Studies Towards Photoaerobic Cycloamination Reactions via Selenium-π-Acid Catalysis

Dissertation

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Abbreviations

°C	degree Celsius
Å	angstrom
Ac	acetyl
AcOH	acetic acid
aq.	aqueous
BINOL	1,1‘-bi-2-naphthol
Bn	benzyl
Boc	*tert*-butoxycarbonyl
calcd.	calculated
conc.	concentrated
COSY	Correlation Spectroscopy
CV	Cyclic Voltammerty
Cy	cyclohexyl
d	day(s) or douplet
DAD	Diode Array Detector
DCE	1,2-dichloroethane
DCM	dichloromethane
de	diastereomeric excess
DEE	diethylether
δ	chemical shift
DFT	Density Functional Theory
DIAD	diisopropyl azodicarboxylate
DMF	dimethylformamide
DMSO	dimethylsulfoxide
dr	diastereomeric ratio
E	electrophile
EDG	electron donating group
ee	enantiomeric excess
EI	Electron Impact

er	enantiomeric ratio
Et	ethyl
eq.	equivalent(s)
ESI	Electrospray Ionization
EtOAc	ethyl acetate
EtOH	ethanol
EWG	electron withdrawing group
Fc	ferrocene
g	gram(s)
HFIP	1,1,1,3,3,3-hexafluoropropan-2-ol
HPLC	High-Performance Liquid Chromatography
HSQC	Heteronuclear Single Quantum Coherence
HRMS	High Resolution Mass Spectrometry
^{i}Pr	*iso*-propyl
IR	Infrared
J	coupling constant
k	kilo
λ	wavelength
L	liter(s)
LA	Lewis acid
LB	Lewis base
LED	Light Emitting Diode
lx	lux
m	milli or multiplet
m	meta
M	molar (mol/L)
m-CPBA	*meta*-chloroperbenzoic acid
Me	methyl
MeCN	acetonitrile
MeOH	methanol
Mes	mesitylene

MHz	megahertz
µ	micro
min	minute(s)
m.p.	melting point
Ms	mesyl
MS	Mass Spectrometry
NBS	*N*-bromosuccinimide
^{n}Bu	*n*-butyl
NFSI	*N*-fluorobenzenesulfonimide
Nm	nanometer(s)
NMR	Nuclear Magnetic Resonance
h	hour(s)
NOESY	Nuclear Overhauser Effect Spectroscopy
Np	neopentyl
Ns	nosyl
Nu	nucleophile
o	ortho
p	para
PE	petroleum ether
pH	*pondus hydrogeni*
Ph	phenyl
pk_a	acid dissociation constant
PMB	*p*-methoxybenzyl
ppm	parts per million
q	quartet
quint	quintet
R	arbitrary rest
rac	racemic
R_f	retention factor
rpm	revolutions per minute
r.t.	room temperature

s	singlet
sat.	saturated
sept	septet
sex	sextet
SHOP	Shell Higher Olefin Process
t	triplet
TAPT	2,4,6-tris(*p*-anisyl) pyrylium tetrafluoroborate
TBS	*tert*-butyldimethylsilyl
^{t}Bu	*tert*-butyl
Tf	trifluoromethanesulfonate
THF	tetrahydrofuran
TIPP	2,4,6-triisopropylphenyl
TLC	Thin layer chromatography
Tol	tolyl
TM	transition metal
TMB	1,3,5-trimethoxybenzene
TMS	trimethylsilyl
Ts	tosyl
UV	ultraviolet

1 Introduction

1.1 Oxidative functionalization of alkenes

Oxidative functionalizations of alkenes represent one of the cornerstone processes for the synthesis of fine chemicals and pharmaceuticals in the field of chemical research and industry.[1,2,3] A big advantage of these processes lies in the unification of two reaction steps, namely the formation of a new bond (C-C, C-N, C-O, C-Hal) and an oxidation.[4] In this way, about two million tons of acetaldehyde (**1**) are produced by the Wacker process[5–7], about one million tons of linear α-olefins (**2**) by the SHOP process per year[8–11] and countless pharmaceuticals such as Naproxen (**3**) and (*R*)-4-(pyridin-3-yl)butane-1,2-diol (**4**) by the Heck reaction (Figure 1).[12–16]

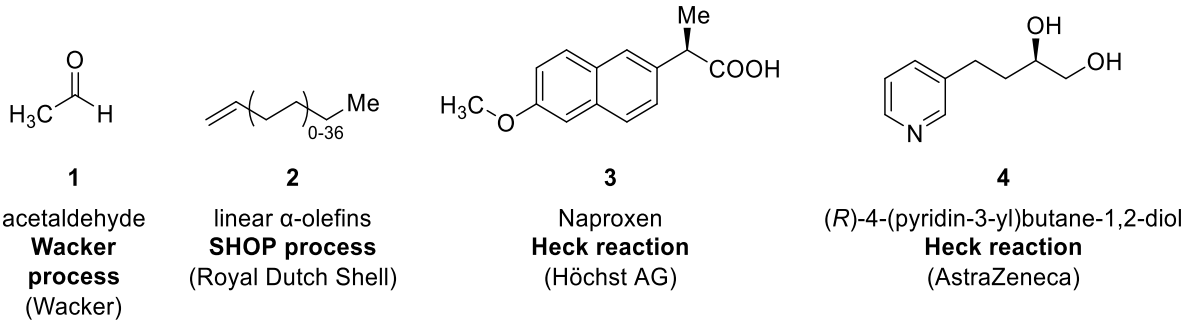
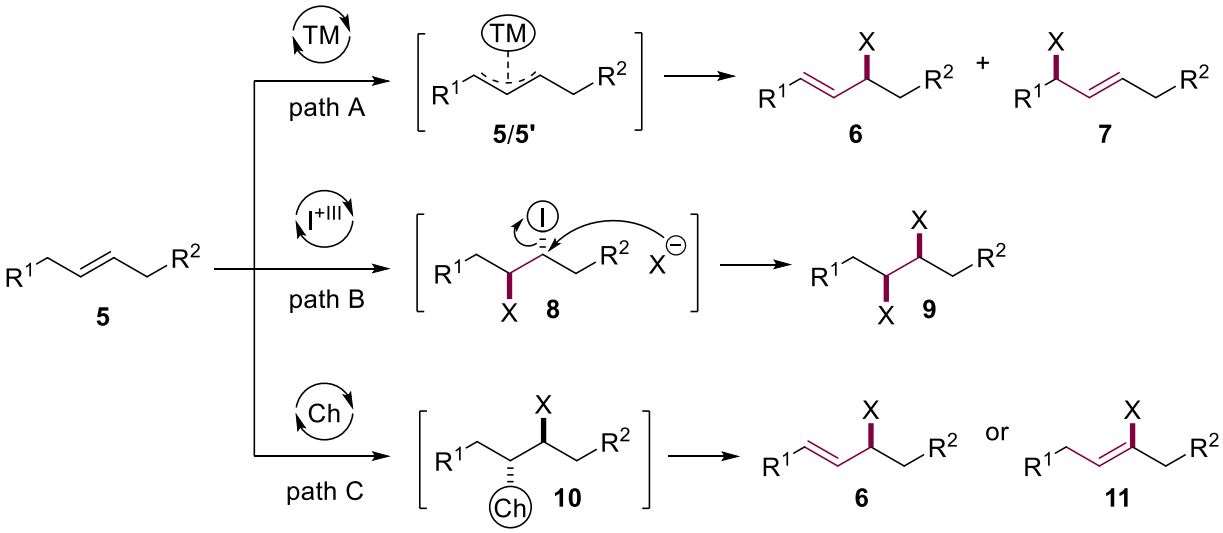


Figure 1. Fine chemicals and pharmaceuticals produced *via* oxidative alkene functionalizations.[5–16]

Oxidative aminations are nowadays among the most researched subcategories in the realm of oxidative alkene functionalization,[17–21] because the direct implementation of a nitrogen moiety into a carbon framework can enable the quick assembly of pharmaceutically relevant molecules.[22] Unarguably, most of these processes rely on the impressive catalytic potency of transition metal (TM) catalysts containing the elements Pd[17–19] or Cu.[20,21] Since the pioneering works of Heck[23] and Trost[24] in the 1960s and 1970s, a vast number of examples has been explored and optimized for industrial purposes, and at the same time these catalytic reactions are still major constituent of todays` research.[25] However, these catalysts also come with their disadvantages and weaknesses. In addition to the enormous costs and the toxicity of TMs in several cases, these catalysts often suffer from the property of undergoing *β*-hydride eliminations.[26] These can be desirable *e.g.* for the SHOP process, but for other cases, they often lead to the formation of regioisomeric side products (Scheme 1, path A).[27] Modern examples to overcome these issues partially were presented *e.g.*

by Stahl *et al.*,[17] Bower *et al.*[28,29] and Yoon *et al.*,[4] covering the synthesis of *N*-heterocycles, or by White *et al.*[30] for the amination of terminal alkenes. Notably, all these techniques require specific structural criteria of the alkenes or are limited to only a specific group of products to ensure the proper regioselective outcome. These specifications can either be the necessity to generate only terminal or conjugated alkenes,[31] the presence of quaternary carbons within the product to prohibit possible double bond migration[29] or the presence of a trisubstituted alkene within the substrate.[4] Hence, although the activation of terminal and cyclic alkenes is manageable for TMs, acyclic internal alkenes are still accompanied with the aforementioned difficulties, especially for sterically demanding TM catalysts.[32] This group of alkenes is particularly interesting because of their availability in large quantities through petrochemical processes and their inexpensiveness.[33] A solution to this limitation can be provided by main group catalysts, which provide an entirely different reaction pathway compared to TMs.[2,3] While TM catalysis proceeds *via* comparatively weak coordinative interactions, which enable the migration of a double bond, main group organocatalysts prevent this migration by strong covalent interactions and thereby proceed very regioselectively.[34] In this context, hypervalent iodine species have been proven to be privileged candidates.[2] Especially for regioselective difunctionalizations, I^{+III} species have proven to be practicable as catalysts in combination with an appropriate oxidant (Scheme 1, path B).[35,36] Notably, here, the difunctionalization is the preferred pathway over the elimination pathway regenerating the double bond, because of the high polarization of the C-I bond[37], which facilitates a second nucleophilic substitution. In this area, Muniz *et al.*[36,38], Wirth *et al.*[39] and Jacobsen *et al.*[40] have made major contributions regarding the reaction scope of stereoselective protocols. While only few I^{+III} catalyzed techniques cover the allylic or vinylic functionalization of internal alkenes, chalcogen catalysts, especially with sulfur or selenium, are at the top of this race here (Scheme 1, path C).[3,41,42,43] Here, the second step can also involve an elimination step rather than a substitution due to the inertness of the C-Se bond towards nucleophiles.[44]



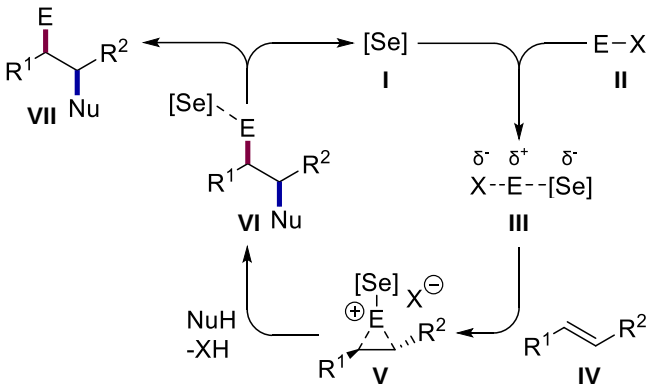
Scheme 1. Typical reaction profiles and products from TM, I^{+III} and chalcogen (Ch) -catalyzed reactions.

Besides a large amount of racemic functionalizations, only few stereoselective ones have been developed over the years, although stoichiometric selenofunctionalizations can be traced back to the 1920s.[45] Hence, the research on new catalytic manifolds for these reaction types represents one of the major challenges in the realm of method oriented organic chemistry. In the following sections, a general overview over the activation modes of selenium catalysts, the underlying mechanism of alkene activation through chalcogen catalysis, and representative examples is given.

1.2 Concepts of selenium catalysis

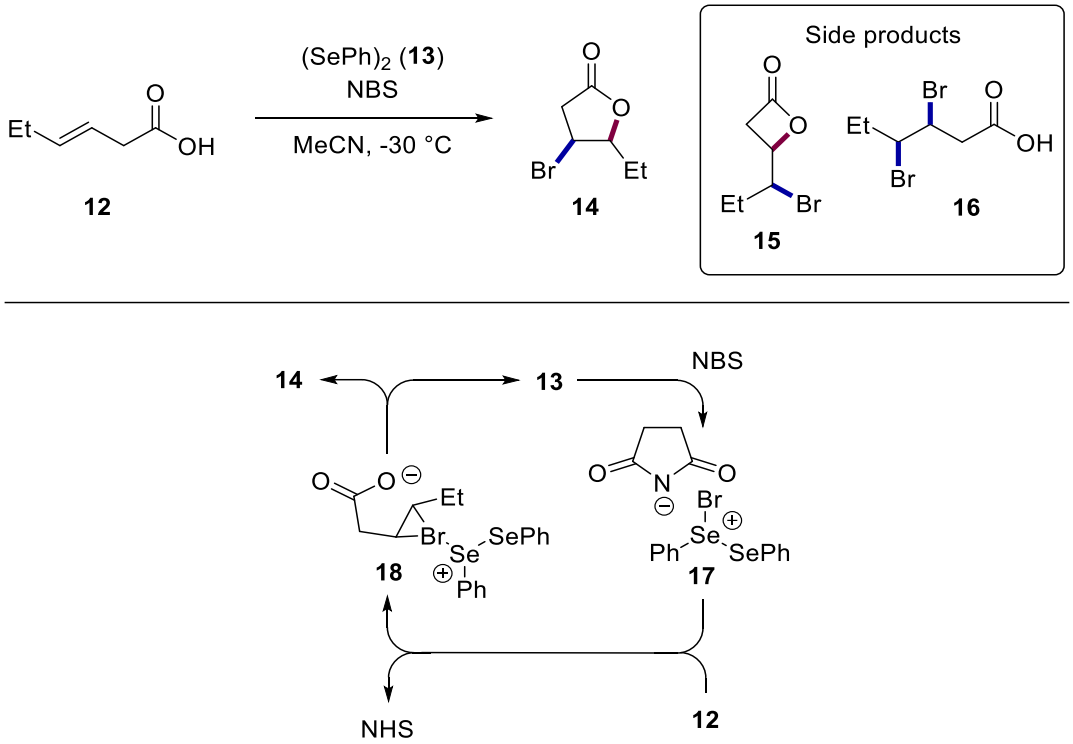
1.2.1 Lewis basic selenium catalysis

To learn about the different selenium-catalyzed oxidative alkene functionalizations, it is first important to understand the mechanisms of selenium catalysis. Two different activation modes of the selenium moiety can trigger a catalytic turnover.[3] One is the Lewis basic activation of an electrophile by the selenium catalyst (Scheme 2).[46] Here, in general, catalyst **I** interacts with substrate **II** in such an extent that the electrophilic moiety of **II** is positively polarized and can be added onto a nucleophilic species like an alkene (**IV**). The resulting planar iranium ion **V** can be attack by a nucleophile in such a way that the addition proceeds in a *trans*-fashion leading to **VI**. From here, Lewis basic selenium catalyst **I** is regenerated, and addition product **VII** can be released.



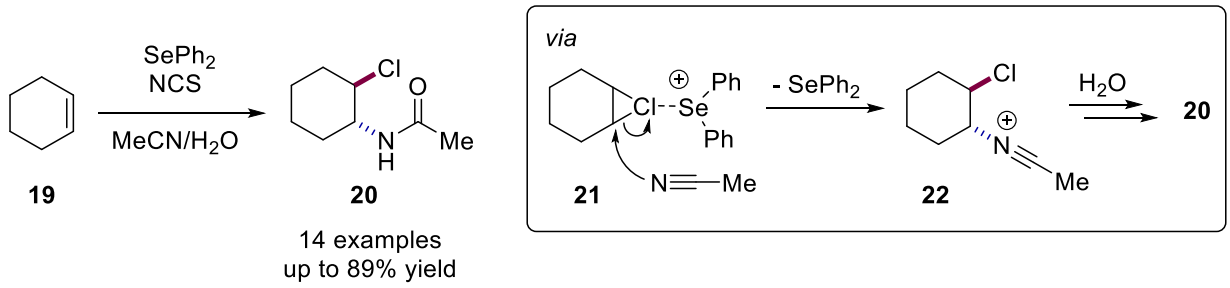
Scheme 2. Mechanism of Lewis basic selenium catalysis.[46]

Although this type of selenium catalysis has not existed for a long time, more and more examples have emerged in recent years.[47,48] Among the first reports of Lewis basic selenium catalysis is the work from Tunge *et al.* within halolactonization reactions (Scheme 3).[49] Herein, the authors proposed that selenium catalyst $(SePh)_2$ (**13**) was activated by the electrophilic bromine source NBS and added to the double bond of alkenoic acid **12**. The intermolecular attack of the acid moiety led to the opening of bromonium ion **18**, the release of bromolactone **14** and the regeneration of **13**. Against this mechanistic proposal, the addition of Lewis acidic **17** onto the double bond of **12** leading to a seleniranium intermediate and subsequent nucleophilic bromide substitution would also descrie a feasible pathway for this catalysis. Notably, Tunge et *al.* also reported of the formation of **15** when no catalyst is added and **16** as a byproduct during the reaction in presence of the catalyst. Further, by the replacement of **13** with phenyl selenyl bromide or *N*-phenylselenopthalimide, the amount of side product **15** increased. Hence, the authors suspected no oxidative cleavage of original catalyst **13** during the reaction.



Scheme 3. Bromolactonization reaction *via* Lewis basic selenium catalysis.[49]

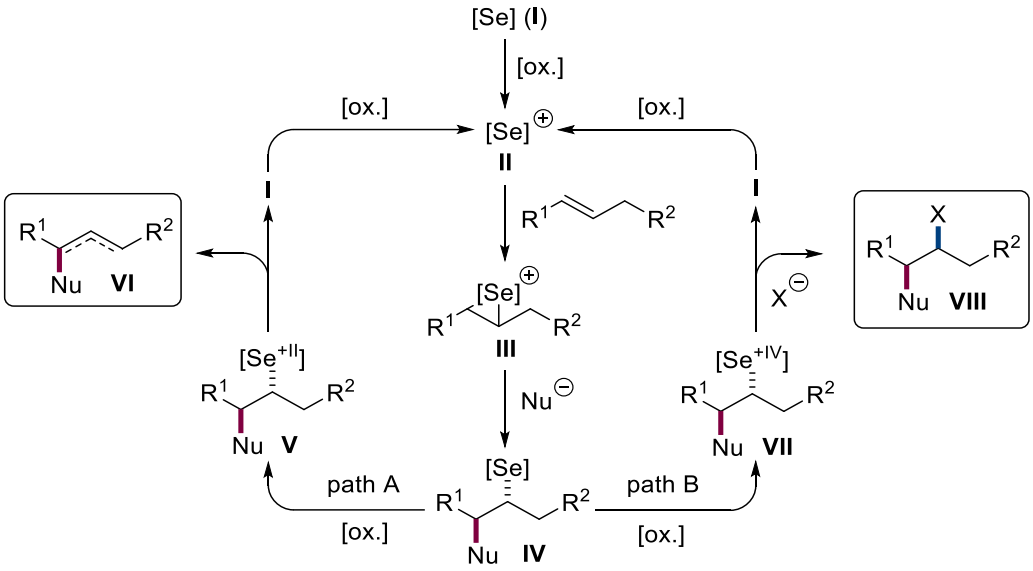
A more recent example of a Lewis basic selenium catalysis was achieved by Yeung *et al.* in 2013 (Scheme 4).[47] By the treatment of simple alkenes (**19**) with NCS and $SePh_2$ in $MeCN/H_2O$, a group of chloroamides (**20**) was obtained in very good yields of up to 89%. Mechanistically, this reaction proceeded in close analogy to the one in Scheme 3. However, here, the intramolecular nucleophilic attack from the acid moiety of **18** leading to **14** was replaced by an intermolecular attack of MeCN, which was eventually quenched by H_2O, generating **20**.



Scheme 4. Chloramination reaction *via* Lewis basic selenium catalysis.[47]

1.2.2 Lewis acidic selenium catalysis

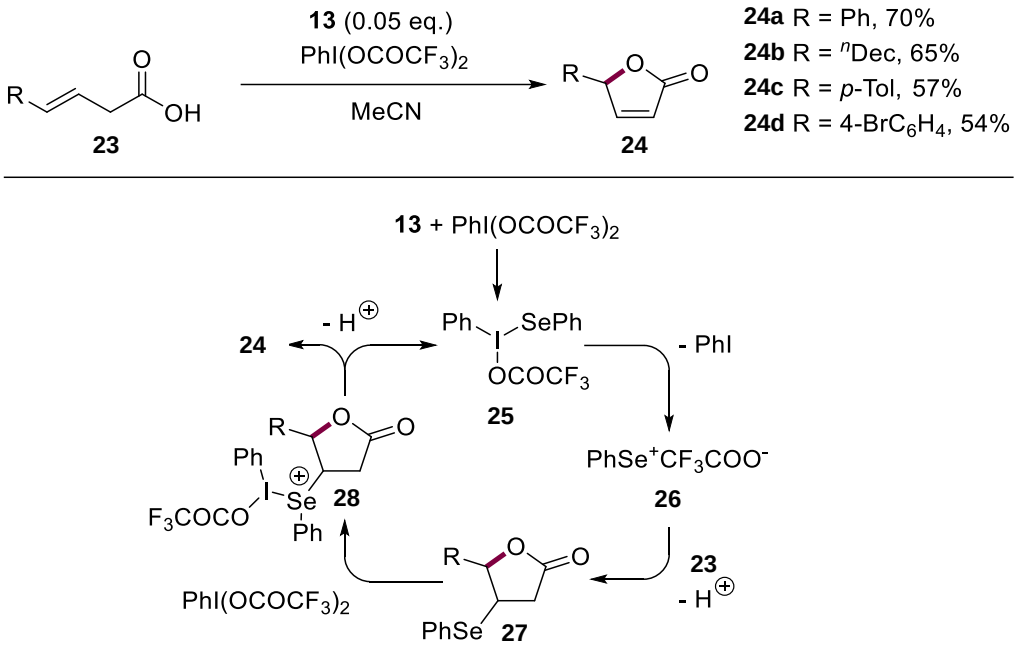
The second type of Selenium catalysis is the Lewis acidic activation mode, which evolved from electrophilic selenofunctionalizations that have already been known for decades.[50] With this type of activation two different products can be obtained (Scheme 5).[3] The mechanism starts with the oxidation of the selenium species to form **II**. For this process different oxidants are commonly used such as persulfates, hypervalent iodine reagents, *N*-fluorinated reagents, and even electrochemical as well as photochemical oxidation techniques.[41] Upon the addition of selenonium ion **II** to an alkene to form seleniranium ion **III**, the attack of a nucleophile leads to selenofunctionalized intermediate **IV**. From here, the path can split off into different routes. First, an oxidation leading to Se^{+II} species **V** can afford the allylic or vinylic functionalization product **VI** upon deselenylation and **II** is regenerated by another oxidation (Scheme 5, path A). Second, **IV** can be oxidized to the respective Se^{+IV} moiety **VII**, whereupon another substitution of the selenium moiety produces difunctionalized product **VIII**. Again, eliminated **I** is oxidized to **II** to close the catalytic cycle (Scheme 5, path B).



Scheme 5. Mechanism of Lewis acidic selenium catalysis.[3]

For this type of catalysis, many approaches were developed.[3,51] Exemplary among these are the contributions from Tiecco *et al*., which have already found attention in 2002.[52] Using a catalytic amount of a selenium catalyst and an excess of persulfate as a terminal oxidant, a small group of allylic alcohols and a *γ*-butenolide were obtained directly from simple alkenes without isolation of the intermediate selenium adducts.

The herein reported lactonization towards the *γ*-butenolide moiety was studied in more detail by Wirth *et al.* five years later, who could propose the underlying mechanism with all relevant species based on NMR measurements (Scheme 6).[53] After an activation of **13** by $PhI(OCOCF_3)_2$ hypervalent iodine reagent **25** is formed. PhI is eliminated from **25** generating electrophilic selenium species **26**. Then, **26** reacts with *β*,*γ*-unsaturated acid **23** in a cyclization reaction, which yields **27**. From here, another $PhI(OCOCF_3)_2$ initiates the elimination of the selenium moiety *via* **28**, which leads to the formation of lactone **24** and regeneration of **25**.



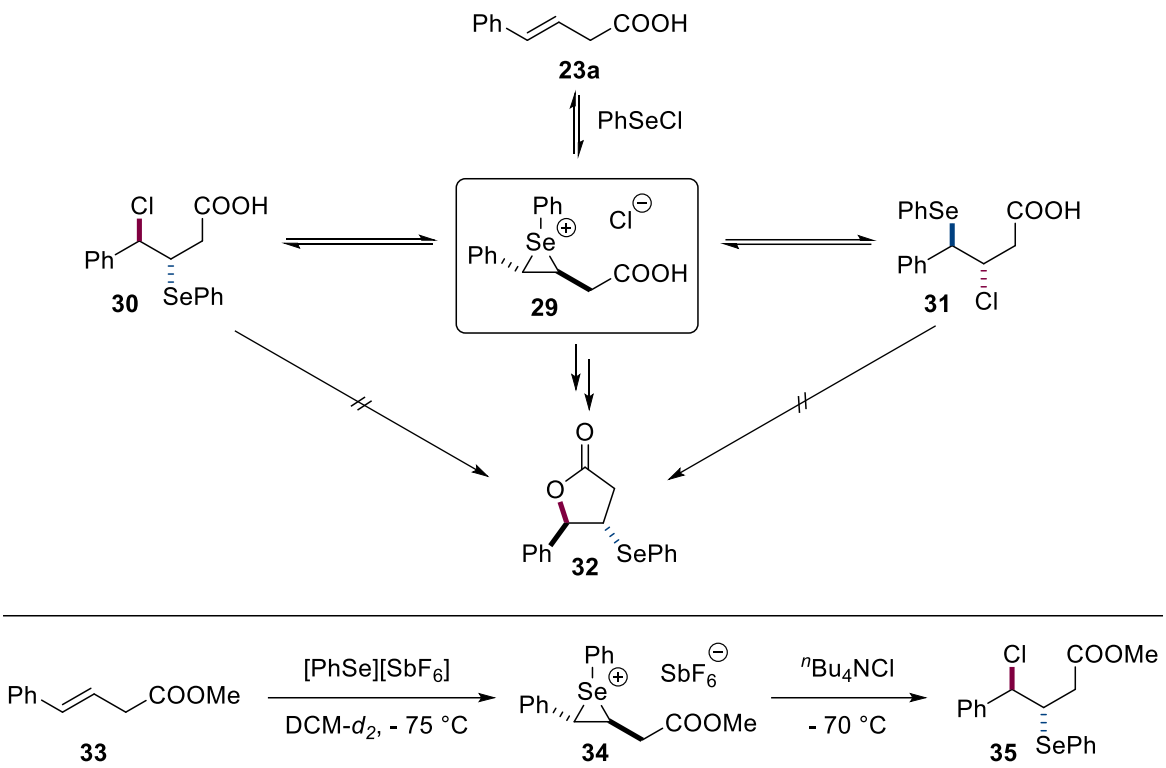
Scheme 6. Selected scope and mechanism of the lactonization *via* Lewis acidic selenium catalysis.[53]

Notably, this cyclization was also tried in an enantioselective fashion with self-developed chiral diselenides from the Wirth group, but only minor success was achieved (up to 22% *ee* for **24b**). When conducting the reaction at -100 °C and with stoichiometric amounts of the chiral catalyst, **24a** could indeed be obtained in 72% *ee*. Nevertheless, the selectivity was found to be very temperature dependent, since the *ee* value of the same reaction at room temperature dropped again to 26%. With these early results Wirth *et al.* could already show that indeed stereoselective selenium-catalyzed lactonizations are possible, but at the same time indicated that there is still much room for improvements.

1.2.3 Mechanistic investigations

In all Lewis acidic selenium catalysis protocols, the seleniranium ion is the deciding reactive intermediate which determines the regio- and stereochemical outcome of the reaction.[54] Although the presence of seleniranium salts could be supported by the isolation and characterization of seleniranium salts in 1974[55] and knowledge that ring opening of a seleniranium ion typically proceeds in an *anti*-fashion,[56] it was not until 2006, when Denmark *et al.* could confirm its presence within their study on selenolactonization reactions (Scheme 7, above).[57] Herein, they found out that at −70 °C the treatment of **23a** with PhSeCl led to chlorinated Markovnikov adduct **30**. Heating up the reaction to −20 °C, the cyclization towards lactone **32** occurred, while also the reversal to starting material **23a** and the formation of small amounts of *anti*-Markovnikov adduct **31** were detected. From this, the authors derived that (1) the attack of an endogenous nucleophile can indeed outcompete the internal cyclization, (2) the formation of **30** is reversible and (3) **30** and **31** most probably stand in an equilibrium *via* **29**, because neither the cyclization of **30**, nor the one of **31** would afford **32**. Instead, in the case of **30**, the cyclization would lead to a diastereomer of **32**, while in the case of **31** another constitutional isomer would emerge. As was shown within the experiments, the formation of the seleniranium ion is reversible and therefore exemplifies a case of dynamic covalent bonding.[58] This unique reaction profile of selenonium ions towards π-bonds has contributed to their reference to as selenium-π-acid catalysts.[3]

To investigate whether the attack by the endogenous nucleophile is preferred to the attack by the exogenous nucleophile, a control experiment was executed (Scheme 7, below). Therefore, the acid moiety of **23a** was protected as an ester (**33**) to prohibit the internal cyclization and examine the behavior of endogenous nucleophiles. The treatment of ester **33** with [PhSe][SbF_6] as a selenating agent led to the formation of seleniranium ion **34**, which could be characterized *via* NMR spectroscopy and could be converted to chlorinated **35** by the addition of $^{n}Bu_4NCl$. From this study, it could be concluded that the choice of the oxidant in these reactions needs to be considered carefully, since a competition between exogenous and endogenous nucleophile can occur.



Scheme 7. Mechanistic process of the selenolactonization (above), control experiment with **33** showing that the exogenous nucleophile can outcompete the endogenous nucleophile (below).[57]

To further gain knowledge about this specific interaction, in 2014, Denmark *et al.* were able to characterize the properties of seleniranium ions (Figure 2).[59] From calculations on carbosulfenylation reactions, they discovered that the activation towards the olefin stems very likely from two decisive electronic interactions with the selenonium moiety. First, the interaction of the olefinic π-orbital with the σ*-orbital of the chalcogen, and second, an interaction between one of the lone pair of electrons on the chalcogen with the π* of the olefin can serve for the initial coordination of these moieties. Notably, this mechanism of bonding is reminiscent of the Dewar-Chatt-Duncanson model,[60] which explains the association of a transition metal to an olefin.[59] Here, a donation of the olefinic π-orbital to the d*-orbital of the metal and a back-donation from a filled d-orbital to the π*-orbital of the olefin lead to the activation or ligation of the olefin.

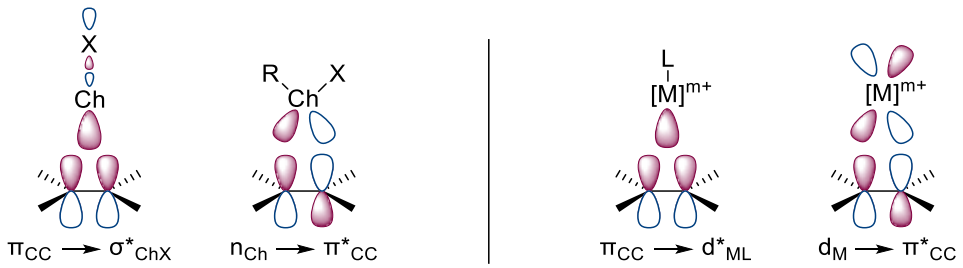
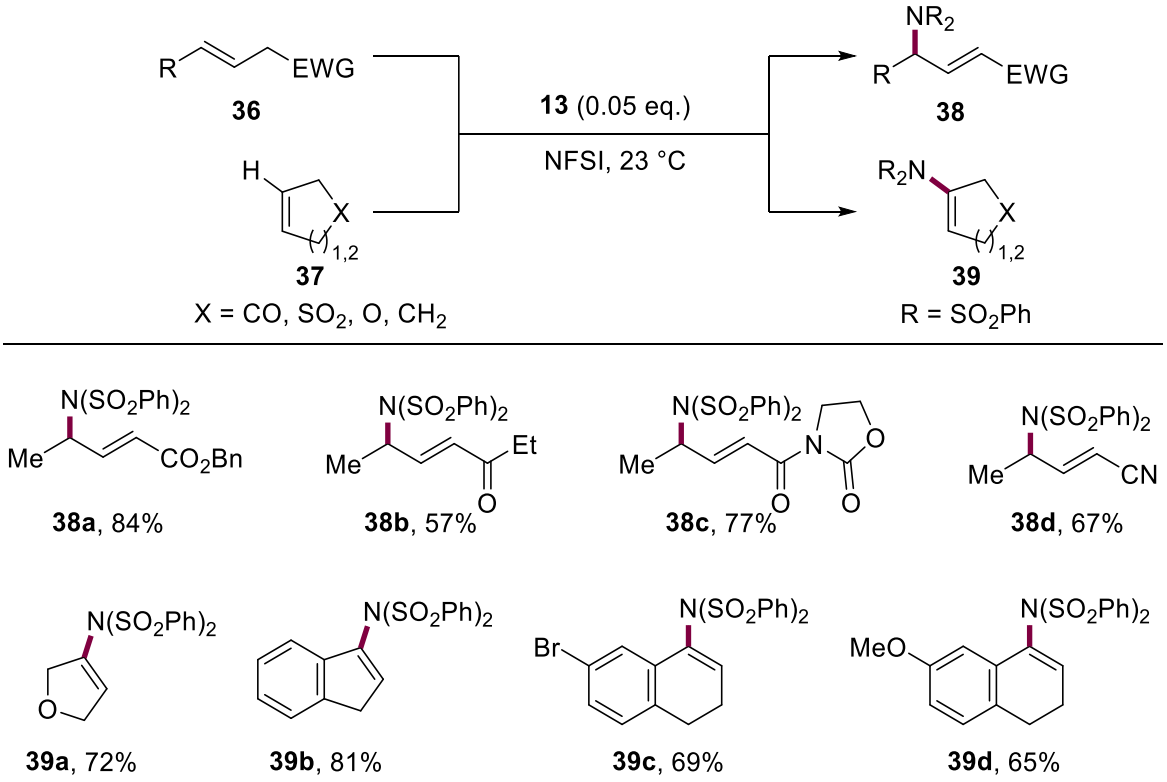


Figure 2. Comparison of olefin activation: selenium-π-acid catalysis (left), Dewar-Chatt-Duncanson (right).[59]

1.3 Selenium-catalyzed amination reactions

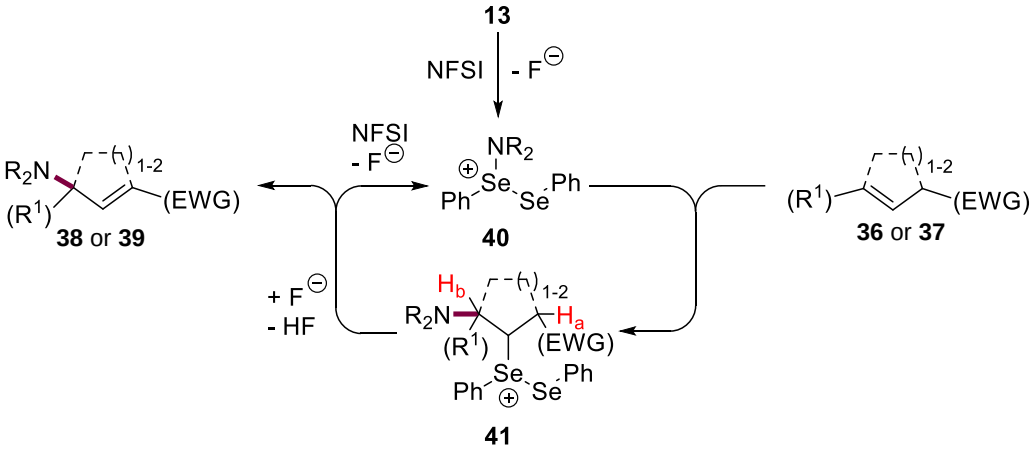
The direct amination of olefins represents a useful method for the formation of C-N bonds in organic compounds. As mentioned in section 1.1, these kinds of reactions can take place *via* TM catalyzed processes[28,30,31], hypervalent iodine[61] or selenium-catalyzed protocols.[3] The latter were first reported in 2013 by Breder *et al.* by the direct amination of non-activated alkenes with NFSI in good to excellent yields (Scheme 8).[62] Notably, this protocol showed a pronounced regioselectivity towards the incorporation of the double bond within the carbon framework. With acyclic substrates, conjugated allylamines (**38a-d**) were formed predominantly, while in the case of cyclic ones, vinylamines (**39a-d**) were obtained as the main products in moderate to good yields of up to 84%.



Scheme 8. Selected scope of the selenium-catalyzed intermolecular amination on internal alkenes **36** and **37**. EWG: electron withdrawing group.[62]

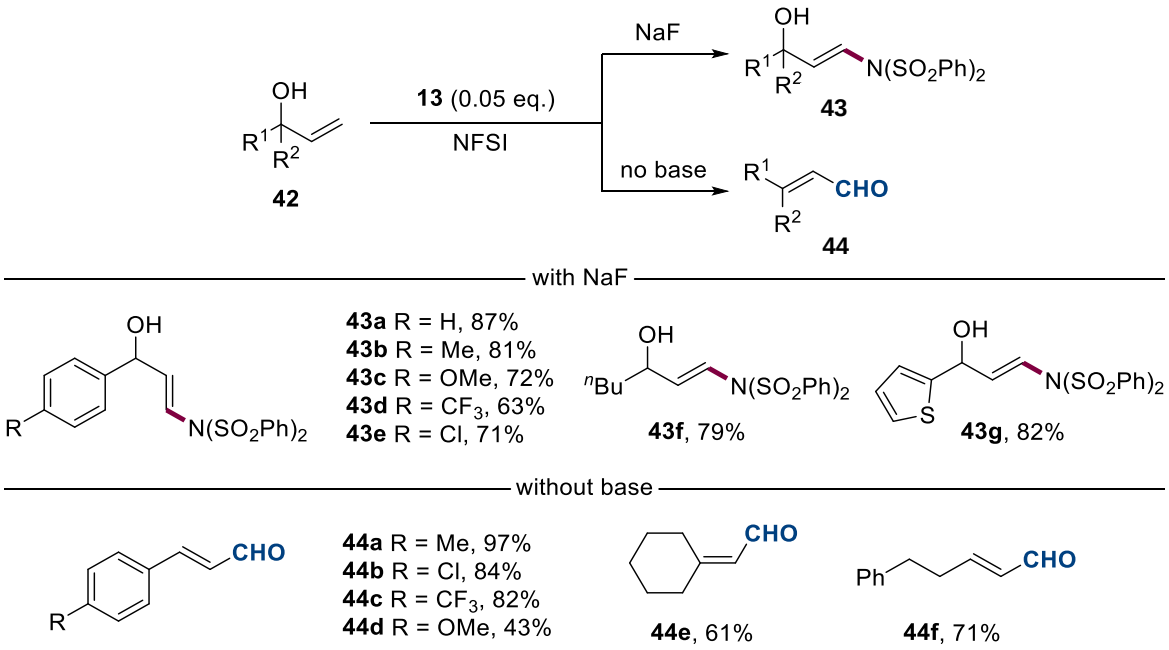
From control experiments it was found that electrophilic PhSeBr cannot catalyze the reaction under the reported conditions, but that the interplay between NFSI and $(SePh)_2$ (**13**) is crucial for the reaction development. Based on these findings the authors postulate the following mechanism (Scheme 9). **13** performs a nucleophilic attack on NFSI to eliminate fluoride and form intermediate **40**. Then, alkene **36** or **37** adds to **40** and generates cationic adduct **41**, which subsequently undergoes an

elimination (H_a or H_b) to yield **38** or **39**. In cyclic systems, where the allylic EWG was absent, the elimination from intermediate **41** most likely occurs at H_b rather than on H_a to form a conjugated system with the sulfonamide. Hence, this could explain the formation of vinylic products when starting from cyclic olefins.

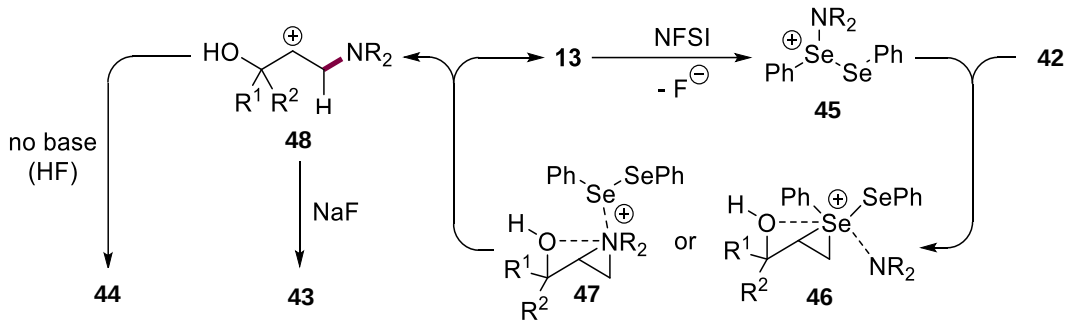


Scheme 9. Mechanism of the selenium-catalyzed intermolecular allylic amination.[62]

The scope of this protocol was expanded by Zhao *et al.* in 2015, who managed to perform the amination on terminal allylic alcohols (**42**) in the presence of a base (Scheme 10).[63] Thereby, it was noticed that in the absence of a base, *α*,*β*-unsaturated carbonyl moieties **44** were generated. With NaF, vinylic amines (**43**) were formed exclusively. This regioselectivity was assumed to be induced by the allylic hydroxy group. Hence, control experiments with protected alcohols were performed, which showed that protected alcohol moieties indeed lead to the same regioisomer, but in lowered yields. From this, the authors concluded that an interaction between a lone pair of the oxygen and the intermediately formed cation of **46** or **47** could be the cause for the formation of the vinylic amines, as shown in the proposed mechanism (Scheme 11). The decreasement in yield in case of the protected alcohols most probably occurred due to the worsened electron donation of the oxygen in comparison to the free alcohol. Regarding the mechanism, the reaction presumably starts also with the oxidation **13** by NFSI leading to intermediate **45** (Scheme 11). Electrophilic addition of **45** to the substrate **42** leads to the formation of either **46** or **47**, the regioselectivity of which is controlled by the alcohol. Upon elimination of the catalyst, **48** is generated, which in the presence of a base yields vinylamines **43a-g**, but in the absence undergoes another elimination step triggered by HF towards *α*,*β*-unsaturated carbonyls **44a-f**.

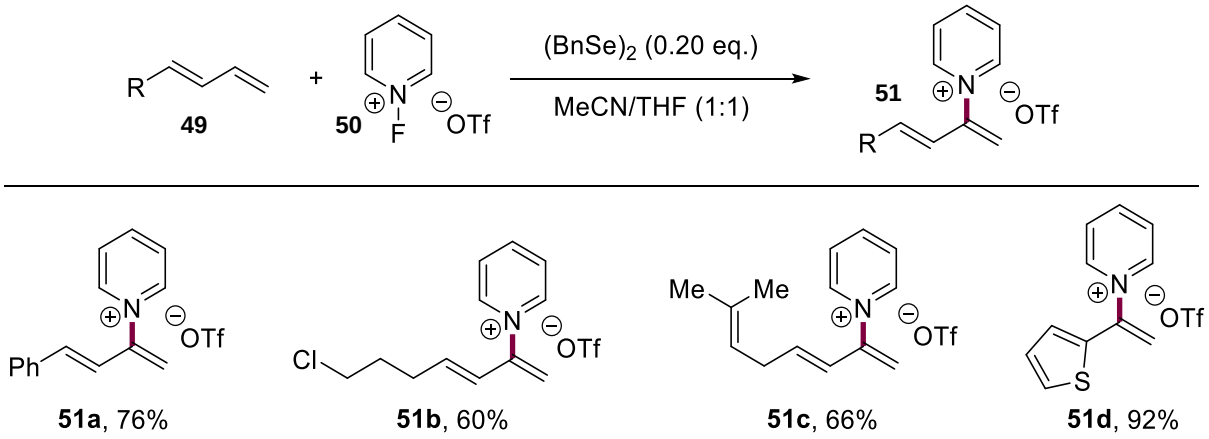


Scheme 10. Selected scope of the selenium-catalyzed intermolecular amination of terminal allylic alcohols **42**.[63]



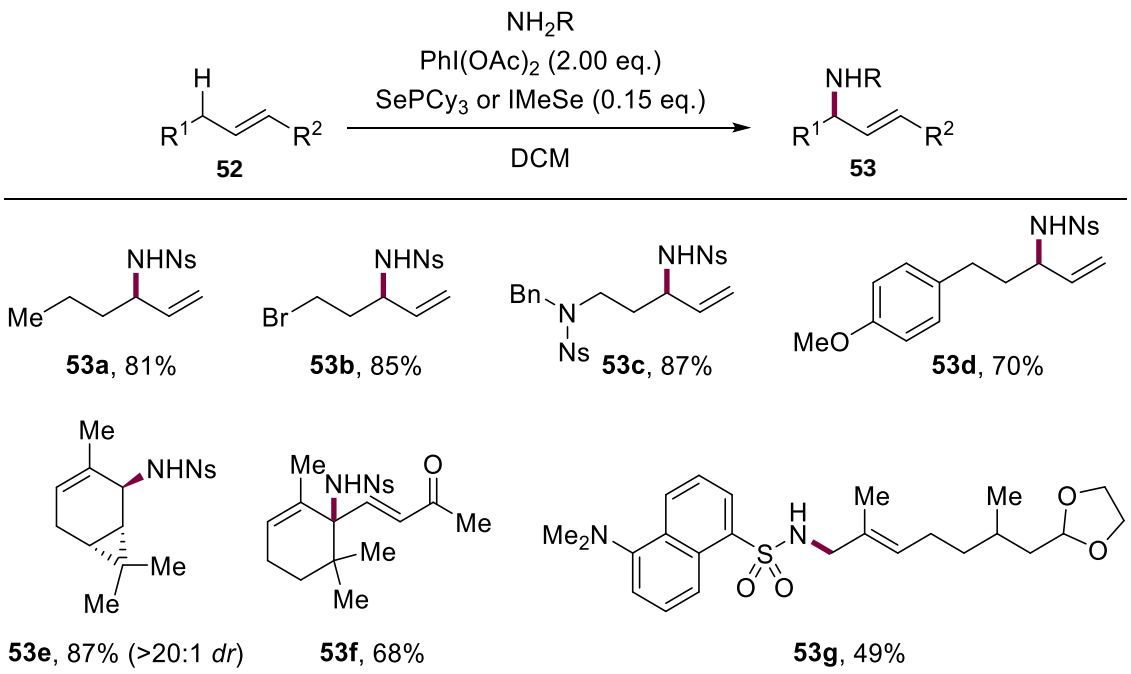
Scheme 11. Mechanism of the selenium-catalyzed intermolecular amination of terminal allylic alcohols **42**.[63]

Two years later, the same group developed an amination of 1,3-dienes (**49**) using *N*-fluoropyridinium triflate (**50**), which serves as the amine source as well as the oxidant, in the presence of $(BnSe)_2$ as the catalyst (Scheme 12).[64] In contrast to former Heck-type reactions that exclusively led to the functionalization at the C-1 position of 1,3-dienes, this protocol enables the functionalization at C-2. Given the synthetic importance of 1,3-dienes, this protocol diversified the scope of this particular class of compounds.[64] Notably, the reaction conditions demanded a high catalyst loading of 0.20 eq., which was needed because of partial oxidative degradation of the catalyst. The high regioselectivity towards the terminal olefinic moiety of 1,3-dienes **49** and the Markovnikov selectivity of this reaction lead to the formation of an array of 2-pyridinium-1,3 butadienes (**51a-d**).



Scheme 12. Selected scope of the selenium-catalyzed intermolecular amination of dienes **49**.[64]

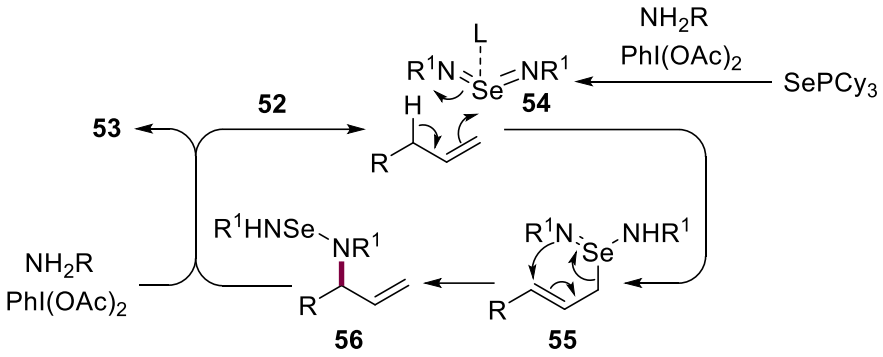
In 2020 an advanced protocol for intermolecular amination was developed by Michael *et al.*, in which a large group of olefins containing mono-, di- and even trisubstituted double bonds could be reacted using $SePCy_3$ as a catalyst for terminal and IMeSe for internal alkenes (Scheme 13).[65] Regarding this high tolerance towards the substitutional pattern of the alkene, this method represented an advance over previous ones.[62–64] In addition to a huge range of products (**53a-g**), which carried various functional groups or were derivatives from naturally occurring compounds, the group also explored the underlying reaction mechanism (Scheme 14).



Scheme 13. Selected scope of the selenium catalyzed intermolecular amination of mono-, di- and trisubstituted olefins **52**.[65]

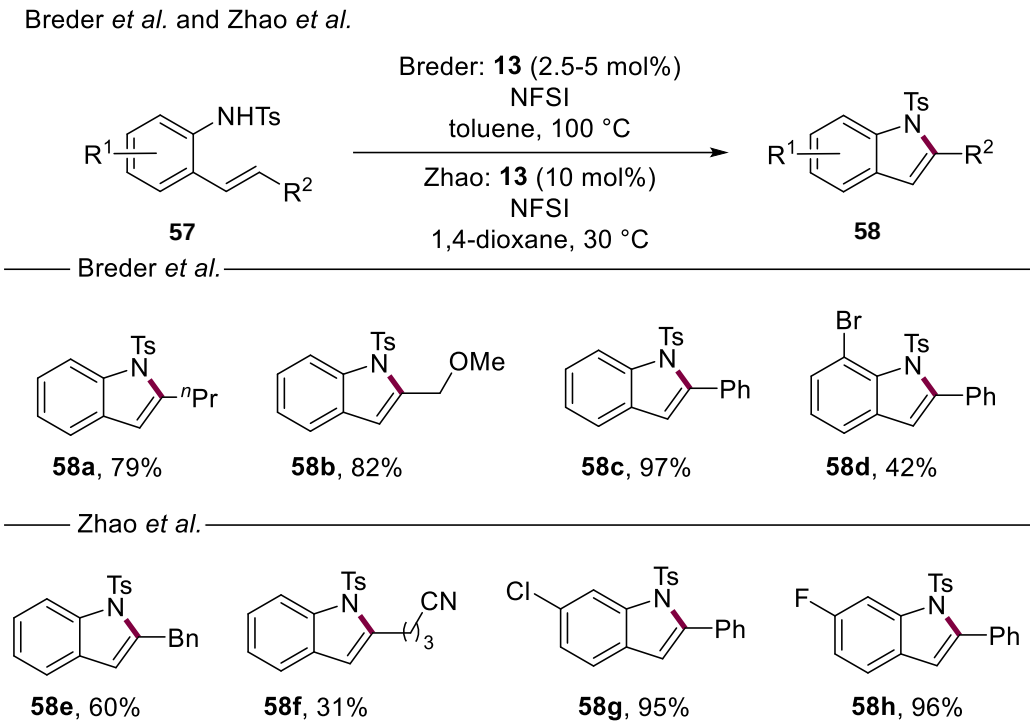
From ^{77}Se, ^{31}P NMR experiments and DFT calculations, which gave indications about the catalytic active species and stable intermediates, they concluded that phosphine

selenide $SePCy_3$ is first oxidized by $PhI(OAc)_2$ and the sulfonamide to selenium(bisimide) **54** (Scheme 14). Then, an ene Reaction leads to intermediate **55**, which undergoes a [2,3]-sigmatropic shift to yield **56**. Eventually, the active catalyst is regenerated and allylamine **53** is released upon another oxidation.



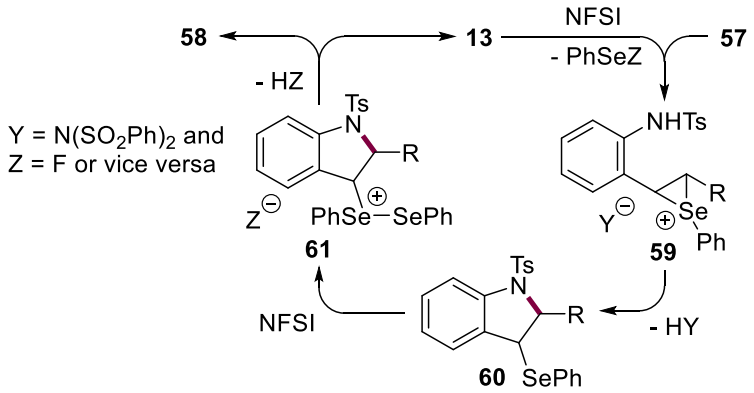
Scheme 14. Proposed mechanism for the selenium-catalyzed intermolecular amination of mono-, di- and trisubstituted olefins **52**.[65]

The first intermolecular amination *via* selenium-π-acid catalysis was reported by Breder *et al.*[51] and shortly thereafter by Zhao *et al.*,[66] where in both cases 2-vinyl substituted phenyl tosylamides **57** were converted to indoles **58a-h**. While in the case of Breder *et al.* the reactions were conducted in toluene at 100 °C, Zhao *et al.* were able to decrease the temperature to 30 °C in 1,4 dioxane, however with a higher catalyst loading (Scheme 15). Both procedures yielded a broad range of alkylated and arylated indoles with a remarkable functional group tolerance.



Scheme 15. Selected scope of the selenium-catalyzed intramolecular amination towards indoles **58**.[51,66]

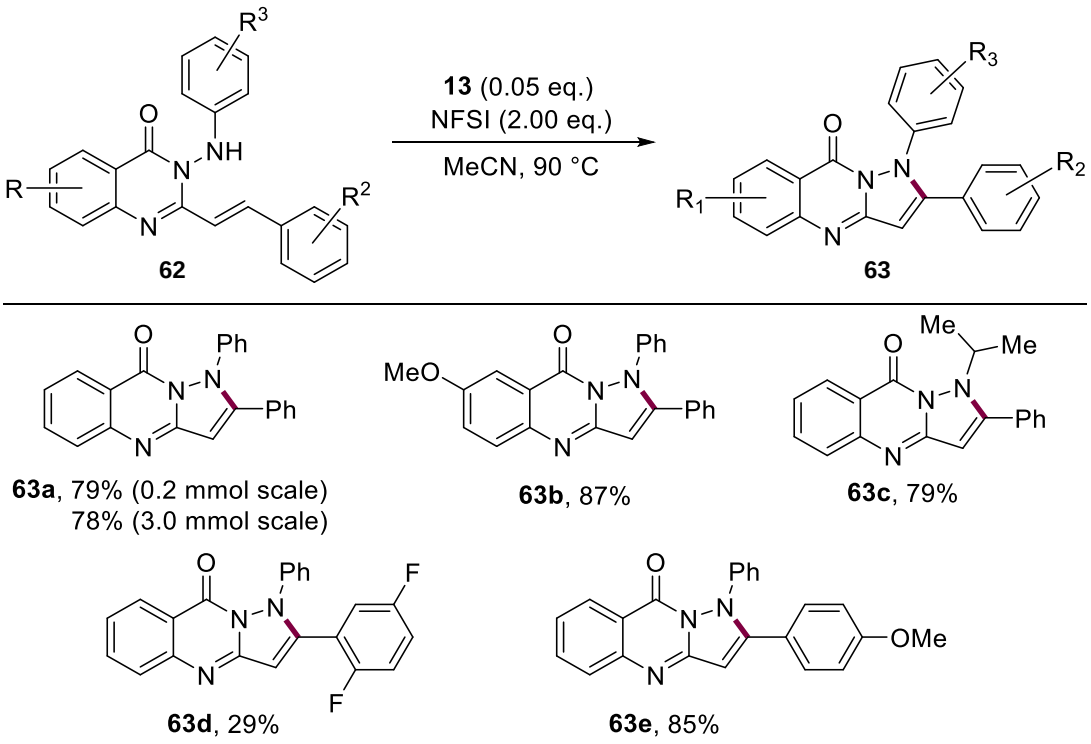
By conducting several control experiments, which showed that oxidative fragmentation and recombination of the the Se-Se bond during the reaction can occur, Breder *et al.* postulated the following mechanism (Scheme 16). $(SePh)_2$ (**13**) is oxidized by NFSI and adds to the double bond of substrate **57** leading to seleniranium ion **59**. From here, nucleophilic attack of the amine generates selenated intermediate **60**. A second oxidation by NFSI leads to salt **61**, which after deprotonation yields the desired indole **58**.



Scheme 16. Mechanism of the selenium-catalyzed intramolecular amination towards indoles **58**.[51]

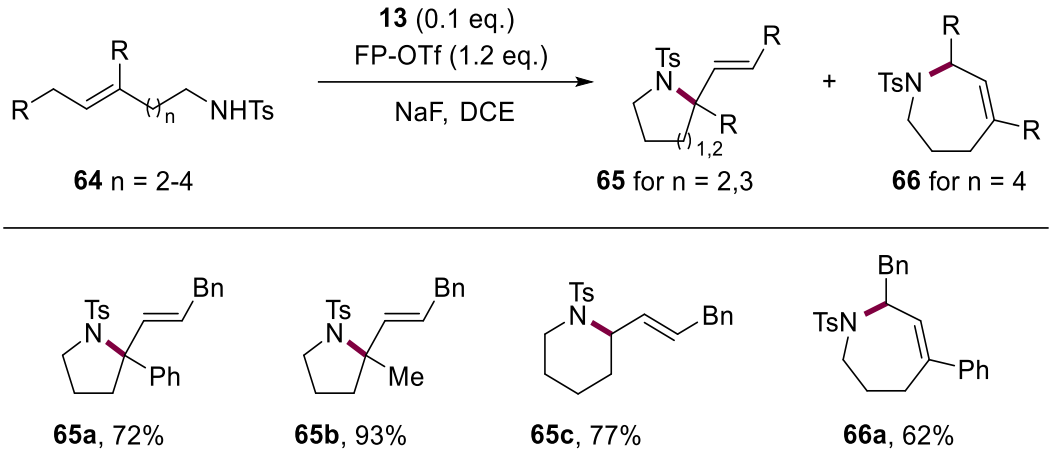
As a complementary work, Chen *et al.* applied a similar protocol for the synthesis of 1,2-diarylpyrazolo[5,1-*b*]quinazolin-9(1*H*)-ones (**63a-e**), which further emphasizes the wide application range of this catalytic regime (Scheme 17).[67] They also showed that

this reaction could be scaled up to 3 mmol with only marginal loss in yield (Scheme 17, **63a**).



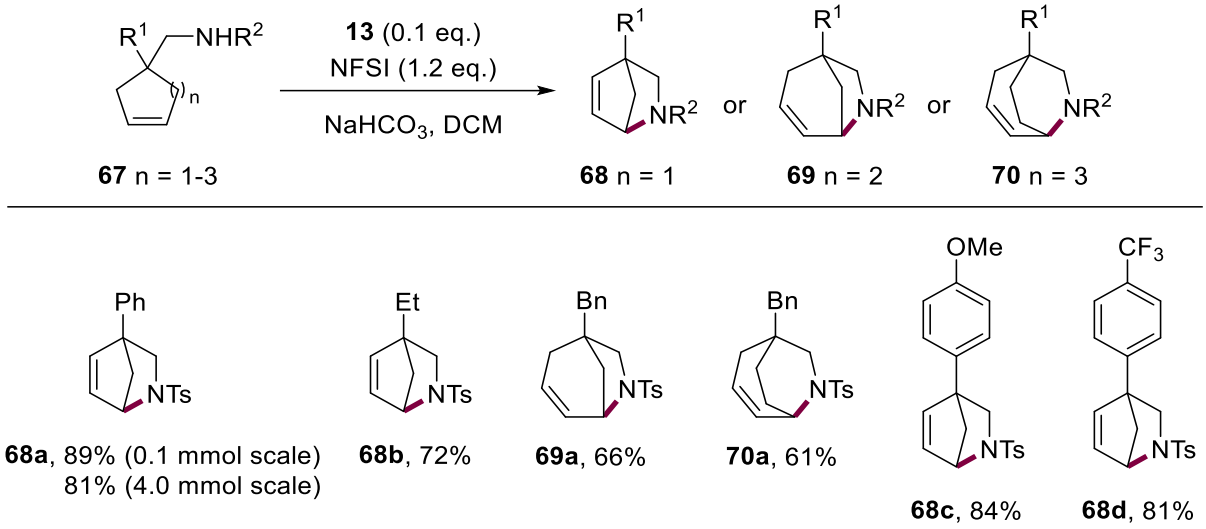
Scheme 17. Selected scope of the selenium-catalyzed intramolecular amination towards 1,2-diarylpyrazolo[5,1-*b*]quinazolin-9(1*H*)-ones **63**.[67]

In 2016, Zhao *et al.* discovered an impressive intramolecular cycloamination of unbiased alkenes *via* selenium catalysis (Scheme 18).[68] Using **13** and *N*-fluoropyridinium trifluoromethanesulfonate (FP-OTf) as the oxidant, they were able to convert substrates **64** to 2-vinyl substituted pyrrolidines and piperidines (**65**) depending on the double bond position within the substrate. Remarkably, even tetrahydroazepine moieties **66** could be obtained when the amount of NaF was halved, which was rationalized by a protic isomerization of **65**. By the aid of NMR experiments the authors were able to assign PhSeX (X = F, OTf) as the catalytically active species to generate a selenated intermediate. Furthermore, FP-OTf was identified as the crucial oxidizing agent that converts the selenated intermediate to the respective product. Based on these findings, the mechanism was proposed to proceed in close analogy to the one reported by Breder *et al.* (Scheme 16).[51] By this method, Zhao *et al.* were able to broaden the scope of selenium-catalyzed reactions with a regioselective synthesis of *N*-heterocycles (Scheme 18, **65a-c**, **66a**).



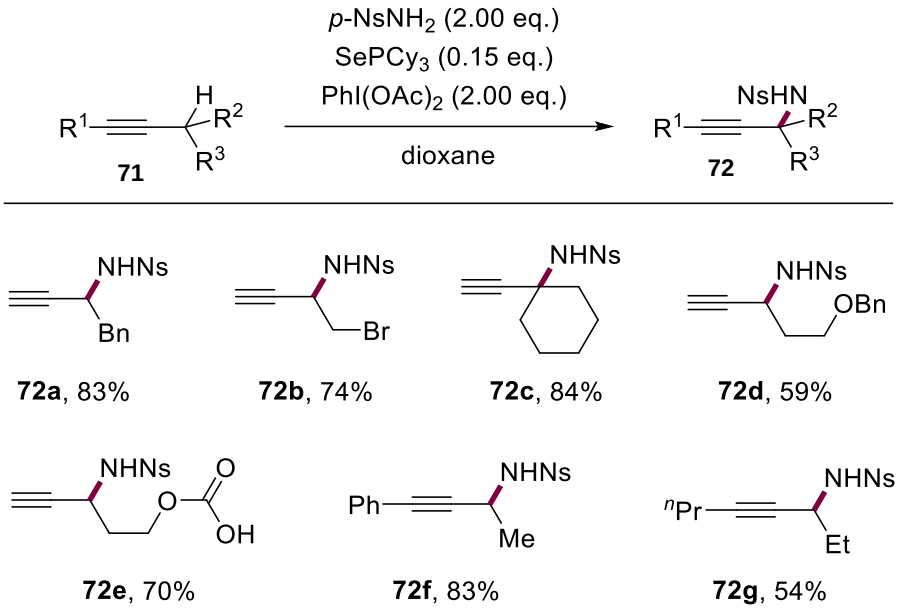
Scheme 18. Selected scope of the selenium-catalyzed intramolecular amination of unbiased alkenes **64**.[68]

Considering the fact, that *N*-bridged heterocycles count to frequently encountered motifs within natural products but are considerably hard to synthesize because of their ring strain,[69] Yao *et al.* developed a selenium-catalyzed process for the assembly of bicyclic structures **68a-d**, **69a** and **70a** (Scheme 19).[69] By the treatment of **67** with diselane **13**, NFSI as the oxidant and $NaHCO_3$, an array of 4-substituted 2-azabicyclo[2.2.1]heptenes **68**, which are generally unobtainable from *aza*-Diels-Alder reactions,[69] were obtained from **67** (n = 1). The higher anaolgues, azabicyclo[3.2.1]oct-3-enes **69** and azabicyclo[3.2.2]non-3-enes **70**, could thereby be constructed from cyclohex-3-en-1-ylmethanamine derivatives **67** (n = 2) and cyclohept-3-en-1-ylmethanamine derivatives **67** (n = 3), respectively. The practicability of this protocol could be confirmed by the scale-up reaction of **67a** (n = 1), in which only 5 mol% of **13** instead of 10 mol% could be used to generate **68a** in similar amounts as in the smaller approach (Scheme 19).



Scheme 19. Selected scope of the selenium-catalyzed intramolecular amination towards *N*-bridged bicycles.[69]

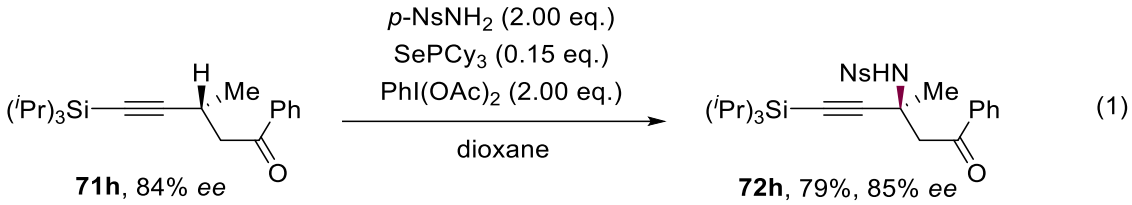
Selenium catalysis was recently also used for the construction of C-N bonds in unfunctionalized alkynes. In this context, Michael *et al.* could use the same catalytic protocol as shown in Scheme 14 for the propargylic amination of alkynes to give propargylic amines **72a-e** (Scheme 20).[70] Among the broad scope of products, even carboxylic acids were well tolerated showing the robustness of this protocol towards Brønstedt acids (Scheme 20, **72e**).



Scheme 20. Selected scope of the selenium-catalyzed propargylic amination of alkynes **71**.[70]

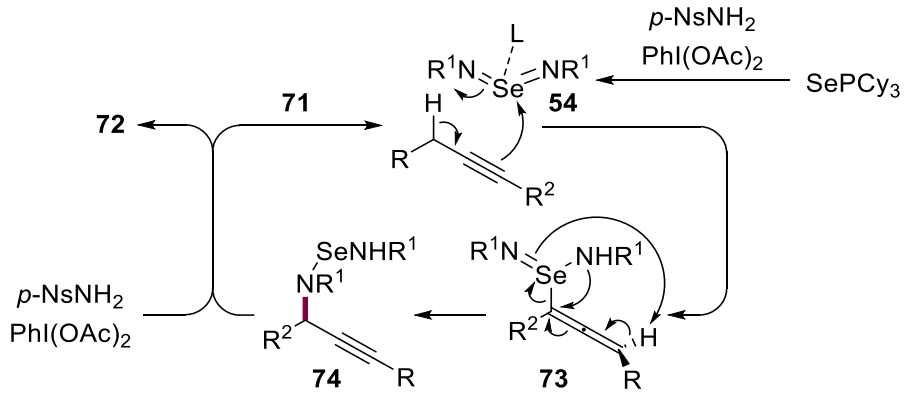
In analogy to the catalytic cycle shown in Scheme 14, it was assumed that this reaction also proceeds *via* an ene Reaction and a [2,3]-sigmatropic rearrangement. Since both events run suprafacially,[65,70] the stereocenter of enantioenriched substrate **71h**

(Figure 3, 84% *ee*) was expected to be preserved, and indeed, the product of this reaction (**72h**) showed complete retention of the stereocenter with 85% *ee* (Equation 1).



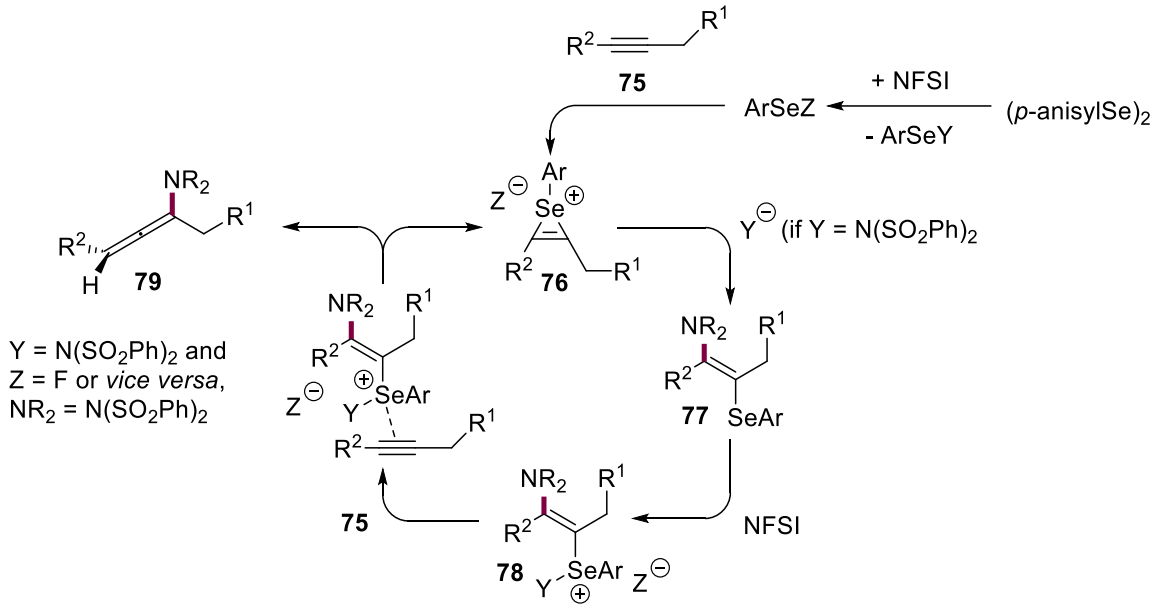
(1)

This result, together with kinetic isotope effect measurements of the propargylic hydrogen and DFT calculations, lead to the following prediction of the mechanism (Scheme 21). After initial oxidation of the phosphine selenide catalyst $SePCy_3$ to bis(imide) **54**, an ene Reaction produces allenylselenium **73**. After [2,3]-sigmatropic rearrangement and oxidative cleavage of the catalyst, propargylic amine **72** is released. Notably, for substrates like **71c** carrying two carbon residues in propargylic position, a different mechanism must proceed, since the generation of allenoic intermediate **73** would not be feasible.



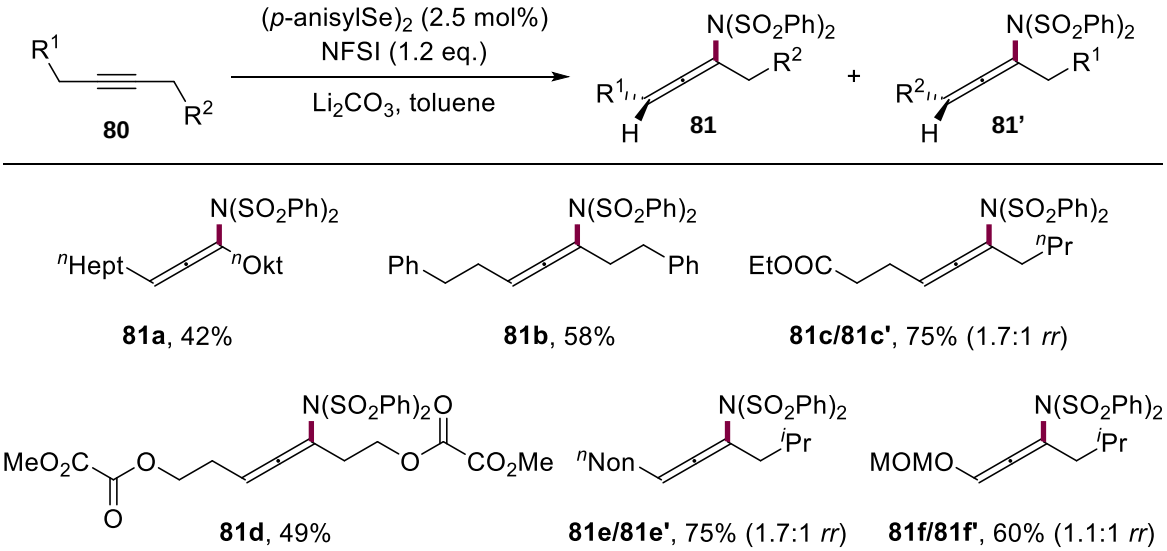
Scheme 21. Mechanism of the selenium-catalyzed propargylic amination of alkynes **71**.[70]

Another activation of alkynes was observed by Breder *et al.*, when treating alkynes **75** with (*p*-anisylSe)$_2$, and NFSI.[71] Studies on this reaction revealed that the reaction proceeds *via* monoselenated intermediate **77** and that the presence of the alkyne substrate **75**, which presumably acts as a Lewis base, is needed to perform the oxidative elimination step from **78** (Scheme 22).



Scheme 22. Mechanism of the selenium-catalyzed aminoallenylation.[71]

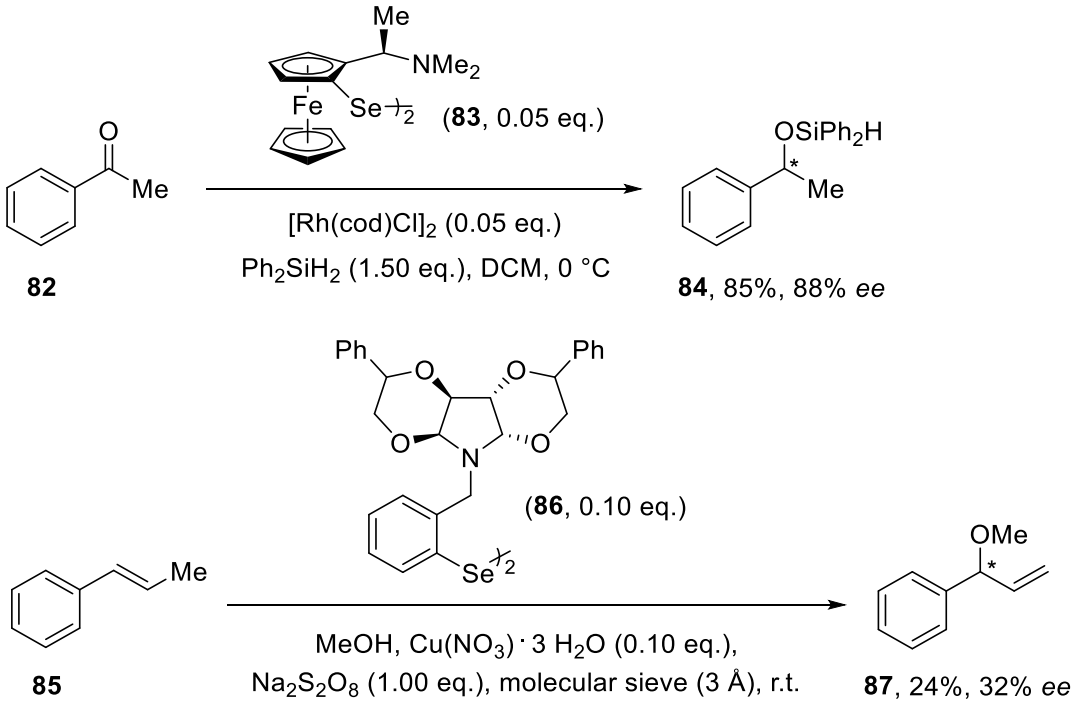
The protocol could be used for the assembly of differently equipped aminoallenes (Scheme 23), a class of compounds, which is interesting in the field of asymmetric synthesis because of the given axial chirality of allenes.[72] While unsymmetrical alkynes lead to an isomeric mixture of the respective amino allene (Schemes 23, **81c/c'**, **81e/e'** and **81f/f'**), only one isomer could be obtained with symmetric alkynes (Scheme 23, **81a**, **81b** and **81d**). Recently, an enantioselective variant of this allenylation was explored by Peixoto *et al.*, however, here, stoichiometric amounts of the chiral selenium moiety were required.[73]



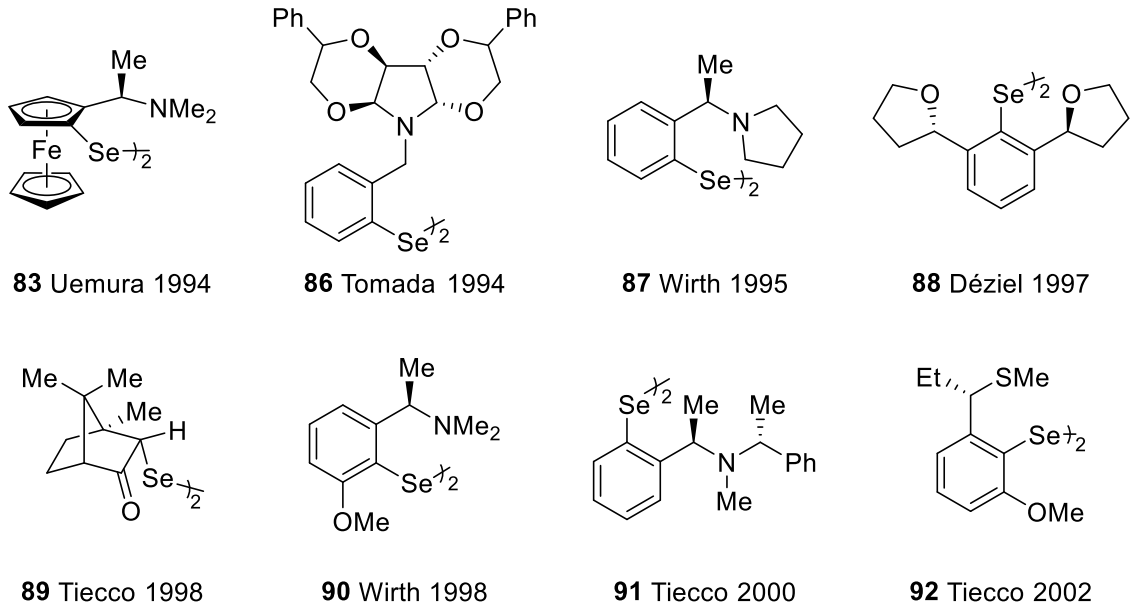
Scheme 23. Selected scope of the selenium-catalyzed aminoallenylation.[71]

1.4 Recent developments in stereoselective selenium-π-acid catalysis

As seen from the previous section, selenium catalysis has been successfully employed in the racemic functionalization of C-C multiple bonds. Chiral selenium catalysis, on the contrary, is a rather underdeveloped area, despite the research on stereoselective selenofunctionalizations is rather exploited and the first potent catalysts were already reported in 1994.[74,75] Back then, using chiral diselenide **83** as a ligand for the Rh^{+I} catalyst, Uemura *et al.* could reduce acetophenone (**82**) to the respective silylether **84** with 88% *ee* (Scheme 24, top).[74] In the same year Tomada *et al.* found that the stereoselective selenofunctionalization of *β*-methyl styrene (**85**) and the subsequent elimination of the selenium moiety can proceed with a catalytic turnover using catalyst **86** (Scheme 24, bottom).[75] Thereafter, various other groups joined into this research area and yielded a range of differently constructed chiral selenium catalysts (Figure 3).[43,74,75]



Scheme 24. First reported asymmetric selenium-catalyzed reactions.[74,75]

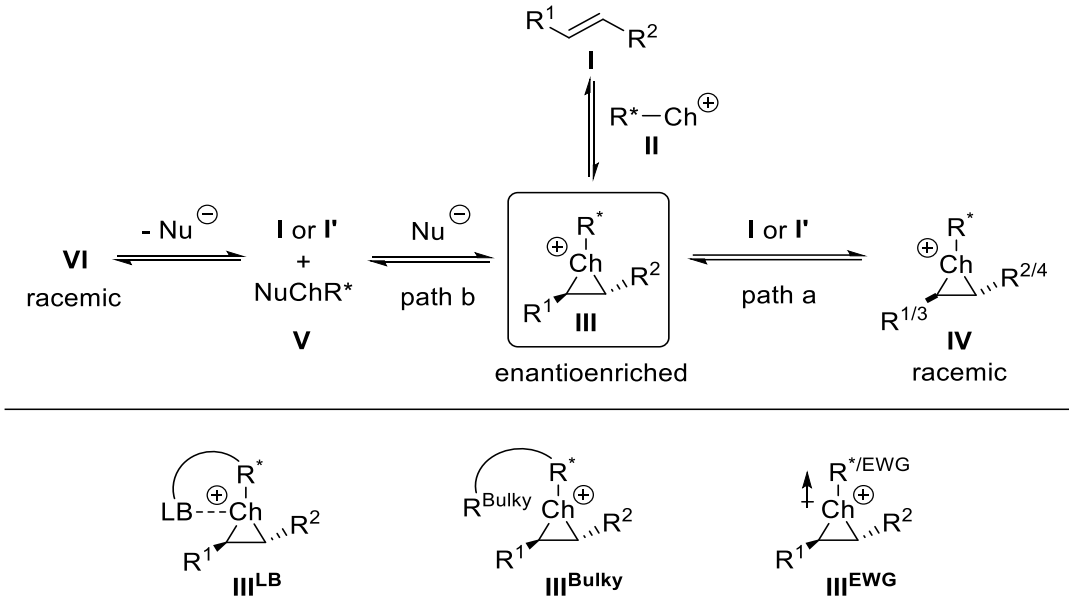


83 Uemura 1994 **86** Tomada 1994 **87** Wirth 1995 **88** Déziel 1997

89 Tiecco 1998 **90** Wirth 1998 **91** Tiecco 2000 **92** Tiecco 2002

Figure 3. Early examples of chiral selenium catalysts.[43,74,75]

Besides these early approaches, Denmark *et al.*[76] and Wirth *et al.*[77] have made major contributions in this area by the investigation of how chalcogenium ions obtained after the oxidation of selenides add onto double bonds (Scheme 25, above). Herein, both groups could show within NMR studies that the addition of a chalcogenium ion **II** to alkene **I** is reversible, and that the readdition to another or the same alkene (**I'** with R^3/R^4 or **I** with R^1/R^2) leads to racemization of chalcogeniranium ion **III** (path a). Also, an addition-elimination process of nucleophile to **III** can have the same effect (path B). In these ways, the native stereoinformation of **III** can be lost. Radom *et al.* and Borodkin *et al.* could support these experimental findings by computational studies.[78] To overcome this racemization process, three possible solutions regarding the catalyst design could be made (Scheme 25 below). First, an internal Lewis basic side moiety on R* could stabilize chalcogeniranium ion **III** and support its configurational stability. Second, a sterical demanding group on R*, which in proximity to the catalytically active center, could potentially prevent the nucleophilic attack from the hindered side. Third, an electron withdrawing effect of R* could lead to the destabilization of **III** and therefor accelerate a nucleophilic attack.[43,79]

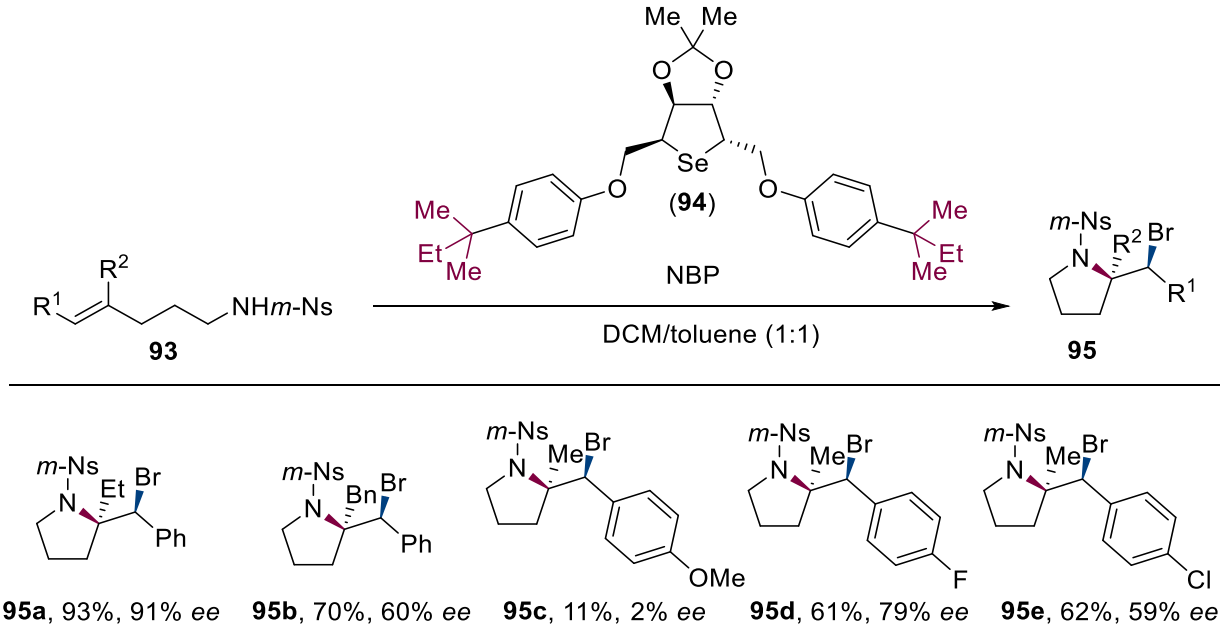


Scheme 25. Above: loss of stereoinformation of **III** by olefin exchange (path a) and nucleophilic addition-elimination (path b), below: possibilities for catalyst design to overcome racemization processes.[43,76,77,79]

In 1998, Wirth *et al.* could meet two of these criteria by the design of catalyst **90** (Figure 3).[80] On the one hand, it contains two Lewis basic side moieties for a possible stabilization of the seleniranium ion, and on the other hand contains a sterically demanding methyl group and thereby could reach 75% *ee* in methoxylation reactions on using styrenes as substrates. Another convenient example that correlates with the desired structure of a chiral selenium catalyst was reported by Tiecco *et al.* in the same year (Figure 3, **89**).[81] Herein, a Lewis basic carbonyl group and a sterically shielding (1*R*)-(+)-camphor unit connected to a diselenide enabled an asymmetric selenomethoxylation of an array of styrylic, as well as unconjugated cyclic and acyclic alkenes. Remarkably, these structural criterions are still to be found in modern chiral selenium catalysts.

As a sustainable approach towards catalyst design, Yeung *et al*. developed C_2-symmetric selenium catalyst **94**, which can be assembled from readily available mannitol (Scheme 26).[82] This catalyst was capable of constructing two stereocenters simultaneously within bromocycloamination reactions on alkenoic sulfonamides **93**. Notably, *o*-Ns (Ns = nosyl) and *p*-Ns bearing substrates **93** were shown to decrease the enantioselectivity of the reaction in comparison to *m*-Ns substituted ones, which indicates a spatial interaction of the substrate with the catalyst at this position. With the optimized catalyst bearing two sterically demanding ^{t}Pentyl (marked in red) moieties on the 4-position of the arenes and *N*-bromophthalimide as the optimized bromide

source, 2-bromomethylpyrrolidines **95** were obtained with the best yields and selectivities for alkyl substituents for R^2 while R^1 was phenyl (**95a** with 91% *ee*), only moderate ones when R^1 was exchanged with deactivated arenes (**95d** and **95e**), but completely diminished ones with electron rich arenes for R^1 (**95c**). Hence, despite showing major improvements in terms of selectivity compared to earlier protocols, this cyclization has to be considered very substrate specific, and the research on more tolerant reactions was ongoing.

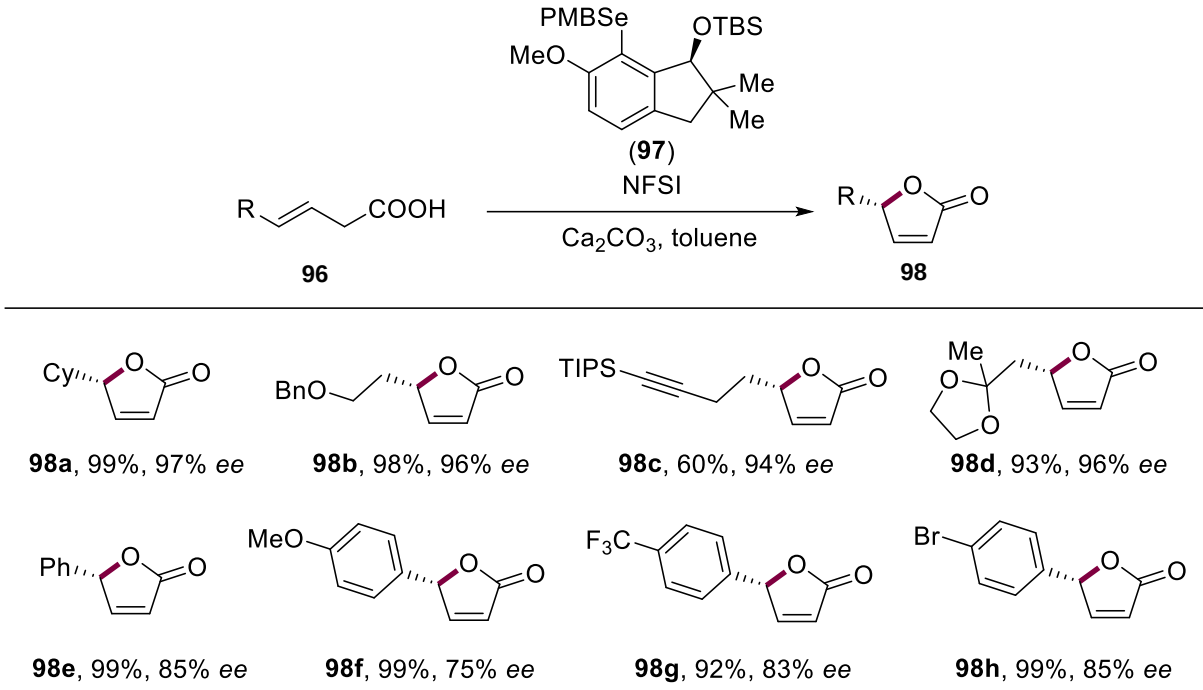


95a, 93%, 91% *ee* **95b**, 70%, 60% *ee* **95c**, 11%, 2% *ee* **95d**, 61%, 79% *ee* **95e**, 62%, 59% *ee*

Scheme 26. Selected scope of the enantioselective bromolactonizations *via* selenium catalysis.[82]

In 2016, Maruoka *et al.* developed the first highly enantioselective reaction by means of a lactonization reaction using a chiral selenium catalyst (Scheme 27).[83] Herein they could show that indanone derived precatalyst **97** enabled the conversion of alkenoic acids **96** to the respective lactones **98** in up to 99% yield and 97% *ee* (Scheme 27, **98a**). Here, under oxidative conditions the PMB group from **97** was cleaved off, which enabled the stereospecific attack of the selenonium moiety on the alkene. The authors speculated that the high selectivity of this attack arose from the rigidity of the catalyst, which was due to the TBS group that is in proximity to the catalytically active center. On the contrary, in former stereoselective selenium-catalyzed reactions the selectivity was mainly achieved by an interaction between the catalyst and a Lewis basic side chain of the substrate.[77,84–86] For arylated substrates, high selectivities could only be achieved by the replacement of $CaCO_3$ with $TMSOCOCF_3$ and were still decreased in comparison to the ones of alkylated substrates (**96a-d** *vs.* **96e-h**). The obtained

butenolides **98** could be reduced to the respective (*Z*)-allyl alcohols in consistently high *ee* values. Furthermore, the same group showed that catalyst **97** could be accessed in 6 steps in a scaled-up synthesis starting from commercially available 6-methoxy-1-indanone.[87] With these outstanding findings a new era of asymmetric protocols in the field of selenium catalysis was ushered, leading to a substantial number of contributions by other working groups, some of which will be discussed below.

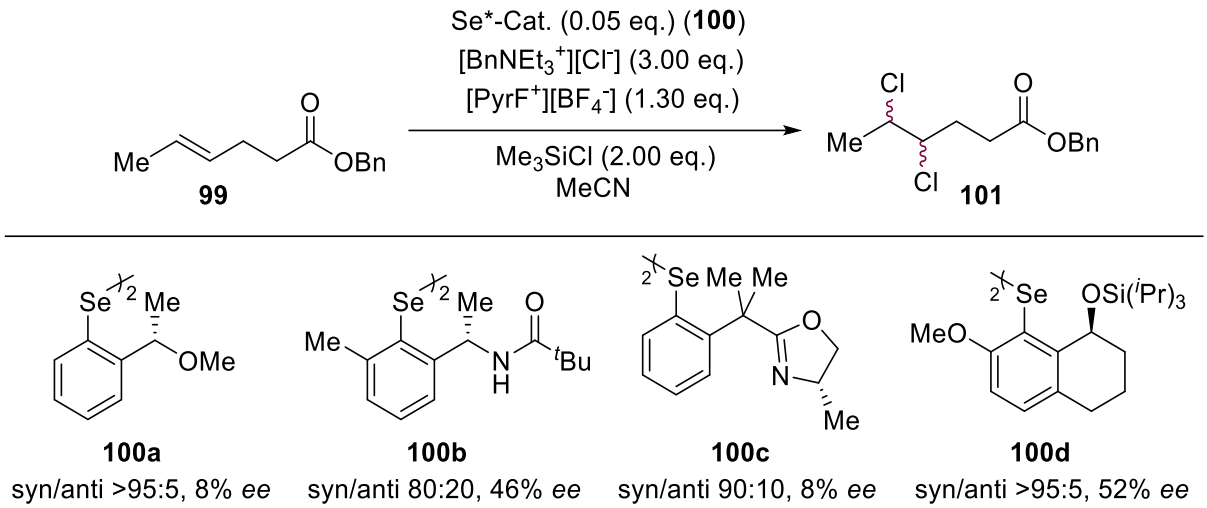


98a, 99%, 97% *ee* **98b**, 98%, 96% *ee* **98c**, 60%, 94% *ee* **98d**, 93%, 96% *ee*

98e, 99%, 85% *ee* **98f**, 99%, 75% *ee* **98g**, 92%, 83% *ee* **98h**, 99%, 85% *ee*

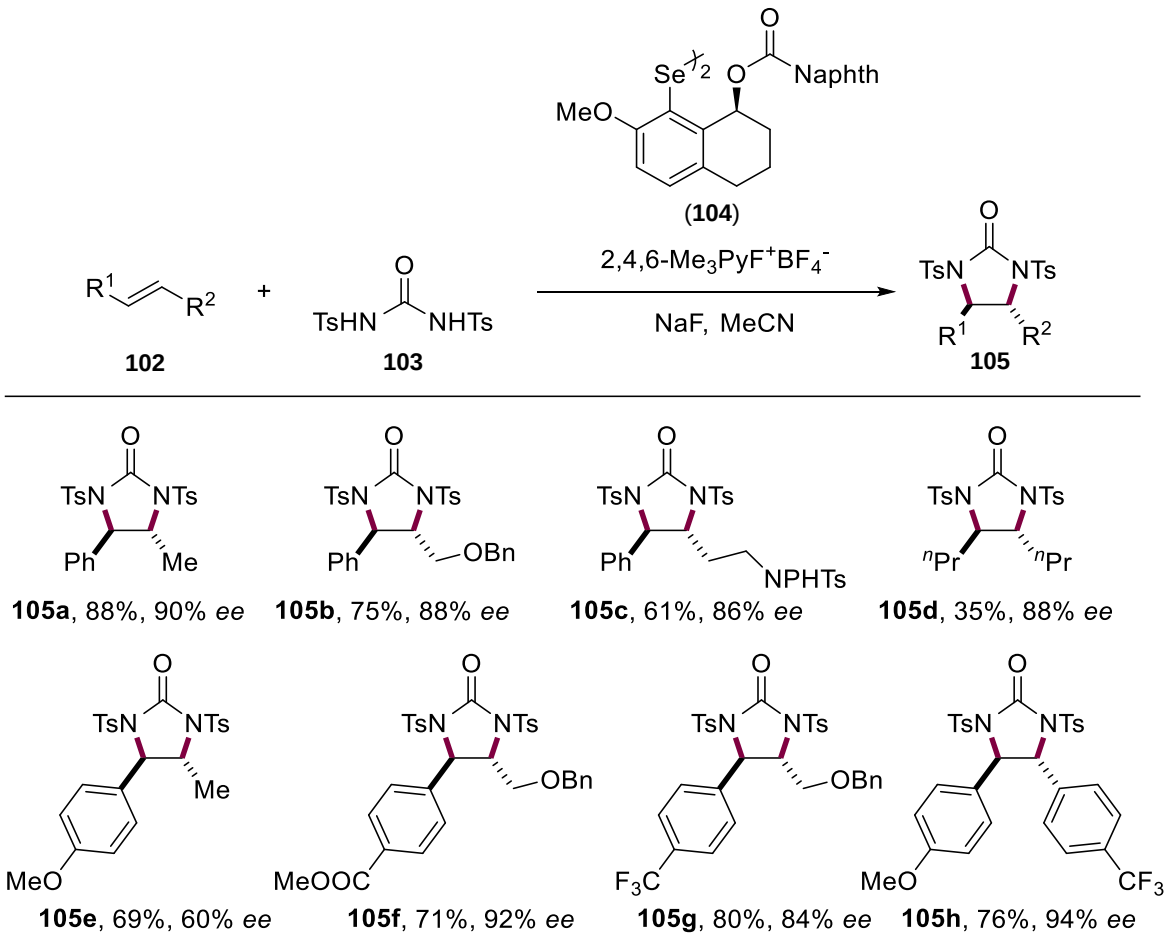
Scheme 27. Selected scope of the enantioselective lactonization *via* selenium catalysis.[83]

In 2019, Denmark *et al.* joined this race by investigating new chiral scaffolds for selenium catalysts studying the performance of diselenides bearing ether (**100a**), carbonyl (**100b**), oxazoline (**100c**) or bicyclic moieties (**100d**) to achieve enantioselective dichlorination reactions (Scheme 28).[88] Thereby, this protocol represented the first selenium-catalyzed difunctionalization reaction. Among the tested catalysts, **100d** performed the best with a selectivity value of 52% *ee*. This rather low value was assumed to be the result of an equilibrium arising during the catalytic cycle, which leads to the racemization of the product.



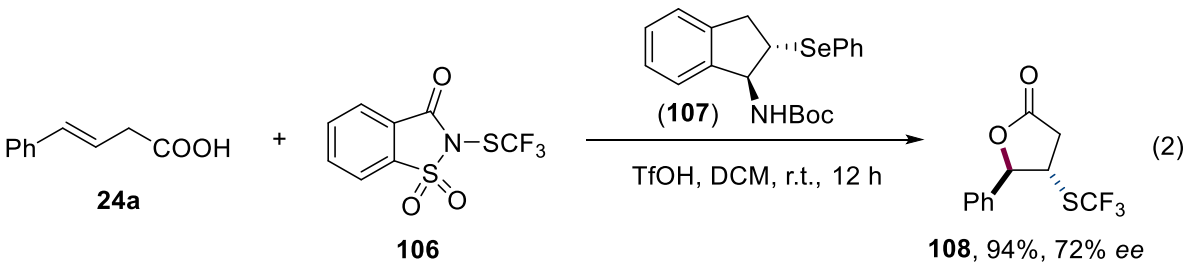
Scheme 28. Exemplary scope of chiral selenium catalysts tested within stereoselective dichlorination reactions.[88]

However, a similar catalyst like **100d** bearing a naphthoic acid ester (**104**) instead of the triisopropylsilyl ether performed very well in diamination reactions (Scheme 29).[89] The reaction showed a remarkable tolerance with regard to the substitutional pattern of the olefin, since diamines carrying either two aryl (**105h**), one aryl and one alkyl (**105a-c**, **105e-g**), and even two alkyl moieties (**105d**) were accessed in consistently high *ee* values. In addition, this transformation was very sustainable and practicable at the same time, since the diamination was achieved by naturally derived *N*,*N*`-bistosyl urea, which can be cleaved off easily by acidic treatment, giving rise to enantioenriched primary diamines.



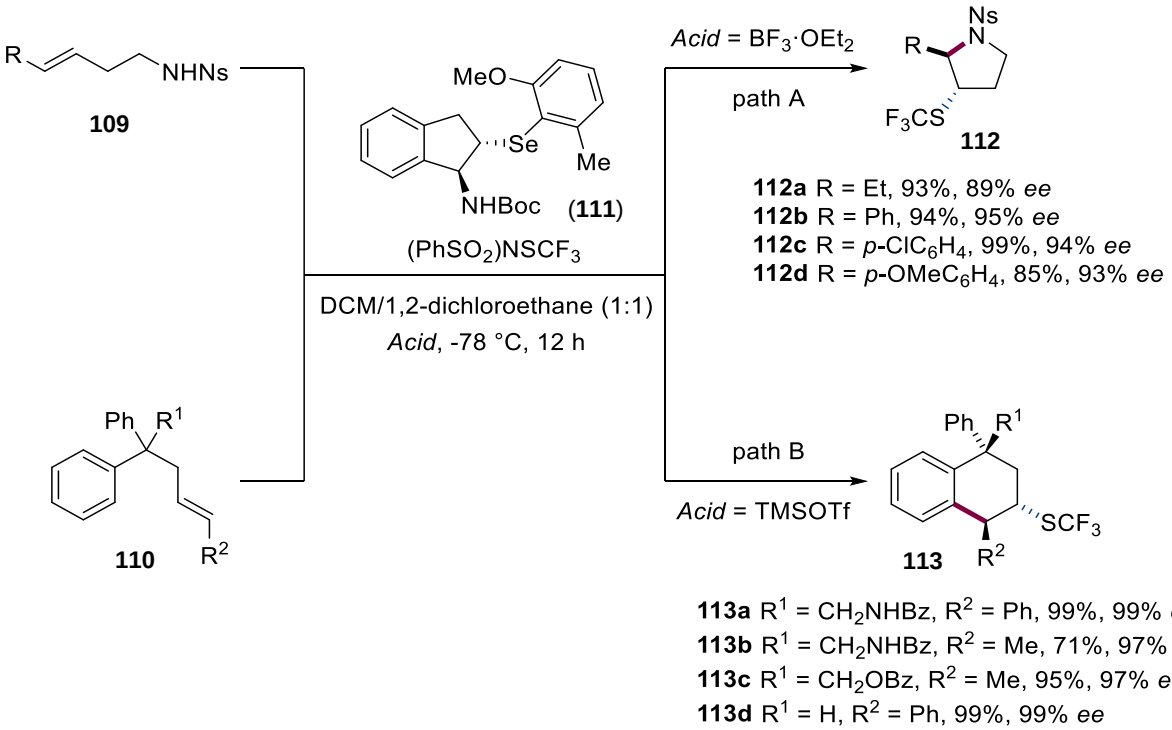
Scheme 29. Selected scope of the enantioselective diamination *via* selenium catalysis.[89]

Zhao *et al.* could show that indane-based chiral selenium catalysts (**107** and **111**) were highly practical for different difunctionalization reactions (Equation 2 and Scheme 30).[90] For trifluoromethylating lactonizations, the authors found that among the tested sulfide and selenide-based catalysts, **107** gave the desired product in 94% yield and 72% *ee* (Equation 2).



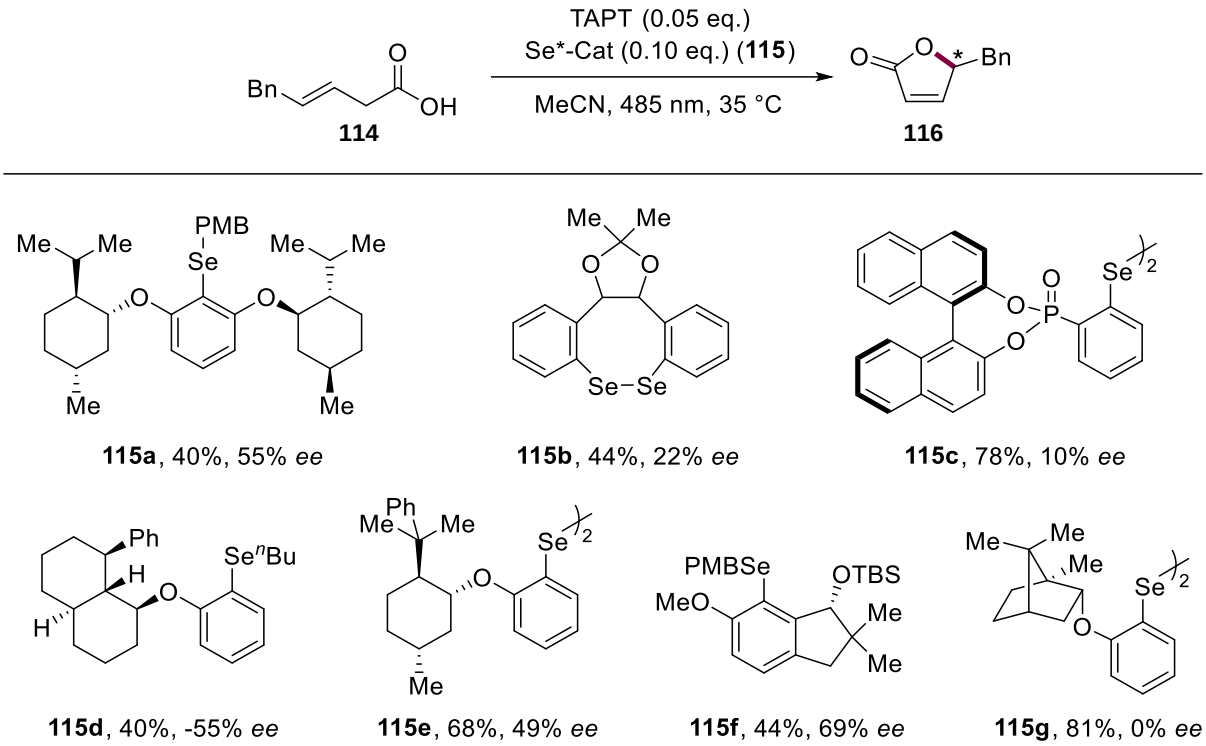
In consecutive research by the same group, it was discovered that 1-methoxy, 6-methyl modified catalyst **111** performs very well within trifluoromethylating amino-[91] and carbocyclizations[92] (Scheme 30). In both cases the very same conditions including $(PhSO_2)_2NSCF_3$ as the SCF_3 source were used. The acid however, which

affects the activation of **111**, was switched from $BF_3{\cdot}OEt_2$ (path A) to TMSOTf (path B). Thus, for both cases, the desired bifunctionalized products (**112** and **113**) were obtained in very good yields and selectivities of up to 95% *ee* for the aminocyclization (path A) and 99% *ee* for the carbocyclization (path B).



Scheme 30. Selected scope of the diastereoselective trifluorothiomethylating aminocyclization (path A) and carbocyclization (path B).[91]

In 2019 Breder *et al.* continued the investigations on chiral scaffolds for selenium catalysts (Scheme 31).[93] Among the tested candidates (**115a-g**) for the conducted photoaerobic lactonization reactions, **115f**, which was the catalyst designed by Maruoka *et al.*,[83] performed best with an *ee* value of 69%. Other catalysts carrying a menthol (**115a**), phenmenthol (**115e**) or chiral decalinol unit (**115d**) only performed mediocrely, and binol- and camphor-derived catalysts **115c** and **115g** showed little to no stereoinduction. Although many different reasonable moieties were tried as chiral backbones for selenium catalysts, only moderately good selectivities in comparison to former catalysts were reached. However, Breder *et al.* mentioned that the increase of *ee* value from **115e** to **115d** could be very likely due to a superior cation-π-interaction of the generated selenonium ion and the phenyl moiety.[93] This would add a new type of stereoinducing factor within electrophilic selenium catalysis to the ones reported by Denmark *et al.*[79] and Wirth *et al.*[43] (*cf*. Scheme 25, below).

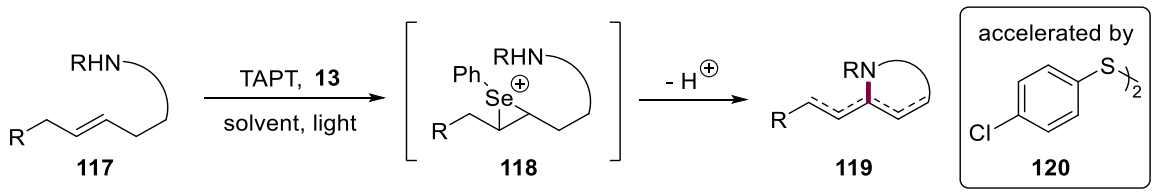


Scheme 31. Exemplary scope of chiral selenium catalysts tested within enantioselective photoaerobic lactonization reactions. TAPT: 2,4,6-tris(*p*-anisyl)pyrylium tetrafluoroborate.[93]

In conclusion, chiral selenium catalysis has rapidly evolved in the last years. Major contributions from Maruoka *et al.*,[83] Denmark *et al.*,[88,89] Wirth *et al.*,[77,85,86] Zhao *et al.*[90–92] and Yeung *et al.*[82] have proven that this branch of catalysis can reach high selectivity values. However, until now, the range of reaction types is rather limited to only lactonization or difunctionalization reactions. Hence it is highly desirable and promising to explore more reaction types since many others have already been reported as a racemic version.[62,65,68]

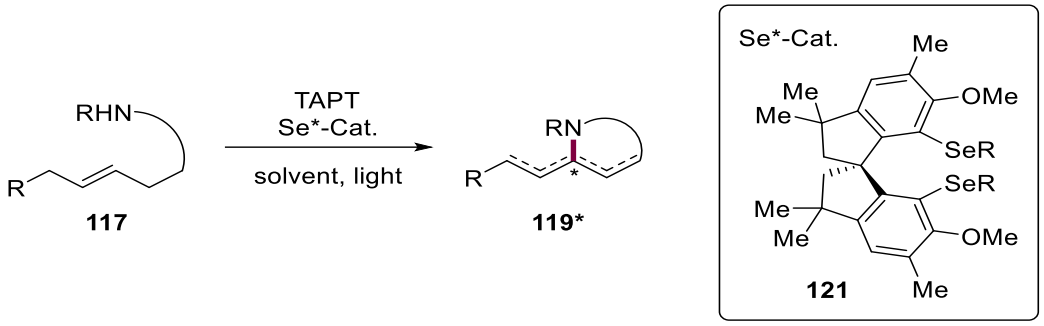
2 Objectives

The aim of this thesis was the development of a synthetic procedure for cycloamination reactions *via* selenium-π-acid catalysis. In this context, the recently developed dual selenium/photoredox catalysis by Breder *et al.*[94–97] should provide the catalytic basis for the desired transformation (Scheme 32). Here, $(SePh)_2$ (**13**) should act as an organocatalyst, which activates the alkene upon oxidation of the aerobically regenerating photocatalyst TAPT as described in former works.[95–97] Therefore, in comparison to previous works on selenium catalyzed cycloaminations this strategy would bring the advantage of omitting superstoichiometrically used oxidants, such as NFSI[51] or $PhI(OAc)_2$.[65] Further, this reaction could be executed under ambient conditions and the protocol would be operationally simple. Also, the switch from commonly used *N*-halogenated oxidants to a photocatalytic cycle could potentially prevent side reactions from endogenous nucleophiles.[57]



Scheme 32. Schematic proposal for a photoaerobic selenium-π-acid catalyzed cycloamination.

During the course of investigation, the addition of disulfide **120** (Scheme 32) was found to accelerate the reaction rate in many cases. Hence, another objective was the elucidation of the mechanism of this reaction, and especially of the role of **120**. Furthermore, since stereoselective functionalizations of alkenes constitute a promising, yet underdeveloped area, *cf.* section 1.4, the enhancement of the racemic protocol into a stereoselective one was also of major interest during this enterprise. Therefore, a chiral selenium catalyst based on a spirobiindane backbone (**121**), which was shown recently to produce good enantioselectivites within lactonization reactions, should provide the basis for enantioselective cycloaminations (Equation 3).[98]



(3)

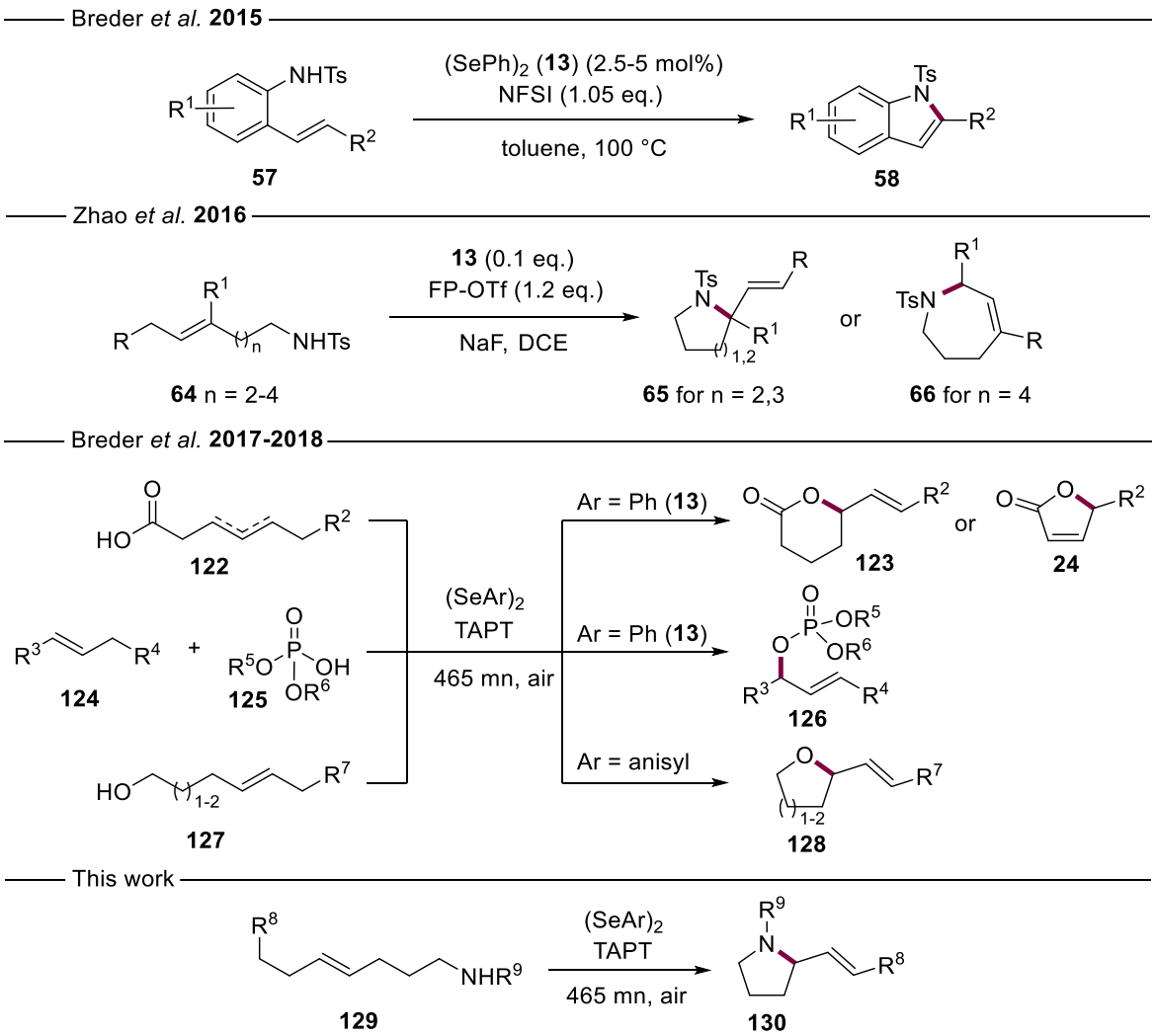
Eventually, to show the applicability of the designed protocol, the stereoselective cycloamination should be applied as a key step for the total assembly of biologically relevant compounds.

3 Results and discussion

3.1 Racemic photoaerobic cycloamination *via* selenium-π-acid catalysis

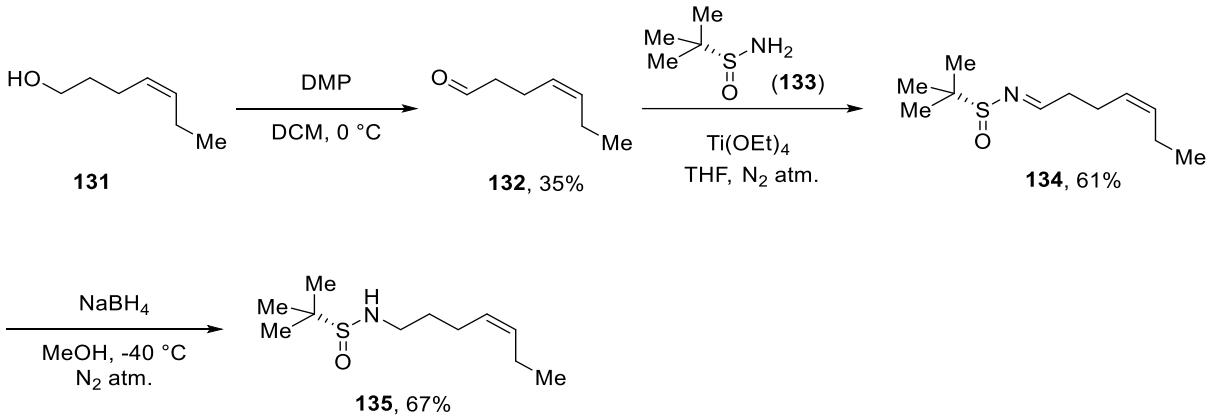
3.1.1 Preliminary investigations and optimization

In 2015, Breder *et al.* developed the first aminocyclization *via* selenium-π-acid catalysis using a catalytic system consisting of $(SePh)_2$ (**13**) as the catalyst and *N*-fluorobenzenesulfonimide (NFSI) as the terminal oxidant, which was used in superstoichiometric amounts (Scheme 33, above).[51] One year later, Zhao *et al.* investigated a similar potocol for the cyclization of internal, non-activated alkenes (Scheme 33, center above).[68]



Scheme 33. Cycloamination by Breder *et al.* (above),[51] Zhao *et al.* (center above)[68], photoaerobic functionalizations by Breder *et al.* (center below)[95–97], photoaerobic cycloamination as the aim of this work (below).

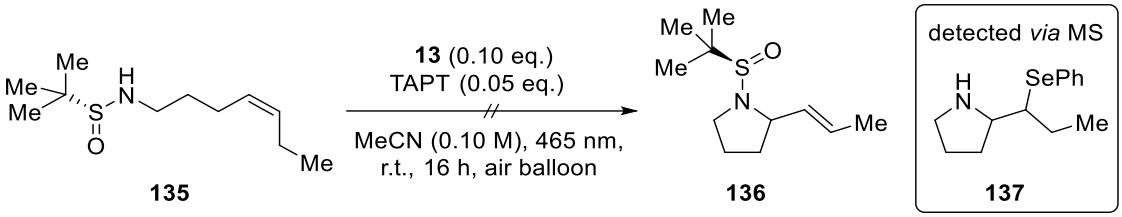
Shortly after, several protocols from Breder *et al.* were reported, demonstrating the replacement of these chemical oxidants by an oxidative photocatalytic cycle within etherification[97], esterification[95] and phosphatidation[96] reactions (Scheme 33, center below). Based on these previous findings, the question arose, whether a similar protocol could also be applied for a corresponding intramolecular amination leading to *N*-heterocyclic moieties (Scheme 33, below). To pursue this question, (*R*,*Z*)-*N*-(hept-4-en-1-yl)-2-methylpropane-2-sulfinamide (**135**) was chosen as a model substrate for a photoaerobic cycloamination *via* selenium-π-acid catalysis (Scheme 34). This choice was made for the following reasons. First, the same compound was shown to perform the intended cyclization within works from Stahl *et al.* using a Pd catalyst instead of an organocatalyst.[99] Second, the intended cycloamination was shown to proceed stereoselectively because of the (*R*)-configurated stereocenter of the applied sulfinamide. Third, this substrate does not contain any stabilizing moiety in proximity to the double bond, hence the cyclization would indisputably occur on a non-activated alkene. Hence, **135** was synthesized according to the procedure reported by Stahl *et al.*[99], where after Dess-Martin oxidation from **131**, a sulfinimidation by Lewis acid acitvation led to the respective imine **134** (Scheme 34). Then, **134** was reduced to the intended sulfinamide **135** in overall moderate yields (14% over 3 steps).



Scheme 34. Three-step synthesis of **135** as a model substrate.[99]

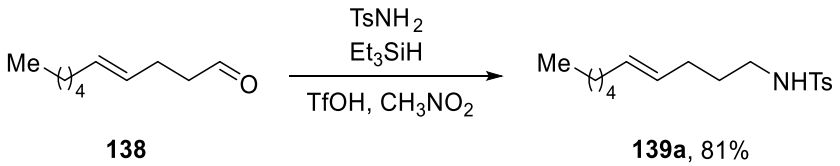
The obtained substrate was exposed to the conditions reported by Breder *et al.* using 0.10 eq. **13** and 0.05 eq. TAPT in MeCN (0.1 M, Equation 4).[95] While the intended formation of **136** did not take place, small amounts of **137** were detected *via* mass spectrometry (MS). As a potential side reaction, the oxidative cleavage of the protecting group can be excluded since the excited TAPT is neither capable of oxidizing the sulfinamide, nor the olefinic moiety of **135**.[100] This fragmentation most

likely occurs during the MS measurement itself. Therefrom, it can be derived that **135** indeed undergoes a cyclization, but only generates small amounts of the intended protected intermediate. Given that the generation of a synthetically useful amount of **136** from **135** has proven to be problematic, another class of *N*-nucleophiles should be tried. This change possibly leads to the formation of larger amount of a cyclized product and the retention of the protecting group. Since similar reactions have also been reported with sulfonamides, the focus was now set on those as potential nucleophiles.[51,101]



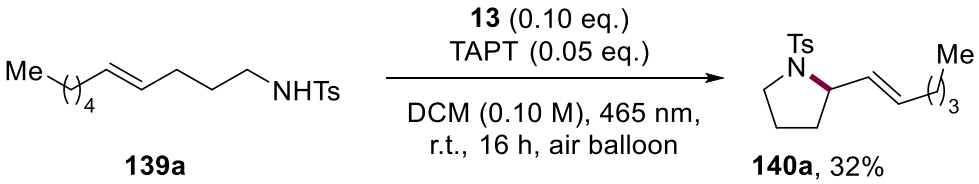
(4)

For this reason, (*E*)-*N*-(Dec-4-en-1-yl)-4-methylbenzenesulfonamide (**139a**) was synthesized by a TfOH catalyzed reductive sulfonamidation protocol from Roth *et al.* (Equation 5).[102]



(5)

Substrate **139a** was again tested under the aforementioned photoaerobic selenium-π-acid catalyzed conditions and led to cyclized product **140a** in 32% yield (Equation 6). The cyclization proceeded in a *5-exo-trig* fashion, which was reported accordingly in other works.[95,97]



(6)

The structure of **140a** could be confirmed *via* 2D-NMR (^{1}H/^{1}H COSY) spectroscopy, showing the representative correlations of the suggested structure (Figure 4). Here, the correlations at 4.08/5.30 ppm, which indicates the ^3J coupling from H^1 to H^2, and at 5.30/5.59 ppm, which shows the ^3J coupling of the olefinic protons H^2 and H^3, are of particular relevance. This structural determination is also supported by the coupling

constants between H^1 and H^2 of 6.9 Hz and 15.2 Hz for H^2 and H^3 indicating an (*E*)-configurated double bond.

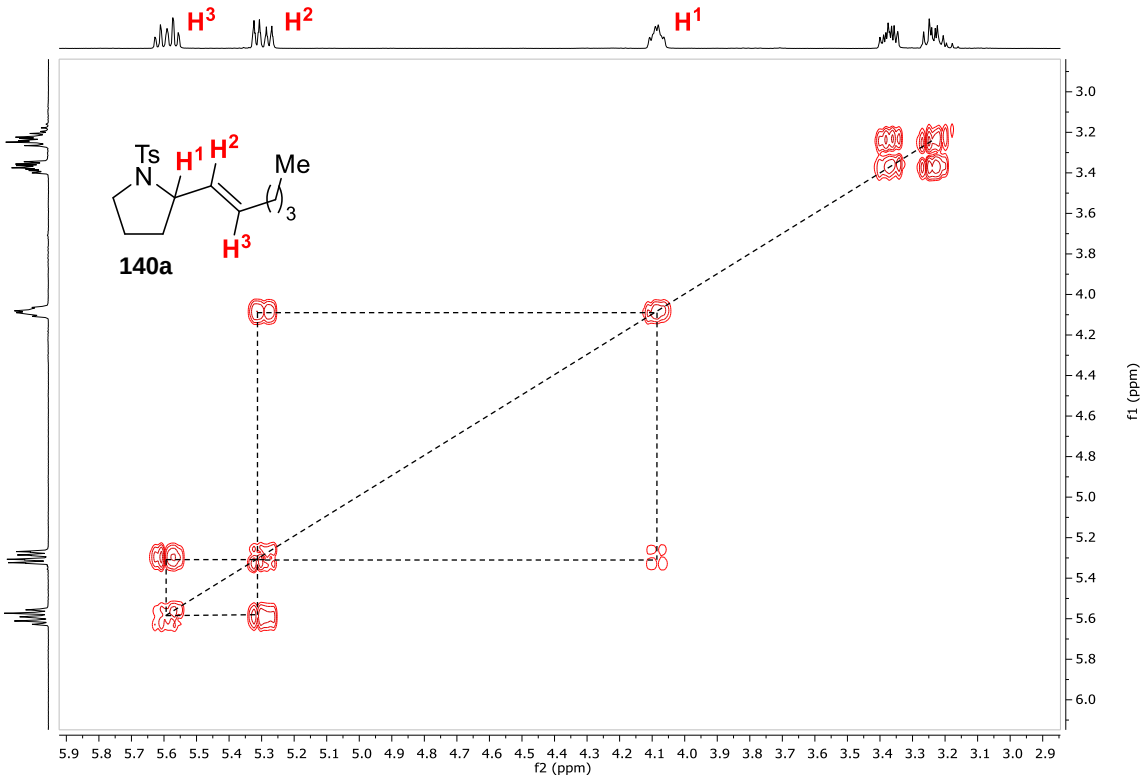


Figure 4. Section of the 2D-NMR ($^1H/^1H$ COSY) of **140a**.

Moreover, the spectrum of **140a** is concordant with the one reported by Cossy *et al.*, where it was obtained from a Rh-catalyzed cyclization (Figure 5).[103]

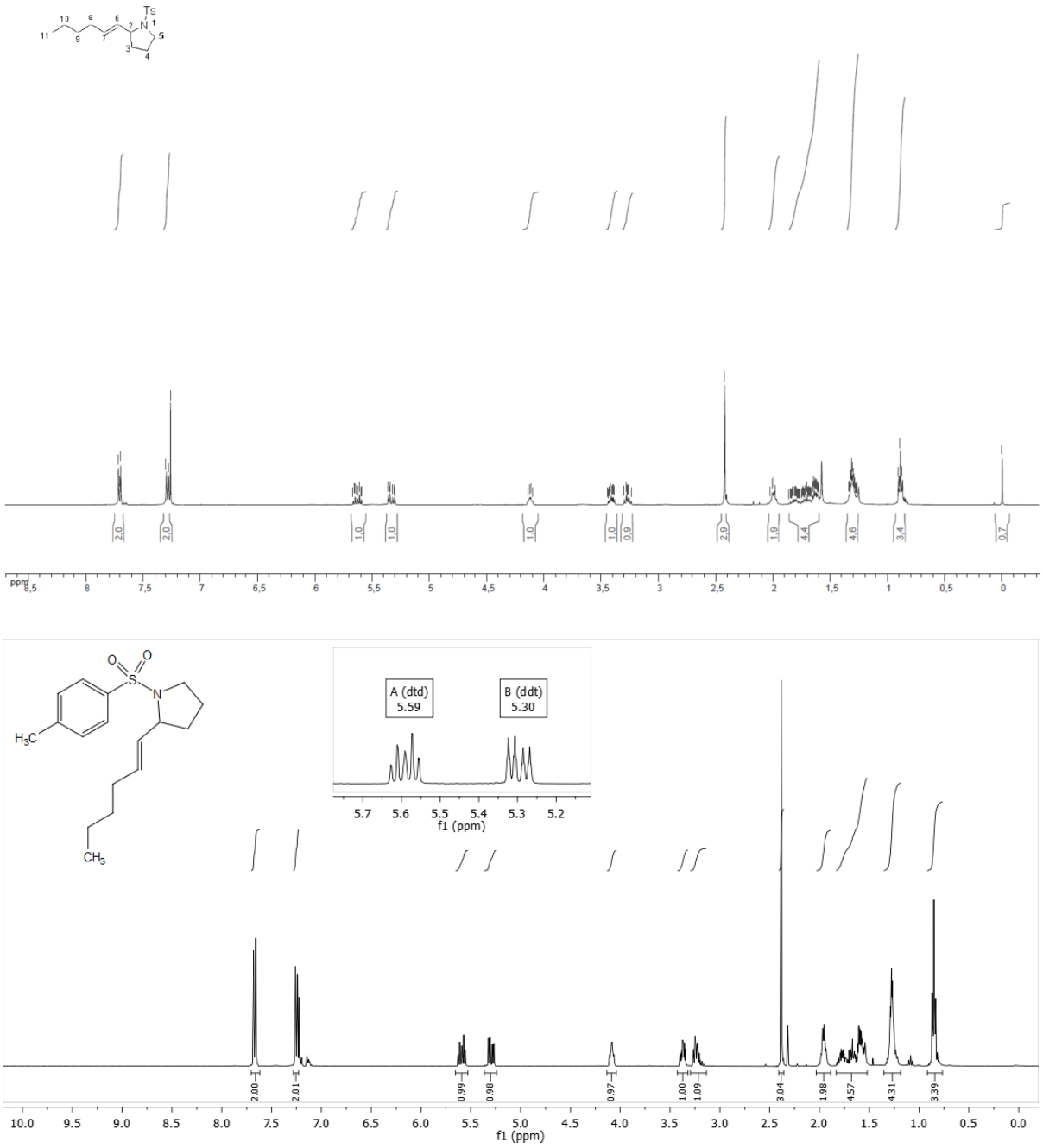
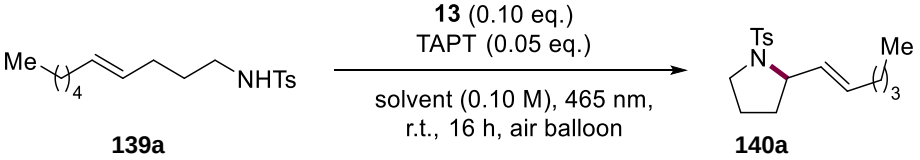


Figure 5. Comparison of ^{1}H-NMR spectra for **140a**: Cossy *et al.* (above)[103], own (below).

With the certainty of this result, the focus was set on the optimization of this reaction (Table 1). Next to DCM other polar solvents, as acetone, MeCN and DMSO were tested without an increasement of the yield (Table 1, Entries 1-4). Otherwise in less polar or aromatic media, the reaction yield could be enhanced, among them *o*-xylene gave the best yield of 75% (Table 1, Entry 12). This trend is rather unexpected considering that the photocatalyst does not dissolve in unpolar solvents but is rather present as finely suspended particles during the reaction. Further fine tuning of the reaction conditions by the addition of bases, which were meant to increase the

nucleophilicity of the sulfonamide group by Lewis basic interaction or abstraction of the respective proton, did also not lead to an enlargement in yield (Table 1, Entries 14-21). Interestingly, with Li_2CO_3, Cs_2CO_3, KF or K_2CO_3 the cyclization process was shut down completely (Table 1, Entries 13, 15, 16 and 20). Furthermore, the conduction of the reaction under a pure O_2 atmosphere or the addition of molecular sieve for the absorption of generated H_2O during the reaction was not beneficial (Table 1, Entries 21-22). Changes of the photocatalyst loading led to significantly lowered yields (Table 1, Entries 23-24). On the other hand, altering the concentration of substrate affected the conversion of the substrate to **140a** significantly. While at a halved concentration of 0.05 M the reaction just gave 33%, a doubled concentration of 0.20 M gave 84% of the desired product (Table 1, Entries 25-26). Eventual control experiments revealed that both catalysts, light, and air were crucial for the reaction (Table 1, Entries 27-30).

Table 1. Optimization of the racemic cycloamination.



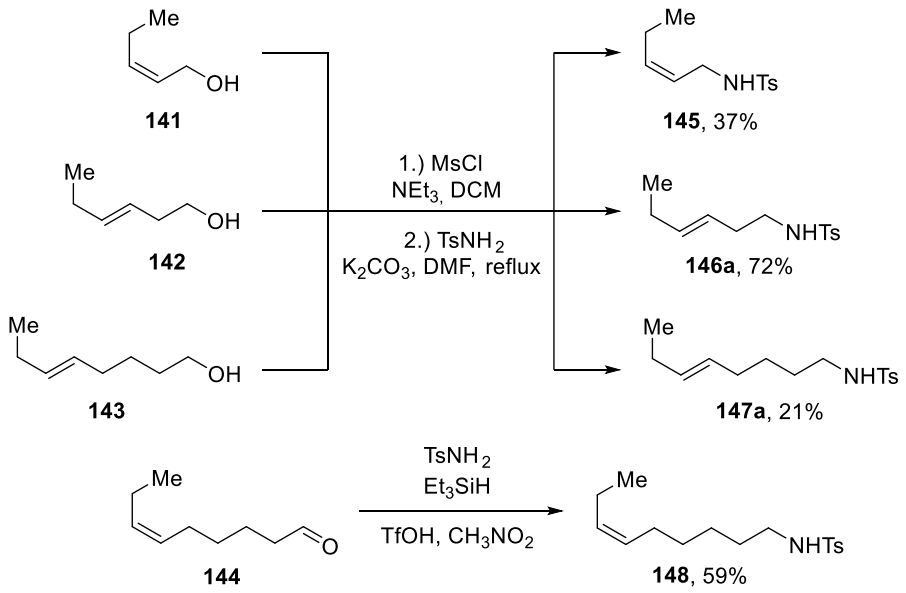
139a **140a**

Entry	Solvent	Comment	Conversion [%]	NMR-Yield [%][a]
1	DCM	-	100	32
2	acetone	-	21	21
3	MeCN	-	100	0
4	DMSO	-	47	0
5	toluene	-	100	48
6	CCl_4	-	100	55
10	$PhCF_3$	-	100	26
12	*o*-xylene	-	100	75
13	*o*-xylene	+ 0.80 eq. Li_2CO_3	3	0
14	*o*-xylene	+ 0.80 eq. Na_2HPO_4	100	70
15	*o*-xylene	+ 0.80 eq. Cs_2CO_3	100	0
16	*o*-xylene	+ 0.80 eq. KF	100	0
17	*o*-xylene	+ 0.80 eq. CaF_2	100	44
18	*o*-xylene	+ 0.80 eq. Na_2CO_3	19	8
19	*o*-xylene	+ 0.80 eq. $NaHCO_3$	100	36
20	*o*-xylene	+ 0.80 eq. K_2CO_3	24	0
21	*o*-xylene	+ molecular sieve (4 Å)	50	19
22	*o*-xylene	under O_2 atmosphere	100	58

23	*o*-xylene	with 10 mol% of TAPT	75	25
24	*o*-xylene	with 2.5 mol% of TAPT	79	15
25	*o*-xylene	0.05 M instead	67	33
26	*o*-xylene	0.20 M instead	100	**84 (79)**[b]
27[c]	*o*-xylene	without $(PhSe)_2$	59	0
28	*o*-xylene	without TAPT	4	0
29	*o*-xylene	under Ar atmosphere	32	0
30	*o*-xylene	without light irradiation	0	0

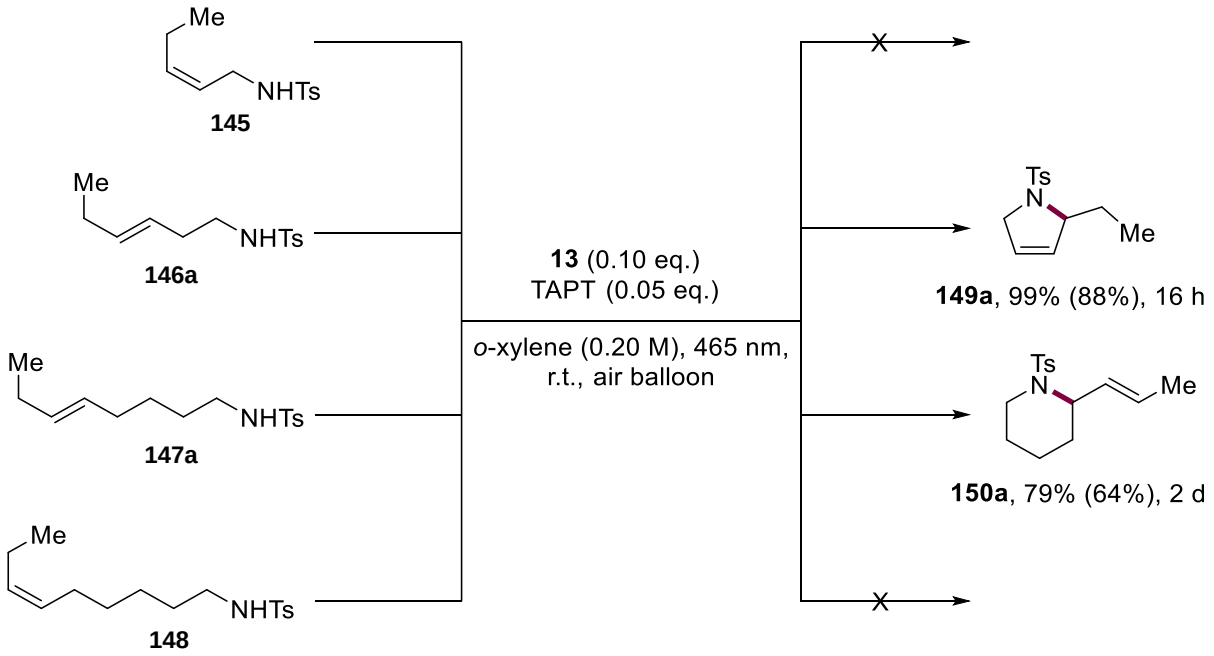
[a]1,3,5-trimethoxybenzene as internal standard. [b]isolated yield in parenthesis. [c]control experiments shaded in grey.

With the optimized conditions in hand, the range of accessible *N*-heterocyclic products was researched (Scheme 35). Hereby, the focus was set on accessing alternate ring sizes, which was suspected to be controllable depending on the position of the double bond with respect to the *N*-moiety. The substrates required for this were synthesized as follows. (*Z*)-4-methyl-*N*-(pent-2-en-1-yl)benzenesulfonamide (**145**), (*E*)-*N*-(Hex-3-en-1-yl)-4-methylbenzenesulfonamide (**146a**) and (*E*)-4-Methyl-*N*-(oct-5-en-1-yl)benzene-sulfonamide (**147a**) were obtained in 37%, 72% and 21%, respectively, by the mesylation of the corresponding alcohols and subsequent substitution with $TsNH_2$.[101] (*Z*)-4-methyl-*N*-(non-6-en-1-yl)benzenesulfonamide (**148**) was again obtained by the aforementioned TfOH catalyzed protocol *via* reductive sulfonamidation.[102]



Scheme 35. Synthesis of substrates for the elucidation of different cyclization possibilities.[101,102]

These substrates could be tested consecutively under the optimized catalytic conditions, whereupon substrates **145** and **148** did not undergo the intended cyclization, while substrates **146a** and **147a** did (Scheme 36). More specifically, substrate **146a** underwent a *5-endo-trig* cyclization process yielding a 3-pyrrolin moiety **149a**, while substrate **147a** underwent a *6-exo-trig* cyclization yielding pyrrolidine ring **150a**.



Scheme 36. Cyclization attempts of substrates bearing double bonds in different distances from the *N*-terminus.

The spectra of both structures (**149a** and **150a**) are in agreement with the ones reported from Cossy *et al.*[103] and Eilbracht *et al.*[104] (Figures 6 and 7). From this outcome, three features of these reactions were noticeable. First, the double bond of the products is formed in a Hofmann fashion in all cases, which is further analyzed in section 3.4. Second, the *5-endo-trig* cyclization of 4,5-unsaturated tosylamides represents a unfavored type of cyclization according to the Baldwin rules.[105] Third, in all cases, the crude NMR data only indicate the conversion to the respective ring moiety indicating the high regioselectivity of this transformation. All manageable aminocyclizations are summarized in Scheme 37.

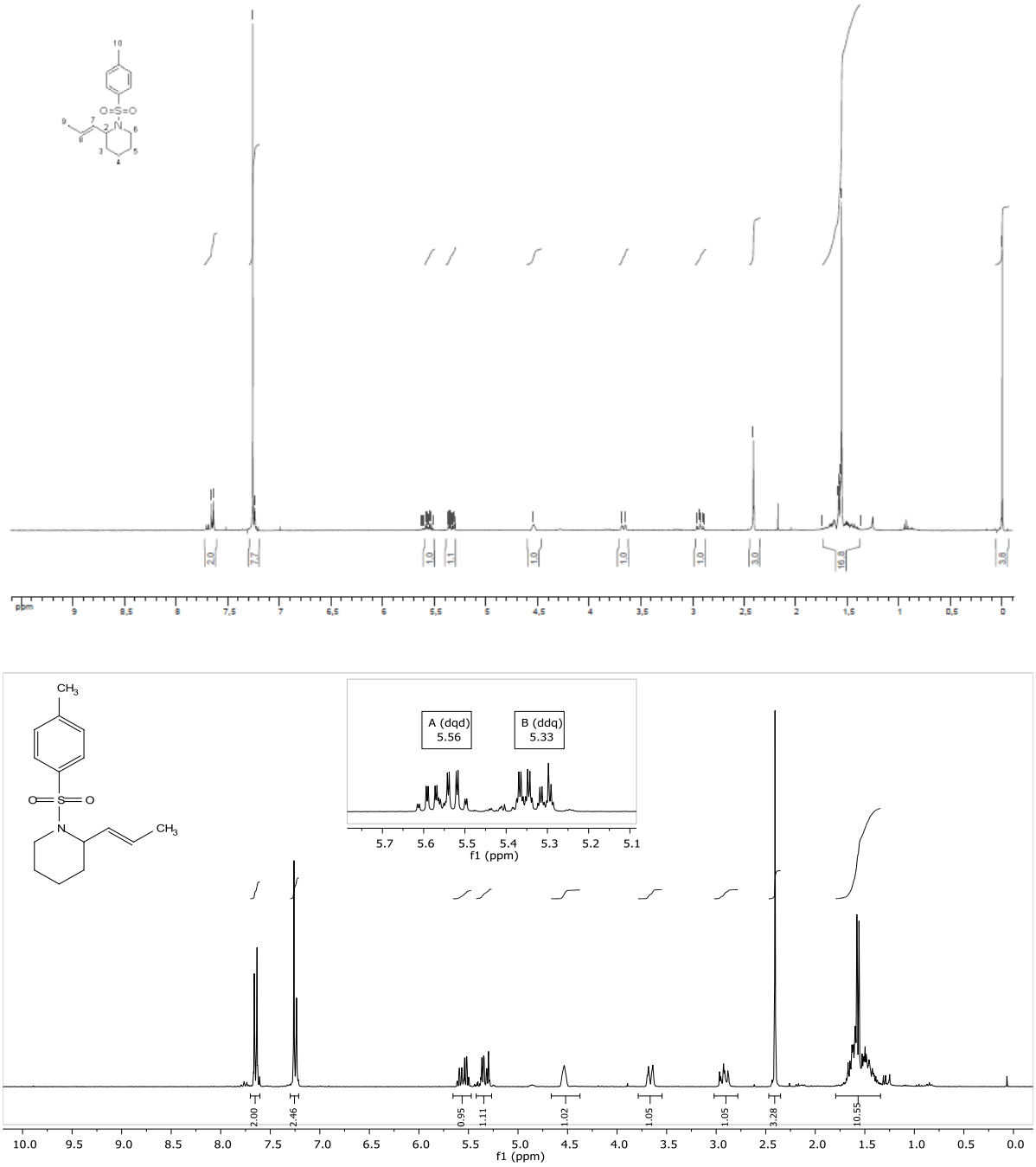


Figure 6. Comparison of ^{1}H-NMR spectra for **150a**: Cossy *et al.* (above)[103], own (below).

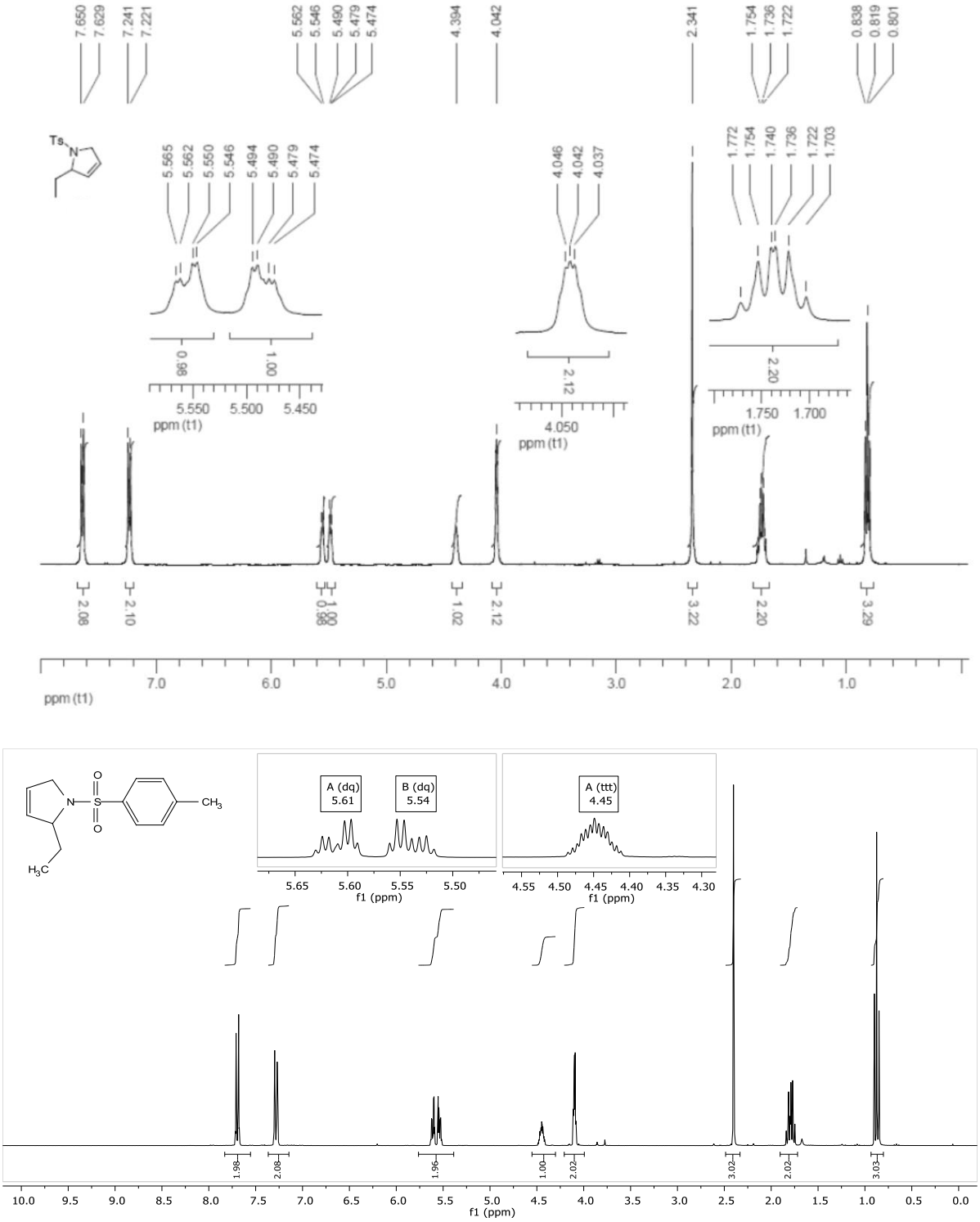
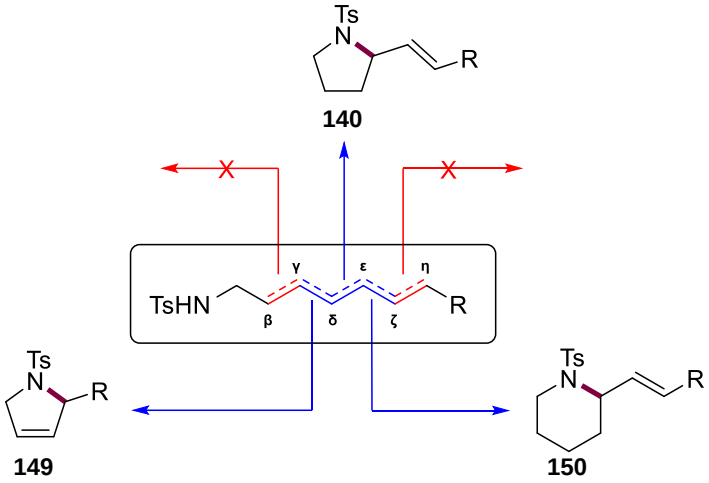


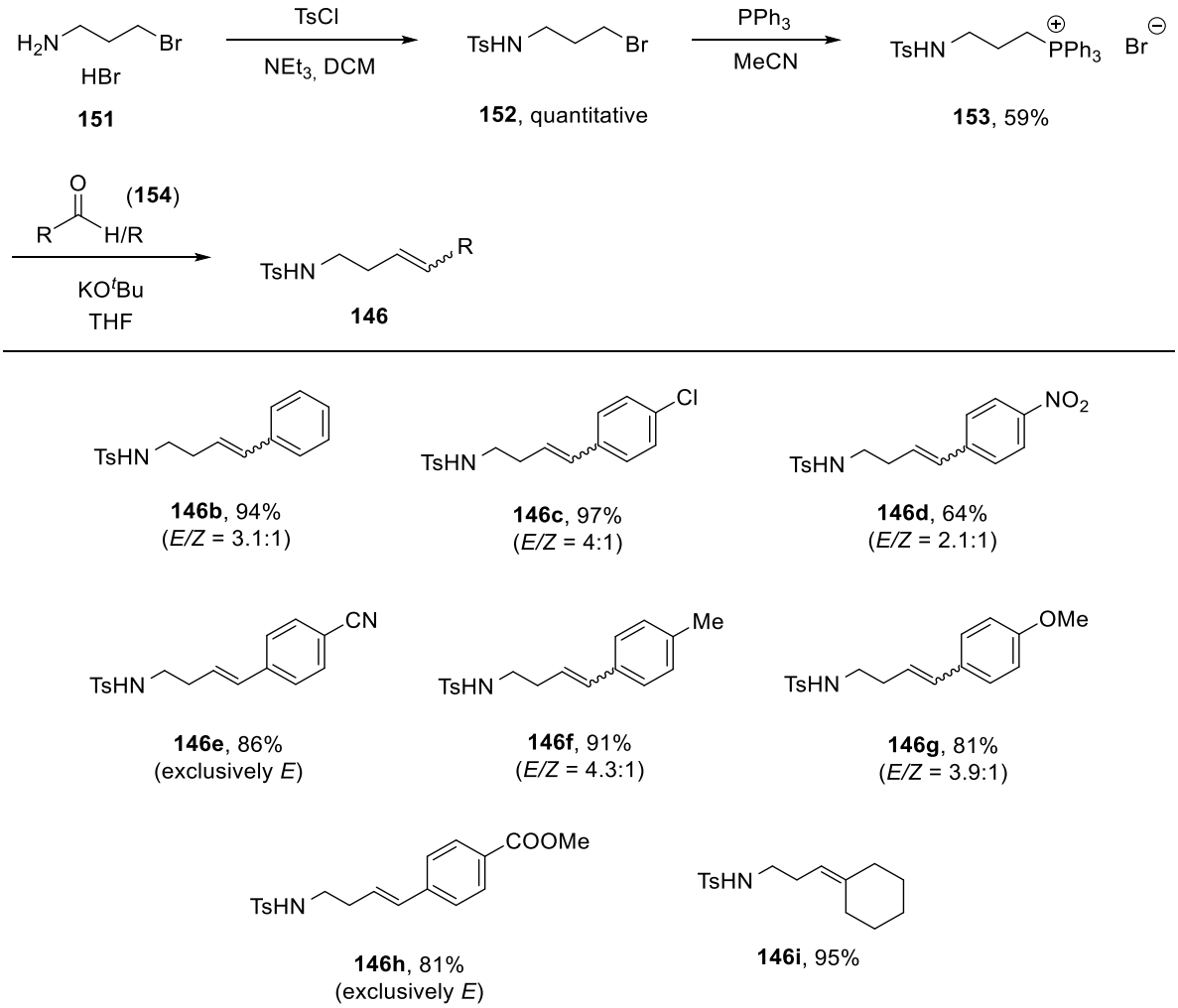
Figure 7. Comparison of ^{1}H-NMR spectra for **149a**: Eilbracht *et al.* (above)[104], own (below).



Scheme 37. Summary of possible cyclization operations towards structural motifs of **140**, **149** and **150**.

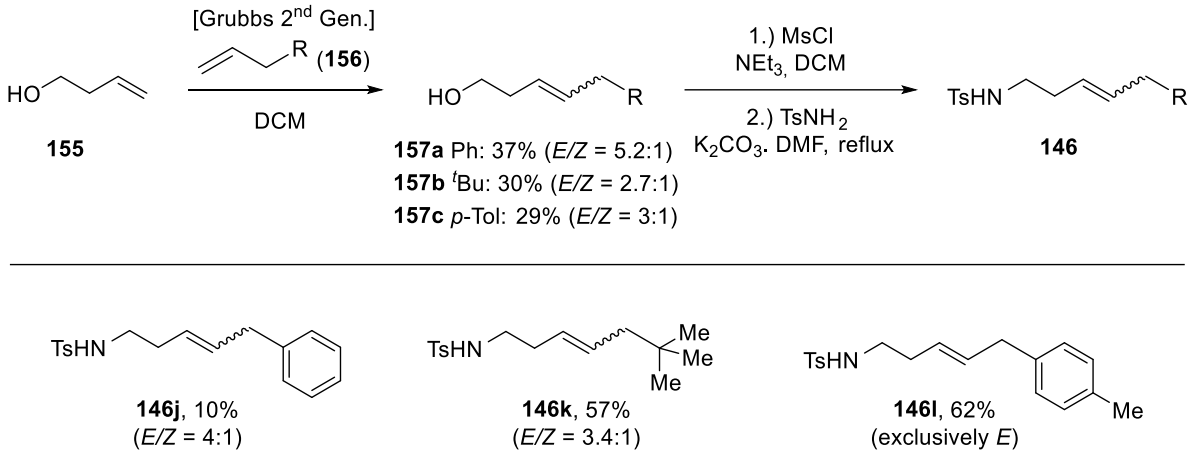
3.1.2 Synthesis of substrates

To further show the utility of this photocatalytic protocol a set of substrates bearing their double bond in suitable positions were synthesized using different synthetic procedures. 4,5-Unsaturated tosylamides **146** bearing different moieties on the olefinic part were synthesized according to Scheme 38. 3-Bromopropylamine hydrobromide (**151**) was converted to the respective tosylamide (**152**) in quantitative yields, and then to the Wittig salt **153**, which served as a common precursor for substrates **146b-i**.[95,106] Overall, while the yields of the Wittig Reactions ranged from good to very good yields (64-97%), the diastereoselectivity with regard to *E/Z* ratios of the constructed double bonds was rather low. The preferred diastereomer was the (*E*)-isomer among all cases, which is atypical for the Wittig Reaction.



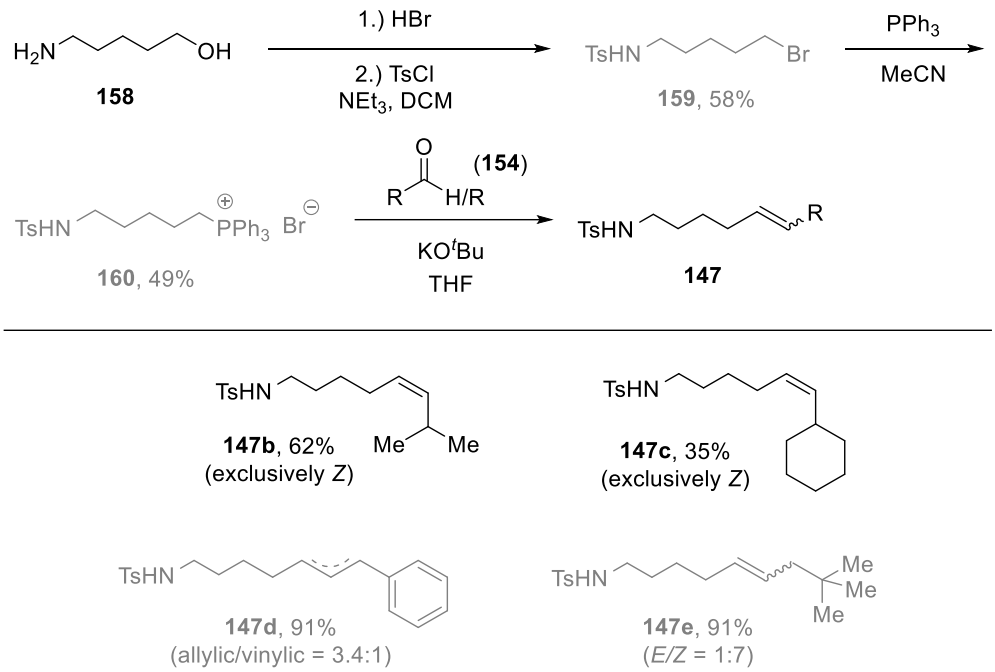
Scheme 38. Synthesis of 4,5-unsaturates tosylamides **146b-i** *via* Wittig Reaction.[95,106]

Substrates **146j-l** could be synthesized through a sequence of Grubbs Metathesis between but-3-en-1-ol (**155**) and different allylic moieties (**156**), following mesylation of the primary alcohol and basic substitution with $TsNH_2$ (Scheme 39).[101,107] Here, the yields of **146j-l** were only poor to moderate. As with the former Wittig Reactions these substrates were also received as an isomeric mixture with a larger content of the (*E*)-isomer. However, here, the selectivity can be inferred from the thermodynamic driving force of the Grubbs Metathesis.



Scheme 39. Synthesis of 4,5-unsaturates tosylamides **146j-l** *via* Grubbs Metathesis.[101,107]

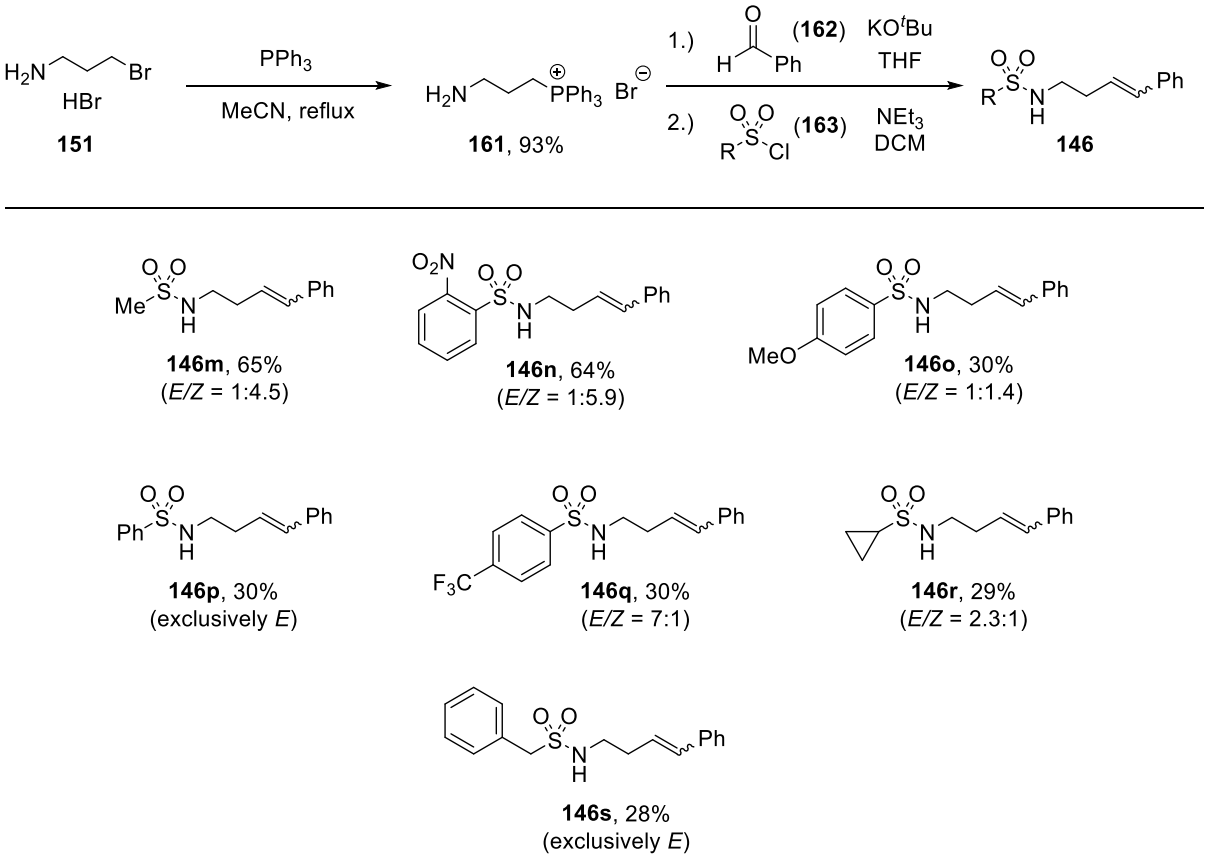
For substrates **147b-e**, again, a Wittig Reaction was sufficient to build up the decisive olefin (Scheme 40). However, the synthesis sequence commenced with commercially available 5-aminopentan-1-ol (**158**). From there, a bromide substitution with watery HBr solution was conducted, before a tosylamination and Wittig salt formation yielded **159** in 58% and **160** in 49%. Among the substrates obtained within this synthesis, one can notice, that in opposite to **147b-l** the (*Z*)-isomer was favored or received exclusively.[95]



Scheme 40. Synthesis of 6,7-unsaturated tosylamides **147b-e** *via* Wittig Reaction, **159**, **160**, **147d** and **147e** were synthesized by T. Appleson. **147d** was obtained as a mixture of allylic/vinylic product (3.4:1).[95]

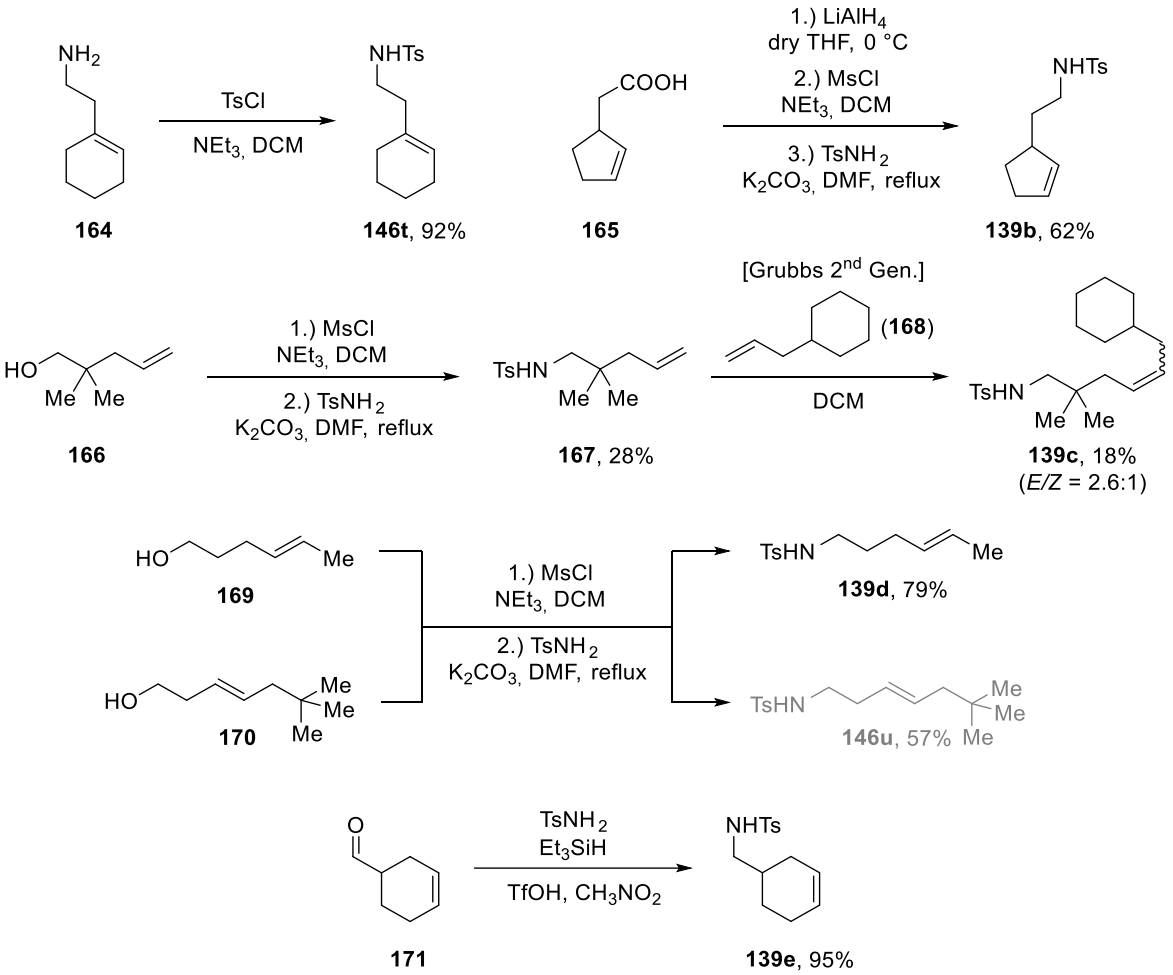
To further show the tolerance of the reaction with respect to the protecting group, **146m-s** were synthesized as appropriate substrates (Scheme 41). All of these were

obtained through the Wittig salt formation from 3-bromopropylamine hydrobromide (**151**) to **161** in very good yields.[106] Then, a Wittig Reaction and a follow up sulfonamidation by different sulfonyl chlorides led to the intended substrates **146m-s**.[95] Notably, no imine formation was observed between the primary amine and the carbonyl compound, indicating the superior nucleophilicity of the ylide moiety.



Scheme 41. Synthesis of 4,5-unsaturated sulfonamides **146m-s** *via* Wittig Reaction and sulfonamidation.[95,106]

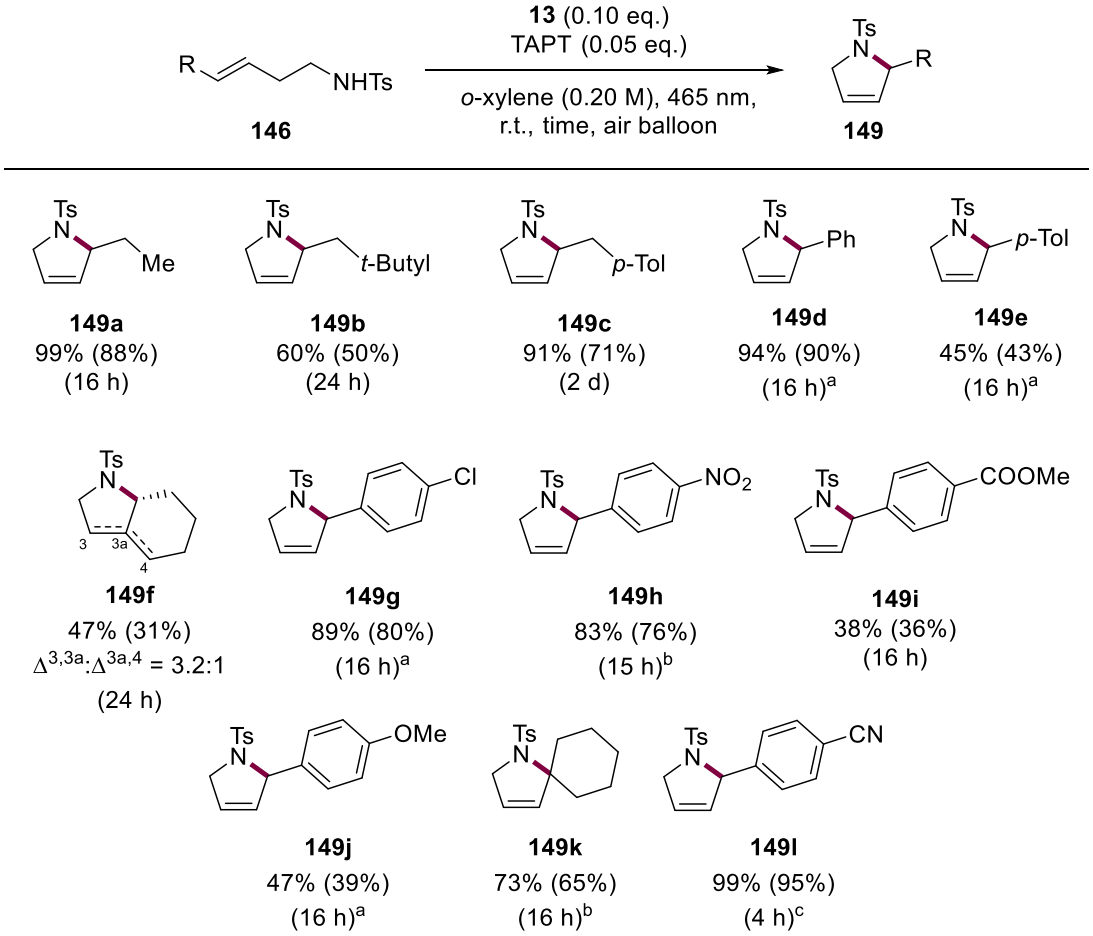
In addition to these substrates, others could be obtained starting from commercially available precursors within different routes (Scheme 42). Thus, substrate **146t** was obtained by direct tosylamination of **164**, **139b** through reduction of **165**, mesylation of the obtained alcohol and $TsNH_2$ substitution. Substrate **139c** contains two methyl groups in geminal position to the amine moiety, hence, the proximate cyclization was believed to be kinetically favored according to the Thorpe Ingold Effect.[108] For its synthesis, 2,2-dimethylpent-4-en-1-ol (**166**) was mesylated and substituted with $TsNH_2$, before a Grubbs Metathesis yielded **139c** as an isomeric mixture of *E/Z* = 2.6:1 in 18% yield. The same mesylation and $TsNH_2$ substitution was applied to receive **139d** in 79% from (*E*)-hex-4-en-1-ol (**169**) and **146u** in 57% from **170**. The reductive sulfonamidation of **170** led to **139e** in very good yields of 95%.[101,102]



Scheme 42. Other applied routes towards 4,5- and 5,6-unsaturated tosylamides **146t**, **146u** and **139b-f**. **146u** was synthesized by T. Appleson.[101,102]

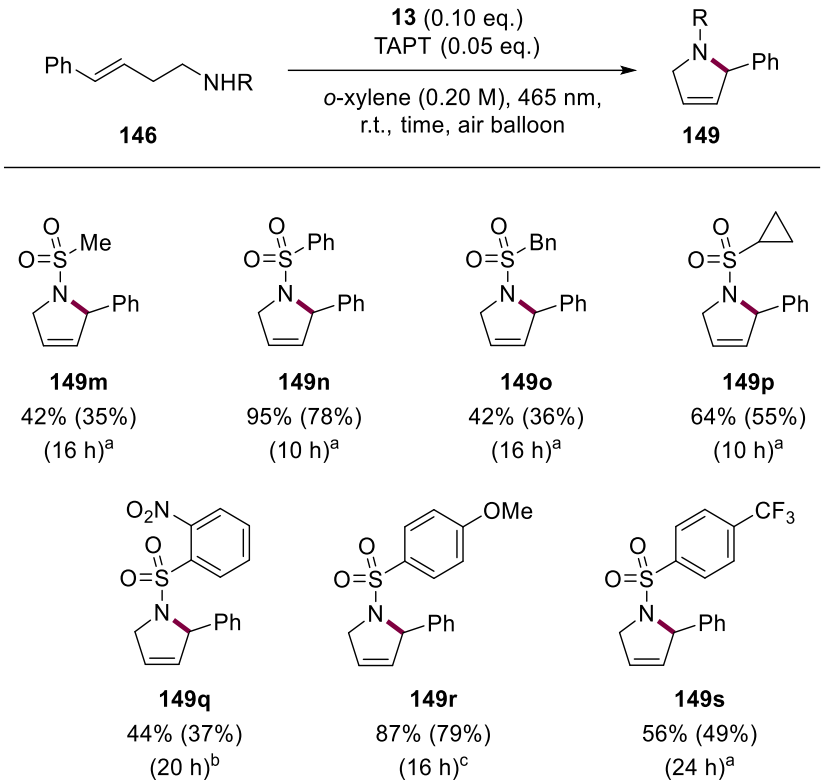
3.1.3 Cyclization reactions

With this broad set of substrates, the intended cyclizations were undertaken (Scheme 43). Targeting 3-pyrrolines **149** simple constituted alkylic and arylic C-frameworks were obtained from good to excellent yields (**149a-e** 45-99%). Notably, even sterically demanding Np-substituted substrate **146u** gave 60% of **149b**, however for the *p*-Tol substituted compound just 45% yield was obtained (**149e**). Also, bi- and spirocyclic substrates underwent the cyclization in synthetically useful yields of 47% and 73%, respectively (**149f** and **149k**). In the case of **149f** two regioisomers were generated. This can most likely be explained by the similar acidity of the protons on C3 and C4. The reaction showed extraordinary tolerance towards functional groups, since halogenated (**149g**), cyanated (**149l**), nitrated (**149h**), ether- (**149j**) or esterificated (**149i**) substrates led to yields ranging from 38-83%.



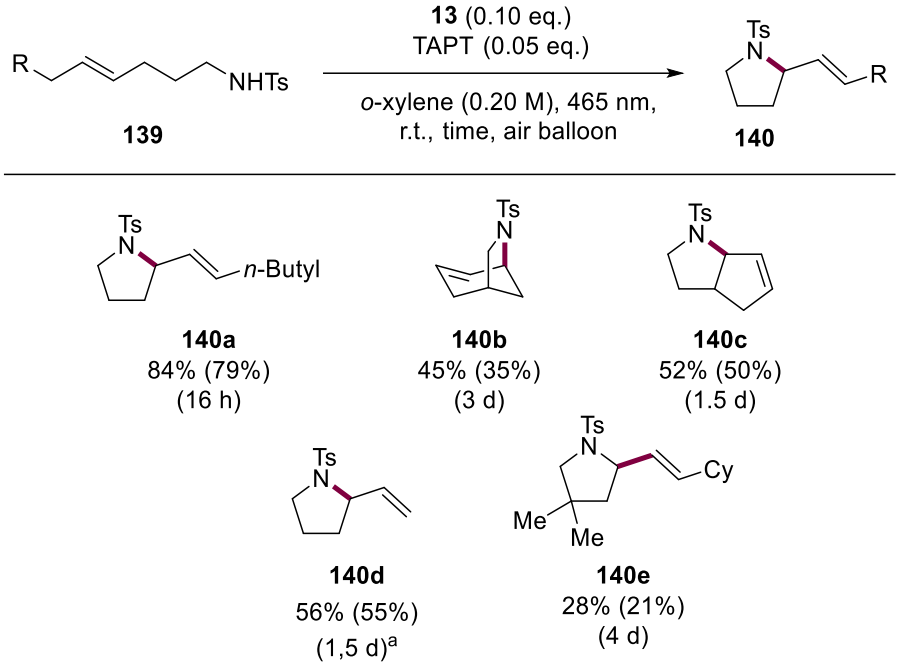
Scheme 43. Product scope of racemic 2-substituted 3-pyrrolines (**149**). ^{1}H-NMR yields determined with 1,3,5-trimethoxybenzene as internal standard, isolated yield in parenthesis. [a]Readdition of **13** and TAPT after 12 h. [b]10 mol% of **120** and 25 mol% *o*-nitrobenzaldehyde as additives. [c]10 mol% of **120** as additive.

The same tolerance was seen for different sulfonamides applied instead of the Ts group within the substrate. Simple alkylated, arylated sulfonamides, as well as heterosubstituted ones gave moderate to good yields from 42-95% (**149m-s**, Scheme 44).



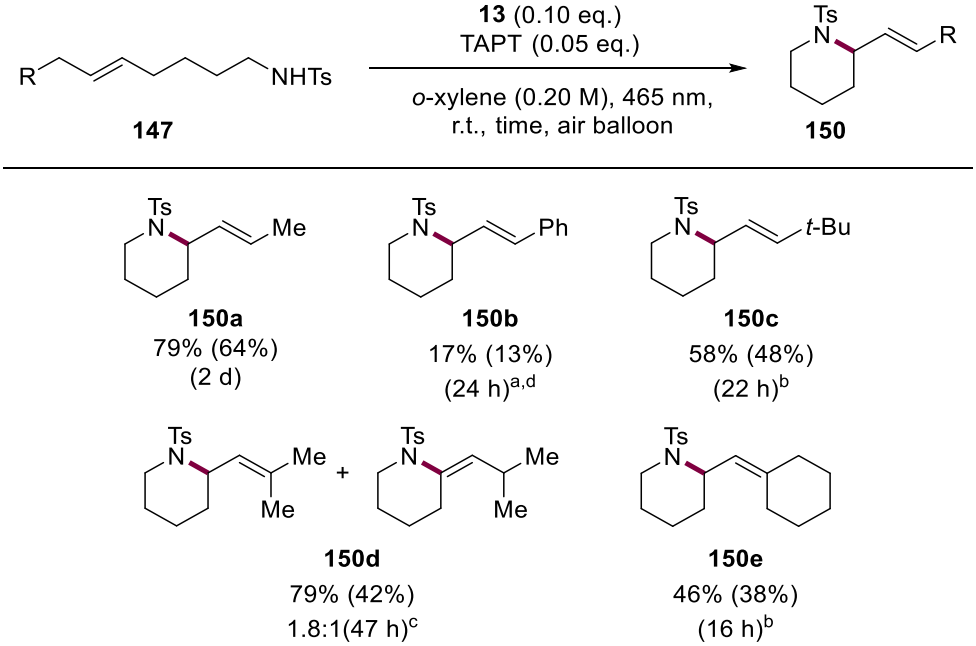
Scheme 44. Product scope of racemic 2-phenyl-3-pyrrolines (**149**) bearing different sulfonamides. ^{1}H-NMR yields determined with 1,3,5-trimethoxybenzene as internal standard, isolated yield in parenthesis. [a]10 mol% of **120** and 25 mol% *o*-nitrobenzaldehyde as additives. [b]Readdition of **13** and TAPT after 16 h. [c]10 mol% of **120** as additive.

Simple alkylated, bicyclic or terminal olefinic pyrrolidines were received in moderate to good yields (**140a-e**, Scheme 45). Even a more challenging, strained bicyclic ringsystem could be obtained in 42% yield (**140b**). The attempt to increase the yield of product **140e** by the application of the two methyl groups in geminal position only gave 28%.



Scheme 45. Product scope of racemic 2-substituted pyrrolidines (**140**). [1]H-NMR yields determined with 1,3,5-trimethoxybenzene as internal standard, isolated yield in parenthesis. [a]Readdition of **13** and TAPT after 24 h.

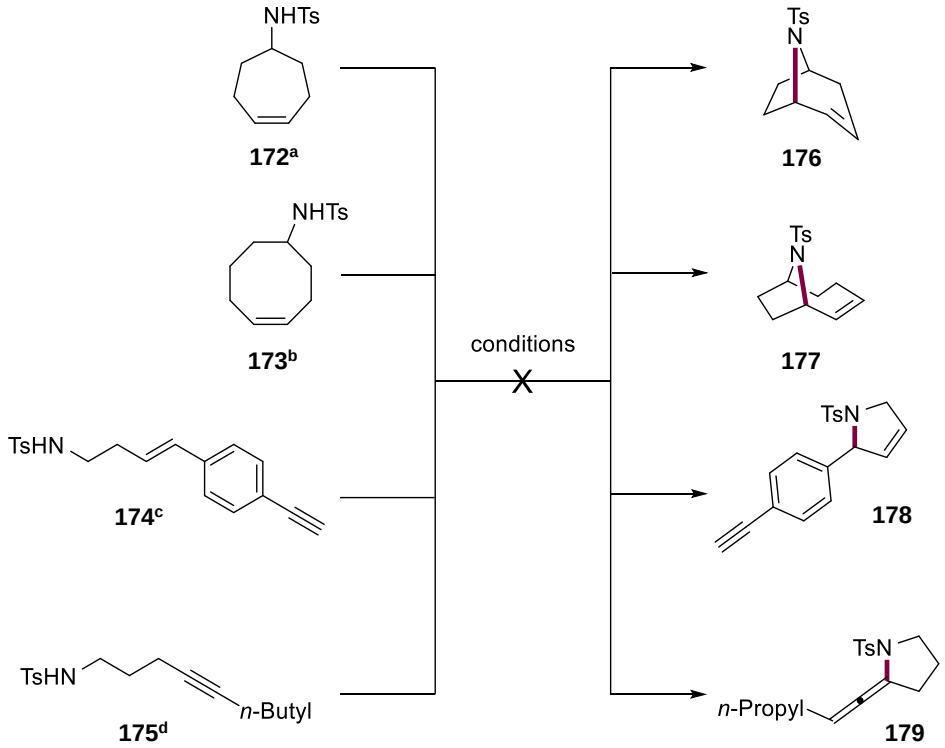
The conversion of 5,6-unsaturated tosylamides **147a-e** gave an array of piperidines with alkyl- and aryl substituents (**150a-e**) in proper yields (Scheme 46). Throughout the scope no preferences regarding the electronic nature of substituents could be examined.



Scheme 46. Product scope of racemic 2-substituted piperidines (**150**). [1]H-NMR yields determined with 1,3,5-trimethoxybenzene as internal standard, isolated yield in parenthesis. [a]10 mol% of **120** and 25 mol% *o*-nitrobenzaldehyde as additives. [b]10 mol% of **120** as additive. [c]10 mol% of **120** and 25 mol% *o*-nitrobenzaldehyde as additives, readdition of **13** and TAPT after 11 h. [d]obtained from **147d**, an allylic/vinylic mixture (3.4:1).

In many cases, the yields could be raised either by the readdition of the catalysts, TAPT and **13**, after the indicated time (*e.g.* for **149d**, **149e** or **149g**) or by the coaddition of disulfide **120** (*e.g.* for **149l**, **149r** or **150c**). The indication that **120** could influence the reaction was derived from the knowledge that diselenides and disulfides can perform scrambling giving rise to interchalcogenated species *via* dynamic covalent bonding.[109] In this way, a more stable leaving group is generated and the elimination of the selenium moiety generating the double bond was suspected to be facilitated.[110] Besides, in some cases the coaddition of *o*-nitrobenzaldehyde was intended to suppress side reactions with $^1O_2$ (*e.g.* for **149m-p**), which can be formed from the excited TAPT.[111] In section 3.4.3 the rate enhancing effect of **120** is further investigated and section 3.3 shows possible side reactions stemming from the presence of $^1O_2$.

Alongside this group of successfully converted substrates, also a minor group of unconvertable ones was discovered (Scheme 47). Herein, an alkyne substituted substrate (**174**) was not converted to the target product (**178**). Despite the higher electron density of alkynes, which would indicate a reaction between the selenonium moiety and the alkyne rather than the alkene, and thereby be in accordance to this outcome, similar electrophilic additions were shown to proceed faster with alkenes than alkynes.[112] Also, the trial to cyclize an internal alkyne moiety to the corresponding allene motive failed (**175** to **179**). This outcome can presumably be reasoned by a consecutive reaction of the allene motive of the product with another catalytic selenonium moiety. All attempts to obtain any N^1-bridged bicyclic ring system did not lead to the respective product in synthetically useful yields, but only led to trace amounts of the desired products (**176** and **177**). Further attempts to raise the yield of tropane structure **176** by the change of solvents (from *o*-xylene to MeCN), an increasement of the diselane loading (**13**, 0.20 eq. instead of 0.10 eq.) or the coaddition of disulfide **120** did not bring an improvement.



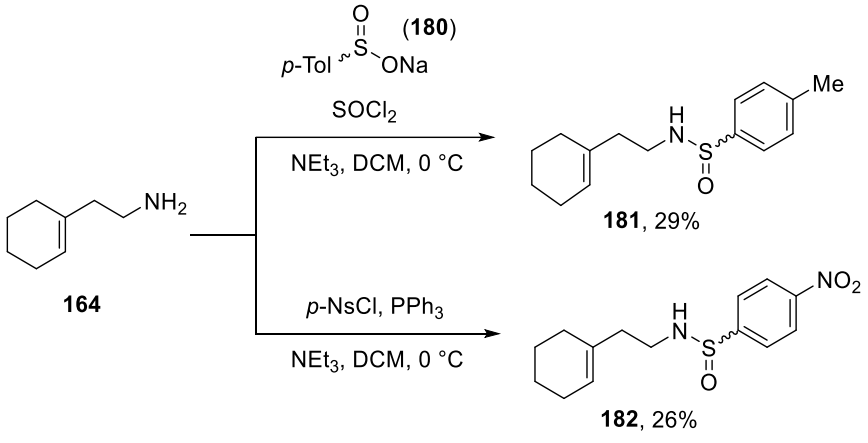
Scheme 47. Unsuccessful attempts of cyclizations. These compounds were synthesized during the bachelor thesis of [a]Simon Kaltenberger[113] or an internship with [b]Marko Boskovic, [c]Alberto Nunez-Bendinelli, [d]Daniel Kolb.

In comparison to recent protocols covering cycloamination reactions, this technique represents the first one, which can afford 3-pyrrolin moieties starting from internal alkenes. This class of compounds has only been made accessible by other procedures like reduction of pyrroles[114], allylic substitution reactions[103,115,116], metathesis reactions[116,117], cyclizations of allenes[118,119], cycloaddition reactions[116,120] or hydroamination reactions[121]. But in contrast to these alternatives, the direct conversion of alkenes with amines to the respective cyclic amines, also referred to as the *aza*-Wacker reaction, unifies the coupling and the oxidative step and therefore represents the most redoxeconomic technique among all.[4,122] A more detailed analysis and possible explanations for the regioselective formation of 3-pyrrolines are described in section 3.4 on the mechanism of this reactions. Further, this reaction is characterized by its operationally simple protocol and setup, which is not dependent on a specific atmosphere, which is a crucial factor for many TM-driven protocols.[123] Lastly, by the use of air as a terminal oxidant, waste producing oxidants, that are frequently used for cycloamination reactions, can be abandoned.[51,62,63,65,66,68]

3.2 Stereoselective photoaerobic cycloamination *via* selenium-π-acid catalysis

3.2.1 Substrate-controlled stereoselective cyclization

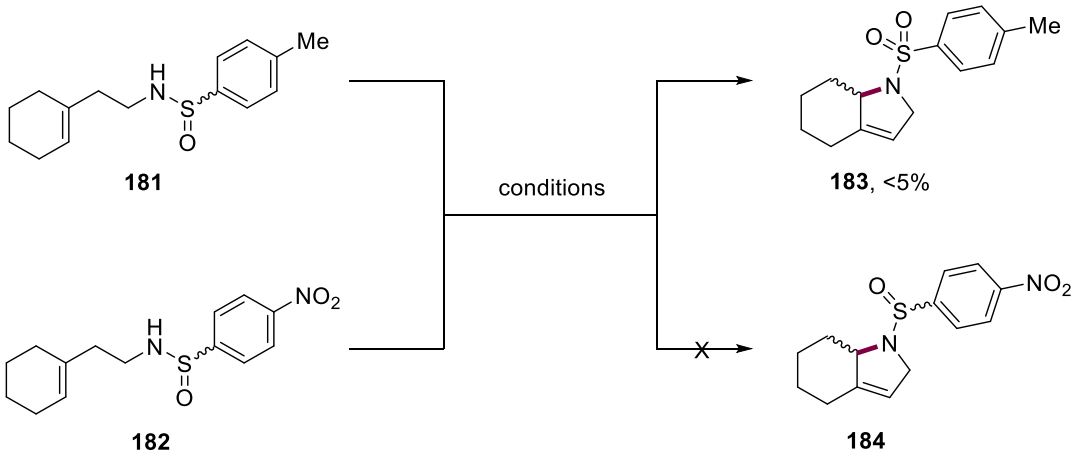
As described in section 1.4 the attention on stereoselective selenium catalysis protocols is constantly rising. In this context, the enhancement of the racemic reaction described in section 3.1 to a stereoselective version would describe a rapid and economic technique to obtain the respective enantiomerically enriched *N*-heterocycles in comparison to former techniques.[116,119,124] For this purpose, the sulfonyl group on the amine should be replaced by a chiral auxiliary, which could potentially induce its stereoinformation to the olefinic part. Hence, their reduced derivatives, sulfinamides, provide potential candidates. However, as described in section 3.1.1, ^{t}Bu-sulfinamide **135** did not perform the intended cyclization, but side reactions that led to the degradation of **136**. In another attempt to perform the cyclization in a stereoselective manner, the ^{t}Bu moiety was exchanged by a *p*-Tol and *p*-nitrophenyl moiety (Scheme 48). In this way the nucleophilicity of the sulfinamide was ment to be altered, which could potentially prevent the side reaction. For this purpose, **181** and **182** were synthesized from **164**. **181** was obtained in 29% yield through the treatment of **164** with 4-methylbenzenesulfinate and $SOCl_2$, **182** in 26% through a reductive sulfinamidation.[125]



Scheme 48. Synthesis of other sulfinamides **181** and **182** for the stereoselective cyclization.[125]

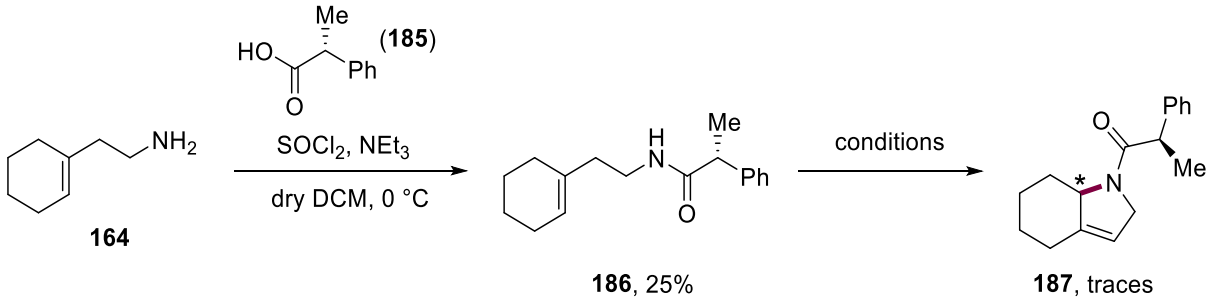
However, in the case of **181**, the photoaerobic cyclization led only to low amounts of oxidized and cyclized sulfonamide **183**, which could be compared with the NMR spectrum of **149f** from the racemic cyclization and detected by MS (Scheme 49).

Notably, if the oxidation process to the sulfonamide happened after the intended cyclization, this reaction could indeed be a stereoselective cycloamination, but since the yield was synthetically unusable, the research on the stereoselective outcome of this reaction was not continued. For **182** neither the cyclized sulfinamide, nor the respective sulfonamide could be detected. Hence, the research on sulfinamide protecting groups for this cyclization was terminated at this point.



Scheme 49. Stereoselective cyclization trial for **181** and **182**.

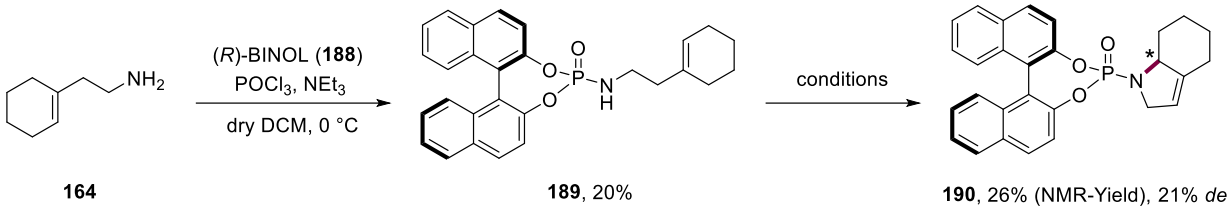
Next, a chiral amino acid moiety should be tested for the cyclization. Similar approaches were reviewed by Bueno *et al.* and Diaz-Muños *et al.* showing that the use of chiral amino acids as auxiliaries is a frequently encountered technique in the realm of stereoselective transformations.[126] For this purpose, **164** was amidated by treatment with (*R*)-2-phenylpropanoic acid (**185**) and $SOCl_2$ to obtain (*R*)-*N*-(2-(cyclohex-1-en-1-yl)ethyl)-2-phenylpropanamide (**186**) in 25% yield (Scheme 50). Unfortunately, the exposure of **186** under the optimized conditions only lead to trace amounts of the intended cyclization product **187**, which could be confirmed by MS.



Scheme 50. Synthesis of chiral amide **186** and stereoselective cyclization trial.

Inspired from the work of Yamamoto *et al.*[127] and Fuji *et al.*[128], a chiral BINOL backbone should be applied to amine **164**. BINOLs are commonly used as chiral

catalyst backbones, because of their remarkable stereoinducing character. However, since different types are naturally derived, abundantly available and in many cases commercial, a stoichiometric use of BINOLs as chiral auxiliary is also feasible, even though the cyclization would entail a bad atom economy.[127,128,129] To test this directing group strategy, (*R*)-BINOL (**188**) was treated with $POCl_3$ and amine **164** leading to the intended phosphonamide **189** in 20% yield (Scheme 51).[130] The cyclization of substrate **189** led to the desired cyclized structure **190** in 26% of NMR-yield and 21% *de*, which could both be derived from the crude NMR of the reaction. The ^{1}H-NMR spectrum of isolated **190** shows the respective two sets of signals for each diastereomer in an increased *de* value of 36% (Figure 8).



Scheme 51. Synthesis of **189** and stereoselective cyclization trial.[130]

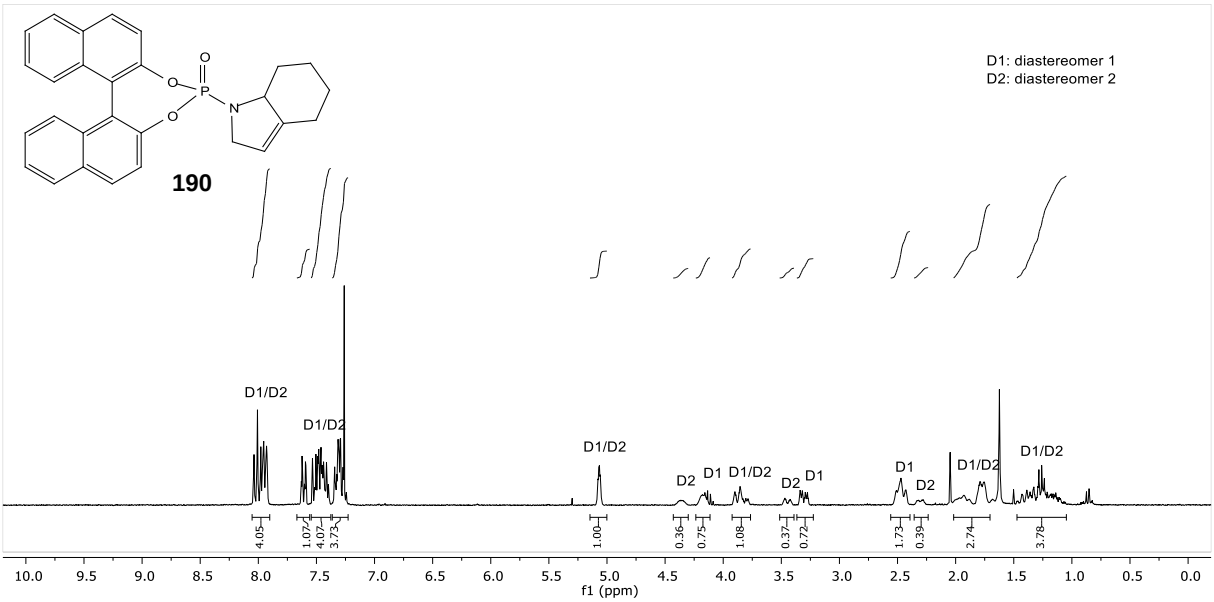
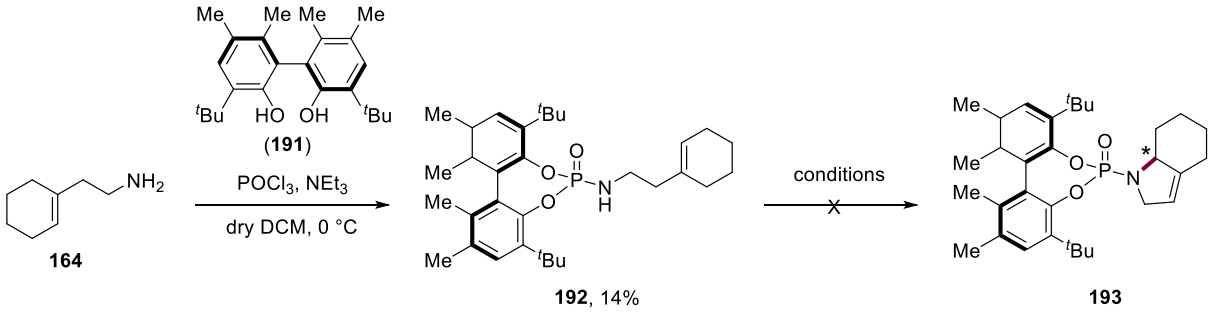


Figure 8. ^{1}H-NMR spectrum of isolated **190** as a diastereomeric mixture.

