Photoredox selenium-π-acid multicatalyzed cyclizations and rearrangement reactions

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„In Fragen der Wissenschaft
ist die Autorität von Tausenden
nicht die bescheidene Argumentation
einer einzelnen Person wert.“
(Galileo Galilei)

1 Table of Contents

1.1 General Abbreviations

Å	Angstrom
a.q.	aqueous
APCI	atmospheric pressure chemical ionization
ATR	attenuated total reflection
calcd.	calculated
cat.	catalytic
cm^{-1}	reciprocal centimeters
cm^2	square centimeters
conv.	conversion
dr	diastereomeric ratio
ee	enantiomeric excess
EI	electron impact ionization
ELS	evaporative light scattering
HRMS	high resolution mass spectrometry
equiv	equivalents
ESI	electron spray ionization
eV	electron volts
EWG	electron withdrawing group
fs	femto seconds
FT-IR	Fourier transformed infrared signal
h	hour
HAT	hydrogen atom transfer
hv	photon induced chemical reaction
IR	Infrared (spectroscopy)
LED	light emitting diode
lm/m	lumen per meter
+M-effect	positive mesomeric effect
M	molarity
mA	milli ampere
MHz	mega Hertz
mmol	milli mole
MP	melting point
MS	mass spectrometry
m/z	mass to charge ratio
n.d.	not determined
Nm	nanometer
NMR	nuclear magnetic resonance spectroscopy
NOESY	Nuclear Overhauser enhancement spectroscopy
Nuc	nucleophile
p.A.	por analysi
PC	photocatalyst
PCET	proton coupled electron transfer
ppm	parts per million
ref	reflux
R_f	retarding factor
r.t.	room temperature
sat. aq.	saturated aqueous
SCE	standard calomel electrode
SDET	stimulated doublet-doublet electron transfer
SET	single electron transfer
S_N	nucleophilic substitution
S_NAr	nucleophilic aromatic substitution
TLC	thin layer chromatography
TS	transition state
UV-Vis	ultraviolet to visible light range
V/V	volumetric ratio
wt%	weight percentage

1 Table of Contents

Chemical Abbreviations

ΔT	temperature change
Δt	time change
v	wave number
δ	chemical shift
µmol	micro moles
µs	micro seconds

1.2 Chemical Abbreviations

Ac	acetate
AgOAc	silver(I)acetate
$AgSbF_6$	silver(I)hexafluoroantimonate
AIBN	azo-bis-(isobutylonitril)
$AlCl_3$	aluminum chloride
Ar*	chiral aryl group
ArOH	generic aromatic alcohol
ArSe	generic aryl selenide
ArSeH	generic aryl selenol
$Bi(OTf)_3$	bismuth(III)triflate
Bn	benzyl
Bn-Br	benzyl bromide
BnHN	benzylamine
BnOH	benzyl alcohol
Boc	*tert*-butyloxycarbonyl
BocO	*tert*-butyloxycarbonyloxide
Bpin	pinacol borane
^{t}Bu	*tert*-butyl
^{n}BuLi	*n*-butyllithium
$^{n}Bu_3N$	tri-*n*-butylamine
$^{n}Bu_4NBr$	Tetra-*n*-butylamino bromide
^{t}BuO	*tert*-butoxide
Bu_3SnH	tributyltin hydride
Br_2	elemental bromine
$CaBr_2xH_2O$	calcium bromide monohydrate
$CaCO_3$	calcium carbonate
CaF_2	calcium fluoride
C_6D_6	deuterated benzene
$CDCl_3$	deuterated chloroform
CDI	*N*,*N*'-carbonyldiimidazole
$[(p\text{-}CF_3\text{-}C_6F_4)_3P]AuCl$	(4-trifluoromethylphenyl)phosphine gold(I)chloride
$CHCl_3$	chloroform
p-Cl-Ar	generic *para*-chloroarene
$(4\text{-Cl-ArS})_2$	1,2-bis(4-chlorophenyl)disulfane
CN	nitrile
CO_2	carbondioxide
Cp	cyclopentyl
$CuCl_2$	copper(II)chloride
$Cu(NO_3)_2xH_2O$	copper(II)nitrate monohydrate
CuI	copper(I)iodide
Cy	cyclohexyl
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene

1 Table of Contents

Chemical Abbreviations

DCE	1,2-dichloroethane	HBr	hydrobromic acid
DCM	dichloromethane	HBR_2	generic alkyl borane
DCN	dicyanonapthalene	HCl	hydrochloric acid
DHP	2,3-dihydro-4*H*-pyran	$(HCOH)_n$	para-formaldehyde
4-DMAP	4-(dimethylamino)-pyridin	(het)Ar	generic heteroaromate
DMF	dimethylformamide	HFIP	hexafluoroisopropanol
DMP	*Dess-Martin*-periodinane	$Hg(OAc)_2$	mercury(II)acetate
DMSO	dimethylsulfoxide	$Hg/Tl(OTf)_2$	mercury(II) or thallium(II) triflate
D_2O	deuteriumoxide	HI	hydrogen iodide
DPA	diphenylamin	H_2O	water
dppe	1,2-bis(diphenylphosphino)ethane	H_3O^+	hydroxonium-ion
Et	ethyl	H_2O_2	hydrogen peroxide
Et_2NH_2	diethylamine	HOAc	acetic acid
Et_2O	diethylether	I_2	elemental iodine
EtOAc	ethyl acetate	$InCl_3$	indium(III)chloride
EtOH	ethanol	IPN	isophthalonitrile
F_3C	trifluoromethyl	$Ir(ppy)_3$	tris(2-phenylpyridine)iridium
$FeBr_3$	iron(III)bromide	K_2CO_3	potassium carbonate
$FeCl_3$	iron(III)chloride	KOAc	potassium acetate
$FeCl_3x6H_2O$	iron(III)chloride hexahydrate	KO^tBu	potassium *tert*-butoxide
Fmoc	9-fluorenylmethoxycarbonyl	$K_2S_2O_8$	potassium persulfate
FP-OTf	*N*-fluoropyridinium triflate	$LiAlH_4$	Lithium aluminum hydride
2F-Pyr	2-fluoropyridine	Li_2CO_3	lithium carbonate
Grubbs Gen. 2	(1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichlor(phenylmethylen)(tricyclohexylphosphan)ruthenium	$LiOHxH_2O$	lithium hydroxide monohydrate
		[M]	generic metal-ligand complex
H_2	elemental hydrogen	*m*CPBA	*meta*-chloroperoxybenzoic acid
hal	halogen	Me	methyl
		MeCN	acetonitrile

1 Table of Contents

Chemical Abbreviations

$MeCN\text{-}d_3$	deuterated acetonitrile	Na_2SO_4	sodium sulfate
$(4\text{-}Me\text{-}ArSe)_2$	1,2-di-*p*-tolyldiselane	NBoc	Boc protected amine
Men	1s-(+)-menthyl	NCS	*N*-chlorosuccinimide
$(2\text{-}MeO\text{-}ArSe)_2$	1,2-bis(2-methoxy-phenyl)diselane	$N(CH_2\text{-}o\text{-}pyridine)_2$	*N*,*N*-bis(pyridin-2-ylmethyl)methanamine
$(2,4\text{-}MeO\text{-}ArSe)_2$	1,2-bis(2,4-dimethoxy-phenyl)diselane	NEt_3	triethylamine
$(2,6\text{-}MeO\text{-}ArSe)_2$	1,2-bis(2,6-dimethoxy-phenyl)diselane	NFSI	*N*-fluorobenzenesulfonimide
$(3,5\text{-}MeO\text{-}ArSe)_2$	1,2-bis(3,5-dimethoxy-phenyl)diselane	NH_4OAc	ammonium acetate
		NH_4Cl	ammonium chloride
$(4\text{-}MeO\text{-}ArSe)_2$	1,2-bis(4-methoxy-phenyl)diselane	2-NO-benzaldehyde	2-nitrobenzaldehyde
Mes	mesyl	N-PSP	*N*-phenylselenophthalimide
Me_3Si	trimethylsilyl	Ns	nosyl
Me-X	generic methyl halide	$(NH_4)_2S_2O_8$	ammonium persulfate
MeOH	methanol	NTos	tosylamide
Mg	elemental magnesium	O_2	elemental oxygen
$MgSO_4$	magnesium sulfate	$^1O_2$	singlet oxygen
$Mn(pic)_3$	Manganese(III)picolinate	O_3	ozone
N_2	elemental nitrogen	OAc	acetoxy
$NaBH_4$	sodium borohydride	OTBDMS	*tert*-butyldimethylsilylether
Na_2CO_3	sodium carbonate	OsO_4	osmium(VIII)oxide
NaF	sodium fluoride	^-OTf	triflate
NaH	sodium hydride	*p*-anisyl	*para*-methoxyphenyl
$NaHCO_3$	sodium hydrogen carbonate	Pd(0)	palladium(0)
Na_2HPO_4	disodium hydrogen phosphate	Pd/C	palladium(0) on activated charcoal
NaH_2PO_4	sodium dihydrogen phosphate	$PdCl_2$	palladium(II)chloride
NaOAc	sodium acetate	$[Pd_2(dba)_3]_3xCHCl_3$	tris(dibenzylideneacetone)dipalladium(0)-chloroformadduct
NaOH	sodium hydroxide	$Pd(OAc)_2$	palladium(II)acetate
Naph	2-napthyl	PE	petroleum ether (isohexanes)
Na_2SO_3	sodium sulfite		

1 Table of Contents

Chemical Abbreviations

P-ester	phosphonic acid ester
Ph	phenyl
$PhCCl_3$	α,α,α-trichlorotoluene
^{i}Pr	isopropyl
$(PhSe)_2$	diphenyldiselenide
PhSeBr	phenylselenyl bromide
PhSeCl	phenylselenyl chloride
PhSeOR	Generic phenylseleno-late
PhSeX	generic phenylselenate
$PhSiH_3$	phenylsilane
PIFA	[bis(trifluorace-toxy)iodo]benzene
PivNH	pivalic amide
PMB	*para*-methoxybenzyl
$POCl_3$	phosphoroxychloride
PS-TBD	polystyrene supported 1,5,7-triazabicy-clo[4.4.0]dec-5-ene
PS-TsOH	Polystyrene supported toluenesulfonic acid
RB	Rosebengal disodium salt
R_2CuLi	generic organic cuprate reagent
$Rh_2(OAc)_4$	rhodium(II)acetate dimer
R_2NH	generic secondary amine
ROH	generic alcohol
SePh or PhSe	phenylselenide
S-ester	sulfonic acid ester
TAPT	2,4,6-tris(4-methoxy-phenyl)pyrylium tetra-fluoroborate
TFA	trifluoroacetic acid
Tf_2O	triflic anhydride
THF	tetrahydrofurane
TMS	trimethylsilane
Tos	Tosyl
TsOH	*para*-toluenesulfonic acid
$TsOHxH_2O$	*para*-toluenesulfonic acid monohydrate
TXT	1,3,6,8-tetramethoxy-9-(o-tolyl)thioxanthylium triflate
$Yb(OTf)_3$	yitterbium(III)triflate
Zn	elemental zinc
$ZnCl_2$	zinc(II)chloride
Zn-Cu-couple	Zinc-copper alloy (3mol% Cu)

2 Introduction

2.1 Alkenes as a versatile synthetic platform

Alkenes represent one of the most important carbon sources[1] for the synthesis of fine chemicals owing to their adaptive reactivity, which allow for a multitude of different transformations ranging from pericyclic- over transition metal catalyzed- to simple addition reactions.[1,2] Being more precise, one can differentiate between two major concepts of influencing the alkene reactivity, the chemical surrounding of the π-bond, and the strategic choice of reagents.

Concerning the chemical structure, an unfunctionalized alkene acts as a nucleophile with increasing nucleophilicity based on the number of substituents as well as further conjugation with more C-C double bonds.[2] Adding suitable electrophiles results in an addition reaction in which case the π-bond is converted into two new σ-bonds (Figure 1).[2] Depending on the chosen electrophile, the transformation can be rendered either an oxidative process, where both carbon atoms of the former double bond are formally oxidized (see products **IIIa-2.1** to **IIId-2.1** in Figure 1), a redox neutral process in which case one carbon of the former double bond is oxidized whereas the other one is reduced (products **IIa-2.1** to **IIc-2.1** in Figure 1) or a reductive process where both carbon atoms get reduced (product **IIg-2.1**).[2]

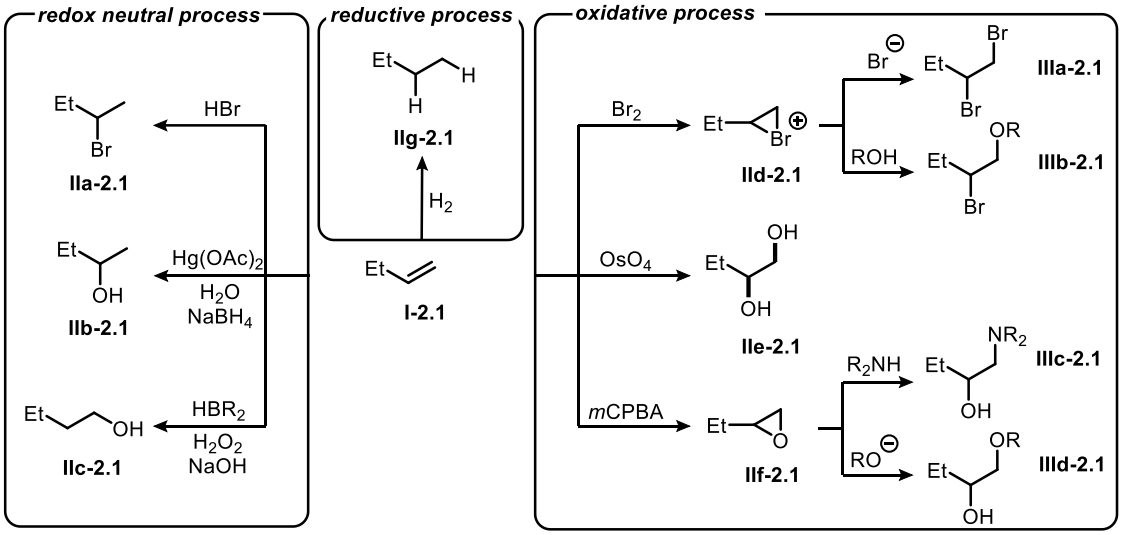


Figure 1: Systematic overview of selected examples of addition reactions to alkenes.[2]

Additionally, the electrophilic addition reaction to unsymmetrically substituted alkenes becomes regioselective according to Markovnikov's rule,[3] stating that the electrophile first adds to the less substituted carbon atom. With the proper choice of reagents however, the opposite addition pattern can be achieved (compare structures **IIb-2.1** and **IIc-2.1** in Figure 1), allowing for additional versatility in the buildup of fine chemical originating from the same starting material. Similar observations were obtained in radical mediated reactions where, the most stable radical intermediate is formed from the alkene thus commonly giving rise to *anti*-Markovnikov products.[4]

More drastic changes in the reactivity are observed when an alkene is conjugated to an electron withdrawing group as the resulting polarization of the C–C double bond leads to a significant increase in electrophilicity of the terminal carbon atom.[2] These changes now allow for the attack of nucleophiles and if the double bond has a suitable leaving group attached, even substitution reactions (similar to S_NAr) are possible.[2]

As the more electronegative heteroatoms (relative to carbon) are exceedingly facile accessed as nucleophilic species, the latter discussed electrophilic reactivity of alkenes becomes more attractive to achieve simple incorporation of such moieties. To access this mode of transformation without the necessity of a conjugated electron withdrawing group, transition metal catalysis has emerged as a useful tool to alter the overall reactivity of the π-bond.[2]

In general terms, the reaction is initiated by the coordination of the metal to the π-orbital of the alkene as described in the Dewar-Chatt-Duncanson model. According to this model, the alkene donates electron from the π-orbital into a set of d-orbitals from the metal whereas filled d-orbitals on the metal donate electrons into the π*-orbitals thus weakening the bond overall[5] and making the olefin more susceptible to nucleophilic attacks.[2,3]

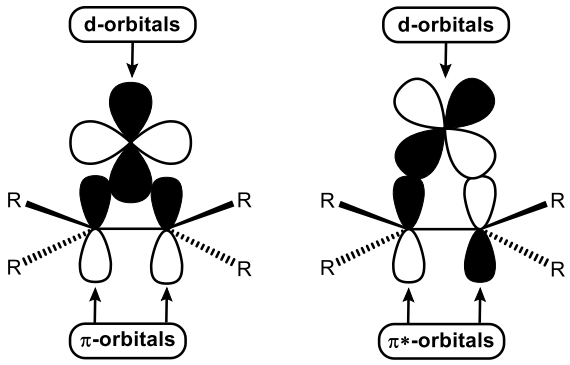
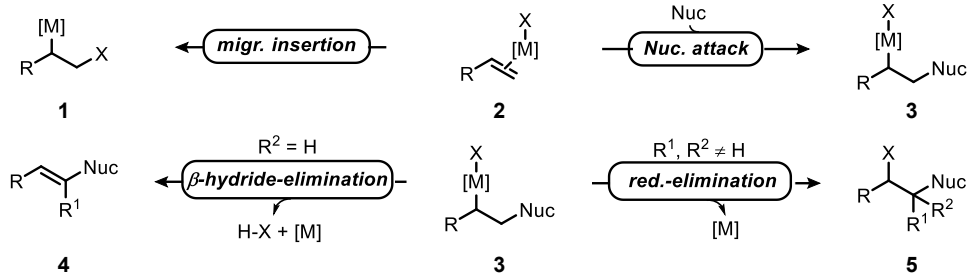


Figure 2: Dewar-Chatt-Duncanson model describing the activation of olefins by metal coordination.[5]

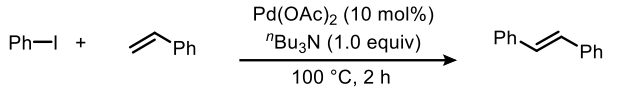
Then either the attack of an external nucleophile onto the double bond or in contrast to this a migratory insertion of a ligand surrounding the metal center (Scheme 1, structure **1**) follows in the reaction mechanism.[2] In both cases σ-bond formation between the metal and the other carbon atom of the former π-bond (structure **3**) then concludes the temporal addition to the former olefin. Further reaction progression is then depending on the conditions as well as the nature of the alkene, either favoring β-hydride elimination (structure **4**) or reductive elimination (structure **5**) when no hydrogen atoms in β-position to the metal atom are available.[2]

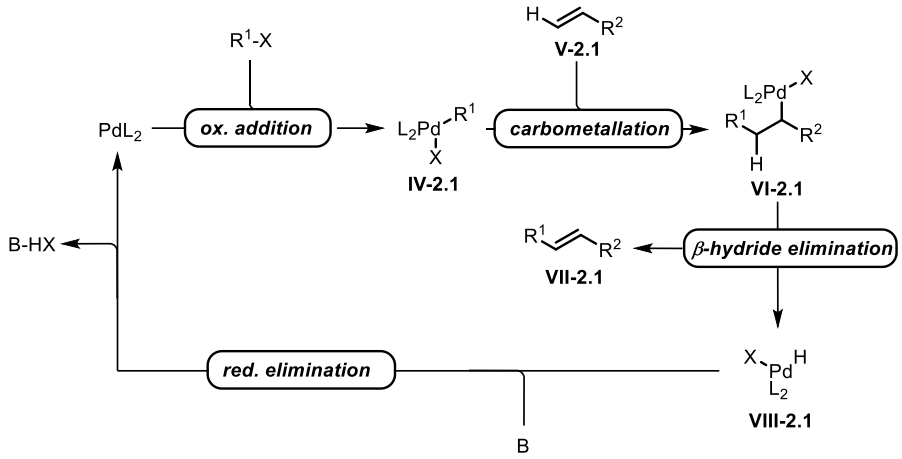
Alkenes as a versatile synthetic platform



Scheme 1: Generalized depiction for the reactivity possibilities when using metals **[M]** and alkenes and the termination possibilities.[2]

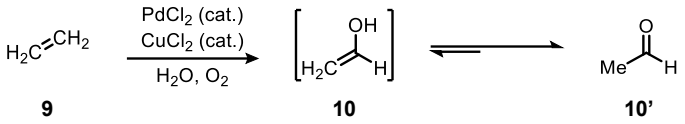
Prominent examples of these modes of reactivity include palladium catalyzed cross couplings such as the Heck coupling (Equation 2.1),[6] the Suzuki coupling and the Stille coupling, all developed to serve different needs when coupling alkenes with alkenes or arenes.[2,6,7] The Heck coupling reported by Richard F. Heck in 1972[6] as an example, follows a reaction mechanism of oxidative addition of the palladium catalyst into the phenyl-iodine bond (depictured as **R^1-X** in Scheme 2) followed by carbometallation and β-hydride elimination (Scheme 2).[2,6]





Scheme 2: Reaction mechanism for the Heck coupling with additional base (**B**). **L =** ligand (commonly organic phosphorous based).[2]

The Suzuki- and the Stille coupling reactions follow a similar concept where a reductive elimination takes place rather than a β-hydride elimination and the consistency of the coupling component **R^1-X** and the substitution motif on the alkene **V-2.1** vary.[2] Another famous reaction, with a slightly different mechanistical progression and different aim, is the Wacker-Hoechst process to convert an alkene into the corresponding enol which tautomerizes to the aldehyde.[8]



9 **10** **10'**

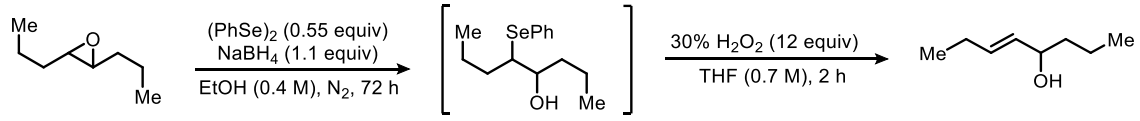
Scheme 3: Simplified equation for the Wacker-Hoechst process. **cat. =** catalytic.

Different reports describe slightly altered reaction progression where upon coordination of the π-bond by the palladium catalyst, the nucleophile (water) either directly attacks the double bond[2] or performs a ligand exchange with one of the chlorine atoms of the palladium catalyst and the reaction then progresses according to Scheme 2.[8]

However, as advantageous as these transformations are, they have the common drawback of employing precious metal catalysts such as for example palladium, resulting in elevated costs.[2,9] Furthermore due to the activation mode of these transition metal catalysts (coordinative bonding) a reattack on the reaction product in a similar fashion as the starting materials is possible, therefore often causing product mixtures. Issues arise if the structural backbone of the starting material allows for multiple β-hydride eliminations which commonly leads to a π-bond isomerization processes climaxing in the most stable π-bond obtainable. Less stable isomers such as terminal olefins can therefore not be obtained, as isomerization processes commonly lead to higher substituted alternatives.[10,11] To counteract the increasing cost of precious metals,[9] as well as the prevailing selectivity issues, the interest for metal free reagents promoting a nucleophilic alkene reactivity by σ-bond activation became more relevant over time.

2.2 Selenium-π-acid catalysis

A class of compounds fitting into the desired description of being cost effective and serving the desired reactivity pattern are organic selenides.[12–14] Already in 1973, K. B. Sharpless and R. F. Lauer, described the use of *in situ* generated $PhSe^-$ as means for converting a generated epoxide **11** into the corresponding allylic alcohol **13** (Scheme 4).[15] Their developed process amounts to a two-step procedure, where in the first step $PhSe^-$ opens up the epoxide and forms the selenofunctionalized intermediate **12**.[15] In a consecutive step, the selenium moiety is then eliminated by oxidation with H_2O_2, giving rise to the allylic alcohol **13**.[15]

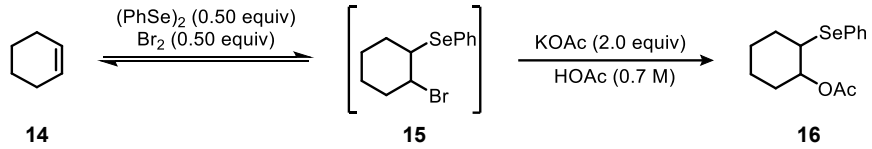


11 **12** **13** 98%

Scheme 4: Reaction example for the process developed by Sharpless and Lauer.[15] Isolated yield reported. The intermediate **12** is used without isolation procedures.

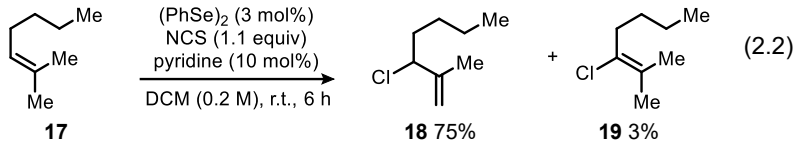
Following the above presented usage of organic selenides as nucleophiles, one year later, the first application of an electrophilic selenium species was then reported by the same authors.[16] Utilizing PhSeX (X = Cl, Br, OAc) as readily available $PhSe^+$ source, the authors investigated the

transformation of cyclic alkenes into the corresponding allylic acids/ethers by an addition-elimination mechanism.[16] In the first step, PhSeX performs a reversible addition reaction to the alkene and subsequent displacement of the X-group with the added nucleophile then delivers the selenofunctionalized compound **16** (Scheme 5). In analogy to the above presented concept (Scheme 4), the PhSe-residue is then oxidatively eliminated by the addition of H_2O_2.[16]



Scheme 5: Example reaction for the application of selenides as electrophiles as described by Sharpless and Lauer.[16] The active PhSeBr species is generated *in situ* by reaction of Br_2 with $(PhSe)_2$ prior to the addition of alkene **14**. Intermediate **15** is not isolated and reacts directly to **16** under the reaction conditions.

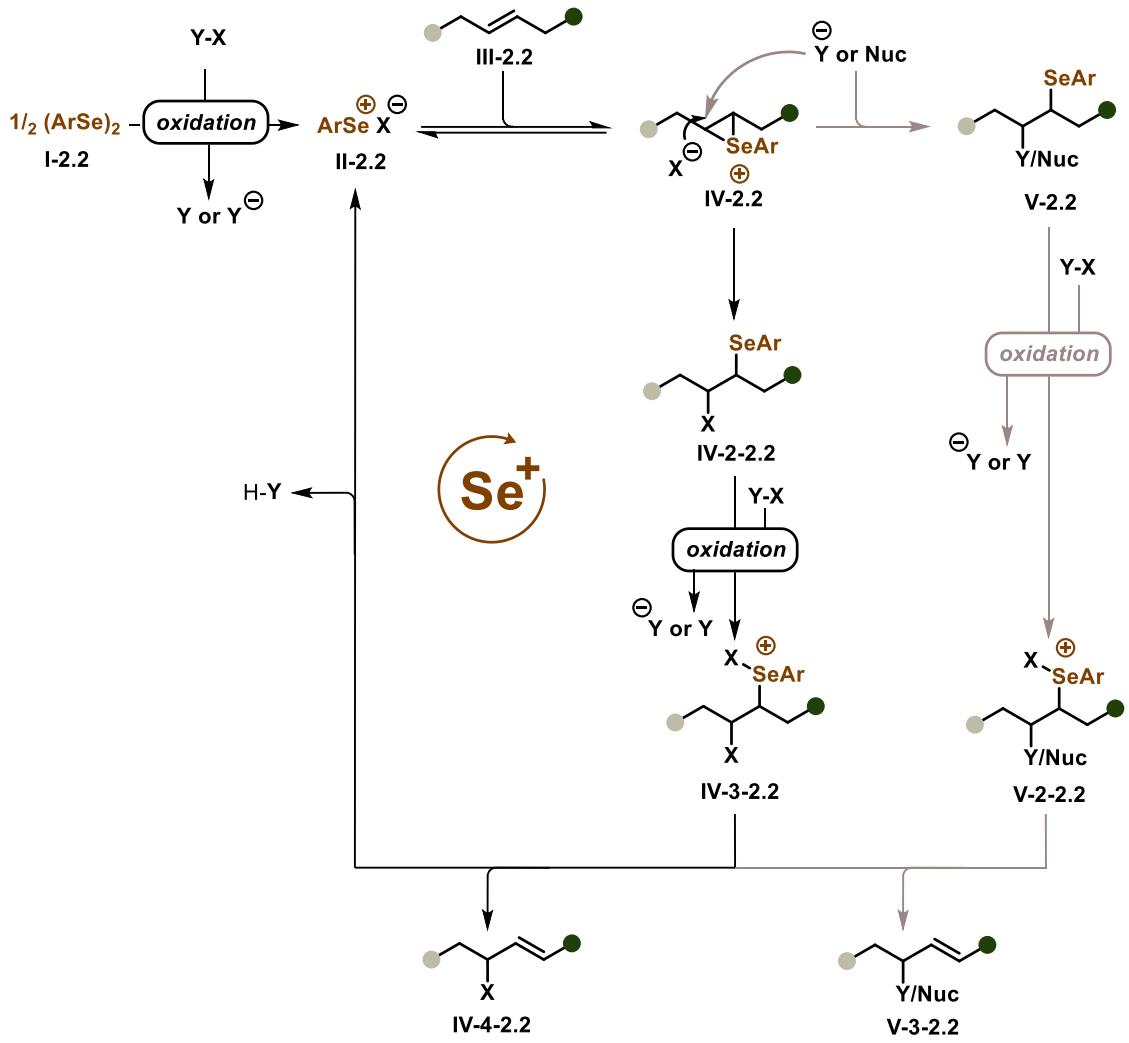
Five years later, the first report on a reaction profile, catalytic in organic diselenide, was then again published by the Sharpless group, when developing a synthesis of allylchlorides (Equation 2.2).[17]



(2.2)

In their proposal about the reaction progression, they postulate an *in situ* generation of PhSeCl by the reaction of $(PhSe)_2$ with NCS which then undergoes the same transformation as described in Scheme 5.[17] Furthermore, they hypothesize that NCS also mediates the elimination of the PhSe-moiety in the intermediate, thus regenerating the catalytic active species.[17]

Continuing efforts by the Torii group then drew a clearer and more general picture of the reaction mechanism, when they investigated the electrochemical conversion of alkenes to allylic alcohols and ethers with catalytic amounts of $(PhSe)_2$.[18] The catalytic cycle commences by the oxidative cleavage of the relatively weak Se–Se σ-bond (44 kcal/mol)[19] and thereby converted into the active electrophilic ArSeX-species **II-2.2** (X represents the counter anion originating from the oxidant after the successful oxidation reaction).[12,14,17,18,20–27]



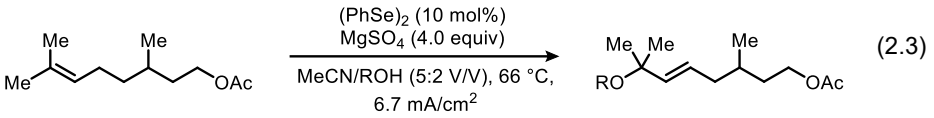
Scheme 6: Generalized mechanism postulated for the catalytic application of organic diselenides.[17,18,23]

The catalytically active species **II-2.2** formed exhibits exceptional chemoselectivity towards π-bonds[23,28] and therefore attacks olefin **III-2.2**,[17,18,20–25,27,29] forming seleniranium-ion **IV-2.2** as an intermediate (Scheme 6).[12,14,23,27,29] From there on, the reaction progression is strongly dependent on the reaction conditions, mainly on the choice of oxidant but nonetheless with constant regioselectivity,[12,18,21] resulting in *anti*-orientation of the ArSe-group and the attacking nucleophile.[21,29] Regarding the first catalytic example reported by the Sharpless group in 1979,[17] the chosen oxidant NCS for example generates PhSeCl *in situ*, with the chloride-anion (**X**$^-$ in Scheme 6) directly serving as nucleophile. After opening the seleniranium-ion **IV-2.2**, the product **IV-2-2.2** is obtained. Alternatively, also the remaining fragment of the oxidant could serve as a nucleophile (**Y** $^-$ in Scheme 6), which is observed when, for example, employing NFSI as terminal oxidant (*vide infra*).[13,30] At last, also external nucleophiles can be applied either if neither part of the previous oxidant (**X** $^-$ or **Y** $^-$**/Y** in Scheme 6) shows sufficient nucleophilic character (c.f. photoredox pathway),[31–33] (structure **V-2.2** in Scheme 6) or as a consecutive process from initial reactivity with the endogenous nucleophile.[34] The addition products **IV-2-2.2** and **V-2.2** then react with another equivalent of oxidant to form the respective cationic species **IV-3-2.2** and **V-2-2.2** which then undergo an elimination

process in combination with a deprotonation to form the vinylic substituted olefins **IV-4-2.2** and **V-3-2.2**.[12,18,20–25,27] As an alternative, distinct literature also report on an attack of another equivalent of an electrophilic selenium species ($ArSe^+$) with the addition products **IV-2-2.2** and **V-2.2**, thereby propagating the catalytic cycle.[14] Furthermore, limited sources describe a nucleophilic substitution of the ArSe-residue instead of elimination, leading to addition products with complete loss of the olefine.[35]

2.2.1. Oxygen based nucleophiles applied in selenium-π-acid catalysis

The possibilities outlined with this concept have led to a multitude of synthetic applications since its initial halogenation reactions (Equation 2.2) starting off in 1979.[17] Another class of nucleophiles that found early on applications are oxygen based nucleophiles, starting with the electrochemical approach by the Torii group in 1981 (Equation 2.3).[18]



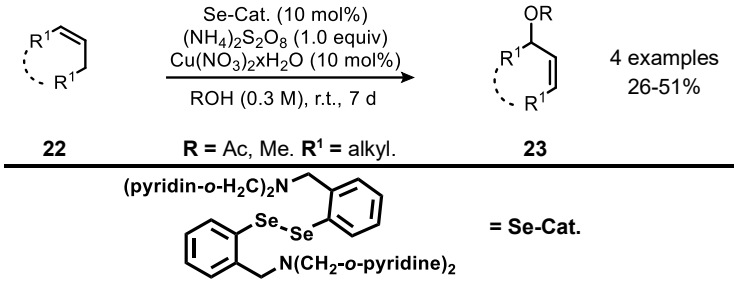
(2.3)

20

21a 82% **R =** Me
21b 80% **R =** H

Their reaction conditions allowed them to convert alkenes into the corresponding allylic alcohols or alternatively into the MeO-ethers if the co-solvent water is replaced by methanol. They proposed a cleavage of the Se–Se σ-bond though oxidation on the Pt-foil-electrode and successive reactivity with the co-solvent to form the active species PhSeOR (equivalent to structure **II-2.2** in Scheme 6), which then reacts with the alkene. Consecutive electrochemical oxidation then leads to elimination of the PhSe-residue which releases the corresponding allylic functionalized products (e.g. Equation 2.3), with $MgSO_4$ being added to avoid overoxidation of the PhSe-moiety and thus preserving the catalytic cycle.[18]

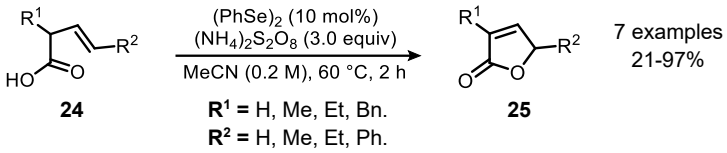
The first organocatalytic approach employing oxygen nucleophiles was then reported more than a decade later, when the Tomoda group published their work on an alike transformation of alkenes to allylic ethers and esters.[24] Similar to their predecessors, they also employed their nucleophile of choice (MeOH or HOAc) in solvent quantities but instead of commercially available $(PhSe)_2$, they resorted to pre-synthesized alternatives (Scheme 7).[24]



Scheme 7: Synthesis of allylic ester/ether developed by the Tomoda group. Isolated yields reported.[24]
$N(CH_2$-*o*-pyridine$)_2$ = *N*,*N*-bis(pyridin-2-ylmethyl)methanamine.

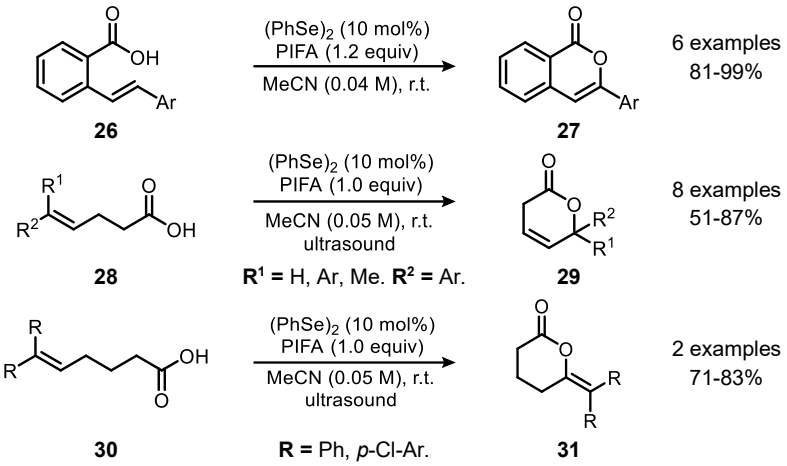
To prevent degradation of the catalytic system by overoxidation, they installed nitrogen-moieties adjacent to the selenium-atoms (Scheme 7) and added catalytic amounts of $Cu(NO_3)_2xH_2O$ which they deemed to be essential for initial Se–Se σ-bond cleavage.[24] Ensuring that the solvent is the nucleophile attacking the seleniranium-ion, they chose $(NH_4)_2S_2O_8$ as stochiometric oxidant which does not release any nucleophilic species upon a reactive turnover. One year later, the Santi group revealed further improvement to the above presented reaction template by employing an excess amount of $(NH_4)_2S_2O_8$ and raising the temperature to 60 °C. In doing so, they were able to utilize commercially available $(PhSe)_2$ to achieve the desired transformation in a now reasonable timeframe (2-7 h compared to 7 d in Scheme 7).[20] The only drawback of their strategy now was that they were relying on an allylic EWG in the starting material to enhance the acidity of the adjacent protons and therefore facilitate the deprotonation leading to the elimination product formation.[20]

Transitioning from intermolecular processes to intramolecular reactions, the Santi group in the same year also reported the first lactonization reaction catalyzed by an organic diselenide catalyst.[25] Minor adjustments to their previously reported synthesis of allylic alcohols and esters[20] were sufficient to convert a series of β,γ-unsaturated acids into the corresponding butenolides **25** (Scheme 8).[25]



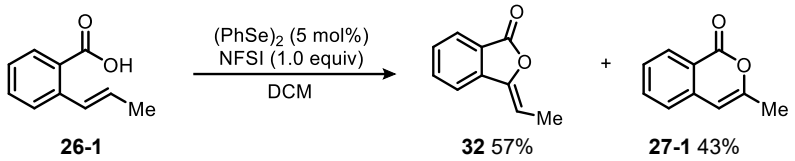
Scheme 8: Lactonization reaction developed by the Santi group. Isolated yields reported.[25]

The Wirth group then expanded the range of application by first exchanging ammonium-persulfate with PIFA ([bis(trifluoracetoxy)iodo]benzene) allowing for the same transformation depicted in Equation 2.3 with lower oxidant loadings (1.05 equiv) as well as lower catalyst loading (5 mol%) in the same timeframe at room temperature.[22] Secondly, they also disclosed the successful synthesis of isocumarine structural motifs **27** as well as 3,6-dihydro-2H-pyran-2-ones **29** and (methylene)tetrahydro-2H-pyran-2-ones **31** by utilizing an adjusted set of reaction conditions and different substituted alkenoic acid **26**, **28** and **30** (Scheme 9).[28,36] Although they obtained excellent yields in all of their transformations in a reasonable timeframe, their procedures were limited to π-bonds conjugated with at least one aryl group to ensure sufficient acidity for the proton to be eliminated along with the PhSe-residue.[28]



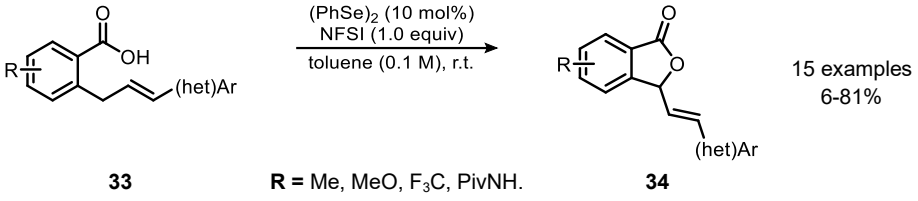
Scheme 9: Synthesis of lactones developed by the Wirth group. Isolated yields reported. ***p*-Cl-Ar =** *para*-chloro-phenyl.[28,36]

The need for aromatic conjugation of the reacting olefin became even more apparent when the Breder group, following the previous results of the Wirth group, attempted the synthesis of isobenzofuranones **32** by utilizing 2-allylbenzoic acid **26** and NFSI as terminal oxidant but ended up having a mixture of the desired compound **32** and isocumarine **27-1** (Scheme 10).[26]



Scheme 10: Product mixture obtained by the Breder group when trying to synthesize isobenzofuranones **32**.[26]

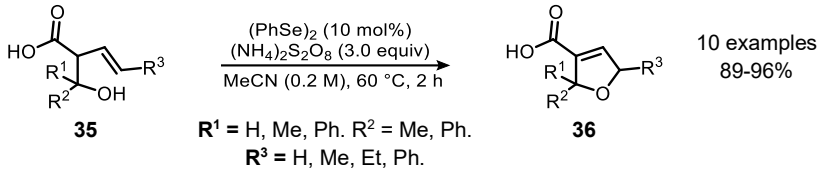
As they were not able to resolve this selectivity issue by any means, they concluded that the (mechanistical-) issue is related to kinetic preference for 5-*exo*-trig versus 6-*endo*-trig and therefore they chose to elongate the carbon chain from vinylated substrate **26-1** to allylic alternative **33**.[26] Again, they did not obtain their desired isobenzofuranone motif **32** but rather the isomer **34** (Scheme 11).



Scheme 11: Synthesis of isobenzofuranones **34** developed by the Breder group. Isolated yields reported. **PivNH =** pivalic-amide. **(het)Ar =** (hetero)aromatic group.[26]

Mechanistically, the authors attributed this reaction outcome to a contribution of the benzylic protons in an undisclosed chain of events, rendering this transformation a novel, overall C(sp^3)-H acyloxylation process.[26]

Concluding the list of oxygen nucleophiles, intramolecular etherification reactions were also initially documented by the Santi group in 1999 after their first reports on the lactonization reaction[20] (discussed above).[21] Utilizing their reactive system composed of catalytic amounts of $(PhSe)_2$ and $(NH_4)_2S_2O_8$, they were able to convert 2-methoxycarbonyl-3-alkenols **35** into their corresponding 2,5-dihydrofuranes **36** in overall excellent yields (Scheme 12). Apart from that, they only report a marginal reaction scope, not including further functional groups apart from the α-acid group which was necessary to drive the reaction.[21]

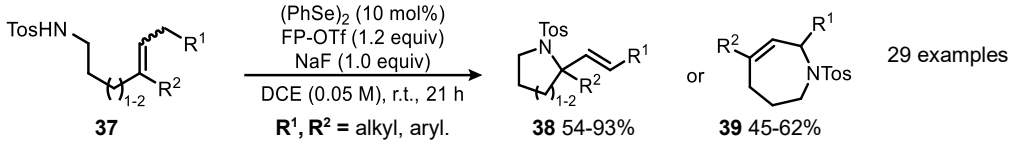


Scheme 12: 2,5-dihydrofuran synthesis developed by the Santi group.[21]

More than a decade later, in 2016, the Zhao group was then able to alter the reaction by extending the relation between the hydroxy group and the alkene by one CH_2-unit, getting rid of the EWG necessity and also reporting a broader scope including functional group tolerance.[12] In similarity to the previously discussed lactonization reaction, the improvement was based on the change of oxidant going from $(NH_4)_2S_2O_8$ to *N*-fluoropyridium-triflate (FP-OTf), allowing the reaction to be carried out at room temperature within a two hours' time frame.[12] Moreover, they were also able to expand the ring size from five- to six-membered heterocycles.[12]

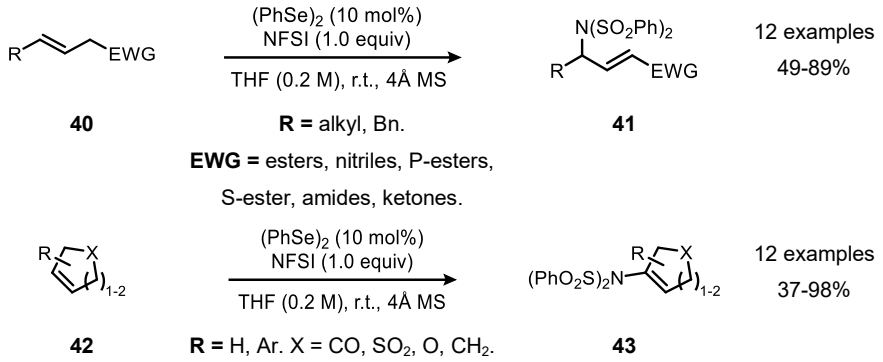
2.2.2. Nitrogen based nucleophiles applied in selenium-π-acid catalysis

In addition to their developed synthesis of tetrahydrofuranes and tetrahydro-2*H*-pyrans, the Zhao group also disclosed a slightly altered set of reaction conditions to allow for the cyclization of olefinic sulfonamides (Scheme 13).[12]



Scheme 13: Formation of *N*-heterocycles reported by the Zhao group. Isolated yields reported.[12]

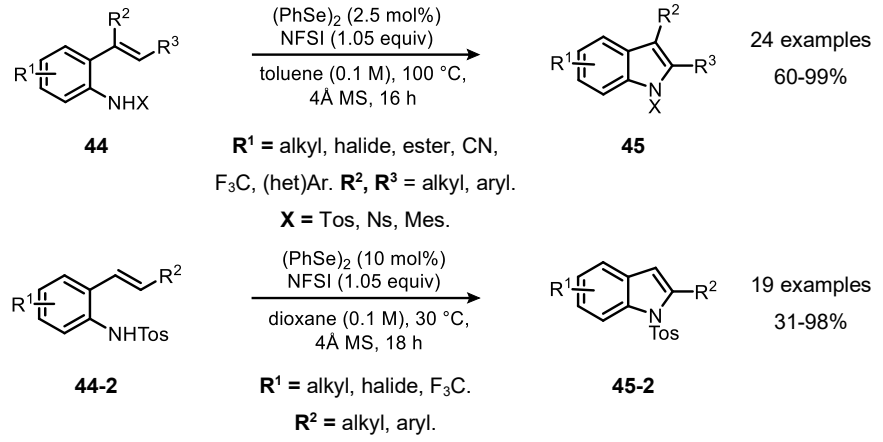
The first report on the application of nitrogen based nucleophiles however was presented by the Breder group in 2013, disclosing their efforts on the allylic and vinylic amination of alkenes.[13] By employing NFSI, they were able to selectively incorporate the *N*-terminus of the oxidant rather than the halide counterpart as it was previously observed by the Sharpless group[17] and Tunge et al.,[37] who observed halogenated products when utilizing NCS as stochiometric oxidant.[13] In combination with 5 mol% of $(PhSe)_2$ as catalyst, 1 equivalent of NFSI was sufficient to convert a series of acyclic **40** and cyclic alkenes **42** into the corresponding allylic and vinylic imides **41** and **43** in moderate to good yields (Scheme 14).[13]



Scheme 14: Vinylic and allylic imidation reported by the Breder group. Isolated yields reported. **P-ester =** phosphoric acid ester, **S-ester =** sulfonic acid ester.[13]

A slightly altered set of conditions as depicted in Scheme 14 was then also used to aminate allylic alcohols[30] or pyridinate terminal dienes.[38]

Referring back to the intramolecular application at the start of this chapter, the first reports of such processes were independently presented by the Breder group and the Zhao group converting *ortho*-allylic anilines into the corresponding (aza-)indoles **45** and **45-2**.[14,39] With only marginal differences in the reaction conditions, the Breder group kept their synthetic focus on different substitution patterns on the indole moiety[14] and the Zhao group presented a broader variety on substituents in selected positions (Scheme 15).[39]



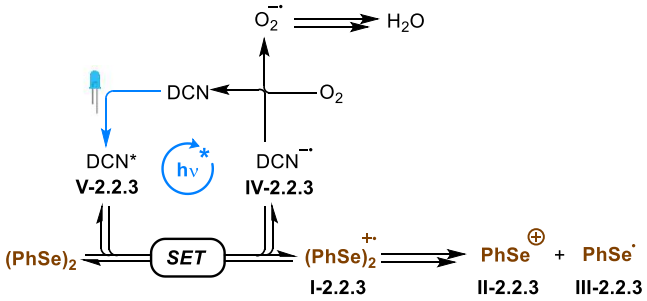
Scheme 15: (Aza-)indole synthesis developed by the Breder group (upper) and the Zhao group (lower). Isolated yields reported in both cases. **Tos =** tosylate, **Ns =** nosylate, **Mes =** mesylate.[14,39]

Irrespectively, both groups enclosed further unique insight into the general reaction applicability such as the intolerance of carboxylic acid derived substituents on the nitrogen atom (modulation of the pK_a of the N-H unit)[14] or that geminal substitution of the double bond results in 1,2-subsitution migration during the cyclization reaction.[39]

2.2.3. Selenium-π-acid photoredox multicatalysis

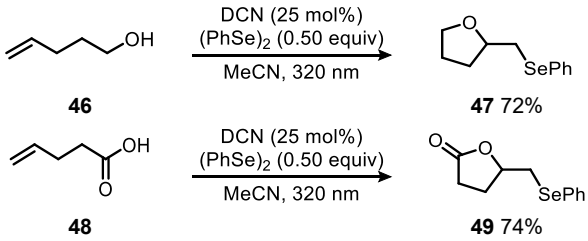
A common drawback of the majority of the above presented applications is their dependence on the proper choice of oxidant, as already disclosed with the probable complications arising from the chemoselectivity issues.[23,26,40] Another recurring issue regarding the use of stoichiometric oxidative chemicals is the question of atom-economy, where stoichiometric amounts of waste material originating from the oxidant, are generated in the catalytic cycle.[31,32,40,41]

Among the electrochemical approaches to tackle these problems,[18,27,42] the possibility to use light irradiation became an interesting vantage point, with initial experiments already published in 1992 by the Pandey group.[19] In their work, they postulate that upon *SET* from an excited photosensitizer (DCN in their case), $(PhSe)_2$ is oxidized to its corresponding radical cation **I-2.2.3** which consecutively undergoes Se–Se σ-bond cleavage, resulting in the a cationic **II-2.2.3** and a radical **III-2.2.3** species (Scheme 16).[19]



Scheme 16: Photocatalytic activation of $(PhSe_2)$ as postulated by the Pandey group. **DCN =** 1,4-dicyanonapthalene.[19]

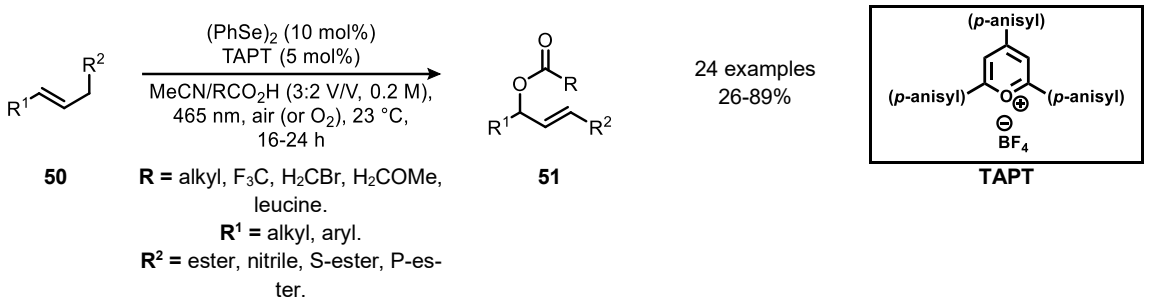
In accordance with the general mechanism depictured in Scheme 6, the cationic species **II-2.2.3** is then attacking the olefin resulting in the addition product formation with a theoretically, unrestricted choice of nucleophiles. As an example, the Pandey group disclosed in their publication an etherification reaction generating furanes and pyranes as well as 5- and 6-membered lactones in overall good yields (Scheme 17).[19]



Scheme 17: Exemplary transformations reported by the Pandey group. Isolated yields reported.[19]

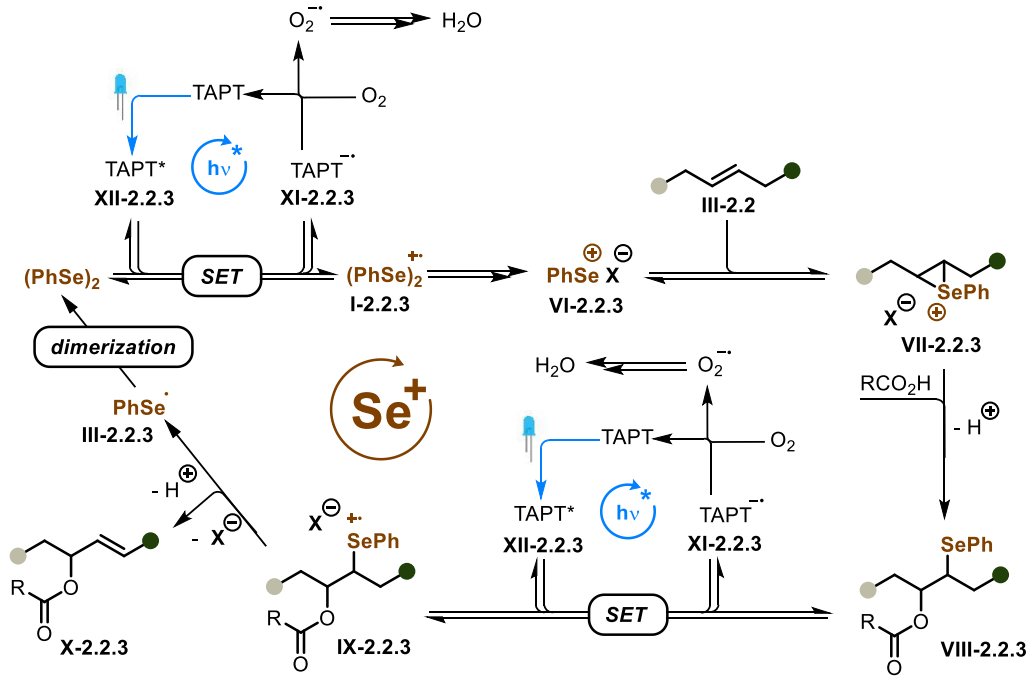
However, as can be seen in the scheme above, the authors did utilize stoichiometric amounts of $(PhSe)_2$ to specifically obtain the addition products **47** and **49** and therefore no information about the elimination of the selenium residue was included at this point.

It took almost two decades for this concept to be re-discovered and being converted to a process utilizing substoichiometric amounts of organic diselenide and mimicking the transformations addressed in Chapter 2.2.2. In 2016, the Breder group was the first team to report about a oxidative functionalization of an olefin using catalytic amounts of $(PhSe)_2$ and TAPT (2,4,6-tris(4-methoxyphenyl)pyrylium tetrafluoroborate) as photocatalyst. The developed process covered a multicatalytic adaption to the, initially in 1992 published, $(PhSe)_2$ induced esterification reaction,[24] thus proving the potential for ambient air as terminal oxidant for such processes (Scheme 18).[31]



Scheme 18: Multicatalytic esterification reaction developed by the Breder group. Isolated yields reported. **P-ester =** phosphoric acid ester, **S-ester =** sulfonic acid ester.[31]

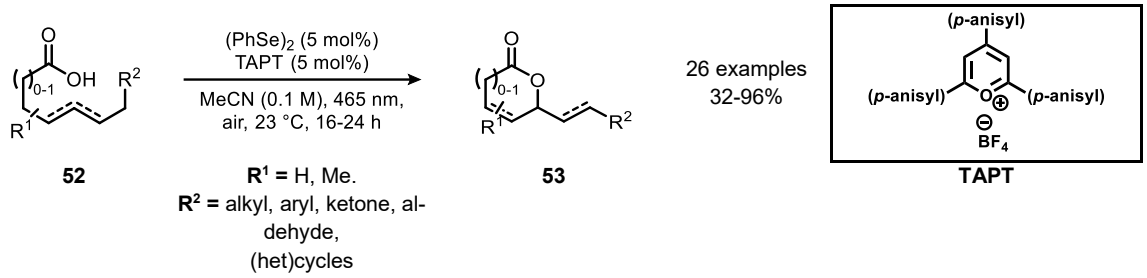
Based on a series of control experiments (NMR and MS analysis), the authors established a reaction mechanism starting from the oxidative cleavage of the diselenide catalyst as described before (Scheme 16).[32]



Scheme 19: Multicatalytic reaction mechanism as postulated by the Breder group. $\mathbf{X}^-$ displays the counter ion of the chosen photocatalyst.[31]

Following the generation of the active species **VI-2.2.3**, an electrophilic attack on the olefin results in formation of the seleniranium-ion **VII-2.2.3** which is opened by nucleophilic attack of the carboxylic acid resulting in the addition product **VIII-2.2.3** (Scheme 19). This intermediate **VIII-2.2.3** then undergoes another *SET* with the excited photocatalyst, forming the radical cation **IX-2.2.3**, which upon deprotonation releases the PhSe-radical **III-2.2.3**. Dimerization of two equivalents of radical **III-2.2.3** then regenerates the catalyst precursor and thereby closes the catalytic cycle.[31]

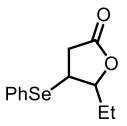
Although this report now included a catalytic application of the organic diselenide, two aspects were still debatable or entirely unclear at this stage. The first of these is the mode of elimination of the selenium-radical-cation moiety after the second *SET* with the photocatalyst and the second one is the actual mechanistic progression turning the diselenide-radical-cation **I-2.2.3** into the active catalyst **VI-2.2.3**. Investing further efforts in implementing this multicatalytic reactivity mode into the general chemical toolbox, one year later, again the Breder group, published their results on the lactonization reaction of alkenoic acids.[32]



52 **R¹ =** H, Me. **R² =** alkyl, aryl, ketone, aldehyde, (het)cycles **53** **TAPT**

Scheme 20: Lactonization reaction developed by the Breder group. Isolated yields reported. **het(cycles) =** heteroatom containing carbocycles.[32]

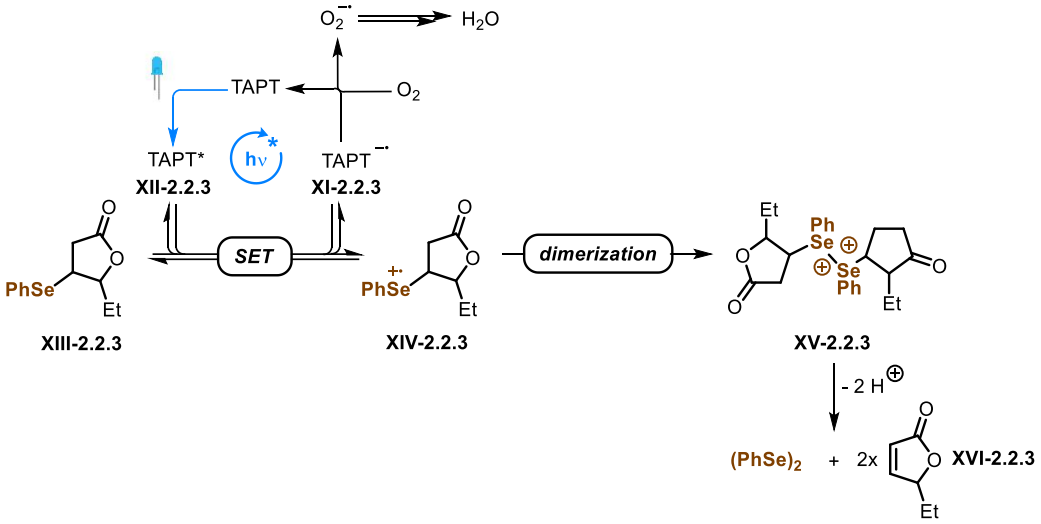
In addition to disclosing their reaction scope, they also reported their mechanistic investigations specifically regarding the formation of the catalytic species **VI-2.2.3** (Scheme 19) and the elimination of the selenium residue from the radical cation to propagate the cycle (analogously to structure **XI-2.2.3** in Scheme 19). During kinetic NMR studies, they observed that prior to any conversion of starting material **52**, the diselenide precursor $(PhSe)_2$ is almost entirely consumed and only after that, starting material conversion is observed.[32] Furthermore, the formation of the addition intermediate **54** (Figure 3) then occurs rapidly and material is accumulated until all $(PhSe)_2$ is used up and only then, product formation is recorded.[32] These results were further assured in control experiments, adding $(PhSe)_2$ and TAPT to a solution of the intermediate **54**, where again no product **53** formation was observed until full conversion of the added $(PhSe)_2$.[32]



54

Figure 3: Mechanistic intermediate used for investigations by the Breder group.[32]

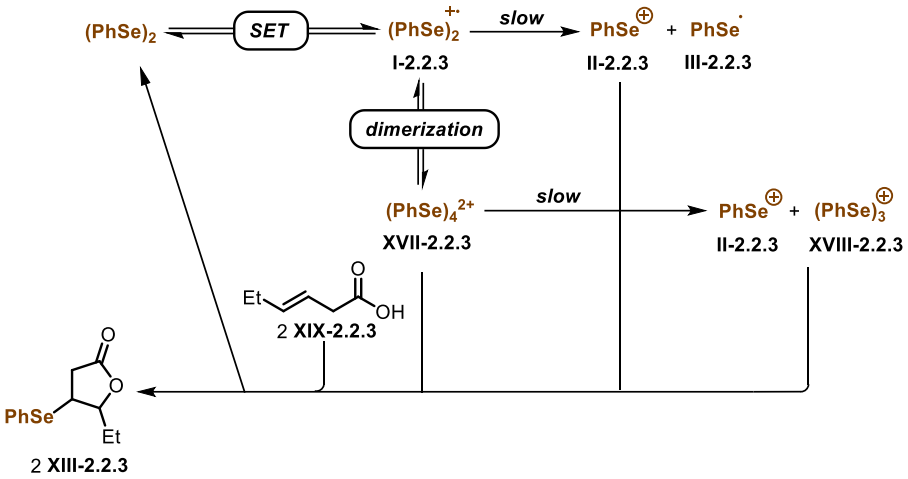
They interpreted these findings in a way that the rate determining step must take place after the formation of intermediate **54** which was proven when monitoring the formation rate of the intermediate **54** depending on the irradiation intensity as well as initial concentration.[32] In order to rationalize this concept, they thought of possible ways to propagate the catalytic cycle and came up with two slightly different ideas. The first was already included in their previous publication and simply involves the elimination of a proton and the PhSe-radical **III-2.2.3** (Scheme 19). The other alternative was that a dimerization of the respective intermediate **XIV-2.2.3** after *SET* (Scheme 21) occurs prior to the elimination step, resulting in the overall elimination of two product molecules **XVI-2.2.3**, two protons and one equivalent of $(PhSe)_2$ (Scheme 21).[32]



Scheme 21: Alternate conclusion of the catalytic cycle envisioned by the Breder and Siewert group.[32]

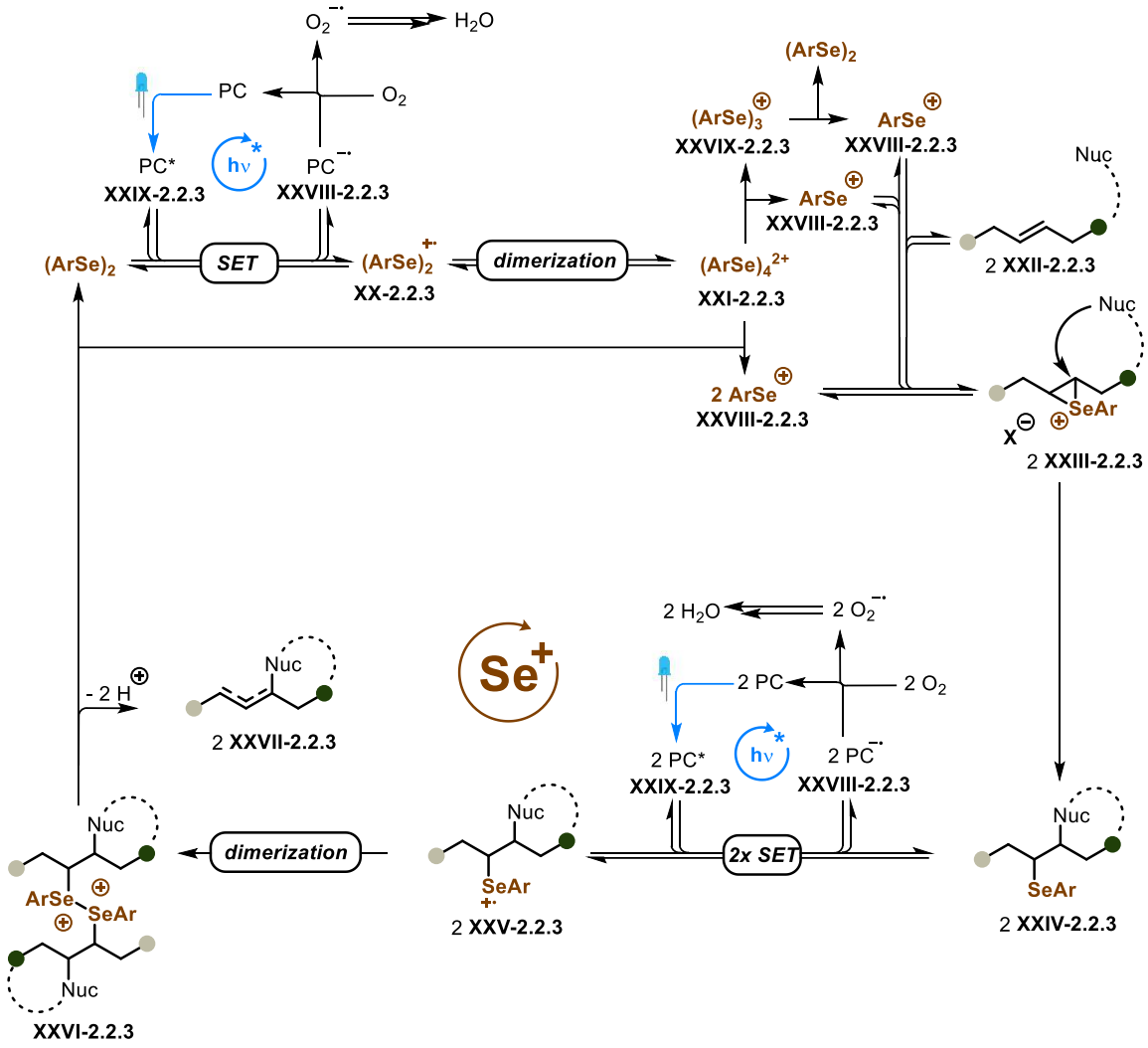
Resorting to mass spectrometry in combination with computational analysis, enough evidence was found to declare the elimination pathway according to Scheme 21 to be the mode of operation.[32] These MS studies also revealed a dominant signal relating to the mass of a trimeric $(ArSe)_3$-cation and computational studies concluded that the formation of a trimeric cation (based on one equivalent of $ArSe^+$ and one equivalent of $(ArSe)_2$) displays an exothermic process. Based on these results, it was further proposed that instead of $ArSe^+$ being the catalytically active species (c.f. structure **VI-2.2.3** in Scheme 19), rather the mentioned cationic trimer serves as the active catalyst due to its rapid formation.[32]

Explicit information on the catalytically active species was then reported one year later, when the Breder group in collaboration with the Siewert group performed cyclovoltammetric analysis on different intermediates of the so far established catalytic cycle.[40] Apart from delivering further evidence to prove the elimination mode depictured in Scheme 21, the groups were also able to draw a picture on the mechanistic progression regarding the initiation of the catalytic cycle (Scheme 22).[40]



Scheme 22: Abbreviated sequence postulated for the formation of the catalytic active selenium species.[40]

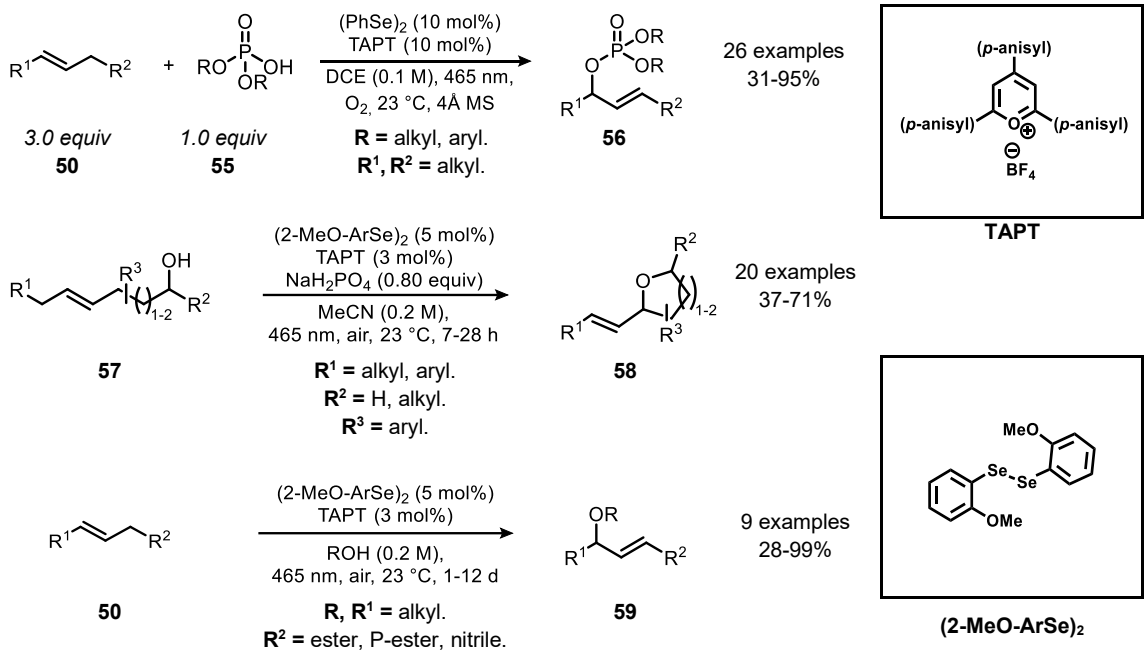
In contrast to the thus far associated catalytic active species $PhSe^+$ and $(PhSe)_3^+$, these investigations concluded that their formation is kinetically inferior to a dimerization process of the radical-cation **I-2.2.3**, and therefore only contribute little to the actual product formation.[40] Instead, a dication-tetramer **XVII-2.2.3** is rapidly formed which then catalyzes two transformations of the starting material **XIX-2.2.3** to the addition intermediate **XIII-2.2.3** while releasing one equivalent of $(PhSe)_2$ in the process to continue the catalytic cycle.[40] Combining all these investigations into one mechanism, a selenium-π-acid photoredox multicatalytic reaction is postulated as follows (Scheme 23). The diaryl-diselenide **$(ArSe)_2$** of choice is firstly oxidized in a *SET* event with the excited state of the chosen photocatalyst **XXIX-2.2.3**. While the resulting radical-anion of the photocatalyst **XXVIII-2.2.3** is converted back to the photocatalyst **PC** by another *SET* with the oxygen provided, the aryl-diselenide-radical-cation **XX-2.2.3** undergoes a dimerization process, which allows for the consecutive attack on two equivalents of provided olefin **XXII-2.2.3**, while also regenerating one equivalent of aryl-diselenide **($ArSe_2$)**. The obtained seleniranium-ions **XIII-2.2.3** are then (intramolecularly-) attacked by the provided nucleophile leading to the addition products **XXIV-2.2.3**, which then undergo a dimerization process after being oxidized by another *SET* mediated by the excited photocatalyst **XXIX-2.2.3**.



