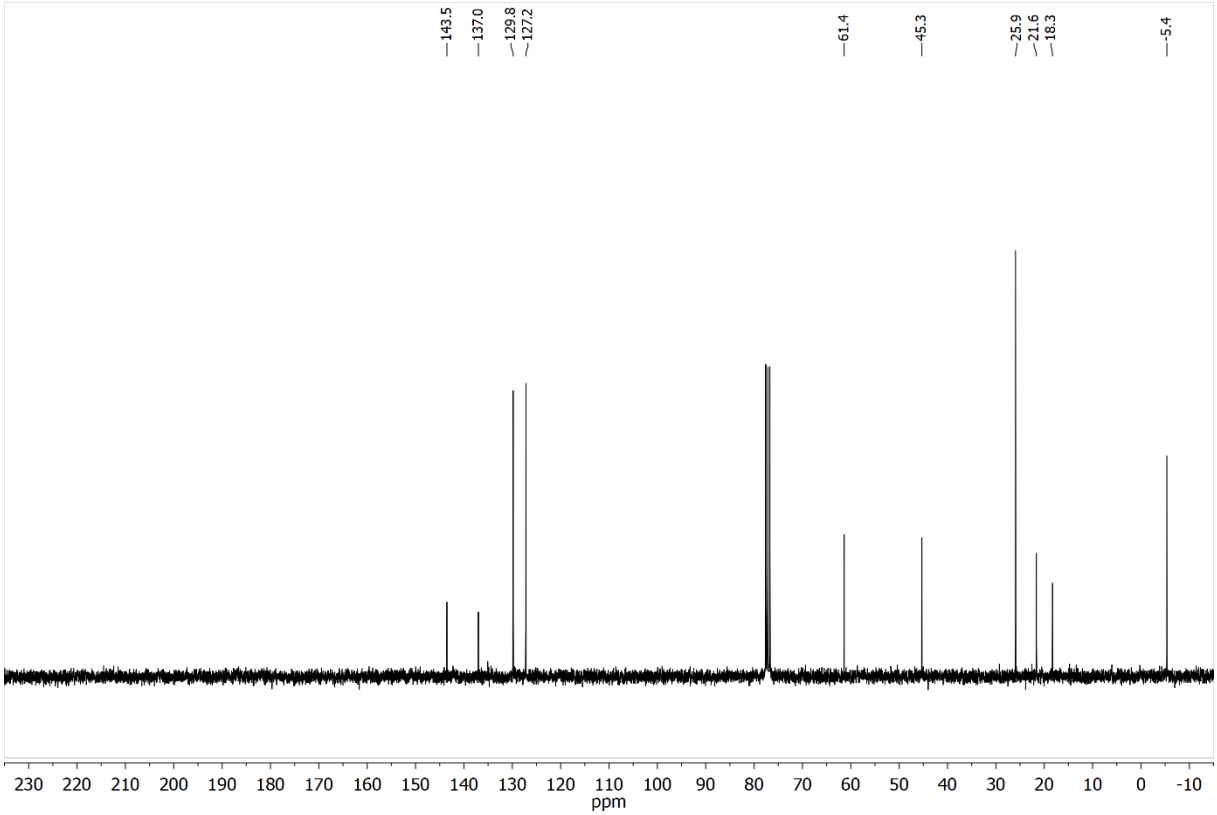
_N_-(2-hydroxyethyl)-4-methylbenzenesulfonamide (2`bl)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

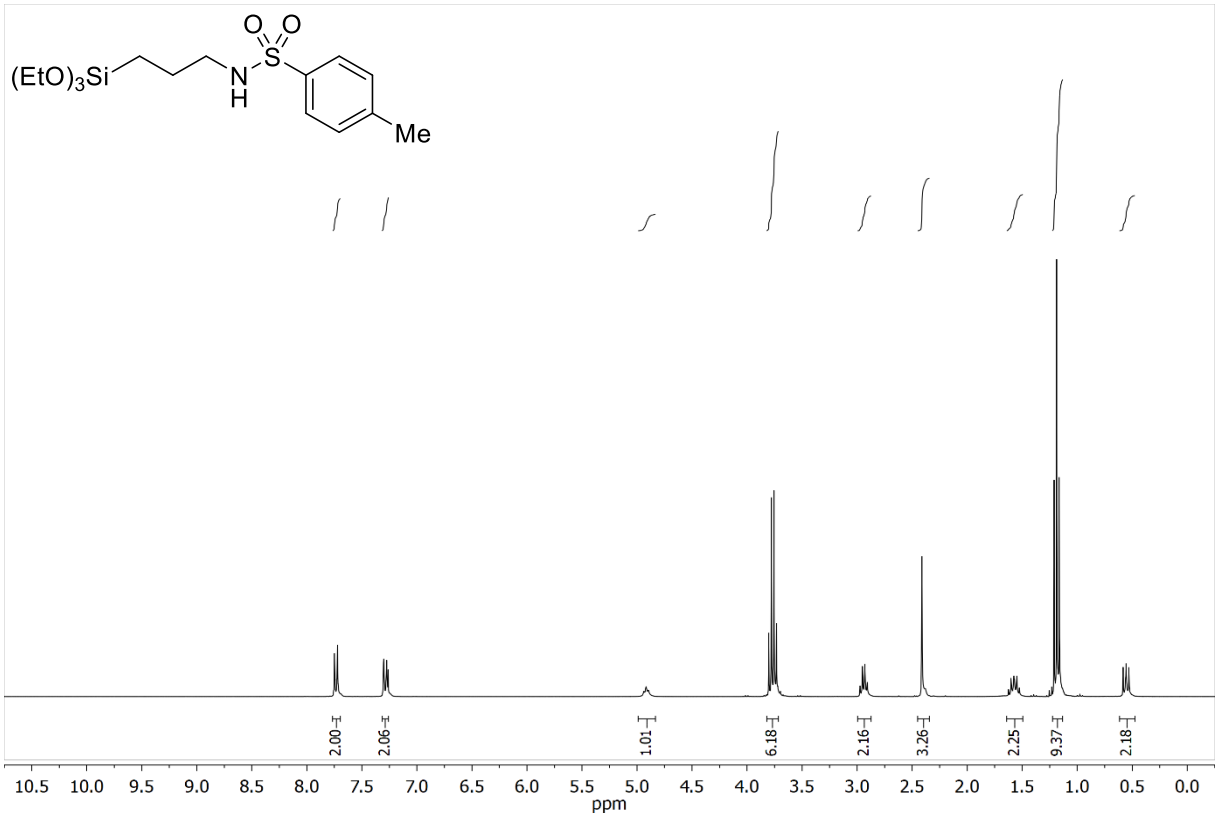
_N_-(2-((_tert_-butyldimethylsilyl)oxy)ethyl)-4-methylbenzenesulfonamide (2bl)

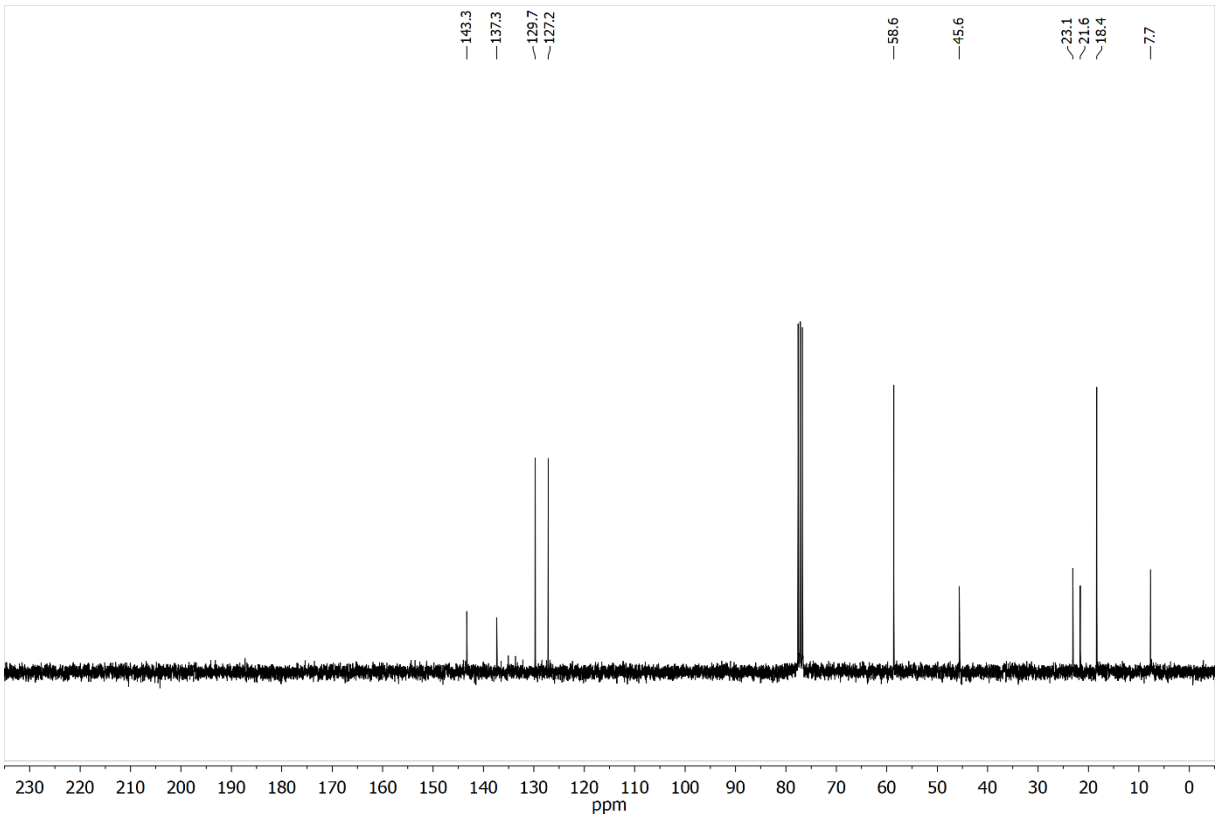




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

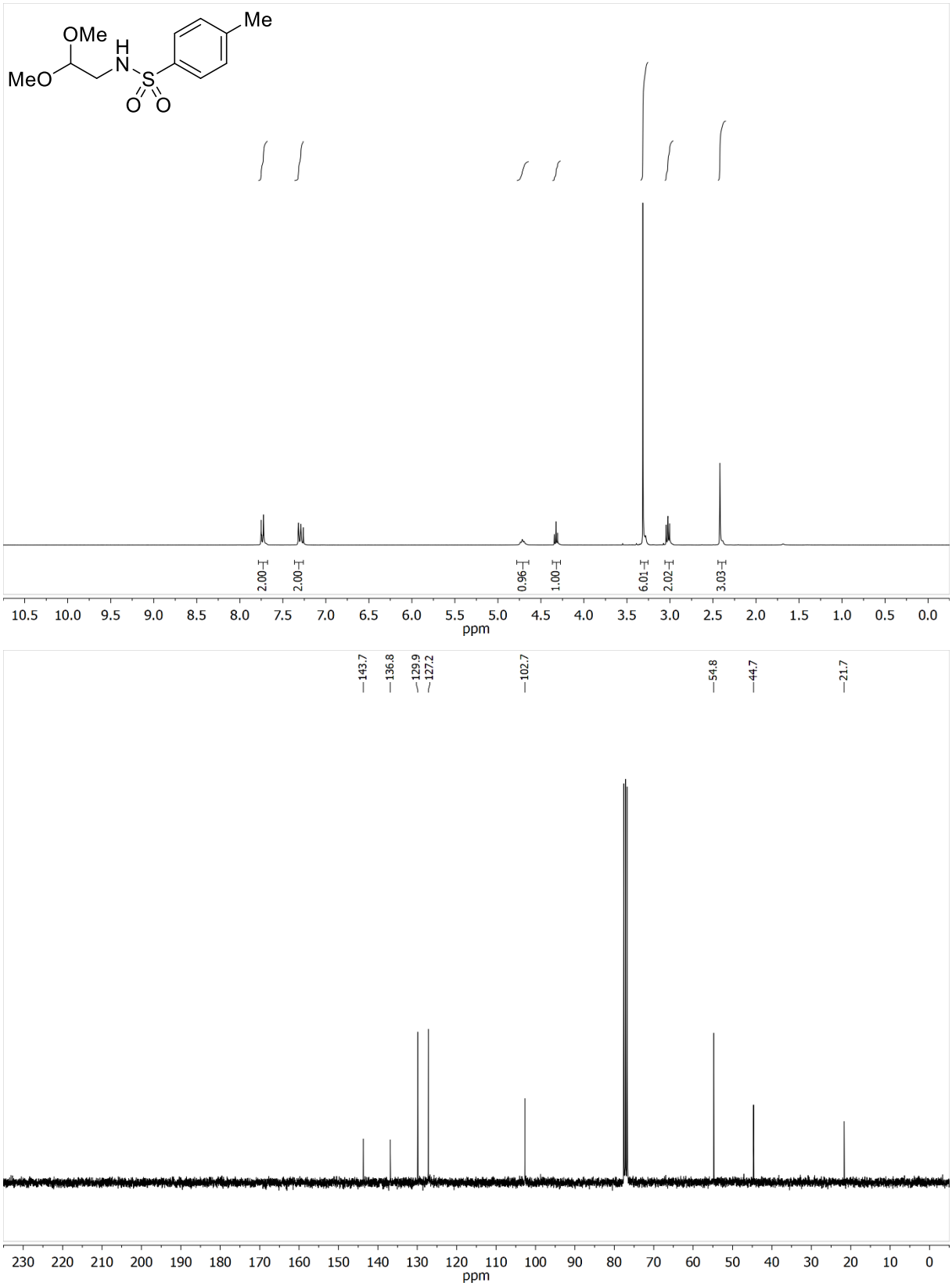
4-methyl-*N*-(3-(triethoxysilyl)propyl)benzenesulfonamide (2bm)





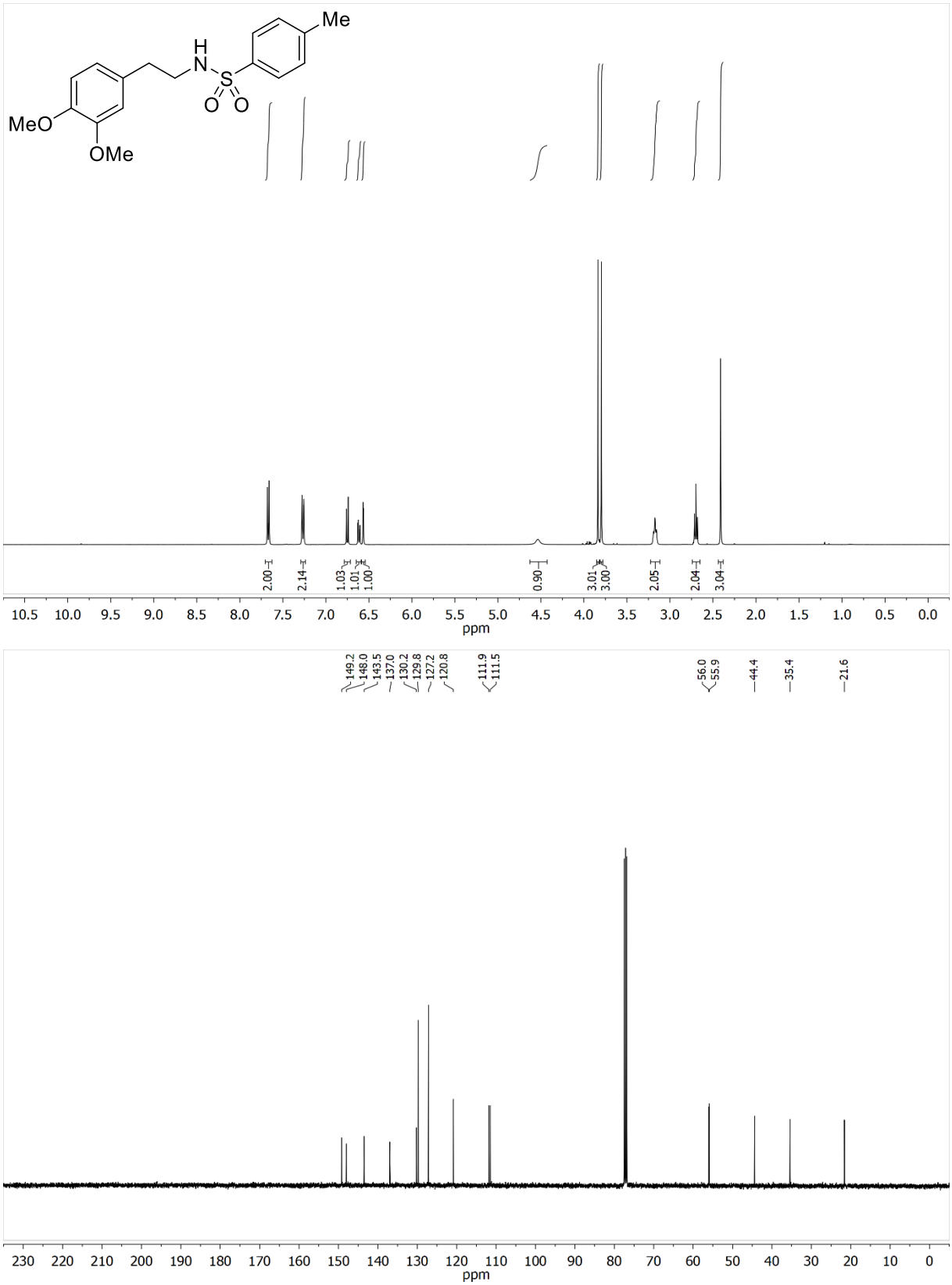
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2,2-dimethoxyethyl)-4-methylbenzenesulfonamide (2bn)



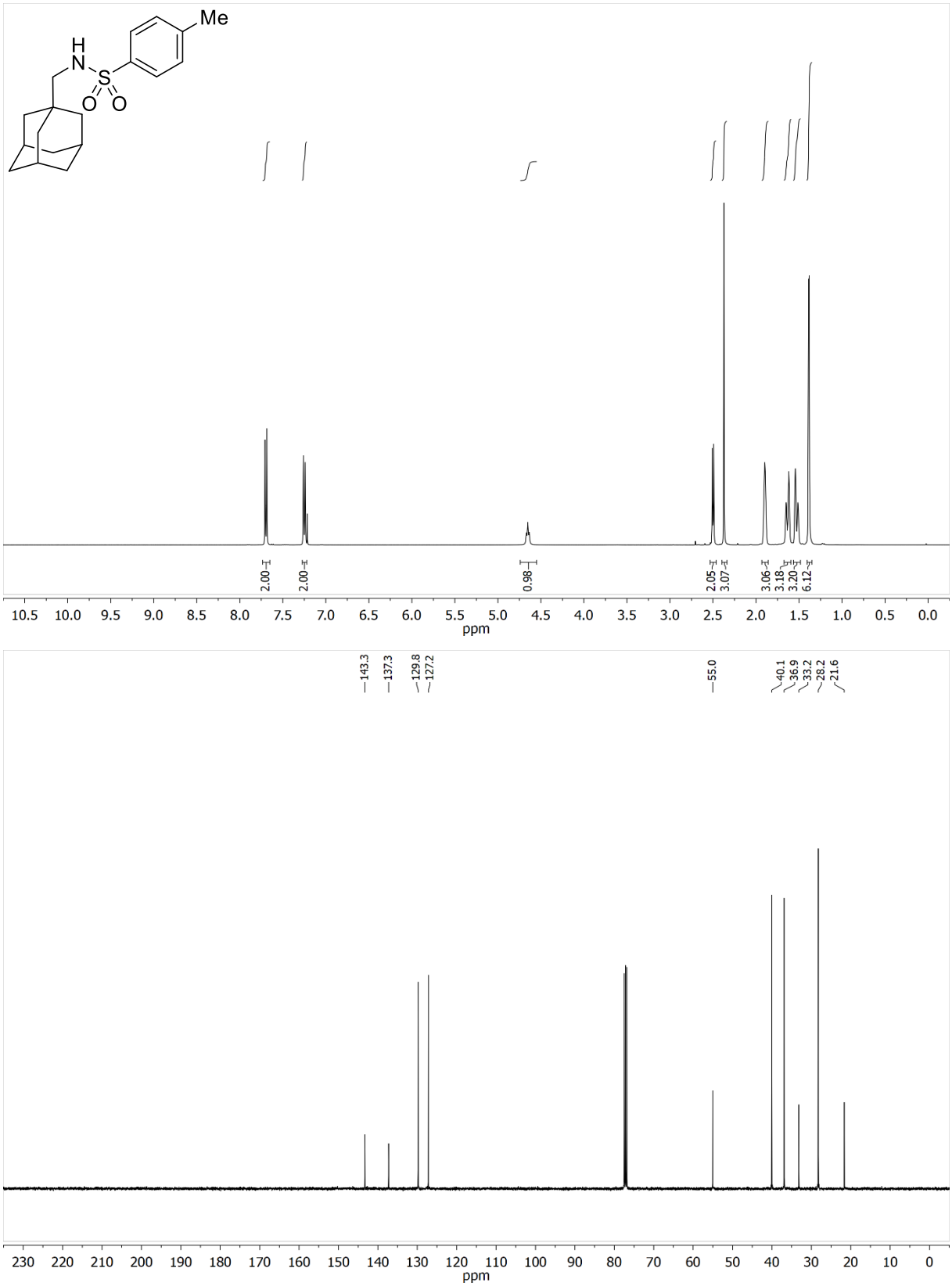
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(3,4-dimethoxyphenethyl)-4-methylbenzenesulfonamide (2bo)



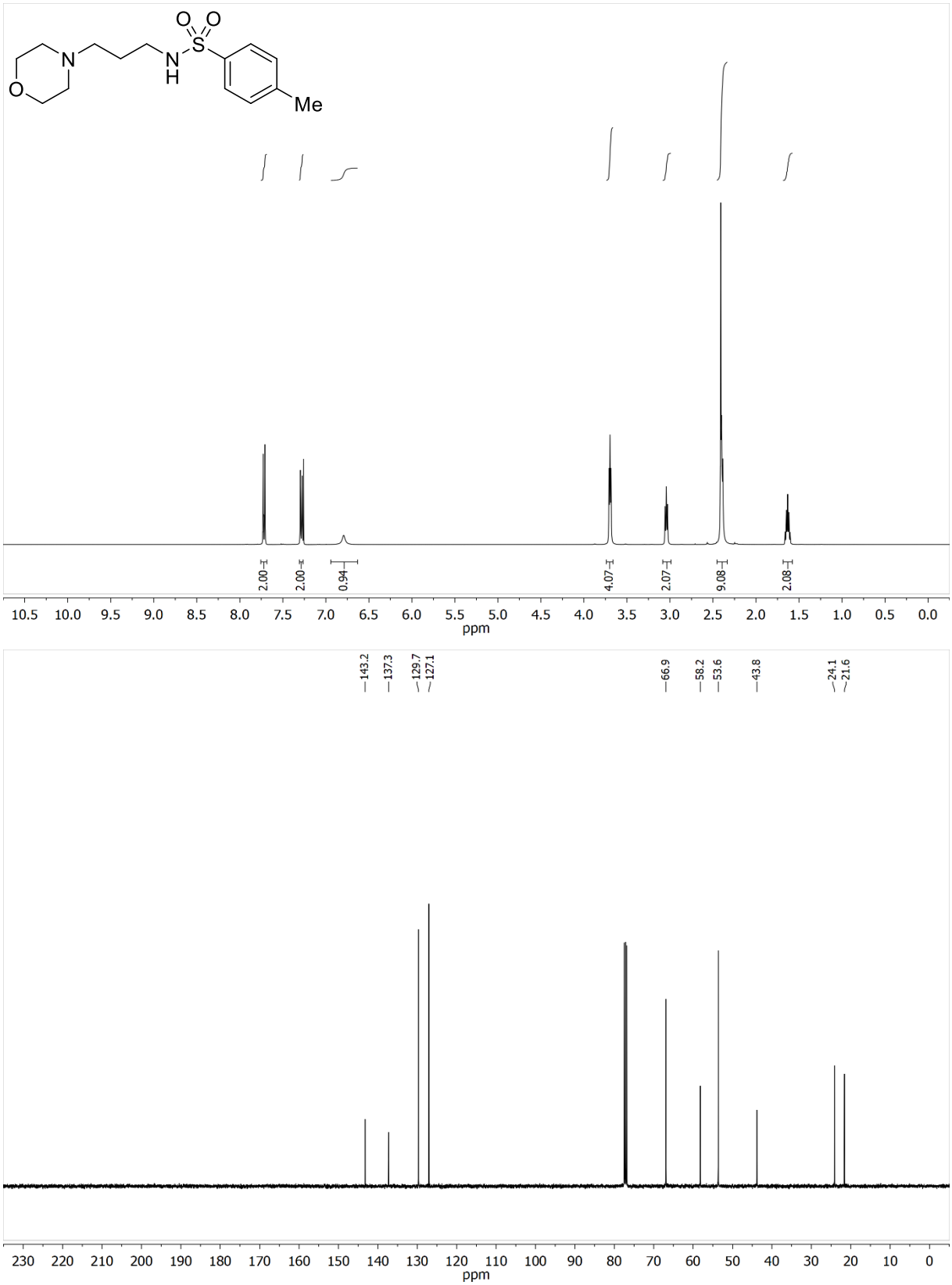
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(((3_r_,5_r_,7_r_)-adamantan-1-yl)methyl)-4-methylbenzenesulfonamide (2bp)



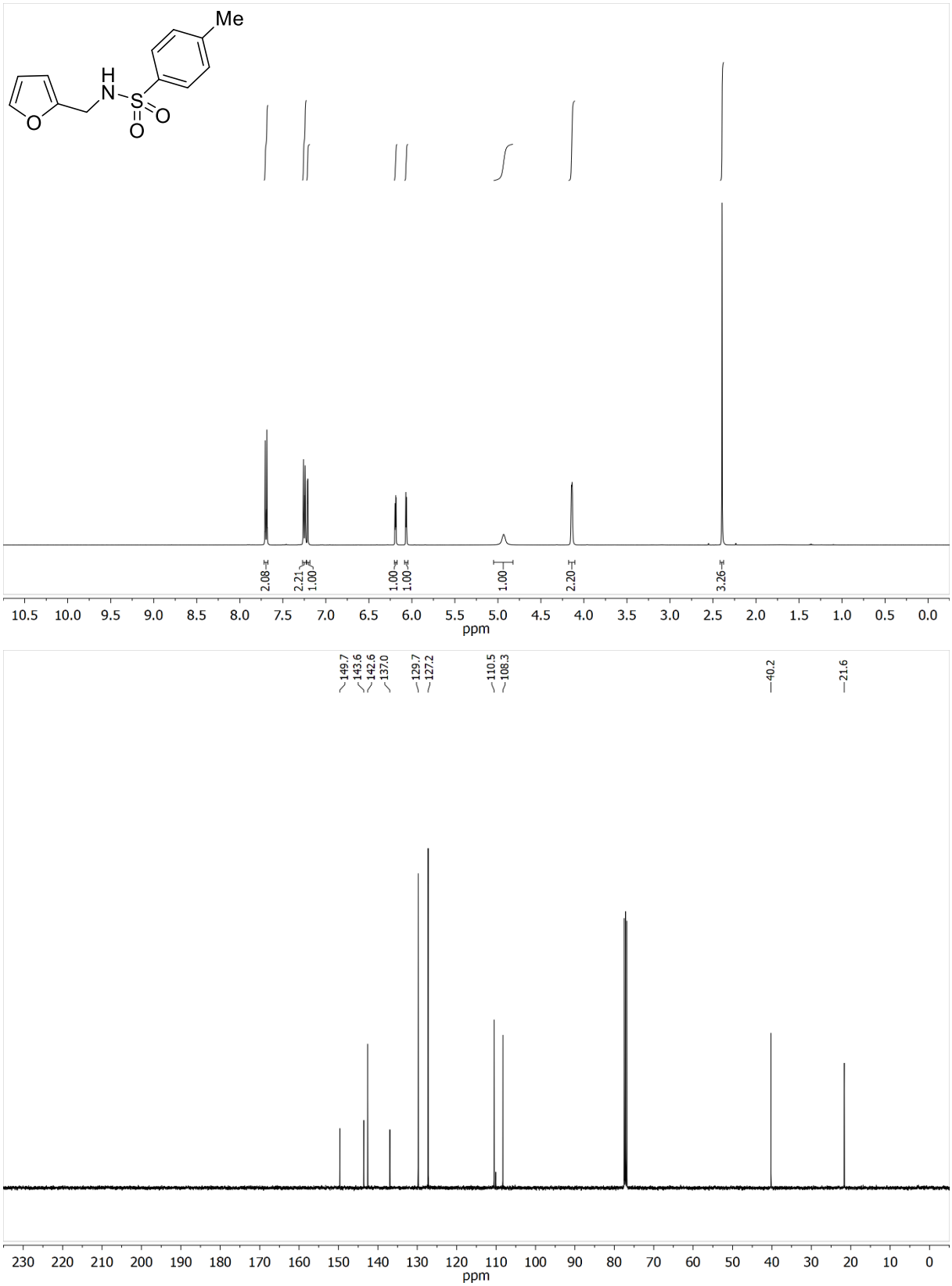
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

4-methyl-*N*-(3-morpholinopropyl)benzenesulfonamide (2bq)



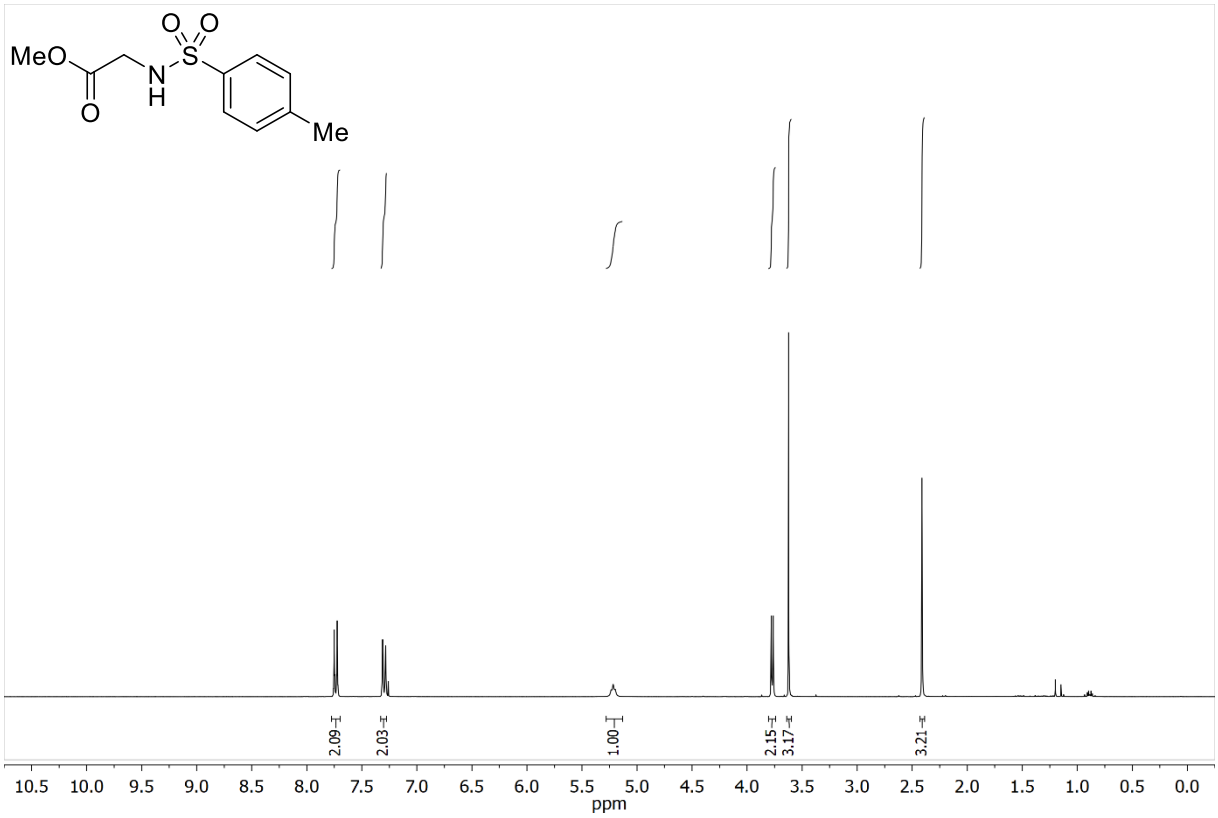
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

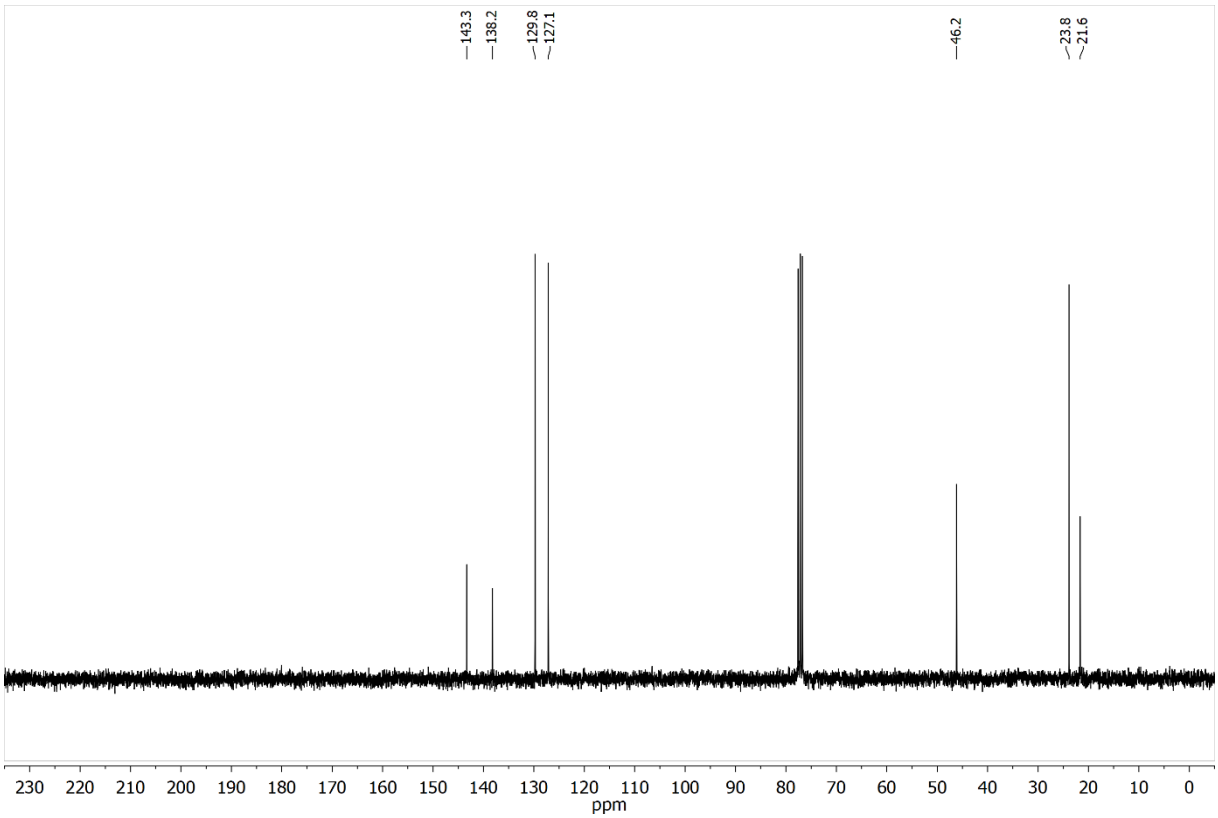
_N_-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (2br)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

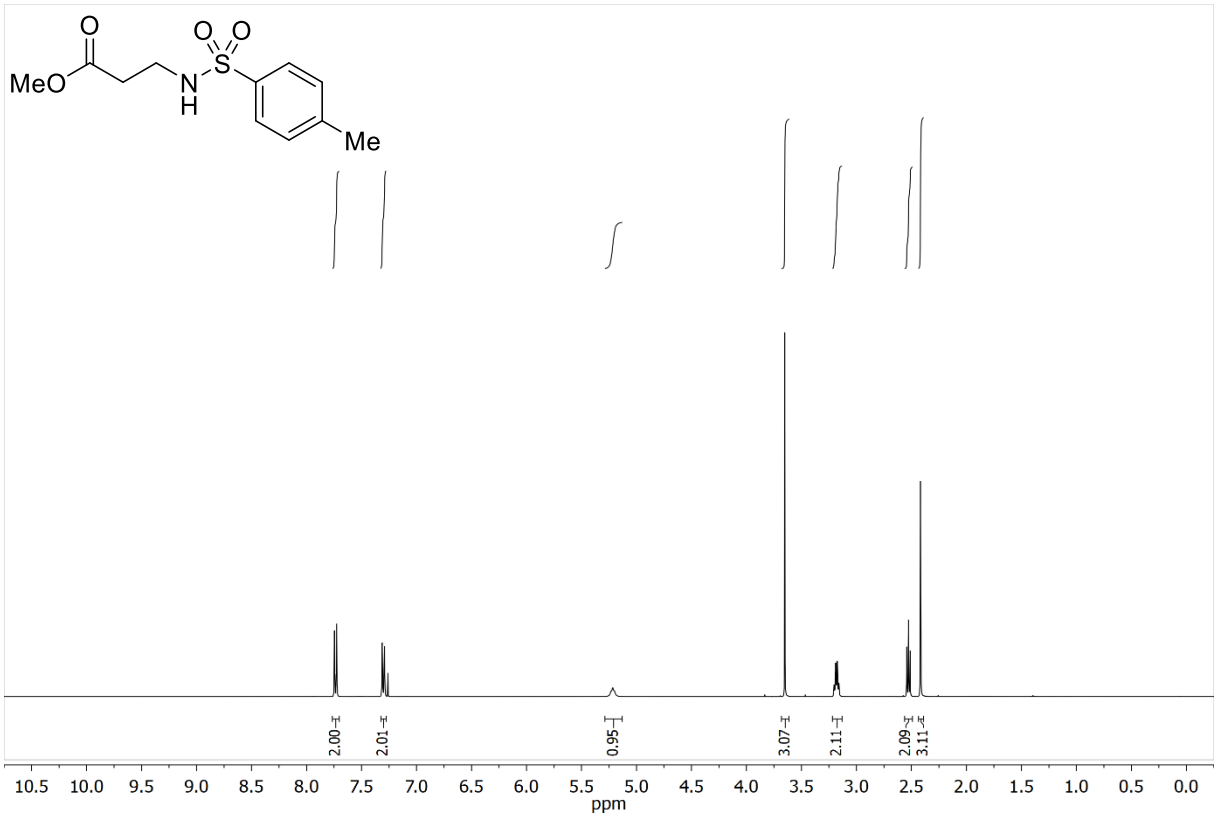
methyl tosylglycinate (2bs)

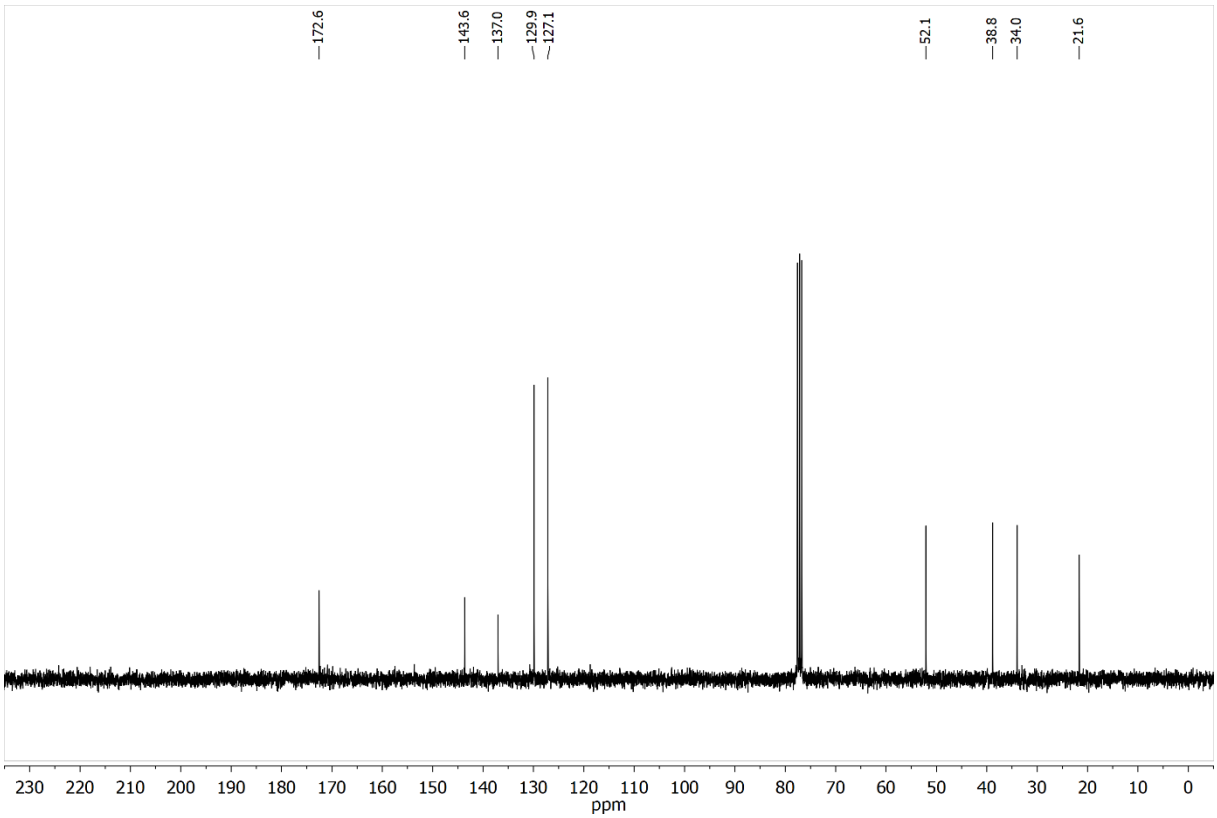




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

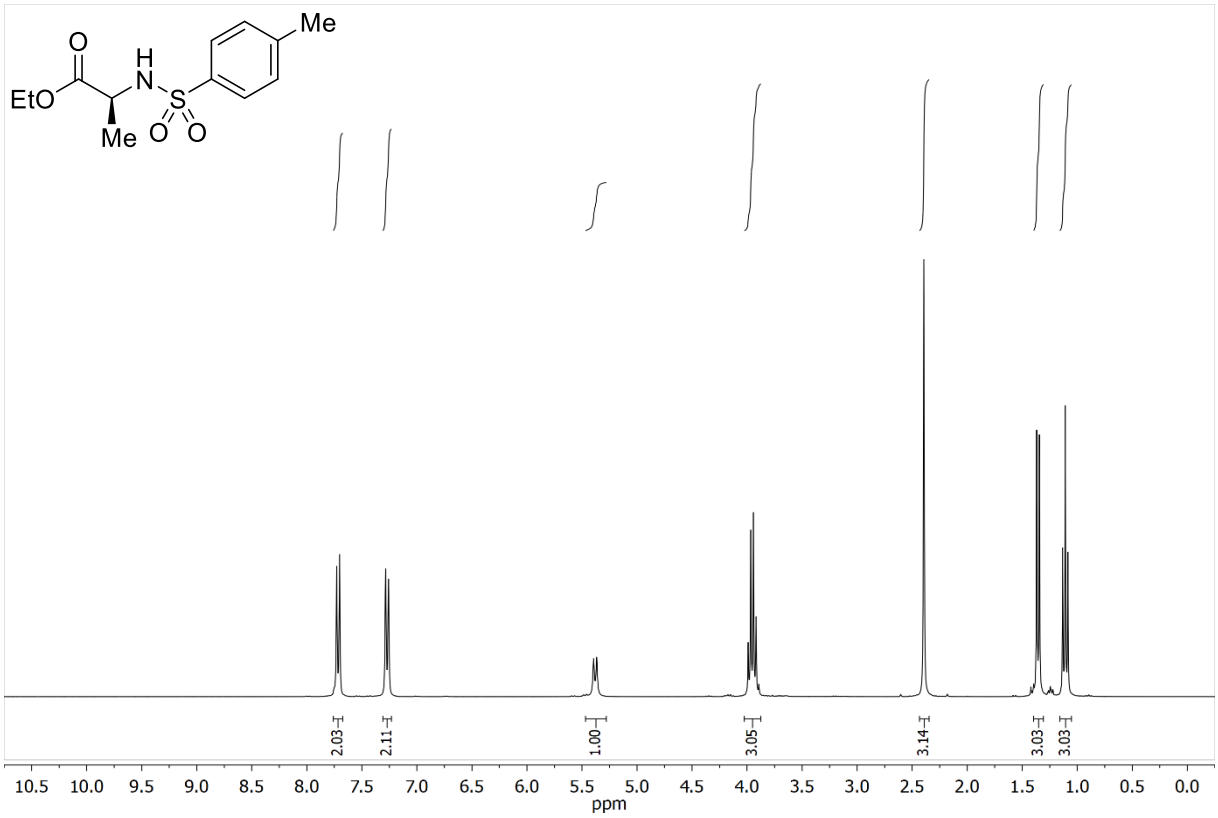
methyl 3-((4-methylphenyl)sulfonamido)propanoate (2bt)

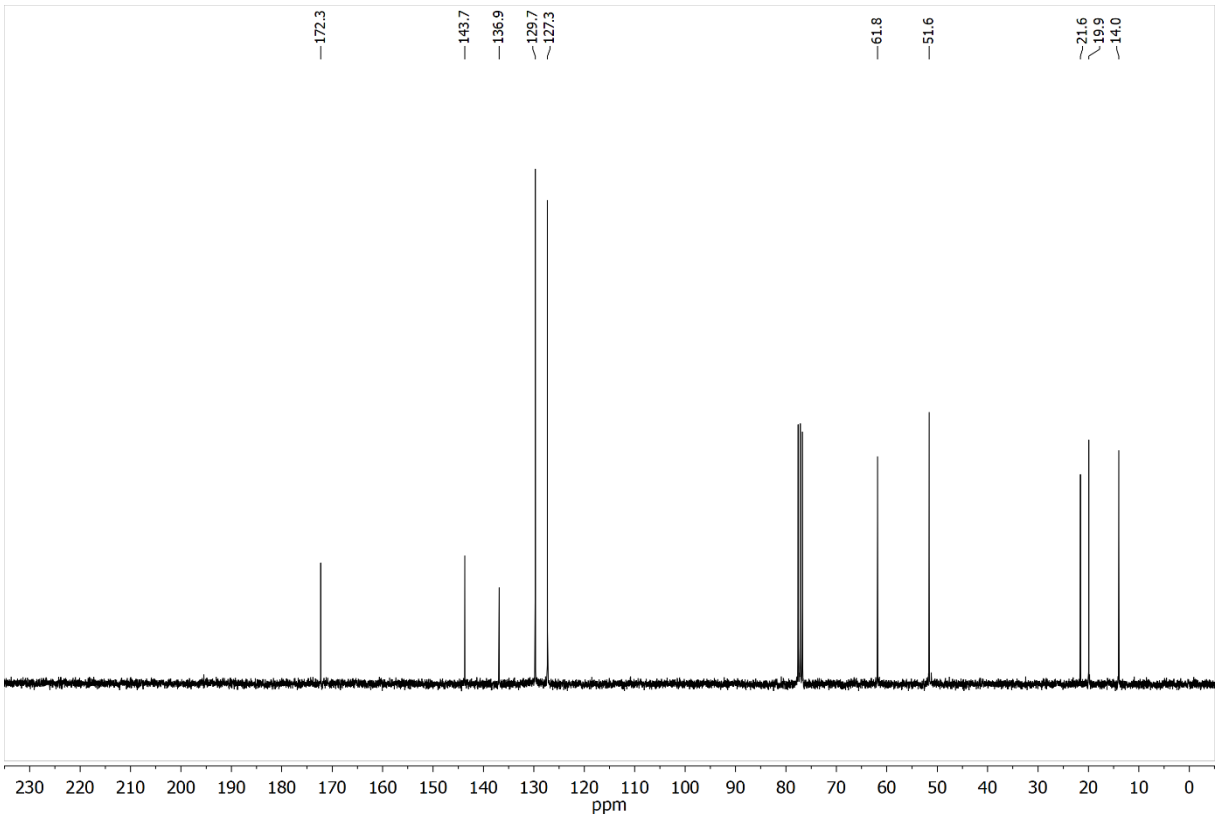




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

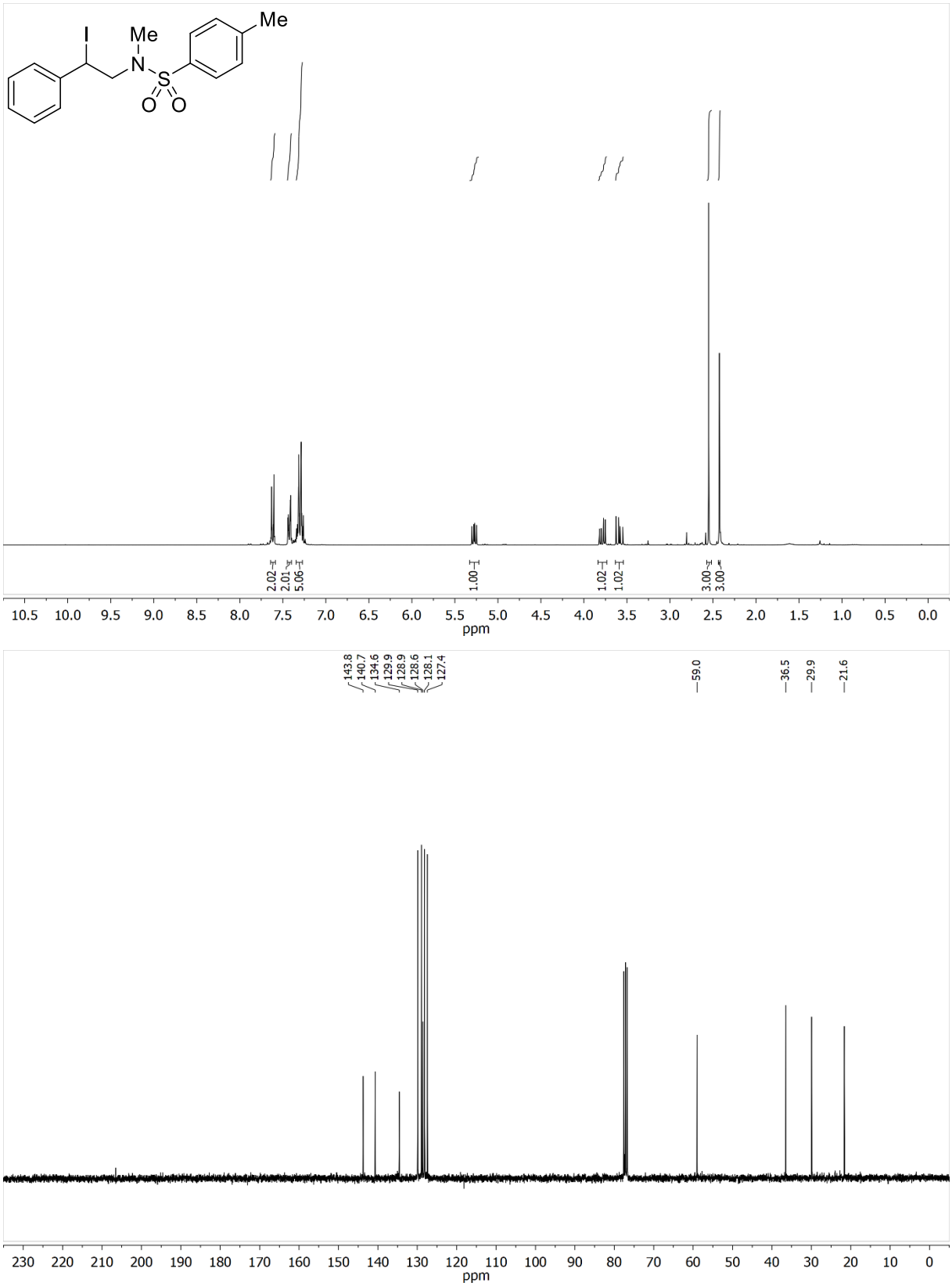
ethyl tosyl-*L*-alaninate (2bu)





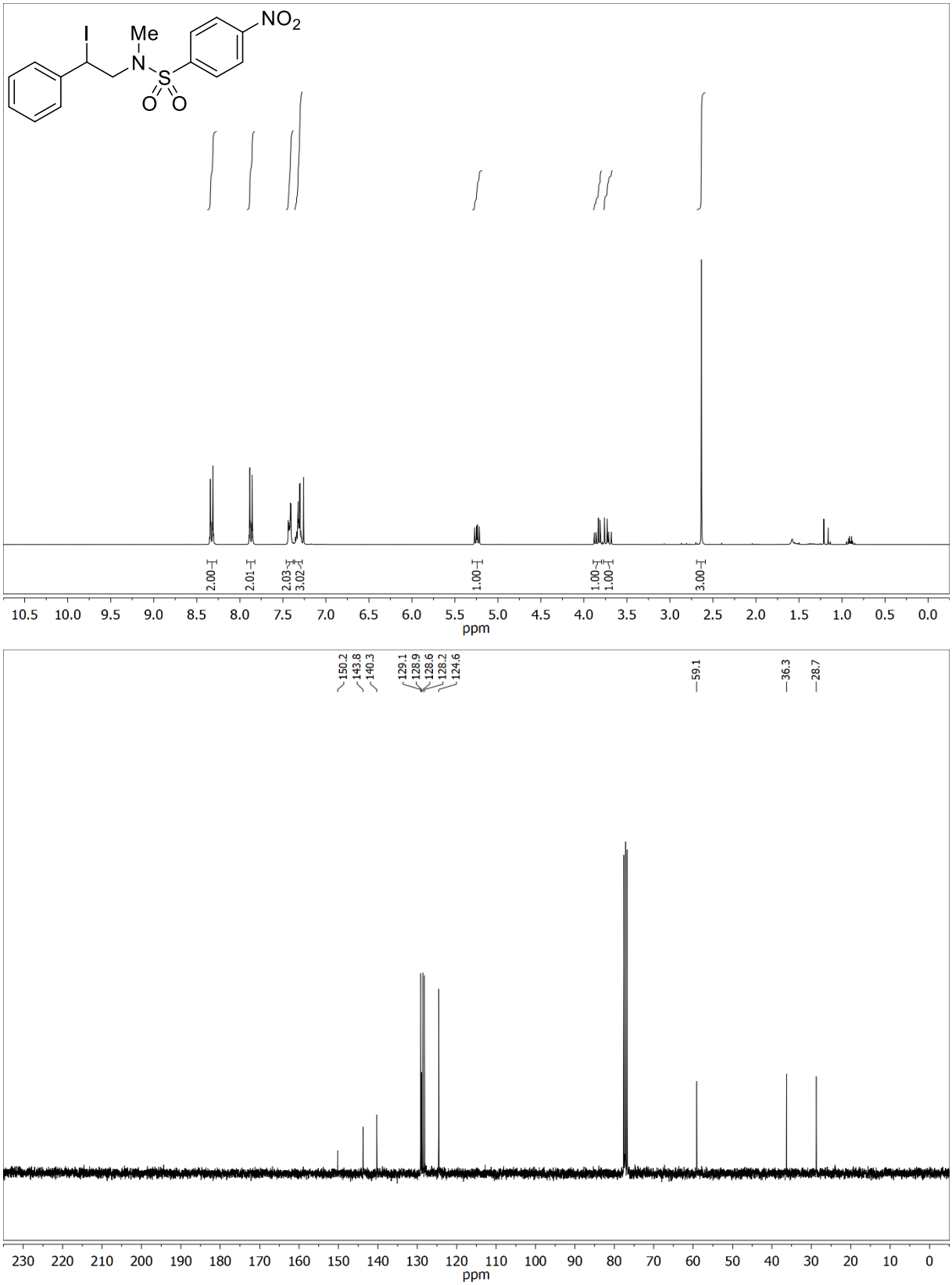
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-2-phenylethyl)-_N_,4-dimethylbenzenesulfonamide (15a)