Following up this finding, a similar phosphonamide was synthesized carrying additional ^{t}Bu substituents at position 3 and 3` of the respective diaryl moiety (**192**, Scheme 52). Through the additional steric repulsion of these groups, the diastereoselectivity was expected to be improved. However, after the synthesis of **192** in 14% by the same protocol as for **189**,[130] the desired cyclization product was not obtained. Hence, not only the formation of the respective substrate seemed to be disfavored in the case of

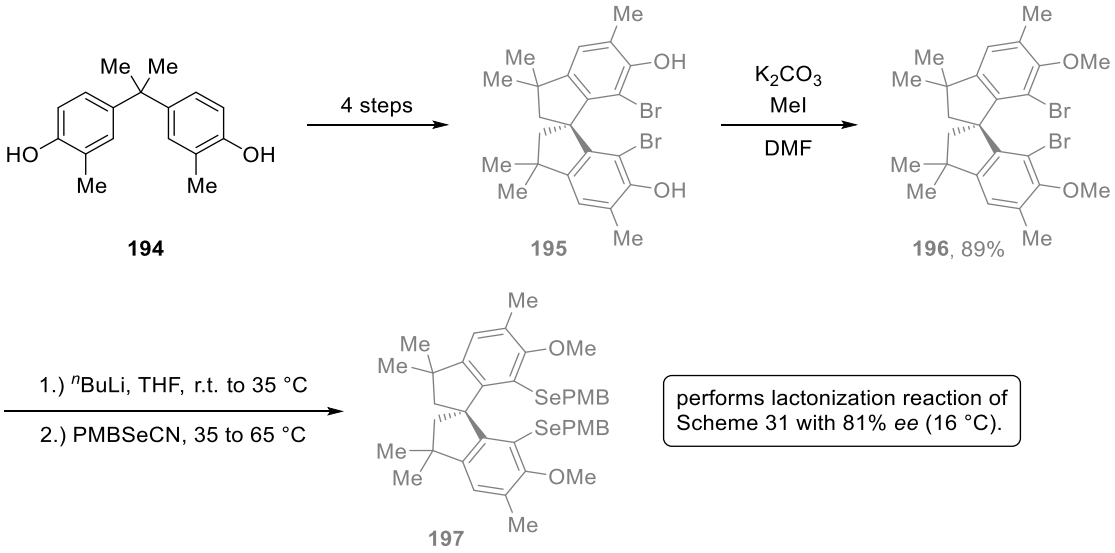
the sterically crowded ^{t}Bu substituted BINOL derivative **192**, but also the cyclization itself was completely prohibited.



Scheme 52. Synthesis of **192** and stereoselective cyclization trial.[130]

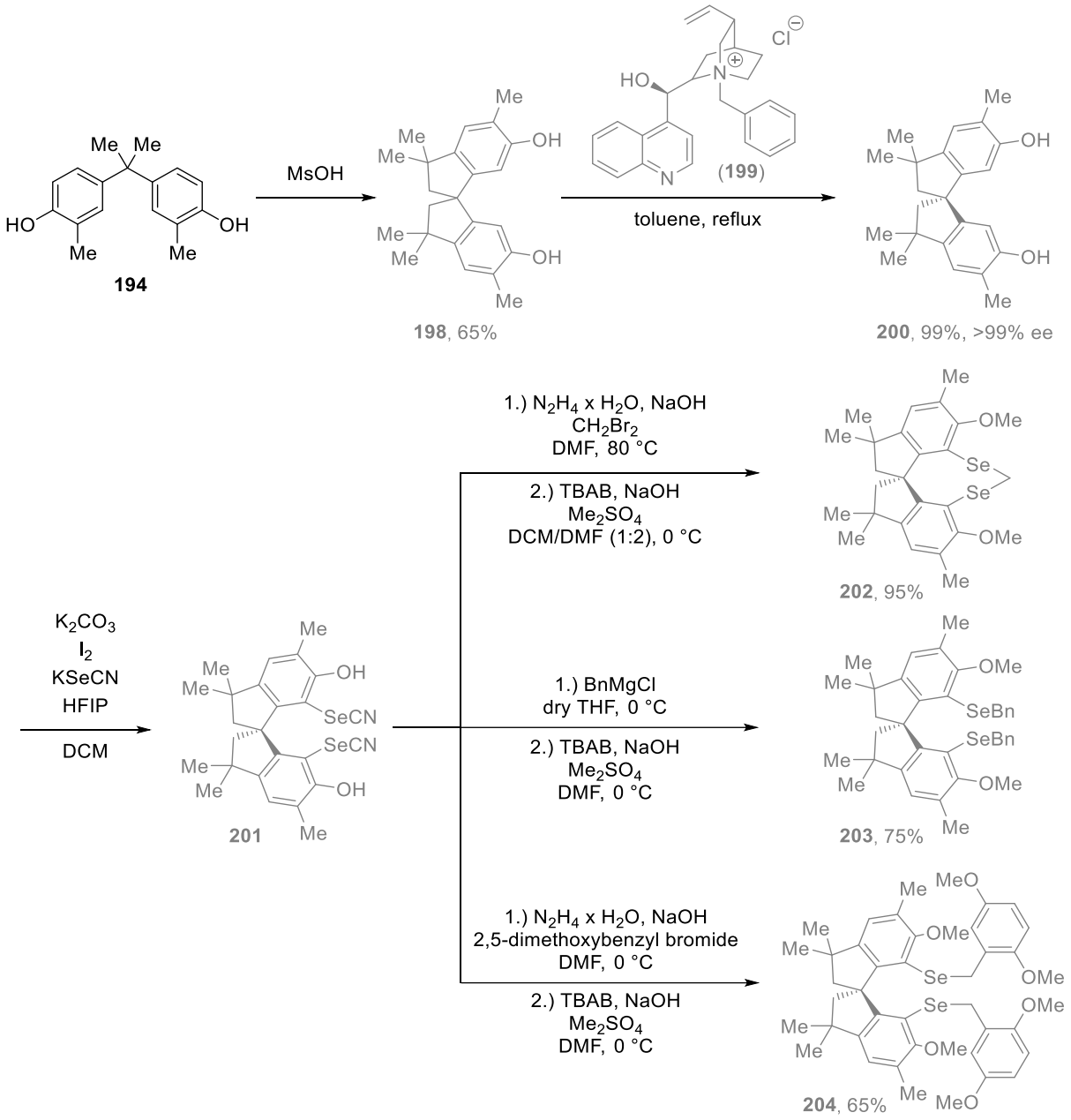
3.2.2 Rational design of a chiral selenium catalyst

Since the substrate-controlled enantioselective cycloamination could only achieve limited success in terms of selectivity and yield, the intended cyclization should be achieved through catalyst control. This type of stereoinduction is generally more favored in terms of chemical sustainability, as the substrate does not need to carry a specifically configured moiety, but the stereoinformation is only induced by the catalyst. Hence, only the catalyst has to carry the stereoinformation instead of each individual substrate.[131] As mentioned in section 1.4, Breder *et al.* have tested several chiral selenium catalysts within lactonization reactions, which proceed similarly to the cycloamination.[93] Among these, the best results were obtained with catalysts **115d-f**. By a structural analysis, the trend was derived that rigid catalysts perform the intended cyclization with better stereocontrol. Therefore, a chiral catalyst based on a rigid spirobiindane system was synthesized by Dr. F. Krätzschmar (Scheme 53).[98] After a literature known procedure by Lin *et al.* yielding intermediate **195**, a basic methylation with MeI led to **196** in 89%.[132] Next, lithium/halogen exchange of the bromides of **196** and selenylation with PMBSeCN could afford **197**. Remarkably, this catalyst was able to convert substrate **114** to the respective lactone in 81% *ee*. This result indicates that the applied spirobiindane backbone of catalyst **197** was very suitable for a proper stereoinduction.



Scheme 53. Synthesis of spirobiindane based selenium catalyst **197** by Dr. F. Krätzschmar.[132,133]

With this knowledge, other chiral selenium catalysts were designed by Dr. T. Lei containing the same chiral backbone of **197**, but with alternated leaving groups on the selenium moiety instead of PMB.[133] The synthesis of these started with the acidic formation of racemic spirobiindane **198** in 65% from bisphenol C (**194**, Scheme 54).[134] After a resolution of racemate **198** with optically pure quinuclidinium salt **199**, **200** was obtained in optically pure form and perfect yield. Next, a selenylation procedure using K_2CO_3, I_2, KSeCN and HFIP yielded intermediate **201**, which served as a precursor for all three selenium catalysts **202-204**. In this way, **202-204** were obtained after methylenation (**202**), benzylation (**203**) or 2,4-dimethoxybenzylation (**204**) of **201**, respectively, and subsequent etherification of the alcohols.



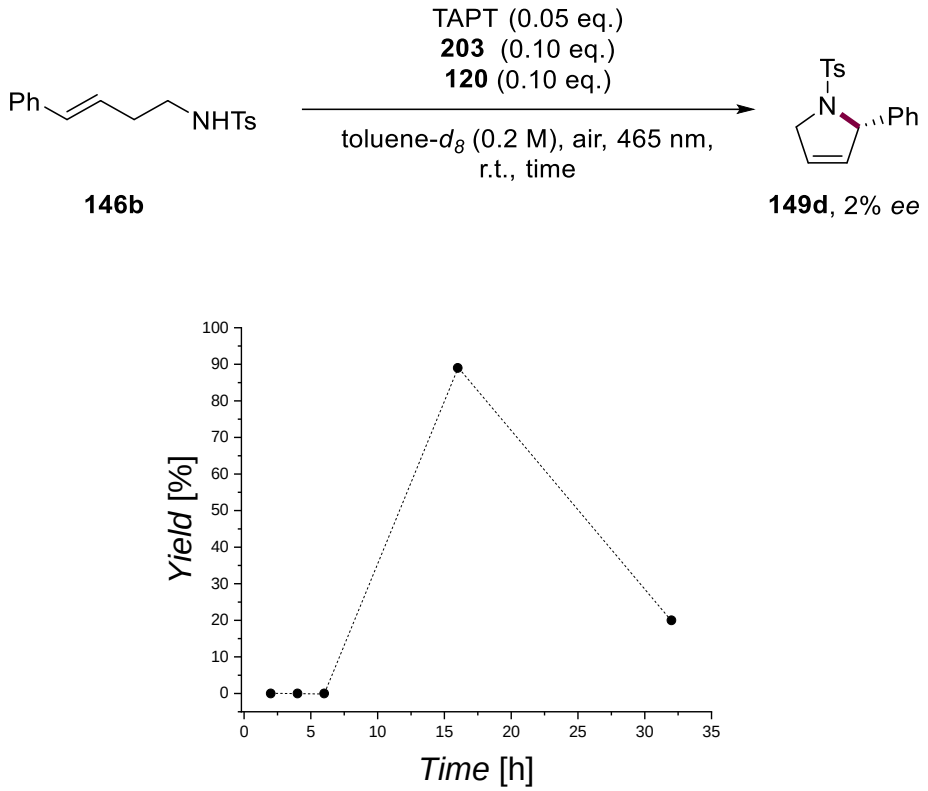
Scheme 54. Synthesis of chiral selenium catalysts **202-204** by Dr. T. Lei.[133,134]

Because of the similarity of the lactonization and the herein reported cycloamination, these catalysts served as a starting point for the enantioselective cycloamination.

3.2.3 Preliminary investigations and optimization

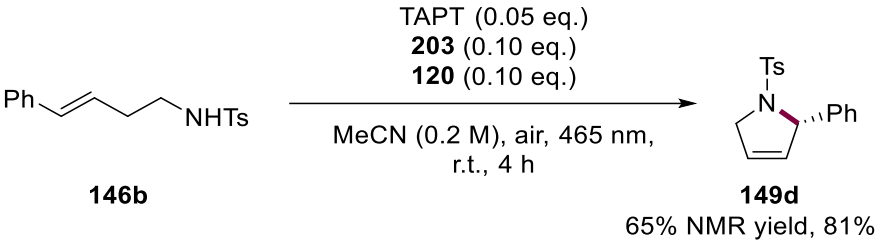
Already within the first study of the prepared catalysts from chapter 3.2.2, substrate **146b** showed a remarkably good conversion (89% after 16 h) to the respective product using chiral catalyst **203**. Thereby, the nonpolar solvent toluene-d_8 was used to track the reaction process directly *via* ^{1}H-NMR spectroscopy (Scheme 55). However, the

reaction only showed little stereoselectivity of 2% *ee*. By comparison of the HPLC traces to the ones reported by Ji *et al.*, the generated stereocenter could be assigned as (*S*)-configurated.[135] Notably, during the reaction it was observed that both, TAPT and **203** were not properly dissolved, but were rather present as finely suspended particles. This could potentially lead to a prolonged reaction time, in which the catalyst could either degrade to an achiral fragment, which is also capable of catalyzing the reaction, or the stereoinformation of the catalyst gets lost due to a multitude of addition/elimination processes onto the olefin as described in section 1.4. Also, it was found that the yield of **149d** significantly drops after 32 h, which indicates that the cyclized product is most likely degrading after a long exposure under the photoaerobic conditions.



Scheme 55. Formation of **149d** within the enantioselective cyclization of **146b** in toluene-d_8 using chiral catalyst **203** monitored *via* ^{1}H-NMR spectroscopy.

Hence, MeCN was chosen as a polar solvent to dissolve both catalysts. Fortunately, this change already led to a product yield of 65% NMR-yield and 81% *ee* (Equation 7). Remarkably, this selectivity value is in the same range of the one obtained within the conducted lactonization reactions using chiral selenium catalyst **197** (Scheme 53). Thus, this finding underlines the capability of a proper stereoinduction using chiral selenium catalysts with a spirobiindane backbone.

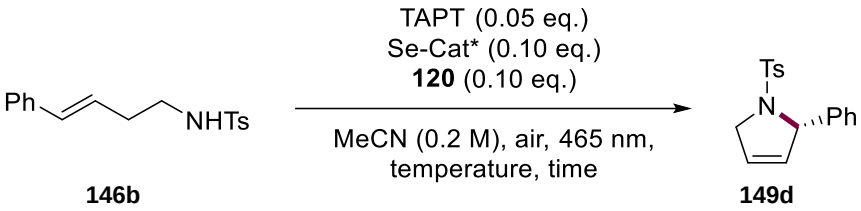


146b **149d**
65% NMR yield, 81% *ee*

(7)

Next, catalysts **202** and **204** were also tested and compared with the performance of catalyst **203** in this reaction (Table 2). Thereby, it was found that catalyst **204** leads to a similar *ee* value, but lower yields of 28%, and catalyst **202** leads to better yields but with a decreased *ee* value of 80%. It was also discovered that the setup of the reaction was a crucial factor. While the *ee* value of **149d** remained the same when the reaction was executed in a photovial or a 100 mL round bottom flask, the change of these setups had a drastic influence on the yield (Table 2, Entry 1 *vs.* 3). This result most likely can be explained by the change of irradiation. While in the photovial only a small irradiation surface led to a lower concentration of excited TAPT and thus lower amounts of yield, the irradiation in a 100 mL round bottom flask led to increased yields by the enlarged irradiation surface. Also, the diffusion rate of molecular oxygen, which was the required terminal oxidant for TAPT, was higher in the 100 mL round bottom flask than in the photovial due to the surface enlargement.

Table 2. Optimization of the chiral selenium catalyst.

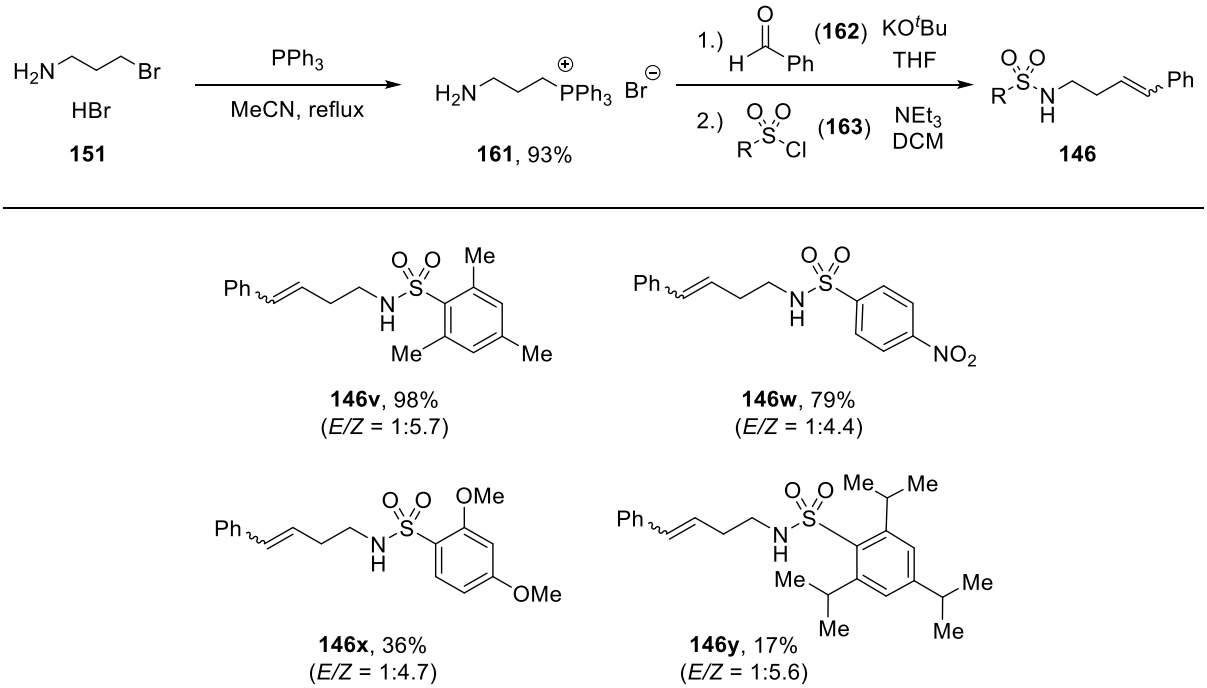


146b **149d**

Entry	Se-Cat*	Setup/ Comment	NMR-Yield [%][a]	*ee* [%][b]
1	**203**	100 mL round bottom flask[c]	**65**	**81**
2	**204**	photovial[d]	28	81
3	**203**	photovial	31	81
4	**202**	photovial	56	80

[a]1,3,5-trimethoxybenzene as internal standard. [b]*ee* determined *via* chiral HPLC. [c]reaction conditions: 4 h, r.t. [d]reaction conditions: 140 min, 55 °C.

Using these established conditions, further fine tuning of the reaction was conducted by the application of different sulfonyl protecting groups. Thereby, it was assumed that the electronic nature as well as the steric change of moieties can influence the attack of the adjacent amine to the activated double bond. For this purpose, in addition to substrates **146m-s** (Scheme 41), another group of substrates, **146v-y**, was synthesized by the formation of Wittig salt **161**, subsequent Wittig Reaction and sulfonamidation (Scheme 56).[95,106]

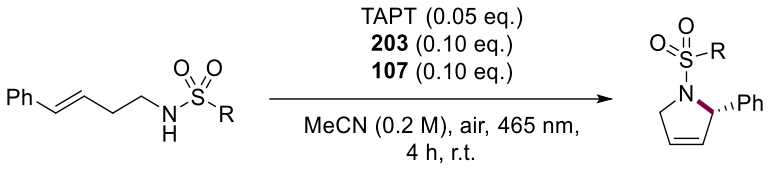


Scheme 56. Synthesis of 4,5-unsaturated sulfonamides **146v-y** *via* Wittig Reaction and subsequent sulfonamidation.[95,106]

With these different sulfonamides in hand, the enantioselective cyclization was conducted. Among all substituents, *o*-nitrophenyl (**146n**, Table 3, Entry 7) performed the best in terms of selectivity (94% *ee*). On the other side, the *p*-nitrophenyl substituted substrate (**146w**, Table 3, Entry 6) only gave 70% *ee*. Replacing *p*-Tol with the sterically more demanding Mes increases the *ee* from 81 to 83% and the yield from 65 to 95% (**146v**, Table 3, Entry 3). The same steric trend was determined for the smaller and unconjugated Me-substituted **146m**, which only gave 75% *ee* (Table 3, Entry 2). However, further enlargement of the substituent to a 2,4,6-TIPP shows only the same *ee* value as in the case of **146y**, but with decreased yields (Table 3, Entry 4). Also, it is notable, that electronically rich substituents like *p*-anisyl (**146o**) and *o*-,*p*-dimethoxyphenyl (**146x**) enhance the stereoselectivity, but at the same time decrease the yield of product (Table 3, Entries 5 and 8). Considering these results, the best

compromise between a high yield paired with a good stereoselectivity was given with substrate **146v** (Table 3, Entry 3). Hence, the Mes moiety was attached to all substrates in the following section.

Table 3. Optimization of the sulfonyl backbone.



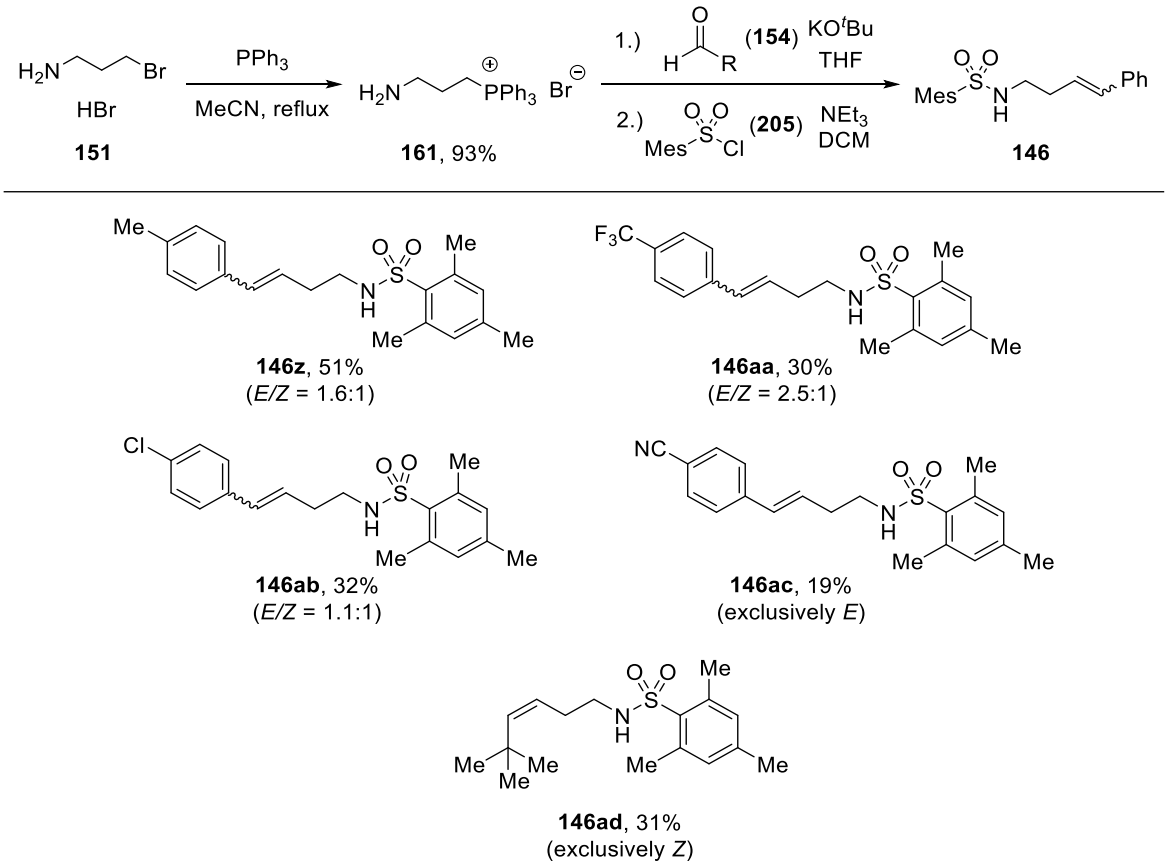
146 **149**

Entry	R	NMR-Yield [%][a]	*ee* [%][b]
1	*p*-Tol (**146b**)	65	81
2	Me (**146m**)	46	75
3	Mes (**146v**)	**95**	**83**
4	2,4,6-TIPP (**146y**)	21	83
5	*p*-anisyl, photovial (**146o**, 0.3 mmol scale)	28	84
6	*p*-nitrophenyl, photovial (**146w**, 0.3 mmol scale)	85	70
7	*o*-nitrophenyl (**146n**)	52	94
8	*o*-, *p*-dimethoxyphenyl (**146x**)	31	86

All reactions were carried out in a 100 mL round bottom flask setup except stated otherwise. [a]1,3,5-trimethoxybenzene as internal standard. [b]*ee* determined *via* chiral HPLC.

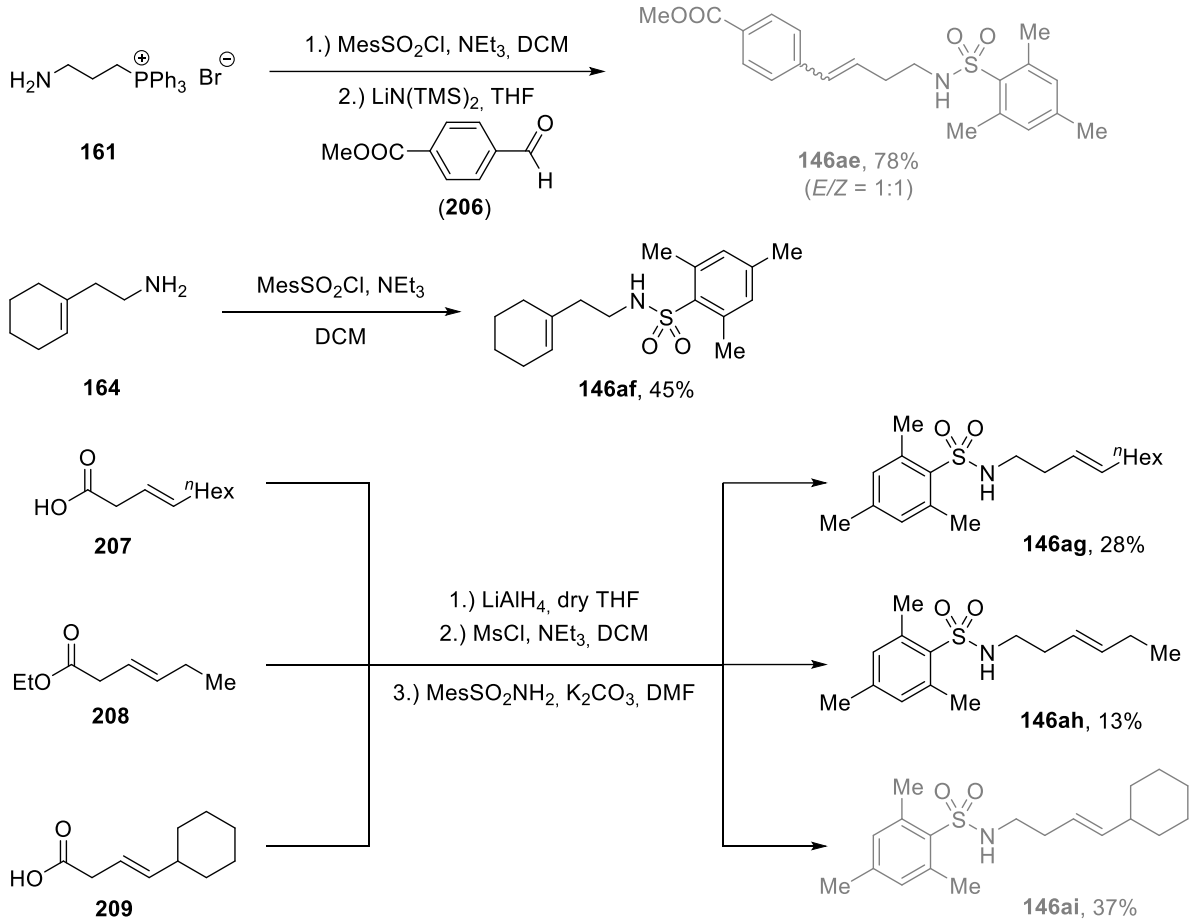
3.2.4 Synthesis of substrates

With the knowledge of the best reaction conditions and sulfonamide protecting group for the substrate, a general route to obtain a broad range of substrates was designed (Scheme 57). Thereby, a group of substrates could be synthesized from the common precursor, (3-aminopropyl)triphenylphosphonium bromide (**161**), which was synthesized from 3-bromopropylamine hydrobromide **151**.[106] From there, different benzaldehyde derivatives (**154**) served as the coupling agents for Wittig Reactions. The following sulfonamidations led to the respective scope of substrates **146z-146ad** ranging from 19 to 51% yield.[95]



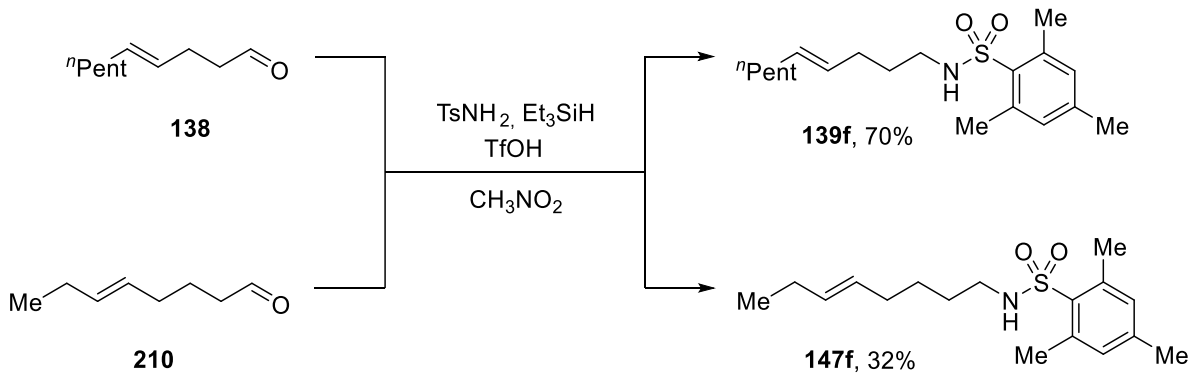
Scheme 57. Synthesis of 4,5-unsaturates mesitylenesulfonamides **146z-146ad** *via* Wittig Reaction.[95,106]

Other synthetic pathways towards 4,5-unsaturated mesitlyensulfonamides included the sulfonamidation of **161** and Wittig Reaction afterwards leading to **146ae** in 78% or direct sulfonamidation of amine **164** to **146af** in 45% yield (Scheme 58). Also, commercial acids or esters (**207-209**) could be used by the reduction with $LiAlH_4$ to the corresponding alcohols, mesylation and eventual basic substitution with mesitylenesulfonamide towards **146ag-146ai**.[101]



Scheme 58. Other applied routes towards 4,5-unsaturated mesitylenesulfonamides **146ae**-**146ai**. **146ae** and **146ai** were synthesized by Dr. T. Lei.[101]

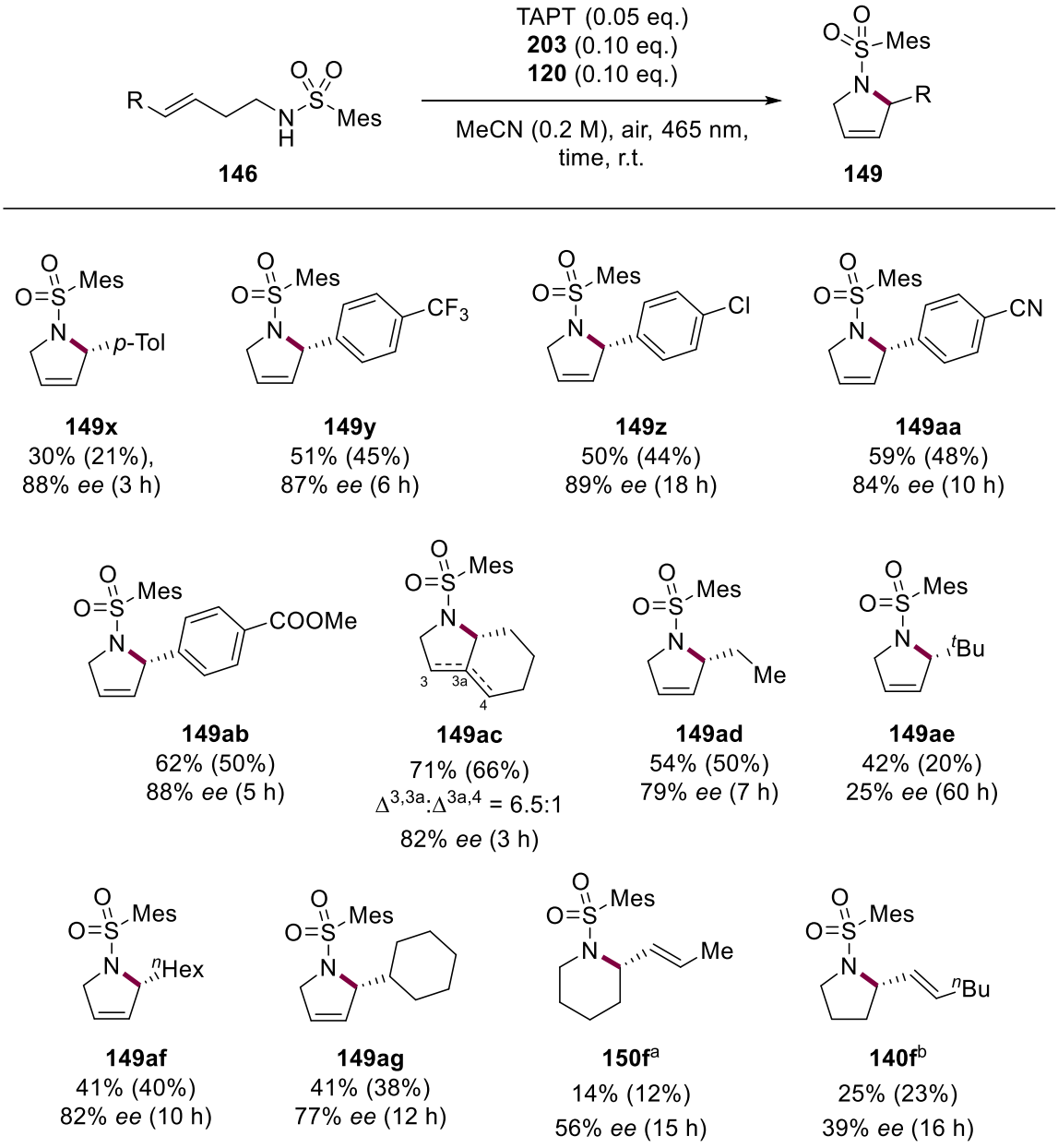
To investigate the compatibility of the enantioselective cycloamination protocol with 5,6-unsaturated and 6,7-unsaturated sulfonamides, as in the case of the racemic reaction, **139f** and **147f** were synthesized using the reductive amidation protocol (Scheme 59).[102]



Scheme 59. Synthesis of 5,6-, and 6,7-unsaturates mesitylenesulfonamides **139f** and **147f** *via* reductive sulfonamidation.[102]

3.2.5 Cyclization reactions

Using the optimized conditions for the enantioselective cycloamination, an array of arylated and alkylated 4,5-unsaturated substates could be converted to the respective 3-pyrrolines (**149x-149ag**) in moderate to good yields and consistent *ee* values (Scheme 60). In the case of the aryl substituted ones, it is noticeable that electronically poor moieties like **149y**, **149aa** and **149ab** can be converted in higher yields (51-62%) than electronically enriched ones (**149x**, 30%).



Scheme 60. Product scope of enantioenriched 2-substituted 3-pyrrolines (**149x-149ag**), pyrrolidines (**140f**) and piperidines (**150f**). ^{1}H-NMR yields determined with 1,3,5-trimethoxybenzene as internal standard, isolated yield in parenthesis. [a]from **147f**. [b]from **139f**.

Remarkably, among this group the *E*/*Z* ratio of the substrates did not influence the outcome of the reaction in terms of selectivity. This special feature of the reaction is discussed further in sections 3.4.3 and 3.4.4.

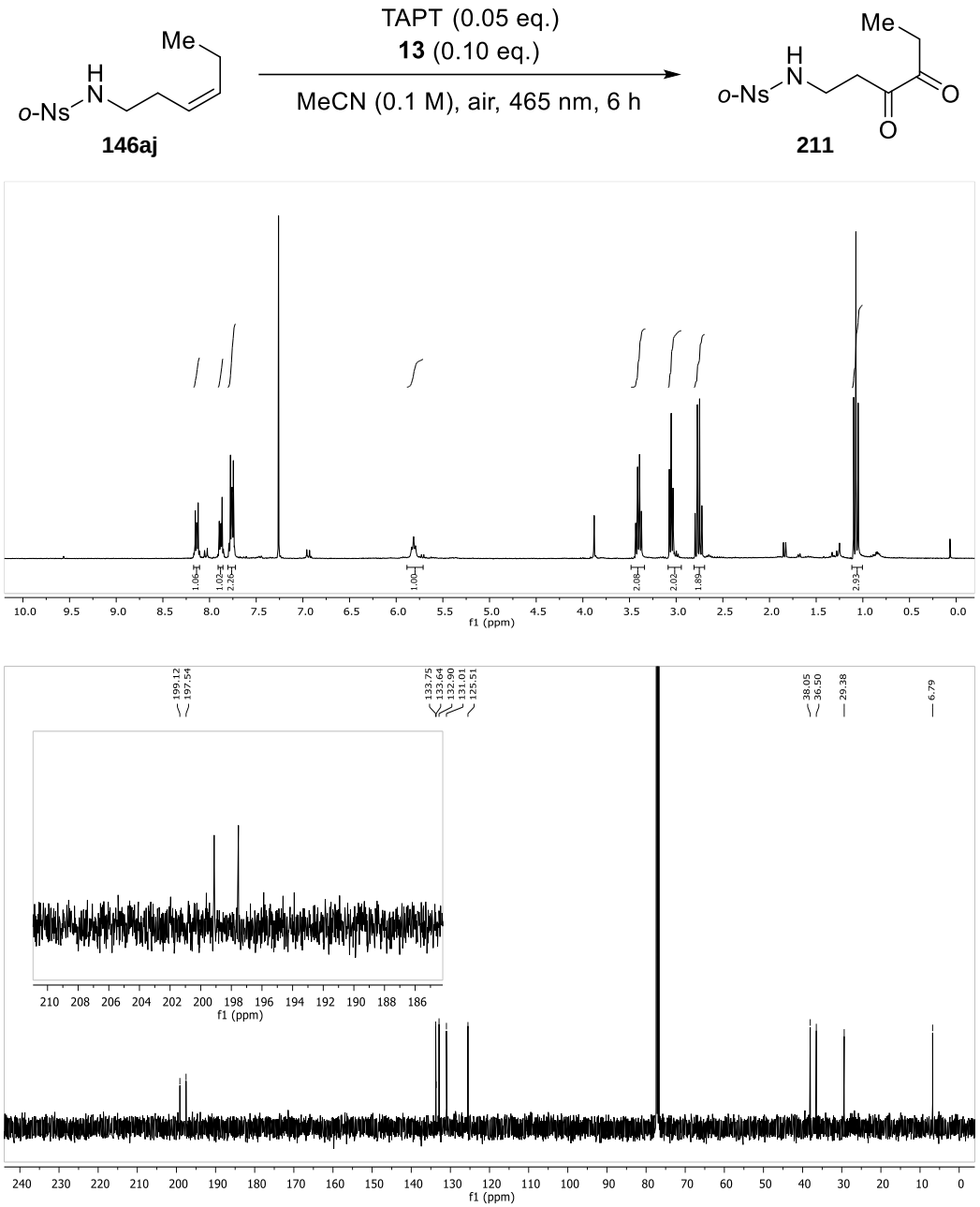
Besides, alkylated substrates were tolerated by this protocol and led to moderate yields with only little loss of *ee* in the case of **149ad**, **149af** and **149ag**, but with drastically declined one for **149ae**, which is counterintuitive considering the sterical demand of the ^{t}Bu group. This could be due to the fact that this substrate was converted only very slowly (60 h) and the stereoinduction of the catalyst was decreased, because of partial degradation of catalyst **203** or a developing racemization process as described in section 1.4. Remarkably, as in the case of the racemic reaction, substrate **146ad** also produced two regioisomers (**149ac**) with the double bond between C3 and C3a or C3a and C4. Furthermore, the conversion of 5,6- and 6,7-unsaturated substrates **139f** and **147f** to the respective pyrrolidine (**140f**) and piperidine (**150f**) took place, but was only marginally successful regarding the yields as well as the enantioselectivities.

Since the racemic version of this reaction already represents the first aminocyclization on alkenes leading to 3-pyrrolines, this enantioselective protocol represents the first asymmetric version towards this class of compounds. More generally, this catalytic protocol exemplifies one of the few reported enantioselective photoredox-catalytic functionalizations of simple alkenes. In the realm of this specific field, the majority of protocols relies on the presence of a heteroatom within the substrate, that can either covalently or noncovalently bind to the active catalyst.[136] Only by this interaction the following asymmetric reaction can be ensured. In contrast, this reaction stands out, because it uses completely unbiased alkenes for the respective cycloamination reactions and the stereoinduction is enabled by the mere interaction of the catalyst with the alkene.

3.3 Unexpected observations during the reaction scope

During the elaboration of the cycloamination protocols, few unexpected reactions within the substrate synthesis and the cyclizations were observed. One was discovered during the reaction of *o*-Ns compound **146aj**, which was attempted to be cyclized to the respective 3-pyrroline but did not show the desired reactivity. Instead, small amounts of a compound were obtained, which showed no signals in the olefinic region

of the ^{1}H-NMR spectrum (Scheme 61 above), two downfield shifted signals in the ^{13}C-NMR spectrum (199.12 and 197.54 ppm, Scheme 61 below) and a strong vibration at 1715 cm^{-1} (Figure 9 above). These measurements suggest that the alkene moiety was converted to a carbonylic one. Since MS revealed a $[M+H]^+$ signal of 315.0 g/mol and also a $[M-H_2O+H]^+$ at 297.0 g/mol (Figure 9 below), which is characteristic for carbonyl moieties, it could be derived that the (*Z*)-configurated double bond of **146aj** was oxidized to the respective dicarbonyl moiety **211**. Hence, both carbons were oxidized from the oxidation state (−I) to (+II), but no oxidative cleavage, which is usually observed in suchlike reactions, was detected.[137]



Scheme 61. Unexpected oxidation of **146aj** to **211**, analysis *via* ^{1}H-NMR (above) and ^{13}C-NMR (below).

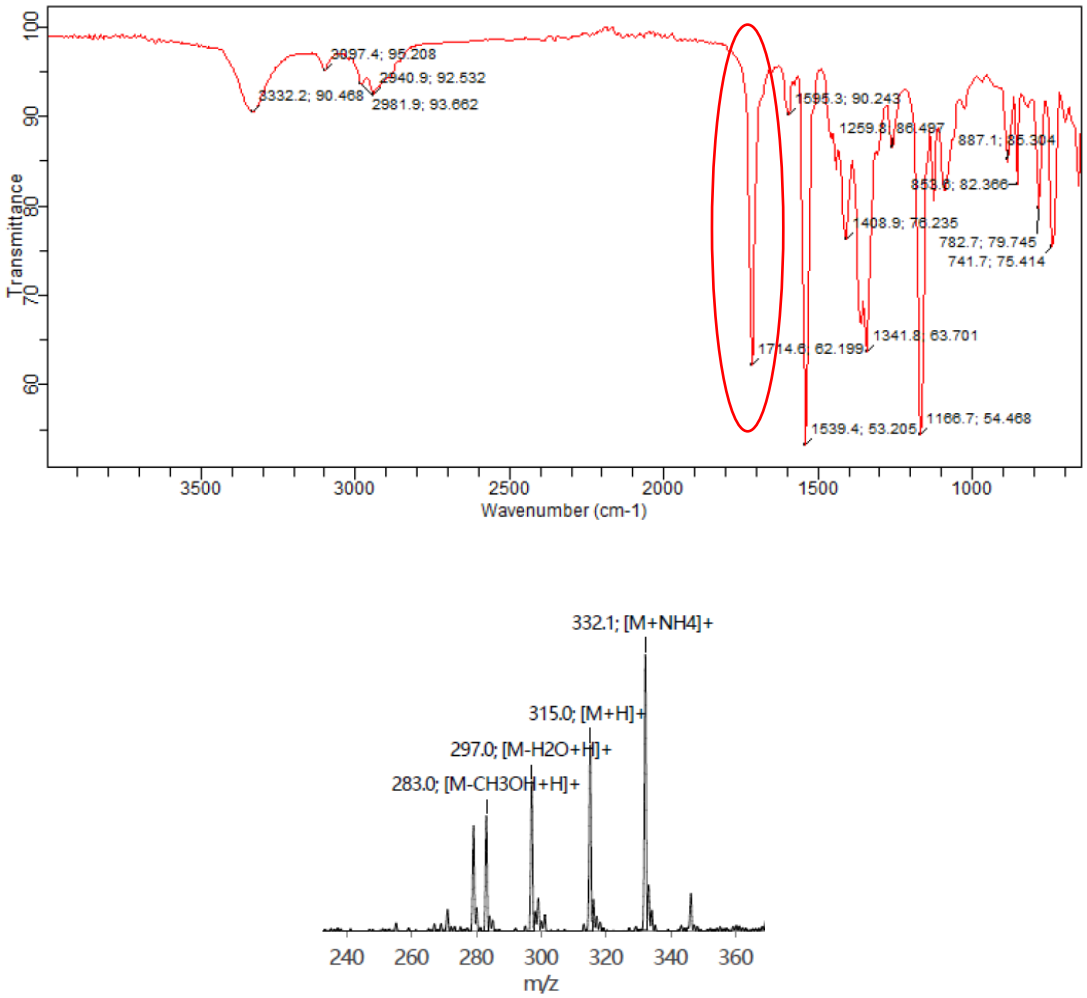
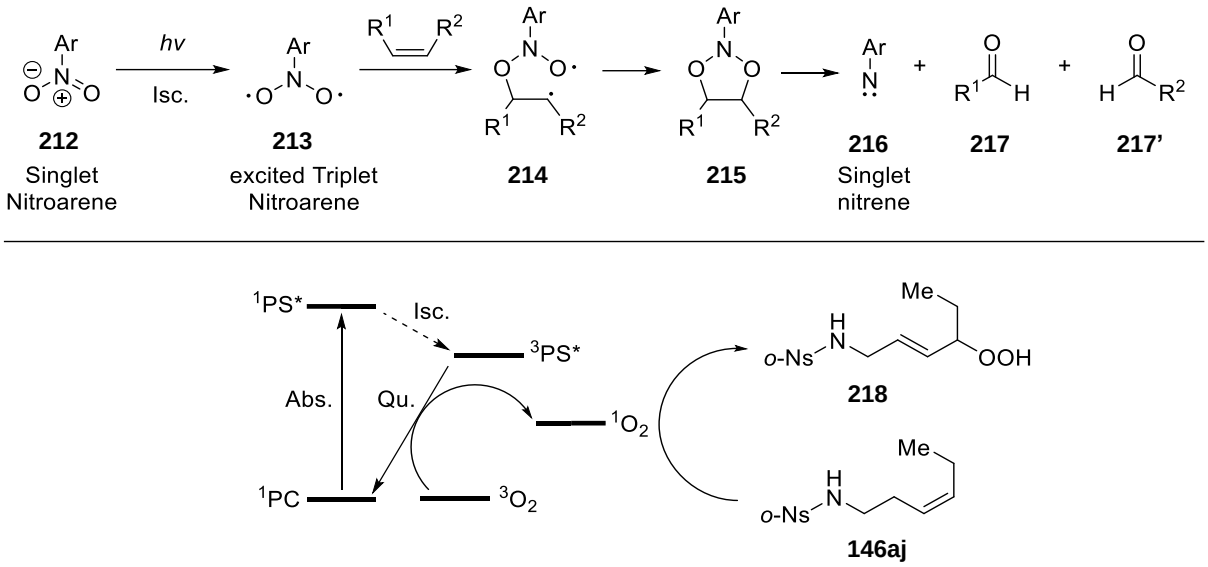


Figure 9. Analysis of **211** *via* IR spectroscopy (above) and MS (below).

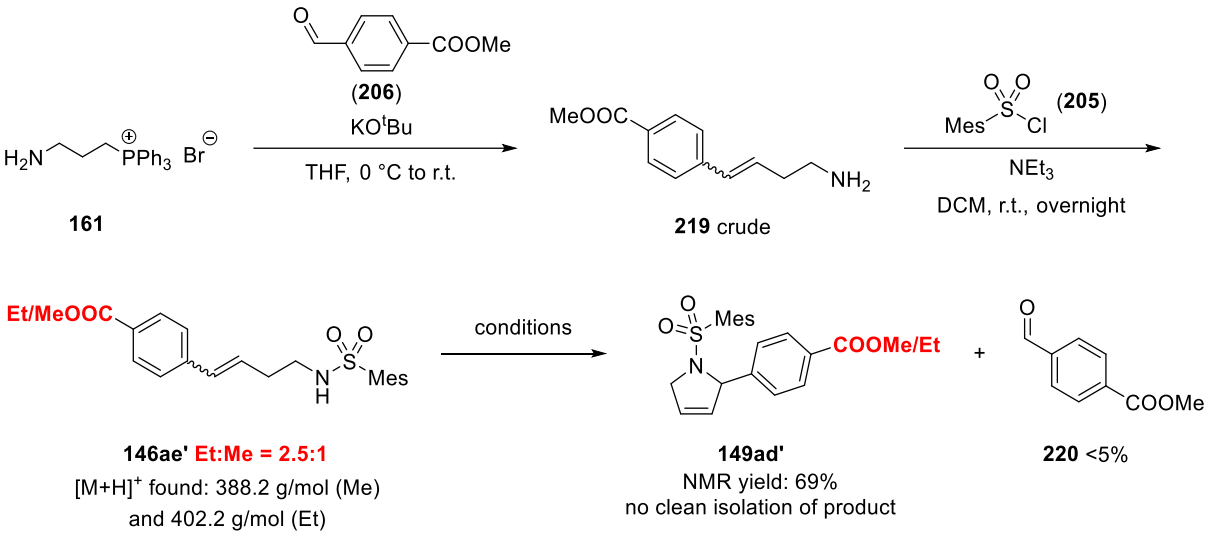
This process could potentially be induced by the nitro group of the *o*-Ns protecting group. Leonori *et al.*[137] report that such an oxidation typically leads to the cleavage of the two generated carbonyl moieties *via* the opening of a difunctionalized nitroarene (Scheme 62, above), however in this case the bond between the two carbonyl moieties was conserved. Another possibility for the formation of **211** could be the oxidation with $^1O_2$ within a Schenck-Ene Reaction (Scheme 62, below).[138] Potentially, $^1O_2$ could be formed by a triplet energy transfer from the photocatalyst, that has been excited and performed an inter system crossing from the excited singlet to the excited triplet state. Nevertheless, this kind of oxidation would lead to allylic peroxide **218** or its regioisomer, hence a follow-up reaction is needed to generate **211**, and, moreover, the reaction rate of dialkylic olefins is typically very low.[138]

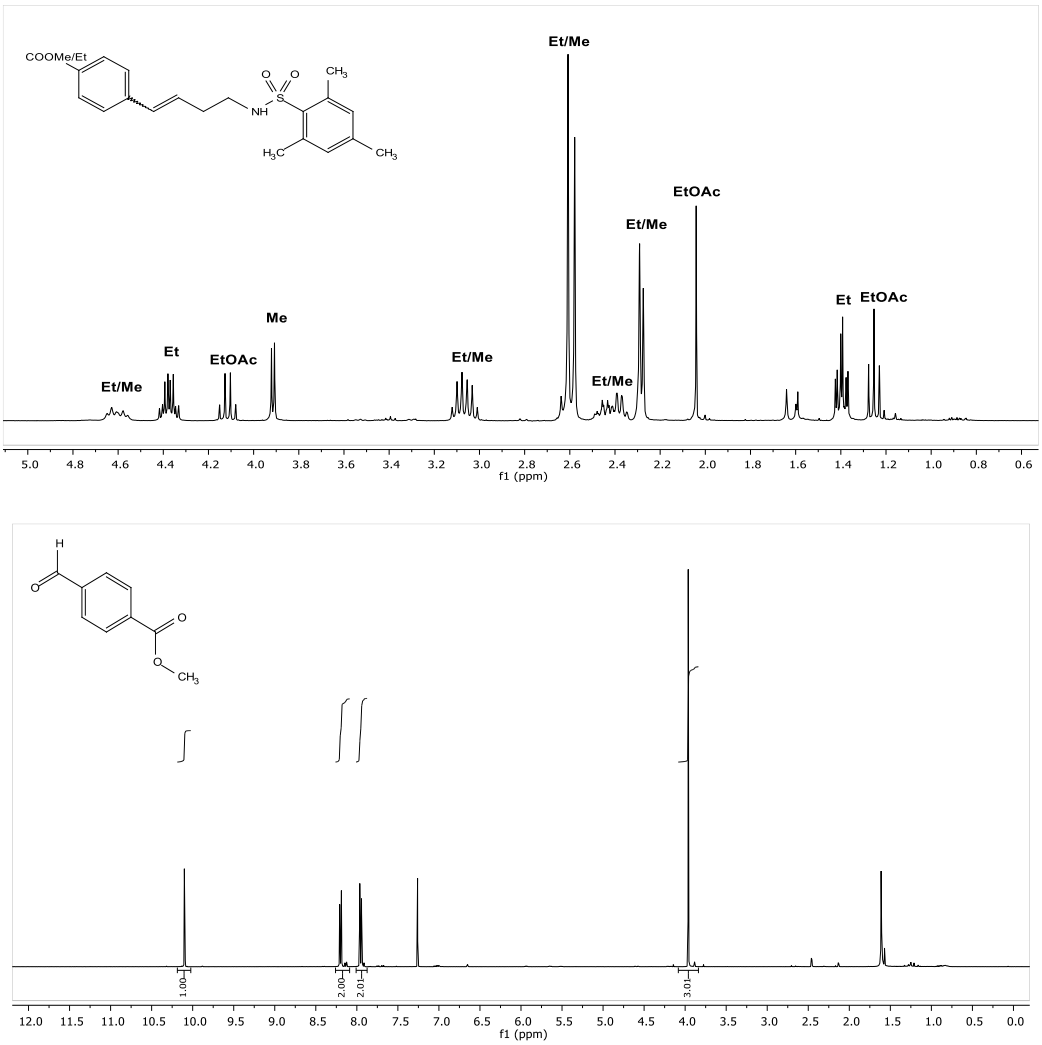


Scheme 62. Oxidative cleavage of alkenes *via* excited nitroarenes (above)[137], formation of $^1O_2$ and follow-up Schenck-Ene Reaction of **146aj**. Abs.: absorbance; Isc.: intersystem crossing; Qu.: luminescence quenching (below)[138].

Another unexpected event was the transesterification of compound **146ae'** (Scheme 63). During the elaboration of the reaction scope for the asymmetric protocol, the Wittig Reaction of **161** yielded the primary amine **219** as the expected methylester, but in the next step, crude **219** was sulfonaminated with $MesSO_2Cl$ (**205**) under basic conditions and **146ae'** was obtained as a mixture of the methyl and ethyl ester, which could be conformed *via* MS and ^{1}H-NMR spectroscopy (Scheme 63). During the isolation and purification of **146ae'**, two possible routes, where an ethyl group could be exchanged, can be discussed. First, the crude mixture of the reaction from **219** to **146ae'** was extracted with DEE. Here, the transesterification of **146ae'** is unplausible, because of the low reactivity of DEE within substitution reactions. Second, the purification of extracted **146ae'** was performed by column chromatography using PE and EtOAc as eluents. Thereby, a transesterification could be a possible consequence, because the silica gel from the column creates a slightly acidic media, which is necessary for ester cleavages, as well as esterifications. The following cyclization led again to a mixture of cyclized methylated and ethylated ester with a combined NMR-yield of 69% (Scheme 63, **149ad'**). Next to the desired product, **220** could be separated from the reaction mixture as a side product. A most likely reason for the formation of **220** is the oxidative cleavage of the styrylic double bond by a [2+2] cycloadditon with $^1O_2$ and a follow-up electrocyclic ringopening.[139] Since the mixture of the esters could not be separated and thereby prevented a proper analysis of the compounds, another

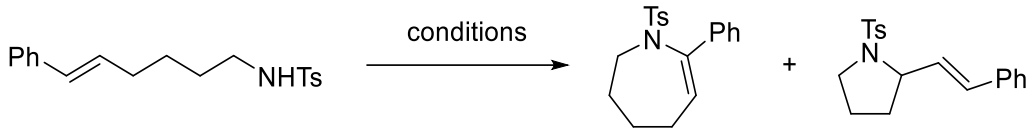
synthetic procedure was used to afford the pure methylated ester of **146ae**, which was shown in section 3.2.4 (Scheme 58).





Scheme 63. Transesterification and ^{1}H-NMR spectrum of **146ae'** (center) and formation of **220** as a side product (below).

Within an experiment to trigger a *7-endo-trig* cyclization, **221** was used as the substrate of choice (Equation 8). Here, only the *7-endo-trig* cyclization was expected, which is a preferred process according to the Baldwin rules,[105] since the competing *exo*-cyclization would not lead to the regeneration of the double bond due to the adjacent phenyl ring. Unexpectedly, the reaction led to a 2:1 mixture of inseparable products, **222** and **140g**. For the mixture only one mass of 328.1 g/mol could be detected as the $[M+H]^+$ signal.



221 **222** **140g**

2:1 mixture, $[M+H]^+$ found: 328.1 g/mol

The signals could be attributed to the respective compounds *via* 2D-NMR spectroscopy (Figure 10). From the major set of signals only few could be analyzed separately because of overlap. The signal at 3.78 ppm and one at ~3.50 ppm, which is overlapping with a signal from the other compound, most likely can be assigned to the α-protons of the amine, because of the characteristic chemical shift and the coupling constant 11.6 Hz, which indicates a vicinal coupling. The signal at 5.64 ppm is a duplet of duplets and most probably can be assigned to an olefinic moiety that only couples to an adjacent methylene moiety. The proton signals derived from the alkyl moieties are overlapping in the region between 1.00-2.10 ppm and are therefore unusable for a clear assignment. Based on this analysis, the 7-membered ring motive of **222** can be suggested as a possible structure, which can be rationalized by a *7-endo-tet* cyclization (Scheme 64, path A). The minor set of signals is identical to the one of **140g**, which was obtained by a *5-exo-trig* cyclization during the elaboration of the racemic scope of this reaction (Figure 11). In this case the cyclization most likely occurred in an allylic fashion, which was already observed by Breder *et al.* in former works.[140] Here, this outcome can be rationalized by the formation of an intermediate allylselane that undergoes a S_N2' reaction (Scheme 64, path B).

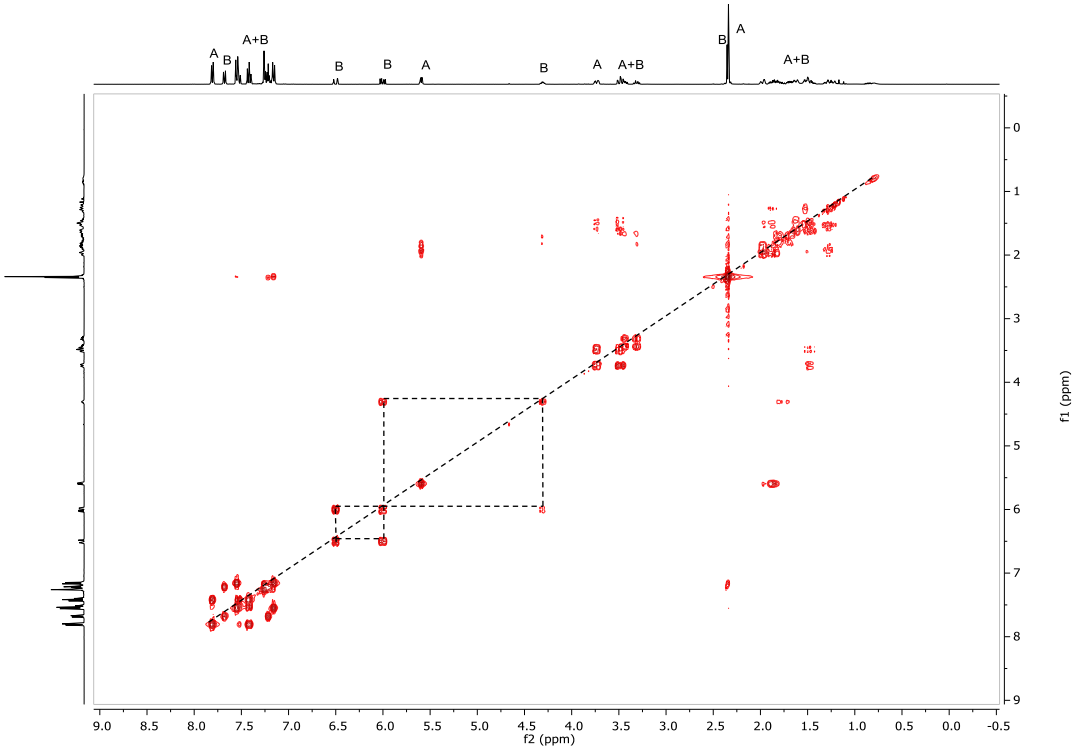


Figure 10. Assignment of the two signal sets for **222** (A) and **140g** (B) (2:1) *via* 2D-NMR spectroscopy (COSY). Decisive correlations for B are assigned.

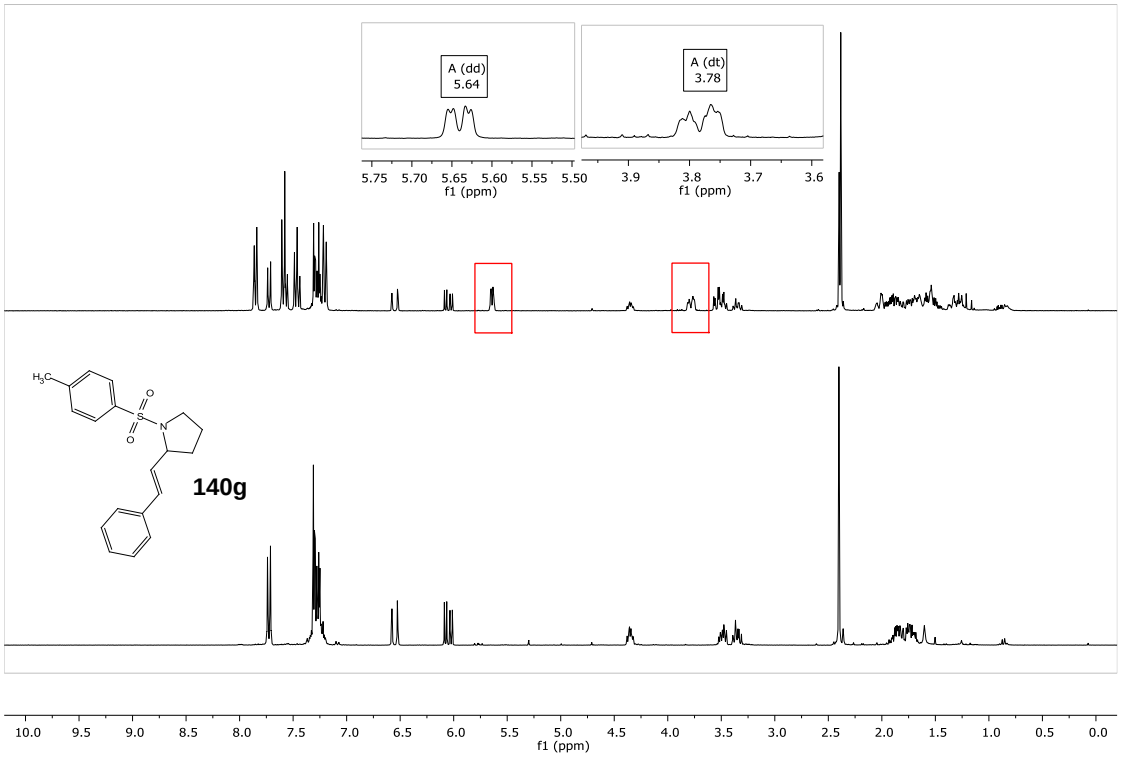
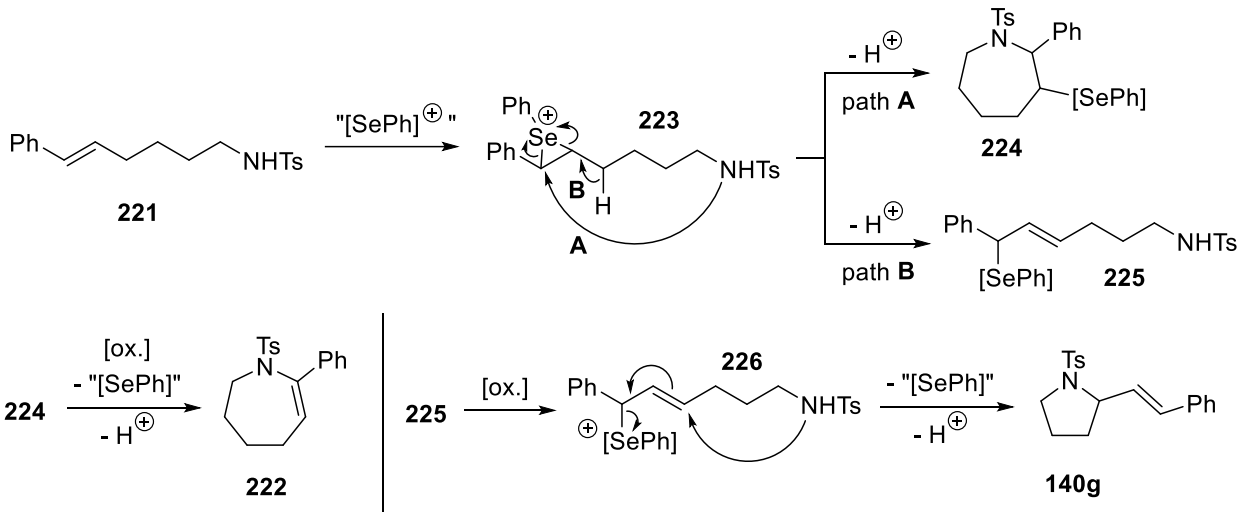


Figure 11. ^{1}H-NMR spectrum of **222** and **140g** (2:1, above) and comparison to the one of pure **140g** (below).

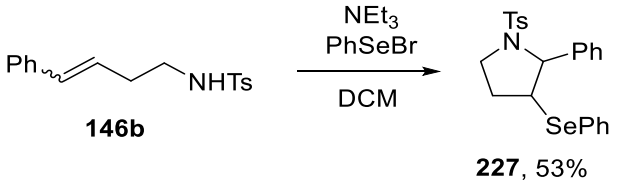


Scheme 64. Mechanistic proposal for the formation of **222** and **140g**.

3.4 Mechanistic investigations of the cycloamination

3.4.1 Initial rate experiments

For the elucidation of the mechanism of this reaction, the potential intermediate **227** of substrate **146b** was synthesized according to Breder *et al.* in 53% yield (Equation 9).[95] The assumption that **227** could be the intermediate of this reaction was derived from former works on lactonization reactions using the same catalytic regime.[110] Moreover, small amounts of **227** could be detected *via* MS in the photoaerobic cyclization of **146b**.



(9)

With **227** in hand, the product formation starting from substrate **146b** or intermediate **227** was measured over time *via* ^{1}H-NMR-spectrometry (Figure 12). By comparison of the product formation rate *via* the course of both graphs, it is noticeable, that both compounds produce **149d** within a similar time frame. This indicates that the cyclization to intermediate **227** happens quickly, and that the second step, the elimination of the selenium moiety and the resulting double bond formation, is rate determining.

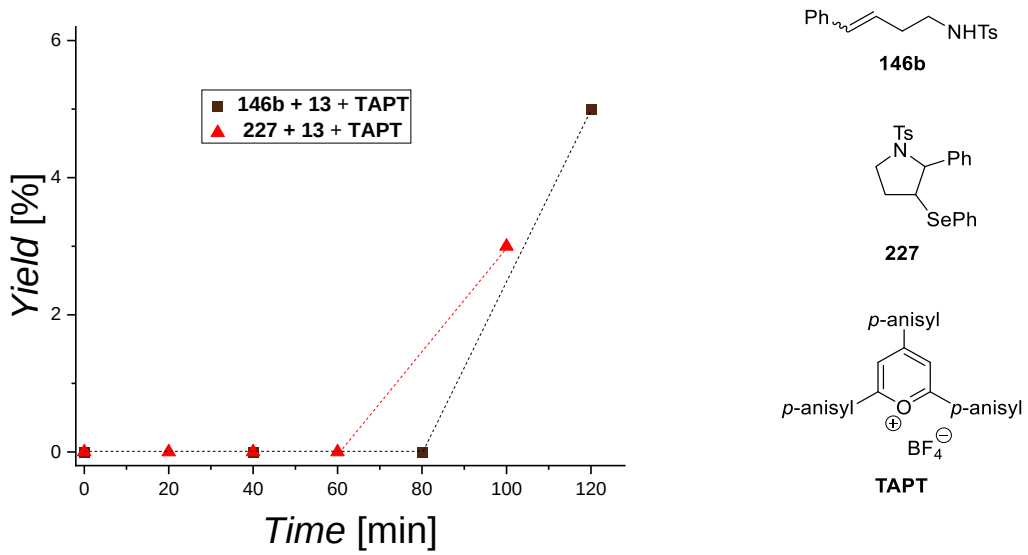
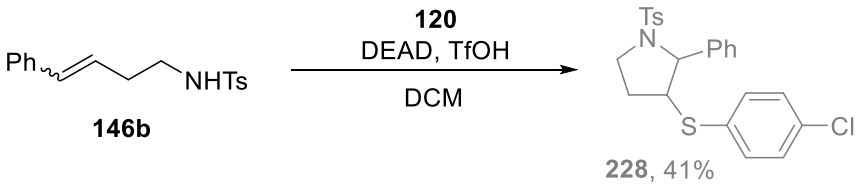


Figure 12. Comparison of the reaction course starting from **146b** or **227** *via* ^{1}H-NMR spectroscopy.

Next, since the reaction was found to be accelerated by the coaddition of disulfide **120**, the influence of this compound was examined by a similar experiment. Therefore, the presence of an alternate intermediate bearing the S-moiety in analogy to **227** must also be assumed. For this purpose, **228** was synthesized by T. Appleson according to Zhao *et al.* in 41% yield (Equation 10).[141]



(10)

In the reaction conducted with disulfide **120** a drastic increase of the slope was detectable when starting from substrate **146b** (Figure 13, orange ball). It is noticeable that after an initiation phase of 20 min without product formation, the formation of **149d** emerges linearly. From this one can derive that in the first segment the fast cyclization to the intermediate happens exclusively. Only afterwards, the second oxidation participates and leads to the formation of **149d**. For the comparison of the initial rates, the reaction was repeated with possible intermediated **227** and **228**.

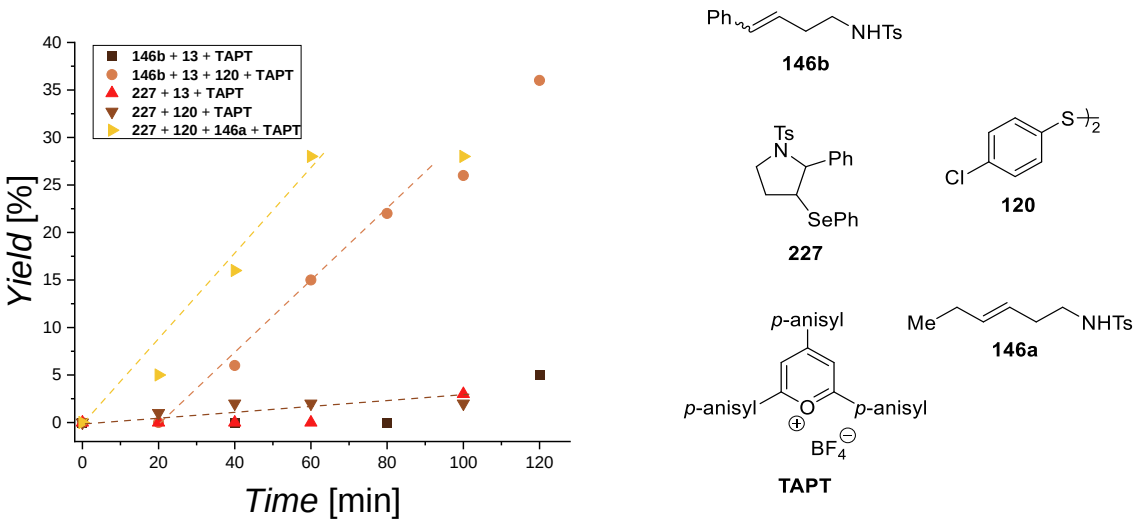


Figure 13. Initial rate experiment.[142]

In the case of **228**, neither with **13**, nor with **120** a considerable quantity of product was formed. However, in the case of **227**, product formation could be detected already after 20 min, but with a lower rate (Figure 13, brown triangle). Taking into consideration, that during the reaction **13** is formed in stoichiometric amounts, which is expected to be a quencher of this reaction, the experiment was repeated with the addition of alkene **146a**. Thereby, **146a** served as a scavenger for the generated **13**. In this case, a similar slope in comparison to **146b** with disulfide **120** was obtained (Figure 13, yellow triangle). Notably, in this experiment product formation starts immediately, which underpins the previous assumption of an initiation phase when starting from **146b**.

3.4.2 Stern-Volmer quenching experiments

The fluorescence quenching of the excited photocatalyst for **13**, **120** and **227** was measured and compared within a Stern-Volmer experiment, which was conducted by T. Appleson (Figure 14).[142,143] From this, one can derive that **13** is the fastest quencher of excited TAPT, followed by **120** and finally **227** (Table 4). Hence, **13** is most likely oxidized at first and activates the olefinic moiety of the substrate to trigger the cyclization to **227**. After full consumption of **13**, **120** is oxidized, and finally **227**.

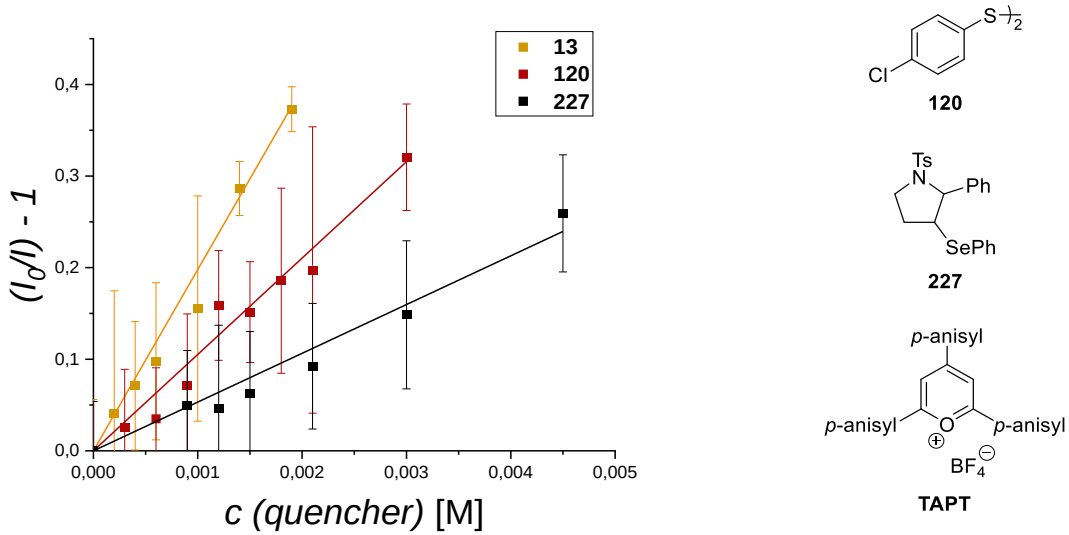


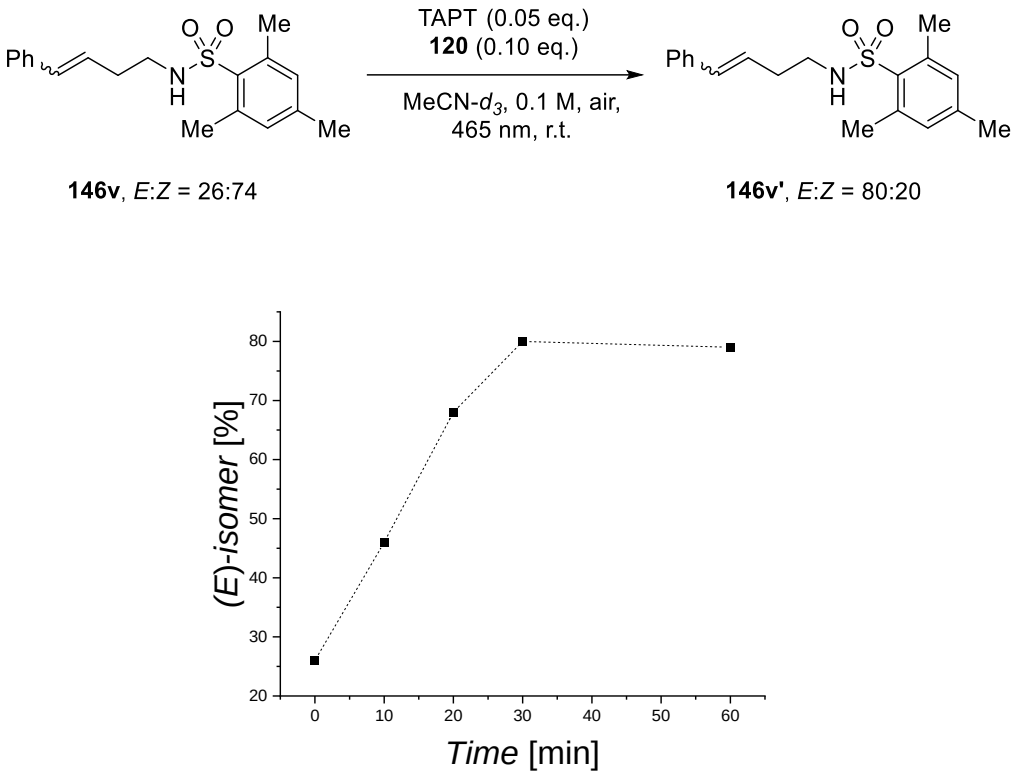
Figure 14. Stern-Volmer plot of **13**, **120** and **227** with the quencher TAPT (from T. Appleson).[142]

Table 4. Stern-Volmer constants derived from the slope of the Stern-Volmer plot (from T. Appleson).[142]

Quencher	Stern-Volmer constant [M^{-1}]
13	198 ± 2
120	105 ± 4
227	53.2 ± 2.5

3.4.3 *E/Z* isomerization of substrates under the reaction conditions

Since many of the substrates were obtained and used as an *E/Z* mixture of isomers, but gave rather consistent yields in the cyclizations, it was assumed that the *E/Z* ratio of the substrates is changing during the course of the reaction. This could lead to the enrichment of one isomer and therefor show that the reactions run independently of the *E*/*Z* ratio of the substrates. Hence, substrate **146v** was exposed to the applied photocatalytic conditions without the selenium catalyst (Scheme 65, above). Thereby, the *E/Z* ratio of the individual samples was determined *via* ^{1}H-NMR spectroscopy depending on the reaction time (Scheme 65, below).



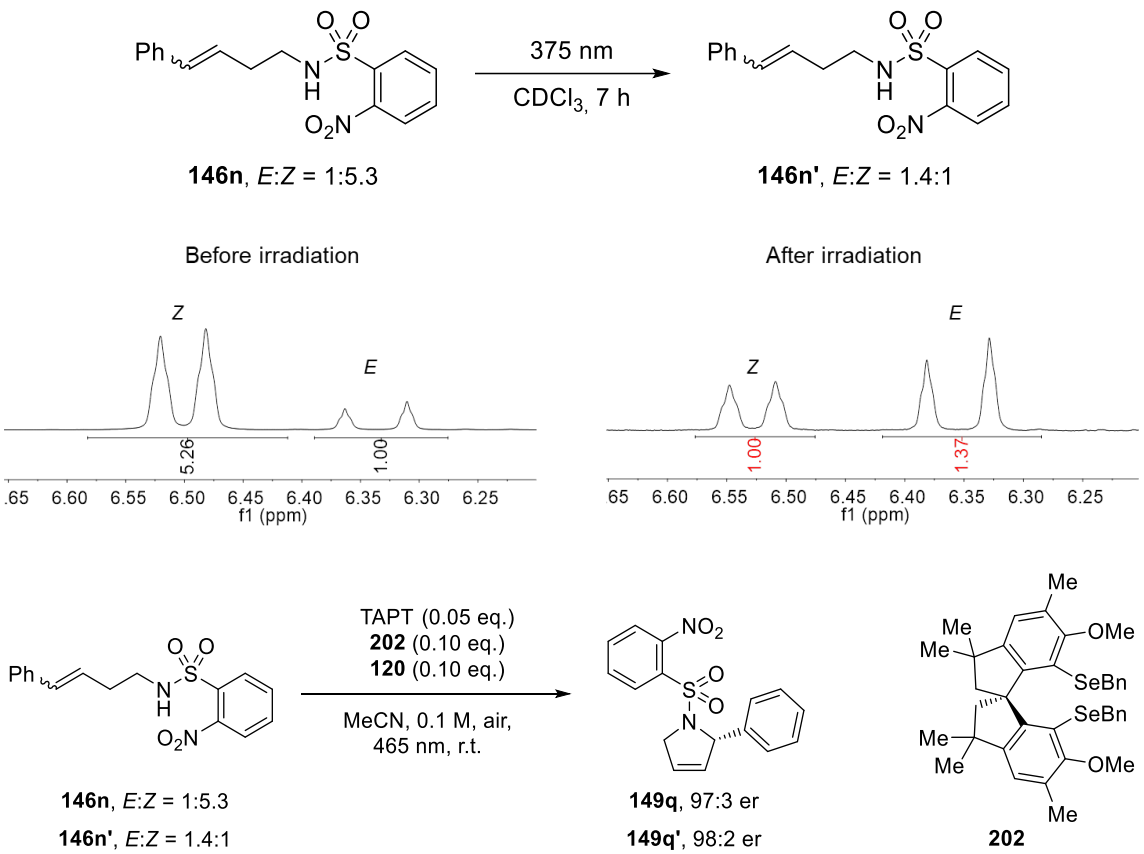
Scheme 65. Development of the *E/Z* isomerization of **146v**.[133]

Starting from an isomeric mixture of *E/Z* = 26:74, the amount of (*E*)-isomer is continuously rising until a threshold of *E/Z* = 80:20 is reached after 30 min. From this result, it was derived that arylic substrate **146v** performs an *E/Z* isomerization leading to the enrichment of the (*E)*-isomer, which is significantly faster than the actual cyclization process. Similar light induced isomerization processes with disulfide catalysts, that are comparable to the one used herein, were reviewed by Patehebieke.[144] Thus, it is assumed that all arylated systems of the substrate scope undergo a similar preisomerization process before the intended cyclization takes place.

3.4.4 Independence of the *E/Z* ratio for the stereoselectivity

To underpin the finding of section 3.4.3, the cycloamination should be conducted starting from two different *E*/*Z* mixtures of one substrate. For this purpose, substrate **146n** bearing an initial *E*/*Z* ratio of 1:5.3 was subjected to UV light (Scheme 66, above). Thereby, the *E*/*Z* ratio could be changed to 1.4:1, which could be detected *via* ^{1}H-NMR spectroscopy (Scheme 66, center). Next, the enantioselective cycloamination was performed on both isomeric mixtures (**146n** and **146n'**) and the results indicated that both isomeric mixtures led to the same selectivities (Scheme 66, below). Hence, this

result underpins the finding described in section 3.4.3 and it can be derived that the selectivity of this protocol runs independently of the initial isomeric ratio.



Scheme 66. *E/Z* isomerization of **146n** with UV light (above), ^{1}H-NMR spectroscopic determination of *E/Z* ratios before and after UV irradiation (center), reaction showing the independence of *E/Z* ratio for the enantioselectivity (below).[133]

3.4.5 Cyclovoltammetric experiments

All cyclic voltammetry (CV) experiments were conducted by H. Pesch.[142] Therefore, the model reaction between **146b** and (*p*-anisylSe)$_2$ was analyzed. For (*p*-anisylSe)$_2$ an irreversible oxidation could be determined at E_p = 0.74 V (*vs.* $Fc^{+|0}$ in MeCN) or at E_p = 0.84 V (*vs.* $Fc^{+|0}$ in fluorobenzene, Figure 15). With increased scan rate the peak shifts and the oxidation remains irreversible for scan rates up to 2 Vs^{-1}, which indicates a subsequent chemical reaction after oxidation. A similar behavior was previously reported.[110] From scan rate dependent measurements, it could be derived that this peak refers to an one-electron oxidation. Next, the CV of 1.0 eq. (*p*-anisylSe)$_2$ together with 5.0 eq. of **146b** was measured. Besides the first oxidation peak from (*p*-anisylSe)$_2$ the graph shows an additional one at E_p = 0.90 V (*vs.* $Fc^{+|0}$ in MeCN), which shows the

same characteristics as the first oxidation peak, and therefore also correlates to an one-electron oxidation and to the induction of a follow-up chemical reaction. By the direct comparison with the CV of **227'** (Figure 15, right, synthesized by T. Appleson), it could be derived, that this peak indeed arises from the oxidation of **227'**. The current does not increase in the CV experiment, because only one turnover on the time scale of the CV was reached. Hence, it can be deduced that the release of the catalyst from oxidized **227'** occurs very slowly in comparison to the former two steps.

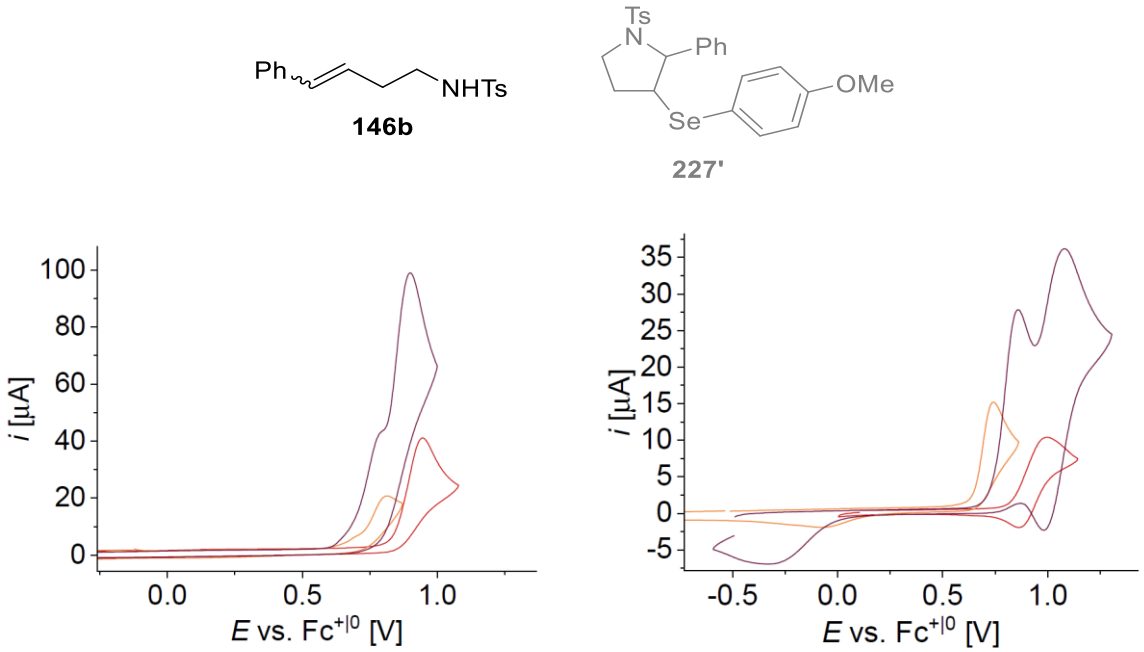


Figure 15. CV measurements of (*p*-anisylSe)$_2$ (orange), (*p*-anisylSe)$_2$ and **146b** (dark brown), and **227'** (light brown) in MeCN (left, 0.1 M ^{n}Bu$_4$NPF$_6$) and fluorobenzene (right, 0.1 M ^{n}Bu$_4$B(C$_6$F$_5$)$_4$), v = 0.2 Vs^{-1}. These graphs were directly taken from Graf *et al.* and measured by H. Pesch.[142]

Digital simulation of scan rate depentent measurements suggest a second order reaction rate.[142] Notably, the oxidation potentials of (*p*-anisylSe)$_2$ and **227'** are both lower than the ones of **13** (E_p = 0.96 V *vs.* Fc$^{+|0}$ in fluorobenzene) and **227** (E_p = ~1.24 V *vs.* Fc$^{+|0}$ in fluorobenzene), which were used in the photoaerobic protocols, because of the electron donating methoxy group. However, the reduction potential of excited TAPT (E_p = 1.35 V *vs.* Fc$^{+|0}$ in MeCN) is still sufficient to oxidize both moieties.[145]

To unveil the rate enhancing effect of disulfide **120**, which was observed in the initial rate experiment, the CV of **120** was recorded (Figure 16). The graph shows one irreversible oxidation peak at E_p = 1.26 V (*vs.* Fc$^{+|0}$ in MeCN). With increasing scan rate the peak shifts and stays irreversible for scan rates up to 2 Vs^{-1}. Notably, in fluorobenzene an oxidation potential of E_p = 1.32 V (*vs.* Fc$^{+|0}$) was measured, which is reversible for scan rates >0.2 Vs^{-1}. Hence, the follow-up reaction in fluorobenzene is

slower than the one in MeCN. According to the Randles-Ševčík equation, which was applied for scan rate dependent measurements, this process corresponds to an one-electron oxidation.[142] Further, the half-life of **120**$^+$ could be determined with a value of 1.4 s. Again, digital simulation of the CV data revealed a second order reaction rate, and thereby leads to the formation of a dimeric dication. Notably, similar chalcogen cations have been characterized.[146] Since the oxidation potential of the excited TAPT exceeds the one of **120** the formation of the sulfinated intermediate **228** would be feasible- in analogy to the formation of **227**. Therefore, the CV of **228** was measured showing an oxidation peak at E_p = 1.39 V (*vs.* $Fc^{+|0}$ in fluorobenzene). Since this exceeds the reduction potential of excited TAPT an oxidation of **228** can be excluded, which was consistent with the results from the initial rate experiment, where no product formation was obtained from **228**. From these results, which indicate that excited TAPT is capable of oxidizing **120** and that **120**$^+$ is rather stable in nonpolar solvents, and the ones used within the initial rate experiment, which showed that the presence of **120** accelerates the elimination of the catalyst from **227**, it was surmised that **120**$^+$ could serve as an electron hole reservoir, which interacts with intermediate **227'** and thereby facilitates the elimination. For this reason, the CV of **227'** in the presence of **120** was measured (Figure 16). When applying a potential that is below the oxidation potential of **120**, but over of **227'** no change of the current was observed and both events stayed reversible indicating no interaction between oxidized **227'**$^+$ and **120**. After a potential was applied that exceeds the one of **120**, both events became irreversible. Notably, the reduction curve showed one reduction peak with a decreased reversibility than in the case of both moieties coexisting. Hence, this indicates a chemical interaction between **120**$^+$ and **227'**$^+$.

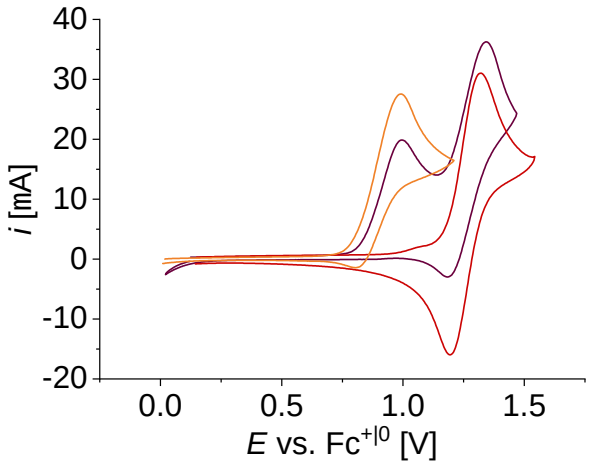


Figure 16. CV measurements of **227'** (orange), $c_{230'}$ = 4 mM, **120** (red), c_{120} = 4 mM, and a mixture of **227'** and **120** (dark brown) in fluorobenzene, 0.1 M $^{n}Bu_4B(C_6F_5)_4$, scan rate v = 0.2 Vs^{-1}. This graph was directly taken from Graf *et al.* and measured by H. Pesch.[142]

When the concentration of **227'** was elevated, an additional peak could be detected at E_p = 1.08 V (*vs.* $Fc^{+|0}$ in fluorobenzene, Figure 17, marked with red arrow), which is in between the reduction potentials of **227'** (E_p = 0.89 V *vs.* $Fc^{+|0}$ in fluorobenzene) and **120** (E_p = 1.20 V *vs.* $Fc^{+|0}$ in fluorobenzene). This new feature could indicate the formation of an interchalcogenated species.

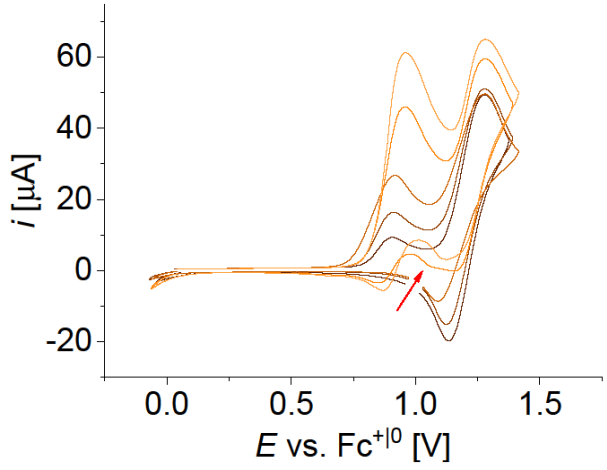


Figure 17. CV measurements of **120**, with various amounts of **227'**, $c_{227'}$ = 1, 2, 4, 6, 8 mM, c_{120} = 4 mM in fluorobenzene, 0.1 M $^{n}Bu_4B(C_6F_5)_4$), scan rate v = 0.4 Vs^{-1}. This graph was directly taken from Graf *et al.* and measured by H. Pesch.[142]

To validate this result, another CV containing $PhSePF_6$, which was formed *in situ*, and **120** was expected to show a similar interaction. Thereby, the generated $PhSePF_6$ showed an irreversible oxidation peak at E_p = 1.37 V and a reduction peak at E_p = 0.73 V (Figure 18). For both moieties together one new oxidation peak at a lower potential than for both individual species were observed. Further, the oxidation of **120**

to **120**$^{+}$ becomes an irreversible process meaning that it is condumed by this process. This result underpins the presence of an interchalcogenated species herein and during the elimination process.

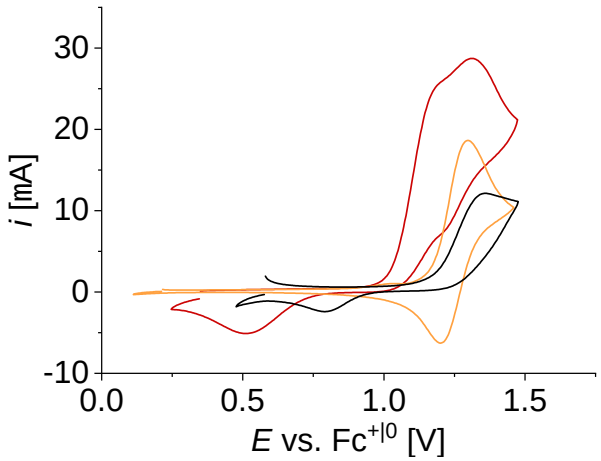
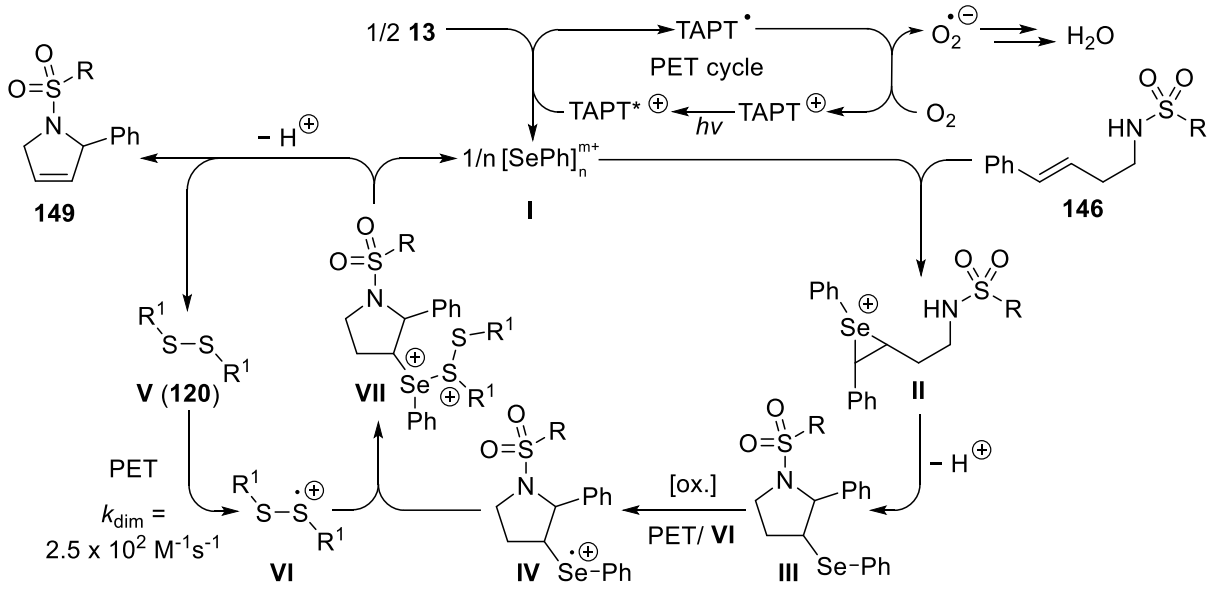


Figure 18. CV of **120** (orange), $c_{\mathbf{120}}$ = 4 mM, $PhSePF_6$ (dark brown), c_{PhSePF_6} = 6 mM, and a mixture of **120** and $PhSePF_6$ (light brown) in fluorobenzene, 0.1 M $^{n}Bu_4B(C_6F_5)_4$), scan rate v = 0.05 Vs^{-1}. This graph was directly taken from Graf *et al.* and measured by H. Pesch.[142]

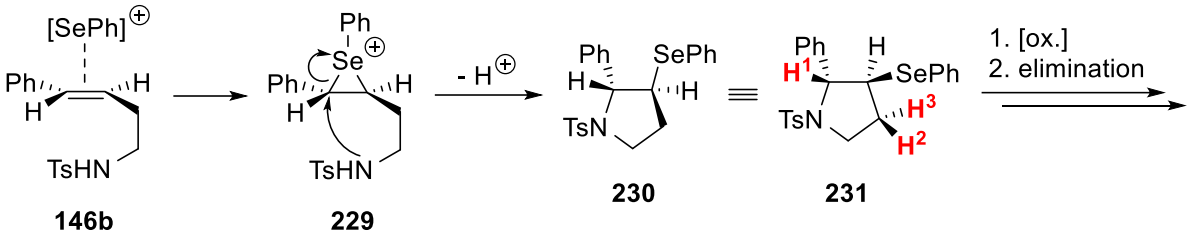
3.4.6 Mechanistic proposal

Taking all information obtained from the initial rate experiment, Stern-Volmer experiment and CV experiments together, the following mechanism is proposed (Scheme 67). Upon oxidation of the selenium catalyst, in this case shown for $(SePh)_2$ (**13**), by excited TAPT, **I** is formed.[110] This species is added to the olefinic moiety of substrate **146** and forms seleniranium ion **II**. The intended cyclization can take place leading to **III** after deprotonation. This process runs until all of **13** is consumed into intermediate **III**. Next, disulfide **V** (**120**) can be oxidized by the excited photocatalyst to generate **VI**. Notably, **VI** possesses a long thermal half-life, and can therefore serve as an electron hole reservoir. From here, **III** can be oxidized either by photoexcited TAPT again or by **VI** to the respective radical cation **IV**. **VI** most likely combines with **IV** yielding the interchalcogenated dicationic species **VII**. Another deprotonation from this highly unstable species leads to the release of disulfide **V** (**120**), the active selenium catalyst **I** and generates product **149**.



Scheme 67. Proposed mechanism for the photoaerobic cycloamination. PET: photoinduced electron transfer. Note: under electrochemical conditions a dimerization of **IV** (k_{dim} = 2.2 x 10^3 $M^{-1}s^{-1}$ for **227'**) and subsequent elimination to afford **149** was proposed, because the oxidation of **V** (**120**) would not be feasible.[142]

Notably, the elimination process from **VII** to **149** could run in two different positions leading either to the Saytzeff or the Hofmann product (Scheme 67). Since only the Hofmann product was observed, the elimination of H^1 must be disfavored or the one of H^2 or H^3 is favored (Scheme 68, **231**). Both, the E1 and $E1_{cb}$ mechanism, would favor the elimination of H^1, because the intermediately generated carbanion could be stabilized through the adjacent phenyl moiety, and hence lead to the Markovnikov product. Concomitantly, the pk_a value of H^1 is lower in comparison to H^2 and H^3. Therefore, the elimination process most likely proceeds according to an E2 mechanism, in which a base can only achieve the deprotonation of H^2 or H^3. This would be in agreement with the results from the CV experiments, which indicate a bimolecular reaction for this step (see section 3.4.5). Also, from a stereochemical point of view, this would be in accordance with the fact that only H^3 stands in an antiperiplanar position towards the selenium moiety enabling an E2 elimination, when starting from an (*E*)-configurated double bond. This requirement in turn is given by the preisomerization of the substrates discussed in section 3.4.3.



Scheme 68. Schematic analysis of the relative configuration of substituents prior to the elimination process. Note: if the selenonium ion attack would occur from the other face of alkene **146b**, the same relative configuration would be obtained.

However, since no appropriate base is present during the reaction and the addition of bases did not affect the reaction progress, as was reported in section 3.1.1, this mechanistic proposal remains speculative.

3.5 Synthesis of *L*-proline derivatives

During the elaboration of the enantioselective cycloamination, it was noticed that the structural skeleton of **149v** could be used as a precursor for various biologically active prolines derivatives (Figure 19).[147–155] Among those, alkylated and (di-)hydroxylated prolines are prevalent components in different bacteria, mussels or fungi.[150] Thereof, prolines **233** and **234** count to the most interesting motives, because of their extraordinary biological relevance as a potent glycosidase inhibitor (**234**) or as component from the poison of the white death cap fungus, *Amanita virosa* (**233**).[150] For this reason, several asymmetric syntheses have been explored in the last two decades, in which the skeleton of **149v** was used as an intermediate.[147–149]

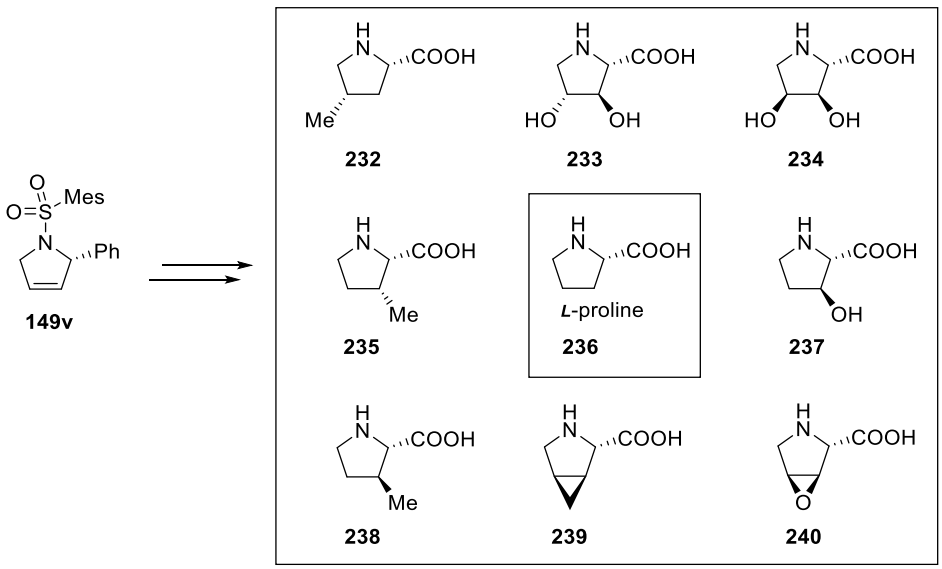
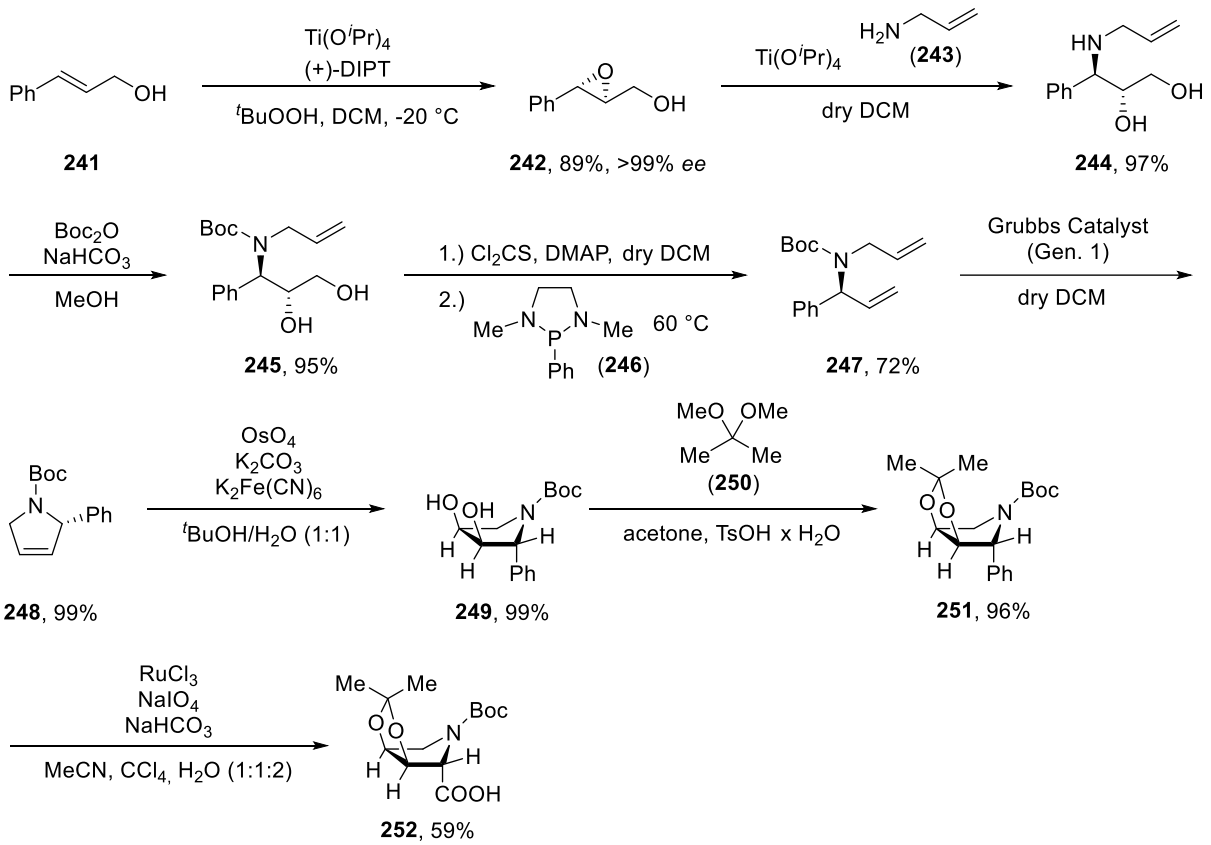


Figure 19. Overview of biologically active proline derivatives similar to **149v**.[147–155]

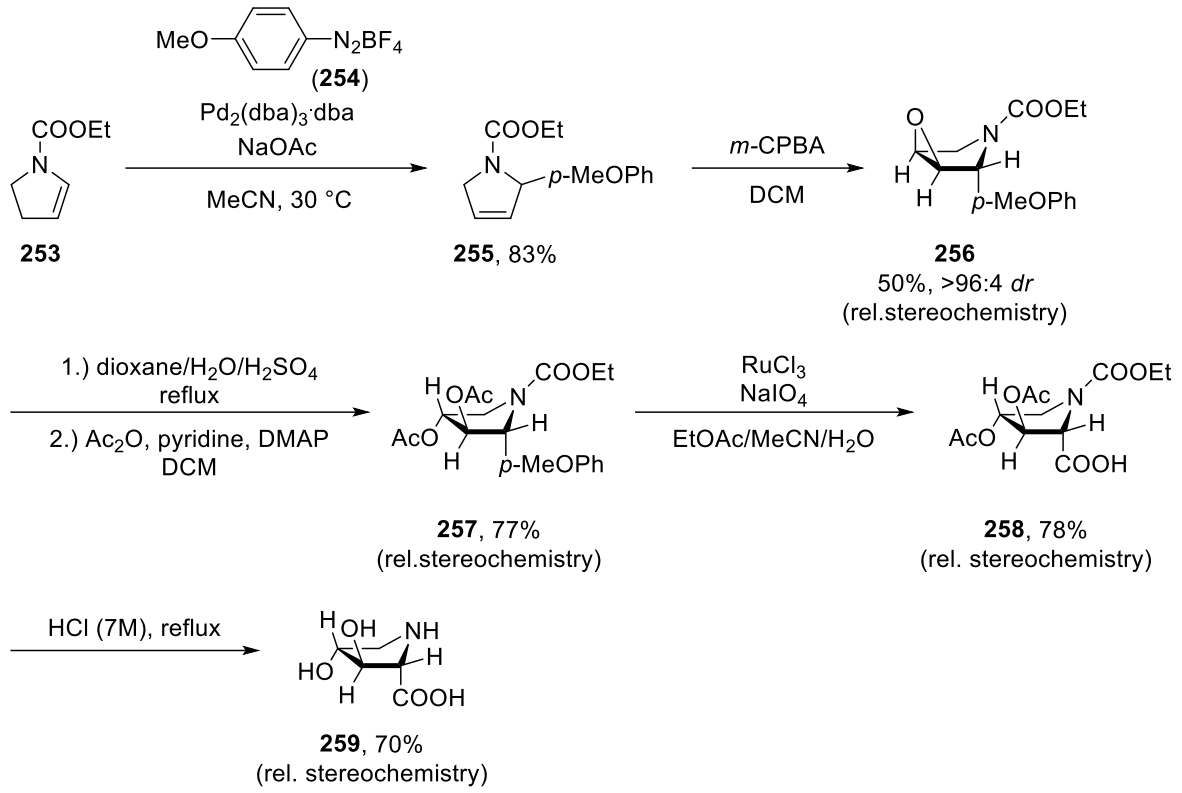
A Boc protected version of **149v** was used *e.g*. by Riera *et al.* in 2002 within the total synthesis of protected (2*S*,3*R*,4*S*)-3,4-dihydroxyproline **252** (Scheme 69).[148] After a Sharpless Epoxidation[156] of cinnamyl alcohol **241** to epoxide **242**, a stereoselective opening with $Ti(O^iPr)_4$ and allylamine **243** yielded aminodiol **244**. The secondary amine was Boc-protected before treatment with thiophosgene to form a thiocarbonate and subsequent pyrolysis with 1,3-dimethyl-2-phenylphosphazolidine (**246**) according to Corey and Hopkins.[157] The obtained bis-allylamine **247** was cyclized by Grubbs Metathesis to **248**, whose structural skeleton is equal to the one of **149v**. The newly formed double bond of **248** was dihydroxylated with OsO_4, the alcohol groups were protected with 2,2-dimethoxypropane (**250**) to the respective full acetal **251** and the synthesis was completed with the oxidation of the phenyl moiety to a carboxylic acid yielding **252** in a total yield of 33% within 9 steps overall.



Scheme 69. Synthesis of protected (2*S*,3*R*,4*S*)-3,4-dihydroxyproline **252**.[148]

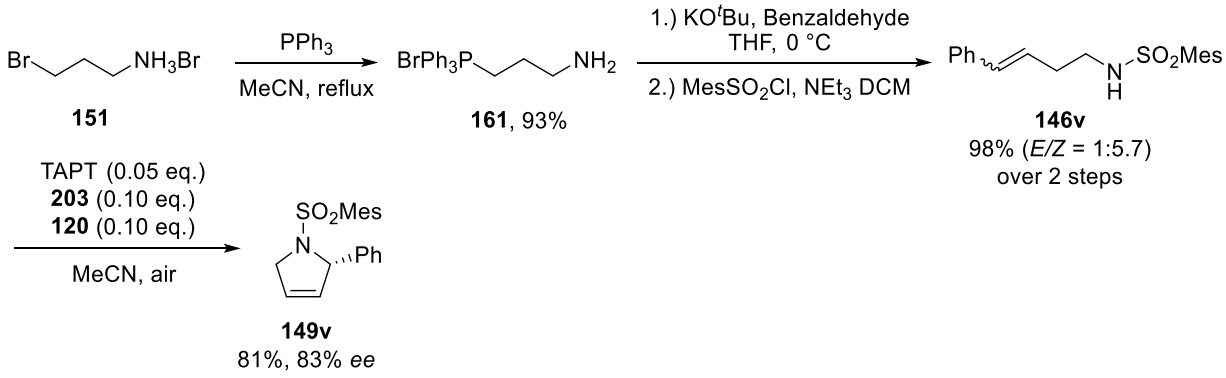
Almost the same motif was used one year later by Correia *et al.* for the total synthesis of racemic 2,3-*trans*-3,4-*trans*-3,4-dihydroxyproline **259** (Scheme 70).[147] The synthesis started with a regioselective Heck Reaction on enecarbamate **253**. Stereoselective epoxidation of **255** with *m*-CPBA yielded racemic **256** in moderate yields, but good diastereoselectivity (>94:6 *dr*). Acidic ring opening of **256** and acetate

protection led to **257** in 77% yield. Then, an oxidation protocol according to the procedures of Sharpless *et al.*[158] and Shioiri *et al.*[159] was applied to oxidize the anisyl moiety of **257** to a carboxylic acid. Finally, all protecting groups were cleaved off by acidic treatment and racemic **259** was obtained within 6 steps and a total yield of 17%.



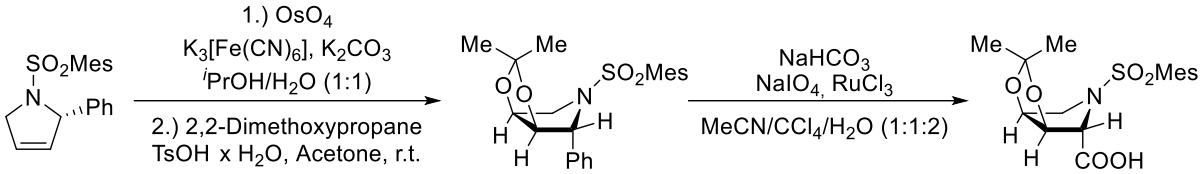
Scheme 70. Synthesis of racemic 2,3-*trans*-3,4-*trans*-3,4-dihydroxyproline **259**.[147]

Our novel synthetic route began with the formation of a phosphonium salt from commercial 3-bromopropyl hydrobromide **151**,[106] followed by Wittig Reaction and amine protection to generate **146v** in 98% yield as an isomeric mixture (*E*/*Z* = 1:5.7, Scheme 71).[95] The enantioselective cycloamination gave **149v** in 81% yield and 83% *ee*. This product was taken as a common precursor for the construction of the envisioned proline derivatives (**261** and **266**).



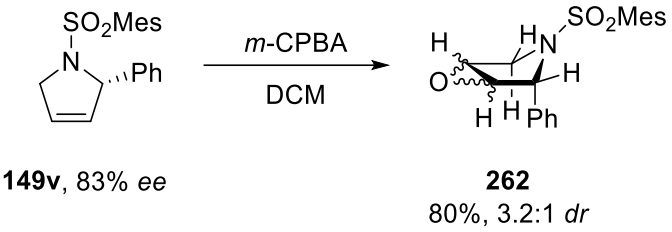
Scheme 71. Synthetic route towards precursor **149v**.[95,106]

For the synthesis of **261**, **149v** was *syn*-dihydroxylated, the diol protected as a full acetal[148] and the final oxidative cleavage of the phenyl moiety[160] could afford (2*S*,3*R*,4*S*)-3,4-dihydroxyproline **261** with 20% yield in total (Scheme 72, 7 steps from **151**). Thereby, this synthesis represents the shortest stereoselective synthesis of this structural motive to date.[147–149]



Scheme 72. Synthetic route towards dihydroxyproline derivative **261**.[148,160]

The second synthesis, towards **266**, commenced with the epoxidation of **149v** (Equation 11). This process was expected to occur stereoselectively because of the sterical hinderance of the phenyl group of **149v**. Therefore, three different epoxidation techniques were tested. The first one was the classic epoxidation using *m*-CPBA according to Correia *et al.*,[147] but in contrast to the reported high disasteroselectivities, a *dr* of only 3.2:1 was obtained (Equation 11). Thereby, the separation of the individual sets of signals could be achieved by COSY (Figure 20). However, no clear assignment of the respective *cis*- and *trans*-epoxidized compounds could be derived from the coupling constants at this stage.



(11)

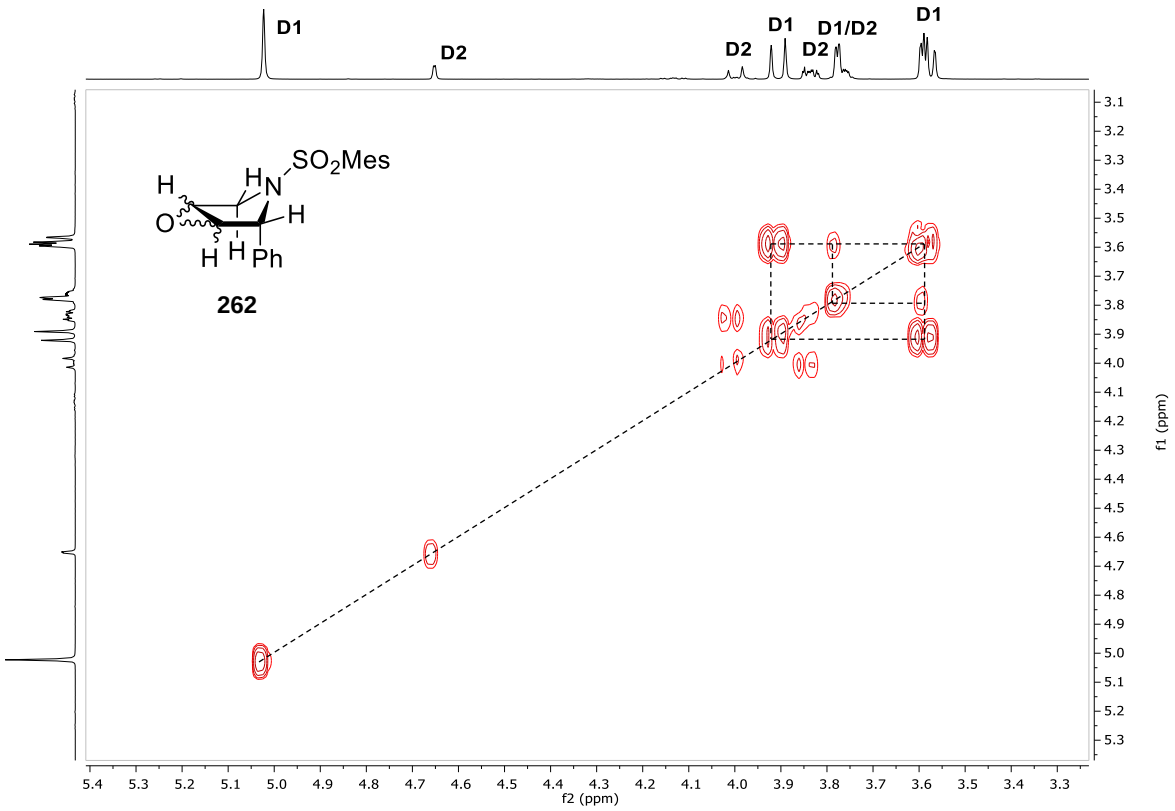
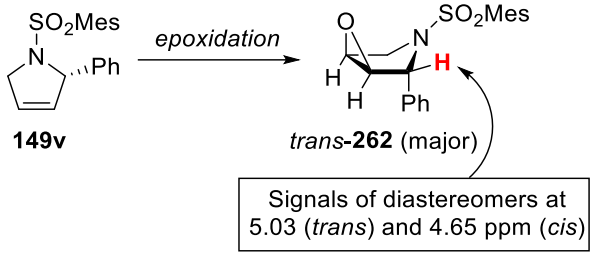
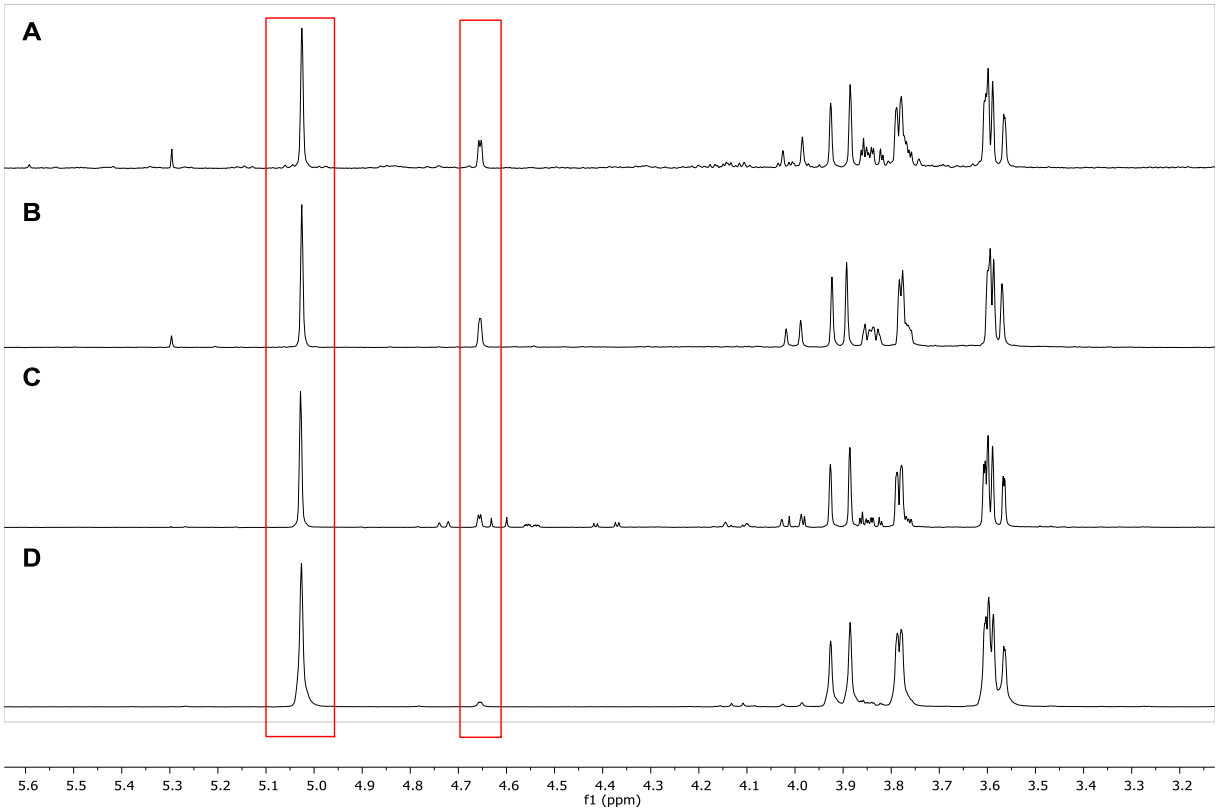


Figure 20. COSY spectrum of the diastereomeric mixture of **262**. D1: diastereomer 1, D2: diastereomer 2. Decisive correlations for D1 are assigned.

Separation trials of the diastereomeric mixture by column chromatography remained unsuccessful. The second epoxidation reaction was performed using an oxone/acetone epoxidation protocol (Scheme 73). Unfortunately, the *dr* obtained herein was even worse (2.5:1) than the one obtained with *m*-CPBA. Even the addition of chiral Shi-Catalyst[161] only led to a *dr* of 7.4:1 and a declined yield of 19%. Hence, another protocol had to be used for the diastereoselective epoxidation. Since the dihydroxylation of the previous synthesis towards **260** proceeded very diastereoselectively, the same protocol was used again for the dihydroxylation of **149v**, and a subsequent Appel Reaction could afford the respective chlorohydrine (Scheme 74, **264**). Notably, one hydroxy group was preserved, which can be explained by the sterical repulsion of the phenyl moiety hindering the attack of the chloride (Scheme 74). Afterwards, the addition of KO^{t}Bu triggered the formation of epoxide **262** in 67% yield, an elevated *ee* value of 89% and >20:1 de. This reaction sequence was possible without purification of the intermediate diol and chlorohydrin (Scheme 75). Given that the dihydroxylation occurs at the opposite face to the phenyl moiety like it was for **260**, and that the Appel Reaction occurs with stereoinversion, the major isomer must therefore be *trans*-**262** (Schemes 73 and 74).

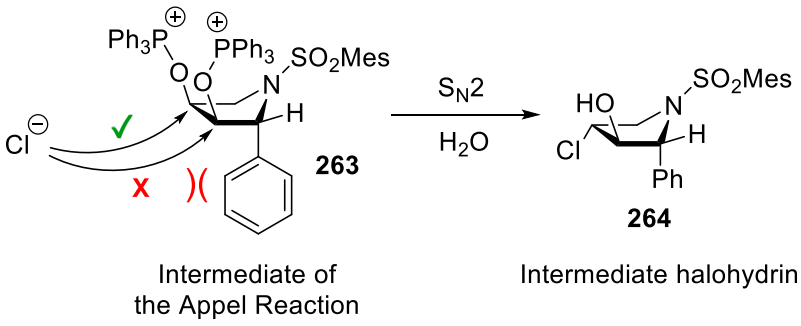


conditions	*dr*	Yield [%]
A *m*-CPBA	3.2:1	80
B oxone, acetone	2.5:1	n.d.
C oxone/Shi-Catalyst	7.4:1	19
D dihydroxylation/Appel Reaction/ epoxidation of chlorohydrin	>20:1	67



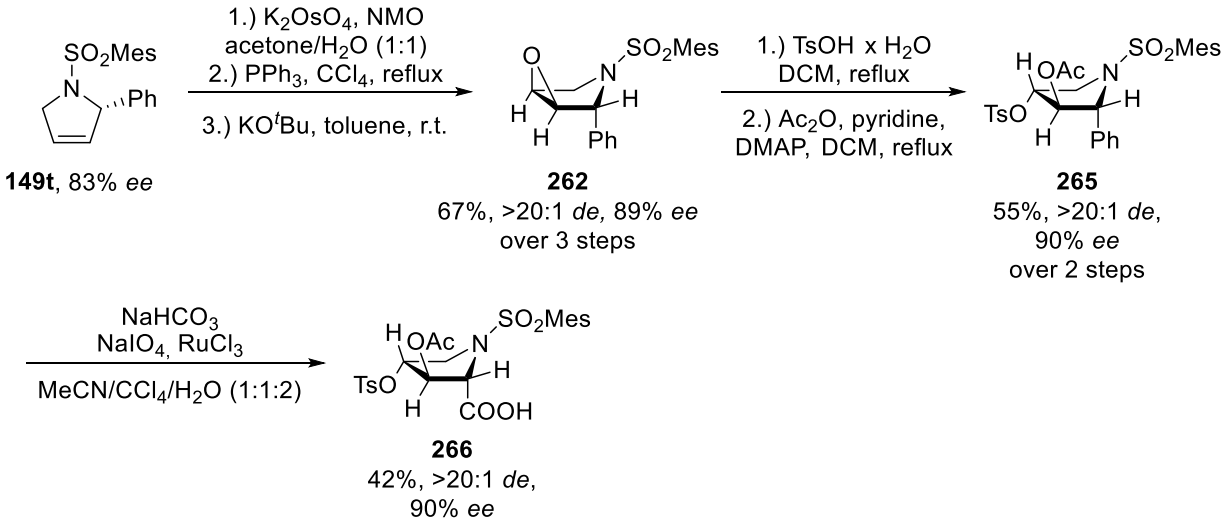
Scheme 73. Comparison of diastereoselectivities of the executed epoxidations *via* ^{1}H-NMR spectroscopy. n. d.: not determined.[161]

The diastereomeric ratios of all executed epoxidations could be determined from the respective ^{1}H-NMR spectra, which are shown in Scheme 73. Thereby, the signal at 5.03 ppm arises from the benzylic proton of the major diastereomer, *trans*-**262**, the one at 4.65 ppm from the minor one, *cis*-**262**.



Scheme 74. Schematic representation of the two possible Appel substitutions.

From **262**, an epoxide opening with TsOH·H_2O and subsequent protection of the free alcohol with acetic anhydride yielded **265** in a moderate yield of 55% and a conserved *ee* value (Scheme 75). Again, the RuO_4 catalyzed oxidation of the phenyl moiety to a carboxylic acid[160] completed the synthesis of **266** in overall 10 steps and a total yield of 11%.



Scheme 75. Synthesis route towards dihydroxyproline derivative **266**.[160]

Although this synthesis does not represent the shortest stereoselective route towards this structural motif, it is the first one, which does not start from a natural feedstock with given stereocenters.[147,162,163] Hence, by this catalytic regime, both enantiomers could be made accessible by the choice of the respective enantiomer of selenium catalyst **203** during the stereoselective cycloamination.

The constitution and relative configuration of the obtained dihydroxyproline derivatives, **261** and **266**, could be derived from a short NMR analysis. For **261** (Figure 21) the singlet at 4.46 ppm can be assigned to H^1, because of its encapsulation to all the surrounding protons and the relatively weak coupling to H^2. The signals at 3.79 and 3.60 ppm correlate with a vicinal coupling constant of 11.4 Hz and therefor can be assigned to H^4 and H^5. The common coupling constant of value 5.9 Hz between the signals at 4.86 and 4.81 ppm and the multiplicity of the latter indicate that H^2 belongs to the signal at 4.86 ppm and H^3 to the one at 4.81 ppm. The value of this coupling constant is typical for a ^3J coupling of *cis*-configurated protons. Unfortunately, no strong NOESY correlations could be detected for **261** giving an indication about its configuration. For **266** (Figure 22), the signals at 3.87 and 3.46 ppm correlate with a coupling constant of 12.0 Hz and therefor most likely derive from the vicinal coupling

of H^9 and H^{10}. Further, the signal at 3.87 ppm and the one at 5.01 ppm share the coupling constant of value 5.6 Hz. This relation and the multiplicity of the signal at 5.01 ppm indicate that this signal is derived from H^8, which can couple with H^7, H^9 and H^{10}. Since no further matching coupling constants could be extracted the assignment of H^7 and H^6 were derived from the multiplicity of the signals and the chemical shift. Regarding the chemical shift, the signal at 5.35 ppm is more likely related to H^7 than to H^6, because of the lowered shielding through the neighboring oxygen. The multiplicity of this signal most probably corresponds to a pseudo triplet, which develops from two duplets that result from coupling with H^6 and H^8. For comparison, the signal at 4.48 ppm only owns one coupling constant and therefore can be assigned to H^6 that only couples with H^7. All correlations could be confirmed with the COSY spectra. Further, the protons H^6, H^7 and H^8 show no correlations in the NOESY spectrum, which indicates the *trans*-configuration of H^6 and H^7, and H^7 and H^8 (Figure 23).

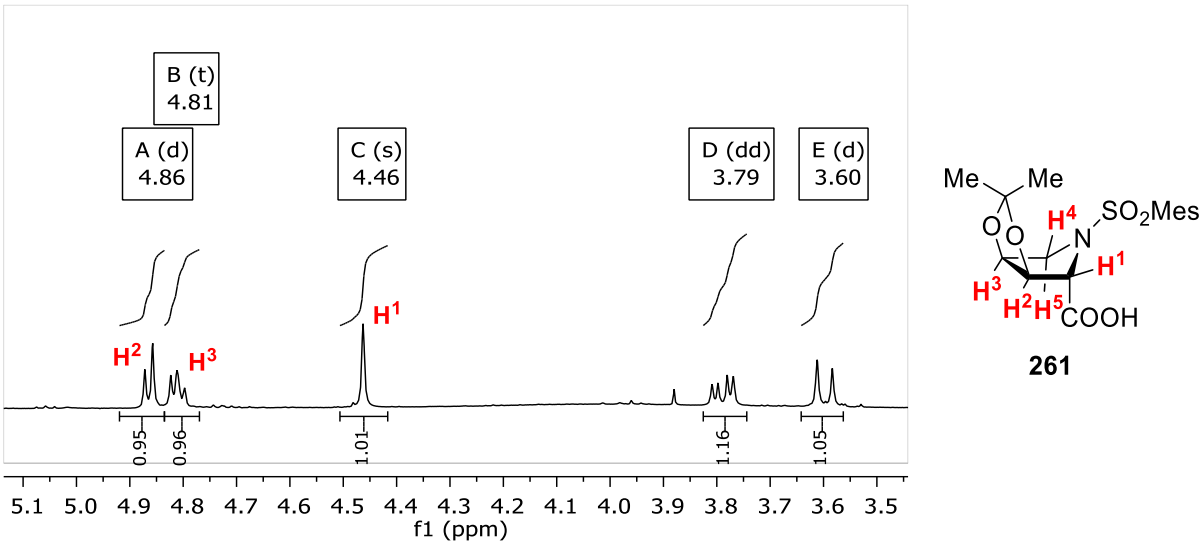


Figure 21. Structural analysis of **261** *via* ^{1}H-NMR spectroscopy.

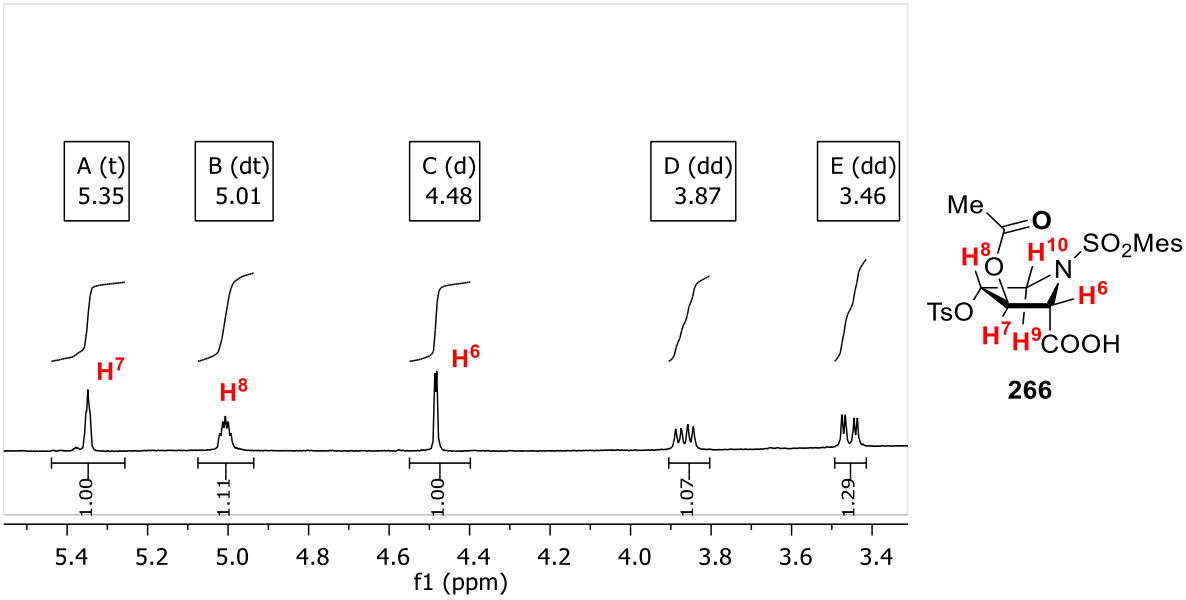


Figure 22. Structural analysis of **266** *via* ^{1}H-NMR spectroscopy.

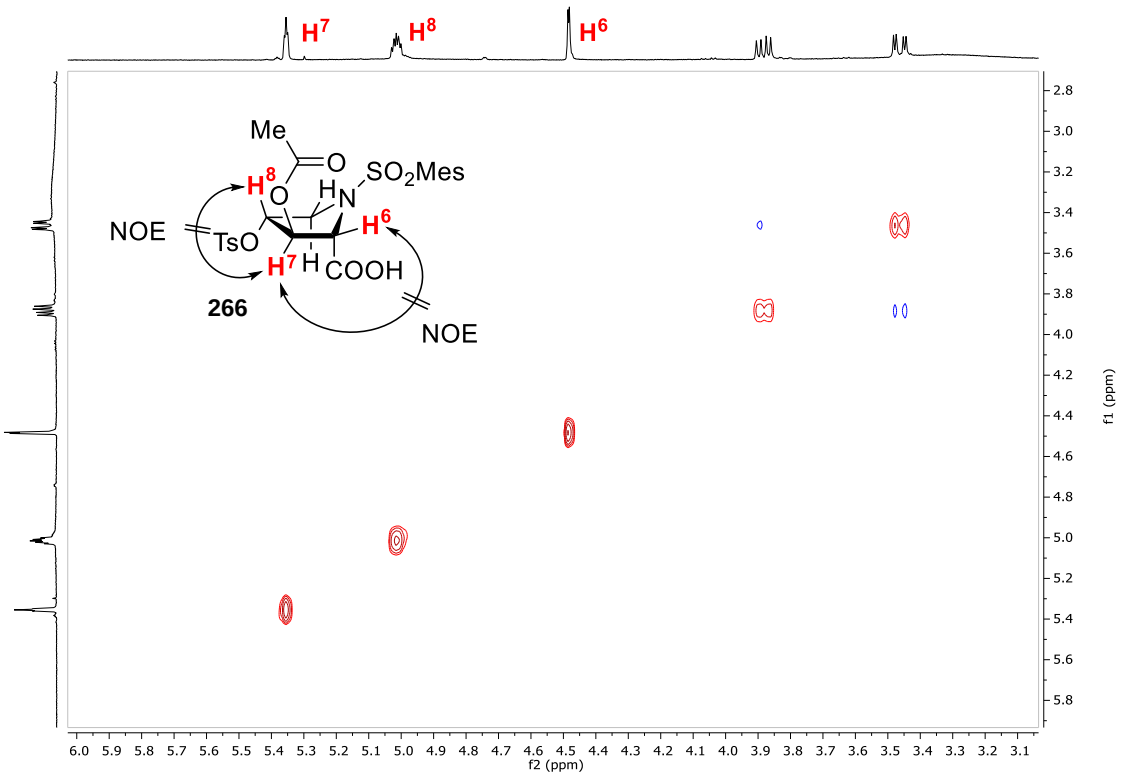
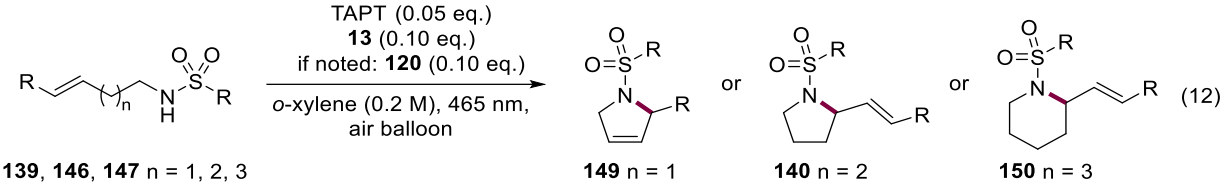


Figure 23. NOESY analysis of compound **266**.

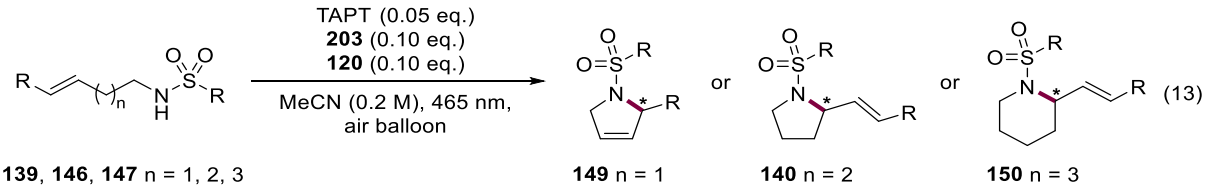
4 Conclusion and outlook

Within the framework of this thesis, three different projects were pursued. First, a photoaerobic protocol for cycloamination reactions *via* selenium-π-acid catalysis was developed. This procedure represents a highly regioselective and operationally simple protocol with pronounced sustainability in comparison to former reported ones. Using the optimized conditions consisting of TAPT as the photocatalyst and $(SePh)_2$ (**13**) as the organocatalyst in *o*-xylene, the reaction enables the synthesis of a manifold of differently equipped pyrrolidines (**140**), piperidines (**150**) and 3-pyrrolines (**149**) from moderate to high yields (Equation 12). For several substrates the reaction rate could be accelerated by the coaddition of disulfide **120**. Hence, the underlying mechanism was elucidated with the help of cyclovoltammetric, fluorescence quenching and initial rate (NMR) experiments, and additionally, the role of **120** as a cocatalyst was investigated.



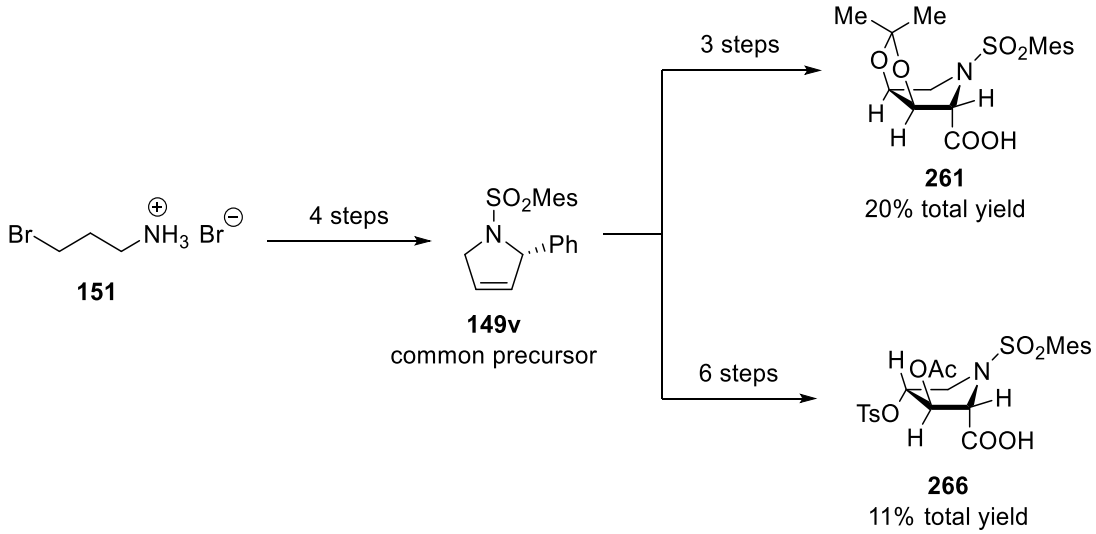
139, **146**, **147** n = 1, 2, 3 **149** n = 1 **140** n = 2 **150** n = 3 (12)

Second, by the design of a chiral selenium catalyst on the basis of a spirobiindane backbone, the racemic transformation could be enhanced to an enantioselective one. Among the tested chiral selenium catalysts and the probed conditions, catalyst **203** in combination with TAPT as the photocatalyst and disulfide **120** as a cocatalyst in MeCN showed the best compromise between a high yield and a good stereoinduction on substrates bearing a mesitylene-2-sulfonyl protecting group on the amine (Equation 13). Using this protocol, an array of 3-pyrrolines (**149**) was successfully synthesized in moderate to good yields and with high enantioselectivities of up to 94% *ee*. Pyrrolidines (**140**) and piperidines (**150**) however could only be obtained in minor yields and enantioselectivities.



139, **146**, **147** n = 1, 2, 3 **149** n = 1 **140** n = 2 **150** n = 3

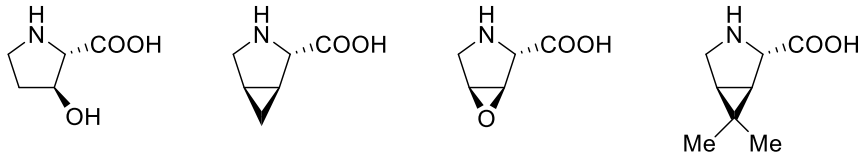
Third, the developed stereoselective protocol was employed as a key step for the assembly of two dihydroxyproline derivatives. Here, the set stereocenter of **149v**, which was obtained from the enantioselective cyclization of **146v**, could be used as an anchor point for the following transformations leading to **261** in 7 steps with a total yield of 20% and to **266** in 10 steps with a total yield of 11%, with conserved enantiomeric excesses in both cases (Scheme 76). For **261** this resembles the shortest synthetic route towards the structural skeleton of enantiomerically enriched 2,3-*trans*-3,4-*cis*-3,4-dihydroxyproline,[147–149] for **266** this route represents the first stereodivergent synthesis.[147,162,163] More precisely, this synthesis does not rely on the given stereocenters from biological feedstocks, but both enantiomers of **266** could be made accessible by choosing the suitable enantiomer of chiral selenium catalyst **203**.



Scheme 76. Synthesis overview of **261** and **266** from their common precursor **149v**.

Based on the results from the photoaerobic cycloamination, for future works, the expansion of this elaborated catalytic regime to an intermolecular version would be highly desirable. For this transformation, the herein used chiral selenium catalysts or analogue structures could also be tested to achieve an intermolecular stereoselective amination. Moreover, the practical application of **149v** could be expanded for the synthesis of other proline derivatives. Given that **149v** can serve as a common

precursor, the structural motives from prolines **237**, **239**, **240** and **267** could very likely be made accessible by literature known procedures (Figure 24).[147,151,152,154]



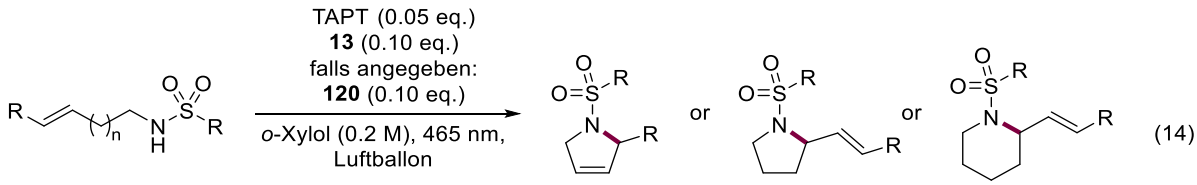
237 **239** **240** **267**

Figure 24. Accessible proline derivatives from **149v**.

In conclusion, the herein developed protocol represents an advancement in the realm of selenium catalysis, not only because it describes the regiospecific cycloamination of alkenes in a greener way in comparison to former techniques,[51,62,63,65,66,68] but also because it provides a new catalytic pathway towards 3-pyrroline moieties, which can even be accessed in enantioenriched form by the help of a chiral selenium catalyst. Further, this work emphasizes the practical use of selenium catalysis for the synthesis of protected natural product.

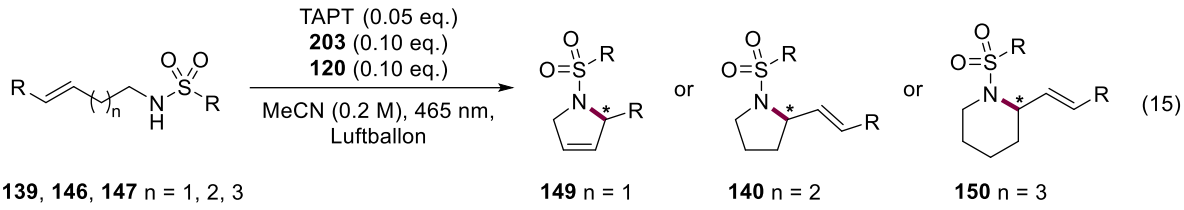
5 Zusammenfassung und Ausblick

Im Rahmen dieser Arbeit wurden drei verschiedene Projekte verfolgt. Zunächst wurde ein photoaerobes Verfahren für Zykloaminierungsreaktionen mittels Selen-π-Säure Katalyse entwickelt. Dieser katalytische Prozess zeichnet sich durch seine hohe Regioselektivität und durch seine einfache und nachhaltige Synthesevorschrift im Vergleich zu vorherigen Verfahren aus. Unter Verwendung der optimierten Bedingungen bestehend aus TAPT, dem Photokatalysator, und $(SePh)_2$ (**13**), dem Organokatalysator, in *o*-Xylol, ermöglicht dieser Prozess die Synthese einer Vielzahl von unterschiedlich ausgestatteten Pyrrolidinen (**140**), Piperidinen (**150**) und 3-Pyrrolinen (**149**) in moderaten bis hohen Ausbeuten (Equation 14). Dabei konnte die Reaktionsgeschwindigkeit mehrerer Substrate durch die Zugabe von Disulfid **120** beschleunigt werden. Deswegen wurde der zugrunde liegende Mechanismus mithilfe von Zyklovoltammetrie, Fluoreszenzlöschung und Anfangsgeschwindigkeits-bestimmung (NMR) aufgeklärt und damit einhergehend die Rolle des Disulfids **120** untersucht.



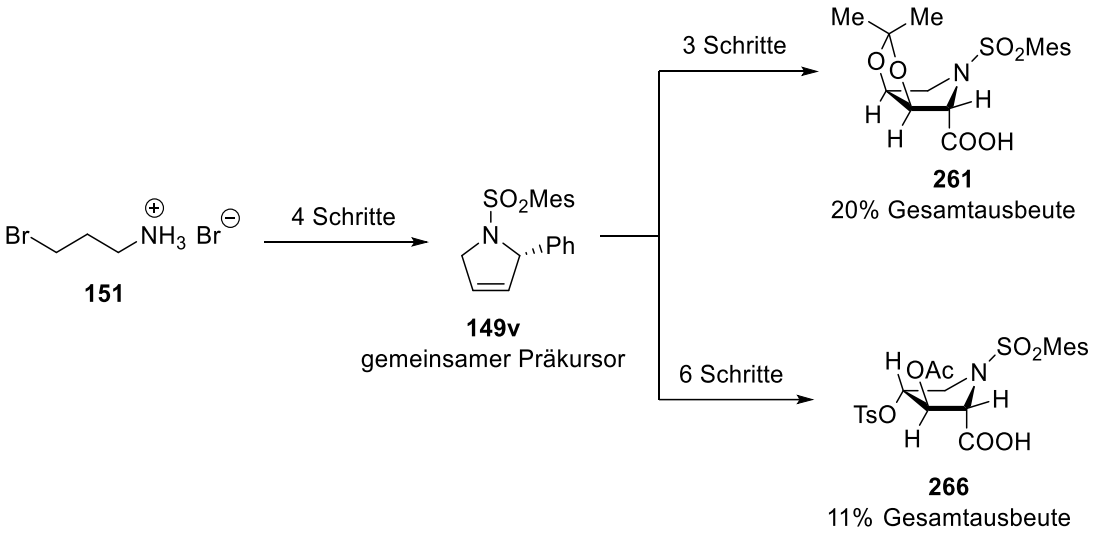
139, **146**, **147** n = 1, 2, 3 **149** n = 1 **140** n = 2 **150** n = 3 (14)

Zweitens konnte unter Zuhilfenahme eines auf einem Spirobiindan Gerüst basierenden chiralen Katalysators die razemische Reaktion zu einer enantioselektiven weiterentwickelt werden. Von den getesteten Katalysatoren konnte Katalysator **203** in Kombination mit TAPT als Photokatalysator und **120** als Co-Katalysator in MeCN den besten Kompromiss zwischen einer hohen Ausbeute und guten Stereoinduktion für Substrate, die eine Mesitylenesulfonyl Schutzgruppe am Amin tragen, erlangen (Equation 15). Durch diese Synthesevorschrift konnte eine Reihe von 3-Pyrrolinen (**149**) in moderaten bis guten Ausbeuten und Enantiomerenüberschüssen von bis zu 94% hergestellt werden. Pyrrolidine (**140**) und Piperidine (**150**) konnten jedoch nur in verminderten Mengen und Selektivitäten erhalten werden.



139, **146**, **147** n = 1, 2, 3 **149** n = 1 **140** n = 2 **150** n = 3

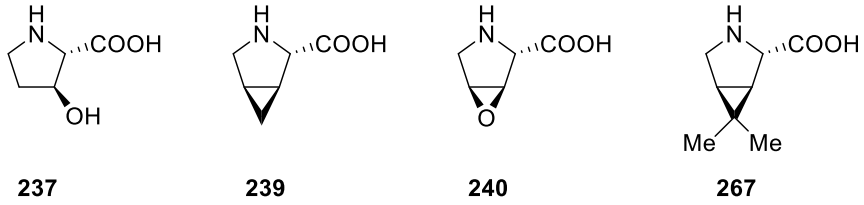
Drittens wurde das entwickelte Verfahren als Schlüsselschritt für den Aufbau zweier Dihydroxyprolinderivative verwendet. Hierbei konnte das durch die enantioselektive Aminierung hergestellte Stereozentrum von **149v** als Ankerpunkt für alle weiteren Transformationen verwendet werden, was zur Herstellung von **261** in insgesamt 7 Schritten mit 20% Ausbeute und **266** in insgesamt 10 Schritten mit 11% Ausbeute führte (Scheme 77). Für **261** stellt diese Syntheseroute die kürzeste zur Erlangung von enantiomerenangereichertem 2,3-*Trans*-3,4-*cis*-3,4-dihydroxyprolin Strukturmotif dar.[147–149] Für **266** stellt diese Route die erste stereodivergente dar, da vorherige Synthesen auf die nativen Stereozentren von natürlich vorkommenden Rohstoffen angewiesen waren und somit lediglich ein einziges Enantiomer zugänglich machten.[147,162,163] Durch die Wahl des passenden Enantiomers von Selenkatalysator **203** für die enantioselektive Zykloaminierung können nun beide Enantiomere von **266** zugänglich gemacht werden.



Scheme 77. Syntheseübersicht von **261** and **266** ausgehend vom gemeinsamen Präkursor **149v**.

Basierend auf den Ergebnissen der photoaeroben Zykloaminierung, ist die Erweiterung dieses Protokolls auf intermolekulare Aminierungen sehr erstrebenswert. Für eine solche Aminierung könnten die hierin verwendeten chiralen Selenkatalysatoren für eine stereoselektive Variante ausgetestet werden. Darüber hinaus könnte die Zykloaminierung auch noch zur Erlangung mehrerer Prolinderivate

verwendet werden. Mit **149v** als gemeinsamen Präkursor könnten die Strukturmotife von **237**, **239**, **240** und **267** durch literaturbekannte Transformationen zugänglich gemacht werden (Figure 25).[147,151,152,154]



237 **239** **240** **267**

Figure 25. Zugängliche Prolinderivative ausgehend von **149v**.

Zusammenfassend stellt das hierin entwickelte Verfahren einen Fortschritt im Bereich der Selenkatalyse dar, nicht nur, da es eine regiospezifische Zykloaminierung ist, die grüner abläuft als vorherige Methoden,[51,62,63,65,66,68] sondern auch, da es eine neue Syntheseroute für 3-Pyrrolinmotife darstellt, die darüber hinaus auch enantiomerenangereichert erhalten werden können. Zudem konnte in dieser Arbeit der praktische Nutzen des entwickelten Verfahrens für die Synthese von geschützten Naturstoffen gezeigt werden.

6 Experimental part

6.1 General methods

All chemicals were purchased from commercial sources and were used without further purification. Solvents were used in p.a. quality or dried according to common procedures if necessary. Purity is estimated to be ≥95% based on ^{1}H-NMR spectroscopic analysis. Irradiation experiments for the racemic amination were performed at λ = 465 nm using commercially available blue LED strips, that were attached to a crystallization beaker (Ø= 140 mm). The applied light intensity was in the range of 4300-4800 lx. Irradiation experiments for the enantioselective amination were performed at λ = 465 nm using custom-made metal blocks and LED irradiation from underneath. The applied light intensity was in the range of 15000-17000 lx.

Chromatography

Thin Layer Chromatography (TLC) was performed on TLC plates from ALUGRAM (Xtra SIL G/UV_{254}). Visualization was enabled by exposure to UV light (λ = 254 nm), and/or treatment with anisaldehyde stain (composition: 250 mL EtOH, 13.4 mL anisaldehyde, 10.0 mL H_2SO_4 conc.). Column chromatography was conducted with Silica from Acros Silica 60 (0.035-0.075 mm, 70-230 mesh ASTM). High Performance Liquid Chromatography (HPLC) was performed with an Agilent 1260 Infinity using columns from Daicel CHIRALPAK (4.6 mm x 25 mm, IA-3, IC-3, ID-3, OD-3). The signals were recorded on a diode array detector (DAD).

Spectroscopy and Spectrometry

Infrared Spectroscopy (IR) was performed on an Agilent Technologies Cary 630 FT-IR spectrometer. High resolution mass spectrometry (HRMS) was measured on an Agilent Q-TOF 6540 UHD or a Jeol AccuTOF GCX. Nuclear Magnetic Resonance (NMR): ^{1}H, ^{13}C, ^{31}P, ^{19}F und ^{77}Se-spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz (^{1}H) and 75 MHz (^{13}C) or on a Bruker Avance 400 spectrometer at 400 MHz (^{1}H), 101 MHz (^{13}C), 162 MHz (^{31}P), 377 MHz (^{19}F) and 76 MHz (^{77}Se). Chemical shifts (δ) are given in ppm. Multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sex = sextet, sept = septet, m = multiplet). Isomeric ratios (*E*/*Z*) were determined by the ratio of ^{1}H-NMR integrals

of the isolated products. Optical rotations were recorded on a Jasco P-2000 polarimeter.

Determination of NMR-yields

For the NMR Yield determination, the solvent of the reaction mixture was evaporated under reduced pressure before work-up. The residue was taken up in $CDCl_3$ (0.6 mL) and 1,3,5-Trimethoxybenzene (TMB) was added as an internal standard. The solvent peak was referenced to 7.26 ppm ($CDCl_3$), then the resonance of the internal standard at 6.03 ppm (s, 3H) was set to an integral of 1.00 and compared to a characteristic olefinic signal of the product. The NMR yield was determined *via* equation (16).

$$\text{NMR Yield [\%]} = \frac{\text{product peak integral}}{1/3} \cdot \frac{\text{m(TMB) [mg]}}{168.19\ \left[\frac{\text{mg}}{\text{mmol}}\right]} \cdot \frac{1}{\text{n(quantitative yield) [mmol]}} \qquad (16)$$

Melting Point

Melting Points were measured on a melting point meter from KRÜSS (M5000).

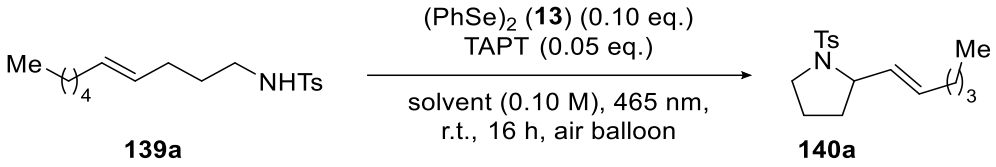
Compounds synthesized by others

Compounds **146d**, **146e**, **146u**, **159**, **160**, **227'** and **228** were synthesized and characterized by T. Appleson. All synthetic procedures and spectroscopic characterizations are described in literature.[142]

Compounds **146ae**, **146ai**, **198**, **199**, **200**, **201**, **202**, **203** and **204** were synthesized and characterized by Dr. T. Lei. All synthetic procedures and spectroscopic characterizations are described in literature.[133]

6.2 Optimization of racemic amination

Table 5. Complete optimization and control experiments of racemic amination.



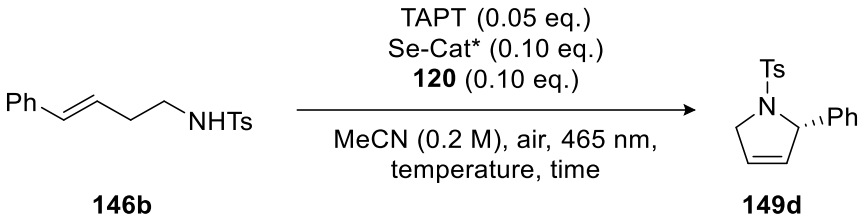
139a **140a**

Entry	Solvent	Comment	Conversion [%]	NMR-Yield [%][a]
1	toluene	-	100	48
2	acetone	-	21	21
3	MeCN	-	100	0
4	DMSO	-	47	0
5	DCM	-	100	32
6	$CHCl_3$	-	100	17
7	CCl_4	-	100	55
8	$C_2H_4Cl_2$	-	100	21
9	$C_2H_2Cl_4$	-	100	12
10	C_6H_5-CF_3	-	100	26
11	cyclohexane	-	39	14
12	*o*-xylene	-	100	75
13	*o*-xylene	+ molecular sieve (4 Å)	50	19
14	*o*-xylene	+ 0.80 eq. Na_2HPO_4	100	70
15	*o*-xylene	+ 0.80 eq. Cs_2CO_3	100	0
16	*o*-xylene	+ 0.80 eq. KF	100	0
17	*o*-xylene	+ 0.80 eq. CaF_2	100	44
18	*o*-xylene	+ 0.80 eq. Na_2CO_3	19	8
19	*o*-xylene	+ 0.80 eq. $NaHCO_3$	100	36
20	*o*-xylene	+ 0.80 eq. K_2CO_3	24	0
21	*o*-xylene	+ 0.80 eq. Li_2CO_3	3	0
22	*o*-xylene	under O_2 atmosphere	100	58
23	*o*-xylene	with 10 mol% of TAPT	75	25
24	*o*-xylene	with 2.5 mol% of TAPT	79	15
25	*o*-xylene	0.20 M instead	100	**84 (79)[b]**
26	*o*-xylene	0.05 M instead	67	33
27[c]	*o*-xylene	without $(PhSe)_2$	59	0
28	*o*-xylene	without TAPT	4	0
29	*o*-xylene	under Ar atmosphere	32	0
30	*o*-xylene	without light irradiation	0	0

[a]1,3,5-trimethoxybenzene as internal standard. [b]isolated yield in parenthesis. [c]control experiments shaded in grey.

6.3 Optimization of enantioselective amination

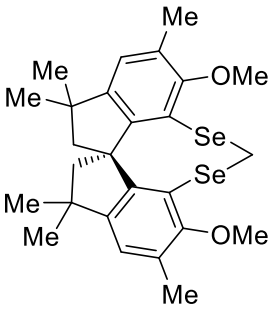
Table 6. Catalyst optimization of enantioselective amination.



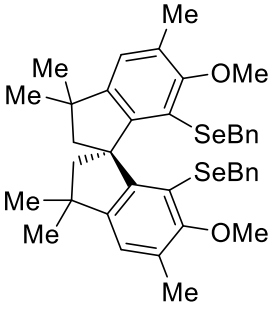
146b **149d**

Entry	Se-Cat*	Setup/ Comment	NMR-Yield [%][a]	*ee* [%][b]
1	**203**	100 mL round bottom flask[c]	**65**	**81**
2	**204**	photovial[d]	28	81
3	**203**	photovial	31	81
4	**202**	photovial	56	80

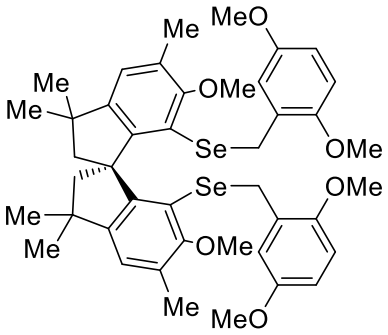
*1,3,5-trimethoxybenzene as internal standard. [b]*ee* determined *via* chiral HPLC. [c]reaction conditions: 4 h, r.t. [d]reaction conditions: 140 min, 55 °C.



202

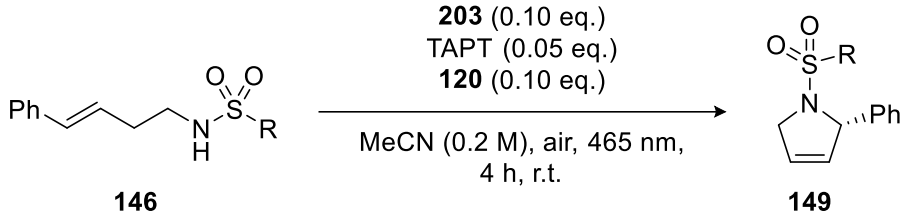


203



204

Table 7. Reaction condition optimization of enantioselective Amination.



Entry	R	NMR-Yield [%][a]	*ee* [%][b]
1	*p*-Tol	65	81
2	Me	46	75
3	Mes	**95**	**83**
4	2,4,6-TIPP	21	83
5	*p*-anisyl, photovial (0.3 mmol scale)	28	84
6	*p*-nitrophenyl, photovial (0.3 mmol scale)	85	70
7	*o*-nitrophenyl	52	94
8	*o*-, *p*-dimethoxyphenyl	31	86
9	*o*-nitrophenyl, 18 °C	49	n.d.[c]
10	*o*-nitrophenyl, 40 °C	27	n.d.
11	*o*-nitrophenyl, + 0.5 eq. *o*-nitrobenzaldehyde	29	n.d.
12	*o*-nitrophenyl, + 0.25 eq. *o*-nitrobenzaldehyde	43	n.d.
13	*o*-nitrophenyl, + 1.0 eq. Na_2HPO_4	37	n.d.
14	*o*-nitrophenyl, + 5 mg MS (4 Å)	49	n.d.
15	*o*-nitrophenyl, in DCE (instead of MeCN)	34	n.d.
16	*o*-nitrophenyl, + 0.2 eq. Disulfide	39	n.d.
17	*o*-nitrophenyl, + S (instead of Disulfide)	10	n.d.
18	*o*-nitrophenyl, 0.2 M	44	n.d.
19	*o*-nitrophenyl, 0.15 eq. Se-cat*	29	n.d.
20	*o*-nitrophenyl, 0.05 eq. of thioxanthene photocat. instead	4 (14% conv.)	n.d.
21	*o*-nitrophenyl, + 0.25 eq. $P(OEt)_3$	22	n.d.

All reactions were carried out in a 100 mL round bottom flask setup. [a]1,3,5-trimethoxybenzene as internal standard. [b]*ee* determined *via* chiral HPLC. [c]not determined.

6.4 Initial rate experiment

For the initial rate experiments, all reactions were performed in irradiated photovials with applied air balloon on a 0.3 mmol scale of the substrate **146b** and were stirred for the indicated time. Every data point arises from an individual experiment. The shown yields refer to the NMR-yield of the respective experiment. The indicated compounds were added- if noted- in the following stoichiometry: **146b** (1.0 eq., 0.30 mmol), $(SePh)_2$ (**13**) (0.1 eq., 0.03 mmol), **120** (0.1 eq., 0.03 mmol), TAPT (0.05 eq., 0.015 mmol), **146a** (1.0 eq., 0.30 mmol) in 3 mL MeCN. **Note:** Alkene **146a** was used in the indicated experiments for scavenging additionally formed **120** (in the case of the **228**) and **13** (in the case of the **227**), which otherwise would both quench the excited photocatalyst (see Stern-Volmer experiment).

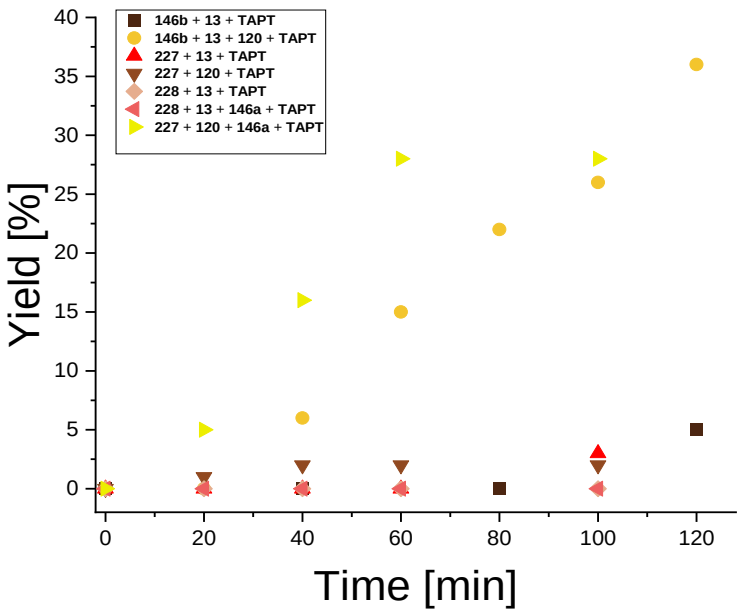


Figure 26. Initial rate experiment.[142]

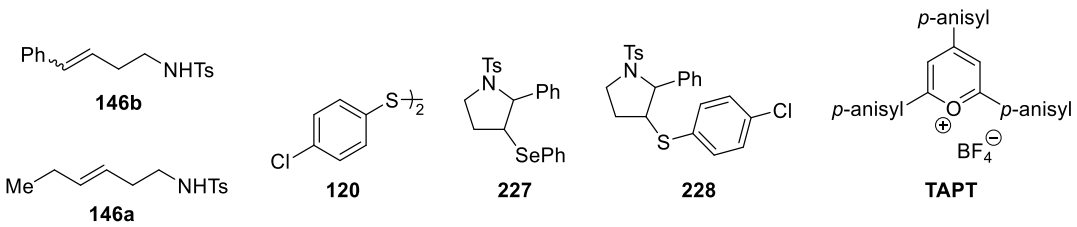


Figure 27. Compounds used for the initial rate experiment and Stern-Volmer plot.

6.5 Stern-Volmer plot

Fluorescence quenching measurements were performed on a JOBINYVON Fluorolog by HORIBA in quartz cuvettes (1 x 1cm) by T. Appleson.[142] For fluorescence quenching measurements, a 0.2 mM stock solution of TAPT, a 2.0 mM stock solution of **13**, a 2.0 and a 6.0 mM stock solution of **120** and a 6.0 mM stock solution of the intermediate **227** in MeCN were prepared. From these stock solutions, samples were prepared with a final TAPT concentration of 10 µM and quencher concentrations in the range of 0-5.7 mM (0-570 eq.). Every measurement was conducted three to five times and an average value of the fluorescence intensity was used for analysis. The obtained intensities $\frac{I_0}{I}$-1 were plotted against the quencher concentration c_q, where I_0 equals the fluorescence intensity of the unquenched photocatalyst derived from the sample containing no quencher and I equals the intensity of the quenched sample. The Stern-Volmer constants K_{SV} of the quenchers were obtained from the slopes of these plots following the Stern-Volmer equation (17).

$$\frac{I_0}{I}\text{-}1 = K_{SV} \cdot c_q \tag{17}$$

Fluorescence quenching was conducted at an absorption λ_{Abs} = 443 nm and an emission λ_{Em} = 540 nm. The resulting Stern-Volmer constants are summarized in Table 8.

Table 8. Stern-Volmer constants for the quenching of TAPT (from T. Appleson).[142]

Quencher	Stern-Volmer constant [M^{-1}]
13	198 ± 2
120	105 ± 4
227	53.2 ± 2.5

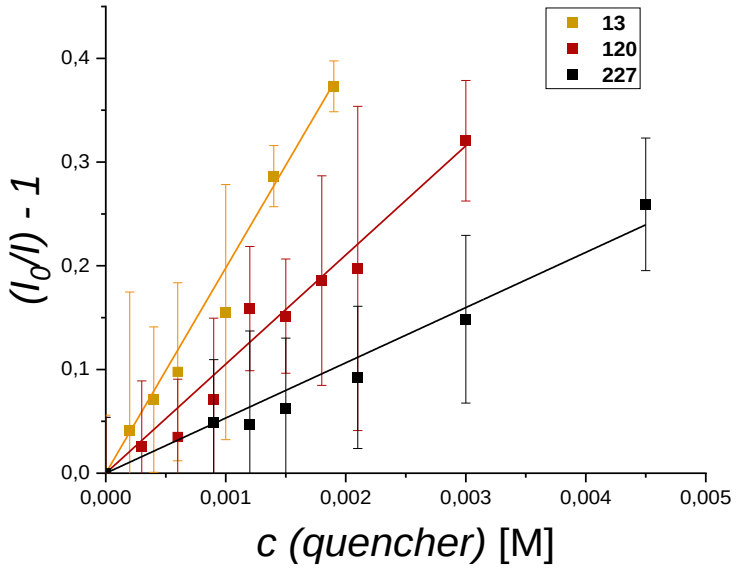
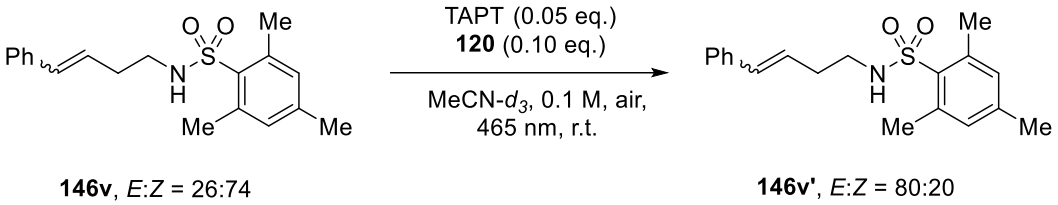


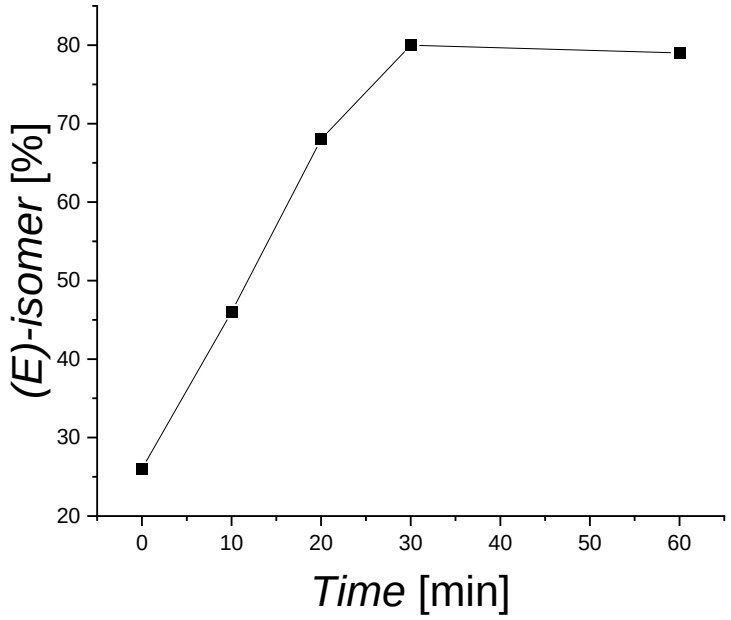
Figure 28. Stern-Volmer quenching experiment (from T. Appleson).[142]

6.6 *E/Z* isomerization of substrates

To a solution of the stated sulfonamide (300 µmol, 1.00 eq.) in MeCN-d_3 (0.1 M, 3 mL) in a photovial were added TAPT (5 mol%) and **120** (10 mol%). The solution was subjected to irradiation at 465 nm and stirred vigorously with a normal stirring bar (750 rpm) at ambient air. The *E/Z* ratio was determined *via* ^{1}H-NMR after the indicated time. Every data point corresponds to an individual experiment.



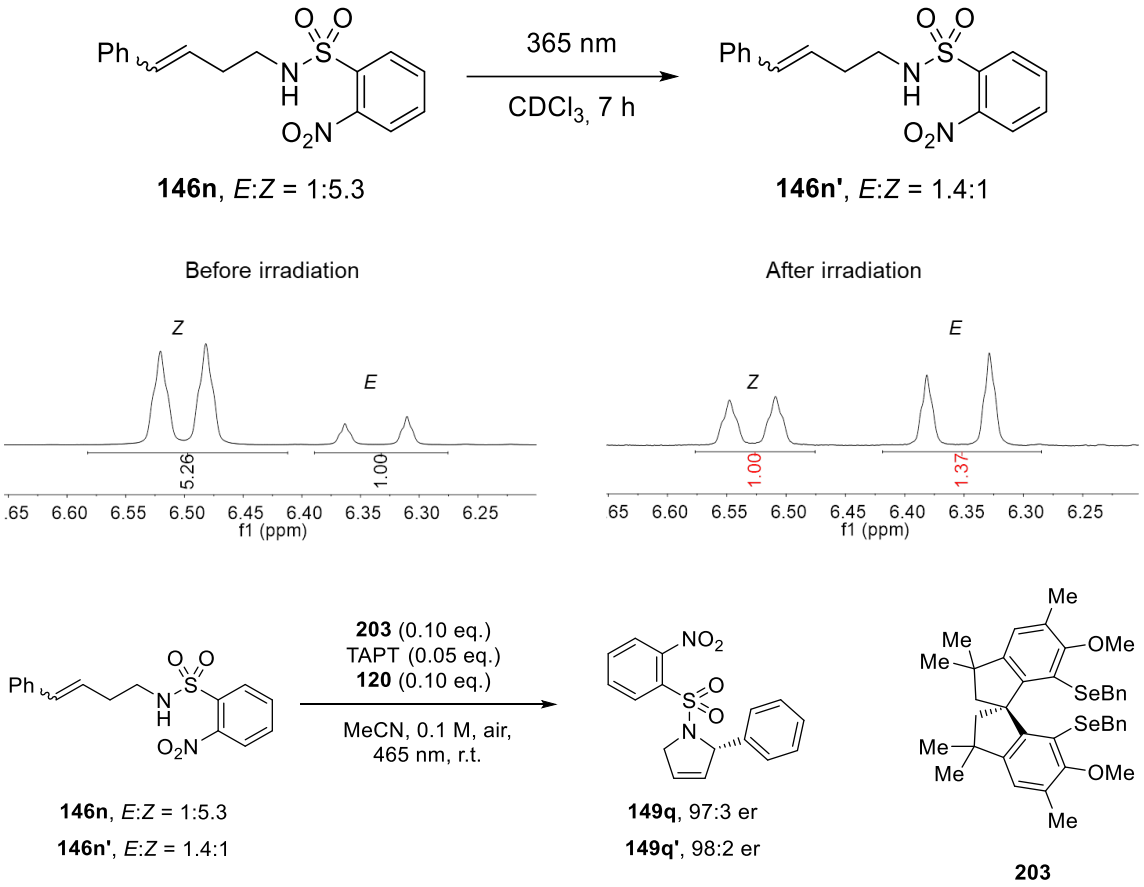
146v, *E*:*Z* = 26:74 **146v'**, *E*:*Z* = 80:20



Scheme 78. *E/Z* isomerization prior to cyclization.[133]

6.7 Independence of *E/Z* ratio of substrates for the stereoselectivity

In a 100 mL round bottom flask a solution of the stated sulfonamide (300 µmol) in $CDCl_3$ (0.1 M, 3 mL) was subjected to irradiation at 365 nm and stirred for 7 h (Scheme 79, above). From the solution a sample was taken to determine the *E/Z* ratio *via* ^{1}H-NMR (Scheme 79, center, besides the change of *E/Z* ratio no development of side products was detected). After evaporation of the solvent, the isomerized product was taken for the cyclization reaction (Scheme 79, below).



Scheme 79. *E/Z* isomerization of substrate with UV light (above), ^{1}H-NMR determination of *E/Z* ratios before and after UV irradiation (center), reaction showing the independence of *E/Z* ratio for the enantioselectivity (below).[133]

6.8 Experimental procedures

6.8.1 General procedures

General procedure A: TfOH catalyzed reductive amination[102]

$TsNH_2$ (1.50 eq.), triethylsilane (1,10 eq.) and trifluoromethanesulfonic acid (0.05 eq.) were added to a solution of the aldehyde (1.00 eq.) in nitromethane (1.0 M) and the mixture was stirred at r.t. for 3 h. Then, 50 mL distilled H_2O were added, and the product was extracted 3x with DCM. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography.

General procedure B: Grubbs Metathesis[107]

To a solution of Grubbs 2nd generation catalyst (0.01 eq.) in DCM under N_2 atmosphere the alkene (1.00 eq.) and the allyl moiety (1.00 eq.) were added simultaneously. The reaction mixture was stirred at r.t. for the indicated time. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography.

General procedure C: Mesylation of alcohol and sulfonamidation[101]

To a solution of the alcohol (1.00 eq.) in DCM (0.1 M), NEt_3 (3.70 eq.) and MsCl (1.60 eq.) were added sequentially at 0 °C and the reaction progress was monitored *via* TLC. Upon completion, 50 mL distilled H_2O were added, and the product was extracted 3x with DCM. The solvent was evaporated under reduced pressure and the crude product was used without further purification. The mesylated alcohol was dissolved in DMF (0.1 M), then, the indicated amount of $TsNH_2$ and K_2CO_3 (7.40 eq.) were added. The solution was stirred for 1 d at 100 °C. The reaction was cooled to r.t. and neutralized by dropwise addition of aq. HCl solution (1 M). The product was extracted 3x with DEE. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography.

General procedure D: Wittig Reaction[95]

To a suspension of the appropriate phosphonium bromide (2.00 eq.) in THF (0.6 M) KO^{t}Bu (4.00 eq.) was added at 0 °C and the mixture stirred for 30 min. A solution of the carbonyl (1.00 eq.) in THF (2.0 M) was added dropwise at 0 °C, the solution was allowed to warm to r.t. and stirred until full conversion was detected *via* TLC. Sat. aq.

NH_4Cl was added, the mixture was extracted 3x with DEE. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography.

General procedure E: Sulfonamidation of amine[51]

To a solution of the amine (1.00 eq.) in DCM (0.1 M), the indicated amount of NEt_3 and the appropriate sulfonylchloride were added at r.t. and the solution was stirred overnight. Then, 50 mL distilled H_2O were added, and the crude product was extracted 3x with DCM. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography.

General procedure F: Photoaerobic racemic amination

To a solution of the sulfonylaminde (1.00 eq.) in *o*-xylene (0.2 M) $(PhSe)_2$ (**13**, 0.10 eq.) and TAPT (0.05 eq.) were added in a 250 mL round bottom flask. The suspension was subjected to irradiation at 465 nm and stirred vigorously with a cross shaped stirring bar (750 rpm) at ambient air for the given time. If indicated, $(4\text{-}ClPhS)_2$ (**120**, 0.10 eq.) or 2-nitrobenzaldehyde (0.25 eq.) were added to the suspension right away or **13** (0.10 eq.) and TAPT (0.05 eq.) were re-added after the indicated time. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography.

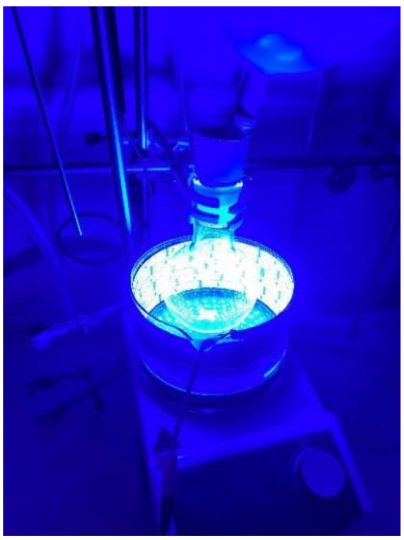


Figure 29. Reaction setup for the racemic Amination.

General procedure G: Wittig Reaction and subsequent sulfonamidation[95]

To a suspension of the appropriate phosphonium bromide (2.00 eq.) in THF (0.6 M), KO*t*Bu (4.00 eq.) was added at 0 °C. The mixture was stirred for 30 min at 0 °C. A solution of the carbonyl compound (1.50 eq.) in THF (2.0 M) was added dropwise at 0 °C. The solution was allowed to warm to r.t. and stirred until full conversion was detected *via* TLC. Brine was added and the mixture was extracted 3x with DEE. The solvent was evaporated under reduced pressure and the crude product was subsequently dissolved in 50 mL DCM. The indicated amount of NEt_3 and sulfonylchloride were added at r.t. and the solution was stirred overnight. Then, 50 mL of distilled H_2O were added, and the crude product was extracted 3x with DCM. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography.

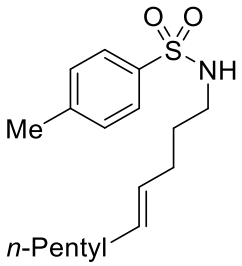
General procedure H: Photoaerobic enantioselective amination

To a solution of the stated sulfonamide (500 µmol or 300 µmol, 1.00 eq.) in MeCN (0.1 M, 5 mL or 3 mL) in a 100 mL round bottom flask were added TAPT (25.0 µmol, 12.1 mg or 15.0 µmol, 7.30 mg, 0.05 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (**203**, 50.0 µmol, 35.0 mg or 30.0 µmol, 21.2 mg, 0.10 eq.) and $(4\text{-ClPhS})_2$ (**120**, 50.0 µmol, 14.4 mg or 30.0 µmol, 8.67 mg, 0.10 eq.). The solution was subjected to irradiation at 465 nm and stirred vigorously with a cross shaped stirring bar (750 rpm) at ambient air until the full conversion of the substrate. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography.

Figure 30. Reaction setup for the enantioselective Amination.

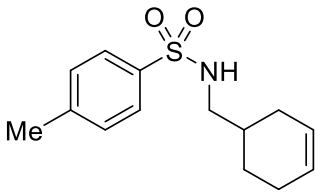
6.8.2 Substrate synthesis for the racemic amination

(*E*)-*N*-(Dec-4-en-1-yl)-4-methylbenzenesulfonamide (139a)



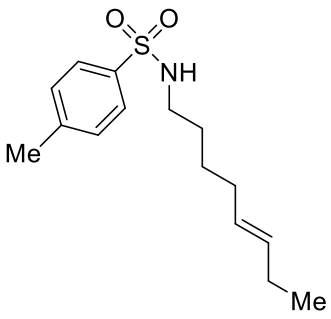
According to General procedure A: (*E*)-Dec-4-enal (2.38 mL, 13.0 mmol, 1.00 eq.), $TsNH_2$ (3.33 g, 19.5 mmol, 1.50 eq.), triethylsilane (2.28 mL, 14,3 mmol, 1.10 eq.), TfOH (57.4 µL, 648 µmol, 0.05 eq.). Eluting with PE/EtOAc 20:1→9:1. Isolated yield: 3.24 g (10.5 mmol, 81%, yellowish oil). **TLC** R_f = 0.23 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 2926, 2855, 1599, 1439, 1327, 1159, 1096, 969, 987, 813. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.79 – 7.64 (m, 2H), 7.38 – 7.27 (m, 2H), 5.46 – 5.17 (m, 2H), 4.46 (t, *J* = 6.2 Hz, 1H), 2.93 (td, *J* = 7.0, 6.2 Hz, 2H), 2.43 (s, 3H), 2.04 – 1.84 (m, 4H), 1.59 – 1.42 (m, 2H), 1.37 – 1.15 (m, 6H), 0.95 – 0.81 (m, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.3, 137.0, 131.9, 129.7, 128.4, 127.1, 42.7, 32.5, 31.4, 29.5, 29.3, 29.2, 22.5, 21.5, 14.1. **HRMS** (ESI) calcd. for $[C_{17}H_{28}NO_2S]^+$ $(M+H)^+$, m/z = 310.1671, found 310.1684.

N-(Cyclohex-3-en-1-ylmethyl)-4-methylbenzenesulfonamide (139e)



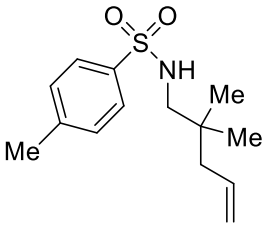
According to General procedure A: Cyclohex-3-ene-1-carbaldehyde (0.20 mL, 1.81 mmol, 1.00 eq.), $TsNH_2$ (464 mg, 2.71 mmol, 1.50 eq.), triethylsilane (317 µL, 2.00 mmol, 1.10 eq.), TfOH (8.00 µL, 90.3 µmol, 0.05 eq.). Eluting with PE/EtOAc 20:1→9:1. Isolated yield: 455 mg (1.71 mmol, 95%, white solid). **TLC** R_f = 0.40 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 3027, 2919, 1599, 1495, 1431, 1320, 1156, 1092, 1062, 813. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.82 – 7.67 (m, 2H), 7.41 – 7.25 (m, 2H), 5.83 – 5.32 (m, 2H), 4.80 (t, *J* = 6.4 Hz, 1H), 2.84 (t, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 2.15 – 1.90 (m, 3H), 1.68 (dtdd, *J* = 14.9, 12.8, 6.0, 4.7 Hz, 3H), 1.29 – 1.08 (m, 1H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.3, 137.0, 129.7, 127.1, 127.0, 125.4, 48.5, 33.7, 29.1, 26.0, 24.4, 21.6. **HRMS** (ESI) calcd. for $[C_{14}H_{19}NO_2S]^+$ $(M+H)^+$, m/z = 266.1209, found 266.1211.

(*E*)-4-Methyl-*N*-(oct-5-en-1-yl)benzenesulfonamide (147a)



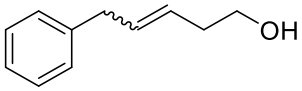
According to General procedure A: (*E*)-5-Octenal (1.00 g, 7.92 mmol, 1.00 eq.), $TsNH_2$ (2.04 g, 11.9 mmol, 1.50 eq.), triethylsilane (1.39 mL, 8.72 mmol, 1.10 eq.), TfOH (35.0 µL, 396 µmol, 0.05 eq.). Eluting with PE/EtOAc 9:1. Isolated yield: 461 mg (1.64 mmol, 21%, colorless oil). **TLC** R_f = 0.40 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3284, 2960, 2933, 2870, 1457, 1327, 1159, 1096, 969, 816. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.75 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.02 (m, 2H), 5.53 – 5.14 (m, 2H), 5.06 (t, *J* = 6.1 Hz, 1H), 2.88 (td, *J* = 7.0, 6.1 Hz, 2H), 2.40 (s, 3H), 2.05 – 1.77 (m, 4H), 1.53 – 1.21 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.3, 137.0, 132.5, 129.7, 128.4, 127.1, 43.1, 31.9, 28.9, 26.4, 25.6, 21.5, 13.9. **HRMS** (ESI) calcd. for $[C_{15}H_{24}NO_2S]^+$ $(M+H)^+$, m/z = 282.1522, found 282.1525.

***N*-(2,2-Dimethylpent-4-en-1-yl)-4-methylbenzenesulfonamide (167)**



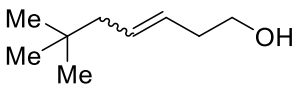
According to General procedure A: 2,2-Dimethylpent-4-enal (825 mg, 7.35 mmol, 1.00 eq.), $TsNH_2$ (1.89 g, 11.0 mmol, 1.50 eq.), triethylsilane (1.29 mL, 8.09 mmol, 1.10 eq.), TfOH (32.5 µL, 368 µmol, 0.05 eq.). Eluting with PE/EtOAc 20:1. Isolated yield: 552 mg (2.06 mmol, 28%, colorless oil). **TLC** R_f = 0.59 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3288, 3075, 2967, 2922, 2874, 1640, 1599, 1454, 1420, 1327, 1163, 1096, 999, 917, 842. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.93 – 7.63 (m, 2H), 7.32 – 7.14 (m, 2H), 5.80 – 5.56 (m, 1H), 5.49 (t, *J* = 6.8 Hz, 1H), 5.02 – 4.90 (m, 2H), 2.62 (d, *J* = 6.9 Hz, 2H), 2.37 (s, 3H), 1.92 (dt, *J* = 7.5, 1.2 Hz, 2H), 0.81 (s, 6H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.2, 137.0, 134.3, 129.7, 127.0, 117.8, 52.8, 43.9, 34.1, 24.8, 21.5. **HRMS** (ESI) calcd. for $[C_{14}H_{22}NO_2S]^+$ $(M+H)^+$, m/z = 268.1366, found 268.1372.

5-Phenylpent-3-en-1-ol (157a)



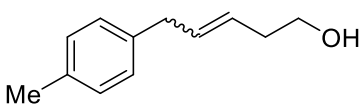
According to General procedure B: Grubbs 2nd generation catalyst (198 mg, 232 µmol, 0.01 eq.), but-3-en-1-ol (1.69 g, 23.2 mmol, 1.00 eq.) and allylbenzene (2.75 g, 23.2 mmol, 1.00 eq.) in 40 mL DCM for 2 d. Eluting with PE/EtOAc 20:1. Isolated yield: 1.39 g (8.57 mmol, 37%, brownish oil) as a mixture of isomers (*E*:*Z* = 5.2:1). **TLC** R_f = 0.16 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3370, 3027, 2885, 1718, 1689, 1603, 1495, 1454, 1178, 1029, 969. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.47 – 7.07 (m, 5H), 5.74 (dtt, *J* = 15.0, 6.7, 1.6 Hz, 1H), 5.63 – 5.41 (m, 1H), 3.73 – 3.61 (m, 2H), 3.43 (dd, *J* = 22.4, 7.0 Hz, 2H), 2.52 – 2.25 (m, 2H), 2.12 (s, 1H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 140.6, 132.3, 128.5, 128.5, 127.6, 126.1, 62.1, 39.2, 36.0, 33.7. **HRMS** (EI) calcd. for $[C_{11}H_{12}]^{\cdot+}$ $(M–H_2O)^{\cdot+}$, m/z = 144.0939, found 144.0934.

6,6-Dimethylhept-3-en-1-ol (157b)



According to General procedure B: Grubbs 2nd generation catalyst (98.8 mg, 116 µmol, 0.01 eq.), but-3-en-1-ol (838 g, 11.6 mmol, 1.00 eq.) and 4,4-dimethylpent-1-ene (1.14 g, 11.6 mmol, 1.00 eq.) in 40 mL DCM for 5 d. Eluting with PE/EtOAc 99:1→20:1. Isolated yield: 490 mg (3.44 mmol, 30%, brownish oil) as a mixture of isomers (*E*:*Z* = 2.7:1). **TLC** R_f = 0.21 (9:1 PE/EtOAc). **IR** [cm^{-1}] 2952, 2863, 2363, 2337, 1737, 1457, 1364, 1215. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 5.70 – 5.10 (m, 2H), 3.54 (td, *J* = 6.6, 1.1 Hz, 2H), 2.34 – 2.10 (m, 2H), 1.85 (ddd, *J* = 20.0, 7.5, 1.2 Hz, 2H), 0.81 (d, *J* = 8.7 Hz, 9H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 130.8, 129.7, 128.1, 126.6, 62.1, 62.1, 47.2, 41.2, 30.7, 29.2. **HRMS** (EI) calcd. for $[C_9H_{18}O]^{\cdot+}$ $(M)^{\cdot+}$, m/z = 142.1358, found 142.1350.

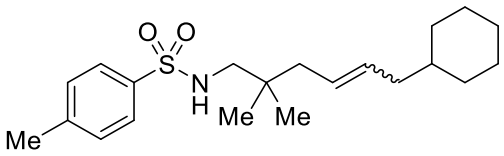
5-(*p*-Tolyl)pent-3-en-1-ol (157c)



This compound was synthesized during an internship with Daniel Kolb. According to General procedure B: Grubbs 2nd generation catalyst (88.9 mg, 105 µmol, 0.01 eq.), but-3-en-1-ol (754 mg, 10.5 mmol, 1.00 eq.) and 1-allyl-4-methyl-benzene (1.38 g, 10.5 mmol, 1.00 eq.) in 40 mL DCM for 1 d. Eluting with PE/EtOAc 9:1. Isolated yield: 532 mg (3.02 mmol,

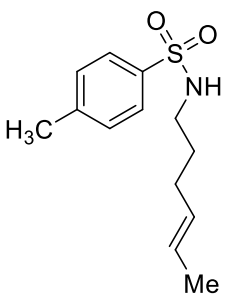
29%, brownish oil) as a mixture of isomers (*E*:*Z* = 3:1). **TLC** R_f = 0.16 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3373, 2922, 1722, 1685, 1607, 1513, 1431, 1178, 1044, 969, 805. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.26 (d, *J* = 2.2 Hz, 4H), 6.07 – 5.53 (m, 2H), 3.78 (dt, *J* = 10.0, 6.7 Hz, 2H), 3.67 – 3.30 (m, 3H), 2.66 – 2.37 (m, 5H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 137.7, 135.5, 132.2, 129.3, 128.6, 127.6, 62.2, 38.9, 36.1, 21.2. **HRMS** (EI) calcd. for $[C_{12}H_{16}O]^{\cdot+}$ $(M)^{\cdot+}$, m/z = 176.1201, found 176.1195.

N-(6-Cyclohexyl-2,2-dimethylhex-4-en-1-yl)-4-methylbenzenesulfonamide (139c)



According to General procedure B: Grubbs 2nd generation catalyst (159 mg, 187 µmol, 0.10 eq.), *N*-(2,2-dimethylpent-4-en-1-yl)-4-methylbenzenesulfonamide (500 mg, 1.87 mmol, 1.00 eq.) and allylcyclohexane (232 mg, 1.87 mmol, 1.00 eq.) in 6.5 mL DCM for 1 d. Eluting with PE/EtOAc 20:1. Isolated yield: 120 mg (330 µmol, 18%, colorless oil) as a mixture of isomers (*E*:*Z* = 2.6:1). **TLC** R_f = 0.55 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3295, 2926, 2855, 2363, 2341, 1703, 1599, 1450, 1334, 1215, 1159, 1096, 973, 910, 842, 842, 816, 708, 664. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.95 – 7.60 (m, 2H), 7.50 – 7.04 (m, 2H), 5.56 – 5.10 (m, 2H), 5.05 – 4.90 (m, 1H), 2.65 (dd, *J* = 8.8, 6.9 Hz, 2H), 2.37 (s, 3H), 1.95 – 1.76 (m, 4H), 1.74 – 1.53 (m, 5H), 1.31 – 1.04 (m, 4H), 0.83 (m, 8H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.2, 143.2, 137.1, 132.5, 131.2, 129.7, 127.1, 126.4, 125.3, 122.8, 118.2, 53.2, 52.8, 42.8, 40.7, 38.3, 38.0, 37.1, 35.1, 34.7, 34.3, 34.3, 33.1, 26.6, 26.4, 24.9, 24.8, 21.5. **HRMS** (ESI) calcd. for $[C_{21}H_{34}NO_2S]^{\cdot+}$ $(M)^{\cdot+}$, m/z = 364.2305, found 364.2308.