Scheme 23: Selenium-π-acid photoredox multicatalytic reaction mechanism based on the investigations made by the Breder group and corresponding collaborators.[32,40] **X**$^-$ represents the counter-ion provided by the photocatalyst.

Subsequent elimination of two protons and one equivalent of **(ArSe)$_2$** concludes the cycle, while obtaining two equivalents of product **XVII-2.2.3**.

Following these mechanistic investigations, the Breder group continued providing application examples such as the phosphatation and inter- as well as intramolecular- etherification of unactivated alkenes (Scheme 24).[33,41]



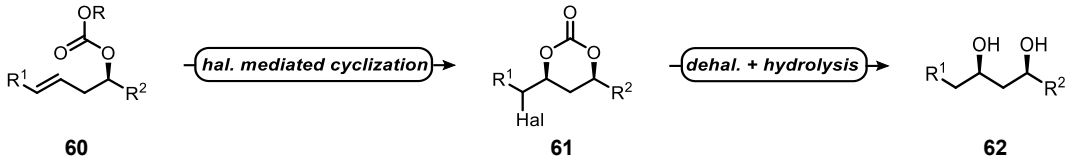
Scheme 24: Application of selenium-π-acid photoredox multicatalysis reported by the Breder group. NMR-yields reported.[33,41]

With a range of 28-99% overall reported yield for the developed processes, the only complications according to the authors originated from either isolation issues due to hydrolysis of the phosphonic esters,[41] or limitations regarding the choice of nucleophile due to the necessary application as reaction solvent.[33] Explicitly, the intermolecular etherification reaction was documented to be a less fruitful process as starting material **50** was restrained to incorporate an electron withdrawing group, the reaction had to be conducted in the nucleophile as solvent and the overall time exceeded several days.[33]

Nonetheless, with these reports a significant portion of available oxygen nucleophiles has been covered ranging from carboxylic acids, over alcohols (intramolecular as well as intermolecular) on to phosphoric acids. However, including the transformations reported with stochiometric oxidant, there are further oxygen nucleophiles, that have thus far not been utilized.

2.3 Cyclic carbonates

One of the oxygen based nucleophiles in question are carbonate groups (or also known as carbonic acid esters), consisting of two alkyl- or aryloxy groups flanking the carbonyl group.[43] Carbonates can be found either with symmetric or asymmetric substitution pattern as well as part of a cycle or acyclic.[43] Apart from imminent decarboxylation resulting from hydrolysis of either of the flanking alkyl - or aryloxy groups,[44] especially cyclic carbonates show great reactive versatility allowing for a multitude of transformations based on the carbon backbone.[45–49] Among the most prominent synthetic applications are the stereoselective syntheses of 1,n-diol motifs based on stereoselective cyclization of acyclic carbonates and subsequent hydrolysis (Scheme 25).[45,50–53]



Scheme 25: Example concept for utilizing cyclic carbonates as means to selectively synthesize a *syn*-1,3-diol **62**.[45,50,54] The shown concept is based on a carbonate synthesis based on the use of halogens (**hal.**) and the cyclization was determined to generally favor the *cis*-configuration. **dehal. =** dehalogenation.[45,49,54,55]

Further valuable transformations are affected by the carbon backbone, where especially the iodo-carbonates **65** (synthetic detail *vide infra*) have been converted to a series of follow up products using different conditions (Figure 4). Possible transformations include simple opening of the carbonate resulting in an open chain carbonate **66** or with additional epoxidation of the liberated OH-group **64**. Also, complete hydrolysis of the carbonate is feasible (Scheme 25) and additionally one of the resulting OH-groups can be used in an epoxidation reaction whereas the iodine serves as a leaving group (structure **67**, Figure 4).[45] Concerning the consecutive epoxidation reactions, it has to be noted, that these reaction also occur with good stereoselectivity and therefore this reaction protocol has been applied to a number of total syntheses over the years.[56–61] Furthermore, by basic elimination of the iodine, enol carbonate **63** can be obtained, which serves as a “masked aldol synthon” being liberated by further treatment with a nucleophile, opening up the carbonate.[47]

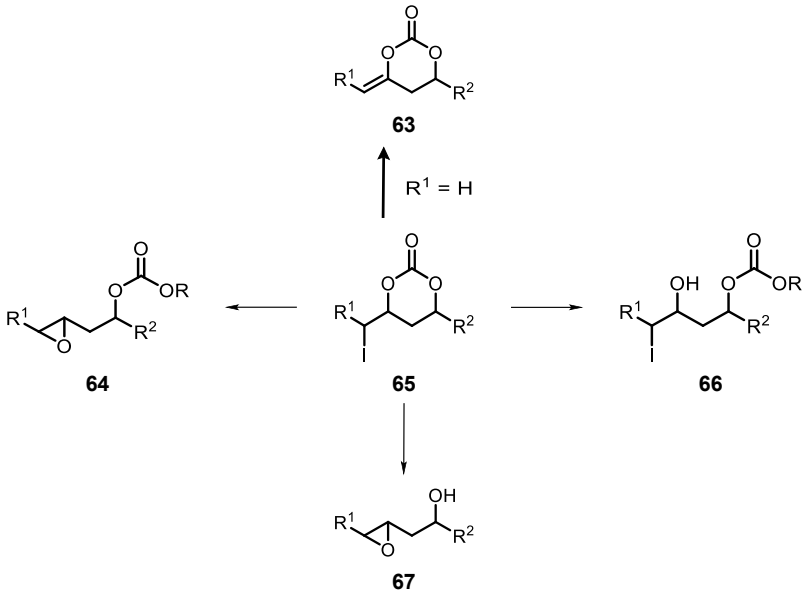


Figure 4: Possible further transformations of iodo-carbonates.[45,47]

The opening of cyclic carbonates furthermore represents a common concept regarding polymer chemistry, as a way of obtaining valuable acyclic polymeric materials[62–66] in a more controllable setting compared to similar processes using either epoxides or isonitriles.[48] Thereby obtained polymers exhibit significant biodegradability[46,64,65,67,68] and therefore find application also in biomedical fields.[64,65,69] Furthermore, when using cyclic carbonates with an additional olefin moiety, two-fold

polymerization allows for cross coupling and therefore extended synthetic opportunities[48] such as synthetic glass for example.[43,46,63,70]

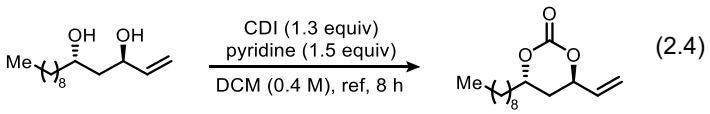
Regarding non-synthetic value, cyclic carbonates found broad application as base labile protecting groups for 1,n-diols,[51,68,71–73] as well as an early day aid to determine their relative configuration.[74,75] They also occur in natural products,[43,68] in selected pharmaceutical products and fine chemicals,[66] or find applications as solvents or electrolytes in batteries.[43,62,63,66,73]

2.3.1. Synthesis of cyclic carbonates

Having outlined the value of the functional group, it stands to reason that over the years multiple ways for the synthesis of cyclic carbonates have been disclosed, each serving different needs. These approaches can overall be categorized by addressing the following three questions:

1) What is the synthetic aim and what kind of further transformations are needed?
2) Which functional groups are included in the starting material?
3) What is the desired ring size?

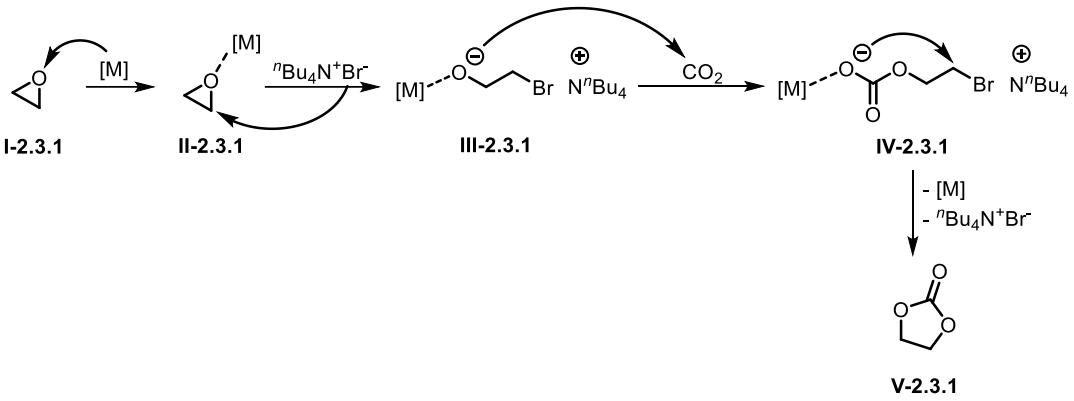
One of the most commonly found procedure employs the use of 1,n-diols as starting material in combination with a “CO-transfer” reagent (Equation 2.4, example by the Evans group)[76] such as phosgene,[74,75,77] triphosgene,[71] CDI (*N,N’*-carbonyl diimidazole),[76,78] 4-nitrophenylchloroformate[62,79] or others,[80] with initial reports dating back to the 1930s.[75]



68 **69** 90% (2.4)

Although this protocol allows for the simple installation of the cyclic carbonate moiety in generally good yields with toleration of various ring sizes such as 5-[75] and 6-membered[74,76] rings, the necessary presence of the 1,n-diol motif in the starting material defeats the synthetic value of implementing said functional group in a stereospecific manner.

A different concept focuses on the use of epoxides as synthetic precursor material which are either generated *in situ*[66,73,81] or directly applied as starting material.[48,63,68,82,83,84,85] In general, one can differentiate between two modes of reactivity depending on the reaction conditions. The first mechanistic progression is reported to proceed by overall formal insertion of CO_2 (provided as reaction atmosphere) into one C–O σ-bond of the epoxide.[63,68,81,82,84] To allow for the insertion to take place, the epoxide is activated by metal coordination **II-2.3.1**, then opens up resulting in a stabilized carbocation or a positive polarized carbon atom in **III-2.3.1** if an additional weak nucleophilic base is used to enforce the epoxide opening. The also liberated oxy-anion then performs a nucleophilic attack on a CO_2 molecule and concluding attack of the *in situ* generated carbonate-anion **IV-2.3.1** back on the carbo-cation (or the positive polarized carbon-atom) terminates the CO_2 insertion and a 5-membered cyclic carbonate **V-2.3.1** is obtained in the process (Scheme 26).[63,68,81,82,84]



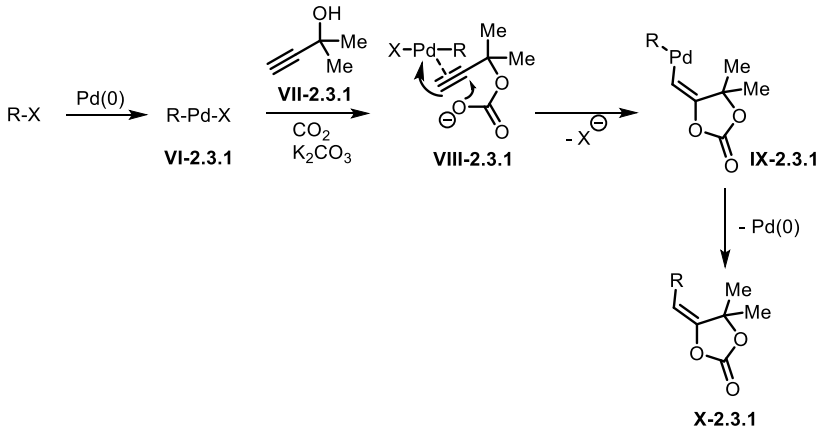
Scheme 26: Mechanistic example for the formal CO_2 insertion procedure. **[M]** is representing various metal-salen-complexes used by the authors.[63,86]

The second concept follows similar reactivity but instead of a nucleophilic attack on CO_2, the epoxide is opened up carboxyl-anion of various origin.[66,73] The liberated oxy-anion (from the formed epoxide) is then attacking the carbonyl-carbon atom closing the cyclic carbonate in a transesterification process.[66,73]

Although there are limited reports performing the same transformations with oxetanes (limited scope and only moderate yields), this reaction concept is limited to the synthesis of 5-membered cyclic carbonate system thereby reducing its overall value.[64,73,87]

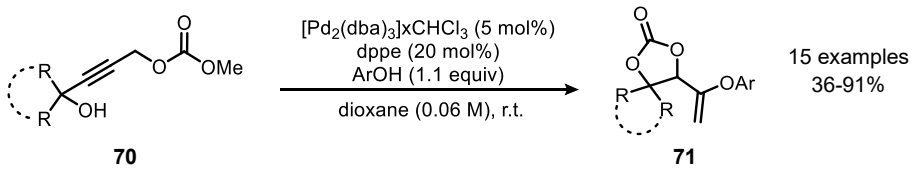
The most versatile approach for the synthesis of cyclic carbonates is based on the application of unsaturated alcohols, allowing for a multitude of structural outcomes depending on the choice of olefin (double- vs. triple bond), the amount of carbon chain units between the alcohol and the olefin, and the choice of reagents.

Beginning with propargylic alcohols, literature reports can be found either generating the acyclic carbonate as an intermediate[46,70,88–97] with the use of CO_2 and a strong base or using a ^{t}BuO-carbonate as starting material.[98,99] If the propargylic alcohol **VII-2.3.1** (Scheme 27) is used as a starting material, the *in situ* formation to the carbonate is achieved by deprotonation of the hydroxy group which then attacks CO_2 supplied in the reaction atmosphere (compare Scheme 26, **III-2.3.1** to **IV-2.3.1**). [46,70,88–97] Meanwhile, the triple bond is activated by (metal-) coordination (e.g. Pd, Cu, Co) which allows for an intramolecular attack of the carbonate functional group (either the anion or the ^{t}BuO-carbonate) closing the cycle.[46,70,88,90–99] Reductive elimination of the metal (either with an additional base or a subsequent cross coupling event),[91–93] results in the formation of the enol-carbonates **X-2.3.1** (Scheme 27).



Scheme 27: Mechanistic rational for the synthesis of cyclic carbonates, using propargylic alcohols, as reported by Uemura et al.[91]

Additional reports can be found disclosing a slightly altered reaction progression centered around the reversible CO_2 elimination from a propargylic alcohol bound to a methyl-carbonate **70** as starting material. This variation has the consequence that instead of enol-carbonate **X-2.3.1**, allylic carbonates **71** are obtained with aryl-alcohols as nucleophiles (Scheme 28).[68,85,100,101]

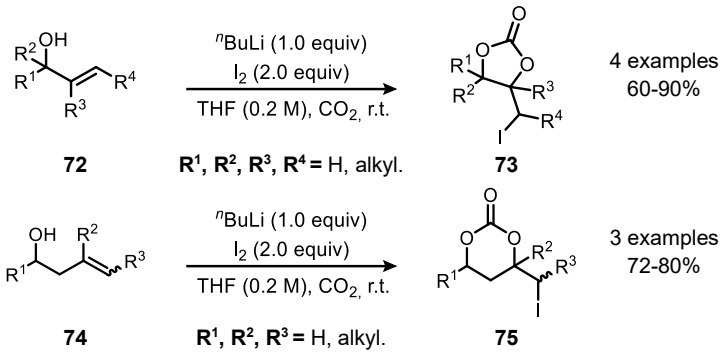


Scheme 28: Example for the altered product formation as reported by the Ihara group. Isolated yields reported.[100]

Although there are limited examples for the synthesis of 6-membered cyclic carbonates,[98] the application of homoallylic alcohols has been proven to be more suitable for such ring sizes. Furthermore among those methods, one can differentiate between exclusive oxidative processes[53,65,102] and (potential-) redox neutral concepts[45,49,50,52,54–61,103,104] in which case especially the latter become more interesting in the context of modern chemical process development.[105]

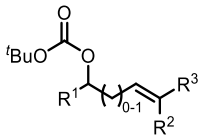
Whereas the exact structural outcome and the reaction progression for the oxidative processes are strongly dependent on the reaction conditions, the (potential-) redox neutral concepts follow one general idea which possesses strong similarity to the reaction concept for the selenium-π-acid reported in Chapter 2.2. Commonly, the alkene is activated by an electrophilic halide species (iodine or bromine) and the resulting haliranium-ion is then opened by an attack of the carbonate functional group, closing the cycle.[45,49,50,54–61,103,104]

The first report on this concept was provided in 1981 by Cardillo et al.[50] using allylic and homoallylic alcohols in combination with ^{n}BuLi as base, CO_2 and stochiometric iodine to obtain both 5- and 6-membered cyclic iodo-carbonates in a one-pot transformation (Scheme 29).



Scheme 29: Cyclocarbonate synthesis reported by Cardillo et al.[50]

Even though these initial reports included successful examples for both 5- and 6-membered cyclic carbonates, the overall reaction scope presented includes only 7 examples with no mentioning of functional group tolerance.[50] Furthermore, the authors did not report on a halogen elimination step to remove the iodine therefore, instead, they mentioned a Barton-McCombie reaction, reductively removing the iodine and consecutive basic hydrolysis of the cyclic carbonate selectively obtaining the *syn*-1,3-diol.[50] With extended focus on the stereoselectivity of the cyclization reaction,[54] one year later, also the first reports using acyclic ^{t}BuO-carbonates **76** as starting materials (Figure 5), were published.[45,104]



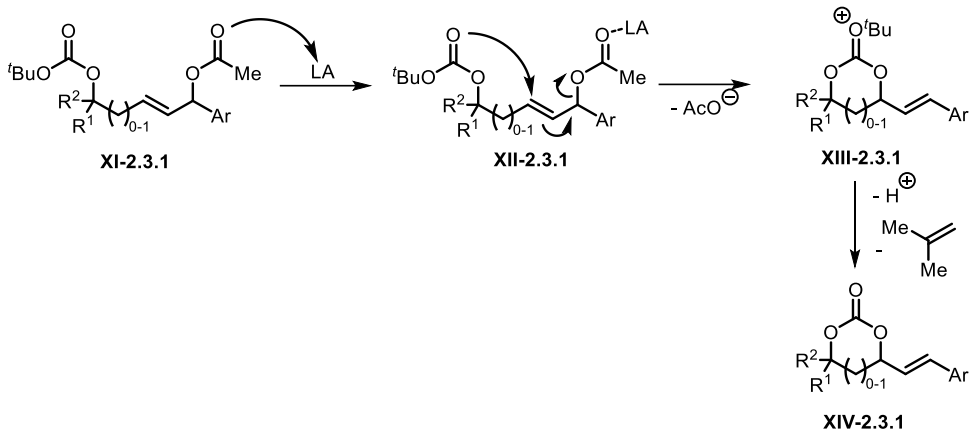
76

Figure 5: General representation for the first applied ^{t}BuO-carbonates **76**.

However, apart from disclosing the possibility to use acyclic carbonates **76**, instead of generating them *in situ*, no further progress was reported neither in terms of reaction scope, nor reaction yield, nor the selectivity of the cyclization process (dr values range from 4:1 to 13:1 for the *in situ* generated carbonates and from 4:1 to 10:1 for the ^{t}BuO-carbonate **76** as starting material), all favoring the *cis*-isomer for 6-membered rings.[45] A decade later, an improvement in the dr values was then reported when changing from stoichiometric iodine to stoichiometric iodine-bromide and significantly reducing the reaction temperature to - 80°C.[49,55] Still, the concept did not include the elimination of the halide and the overall applicability was limited, only reporting 13-examples with moderate functional group incorporation.[49,55]

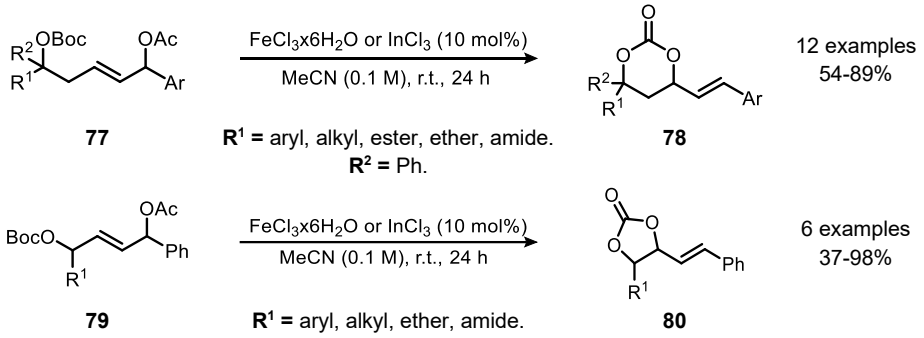
In contrast to all the above presented methods, which are oxidative in nature but did not include an elimination step to regain the olefin (e.g. one report by Bates et al.),[106] there has thus far been only one such approach reported by Cornil et al. in 2014.[52] Their work is based on the activation of an allylic acetate by Lewis-acid catalysis (Scheme 30, structure **XII-2.3.1**), thereby increasing the electrophilicity of the C–C double bond.[52] The olefin is then attacked by the incorporated allylic or

homoallylic *t*BuO-carbonate-group and subsequently regained by elimination of the AcO-group (Scheme 30).



Scheme 30: Mechanistic progression from the reports by Cornil et al. using a Lewis-acid (**LA**) as catalyst.[52]

Not only does this protocol display the elimination step to regain the olefin, the authors also were able to promote the desired reaction using only catalytic amounts of $FeCl_3x6H_2O$ or $InCl_3$ as Lewis-acids. Their reported reaction scope includes nine examples for 6-membered cyclic carbonates and five examples for 5-membered rings with overall isolated yields ranging from 37-98%, an average diastereomeric ratio of 35:10 and good functional group tolerance (Scheme 31).[52]

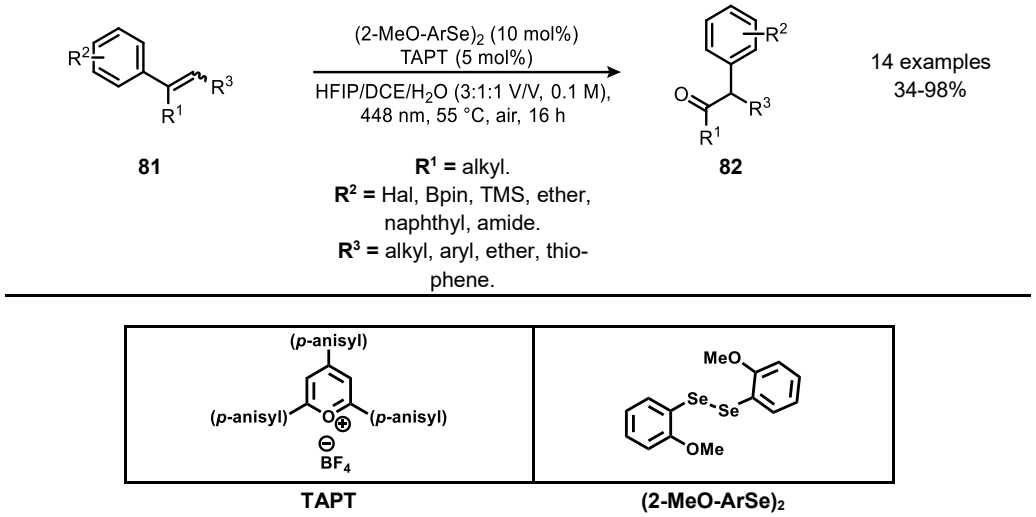


Scheme 31: Cyclic carbonate synthesis reported by Cornil et al. Isolated yields are reported.[52]

However, the protocol still includes limitations such as the fact that no primary carbonates **77** and **79** were tolerated and the obtained π-bond in the products **78** and **80** has to be conjugated with an aryl group. Furthermore, the reactivity of the olefin is based on the presence of the AcO-group, serving as a leaving group in the overall process. Referring back to the previous chapter, explaining the reactivity mode of selenium-π-acid catalysis as well as considering the halogen mediated syntheses of cyclic carbonates, it stands to reason that these limitations (necessity of the OAc-activation group and the aromatic conjugation in the products) of the hereby presented approach by Cornil et al.[52] could be resolved by employing a selenium-π-acid catalyst rather than the used Lewis-acid catalysts.

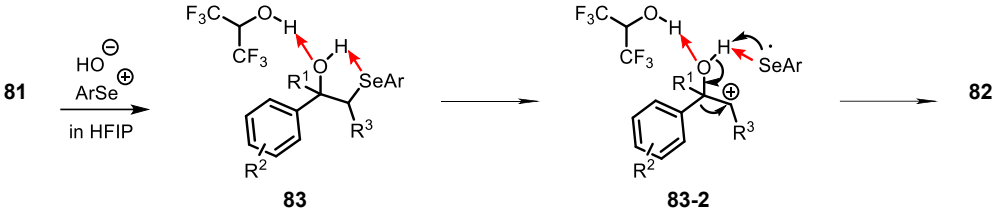
2.4 Selenium-π-acid catalyzed rearrangement reactions

Remaining with the idea of further oxygen based nucleophiles in selenium-π-acid catalyzed transformations of alkenes, the use of water as a nucleophile, resulting in the corresponding allylic alcohols (Equation 2.3) was already covered before.[18] However, novel reactivity of using water as a nucleophile was recently developed by the Breder group, transforming stilbenes **81** into the corresponding ketones **82** by a migratory Tsuji-Wacker oxidation (Scheme 32).[107]



Scheme 32: Tsuji-Wacker oxidation developed by the Breder group. **Bpin =** pinacol-borane, **TMS =** trimethylsilane, **Hal =** halogen. NMR yields reported.[107]

The conceptual basis for this protocol were prior results by the same group, in which they submitted selenohydrins **83** (Scheme 33) to a photoredox cycle that resulted in the substitution (rather than elimination) of the ArSe-residue and furnished the corresponding ketone as reaction product after a semipinacol type I[108] rearrangement.[109]



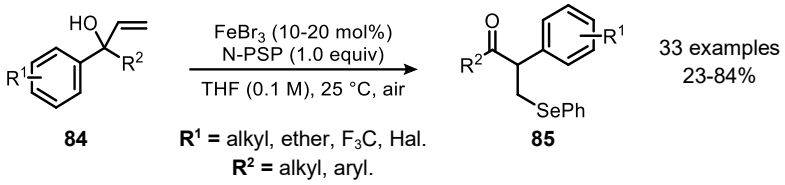
Scheme 33: Initial anticipated reaction progression for the 1,2-aryl migration based for the rearrangement of selenohydrins **83**, reported by the Breder group.[109]

The report also included mechanistic investigations attempting to explain the observed changes in the reactivity and concluded, that an existing H-bond interaction between the OH-group and the neighboring selenium residue (Scheme 33) modulated the nucleofugality and thus enabled S_N reactivity.[107,109] In more detail, the authors postulated that upon cleavage of the C–Se σ-bond, this H-bond interaction fixates the ArSe-group in close proximity to the carbon back bone until the aryl migration takes place (Scheme 33).[109]

By using water as a nucleophile and a suitable alkene, the beforehand mentioned Tsuji-Wacker oxidation (Scheme 32) then followed, allowing the use of substoichiometric amounts of diselenides with photoredox catalysis as a catalytic co-cycle. A fundamental limitation that has not been overcome thus far is the restriction regarding the composition of the applied alkene, where only non-terminal styrene derivatives **81** showed successful product **82** formation.[107] Nonetheless, the presented results clearly show, that a migratory reaction is indeed feasible under selenium-π-acid photoredox multicatalysis allowing for further speculations regarding substrates that could be used as starting materials. As such, *tertiary* allylic alcohols could be potential candidates in which case the activation of the olefin by the selenium catalyst triggers a migration event forming α,β-unsaturated ketones upon elimination.

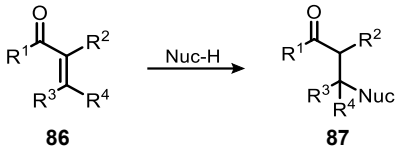
2.5 α,β-unsaturated ketones

A partial example of such a process has already been established by the Yu group in 2017, when they reported a 1,2-aryl migration induced by $FeBr_3$ promoting phenylselenylation (Scheme 34).[110]



Scheme 34: Rearrangement reaction developed by the Yu group. **N-PSP** = *N*-(phenylseleno)phthalimide. Isolated yields reported.[110]

A complete catalytic cycle (including consecutive elimination of the PhSe-group) would conclude in a α,β-unsaturated ketone as a vital functional group, found in various natural products,[111–115] fragrances,[116] as well as pharmaceuticals[112,114,115,117–119] with a multitude of potential applications (anti- viral, cancer, and inflammatory).[117] In terms of synthetic value, the most prominent is the application in Michael type addition reactions (Scheme 35),[113,118–134] which display a major tool for the formation of C-C or C-X σ-bonds[121,123,128] and thereby represent a key step in the synthesis of natural-[115,128] and pharmacological products.[122,124]

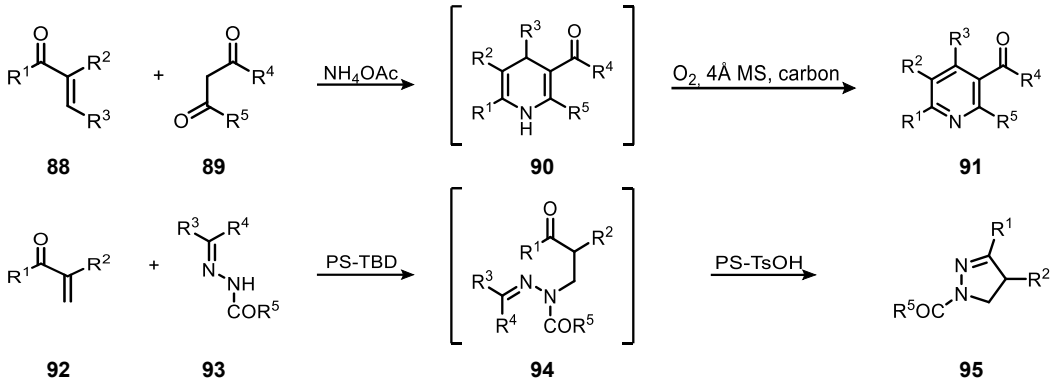


Scheme 35: Minimalistic representation of the concept behind the Michael addition.

Overall, there exist a vast number of different protocols which make use of the initial idea of the Michael addition[120] to allow for the conjugated addition of different nucleophiles (**Nuc-H** in Scheme 35) based on various hetero atoms such as nitrogen,[121,122,129,131,134] oxygen,[123,130] phosphorus[125,132] and sulfur[127,133] to the unsaturated ketone **86** thus underlining on one side the versatility

of the reaction protocol but on the other side also the possibilities using α,β-unsaturated ketones as starting materials.

Beyond the Michael type additions, other noteworthy synthetic applications of α,β-unsaturated ketones include addition reactions to the alkene,[113,135] Diels-Alder reactions,[113,136] conjugated additions of cuprates[113,137] and the Morita-Baylis-Hilman reaction.[113,138] More specific, target-oriented applications are the synthesis of highly functionalized pyridines **91**[139] and 3,4-substituted pyrazolines **95**,[140] both being viable core structures in the realm of biochemistry (Scheme 36).[139,140]



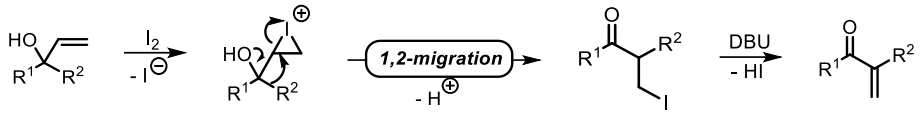
Scheme 36: General concepts for the synthesis of highly subst. pyridines **91** (above)[139] and pyrazolines **95** (below).[140] **PS-TBD** = polystyrene supported 1,5,7-triazabicyclo[4.4.0]dec-5-ene, **PS-TsOH** = polystyrene supported *para*-toluene-sulfonic acid.

From the few examples depicture in the schemes above (Scheme 35 and Scheme 36), it becomes obvious that the term α,β-unsaturated ketone allows for a multitude of substitution patterns, ranging from a fully substituted pattern (structure **86**) to terminal, single substituted alkenes (structure **92**, R^2 = H). Among those, terminal alkenes as represented in structure **92**, are considered to be of elevated relevance, as they represent the most significant synthon in chemical synthesis and additionally being present in a wide variety of natural products or in material sciences.[141]

2.5.1. Syntheses of (terminal-) α,β-unsaturated ketones

Regarding the value of α,β-unsaturated ketones, it becomes obvious that a number of different approaches have been reported to allow for the synthesis of this particular functional group, based on different starting materials. Addressing the idea of a rearrangement of allylic alcohols, which are easily prepared from simple ketones and commercial vinyl magnesium bromide,[114] there are indeed several reports found which achieve the desired transformation by applying individual reaction conditions.

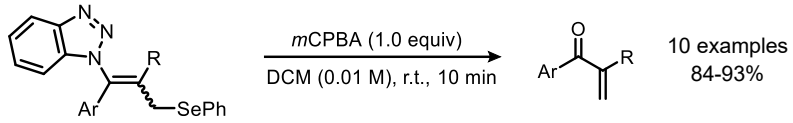
The first report for such a concept was published in 1995 by the Ciganek group and employed a two-step protocol with stochiometric iodine and DBU as base.[142] The reaction is postulated to progress by initial formation of an iodonium-ion **97** which is opened up by the migration of one of the substituents giving rise to the β-iodo-ketone **98**. Consecutive treatment with DBU furnishes the α,β-unsaturated ketone target structure **92** (Scheme 37).[142]



96 **97** **98** **92**

Scheme 37: Reaction progression reported by the Ciganek group. **DBU =** 1,8-diazabicyclo(5.4.0)undec-7-ene.[142]

However, this initial report had a major focus on cyclic systems and therefore did only include one acyclic substrate (R^1 and R^2 = Ph, 77% yield) using excess amounts of iodine (1.2 equiv), AgOAc (1.2 equiv) and DBU (4.8 equiv) in benzene.[142] Several years later, this concept was taken up by the Kim group when they used benzotriazole-PhSe-substituted alkenes **99** which underwent a similar transformation upon oxidation of the PhSe-moiety by *m*CPBA and elimination of the benzotriazole group (Scheme 38).[143]

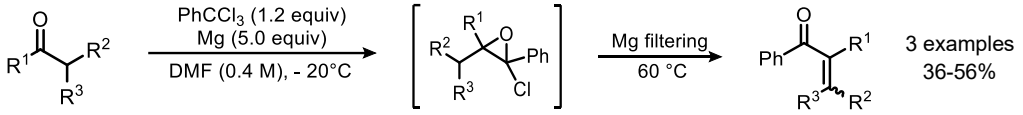


99 **R =** alkyl, aryl. **100**

Scheme 38: Reaction developed by the Kim group. Isolated yields reported.[143]

Although they were able to report an improved reaction scope of ten examples with excellent yields, the overall concept suffers from a complex starting material **99** which offers only limited possibilities for modifications as reported by the authors.[143]

Five years later, Aaziz et al. then resorted back to using simple alkenes as starting materials and applying a Grignard reaction to transform them into the corresponding epoxides **102** with α,α,α-trichlorotoluene. Consecutive thermal driven rearrangement and elimination of the chlorine atom then furnishes the target unsaturated ketones **103** in acceptable to good yields (Scheme 39).[144]



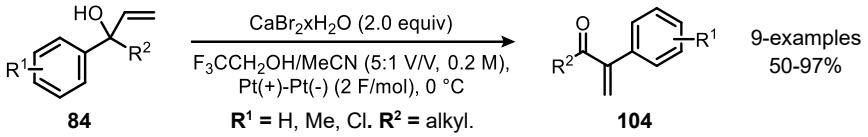
101 **R^1, R^2, R^3 =** alkyl. **102** **103**

Scheme 39: Reaction progression developed by Aaziz et al. Isolated yields reported.[144]

Again, the entire reaction scope only covers eight examples among which there are only 3 acyclic products and among those only one with a terminal double bond (55% yield).[144] Furthermore, the structural outcome is limited by the use of α,α,α-trichlorotoluene which is incorporated into the target product scaffold (Ph-group as α-substituent in the product ketone **103**).

Apart from limited reaction scope, the thus far presented methods all suffer from low atom-economy and in several cases also step-economy. With regards to the atom-economy problem, the Onomura group then set out to develop an electrochemical approach to enable the rearrangement of allylic alcohols, without the use of excess amounts of additional chemicals such as external oxidants.[114]

According to their work, the reaction is mediated by halide ions (chloride or bromide), which are employed in the form of the corresponding alkaline earth metal salts and are then oxidized at the platinum electrodes. The resulting cations then attack the alkene and the reaction concludes similar to the initial iodine report (Scheme 37).[114] The selling point of this approach, in contrast to the earlier mentioned iodine process for example, is that the eliminated halide anions then take part in further product formation (by re-oxidation on the platinum electrode) and are not terminally scavenged by an additional added base. Applying their concept, the Onomura group was able to convert up to nine vinylic alcohols into their corresponding terminal α,β-unsaturated ketones in good to excellent yields (Scheme 40).[114]

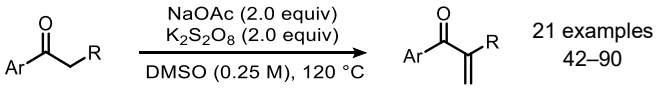


84 **R¹ =** H, Me, Cl**. R² =** alkyl. **104**

Scheme 40: Set of reaction conditions developed by the Onomura group. Isolated yields reported.[114]

Although they were able to reduce the amount of excess chemicals needed, the delivered protocol still requires 2 equivalents of halide source to operate at optimal efficiency. Furthermore, the versatility of the reaction scope still leaves room for improvement, especially regarding the α-position of the product ketone **104**, where only alkyl groups were reported.[114]

Naturally, there are other methodologies aiming at the synthesis of (terminal-) α,β-unsaturated ketones starting from divers starting materials apart from allylic alcohols. Among the most prominent one is the α-CH-functionalization[111,113,115,119,133,141,145–150] such as for example the Mannich reaction[111,115,151] with additional elimination of the amine group. A generalized reaction progression can be described as follows: The ketone which is used as starting material is partially enolized either by acid or base catalysis, then attacking a C1-source such as DMF,[141] (para-) formaldehyde,[113,145,148] *N,N*-tetramethylen-ethane-diamine,[133] trioxymethylene,[119] DMSO,[149] dibromomethane,[115] or DMF-dimethylacetale.[147] Consecutive elimination of the thereby introduced functional group, initiated by different means (basicity,[115,145,148] acidity,[113,119,133,146] oxidation,[141,149] reduction)[147] then results in the α,β-unsaturated ketone motif.



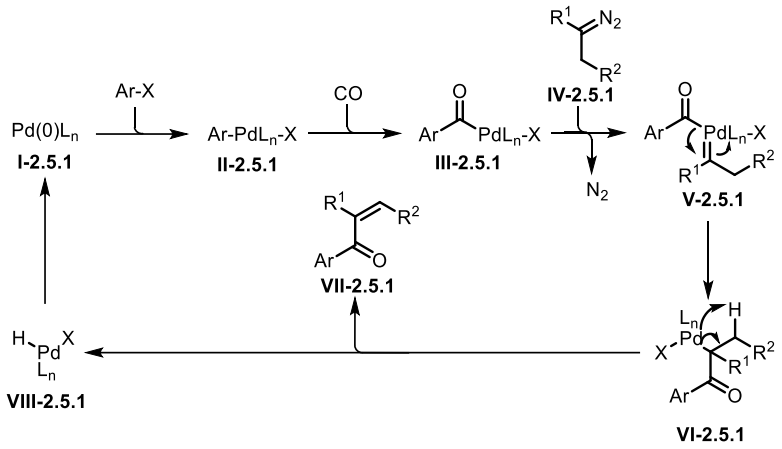
105 **R =** H, alkyl, aryl. **100**

Scheme 41: Example for the α-CH functionalization protocol. Conditions from reports by the Guo group. Isolated yields reported.[149]

An adapted concept also has been reported using silyl-enol-ethers as starting materials rather than forming the enol *in situ* by acid/base catalysis.[111,152] Although the general idea is widespread and therefore, in summary a broad reaction scope has been achieved, individual reports often lack said broad applicability regarding suitable substrates. These structural limitations mostly arise in terms of functional group incorporation as well as minor reports for versatile geminal substituted terminal

alkenes, as the focus is often either on cyclic substrates or single substituted terminal alkenes as products.[111,113,115,119,133,141,145–150,152] Another drawback in contrast to the previously reported rearrangement protocols is the fact, that these α-CH-functionalizations are formal two component reactions using further stoichiometric reagents (terminal oxidant, base or else) amounting to a disadvantage with regards to atom-economy.

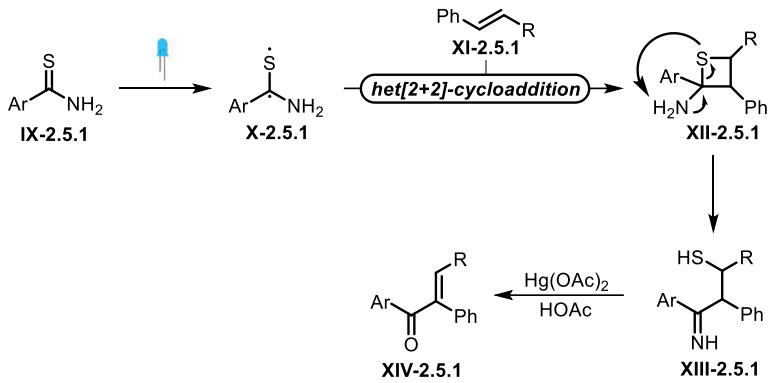
Another less common concept found in literature is the palladium catalyzed insertion of an Ar-group and CO in a benzylic diazo compound. After coordination of both the aryl group and CO by the Pd-catalyst, the latter then inserts in the Ar-Pd bond (structure **III-2.5.1**). This complex is then reacting with a provided diazo-compound **IV-2.5.1** forming a palladium-carbene **V-2.5.1** upon liberation of nitrogen gas (Scheme 42).[153,154]



Scheme 42: Postulated reaction mechanism for the synthesis of α,β-unsaturated ketones using palladium catalysis.[153,154]

Rearrangement and reductive elimination of the palladium catalyst then furnishes the α,β-unsaturated ketone **VII-2.5.1** as reaction product.[153,154] A disadvantage of this concept, however, lies in the limitations regarding the substitution pattern of the product **VII-2.5.1** being restricted to two aryl substituents in both α-positions.[153,154] These limitations arise on one side by the initial coordination of Ar–X to the palladium catalyst **I-2.5.1**, which does not work for a sp^3-hybridized carbon atom and on the other side by the composition of the diazo-compound **IV-2.5.1**, which requires aryl-conjugation for stability and accessibility (position R^1 in structure **IV-2.5.1**). Furthermore, like in the case of the α-CH-functionalization concept, the palladium catalysis concept displays a two component setup (Ar–X and the diazo-compound **IV-2.5.1**) as well as other stoichiometric reagents (terminal oxidant, base)[153,154] making this approach also unfavorable in terms of atom-economy comparing with the rearrangement idea.

The last concept is the light induced het[2+2]-cycloaddition between an alkene and a carbothioamide **IX-2.5.1**.[155] Consecutive C–S σ-bond cleavage results in an imine and a free SH-group (structure **XIII-2.5.1**) which is then eliminated under acidic conditions using $Hg(OAc)_2$ in acetic acid as solvent thereby also converting the imine into the ketone **XIV-2.5.1**.[155]

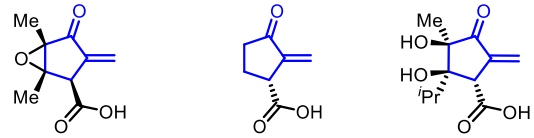


Scheme 43: Reaction progression for the light induced het[2+2]-cycloaddition procedure developed by the *Oda* group.[155]

Although this approach is unique with regards to reaction concept (Scheme 43), the authors were only able to report a total number of 6 examples (81-92% isolated yields) of product structures being limited to arylic-carbothioamides **IX-2.5.1** and styrene derivatives **XI-2.5.1**. Furthermore, the overall process also includes two reaction steps with the second one being necessary to remove the thiol and regain the carbonyl group.

2.6 2-Methylenecyclopentan-1-ones

As already indicated before, several of the mentioned synthetic approaches for α,β-unsaturated ketones have a dominant focus on the synthesis of cyclic structures rather than acyclic ones. Among those cyclic structural motifs, 2-methylenecyclopentan-1-ones received elevated attention, representing a vital group, present in various natural-, biological active products such as Methylenomycin-A (**106**),[146,156,157] Sarcomycin (**107**)[156–159] and Xanthocidin (**108**),[157] each being labeled to express anti-biotic properties (Figure 6).[11,146,156–160]



106 Methylenomycin A **107** Sarcomycin **108** Xanthocidin

Figure 6: Example of biological active compounds based on 2-methylenecyclopentan-1-ones (core highlighted in blue).[156,157,159]

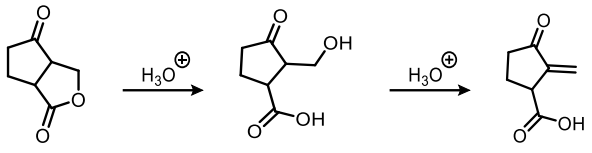
In addition, 2-methylenecyclopentan-1-ones display an important (key-) intermediate for the total synthesis of various natural products such as (+)-Laurene,[161,162] A-Ring Aromatic Trichothecanes,[160,163] (-)-Debromoaplysin and (-)-Aplysin,[164] and various more.[165–167]

2.6.1. Syntheses of 2-methylenecyclopentan-1-ones

Regarding the synthesis of 2-methylenecyclopentan-1-ones, similar approaches to the earlier discussed acyclic methodologies (chapter 2.5.1) can be found throughout literature. Among the most

common principle is the α-CH-functionalization (compare with Scheme 41) using either formaldehyde[156,168] or quaternary-amines[169–172] as C1-source. A drawback of this method is the regioselectivity of the functionalization regarding the two α-positions of the carbonyl group, indicating a formation of product mixtures. The reported literature examples however are all listed in total synthesis projects and include solely cyclopentanones where one α-position is sterically blocked[168,170–172] or does not provide any protons for abstraction[156,169] thereby enabling for (selective-) product formation.

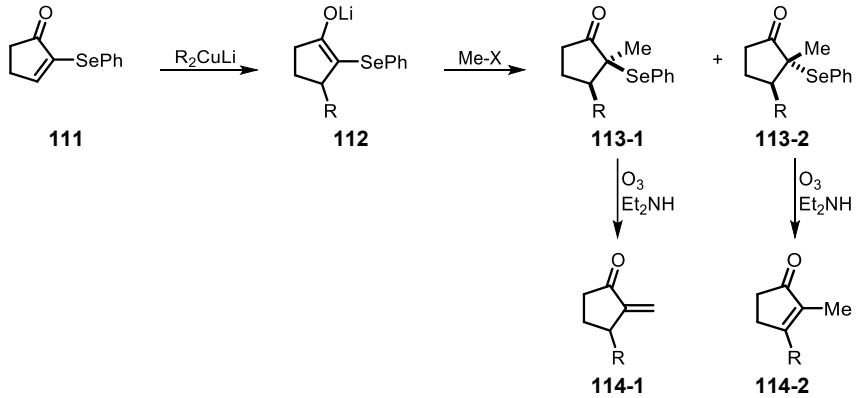
Similar, elimination-based concepts can be found either using 2-phenylselenylenones **111**[173,174] or cyclopentanones with a 1-2-annulation of a lactone **109**.[157,159] Whereas the second of these two methods exhibits mechanistic simplicity by solely being based on the acid-mediated hydrolysis of the annulated lactone with consecutive water elimination under the acidic conditions (Scheme 44),[157,159] the mechanistic rational of the application of the 2-phenylselenylenones **111** involves more complexity.



109 **110** **107-1**

Scheme 44: Simplified concept for the synthesis of 2-methylenecyclopentan-1-ones by hydrolysis of 1-2-annulated lactones **109**.[159]

The reaction sequence is initiated by a conjugated addition to the olefin **111**, using an organic cuprate as reagent (Scheme 45) and concluding addition of a methyl-halide reagent then furnishes the addition product as a mixture of diastereomers **113-1** and **113-2** (Scheme 45).[173]



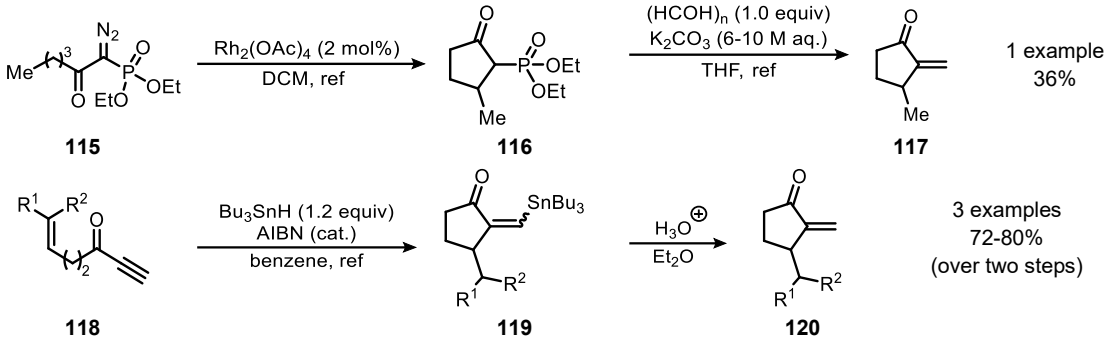
111 **112** **113-1** **113-2** **114-1** **114-2**

Scheme 45: Abbreviated concept for the synthesis of 2-methylenecyclopentan-1-ones using 2-phenylselenylenones **111** as starting materials.[173]

As a significant disadvantage, by oxidative elimination, only one of the two diastereomers results in the formation of the desired 2-methylenecyclopentan-1-one **114-1**, while the other diastereomer forms a different configurational isomer **114-2**.[173]

Regarding the applicability of these two methods, much like in the case of the already mentioned α-CH-functionalizations, most applications are either part of a total synthesis or display intermediate character. Therefore, the overall number of synthesized examples (by these methods) is marginal and the structural diversifications reported rather target oriented than general.[157,159,173,174]

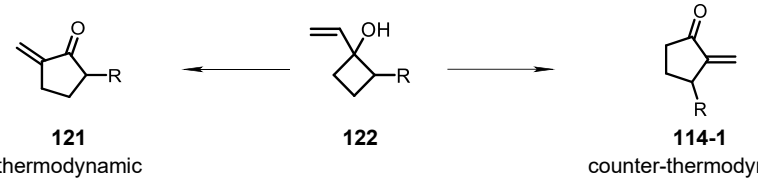
Further, conceptionally more unique methods, include the rhodium catalyzed cyclization of α-diazophosphate-ester **115** with a consecutive Horner-Wadsworth-Emmons reaction[175] and a radical mediated cyclization reaction between an alkene and an alkyne (Scheme 46).[176]



Scheme 46: Systematic overview of the syntheses of 2-methylenecyclopentan-1-ones using α-diazophosphate-esters (above) and an alkene with an alkyne (below). Isolated yields reported.[175,176] **cat. =** catalytic.

Again, the major drawback of these two methods include step-economy (both methods consist of two individual reaction steps) and only a scarce amount of representative application examples provided (only 4 total examples for both methods combined with only carbon chains and one acid functionality as additional functional group).[175,176]

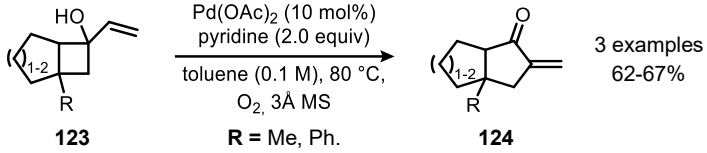
The most featured synthetic method for the synthesis of 2-methylenecyclopentan-1-ones is based on a ring expansion process[177] from an α-unsaturated cyclobutanol-moiety,[10,11,160–167,177–188] similar to the rearrangement concept discussed in chapter 2.5.1 regarding the 1,2-aryl migration (e. g. Scheme 37). In addition to the acyclic methodologies, the present ring strain is further favoring the ring expansion reaction[187] and especially for vinylic cyclobutane moieties, the π-system is more prone to Markovnikov-controlled electrophilic attacks thereby further facilitating the ring enlargement reaction.[189] Another aspect that differs from the acyclic migration reaction is the now relevant question of regioselectivity – which α-bond of the olefinic cyclobutanol is migrating – potentially leading to two energetically different products (thermodynamic vs. counter-thermodynamic product, Scheme 47).



Scheme 47: Schematic difference between the thermodynamic product **121** and the sterically more encumbered counter-thermodynamic product **114-1**.

2-Methylenecyclopentan-1-ones

Starting off with methods favoring the formation of the thermodynamic product, the only selective procedure employs the activation of the π-bond of an vinylic cyclobutanol **123** by palladium catalysis with subsequent migration of the sterically less demanding carbon chain (Scheme 48).[186,187]

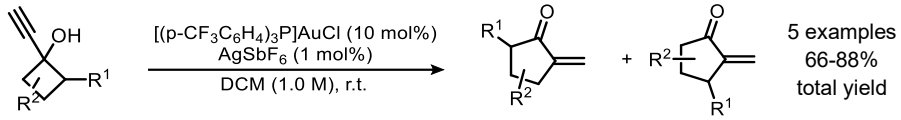


123 **R =** Me, Ph. **124**

Scheme 48: Ring expansion protocol reported by the Uemura group. Isolated yields reported.[186,187]

Although the authors were able to report selective formation and isolation of the thermodynamic products **124**, the overall applicability remains elusive as only three examples were shown, each consisting of a bicyclic core structure.[186,187]

A similar approach was reported by Markham et al. using propargylic cyclobutanols rather than vinylic ones with a gold catalyst to activate the alkyne.[185] According to their report, the outcome of their transformation seems to be strongly dependent on the structural composition of the starting alcohol **125** as sterically demanding spirocyclic structure were reported to result in selective formation of the counter-thermodynamic product, whereas less steric demanding substrates result in a mixture favoring the thermodynamic product (Scheme 49).[185]



125 **R¹, R²** = alkyl **126-1** **126-2**

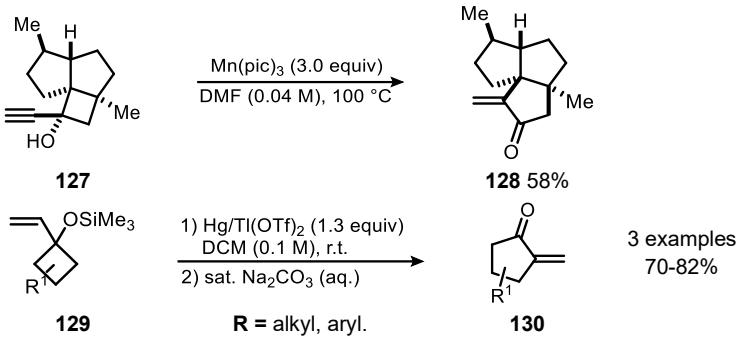
Scheme 49: Ring expansion developed by Markham et al. NMR yields reported.[185]

A similar dependency for the reaction outcome was reported by the Reusch group in their initial report on the ring expansion of vinylic cyclobutanols employing a two-step protocol based on initial epoxidation and subsequent epoxide opening triggering the ring enlargement.[178] According to their work, the ring expansion is directly influenced by the relative stereochemistry between the quaternary carbon atom carrying the epoxide and fused 6-membered cycle backbone.[178] By differentiating between these two diastereomers, the authors were able to selectively synthesize either the thermodynamic (75% isolated yield) or the counter-thermodynamic product (78% isolated yield), but not for more than one isolated case.

Switching over to the methods resulting in counter-thermodynamic product formation there exist complimentary protocols based on the previous mentioned epoxidation strategy[161,162,178] as well as palladium catalysis approaches.[10,11,160,162–167,179,184] While in the case of the epoxidation protocols, the change of regioselectivity was simply observed by using non-bicyclic substrates,[161,162] the palladium catalyzed protocols rely on the application of protected alcohol groups (as ethers or silyl ethers)[162–164,167,179,184] to avoid double bond isomerization by reattacking of the palladium catalyst.[10,11,166] Again though, all found sources only respond to one-time applications of these reaction

concepts (some of these even use stochiometric amounts of palladium)[162–164] without explicitly reporting a reaction scope or optimization studies.

In addition to these methods there also exist limited reports on a radical approach mediated by trivalent manganese and propargylic cyclobutanols[181–183] and a mechanistic similar approach regarding the epoxidation concept but using mercury- or thallium salts instead of an epoxide.[177,180,188]



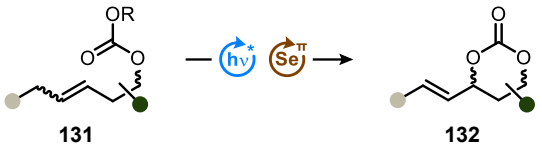
Scheme 50: Example procedures for the manganese catalyzed reaction protocol (above) and the mercury/thallium-salt concept (below). **Pic** = picolinate. Isolated yields reported for both cases.[177,181]

Unfortunately, again the major drawback is the reported applicability with only limited given examples (two for the mercury/thallium protocol and three for the manganese protocol) in addition to having a low atom-economy by using at least stochiometric amounts of additional (toxic-) reagents that do not end up being part of the target molecule.

In summary, all the outlined methods for the synthesis of 2-methylenecyclopentan-1-ones report to a close array of substrates, leaving room for improvement regarding the applicable substrates as well as the overall reaction protocol. Furthermore, even though the ring expansion protocols prove to be more interesting in terms of step economy, there have been no reports on the explicit development of such concepts especially regarding counter-thermodynamic product formation, where only application in total synthesis can be found.

3 Objectives

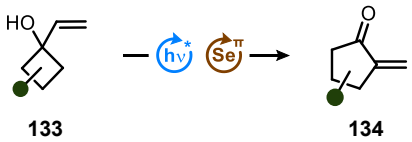
The concise aim of this work can be summarized under the main goal of expanding the applications of selenium-π-acid catalysis and thus further establish the overall concept. The first task under this premise is then to finalize the implementation of carbonate functional groups as suitable oxygen based nucleophiles (Scheme 51) started in the preceding Master's Thesis.[190]



Scheme 51: General equation for the application of carbonates as oxygen based nucleophiles.

As most of the reaction screening has already been covered within the Master's Thesis,[190] the remaining screening task is focused on the development of a reaction setup, that allows for temperature control, as well as reliable light irradiation over time, to enhance the overall reproducibility. Apart from that, a further challenge that needs to be addressed is the design of a versatile synthetic pathway allowing for the synthesis of a multitude of structural relevant starting materials **131**. Based on a reaction scope, a further opportunity is given to establish certain characteristics of the process such as relevance of the configuration of the double bond in the starting material **131** and if the reaction follows the *cis*-selectivity that is found in related literature.[50,52,55]

Moving away from carbonates, the next project then involves the development of ring expansion reaction for vinylic cyclobutanols **133** (Scheme 52). Orienting ourselves at the literature presented in the introduction (chapter 2.6.1), project collaborators already developed suitable reaction conditions for an achiral process, so the first question is if there is a possibility to adapt these conditions to a chiral process.

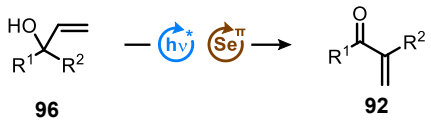


Scheme 52: Reaction concept developed by project collaborators.

Furthermore, the challenge of finding suitable synthetic procedures allowing for the synthesis of a broad array of starting materials **133** has to be faced in order to able to present a viable reaction scope underlining the value of the process. Based on a significant broad scope, the regioselectivity of the ring expansion process (contra-thermodynamic vs. thermodynamic product formation) has to be analyzed, as well as stereoretention of present stereocenters to be able to postulate a mechanistic rational for the transformation and possible explanations for the examined selectivities.

In parallel to this project, it is desired to establish a reactivity concept that could be applied to acyclic allylic alcohols **96**, as foundational work to support this idea has already been provided in literature (Scheme 34).[110] An important point of this concept is then the migration selectivity for different

substitutional patterns (R^1 vs. R^2, Scheme 53) and ranking this selectivity among other procedures that achieve the same transformation.



96 **92**

Scheme 53: Anticipated selenium-π-acid catalyzed migration reaction

It is also envisioned that the possibility for substitution of the selenium residue by a nucleophile rather than elimination would be feasible, allowing for a facile buildup of more complex carbon scaffolds in a single reaction step. To realize this idea, it is necessary to establish corresponding reaction conditions as well as a precisely defined scope of tolerated nucleophiles and respective acyclic vinylic alcohols **96**.

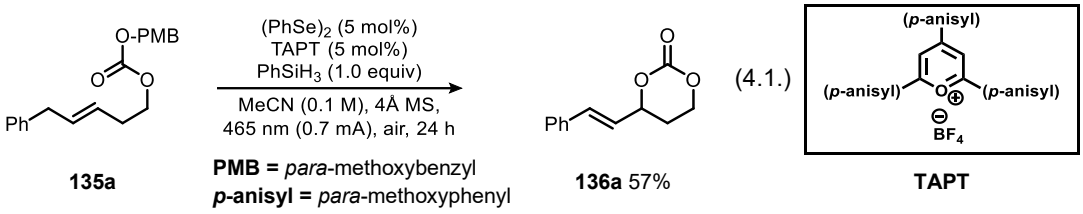
4 Results and Discussion

4.1 Synthesis of 1,3-dioxan-2-ones

A significant share of the reaction optimizations, as well as the development of a synthetic route for the starting material synthesis has already been discussed in the corresponding Master's Thesis "Synthesis of Cyclic Carbonates Mediated by Photoaerobic Selenium-π-Acid Catalysis" with the aim of developing a synthesis for 1,3-dioxan-2-ones (6-membered cyclic carbonates).[190] In continuing studies, further optimizations to the reaction conditions and the reaction setup, as well as a new robust route for the starting material synthesis had to be devised.

4.1.1. Optimization studies

As mentioned, a set of optimized reaction conditions was developed in the preceding Master's Thesis.[190] A summary of said conditions applied to the screening substrate **135a** is shown below in equation 4.1.



135a

PMB = *para*-methoxybenzyl
***p*-anisyl =** *para*-methoxyphenyl

136a 57%

TAPT

Remaining deficits of the above shown reaction setup included the lack of temperature control, as well as the incapability to precisely determine the reaction temperature and the intensity of the irradiation. As the reaction vessel can neither be heated nor cooled, the overall temperature in the utilized irradiation setup (Figure 7) is governed by the reaction itself as well as by the heat emitted by the LED strips. Especially the latter factor is difficult to reproduce when the reaction vessel is not placed at the exact same spot for each consecutive reaction.

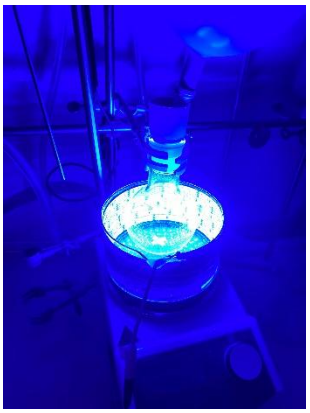


Figure 7: Reaction setup used for the first reaction optimization.

Also, the intensity of the irradiation is strongly dependent on the distance between the flask and the LED strip and beyond that the intensity was found to be furthermore subjected to general

deterioration based on the extended use. To circumvent these drawbacks, we improved the setup to a single, high power LED setup, which is mounted underneath an aluminum block, that can carry two 100 mL flasks (Figure 8). With these adaptations, we now were able to regulate the reaction temperature either by simply circulating cooling tap water through the system or by connecting a suitable thermostat additionally enabling heating up a circulating water/ethyleneglycole mixture.

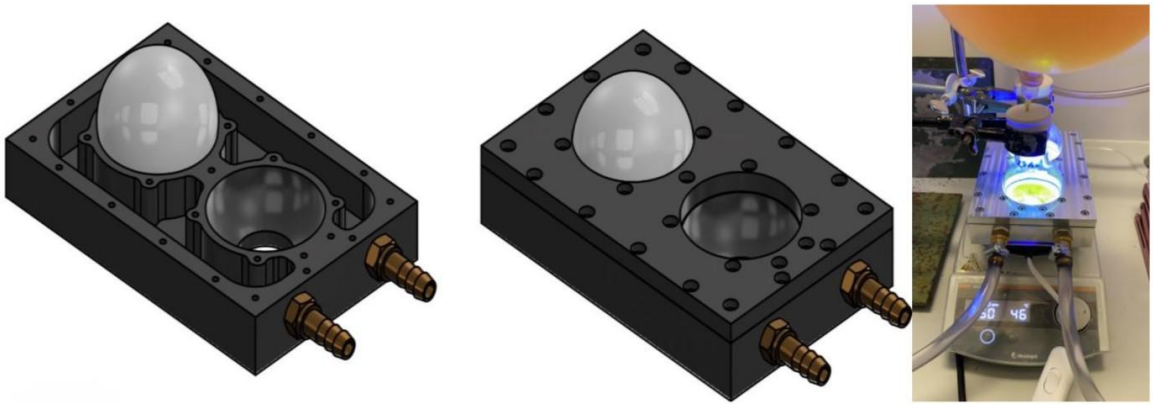
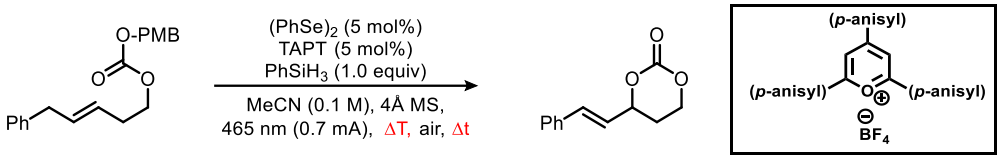


Figure 8: Left, technical drawing of the manufactured cooling block system. Right, actual representation of the irradiation setup.

With this new setup at hand, we first began to find the accurate temperature to reproduce the results from the previous setup. From there on, we set out to further optimize the conditions aimed at increasing yield while reducing side reactivity and degradation processes.

The first reaction was performed using water at a temperature of 19 °C (Table 1, entry 1). However, after 4 h of reaction time neither product formation nor significant conversion of starting material let us believe that elevated temperatures are indeed necessary for successful reaction progression. As temperature readings in the previous setups concluded in temperature roughly above 35 °C during the irradiation process, we continued investigations starting from 40 °C going upwards. As 40 °C still led to no significant improvement in yield and conversion (entry 2), we doubled the reaction time and further increased the temperature to first observe definite product formation after 8 h at 50 °C (entry 4). Owing to the time intensive initiation phase that selenium-π-acid photoredox multicatalytic processes have to undergo before product formation,[40,191] we further increased reaction times and found suitable conditions at 18 h of reaction time at 55 °C (entry 11). Due to possible solvent evaporation and the fact that extended reaction times result in raised product degradation (comparing entries 5, 8-10, also known from previous studies),[190] we objected to the further increase of temperature and remained with 55 °C. We then attempted to alter from the screening scale conditions (0.50 mmol) to the chosen scope scale of 1.0 mmol, where unfortunately simple adaption of the parameters was not successful (entry 12) as the increase in total volume caused a decrease in absorbed light intensity according to Lambert-Beer's law.[192] Further elongated reaction times while maintaining the temperature at 55 °C then resulted in acceptable product formation even at a scale of 1.0 mmol (entry 13).

Table 1: Overview of the temperature and time screening

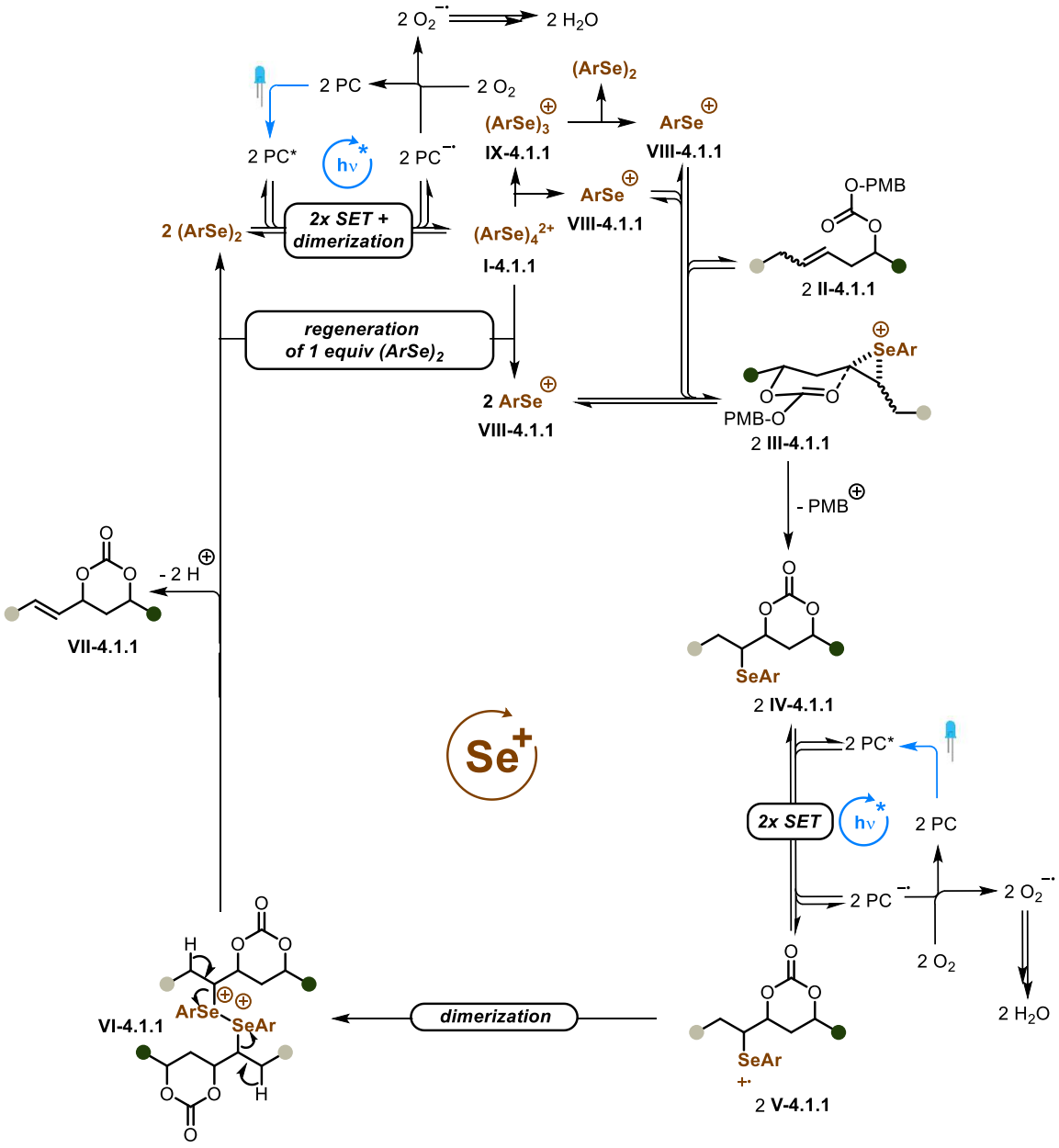


135a **136a** **TAPT**

Entry	Δt [h]	ΔT [°C]	NMR Yield	Conversion
1	4	19	0%	2%
2	4	40	0%	6%
3	8	40	0%	6%
4	8	50	8%	22%
5	24	45	18%	34%
6	24	55	49%	81%
7	27	50	27%	53%
8	28	55	43%	82%
9	20	55	55%	85%
10	16	55	46%	73%
11	18	55	56%	84%
12[a)]	18	55	24%	44%
13[a)]	40	55	52%	81%

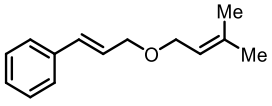
Reactions were performed on a 0.50 mmol scale in MeCN-d_3 (0.1 M) with 5 mol% of $(PhSe)_2$ and TAPT, $PhSiH_3$ (1.0 equiv) and 4Å MS (10 mg/mmol). The reactions were irradiated by blue LEDs (465 nm, 0.7 mA) at the given temperature under an atmosphere of air (balloon) for the given reaction time. NMR Yields were determined by using 1,3,5-trimethoxybenzene as an internal standard. a) reactions were performed on a 1.0 mmol scale.