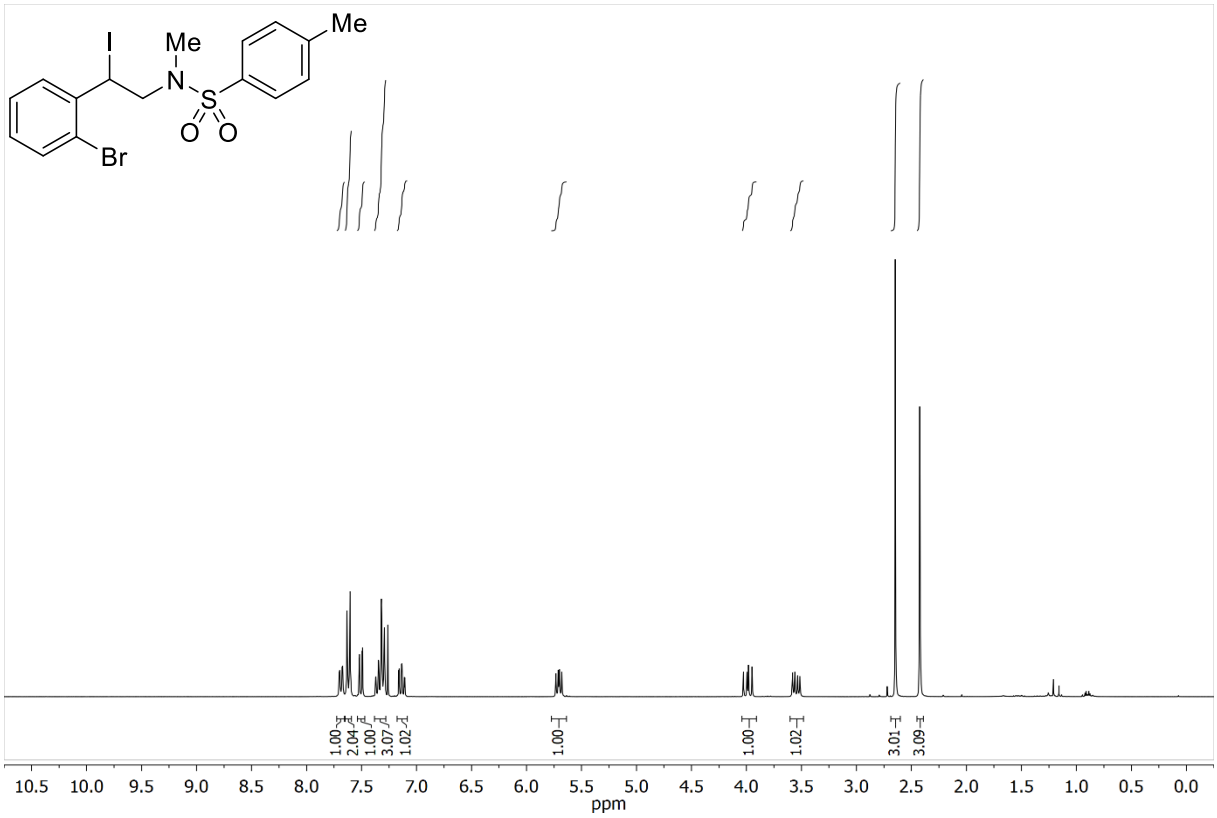
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

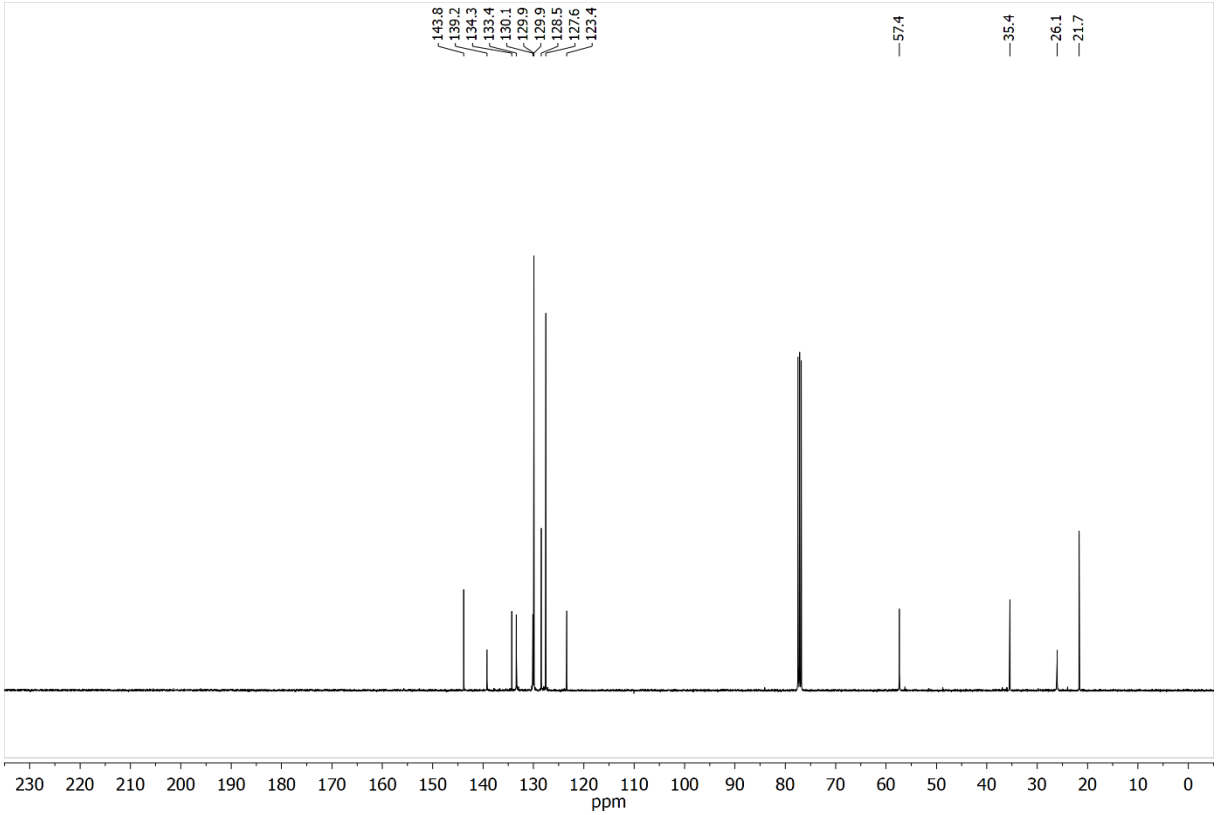
_N_-(2-iodo-2-phenylethyl)-_N_-methyl-4-nitrobenzenesulfonamide (Ns-15a)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

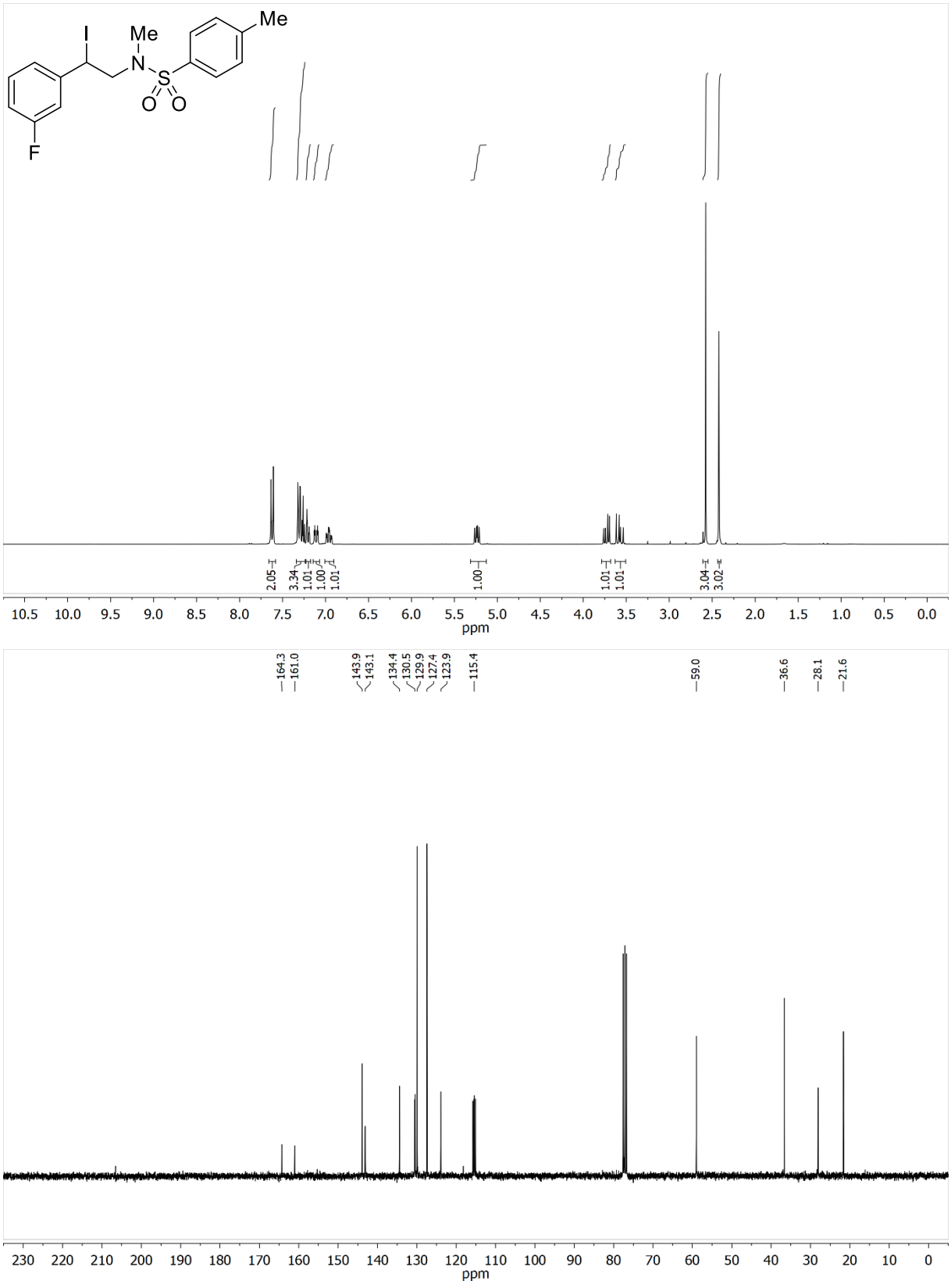
_N_-(2-(2-bromophenyl)-2-iodoethyl)-_N_,4-dimethylbenzenesulfonamide (15b)



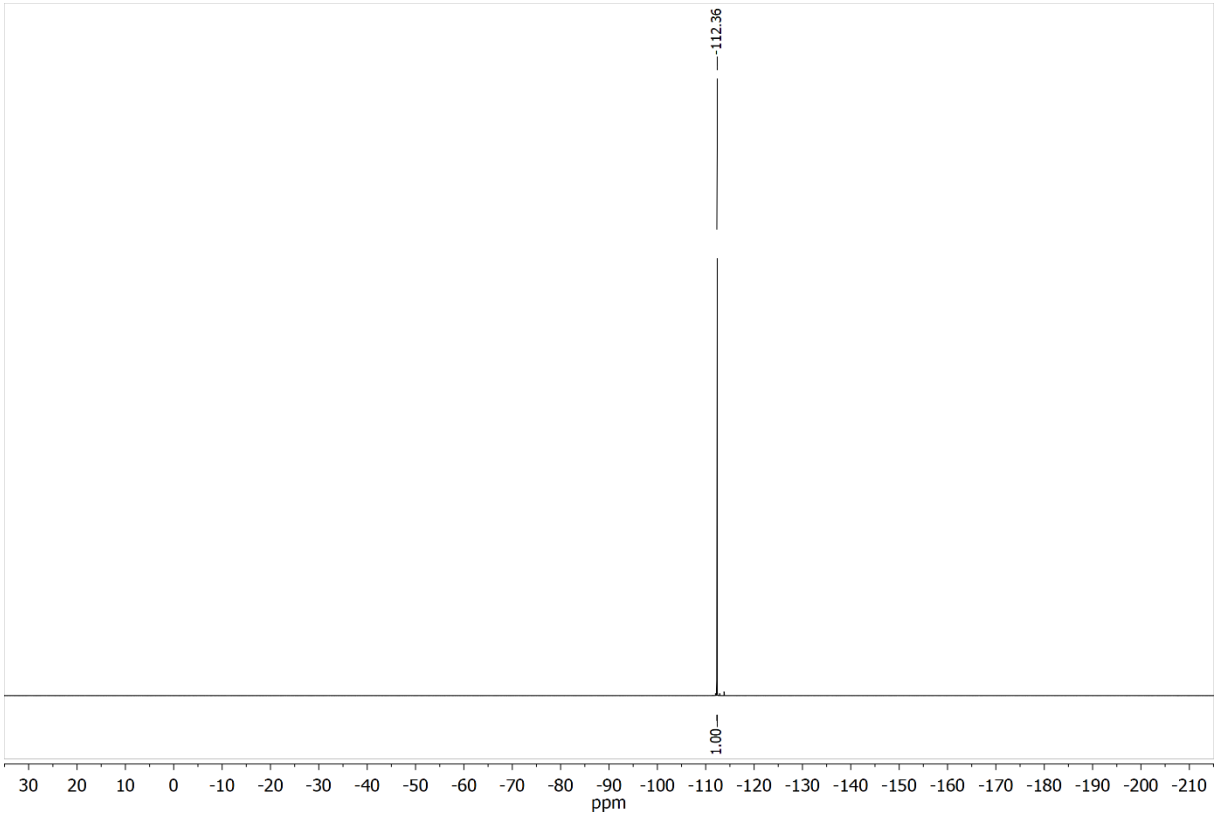


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-(3-fluorophenyl)-2-iodoethyl)-_N_,4-dimethylbenzenesulfonamide (15c)

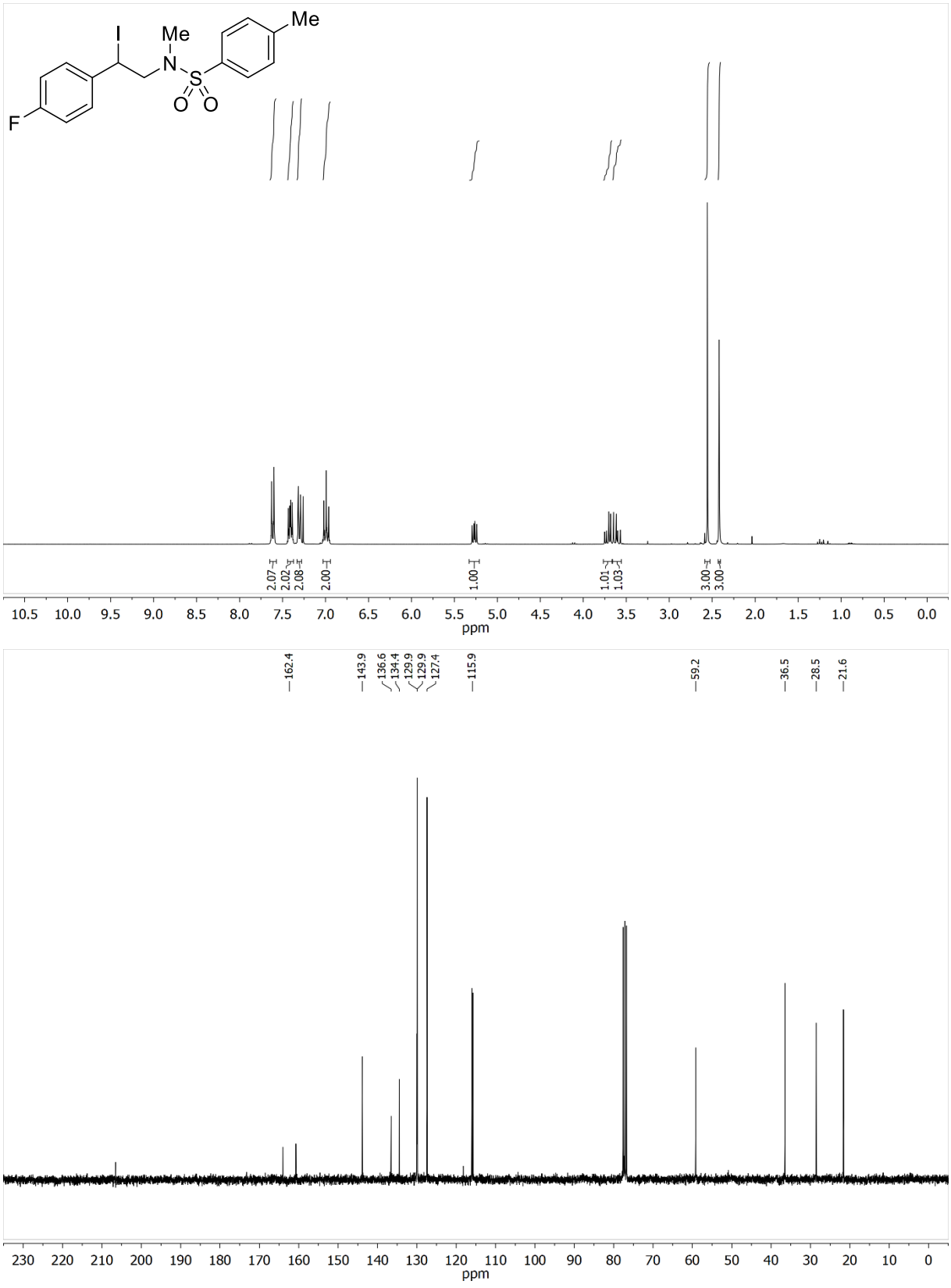


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

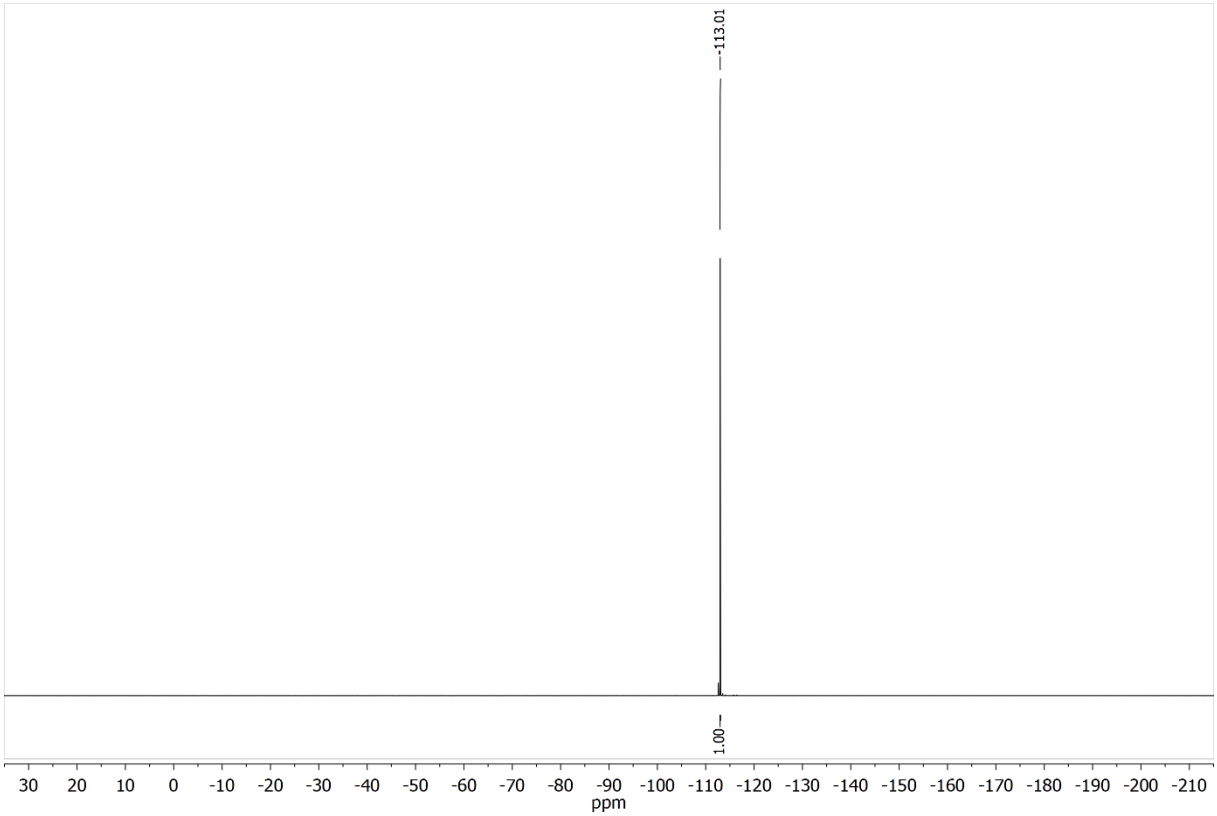


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-(4-fluorophenyl)-2-iodoethyl)-_N_,4-dimethylbenzenesulfonamide (15d)

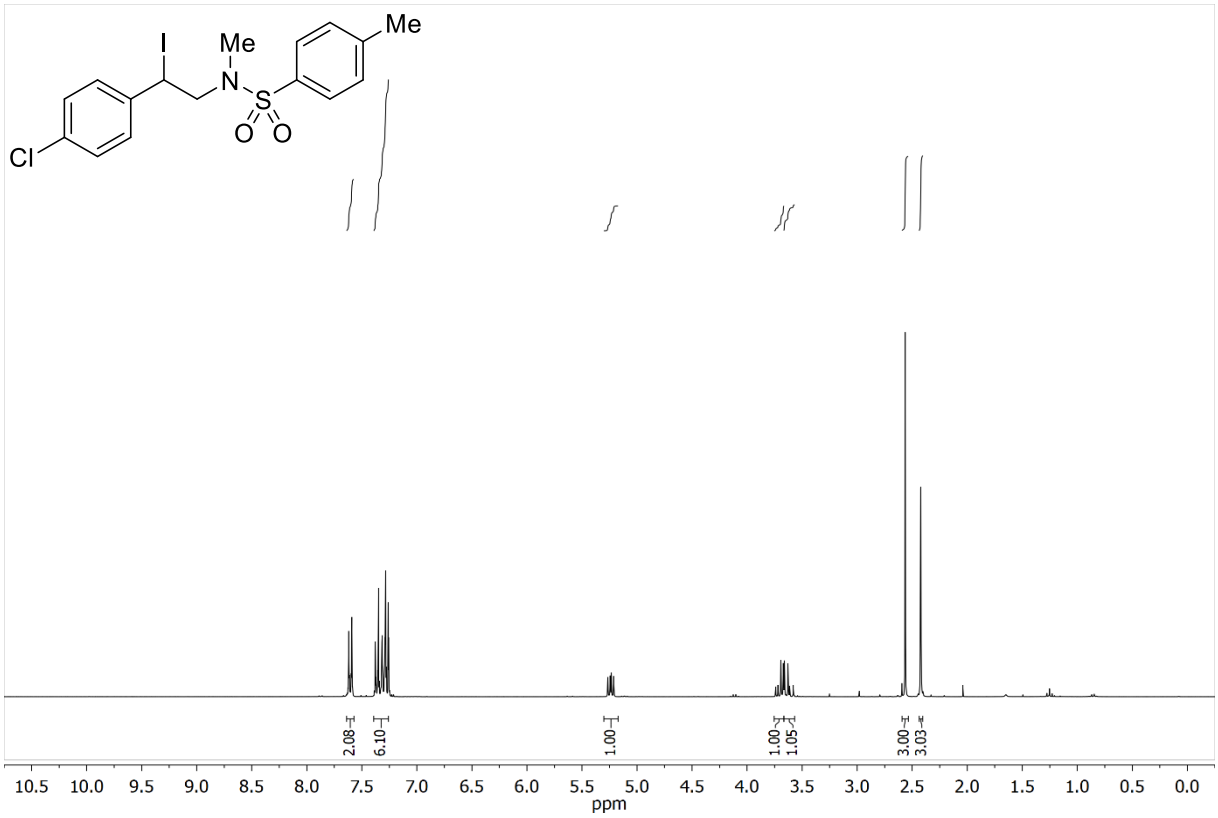


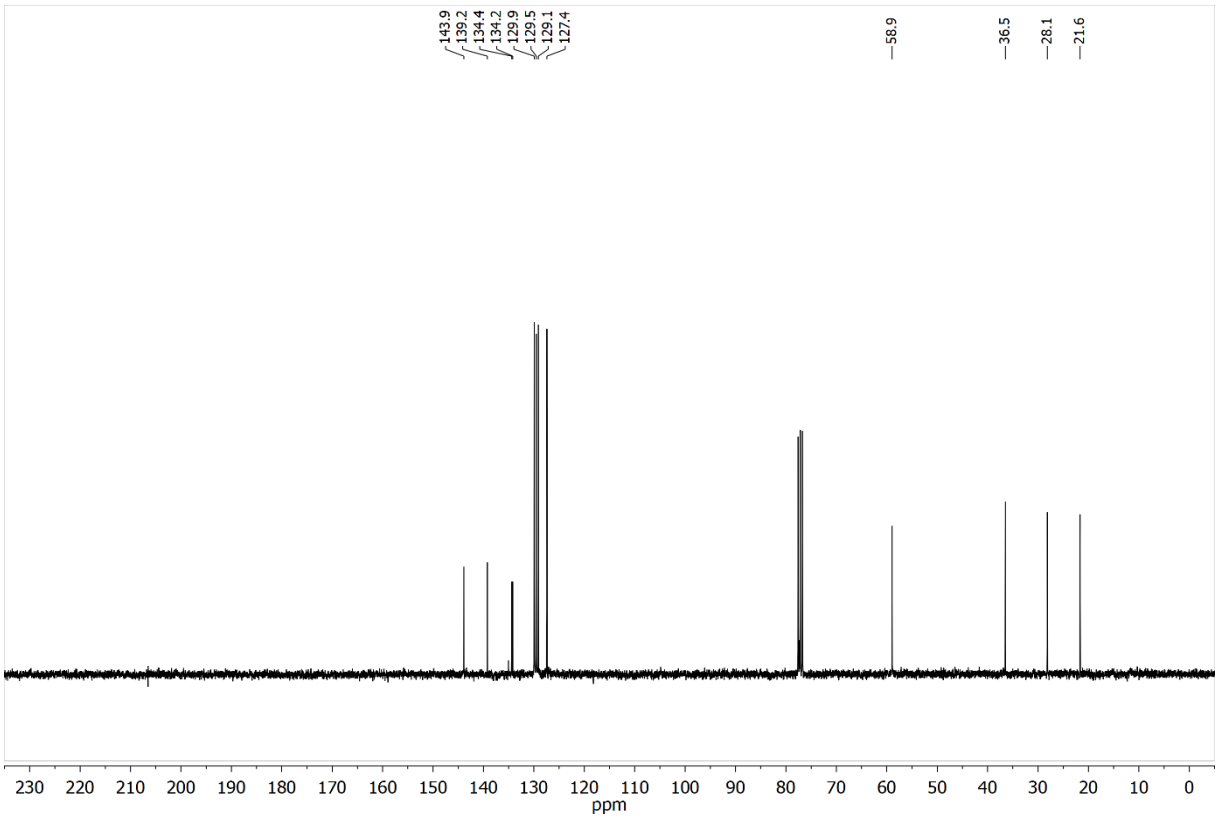
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

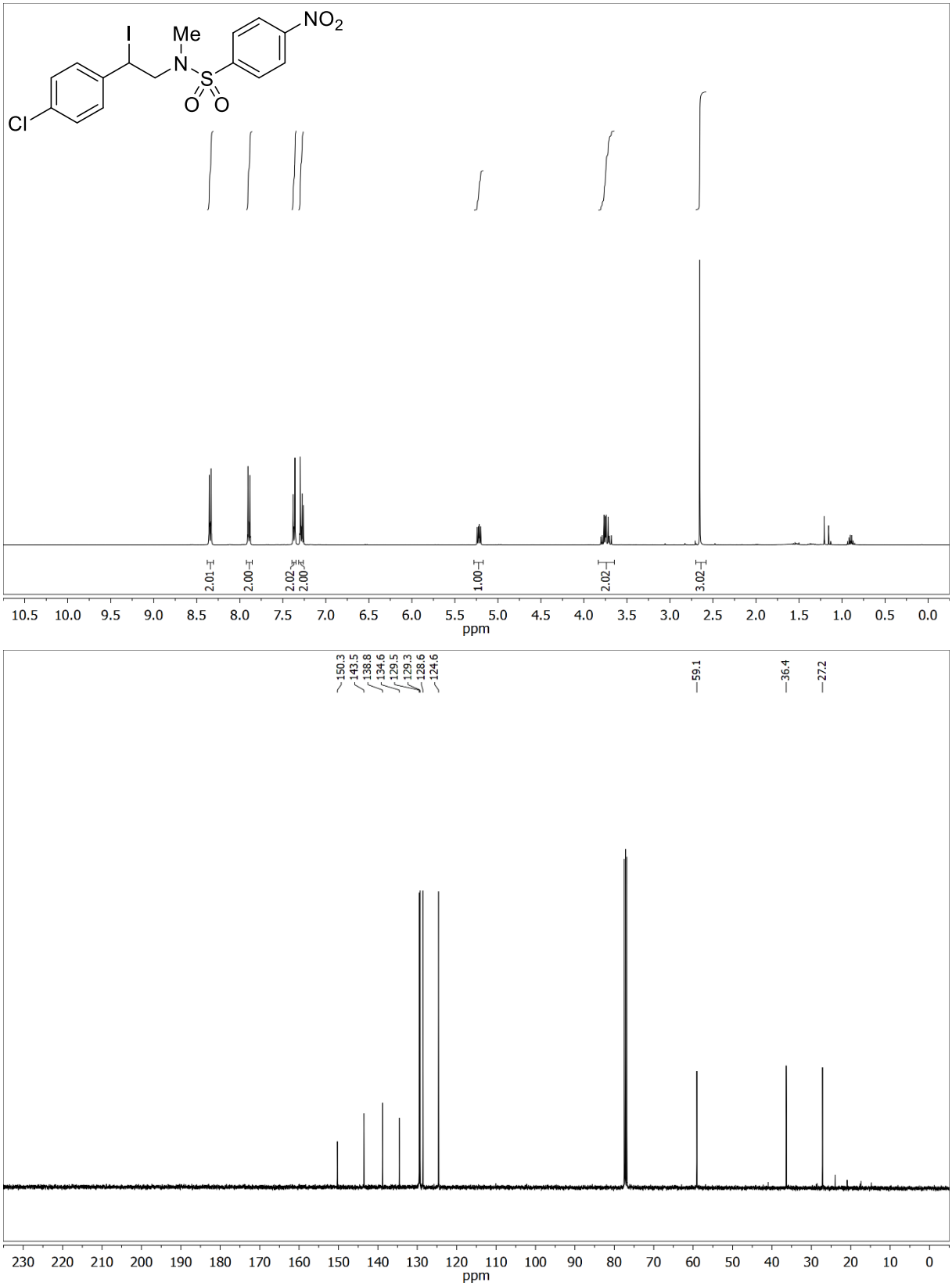
_N_-(2-(4-chlorophenyl)-2-iodoethyl)-_N_,4-dimethylbenzenesulfonamide (15e)





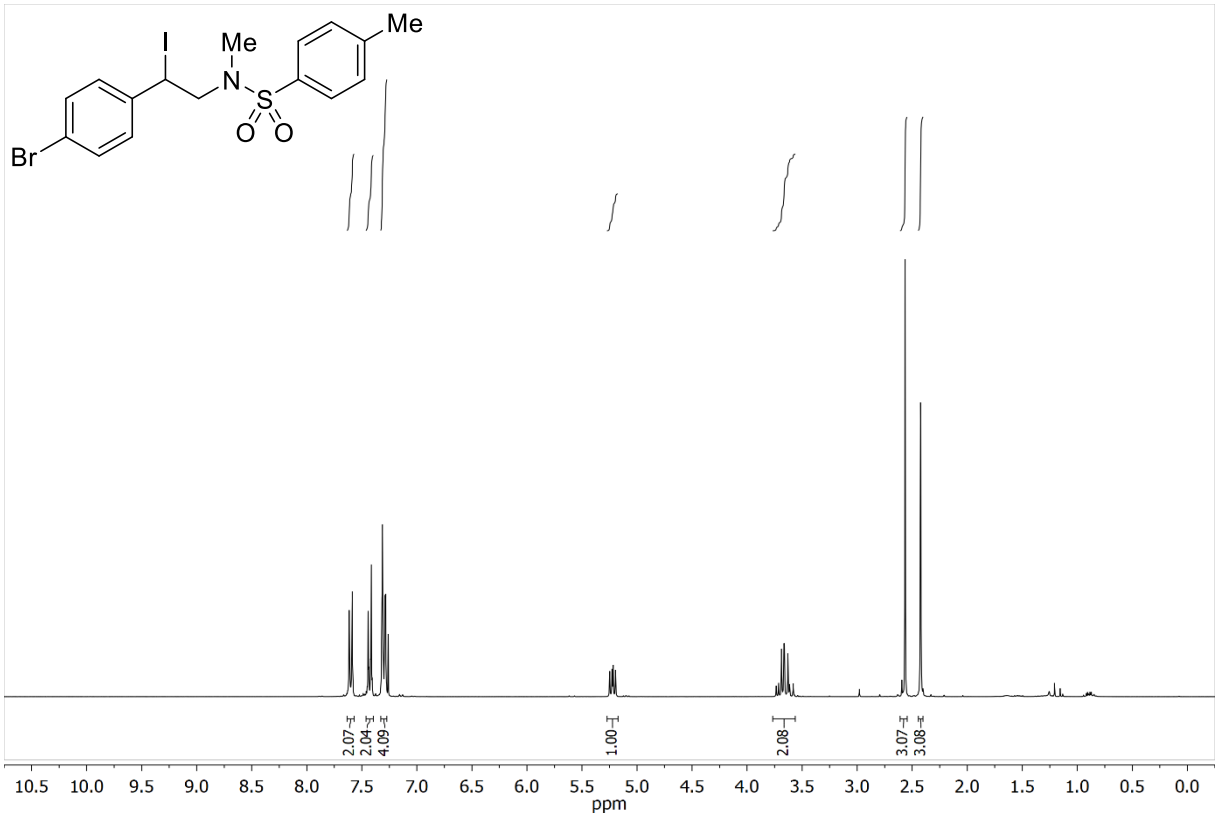
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

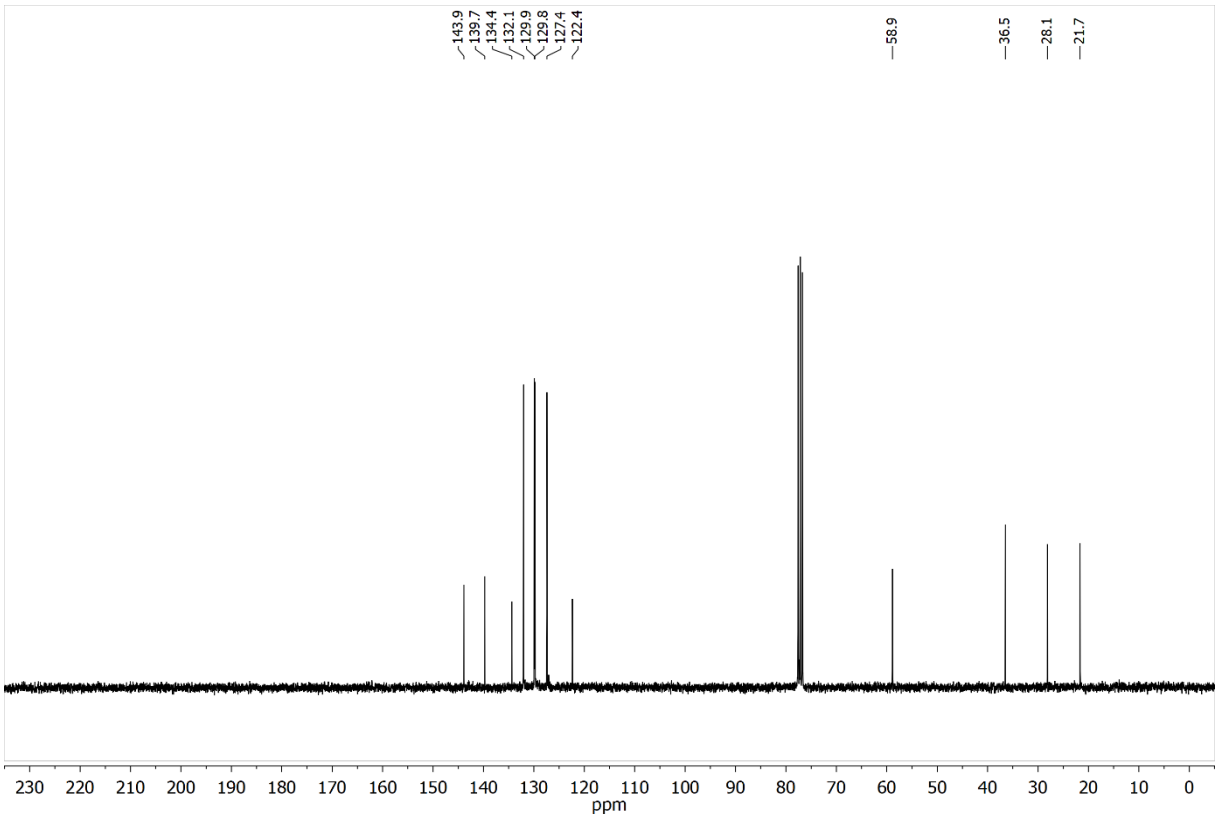
_N_-(2-(4-chlorophenyl)-2-iodoethyl)-_N_-methyl-4-nitrobenzenesulfonamide (Ns-15e)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

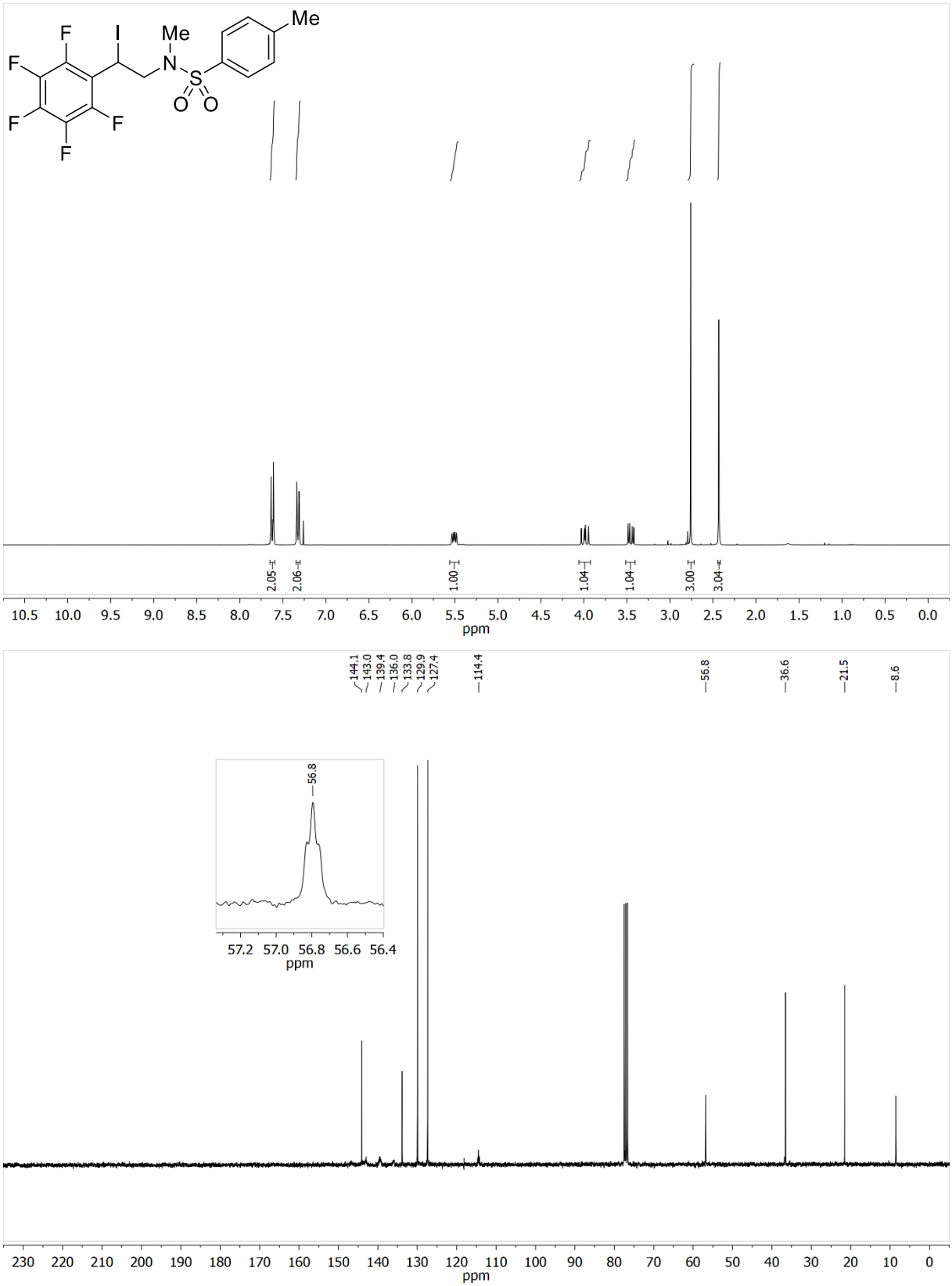
_N_-(2-(4-bromophenyl)-2-iodoethyl)-_N_,4-dimethylbenzenesulfonamide (15f)



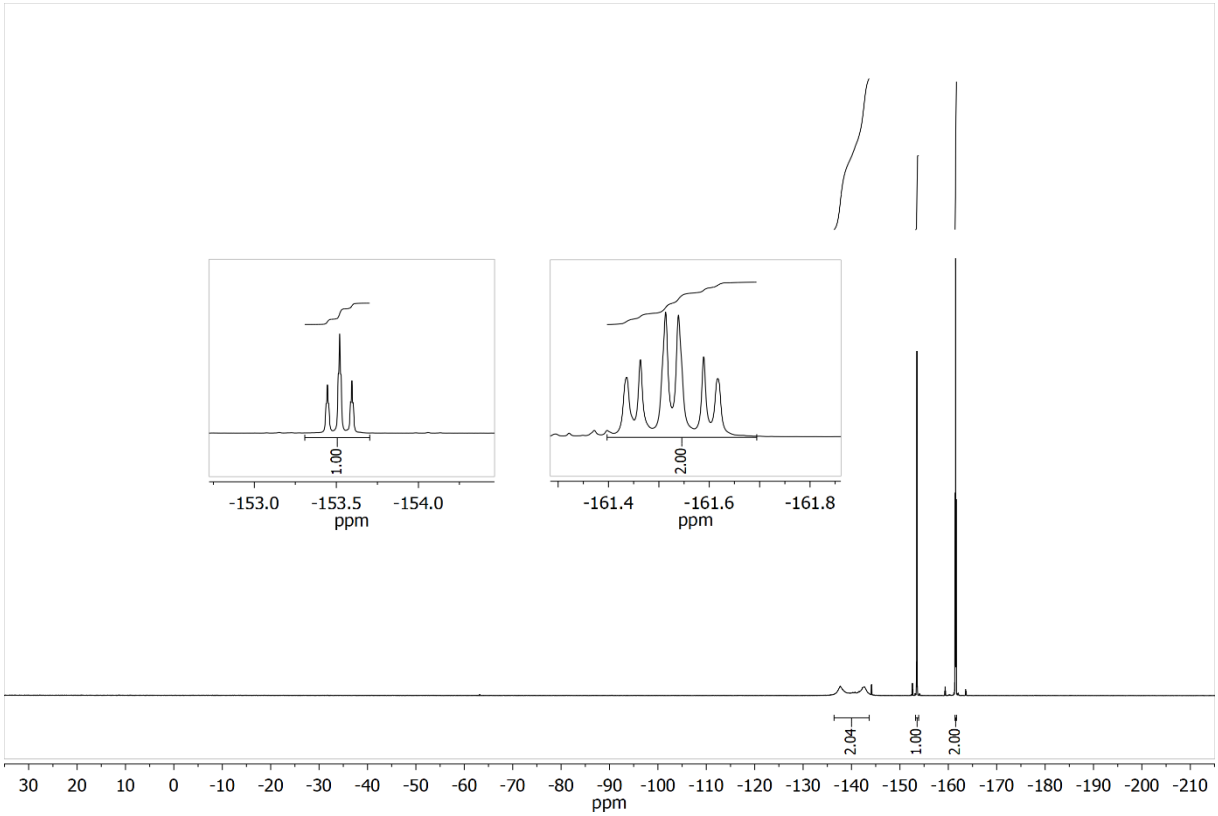


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-2-(perfluorophenyl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15g)

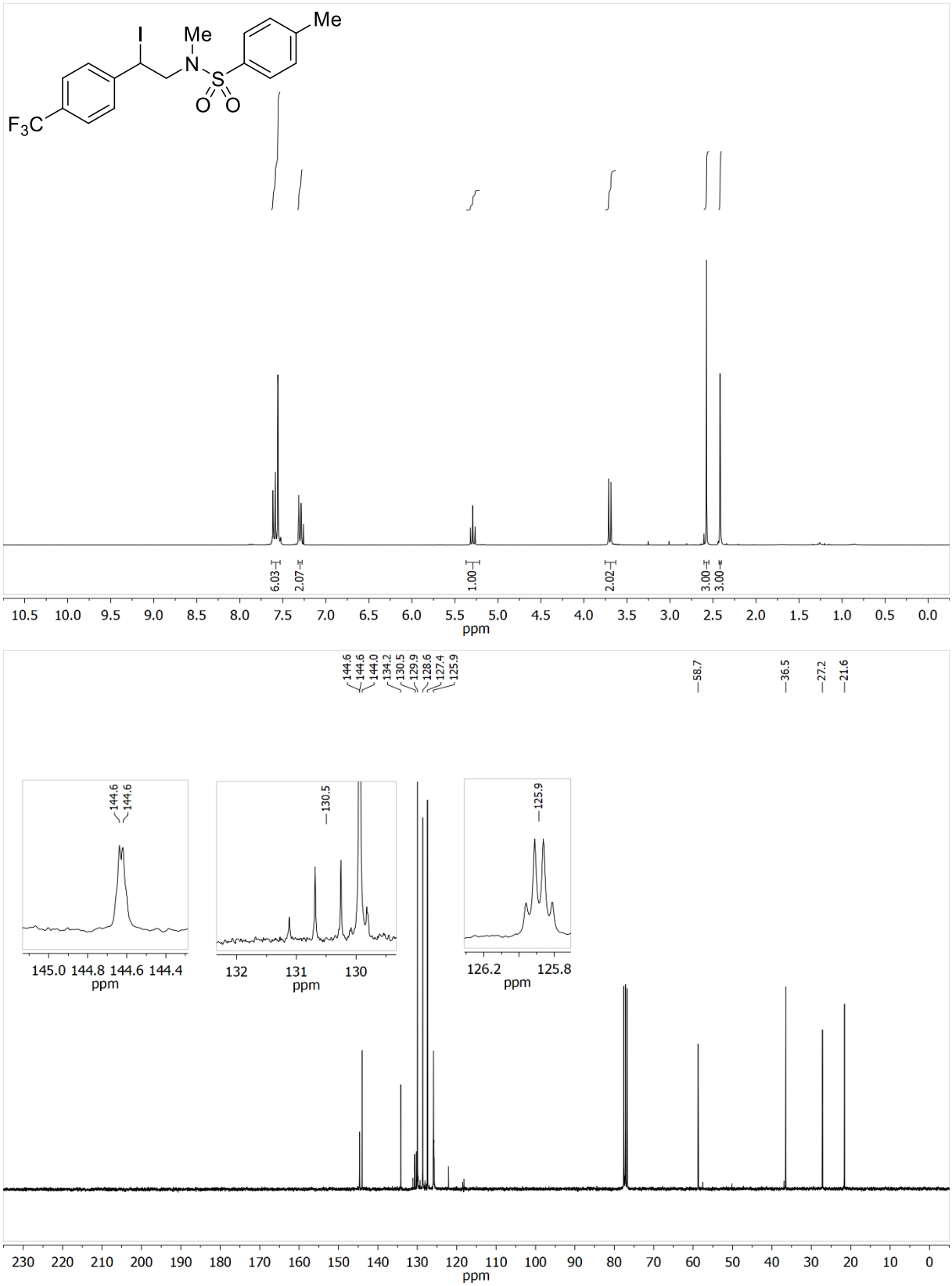


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

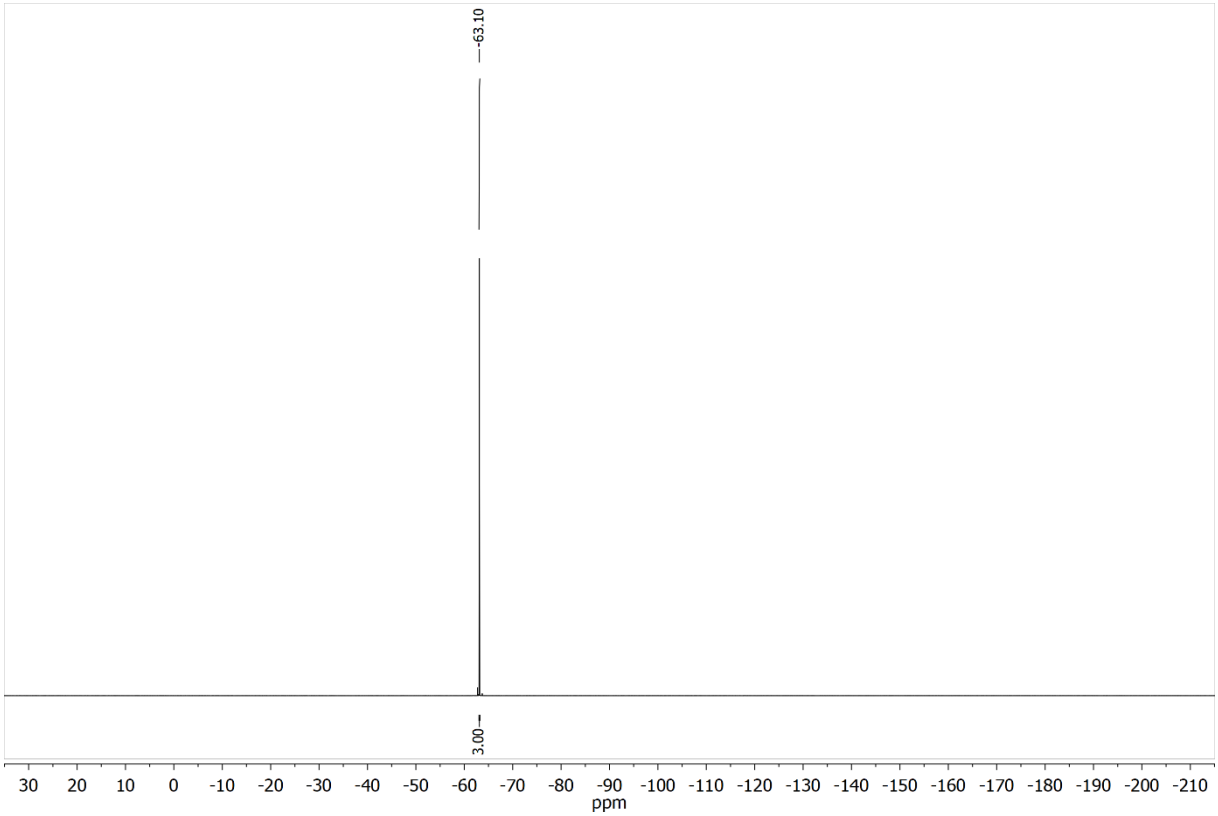


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-2-(4-(trifluoromethyl)phenyl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15h)

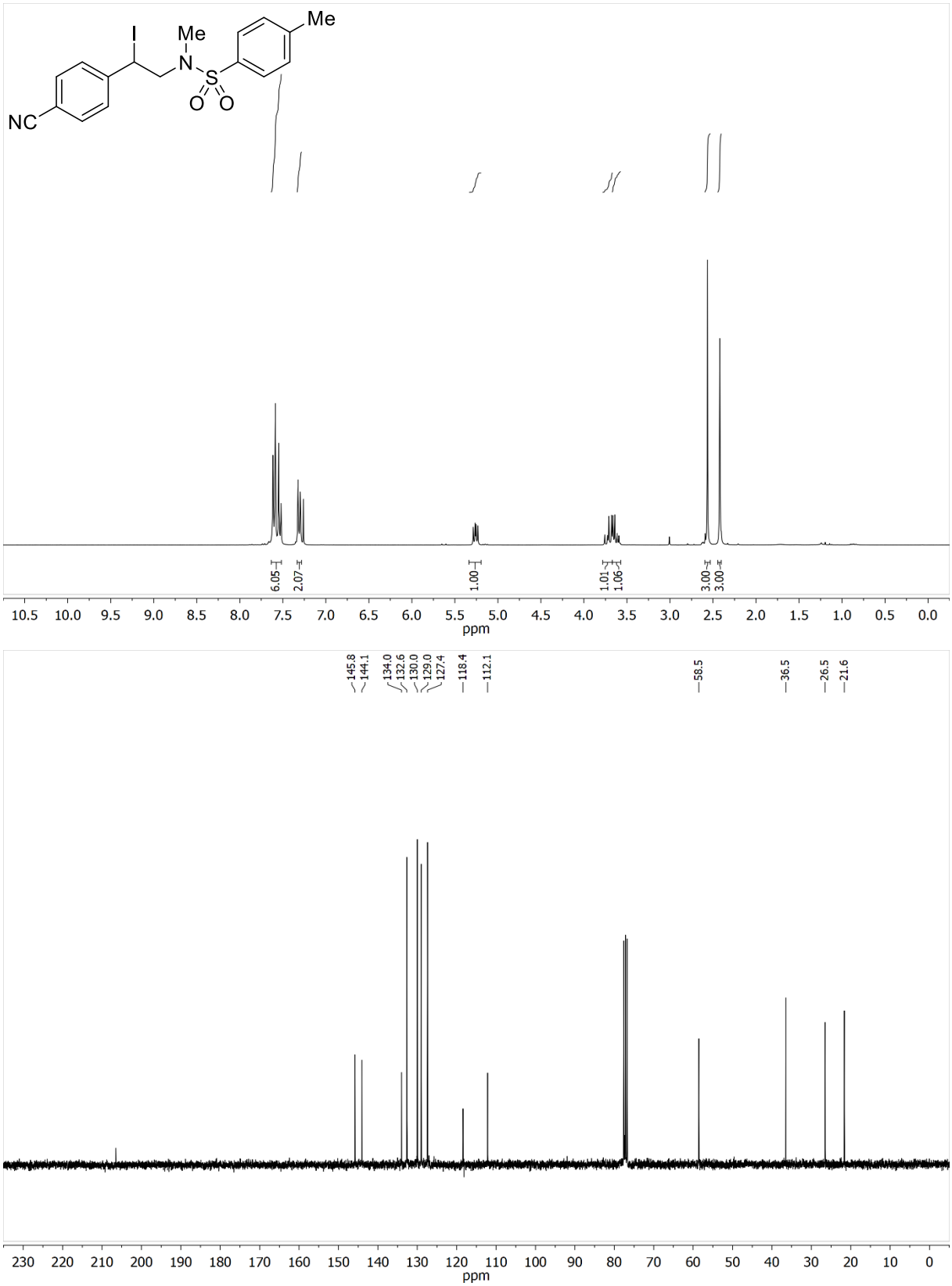


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.