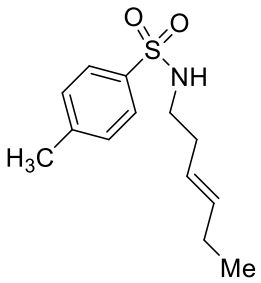
(*E*)-*N*-(Hex-4-en-1-yl)-4-methylbenzenesulfonamide (139d)



According to general procedure C: (*E*)-Hex-4-en-1-ol (851 mg, 8.50 mmol, 1.00 eq.), NEt_3 (3.18 g, 31.4 mmol, 3.70 eq.), MsCl (1.56 g, 13.6 mmol, 1.60 eq.) in 90 mL DCM, then K_2CO_3 (8.69 g, 62.9 mmol, 7.40 eq.) and $TsNH_2$ (12.5 g, 73.1 mmol, 8.60 eq.) in 90 mL DMF. Eluting with PE/EtOAc 9:1→4:1. Isolated yield: 1.70 g (6.71 mmol, 79%, yellowish oil). **TLC** R_f = 0.44 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 2933, 2855, 1599, 1666, 1495, 1320, 1156, 1092, 965.

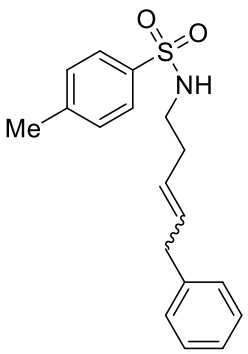
^{1}H-NMR (300 MHz, Chloroform-*d*): δ (ppm) = 7.73 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 5.68 – 4.67 (m, 3H), 2.91 – 2.79 (m, 2H), 2.39 (d, *J* = 1.4 Hz, 3H), 1.98 – 1.82 (m, 2H), 1.62 – 1.36 (m, 5H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.2, 129.8, 129.7, 127.1, 125.9, 42.6, 29.5, 29.2, 21.5, 17.9. **HRMS** (ESI) calcd. for $[C_{13}H_{20}NO_2S]^+$ $(M+H)^+$, m/z = 254.1209, found 254.1210.

(*E*)-*N*-(Hex-3-en-1-yl)-4-methylbenzenesulfonamide (146a)



According to general procedure C: (*E*)-Hex-3-en-1-ol (1.10 g, 11.0 mmol, 1.00 eq.), NEt_3 (4.11 g, 40.6 mmol, 3.70 eq.), MsCl (2.01 g, 17.6 mmol, 1.60 eq.) in 116 mL DCM, then K_2CO_3 (11.2 g, 81.3 mmol, 7.40 eq.) and $TsNH_2$ (7.52 g, 49.9 mmol, 4.00 eq.) in 116 mL DMF. Eluting with PE/EtOAc 20:1→9:1. Isolated yield: 1.99 g (7.85 mmol, 72%, colorless oil). **TLC** R_f = 0.54 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 2963, 2933, 1599, 1424, 1320, 1156, 1092. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.77 – 7.68 (m, 2H), 7.33 – 7.24 (m, 2H), 5.43 (dtt, *J* = 15.2, 6.2, 1.3 Hz, 1H), 5.16 (dtt, *J* = 15.3, 6.9, 1.6 Hz, 1H), 4.91 (t, *J* = 6.0 Hz, 1H), 2.92 (td, *J* = 6.8, 5.9 Hz, 2H), 2.39 (s, 3H), 2.09 (qq, *J* = 6.7, 1.1 Hz, 2H), 1.92 (qdq, *J* = 7.4, 6.2, 1.2 Hz, 2H), 0.89 (t, *J* = 7.5 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.3, 137.0, 135.8, 129.7, 127.1, 124.4, 42.8, 32.4, 25.5, 21.5, 13.6. **HRMS** (ESI) calcd. for $[C_{13}H_{20}SO_2S]^+$ $(M+H)^+$, m/z = 254.1209, found 254.1210.

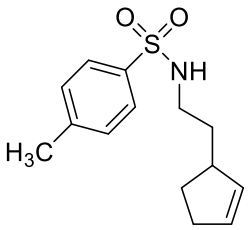
4-Methyl-*N*-(5-phenylpent-3-en-1-yl)benzenesulfonamide (146j)



According to general procedure C: 5-Phenylpent-3-en-1-ol (1.39 mg, 8.57 mmol, 1.00 eq.), NEt_3 (3.21 g, 31.7 mmol, 3.70 eq.), MsCl (1.57 g, 13.7 mmol, 1.60 eq.) in 90 mL DCM, then K_2CO_3 (8.76 g, 63.4 mmol, 7.40 eq.) and $TsNH_2$ (12.6 g, 73.7 mmol, 8.60 eq.) in 90 mL DMF. Eluting with PE/EtOAc 4:1. Isolated yield: 271 mg (0.86 mmol, 10%, colorless oil) as a mixture of isomers (*E*:*Z* = 5.5:1). **TLC** R_f = 0.31 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3478, 3273, 3064, 3030, 2926, 1599, 1707, 1495, 1450, 1420, 1323, 1223, 1156, 1092. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = δ 7.84 – 7.69 (m, 2H), 7.37 – 7.06 (m, 7H), 5.73

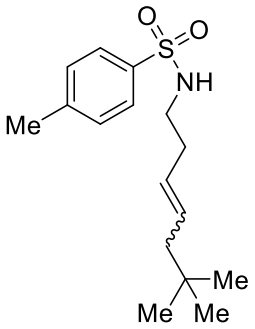
– 5.50 (m, 1H), 5.46 – 5.17 (m, 1H), 5.07 – 4.74 (m, 1H), 3.38 – 3.21 (m, 2H), 3.01 (p, *J* = 6.8 Hz, 2H), 2.42 (s, 3H), 2.33 – 2.02 (m, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.4, 140.3, 137.0, 132.7, 131.6, 129.7, 128.5, 128.5, 128.3, 127.2, 127.1, 126.1, 126.1, 125.9, 118.2, 42.7, 39.0, 33.5, 32.5, 27.6, 21.6. **HRMS** (ESI) calcd. for $[C_{18}H_{21}NO_2S]^+$ $(M+H)^+$, m/z = 316.1366, found 316.1367.

N-(Cyclopent-2-en-1-ylmethyl)-4-methylbenzenesulfonamide (139b)



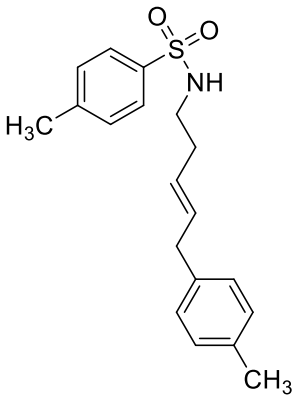
To a suspension of $LiAlH_4$ (1.50 g, 39.6 mmol, 2.50 eq.) in 80 mL THF at 0 °C, a solution of cyclopent-2-eneacetic acid (2.00 g, 15.6 mmol, 1.00 eq.) in 16 mL THF was added slowly. The mixture was stirred overnight at r.t., then cooled to 0 °C again and quenched carfully with 100 mL distilled H_2O. The crude product was extracted 3x with DCM and the solvent was evaporated under reduced pressure. The residue was used without further purification in the next step. According to general procedure C: the crude alcohol (1.70 g), NEt_3 (5.67 g, 56.1 mmol, 3.70 eq.), MsCl (2.78 g, 24.3 mmol, 1.60 eq.) in 160 mL DCM, then K_2CO_3 (15.5 g, 112 mmol, 7.40 eq.) and $TsNH_2$ (13.0 g, 75.8 mmol, 5.00 eq.) in 160 mL DMF. Eluting with PE/EtOAc 20:1. Isolated yield: 2.51 g (9.46 mmol, 62%, yellowish oil). **TLC** R_f = 0.44 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3273, 3049, 2930, 2855, 1662, 1599, 1435, 1323, 1156, 1092. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.83 – 7.68 (m, 2H), 7.37 – 7.27 (m, 2H), 5.71 (dq, *J* = 5.8, 2.3 Hz, 1H), 5.55 (dq, *J* = 5.8, 2.1 Hz, 1H), 4.44 (t, *J* = 6.2 Hz, 1H), 2.97 (td, *J* = 7.4, 6.2 Hz, 2H), 2.64 (ttt, *J* = 8.5, 6.3, 2.3 Hz, 1H), 2.43 (s, 3H), 2.36 – 2.15 (m, 2H), 2.10 – 1.86 (m, 1H), 1.71 – 1.15 (m, 4H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.4, 136.9, 133.8, 131.3, 129.7, 127.1, 42.7, 41.9, 35.7, 31.9, 29.5, 21.6. **HRMS** (ESI) calcd. for $[C_{14}H_{20}NO_2S]^+$ $(M+H)^+$, m/z = 266.1209, found 266.1209.

N-(6,6-Dimethylhept-3-en-1-yl)-4-methylbenzenesulfonamide (146k)



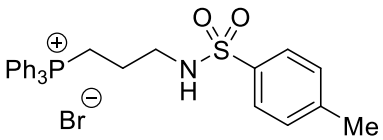
According to general procedure C: 6,6-Dimethylhept-3-en-1-ol (270 mg, 1.90 mmol, 1.00 eq.), NEt_3 (711 mg, 7.02 mmol, 3.70 eq.), MsCl (348 mg, 3.04 mmol, 1.60 eq.) in 20 mL DCM, then K_2CO_3 (1.94 g, 14.1 mmol, 7.40 eq.) and $TsNH_2$ (2.79 g, 16.3 mmol, 8.60 eq.) in 20 mL DMF. Eluting with PE/EtOAc 9:1→4:1. Isolated yield: 320 mg (1.08 mmol, 57%, colorless oil) as a mixture of isomers (*E*:*Z* ≈ 3.4:1). **TLC** R_f = 0.44 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 2952, 2866, 1599, 1485, 1431, 1364, 1327, 1159, 1096, 973, 813. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.73 (dq, *J* = 8.5, 1.9 Hz, 2H), 7.31 – 7.19 (m, 2H), 5.62 – 4.94 (m, 3H), 2.90 (tt, *J* = 7.0, 5.4 Hz, 2H), 2.35 (s, 3H), 2.11 (qd, *J* = 7.0, 1.4 Hz, 2H), 1.77 (ddd, *J* = 7.4, 4.0, 1.2 Hz, 2H), 0.83 – 0.74 (m, 9H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.2, 137.1, 137.0, 131.0, 130.1, 129.7, 127.7, 127.2, 127.1, 127.1, 127.1, 126.3, 47.0, 46.6, 45.3, 42.9, 41.0, 32.6, 31.1, 30.7, 29.2, 29.2, 27.5, 21.5. **HRMS** (ESI) calcd. for $[C_{16}H_{26}NO_2S]^+$ $(M+H)^+$, m/z = 296.1679, found 296.1682.

(*E*)-4-Methyl-*N*-(5-(*p*-tolyl)pent-3-en-1-yl)benzenesulfonamide (146l)



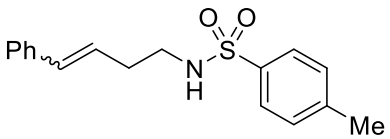
This compound was synthesized during an internship with Daniel Kolb. According to general procedure C: 5-(*p*-Tolyl)pent-3-en-1-ol (468 mg, 2.66 mmol, 1.00 eq.), NEt_3 (994 mg, 9.82 mmol, 3.70 eq.), MsCl (487 mg, 4.25 mmol, 1.60 eq.) in 28 mL DCM, then K_2CO_3 (2.72 g, 19.7 mmol, 7.40 eq.) and $TsNH_2$ (3.91 g, 22.8 mmol, 8.60 eq.) in 28 mL DMF. Eluting with PE/EtOAc 9:1. Isolated yield: 539 mg (1.64 mmol, 62%, colorless oil) exclusively *E*-isomer. **TLC** R_f = 0.34 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 3023, 2922, 1599, 1513, 1431, 1323, 1156, 1096, 969. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.01 – 7.75 (m, 2H), 7.44 – 7.25 (m, 2H), 7.24 – 6.96 (m, 4H), 5.84 – 5.22 (m, 3H), 3.29 (d, *J* = 6.8 Hz, 2H), 3.05 (p, *J* = 6.7 Hz, 2H), 2.41 (d, *J* = 3.2 Hz, 3H), 2.37 (s, 3H), 2.31 – 2.09 (m, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.4, 137.4, 137.2, 132.8, 129.8, 129.2, 128.5, 127.2, 127.0, 42.9, 38.6, 32.6, 21.6, 21.1. **HRMS** (ESI) calcd. for $[C_{19}H_{24}NO_2S]^+$ $(M+H)^+$, m/z = 330,1522 found 330.1524.

(3-((4-Methylphenyl)sulfonamido)propyl)triphenylphosphonium bromide (153)[106]



To a solution of 3-bromopropylamine hydrobromide (10.0 g, 46.0 mmol, 1.00 eq.) in 200 ml DCM, NEt_3 (19.1 mL, 137 mmol, 3.00 eq.) and TsCl (8.70 g, 46.0 mmol, 1.00 eq.) were added dropwise at 0 °C. The solution was stirred for 2 h at r.t., then quenched with 200 mL H_2O. The mixture was extracted 3x with DCM and the solvent was evaporated under reduced pressure. The residue was dissolved in 60 mL MeCN, PPh_3 (14.4 g, 54.8 mmol, 1.20 eq.) was added and the solution was refluxed at 82 °C overnight. The crude mixture was cooled down to r.t., then put into the freezer for 1 h. The white precipitate was filtered off and washed 5× with 50 mL EtOAc, then dried under high vacuum. Isolated yield: 14.9 g (27.1 mmol, 59%, white solid). **TLC** R_f = 0.68 (1:1 DCM/MeOH). **IR** [cm^{-1}] 3407, 2878, 2818, 2065, 1588, 1513, 1484, 1439, 1338, 1159, 1111, 995, 742, 690. **^{1}H-NMR** (400 MHz, MeOD-*d*$_3$): δ (ppm) = 8.07 – 7.55 (m, 17H), 7.42 – 7.23 (m, 2H), 3.50 – 3.35 (m, 2H), 3.04 (td, *J* = 6.5, 1.0 Hz, 2H), 2.39 (s, 3H), 1.89 – 1.70 (m, 2H). **^{13}C-NMR** (75 MHz, MeOD-*d*$_3$): δ (ppm) = 143.4, 137.3, 135.0, 135.0, 133.5, 133.3, 130.3, 130.1, 129.5, 126.6, 118.8, 117.6, 42.5, 42.3, 22.9, 22.9, 20.1, 19.3, 18.6. **^{31}P-NMR** (162 MHz, MeOD-*d*$_3$): δ (ppm) = 23.9. **HRMS** (ESI) calcd. for $[C_{28}H_{29}NO_2PS]^+$ $(M)^+$, m/z = 474.1651, found 474.1651.

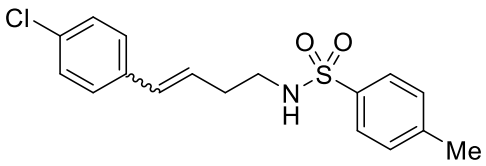
4-Methyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146b)



According to General procedure D: (3-((4-methylphenyl)sulfonamido)propyl)triphenylphosphonium bromide (4.00 g, 7.21 mmol, 2.00 eq.), KO^{t}Bu (1.62 g, 14.4 mmol, 4.00 eq.) in 12 mL THF and benzaldehyde (383 mg, 3.61 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 20:1→9:1. Isolated yield: 1.02 g (3.38 mmol, 94%, white solid) as a mixture of isomers (*E*:*Z* = 3.1:1). **TLC** R_f = 0.25 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3273, 3027, 2926, 2870, 1599, 1495, 1420, 1320, 1156, 1092, 965, 910, 813, 731, 693. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.86 – 7.63 (m, 2H), 7.37 – 7.13 (m, 7H), 6.35 (dt, *J* = 15.9, 1.4 Hz, 1H), 5.99 (dt, *J* = 15.9, 7.1 Hz, 1H), 4.90 (dt, *J* = 20.5, 6.1 Hz, 1H), 3.27 – 2.91 (m, 2H), 2.57 – 2.19 (m, 5H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.4, 143.4, 136.9, 136.9, 136.9, 136.8, 133.0, 131.9, 129.8, 129.7, 128.7, 128.5, 128.3, 127.7, 127.4, 127.2, 127.1, 127.0, 126.2,

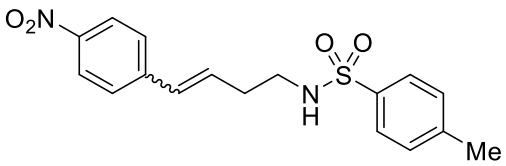
125.7, 43.0, 42.6, 33.0, 28.7, 21.6. **HRMS** (ESI) calcd. for $[C_{17}H_{20}NO_2S]^+$ $(M+H)^+$, m/z = 302.1209, found 302.1207.

N-(4-(4-Chlorophenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (146c)



According to General procedure D: (3-((4-methylphenyl)sulfonamido)propyl)triphenylphosphonium bromide (2.00 g, 3.61 mmol, 2.00 eq.), KO*t*Bu (810 mg, 7.21 mmol, 4.00 eq.) in 6 mL THF and 4-chlorobenzaldehyde (254 mg, 1.80 mmol, 1.00 eq.) in 0.9 mL THF. Eluting with PE/EtOAc 9:1→6:1. Isolated yield: 590 mg (1.76 mmol, 97%, brownish solid) as a mixture of isomers (*E*:*Z* = 4.2:1). **TLC** R_f = 0.23 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 3030, 2930, 2874, 1595, 1491, 1409, 1323, 1211, 1159, 1092, 1014, 969. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.82 – 7.62 (m, 2H), 7.31 – 7.02 (m, 6H), 6.51 – 6.16 (m, 1H), 6.09 – 5.41 (m, 1H), 5.23 (dt, *J* = 17.3, 6.1 Hz, 1H), 3.04 (dq, *J* = 10.0, 6.7 Hz, 2H), 2.48 – 2.22 (m, 5H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.5, 136.8, 135.5, 135.3, 132.8, 132.6, 131.6, 130.5, 130.0, 129.8, 129.7, 128.6, 128.5, 128.4, 127.4, 127.1, 127.0, 126.7, 42.9, 42.6, 33.0, 28.7, 21.6. **HRMS** (ESI) calcd. for $[C_{17}H_{19}ClNO_2S]^+$ $(M+H)^+$, m/z = 336,0820 found 336.0823.

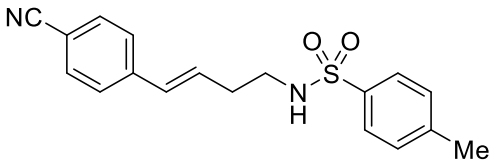
4-Methyl-*N*-(4-(4-nitrophenyl)but-3-en-1-yl)benzenesulfonamide (146d)



According to General procedure D: (3-((4-methylphenyl)sulfonamido)propyl)triphenylphosphonium bromide (4.00 g, 7.21 mmol, 2.00 eq.), KO*t*Bu (1.62 g, 14.4 mmol, 4.00 eq.) in 12 mL THF and 4-nitrobenzaldehyde (545 mg, 3.61 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 20:1→9:1. Isolated yield: 795 mg (2.30 mmol, 64%, brown solid) as a mixture of isomers (*E*:*Z* = 2.1:1). **TLC** R_f = 0.13 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3288, 2933, 1595, 1517, 1342, 1159, 1096, 861, 816, 664. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 8.32 – 7.98 (m, 2H), 7.93 – 7.59 (m, 2H), 7.48 – 7.25 (m, 4H), 6.44 (dt, *J* = 15.8, 1.4 Hz, 1H), 6.23 (dt, *J* = 15.9, 7.0 Hz, 1H), 4.67 (dt, *J* = 26.8, 6.4 Hz, 1H), 3.11 (dq, *J* = 18.2, 6.6 Hz, 2H), 2.62 – 2.22 (m, 5H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 146.8, 146.5, 143.6, 143.4, 143.3, 140.0, 136.9, 136.9, 131.5,

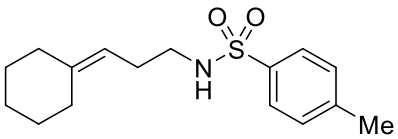
131.2, 131.0, 130.1, 129.8, 129.8, 129.3, 127.1, 127.0, 126.7, 124.0, 123.6, 42.7, 42.3, 33.3, 29.0, 21.6, 21.5. **HRMS** (ESI) calcd. for $[C_{17}H_{19}N_2O_4S]^+$ $(M+H)^+$, m/z = 347.1060, found 347.1061.

(*E*)-*N*-(4-(4-Cyanophenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (146e)



According to General procedure D: (3-((4-methylphenyl)sulfonamido)propyl)triphenylphosphonium bromide (4.00 g, 7.21 mmol, 2.00 eq.), KO*t*Bu (1.62 g, 14.4 mmol, 4.00 eq.) in 12 mL THF and 4-formylbenzonitrile (473 mg, 3.61 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 9:1→4:1. Isolated yield: 1.01 g (3.09 mmol, 86%, yellowish solid) exclusively *E*-isomer. **TLC** R_f = 0.13 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3276, 3034, 2930, 2874, 2225, 1707, 1603, 1498, 1413, 1327, 1156, 1092, 969. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.85 – 7.68 (m, 2H), 7.64 – 7.45 (m, 2H), 7.30 (ddd, *J* = 18.5, 7.5, 1.4 Hz, 4H), 6.48 – 6.28 (m, 1H), 6.17 (dt, *J* = 15.9, 7.0 Hz, 1H), 5.01 (t, *J* = 6.2 Hz, 1H), 3.09 (q, *J* = 6.5 Hz, 2H), 2.59 – 2.26 (m, 5H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.6, 141.4, 136.8, 132.3, 131.4, 130.2, 129.8, 127.1, 126.6, 110.5, 42.4, 33.2, 21.6. **HRMS** (ESI) calcd. for $[C_{18}H_{19}N_2O_2S]^+$ $(M+H)^+$, m/z = 327.1162, found 327.1163.

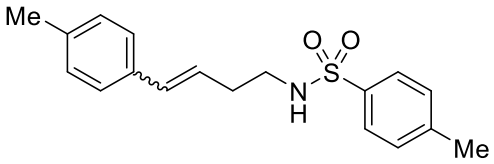
N-(3-Cyclohexylidenepropyl)-4-methylbenzenesulfonamide (146i)



According to General procedure D: (3-((4-methylphenyl)sulfonamido)propyl)triphenylphosphonium bromide (4.00 g, 7.21 mmol, 2.00 eq.), KO*t*Bu (1.62 g, 14.4 mmol, 4.00 eq.) in 12 mL THF and cyclohexanone (354 mg, 3.61 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 9:1. Isolated yield: 1.01 g (3.44 mmol, 95%, yellowish solid). **TLC** R_f = 0.40 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 2926, 2855, 1599, 1446, 1323, 1156, 1096, 1021. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.72 – 7.59 (m, 2H), 7.17 (s, 2H), 5.16 (t, *J* = 6.0 Hz, 1H), 4.79 (tt, *J* = 7.3, 1.3 Hz, 1H), 2.79 (q, *J* = 7.0 Hz, 2H), 2.30 (s, 3H), 2.04 (q, *J* = 7.2 Hz, 2H), 1.96 – 1.78 (m, 4H), 1.36 (dp, *J* = 15.9, 4.7 Hz, 6H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.1,

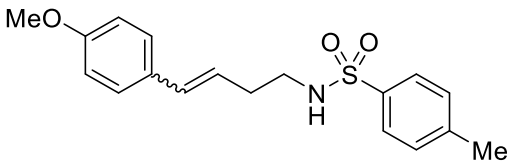
137.0, 129.6, 127.1, 116.5, 43.3, 37.0, 28.7, 28.5, 27.8, 27.3, 26.7, 21.5. **HRMS** (ESI) calcd. for $[C_{16}H_{24}NO_2S]^+$ $(M+H)^+$, m/z = 294.1522, found 294.1531.

4-Methyl-*N*-(4-(*p*-tolyl)but-3-en-1-yl)benzenesulfonamide (146f)



This compound was synthesized during an internship with Alberto Nunez-Bendinelli. According to General procedure D: (3-((4-methylphenyl)sulfonamido)propyl)triphenylphos-phonium bromide (4.00 g, 7.21 mmol, 2.00 eq.), KO^{t}Bu (1.62 g, 14.4 mmol, 4.00 eq.) in 12 mL THF and 4-methylbenzaldehyde (433 mg, 3.61 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 4:1. Isolated yield: 1.03 g (3.27 mmol, 91%, white solid) as a mixture of isomers (*E*:*Z* = 4.3:1). **TLC** R_f = 0.33 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3276, 3023, 2922, 2870, 1707, 1599, 1513, 1420, 1364, 1323, 1223, 1156, 1092, 969. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.85 – 7.71 (m, 2H), 7.30 – 7.03 (m, 6H), 6.32 (d, *J* = 15.8 Hz, 1H), 5.96 (dtt, *J* = 14.2, 7.1, 1.6 Hz, 1H), 5.39 – 5.06 (m, 1H), 3.08 (q, *J* = 6.3 Hz, 2H), 2.55 – 2.29 (m, 8H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.4, 143.3, 137.1, 137.0, 134.3, 132.7, 129.8, 129.2, 127.2, 126.1, 124.8, 42.8, 33.0, 21.6, 21.3. **HRMS** (ESI) calcd. for $[C_{18}H_{22}NO_2S]^+$ $(M+H)^+$, m/z = 316.1366, found 316.1365.

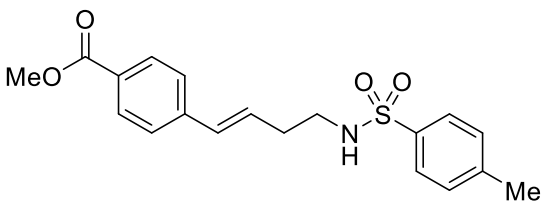
***N*-(4-(4-Methoxyphenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (146g)**



According to General procedure D: (3-((4-methylphenyl)sulfonamido)propyl)triphenyl-phosphonium bromide (4.00 g, 7.21 mmol, 2.00 eq.), KO^{t}Bu (1.62 g, 14.4 mmol, 4.00 eq.) in 12 mL THF and 4-methoxylbenzaldehyde (491 mg, 3.61 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 4:1. Isolated yield: 965 mg (2.91 mmol, 81%, brownish solid) as a mixture of isomers (*E*:*Z* = 3.9:1). **TLC** R_f = 0.33 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 2937, 2840, 1607, 1513, 1442, 1327, 1249, 1156, 1092, 1033, 969. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.86 – 7.61 (m, 2H), 7.37 – 7.07 (m, 4H), 6.83 (dq, *J* = 9.7, 3.0, 2.6 Hz, 2H), 6.52 – 6.15 (m, 1H), 5.82 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.62 (dt, *J* = 13.5, 6.1 Hz, 1H), 3.80 (d, *J* = 3.0 Hz, 3H), 3.06 (p, *J* = 6.6 Hz, 2H), 2.57 – 2.25 (m, 5H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 159.1, 143.4, 136.9, 132.6,

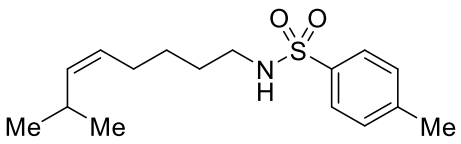
129.9, 129.7, 129.6, 127.3, 127.2, 127.1, 123.3, 114.0, 113.7, 55.3, 42.7, 33.0, 21.6. **HRMS** (ESI) calcd. for $[C_{18}H_{22}NO_3S]^+$ $(M+H)^+$, m/z = 332.1315, found 332.1315.

Methyl (*E*)-4-(4-((4-methylphenyl)sulfonamido)but-1-en-1-yl)benzoate (146h)



This compound was synthesized during an internship with Alberto Nunez-Bendinelli. According to General procedure D: (3-((4-methylphenyl)sulfonamido)propyl)triphenylphosphonium bromide (4.00 g, 7.21 mmol, 2.00 eq.), KO^{t}Bu (1.62 g, 14.4 mmol, 4.00 eq.) in 12 mL THF and methyl 4-formylbenzoate (592 mg, 3.61 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 9:1→4:1. Isolated yield: 288 mg (2.91 mmol, 81%, white solid) exclusively *E*-isomer. **TLC** R_f = 0.18 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 2952, 1718, 1602, 1439, 1316, 1275, 1178, 1152, 1111, 1081, 1049, 965, 869, 760, 701, 664. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.00 – 7.87 (m, 2H), 7.78 – 7.66 (m, 2H), 7.37 – 7.21 (m, 4H), 6.48 – 6.30 (m, 1H), 6.12 (dt, *J* = 15.8, 7.0 Hz, 1H), 4.70 (t, *J* = 6.2 Hz, 1H), 3.90 (s, 3H), 3.11 (q, *J* = 6.5 Hz, 2H), 2.47 – 2.32 (m, 5H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 166.9, 143.5, 141.3, 136.9, 132.3, 129.9, 129.8, 128.9, 128.6, 127.1, 126.0, 125.8, 52.1, 42.4, 33.2, 21.6. **HRMS** (ESI) calcd. for $[C_{19}H_{22}NO_2S]^+$ $(M+H)^+$, m/z = 360.1264, found 360.1268.

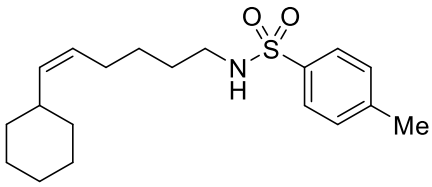
(*Z*)-4-Methyl-*N*-(7-methyloct-5-en-1-yl)benzenesulfonamide (147b)



According to General procedure D: (5-((4-methylphenyl)sulfonamido)pentyl)triphenylphosphonium 4-methylbenzenesulfonate (5.00 g, 7.42 mmol, 2.00 eq.), KO^{t}Bu (1.67 g, 14.8 mmol, 4.00 eq.) in 12 mL THF and isobutyraldehyde (268 mg, 3.71 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 20:1. Isolated yield: 682 mg (2.31 mmol, 62%, yellowish oil) exclusively *Z*-isomer. **TLC** R_f = 0.44 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3288, 2997, 2956, 2866, 1737, 1655, 1599, 1461, 1424, 1327, 1159, 1096, 973, 861, 816, 734, 664. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.82 – 7.63 (m, 2H), 7.36 – 7.16 (m, 2H), 5.30 (t, *J* = 6.1 Hz, 1H), 5.19 – 4.95 (m, 2H), 2.87 (q, *J* = 6.7 Hz, 2H), 2.47 (dh, *J* = 8.4, 6.6 Hz, 1H), 2.38 (s, 3H), 2.03 – 1.77 (m, 2H), 1.53 – 1.34 (m, 2H), 1.33 – 1.17 (m, 2H), 0.90 – 0.79 (m, 6H). **^{13}C-NMR**

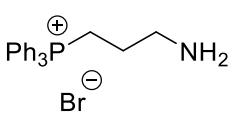
(75 MHz, Chloroform-*d*): δ (ppm) = 143.2, 138.0, 137.0, 129.7, 127.1, 126.6, 43.1, 29.0, 26.7, 26.7, 26.4, 23.2, 21.5. **HRMS** (ESI) calcd. for $[C_{16}H_{26}NO_2S]^+$ $(M+H)^+$, m/z = 296.1679, found 296.1681.

(*Z*)-*N*-(6-Cyclohexylhex-5-en-1-yl)-4-methylbenzenesulfonamide (147c)



According to General procedure D: (5-((4-methylphenyl)sulfonamido)pentyl)triphenylphosphonium 4-methylbenzenesulfonate (5.00 g, 7.42 mmol, 2.00 eq.), KO^{t}Bu (1.67 g, 14.8 mmol, 4.00 eq.) in 12 mL THF and cyclohexanecarbaldehyde (416 mg, 3.71 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 20:1. Isolated yield: 430 mg (1.28 mmol, 35%, yellowish oil) exclusively *Z*-isomer. **TLC** R_f = 0.44 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 2997, 2922, 2851, 2363, 1651, 1599, 1446, 1327, 1159, 1096, 891, 813, 667. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.75 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.35 – 4.99 (m, 2H), 4.73 (t, *J* = 6.1 Hz, 1H), 2.91 (q, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 2.15 (tdd, *J* = 12.2, 7.3, 3.8 Hz, 1H), 1.97 (td, *J* = 7.3, 6.2 Hz, 2H), 1.75 – 1.39 (m, 8H), 1.37 – 0.91 (m, 8H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.3, 137.0, 136.7, 129.7, 127.1, 127.0, 43.2, 36.3, 33.3, 33.2, 29.1, 27.0, 26.1, 26.0, 21.6. **HRMS** (ESI) calcd. for $[C_{19}H_{30}NO_2S]^+$ $(M+H)^+$, m/z = 336.1992, found 336.1992.

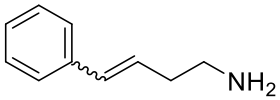
(3-Aminopropyl)triphenylphosphonium bromide (161)[106]



3-Bromopropylamine hydrobromide (20.0 g, 91.4 mmol, 1.00 eq.) was dissolved in 120 mL MeCN, PPh_3 (24.0 g, 91.4 mmol, 1.00 eq.) was added and the solution was refluxed at 82 °C overnight. The crude mixture was cooled down to r.t., then put into the freezer for 1 h. The white precipitate was filtered off and washed 5× with 25 mL EtOAc, then dried under vacuum. Isolated yield: 34.1 g (85.2 mmol, 93%, white solid). **TLC** R_f = 0.70 (1:1 DCM/MeOH). **IR** [cm^{-1}] 3418, 2971, 2922, 1618, 1510, 1435, 1241, 1111, 995, 738, 686. **^{1}H-NMR** (400 MHz, MeOD-d_3): δ (ppm) = 8.25 – 7.46 (m, 15H), 3.80 – 3.60 (m, 2H), 3.30 – 3.19 (m, 2H), 2.17 – 2.00 (m, 2H). **^{13}C-NMR** (101 MHz, MeOD-d_3): δ (ppm) = 135.2, 135.1, 133.6, 133.5, 130.4, 130.3, 118.3, 117.4, 39.4, 39.2, 20.5, 20.5, 19.6, 19.0. **^{31}P-NMR**

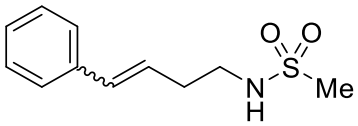
(162 MHz, MeOD-d_3): δ (ppm) = 23.7. **HRMS** (ESI) calcd. for $[C_{21}H_{23}NP]^+$ $(M)^+$, m/z = 320.1563, found 320.1562.

4-Phenylbut-3-en-1-amine[95]



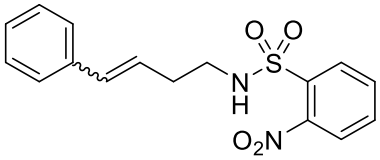
To a suspension of (3-aminopropyl)triphenylphosphonium bromide (4.00 g, 10.0 mmol, 2.00 eq.) in 16.6 mL THF (0.6 M) KO^{t}Bu (2.24 g, 20.0 mmol, 4.00 eq.) was added at 0 °C and the mixture stirred for 30 min. A solution of benzaldehyde (530 mg, 5.00 mmol, 1.00 eq.) in 2.5 mL THF (2.0 M) was added dropwise, the solution was allowed to warm to r.t. and stirred for further 2 h. The reaction was quenched with aq. HCl solution (0.1 M, pH 1) and DEE was added. The watery phase was separated, basified with sat. aq. Na_2CO_3 solution and the crude mixture was extracted in DEE. The solvent was evaporated under reduced pressure and the crude product was used without further purification for further synthesis.

***N*-(4-Phenylbut-3-en-1-yl)methanesulfonamide (146m)**



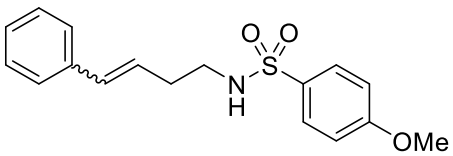
According to General procedure E: Crude 4-phenylbut-3-en-1-amine (735 mg, 4.99 mmol, 1.00 eq.), NEt_3 (1.01 g, 9.98 mmol, 2.00 eq.) and MsCl (572 mg, 4.99 mmol, 1.00 eq.) in 50 mL DCM. Eluting with PE/EtOAc 4:1→2:1. Isolated yield: 735 mg (3.26 mmol, 65%, yellowish solid) as a mixture of isomers (*E*:*Z* = 1:4.5). **TLC** R_f = 0.10 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3288, 3056, 3023, 2933, 1495, 1439, 1409, 1320, 1077, 973. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.47 – 7.11 (m, 5H), 6.68 – 6.37 (m, 1H), 5.62 (dt, *J* = 11.6, 7.2 Hz, 1H), 5.01 (dt, *J* = 18.3, 6.0 Hz, 1H), 3.34 – 3.10 (m, 2H), 2.87 (d, *J* = 19.2 Hz, 3H), 2.67 – 2.39 (m, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 137.0, 137.0, 133.0, 131.8, 128.7, 128.7, 128.4, 127.9, 127.5, 127.1, 126.2, 126.0, 43.1, 42.8, 40.1, 33.6, 29.2. **HRMS** (ESI) calcd. for $[C_{11}H_{16}NO_2S]^+$ $(M+H)^+$, m/z = 226.0896, found 226.0904.

2-Nitro-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146n)



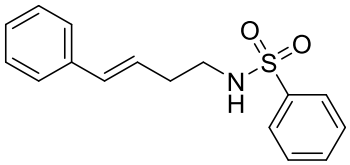
According to General procedure E: Crude 4-phenylbut-3-en-1-amine (185 mg, 1.26 mmol, 1.00 eq.), NEt_3 (254 mg, 2.51 mmol, 2.00 eq.) and 2-nitrobenzenesulfonyl chloride (172 mg, 1.51 mmol, 1.20 eq.) in 10 mL DCM. Eluting with PE/EtOAc 4:1. Isolated yield: 266 mg (0.80 mmol, 64%, yellow oil) as a mixture of isomers (*E*:*Z* = 1:5.9). **TLC** R_f = 0.23 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3340, 3094, 3019, 2941, 2885, 1536, 1495, 1443, 1409, 1342, 1163, 1074, 854, 768, 738, 701. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 8.17 – 7.98 (m, 1H), 7.77 – 7.55 (m, 3H), 7.33 – 7.06 (m, 5H), 6.49 (dd, *J* = 11.6, 1.9 Hz, 1H), 5.48 (dt, *J* = 11.6, 7.2 Hz, 1H), 5.38 (q, *J* = 6.7, 6.2 Hz, 1H), 3.23 (dq, *J* = 17.9, 6.6 Hz, 2H), 2.44 (dqd, *J* = 36.8, 6.9, 1.6 Hz, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 147.9, 147.8, 136.8, 136.7, 133.7, 133.7, 133.6, 133.6, 133.4, 132.9, 132.3, 130.9, 130.8, 128.6, 128.6, 128.5, 128.3, 127.5, 127.2, 127.1, 126.2, 125.4, 125.4, 125.3, 43.8, 43.5, 33.2, 28.7. **HRMS** (ESI) calcd. for $[C_{16}H_{16}N_2O_4SNa]^+$ $(M+Na)^+$, m/z = 355.0723, found 355.0724.

4-Methoxy-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146o)



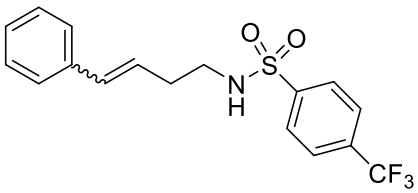
According to General procedure E: Crude 4-phenylbut-3-en-1-amine (478 mg, 3.25 mmol, 1.00 eq.), NEt_3 (657 mg, 6.49 mmol, 2.00 eq.) and 4-methoxy-benzenesulfonyl chloride (805 mg, 3.90 mmol, 1.20 eq.) in 50 mL DCM. Eluting with PE/EtOAc 20:1→4:1. Isolated yield: 312 mg (983 µmol, 30%, yellow oil) as a mixture of isomers (*E*:*Z* = 1:1.4). **TLC** R_f = 0.18 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3280, 3060, 3019, 2971, 2840, 1741, 1595, 1498, 1443, 1364, 1327, 1260, 1156, 1096, 1029. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.95 – 7.64 (m, 2H), 7.38 – 7.12 (m, 5H), 7.03 – 6.83 (m, 2H), 6.60 – 6.22 (m, 1H), 6.09 – 5.41 (m, 1H), 4.98 (d, *J* = 18.6 Hz, 1H), 3.83 (s, 3H), 3.05 (dq, *J* = 11.6, 6.7, 6.0 Hz, 2H), 2.41 (dqd, *J* = 33.4, 6.9, 1.6 Hz, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 162.9, 162.8, 137.0, 136.9, 133.2, 133.1, 132.9, 131.8, 131.5, 131.4, 129.3, 129.3, 129.2, 128.7, 128.5, 128.5, 128.3, 127.7, 127.4, 127.0, 126.2, 126.2, 126.0, 125.8, 117.6, 114.3, 114.3, 114.2, 55.6, 45.8, 43.0, 42.6, 38.5, 33.0, 28.7, 27.5. **HRMS** (ESI) calcd. for $[C_{17}H_{20}NO_3S]^+$ $(M+H)^+$, m/z = 318.1158, found 318.1157.

(*E*)-*N*-(4-Phenylbut-3-en-1-yl)benzenesulfonamide (146p)



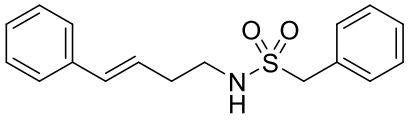
According to General procedure E: Crude 4-phenylbut-3-en-1-amine (710 mg, 4.82 mmol, 1.00 eq.), NEt_3 (1.71 g, 16.9 mmol, 3.50 eq.) and benzenesulfonyl chloride (852 mg, 4.82 mmol, 1.00 eq.) in 50 mL DCM. Eluting with PE/EtOAc 5.7:1. Isolated yield: 419 mg (1.46 mmol, 30%, yellow oil) exclusively *E*-isomer. **TLC** R_f = 0.31 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3284, 3064, 3027, 2941, 1737, 1495, 1446, 1424, 1326, 1215, 1159, 1096, 969, 835, 753, 723, 693. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.00 – 7.79 (m, 2H), 7.62 – 7.40 (m, 3H), 7.34 – 7.13 (m, 5H), 6.35 (dt, *J* = 15.9, 1.4 Hz, 1H), 6.00 (dt, *J* = 15.9, 7.1 Hz, 1H), 5.20 (t, *J* = 6.1 Hz, 1H), 3.10 (q, *J* = 6.5 Hz, 2H), 2.36 (qd, *J* = 6.9, 1.4 Hz, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 139.9, 136.9, 133.0, 132.7, 129.2, 128.6, 127.5, 127.1, 126.2, 125.8, 42.7, 33.1. **HRMS** (ESI) calcd. for $[C_{16}H_{18}NO_2S]^+$ $(M+H)^+$, m/z = 288,1053 found 288.1056.

***N*-(4-Phenylbut-3-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (146q)**



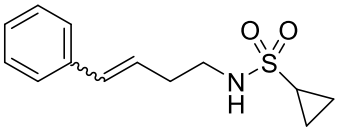
According to General procedure E: Crude 4-phenylbut-3-en-1-amine (550 mg, 3.74 mmol, 1.00 eq.), NEt_3 (1.32 g, 13.1 mmol, 3.50 eq.) and 4-(trifluoromethyl)benzenesulfonyl chloride (914 mg, 3.74 mmol, 1.00 eq.) in 50 mL DCM. Eluting with PE/EtOAc 9:1. Isolated yield: 398 mg (1.12 mmol, 30%, yellowish solid) as a mixture of isomers (*E*:*Z* = 7:1). **TLC** R_f = 0.18 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3284, 3060, 3030, 2930, 1405, 1323, 1167, 1133, 1096, 1062, 1018, 969, 842, 746, 712. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.07 – 7.84 (m, 2H), 7.81 – 7.60 (m, 2H), 7.47 – 7.07 (m, 5H), 6.64 – 6.27 (m, 1H), 5.97 (dt, *J* = 15.9, 7.1 Hz, 1H), 5.15 – 4.68 (m, 1H), 3.14 (q, *J* = 6.5 Hz, 2H), 2.55 – 2.30 (m, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.6, 136.7, 135.0, 134.5, 134.1, 134.0, 133.7, 133.4, 132.4, 128.6, 128.5, 128.3, 127.6, 127.5, 127.2, 127.2, 126.4, 126.3, 126.3, 126.2, 126.1, 125.2, 125.1, 121.4, 43.0, 42.7, 33.1, 28.6. **^{19}F NMR** (377 MHz, Chloroform-*d*): δ (ppm) = -63.6. **HRMS** (ESI) calcd. for $[C_{17}H_{17}F_3NO_2S]^+$ $(M+H)^+$, m/z = 356,0927 found 356.0930.

(*E*)-1-Phenyl-N-(4-phenylbut-3-en-1-yl)methanesulfonamide (146s)



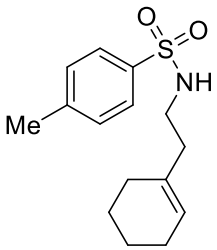
According to General procedure E: Crude 4-phenylbut-3-en-1-amine (710 mg, 4.82 mmol, 1.00 eq.), NEt_3 (1.71 g, 16.9 mmol, 3.50 eq.) and phenylmethanesulfonyl chloride (919 mg, 4.82 mmol, 1.00 eq.) in 50 mL DCM. Eluting with PE/EtOAc 5.7:1. Isolated yield: 410 mg (1.36 mmol, 28%, yellowish solid) exclusively *E*-isomer. **TLC** R_f = 0.30 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3288, 3060, 3030, 2930, 1599, 1495, 1454, 1409, 1264, 1200, 1152, 1074, 969, 895, 831, 783, 746, 697. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.46 – 7.13 (m, 10H), 6.54 – 6.34 (m, 1H), 6.05 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.54 (t, *J* = 6.0 Hz, 1H), 4.24 (s, 2H), 3.08 (q, *J* = 6.4 Hz, 2H), 2.37 (qd, *J* = 6.8, 1.4 Hz, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 136.9, 133.1, 130.7, 129.4, 128.9, 128.8, 128.6, 127.5, 126.2, 125.7, 58.8, 43.2, 33.9. **HRMS** (ESI) calcd. for $[C_{17}H_{20}NO_2S]^+$ $(M+H)^+$, m/z = 302.1209, found 302.1213.

***N*-(4-Phenylbut-3-en-1-yl)cyclopropanesulfonamide (146r)**



According to General procedure E: Crude 4-phenylbut-3-en-1-amine (710 mg, 4.82 mmol, 1.00 eq.), NEt_3 (1.71 g, 16.9 mmol, 3.50 eq.) and cyclopropanesulfonyl chloride (678 mg, 4.82 mmol, 1.00 eq.) in 50 mL DCM. Eluting with PE/EtOAc 4:1. Isolated yield: 347 mg (1.38 mmol, 29%, yellowish solid) as a mixture of isomers (*E*:*Z* = 2.3:1). **TLC** R_f = 0.30 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3284, 3056, 3023, 2937, 1495, 1420, 1327, 1193, 1148, 1074, 969, 939, 895, 768, 701. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.51 – 7.03 (m, 5H), 6.72 – 6.35 (m, 1H), 6.27 – 5.48 (m, 1H), 4.49 (dt, *J* = 20.0, 6.2 Hz, 1H), 3.28 (dq, *J* = 12.9, 6.6 Hz, 2H), 2.68 – 2.45 (m, 2H), 2.45 – 2.23 (m, 1H), 1.28 – 1.06 (m, 2H), 1.04 – 0.83 (m, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 136.9, 133.2, 132.1, 128.7, 128.6, 128.3, 127.7, 127.5, 127.1, 126.2, 125.7, 43.2, 42.9, 33.8, 30.2, 30.1, 29.3, 27.4, 6.5, 5.4. **HRMS** (ESI) calcd. for $[C_{13}H_{18}NO_2S]^+$ $(M+H)^+$, m/z = 252.1053, found 252.1055.

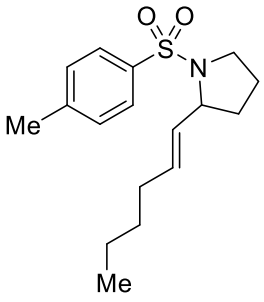
N-(2-(Cyclohex-1-en-1-yl)ethyl)-4-methylbenzenesulfonamide (146t)



According to General procedure E: 2-(Cyclohex-1-en-1-yl)ethan-1-amine (898 mg, 7.17 mmol, 1.00 eq.), NEt_3 (2.18 g, 21.5 mmol, 3.00 eq.) and TsCl (1.50 g, 7.89 mmol, 1.10 eq.) in 72 mL DCM. Eluting with DCM. Isolated yield: 1.85 g (6.62 mmol, 92%, white solid). **TLC** R_f = 0.41 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3496, 3280, 2930, 1707, 1659, 1599, 1495, 1439, 1323, 1156, 1092, 954, 917. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.80 – 7.67 (m, 2H), 7.36 – 7.28 (m, 2H), 5.38 (tq, *J* = 3.8, 1.4 Hz, 1H), 4.32 (s, 1H), 3.00 (td, *J* = 6.5, 5.5 Hz, 2H), 2.43 (s, 3H), 2.05 (td, *J* = 6.6, 1.4 Hz, 2H), 2.00 – 1.88 (m, 2H), 1.78 – 1.63 (m, 2H), 1.60 – 1.44 (m, 4H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.4, 136.8, 133.4, 129.7, 127.1, 124.9, 40.4, 37.3, 27.5, 25.2, 22.6, 22.2, 21.6. **HRMS** (ESI) calcd. for $[C_{15}H_{22}NO_2S]^+$ $(M+H)^+$, m/z = 280.1366, found 280.1364.

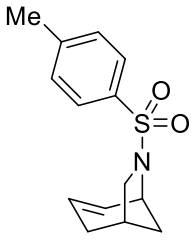
6.8.3 Racemic synthesis of 3-pyrrolines, pyrrolidines and piperidines

2-(Hex-1-en-1-yl)-1-tosylpyrrolidine (140a)



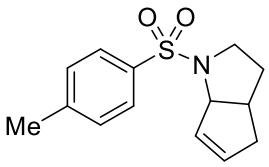
According to General procedure F: (*E*)-*N*-(Dec-4-en-1-yl)-4-methylbenzenesulfonamide (112 mg, 362 µmol, 1.00 eq.), TAPT (8.80 mg, 18.0 µmol, 0.05 eq.) and $(PhSe)_2$ (11.3 mg, 36.0 µmol, 0.10 eq.) in 1.8 mL *o*-xylene for 16 h. Eluting with PE/EtOAc 20:1. NMR yield: 93.0 mg (302 µmol, 84%), isolated yield: 88.0 mg (286 µmol, 79%, colorless oil). **TLC** R_f = 0.57 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3030, 2956, 2930, 2870, 1599, 1495, 1457, 1402, 1346, 1260, 1197, 1096, 1059, 969, 816, 708. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.71 – 7.62 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.59 (dtd, *J* = 14.8, 6.7, 1.1 Hz, 1H), 5.30 (ddt, *J* = 15.2, 6.7, 1.5 Hz, 1H), 4.09 (td, *J* = 6.9, 3.5 Hz, 1H), 3.37 (ddd, *J* = 10.0, 7.4, 4.6 Hz, 1H), 3.30 – 3.14 (m, 1H), 2.38 (s, 3H), 1.96 (qd, *J* = 6.8, 3.6 Hz, 2H), 1.83 – 1.52 (m, 5H), 1.35 – 1.19 (m, 4H), 0.92 – 0.77 (m, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.0, 135.7, 132.0, 130.1, 129.5, 127.5, 61.6, 48.6, 32.8, 31.8, 31.3, 23.9, 22.3, 21.5, 14.0. **HRMS** (ESI) calcd. for $[C_{17}H_{26}NO_2S]^+$ $(M+H)^+$, m/z = 308.1679, found 308.1681.

6-Tosyl-6-azabicyclo[3.2.1]oct-3-ene (140b)



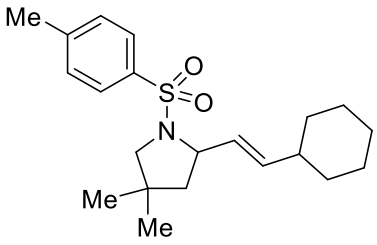
According to General procedure F: *N*-(Cyclohex-3-en-1-ylmethyl)-4-methylbenzenesulfonamide (100 mg, 377 µmol, 1.00 eq.), TAPT (9.20 mg, 19.0 µmol, 0.05 eq.) and $(PhSe)_2$ (11.8 mg, 38.0 µmol, 0.10 eq.) in 1.85 mL *o*-xylene for 3 d. Eluting with PE/EtOAc 20:1. NMR yield: 45.0 mg (171 µmol, 45%), isolated yield: 35.0 mg (133 µmol, 35%, white solid). **TLC** R_f = 0.38 (4:1 PE/EtOAc). **m.p.** 104 °C. **IR** [cm^{-1}] 3034, 2952, 2889, 2837, 1599, 1495, 1450, 1383, 1338, 1256, 1156, 1096, 1051, 1018, 910, 820, 708, 671. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.73 – 7.67 (m, 2H), 7.31 – 7.25 (m, 2H), 6.03 – 5.88 (m, 1H), 5.52 (dddt, *J* = 9.3, 3.8, 2.8, 0.9 Hz, 1H), 4.21 (ddd, *J* = 5.9, 4.9, 0.9 Hz, 1H), 3.48 (ddd, *J* = 10.2, 6.3, 2.0 Hz, 1H), 3.15 (d, *J* = 10.2 Hz, 1H), 2.58 – 2.48 (m, 1H), 2.41 (s, 3H), 2.34 (dq, *J* = 4.7, 2.5 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.62 (d, *J* = 10.9 Hz, 1H), 1.44 – 1.33 (m, 1H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.1, 136.1, 130.0, 129.5, 127.6, 127.5, 54.5, 54.0, 34.9, 33.7, 33.4, 21.6. **HRMS** (ESI) calcd. for $[C_{14}H_{18}NO_2S]^+$ $(M+H)^+$, m/z = 264.1053, found 264.1053.

1-Tosyl-1,2,3,3*a*,4,6*a*-hexahydrocyclopenta[*b*]pyrrole (140c)



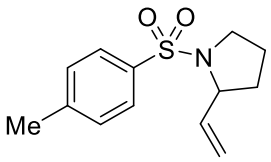
According to General procedure F: *N*-(2-(Cyclopent-2-en-1-yl)ethyl)-4-methylbenzenesulfonamide (200 mg, 754 µmol, 1.00 eq.), TAPT (18.3 mg, 37.7 µmol, 0.05 eq.) and $(PhSe)_2$ (23.5 mg, 75.4 µmol, 0.10 eq.) in 3.75 mL *o*-xylene for 1.5 d. Eluting with PE/EtOAc 20:1. NMR yield: 104 mg (395 µmol, 52%), isolated yield: 99.0 mg (376 µmol, 50%, brown oil). **TLC** R_f = 0.46 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3064, 2926, 2855, 1733, 1599, 1454, 1346, 1264, 1234, 1159, 1096, 1029, 895, 850, 816, 749, 723. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.79 – 7.65 (m, 2H), 7.35 – 7.28 (m, 2H), 5.90 – 5.63 (m, 2H), 4.55 (dq, *J* = 7.8, 1.8 Hz, 1H), 3.37 (ddd, *J* = 9.8, 6.8, 4.5 Hz, 1H), 3.06 (ddd, *J* = 9.9, 8.6, 6.4 Hz, 1H), 2.68 – 2.40 (m, 5H), 2.11 (dp, *J* = 16.9, 2.2 Hz, 1H), 1.84 (dddd, *J* = 12.6, 8.1, 6.4, 4.5 Hz, 1H), 1.67 – 1.39 (m, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.3, 134.7, 131.9, 131.3, 129.6, 127.6, 70.1, 48.3, 39.9, 38.0, 32.4, 21.6. **HRMS** (ESI) calcd. for $[C_{14}H_{18}NO_2S]^+$ $(M+H)^+$, m/z = 264.1053, found 264.1053.

(*E*)-2-(2-Cyclohexylvinyl)-4,4-dimethyl-1-tosylpyrrolidine (140e)



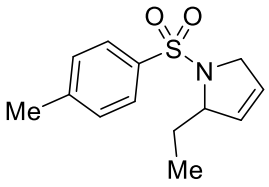
According to General procedure F: *N*-(6-Cyclohexyl-2,2-dimethylhex-4-en-1-yl)-4-methylbenzenesulfonamide (117 mg, 312 µmol, 1.00 eq.), TAPT (7.82 mg, 16.1 µmol, 0.05 eq.) and $(PhSe)_2$ (10.2 mg, 32.2 µmol, 0.10 eq.) in 1.6 mL *o*-xylene for 96 h. Eluting with PE/EtOAc 40:1. NMR yield: 32.0 mg (88.5 µmol, 28%), isolated yield: 24.0 mg (66.4 µmol, 21%, yellow oil). **TLC** R_f = 0.76 (4:1 PE/EtOAc). **IR** [cm^{-1}] 2926, 2855, 1599, 1495, 1450, 1349, 1215, 1195, 1055, 962, 928, 816, 760, 708, 667. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.68 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 0.9 Hz, 2H), 5.49 (dd, *J* = 15.4, 6.3 Hz, 1H), 5.26 (ddd, *J* = 15.5, 7.8, 1.3 Hz, 1H), 4.01 (q, *J* = 7.9 Hz, 1H), 3.34 – 3.08 (m, 2H), 2.42 (s, 3H), 1.97 – 1.80 (m, 1H), 1.80 – 1.43 (m, 8H), 1.35 – 1.08 (m, 3H), 1.05 (s, 5H), 0.77 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.9, 137.8, 136.4, 129.3, 128.5, 127.6, 62.1, 61.3, 48.1, 40.0, 37.3, 32.6, 26.5, 26.2, 26.1, 26.0, 21.5. **HRMS** (ESI) calcd. for $[C_{21}H_{32}NO_2S]^+$ $(M+H)^+$, m/z = 362.2148, found 362.2155.

1-Tosyl-2-vinylpyrrolidine (140d)



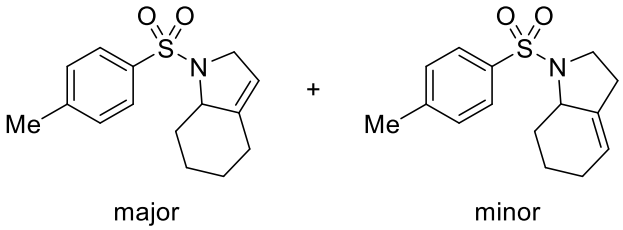
According to General procedure F: *N*-(Hex-4-en-1-yl)-4-methylbenzenesulfonamide (165 mg, 651 µmol, 1.00 eq.), TAPT (15.8 mg, 32.6 µmol, 0.05 eq.) and $(PhSe)_2$ (20.3 mg, 65.1 µmol, 0.10 eq.) in 3.25 mL *o*-xylene for 24 h, TAPT (10.0 mg, 20.5 µmol, 0.03 eq.) was re-added and the reaction was stirred for another 12 h. Eluting with PE/EtOAc 20:1. NMR yield: 91.0 mg (362 µmol, 56%), isolated yield: 90.0 mg (358 µmol, 55%, brownish solid). **TLC** R_f = 0.46 (4:1 PE/EtOAc). **m.p.** 64 °C. **IR** [cm^{-1}] 3064, 2978, 2930, 2878, 1599, 1495, 1450, 1402, 1346, 1197, 1159, 1096, 1051, 1010, 924, 820, 757, 708. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.82 – 7.65 (m, 2H), 7.39 – 7.27 (m, 2H), 5.81 (ddd, *J* = 17.0, 10.2, 6.0 Hz, 1H), 5.47 – 4.93 (m, 2H), 4.30 – 3.89 (m, 1H), 3.45 (ddd, *J* = 10.2, 7.4, 4.4 Hz, 1H), 3.23 (dt, *J* = 9.9, 7.4 Hz, 1H), 2.43 (s, 3H), 1.89 – 1.53 (m, 4H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.3, 138.7, 135.2, 129.6, 127.6, 115.3, 61.9, 48.8, 32.3, 23.8, 21.5. **HRMS** (ESI) calcd. for $[C_{13}H_{18}NO_2S]^+$ $(M+H)^+$, m/z = 252.1053, found 252.1053.

1-((2-Ethylcyclopent-3-en-1-yl)sulfonyl)-4-methylbenzene (149a)



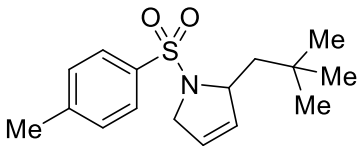
According to General procedure F: *N*-(Hex-3-en-1-yl)-4-methylbenzenesulfonamide (227 mg, 896 µmol, 1.00 eq.), TAPT (0.05 eq.) and $(PhSe)_2$ (0.10 eq.) in 4.5 mL *o*-xylene for 16 h. Eluting with PE/EtOAc 99:1→32.3:1. NMR yield: 223 mg (887 µmol, 99%), isolated yield: 199 mg (792 µmol, 88%, yellow oil). **TLC** R_f = 0.46 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3068, 2967, 2874, 1726, 1599, 1461, 1334, 1159, 1092, 813, 708. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.79 – 7.55 (m, 2H), 7.37 – 7.15 (m, 2H), 5.69 – 5.38 (m, 2H), 4.45 (tdp, *J* = 5.5, 3.7, 1.9 Hz, 1H), 4.21 – 3.99 (m, 2H), 2.40 (s, 3H), 1.79 (qd, *J* = 7.5, 5.3 Hz, 2H), 0.87 (t, *J* = 7.5 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.3, 134.9, 129.7, 129.4, 127.4, 124.9, 68.2, 55.8, 28.8, 21.5, 8.5. **HRMS** (ESI) calcd. for $[C_{13}H_{18}NO_2S]^+$ $(M+H)^+$, m/z = 252.1053, found 252.1055.

1-Tosyl-2,4,5,6,7,7*a*-hexahydro-1H-indole and 1-Tosyl-2,3,5,6,7,7*a*-hexahydro-1H-indole (isomeric ratio: 3.2:1, 149f and 149f')



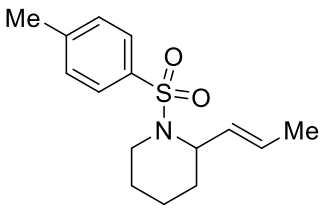
According to General procedure F: *N*-(2-(Cyclohex-1-en-1-yl)ethyl)-4-methylbenzenesulfonamide (228 mg, 816 µmol, 1.00 eq.), TAPT (19.8 mg, 40.8 µmol, 0.05 eq.) and $(PhSe)_2$ (25.5 mg, 81.6 µmol, 0.10 eq.) in 4.1 mL *o*-xylene for 24 h. Eluting with PE/EtOAc 9:1. NMR yield: 107 mg (386 µmol, 47%), isolated yield: 70.0 mg (252 µmol, 31%, white solid) as a mixture of isomers (3.2:1). **TLC** R_f = 0.43 (4:1 PE/EtOAc). **m.p.** 93 °C. **IR** [cm^{-1}] 3064, 2933, 2859, 1599, 1495, 1446, 1402, 1342, 1234, 1163, 1100, 816, 708. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.77 – 7.66 (m, 2H), 7.31 (dd, *J* = 8.2, 3.7 Hz, 2H), 5.14 (t, *J* = 2.0 Hz, 1H), 4.22 – 3.24 (m, 3H), 2.55 – 2.32 (m, 5H), 2.07 – 1.67 (m, 3H), 1.48 – 1.06 (m, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.2, 141.8, 137.4, 134.9, 129.7, 127.5, 121.2, 114.2, 66.5, 58.7, 54.9, 47.6, 36.4, 29.9, 28.4, 26.4, 24.3, 23.9, 21.5, 20.3. **HRMS** (ESI) calcd. for $[C_{15}H_{20}NO_2S]^+$ $(M+H)^+$, m/z = 278.1209, found 278.1209.

2-Neopentyl-1-tosyl-2,5-dihydro-1H-pyrrole (149b)



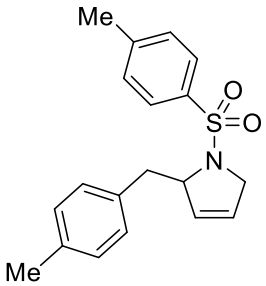
According to General procedure F: *N*-(6,6-Dimethylhept-3-en-1-yl)-4-methylbenzenesulfonamide (205 mg, 694 µmol, 1.00 eq.), TAPT (16.9 mg, 34.7 µmol, 0.05 eq.) and $(PhSe)_2$ (21.7 mg, 69.4 µmol, 0.10 eq.) in 3.5 mL *o*-xylene for 24 h. Eluting with PE/EtOAc 20:1. NMR yield: 123 mg (419 µmol, 60%), isolated yield: 101 mg (344 µmol, 50%, white solid). **TLC** R_f = 0.54 (4:1 PE/EtOAc). **m.p.** 92 °C. **IR** [cm^{-1}] 3068, 2952, 2870, 1599, 1469, 1398, 1342, 1249, 1197, 1163, 1092, 1062, 816, 708. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.78 – 7.64 (m, 2H), 7.36 – 7.27 (m, 2H), 5.69 (dq, *J* = 6.5, 2.2 Hz, 1H), 5.54 (dq, *J* = 6.2, 1.9 Hz, 1H), 4.40 (ddp, *J* = 10.1, 4.5, 2.2 Hz, 1H), 4.25 – 3.96 (m, 2H), 2.42 (s, 3H), 2.10 (dd, *J* = 13.9, 2.3 Hz, 1H), 1.50 (dd, *J* = 13.8, 10.2 Hz, 1H), 0.99 (s, 9H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.3, 134.7, 131.7, 129.7, 127.5, 123.7, 65.0, 54.8, 51.2, 30.2, 30.1, 21.6. **HRMS** (ESI) calcd. for $[C_{16}H_{23}NO_2S]^+$ $(M+H)^+$, m/z = 294.1522, found 294.1524.

(*E*)-2-(Prop-1-en-1-yl)-1-tosylpiperidine (150a)



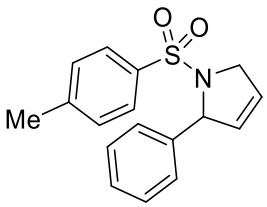
According to General procedure F: (*E*)-4-Methyl-*N*-(oct-5-en-1-yl)benzenesulfonamide (150 mg, 533 µmol, 1.00 eq.), TAPT (13.0 mg, 26.7 µmol, 0.05 eq.), $(PhSe)_2$ (16.6 mg, 53.3 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (15.3 mg, 53.3 µmol, 0.10 eq.) and 2-nitrobenzaldehyde (20.1 mg, 133 µmol, 0.25 eq.) in 2.7 mL *o*-xylene for 24 h, TAPT (13.0 mg, 26.7 µmol, 0.05 eq.) and $(PhSe)_2$ (16.6 mg, 53.3 µmol, 0.10 eq.) were re-added and the reaction was stirred for another 2 h. Eluting with PE/EtOAc 20:1. NMR yield: 118 mg (422 µmol, 79%), isolated yield: 95.0 mg (340 µmol, 64%, colorless oil). **TLC** R_f = 0.54 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3027, 2937, 2859, 1599, 1495, 1446, 1379, 1334, 1215, 1150. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.70 – 7.60 (m, 2H), 7.30 – 7.21 (m, 2H), 5.56 (dqd, *J* = 15.4, 6.4, 1.3 Hz, 1H), 5.42 – 5.27 (m, 1H), 4.66 – 4.37 (m, 1H), 3.66 (dtd, *J* = 12.8, 2.7, 1.3 Hz, 1H), 3.02 – 2.78 (m, 1H), 2.41 (s, 3H), 1.77 – 1.35 (m, 9H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.7, 137.7, 129.3, 128.3, 127.5, 127.3, 54.8, 41.7, 30.5, 25.2, 21.5, 19.0, 17.8. **HRMS** (ESI) calcd. for $[C_{15}H_{22}NO_2S]^+$ $(M+H)^+$, m/z = 280.1366, found 280.1368.

2-(4-Methylbenzyl)-1-tosyl-2,5-dihydro-1H-pyrrole (149c)



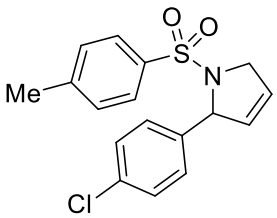
This compound was synthesized during an internship with Daniel Kolb. According to General procedure F: 4-Methyl-*N*-(5-(*p*-tolyl)pent-3-en-1-yl)benzenesulfonamide (147 mg, 446 µmol, 1.00 eq.), TAPT (10.9 mg, 22.3 µmol, 0.05 eq.) and $(PhSe)_2$ (13.9 mg, 44.6 µmol, 0.10 eq.) in 2.2 mL *o*-xylene for 2 d. Eluting with PE/EtOAc 20:1. NMR yield: 133 mg (406 µmol, 91%), isolated yield: 107 mg (327 µmol, 71%, yellow oil). **TLC** R_f = 0.43 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3023, 2922, 2866, 1730, 1599, 1513, 1446, 1402, 1338, 1163, 1092, 1055, 850, 813, 708. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.83 – 7.62 (m, 2H), 7.36 – 7.27 (m, 2H), 7.19 – 7.01 (m, 4H), 5.63 – 5.37 (m, 2H), 4.61 (ddtt, *J* = 7.6, 5.0, 2.4, 1.4 Hz, 1H), 4.13 – 3.90 (m, 2H), 3.25 (dd, *J* = 13.2, 3.6 Hz, 1H), 2.90 (dd, *J* = 13.2, 8.7 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.5, 135.9, 134.7, 134.2, 129.8, 129.3, 128.9, 127.4, 125.0, 68.6, 55.8, 42.8, 21.6, 21.1. **HRMS** (ESI) calcd. for $[C_{19}H_{22}NO_2S]^+$ $(M+H)^+$, m/z = 328.1366, found 328.1368.

2-Phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (149d)



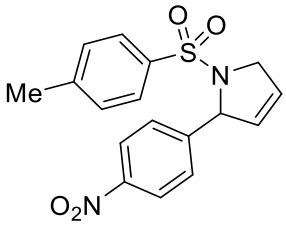
According to General procedure F: 4-Methyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (120 mg, 389 µmol, 1.00 eq.), TAPT (9.68 mg, 19.9 µmol, 0.05 eq.) and $(PhSe)_2$ (12.4 mg, 39.8 µmol, 0.10 eq.) in 2.0 mL *o*-xylene for 12 h, TAPT (9.68 mg, 19.9 µmol, 0.05 eq.) and $(PhSe)_2$ (12.4 mg, 39.8 µmol, 0.10 eq.) were re-added and the reaction was stirred for another 4 h. Eluting with PE/EtOAc 20:1→11.5:1. NMR yield: 112 mg (374 µmol, 94%), isolated yield: 107 mg (357 µmol, 90%, white solid). **TLC** R_f = 0.35 (4:1 PE/EtOAc). **m.p.** 130 °C. **IR** [cm^{-1}] 3064, 3034, 2922, 2866, 1599, 1495, 1454, 1342, 1163, 1096, 1059, 816, 760, 697, 667. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.55 – 7.48 (m, 2H), 7.37 – 7.23 (m, 5H), 7.22 – 7.16 (m, 2H), 5.79 (dq, *J* = 6.0, 2.0 Hz, 1H), 5.65 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.52 (dq, *J* = 4.7, 2.2 Hz, 1H), 4.41 – 4.19 (m, 2H), 2.38 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.2, 140.5, 135.5, 130.6, 129.5, 128.5, 127.8, 127.3, 124.5, 118.2, 70.3, 55.4, 21.5. **HRMS** (ESI) calcd. for $[C_{17}H_{18}NO_2S]^+$ $(M+H)^+$, m/z = 300.1053, found 300.1055.

2-(4-Chlorophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole (149g)



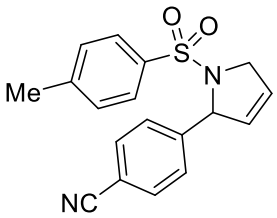
According to General procedure F: *N*-(4-(4-Chlorophenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (162 mg, 482 µmol, 1.00 eq.), TAPT (11.7 mg, 24.1 µmol, 0.05 eq.) and $(PhSe)_2$ (15.1 mg, 48.2 µmol, 0.10 eq.) in 2.4 mL *o*-xylene for 12 h, TAPT (11.7 mg, 24.1 µmol, 0.05 eq.) and $(PhSe)_2$ (15.1 mg, 48.2 µmol, 0.10 eq.) were re-added and the reaction was stirred for another 4 h. Eluting with PE/EtOAc 20:1→11.5:1. NMR yield: 144 mg (431 µmol, 89%), isolated yield: 129 mg (386 µmol, 80%, brownish oil). **TLC** R_f = 0.35 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3064, 2922, 2870, 1733, 1595, 1491, 1405, 1346, 1249, 1163, 1088, 1059, 813, 734. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.57 – 7.47 (m, 2H), 7.28 – 7.13 (m, 6H), 5.80 (dq, *J* = 6.1, 2.0 Hz, 1H), 5.61 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.47 (dq, *J* = 4.9, 2.3 Hz, 1H), 4.45 – 4.05 (m, 2H), 2.40 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.4, 139.1, 135.3, 133.6, 130.2, 129.6, 128.7, 128.6, 127.2, 125.0, 69.5, 55.4, 21.5. **HRMS** (ESI) calcd. for $[C_{17}H_{17}ClNO_2S]^+$ $(M+H)^+$, m/z = 334.0663, found 334.0663.

2-(4-Nitrophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole (149h)



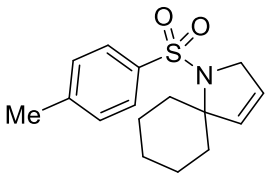
According to General procedure F: 4-Methyl-*N*-(4-(4-nitrophenyl)but-3-en-1-yl)benzenesulfonamide (123 mg, 355 µmol, 1.00 eq.), TAPT (8.63 mg, 17.8 µmol, 0.05 eq.), $(PhSe)_2$ (11.1 mg, 35.5 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (10.2 mg, 35.5 µmol, 0,10 eq.) and 2-nitrobenzaldehyde (13.4 mg, 88.8 µmol, 0.25 eq.) in 1.8 mL *o*-xylene for 15 h, Eluting with PE/EtOAc 9:1→4:1. NMR yield: 102 mg (296 µmol, 83%), isolated yield: 93.0 mg (270 µmol, 76%, brownish solid). **TLC** R_f = 0.22 (4:1 PE/EtOAc). **m.p.** 135 °C. **IR** [cm^{-1}] 3079, 2922, 2866, 1722, 1692, 1599, 1521, 1346, 1163, 1096, 1062, 857, 820, 753. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.21 – 8.11 (m, 2H), 7.65 – 7.54 (m, 2H), 7.50 – 7.42 (m, 2H), 7.29 – 7.20 (m, 2H), 5.85 (dq, *J* = 6.1, 1.9 Hz, 1H), 5.59 (ddq, *J* = 17.1, 6.3, 2.1 Hz, 2H), 4.33 (dt, *J* = 4.3, 2.1 Hz, 2H), 2.41 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 148.0, 143.9, 134.7, 131.5, 129.8, 129.4, 128.0, 127.3, 125.9, 123.8, 69.5, 55.7, 21.6. **HRMS** (ESI) calcd. for $[C_{17}H_{17}N_2O_4S]^+$ $(M+H)^+$, m/z = 345.0904, found 345.0905.

4-(1-Tosyl-2,5-dihydro-1H-pyrrol-2-yl)benzonitrile (149l)



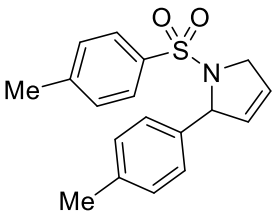
According to General procedure F: (*E*)-*N*-(4-(4-Cyanophenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (165 mg,505 µmol, 1.00 eq.), TAPT (12.3 mg, 25.3 µmol, 0.05 eq.), $(PhSe)_2$ (15.8 mg, 55.6 µmol, 0.10 eq.) and 1,2-bis(4-chlorophenyl)disulfane (14.5 mg, 55.6 µmol, 0.10 eq.) in 2.5 mL *o*-xylene for 4 h. Eluting with PE/EtOAc 9:1→4:1. NMR yield: 163 mg (502 µmol, 99%), isolated yield: 155 mg (478 µmol, 95%, yellow solid). **TLC** R_f = 0.18 (4:1 PE/EtOAc). **m.p.** 147 °C. **IR** [cm^{-1}] 3064, 2922, 2870, 2229, 1599, 1495, 1413, 1342, 1252, 1163, 1092, 1059, 1018, 962, 820, 760, 708. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.62 – 7.54 (m, 4H), 7.43 – 7.36 (m, 2H), 7.29 – 7.21 (m, 2H), 5.83 (dq, *J* = 6.2, 2.0 Hz, 1H), 5.61 (dq, *J* = 6.3, 2.2 Hz, 1H), 5.52 (ddt, *J* = 5.6, 3.9, 2.1 Hz, 1H), 4.32 (q, *J* = 2.4 Hz, 2H), 2.41 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 146.0, 143.8, 134.8, 132.4, 129.7, 129.5, 127.9, 127.3, 125.8, 118.7, 111.6, 69.8, 55.7, 21.6. **HRMS** (ESI) calcd. for $[C_{18}H_{17}N_2O_2S]^+$ $(M+H)^+$, m/z = 325.1005, found 325.1007.

1-Tosyl-1-azaspiro[4.5]dec-3-ene (149k)



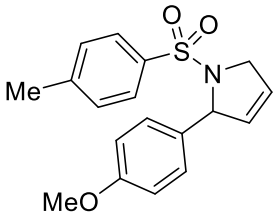
According to General procedure F: *N*-(3-Cyclohexylidenepropyl)-4-methylbenzenesulfonamide (148 mg, 504 µmol, 1.00 eq.), TAPT (12.3 mg, 25.2 µmol, 0.05 eq.), $(PhSe)_2$ (15.7 mg, 50.4 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.5 mg, 50.4 µmol, 0.10 eq.) and 2-nitrobenzaldehyde (19.1 mg, 126 µmol, 0.25 eq.) in 2.5 mL *o*-xylene for 16 h. Eluting with PE/EtOAc 20:1. NMR yield: 107 mg (367 µmol, 73%), isolated yield: 95.0 mg (326 µmol, 65%, yellowish oil). **TLC** R_f = 0.48 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3068, 2930, 2863, 1730, 1599, 1495, 1454, 1402, 1368, 1331, 1159, 1126, 1100, 1070, 1006, 902, 816, 723. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.86 – 7.64 (m, 2H), 7.36 – 7.13 (m, 2H), 6.11 (dt, *J* = 6.6, 2.3 Hz, 1H), 5.66 (dt, *J* = 6.6, 2.0 Hz, 1H), 4.11 (t, *J* = 2.2 Hz, 2H), 2.40 (s, 5H), 1.85 – 1.59 (m, 5H), 1.42 – 1.22 (m, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.7, 138.6, 132.8, 129.4, 127.2, 122.3, 75.9, 55.1, 37.2, 25.2, 24.6, 21.5. **HRMS** (ESI) calcd. for $[C_{16}H_{22}NO_2S]^+$ $(M+H)^+$, m/z = 292.1366, found 292,1367.

2-(*p*-Tolyl)-1-tosyl-2,5-dihydro-1H-pyrrole (149e)



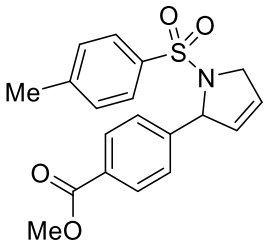
This compound was synthesized during an internship with Alberto Nunez-Bendinelli. According to General procedure F: 4-Methyl-*N*-(4-(*p*-tolyl)but-3-en-1-yl)benzenesulfonamide (160 mg, 507 µmol, 1.00 eq.), TAPT (12.3 mg, 25.4 µmol, 0.05 eq.) and $(PhSe)_2$ (15.8 mg, 50.7 µmol, 0.10 eq.) in 2.5 mL *o*-xylene for 12 h, TAPT (12.3 mg, 25.4 µmol, 0.05 eq.) and $(PhSe)_2$ (15.8 mg, 50.7 µmol, 0.10 eq.) were re-added and the reaction was stirred for further 4 h. Eluting with PE/EtOAc 20:1. NMR yield: 72.0 mg (230 µmol, 45%), isolated yield: 69.0 mg (220 µmol, 43%, colorless oil). **TLC** R_f = 0.38 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3030, 2922, 2863, 2863, 1748, 1651, 1599, 1457, 1398, 1346, 1163, 1096, 1059, 1021, 813, 779, 813. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.58 – 7.47 (m, 2H), 7.24 – 7.03 (m, 6H), 5.77 (dq, *J* = 6.0, 2.0 Hz, 1H), 5.63 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.47 (dq, *J* = 4.9, 2.3 Hz, 1H), 4.43 – 4.15 (m, 2H), 2.39 (s, 3H), 2.33 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.1, 137.6, 135.5, 130.7, 129.4, 129.1, 127.3, 127.2, 124.4, 70.0, 55.4, 21.5, 21.2. **HRMS** (ESI) calcd. for $[C_{18}H_{20}NO_2S]^+$ $(M+H)^+$, m/z = 314.1209, found 314.1210.

2-(4-Methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole (149j)



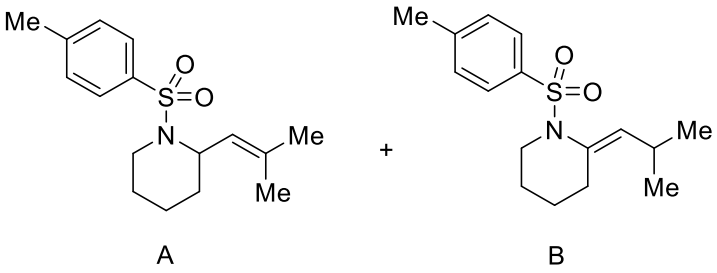
According to General procedure F: *N*-(4-(4-Methoxyphenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (168 mg, 507 µmol, 1.00 eq.), TAPT (12.3 mg, 25.3 µmol, 0.05 eq.) and $(PhSe)_2$ (15.8 mg, 50.7 µmol, 0.10 eq.) in 2.5 mL *o*-xylene for 12 h, TAPT (12.3 mg, 25.3 µmol, 0.05 eq.) and $(PhSe)_2$ (15.8 mg, 50.7 µmol, 0.10 eq.) were re-added and the reaction was stirred for further 4 h. Eluting with PE/EtOAc 20:1. NMR yield: 79.0 mg (240 µmol, 47%), isolated yield: 65.0 mg (197 µmol, 39%, yellowish oil). **TLC** R_f = 0.28 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3001, 2926, 2866, 2359, 1610, 1513, 1465, 1346, 1290, 1245, 1163, 1107, 1036, 820. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.53 – 7.46 (m, 2H), 7.23 – 7.11 (m, 4H), 6.87 – 6.75 (m, 2H), 5.78 (dq, *J* = 6.0, 2.0 Hz, 1H), 5.63 (dq, *J* = 6.3, 2.2 Hz, 1H), 5.48 (dq, *J* = 4.8, 2.3 Hz, 1H), 4.39 – 4.15 (m, 2H), 3.79 (s, 3H), 2.38 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 159.3, 143.0, 135.7, 132.6, 130.7, 129.4, 128.6, 127.2, 124.4, 113.8, 69.7, 55.3, 55.2, 21.5. **HRMS** (ESI) calcd. for $[C_{18}H_{20}NO_3S]^+$ $(M+H)^+$, m/z = 330.1158, found 330.1162.

Methyl 4-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)benzoate (149i)



This compound was synthesized during an internship with Alberto Nunez-Bendinelli. According to General procedure F: Methyl-4-(4-((4-methylphenyl)sulfonamido)but-1-en-1-yl)benzoate (150 mg, 416 µmol, 1.00 eq.), TAPT (10.1 mg, 20.8 µmol, 0.05 eq.) and $(PhSe)_2$ (13.0 mg, 41.6 µmol, 0.10 eq.) in 2.1 mL *o*-xylene for 16 h. Eluting with PE/EtOAc 20:1→9:1. NMR yield: 56.0 mg (157 µmol, 38%), isolated yield: 54.0 mg (151 µmol, 36%, yellow solid). **TLC** R_f = 0.20 (4:1 PE/EtOAc). **m.p.** 108 °C. **IR** [cm^{-1}] 2997, 2952, 2866, 1718, 1610, 1435, 1346, 1275, 1163, 1100, 1059, 1018, 962, 813, 768, 708, 667. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 8.10 – 7.86 (m, 2H), 7.67 – 7.53 (m, 2H), 7.41 – 7.33 (m, 2H), 7.29 – 7.16 (m, 2H), 5.85 (dq, *J* = 6.1, 2.0 Hz, 1H), 5.67 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.59 (dq, *J* = 5.0, 2.4 Hz, 1H), 4.48 – 4.23 (m, 2H), 3.96 (s, 3H), 2.43 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 166.8, 145.7, 143.5, 135.3, 130.0, 129.9, 129.6, 129.6, 127.3, 127.2, 125.2, 69.9, 55.6, 52.1, 21.5. **HRMS** (ESI) calcd. for $[C_{19}H_{20}NO_4S]^+$ $(M+H)^+$, m/z = 358.1108, found 358.1109.

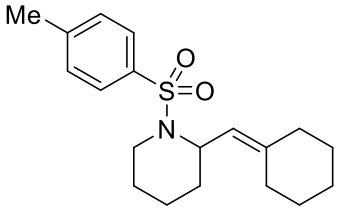
(2-(2-Methylpropylidene)-1-tosylpiperidine (A) and 2-(2-Methylprop-1-en-1-yl)-1-tosylpi-peridine (B) (isomeric ratio: 1.8:1, 150d and 150d')



A + B

According to General procedure F: (*Z*)-4-Methyl-*N*-(7-methyloct-5-en-1-yl)benzenesulfonamide (143 mg, 484 µmol, 1.00 eq.), TAPT (11.8 mg, 24.2 µmol, 0.05 eq.), $(PhSe)_2$ (15.1 mg, 48.4 µmol, 0.10 eq.) and and 1,2-bis(4-chlorophenyl)disulfane (13.9 mg, 48.4 µmol, 0.10 eq.) in 2.4 mL *o*-xylene for 11 h, TAPT (11.8 mg, 24.2 µmol, 0.05 eq.) and $(PhSe)_2$ (15.1 mg, 48.4 µmol, 0.10 eq.) were re-added and the reaction was stirred for further 1.5 h. Eluting with PE/EtOAc 20:1. NMR yield: 112 mg (382 µmol, 79%), isolated yield: 59.0 mg (202 µmol, 42%, colorless oil). **TLC** R_f = 0.58 (4:1 PE/EtOAc). **IR** [cm^{-1}] 2937, 2866, 1599, 1446, 1338, 1264, 1219, 1156, 1092, 932, 816, 731. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.82 – 7.70 (B, m, 2H), 7.63 – 7.56 (A+B, m, 2H+2H), 7.31 (B, d, *J* = 8.1 Hz, 2H), 7.27 – 7.22 (A+B, m, 2H+2H), 5.11 (A, dp, *J* = 9.3, 1.5 Hz, 1H), 4.79 (A, ddd, *J* = 8.2, 5.0, 2.2 Hz, 1H), 4.30 (B, dt, *J* = 13.6, 6.4 Hz, 1H), 3.79 – 3.62 (A+B, m, 2H+2H), 3.37 (B, dd, *J* = 11.6, 2.0 Hz, 1H), 3.02 – 2.66 (A+B. m, 1H+1H), 2.44 (B, s, 3H), 2.43 (A, s, 3H), 2.35 – 2.19 (A, m, 1H), 1.86 – 1.73 (A+B, m, 1H+1H), 1.72 – 1.41 (A+B, m, 10H+6H), 1.28 (B, d, *J* = 6.7 Hz, 3H), 1.20 – 1.07 (A, m, 1H), 1.02 (B, d, *J* = 6.5 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.0, 142.6, 138.8, 137.1, 134.3, 133.9, 131.03, 129.7, 129.1, 129.0, 127.5, 127.3, 127.2, 119.9, 57.4, 56.6, 51.5, 41.7, 40.9, 31.4, 27.4, 25.7, 25.6, 25.3, 23.1, 22.7, 21.5, 21.5, 19.0, 18.1, 18.0, 17.5. **HRMS** (ESI) calcd. for $[C_{16}H_{24}NO_2S]^+$ $(M+H)^+$, m/z = 294.1522, found 294.1521.

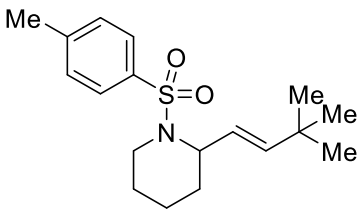
2-(Cyclohexylidenemethyl)-1-tosylpiperidine (150e)



According to General procedure F: (*Z*)-*N*-(6-Cyclohexylhex-5-en-1-yl)-4-methylbenzenesulfonamide (153 mg, 456 µmol, 1.00 eq.), TAPT (11.1 mg, 22.8 µmol, 0.05 eq.), $(PhSe)_2$ (14.2 mg, 45.6 µmol, 0.10 eq.) and and 1,2-bis(4-chlorophenyl)disulfane (13.1 mg, 45.6 µmol, 0.10 eq.) in 2.6 mL *o*-xylene for 16 h. Eluting with PE/EtOAc 20:1. NMR yield: 70.0 mg (210 µmol,

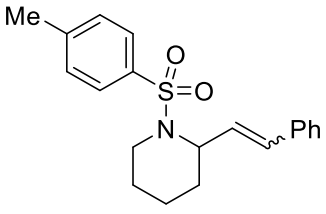
46%), isolated yield: 58.0 mg (174 µmol, 38%, colorless oil). **TLC** R_f = 0.24 (4:1 PE/EtOAc). **IR** [cm^{-1}] 2926, 2855, 2363, 1446, 1341, 1159, 1096, 1055, 936, 816, 731, 664. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.81 – 7.53 (m, 2H), 7.33 – 7.15 (m, 2H), 5.15 – 4.23 (m, 2H), 3.79 – 3.43 (m, 1H), 3.07 – 2.74 (m, 1H), 2.41 (d, *J* = 6.9 Hz, 3H), 2.20 – 2.06 (m, 2H), 2.02 – 0.96 (m, 14H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.6, 141.5, 137.1, 129.1, 127.7, 116.8, 50.6, 41.6, 37.0, 32.2, 29.0, 28.2, 27.5, 26.6, 25.4, 21.5, 19.0. **HRMS** (ESI) calcd. for $[C_{19}H_{28}NO_2S]^+$ $(M+H)^+$, m/z = 334.1835, found 334.1837.

(*E*)-2-(3,3-Dimethylbut-1-en-1-yl)-1-tosylpiperidine (150c)



This compound was synthesized during an internship with Alberto Nunez-Bendinelli. According to General procedure F: *N*-(8,8-Dimethylnon-5-en-1-yl)-4-methylbenzenesulfonamide (170 mg, 526 µmol, 1.00 eq.), TAPT (12.8 mg, 26.3 µmol, 0.05 eq.), $(PhSe)_2$ (16.4 mg, 52.6 µmol, 0.10 eq.) and 1,2-bis(4-chlorophenyl)disulfane (15.1 mg, 52.6 µmol, 0.10 eq.) in 2.6 mL *o*-xylene for 22 h. Eluting with PE/EtOAc 4:1. NMR yield: 98.0 mg (305 µmol, 58%), isolated yield: 81.0 mg (252 µmol, 48%, colorless liquid). **TLC** R_f = 0.71 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3437, 2944, 2866, 1599, 1457, 1338, 1215, 1156, 1096, 1059, 973, 932, 816, 723. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.74 – 7.56 (m, 2H), 7.30 – 7.18 (m, 2H), 5.51 (dd, *J* = 15.8, 1.5 Hz, 1H), 5.19 (dd, *J* = 15.8, 6.1 Hz, 1H), 4.55 (s, 1H), 3.70 (d, *J* = 12.4 Hz, 1H), 3.08 – 2.72 (m, 1H), 2.40 (s, 3H), 1.74 – 1.38 (m, 6H), 0.89 (s, 9H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 144.0, 142.7, 138.0, 129.4, 127.4, 121.1, 54.8, 41.7, 32.9, 30.9, 29.4, 25.3, 21.5, 19.0. **HRMS** (ESI) calcd. for $[C_{18}H_{28}NO_2S]^+$ $(M+H)^+$, m/z = 322.1835, found 322.1837.

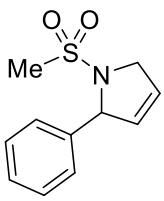
2-Styryl-1-tosylpiperidine (150b)



According to General procedure F: 4-Methyl-*N*-(7-phenylhept-5-en-1-yl)benzenesulfonamide (allylic:vinylic mixture of 3.4:1, 166 mg, 483 µmol, 1.00 eq.), TAPT (11.8 mg, 24.2 µmol, 0.05 eq.), $(PhSe)_2$ (15.1 mg, 48.3 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (13.9 mg, 48.3 µmol, 0.10 eq.) and 2-

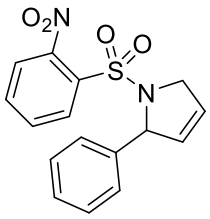
nitrobenzaldehyde (18.2 mg, 121 µmol, 0.25 eq.) in 2.4 mL *o*-xylene for 16 h. Eluting with PE/EtOAc 20:1. NMR yield: 21.0 mg (62 µmol, 17% from allylic substrate), isolated yield: 17.0 mg (50 µmol, 13% from allylic substrate, colorless oil) as a mixture of isomers (*E*/*Z* = 15:1). **TLC** R_f = 0.31 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3027, 2937, 2859, 1599, 1495, 1450, 1338, 1267, 1208, 1159, 1095, 1059, 939, 852, 816, 753, 723, 693, 664. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.97 – 7.53 (m, 2H), 7.51 – 6.92 (m, 8H), 6.35 (dd, *J* = 16.1, 1.5 Hz, 1H), 5.93 (dd, *J* = 16.1, 6.3 Hz, 1H), 5.01 – 4.55 (m, 1H), 3.86 – 3.47 (m, 1H), 3.16 – 2.83 (m, 1H), 2.30 (s, 3H), 1.72 (dt, *J* = 7.8, 3.5 Hz, 2H), 1.65 – 1.32 (m, 4H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.9, 137.4, 136.6, 132.2, 129.5, 128.5, 127.6, 127.5, 126.3, 126.3, 55.1, 42.0, 30.7, 25.2, 21.4, 19.3. **HRMS** (ESI) calcd. for $[C_{20}H_{24}NO_2S]^+$ $(M+H)^+$, m/z = 342,1522, found 342,1524.

1-(Methylsulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (149m)



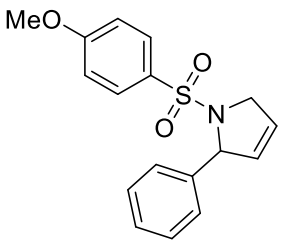
According to General procedure F: *N*-(4-Phenylbut-3-en-1-yl)methanesulfonamide (117 mg, 519 µmol, 1.00 eq.), TAPT (12.6 mg, 26.0 µmol, 0.05 eq.), $(PhSe)_2$ (16.2 mg, 51.9 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.9 mg, 51.9 µmol, 0.10 eq.) and 2-nitrobenzaldehyde (19.6 mg, 130 µmol, 0.25 eq.) in 2.6 mL *o*-xylene for 16 h. Eluting with PE/EtOAc 4:1. NMR yield: 49.0 mg (219 µmol, 42%), isolated yield: 40.0 mg (179 µmol, 35%, brown solid). **TLC** R_f = 0.15 (4:1 PE/EtOAc). **m.p.** 119 °C. IR [cm^{-1}] 3064, 3030, 2930, 2870, 1722, 1603, 1495, 1413, 1327, 1256, 1197, 1152, 1074, 965, 835, 757, 697. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.39 – 7.22 (m, 5H), 5.91 (dq, *J* = 6.1, 2.0 Hz, 1H), 5.74 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.53 (dq, *J* = 6.5, 2.2 Hz, 1H), 4.42 (dq, *J* = 14.4, 2.3 Hz, 1H), 4.22 (ddt, *J* = 14.4, 5.9, 2.1 Hz, 1H), 2.45 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 139.8, 130.5, 128.8, 128.3, 127.5, 124.9, 69.8, 55.1, 38.3. **HRMS** (ESI) calcd. for $[C_{11}H_{14}NO_2S]^+$ $(M+H)^+$, m/z = 224.0740, found 224.0741.

1-((2-Nitrophenyl)sulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (149q)



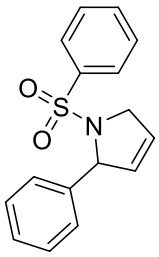
According to General procedure F: 2-Nitro-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (162 mg, 487 µmol, 1.00 eq.), TAPT (11.9 mg, 24.4 µmol, 0.05 eq.) and $(PhSe)_2$ (15.2 mg, 48.7 µmol, 0.10 eq.) in 2.4 mL *o*-xylene for 16 h, TAPT (11.9 mg, 24.4 µmol, 0.05 eq.) and $(PhSe)_2$ (15.2 mg, 48.7 µmol, 0.10 eq.) were re-added and the reaction was stirred for further 4 h. Eluting with PE/EtOAc 7.3:1→6.7:1. NMR yield: 71.0 mg (215 µmol, 44%), isolated yield: 60.0 mg (182 µmol, 37%, brownish oil). **TLC** R_f = 0.20 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3094, 3034, 2881, 1748, 1543, 1357, 1170, 1133, 1088, 854, 760, 697. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 7.63 – 7.42 (m, 2H), 7.41 – 7.32 (m, 1H), 7.30 – 7.14 (m, 6H), 6.06 – 5.89 (m, 1H), 5.77 (ddp, *J* = 8.4, 6.5, 2.2 Hz, 2H), 4.73 – 4.52 (m, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 147.7, 139.2, 133.5, 132.8, 131.0, 130.6, 130.2, 128.4, 128.1, 127.6, 124.5, 123.5, 70.5, 56.0. **HRMS** (ESI) calcd. for $[C_{16}H_{15}N_2O_4S]^+$ $(M+H)^+$, m/z = 331.0747, found 331.0744.

1-((4-Methoxyphenyl)sulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (149r)



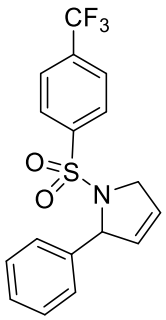
According to General procedure F: 4-Methoxy-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (166 mg, 523 µmol, 1.00 eq.), TAPT (12.7 mg, 26.2 µmol, 0.05 eq.), $(PhSe)_2$ (16.3 mg, 52.3 µmol, 0.10 eq.) and 1,2-bis(4-chlorophenyl)disulfane (15.0 mg, 52.3 µmol, 0.10 eq.) in 2.6 mL *o*-xylene for 16 h. Eluting with PE/EtOAc 20:1. NMR yield: 144 mg (457 µmol, 87%), isolated yield: 131 mg (415 µmol, 79%, white solid). **TLC** R_f = 0.22 (4:1 PE/EtOAc). **m.p.** 95 °C. **IR** [cm^{-1}] 3034, 2922, 2848, 1651, 1595, 1498, 1457, 1416, 1341, 1305, 1260, 1159, 1096, 1029, 835, 760, 697. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.62 – 7.49 (m, 2H), 7.33 – 7.17 (m, 5H), 6.92 – 6.78 (m, 2H), 5.79 (dq, *J* = 6.1, 2.0 Hz, 1H), 5.66 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.51 (dq, *J* = 4.6, 2.2 Hz, 1H), 4.35 (dq, *J* = 14.5, 2.3 Hz, 1H), 4.25 (ddt, *J* = 14.5, 5.7, 2.1 Hz, 1H), 3.84 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 162.7, 140.5, 130.7, 130.3, 129.3, 128.5, 127.8, 127.3, 124.5, 114.0, 70.2, 55.6, 55.4. **HRMS** (ESI) calcd. for $[C_{17}H_{18}NO_3S]$ $(M+H)^+$, m/z = 316.1002, found 316.1003.

2-Phenyl-1-(phenylsulfonyl)-2,5-dihydro-1H-pyrrole (149n)



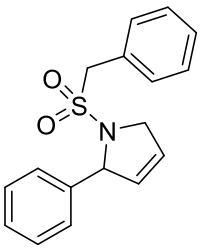
According to General procedure F: (*E*)-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (144 mg, 501 µmol, 1.00 eq.), TAPT (12.2 mg, 25.1 µmol, 0.05 eq.), $(PhSe)_2$ (15.6 mg, 50.1 µmol, 0.10 eq.) and 1,2-bis(4-chlorophenyl)disulfane (14.4 mg, 50.1 µmol, 0.10 eq.) in 2.5 mL *o*-xylene for 10 h. Eluting with PE/EtOAc 20:1. NMR yield: 136 mg (477 µmol, 95%), isolated yield: 111 mg (389 µmol, 78%, white solid). **TLC** R_f = 0.29 (4:1 PE/EtOAc). **m.p.** 107 °C. **IR** [cm^{-1}] 304, 3034, 2870, 1495, 1446, 1342, 1167, 1096, 831, 757, 723, 693. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.66 – 7.54 (m, 2H), 7.55 – 7.44 (m, 1H), 7.42 – 7.33 (m, 2H), 7.31 – 7.17 (m, 5H), 5.81 (dq, *J* = 6.0, 2.0 Hz, 1H), 5.67 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.55 (dq, *J* = 6.7, 2.2 Hz, 1H), 4.46 – 4.20 (m, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 140.2, 138.6, 132.3, 130.6, 128.8, 128.5, 127.9, 127.4, 127.1, 124.5, 70.3, 55.4. **HRMS** (ESI) calcd. for $[C_{16}H_{15}NO_2S]^{\cdot+}$ $(M)^{\cdot+}$, m/z = 285.0818, found 285.0820.

2-Phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-2,5-dihydro-1H-pyrrole (149s)



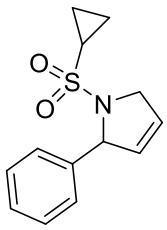
According to General procedure F: *N*-(4-phenylbut-3-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (183 mg, 515 µmol, 1.00 eq.), TAPT (12.5 mg, 25.8 µmol, 0.05 eq.), $(PhSe)_2$ (16.1 mg, 51.5 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.8 mg, 51.5 µmol, 0.10 eq.) and 2-nitrobenzaldehyde (19.5 mg, 129 µmol, 0.25 eq.) in 2.6 mL *o*-xylene for 24 h. Eluting with PE/EtOAc 20:1. NMR yield: 106 mg (300 µmol, 58%), isolated yield: 90.0 mg (255 µmol, 49%, brownish oil). **TLC** R_f = 0.35 (4:1 PE/EtOAc). **IR** [cm^{-1}] 2926, 2855, 1737, 1457, 1405, 1353, 1323, 1260, 1170, 1133, 1111, 1062, 1014, 842, 798, 716. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.56 (s, 4H), 7.32 – 7.09 (m, 5H), 5.88 (dq, *J* = 6.1, 1.9 Hz, 1H), 5.71 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.59 (dq, *J* = 6.4, 2.2 Hz, 1H), 4.47 (dq, *J* = 14.2, 2.3 Hz, 1H), 4.26 (ddt, *J* = 14.2, 5.8, 2.1 Hz, 1H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) =142.7, 139.2, 134.0, 133.5, 130.5, 128.5, 128.2, 127.6, 127.3, 125.8, 125.8, 125.7, 125.7, 124.5, 70.3, 55.3. **^{19}F NMR** (377 MHz, Chloroform-*d*): δ (ppm) = -63.7. **HRMS** (ESI) calcd. for $[C_{17}H_{15}F_3NO_2S]^+$ $(M+H)^+$, m/z = 354.0770, found 354.0074.

1-(Benzylsulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (149o)



According to General procedure F: (*E*)-1-Phenyl-*N*-(4-phenylbut-3-en-1-yl)methanesulfonamide (150 mg, 498 µmol, 1.00 eq.), TAPT (12.1 mg, 24.9 µmol, 0.05 eq.), $(PhSe)_2$ (15.5 mg, 49.8 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.3 mg, 49.8 µmol, 0.10 eq.) and 2-nitrobenzaldehyde (18.8 mg, 124 µmol, 0.25 eq.) in 2.5 mL *o*-xylene for 16 h. Eluting with PE/EtOAc 32:1. NMR yield: 62.0 mg (207 µmol, 42%), isolated yield: 53.0 mg (177 µmol, 36%, white solid). **TLC** R_f = 0.29 (4:1 PE/EtOAc). **m.p.** 140 °C. **IR** [cm^{-1}] 3030, 2971, 2922, 2855, 1741, 1454, 1368, 1215, 1156, 1074, 831, 783, 697. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.58 – 7.27 (m, 8H), 7.22 – 7.03 (m, 2H), 5.85 (dq, *J* = 6.0, 1.9 Hz, 1H), 5.72 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.56 (dq, *J* = 6.3, 2.2 Hz, 1H), 4.27 (dq, *J* = 14.4, 2.3 Hz, 1H), 3.90 (d, *J* = 13.8 Hz, 1H), 3.84 – 3.62 (m, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 140.0, 130.8, 129.8, 129.1, 128.7, 128.5, 128.5, 127.9, 125.3, 70.0, 58.8, 55.9. **HRMS** (ESI) calcd. for $[C_{17}H_{18}NO_2S]^+$ $(M+H)^+$, m/z = 300.1053, found 300.1056.

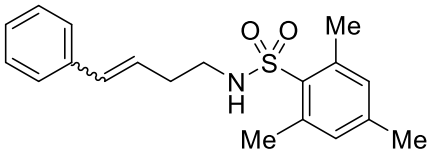
1-(Cyclopropylsulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (149p)



According to General procedure F: *N*-(4-phenylbut-3-en-1-yl)cyclopropanesulfonamide (215 mg, 855 µmol, 1.00 eq.), TAPT (20.8 mg, 42.8 µmol, 0.05 eq.), $(PhSe)_2$ (26.7 mg, 85.5 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (24.6 mg, 85.5 µmol, 0.10 eq.) and 2-nitrobenzaldehyde (32.3 mg, 214 µmol, 0.25 eq.) in 4.3 mL *o*-xylene for 26 h. Eluting with PE/EtOAc 20:1. NMR yield: 136 mg (545 µmol, 64%), isolated yield: 117 mg (469 µmol, 55%, brownish oil). **TLC** R_f = 0.29 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3034, 2926, 2855, 1730, 1689, 1495, 1454, 1394, 1338, 1252, 1152, 1085, 1003, 932, 891, 831, 760, 701. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.41 – 7.27 (m, 5H), 5.93 (dq, *J* = 6.1, 2.0 Hz, 1H), 5.77 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.63 (dt, *J* = 5.9, 2.3 Hz, 1H), 4.53 (dq, *J* = 14.2, 2.3 Hz, 1H), 4.31 (ddt, *J* = 14.2, 5.9, 2.0 Hz, 1H), 1.92 (tt, *J* = 8.0, 4.9 Hz, 1H), 1.09 (ddt, *J* = 9.9, 7.1, 4.7 Hz, 1H), 0.94 – 0.83 (m, 1H), 0.78 (dddd, *J* = 8.9, 8.0, 6.7, 4.6 Hz, 1H), 0.66 – 0.54 (m, 1H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 140.9, 130.7, 128.6, 128.1, 127.5, 124.7, 69.9, 55.5, 29.4, 4.9, 4.8. **HRMS** (ESI) calcd. for $[C_{13}H_{15}NO_2S]^{\cdot+}$ $(M)^{\cdot+}$, m/z = 249.0818, found 249.0812.

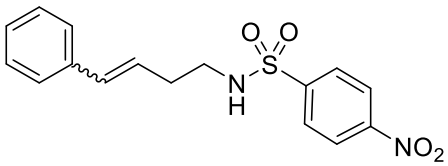
6.8.4 Substrate synthesis for the enantioselective amination

2,4,6-Trimethyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146v)



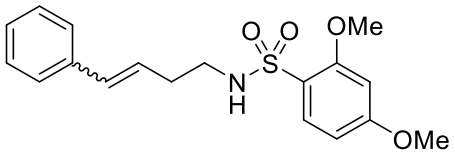
Following General procedure G: Crude 4-phenylbut-3-en-1-amine (1,50 g, 10.2 mmol, 1.00 eq.), NEt_3 (2,06 g, 20.4 mmol, 2.00 eq.) and 2,4,6-trimethylbenzenesulfonyl chloride (2,67 g, 12.2 mmol, 1.20 eq.) in 50 mL DCM. Eluting with PE/EtOAc 4:1. Isolated yield: 3,29 g (10.0 mmol, 98%, yellow solid) as a mixture of isomers (*E*:*Z* = 1:5.7). **TLC** R_f = 0.23 (4:1 PE/EtOAc). **m.p.** 46.3 °C. **IR** [cm^{-1}] 3306, 3023, 2975, 2937, 1603, 1566, 1495, 1446, 1405, 1320, 1185, 1152, 1077, 1033, 969, 917, 854, 768, 701. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.38 – 7.13 (m, 5H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.59 – 6.23 (m, 1H), 6.06 – 5.38 (m, 1H), 4.82 (dt, *J* = 21.4, 6.2 Hz, 1H), 3.05 (dq, *J* = 13.3, 6.6 Hz, 2H), 2.62 (d, *J* = 7.8 Hz, 6H), 2.52 – 2.32 (m, 2H), 2.30 (d, *J* = 3.6 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.2, 142.1, 139.1, 139.0, 136.8, 133.8, 133.7, 133.0, 132.0, 132.0, 131.9, 128.7, 128.6, 128.3, 127.9, 127.5, 127.0, 126.1, 125.9, 42.5, 42.1, 33.0, 28.6, 23.0, 23.0, 21.0. **HRMS** (ESI) calcd. for $[C_{19}H_{23}NO_2S]^+$ ($[M+H]^+$), m/z = 330.1522, found 330.1527.

4-Nitro-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146w)



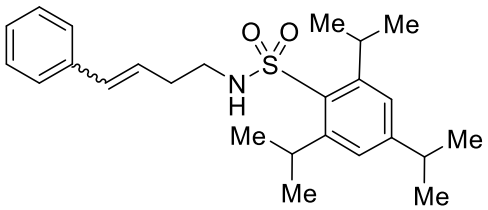
Following General procedure G: Crude 4-phenylbut-3-en-1-amine (1.50 g, 10.2 mmol, 1.00 eq.), NEt_3 (2.06 g, 20.4 mmol, 2.00 eq.) and 4-nitrobenzenesulfonyl chloride (1.13 g, 5.09 mmol, 0.50 eq.) in 50 mL DCM. Eluting with PE/EtOAc 9:1. Isolated yield: 1.33 g (4.00 mmol, 79%, yellow oil) as a mixture of isomers (*E*:*Z* = 1:4.4). **TLC** R_f = 0.10 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3295, 3105, 3023, 2937, 2870, 1607, 1528, 1405, 1349, 1312, 1163, 1092, 969, 943, 854, 794, 738, 686. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.34 – 8.15 (m, 2H), 8.11 – 7.81 (m, 2H), 7.34 – 7.09 (m, 5H), 6.53 (dt, *J* = 11.5, 1.9 Hz, 1H), 5.46 (dt, *J* = 11.6, 7.2 Hz, 1H), 4.89 (dt, *J* = 27.8, 6.0 Hz, 1H), 3.18 (p, *J* = 6.7 Hz, 2H), 2.42 (dqd, *J* = 15.0, 6.7, 1.6 Hz, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 150.0, 149.9, 146.0, 145.9, 136.5, 136.5, 133.6, 132.6, 128.6, 128.6, 128.3, 128.3, 128.1, 127.8, 127.3, 126.9, 126.1, 125.0, 124.4, 124.4, 43.1, 42.8, 33.2, 28.6. **HRMS** (ESI) calcd. for $[C_{16}H_{17}N_2O_4S]^+$ ($[M+H]^+$), m/z = 333.0904, found 333.0910.

2,4-Dimethoxy-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146x)



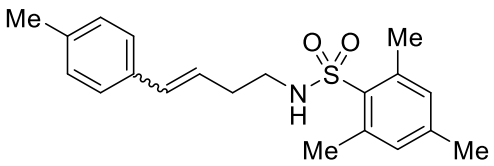
Following General procedure G: Crude 4-phenylbut-3-en-1-amine (0.70 g, 4.75 mmol, 1.00 eq.), NEt_3 (962 mg, 9.51 mmol, 2.00 eq.) and 2,4-dimethoxybenzenesulfonyl chloride (1.13 g, 5.09 mmol, 1.00 eq.) in 50 mL DCM. Eluting with PE/EtOAc 9:1. Isolated yield: 601 mg (1.73 mmol, 36%, yellow oil) as a mixture of isomers (*E*:*Z* = 1:4.7). **TLC** R_f = 0.11 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3314, 3012, 2945, 2844, 1595, 1491, 1465, 1327, 1260, 1215, 1159, 1077, 1025, 939, 839, 798, 734, 682. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.78 (t, *J* = 8.0 Hz, 1H), 7.32 – 7.02 (m, 5H), 6.57 – 6.21 (m, 3H), 5.47 (dt, *J* = 11.8, 7.1 Hz, 1H), 5.16 (t, *J* = 6.3 Hz, 1H), 3.86 – 3.65 (m, 6H), 2.95 (p, *J* = 6.8 Hz, 2H), 2.44 (qd, *J* = 7.0, 1.8 Hz, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 164.8, 157.7, 157.6, 136.9, 136.9, 132.7, 131.9, 131.9, 131.4, 128.7, 128.6, 128.6, 128.5, 128.3, 128.1, 127.4, 126.9, 126.2, 126.1, 119.3, 119.3, 104.6, 99.2, 60.4, 56.2, 55.8, 43.3, 42.9, 32.7, 28.6, 21.1, 14.3. **HRMS** (ESI) calcd. for $[C_{18}H_{22}NO_4S]^+$ ($[M+H]^+$), m/z = 348.1264, found 348.1268.

2,4,6-Triisopropyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146y)



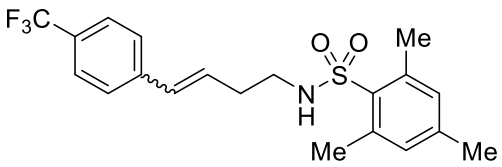
Following General procedure G: Crude 4-phenylbut-3-en-1-amine (0.90 g, 6.11 mmol, 1.00 eq.), NEt_3 (1.24 mg, 12.2 mmol, 2.00 eq.) and 2,4,6-triisopropylbenzenesulfonyl chloride (1.85 g, 6.11 mmol, 1.00 eq.) in 50 mL DCM. Eluting with PE/EtOAc 9:1. Isolated yield: 0.42 g (1.02 mmol, 17%, yellow oil) as a mixture of isomers (*E*:*Z* = 1:5.6). **TLC** R_f = 0.53 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3302, 3056, 3012, 2960, 2870, 1737, 1603, 1562, 1495, 1461, 1424, 1364, 1320, 1256, 1197, 1152, 1103, 1074, 1044, 939, 883, 854, 805, 768, 701. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.36 – 7.15 (m, 7H), 6.64 – 6.33 (m, 1H), 5.54 (dt, *J* = 11.7, 7.3 Hz, 1H), 4.52 (dt, *J* = 21.2, 6.2 Hz, 1H), 4.31 – 4.06 (m, 2H), 3.52 – 2.81 (m, 3H), 2.50 (dqd, *J* = 31.3, 6.9, 1.6 Hz, 2H), 1.89 – 1.18 (m, 18H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 154.6, 152.7, 150.4, 150.3, 136.8, 133.3, 132.2, 132.1, 132.1, 128.6, 128.6, 128.3, 127.7, 127.5, 127.0, 126.1, 125.7, 124.5, 124.3, 123.8, 42.6, 42.2, 34.6, 34.2, 29.8, 29.6, 29.0, 28.7, 24.9, 24.4, 24.0, 23.6. **HRMS** (ESI) calcd. for $[C_{25}H_{36}NO_2S]^+$ ($[M+H]^+$), m/z = 414.2461, found 414.2468.

2,4,6-Trimethyl-*N*-(4-(*p*-tolyl)but-3-en-1-yl)benzenesulfonamide (146z)



Following General procedure G: (3-Aminopropyl)triphenylphosphonium bromide (5.00 g, 12.5 mmol, 2.00 eq.), KO^{t}Bu (2.80 g, 25.0 mmol, 4.00 eq.) in 21 mL THF, 4-methylbenzaldehyde (1.13 g, 9.37 mmol, 1.50 eq.) in 3.1 mL THF, NEt_3 (1.88 g, 18.6 mmol, 2.00 eq.) and 2,4,6-trimethylbenzenesulfonyl chloride (2.44 g, 11.2 mmol, 1.20 eq.). Eluting with PE/EtOAc 9:1. Isolated yield: 1.63 g (4.75 mmol, 51%, brown oil) as a mixture of isomers (*E*:*Z* = 1.6:1). **TLC** R_f = 0.23 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3310, 3015, 2926, 2855, 1603, 1586, 1513, 1454, 1405, 1320, 1189, 1156, 1081, 969, 850, 753. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.21 – 7.04 (m, 4H), 6.93 (d, *J* = 10.7 Hz, 2H), 6.31 (dt, *J* = 15.8, 1.4 Hz, 1H), 5.90 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.57 (dt, *J* = 29.8, 6.2 Hz, 1H), 3.04 (dq, *J* = 16.8, 6.5 Hz, 2H), 2.61 (d, *J* = 8.2 Hz, 6H), 2.50 – 2.32 (m, 5H), 2.30 (d, *J* = 5.3 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.2, 142.1, 139.1, 137.3, 136.8, 134.0, 133.8, 133.7, 133.6, 133.1, 132.0, 132.0, 129.3, 129.0, 128.6, 127.0, 126.0, 124.6, 42.5, 42.1, 32.9, 28.5, 23.0, 23.0, 21.2, 21.0. **HRMS** (ESI) calcd. for $[C_{20}H_{26}NO_2S]^+$ ([M+H]$^+$), m/z = 3441679, found 344.1683.

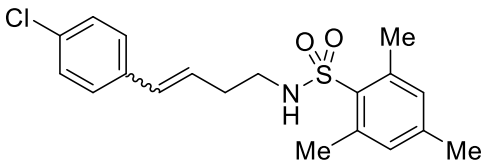
2,4,6-Trimethyl-*N*-(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)benzenesulfonamide (146aa)



Following General procedure G: (3-Aminopropyl)triphenylphosphonium bromide (5.00 g, 12.5 mmol, 2.00 eq.), KO^{t}Bu (2.80 g, 25.0 mmol, 4.00 eq.) in 21 mL THF, 4-(trifluoromethyl)benzaldehyde (1.63 g, 9.37 mmol, 1.50 eq.) in 3.1 mL THF, NEt_3 (1.88 g, 18.6 mmol, 2.00 eq.) and 2,4,6-trimethylbenzenesulfonyl chloride (2.44 g, 11.2 mmol, 1.20 eq.). Eluting with PE/EtOAc 9:1. Isolated yield: 1.10 g (2.77 mmol, 30%, yellow solid) as a mixture of isomers (*E*:*Z* = 2.5:1). **TLC** R_f = 0.41 (4:1 PE/EtOAc). **m.p.** 97.0 °C. **IR** [cm^{-1}] 3310, 2974, 2941, 1741, 1614, 1566, 1454, 1416, 1327, 1230, 1156, 1122, 1066, 969, 854, 816, 779. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.52 (t, *J* = 8.0 Hz, 2H), 7.40 – 7.21 (m, 2H), 6.91 (d, *J* = 6.3 Hz, 2H), 6.62 – 6.22 (m, 1H), 6.20 – 5.47 (m, 1H), 4.97 (dt, *J* = 19.5, 6.2 Hz, 1H), 3.06 (dq, *J* = 16.2, 6.6 Hz,

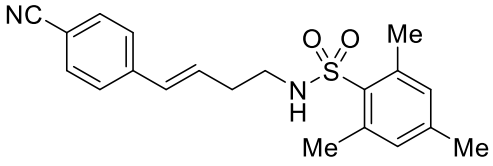
2H), 2.60 (d, *J* = 10.4 Hz, 6H), 2.47 – 2.32 (m, 2H), 2.28 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.3, 140.4, 139.1, 139.0, 133.7, 133.7, 132.0, 132.0, 131.6, 130.5, 130.1, 129.3, 128.9, 128.9, 128.6, 126.3, 126.0, 125.5, 125.4, 125.4, 125.3, 125.2, 125.1, 125.1, 122.4, 42.3, 41.9, 33.1, 28.7, 23.0, 22.9, 20.9, 20.9. **^{19}F NMR** (377 MHz, Chloroform-*d*): δ (ppm) = -63.0 (*E*), -63.0 (*Z*). **HRMS** (ESI) calcd. for $[C_{20}H_{23}F_3NO_2S]^+$ ($[M+H]^+$), m/z = 398.1396, found 398.1400.

N-(4-(4-Chlorophenyl)but-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (146ab)



Following General procedure G: (3-Aminopropyl)triphenylphosphonium bromide (5.00 g, 12.5 mmol, 2.00 eq.), KO^{t}Bu (2.80 g, 25.0 mmol, 4.00 eq.) in 21 mL THF, 4-chlorobenzaldehyde (1.32 g, 9.37 mmol, 1.50 eq.) in 3.1 mL THF, NEt_3 (1.88 g, 18.6 mmol, 2.00 eq.) and 2,4,6-trimethylbenzenesulfonyl chloride (2.44 g, 11.2 mmol, 1.20 eq.). Eluting with PE/EtOAc 9:1. Isolated yield: 1.10 g (3.02 mmol, 32%, yellowish solid) as a mixture of isomers (*E*:*Z* = 1.1:1). **TLC** R_f = 0.43 (4:1 PE/EtOAc). **m.p.** 53.3 °C. **IR** [cm^{-1}] 3302, 2978, 2937, 2363, 1730, 1603, 1566, 1491, 1454, 1405, 1323, 1185, 1156, 1092, 969, 939, 846, 716. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.26 (dt, *J* = 8.8, 2.2 Hz, 2H), 7.21 – 7.15 (m, 1H), 7.13 – 7.03 (m, 1H), 6.92 (dq, *J* = 9.2, 0.7 Hz, 2H), 6.55 – 6.15 (m, 1H), 6.03 – 5.34 (m, 1H), 4.77 – 4.30 (m, 1H), 3.05 (dq, *J* = 11.3, 6.5 Hz, 2H), 2.60 (d, *J* = 8.5 Hz, 6H), 2.45 – 2.27 (m, 5H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.2, 142.2, 139.0, 139.0, 135.3, 135.1, 133.6, 133.6, 133.1, 132.8, 132.1, 132.0, 132.0, 130.9, 129.9, 128.7, 128.4, 127.3, 126.5, 42.4, 41.9, 33.0, 28.6, 23.0, 23.0, 21.0. **HRMS** (ESI) calcd. for $[C_{19}H_{23}ClNO_2S]^+$ ($[M+H]^+$), m/z = 364.1133, found 364.1135.

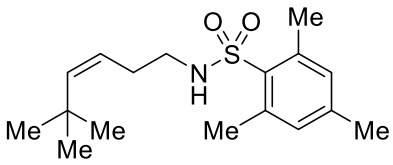
(E)-N-(4-(4-Cyanophenyl)but-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (146ac)



Following General procedure G: (3-Aminopropyl)triphenylphosphonium bromide (5.00 g, 12.5 mmol, 2.00 eq.), KO^{t}Bu (2.80 g, 25.0 mmol, 4.00 eq.) in 21 mL THF, 4-formylbenzonitrile (1.23 g, 9.37 mmol, 1.50 eq.) in 3.1 mL THF, NEt_3 (1.88 g, 18.6 mmol, 2.00 eq.) and 2,4,6-trimethylbenzenesulfonyl chloride (2.44 g, 11.2 mmol,

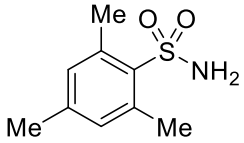
1.20 eq.). Eluting with PE/EtOAc 9:1. Isolated yield: 640 mg (1.81 mmol, 19%, yellow solid) as the (*E*)-isomer exclusively. **TLC** R_f = 0.24 (4:1 PE/EtOAc). **m.p.** 133.8 °C. **IR** [cm^{-1}] 3310, 3034, 2978, 2941, 2226, 1603, 1506, 1454, 1409, 1323, 1189, 1156, 1081, 969, 857. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.56 – 7.49 (m, 2H), 7.39 – 7.28 (m, 2H), 6.92 (s, 2H), 6.43 – 6.26 (m, 1H), 6.14 (dt, *J* = 15.9, 6.9 Hz, 1H), 4.93 (t, *J* = 6.2 Hz, 1H), 3.08 (q, *J* = 6.5 Hz, 2H), 2.60 (s, 6H), 2.38 (qd, *J* = 6.6, 1.3 Hz, 2H), 2.28 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.3, 141.4, 139.0, 133.6, 132.3, 132.0, 131.4, 130.4, 126.6, 119.0, 110.5, 41.8, 33.2, 23.0, 21.0. **HRMS** (ESI) calcd. for $[C_{20}H_{23}N_2O_2S]^+$ ($[M+H]^+$), m/z = 355.1475, found 355.1480.

(Z)-N-(5,5-Dimethylhex-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (146ad)



Following General procedure G: (3-Aminopropyl)triphenylphosphonium bromide (5.00 g, 12.5 mmol, 2.00 eq.), KO^{t}Bu (2.80 g, 25.0 mmol, 4.00 eq.) in 21 mL THF, pivalaldehyde (807 mg, 9.37 mmol, 1.50 eq.) in 3.1 mL THF, NEt_3 (1.89 g, 18.7 mmol, 2.00 eq.) and 2,4,6-trimethylbenzenesulfonyl chloride (2.45 g, 11.2 mmol, 1.20 eq.). Eluting with PE/EtOAc 9:1. Isolated yield: 890 mg (2.88 mmol, 31%, yellowish solid) as the (*Z*)-isomer exclusively. **TLC** R_f = 0.76 (4:1 PE/EtOAc). **m.p.** 67.9 °C. **IR** [cm^{-1}] 3306, 2952, 2870, 1603, 1566, 1461, 1405, 1364, 1320, 1234, 1189, 1152, 1074, 1033, 895, 850, 783, 731. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.02 – 6.87 (m, 2H), 5.43 (dt, *J* = 11.9, 1.8 Hz, 1H), 4.93 (dt, *J* = 12.0, 7.4 Hz, 1H), 4.44 (t, *J* = 6.2 Hz, 1H), 2.91 (q, *J* = 6.8 Hz, 2H), 2.63 (s, 6H), 2.44 – 2.25 (m, 5H), 1.06 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 143.4, 142.2, 139.1, 133.5, 132.0, 123.5, 42.7, 33.3, 31.0, 28.3, 23.0, 20.9. **HRMS** (ESI) calcd. for $[C_{17}H_{28}NO_2S]^+$ ($[M+H]^+$), m/z = 310.1835, found 310.1840.

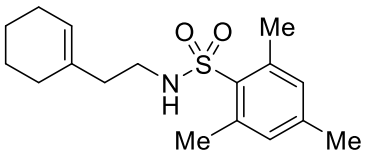
2,4,6-Trimethylbenzenesulfonamide



To a solution of 2,4,6-Trimethylbenzenesulfonyl chloride (4,40 g, 20.1 mmol, 1.00 eq.) in $CHCl_3$ (30 mL) was added NH_3 aq. (7.56 mL, 101 mmol, 5.00 eq., 28% solution). After stirring vigorously for 2 h at r.t., the reaction mixture was extracted with DCM and the solvent was evaporated under reduced pressure to give the corresponding sulfonamide. Isolated yield: 3.36 g (16.9 mmol, 84%, white solid). **TLC** R_f = 0.27 (DCM). **m.p.** 142.7 °C. **IR** [cm^{-1}] 3370, 3261, 3023, 2971, 2937, 1603, 1554, 1454, 1402, 1331,

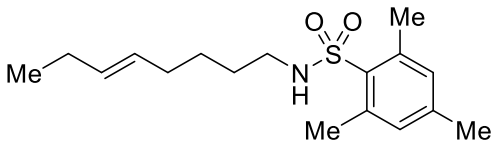
1148, 1055, 880, 667. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 6.96 (s, 2H), 4.82 (s, 2H), 2.65 (s, 6H), 2.30 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 142.2, 138.2, 136.0, 131.9, 22.9, 20.9. **HRMS** (ESI) calcd. for $[C_9H_{14}NO_2S]^+$ ($[M+H]^+$), m/z = 200.0740, found 200.0740.

N-(2-(Cyclohex-1-en-1-yl)ethyl)-2,4,6-trimethylbenzenesulfonamide (146af)



Following General procedure E: 2-(Cyclohex-1-en-1-yl)ethan-1-amine (1.00 g, 7.99 mmol, 1.00 eq.), NEt_3 (1.62 g, 16.0 mmol, 2.00 eq.) and 2,4,6-trimethylbenzenesulfonyl chloride (1.75 g, 7.99 mmol, 1.00 eq.) in 50 mL DCM. Eluting with PE/EtOAc 9:1. Isolated yield: 1.11 g (3.62 mmol, 45%, white solid). **TLC** R_f = 0.58 (4:1 PE/EtOAc). **m.p.** 54.6 °C. **IR** [cm^{-1}] 3306, 2926, 1737, 1603, 1566, 1439, 1405, 1320, 1185, 1152, 1059, 985, 917, 850, 753. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 6.95 (s, 2H), 5.40 (dq, *J* = 3.8, 1.9 Hz, 1H), 4.45 (t, *J* = 5.8 Hz, 1H), 2.93 (q, *J* = 6.2 Hz, 2H), 2.62 (s, 6H), 2.30 (s, 3H), 2.11 – 2.01 (m, 2H), 2.01 – 1.90 (m, 2H), 1.69 (dt, *J* = 7.4, 3.6 Hz, 2H), 1.52 (qd, *J* = 4.4, 1.9 Hz, 4H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.1, 139.1, 133.6, 133.4, 131.9, 124.9, 39.8, 37.3, 27.4, 25.2, 23.0, 22.6, 22.2, 21.0. **HRMS** (ESI) calcd. for $[C_{17}H_{26}NO_2S]^+$ ($[M+H]^+$), m/z = 308.1679, found 308.1685.

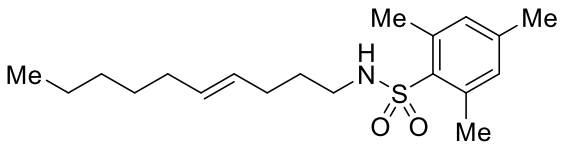
(E)-2,4,6-Trimethyl-*N*-(oct-5-en-1-yl)benzenesulfonamide (147f)



2,4,6-Trimethylbenzenesulfonamide (2.37 g, 11.9 mmol, 1.50 eq.), triethylsilane (1.01 g, 8.72 mmol, 1.10 eq.) and trifluoromethanesulfonic acid (59.5 mg, 396 µmol, 0.05 eq.) were added to a solution of *(E)*-oct-5-enal (1.00 g, 7.92 mmol, 1.00 eq.) in nitromethane (6.40 mL, 1.0 M) and the mixture was stirred for 3 h at r.t. Then, 50 mL distilled H_2O were added, and the product was extracted 3x with DCM. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 20:1. Isolated yield: 710 mg (2.52 mmol, 32%, colorless oil). **TLC** R_f = 0.36 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3310, 2930, 2859, 1603, 1566, 1439, 105, 1323, 1185, 1156, 1081, 1036, 969, 921, 850, 753. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 6.95 (q, *J* = 0.7 Hz, 2H), 5.45 – 5.20 (m, 2H), 4.47 (t, *J* = 6.2 Hz, 1H), 3.00 – 2.70 (m, 2H), 2.63 (s, 6H), 2.30 (s, 3H), 2.00 – 1.80 (m, 4H), 1.43 (dddd, *J* = 12.5, 8.2, 6.1, 1.2 Hz, 2H), 1.35 –

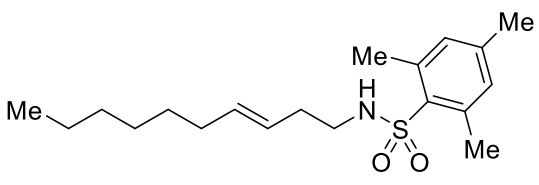
1.23 (m, 2H), 0.94 (td, *J* = 7.4, 2.4 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.1, 139.1, 133.6, 132.7, 131.9, 128.3, 42.5, 31.9, 29.0, 26.5, 25.6, 23.0, 20.9, 13.9. **HRMS** (ESI) calcd. for $[C_{17}H_{28}NO_2S]^+$ ($[M+H]^+$), m/z = 310.1835, found 310.1841.

(E)-*N*-(Dec-4-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (139f)



2,4,6-Trimethylbenzenesulfonamide (1.94 g, 9.72 mmol, 1.50 eq.), triethylsilane (829 mg, 7.13 mmol, 1.10 eq.) and trifluoromethanesulfonic acid (48.6 mg, 324 µmol, 0.05 eq.) were added to a solution of *(E)*-dec-4-enal (1.00 g, 6.48 mmol, 1.00 eq.) in nitromethane (5.20 mL, 1.0 M) and the mixture was stirred for 3 h at r.t. Then, 50 mL distilled H_2O were added, and the product was extracted 3x with DCM. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 20:1. Isolated yield: 1.54 g (4.56 mmol, 70%, colorless oil). **TLC** R_f = 0.36 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3302, 2926, 2855, 1741, 1603, 1586, 1454, 1409, 1323, 1215, 1156, 1081, 1032, 969, 850, 738. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 6.95 (s, 2H), 5.45 – 5.06 (m, 2H), 4.58 (s, 1H), 2.88 (q, *J* = 6.8 Hz, 2H), 2.63 (s, 6H), 2.29 (s, 3H), 2.00 – 1.81 (m, 4H), 1.50 (p, *J* = 7.1 Hz, 2H), 1.25 (tdd, *J* = 13.2, 8.8, 4.5 Hz, 6H), 0.94 – 0.79 (m, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.1, 139.1, 133.7, 132.3, 131.9, 128.4, 42.0, 32.5, 31.4, 29.6, 29.2, 29.2, 23.0, 22.5, 20.9, 14.1. **HRMS** (ESI) calcd. for $[C_{19}H_{32}NO_2S]^+$ ($[M+H]^+$), m/z = 338.2148, found 338.2147.

(*E*)-*N*-(Dec-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (146ag)

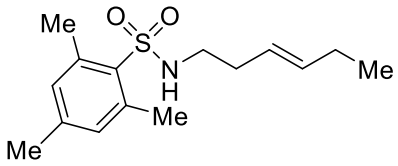


To a solution of (*E*)-dec-3-enoic acid (2,00 g, 11.8 mmol, 1.00 eq.) in 20 mL dry THF, $LiAlH_4$ (1.34 g, 35.2 mmol, 3.00 eq.) was added slowly at 0 °C under N_2 atmosphere. The reaction was stirred for 1 h, then distilled H_2O was added slowly and the mixture was extracted 3x with DEE. The solvent was evaporated under reduced pressure and the crude product was dissolved in 50 mL DCM. Next, NEt_3 (2.38 g, 23.6 mmol, 2.00 eq.) and MsCl (1.35 g, 11.8 mmol, 1.00 eq.) were added and the solution was stirred at r.t.

overnight. The solvent was evaporated under reduced pressure and the crude product was used without further purification for further synthesis.

Crude (*E*)-dec-3-en-1-yl methanesulfonate (2.76 g, 11.8 mmol, 1.00 eq.) was dissolved in 124 mL DMF, then, 2,4,6-Trimethylbenzenesulfonamide (3.05 g, 15.3 mmol, 1.30 eq.) and K_2CO_3 (8.14 g, 58.9 mmol, 5.00 eq.) were added. The solution was stirred overnight at 90 °C. The reaction was cooled to r.t. and neutralized by dropwise addition of aq. HCl solution (1.0 M). The product was extracted 3x with DEE. The solvent was removed under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1. Isolated yield: 1.12 g (3.32 mmol, 28% (over three steps), colorless oil). **TLC** R_f = 0.34 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3302, 2926, 2855, 1603, 1454, 1405, 1323, 1185, 1156, 1081, 969, 850, 760. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 6.95 (s, 2H), 5.43 (dtt, *J* = 14.7, 6.6, 1.3 Hz, 1H), 5.17 (dtt, *J* = 15.3, 6.9, 1.4 Hz, 1H), 4.57 (t, *J* = 6.0 Hz, 1H), 2.93 – 2.85 (m, 2H), 2.61 (s, 6H), 2.29 (s, 3H), 2.11 (qd, *J* = 6.6, 1.2 Hz, 2H), 1.93 (t, *J* = 6.7 Hz, 2H), 1.34 – 1.15 (m, 8H), 0.93 – 0.80 (m, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.1, 139.0, 134.8, 133.6, 131.9, 125.4, 42.0, 32.6, 32.3, 31.7, 29.3, 28.9, 23.0, 22.6, 20.9, 14.1. **HRMS** (ESI) calcd. for $[C_{19}H_{32}NO_2S]^+$ ($[M+H]^+$), m/z = 338.2148, found 338.2149.

(*E*)-*N*-(Hex-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (146ah)



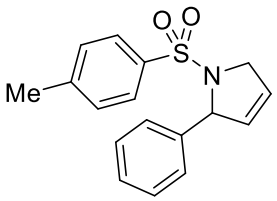
To a solution of Ethyl (*E*)-hex-3-enoate (2,00 g, 14.1 mmol, 1.00 eq.) in 20 mL dry THF, $LiAlH_4$ (1.07 g, 28.1 mmol, 2.00 eq.) was added slowly at 0 °C under N_2 atmosphere. The reaction was stirred for 1 h, then distilled H_2O was added slowly and the mixture was extracted 3x with DEE. The solvent was evaporated under reduced pressure and the crude product was dissolved in 50 mL DCM. Next, NEt_3 (3.90 mL, 28.0 mmol, 2.00 eq.) and MsCl (1.60 g, 14.0 mmol, 1.00 eq.) were added and the solution was stirred overnight at r.t.. The solvent was evaporated under reduced pressure and the crude product was used without further purification for further synthesis.

Crude (*E*)-Hex-3-en-1-yl methanesulfonate (1.00 g, 5.61 mmol, 1.00 eq.) was dissolved in 60 mL DMF, then, 2,4,6-Trimethylbenzenesulfonamide (2.24 g, 11.2 mmol, 2.00 eq.) and K_2CO_3 (3.88 g, 28.1 mmol, 5.00 eq.) were added. The solution was stirred overnight at 90 °C. The reaction was cooled to r.t. and neutralized

by dropwise addition of aq. HCl solution (1.0 M). The product was extracted 3x with DEE. The solvent was removed under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1. Isolated yield: 510 mg (1.81 mmol, 13% (over three steps), colorless oil). **TLC** R_f = 0.46 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3302, 3026, 2963, 2874, 1603, 1566, 1454, 1405, 1320, 1152, 1077, 969, 850. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 6.93 (s, 2H), 5.45 (dtt, *J* = 15.3, 6.3, 1.4 Hz, 1H), 5.16 (dtt, *J* = 15.4, 7.0, 1.6 Hz, 1H), 4.69 (t, *J* = 6.2 Hz, 1H), 2.90 (q, *J* = 6.4 Hz, 2H), 2.61 (s, 6H), 2.10 (qd, *J* = 6.7, 1.2 Hz, 2H), 1.95 (qdd, *J* = 7.5, 6.2, 1.3 Hz, 2H), 0.92 (t, *J* = 7.5 Hz, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 142.1, 139.0, 136.0, 133.7, 131.9, 124.6, 42.0, 32.3, 25.5, 22.9, 20.9, 13.6. **HRMS** (ESI) calcd. for $[C_{15}H_{24}NO_2S]^+$ ($[M+H]^+$), m/z = 282.1522, found 282.1526.

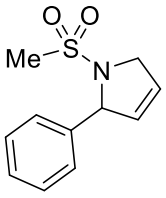
6.8.5 Enantioselective synthesis of 3-pyrrolines, pyrrolidines and piperidines

2-Phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (149d)*



Following General procedure H: 4-Methyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (150 mg, 498 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.0 mg, 50.0 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.3 mg, 50.0 µmol, 0.10 eq.) and TAPT (12.1 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 5 h. Eluting with PE/EtOAc 9:1. NMR yield: 97.0 mg (324 µmol, 65%), isolated yield: 81.0 mg (271 µmol, 54%, white solid, 90.5:9.5 *er*). **TLC** R_f = 0.35 (4:1 PE/EtOAc). **m.p.** 130 °C. **IR** [cm^{-1}] 3064, 3030, 2922, 2855, 1595, 1491, 1454, 1338, 1159, 1092, 1059, 913, 816, 757, 693. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.55 – 7.48 (m, 2H), 7.37 – 7.23 (m, 5H), 7.22 – 7.16 (m, 2H), 5.79 (dq, *J* = 6.0, 2.0 Hz, 1H), 5.65 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.52 (dq, *J* = 4.7, 2.2 Hz, 1H), 4.41 – 4.19 (m, 2H), 2.38 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.2, 140.5, 135.5, 130.6, 129.5, 128.5, 127.8, 127.3, 124.5, 118.2, 70.3, 55.4, 21.5. **HRMS** (ESI) calcd. for $[C_{17}H_{18}NO_2S]^+$ ([M+H]$^+$), m/z = 300.1053, found 300.1055. **HPLC** (OD-3, hexane:^{i}PrOH 85:15, flow rate 1.0 ml/min, 25 °C) t_R = 7.921 min (major), 8.953 min (minor). **Optical rotation** $[\alpha]_D^{20}$ = −255.4 (*c* 1.0, $CHCl_3$).

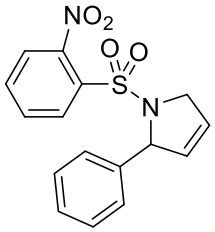
1-(Methylsulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149m)*



Following General procedure H: *N*-(4-Phenylbut-3-en-1-yl)methanesulfonamide (68 mg, 302 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (21.2 mg, 30.1 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (8.67 mg, 30.1 µmol, 0.10 eq.) and TAPT (7.34 mg, 15.1 µmol, 0.05 eq.) in 3 mL MeCN for 10 h. Eluting with PE/EtOAc 4:1. NMR yield: 31.0 mg (139 µmol, 46%), isolated yield: 25.0 mg (112 µmol, 37%, brown solid, 87.5:12.5 *er*). **TLC** R_f = 0.15 (4:1 PE/EtOAc). **m.p.** 119 °C. **IR** [cm^{-1}] 3064, 3030, 2930, 2870, 1722, 1603, 1495, 1413, 1327, 1256, 1197, 1152, 1074, 965, 835, 757, 697. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.39 – 7.22 (m, 5H), 5.91 (dq, *J* = 6.1, 2.0 Hz, 1H), 5.74 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.53 (dq, *J* = 6.5, 2.2 Hz, 1H), 4.42 (dq, *J* = 14.4, 2.3 Hz,

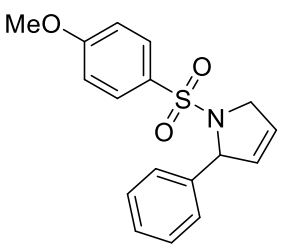
1H), 4.22 (ddt, *J* = 14.4, 5.9, 2.1 Hz, 1H), 2.45 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 139.8, 130.5, 128.8, 128.3, 127.5, 124.9, 69.8, 55.1, 38.3. **HRMS** (ESI) calcd. for $[C_{11}H_{14}NO_2S]^+$ ($[M+H]^+$), m/z = 224.0740, found 224.0741. **HPLC** (OD-3, hexane:^{i}PrOH 85:15, flow rate 1.0 ml/min, 25 °C) t_R = 9.742 min (major), 10.912 min (minor). **Optical rotation** $[\alpha]_D^{20}$ = −231.5 (*c* 0.5, $CHCl_3$).

1-((2-Nitrophenyl)sulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149q)*



Following General procedure H: 2-Nitro-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (167 mg, 502 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.3 mg, 50.0 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.4 mg, 50.0 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 5 h. Eluting with PE/EtOAc 9:1→4:1. NMR yield: 86.0 mg (260 µmol, 52%), isolated yield: 52.0 mg (157 µmol, 31%, brown liquid, 97:3 *er*). **TLC** R_f = 0.20 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3090, 3034, 2922, 1744, 1543, 1495, 1357, 1170, 1129, 1088, 854, 746, 697. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.52 – 7.40 (m, 2H), 7.36 – 7.28 (m, 1H), 7.28 – 7.09 (m, 6H), 5.93 (ddt, *J* = 4.5, 2.8, 1.6 Hz, 1H), 5.73 (tp, *J* = 6.3, 2.1 Hz, 2H), 4.59 (tt, *J* = 4.3, 2.1 Hz, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 147.6, 139.1, 133.4, 132.8, 130.9, 130.5, 130.1, 128.4, 128.1, 127.6, 124.4, 123.5, 70.5, 55.9. **HRMS** (ESI) calcd. for $[C_{16}H_{15}N_2O_4S]^+$ ($[M+H]^+$), m/z = 331.0747, found 331.0744. **HPLC** (OD-3, hexane:^{i}PrOH 85:15, flow rate 1.0 ml/min, 25 °C) t_R = 12.979 min (minor), 13.773 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −193.8 (*c* 0.54, $CHCl_3$).

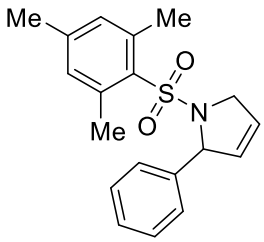
1-((4-Methoxyphenyl)sulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149r)*



Following General procedure H: 4-methoxy-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (95.0 mg, 300 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (21.0 mg, 30.0 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (8.60 mg, 30.0 µmol, 0.10 eq.) and TAPT (7.28 mg, 15.0 µmol, 0.05 eq.) in 3 mL MeCN for 3 h. Eluting with PE/EtOAc 9:1. NMR yield: 26.0 mg (82.4 µmol, 28%), isolated yield:

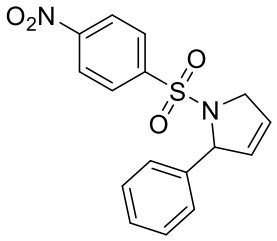
19.0 mg (60.0 µmol, 20%, white solid, 92:8 *er*). **TLC** R_f = 0.22 (4:1 PE/EtOAc). **m.p.** 95 °C. **IR** [cm^{-1}] 3034, 2922, 2848, 1651, 1595, 1498, 1457, 1416, 1341, 1305, 1260, 1159, 1096, 1029, 835, 760, 697. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.62 – 7.49 (m, 2H), 7.33 – 7.17 (m, 5H), 6.92 – 6.78 (m, 2H), 5.79 (dq, *J* = 6.1, 2.0 Hz, 1H), 5.66 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.51 (dq, *J* = 4.6, 2.2 Hz, 1H), 4.35 (dq, *J* = 14.5, 2.3 Hz, 1H), 4.25 (ddt, *J* = 14.5, 5.7, 2.1 Hz, 1H), 3.84 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 162.7, 140.5, 130.7, 130.3, 129.3, 128.5, 127.8, 127.3, 124.5, 114.0, 70.2, 55.6, 55.4. **HRMS** (ESI) calcd. for $[C_{17}H_{18}NO_3S]^+$ ($[M+H]^+$), m/z = 316.1002, found 316.1003. **HPLC** (OD-3, hexane:^{i}PrOH 85:15, flow rate 1.0 ml/min, 25 °C) t_R = 11.315 min (major), 13.488 min (minor). **Optical rotation** $[\alpha]_D^{20}$ = −209.6 (*c* 1.0, $CHCl_3$).

1-(Mesitylsulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149v)*



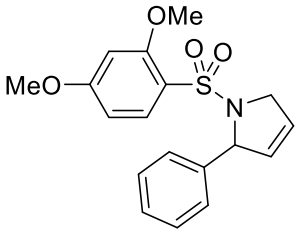
Following General procedure H: 2,4,6-Trimethyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (165 mg, 501 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.2 mg, 50.0 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.4 mg, 50.0 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 3 h. Eluting with PE/EtOAc 9:1. NMR yield: 156 mg (476 µmol, 95%), isolated yield: 133 mg (406 µmol, 81%, brown oil, 91.5:8.5 *er*). **TLC** R_f = 0.60 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3064, 3030, 2974, 2937, 2866, 1603, 1566, 1491, 1405, 1316, 1189, 1156, 1062, 1029, 984, 854, 760, 693. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.12 – 7.03 (m, 3H), 7.03 – 6.94 (m, 2H), 6.68 (d, *J* = 1.0 Hz, 2H), 5.91 (dq, *J* = 6.2, 2.0 Hz, 1H), 5.67 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.57 – 5.39 (m, 1H), 4.58 (ddt, *J* = 14.4, 3.1, 2.2 Hz, 1H), 4.17 (ddt, *J* = 14.3, 5.8, 2.0 Hz, 1H), 2.46 (s, 6H), 2.16 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.4, 140.1, 139.8, 132.7, 131.5, 130.7, 127.9, 127.4, 127.0, 124.6, 69.5, 54.8, 22.7, 20.8. **HRMS** (ESI) calcd. for $[C_{19}H_{22}NO_2S]^+$ ($[M+H]^+$), m/z = 328.1366, found 328.1365. **HPLC** (OD-3, hexane:^{i}PrOH 85:15, flow rate 1.0 ml/min, 25 °C) t_R = 6.305 min (minor), 6.788 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −155.1 (*c* 1.0, $CHCl_3$).

1-((4-Nitrophenyl)sulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149$^{p\text{-}NO_2}$)*



Following General procedure H: 4-Nitro-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (100 mg, 301 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (21.1 mg, 30.0 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (8.64 mg, 30.0 µmol, 0.10 eq.) and TAPT (7.32 mg, 15.0 µmol, 0.05 eq.) in 3 mL MeCN for 3.5 h. Eluting with PE/EtOAc 9:1. NMR yield: 84.0 mg (254 µmol, 85%), isolated yield: 69.0 mg (209 µmol, 69%, brownish solid, 85:15 *er*). **TLC** R_f = 0.35 (4:1 PE/EtOAc). **m.p.** 180 °C. **IR** [cm^{-1}] 3105, 3034, 2870, 1715, 1607, 1528, 1495, 1170, 1111, 1074, 1014, 857, 738, 693. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.18 – 8.01 (m, 2H), 7.59 – 7.50 (m, 2H), 7.30 – 7.17 (m, 3H), 7.15 – 7.08 (m, 2H), 5.91 (dq, *J* = 6.1, 2.0 Hz, 1H), 5.73 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.63 (dq, *J* = 6.3, 2.2 Hz, 1H), 4.51 (dq, *J* = 14.1, 2.2 Hz, 1H), 4.25 (ddt, *J* = 14.1, 5.8, 2.1 Hz, 1H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 149.5, 145.2, 138.9, 130.4, 128.6, 128.4, 127.9, 127.8, 124.5, 123.8, 70.4, 55.3. **HRMS** (ESI) calcd. for $[C_{16}H_{15}N_2O_4S]^+$ ([M+H]$^+$), m/z = 331.0747, found 331.0745. **HPLC** (OD-3, hexane:^{i}PrOH 85:15, flow rate 1.0 ml/min, 25 °C) t_R = 17.408 min (major), 22.022 min (minor). **Optical rotation** $[\alpha]_D^{20}$ = −17.5 (*c* 1.0, $CHCl_3$).

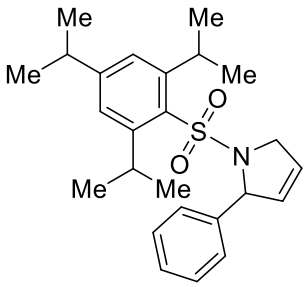
1-((2,4-Dimethoxyphenyl)sulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149$^{o,p\text{-}OMe}$)*



Following General procedure H: 2,4-Dimethoxy-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (174 mg, 501 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.2 mg, 50.0 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.4 mg, 50.0 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 5 h. Eluting with PE/EtOAc 9:1. NMR yield: 53.0 mg (153 µmol, 31%), isolated yield: 36.0 mg (104 µmol, 21%, brown oil, 93:7 *er*). **TLC** R_f = 0.13 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3355, 2922, 2855, 1659, 1595, 1469, 1416, 1334, 1260, 1215, 1159, 1081, 1025, 831, 760, 71. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.73 – 7.61 (m, 1H), 7.25 – 7.11 (m, 5H), 6.36 (d, *J* = 7.5 Hz, 2H), 5.85 (dq, *J* = 6.2, 2.0 Hz, 1H), 5.70 (dq, *J* = 6.4, 2.3 Hz, 1H), 5.60 (dq, *J* = 4.6, 2.1 Hz, 1H), 4.54 – 4.26 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 164.5,

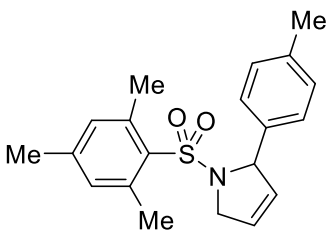
158.1, 140.6, 133.5, 130.6, 128.2, 127.5, 127.1, 124.8, 119.9, 103.9, 99.2, 69.9, 55.9, 55.7. **HRMS** (ESI) calcd. for $[C_{18}H_{20}NO_4S]^+$ ([M+H]$^+$), m/z = 346.1108, found 346.1107. **HPLC** (IC-3, hexane:^{i}PrOH 60:40, flow rate 0.9 ml/min, 25 °C) t_R = 46.901 min (major), 54.451 min (minor). **Optical rotation** $[\alpha]_D^{20}$ = −160.1 (*c* 1.0, $CHCl_3$).

2-Phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-2,5-dihydro-1*H*-pyrrole (149^{TIPP})*



Following General procedure H: 2,4,6-Triisopropyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (204 mg, 493 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (34.7 mg, 49.3 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.2 mg, 49.3 µmol, 0.10 eq.) and TAPT (12.0 mg, 24.7 µmol, 0.05 eq.) in 5 mL MeCN for 5 h. Eluting with PE/EtOAc 9:1. NMR yield: 43.0 mg (104 µmol, 21%), isolated yield: 39.0 mg (95.0 µmol, 19%, yellow oil, 91.5:8.5 *er*). **TLC** R_f = 0.68 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3064, 3034, 2960, 2870, 1603, 1562, 1495, 1461, 1424, 1316, 1260, 1197, 1156, 1107, 962, 883, 757, 697. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.24 – 7.09 (m, 5H), 7.04 (s, 2H), 5.92 (dt, *J* = 5.9, 2.0 Hz, 1H), 5.74 (ddt, *J* = 8.3, 4.7, 2.2 Hz, 2H), 4.49 (dq, *J* = 13.8, 2.0 Hz, 1H), 4.13 – 3.96 (m, 3H), 2.84 (hept, *J* = 7.0 Hz, 1H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.13 (d, *J* = 6.7 Hz, 6H), 1.08 (d, *J* = 6.7 Hz, 6H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 153.1, 151.4, 140.3, 131.5, 130.7, 128.2, 127.7, 127.7, 124.9, 123.6, 69.2, 54.7, 34.2, 29.2, 25.0, 24.6, 23.6, 23.6. **HRMS** (ESI) calcd. for $[C_{25}H_{34}NO_2S]^+$ ([M+H]$^+$), m/z = 412.2305, found 412.2307. **HPLC** (OD-3, hexane:^{i}PrOH 95:5, flow rate 1.0 ml/min, 25 °C) t_R = 8.007 min (major), 8.936 min (minor). **Optical rotation** $[\alpha]_D^{20}$ = −93.5 (*c* 1.0, $CHCl_3$).

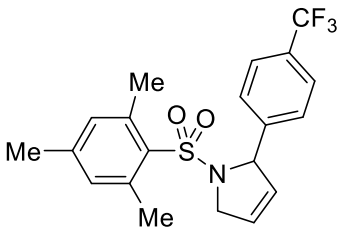
1-(Mesitylsulfonyl)-2-(p-tolyl)-2,5-dihydro-1*H*-pyrrole (149x)*



Following General procedure H: 2,4,6-Trimethyl-*N*-(4-(*p*-tolyl)but-3-en-1-yl)benzenesulfonamide (172 mg, 501 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.2 mg, 50.0 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)-

disulfane (14.4 mg, 50.0 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 3 h. Eluting with PE/EtOAc 9:1. NMR yield: 51.0 mg (149 µmol, 30%), isolated yield: 36.0 mg (105 µmol, 21%, yellow oil, 94:6 *er*). **TLC** R_f = 0.60 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3027, 2922, 2863, 1715, 1603, 1569, 1513, 1454, 1416, 1383, 1320, 1185, 1156, 1092, 1062, 1036, 984, 850, 813, 779, 723, 675. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 6.88 (s, 4H), 6.68 (q, *J* = 0.7 Hz, 2H), 5.89 (dq, *J* = 6.2, 2.0 Hz, 1H), 5.66 (dq, *J* = 6.3, 2.2 Hz, 1H), 5.46 (ddt, *J* = 5.2, 3.1, 2.1 Hz, 1H), 4.54 (ddt, *J* = 14.3, 3.0, 2.2 Hz, 1H), 4.16 (ddt, *J* = 14.3, 5.8, 2.0 Hz, 1H), 2.46 (s, 6H), 2.23 (s, 3H), 2.17 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.3, 140.1, 137.2, 136.8, 132.8, 131.5, 130.8, 128.5, 127.0, 124.4, 69.3, 54.7, 22.7, 21.0, 20.8. **HRMS** (ESI) calcd. for $[C_{20}H_{24}NO_2S]^+$ ($[M+H]^+$), m/z = 342.1522, found 342.1520. **HPLC** (OD-3, hexane:^{i}PrOH 90:10, flow rate 1.0 ml/min, 25 °C) t_R = 6.677 min (minor), 7.455 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −149.4 (*c* 1.0, $CHCl_3$).

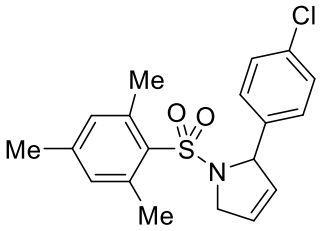
1-(Mesitylsulfonyl)-2-(4-(trifluoromethyl)phenyl)-2,5-dihydro-1*H*-pyrrole (149y)*



Following General procedure H: 2,4,6-Trimethyl-*N*-(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)benzenesulfonamide (200 mg, 503 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.4 mg, 50.3 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.5 mg, 50.3 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.2 µmol, 0.05 eq.) in 5 mL MeCN for 6 h. Eluting with PE/EtOAc 9:1. NMR yield: 102 mg (258 µmol, 51%), isolated yield: 90.0 mg (228 µmol, 45%, yellow solid, 93.5:6.5 *er*). **TLC** R_f = 0.50 (4:1 PE/EtOAc). **m.p.** 98 °C. **IR** [cm^{-1}] 2937, 2870, 1733, 1607, 1457, 1420, 1382, 1327, 1159, 1126, 1066, 1021, 988, 850, 701, 678. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 2H), 5.96 (dq, *J* = 6.3, 2.1 Hz, 1H), 5.65 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.51 (tt, *J* = 5.5, 2.4 Hz, 1H), 4.63 (ddt, *J* = 14.4, 3.3, 2.3 Hz, 1H), 4.24 (ddt, *J* = 14.5, 5.9, 2.1 Hz, 1H), 2.46 (s, 6H), 2.13 (s, 3H).**^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.7, 143.7, 142.9, 140.0, 132.6, 131.6, 129.9, 129.5, 127.3, 125.4, 124.8, 124.8, 124.7, 124.7, 69.0, 55.1, 22.7, 20.6. **^{19}F-NMR** (376 MHz, Chloroform-*d*): δ (ppm) = -63.1. **HRMS** (ESI) calcd. for $[C_{20}H_{21}F_3NO_2S]^+$ ($[M+H]^+$), m/z = 396.1240, found 396.1241.

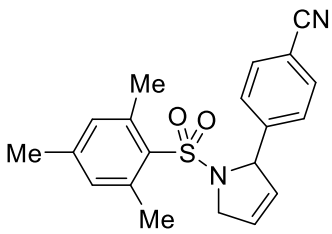
HPLC (OD-3, hexane:^{i}PrOH 90:10, flow rate 1.0 ml/min, 25 °C) t_R = 6.893 min (minor), 8.905 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −7.5 (*c* 1.0, $CHCl_3$).

2-(4-Chlorophenyl)-1-(mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrole (149z)*



Following General procedure H: *N*-(4-(4-Chlorophenyl)but-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (182 mg, 500 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.2 mg, 50.0 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.4 mg, 50.0 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 18 h. Eluting with PE/EtOAc 9:1. NMR yield: 90.0 mg (249 µmol, 50%), isolated yield: 80.0 mg (221 µmol, 44%, yellow oil, 94.5:5.5 *er*). **TLC** R_f = 0.53 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3030, 2926, 2862, 1737, 1603, 1491, 1409, 1379, 1320, 1185, 1156, 1088, 1062, 1014, 988, 820, 790, 719, 667. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.06 – 6.93 (m, 2H), 6.93 – 6.81 (m, 2H), 6.71 – 6.58 (m, 2H), 5.89 (dq, *J* = 6.2, 2.0 Hz, 1H), 5.59 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.41 (dt, *J* = 5.5, 2.7 Hz, 1H), 4.52 (ddt, *J* = 14.4, 3.3, 2.2 Hz, 1H), 4.12 (ddt, *J* = 14.4, 5.8, 2.1 Hz, 1H), 2.42 (d, *J* = 0.6 Hz, 6H), 2.16 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.8, 140.0, 138.3, 133.3, 132.6, 131.6, 130.2, 128.4, 128.0, 125.1, 68.8, 54.8, 22.7, 20.8. **HRMS** (ESI) calcd. for $[C_{19}H_{21}ClNO_2S]^+$ ($[M+H]^+$), m/z = 362.0976, found 362.0979. **HPLC** (OD-3, hexane:^{i}PrOH 90:10, flow rate 1.0 ml/min, 25 °C) t_R = 7.334 min (minor), 9.072 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −97.1 (*c* 0.34, $CHCl_3$).

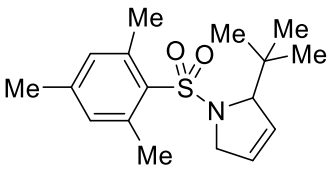
4-(1-(Mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrol-2-yl)benzonitrile (149aa)*



Following General procedure H: *N*-(4-(4-Cyanophenyl)but-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (177 mg, 499 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.1 mg, 50.0 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.3 mg, 50.0 µmol, 0.10 eq.) and TAPT (12.1 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 10 h. Eluting with PE/EtOAc 9:1. NMR yield: 103 mg (292 µmol, 59%), isolated yield: 85.0 mg (241 µmol, 48%, yellowish solid, 92:8

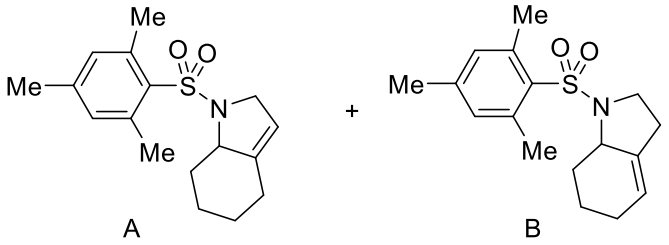
er). **TLC** R_f = 0.30 (4:1 PE/EtOAc). **m.p.** 101 °C. **IR** [cm^{-1}] 2926, 2866, 2229, 1607, 1566, 1506, 1457, 1413, 1320, 1260, 1189, 1156, 1096, 1062, 1033, 988, 850, 760, 719, 671. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.44 – 7.34 (m, 2H), 7.18 – 7.05 (m, 2H), 6.70 (dd, *J* = 1.3, 0.7 Hz, 2H), 5.98 (dq, *J* = 6.2, 2.0 Hz, 1H), 5.64 (dq, *J* = 6.4, 2.2 Hz, 1H), 5.54 (dq, *J* = 5.4, 2.4 Hz, 1H), 4.58 (ddt, *J* = 14.4, 3.2, 2.2 Hz, 1H), 4.19 (ddt, *J* = 14.5, 5.9, 2.0 Hz, 1H), 2.46 (d, *J* = 0.6 Hz, 6H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 143.0, 140.1, 132.4, 131.8, 131.6, 129.5, 127.7, 125.9, 118.5, 111.2, 69.0, 55.1, 22.7, 20.8. **HRMS** (ESI) calcd. for $[C_{20}H_{21}N_2O_2S]^+$ ($[M+H]^+$), m/z = 353.1318, found 353.1317. **HPLC** (OD-3, hexane:^{i}PrOH 90:10, flow rate 1.0 ml/min, 25 °C) t_R = 14.552 min (minor), 19.598 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −126.1 (*c* 1.0, $CHCl_3$).

2-(*Tert*-butyl)-1-(mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrole (149ae)*



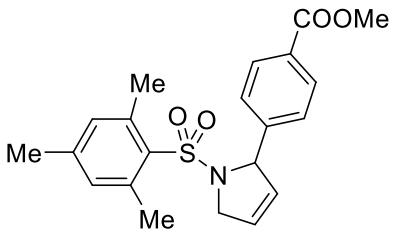
Following General procedure H: *N*-(5,5-dimethylhex-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (155 mg, 501 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.2 mg, 50.1 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.4 mg, 50.1 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 60 h. Eluting with PE/EtOAc 20:1. NMR yield: 65.0 mg (211 µmol, 42%), isolated yield: 31.0 mg (100 µmol, 20%, colorless liquid, 62.5:37.5 *er*). **TLC** R_f = 0.70 (4:1 PE/EtOAc). **IR** [cm^{-1}]. 2930, 2855, 1737, 1674, 1607, 1461, 1364, 1327, 1215, 1156, 1070, 1018, 947, 902, 854, 783, 667. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 6.94 (d, *J* = 1.1 Hz, 2H), 5.87 (s, 2H), 4.61 – 4.47 (m, 1H), 4.30 – 4.15 (m, 1H), 3.81 – 3.61 (m, 1H), 2.66 (s, 6H), 2.29 (s, 3H), 0.82 (s, 9H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.5, 140.5, 133.0, 132.0, 129.3, 127.1, 75.9, 55.5, 36.9, 26.4, 23.1, 21.0. **HRMS** (ESI) calcd. for $[C_{17}H_{26}NO_2S]^+$ ($[M+H]^+$), m/z = 308.1679, found 308.1676. **HPLC** (OD-3, hexane:^{i}PrOH 99:1, flow rate 1.0 ml/min, 25 °C) t_R = 10.028 min (minor), 11.962 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −17.1 (*c* 1.0, $CHCl_3$).

1-(Mesitylsulfonyl)-2,4,5,6,7,7a-hexahydro-1*H*-indole (A) and 1-(Mesitylsulfonyl)-2,3,5,6,7,7a-hexahydro-1*H*-indole (B) (149ac and 149ac')*



Following General procedure H: *N*-(2-(Cyclohex-1-en-1-yl)ethyl)-2,4,6-trimethylbenzenesulfonamide (155 mg, 504 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.4 mg, 50.4 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.5 mg, 50.4 µmol, 0.10 eq.) and TAPT (12.3 mg, 25.2 µmol, 0.05 eq.) in 5 mL MeCN for 3 h. Eluting with PE/EtOAc 20:1. NMR yield: 109 mg (357 µmol, 71%), isolated yield: 102 mg (357 µmol, 66%, brownish solid, 91:9 *er*). **TLC** R_f = 0.65 (4:1 PE/EtOAc). **m.p.** 89 °C. **IR** [cm^{-1}] 2937, 2859, 2363, 1603, 1566, 1446, 1405, 1316, 1189, 1156, 1100, 1062, 1029, 854, 798, 678. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 6.94 (s, 2H, A+B), 5.53 (d, *J* = 4.0 Hz, 1H, B), 5.23 (q, *J* = 2.0 Hz, 1H, A), 4.30 (q, *J* = 4.5 Hz, 1H, A), 4.19 (dtd, *J* = 13.0, 3.2, 1.8 Hz, 1H, A), 4.01 (s, 1H, B), 3.87 – 3.73 (m, 1H, A), 3.56 (ddd, *J* = 10.2, 9.4, 3.1 Hz, 1H, B), 3.03 (ddd, *J* = 10.2, 9.2, 7.1 Hz, 1H, B), 2.65 (d, *J* = 1.5 Hz, 6H, A+B), 2.47 (ddt, *J* = 13.7, 4.3, 2.0 Hz, 1H, A+B), 2.29 (s, 3H, A+B), 2.04 – 1.88 (m, 2H, A+B), 1.83 – 1.62 (m, 2H, A+B), 1.39 – 1.01 (m, 3H, A+B). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.5, 142.4, 141.9, 140.2, 140.1, 138.3, 133.3, 131.9, 131.8, 129.8, 129.0, 120.7, 114.1, 92.9, 77.3, 65.3, 57.7, 55.3, 53.8, 46.2, 35.1, 30.3, 28.8, 28.4, 26.5, 24.3, 23.9, 22.9, 22.8, 21.0, 20.4. **HRMS** (ESI) calcd. for $[C_{17}H_{24}NO_2S]^+$ ($[M+H]^+$), m/z = 306.1522, found 306.1529. **HPLC** (IC-3, hexane:^{i}PrOH 95:5, flow rate 1.0 ml/min, 25 °C) t_R = 43.360 min (major), 45.469 min (minor). **Optical rotation** $[\alpha]_D^{20}$ = +61.5 (*c* 1.0, $CHCl_3$).

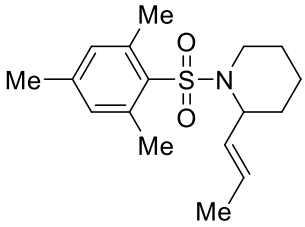
Methyl 4-(1-(mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrol-2-yl)benzoate (149ab)*



Following General procedure H: Methyl-4-(4-((2,4,6-trimethylphenyl)sulfonamido)but-1-en-1-yl)benzoate (194 mg, 501 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.2 mg,

50.1 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.4 mg, 50.1 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 5 h. Eluting with PE/EtOAc 9:1. NMR yield: 119 mg (309 µmol, 62%), isolated yield: 98.0 mg (254 µmol, 50%, colorless oil, 94:6 *er*). **TLC** R_f = 0.4 (PE:EtOAc, 4:1). **IR** [cm^{-1}] 2930, 2863, 1722, 1607, 1439, 1316, 1279, 1189, 1156, 1111, 1062, 1021, 969, 854, 816, 772, 701, 678. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 7.82 – 7.67 (m, 2H), 7.11 – 6.98 (m, 2H), 6.66 (s, 2H), 5.95 (dq, *J* = 6.2, 2.0 Hz, 1H), 5.66 (dq, *J* = 6.3, 2.2 Hz, 1H), 5.59 – 5.46 (m,, 1H), 4.60 (ddt, *J* = 14.4, 3.1, 2.2 Hz, 1H), 4.20 (ddt, *J* = 14.4, 5.8, 2.1 Hz, 1H), 3.89 (s, 3H), 2.46 (s, 6H), 2.13 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = δ 166.8, 144.9, 142.8, 140.1, 132.5, 131.6, 130.0, 129.3, 129.2, 127.0, 125.3, 69.1, 55.0, 52.1, 22.7, 20.7. **HRMS** (ESI) calcd. for $[C_{21}H_{24}NO_4S]^+$ ($[M+H]^+$), m/z = 186.1421, found 186.1421. **HPLC** (IC-3, hexane:^{i}PrOH 80:20, flow rate 1.0 ml/min, 25 °C) t_R = 33.958 min (minor), 35.147 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −226.2 (*c* 1.0, $CHCl_3$).

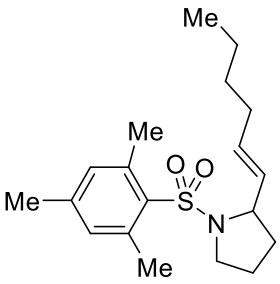
1-(Mesitylsulfonyl)-2-(prop-1-en-1-yl)piperidine (150f)*



Following General procedure H: 2,4,6-Trimethyl-*N*-(oct-5-en-1-yl)benzenesulfonamide (160 mg, 517 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (36.3 mg, 51.7 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.9 mg, 51.7 µmol, 0.10 eq.) and TAPT (12.6 mg, 25.9 µmol, 0.05 eq.) in 5 mL MeCN for 15 h. Eluting with PE/EtOAc 20:1. NMR yield: 22.0 mg (71.6 µmol, 14%), isolated yield: 19.0 mg (62.0 µmol, 12%, colorless oil, 78:22 *er*) as a mixture of isomers (*E*:*Z* = 1:7.3).. **TLC** R_f = 0.73 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3027, 2933, 2859, 1730, 1603, 1532, 1454, 1405, 1320, 1208, 1152, 1115, 1066, 1010, 969, 854, 820, 727, 667. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 6.97 – 6.87 (m, 2H), 5.93 – 5.23 (m, 2H), 4.42 (s, 1H), 3.44 – 3.19 (m, 1H), 3.09 (ddd, *J* = 12.9, 11.8, 2.7 Hz, 1H), 2.60 (s, 6H), 2.29 (s, 3H), 1.81 – 1.71 (m, 1H), 1.67 – 1.64 (m, 2H), 1.60 – 1.52 (m, 5H), 1.48 – 1.36 (m, 1H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 141.9, 140.1, 133.5, 131.8, 128.4, 128.2, 53.7, 40.9, 29.7, 25.3, 22.8, 20.9, 19.5, 18.0. **HRMS** (ESI) calcd. for $[C_{17}H_{26}NO_2S]^+$ ($[M+H]^+$), m/z = 308.1679, found 308.1682. **HPLC** (IC-3, hexane:^{i}PrOH

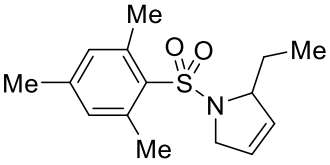
95:5, flow rate 1.0 ml/min, 25 °C) t_R = 22.334 min (major), 25.657 min (minor). **Optical rotation** $[\alpha]_D^{20}$ = +4.5 (*c* 0.73, $CHCl_3$).

(*E*)-2-(Hex-1-en-1-yl)-1-(mesitylsulfonyl)pyrrolidine (140f)*



Following General procedure H: *N*-(dec-4-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (160 mg, 474 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (33.3 mg, 47.4 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (13.6 mg, 47.4 µmol, 0.10 eq.) and TAPT (11.5 mg, 23.7 µmol, 0.05 eq.) in 5 mL MeCN for 16 h. Eluting with PE/EtOAc 20:1. NMR yield: 39.0 mg (116 µmol, 25%), isolated yield: 36.0 mg (107 µmol, 23%, colorless oil, 69.5:30.5 *er*) as the (*E*)-isomer exclusively. **TLC** R_f = 0.68 (4:1 PE/EtOAc). **IR** [cm^{-1}] 2930, 2874, 1603, 1586, 1457, 1409, 1316, 1189, 1152, 1059, 969, 917, 854, 787, 753, 675. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 6.88 (d, *J* = 1.1 Hz, 2H), 5.29 (dtd, *J* = 15.3, 6.6, 0.9 Hz, 1H), 4.97 (ddt, *J* = 15.2, 8.1, 1.5 Hz, 1H), 4.16 (td, *J* = 7.9, 5.2 Hz, 1H), 3.59 (dt, *J* = 9.9, 7.1 Hz, 1H), 3.30 (dt, *J* = 9.9, 6.4 Hz, 1H), 2.60 (s, 6H), 2.26 (s, 3H), 2.07 (dq, *J* = 12.2, 7.4 Hz, 1H), 1.92 – 1.83 (m, 2H), 1.66 (ddd, *J* = 12.8, 6.5, 1.4 Hz, 3H), 1.22 – 0.99 (m, 4H), 0.83 (t, *J* = 7.2 Hz, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 140.9, 139.0, 133.1, 130.8, 130.6, 128.2, 60.3, 46.5, 32.9, 30.5, 29.8, 23.1, 21.9, 21.2, 19.9, 12.9. **HRMS** (ESI) calcd. for $[C_{19}H_{30}NO_2S]^+$ ($[M+H]^+$), m/z = 336.1992, found 336.1999. **HPLC** (IC-3, hexane:^{i}PrOH 95:5, flow rate 1.0 ml/min, 25 °C) t_R = 29.725 min (major), 36.392 min (minor). **Optical rotation** $[\alpha]_D^{20}$ = +1.5 (*c* 0.17, $CHCl_3$).

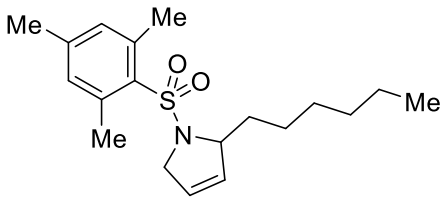
2-Ethyl-1-(mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrole (149ad)*



Following General procedure H: (*E*)-*N*-(Hex-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (141 mg, 501 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.2 mg, 50.1 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.4 mg, 50.1 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.1 µmol, 0.05 eq.) in 5 mL MeCN for 7 h. Eluting with PE/EtOAc 20:1. NMR yield: 76.0 mg (272 µmol, 54%), isolated yield: 70.0 mg

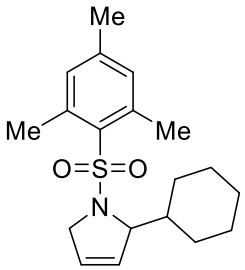
(250 µmol, 50%, white solid, 89.5:10.5 *er*). **TLC** R_f = 0.45 (9:1 PE/EtOAc). **m.p.** 62 °C. **IR** [cm^{-1}] 2967, 2930, 2874, 2356, 1603, 1457, 1320, 1156, 1096, 1062, 854, 671. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 6.94 (s, 2H), 5.75 (dq, *J* = 5.8, 1.9 Hz, 1H), 5.68 (dq, *J* = 6.3, 2.1 Hz, 1H), 4.68 (dddt, *J* = 7.5, 5.5, 3.9, 2.0 Hz, 1H), 4.25 (dq, *J* = 14.3, 2.2 Hz, 1H), 3.85 (ddt, *J* = 14.3, 5.6, 1.9 Hz, 1H), 2.65 (s, 6H), 2.29 (s, 3H), 1.56 (dddd, *J* = 12.0, 9.7, 7.0, 3.9 Hz, 1H), 1.42 (dt, *J* = 14.0, 7.2 Hz, 1H), 0.76 (t, *J* = 7.4 Hz, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 142.5, 140.2, 133.2, 131.9, 129.5, 125.0, 67.1, 54.9, 27.6, 22.8, 21.0, 8.6. **HRMS** (ESI) calcd. for $[C_{15}H_{22}NO_2S]^+$ ($[M+H]^+$), m/z = 280.1366, found 280.1369. **HPLC** (OD-3, hexane:^{i}PrOH 95:5, flow rate 1.0 ml/min, 25 °C) t_R = 6.658 min (minor), 7.020 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −188.8 (*c* 1.0, $CHCl_3$).

2-Hexyl-1-(mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrole (149af)*



Following General procedure H: (*E*)-*N*-(Dec-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (169 mg, 501 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzyl-selane) (35.2 mg, 50.1 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.4 mg, 50.1 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 10 h. Eluting with PE/EtOAc 99:1. NMR yield: 69.0 mg (206 µmol, 41%), isolated yield: 67.0 mg (200 µmol, 40%, colorless oil, 91:9 *er*). **TLC** R_f = 0.24 (9:1 PE/EtOAc). **IR** [cm^{-1}] 2926, 2855, 2356, 1737, 1603, 1454, 1316, 1156, 1092, 1059, 854, 671. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 6.94 (s, 2H), 5.71 (dtd, *J* = 8.3, 6.3, 1.8 Hz, 2H), 4.68 (dtq, *J* = 7.6, 3.9, 2.1 Hz, 1H), 4.29 (dq, *J* = 14.5, 2.1 Hz, 1H), 3.87 (ddt, *J* = 14.5, 5.7, 1.8 Hz, 1H), 2.65 (s, 6H), 2.29 (s, 3H), 1.55 – 1.41 (m, 1H), 1.39 – 1.02 (m, 9H), 0.85 (t, *J* = 7.2 Hz, 3H).**^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 142.5, 140.2, 133.4, 131.9, 130.0, 124.7, 66.2, 54.7, 34.7, 31.7, 29.1, 24.4, 22.9, 22.5, 21.0, 14.1. **HRMS** (ESI) calcd. for $[C_{19}H_{30}NO_2S]^+$ ($[M+H]^+$), m/z = 336.1992, found 336.1992. **HPLC** (OD-3, hexane:^{i}PrOH 98:2, flow rate 1.0 ml/min, 25 °C) t_R = 7.447 min (minor), 8.394 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −122.8 (*c* 1.0, $CHCl_3$).

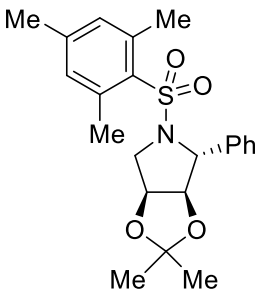
2-Cyclohexyl-1-(mesitylsulfonyl)-2,5-dihydro-1H-pyrrole (149ag)*



Following General procedure H: (*E*)-*N*-(4-Cyclohexylbut-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (168 mg, 501 µmol, 1.00 eq.), (6,6'-dimethoxy-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(benzylselane) (35.2 mg, 50.0 µmol, 0.10 eq.), 1,2-bis(4-chlorophenyl)disulfane (14.4 mg, 50.0 µmol, 0.10 eq.) and TAPT (12.2 mg, 25.0 µmol, 0.05 eq.) in 5 mL MeCN for 12 h. Eluting with PE/EtOAc 99:1. NMR yield: 69.0 mg (207 µmol, 41%), isolated yield: 64.0 mg (191 µmol, 38%, yellowish oil, 88.5:11.5 *er*). **TLC** R_f = 0.47 (9:1 PE/EtOAc). **IR** [cm^{-1}] 2922, 2851, 1603, 1586, 1450, 1405, 1316, 1271, 1185, 1156, 1092, 1059, 1021, 977, 943, 850, 775, 731, 671. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 6.95 (s, 2H), 5.81 – 5.61 (m, 2H), 4.60 (ddq, *J* = 5.8, 4.0, 2.1 Hz, 1H), 4.21 (dq, *J* = 14.4, 2.2 Hz, 1H), 3.80 (ddt, *J* = 14.1, 5.3, 1.9 Hz, 1H), 2.64 (s, 6H), 2.30 (s, 3H), 1.74 – 1.37 (m, 6H), 1.17 – 0.70 (m, 5H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 266.3, 266.1, 142.6, 140.3, 133.3, 131.9, 127.5, 125.5, 71.2, 55.0, 42.3, 30.0, 26.9, 26.6, 26.5, 25.9, 22.8, 21.0. **HRMS** (ESI) calcd. for $[C_{19}H_{28}NO_2S]^+$ ($[M+H]^+$), m/z = 334.1835, found 334.1838. **HPLC** (OD-3, hexane:^{i}PrOH 99:1, flow rate 1.0 ml/min, 25 °C) t_R = 10.577 min (minor), 17.214 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −57.8 (*c* 1.0, $CHCl_3$).

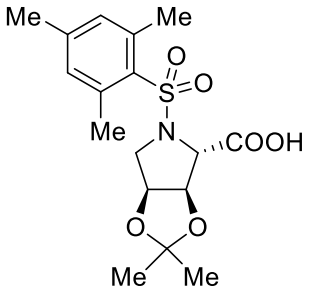
6.8.6 Synthesis of dihydroxyproline analogues

(3a*R*,4*R*,6a*S*)-5-(Mesitylsulfonyl)-2,2-dimethyl-4-phenyltetrahydro-4H-[1,3]dioxolo[4,5-c]pyrrole (260)[148]



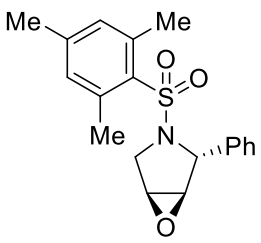
To a solution of 1-(Mesitylsulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (657 mg, 2.01 mmol, 1.0 eq.) in ^{t}BuOH (14.8 mL) and H_2O (14.8 mL), potassium hexacyanoferrate (1.98 g, 6.02 mmol, 3.0 eq.) and K_2CO_3 (832 mg, 6.02 mmol, 3.0 eq.) were added. The mixture was stirred for 15 min at r.t. and a solution of OsO_4 (3.00 mL, 2.5 wt% in ^{t}BuOH) was added slowly. After 24 h of stirring, DEE was added, and the crude product was extracted 3x in DEE. The combined organic layers were washed with brine. The solvent was evaporated under reduced pressure to give the diol as an intermediate, which was used without further purification. The crude diol was dissolved in acetone (28 mL), then 2,2-dimethoxypropane (1.04 g, 10.0 mmol, 5.0 eq.) and *p*-TsOH×H_2O (38.2 mg, 0.20 mmol, 0.1 eq.) were added. After stirring overnight, the solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography (PE/EtOAc = 9:1) to provide the target compound as a yellowish oil (449 mg, 1.12 mmol, 56%, 91.5:8.5 *er*). **TLC** R_f = 0.41 (PE:EtOAc, 9:1). **IR** [cm^{-1}] 3030, 2982, 2937, 2874, 1603, 1454, 1379, 1326, 1275, 1241, 1211, 1156, 1107, 1055, 973, 857, 753, 701, 675. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 7.37 – 7.18 (m, 5H), 6.91 (s, 2H), 5.22 (s, 1H), 4.86 (td, *J* = 5.5, 1.5 Hz, 1H), 4.74 (dd, *J* = 5.9, 1.1 Hz, 1H), 3.80 (dd, *J* = 11.8, 5.1 Hz, 1H), 3.70 (dd, *J* = 11.8, 1.6 Hz, 1H), 2.64 (s, 6H), 2.30 (s, 3H), 1.48 (s, 3H), 1.32 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 142.3, 139.9, 138.3, 133.6, 131.8, 128.6, 127.6, 126.5, 112.3, 87.7, 79.2, 69.4, 53.3, 26.3, 24.7, 23.3, 20.9. **HRMS** (ESI) calcd. for $[C_{22}H_{28}NO_4S]^+$ ($[M+H]^+$), m/z = 402.1734, found 402.1739. **HPLC** (IC-3, hexane:^{i}PrOH 97:3, flow rate 1.0 ml/min, 25 °C) t_R = 85.932 min (minor), 94.331 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −14.8 (*c* 1.0, $CHCl_3$).

(3a*R*,4*S*,6a*S*)-5-(Mesitylsulfonyl)-2,2-dimethyltetrahydro-4H-[1,3]dioxolo[4,5-c]pyrrole-4-carboxylic acid (261)[148]



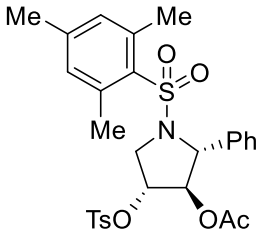
To a solution of (3a*R*,4*R*,6a*S*)-5-(mesitylsulfonyl)-2,2-dimethyl-4-phenyltetrahydro-4*H*-[1,3]diox-olo[4,5-*c*]pyrrole (120 mg, 299 µmol, 1.00 eq.) in a 1:1:2 mixture of CCl_4/MeCN/H_2O (1.9 mL/ 1.9 mL/ 3.9 mL) was added sodium bicarbonate (419 mg, 4.99 mmol, 16.7 eq.) and the mixture was stirred until both phases were clear. Sodium periodate (1.25 g, 5.86 mmol, 19.6 eq.) was added at r.t. and the mixture stirred for further 15 min. Ruthenium trichloride hydrate (6.74 mg, 30.0 µmol, 0.10 eq.) was added and the mixture vigorously stirred at 30 °C for 3 d. Then, DEE (50 mL) and a watery K_2CO_3 solution (1.0 M, 50 mL) were added, and the crude product was extracted in the basic watery phase. The collected watery phase was acidified by a watery HCl solution (1.0 M, 100 mL) and the compound was extracted in DEE (3x 50 mL). The organic phases were collected, and the solvent was evaporated under reduced pressure. Again, DEE (50 mL) and water (50 mL) were added, and the compound was extracted in the organic phase. The solvent was evaporated under reduced pressure to provide the product as a yellowish oil (54.0 mg, 146 µmol, 48%, 92.5:7.5 *er*). **TLC** R_f = 0.60 (DCM:MeOH, 9:1). **IR** [cm^{-1}] 2982, 2937, 2356, 1730, 1603, 1457, 1379, 1331, 1275, 1241, 1211, 1159, 1111, 1055, 872, 675. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 6.94 (s, 2H), 4.86 (d, *J* = 5.9 Hz, 1H), 4.81 (t, *J* = 5.2 Hz, 1H), 4.46 (s, 1H), 3.79 (dd, *J* = 11.5, 4.6 Hz, 1H), 3.60 (d, *J* = 11.4 Hz, 1H), 2.64 (s, 6H), 2.29 (s, 3H), 1.37 (s, 3H), 1.27 (s, 3H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 173.4, 142.8, 140.3, 132.7, 132.0, 112.5, 83.1, 79.2, 66.4, 53.0, 25.9, 24.3, 23.1, 21.0. **HRMS** (ESI) calcd. for $[C_{17}H_{24}NO_6S]^+$ ($[M+H]^+$), m/z = 370.1319, found 370.1324. **HPLC** (IC-3, hexane:^{i}PrOH 90:10 +0.1% TFA, flow rate 1.0 ml/min, 25 °C) t_R = 36.001 min (minor), 43.779 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −16.5 (*c* 0.1, $CHCl_3$).

(1*R*,2*R*,5*S*)-3-(Mesitylsulfonyl)-2-phenyl-6-oxa-3-azabicyclo[3.1.0]hexane (262)



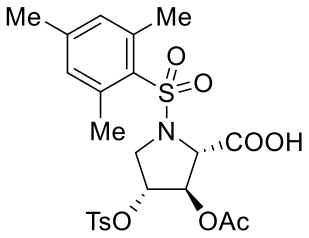
To a solution of (*S*)-1-(mesitylsulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (1.10 g, 3.36 mmol, 1.00 eq.) in a mixture of 20 mL acetone and 13.4 mL distilled H_2O was added 4-methylmorphilone-*N*-oxide (866 mg, 7.39 mmol, 2.20 eq.) and potassium osmate dihydrate (61.9 mg, 168 µmol, 0.05 eq.). The reaction was stirred overnight, then quenched with 100 mL distilled H_2O and extracted in DEE. After evaporation of the solvent the crude product was dissolved in 80 mL CCl_4 and PPh_3 (3.48 g, 13.3 mmol, 4.00 eq.) were added. The reaction was refluxed at 80 °C for 3 h, quenched with 200 mL distilled H_2O and extracted in DCM (3x 100 mL). After evaporation of the solvent, 30 mL toluene were added, and the dark blue precipitate was filtered off. To the remaining solution KO*t*Bu (372 mg, 3.32 mmol, 1.00 eq.) was added, and the solution was stirred at r.t. for 1 h. The reaction was quenched with 100 mL distilled H_2O and extracted in DEE (3x 50 mL). The solvent was removed under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 8:2 (+1% NEt_3). Isolated yield: 759 mg (2.21 mmol, 67% (over three steps), colorless oil, >20:1 *dr*, 94.5:5.5 *er*). **TLC** R_f = 0.40 (8:2 PE/EtOAc). **IR** [cm^{-1}] 3034, 2922, 2870, 1603, 1495, 1454, 1402, 1323, 1215, 1156, 1088, 1033, 980, 913, 850, 820, 760, 701, 671. ^{1}H-NMR (300 MHz, Chloroform-*d*): δ (ppm) = 7.26 (td, *J* = 4.5, 3.8, 1.6 Hz, 3H), 7.14 (dt, *J* = 6.9, 2.3 Hz, 2H), 6.84 (s, 2H), 5.03 (s, 1H), 3.91 (d, *J* = 12.1 Hz, 1H), 3.78 (dd, *J* = 2.9, 1.1 Hz, 1H), 3.64 – 3.49 (m, 2H), 2.51 (s, 6H), 2.24 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 142.6, 140.2, 137.5, 132.9, 131.9, 128.7, 128.1, 126.7, 63.2, 59.6, 55.0, 48.2, 23.0, 20.9. **HRMS** (ESI) calcd. for $[C_{19}H_{22}NO_3S]^+$ ($[M+H]^+$), m/z = 344.1315, found 344.1318. **HPLC** (IA-3, hexane:*i*PrOH 95:5, flow rate 1.0 ml/min, 25 °C) t_R = 18.131 min (major), 20.355 min (minor). **Optical rotation** $[\alpha]_D^{20}$ = −16.1 (*c* 1.0, $CHCl_3$).

(2*R*,3*R*,4*R*)-1-(Mesitylsulfonyl)-2-phenyl-4-(tosyloxy)pyrrolidin-3-yl acetate (265)



To a solution of (1*R*,2*R*,5*S*)-3-(mesitylsulfonyl)-2-phenyl-6-oxa-3-azabicyclo[3.1.0]hexane (320 mg, 932 µmol, 1.00 eq.) in 100 mL DCM was added TsOH x H_2O (709 mg, 3.73 mmol, 4.00 eq.) and the solution was refluxed at 44 °C until full consumption of the starting material. Then, 100 mL distilled H_2O were added, and the reaction was extracted in DCM (3x 100 mL). After evaporation of the solvent the crude product was dissolved in 50 mL DCM, pyridine (368 mg, 375 µL, 4.65 mmol, 5.00 eq.), acetic anhydride (475 mg, 4.65 mmol, 5.00 eq.) and 4-dimethylaminopyridine (11.4 mg, 93.1 µmol, 0.10 eq.) were added. The solution was refluxed again at 44 °C for 1 h, quenched with 100 mL distilled H_2O and the crude product extracted in DCM (3x 50 mL). The solvent was removed under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 8:2. Isolated yield: 287 mg (515 µmol, 55% (over two steps), yellow oil, >20:1 *dr*, 95:5 *er*). **TLC** R_f = 0.33 (8:2 PE/EtOAc). **IR** [cm^{-1}] 3034, 2982, 2937, 1748, 1603, 1495, 1454, 1368, 1327, 1223, 1178, 1036, 977, 906, 835, 742. ^{1}H-NMR (300 MHz, Chloroform-*d*): δ (ppm) = 7.90 – 7.69 (m, 2H), 7.52 – 7.42 (m, 2H), 7.32 – 7.16 (m, 5H), 6.90 (s, 2H), 5.30 – 5.13 (m, 2H), 4.96 (d, *J* = 2.5 Hz, 1H), 4.26 (dd, *J* = 12.2, 4.9 Hz, 1H), 4.07 – 3.98 (m, 1H), 2.65 (s, 6H), 2.63 (s, 3H), 2.37 (s, 3H), 2.24 (s, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 169.2, 145.4, 142.8, 139.8, 136.2, 132.9, 132.6, 131.7, 130.0, 127.9, 127.7, 127.6, 127.0, 82.4, 80.2, 67.9, 52.5, 22.9, 21.7, 20.8, 20.7. **HRMS** (ESI) calcd. for $[C_{28}H_{32}NO_7S_2]^+$ ($[M+H]^+$), m/z = 558.1615, found 558.1621. **HPLC** (IA-3, hexane:^{i}PrOH 95:5, flow rate 1.0 ml/min, 25 °C) t_R = 38.569 min (minor), 45.607 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −3.6 (*c* 0.3, $CHCl_3$).

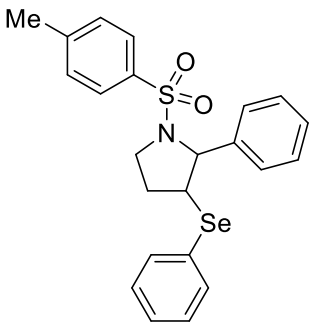
(2*S*,3*R*,4*R*)-3-Acetoxy-1-(mesitylsulfonyl)-4-(tosyloxy)pyrrolidine-2-carboxylic acid (266)[148]



To a solution of (2*R*,3*R*,4*R*)-1-(mesitylsulfonyl)-2-phenyl-4-(tosyloxy)pyrrolidin-3-yl acetate (160 mg, 286 µmol, 1.00 eq.) in a 1:1:2 mixture of CCl_4/MeCN/H_2O (2.2 mL/ 2.2 mL/ 4.5 mL) was added sodium bicarbonate (402 mg, 4.79 mmol, 16.7 eq.) and the mixture was stirred until both phases were clear. Sodium periodate (614 mg, 2.87 mmol, 10.0 eq.) was added at and the mixture stirred for further 15 min. Ruthenium trichloride hydrate (12.9 mg, 57.4 µmol, 0.20 eq.) was added and the mixture vigorously stirred at r.t. for 5 d. The reaction was quenched with 100 mL H_2O, acidified with 100 mL aq. HCl solution (1 M), and the crude product extracted in DCM (3x 50 mL). The solvent was removed under reduced pressure and the crude product was purified *via* column chromatography. Eluting with DCM/MeOH 95:5. Isolated yield: 63.0 mg (120 µmol, 42%, yellow oil, >20:1 *dr*, 95:5 *er*). **TLC** R_f = 0.41 (9:1 DCM/MeOH). **IR** [cm^{-1}] 3220, 2978, 2940, 1752, 1603, 1372, 1327, 1223, 1178, 1055, 977, 910, 734, 671. ^{1}H-NMR (400 MHz, Chloroform-*d*): δ (ppm) = 7.86 – 7.64 (m, 2H), 7.44 – 7.30 (m, 2H), 6.95 (s, 2H), 5.35 (t, *J* = 2.2 Hz, 1H), 5.01 (dt, *J* = 5.8, 3.1 Hz, 1H), 4.48 (d, *J* = 1.8 Hz, 1H), 3.87 (dd, *J* = 12.1, 5.6 Hz, 1H), 3.46 (dd, *J* = 12.0, 3.4 Hz, 1H), 2.60 (s, 6H), 2.46 (s, 3H), 2.30 (s, 3H), 2.08 (d, *J* = 12.2 Hz, 3H). **^{13}C-NMR** (151 MHz, Chloroform-*d*): δ (ppm) = 169.6, 169.5, 145.7, 143.8, 140.8, 132.7, 132.1, 131.0, 130.1, 127.9, 79.4, 78.4, 63.3, 51.4, 22.9, 21.7, 21.0, 20.6. **HRMS** (ESI) calcd. for $[C_{23}H_{28}NO_9S_2]^+$ ($[M+H]^+$), m/z = 526.1200, found 526.1205. **HPLC** (IA-3, hexane:^{i}PrOH 85:15 +0.1% TFA, flow rate 1.0 ml/min, 25 °C) t_R = 20.573 min (minor), 22.559 min (major). **Optical rotation** $[\alpha]_D^{20}$ = −16.2 (*c* 0.1, $CHCl_3$).