Being able to utilize the improved reaction setup, we also intended to rethink our catalytic system in order to minimize/prevent degradation processes. According to the postulated reaction mechanism (Scheme 54 also compare Scheme 23), the chosen photocatalyst **PC** needs to have a sufficiently high oxidation potential to activate the corresponding diselenide catalyst **$(ArSe)_2$**, but also the selenated intermediate **IV-4.1.1**. On the other hand, the activated selenium species **I-4.1.1** as well as the successive seleniranium ion **III-4.1.1**, need to exhibit high enough electrophilicity to promote the first the electrophilic attack on the olefin and then the consecutive nucleophilic attack of the carbonate functional group.



Scheme 54: Postulated reaction mechanism for the formation of the cyclic carbonates according to known literature.[32,40]

As we assumed that oxidation of the conjugated π-bond in the resulting product **VII-4.1.1**, becomes more facile with a photocatalyst **PC** exhibiting higher excited state oxidation potential we set out to test different electron rich diselenides **(ArSe)$_2$**, allowing for weaker oxidizing conditions. A benchmark value that was used to choose potential combinations, is the oxidation potential of styrene **137** (+1.42 eV vs. SCE)[193] (Figure 9).

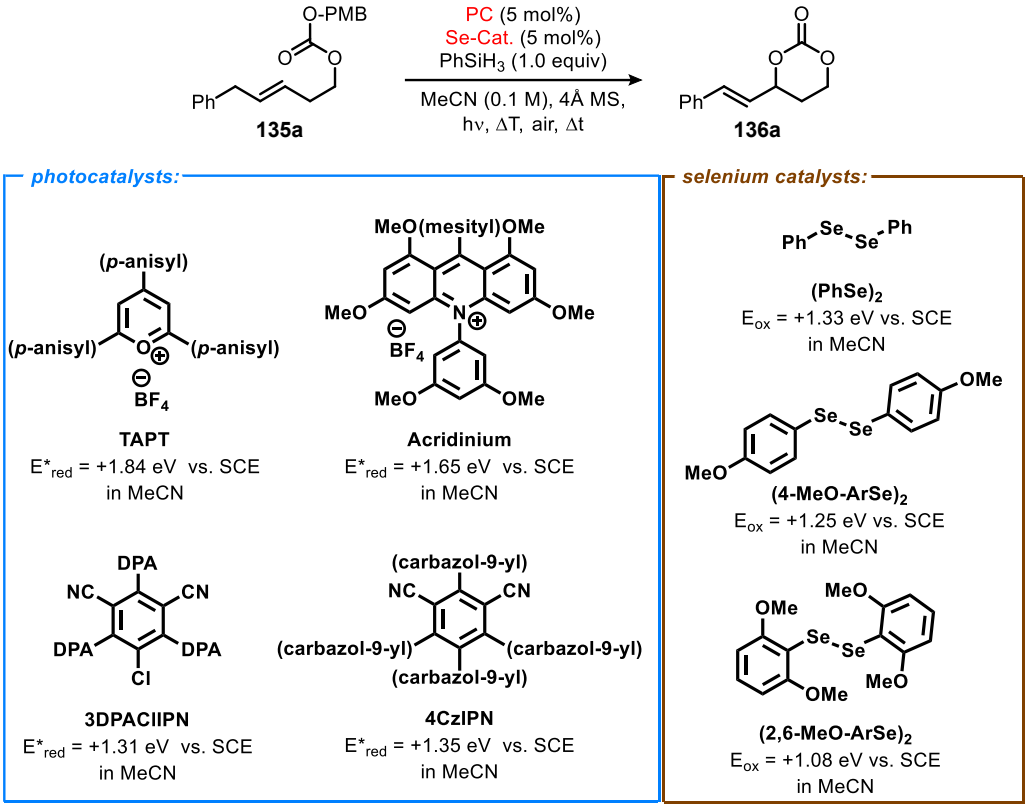


137

Figure 9: Styrene structural motif with known oxidation potential which was used as a reference.

In addition, we also imagined a beneficial effect when choosing electron poor diselenides **$(ArSe)_2$**, leading to more nucleophilic intermediates **I-4.1.1** and **III-4.1.1** which we anticipated to enhance reaction kinetics favoring product formation over degradation processes. An overview of available catalyst combinations (prepared by different members of the group in independent studies) and the corresponding results are listed in Table 2.

Table 2: Complete overview of the catalyst screening



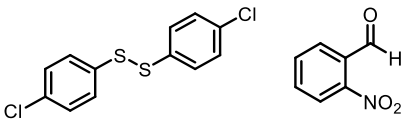
Entry	Photocatalyst [5 mol%]	Se-Catalyst [5 mol%]	NMR Yield	Conversion
1[b)e)]	Acridinium	$(4\text{-MeO-ArSe})_2$	15%	73%
2[b)e)]	Acridinium	$(PhSe)_2$	20%	83%
3[a)e)]	TAPT	$(4\text{-MeO-ArSe})_2$	14%	46%
4[c)]	4CzIPN	$(2,6\text{-MeO-ArSe})_2$	6%	50%
5[c)]	3DPAClIPN	$(4\text{-MeO-ArSe})_2$	5%	38%
6[c)]	4CzIPN	$(PhSe)_2$	0%	38%
7[d)]	TAPT	$(PhSe)_2$	56%	84%

Reactions were performed on a 0.50 mmol scale in MeCN-d_3 (0.1 M) with 5 mol% of each catalyst under an atmosphere of air (balloon). NMR Yields were determined by using 1,3,5-trimethoxybenzene as an internal standard. **DPA**: diphenylamine. a) The reactions were run in the crystallization beaker irradiation setup using 465 nm LEDs for 16 h. b) The reaction was performed in a simple round flask and irradiated at 427 nm using a *Kessil*-Lamp for 16 h. c) $PhSiH_3$ (1.0 equiv) and 4Å MS (10 mg/mmol) were added and the reaction irradiated for 38 h at 448 nm (0.7 mA) in the cooling block setup at 55 °C. d) Optimized reaction conditions c.f. Table 1, entry 11. e) Reaction were conducted in the corresponding Masters' Thesis.[190]

All values for oxidation potentials were taken from literature (or mathematically converted using literature tables)[194] for the photocatalysts,[195,196,197] as well as for the selenium catalysts.[40,198] Entries 1-3 were already performed and analyzed in the related Master's Thesis[190] and were performed prior to complete reaction optimization, which is the reason why the reaction conditions differ in comparison to entries 4-6. Nonetheless, it was decided to include these results to deliver a complete picture about the mechanistic analysis.

In summary, we observed that electron rich diselenides (**(4-MeO-ArSe)$_2$** and **(2,6-MeO-ArSe)$_2$**) (entries 1, 3-4) paired with photocatalysts having a lower excited state oxidation potential compared to **TAPT**, results in decreasing product formation. The conclusion drawn from these results were, that either the diselenides **(4-MeO-ArSe)$_2$** and **(2,6-MeO-ArSe)$_2$** do not produce strong electrophiles **I-4.1.1** and/or **III-4.1.1**, or the photocatalysts apart from **TAPT** do not possess enough oxidation power, to produce the intermediate **V-4.1.1**, as proposed in Scheme 54. Furthermore, when comparing the obtained NMR yields with the conversion in all entries, it becomes obvious that even the lower excited state oxidation potentials from **4CzIPN** and **3DPAClIPN** are sufficient to effectively degrade starting material **135a** and/or the product **136a**, which is why we abstained from using electron poor diselenides in combination with photocatalysts with higher excited state oxidation potentials.

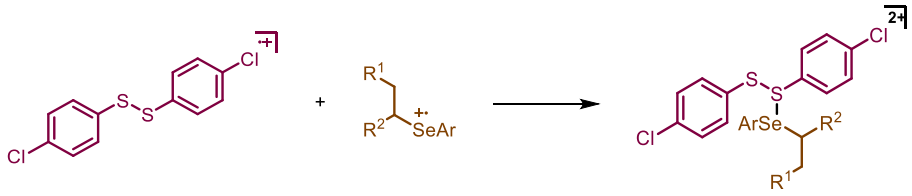
Another way we anticipated to positively influence the reaction outcome was the use of selective additives such as 1,2-bis(4-chlorophenyl)disulfane (**138**) and 2-nitrobenzaldehyde (**139**).



138 **139**

Figure 10: Representation of further chosen additives. left: 1,2-bis(4-chlorophenyl)disulfane (**138**). right: 2-nitrobenzaldehyde (**139**).

In independent studies regarding intramolecular amination reactions, we disclosed a positive effect on the reaction yield as well as reaction kinetics, when adding equimolar amounts of the chosen diselenide catalyst and the shown disulfide **138**.[191] Kinetic studies, showed that the disulfide **138** (upon one electron oxidation under the reaction conditions) forms unsymmetrical S-Se σ-bonded moieties **141** (Scheme 55), which more rapidly release a catalytic active species ($ArSe^+$) in the elimination step that reforms the π-bond.[199] This positively affects the overall reaction kinetics as the rate determining step being the elimination of catalyst precursor $(ArSe)_2$ after dimerization of two equivalents of the oxidized selenofunctionalized intermediate **140** (or structure **V-4.1.1** to **VI-4.1.1** in Scheme 54).[32,40]

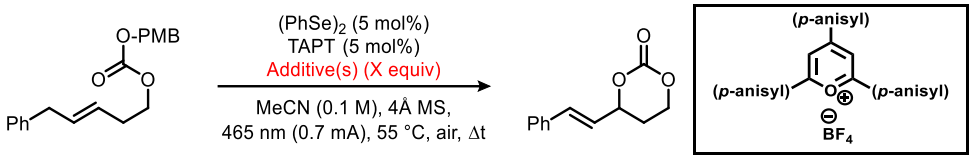


138 140 141

Scheme 55: Postulation for the formation of the Se-S agglomerate.[199]

2-Nitrobenzaldehyde (**139**) on the other side is declared to suppress singlet oxygen generation which has been quantified by monitoring reversible trapping with anthracene.[200] Said literature also proposes that excited 2-nitrobenzaldehyde (**139**) preferentially interacts with formed singlet oxygen producing the corresponding benzoic acid and thus preventing similar (oxidative-) side reactivities on other substrates such as fatty acids and organic dyes.[200] In similar fashion, we anticipated that the above mentioned aldehyde **139** would aid in the reduction of side reactivity stemming from a potential oxidative attack of singlet oxygen on present C–C π-bonds and additionally increase stability of the utilized selenium catalysts by preventing the irreversible formation of selenoxides which are catalytically less active.[191,201] Aiming for maximizing positive effects, we employed both, the disulfide **138**, the aldehyde **139** and the already utilized $PhSiH_3$ additive, in varying combinations (Table 3).

Table 3: Overview of the expanded additive screening



135a 136a TAPT

Entry	$PhSiH_3$ [1.0 equiv]	disulfide 138 [5 mol%]	aldehyde 139 [25 mol%]	NMR Yield	Conversion
1	✓	-	-	28%	48%
2	✓	✓	-	12%	40%
3[a), b)]	-	-	✓	24%	56%
4[a)]	✓	-	✓	19%	39%

Reactions were performed on a 0.50 mmol scale in MeCN-d_3 (0.1 M) with 5 mol% of TAPT and 5 mol% of $(PhSe)_2$. The listed additives and 4Å MS (10 mg/mmol) were added and the reaction irradiated for 9 h at 448 nm (0.7 mA) in the cooling block setup at 55 °C under an atmosphere of air (balloon). NMR Yields were determined by using 1,3,5-trimethoxybenzene as an internal standard. a) Irradiated for 18 h at 448 nm (0.7 mA) in the cooling block setup at 55 °C under an atmosphere of air (balloon). b) no 4Å MS was added.

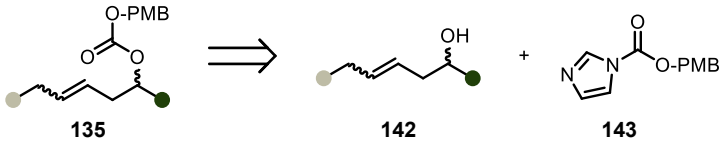
To assess if a kinetic enhancement actually is in operation, we reduced the reaction time from 18 h (maximum conversion for 0.50 mmol setup) to 9 h and analyzed the outcome without further deviations from previous optimal conditions (entry 1). Unfortunately, no enhancement of the overall reaction rate is observed when disulfide **138** was additionally added, as the observed yield is lower at almost similar conversion when compared with entry 1. Likewise, ineffectiveness could also be reported for aldehyde **139**, which did not show any form of improvement, neither when used as

sole additive (entry 3), nor when used in combination with the already tested additive $PhSiH_3$ (entry 4). Resorting to a reaction time of 18 h (optimal conversion under non-altered conditions, Table 1, entry 11), both reactions with aldehyde **139** as additive reported a slower conversion rate only reaching roughly 50% (entries 3-4) in the same timeframe. Additionally, the ratio of product formation to starting material conversion is only marginally affected and even slightly worse, leaving us with the conclusion that the application of aldehyde **139** does not improve our reaction system.

With these results obtained, we terminated further optimization attempts and started shifting the focus on the applicability of the developed method and related to that, the revisal of the synthetic route for the synthesis of suitable starting materials.

4.1.2. Starting material synthesis

Prior to any change in the synthesis of starting material **135**, we reconciled that we would remain with the PMB-leaving group as it was initially intended and utilized in the screening substrate **135a**.[190] Furthermore, we also envisioned to focus on the coupling reaction between 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (**143**) and a given allylic alcohol **142** (Scheme 56) which was used in the successful generation of the screening substrate **135a**.[190]

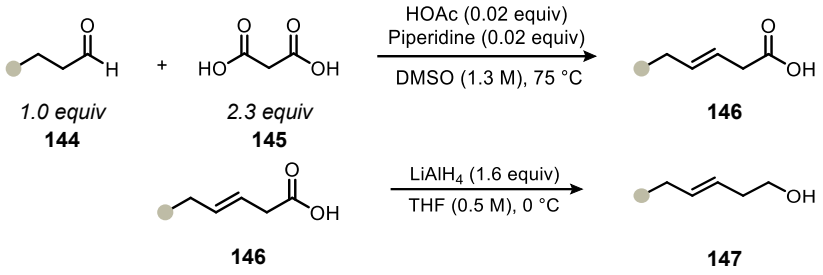


135 **142** **143**

Scheme 56: Retrosynthetic pathway for the synthesis of the acyclic carbonates **135**.

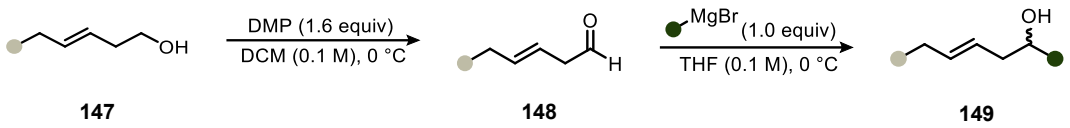
However, we were uncertain if the thus far used reaction conditions could be applied to a broader reaction scope, as side reactions could already be recorded in previous attempts.[190] Nonetheless we anticipated that this retrosynthetic analysis was the most facile way of selectively generating a broad variety of asymmetric substituted acyclic carbonates **135** by simply using structurally flexible alcohol precursors **142** in a converging synthesis. The structural diversification is then solely depending on the alcohol **142**, where we envisioned two positions for altering the basic carbon chain. The first adjustable C-atom carries the hydroxy group (green in Scheme 56), enabling the synthesis of acyclic carbonates **135**, based on secondary- and possible tertiary alcohols of different steric impact. From these modifications we anticipated an increased product formation based on Thorpe-Ingold-Effect, as increasing substitution on a carbon center results in angle compression and thereby favors cyclization reactions by minimizing the mobility of the carbon chain.[202,203] The second modifiable C-atom is located in vinylic position on the other end of the carbon chain (beige in Scheme 56) and was mainly anticipated to display functional group tolerance. At last, we sought out to only use either *E*- or *Z*-configurated π-bonds to avoid possible complications and reactivity differences.

The first route that was already used in the synthesis of the screening material **135a** is based on primary alcohol **147**, which is obtained from a Knoevenagel Condensation[32] from a commercially available aldehyde **144** and subsequent reduction with $LiAlH_4$ (Scheme 57).[204]



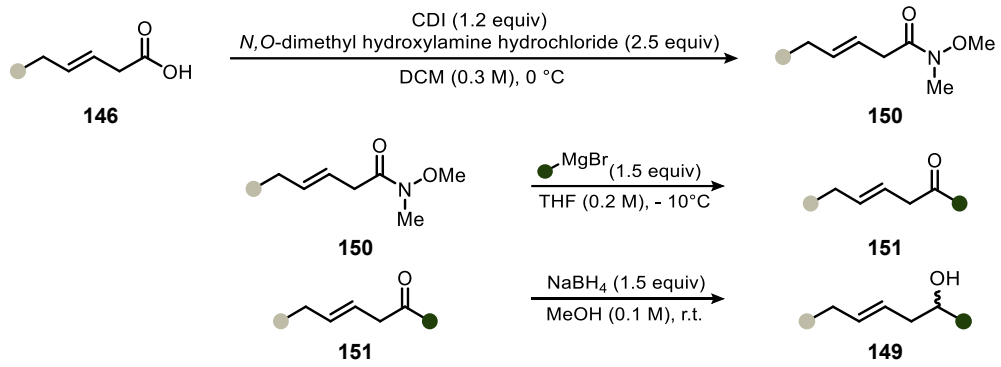
Scheme 57: Reaction template for the synthesis of primary allylic alcohols **147**.

Apart from serving themselves as suitable starting materials for the coupling reaction illustrated in retrospective in Scheme 56, the obtained alcohols **147** were then also meant to be further transformed into their secondary or tertiary counterparts **147-2** by means of selective oxidation with Dess-Martin-Periodinane[205] and consecutive treatment with suitable Grignard reagents (Scheme 58).[206]



Scheme 58: Reaction template for the transformation of primary alcohols **147** to their secondary analogues **149**.

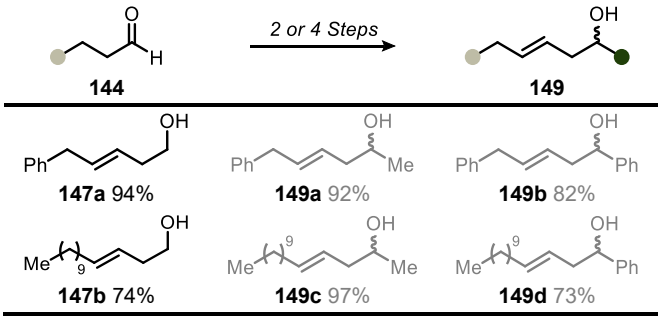
The major issue with this synthesis plan turned out to be the stability of the aldehyde Fehler! Verweisquelle konnte nicht gefunden werden. whereas both, isolation, and purification attempts resulted in partial isomerization of the π-bond to form a conjugated system.[190] In order to circumvent this issue, the aldehyde **148** had to be used directly without purification processes, resulting in yields below 20% in the following Grignard reaction.[190] To address this problem, we then thought of approaching the introduction of secondary substituent in an earlier stage, therefore avoiding the need for aldehyde Fehler! Verweisquelle konnte nicht gefunden werden.. The adapted synthesis plan again relied on the Knoevenagel Condensation to form the alkenoic acid **146**, but instead of reduction to the primary alcohol **147**, it was transformed into Weinreb Amide **150**[14] and from there on the secondary substituent was introduced by a Grignard reaction.[207] Final reduction of the obtained ketone **151** was then envisioned by reduction with $NaBH_4$ (Scheme 59).[208]



Scheme 59: Synthesis route based on Weinreb Amides.

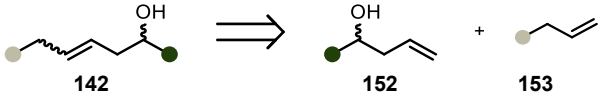
Following this concept, we were able to synthesize six different *E*-selective alcohols **149**, using commercial available 3-phenylpropanal and dodecanal as starting aldehydes **144**, and MeMgBr as well as PhMgBr as commercial Grignard reagents (Table 4). Unfortunately, this pathway was still limited to a small number of commercially available aldehydes **144** that have at least two unfunctionalized carbon atom between the aldehyde and further functional groups and only the above mentioned Grignard reagents showed successful product formation when reacting with the Weinreb Amide **150**. Other Grignard reagents were tested and also the corresponding Li-organyls were not nucleophilic enough and potentially solely reacted as bases.[209]

Table 4: Scope for the synthesis of *E*-selective alcohols **142**



Gray toned substrates were synthesized by MSc. Carolin Nagel.[203,209] Reported isolated yields correspond to the last step in the respective reaction procedure.

Anticipating that the examples listed above (**147a-b** and **149a-d**) would be enough to demonstrate that the configuration of the π-bond has no significant impact on the outcome of the cyclization reaction, when compared with corresponding *E/Z*-mixtures, we thought of different ways to assemble the alcohol **142** and found a viable option in utilizing cross coupling metathesis (Scheme 60).

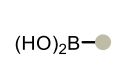
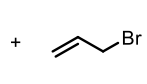
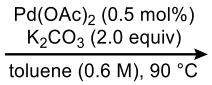
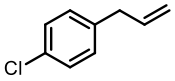
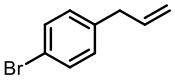
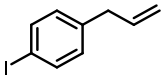
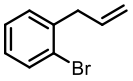
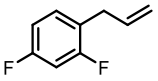
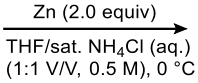
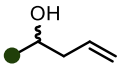
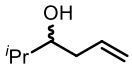
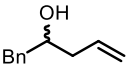


Scheme 60: Concept for the cross coupling metathesis.

The advantages of this approach were easy access to both starting materials **152** and **153**, but also a reduction in total number of reaction steps required. In this context it should also be noted that to

arrive at the desired reaction scope, a selective number of alkenes **153** and allylic alcohols **152** were additionally synthesized using respective procedures. Among those a Suzuki coupling[210] between an aromatic boronic ester **154** and allyl bromide (**155**) was used to generate selective terminal alkenes **153** in overall good yields (Table 5, upper part). On the other side, additional allylic alcohols **152** were prepared using a Barbier reaction, to couple chosen aldehydes **156** with allyl bromide (**155**) (Table 5, lower part).[211]

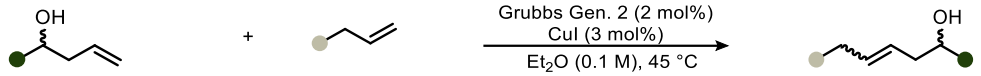
Table 5: Scope overview for the Suzuki coupling and the Barbier reaction

Suzuki coupling				
				
1.0 equiv **154**	*11 equiv* **155**		**153**	
				
153a 60%	**153b** 36%	**153c** 82%	**153d** 56%	**153e** 82%
Barbier reaction				
				
1.0 equiv **156**	*2.0 equiv* **155**		**152**	
				
152a 80%			**152b** 35%	

Isolated yields reported.

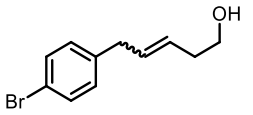
Coupling alkenes **153** and the allylic alcohols **152** synthesized, as well as commercially available alternatives, in the cross coupling metathesis, gave rise to the total scope for the allylic alcohols **142** presented in Table 6. The metathesis reaction was performed using Grubbs Gen. 2 catalyst in combination with CuI, whereas the iodine is postulated to extend the lifetime of the catalyst resulting in better yields.[212] Products **142a-x** were obtained in acceptable to good yields with notable trends being the increase in *E/Z*-ratio with increase in bulk of the secondary substituent (c.f. **142t** and **142v**) as well as potentially lower yields for alkenes with electron withdrawing substituents **153** (c.f. **142f** and **142o**). However, the values listed in Table 6 correspond to the isolated material, therefore any deviations resulting from purification processes cannot be excluded.

Table 6: Scope overview for the cross coupling metathesis

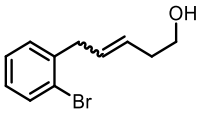


1.0 – 3.0 equiv **152** | *1.0 – 3.0 equiv* **153** | **142**

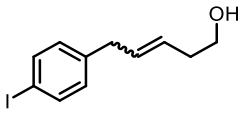
primary substrates:



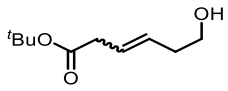
142a 57%, 49:10 *E/Z*



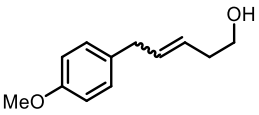
142b 54%, 44:10 *E/Z*



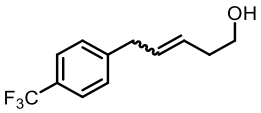
142c 53%, 51:10 *E/Z*



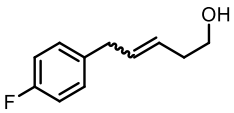
142d 56%, 52:10 *E/Z*



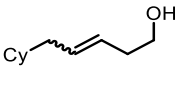
142e 45%, 45:10 *E/Z*



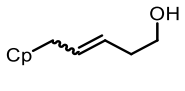
142f 34%, 46:10 *E/Z*



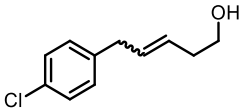
142g 52%, 50:10 *E/Z*



142h 24%, 41:10 *E/Z*

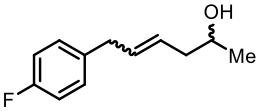


142i 54%, 34:10 *E/Z*

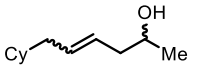


142j 56%, 50:10 *E/Z*

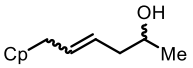
secondary/tertiary substrates:



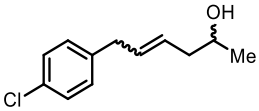
142k 54%, 54:10 *E/Z*



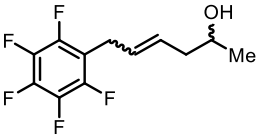
142l 38%, *E/Z* n.d.



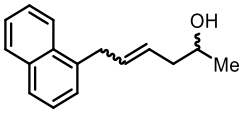
142m 40%, *E/Z* n.d.



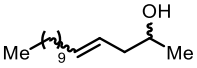
142n 45%, 52:10 *E/Z*



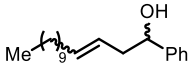
142o 20%, 46:10 *E/Z*



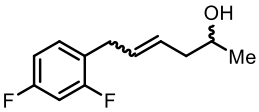
142p 40%, 50:10 *E/Z*



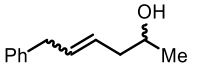
142q 31%, *E/Z* n.d.



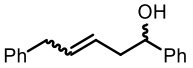
142r 25%, 46:10 *E/Z*



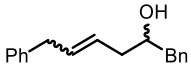
142s 48%, 48:10 *E/Z*



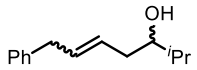
142t 43%, 55:10 *E/Z*



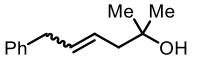
142u 24%, 40:10 *E/Z*



142v 30%, 63:10 *E/Z*



142w 18%, 46:10 *E/Z*



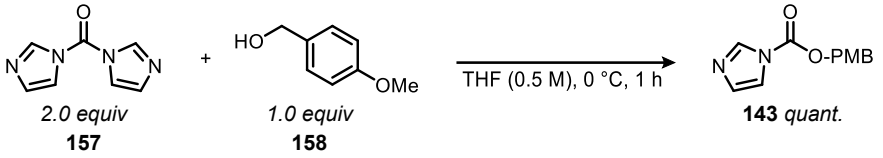
142x 51%, 51:10 *E/Z*

Isolated yields reported. *E*/*Z*-ratios correspond to isolated material. Explicit ratios of starting materials **152** and **153**, depend on the starting material used. **Grubbs Gen. 2 =** Grubbs second generation catalyst.

In summary, the scope provided a broad array of valuable motifs ranging from primary substituted alcohols (**142a-j**) to secondary alcohols with varying steric demand (**142t-w**) and even a tertiary alcohol **142x** was successfully synthesized. Of elevated interest were substrates **142e** and **142f** to provide insight in the relevance of the electronic nature (electron withdrawing vs. electron donating) of the terminal substituent regarding the stability towards degradation, as well as the comparison between primary alcohols **142g-j** and their secondary counterparts **142k-n** to test for potential improved yields by limiting free structural movement similar to a Thorpe-Ingold-Effect, thereby facilitating the cyclization. Structures **142t-w** were specifically designed to prove our hypothesis that an increase in steric bulk would result in larger dr values in the final cyclization reaction, as it is also postulated in literature regarding similar transformations.[52,213–216] At last, compounds **142q-r** and **142t-u** represented the *E/Z*-mixtures to the previously synthesized *E*-selective structures **147a-b**

and **149a-d** which allowed for analysis of the potential reactivity difference between different conjugated π-bonds.

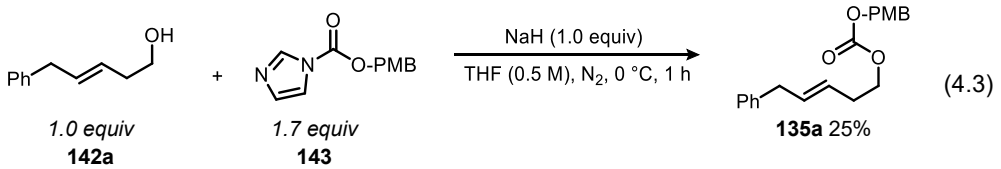
Having established a valid substrate scope for the alcohol **142,** the next step was then to revise the synthesis of the coupling partner **143**, as well the coupling reaction itself, whereas the first proved to be less problematic, as we could simply use the adapted procedure by Wu et al.[217] already used in the corresponding Master's Thesis (Equation 4.2).[190]



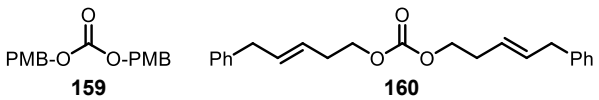
2.0 equiv **157** *1.0 equiv* **158** **143** *quant.* (4.2)

Compound **143** proved problematic, as it was slowly degrading upon isolation, requiring a direct use after synthesis. Furthermore, upon cooling down to r.t., compound **143** transformed from a transparent oil to a sticky colorless grease, enforcing a necessity for dilution before it could be added to the consecutive reaction.

The coupling reaction was then initially performed under highly basic conditions, deprotonating the exhibited alcohol **142a** with NaH at 0 °C. After a reaction time of 1 hour, the coupling partner **143** was added and the combined mixture stirred for 1 more hour and then promptly quenched to minimize side reactivity (Equation 4.3).[190,217]



1.0 equiv **142a** *1.7 equiv* **143** **135a** 25% (4.3)



159 **160**

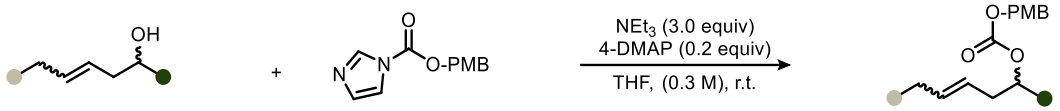
Figure 11: Side products from the above described carbonate synthesis.

Nonetheless, the reaction shown above suffered severely from side product formation of which, two could be isolated and identified as the two alternative, symmetrical substituted, acyclic carbonate motifs **159** and **160** (Figure 11).[190] Although not deeply investigated, we anticipated that these products result from decomposition processes of compound **143** and simple transesterification reactions made possible in the strongly basic reaction media. Furthermore, the reaction outcome became even worse when trying to apply other alcohols **142** such as compound **142b** in which case product formation was still observed but clean separation from other impurities was not possible and other tested substrates showed no product formation at all.[190]

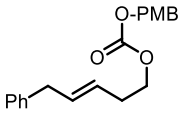
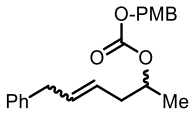
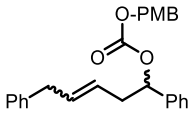
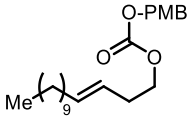
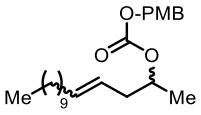
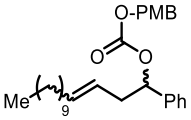
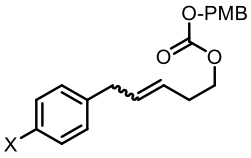
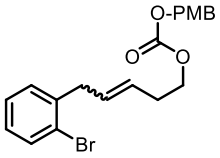
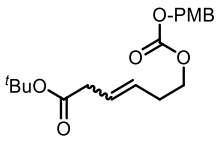
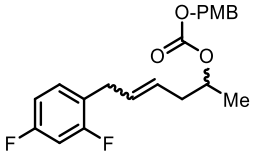
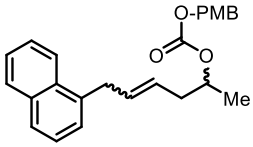
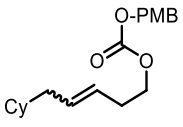
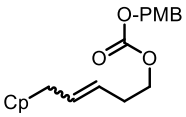
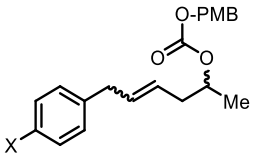
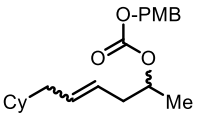
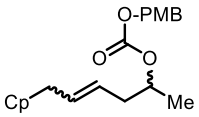
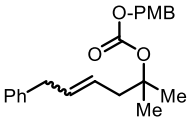
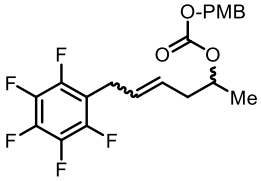
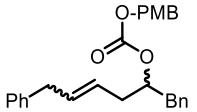
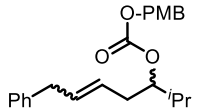
As it was obvious to us, that the mayor issue with the above-mentioned reaction (Equation 4.3) setup laid within the strong basic media, we thought about using less basic conditions to drive the reaction solely to the compounds of interest and disfavor other transesterification processes. A

practical solution was found, when applying adapted Steglich Esterification conditions, utilizing triethylamine as a weaker base to activate the alcohol **142** and 4-(dimethylamino)-pyridin (4-DMAP) in catalytic amounts to increase the reactivity of the carbamate **143**.[218] Although the reaction times severely increased from 1 hour to roughly 2 days, side product formation of **159** and **160** could be reduced, resulting in improved yields and easier isolation procedures allowing for the synthesis of a broad variety of acyclic carbonates **135**, from the alcohols **142**, **147** and **149** listed in Table 4 and Table 6. The only non-successful transformation was observed when applying tertiary alcohol **142x**, in which case not even extended reaction times over 2 weeks showed any signs of product formation. We attributed this observation to the diminished reactivity of the tertiary alcohol in esterification reactions but also the fact, that we were not utilizing an acid as counterpart but rather a carbamate. Said carbamate functionality is known to obtain more structural rigidity due to the additional delocalization of electrons from the bound nitrogen atom when compared with a simple acid function.[219] In this context it seems more logical, that this additional delocalization feature also reduces the electrophilicity of the carbonyl C-atom therefore making it less prone to substitution reactions, at least in the conditions we applied. An overview of the acyclic carbonates **135** synthesized in listed in Table 7. Comparing the *E/Z*-ratio of the acyclic carbonates **135** with their alcohol precursors **142**, it is reasonable to say, that the carbonate formation (Table 7) had no impact on the previous obtained configuration of the π-bond and in limited cases such as **135q-r**, and **135x-z**, we attribute the rather significant changes in *E/Z*-ratio to incomplete isolation of both isomers during column chromatography. Analyzing primary carbonates bearing different functional groups **135g-n** and **135q-r**, no significant impact on the reaction outcome is observed especially when taking a closer look at substrates **135i-j** and **135n**. Whereas the first and the latter represent electron withdrawing functionalities, substrate **135i** can be declared as an electron donating functionality. Indifferently however, the yields of these three individual substrates show no clear trend indicating any preferences for either electron withdrawing or electron donating functional group. In this aspect it also has to be mentioned that the actual yield for **135i** was estimated to be much higher but due to separation issues from the side product **159**, the material had to be recrystallized and only the *E*-fraction of **135i** could be isolated. Lastly, comparing the yield of the primary carbonates with their secondary counterparts (if available), one might declare a trend of decreasing yield, with more space consuming secondary substituents (comparing substrates **135a** with **135w**, **135y** and **135z**). This observation holds true for most primary/secondary carbonate pairs listed in Table 7, whereas the extent of the decrease is not unanimous and the trend even inverts in the examples of substrates **135a** vs. **135b**, **135c**, **135f**. However, as the values presented only correspond to isolated material, we cannot neglect the impact of improper isolation and other deviations during the workup process.

Table 7: Scope Overview for the synthesis of carbonates **135**



1.0 equiv **142** | *1.5 equiv* **143** | **135**

 **135a** 60%	 **135b** 76%, only *E* **135bb** 80%, *E/Z* 47:10	 **135c** 85%, only *E* **135cc** 59%, *E/Z* 33:10	 **135d** 82%
 **135e** 77%, only *E* **135ee** 82%, *E/Z* n.d.	 **135f** 86%, only *E* **135ff** 57%, *E/Z* 33:10	 **135g X = Br** 53%, *E/Z* 46:10 **135h X = I** 62%, *E/Z* 45:10 **135i X = OMe** 27%, only *E* **135j X = CF_3** 74%, *E/Z* 45:10 **135k X = F** 68%, *E/Z* 42:10 **135l X = Cl** 53%, *E/Z* 53:10	 **135m** 74% *E/Z* 46:10
 **135n** 40%, *E/Z* 45:10	 **135o** 44%, *E/Z* 43:10	 **135p** 38%, *E/Z* 51:10	 **135q** 78%, *E/Z* 29:10
 **135r** 57%, *E/Z* 50:10	 **135s = F** 49%, *E/Z* 39:10 **135t = Cl** 43%, *E/Z* 43:10	 **135u** 17%, *E/Z* 32:10	 **135v** 44%, *E/Z* 46:10
 **135w** 0%	 **135x** 57%, *E/Z* 61:10	 **135y** 65%, *E/Z* 46:10	 **135z** 40%, *E/Z* 22:10

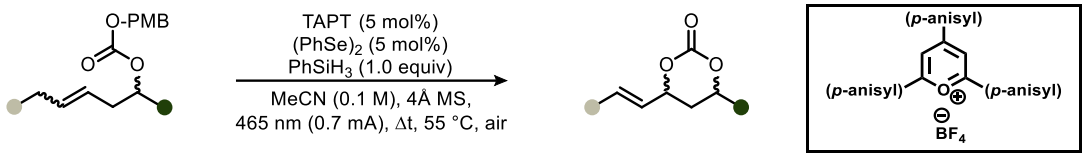
Substrates that are grayed out were synthesized by MSc. Carolin Nagel.[203,209] Isolated yields reported. *E/Z*-ratios correspond to isolated material.

To conclude, utilizing two different pathways for the synthesis of allylic alcohols **142**, we were able to synthesize a broad variety of said alcohols, also being able to synthesize purely *E*-configurated motifs to compare with their *E/Z*-mixture analogues. Transformation into the corresponding acyclic carbonates **135** was then made possible by reinvestigating the reaction conditions, allowing for a wide array of acyclic carbonates **135** that could then be used in the cyclization procedure.

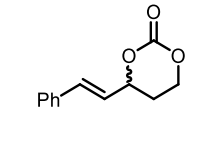
4.1.3. Selenium-π-acid catalyzed cyclization reaction

To investigate the potential of the developed method, we first started to apply the primary carbonates **135** to our reaction conditions. All of the reaction listed below were performed in the same reaction setup using the cooling block system with bottom irradiation, the sole exception being substrate **136a**, which was only performed in the crystallization beaker setup. In order to obtain the best result, we let the reaction stir under irradiation of at least 38 h and then performed TLC analysis to determine the stage of conversion. To minimize the extent of degradation processes, we attempted to stop the irradiation prior to full conversion, which in most cases resulted less than 20% of starting material **135** remaining at the point of NMR analysis. Another important factor that governed the outcome was the stirring and thus the oxygen diffusion into the reaction media, delivering the oxygen needed for the regeneration of the photocatalyst (Scheme 54). Higher stirring rates however not only resulted in increased oxygen concentration within the solution but also affected the concentration of singlet oxygen $^1O_2$ (+0.97 eV vs SCE), formed by TAPT (+1.84 eV vs SCE) as a side reactivity.[220,221] Apart from being relatively longevous, $^1O_2$ displays a highly reactive intermediate due to its singlet character, which enables reactivity with common organic features such as π-bonds or electronic available X-H σ-bonds.[221] The resulting (endo-)peroxides then participate in further reactivity either directly compromising the target compound or *in situ* generation of compounds that will provoke side reactivity. Another found drawback is the possible oxidation of the diselenide catalyst $(PhSe)_2$,[201,221] therefore rendering it inactive for further transformations.[221] As we observed both phenomena, even when additional $^1O_2$ quenchers were applied, we tried to keep the stirring at lower values (< 500 rpm). As we were, however, not able to influence the consistency of the stirring process over the whole irradiation period, we often found ourselves surprised that two identical reaction setups, run in parallel, were at different levels of reaction progression in the same time frame. By visual analysis in combination with the obtained results it was then reasoned that the reaction with less progression suffered from inconsistent stirring, therefore minor oxygen diffusion and thus insufficient photocatalyst regeneration. Furthermore, we also declare this observation to be contributing to the inconsistency in the reaction times, where we have a time span of 24-72 hours (Table 8). This often-drastic change in reaction time then further resulted in elongated light exposure which on one hand contributed to possible degradation by direct oxidation or by reaction with $^1O_2$ which presence we cannot exclude.

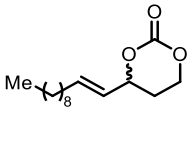
Table 8: Scope overview for the primary 1,3-dioxan-2-ones **136**



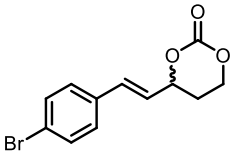
135 **136** **TAPT**



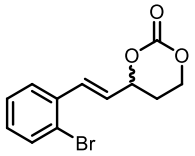
136a[a] 57% (59%), 24 h, conv. n.d.



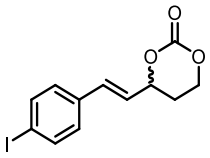
136d[a] 21% (41%), 72 h, 88% conv.



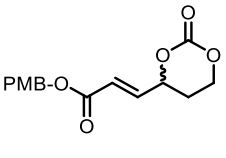
136g 31% (36%), 39 h, 75% conv.



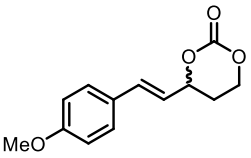
136m 28% (41%), 41 h, 72% conv.



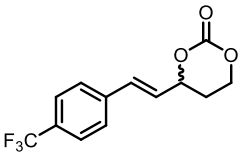
136h -% (23%), 166 h, 84% conv.



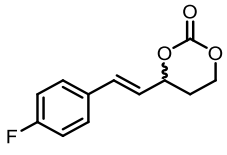
136n[a] 38% (44%), 46 h, 100% conv.



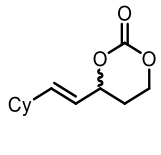
136i -% (>5%), 38 h, 45% conv.



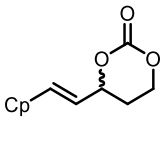
136j 68% (68%), 60 h, 100% conv.



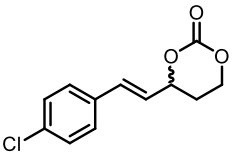
136k 46% (54%), 39 h, 82% conv.



136q 21% (44%), 67 h, 100% conv.



136r 20% (41%), 67 h, 100% conv.



136l 18% (27%), 74 h, 100% conv.

Reactions were performed on a 1.0 mmol scale. NMR yield is given in parentheses. 1,1',2,2'-tetrachlorethane (0.50 equiv) was used as internal standard. a) 1,3,5-trimethoxybenzene (0.50 equiv) was used as internal standard.

An obvious example for the above discussed degradation problematic can be directly seen when comparing substrates **136i** and **136j**. The electron rich nature of the olefin in substrate **136i** should in theory make it more volatile towards oxidative processes in contrast to the electron poor counterpart **136j**, independently whether the cause of degradation is $^1O_2$ or direct oxidation by the photocatalyst. Proving this hypothesis, only traces of product **136i** could be observed in the NMR, whereas product **136j** is among the most profitable reactions within the entire reaction scope. When taking a closer look at the halogen substituted arenes **136g-h** and **136k-m** we could declare a similar trend leading back to the differences in electron distribution, when disregarding the differences in reaction time. Whereas in the fluorinated substrate **136k** a withdrawing inductive effect dominates the electron distribution, electron donating effects become more prominent up to the iodinated substrate **136h**, therefore leading to more electron rich olefins and increased volatility.[2] In the cases of substrates **136d**, and **136p-r**, we also believed that the elongated reaction times are a major cause for the only acceptable yields but we further postulate that the lack of a conjugated π-bond also significantly affects the transformation. The reasoning behind this postulate is that a conjugated π-bond displays a meaningful driving force in the cyclization process and the absence results in a decreased reaction rate leaving more time for catalyst degradation therefore minor product formation and dominant degradation of starting material by irradiation processes.

One last thing that has to be mentioned is a transesterification observed in substrate **136n**. Whereas substrate **136n** is based on the ^{t}Bu-ester **135n**, the same is observed in a NMR spectra

recorded prior to the isolation process where a ^{t}Bu-group is still observable. After isolation by column chromatography however, the signal set of the isolated fraction significantly changed, most noticeable, the loss of the ^{t}Bu-group. On the contrary, the signals belonging to the PMB-group remained and were also correlating to the π-bond signals (Figure 12). We concluded therefore a transesterification process first occurring under the slightly acidic conditions from the column chromatographic resolution facilitated by the high nucleofugacity of ^{t}Bu-group.

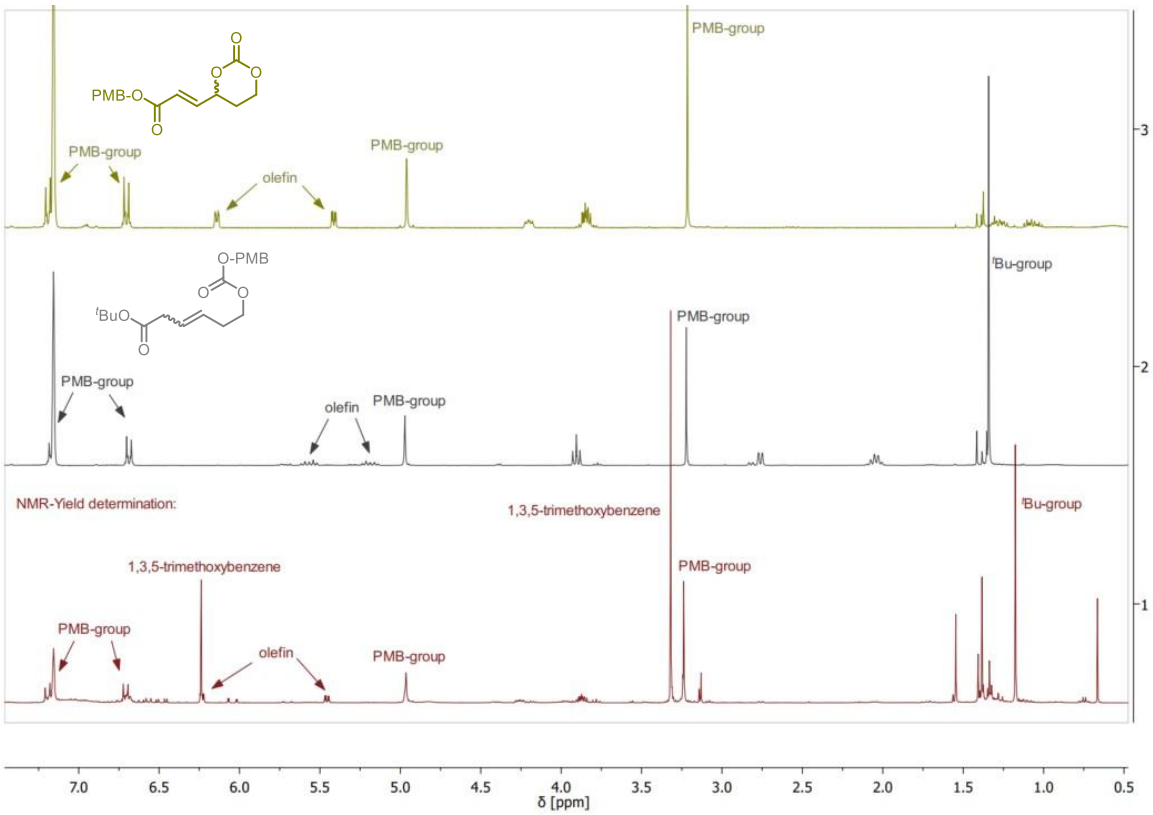
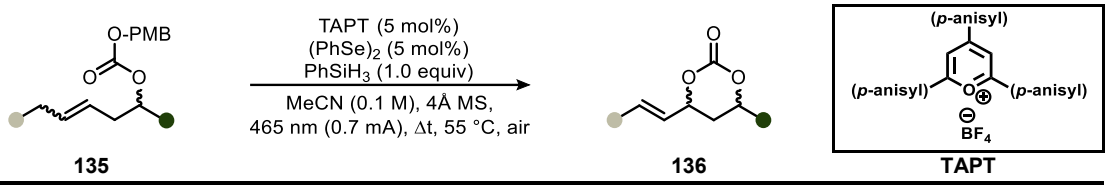


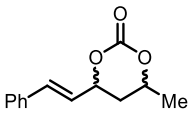
Figure 12: NMR stacking of the isolated material **136**j (olive, top), the used starting material **135**j (grey, middle) and the corresponding NMR yield determination (maroon, bottom), all done in C_6D_6.

We then shifted our focus to our array of secondary substrates, where we still expected all the complications listed above but also anticipated better overall yields due the secondary substitution decreasing the free mobility of the carbon chain and thus facilitate the cyclization reaction.[202] Based on our obtained results, we could conclude that our hypothesis had proven to be right as indeed all secondary cyclic carbonates **136** were formed with an average increase of 20 percentage points (Table 9).

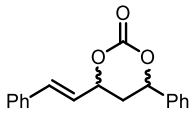
Table 9: Scope overview for the secondary 1,3-dioxan-2-ones **136**



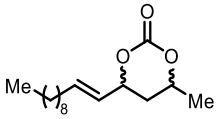
135 **136** **TAPT**



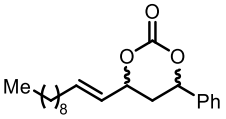
136b 37% (65%), 38 h, 100% conv., 26:10 *cis*/*trans*



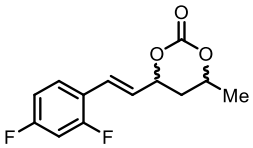
136c 44% (64%), 37 h, 100% conv., 32:10 *cis*/*trans*



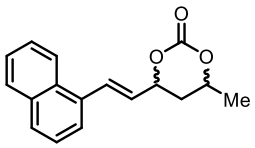
136e 39% (65%), 37 h, 100% conv., 34:10 *cis*/*trans*



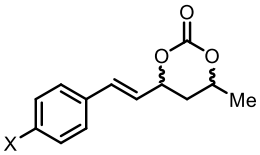
136f 38% (57%), 39 h, 100% conv., 64:10 *cis*/*trans*



136o 62% (70%), 61 h, 100% conv., 25:10 *cis/trans*

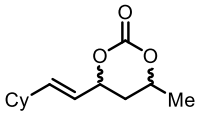


136p 32% (40%), 39 h, 100% conv., 23:10 *cis*/*trans*

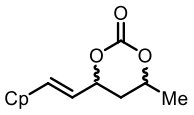


136s X = F 25% (55%), 39 h, 100% conv., 19:10 *cis*/*trans*

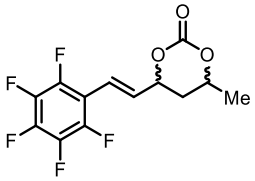
136t X = Cl 43% (65%), 40 h, 22:10 *cis*/*trans*



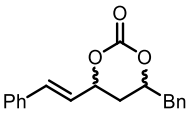
136u 60% (74%), 38 h, 100% conv., 36:10 *cis/trans*



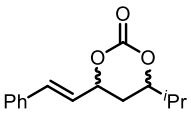
136v 51% (65%), 39 h, 100% conv., 33:10 *cis*/*trans*



136x 49% (64%), 41 h, 81% conv., 20:10 *cis*/*trans*



136y 35% (55%), 39 h, 100% conv., 26:10 *cis*/*trans*

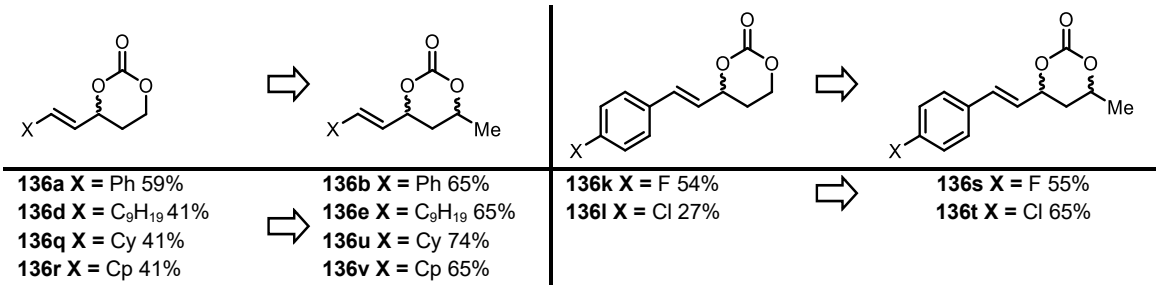


136z 24% (61%), 38 h, 100% conv., 34:10 *cis*/*trans*

Reactions were performed on a 1.0 mmol scale. NMR yield is given in parentheses. 1,1',2,2'-tetrachlorethane (0.50 equiv) was used as internal standard. dr values correspond to isolated material.

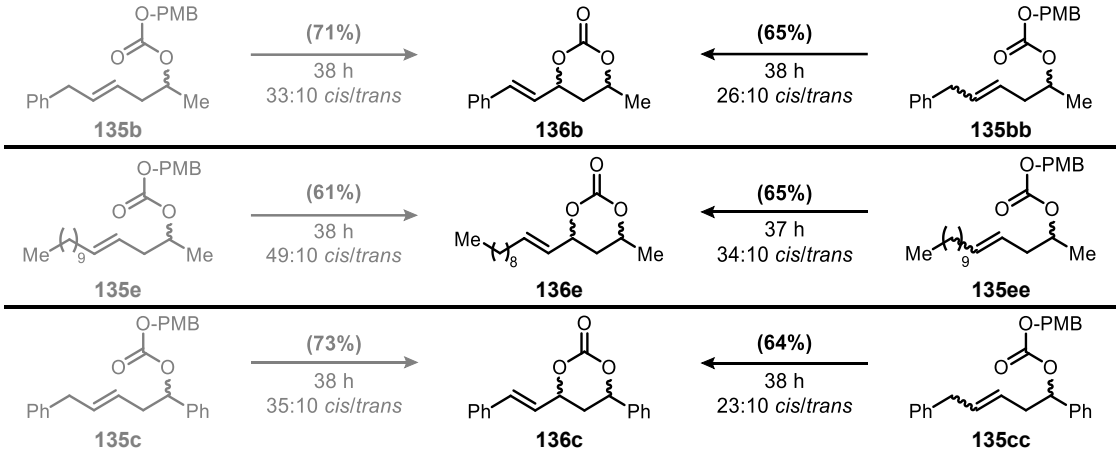
Even more so, the beneficial effect of a secondary substituent could be shown directly, when comparing previously reported primary 1,3-dioxan-2-ones such as **136a, 136d,** and **136k-l** with the now obtained secondary counterparts (Scheme 61). On average, we obtained a 22 percentage point increase in yield when adding a secondary substituent, with the only available exception being the substrate pair **136k** and **136s**, in which case no boosting effect was registered. Unfortunately, as we were not able to synthesize the tertiary starting material **135w**, we could not determine if further substitution would have had an even more beneficial effect on the reaction outcome.

Synthesis of 1,3-dioxan-2-ones Selenium-π-acid catalyzed cyclization reaction



Scheme 61: Overview of the NMR yield enhancement by addition of a secondary substituent.

Another question we could now answer was the impact of the π-bond configuration on the reaction outcome, to be precise whether a double bond isomeric mixture would negatively affect reaction progression and outcome. The work for this part displayed a team effort, as the reaction involving the *E*-selective substrates **135b**, **135c** and **135e** were performed by independent members of the group.[209] In order to be able give definite statements, reaction parameters were kept as constant as possible and therefore only values obtained during the NMR yield determination were used for comparison (Scheme 62).



Scheme 62: Reactivity comparison between double bond isomeric mixtures and pure isomers. NMR yields in parenthesis. dr values taken from the crude NMR. Reactions that are grayed out were performed by MSc. Carolin Nagel.[203,209]

Based on our results, (Scheme 62) going from an isolated π-bond isomer to a mixture imposes only a marginal effect on the reaction yield, whereas the extent of this alteration seems to be different for the aromatic substrates **136b** and **136c** in contrast to the alkyl chain substrate **136e**. A rather more significant and continuous impact however is observed concerning the diastereomeric ratio of the products where isolated *E*-conformers give higher ratios then their mixture counterparts. Trying to explain this behavior, we first tried to understand which diastereomer is favored and what is the mechanistical reasoning for this preference. From a practical viewpoint, a coworker was able to separate both diastereomers from substrate **136b** and we were able to determine the relative configuration using 2D NOESY spectroscopy (Figure 13).[203,209]

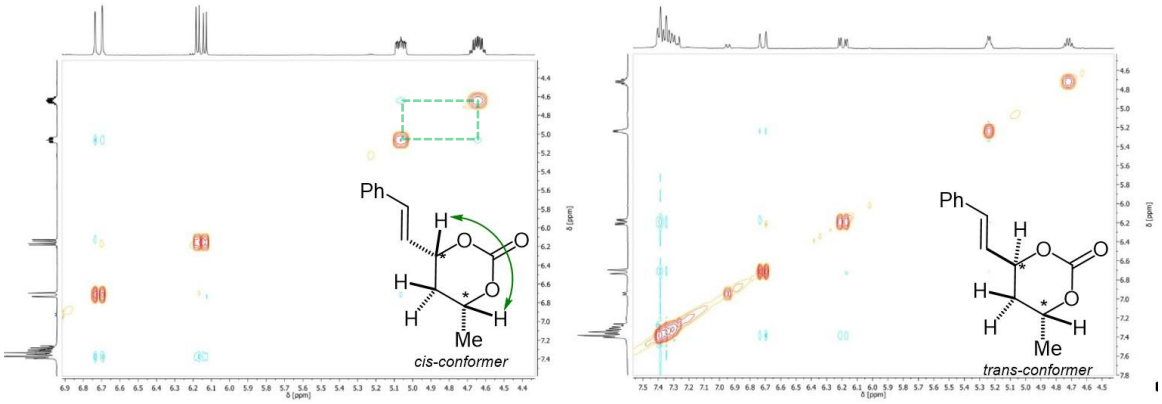


Figure 13: Excerpt of the NOESY spectra for both diastereomers of compound **136b**.[203]

The major fraction was declared the *cis*-diastereomer as a thru space coupling was clearly observed between the two protons at the stereogenic centers (Figure 13). The minor fraction did not provide such an interaction and was therefore complimentary declared as the *trans*-diastereomer (Figure 13). Furthermore, analogous outcomes for similar operating cyclization reaction can be found in literature and these reports also provided us with a theoretical basis to mechanistically prove our observation and generalize it for all our substrates (Figure 14).[52,53,65,103,213,214,216]

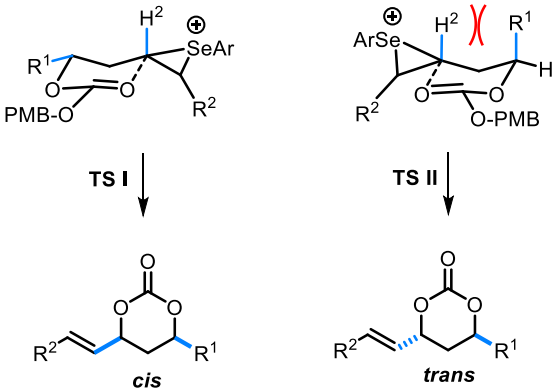
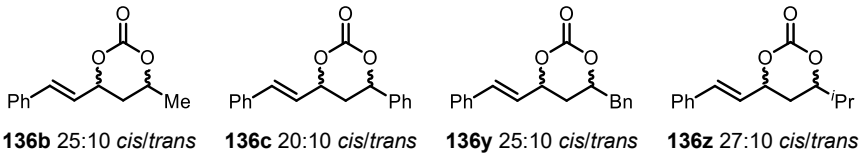


Figure 14: Graphical representation of which transition state (**TS**) translates to which diastereomer.

Comparing both transition states leading to each diastereomer in the Zimmerman-Traxler model, the R^1-group switches between the equatorial plane for the transition state leading to the *cis*-diastereomer (**TS I**) and the axial plane for the transition state leading to the *trans*-conformer (**TS II**). Apart from being energetically disfavored in axial position, the R^1-group in this orientation results in a further increase of energy by causing 1,3-diaxial interaction with proton H^2 thereby significantly disfavoring **TS II** over **TS I**. This lead to the hypothesis that with increasing steric demand of R^1, the diastereomeric ratio should be further shifted to the *cis*-diastereomer, which we could prove practically by comparing the dr values obtained in the NMR yield determination of substrates with sterically more demanding R^1-groups (Figure **15**).

Synthesis of 1,3-dioxan-2-ones Selenium-π-acid catalyzed cyclization reaction



136b 25:10 *cis*/*trans* **136c** 20:10 *cis*/*trans* **136y** 25:10 *cis*/*trans* **136z** 27:10 *cis*/*trans*

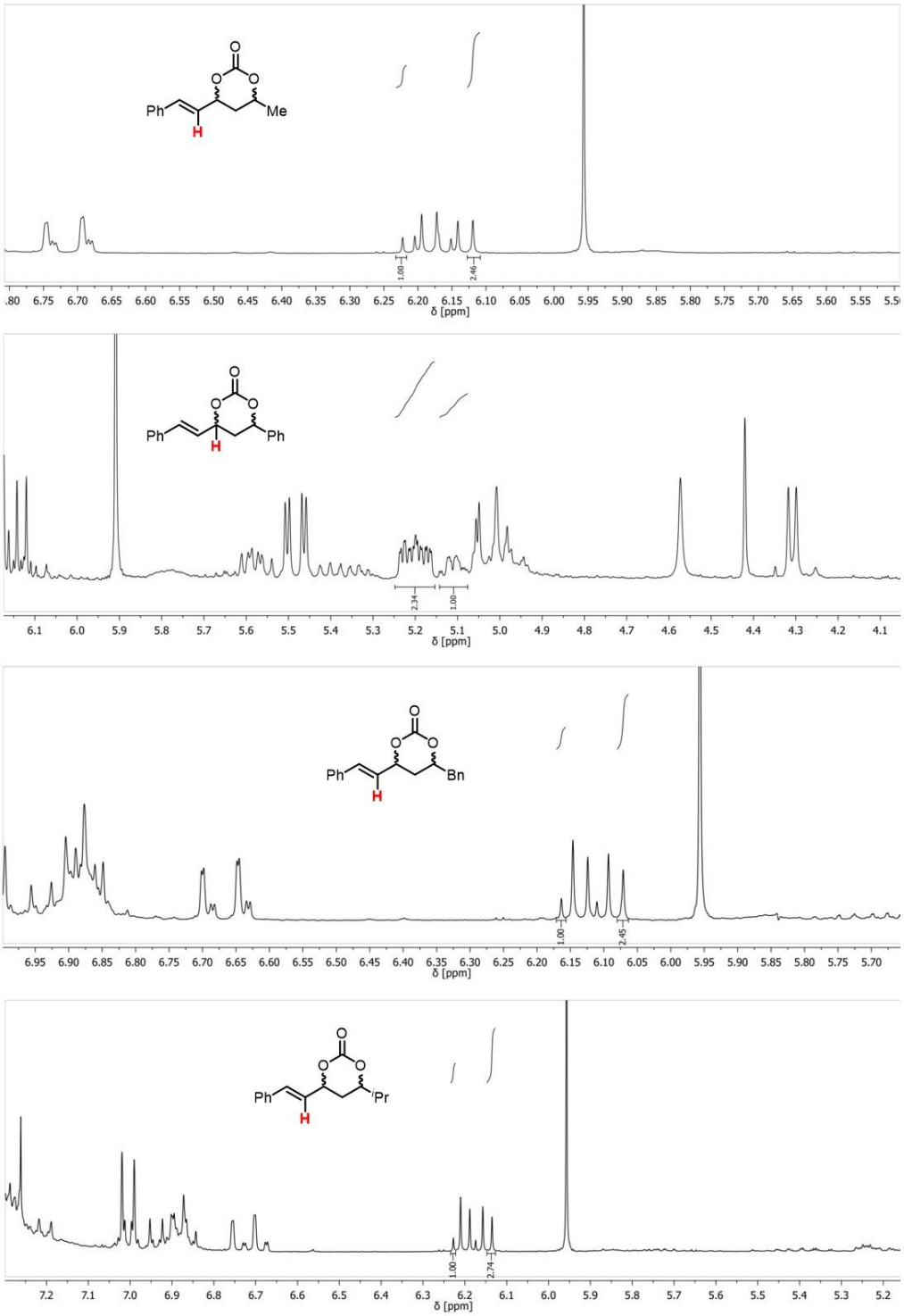
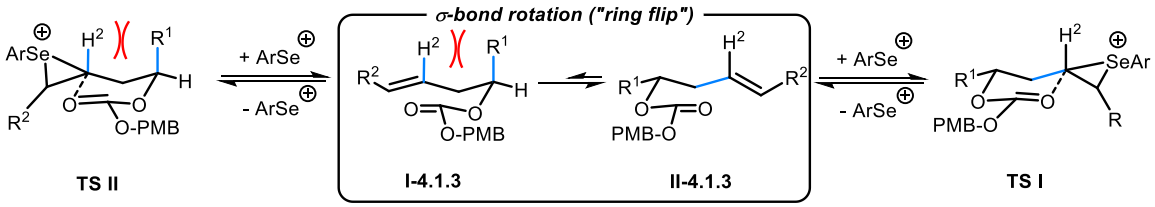


Figure 15: Comparison of the *dr*-values obtained in the NMR yield determination (top) and excerpt of the corresponding NMRs (bottom).

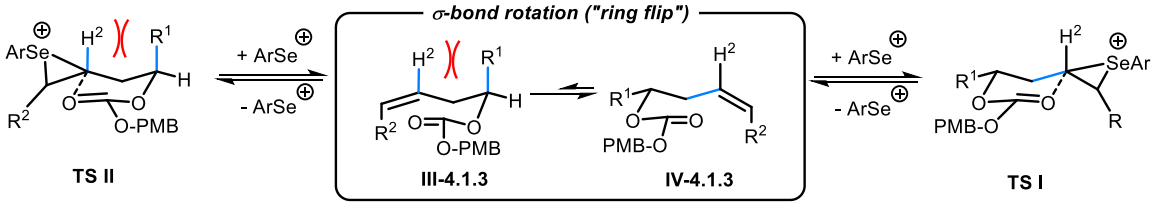
Although the impact is rather small, the sterically more demanding ^{i}Pr-group in **136z** already shows slightly better selectivity than the smaller Me-group (structure **136b**) or the flat Ph-group (structure **136c**). However, without also replacing the proton H^2 with more bulky residues, more prominent changes seemed to be less likely.

Having investigated the steric outcome of the major diastereomer, we came back to the question of how the configuration of the double bond might affect the reaction pathway. Starting off with the *E*-isomer, we considered the necessities for the formation of each transitions state (**TS I** and **TS II**) and concluded that a simple σ-bond rotation (blue bond, Scheme 63) controls the continuing reactivity. By applying a Zimmerman-Traxler model, said σ-bond rotation can be envisioned with a “ring flip” in which case we end up with a pro-*trans* arrangement **I-4.1.3** and a pro-*cis* arrangement **II-4.1.3**, each leading to the respective diastereomer they are named after (Scheme 63). However, based on the fact, that the pro-*trans* arrangement **I-4.1.3** is higher in energy due to the axial orientation of the R^1-group and the therefore resulting additional 1,3-diaxial tension (depictured between R^1 and H^2, Scheme 63), the pro-*cis* arrangement **II-4.1.3** is favored and therefore also the *cis*-product **136**.



Scheme 63: Stereochemical explanation for the favorable formation of the *cis*-product **136** starting from the *E*-isomer **135**.

Analogous evaluation of the reaction pathway for the *Z*-isomer led to unaltered observations as the same conclusions drawn for the *E*-Isomer could also be applied here. The major factor determining selectivity again resides within the consequence that the molecular arrangement leading to the transition state favoring the *trans*-product **136** is energetically disfavored due to a 1,3-diaxial tension and thus the *cis*-product **136** will be major outcome.