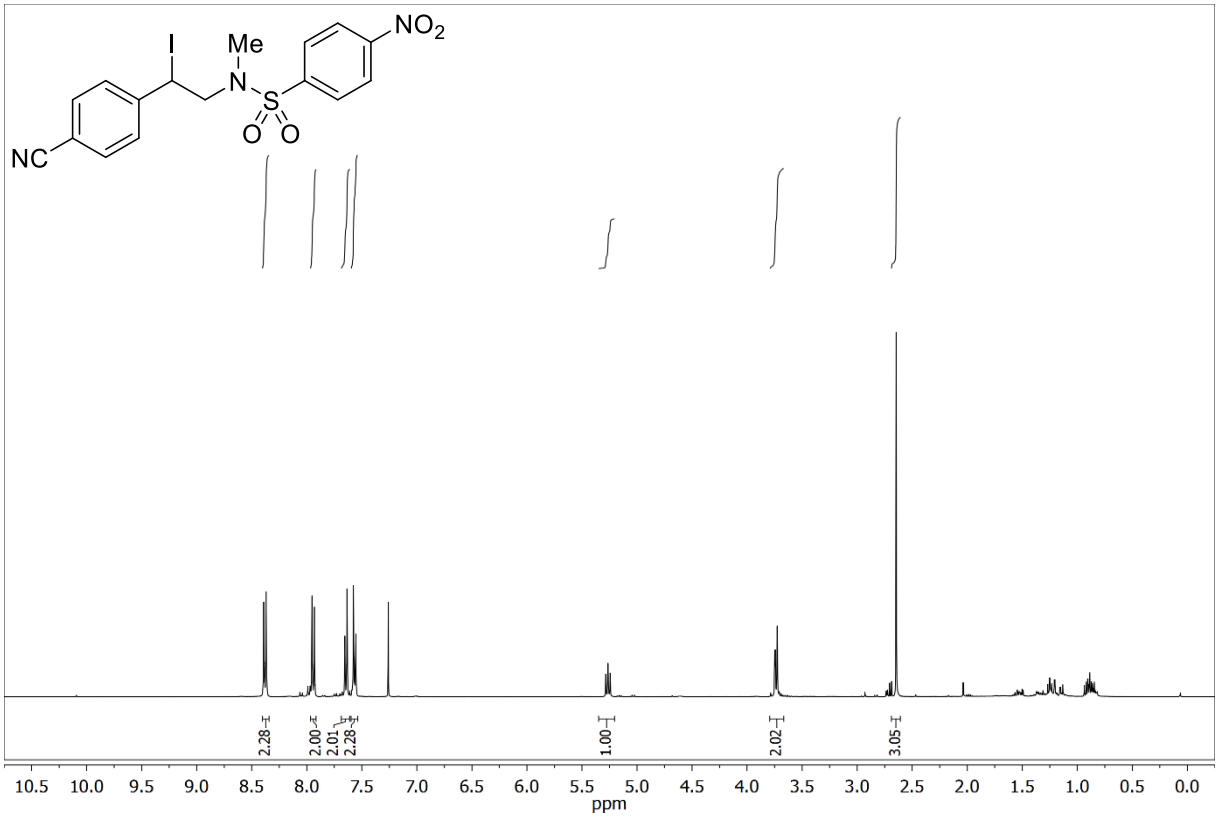
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; Third image: ^{19}F-NMR; NMR-solvent: $CDCl_3$.

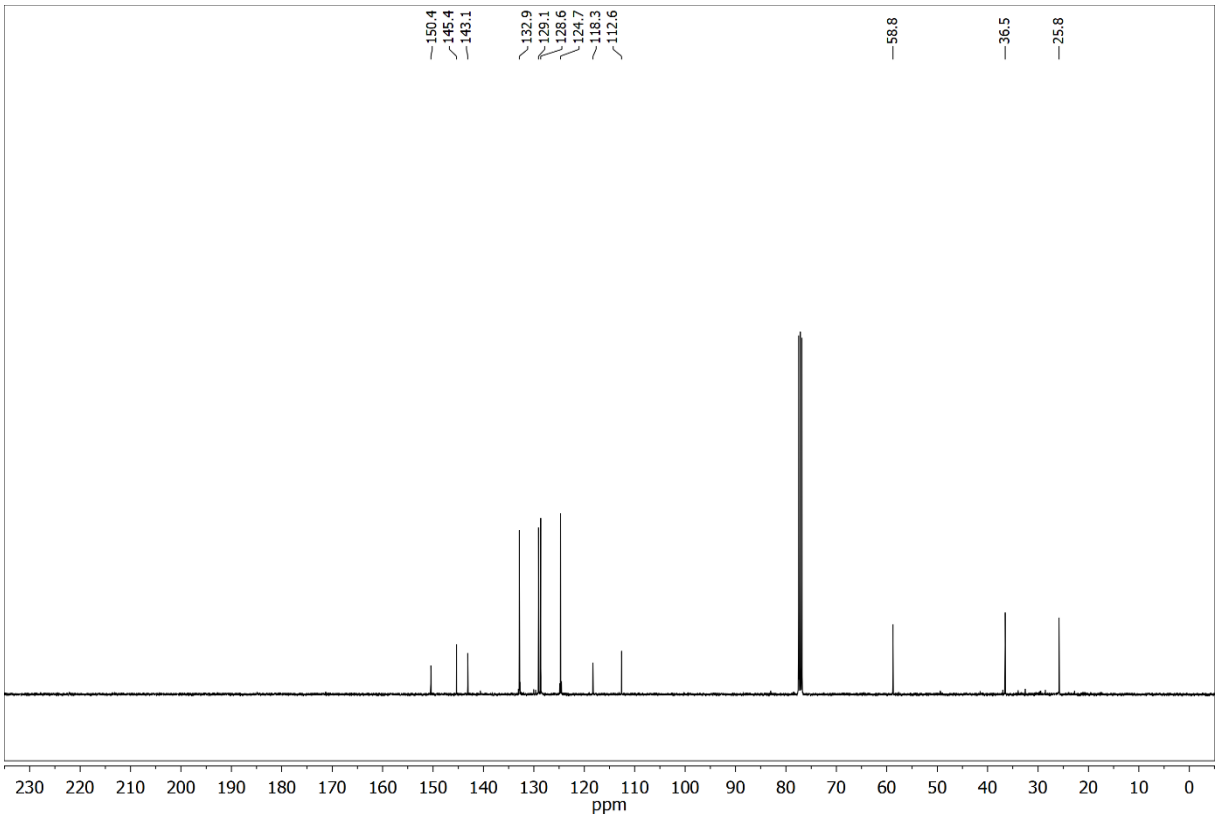
_N_-(2-(4-cyanophenyl)-2-iodoethyl)-_N_,4-dimethylbenzenesulfonamide (15i)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

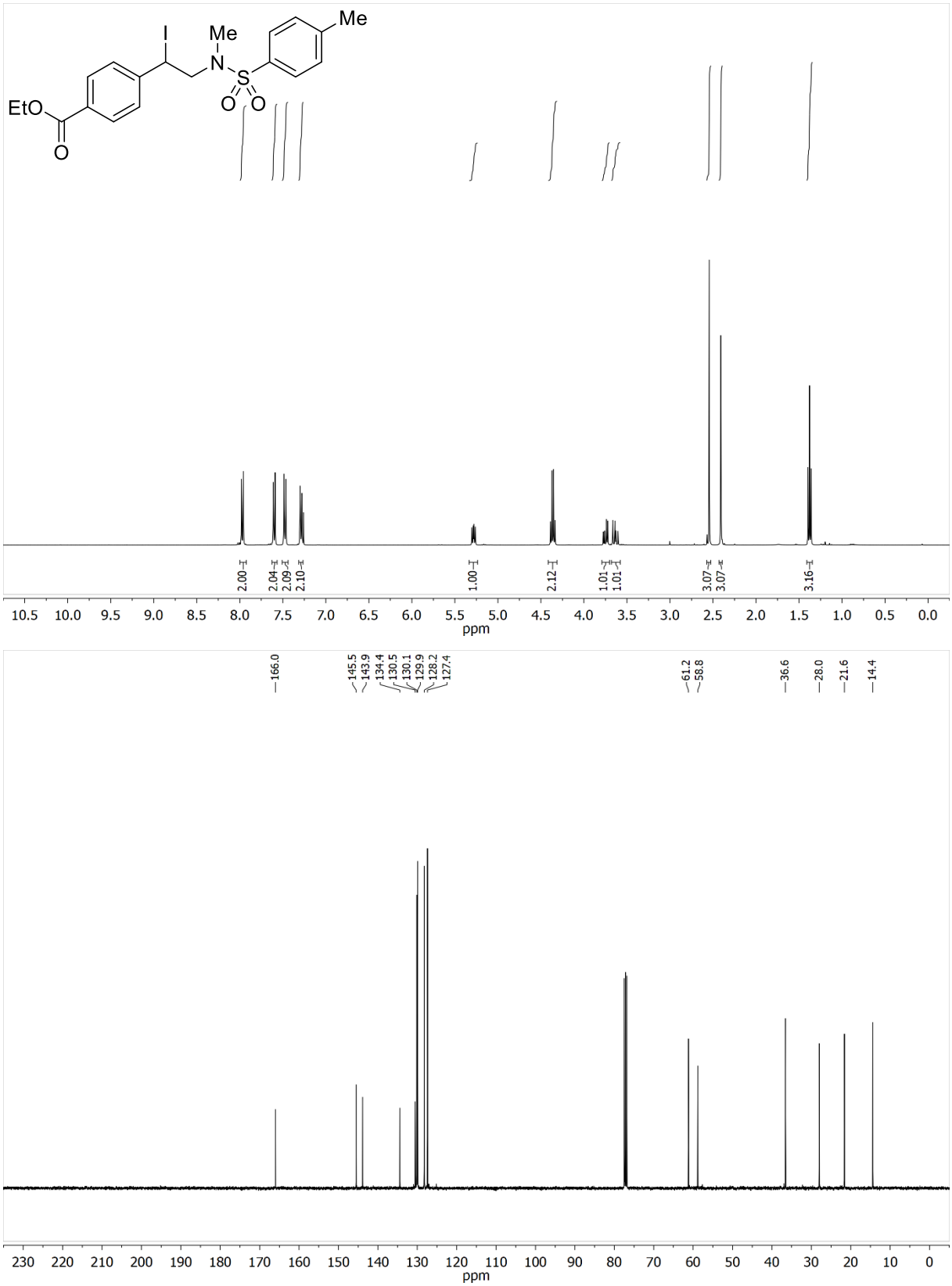
***N*-(2-(4-cyanophenyl)-2-iodoethyl)-*N*-methyl-4-nitrobenzenesulfonamide (Ns-15i)**





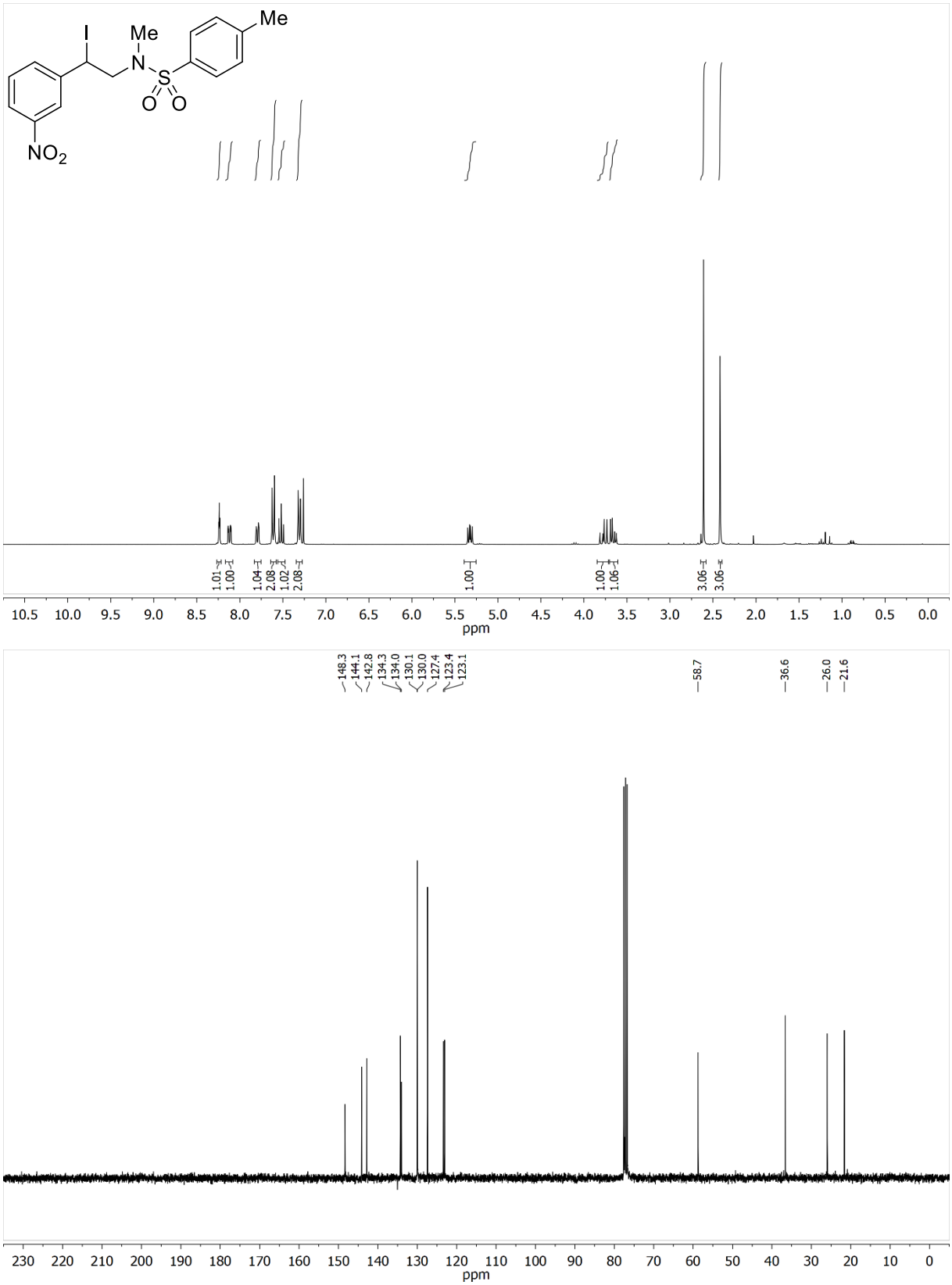
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

ethyl 4-(2-((*N*,4-dimethylphenyl)sulfonamido)-1-iodoethyl)benzoate (15j)



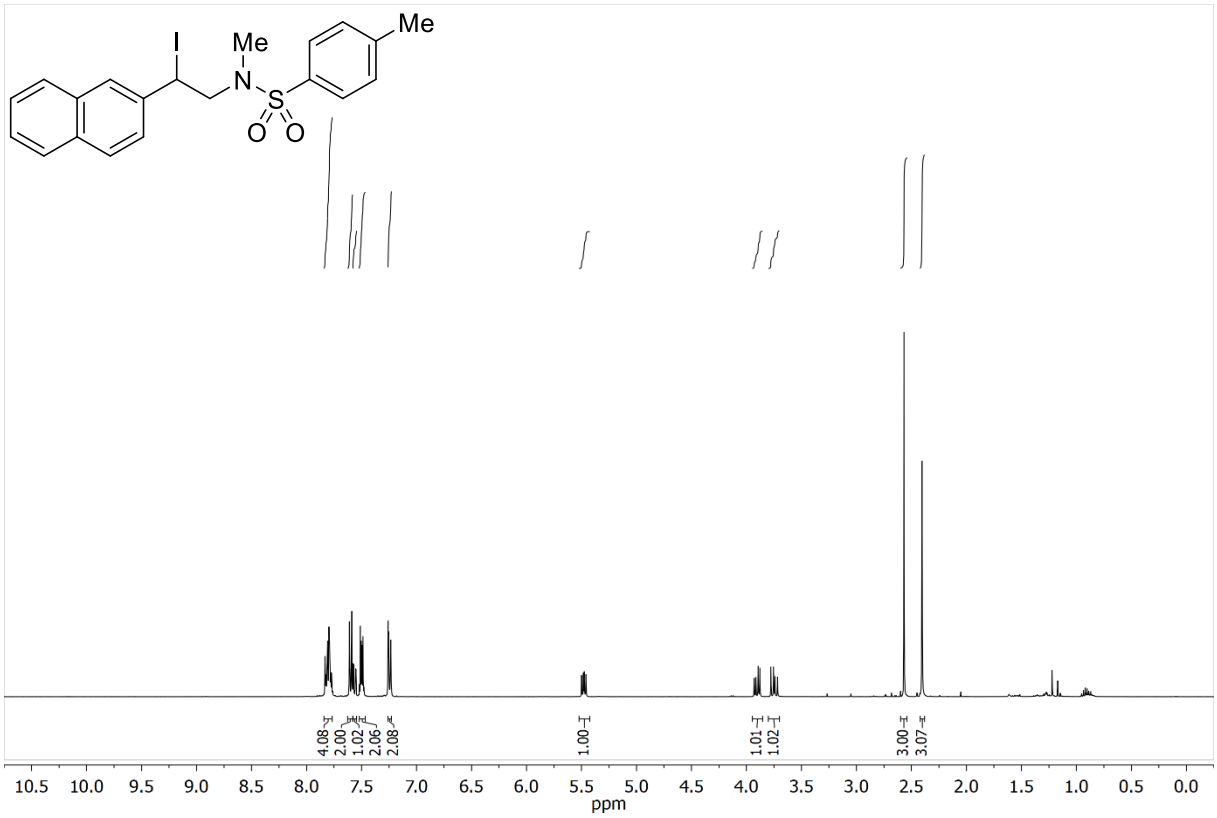
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

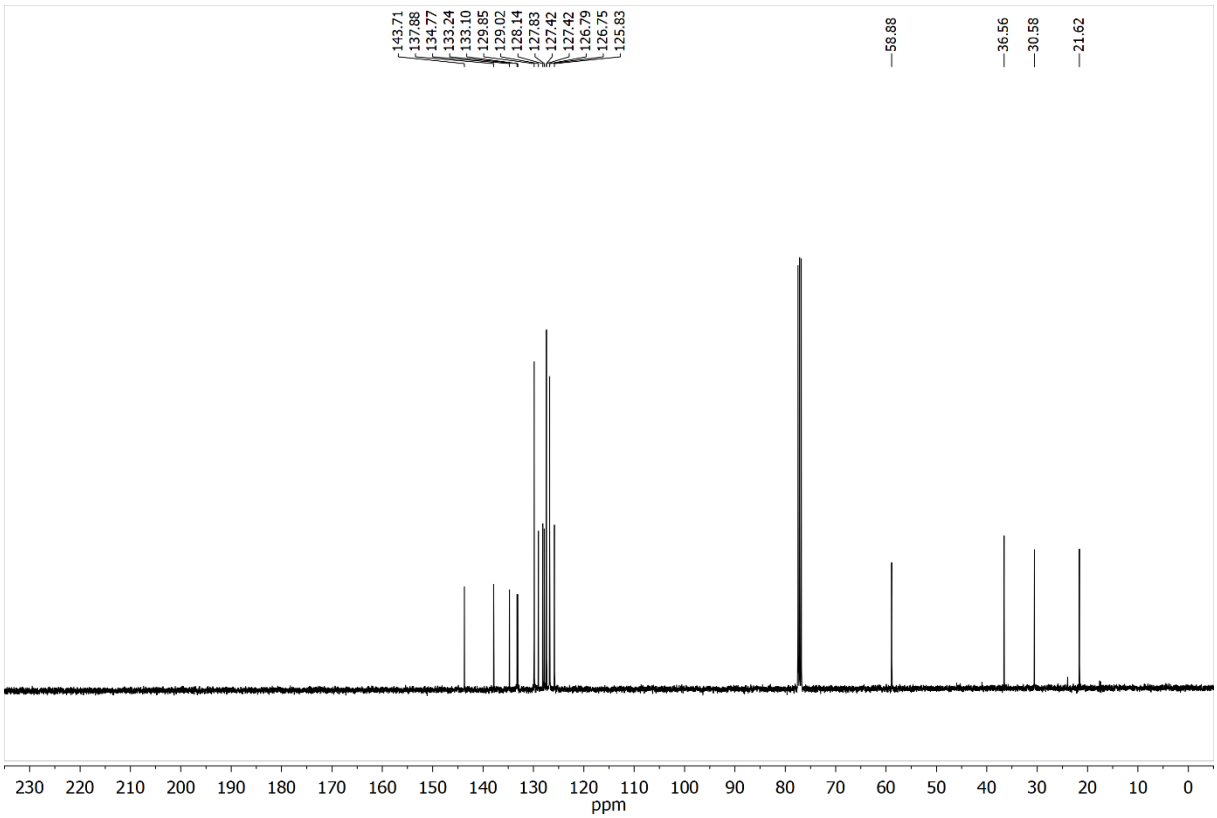
_N_-(2-iodo-2-(3-nitrophenyl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15k)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

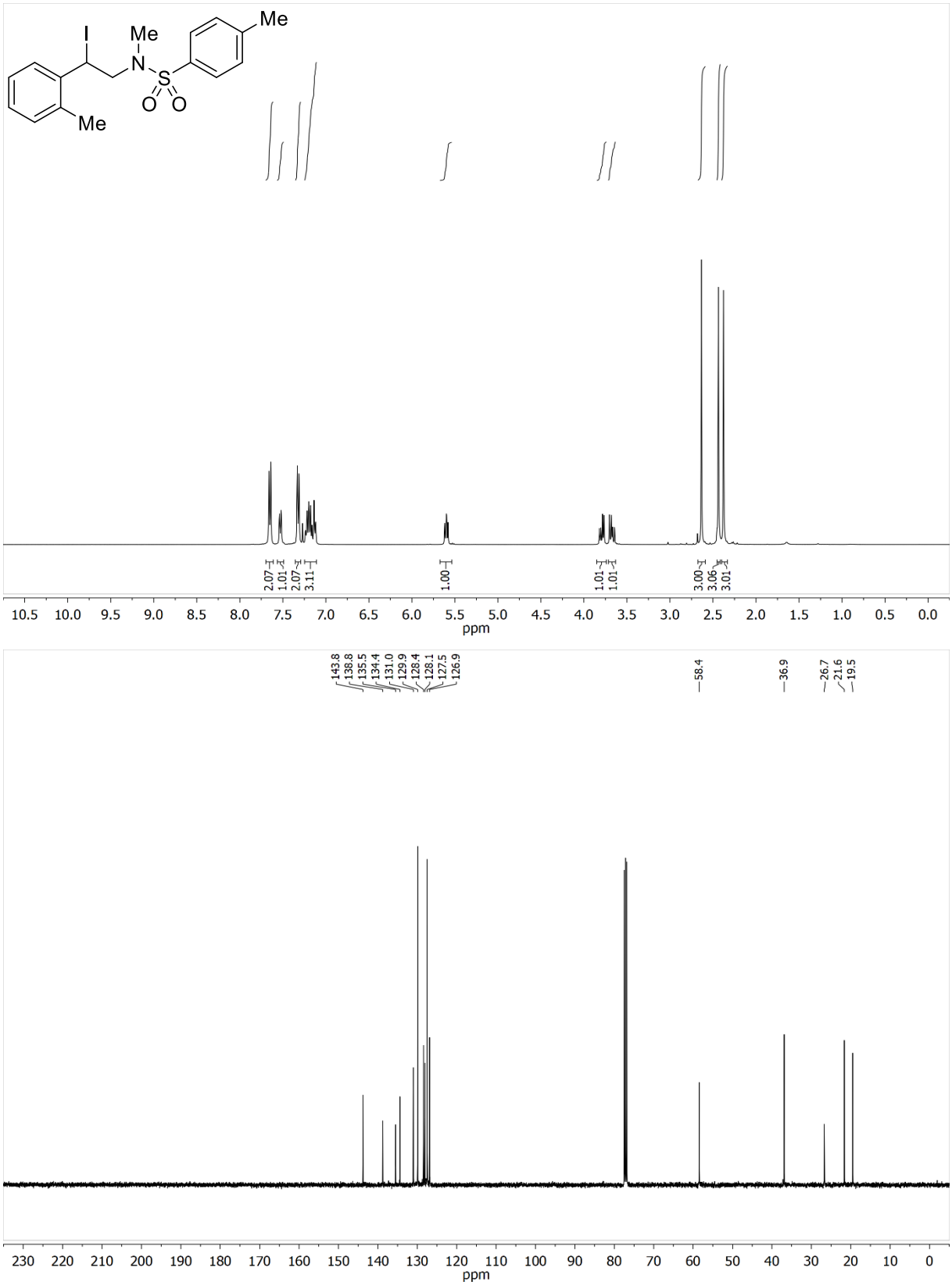
_N_-(2-iodo-2-(naphthalen-2-yl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15l)





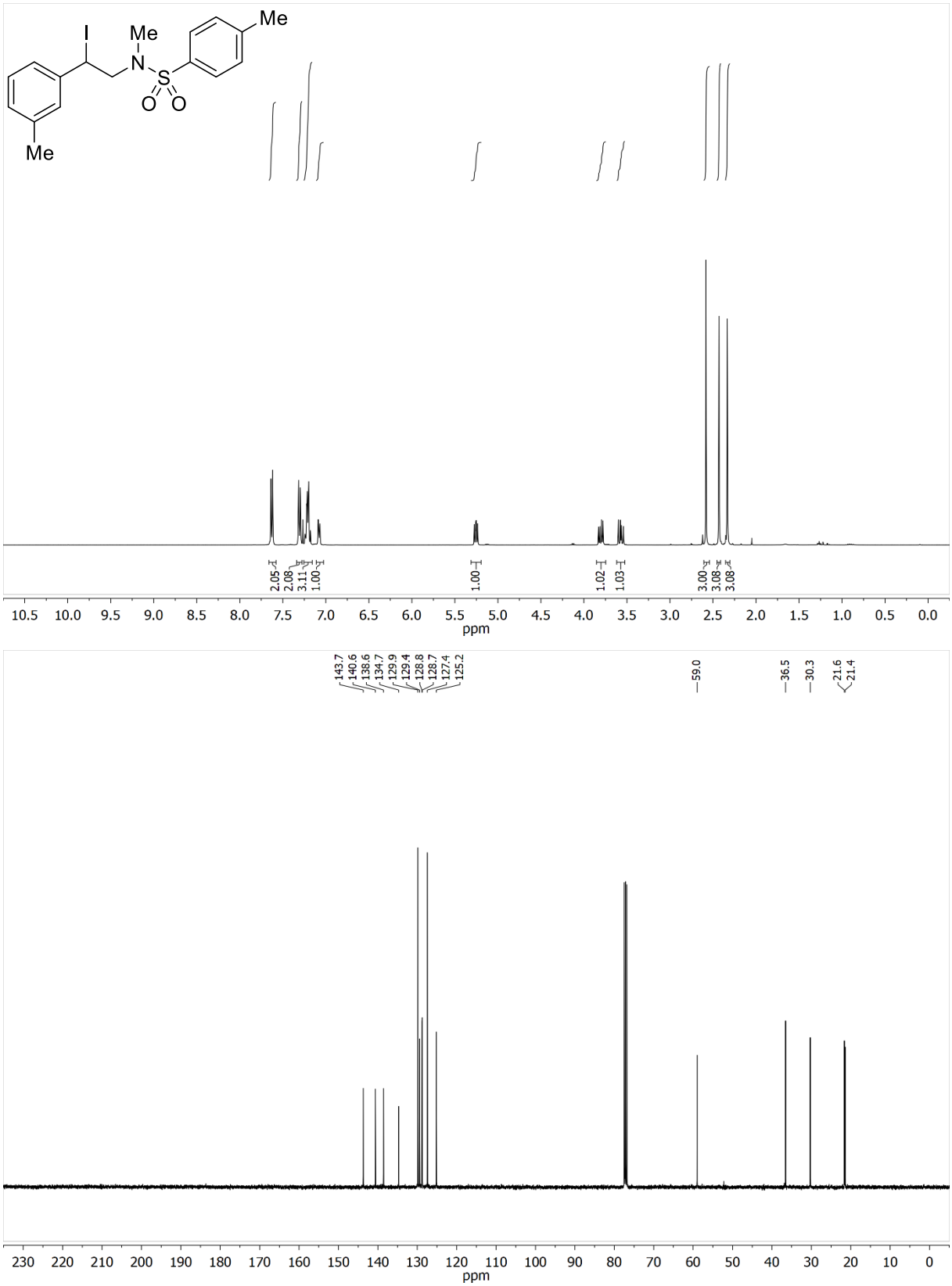
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-2-(_o_-tolyl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15n)



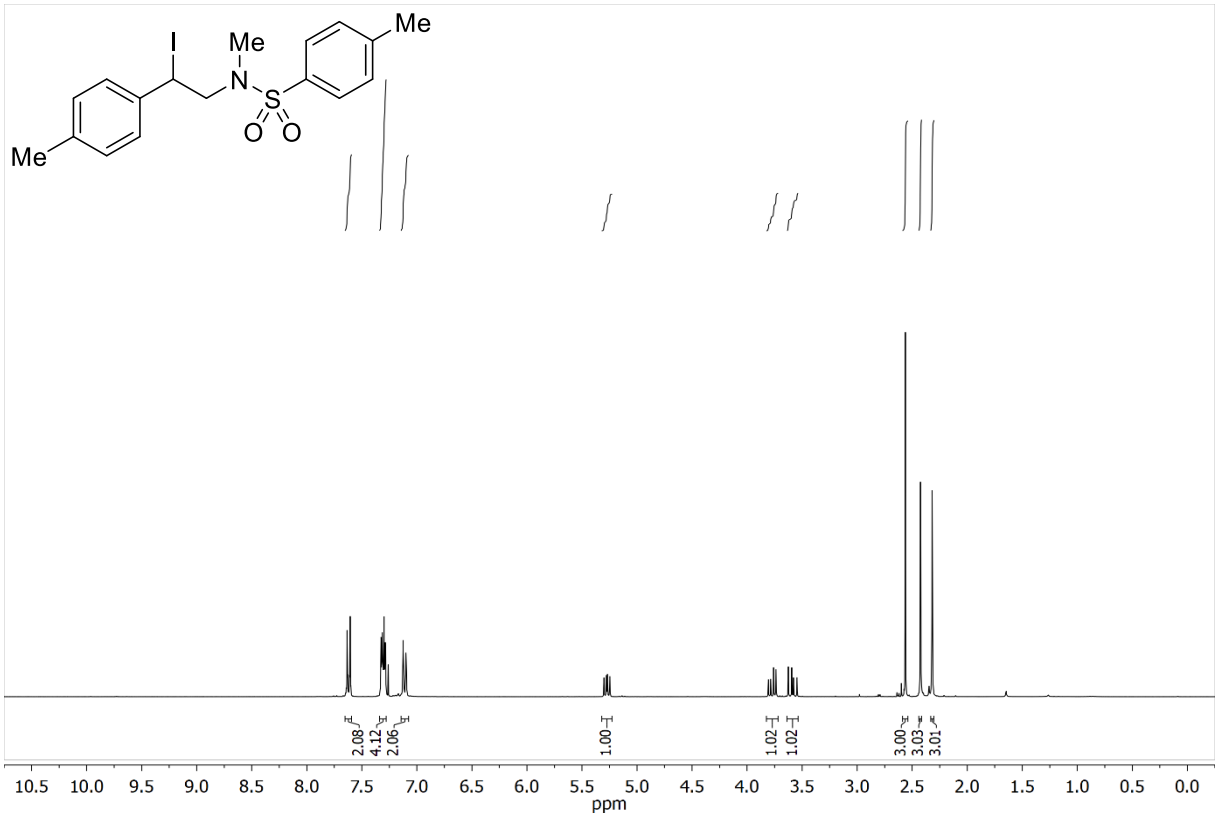
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

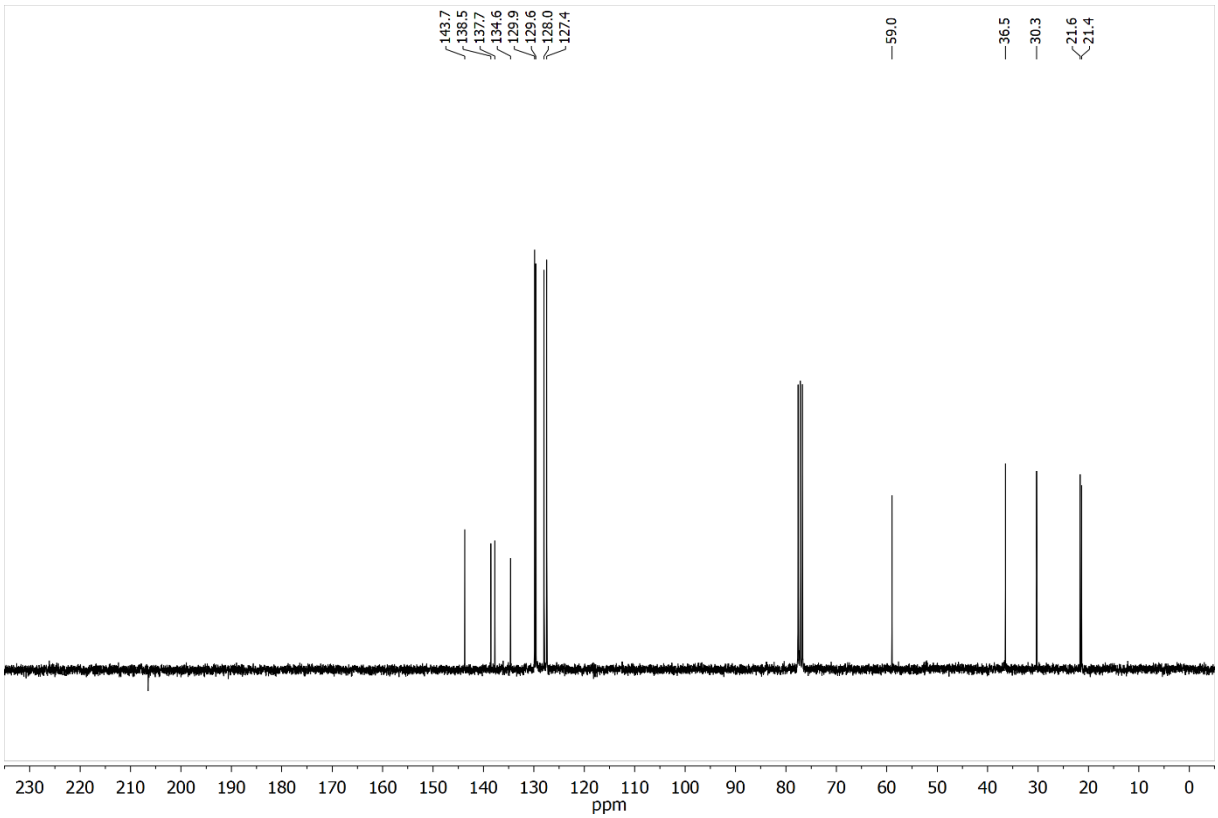
_N_-(2-iodo-2-(_m_-tolyl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15o)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

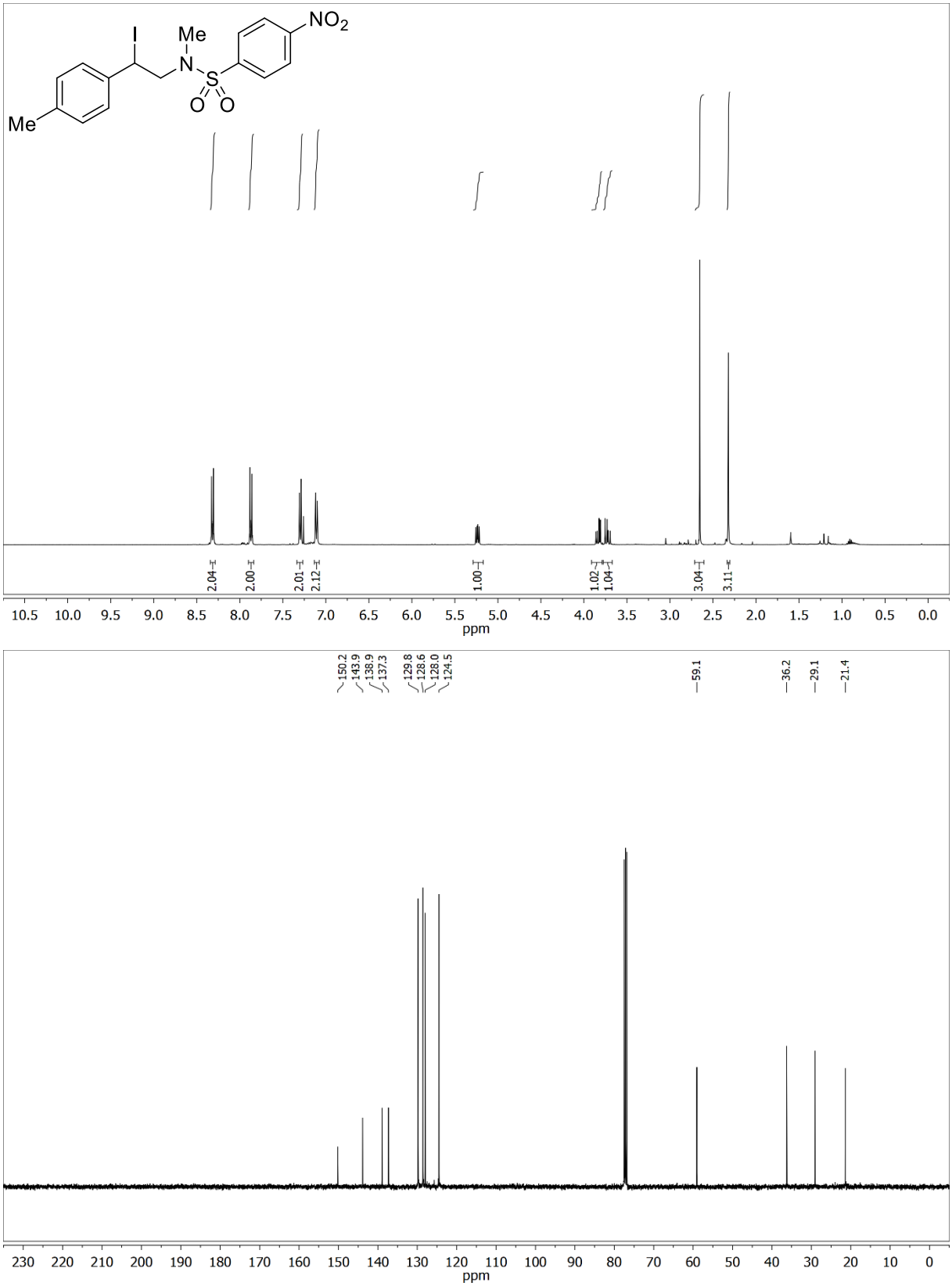
_N_-(2-iodo-2-(_p_-tolyl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15p)





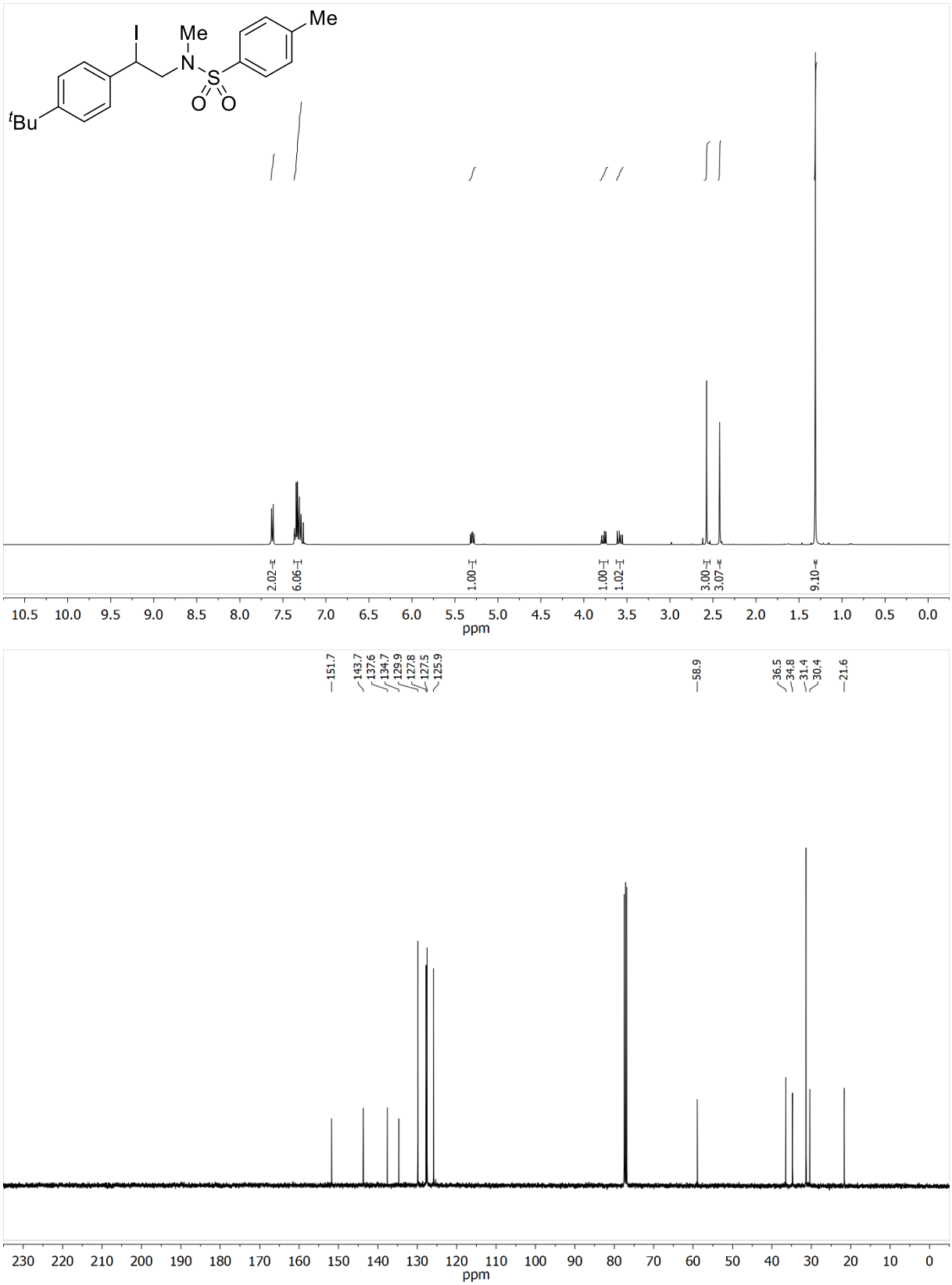
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-2-(_p_-tolyl)ethyl)-_N_-methyl-4-nitrobenzenesulfonamide (Ns-15p)



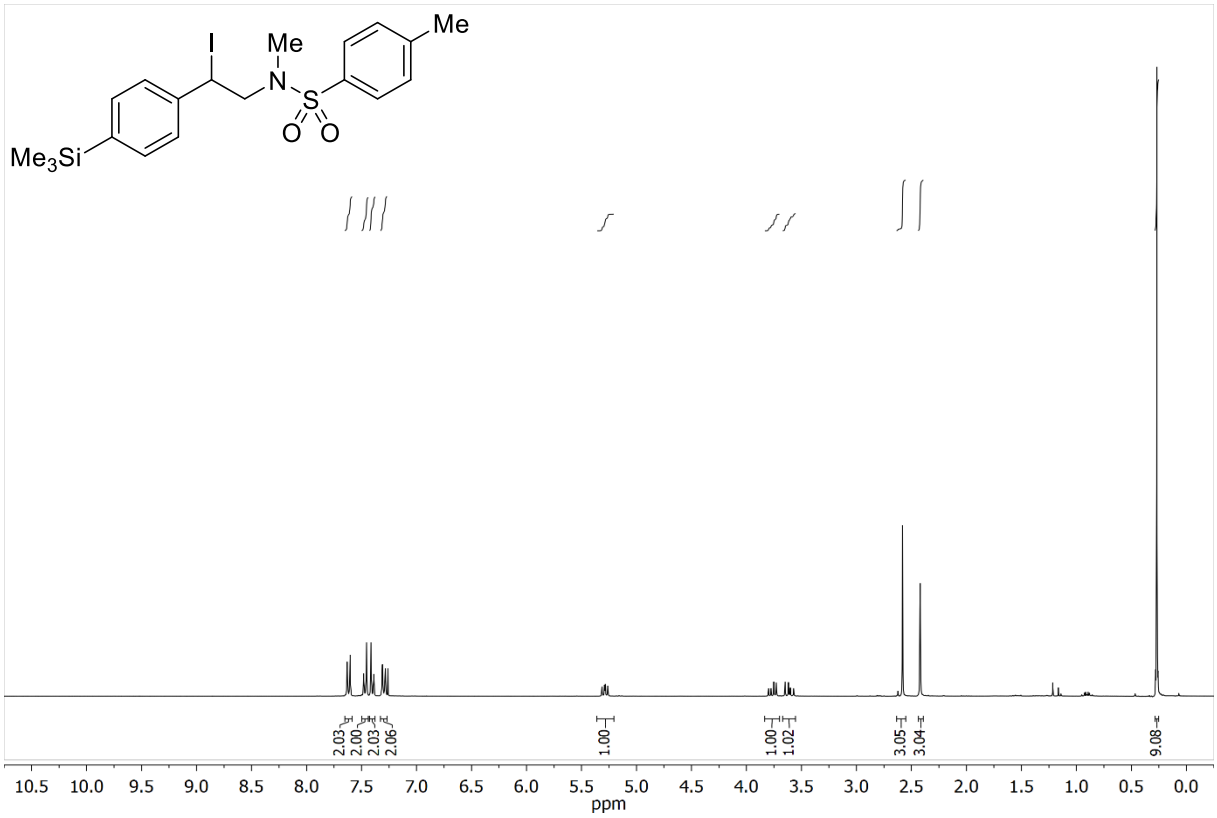
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

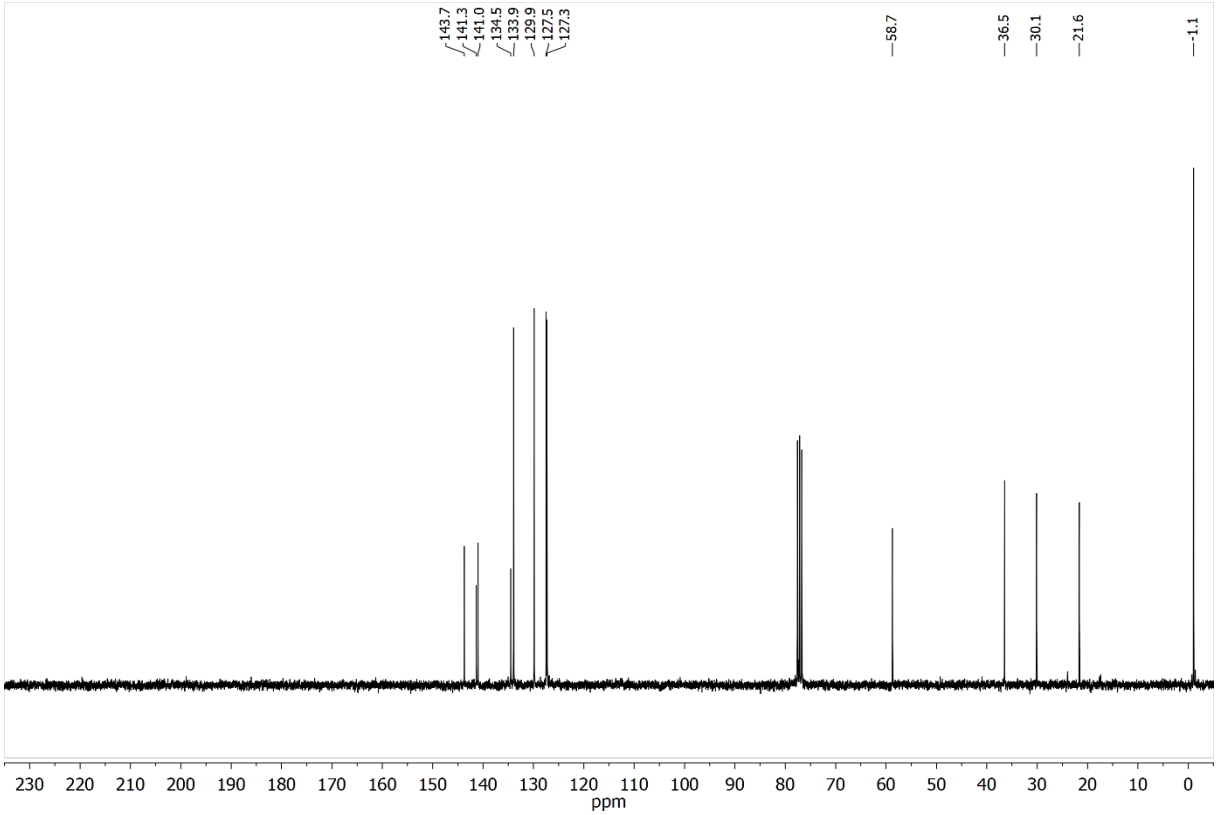
_N_-(2-(4-(_tert_-butyl)phenyl)-2-iodoethyl)-_N_,4-dimethylbenzenesulfonamide (15q)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

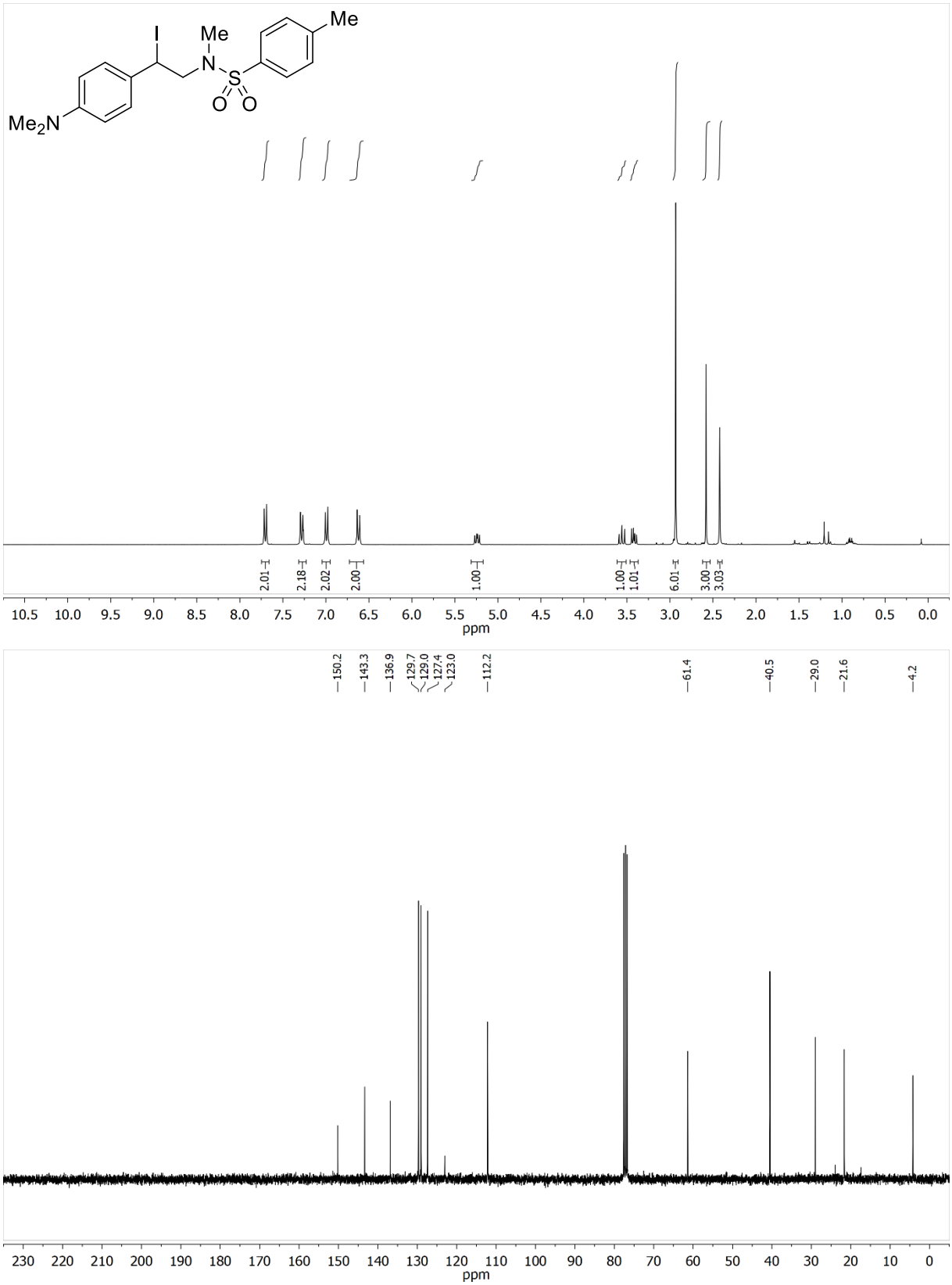
_N_-(2-iodo-2-(4-(trimethylsilyl)phenyl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15r)