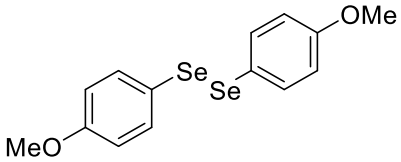
6.8.7 Synthesis of catalysts and reaction intermediates

2-Phenyl-3-(phenylselanyl)-1-tosylpyrrolidine (227)[95]



To a solution of 4-methyl-N-(4-phenylbut-3-en-1-yl)benzene-sulfonamide (3.00 g, 9.95 mmol, 1.00 eq.) and NEt_3 (1.39 mL, 9.95 mmol, 1.00 eq.) in dry DCM (50 mL) under a N_2 atmosphere was added PhSeBr (2.58 g, 11.0 mmol, 1.10 eq.). The resulting solution was stirred at ambient temperature overnight, then quenched with H_2O. The reaction mixture was washed with 1 M HCl solution, sat. aq. $NaHCO_3$ and brine and the aq. phase was extracted with DCM (50 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with DCM. Isolated yield: 2.40 g (5.26 mol, 53%, brown oil). **TLC** R_f = 0.41 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3064, 3030, 2955, 1599, 1476, 1599, 1439, 1346, 1260, 1211, 1156, 1096, 1047, 1006, 906, 813, 693, 667, 727. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.79 – 7.68 (m, 2H), 7.42 – 7.16 (m, 12H), 4.71 (d, *J* = 2.6 Hz, 1H), 3.79 (ddd, *J* = 9.4, 7.5, 3.2 Hz, 1H), 3.71 – 3.53 (m, 2H), 2.47 (s, 3H), 2.33 (dddd, *J* = 13.4, 9.5, 7.5, 5.9 Hz, 1H), 1.79 (ddt, *J* = 13.3, 6.6, 3.2 Hz, 1H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 266.8, 143.6, 142.0, 135.1, 135.0, 134.9, 134.5, 131.5, 129.6, 129.3, 129.3, 128.5, 128.3, 128.2, 127.8, 127.5, 126.1, 69.3, 49.7, 48.3, 30.2, 21.7. **^{77}Se-NMR** (76 MHz, Chloroform-*d*): δ (ppm) = 377.8. **HRMS** (ESI) calcd. for $[C_{23}H_{24}NO_2SSe]^+$ $(M+H)^+$, m/z = 458.0588, found 458.0694.

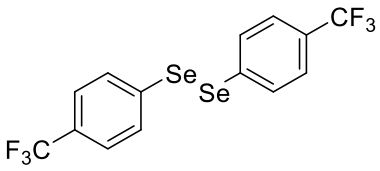
1,2-Bis(4-methoxyphenyl)diselane (13^{OMe})[110]



To a solution of 1-iodo-4-methoxybenzene (23.4 g, 100 mmol, 1.00 eq.) and selenium powder (23.7 g, 300 mmol, 3.00 eq.) in dry DMSO (300 mL) were added CuI (1.90 g, 10.0 mmol, 0.10 eq.) and K_3PO_4 (63.7 g, 300 mmol, 3.00 eq.). The resulting mixture was then heated under an N_2 atmosphere at 90 °C for 18 h. The reaction was cooled to r.t. and excess K_3PO_4 and selenium powder was removed by filtration. Then, 300 mL distilled H_2O were added, and the reaction was extracted in DEE (3x 200 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 99:1→9:1. Isolated yield: 8.15 g (21.9 mmol, 44%, orange

crystals). **TLC** R_f = 0.40 (9:1 PE/EtOAc). **m.p.** 51 °C. **IR** [cm^{-1}] 3060, 3001, 2937, 2900, 2833, 1584, 1487, 1461, 1402, 1286, 1245, 1170, 1103, 1070, 1029, 820. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.75 – 7.34 (m, 4H), 7.04 – 6.56 (m, 4H), 3.80 (s, 6H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 160.1, 135.5, 122.0, 114.8, 55.4. **^{77}Se-NMR** (76 MHz, Chloroform-*d*): δ (ppm) = 503.4. **HRMS** (ESI) calcd. for $[C_{14}H_{14}NaO_2Se_2]^+$ $(M+Na)^+$, m/z = 396.9191, found 396.9194.

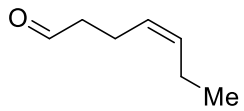
1,2-Bis(4-(trifluoromethyl)phenyl)diselane (13^{CF_3})[110]



Under N_2 atmosphere, magnesium (1.08 g, 44.4 mmol, 1.00 eq.) was added to a solution of 1-bromo-4-(trifluoromethyl)benzene (10.0 g, 44.4 mmol, 1.00 eq.) in 130 mL dry DEE. The reaction was brought to a gentle reflux and let stirring for another 30 min. Then, Selenium powder (7.02 g, 88.9 mmol, 2.00 eq.) were added slowly and the reaction was stirred for another 30 min. After cooling to r.t., the reaction was poured into a mixture of aq. HCl solution (1 M) and crushed ice. The crude product was extracted with DEE (3x 100 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 99:1→9:1. Isolated yield: 3.70 g (8.26 mmol, 37%, orange crystals). **TLC** R_f = 0.90 (9:1 PE/EtOAc). **m.p.** 55 °C. **IR** [cm^{-1}] 2919, 1599, 1398, 1320, 1163, 1118, 1070, 1010, 951, 824, 775, 723, 686. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.78 – 7.65 (m, 4H), 7.60 – 7.44 (m, 4H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 134.8, 130.7, 130.6, 130.2, 129.7, 126.2, 126.2, 126.1, 126.1, 125.7, 122.0. **^{77}Se-NMR** (76 MHz, Chloroform-*d*): δ (ppm) = 452.4. **^{19}F-NMR** (376 MHz, Chloroform-*d*): δ (ppm) = -63.2. **HRMS** (ESI) calcd. for $[C_{14}H_8F_6Se_2]^{\cdot+}$ $(M)^{\cdot+}$, m/z = 449.8863, found 449.8847.

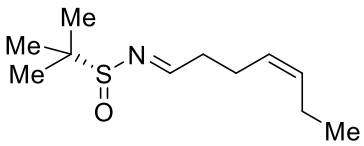
6.8.8 Synthesis of unconvertable substrates

(*Z*)-Hept-4-enal (132)



To a solution of (*Z*)-hept-4-en-1-ol (85.0 mg, 100 µL, 744 µmol, 1.00 eq.) in 10 mL DCM was added Dess-Martin periodinane (631 mg, 1.49 mmol, 2.00 eq.) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The mixture was quenched with aq. $NaHCO_3$ solution (2x 100 mL) and extracted in DCM. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1. Isolated yield: 29.3 mg (261 µmol, 35%, yellowish oil). **TLC** R_f = 0.90 (9:1 PE/EtOAc). **IR** [cm^{-1}] 2963, 2933, 2874, 2721, 1726, 1457, 1413, 1141, 969. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 9.77 (t, *J* = 1.6 Hz, 1H), 5.51 – 5.17 (m, 2H), 2.53 – 2.44 (m, 2H), 2.42 – 2.31 (m, 2H), 2.15 – 1.94 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 202.3, 133.3, 126.5, 43.9, 20.5, 20.0, 14.2. **HRMS** (EI) calcd. for $[C_7H_{12}O]^{\bullet+}$ $(M)^{\bullet+}$, m/z = 112.0888, found 112.0878.

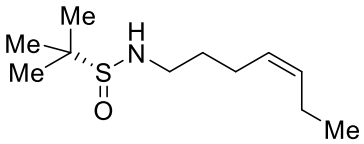
(*R*)-*N*-((1*E*,4*Z*)-Hept-4-en-1-ylidene)-2-methylpropane-2-sulfinamide (134)[99]



(*Z*)-Hept-4-enal (85 mg, 100 µL, 758 µmol, 1.00 eq.) was dissolved in THF (5 mL) in a roundbottomed flask purged with N_2. Then (*R*)-(+)-2-methyl-2-propanesulfinamide (110 mg, 909 µmol, 1.20 eq.) was added. Finally, $Ti(OEt)_4$ (398 mg, 1.74 mmol, 2.30 eq.) was added to the stirring solution. This was allowed to stirr at r.t. under N_2 until consumption of the starting sulfinamide was determined by TLC. The solution was then poured into a stirring solution of brine, filtered over celite, and washed with EtOAc. The organic layer was separated from the aq. layer, washed with EtOAc. The organic layers were combined, dried over $MgSO_4$ and filtrated. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1→1:1. Isolated yield: 99.0 mg (460 µmol, 61%, yellowish oil). **TLC** R_f = 0.50 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3206, 2956, 2922, 2855, 1461, 1178, 1051, 969. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.07 (t, *J* = 4.5 Hz, 1H), 5.53 – 5.25 (m, 2H), 2.58 (tdd, *J* = 6.8, 4.5, 0.9 Hz, 2H), 2.42 – 2.30 (m, 2H), 2.12 – 1.98 (m, 2H), 1.19 (s, 9H), 0.97 (t, *J* = 7.5 Hz, 3H). **^{13}C-NMR** (101 MHz,

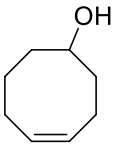
Chloroform-*d*): δ (ppm) = 169.0, 133.3, 126.8, 56.5, 36.2, 23.1, 22.4, 22.3, 20.6, 14.2. **HRMS** (ESI) calcd. for $[C_{11}H_{22}NOS]^+$ $(M+H)^+$, m/z = 216.1417, found 216.1414.

(*R*,*Z*)-*N*-(Hept-4-en-1-yl)-2-methylpropane-2-sulfinamide (135)[99]



(*R*)-*N*-((1*E*,4*Z*)-hept-4-en-1-ylidene)-2-methylpropane-2-sulfinamide (75.0 mg, 348 µmol, 1.00 eq.) was dissolved in methanol (5 mL). This solution was purged with N_2 and cooled to −40 ºC. Then $NaBH_4$ (13.8 mg, 366 µmol, 1.05 eq.) was added, and the solution was slowly warmed to r.t. overnight. The reaction was quenched with saturated aq. NH_4Cl solution, and the aq. layer was washed with DCM (2x 50 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 1:1. Isolated yield: 51.0 mg (235 µmol, 67%, yellowish oil). **TLC** R_f = 0.29 (6:4 PE/EtOAc). **IR** [cm^{-1}] 3264, 2963, 2874, 1260, 1092, 1029, 801. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 5.39 – 5.14 (m, 2H), 3.19 (q, *J* = 5.5, 4.3 Hz, 1H), 3.16 – 2.89 (m, 2H), 2.07 – 1.84 (m, 4H), 1.54 (p, *J* = 7.1 Hz, 2H), 1.12 (s, 9H), 0.86 (t, *J* = 7.5 Hz, 3H).**^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 132.5, 127.8, 55.5, 45.2, 30.9, 24.2, 22.6, 20.5, 14.3. **HRMS** (ESI) calcd. for $[C_{11}H_{23}NOS]^+$ $(M+H)^+$, m/z = 218.1574, found 218.1576.

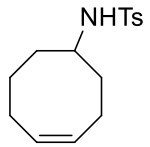
(*Z*)-Cyclooct-4-en-1-ol (173^S)



This compound was synthesized during an internship with Marko Boskovic. To a solution of 1-5-cyclooctadiene (3.00 mL, 24.4 mmol, 1.00 eq.) in 50 mL DCM, *m*CPBA (4.21 g, 24.4 mmol, 1.0eq.) was added slowly at 0 °C and stirred at r.t. overnight. The reaction was quenched with sat aq. $NaHCO_3$ solution (50 mL) and washed with distilled H_2O (2x 50 mL). After evaporation of the solvent the crude product was dissolved in 20 mL dry THF under N_2 atmosphere and the solution was cooled to 0 °C. Then, $LiAlH_4$ (1.27 g, 33.5 mmol, 14.0 eq.) was slowly added, the reaction was stirred at r.t. overnight and quenched with 50 mL distilled H_2O. The product was extracted in DEE (3x 50 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1. Isolated yield: 1.42 g (11.2 mmol, 47%, colorless oil). **TLC** R_f = 0.43

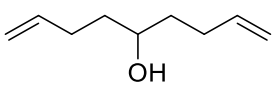
(9:1 PE/EtOAc). **IR** [cm^{-1}] 3347, 3079, 2930, 2859, 1711, 1461, 1424, 1144, 1096, 992, 921, 727, 671. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 5.81 – 5.42 (m, 2H), 3.77 (dddd, *J* = 9.4, 8.2, 4.4, 1.1 Hz, 1H), 2.47 – 1.35 (m, 12H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 130.1, 129.5, 72.7, 37.7, 36.3, 25.7, 24.9, 22.8. **HRMS** (EI) calcd. for $[C_8H_{15}O]^{\bullet+}$ $(M)^{\bullet+}$, m/z = 126.1045, found 126.1043.

(*Z*)-*N*-(Cyclooct-4-en-1-yl)-4-methylbenzenesulfonamide (173)



This compound was synthesized during an internship with Marko Boskovic. To a solution of (*Z*)-cyclooct-4-en-1-ol (100 mg, 792 µmol, 1.00 eq.) in 8.5 mL DCM was added NEt_3 (407 µL, 297 mg, 2.93 mmol, 3.70 eq.) and MsCl (98.1 µL, 145 mg, 1.27 mmol, 1.60 eq.) at 0 °C. After completion of the reaction (check *via* TLC), 50 mL distilled H_2O and 50 mL DCM were added, and the organic phase was separated. The solvent was evaporated under reduced pressure and the crude product was used without further purification in the next step. Crude (*Z*)-cyclooct-4-en-1-yl methanesulfonate was dissolved in 8.5 mL DMF, then $TsNH_2$ (1.17 g, 6.81 mmol, 8.60 eq.) and K_2CO_3 (810 mg, 5.86 mmol, 7.40 eq.) were added, and the reaction was heated to reflux overnight. The reaction was quenched with 50 mL aq. HCl solution (1 M) and extracted in DEE (3x 50 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1. Isolated yield: 47.0 mg (168 µmol, 21%, colorless oil). **TLC** R_f = 0.24 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3276, 3019, 2930, 2855, 1737, 1439, 1327, 1215, 1096, 816, 664. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.83 – 7.65 (m, 2H), 7.33 – 7.23 (m, 2H), 5.69 – 5.47 (m, 2H), 5.09 – 4.85 (m, 1H), 3.33 (pd, *J* = 7.8, 7.2, 4.2 Hz, 1H), 2.40 (s, 3H), 2.36 – 1.15 (m, 10H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.1, 138.2, 130.1, 129.6, 129.5, 127.0, 53.8, 36.0, 34.7, 25.8, 25.6, 23.2, 21.5. **HRMS** (ESI) calcd. for $[C_{15}H_{22}NO_2S]^+$ $(M+H)^+$, m/z = 280.1370, found 280.1366.

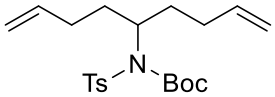
Nona-1,8-dien-5-ol (172^{S1})[164]



This compound was synthesized during the bachelors thesis with Simon Kaltenberger. In a 250 mL Schlenk flask, but-3-en-1-ylmagnesium bromide (40 mL, 0.5 M solution in THF, 20 mmol, 2.00 eq.) was dissolved

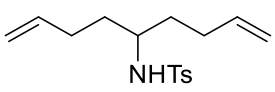
in 22 mL THF and cooled to 0 °C. Ethyl formate (0.8 mL, 9,9 mmol, 1.00 eq.) was added slowly and the reaction was stirred at r.t. overnight. The reaction was quenched with a 50 mL sat. aq. NH_4Cl solution and the crude product was extracted in EtOAc (3x 50 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 8:2. Isolated yield: 47.0 mg (168 µmol, 21%, colorless oil). **TLC** R_f = 0.38 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3347, 3079, 2978, 2930, 1640, 1446. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 5.82 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 2H), 5.09 – 4.87 (m, 4H), 3.62 (tt, *J* = 7.4, 4.9 Hz, 1H), 2.35 – 1.98 (m, 4H), 1.92 – 1.75 (m, 1H), 1.65 – 1.40 (m, 4H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 160.8, 137.4, 115.2, 73.1, 33.2, 29.4. **HRMS** (ESI) calcd. for $[C_9H_{15}O]^+$ $(M-H)^+$, m/z = 139.1117, found 139.1121.

Tert-Butyl nona-1,8-dien-5-yl(tosyl)carbamate (172^{S2})[165]



This compound was synthesized during the bachelors thesis with Simon Kaltenberger. To a solution of Nona-1,8-dien-5-ol (1.00 g, 7.10 mmol, 1.00 eq.) in 26 ml benzene under N_2 atmosphere PPh_3 (2.81 g, 11.0 mmol, 1.50 eq.) and *tert*-butyl tosylcarbamate (2.71 g, 10.0 mmol, 1.40 eq.) were added. To the turbid solution was added diisopropylazodicarboxylate (1.80 mL, 9.20 mmol, 1.30 eq.) slowly and the solution was stirred at r.t. overnight. The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 20:1. Isolated yield: 2.08 g (5.30 mmol, 74%, colorless oil). **TLC** R_f = 0.42 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3089, 2982, 2933, 1722, 1640, 1599, 1453, 1353, 1279, 1148. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.82 – 7.69 (m, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 5.77 (ddt, *J* = 16.6, 10.1, 6.3 Hz, 2H), 5.11 – 4.79 (m, 4H), 2.36 (s, 3H), 2.16 – 1.90 (m, 6H), 1.76 (ddt, *J* = 12.7, 9.3, 5.8 Hz, 2H), 1.40 – 1.23 (m, 9H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 150.9, 144.0, 137.7, 137.5, 129.0, 128.3, 115.0, 83.9, 59.1, 32.9, 31.1, 27.9, 21.5. **HRMS** (ESI) calcd. for $[C_{21}H_{31}NNaO_4S]^+$ $(M+Na)^+$, m/z = 416.1866, found 416.1863.

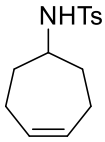
4-Methyl-*N*-(nona-1,8-dien-5-yl)benzenesulfonamide (172^{S3})[166]



This compound was synthesized during the bachelors thesis with Simon Kaltenberger. To a solution of *tert*-Butyl nona-1,8-dien-5-

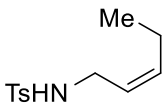
yl(tosyl)carbamate (1.75 g, 4.50 mmol, 1.00 eq.) in 18 mL DCM was added TFA (9,80 mL, 127 mmol, 29.0 eq.) portionwise over a period of 2.5 h. Then, another 18 mL of DCM were added, and the solution was neutralized slowly by the addition of a sat. aq. $NaHCO_3$ solution. The crude product was extracted in DCM (3x 50 mL). The solvent was evaporated under reduced pressure to yield the desired product. Isolated yield: 1.06 g (3.60 mmol, 81%, yellow oil). **TLC** R_f = 0.50 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3276, 3075, 2978, 2926, 2859, 1640, 1599, 1494, 1423, 1320, 1156. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.86 – 7.62 (m, 2H), 7.40 – 7.07 (m, 2H), 5.60 (ddt, *J* = 17.7, 9.6, 6.6 Hz, 2H), 5.31 (d, *J* = 8.5 Hz, 1H), 4.99 – 4.64 (m, 4H), 3.30 – 3.12 (m, 1H), 2.38 (s, 3H), 1.92 (dqt, *J* = 9.4, 8.2, 6.6 Hz, 4H), 1.57 – 1.24 (m, 4H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.1, 138.5, 137.7, 129.6, 127.0, 115.0, 53.2, 34.0, 29.5, 21.5. **HRMS** (ESI) calcd. for $[C_{16}H_{24}NO_2S]^+$ $(M+H)^+$, m/z = 294.1522, found 294.1523.

N-(Cyclohept-4-en-1-yl)-4-methylbenzenesulfonamide (172)[19]



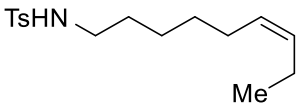
This compound was synthesized during the bachelors thesis with Simon Kaltenberger. In a 250 mL Schlenk flask with applied reflux condenser, 4-Methyl-*N*-(nona-1,8-dien-5-yl)benzenesulfonamide (616 mg, 2.10 mmol, 1.00 eq.) was dissolved in 82 mL dry toluene under N_2 atmosphere. The solution was stirred and heated to reflux and a solution of Grubbs 1st generation catalyst (86.0 mg, 0.10 mmol, 0.05 eq.) in 1.8 mL dry toluene was added. The reaction was refluxed for 1.5 h. Afterwards, the solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 20:1. Isolated yield: 239 mg (0.90 mmol, 43%, colorless solid). **TLC** R_f = 0.23 (9:1 PE/EtOAc). **m.p.** 103 °C. **IR** [cm^{-1}] 3265; 3019; 2939; 2848; 1655; 1599; 1495; 1438; 1320; 1156. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.91 – 7.70 (m, 2H), 7.35 – 7.15 (m, 2H), 5.66 (ddd, *J* = 4.1, 2.7, 1.2 Hz, 2H), 5.36 (d, *J* = 7.6 Hz, 1H), 3.47 – 3.23 (m, 1H), 2.39 (s, 3H), 2.21 – 1.65 (m, 6H), 1.38 (dddd, *J* = 13.6, 10.7, 8.8, 2.1 Hz, 2H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.1, 138.2, 131.6, 129.7, 127.0, 56.0, 33.9, 24.0, 21.6. **HRMS** (ESI) calcd. for $[C_{14}H_{20}NO_2S]^+$ $(M+H)^+$, m/z = 266.1209, found 266.1213.

(*Z*)-4-Methyl-*N*-(pent-2-en-1-yl)benzenesulfonamide (145)



To a solution of (*Z*)-pent-2-en-1-ol (597 mg, 700 µL, 6.93 mmol, 1.00 eq.) in 55 mL DCM was added NEt_3 (2.60 g, 3.58 mL, 25.7 mmol, 3.70 eq.) and MsCl (1.27 g, 858 µL, 11.1 mmol, 1.60 eq.) at 0 °C. After completion of the reaction (check *via* TLC), 50 mL distilled H_2O and 100 mL DCM were added, and the organic phase was separated. The solvent was evaporated under reduced pressure and the crude product was used without further purification in the next step. Crude (*Z*)-pent-2-en-1-yl methanesulfonatewas dissolved in 50 mL DMF, then $TsNH_2$ (10.2 g, 59.6 mmol, 8.60 eq.) and K_2CO_3 (2.88 mg, 51.3 mmol, 7.40 eq.) were added, and the reaction was heated to reflux overnight. The reaction was quenched with 50 mL aq. HCl solution (1 M) and extracted in DEE (3x 100 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1. Isolated yield: 610 mg (2.55 mmol, 37%, yellowish oil). **TLC** R_f = 0.24 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3273, 2967, 2930, 2878, 1722, 1599, 1428, 1323, 1156, 1096, 813, 664. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.80 – 7.68 (m, 2H), 7.35 – 7.27 (m, 2H), 5.48 (dtt, *J* = 10.4, 7.4, 1.5 Hz, 1H), 5.23 (dtt, *J* = 10.4, 7.0, 1.6 Hz, 1H), 4.51 (t, *J* = 5.7 Hz, 1H), 3.76 – 3.46 (m, 2H), 2.43 (s, 3H), 2.04 – 1.85 (m, 2H), 0.90 (t, *J* = 7.5 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.5, 136.9, 136.3, 129.7, 127.2, 123.2, 40.0, 21.6, 20.6, 14.0. **HRMS** (ESI) calcd. for $[C_{12}H_{28}NO_2S]^+$ $(M+H)^+$, m/z = 240.1053, found 240.1055.

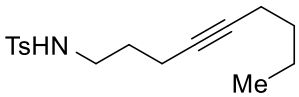
(*Z*)-4-Methyl-N-(non-6-en-1-yl)benzenesulfonamide (148)



This compound was synthesized during the bachelors thesis with Simon Kaltenberger. According to General procedure A: (*Z*)-Non-6-enal (500 µL, 424 mg, 3.02 mmol, 1.00 eq.), $TsNH_2$ (776 mg, 4.53 mmol, 1.50 eq.), triethylsilane (531 µL, 386 mg, 3.32 mmol, 1.10 eq.), TfOH (13.4 µL, 22.7 mg, 151 µmol, 0.05 eq.). Eluting with PE/EtOAc 99:1→9:1. Isolated yield: 530 mg (1.79 mmol, 59%, yellow oil). **TLC** R_f = 0.36 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3507, 3273, 2933, 2863, 1707, 1424, 1361, 1327, 1223, 1156, 1092, 816. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.79 – 7.67 (m, 2H), 7.31 – 7.20 (m, 2H), 5.38 – 5.12 (m, 3H), 2.85 (td, *J* = 7.2, 6.1 Hz, 2H), 2.37 (s, 3H), 2.07 – 1.83 (m, 4H), 1.41 (dd, *J* = 8.3, 5.8 Hz, 2H), 1.22 (dq, *J* = 7.3, 3.5, 3.1 Hz, 4H), 0.88 (t, *J* = 7.5 Hz, 3H). **^{13}C-NMR**

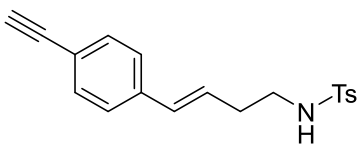
(75 MHz, Chloroform-*d*): δ (ppm) = 143.2, 137.0, 131.8, 129.6, 128.8, 127.1, 43.1, 29.4, 29.2, 26.8, 26.1, 21.5, 20.5, 14.4. **HRMS** (ESI) calcd. for $[C_{16}H_{26}NO_2S]^+$ $(M+H)^+$, m/z = 296.1679, found 296.1685.

4-Methyl-*N*-(non-4-yn-1-yl)benzenesulfonamide (175)



This compound was synthesized during an internship with Daniel Kolb. To a solution of 1-Chlorononon-4-yne (368 mg, 2.32 mmol, 1.00 eq.) in 24 ml DMF was added $TsNH_2$ (2.94 g, 17.2 mmol, 7.40 eq.) and 2.76 g K_2CO_3 (2.76 g, 20.0 mmol, 8.60 eq.). The mixture was heated to reflux until completion (check *via* TLC, 2 h). The reaction was quenched with distilled H_2O and the crude product was extracted in DEE (3x 50 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 20:1. Isolated yield: 332 mg (1.13 mmol, 49%, yellow oil). **TLC** R_f = 0.40 (8:2 PE/EtOAc). **IR** [cm^{-1}] 3276, 2930, 2874, 1707, 1599, 1424, 1323, 1156, 1092, 813. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.69 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.14 (m, 2H), 5.25 (t, *J* = 6.3 Hz, 1H), 2.94 (q, *J* = 6.5 Hz, 2H), 2.34 (s, 3H), 2.13 – 1.93 (m, 4H), 1.53 (q, *J* = 6.8 Hz, 2H), 1.40 – 1.18 (m, 4H), 0.80 (t, *J* = 7.1 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 143.3, 136.9, 129.7, 127.1, 81.4, 78.4, 42.4, 31.0, 28.6, 21.9, 21.5, 18.3, 16.1, 13.6. **HRMS** (ESI) calcd. for $[C_{16}H_{24}NO_2S]^+$ $(M+H)^+$, m/z = 294.1522, found 294.1525.

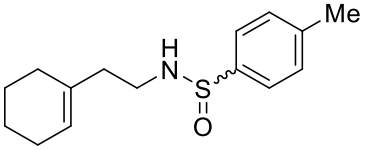
(*E*)-*N*-(4-(4-Ethynylphenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (174)



According to General procedure D: (3-((4-methylphenyl)sulfonamido)propyl)triphenylphos-phonium bromide (4.00 g, 7.21 mmol, 2.00 eq.), KO^{t}Bu (1.62 g, 14.4 mmol, 4.00 eq.) in 12 mL THF and 4-ethynylbenzaldehyde (469 mg, 3.61 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 9:1. Isolated yield: 490 mg (1.51 mmol, 42%, yellow oil) exclusively *E*-isomer. **TLC** R_f = 0.42 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3481, 3265, 3064, 2926, 1703, 1603, 1409, 1327, 1156, 1092, 1014, 816, 664. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.80 – 7.68 (m, 2H), 7.43 – 7.33 (m, 2H), 7.29 – 7.13 (m, 4H), 6.38 – 6.21 (m, 1H), 6.01 (dt, *J* = 15.9, 7.0 Hz, 1H), 5.11 (t, *J* = 6.1 Hz, 1H), 3.16 – 2.98 (m, 3H), 2.43 – 2.29 (m, 5H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ

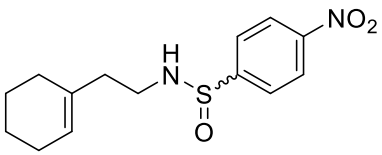
(ppm) = 143.5, 137.4, 136.8, 132.3, 132.2, 129.7, 127.3, 127.1, 126.0, 120.8, 83.7, 42.5, 33.1, 21.6. **HRMS** (ESI) calcd. for $[C_{19}H_{20}NO_2S]^+$ $(M+H)^+$, m/z = 326.1209, found 326.1210.

(*Rac*)-*N*-(2-(Cyclohex-1-en-1-yl)ethyl)-4-methylbenzenesulfinamide (181)



Sodium 4-methylbenzenesulfinate (1.00 g, 5.61 mmol, 1.00 eq.) was dissolved in dry DCM (40 mL) and cooled to 0 °C. To the solution thionylchloride (407 µL, 668 mg, 5.61 mmol, 1.00 eq.) were added slowly. After 10 min of stirring at 0 °C, 2-(cyclohex-1-en-1-yl)ethan-1-amine (703 mg, 5.61 mmol, 1.00 eq.) and NEt_3 (908 µL, 888 mg, 11.2 mmol, 2.00 eq.) were added sequentially and the solution was stirred overnight. The reaction was quenched with distilled H_2O and the crude product was extracted in DCM (3x 50 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1. Isolated yield: 424 mg (1.61 mmol, 29%, yellow oil). **TLC** R_f = 0.21 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3213, 2926, 1491, 1439, 1402, 1088, 1059, 813. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.59 – 7.39 (m, 2H), 7.28 – 7.11 (m, 2H), 5.37 (tq, *J* = 2.9, 1.4 Hz, 1H), 4.12 (dd, *J* = 7.0, 5.0 Hz, 1H), 3.09 (dtd, *J* = 11.9, 6.9, 5.0 Hz, 1H), 2.70 (dq, *J* = 12.2, 6.8 Hz, 1H), 2.32 (s, 3H), 2.10 – 1.99 (m, 2H), 1.90 (ddt, *J* = 6.1, 4.2, 2.1 Hz, 2H), 1.82 – 1.68 (m, 2H), 1.56 – 1.39 (m, 4H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 141.2, 141.0, 134.2, 129.5, 126.0, 124.0, 38.6, 37.9, 27.8, 25.2, 22.8, 22.3, 21.3. **HRMS** (ESI) calcd. for $[C_{15}H_{22}NOS]^+$ $(M+H)^+$, m/z = 264.1417, found 264.1420.

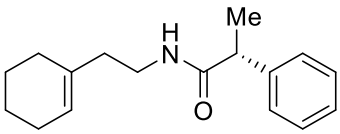
***N*-(2-(Cyclohex-1-en-1-yl)ethyl)-4-nitrobenzenesulfinamide (182)**



To a solution of 4-nitrobenzenesulfonyl chloride (1.00 g, 4.51 mmol, 1.00 eq.) in 15 mL DCM was added NEt_3 (4.57 g, 6.29 mL, 45,1 mmol, 10.0 eq.) and the mixture was cooled to 0 °C. A second solution of PPh_3 (1.18 g, 4.51 mmol, 1.00 eq.) and 2-(cyclohex-1-en-1-yl)ethan-1-amine (565 mg, 4.51 mmol, 1.00 eq.) in 15 mL DCM was added to the first solution over a period of 1 h and the reaction was stirred for another 1 h. The reaction was quenched with 100 mL distilled H_2O and extracted in DCM (3x 50 mL). The solvent was evaporated under reduced pressure and the crude product

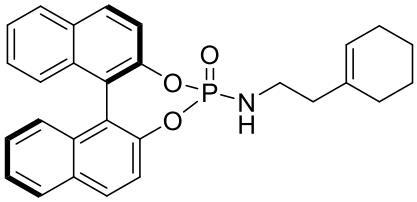
was purified *via* column chromatography. Eluting with PE/EtOAc 9:1→8:2. Isolated yield: 351 mg (1.19 mmol, 26%, yellowish oil). **TLC** R_f = 0.24 (8:2 PE/EtOAc). **IR** [cm^{-1}] 3217, 2930, 2860, 1603, 1528, 1439, 1346, 1062, 921, 854, 746, 686. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.47 – 8.22 (m, 2H), 7.98 – 7.78 (m, 2H), 5.48 (td, *J* = 3.5, 1.7 Hz, 1H), 4.25 (s, 1H), 3.21 (dtd, *J* = 11.7, 6.9, 4.6 Hz, 1H), 2.69 (dq, *J* = 12.3, 6.7 Hz, 1H), 2.14 (t, *J* = 6.7 Hz, 2H), 1.99 (ddt, *J* = 6.6, 4.7, 2.4 Hz, 2H), 1.80 (dd, *J* = 12.1, 7.3 Hz, 2H), 1.57 (ddtd, *J* = 12.1, 7.5, 4.9, 2.2 Hz, 4H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 151.2, 149.4, 133.8, 127.5, 124.4, 123.9, 38.4, 38.0, 27.7, 25.2, 22.7, 22.3. **HRMS** (ESI) calcd. for $[C_{14}H_{19}N_2O_3S]^+$ $(M+H)^+$, m/z = 295.1111, found 295.1115.

(*R*)-*N*-(2-(Cyclohex-1-en-1-yl)ethyl)-2-phenylpropanamide (186)



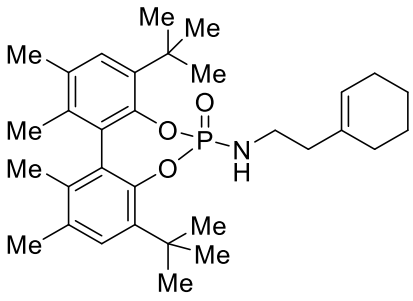
To a solution of (*R*)-2-phenylpropanoic acid (1.00 g, 6.66 mmol, 1.00 eq.) in 15 mL dry DCM thionylchloride (483 µL, 792 mg, 6.66 mmol, 1.00 eq.) was added at 0 °C. The solution was stirred for 10 min, then NEt_3 (2.78 mL, 2.02 g, 19.9 mmol, 3.00 eq.) was added and 2-(cyclohex-1-en-1-yl)ethan-1-amine (832 mg, 926 µL, 6.64 mmol, 1.00 eq.) slowly. After 1 h of stirring, the reaction was carefully quenched with distilled H_2O, and the crude product was extracted in DCM (3x 50 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1. Isolated yield: 430 mg (1.67 mmol, 25%, colorless oil). **TLC** R_f = 0.19 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3295, 3064, 2930, 1648, 1551, 1450, 1372, 1234, 701. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 7.33 – 7.14 (m, 6H), 5.63 (s, 1H), 5.17 (tt, *J* = 3.6, 1.5 Hz, 1H), 3.52 (q, *J* = 7.2 Hz, 1H), 3.19 (tdd, *J* = 13.2, 6.6, 5.3 Hz, 2H), 2.02 – 1.93 (m, 2H), 1.83 (tq, *J* = 5.7, 1.9 Hz, 2H), 1.79 – 1.71 (m, 2H), 1.54 – 1.35 (m, 8H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 174.1, 141.4, 134.3, 128.8, 127.7, 127.1, 123.7, 47.0, 37.4, 37.0, 27.6, 25.1, 22.7, 22.3, 18.3. **HRMS** (ESI) calcd. for $[C_{17}H_{24}NO]^+$ $(M+H)^+$, m/z = 258.1852, found 258.1858.

(4*R*)-4-((2-(Cyclohex-1-en-1-yl)ethyl)amino)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (189)



(*R*)-BINOL (1.00 g, 3.49 mmol, 1.00 eq.) and NEt_3 (1.95 mL, 1.41 g, 14.0 mmol, 4.00 eq.) were dissolved in dry DCM (20 mL), cooled to 0 °C and $POCl_3$ (359 µL, 589 mg, 3.84 mmol, 1.10 equiv.) was added. The mixture was stirred overnight, then added to a solution of 2-(cyclohex-1-en-1-yl)ethan-1-amine (440 mg, 3.51 mmol, 1.00 eq.) and NEt_3 (0.98 mL, 711 mg, 7.03 mmol, 2.00 eq.) and stirred at r.t. overnight. The reaction was quenched with distilled H_2O, and the crude product was extracted in DCM (3x 50 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1→6:4. Isolated yield: 313 mg (687 µmol, 20%, yellowish oil). **TLC** R_f = 0.45 (6:4 PE/EtOAc). **IR** [cm^{-1}] 3206, 3060, 2926, 2855, 1510, 1461, 1435, 1327, 1260, 1230, 1100, 992, 969, 906, 869, 816, 749. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.05 – 7.88 (m, 4H), 7.67 – 7.19 (m, 8H), 5.43 (tt, *J* = 3.8, 1.5 Hz, 1H), 3.14 – 2.98 (m, 1H), 2.93 (dddd, *J* = 12.6, 8.9, 5.4, 1.8 Hz, 1H), 2.14 – 2.01 (m, 2H), 2.00 – 1.69 (m, 4H), 1.70 – 1.33 (m, 4H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 147.6, 147.5, 146.7, 146.6, 133.7, 132.4, 132.2, 131.8, 131.5, 131.2, 130.9, 128.5, 128.5, 127.2, 127.0, 126.8, 126.6, 125.7, 125.6, 124.5, 121.8, 121.7, 121.3, 121.3, 121.1, 121.0, 120.8, 120.8, 39.8, 39.7, 39.6, 31.0, 27.7, 25.2, 22.8, 22.3. **^{31}P-NMR** (162 MHz, Chloroform-*d*): δ (ppm) = 7.6. **HRMS** (ESI) calcd. for $[C_{28}H_{27}NO_3P]^+$ $(M+H)^+$, m/z = 456.1723, found 456.1726.

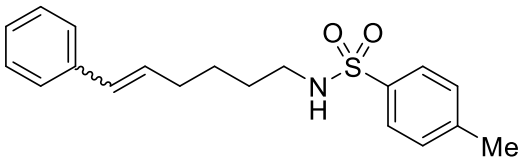
4,8-Di-*tert*-butyl-6-((2-(cyclohex-1-en-1-yl)ethyl)amino)-1,2,10,11-tetramethyldibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide (192)



(*Rac*)-3,3'-di-tert-butyl-5,5',6,6'-tetramethyl-[1,1'-biphenyl]-2,2'-diol (1.00 g, 2.82 mmol, 1.00 eq.) and NEt_3 (1.57 mL, 1.14 g, 11.3 mmol, 4.00 eq.) were dissolved in dry DCM (20 mL), cooled to 0 °C and $POCl_3$ (290 µL, 476 mg, 3.10 mmol, 1.10 equiv.) was added. The mixture was stirred overnight, then added to a solution of 2-(cyclohex-1-en-1-yl)ethan-1-amine (350 mg, 2.80 mmol, 1.00 eq.) and NEt_3

(0.78 mL, 566 mg, 5.59 mmol, 2.00 eq.) and stirred at r.t. overnight. The reaction was quenched with distilled H_2O, and the crude product was extracted in DCM (3x 50 mL). The solvent was evaporated under reduced pressure and the crude product was purified *via* column chromatography. Eluting with PE/EtOAc 9:1→4:1. Isolated yield: 210 mg (401 µmol, 14%, yellow oil). **TLC** R_f = 0.33 (6:4 PE/EtOAc). **IR** [cm^{-1}] 3161, 2960, 2870, 1715, 1439, 1305, 1223, 1118, 906, 805, 723. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 7.18 (d, *J* = 6.2 Hz, 2H), 5.37 (td, *J* = 3.6, 1.8 Hz, 1H), 2.85 (dt, *J* = 12.4, 6.3 Hz, 1H), 2.57 (ddt, *J* = 15.3, 8.8, 6.6 Hz, 2H), 2.29 – 2.25 (m, 3H), 2.24 (d, *J* = 1.2 Hz, 3H), 2.00 – 1.91 (m, 4H), 1.87 (s, 3H), 1.76 (s, 3H), 1.76 – 1.70 (m, 2H), 1.48 (d, *J* = 22.4 Hz, 22H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 145.8, 145.7, 144.7, 144.6, 137.9, 137.9, 137.7, 137.7, 134.9, 134.9, 134.8, 134.8, 134.0, 133.0, 133.0, 132.7, 132.7, 129.1, 129.0, 128.7, 128.6, 128.6, 128.6, 128.4, 128.4, 124.0, 40.0, 40.0, 39.8, 39.8, 34.9, 34.8, 31.4, 31.3, 27.7, 25.2, 22.8, 22.3, 20.4, 20.3, 16.7, 16.5. **^{31}P-NMR** (162 MHz, Chloroform-*d*): δ (ppm) = 6.6. **HRMS** (ESI) calcd. for $[C_{32}H_{47}NO_3P]^+$ $(M+H)^+$, m/z = 524.3288, found 524.3286.

4-Methyl-*N*-(6-phenylhex-5-en-1-yl)benzenesulfonamide (221)



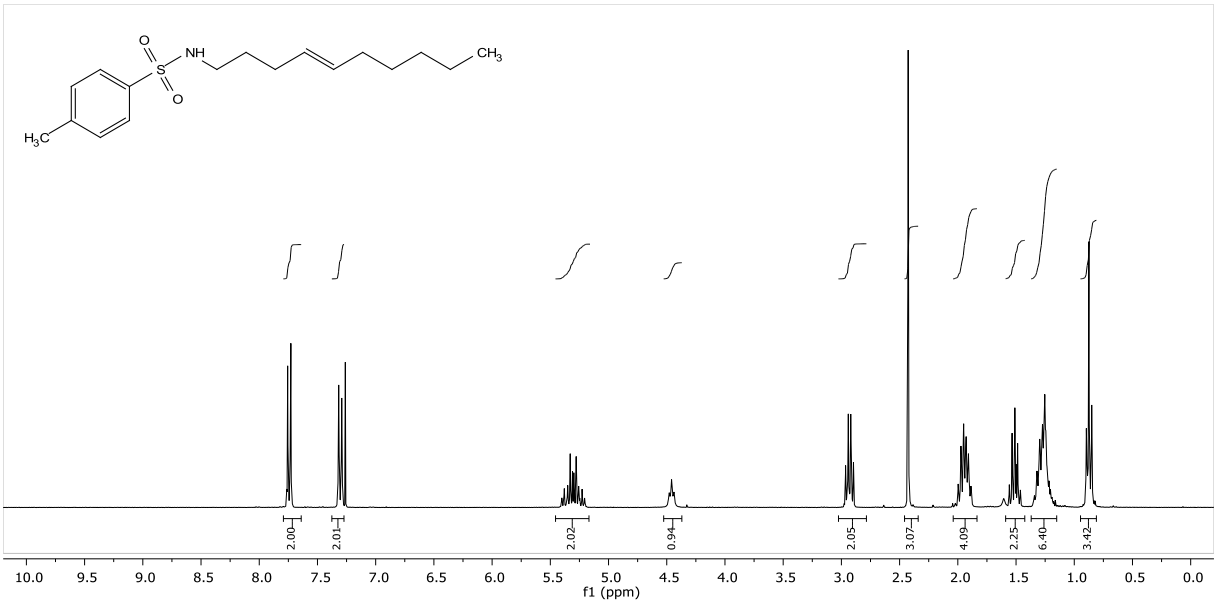
According to General procedure D: (5-((4-methylphenyl) sulfonamido)pentyl)triphenyl-phosphonium 4-methylbenzenesulfonate (5.00 g, 7.42 mmol, 2.00 eq.), KO^{t}Bu (1.67 g, 14.8 mmol, 4.00 eq.) in 12 mL THF and benzaldehyde (661 mg, 3.71 mmol, 1.00 eq.) in 1.8 mL THF. Eluting with PE/EtOAc 20:1. Isolated yield: 651 mg (1.98 mmol, 53%, yellowish oil) as a mixture of isomers (*E*:*Z* = 1:1.2). **TLC** R_f = 0.46 (9:1 PE/EtOAc). **IR** [cm^{-1}] 3276, 3056, 3027, 2930, 2863, 1599, 1495, 1446, 1320, 1156, 1092. **^{1}H-NMR** (400 MHz, Chloroform-*d*): δ (ppm) = 7.81 – 7.66 (m, 2H), 7.41 – 7.27 (m, 5H), 7.25 – 7.14 (m, 2H), 6.58 – 6.21 (m, 1H), 6.21 – 5.46 (m, 1H), 4.45 (dt, *J* = 14.4, 6.4 Hz, 1H), 2.94 (dq, *J* = 20.2, 6.6 Hz, 2H), 2.41 (d, *J* = 3.2 Hz, 3H), 2.35 – 2.04 (m, 2H), 1.59 – 1.34 (m, 4H). **^{13}C-NMR** (101 MHz, Chloroform-*d*): δ (ppm) = 143.4, 137.6, 137.5, 137.0, 137.0, 132.0, 130.4, 129.9, 129.7, 129.7, 129.4, 128.7, 128.5, 128.5, 128.2, 127.1, 127.0, 126.6, 125.9, 125.5, 43.1, 43.1, 32.3, 29.2, 29.1, 27.9, 26.8, 26.2, 21.5. **HRMS** (ESI) calcd. for $[C_{19}H_{24}NO_2S]^+$ $(M+H)^+$, m/z = 330.1522, found 330.1525.

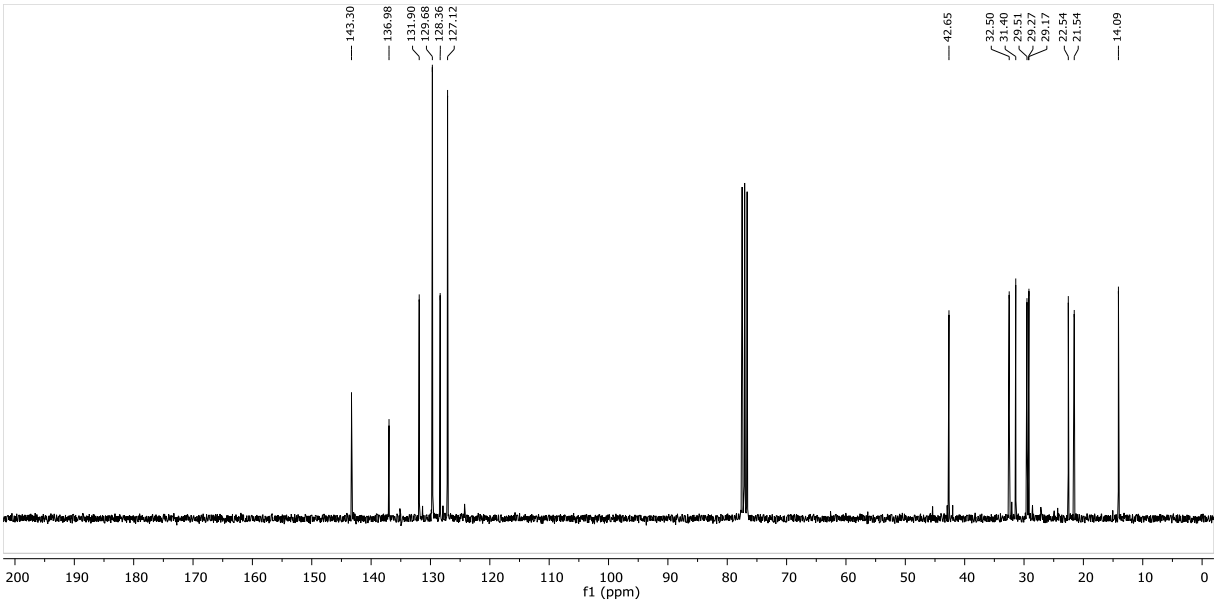
(*Z*)-*N*-(Hex-3-en-1-yl)-2-nitrobenzenesulfonamide (146aj)

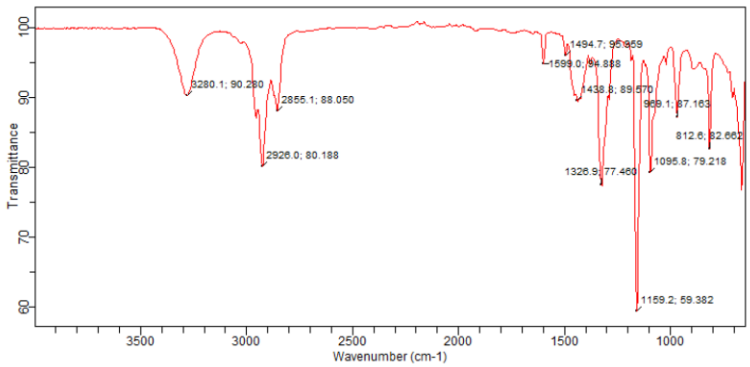
According to general procedure C: (*Z*)-Hex-3-en-1-ol (1.10 g, 11.0 mmol, 1.00 eq.), NEt_3 (4.11 g, 40.6 mmol, 3.70 eq.), MsCl (2.01 g, 17.6 mmol, 1.60 eq.) in 116 mL DCM, then K_2CO_3 (11.2 g, 81.3 mmol, 7.40 eq.) and *o*-$NsNH_2$ (8.88 g, 43.9 mmol, 4.00 eq.) in 116 mL DMF. Eluting with PE/EtOAc 9:1→4:1. Isolated yield: 2.10 g (7.39 mmol, 67%, brown oil). **TLC** R_f = 0.41 (4:1 PE/EtOAc). **IR** [cm^{-1}] 3340, 3097, 3012, 2967, 237, 2878, 1536, 1439, 1409, 1342, 1163, 1070, 854, 783, 731. **^{1}H-NMR** (300 MHz, Chloroform-*d*): δ (ppm) = 8.23 – 8.00 (m, 1H), 7.94 – 7.81 (m, 1H), 7.80 – 7.65 (m, 2H), 5.61 – 5.42 (m, 1H), 5.31 (t, *J* = 5.7 Hz, 1H), 5.23 – 5.06 (m, 1H), 3.12 (q, *J* = 6.6 Hz, 2H), 2.33 – 2.18 (m, 2H), 2.08 – 1.87 (m, 2H), 0.93 (td, *J* = 7.5, 0.8 Hz, 3H). **^{13}C-NMR** (75 MHz, Chloroform-*d*): δ (ppm) = 148.1, 135.8, 133.7, 133.5, 132.8, 131.1, 125.4, 123.6, 43.5, 27.3, 20.6, 14.2. **HRMS** (ESI) calcd. for $[C_{12}H_{17}N_2O_4S]^+$ $(M+H)^+$, m/z = 285.0904, found 285.0905.

6.9 Spectra and HPLC traces

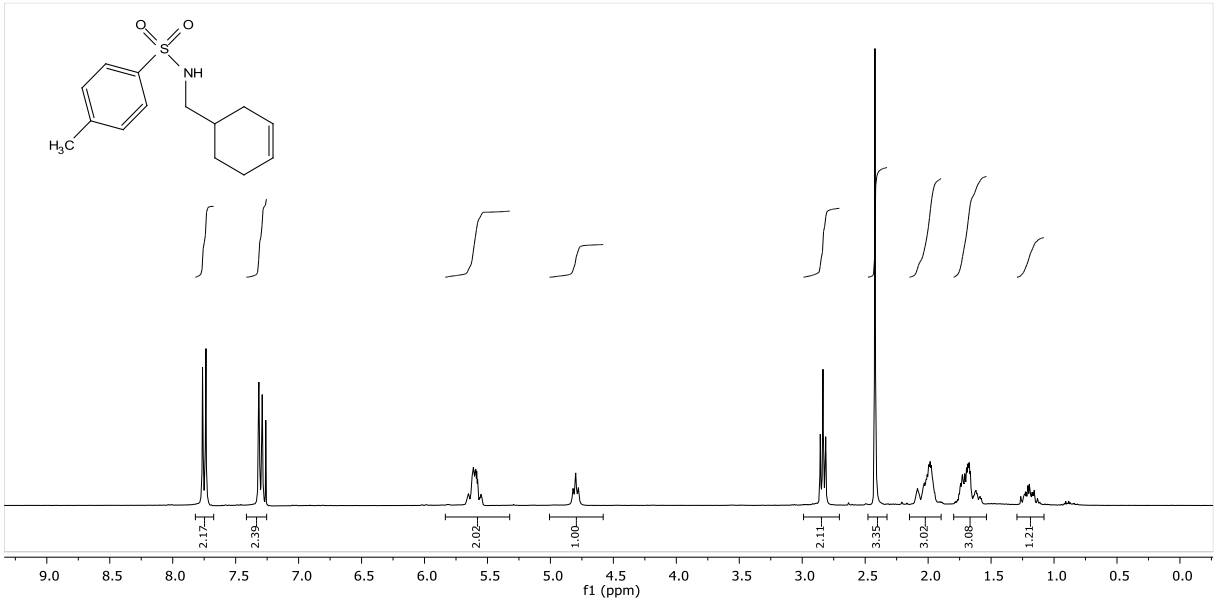
(*E*)-*N*-(Dec-4-en-1-yl)-4-methylbenzenesulfonamide (139a): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

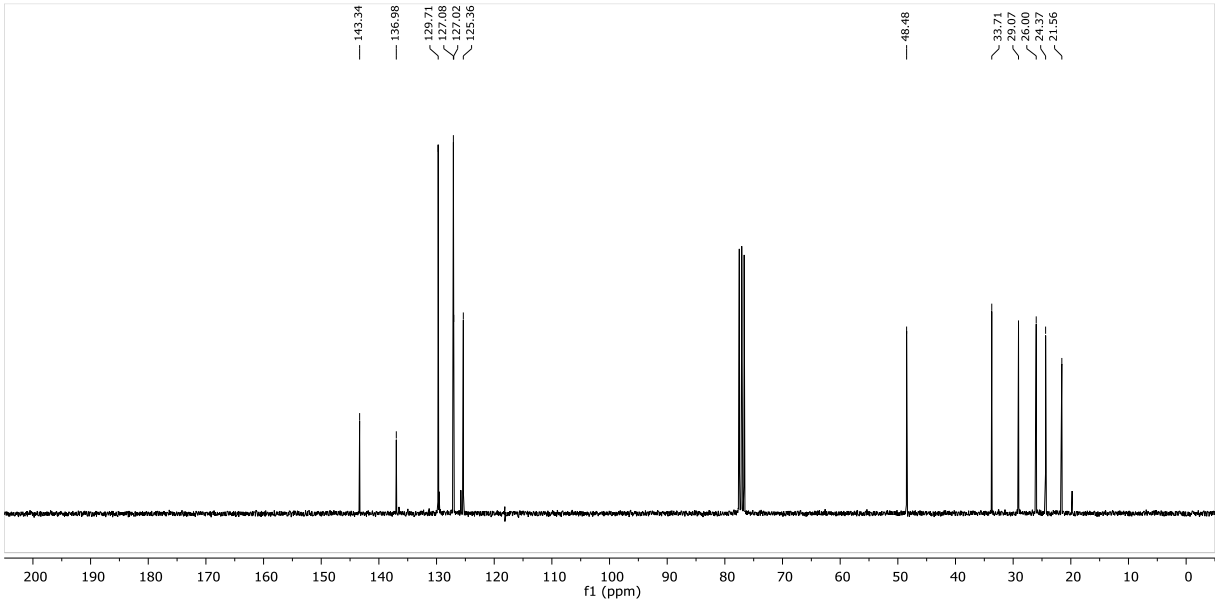


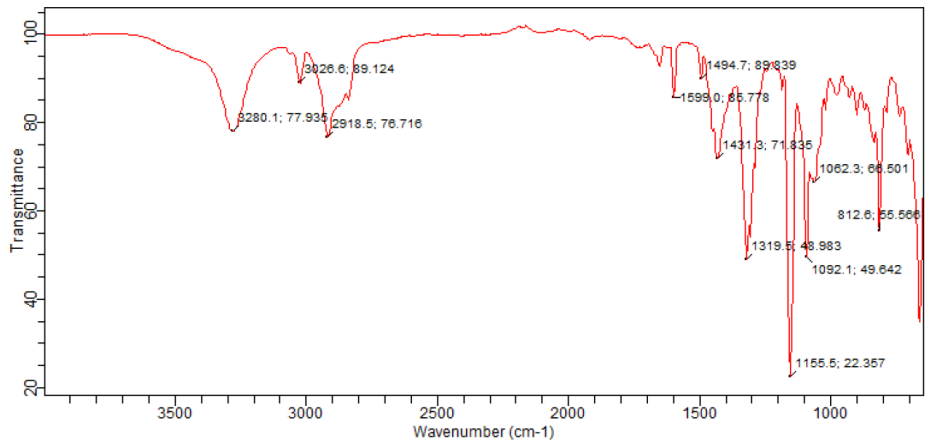




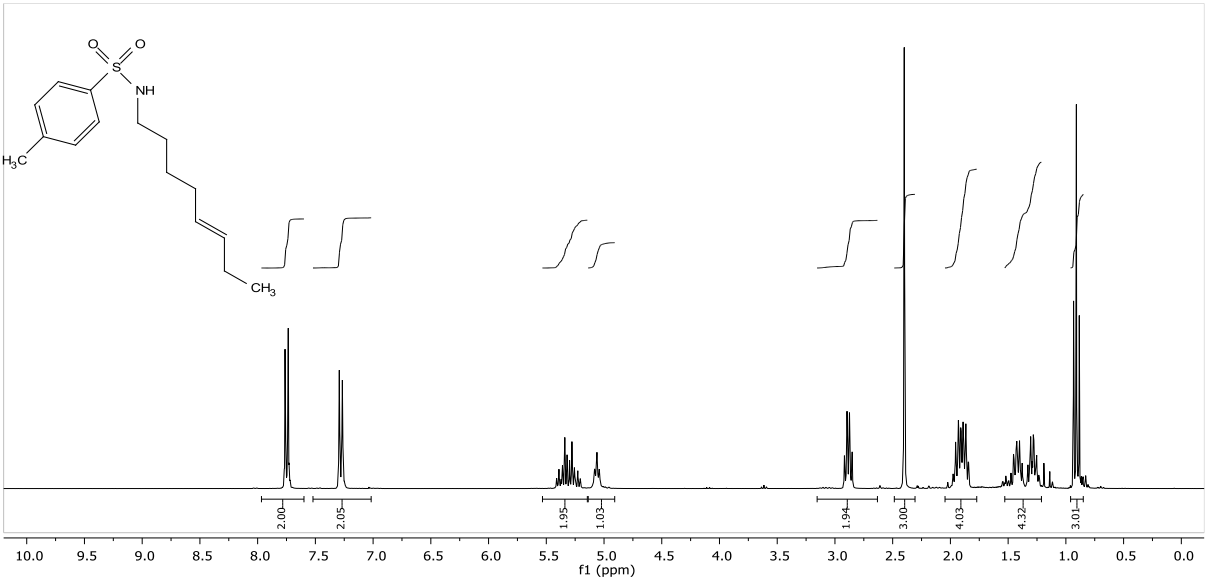
***N*-(Cyclohex-3-en-1-ylmethyl)-4-methylbenzenesulfonamide (139e):** ^{1}H, ^{13}C NMR in $CDCl_3$, IR

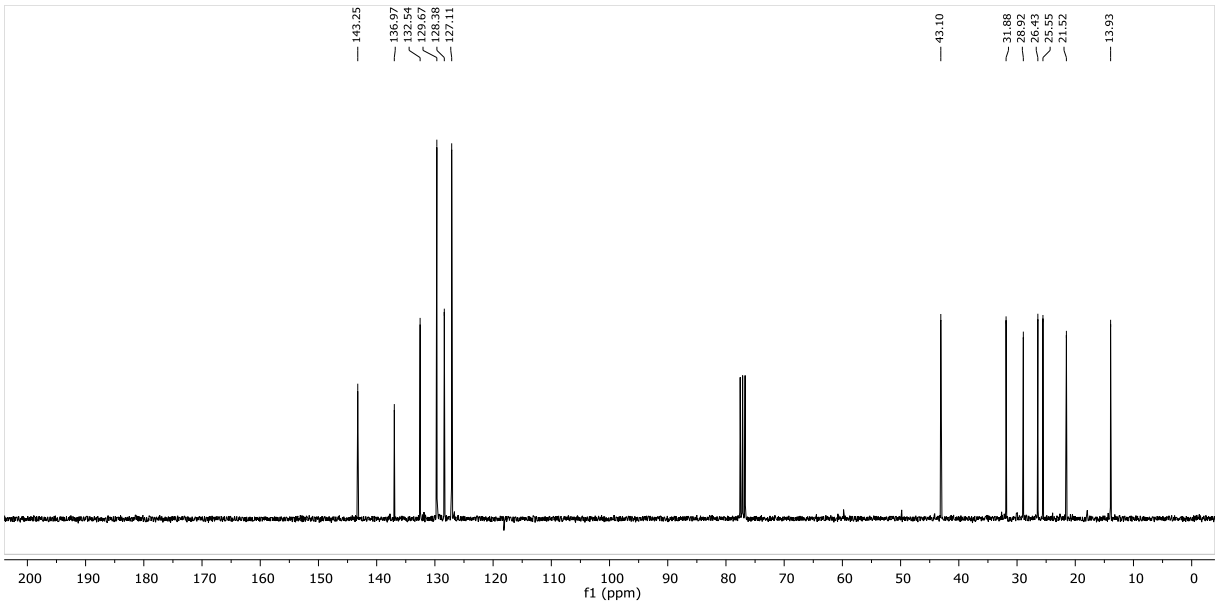


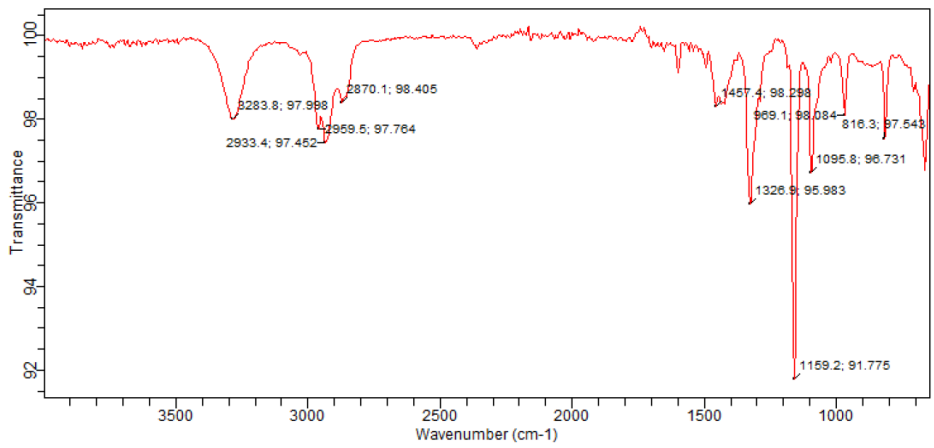




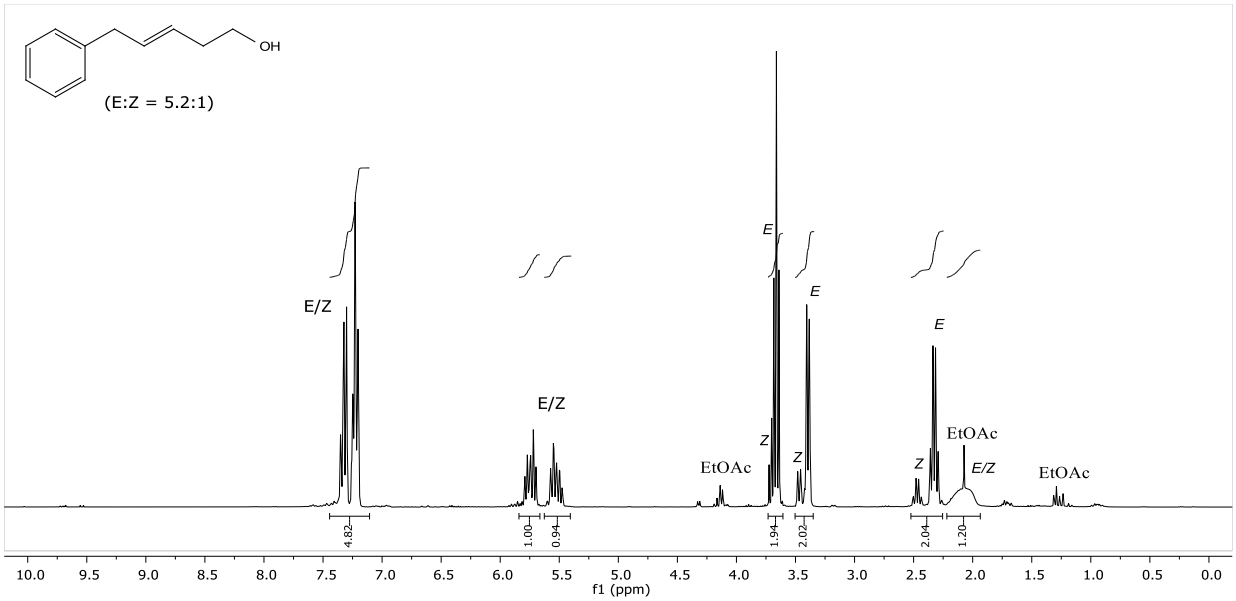
(*E*)-4-Methyl-*N*-(oct-5-en-1-yl)benzenesulfonamide (147a): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

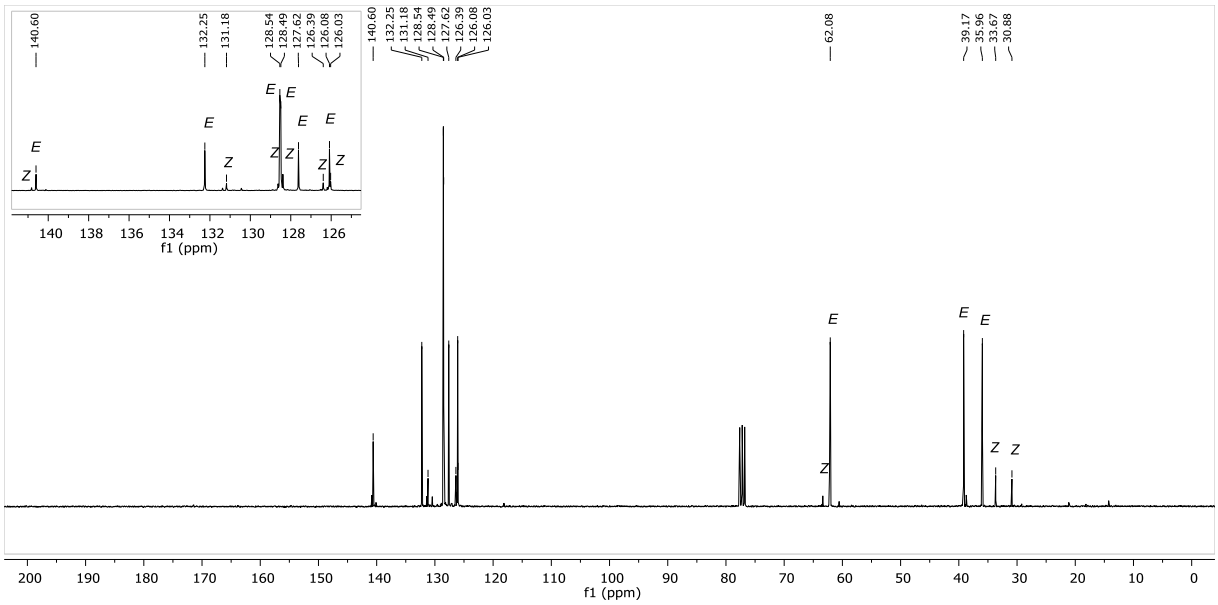


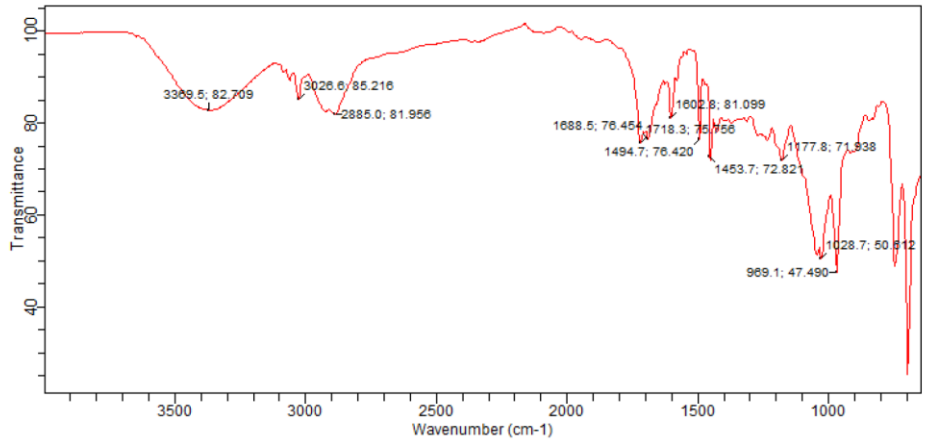




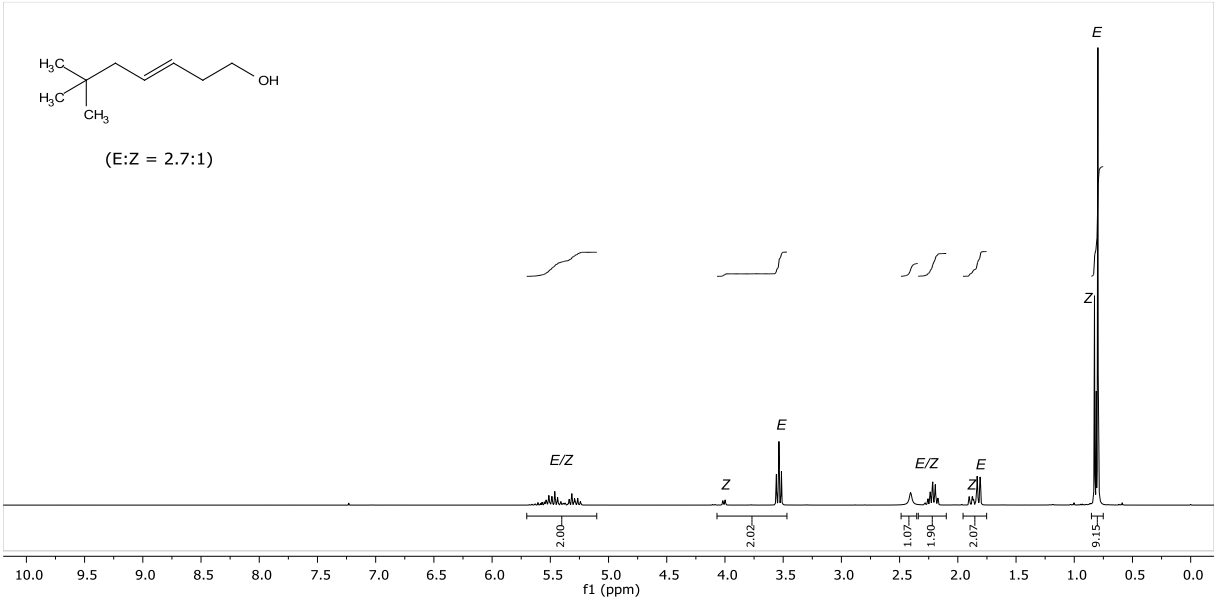
5-Phenylpent-3-en-1-ol (157a): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

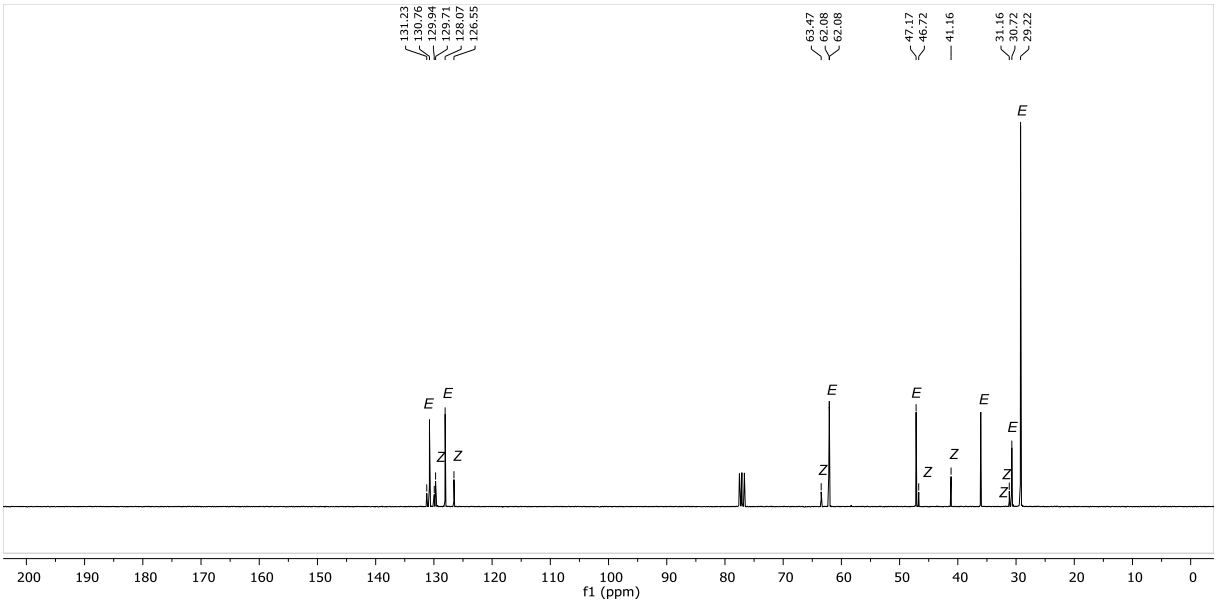


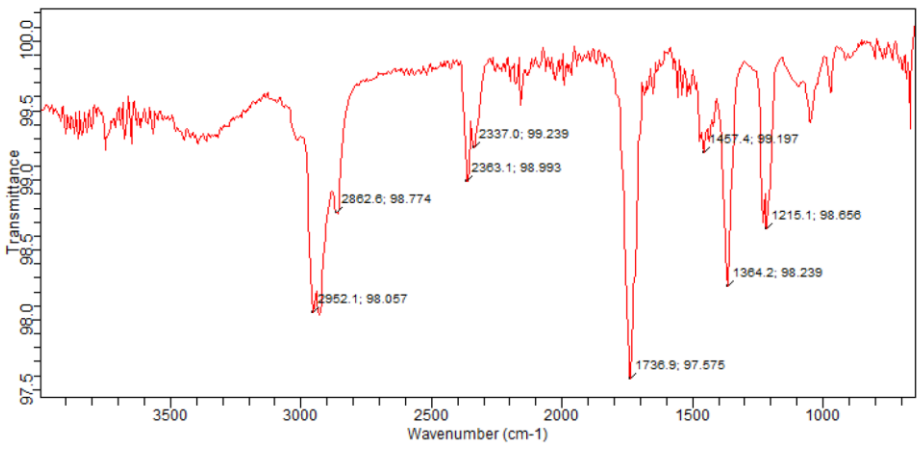




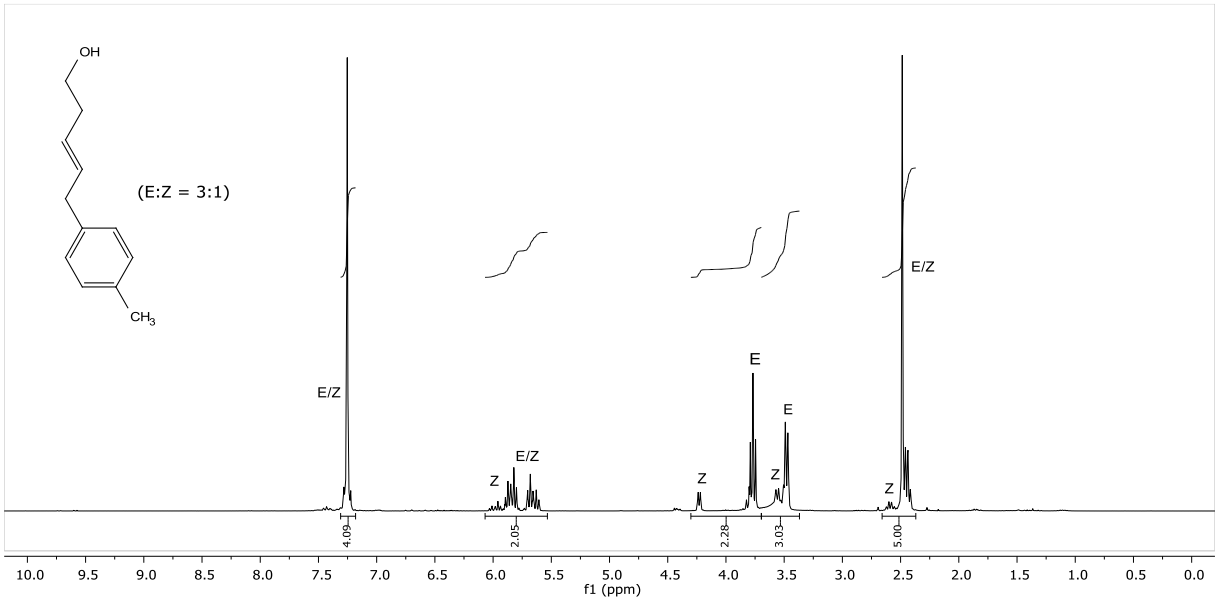
6,6-Dimethylhept-3-en-1-ol (157b): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

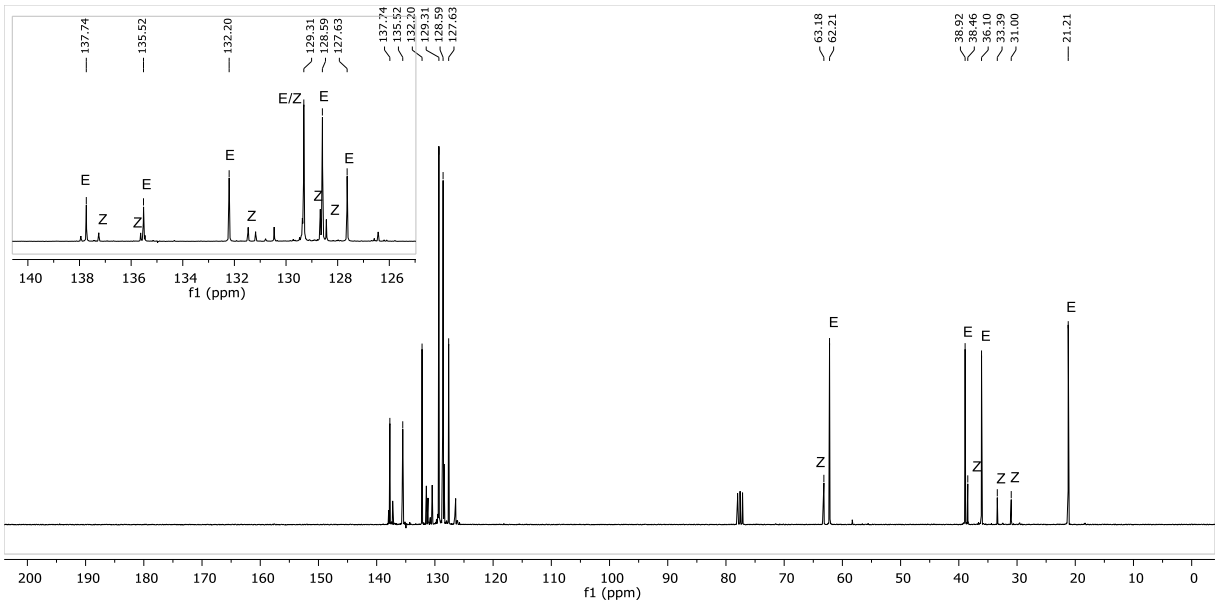


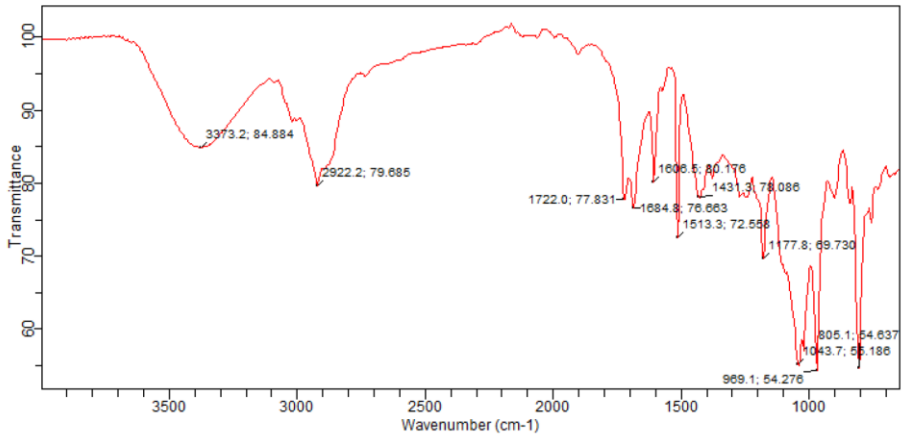




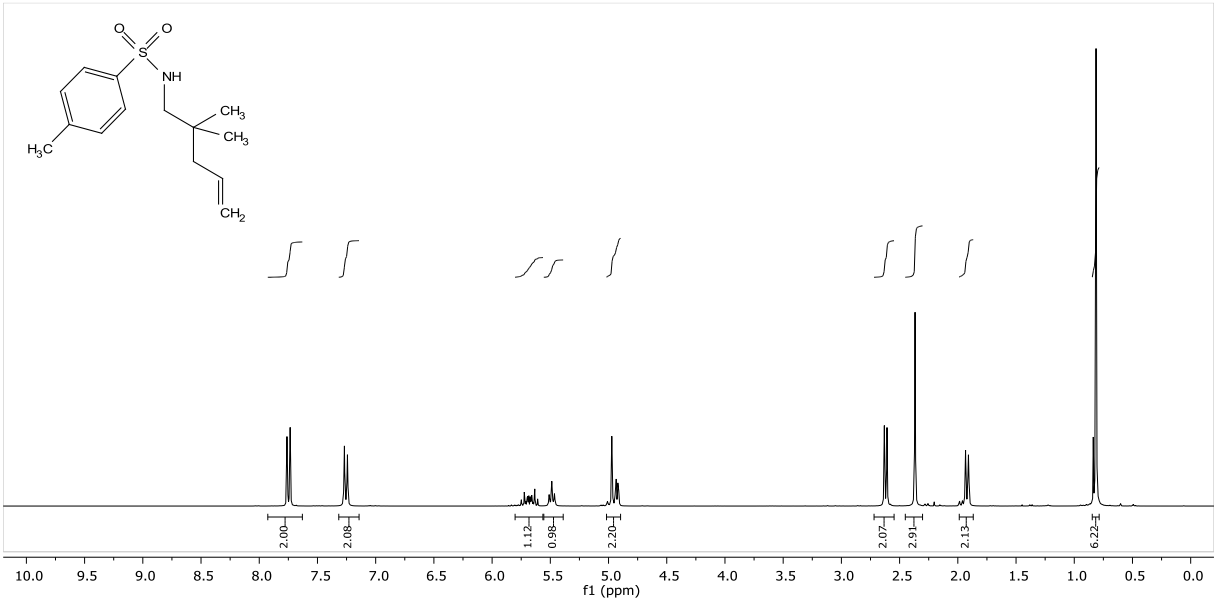
5-(*p*-Tolyl)pent-3-en-1-ol (157c): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

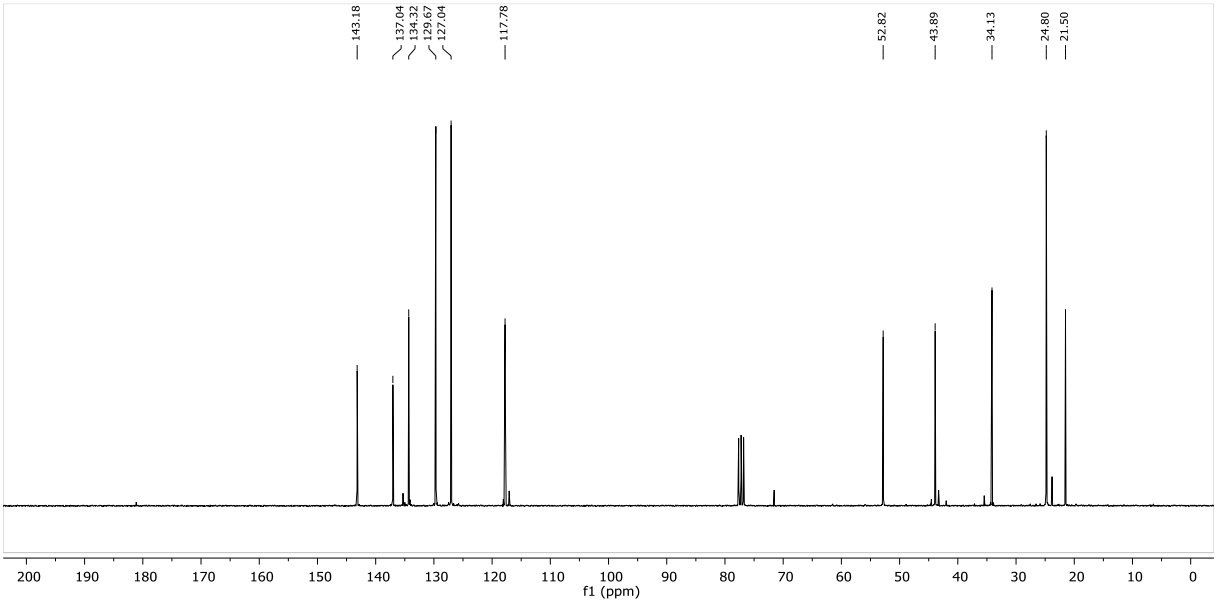


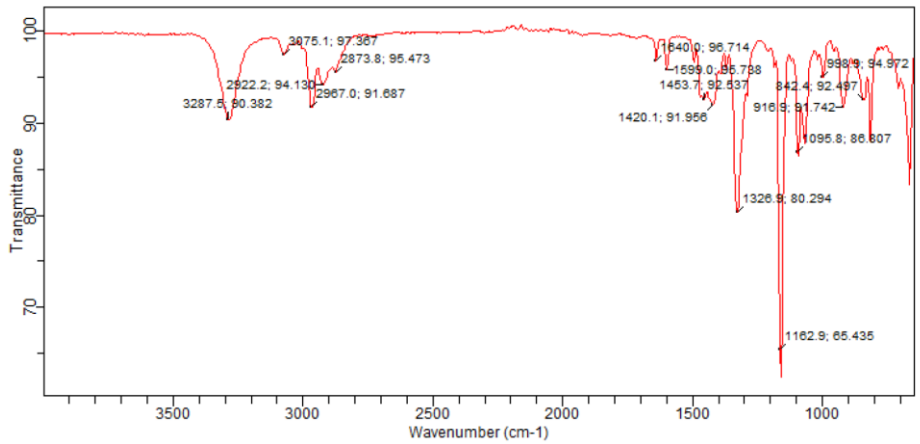




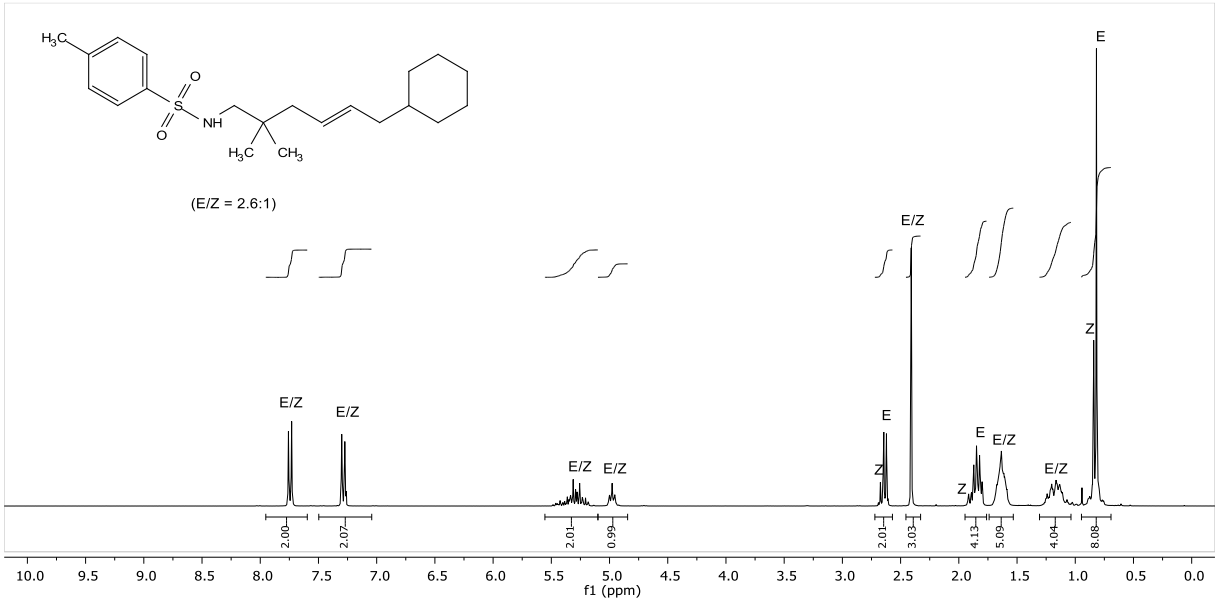
_N_-(2,2-Dimethylpent-4-en-1-yl)-4-methylbenzenesulfonamide (167): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

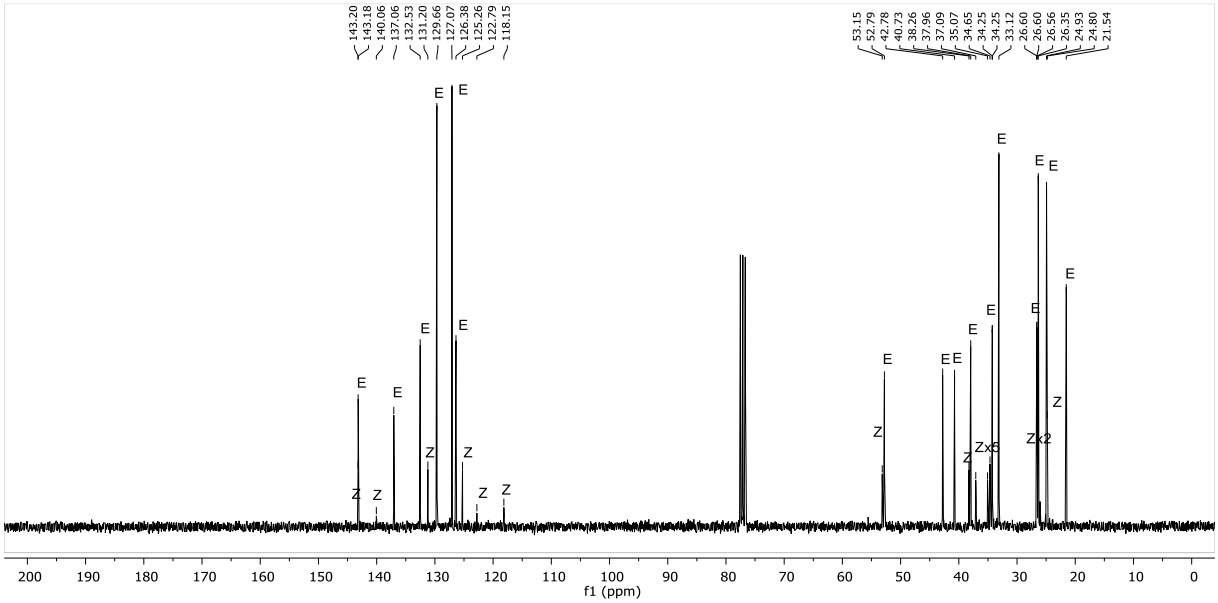


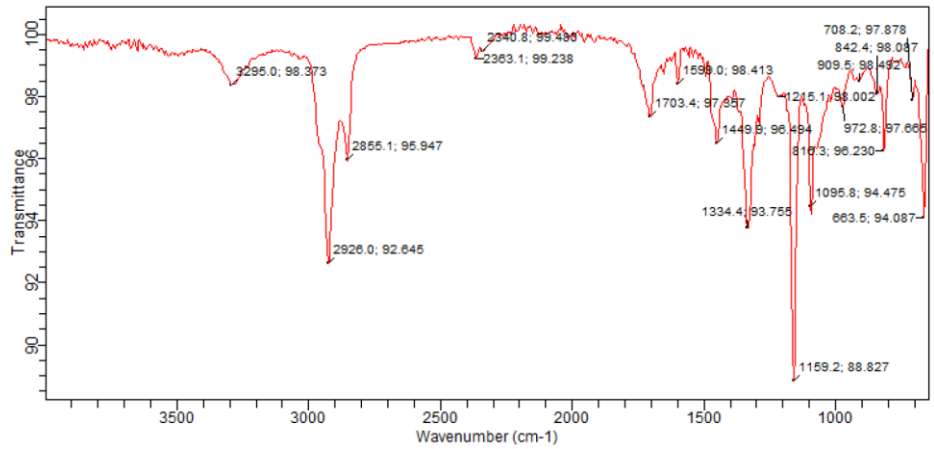




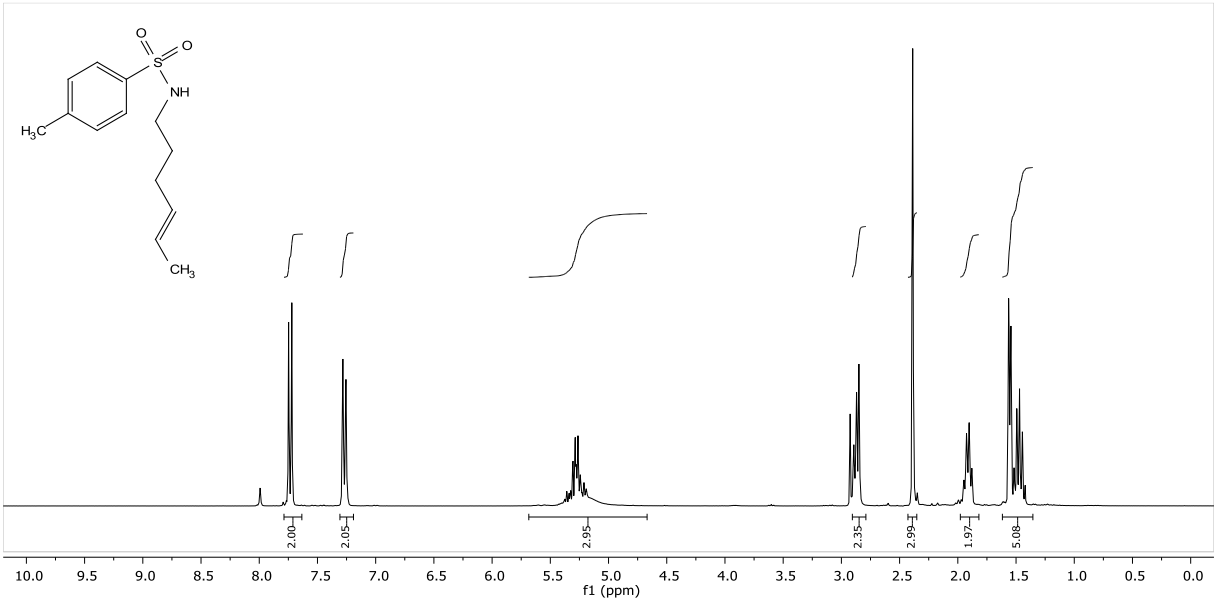
_N_-(6-Cyclohexyl-2,2-dimethylhex-4-en-1-yl)-4-methylbenzenesulfonamide (139c): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

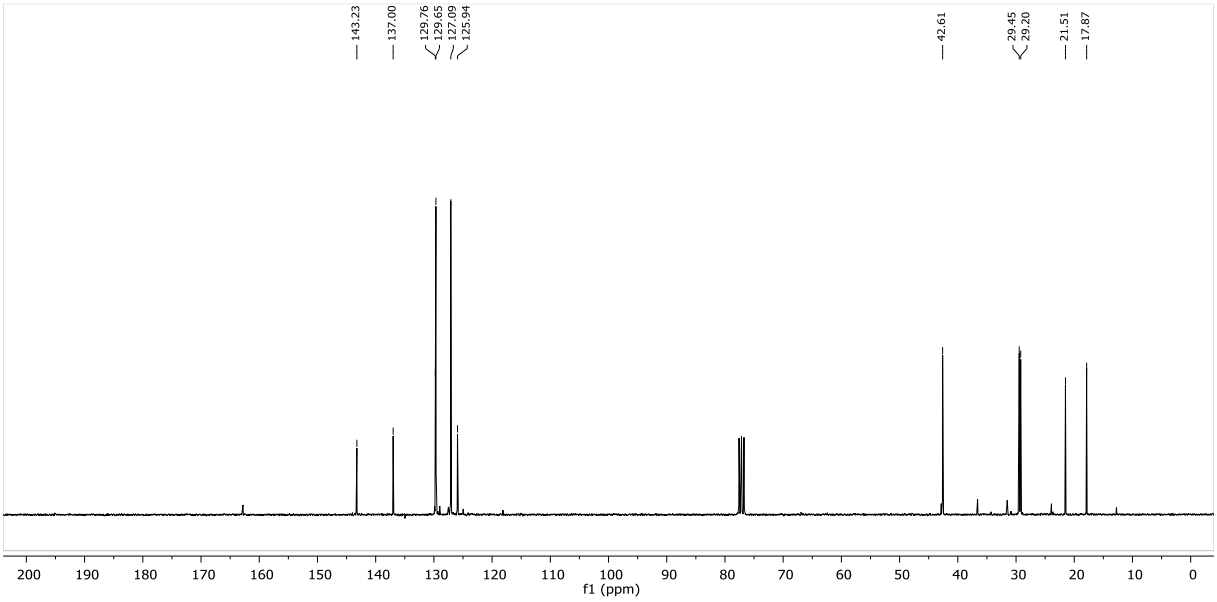


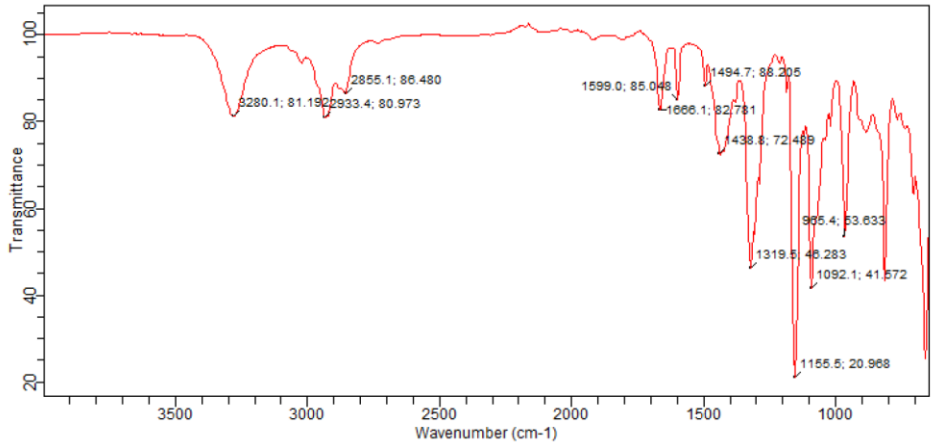




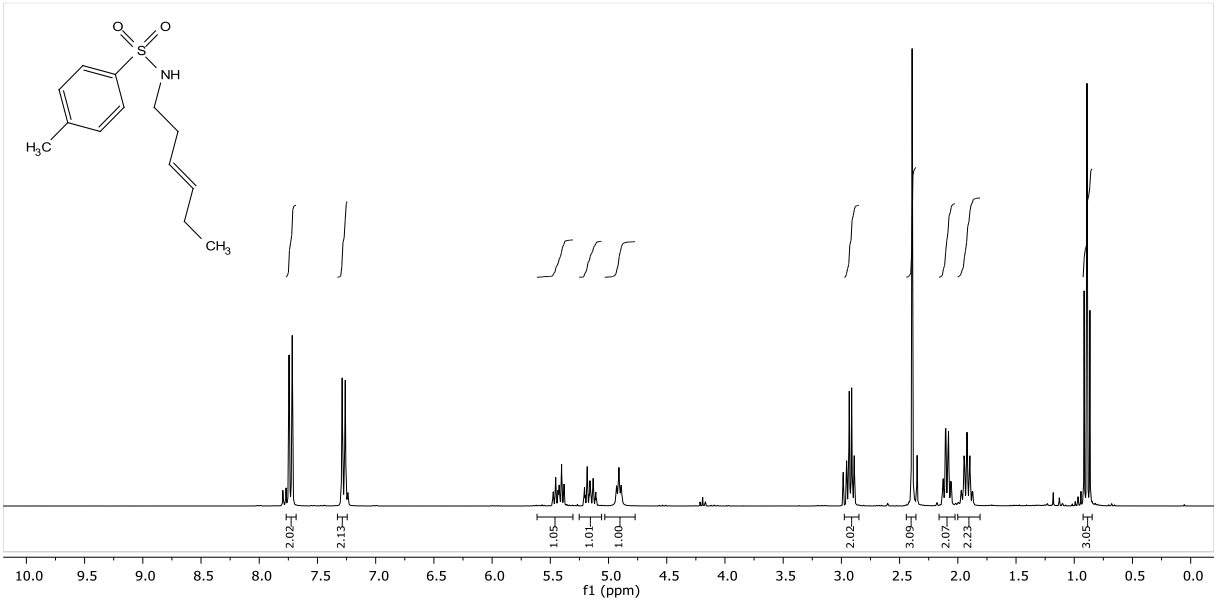
(*E*)-*N*-(Hex-4-en-1-yl)-4-methylbenzenesulfonamide (139d): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

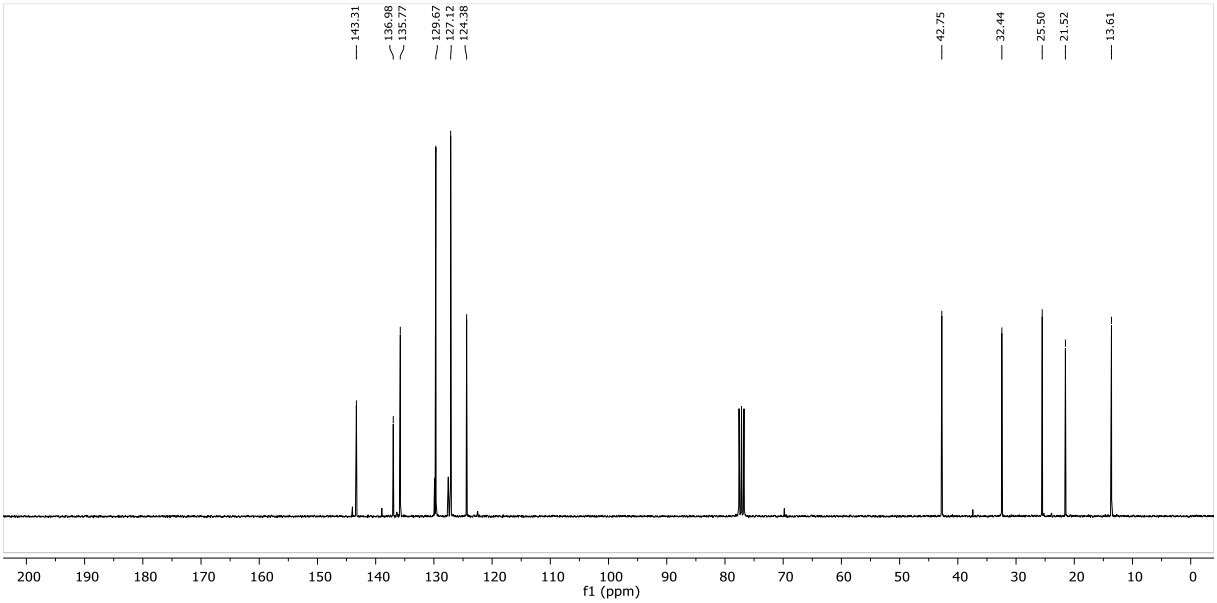


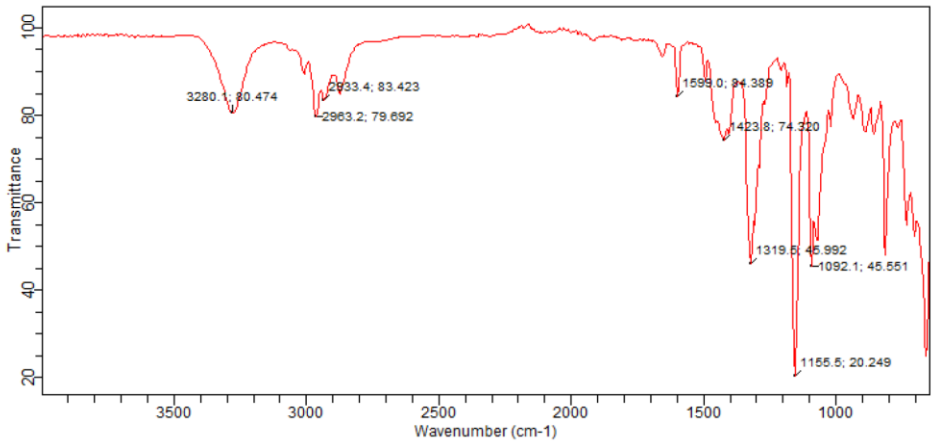




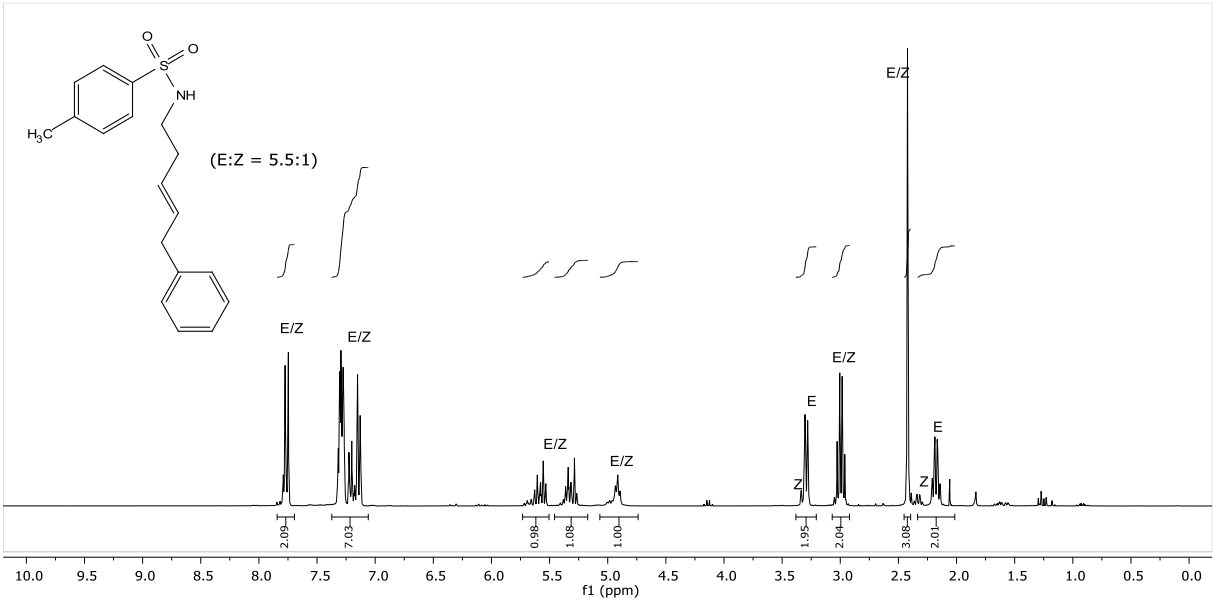
(*E*)-*N*-(Hex-3-en-1-yl)-4-methylbenzenesulfonamide (146a): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

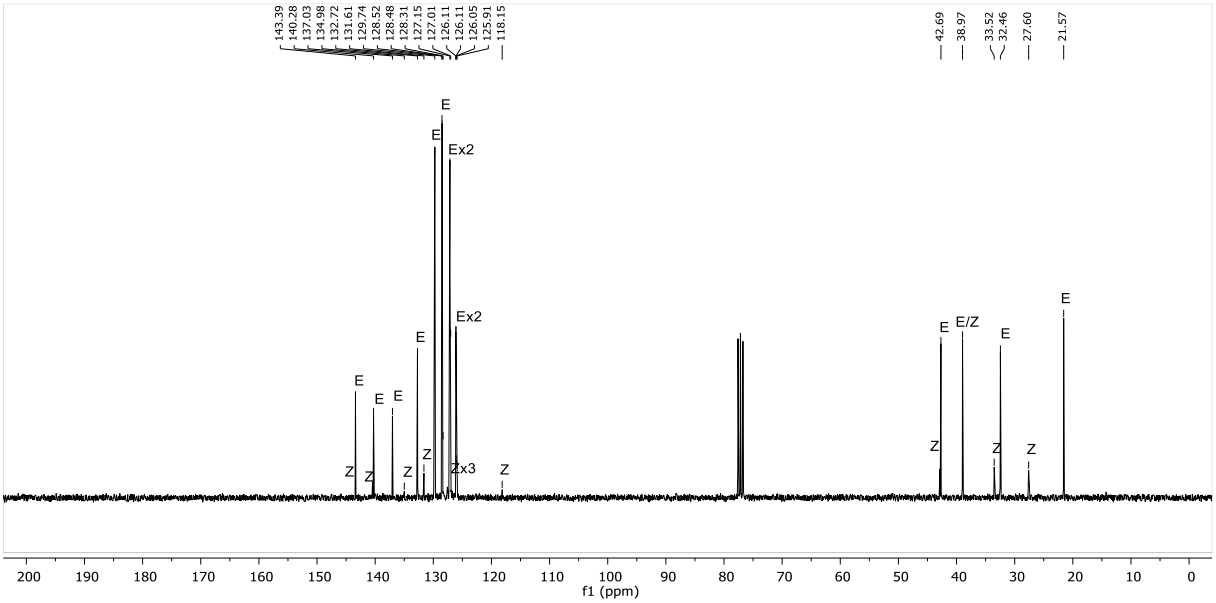


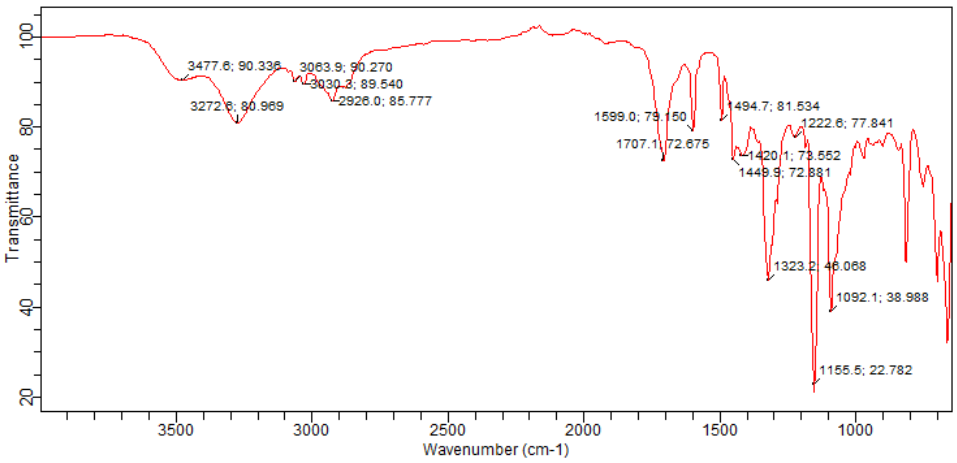




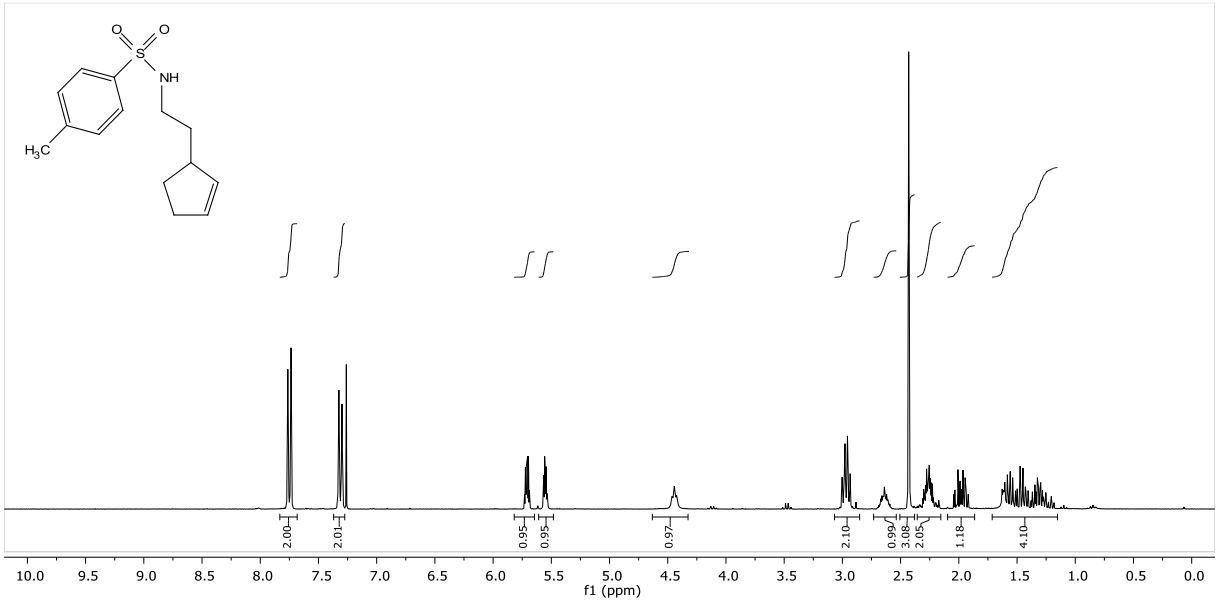
4-Methyl-*N*-(5-phenylpent-3-en-1-yl)benzenesulfonamide (146j): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

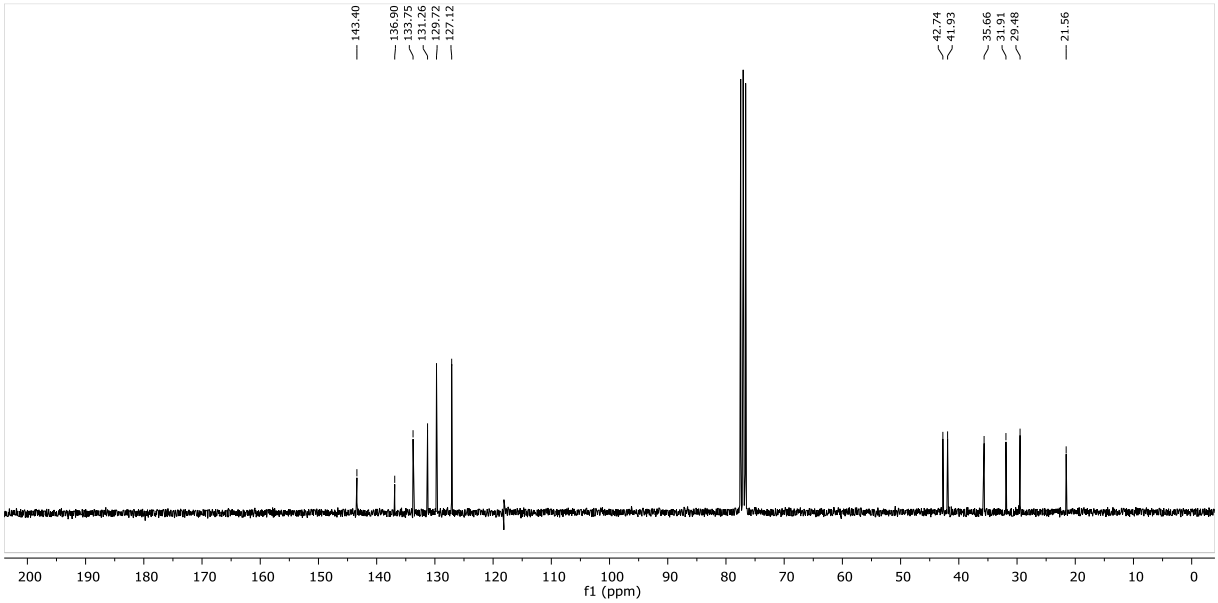


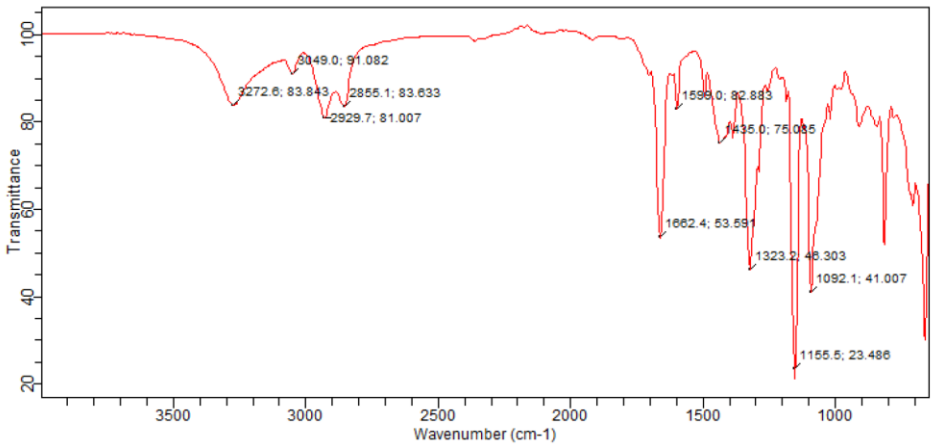




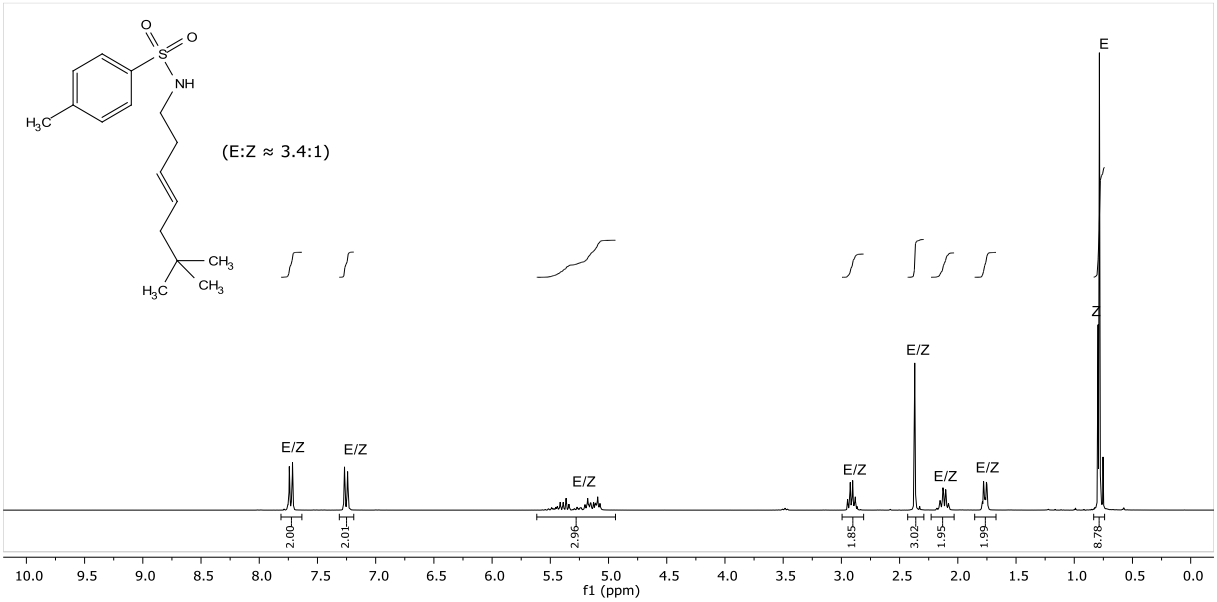
_N_-(Cyclopent-2-en-1-ylmethyl)-4-methylbenzenesulfonamide (139b): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

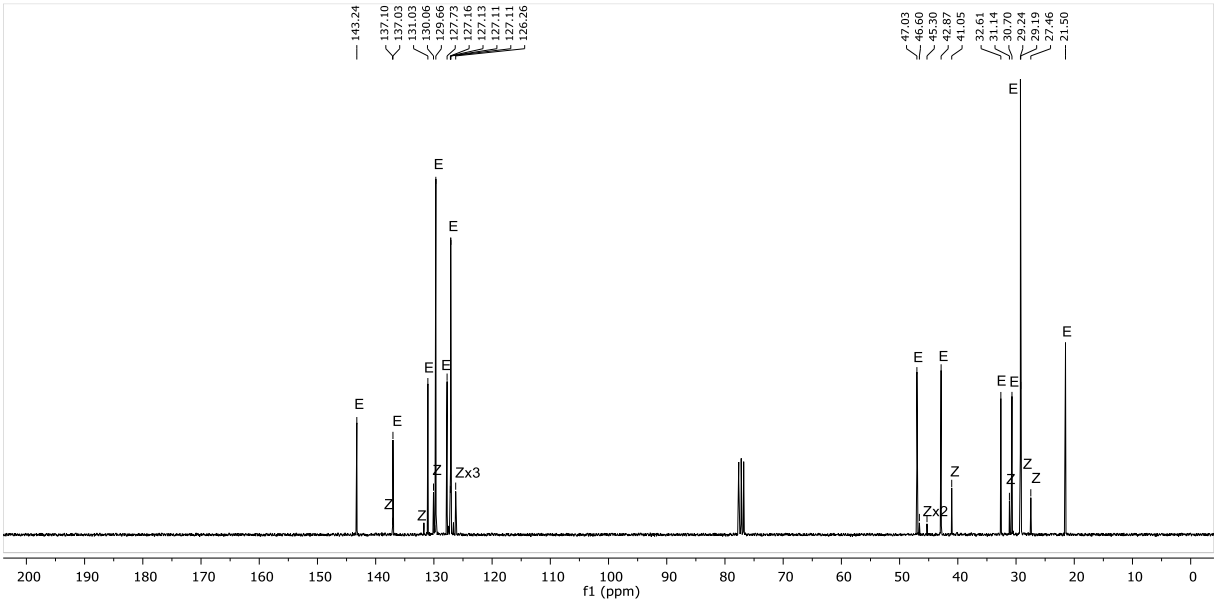


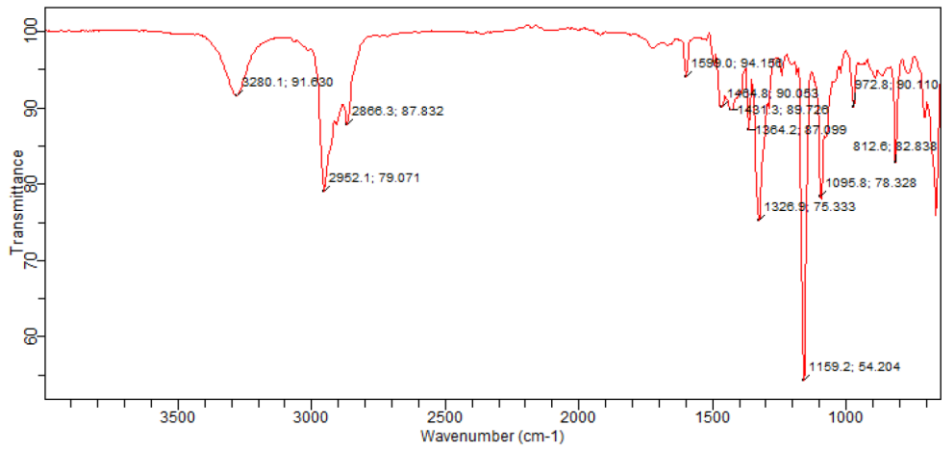




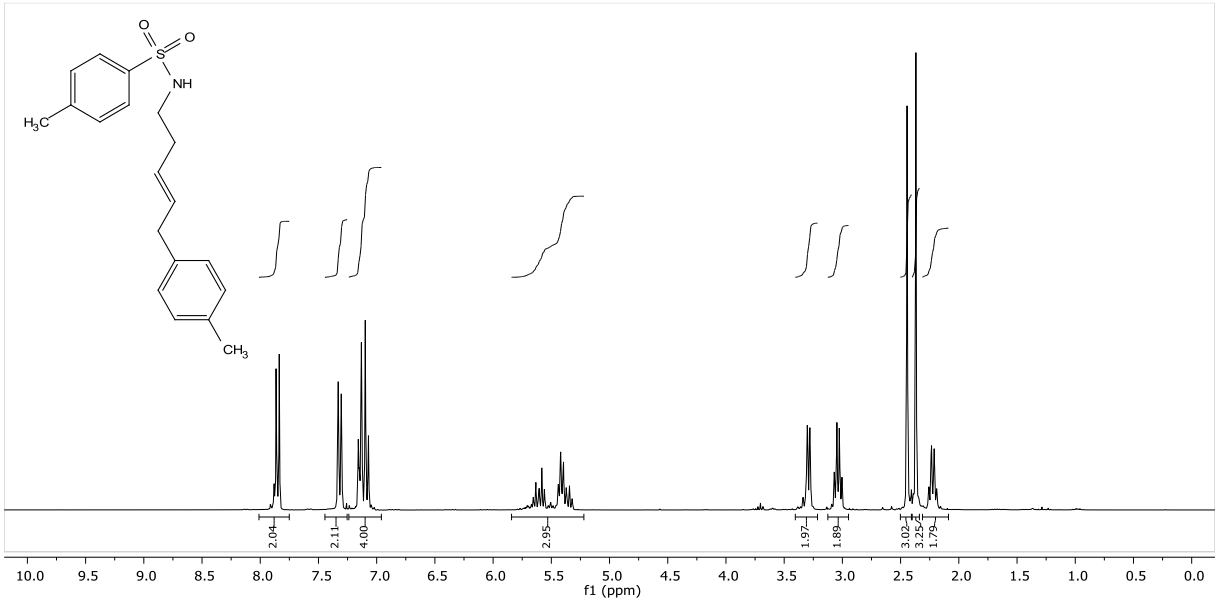
_N_-(6,6-Dimethylhept-3-en-1-yl)-4-methylbenzenesulfonamide (146k): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

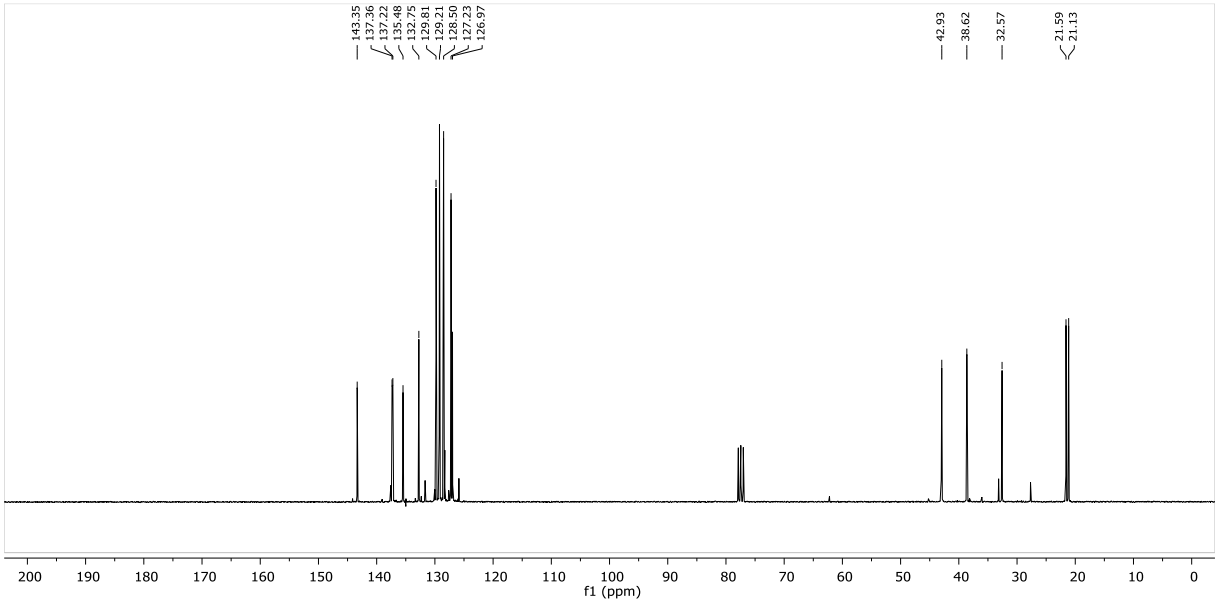


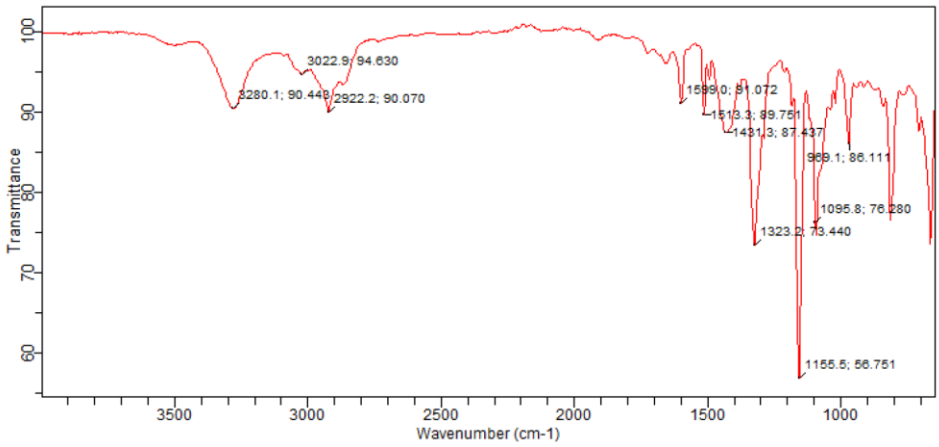




(*E*)-4-Methyl-*N*-(5-(*p*-tolyl)pent-3-en-1-yl)benzenesulfonamide (146l): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

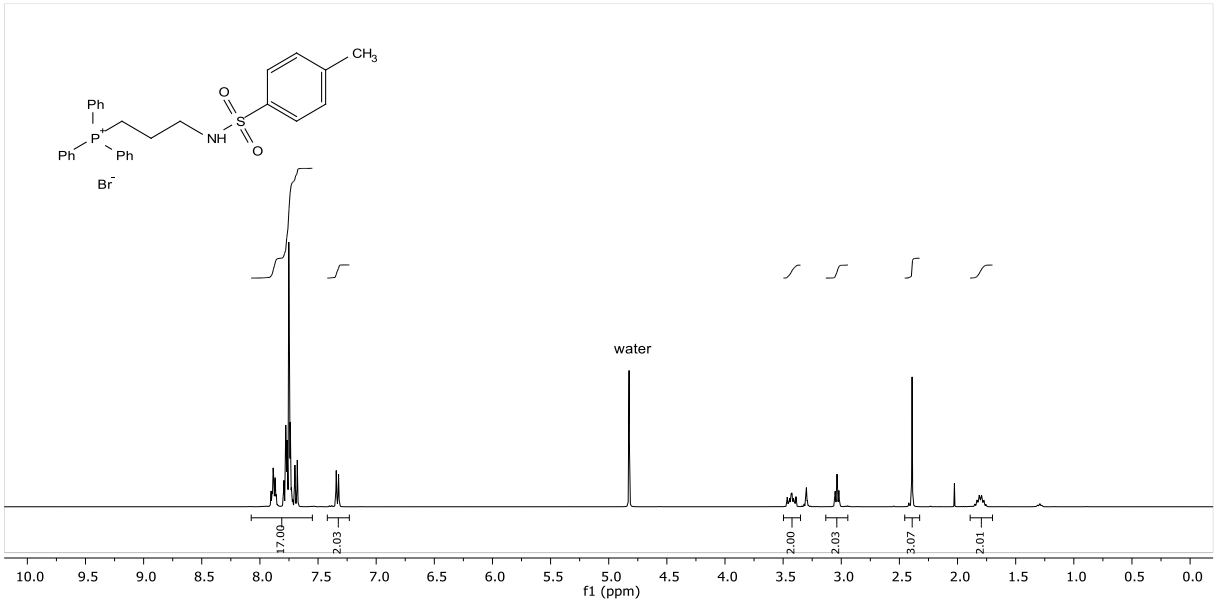


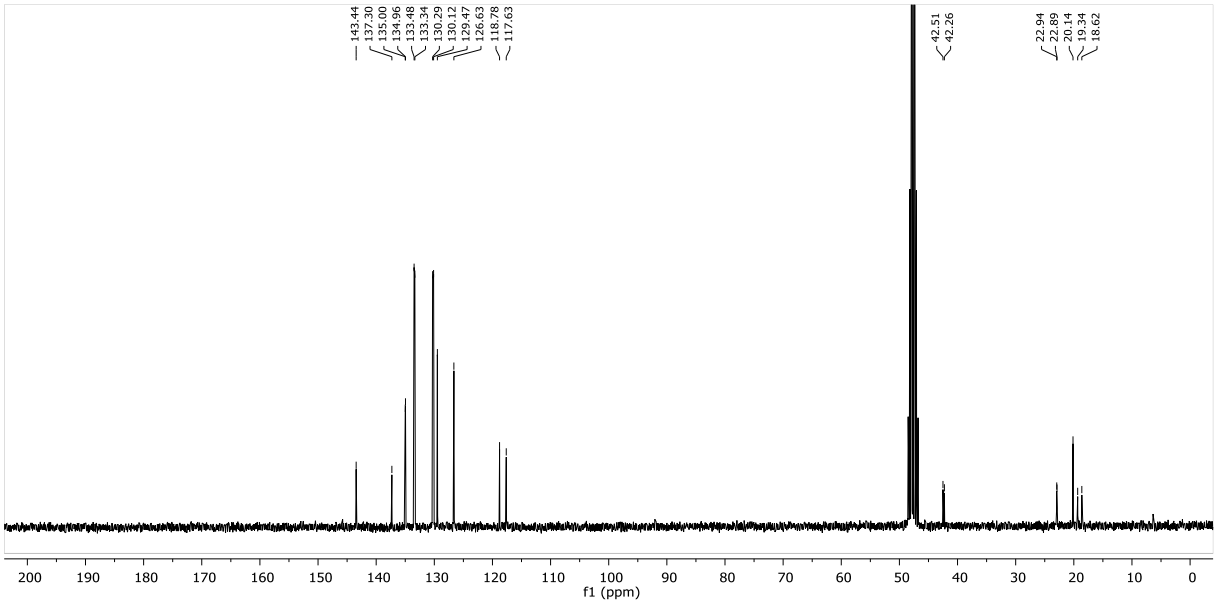


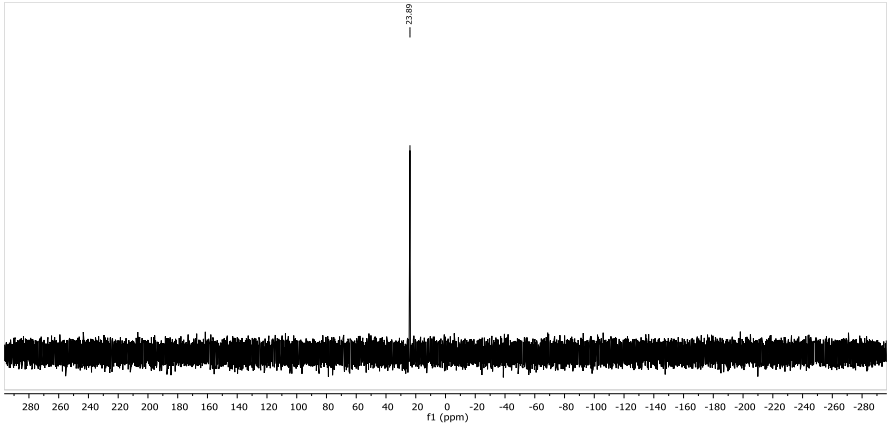


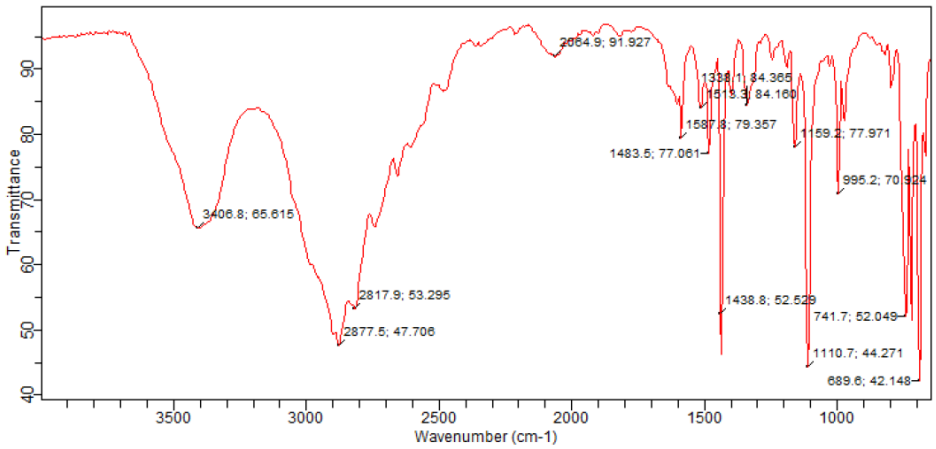
(3-((4-Methylphenyl)sulfonamido)propyl)triphenylphosphonium bromide (153):

^{1}H, ^{13}C, ^{31}P NMR in MeOD-d_3, IR

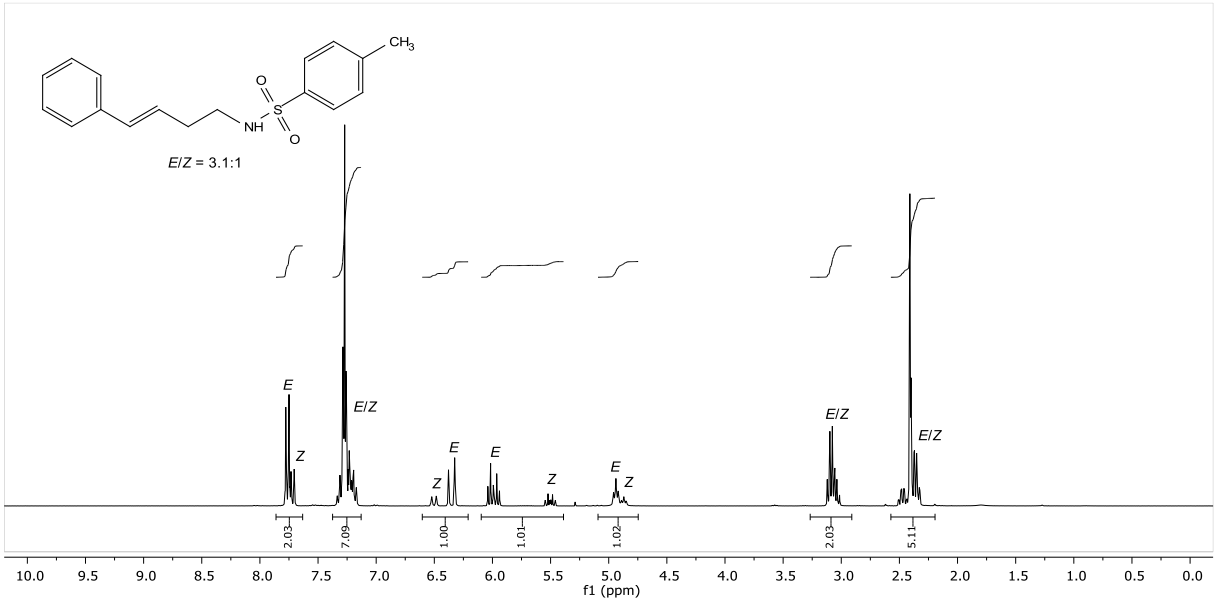


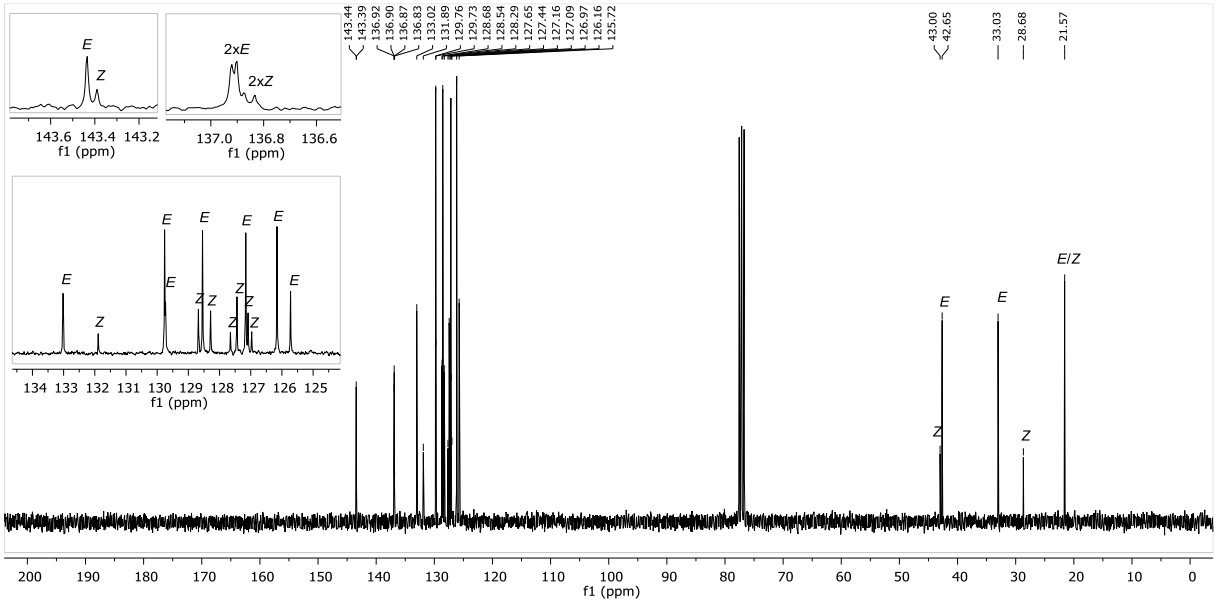


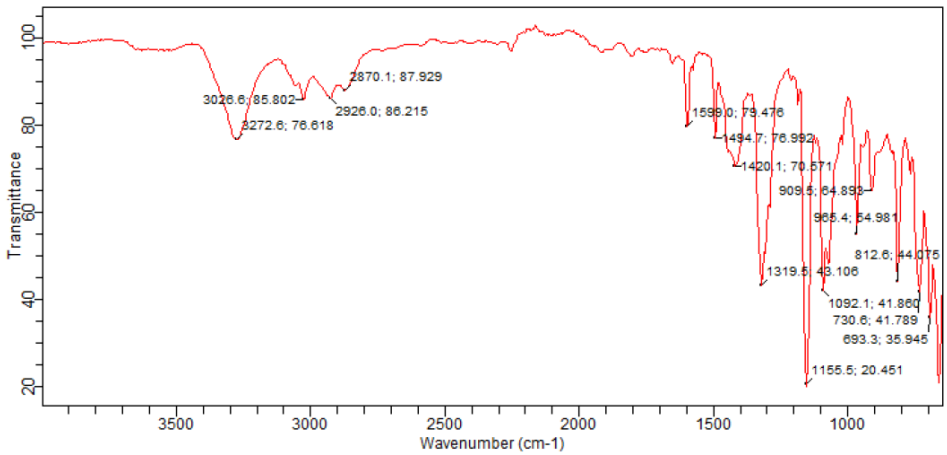



Transmittance
Wavenumber (cm-1)
3406.8; 65.615
2817.9; 53.295
2877.5; 47.706
2664.9; 91.927
1483.5; 77.061
1438.8; 52.529
741.7; 52.049
1110.7; 44.271
689.6; 42.148
995.2; 70.924

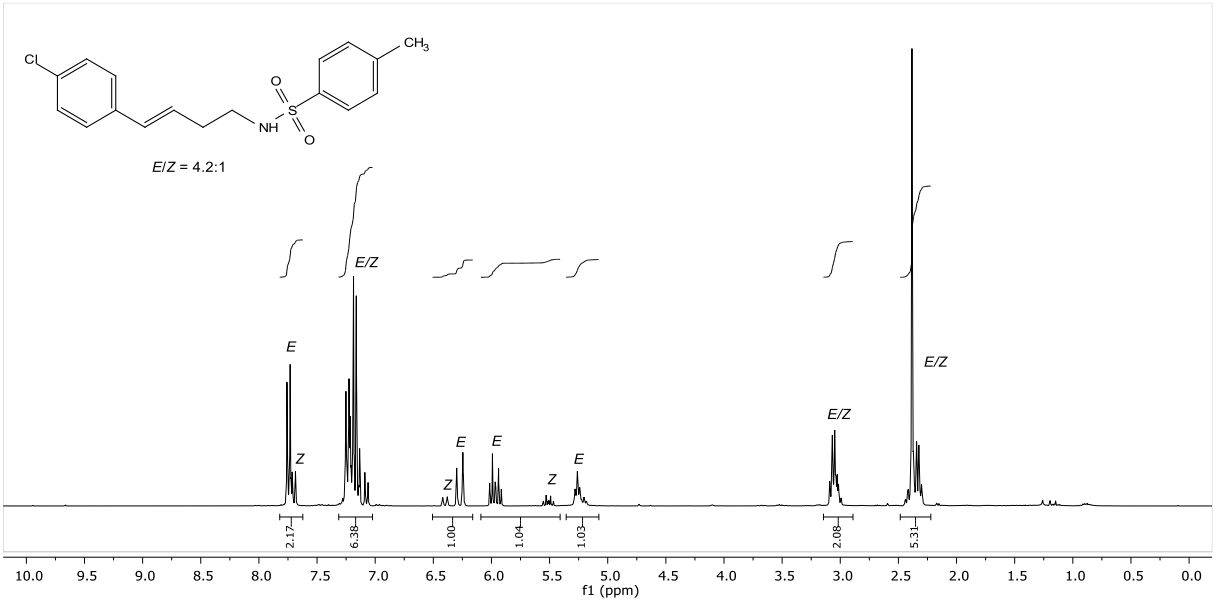
4-Methyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146b): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

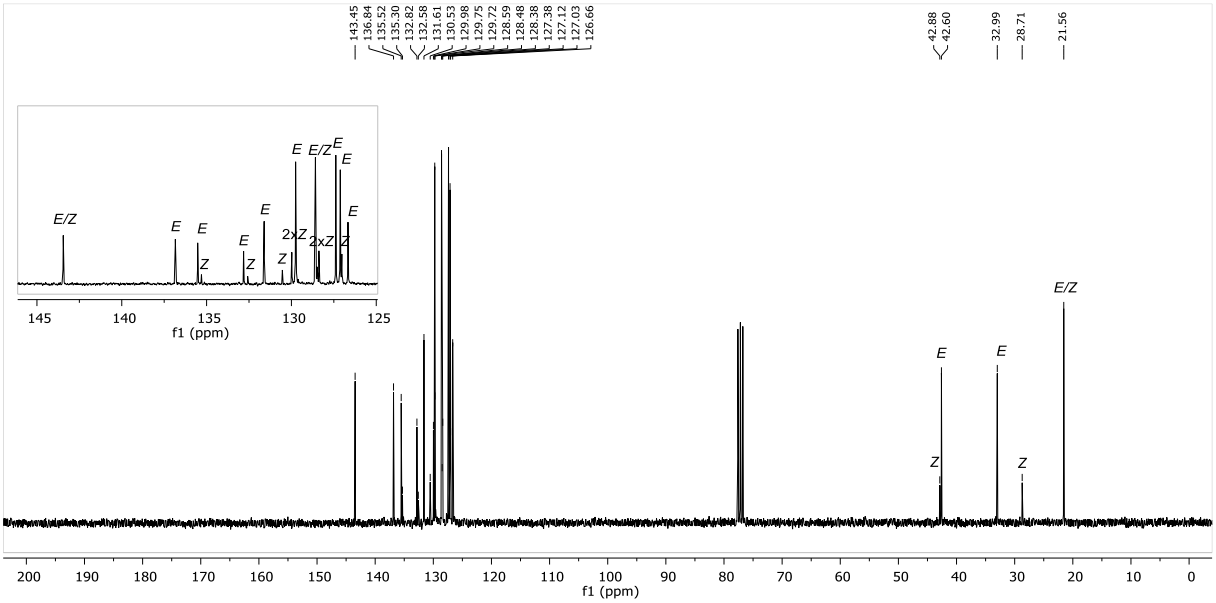


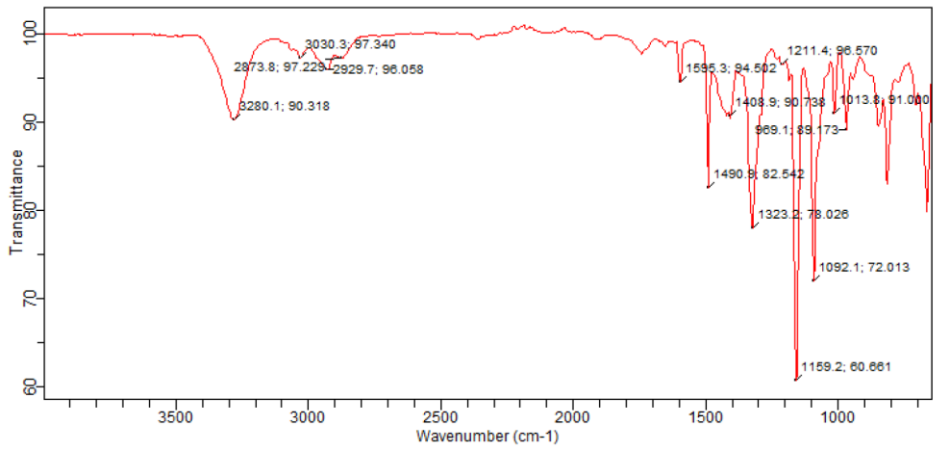




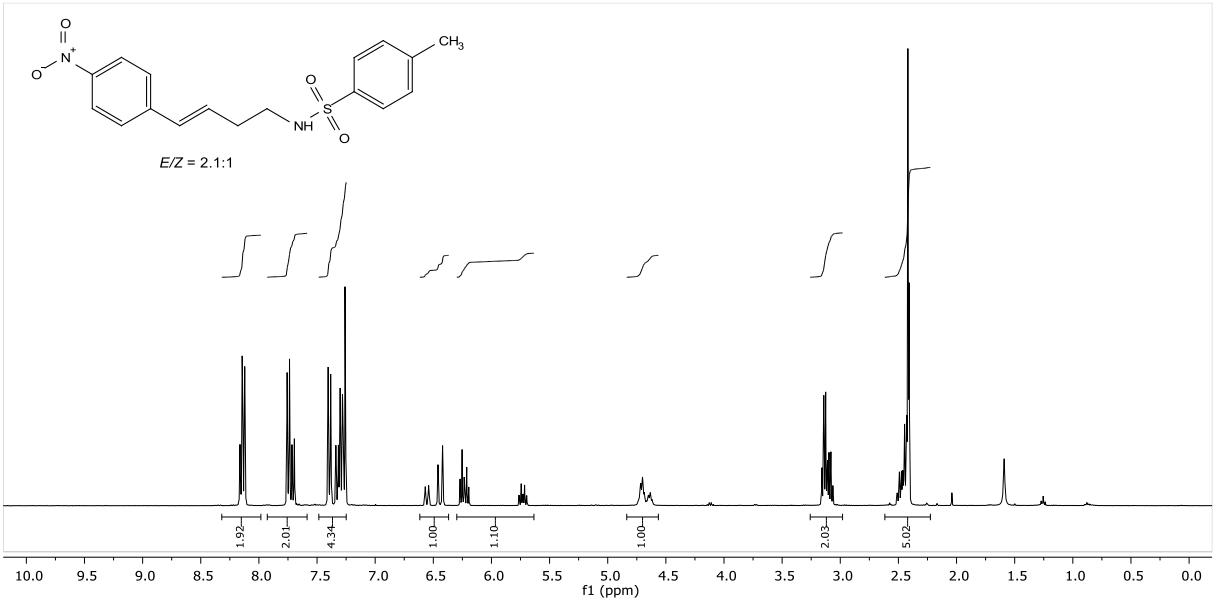
_N_-(4-(4-Chlorophenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (146c): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

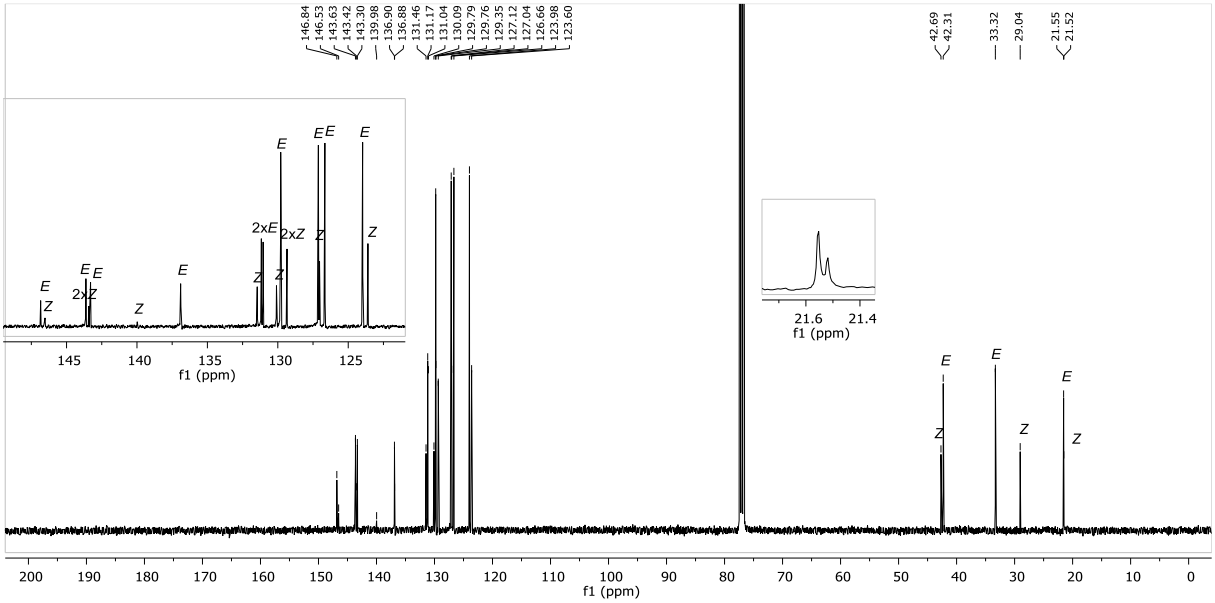


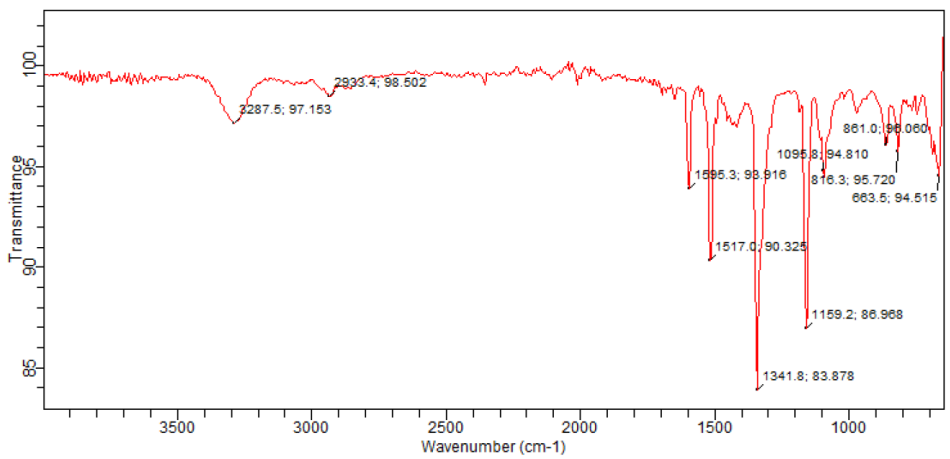




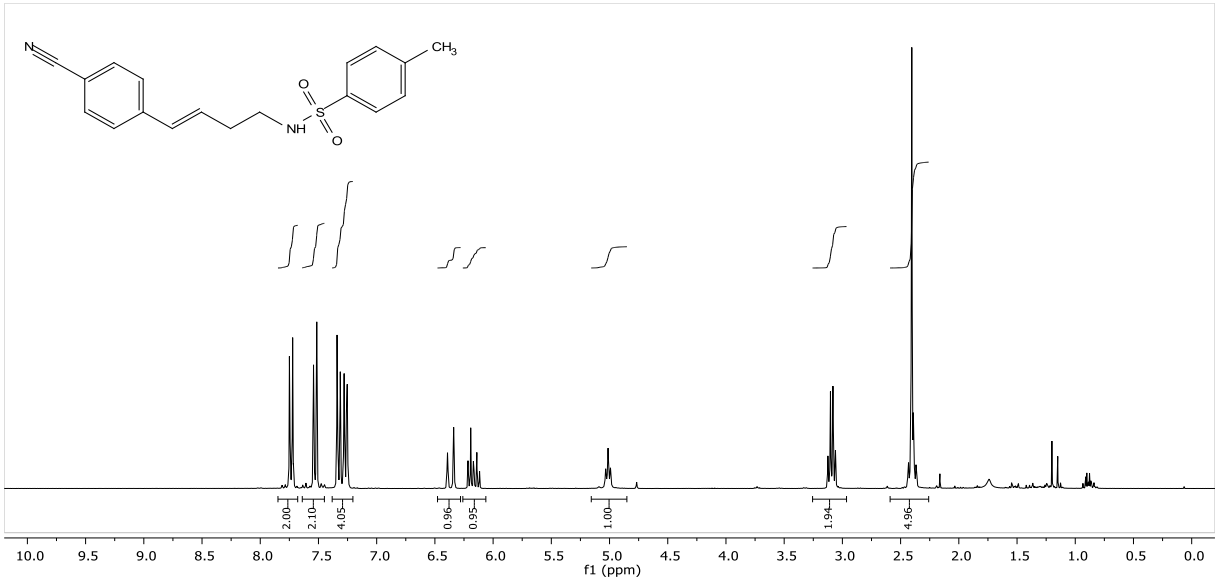
4-Methyl-*N*-(4-(4-nitrophenyl)but-3-en-1-yl)benzenesulfonamide (146d): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

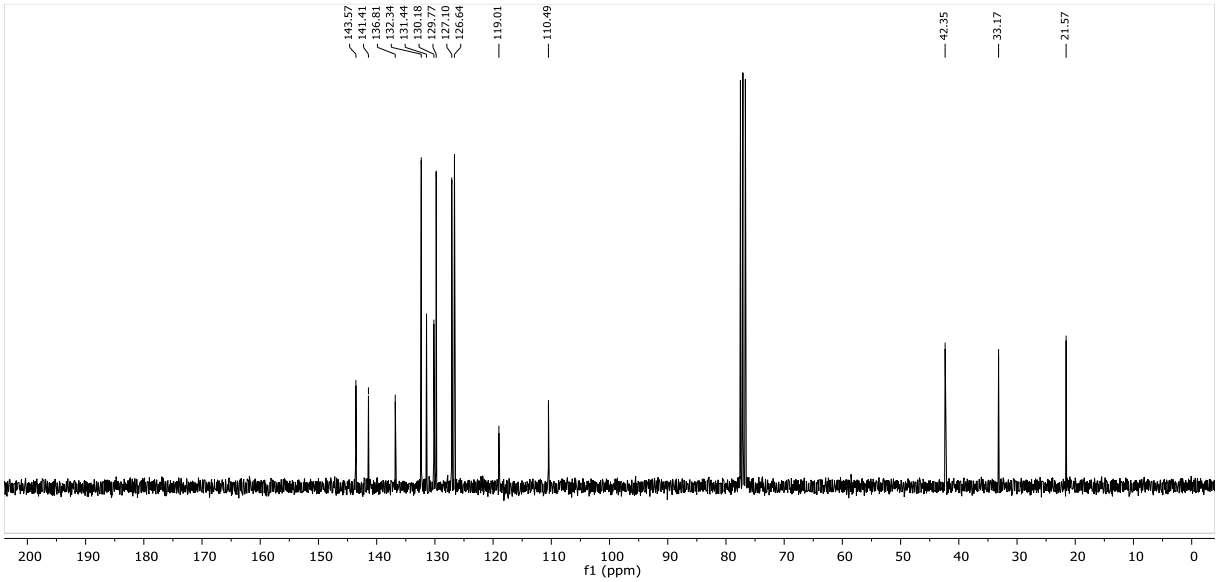


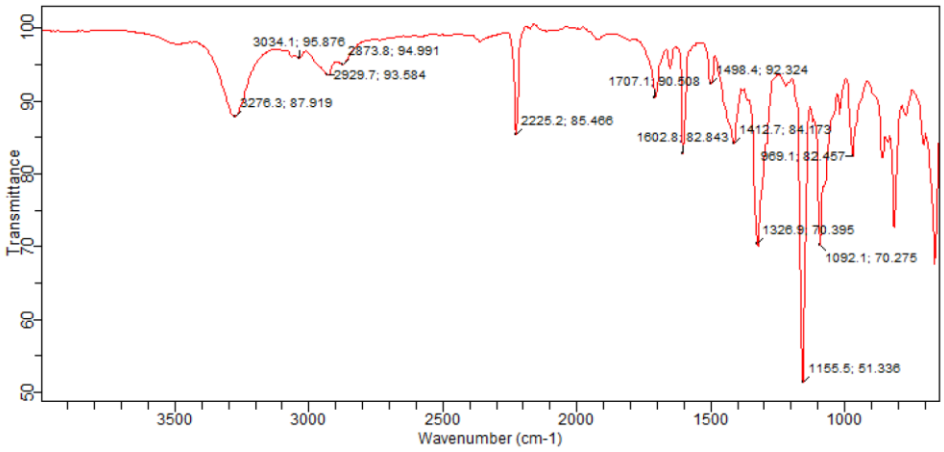




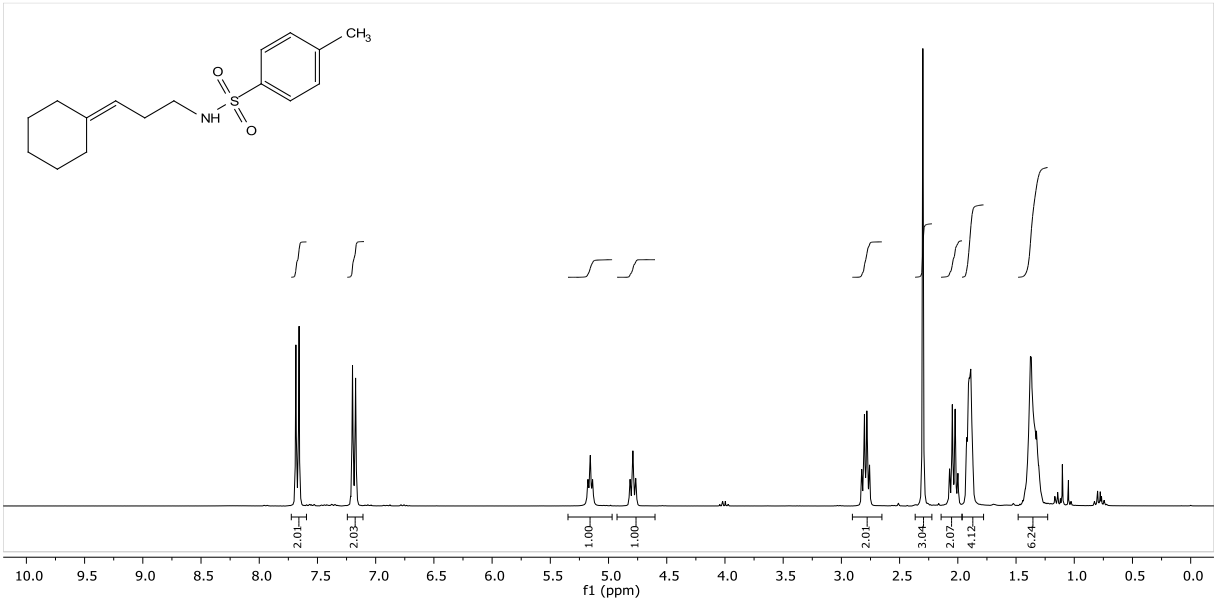
(*E*)-*N*-(4-(4-Cyanophenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (146e): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

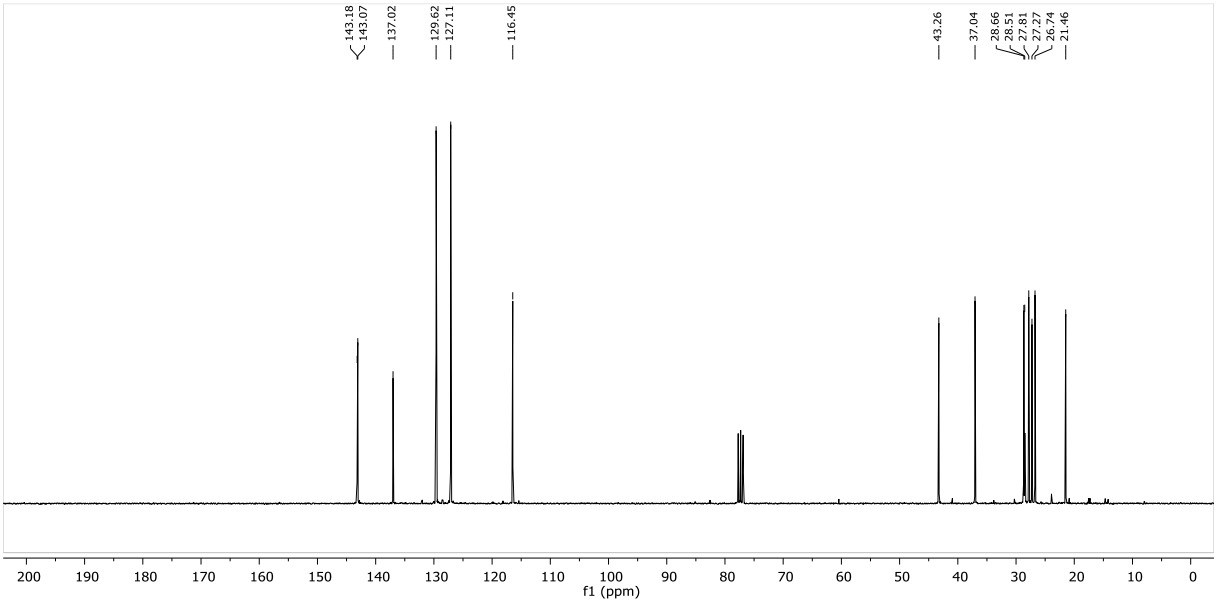


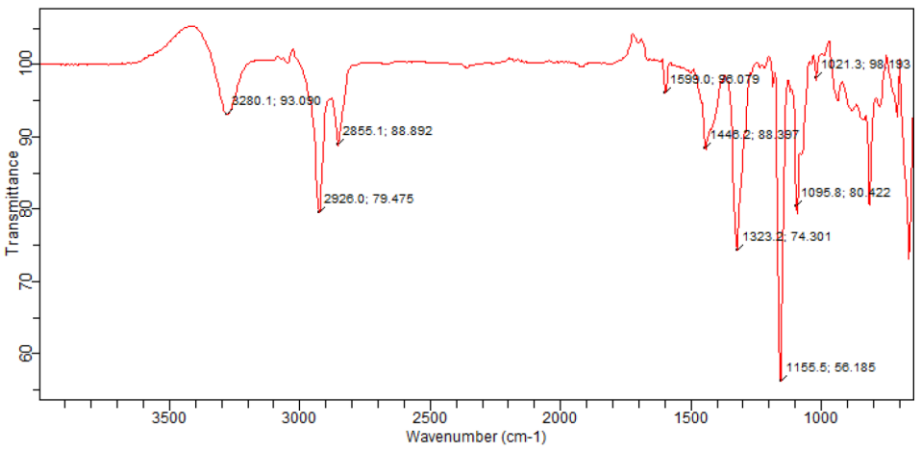




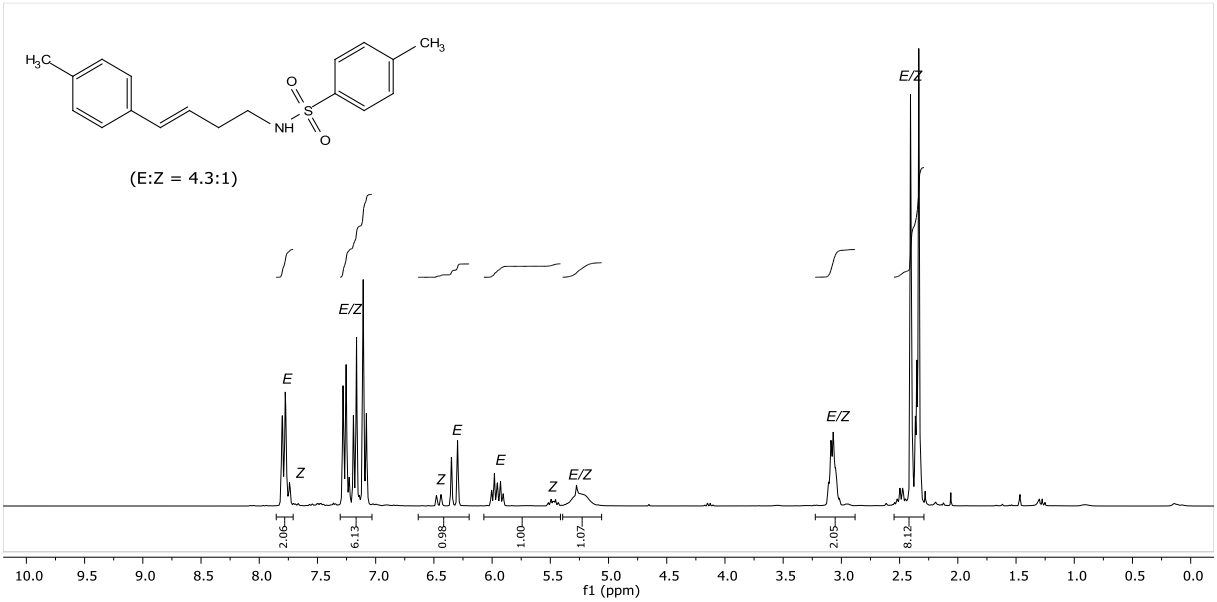
_N_-(3-Cyclohexylidenepropyl)-4-methylbenzenesulfonamide (146i): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

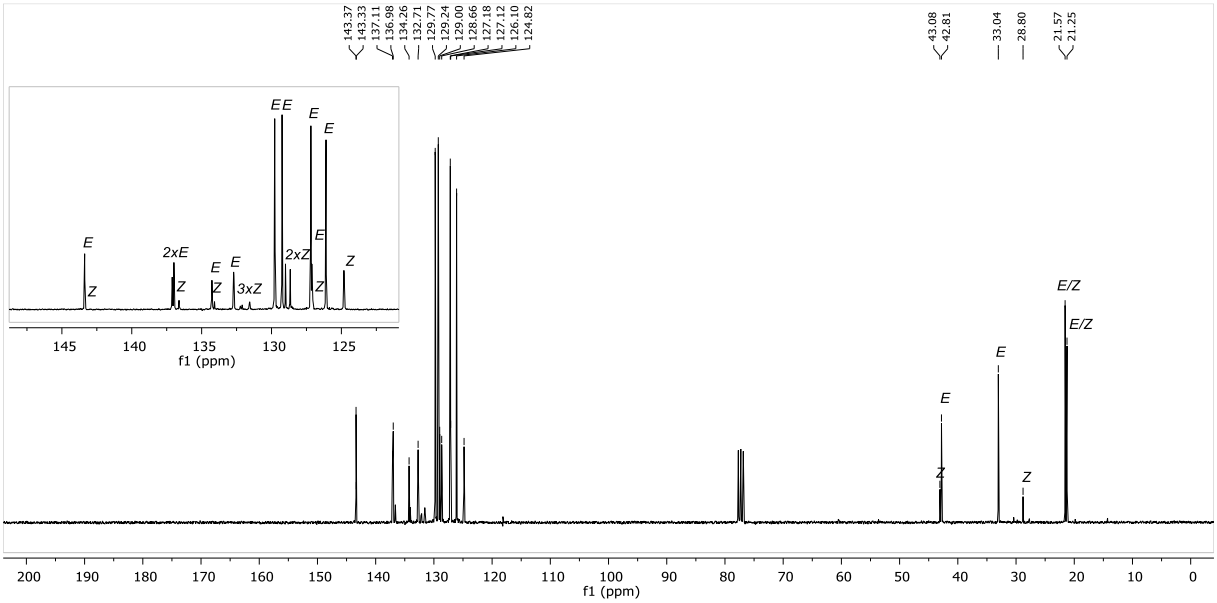


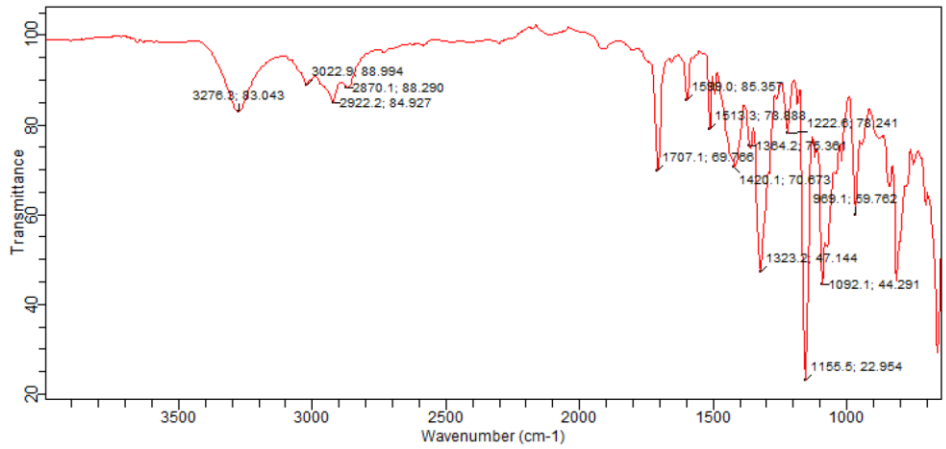




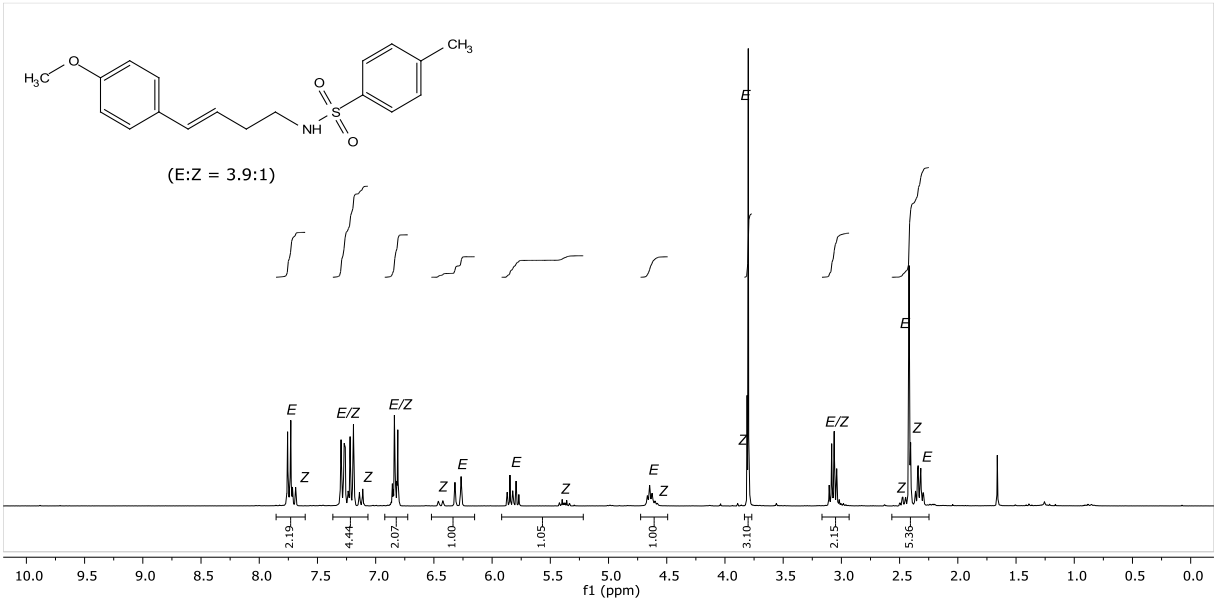
4-Methyl-*N*-(4-(*p*-tolyl)but-3-en-1-yl)benzenesulfonamide (146f): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

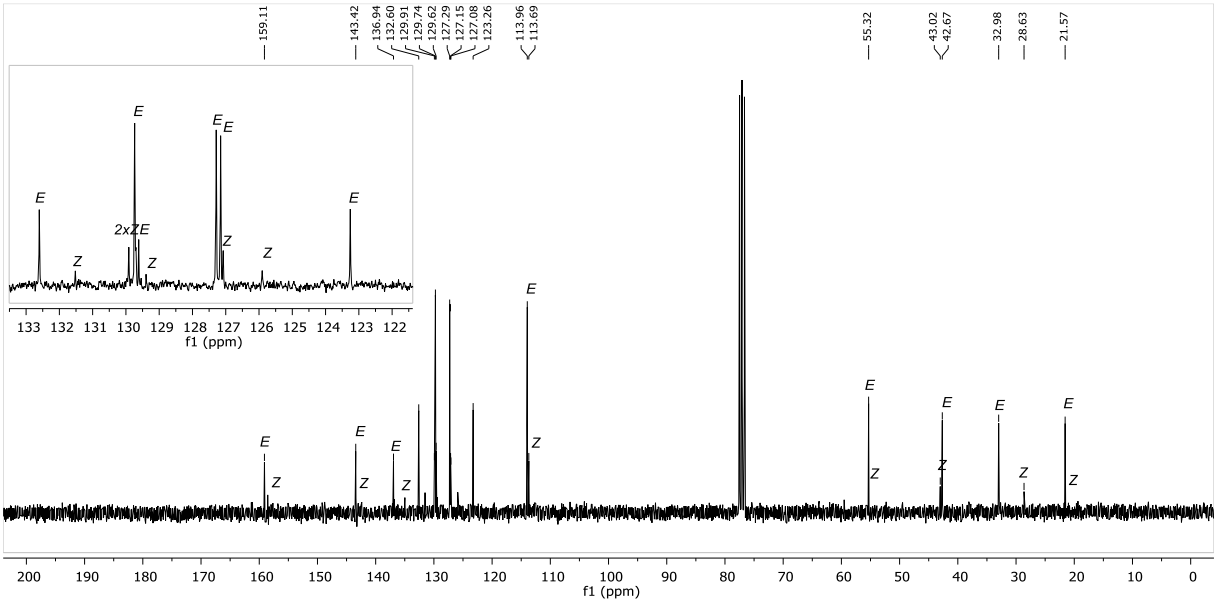


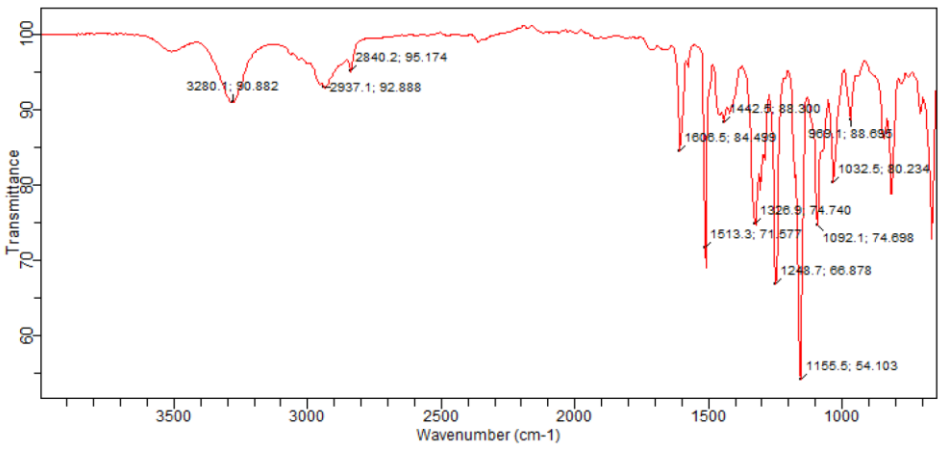




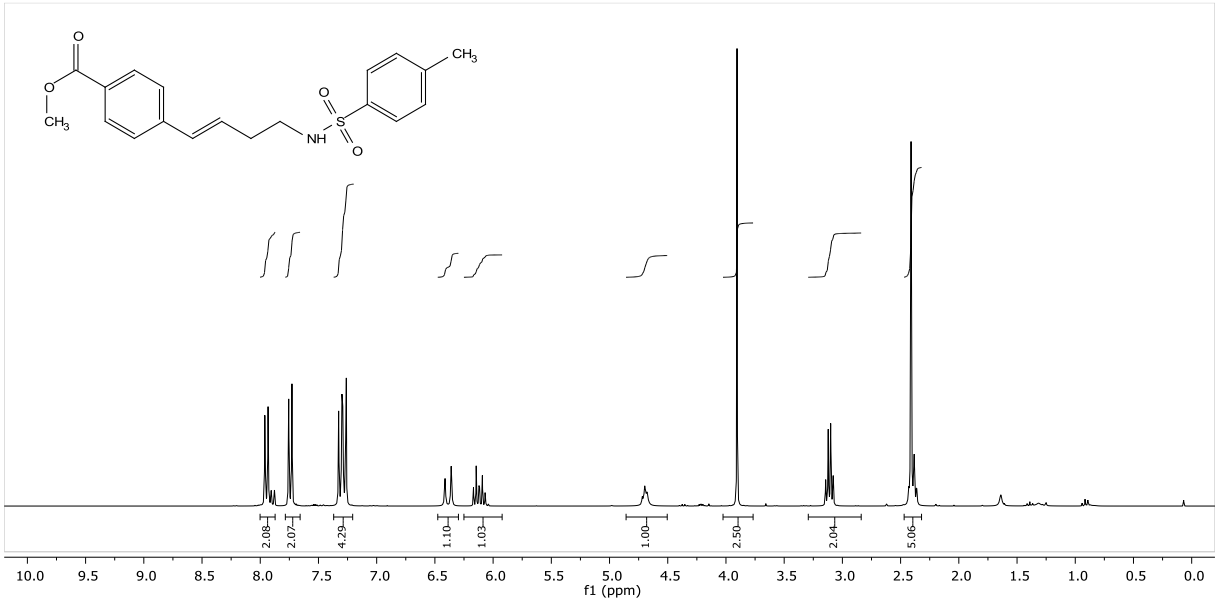
_N_-(4-(4-Methoxyphenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (146g): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

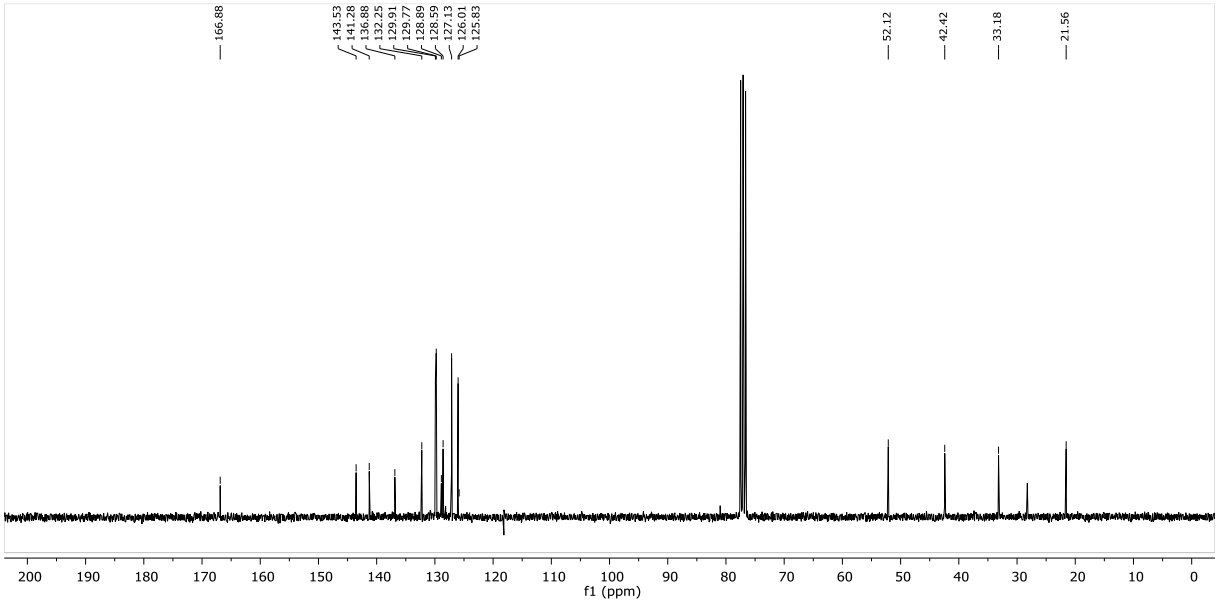


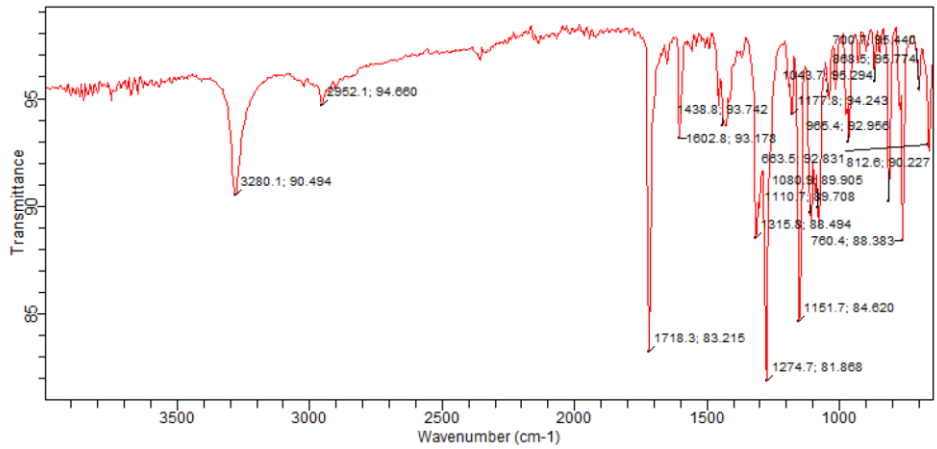




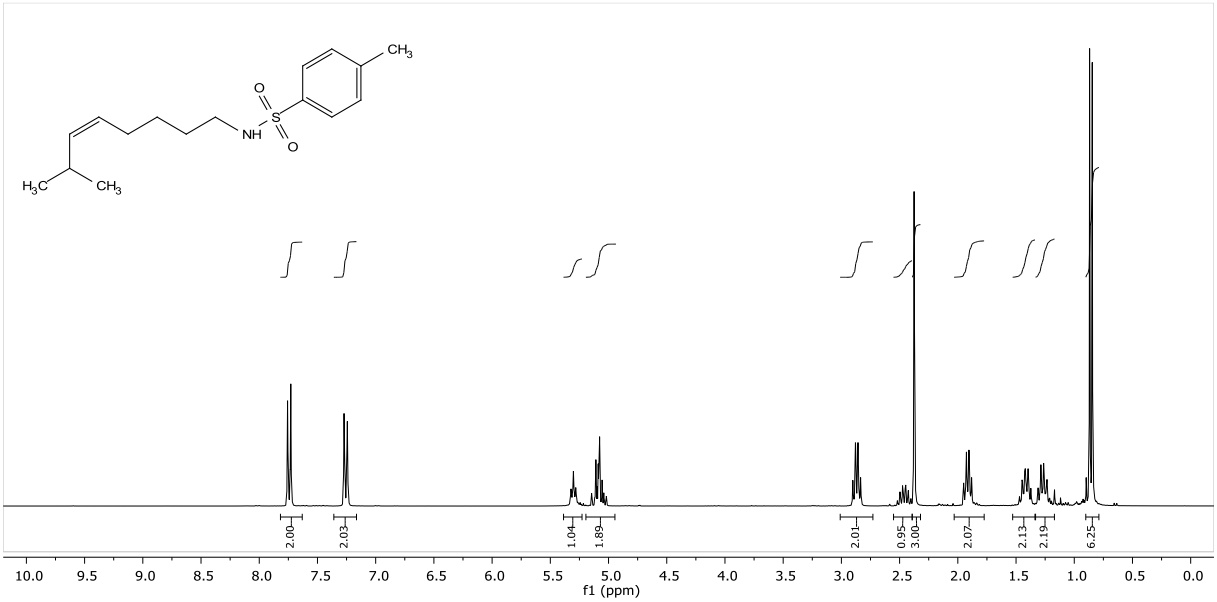
Methyl (*E*)-4-(4-((4-methylphenyl)sulfonamido)but-1-en-1-yl)benzoate (146h): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

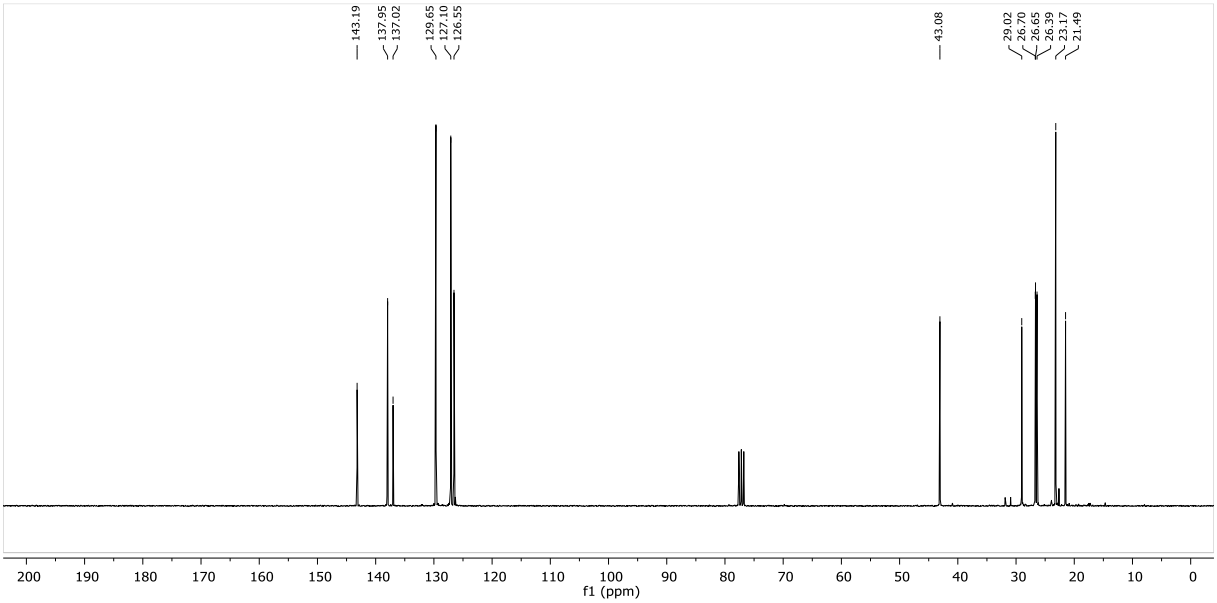


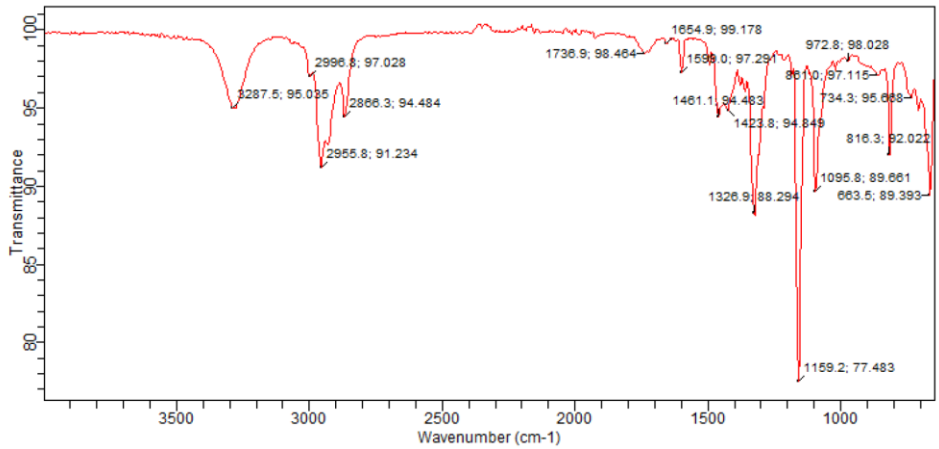




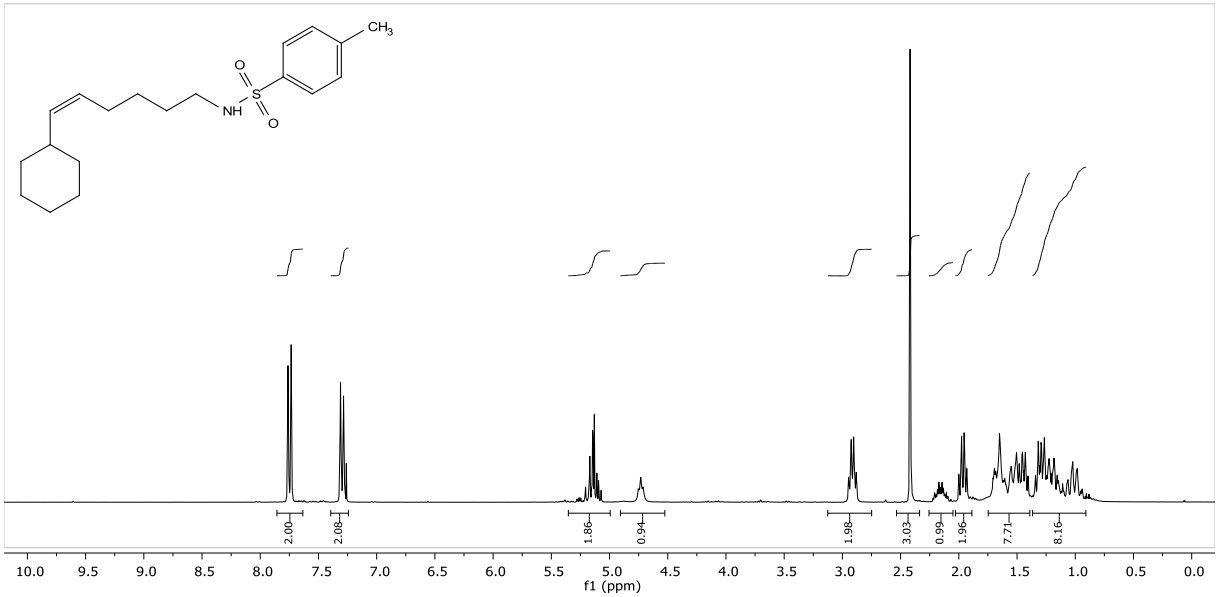
(*Z*)-4-Methyl-*N*-(7-methyloct-5-en-1-yl)benzenesulfonamide (147b): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

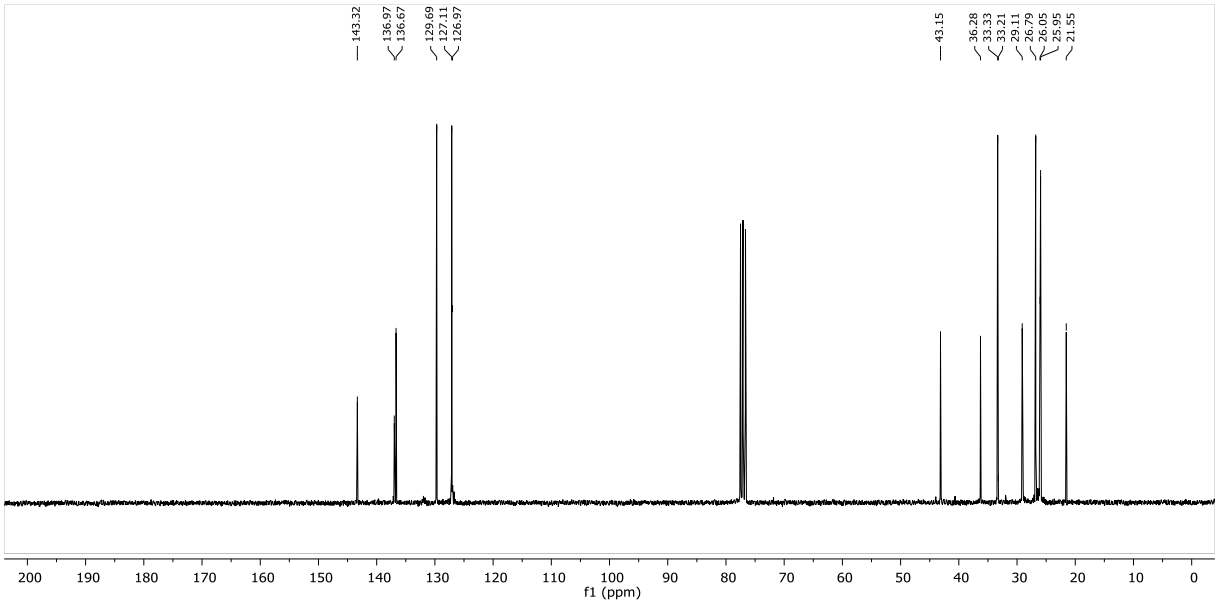


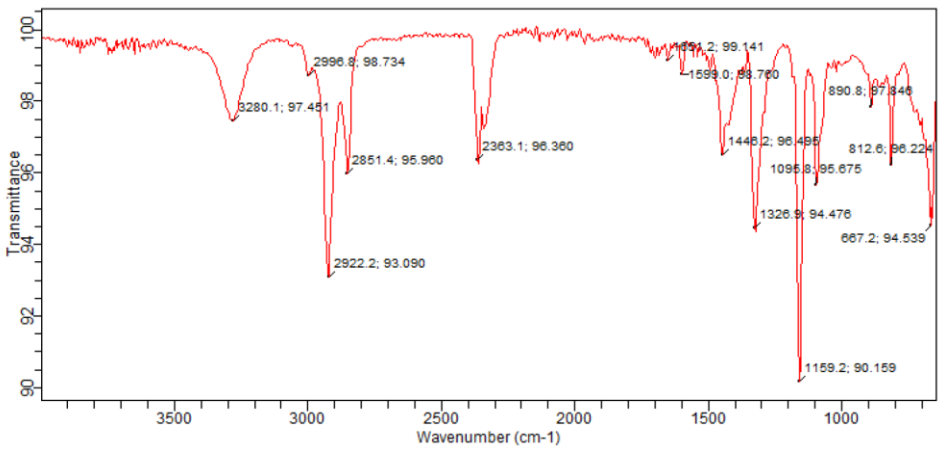




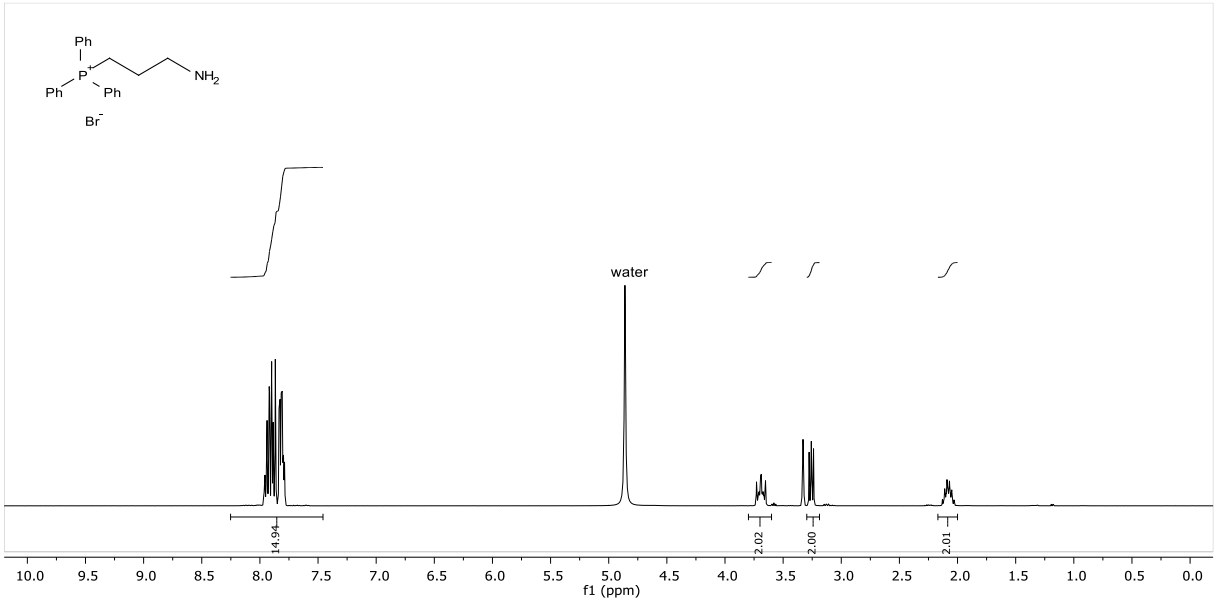
(*Z*)-*N*-(6-Cyclohexylhex-5-en-1-yl)-4-methylbenzenesulfonamide (147c): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