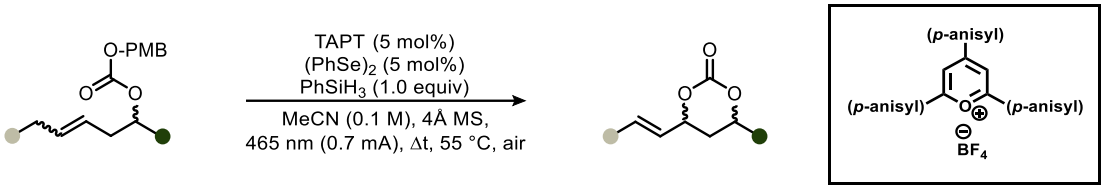


Scheme 64: Stereochemical explanation for the transformation starting from the *Z*-isomer **135**.

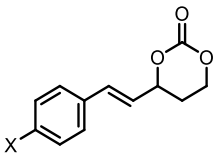
Concluding from these analyses it can be said that the reasoning behind the higher dr values is no direct consequence of the difference regarding *E*- or *Z*- configuration of the alkene starting material as both conformers do not affect the selectivity regarding the mechanistic outcome. However, there are further considerations such as the overall reversibility of the above mentioned steps, that might

have further impact on the stereochemical outcome. This for example is known to lead to an inter-conversion of *Z*- to *E*-alkenes by reversible addition and elimination of the $ArSe^+$-group (going from **III-4.1.3** or **IV-4.1.3** via **TS I** or **TS II** to **II 4.1.3**) before further progression.[191,222] An even more complex implication has been described by the Denmark group reporting on an intermolecular transfer of the $ArSe^+$-moiety from a *Z*- to an *E*-alkene.[223]

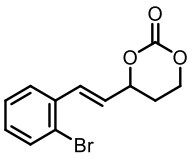
Table 10: Complete overview of the substrate scope for the synthesis of 1,3-dioxan-2-ones **136**



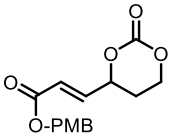
135 **136** **TAPT**



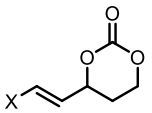
136a[a] 57% (59%), **X =** H
136g 31% (36%), **X =** Br
136h -% (23%), **X =** I
136i -% (>5%), **X =** MeO
136j 68% (68%), **X =** F_3C
136k 46% (54%), **X =** F
136l 18% (27%), **X =** Cl



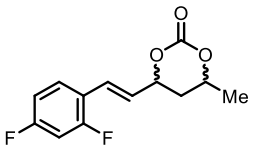
136m 28% (41%)



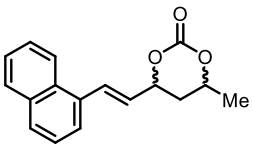
136n[a] 38% (44%)



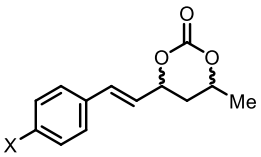
136d[a] 21% (41%),
X = C_9H_{19}
136q 21% (44%),
X = Cy
136r 20% (41%),
X = Cp



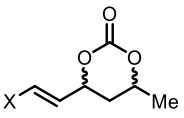
136o 62% (70%), 25:10 dr



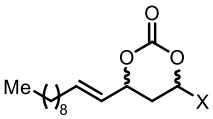
136p 32% (40%), 23:10 dr



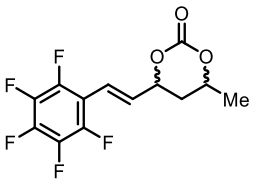
136s 25% (55%),
19:10 dr **X =** F
136t 43% (65%),
22:10 dr **X =** Cl



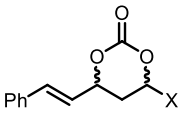
136u 60% (74%),
36:10 dr **X =** Cy
136v 51% (65%),
33:10 dr **X =** Cp



136e 39% (65%), 34:10 dr
X = Me
136f 38% (57%), 64:10 dr
X = Ph



136x 49% (64%), 20:10 dr



136b 37% (65%), 26:10 dr
X = Me
136c 44% (64%), 32:10 dr
X = Ph
136y 35% (55%), 26:10 dr
X = Bn
136z 24% (61%), 34:10 dr
X = ^{i}Pr

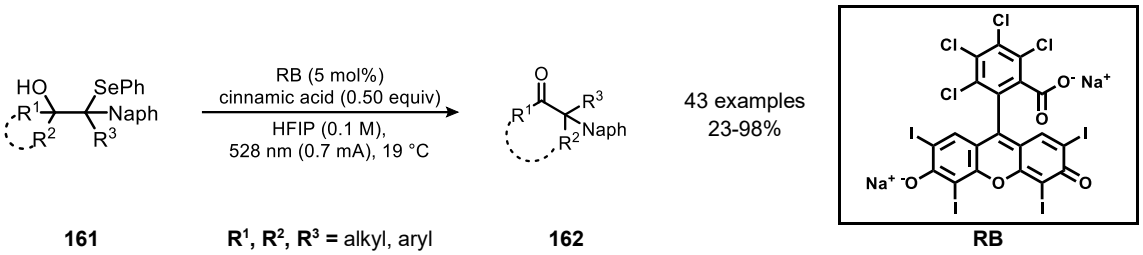
Reactions were performed on a 1.0 mml scale. NMR yield is given in parentheses. 1,1',2,2'-tetrachlorethane (0.50 equiv) was used as internal standard. dr-values correspond to isolated material. The major diastereomer corresponds to the *cis*-diastereomer. a) 1,3,5-trimethoxybenzene (0.50 equiv) was used as internal standard.

However, as no explicit investigations were done regarding this observation it cannot be said that these transfer mechanisms have any implication on the diastereoselectivity and thus the impact of reacting pure *E*-conformers vs. *E*/Z-mixtures (Scheme 62).

Overall comparing our protocol with the existing literature about such transformations (c.f. chapter 2.3.1) our developed method displays the first catalytic synthesis of 1,3-dioxan-2-ones based on simple unactivated olefins regardless of their conformation. Furthermore, we could demonstrate the successful conversion acyclic carbonates **135** with several incorporated functional groups such as substituted arenes, esters and alkyl chains and various secondary substitution (going from H over Me, Ph, Bn to ^{i}Pr) manifesting in a more versatile substrate scope than most previous described methods. In addition to this, all products **136** are obtained with exclusive *E*-selectivity for the regained π-bond and in the cases of the secondary dioxan-2-ones **136** with moderate *cis*-selectivity even for modest steric demanding structures (Table 10).

4.2 Synthesis of 2-methylenecyclopentan-1-ones

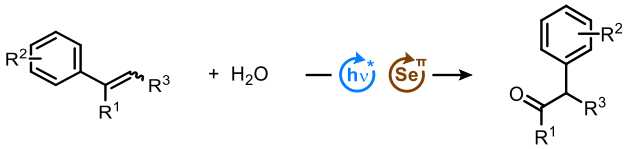
The focus was next shifted towards oxidative rearrangement reactions and thus the access to α,β-unsaturated ketones. Initial results based on this topic were obtained in the working group developing a semipinacol-rearrangement of 1, 2-selenohydrins **161** by means of photocatalytic activation (Scheme 65), thereby accessing highly α-substituted ketones **162**.[109]



161 **R¹, R², R³ =** alkyl, aryl **Naph =** 2-napthyl **162** **RB**

Scheme 65: Exemplary equation for the developed semipinacol rearrangement of selenohydrins. Isolated yields reported.[109]

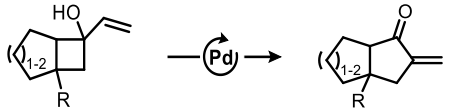
The question was then raised if such a process could be made feasible with a selenium based catalyst and in ongoing research, further improvement of the above mentioned reaction template was successfully implemented by utilizing aromatic conjugated alkenes in combination with water as a nucleophile (Scheme 66).[107]



81 **82**

Scheme 66: Reaction concept for the selenium-π-acid catalyzed synthesis of ketones based on alkenes.[107]

Although yields in the range of 34 to 98% were obtained with the thus far developed concept, a decisive limitation is the range of applicable starting material alkenes **81** where only non-terminal styrene-derivatives were tolerated.[107] Eager to expand the reach of the rearrangement idea, we sought further ways to invoke similar reactivity based on alternate starting materials and it was then decided to attempt a ring expansion of vinylic cyclobutanols to obtain the corresponding 2-methylenecyclopentan-1-ones based on Pd catalyzed reports found in literature (Scheme 48 and Scheme 67).[186,187]

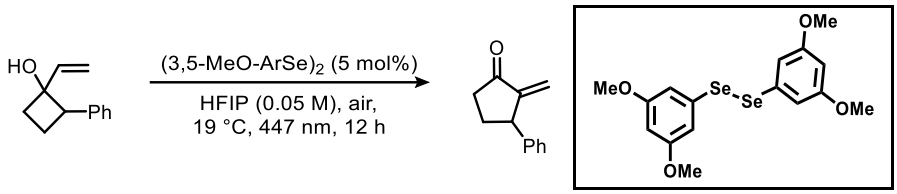


123 **124**

Scheme 67: Pd catalyzed ring expansion of vinyl cyclobutanols **123**.[186,187]

4.2.1. Development of non-stereoselective reaction conditions

Using 2-phenyl-1-vinylcyclobutan-1-ol (**163a**) as starting material in combination with various diselenide-catalysts and TAPT, project collaborators found out that most diselenide catalysts deliver good to excellent yields if the reaction is performed in HIFP as solvent. Best results however were obtained when using $(3,5\text{-MeO-ArSe})_2$ as the diselenide catalyst under blue light (447 nm) irradiation (Scheme 68).[224]



163 **164 (87%)** **$(3,5\text{-MeO-ArSe})_2$**

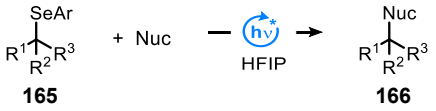
Scheme 68: Reaction conditions for the non-selective ring expansion reaction of vinyl cyclobutanols. Only NMR yield reported.[224]

The most intriguing revelation of the optimization process was that the initial reaction conditions included TAPT as photocatalyst which was later on prove to be unessential to drive the reaction to excellent yields and therefore the reaction was screened again to manifest this outcome.[224]

With this insight, the question about the actual reaction progression was raised as these changes were no longer in accordance with the thus far postulated mechanism (Scheme 23). Although the explicit reaction mechanism for this developed transformation still under investigation at this point, colleagues within the working group have established a reactivity concept for both C–Se σ-bonds as well as Se–Se σ-bonds regarding direct excitation.[225]

The starting point for these investigations was based on the observation that upon irradiation with green light (528 nm) in HFIP as the reaction solvent, arylselenides **165** undergo a substitution

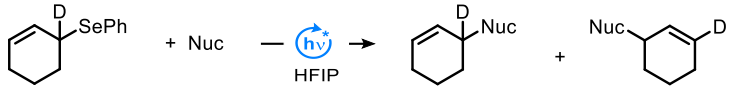
process with various tested nucleophiles (oxygen-, nitrogen-, sulfur- and carbon based) (Scheme 69).[225,226]



165 **166**

Scheme 69: Reaction concept for the light mediated subst. of arylselenides **165**.[225,226]

In this project the similar question arose, as to how the reaction is driven and what is the reactive species absorbing the light, being necessary for the reaction to occur. A first hint was obtained, when experimenting with selectively deuterated starting materials **165** in order to determine which substitution mechanism is active (S_N2 v.s S_N2') by using (cyclohex-2-en-1-yl-1-d)(phenyl)selane (**167**) as starting material **165** (Scheme 70).

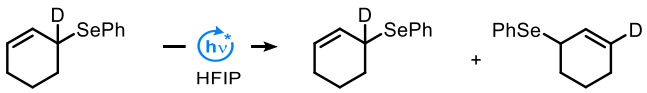


167 **168** **169**

Scheme 70: Experiment done the analyzed the site selectivity for the substitution reaction.

During these experiments, we discovered that the Se-shift already occurs when irradiating compound **167** without any nucleophile present (Figure 16), only in HFIP as the solvent (Table 11). As these observations indicated a reversible C–Se σ-bond cleavage, working group colleagues then continued these investigations to verify the thermal nature of the process,[227]fortified by the acidity of the reaction media and HFIP as solvent building a strong hydrogen bonding network.[225,226]

Table 11: Solvent dependent investigation into the D-shift



167 **167** **167-2**

Entry	Solvent [0.5 M]	Conditions	NMR Ratio [167] and [167-2]
1	**HFIP**	5 °C, 2 h, 528 nm (0.7 mA)	54/46
2	**MeCN**	5 °C, 2 h, 528 nm (0.7 mA)	>10/1
3	**EtOH**	5 °C, 2 h, 528 nm (0.7 mA)	>10/1
4	**THF**	5 °C, 2 h, 528 nm (0.7 mA)	10/1
5	**EtOAc**	5 °C, 2 h, 528 nm (0.7 mA)	>10/1

Reactions were performed on a 0.50 mmol scale (75%-D in starting material) in a vial with screw cap (penetrated with cannulas for air exchange) in the given solvent and given concentration. The vial was irradiated with a green LED (528 nm, 0.7 mA) in the cooling block setup at 5 °C under air for 2 h. The ratio was determined using H^1 NMR spectroscopy and H^2 NMR spectroscopy.

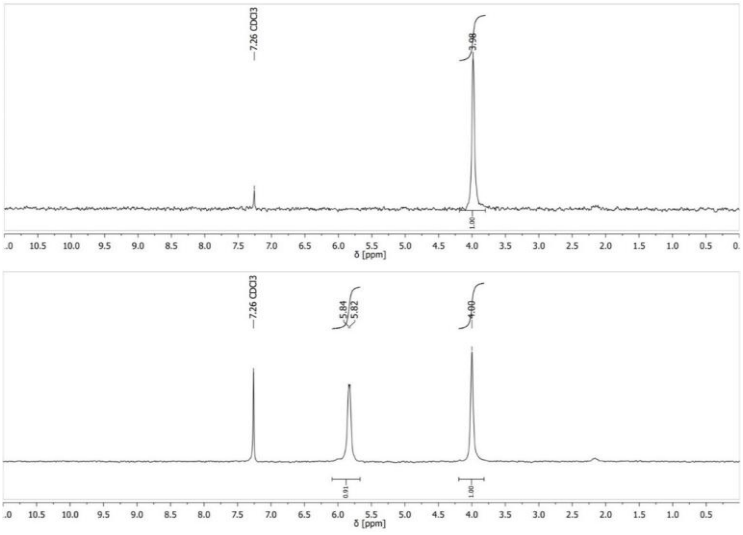


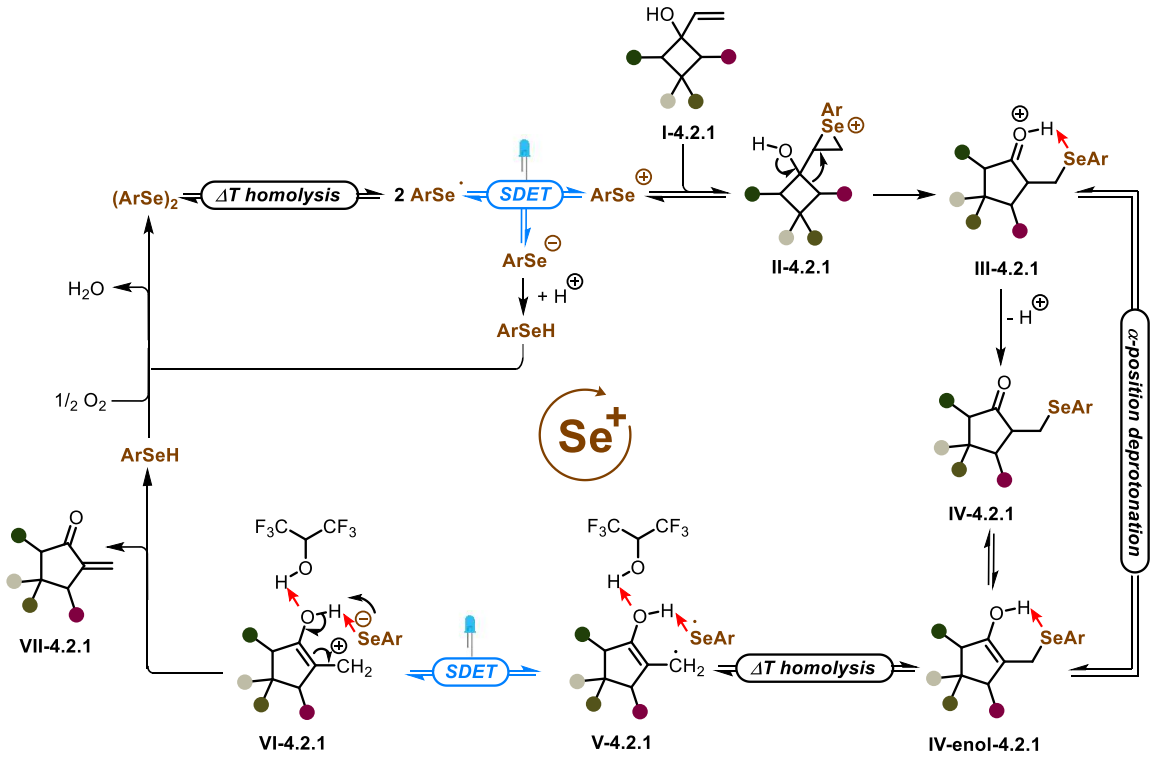
Figure 16: Comparison of the ^{2}H NMR of the starting material **167** before (upper) and after (lower) irradiation when performed in HFIP.

The continuing question then centered around the role of the irradiation, which was deemed necessary for the formation of the substitution products **168** and **169** but seemed to be irrelevant for the C–Se σ-bond cleavage. A first consideration was then the nature of the observed substitution reaction (Scheme 69) which was anticipated to be an ionic process rather than a radical one based on related literature.[228] As ionic species however are energetically not feasible under the thermal conditions due to the unpolar nature of the C–Se σ-bond,[229] a homolytic cleavage was postulated and confirmed by irradiation experiments with different wavelengths as well as transient absorption measurements and theoretical calculations, all indicating the incipient PhSe-radical as the major light absorber.[225,226] This led to the conclusion upon formation, the two radicals undergo a *SDET* (stimulated doublet-doublet electron transfer) where the excited PhSe-radical takes up an electron from the carbon radical, thereby forming two ionic species.[225,226] This transfer is mainly enabled by the caging effects of the solvent HFIP,[225,226,230] keeping both radicals in close proximity.[225,226] This results in the formation of a carbo cation and $PhSe^-$ which now allows for an ionic driven substitution process in accordance with related literature.[228]

To establish the possibility for a full selenium-π-acid catalytic cycle, working group colleagues then conducted an identical set of experiments to determine if analogous reactivity can be achieved by going from a C–Se to a Se–Se σ-bond. Fortunately, due to the lower energy of the Se–Se σ-bond said reactivity is even more facilitated in terms of a more distinct thermal bond homolysis even in less protic media and consecutive coincidental desymmetrization of the two PhSe-radicals by excitation and *SDET*.[225,226] In addition to that, colleagues established another, parallel occurring pathway based on the observation that the applied diselenides themselves act a light absorbers in the near UV region.[225,226] Furthermore, due to the likewise absorption capabilities of the resulting PhSe-radical and $PhSe^+$ the interconversion of both could be traced, whereas analogues experiments were not possible for the C–Se σ-bond reactivity due to the lack of absorption of the carbon-radical and the corresponding carbocation.[225,226] Consecutive transient absorption measurements

for the Se-Se σ-bond reactivity at the µs-timescale then revealed the presence of the $PhSe^+$ and the interconversion of the PhSe-radical to the $PhSe^+$ in the fs-timescale.[225,226] However, the concentration of both observed species in both timescales contradicted the reactivity progression established for the C–Se σ-bond, where due to the generation of the corresponding radical prior to excitation, a very low concentration of the excited state species was anticipated.[225,226] The cumulation of these results then led to the postulation that for the Se–Se σ-bond additionally the initial steps can occur in an inverse fashion compared to the C–Se σ-bond. At first $(PhSe)_2$ gets excited and then the bond homolysis occurs leading to two excited ("hot") PhSe-radicals which can then undergo desymmetrization via coincidental cooling of only one of the radicals, followed by a *SDET* to form $PhSe^+$ and $PhSe^-$.[225,226]

In analogy, we herein postulate similar reaction progression for the $(3,5\text{-MeO-ArSe})_2$ catalyst used in this project and anticipate further reactivity as a combination of reports described by Wu et al.[110] describing a 1,2-aryl migration utilizing stochiometric amount of a $PhSe^+$ source and Nishimura et al.,[186,187] developing the herein discussed ring expansion reaction using catalytic amount of a Pd-catalyst (Scheme 71).



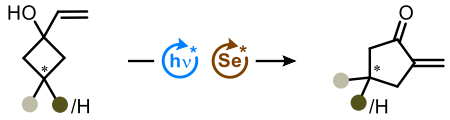
Scheme 71: Mechanistic concept for the developed ring expansion reaction.

Upon formation, the active species **$ArSe^+$** reacts according to the above described literature, firstly attacking the π-bond thus forming the seleniranium-ion **II-4.2.1**. In similar fashion to the Pd-catalysis, the 4-membered ring is then opening up and forming the 5-membered ring **III-4.2.1** after interaction with the seleniranium-ion **II-4.2.1**. The definite nature of this rearrangement however is still under investigation and will be discussed further based on our results in the reaction scope (*vide*

infra). Having formed selenofunctionalized product **IV-4.2.1** we further on postulate that a significant portion is converted into its corresponding enol-form **IV-enol-4.2.1** resulting in an allylic positioned ArSe-group similar to the structural motifs used in the substitution project (Scheme 70).[231] Based on this structure we also hypothesized further reactivity according to the previous discussed mechanistic postulations regarding the thermal homolysis of the Se–C σ-bond and the consecutive *SDET* furnishing **ArSe**$^{\cdot}$ and a carbo-cation in structure **VI-4.2.1** (Scheme 71). **ArSe**$^{\cdot}$ is then abstracting the proton from the H-bond interaction thereby forming the target product **VII-4.2.1** after π-bond isomerization and one equivalent of **ArSeH**. The latter then recombines with another equivalent under oxidative conditions (O_2 from the atmosphere) to reform the catalyst precursor **$(ArSe)_2$** and restart the cycle.

4.2.2. Development of a stereoselective reaction process

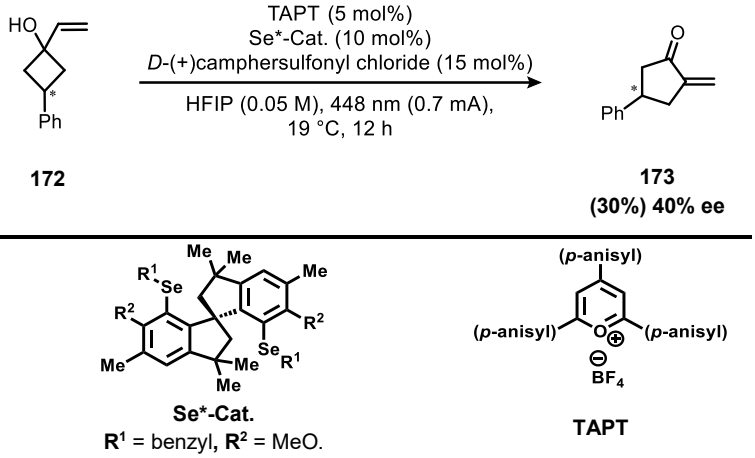
Having established a non-stereoselective reaction process, the primary focus then fell onto the development of a chiral version, starting with most simple 3-subsitutited and 3,3-disubstituted vinyl cyclobutanols **170** (Scheme 72).



170 **171**

Scheme 72: Reaction concept for the chiral ring expansion reaction.

In initial experiments performed by collaborators within our working group it was first confirmed that in contrast to the non-stereoselective process, a photocatalyst was necessary to observe more than 50% conversion of the starting material **170**. Furthermore, even when using a photocatalyst, these experiments could neither report good yields nor good *ee*, with 40% ee at 30% product formation, being the best results (Scheme 73).



172

173
(30%) 40% ee

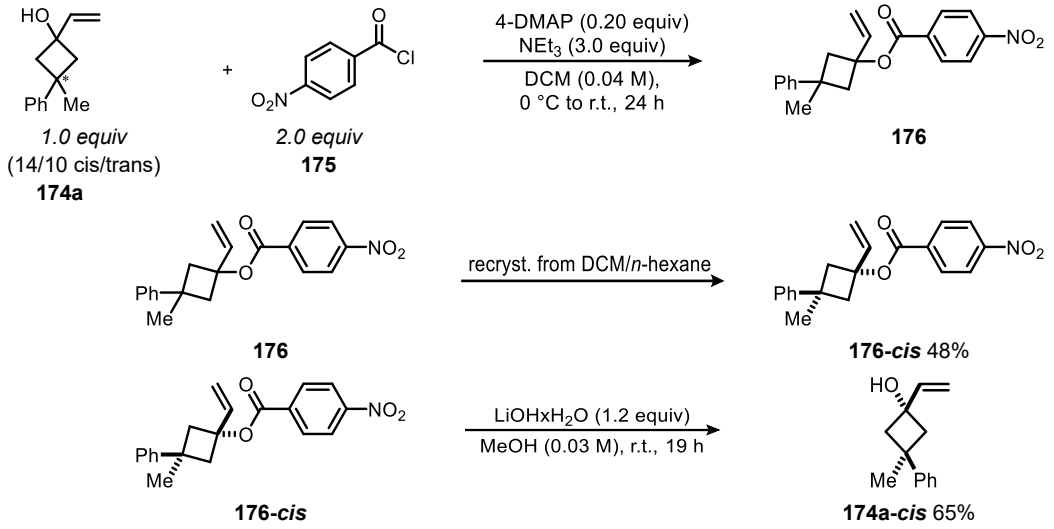
Se*-Cat.
R^1 = benzyl, **R^2** = MeO.

TAPT

Scheme 73: Thus far best reaction conditions for the stereoselective ring expansion reaction. Only NMR yield reported.

During these investigations, we envisioned that a potential issue with the desired setup lies within the starting material **172**, being composed of a mixture of two diastereomers and would therefore lead to substrate control complications with the provided chiral selenium catalyst. As a consequence, a single chiral catalyst could generate both product enantiomers **173** in ratios resembling the dr value of the starting material **172** or productive conversion of one diastereomer would shut down entirely due to a miss-matched case. In the worst case, this could imply that our chiral selenium catalyst is miss-matched with the major diastereomer of our starting material, leaving us with diminished product formation in addition to only poor *ee*-values.

Attempting to improve that situation we set out to find means of diastereomeric resolution before attempting further screening experiments. For reasons of quick access, we switched to the synthesized vinyl cyclobutanol **174a** (procedure discussed in the following chapter) and found a suitable resolution procedure by converting it to the nitrobenzoic acid ester **176** (Scheme 74).[232]



Scheme 74: Reaction sequence for the diastereomeric resolution of alcohol **174a.** Isolated yields reported.

The diastereomers of nitrobenzoic acid ester **176** were then separated by recrystallization of the crude material in DCM by addition of *n*-hexane under reduced temperature (stored in fridge) and 2D NOESY spectroscopy then aided in assigning the relative stereochemistry (Figure 17). Considering the diastereotopic nature of the protons located at the cyclobutane ring, the corresponding signals can be used to determine the relative configuration of the other substituents. Analyzing of the cross relations obtained in the 2D NOESY spectra from our recrystallized material (Figure 17), we were fortunate to observe a clear separation for diastereotopic proton pairs (H^2 and H^3) and furthermore, also the respective coupling to the Me-group and olefin. Concluding that the Me-group only couples to proton H^3 and the olefin only to H^2 was enough evidence for us to assign the relative stereochemistry with the Me-group and the olefin being on different orientations regarding the cyclobutane plane (declared as *cis*-isomer). Base mediated hydrolysis of the ester **176-*cis*** then delivered in the vinylic cyclobutanol **174a-*cis***, without the loss of stereo information (confirmed by 2D NOESY spectroscopy of the alcohol **174a-*cis***, c.f. Experimental Section).[233]

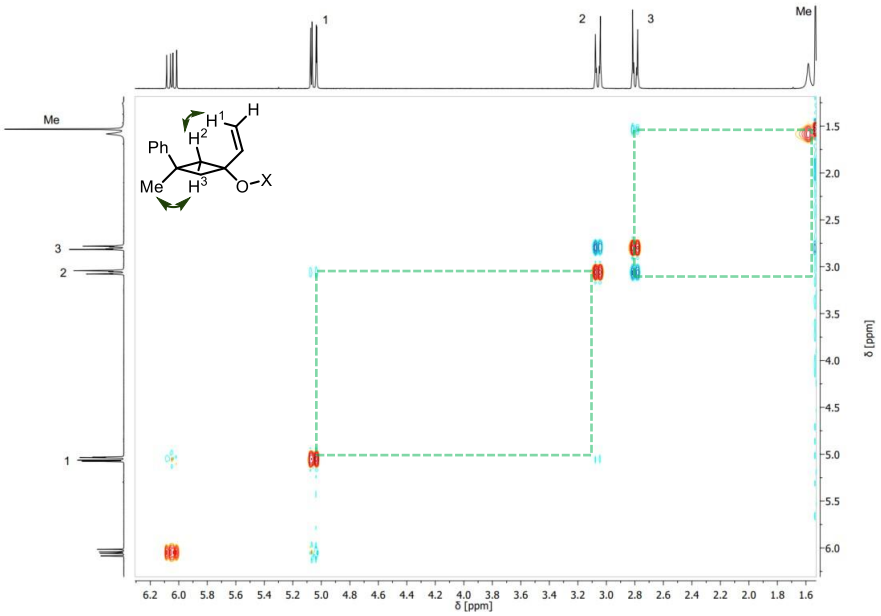
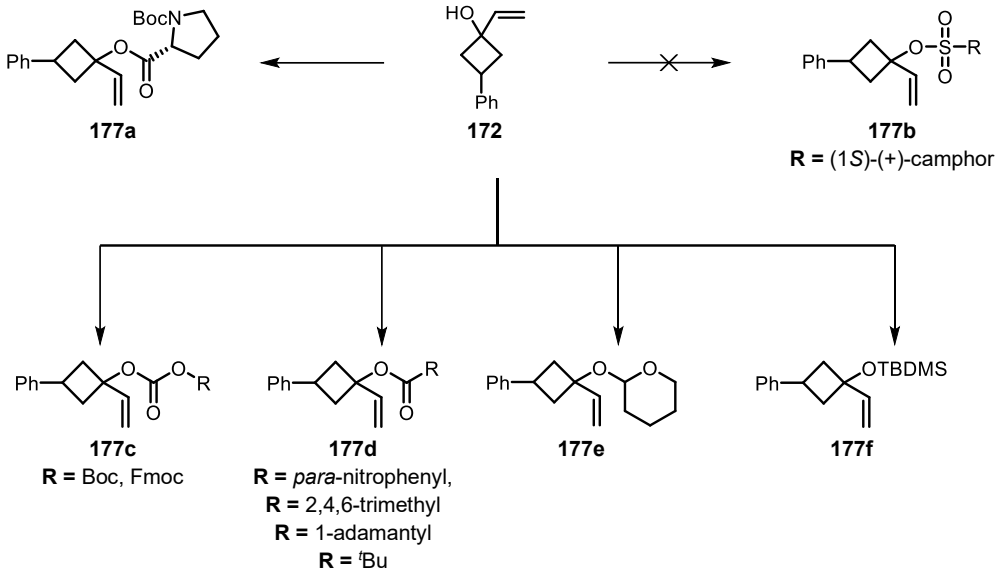


Figure 17: Excerpt of the NOESY spectra for the diastereomeric resolution of **176**.

Unfortunately, clean isolation of the other diastereomer was not successful, as the recrystallization procedure did not completely separate the isomers but rather stepwise enriched one isomer until a certain point where selective crystallization was no longer possible. Furthermore, the above performed resolution procedure showed no effect when applied to substrate **172**, so we had to look for other methods, with a preference for resolution by chromatography to allow easy access to both diastereomers. To do so we tried a number of different substituents on the oxygen atom of the hydroxy group allowing for easy removal after potential separation. Among the diversifications chosen were carbonate moieties **177c** such as Boc- and Fmoc- or different sterically bulky esters **177d** such as the beforehand mentioned *para*-nitrobenzoic acid ester or 2,4,6-trimethylbenzoic acid ester (Scheme 75). Apart from increasing the bulkiness in hope of better separation we also thought of using ways to affect the overall polarity of each diastereomer (to varying extents) by implementing ether functions such as a DHP ether **177e** or a silyl ether **177f**. At last, we also tried to apply reagent controlled reactivity in utilizing chiral reagents such as (1S)-(+)-10-camphorsulfonyl chloride or (L)-*N*-Boc-proline to selectively react with only one of the given diastereomers (structures **177a** and **177b**).

Synthesis of 2-methylenecyclopentan-1-ones Development of a stereoselective reaction process

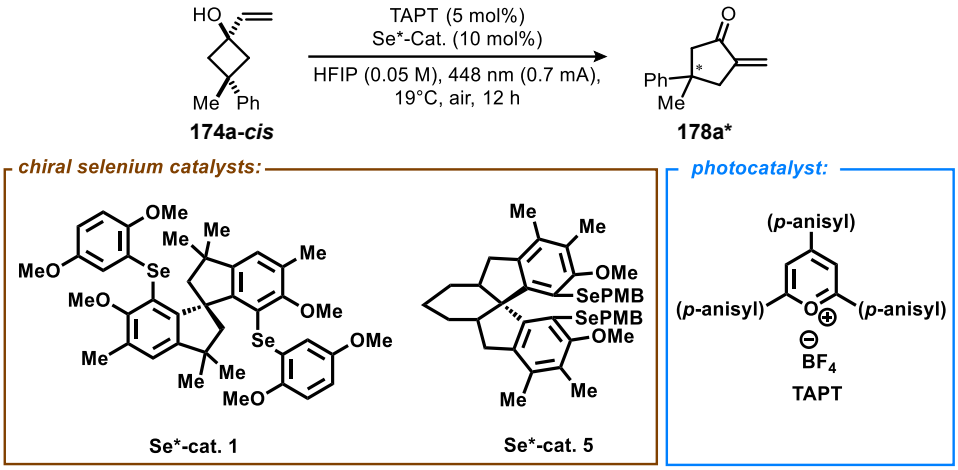


Scheme 75: Attempted diversification of **172** for diastereomeric resolution. **OTBDMS =** *tert*-butyldimethylsilylether.

To our disappointment, none of the above shown reactions allowed for separation of diastereomers by column chromatography (indicated by TLC measurements after confirmed product formation by crude NMR analysis) and thus no isolations were performed. The only exception to this was the silyl ether **177f**, in which case two independent spots were observed on TLC but its unpolar nature made clean separation impractical by the available chromatographic methods.

Before attempting further means of resolution, we decided that it might be more strategic to test if the purified diastereomer **174a-*cis*** results in an improved outcome or if we face further complications by a miss-match with given catalyst. The choice of chiral catalysts was at this point mainly affected by availability and therefore, we only could use the second best catalyst **Se*-Cat. 1**, from previous screenings as well as **Se*-Cat. 5**, which was not used before. Furthermore, we abstained from utilizing further additives to get a clean impression on the effect of diastereomeric purity on the chiral outcome without other implications (Table 12).

Table 12: Overview of the chiral screening using the isolated diastereomer **174a-*cis***



Entry	Se-Cat. [5.0 mol%]	Additive	NMR Yield	Conversion	*ee*
1	**Se*-Cat. 1**	-	54%	87%	49%
2	**Se*-Cat. 5**	-	79%	89%	racemic
3[a)]	**$(3,5\text{-MeO-ArSe})_2$**	-	97%	100%	racemic

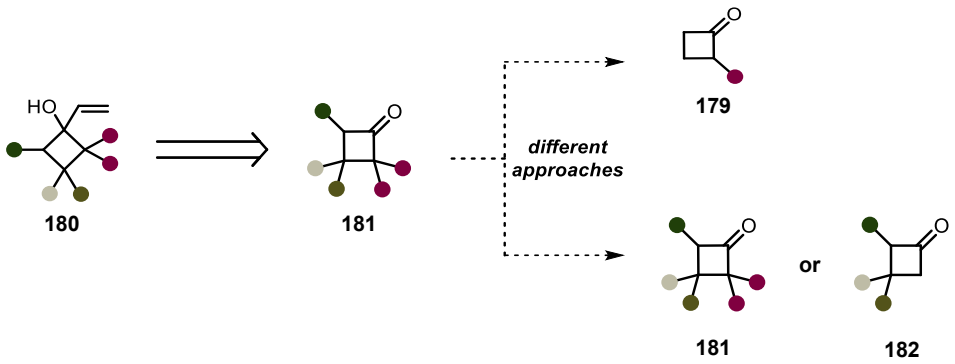
Reactions were performed on a 0.50 mmol scale in a vial with screw cap (penetrated with cannulas for air exchange). The vial was irradiated with a blue LED (448 nm, 0.7 mA) in the cooling block setup at 19 °C under air for 12 h. NMR yields were determined using 1,3-dinitrobenzene as internal standard. a) racemic reaction protocol *vide infra*.

Whereas **Se*-cat. 5** showed no stereoinduction at all, arguably a significant increase in the *ee*-value is observed when using **Se*-cat. 1**, where only 20% *ee* were obtained in previous screenings (Scheme 73). However, one cannot neglect the fact that the screening substrates differ in both cases what we also postulated to have an impact on the outcome regarding the *ee* value. Furthermore, these results included no definite answer about whether the interactions between our diastereomer **174a-*cis*** and the used enantiomer of the chiral catalyst favor a reaction or not (matched vs. miss-matched). To do so, we would need to have access to the other diastereomer of compound **174a-*cis*** or the other enantiomer of the tested chiral selenium catalysts, both of which were not practically feasible and we therefore decided to stop investing in this reaction and continued with the formation of the reaction scope for the achiral concept.

4.2.3. Synthesis of the starting materials

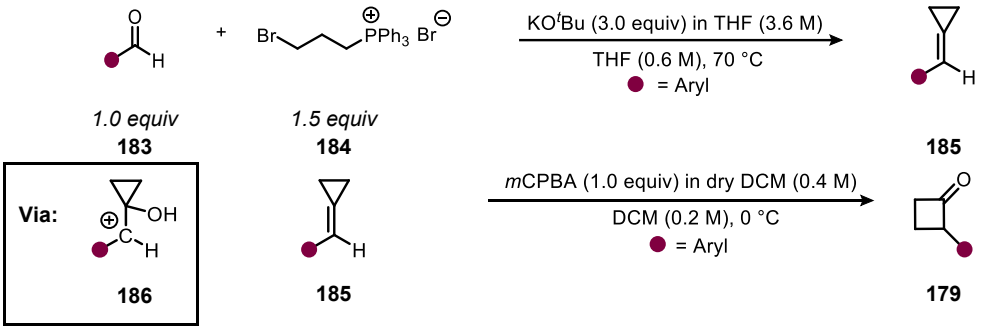
Regarding the substrate synthesis, we early on determined, that a Grignard reaction would be most suitable to generate the allylic alcohol moiety, which had the consequence that we needed to find ways to synthesize different substituted cyclobutanones **181** as precursor materials. As no general procedure allowed for a flexible synthesis of cyclobutanones **181** with different substitution pattern, individual procedures had to be used. Overall synthetic protocols allowing for multiple substitution (structure **181** and **182**) were used, in combination with two procedures allowing for the selective synthesis of cyclobutanones being substituted in the α-position (structure **179** in Scheme 76). The

last concept also aimed at the selective insertion of further functional groups in an existing cyclobutanone skeleton.



Scheme 76: General retrosynthetic analysis for the synthesis of the vinyl cyclobutanols **180**.

In accordance with the screening experiments and the thereby used starting material **163**, the first synthetic protocols applied allowed for the selective synthesis of α-substituted cyclobutanones **179**. Project collaborators obtained these type of substitution patterns based on reports by Ai et al. in a two-step procedure consisting of a Wittig reaction with consecutive epoxidation reaction.[234] In the first step, a commercially available arylated aldehyde **183** is treated with (3-bromopropyl)triphenylphosphonium bromide **184**, delivering the cyclopropylidene **185** after elimination of the bromide by intramolecular attack of the π-bond (Scheme 77).[234]

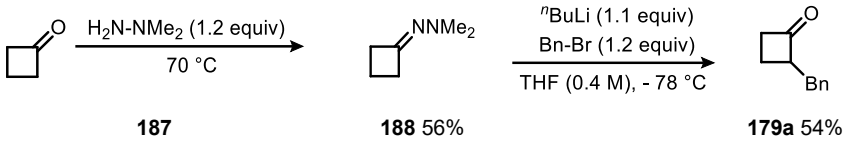


Scheme 77: Overview of the synthesis of α-substituted cyclobutanones **179** with intermediate cation **186**. Reactions were performed by MSc. Daniela Fritsch.[235]

After isolation, these cyclopropylidenes **185** were then epoxidized by treatment with *m*CPBA predissolved in dry DCM (Scheme 77), causing the formed spirocyclic intermediate[236] to open up and rearrange to the desired α-substituted cyclobutanone **179**.[234] Applying this concept, project collaborators were able to synthesize two different substituted cyclobutanones **179** (69% and 98% isolated yields).[224,235]

An apparent limitation of the presented conditions resided within the requirement for a substitution pattern, stabilizing formed cation species **186** to allow for the opening of the epoxide (Scheme 77) which in the cases of non-stabilized alternative does not occur without harsh acidic treatment.[236] However, we used a different method to introduce a non-aromatic substituent in the α-position,

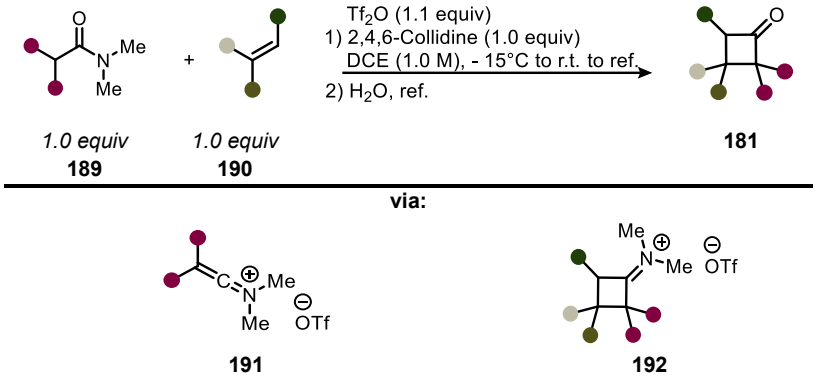
reported by Wu et al.[237] composed of a two-step procedure selectively inserting a benzyl group in otherwise unfunctionalized cyclobutanone (**187**) (Scheme 78).



187 **188** 56% **179a** 54%

Scheme 78: Reaction sequence as proposed by Wu et al.[237] Isolated yields reported.

As reactivity for the nucleophilic attack of Bn-Br is based on enol chemistry, the cyclobutanone (**187**) had to be converted into the corresponding hydrazine **188** as no reactivity was observed otherwise. Moving on to syntheses allowing for different substitutional patterns, the first successful concept was a reaction using *N,N*-dimethylacetamide(-derivatives) **189** under harsh acidic conditions (Scheme 79).[238]



Scheme 79: Acidic mediated [2+2]-cycloaddition reaction and relevant intermediates.

The initial treatment of *N,N*-dimethylacetamide **189** with Tf_2O at temperatures below 0 °C results in the formation of ketiminium-ion **191** (Scheme 79) by water elimination which then undergoes a [2+2]-cycloaddition with the consecutively added alkene **190**.[238] The in parallel added base (2,4,6-collidine) neutralizes the acid and in a second step, the crude material is refluxed with water to hydrolyze the formed iminium-ion **192** to ketone **181**. By applying this reaction template, we were able to observe product formation, even with the prospect of obtaining fully substituted cyclobutanone **181** motifs, depending on the choice of the corresponding acetamide derivative **189**. Overall 8 substrates including the precursor to the vinylic alcohol **174a**, were synthesized by this protocol whereas 7 of these (including substrates with full substitution motif) were contributed by project collaborators.[224,235]

On the downside, the practical application of this template came with severe drawbacks especially regarding selectivity, as the regioselectivity of the cycloaddition is solely determined by steric demand of the used acetamide **189**, which results in noticeable formation of constitutional isomers when using simple *N,N*-dimethylacetamide (Figure 18). A separation of these isomers turned out

to be impossible in some cases or resulted in a tremendous loss of material, therefore resulting in low isolated yields.

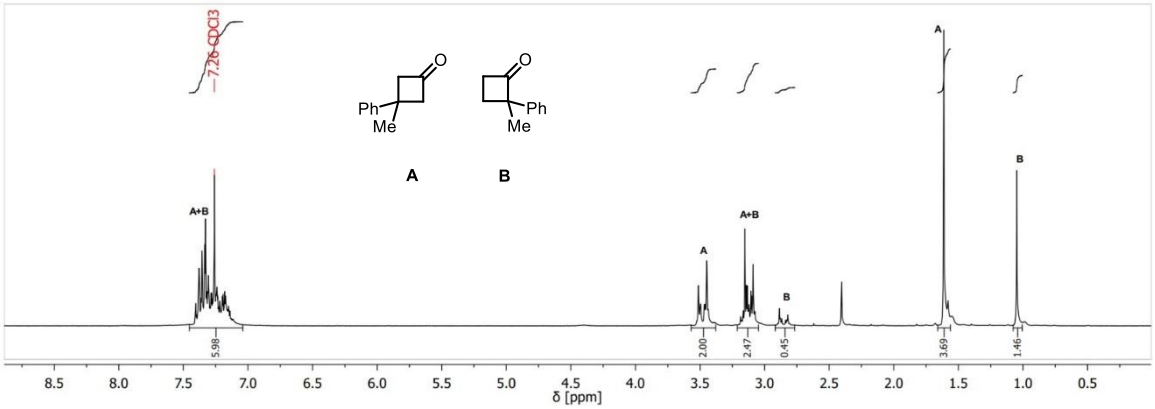


Figure 18: ^{1}H NMR spectra of an incomplete separated mixture of constitutional isomers **A** and **B**.

Another drawback was the side product formation originating from the acidic conditions, causing π-bond isomerization prior to the cyclization process. This rendered the method unapplicable for alkenes which could undergo isomerization to more stable configurations such as allylbenzene derivatives or even allylcyclopentanes. An exemplary case was the desired transformation of 2,3-dimethylbut-1-ene to 3-isopropyl-3-methylcyclobutan-1-one (**A** in Figure 19), where after multiple isolation attempts, 2,2,3,3-tetramethylcyclobutan-1-one (**B** in Figure 19) remained as an impurity, obtained by isomerization of the starting alkene.

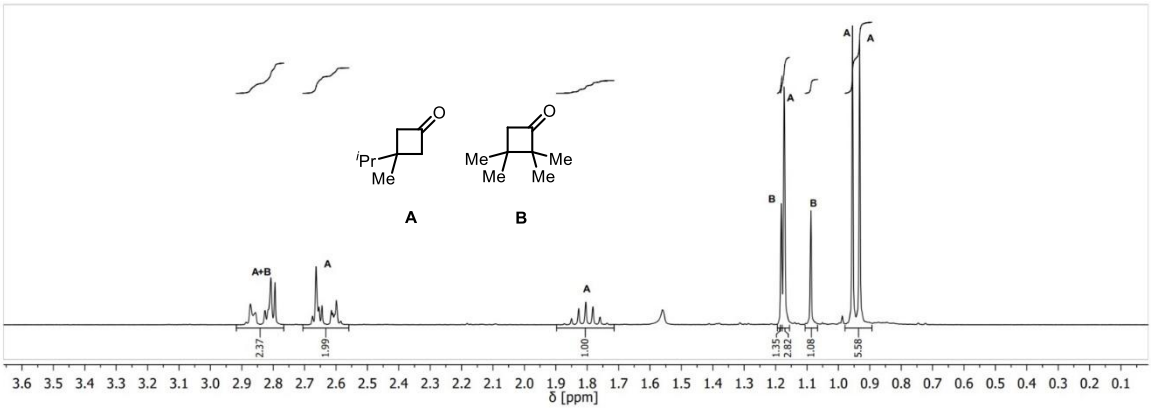
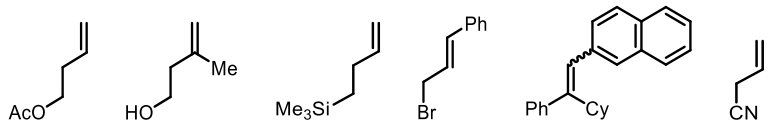


Figure 19: Excerpt of the ^{1}H NMR spectra of the constitutional isomers obtained in the same reaction due to alkene isomerization.

Apart from these observed selectivity issues, the method also remained unsuccessful for the conversion of alkenes baring functional groups such as esters **190a**, silyl groups **190c**, free OH-groups **190b**, nitriles **190f**, free alkyl halides **190d** and conjugated π-bonds between two aromatic systems **190e** (Figure 20).

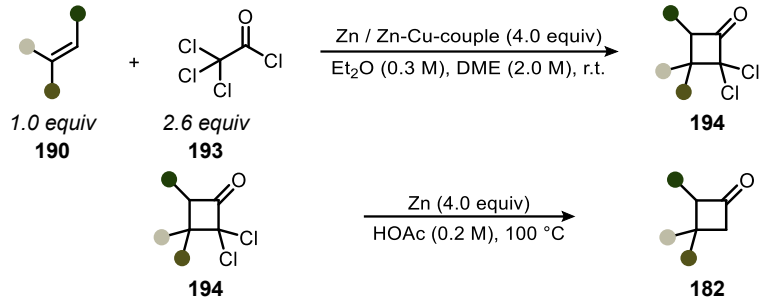
Synthesis of 2-methylenecyclopentan-1-ones Synthesis of the starting materials



190a **190b** **190c** **190d** **190e** **190f**

Figure 20: Excerpt of incompatible alkenes in the acid mediated [2+2]-cycloaddition reaction.

Based on these circumstances we searched for alternative reaction templates and further progress was made in the discovery of a patent describing a reaction protocol using 2,2,2-trichloroacetyl chloride (**193**) as reaction partner for the alkenes. [239] By dehalogenation of said acid chloride by a *SET* from the applied elemental zinc (or a zinc-copper alloy), a dichloroketene is formed (analogous to the ketiminium-ion **191**) which then engages in a [2+2]-cycloaddition forming the intermediate **194** (Scheme 80).[240] $POCl_3$ or 1,2-dimethoxyethane (DME) are common found additives to on one side remove the $ZnCl_2$ byproduct and thus prevent side reactivity as well as on the other side enabling the transformation for sterically demanding alkenes **190**.[241] As the corresponding authors however observed superior results with DME than with $POCl_3$ they remained with said additive in co-solvent quantities (Scheme 80).[239]



1.0 equiv **190** + *2.6 equiv* **193** → **194**

194 → **182**

Scheme 80: Reaction template based on the work patented by the Novartis AG.[239]

Although we were able to confirm the formation the dichlorinated cyclobutanones **194** their clean isolation remained unsuccessful in the multiple attempts and we therefore chose to utilize the crude material after phase separation and concentration without further cleanup processes. Due to this decision, a vast amount of DME remained in the crude material (Figure 21) and thus consecutive reaction could only be set up with approximated net weight of reagents, negatively affecting the overall outcome.

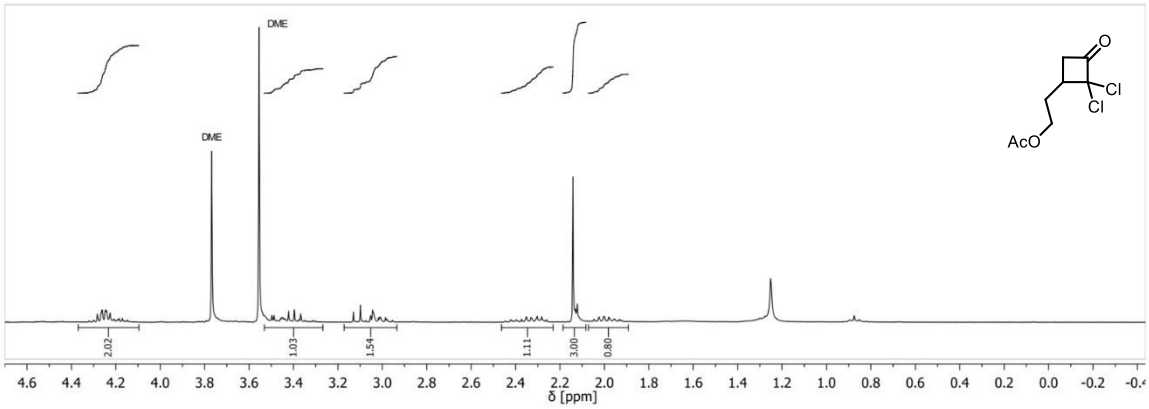
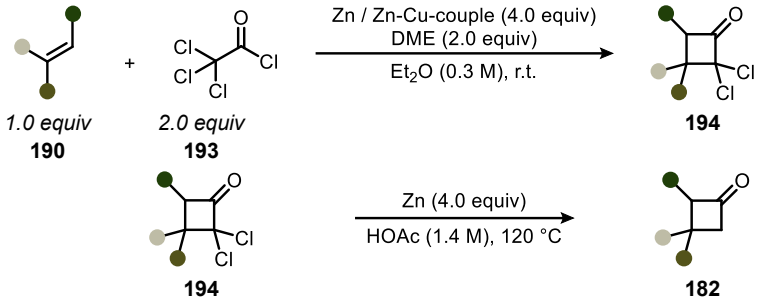


Figure 21: NMR excerpt of the shown dichlorocyclobutanone showing the remaining DME after phase extraction and concentration.

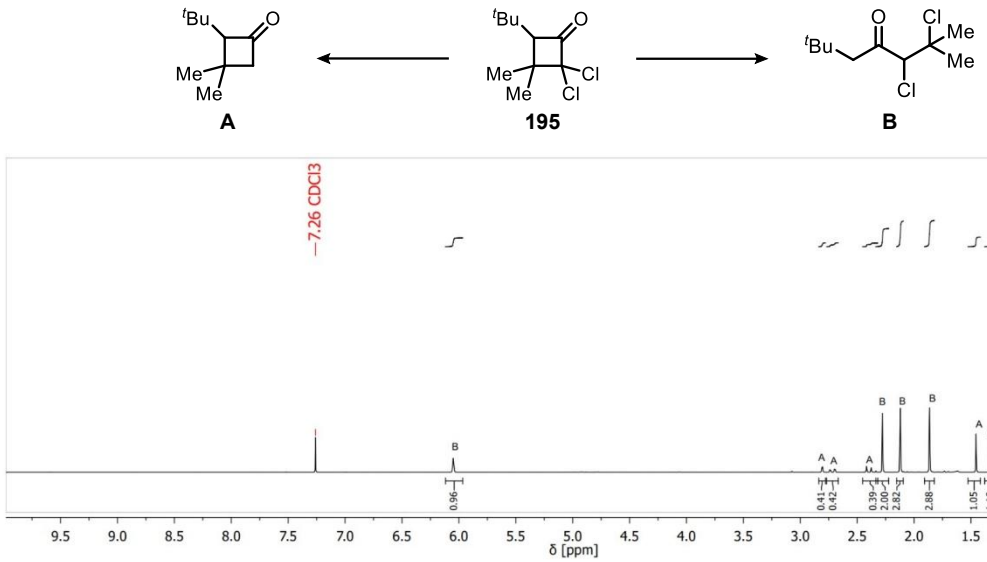
As we further envisioned an impact on reactivity by the remaining DME we updated the initial reaction conditions based on the literature reported by de Blieck et al., reducing the amount of DME from a co-solvent to two equivalents (Scheme 81).[242]



Scheme 81: Reaction protocol reported by de Blieck et al.[242]

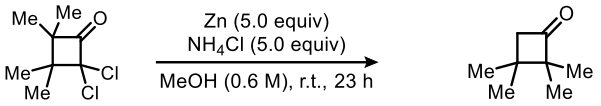
The dehalogenation step on the other side remained nearly unchanged and generally achieved by refluxation of the dichlorinated cyclobutanones **194**, in acetic acid, enabling a substitution of both chlorine atoms by protons delivered from the acetic media. Both applied protocols in general delivered acceptable outcomes with the mere difference that the conditions reported by de Blieck et al. offered improved practicality by using less amount of acetic acid, thus facilitating the workup protocol (Scheme 81). The only blockade that we however encountered during this reaction step was when either using a quaternary substituted alkene **190** (2,3-dimethylbut-2-ene) or an extremely sterically demanding alkene **190** (2,4,4-trimethylpent-2-ene), in which cases a ring opening between the substituents was postulated as a dominating side reaction based on NMR analysis.

Synthesis of 2-methylenecyclopentan-1-ones Synthesis of the starting materials



Scheme 82: Determined side reactivity for steric demanding dichlorocyclobutanone **194a** (top) and corresponding ^{1}H NMR of the mixture obtained after attempted purification by column chromatography (bottom).

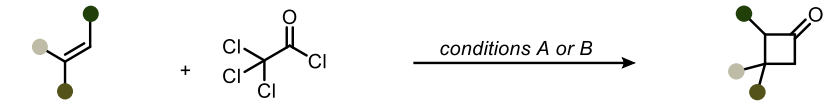
A practical solution was found and applied in the case of the 2,3-dimethylbut-2-ene, where less acidic conditions (reported by Chen et al.) where employed and allowed for the clean isolation of 2,2,3,3-tetramethylcyclobutan-1-one (**182b**) in 16% yield over two steps (Equation 4.4).[243]



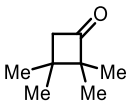
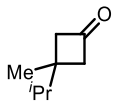
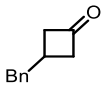
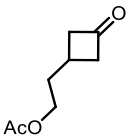
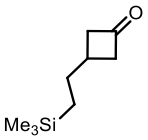
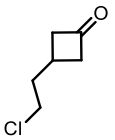
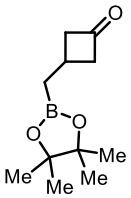
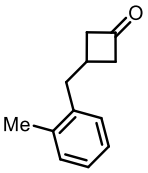
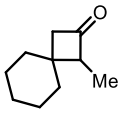
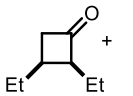
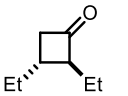
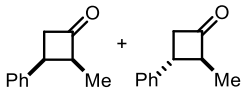
(4.4)

Complementing the results using acetamide derivatives **189** (Scheme 79) we now were able to obtain cyclobutanones **182**, bearing a multitude of functional groups such as esters **182e**, silyl ethers **182f**, halides **182g** and even boronic acids esters **182h**. In addition to that, this protocol also allowed us the synthesis of substrates **182c/d/i**, as well as multiple substituted motifs such as **182j-l**, where in the previous attempts (Scheme 79) selectivity issues as well as isomerization reactions prevented clean product formation (Table 13). However, even at this point, we were still interested in advancing the scope but again ran into limitations which we thought are based on the reaction mechanism itself rather than the synthetic procedure (Figure 22).

Table 13: Combined overview of the substrates generated using trichloroacetyl chloride **193**

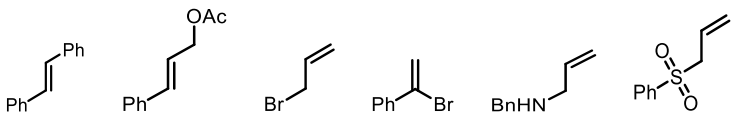


1.0 equiv **190** + *2.0 or 2.6 equiv* **193** → **182**

					
182b 16% conditions B	**182c** 24% conditions B	**182d** 47% conditions B	**182e** 37% conditions A	**182f** 74% conditions A	**182g** 28% conditions B
					
182h 6.0% conditions A	**182i** 35% conditions B	**182j** 43% conditions A	**182k** 43% 39:10 *cis/trans* conditions A		**182l** 16% 52:10 *cis/trans* conditions A

Conditions A correspond to the reaction protocol depictured in Scheme 80 and conditions B to the pathway depicture in Scheme 81. Isolated yields reported. dr values and relative configuration of given examples were determined by 2D NOESY spectroscopy if suitable signals could be identified.

As already discussed for the acidic mediated reaction (Scheme 79) also this procedure did not tolerate conjugated olefins, bridging two aromatic systems **190a**, possibly due to the extended delocalization making the alkene unreactive for the cycloaddition reaction. A similar hypothesis was attributed to the failure of the conversion of alkene **190g** in which case we have a push-pull system again extending the delocalization of the electron enough to prevent the [2+2]-cycloaddition (postulated to be similar for substrate **190k**). Apart from that, there were still a number of functional groups that were not tolerated such as protected amines **190j**, which only formed the corresponding amide with trichloroacetyl chloride (**193**) and bromine incorporated in the carbon scaffold, possibly due to side reactivity with the elemental zinc (Figure 22).

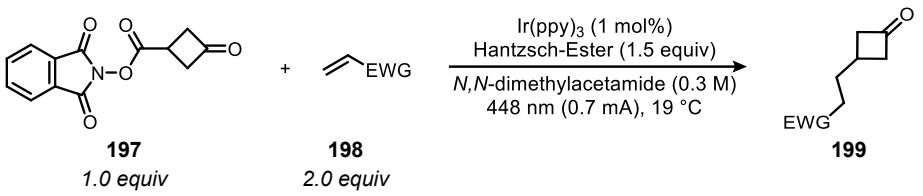


190a **190g** **190h** **190i** **190j** **190k**

Figure 22: List of unsuccessful alkenes in the reaction protocol explained in Scheme 80 and Scheme 81.

To further broaden the reaction scope, a synthetic protocol using photoreductive decarboxylation (Scheme 83) with 1,3-dioxoisoindolin-2-yl 3-oxocyclobutane-1-carboxylate (**197**) in combination with an electron poor alkene **198** was developed based on related literature.[244] Upon reduction, the ester moiety is eliminated by a decarboxylation process leaving a secondary C-centered radical which then attacks the electron poor alkene **198**. The applied Hantzsch-Ester serves a dual purpose by regenerating the photocatalyst as well as delivering an H-atom to conclude the product

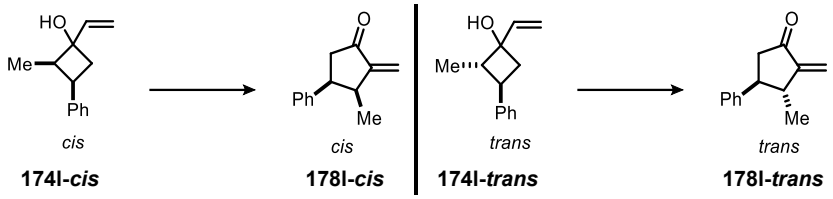
formation and thereby achieving further incorporation of functional groups in the existing cyclobutanone moiety **199**.[245]



Scheme 83: Photoreductive decarboxylation procedure developed by a Dr. Tao Lei.[224]

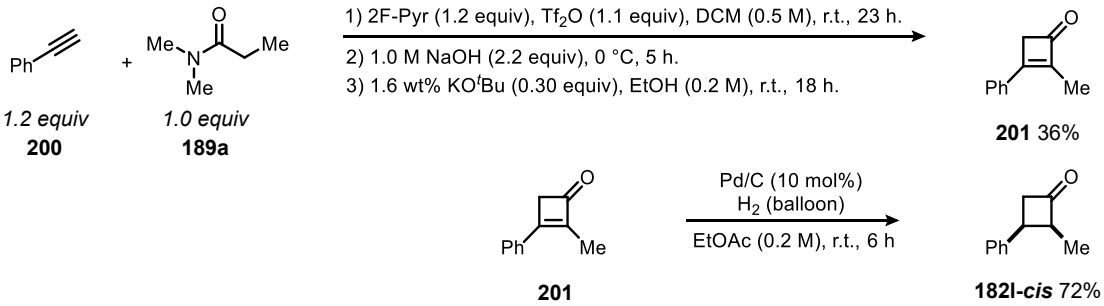
This protocol was then attempted with three different electron poor alkenes **198**, of which only (vinylsulfonyl)benzene resulted in sufficient reaction yield (27%) to be of further use. Acrylonitrile and 4,4,5,5-tetramethyl-2-vinyl-1,3,2-dioxaborolane both resulted in inferior yields and major isolation issues, which caused us to neglect them for further consideration.

One last thought that had to be realized was the stereospecific synthesis of each diastereomer of cyclobutanone **182l** aimed to prove the stereoretention of the ring enlargement procedure (Scheme 84).



Scheme 84: Experiments to prove stereoretention of the ring expansion reaction.

Whereas the *trans*-diastereomer **174l-*trans*** was only obtained after diastereomeric resolution (analogous to Scheme 74), the *cis*-diastereomer could be obtained by a linear three step procedure starting from phenylacetylene (**200**) (Scheme 85).[246] The first step is mechanistically equivalent to the concept already discussed above (Scheme 79), with the exception that a triple bond is present and in order to achieve the desired configuration of the π-bond in product **201**, the crude material had to be additionally submitted to basic conditions (step 3), allowing for isomerization to occur.[246]



Scheme 85: Reaction protocol for the stereoselective synthesis of **182l-*cis***.[246] **2F-Pyr =** 2-fluoropyridine.

The second part was then a simple *cis*-selective hydrogenation using Pd on activated charcoal under an atmosphere of H_2 gas.[246] Stereochemistry was then confirmed by comparison with the previously obtained mixture **182l** (Figure 23) as well 2D NOESY spectroscopy (Figure 24).

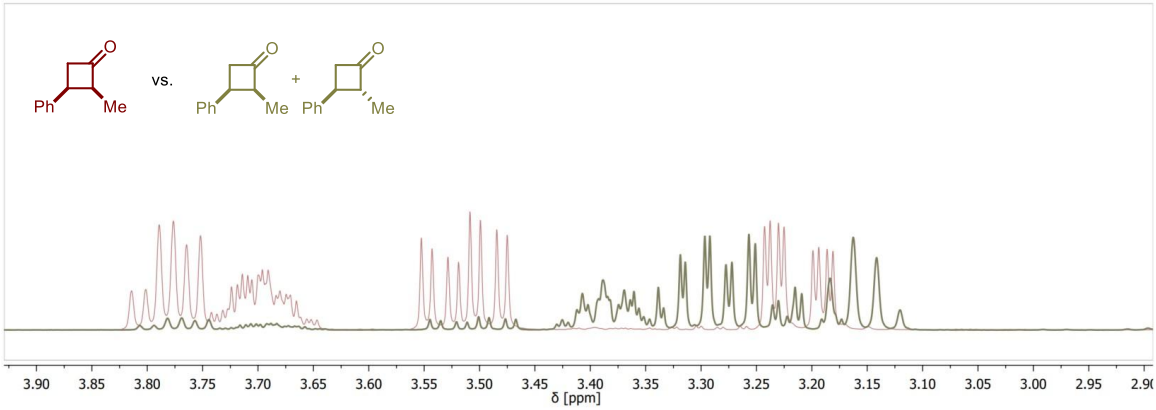


Figure 23: NMR overlap between the mixture of diastereomers **182l** (olive) and the isolated diastereomer **182l-*cis*** (maroon).

The spectral overlap clearly shows that the minor fraction obtained in the mixture translates to the sole component obtained in the reaction pathway described in Scheme 85 and the recorded NOESY spectra also conveys the same information. Based on the assignment of H^2 having the only cross coupling with the Me-group, on can identify identically strong signal to the proton $H^{1'}$ and H^3 which were individually assigned by the coupling constants and the coupling pattern (H^1 and $H^{1'}$ each include a coupling constant of 17.6 Hz which is an indication for geminal coupling).[247] This visible correlation between the protons $H^{1'}$, H^2 and H^3 for us validated the previous assigned *cis*-configuration as it was also claimed in the corresponding literature.[246]

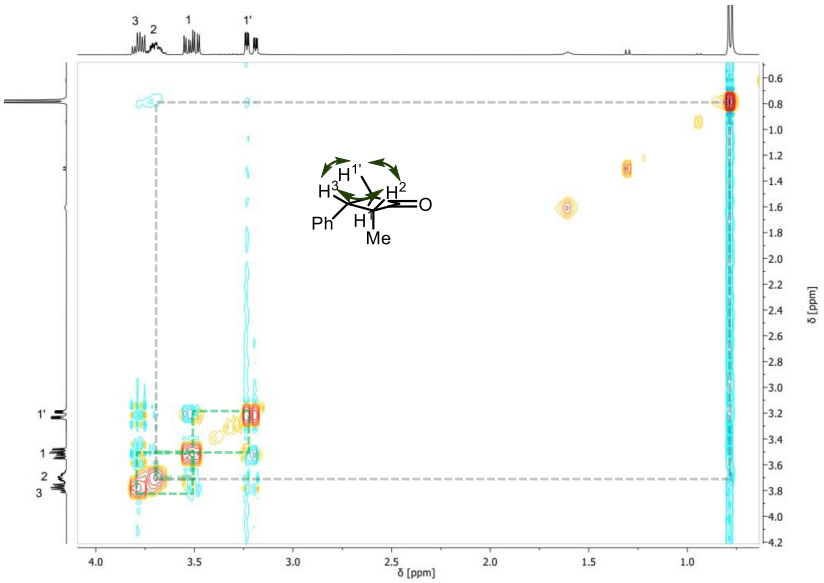
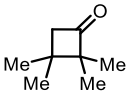
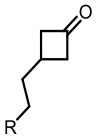
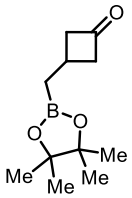
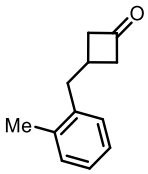
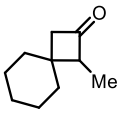
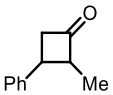
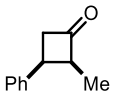


Figure 24: NOESY excerpt for the cyclobutanone **182l-*cis*** only the cross couplings of interest where highlighted (grey and green).

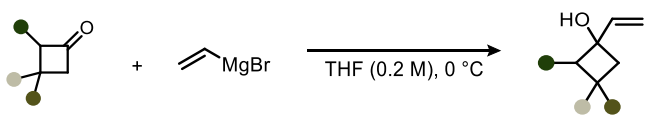
Concluding the synthesis of cyclobutanones **182**, a joined overview of all obtained substrate motifs is listed below, including carbon scaffolds selectively substituted in either 2-(substrates **179a**) or 3-position **182d-l** also including geminal 3,3-disubstitutional motifs (substrates **182a/c**). Furthermore, also a number of different functional groups ranging from pinacolboranes **182h** over esters **182e**, silyl ethers **182f** to sulfones **199a** and halide substituted carbon moieties **182g** could be included with an elevated interest being substrates substituted at multiple positions (**182b/j/k/l/l-*cis***) as we expected site selectivity in the developed ring expansion reaction. As this selectivity is determined by the mechanistic nature of the rearrangement reaction, further mechanistical insight could be obtained this way as well as further value when compared with existing literature (chapter 2.6.1).