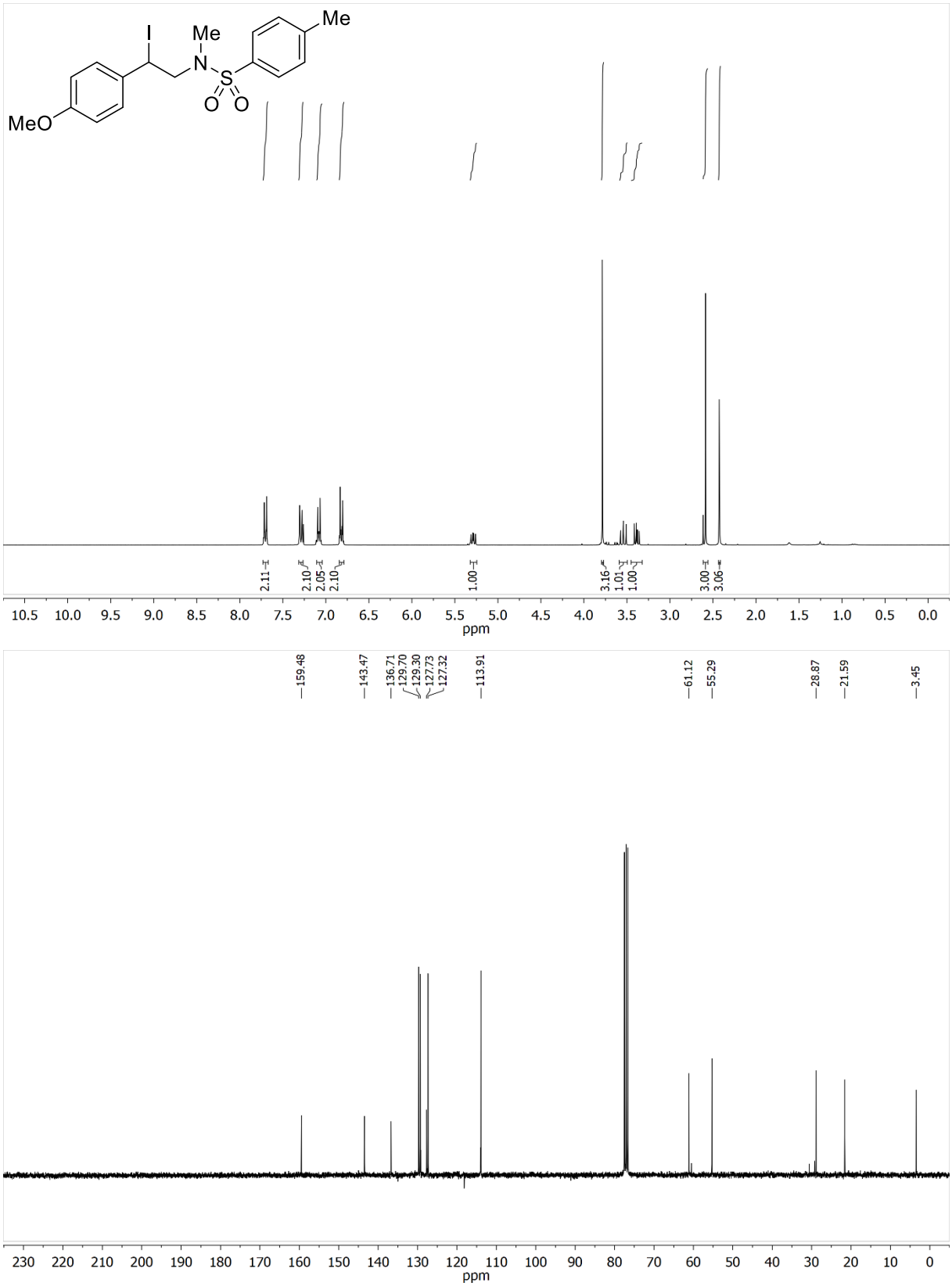
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-(4-(dimethylamino)phenyl)-2-iodoethyl)-_N_,4-dimethylbenzenesulfonamide (15s)



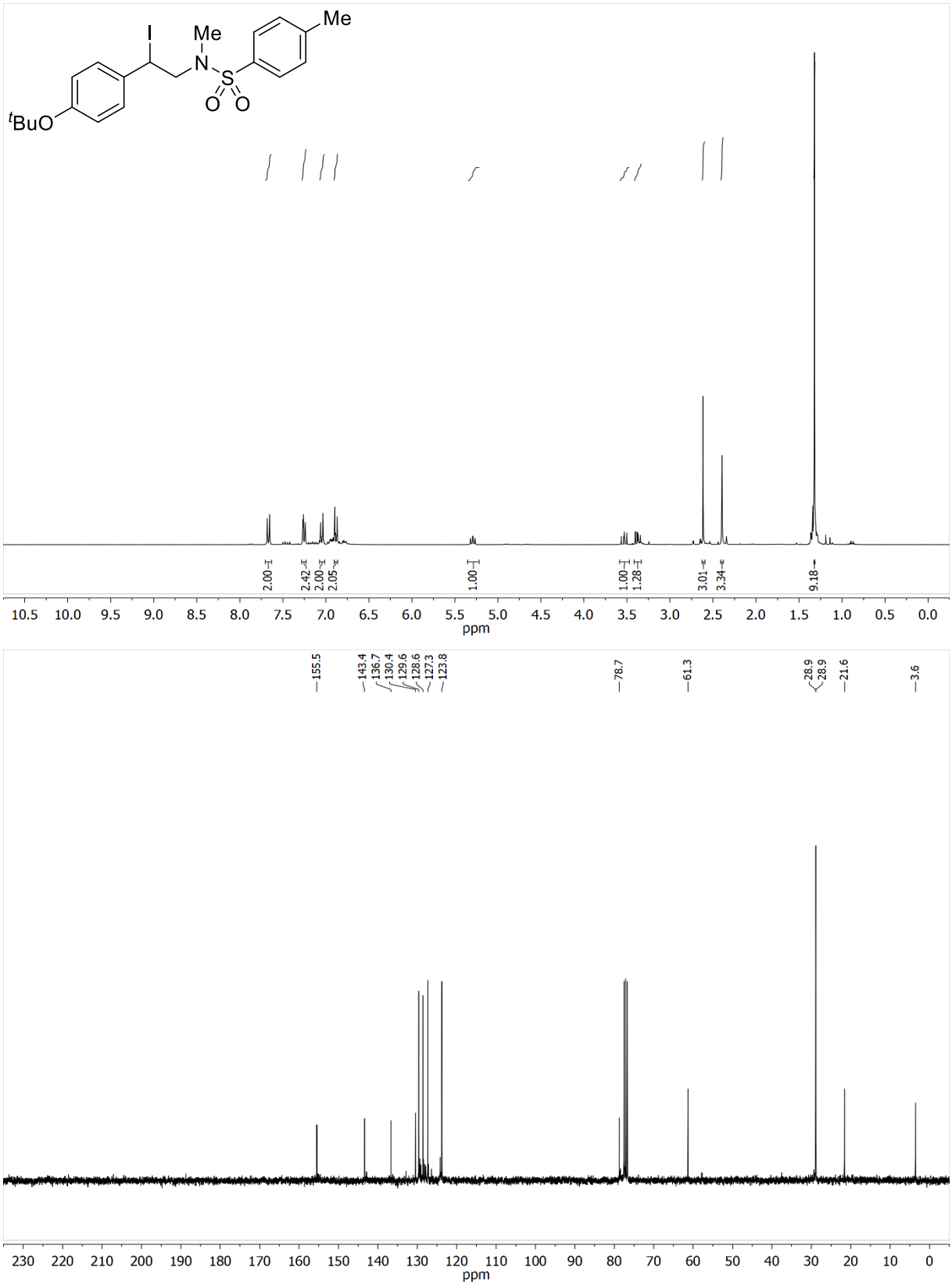
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-2-(4-methoxyphenyl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15u)



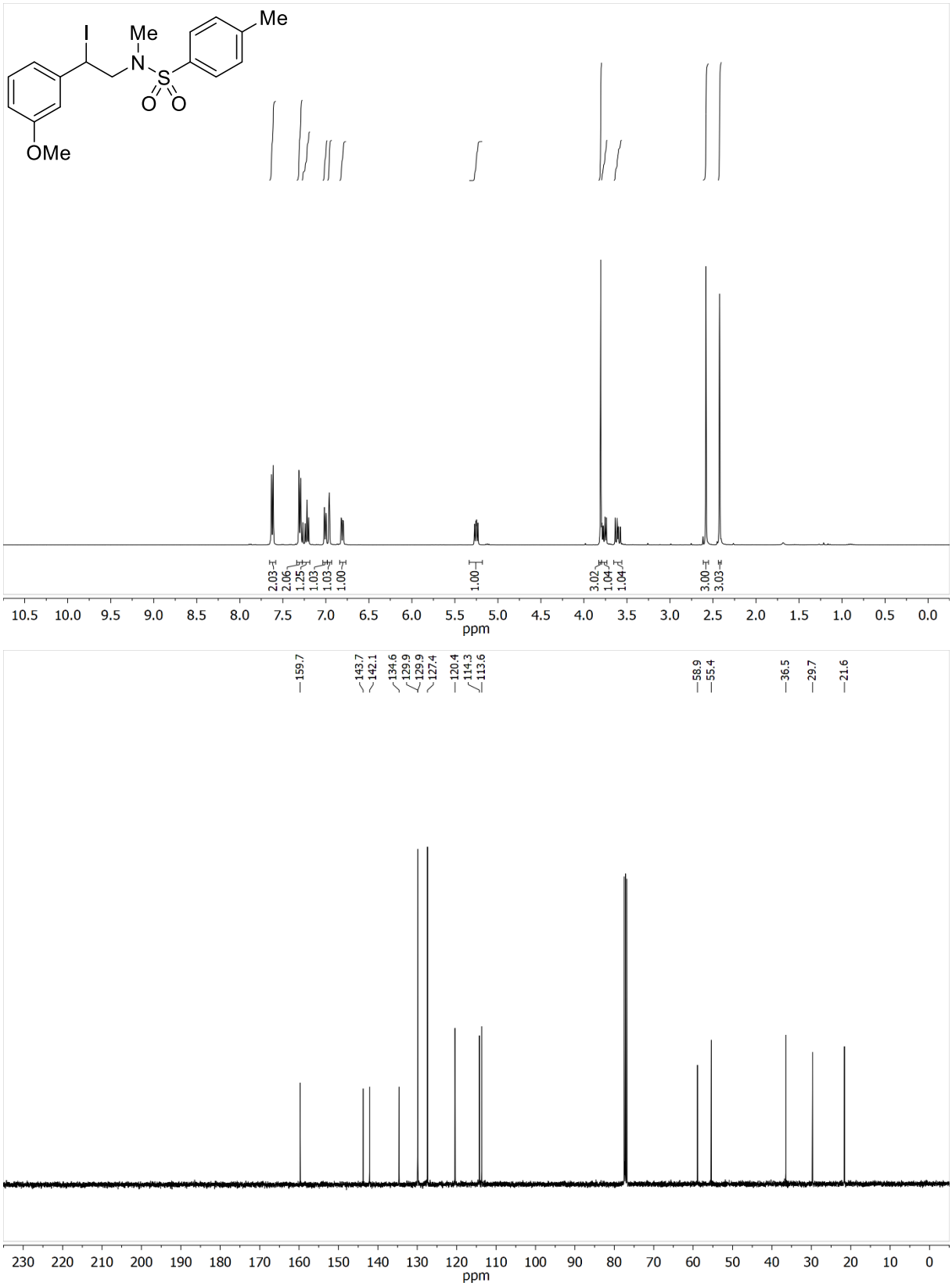
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-(4-(_tert_-butoxy)phenyl)-2-iodoethyl)-_N_,4-dimethylbenzenesulfonamide (15v)



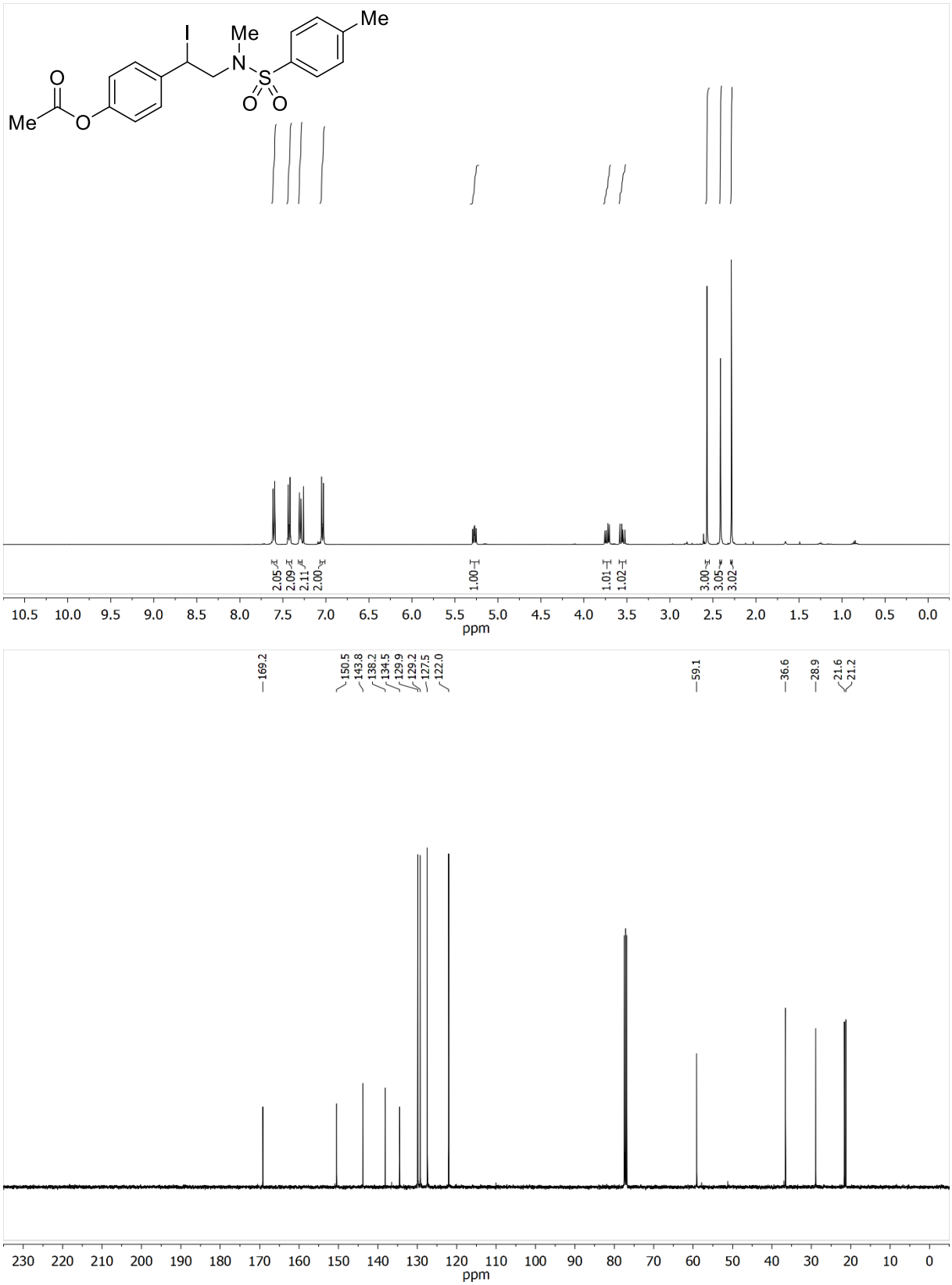
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-2-(3-methoxyphenyl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15w)



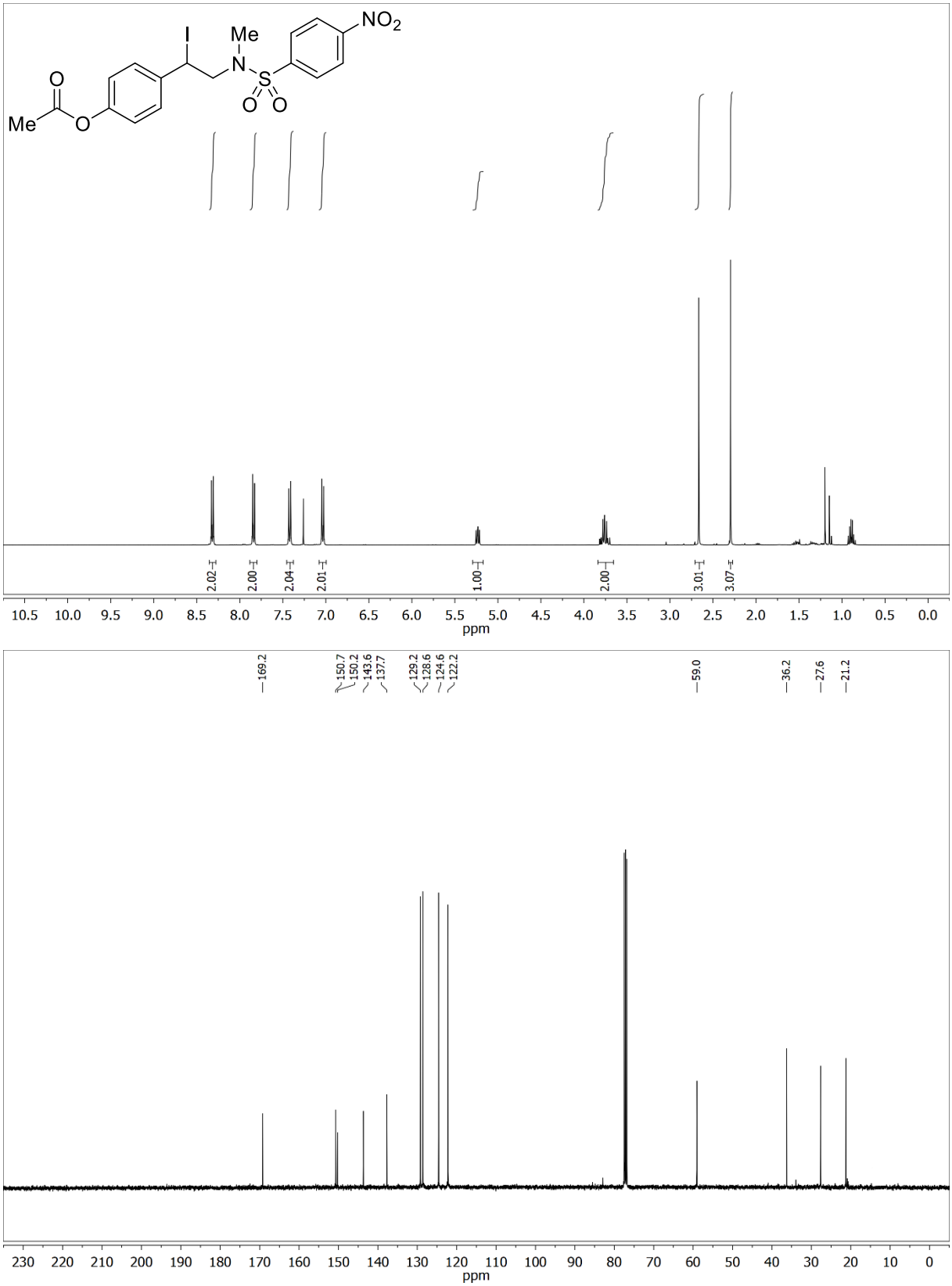
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

4-(2-((*N*,4-dimethylphenyl)sulfonamido)-1-iodoethyl)phenyl acetate (15x)



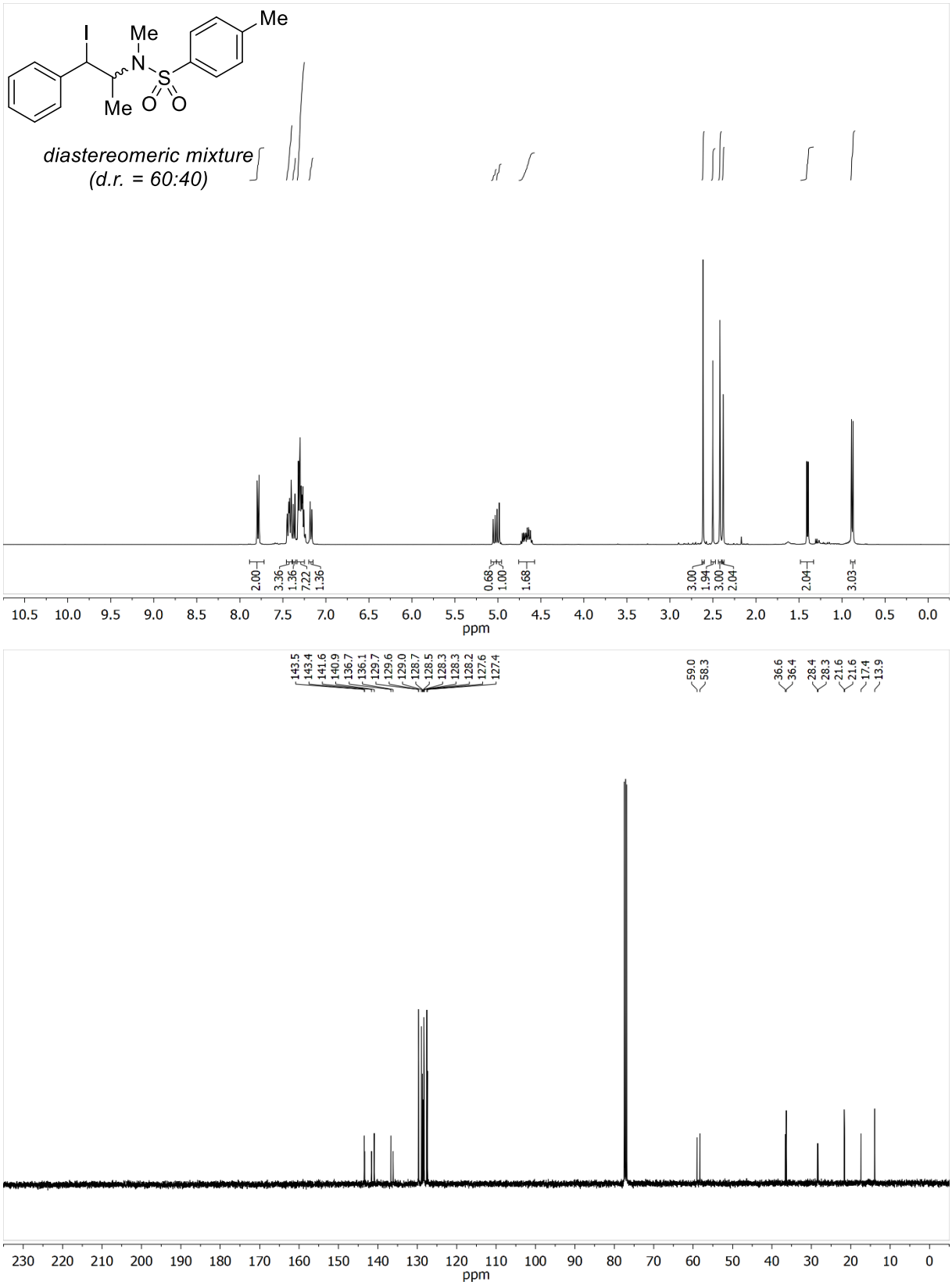
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

4-(1-iodo-2-((*N*-methyl-4-nitrophenyl)sulfonamido)ethyl)phenyl acetate (Ns-15x)



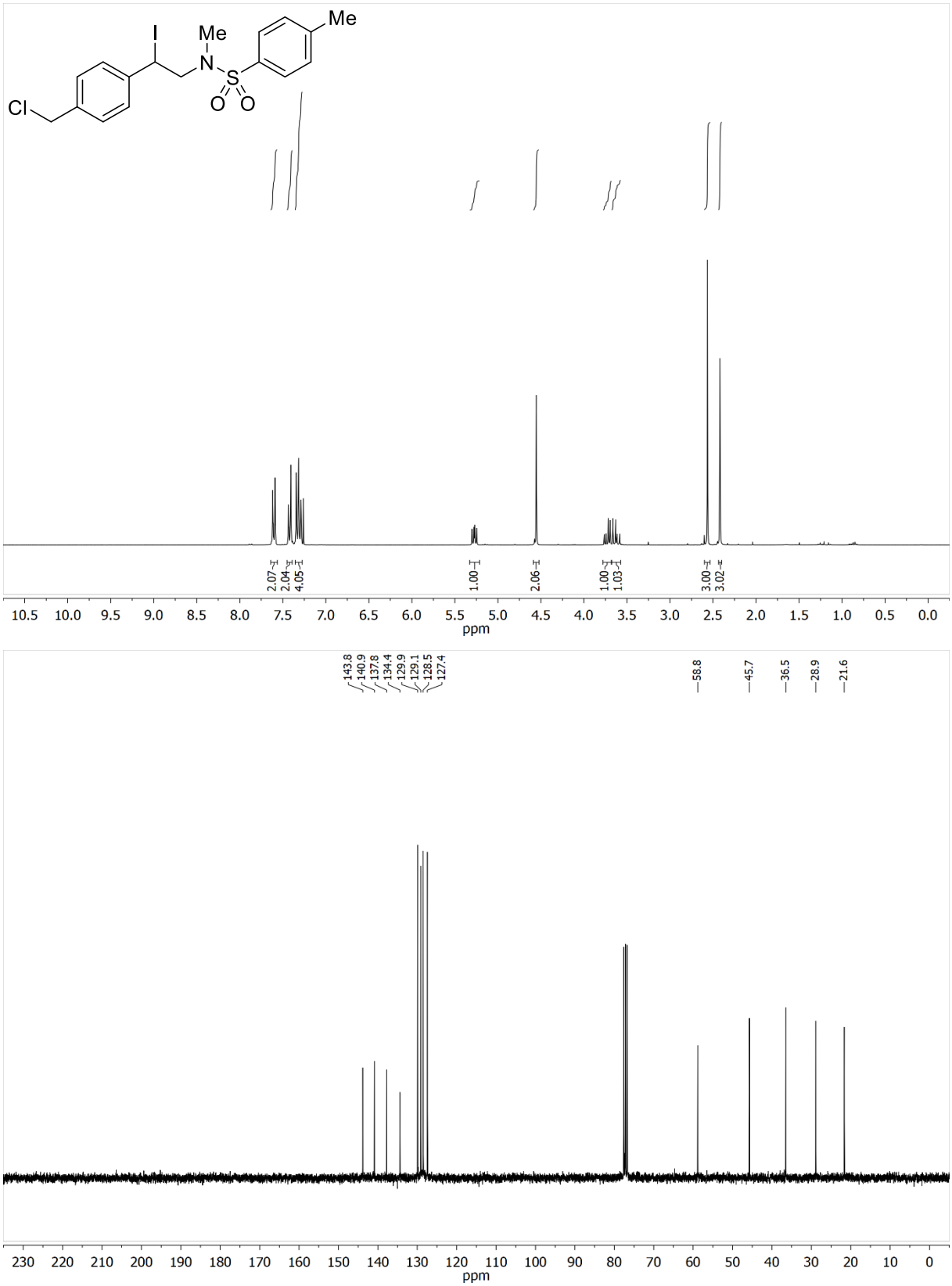
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(1-iodo-1-phenylpropan-2-yl)-_N_,4-dimethylbenzenesulfonamide (d.r. 60:40) (15z)



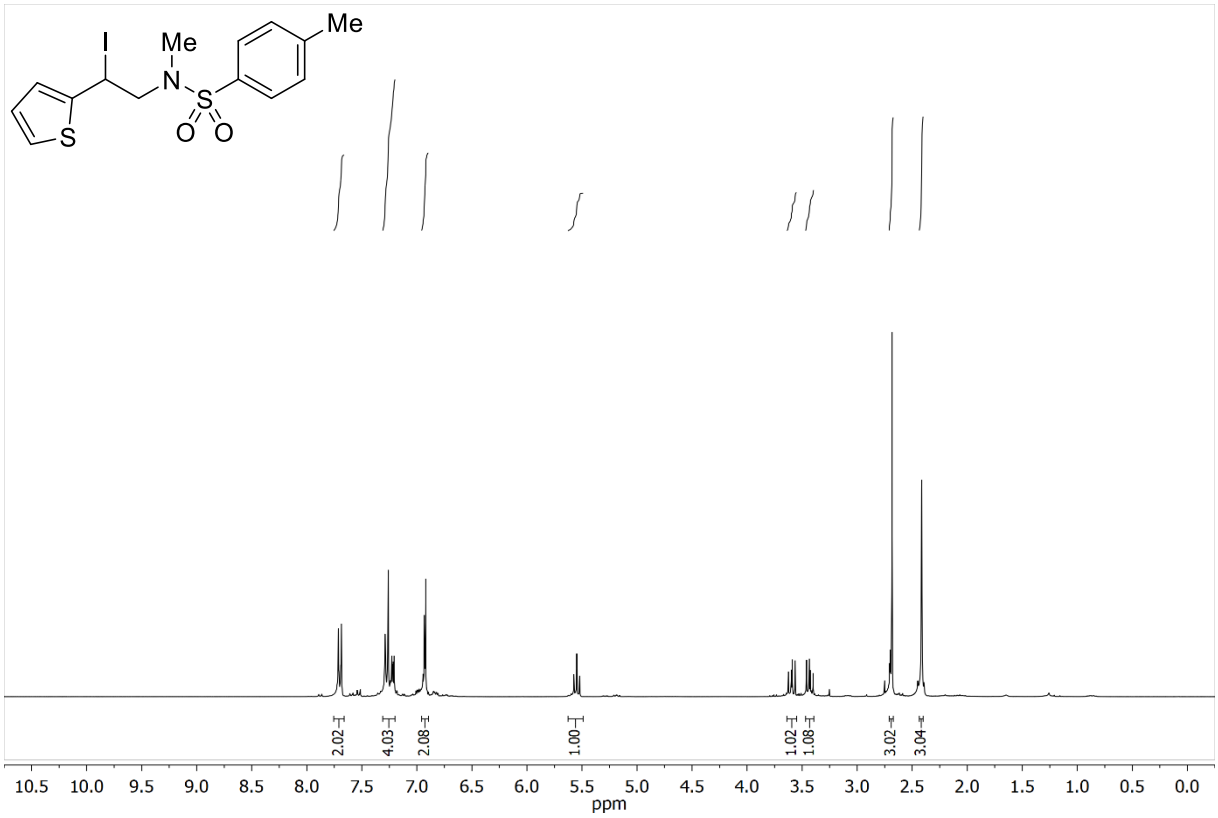
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

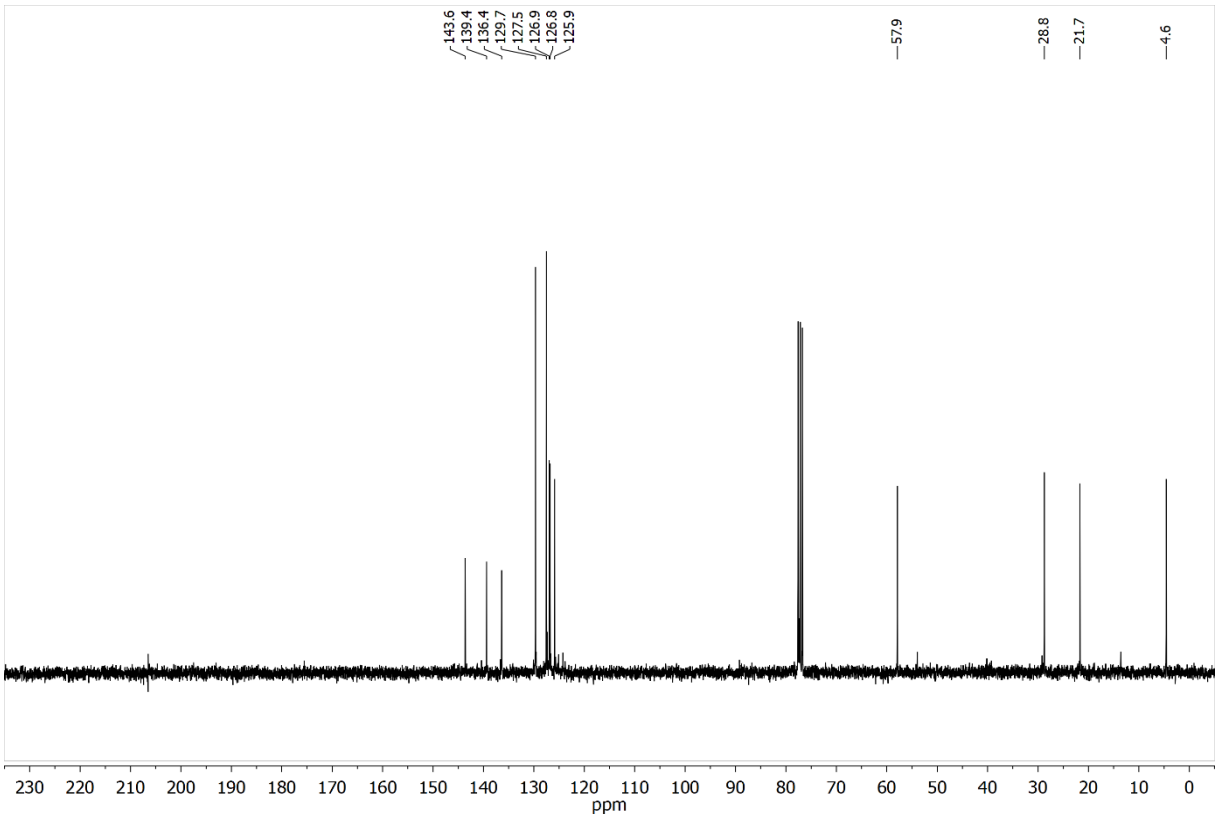
_N_-(2-(4-(chloromethyl)phenyl)-2-iodoethyl)-_N_,4-dimethylbenzenesulfonamide (15ad)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

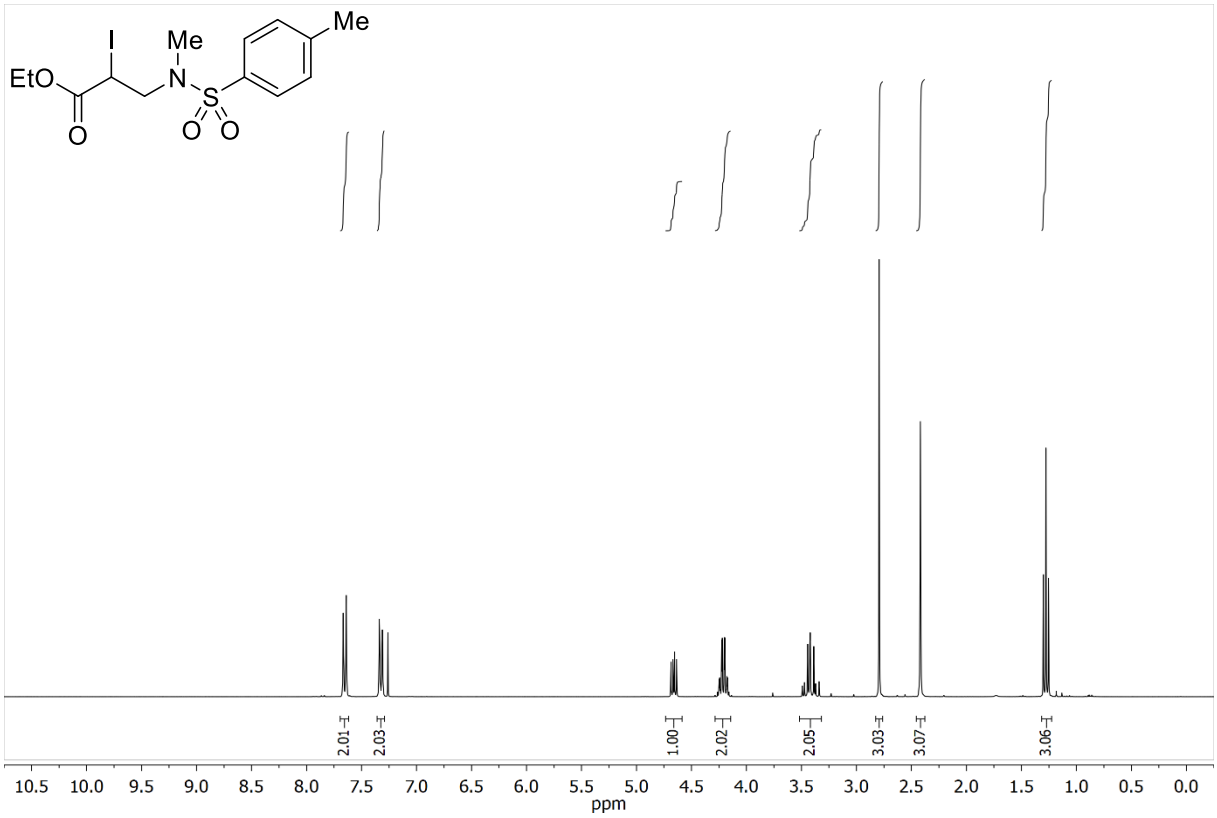
_N_-(2-iodo-2-(thiophen-2-yl)ethyl)-_N_,4-dimethylbenzenesulfonamide (15af)

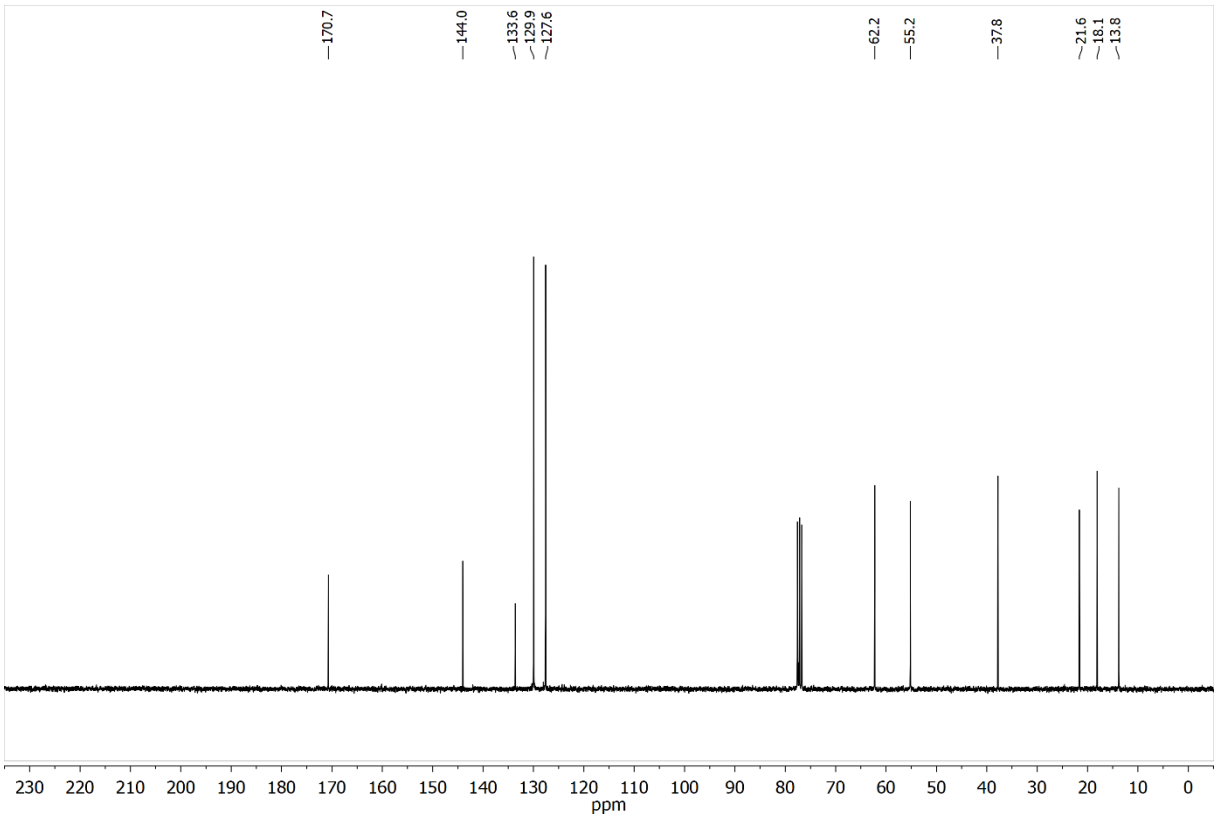




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

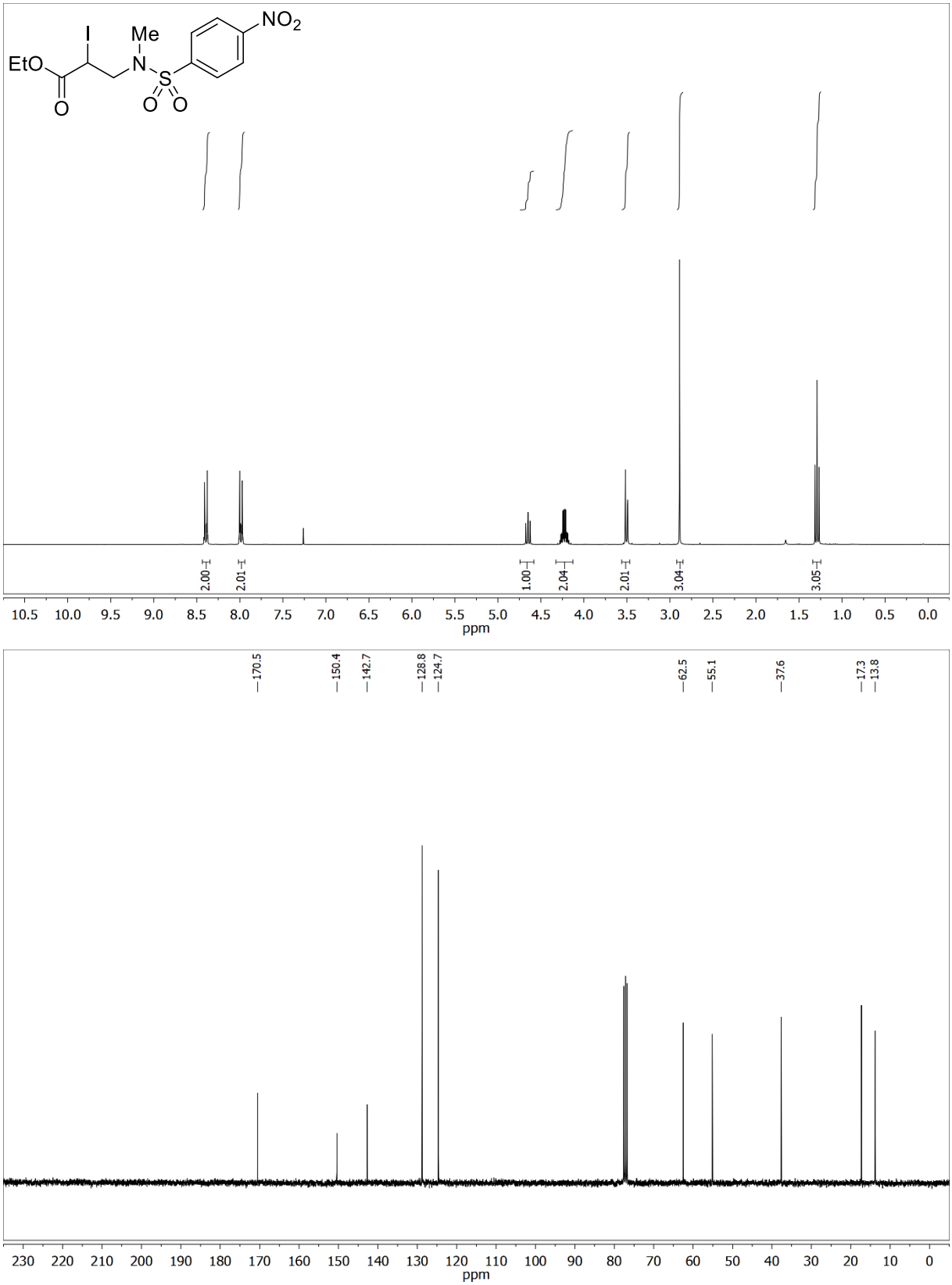
ethyl 3-((*N*,4-dimethylphenyl)sulfonamido)-2-iodopropanoate (15ai)





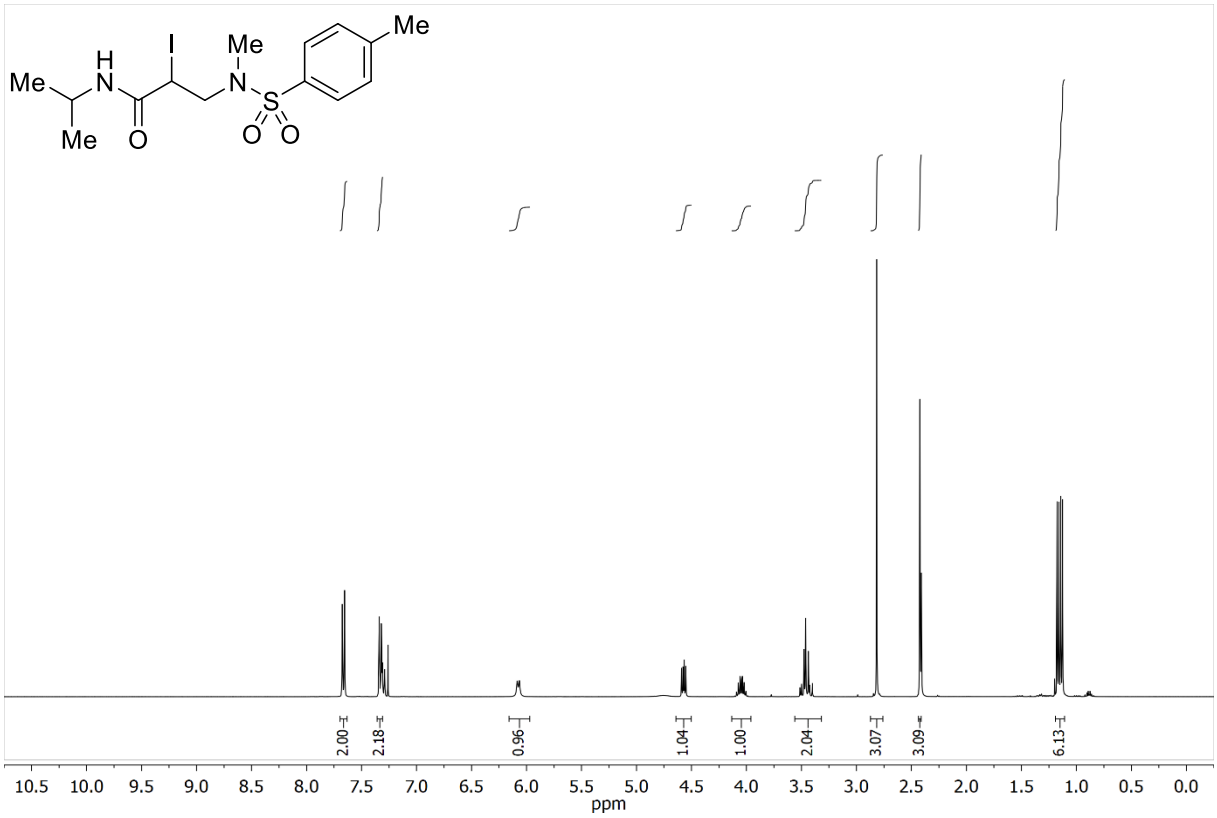
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

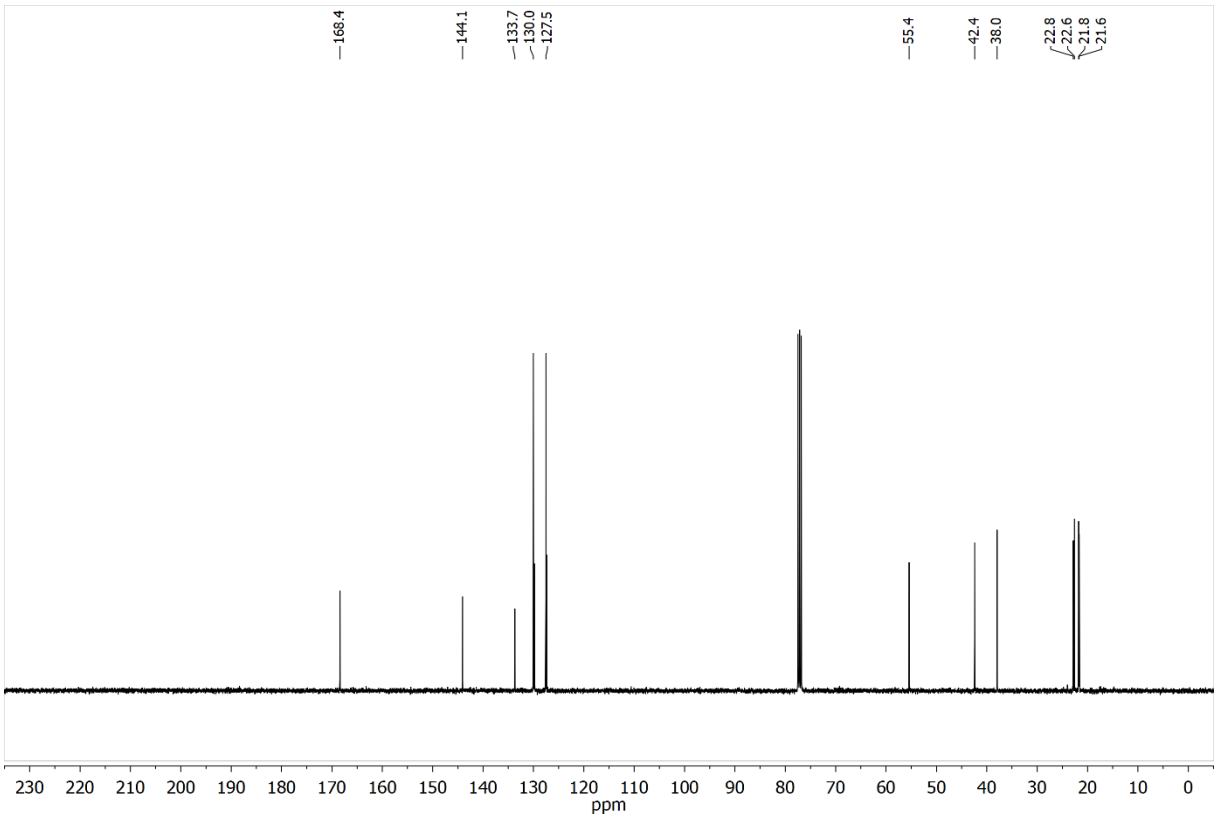
ethyl 2-iodo-3-((*N*-methyl-4-nitrophenyl)sulfonamido)propanoate (Ns-15ai)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

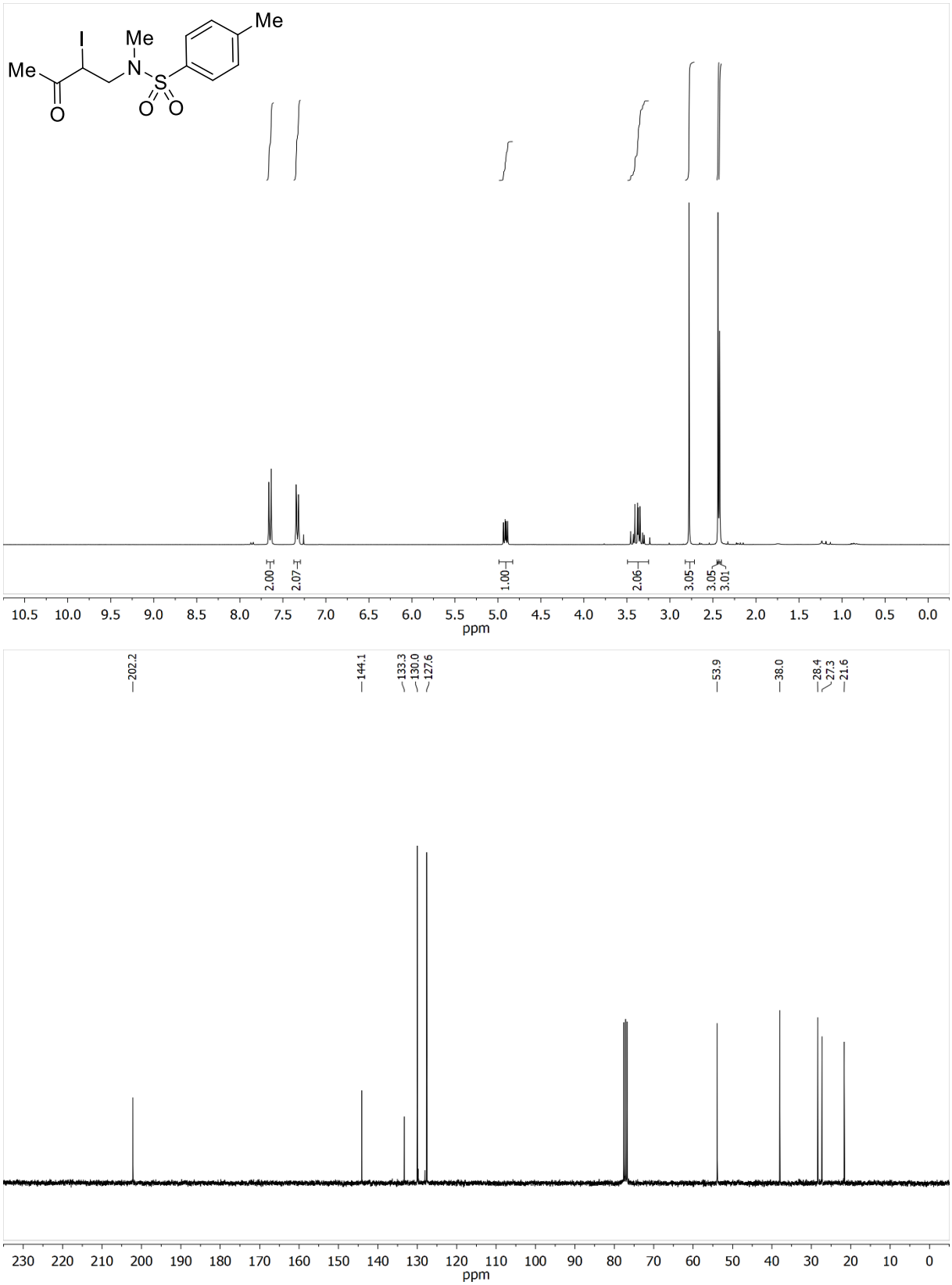
3-((*N*,4-dimethylphenyl)sulfonamido)-2-iodo-*N*-isopropylpropanamide (15aj)