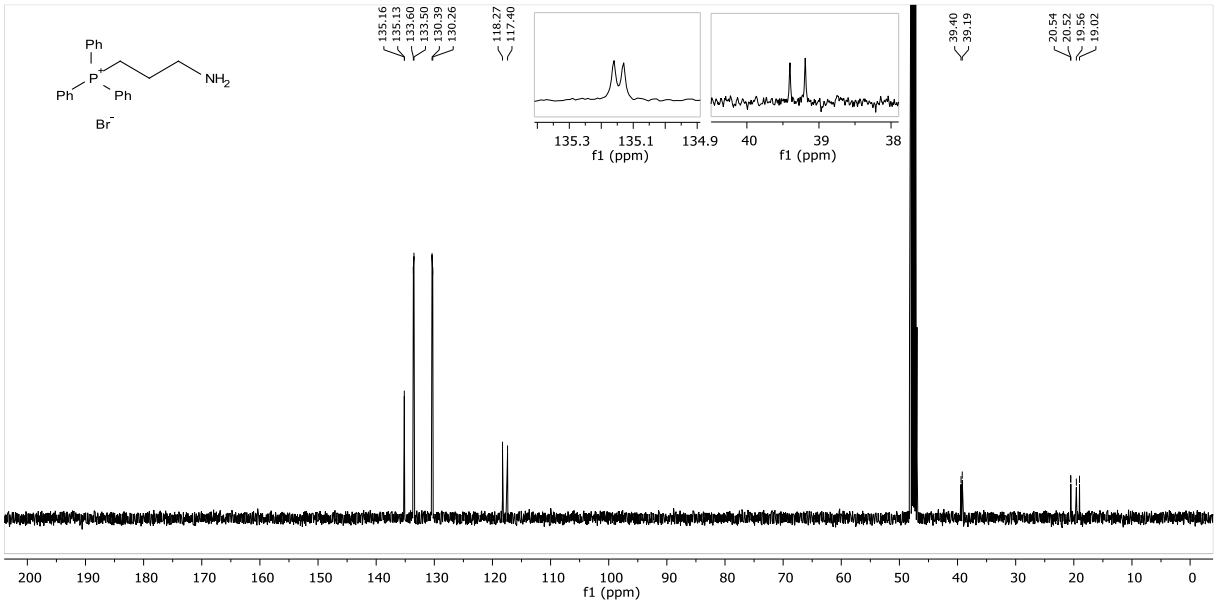


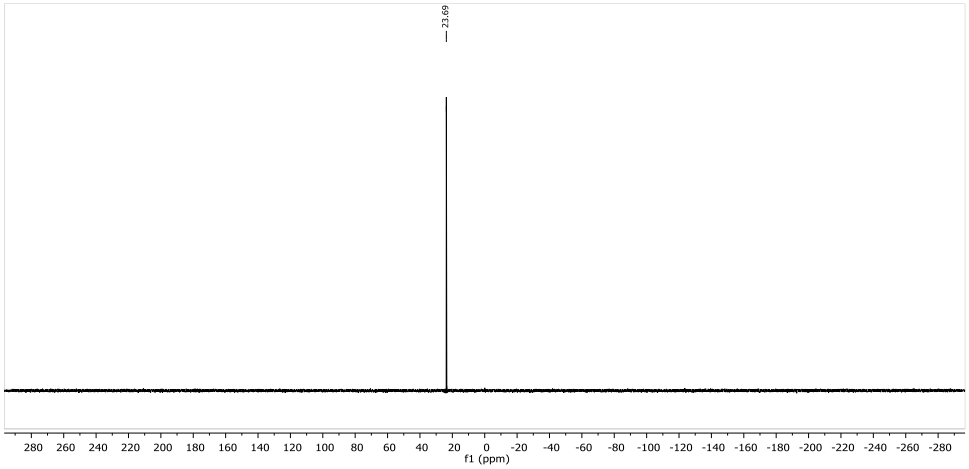


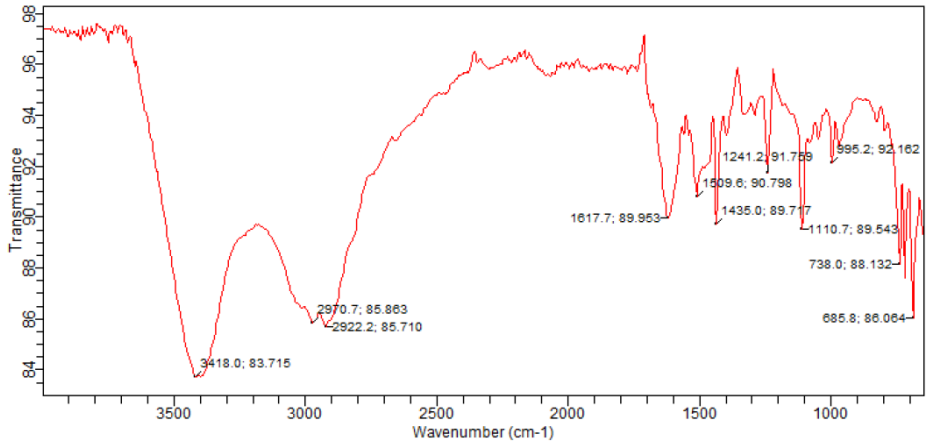


(3-Aminopropyl)triphenylphosphonium bromide (161): ^{1}H, ^{13}C, ^{31}P NMR in MeOD-d_3, IR

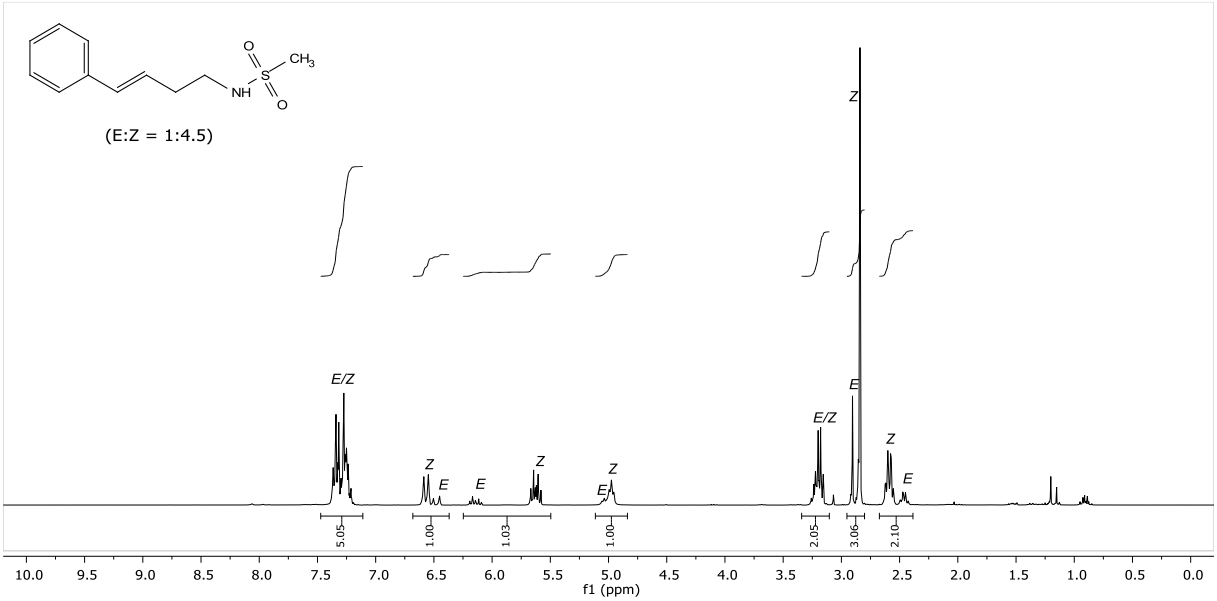


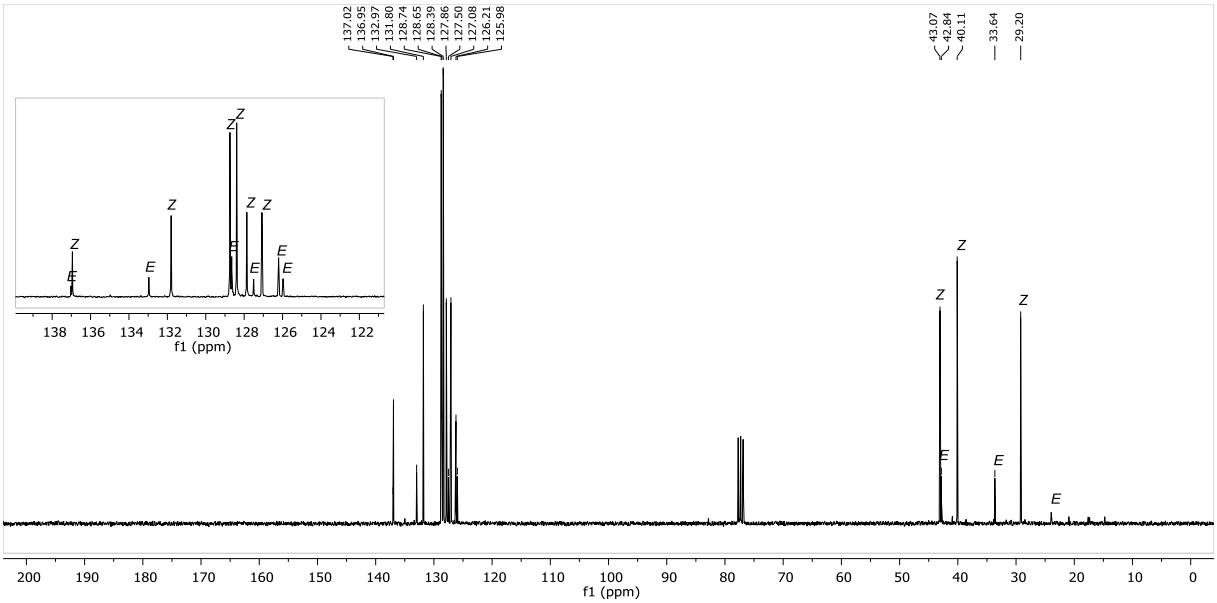


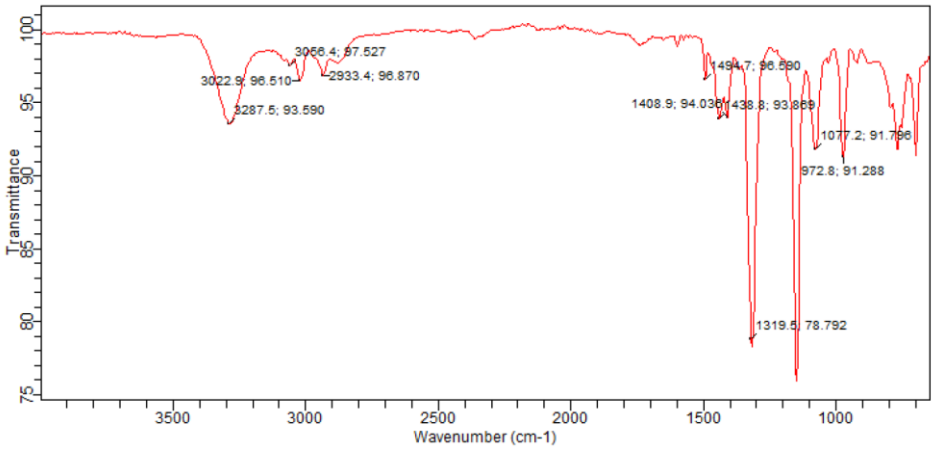



Transmittance
98
96
94
92
90
88
86
84
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
3418.0; 83.715
2970.7; 85.863
2922.2; 85.710
1617.7; 89.953
1509.6; 90.798
1435.0; 89.717
1241.2; 91.759
1110.7; 89.543
995.2; 92.162
738.0; 88.132
685.8; 86.064

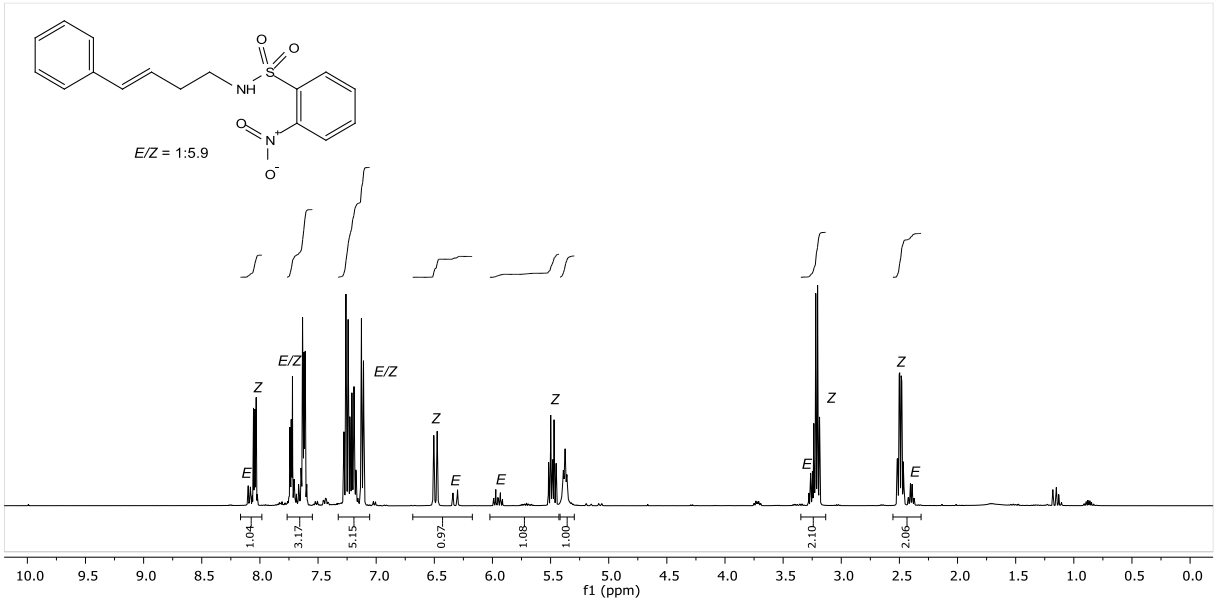
_N_-(4-Phenylbut-3-en-1-yl)methanesulfonamide (146m): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

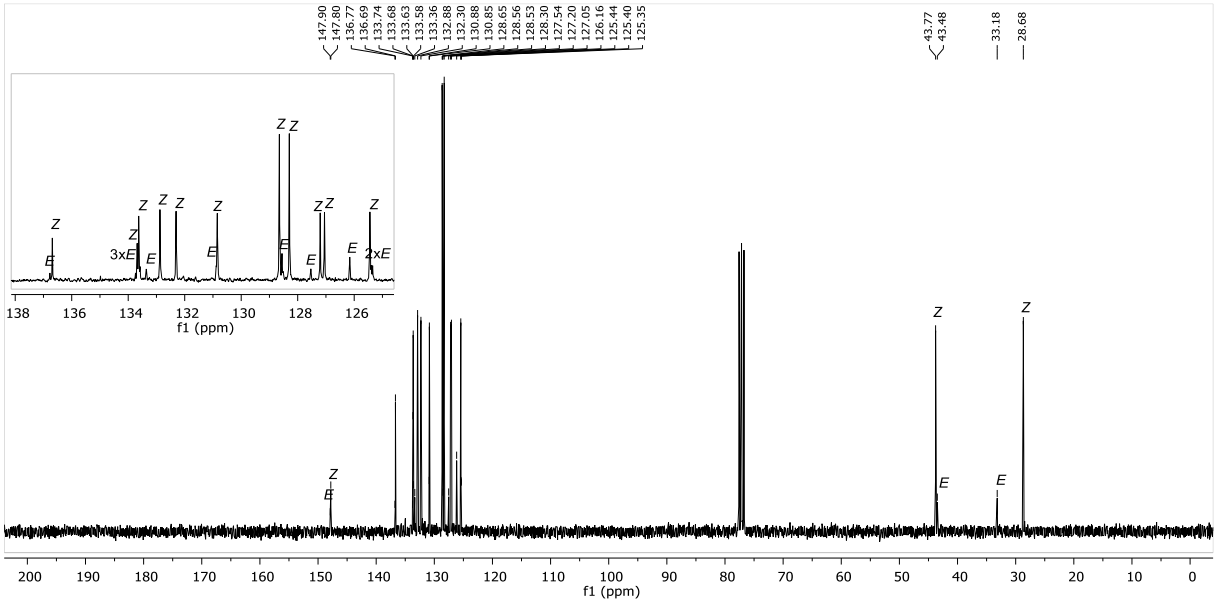


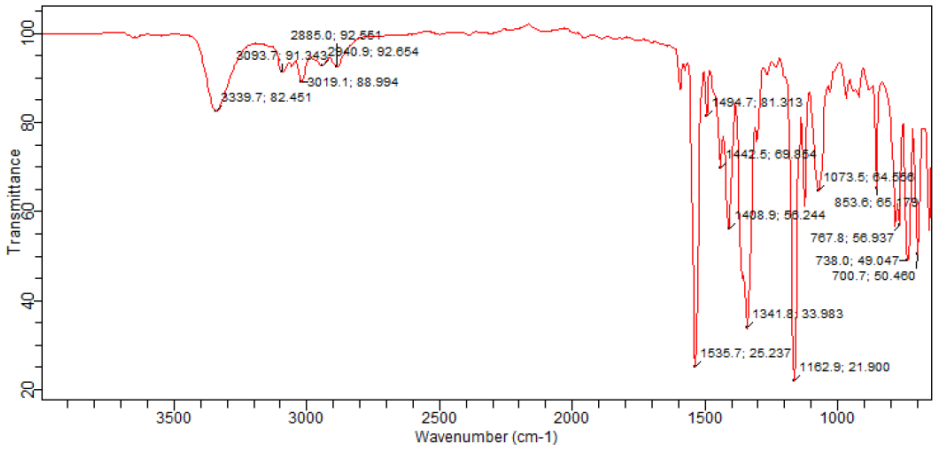




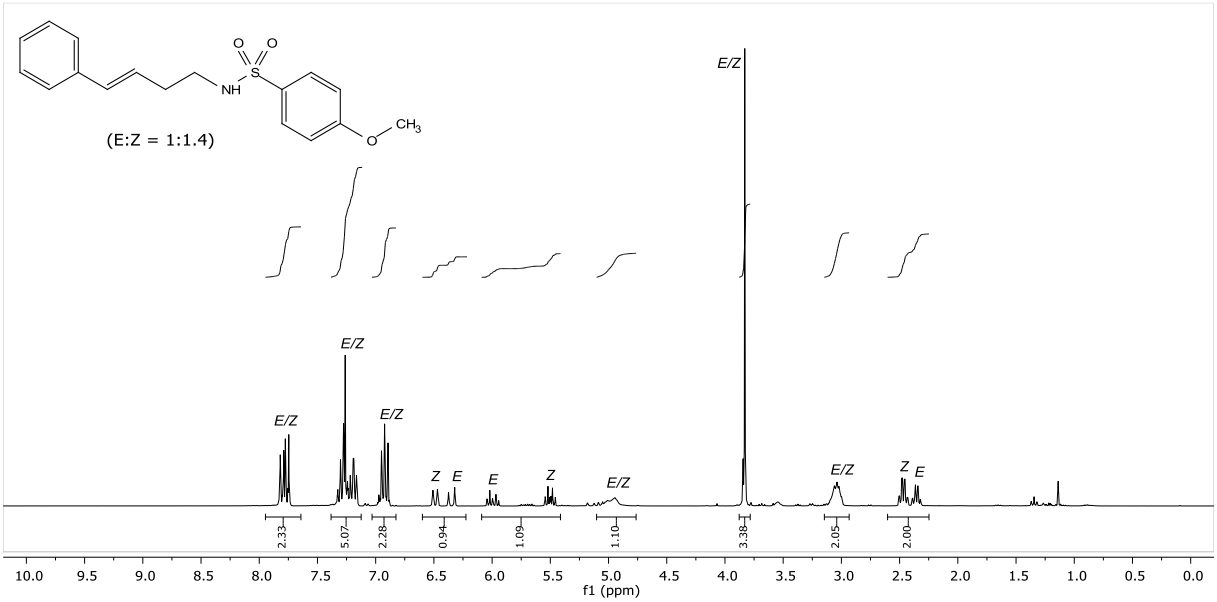
2-Nitro-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146n): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

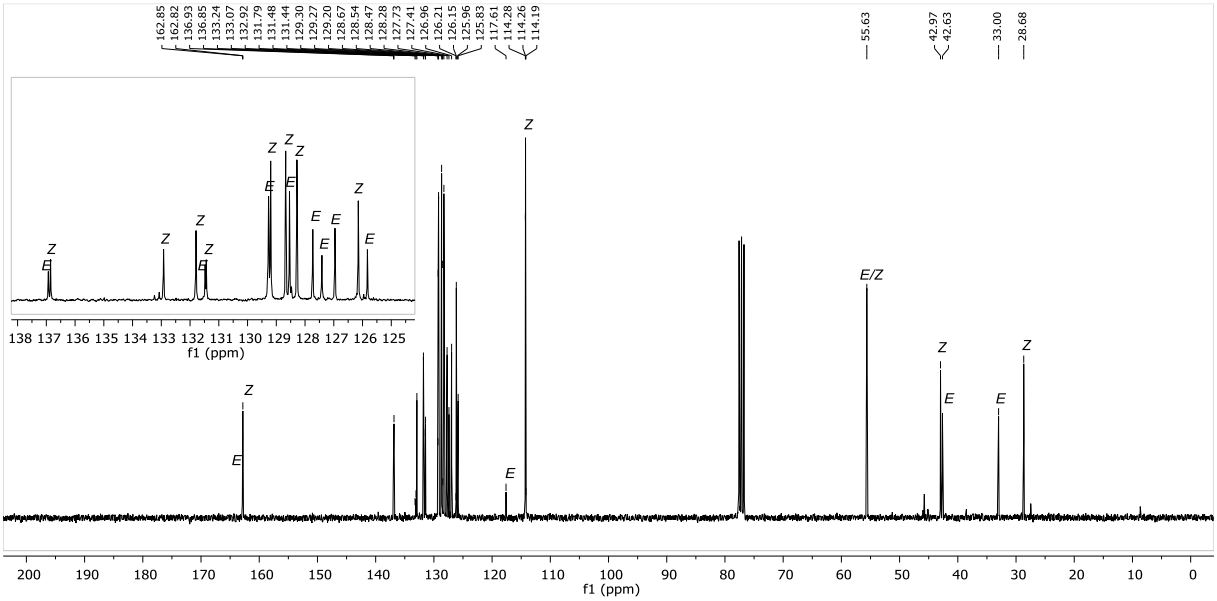


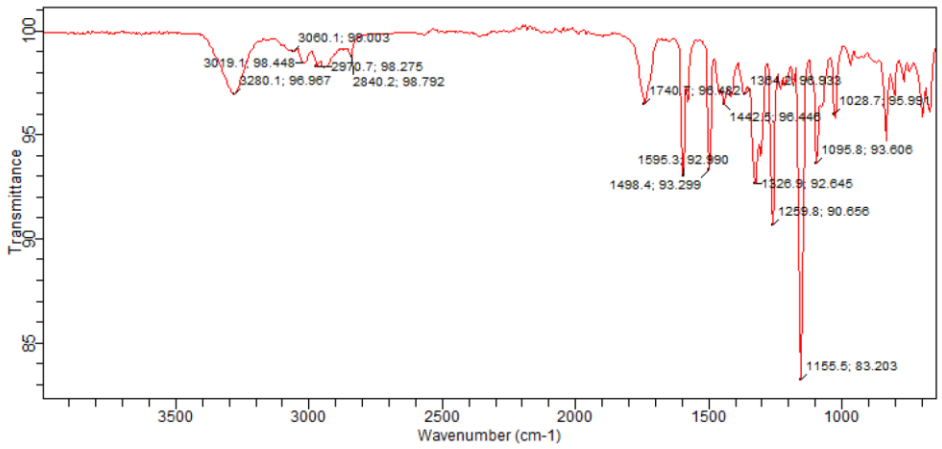




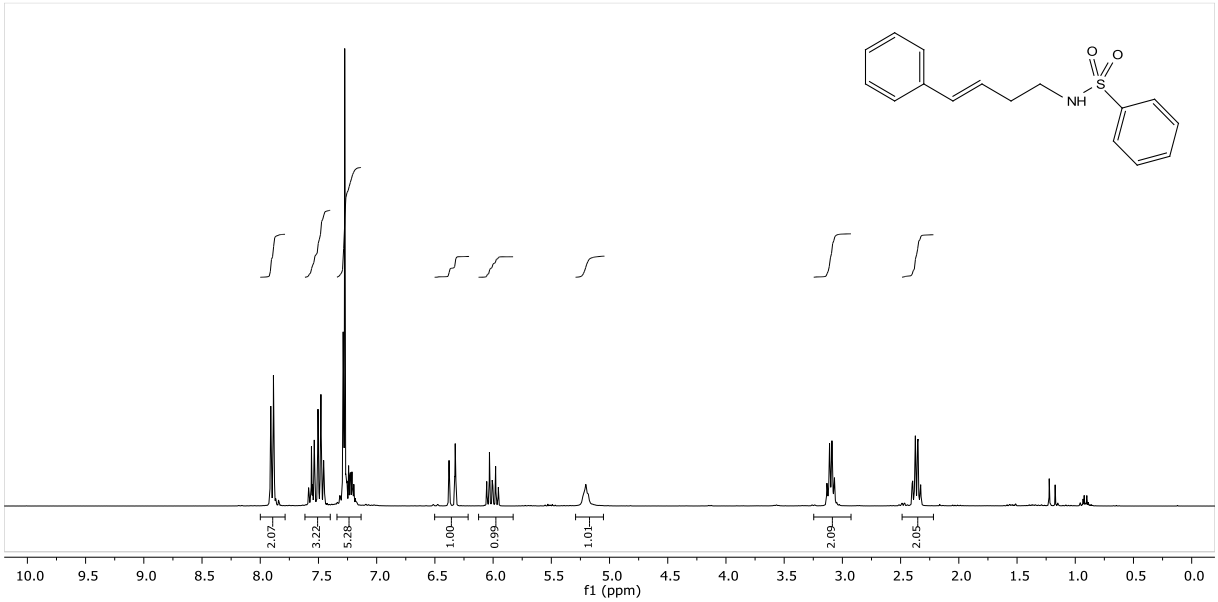
4-Methoxy-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146o): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

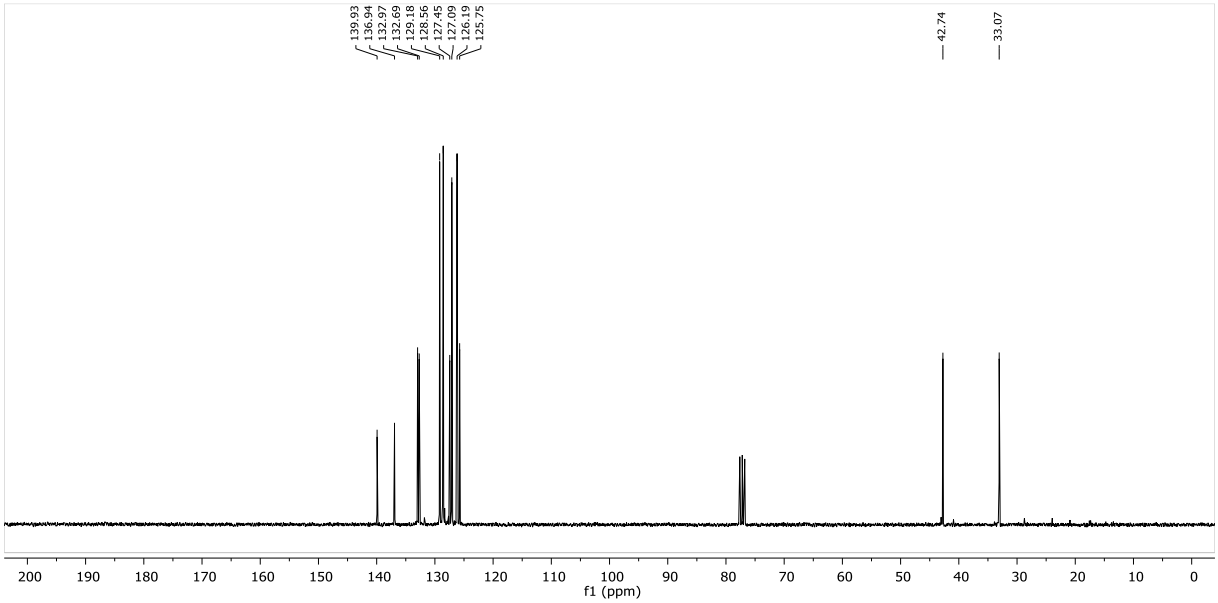


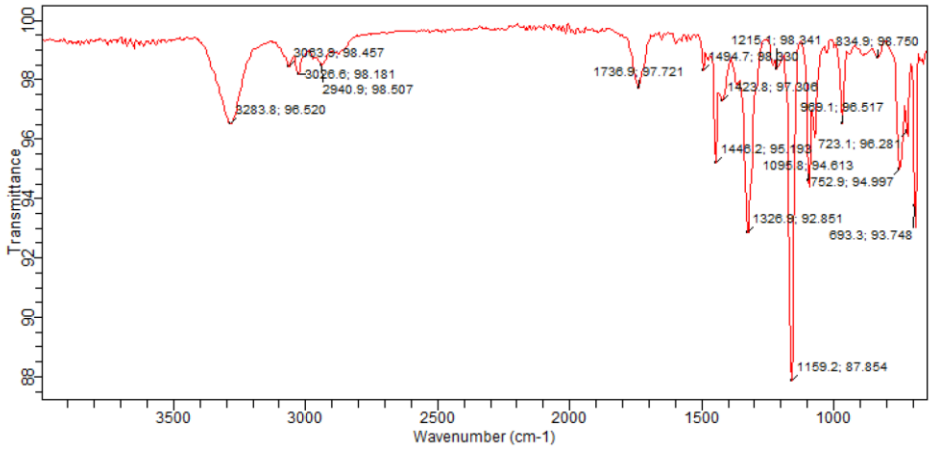




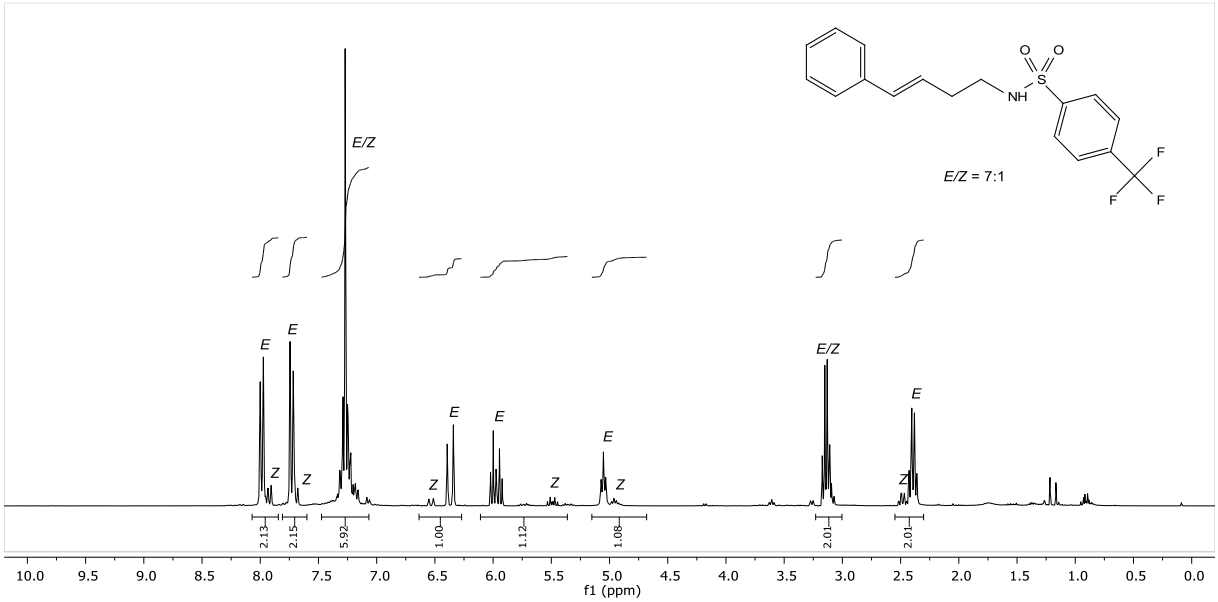
(*E*)-*N*-(4-Phenylbut-3-en-1-yl)benzenesulfonamide (146p): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

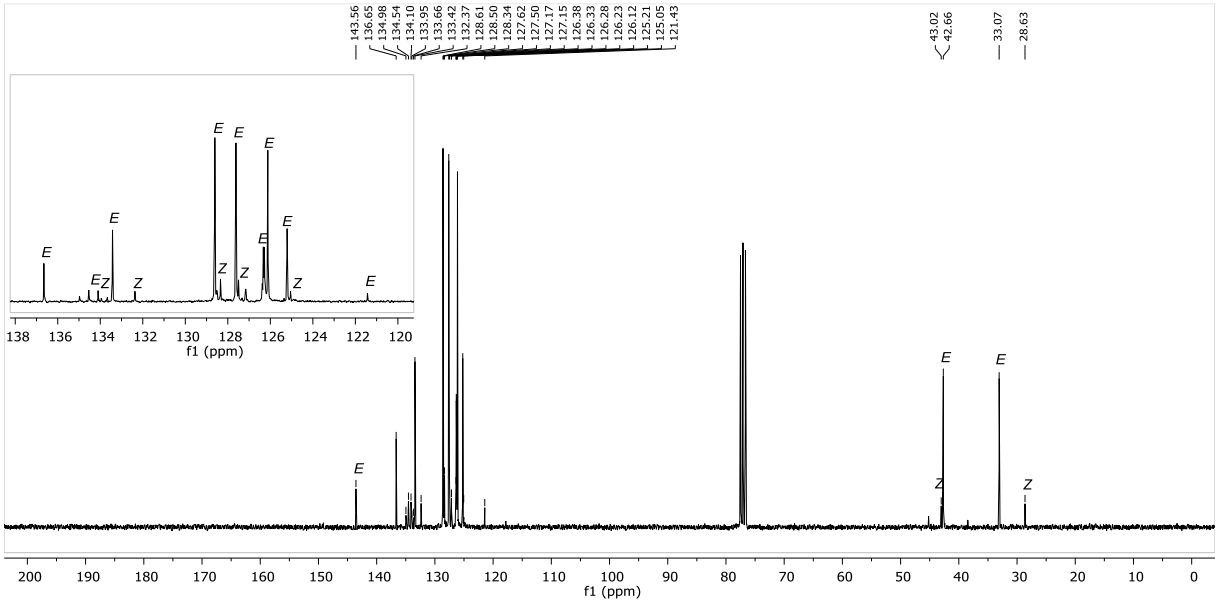


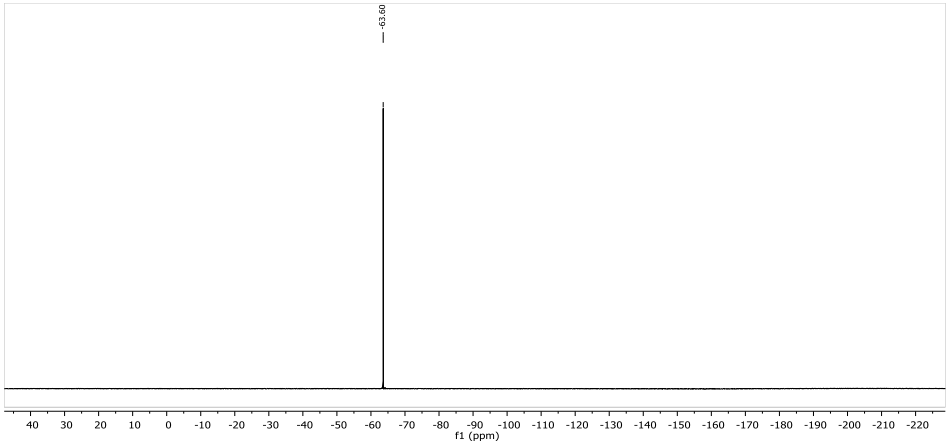


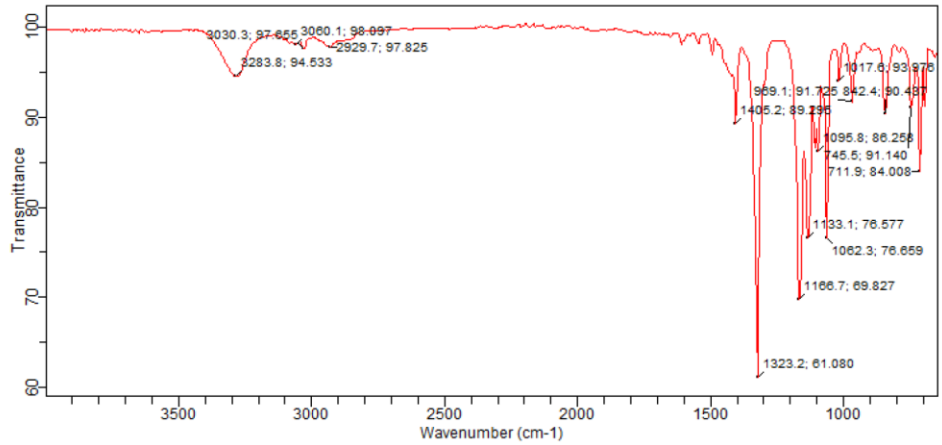


_N_-(4-Phenylbut-3-en-1-yl)-4-(trifluoromethyl)benzenesulfonamide (146q): ^{1}H, ^{13}C, ^{19}F NMR in $CDCl_3$, IR

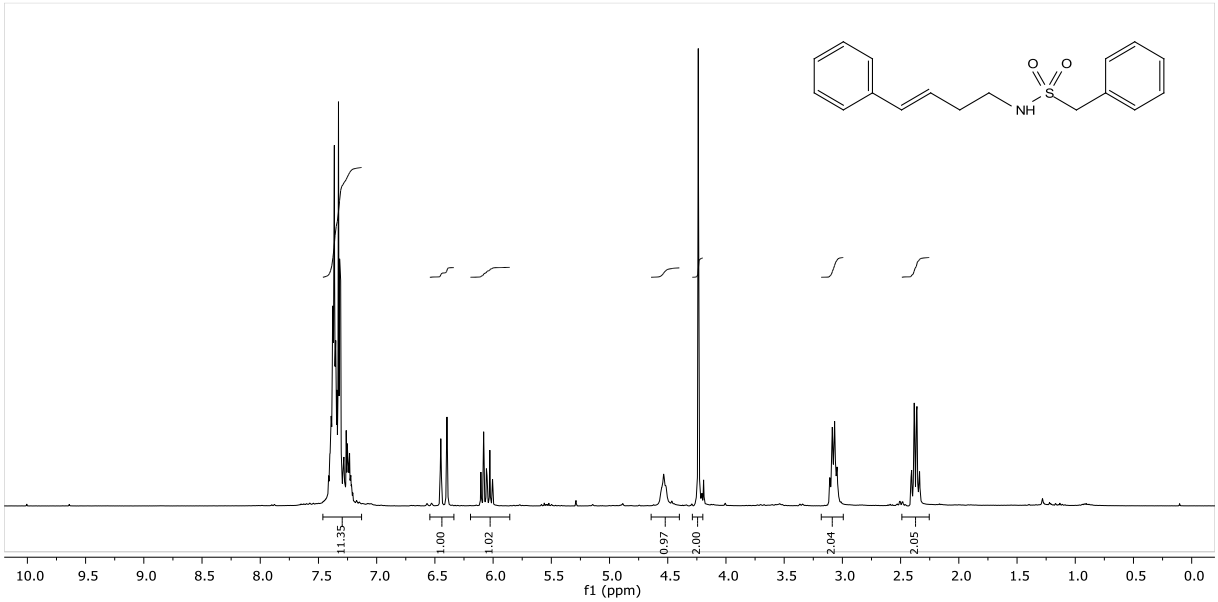


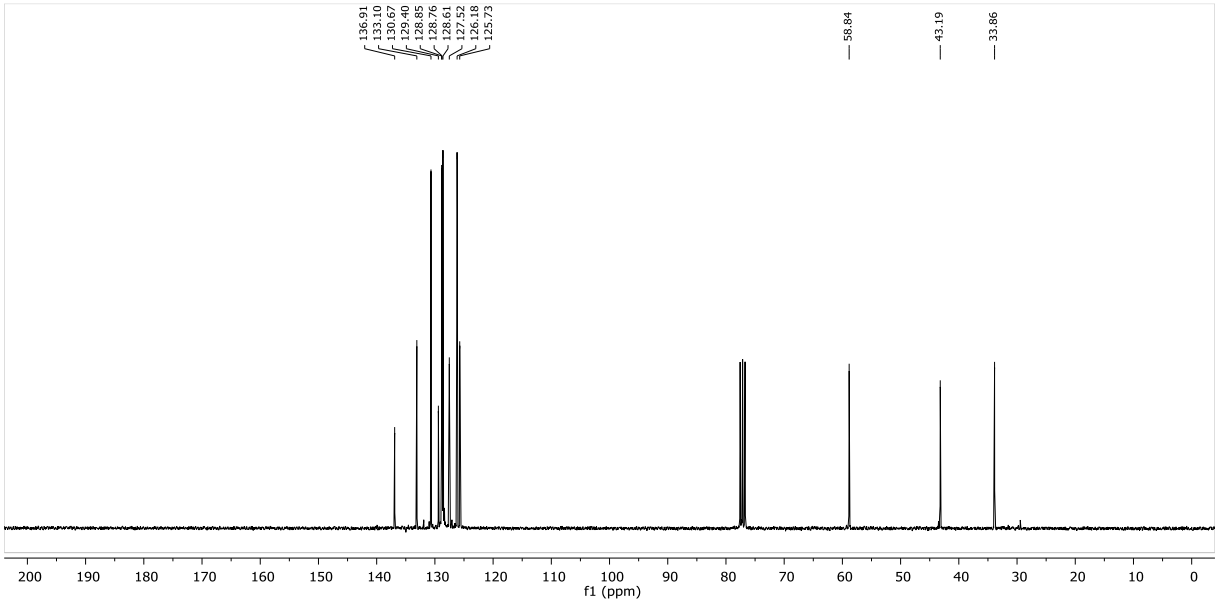


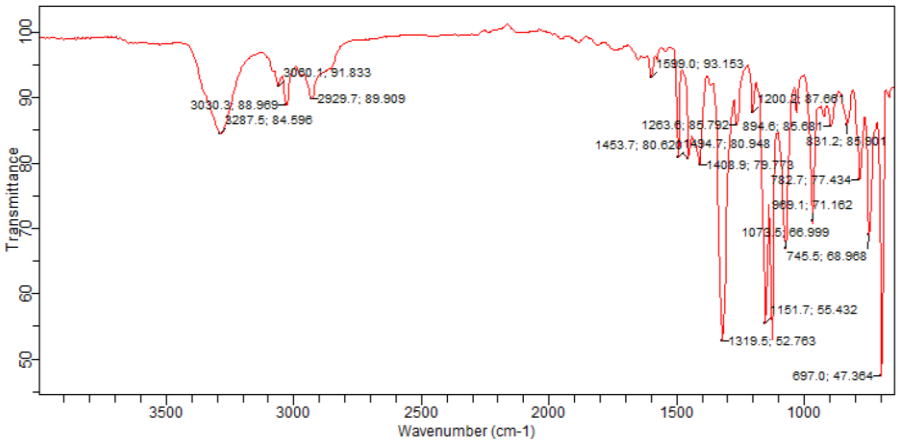



Transmittance
100
90
80
70
60
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
3030.3; 97.655
3060.1; 98.097
2929.7; 97.825
3283.8; 94.533
1323.2; 61.080
1166.7; 69.827
1133.1; 76.577
1062.3; 76.659
1095.8; 86.256
745.5; 91.140
711.9; 84.008

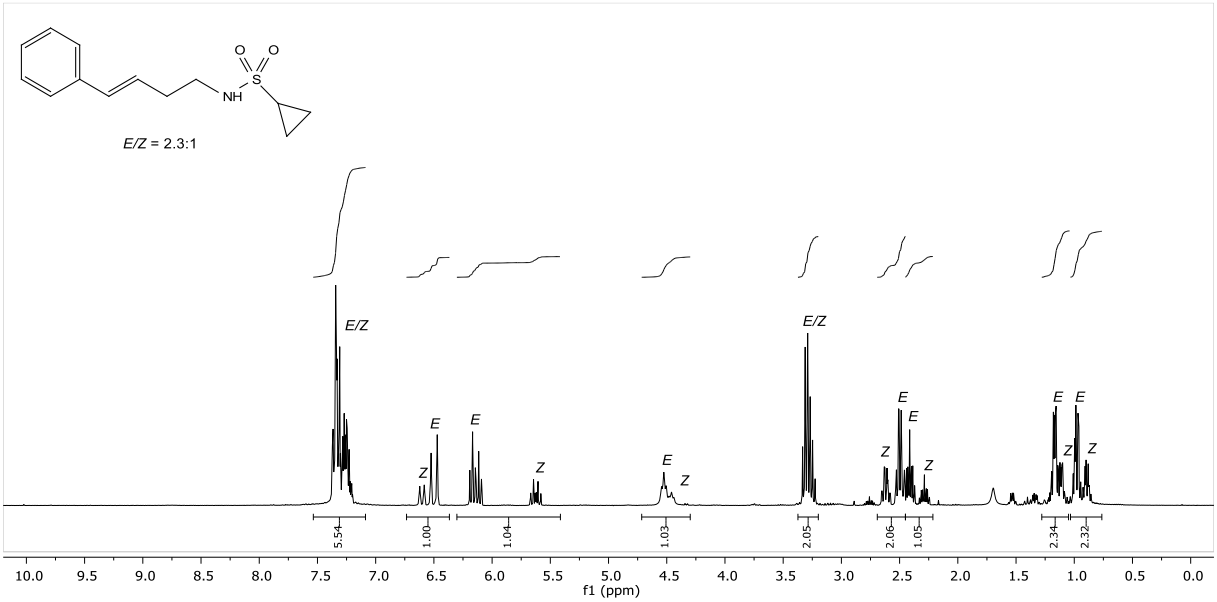
(*E*)-1-Phenyl-N-(4-phenylbut-3-en-1-yl)methanesulfonamide (146s): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

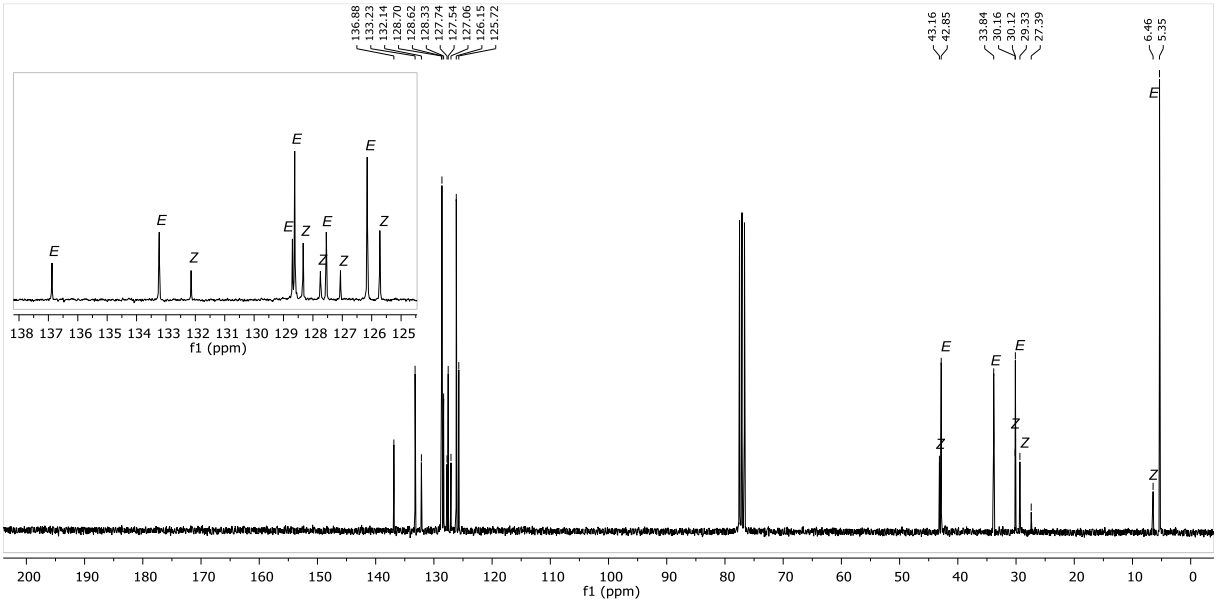


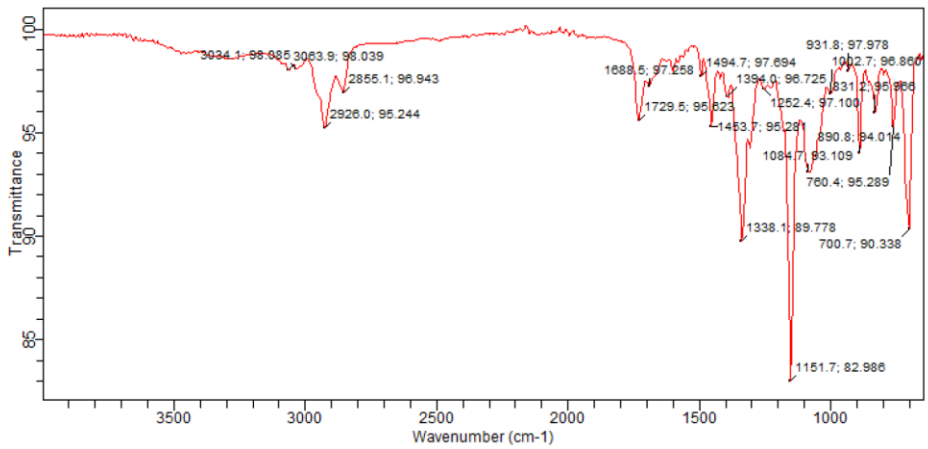




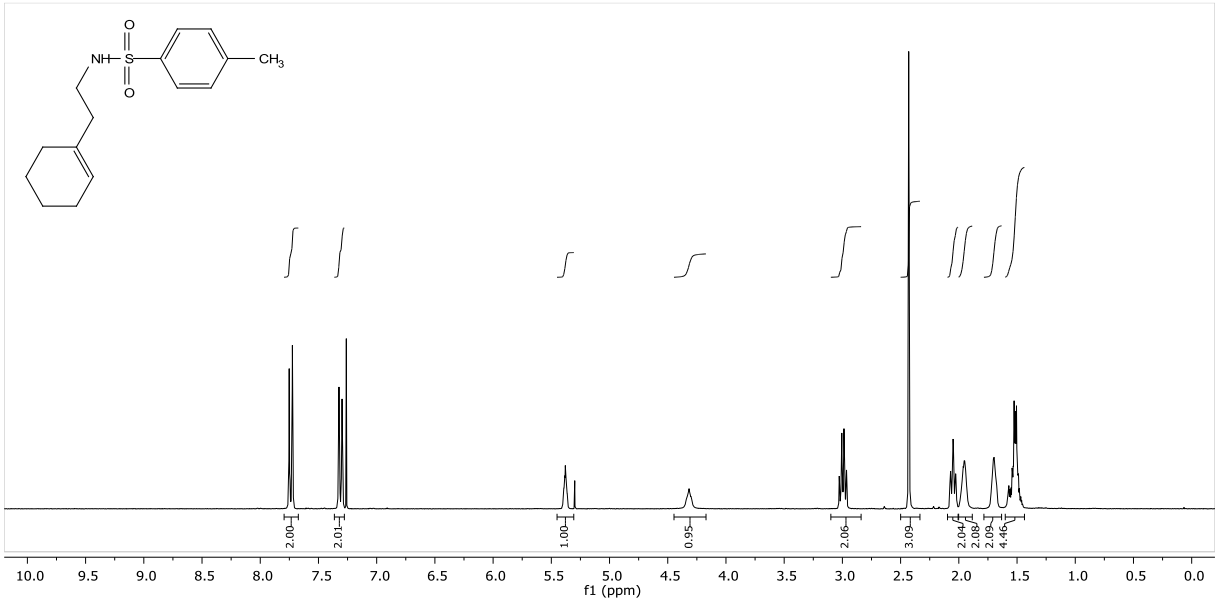
_N_-(4-Phenylbut-3-en-1-yl)cyclopropanesulfonamide (146r): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

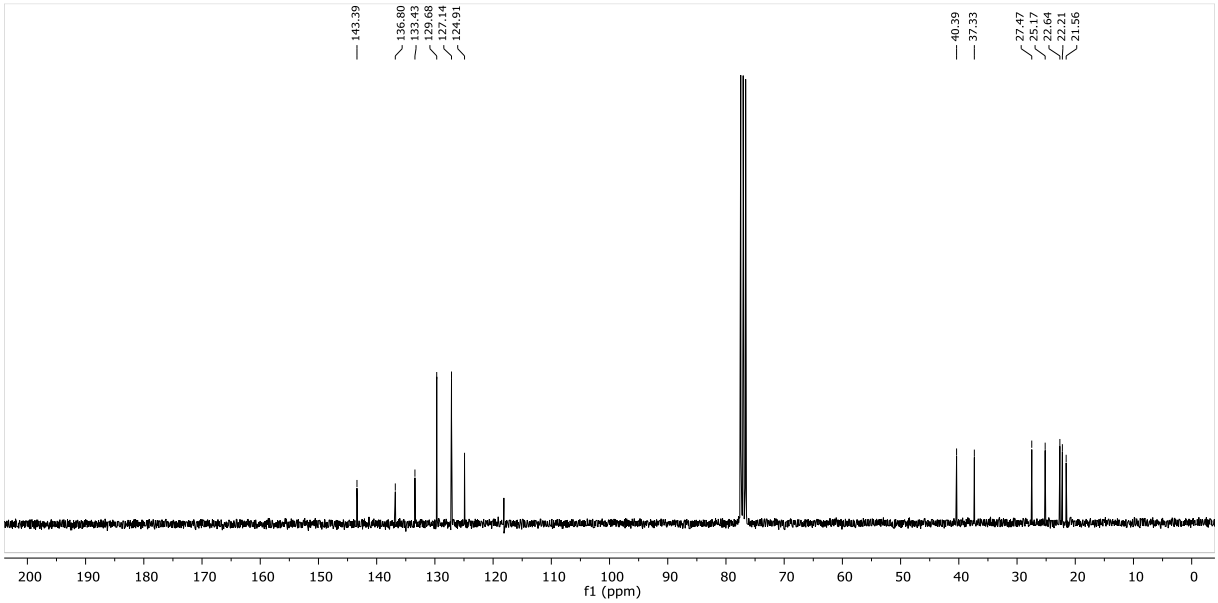


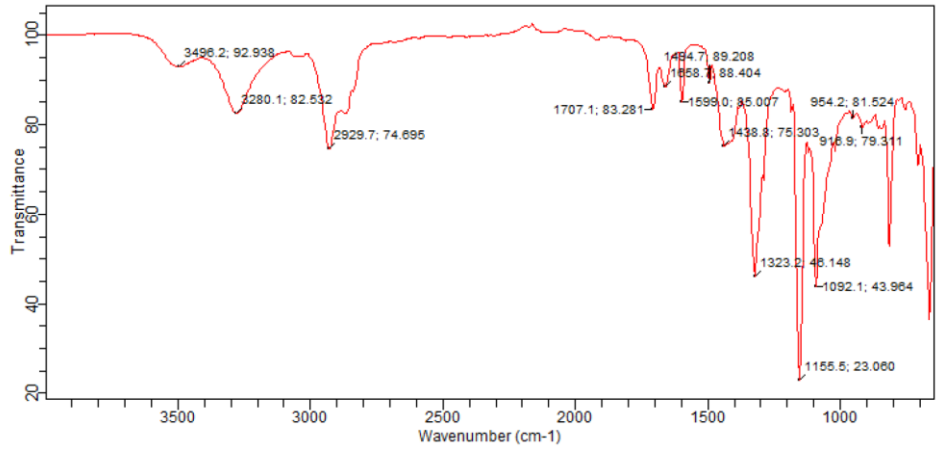




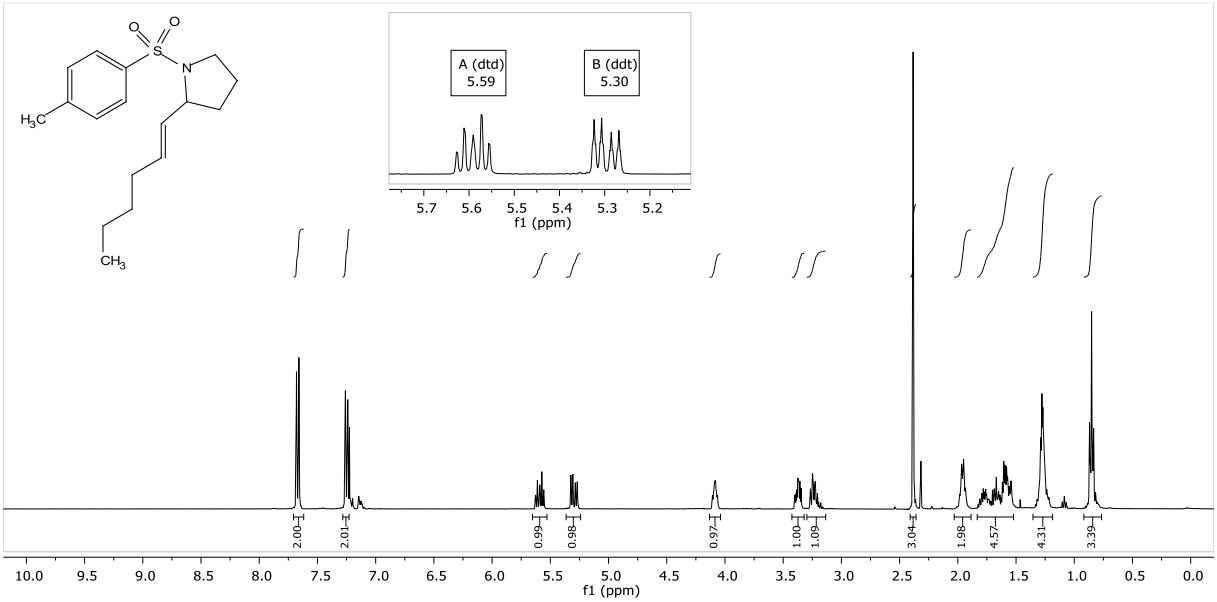
_N_-(2-(Cyclohex-1-en-1-yl)ethyl)-4-methylbenzenesulfonamide (146t): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

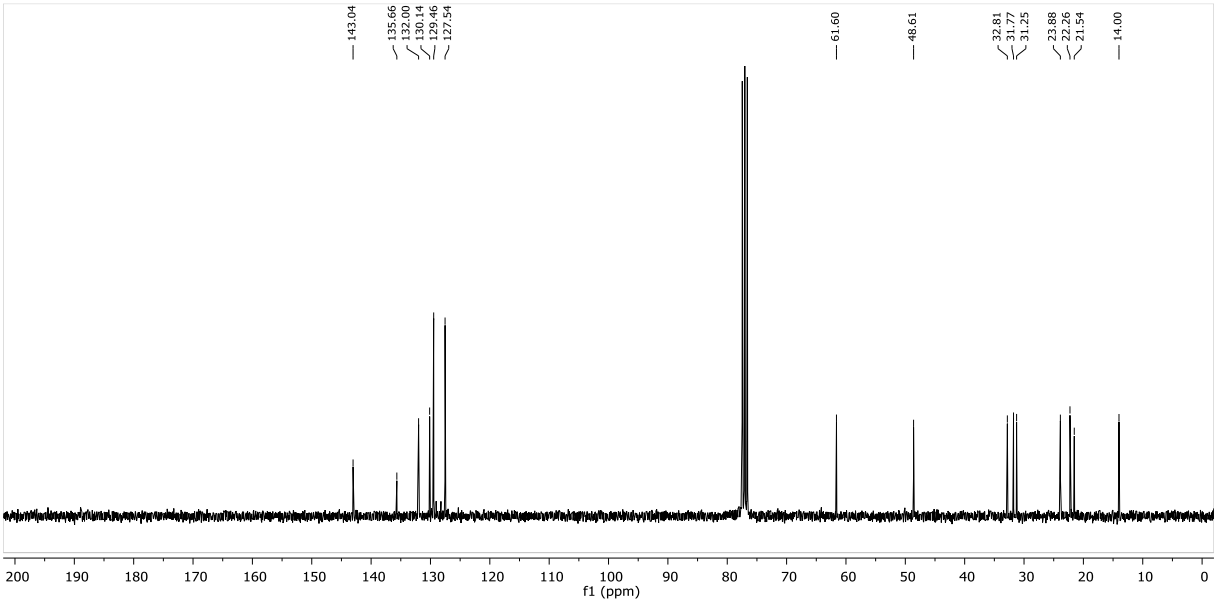


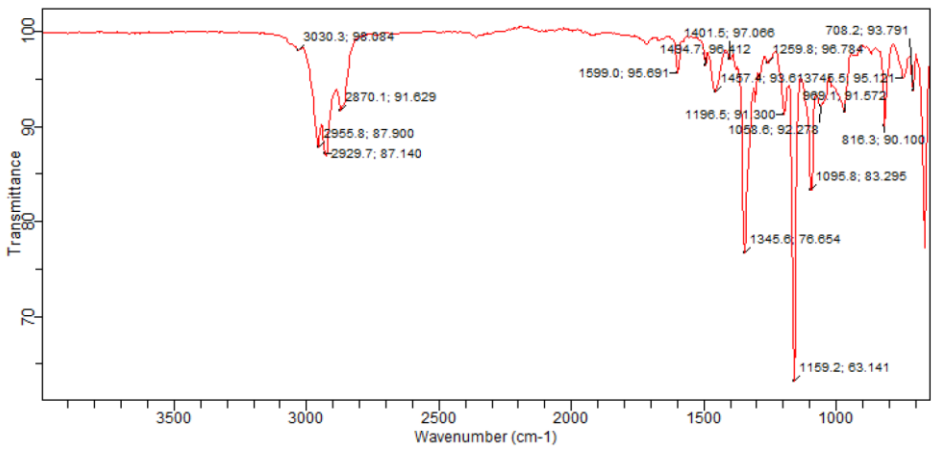


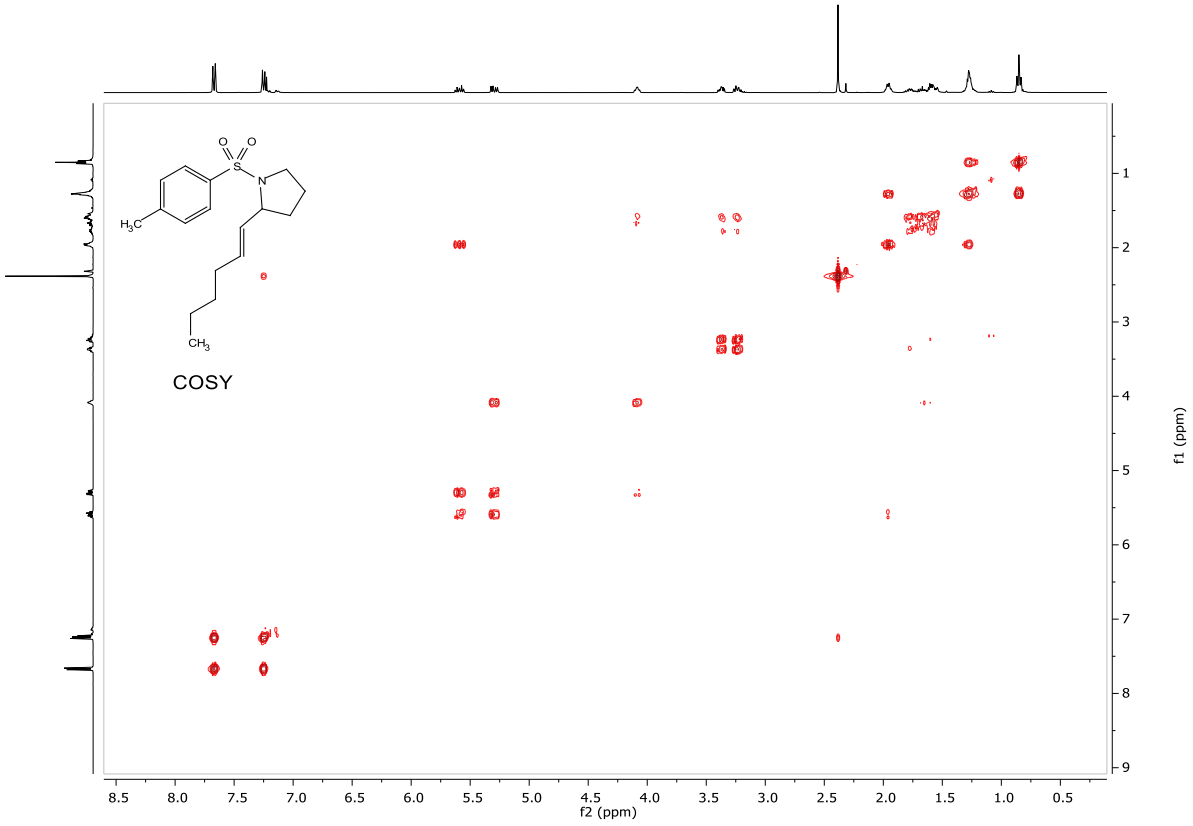


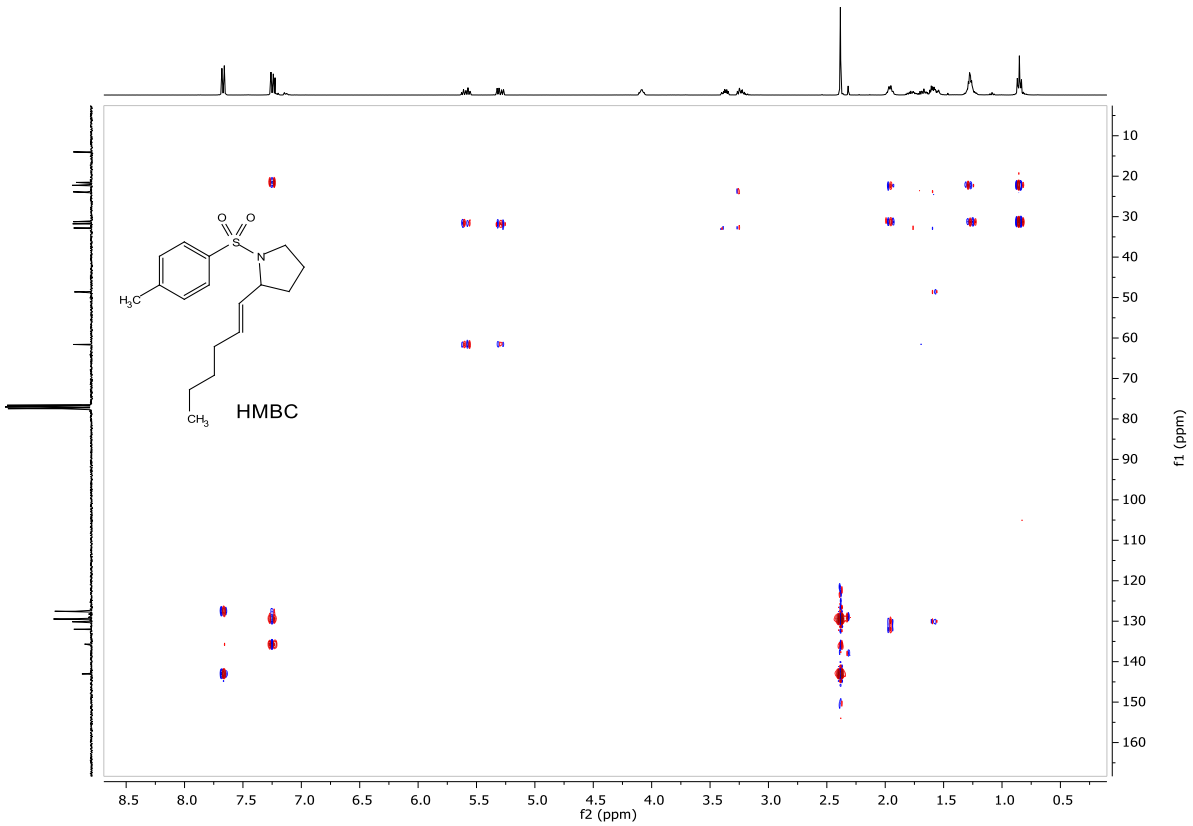
2-(Hex-1-en-1-yl)-1-tosylpyrrolidine (140a): ^{1}H, ^{13}C NMR in $CDCl_3$, IR, COSY, HMBC, HSQC

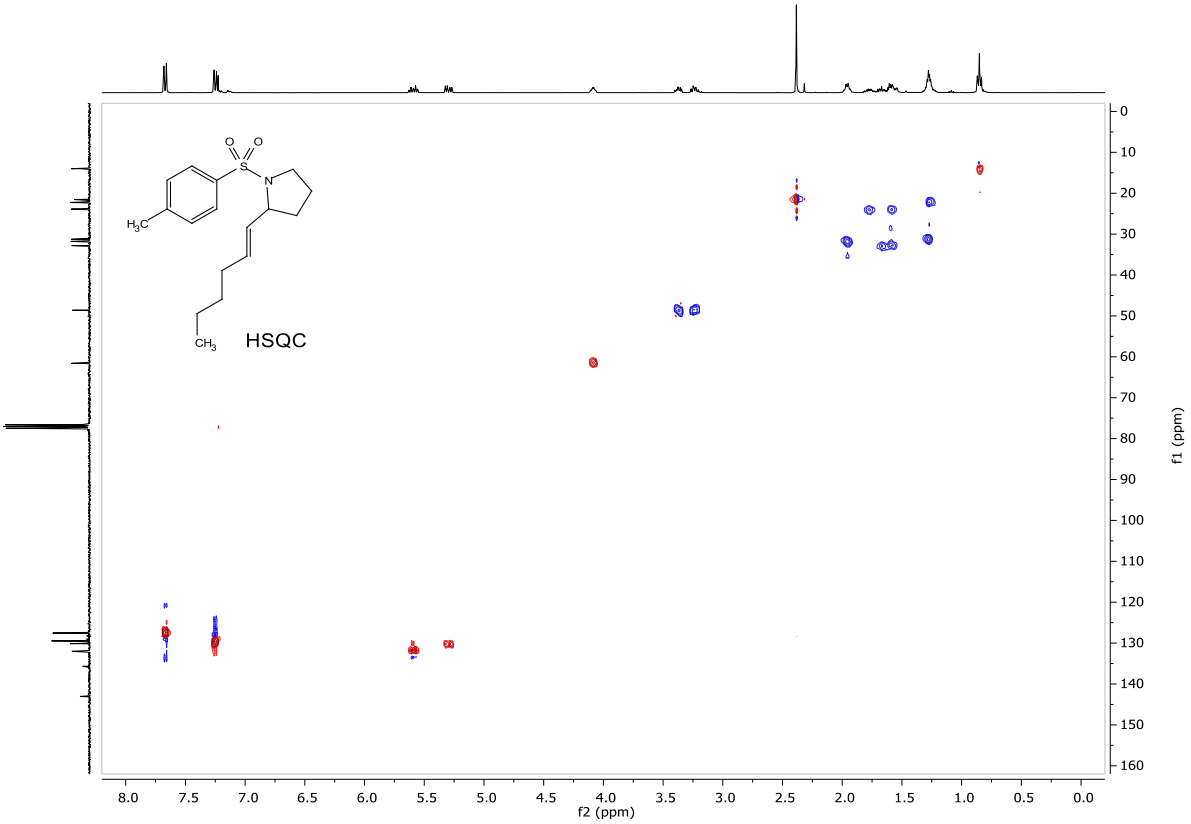




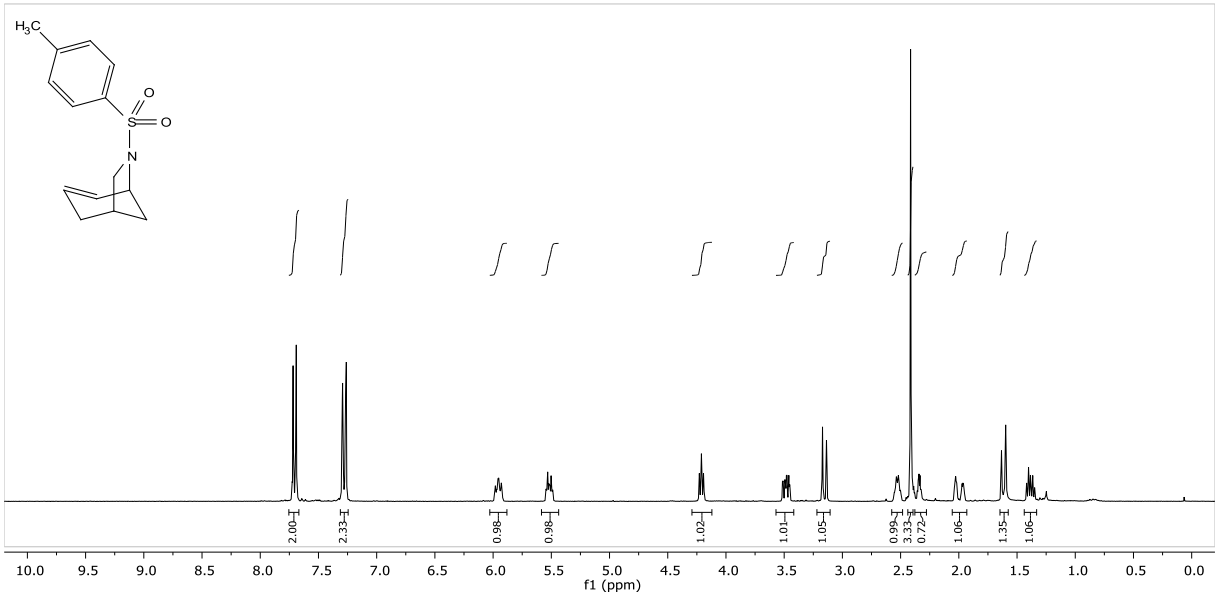


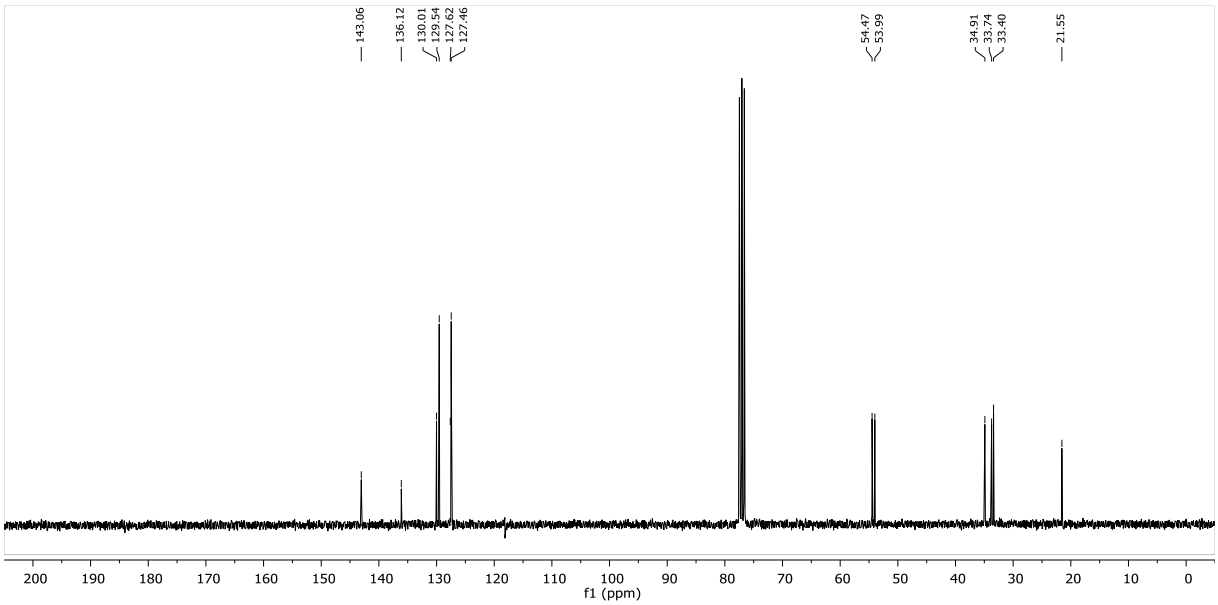

COSY
f2 (ppm)
f1 (ppm)

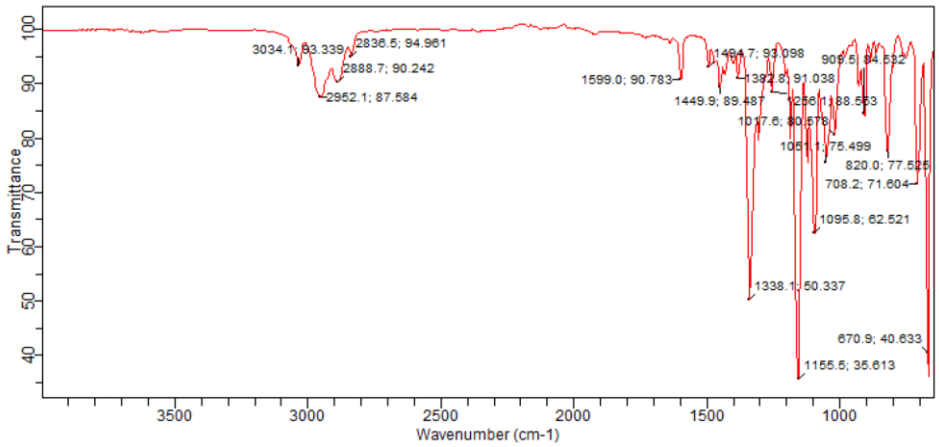

HMBC
f2 (ppm)
f1 (ppm)


HSQC
f2 (ppm)
f1 (ppm)

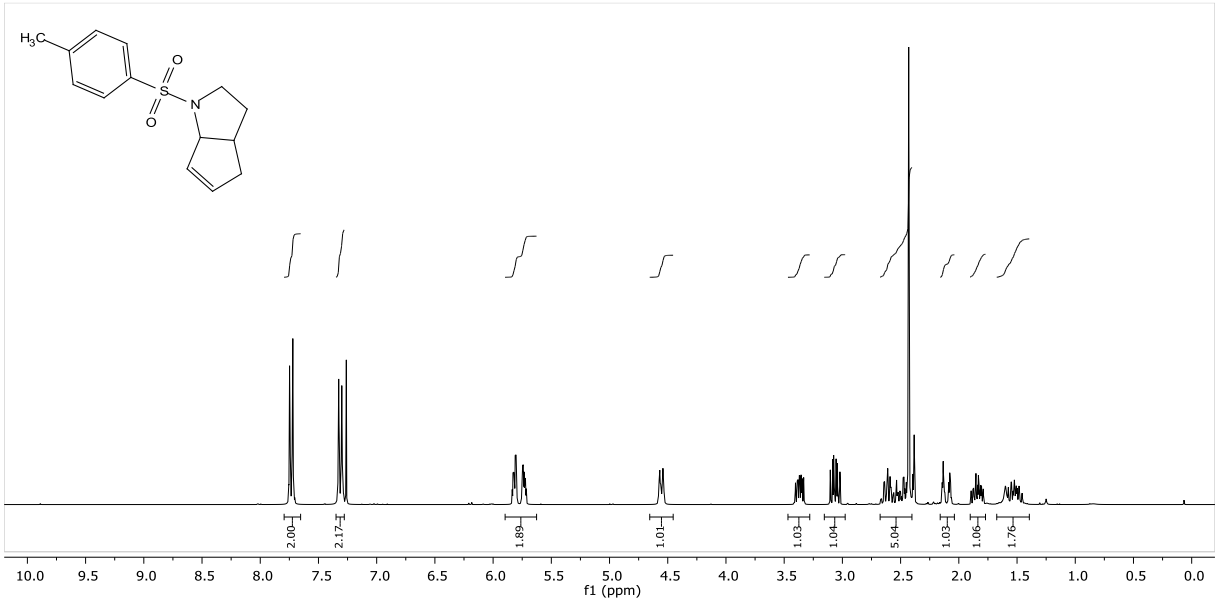
6-Tosyl-6-azabicyclo[3.2.1]oct-3-ene (149b): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

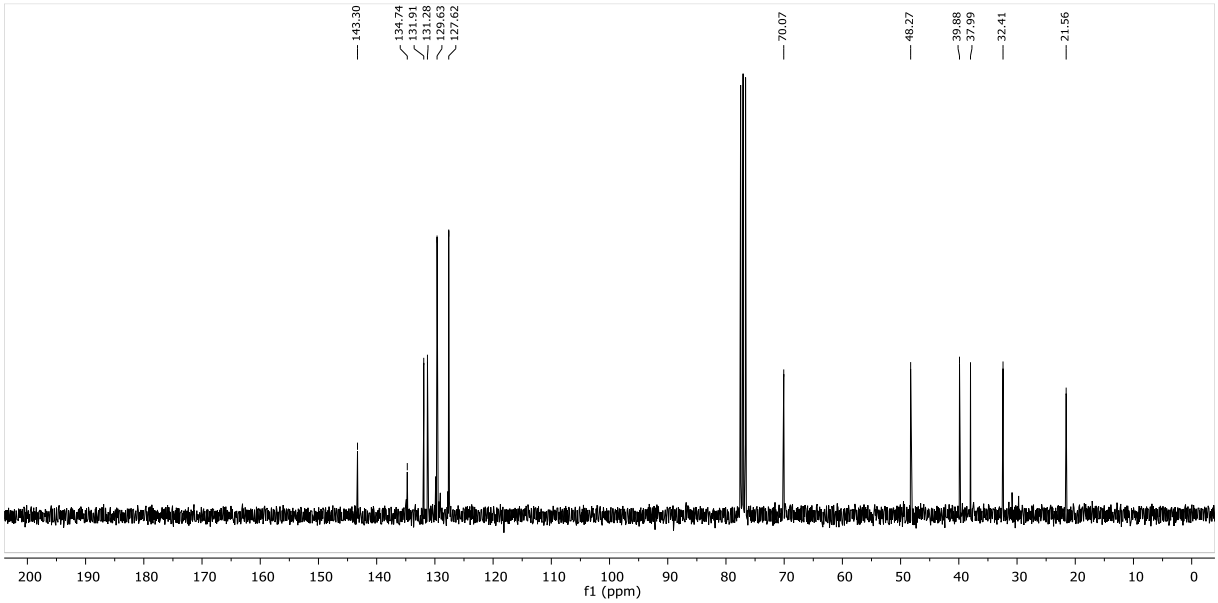


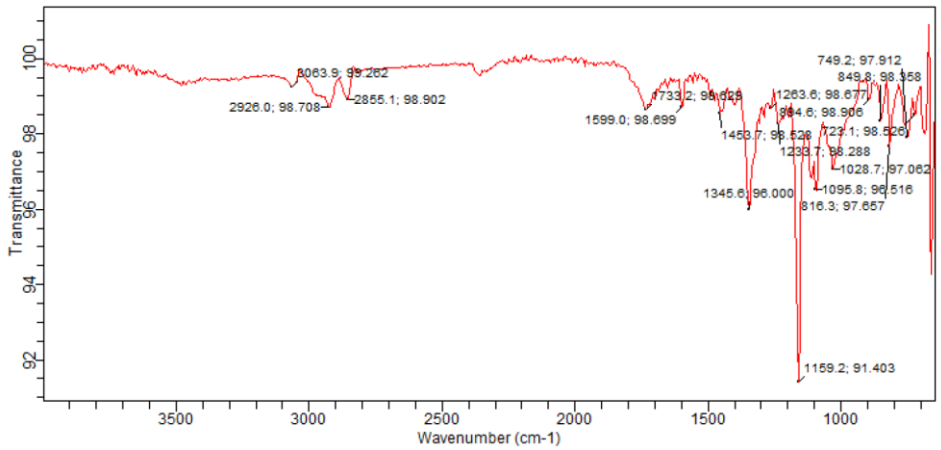




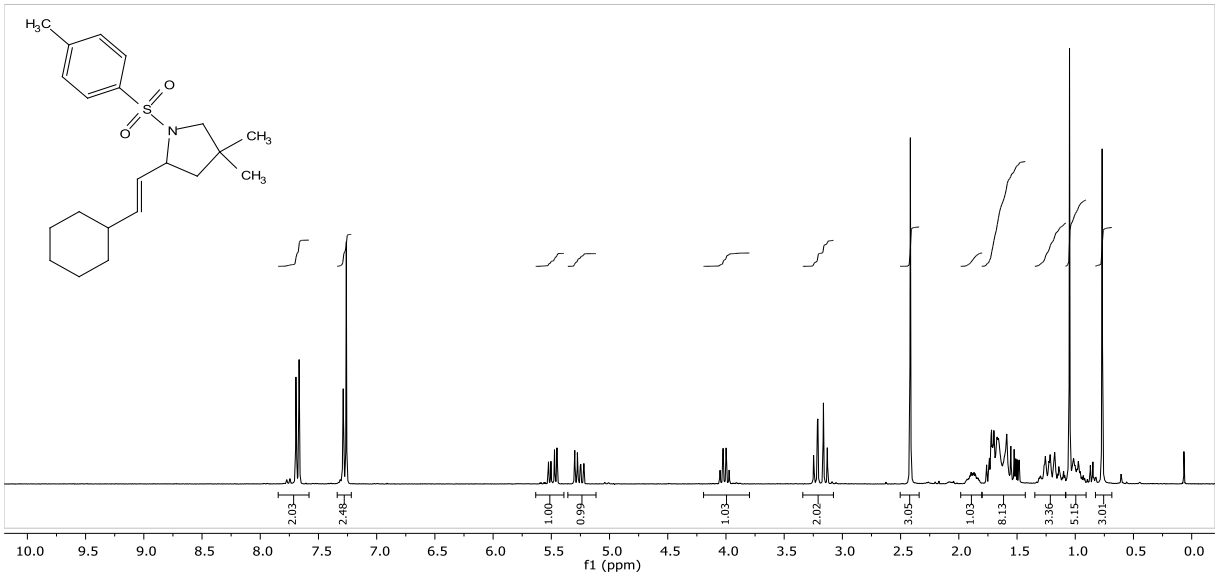
1-Tosyl-1,2,3,3*a*,4,6*a*-hexahydrocyclopenta[*b*]pyrrole (140c): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

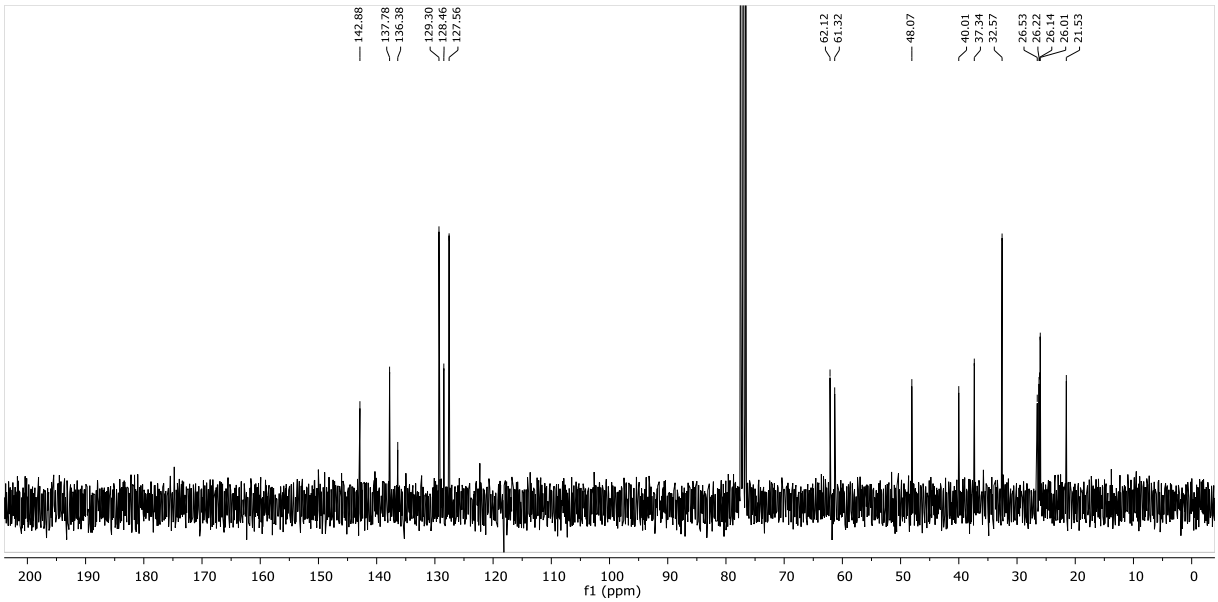


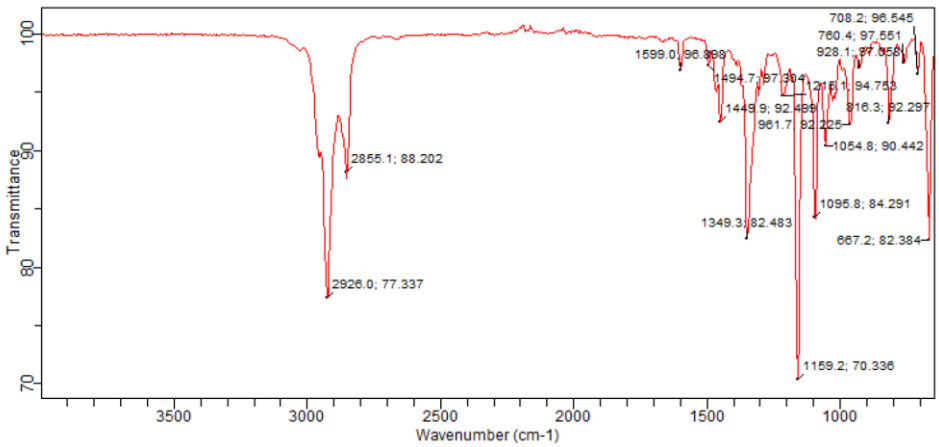




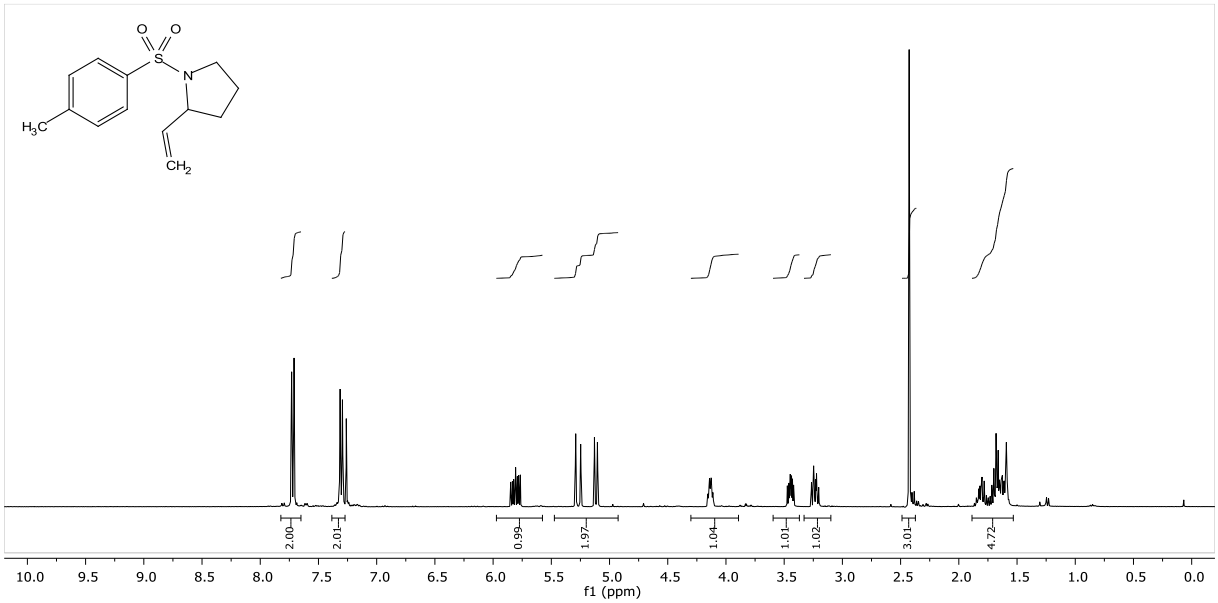
(*E*)-2-(2-Cyclohexylvinyl)-4,4-dimethyl-1-tosylpyrrolidine (140e): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

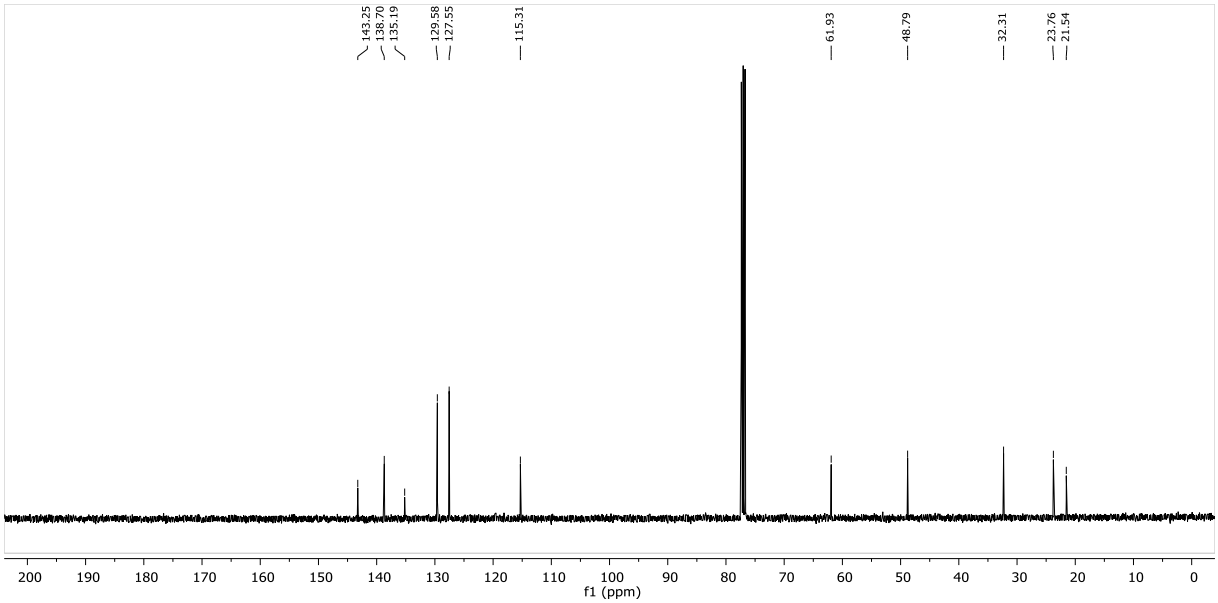


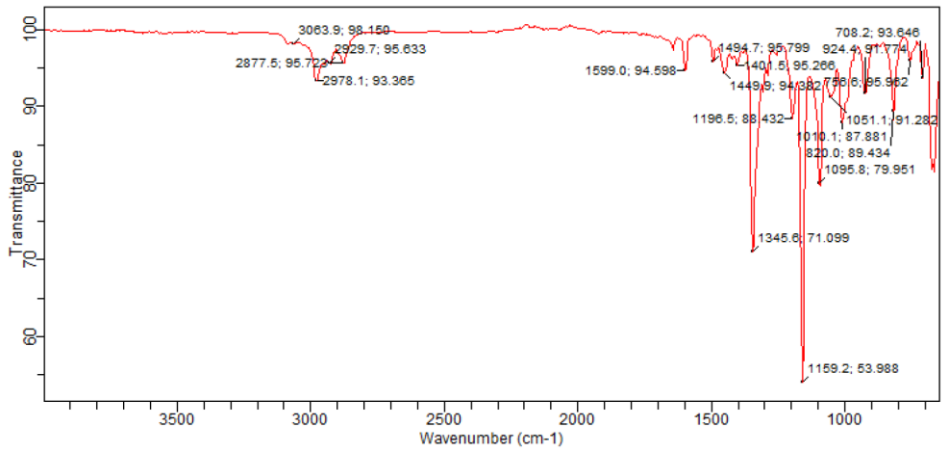




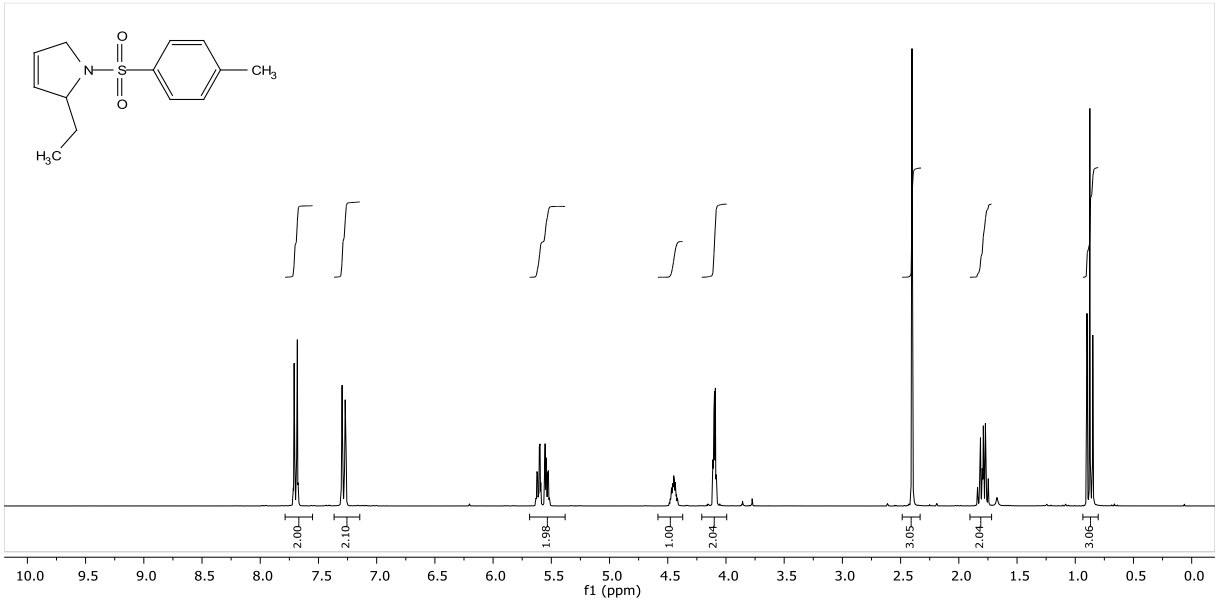
1-Tosyl-2-vinylpyrrolidine (140d): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

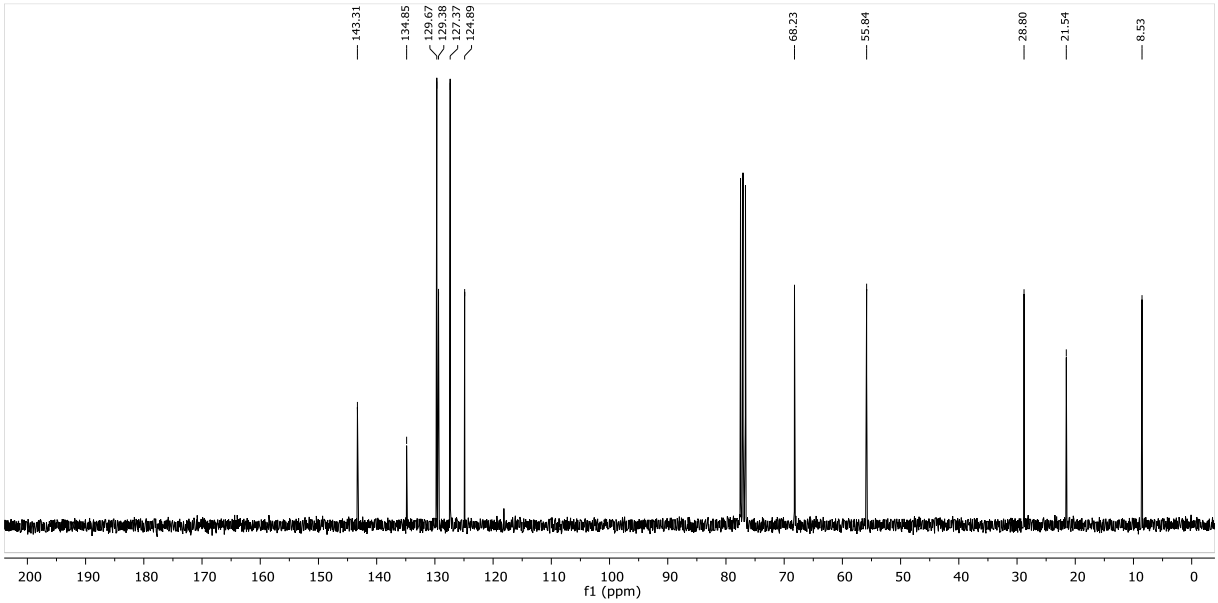


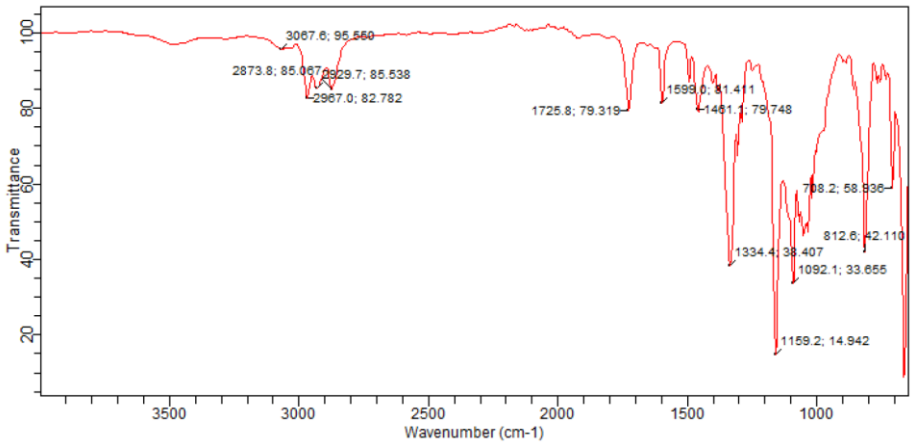




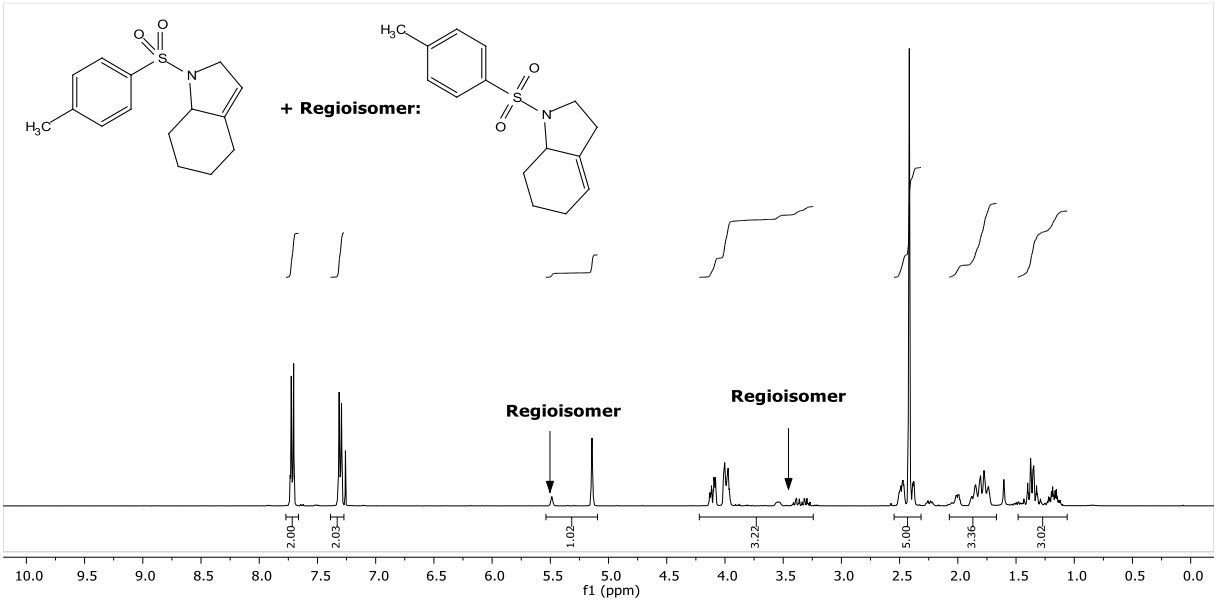
1-((2-Ethylcyclopent-3-en-1-yl)sulfonyl)-4-methylbenzene (149a): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

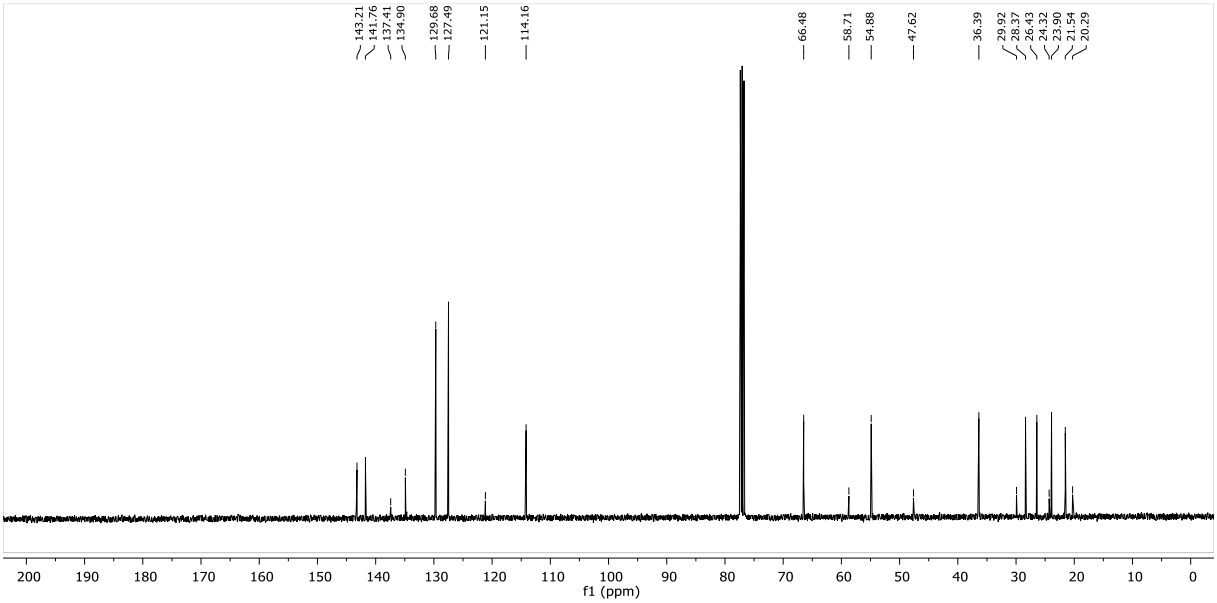


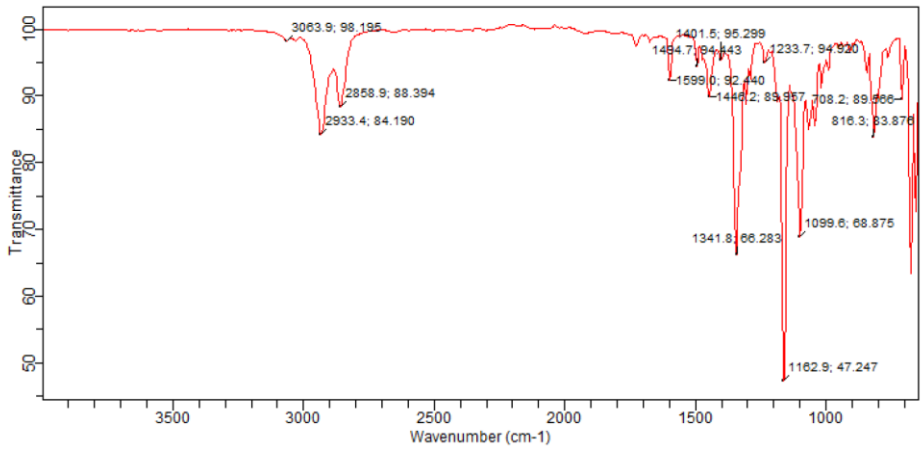




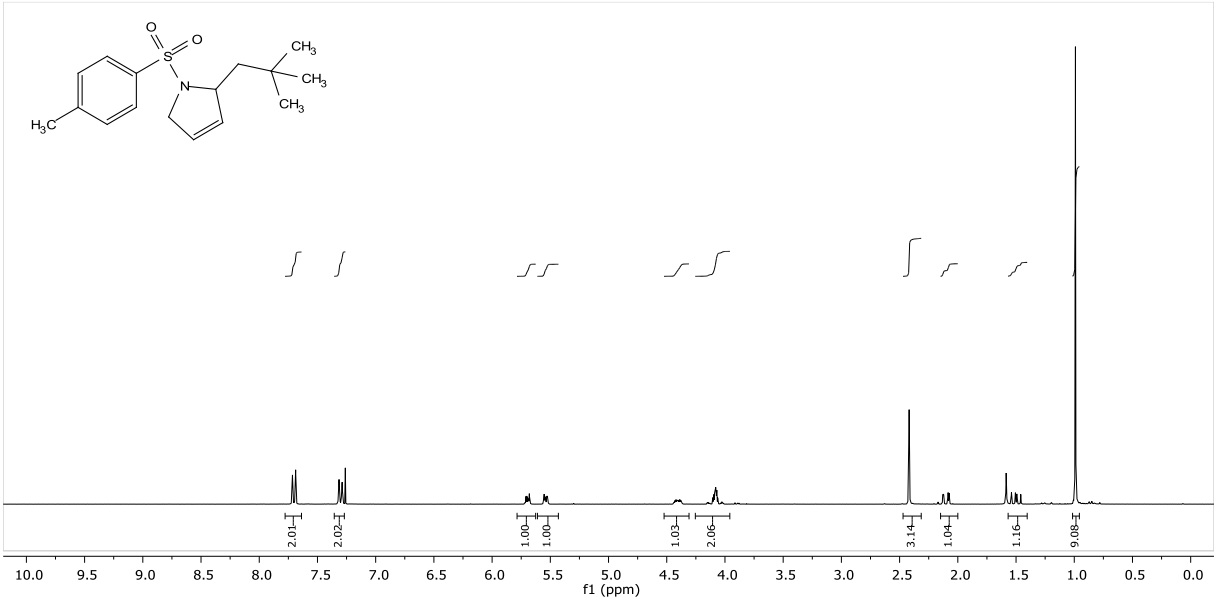
1-Tosyl-2,4,5,6,7,7*a*-hexahydro-1H-indole and 1-Tosyl-2,3,5,6,7,7*a*-hexa-hydro-1H-indole (minor, Regioisomer) (149f and 149f'): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

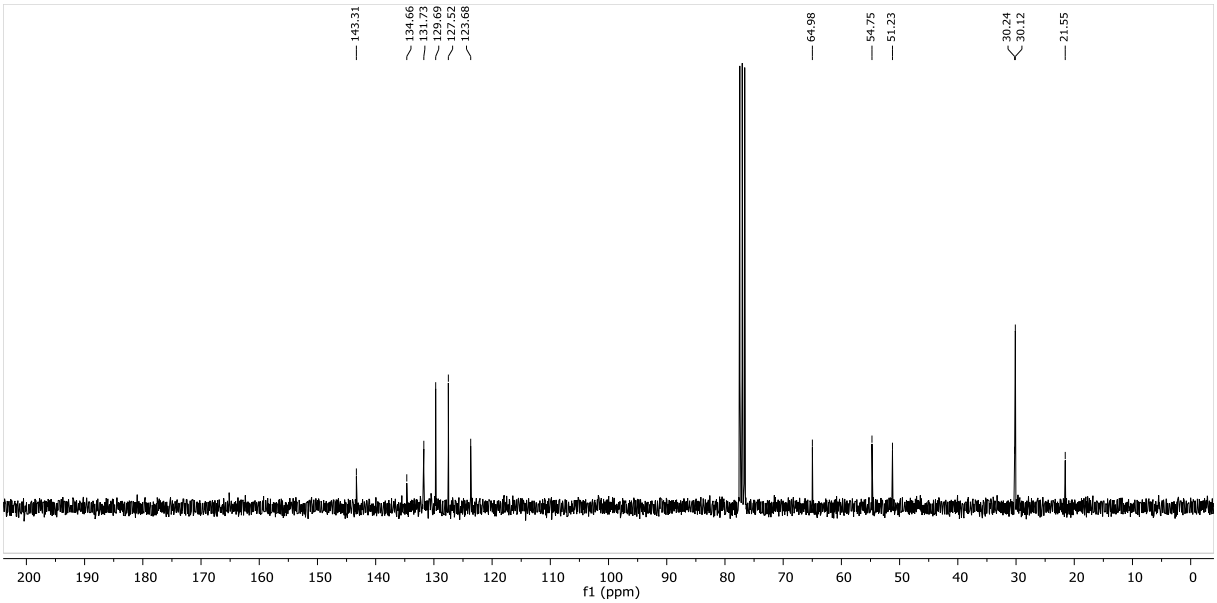


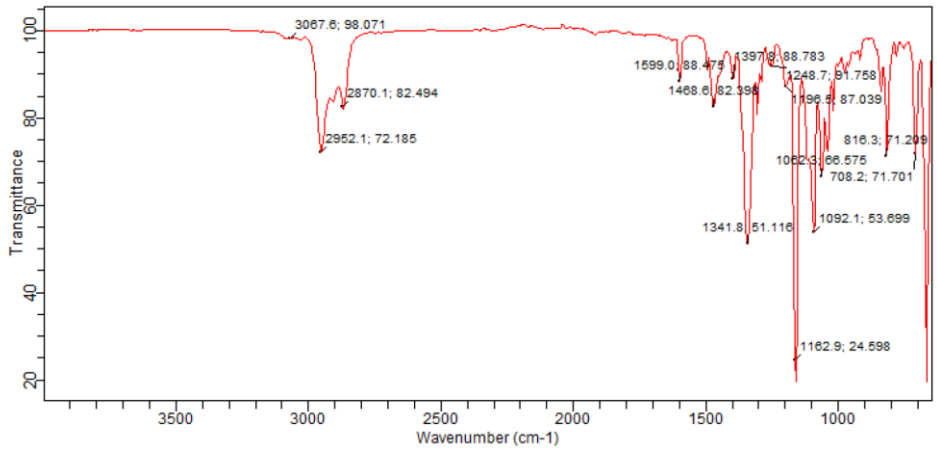




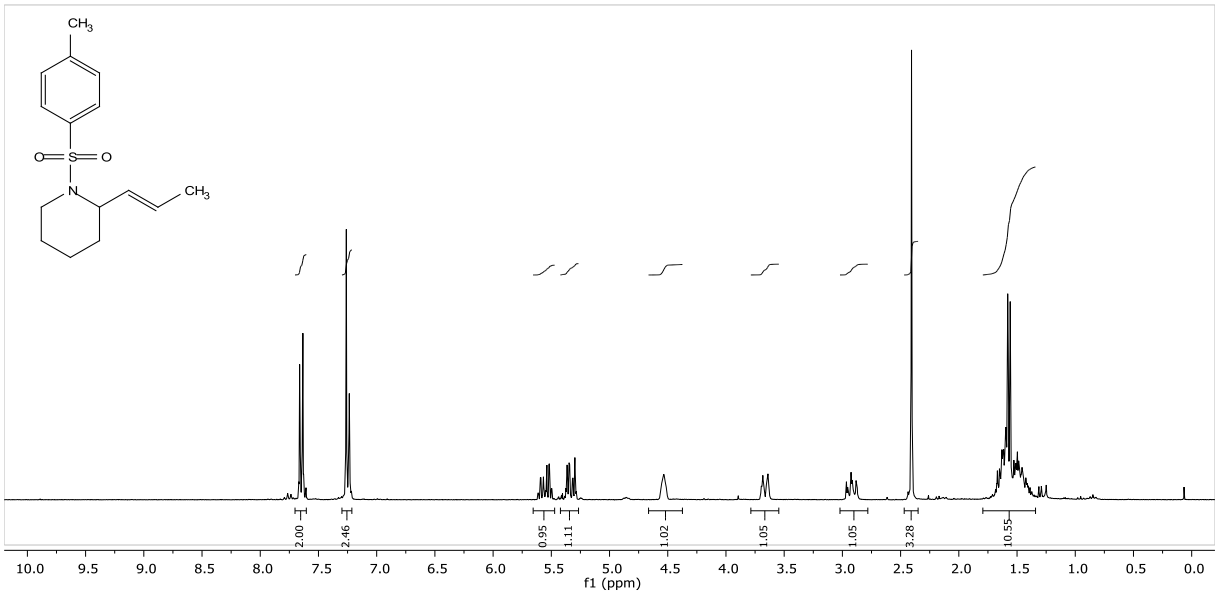
2-Neopentyl-1-tosyl-2,5-dihydro-1H-pyrrole (149b): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

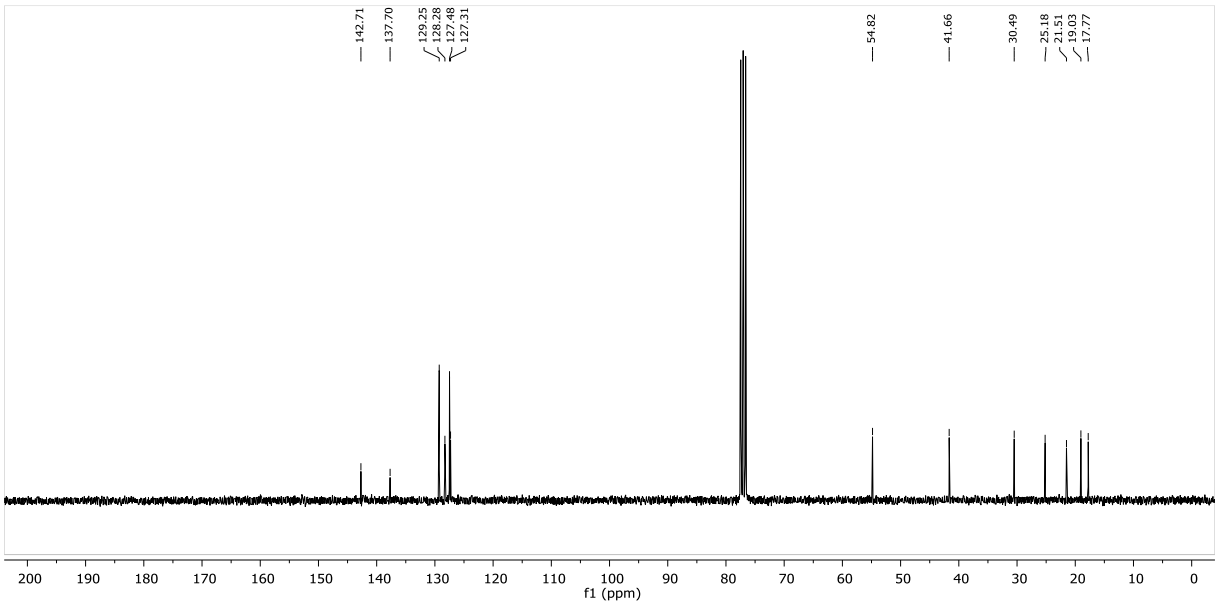


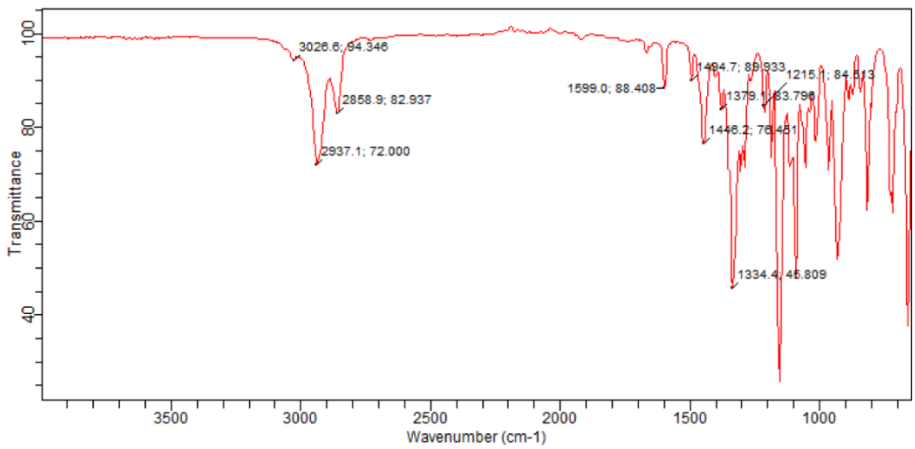




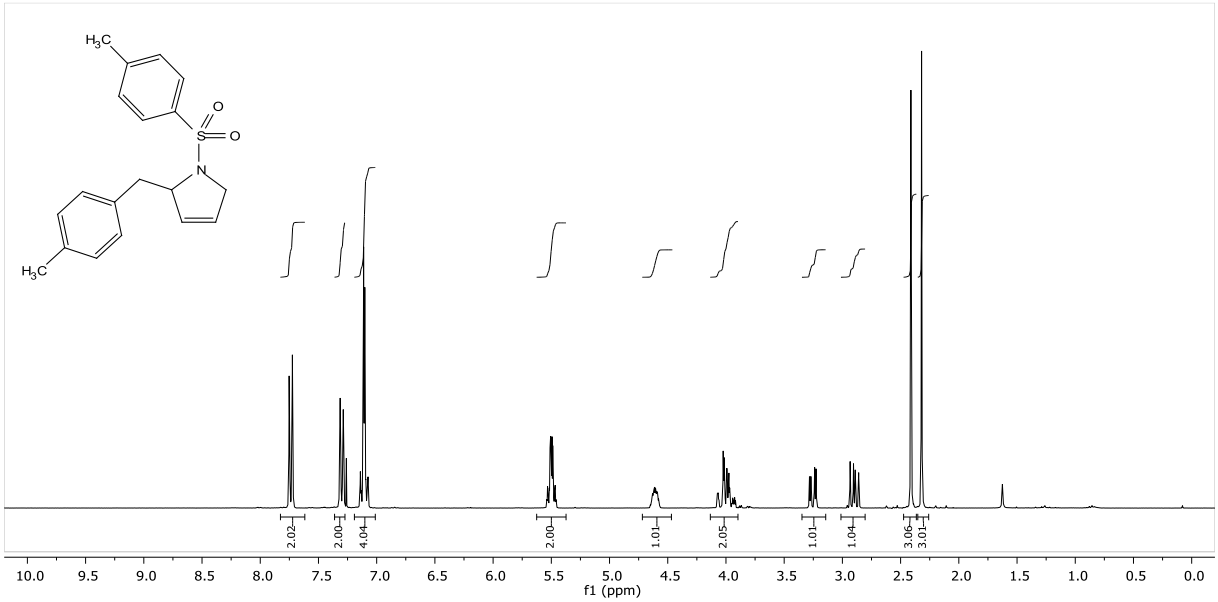
(*E*)-2-(Prop-1-en-1-yl)-1-tosylpiperidine (150a): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

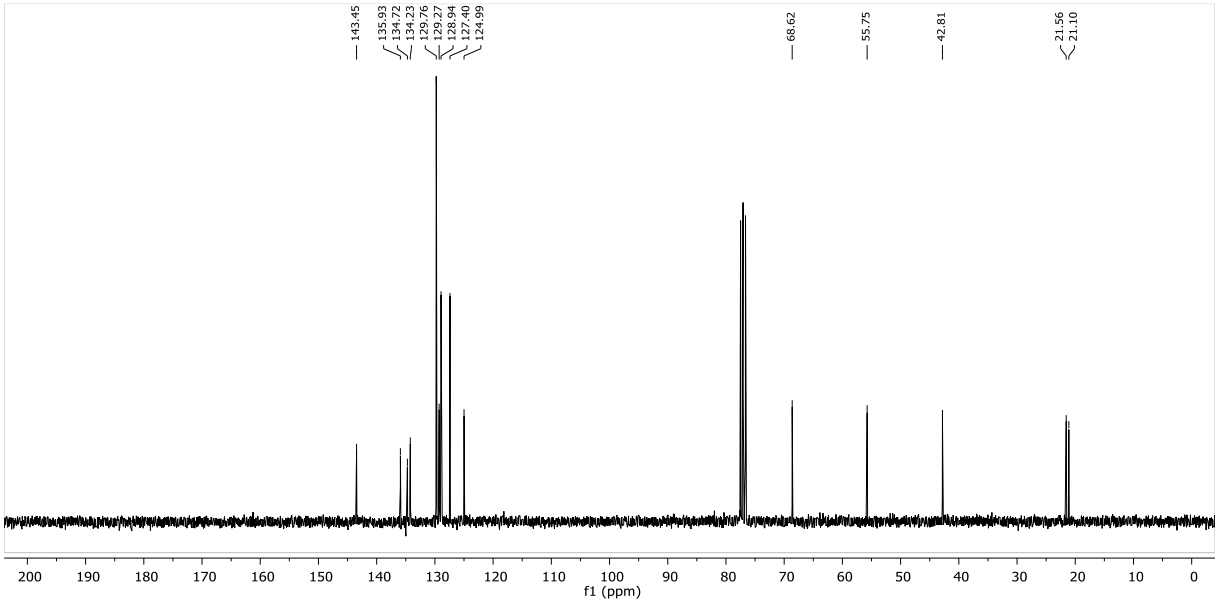


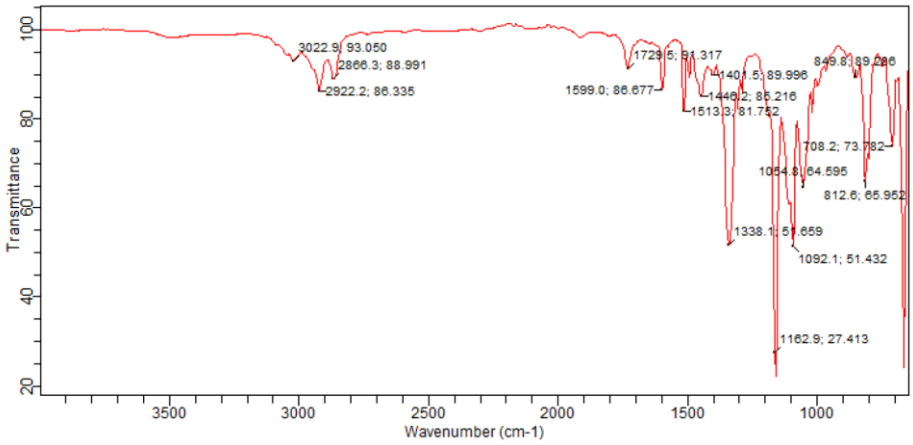




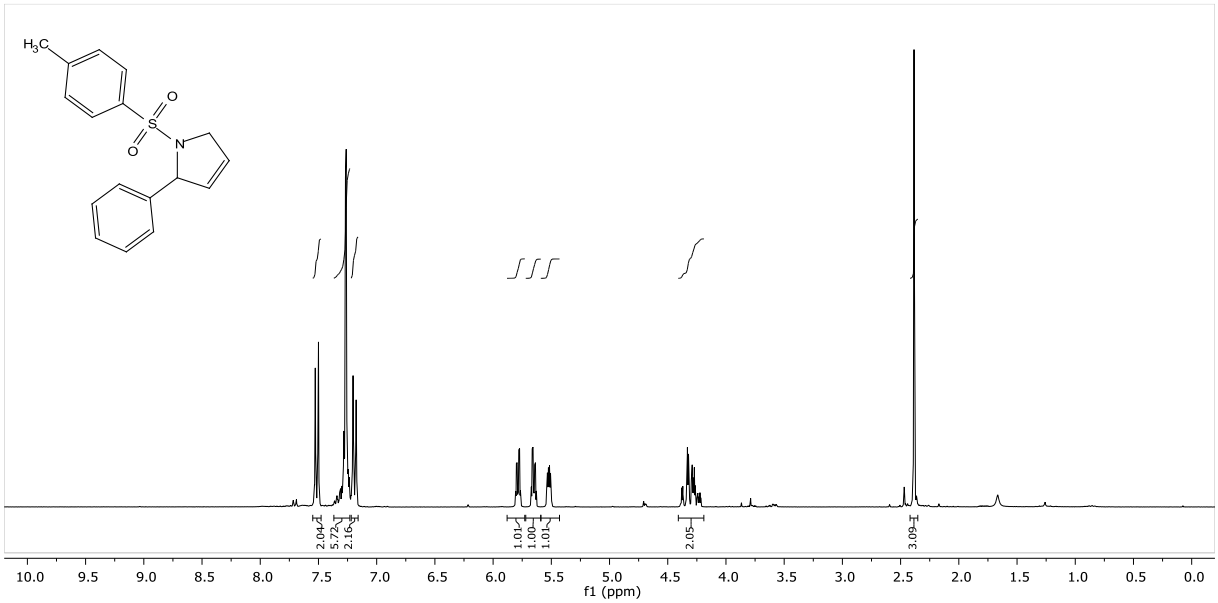
2-(4-Methylbenzyl)-1-tosyl-2,5-dihydro-1H-pyrrole (149c): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

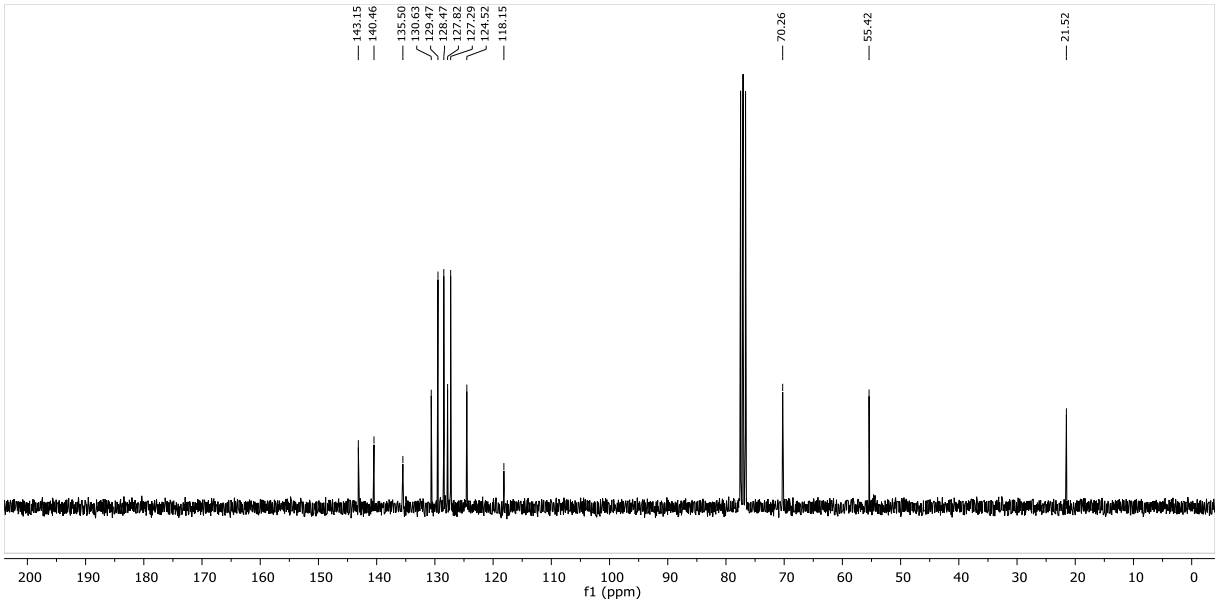


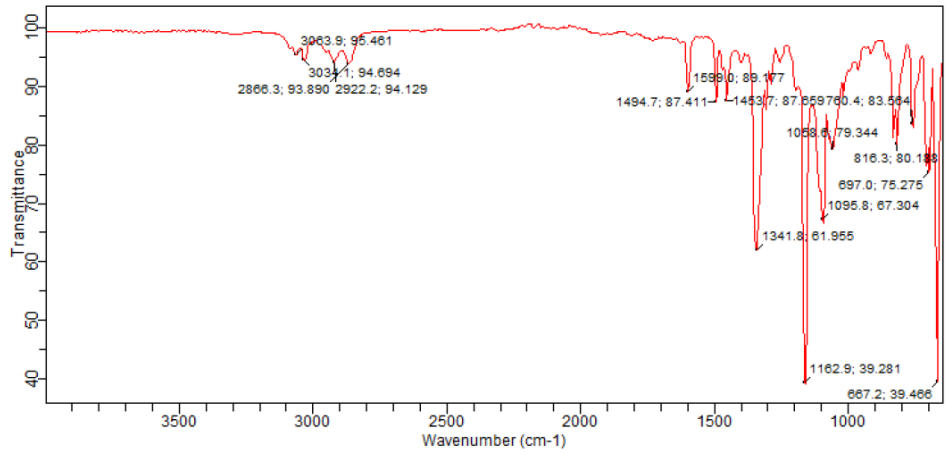




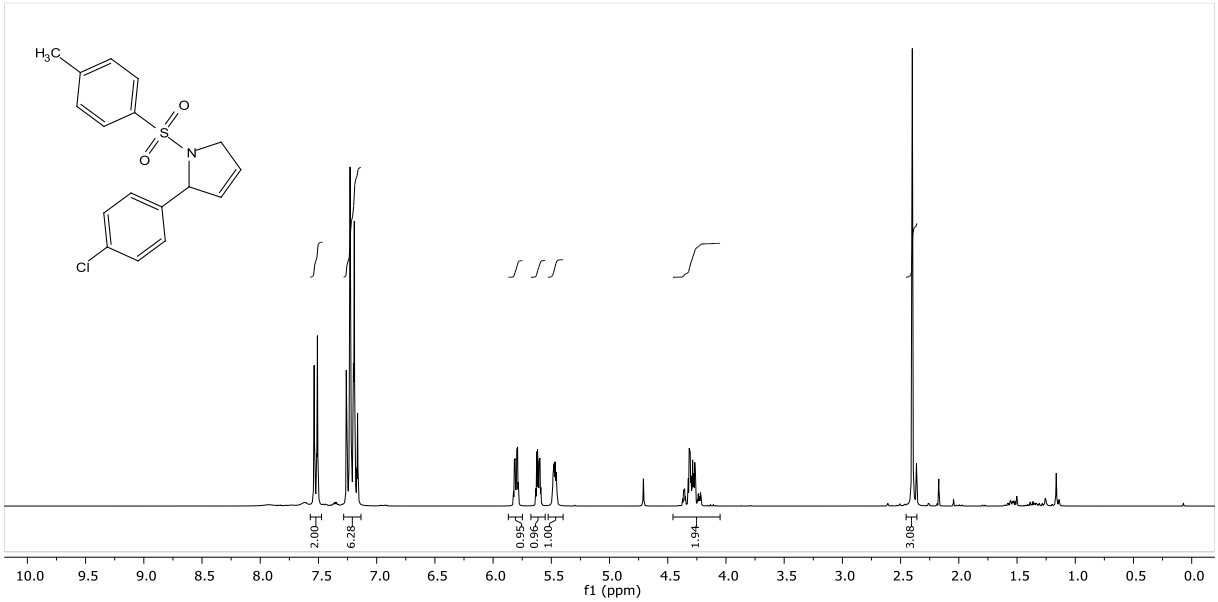
2-Phenyl-1-tosyl-2,5-dihydro-1H-pyrrole (149d): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

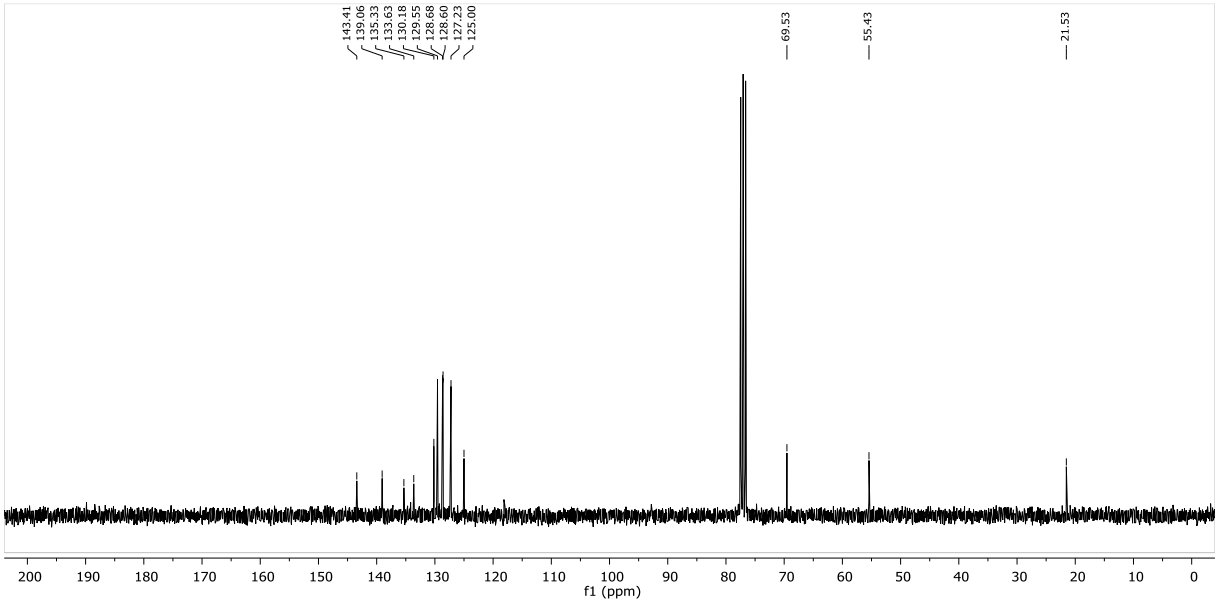


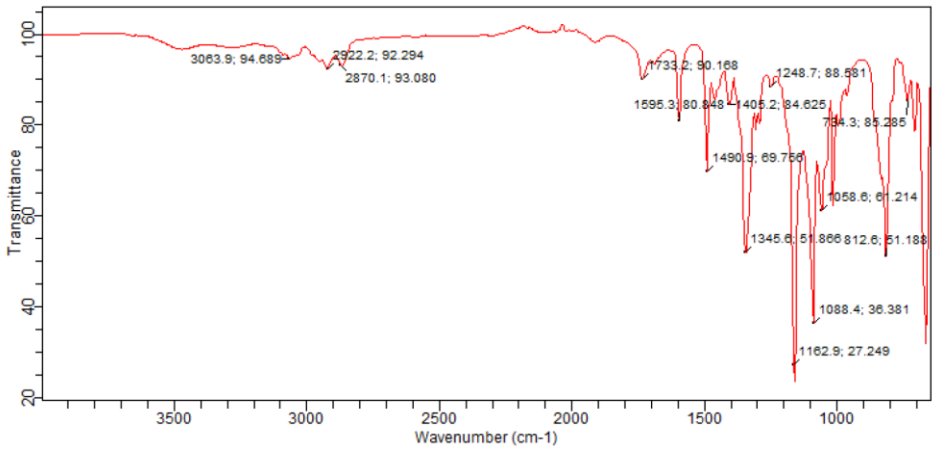




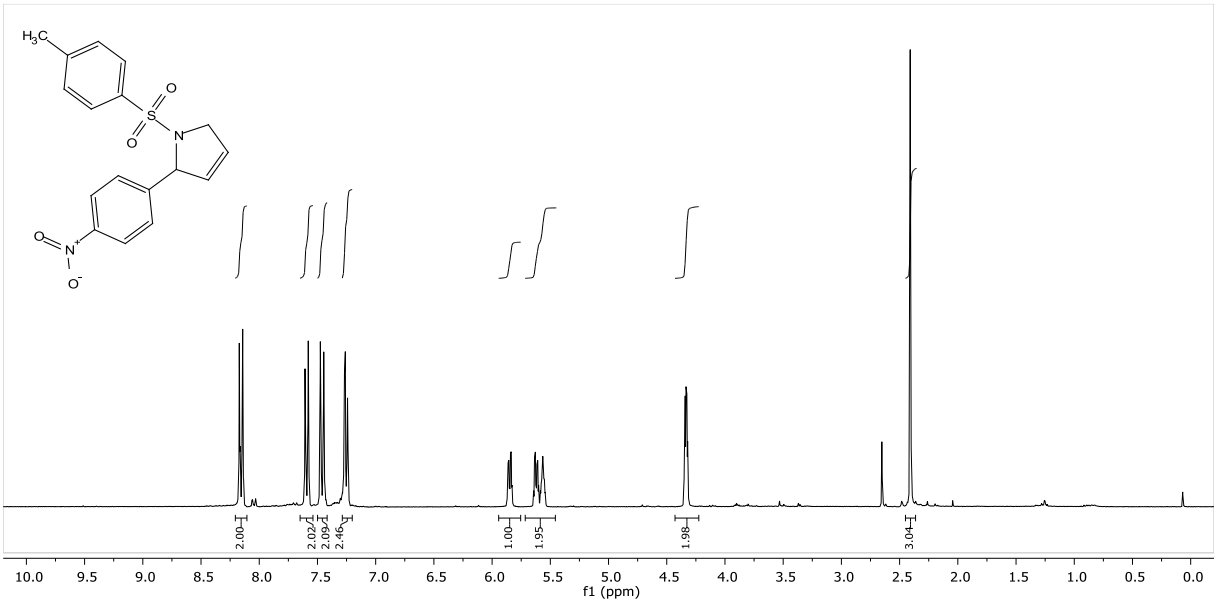
2-(4-Chlorophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole (149g): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

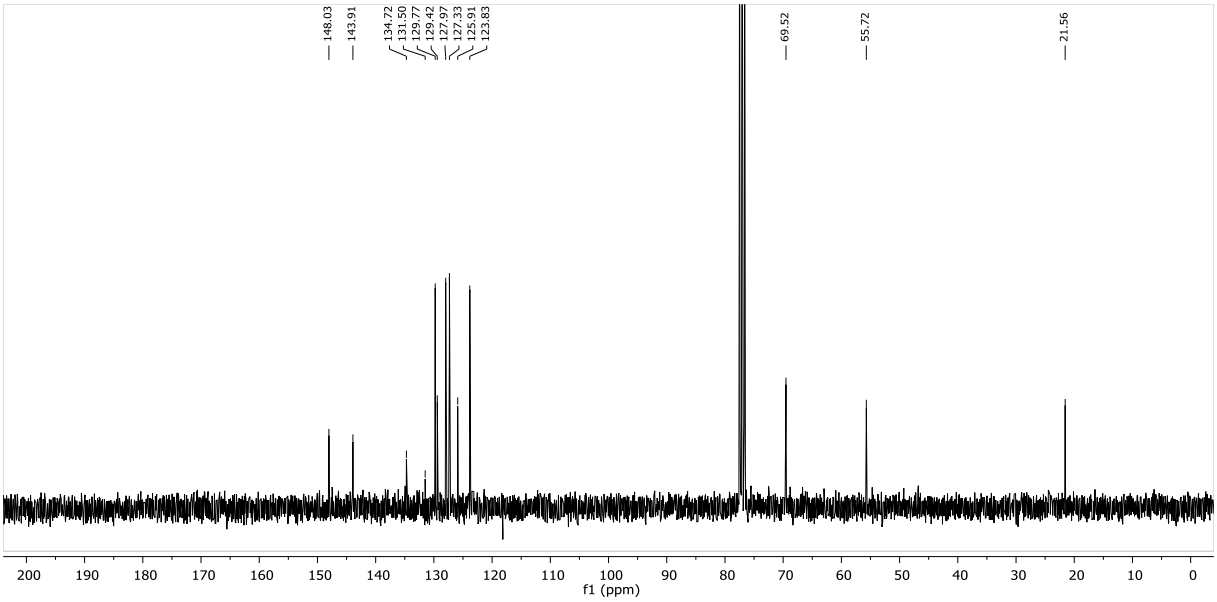


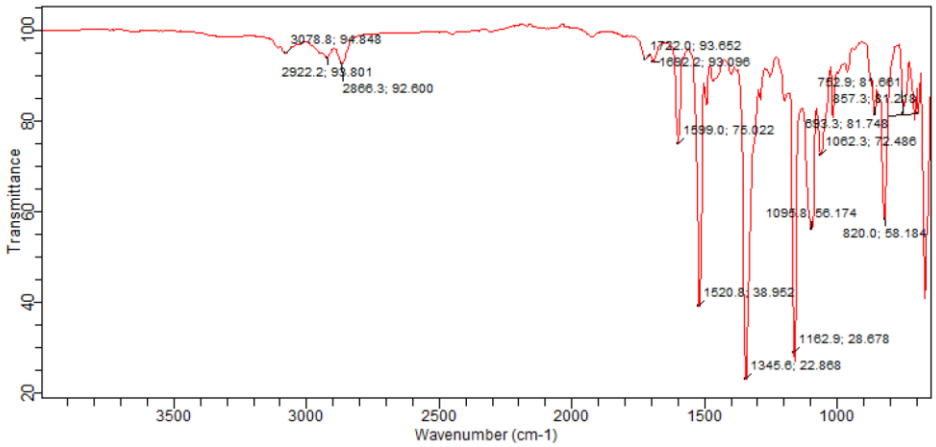




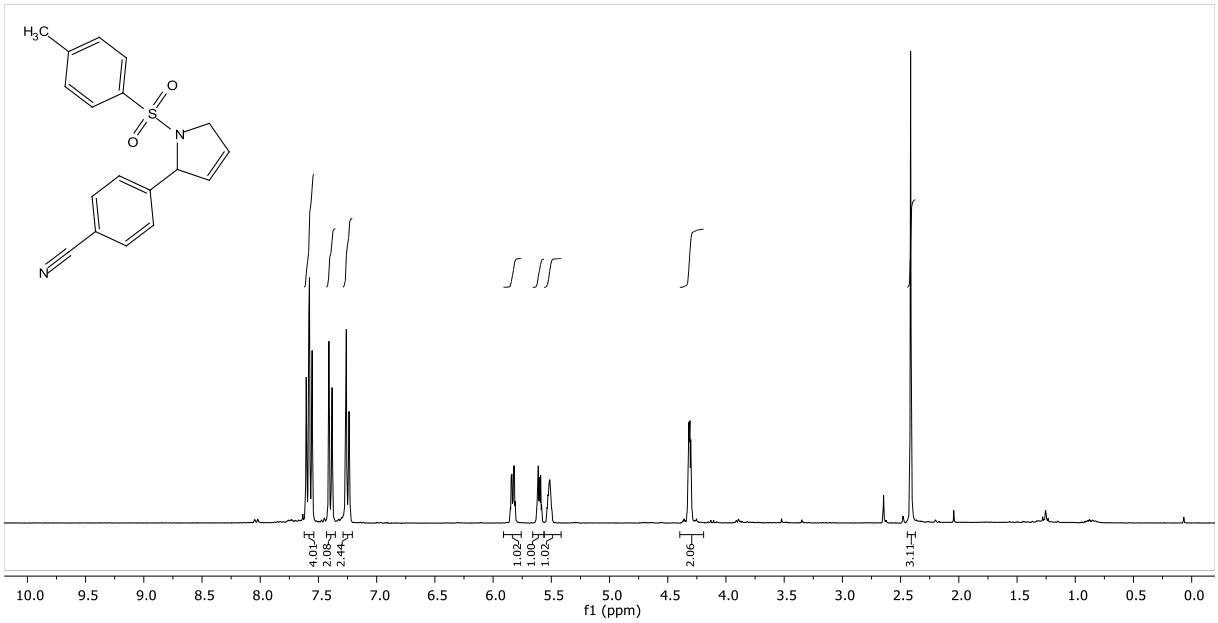
2-(4-Nitrophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole (149h): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

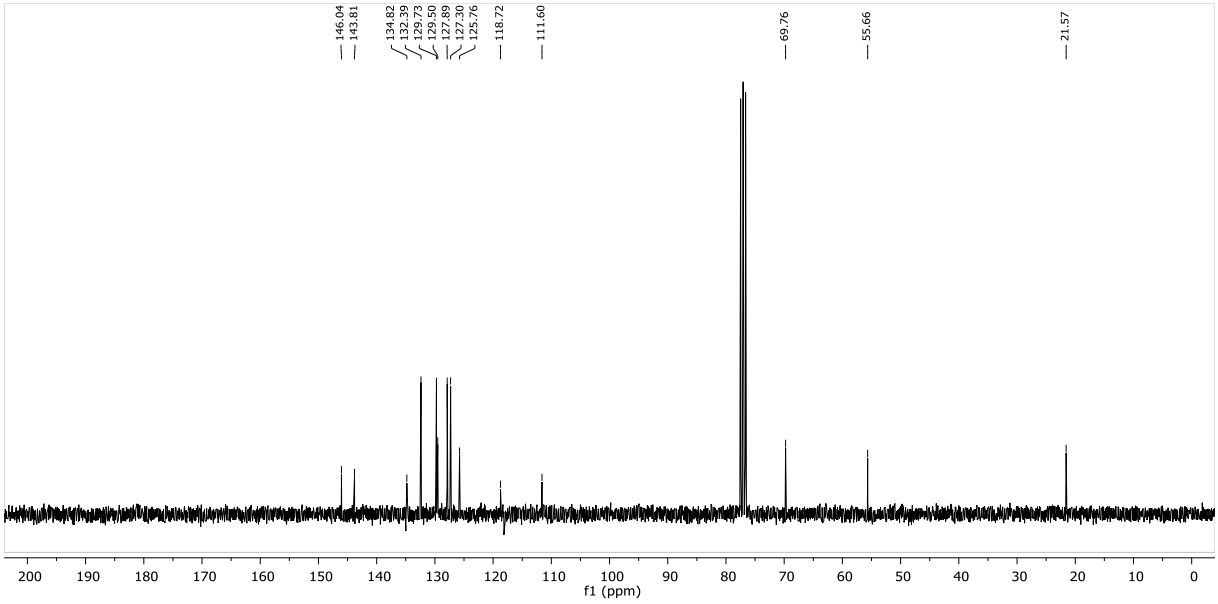


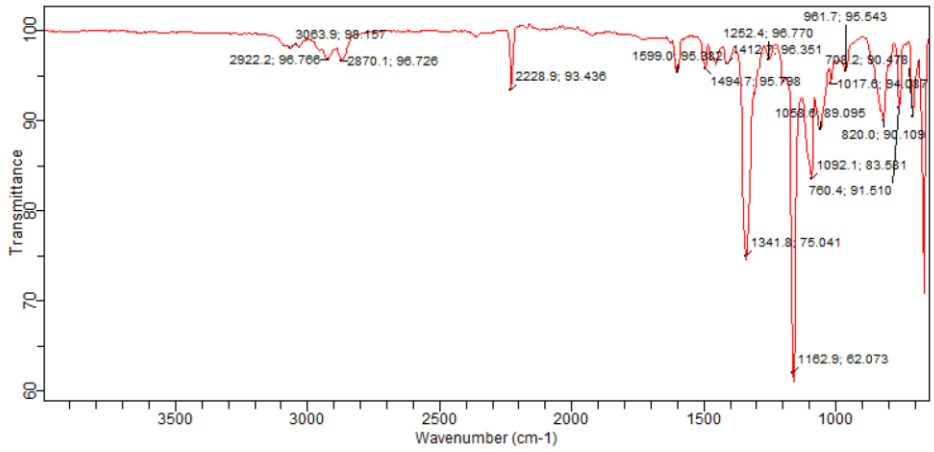




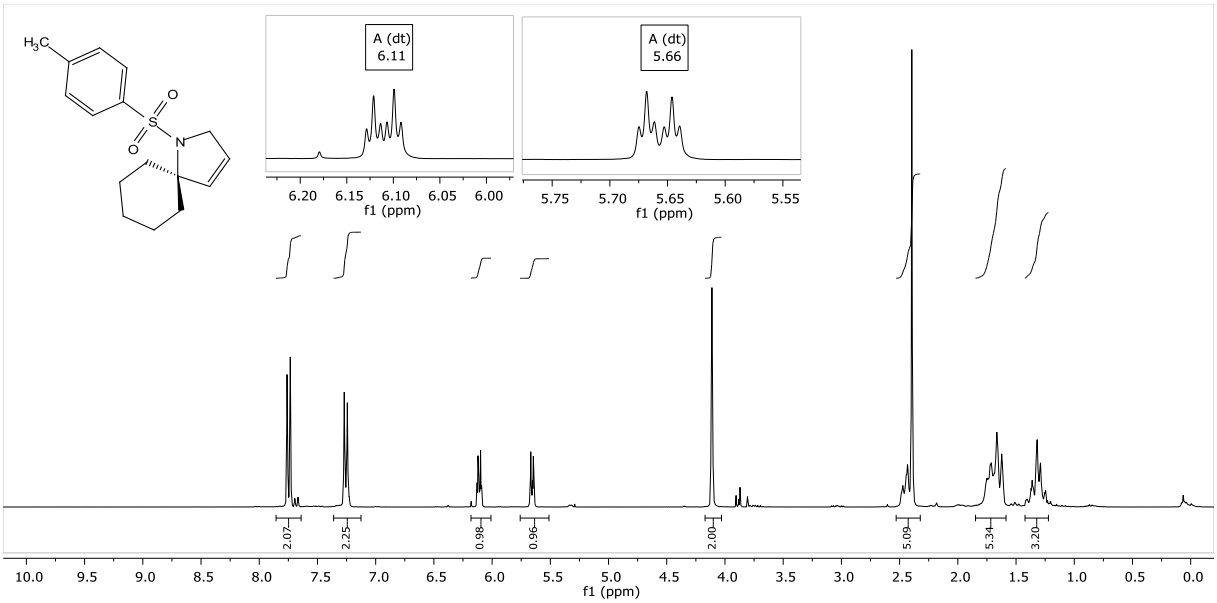
4-(1-Tosyl-2,5-dihydro-1H-pyrrol-2-yl)benzonitrile (149l): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

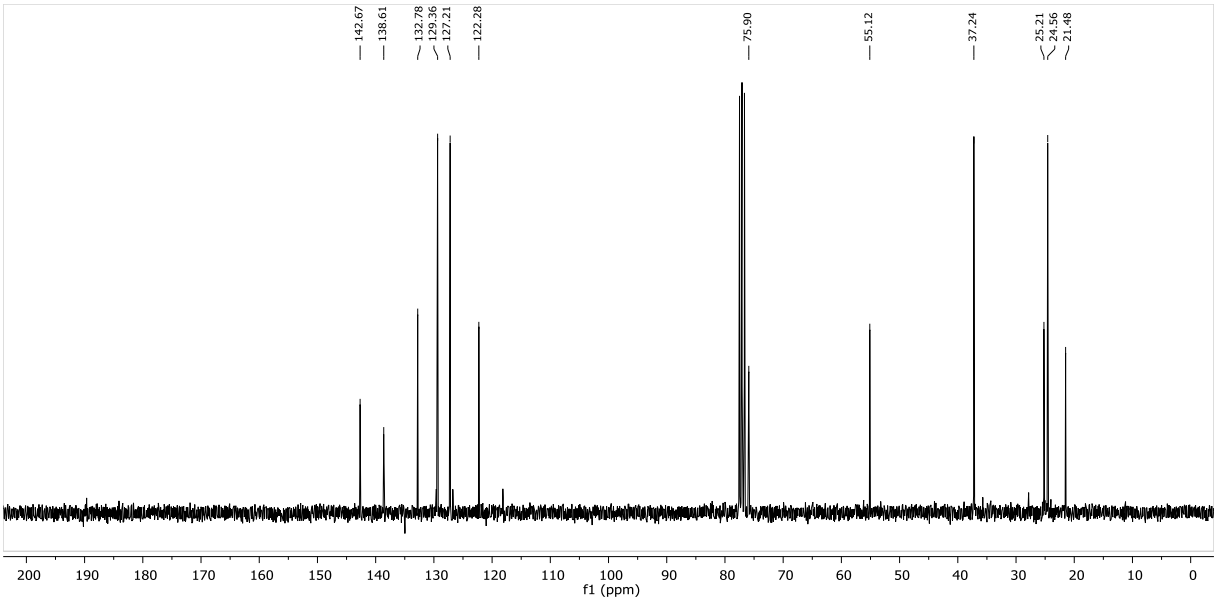


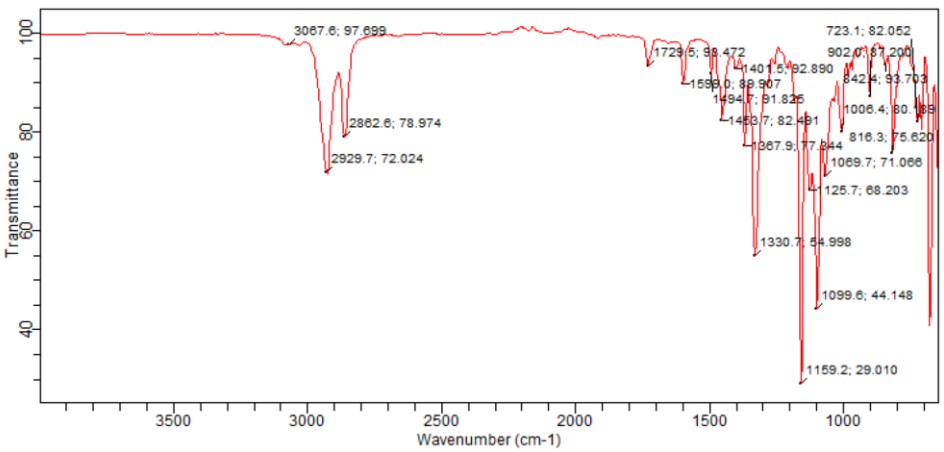




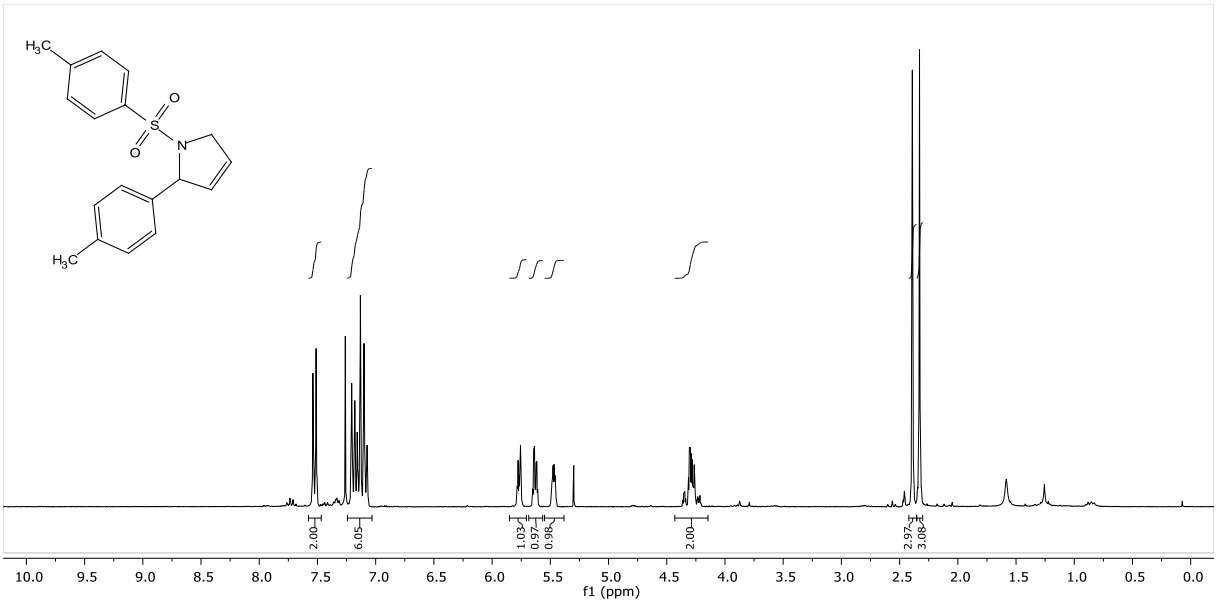
1-Tosyl-1-azaspiro[4.5]dec-3-ene (149k): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

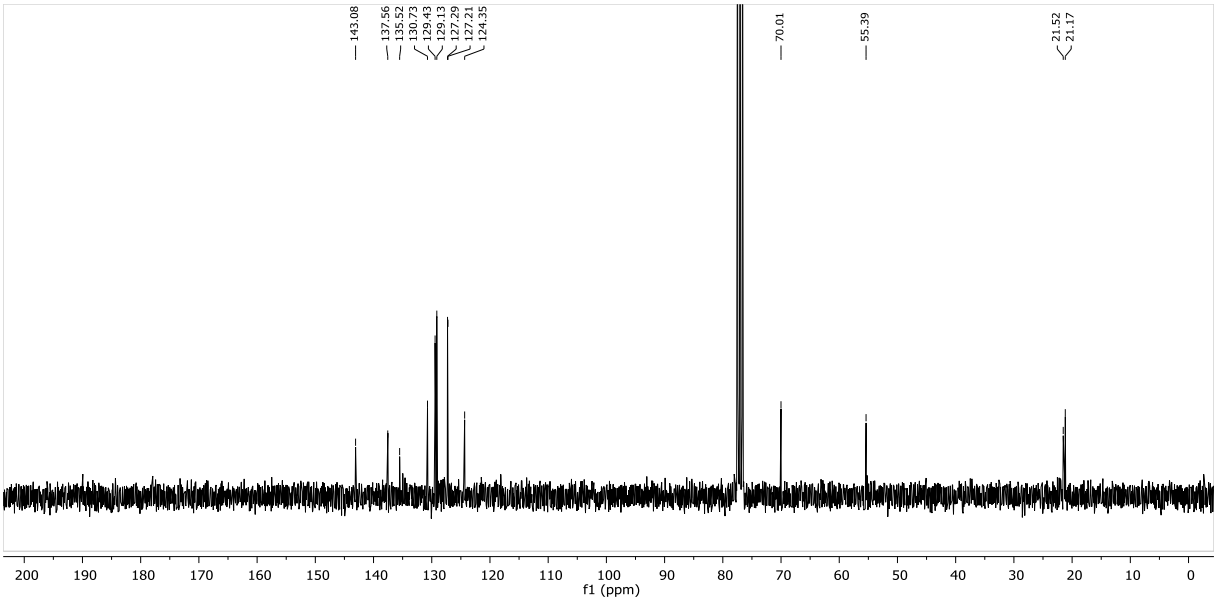


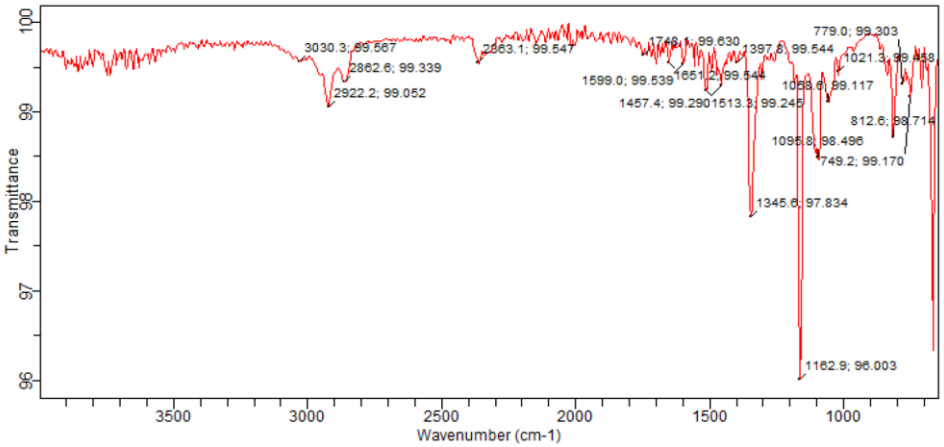




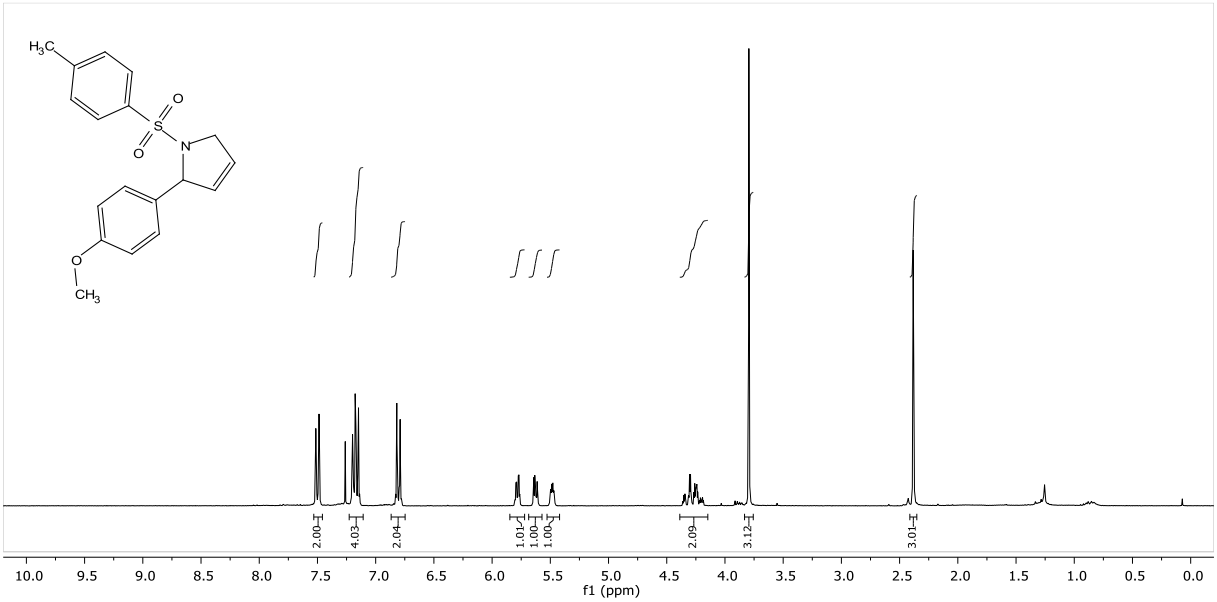
2-(*p*-Tolyl)-1-tosyl-2,5-dihydro-1H-pyrrole (149e): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

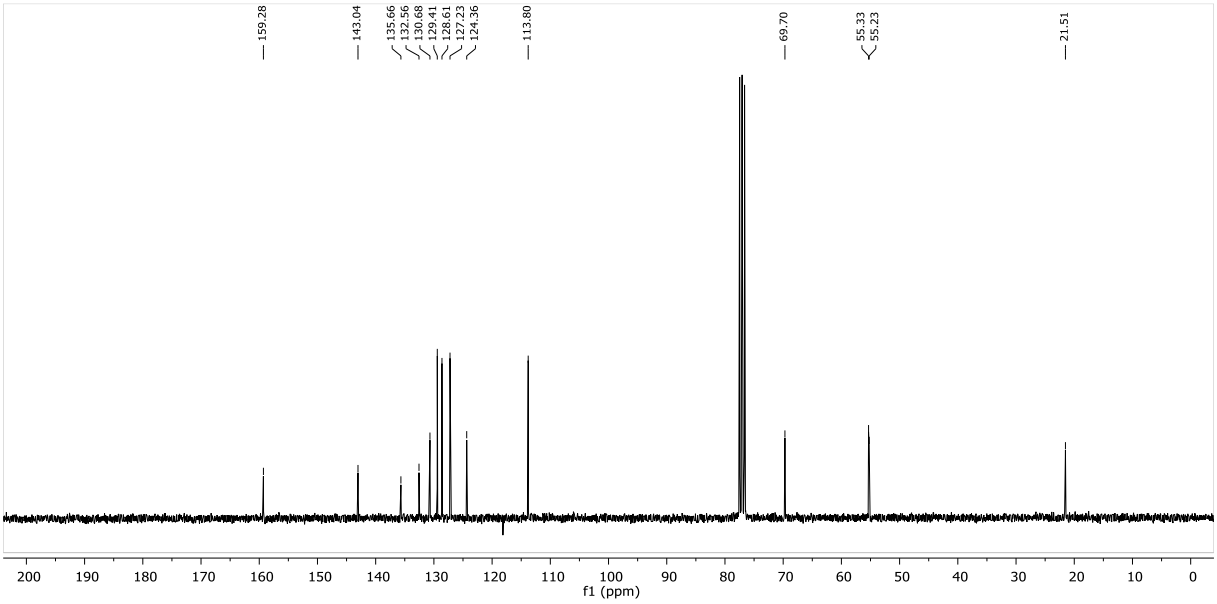


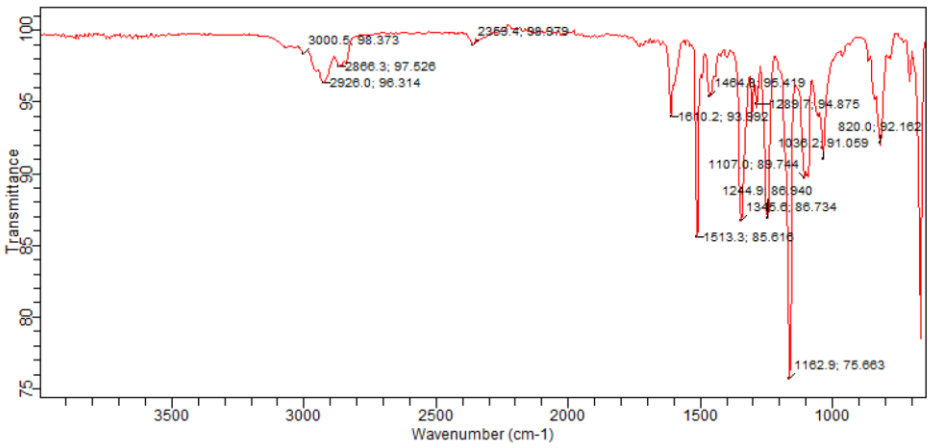




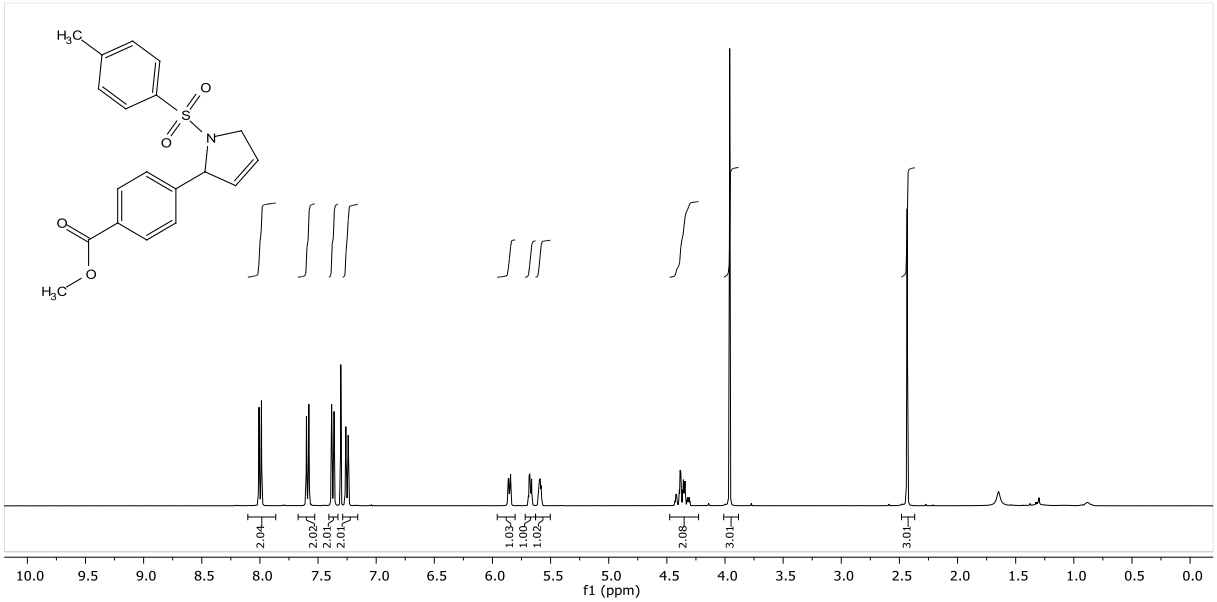
2-(4-Methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole (149j): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

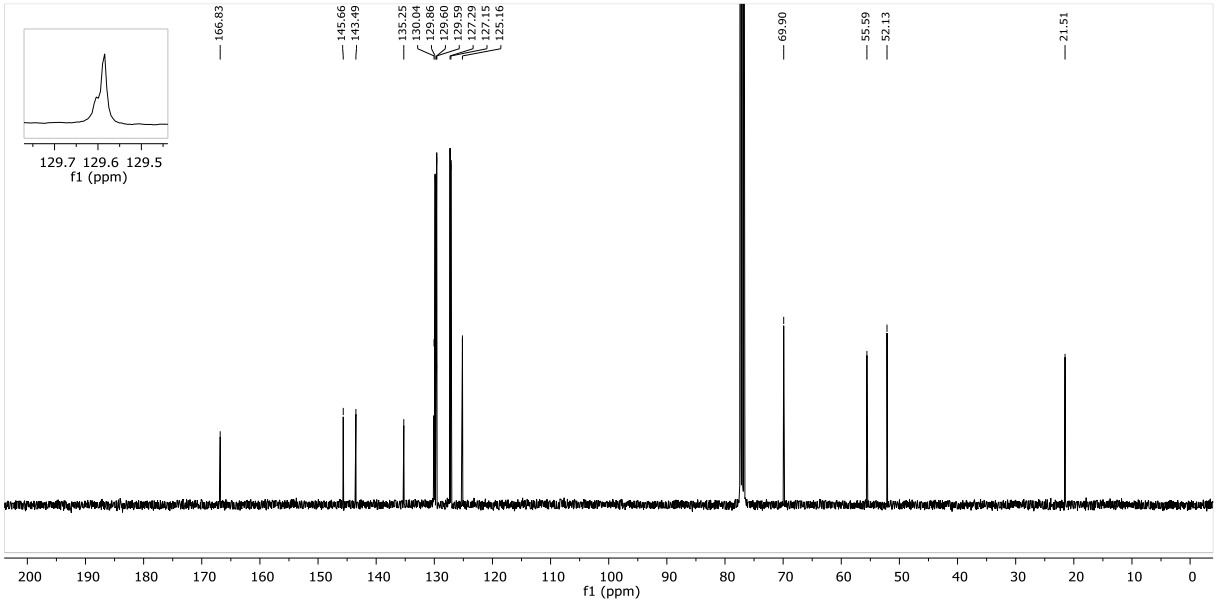


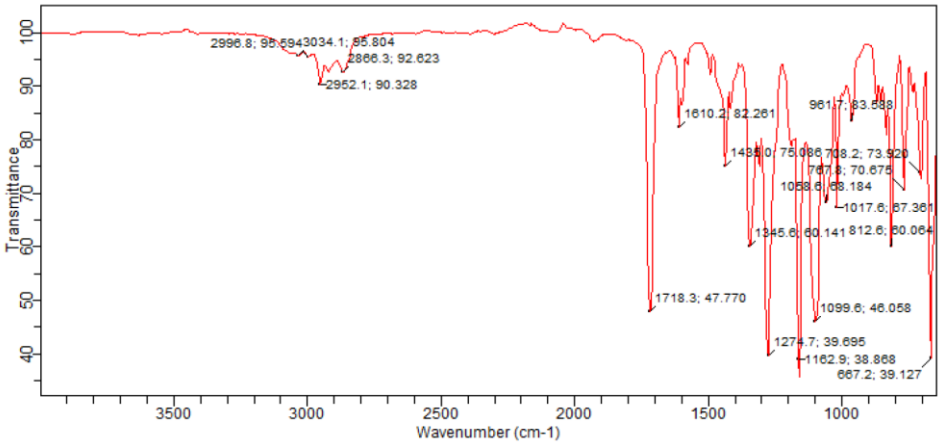




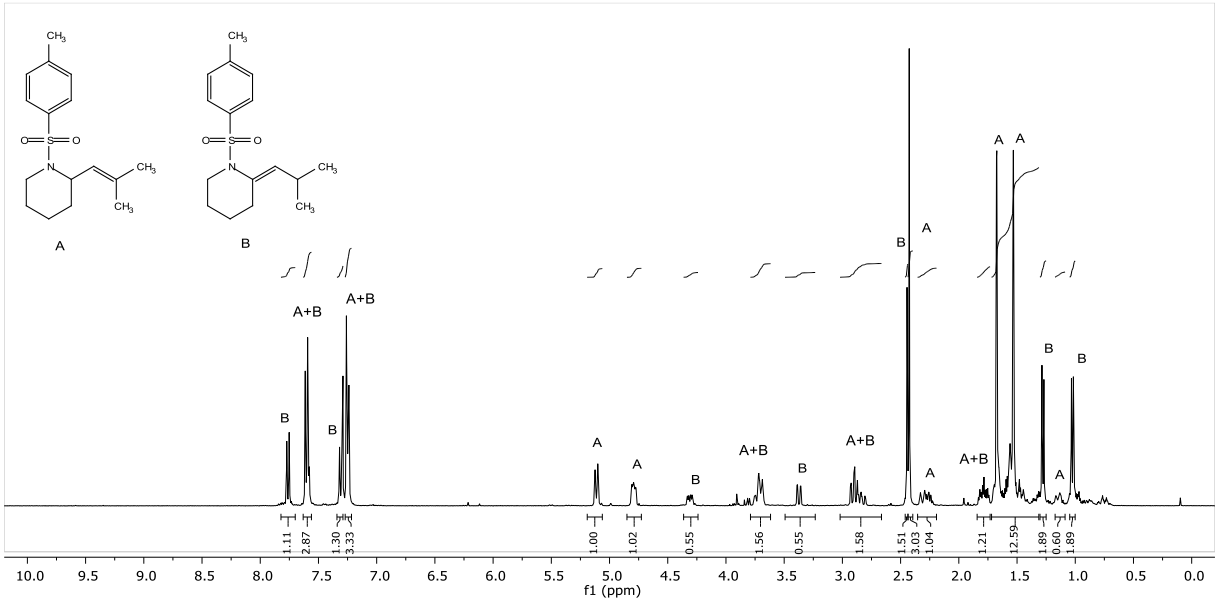
Methyl 4-(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)benzoate (149i): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

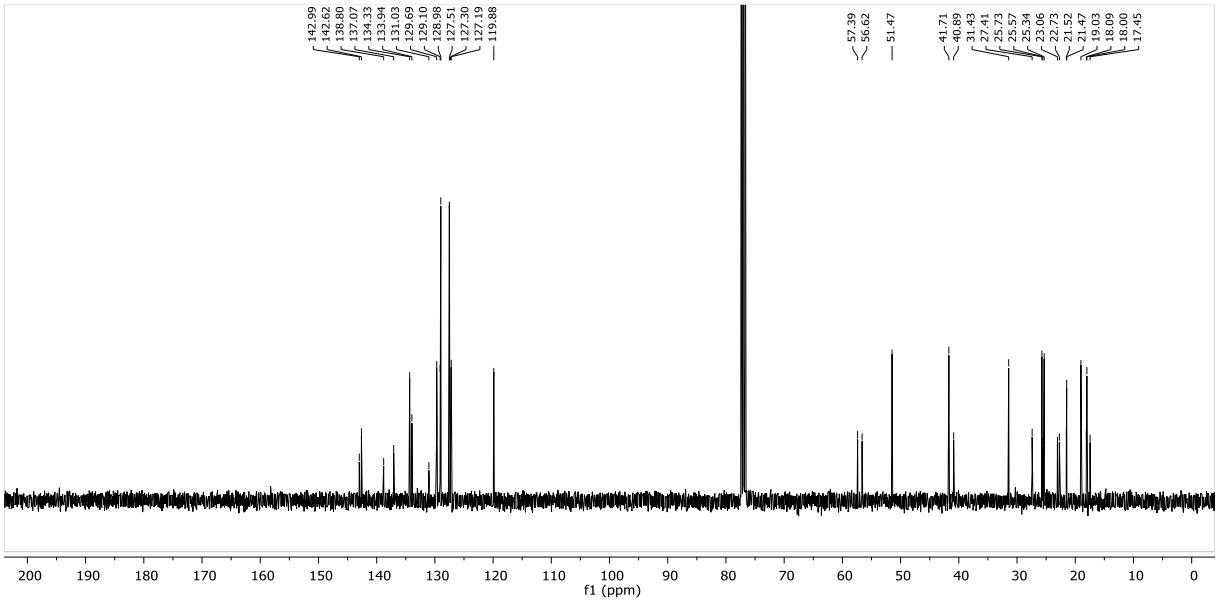


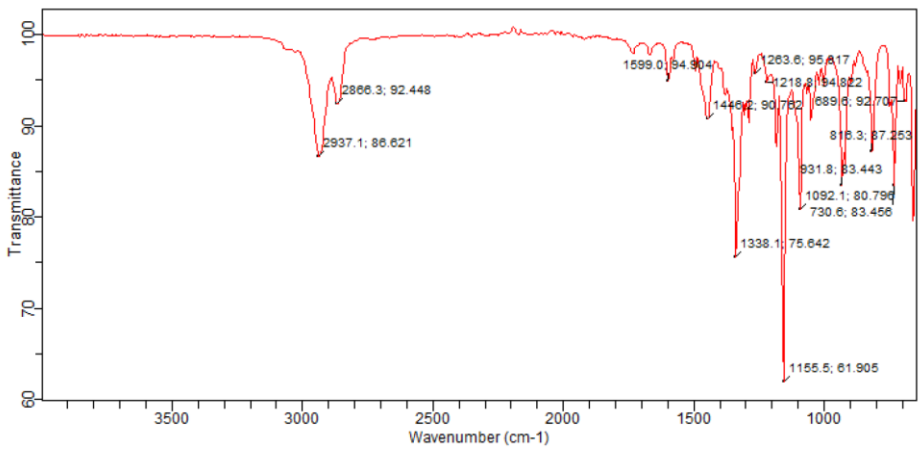




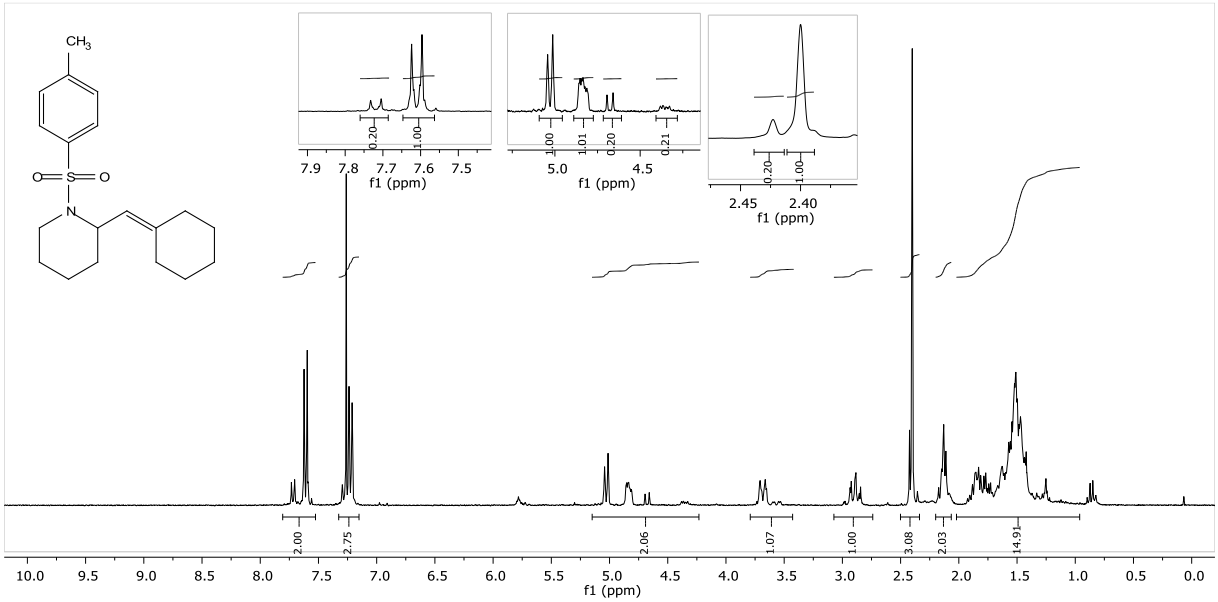
(2-(2-Methylpropylidene)-1-tosylpiperidine (A) and 2-(2-Methylprop-1-en-1-yl)-1-tosylpi-peridine (B) (150d and 150d'): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

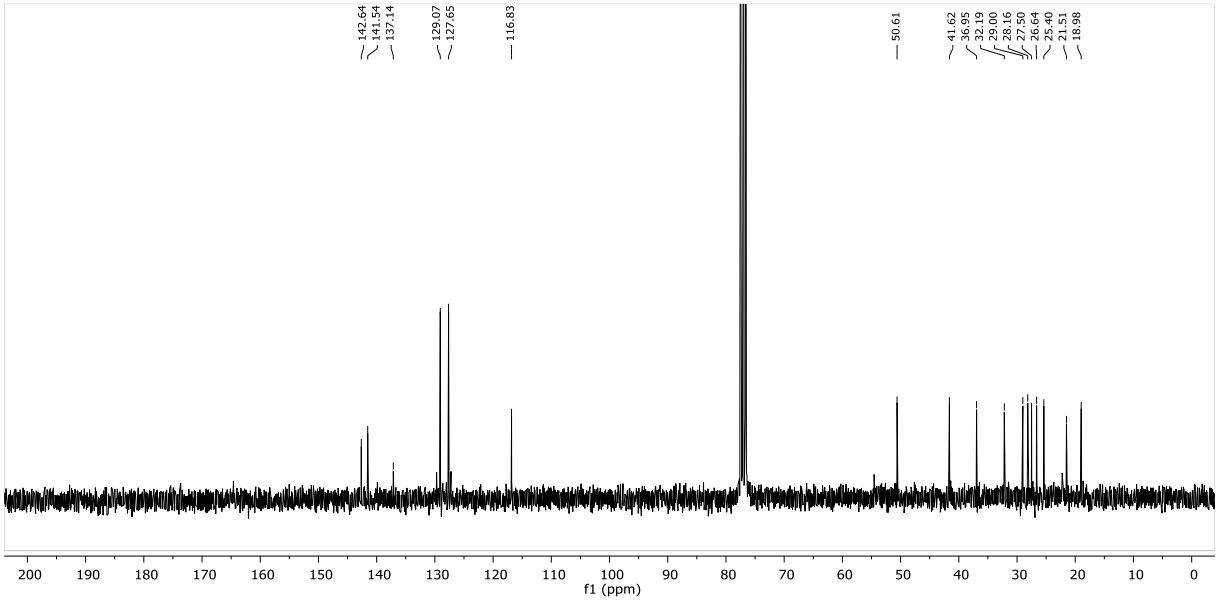


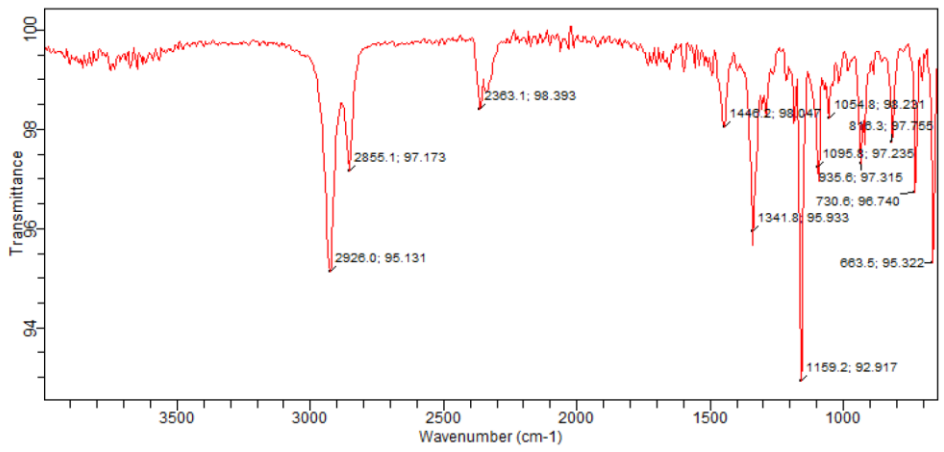




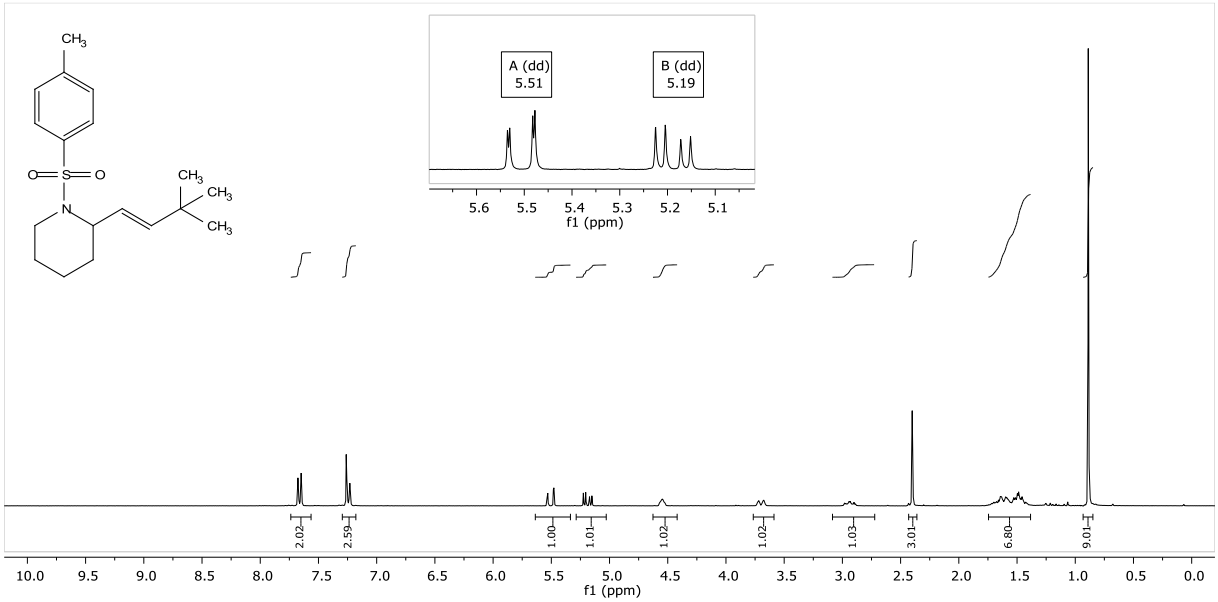
2-(Cyclohexylidenemethyl)-1-tosylpiperidine (2 Rotamers, 150e): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

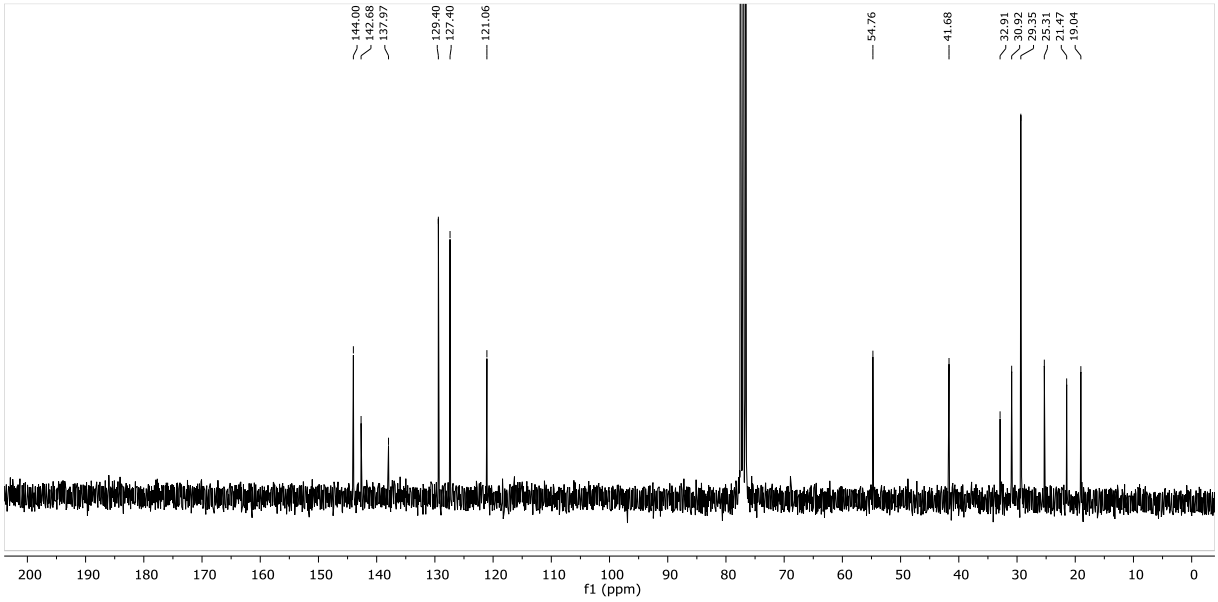


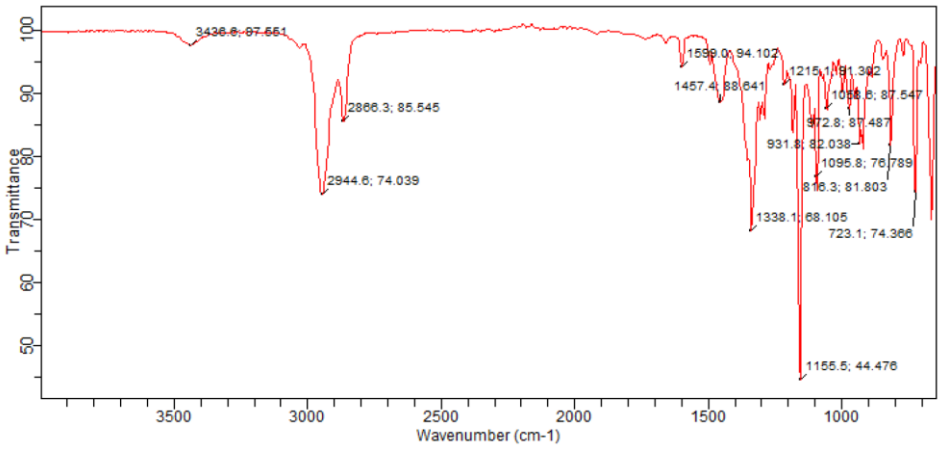




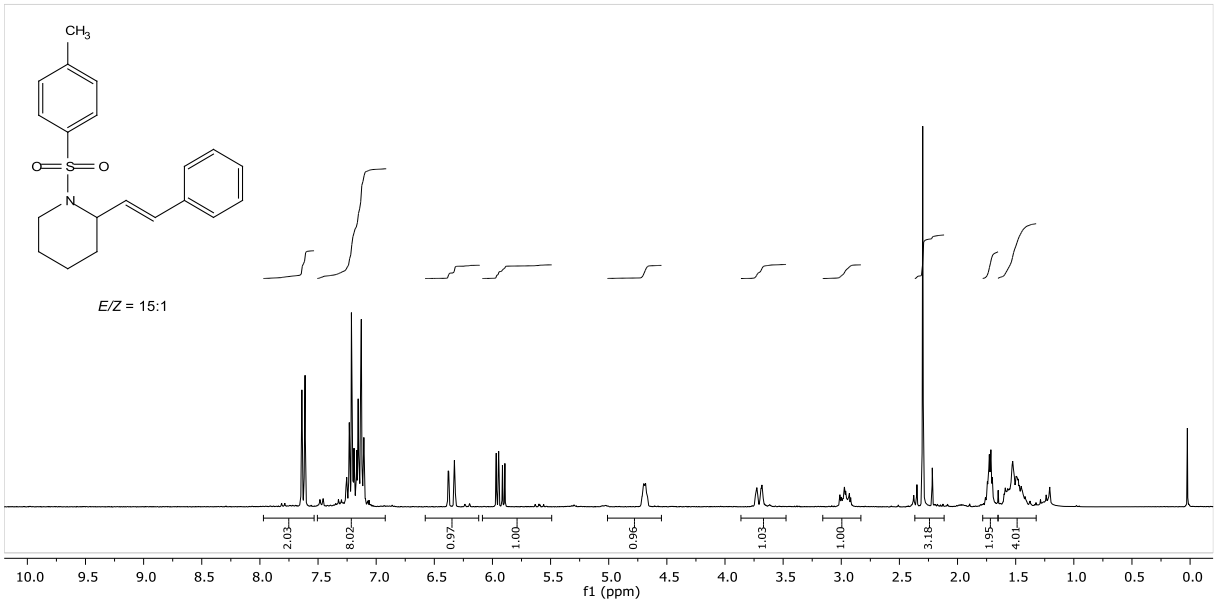
(*E*)-2-(3,3-Dimethylbut-1-en-1-yl)-1-tosylpiperidine (150c): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