Table 14: Complete overview of all synthesized cyclobutanones **182**

Versatile starting materials	*multiple conditions* → **182**				
					
179a 54%	**182b** 16%	**182a** 14% **R¹ =** Me, **R² =** Ph **182c** 24%, **R¹=** Me, **R² =** ^{i}Pr	**182d** 47%	**182e** 74%, **R =** OAc **182f** 37%, **R =** $SiMe_3$ **182g** 28%, **R =** Cl **199a** 27%, **R =** SO_2Ph	**182h** 6%
					
182i 35%	**182j** 43%	**182k** 43% 39:10 *cis*/*trans*	**182l** 16% 52:10 *cis*/*trans*	**182l-*cis*** 72%	

Reported isolated yields correspond to the last step in the respective reaction procedure. dr values and relative configuration of given examples were determined by 2D NOESY spectroscopy if suitable signals could be identified (for explicit details see experimental section).

The final step in the in the starting material synthesis then merged in a Grignard reaction with commercially available vinylmagnesium bromide (**202**) as mentioned at the beginning of this chapter (Scheme 86).[248]

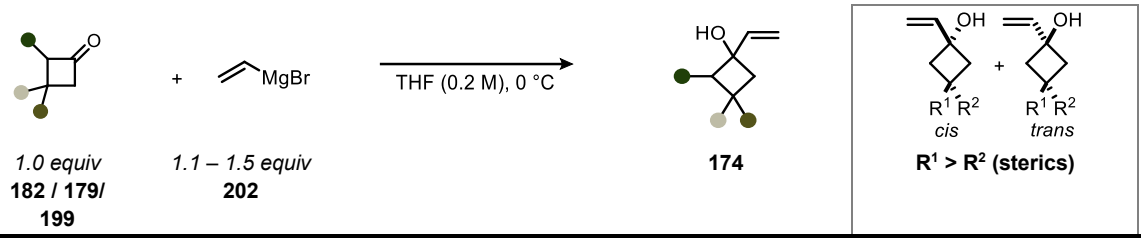


1.0 equiv **182** *1.1 – 1.5 equiv* **202** **174**

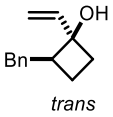
Scheme 86: Reaction equation for the Grignard reaction.[248]

In contrast to the synthesis of the cyclobutanones, the Grignard reaction was applicable to all the above listed substrates (Table 14) and additional commercially available compounds, without complications (Table 15). On the other side, the Grignard reaction introduced another stereocenter, which lead to analytical difficulties as most substrates were isolated in a set of diastereomers (with their corresponding enantiomers). Nonetheless, we attempted an analysis in each case, leading to the conclusion, that one might declare a preference for *trans*-configuration between the olefin and the substituent with the highest priority (based on steric demand) in β-position. This declaration is also valid when analyzing the α-substituted substrate **174q**, in which cases only *trans*-configurated product was obtained and could be identified as such by 2D NOESY analysis (c.f. experimental section) (Table 15). This also matched our expectations as we anticipated the larger substituents to avoid each other, therefore to a certain extent directing the attack of the Grignard reagent on the carbonyl group. On the contrary, the overall minimization of the dipole moment within the structure favors an alignment in which the present hydroxy group and a substituent $\mathbf{R^1}$ with polarizing functional groups (e.g. substrates **174e/p/o**) point in opposite directions in the strained 4-membered ring. This leads to a *cis* alignment of the sterically most demanding substituents in several cases as can be observed in substrates **174e/p/o**. Whereas in the cases of single substituted cyclobutanones **182** only two diastereomers were obtained in varying ratios, that number increased to a maximum of four diastereomers for multiple substituted cyclobutanones **182**, resulting in complex NMR spectra with overlap of the signals originating from the isomers. In these cases (**174k/l**) the recorded 2D NOESY spectra alone did not result in definite statements about the stereochemistry in the preferred product but other empirical aspects had to be considered to postulate the order of preference regarding the stereochemistry (experimental section). Among those empirical aspects we considered the previous declared selectivity for a *trans*-relation between the olefin and the most steric encumbering neighbor as well as the ratio of isomers that was determined for the starting material ketones **182k/l** (experimental section).

Table 15: Complete overview of the performed Grignard reactions

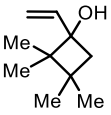


1.0 equiv **182 / 179/ 199** | *1.1 – 1.5 equiv* **202** | **174** | **$R^1 > R^2$ (sterics)**

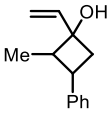


trans

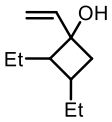
174q 56%



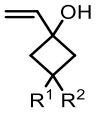
174b 59%



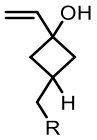
174l 53%[a)]



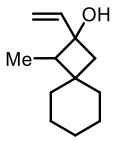
174k 40%[a)]



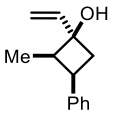
174a 66%, **R^1 =** Me, **R^2 =** Ph, 14/10 *trans* / *cis*. **174c** 41%, **R^1 =** Me, **R^2 =** ^{i}Pr, 19/10 *trans* / *cis*. **174d** 60%, **R^1 =** Bn, **R^2 =** H, 37/10 *trans* / *cis*. **174m** 40%, **R^1 =** CN, **R^2 =** H, 13/1 *trans* / *cis*. **174n** 31%, **R^1 =** CO_2Et, **R^2 =** H, 66/10 *trans* / *cis*.



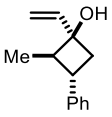
174e 53%, **R =** CH_2OAc, 46/10 *cis* / *trans*. **174f** 74%, **R =** CH_2SiMe_3, 35/10 *cis* / *trans*. **174g** 31%, **R =** CH_2Cl, 16/1 *trans* /*cis*. **174h** 25%, **R =** Bpin, 40/10 *trans* / *cis*. **174i** 56%, **R =** (2-methylphenyl), 38/10 *trans* / *cis*. **174p** 47%, **R =** CH_2SO_2Ph, 39/10 *cis* / *trans*. **174o** 29%, **R =** Br, 59/10 *cis* / *trans*.



174j 77%, 10/1 *trans* / *cis*.



174l-*cis* 77%



174l-*trans* 83%[c)]

dr values and relative configuration of given examples were determined by 2D NOESY spectroscopy if suitable signals could be identified (for explicit details see experimental section). Isolated yields reported. a) complex mixture of isomers obtained (for possible analysis see experimental section). b) yield reported over two steps, as previous step was not isolatable. c) obtained via diastereomeric resolution of **174l** using a procedure analog to Scheme 74. **Bpin =** 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl).

Also as mentioned before, substrate **174l-*trans***, could not be accessed directly via the presented Grignard reaction but rather from a diastereomeric resolution procedure from substrate **174l** (analog to Scheme 74). Comparison of the NMR data for both substrates **174l-*cis*** and **174l-*trans*** then confirmed the relative stereochemistry in both cases (Figure 25).

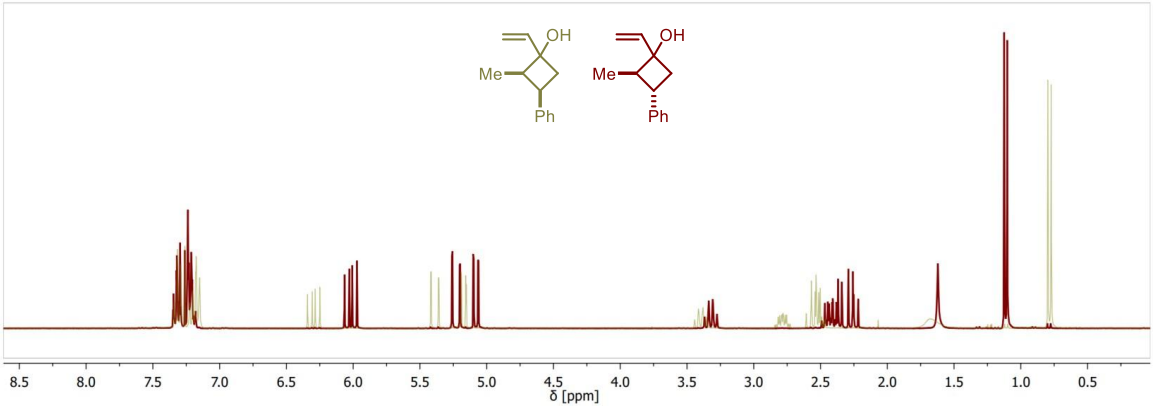


Figure 25: ^{1}H NMR comparison of **174l-*trans*** (maroon) and **174l-*cis*** (olive).

The stacked ^{1}H NMR of both compounds clearly show differences in chemical shifts, most importantly in the region from 2.0 ppm to 3.5 ppm where the protons of the cyclobutane ring are located.

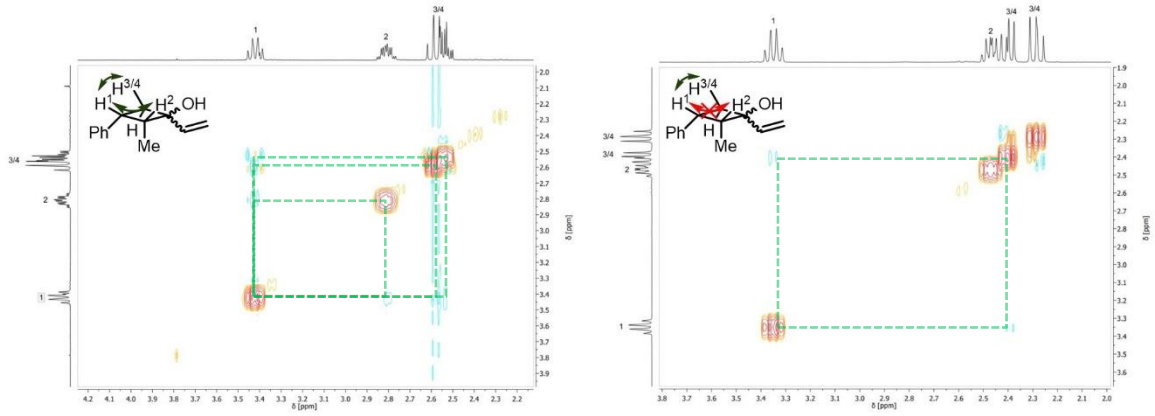


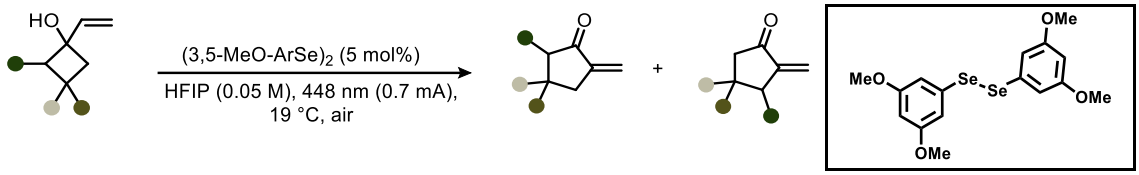
Figure 26: NOESY excerpt comparison of **174l-*cis*** (left) and **174l-*trans*** (right).

In addition, the comparison of both 2D NOESY spectra further confirmed the anticipated relative stereochemistry (Figure 26), where a through space coupling between H^1 and H^2 was observed in the case for the previously declared *cis*-isomer and a lack of said respective coupling in the *trans*-isomer.

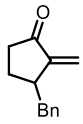
4.2.4. Substrate Scope for the ring expansion reaction

Having established a viable number of vinylic cyclobutanols **174**, we then set out to submit them to the developed reaction conditions, where we were pleased to see, that the reported excellent NMR yield of 87%, obtained in the reaction optimization procedure (Scheme 68) turned out to be a valid benchmark for nearly all NMR yields obtained throughout the entire rection scope (Table 16). Independently of substitutional pattern or the incorporation of functional groups, at full conversion, we were able to report excellent yields with 92% NMR yield **178o** being the lowest number for reactions that produce a single stereocenter. Results deviating from this statement only included reactions that concluded in the formation of multiple isomers or substrates that did not reach 100% conversion even after elongated reaction times (e. g. **178p**).[224]

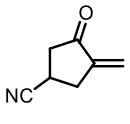
Table 16: Scope overview for the ring expansion reaction



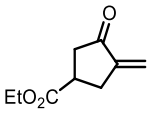
174 **178 (main + side)** **$(3,5\text{-MeO-ArSe})_2$**



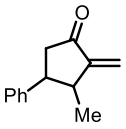
178q
70% (95%)



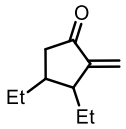
178m – (0%),
0% conv.



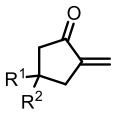
178n – (0%),
0% conv.



178l-main 72% (92%),
47/10 *trans* / *cis*

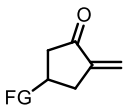


178k 44% (80%),
38/10 *trans* / *cis*



carbon scaffold:

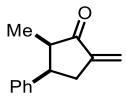
178a 85% (97%), **R^1 =** Ph, **R^2 =** Me. **178c** 88% (95%), **R^1 =** Me, **R^2 =** ^{i}Pr. **178d** 78% (97%), **R^1 =** Bn, **R^2 =** H. **178i** 48% (94%), **R^1 =** (2-methylphenyl), **R^2 =** H.



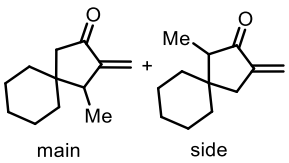
functional groups:

178e 79% (99%)**, R =** $(CH_2)_2OAc$. **178f** 82% (91%), **R =** $(CH_2)_2SiMe_3$. **178g** 66% (96%), **R =** $(CH_2)_2Cl$. **178h** 57% (96%), **R =** CH_2Bpin. **178p**[a,b] n.d. (57%), **R =** $(CH_2)_2SO_2Ph$. **178o**[c] - (92%), **R =** CH_2Br.

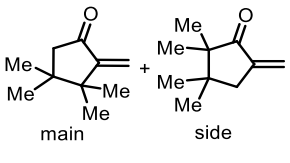
multiple substitution:



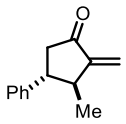
178l-side[b] n.d% (5.0%)



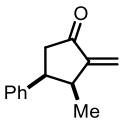
178j 70% (75% + 4%),
22/1 main / side



178b 91% (91% + 9%),
97/10 main / side



178l-*trans*
79% (98%)



178l-*cis*
62% (94%)

Reactions were performed on a 0.50 mmol scale. NMR yield is given in parentheses. 1,3-dinitrobenzene (0.50 equiv) was used as internal standard. a) no full conversion. b) incomplete isolation. c) degradation on column. Reactions were run until full conversion if not stated otherwise. dr values and relative configuration of given examples were determined by 2D NOESY spectroscopy if suitable signals could be identified (for explicit details see experimental section).

However, even in these cases, the difference in product yield and conversion is marginal (c.f. experimental section), indicating that the reaction progress was most likely terminated by catalyst degradation and the yields would align with the examples that reached full conversion. Unfortunately, as the detailed mechanism was not entirely established at this point, we are not able to deliver any hypothesis as to how the enhanced deactivation rate of the catalyst is explained in those cases or even how we could prevent these circumstances.

A notable exception however was found in the cases of substrates **178m** and **178n** where no product formation was observed at all, even when an additional photoredox catalyst was applied. Mechanistically this indicated to us, that the reason for the reaction inhibition does not come from the selenium catalyst or its activation mode, but rather from the rearrangement procedure itself. Based on the mechanistic hypothesis made in Scheme 71 and the results from the experiments **178m** and

178n, we anticipate that the seleniranium-ion **II-4.2.1** is formed but the rearrangement does not conclude due to the electronic nature of these substrates. As a requirement for the migration includes the cleavage of one of the C–C σ-bonds (Figure 27) it was first questioned as to how this bond cleavage occurs especially regarding a present selectivity, which leads to different products if the corresponding σ-bonds are chemically different.

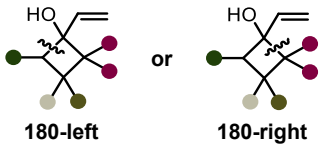
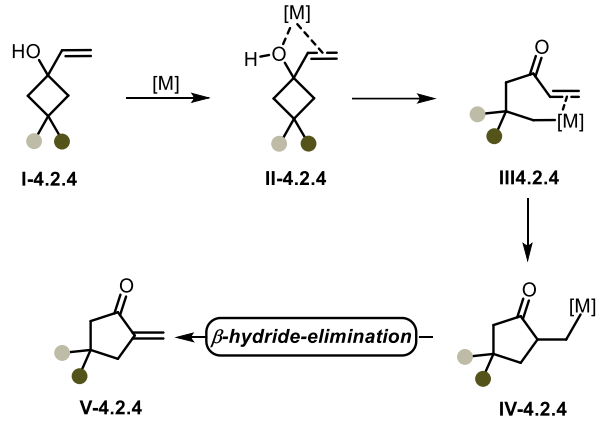


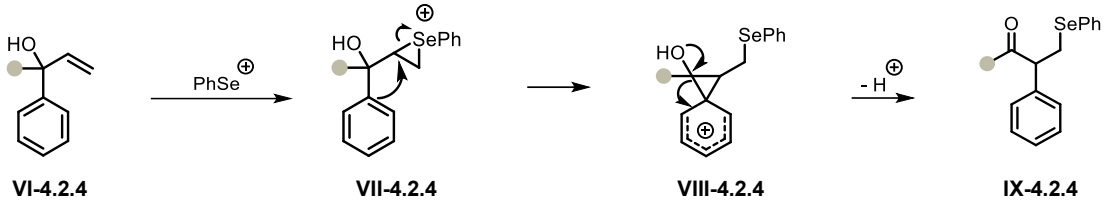
Figure 27: Visual representation of the possible σ-bond cleavages.

The mechanistic rational for said bond cleavage is then defined by the reagents used and in general two major differences can be found throughout literature. Performing the reaction with transition metals such as Pd or Ru, the metal is first chelated between the hydroxy group and the π-bond (Scheme 87, structure **II-4.2.4**) and by this activation mode β-C-scission is then achieved by formation of a carbon-metal σ-complex **III-4.2.4**. The ring expansion product is then formed upon migratory insertion (structure **IV-4.2.4**) and β-hydride elimination.[110,186,187,249,250] The selectivity for the β-C scission in this case is dominated by steric implications, making a secondary carbon atom more preferential in comparison with a tertiary one.[187]



Scheme 87 Literature based rearrangement progression when using transition metals [M].

However, as selenium reactivity is centered around σ-orbitals, the above mentioned reaction steps are not feasible and therefore we anticipate a different progression in alignment with the concept reported by Wu et al. who reported a 1,2-aryl migration mediated by a Lewis-acidic Fe-catalyst and stochiometric amount of a $PhSe^+$ source.[110] The mechanism is centered around a Type II semipinacol rearrangement which is achieved by the generation of an electrophilic carbon center in β-position to the alcohol **VI-4.2.4**. [108] To achieve the migration reaction, the authors describe an interplay between the migrating aryl substituent and the seleniranium-ion (structure **VII-4.2.4**) in form of a Wheland-complex **VIII-4.2.4** whereas further stabilization of positive charges is obtained by the adjacent oxygen atom (Scheme 88).



Scheme 88: Excerpt of the mechanism reported by Wu et al.[110]

This concept seems plausible for their list of applications, as the authors almost exclusively use substrates **VI-4.2.4** that carry at least one aryl group, whereas the sole successfully reported deviating substrate is 1-vinylcyclobutan-1-ol. In this case, an intermediate as displayed in structure **VIII-4.2.4** is impossible as we have to consider sp^3-hybridized C-atoms rather than sp^2-hybridzed ones meaning that initial C–C bond cleavage is required for the migration to occur. In this context it is not surprising that the only successful transformation (without an aryl group) is a cyclobutane ring because of its comparatively weak C–C σ-bonds due to the ring geometry, resulting in significant strain. This ring strain is furthermore forcing the non-bonded carbon atoms in close proximity resulting in repulsion which elongates and thus further weakens the C–C σ-bonds.[251] Going back now to the start of this discussion, these considerations could explain the inertness of substrates **174m** and **174n**, as in related literature it has been shown, that a trifluoromethyl group as a substituent on a cyclobutane ring causes a flattening of the ring geometry as well as an elongation of the C-C σ-bonds of the ring.[252] As we anticipate a similar impact by a nitrile or ester group, this bond elongation would have a negative impact on the needed orbital overlap to achieve the ring expansion reaction (Figure 28).

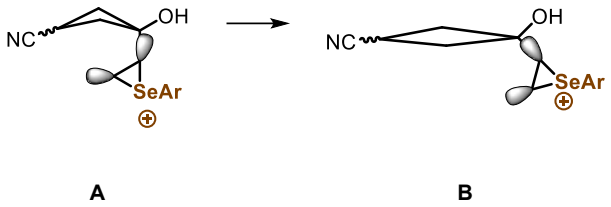
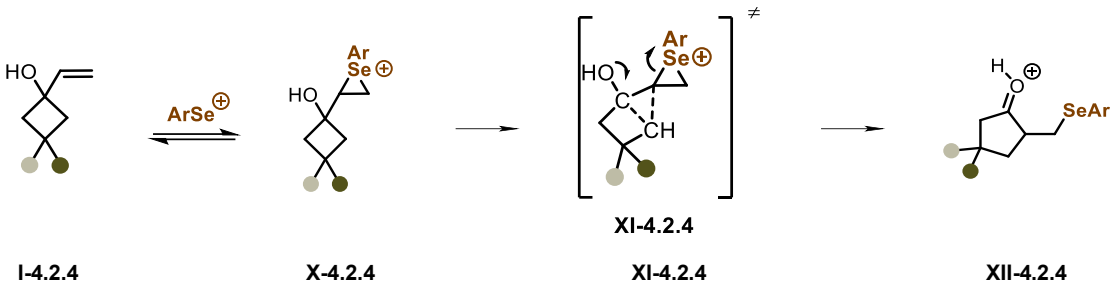


Figure 28: Postulated flattening and bond elongation imposed by the electron withdrawing nitrile group.

Going further, the electronic nature of the bond cleavage (radical vs. ionic) is then reported to be determined by the nucleophile attacking the π-bond indicating a heterolytic bond cleavage based on the cationic nucleophile applied (Scheme 88).[253] Applying these information to our reaction template let us conclude, that a heterolytic bond cleavage appears to be more suitable as a radical reaction progression would be based on a radical attack on the olefin, which would be feasible without irradiation as the Se–Se σ-bond homolysis was determined to be a thermal process (c. f. chapter 4.2.1).

As already indicated in Figure 28, we postulated that the successful reactivity is significantly affected by the alignment of the orbitals needed for the migration step. Envisioning a concerted

reaction progression (Scheme 89), the transition state **XI-4.2.4** is considered crucial as only anti-periplanar alignment of the σ-C-Se orbitals and the orbitals from the migrating group allow for a successful transformation.



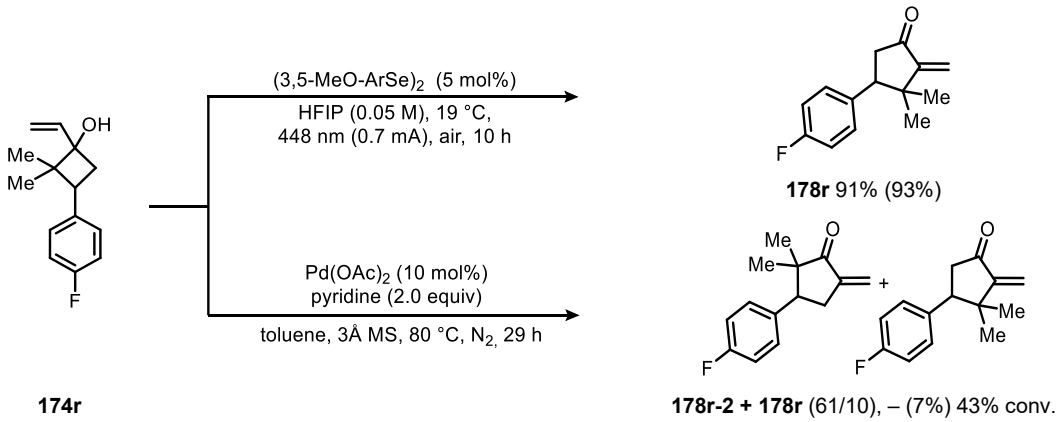
I-4.2.4 **X-4.2.4** **XI-4.2.4** **XII-4.2.4**

XI-4.2.4

Scheme 89: Rational for the C-C σ-bond cleavage, based on the catalytic active species $ArSe^+$.

Concluding from this postulation we formed the hypothesis that a successful reaction is based on two aspects. The first one being the liability of the C-C bond that needs to be broken and the second one being the geometry of the resulting transition state **XI-4.2.4**, which affects the necessary orbital overlap. As mentioned prior, a substitution on the cyclobutane ring has the consequence of elongating and thus weakening the bonds,[252] therefore facilitating adjacent bond cleavages. However, with increasing electron withdrawing capabilities of the substituent, the ring flattening and thus worsening of the necessary orbital overlap (Figure 28) can disfavor the transformation as seen in the substrates **174m** and **174n**.[252]

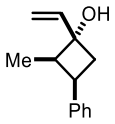
Overall though, this represents the opposite selectivity in contrast to the Pd-mediated concept in Scheme 87, where the dominant migration occurs from the sterically less hindered position.[110,186,187,249,250] We could then indirectly prove our postulated concerted pathway (Scheme 89) by the chemoselectivity that is generally observed in our reaction scope, starting with the α-subst. starting material **174q**, where exclusive formation of a single product (**178q**) was observed. Furthermore, among the two theoretical outcomes, only the product was formed where the higher substituted C–C σ-bond was migrating, which is in direct contrast to the ring enlargement mechanism postulated for the reaction using catalytic amounts of Pd.[187] To explicitly prove this difference in reactivity, a project collaborator submitted starting material **174r** additionally to the conditions described by Nishimura et al.[187] validating if a change in the selectivity for the migrating C–C σ-bond can be observed or not (Scheme 90).



Scheme 90: Reactivity comparison between a Pd-catalyzed reaction and our developed selenium catalyzed process.[224,235] For the Pd-catalyzed reaction, only NMR related values are reported. [186,187]

Not only did the Pd reaction result in the other isomer **178r-2** as major fraction, but also the outcome in its entirety is significantly worse with only 7% total product formation and less than 50% conversion after 29 h. Our developed reaction procedure on the other side resulted in exclusive formation of **178r** in nearly quantitative yields and only 1/3 of the reaction time. A possible reason for the inferior yields of the Pd catalysis, was postulated to be the reported isomerization of the π-bond by re-coordination of the Pd catalyst and the consecutive β-hydride elimination to form the thermodynamically more favored higher substituted double bond.[10]

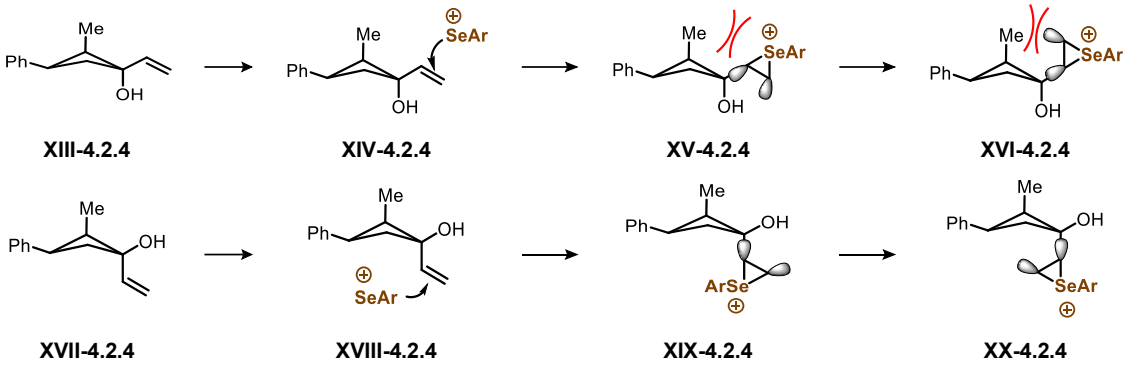
Continuing, the above presented selectivity preference for the migration of higher substituted C–C σ-bond is present throughout the entire scope. Although we obtained a mixture of product isomers in several cases, the isomer in which the sterically more demanding group has migrated (counter-thermodynamic) is always favored by at least a factor of 10. A sole exception to this observation is a substrate which was derived from a fully substituted allylic cyclobutanol motif where not only a smaller ratio of constitutional isomers was observed, but also the less substituted carbon center migrated preferentially.[224,235] We attributed this change in selectivity to steric inhibition affecting the directionality of the attack of the selenium catalyst and thereby increasing the (energetic-) differences for the migration of each individual carbon chain based on molecular motion. The basis for this postulation was found, when analyzing the combined results for the transformations of **178l, 178l-*cis*** and **178l-*trans*** which were at first only aimed to prove the stereoretention of the ring enlargement reaction. During these experiments the formation of the side product **178l-side**, could only be observed when applying the diastereomeric mixture **174l** composed of all four possible relations between the substituents. By analyzing the 2D NOESY experiment from the purified material from **178l-side** as well as considering the ratio of isomers in the starting material **174l** we then concluded that the major diastereomer causing the formation of the side product can only be the *all-cis*-isomer **174l-*all-cis*** (Figure 29) which is only present in the starting material mixture **174l**.



174l-*all-cis*

Figure 29: Diastereomer that was anticipated to cause the majority of side product formation **178l-side**.

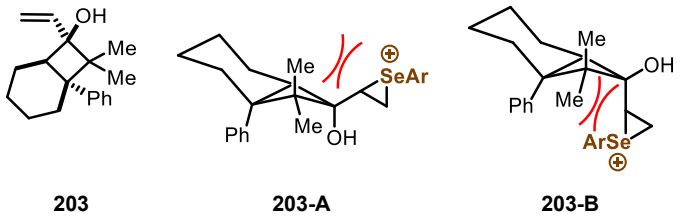
In order to visualize potential difference, we decided to compare the above shown **174l-*all-cis*** isomer with **174l-*cis*** (Table 15) where only one stereogenic center is altered. Considering the necessity of anti-periplanar alignment of the σ-C-Se bond orbital and the σ-orbital involved in the bond migration (Scheme 89) reactivity will preferably occur on the side of the (unsymmetric) ring moiety which has the strongest overlap. The major difference between the two compared isomers is that for the **174l-*all-cis*** isomer (**XIII-4.2.4** in Scheme 91), steric strain causes the orbitals to bend away from the higher substituted carbon chain (**XV-4.2.4** and **XVI-4.2.4** in Scheme 91) thereby favoring the orbital overlap for the less substituted carbon chain. In contrast to this, the inversion of the stereogenic center in **174l-*cis*** (**XIII-4.2.4** in Scheme 91) prevents the beforehand mentioned steric impact. The resulting seleniranium conformers (**XIX-4.2.4** and **XX-4.2.4** in Scheme 91) are not affected by steric repulsion and the relevant σ*-C-Se bond orbitals point toward the non-substituted plane of the 4-membered ring (Scheme 91). This has the consequence that the seleniranium ion for the **174l-*cis*** isomer does not distinguish between both possible carbon chains and the more favorable (higher substituted) bond is migrating preferentially.



Scheme 91: Anticipated impact on the necessary orbital overlap for the desired bond migration imposed by the stereochemical relation between the methyl group and the vinyl group.

Concluding from these comparisons, we generally postulated, that a *cis*-configuration between the olefin and the substituent in β-position results in notable steric impact for the corresponding seleniranium ions which leads to the formation of the thermodynamic side products (further examples: **178b** and **178j**). An extreme case relating to this postulate is the substrate mentioned at the beginning of this discussion **203**. Due to the geminal disubstitution the relative sterical relation between the vinyl group and the adjacent substituent become less relevant, as in contrast to the discussion above, now both planes of the ring impose unsymmetric steric repulsion on the formed seleniranium ions (**203-A** and **203-B** in Figure 30). In addition to this, the fused 6-membered ring enhanced this

steric repulsion by making the overall structure more rigid leading to and overall favored migration of the less substitution alkyl chain.



203 **203-A** **203-B**

Figure 30: Steric representation of the two possible seleniranium-ion based on the bicyclic starting material.

Regarding the migration of the respective C–C σ-bond, we could further determine, that said migrations occur without bond rotations thereby allowing for retention of present relative stereocenters as exemplified in the substrates **178l-*cis*** and **178l-*trans***. The 2D NOESY experiments directly confirmed the retention of the stereochemical information for the *cis*-diastereomer **178l-*cis*** (Figure 31), whereas the *trans*-diastereomer could only be indirectly confirmed by comparison of the ^{1}H NMR spectra of the isolated diastereomers **178l-*cis*** and **178l-*trans***, with the beforehand obtained diastereomeric mixture **178l** (Figure 31).

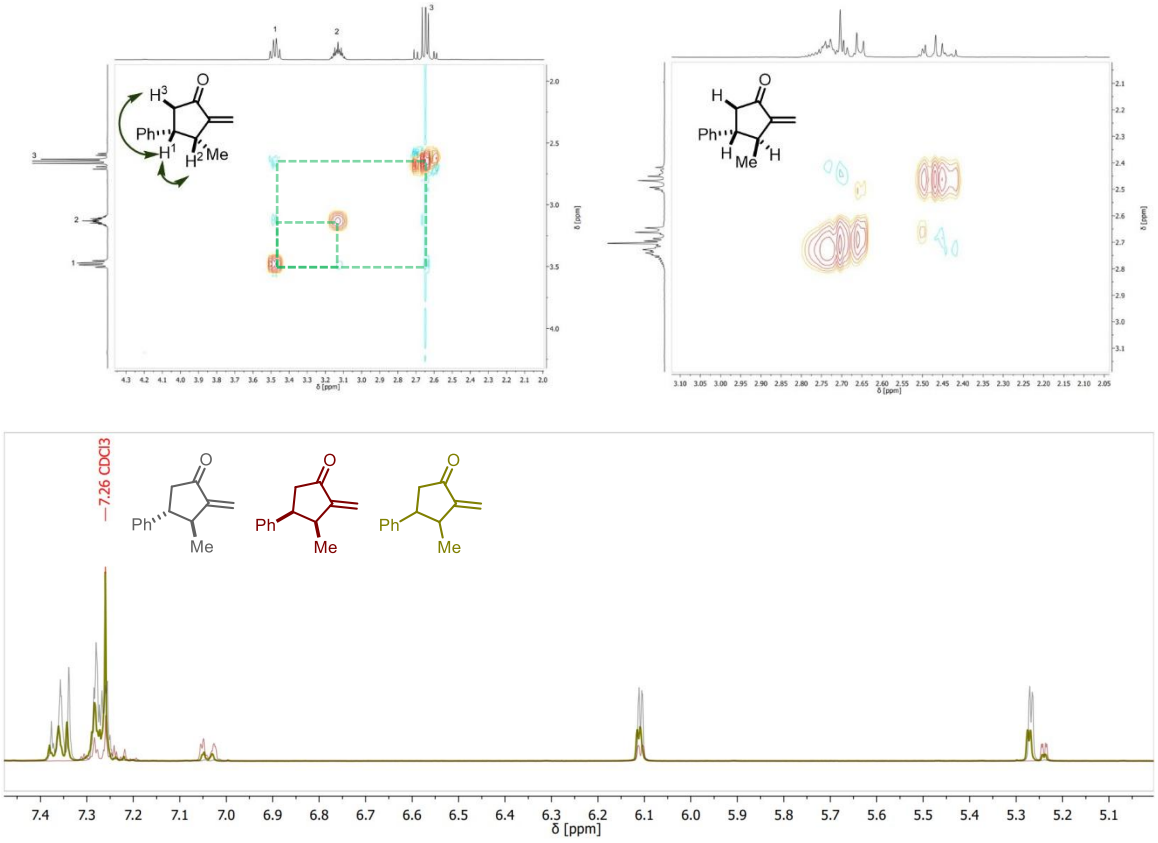


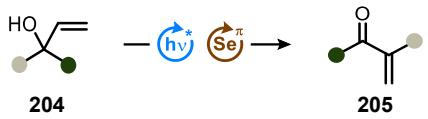
Figure 31: 2D NOESY comparison between the *cis*-diastereomer (upper left) and the *trans*-diastereomer (upper right) and excerpt of the stacked ^{1}H NMRs of the *cis*-diastereomer (below, maroon), the *trans*-diastereomer (below, grey) and the mixture (below, olive).

The excerpt of the ^{1}H NMR clearly shows, that the products obtained in the reactions **178l-*cis*** and **178l-*trans*** add up to the mixture **178l**, which translates to the conclusion, that the grey signal set must belong to the *trans*-diastereomer with the *cis*-diastereomer already being determined.

Summarizing this project, we have developed a synthetic protocol for the ring expansion reaction of vinylic cyclobutanols, representing a complementary method to known Pd-catalyzed processes, by obtaining opposite configurational isomers. In our case, the rearrangement process is mostly dominated by electronic factors but increasing steric tension regarding the substitution pattern can contribute to the observed selectivity and even alter the preference. In addition to this, we could exclude C-C σ-bond rotation movements during the migration step, thus ensuring stereoretention of already existing chiral centers. Furthermore, our reaction template represents a novelty regarding the number of applications as we were able to present reasonable functional group tolerance and in total over 25 examples, where previously only marginal examples per publication could be found (chapter 2.6.1).

4.3 1,2-aryl migration reaction

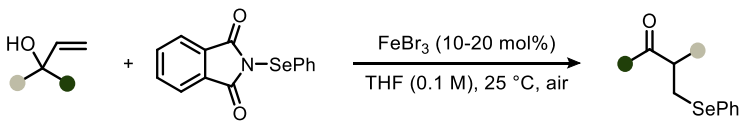
Simultaneously to above discussed reaction development, we wondered whether the reaction conditions could be applied to an acyclic system thereby further expanding the scope of applications. The fundamental idea then was to utilize different substituted allylic alcohols **204** and transform them into the related α,β-unsaturated ketones **205** (Scheme 92).



204 **205**

Scheme 92: Reaction concept for the acyclic rearrangement reaction.

Evidence for a possible successful implementation of such a process has already been reported by Wu et al.[110] who performed this type of reaction using stochiometric amounts of a $PhSe^+$ source **206** (Scheme 93 for more details Scheme 34). These reports indicated for us that the desired type II semipinacol rearrangement is indeed feasible, however, the remaining questions was if the same would hold true for a catalytic process with concluding elimination of the selenium moiety in structure **207** with a photoredox setup.

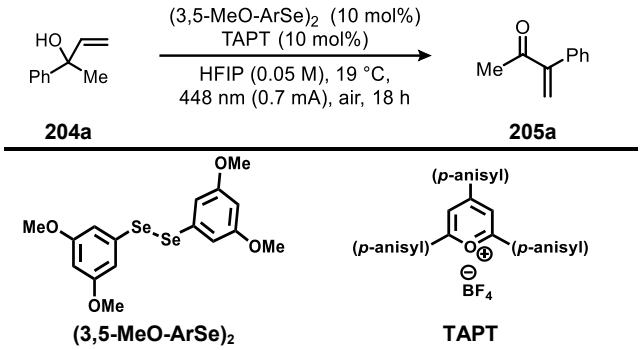


1.0 equiv **204** *1.0 equiv* **206** **207**

Scheme 93: Reaction developed by Wu et al.[110]

4.3.1. Reaction conditions for the formation α,β-unsaturated ketones

The investigations were initiated by first applying the optimized reaction conditionsthat were developed for the ring expansion reaction to 2-phenylbut-3-en-2-ol (**204a**) as chosen starting material (Scheme 94).



Scheme 94: Reaction setup for the first experiment aiming at the catalytic mediated 1,2-aryl migration of allylic alcohols **204a**.

The initial experiment indeed revealed new signal sets in the ^{1}H NMR which we attributed to the methylene group of the product **205a** (Figure 32). However, we also realized that the reaction was not at full conversion which is why we first started to monitor the reaction time before further changes were applied (Table 17).

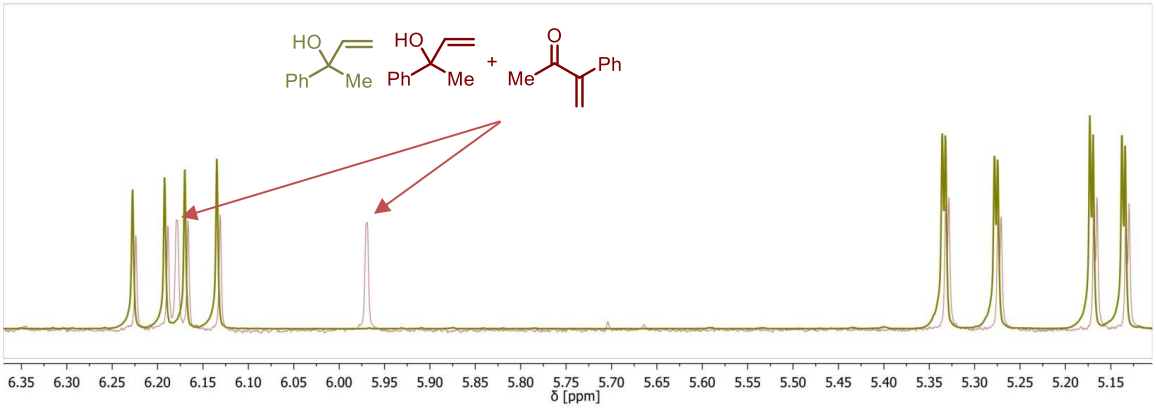
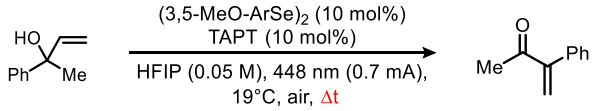


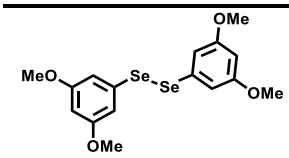
Figure 32: ^{1}H NMR overlap excerpt of the starting material **204a** (olive) and the crude NMR (maroon).

1,2-aryl migration reaction Reaction conditions for the formation α,β-unsaturated ketones

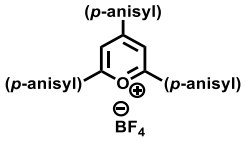
Table 17: Screening of reaction time for the 1,2-aryl migration



204a **205a**



(3,5-MeO-ArSe)$_2$



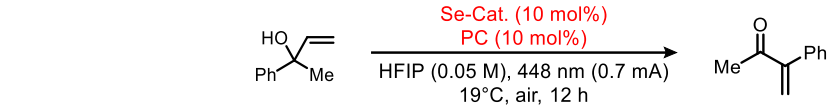
TAPT

Entry	Se-Cat. [10 mol%]	PC [10 mol%]	Δt [h]	Conversion	NMR Yield
1[a)]	**(3,5-MeO-ArSe)$_2$**	**TAPT**	18	<100%	n.d.
2	**(3,5-MeO-ArSe)$_2$**	**TAPT**	41	100%	24%
3	**(3,5-MeO-ArSe)$_2$**	**TAPT**	12	66%	22%

Reactions were performed on a 0.50 mmol scale in a vial with screw cap (penetrated with cannulas for air exchange). The vial was irradiated with a blue LED (448 nm, 0.7 mA) in the cooling block setup at 19 °C under air for the given time. NMR yields were determined using 1,3-dinitrobenzene as internal standard. a) no NMR yield was determined.

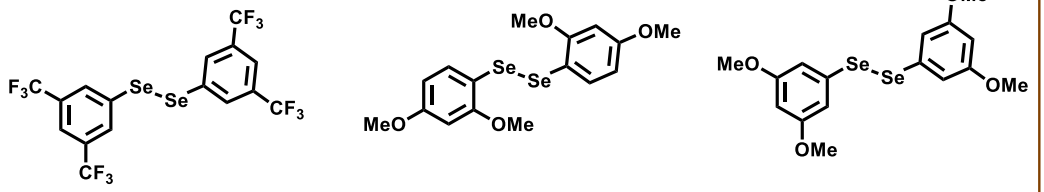
Unfortunately, this did not have the desired outcome, as we only observed a minimal difference in NMR yield unaffected of whether we let the reaction run for 12 h or 41 h. In combination with the fact that the difference in conversion was much more formative, we concluded a more drastic impact from side reactivity which is dominant under these chosen conditions. To analyze the origin of this side reactivity we chose to change the combination of catalysts to alternating combinations, either avoiding high oxidation potentials (TAPT = +1.84 eV vs. SCE)[197] or using more electron deficient selenium catalysts to positively affect the driving force for the aryl migration (Table 18).

Table 18: Overview of the first catalyst screening for the 1,2-aryl migration



204a **205a**

selenium catalysts:

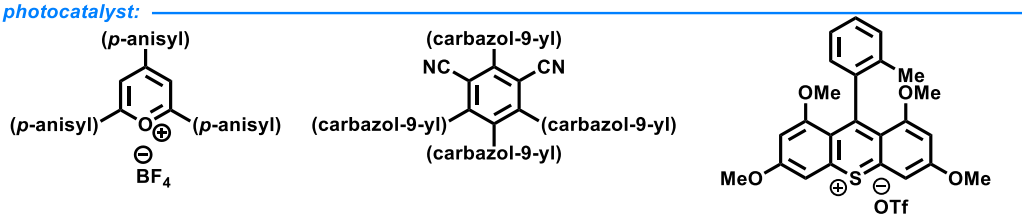


$(3,5\text{-}F_3C\text{-}ArSe)_2$
E_{ox} = +1.71 eV vs. SCE in MeCN

$(2,4\text{-}MeO\text{-}ArSe)_2$
E_{ox} = +0.98 eV vs. SCE in MeCN

$(3,5\text{-}MeO\text{-}ArSe)_2$
E_{ox} = +1.29 eV vs. SCE in MeCN

photocatalyst:



TAPT
E^*_{red} = +1.84 eV vs. SCE in MeCN

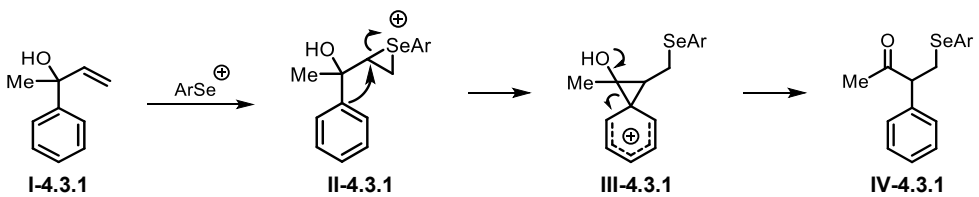
4CzIPN
E^*_{red} = +1.35 eV vs. SCE in MeCN

TXT
E^*_{red} = +1.76 eV vs. SCE in MeCN

Entry	Se-Cat. [10 mol%]	PC [10 mol%]	Δt [h]	Conversion	NMR Yield
1	**$(3,5\text{-}F_3C\text{-}ArSe)_2$**	**TAPT**	12	100%	2%
2	**$(2,4\text{-}MeO\text{-}ArSe)_2$**	**4CzIPN**	12	34%	0%
3	**$(3,5\text{-}MeO\text{-}ArSe)_2$**	**TXT**	12	79%	19%

Reactions were performed on a 0.50 mmol scale in a vial with screw cap (penetrated with cannulas for air exchange). The vial was irradiated with a blue LED (448 nm, 0.7 mA, TAPT) or a green LED (528 nm, 0.7 mA, 4CzIPN, TXT) in the cooling block setup at 19 °C under air for the given time. NMR yields were determined using 1,3-dinitrobenzene as internal standard. Values for redox potentials were taken from the corresponding literature.[40,194,196,197,254]

Again, the reaction outcomes were oppositional to our expectations, but they allowed us minor insight into the reaction problematics regarding the mechanistic progression. Initially, it was assumed that electron poor selenium catalysts would enhance the overall reactivity by forming more electrophilic seleniranium-ions **II-4.3.1** thus favoring the attack of the adjacent aryl group, forming the Wheland-Complex **III-4.3.1** (Scheme 95).



I-4.3.1 **II-4.3.1** **III-4.3.1** **IV-4.3.1**

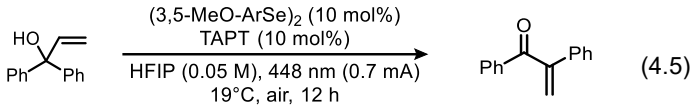
Scheme 95: Excerpt of the proposed reaction mechanism, depictured for substrate **204a**.

However, based on the results obtained in the respective catalyst screening, we had to rethink this postulate as not only inferior yields were observed but even more so, the quality of the obtained crude NMRs were significantly worse when using the more electron deficient diselenide **(3,5-F_3C-ArSe)$_2$**, indicating increased side reactivity (Table 18, entry 1). This meant that the electrophilicity of the respective catalytic species $ArSe^+$ and the seleniranium-ion **II-4.3.1** were not the major cause for the inferior yields but rather degradative processes, either affecting the starting material **204a**, the product **205a** or both. We then considered the starting material **204a** with its isolated π-bond to be more susceptible to oxidation rather than the ketone (EWG) conjugated π-bond in the product **205a**, which could be verified by comparing the results from the catalyst screening (Table 18) with the results prior to it (Table 17). Whereas on one side **TAPT** in combination with **(3,5-MeO-ArSe)$_2$** results in 22% of product formation at 66% conversion (Table 17, entry 3), **4CzIPN** with a lower excited state oxidation potential and the electron rich **(2,4-MeO-ArSe)$_2$** catalyst gave no product and only 34% conversion (Table 18, entry 2). This means that successful product **205a** formation requires a photocatalyst-diselenide combination resulting in a catalytic active species $ArSe^+$ exhibiting sufficient nucleophilicity to promote the aryl migration (Scheme 95, stage **II-4.3.1** to stage **III-4.3.1**) as termination at the stage of the selenofunctionalized intermediate **IV-4.3.1** could be excluded by analysis of the crude NMR spectra. These observations also imply that the product formation is energetically inferior to the degradation of the starting material **204a** based on the fact that significant consumption of **204a** is observed in both cases, whereas product **205a** is only obtained when using the stronger oxidant **TAPT**. The thus far postulated requirement for the photocatalyst-diselenide combination was then further established in the last experiment (Table 18, entry 3) where we used the initial selenium catalyst **(3,5-MeO-ArSe)$_2$** with **TXT** as weaker oxidizing photocatalyst (compared to **TAPT**) under green light irradiation, obtaining a slightly inferior yield and slightly higher conversion compared to the original conditions (Table 17, entry 2).

Overall, the results from these experiments proved to us that the major complication in the reaction concept arises from the photocatalytic driven degradation of the starting material **204a** with a strong correlation between the excited state oxidation potential of the photocatalyst and rate of degradation. The catalytic active selenium species on the other side needs to exhibit sufficient electrophilicity to enable product formation but even highly electrophilic selenium species alone cannot change the reaction preference to favor the product formation over the starting material degradation.

Intending to analyze the lability of the starting material under the reaction conditions, we tested a different substituted vinylic alcohol **204b** before making additional changes to the reaction conditions (Equation 4.5). Substrate **204b** was then chosen, based on the availability and the hypothesis that a biarylated allylic alcohol **204** would exhibit a higher migration tendency due to additional stabilization by +M-effects of the remaining arene as well as having two (identical) migratable groups instead of one.

1,2-aryl migration reaction Reaction conditions for the formation α,β-unsaturated ketones



204b **205b** 23%
80% conversion (4.5)

To our disappointment, the obtained NMR yield was no different to the previous substrate **204a**, indicating that the degradation issue is mostly independent on the substitution pattern. However, when analyzing the corresponding crude NMR to determine the NMR yield, we came across a new signal indicating a possible side reactivity (Figure 33).

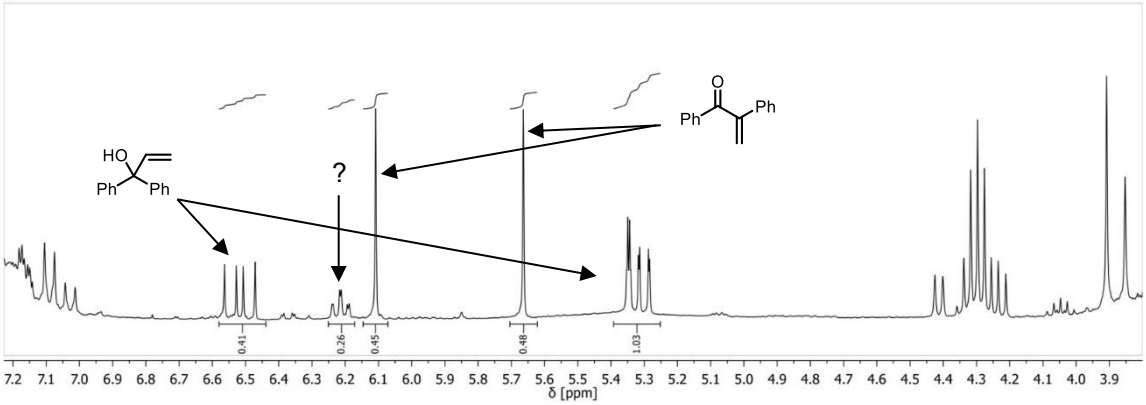
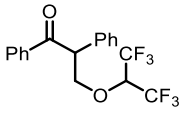


Figure 33: ^{1}H NMR excerpt of the NMR yield determination, indicating a new signal set.

This newly found signal was then hypothesized to originate from an alternative product in which case we either observe a conjugated addition reaction to our product **205b** by the solvent HFIP or the selenium residue was not eliminated to reform the double bond but rather directly substituted by HFIP (Figure 34).



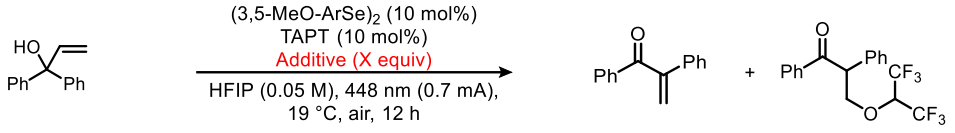
208

Figure 34: Anticipated side product in the migration reaction.

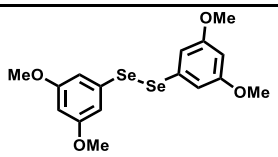
During the investigations into the formation of this side product **208** (*vide infra*) we discovered that the moderate acidity of the solvent HFIP is a cause for its formation and therefore it was decided to test if basic additives would sufficiently counteract the solvent acidity and consecutively favor the formation of the elimination product **205**. [255] In the first reactions we tested an inorganic derived base in comparison to an organic counterpart (Table 19) and observed that the reaction using DBU (Table 19, entry 2) nearly prevented any product formation, whereas Li_2CO_3 already showed tremendous improvement by almost leveling the values for conversion and NMR yield (Table 19, entry 1). Hoping to further exploit this observation, we extended the reaction time only to find advanced conversion but slightly decreased NMR yields, most likely attributed to degradation/deactivation of the catalytic system by the base. To check for a similar pattern, we tested further inorganic

bases and found out that other carbonate based bases all followed this degradation/deactivation postulate especially in the cases of Na_2CO_3 and K_2CO_3 where no light emission by the photocatalyst was observed after several hours (entries 4-5). The low conversion is therefore explained by complete shutdown of both the desired reaction and photocatalytic driven degradation processes.

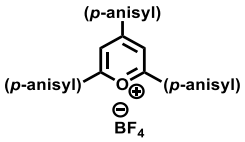
Table 19: Screening of basic additives for the aryl migration



204b **205b** **208**



(3,5-MeO-ArSe)$_2$



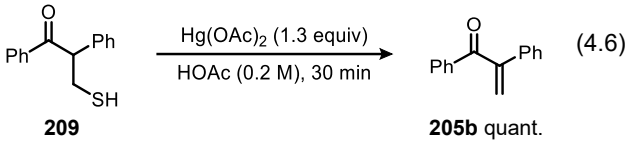
TAPT

Entry	Se-Cat. [10 mol%]	PC [10 mol%]	Additive	Δt [h]	Conversion	NMR Yield [205b]	NMR Yield [208]	∑ NMR Yield
1	**(3,5-MeO-ArSe)$_2$**	**TAPT**	Li_2CO_3 (2.0 equiv)	12	58%	48%	25%	73%
2	**(3,5-MeO-ArSe)$_2$**	**TAPT**	DBU (2.0 equiv)	12	70%	2.5%	5%	7.5%
3	**(3,5-MeO-ArSe)$_2$**	**TAPT**	Li_2CO_3 (2.0 equiv)	20	88%	44%	15%	59%
4	**(3,5-MeO-ArSe)$_2$**	**TAPT**	K_2CO_3 (2.0 equiv)	12	9%	9%	0%	9%
5	**(3,5-MeO-ArSe)$_2$**	**TAPT**	Na_2CO_3 (2.0 equiv)	12	33%	12%	0%	12%
6	**(3,5-MeO-ArSe)$_2$**	**TAPT**	$CaCO_3$ (2.0 equiv)	12	70%	21%	16%	37%
7	**(3,5-MeO-ArSe)$_2$**	**TAPT**	NaH_2PO_4 (2.0 equiv)	12	59%	19%	9%	28%
8	**(3,5-MeO-ArSe)$_2$**	**TAPT**	Na_2HPO_4 (2.0 equiv)	12	50%	25%	12%	37%
9	**(3,5-MeO-ArSe)$_2$**	**TAPT**	CaF_2 (2.0 equiv)	12	72%	21%	12%	33%

Reactions were performed on a 0.50 mmol scale in a vial with screw cap (penetrated with cannulas for air exchange). The vial was irradiated with a blue LED (448 nm, 0.7 mA) in the cooling block setup at 19 °C under air for the given time. NMR yields were determined using 1,3-dinitrobenzene as internal standard.

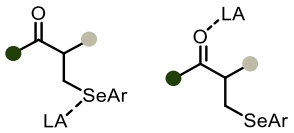
As phosphate and fluorine bases (entries 7-9) also were not able to improve the results we also tested different additives hoping to improve the outcome by different approaches. Among the additives tested were the already in chapter 4.1.1 discussed disulfide **138** and *para*-nitrobenzaldehyde (**139**), again with the aim to enhance reaction kinetics and reduce potential $^1O_2$ based side reactivity. Furthermore, we also questioned if an additional Lewis-acid would have a favorable

influence on the reaction outcome based on the literature reported in 1992 by Oda et al.[155] where a thiol residue **209** is eliminated under acidic conditions with $Hg(OAc)_2$ (Equation 4.6).



209 **205b** quant. (4.6)

As it was not explicitly stated by the authors, we anticipated that the role of the acidic media was to amplify the nucleofugacity of the thiol group by protonation, as well as shifting the electron density further towards the carbonyl group upon its protonation. The question then was, if the application of a Lewis-acid would serve a similar purpose in enhancing the nucleofugacity of the selenium residue in the selenofunctionalized intermediate **207**, either by direct coordination between the selenium atom and the Lewis-acid, or by coordination to the carbonyl group (Figure 35).



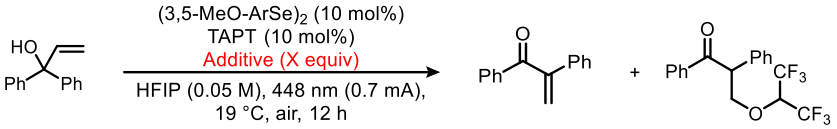
207-1 **207-2**

Figure 35: Hypothesized influence of a Lewis-acid (LA) on the nucleofugacity of the ArSe-residue.

The results of this additive screening, however clearly revealed that the application of Lewis-acids did not show the anticipated reaction improvement as only in one of three experiments, the formation of the product was observed (Table 20, entries 4-6). Whereas in the case of $AlCl_3$ (Table 20, entry 6) the outcome was simply inferior to the setup using Li_2CO_3 (Table 19, entry 3), the application of $FeCl_3$ and $Yb(OTf)_3$ (Table 20, entries 4-5) resulted in the promotion of undeclared side reactivity as neither product **205b** nor side product **208** formation was determined at full conversion.

Also, the utilization of disulfide **138** remained ineffective (Table 20, entry 1) leading to lower yields and higher conversion in comparison to Li_2CO_3 (Table 19, entry 1), whereas the nitrobenzaldehyde **139** initially looked promising reporting a similar conversion to yield ratio as Li_2CO_3 (Table 20, entry 2), although with slower progression rate. By combining the aldehyde **139** and Li_2CO_3 we then hoped for cumulative further improvement of the conversion rate as well as the beneficial effects on the reaction yield which unfortunately was not the case as no significant change neither in yield nor conversion was detected (Table 20, entry 3).

Table 20: Overview of the second additive screening.



204b **205b** **208**

(3,5-MeO-ArSe)$_2$ **TAPT**

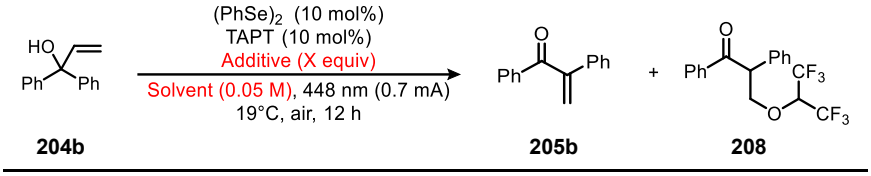
En-try	Additive	Δt [h]	Conversion	NMR Yield [205b]	NMR Yield [208]	∑ NMR Yield
1	(*p*-Cl-ArS)$_2$ **138** (10 mol%)	12	92%	20%	5%	25%
2	2-NO$_2$-benzaldehyde **139** (25 mol%)	12	55%	19%	10%	29%
3	2-NO$_2$-benzaldehyde **139** (25 mol%) + Li_2CO_3 (2.00 equiv)	12	63%	21%	9%	30%
4	$FeCl_3$ (20 mol%)	12	100%	0%	0%	0%
5	$Yb(OTf)_3$ (20 mol%)	12	100%	0%	0%	0%
6	$AlCl_3$ (20 mol%)	12	73%	17%	n.d.	17%

Reactions were performed on a 0.50 mmol scale in a vial with screw cap (penetrated with cannulas for air exchange). The vial was irradiated with a blue LED (448 nm, 0.7 mA) in the cooling block setup at 19 °C under air for the given time. NMR yields were determined using 1,3-dinitrobenzene as internal standard.

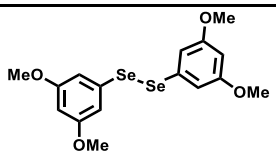
We then centered our focus for improvement back to the matter of the persistent acidity in the reaction media as we could observe the formation of the side product **208** throughout most experiments that led to significant formation of the target molecule **205b** (Table 19 and Table 20). At first, we then wanted to establish the possibility to use the commercial available (PhSe)$_2$ (+1.33 eV vs. SCE)[40] instead of the pre-synthesized (3,5-MeO-ArSe)$_2$ (+1.29 eV vs. SCE)[40] to enhance the practicality. As this exchange of catalyst had no observable impact on the reaction outcome, (Table 21, entry 1), we continued further experiments using (PhSe)$_2$ and aimed at changing the reaction solvent to counteract the acidity.

1,2-aryl migration reaction Reaction conditions for the formation α,β-unsaturated ketones

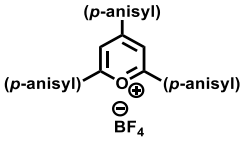
Table 21: Screening of multiple parameters for the aryl migration reaction



204b **205b** **208**



(3,5-MeO-ArSe)$_2$



TAPT

Entry	Se-Cat. [10 mol%]	Solvent [0.05 M]	Additive	Δt [h]	Conversion	NMR Yield [205b]	NMR Yield [208]	∑ NMR Yield
1	**(PhSe)$_2$**	HIFP	Li_2CO_3 (2.0 equiv)	12	100%	47%	25%	72%
2	**(PhSe)$_2$**	MeCN	Li_2CO_3 (2.0 equiv)	12	80%	19%	0%	19%
3	**(PhSe)$_2$**	HFIP	Li_2CO_3 (1.0 equiv)	12	100%	45%	23%	68%
4	**(PhSe)$_2$**	HFIP	Li_2CO_3 (4.0 equiv)	12	100%	45%	25%	70%
5	**(PhSe)$_2$**	HFIP	NEt_3 (3.0 equiv)	12	100%	10%	34%	44%
6	**(PhSe)$_2$**	HFIP	NaOH (2.0 equiv)	12	100%	11%	n.d.	11%
7	**(PhSe)$_2$**	HFIP/MeCN (1:1 V/V)		12	100%	62%	0%	62%
8	**(PhSe)$_2$**	HFIP/MeCN (1:1 V/V)	Li_2CO_3 (1.0 equiv)	12	100%	25%	11%	36%
9	**(PhSe)$_2$**	HFIP/MeCN (1:2 V/V)		12	100%	50%	0%	50%
10	**(PhSe)$_2$**	HFIP/MeCN (2:1 V/V)		12	100%	64%	0%	64%
11	**(PhSe)$_2$**	HFIP/MeCN (3:1 V/V)		12	100%	62%	0%	62%
12	**(PhSe)$_2$**	HFIP/MeCN (4:1 V/V)		12	100%	58%	0%	58%

Reactions were performed on a 0.50 mmol scale in a vial with screw cap (penetrated with cannulas for air exchange). The vial was irradiated with a blue LED (448 nm, 0.7 mA) in the cooling block setup at 19 °C under air for the given time. NMR yields were determined using 1,3-dinitrobenzene as internal standard.

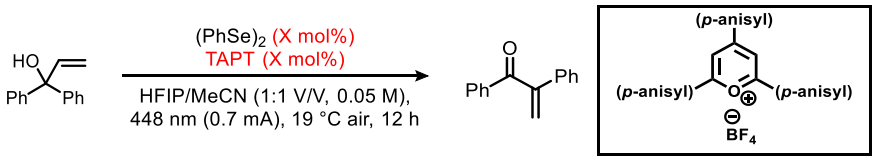
Starting by using MeCN as reaction solvent we however observed a downgrade of the reaction outcome, thereby postulating the necessity for HFIP in the reaction media. We decided to use HFIP again but then intended to affect the acidity by changing the equivalents of Li_2CO_3 (Table 21, entries 3-4) as well as using other stronger bases (Table 21, entries 5-6). Whereas the amount of Li_2CO_3 did not affect the reaction outcome at all, a significant increase of the yield for the side product **208** could be determined when using stronger bases which we attributed to the enhanced nucleophilicity of the deprotonated hexafluoroisopropylate in comparison with the protonated alcohol. A breakthrough was then achieved when instead of using additional bases, the amount of HFIP

was halved by conducting the reaction in a solvent mixture of HFIP and MeCN (Table 21, entry 7). Combinations based on other solvents (DCM, THF etc.) were also tested but no reactivity was observed either due to solubility issues of the photocatalyst or miscibility complications between the respective solvents. Also, when adding Li_2CO_3, the results deteriorated again (Table 21, entry 8) and even so the volumetric ratio of HFIP and MeCN had only minor impact but started to produce inferior results, when increasing the MeCN content or going above a 3:1 V/V HFIP/MeCN ratio (Table 21, entries 9,12).

Apart from definite progress in the reaction outcome, these experiments gave us further insight into the mechanistic progression starting with the necessity for HFIP as strong H-bonding agent[230,231] as well as the drawback originating from the use of HFIP acting as a nucleophile and thus promoting side reactivities especially in strongly basic media.

At last, we then wanted to check the impact of the catalyst loading on the reaction outcome (Table 22), where we determined that a 50% reduction of the catalyst loading likewise halved the yield for the product **205b** (Table 22, entry 1). Doubled catalyst loading on the other side only marginally affect the product formation, which was not enough for us to continue with these reaction parameters (Table 22, entry 2).

Table 22: Catalyst loading screening



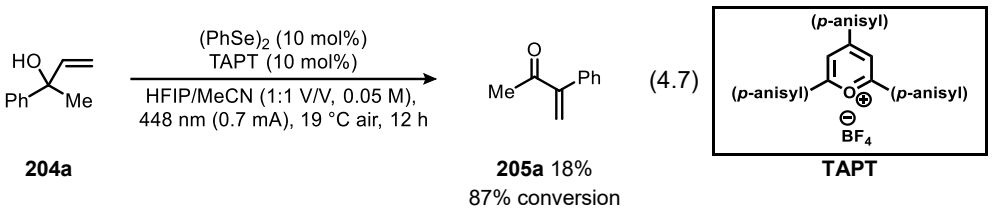
204b **205b** **TAPT**

Entry	Se-Cat.	PC	Solvent [0.05 M]	Additive	Δt [h]	Conversion	NMR Yield
1	**$(PhSe)_2$ (5 mol%)**	**TAPT (5 mol%)**	HFIP/MeCN (1:1 V/V)	-	12	90%	33%
2	**$(PhSe)_2$ (20 mol%)**	**TAPT (20 mol%)**	HFIP/MeCN (1:1 V/V)	-	12	100%	71%
3	**$(PhSe)_2$ (10 mol%)**		HFIP/MeCN (1:1 V/V)	-	12	50%	9.0%

Reactions were performed on a 0.50 mmol scale in a vial with screw cap (penetrated with cannulas for air exchange). The vial was irradiated with a blue LED (448 nm, 0.7 mA) in the cooling block setup at 19 °C under air for the given time. NMR yields were determined using 1,3-dinitrobenzene as internal standard.

In this context we then also checked the necessity for the photocatalyst which in contrast to the previous discussed project (chapter 4.2) was required here to achieve valid product formation (Table 22, entry 3). Even more interesting however was the discovery, that even without the photocatalyst we had 50% conversion of starting material which led us to the conclusion that the degradation of the starting material cannot only be attributed to oxidative processes mediated by the photocatalyst but is also fueled by other aspects of the reaction conditions. Based on this input, we then decided to test the new set of conditions on the initial aryl-alkyl vinylic alcohol **204a** (Equation 4.7) before envisioning further changes. To our disapproval however, all the adaptions had no

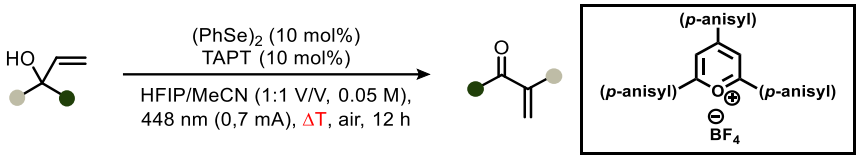
positive impact on the reaction outcome as we observed unchanged NMR yield and conversion in comparison with the initial results in Table 17 (entry 3).



204a **205a** 18%
87% conversion
TAPT

As the only difference between the substrates **204a** and **204b** is centered around the substitution pattern of the allylic alcohol, we anticipated that in the case of the biarylic substrate **204b** the migration of one Ph-group is energetically further facilitated by the mesomeric effects of the second Ph-group. As the same extent for charge stabilization cannot be allocated to the Me-group in starting material **204a** we derived at the conclusion the aryl migration in this case is higher in energy and therefore less feasible at the given temperature of 19 °C. This postulate could further on be proven as we observed a significant improvement when elevating the reaction temperature from 19 °C to a maximum of 50 °C, thereby increasing the yield from the initial 18% to 49% (Table 23, entry 2) and even to 61% when additionally doubling the catalyst loading (Table 23, entry 3). We then also checked the relevance of the temperature for the biarylic substrate **204b** and could thereby also further improve this setup by using 35 °C instead of 19 °C (Table 23, entry 4). An increasement beyond 35 °C however resulted in slightly less product formation, thus indicating temperature dependent degradation which in combination with the boiling points from the respective solvent prevented us from testing even higher temperatures.