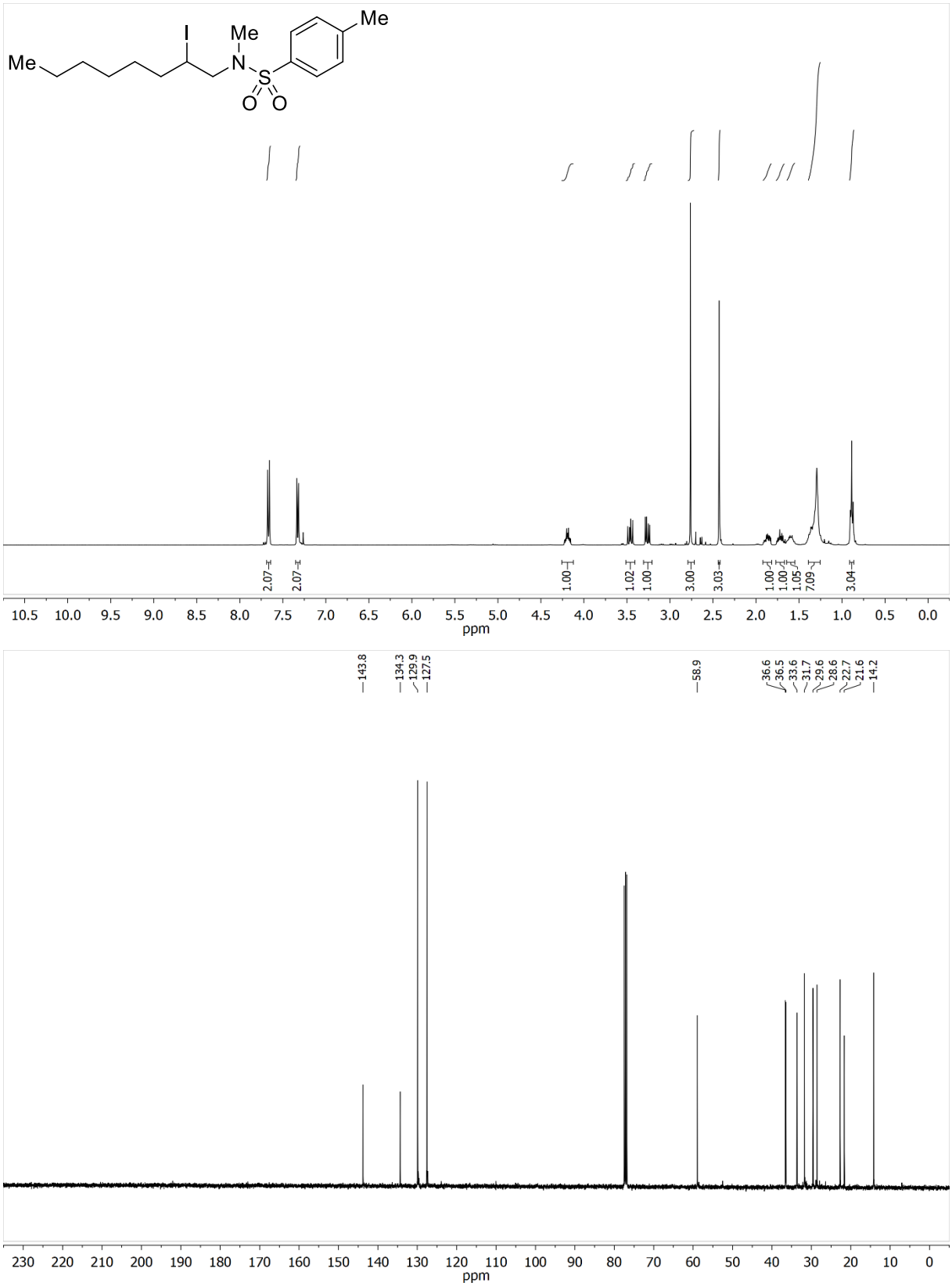
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-3-oxobutyl)-_N_,4-dimethylbenzenesulfonamide (15ak)



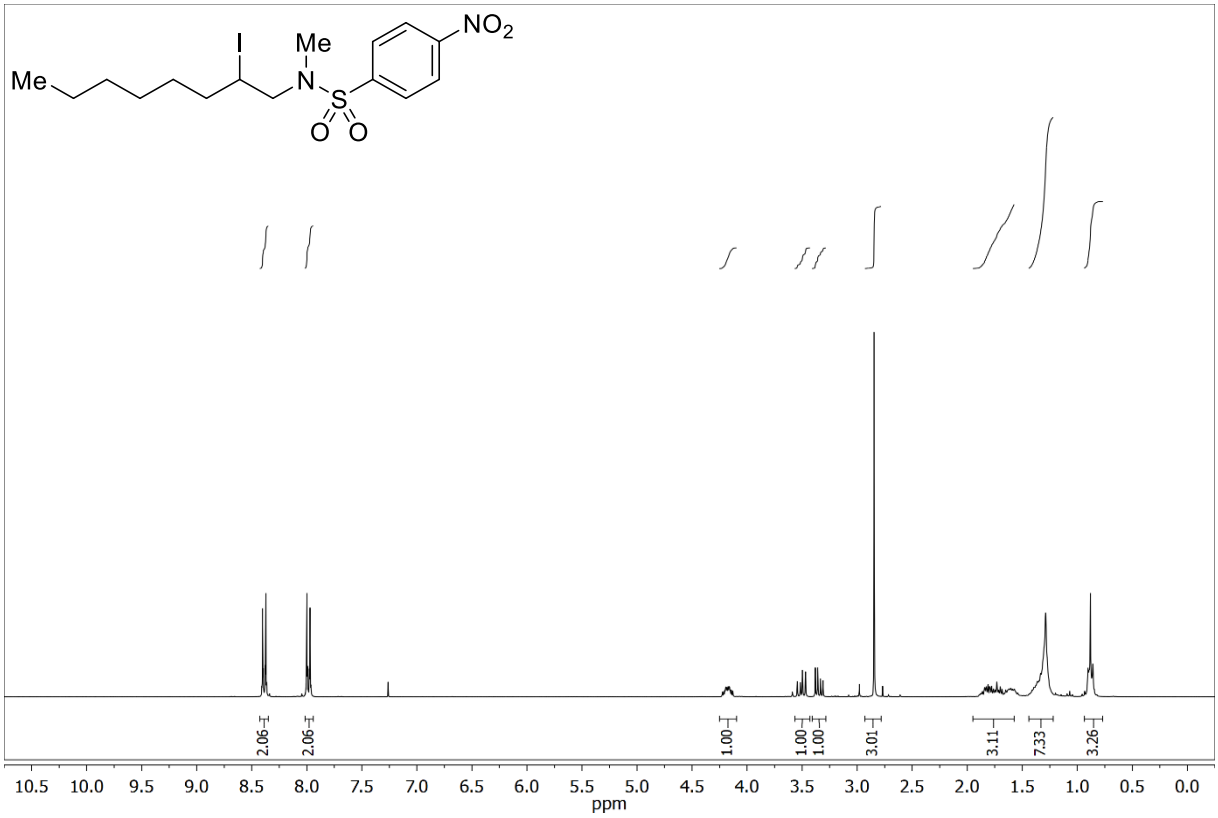
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

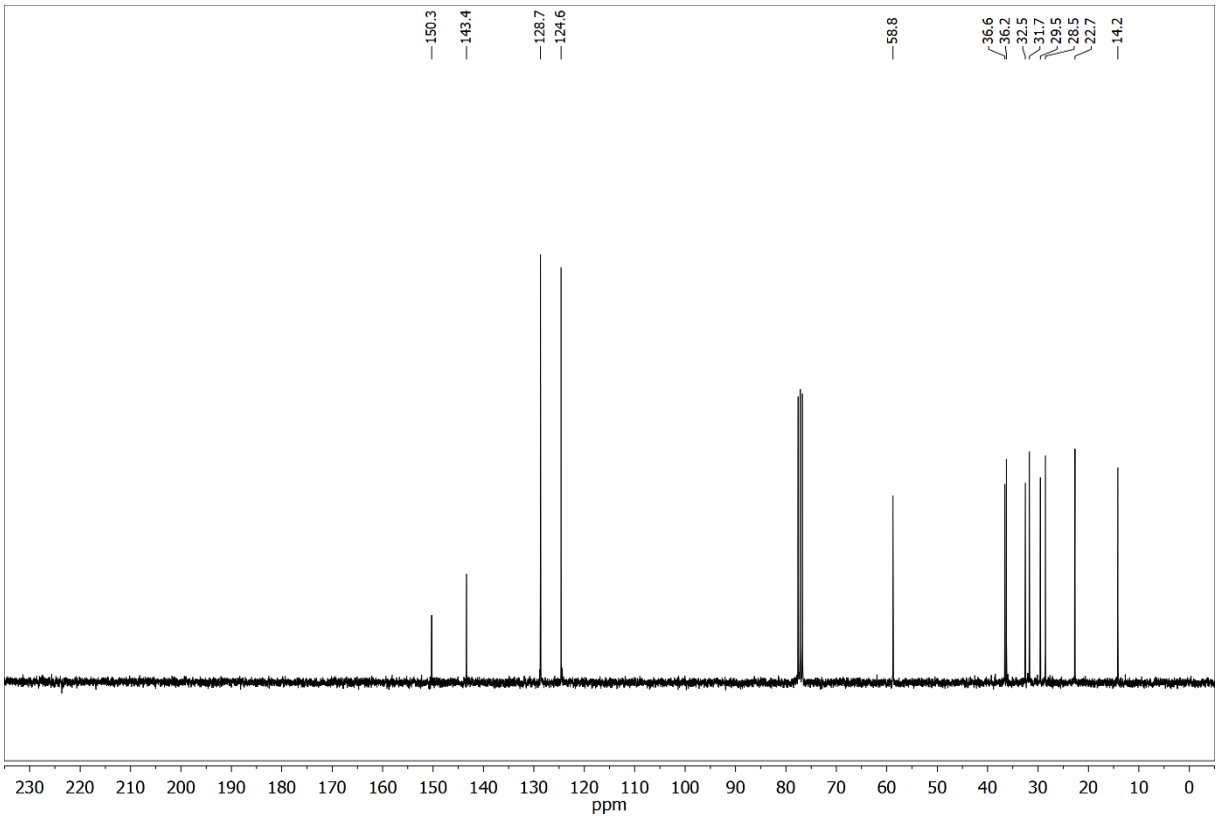
_N_-(2-iodooctyl)-_N_,4-dimethylbenzenesulfonamide (15an)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

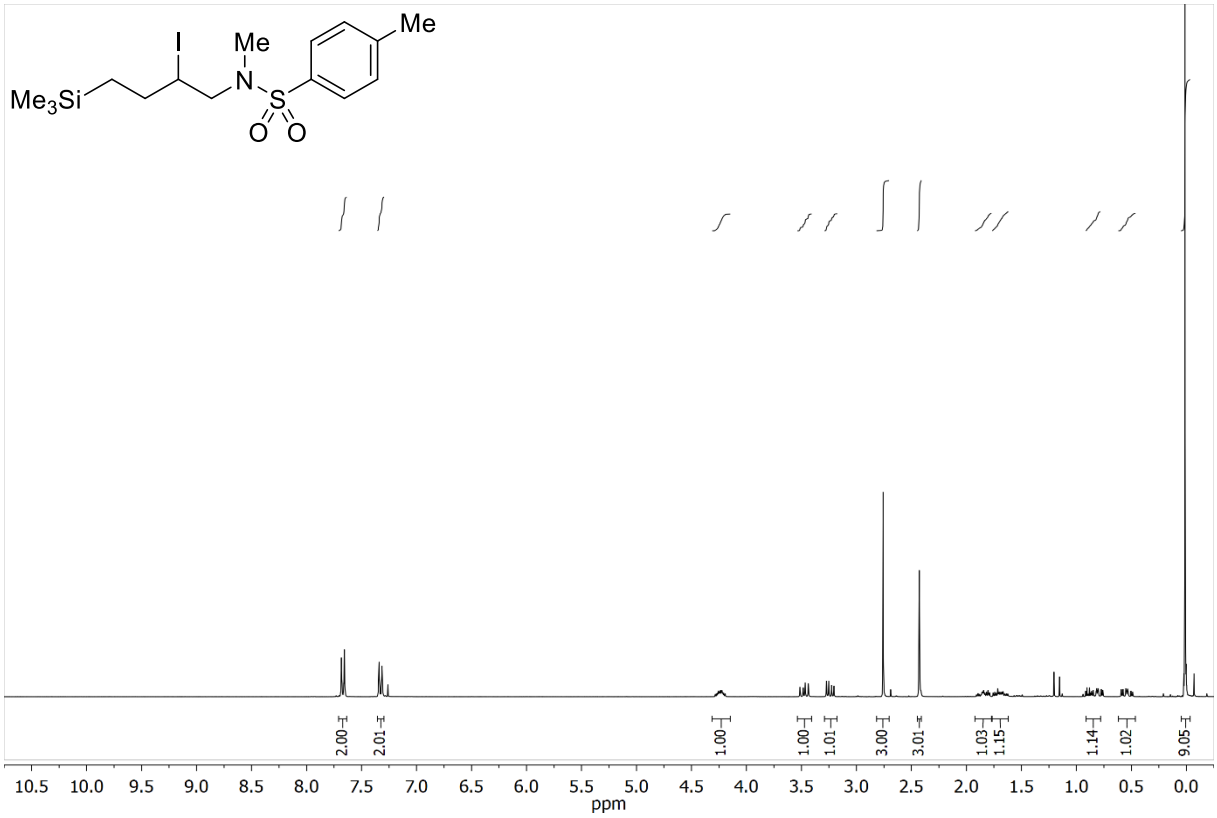
_N_-(2-iodooctyl)-_N_-methyl-4-nitrobenzenesulfonamide (Ns-15an)

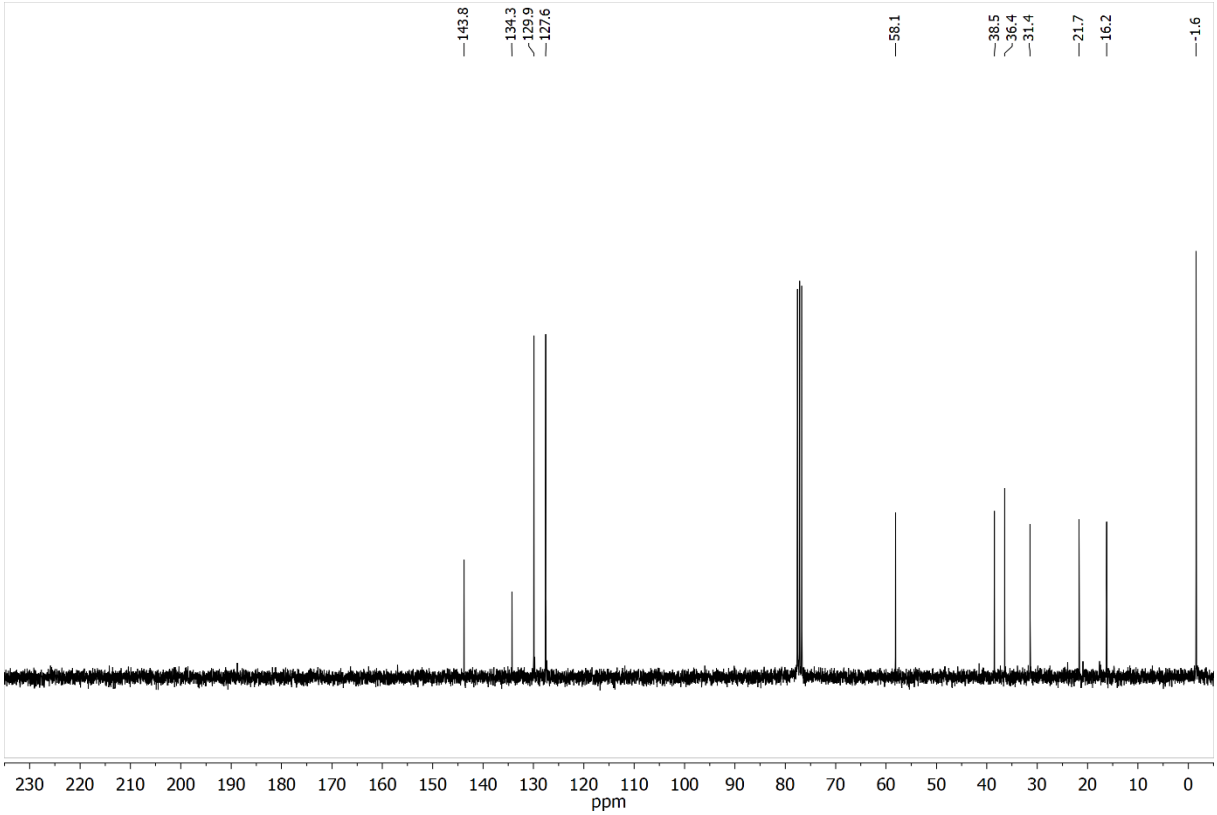




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

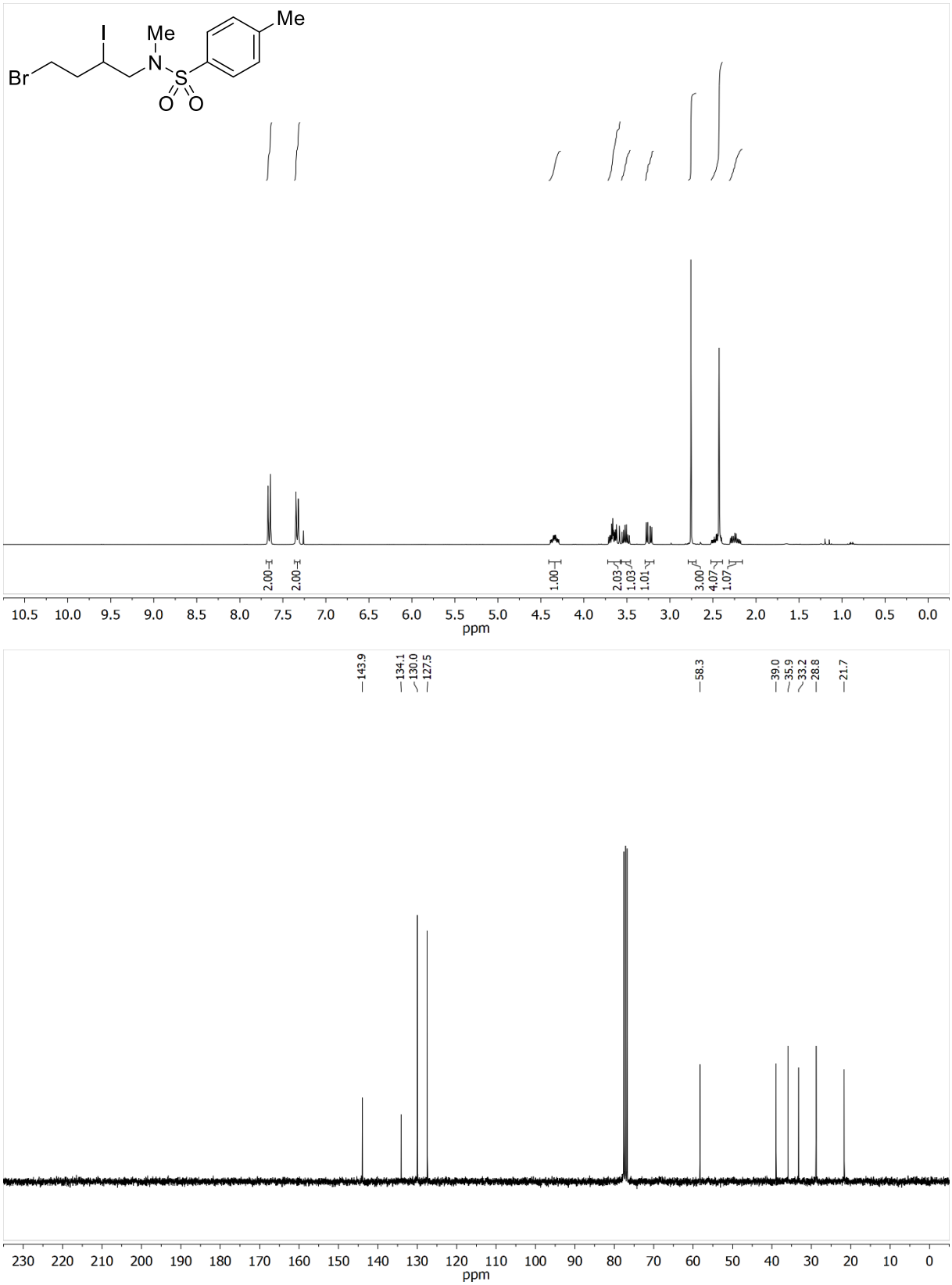
_N_-(2-iodo-4-(trimethylsilyl)butyl)-_N_,4-dimethylbenzenesulfonamide (15ao)





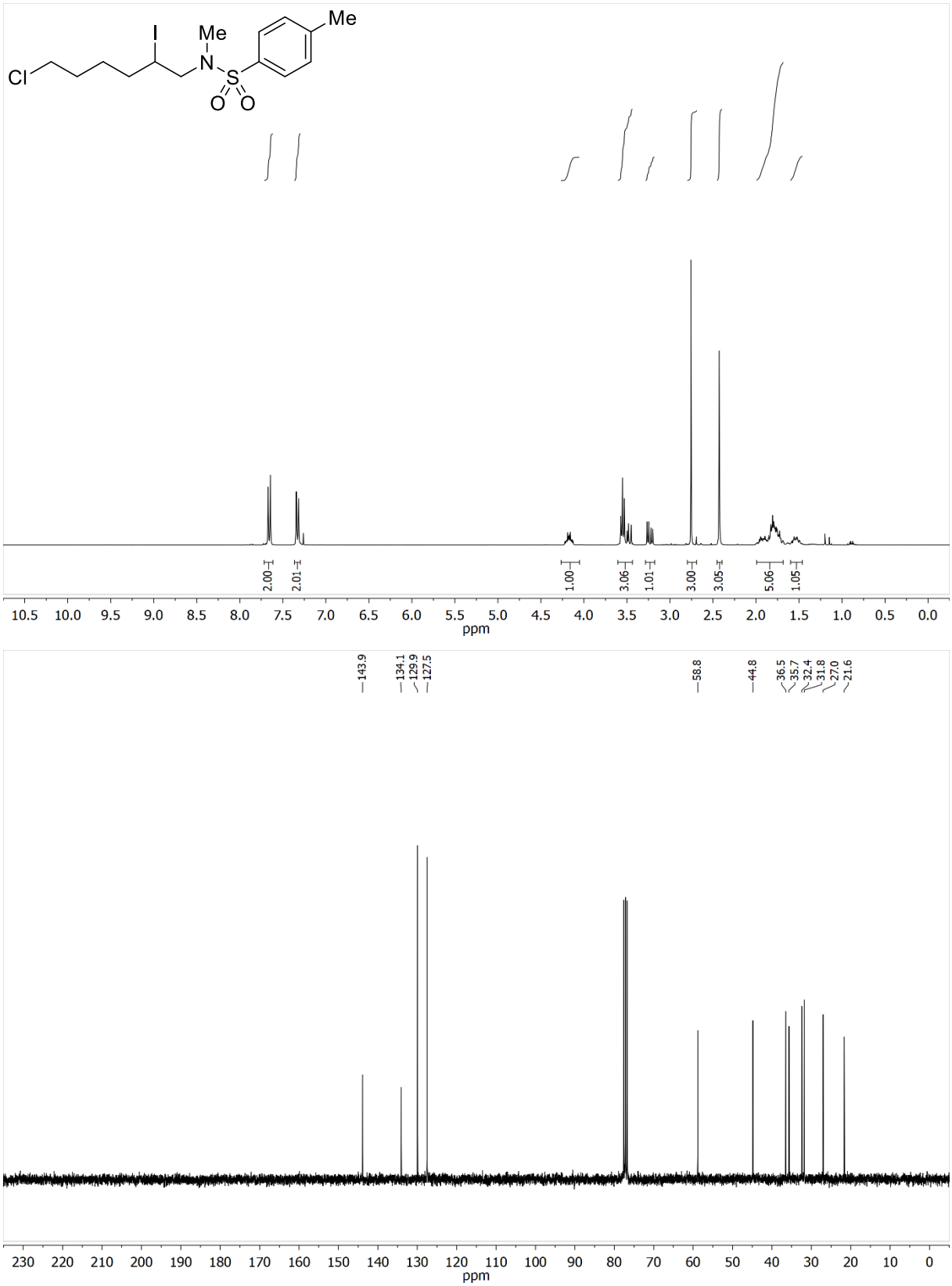
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(4-bromo-2-iodobutyl)-_N_,4-dimethylbenzenesulfonamide (15ap)



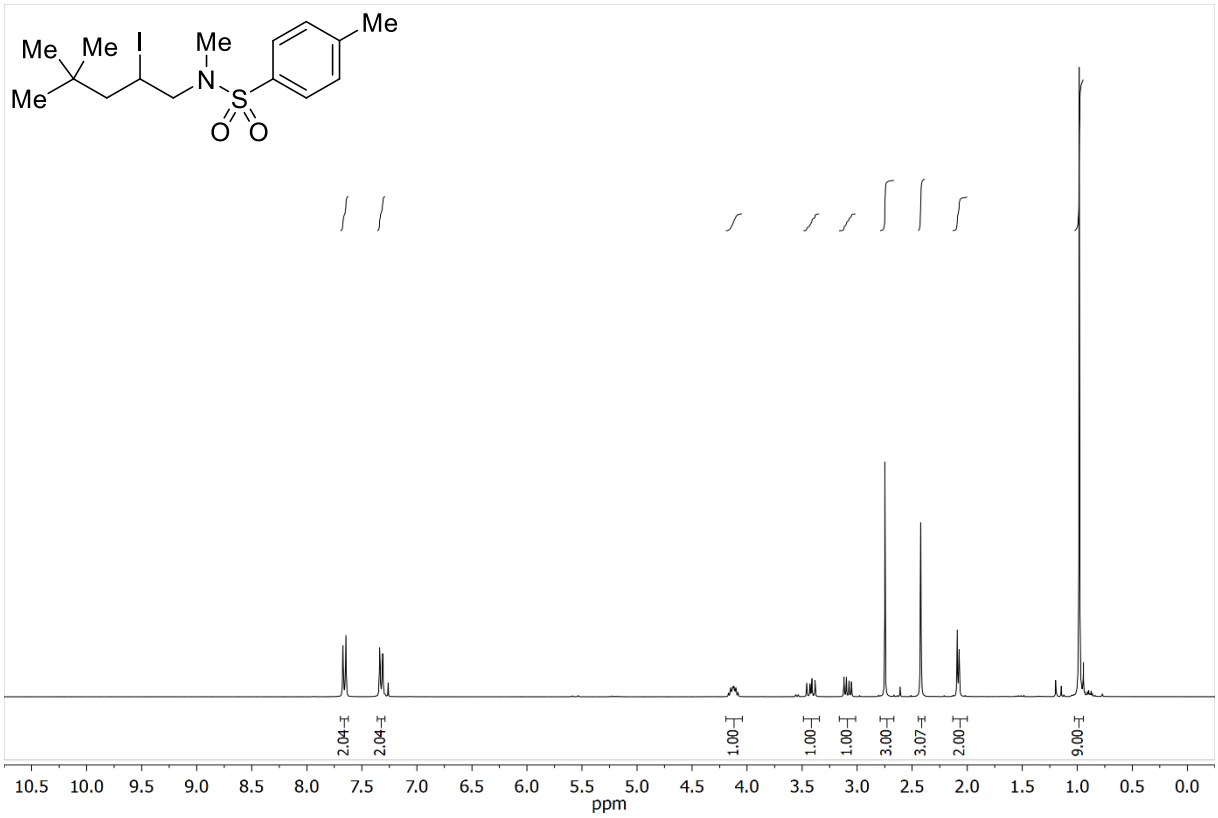
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

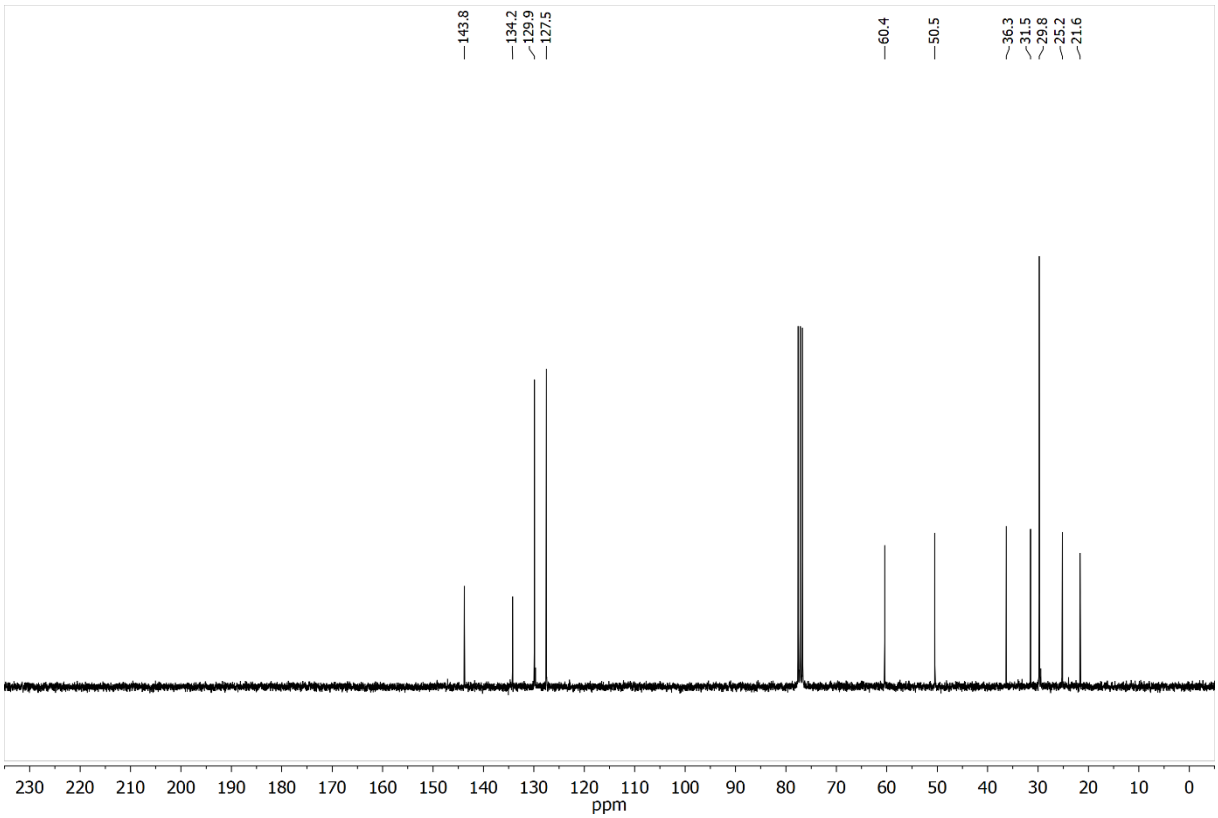
_N_-(6-chloro-2-iodohexyl)-_N_,4-dimethylbenzenesulfonamide (15aq)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

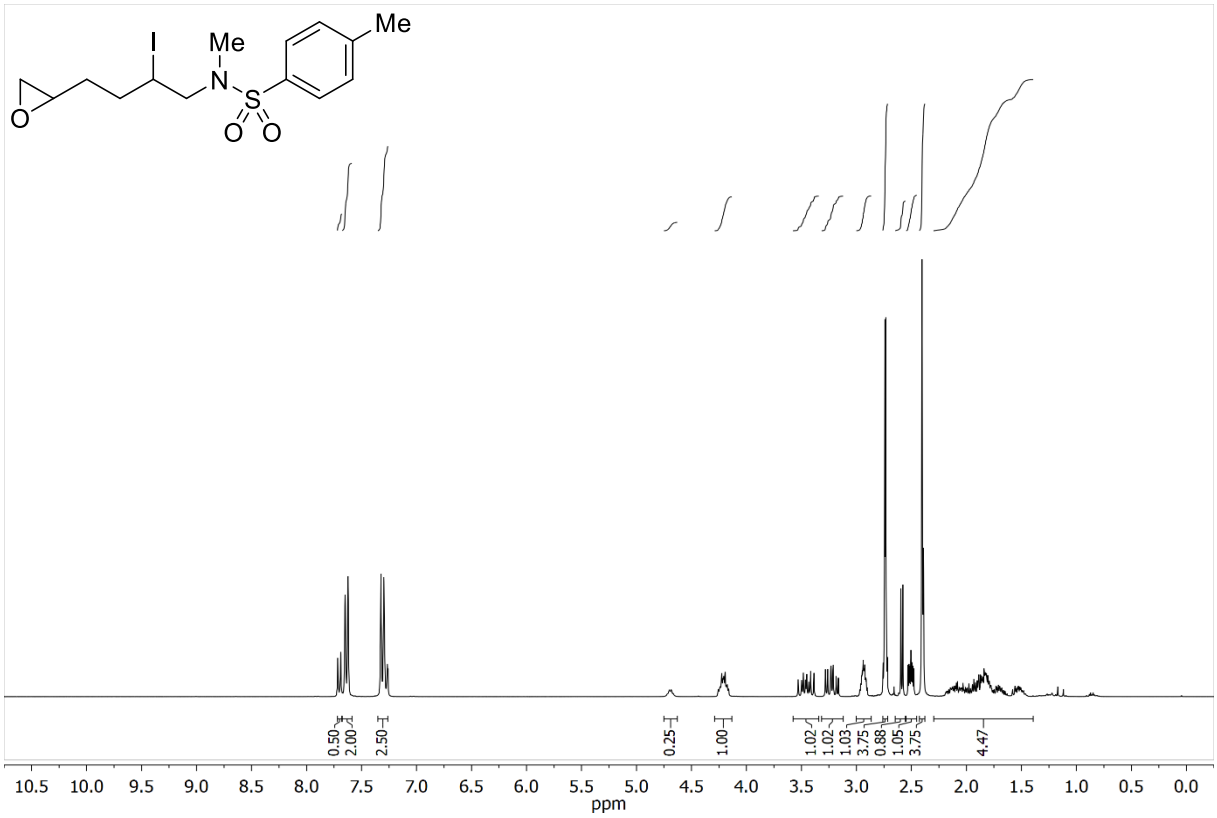
_N_-(2-iodo-4,4-dimethylpentyl)-_N_,4-dimethylbenzenesulfonamide (15ar)

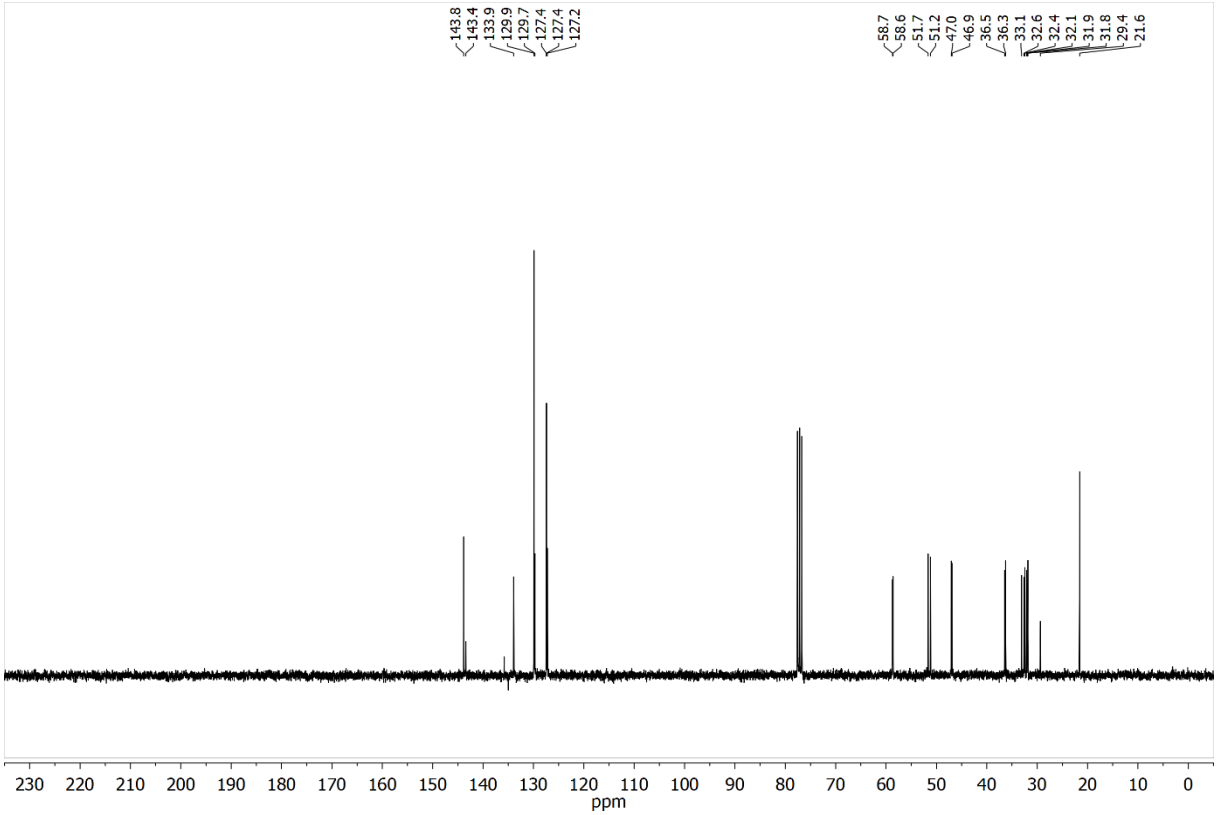




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

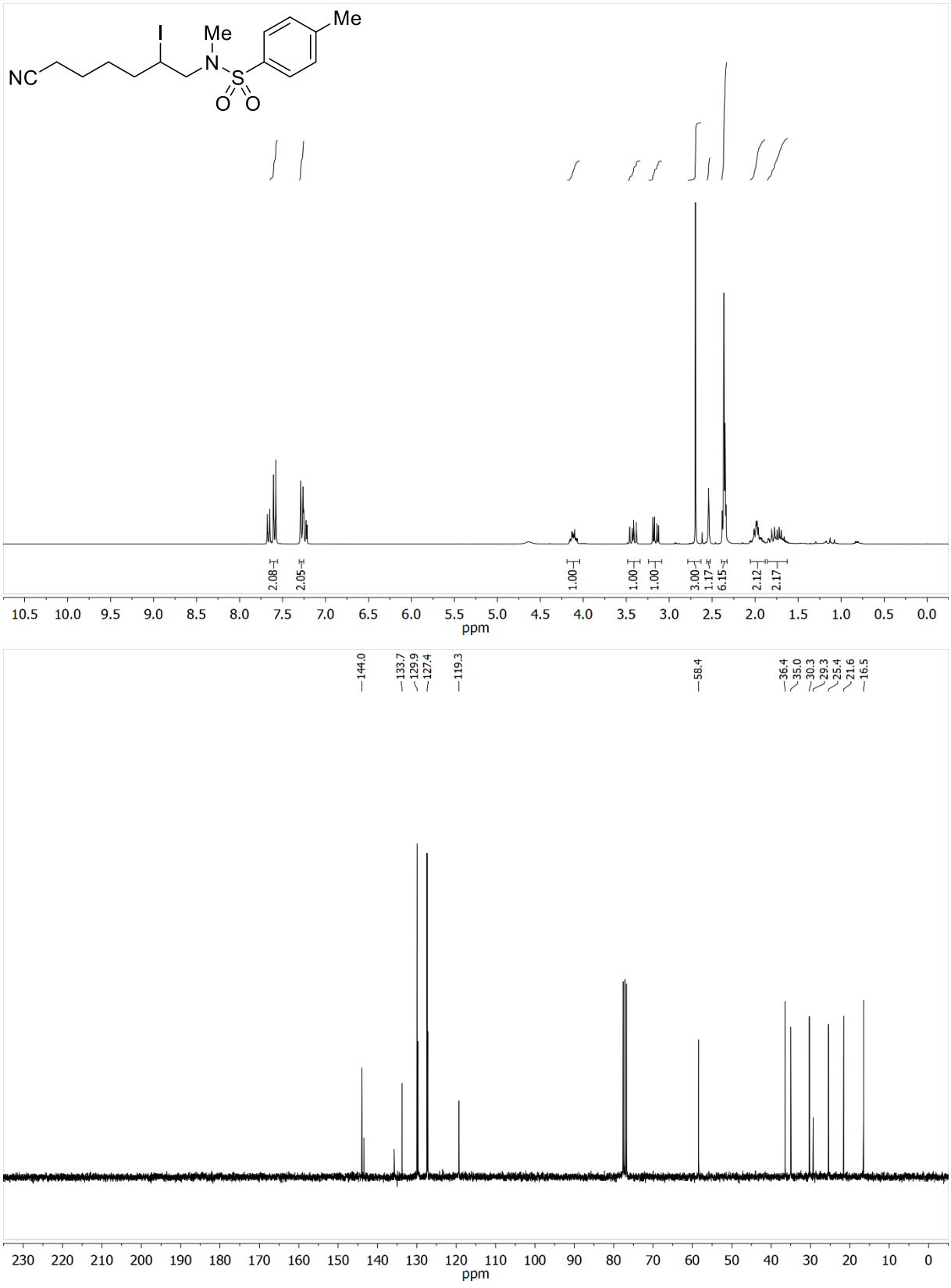
_N_-(2-iodo-4-(oxiran-2-yl)butyl)-_N_,4-dimethylbenzenesulfonamide (d.r. = 80:20) (15as)





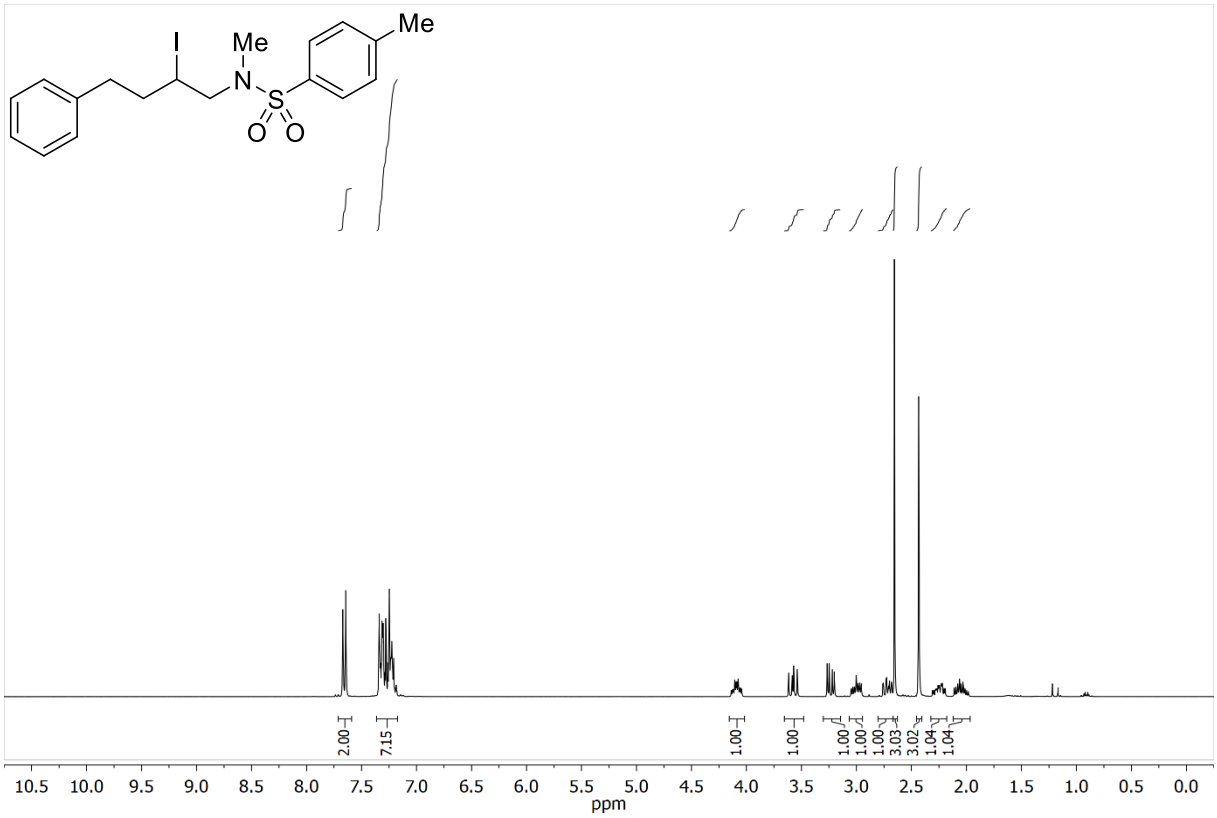
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

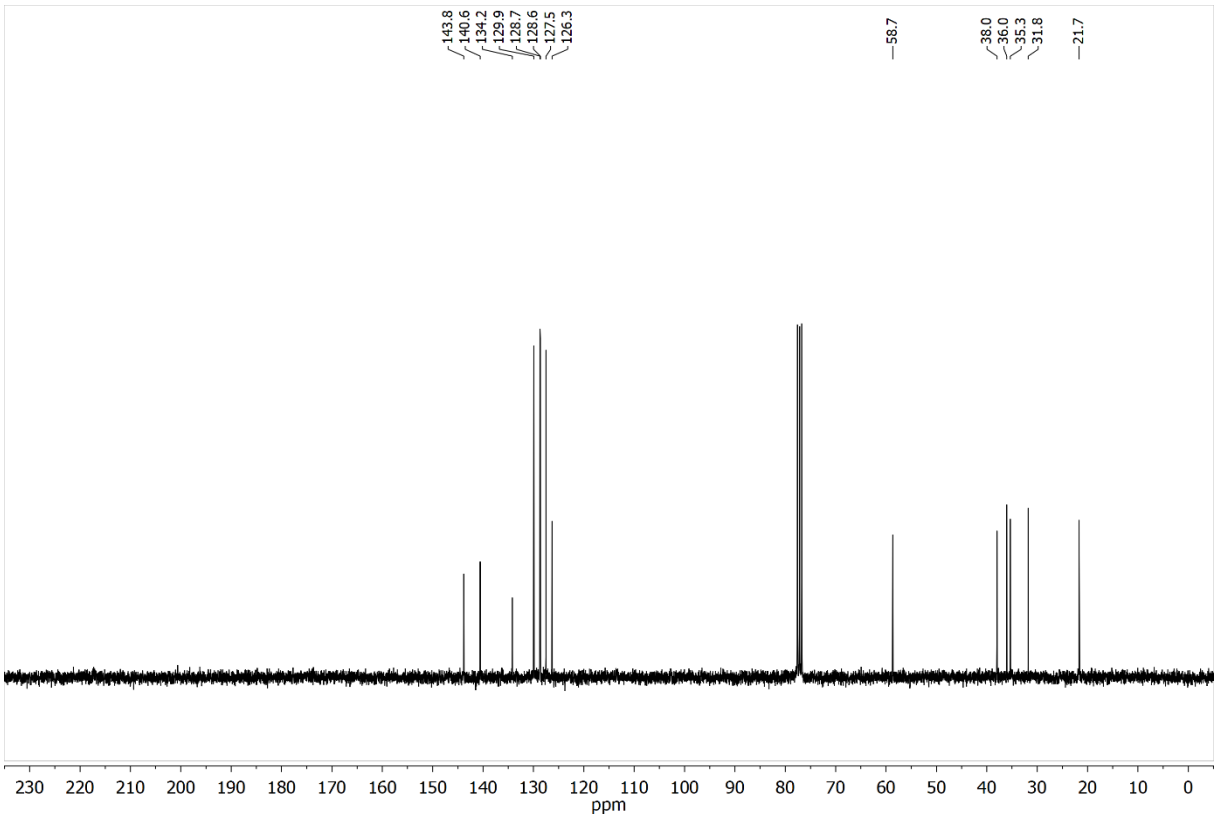
_N_-(6-cyano-2-iodohexyl)-_N_,4-dimethylbenzenesulfonamide (15at)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

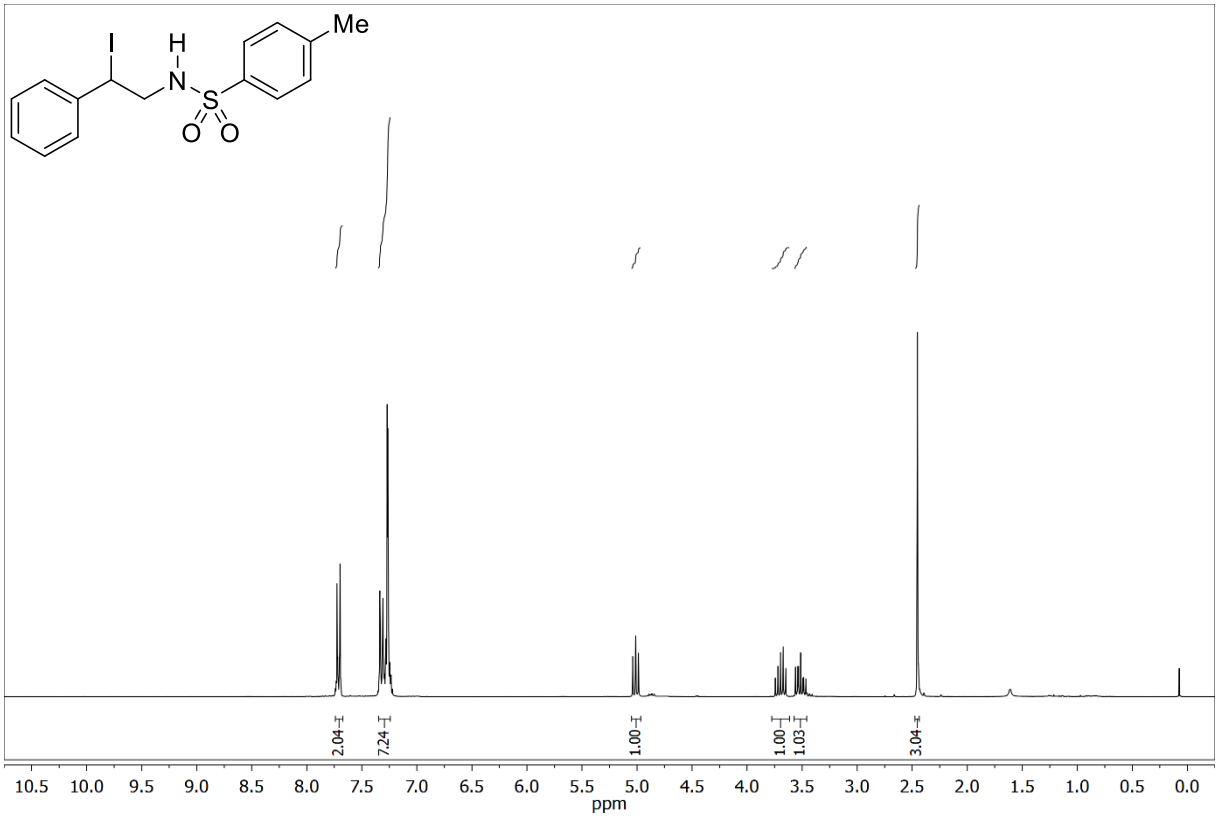
_N_-(2-iodo-4-phenylbutyl)-_N_,4-dimethylbenzenesulfonamide (15au)

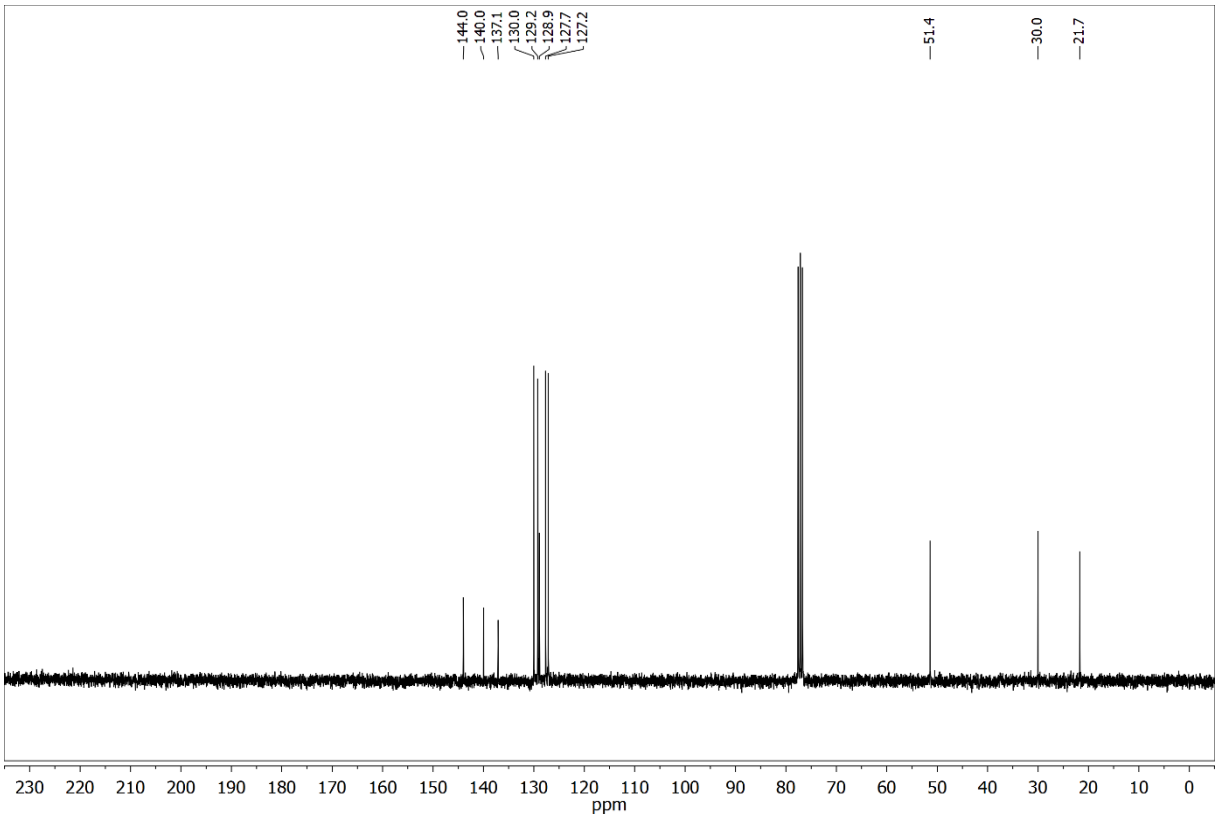




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

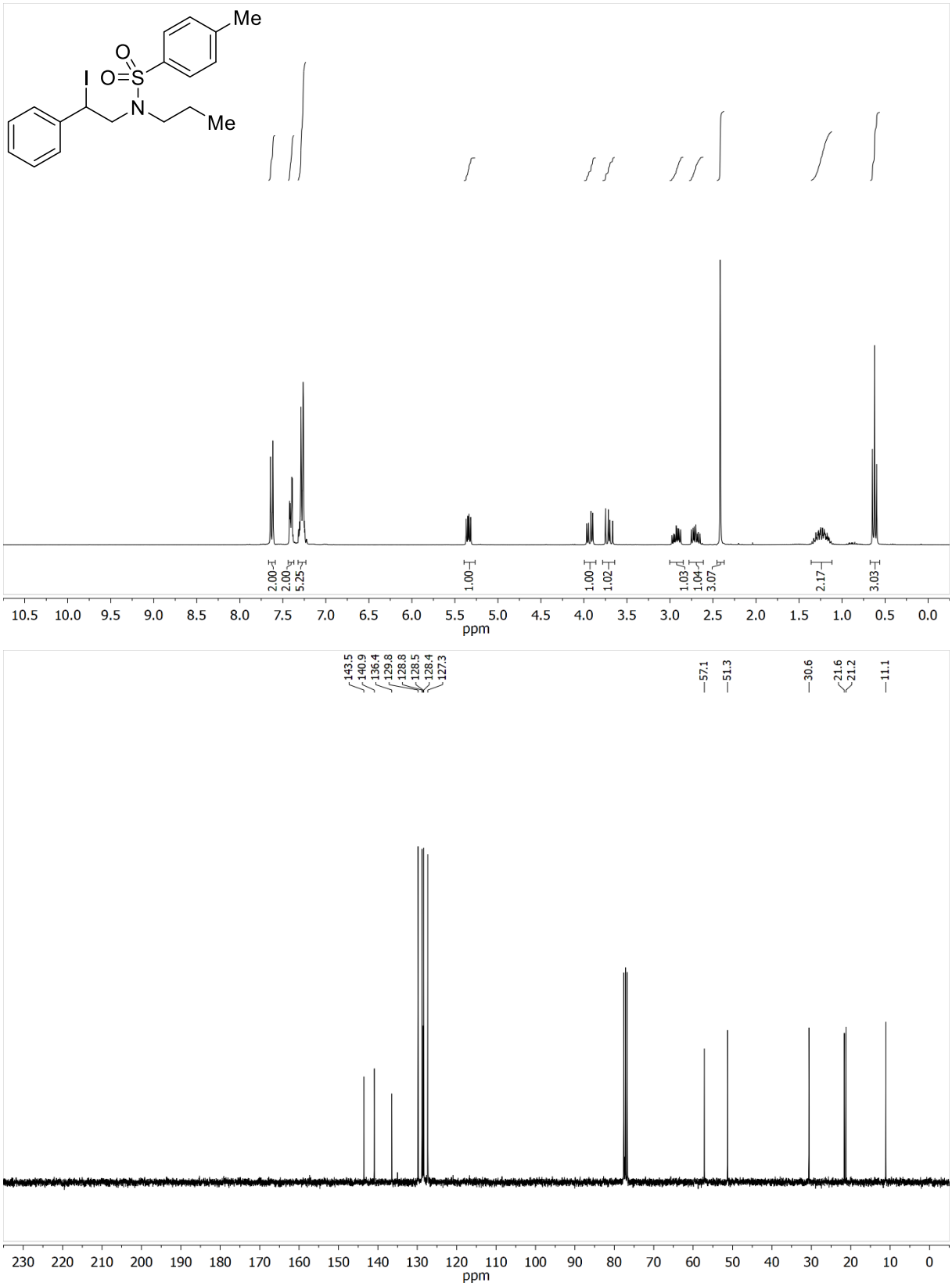
_N_-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bc)