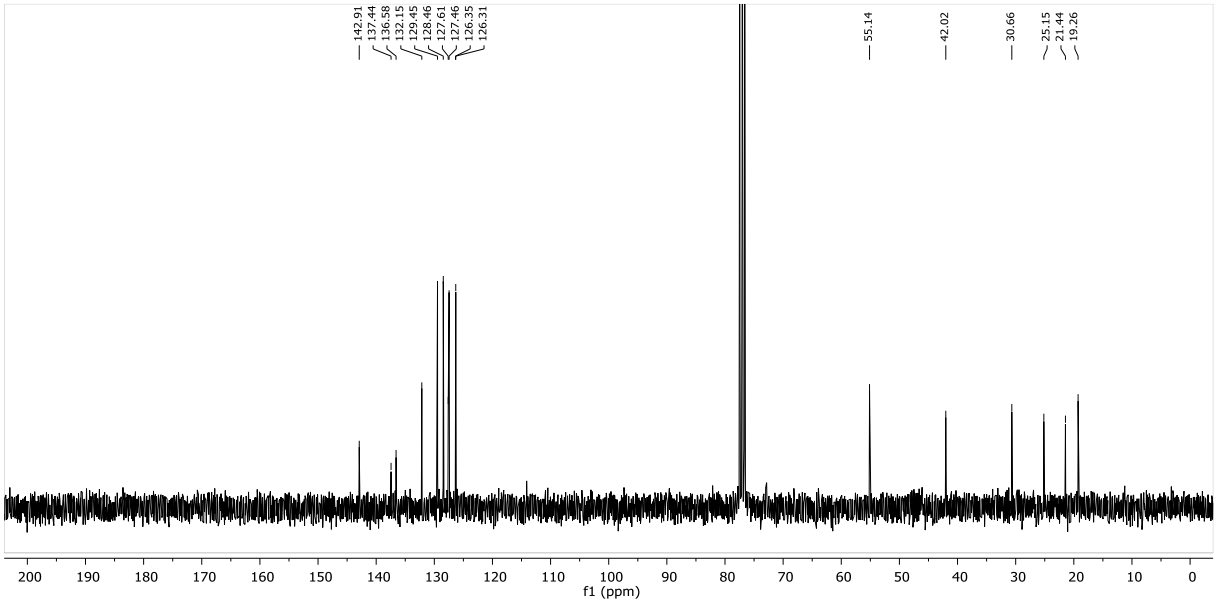


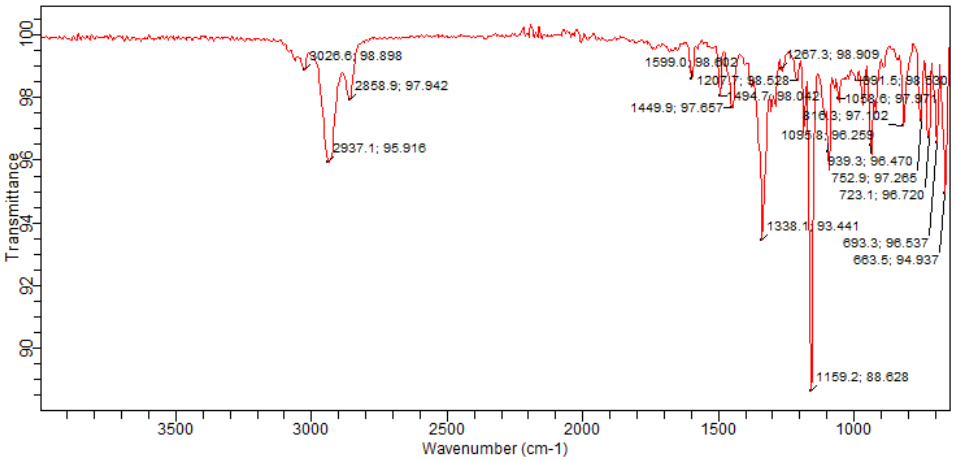




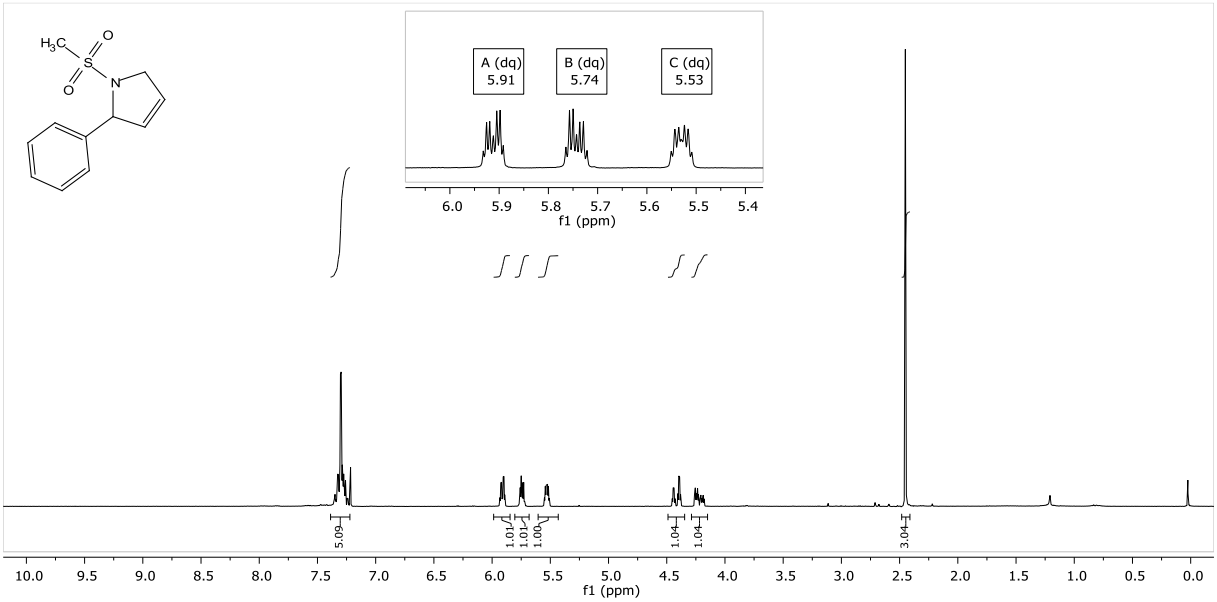
2-Styryl-1-tosylpiperidine (150b): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

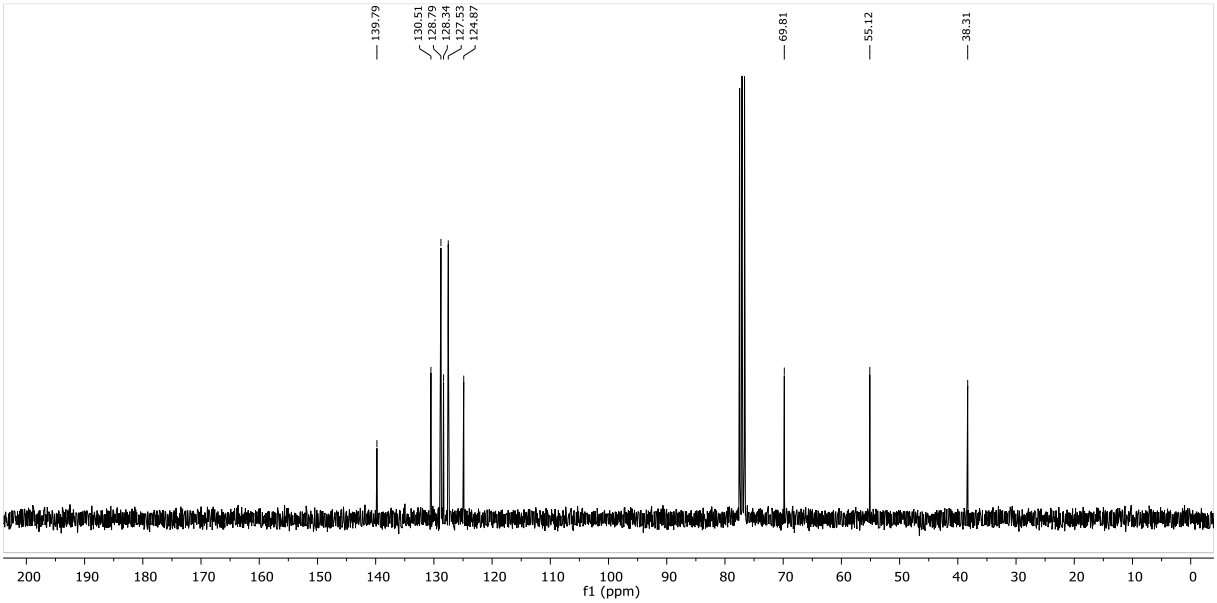


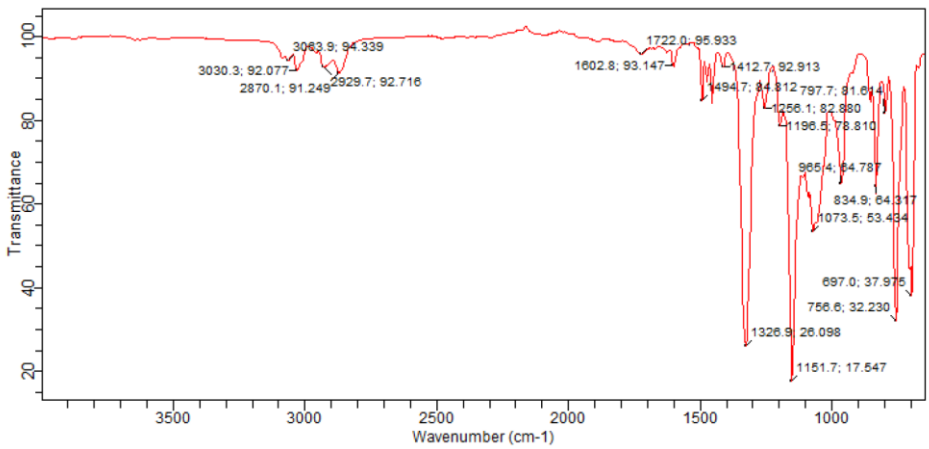




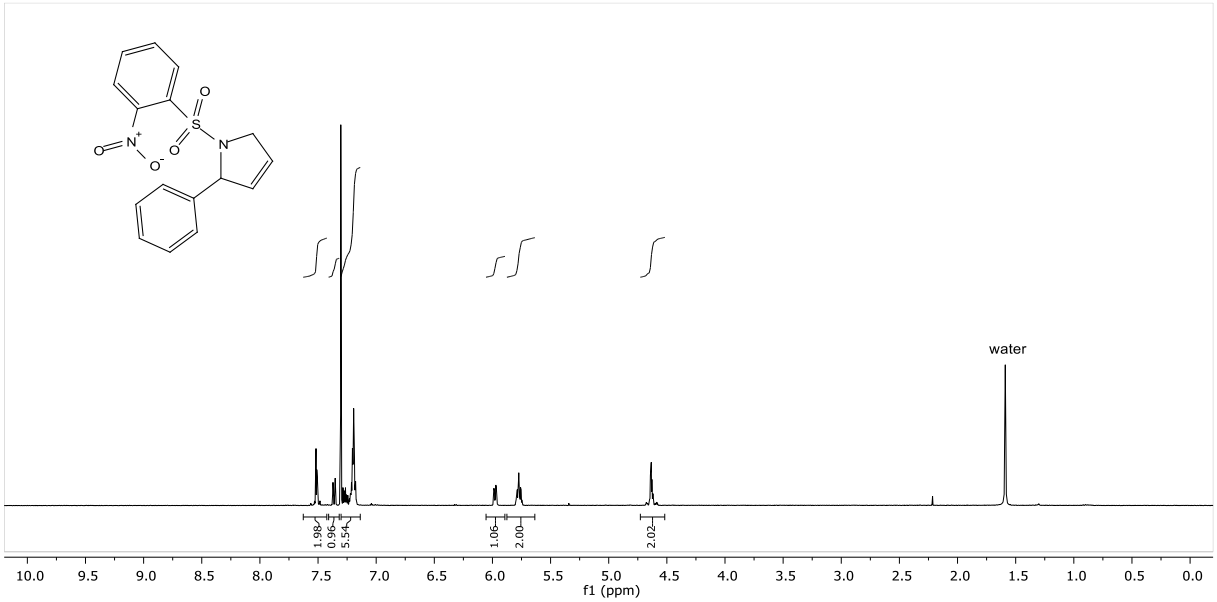
1-(Methylsulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (149m): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

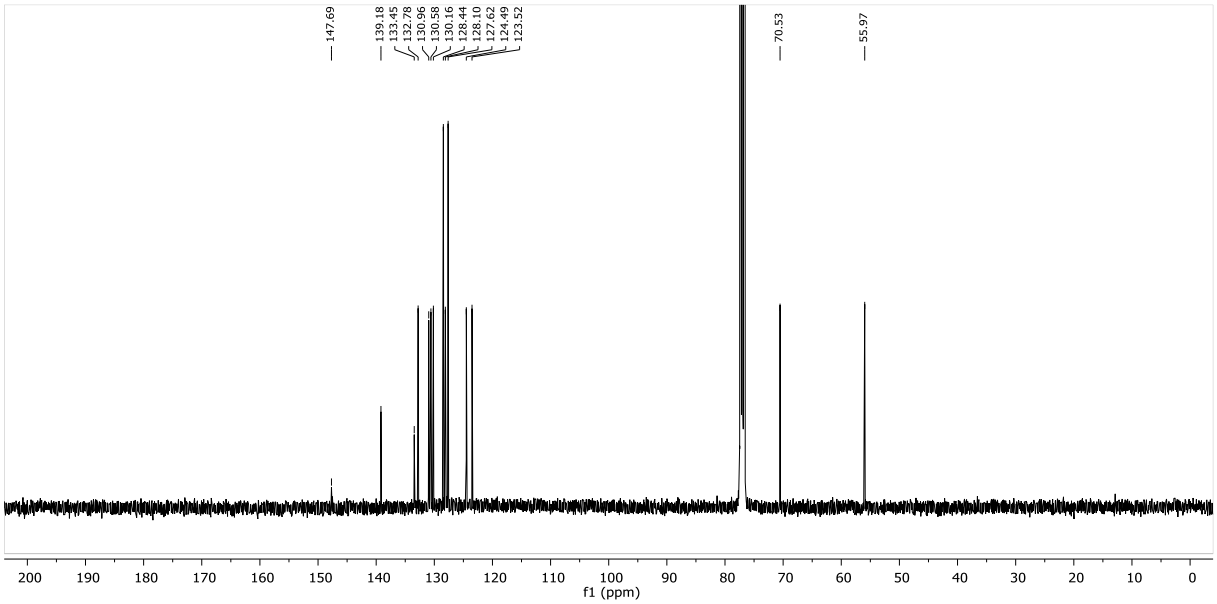


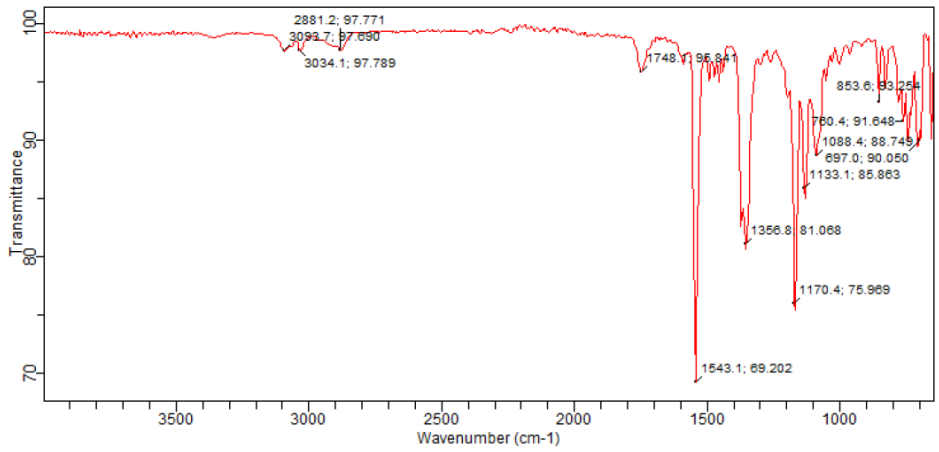




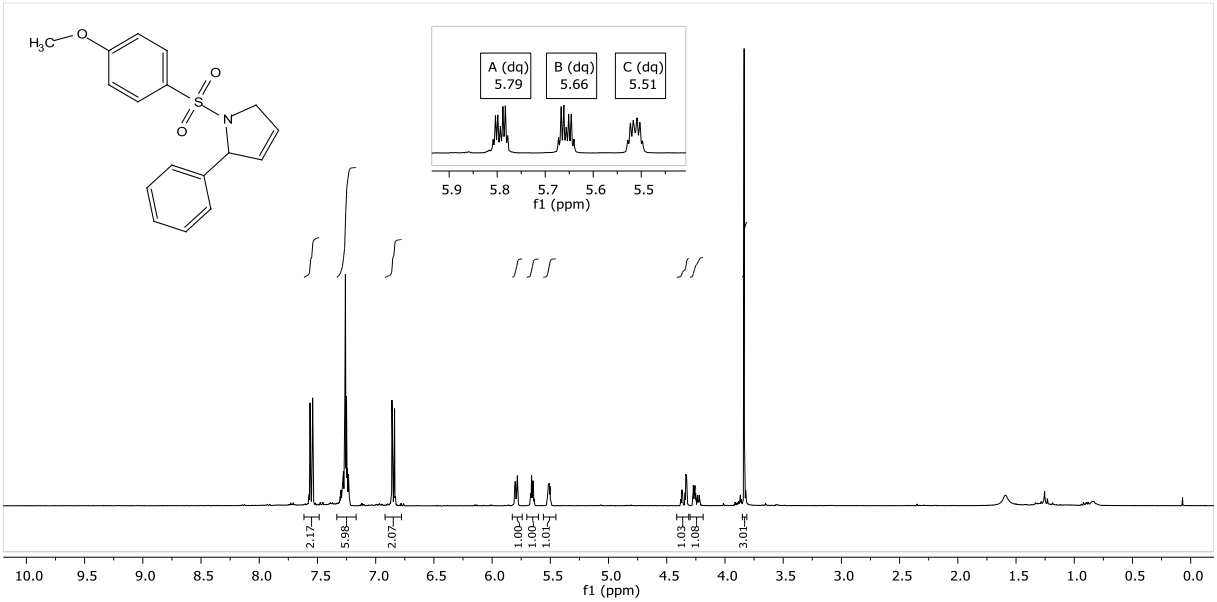
1-((2-Nitrophenyl)sulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (149q): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

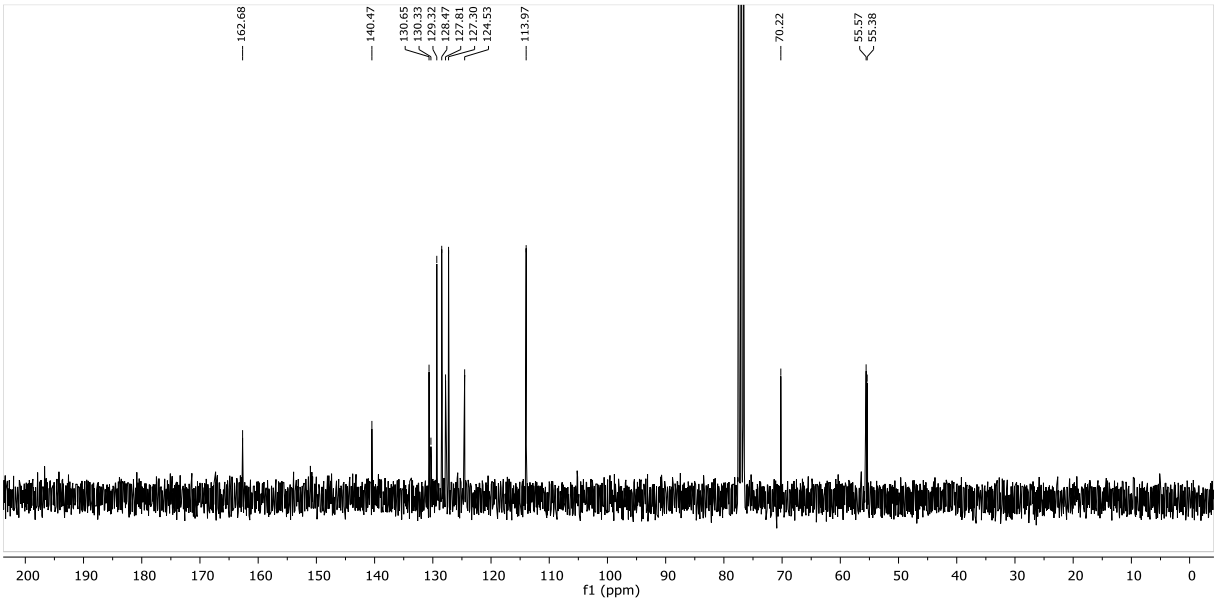


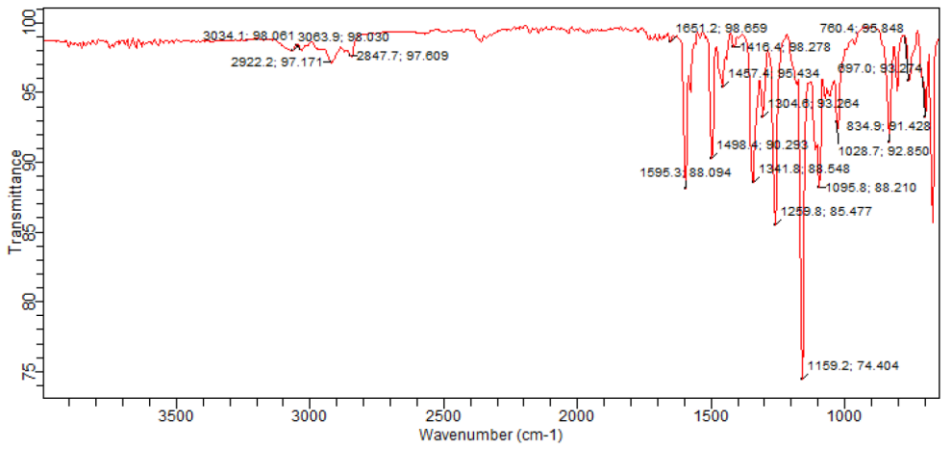




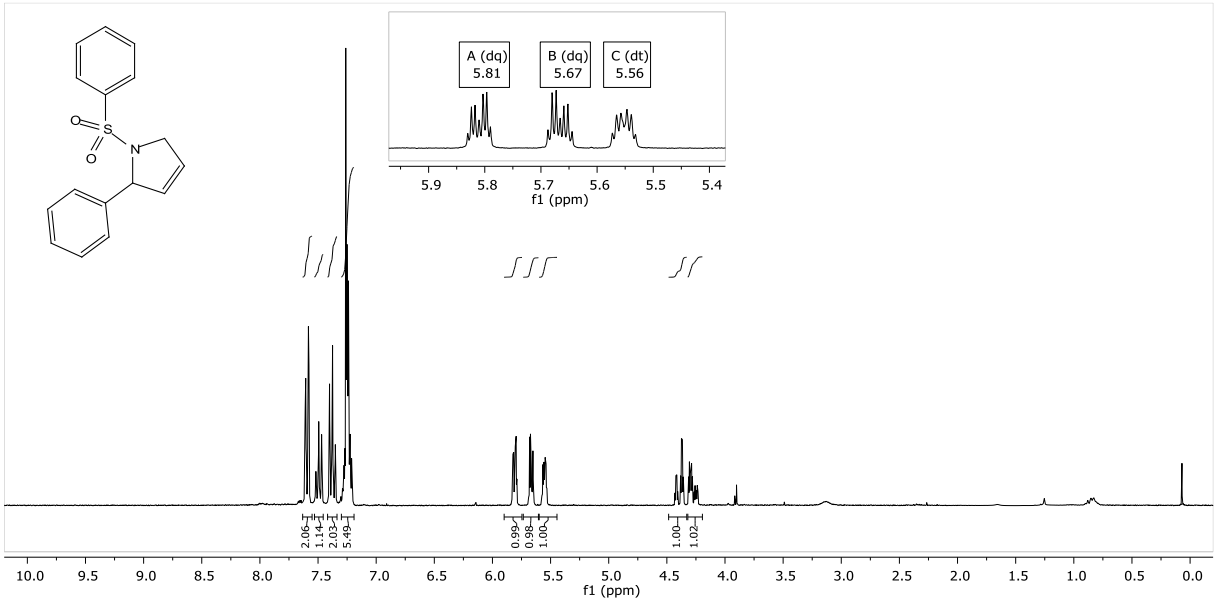
1-((4-Methoxyphenyl)sulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (149r): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

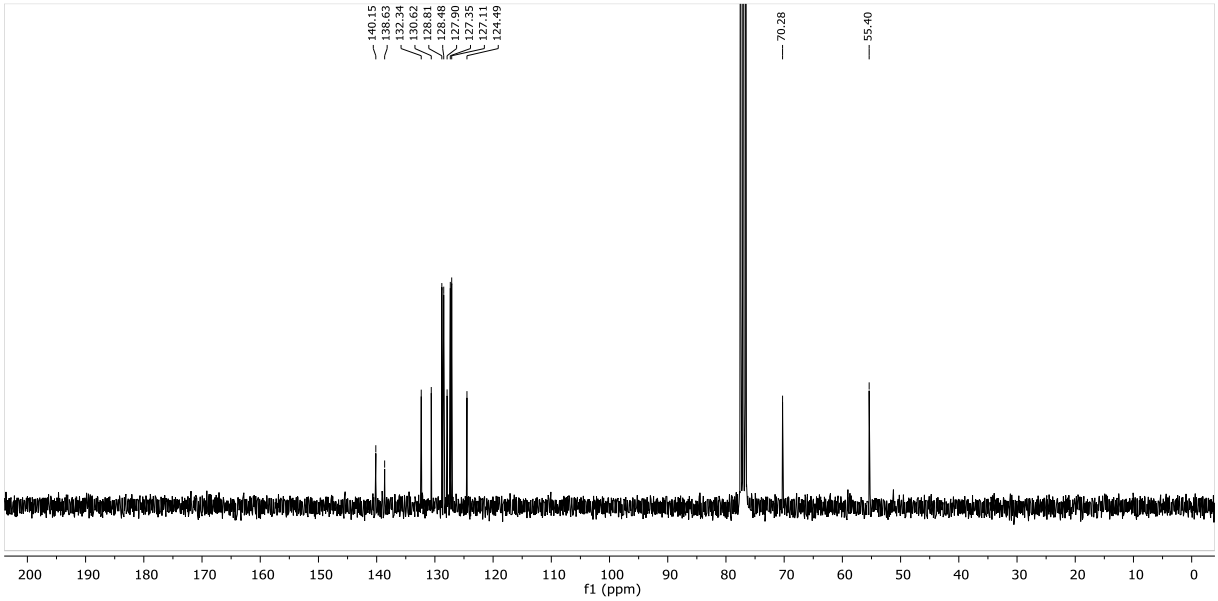


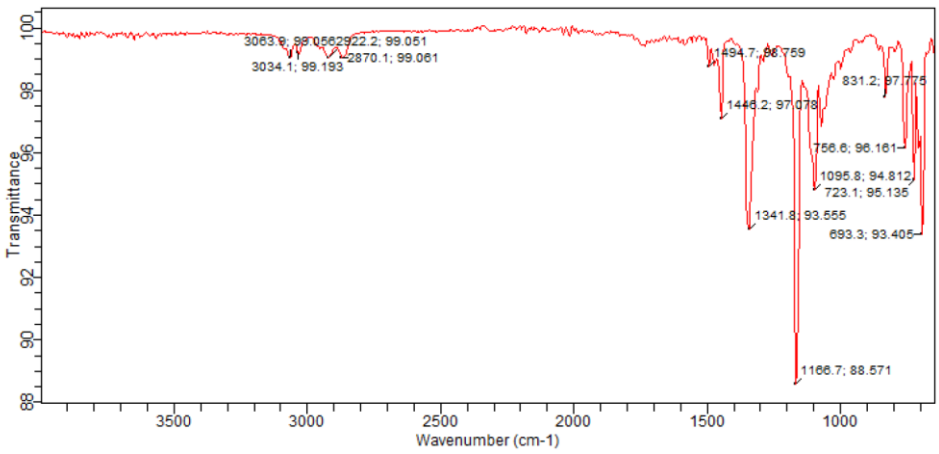




2-Phenyl-1-(phenylsulfonyl)-2,5-dihydro-1H-pyrrole (149n): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

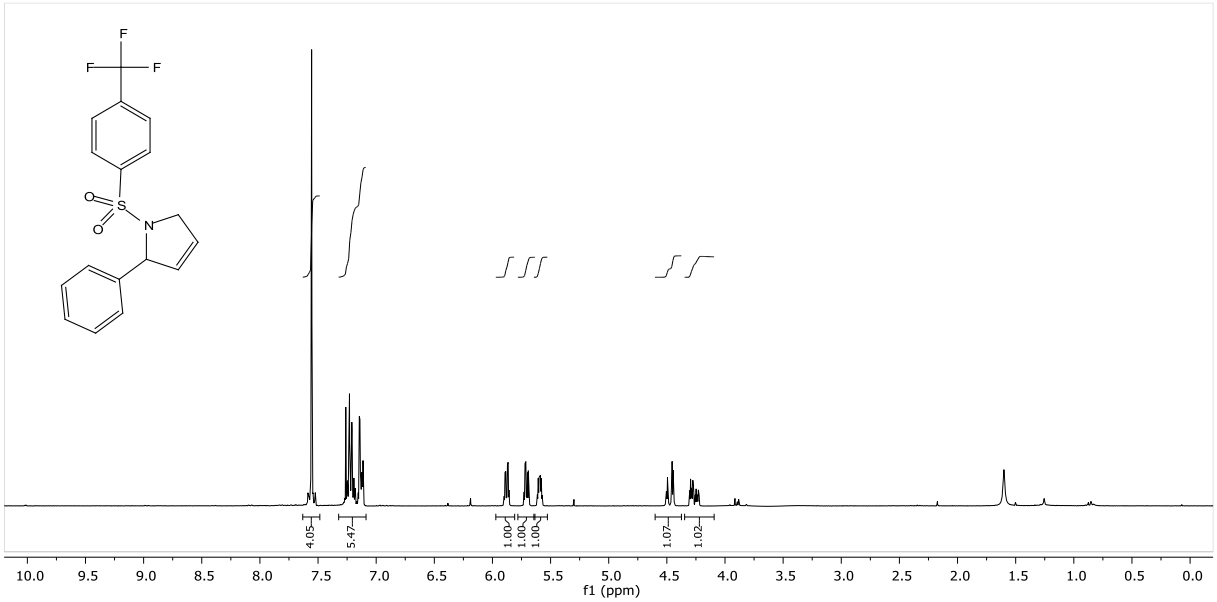


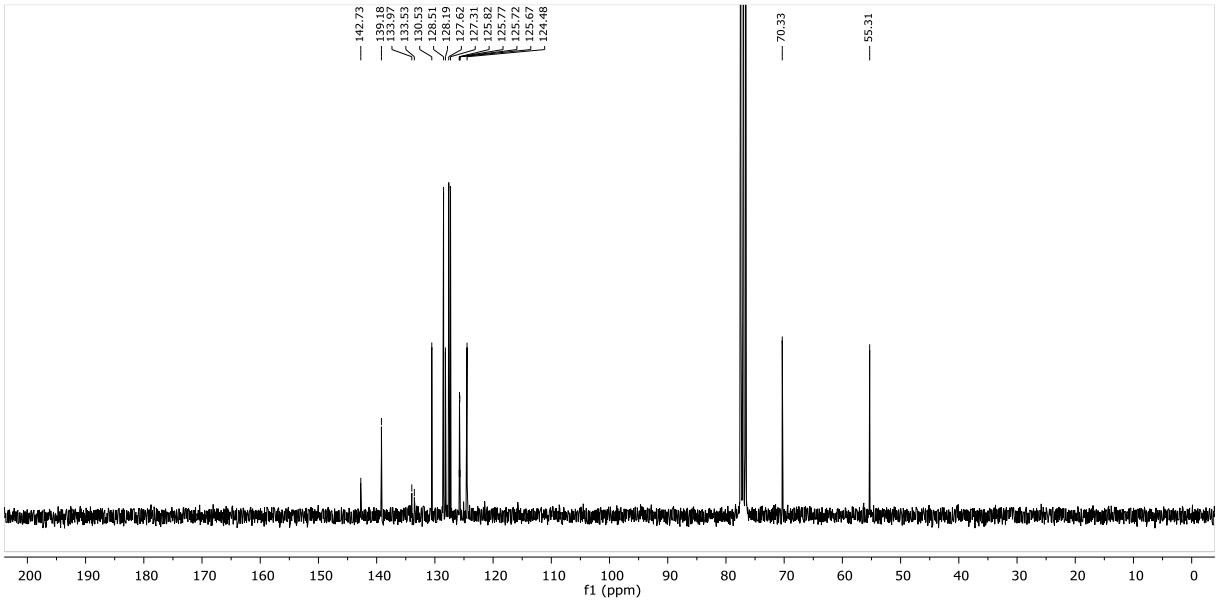


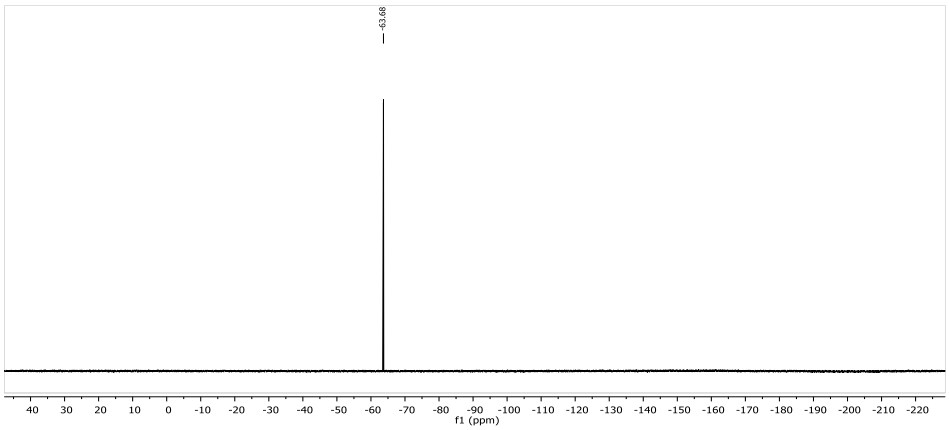


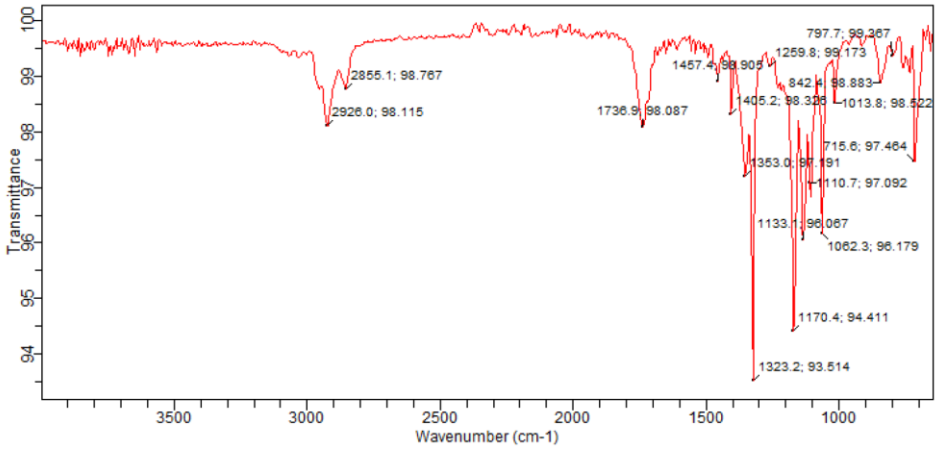
2-Phenyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-2,5-dihydro-1H-pyrrole (149s):

^{1}H, ^{13}C, ^{19}F NMR in $CDCl_3$, IR

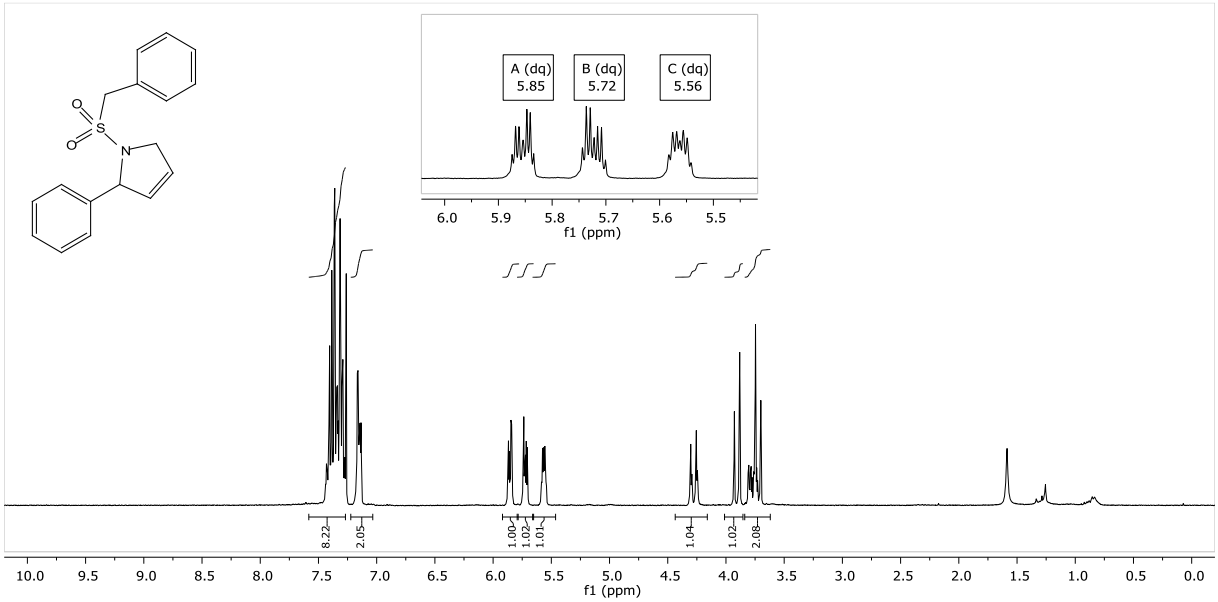


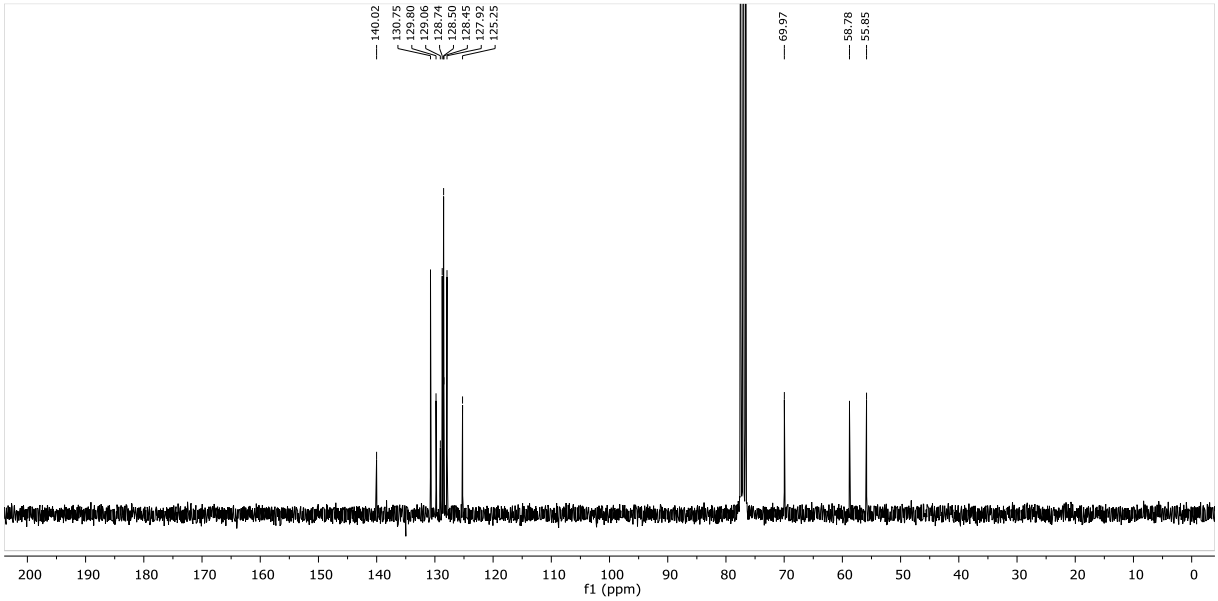


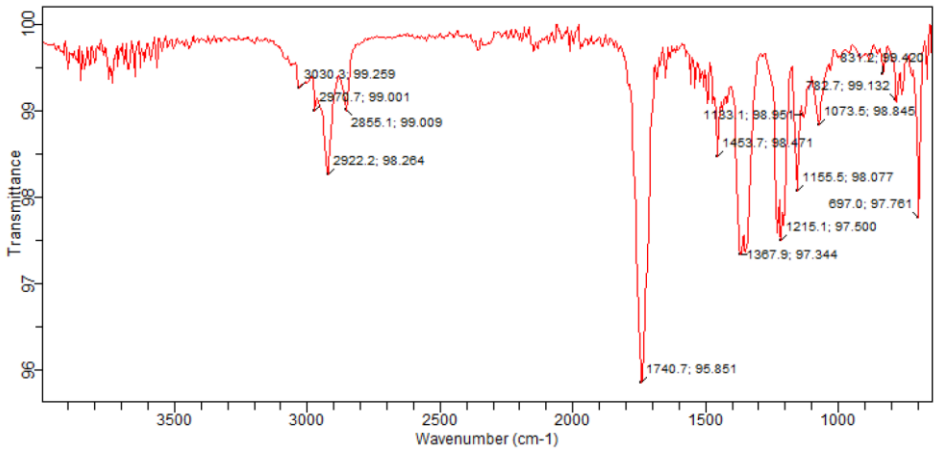



Transmittance
100
99
98
97
96
95
94
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
2855.1; 98.767
2926.0; 98.115
1736.9; 98.087
1457.4; 98.905
1259.8; 99.173
797.7; 99.367
842.4; 98.883
1405.2; 98.336
1013.8; 98.522
715.6; 97.464
1353.0; 97.191
1110.7; 97.092
1133.1; 96.067
1062.3; 96.179
1170.4; 94.411
1323.2; 93.514

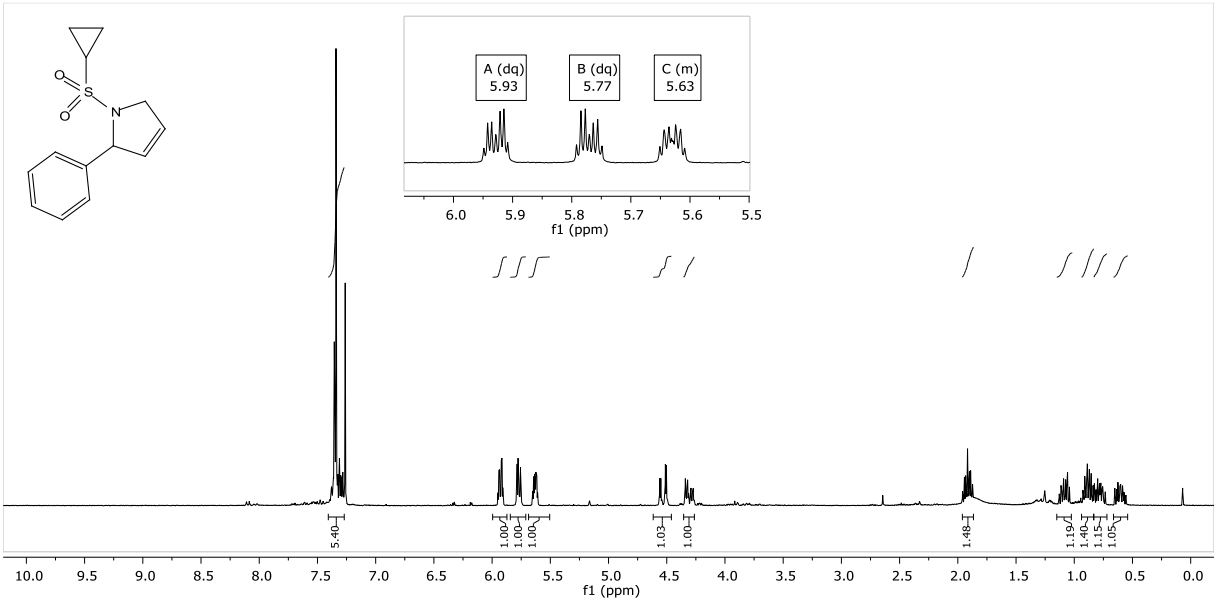
1-(Benzylsulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (149o): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

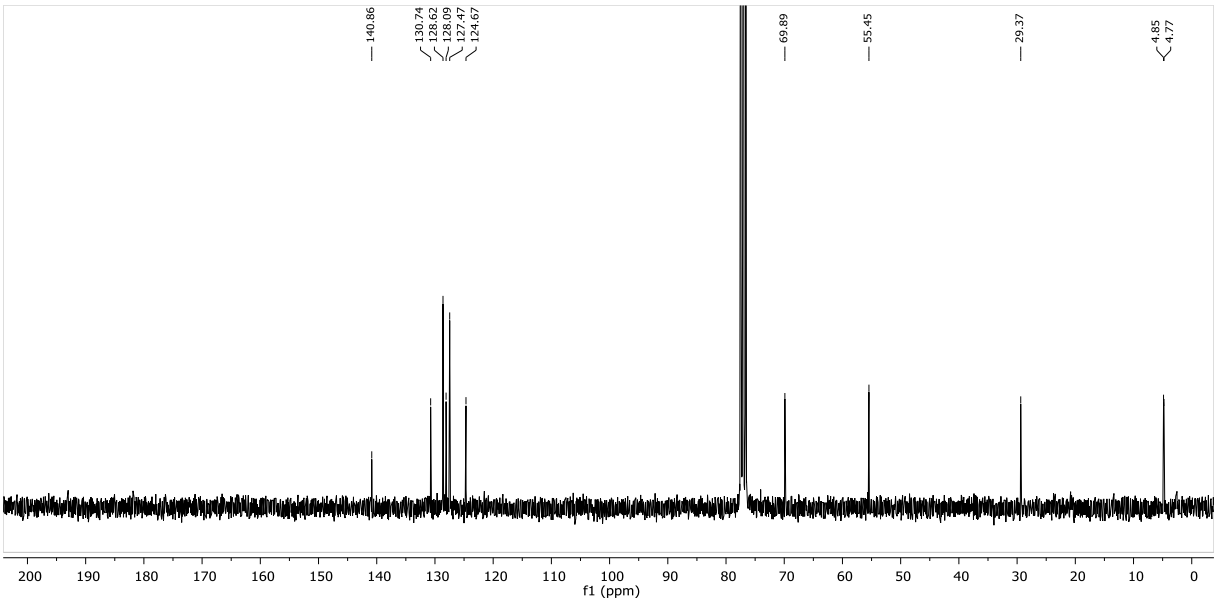


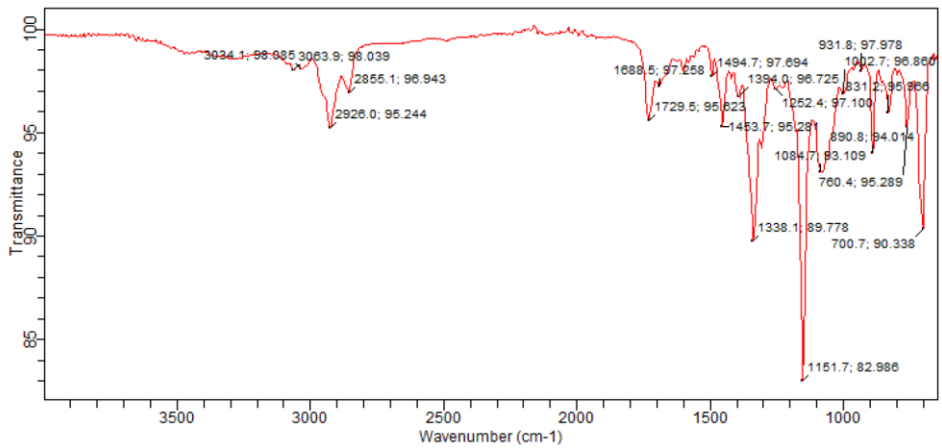




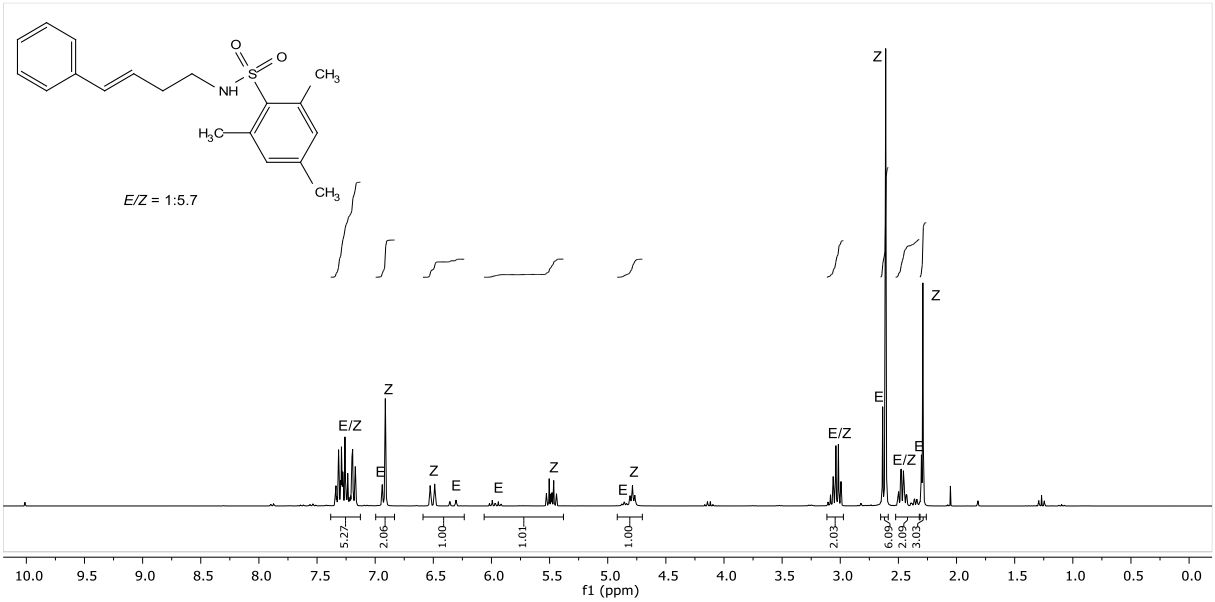
1-(Cyclopropylsulfonyl)-2-phenyl-2,5-dihydro-1H-pyrrole (149p): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

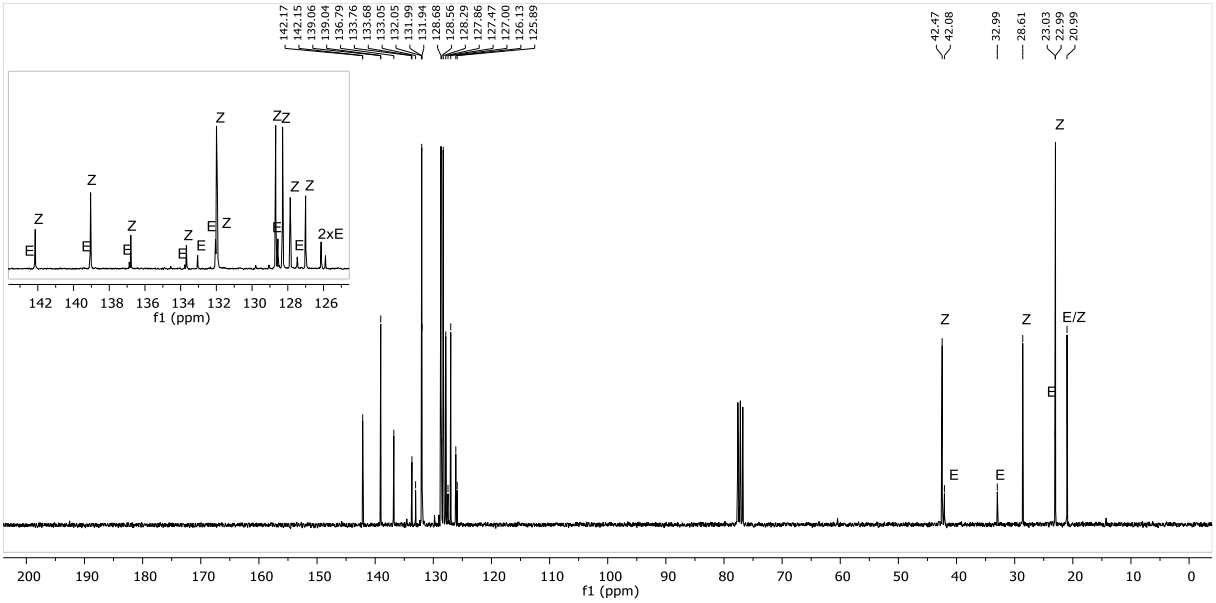


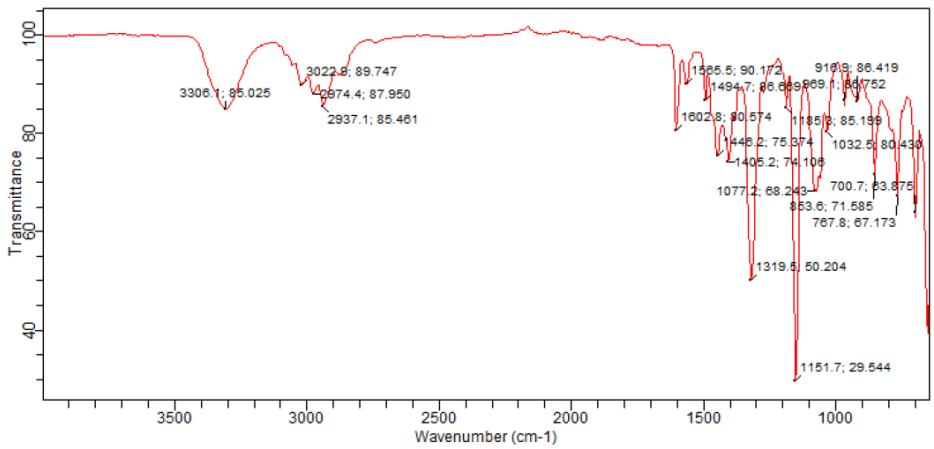




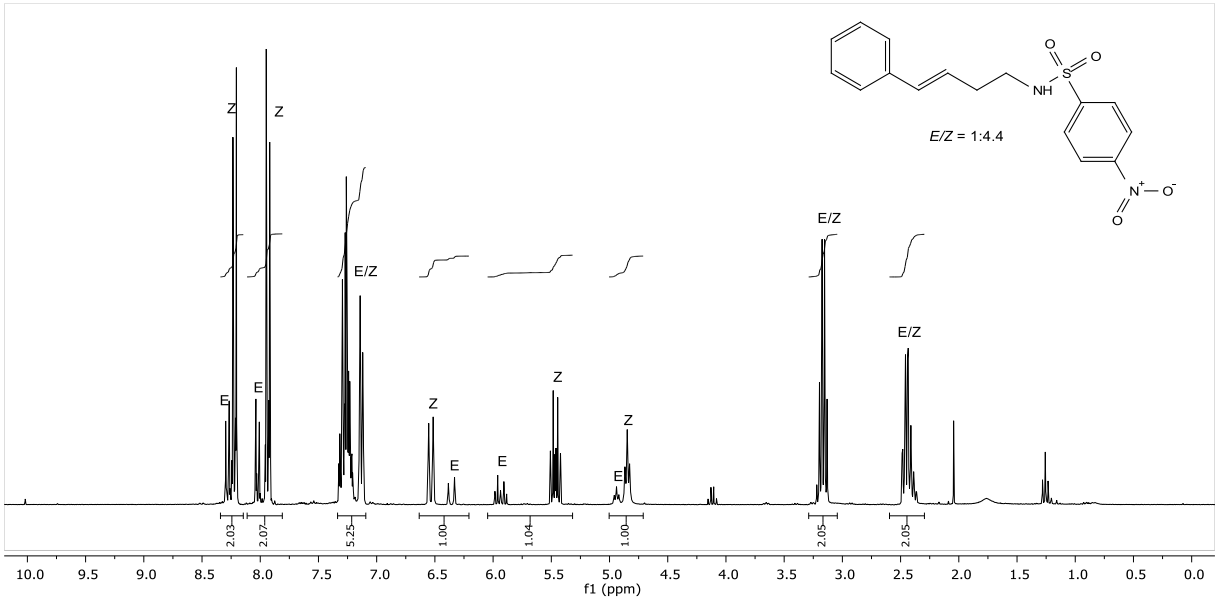
2,4,6-Trimethyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146v): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

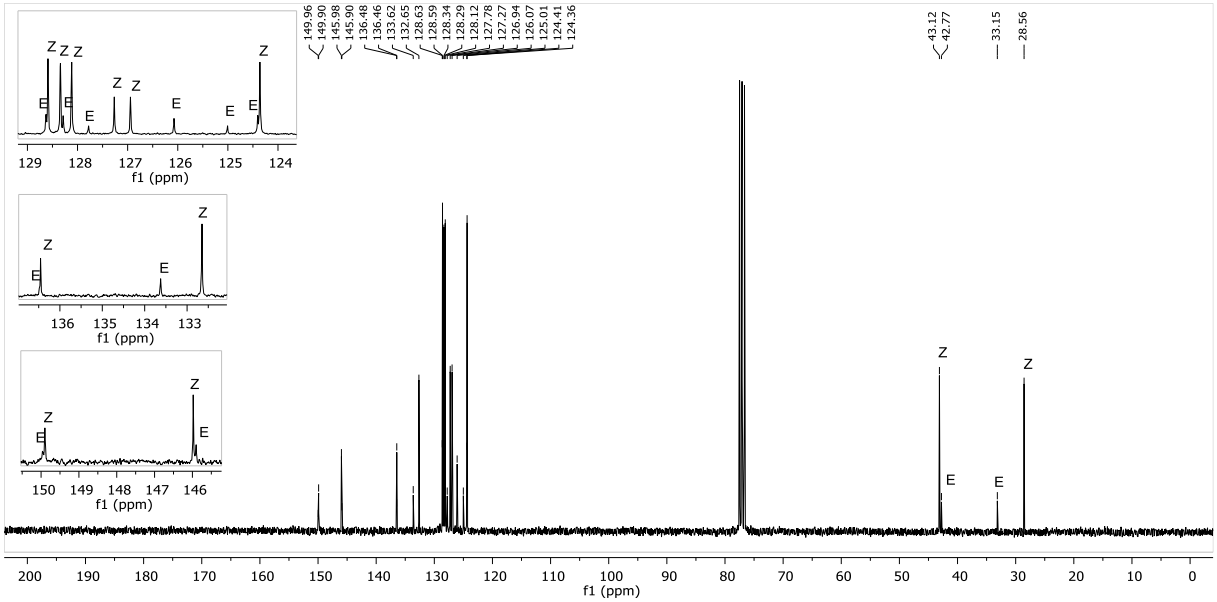


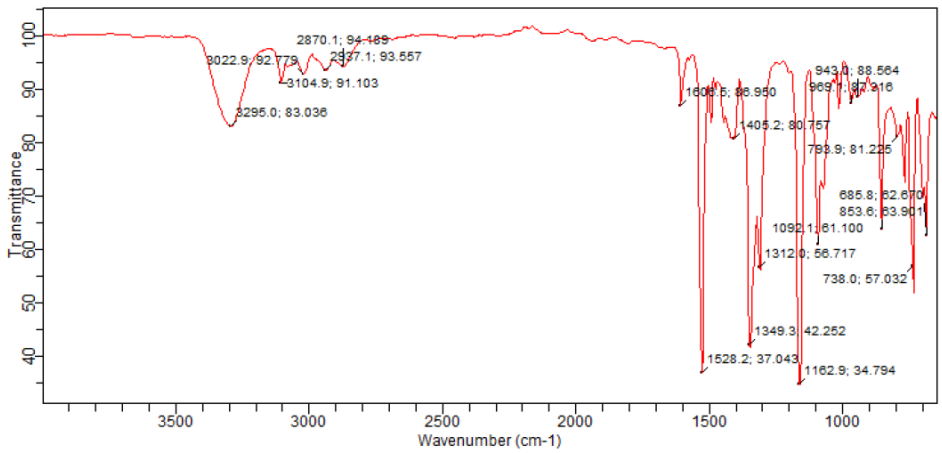




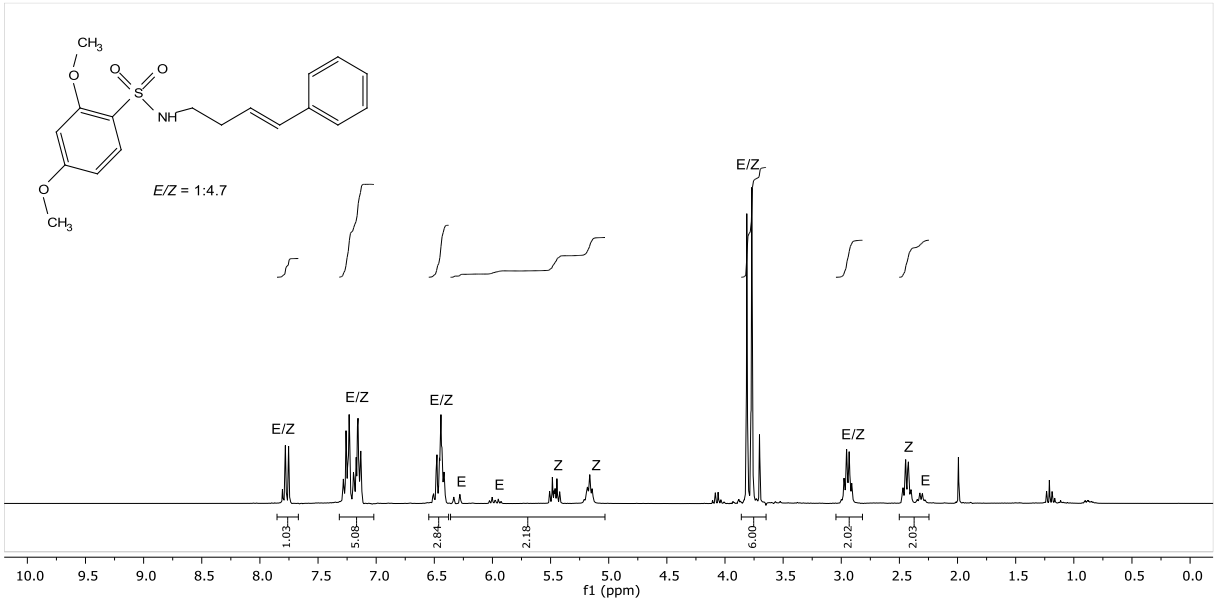
4-Nitro-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146w): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

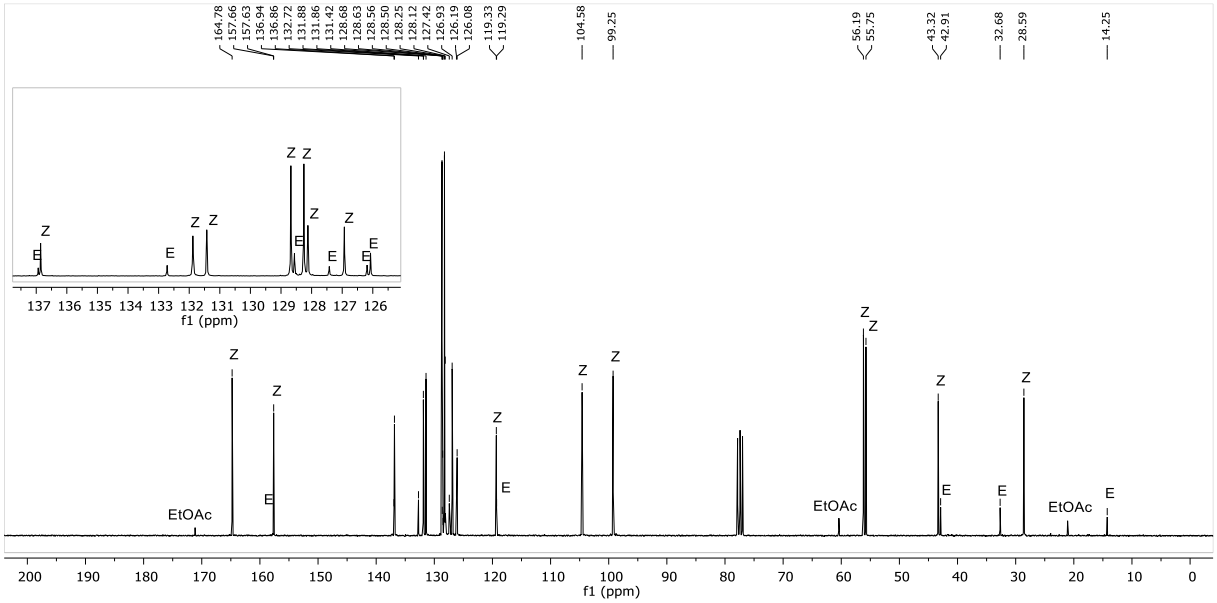


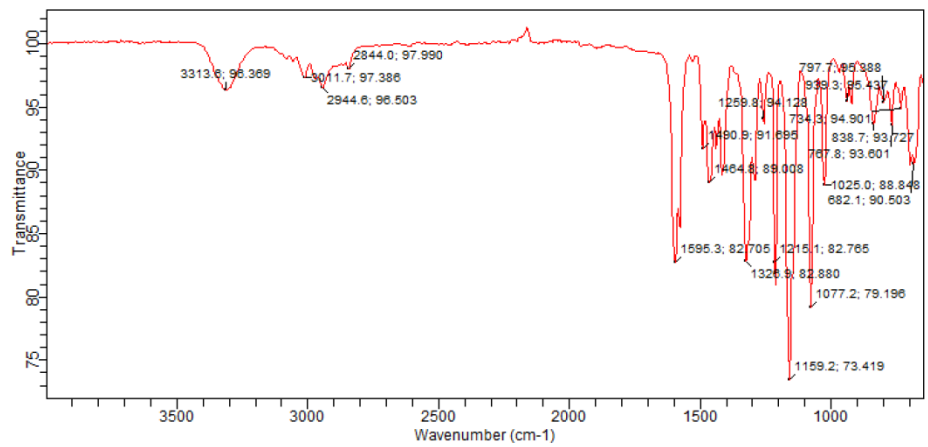




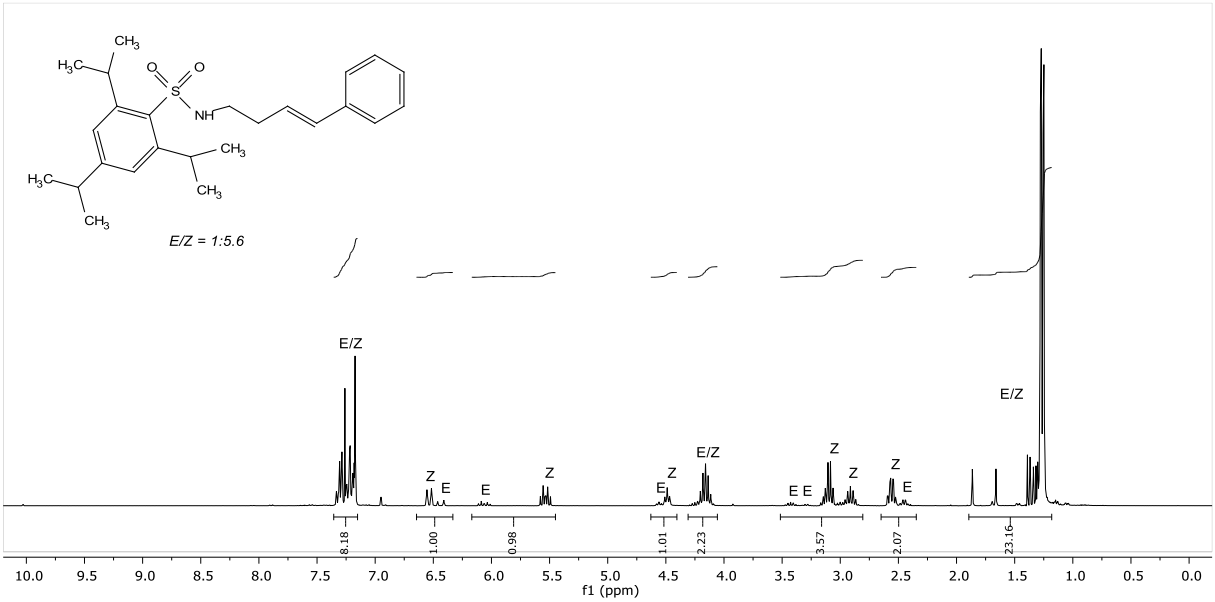
2,4-Dimethoxy-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146x): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

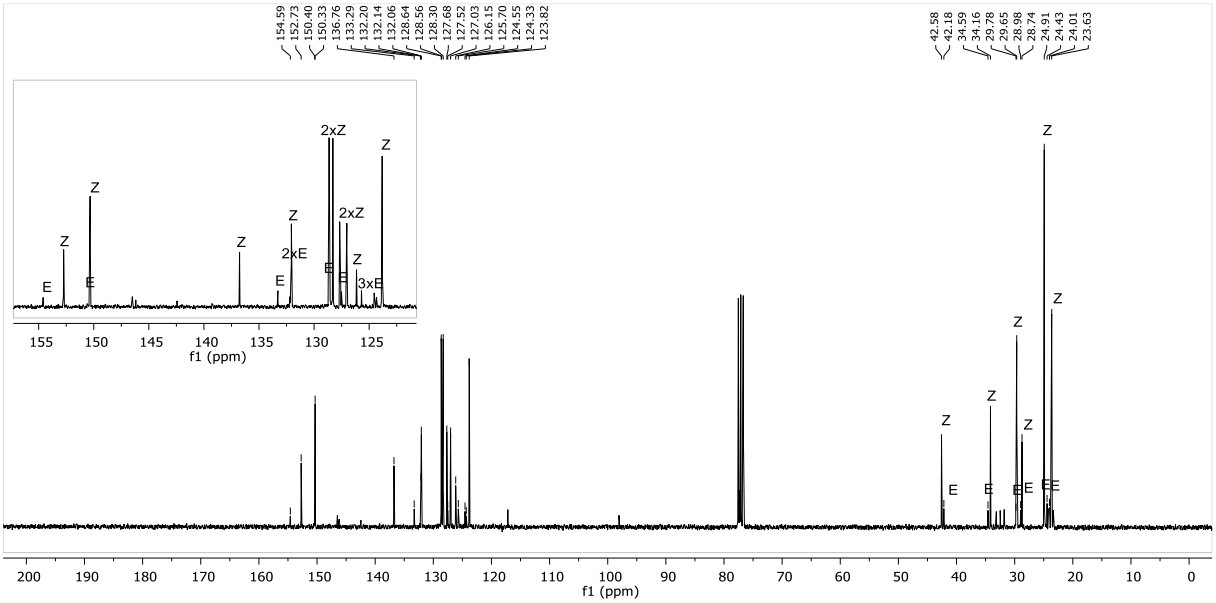


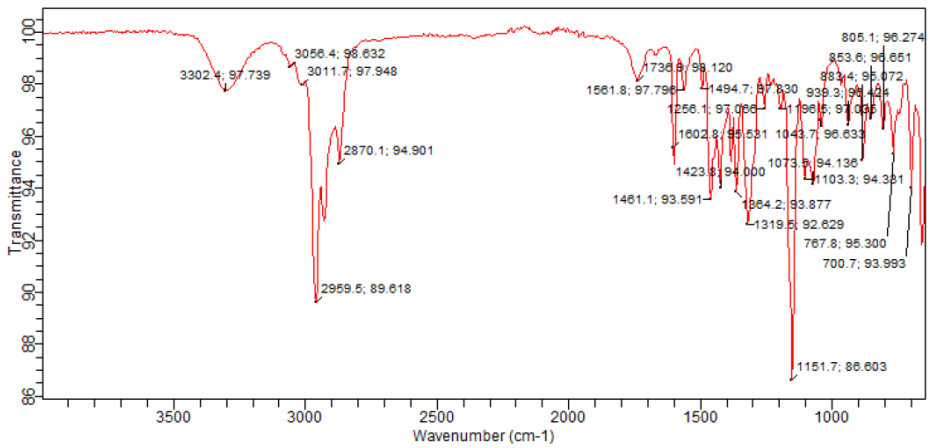




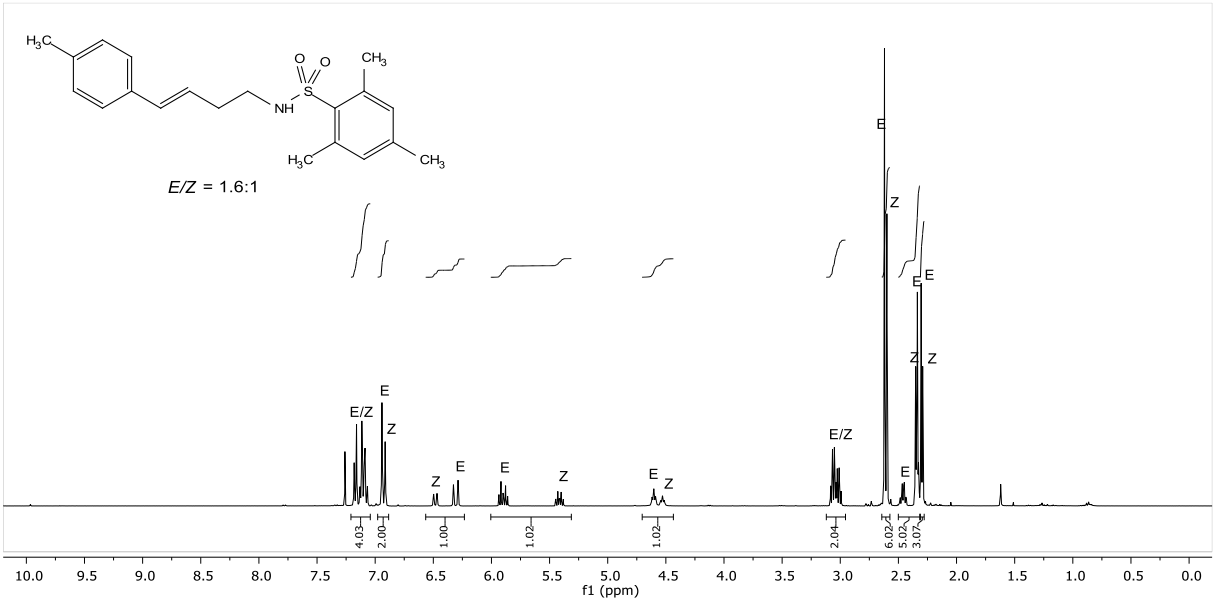
2,4,6-Triisopropyl-*N*-(4-phenylbut-3-en-1-yl)benzenesulfonamide (146y): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

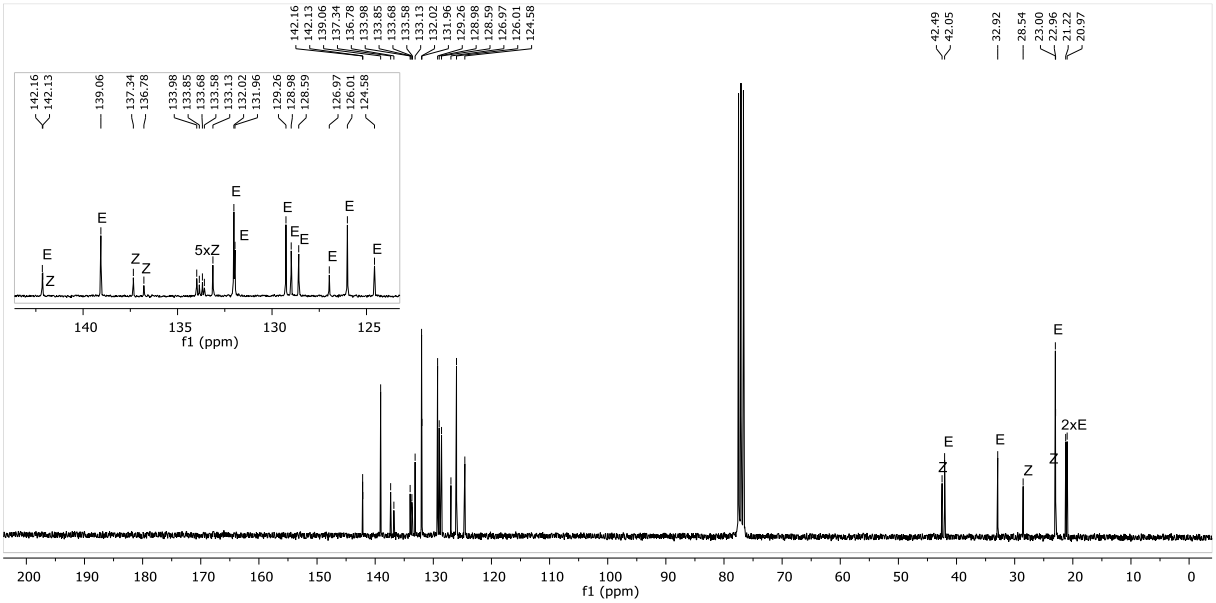


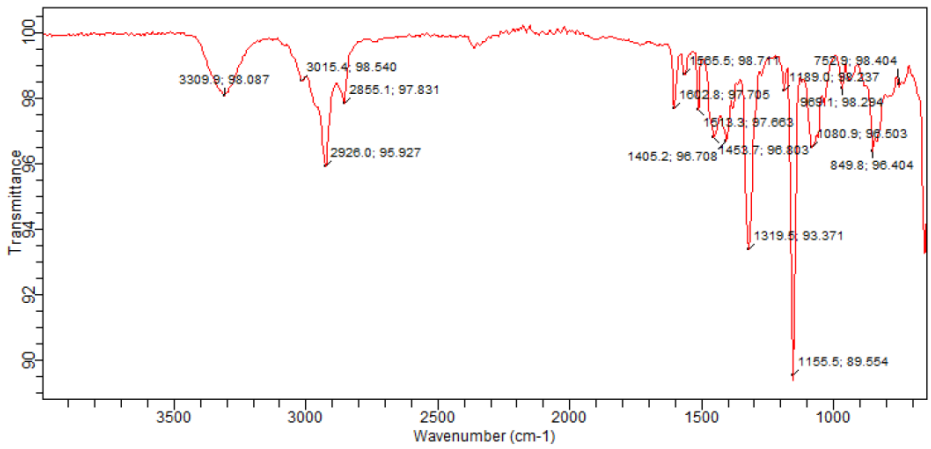




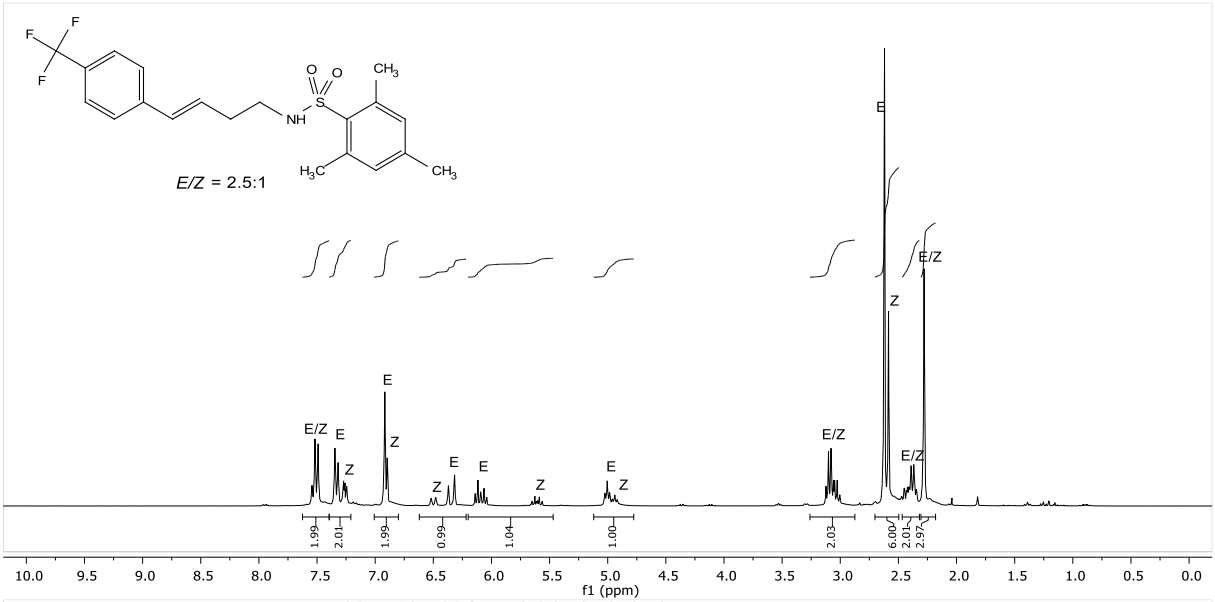
2,4,6-Trimethyl-*N*-(4-(*p*-tolyl)but-3-en-1-yl)benzenesulfonamide (146z): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

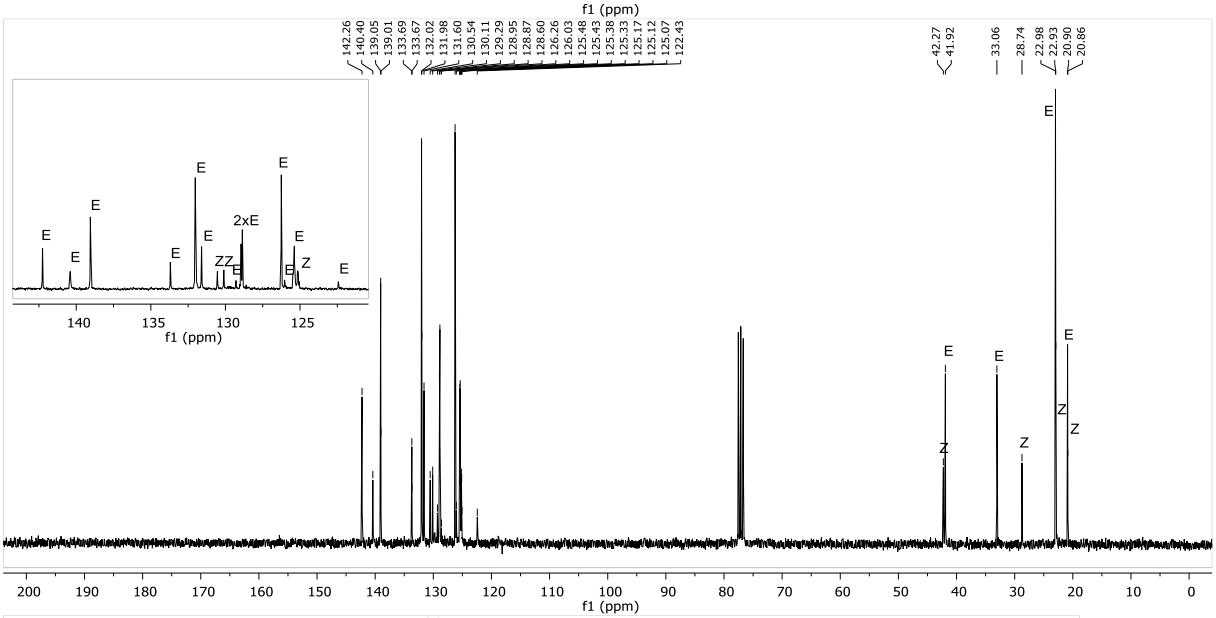


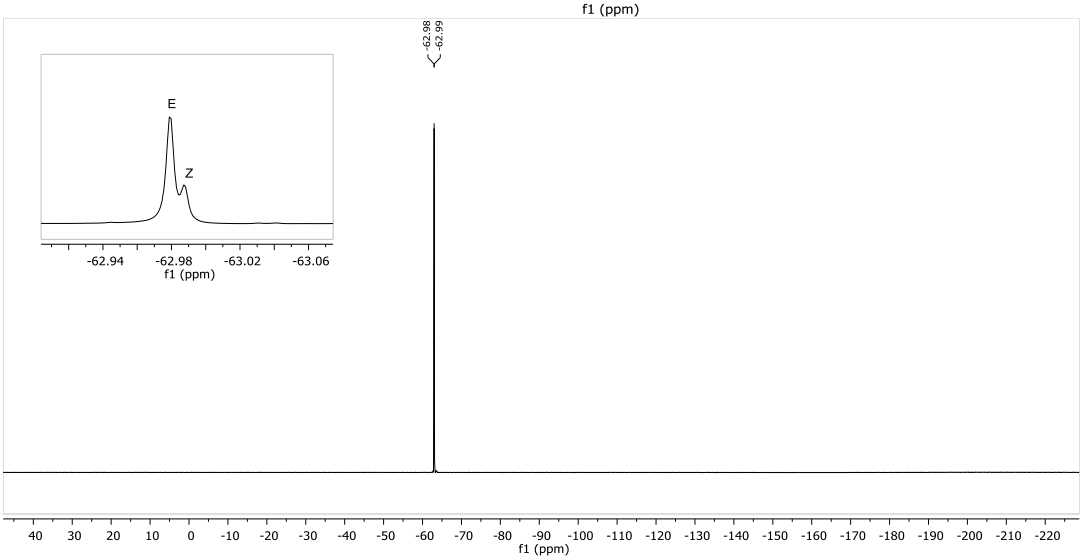


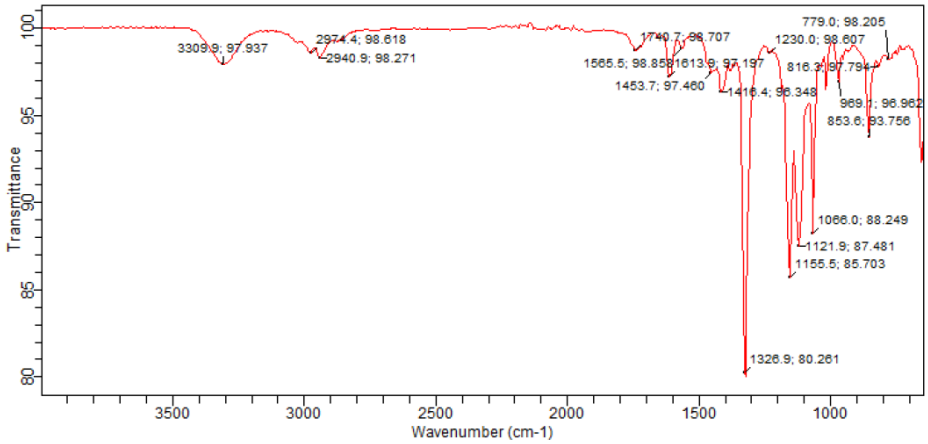


2,4,6-Trimethyl-*N*-(4-(4-(trifluoromethyl)phenyl)but-3-en-1-yl)benzenesulfonamide (146aa): ^{1}H, ^{13}C, ^{19}F NMR in $CDCl_3$, IR



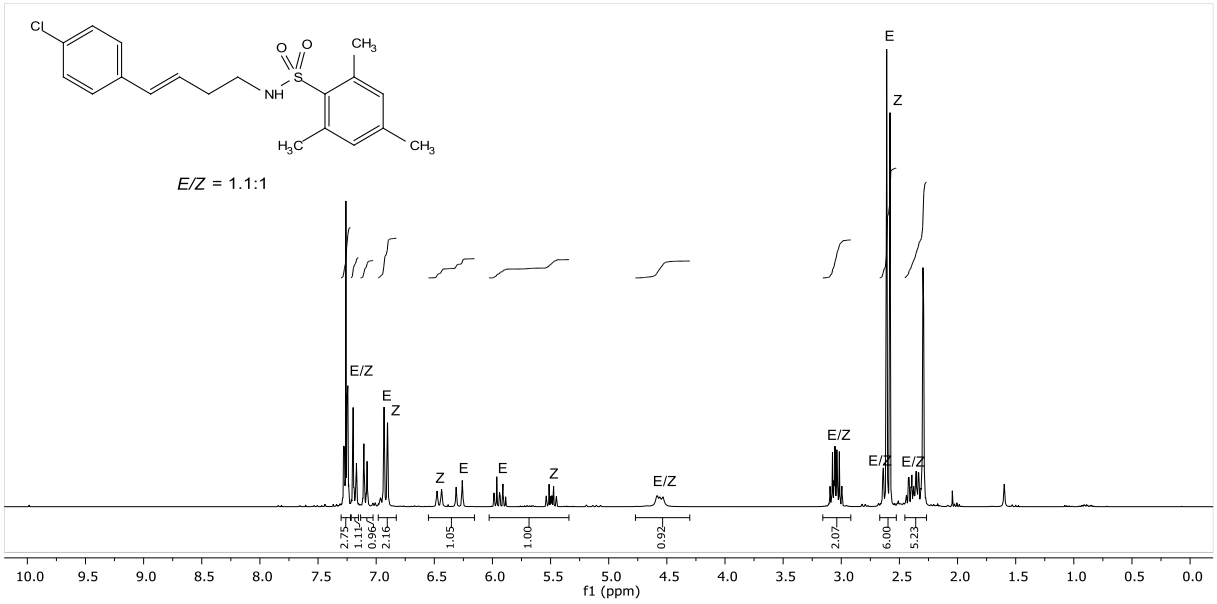


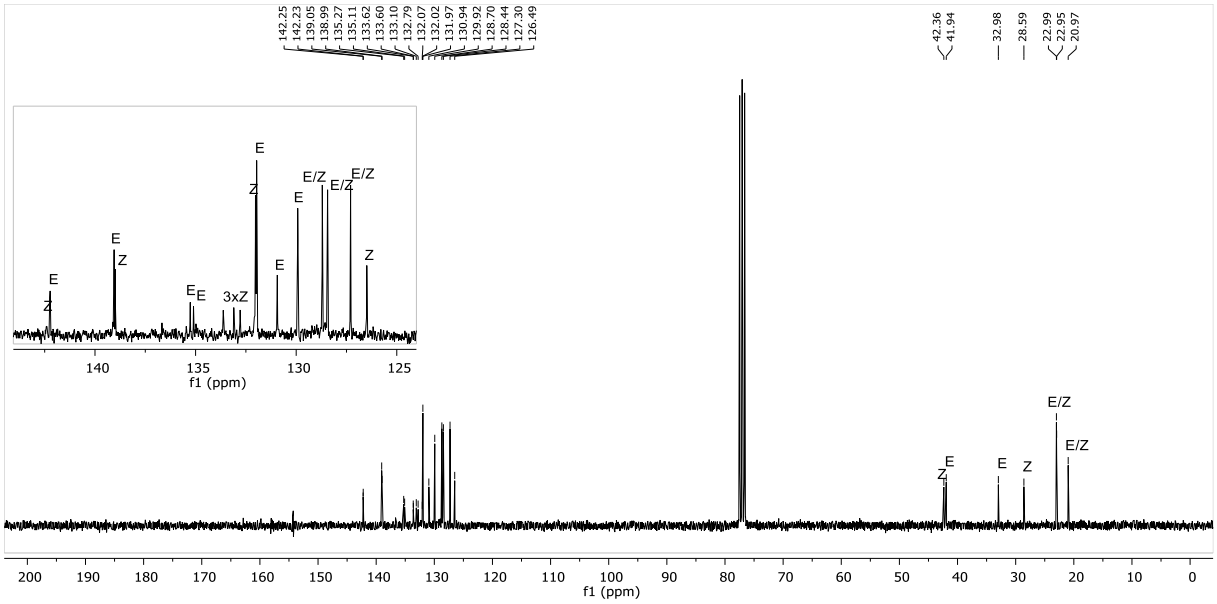


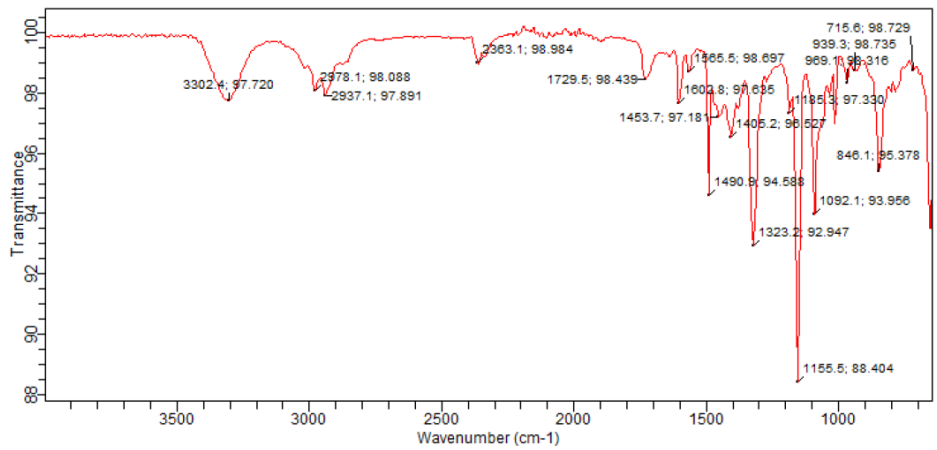

Transmittance
Wavenumber (cm-1)
3309.9; 97.937
2974.4; 98.618
2940.9; 98.271
1740.7; 98.707
1565.5; 98.858
1613.9; 97.197
1453.7; 97.460
1416.4; 96.348
1326.9; 80.261
1230.0; 98.607
816.3; 97.794
779.0; 98.205
969.7; 96.962
853.6; 93.756
1066.0; 88.249
1121.9; 87.481
1155.5; 85.703

N-(4-(4-Chlorophenyl)but-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (146ab):

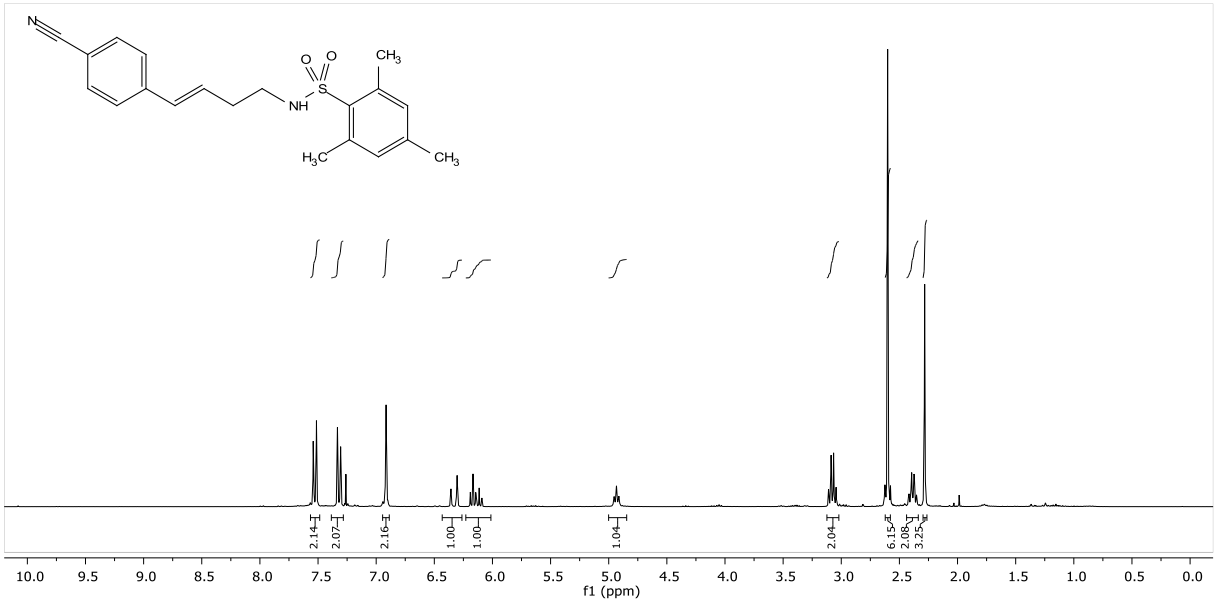
^{1}H, ^{13}C NMR in $CDCl_3$, IR

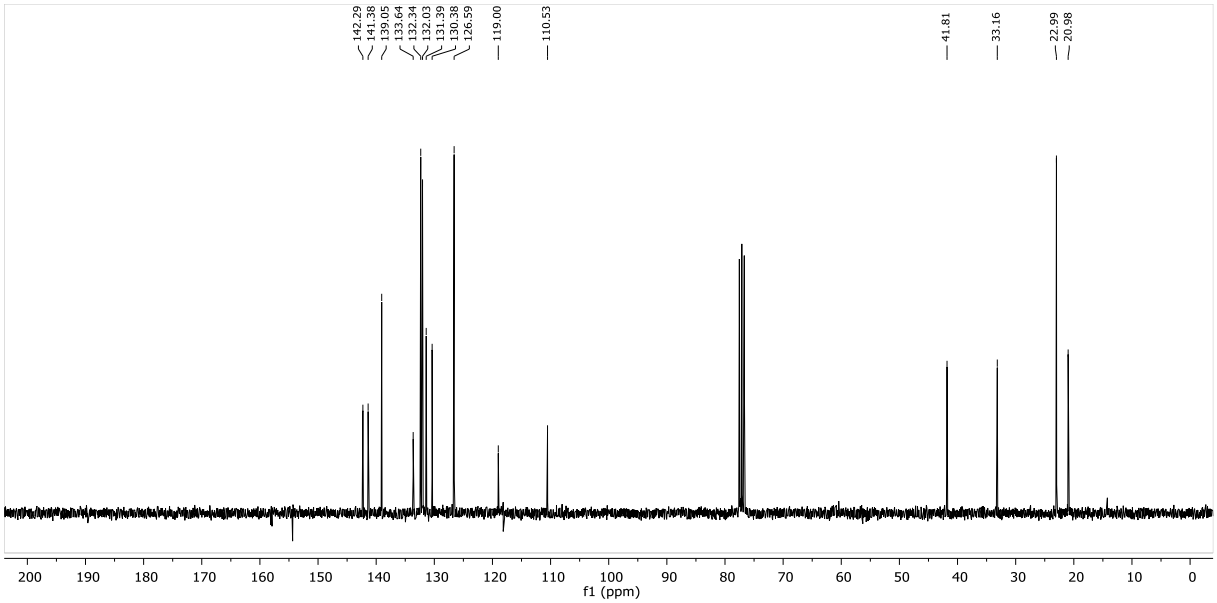


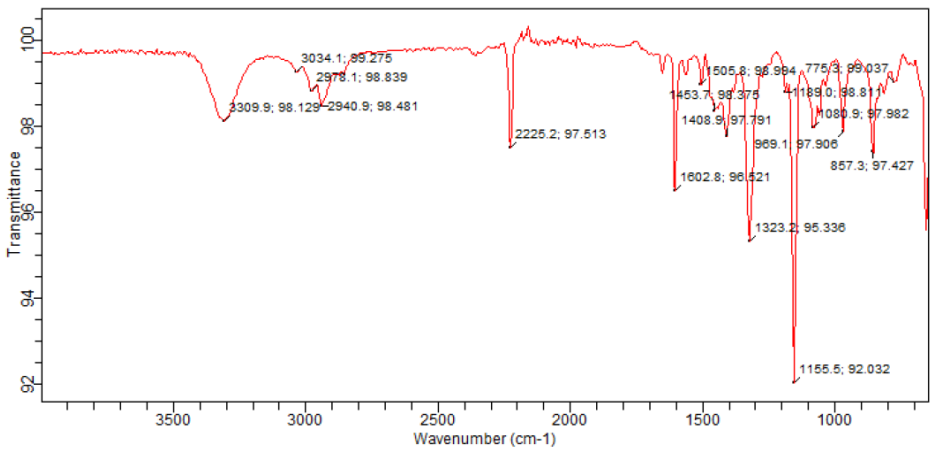




***(E)-N*-(4-(4-Cyanophenyl)but-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (146ac):** ^{1}H, ^{13}C NMR in $CDCl_3$, IR

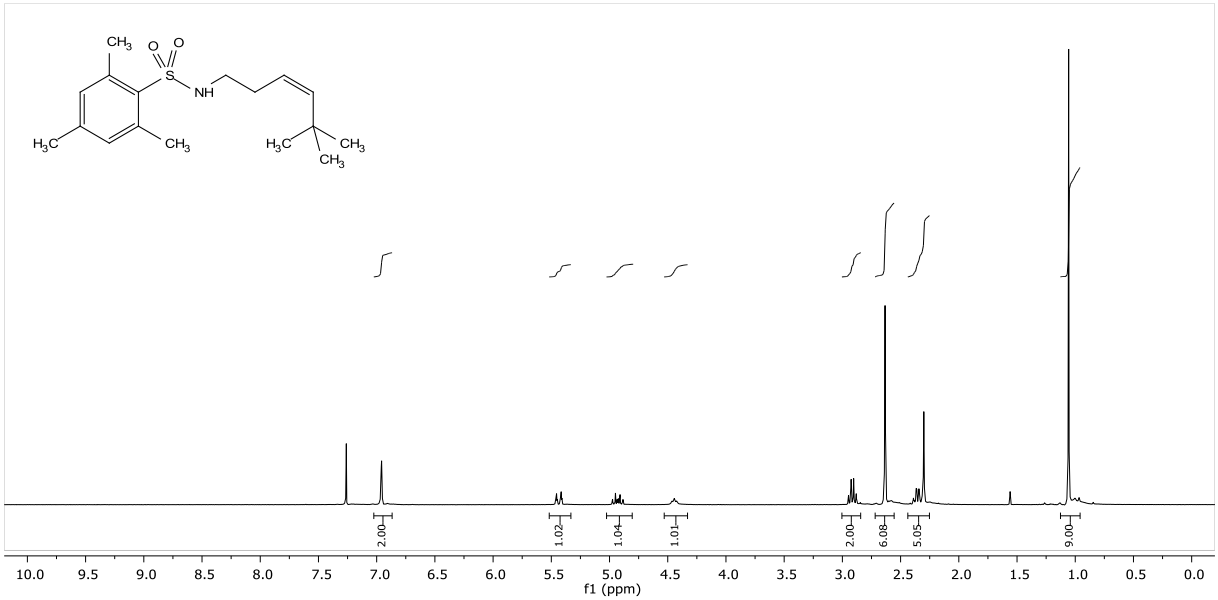


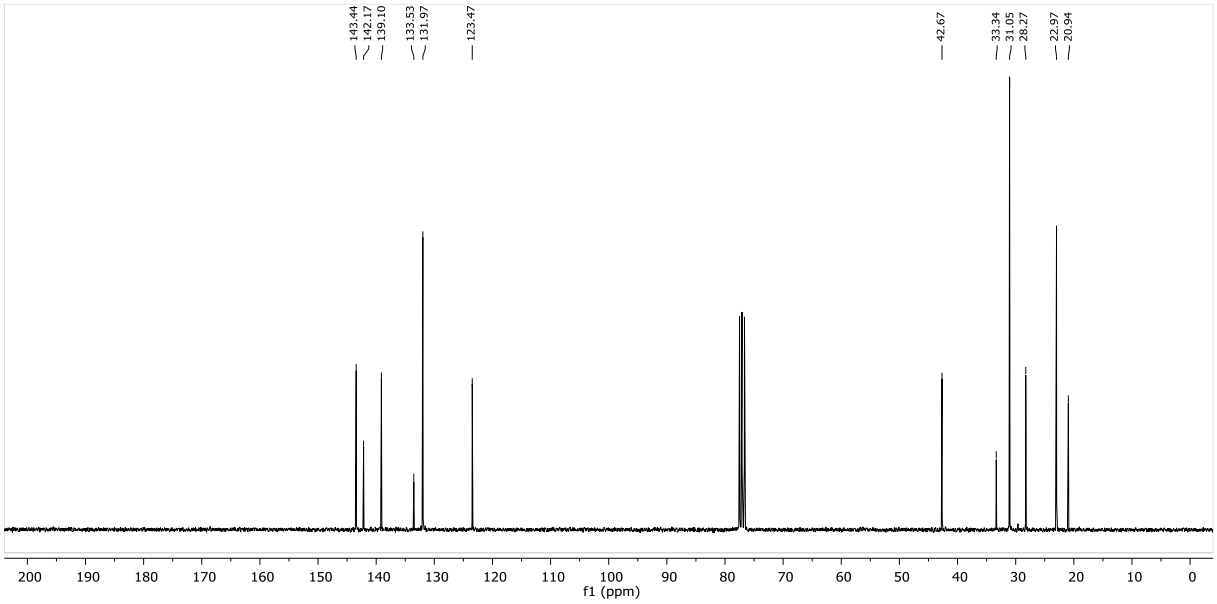


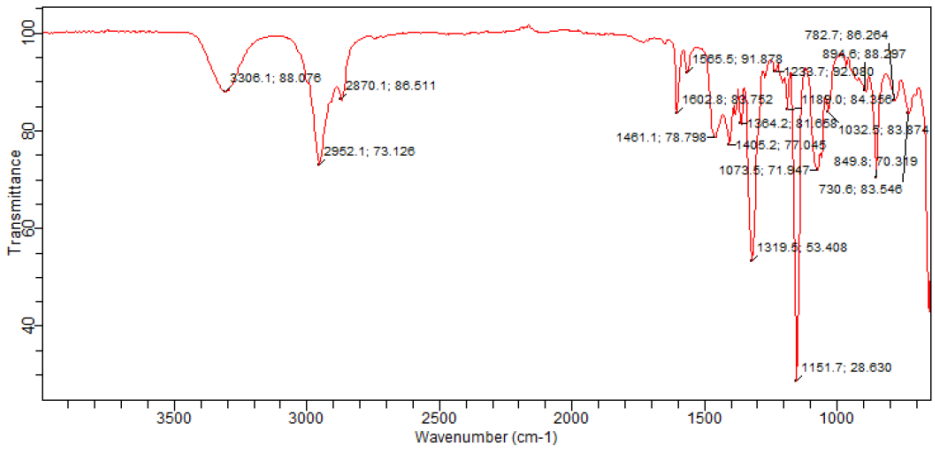


_(Z)-N_-(5,5-Dimethylhex-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (146ad):

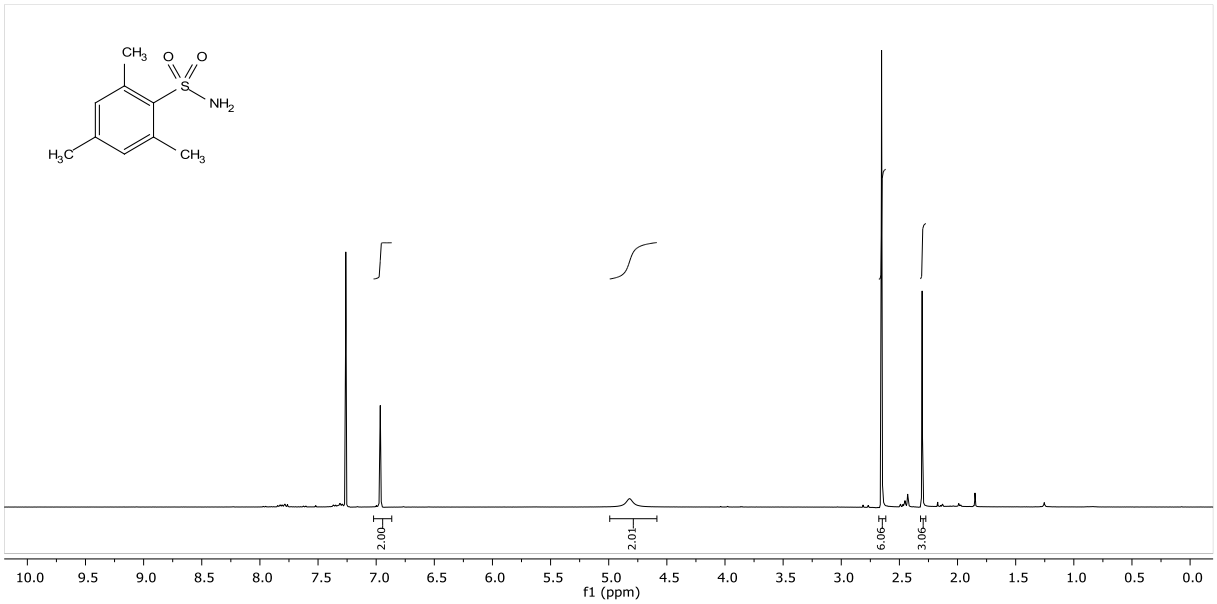
^{1}H, ^{13}C NMR in $CDCl_3$, IR

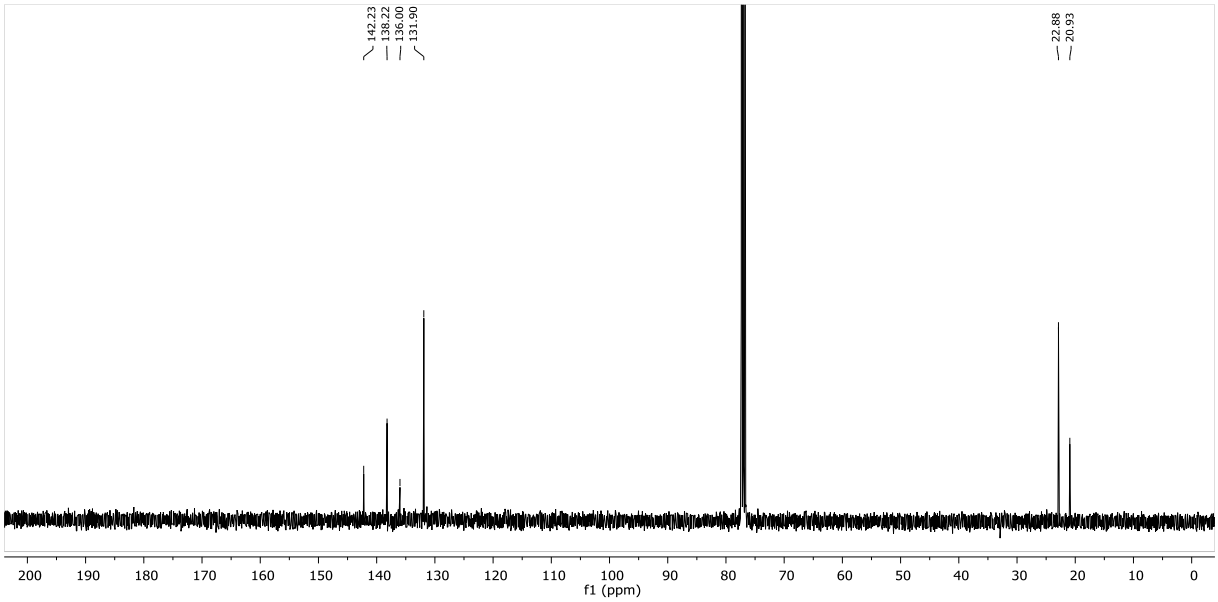


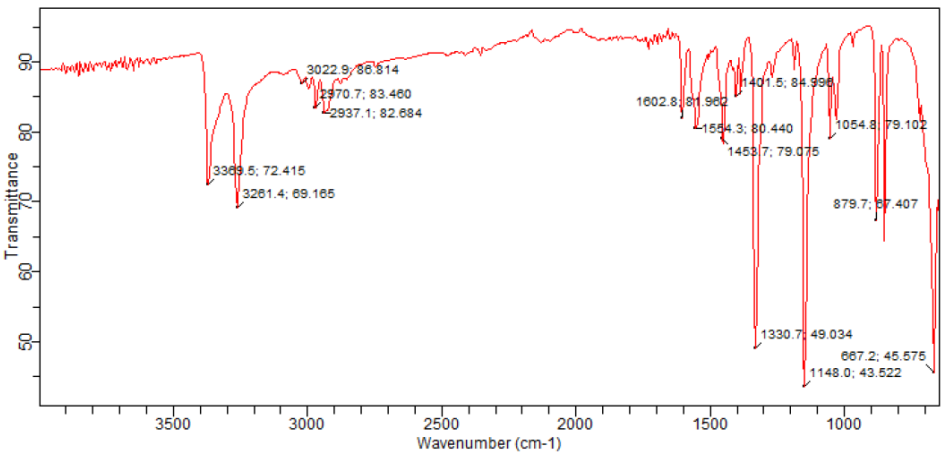




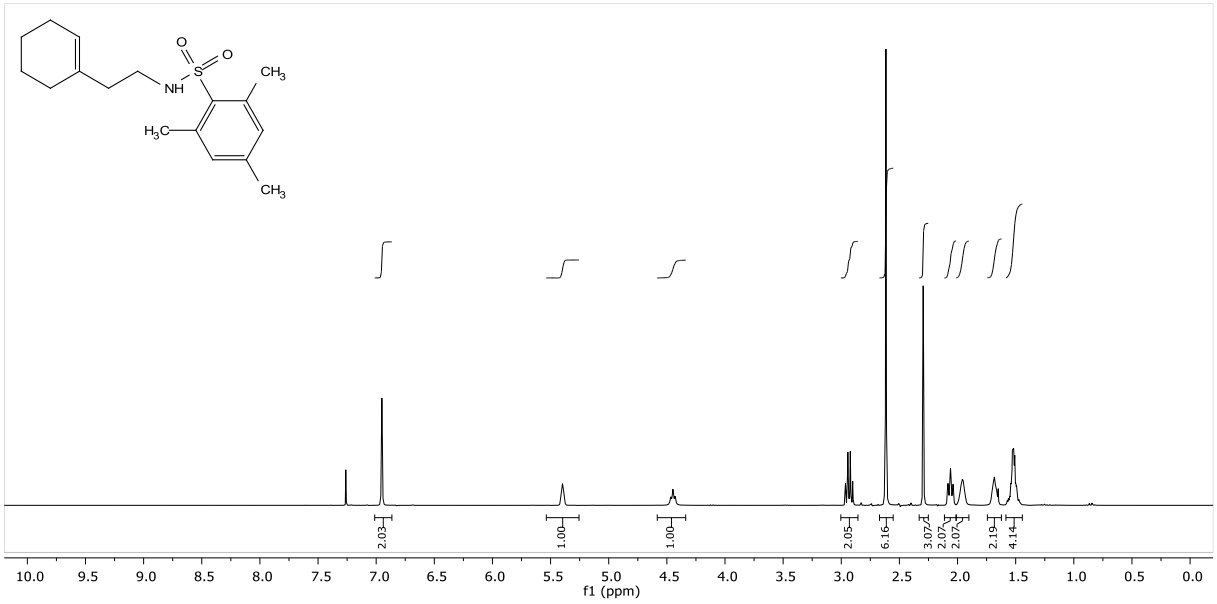
2,4,6-Trimethylbenzenesulfonamide: ^{1}H, ^{13}C NMR in $CDCl_3$, IR

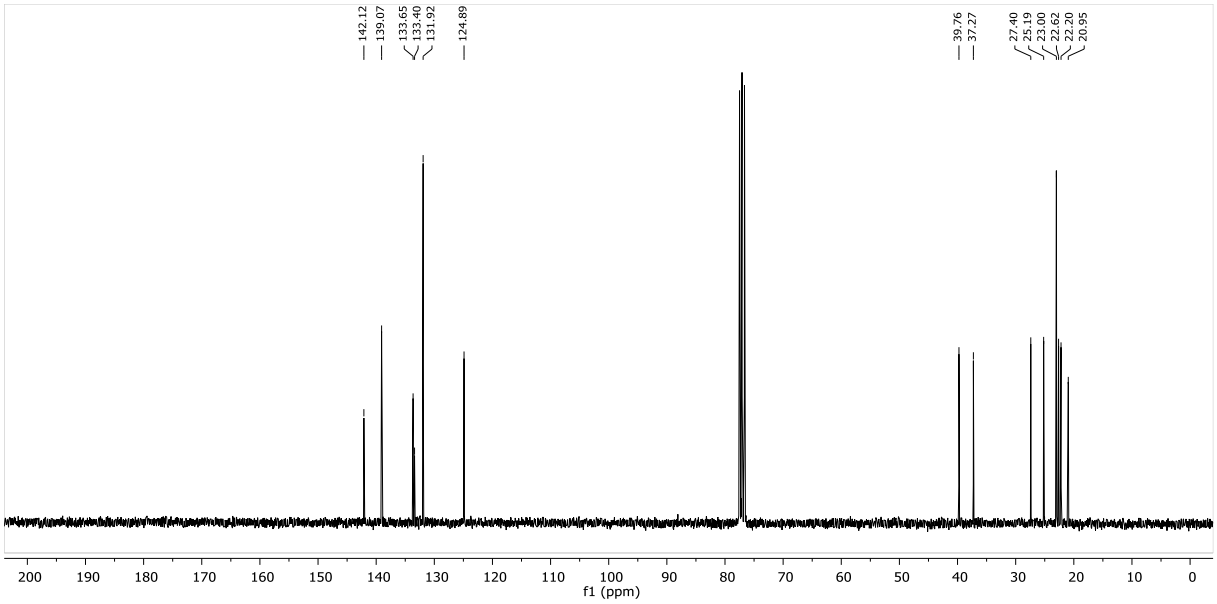


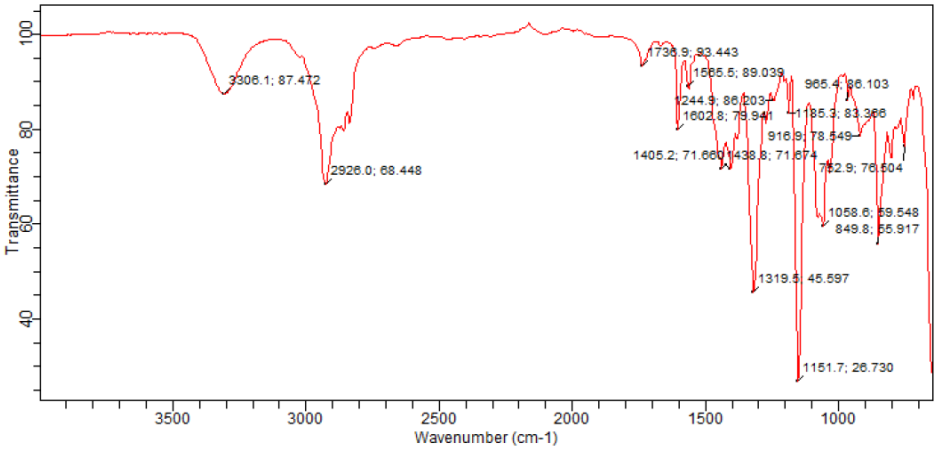




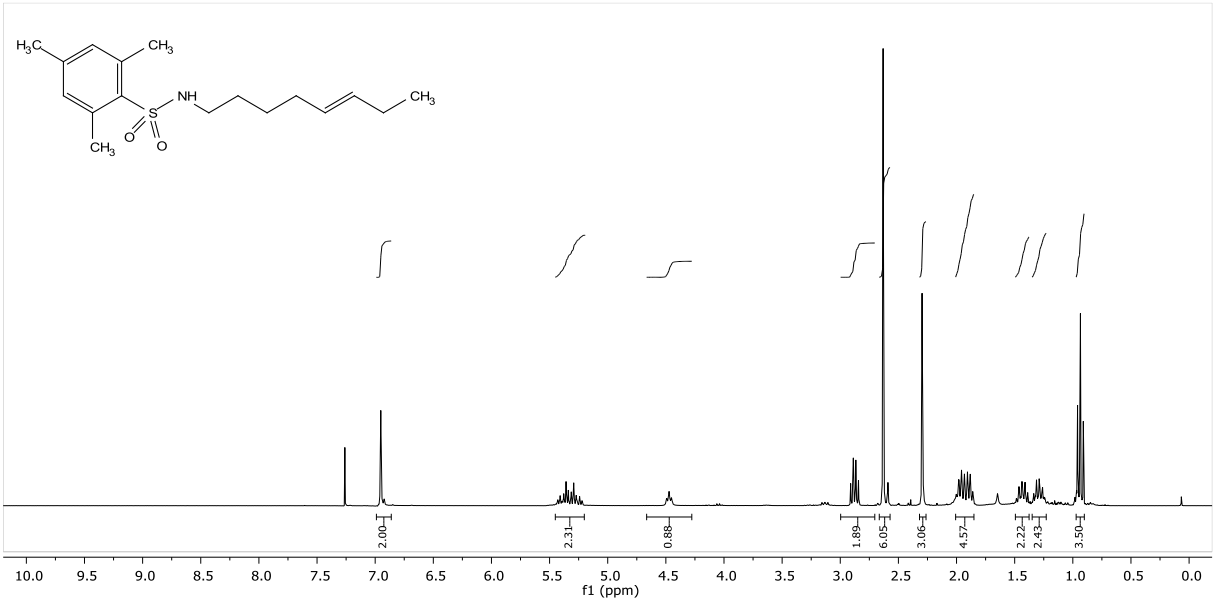
_N_-(2-(Cyclohex-1-en-1-yl)ethyl)-2,4,6-trimethylbenzenesulfonamide (146af): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

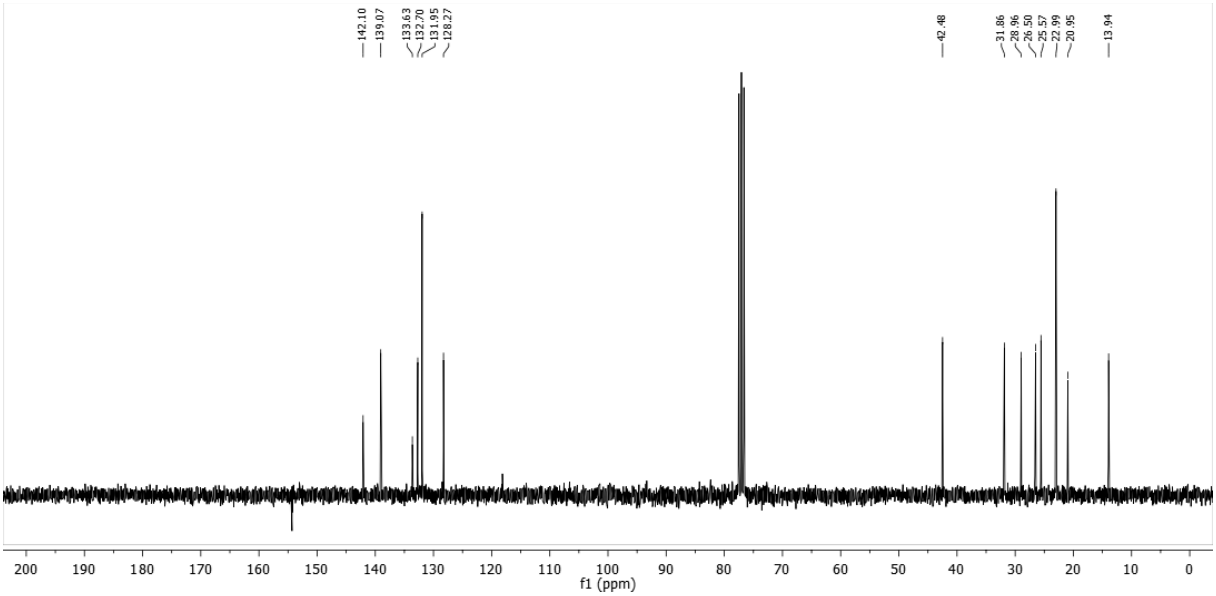


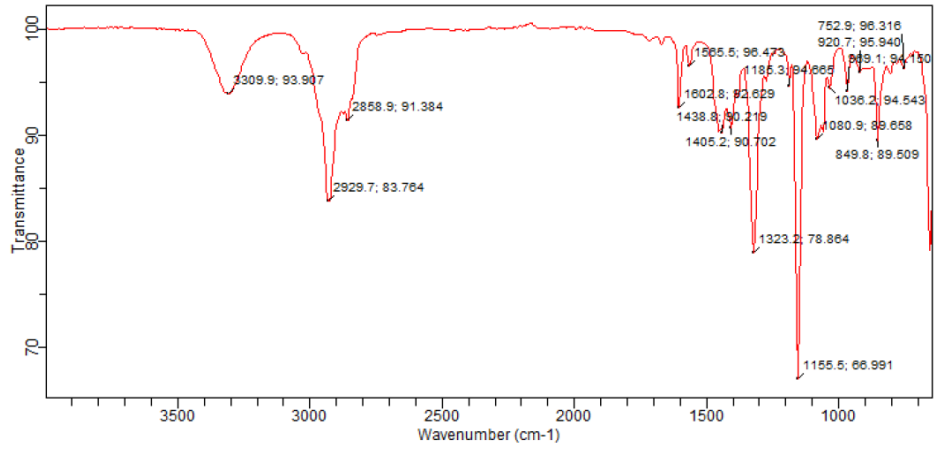




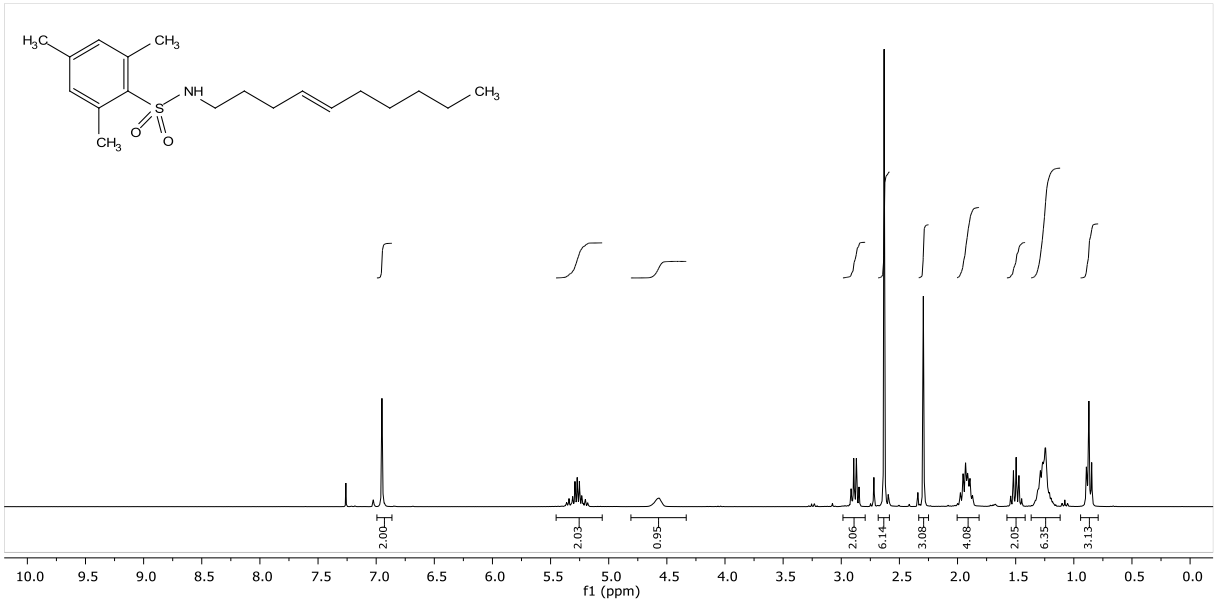
***(E)*-2,4,6-Trimethyl-N-(oct-5-en-1-yl)benzenesulfonamide (147f):** ^{1}H, ^{13}C NMR in $CDCl_3$, IR

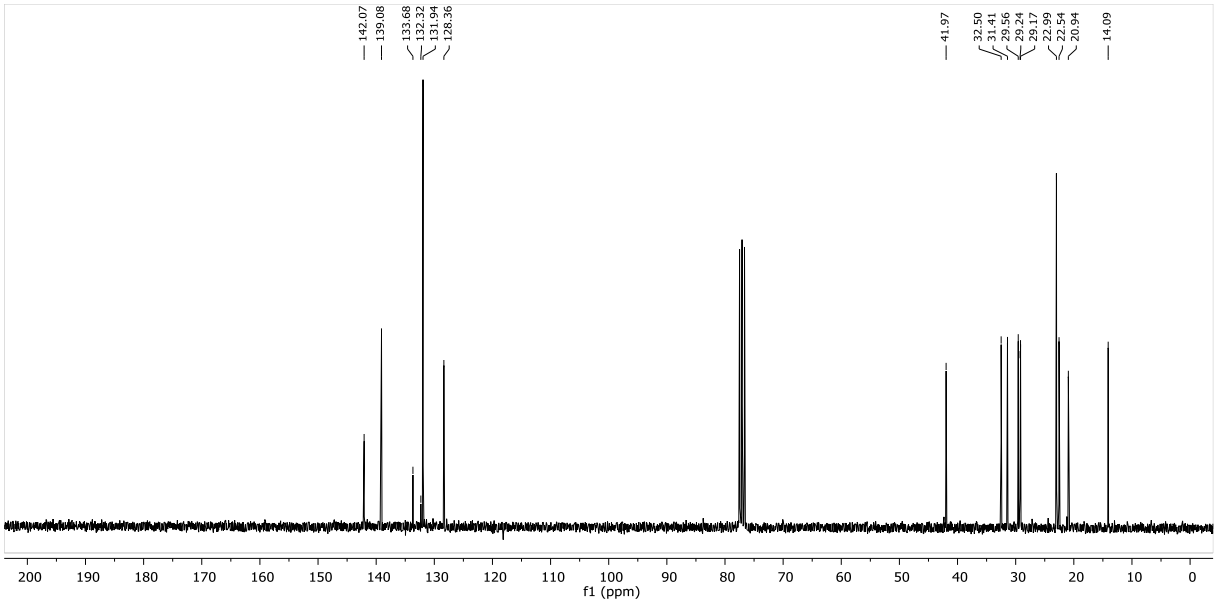


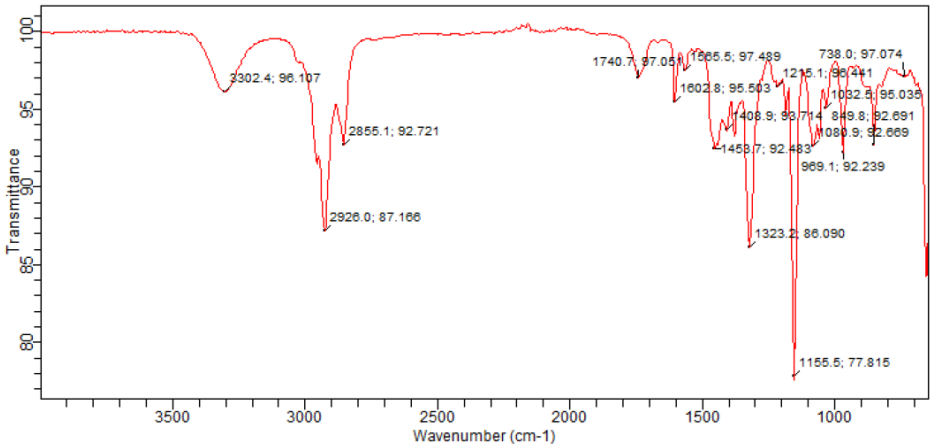




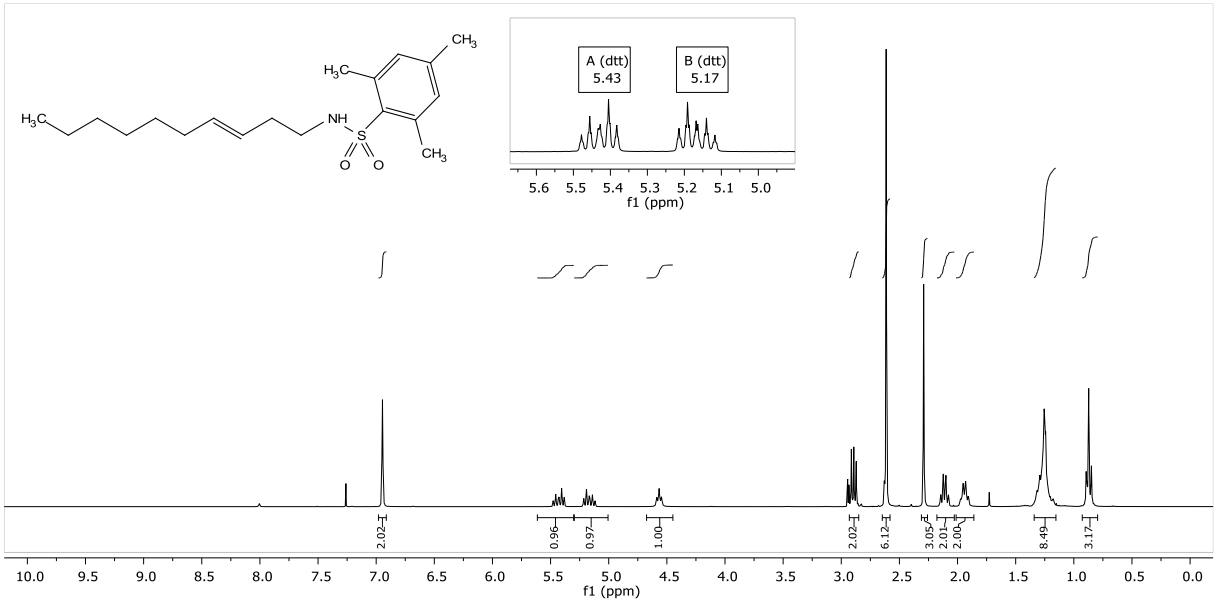
***(E)-N*-(Dec-4-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (139f):** ^{1}H, ^{13}C NMR in $CDCl_3$, IR

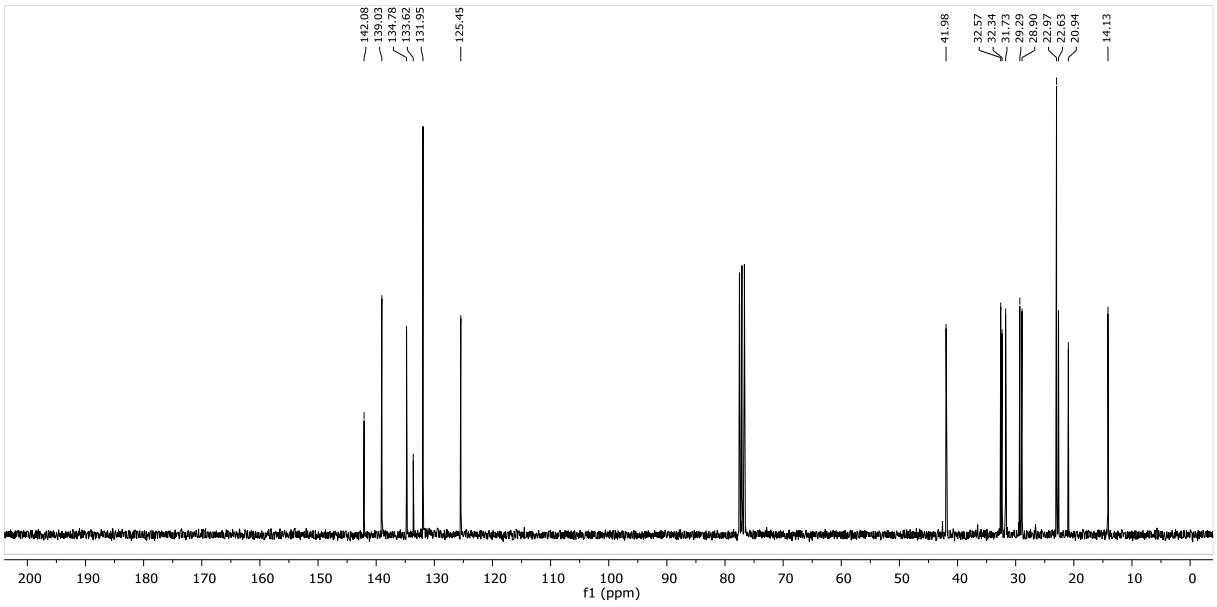


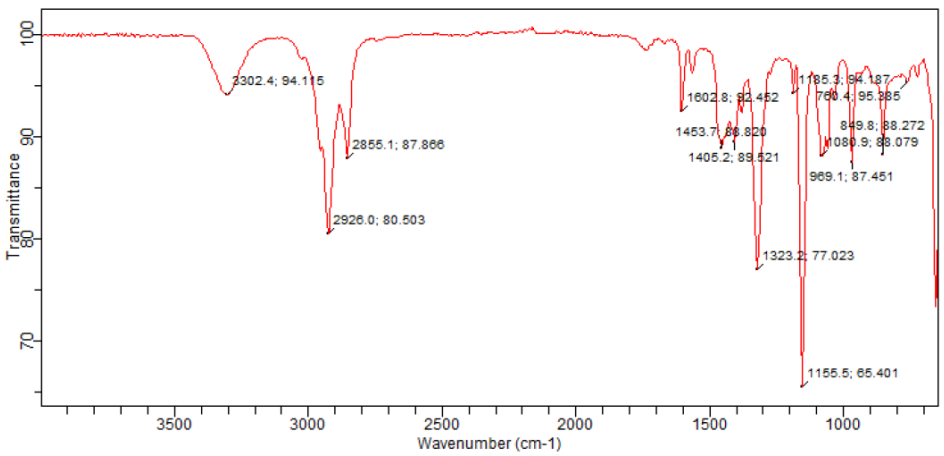




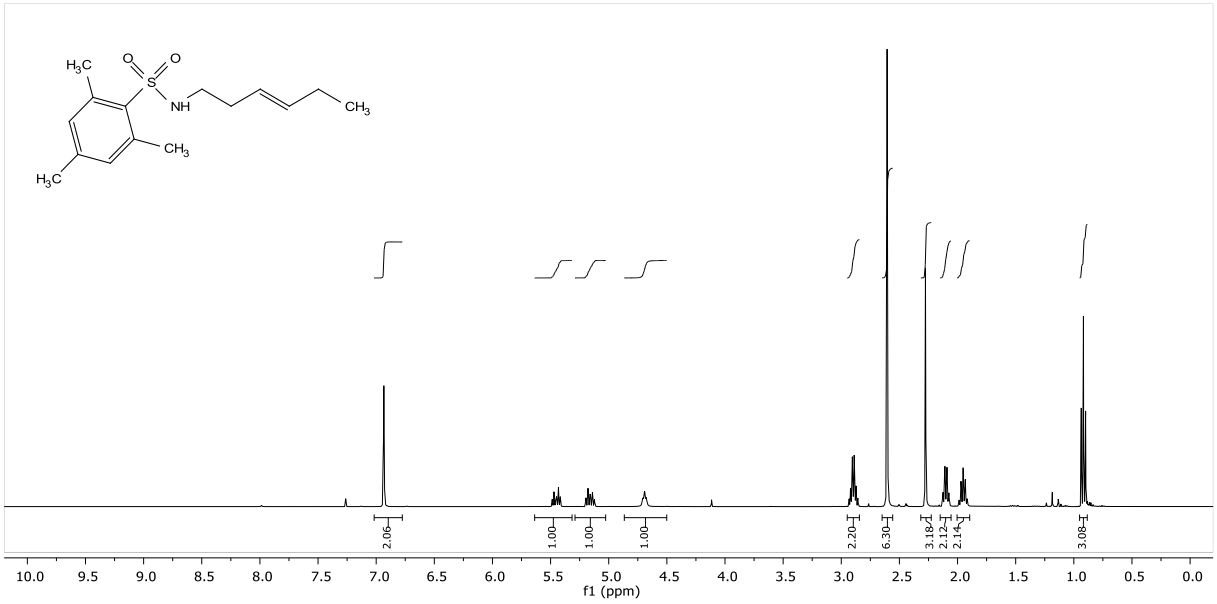
(*E*)-*N*-(Dec-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (146ag): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

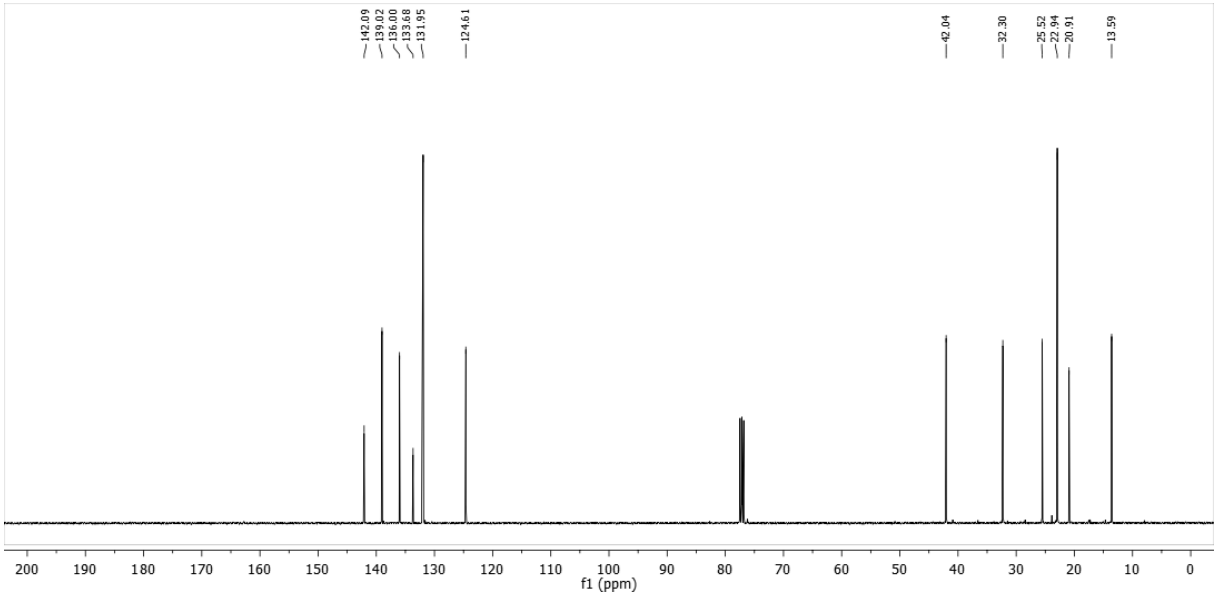


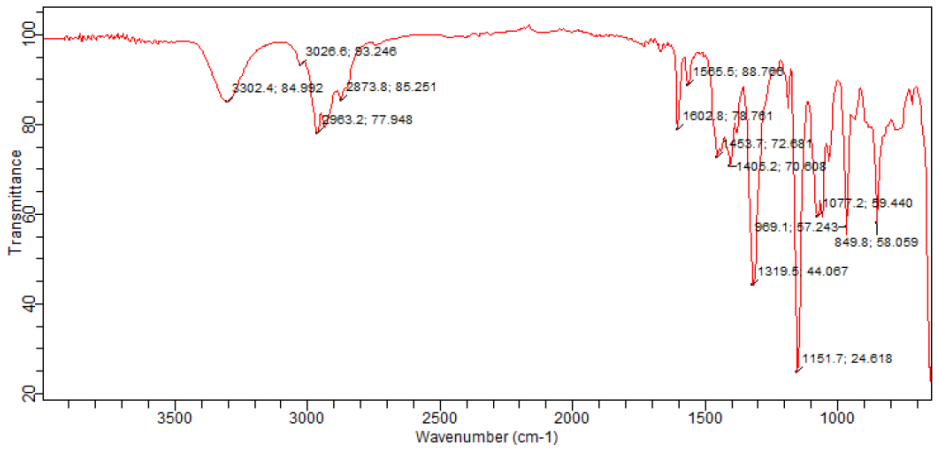




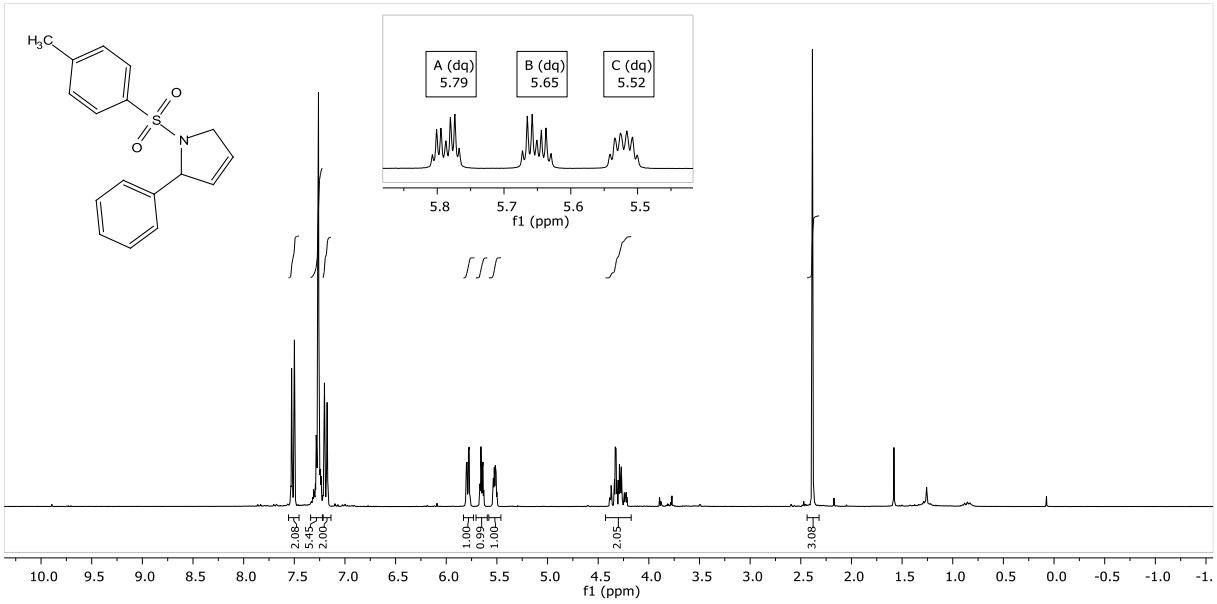
(*E*)-*N*-(Hex-3-en-1-yl)-2,4,6-trimethylbenzenesulfonamide (146ah): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

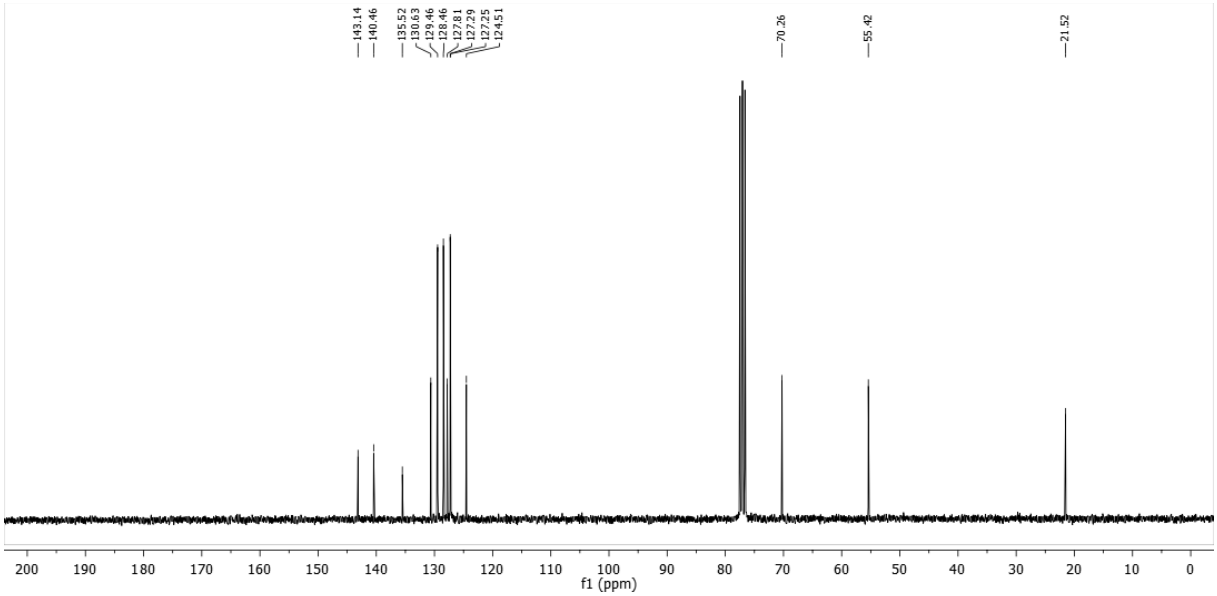


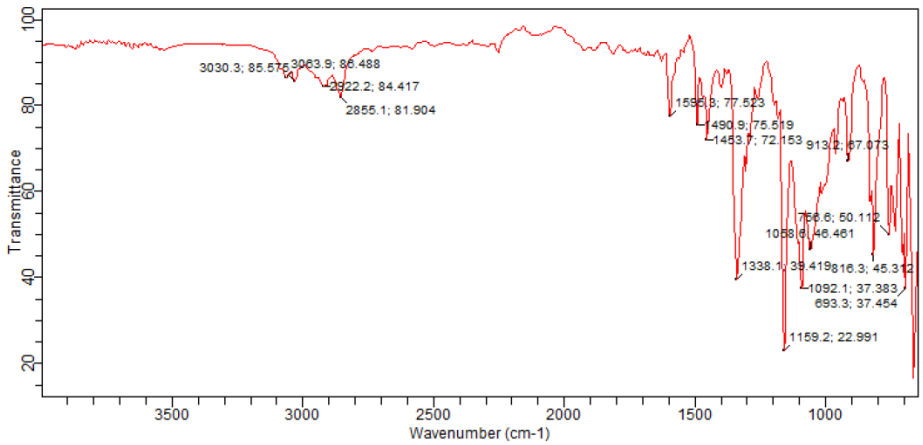


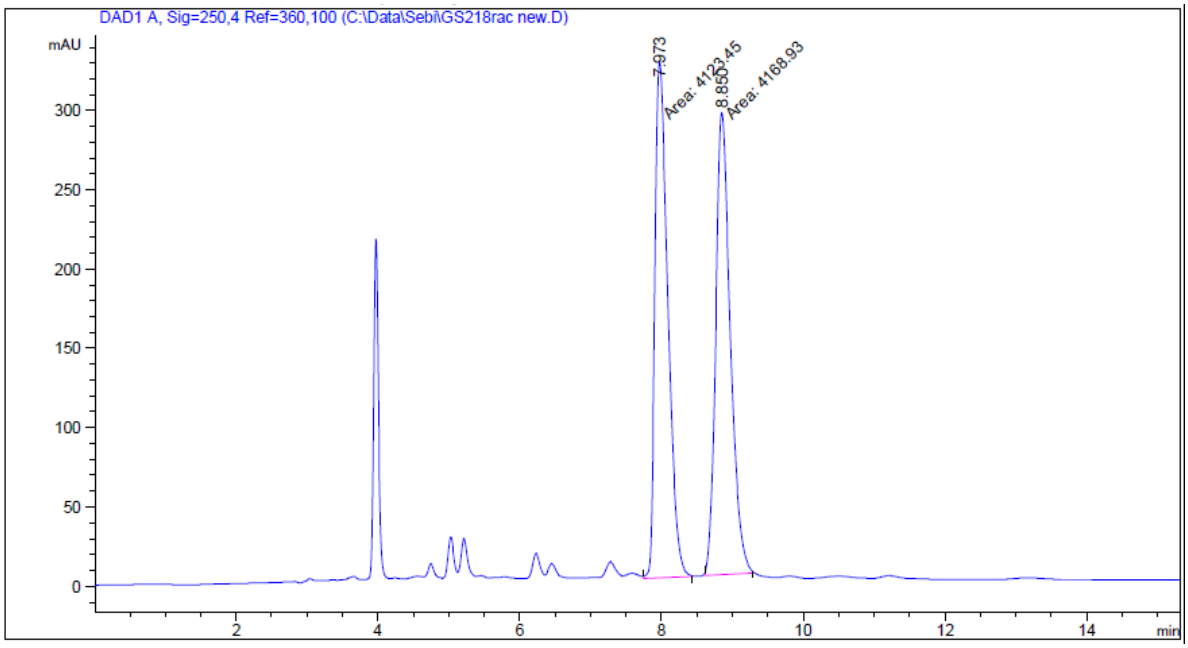


2-Phenyl-1-tosyl-2,5-dihydro-1*H*-pyrrole (149d)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

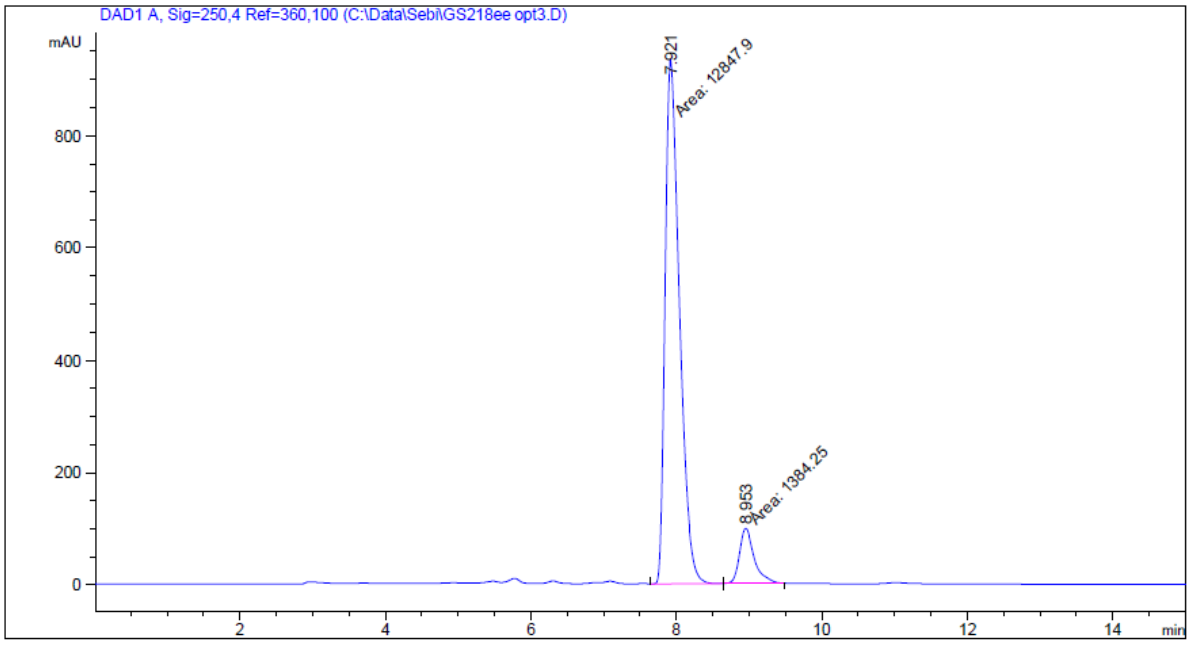






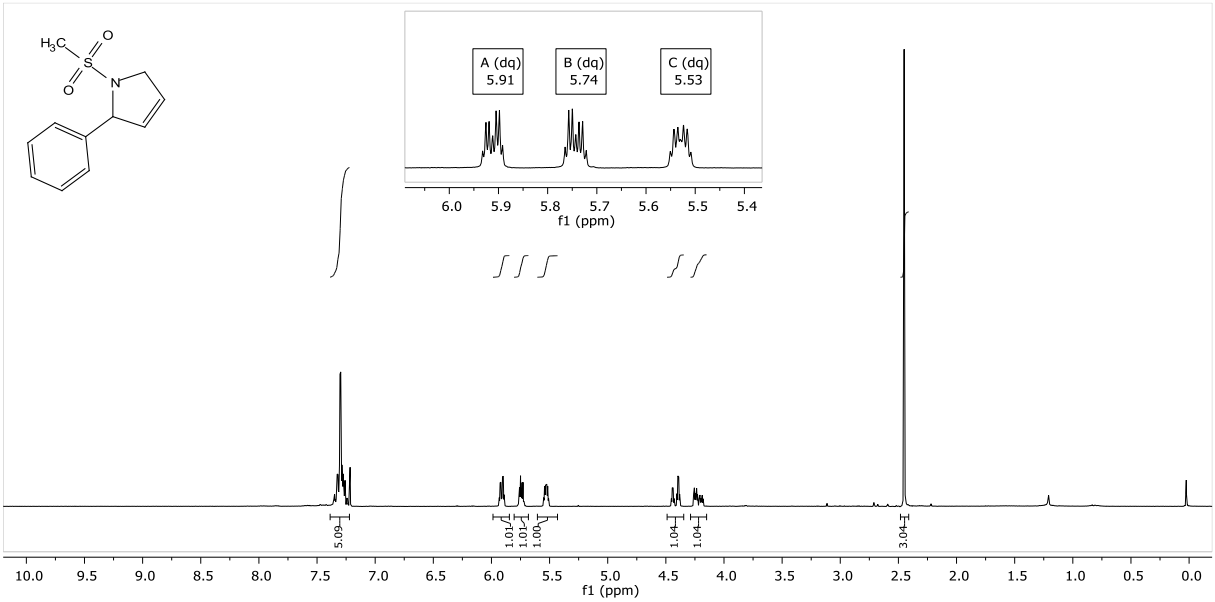


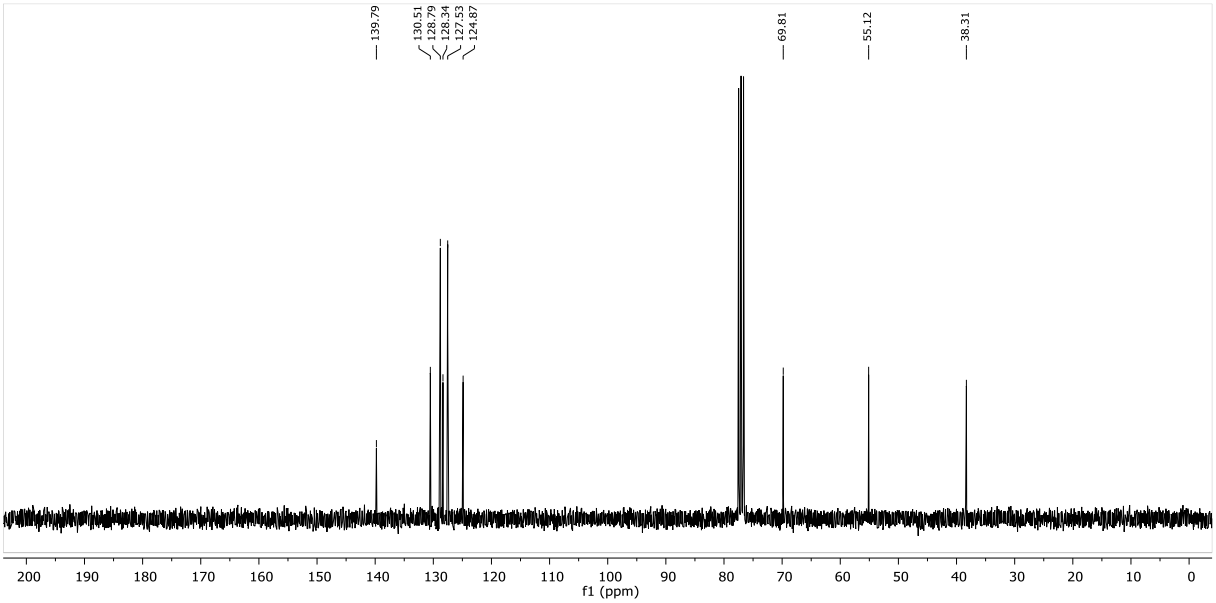
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.973	MM	0.2111	4123.45410	325.58704	49.7258
2	8.850	MM	0.2382	4168.93213	291.68802	50.2742

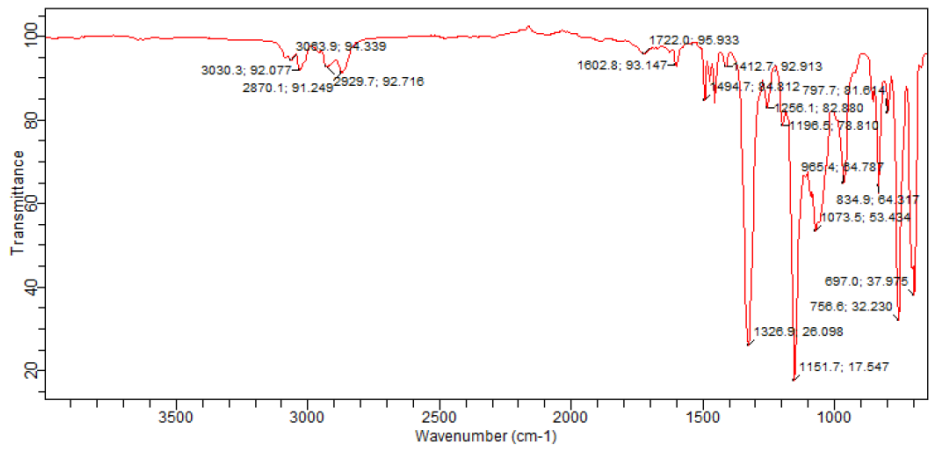


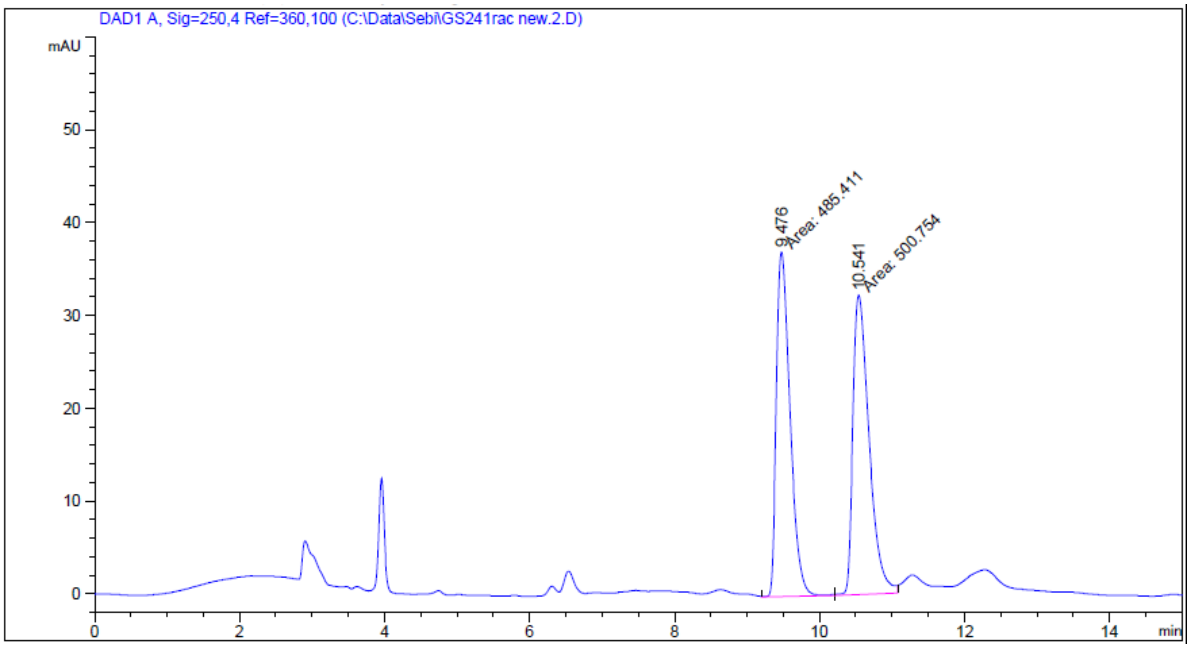
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.921	MM	0.2296	1.28479e4	932.68365	90.2738
2	8.953	MM	0.2344	1384.25171	98.40445	9.7262

1-(Methylsulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149m)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

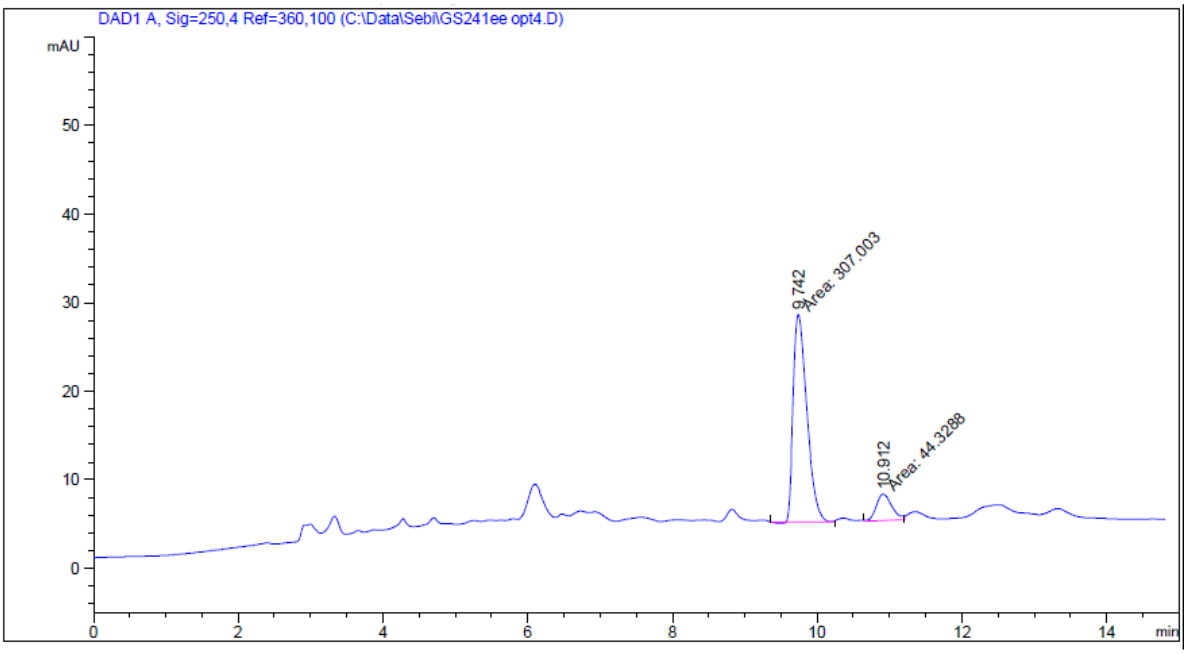






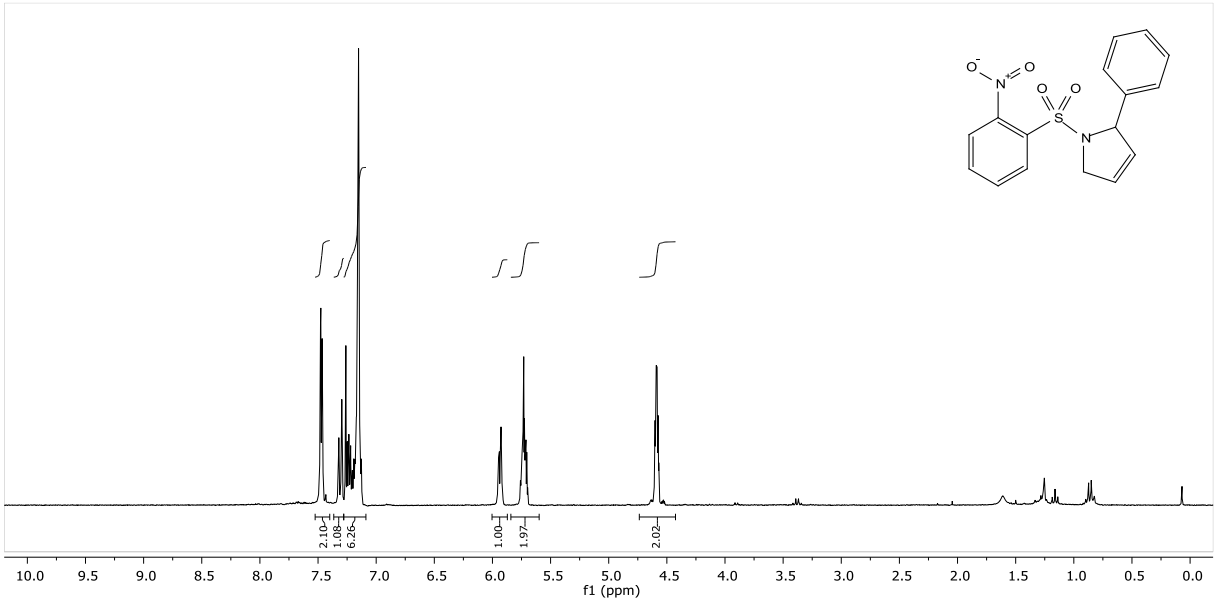


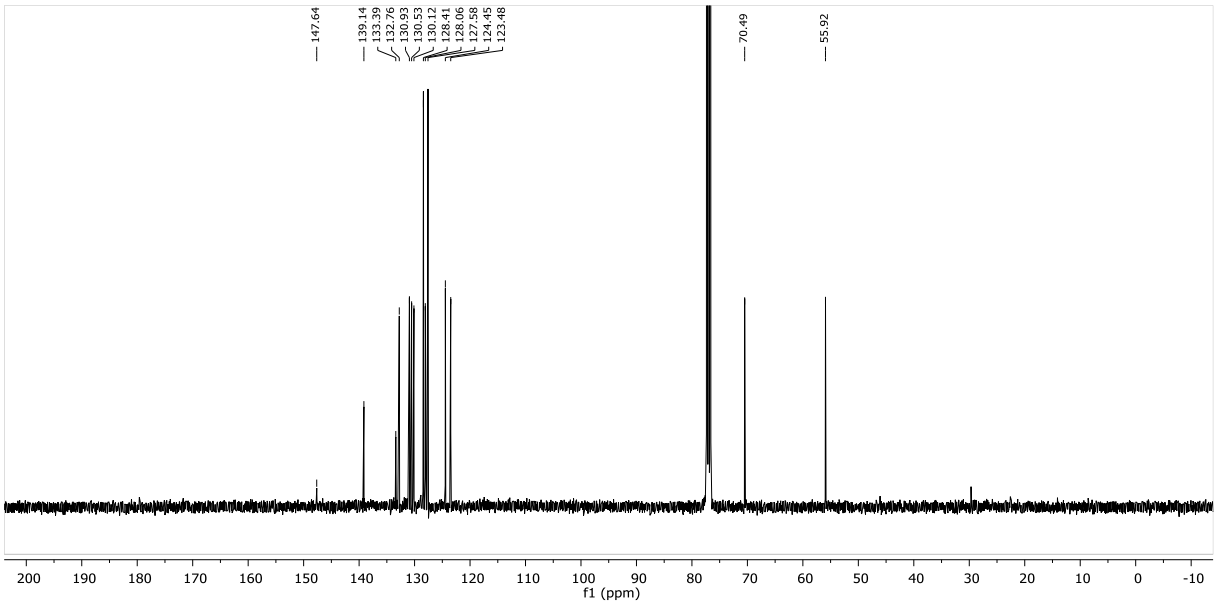
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.476	MM	0.2178	485.41095	37.14945	49.2221
2	10.541	MM	0.2585	500.75409	32.28336	50.7779

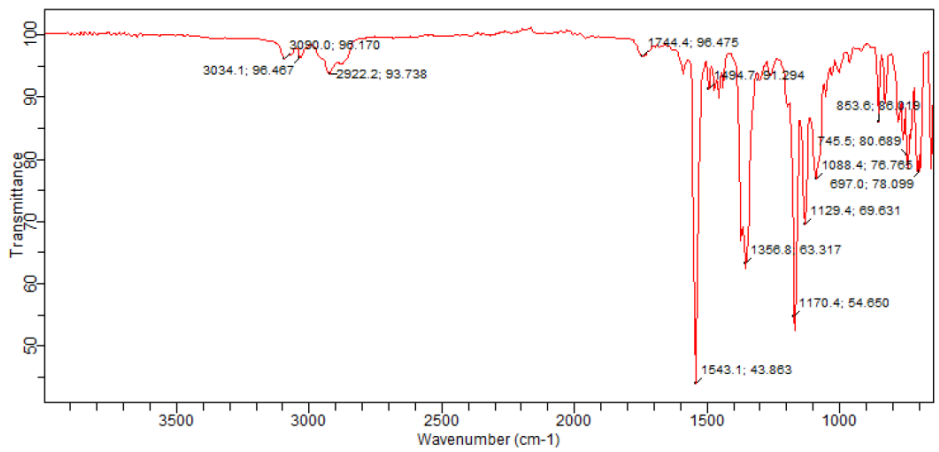


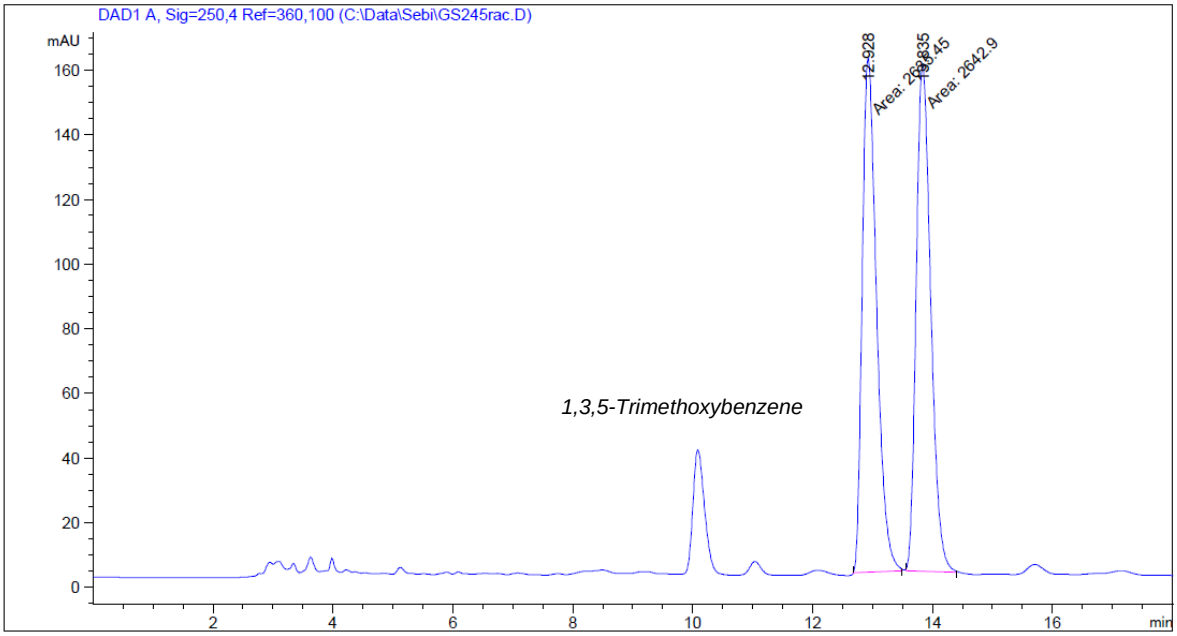
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.742	MM	0.2183	307.00272	23.44176	87.3826
2	10.912	MM	0.2494	44.32875	2.96228	12.6174

1-((2-Nitrophenyl)sulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149q)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces



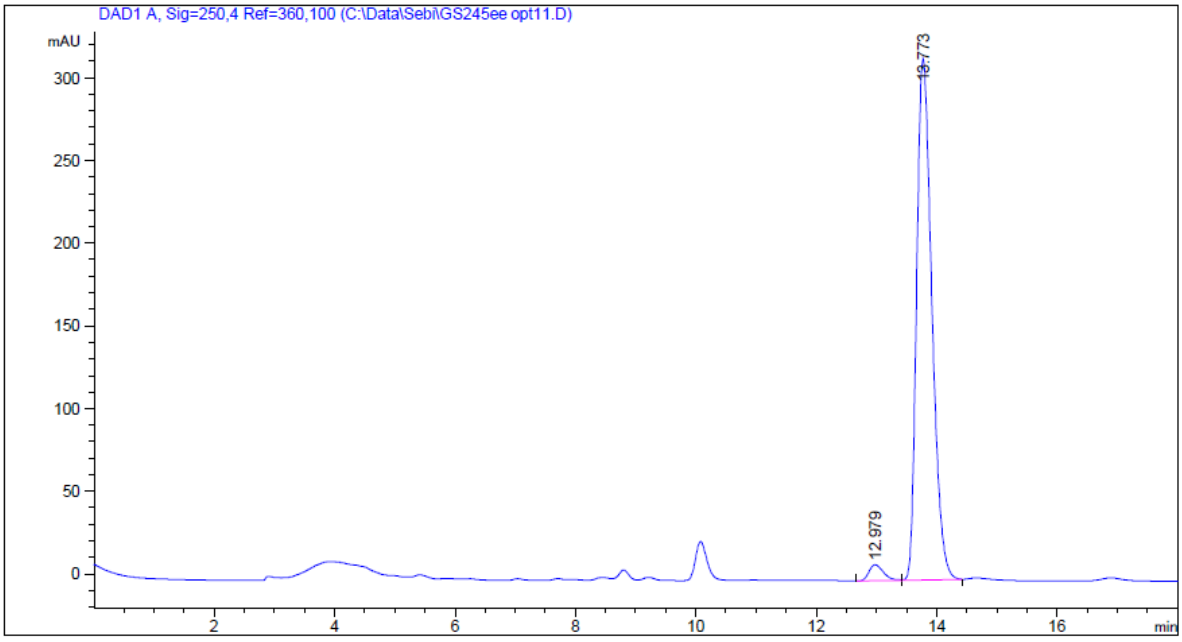






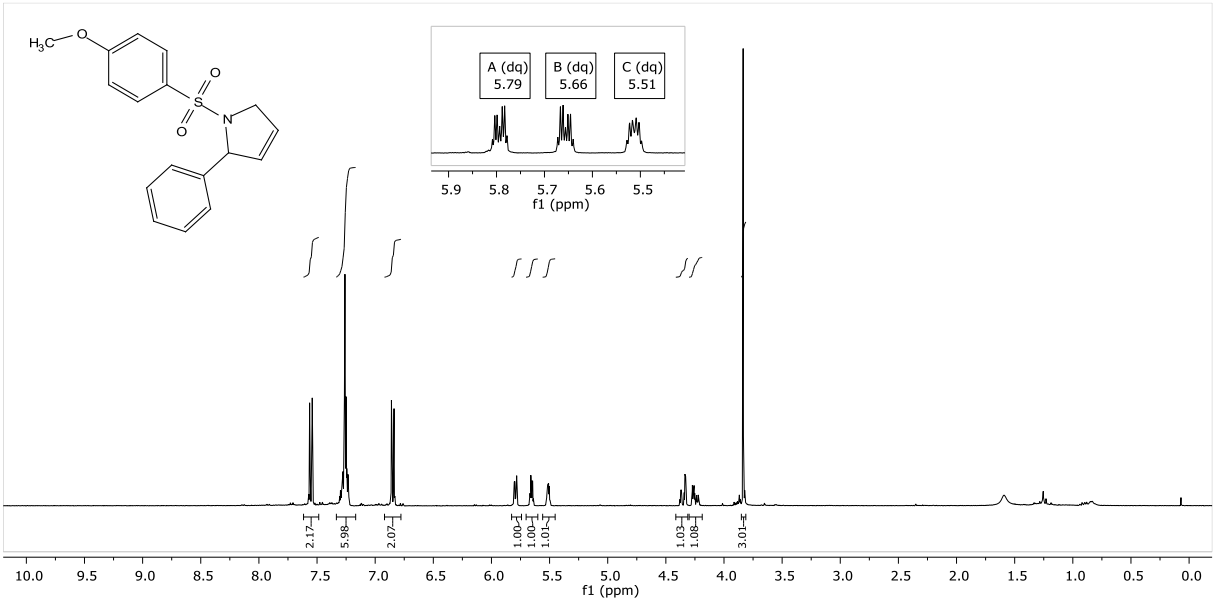
Signal 1: DAD1 A, Sig=250,4 Ref=360,100

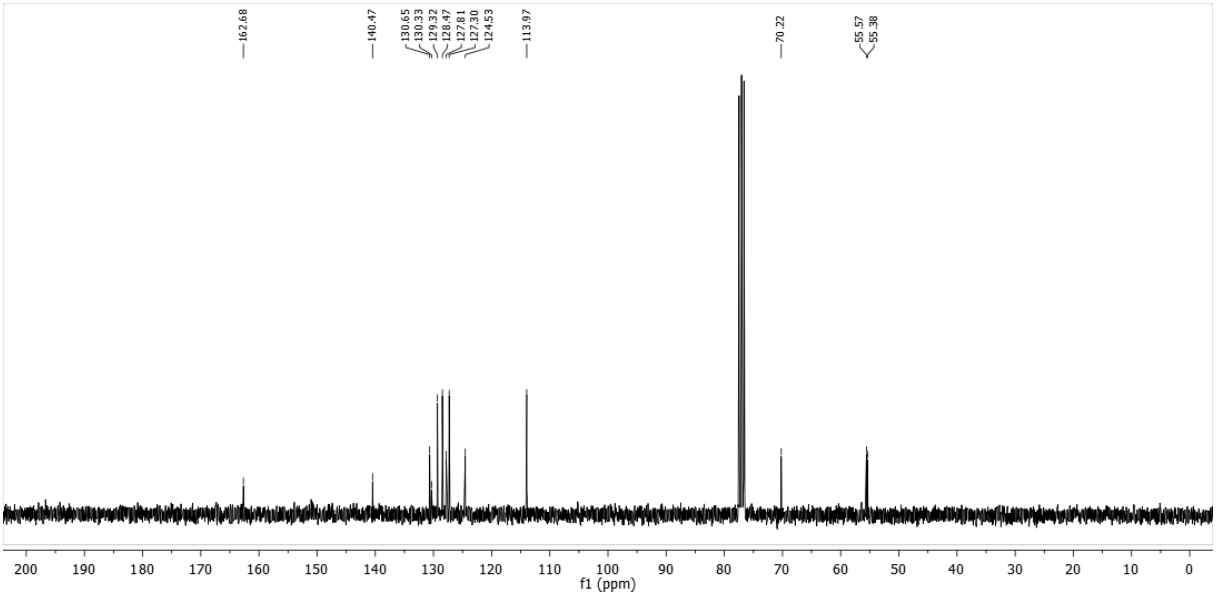
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.928	MM	0.2761	2635.45386	159.08649	49.9295
2	13.835	MM	0.2802	2642.89575	157.19418	50.0705

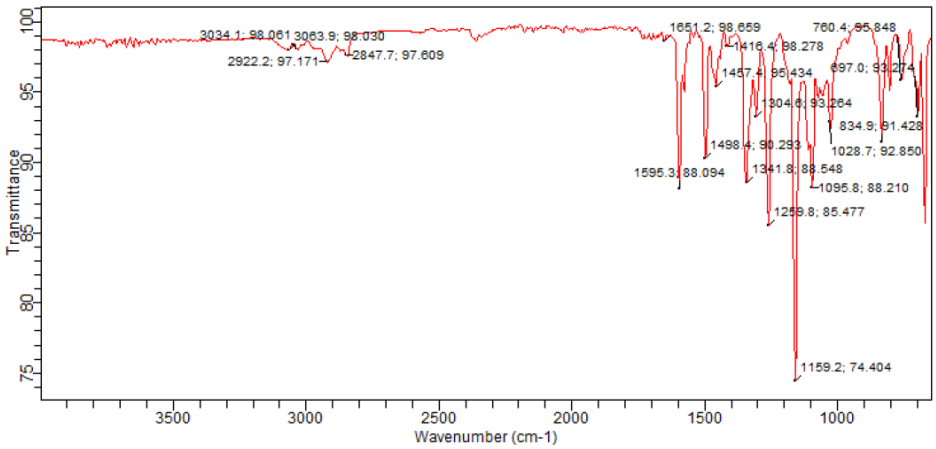


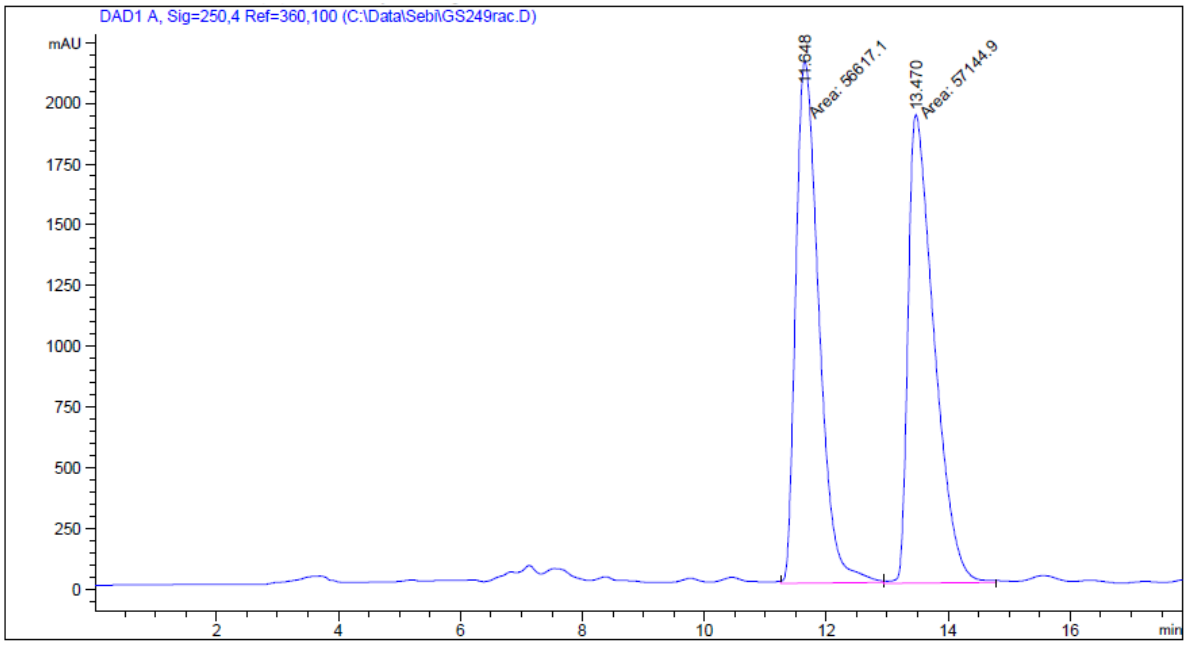
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.979	BV	0.2574	160.75589	9.69776	2.8275
2	13.773	VB	0.2725	5524.74512	315.24750	97.1725

1-((4-Methoxyphenyl)sulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149r)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

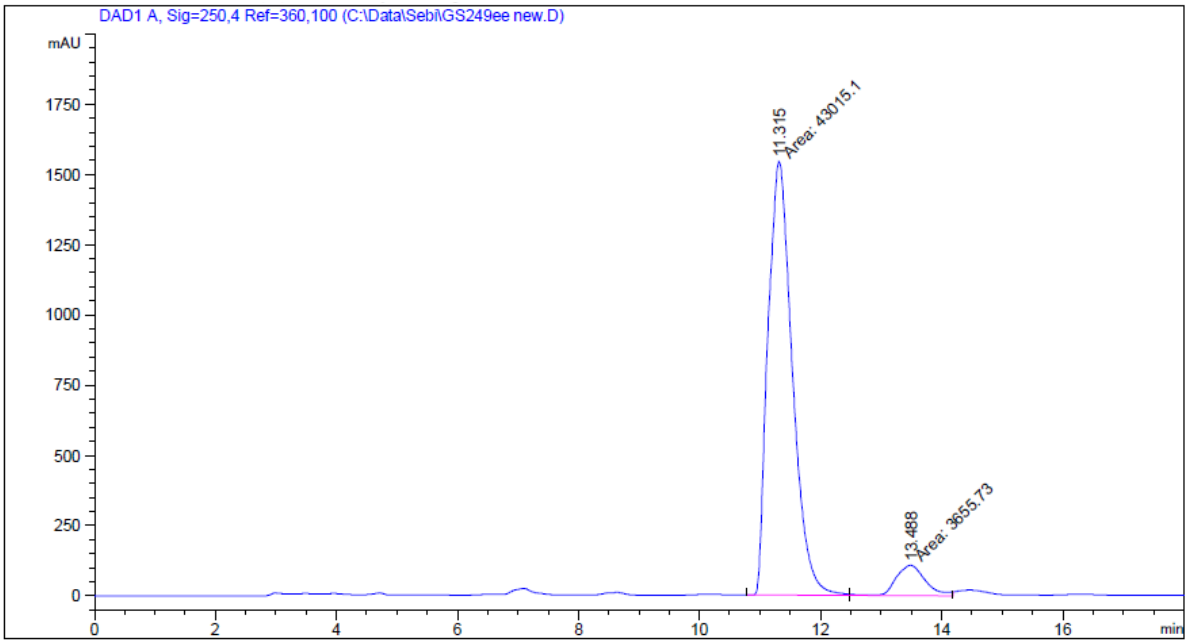






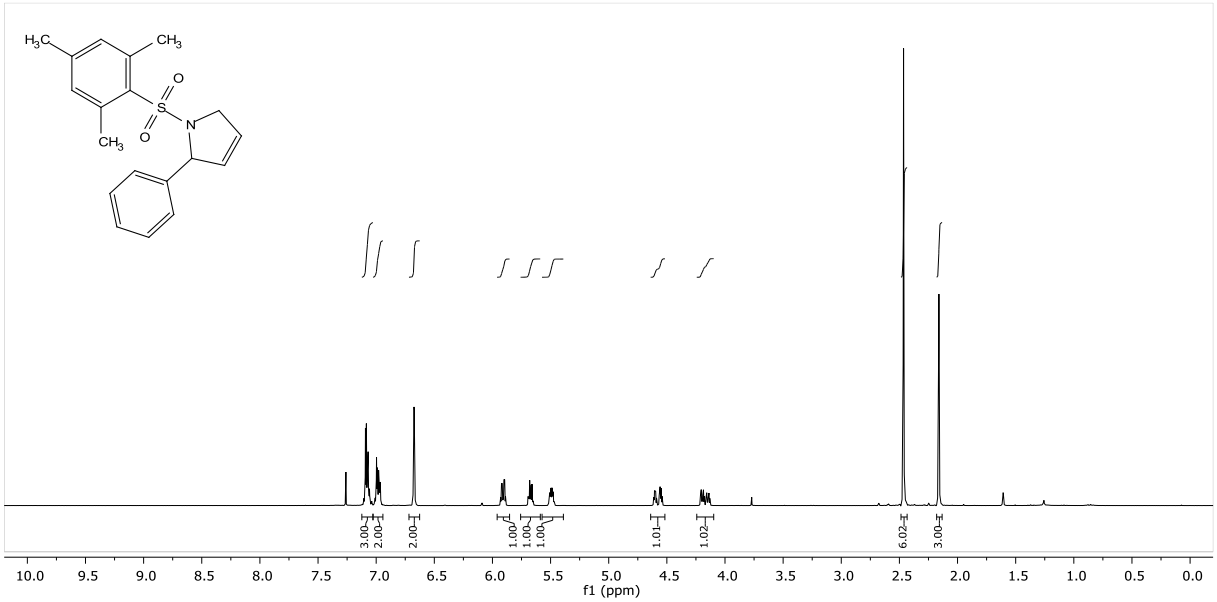


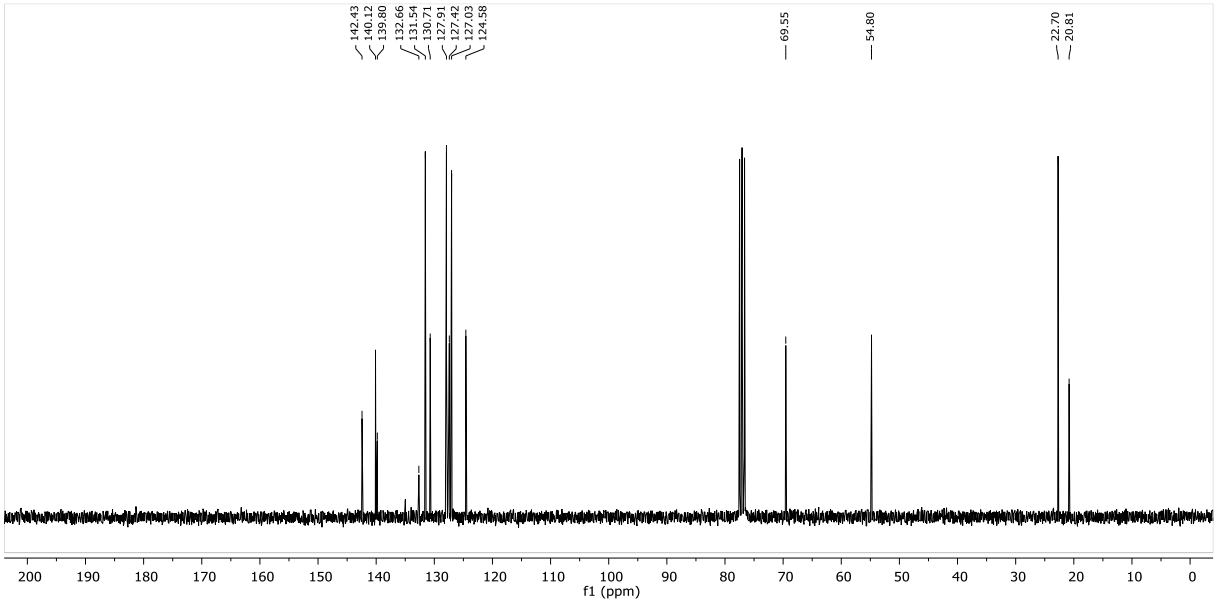
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.648	MM	0.4393	5.66171e4	2148.02490	49.7680
2	13.470	MM	0.4941	5.71449e4	1927.55786	50.2320

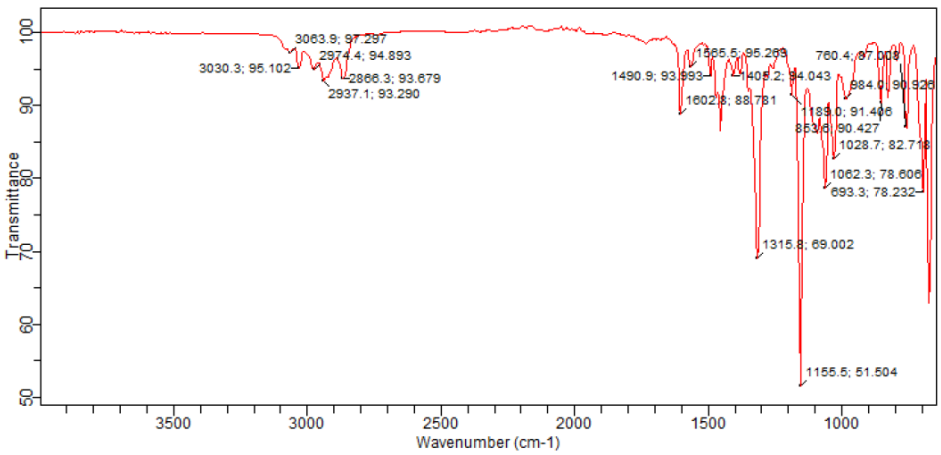


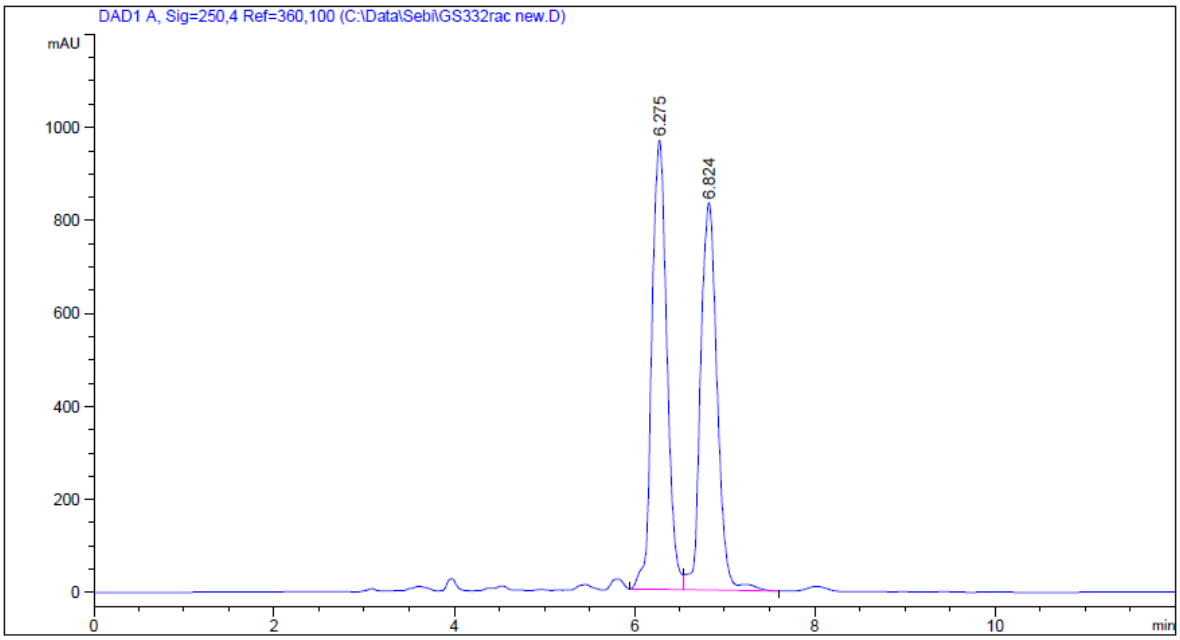
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.315	MM	0.4647	4.30151e4	1542.71985	92.1670
2	13.488	MM	0.5616	3655.72705	108.49354	7.8330

1-(Mesitylsulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149v)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