Table 23: Temperature screening for both substrate motifs



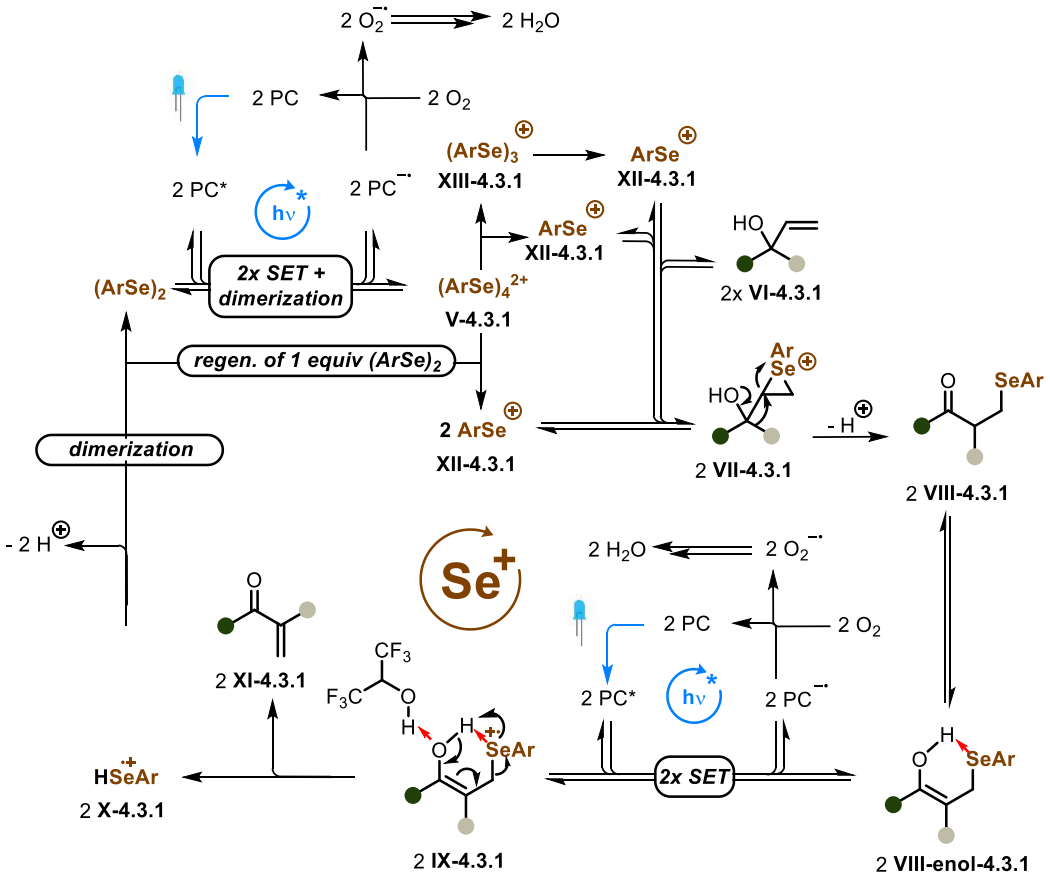
204 **205** **TAPT**

Entry	Subst.	Se-Catalyst [10 mol%]	PC [10 mol%]	ΔT	Δt [h]	Conversion	NMR Yield
1	**Ph/Me**	**$(PhSe)_2$**	**TAPT**	35 °C	12	100%	39%
2	**Ph/Me**	**$(PhSe)_2$**	**TAPT**	50 °C	12	100%	49%
3	**Ph/Me**	**$(PhSe)_2$ (20 mol%)**	**TAPT (20 mol%)**	50 °C	12	100%	61%
4	**Ph/Ph**	**$(PhSe)_2$**	**TAPT**	35 °C	12	100%	74%
5	**Ph/Ph**	**$(PhSe)_2$**	**TAPT**	50 °C	12	100%	67%
6	**Ph/Ph**	**$(PhSe)_2$ (20 mol%)**	**TAPT (20 mol%)**	35 °C	12	100%	72%

Reactions were performed on a 0.50 mmol scale in a vial with screw cap (penetrated with cannulas for air exchange). The vial was irradiated with a blue LED (448 nm, 0.7 mA) in the cooling block setup at the given temperature under air for the given time. NMR yields were determined using 1,3-dinitrobenzene as internal standard.

Having completed the reaction optimization at this point, allowed us to postulate a potential reaction mechanism based on individual results of our screening experiments, as well as corresponding

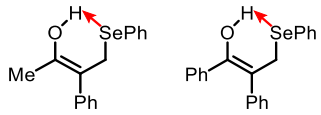
literature regarding the migration reaction,[110] and the known selenium-π-acid photoredox multicatalytic process.[32,40] According to said literature, the catalytic cycle is initiated by the photocatalytic generation of the catalytic active selenium species **V-4.3.1**, which then attacks the olefin resulting in the seleniranium-ion **VII-4.3.1** (Scheme 96) analogues to the mechanism discussed in chapter 4.1.1 (Scheme 54). The seleniranium-ion **VII-4.3.1** then undergoes the aryl migration reaction, which is as previously established, energetically depending on the substitution pattern thereby requiring higher temperature for substrates with one alkyl instead of an aryl substituent. Until this stage, the reaction progression is in direct alignment with the reports by Wu et al. who intended the isolation of the selenofunctionalized product **VIII-4.3.1**.[110] Going further however, we questioned the mode of elimination as we were presented with a ArSe-group exhibiting diminished nucleofugality upon photochemical oxidation (Se^{III}-species) when attached to a primary carbon center rather than a *tertiary* one.[109,256] As we could therefore exclude a direct oxidative elimination as presented in Scheme 54 we came up with the hypothesis that the ketone **VIII-4.3.1** forms its corresponding enol **VIII-enol-4.3.1** under the acidic conditions thereby engaging in an intramolecular H-bonding interaction enhancing the nucleofugality of the ArSe-group.[109]



Scheme 96: Mechanistical hypothesis for the 1,2-aryl migration reaction.[32,40]

Furthermore, this H-bonding arranges the molecule in a 6-membered ring like structure, which enables an electrocyclic reaction upon excitation and dimerization. By shifting 6-electrons (**IX-4.3.1**), the elimination of the ArSe-groups is thereby energetically facilitated, resulting in two equivalents

of product and two equivalents of the arylselenol-radical-cation **X-4.3.1**, which dimerize upon deprotonation to close the catalytic cycle.[109] Apart from delivering an idea as to why the ArSe-elimination is observed from a primary carbon atom, this hypothesis would also contribute to the reasoning for the reactivity difference between biarylated substrate **VI-4.3.1** and aryl-alkyl-substituted alternatives by considering the extent of enolization for each case. As already stated previously in this discussion we consider the acidic reaction media to be the major factor regarding the extent of enolization independent on the structural composition of the starting material. When however comparing the two screened substrates **204a** and **204b**, the driving force to form the enol was estimated to be significantly higher for substrate **204b**, as the formed C–C double bond is conjugated between two aromatic system rather than only one in substrate **204a** (Figure 36).



210a **210b**

Figure 36: Comparison of the possible enol forms from both screened substrates. H-bonding interaction marked in red.

As further reactivity is anticipated to be based on this isomer, the reaction kinetics are better for a structural motif in which case the enol formation is more prominent.

4.3.2. Investigation in a potential substitution process

As already stated in the previous chapter, switching to the biarylated substrate **204b**, initially revealed a new signal set (Figure 33) that remained present throughout the screening experiments until the final adjustments. A particular clean example for this side product was obtained when applying NEt_3 as a base (Table 21, entry 5) where a total of three NMR signals were observed to relate to each other by means of signal integrals (Figure 37).

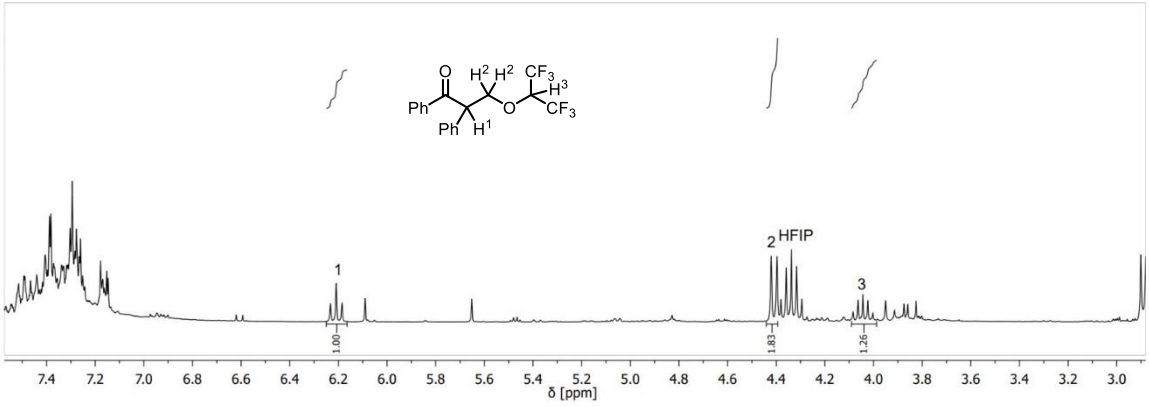
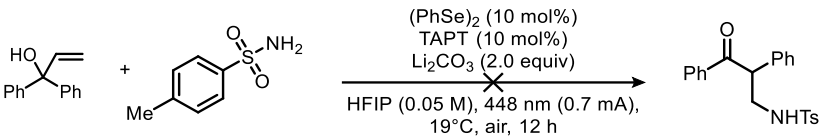


Figure 37: ^1H NMR excerpt cleanly showing the formed side product.

Based on the coupling pattern of the obtained NMR signals (triplet and doublet) as well as the respectively high chemical shifts (both above 4.00 ppm) and other reports from individual group members in unrelated projects, we assumed the signal set to originate from a side product based on the formal nucleophilic substitution of the ArSe-group with HFIP. Mechanistically, we anticipated, that said product formation occurs either as a substitution alternative to the elimination (Scheme 96) depending on the reaction conditions or displays a consecutive conjugated addition to the elimination product **205**. As independent reports made within our working group successfully exploited the substitution potential of allylic selenides under green light irradiation,[231] we began to question if a similar reactivity might be enabled by **VIII-enol-4.3.1** (Scheme 96). In this context, we then postulated that the magnitude of substitution product formation is rather based on the HFIP quantity (used as solvent), than its nucleophilicity, which is being reduced due to electron withdrawing F_3C-groups. Therefore, we initially were interested if this substitution process can be influenced with stronger nucleophiles.

Selecting the thus far best conditions for the side product formation (Table 21, entry 1), the first nucleophile we tested was *para*-toluenesulfonic amide (**211**) (Equation 4.8), performing well in the parallel developed substitution project.[231]



(4.8)

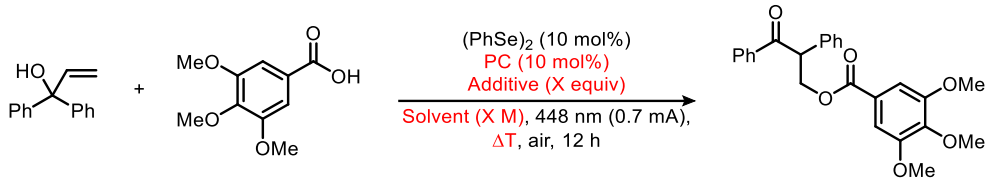
1.0 equiv **204b** *2.0 equiv* **211** **212**

Unfortunately, the only formed products based on the crude NMR, were HFIP substituted product **208** (24%) and the elimination product **205b** (40%). In a similar manner we tested 4-chloro-1H-pyrazole (successfully applied in another project),[257] even exchanging the solvent with MeCN or DCE to avoid the competing reaction with HFIP, but again no formation of the desired substitution product could be reported. A first improvement was observed using 3,4,5-trimethoxybenzoic acid (**213**) in HFIP, where we attributed the presence of a singlet relating the three MeO-groups to the already established signals of the carbon backbone (Figure 37, signal 1 and signal 2) to a successful product formation with the acid **213** (50%) as nucleophile, replacing HFIP. However, within this first experiment, we also obtained 32% of the elimination product, indicating a further need for optimization.

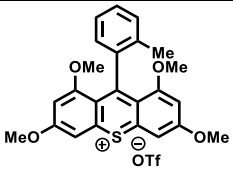
Unfortunately, none of the attempted changes resulted in any improvement to the product formation or had any impact on the formation of the elimination product (Table 24). Among the changes made, we tested various additives like the beforehand employed Li_2CO_3 (Table 24, entry 2) or additional non-nucleophilic acids to enhance the nucleofugality of the selenium residue (Table 24, entries 7-8), however only obtaining inferior results or complete absence of product formation. In the same context, we tested a different photocatalyst (Table 24, entry 3) as well a different solvent (Table 24, entry 4) and different solvent concentration (Table 24, entry 9) sadly consequently worsen the reaction outcome significantly. Also, any temperature related changes (Table 24, entries 11-12) did not improve the situation, but based on these results we could conclude that higher

temperatures are less advantageous than lower ones. Even though none of the thus far changed parameters improved our reaction concept, selected results gave us further insight into the reaction progression thereby allowing us to anticipate as to how the conditions need to be adapted to favor the substitution product formation. One of these experiments was a setup run for an extended time period (Table 24, entry 10), to see if there is a possibility that the elimination product can be considered an intermediate in the formation of the substitution product (conjugated addition reaction). By this logic we would have expected an increase in substitution product yield over extended time while the yield for the elimination product would decrease. As both substitution product and elimination product entirely vanished after 24 hours, the result remained inconclusive. However, in addition to the previous chapter about the elimination reaction, this experiment now also established the volatility of the elimination product **205**, thereby stating a further limitation of the overall reaction concept. The second important insight was gained upon the change of equivalents of the nucleophile (Table 24, entries 5-6), where deviations in both directions showed inferior yields, but in the same instance higher amounts of nucleophilic acid **213** were found to improve the ratio of substitution product to elimination product (1:1 ratio for 1.0 equiv of acid **213**, up to 2:1 for 4.0 equiv).

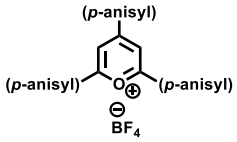
Table 24: Screening overview for the substitution Reaction using 3,4,5-trimethoxybenzoic acid (**213**)



1.0 equiv **204b** | **X equiv** **213** | **214**



TXT



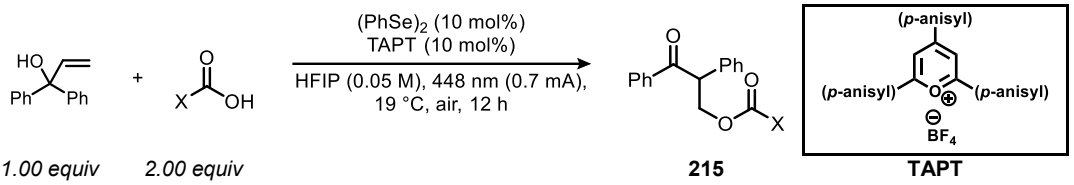
TAPT

Entry	PC [10 mol%]	Solvent [0.05 M]	Nuc [equiv]	Additive	Δt [h]	Conversion	NMR Yield [214]	NMR Yield [205b]	∑ NMR Yield
1	**TAPT**	HFIP	2.0		12	100%	50%	32%	82%
2	**TAPT**	HFIP	2.0	Li_2CO_3 (2.0 equiv)	12	100%	44%	28%	72%
3	**TXT**	HFIP	2.0		12	100%	18%	22%	40%
4	**TAPT**	MeCN	2.0		12	100%	0%	25%	25%
5	**TAPT**	HFIP	1.0		12	100%	34%	35%	69%
6	**TAPT**	HFIP	4.0		12	100%	40%	20%	60%
7	**TAPT**	HFIP	2.0	$AlCl_3$ (1.0 equiv)	12	100%	0%	0%	0%
8	**TAPT**	HFIP	2.0	TFA (0.50 equiv)	12	100%	0%	0%	0%
9	**TAPT**	HFIP (0.1 M)	2.0		12	100%	19%	1%	20%
10	**TAPT**	HFIP	2.0		24	100%	0%	4%	4%
11[a)]	**TAPT**	HFIP	2.0		12	100%	15%	3%	18%
12[b)]	**TAPT**	HFIP	2.0		12	100%	32%	17%	49%

Reactions were performed on a 0.50 mmol scale in a vial with screw cap (penetrated with cannulas for air exchange). The vial was irradiated with a blue LED (448 nm, 0.7 mA, TAPT) or a green LED (528 nm, 0.7 mA, TXT) in the cooling block setup at 19 °C under air for the given time. NMR yields were determined using 1,3-dinitrobenzene as internal standard. a) reaction was run at 30 °C. b) reaction was run at 9 °C.

Based on this observation, we concluded, that in order to achieve dominant substitution reaction, we had to finetune the acidity within the reaction system to outbalance the side reactivities (e.g. Table 24, entry 8) such as the formation of the elimination product **205**. As the application of more than four equivalents of 3,4,5-trimethoxybenzoic acid (**213**) would have resulted in solubility issues, we first checked for alternatives and found that acetic acid (pK_A = 4.76)[258] was a suitable choice whereas TFA (pK_A = 0.23)[259] in the applied quantities already resulted in a too acidic media preventing product formation (Table 25).

Table 25: Different acidic Nucleophiles

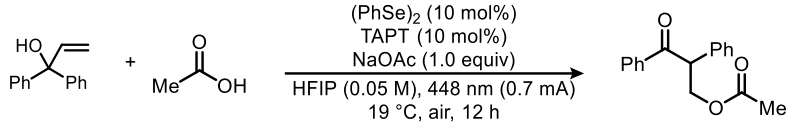


1.00 equiv **204b** *2.00 equiv* **215** **215** **TAPT**

Entry	Solvent [0.05 M]	X	Δt [h]	Conversion	NMR Yield [215]	NMR Yield [205b]	∑ NMR Yield
1	HFIP	CH_3	12	100%	50%	5%	55%
2	HFIP	CF_3	12	100%	0%	0%	0%

Reactions were performed on a 0.50 mmol scale in a vial with screw cap (penetrated with cannulas for air exchange). The vial was irradiated with a blue LED (448 nm, 0.7 mA) in the cooling block setup at 19 °C under air for the given time. NMR yields were determined using 1,3-dinitrobenzene as internal standard.

Consecutive experiments with varying amounts of acetic acid then revealed that 10 equivalents result in the best product to side product ratio (17:1) under water cooling (19 °C), whereas less equivalents significantly decreased the yield and the product ratio (1.0 equiv result in 23% elimination product and 12% substitution product). The last thing we then checked was if a buffer system based on acetic acid and a corresponding acetate salt would further improve the product formation by counteracting the rapid increase in acidity while unchanging the amount of nucleophile provided. However, among tested NaOAc and KOAc, only the first showed improvement to the reaction outcome (Equation 4.9), whereas KOAc resulted in inferior product formation.

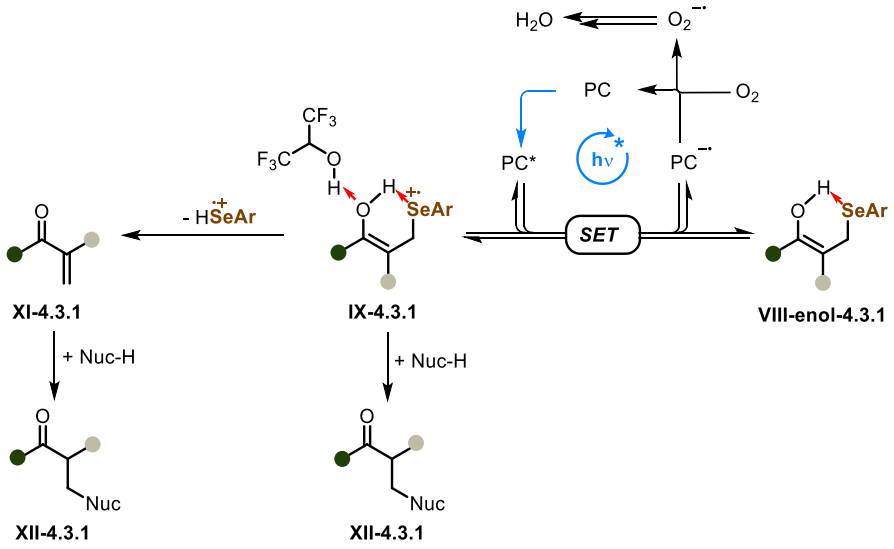


(4.9)

1.0 equiv **204b** *10 equiv* **215a** **215a** 64%

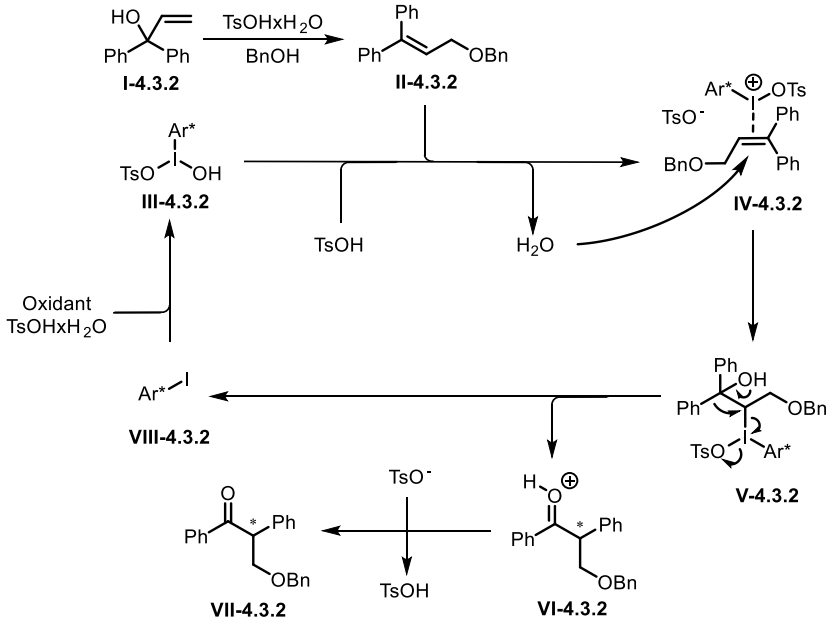
Increasing amounts of NaOAc, However, again tipped the scales towards the elimination product and also when we attempted to replace the 10 equivalents of acetic acid **215a** by stronger, non-nucleophilic acids (therefore using less amount of acid in total) such as H_2SO_4 and H_3PO_4 no improvement and mostly significant reduced yields were obtained.

As, we then unsuccessfully attempted to port the conditions over to the aryl-alkyl substrate **204a** and remained clueless as how to further affect the reaction progression, we scouted related literature and came across a publication from the Gong group developing a similar transformation using a chiral hypervalent iodine catalyst and an excess of a terminal oxidant.[260] In contrast to the reaction progression that we anticipated, being composed of the previous discussed regarding the formation of the elimination product **205** with adaptations regarding a nucleophilic attack (Scheme 97), the Gong group postulated a different reaction progression with an initial step being the acidic mediated alcohol elimination facilitated by the simultaneous attack of the given nucleophile (BnOH) (Scheme 98).



Scheme 97: Mechanistic adaptation to the previous elimination mechanism (Scheme 96) signifying the anticipated pathways for the formation of the substitution product **XII-4.3.1**.

The rearranged double bond **II-4.3.2** is then activated by the (chiral-)-iodine catalyst enabling the re-attack of the previously eliminated H_2O thereby forcing the aryl migration and the formation of the corresponding ketone **VII-4.3.2** (Scheme 98).

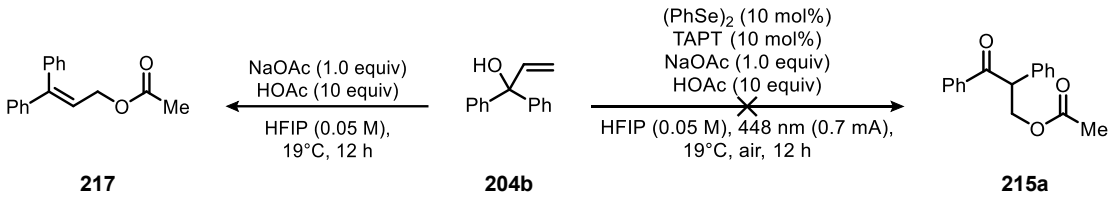


Scheme 98: Reaction mechanism described by the *Gong* group.[260]

To validate their postulation, they performed different experiments among which they also quenched their reaction after five minutes to quantitively obtain the product **II-4.3.2**. By resubmitting product **II-4.3.2** to the reaction conditions they were then able to confirm the formation of the target product **VII-4.3.2**, thereby proving its relevance in the reaction progression.[260] This intermediate further explains their observed limitation regarding the reaction scope, as the authors were only

able to convert biarylic-substrates **I-4.3.2** as in the case of monoarylated substrates **I-4.3.2** harsher (more acidic) conditions are required to enable the water elimination (**I-4.3.2** to **II-4.3.2**).[261]

Being presented with this reaction concept, we began to question if said progression could also be present in our attempted transformation and further on if this would have any implications on our thus far postulated product formation (Scheme 97). As we had independently established that our utilized selenium-catalysts show no reactivity with geminal biarylic substituted double bonds,[107] the reaction step from **II-4.3.2** to **V-4.3.2** is most likely improbable leading to the accumulation of product **II-4.3.2**. As the corresponding NMR signals for this intermediate **II-4.3.2** theoretically possess enough similarity to our postulated substitution product **215a** (one low field shifted doublet and one low field shifted triplet) we decided to repeat the early quenching experiment proposed by the Gong group. In this experiment, we obtained complete conversion of the starting material **204b** and clean formation of the above discussed NMR pattern (one doublet and one triplet), which we thus far have attributed to the substitution product **215a** (Scheme 99). In accordance with the reports by the Gong group however, we had to revise our so far made postulation and concluded that initial intended substitution was never observed.



217 **204b** **215a**

Scheme 99: Comparison between anticipated reactivity and actual reactivity.

Even though this meant that all thus far made screening results were incorrect regarding the initial false product declaration, this excursion still imposed straightforward value as it delivered an explanation towards the acidic mediated side reactivity which was also present at the beginning of the screening for the elimination reaction.

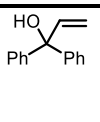
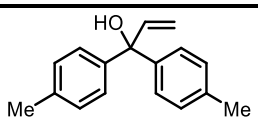
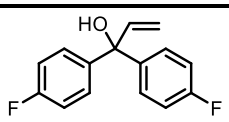
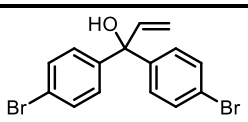
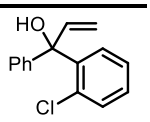
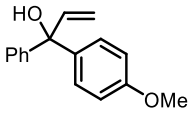
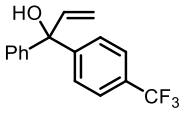
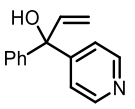
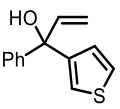
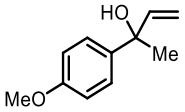
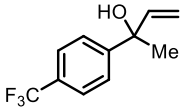
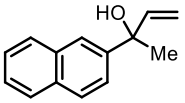
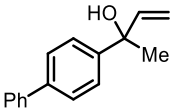
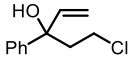
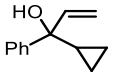
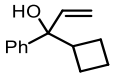
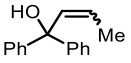
4.3.3. Synthesis of the starting materials

Having concluded the screening experiments, we continued with the synthesis of starting materials to be applied in the elimination reaction. On a positive side note compared to the other projects discussed in this work (chapter 4.1 and 4.2), the synthetic route in this case demanded less steps, only consisting of a Grignard reaction with selected ketones.[248] Said ketones were thereby reacted with commercial vinylmagnesium bromide (**202**) with the sole exception being substrate **204s** which was synthesized using prop-1-en-1-ylmagnesium bromide in order to check for reactivity implication with non-terminal double bond. Apart from that, the remaining synthesized substrates **204** can be divided into four major groups, representing different aspects that we wanted to test in the concluding migration reaction (Table 26). The compounds **204b-e** are based on symmetrically substituted ketones **218** and are merely prove of concept, whereas the substrates **204f-j** are biarylated but consist of two electronically different aryl groups aimed at taking a closer look at

migration selectivity. As said migration selectivity is postulated to be depending on the electronic nature of the arene,[110] these substrates were meant to verify this postulate in our concept, as well as delivering values to rationalize the preferred reactivity of electron rich arenes and rank it among other reports. Furthermore, this group also includes substrates **204i** and **204j** containing a heteroaromatic moiety to check their tolerance by the reaction conditions. The third group (substrates **204a/k-n**) is composed of substrates that contain a Me-group as one substituent in combination with various aromatic systems to analyze the explicit impact of the composition of the aromatic group (electronrich vs. electronpoor) on the migration tendency as well as the (degradative-) side reactivity. Concluding, the last group (substrates **204o-r**) contains substrates with varying alkyl substituents and a consistent phenyl group aimed to investigate the (steric-) impact of different alkyl chains.

Table 26: Overview of the synthesized vinylic alcohols **204**

1.0 equiv **218** | *1.1 – 2.0 equiv* **202** | **204**

 **204b** 87%	 **204c** 87%	 **204d** 89%	 **204e** 83%	 **204f** 83%
 **204g** 96%	 **204h** 33%	 **204i** 9.0%	 **204j** 67%	 **204a** 50%
 **204k** 51%	 **204l** 50%	 **204m** 40%	 **204n** 97%	 **204o (72%)**
 **204p** 63%	 **204q** 66%	 **204r** 86%	 **204s**[a] 47%, 16/10 *E/Z*	

Isolated yields reported. a) substrate was synthesized using prop-1-en-1-ylmagnesium bromide (2.0 equiv, 0.5 M in THF).

Regarding the Grignard reaction itself, we would have postulated that the product formation would correlate with the electrophilicity of the carbonyl-C-atom as well as the steric demand of the two α-substituents. As we however did not record NMR yields and the isolation protocol significantly differed in some cases, we cannot deliver a definite statement if the theoretical reactivity pattern holds true or not. A detrimental example for this difference in the workup protocol is substrate **204i**, where multiple chromatography steps had to applied in contrast to the other substrates which were obtained in good to excellent yields in several cases even without the necessity for column chromatography. Notable tendencies however are the observation that biarylated substrates **204b-j** on average record better isolated yields than the aryl-alkyl counterparts **204a** and **204k-r** indicating the unfavorable steric impact of the alkyl groups in contrast to an aryl group.

4.3.4. Reaction scope for the aryl migration reaction

We then set out to submit the starting materials **204** to our reaction conditions, where a first common observation was that upon isolation, an unknown signal set, neither related to the product nor the starting material, remained inseparable from our target compound **205**. An extreme case of this inseparable side product was obtained in the reaction of substrate **204p**, in which the analysis of the additional signal pattern allowed for the conclusion, that every product signal with the exception of the two olefinic protons (used for NMR-yield determination) was obtained twice with deviating integrals. Based on this observation we anticipated that the additional signals correspond to the initial ketone **218p**, which could further on be validated by an overlap with a therefore recorded ^{1}H NMR of cyclopropyl(phenyl)methanone (**218p**) (Figure 38).

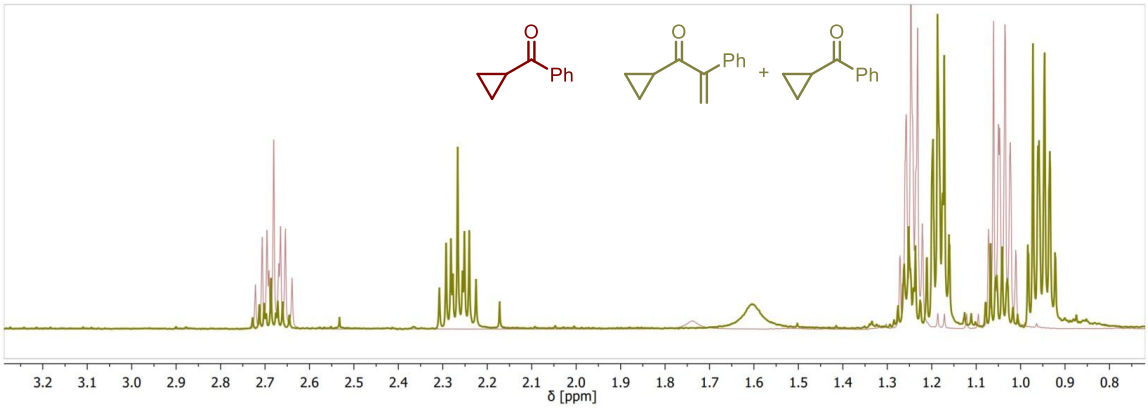
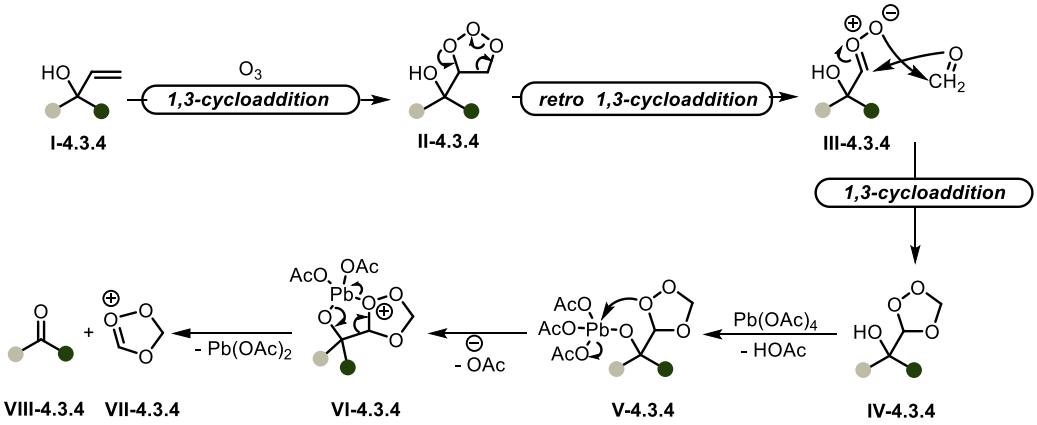


Figure 38: Excerpt of the ^{1}H NMR overlap between the initial ketone **218p** (maroon) and the product mixture **205p** (olive).

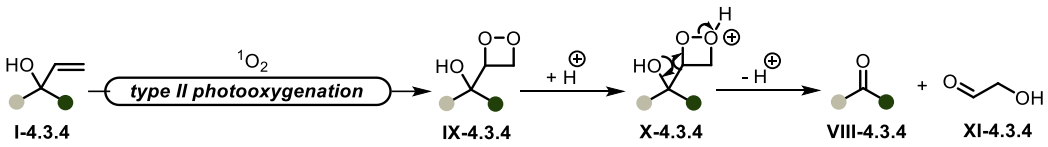
To further support this discovery, we then consolidated literature to determine if an inversion of our previously discussed Grignard reaction (chapter 4.3.3) has been reported and if we could find similarities with our photocatalytic system thereby explaining this reactivity. Among the sources we found, only the López group reported explicit conditions to drive this kind of reactivity, based on a Crigee oxidation[262] using ozone and $Pb(OAc)_4$ (Scheme 100).[263]



Scheme 100: Mechanism postulated by the López group.[263]

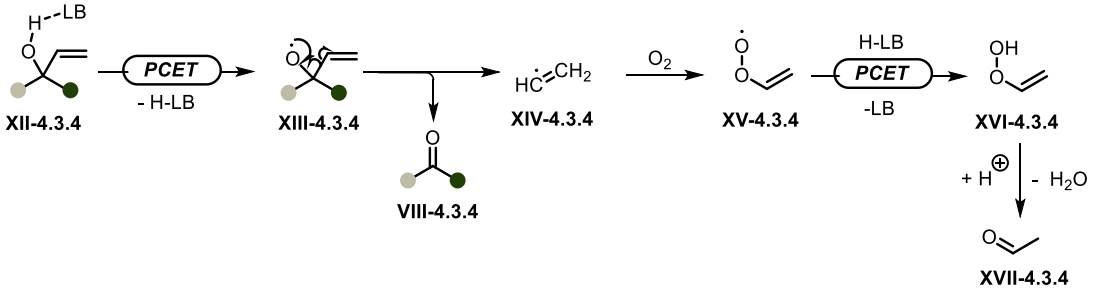
The key steps in their postulated mechanism are the formation of the secondary ozonide **IV-4.3.4** and consecutive chelation of $Pb(OAc)_4$ (structure **VI-4.3.4)**. This bicyclic arrangement **VI-4.3.4** then collapses, releasing the target ketone **VIII-4.3.4**, $Pb(OAc)_2$ and the ozonide **VII-4.3.4**, which we anticipate is further degraded by the acidic conditions, but as such not explicitly stated by the authors.

However, as we had neither O_3 nor $Pb(OAc)_4$ in our reaction, we first speculated that similar reactivity under the photocatalytic condition might be achieved with *in situ* formed $^1O_2$ performing a type II photooxygenation reaction.[264] Upon protonation in the slightly acidic media, the intermediate **X-4.3.4** could rearrange thereby cleaving off the initial ketone **VIII-4.3.4** and 2-hydroxyethanal **XI-4.3.4** as a volatile side product (Scheme 101).



Scheme 101: Speculated pathway for the regeneration of the initial ketone VIII under our reaction conditions.

We also found more generalized alternatives, based on a *PCET* involving the hydroxy group in the starting material **204** forming an *O*-centered radical.[265,266] This radical then undergoes β-scission cleaving of the most stable carbon-centered radical resulting in the target ketone **218** and a side product that depends on the reaction conditions.[266] Transferring this concept onto our reaction conditions would require the diselenide to act as a Lewis-base thus allowing for a *PCET* to generate the *O*-centered radical **XIII-4.3.4** (Scheme 102). Rearrangement of this radical would then cleave off the observed starting material ketone **VIII-4.3.4** and an ethene-radical **XIV-4.3.4** that further decomposes under the reaction conditions to volatile acetaldehyde **XVII-4.3.4**, by reaction with O_2 from the atmosphere.



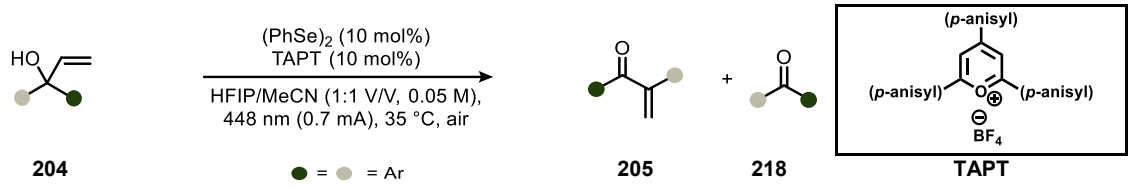
Scheme 102: Postulated reaction progression according to the β-scission mechanism. **LB =** Lewis base.

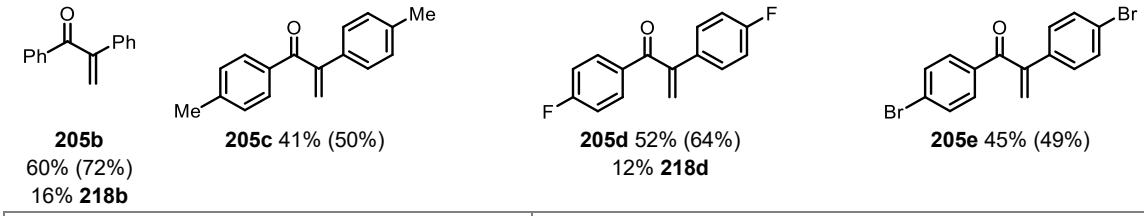
Further literature that strengthens this postulate includes a review by Ortgies et al. reporting about the application of diselenides as Lewis-bases,[23] and independent reports by the Knowles group reporting a photocatalytic generation of an *O*-centered radical by a *PCET*, although with a thiol as HAT reagent, thereby achieving β-C-scission.[265] Including the reports by the Huang group, transforming allylic alcohol **204a** to acetophenone with $Bi(OTf)_3$ as Lewis base and an *in situ* generated

Ag^{2+}-species as electron acceptor,[266] we were confident that the coalition of these individual sources validate our postulate (Scheme 102), explaining the formation of the side product **VIII-4.3.4**.

Continuing with the product scope we first applied the biarylated substrate to their respective set of conditions (Table 27), where we observed the formation of the discussed side product **218** especially for substrates incorporating electron neutral or electron poor arenes. However, regarding the postulated mechanism for the side product formation (Scheme 102) we would have anticipated the exact opposite outcome as the formation of the *O*-centered radical is declared to be a consequence of initial oxidation of the adjacent arene ring with a consecutive intramolecular *SET* from the OH-group upon simultaneous deprotonation (described by the Knowles group).[265] By this postulate, substrates **204**, with an electron rich arene should facilitate the side product formation in contrast to electron poor counterparts which is in direct contrast to our made observations. As we however, due to signal overlap in the crude NMR, were only able to report the yield for the side products **218** regarding purified material, we cannot account for the impact of deviating separability between the target product **205** and the side products **218** in each individual case, thereby affecting our final observation.

Table 27: Scope overview of the biarylated substrates





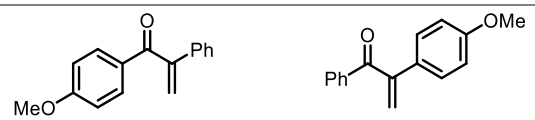
205b 60% (72%) 16% **218b**

205c 41% (50%)

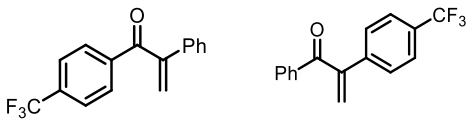
205d 52% (64%) 12% **218d**

205e 45% (49%)

205f-1 48% (70%) **+ 205f-2** – (0%)



205g-1 – (0%) **+ 205g-2** 23% (25%)



205h-1 44% (61%) **+ 205h-2** – (0%) 12% **218h**

205i-1 – (0%) **+ 205i-2** – (0%) 13% conversion

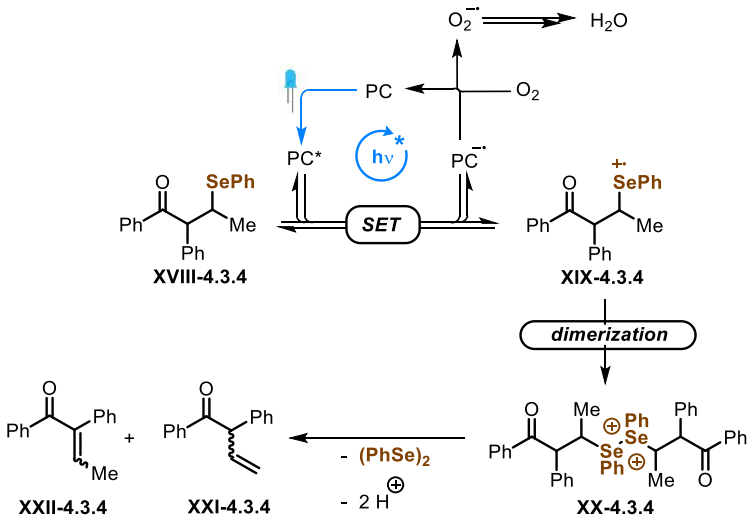
205j-1 – (<5%) **+ 205j-2** – (<5%)

205s-1 – (0%) **+ 205s-2** – (0%)

Reactions were performed on a 0.50 mmol scale. NMR yield is given in parentheses. 1,3-dinitrobenzene (0.50 equiv) was used as internal standard. Yield for side product only determined after workup. Reactions were run until full conversion if not stated otherwise.

Regardless of this observed side product formation, we obtained overall (NMR-) yields in the range of 5-70% and even more interesting, a remarkable selectivity of the aryl-migration, where in all experiments with two different arene systems, exclusively formation of one product could be determined in the crude NMR. The observed selectivity corresponds to the preferred migration of the more electron rich arene (e.g. products **205f-1**, **205g-2**, **205h-1**) which is in accordance with the mechanistic postulation made by Wu et al. (Scheme 95) as well as the results obtained by the same group.[110] Overall unsuccessful product formation however was observed in the cases of the heteroaromatic substrates **204i** and **204j** yielding on average less than 5% NMR yield and in the case of **204i** even only 13% of conversion. Whereas the low yields for product **205i** could therefore be attributed to the deactivation of the diselenide due to known non-bonding interactions with the basic nitrogen from the pyridine ring,[267] we based the low product yield (at full conversion) for the thiophene substrate **204j** on dominant side reactivity (polymerization) stemming from the oxidation of the thiophene ring (≈ +1.6 eV vs. SCE in MeCN).[268] In similar fashion, we also attributed the comparatively low (NMR) yield for substrate **205g-2** (25%) to side reactivity, but in this case postulating enhanced (photocatalytic-) degradation (c.f. discussions in chapter 4.3.1 and 4.3.2), facilitated by the electron rich nature of the anisyl ring. Conveniently, the opposite behavior was observed by substrate **205h-1**, where in accordance to our expectation, the electron poor F_3C-arene imposes enhanced stability towards (photocatalytic-) degradation (starting material **204h** and product **205h-1**), resulting in a more superior (NMR-) yield of 70%.

Mechanistically more surprising however was the unsuccessful formation of neither the conjugated product **205s-1** nor the terminal alkene **205s-2** as we anticipated a facilitated elimination of the PhSe-group from the functionalized intermediate **XVIII-4.3.4** due to the additional abstractable protons and the carbon atom, the PhSe-group is attached to.[109,256] Based on these assumptions we anticipated a reaction progression according to the initial experiments reported by the Breder group (Scheme 23), with a direct oxidation and dimerization of the intermediate **XVIII-4.3.4** without the necessity for the enol **VIII-enol-4.3.2** (Scheme 96) formation (Scheme 103).

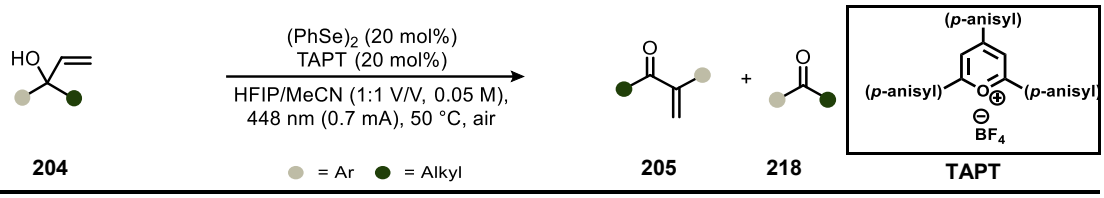


Scheme 103: Potential mechanistic adaption for the substrate **204s** based on known literature.[32]

As however no product formation was observed (full conversion) and implications regarding the formation of the selenofunctionalized intermediate **XVIII-4.3.4** (Scheme 96) by the additional Me-group were excluded, the facilitated reaction progression as described in Scheme 103 was declared not operational. Instead, we then concluded that the additional Me-group enhances the formation of the side products **218** (Scheme 102) by facilitating the formation of the hypothesized cleaved off radical **XIV-4.3.4**.

The persistent presence of this side reactivity was then further confirmed when we submitted the aryl-alkyl substrates to the respective set of conditions, where again said side products **218** were obtained in limited cases (Table 28).

Table 28: Overview of the aryl-alkyl substrates **205**



204 **205** **218** **TAPT**

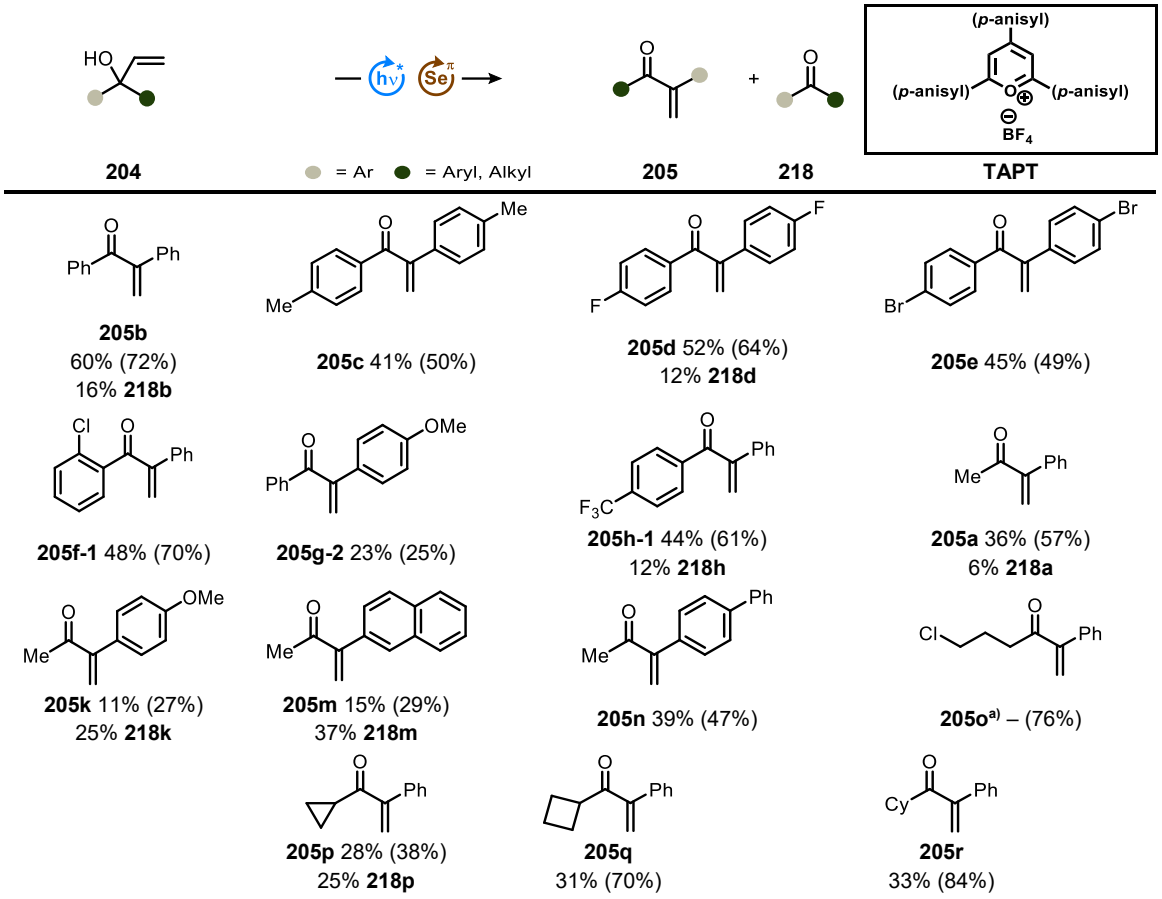
205a 36% (57%) 6% **218a**	**205k** 11% (27%) 25% **218k**	**205l** – (0%)	**205m** 15% (29%) 37% **218m**	**205n** 39% (47%)
205o[a] – (76%)	**205p** 28% (38%) 25% **218p**	**205q** 31% (70%)	**205r** 33% (84%)	

Reactions were performed on a 0.50 mmol scale. NMR yield is given in parentheses. 1,3-dinitrobenzene (0.50 equiv) was used as internal standard. a) degradation upon column chromatography. Yield for side product only determined after workup. Reaction run until full conversion if not stated otherwise.

In similarity to the biarylic substrates **205** discussed prior, we also anticipated a higher degree of side reactivity regarding more facile oxidized arene substituents, which can indeed be observed when comparing substrates **205a**, **205k** and **205m** regarding the oxidation potential of their (isolated) aromatic rings.[269] Nonetheless, also in this list of substrates, we came to the conclusion that the observation of the side product **218** is majorly affected by the workup necessity as exemplified by substrates **205p**, **205q** and **205r** were we (based on the postulation for the side product **218** formation in Scheme 102), expected similar degrees of side reactivity. As we however obtained isolated material for the substrates **205q** and **205r** even though all three substrates (**204p**, **204q**, **204r**) incorporate the same arene system (Ph-group), we assumed that the increasing steric demand of the carbocycle substituent resulted in improved separability. The steric demand of the adjacent alkyl chain was furthermore found to have a positive influence on the NMR yields (38% (**205p**) to 84% (**205r**)), which we explained by the additional driving force for the aryl migration through resolving steric tension in the starting material **204**. On the contrary, the electron density of the arene substituent appeared to have an even more detrimental impact on the (NMR-) yield, although only negative consequences were observed in both extremes (**205k** and **205l**). Whereas

we already established that arenes with lower oxidation potential result in increased side product formation and more facile degradation by the reaction conditions, the incorporation of an electron poor arene **204l** appears to constitute an energetic inhibition concerning the formation of the Wheland-Complex **III-4.3.1** (Scheme 95) thereby preventing any product formation. The latter observation also explains the observed migration selectivity in the case of the biarylic substrates **204h**. In summary, we were able to develop a reaction concept that allows for a 1,2-aryl migration with a thus far unprecedented range of application based on easily obtained allylic alcohols **204** as starting materials. Furthermore, the developed conditions include no additional (stochiometric) reagents apart from the two catalysts and uses air as a terminal oxidant resulting in water as the sole byproduct. The products are obtained in moderate to good yields regardless of the substitution pattern (biarylic vs. aryl-alkyl) and excellent migration selectivity regarding biarylic substrates with exclusive migration of the more electron rich arene (Table 29). A thus far unavoidable drawback however is the formation of the side products **218,** resulting in an isolation issue that has to be addressed further to enhance the competitiveness of our method among other protocols allowing the synthesis for α,β-unsaturated ketones **205**.

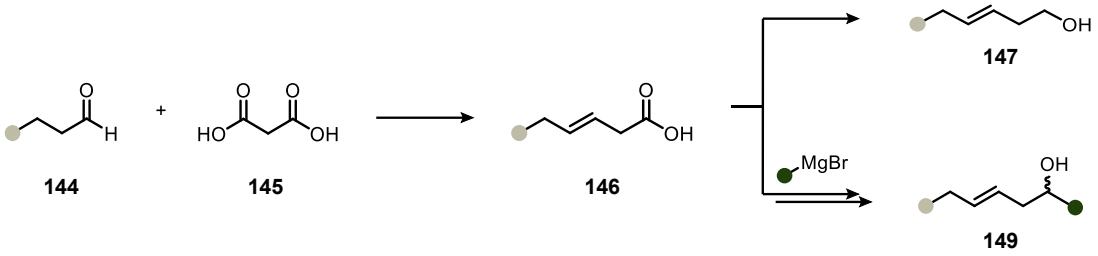
Table 29: Overview of the successful aryl migration reactions



Reactions were performed on a 0.50 mmol scale. NMR yield is given in parentheses. 1,3-dinitrobenzene (0.50 equiv) was used as internal standard. a) degradation upon column chromatography. Reactions were run until full conversion if not stated otherwise.

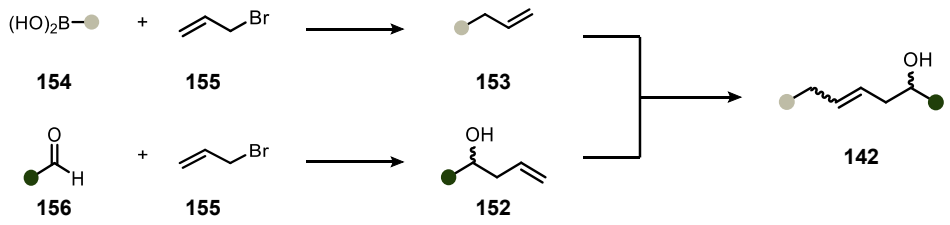
5 Summary and Outlook

The herein presented work is a continuation and likewise an expansion of the preliminary reports on selenium-π-acid catalyzed functionalizations published by the Breder group.[14,31–33,41] Based on their latest reports about the aerobic allylation of alcohols[33] and the multi selenium-π-acid/photoredox catalyzed lactonization reaction[32] the question was raised, if the scope of oxygen nucleophile could be extended to organic carbonates as a non protic species. A large portion of the development of the reaction conditions such as catalyst loading, catalyst combinations, solvent and additive changes, was already discussed in the corresponding Master's Thesis[190] and now finalized in terms of testing selective further additives and catalysts as well as the optimization of the overall reaction setup allowing for temperature control and constant irradiation over time. Concluding the development of the reaction conditions, the major task then was to find a suitable synthetic route to allow for the synthesis of a broad variety of substrates. During the investigations, we were able to implement two different procedures each serving a different purpose. The first route was designed to deliver *E*-selective substrates **147** and **149** for mechanistic investigations (Scheme 104), but unfortunately saw extreme limitation regarding commercial available starting materials.



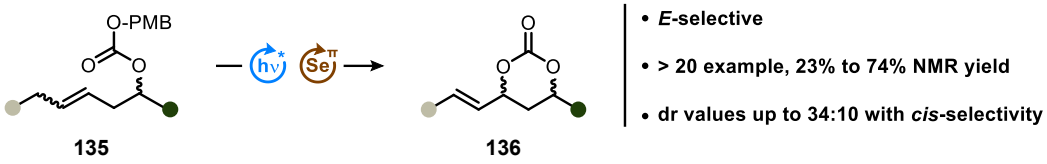
Scheme 104: Abbreviated compilation of the *E*-selective starting material synthesis.

The alternative developed procedure did not result in selective double bond formation, however the overall procedure was significantly shorter and a larger number of viable starting materials **152** and **153** were commercially available (Scheme 105).



Scheme 105: Abbreviated overview for the unselective starting material synthesis.

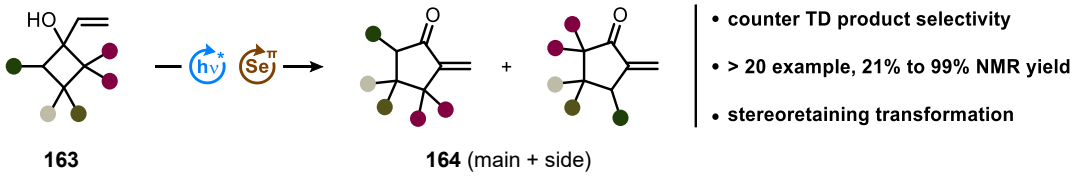
Products from both reaction were then converted into the corresponding acyclic carbonates using a modified Steglich-Esterification and pre-synthesized 1H-imidazole-1-carboxylate (**143**) as coupling partner (Table 7). Consecutive application of the acyclic carbonates **135** in our developed reaction conditions enabled the desired transformation in moderate to good yields with in general better yields for secondary substrates **135** (Scheme 106 and Table 10).



Scheme 106: Summary for the developed cyclic carbonate **136** synthesis.

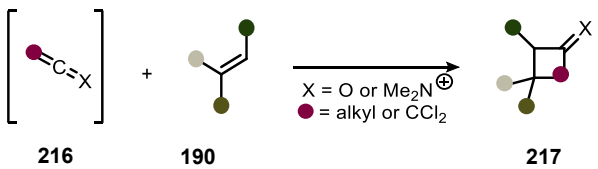
Following these results, we then presented a mechanistic hypothesis explaining the preferred formation of the *cis*-isomer with a Zimmerman-Traxler model, displaying the steric tensions present in the transition state leading to the *trans*-isomer (Figure 14). We then also analyzed the impact of the initial π-bond configuration on the dr value in the products, where we came to the conclusion (based on a Zimmerman-Traxler like model) that a *Z*-configured olefin based on steric tension partially favors the formation of the *trans*-product, whereas the *E*-isomer exclusively favors the *cis*-product.[203]

Moving away from oxygen based nucleophiles, the second topic then evolved around selenium-π-acid mediated rearrangement reactions, more explicitly the ring enlargement reaction of vinylic cyclobutanols **163** (Scheme 107).



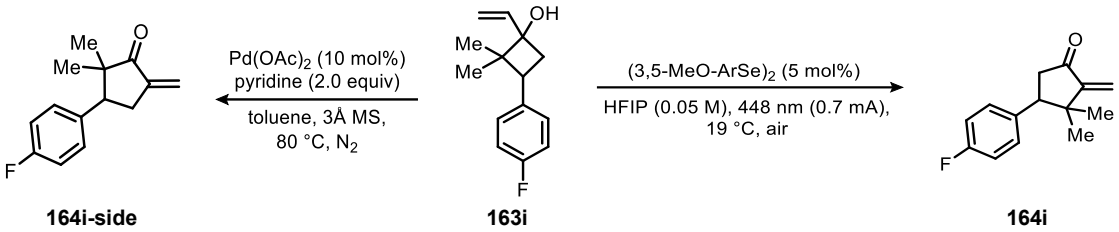
Scheme 107: Investigated reaction concept for the ring enlargement reaction.

As the racemic reaction conditions were already extensively investigated by fellow coworkers, the first task then was to adapt the process and turning it into a chiral procedure, which remained unsuccessful as we were not able to generally separate the diastereomers of the starting material **163** and thereby could not avoid substrate controlled reactivity. Moving further, the focus was then set on the synthesis of the starting material **163**, which concluded in individual reaction procedures serving different needs, as no general procedure tolerating a broad variety of substrates and exhibiting the needed selectivity was found. Apart from specific reactions aimed at the selective generation of certain scaffolds (Scheme 78, Scheme 83 and Scheme 85) a rather general employed method was a [2+2]-cycloaddition between an *in situ* generated ketene **216** and a suitable alkene **190** (Scheme 108).



Scheme 108: Generalized reaction concept for the [2+2]-cycloaddition.

Submitting the obtained cyclobutanones **181** to a general applicable Grignard reaction using literature conditions gave rise to a broad variety of vinyl cyclobutanols **163** which in turn could then be used in the ring expansion protocol. The final ring expansion reaction then delivered the target products **164** in good to excellent yields and thus far not observed selectivity concerning the ring expansion process. Whereas alternate Pd catalyzed reported methods preferably insert the methylene unit in the less steric demanding position,[10,186,187] we discovered that our selenium-π-acid catalyzed process results in the exact opposite product formation which was explicitly determined by a coworker using **163i** as starting material (Scheme 109).

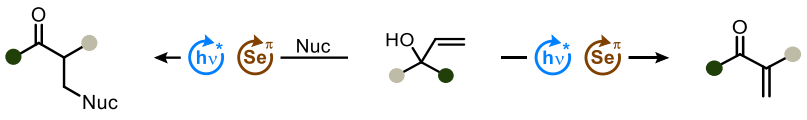


164i-side **163i** **164i**

Scheme 109: Control experiment performed by a coworker to exemplify the selectivity difference.

As of now, the project is in its final stages with a few extra substrates being prepared in addition to what is presented in this work. The majority of resources is however still focused on the confirmation of the reaction mechanism where colleagues observed the irrelevance of the photocatalyst, thereby extensively changing the thus far postulated reaction (Scheme 23).

The last project covered in this work then was the acyclic adaption of the ring expansion reaction, where we in addition to a time intensive reaction optimization study, also at first anticipated that we have the potential to further derivatize the reaction by allowing for nucleophilic substitution rather than elimination (Scheme 110).



218 **204** **205**

Scheme 110: Two anticipated reaction concepts based on the same starting material **204**.

As the initial evidence for the substitution product **218** was declared wrong later on, we kept the focus on the elimination process with starting materials **204** simply obtained by a Grignard reaction with commercially available ketones Fehler! Verweisquelle konnte nicht gefunden werden.. With a small substrate scope thereby readily available (Table 29) we were able to verify our postulations regarding the preferred migration selectivity for arenes with higher electron density, as well as the reactivity differences between versatile substituted allylic alcohols **204** (biarylic vs. aryl-alkyl), resulting in slightly altered reaction conditions in each case. Nonetheless with our developed conditions we obtained a thus far unprecedented number of products **205** (regarding this synthesis method), in moderate to good yields, with the major drawbacks being an observed side reactivity that transfers the starting material **204** back to the starting ketone **218**, as well as other degradative

processes affecting both the starting material **204** and the product **205**. Whereas we were positive to have found a viable mechanism for the formation of the ketone **218**, explicit experiments would have to be conducted to verify its accuracy and further on preventing it.

6 Experimental Section

6.1 General remarks

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 (if not stated otherwise). Common solvents (EtOAc, PE, Et_2O and DCM) were distilled before further use. Dry solvents were obtained from commercial sources or taken from an MBraun solvent purification system (THF, toluene, Et_2O, DCM). Celite 545 gebr. from Fluka, was used for filtration if mentioned in the procedure.

Irradiation experiments were performed at λ = 465 nm using commercially available blue LED strips (2835 super bright SMD-LEDs, 100 diodes/m, 400 lm/m, 24 V, 12 W) or in a manufactured cooling block with bottom irradiation using the following LEDs:

465 nm, 700 mA, LT-1164 Seoul 3.5 W Star

448 nm, 700 mA, LT-1013 Luxeon REBEL

448 nm, 700 mA, LXML-PR01-0500 Luxeon REBEL

528 nm, 700 mA, LT-1966 OSRAM Oslon SSL 80

All mounted on a cooling block.

The temperature was controlled using a Julabo CORIO CD-601F and CORIO CD-200F filled with a 1:1 V/V mixture of ethylene glycol and water.

Thin-layer chromatography (TLC): MACHEREY-NAGEL, TLC plates Alugram® Sil G/UV254. R_f values are reported from covered substance distance to covered solvent distance. Visualization of the developed chromatogram was performed by fluorescence quenching at 254 nm and staining with ceric ammonium molybdate, *para*-anisaldehyde or potassium permanganate. Chromatography: Separations were carried out on Acros Silica 60 (0.035-0.70 mm, 70-230 mesh ASTM) using forced flow or automated using a puriFlash 5.020 system with UV-Vis (200-800 nm) and ELS detection. Empty cartridges were filled manually with the silica mentioned above.

Melting points were determined on a Krüss M5000 melting point meter. Values were noted without mathematical correction.

IR (ATR) spectra was recorded on an Agilent Technologies Cary 630 FT-IR spectrometer.

High resolution mass spectrometry (HRMS) was recorded on an Agilent Q-TOF 6540 UHD or Jeol Accu TOF GCX and ThermoQuest Finnigan TSQ 7000. *In situ* mass spectrometry was performed on a Advion CMS Expression L System with and APCI ionization source.

NMR (^{1}H, ^{13}C) spectra were recorded at 300 MHz (^{1}H), 75 MHz (^{13}C) respectively, on a Bruker Avance 300 or at 400 MHz (^{1}H), 101 MHz (^{13}C), 376 MHz (^{19}F), 128 MHz (^{11}B), 61 MHz (^{2}H) on a Bruker Avance 400, a Bruker Avance III HD 400, or at 600 MHz (^{1}H), 151 MHz (^{13}C) on a Bruker Avance III HD 600 spectrometer in chloroform-*d*, if not otherwise specified. Chemical shifts (δ) are

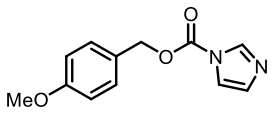
given in ppm. Multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, h = sextet, hept = septet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dddd = doublet of doublet of doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, ddt = doublet of doublet of triplet, dtt = doublet of triplet of triplet, dtd = doublet of triplet of doublet, dtq = doublet of triplet of quartet, dqd = doublet of quartet of doublet, dddt = doublet of doublet of doublet of triplet, dtdd = doublet of triplet of doublet of doublet, ddq = doublet of doublet of quartet, ddddd = doublet of doublet of doublet of doublet of doublet, td = triplet of doublet, tt = triplet of triplet, tq = triplet of quartet, tdd = triplet of doublet of doublet, tdt = triplet of doublet of triplet, ttd = triplet of triplet of doublet, qd = quartet of doublet, qt = quartet of triplet, qq = quartet of quartet, qdd = quartet of doublet of doublet, dp = doublet of quintet, pd = quintet of doublet).

6.2 Project “synthesis of 1,3-dioxan-2-ones”

Analytic data for this project are featured in the following literature: ”*Eur. J. Org. Chem.* **2023**, *26*, e202201180 (1 of 5)“.[203]

6.2.1. Synthesis of starting materials

4-Methoxybenzyl 1*H*-imidazole-1-carboxylate (143)



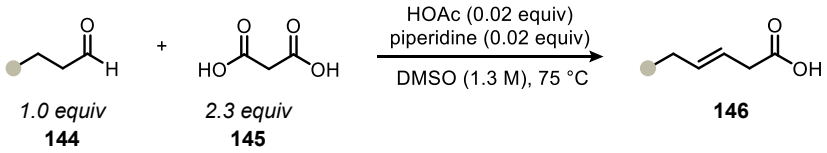
A round flask was equipped with CDI (5.0 g, 31 mmol, 2.0 equiv), cooled to 0 °C and dissolved in THF (60 mL, 0.5 M). After the slow addition of (4-methoxyphenyl)methanol (2.1 g, 15 mmol, 1.0 equiv) the yellow suspension was stirred at 0 °C for 1 h. The crude mixture was partially concentrated. The concentrated liquid phase was filtrated over a column containing silica gel with Et_2O as solvent to yield 3.4 g (15 mmol, 99%) of 4-methoxybenzyl 1*H*-imidazole-1-carboxylate as a colorless oil.

*The product was synthesized using the following procedure.[217]

*The product exhibited increased degradation, therefore no HRMS could be recorded.

TLC: R_f = 0.48 (Et_2O). **IR** (ATR): ṽ [cm^{-1}] = 3131, 3004, 2960, 2840, 1752, 1614, 1513, 1469, 1398, 1316, 1282, 1238, 1167, 1033, 1003, 828, 768. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 8.13 (t, *J* = 1.1 Hz, 1H), 7.45–7.31 (m, 3H), 7.04 (dd, *J* = 1.7, 0.8 Hz, 1H), 6.96–6.89 (m, 2H), 5.35 (s, 2H), 3.82 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 160.5, 137.3, 130.9, 130.7, 130.2, 126.2, 117.3, 114.3, 70.0, 55.5.

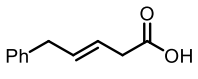
General Procedure A-1: Knoevenagel condensation[32]



Scheme 111: Reaction equation for the Knoevenagel condensation.

Malonic acid (2.3 equiv) was dissolved in DMSO (1.3 M) in a 3-neck round flask, equipped with reflux condenser and dropping funnel. To the solution were added HOAc (0.02 equiv) and piperidine (0.02 equiv) and the mixture was heated to 65 °C. At this temperature the respective aldehyde (1.0 equiv) was added via the dropping funnel and the reaction was stirred at 75 °C for the given reaction time. The reaction was quenched by the addition of H_2O and the solution was extracted with Et_2O (3x) and washed with brine. After drying over Na_2SO_4 or $MgSO_4$ and concentration, purification by column chromatography was applied if necessary to give the title compound.