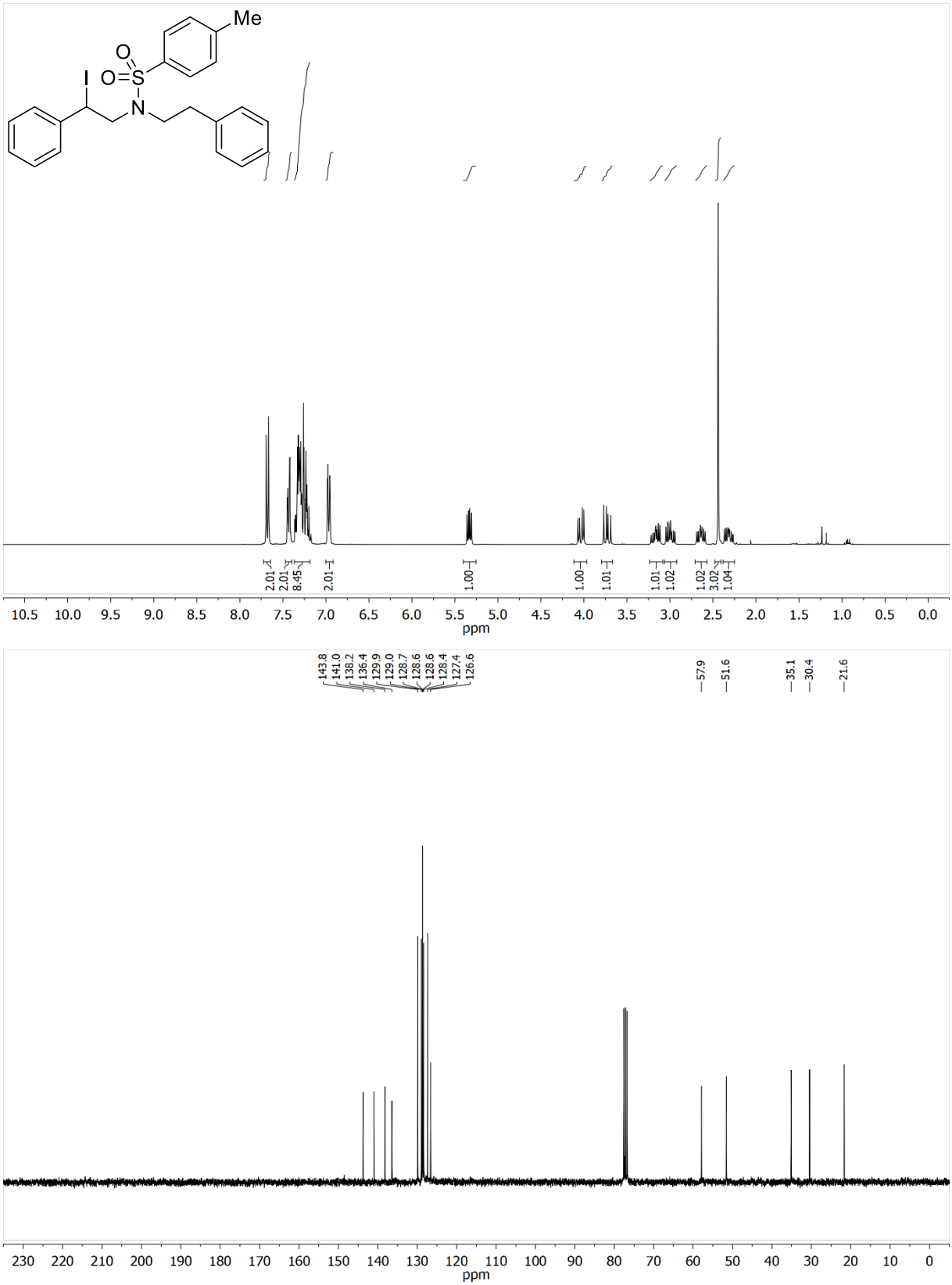
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-2-phenylethyl)-4-methyl-_N_-propylbenzenesulfonamide (15bg)



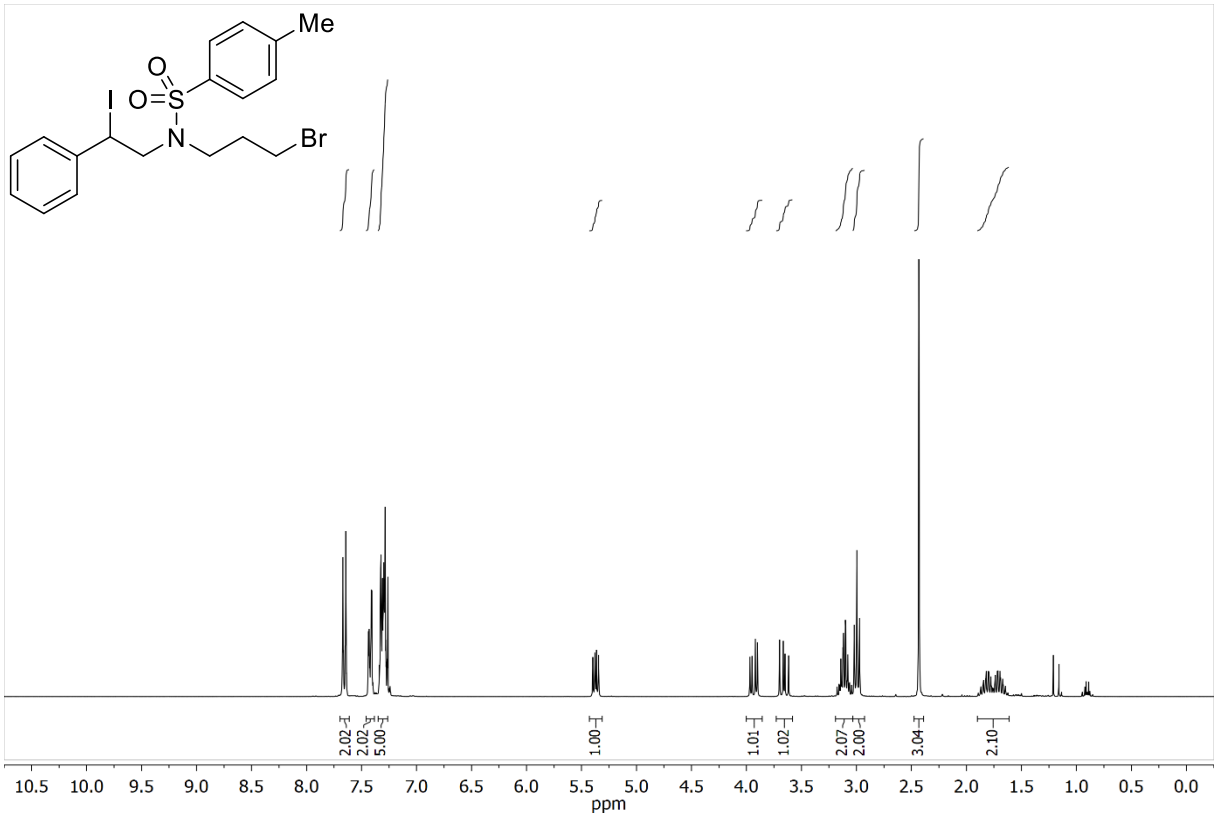
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

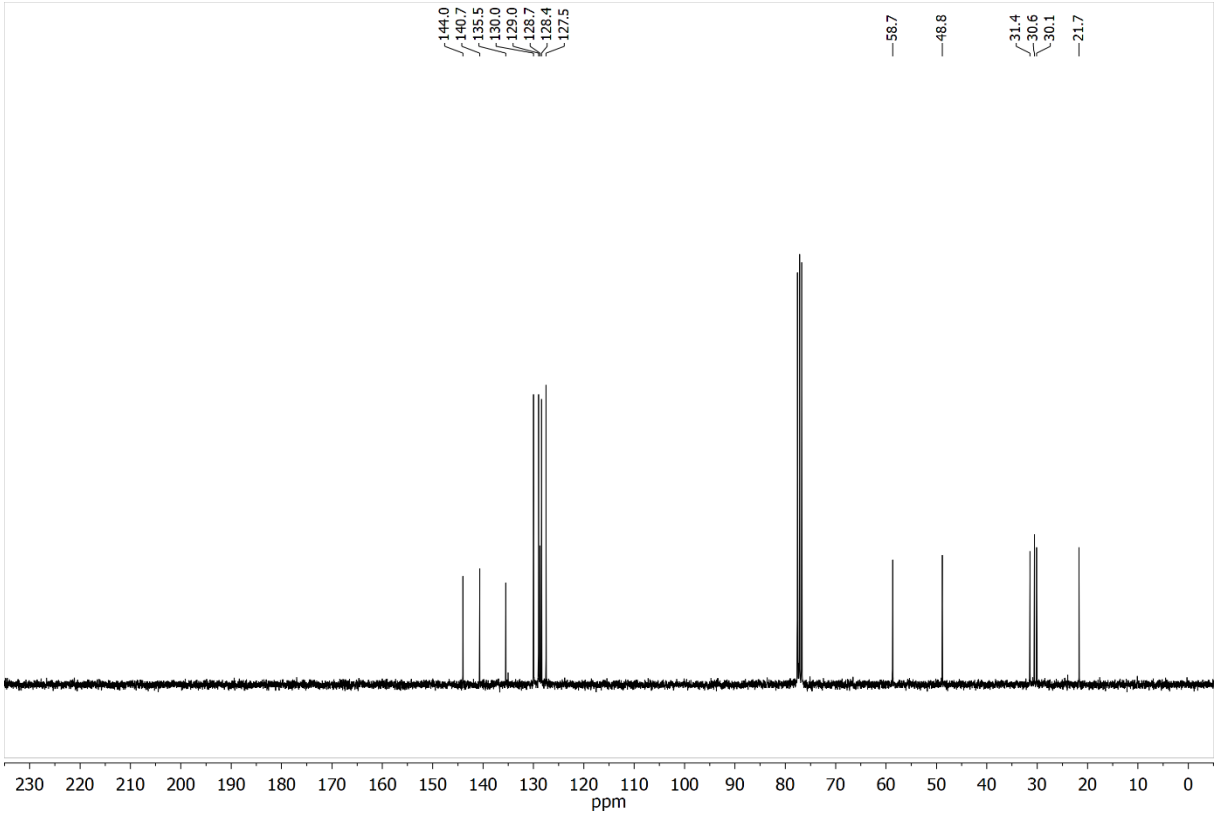
_N_-(2-iodo-2-phenylethyl)-4-methyl-_N_-phenethylbenzenesulfonamide (15bh)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

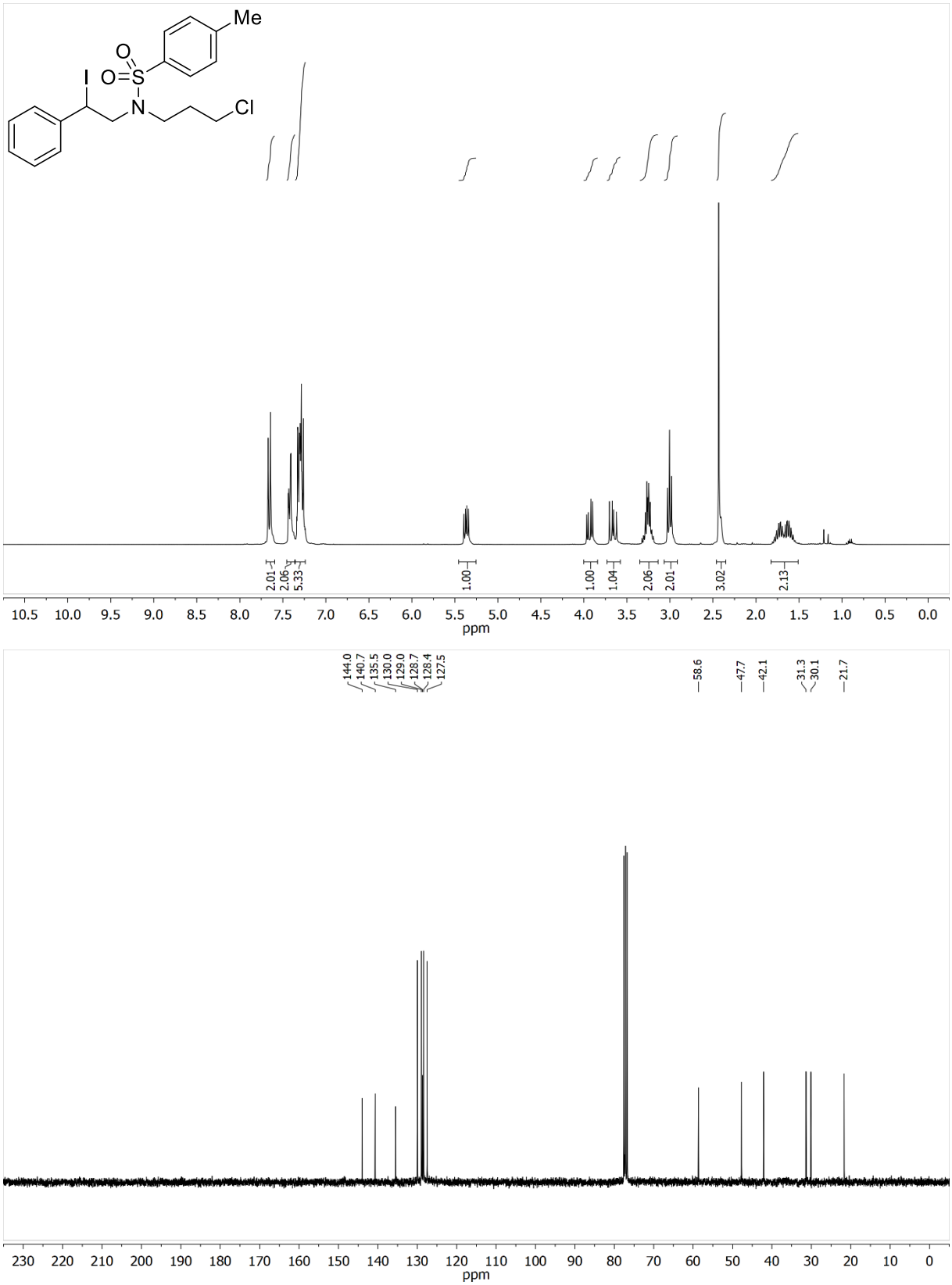
_N_-(3-bromopropyl)-_N_-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bi)





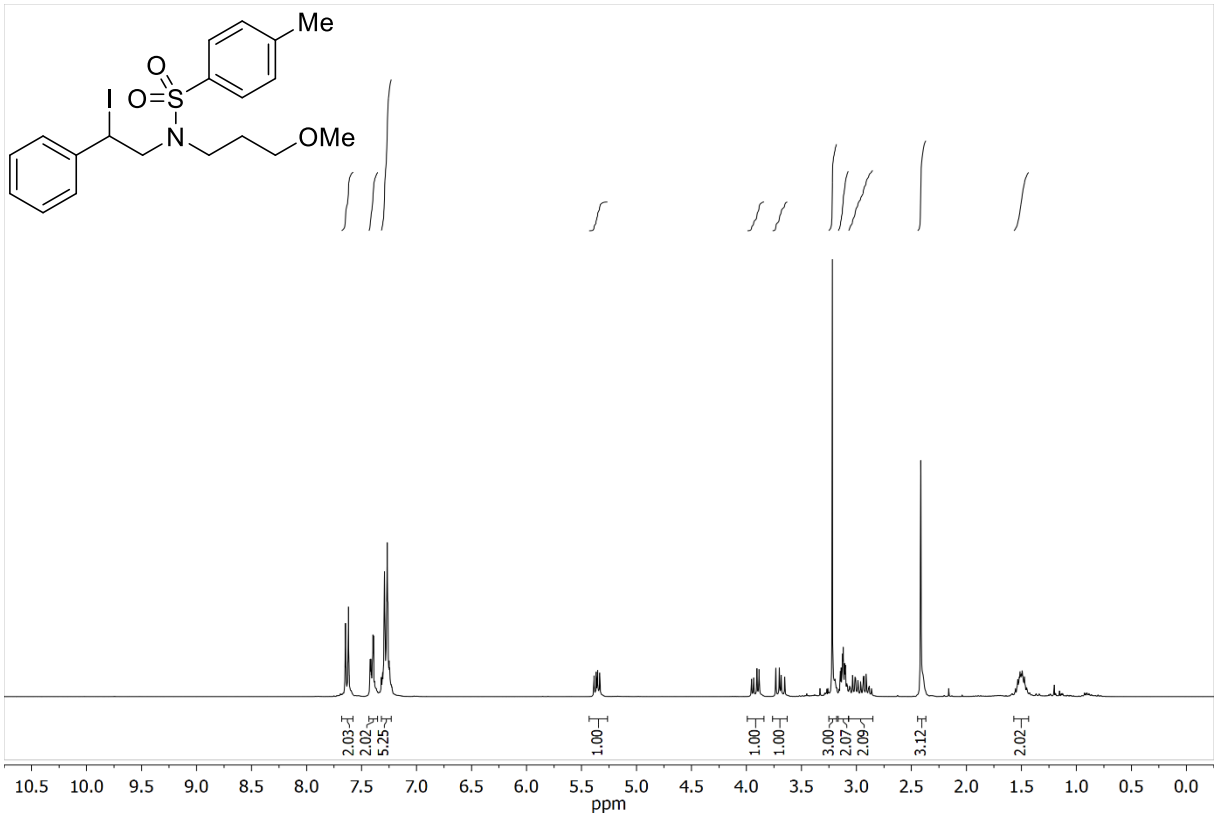
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

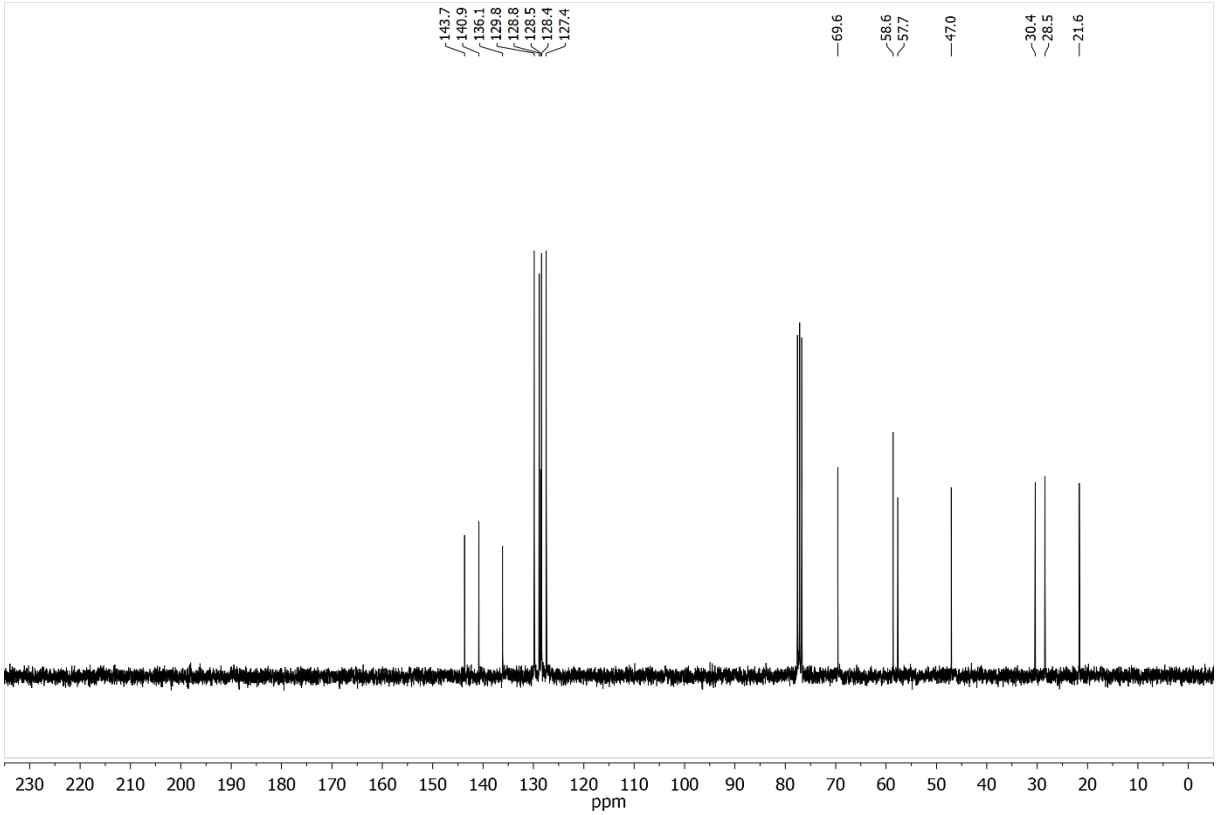
_N_-(3-chloropropyl)-_N_-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bj)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

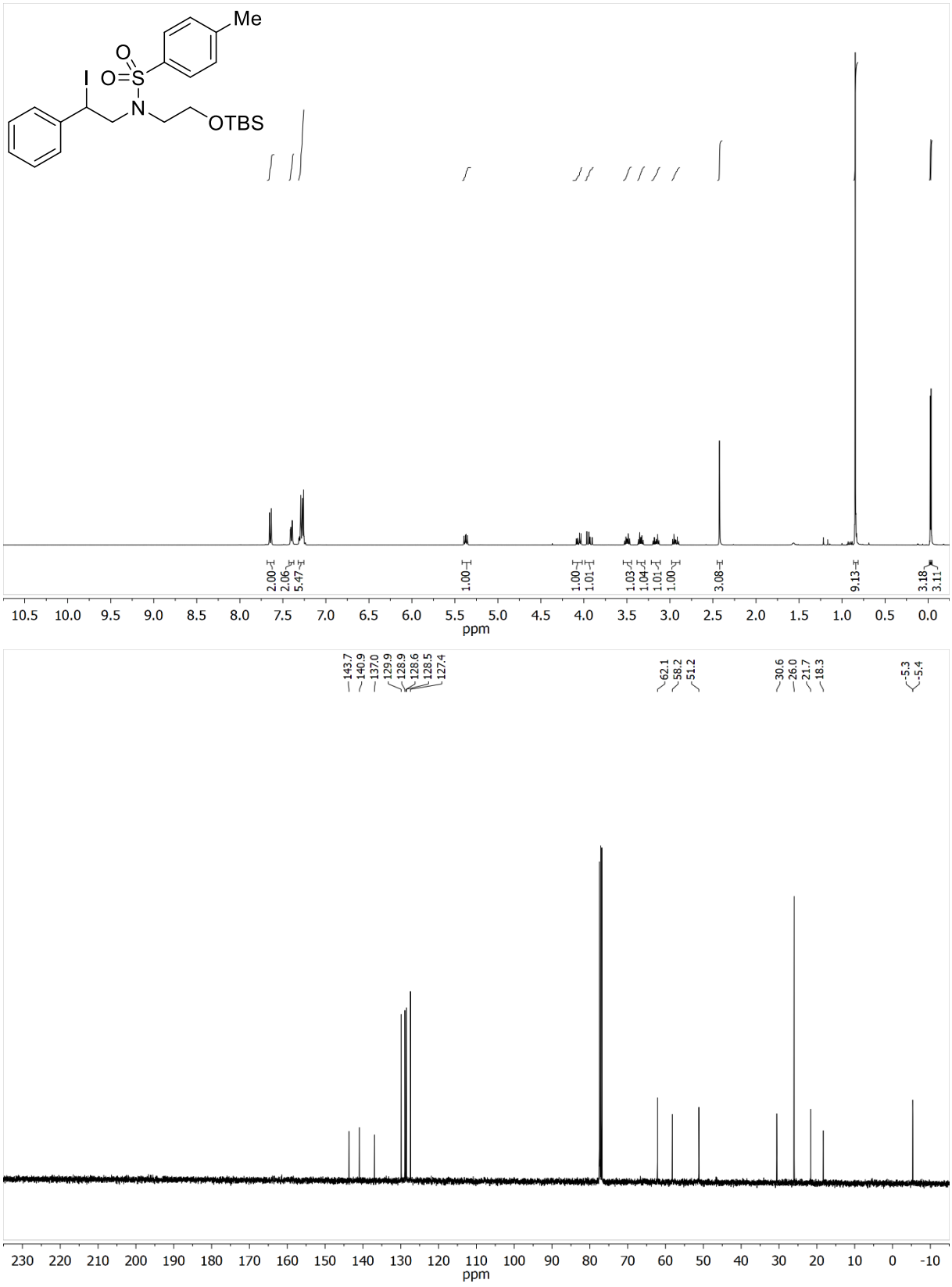
_N_-(2-iodo-2-phenylethyl)-_N_-(3-methoxypropyl)-4-methylbenzenesulfonamide (15bk)





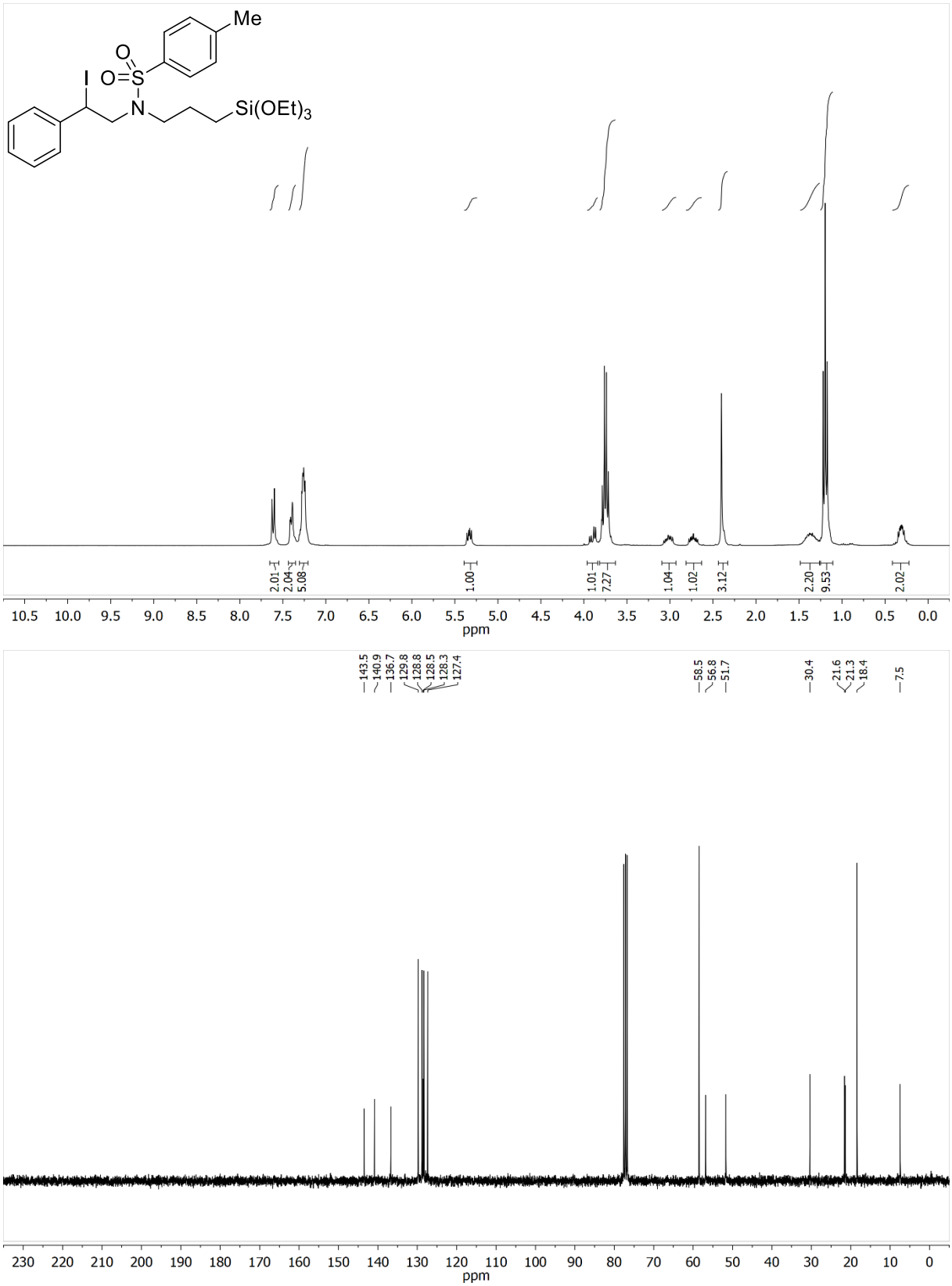
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-((_tert_-butyldimethylsilyl)oxy)ethyl)-_N_-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bl)



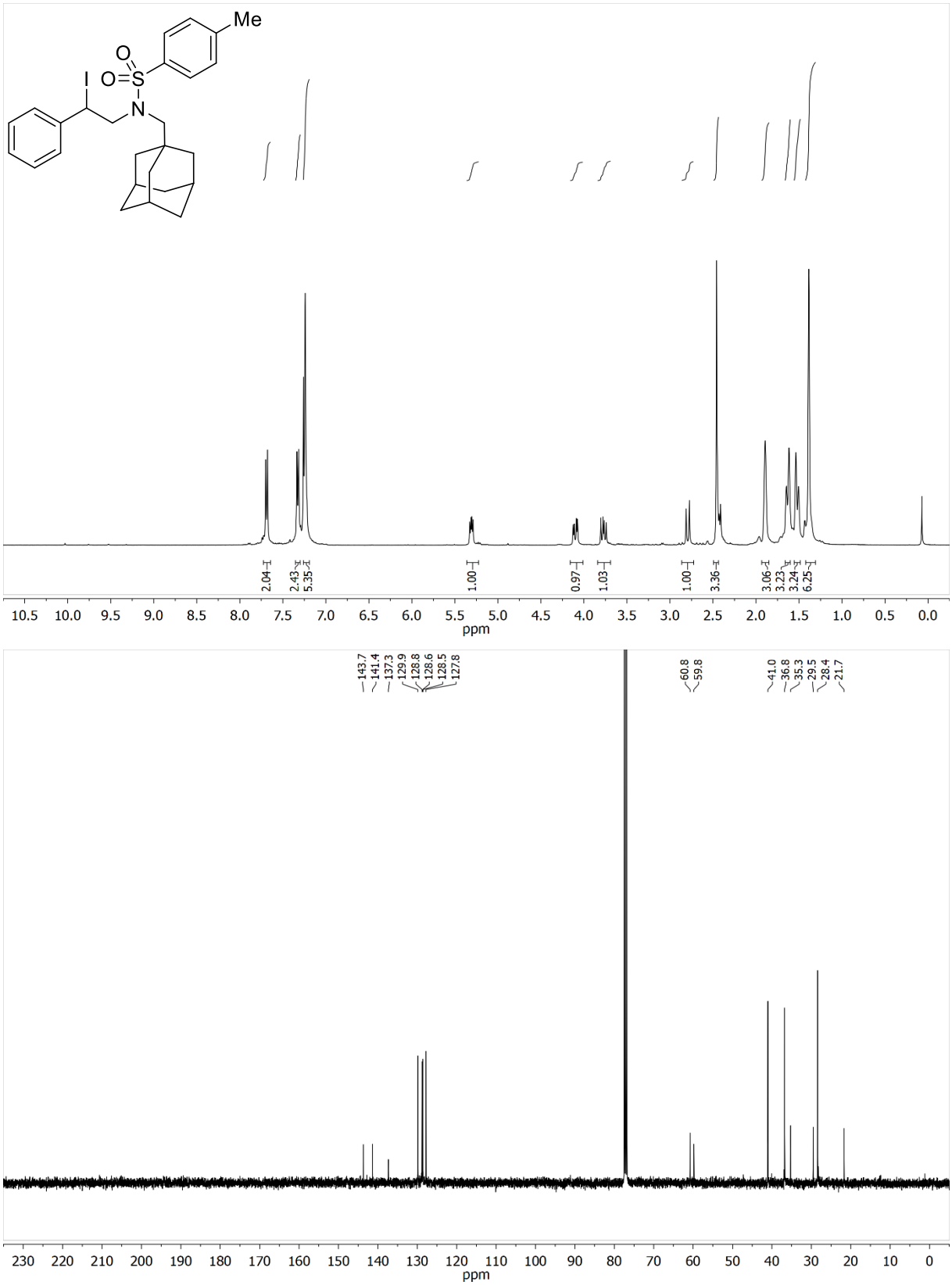
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-2-phenylethyl)-4-methyl-_N_-(3-(triethoxysilyl)propyl)benzenesulfonamide (15bm)



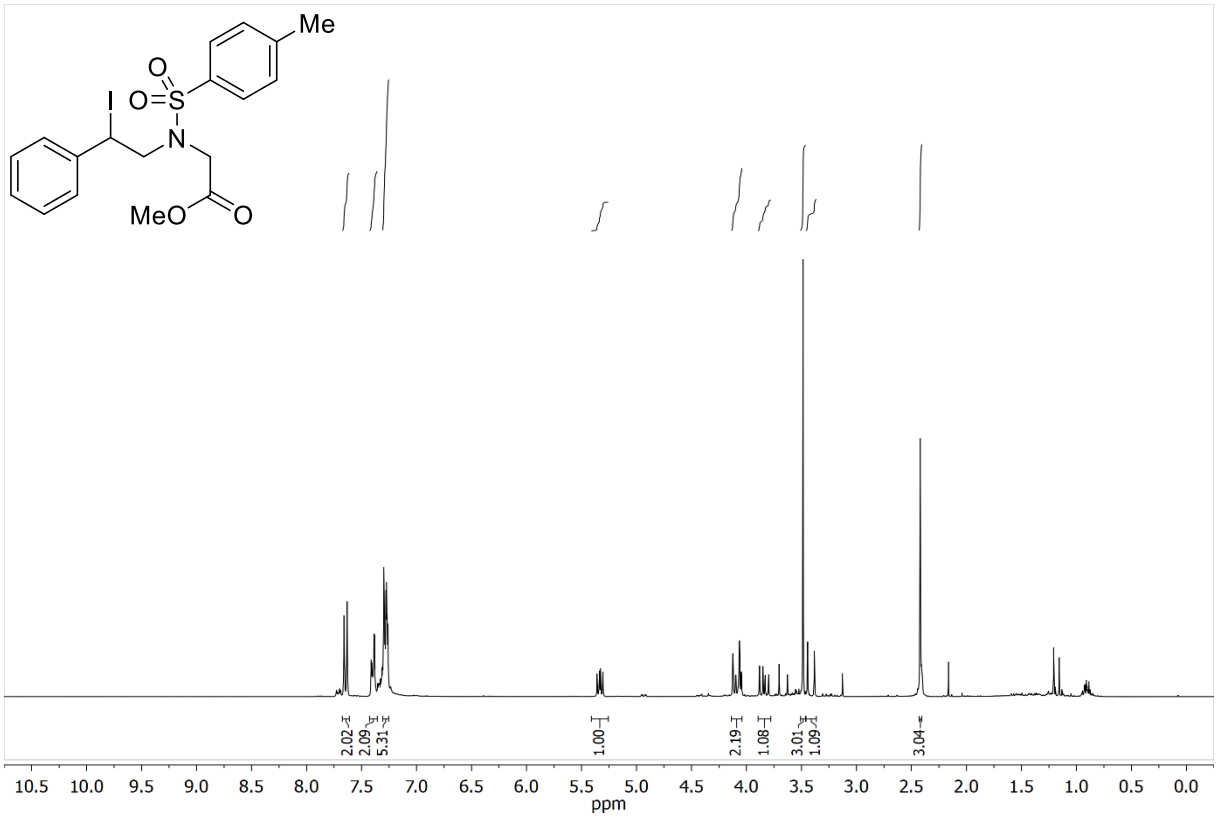
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

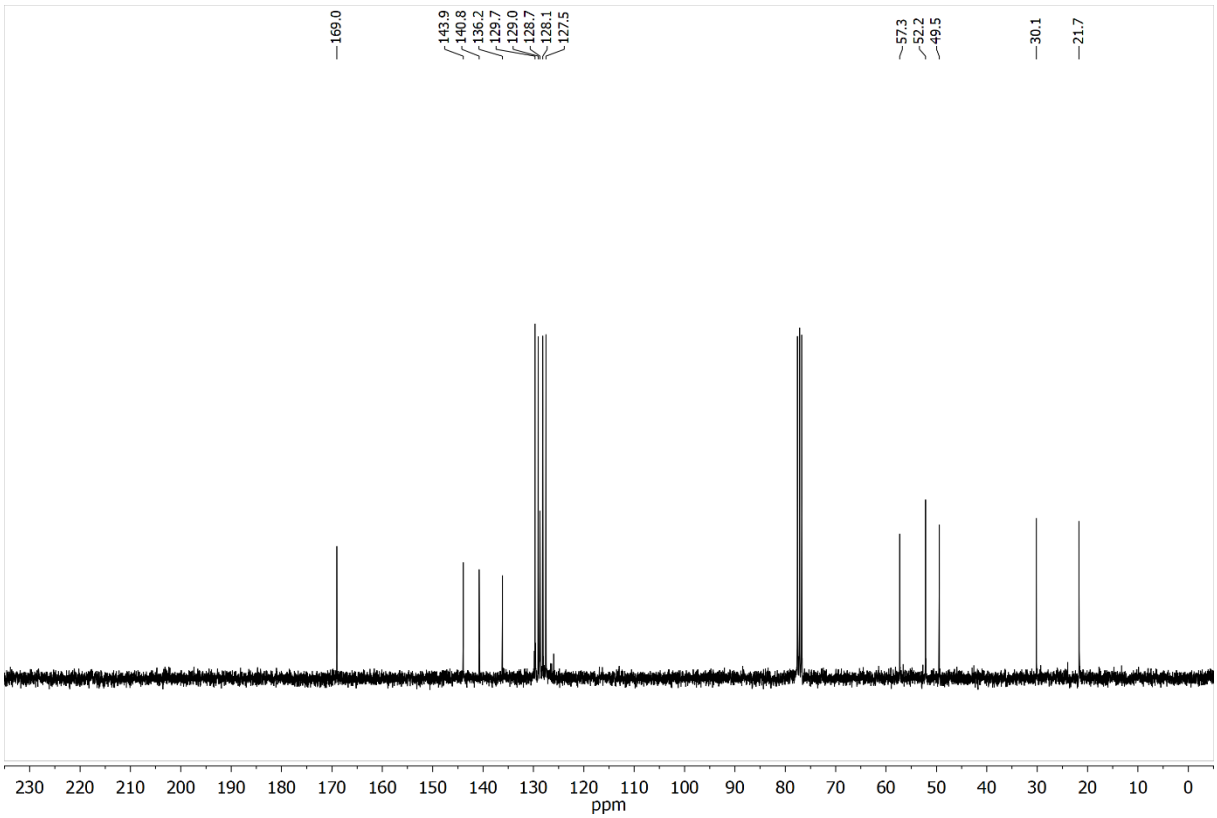
_N_-(((3_r_,5_r_,7_r_)-adamantan-1-yl)methyl)-_N_-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bp)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

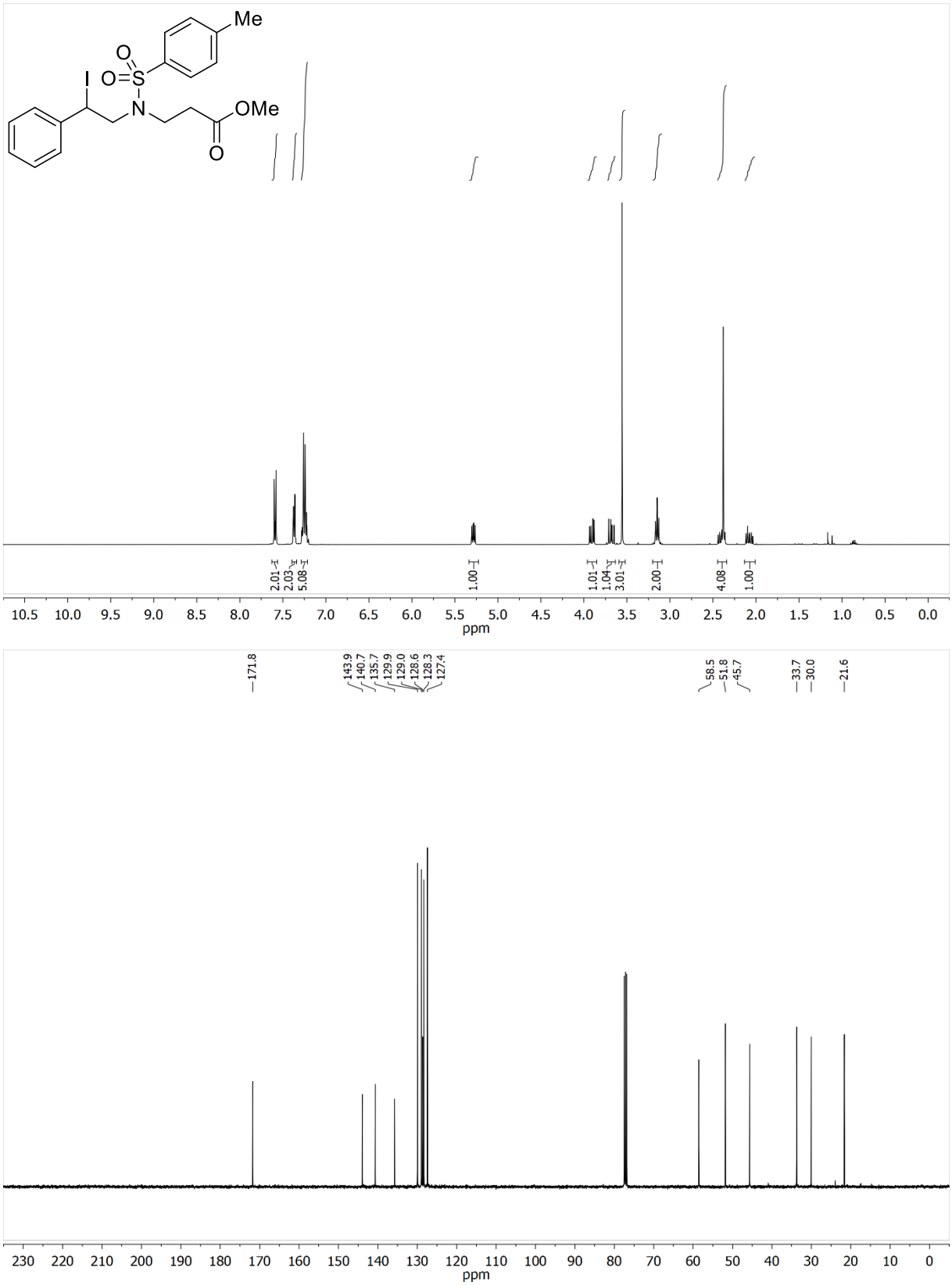
methyl *N*-(2-iodo-2-phenylethyl)-*N*-tosylglycinate (15bs)





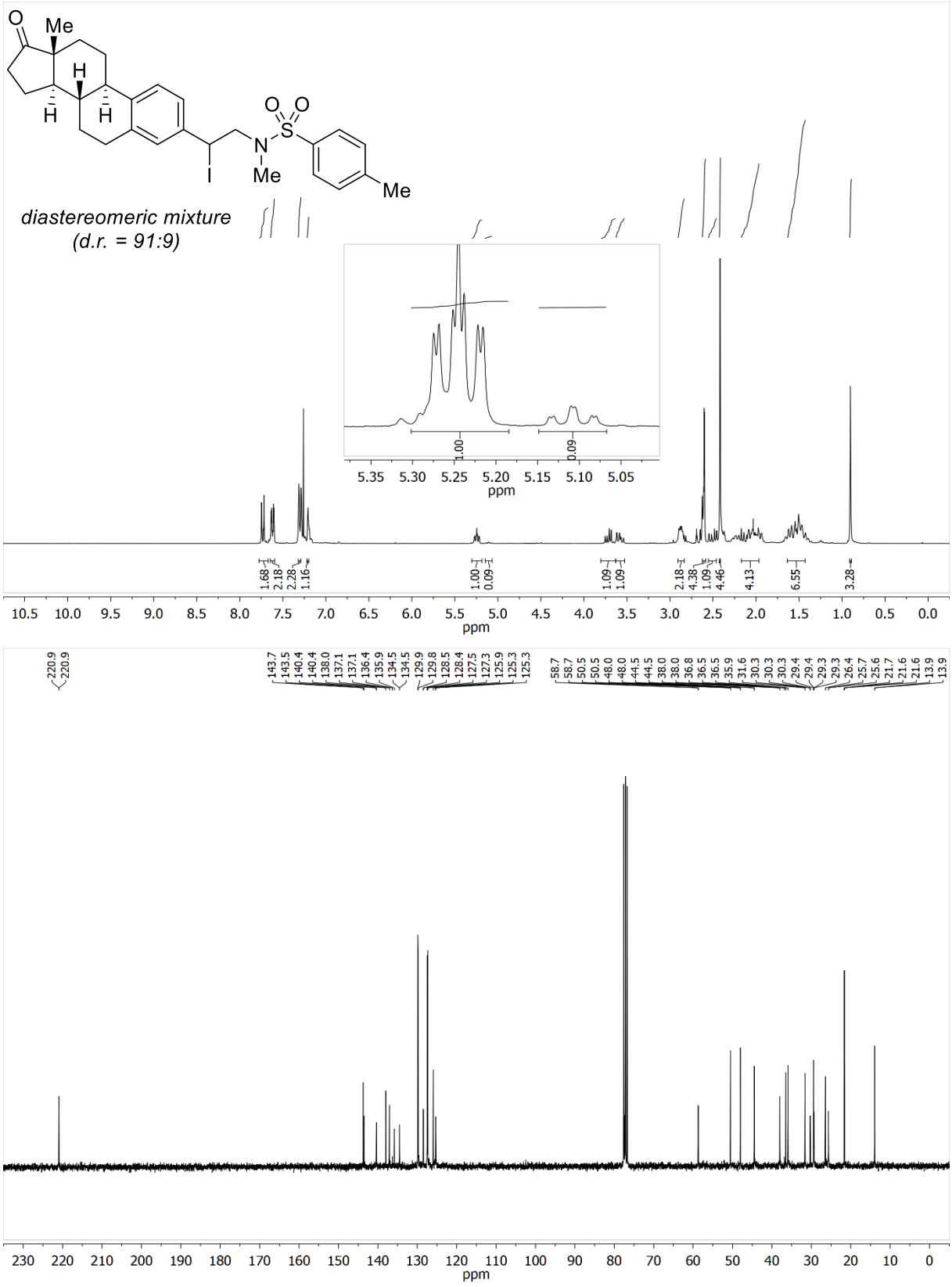
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

methyl 3-((*N*-(2-iodo-2-phenylethyl)-4-methylphenyl)sulfonamido)propanoate (15bt)



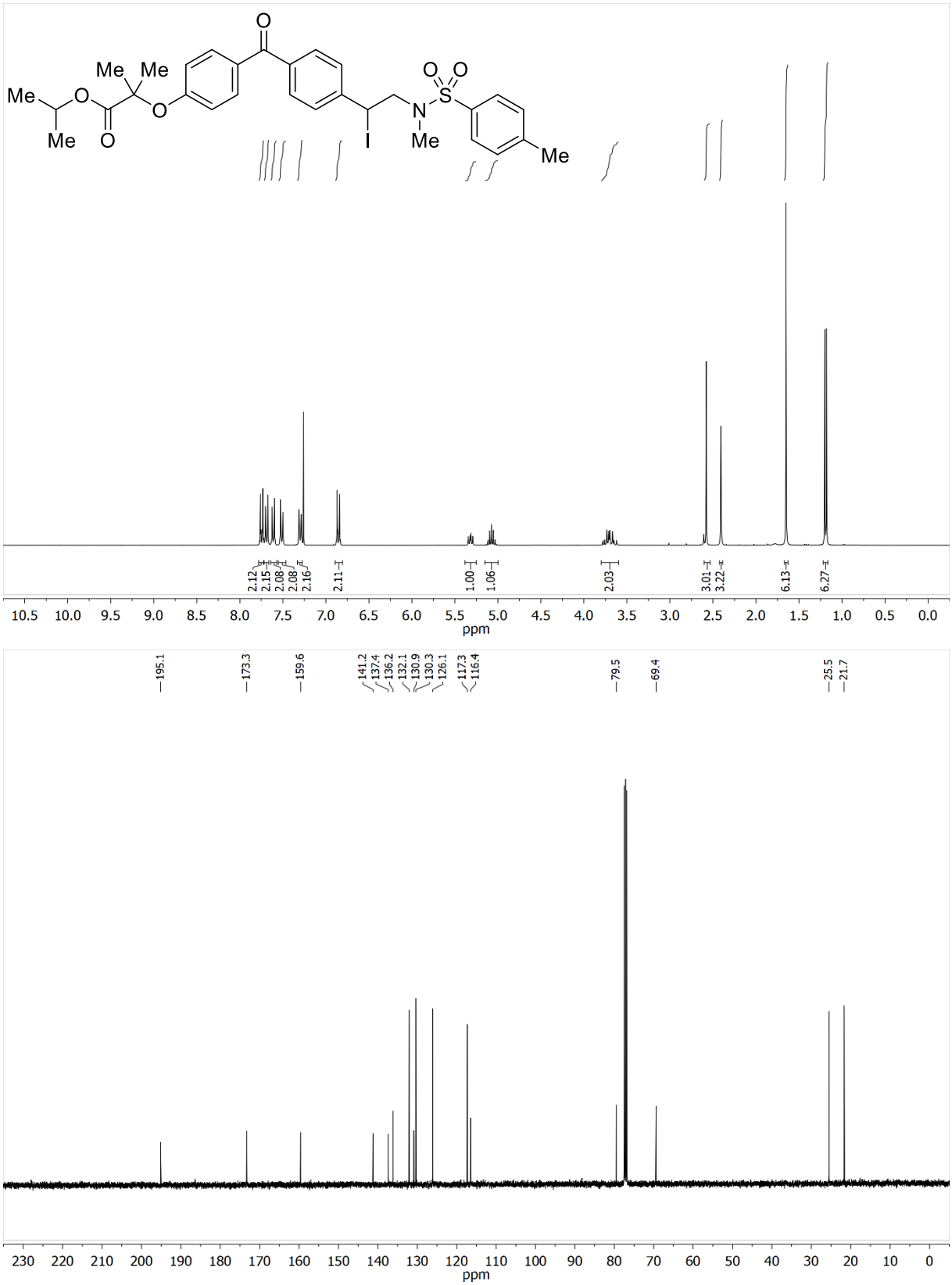
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(2-iodo-2-((8_S_,9_R_,13_R_,14_R_)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6_H_-cyclopenta[_a_]phenanthren-3-yl)ethyl)-_N_,4-dimethylbenzenesulfonamide (d.r. = 91:9) (15bv)



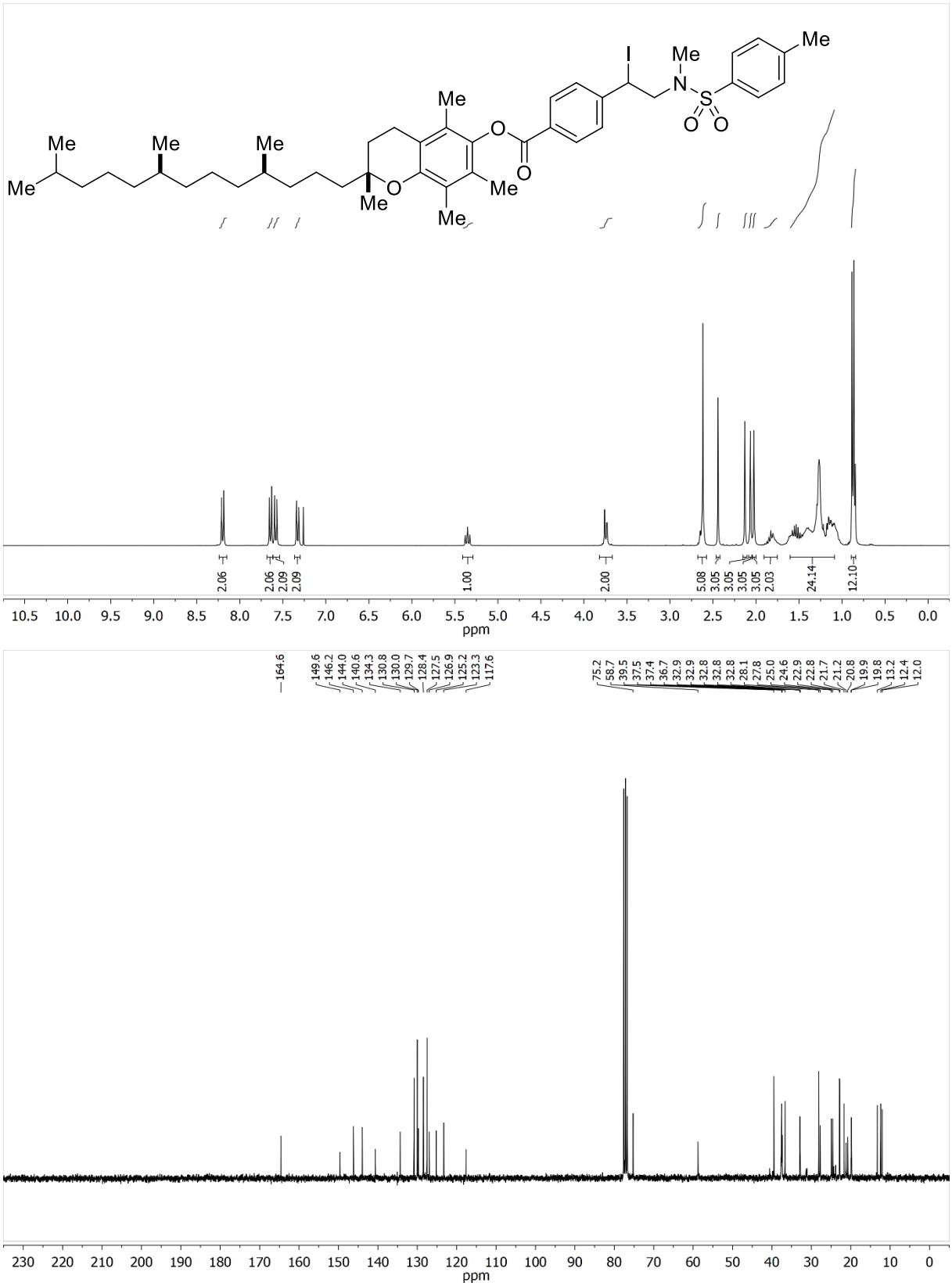
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

isopropyl 2-(4-(4-(2-((*N*,4-dimethylphenyl)sulfonamido)-1-iodoethyl)benzoyl)phenoxy)-2-methylpropanoate (15bw)