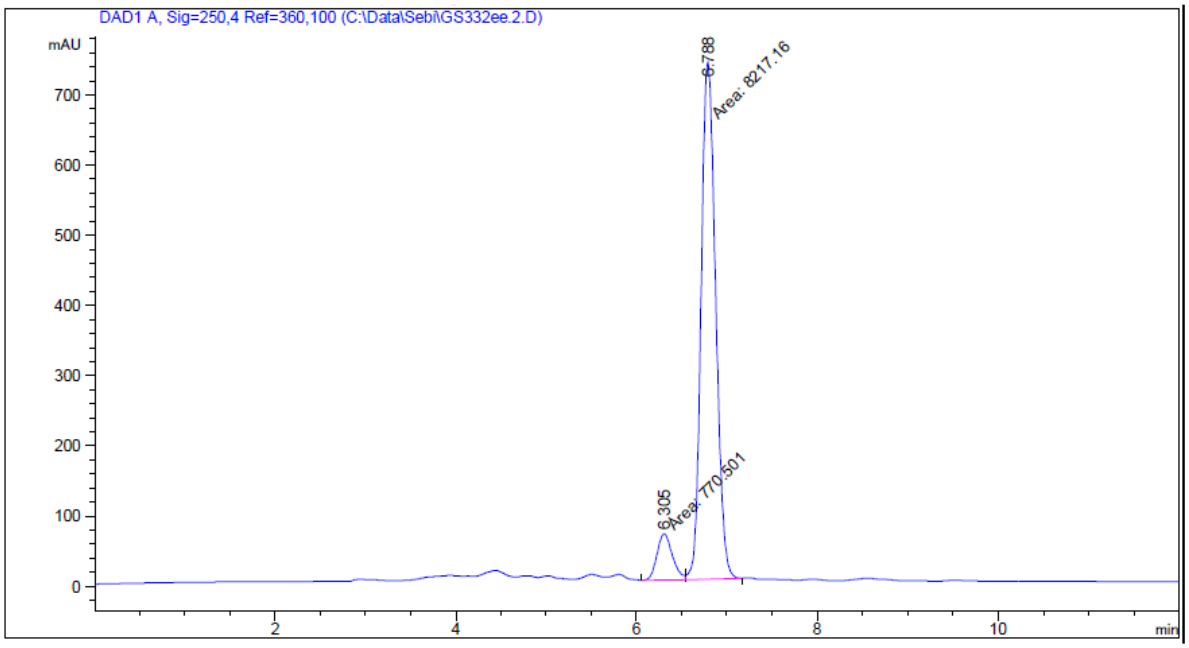






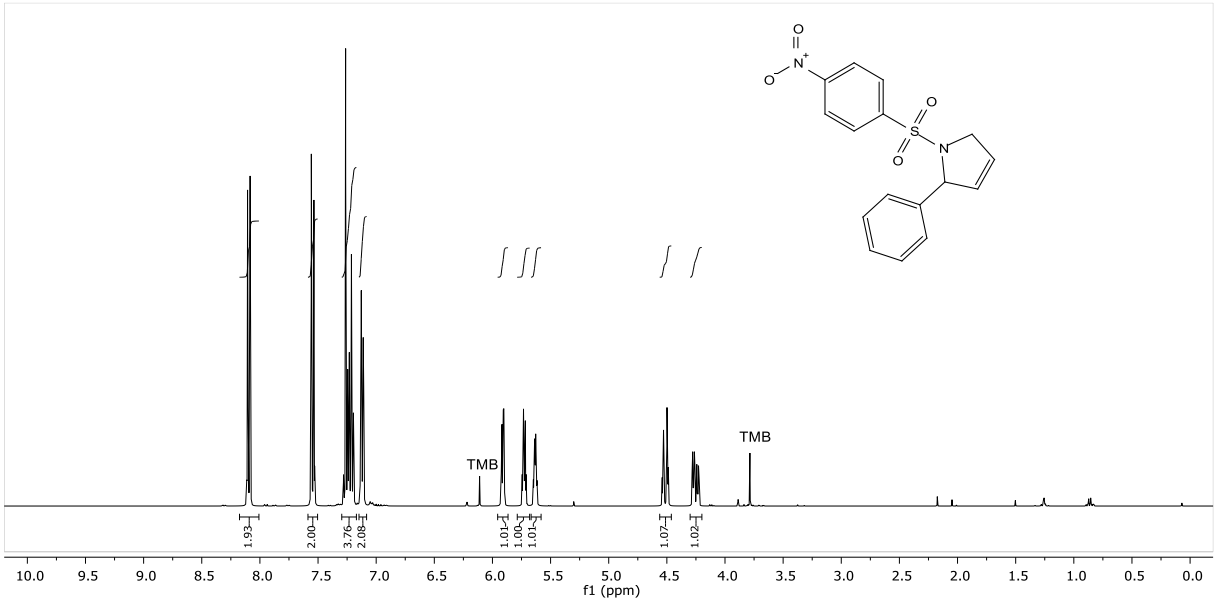


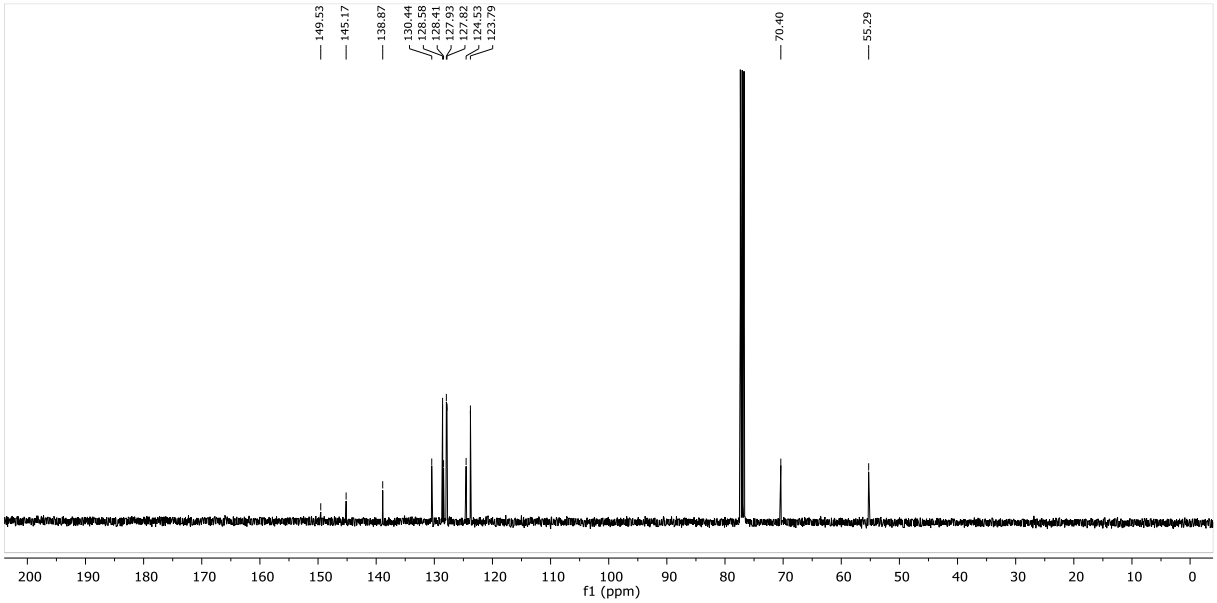
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.275	BV	0.1859	1.12450e4	965.20996	51.3393
2	6.824	VV R	0.2009	1.06583e4	832.39984	48.6607

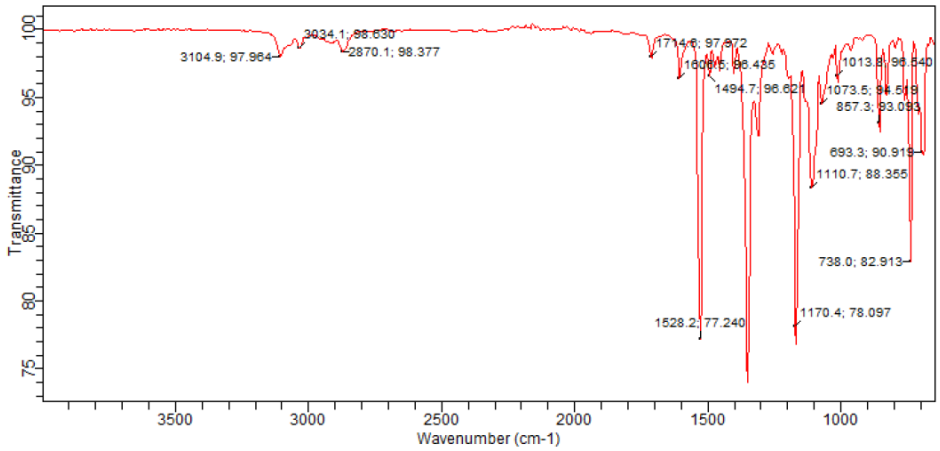


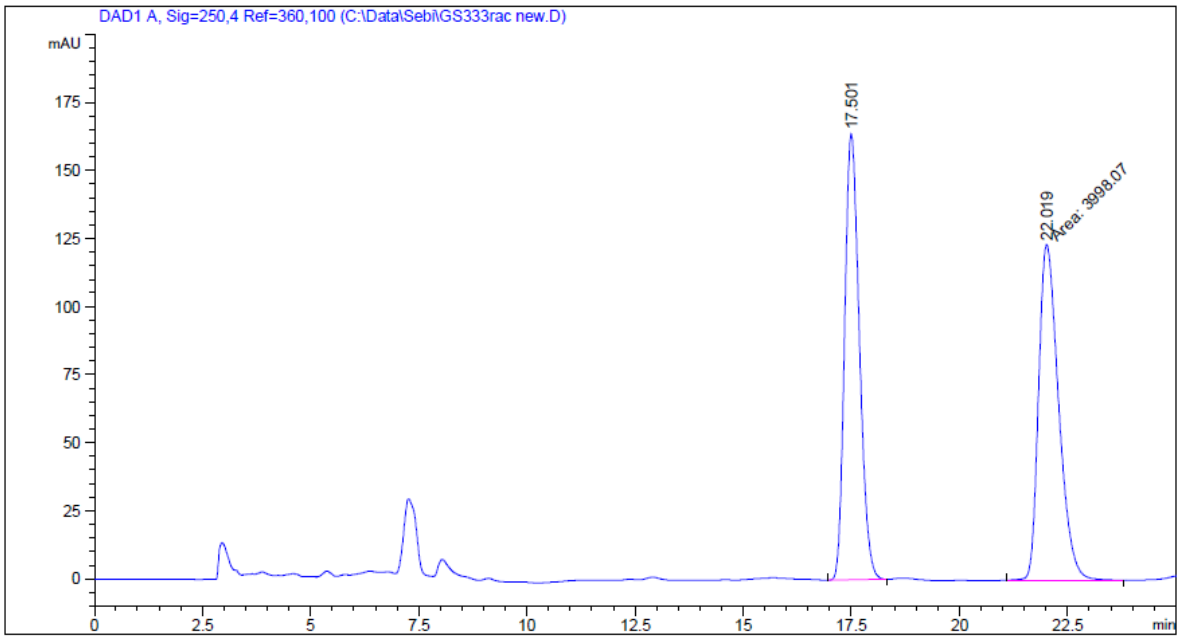
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.305	MM	0.1957	770.50067	65.62192	8.5729
2	6.788	MM	0.1857	8217.15723	737.30292	91.4271

1-((4-Nitrophenyl)sulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149$^{p\text{-}NO_2}$)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

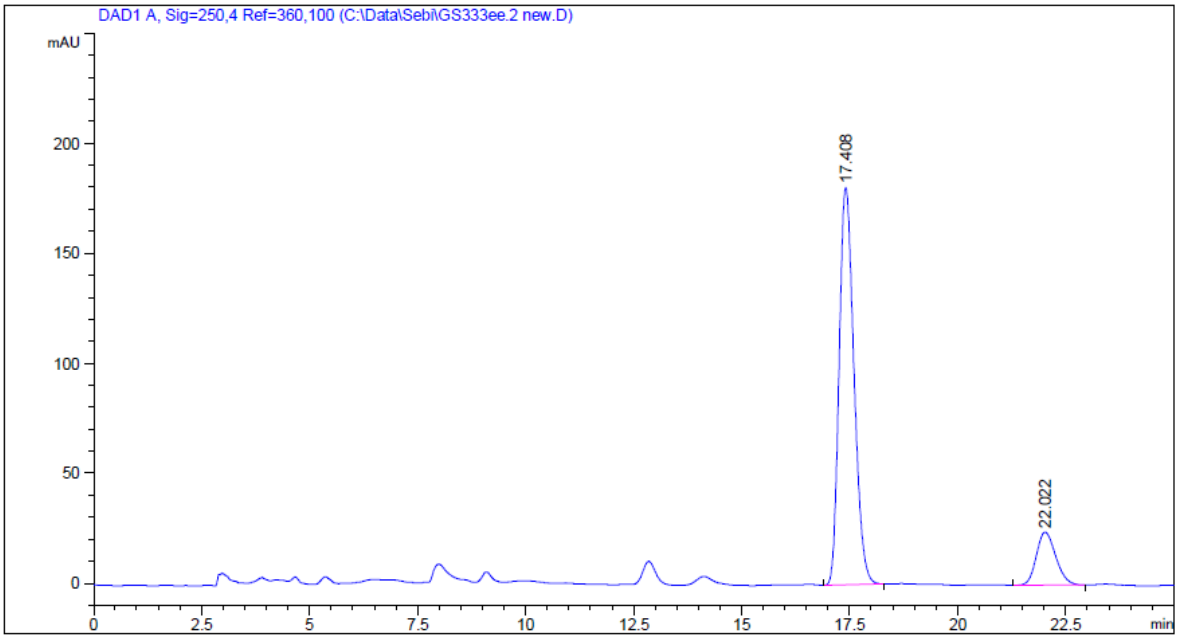








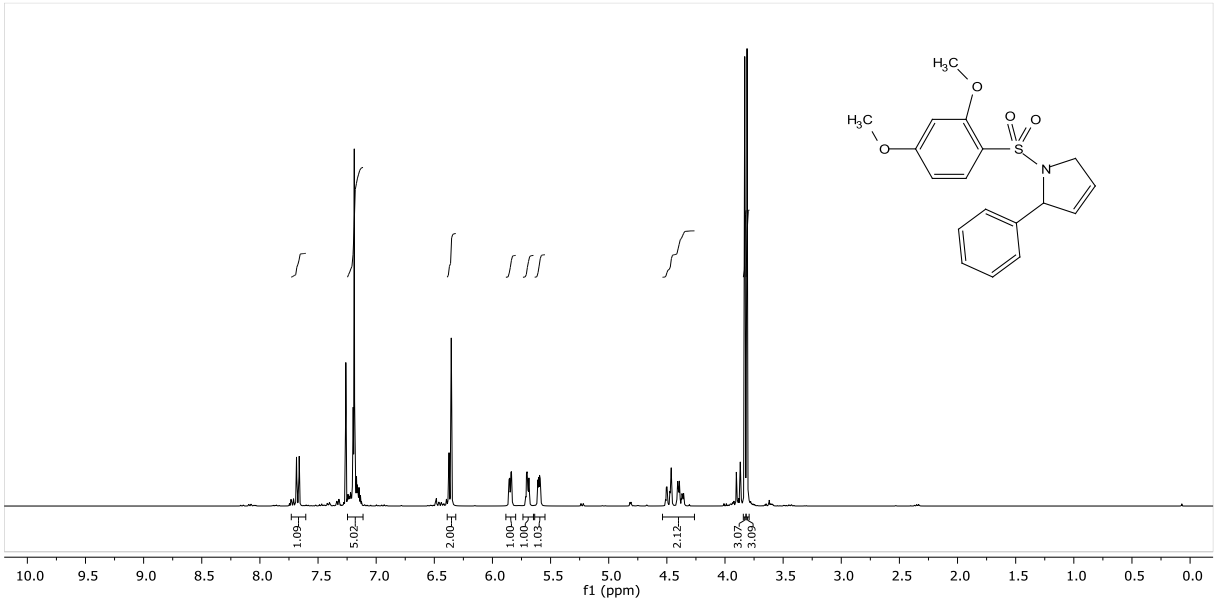
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.501	BB	0.3681	3876.62500	163.78168	49.2289
2	22.019	MM	0.5398	3998.06616	123.44219	50.7711

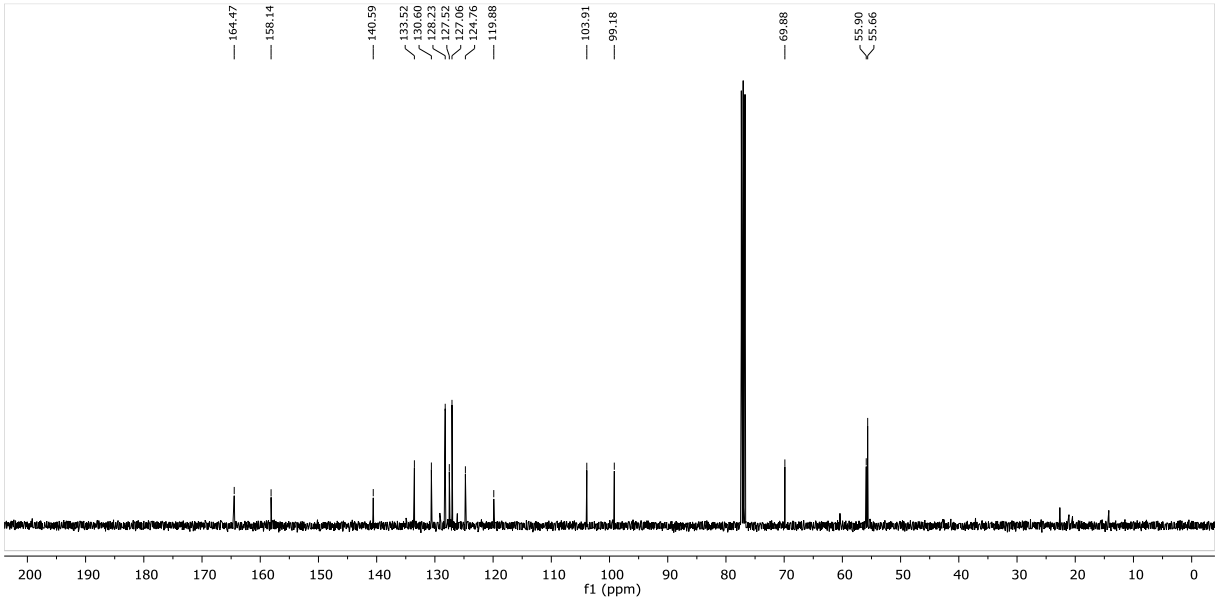


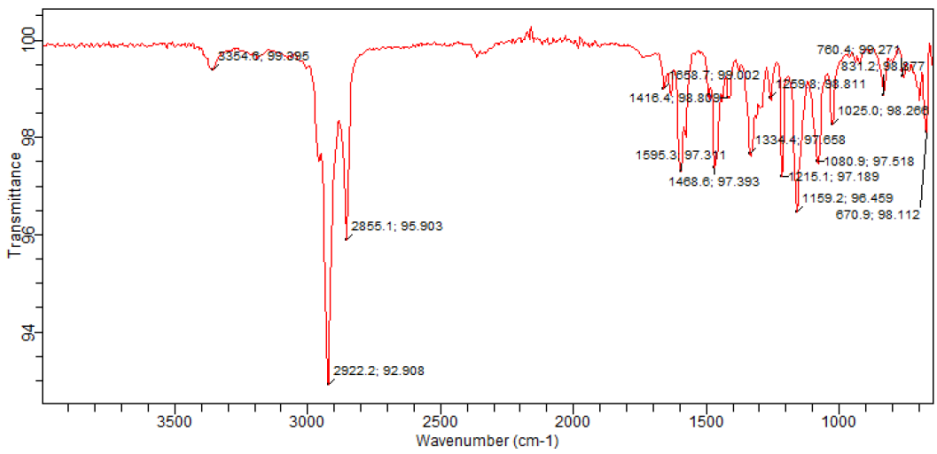
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.408	BB	0.3698	4303.31982	180.71715	85.1332
2	22.022	BB	0.4836	751.48566	24.11068	14.8668

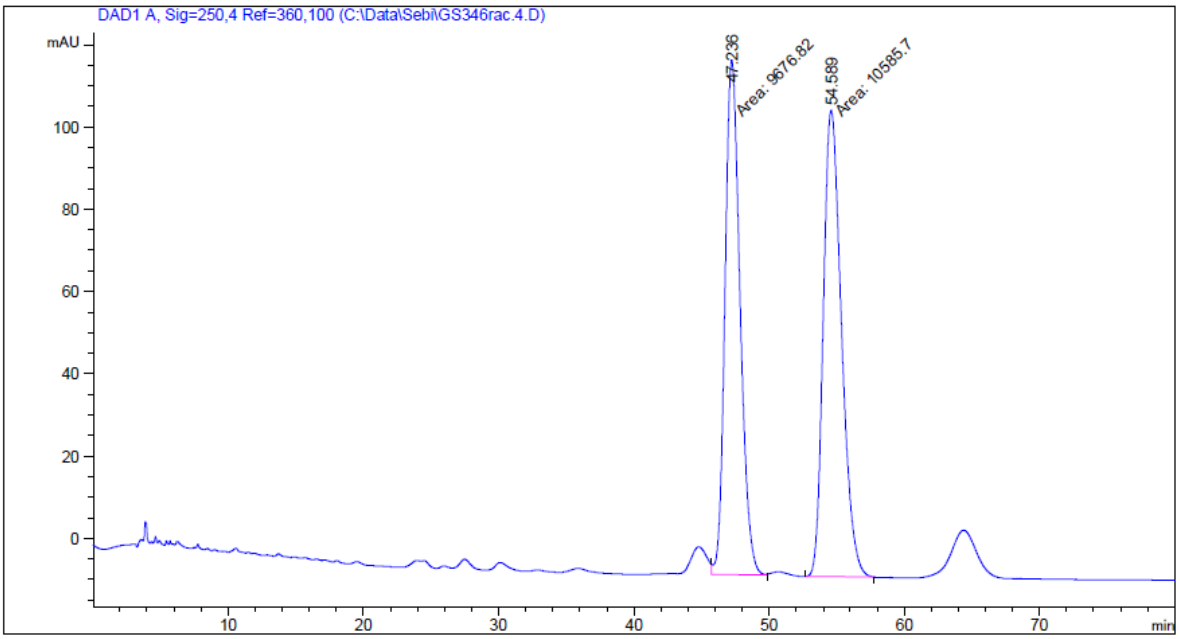
1-((2,4-Dimethoxyphenyl)sulfonyl)-2-phenyl-2,5-dihydro-1*H*-pyrrole (149$^{o,p\text{-OMe}}$)*:

^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

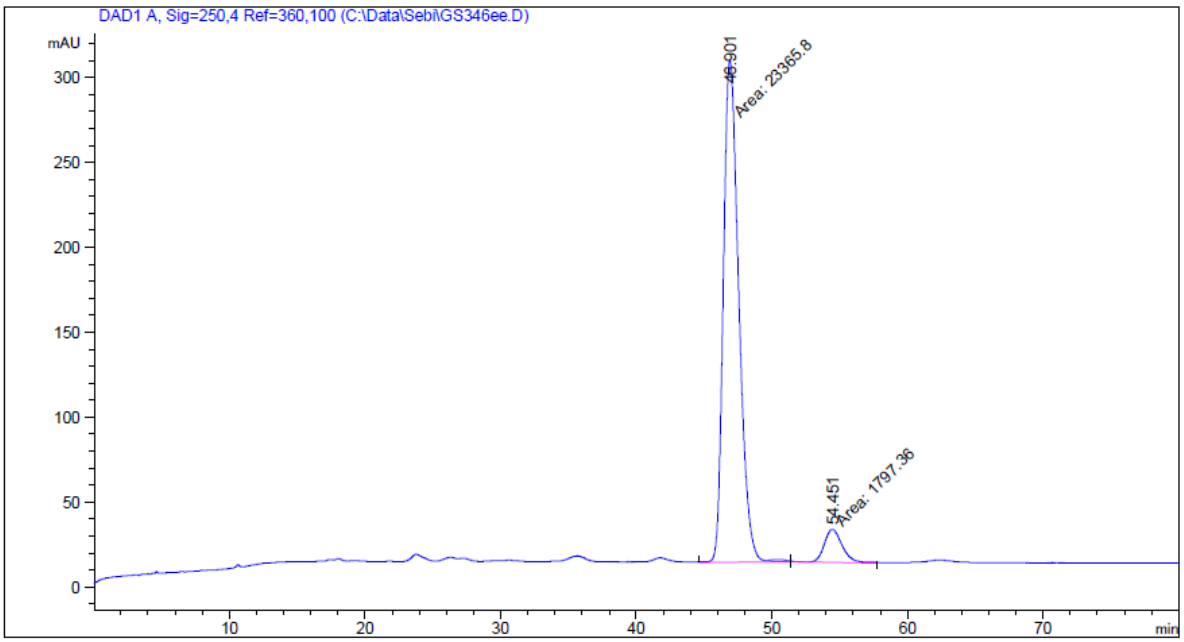








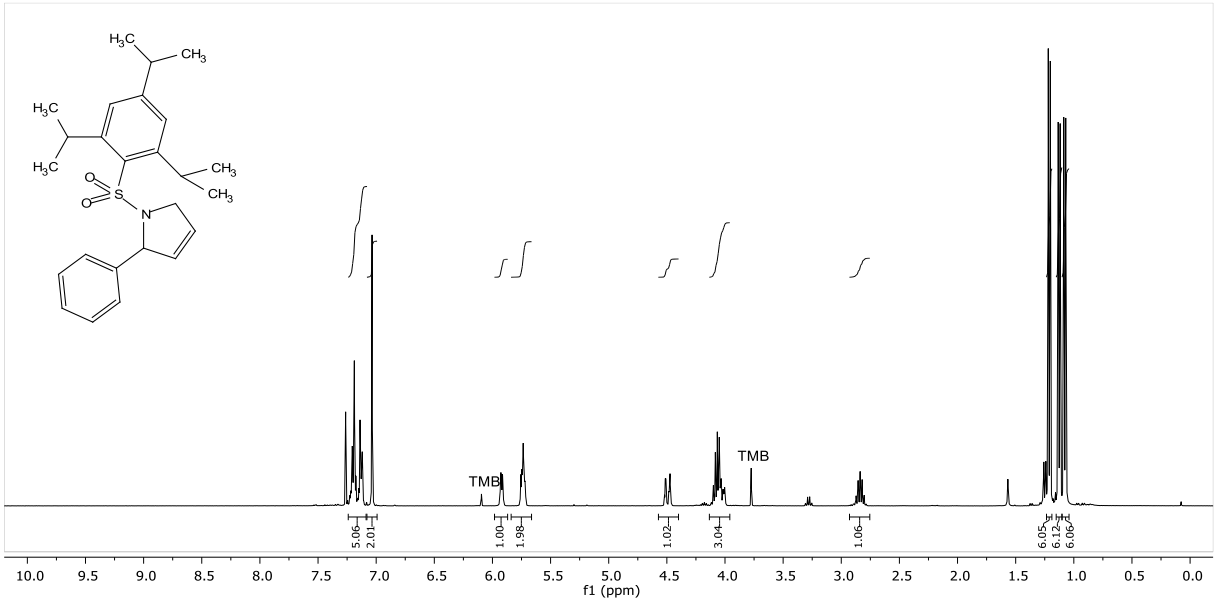
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.236	MM	1.2886	9676.81934	125.16350	47.7572
2	54.589	MM	1.5570	1.05857e4	113.31479	52.2428

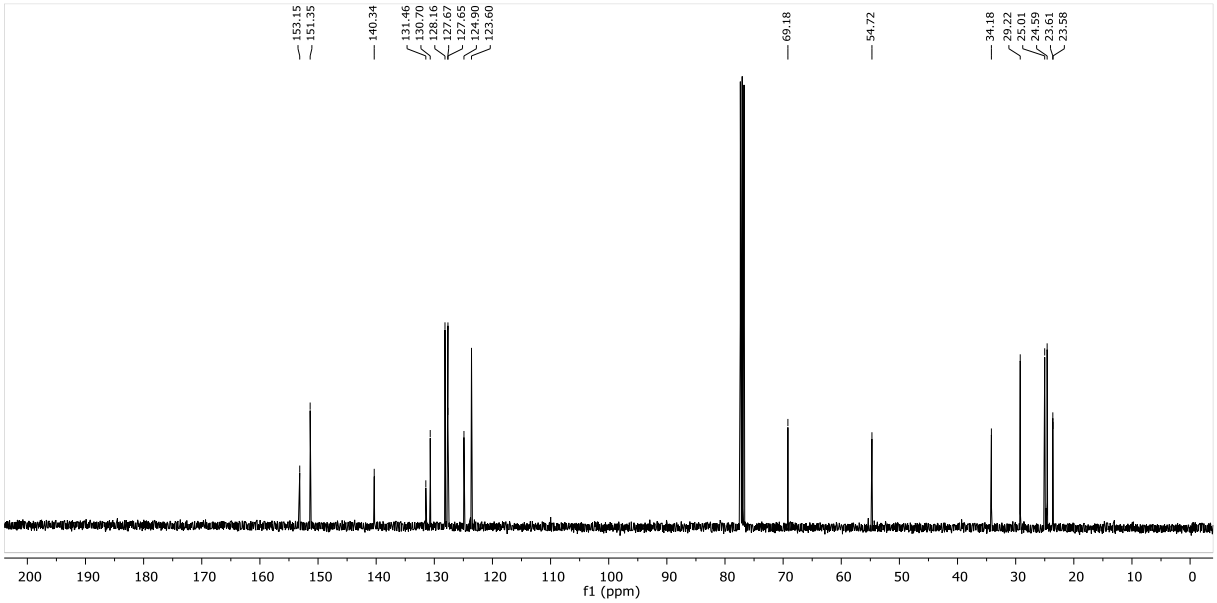


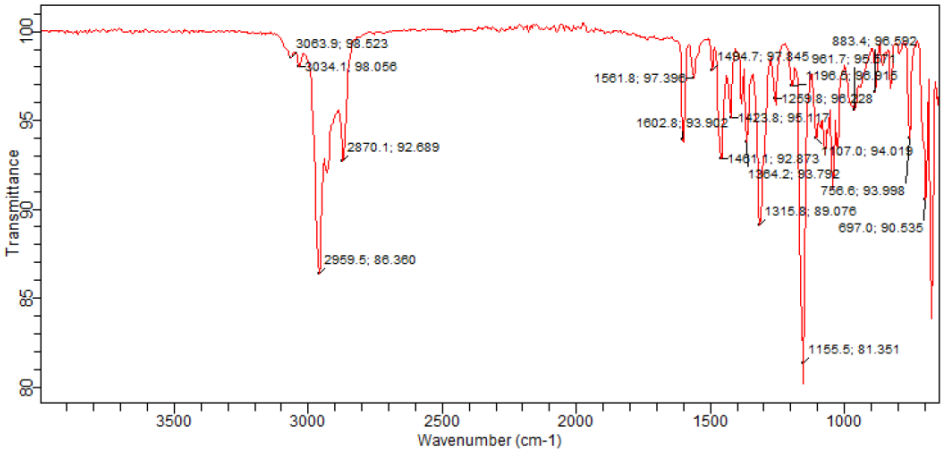
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.901	MM	1.3189	2.33658e4	295.25897	92.8572
2	54.451	MM	1.5390	1797.36255	19.46442	7.1428

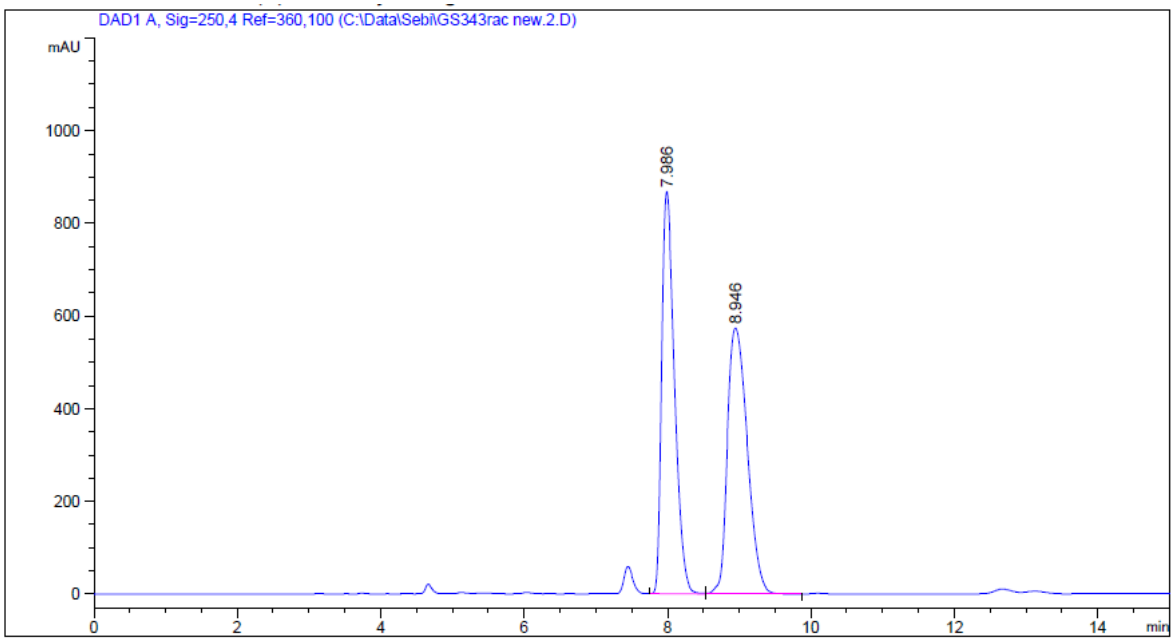
2-Phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-2,5-dihydro-1*H*-pyrrole (149^{TIPP})*:

^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

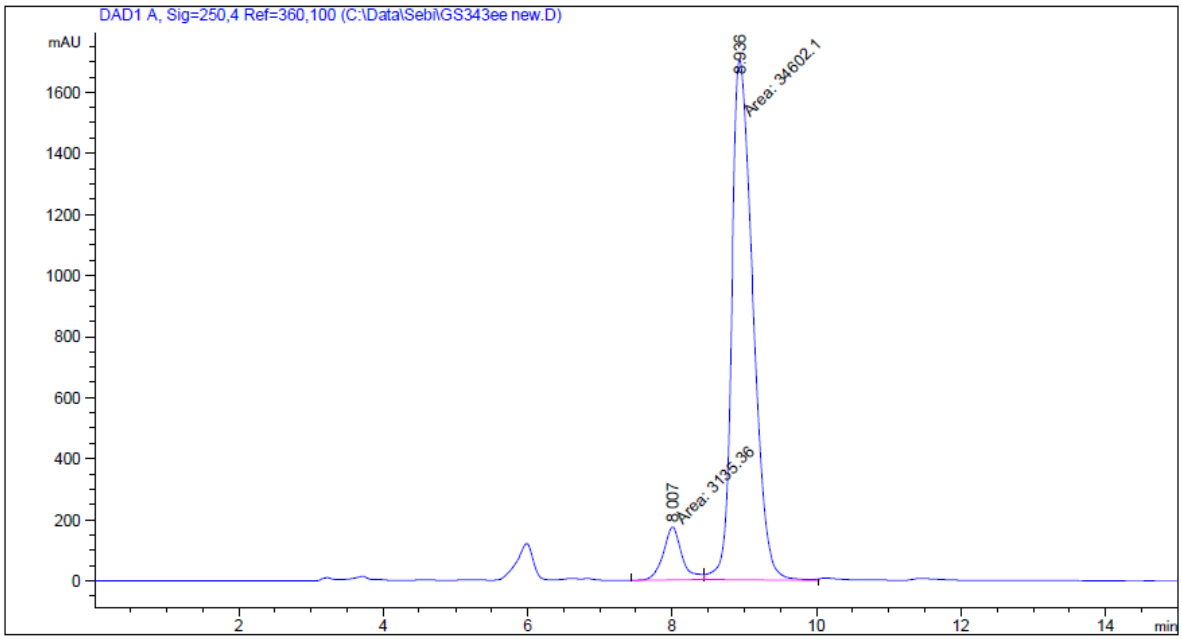






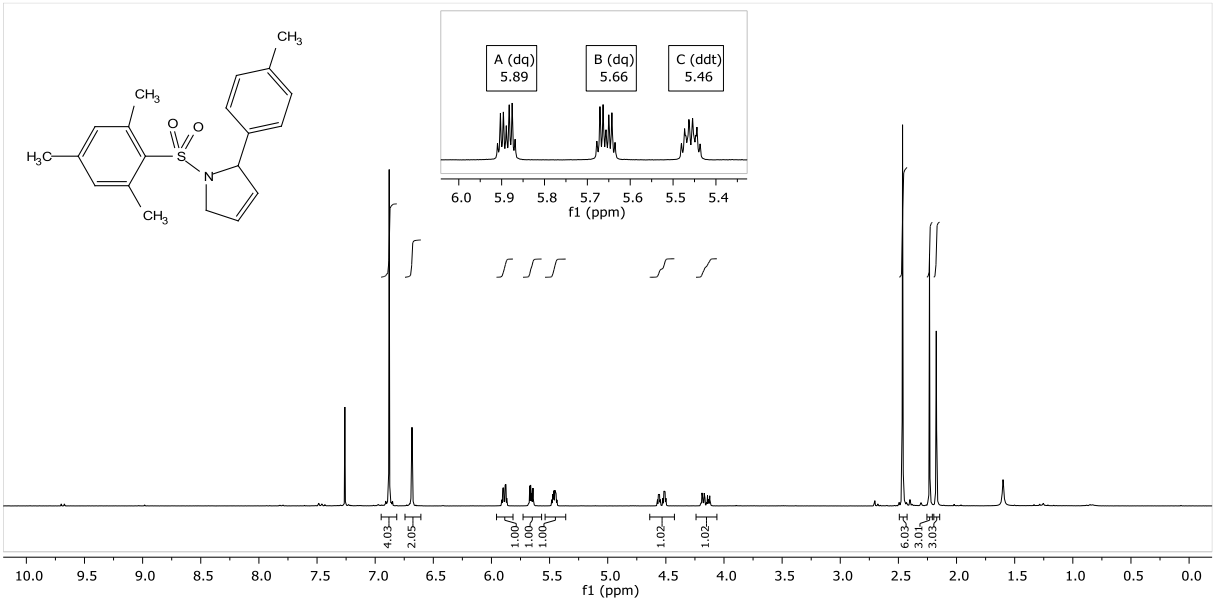


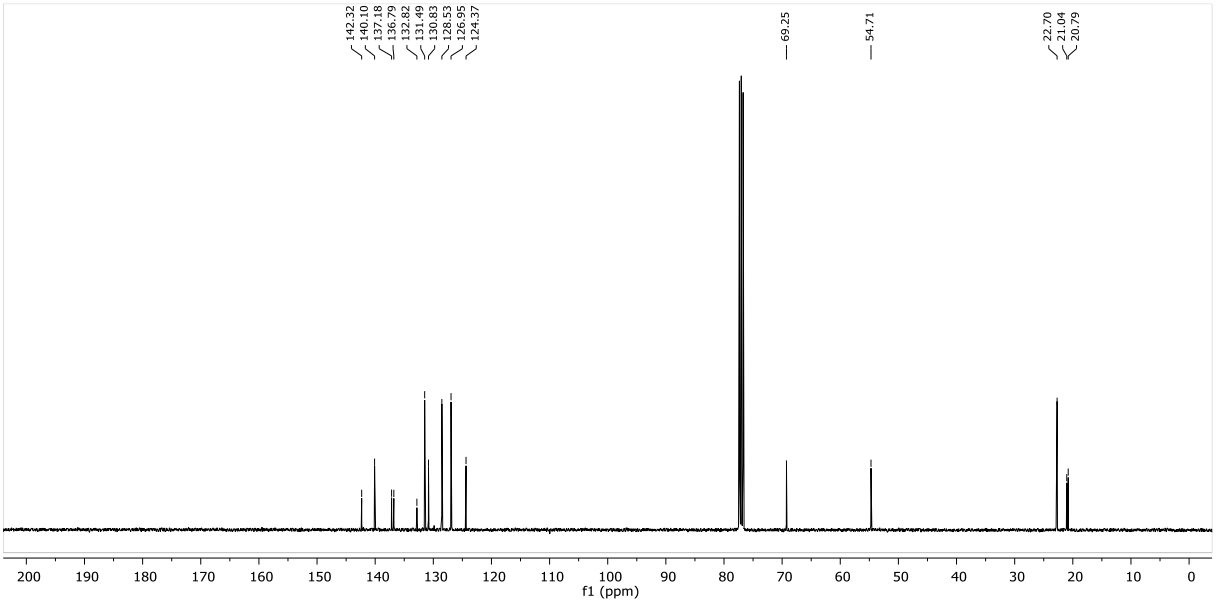
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.986	BV	0.1926	1.07644e4	868.28442	49.3299
2	8.946	VB	0.3088	1.10569e4	573.85175	50.6701

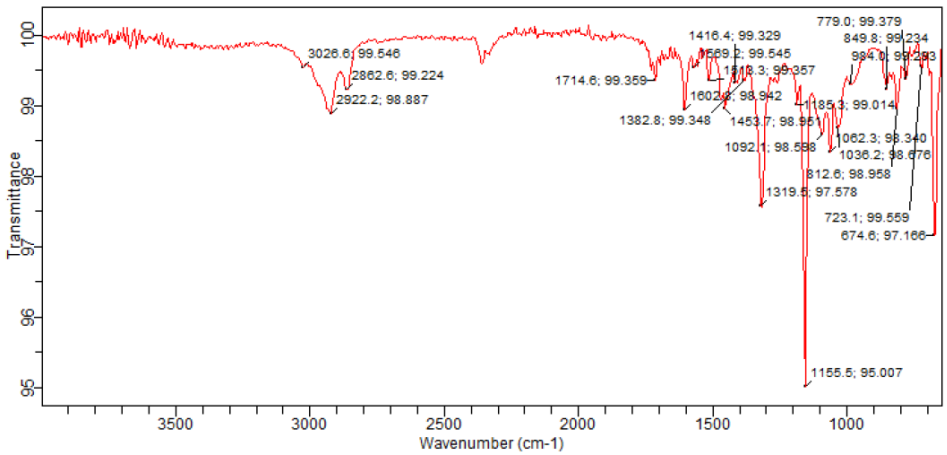


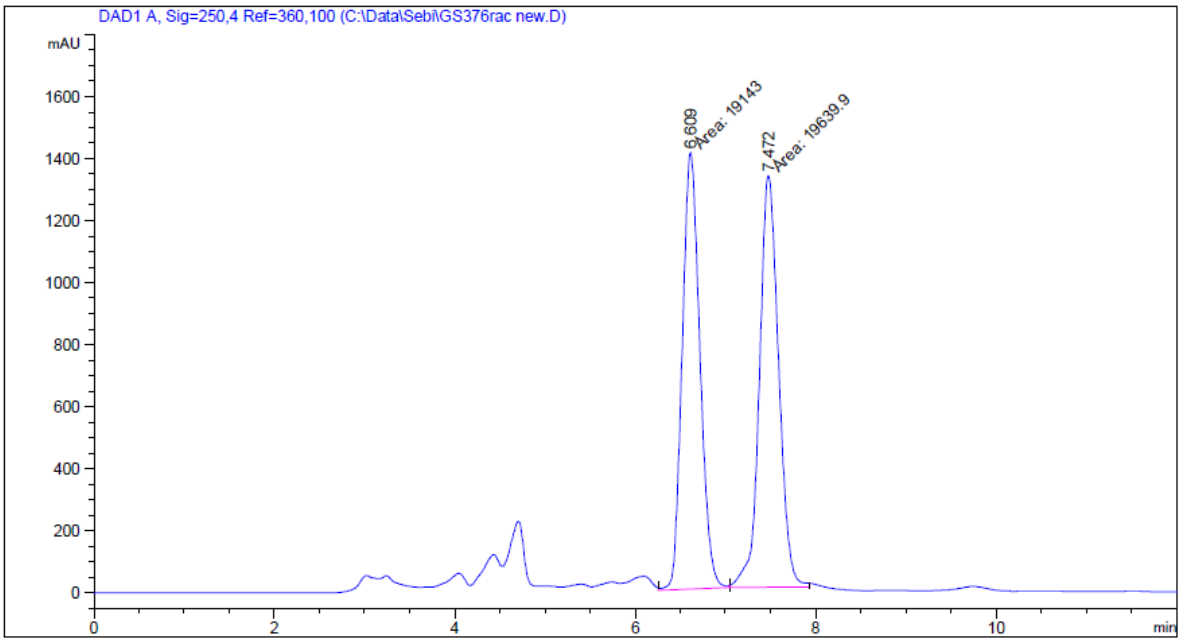
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.007	MM	0.3014	3135.36133	173.36520	8.3084
2	8.936	MM	0.3385	3.46021e4	1703.76233	91.6916

1-(Mesitylsulfonyl)-2-(p-tolyl)-2,5-dihydro-1*H*-pyrrole (149x)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

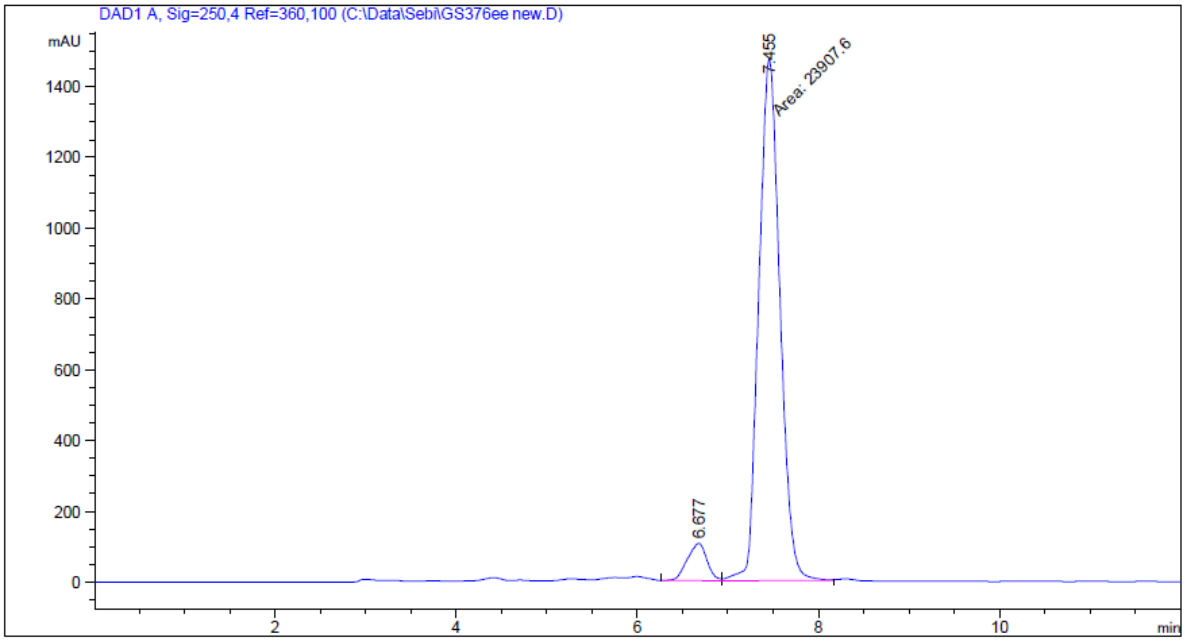








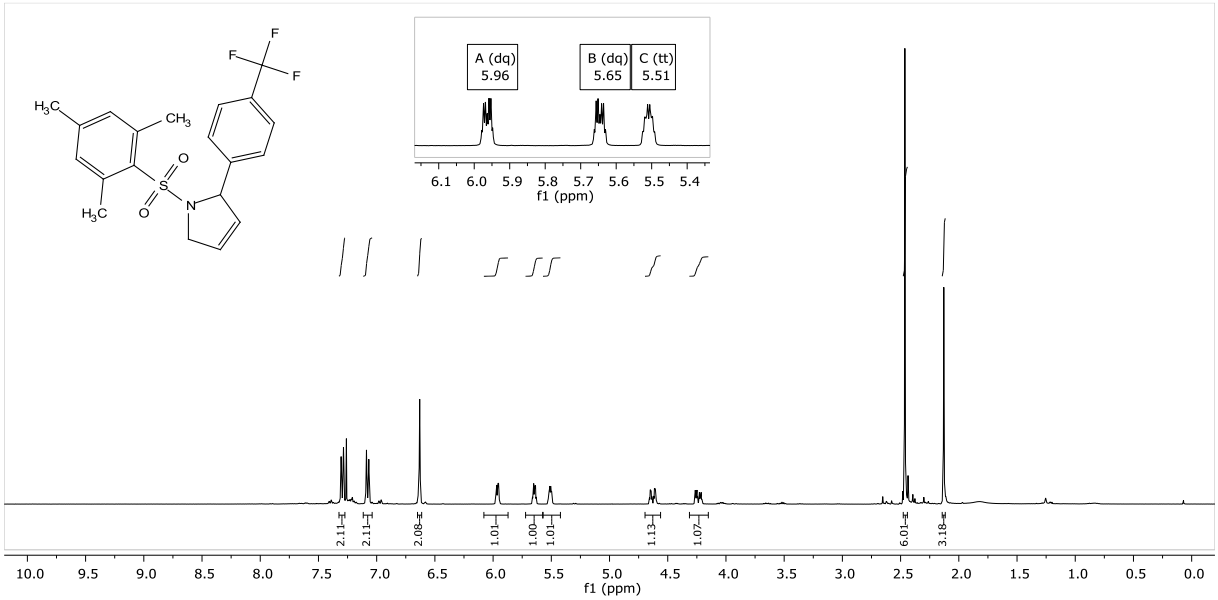
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.609	MM	0.2269	1.91430e4	1405.84705	49.3594
2	7.472	MM	0.2465	1.96399e4	1327.83606	50.6406

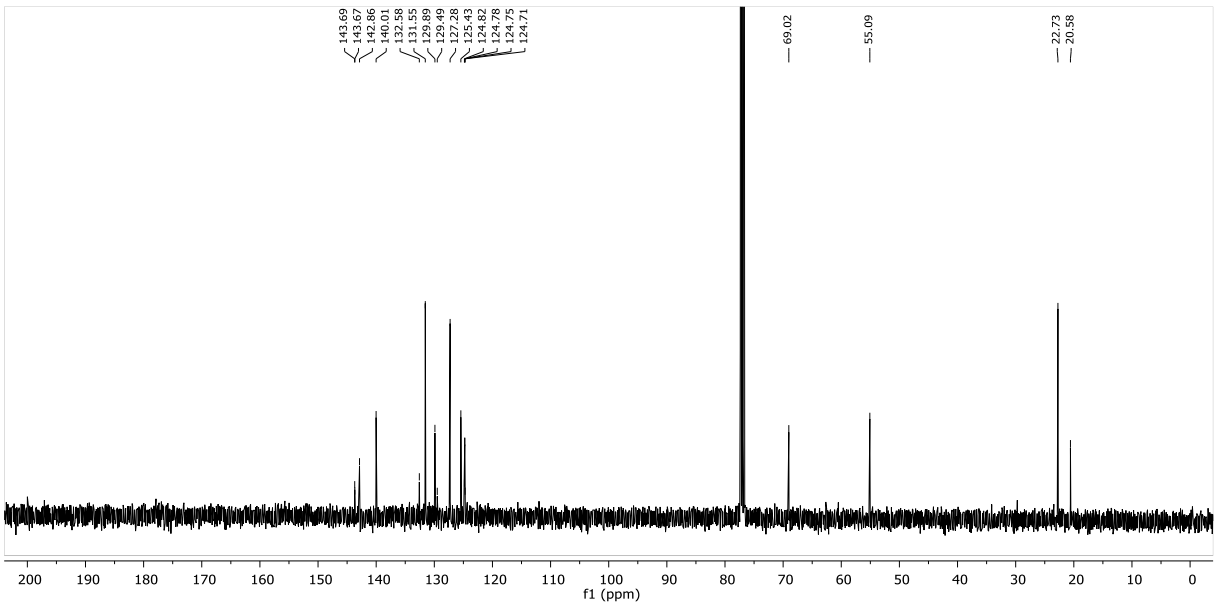


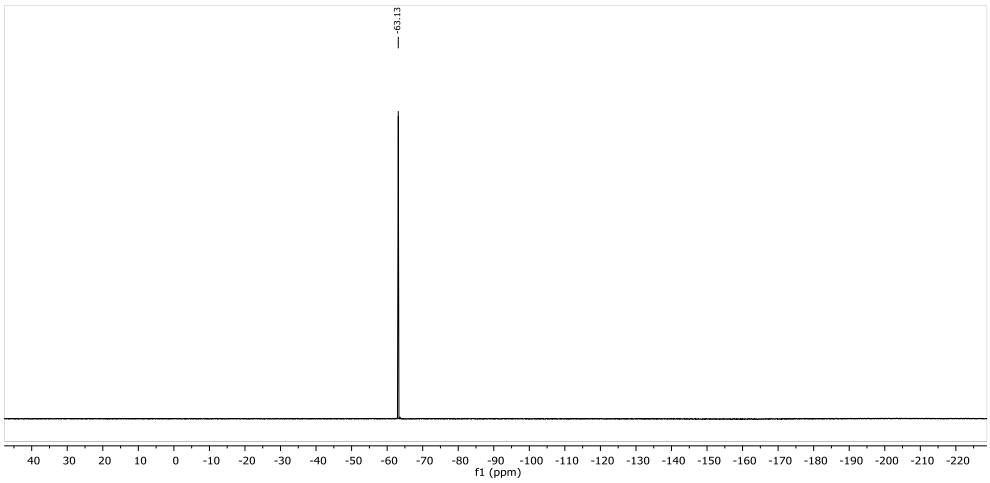
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.677	BV	0.2522	1593.59058	105.50451	6.2491
2	7.455	MM	0.2701	2.39076e4	1475.46643	93.7509

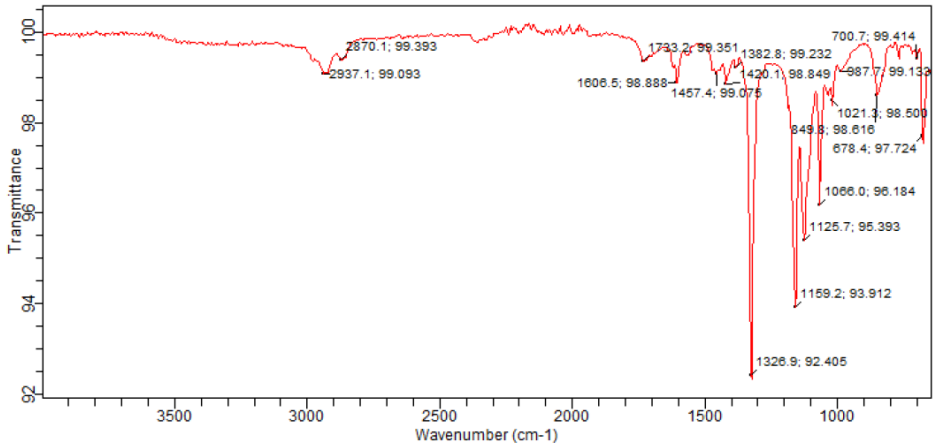
1-(Mesitylsulfonyl)-2-(4-(trifluoromethyl)phenyl)-2,5-dihydro-1*H*-pyrrole (149y)*:

^{1}H, ^{13}C, ^{19}F NMR in $CDCl_3$, IR, HPLC traces








Transmittance
100
98
96
94
92
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
2870.1; 99.393
2937.1; 99.093
1733.2; 99.351
1606.5; 98.888
1457.4; 99.075
1382.8; 99.232
1420.1; 98.849
700.7; 99.414
987.7; 99.133
1021.3; 98.509
849.8; 98.616
678.4; 97.724
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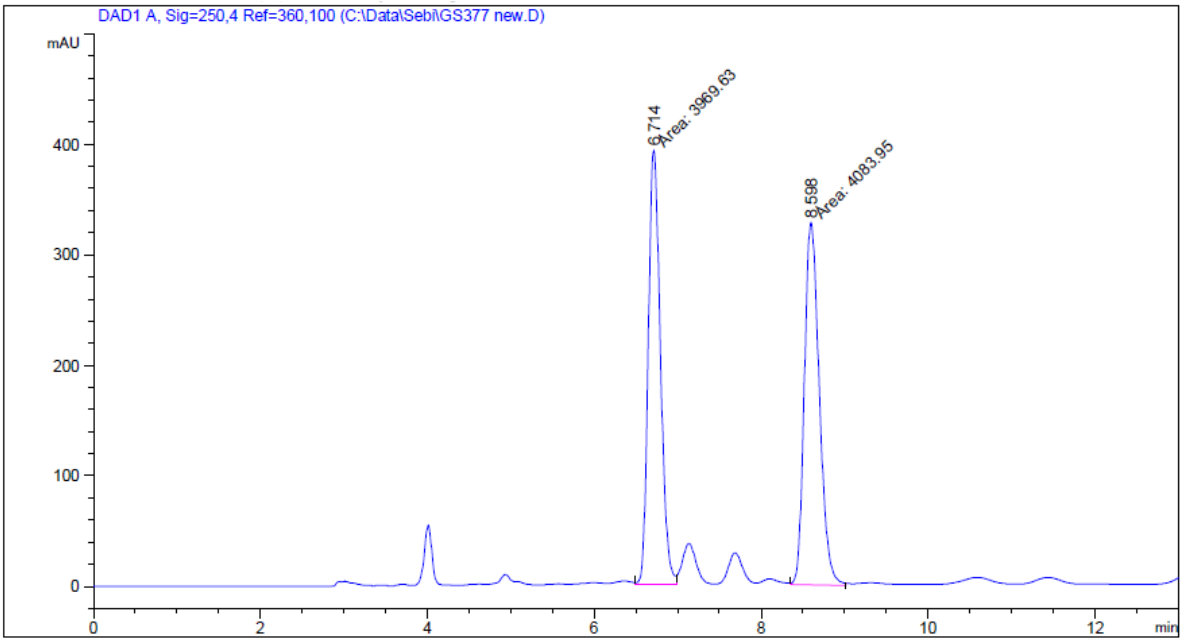
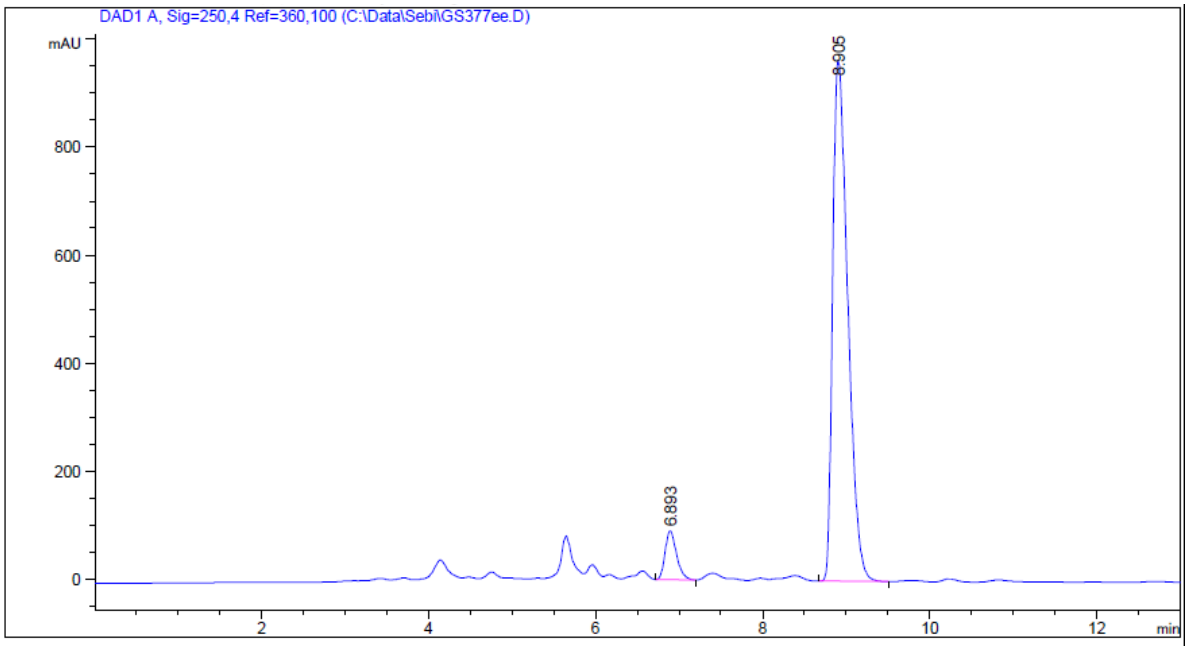
1125.7; 95.393
1159.2; 93.912
1326.9; 92.405

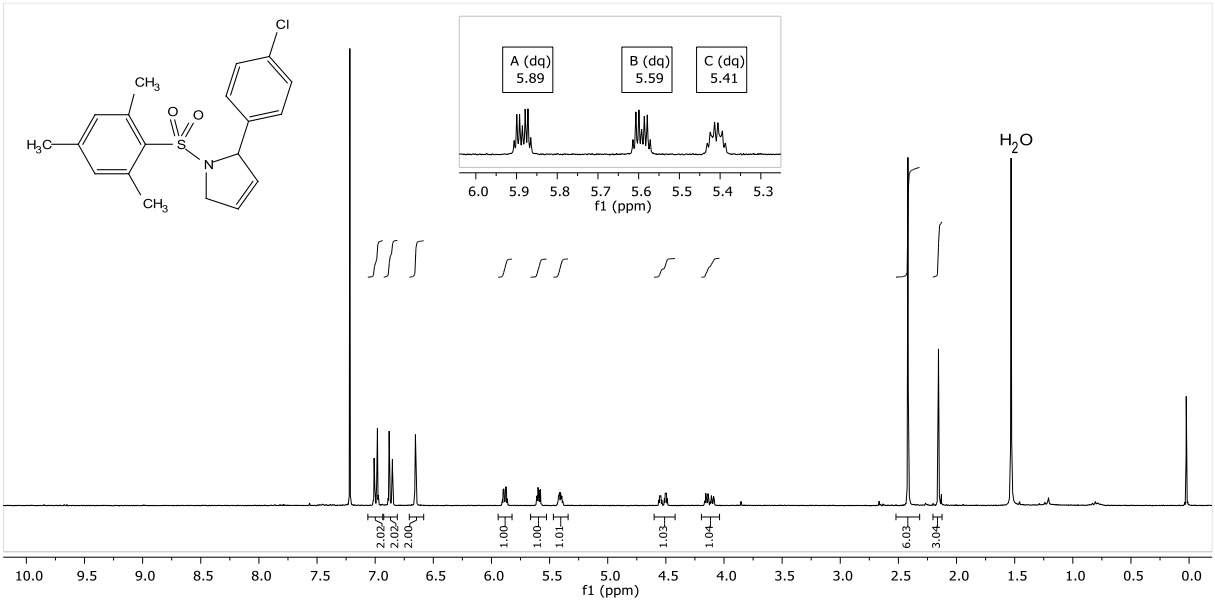


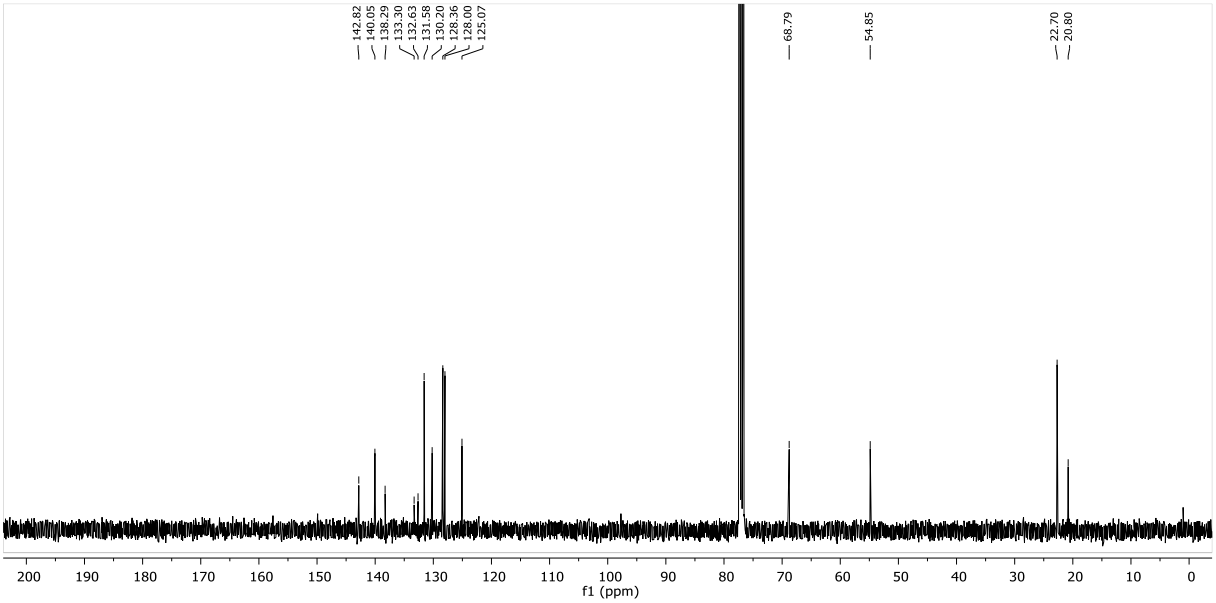
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.714	MM	0.1685	3969.63330	392.67990	49.2903
2	8.598	MM	0.2075	4083.94580	328.06671	50.7097

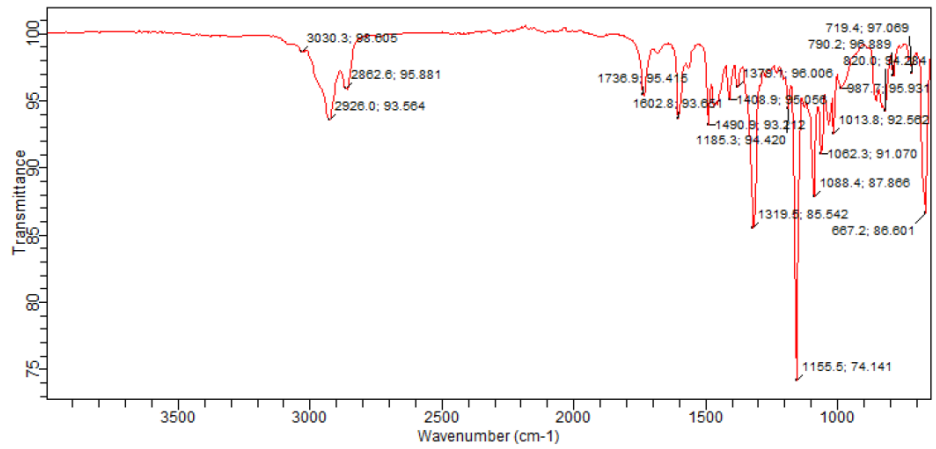


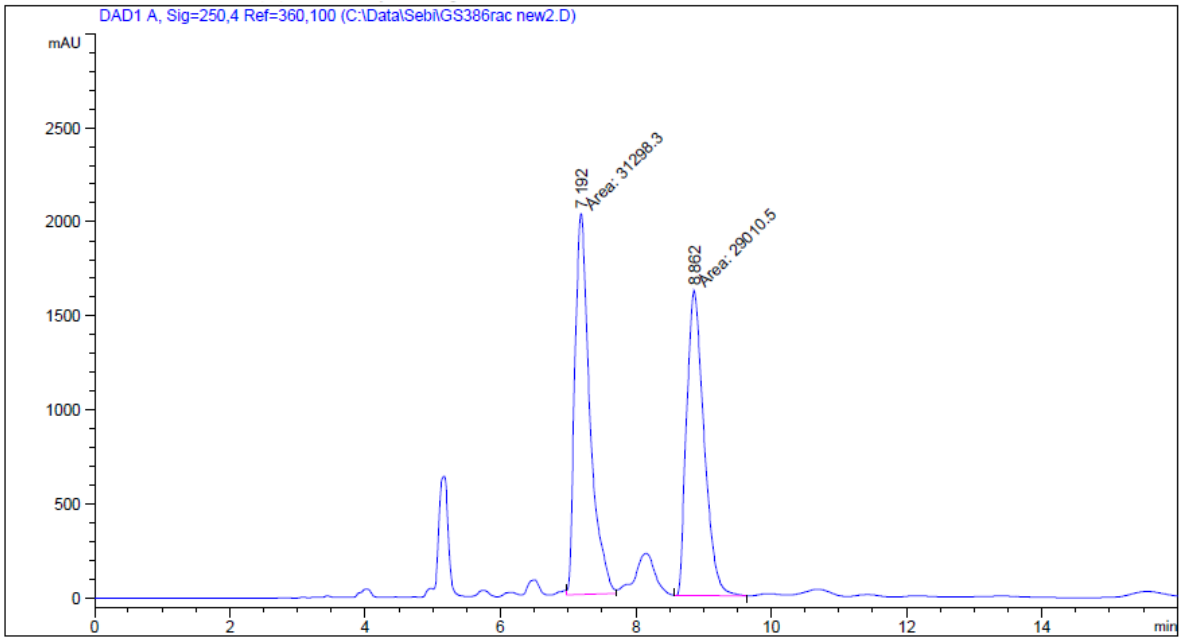
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.893	BB	0.1476	858.41058	89.71965	6.6295
2	8.905	BB	0.1946	1.20900e4	961.93457	93.3705

2-(4-Chlorophenyl)-1-(mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrole (149z)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

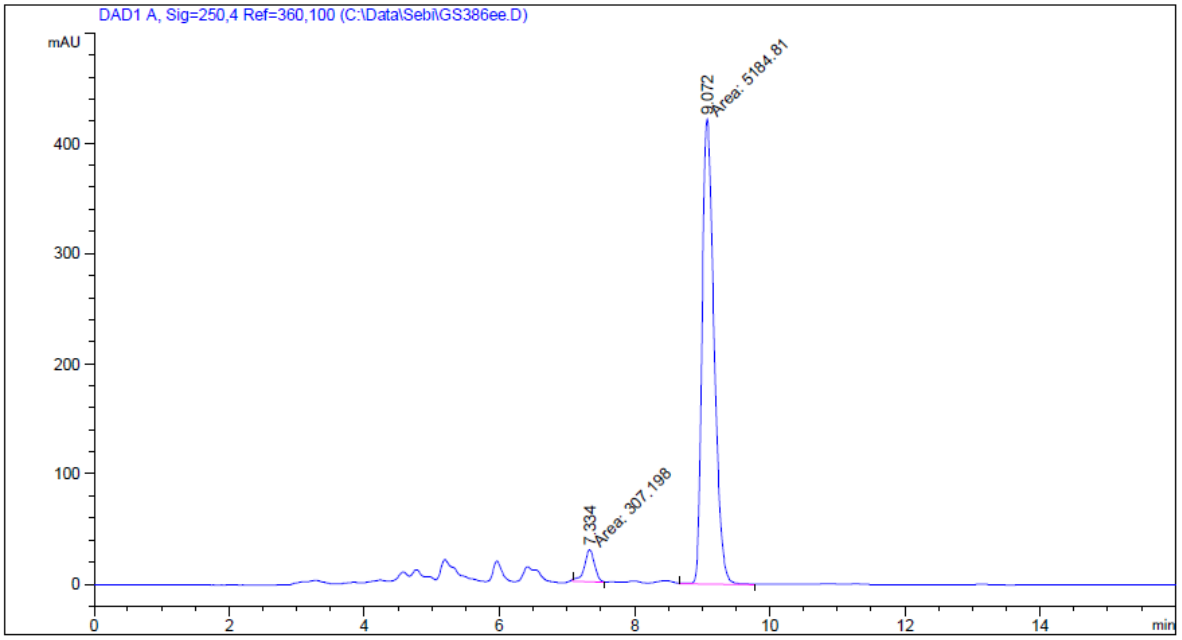






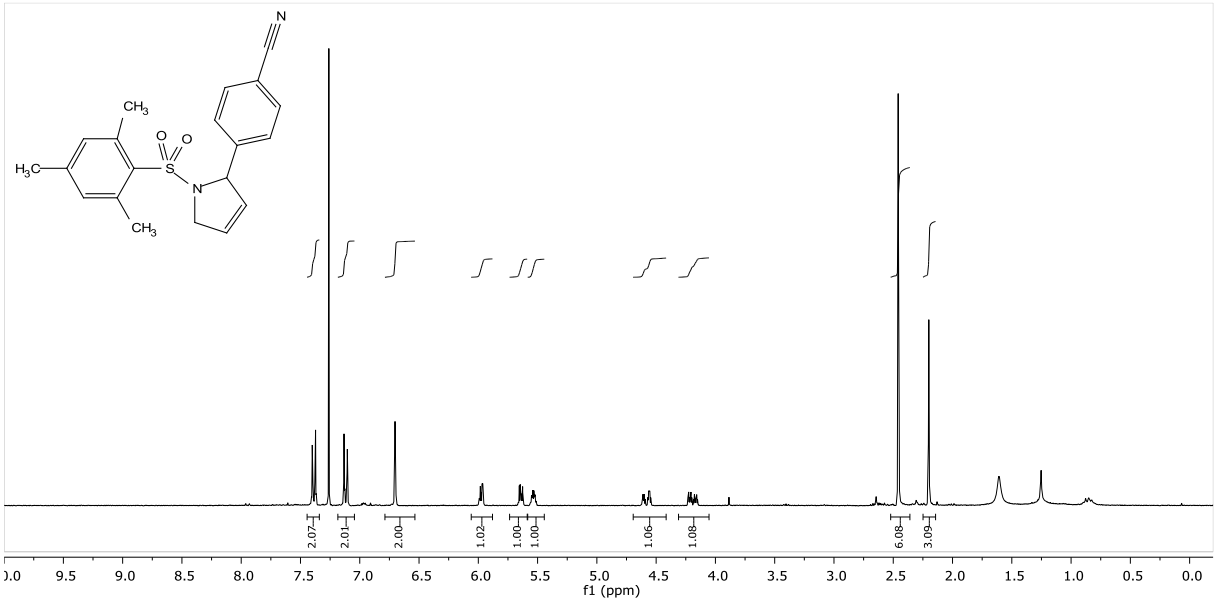


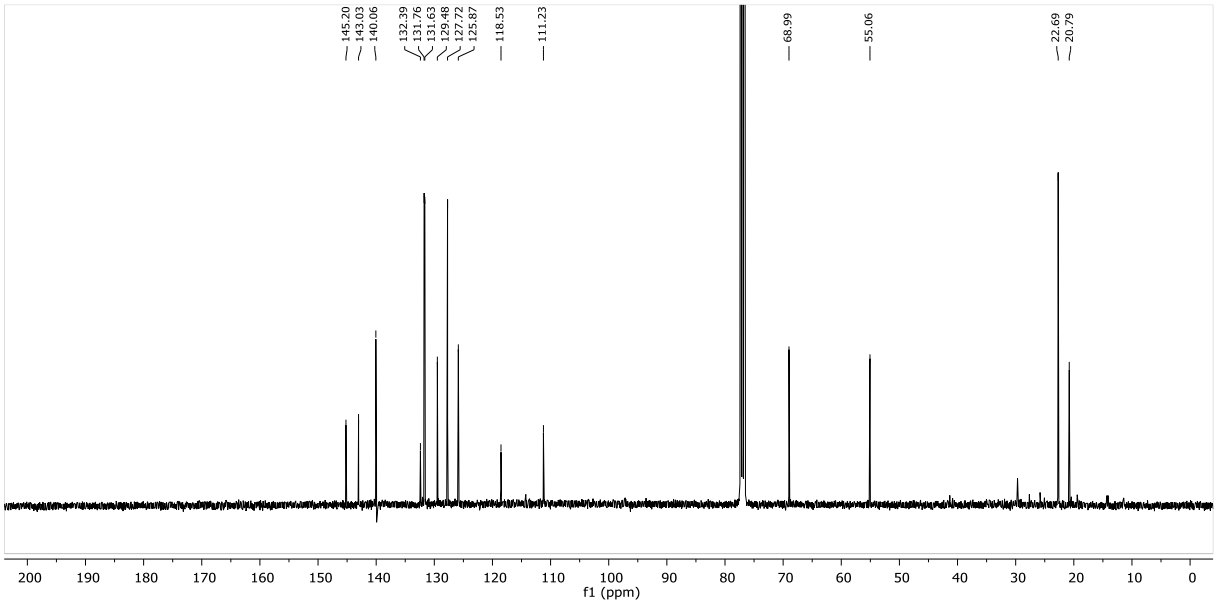
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.192	MM	0.2575	3.12983e4	2026.14270	51.8967
2	8.862	MM	0.2977	2.90105e4	1624.32507	48.1033

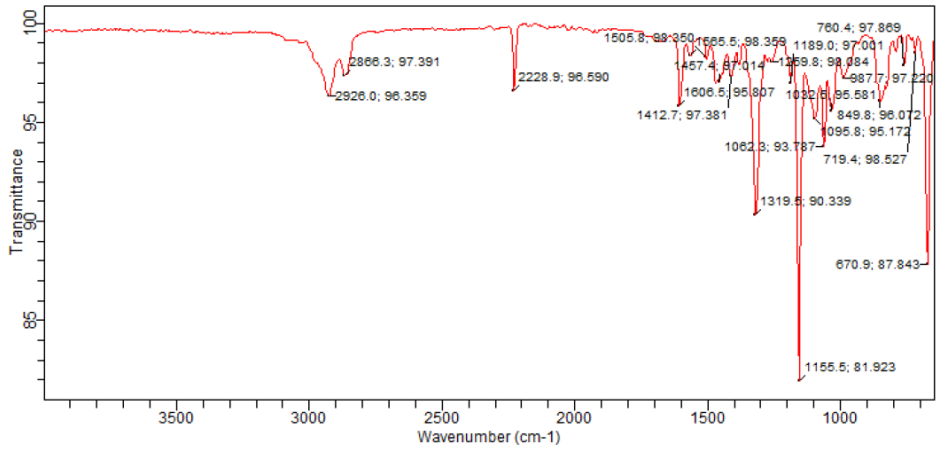


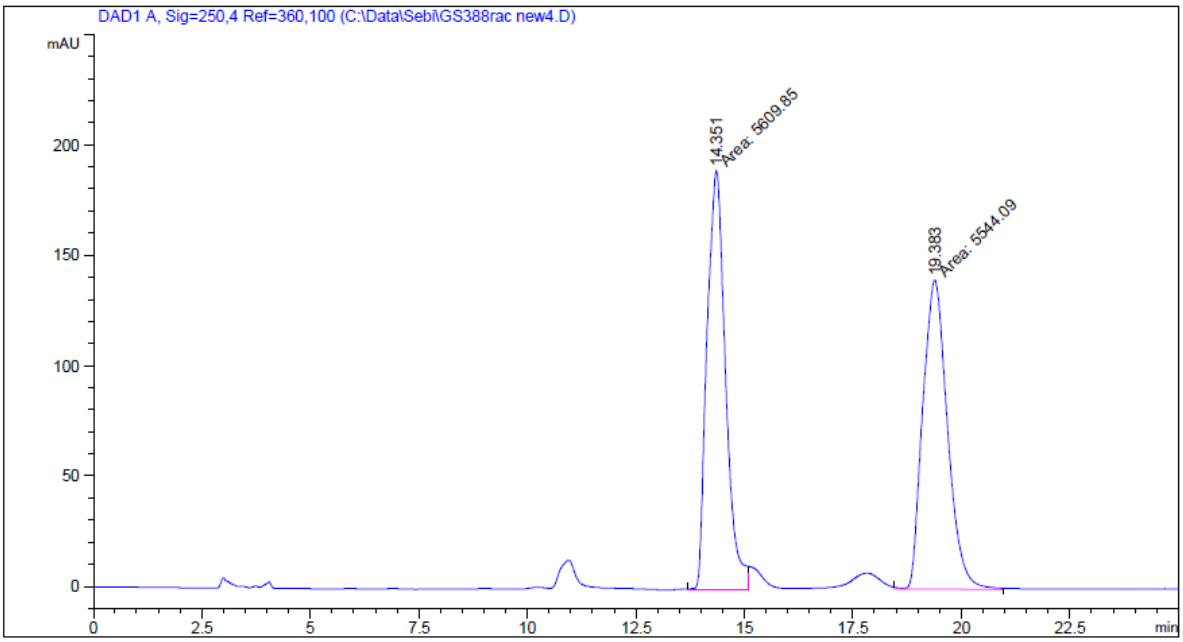
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.334	MM	0.1764	307.19830	29.03017	5.5936
2	9.072	MM	0.2048	5184.80664	421.86496	94.4064

4-(1-(Mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrol-2-yl)benzonitrile (149aa)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

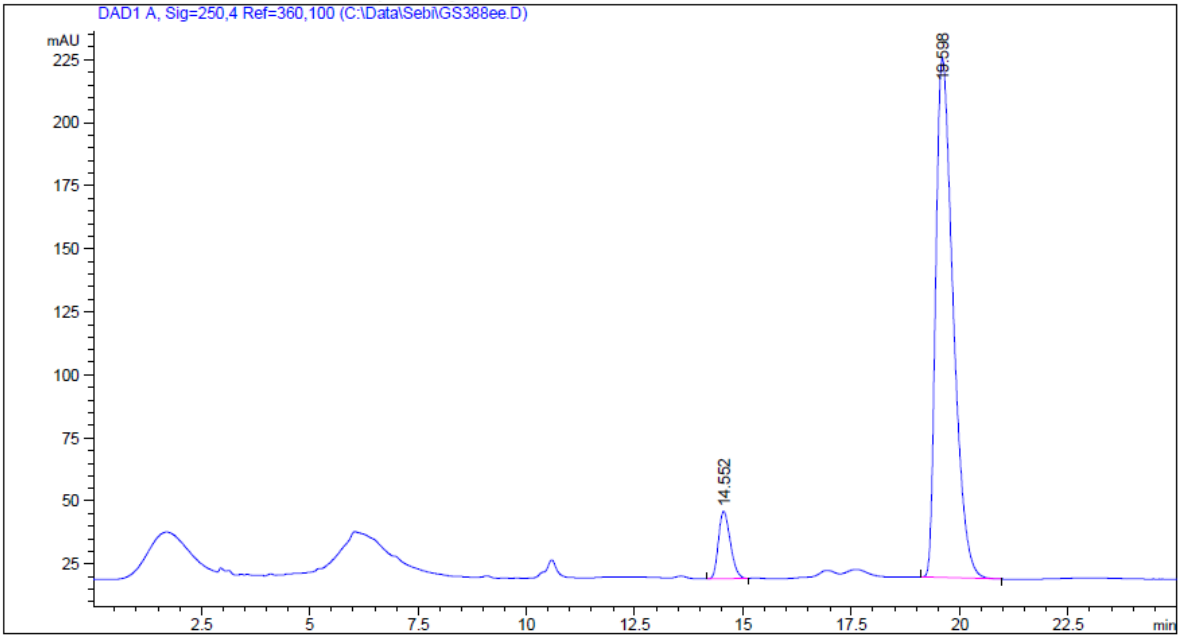






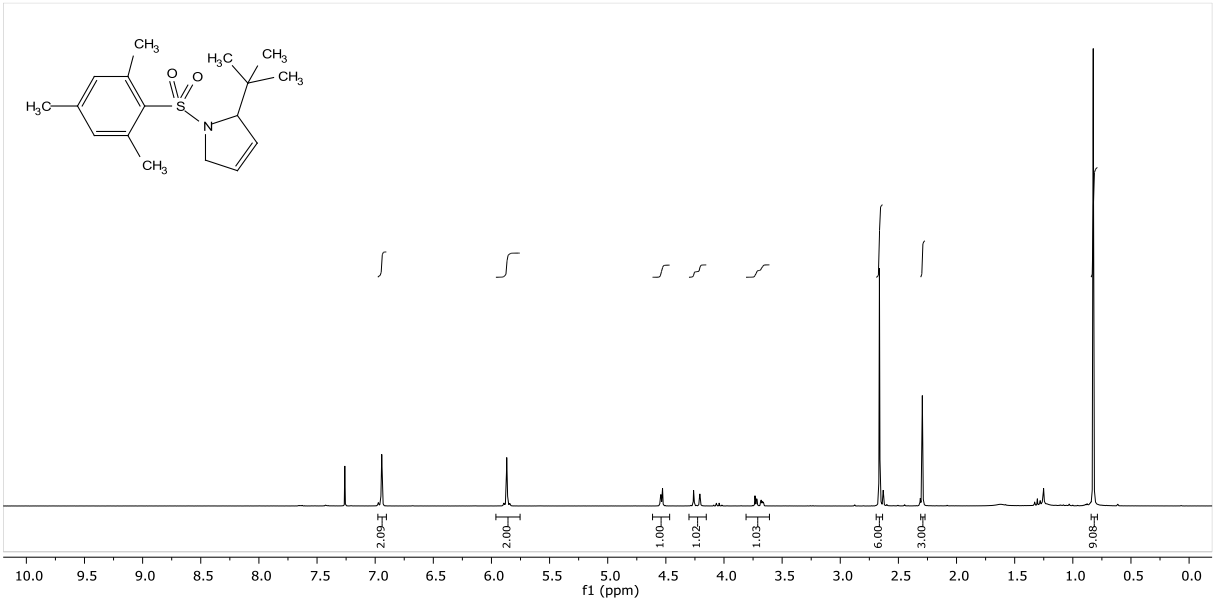


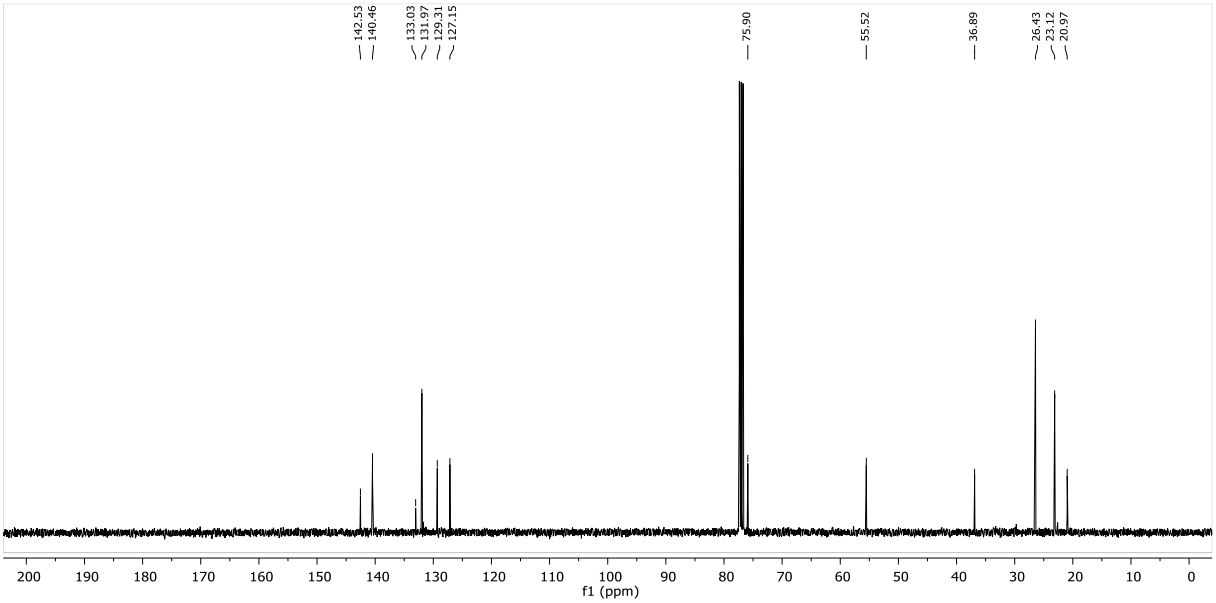
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.351	MM	0.4930	5609.85400	189.63557	50.2948
2	19.383	MM	0.6599	5544.09229	140.01308	49.7052

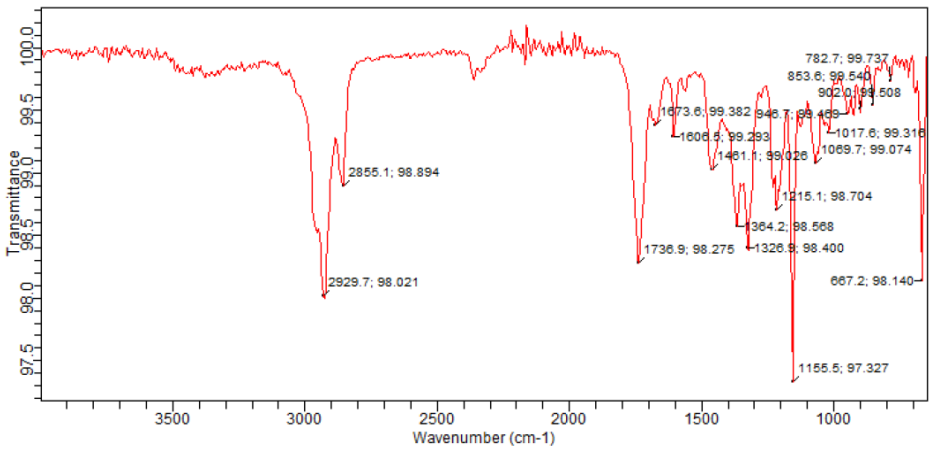


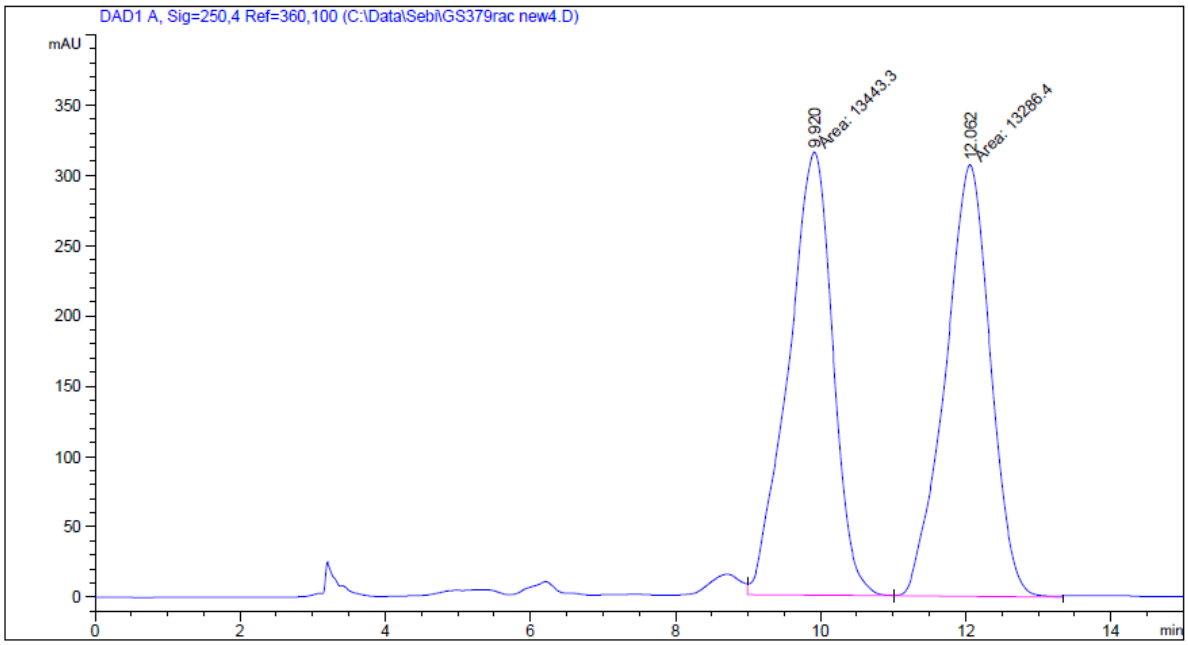
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.552	BB	0.2955	508.49820	26.78134	8.1439
2	19.598	BB	0.4287	5735.40576	206.05281	91.8561

2-(*Tert*-Butyl)-1-(mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrole (149ae)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

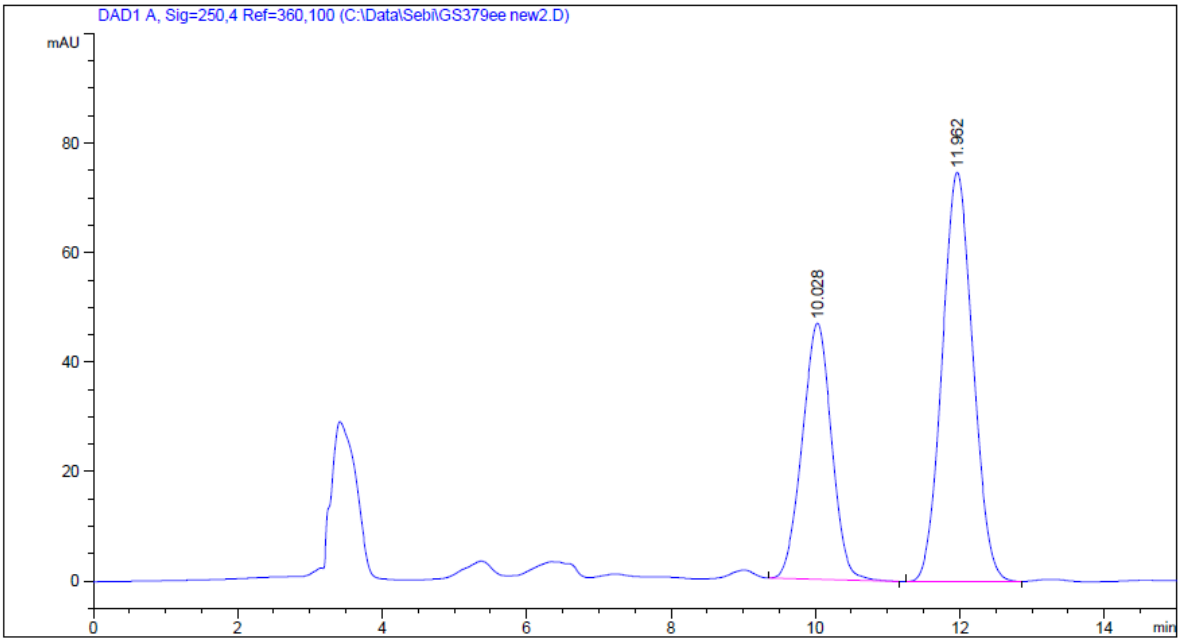






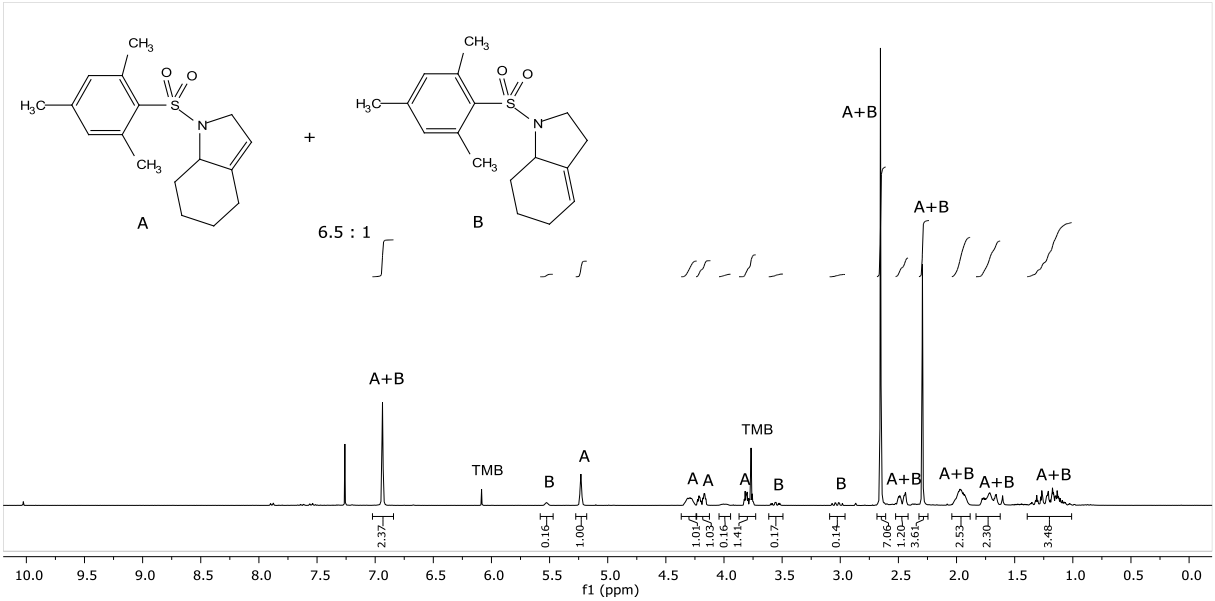


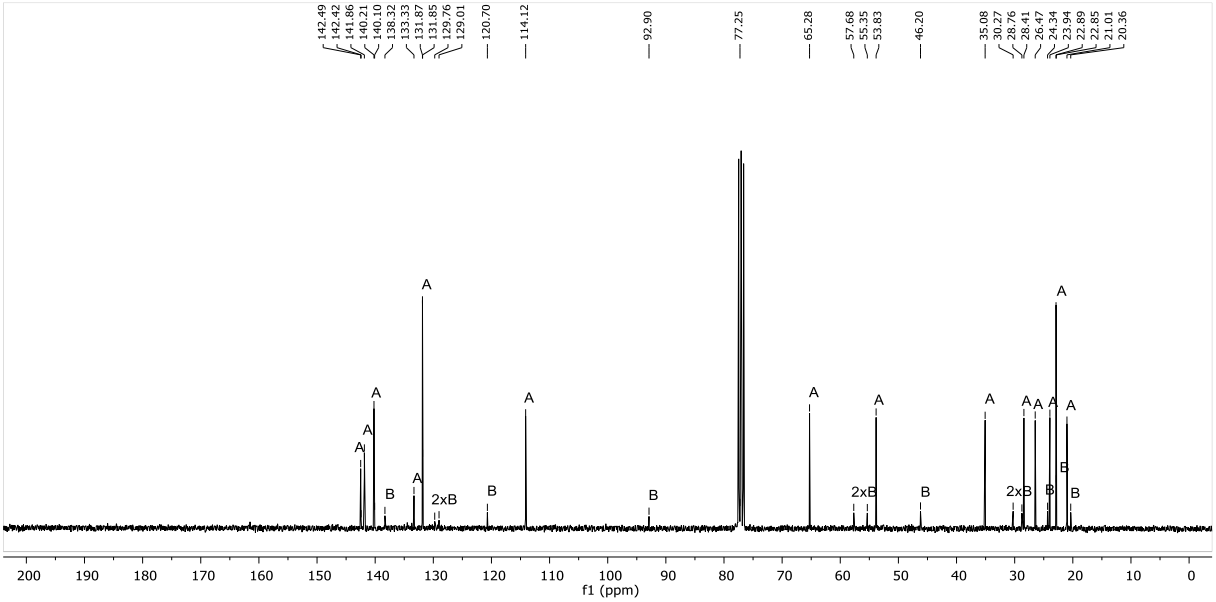
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.920	MM	0.7111	1.34433e4	315.08554	50.2935
2	12.062	MM	0.7214	1.32864e4	306.97073	49.7065

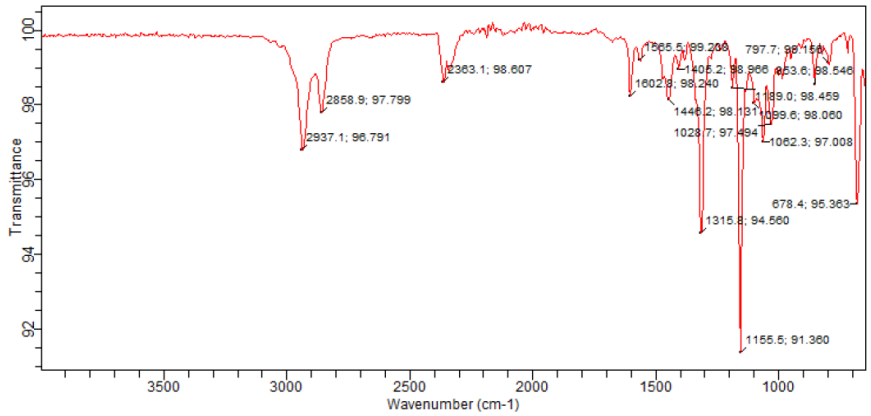


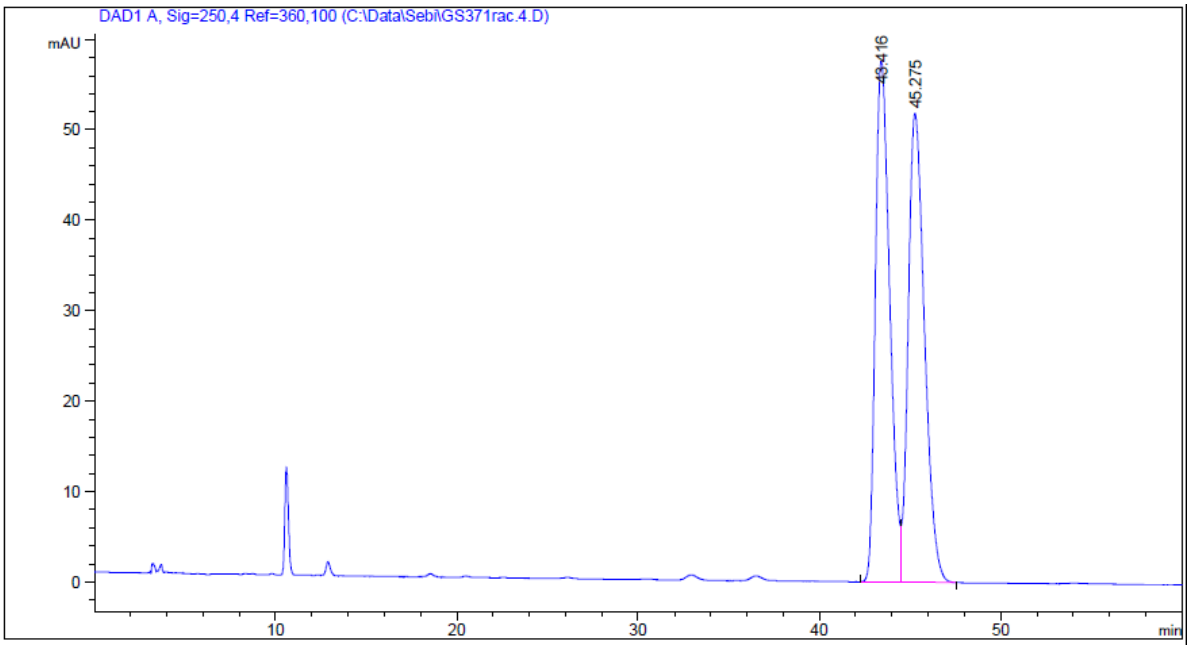
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.028	BB	0.4447	1318.81995	46.80371	37.3882
2	11.962	BB	0.4688	2208.55054	74.72631	62.6118

1-(Mesitylsulfonyl)-2,4,5,6,7,7a-hexahydro-1*H*-indole (A) and 1-(Mesitylsulfonyl)-2,3,5,6,7,7a-hexahydro-1*H*-indole (B) (149ac and 149ac')*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

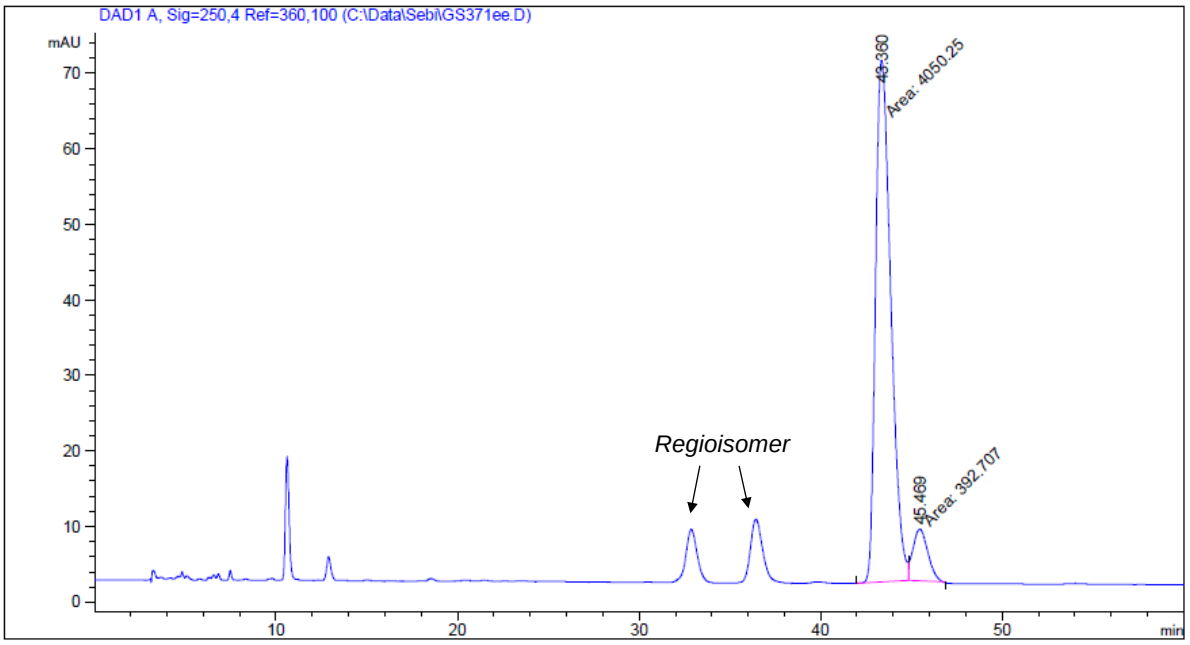






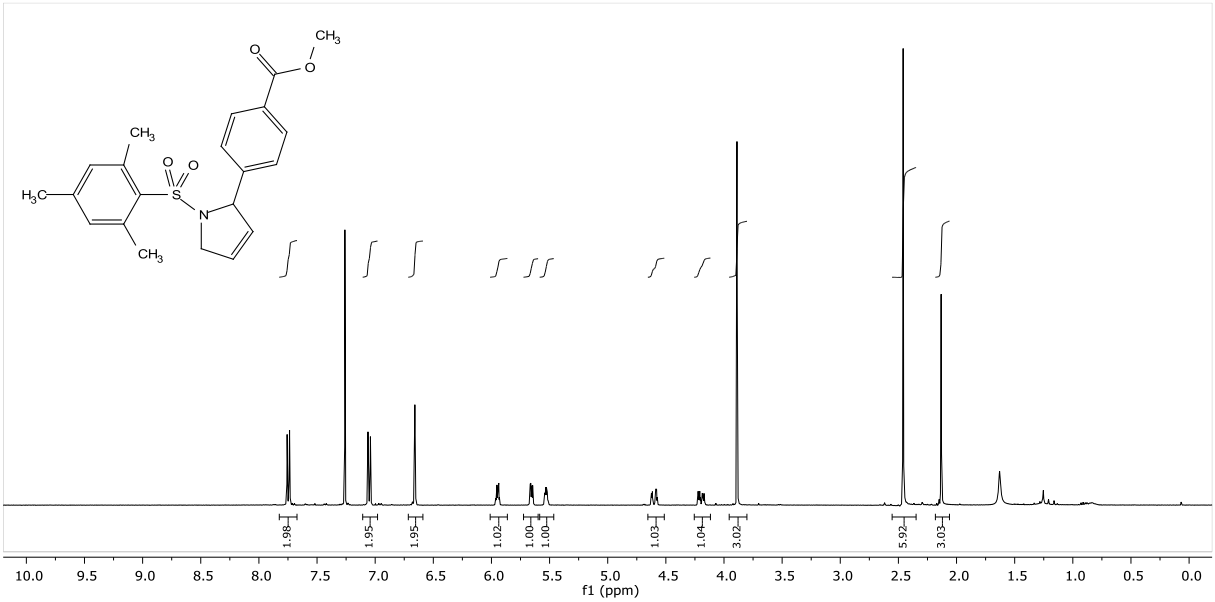


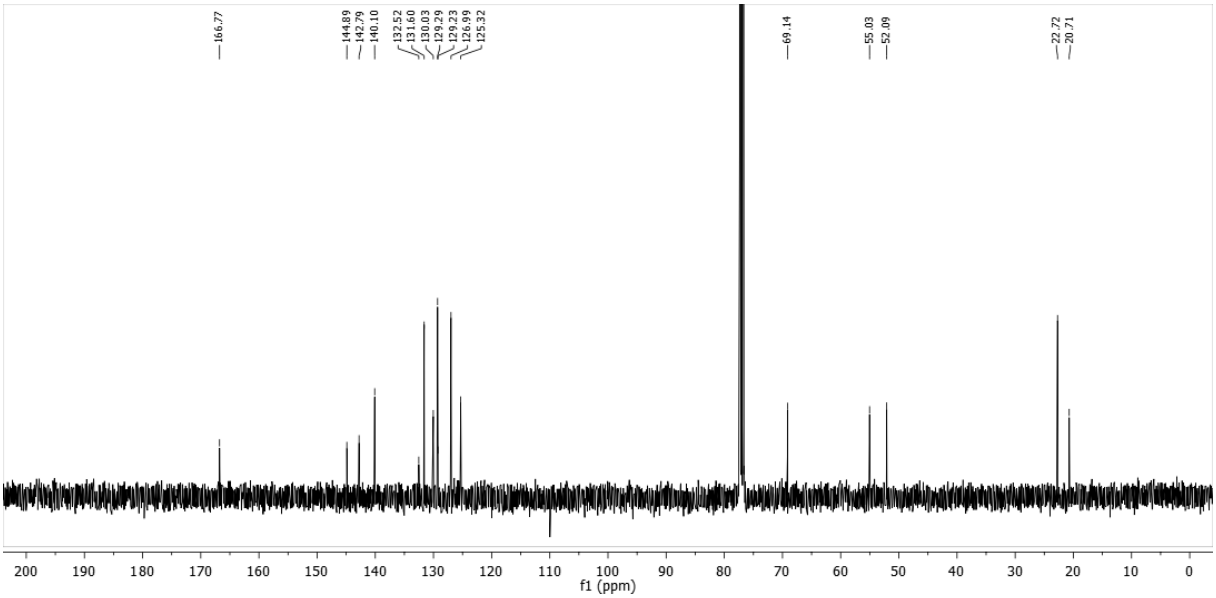
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.416	BV	0.8579	3169.78979	57.60741	49.4332
2	45.275	VB	0.9512	3242.47534	51.87461	50.5668

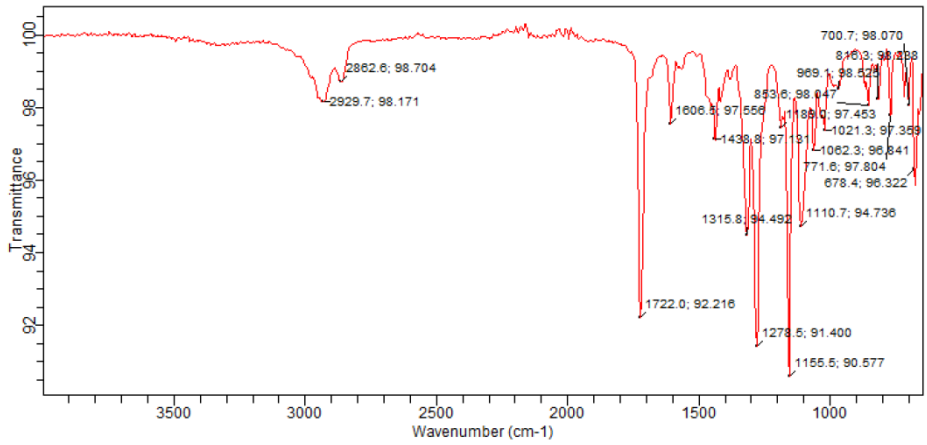


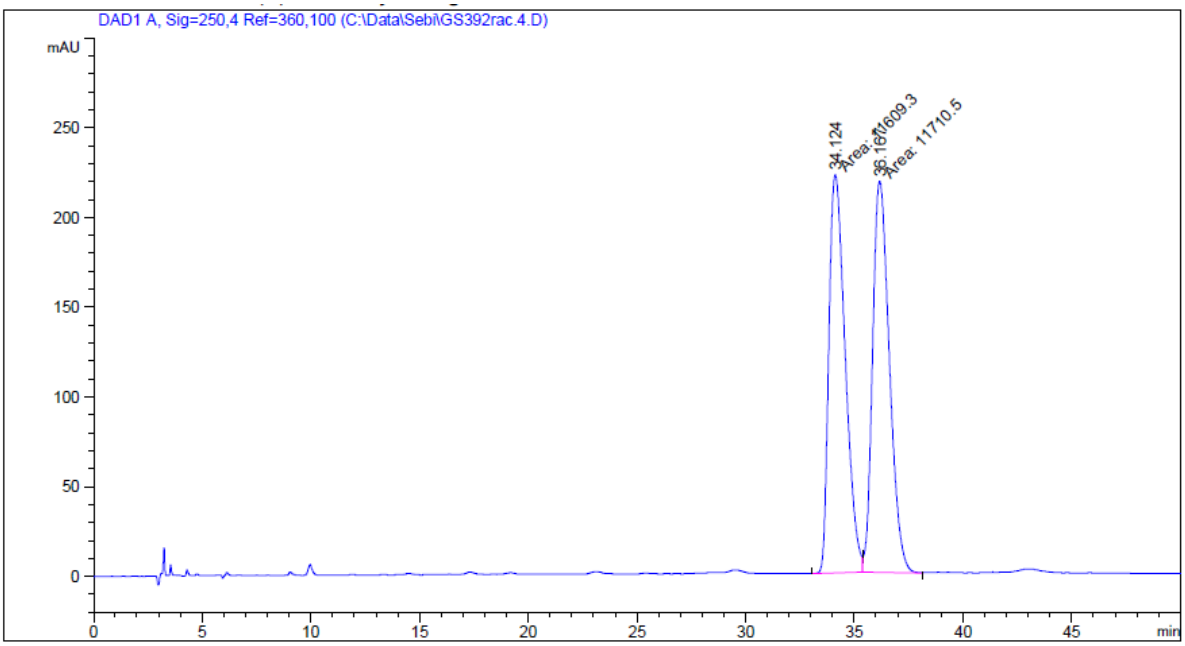
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.360	MM	0.9763	4050.24731	69.13988	91.1611
2	45.469	MM	0.9527	392.70676	6.87027	8.8389

Methyl 4-(1-(mesitylsulfonyl)-2,5-dihydro-1H-pyrrol-2-yl)benzoate (149ab)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

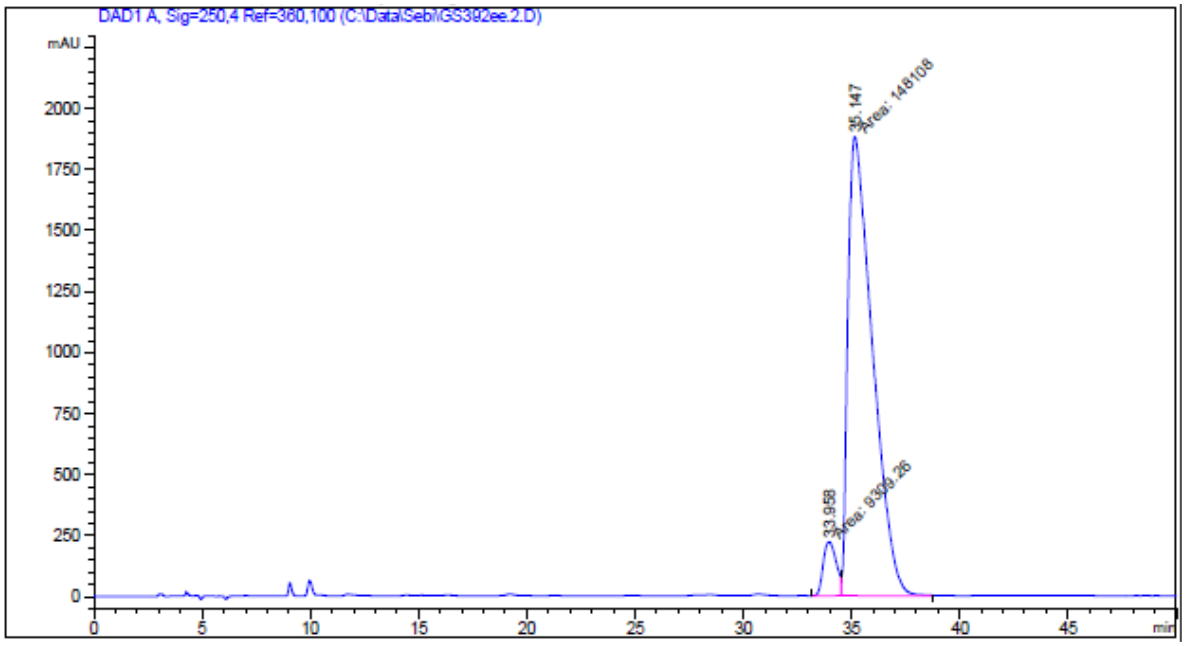






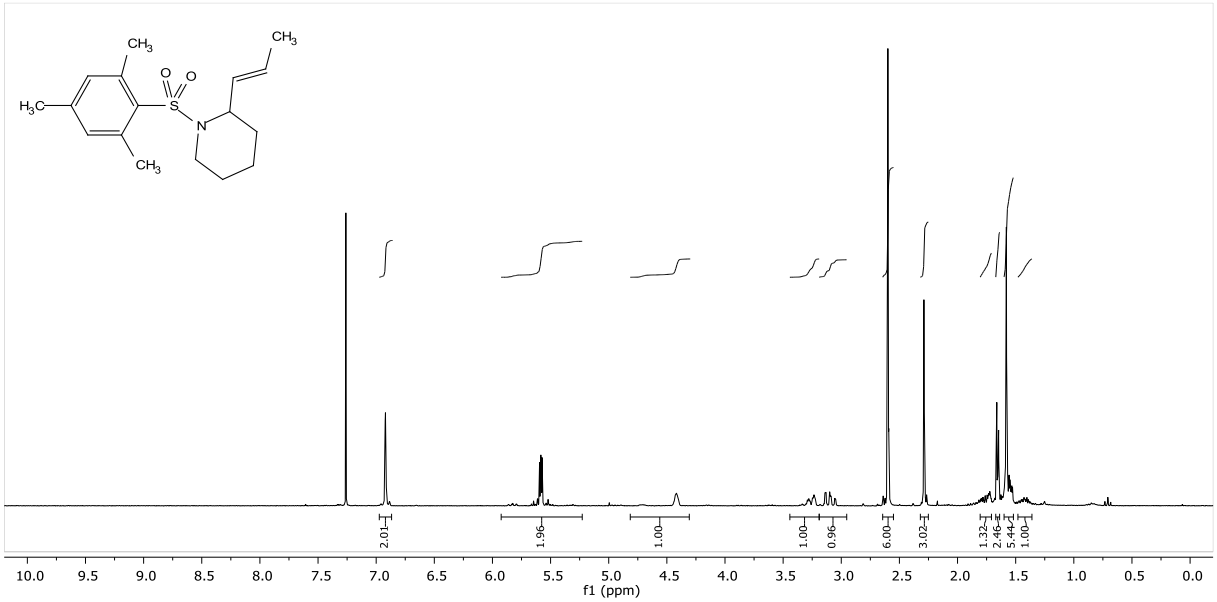


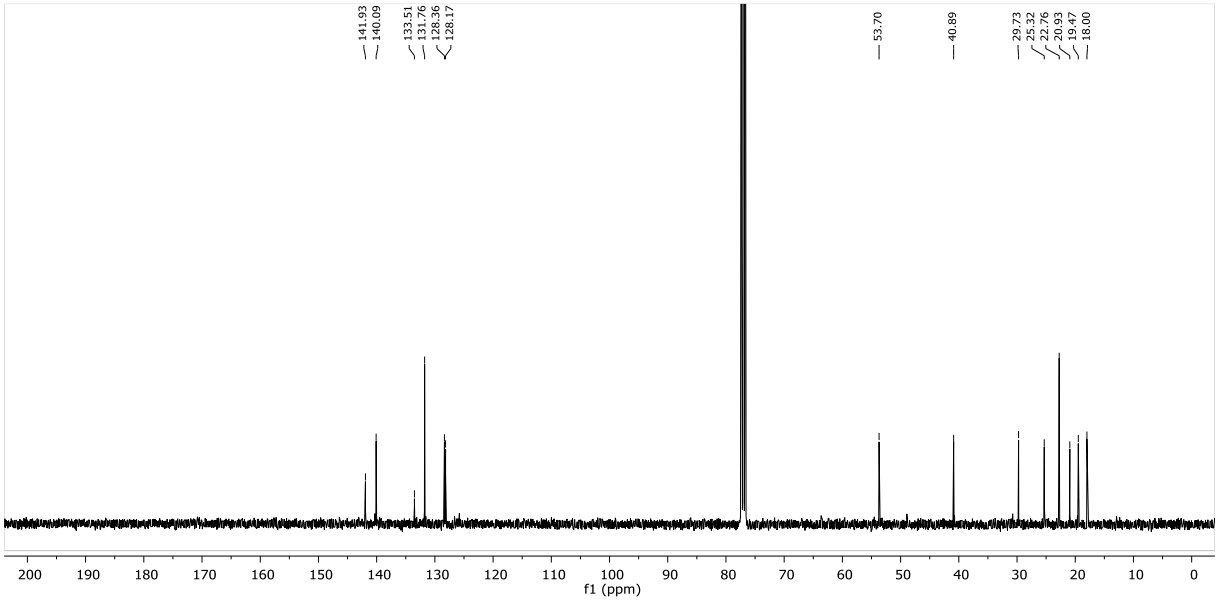
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.124	MM	0.8727	1.16093e4	221.72552	49.7830
2	36.167	MM	0.8958	1.17105e4	217.88553	50.2170

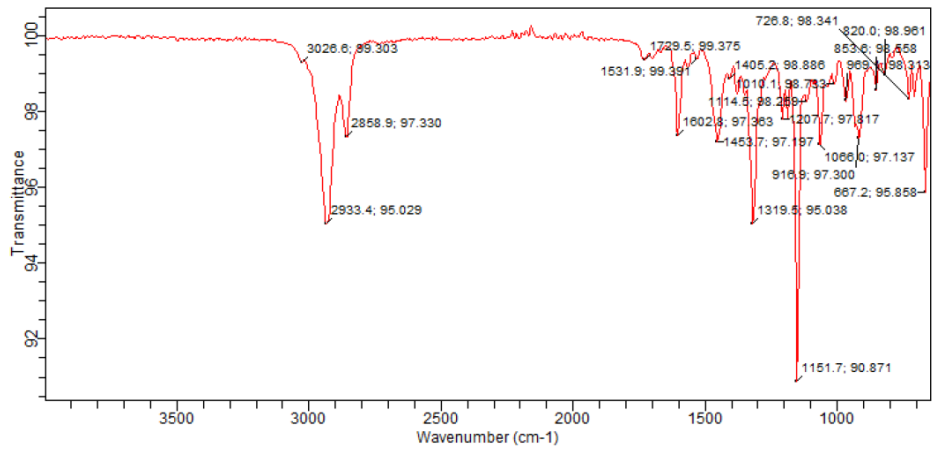


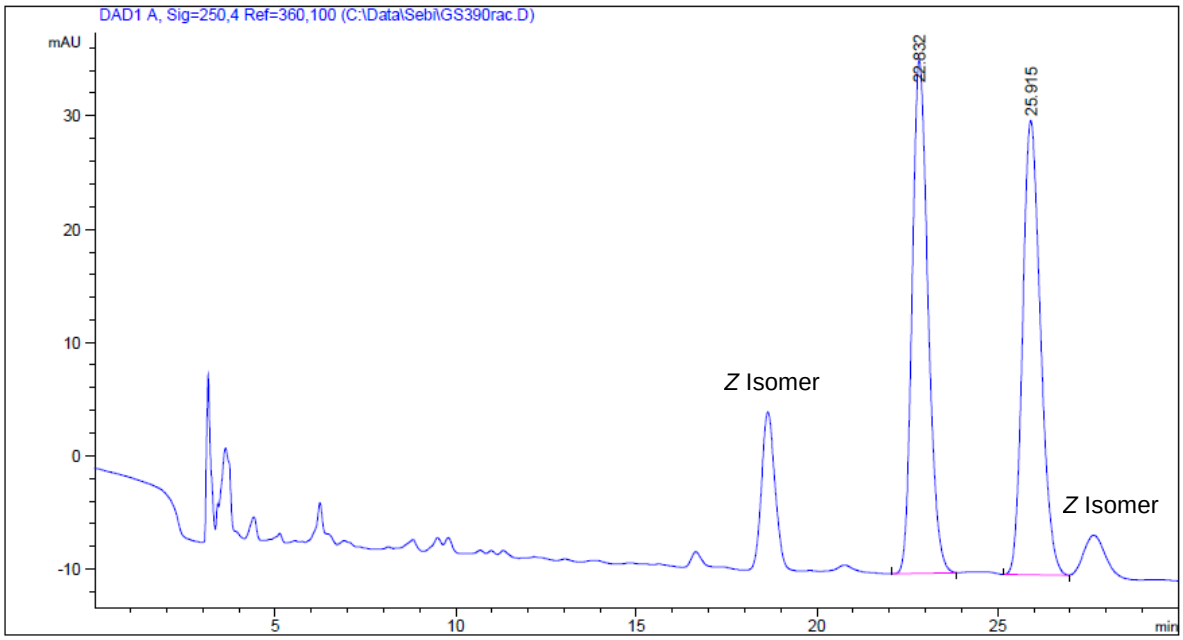
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.958	MM	0.7005	9309.25977	221.48358	5.9137
2	35.147	MM	1.3120	1.48108e5	1881.40430	94.0863

1-(Mesitylsulfonyl)-2-(prop-1-en-1-yl)piperidine (150f)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

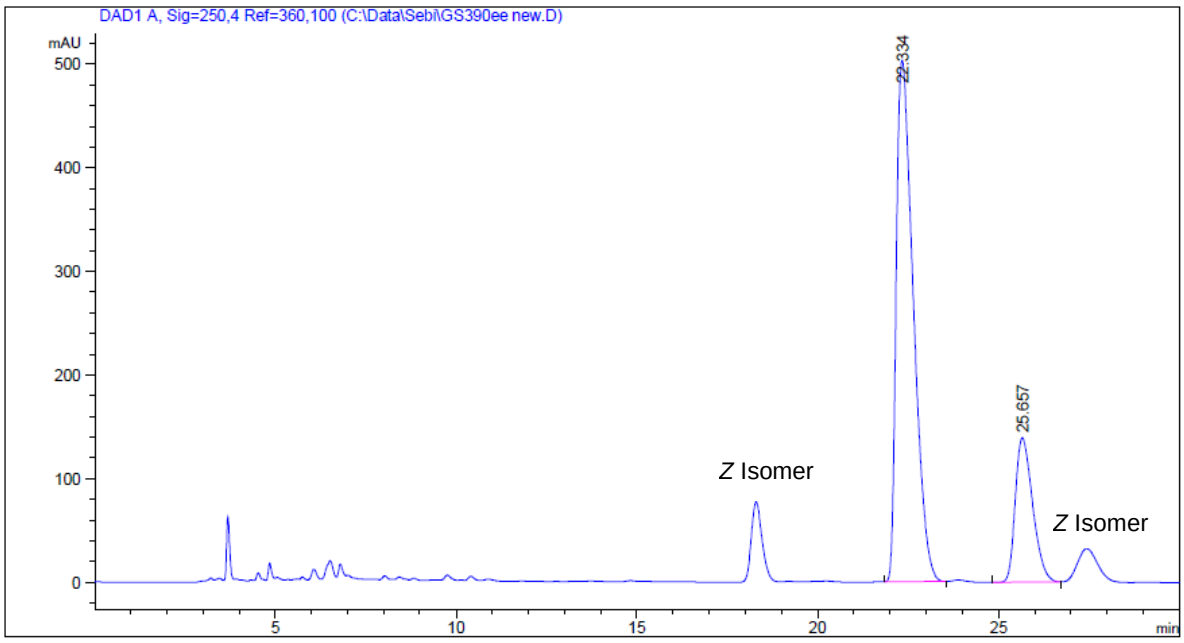






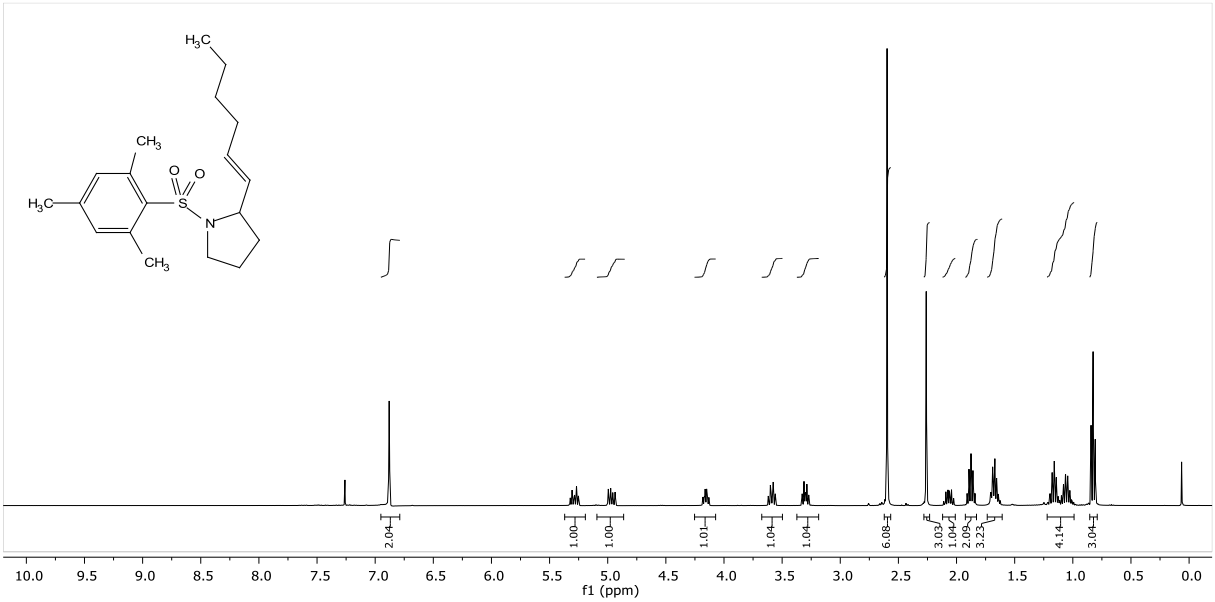


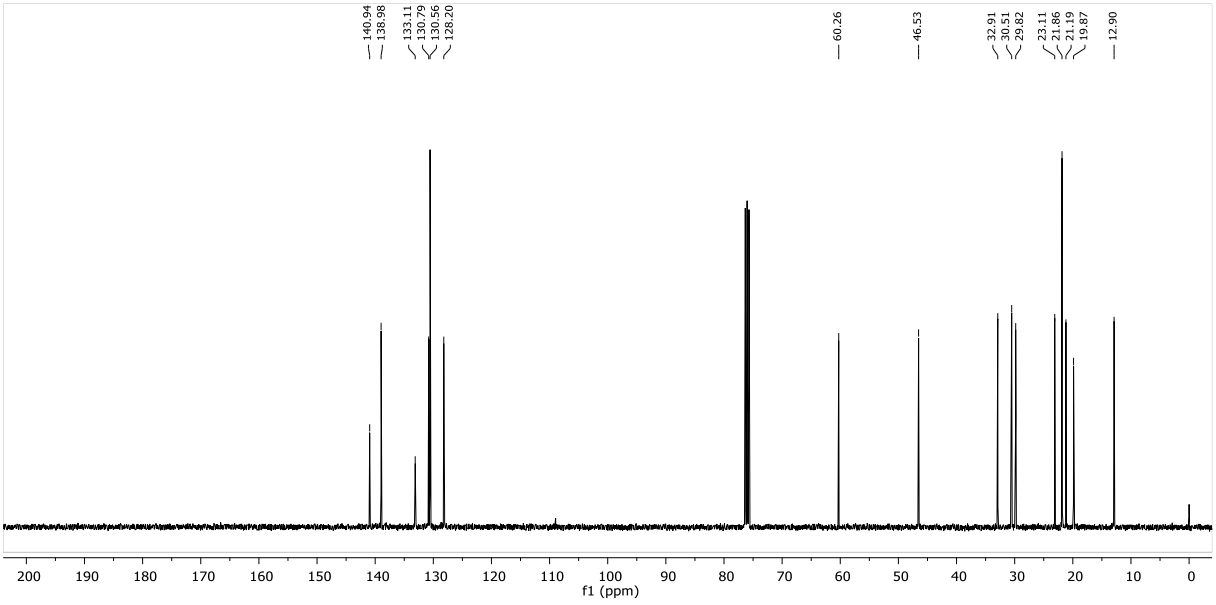
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.832	BB	0.4702	1385.08887	45.36264	50.1358
2	25.915	BB	0.5304	1377.58752	40.13597	49.8642

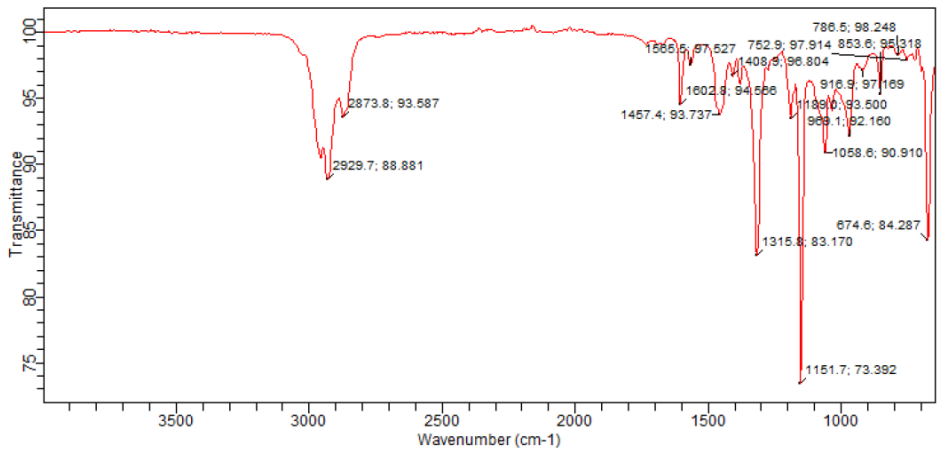


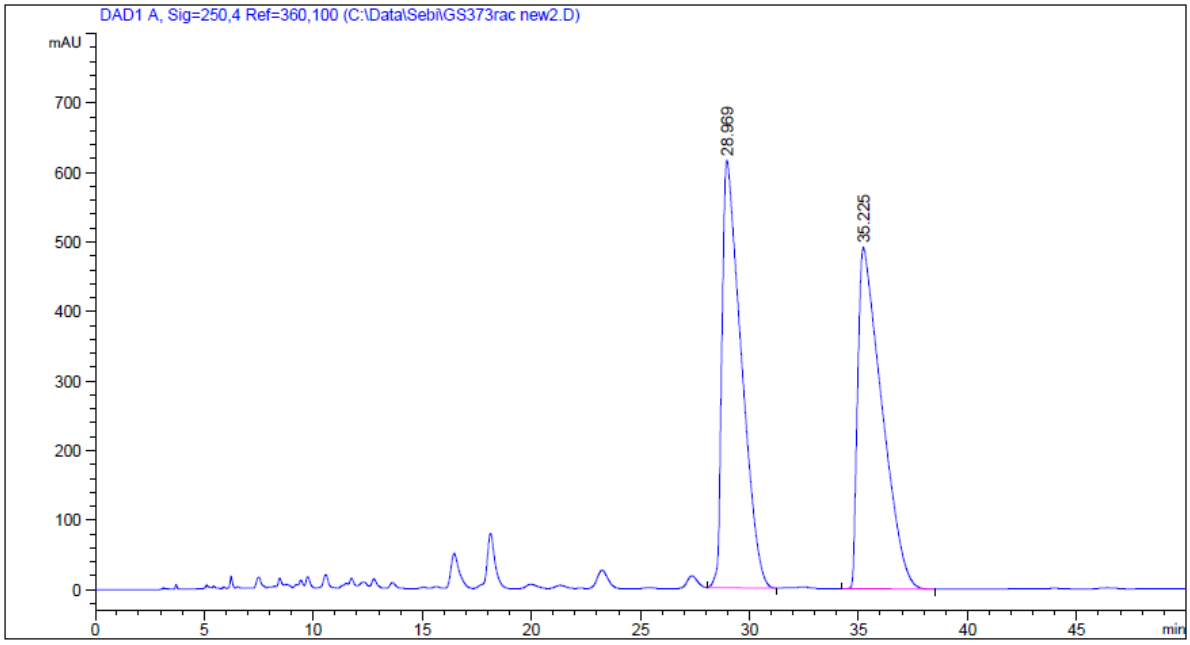
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.334	BB	0.5074	1.64516e4	503.26324	77.9155
2	25.657	BB	0.5196	4663.07666	139.63063	22.0845

(*E*)-2-(Hex-1-en-1-yl)-1-(mesitylsulfonyl)pyrrolidine (140f)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

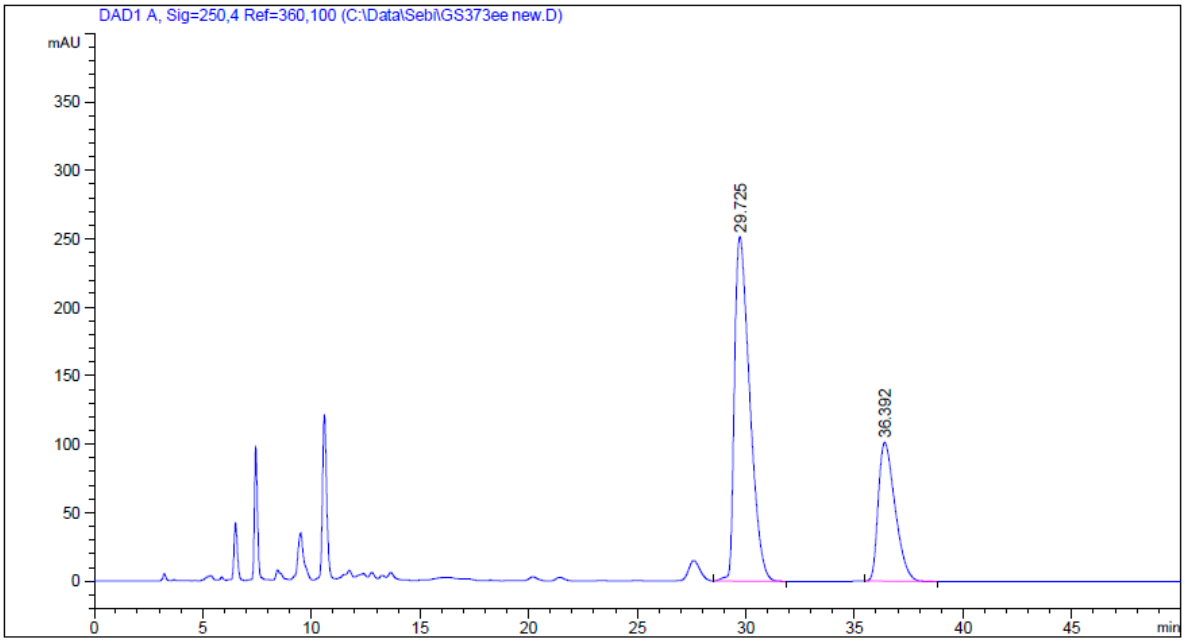






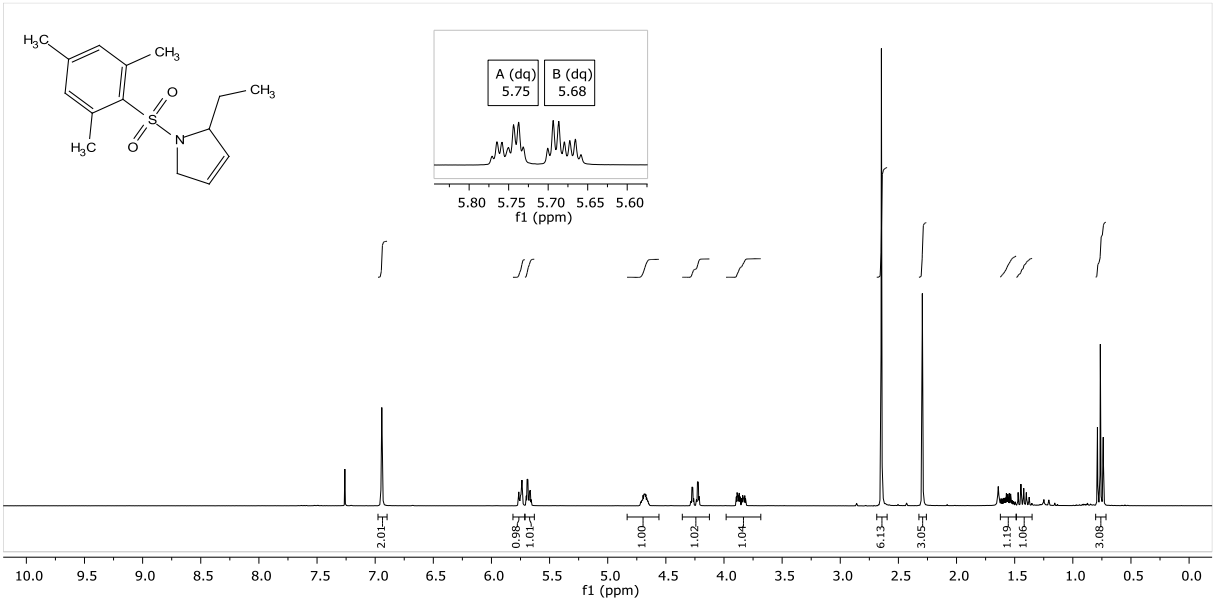


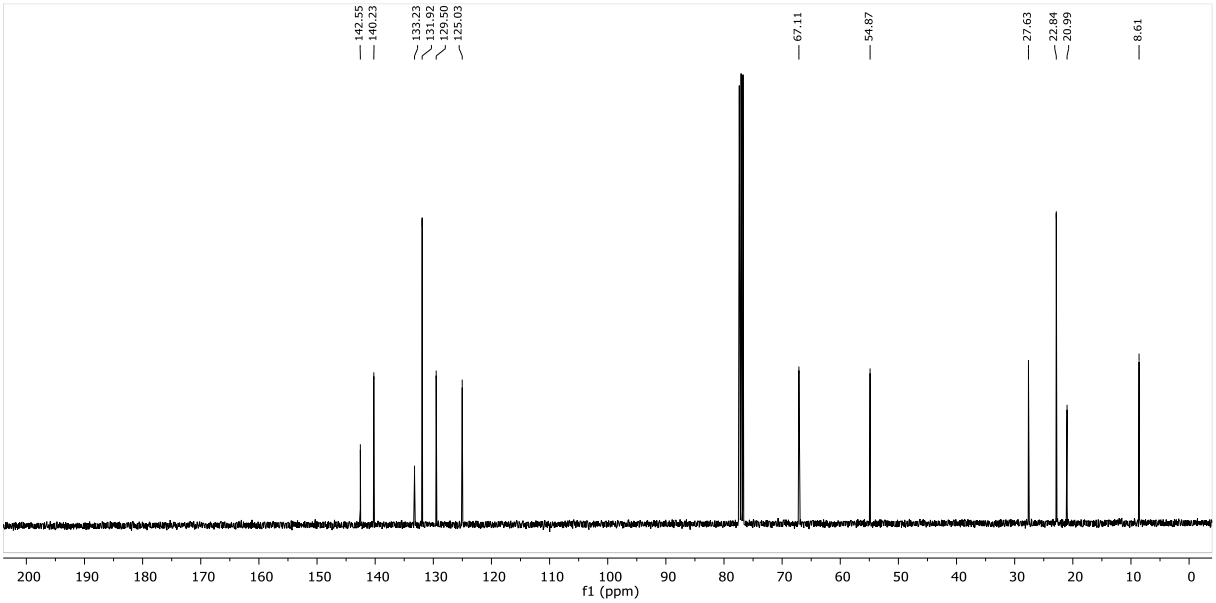
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.969	BB	0.8803	3.77604e4	615.03290	50.1893
2	35.225	BB	1.1029	3.74754e4	490.75143	49.8107

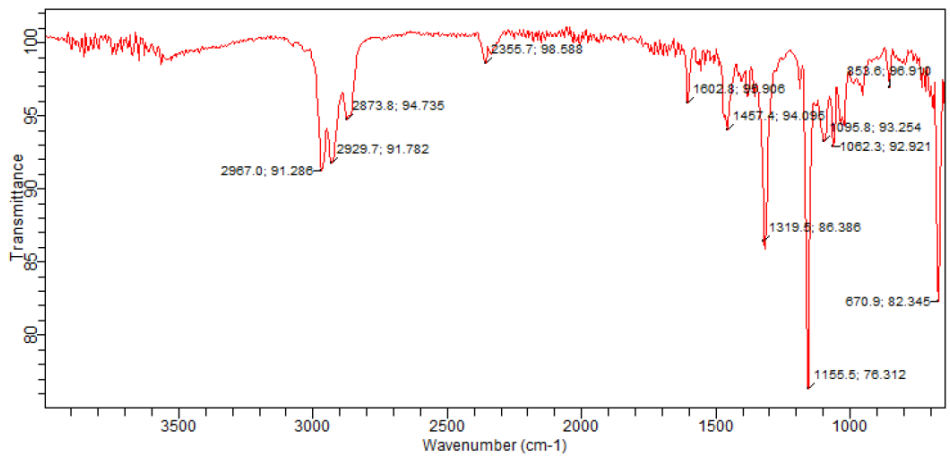


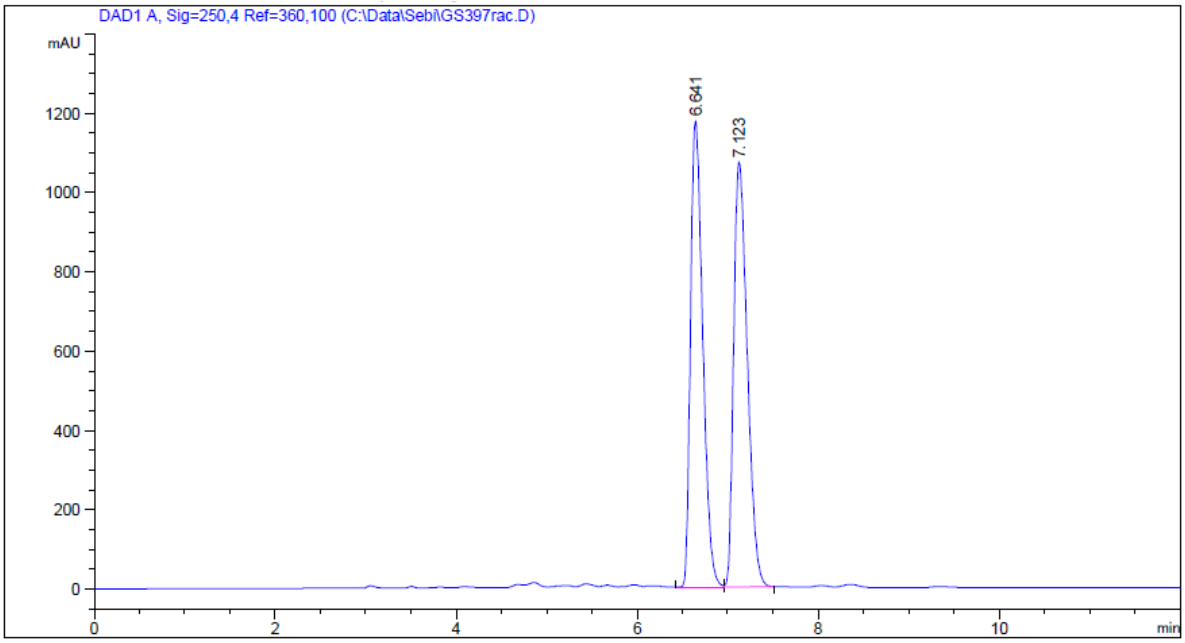
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.725	BB	0.7457	1.22443e4	251.64601	69.2731
2	36.392	BB	0.8219	5431.10596	101.23749	30.7269

2-Ethyl-1-(mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrole (149ad)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

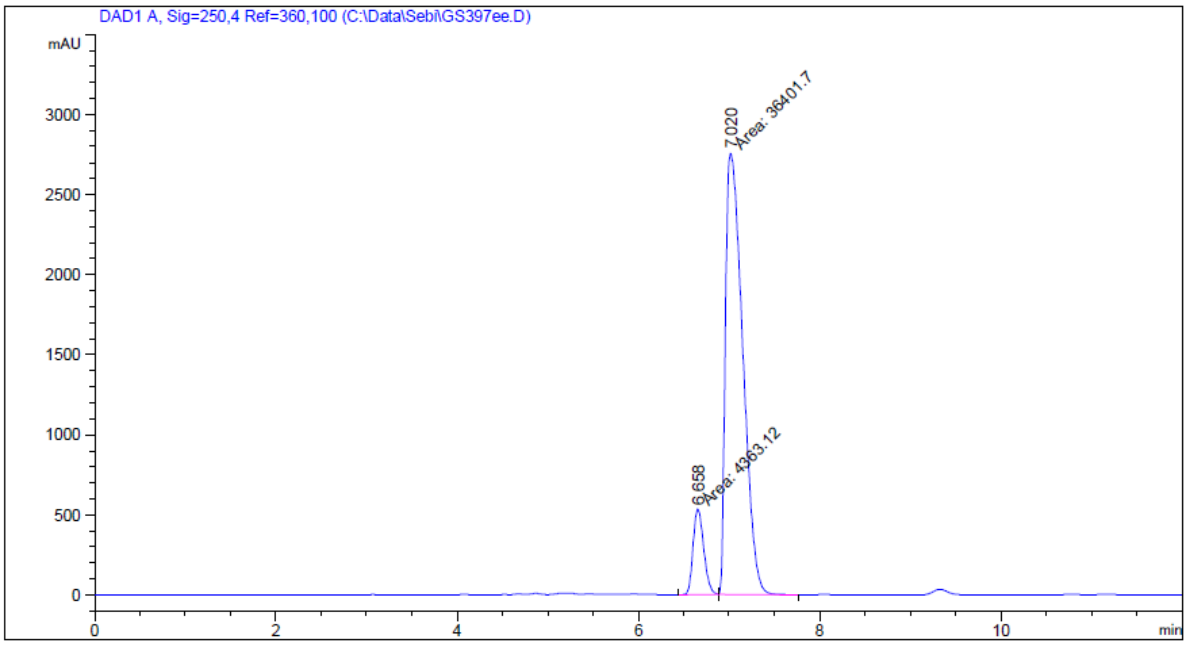






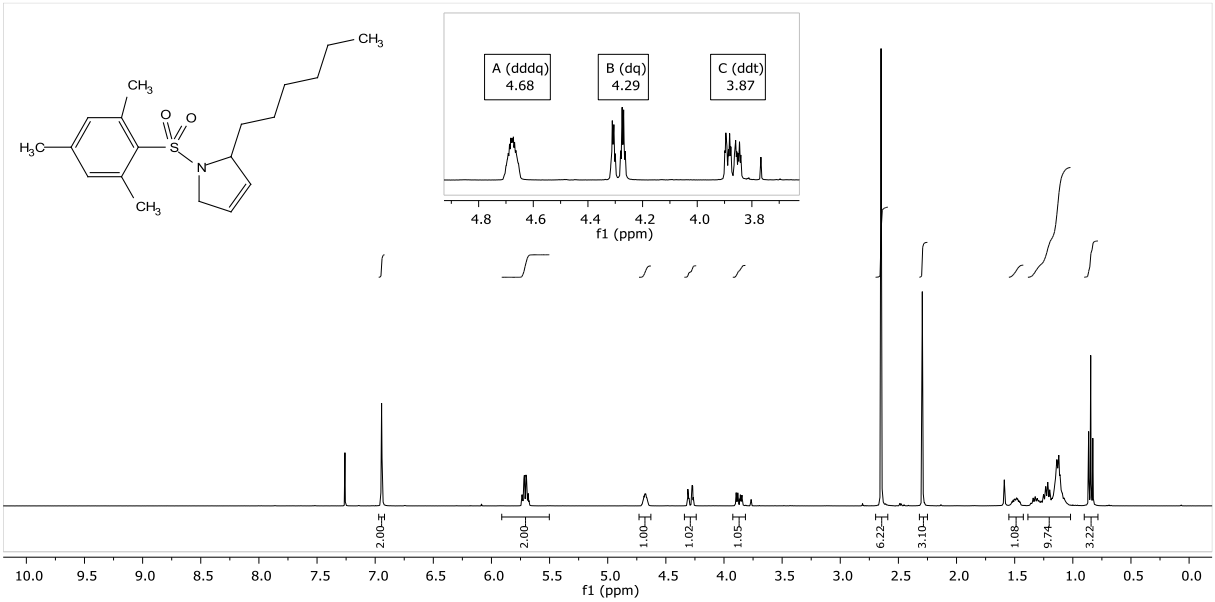


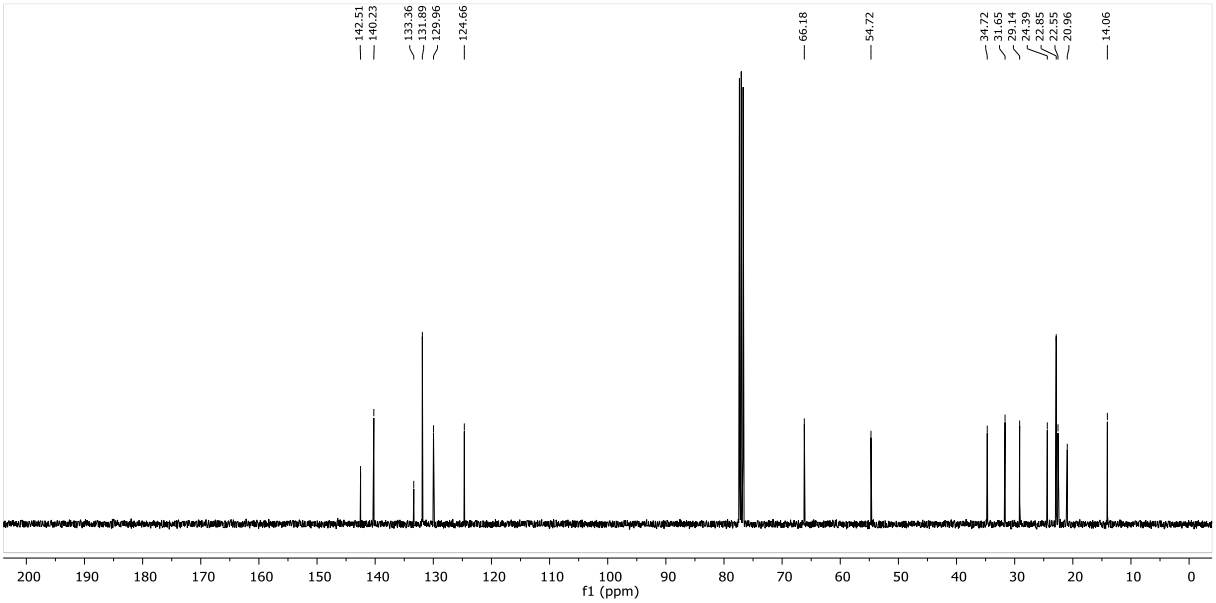
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.641	BV	0.1473	1.10030e4	1174.66052	49.6160
2	7.123	VB	0.1639	1.11733e4	1069.73962	50.3840

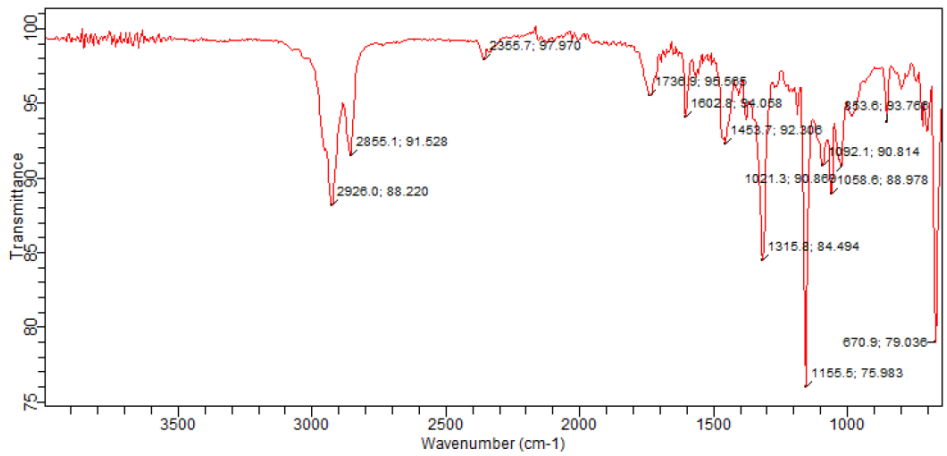


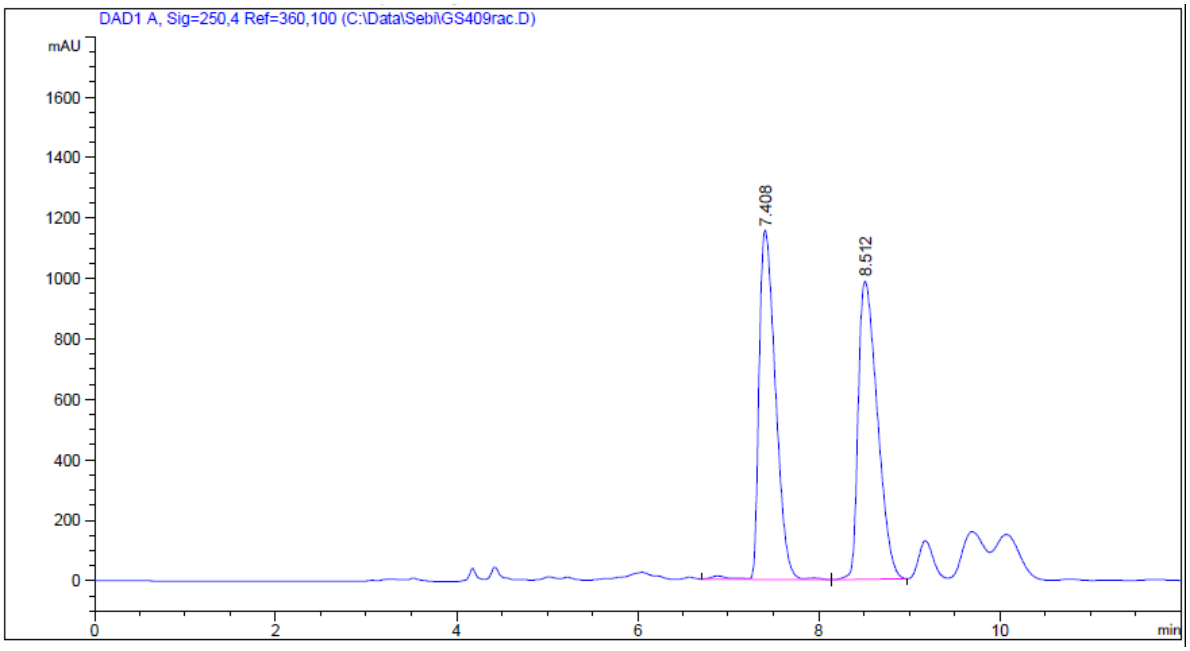
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.658	MM	0.1360	4363.12402	534.74866	10.7032
2	7.020	MM	0.2200	3.64017e4	2757.18896	89.2968

2-Hexyl-1-(mesitylsulfonyl)-2,5-dihydro-1*H*-pyrrole (149af)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

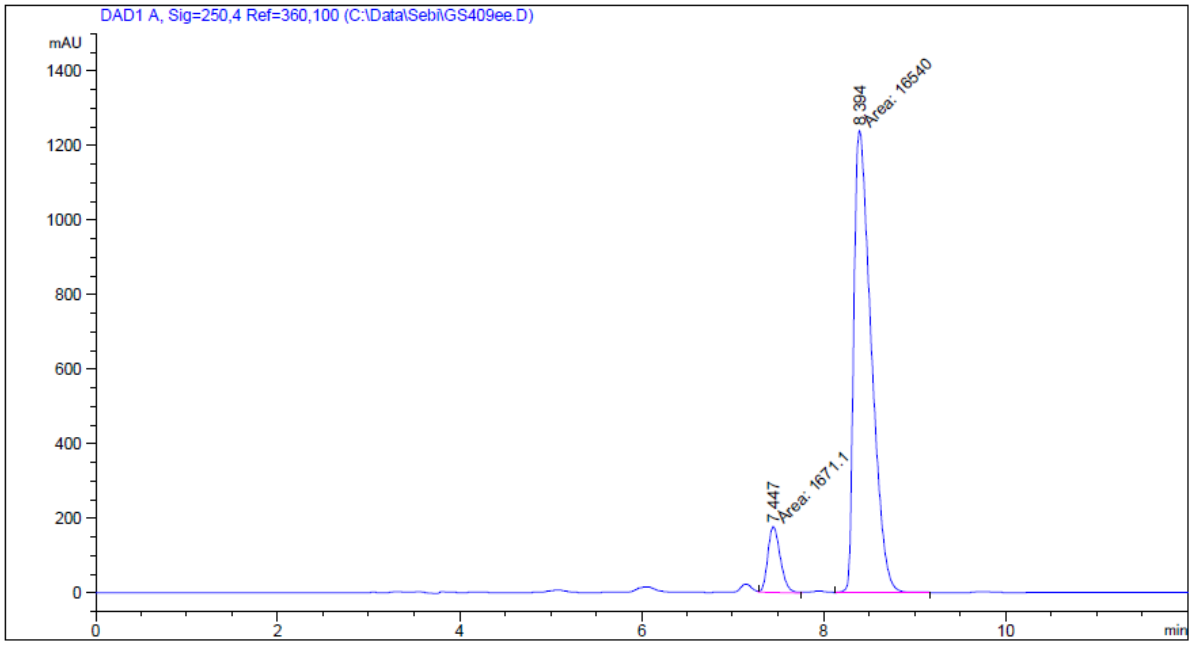






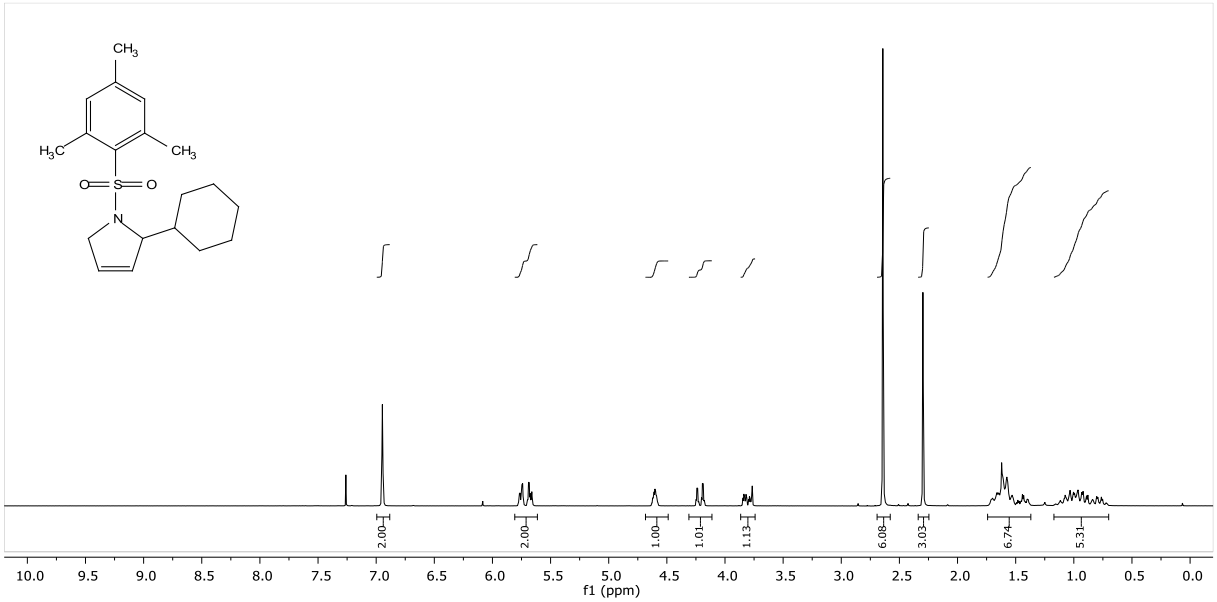


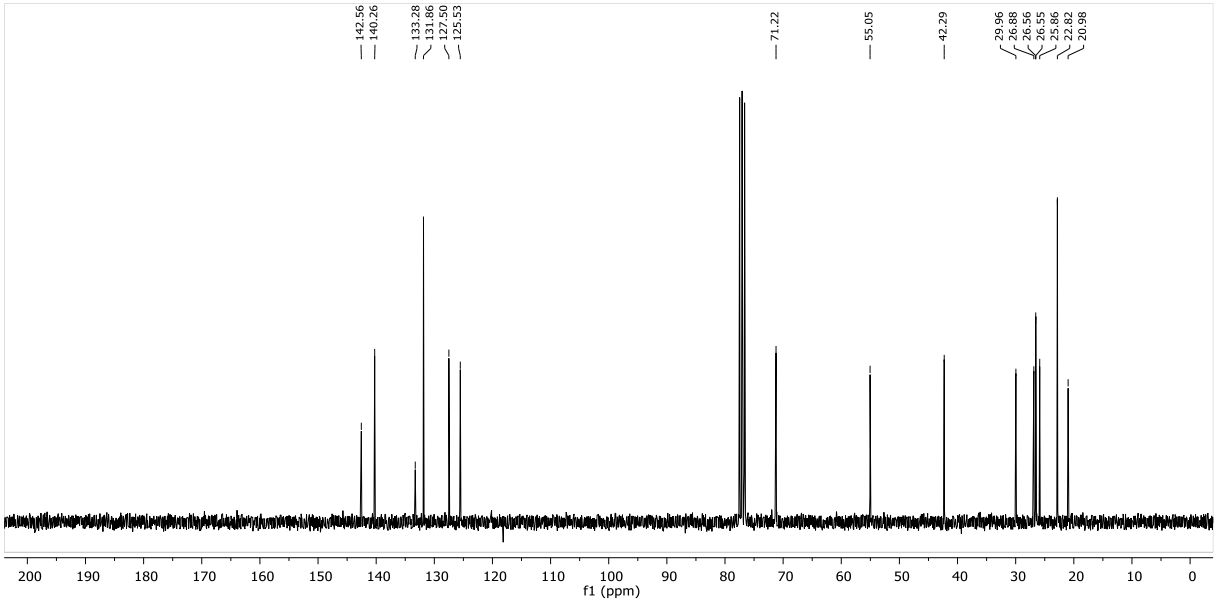
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.408	VV R	0.1949	1.45403e4	1154.33704	50.1291
2	8.512	BB	0.2309	1.44654e4	987.32990	49.8709

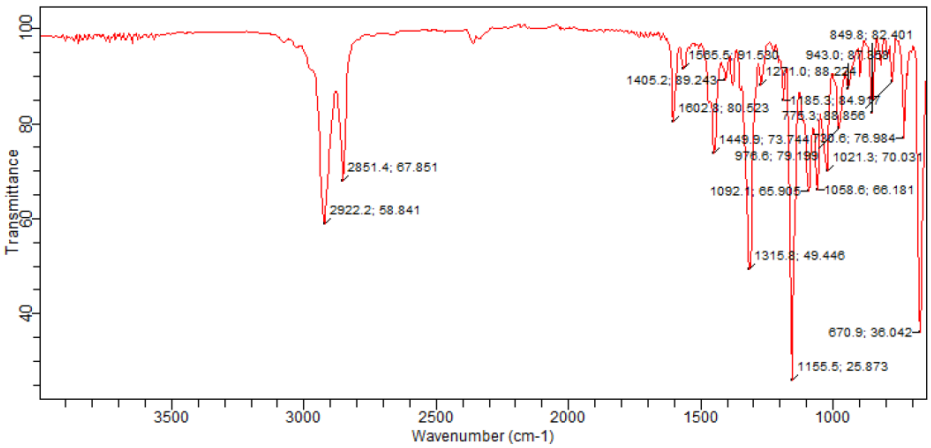


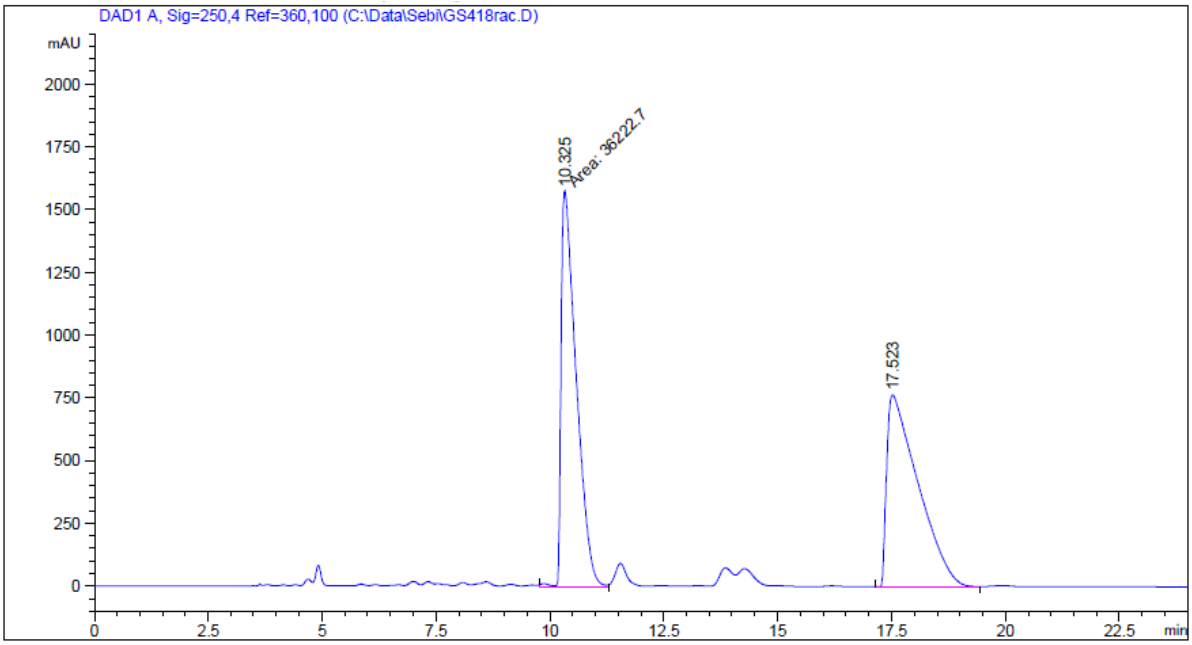
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.447	MM	0.1582	1671.10193	176.03351	9.1763
2	8.394	MM	0.2220	1.65400e4	1241.85999	90.8237

2-Cyclohexyl-1-(mesitylsulfonyl)-2,5-dihydro-1H-pyrrole (149ag)*: ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

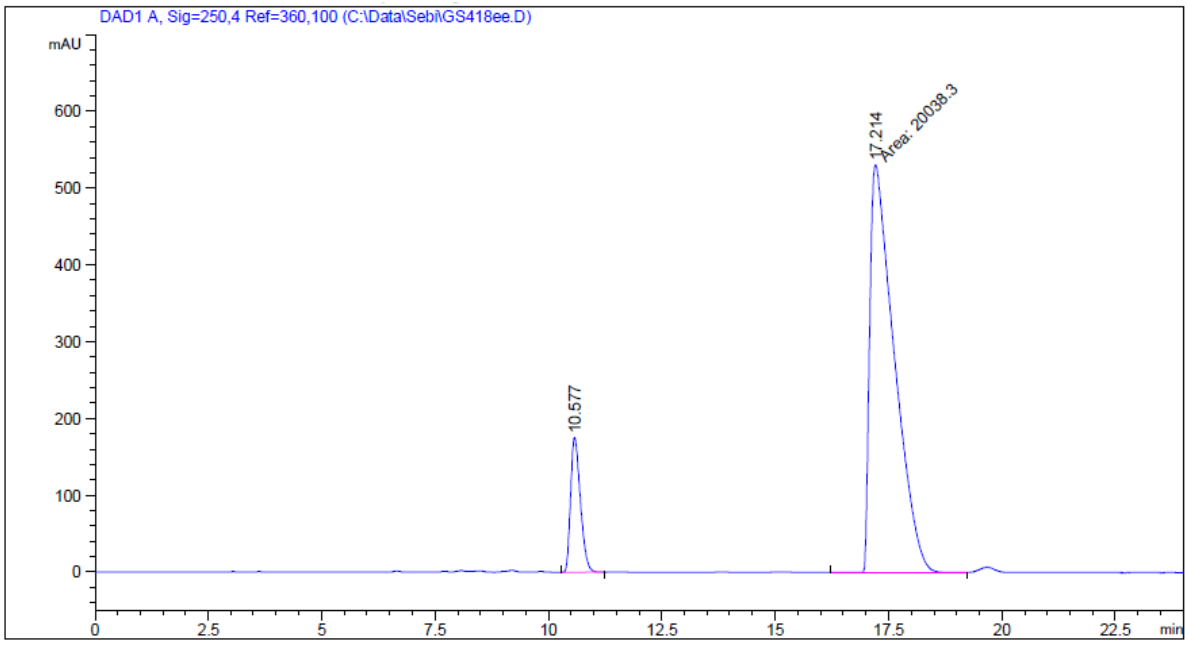






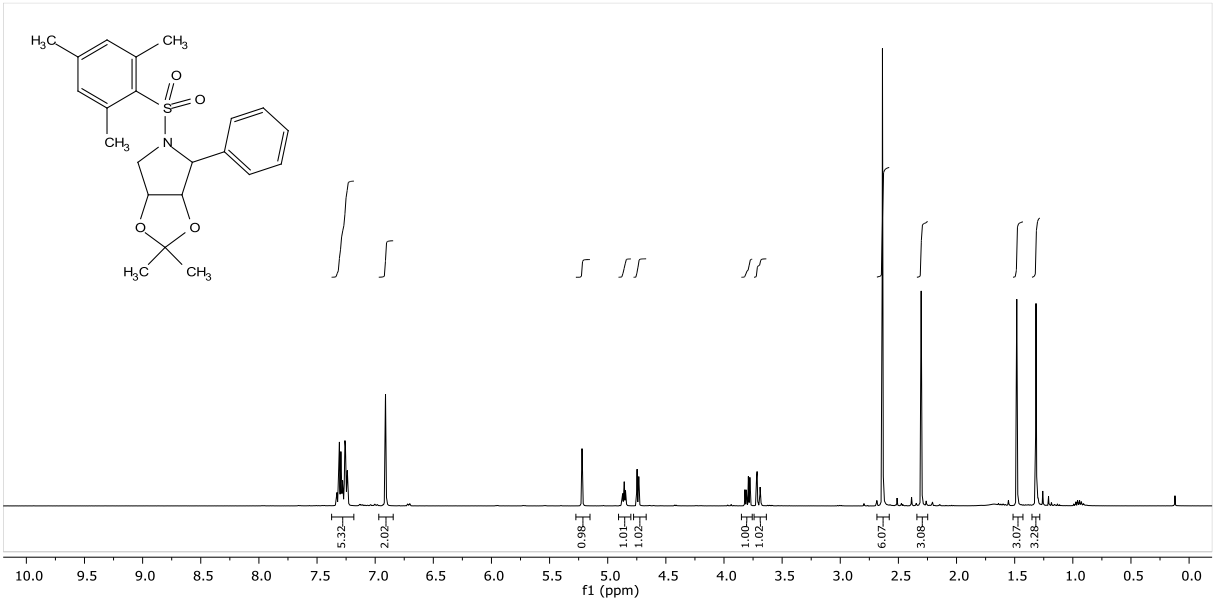


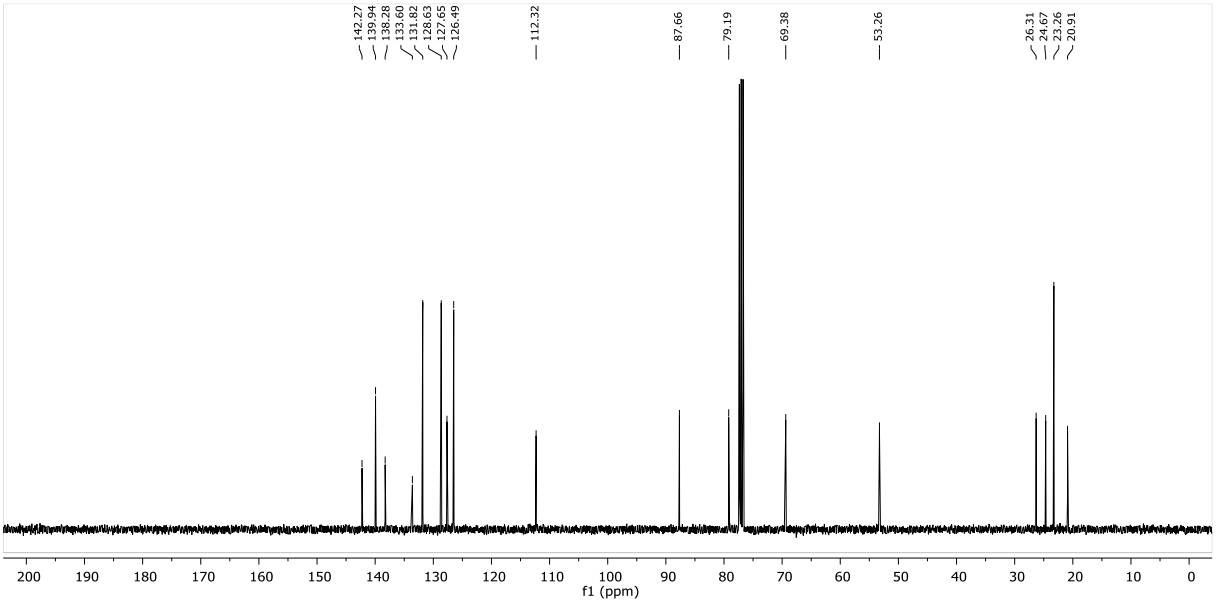
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.325	MM	0.3828	3.62227e4	1577.01404	49.8708
2	17.523	BB	0.6902	3.64104e4	763.73151	50.1292

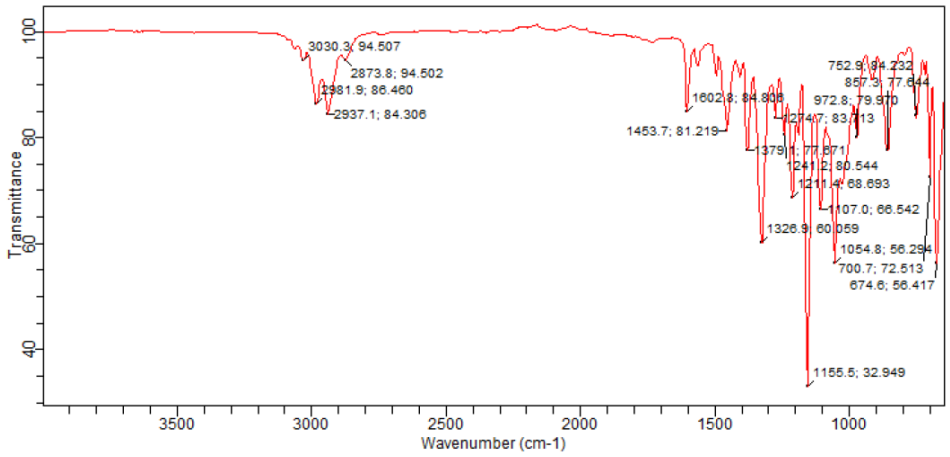


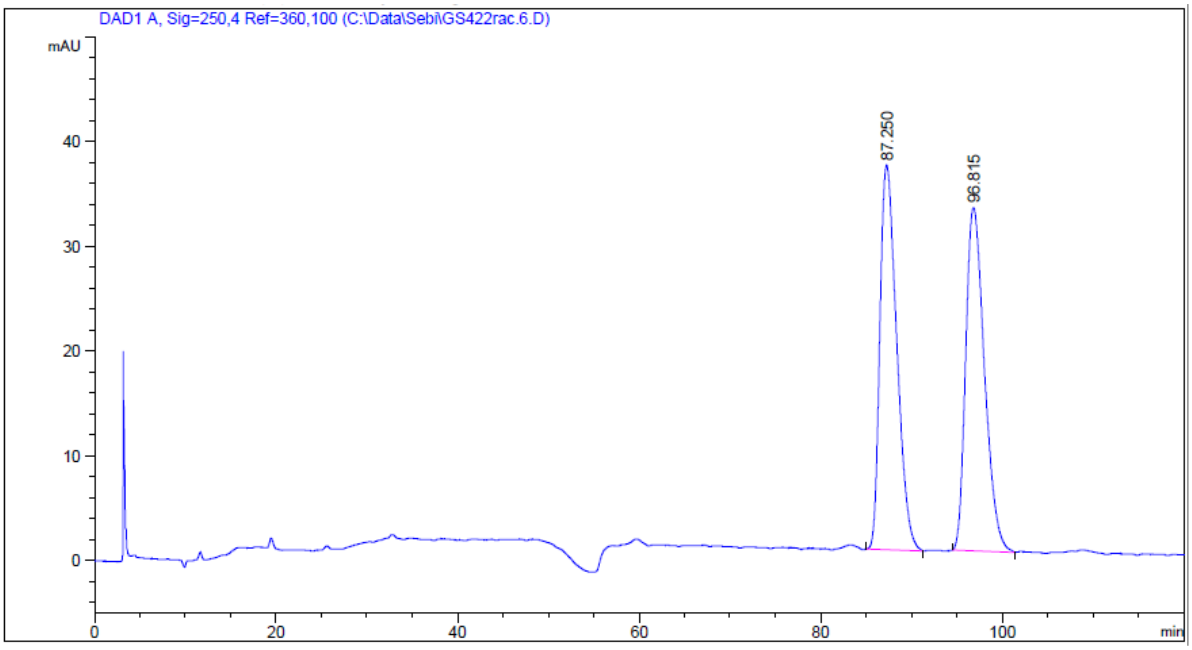
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.577	BB	0.2310	2629.94336	175.32954	11.6019
2	17.214	MM	0.6280	2.00383e4	531.81653	88.3981

(3a*R*,4*R*,6a*S*)-5-(Mesitylsulfonyl)-2,2-dimethyl-4-phenyltetrahydro-4H-[1,3]dioxolo[4,5-c]pyrrole (260): ^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

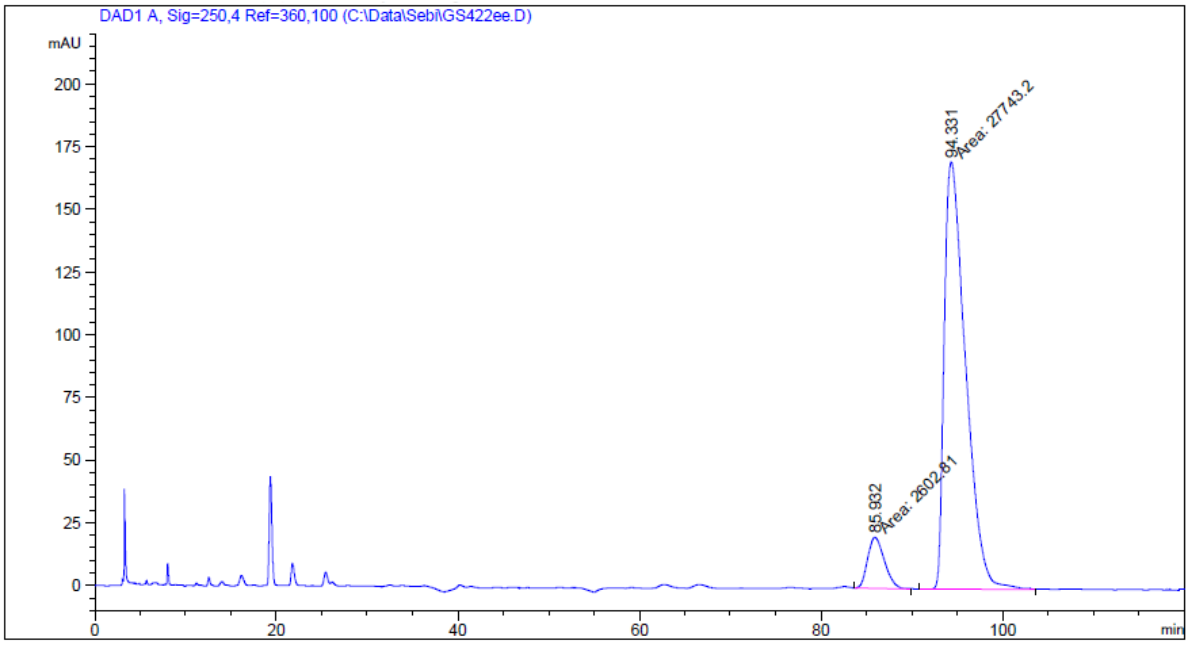






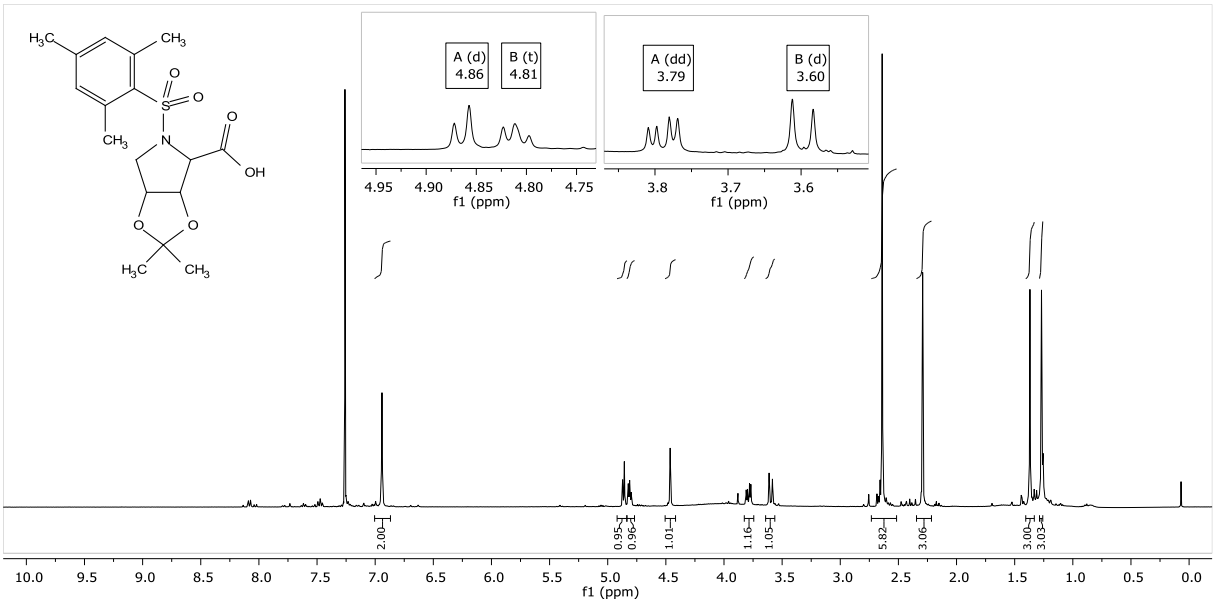


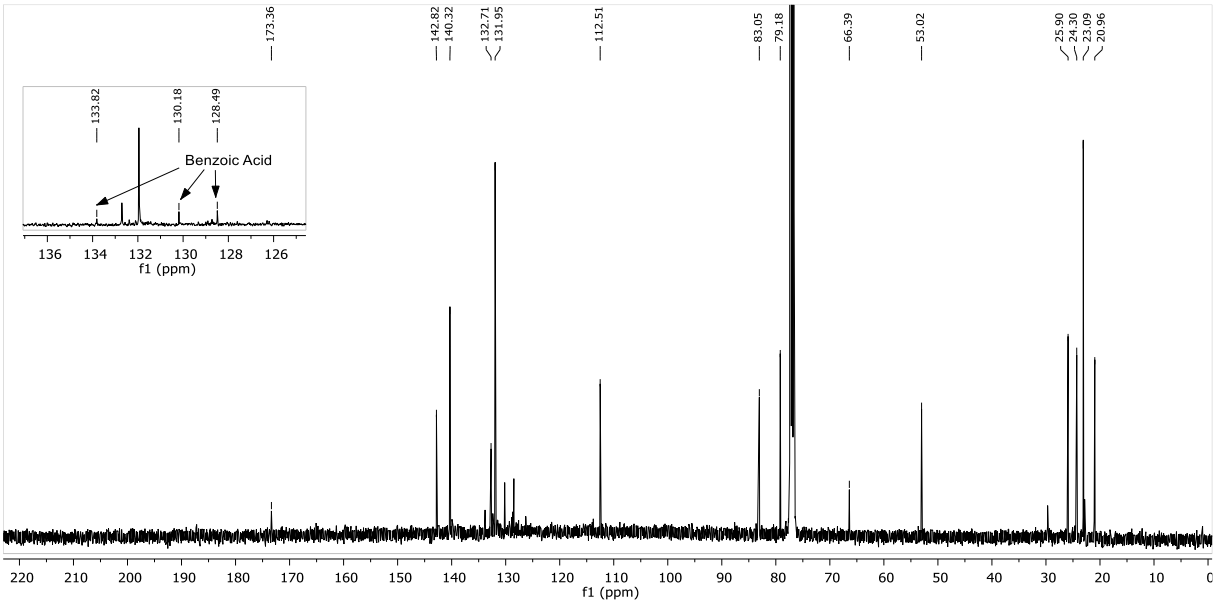
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	87.250	BB	1.5714	4723.82959	36.75608	50.1159
2	96.815	BB	1.7424	4701.97168	32.80088	49.8841

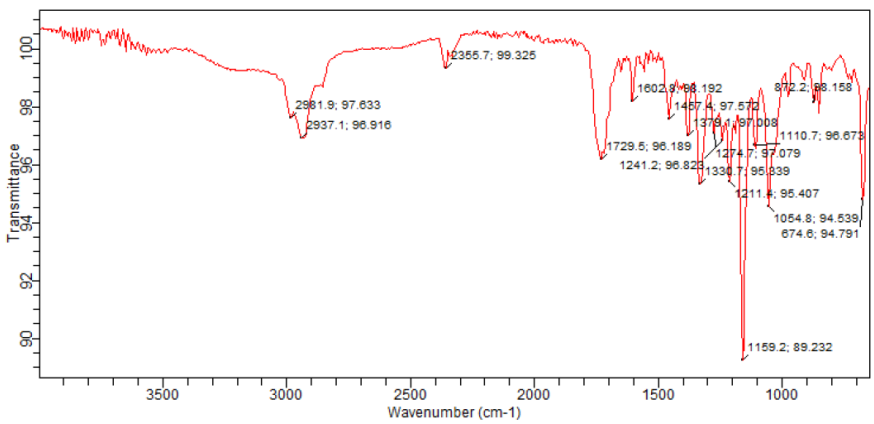


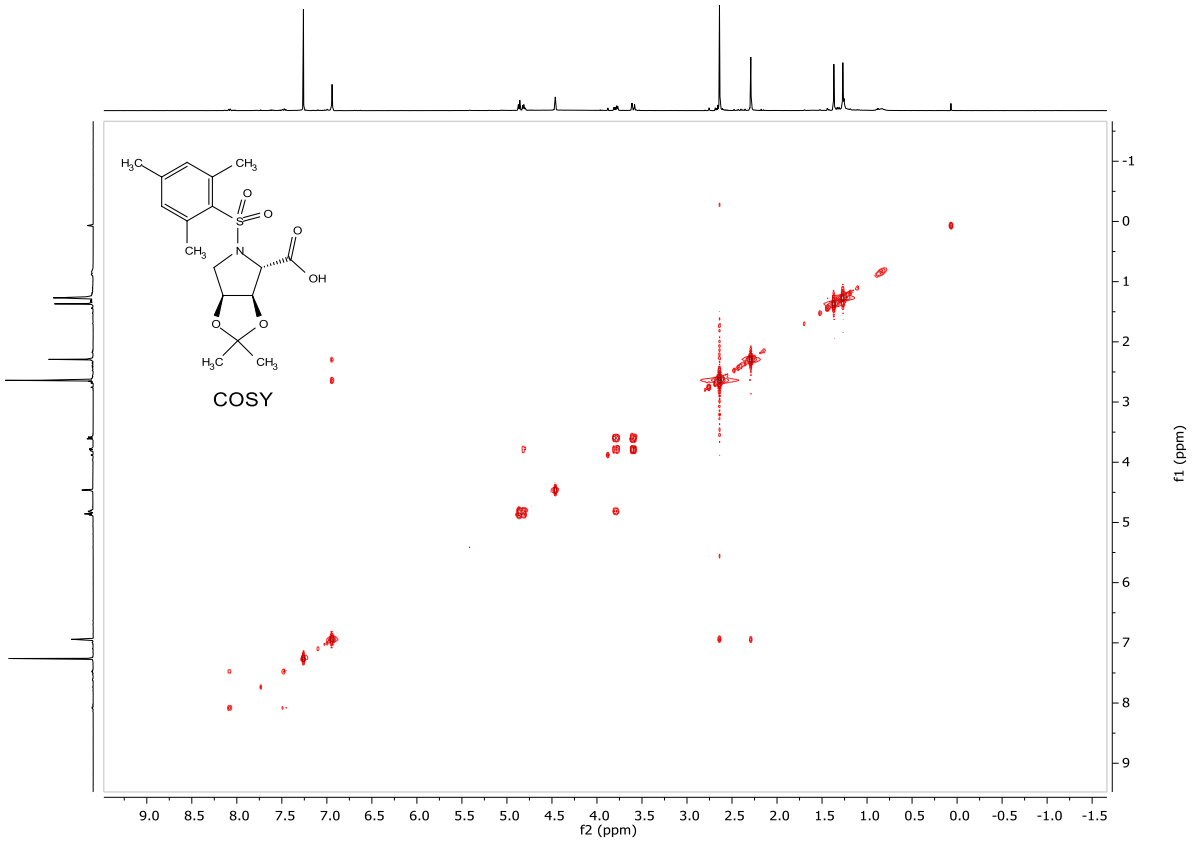
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	85.932	MM	2.1367	2602.81396	20.30204	8.5771
2	94.331	MM	2.7144	2.77432e4	170.34502	91.4229

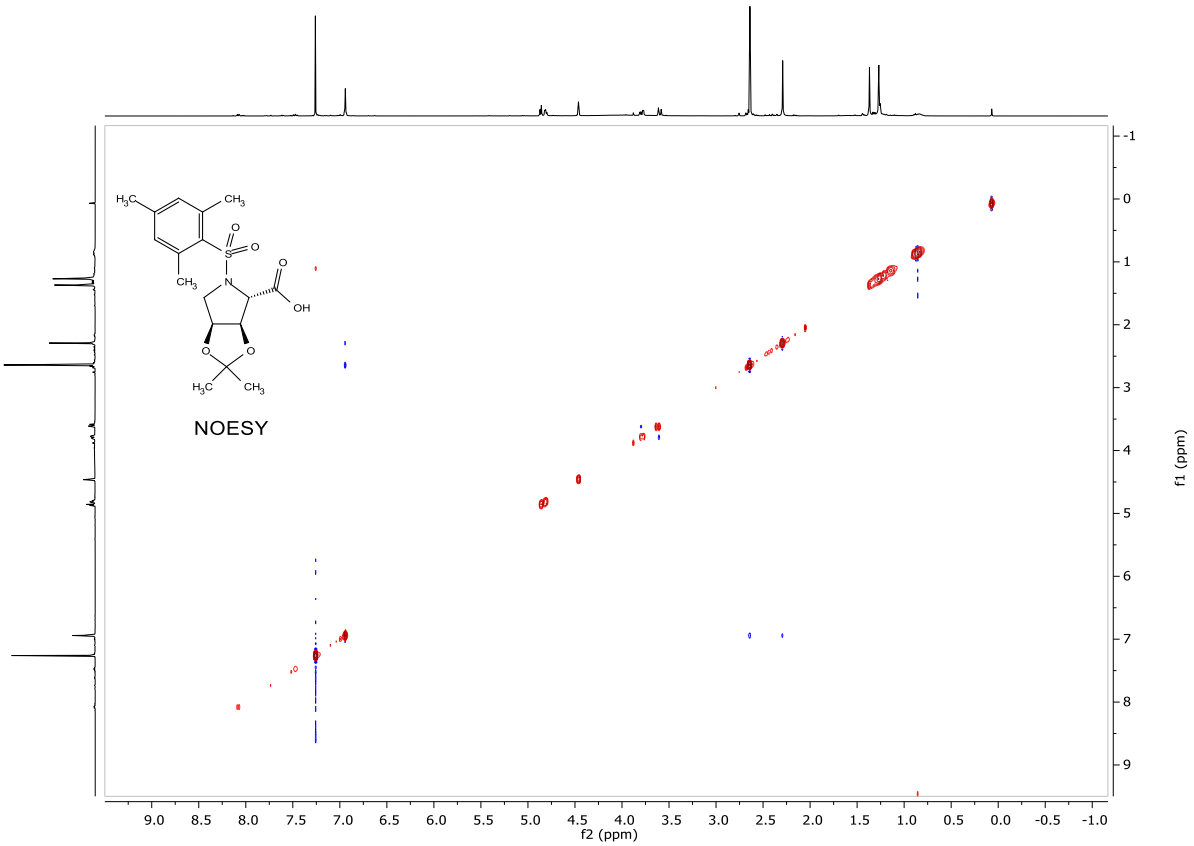
(3a*R*,4*S*,6a*S*)-5-(Mesitylsulfonyl)-2,2-dimethyltetrahydro-4H-[1,3]dioxolo[4,5-c]pyrrole-4-carboxylic acid (261): ^{1}H, ^{13}C NMR in $CDCl_3$, IR, COSY, NOESY, HPLC traces