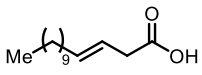
(*E*)-5-Phenylpent-3-enoic acid



According to **General Procedure A-1**: malonic acid (35 g, 0.34 mol, 2.2 equiv) was diluted in DMSO (250 mL, 1.3 M) and HOAc (0.18 g, 2.9 mmol, 0.02 equiv), piperidine (0.27 mg, 3.1 mmol, 0.02 equiv) and phenylpropanal (20 g, 0.15 mol, 1.0 equiv) were added. Reaction time 3 h. Extracted Et_2O (10x 100 mL), washed with brine (1x 30 mL), dried over Na_2SO_4. Isolated yield: 23 g (0.13 mmol, 85%).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3027, 2904, 1703, 1495, 1405, 1219, 969, 746, 697. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.37–7.24 (m, 2H), 7.24–7.14 (m, 3H), 5.84–5.70 (m, 1H), 5.63 (dtt, *J* = 15.1, 6.9, 1.2 Hz, 1H), 3.40 (d, *J* = 6.5 Hz, 2H), 3.13 (dq, *J* = 6.6, 1.1 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 178.2, 139.9, 133.9, 128.5, 128.5, 126.2, 122.3, 38.9, 37.7. **HRMS** (EI) calcd. for $[C_{11}H_{12}O_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 176.0832, found 176.0833.

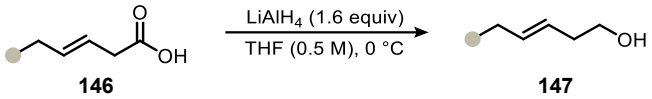
(*E*)-Tetradec-3-enoic acid



According to **General Procedure A-1**: malonic acid (13 g, 0.12 mol, 2.1 equiv) was diluted in DMSO (92 mL, 1.3 M) and HOAc (0.06 mL, 1.1 mmol, 0.02 equiv), piperidine (0.10 mL, 1.0 mmol, 0.02 equiv) and dodecanal (11 g, 57 mmol, 1.0 equiv) were added. Reaction time 4 h. Extracted Et_2O (3x 100 mL), washed with brine (1x 50 mL), dried over Na_2SO_4. Eluting with PE/EtOAc 9:1 + 1V% TFA. Isolated yield: 9.5 g (42 mmol, 74%).

TLC: R_f = 0.31 (PE/EtOAc 9:1 + 1V% TFA). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2922, 2851, 1692, 1469, 1428, 1293, 1241, 965, 928. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.69–5.38 (m, 2H), 3.17-2.97 (m, 2H), 2.03 (q, *J* = 6.6 Hz, 2H), 1.26 (s, 17H), 0.96-0.77 (m, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 177.6, 135.7, 120.6, 37.7, 32.5, 31.9, 29.6, 29.5, 29.4, 29.2, 29.1, 22.7, 14.1. **HRMS** (ESI) calcd. for $[C_{14}H_{27}O_2]^+$ $(M+H)^+$: m/z = 227.2006, found 227.2008.

General Procedure A-2: $LiAlH_4$ reduction[204]

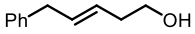


146 **147**

Scheme 112: Reaction equation for the $LiAlH_4$ reduction.

A dried Schlenk flask was equipped with $LiAlH_4$ (1.6 equiv) and suspended in dry THF (0.5 M). The suspension was cooled to 0 °C and the corresponding acid from reaction **A-1** (1.0 equiv) was added dropwise to minimized gas evaporation. The mixture was allowed to warm to rt. After complete conversion was determined by TLC analysis, the mixture was again cooled to 0 °C and quenched with H_2O and 1.0 M NaOH. After stirring for 1 h, the grey precipitate was filtered off, rinsed with THF, and concentrated in vacuum to give the title compound.

(*E*)-5-Phenylpent-3-en-1-ol (147a)

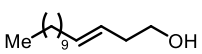


According to **General Procedure A-2**: $LiAlH_4$ (2.7 g, 71 mmol, 1.6 equiv) was diluted in dry THF (140 mL, 0.5 M) and (*E*)-5-phenylpent-3-enoic acid (8.0 g, 46 mmol, 1.0 equiv) diluted in dry THF (40 mL) was added. Reaction time 2 h. Isolated yield: 6.9 g (43 mmol, 94%).

*Data are in accordance with cited literature.[270]

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3325, 2926, 1603, 1495, 1454, 1044, 969, 742, 697. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.36–7.24 (m, 2H), 7.29–7.13 (m, 4H), 5.73 (dtt, *J* = 14.7, 6.6, 1.3 Hz, 1H), 5.58–5.40 (m, 1H), 3.66 (t, *J* = 6.3 Hz, 2H), 3.37 (d, *J* = 6.7 Hz, 2H), 2.31 (dtd, *J* = 7.4, 6.3, 1.1 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 140.5, 132.6, 128.5, 128.5, 127.5, 126.1, 62.1, 39.1, 35.9. **HRMS** (EI) calcd. for $[C_{11}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 162.1045, found 162.1337.

(*E*)-Tetradec-3-en-1-ol (147b)

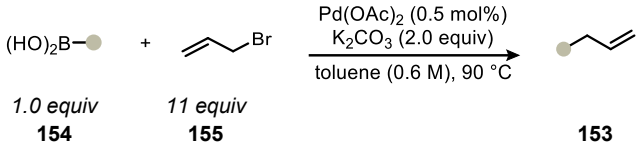


According to **General Procedure A-2**: $LiAlH_4$ (2.3 g, 60 mmol, 1.4 equiv) was diluted in dry THF (100 L, 0.6 M) and (*E*)-tetradec-3-enoic acid (9.5 g, 42 mmol, 1.0 equiv) diluted in dry THF (10 mL) was added. Reaction time 20 h. Isolated yield: 6.6 g (31 mmol, 74%).

*Data are in accordance with cited literature.[271]

IR (ATR): v [cm^{-1}] = 3332, 2922, 2855, 1782, 1465, 1047, 969. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.56 (dtt, *J* = 15.6, 6.5, 1.2 Hz, 1H), 5.37 (dtt, *J* = 15.2, 6.9, 1.3 Hz, 1H), 3.62 (t, *J* = 6.2 Hz, 2H), 2.33–2.19 (m, 2H), 2.01 (q, *J* = 6.6 Hz, 2H), 1.26 (s, 17H), 0.94–0.80 (m, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 134.5, 125.6, 118.2, 62.0, 36.0, 32.7, 31.9, 29.7, 29.5, 29.5, 29.4, 29.2, 22.7, 14.2. **HRMS** (EI) calcd. for $[C_{14}H_{28}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 212.2140, found 212.2159.

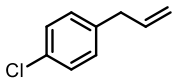
General procedure B-1: Suzuki coupling[210]



Scheme 113: Reaction equation for the Suzuki coupling.

A dried Schlenk tube was equipped with the respective boronic acid (1.0 equiv), $Pd(OAc)_2$ (0.5 mol%) and K_2CO_3 (2.0 equiv). Dry Toluene (0.6 M) and allylbromide (11 equiv) were added and the suspension was heated up to 90 °C and stirred at that temperature for the respective time. The mixture was filtered, washed with Et_2O, and concentrated to afford the title compound.

1-Allyl-4-chlorobenzene (153a)

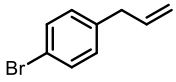


According to **General Procedure B-1**: (4-chlorophenyl)boronic acid (8.1 g, 52 mmol, 1.0 equiv), $Pd(OAc)_2$ (60 mg, 0.27 mmol, 0.5 mol%), K_2CO_3 (14 g, 0.10 mol, 2.0 equiv) were dissolved in dry toluene (100 mL, 0.5 M) and allylbromide (44 mL, 0.51 mol, 10 equiv) was added. Reaction time 21 h. Isolated yield: 4.7 g (31 mmol, 60%).

*Data are in accordance with cited literature.[272]

IR (ATR): ṽ [cm^{-1}] = 3079, 3004, 2982, 2907, 1640, 1491, 1431, 1252, 1088, 1018, 917, 835, 798. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.32–7.21 (m, 2H), 7.17–7.05 (m, 2H), 6.04–5.83 (m, 1H), 5.10 (t, *J* = 1.5 Hz, 1H), 5.05 (dq, *J* = 7.7, 1.6 Hz, 1H), 3.36 (dt, *J* = 6.6, 1.5 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 138.5, 136.9, 131.8, 130.0, 128.5, 116.2, 39.5. **HRMS** (EI) calcd. for $[C_9H_9Cl]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 152.0393, found 152.0385.

1-Allyl-4-bromobenzene (153b)

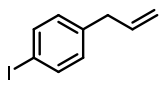


According to **General Procedure B-1**: (4-bromophenyl)boronic acid (8.2 g, 41 mmol, 1.0 equiv), $Pd(OAc)_2$ (46 mg, 0.21 mmol, 0.5 mol%), K_2CO_3 (11 g, 80 mmol, 2.0 equiv) were dissolved in dry toluene (80 mL, 0.5 M) and allylbromide (5.8 g, 48 mmol, 1.2 equiv) was added. Reaction time 17 h. Isolated yield: 2.9 g (15 mmol, 36%).

*Data are in accordance with cited literature.[273]

IR (ATR): ṽ [cm^{-1}] = 3079, 2982, 2911, 2363, 1640, 1487, 1431, 1405, 1074, 1014, 917, 835, 794. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.47–7.36 (m, 2H), 7.12–7.01 (m, 2H), 6.04–5.81 (m, 1H), 5.14–5.00 (m, 2H), 3.34 (dd, *J* = 6.6, 1.5 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 139.0, 136.8, 131.5, 130.4, 119.9, 116.3, 39.6. **HRMS** (EI) calcd. for $[C_9H_9Br]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 195.9888, found 195.9887.

1-Allyl-4-iodobenzene (153c)

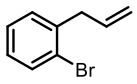


According to **General Procedure B-1**: (4-iodophenyl)boronic acid (5.1 g, 20 mmol, 1.0 equiv), $Pd(OAc)_2$ (24 mg, 0.10 µmol, 0.5 mol%), K_2CO_3 (5.7 g, 41 mmol, 2.0 equiv) were dissolved in dry toluene (40 mL, 0.5 M) and allylbromide (17 mL, 0.20 mmol, 9.6 equiv) was added. Reaction time 19 h. Isolated yield: 4.1 g (17 mmol, 82%).

*Data are in accordance with cited literature[273]

IR (ATR): ṽ [cm^{-1}] = 3075, 3004, 2978, 2904, 2837, 1640, 1484, 1431, 1398, 1059, 1006, 917, 831, 790. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.68–7.53 (m, 2H), 7.01–6.87 (m, 2H), 6.02–5.81 (m, 1H), 5.10 (t, *J* = 1.5 Hz, 1H), 5.05 (dq, *J* = 7.5, 1.5 Hz, 1H), 3.33 (dd, *J* = 6.7, 1.5 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 139.7, 137.4, 136.7, 130.7, 116.3, 91.2, 39.7. **HRMS** (EI) calcd. for $[C_9H_9I]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 243.9749, found 243.9748.

1-Allyl-2-bromobenzene (153d)

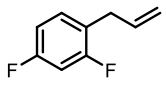


According to **General Procedure B-1**: (2-bromophenyl)boronic acid (9.0 g, 45 mmol, 1.0 equiv), $Pd(OAc)_2$ (50 mg, 0.22 µmol, 0.5 mol%), K_2CO_3 (12 g, 89 mmol, 2.0 equiv) were dissolved in dry toluene (80 mL, 0.6 M) and allylbromide (41 mL, 0.50 mol, 11 equiv) was added. Reaction time: 19 h. Isolated yield: 4.9 g (25 mmol, 56%).

*Data are in accordance with cited literature.[274]

IR (ATR): ṽ [cm^{-1}] = 3064, 3012, 2982, 2919, 2855, 1640, 1469, 1439, 1260, 1025, 995, 917, 749, 667. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.57–7.52 (m, 1H), 7.32–7.17 (m, 2H), 7.08 (ddd, *J* = 8.0, 6.2, 2.9 Hz, 1H), 5.98 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.16–5.02 (m, 2H), 3.51 (dt, *J* = 6.5, 1.5 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 139.4, 135.6, 132.8, 130.4, 127.8, 127.5, 124.6, 116.6, 40.2. **HRMS** (EI) calcd. for $[C_9H_9Br]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 195.9883, found 195.9885.

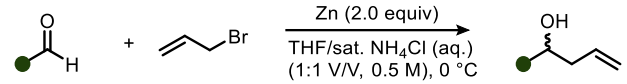
1-Allyl-2,4-difluorobenzene (153e)



According to **General Procedure B-1**: (2,4-difluorophenyl)boronic acid (7.6 g, 48 mmol, 1.0 equiv), $Pd(OAc)_2$ (54 mg, 0.24 mmol, 0.5 mol%), K_2CO_3 (13 g, 96 mmol, 2.0 equiv) were dissolved in dry toluene (97 mL, 0.5 M) and allylbromide (42 mL, 0.49 mmol, 10 equiv) was added. Reaction time 20 h. Isolated yield: 3.3 g (22 mmol, 82%).

IR (ATR): ṽ [cm^{-1}] = 3012, 2971, 2941, 1737, 1506, 1364, 1215, 1141, 910, 734. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.14 (q, *J* = 7.9 Hz, 1H), 6.86–6.73 (m, 2H), 5.93 (ddt, *J* = 16.8, 10.3, 6.5 Hz, 1H), 5.13–4.99 (m, 2H), 3.36 (d, *J* = 6.5 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 162.5 (dd, *J* = 81.9, 11.8 Hz, C-F), 159.6, 135.6, 131.1 (dd, *J* = 9.5, 6.4 Hz, C-F), 122.7 (dd, *J* = 16.1, 3.8 Hz, C-F), 116.3, 111.0 (dd, *J* = 20.9, 3.8 Hz, C-F), 103.6 (t, *J* = 25.6 Hz, C-F), 32.4. **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 113.9 (d, *J* = 6.8 Hz, F-F), - 114.8 (d, *J* = 6.8 Hz, F-F) **HRMS** (EI) calcd. for $[C_9H_8F_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 154.0594, found 154.0601.

General Procedure B-2: Barbier-type reaction[211]

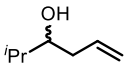


1.0 equiv **156** *2.0 equiv* **155** **152**

Scheme 114: Reaction equation for the Barbier-type reaction.

Allylbromide (2.0 equiv) was diluted in THF (1.0 M), zinc dust (2.0 equiv) was added, and the suspension was cooled to 0 °C. To the suspension was added the respective aldehyde (1.0 equiv) and dropwise over 30 min NH_4Cl sat. aq. (equal volume to THF). The reaction was allowed to warm to rt and stirred for the given time. To the solution was added H_2O and 1.0 M HCl until the white precipitate was completely dissolved and the organic phase was extracted with Et_2O. After concentration the residue was purified by column chromatography to give the title compound.

2-Methylhex-5-en-3-ol (152a)

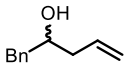


According to **General Procedure B-2**: allylbromide (34 g, 0.28 mol, 2.1 equiv), zinc dust (18 g, 0.28 mmol, 2.1 equiv) were diluted in THF (140 mL, 1.0 M) and 2-methylpropanal (9.5 g, 0.13 mol, 1.0 equiv) was added. Reaction time 23 h. Extracted with Et_2O (2x 100 mL). Partial concentration due to volatility. Isolated yield: 18 g as a mixture of 66wt% 2-methylhex-5-en-3-ol (12 g, 0.11 mmol, 80%) and 34wt% THF.

*Data are in accordance with cited literature.[275]

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3452, 2967, 1700, 1640, 1469, 1435, 1394, 1264, 1111, 1074, 992, 917, 865, 813, 705. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.84 (dddd, *J* = 16.9, 10.6, 8.1, 6.2 Hz, 1H), 5.23-5.07 (m, 2H), 3.43 (ddt, *J* = 8.8, 5.5, 3.4 Hz, 1H), 2.33 (dddt, *J* = 15.5, 6.3, 3.4, 1.4 Hz, 1H), 2.22–2.04 (m, 1H), 1.84-1.62 (m, 2H), 0.94 (dd, *J* = 6.8, 4.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 135.5, 118.2, 75.8, 68.8 (THF), 38.9, 33.2, 25.7 (THF), 18.8, 17.7. **HRMS** (APCI) calcd. for $[C_7H_{13}O]^{+\cdot}$ $(M\text{-}H)^{+\cdot}$: m/z = 113.0961, found 113.0963.

1-Phenylpent-4-en-2-ol (152b)



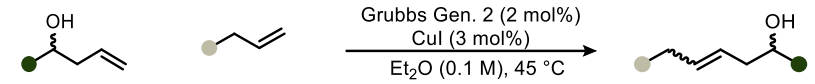
According to **General Procedure B-2**: allylbromide (20 g, 0.17 mol, 1.9 equiv), zinc dust (11 g, 0.17 mmol, 1.9 equiv) were diluted in THF (84 mL, 1.0 M) and phenylacetaldehyde (10 g, 83 mmol, 1.0 equiv) was added. Reaction time 15 h. Extracted with Et_2O (3x 100 mL). Eluting with PE/EtOAc 50:1 Isolated yield: 4.7 g (29 mmol, 35%).

*Data are in accordance with cited literature.[276]

TLC: R_f = 0.10 (PE/EtOAc 50:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3563, 3407, 3068, 3030, 2922, 1640, 1603, 1495, 1454, 1077, 1033, 999, 917, 746, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.14 (m, 5H), 5.98–5.75 (m, 1H), 5.25–5.09 (m, 2H), 3.89 (ttd, *J* = 7.9, 4.8, 3.3 Hz, 1H), 2.91–2.65

(m, 2H), 2.43–2.13 (m, 2H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 138.5, 134.8, 129.6, 128.7, 126.6, 118.3, 71.8, 43.4, 41.3. **HRMS** (APCI) calcd. for $[C_{11}H_{18}NO]^+$ $(M+NH_4)^+$: m/z = 180.1383, found 180.1383.

General procedure B-3: cross coupling metathesis[212]



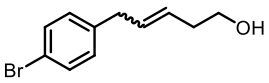
1.0 – 3.0 equiv **152** *1.0 – 3.0 equiv* **153** **142**

Scheme 115: Reaction equation for the Cross Coupling Metathesis.

The product from reaction **A-1** or commercial alternatives (1.0 equiv), the product from reaction **A-2** or commercial alternatives (1.0–3.0 equiv), Grubbs second generation catalyst (Grubbs Gen. 2) (2 mol%) and CuI (3 mol%) were dissolved in Et_2O (0.1 M) and refluxed at 45 °C for the respective time. The mixture was cooled to r.t., and volatiles were removed under reduced pressure. The residue was purified by column chromatography to give the title compound.

*This procedure represents the case if A-2 (or its commercial derivative) is volatile if not, the equivalents with respect to A-1 are inverted.

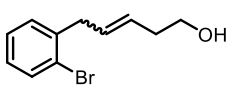
5-(4-Bromophenyl)pent-3-en-1-ol (142a)



According to **General Procedure B-3**: 1-allyl-4-bromobenzene (2.5 g, 13 mmol, 1.0 equiv), but-3-en-1-ol (2.8 g, 38 mmol, 3.0 equiv), Grubbs Gen. 2 (0.22 g, 0.25 mmol, 2 mol%) and CuI (79 mg, 0.42 mmol, 3 mol%) were dissolved in Et_2O (120 mL, 0.1 M). Reaction time 3 h. Eluting with PE to PE/EtOAc 4:1. Isolated yield: 1.8 g (7.2 mmol, 57%) as a mixture of isomers (49:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 4:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 1487, 1070, 1014, 969, 906, 885, 801, 727. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.46–7.35 (m, 2H, *E/Z*), 7.12–7.00 (m, 2H, *E/Z*), 5.75–5.61 (m, 1H, *E/Z*), 5.60–5.39 (m, 1H, *E/Z*), 3.68 (2xt, *J* = 6.4 Hz, 2H, *E/Z*), 3.38 (d, *J* = 7.6 Hz, 2H, *Z*), 3.31 (d, *J* = 6.6 Hz, 2H, *E*), 2.50–2.36 (m, 2H, *Z*), 2.38–2.23 (m, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 139.7 (*Z*), 139.5 (*E*), 132.2 (*Z*) 131.8 (*Z*), 131.7 (*E*), 131.5 (*E*), 131.5 (*E*), 130.7 (*Z*), 130.2 (*E*), 130.1 (*E*), 129.0 (*Z*), 128.6 (*Z*), 128.1 (*E*), 127.0 (*Z*), 126.8 (*Z*), 119.8 (*E*), 62.2 (*Z*), 62.0 (*E*), 38.4 (*E*), 35.9 (*E*), 33.0 (*Z*), 30.8 (*Z*). **HRMS** (EI) calcd. for $[C_{11}H_{13}BrO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 240.0150, found 240.0140.

5-(2-Bromophenyl)pent-3-en-1-ol (142b)

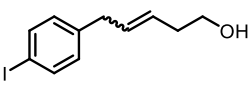


According to **General Procedure B-3**: 1-allyl-2-bromobenzene (4.7 g, 24 mmol, 1.0 equiv), but-3-en-1-ol (5.2 g, 72 mmol, 3.0 equiv), Grubbs Gen. 2 (0.40 g, 0.47 mmol, 2 mol%) and CuI (0.14 g, 0.72 mmol, 3 mol%) were dissolved

in Et_2O (200 mL, 0.1 M). Reaction time 5 h. Eluting with PE/EtOAc 4:1. Isolated yield: 3.1 g (13 mmol, 54%) as a mixture of isomers (44:10 *E/Z*).

TLC: R_f = 0.22 (PE/EtOAc 4:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3347, 2930, 1778, 1469, 1439, 1025, 969, 749. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.54 (dd, *J* = 7.9, 1.3 Hz, 1H, *E/Z*), 7.29–7.18 (m, 2H, *E/Z*), 7.07 (ddd, *J* = 7.9, 6.7, 2.4 Hz, 1H, *E/Z*), 5.75–5.65 (m, 1H, *E/Z*), 5.62–5.53 (m, 1H, *Z*), 5.47 (dtt, *J* = 15.5, 7.0, 1.5 Hz, 1H, *E*), 3.71 (t, *J* = 6.5 Hz, 2H, *Z*), 3.65 (t, *J* = 6.3 Hz, 2H, *E*), 3.56–3.52 (m, 2H, *Z*), 3.48 (dd, *J* = 6.5, 1.3 Hz, 2H, *E*), 2.53–2.40 (m, 2H, *Z*), 2.31 (dtd, *J* = 7.3, 6.2, 1.2 Hz, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 139.8 (*E/Z*), 132.8 (*E*), 132.8 (*Z*), 130.6 (*E*), 130.4 (*E*), 130.0 (*Z*), 129.7 (*Z*), 128.3 (*E/Z*), 127.8 (*E*), 127.8 (*Z*), 127.6 (*E*), 127.2 (*Z*), 124.5 (*E*), 110.0 (*Z*), 62.3 (*Z*), 61.9 (*E*), 39.2 (*E*), 36.0 (*E*), 34.1 (*Z*), 31.1 (*Z*). **HRMS** (EI) calcd. for $[C_{11}H_{13}BrO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 240.0150, found 240.0140.

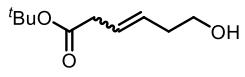
5-(4-Iodophenyl)pent-3-en-1-ol (142c)



According to **General Procedure B-3**: 1-allyl-4-iodobenzene (3.9 g, 16 mmol, 1.0 equiv), but-3-en-1-ol (3.5 g, 48 mmol, 3.0 equiv), Grubbs Gen. 2 (0.27 g, 0.32 mmol, 2 mol%) and CuI (91 mg, 0.48 µmol, 3 mol%) were dissolved in Et_2O (150 mL, 0.1 M). Reaction time 4 h. Eluting with PE/EtOAc 4:1. Isolated yield: 2.4 g (8.5 mmol, 53%) as a mixture of isomers (51:10 *E/Z*).

TLC: R_f = 0.22 (PE/EtOAc 4:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3321, 2878, 1484, 1424, 1398, 1044, 969, 831, 794, 708. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.68–7.52 (m, 2H, *E/Z*), 6.94 (dd, *J* = 7.5, 5.4 Hz, 2H, *E/Z*), 5.67 (dtt, *J* = 14.3, 6.5, 1.3 Hz, 1H, *E/Z*), 5.59–5.40 (m, 1H, *E/Z*), 3.68 (2xt, *J* = 6.4 Hz, 2H, *E/Z*), 3.38 (d, *J* = 7.4 Hz, 2H, *Z*), 3.30 (d, *J* = 6.6 Hz, 2H, *E*), 2.43 (q, *J* = 7.0 Hz, 2H, *Z*), 2.37–2.23 (m, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 140.2 (*E/Z*), 137.5 (*Z*), 137.5 (*E*), 131.7 (*E*), 130.6 (*E/Z*), 130.4 (*Z*), 128.1 (*E*), 126.9 (*Z*), 91.1 (*E/Z*), 62.2 (*Z*), 62.0 (*E*), 38.6 (*E*), 35.9 (*E*), 33.1 (*Z*), 30.8 (*Z*). **HRMS** (EI) calcd. for $[C_{11}H_{13}IO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 288.0007, found 288.0011.

***tert*-Butyl 6-hydroxyhex-3-enoate (142d)**

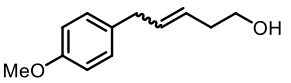


According to **General Procedure B-3**: *tert*-butyl but-3-enoate (3.8 g, 27 mmol, 1.0 equiv), but-3-en-1-ol (5.8 g, 81 mmol, 3.0 equiv), Grubbs Gen. 2 (0.46 mg, 0.54 mmol, 2 mol%) and CuI (0.16 g, 0.82 mmol, 3 mol%) were dissolved in Et_2O (250 mL, 0.1 M). Reaction time 24 h. Eluting with PE/EtOAc 6:1. Isolated yield: 2.8 g (15 mmol, 56%) as a mixture of isomers (52:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 6:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3421, 2978, 2933, 1730, 1368, 1293, 1256, 1148, 1051, 969. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.00–6.75 (m, 1H, *Z*), 5.86–5.40 (m, 1H *Z* + 2H *E*), 3.66 (dd, *J* = 7.6, 4.5 Hz, 2H, *E/Z*), 3.04 (dd, *J* = 6.7, 0.8 Hz, 2H, *Z*), 2.97 (dd, *J* = 6.6, 1.0 Hz, 2H, *E*), 2.39–2.18 (m, 2H, *E/Z*), 1.46 (2xs, 9H, *E/Z*). **^{13}C NMR** (75 MHz, Chloroform-*d*):

δ [ppm] = 147.1 (*E/Z*), 130.1 (*E/Z*), 125.8 (*E/Z*), 123.5 (*E/Z*), 118.1 (*E/Z*), 80.7 (*E/Z*), 61.7 (*E/Z*), 39.3 (*E/Z*), 35.9 (*E/Z*), 28.1 (*E/Z*). **HRMS** (APCI) calcd. for $[C_{10}H_{22}NO_3]^+$ $(M+NH_4)^+$: m/z = 204.1594, found 204.1595.

5-(4-Methoxyphenyl)pent-3-en-1-ol (142e)

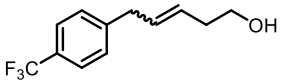


According to **General Procedure B-3**: 4-allylanisole (1.0 g, 6.8 mmol, 1.0 equiv), but-3-en-1-ol (1.4 g, 20 mmol, 2.9 equiv), Grubbs Gen. 2 (0.11 g, 0.13 mmol, 2 mol%) and CuI (42 mg, 0.22 mmol, 3 mol%) were dissolved in Et_2O (68 mL, 0.1 M). Reaction time 19 h. Eluting with PE/EtOAc 4:1. Isolated yield: 0.59 g (3.1 mmol, 45%) as a mixture of isomers (45:10 *E/Z*).

*Data are in accordance with cited literature.[270]

TLC: R_f = 0.12 (PE/EtOAc 4:1). **IR** (ATR): ṽ [cm^{-1}] = 3358, 2937, 2907, 2837, 1610, 1513, 1465, 1301, 1245, 1178, 1036, 969, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.17–7.04 (m, 2H, *E/Z*), 6.89-6.78 (m, 2H, *E/Z*), 5.70 (dtt, *J* = 14.7, 6.6, 1.3 Hz, 1H, *E/Z*), 5.58–5.38 (m, 1H, *E/Z*), 3.79 (2xs, 3H, E/Z), 3.68 (2xt, *J* = 6.4 Hz, 2H, *E/Z*), 3.38 (d, *J* = 7.8 Hz, 2H, *Z*), 3.30 (d, *J* = 6.7 Hz, 2H, *E*), 2.51-2.38 (m, 2H, *Z*), 2.30 (dtd, *J* = 7.4, 6.3, 1.1 Hz, 2H, *E*). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 206.5 (*E/Z*), 157.9 (*E/Z*), 135.0 (*E/Z*), 133.0 (*E*), 132.5 (*Z*), 129.4 (*E*), 129.2 (*Z*), 127.1 (*E/Z*), 113.9 (*Z*), 113.9 (*E*), 62.1 (*E*), 59.5 (*Z*), 55.3 (*E/Z*), 38.2 (*E*), 35.9 (*E*), 35.8 (*Z*), 34.2 (*Z*). **HRMS** (EI) calcd. for $[C_{12}H_{16}O_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 192.1150, found 192.1140.

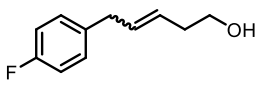
5-(4-(Trifluoromethyl)phenyl)pent-3-en-1-ol (142f)



According to **General Procedure B-3**: 1-allyl-4-(trifluoromethyl)benzene (2.0 g, 11 mmol, 1.0 equiv), but-3-en-1-ol (1.6 g, 22 mmol, 2.1 equiv), Grubbs Gen. 2 (0.18 g, 0.21 mmol, 2 mol%) and CuI (65 mg, 0.34 mmol, 3 mol%) were dissolved in Et_2O (110 mL, 0.1 M). Reaction time 19 h. Eluting with PE to PE/EtOAc 9:1. Isolated yield: 0.82 g (3.6 mmol, 34%) as a mixture of isomers (46:10 *E/Z*).

TLC: R_f = 0.10 (PE/EtOAc 9:1). **IR** (ATR): ṽ [cm^{-1}] = 3347, 2993, 1617, 1416, 1323, 1162, 1118, 1066, 1021, 969, 849. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.54 (d, *J* = 8.0 Hz, 2H, *E/Z*), 7.29 (d, *J* = 7.8 Hz, 2H, *E/Z*), 5.70 (dtt, *J* = 16.4, 6.7, 1.3 Hz, 1H, *E/Z*), 5.63–5.48 (m, 1H, *E/Z*), 3.71 (t, *J* = 6.5 Hz, 2H, *Z*), 3.67 (t, *J* = 6.3 Hz, 2H, *E*), 3.49 (d, *J* = 7.4 Hz, 2H, *Z*), 3.42 (d, *J* = 6.7 Hz, 2H, *E*), 2.45 (h, *J* = 6.5 Hz, 2H, *Z*), 2.32 (qd, *J* = 6.4, 1.3 Hz, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.6 (*E/Z*), 131.2 (*E*), 130.1 (*Z*), 128.8 (*E*), 128.6 (*Z*), 128.6 (*E*), 128.3 (*Z*), 127.3 (*E/Z*), 125.7 (*E/Z*), 125.4 (q, *J* = 3.8 Hz, C-F, *E/Z*), 123.0 (*E/Z*), 62.2 (*Z*), 62.0 (*E*), 38.9 (*E*), 35.9 (*E*), 33.4 (*Z*), 30.8 (*Z*). **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = -62.9 (s, *E/Z*). **HRMS** (EI) calcd. for $[C_{12}H_{13}F_3O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 230.0918, found 230.0915.

5-(4-Fluorophenyl)pent-3-en-1-ol (142g)

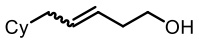


According to **General Procedure B-3**: 1-allyl-4-fluorobenzene (5.3 g, 39 mmol, 1.0 equiv), but-3-en-1-ol (7.8 g, 0.11 mol, 2.8 equiv), Grubbs Gen. 2 (0.62 g, 0.74 mmol, 2 mol%) and CuI (0.21 g, 1.1 mmol, 3 mol%) were dissolved in Et_2O (250 mL, 0.2 M). Reaction time 22 h. Eluting with PE/EtOAc 6:1. Isolated yield: 3.6 g (20 mmol, 52%) as a mixture of isomers (50:10 *E/Z*).

*Data are in accordance with cited literature[270]

TLC: R_f = 0.12 (PE/EtOAc 6:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3340, 2930, 1603, 1510, 1431, 1223, 1156, 1047, 969, 824. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.20–7.06 (m, 3H, *E/Z*), 7.04–6.90 (m, 2H, *E/Z*), 5.69 (dtt, *J* = 15.8, 6.7, 1.2 Hz, 1H, *E/Z*), 5.58–5.39 (m, 1H, *E/Z*), 3.68 (2xt, *J* = 6.4 Hz, 2H, *E/Z*), 3.41 (d, *J* = 7.5 Hz, 2H, *Z*), 3.33 (d, *J* = 6.7 Hz, 2H, *E*), 2.51–2.37 (m, 2H, *Z*), 2.38–2.24 (m, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 132.3 (*E/Z*), 129.8 (d, *J* = 7.8 Hz, C-F, *E/Z*), 127.7 (*E/Z*), 115.2 (d, *J* = 21 Hz, C-F, *E/Z*), 62.1 (*E/Z*), 38.3 (*E/Z*), 35.9 (*E/Z*). **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 118.0 (s, *E*), - 118.1 (s, *Z*). **HRMS** (EI) calcd. for $[C_{11}H_{13}FO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 180.0950, found 180.0948.

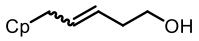
5-Cyclohexylpent-3-en-1-ol (142h)



According to **General Procedure B-3**: allylcyclohexane (5.5 g, 44 mmol, 1.0 equiv), but-3-en-1-ol (6.4 g, 89 mmol, 2.0 equiv), Grubbs Gen. 2 (0.55 g, 0.88 mmol, 2 mol%) and CuI (0.26 g, 1.4 mmol, 3 mol%) were dissolved in Et_2O (220 mL, 0.1 M). Reaction time 20 h. Eluting with PE/EtOAc 6:1 and PE/EtOAc 12:1. Isolated yield: 1.8 g (10 mmol, 24%) as a mixture of isomers (41:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 6:1) and 0.06 (12:1 PE/EtOAc). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3317, 2922, 2851, 1446, 1044, 969, 731. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.61–5.49 (m, 1H, *E/Z*), 5.47–5.26 (m, 1H, *E/Z*), 3.71–3.55 (m, 2H, *E/Z*), 2.40–2.20 (m, 2H, *E/Z*), 2.02–1.85 (m, 2H, *E/Z*), 1.77–1.56 (m, 6H, *E/Z*), 1.36–1.06 (m, 4H, *E/Z*), 0.99–0.76 (m, 2H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 132.6 (*E*), 132.5 (*E*) 131.7 (*Z*), 131.6 (*Z*), 126.8 (*E*), 125.6 (*Z*), 62.2 (*Z*), 62.0 (*E*), 40.7 (*E)*, 38.2 (*Z*), 37.9 (*E*), 36.0 (*E*), 35.1 (*Z*), 33.1 (*E/Z*), 30.9 (*Z*), 26.5 (*E*), 26.5 (*Z*), 26.3 (*E/Z*). **HRMS** (EI) calcd. for $[C_{11}H_{20}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 168.1514, found 168.1512.

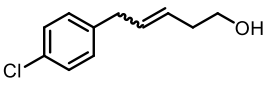
5-Cyclopentylpent-3-en-1-ol (142i)



According to **General Procedure B-3**: allylcyclopentane (4.9 g, 45 mmol, 1.0 equiv), but-3-en-1-ol (6.6 g, 91 mmol, 2.1 equiv), Grubbs Gen. 2 (0.76 g, 0.89 mmol, 2 mol%) and CuI (0.25 g, 1.3 mmol, 3 mol%) were dissolved in Et_2O (300 mL, 0.1 M). Reaction time 20 h. Eluting with PE to PE/EtOAc 100:1. Isolated yield: 3.7 g (24 mmol, 54%) as a mixture of isomers (34:10 *E/Z*).

TLC: R_f = 0.18 (PE/EtOAc 100:1). **IR** (ATR): ṽ [cm^{-1}] = 3336, 2945, 2866, 1947, 1722, 1633, 1450, 1044, 969. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.62–5.49 (m, 1H, *E/Z*), 5.45–5.28 (m, 1H, *E/Z*), 3.63 (2xt, *J* = 6.3 Hz, 2H, *E/Z*), 2.28 (2xq, *J* = 6.6 Hz, 2H, *E/Z*), 2.14–1.96 (m, 2H, *E/Z*), 1.92–1.37 (m, 8H, *E/Z*), 1.11 (dddd, *J* = 12.2, 10.5, 6.2, 2.3 Hz, 2H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 133.8 (*E*), 132.8 (*Z*), 126.1 (*E*), 125.1 (*Z*), 62.4 (*Z*), 62.0 (*E*), 40.3 (*Z*), 39.9 (*E*), 39.1 (*E/Z*), 36.0 (*E/Z*), 33.4 (*E/Z*), 32.3 (*Z*), 32.2 (*E*), 30.9 (*Z*), 30.9 (*E*), 25.1 (*Z*), 25.1 (*E*). **HRMS** (EI) calcd. for $[C_{10}H_{16}]^{+\cdot}$ $(M\text{-}H_2O)^{+\cdot}$: m/z = 136.1247, found 136.1283.

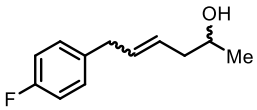
5-(4-Chlorophenyl)pent-3-en-1-ol (142j)



According to **General Procedure B-3**: 1-allyl-4-chlorobenzene (4.5 g, 30 mmol, 1.0 equiv), but-3-en-1-ol (6.4 g, 89 mmol, 3.0 equiv), Grubbs Gen. 2 (0.50 g, 0.59 mmol, 2 mol%) and CuI (0.17 g, 0.89 mmol, 3 mol%) were dissolved in Et_2O (200 mL, 0.1 M). Reaction time 4 h. Eluting with PE to PE/EtOAc 4:1. Isolated yield: 3.3 g (17 mmol, 56%) as a mixture of isomers (50:10 *E/Z*).

TLC: R_f = 0.18 (PE/EtOAc 4:1). **IR** (ATR): ṽ [cm^{-1}] = 3336, 2930, 1491, 1428, 1092, 1044, 969, 801. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.31–7.20 (m, 2H, *E/Z*), 7.17–7.03 (m, 2H, *E/Z*), 5.76–5.61 (m, 1H, *E/Z*), 5.59–5.40 (m, 1H, *E/Z*), 3.68 (2xt, *J* = 6.4 Hz, 2H, *E/Z*), 3.40 (d, *J* = 7.4 Hz, 2H, *Z*), 3.33 (d, *J* = 6.6 Hz, 2H, *E*), 2.43 (dtd, *J* = 7.2, 6.5, 1.5 Hz, 2H, *Z*), 2.34–2.24 (m, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 152.3 (*E/Z*), 138.9 (*E/Z*), 131.9 (*E*), 131.8 (*Z*), 130.8 (*E/Z*), 129.8 (*E*), 129.7 (*Z*), 128.6 (*Z*), 128.5 (*E*), 128.0 (*E/Z*), 126.8 (*E/Z*), 62.2 (*Z*), 62.0 (*E*), 38.4 (*E/Z*), 35.9 (*E*), 32.9 (*Z*). **HRMS** (EI) calcd. for $[C_{11}H_{13}ClO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 196.0655, found 196.0646.

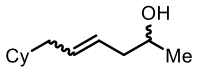
6(4-Fluorophenyl)hex-4-en-2-ol (142k)



According to **General Procedure B-3**: 1-allyl-4-fluorobenzene (2.1 g, 15 mmol, 1.0 equiv), pent-4-en-2-ol (2.5 g, 30 mmol, 2.0 equiv), Grubbs Gen. 2 (0.25 g, 0.29 mmol, 2 mol%) and CuI (84 mg, 0.44 mmol, 3 mol%) were dissolved in Et_2O (100 mL, 0.1 M). Reaction time 20 h. Eluting with PE to PE/EtOAc 19:1. Isolated yield: 1.6 g (8.2 mmol, 54%) as a mixture of isomers (54:10 *E/Z*).

TLC: R_f = 0.10 (PE/EtOAc 19:1). **IR** (ATR): ṽ [cm^{-1}] = 3343, 2967, 2926, 1602, 1508, 1218, 1155, 1121, 1077, 989, 969, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.19–7.06 (m, 2H, *E/Z*), 7.04–6.91 (m, 2H, *E/Z*), 5.77–5.57 (m, 1H, *E/Z*), 5.59–5.41 (m, 1H, *E/Z*), 3.97–3.73 (m, 1H, *E/Z*), 3.40 (d, *J* = 7.5 Hz, 2H, *Z*), 3.34 (d, *J* = 6.6 Hz, 2H, *E*), 2.40–2.06 (m, 2H, *E/Z*), 1.24 (d, *J* = 6.2 Hz, 3H, *Z*), 1.19 (d, *J* = 6.2 Hz, 3H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 162.6 (*E*), 160.2 (*Z*), 136.1 (*E/Z*), 132.7 (*E*), 131.2 (*Z*), 129.8 (d, *J* = 7.8 Hz, C-F, *E*), 129.7 (d, *J* = 7.8 Hz, C-F, *Z*), 127.7 (*E*), 126.4 (*Z*), 115.2 (d, *J* = 21 Hz, C-F, *Z*), 115.2 (d, *J* = 21 Hz, C-F, *E*), 67.3 (*E/Z*), 42.4 (*E*), 38.3 (*E*), 37.1 (*Z*), 32.8 (*Z*), 23.0 (*Z*), 22.8 (*E*). **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 118.0 (s, *E*), - 118.1 (s, *Z*). **HRMS** (EI) calcd. for $[C_{12}H_{15}FO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 194.1107, found 194.1104.

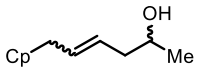
6-Cyclohexylhex-4-en-2-ol (142l)



According to **General Procedure B-3**: allylcyclohexane (5.0 g, 40 mmol, 1.0 equiv), pent-4-en-2-ol (3.5 g, 40 mmol, 1.0 equiv), Grubbs Gen. 2 (0.67 g, 0.79 mmol, 2 mol%) and CuI (0.23 g, 1.2 mmol, 3 mol%) were dissolved in Et_2O (300 mL, 0.1 M). Reaction time 3 h. Eluting with PE/EtOAc 30:1. Isolated yield: 2.8 g (15 mmol, 38%) as a mixture of isomers (*E/Z* n.d., *E*-major fraction).

TLC: R_f = 0.12 (PE/EtOAc 30:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3362, 2967, 2922, 2851, 1446, 1372, 1349, 1312, 1118, 1077, 969, 939, 842. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.63–5.44 (m, 1H, *E/Z*), 5.45-5.26 (m, 1H, *E/Z*), 3.78 (dqd, *J* = 7.7, 6.1, 4.4 Hz, 1H, *E/Z*), 2.21 (dddd, *J* = 13.6, 6.1, 4.8, 1.2 Hz, 1H, *E/Z*), 2.16–2.00 (m, 1H, *E/Z*), 2.01–1.86 (m, 2H, *E/Z*), 1.78–1.54 (m, 6H, *E/Z*), 1.36–1.06 (m, 6H, *E/Z*), 1.01–0.77 (m, 2H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 133.3 (*E*), 132.1 (*Z*), 126.8 (*E*), 125.6 (*Z*), 67.8 (*Z*), 67.2 (*E*), 42.6 (*E*), 40.7 (*E*), 38.3 (*Z*), 38.0 (*E*), 37.2 (*Z*), 35.2 (*Z*), 33.2 (*Z*), 33.1 (*E*), 26.6 (*E*/*Z*), 26.4 (*E/Z*), 22.8 (E/*Z*), 22.6 (*E/Z*). **HRMS** (EI) calcd. for $[C_{12}H_{20}]^{+\cdot}$ $(M\text{-}H_2O)^{+\cdot}$: m/z = 164.1560, found 164.1555.

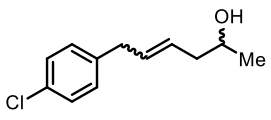
6-Cyclopentylhex-4-en-2-ol (142m)



According to **General Procedure B-3**: allylcyclopentane (5.1 g, 46 mmol, 1.0 equiv), pent-4-en-2-ol (4.0 g, 46 mmol, 1.0 equiv), Grubbs Gen. 2 (0.78 g, 0.92 mmol, 2 mol%) and CuI (0.27 g, 1.4 mmol, 3 mol%) were dissolved in Et_2O (300 mL, 0.1 M). Reaction time 4 h. Eluting with PE to PE/EtOAc 9:1. Isolated yield: 3.1 g (18 mmol, 40%) as a mixture of isomers (*E/Z* n.d. *E*-major fraction).

TLC: R_f = 0.15 (PE/EtOAc 9:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3351, 2948, 2870, 1454, 1372, 1118, 1074, 969, 939. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.65–5.47 (m, 1H, *E/Z*), 5.46–5.33 (m, 1H, *E/Z*), 3.87-3.69 (m, 1H, *E/Z*), 2.30–1.97 (m, 4H, *E/Z*), 1.93–1.41 (m, 8H, *E/Z*), 1.30–1.02 (m, 5H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 134.2 (*E*), 132.9 (*Z*), 126.2 (*E*), 125.2 (*Z*), 67.8 (*Z*), 67.2 (*E*), 42.6 (*E*), 40.3 (*Z*), 39.9 (*E*), 39.1 (*E*), 37.3 (*Z*), 33.5 (*Z*), 32.4 (*Z*), 32.3 (*Z*), 32.3 (*E*), 33.2 (*E*), 25.2 (*E*), 25.1 (*Z*), 22.8 (*Z*), 22.6 (*E*). **HRMS** (EI) calcd. for $[C_{11}H_{18}]^{+\cdot}$ $(M\text{-}H_2O)^{+\cdot}$: m/z = 150.1403, found 150.1399.

6-(4-Chlorophenyl)hex-4-en-2-ol (142n)

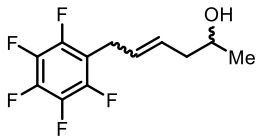


According to **General Procedure B-3**: 1-allyl-4-chlorobenzene (4.5 g, 30 mmol, 1.0 equiv), pent-4-en-2-ol (5.0 g, 58 mmol, 2.0 equiv), Grubbs Gen. 2 (0.50 g, 0.59 µmol, 2 mol%) and CuI (0.17 g, 0.89 mmol, 3 mol%) were dissolved in Et_2O (250 mL, 0.1 M). Reaction time 4 h. Eluting with PE/EtOAc 9:1. Isolated yield: 2.8 g (13 mmol, 45%) as a mixture of isomers (52:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 9:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3362, 2967, 2907, 1491, 1431, 1375, 1126, 1092, 1014, 969, 939, 805. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.29–7.22 (m, 2H, *E/Z*),

7.16–7.05 (m, 2H, *E/Z*), 5.76–5.60 (m, 1H, *E/Z*), 5.58–5.48 (m, 1H, *E/Z*), 3.95–3.74 (m, 1H, *E/Z*), 3.40 (d, *J* = 7.2 Hz, 2H, *Z*), 3.33 (d, *J* = 6.5 Hz, 2H, *E*), 2.43–2.07 (m, 2H, *E/Z*), 1.24 (d, *J* = 6.2 Hz, 3H, *Z*), 1.19 (d, *J* = 6.2 Hz, 3H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 138.9 (*E/Z*), 132.3 (*E/Z*), 131.8 (*E/Z*), 129.8 (*E/Z*), 129.7 (*E/Z*), 128.5 (*E/Z*), 128.0 (*E/Z*), 67.3 (*E/Z*), 42.4 (*E/Z*), 38.4 (*E/Z*), 37.1 (*E/Z*), 22.8 (*E/Z*). **HRMS** (EI) calcd. for $[C_{12}H_{15}ClO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 210.0811, found 210.0800.

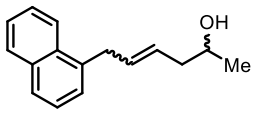
6-(Perfluorophenyl)hex-4-en-2-ol (142o)



According to **General Procedure B-3**: 1-allyl-2,3,4,5,6-pentafluorobenzene (7.2 g, 35 mmol, 1.0 equiv), pent-4-en-2-ol (3.0 g, 35 mmol, 1.0 equiv), Grubbs Gen. 2 (0.59 g, 0.69 mmol, 2 mol%) and CuI (0.20 g, 1.0 mmol, 3 mol%) were dissolved in Et_2O (300 mL, 0.1 M). Reaction time 4 h. Eluting with PE to PE/EtOAc 19:1. Isolated yield: 1.9 g (7.0 mmol, 20%) as a mixture of isomers (46:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 19:1). **IR** (ATR): ṽ [cm^{-1}] = 3362, 2974, 2930, 1506, 1122, 962. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.71–5.44 (m, 2H, *E/Z*), 3.81 (dqd, *J* = 7.2, 6.2, 5.0 Hz, 1H, *E/Z*), 3.51–3.34 (m, 2H, *E/Z*), 2.36 (q, *J* = 6.8 Hz, 2H, *Z*), 2.27–2.04 (m, 2H, *E*), 1.25 (d, *J* = 6.2 Hz, 3H, *Z*), 1.17 (d, *J* = 6.2 Hz, 3H, *E*). **^{13}C NMR** (151 MHz, Chloroform-*d*): δ [ppm] = 145.7 (ddt, *J* = 2.4, 8.6, 4.1 Hz, C-F, *E/Z*), 144.1 (ddd, *J* = 15.0, 8.5, 3.9 Hz, C-F, *E/Z*), 140.6 (m, C-F, *Z*), 138.9 (tt, *J* = 13.5, 5.2 Hz, C-F, *Z*), 138.3 (dddd, *J* = 17.6, 12.7, 5.1, 2.1 Hz, C-F, *E*), 136.7 (m, C-F, *E*), 129.2 (*E*), 128.3 (*Z*), 127.9 (*E*), 126.7 (*Z*), 113.8 (m, C-F, *Z*), 113.5 (td, *J* = 18.7, 3.9 Hz, C-F, *E*), 67.6 (*Z*), 67.2 (*E*), 42.1 (*E*), 36.9 (*Z*), 25.4 (*Z*), 22.8 (*E*). **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 144.7 (m, F-F, *E/Z*), - 158.0 (t, *J* = 20.8 Hz, F-F, *E/Z*), - 163.2 (m, F-F, *E/Z*). **HRMS** (EI) calcd. for $[C_{12}H_9F_5]^{+\cdot}$ $(M\text{-}H_2O)^{+\cdot}$: m/z = 248.0619, found 248.0602.

6-(Naphthalen-1-yl)hex-4-en-2-ol (142p)

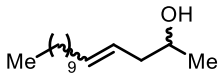


According to **General Procedure B-3**: 1-allylnapthalene (5.1 g, 30 mmol, 1.0 equiv), pent-4-en-2-ol (2.6 g, 30 mmol, 1.0 equiv), Grubbs Gen. 2 (0.51 g, 0.60 mmol, 2 mol%) and CuI (0.17 g, 0.90 mmol, 3 mol%) were dissolved in Et_2O (300 mL, 0.1 M). Reaction time 5 h. Eluting with PE to PE/EtOAc 19:1. Isolated yield: 2.7 g (12 mmol, 40%) as a mixture of isomers (50:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 19:1). **IR** (ATR): ṽ [cm^{-1}] = 3362, 3042, 2967, 2922, 1595, 1510, 1398, 1126, 1077, 969, 939, 779. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 8.11–7.98 (m, 1H, *E/Z*), 7.94–7.82 (m, 1H, *E/Z*), 7.74 (d, *J* = 8.1 Hz, 1H, *E/Z*), 7.57–7.41 (m, 2H, *E/Z*), 7.41 (dd, *J* = 8.2, 7.0 Hz, 1H, *E/Z*), 7.34 (dd, *J* = 7.0, 1.3 Hz, 1H, *E/Z*), 5.85 (dtt, *J* = 15.3, 6.3, 1.3 Hz, 1H, *E/Z*), 5.69–5.44 (m, 1H, *E/Z*), 3.99-3.70 (m, 3H, *E/Z*), 2.43 (ddq, *J* = 21.6, 14.6, 7.1 Hz, 2H, *Z*), 2.31–2.05 (m, 2H, *E*), 1.28 (d, *J* = 6.1 Hz, 3H, *Z*), 1.16 (d, *J* = 6.2 Hz, 3H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 136.5 (*E/Z*), 133.9 (*E/Z*), 132.5 (*E/Z*), 131.9 (*E/Z*), 128.8 (*E/Z*), 127.8 (*E/Z*), 127.0 (*E/Z*),

126.2 (*E/Z*), 125.8 (*E/Z*), 125.7 (*E/Z*), 125.6 (*E/Z*), 124.0 (*E/Z*), 67.3 (*E/Z*), 42.5 (*E/Z*), 36.3 (*E/Z*), 22.7 (*E/Z*). **HRMS** (EI) calcd. for $[C_{16}H_{18}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 226.1358, found 226.1358.

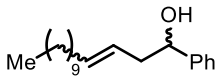
Pentadec-4-en-2-ol (142q)



According to **General Procedure B-3**: dodec-1-ene (5.0 g, 30 mmol, 1.0 equiv), pent-4-en-2-ol (2.6 g, 30 mmol, 1.0 equiv), Grubbs Gen. 2 (0.51 g, 0.60 mmol, 2 mol%) and CuI (0.17 g, 0.90 mmol, 3 mol%) were dissolved in Et_2O (300 mL, 0.1 M). Reaction time 4 h. Eluting with PE to PE/EtOAc 19:1. Isolated yield: 2.1 g (9.2 mmol, 31%) as a mixture of isomers (*E/Z* n.d. *E*-major fraction).

TLC: R_f = 0.12 (PE/EtOAc 19:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3347, 2960, 2922, 2855, 1461, 1375, 1118, 1077, 969, 943, 723. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.63–5.46 (m, 1H, *E/Z*), 5.39 (dddt, *J* = 15.3, 7.7, 6.3, 1.2 Hz, 1H, *E/Z*), 3.78 (dqd, *J* = 7.7, 6.2, 4.6 Hz, 1H, *E/Z*), 2.30–2.13 (m, 1H, *E/Z*), 2.05 (dq, *J* = 7.3, 6.9 Hz, 3H, *E/Z*), 1.41–1.12 (m, 19H, *E/Z*), 0.93–0.82 (m, 3H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 134.9 (*E*), 133.6 (*Z*), 125.7 (*E*), 125.0 (*Z*), 67.2 (*E/Z*), 42.6 (*E*), 37.2 (*Z*), 32.7 (*E*), 31.9 (*E/Z*), 29.6 (*E/Z*), 29.5 (*E/Z*), 29.5 (*E/Z*), 29.4 (*E/Z*), 29.2 (*E/Z*), 27.4 (*Z*), 22.7 (*E/Z*), 22.6 (*E/Z*), 14.1 (*E/Z*). **HRMS** (EI) calcd. for $[C_{15}H_{28}]^{+\cdot}$ $(M\text{-}H_2O)^{+\cdot}$: m/z = 208.2186, found 208.2182.

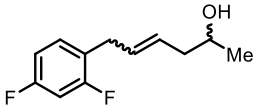
1-Phenyltetradec-3-en-1-ol (142r)



According to **General Procedure B-3**: Dodec-1-ene (11 g, 68 mmol, 2.0 equiv), 1-phenylbut-3-en-1-ol (5.1 g, 34 mmol, 1.0 equiv), Grubbs Gen. 2 (0.58 g, 0.68 mmol, 2 mol%) and CuI (0.20 g, 1.1 mmol, 3 mol%) were dissolved in Et_2O (250 mL, 0.1 M). Reaction time 21 h. Eluting with PE/EtOAc 99:1. Isolated yield: 2.5 g (8.7 mmol, 25%) as a mixture of isomers (46:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 99:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3388, 3064, 3030, 2922, 2855, 1495, 1454, 1047, 969, 757, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.35 (d, *J* = 4.4 Hz, 4H, *E/Z*), 7.33–7.22 (m, 1H, *E/Z*), 5.67–5.49 (m, 1H, *E/Z*), 5.48–5.30 (m, 1H, *E/Z*), 4.70 (tdd, *J* = 7.9, 5.1, 2.9 Hz, 1H, *E/Z*), 2.67-2.23 (m, 2H, *E/Z*), 2.12–1.95 (m, 3H, *E/Z*), 1.26 (s, 16H, *E/Z*), 0.96-0.80 (m, 3H, *E/Z*).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.1 (*E/Z*), 135.4 (*E/Z*), 133.9 (*E/Z*), 128.4 (*Z*), 128.4 (*E*), 127.4 (*E/Z*), 125.9 (*Z*), 125.8 (*E*), 125.4 (*E/Z*), 73.5 (*E/Z*), 42.9 (*E/Z*), 32.7 (*E/Z*), 31.9 (*E/Z*), 29.7 (*E/Z*), 29.5 (*E/Z*), 29.4 (*E/Z*), 29.4 (*E/Z*), 29.2 (*E/Z*), 22.7 (*E/Z*), 14.1 (*E/Z*). **HRMS** (APCI) calcd. for $[C_{20}H_{31}]^+$ $(M\text{-}OH^-)^+$: m/z = 271.2420, found 271.2426.

6-(2,4-Difluorophenyl)hex-4-en-2-ol (142s)

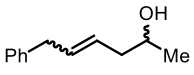


According to **General Procedure B-3**: 1-allyl-2,4-difluorobenzene (3.3 g, 21 mmol, 1.0 equiv), pent-4-en-2-ol (3.6 g, 42 mmol, 2.0 equiv),

Grubbs Gen. 2 (0.36 g, 0.48 mmol, 2 mol%) and CuI (0.13 g, 0.66 mmol, 3 mol%) were dissolved in Et_2O (220 mL, 0.1 M). Reaction time 4 h. Eluting with PE/EtOAc 9:1. Isolated yield: 2.2 g (10 mmol, 48%) as a mixture of isomers (48:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 9:1). **IR** (ATR): ṽ [cm^{-1}] = 3362, 2971, 2926, 1603, 1506, 1428, 1275, 1137, 1088, 965, 850. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.20–7.06 (m, 1H, *E/Z*), 6.87–6.70 (m, 2H, *E/Z*), 5.73–5.56 (m, 1H, *E/Z*), 5.60–5.42 (m, 1H, *E/Z*), 3.93–3.74 (m, 1H, *E/Z*), 3.39 (d, *J* = 6.9 Hz, 2H, *Z*), 3.34 (d, *J* = 6.4 Hz, 2H, *E*), 2.43–2.07 (m, 2H, *E/Z*), 1.24 (d, *J* = 6.1 Hz, 3H, *Z*), 1.18 (d, *J* = 6.2 Hz, 3H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 162.7 (*E/Z*), 160.3 (*E/Z*), 130.9 (*E*), 129.5 (*Z*), 128.1 (*E/Z*), 127.1 (*E*), 126.1 (*Z*), 123.2 (dd, *J* = 16.0, 3.8 Hz, C-F, *E/Z*), 111.0 (dd, *J* = 20.9, 3.8 Hz, C-F, *E/Z*), 103.7 (t, *J* = 25.6 Hz, C-F, *E/Z*), 67.7 (*Z*) 67.2 (*E*), 42.4 (*E*), 37.0 (*Z*), 31.5 (*E*), 26.3 (*Z*), 23.0 (*Z*), 22.8 (*E*). **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 113.9 (d, *J* = 6.7 Hz, F-F, *E*), - 114.1 (d, *J* = 6.6 Hz, F-F, *Z*), - 114.6 (d, *J* = 6.8 Hz, F-F, *Z*), - 114.9 (d, *J* = 6.7 Hz, F-F, *E*). **HRMS** (EI) calcd. for $[C_{12}H_{12}F_2]^{+\cdot}$ $(M\text{-}H_2O)^{+\cdot}$: m/z = 194.0904, found 194.0555.

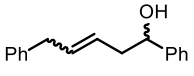
6-Phenylhex-4-en-2-ol (142t)



According to **General Procedure B-3**: allylbenzene (5.1 g, 43 mmol, 1.0 equiv), pent-4-en-2-ol (7.4 g, 86 mmol, 2.0 equiv), Grubbs Gen. 2 (0.73 g, 0.86 mmol, 2 mol%) and CuI (0.24 g, 1.3 mmol, 3 mol%) were dissolved in Et_2O (250 mL, 0.2 M). Reaction time 4 h. Eluting with PE to PE/EtOAc 9:1. Isolated yield: 3.3 g (18 mmol, 43%) as a mixture of isomers (55:10 *E/Z*).

TLC: R_f = 0.14 (PE/EtOAc 9:1). **IR** (ATR): ṽ [cm^{-1}] = 3340, 3027, 2967, 2900, 1495, 1454, 1126, 1074, 969, 939, 746, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.30 (tq, *J* = 7.0, 1.1 Hz, 2H, *E/Z*), 7.24–7.14 (m, 3H, *E/Z*), 5.72 (dtt, *J* = 15.6, 6.6, 1.2 Hz, 1H, *E/Z*), 5.52 (dddt, *J* = 15.5, 7.9, 6.5, 1.4 Hz, 1H, *E/Z*), 3.99–3.75 (m, 1H, *E/Z*), 3.49–3.43 (m, 2H, *Z*), 3.38 (d, *J* = 6.7 Hz, 2H, *E*), 2.48–2.07 (m, 2H, *E/Z*), 1.25 (d, *J* = 6.2 Hz, 3H, *Z*), 1.20 (d, *J* = 6.2 Hz, 3H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 140.6 (*E/Z*), 133.1 (*E/Z*), 128.6 (*E/Z*), 128.5 (*E/Z*), 127.6 (*E/Z*), 126.2 (*E/Z*), 67.4 (*E/Z*), 42.6 (*E*), 39.3 (*E*), 37.3 (*Z*), 33.8 (*Z*), 22.9 (*E/Z*). **HRMS** (APCI) calcd. for $[C_{12}H_{20}NO]^+$ $(M+NH_4)^+$: m/z = 194.1539, found 194.1540.

1,5-Diphenylpent-3-en-1-ol (142u)

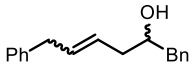


According to **General Procedure B-3**: allylbenzene (8.0 g, 68 mmol, 2.0 equiv), 1-phenylbut-3-en-1-ol (5.0 g, 34 mmol, 1.0 equiv), Grubbs Gen. 2 (0.58 g, 0.69 µmol, 2 mol%) and CuI (0.20 g, 1.1 mmol, 3 mol%) were dissolved in Et_2O (250 mL, 0.1 M). Reaction time 21 h. Eluting with PE to PE/EtOAc 30:1. Isolated yield: 1.9 g (8.1 mmol, 24%) as a mixture of isomers (40:10 *E/Z*).

*Data are in accordance with cited literature.[277]

TLC: R_f = 0.06 (PE/EtOAc 30:1). **IR** (ATR): ṽ [cm^{-1}] = 3362, 3026, 2899, 1602, 1494, 1453, 1028, 969, 745, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.43–7.24 (m, 7H, *E/Z*), 7.25–7.07 (m, 3H, *E/Z*), 5.85–5.62 (m, 1H, *E/Z*), 5.63–5.42 (m, 1H, *E/Z*), 4.88–4.67 (m, 1H, *E/Z*), 3.37 (2xt, *J* = 6.9 Hz, 2H, *E/Z*), 2.76–2.56 (m, 2H, *Z*), 2.49 (tdd, *J* = 7.4, 3.1, 1.1 Hz, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ [ppm] = 144.0 (*E/Z*), 140.4 (*E/Z*), 133.2 (*E/Z*), 128.6 (*Z*), 128.5 (*Z*), 128.5 (*E*) 128.4 (*E*), 128.4 (*E*), 128.4 (*Z*), 127.6 (*Z*), 127.5 (*E*), 127.2 (*E*), 126.2 (*Z*), 126.2 (*Z*), 126.0 (*E*), 125.9 (*E/Z*), 73.7 (*E/Z*), 42.6 (*E*), 39.1 (*E*), 37.3 (*Z*), 33.7 (*Z*). **HRMS** (EI) calcd. for $[C_{17}H_{16}]^{+\cdot}$ $(M\text{-}H_2O)^{+\cdot}$: m/z = 220.1247, found 220.1243.

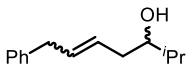
1,6-Diphenylhex-4-en-2-ol (142v)



According to **General Procedure B-3**: allylbenzene (6.9 g, 58 mmol, 2.0 equiv), 1-phenylpent-4-en-2-ol (4.7 g, 29 mmol, 1.0 equiv), Grubbs Gen. 2 (0.51 g, 0.60 µmol, 2 mol%) and CuI (0.17 g, 0.90 µmol, 3 mol%) were dissolved in Et_2O (200 mL, 0.1 M). Reaction time 21 h. Eluting with PE to PE/EtOAc 19:1. Isolated yield: 2.2 g (8.6 mmol, 30%) as a mixture of isomers (63:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 19:1). **IR** (ATR): ṽ [cm^{-1}] = 3571, 3422, 3064, 3027, 2919, 1603, 1495, 1454, 1077, 1029, 973, 746, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.41–7.11 (m, 10H, *E/Z*), 5.86-5.47 (m, 2H, *E/Z*), 4.30 (d, *J* = 7.2 Hz, 1H, *Z*), 4.00–3.78 (m, 1H, *E*), 3.44 (d, *J* = 7.3 Hz, 2H, *Z*), 3.39 (d, *J* = 6.7 Hz, 2H, *E*), 2.93–2.66 (m, 2H, *E/Z*), 2.47–2.13 (m, 2H, *E/Z*). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 140.6 (*E/Z*), 138.6 (*E/Z*), 135.1 (*E/Z*), 133.1 (*E/Z*), 131.5 (*E/Z*), 129.5 (*E/Z*), 128.6 (*E/Z*), 128.6 (*E/Z*), 128.6 (*E/Z*), 127.5 (*E/Z*), 126.6 (*E/Z*), 126.1 (*E/Z*), 72.1 (*E/Z*), 43.4 (*E/Z*), 40.0 (*E*), 39.3 (*E*), 34.8 (*Z*), 33.8 (*Z*). **HRMS** (APCI) calcd. for $[C_{18}H_{24}NO]^+$ $(M+NH_4)^+$: m/z = 270.1857, found 270.1852.

2-Methyl-7-phenylhept-5-en-3-ol (142w)

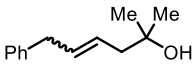


According to **General Procedure B-3**: allylbenzene (6.2 g, 52 mmol, 1.0 equiv), 2-methylhex-5-en-3-ol (18 g, 0.10 mol, 2.0 equiv, 66 wt% in THF), Grubbs Gen. 2 (0.86 g, 1.0 mmol, 2 mol%) and CuI (0.30 g, 1.6 mmol, 3 mol%) were dissolved in Et_2O (300 mL, 0.2 M). Reaction time 5 h. Eluting with PE to PE/EtOAc 30:1. Isolated yield: 1.9 g (9.3 mmol, 18%) as a mixture of isomers (46:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 30:1). **IR** (ATR): ṽ [cm^{-1}] = 3407, 3064, 3027, 2960, 2900, 1603, 1495, 1387, 1267, 1178, 1126, 1029, 973, 872, 746, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.36–7.22 (m, 2H, *E/Z*), 7.19 (td, *J* = 7.0, 1.3 Hz, 3H, *E/Z*), 5.82–5.66 (m, 1H, *E/Z*), 5.64–5.47 (m, 1H, *E/Z*), 3.49-3.41 (m, 1H, *Z*), 3.41–3.33 (m, 1+2H, *E* + *E/Z*), 2.39–2.23 (m, 1H, *E/Z*), 2.09 (dddd, *J* = 14.0, 8.8, 7.9, 0.9 Hz, 1H, *E/Z*), 1.80–1.61 (m, 1H, *E/Z*), 1.03–0.86 (m, 6H, *E/Z*). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 140.7 (*E/Z*), 132.9 (*E*), 131.5 (*Z*), 129.8 (*Z*), 128.6 (*E/Z*), 128.2 (*E*), 127.0 (*Z*) 126.2 (*E*), 75.8 (*E/Z*), 39.3 (*E/Z*), 37.7 (*E*), 33.8 (*Z*), 33.2 (*E*), 32.4 (*Z*),

18.9 (*E/Z*), 17.7 (*E/Z*). **HRMS** (APCI) calcd. for $[C_{14}H_{24}NO]^+$ $(M+NH_4)^+$: m/z = 222.1852, found 222.1856.

2-Methyl-6-phenylhex-4-en-2-ol (142x)

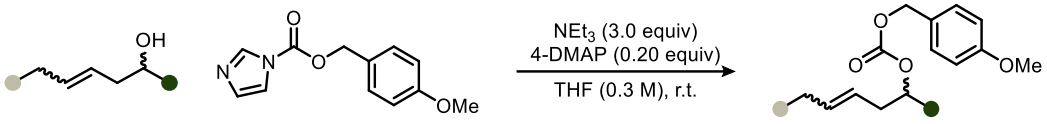


According to **General Procedure B-3**: allylbenzene (8.2 g, 69 mmol, 2.0 equiv), 2-methylpent-4-en-2-ol (4.5 g, 45 mmol, 1.0 equiv), Grubbs Gen. 2 (0.76 g, 0.89 mmol, 2 mol%) and CuI (0.26 g, 1.4 mmol, 3 mol%) were dissolved in Et_2O (300 mL, 0.1 M). Reaction time 4 h. Eluting with PE/EtOAc 30:1. Isolated yield: 2.1 g (11 mmol, 25%) as a mixture of isomers (51:10 *E/Z*).

*Data are in accordance with cited literature (*E*-isomer).[278]

TLC: R_f = 0.06 (PE/EtOAc 30:1). **IR** (ATR): ṽ [cm^{-1}] = 3567, 3384, 3026, 2970, 2926, 1602, 1494, 1453, 1375, 1151, 972, 905, 745, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.36–7.23 (m, 2H, *E/Z*), 7.20 (td, *J* = 6.2, 1.7 Hz, 3H, *E/Z*), 5.87–5.49 (m, 2H, *E/Z*), 3.44 (d, *J* = 7.3 Hz, 2H, *Z*), 3.39 (d, *J* = 6.3 Hz, 2H, *E*), 2.37 (d, *J* = 7.6 Hz, 2H, *Z*), 2.21 (d, *J* = 7.0 Hz, 2H, *E*), 1.27 (s, 6H, *Z*), 1.22 (s, 6H, *E*).**^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 140.6, 133.4, 128.5, 127.0, 126.0, 70.6, 46.9, 39.2, 29.2, 29.1 (all *E*). **HRMS** (EI) calcd. for $[C_{13}H_{16}]^{+\cdot}$ $(M-H_2O)^{+\cdot}$: m/z = 172.1247, found 172.1247.

General procedure C: Adapted Steglich esterification

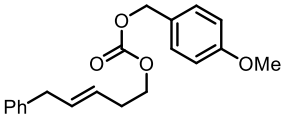


1.0 equiv **142** *1.5 equiv* **143** **135**

Scheme 116: Reaction equation for the adapted Steglich esterification.