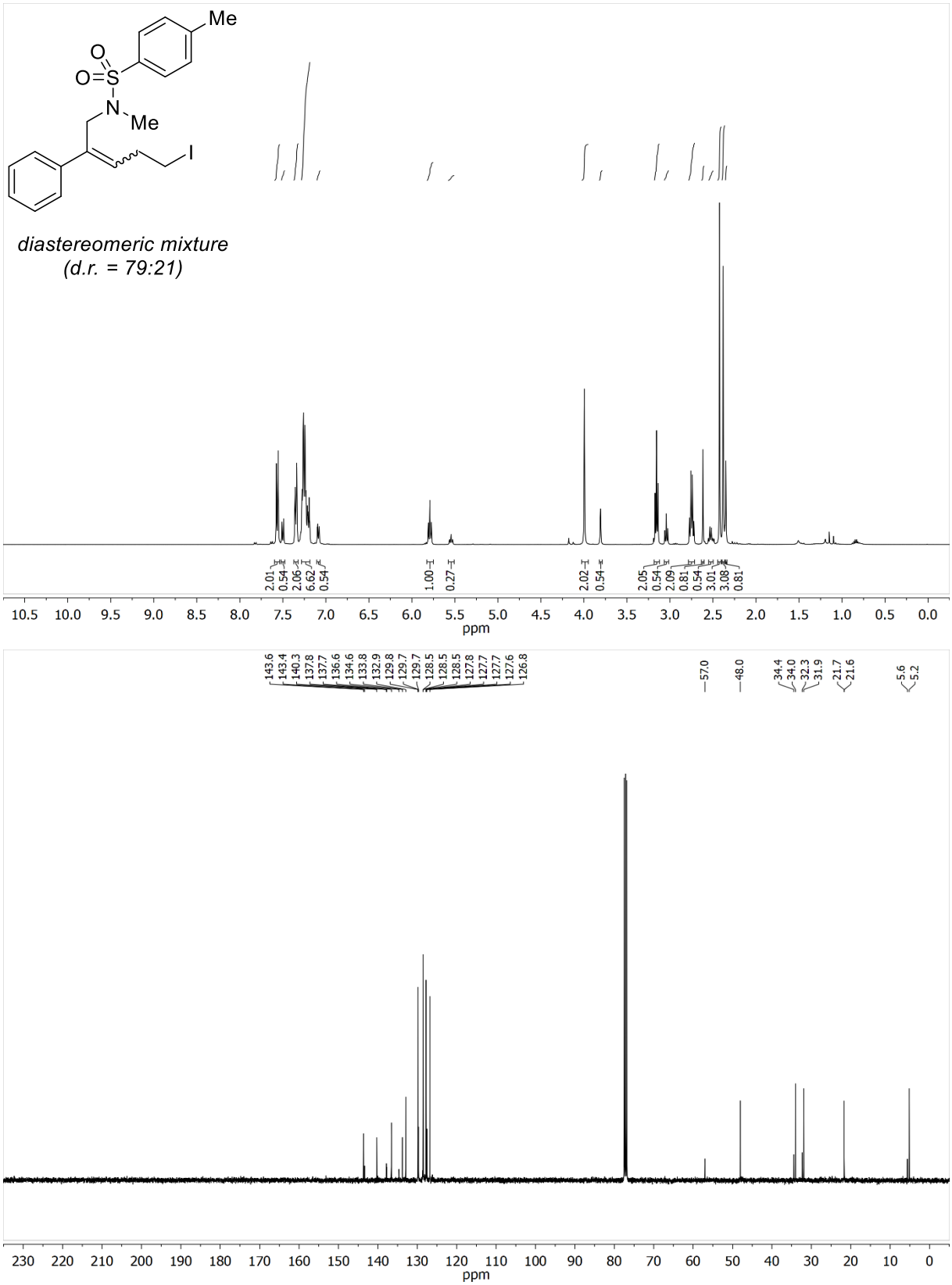
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

(2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-(2-((*N*,4-dimethylphenyl)sulfonamido)-1-iodoethyl)benzoate (15by)



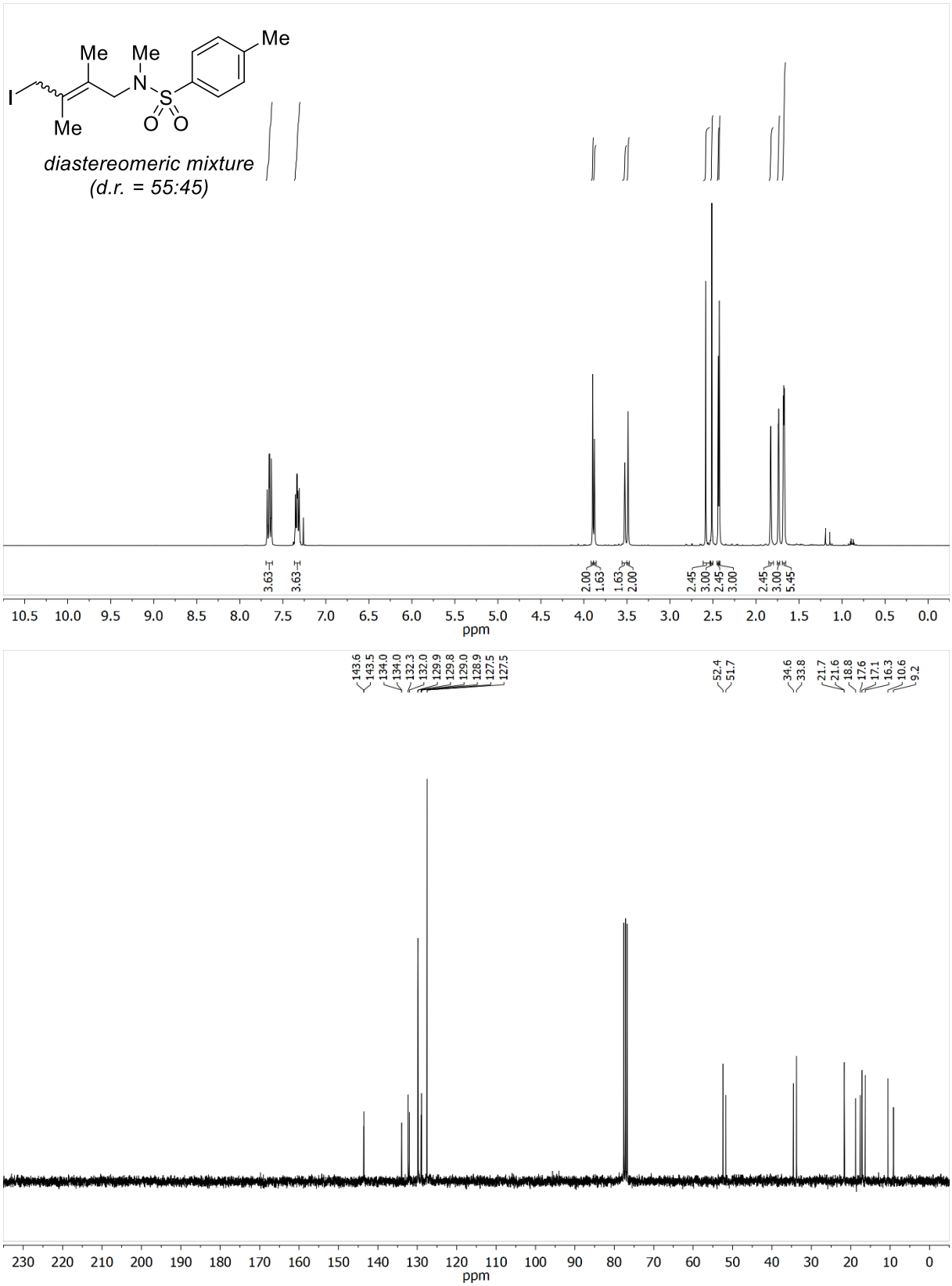
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-(5-iodo-2-phenylpent-2-en-1-yl)-_N_,4-dimethylbenzenesulfonamide (d.r. = 79:21) (15cb)



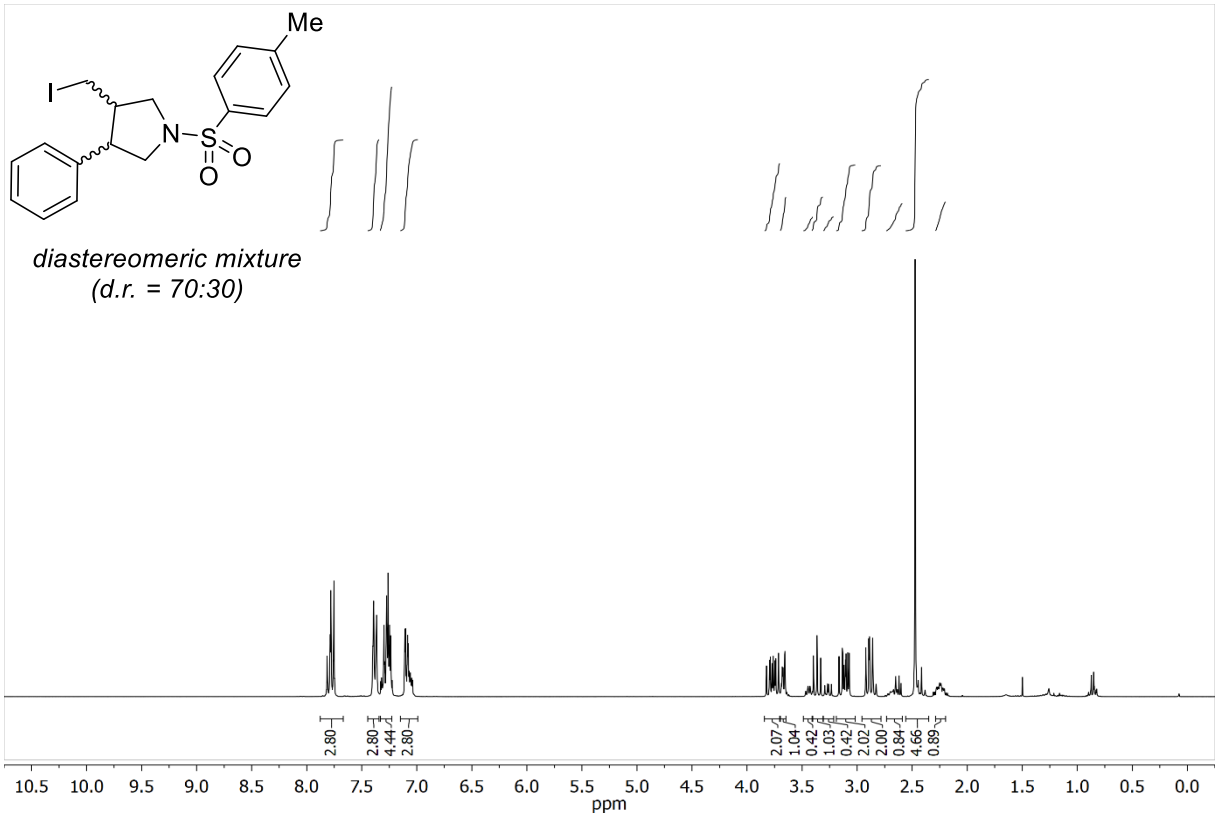
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

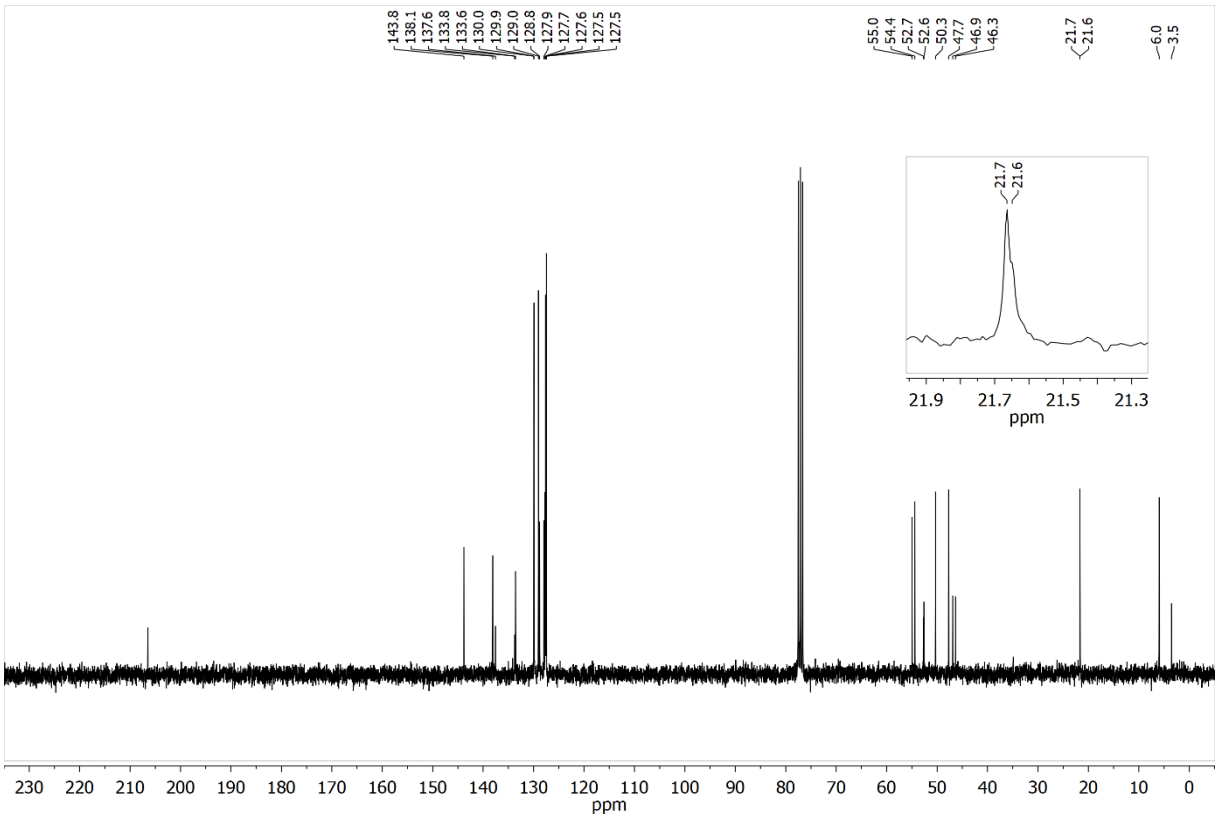
_N_-(4-iodo-2,3-dimethylbut-2-en-1-yl)-_N_,4-dimethylbenzenesulfonamide (d.r. = 55:45) (15cd)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

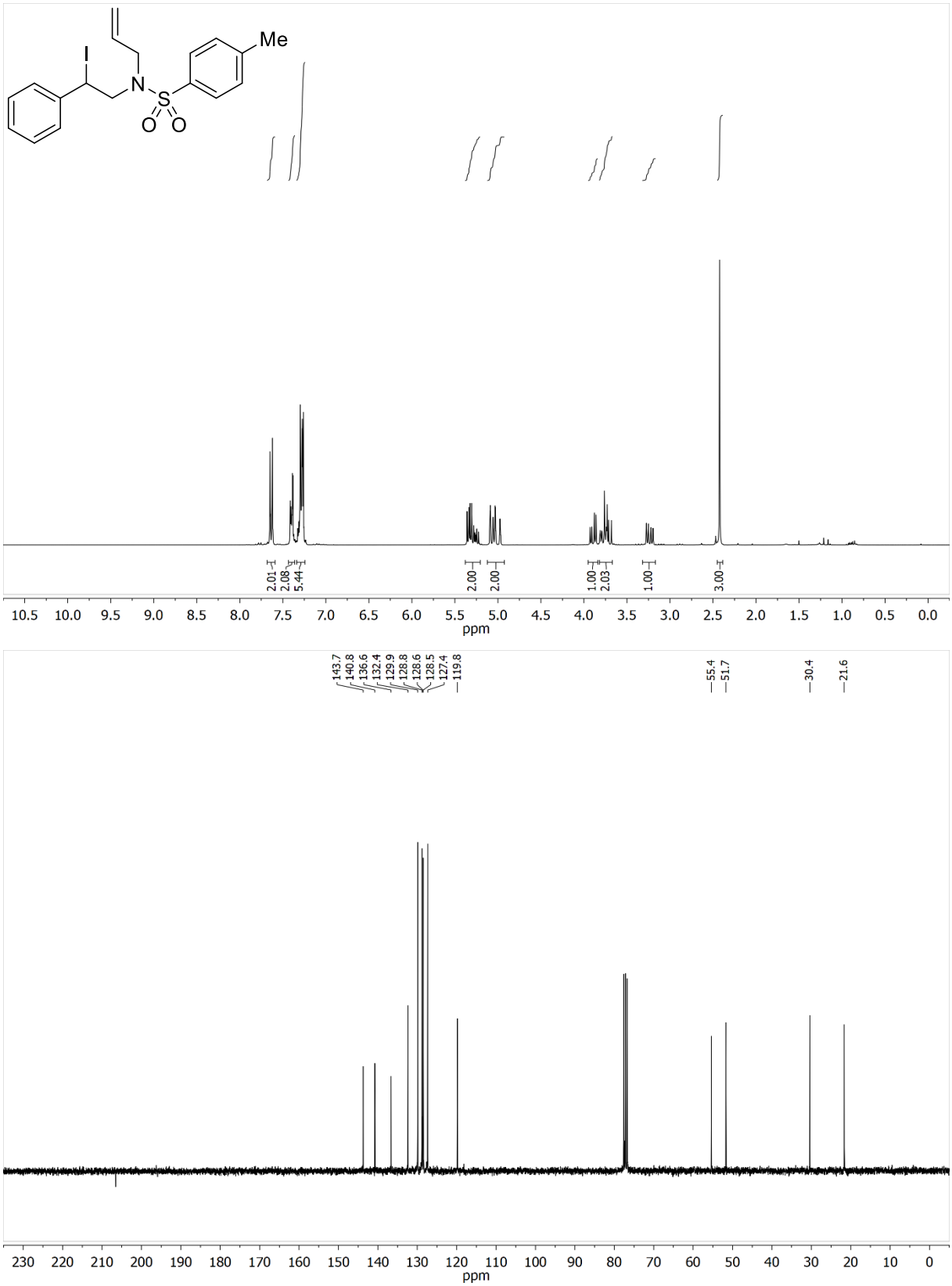
3-(iodomethyl)-4-phenyl-1-tosylpyrrolidine (d.r. = 70:30) (12a)





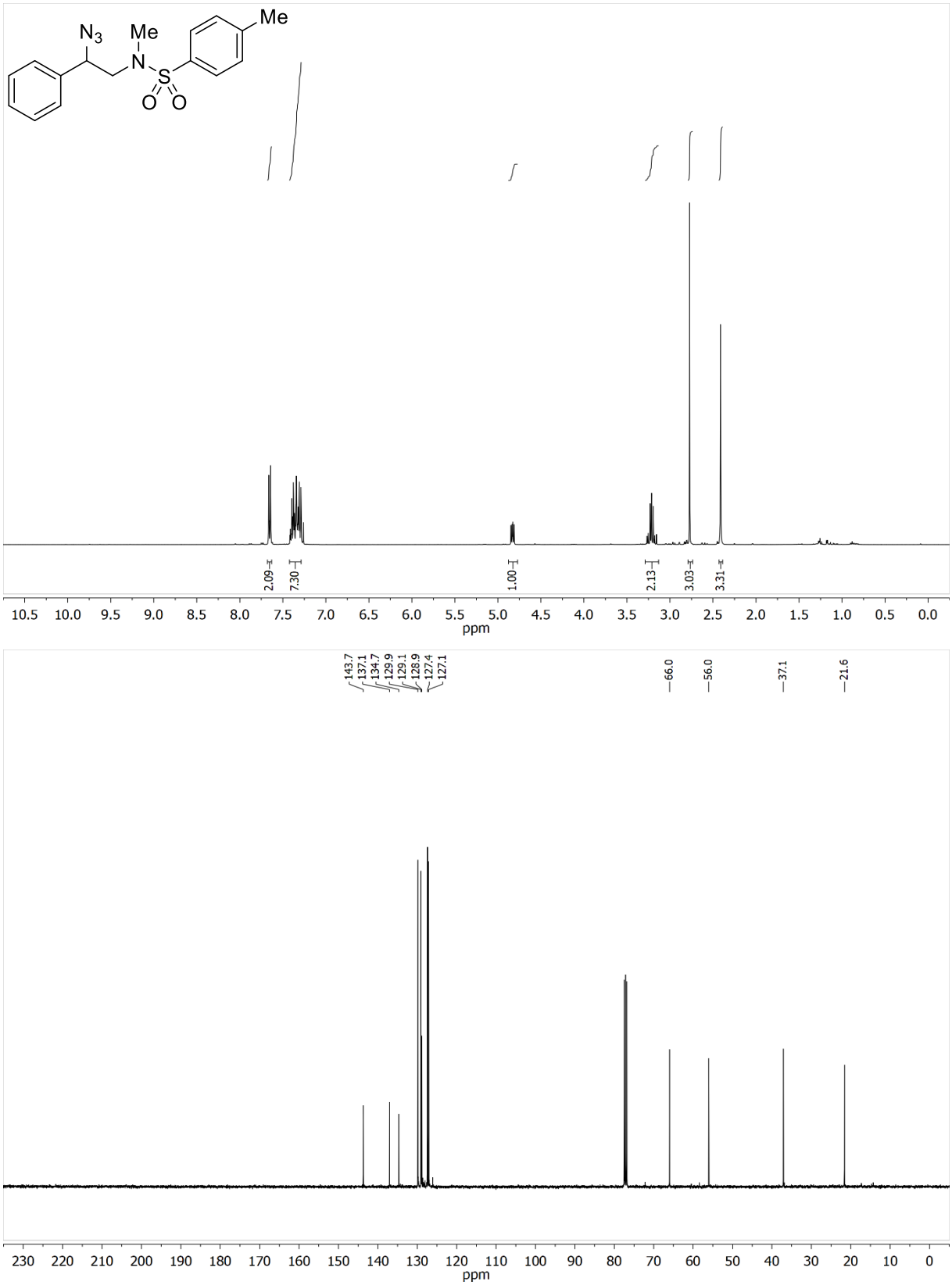
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_-allyl-N-(2-iodo-2-phenylethyl)-4-methylbenzenesulfonamide (15bz)



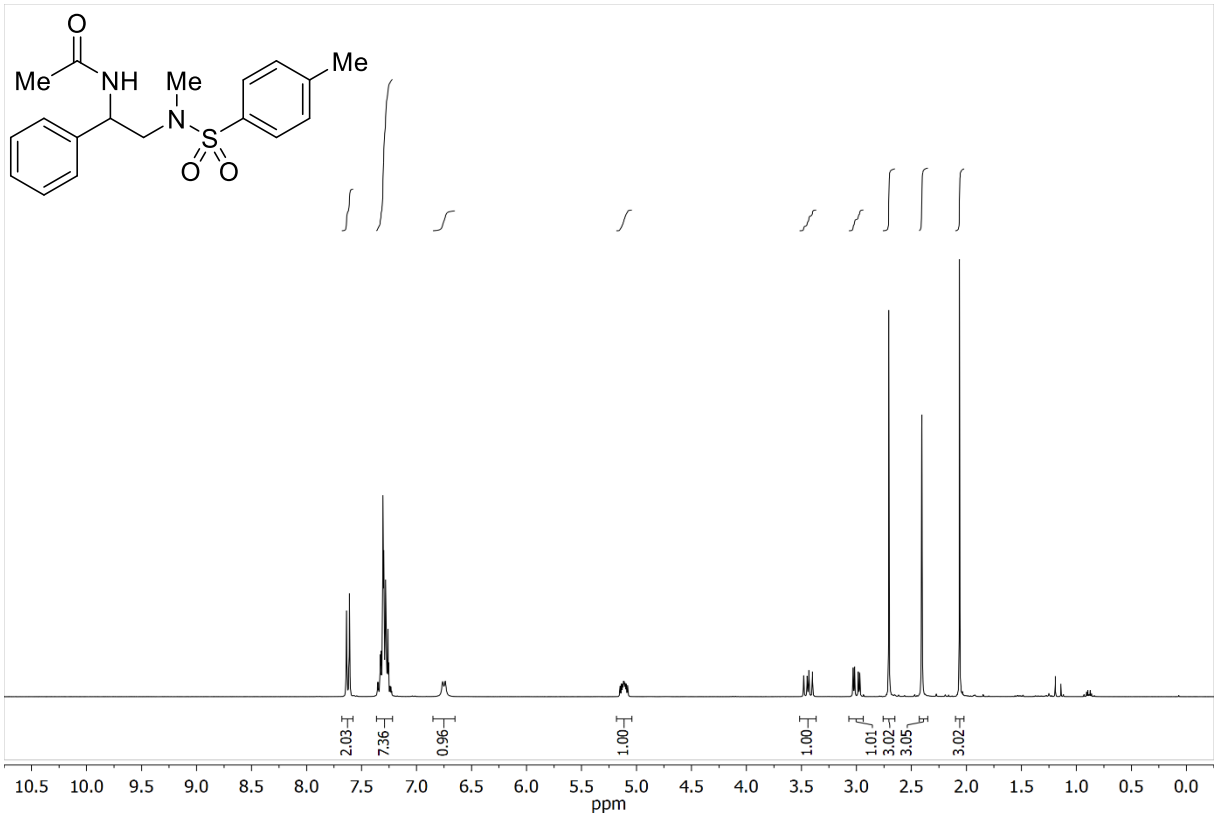
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

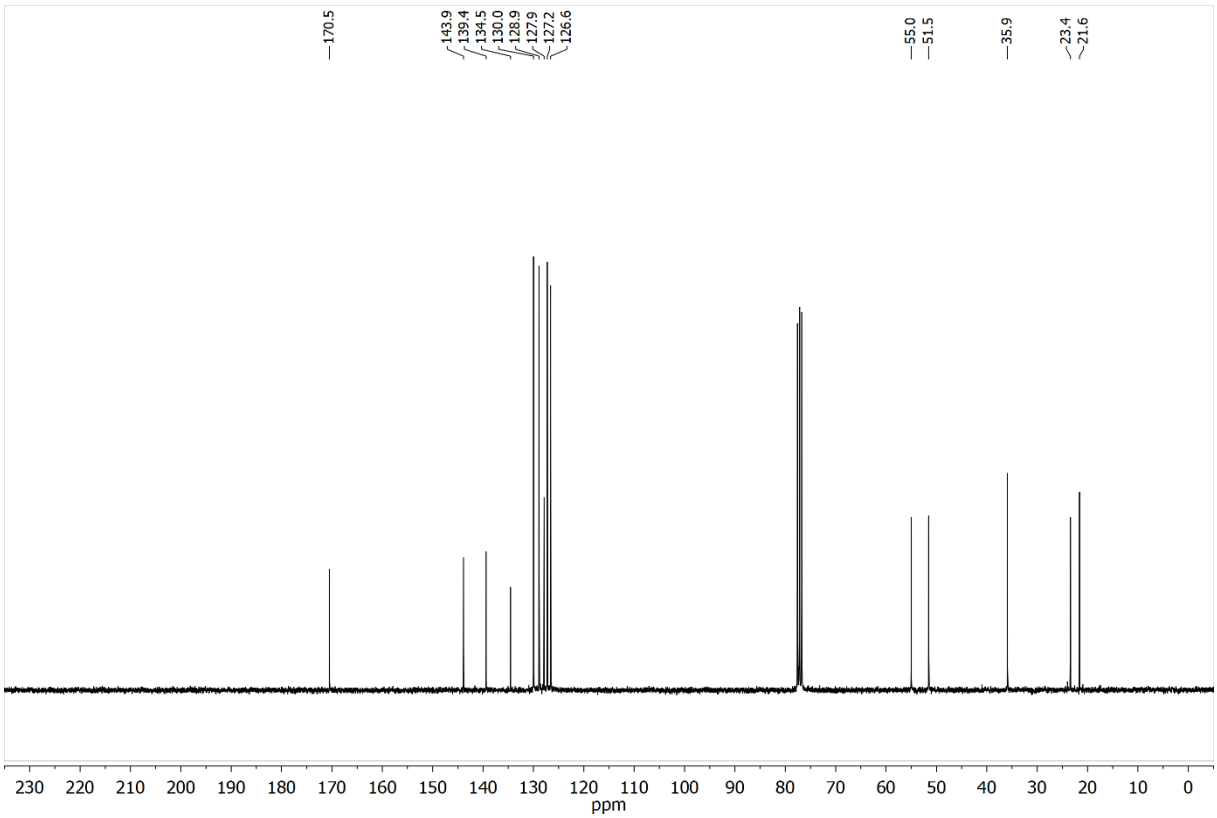
_N_-(2-azido-2-phenylethyl)-_N_,4-dimethylbenzenesulfonamide (16a)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

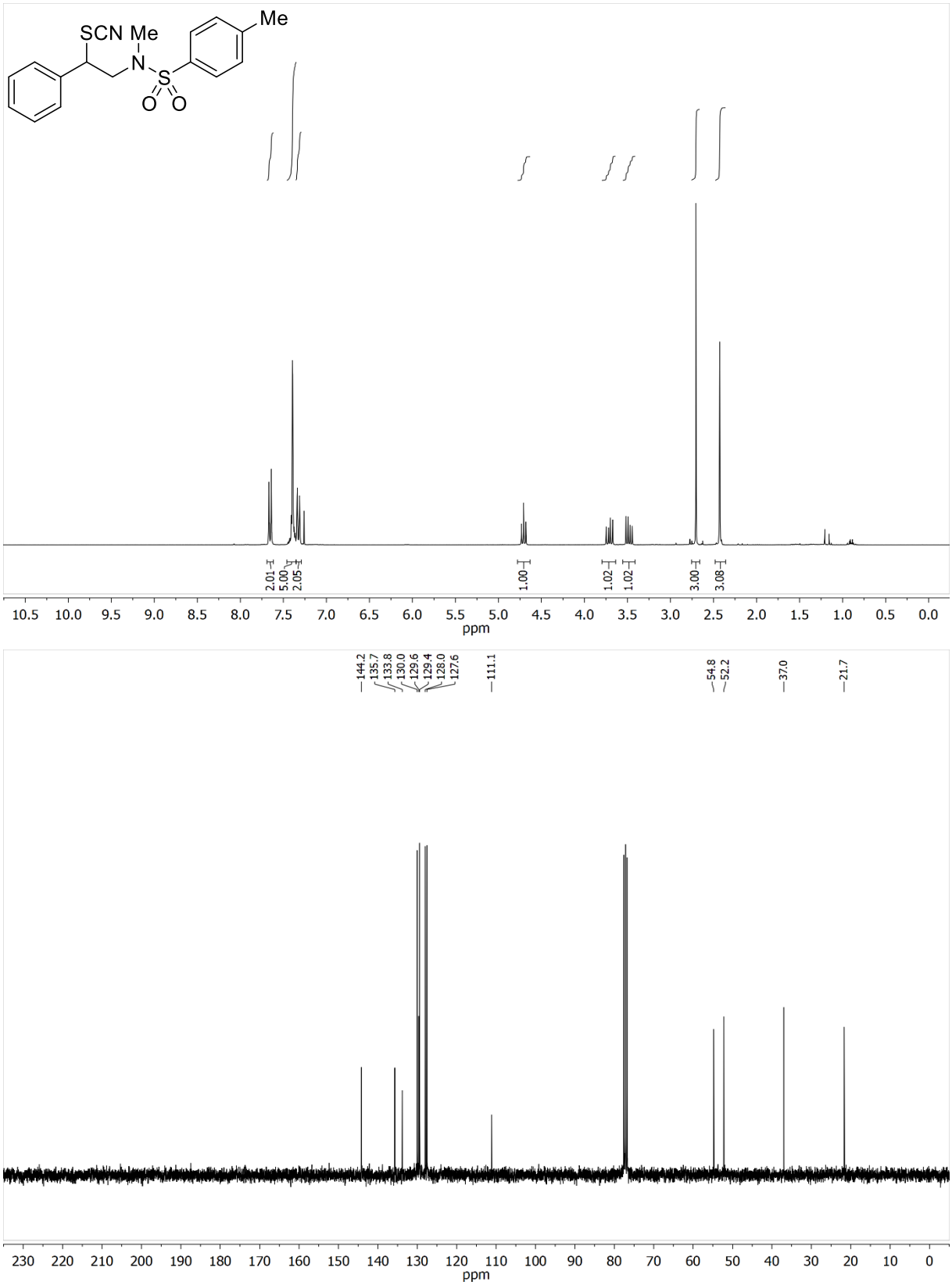
_N_-(2-((_N_,4-dimethylphenyl)sulfonamido)-1-phenylethyl)acetamide (16b)





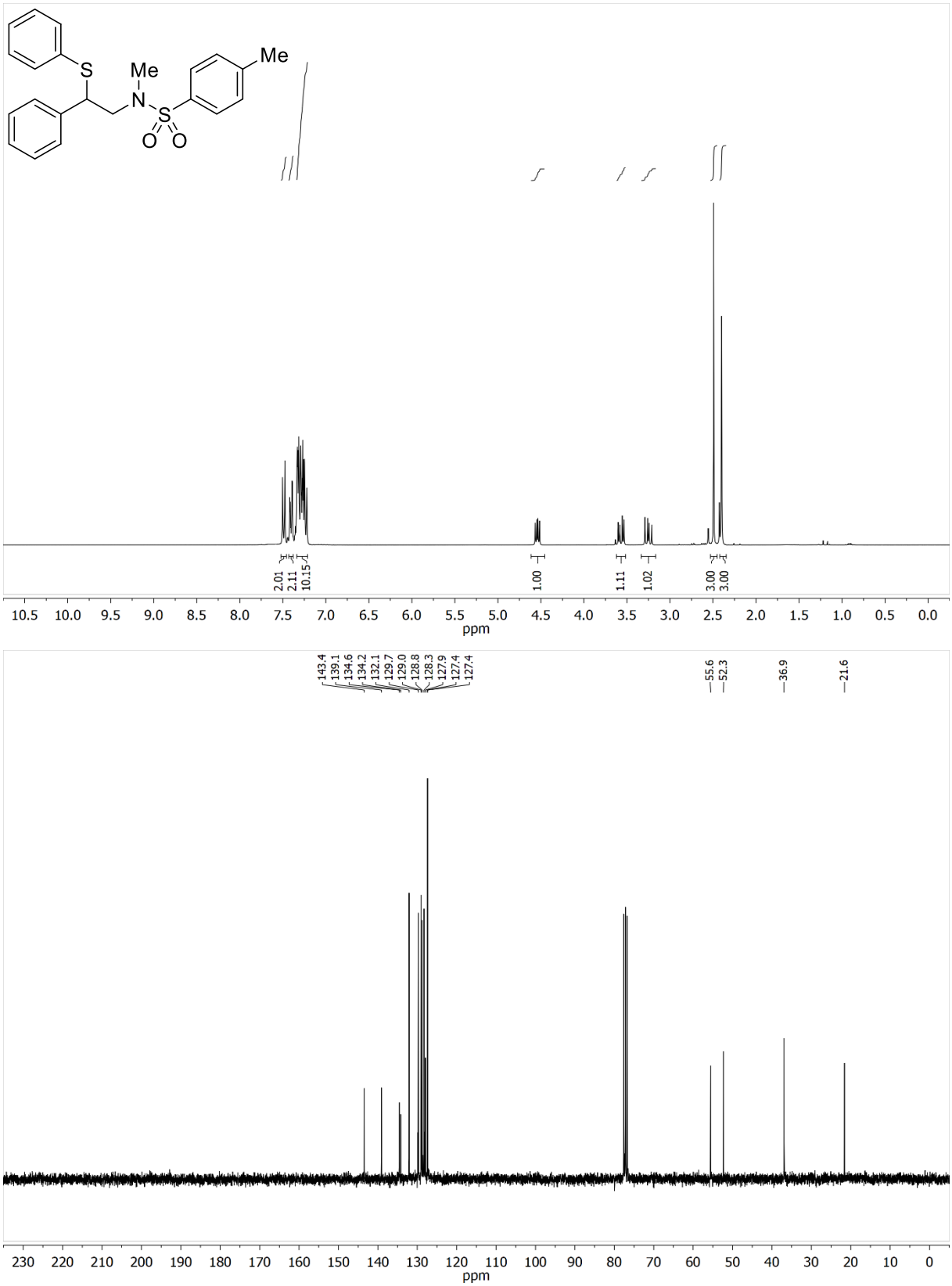
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_,4-dimethyl-_N_-(2-phenyl-2-thiocyanatoethyl)benzenesulfonamide (16c)



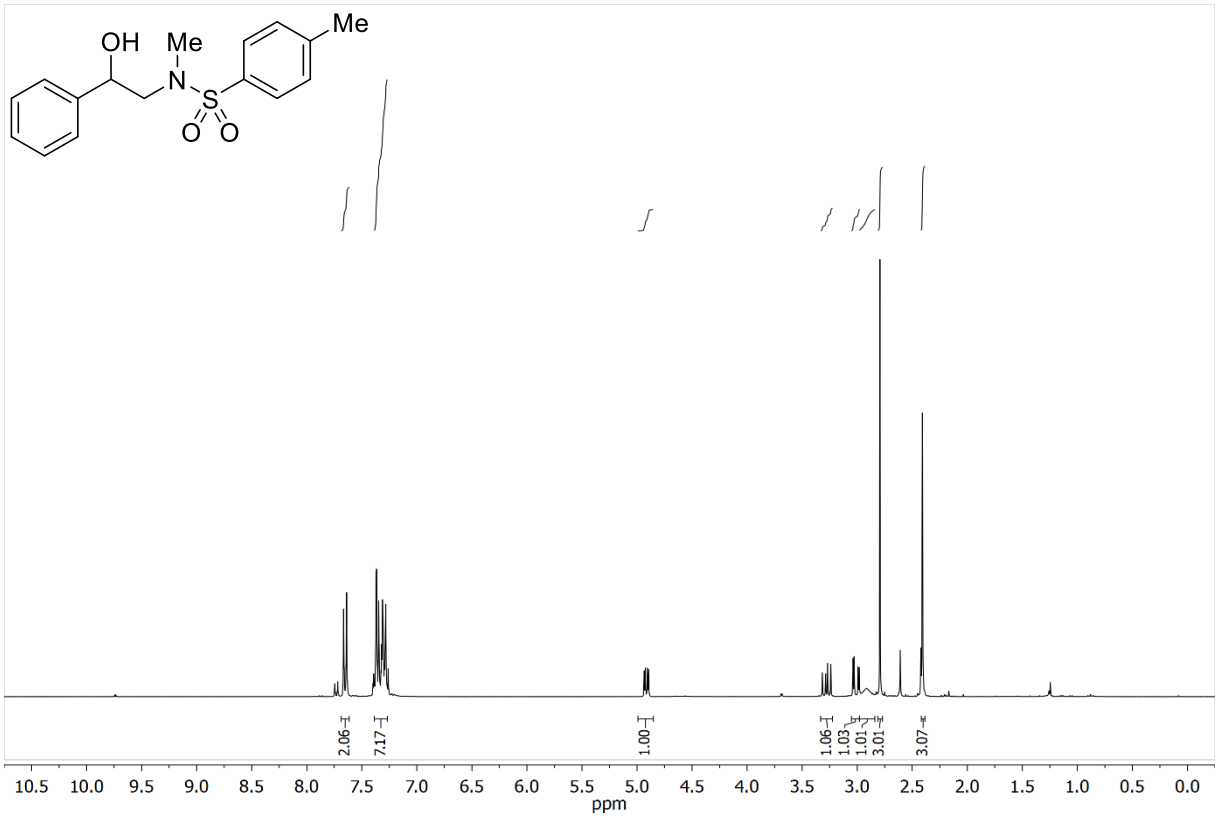
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

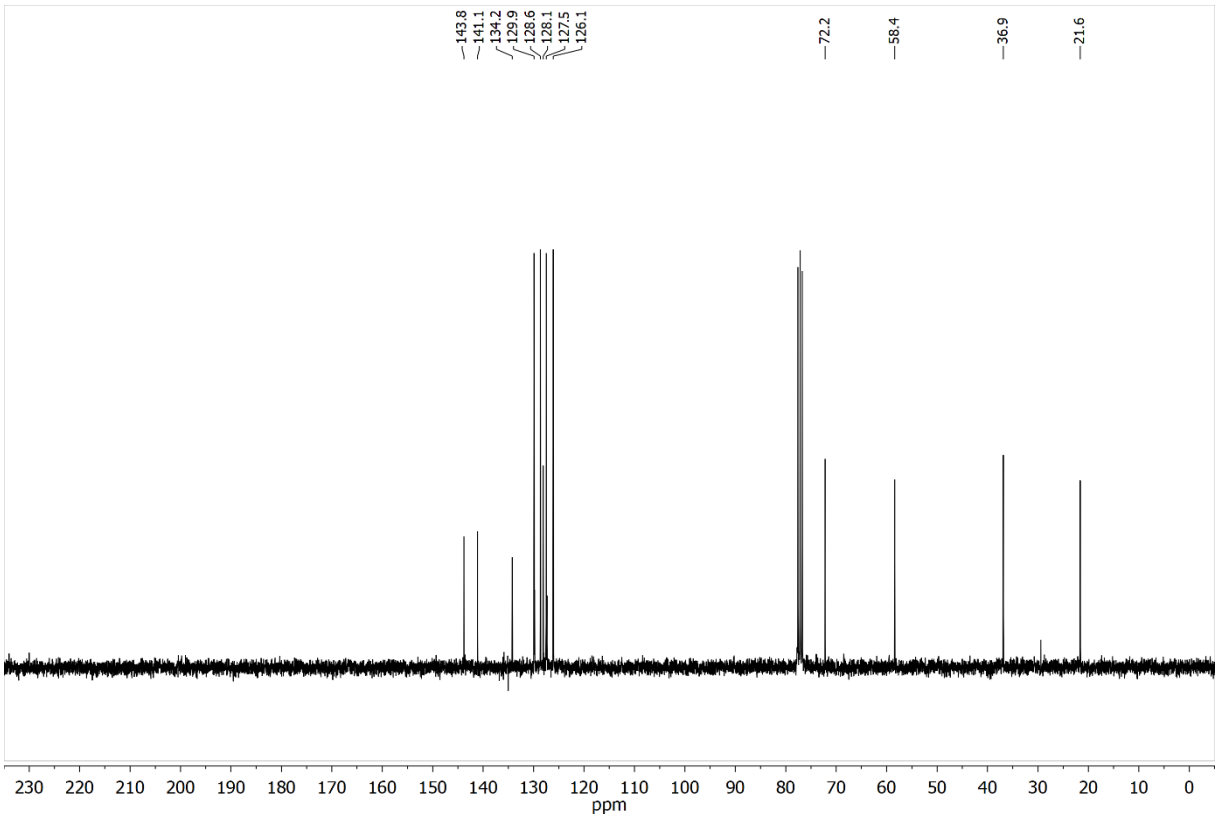
_N_,4-dimethyl-_N_-(2-phenyl-2-(phenylthio)ethyl)benzenesulfonamide (16d)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

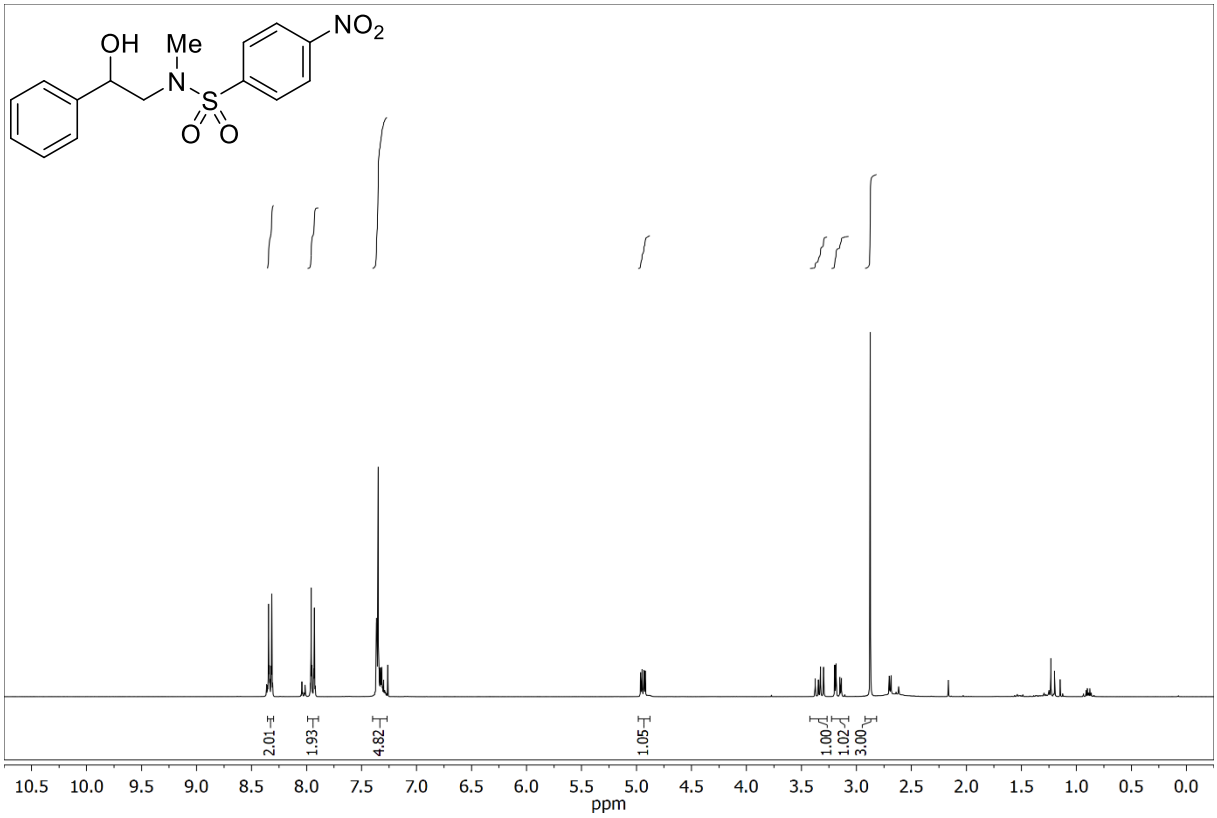
_N_-(2-hydroxy-2-phenylethyl)-_N_,4-dimethylbenzenesulfonamide (16e)

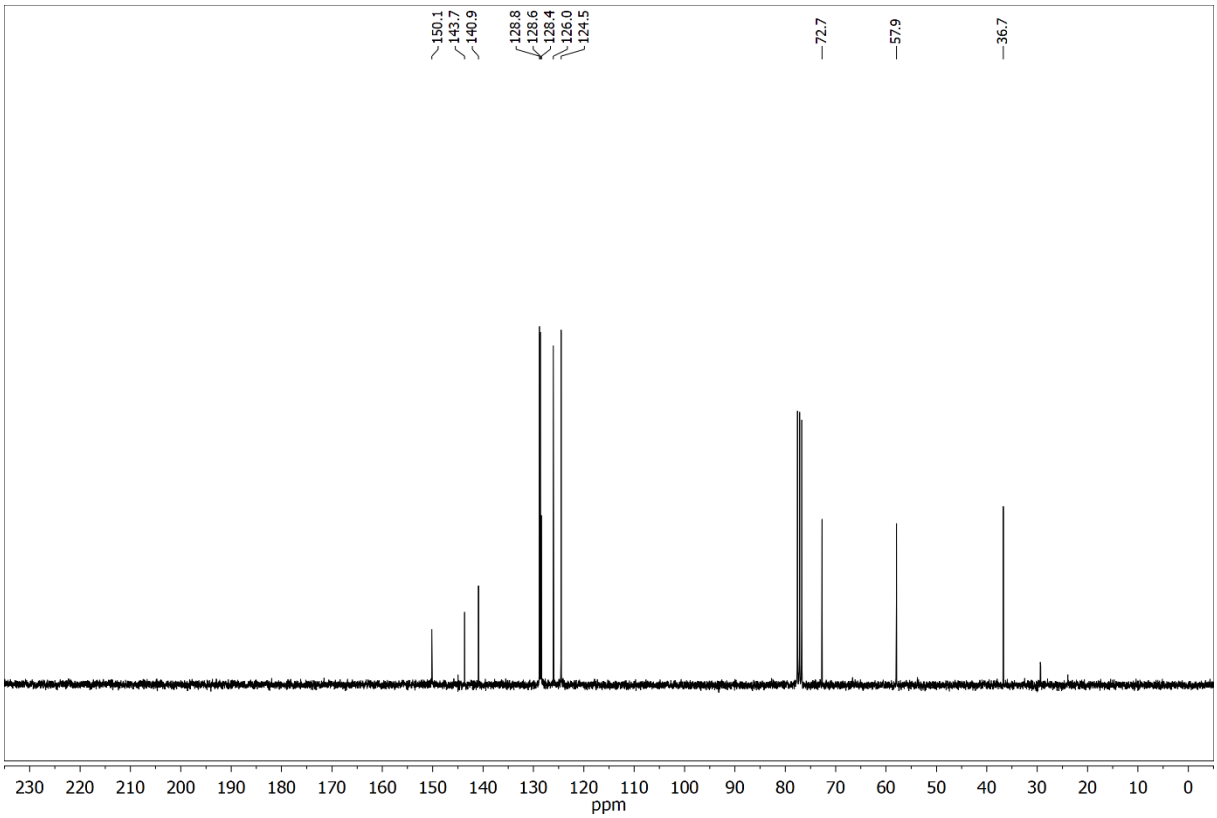




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

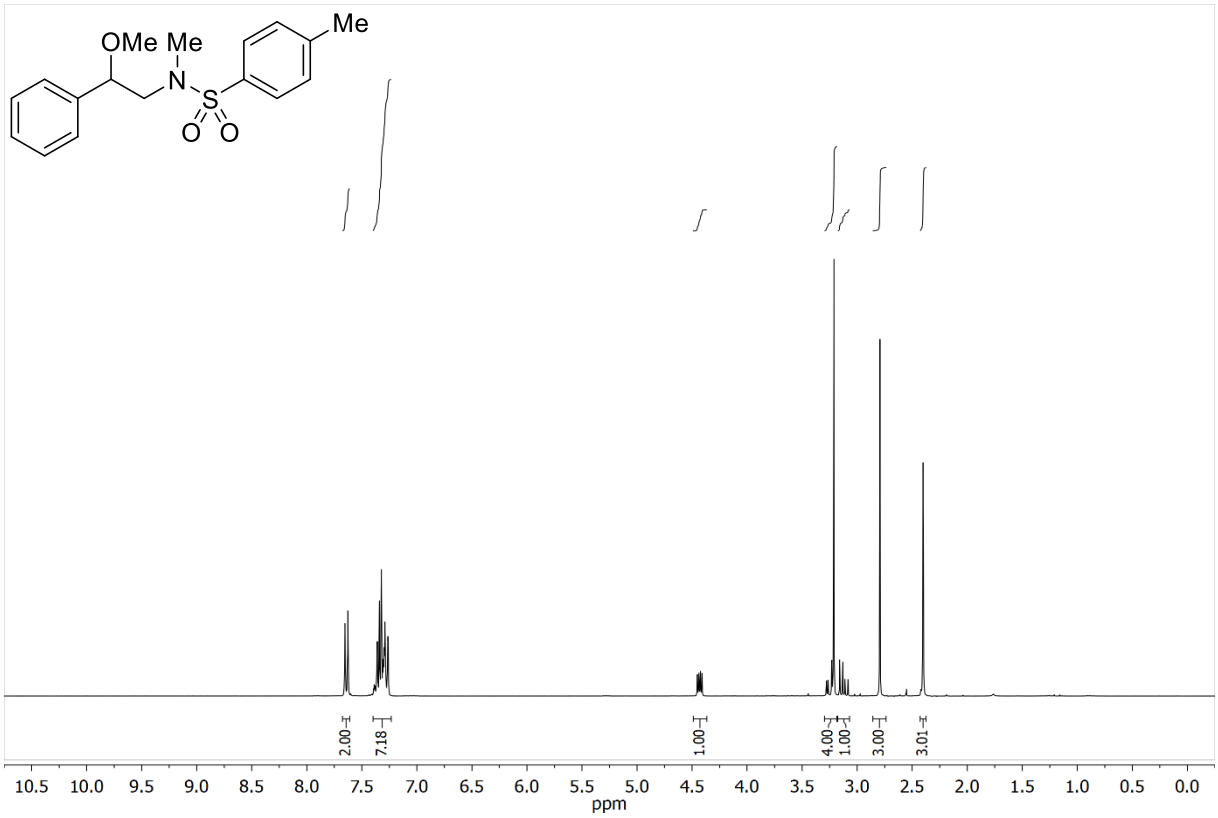
_N_-(2-hydroxy-2-phenylethyl)-_N_-methyl-4-nitrobenzenesulfonamide (Ns-16e)