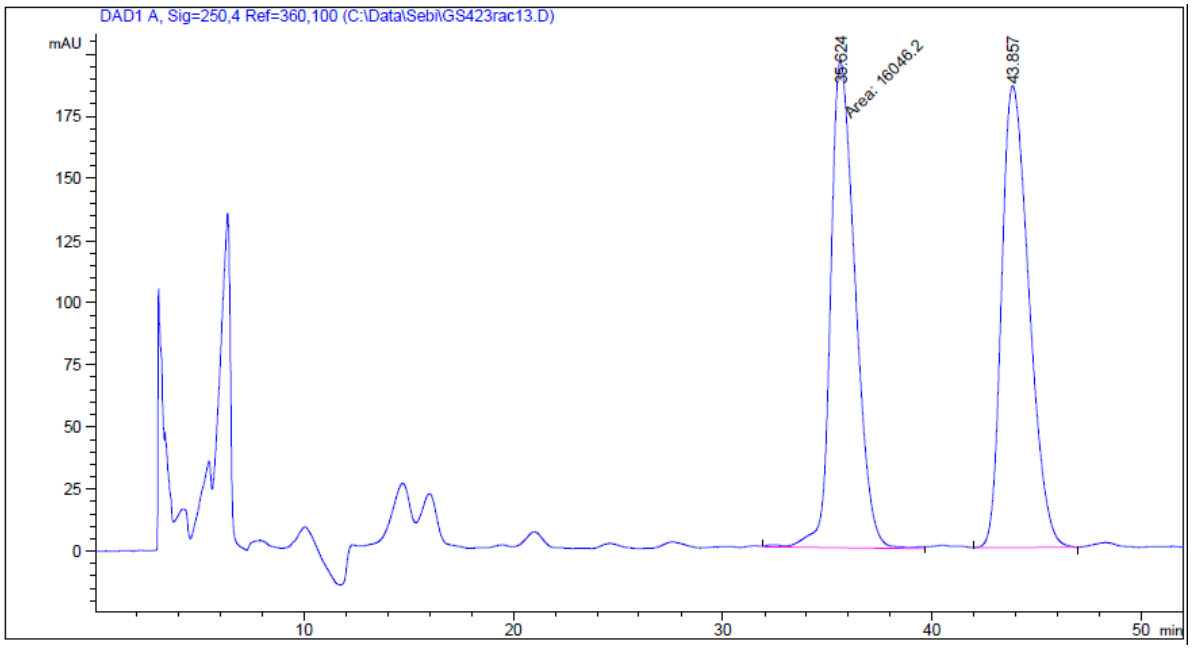




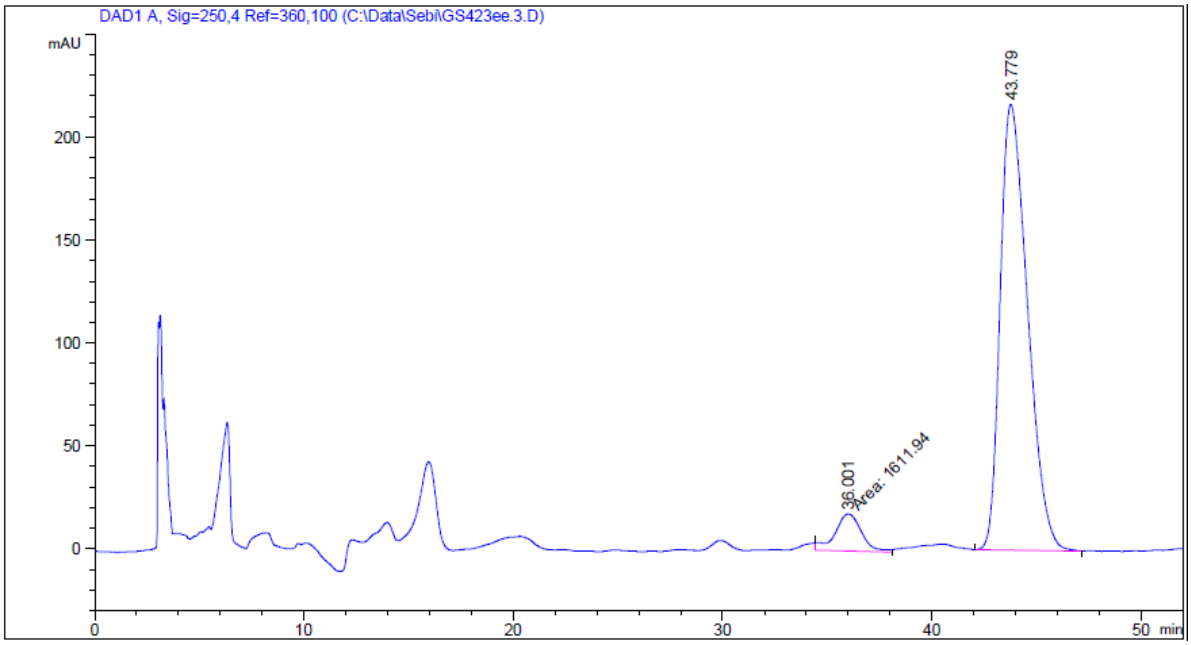



COSY
f2 (ppm)
f1 (ppm)


NOESY
f2 (ppm)
f1 (ppm)



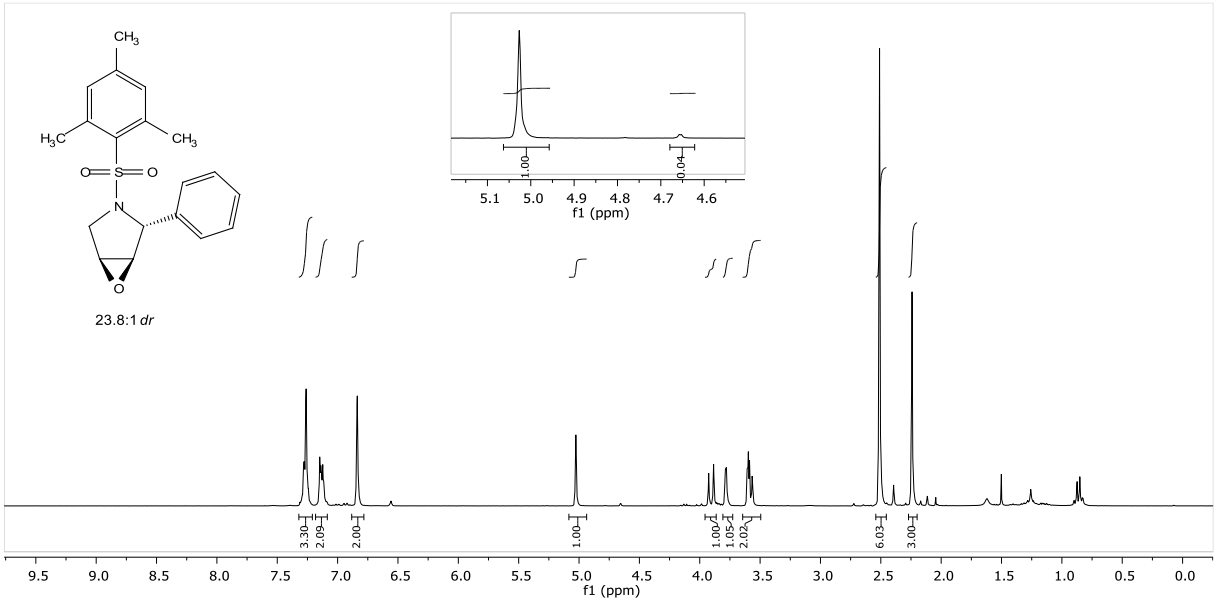
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.624	MM	1.3660	1.60462e4	195.77594	48.7176
2	43.857	BB	1.3952	1.68910e4	185.69447	51.2824

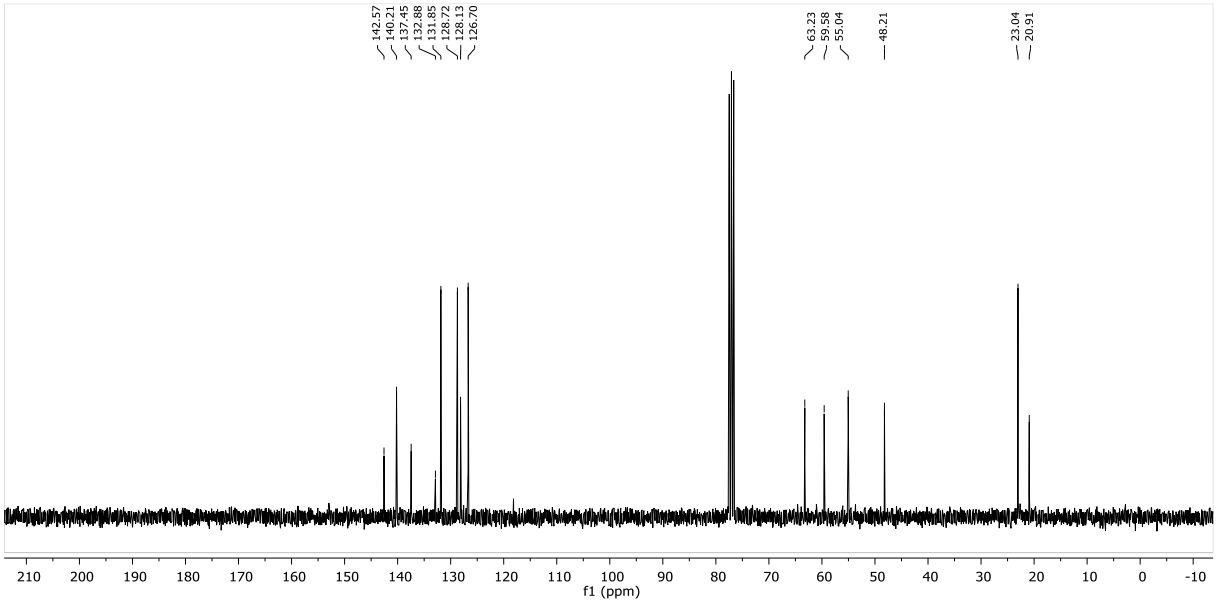


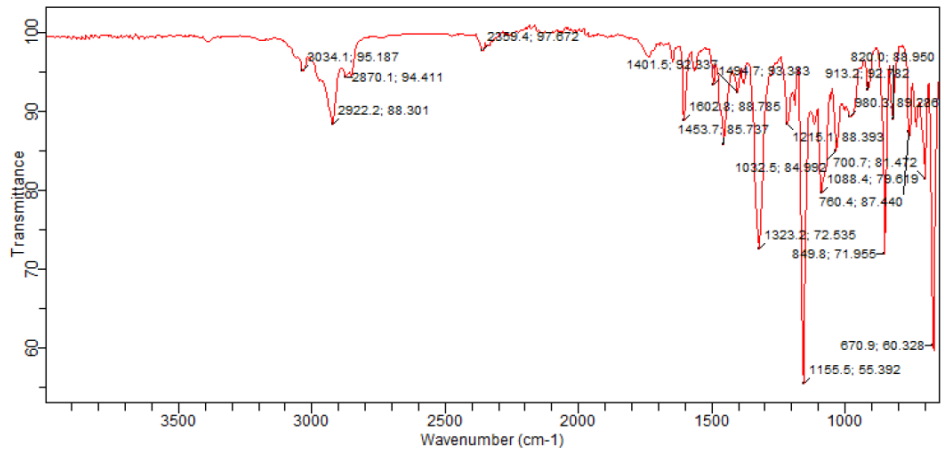
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.001	MM	1.4841	1611.93616	18.10194	7.5788
2	43.779	BB	1.3966	1.96570e4	216.63756	92.4212

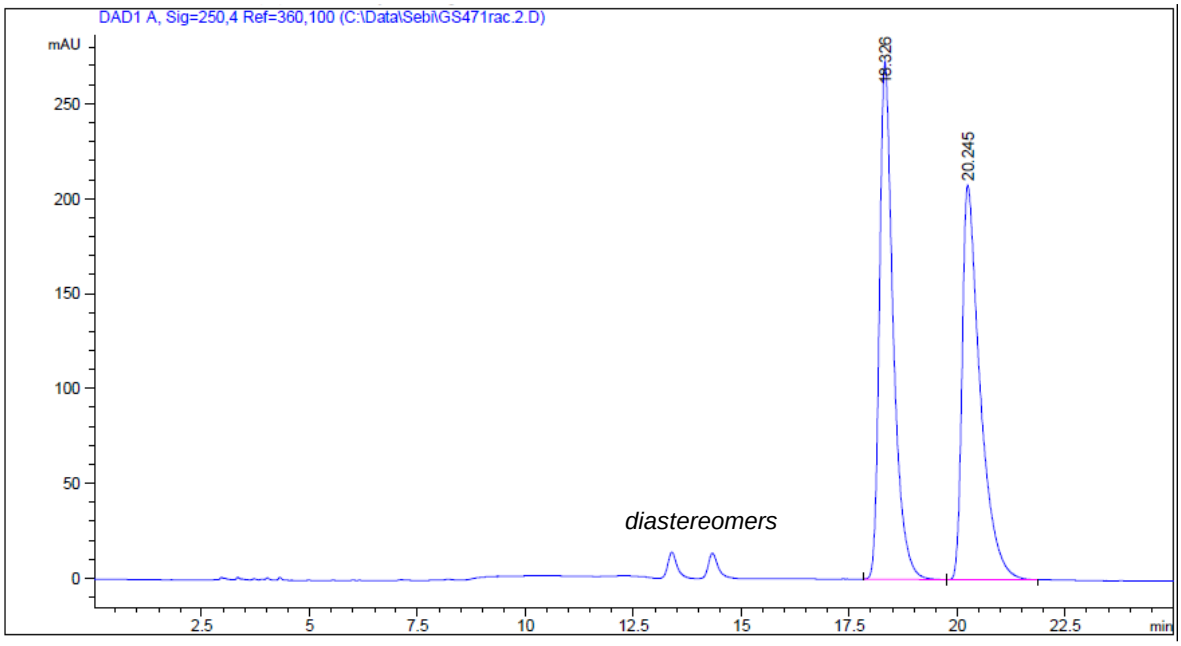
(1*R*,2*R*,5*S*)-3-(Mesitylsulfonyl)-2-phenyl-6-oxa-3-azabicyclo[3.1.0]hexane (262):

^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

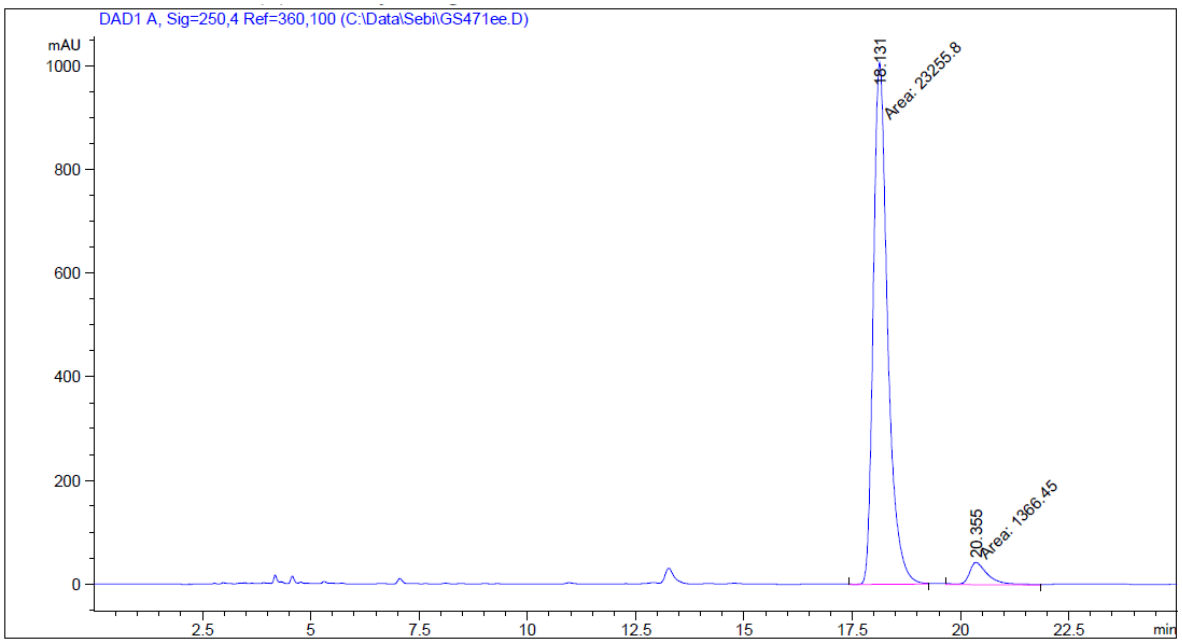








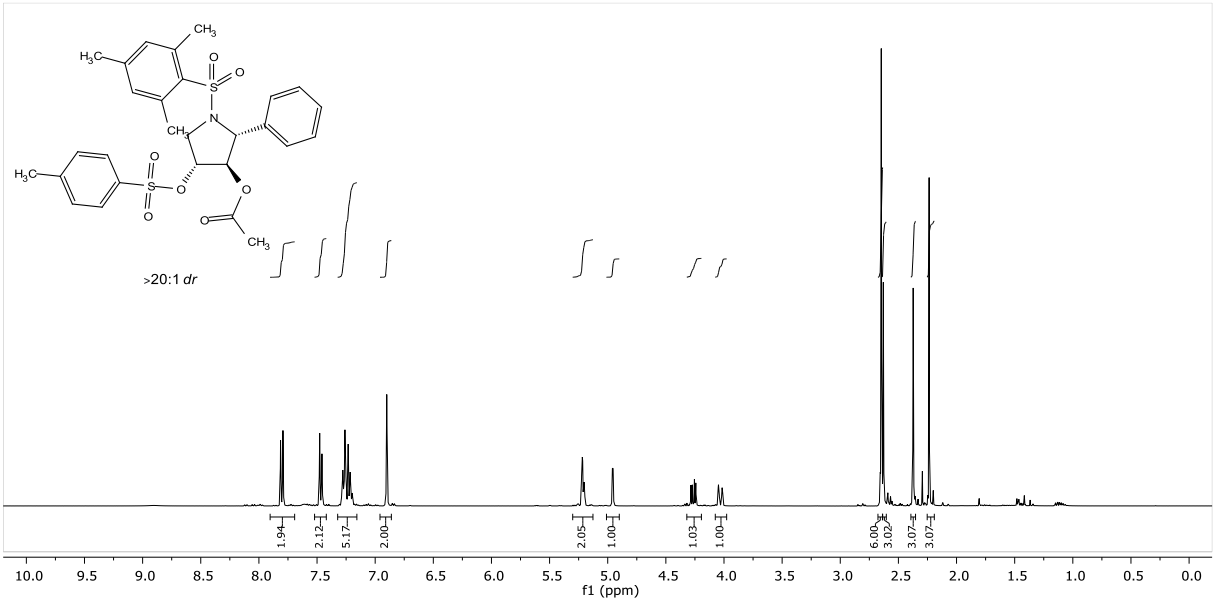
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.326	BB	0.3307	6044.92432	272.56396	50.1652
2	20.245	BB	0.4210	6005.10156	207.88297	49.8348

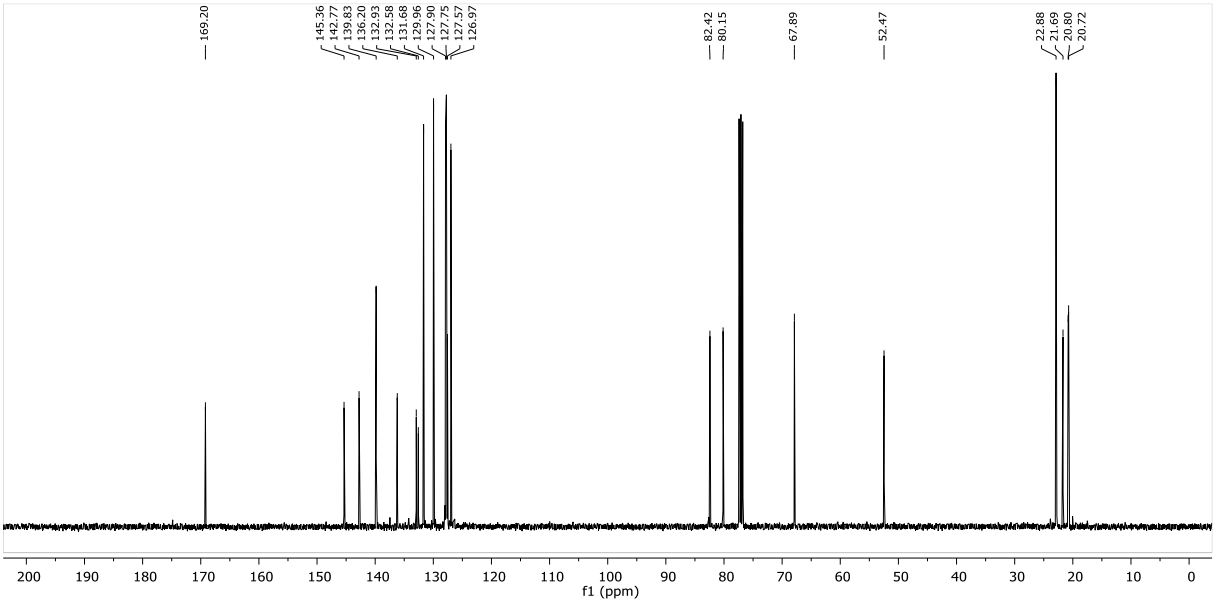


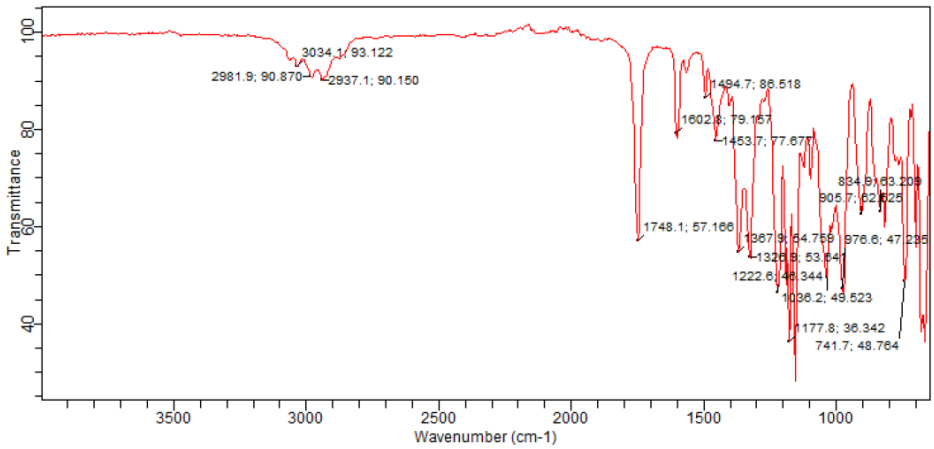
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.131	MM	0.3848	2.32558e4	1007.39606	94.4503
2	20.355	MM	0.5245	1366.44946	43.42229	5.5497

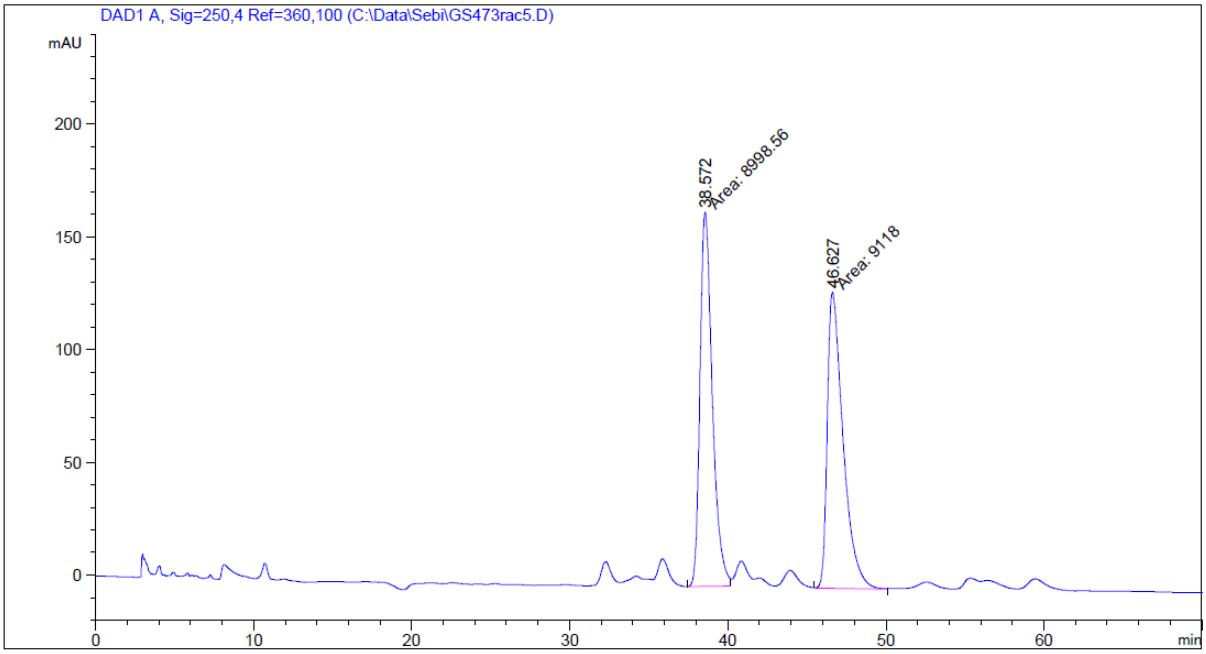
(2*R*,3*R*,4*R*)-1-(Mesitylsulfonyl)-2-phenyl-4-(tosyloxy)pyrrolidin-3-yl acetate (265):

^{1}H, ^{13}C NMR in $CDCl_3$, IR, HPLC traces

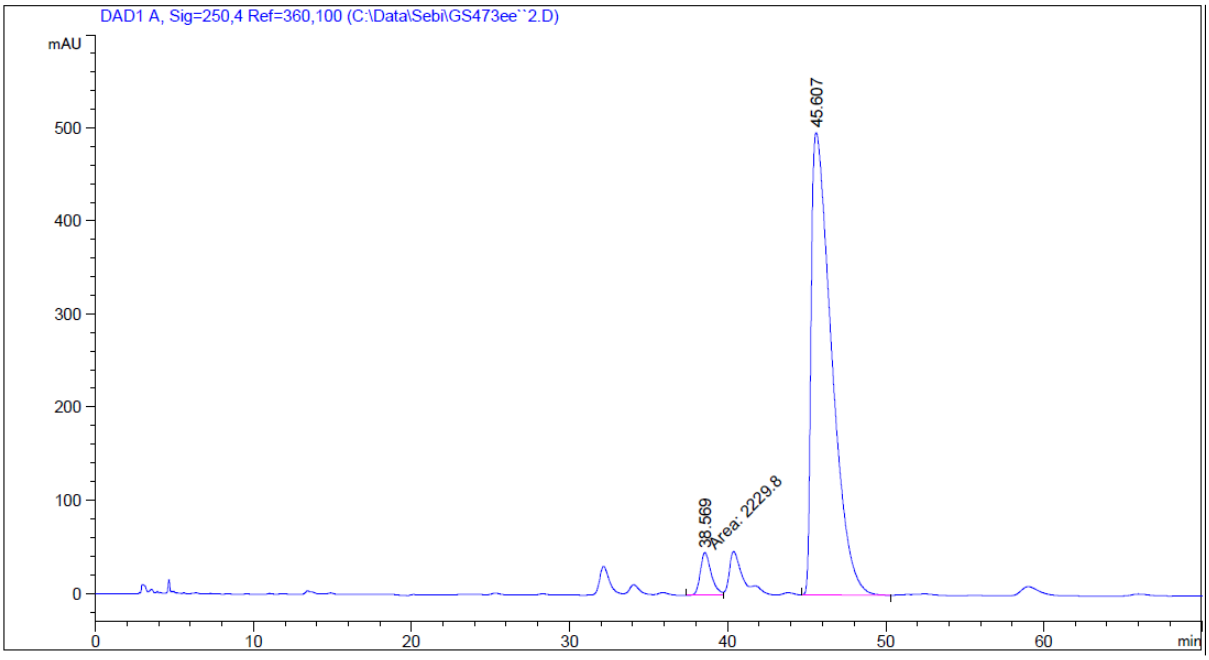






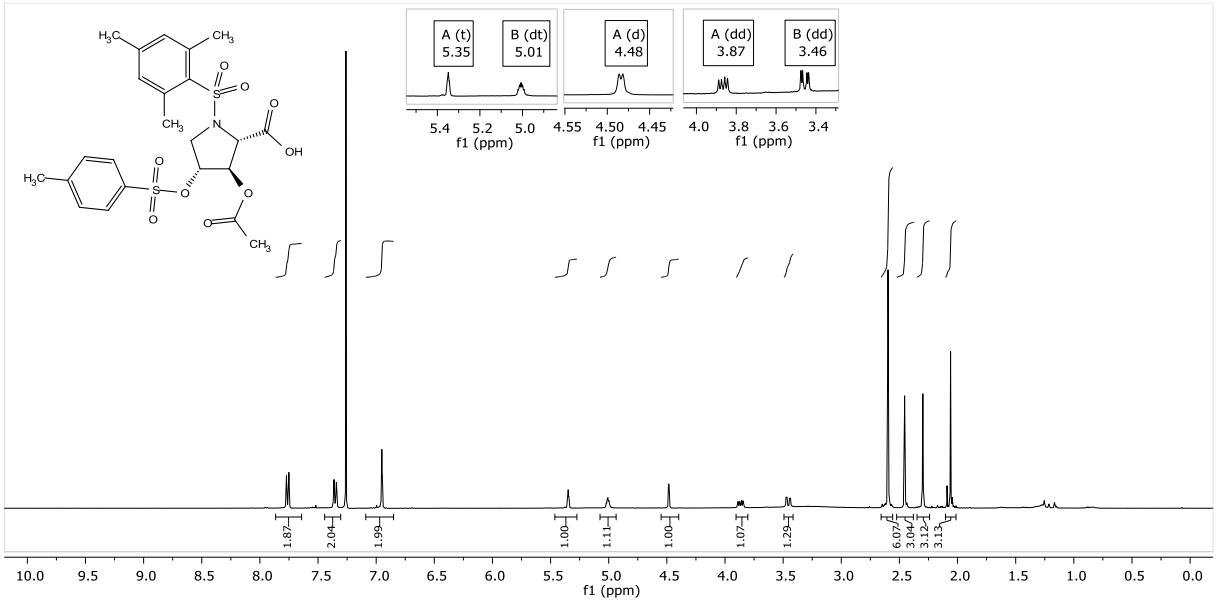


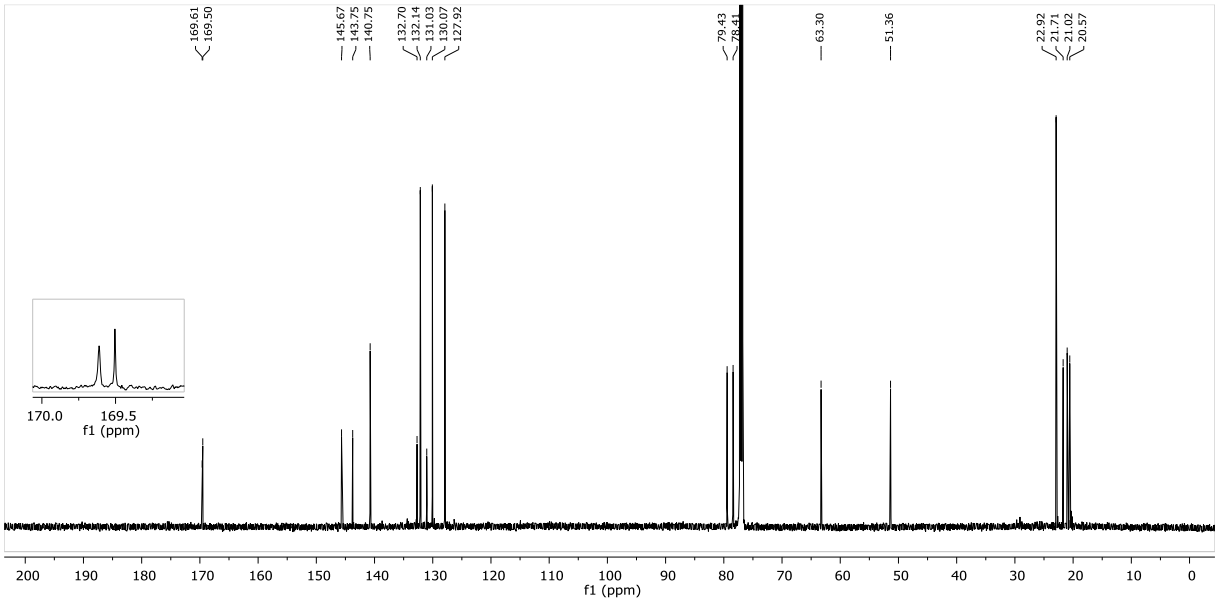
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.572	MM	0.9038	8998.55566	165.94029	49.6703
2	46.627	MM	1.1581	9118.00391	131.21573	50.3297

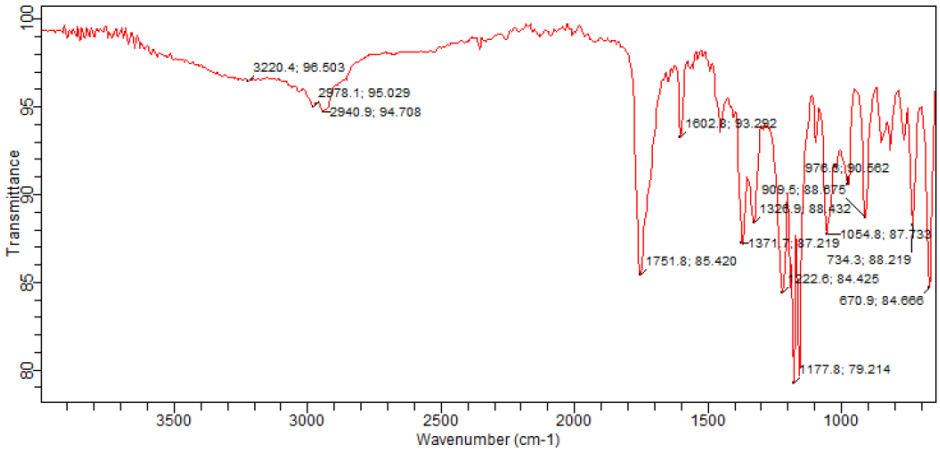


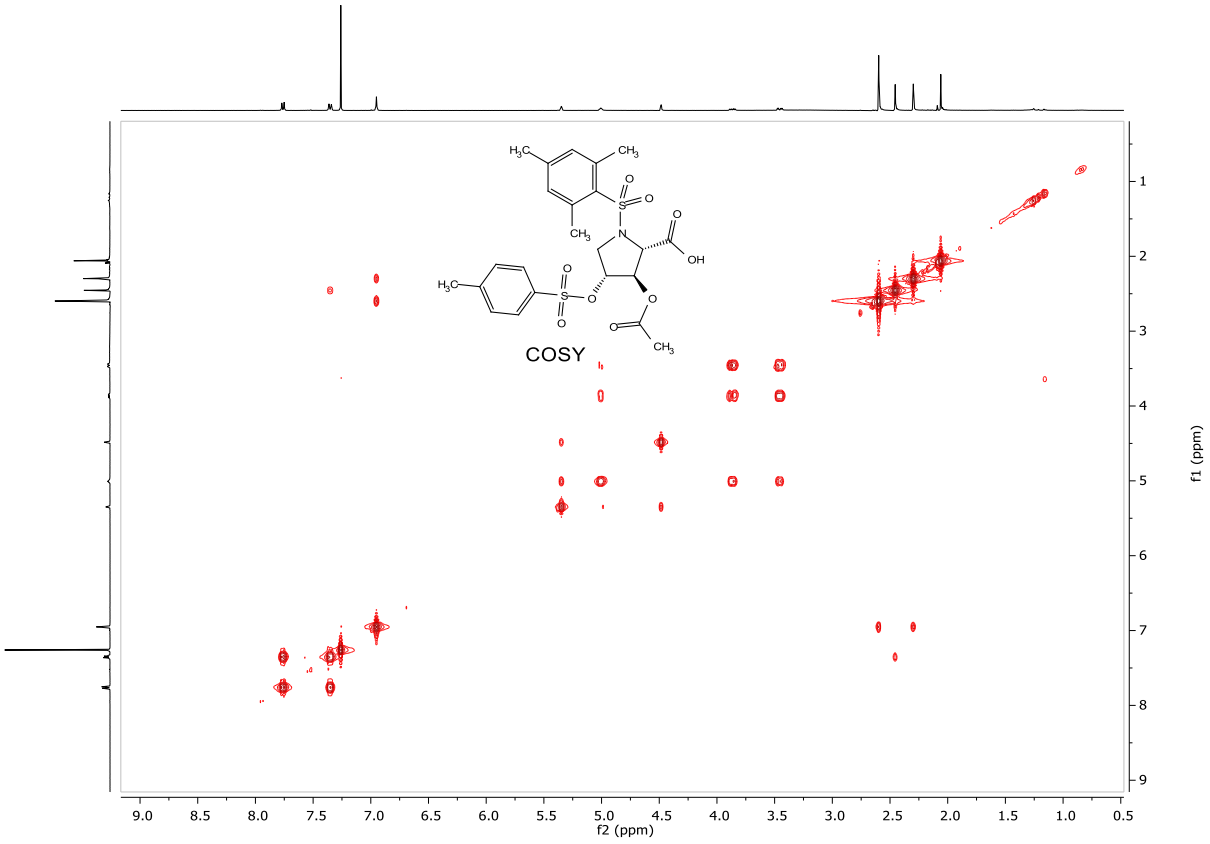
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.569	MM	0.8089	2229.80249	45.94330	4.7778
2	45.607	BB	1.2800	4.44400e4	496.63779	95.2222

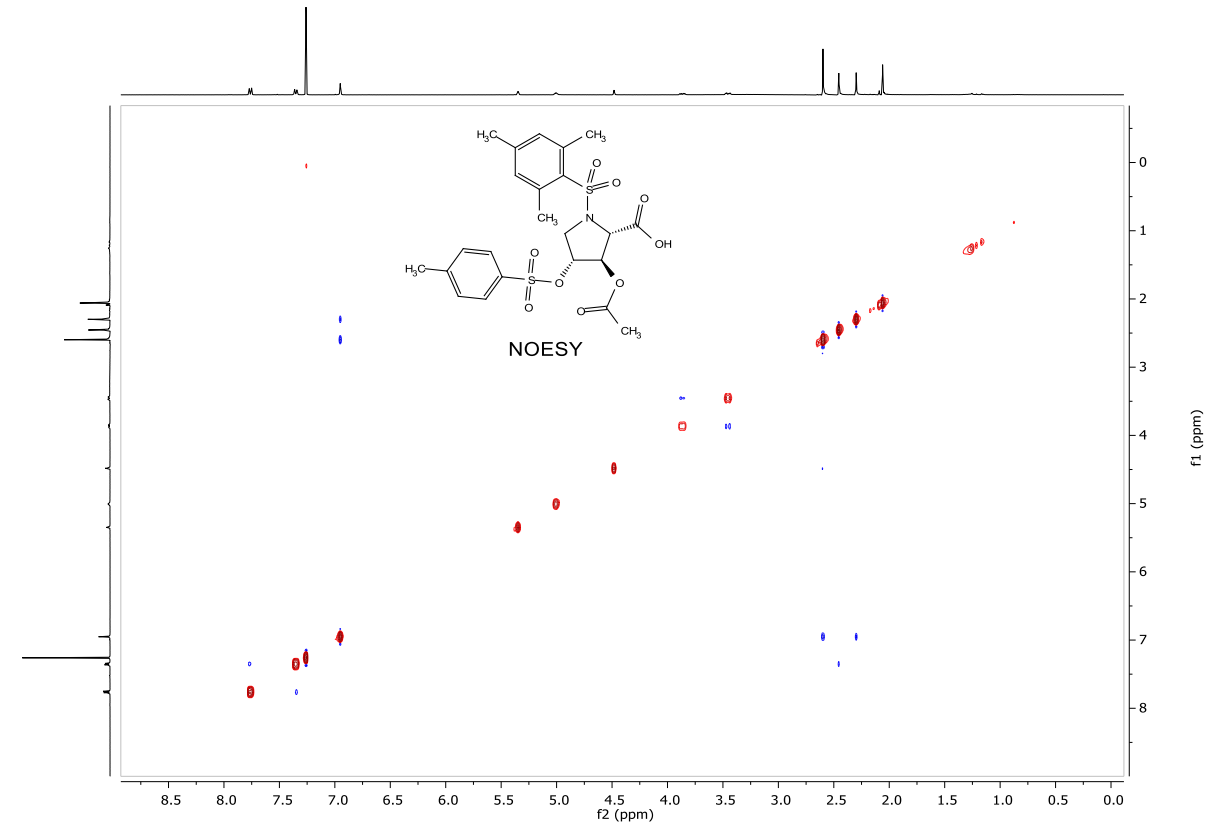
(2*S*,3*R*,4*R*)-3-Acetoxy-1-(mesitylsulfonyl)-4-(tosyloxy)pyrrolidine-2-carboxylic acid (266): ^{1}H, ^{13}C NMR in $CDCl_3$, IR, COSY, NOESY, HPLC traces

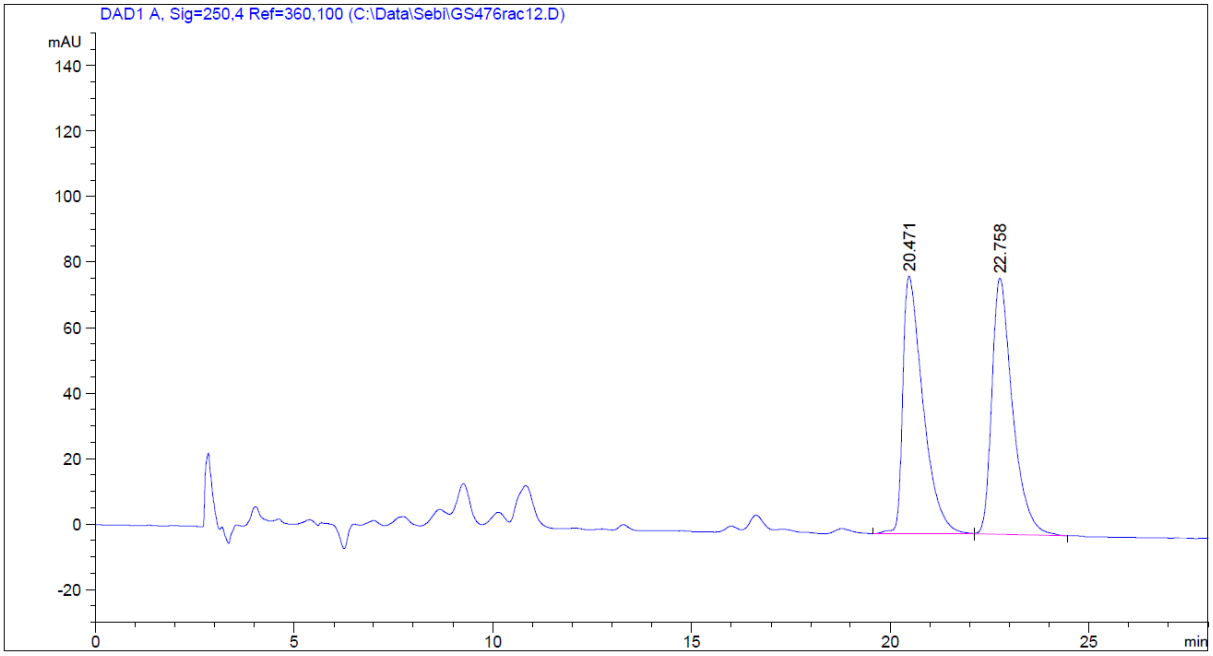




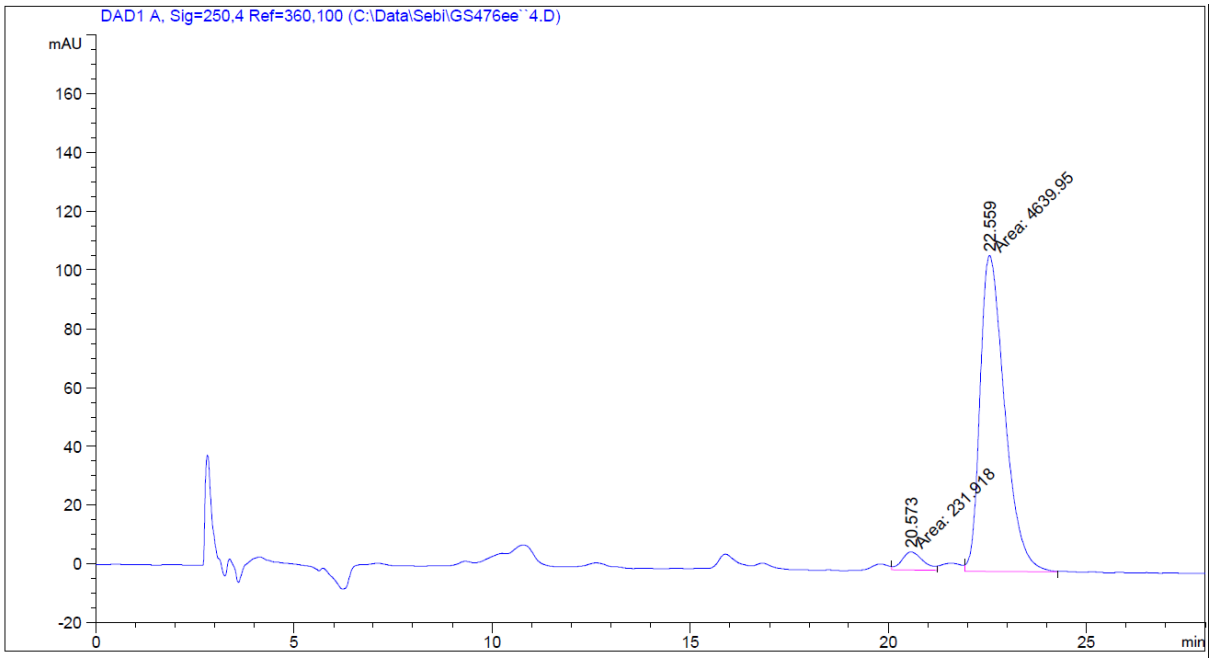



COSY
f2 (ppm)
f1 (ppm)


NOESY
f2 (ppm)
f1 (ppm)

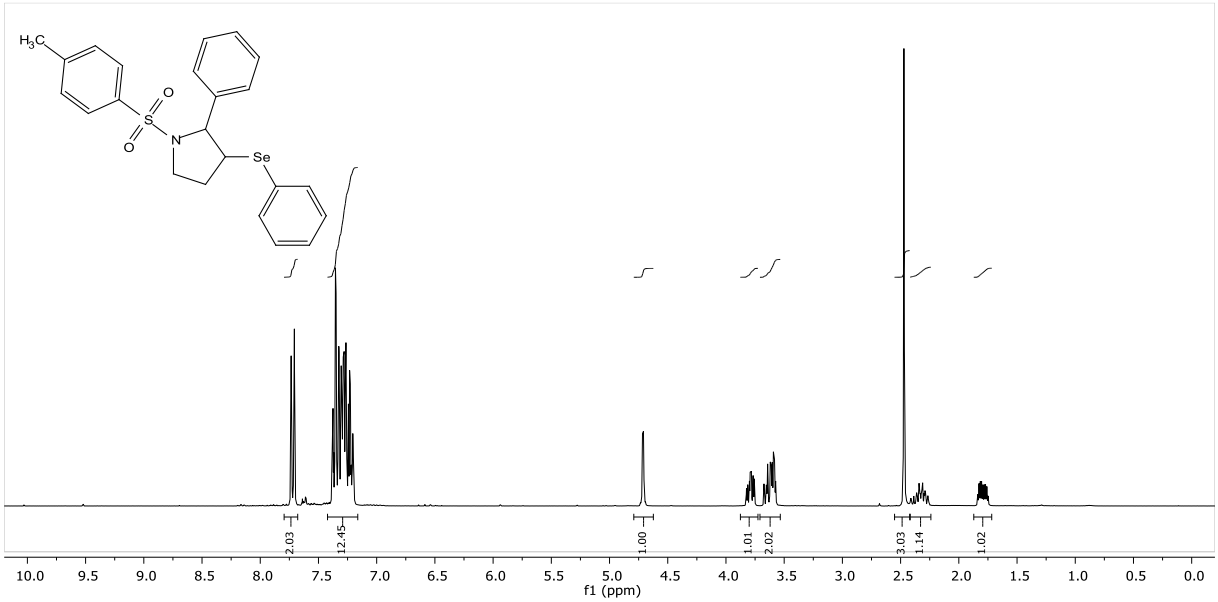


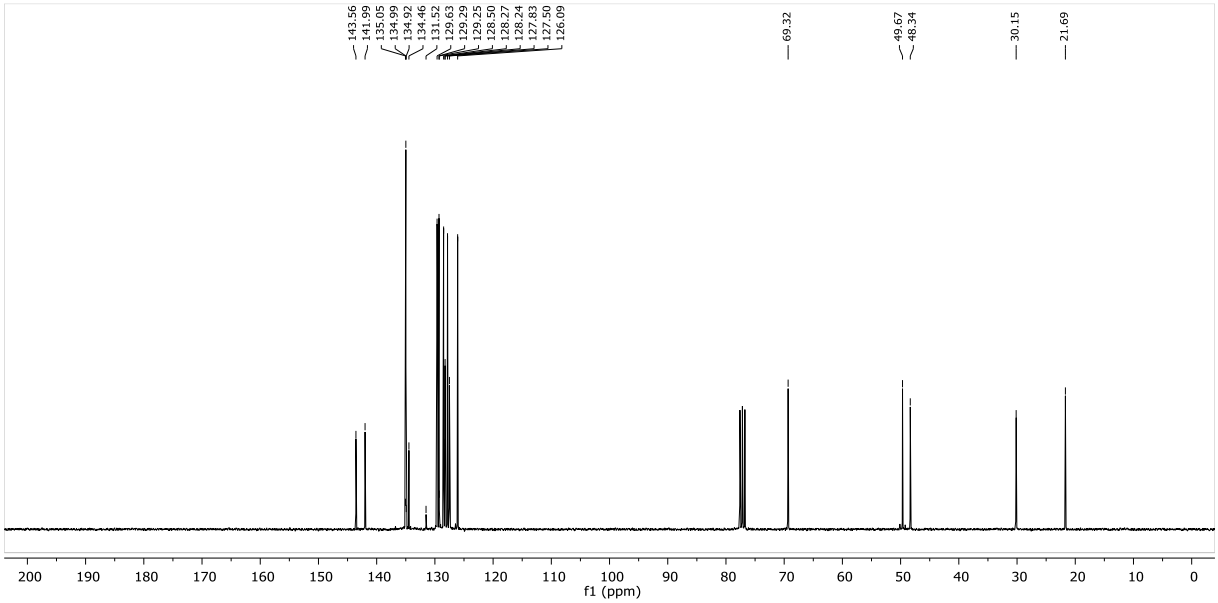
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.471	BB	0.5262	2780.21924	78.69393	49.5876
2	22.758	BB	0.5394	2826.45996	78.24615	50.4124

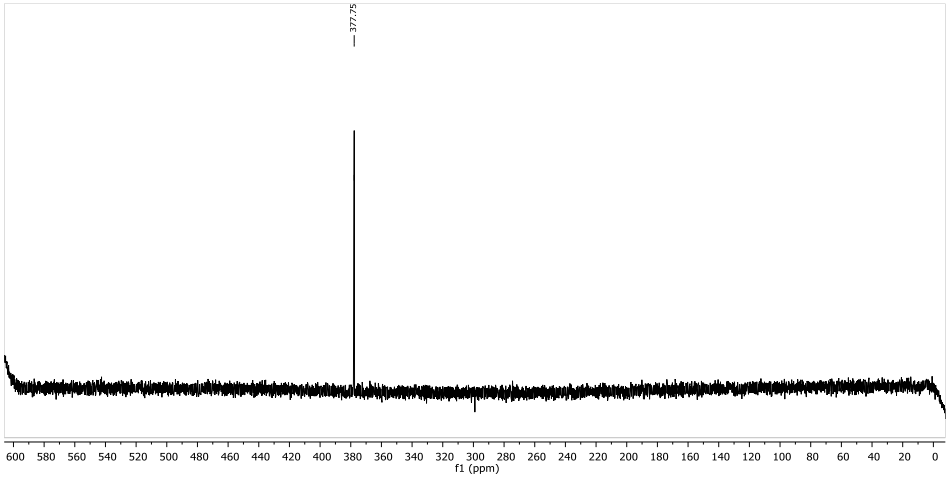


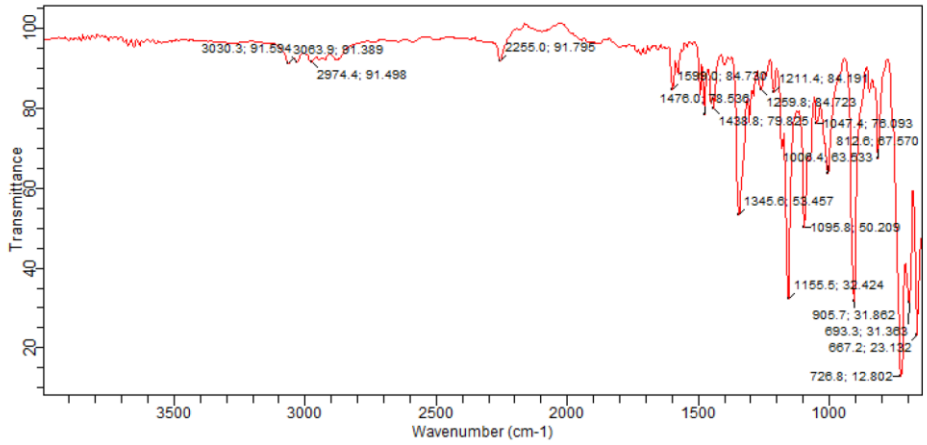
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.573	MM	0.6267	231.91832	6.16807	4.7604
2	22.559	MM	0.7196	4639.95313	107.46580	95.2396

2-Phenyl-3-(phenylselanyl)-1-tosylpyrrolidine (227): ^{1}H, ^{13}C, ^{77}Se NMR in $CDCl_3$, IR

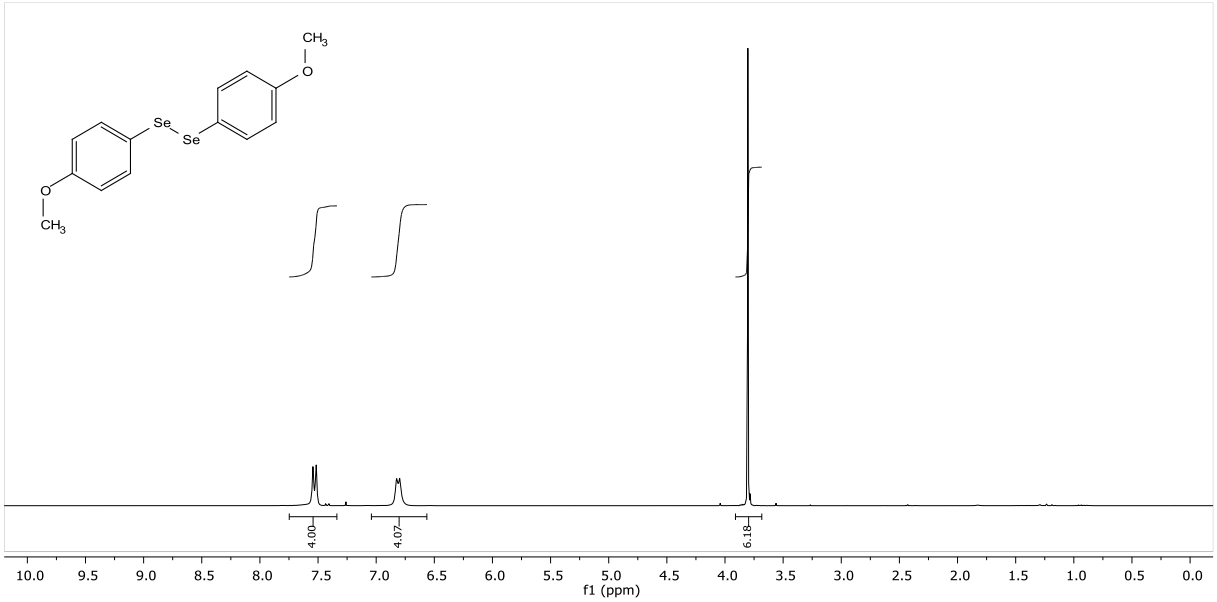


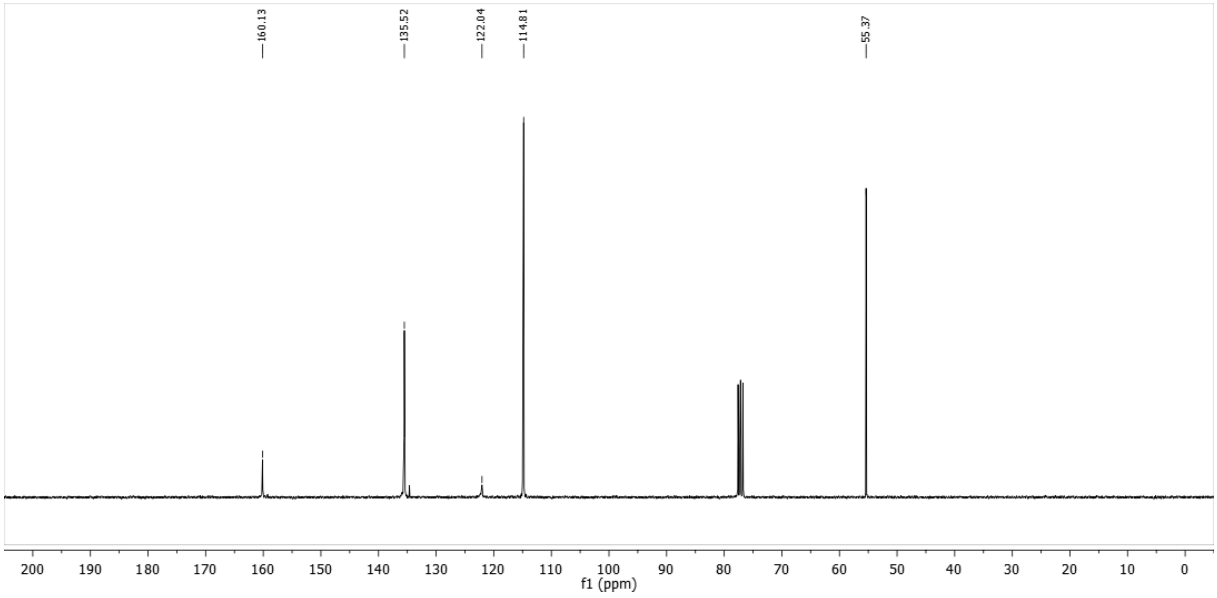


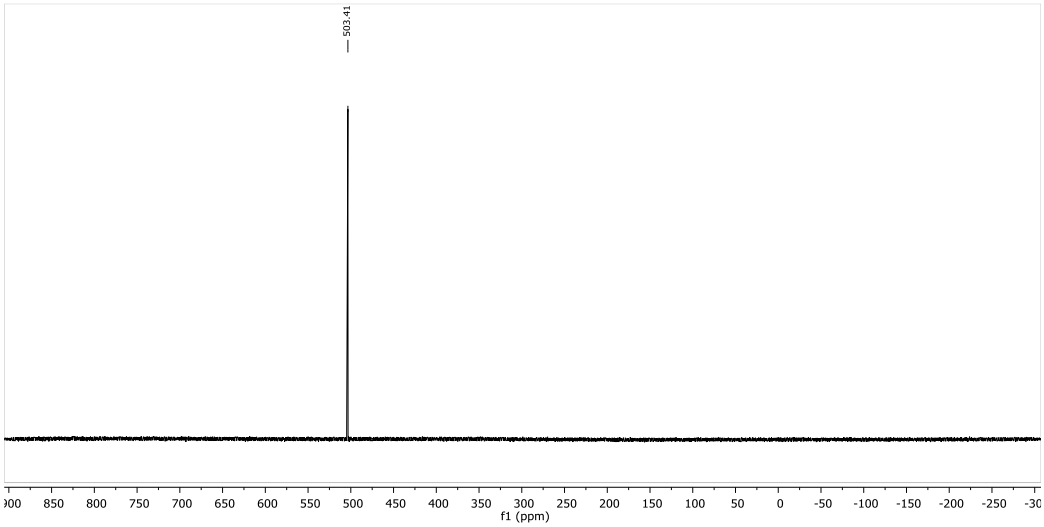


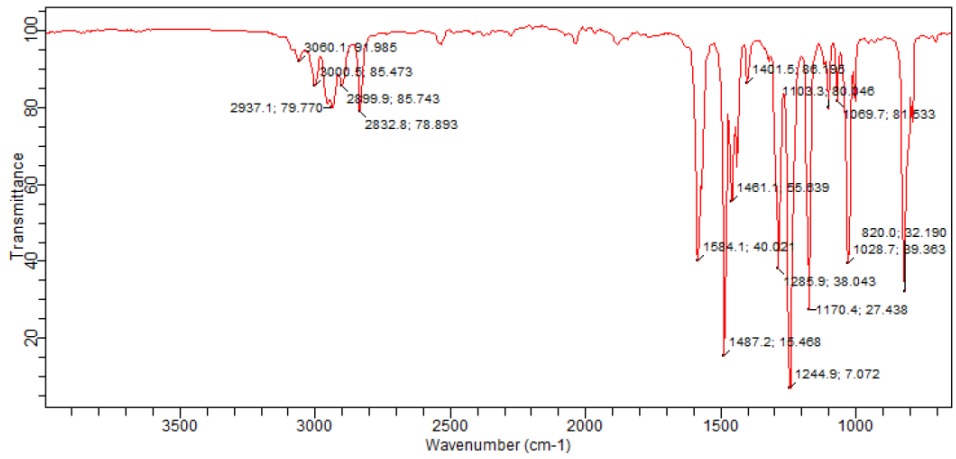

Transmittance
100
80
60
40
20
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
3030.3; 91.594
3063.9; 91.389
2974.4; 91.498
2255.0; 91.795
1598.0; 84.730
1211.4; 84.191
1476.0; 78.536
1259.8; 84.723
1438.8; 79.825
1047.4; 76.093
812.6; 67.570
1006.4; 63.533
1345.6; 53.457
1095.8; 50.209
1155.5; 32.424
905.7; 31.862
693.3; 31.363
667.2; 23.132
726.8; 12.802

1,2-Bis(4-methoxyphenyl)diselane (13^{OMe}): ^{1}H, ^{13}C, ^{77}Se NMR in $CDCl_3$, IR

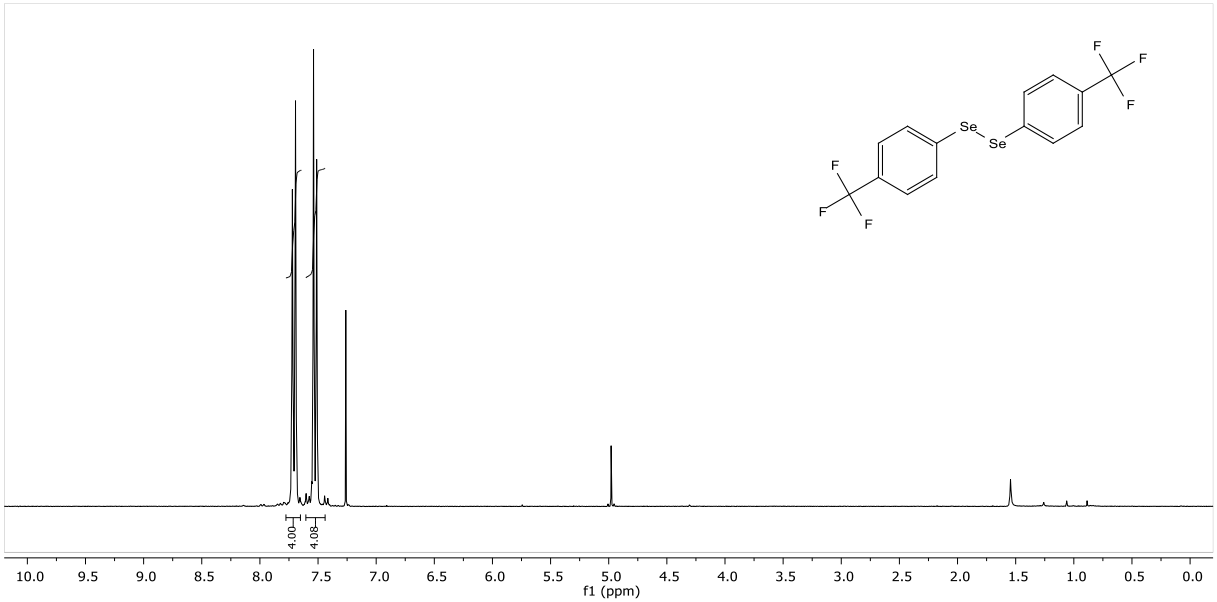


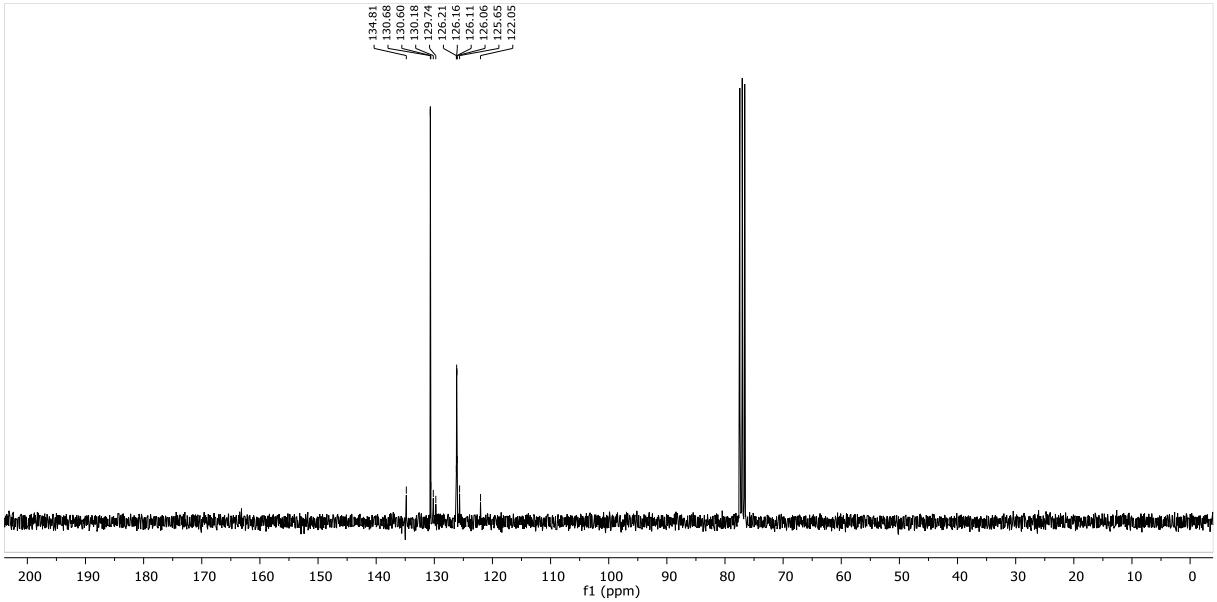


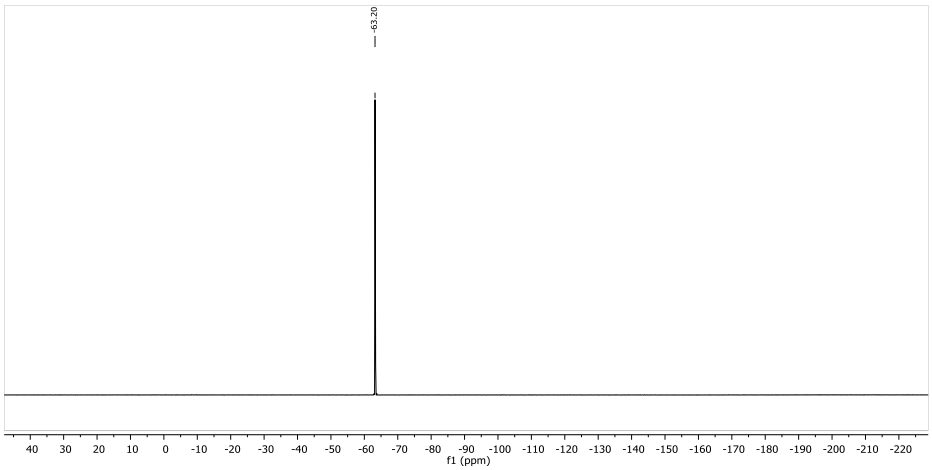


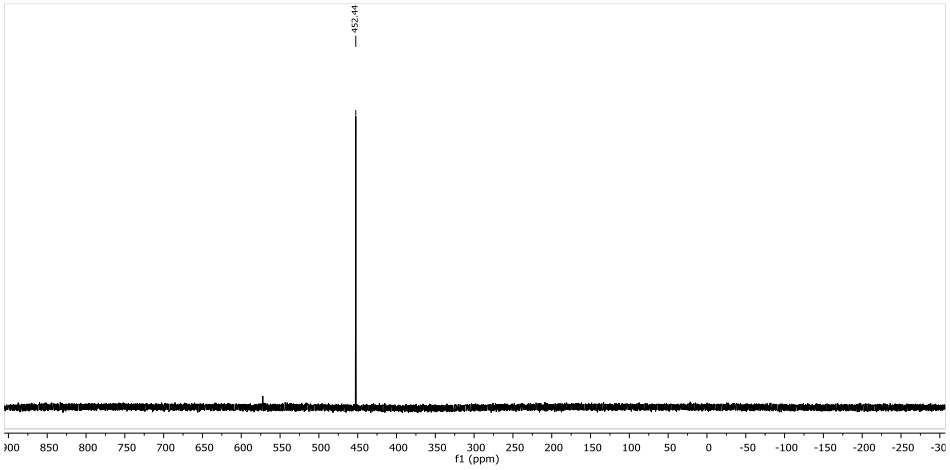

Transmittance
100
80
60
40
20
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
3060.1; 91.985
3000.6; 85.473
2937.1; 79.770
2899.9; 85.743
2832.8; 78.893
1401.5; 86.195
1103.3; 80.946
1069.7; 81.633
1461.1; 85.639
820.0; 32.190
1028.7; 39.363
1584.1; 40.021
1285.9; 38.043
1170.4; 27.438
1487.2; 15.468
1244.9; 7.072

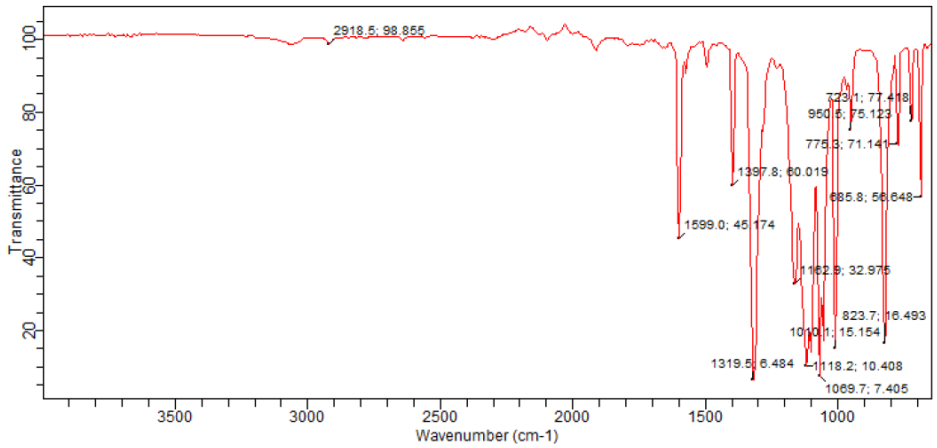
1,2-Bis(4-(trifluoromethyl)phenyl)diselane (13^{CF_3}): ^{1}H, ^{13}C, ^{19}F, ^{77}Se NMR in $CDCl_3$, IR



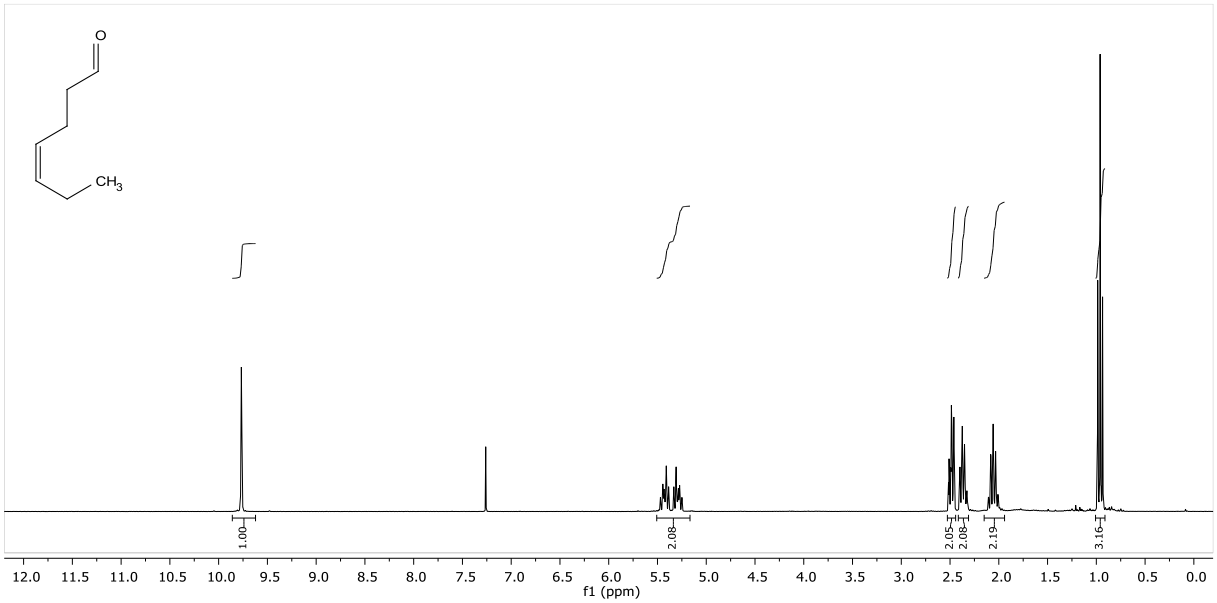


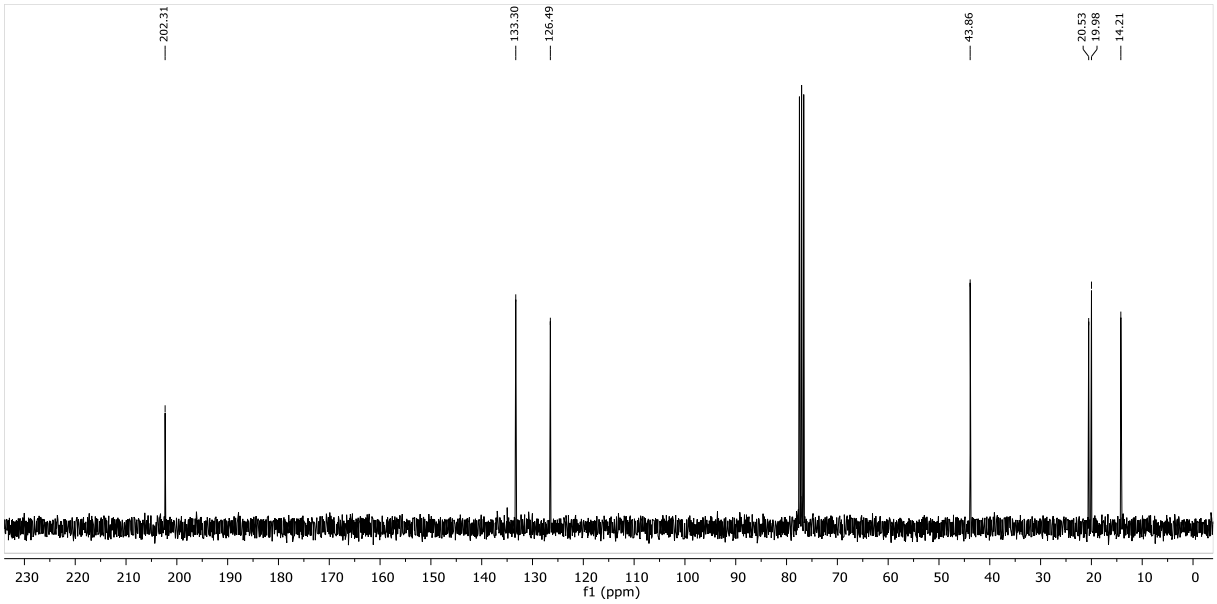


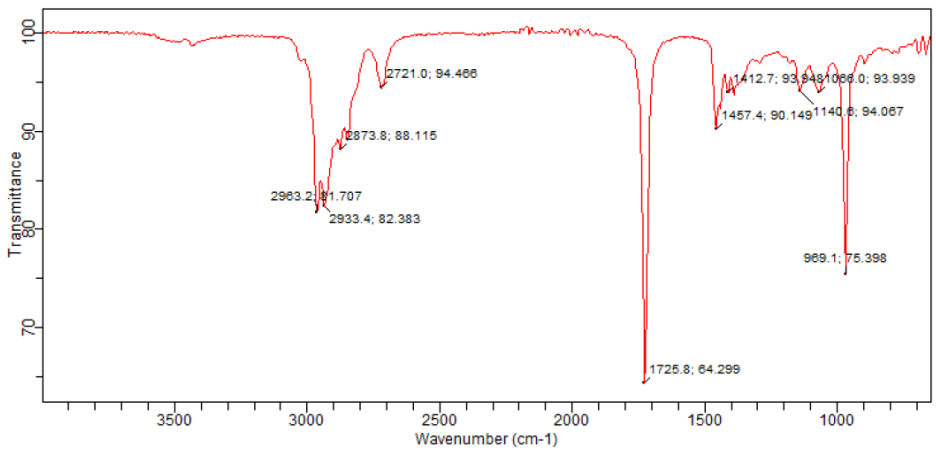

452.44
f1 (ppm)


2918.5; 98.855
1599.0; 45.174
1397.8; 60.019
1319.5; 6.484
1162.9; 32.975
1118.2; 10.408
1069.7; 7.405
1010.1; 15.154
950.6; 75.123
823.7; 16.493
775.3; 71.141
723.1; 77.418
685.8; 56.648
Transmittance
Wavenumber (cm-1)

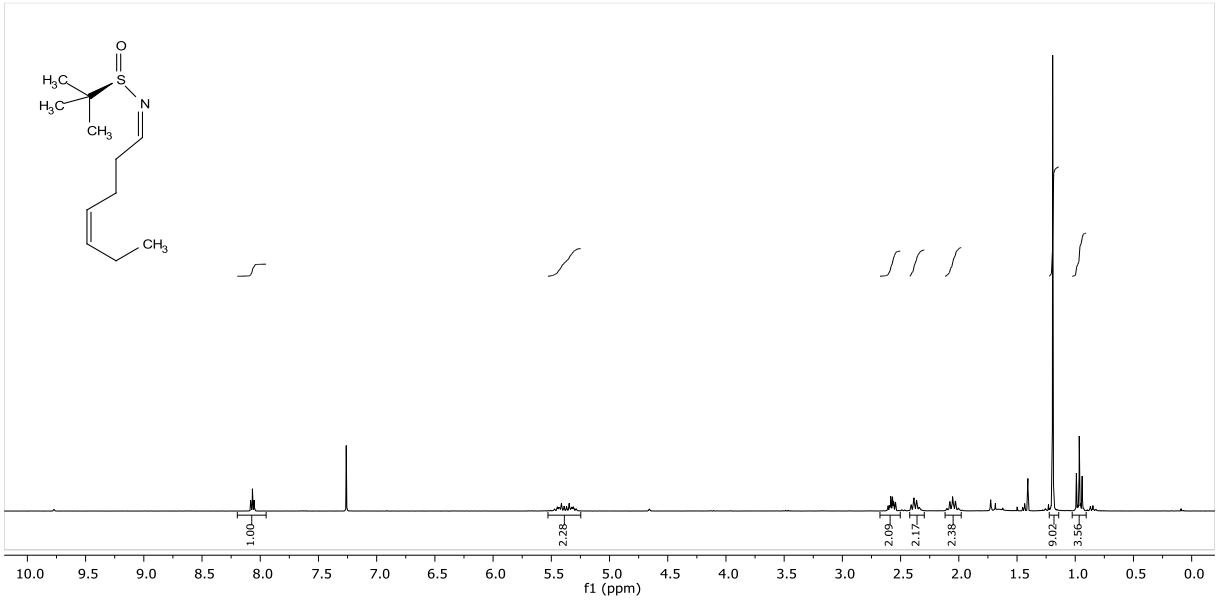
(*Z*)-Hept-4-enal (132): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

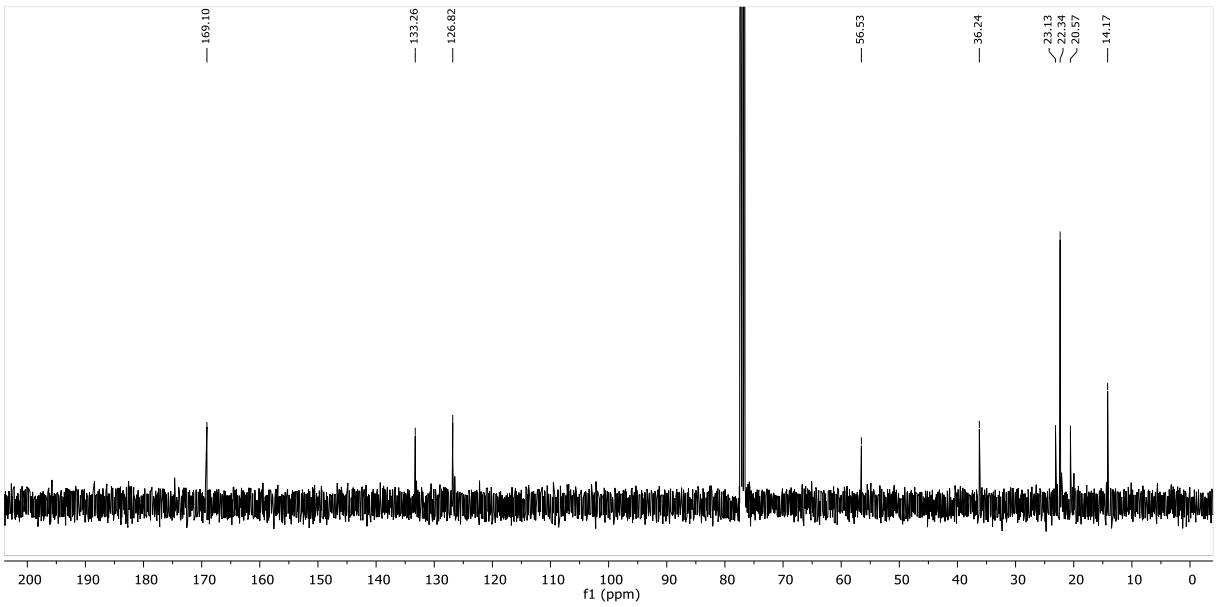


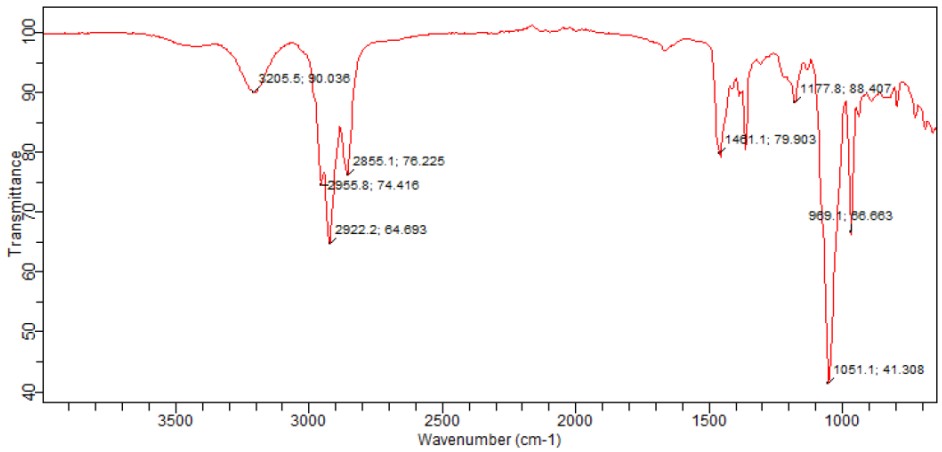




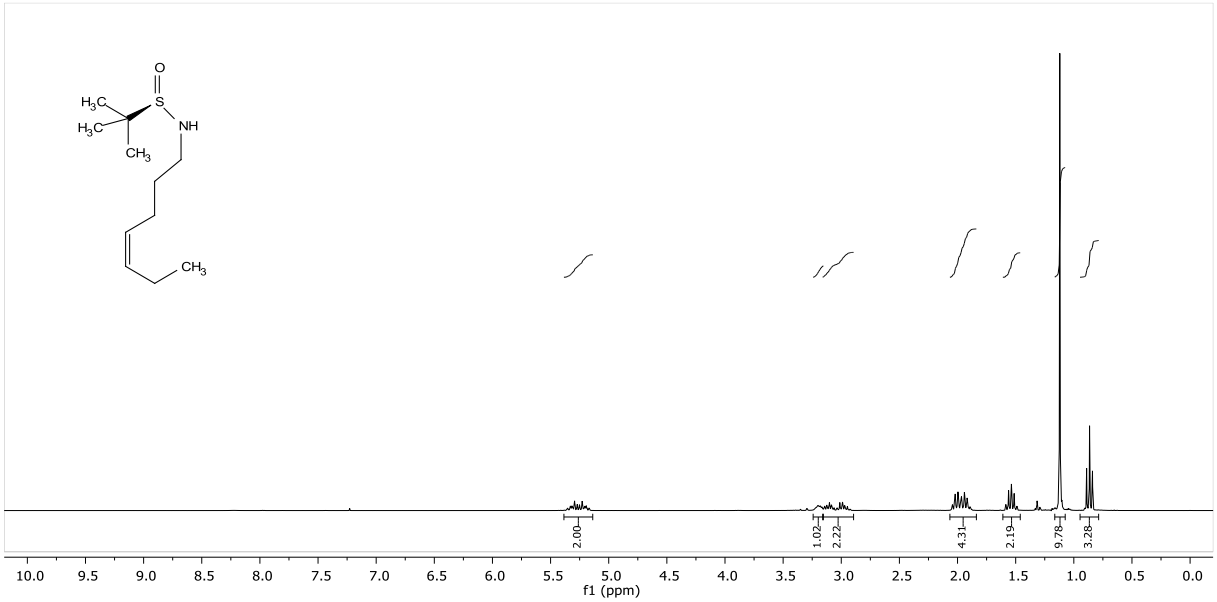
(*R*)-*N*-((1*E*,4*Z*)-Hept-4-en-1-ylidene)-2-methylpropane-2-sulfinamide (134): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

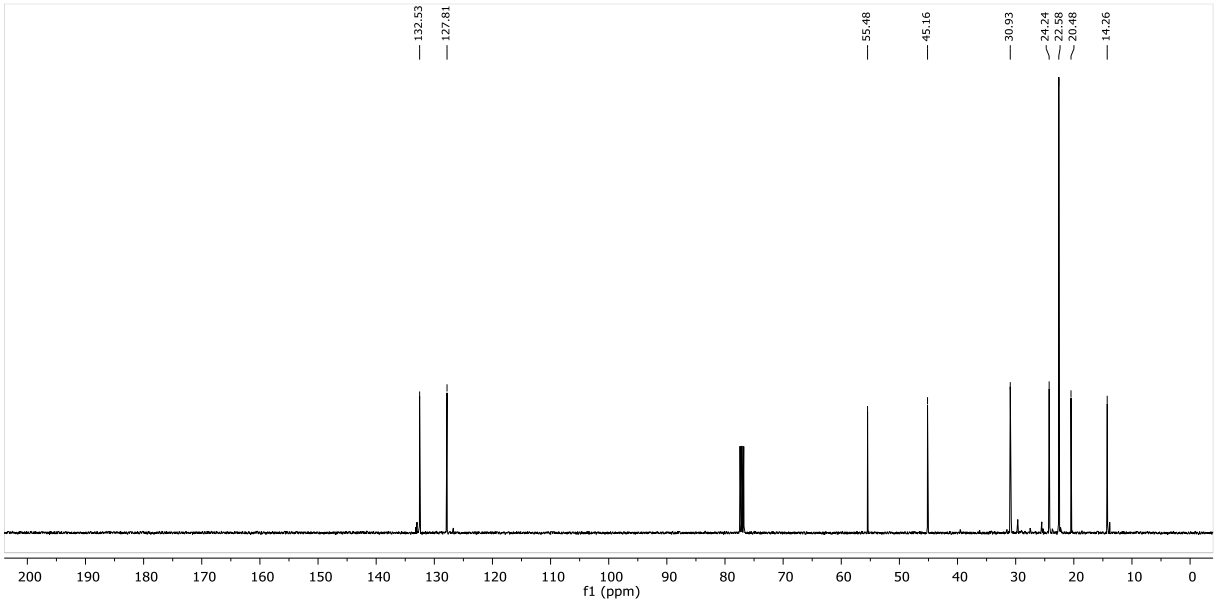


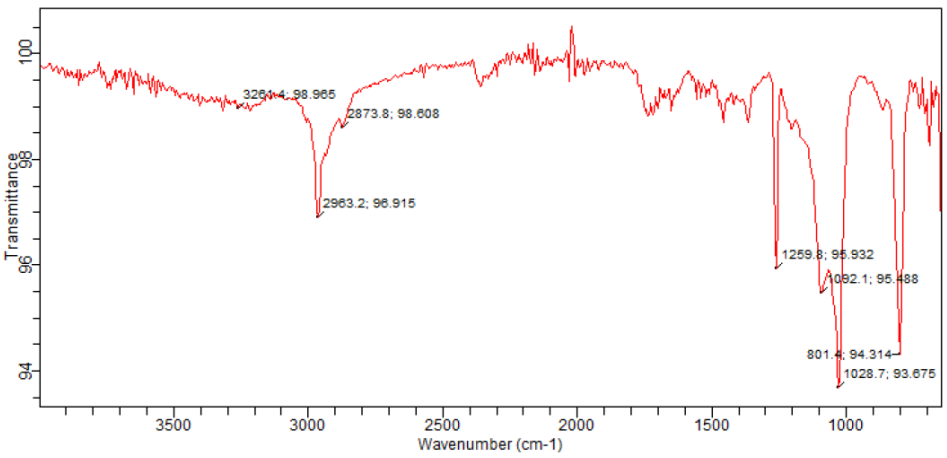




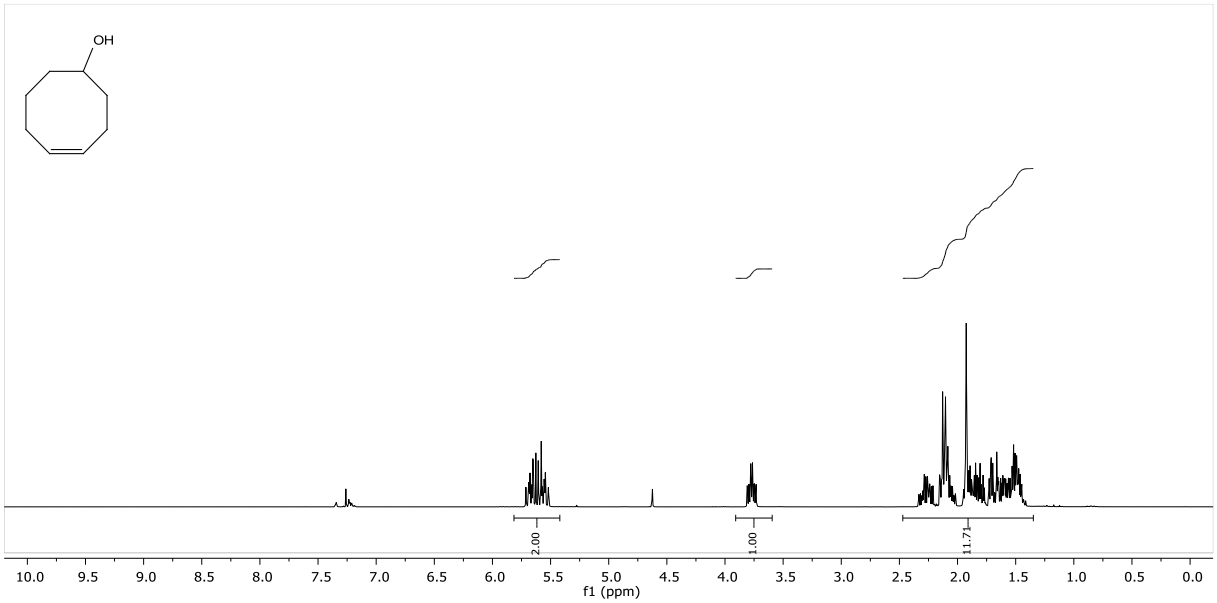
(*R*,*Z*)-*N*-(Hept-4-en-1-yl)-2-methylpropane-2-sulfinamide (135): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

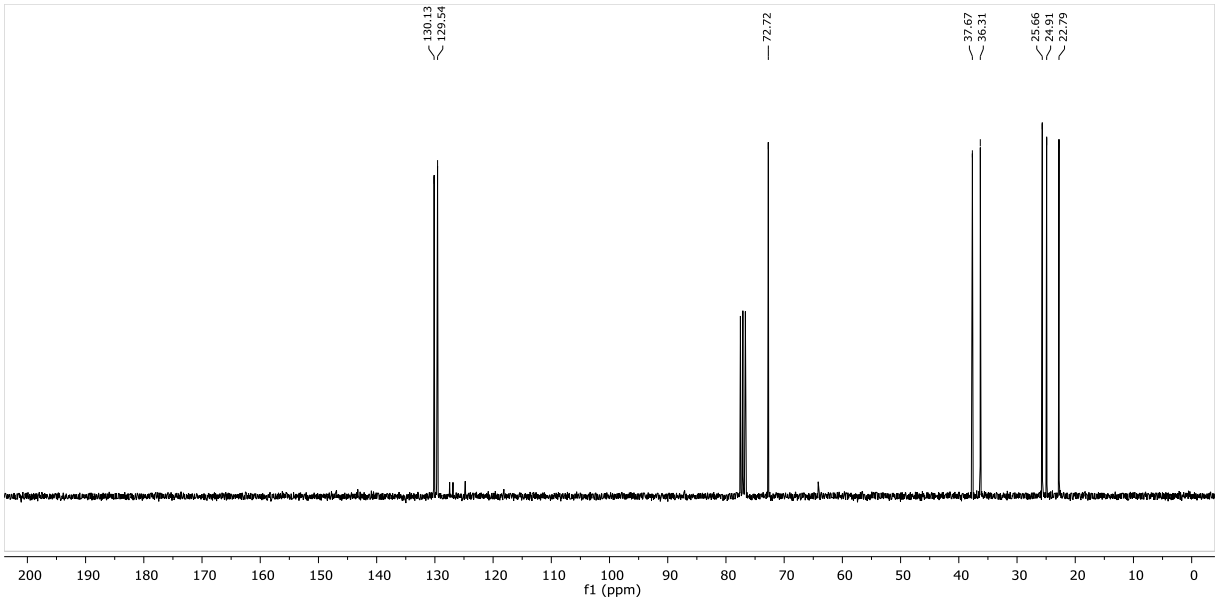


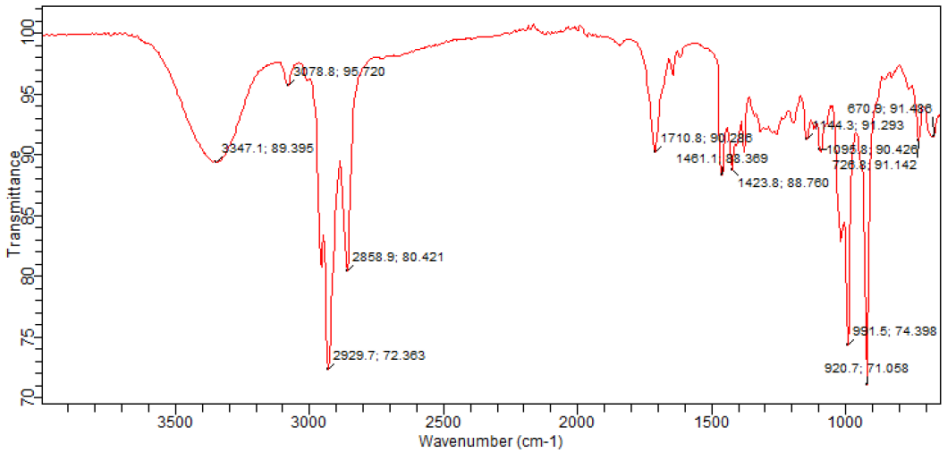




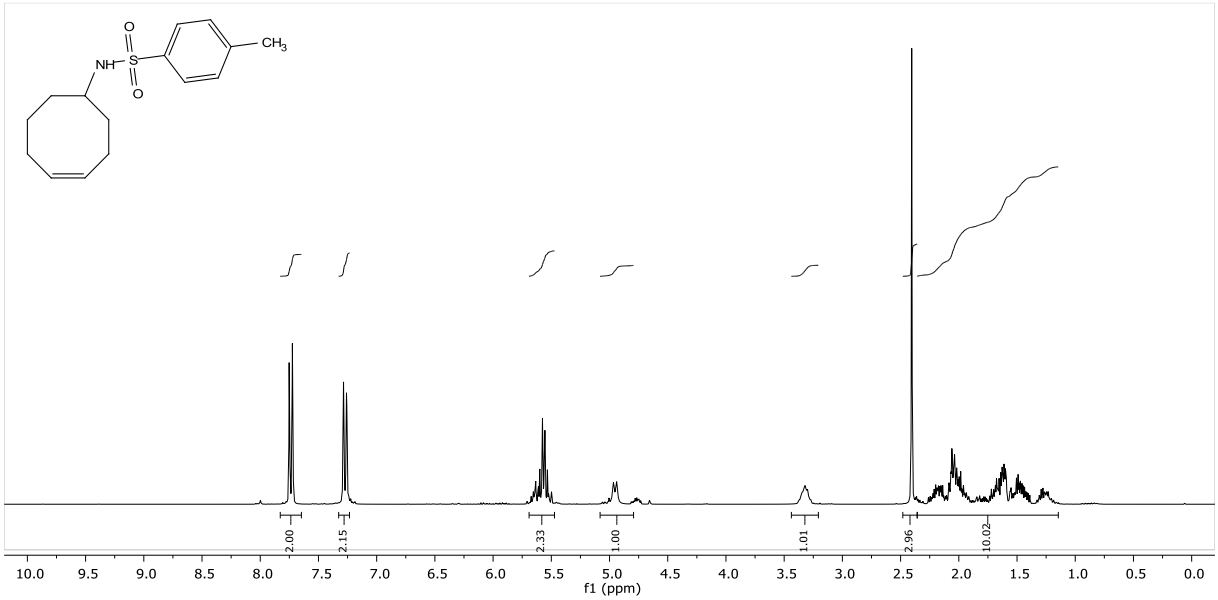
(*Z*)-Cyclooct-4-en-1-ol (173^{S}): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

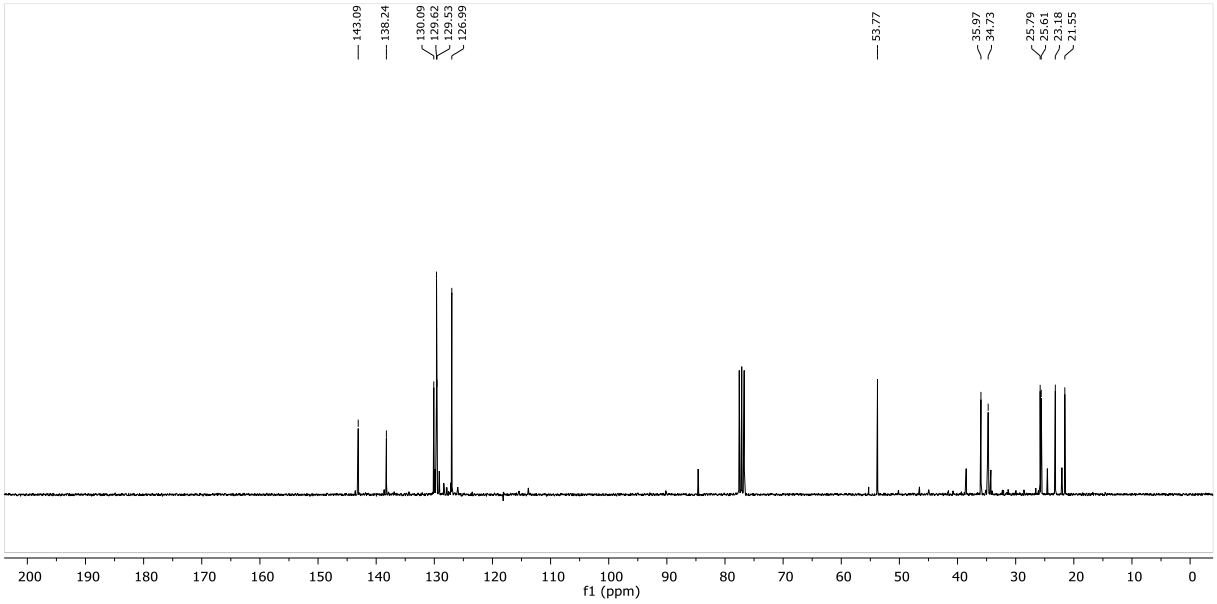


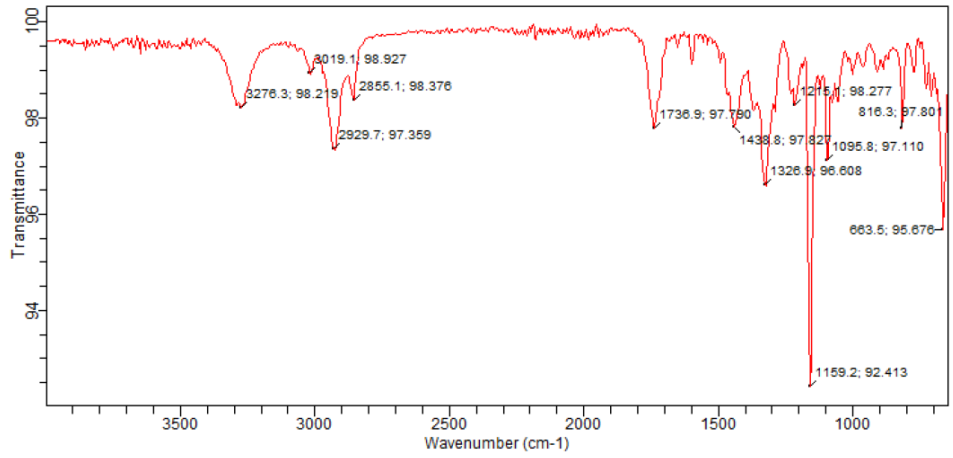




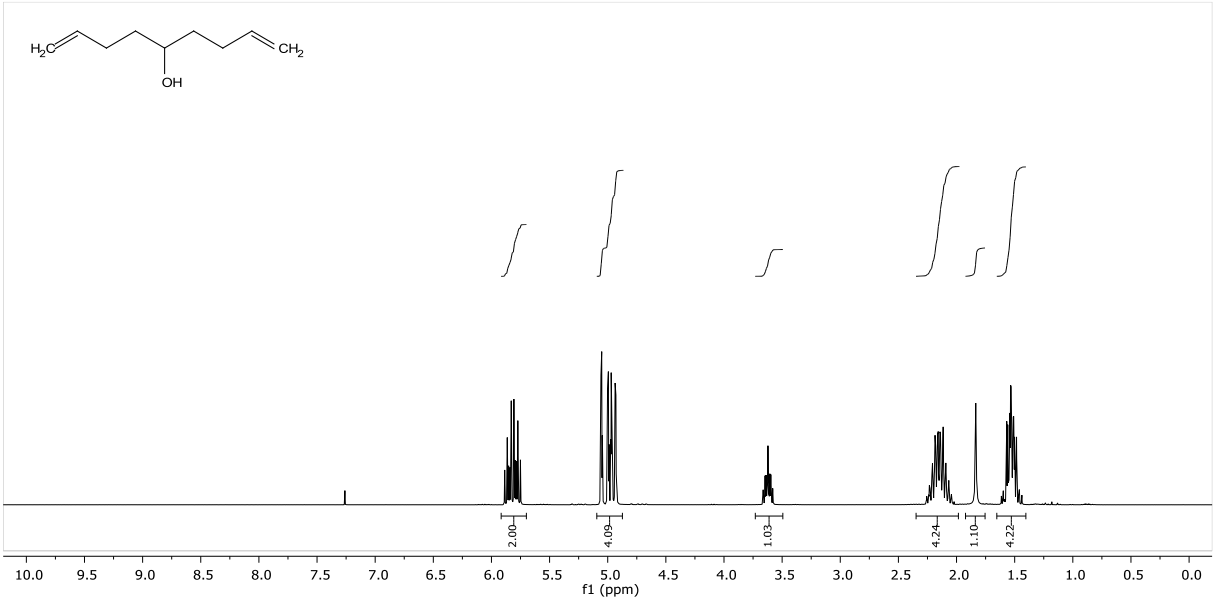
(*Z*)-*N*-(Cyclooct-4-en-1-yl)-4-methylbenzenesulfonamide (173): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

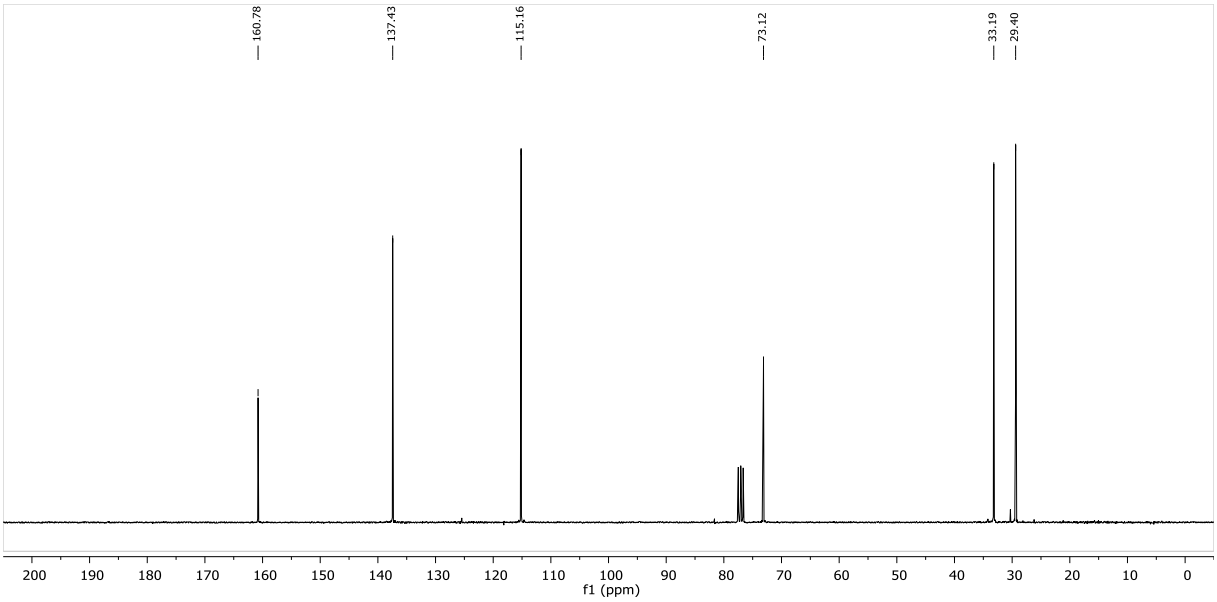


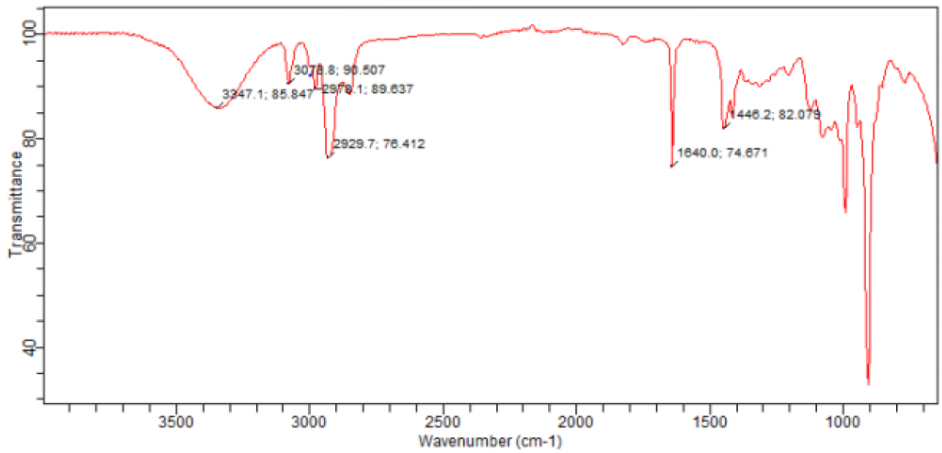




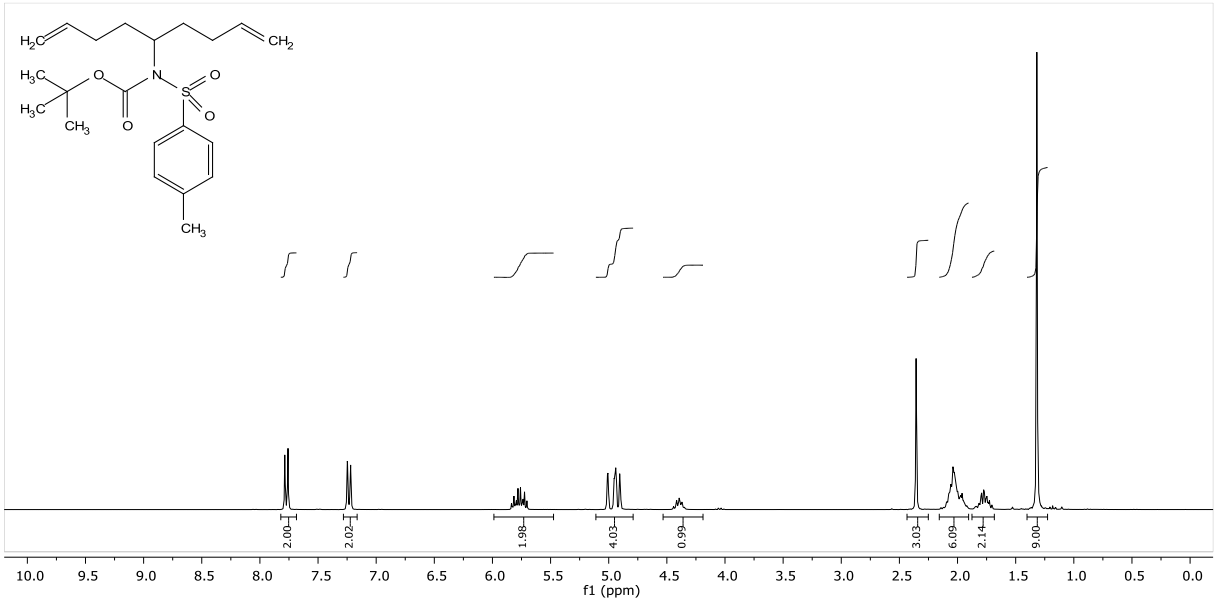
Nona-1,8-dien-5-ol (172^{S1}): ^{1}H, ^{13}C NMR in $CDCl_3$, IR[113]

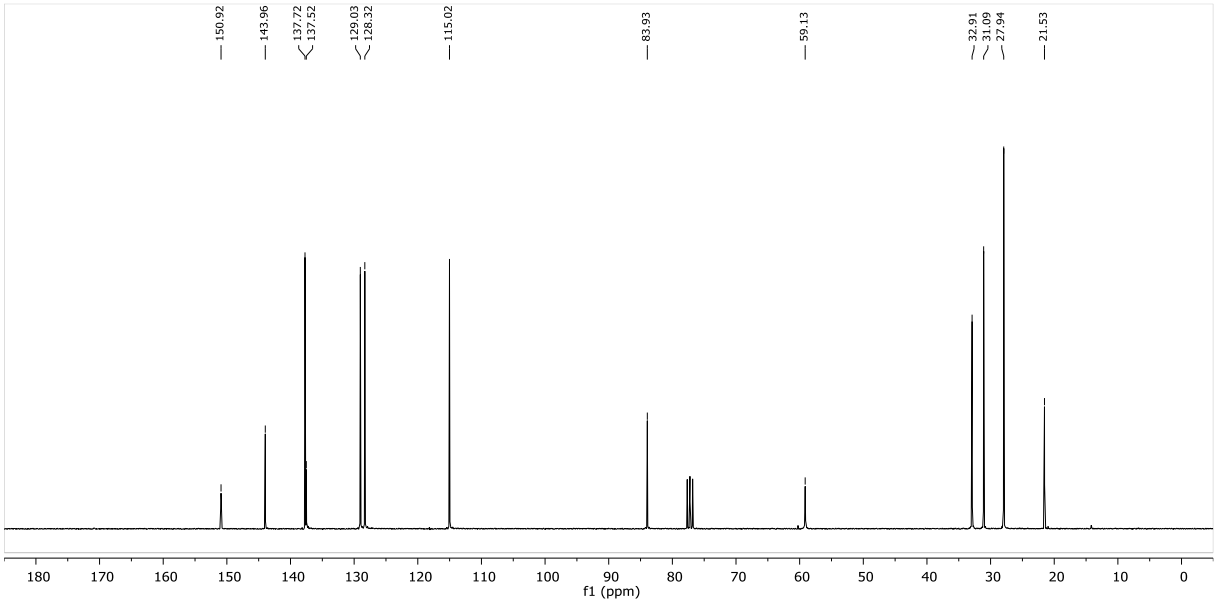


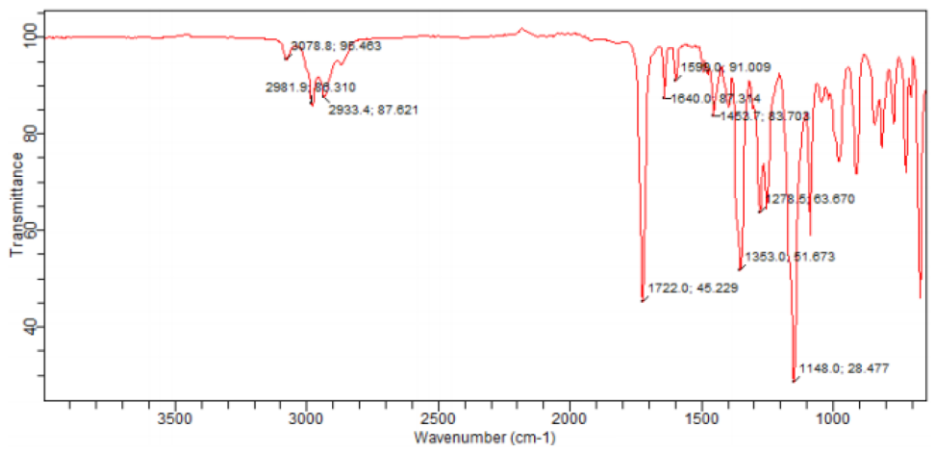




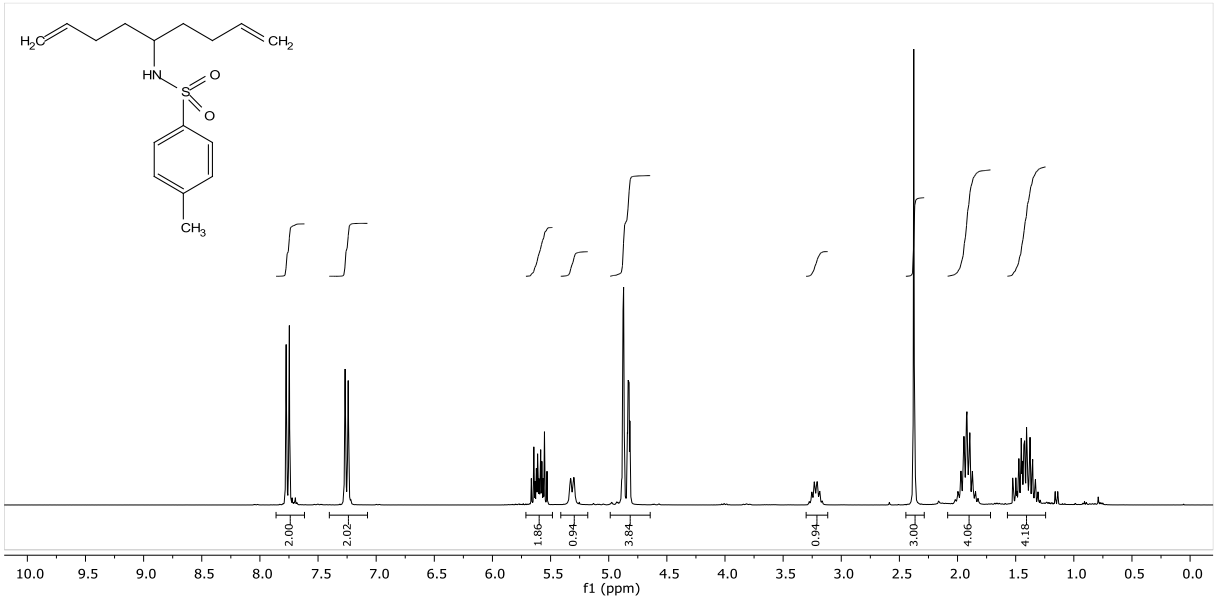
***Tert*-Butyl nona-1,8-dien-5-yl(tosyl)carbamate (172^{S2}):** ^{1}H, ^{13}C NMR in $CDCl_3$, IR[113]

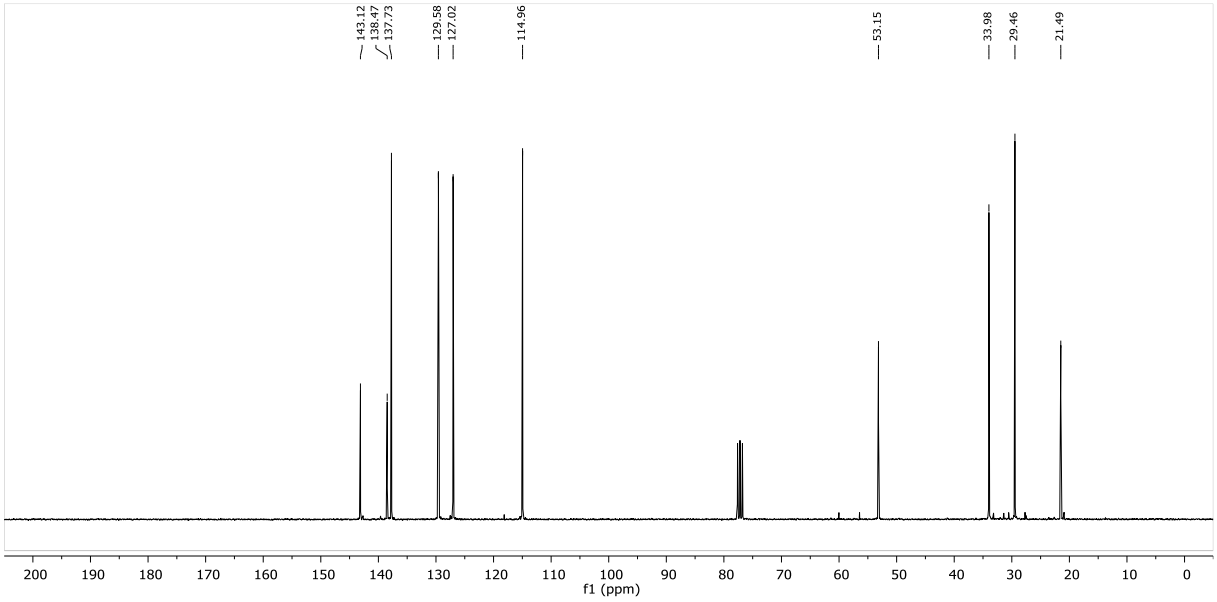


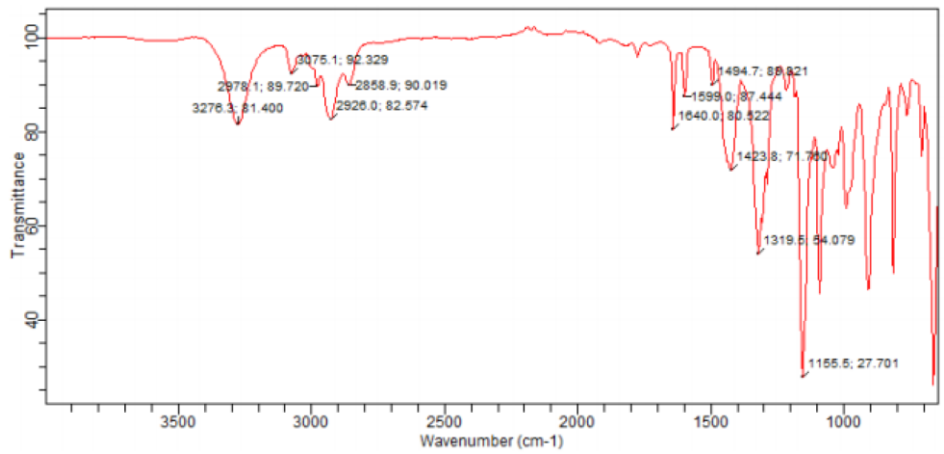




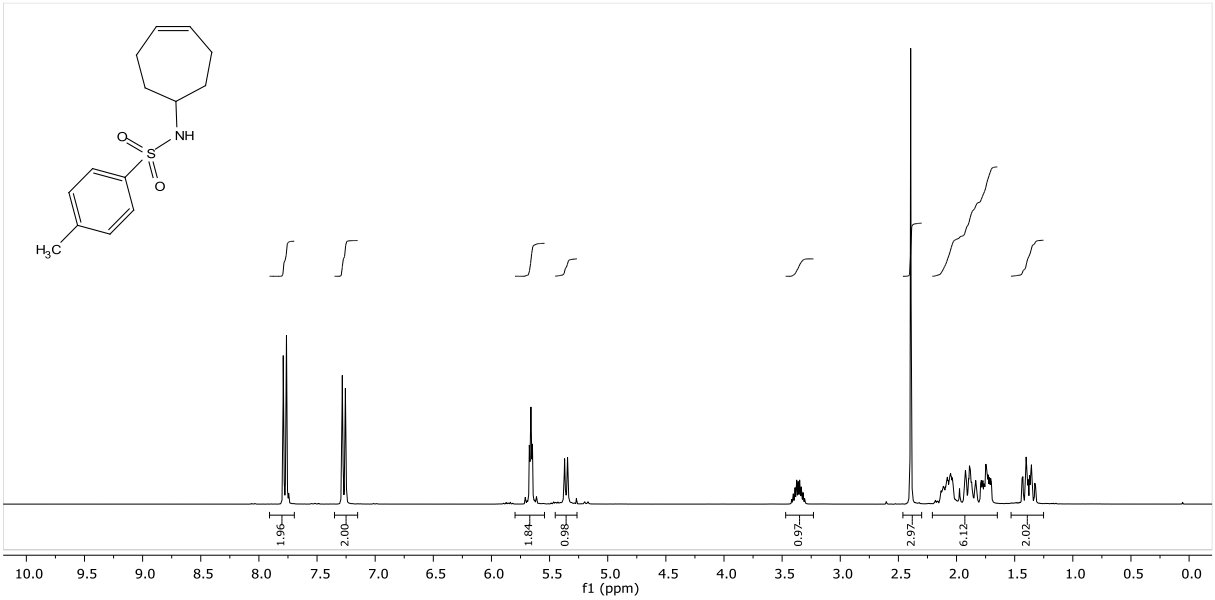
4-Methyl-*N*-(nona-1,8-dien-5-yl)benzenesulfonamide (172^{S3}): ^{1}H, ^{13}C NMR in $CDCl_3$, IR[113]

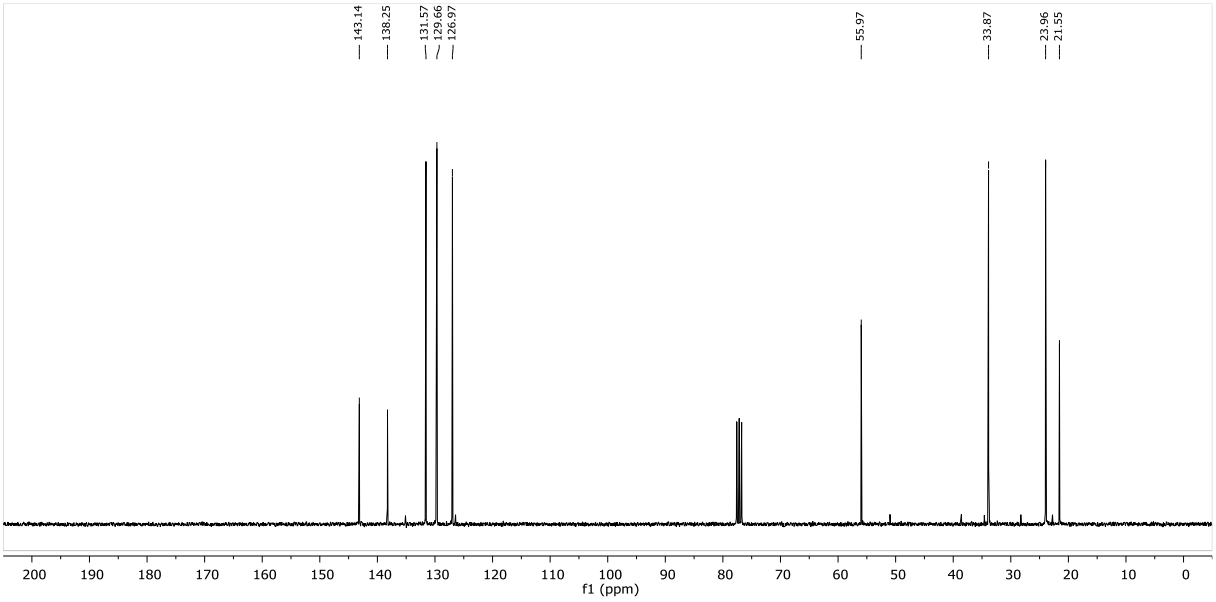


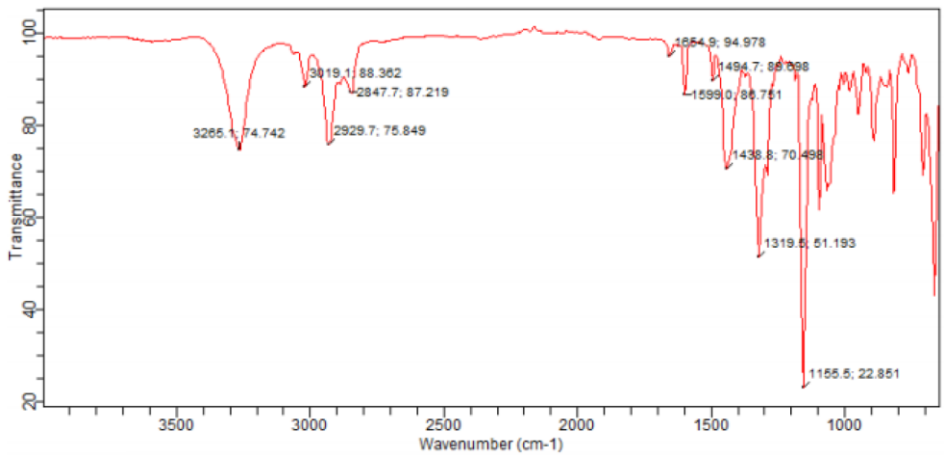




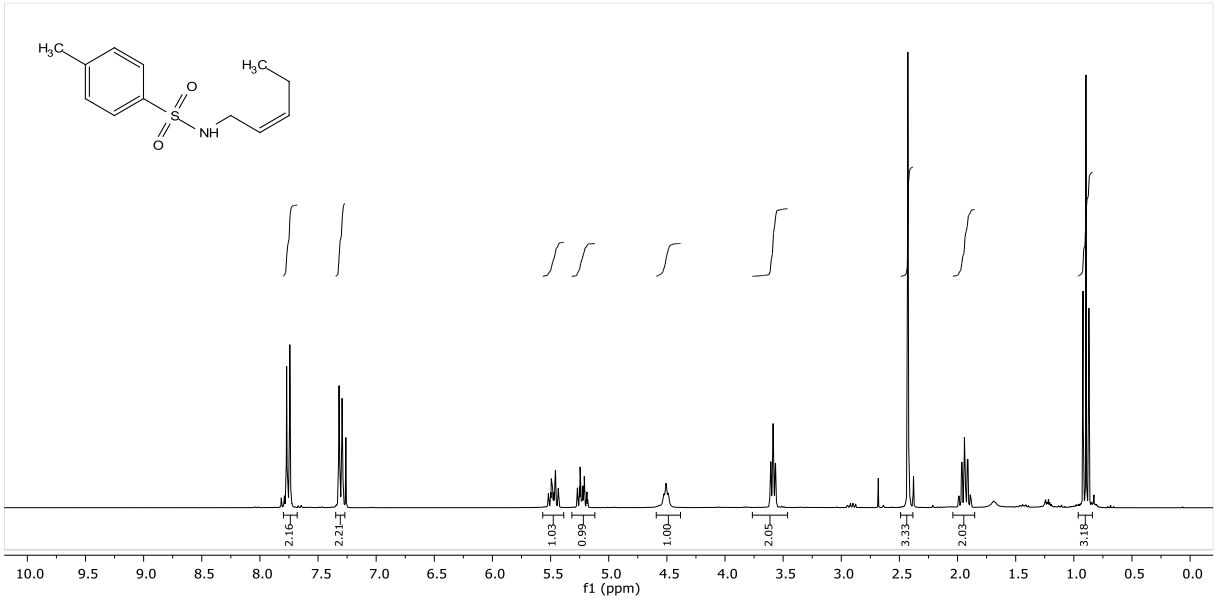
***N*-(Cyclohept-4-en-1-yl)-4-methylbenzenesulfonamide (172):** ^{1}H, ^{13}C NMR in $CDCl_3$, IR[113]

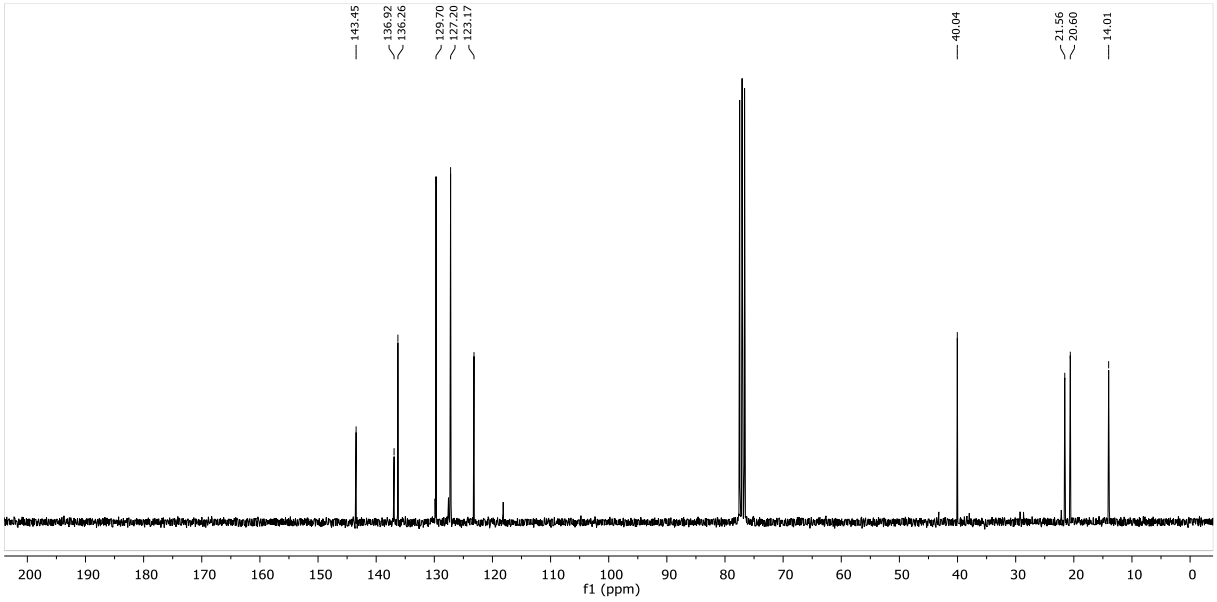


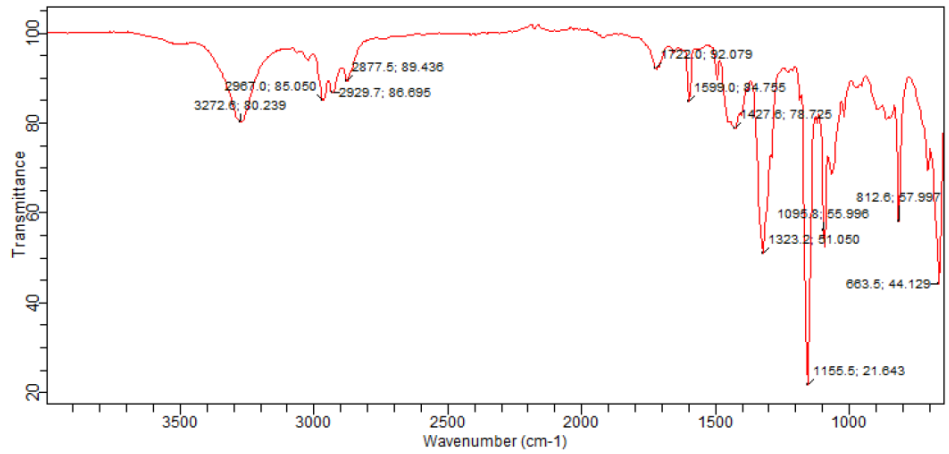




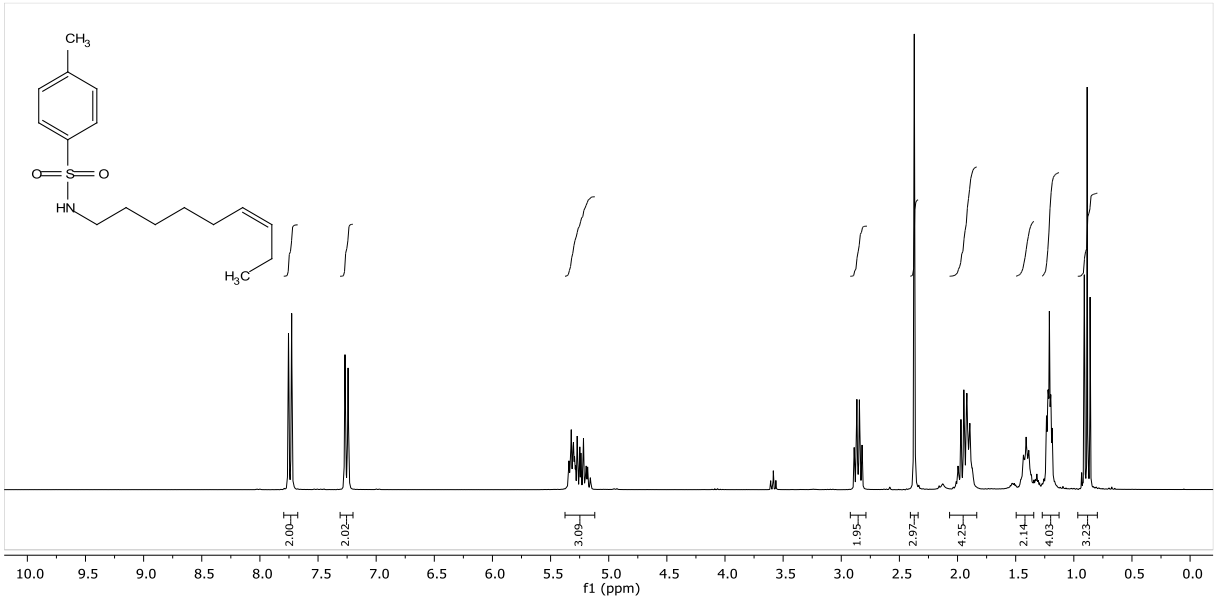
(*Z*)-4-Methyl-*N*-(pent-2-en-1-yl)benzenesulfonamide (145): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

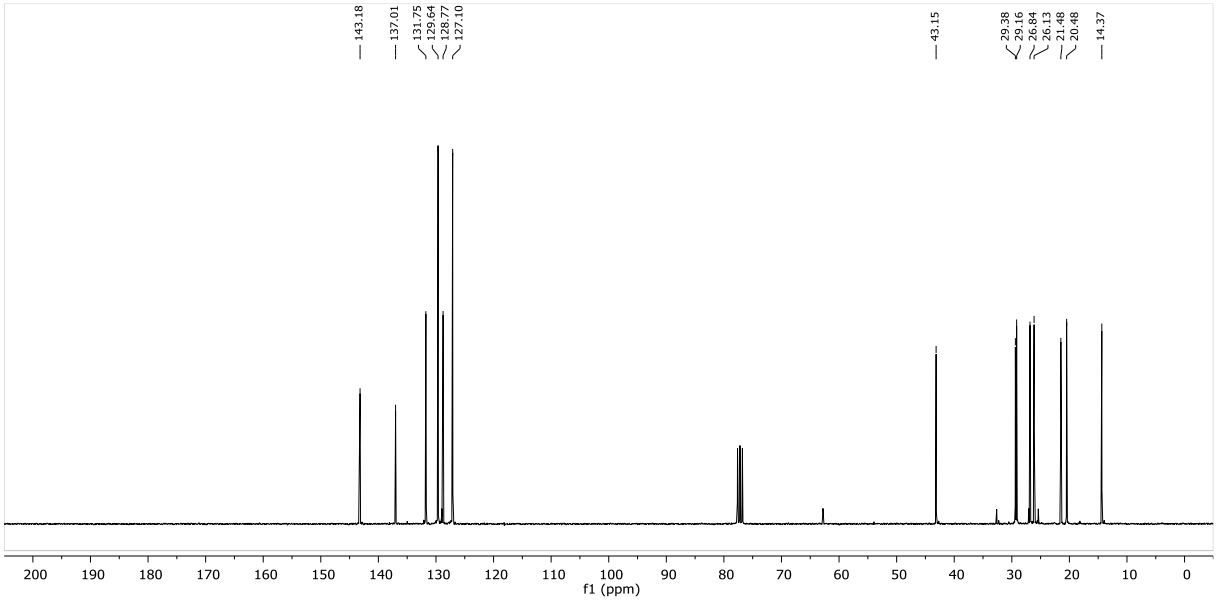


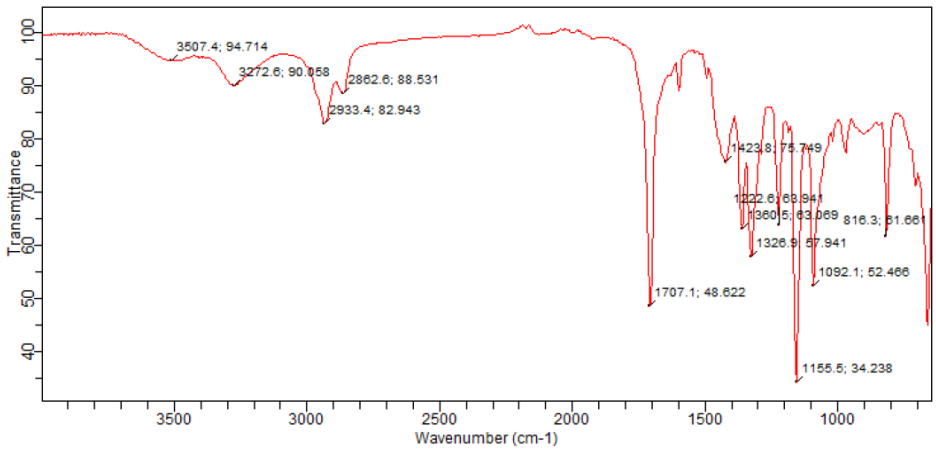




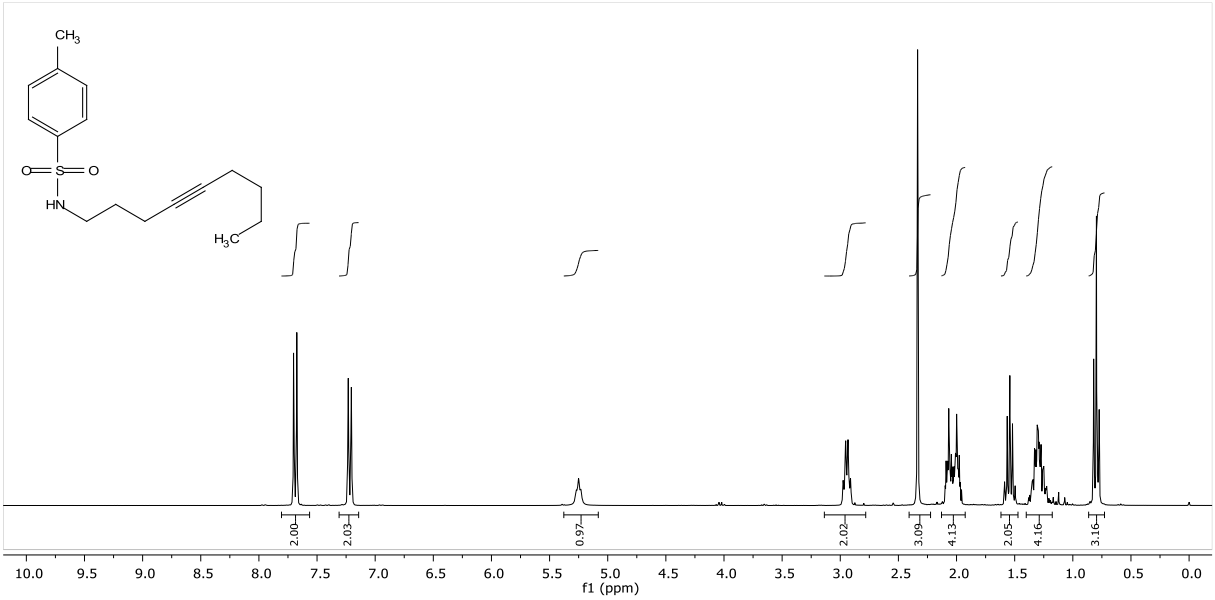
(*Z*)-4-Methyl-*N*-(non-6-en-1-yl)benzenesulfonamide (148): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

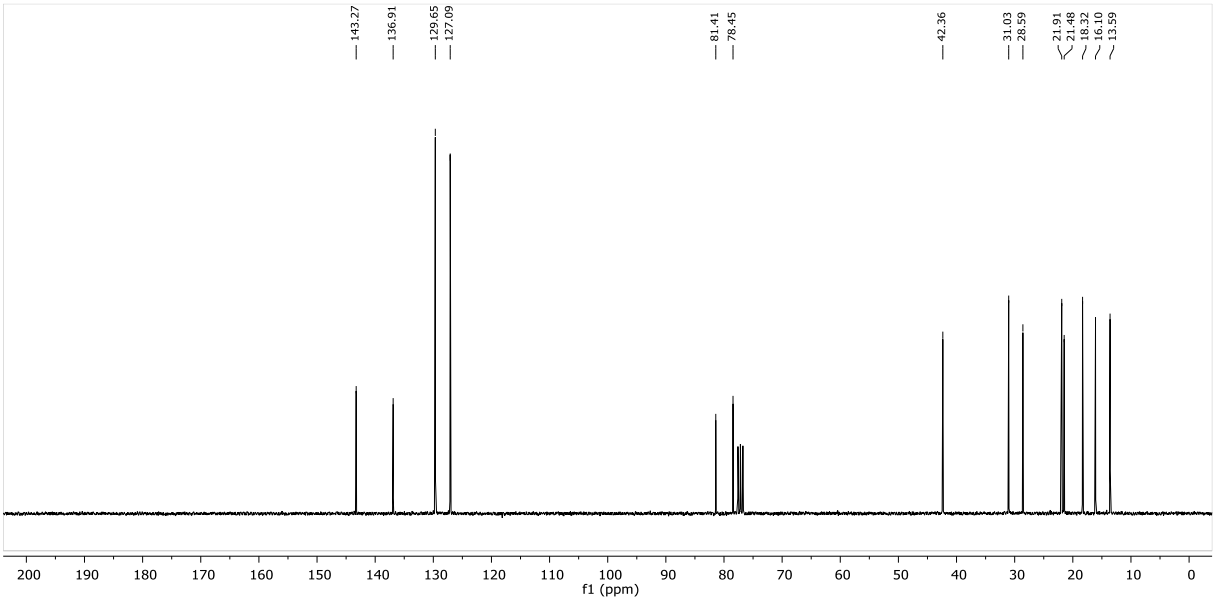


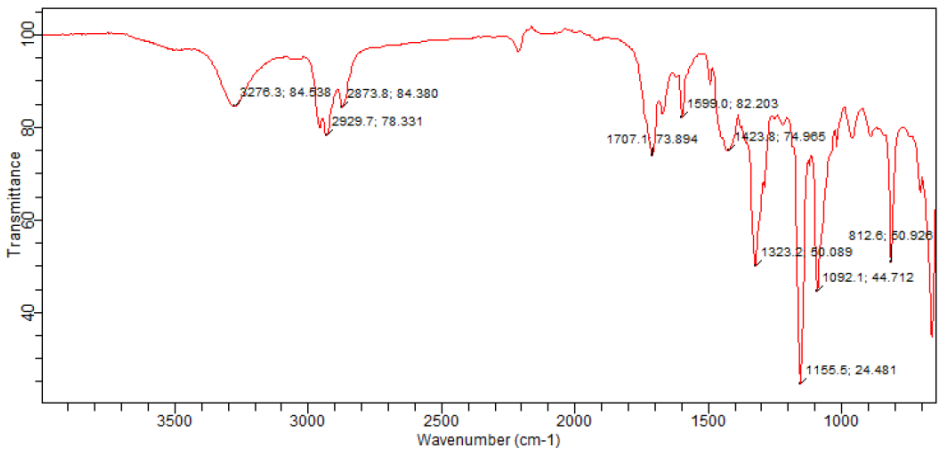




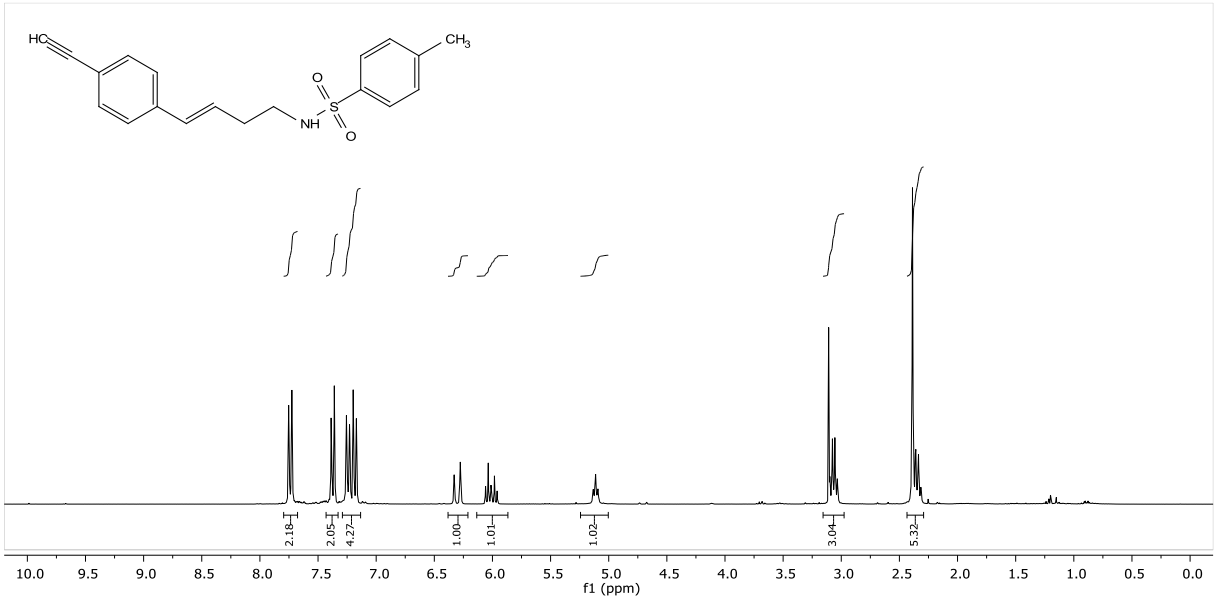
4-Methyl-*N*-(non-4-yn-1-yl)benzenesulfonamide (175): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

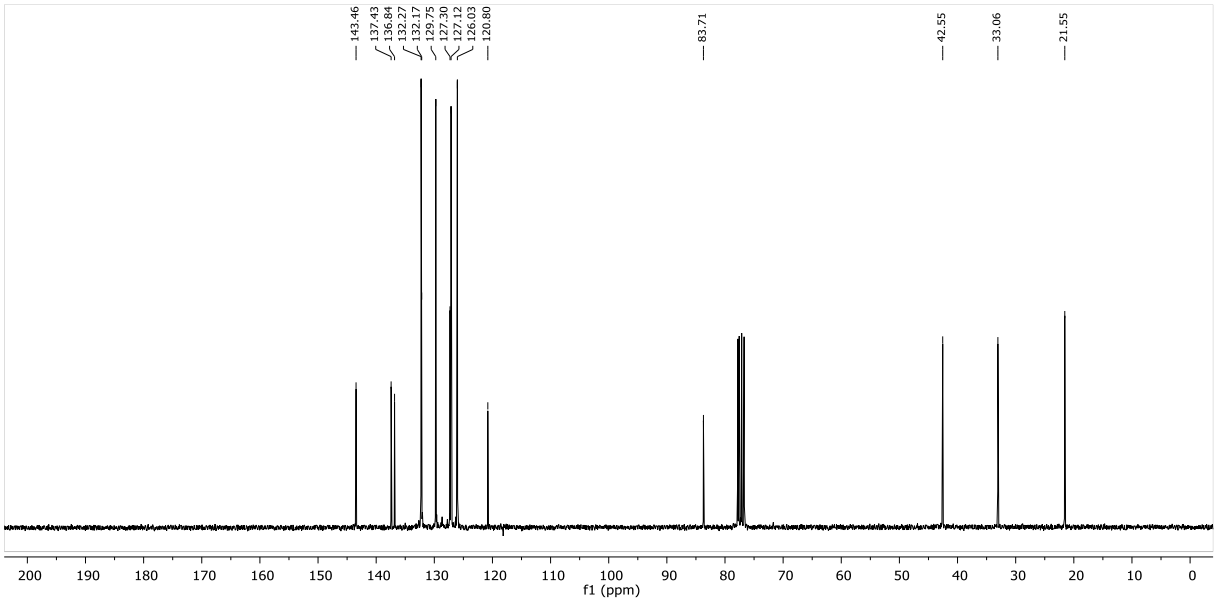


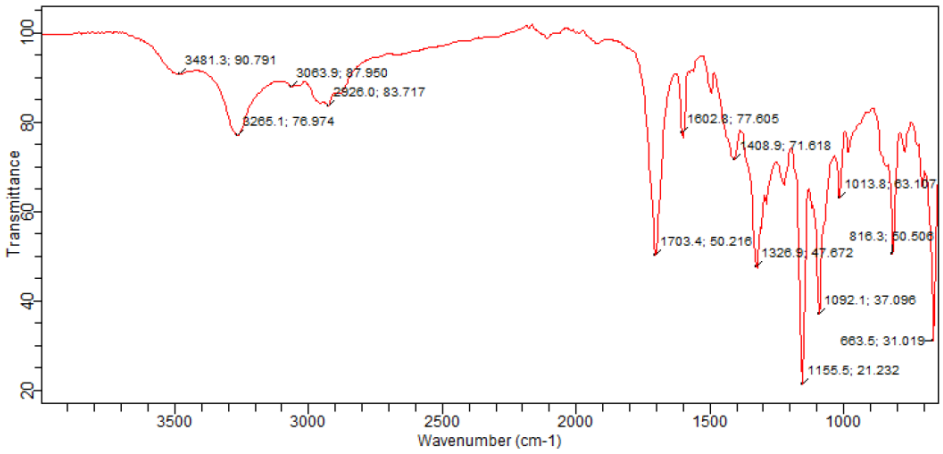




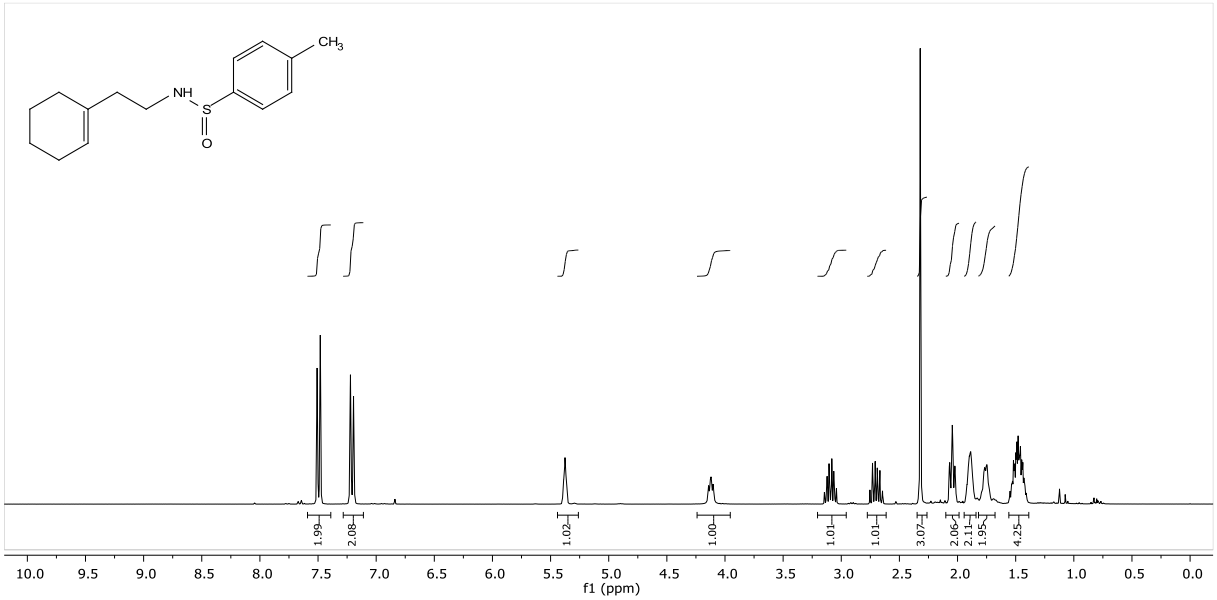
(*E*)-*N*-(4-(4-Ethynylphenyl)but-3-en-1-yl)-4-methylbenzenesulfonamide (174): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

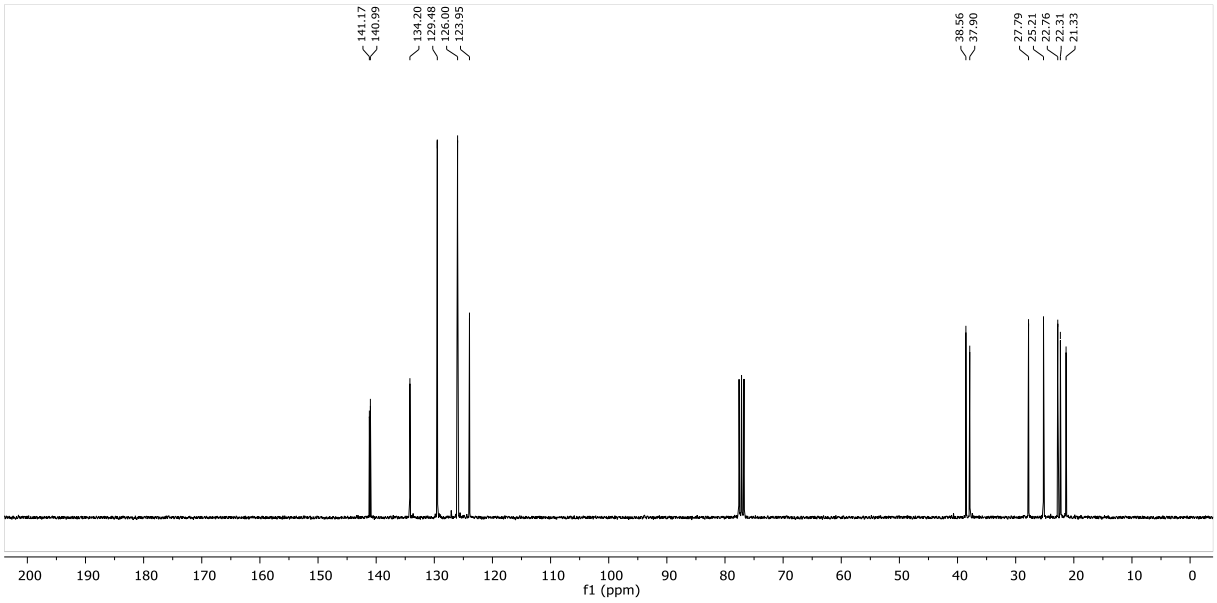


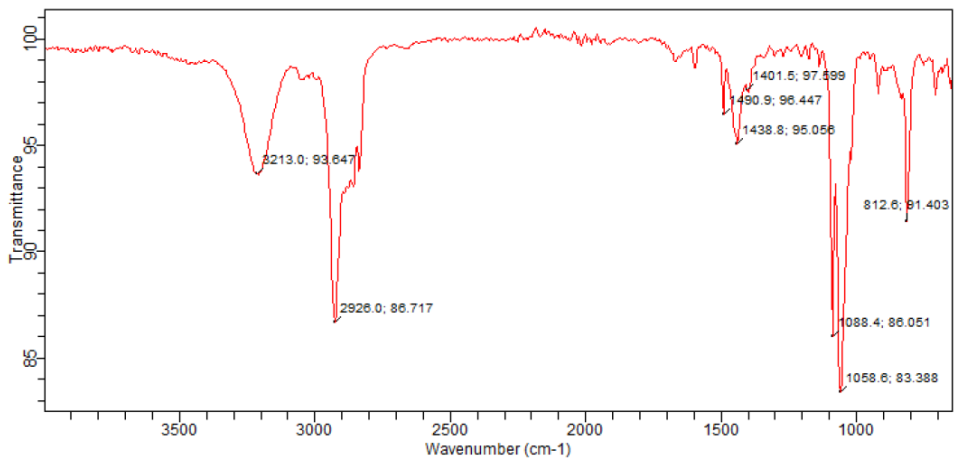




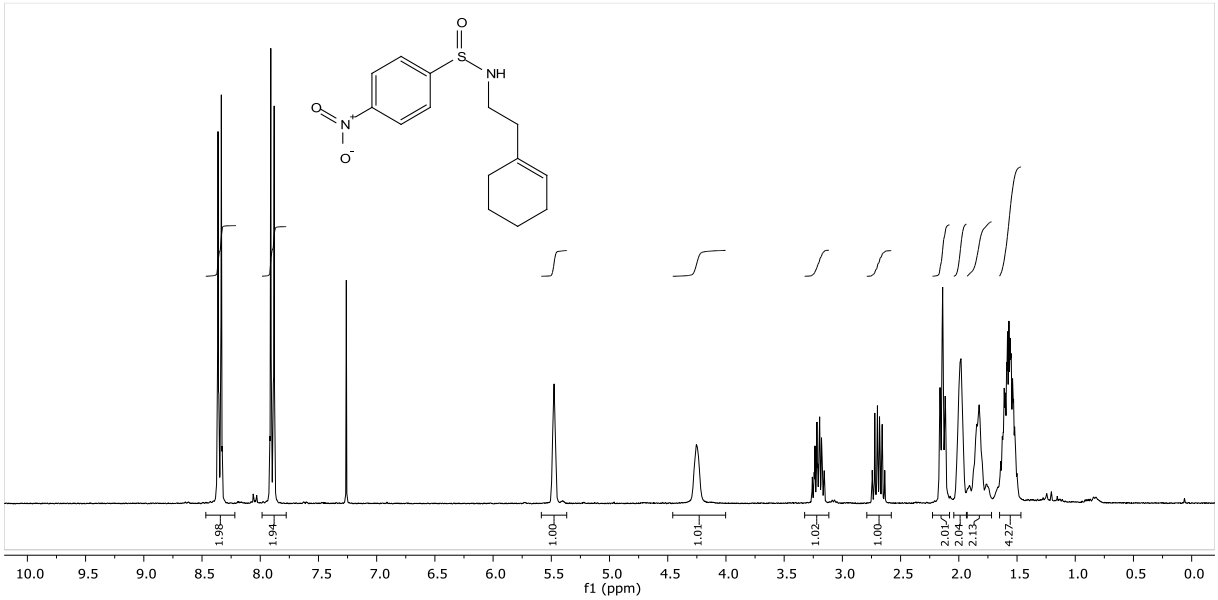
(*Rac*)-*N*-(2-(Cyclohex-1-en-1-yl)ethyl)-4-methylbenzenesulfinamide (181): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

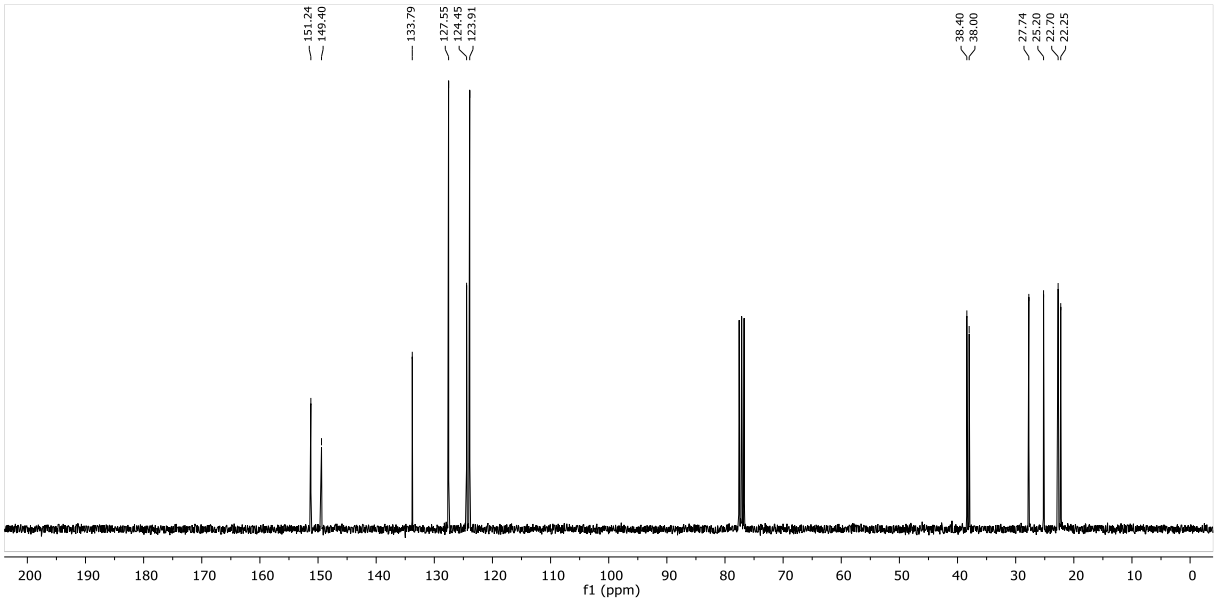


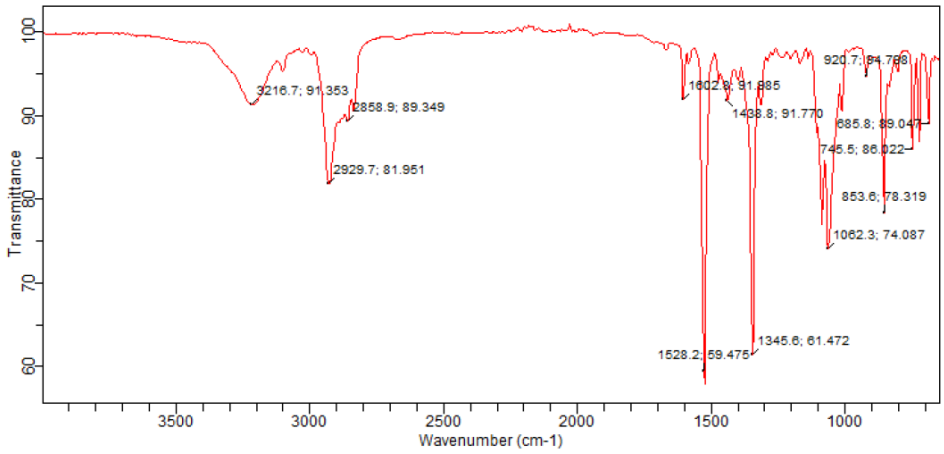




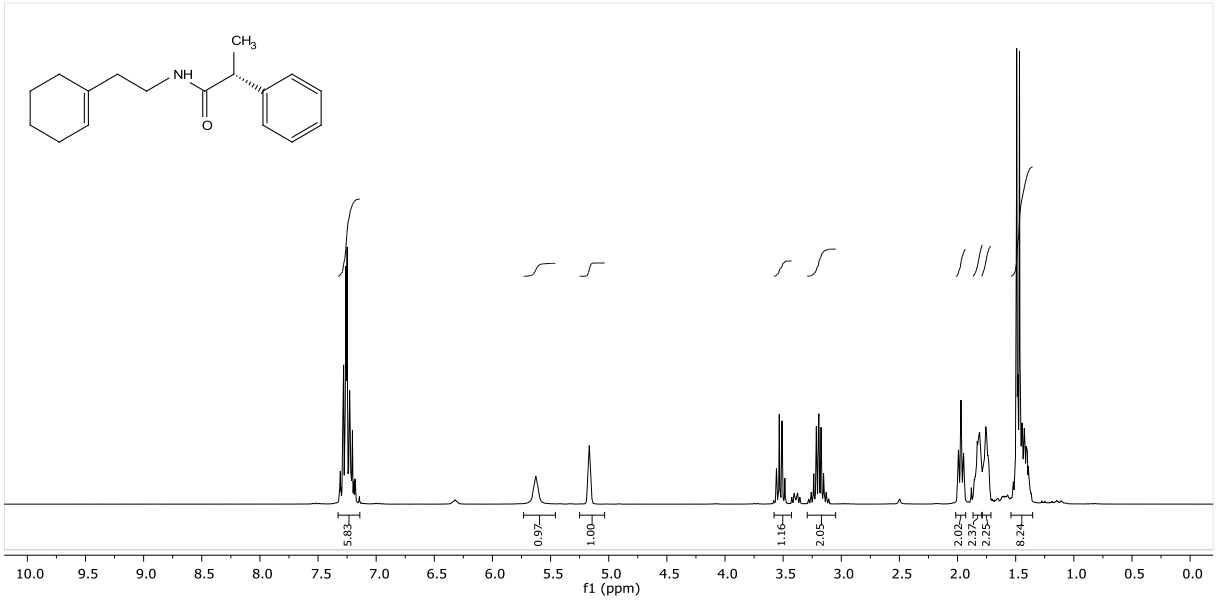
***N*-(2-(Cyclohex-1-en-1-yl)ethyl)-4-nitrobenzenesulfinamide (182):** ^{1}H, ^{13}C NMR in $CDCl_3$, IR

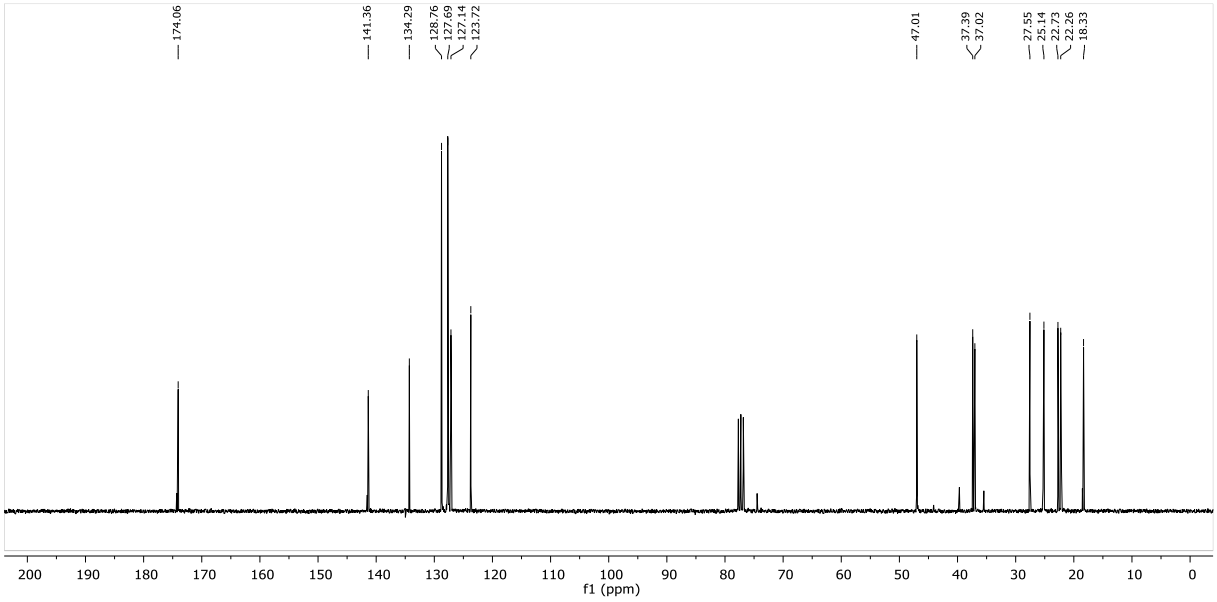


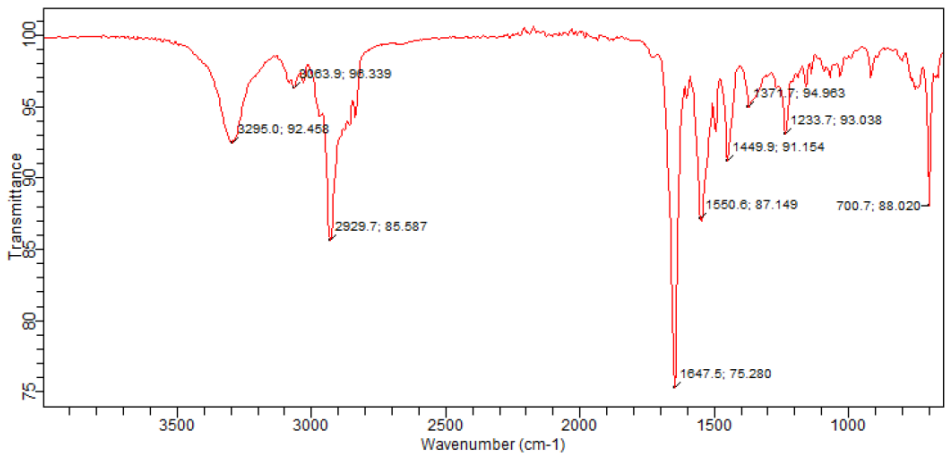




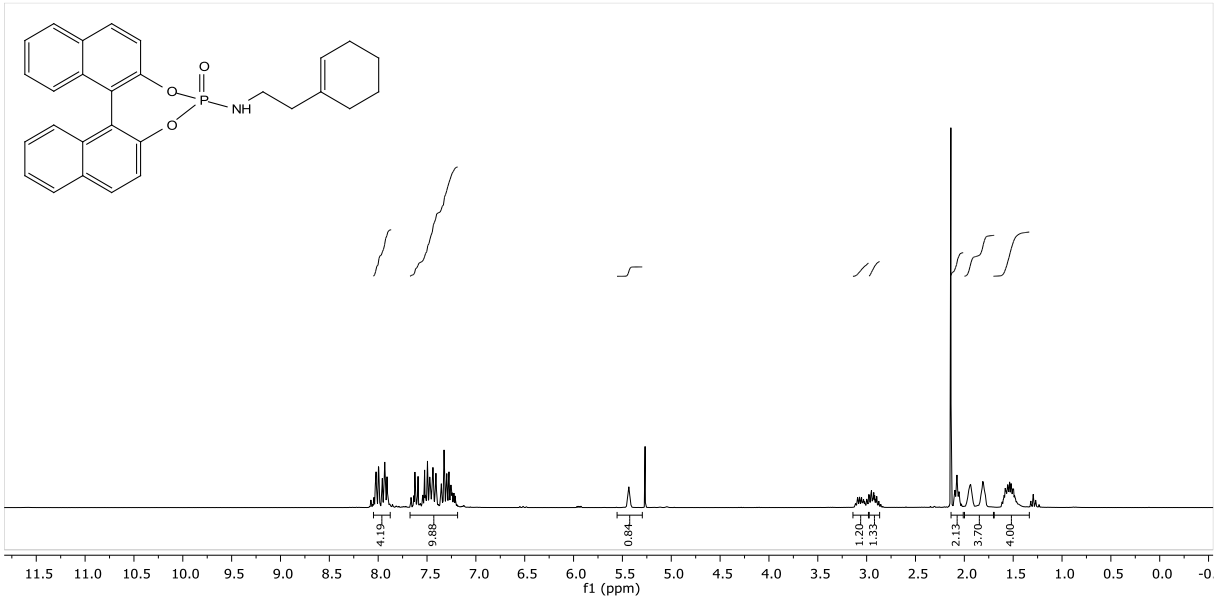
(*R*)-*N*-(2-(Cyclohex-1-en-1-yl)ethyl)-2-phenylpropanamide (186): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

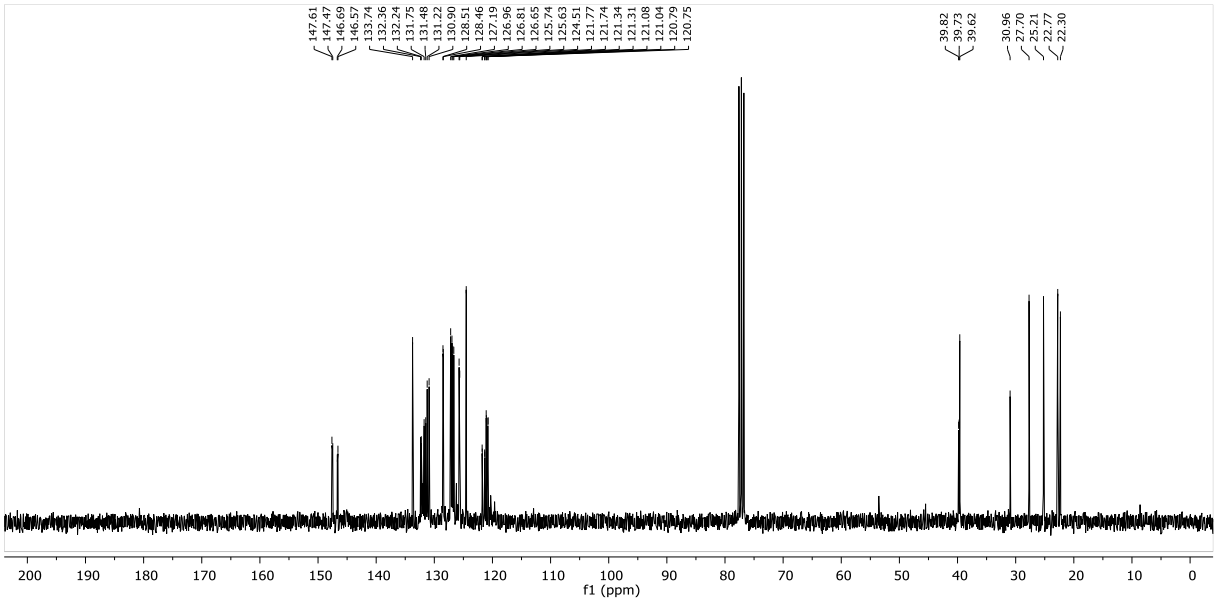


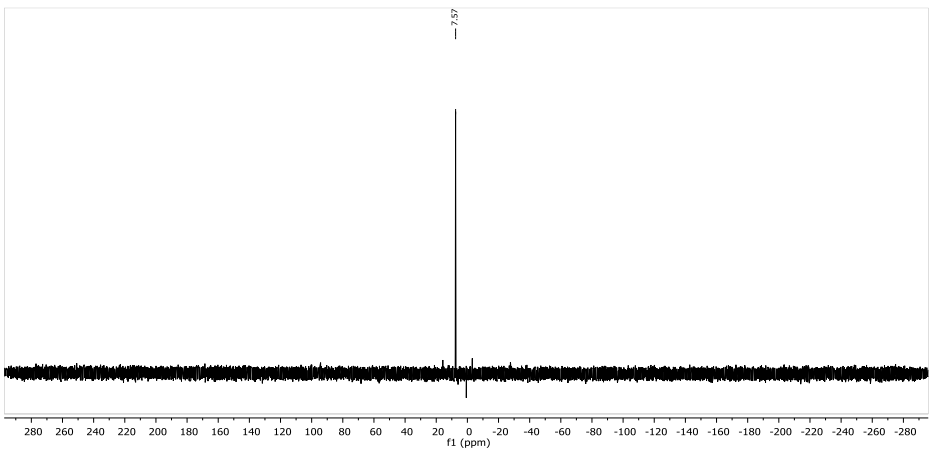


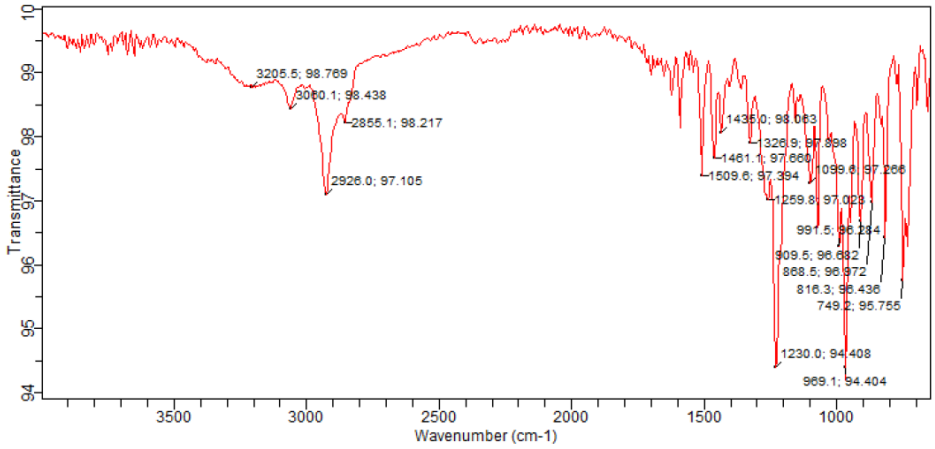


(4*R*)-4-((2-(Cyclohex-1-en-1-yl)ethyl)amino)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (189): ^{1}H, ^{13}C, ^{31}P NMR in $CDCl_3$, IR

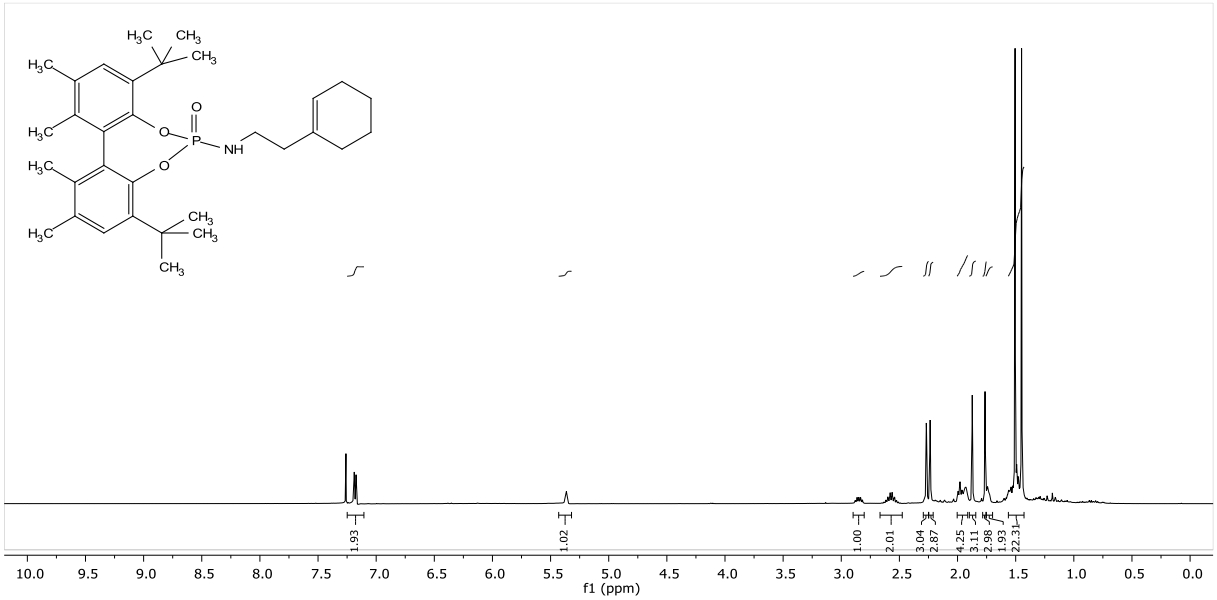


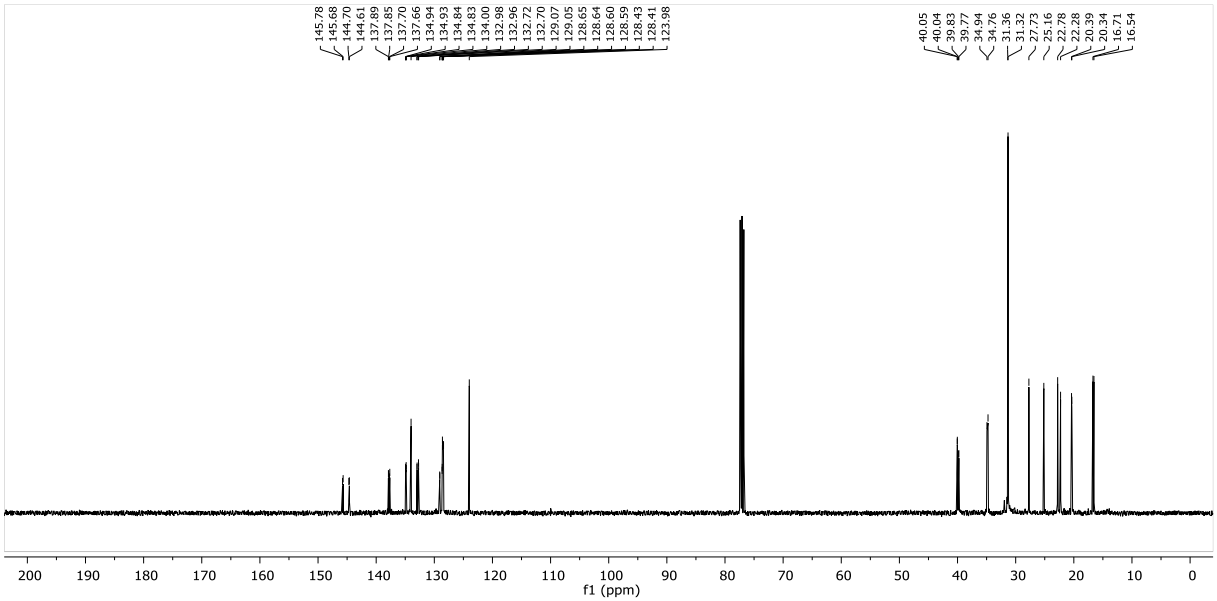


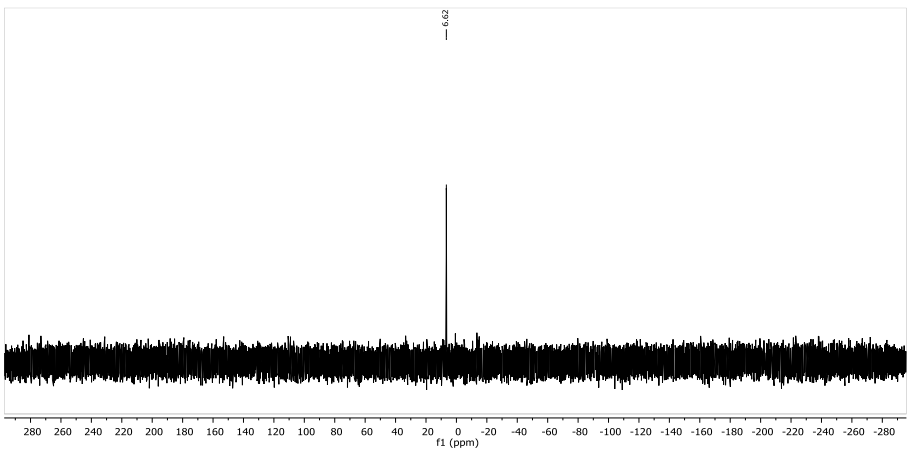


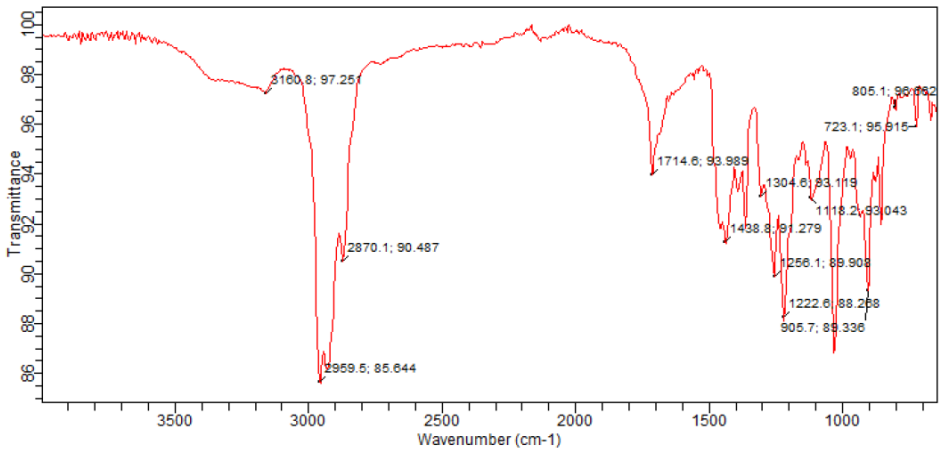

Transmittance
Wavenumber (cm-1)
3205.5; 98.769
3060.1; 98.438
2855.1; 98.217
2926.0; 97.105
1435.0; 98.063
1326.9; 97.898
1461.1; 97.666
1509.6; 97.394
1259.8; 97.023
991.5; 96.184
909.5; 96.082
868.5; 96.072
816.3; 96.436
749.2; 95.755
1230.0; 94.408
969.1; 94.404

4,8-Di-*tert*-butyl-6-((2-(cyclohex-1-en-1-yl)ethyl)amino)-1,2,10,11-tetramethyldibenzo[d,f][1,3,2]dioxaphosphepine 6-oxide (192): ^{1}H, ^{13}C, ^{31}P NMR in $CDCl_3$, IR

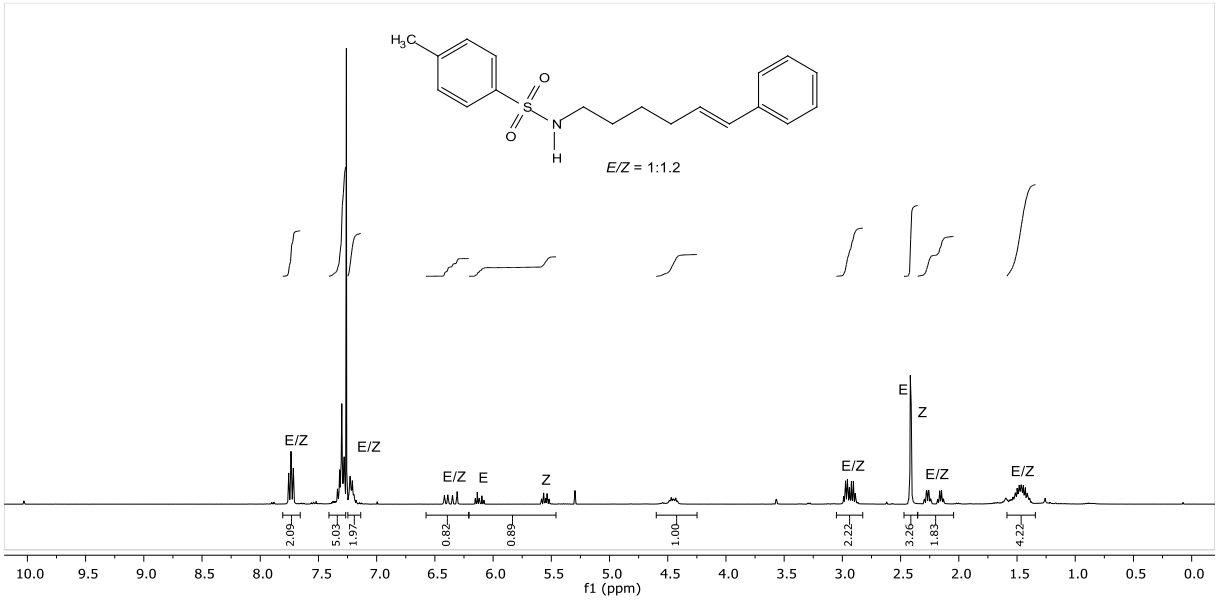


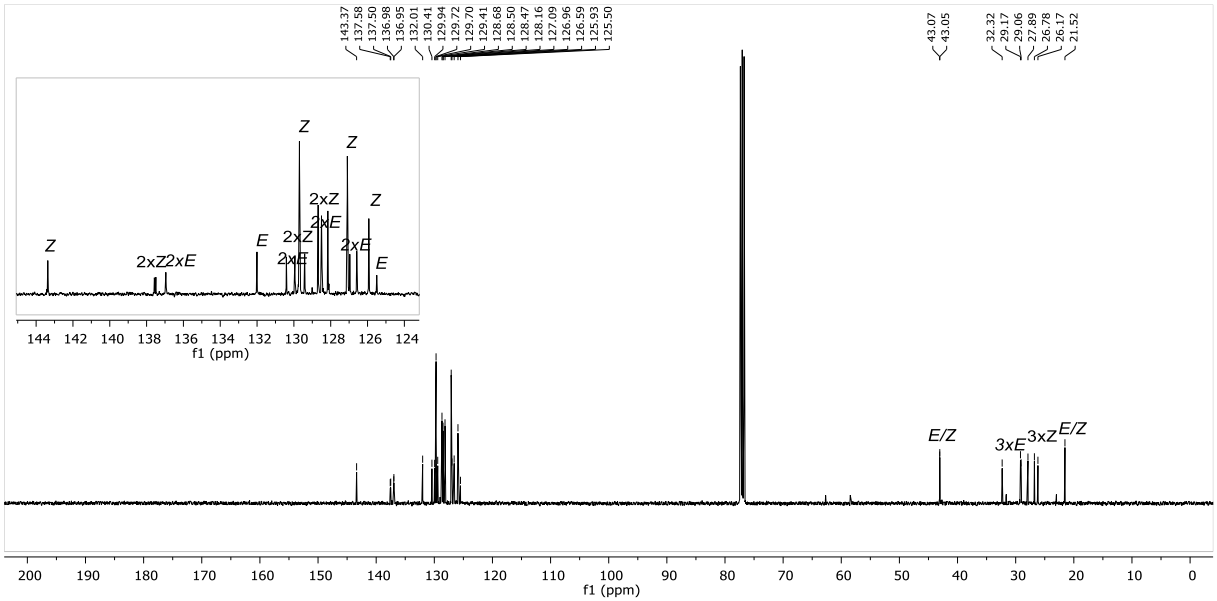


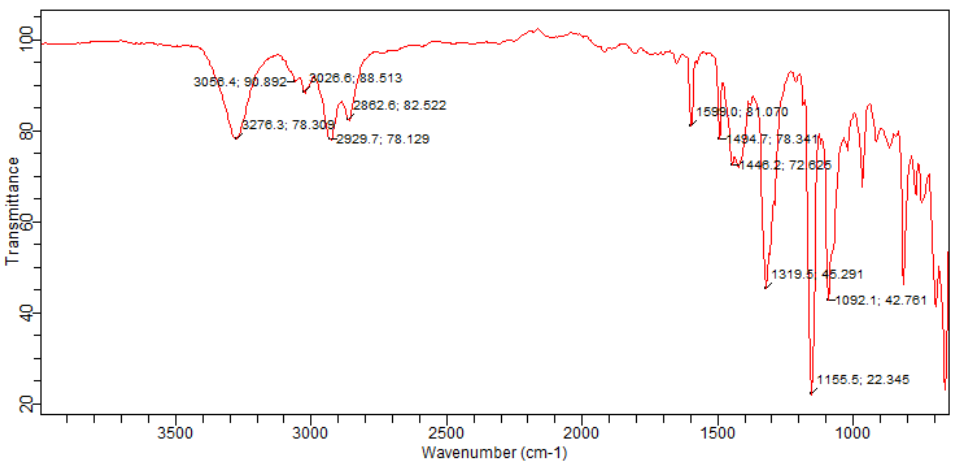



Transmittance
Wavenumber (cm-1)
3160.8; 97.251
2870.1; 90.487
2959.5; 85.644
1714.6; 93.989
1304.6; 93.119
1438.8; 91.279
1256.1; 89.908
1222.6; 88.258
905.7; 89.336
723.1; 95.915
805.1; 96.892
1118.2; 93.043

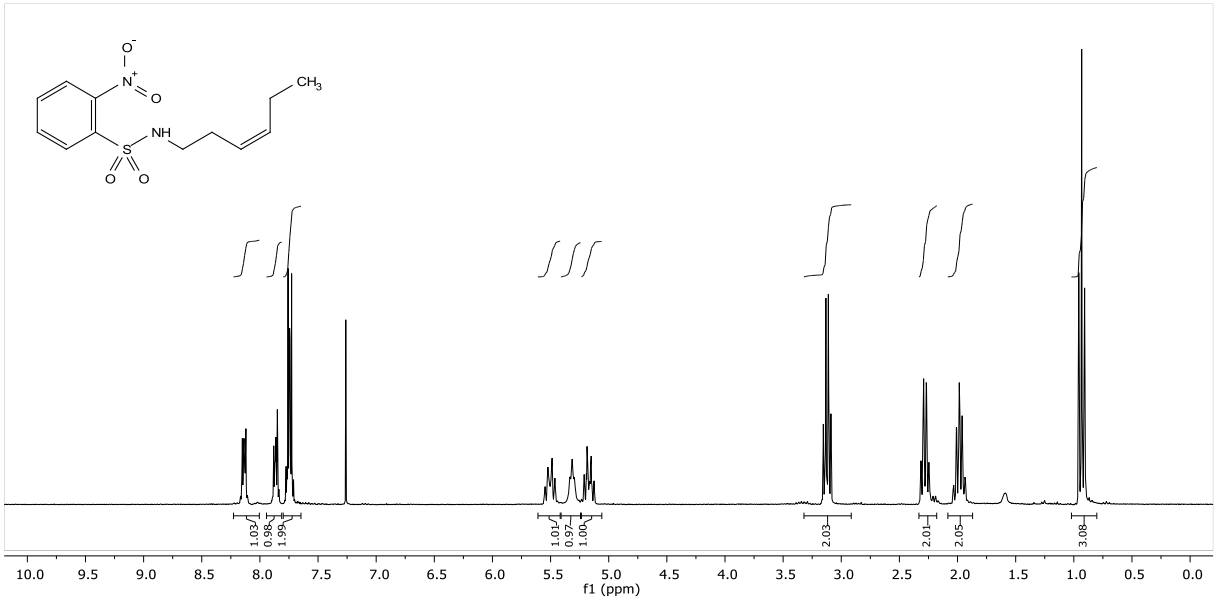
4-Methyl-*N*-(6-phenylhex-5-en-1-yl)benzenesulfonamide (221): ^{1}H, ^{13}C NMR in $CDCl_3$, IR

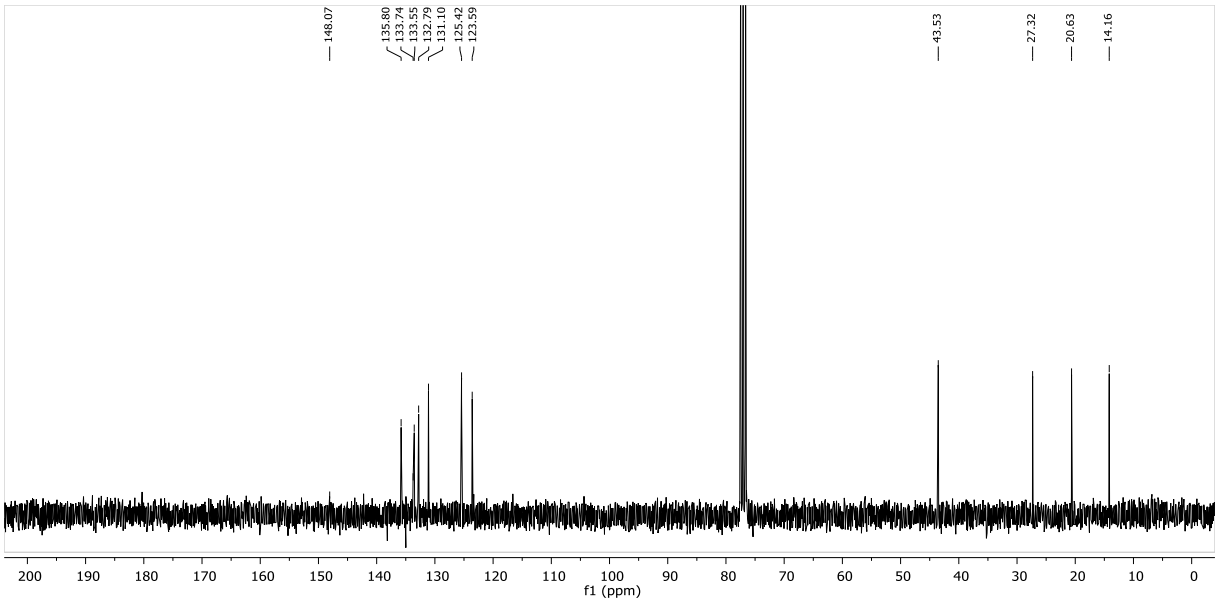


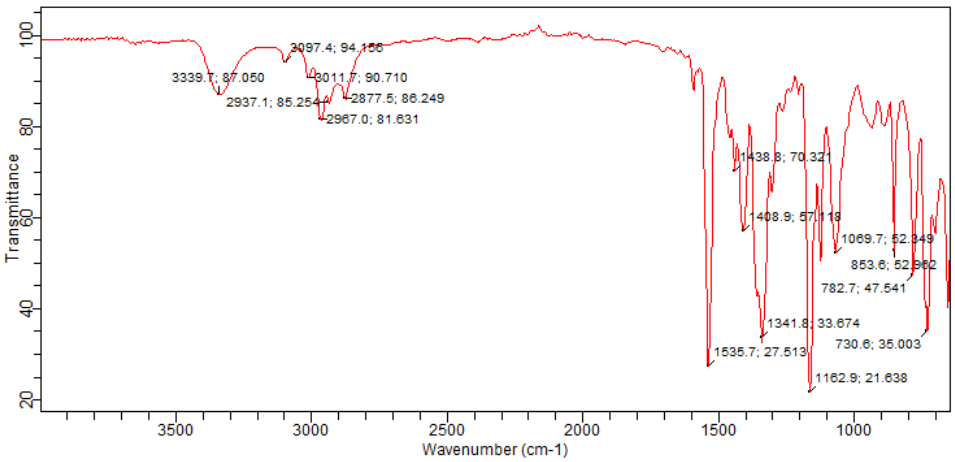




(*Z*)-*N*-(Hex-3-en-1-yl)-2-nitrobenzenesulfonamide (146aj): ^{1}H, ^{13}C NMR in $CDCl_3$, IR







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9 Declaration

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 reference to the literature, license, and acknowledgment of collaborative research.

Regensburg, 05.06.2024

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Sebastian Graf