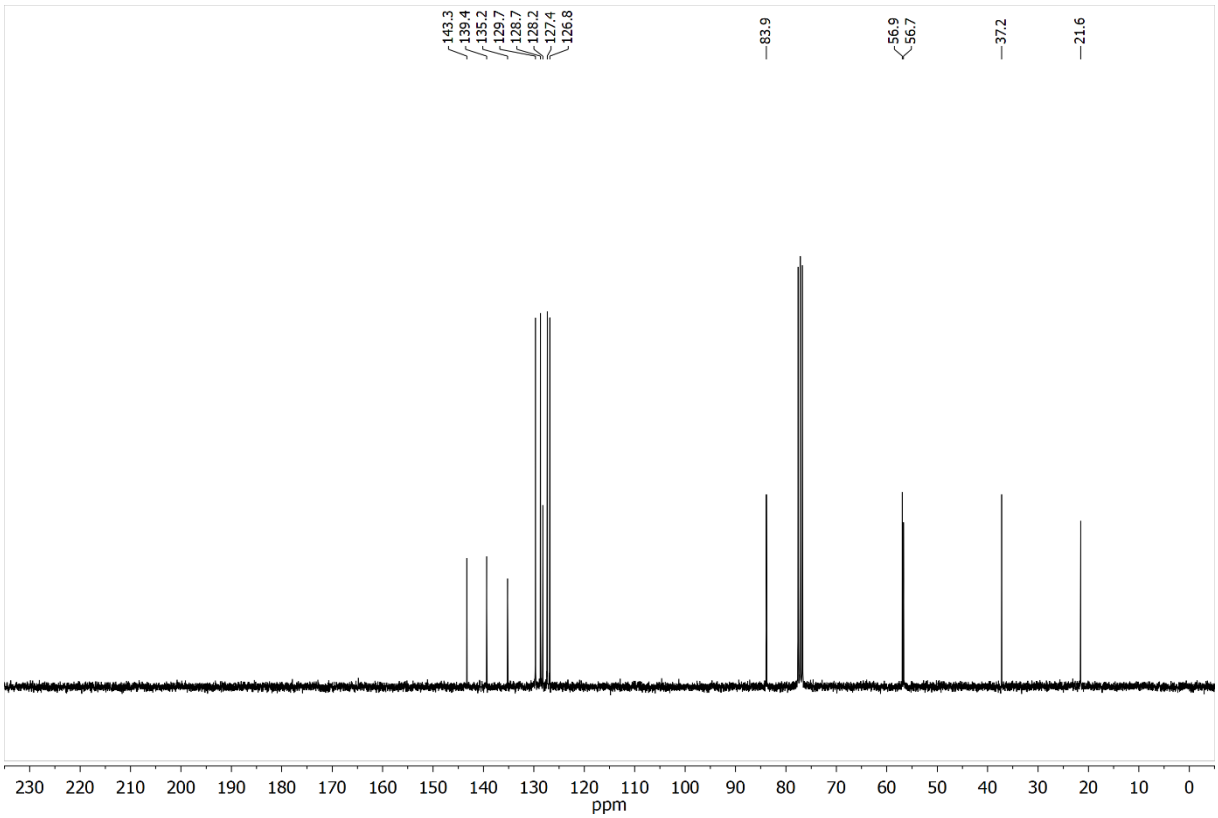




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

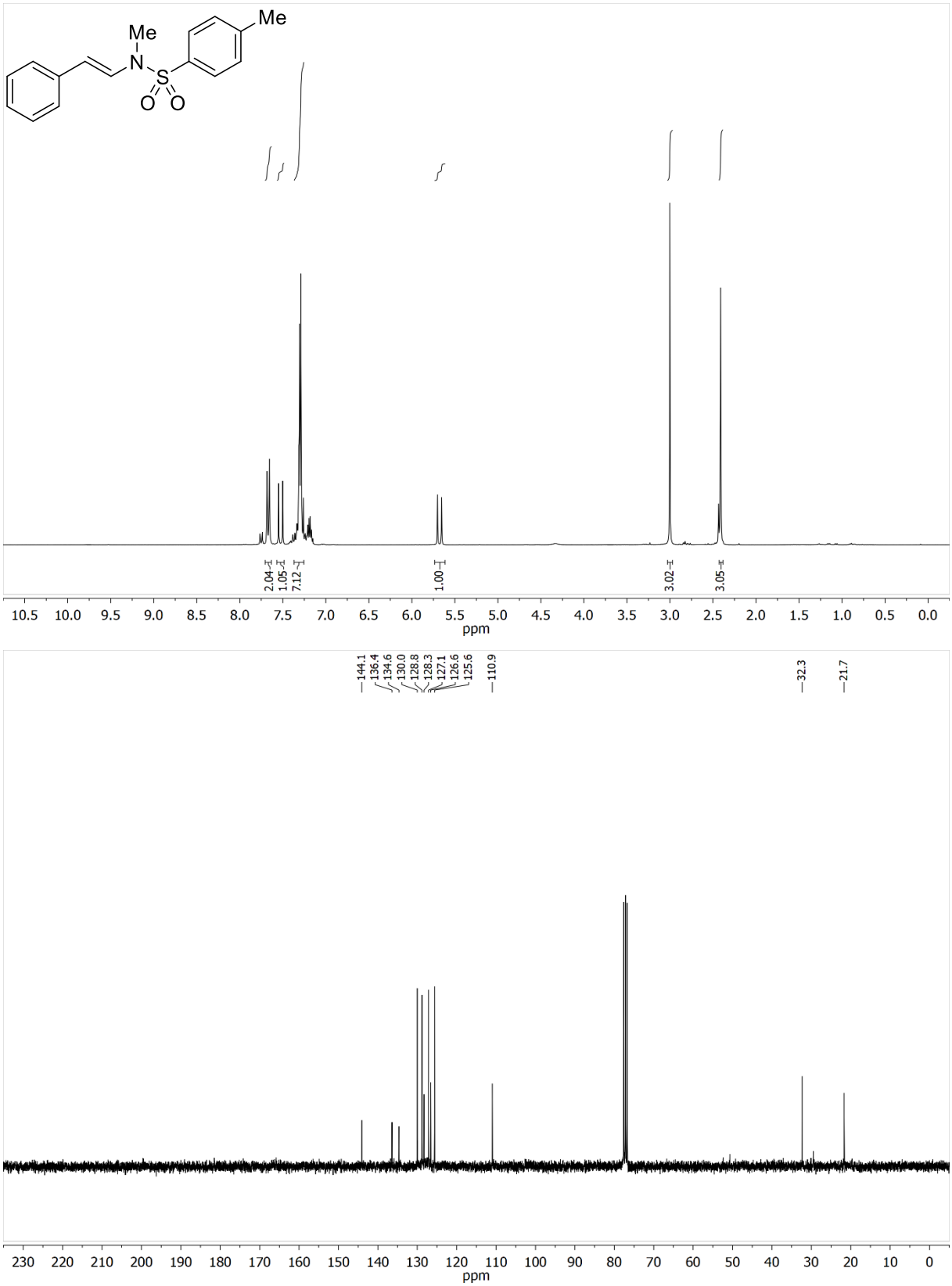
_N_-(2-methoxy-2-phenylethyl)-_N_,4-dimethylbenzenesulfonamide (16f)





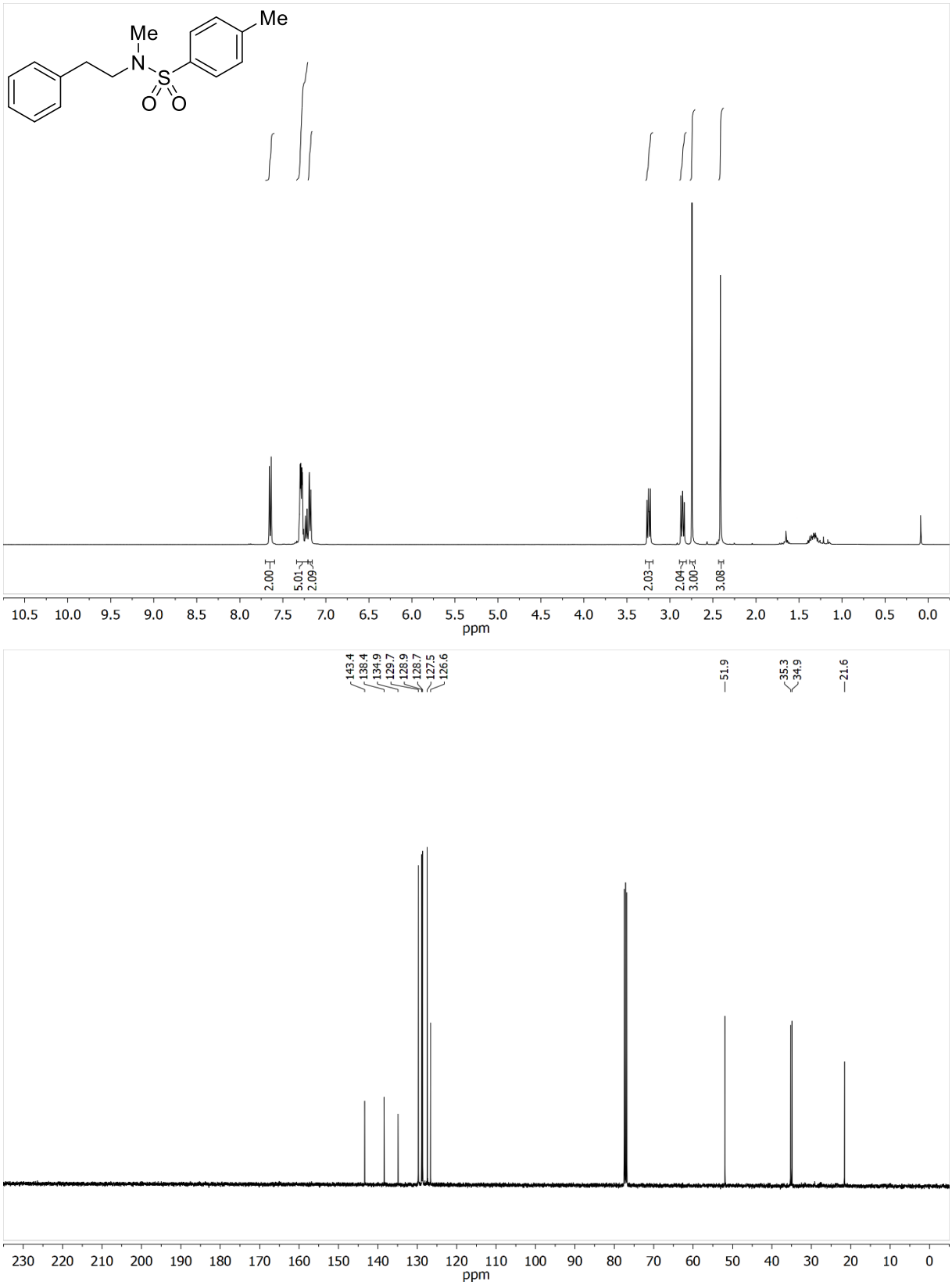
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

(*E*)-*N*,4-dimethyl-*N*-styrylbenzenesulfonamide (17)



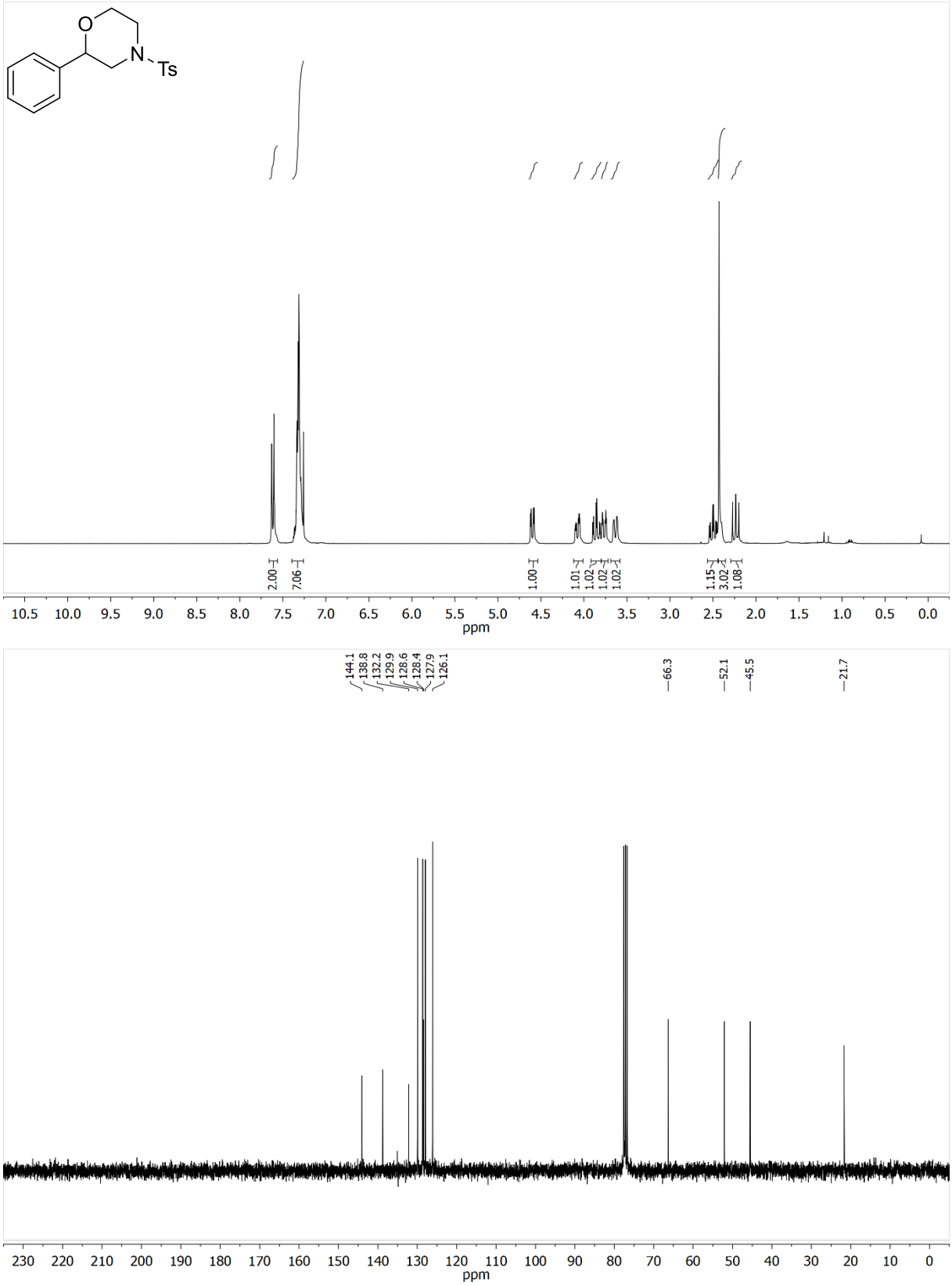
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

_N_,4-dimethyl-_N_-phenethylbenzenesulfonamide (18)



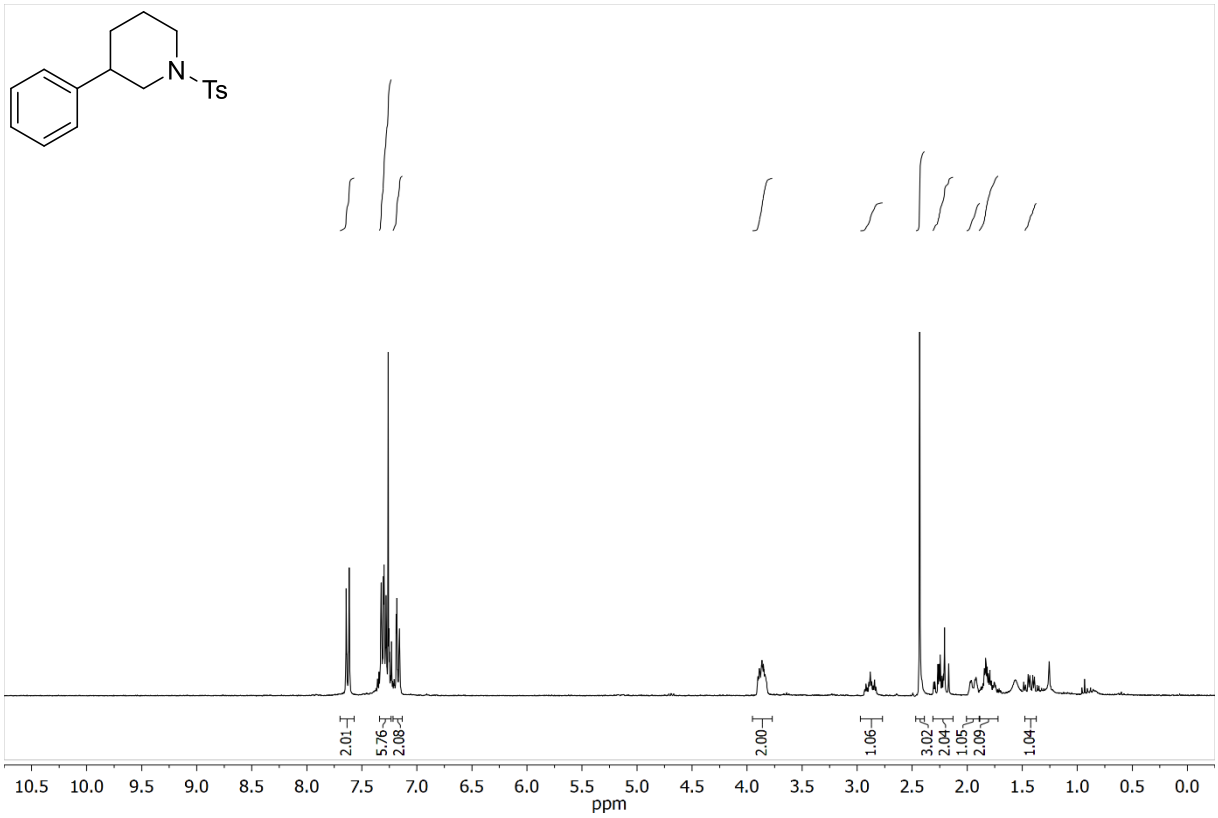
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

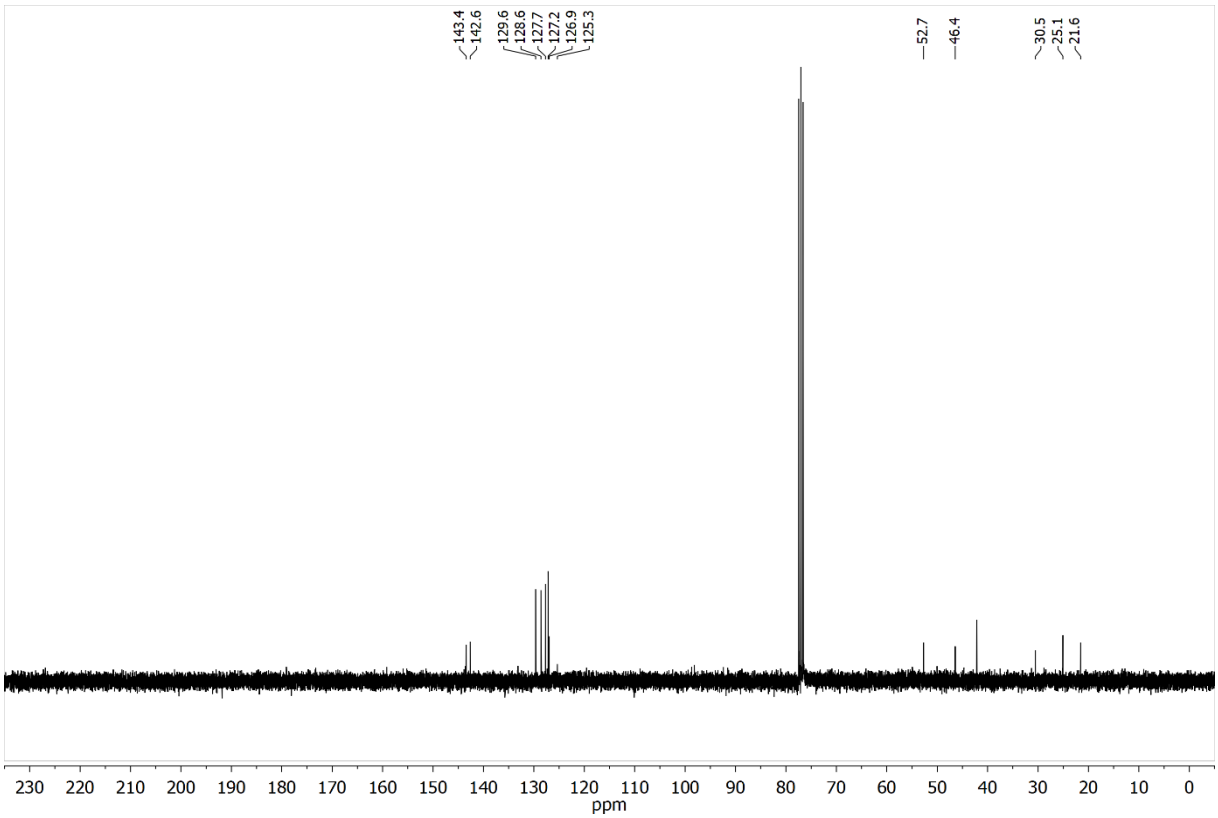
2-phenyl-4-tosylmorpholine (23)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

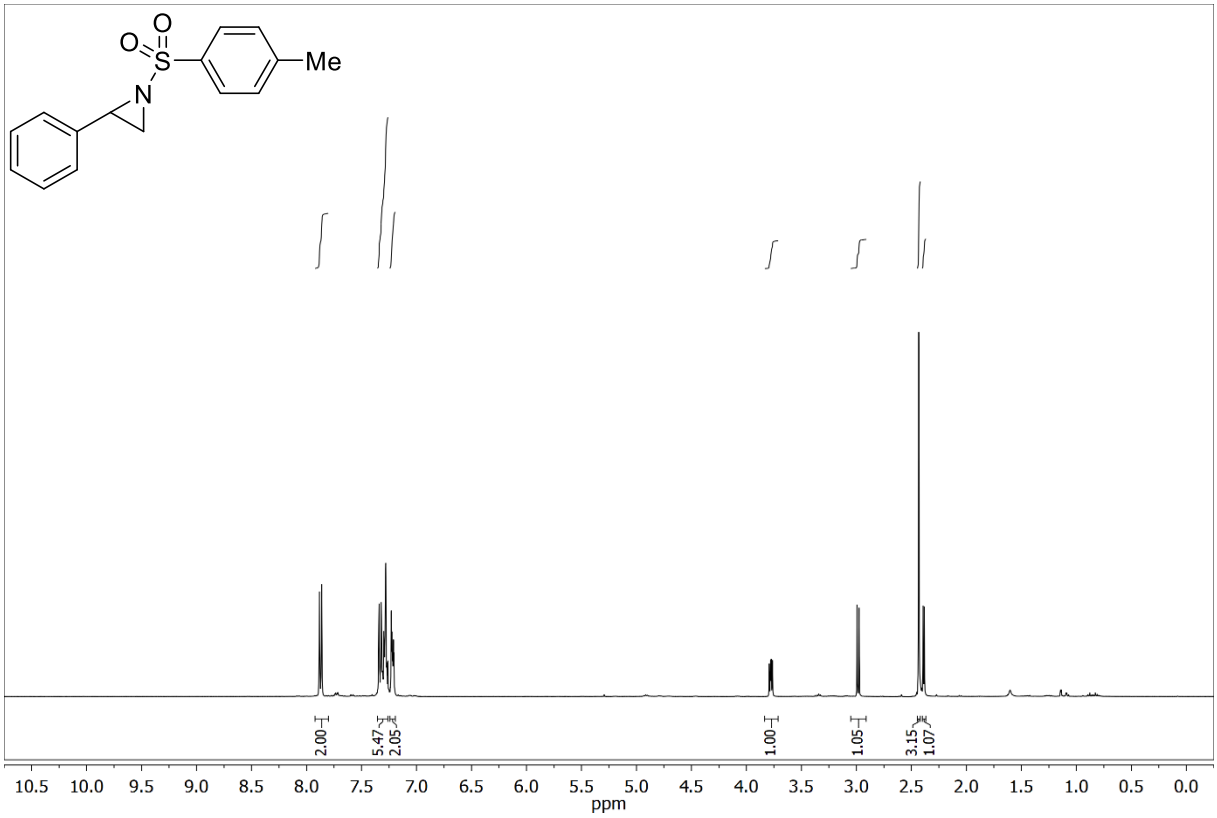
3-phenyl-1-tosylpiperidine (25)

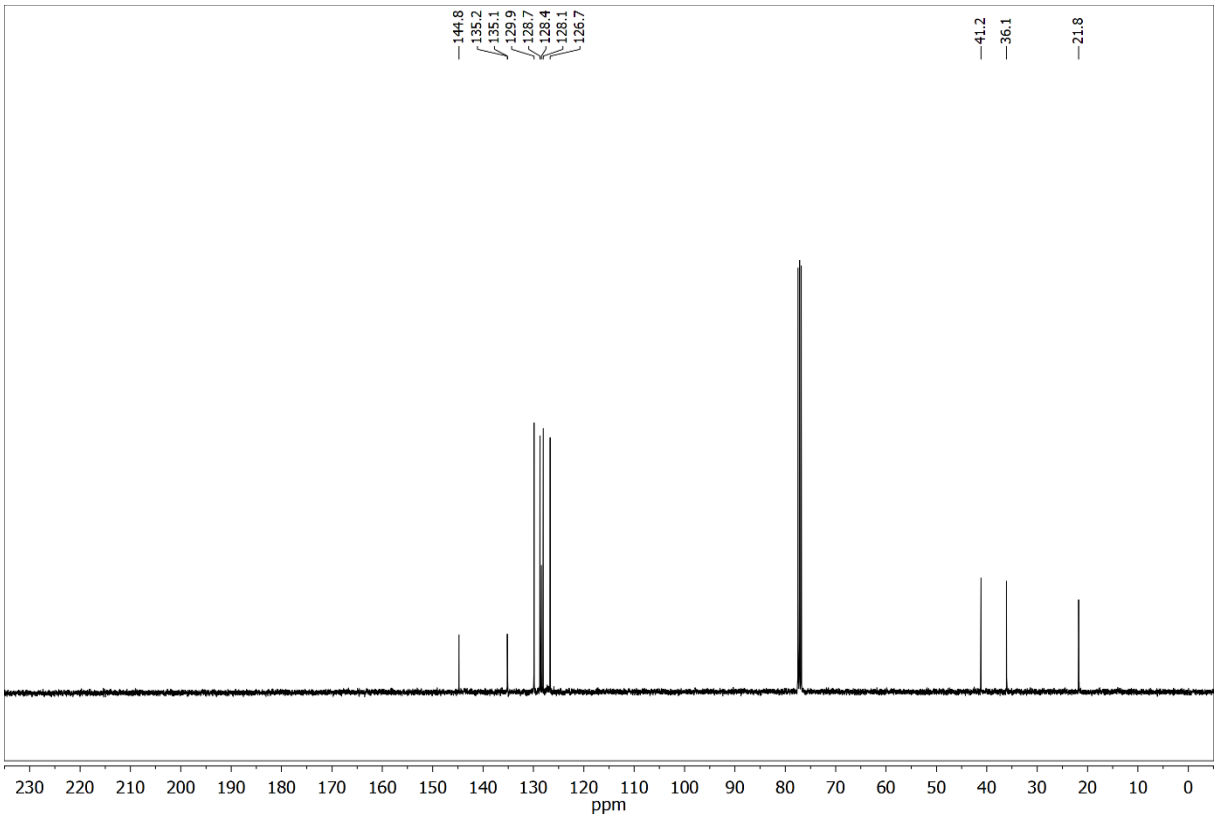




First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

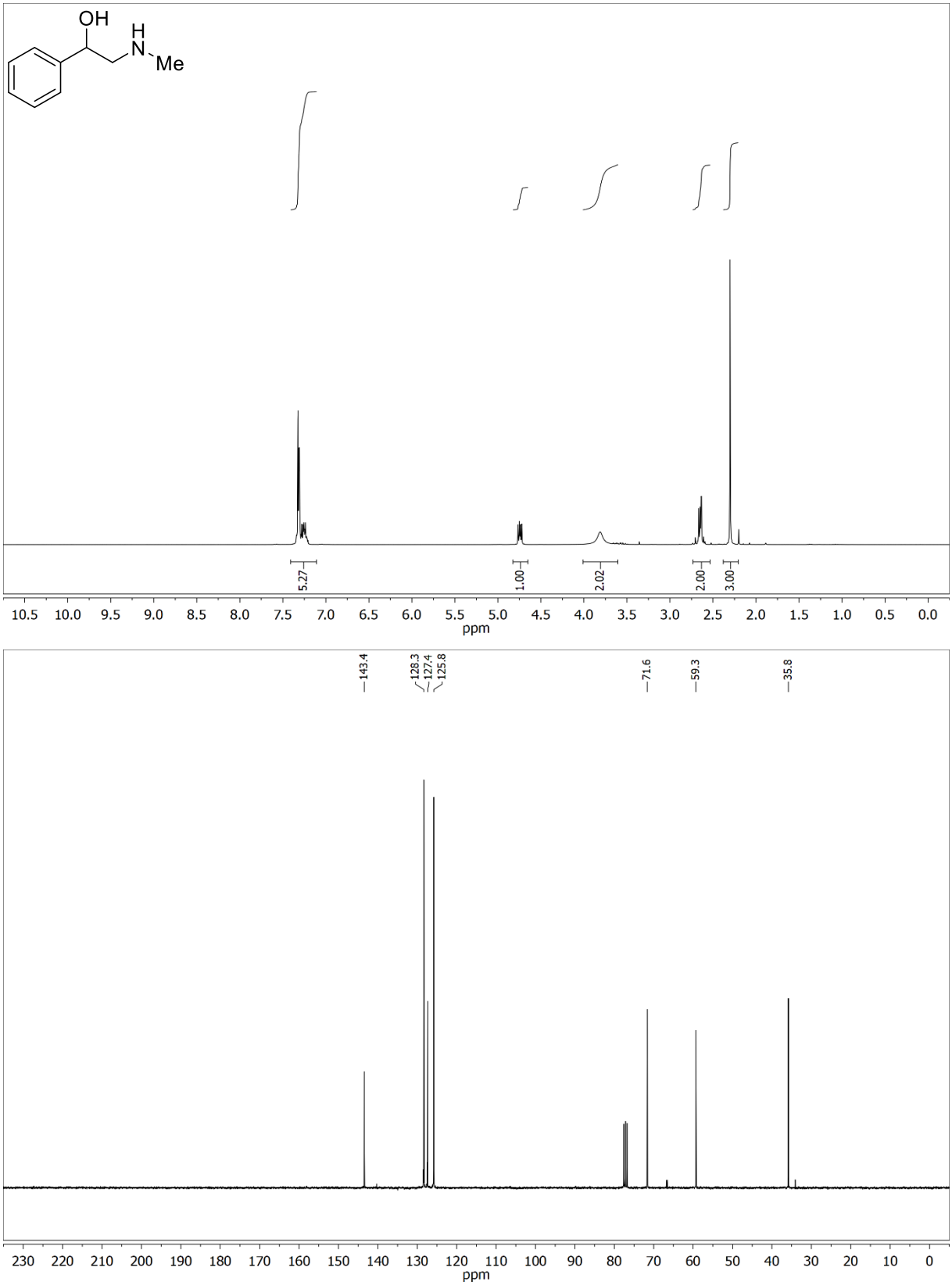
2-phenyl-1-tosylaziridine (26)





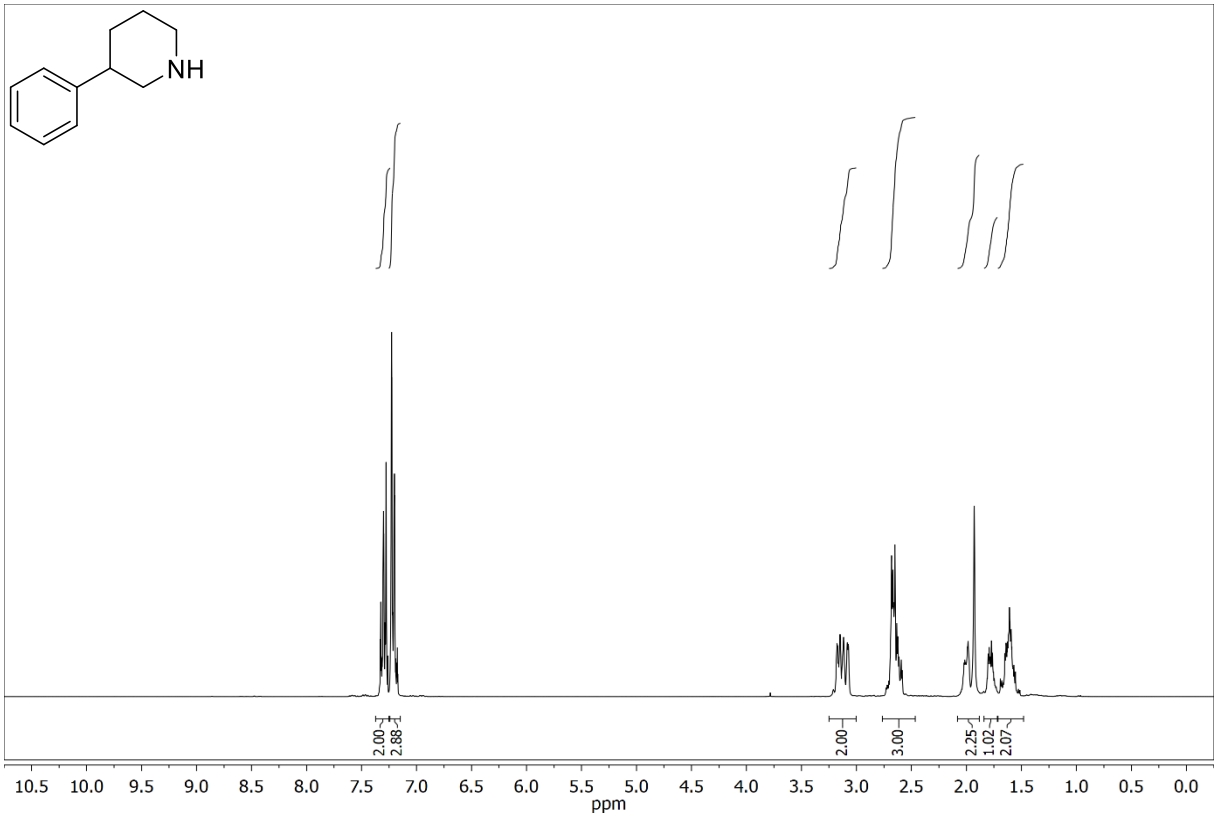
First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

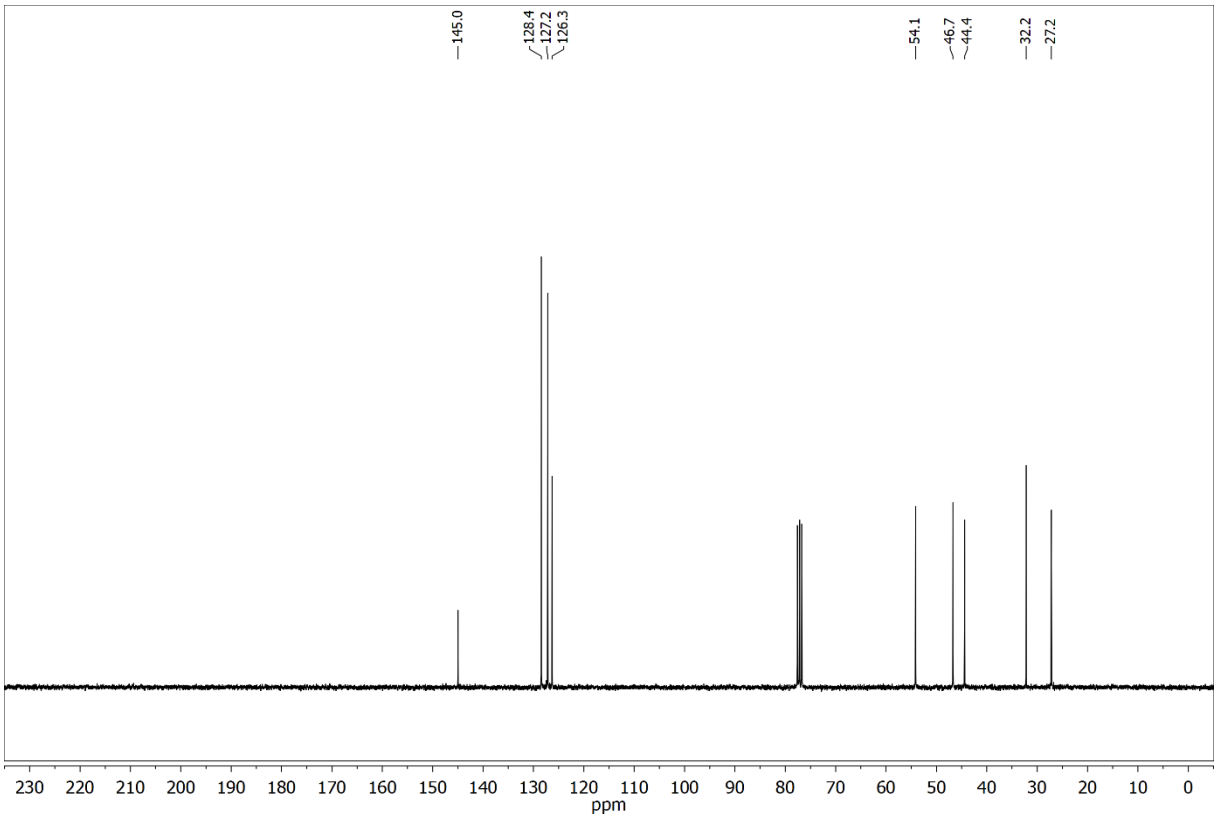
2-(methylamino)-1-phenylethan-1-ol (30)



First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

3-phenylpiperidine (31)

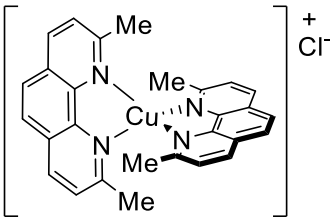


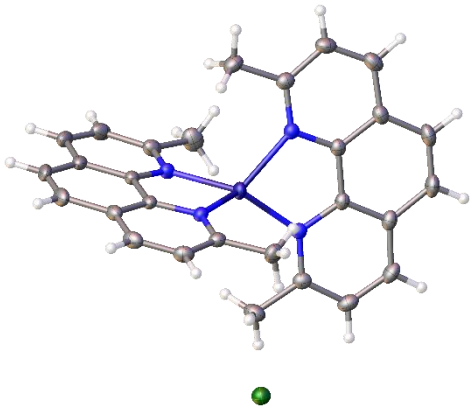


First image: ^{1}H-NMR; Second image: ^{13}C-NMR; NMR-solvent: $CDCl_3$.

8.6 X-Ray Analysis Data

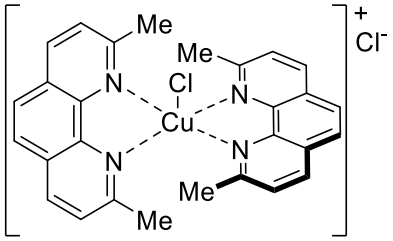
[Cu(dmp)$_2$]Cl

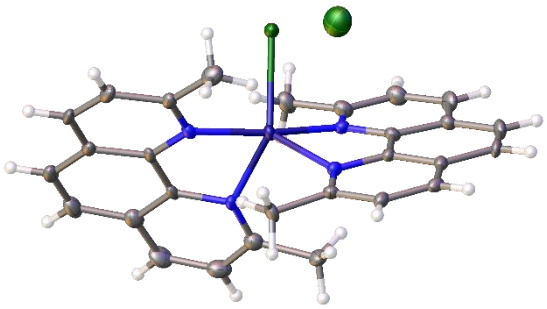




Formula	$C_{28}H_{26}ClCuN_4O$
$D_{calc.}$/ g cm^{-3}	1.448
μ/mm^{-1}	2.490
Formula Weight	533.52
Colour	clear red
Shape	plate
Size/mm^3	0.29×0.10×0.03
T/K	123.01(10)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	13.9217(3)
b/Å	17.3449(3)
c/Å	10.13873(18)
α/°	90
β/°	90.7692(17)
γ/°	90
V/Å^3	2447.98(8)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	CuK_α
Θ_{min}/°	4.072
Θ_{max}/°	74.092
Measured Refl.	14194
Independent Refl.	4779
Reflections with I > 2(I)	4420
R_{int}	0.0187
Parameters	323
Restraints	0
Largest Peak	0.300
Deepest Hole	-0.367
GooF	1.046
wR_2 (all data)	0.0752
wR_2	0.0730
R_1 (all data)	0.0287
R_1	0.0261
Creation Method Solution Refinement	Olex2 1.2-alpha (compiled 2018.07.26 svn.r3523 for OlexSys, GUI svn.r5532)

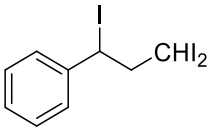
[Cu(dmp)$_2$Cl]Cl (CCDC: 1922265)

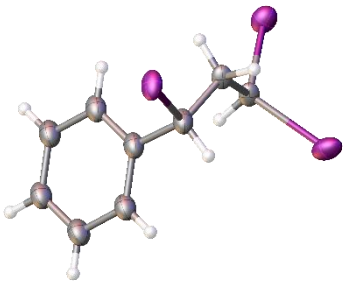




Formula	$C_{28}H_{24}Cl_2CuN_4$
$D_{calc.}$/ g cm^{-3}	1.240
μ/mm^{-1}	2.869
Formula Weight	550.95
Colour	green
Shape	needle
Size/mm^3	0.29×0.07×0.07
T/K	293(2)
Crystal System	monoclinic
Flack Parameter	0.412(17)
Hooft Parameter	0.420(6)
Space Group	*Pn*
a/Å	7.42340(10)
b/Å	24.9768(6)
c/Å	15.9408(3)
α/°	90
β/°	92.784(2)
γ/°	90
V/Å^3	2952.14(10)
Z	4
Z'	2
Wavelength/Å	1.54184
Radiation type	CuK_α
Θ_{min}/°	3.539
Θ_{max}/°	74.030
Measured Refl.	18773
Independent Refl.	9748
Reflections with I > 2(I)	8967
R_{int}	0.0235
Parameters	640
Restraints	2
Largest Peak	0.952
Deepest Hole	-0.375
GooF	1.059
wR_2 (all data)	0.1164
wR_2	0.1135
R_1 (all data)	0.0449
Creation Method Solution	ShelXL-2016/6
	ShelXT 2014/5 (Sheldrick, 2014)
Refinement	ShelXL-2016/6 (Sheldrick, 2016)

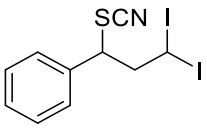
(1,3,3-triiodopropyl)benzene (25a) (CCDC: 2013498)

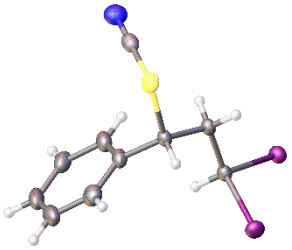




Formula	$C_9H_9I_3$
$D_{calc.}$/ g cm^{-3}	2.688
μ/mm^{-1}	59.467
Formula Weight	497.86
Colour	clear light yellow
Shape	prism
Size/mm^3	0.15×0.08×0.04
T/K	123.01(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	10.0057(4)
b/Å	6.5063(3)
c/Å	19.3960(7)
α/°	90
β/°	102.991(4)
γ/°	90
V/Å^3	1230.36(9)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K$_\alpha$
Θ_{min}/°	4.612
Θ_{max}/°	74.474
Measured Refl.	30217
Independent Refl.	2476
Reflections with I > 2(I)	2288
R_{int}	0.1153
Parameters	195
Restraints	222
Largest Peak	0.994
Deepest Hole	-0.888
GooF	1.226
wR_2 (all data)	0.0934
wR_2	0.0901
R_1 (all data)	0.0464
R_1	0.0422

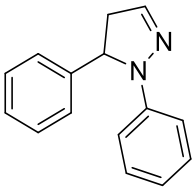
(3,3-diiodo-1-thiocyanatopropyl)benzene (34a) (CCDC: 2013499)

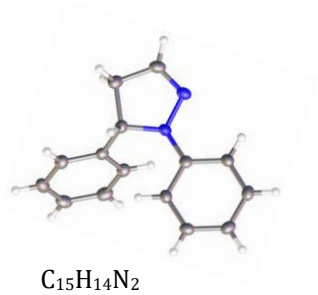




Formula	$C_{10}H_9I_2NS$
$D_{calc.}$/ g cm^{-3}	2.278
μ/mm^{-1}	5.159
Formula Weight	429.04
Colour	clear light yellow
Shape	prism
Size/mm^3	0.25×0.10×0.08
T/K	123.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	6.5392(2)
b/Å	23.2657(7)
c/Å	8.6352(3)
α/°	90
β/°	107.806(4)
γ/°	90
V/Å^3	1250.82(8)
Z	4
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K_α
Θ_{min}/°	3.034
Θ_{max}/°	32.389
Measured Refl's.	10829
Ind't Refl's	4130
Refl's with I > 2(I)	3433
R_{int}	0.0340
Parameters	224
Restraints	246
Largest Peak	1.464
Deepest Hole	-1.155
GooF	1.063
wR_2 (all data)	0.0741
wR_2	0.0691
R_1 (all data)	0.0471
R_1	0.0357

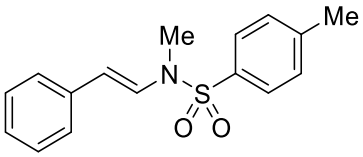
1,5-diphenyl-4,5-dihydro-*1H*-pyrazole (36a) (CCDC: 2013500)

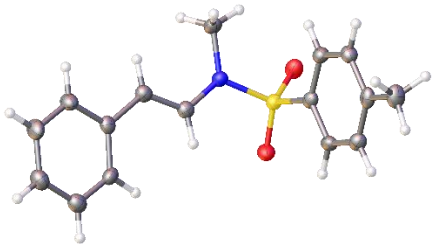




Formula	$C_{15}H_{14}N_2$
$D_{calc.}$/ g cm^{-3}	1.312
μ/mm^{-1}	0.605
Formula Weight	222.28
Colour	clear light yellow
Shape	needle
Size/mm^3	0.38×0.07×0.05
T/K	123.01(10)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	9.1627(3)
b/Å	5.59611(16)
c/Å	22.3891(6)
α/°	90
β/°	101.368(3)
γ/°	90
V/Å^3	1125.48(6)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	CuK_α
Θ_{min}/°	4.028
Θ_{max}/°	73.583
Measured Refl's.	6745
Ind't Refl's	2223
Refl's with I > 2(I)	1998
R_{int}	0.0273
Parameters	154
Restraints	0
Largest Peak	0.301
Deepest Hole	-0.285
GooF	1.046
wR_2 (all data)	0.1083
wR_2	0.1038
R_1 (all data)	0.0445
R_1	0.0398

(*E*)-*N*,4-dimethyl-*N*-styrylbenzenesulfonamide (17)





Formula	$C_{16}H_{17}NO_2S$
$D_{calc.}$/ g cm^{-3}	1.329
μ/mm^{-1}	2.005
Formula Weight	287.36
Colour	clear colourless
Shape	prism-shaped
Size/mm^3	0.25×0.09×0.05
T/K	123.00(10)
Crystal System	orthorhombic
Flack Parameter	-0.01(3)
Hooft Parameter	-0.031(19)
Space Group	$P2_12_12_1$
a/Å	6.2494(2)
b/Å	7.7921(3)
c/Å	29.4965(8)
α/°	90
β/°	90
γ/°	90
V/Å^3	1436.36(8)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K$_\alpha$
Θ_{min}/°	5.873
Θ_{max}/°	66.738
Measured Refl's.	7660
Indep't Refl's	2535
Refl's I≥2 σ(I)	2363
R_{int}	0.0596
Parameters	183
Restraints	0
Largest Peak	0.340
Deepest Hole	-0.383
GooF	1.039
wR_2 (all data)	0.1199
wR_2	0.1162
R_1 (all data)	0.0487

Chapter 9

Personal Appendix

This chapter contains personal appendix like curriculum vitae, a list of publications as well as a list of selected congresses and scientific meetings.

9.1 Curriculum Vitae

Personal Data

Name	Sebastian Wilhelm Engl
Date and place of birth	12.10.1994 in Regensburg, Germany
Nationality	German
Email	engl.sebastian@outlook.de

Education

10/2018 – 01/2022	**PhD Thesis** at the University of Regensburg under supervision of Prof. Dr. Oliver Reiser *"The Unique Character of Copper in Photoredox Catalysis"*
10/2016 – 09/2018	International Elite **Master of Science (M. Sc.)** (grade 1.2) as part of the Elite Network of Bavaria administered by the Bavarian State Ministry of Science and the Arts at the University of Regensburg Thesis under supervision of Prof. Dr. Oliver Reiser: *"Visible Light Mediated Copper Catalyzed Chlorosulfonylation of Alkenes and Alkynes"* (grade: 1.0)
10/2013 – 07/2016	**Bachelor of Science (B. Sc.)** (grade 1.5) at the University of Regensburg Thesis under supervision of Prof. Dr. Oliver Reiser: *"Photoredox katalysierte Synthese substituierter Pyrrolidine"* (grade: 1.0)
09/2005 – 06/2013	**Abitur** (A-level) (grade 1.2) at the Gymnasium Neutraubling, Germany
09/2001 – 07/2005	**Primary School** (grade 1.3), Grundschule Altenthann, Germany

International Experience

10/2019 – 11/2019	Research Project at University of Delhi in **Delhi (India**) under supervision of Prof. Dr. Akilesh K. Verma
09/2017 – 10/2017	Research Project at Merkert Chemistry Center at Boston College in **Boston (USA)** under supervision of Prof. Dr. X. Peter Zhang

Awards, Certificates and Fellowships

since 07/2019	Studienstiftung des deutschen Volkes. Germany`s largest and oldest scholarship foundation.

08/2020	Certificate for Quality Management in Analytical Chemistry
01/2017	Deutschlandstipendium National fellowship program of the Federal Republic of Germany
07/2018	Certificate in a Foreign Language UNIcert Level III for English (GeR-Stufe C1)
01/2017	Certificate for Professional Mentor in Chemistry
12/2016	Certificate for Professional Tutor in Chemistry
10/2016	Award of the Elite Network of Bavaria
07/ 2016	Certificate of Competence for the Chemical Prohibition Ordinance
01/2015	Deutschlandstipendium National fellowship program of the Federal Republic of Germany
07/2013	Award for best absolvent in chemistry (Abitur) by the German Chemical Society (GDCh)
07/2013	Award for the best absolvent in physics (Abitur) by the German Physical Society (DPG)
07/2013	Online-Fellowship E-Fellows.net (Abitur)

Languages

German	Native Language
English	Business Fluent: B2+/C1 according to Abitur, as well as C1 (UNIcert III) certificate
Latin	Basics

Professional References

Prof. Dr. Oliver Reiser
Institut für Organische Chemie
Universität Regensburg, Universitätsstr. 31
93053 Regensburg, Germany
Phone: +49 941 9434631
Email: oliver.reiser@chemie.uni-regensburg.de

Prof. Dr. X. Peter Zhang
Department of Chemistry
Boston College, Chestnut Hill
02467 Massachusetts
Phone: +1 617 552 1483
Email: peter.zhang@bc.edu

Prof. Dr. Akhilesh K. Verma
Department of Chemistry
University of Delhi, New Delhi
110021 Delhi
Email: akhilesh682000@gmail.com
Email: averma@acbr.du.ac.in

9.2 Congress and Scientific Meetings

[1] Exploratory Photochemistry: Light Creates Structure, Halle, Germany, **2021**
Poster Presentation: "*Copper Makes the Difference: Visible-Light-Mediated Atom Transfer Radical Addition Reactions of Iodoform with Olefins*"
Sebastian Engl and Oliver Reiser

[2] 21st Christmas Colloquium of the Institute for Organic Chemistry, Regensburg, Germany, **2019**
Oral Presentation: "Copper rocks the Christmas Tree – From Regensburg to Delhi and back"
Sebastian Engl and Oliver Reiser

[3] J-NOST Conference for Research Scholars, Delhi, India, **2019**
Oral Presentation: „*Unique Avenues in Photocatalysis: Cu(I)- and Cu(II)-catalyzed Chlorosulfonylation of Alkenes and Alkynes.*"
Sebastian Engl and Oliver Reiser

[4] Roche Continents, Salzburg, Austria, **2019**
International seminar week for top-talented students administered by the pharmaceutical company Hoffmann-La Roche

[5] 10th Münster Symposium on Cooperative Effects, Münster, Germany, **2019**
Poster Presentation: "*Economic Synthesis of β-Chlorosulfones via Visible-Light-Mediated Copper(I)- and Copper(II)-Photocatalysis"*
Sebastian Engl, Asik Hossain, Eugen Lutsker and Oliver Reiser

[6] 691st WE-Heraeus-Seminar on Physical Organic Chemistry, Bonn, Germany, **2019**
Poster Presentation: "*Visible-Light-Mediated Chlorosulfonylation of Alkenes and Alkynes: Introducing the Cu(II) Complex [Cu(dap)Cl_2] in ATRA Reactions*"
Sebastian Engl, Asik Hossain, Eugen Lutsker and Oliver Reiser

[7] 26th Lecture Conference on Photochemistry, Munich, Germany, **2018**
Poster Presentation: "*Copper Mediated Photoredox Catalyzed Iodoperfluoroalkylation of Alkenes and Alkynes*"
Eugen Lutsker, Sebastian Engl, Christian Kaiser, Thomas Rawner and Oliver Reiser

[8] Boston College Graduate Student Symposium, Dover, Massachusetts, USA, **2017**
Poster Presentation: "*Asymmetric Radical Reactions with In-Situ generated Diazo Compounds via Co(II)-based MRC*"
Yong Wang, Xin Wen, Jing Ke, Sebastian Engl und X. Peter Zhang

9.3 List of Publications

[1] Henriquez, M. A.; Engl, S.; Jaque, P.; Gonzalez, I. A.; Natali, M.; Reiser, O.; Cabrera, A. R., Phosphine evaluation on a new series of heteroleptic copper(I) photocatalysts with dpa ligand [Cu(dpa)(*P*,*P*)]BF_4. *Eur. J. Inorg. Chem.* **2021**, 4020-4029.

[2] Engl, S.; Reiser, O., Catalyst-Free Visible-Light-Mediated Iodoamination of Olefins and Synthetic Application. *Org. Lett.* **2021**, *23*, 5581-5586.

[3] Engl, S.; Reiser, O., Copper Makes the Difference: Visible-Light-Mediated Atom Transfer Radical Addition Reactions of Iodoform with Olefins. *ACS Catal.* **2020**, *10*, 9899-9906.
Highlighted in *Synfacts* **2020,** 16(*11*), 1304.

[4] Fayad, R.; Engl, S.; Danilov, E. O.; Hauke, C. E.; Reiser, O.; Castellano, F. N., Direct Evidence of Visible Light-Induced Homolysis in Chlorobis(2,9-dimethyl-1,10-phenanthroline)copper(II). *J. Phys. Chem. Lett.* **2020**, *11*, 5345-5349.

[5] Engl, S.; Reiser, O., Making Copper Photocatalysis Even More Robust and Economic: Photoredox Catalysis with $[Cu^{II}(dmp)_2Cl]Cl$. *Eur. J. Org. Chem.* **2020**, 1523-1533.
Highlighted as Very Important Paper (VIP).
Highlighted in "ChemistryViews – Magazine of ChemPubSoc Europe"
Awarded as "Top Downloaded Paper 2018-2019".

[6] Hossain, A.†; Engl, S.†; Lutsker, E.†; Reiser, O., Visible-Light-Mediated Regioselective Chlorosulfonylation of Alkenes and Alkynes: Introducing the Cu(II) Complex [Cu(dap)Cl_2] to Photochemical ATRA Reactions. *ACS Catal.* **2019**, *9*, 1103-1109. (†Authors contributed equally).

[7] Engl, S.; Rolka, A., SynCat – Ein Masterstudiengang trifft den Nerv der Zeit. Article in the Journal "Faszination Chemie".

Chapter 10

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Zunächst möchte ich mich an dieser Stelle bei all denjenigen bedanken, die mich während der Anfertigung dieser Doktorarbeit unterstützt haben.

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A special thanks goes also to *Prof. X. Peter Zhang* for the great chance and constant guidance to work in his labs at Boston College in the US. I am very grateful to Prof. X. Peter Zhang for writing recommendation letter for me. Thanks to all *former and present co-workers*, especially *Dr. Yong Wang* and *Dr. Xin Wen* for their great guidance and patience, which led me grow as a scientist.

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Chapter B – Introducing Chlorobis(dmp)copper(II) to Photocatalysis), sowie *Marco Henriquez* und *Prof. Dr. Alan Cabrera* mit weiteren Partnern von ganzem Herzen bedanken.

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Chapter 11

Declaration / Eidesstattliche Erklärung

Herewith I declare that this present thesis is a presentation of my original work prepared single-handed. Wherever contributions from others are involved, all of them are marked clearly, with references to the literature, licenses and acknowledgement of collaborative research.

Regensburg, den 10.01.2022

Engl, Sebastian