The respective olefinic alcohol (1.0 equiv) was diluted in THF (0.3 M) and NEt_3 (3.0 equiv) and 4-dimethylaminopyridine (4-DMAP) (0.20 equiv) were added. Then 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (1.5 equiv) diluted in THF (5.7 M) was added dropwise and the mixture was stirred for the respective time. The mixture was separated between H_2O and Et_2O and further extracted with Et_2O. After washing with brine or H_2O and drying over Na_2SO_4 or $MgSO_4$, the mixture was concentrated and purified by column chromatography to give the title compound.

(*E*)-4-Methoxybenzyl (5-phenylpent-3-en-1-yl) carbonate (135a)

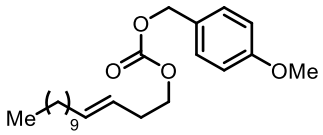


According to **General Procedure C**: (*E*)-5-phenylpent-3-en-1-ol (0.53 g, 3.2 mmol, 1.0 equiv), NEt_3 (1.3 mL, 9.3 mmol, 2.9 equiv) were dissolved in THF (10 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate

(0.94 g, 4.7 mmol, 1.5 equiv), was added. After 24 h 4-DMAP (80 mg, 0.65 mmol, 0.20 equiv) was added. Total reaction time 140 h. Separated between H_2O (15 mL) and Et_2O (15 mL). Extracted with Et_2O (3x 15 mL), washed with H_2O (3x 15 mL) and dried over Na_2SO_4. Eluting with PE/EtOAc 15:1. Isolated yield: 0.64 g (2.0 mmol, 60%).

TLC: R_f = 0.22 (PE/EtOAc 15:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2960, 1737, 1614, 1513, 1454, 1394, 1238, 1174, 1033, 965, 820, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.39–7.22 (m, 4H), 7.23–7.12 (m, 3H), 6.96–6.85 (m, 2H), 5.69 (dtt, *J* = 14.8, 6.7, 1.3 Hz, 1H), 5.47 (dtt, *J* = 15.1, 6.8, 1.4 Hz, 1H), 5.09 (s, 2H), 4.16 (t, *J* = 6.8 Hz, 2H), 3.81 (s, 3H), 3.33 (d, *J* = 6.7 Hz, 2H), 2.40 (qq, *J* = 6.9, 1.1 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.9, 155.2, 140.4, 132.3, 130.3, 128.5, 128.4, 127.5, 126.2, 126.0, 114.0, 69.4, 67.4, 55.3, 39.0, 31.9. **HRMS** (ESI) calcd. for $[C_{20}H_{22}NaO_4]^+$ $(M+Na)^+$: m/z = 349.1410, found 349.1414.

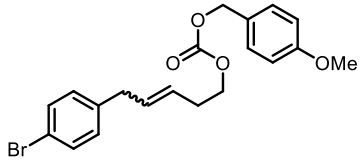
(*E*)-4-Methoxybenzyl tetradec-3-en-1-yl carbonate (135d)



According to **General Procedure C**: (*E*)-tetradec-3-en-1-ol (2.4 g, 11 mmol, 1.0 equiv), 4-DMAP (0.25 g, 2.0 mmol, 0.18 equiv), NEt_3 (4.8 mL, 34 mmol, 3.0 equiv) were dissolved in THF (38 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (3.9 g, 17 mmol, 1.5 equiv), diluted in THF (3.0 mL), was added. Reaction time 46 h. Separated between H_2O (50 mL) and Et_2O (50 mL). Extracted with Et_2O (2x 50 mL), washed with H_2O (1x 50 mL) and dried over Na_2SO_4. Eluting with PE/EtOAc 30:1. Isolated yield: 3.5 g (9.3 mmol, 82%).

TLC: R_f = 0.22 (PE/EtOAc 30:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2926, 2855, 1744, 1614, 1517, 1461, 1394, 1245, 1178, 1036, 969, 824. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.27 (m, 2H), 6.94–6.83 (m, 2H), 5.51 (dtt, *J* = 15.5, 6.4, 1.2 Hz, 1H), 5.35 (dtt, *J* = 15.0, 6.8, 1.2 Hz, 1H), 5.08 (s, 2H), 4.12 (t, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 2.34 (qd, *J* = 7.0, 1.1 Hz, 2H), 1.96 (q, *J* = 6.8 Hz, 2H), 1.25 (s, 16H), 0.97-0.81 (m, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 159.8, 155.2, 134.0, 130.3, 127.5, 124.4, 118.2, 113.9, 69.4, 67.7, 55.3, 32.6, 32.0, 31.9, 29.7, 29.5, 29.4, 29.2, 22.7, 14.2. **HRMS** (ESI) calcd. for $[C_{23}H_{36}NaO_4]^+$ $(M+Na)^+$: m/z = 399.2506, found 399.2513.

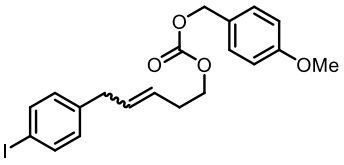
5-(4-Bromophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (135g)



According to **General Procedure C**: 5-(4-bromophenyl)pent-3-en-1-ol (1.4 g, 5.8 mmol, 1.0 equiv), 4-DMAP (0.14 g, 1.2 mmol, 0.20 equiv), NEt_3 (2.4 mL, 17 mmol, 3.0 equiv) were dissolved in THF (20 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (2.1 g, 8.9 mmol, 1.5 equiv), diluted in THF (5.0 mL), was added. Reaction time 72 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 30:1. Isolated yield: 1.3 g (3.1 mmol, 53%) as a mixture of isomers (46:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 30:1). **IR** (ATR): ṽ [cm^{-1}] = 3001, 2960, 2904, 2840, 1744, 1517, 1487, 1245, 1178, 1036, 969, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.44–7.26 (m, 4H, *E/Z*), 7.09–6.98 (m, 2H, *E/Z*), 6.95–6.82 (m, 2H, *E/Z*), 5.72–5.55 (m, 1H, *E/Z*), 5.56–5.37 (m, 1H, *E/Z*), 5.08 (d, *J* = 1.8 Hz, 2H, *E/Z*), 4.17 (2xt, *J* = 6.9 Hz, 2H, *E/Z*), 3.81 (s, 3H, *E/Z*), 3.33 (d, *J* = 7.9 Hz, 2H, *Z*), 3.27 (d, *J* = 6.6 Hz, 2H, *E*), 2.51 (q, *J* = 7.1 Hz, 2H, *Z*), 2.39 (dddd, *J* = 7.9, 6.8, 5.7, 1.2 Hz, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.9 (*E/Z*), 155.2 (*E/Z*), 139.5 (*E*), 139.3 (*Z*), 131.6 (*E*), 131.5 (*Z*), 131.4 (*E/Z*), 130.3 (*E/Z*), 130.3 (*E/Z*), 127.4 (*Z*), 126.9 (*E*), 119.8 (*Z*), 114.0 (*E*), 69.5 (*E/Z*), 67.3 (*E/Z*), 55.3 (*E/Z*), 38.3 (*E/Z*), 31.9 (*E/Z*). **HRMS** (ESI) calcd. for $[C_{20}H_{21}BrNaO_4]^+$ $(M+Na)^+$: m/z = 427.0517, found 427.0517.

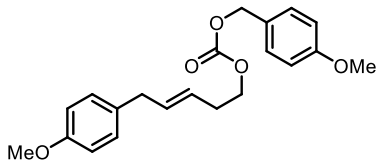
5-(4-Iodophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (135h)



According to **General Procedure C**: 5-(4-iodophenyl)pent-3-en-1-ol (2.0 g, 6.8 mmol, 1.0 equiv), 4-DMAP (0.17 g, 1.4 mmol, 0.20 equiv), NEt_3 (2.9 mL, 21 mmol, 3.1 equiv) were dissolved in THF (20 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (2.4 g, 10 mmol, 1.5 equiv), diluted in THF (3.5 mL), was added. Reaction time 70 h. Separated between H_2O (25 mL) and Et_2O (25 mL). Extracted with Et_2O (2x 20 mL), washed with H_2O (3x 25 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 30:1. Isolated yield: 1.9 g (4.2 mmol, 62%) as a mixture of isomers (45:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 30:1). **IR** (ATR): ṽ [cm^{-1}] = 3001, 2960, 2907, 2837, 1744, 1614, 1513, 1484, 1398, 1245, 1178, 1036, 969, 824, 794. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.62–7.52 (m, 2H, *E/Z*), 7.35–7.29 (m, 2H, *E/Z*), 6.95–6.83 (m, 4H, *E/Z*), 5.70–5.55 (m, 1H, *E/Z*), 5.55–5.38 (m, 1H, *E/Z*), 5.08 (d, *J* = 1.8 Hz, 2H, *E/Z*), 4.17 (2xt, *J* = 6.8 Hz, 2H, *E/Z*), 3.81 (s, 3H, *E/Z*), 3.32 (d, *J* = 7.3 Hz, 2H, *Z*), 3.26 (d, *J* = 6.6 Hz, 2H, *E*), 2.50 (t, *J* = 6.8 Hz, 2H, *Z*), 2.39 (dddd, *J* = 7.8, 6.7, 5.7, 1.1 Hz, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.9 (*E/Z*), 155.2 (*E/Z*), 140.0 (*Z*), 137.5 (*E*), 137.4 (*E/Z*), 131.6 (*E*), 130.6 (*E/Z*), 130.5 (*Z*), 130.3 (*E/Z*), 127.4 (*Z*), 126.9 (*E*), 114.0 (*E/Z*), 91.1 (*E/Z*), 69.5 (*E/Z*), 67.3 (*E*), 67.1 (*Z*), 55.3 (*E/Z*), 38.4 (*E/Z*), 33.0 (*Z*), 31.9 (*E*). **HRMS** (ESI) calcd. for $[C_{20}H_{21}INaO_4]^+$ $(M+Na)^+$: m/z = 475.0377, found 475.0380.

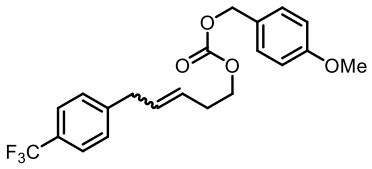
(*E*)-4-Methoxybenzyl (5-(4-methoxyphenyl)pent-3-en-1-yl) carbonate (135i)



According to **General Procedure C**: 5-(4-methoxyphenyl)pent-3-en-1-ol (1.1 g, 5.8 mmol, 1.0 equiv), 4-DMAP (0.14 g, 1.2 mmol, 0.20 equiv), NEt_3 (2.4 mL, 17 mmol, 3.0 equiv) were dissolved in THF (20 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (2.0 g, 8.7 mmol, 1.5 equiv), diluted in THF (2.0 mL), was added. Reaction time 68 h. Separated between H_2O (15 mL) and Et_2O (15 mL). Extracted with Et_2O (2x 15 mL), washed with H_2O (2x 15 mL) and dried over $MgSO_4$. Recrystallized from Et_2O and *n*-hexane in the freezer. Isolated yield: 0.55 g (1.5 mmol, 27%).

IR (ATR): ṽ [cm^{-1}] = 2960, 2907, 2837, 1744, 1614, 1513, 1245, 1178, 1036, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.27 (m, 2H), 7.13–7.01 (m, 2H), 6.94–6.83 (m, 2H), 6.87–6.76 (m, 2H), 5.66 (dtt, *J* = 14.7, 6.7, 1.3 Hz, 1H), 5.44 (dtt, *J* = 15.0, 6.7, 1.4 Hz, 1H), 5.08 (s, 2H), 4.15 (t, *J* = 6.9 Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.26 (d, *J* = 6.7 Hz, 2H), 2.39 (dddd, *J* = 8.0, 6.9, 5.8, 1.2 Hz, 2H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 159.9, 157.1, 155.2, 133.2, 132.7, 132.4, 132.1, 130.3, 129.4, 125.9, 113.9, 113.8, 69.4, 67.5, 55.3, 38.1, 31.9. **HRMS** (ESI) calcd. for $[C_{21}H_{24}NaO_5]^+$ (M+Na)$^+$: m/z = 379.1516, found 379.1519.

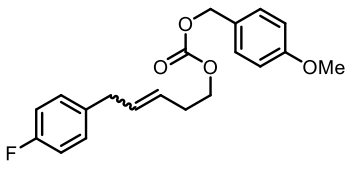
4-Methoxybenzyl (5-(4-(trifluoromethyl)phenyl)pent-3-en-1-yl) carbonate (135j)



According to **General Procedure C**: 5-(4-(trifluoromethyl)phenyl)pent-3-en-1-ol (1.6 g, 6.8 mmol, 1.0 equiv), 4-DMAP (0.16 g, 1.3 mmol, 0.20 equiv), NEt_3 (2.7 mL, 19 mmol, 2.9 equiv) were dissolved in THF (20 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (2.5 g, 11 mmol, 1.6 equiv), diluted in THF (3.0 mL), was added. Reaction time 72 h. Separated between H_2O (20 mL) and Et_2O (20 mL). Extracted with Et_2O (1x 20 mL), washed with H_2O (3x 20 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 50:1. Isolated yield: 2.0 g (5.0 mmol, 74%) as a mixture of isomers (45:10 *E/Z*).

TLC: R_f = 0.10 (PE/EtOAc 50:1). **IR** (ATR): ṽ [cm^{-1}] = 2959, 2907, 2840, 1740, 1613, 1517, 1326, 1241, 1162, 1118, 1066, 1036, 969, 849, 820. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.51 (t, *J* = 8.3 Hz, 2H, *E/Z*), 7.36–7.23 (m, 4H, *E/Z*), 6.93–6.84 (m, 2H, *E/Z*), 5.72–5.59 (m, 1H, *E/Z*), 5.61–5.44 (m, 1H, *E/Z*), 5.09 (s, 2H, *E/Z*), 4.24–4.13 (m, 2H, *E/Z*), 3.80 (s, 3H, *E/Z*), 3.44 (d, *J* = 7.4 Hz, 2H, *Z*), 3.38 (d, *J* = 6.7 Hz, 2H, *E*), 2.58–2.48 (m, 2H, *Z*), 2.41 (qt, *J* = 6.7, 1.2 Hz, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.9 (*E/Z*), 155.2 (*E/Z*), 131.1 (*E/Z*), 130.3 (*Z*), 130.3 (*E*), 128.8 (*E*), 128.7 (*Z*), 127.4 (*E/Z*), 125.9 (*E/Z*), 125.7 (*E/Z*), 125.3 (q, *J* = 4.0 Hz, C-F, *E/Z*), 114.0 (*E/Z*), 69.5 (*Z*), 69.5 (*E*), 67.2 (*E*), 67.0 (*Z*), 55.3 (*E/Z*), 38.7 (*E*), 33.3 (*Z*), 31.9 (*E*), 27.0 (*Z*). **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 62.8 (s). **HRMS** (EI) calcd. for $[C_{21}H_{21}F_3NaO_4]^+$ (M+Na)$^+$: m/z = 417.1284, found 417.1290.

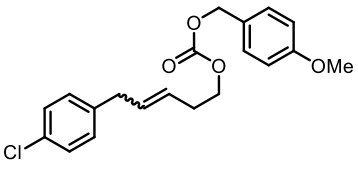
5-(4-Fluorophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (135k)



According to **General Procedure C**: 5-(4-fluorophenyl)pent-3-en-1-ol (1.0 g, 5.6 mmol, 1.0 equiv), 4-DMAP (0.14 g, 1.1 mmol, 0.20 equiv), NEt_3 (2.3 mL, 17 mmol, 3.0 equiv) were dissolved in THF (19 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (2.2 g, 9.5 mmol, 1.7 equiv), diluted in THF (3.0 mL), was added. Reaction time 71 h. Separated between H_2O (10 mL) and Et_2O (10 mL). Extracted with Et_2O (2x 15 mL), washed with H_2O (2x 15 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 100:1. Isolated yield: 1.3 g (3.8 mmol, 68%) as a mixture of isomers (42:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 100:1). **IR** (ATR): ṽ [cm^{-1}] = 2960, 2907, 2840, 1744, 1614, 1513, 1245, 1178, 824. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.37–7.26 (m, 2H, *E/Z*), 7.11 (ddd, *J* = 8.6, 5.8, 3.1 Hz, 2H, *E/Z*), 7.01–6.90 (m, 2H, *E/Z*), 6.95–6.83 (m, 2H, *E/Z*), 5.73–5.57 (m, 1H, *E/Z*), 5.54–5.37 (m, 1H, *E/Z*), 5.09 (2xs, 2H, *E/Z*), 4.17 (2xt, *J* = 6.9 Hz, 2H, *E/Z*), 3.81 (s, 3H, *E/Z*), 3.35 (d, *J* = 7.3 Hz, 2H, *Z*), 3.29 (d, *J* = 6.7 Hz, 2H, *E*), 2.52 (q, *J* = 6.8 Hz, 2H, *Z*), 2.46–2.32 (m, 2H, *E*). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 154.5 (*E/Z*), 150.1 (*E/Z*), 149.8 (*E/Z*), 144.0 (*E/Z*), 135.0 (*E*), 130.6 (*Z*), 126.8 (*Z*), 125.0 (*E*), 124.5 (d, *J* = 7.9 Hz, C-F, *E/Z*), 122.1 (*Z*), 121.2 (*E*), 109.8 (d, *J* = 21.3 Hz, C-F, *E/Z*), 108.6 (*E/Z*), 84.1 (*E/Z*), 64.1 (*E/Z*), 62.0 (*E/Z*), 50.0 (*E/Z*), 32.8 (*E/Z*), 26.6 (*E/Z*). **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 118.1 (s, *E*), - 118.1 (s, *Z*). **HRMS** (ESI) calcd. for $[C_{20}H_{21}FNaO_4]^+$ $(M+Na)^+$: m/z = 367.1316, found 367.1326.

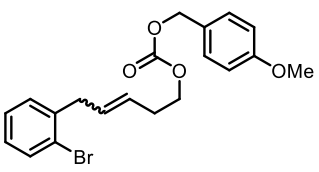
5-(4-Chlorophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (135l)



According to **General Procedure C:** 5-(4-chlorophenyl)pent-3-en-1-ol (2.0 g, 10 mmol, 1.0 equiv), 4-DMAP (0.25 g, 2.1 mmol, 0.20 equiv), NEt_3 (4.2 mL, 30 mmol, 3.0 equiv) were dissolved in THF (34 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (3.6 g, 15 mmol, 1.5 equiv), diluted in THF (5.0 mL), was added. Reaction time 72 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 30:1. Isolated yield: 1.9 g (5.4 mmol, 53%) as a mixture of isomers (53:10 *E/Z*).

TLC: R_f = 0.10 (PE/EtOAc 30:1). **IR** (ATR): ṽ [cm^{-1}] = 3001, 2960, 2907, 2840, 1744, 1614, 1517, 1245, 1178, 1036, 969, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.26 (m, 2H, *E/Z*), 7.28–7.16 (m, 2H, *E/Z*), 7.14–7.02 (m, 2H, *E/Z*), 6.95–6.83 (m, 2H, *E/Z*), 5.64 (dtt, *J* = 14.4, 6.5, 1.2 Hz, 1H, *E/Z*), 5.56–5.37 (m, 1H, *E/Z*), 5.08 (d, *J* = 2.0 Hz, 2H, *E/Z*), 4.17 (2xt, *J* = 6.9 Hz, 2H, *E/Z*), 3.81 (s, 3H, *E/Z*), 3.34 (d, *J* = 7.3 Hz, 2H, *Z*), 3.28 (d, *J* = 6.6 Hz, 2H, *E*), 2.51 (q, *J* = 7.0 Hz, 2H, *Z*), 2.39 (tdt, *J* = 6.8, 5.7, 1.1 Hz, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.9 (*E/Z*), 155.2 (*E/Z*), 138.8 (*E/Z*), 131.7 (*E/Z*), 130.4 (*E/Z*), 130.3 (*E/Z*), 129.8 (*E/Z*), 128.5 (*E/Z*), 127.4 (*Z*), 126.8 (*E*), 114.0 (*E/Z*), 69.4 (*E/Z*), 67.3 (*E*), 67.1 (*Z*), 55.3 (*E/Z*), 38.3 (*E*), 32.9 (*Z*), 31.9 (*E*), 27.0 (*Z*). **HRMS** (ESI) calcd. for $[C_{20}H_{21}ClNaO_4]^+$ $(M+Na)^+$: m/z = 383.1021, found 383.1023.

5-(2-Bromophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (135m)

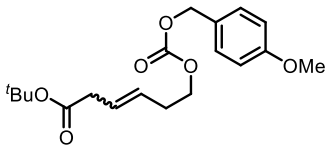


According to **General Procedure C**: 5-(2-bromophenyl)pent-3-en-1-ol (2.7 g, 11 mmol, 1.0 equiv), 4-DMAP (0.28 g, 2.3 mmol, 0.20 equiv), NEt_3 (4.7 mL, 34 mmol, 3.0 equiv) were dissolved in THF (35 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (3.9 g, 17 mmol, 1.5 equiv), diluted in THF (5.0 mL), was added. Reaction time 70 h. Separated between H_2O (25 mL) and Et_2O (25 mL). Extracted with Et_2O (2x 20 mL), washed with H_2O (3x

25 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 30:1. Isolated yield: 3.4 g (8.4 mmol, 74%) as a mixture of isomers (46:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 30:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2960, 2904, 2840, 1741, 1614, 1513, 1469, 1394, 1245, 1178, 1029, 969, 824, 753. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.57–7.48 (m, 1H, *E/Z*), 7.37–7.26 (m, 2H, *E/Z*), 7.26–7.14 (m, 2H, *E/Z*), 7.06 (ddd, *J* = 8.8, 6.5, 2.8 Hz, 1H, *E/Z*), 6.94–6.83 (m, 2H, *E/Z*), 5.76–5.57 (m, 1H, *E/Z*), 5.59–5.39 (m, 1H, *E/Z*), 5.09 (s, 2H, *Z*), 5.08 (s, 2H, *E*), 4.25–4.09 (m, 2H, *E/Z*), 3.81 (s, 3H, *E/Z*), 3.49 (d, *J* = 7.0 Hz, 2H, *Z*), 3.44 (d, *J* = 6.5 Hz, 2H, *E*), 2.55 (q, *J* = 7.1 Hz, 2H, *Z*), 2.45–2.33 (m, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.9 (*E/Z*), 155.2 (*E/Z*), 139.8 (*E/Z*), 132.7 (*E/Z*), 130.4 (*Z*), 130.3 (*E*), 130.3 (*E/Z*), 127.8 (*E/Z*), 127.5 (*E*), 127.4 (*Z*), 127.1 (*E/Z*), 125.8 (*E/Z*), 124.5 (*E/Z*), 114.0 (*E/Z*), 69.4 (*E/Z*), 67.3 (*E/Z*), 55.3 (*E/Z*), 39.1 (*E*), 34.0 (*Z*), 32.0 (*E*), 27.1 (*Z*). **HRMS** (ESI) calcd. for $[C_{20}H_{21}BrNaO_4]^+$ $(M+Na)^+$: m/z = 427.0515, found 427.0521.

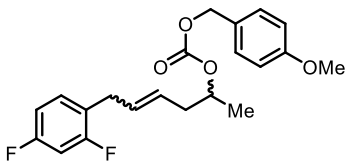
tert-Butyl-6-((((4-Methoxybenzyl)oxy)carbonyl)oxy)hex-3-enoate (135n)



According to **General Procedure C**: *tert*-butyl-6-hydroxyhex-3-enoate (1.1 g, 6.0 mmol, 1.0 equiv), 4-DMAP (0.15 g, 1.2 mmol, 0.20 equiv), NEt_3 (2.5 mL, 18 mmol, 3.0 equiv) were dissolved in THF (20 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (2.2 g, 9.3 mmol, 1.5 equiv), diluted in THF (4.0 mL), was added. Reaction time 69 h. Separated between H_2O (10 mL) and Et_2O (10 mL). Extracted with Et_2O (3x 10 mL), washed with H_2O (3x 10 mL) and dried over $MgSO_4$. Eluting with DCM/PE 7:3. Isolated yield: 0.85 g (2.4 mmol, 40%) as a mixture of isomers (45:10 *E/Z*).

TLC: R_f = 0.24 (DCM/PE 7:3). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2974, 2840, 1733, 1614, 1517, 1457, 1394, 1368, 1241, 1148, 1036, 969, 824. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.27 (m, 2H, *E/Z*), 6.94-6.82 (m, 2H, *E/Z*), 5.84–5.40 (m, 2H, *E/Z*), 5.08 (s, 2H, *E/Z*), 4.23–4.09 (m, 2H, *E/Z*), 3.81 (s, 3H, *E/Z*), 2.99 (dd, *J* = 7.2, 1.6 Hz, 2H, *Z*), 2.93 (dd, *J* = 6.6, 1.1 Hz, 2H, *E*), 2.49–2.31 (m, 2H, *E*), 2.27 (dd, *J* = 8.6, 7.0 Hz, 2H, *Z*), 1.47 (s, 9H, *Z*), 1.43 (s, 9H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 171.1 (*E/Z*), 159.9 (*E/Z*), 155.1 (*E/Z*), 130.3 (*E/Z*), 128.6 (*E/Z*), 127.4 (*E/Z*), 125.7 (*E/Z*), 114.0 (*E/Z*), 80.6 (*E/Z*), 69.4 (*E/Z*), 67.3 (*E/Z*), 55.3 (*E/Z*), 39.3 (*E*), 34.3 (*Z*), 31.9 (*E*), 28.2 (*E/Z*), 27.1 (*Z*). **HRMS** (ESI) calcd. for $[C_{19}H_{30}NO_6]^+$ $(M+NH_4)^+$: m/z = 368.2068, found 368.2071.

6-(2,4-Difluorophenyl)hex-4-en-2-yl (4-methoxybenzyl) carbonate (135o)

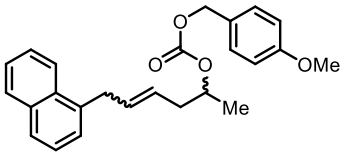


According to **General Procedure C**: 6-(2,4-difluorophenyl)hex-4-en-2-ol (2.2 g, 10 mmol, 1.0 equiv), 4-DMAP (0.25 g, 2.0 mmol, 0.20 equiv), NEt_3 (4.3 mL, 31 mmol, 3.0 equiv) were dissolved in THF (34 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (3.5 g, 15 mmol, 1.5 equiv), diluted in THF (5.0 mL), was added. Reaction time 67 h.

Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 25 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 35:1. Isolated yield: 1.7 g (4.5 mmol, 44%) as a mixture of isomers (43:10 *E/Z*).

TLC: R_f = 0.06 (PE/EtOAc 35:1). **IR** (ATR): ṽ [cm^{-1}] = 3079, 2982, 2840, 1737, 1614, 1506, 1383, 1245, 1178, 1137, 1088, 1036, 965, 917, 850, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.37–7.28 (m, 2H, *E/Z*), 7.19–7.02 (m, 1H, *E/Z*), 6.94–6.83 (m, 2H, *E/Z*), 6.83–6.68 (m, 2H, *E/Z*), 5.68–5.49 (m, 1H, *E/Z*), 5.54–5.36 (m, 1H, *E/Z*), 5.08 (s, 2H, *Z*), 5.06 (s, 2H, *E*), 4.81 (dq, *J* = 14.7, 6.3 Hz, 1H, *E/Z*), 3.81 (s, 3H, *E/Z*), 3.34 (d, *J* = 7.1 Hz, 2H, *Z*), 3.29 (d, *J* = 6.5 Hz, 2H, *E*), 2.52 (dt, *J* = 13.7, 6.6 Hz, 2H, *Z*), 2.47-2.17 (m, 2H, *E*), 1.30 (d, *J* = 6.3 Hz, 3H, *Z*), 1.25 (d, *J* = 6.3 Hz, 3H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.9 (*E/Z*), 154.7 (*E/Z*), 130.9 (dd, *J* = 9.4, 6.5 Hz, C-F, *E/Z*), 130.8 (*E/Z*), 130.3 (*E/Z*), 130.3 (*E/Z*), 127.5 (*E*), 127.5 (*Z*), 126.8 (*E/Z*), 114.0 (*E/Z*), 111.0 (d, *J* = 20.7 Hz, C-F, *E/Z*), 103.6 (t, *J* = 25.8 Hz, C-F, *E/Z*), 74.6 (*E/Z*), 69.3 (*E/Z*), 55.3 (*E/Z*), 38.9 (*E/Z*), 31.3 (*E/Z*), 31.3 (*E/Z*), 19.5 (*E/Z*). **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 114.1 (d, *J* = 6.7 Hz, *E*), - 114.1 (d, *J* = 6.7 Hz, *Z*), - 114.6 (d, *J* = 6.7 Hz, *Z*), - 114.87 (d, *J* = 6.7 Hz, *E*). **HRMS** (ESI) calcd. for $[C_{21}H_{22}F_2NaO_4]^+$ $(M+Na)^+$: m/z = 399.1378, found 399.1381.

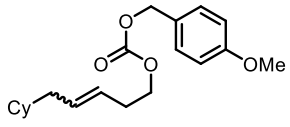
4-Methoxybenzyl (6-(naphthalen-1-yl)hex-4-en-2-yl) carbonate (135p)



According to **General Procedure C**: 6-(naphthalen-1-yl)hex-4-en-2-ol (2.7 g, 12 mmol, 1.0 equiv), 4-DMAP (0.29 g, 2.4 mmol, 0.20 equiv), NEt_3 (4.9 mL, 35 mmol, 3.0 equiv) were dissolved in THF (40 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (4.1 g, 18 mmol, 1.5 equiv), diluted in THF (5.0 mL), was added. Reaction time 45 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 19:1. Isolated yield: 1.7 g (4.4 mmol, 38%) as a mixture of isomers (51:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 19:1). **IR** (ATR): ṽ [cm^{-1}] = 3042, 2978, 2837, 1737, 1614, 1513, 1383, 1245, 1178, 1036, 969, 917, 820, 790. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 8.07–7.94 (m, 1H, *E/Z*), 7.91–7.79 (m, 1H, *E/Z*), 7.72 (dt, *J* = 8.1, 1.1 Hz, 1H, *E/Z*), 7.56–7.43 (m, 2H, *E/Z*), 7.45–7.33 (m, 1H, *E/Z*), 7.39–7.25 (m, 3H, *E/Z*), 6.94–6.81 (m, 2H, *E/Z*), 5.89–5.70 (m, 1H, *E/Z*), 5.64–5.41 (m, 1H, *E/Z*), 5.10 (s, 2H, *Z*), 5.05 (s, 2H, *E*), 4.90 (q, *J* = 6.3 Hz, 1H, *Z*), 4.78 (h, *J* = 6.3 Hz, 1H, *E*), 3.87–3.73 (m, 5H, *E/Z*), 2.56 (ddt, *J* = 42.2, 14.5, 7.1 Hz, 2H, *Z*), 2.46–2.18 (m, 2H, *E*), 1.35 (d, *J* = 6.3 Hz, 3H, *Z*), 1.24 (d, *J* = 6.3 Hz, 3H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.8 (*E/Z*), 154.7 (*E/Z*), 136.5 (*E/Z*), 133.8 (*E/Z*), 132.3 (*E*), 131.9 (*Z*), 130.3 (*Z*), 130.3 (*E*), 128.7 (*E*), 127.6 (*Z*), 126.9 (*E/Z*), 126.5 (*E/Z*), 126.1 (*E/Z*), 125.8 (*E/Z*), 125.6 (*E/Z*), 125.5 (*E/Z*), 124.0 (*E/Z*), 113.9 (*E/Z*), 74.8 (*E/Z*), 69.2 (*E/Z*), 55.3 (*E/Z*), 39.0 (*E*), 36.2 (*E*), 33.9 (*Z*), 31.0 (*Z*), 19.5 (*E/Z*). **HRMS** (ESI) calcd. for $[C_{25}H_{26}NaO_4]^+$ $(M+Na)^+$: m/z = 413.1723, found 413.1728.

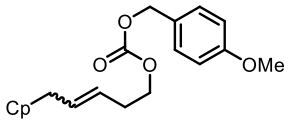
5-Cyclohexylpent-3-en-1-yl (4-methoxybenzyl) carbonate (135q)



According to **General Procedure C**: 5-cyclohexylpent-3-en-1-ol (2.2 g, 13 mmol, 1.0 equiv), 4-DMAP (0.34 g, 2.8 mmol, 0.21 equiv), NEt_3 (5.7 mL, 41 mmol, 3.1 equiv) were dissolved in THF (45 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (4.7 g, 20 mmol, 1.5 equiv), diluted in THF (6.9 mL), was added. Reaction time 92 h. Separated between H_2O (15 mL) and Et_2O (15 mL). Extracted with Et_2O (2x 30 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 99:1. Isolated yield: 3.4 g (10 mmol, 78%) as a mixture of isomers (29:10 *E/Z*).

TLC: R_f = 0.06 (PE/EtOAc 99:1). **IR** (ATR): ṽ [cm^{-1}] = 2922, 2848, 1741, 1614, 1513, 1450, 1394, 1238, 1174, 1111, 1036, 969, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.28 (m, 2H, *E/Z*), 6.94-6.83 (m, 2H, *E/Z*), 5.50 (dtt, *J* = 15.2, 6.9, 1.2 Hz, 1H, *E/Z*), 5.42–5.27 (m, 1H, *E/Z*), 5.08 (s, 2H, *E/Z*), 4.17–4.08 (m, 2H, *E/Z*), 3.81 (s, 3H, *E/Z*), 2.46–2.29 (m, 2H, *E/Z*), 1.97–1.80 (m, 2H, *E/Z*), 1.74-1.54 (m, 5H, *E/Z*), 1.30–1.07 (m, 4H, *E/Z*), 0.84 (q, *J* = 11.8 Hz, 2H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.8 (*E/Z*), 155.2 (*E/Z*), 132.5 (*E/Z*), 130.3 (*E/Z*), 127.5 (*E/Z*), 125.4 (*E/Z*), 124.2 (*E/Z*), 113.9 (*E/Z*), 69.4 (*E/Z*), 67.7 (*E/Z*), 55.3 (*E/Z*), 40.6 (*E/Z*), 38.1 (*E/Z*), 37.9 (*E/Z*), 33.1 (*E/Z*), 33.1 (*E*), 32.0 (*Z*), 26.6 (*Z*), 26.4 (*E*). **HRMS** (ESI) calcd. for $[C_{20}H_{28}NaO_4]^+$ $(M+Na)^+$: m/z = 355.1880, found 355.1880.

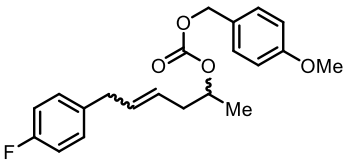
5-Cyclopentylpent-3-en-1-yl (4-methoxybenzyl) carbonate (135r)



According to **General Procedure C**: 5-cyclopentylpent-3-en-1-ol (2.0 g, 13 mmol, 1.0 equiv), 4-DMAP (0.49 g, 4.0 mmol, 0.31 equiv), NEt_3 (8.4 mL, 60 mmol, 4.7 equiv) were dissolved in THF (67 mL, 0.2 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (6.1 g, 26 mmol, 2.0 equiv), diluted in THF (6.0 mL), was added. Reaction time 116 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 15 mL), washed with H_2O (2x 15 mL) and brine (15 mL), and dried over $MgSO_4$. Eluting with PE/EtOAc 99:1. Isolated yield: 2.4 g (7.4 mmol, 57%) as a mixture of isomers (50:1 *E/Z*).

TLC: R_f = 0.06 (PE/EtOAc 99:1). **IR** (ATR): ṽ [cm^{-1}] = 2952, 1744, 1614, 1517, 1454, 1394, 1245, 1178, 1036, 969, 824. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.27 (m, 2H, *E/Z*), 6.95–6.83 (m, 2H, *E/Z*), 5.60–5.43 (m, 1H, *E/Z*), 5.43–5.26 (m, 1H, *E/Z*), 5.08 (s, 2H, *E/Z*), 4.12 (2xt, *J* = 7.0 Hz, 2H, *E/Z*), 3.81 (s, 3H, *E/Z*), 2.48–2.28 (m, 2H, *E/Z*), 2.09–1.92 (m, 2H, *E/Z*), 1.86–1.40 (m, 7H, *E/Z*), 1.20-1.00 (m, 2H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.8 (*E/Z*), 155.2 (*E/Z*), 133.3 (*E*), 132.6 (*Z*), 130.3 (*E/Z*), 127.5 (*E/Z*), 124.9 (*E*), 123.7 (*Z*), 113.9 (*E*), 110.0 (*Z*), 69.3 (*E/Z*), 67.7 (*E/Z*), 55.3 (*E/Z*), 40.1 (*Z*), 39.8 (*E*), 39.0 (*E/Z*), 33.3 (*Z*), 32.3 (*Z*), 32.2 (*E*), 32.0 (*E*), 27.0 (*Z*), 25.1 (*E*). **HRMS** (ESI) calcd. for $[C_{19}H_{26}NaO_4]^+$ $(M+Na)^+$: m/z = 341.1723, found 341.1731.

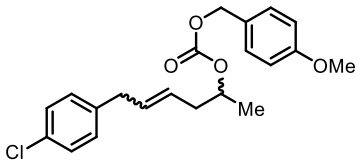
6-(4-Fluorophenyl)hex-4-en-2-yl (4-methoxybenzyl) carbonate (135s)



According to **General Procedure C**: 6-(4-fluorophenyl)hex-4-en-2-ol (1.4 g, 7.3 mmol, 1.0 equiv), 4-DMAP (0.12 g, 1.0 mmol, 0.14 equiv), NEt_3 (2.1 mL, 15 mmol, 2.0 equiv) were dissolved in THF (20 mL, 0.4 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (1.7 g, 7.5 mmol, 1.0 equiv), diluted in THF (5.0 mL), was added. Reaction time 92 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 50:1. Isolated yield: 0.88 g (2.5 mmol, 49%) as a mixture of isomers (39:10 *E/Z*).

TLC: R_f = 0.10 (PE/EtOAc 50:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2932, 1737, 1614, 1513, 1245, 1036. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.26 (m, 2H, *E/Z*), 7.17–7.04 (m, 2H, *E/Z*), 7.01–6.89 (m, 2H, *E/Z*), 6.95–6.83 (m, 2H, *E/Z*), 5.71–5.54 (m, 1H, *E/Z*), 5.53–5.35 (m, 1H, *E/Z*), 5.07 (2xs, 2H, *E/Z*), 4.81 (h, *J* = 6.2 Hz, 1H, *E/Z*), 3.80 (s, 3H, *E/Z*), 3.35 (d, *J* = 7.0 Hz, 2H, *Z*), 3.28 (d, *J* = 6.6 Hz, 2H, *E*), 2.68-2.44 (m, 2H, *Z*), 2.45-2.20 (m, 2H, *E*), 1.31 (d, *J* = 6.2 Hz, 3H, *Z*), 1.27 (d, *J* = 6.3 Hz, 3H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.9 (*E/Z*), 154.8 (*E/Z*), 154.7 (*E/Z*), 138.3 (*Z*), 136.1 (*Z*), 132.5 (*Z*), 130.3 (*E*), 129.8 (d, *J* = 7.8 Hz, C-F, *E/Z*), 127.5 (*Z*), 126.3 (*E*), 115.1 (d, *J* = 21.0 Hz, C-F, *E/Z*), 114.0 (*E/Z*), 77.2 (*E/Z*), 74.7 (*E/Z*), 69.3 (*E/Z*), 55.3 (*E/Z*), 38.9 (*E/Z*), 38.2 (*E/Z*), 19.5 (*E/Z*). **^{19}F NMR** (376 MHz, Chloroform-*d*): δ [ppm] = -118.1 (s). **HRMS** (ESI) calcd. for $[C_{21}H_{23}FNaO_4]^+$ $(M+Na)^+$: m/z = 381.1473, found 381.1472.

6-(4-Chlorophenyl)hex-4-en-2-yl (4-methoxybenzyl) carbonate (135t)

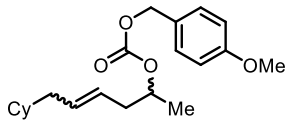


According to **General Procedure C**: 6-(4-chlorophenyl)hex-4-en-2-ol (2.8 g, 13 mmol, 1.0 equiv), 4-DMAP (0.34 g, 2.8 mmol, 0.21 equiv), NEt_3 (5.5 mL, 40 mmol, 3.0 equiv) were dissolved in THF (45 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (3.9 g, 17 mmol, 1.3 equiv), diluted in THF (6.0 mL), was added. Reaction time 66 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 50:1. Isolated yield: 2.1 g (5.7 mmol, 43%) as a mixture of isomers (43:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 50:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2978, 1737, 1614, 1513, 1457, 1383, 1245, 1178, 1137, 1092, 1036, 969, 917, 820, 712. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.26 (m, 2H, *E/Z*), 7.21 (dq, *J* = 8.4, 2.3 Hz, 2H, *E/Z*), 7.14–7.02 (m, 2H, *E/Z*), 6.94–6.83 (m, 2H, *E/Z*), 5.69–5.53 (m, 1H, *E/Z*), 5.45 (dtt, *J* = 15.3, 7.1, 1.3 Hz, 1H, *E/Z*), 5.07 (2xs, 2H, *E/Z*), 4.89–4.70 (m, 1H), 3.81 (s, 3H, *E/Z*), 3.34 (d, *J* = 7.0 Hz, 2H, *Z*), 3.28 (d, *J* = 6.6 Hz, 2H, *E*), 2.43–2.21 (m, 2H, *E/Z*), 1.31 (d, *J* = 6.3 Hz, 3H, *Z*), 1.27 (d, *J* = 6.3 Hz, 3H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.9 (*E/Z*), 154.7 (*E/Z*), 139.0 (*Z*), 138.9 (*E*), 132.1 (*E*), 131.7 (*Z*), 130.8 (*Z*), 130.3 (*E*), 130.3 (*E/Z*), 129.8 (*E*), 129.7 (*Z*), 128.5 (*Z*), 128.5 (*E*), 127.5 (*E*), 127.5 (*Z*), 126.6 (*E*),

125.2 (*Z*), 114.0 (*E/Z*), 74.7 (*E/Z*), 69.3 (*E/Z*), 55.3 (*E/Z*), 38.9 (*E*), 38.3 (*E*), 33.7 (*Z*), 32.9 (*Z*), 19.6 (*Z*), 19.5 (*E*). **HRMS** (ESI) calcd. for $[C_{21}H_{23}ClNaO_4]^+$ $(M+Na)^+$: m/z = 397.1177, found 397.1177.

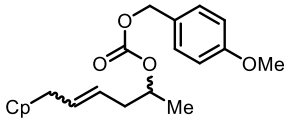
6-Cyclohexylhex-4-en-2-yl (4-methoxybenzyl) carbonate (135u)



According to **General Procedure C**: 6-cyclohexylhex-4-en-2-ol (2.8 g, 15 mmol, 1.0 equiv), 4-DMAP (0.38 g, 3.1 mmol, 0.20 equiv), NEt_3 (6.4 mL, 46 mmol, 3.0 equiv) were dissolved in THF (50 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (5.4 g, 23 mmol, 1.5 equiv), diluted in THF (5.0 mL), was added. Reaction time 68 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 99:1. Isolated yield: 0.93 g (2.7 mmol, 17%) as a mixture of isomers (32:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 99:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2922, 2851, 1741, 1614, 1517, 1450, 1383, 1245, 1178, 1036, 973, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.28 (m, 2H, *E/Z*), 6.94–6.83 (m, 2H, *E/Z*), 5.53–5.39 (m, 1H, *E/Z*), 5.37–5.25 (m, 1H, *E/Z*), 5.07 (s, 2H, *E/Z*), 4.85–4.68 (m, 1H, *E/Z*), 3.81 (s, 3H, *E/Z*), 2.43–2.14 (m, 2H, *E/Z*), 1.89 (2xt, *J* = 6.9 Hz, 2H, *E/Z*), 1.74–1.57 (m, 4H, *E/Z*), 1.32-1.09 (m, 7H, *E/Z*), 0.96–0.75 (m, 3H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 172.4 (*E/Z*), 168.6 (*E/Z*), 159.8 (*E/Z*), 154.7 (*E/Z*), 132.9 (*Z*), 130.2 (*E*), 127.6 (*Z*), 125.4 (*E*), 113.9 (*E/Z*), 75.0 (*E/Z*), 69.2 (*E/Z*), 55.3 (*E/Z*), 40.6 (*E/Z*), 39.1 (*E/Z*), 37.9 (*E/Z*), 33.2 (*Z*), 33.1 (*E*), 33.1 (*E/Z*), 26.6 (*Z*), 26.4 (*E*), 19.4 (*E/Z*). **HRMS** (ESI) calcd. for $[C_{21}H_{30}NaO_4]^+$ $(M+Na)^+$: m/z = 369.2036, found 369.2047.

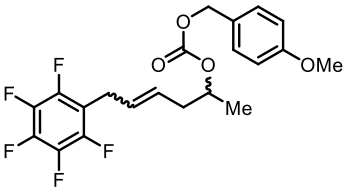
6-Cyclopentylhex-4-en-2-yl (4-methoxybenzyl) carbonate (135v)



According to **General Procedure C**: 6-cyclopentylpent-3-en-1-ol (3.0 g, 18 mmol, 1.0 equiv), 4-DMAP (0.44 g, 3.6 mmol, 0.20 equiv), NEt_3 (7.5 mL, 54 mmol, 3.0 equiv) were dissolved in THF (60 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (6.3 g, 27 mmol, 1.5 equiv), diluted in THF (5.0 mL), was added. Reaction time 49 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (2x 30 mL) and brine (15 mL), and dried over $MgSO_4$. Eluting with PE/EtOAc 99:1. Isolated yield: 2.7 g (8.0 mmol, 44%) as a mixture of isomers (46:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 99:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2948, 2866, 1737, 1614, 1513, 1454, 1383, 1245, 1178, 1133, 1036, 973, 917, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.27 (m, 2H, *E/Z*), 6.94–6.82 (m, 2H, *E/Z*), 5.49 (dtt, *J* = 14.6, 6.6, 1.1 Hz, 1H, *E/Z*), 5.42–5.24 (m, 1H, *E/Z*), 5.07 (s, 2H, *E/Z*), 4.85–4.68 (m, 1H, *E/Z*), 3.81 (s, 3H, *E/Z*), 2.49–2.14 (m, 2H, *E/Z*), 2.09–1.91 (m, 2H, *E/Z*), 1.90-1.41 (m, 7H, *E/Z*), 1.26 (dd, *J* = 6.3, 5.1 Hz, 3H, *E/Z*), 1.18–0.99 (m, 2H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.8 (*E/Z*), 154.8 (*E/Z*), 139.4 (*Z*), 133.8 (*E*), 130.2 (*E*), 127.6 (*Z*), 124.8 (*E/Z*), 113.9 (*E*), 110.0 (*Z*), 75.0 (*E/Z*), 69.2 (*E/Z*), 55.3 (*E/Z*), 39.9 (*E/Z*), 39.1 (*E/Z*), 39.0 (*E/Z*), 32.2 (*E/Z*), 32.2 (*E/Z*), 25.2 (*E*), 25.1 (*Z*), 19.4 (*E/Z*). **HRMS** (ESI) calcd. for $[C_{20}H_{28}NaO_4]^+$ $(M+Na)^+$: m/z = 355.1880, found 355.1882.

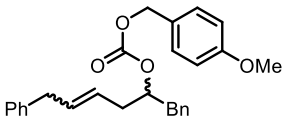
4-Methoxybenzyl (6-(perfluorophenyl)hex-4-en-2-yl) carbonate (135x)



According to **General Procedure C**: 6-(perfluorophenyl)hex-4-en-2-ol (1.9 g, 7.0 mmol, 1.0 equiv), 4-DMAP (0.17 g, 1.4 mmol, 0.20 equiv), NEt_3 (2.9 mL, 21 mmol, 3.0 equiv) were dissolved in THF (24 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (2.4 g, 11 mmol, 1.5 equiv), diluted in THF (5.0 mL), was added. Reaction time 120 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 50:1. Isolated yield: 1.7 g (4.0 mmol, 57%) as a mixture of isomers (61:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 50:1). **IR** (ATR): ṽ [cm^{-1}] = 2982, 1741, 1506, 1249. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.23 (m, 2H, *E/Z*), 6.95–6.83 (m, 2H, *E/Z*), 5.63–5.40 (m, 2H, *E/Z*), 5.07 (s, 2H, *E/Z*), 4.90–4.68 (m, 1H, *E/Z*), 3.81 (s, 3H, *E/Z*), 3.45–3.32 (m, 2H, *E/Z*), 2.60–2.36 (m, 2H, *Z*), 2.39-2.16 (m, 2H, *E*), 1.31 (d, *J* = 6.0 Hz, 3H, *Z*), 1.23 (d, *J* = 6.3 Hz, 3H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.8 (*E/Z*), 154.6 (*E/Z*), 146.1 (m, C-F, *E/Z*), 143.7 (m, C-F, *E/Z*), 141.0 (m, C-F, *Z*), 138.7 (m, C-F, *E/Z* + *E*), 136.2 (m, C-F, *E/Z*), 130.2 (*E/Z*), 128.0 (*E/Z*), 127.8 (*E/Z*), 127.4 (*E/Z*), 113.9 (*E/Z*), 74.3 (*E/Z*), 69.2 (*E/Z*), 55.2 (*E/Z*), 38.7 (*E*), 33.4 (*Z*), 25.3 (*Z*), 19.4 (*E*). **^{19}F NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 144.6 (dd, *J* = 22.3, 8.6 Hz, F-F, *E/Z*), - 158.0 (t, *J* = 20.8 Hz, F-F, *E/Z*), -163.2 (m, F-F, *E/Z*). **HRMS** (ESI) calcd. for $[C_{21}H_{19}F_5NaO_4]^+$ $(M+Na)^+$: m/z = 453.1096, found 453.1096.

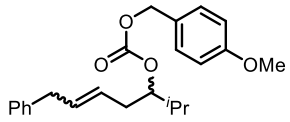
1,6-Diphenylhex-4-en-2-yl (4-methoxybenzyl) carbonate (135y)



According to **General Procedure C**: 1,6-diphenylhex-4-en-2-ol (2.1 g, 8.6 mmol, 1.0 equiv), 4-DMAP (0.23 g, 1.9 mmol, 0.21 equiv), NEt_3 (3.6 mL, 26 mmol, 3.0 equiv) were dissolved in THF (29 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (3.1 g, 13 mmol, 1.5 equiv), diluted in THF (4.5 mL), was added. Reaction time 71 h. Separated between H_2O (20 mL) and Et_2O (20 mL). Extracted with Et_2O (2x 20 mL), washed with H_2O (3x 20 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 30:1. Isolated yield: 2.4 g (5.7 mmol, 65%) as a mixture of isomers (46:10 *E/Z*).

TLC: R_f = 0.12 (PE/EtOAc 30:1). **IR** (ATR): ṽ [cm^{-1}] = 3355, 2922, 2855, 1047, 969, 757, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.37–7.09 (m, 12H, *E/Z*), 6.90–6.82 (m, 2H, *E/Z*), 5.76–5.59 (m, 1H, *E/Z*), 5.55–5.38 (m, 1H, *E/Z*), 5.02 (2xs, 2H, *E/Z*), 4.94 (qd, *J* = 6.9, 5.7 Hz, 1H, *E/Z*), 3.81 (2xs, 3H, *E/Z*), 3.31 (d, *J* = 6.6 Hz, 2H, *E/Z*), 3.08–2.78 (m, 2H, *E/Z*), 2.52–2.42 (m, 2H, *Z*), 2.38–2.26 (m, 2H, *E*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.0 (*E/Z*), 135.4 (*E*), 133.9 (*Z*), 128.4 (*E/Z*), 127.5 (*Z*), 127.4 (*E*), 126.2 (*Z*), 125.8 (*E*), 125.4 (*E*), 124.6 (*Z*), 74.0 (*Z*), 73.5 (*E*), 42.9 (*E*), 37.4 (*Z*), 32.7 (*E*), 31.9 (*E/Z*), 29.7 (*E/Z*), 29.6 (*E/Z*), 29.6 (*E/Z*), 29.5 (*E/Z*), 29.4 (*E/Z*), 29.4 (*E/Z*), 29.3 (*E/Z*), 29.2 (*E/Z*), 27.5 (*E/Z*), 22.7 (*E/Z*), 14.1 (*E/Z*). **HRMS** (ESI) calcd. for $[C_{27}H_{28}NaO_4]^+$ $(M+Na)^+$: m/z = 439.1880, found 439.1886.

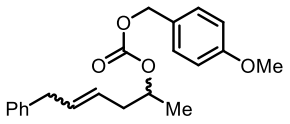
4-Methoxybenzyl (2-methyl-7-phenylhept-5-en-3-yl) carbonate (135z)



According to **General Procedure C**: 2-methyl-7-phenylhept-5-en-3-ol (1.9 g, 9.3 mmol, 1.0 equiv), 4-DMAP (0.29 g, 1.9 mmol, 0.20 equiv), NEt_3 (3.9 mL, 28 mmol, 3.0 equiv) were dissolved in THF (31 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (3.3 g, 14 mmol, 1.5 equiv), diluted in THF (5.0 mL), was added. Reaction time 72 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 25 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 99:1. Isolated yield: 1.4 g (3.7 mmol, 40%) as a mixture of isomers (22:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 99:1). **IR** (ATR): ṽ [cm^{-1}] = 3027, 2963, 2840, 1741, 1614, 1517, 1454, 1387, 1245, 1178, 1036, 969, 824, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.37–7.20 (m, 4H, *E/Z*), 7.22–7.11 (m, 3H, *E/Z*), 6.92–6.82 (m, 2H, *E/Z*), 5.70–5.56 (m, 1H, *E/Z*), 5.45 (dt, *J* = 15.2, 6.9 Hz, 1H, *E/Z*), 5.07 (2xs, 2H, *E/Z*), 4.58 (dt, *J* = 7.2, 5.5 Hz, 1H, *E/Z*), 3.80 (2xs, 3H, *E/Z*), 3.38 (d, *J* = 6.6 Hz, 2H, *Z*), 3.28 (d, *J* = 6.7 Hz, 2H, *E*), 2.54–2.38 (m, 2H, *Z*), 2.36–2.25 (m, 2H, *E*), 1.89 (dp, *J* = 13.1, 6.5 Hz, 1H, *E/Z*), 0.93 (2xd, *J* = 6.8 Hz, 6H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.8 (*E/Z*), 155.2 (*E/Z*), 143.9 (*Z*), 140.6 (*E*), 132.2 (*Z*), 130.1 (*E*), 128.5 (*E*), 128.4 (*Z*), 128.4 (*E*), 127.7 (*Z*), 126.5 (*E*), 125.9 (*E*), 125.2 (*Z*), 113.9 (*E/Z*), 82.5 (*E/Z*), 69.2 (*E/Z*), 55.3 (*E/Z*), 39.0 (*E/Z*), 34.6 (*E/Z*), 31.1 (*E*), 29.3 (*Z*), 18.5 (*E/Z*), 17.5 (*E/Z*). **HRMS** (ESI) calcd. for $[C_{23}H_{28}NaO_4]^+$ $(M+Na)^+$: m/z = 391.1880, found 391.1880.

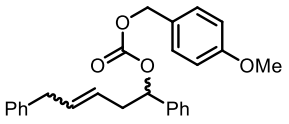
4-Methoxybenzyl (6-phenylhex-4-en-2-yl) carbonate (135bb)



According to **General Procedure C**: 6-phenylhex-4-en-2-ol (3.3 g, 18 mmol, 1.0 equiv), 4-DMAP (0.49 g, 4.0 mmol, 0.22 equiv), NEt_3 (7.8 mL, 56 mmol, 3.0 equiv) were dissolved in THF (61 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (6.2 g, 27 mmol, 1.5 equiv), diluted in THF (9.2 mL), was added. Reaction time 68 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 35:1. Isolated yield: 5.0 g (15 mmol, 80%) as a mixture of isomers (47:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 35:1). **IR** (ATR): ṽ [cm^{-1}] = 3026, 2978, 2836, 1736, 1613, 1513, 1453, 1382, 1244, 1177, 1138, 1036, 969, 918, 853, 820, 747, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.21 (m, 4H, *E/Z*), 7.22–7.13 (m, 3H, *E/Z*), 6.92–6.86 (m, 2H, *E/Z*), 5.66 (dtt, *J* = 14.7, 6.6, 1.2 Hz, 1H, *E/Z*), 5.54–5.39 (m, 1H, *E/Z*), 5.08 (2xs, 2H, *E/Z*), 4.81 (hept, *J* = 6.3 Hz, 1H, *E/Z*), 3.81 (s, 3H, *E/Z*), 3.39 (d, *J* = 7.4 Hz, 2H, *Z*), 3.32 (d, *J* = 6.7 Hz, 2H, *E*), 2.60–2.48 (m, 2H, *Z*), 2.45–2.21 (m, 2H, *E*), 1.31 (d, *J* = 6.3 Hz, 3H, *Z*), 1.27 (d, *J* = 6.3 Hz, 3H, *E*). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 159.9 (*E/Z*), 154.8 (*E/Z*), 140.6 (*E/Z*), 132.8 (*E/Z*), 130.4 (*E/Z*), 128.6 (*E/Z*), 127.6 (*E/Z*), 126.2 (*E/Z*), 114.1 (*E/Z*), 77.6 (*E/Z*), 74.9 (*E/Z*), 69.4 (*E/Z*), 55.4 (*E/Z*), 39.2 (*E/Z*), 19.6 (*E/Z*). **HRMS** (ESI) calcd. for $[C_{21}H_{24}NaO_4]^+$ $(M+Na)^+$: m/z = 363.1567, found 363.1570.

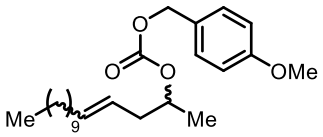
1,5-Diphenylpent-3-en-1-yl (4-methoxybenzyl) carbonate (135cc)



According to **General Procedure C**: 1,5-diphenylpent-3-en-1-ol (1.9 g, 8.0 mmol, 1.0 equiv), 4-DMAP (0.19 g, 1.6 mmol, 0.20 equiv), NEt_3 (3.3 mL, 24 mmol, 3.0 equiv) were dissolved in THF (25 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (2.8 g, 12 mmol, 1.5 equiv), diluted in THF (4.0 mL), was added. Reaction time 157 h. Separated between H_2O (25 mL) and Et_2O (25 mL). Extracted with Et_2O (2x 20 mL), washed with H_2O (3x 20 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 30:1. Isolated yield: 1.9 g (4.7 mmol, 59%) as a mixture of isomers (33:10 *E/Z*).

TLC: R_f = 0.08 (PE/EtOAc 50:1). **IR** (ATR): ṽ [cm^{-1}] = 3063, 3030, 2959, 2907, 2836, 1740, 1613, 1517, 1453, 1382, 1244, 1177, 1032, 969, 913, 823, 749, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ [ppm] = 7.43–7.11 (m, 10H, *E/Z*), 7.06 (dd, *J* = 6.8, 1.7 Hz, 2H, *E/Z*), 6.92–6.84 (m, 2H, *E/Z*), 5.69-5.54 (m, 2H, *E/Z*), 5.48–5.33 (m, 1H, *E/Z*), 5.16–4.96 (m, 2H, *E/Z*), 3.80 (2xs, 3H, *E/Z*), 3.27 (d, *J* = 6.7 Hz, 2H, *E/Z*), 2.87–2.48 (m, 2H, *E/Z*). **^{13}C NMR** (101 MHz Chloroform-*d*) δ [ppm] = 159.8 (*E/Z*), 154.6 (*E/Z*), 140.3 (*E/Z*), 139.5 (*E/Z*), 133.0 (*Z*), 130.3 (*E*), 128.5 (*Z*), 128.5 (*E*), 128.4 (*E/Z*), 128.4 (*Z*), 128.3 (*E*), 128.1 (*E/Z*), 127.4 (*E/Z*), 126.6 (*E/Z*), 126.5 (*E/Z*), 125.9 (*E/Z*), 125.8 (*E/Z*), 113.9 (*E/Z*), 79.7 (*E/Z*), 69.5 (*E/Z*), 55.3 (*E/Z*), 39.6 (*E/Z*), 38.9 (*E/Z*). **HRMS** (ESI) calcd. for $[C_{26}H_{26}NaO_4]^+$ $(M+Na)^+$: m/z = 425.1723, found 425.1726.

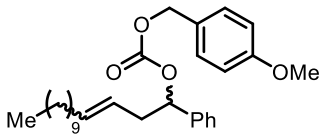
4-Methoxybenzyl pentadec-4-en-2-yl carbonate (135ee)



According to **General Procedure C**: pentadec-4-en-2-ol (2.1 g, 9.2 mmol, 1.0 equiv), 4-DMAP (0.23 g, 1.9 mmol, 0.20 equiv), NEt_3 (3.8 mL, 28 mmol, 3.0 equiv) were dissolved in THF (50 mL, 0.2 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (3.2 g, 14 mmol, 1.5 equiv), diluted in THF (5.0 mL), was added. Reaction time 68 h. Separated between H_2O (30 mL) and Et_2O (30 mL). Extracted with Et_2O (2x 25 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 200:1 to 99:1. Isolated yield: 3.5 g (9.3 mmol, 82%) as a mixture of isomers (*E/Z* n.d., *E*-major fraction).

TLC: R_f = 0.15 (PE/EtOAc 99:1). **IR** (ATR): ṽ [cm^{-1}] = 2926, 2855, 1741, 1614, 1517, 1461, 1379, 1245, 1178, 1040, 969, 917, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.35–7.29 (m, 2H, *E/Z*), 6.94-6.83 (m, 2H, *E/Z*), 5.57–5.41 (m, 1H, *E/Z*), 5.41–5.24 (m, 1H, *E/Z*), 5.07 (s, 2H, *E/Z*), 4.86–4.67 (m, 1H, *E/Z*), 3.81 (s, 3H, *E/Z*), 2.47–2.14 (m, 2H, *E/Z*), 1.97 (p, *J* = 7.0 Hz, 2H, *E/Z*), 1.40–1.17 (m, 19H, *E/Z*), 0.93–0.80 (m, 3H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.8 (*E/Z*), 154.7 (*E/Z*), 134.5 (*E/Z*), 130.2 (*E/Z*), 127.6 (*E/Z*), 124.3 (*E/Z*), 113.9 (*E/Z*), 75.0 (*E/Z*), 69.2 (*E/Z*), 55.3 (*E/Z*), 39.1 (*E/Z*), 32.6 (*E/Z*), 31.9 (*E/Z*), 29.7 (*E/Z*), 29.5 (*E/Z*), 29.4 (*E/Z*), 29.4 (*E/Z*), 29.2 (*E/Z*), 22.7 (*E/Z*), 19.4 (*E/Z*), 14.1 (*E/Z*). **HRMS** (ESI) calcd. for $[C_{24}H_{38}NaO_4]^+$ $(M+Na)^+$: m/z = 413.2662, found 413.2675.

4-Methoxybenzyl (1-phenyltetradec-3-en-1-yl) carbonate (135ff)

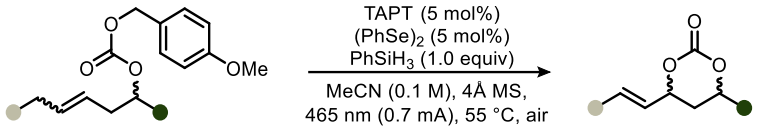


According to **General Procedure C**: 1-phenyltetradec-3-en-1-ol (2.5 g, 8.7 mmol, 1.0 equiv), 4-DMAP (0.22 g, 1.8 mmol, 0.21 equiv), NEt_3 (3.6 mL, 26 mmol, 3.0 equiv) were dissolved in THF (29 mL, 0.3 M) and 4-methoxybenzyl 1*H*-imidazole-1-carboxylate (3.2 g, 14 mmol, 1.6 equiv), diluted in THF (4.5 mL), was added. Reaction time 66 h. Separated between H_2O (20 mL) and Et_2O (20 mL). Extracted with Et_2O (2x 20 mL), washed with H_2O (2x 20 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 50:1. Isolated yield: 2.3 g (5.0 mmol, 57%) as a mixture of isomers (33:10 *E/Z*).

TLC: R_f = 0.10 (PE/EtOAc 50:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2922, 2855, 1744, 1614, 1517, 1457, 1383, 1245, 1178, 1036, 969, 910, 850, 824, 760, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.40–7.21 (m, 7H, *E/Z*), 6.93–6.81 (m, 2H, *E/Z*), 5.55 (dd, *J* = 7.4, 6.3 Hz, 1H, *E/Z*), 5.50–5.40 (m, 1H, *E/Z*), 5.33–5.18 (m, 1H, *E/Z*), 5.12–4.97 (m, 2H, *E/Z*), 3.80 (s, 3H, *E/Z*), 2.79–2.56 (m, 1H, *E/Z*), 2.57–2.42 (m, 1H, *E/Z*), 1.90 (t, *J* = 6.9 Hz, 2H, *E/Z*), 1.35–1.15 (m, 16H, *E/Z*), 0.95–0.82 (m, 3H, *E/Z*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 159.8 (*E/Z*), 154.6 (*E/Z*), 139.7 (*E/Z*), 134.8 (*E/Z*), 130.3 (*E/Z*), 128.4 (*E/Z*), 128.1 (*E*), 127.4 (*Z*), 126.6 (*E/Z*), 123.9 (*E/Z*), 113.9 (*E/Z*), 80.0 (*E/Z*), 69.4 (*E/Z*), 55.3 (*E/Z*), 39.7 (*E/Z*), 32.5 (*E/Z*), 31.9 (*E/Z*), 29.7 (*E/Z*), 29.7 (*E/Z*), 29.5 (*E/Z*), 29.4 (*E/Z*), 29.3 (*E/Z*), 29.1 (*E/Z*), 27.4 (*E/Z*), 22.7 (*E/Z*), 14.1 (*E/Z*). **HRMS** (ESI) calcd. for $[C_{29}H_{40}NaO_4]^+$ $(M+Na)^+$: m/z = 475.2819, found 475.2820.

6.2.2. Synthesis of 1,3-dioxan-2-ones

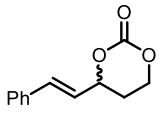
General Procedure D: Selenium-π-acid photoredox dual catalyzed cyclization reaction



Scheme 117: Reaction equation for the selenium-π-acid photoredox multicatalytic synthesis of cyclocarbonates.

The product from **General Procedure C** (1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (5 mol%), diphenyldiselenide (5 mol%) and phenylsilane (1.0 equiv) were added in a 100 mL flask and dissolved in MeCN (0.1 M). After the addition of 4Å molar sieves (10 mg/mmol), the mixture was irradiated with blue light (465 nm, 0.7 mA) at a temperature of 55 °C and an atmosphere of air (balloon) for the given reaction time. The reaction was concentrated, the respective NMR standard (0.50 equiv) added and diluted with chloroform-*d* (10 mL). After NMR analysis, the NMR sample was added back with $CHCl_3$, concentrated and separated between H_2O and EtOAc. After extraction with EtOAc and washing with H_2O, the residue was dried over $MgSO_4$ or Na_2SO_4 and purified by column chromatography.***the reaction time is strongly depended on the consistency of the stirring. Irregular stirring resulted in decreased reaction progression.**

(*E*)-4-Styryl-1,3-dioxan-2-one (136a)



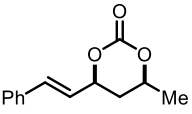
According to **General Procedure D**: (*E*)-4-methoxybenzyl (5-phenylpent-3-en-1-yl) carbonate (0.39 g, 1.2 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (30 mg, 60 µmol, 5 mol%), diphenyldiselenide (19 mg, 60 µmol, 5 mol%), phenylsilane (0.15 g, 1.4 mmol, 1.1 equiv) and 4Å molar sieves (10 mg) were dissolved in MeCN (12 mL, 0.1 M). Reaction time 24 h. 1,3,5-trimethoxybenzene (0.10 g, 0.60 mmol, 0.50 equiv) were added. NMR analysis resulted in 59%. Extracted with EtOAc (1x 10 mL), washed with H_2O (3x 20 mL) and dried over Na_2SO_4. Eluting with *n*-pentane/EtOAc 4:1.

Isolated yield 0.14 g, (0.68 mmol, 57%).

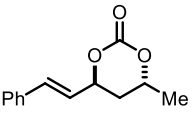
*Reaction was performed in the crystallization beaker setup.

TLC: R_f = 0.08 (*n*-pentane/EtOAc 4:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3027, 1733, 1409, 1245, 1193, 1133, 1103, 969, 746, 693. **^{1}H NMR** (400 MHz, MeCN-d_3): δ [ppm] = 7.52–7.43 (m, 2H), 7.42–7.25 (m, 3H), 6.74 (dd, *J* = 16.0, 1.2 Hz, 1H), 6.33 (dd, *J* = 16.0, 6.6 Hz, 1H), 5.16 (dddd, *J* = 9.5, 6.6, 3.8, 1.2 Hz, 1H), 4.47-4.38 (m, 2H), 2.23 (dq, *J* = 14.5, 3.8 Hz, 1H), 2.14–2.01 (m, 1H). **^{13}C NMR** (101 MHz, MeCN-d_3): δ [ppm] = 149.5, 133.8, 129.7, 129.3, 127.7, 127.1, 118.3, 80.3, 67.8, 27.9. **HRMS** (EI) calcd. for $[C_{11}H_{12}O_1]^{+\cdot}$ $(M - CO_2)^{+\cdot}$: m/z = 160.0883, found 160.0885.

(*E*)-4-Methyl-6-styryl-1,3-dioxan-2-one (136b)



cis



trans

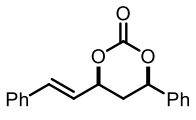
According to **General Procedure D**: 4-methoxybenzyl (6-phenylhex-4-en-2-yl) carbonate (0.34 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (25 mg, 50 µmol, 5 mol%), diphenyldiselenide (15 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (12 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 38 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 65% (25:10 *cis*/*trans*). Separated between EtOAc (30 mL) and H_2O (30 mL).Extracted with EtOAc (3x 20 mL), washed with H_2O (2x 20 mL), brine (1x 20 mL) and dried over Na_2SO_4. Eluting with PE/EtOAc 7:3 then precipitation when 1:1.5 PE/Et_2O was added.

Isolated yield 81 mg (0.37 mmol, 37%) as a mixture of diastereomers (26:10 *cis*/*trans*).

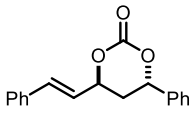
TLC: R_f = 0.10 (PE/EtOAc 7:3). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3060, 3027, 2982, 2933, 1737, 1603, 1495, 1450, 1394, 1301, 1230, 1193, 1141, 1100, 1036, 969, 753, 693. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.47–7.23 (m, 5H, *cis*/*trans*), 6.72 (2xdd, *J* = 15.9, 3.5 Hz, 1H, *cis*/*trans*), 6.18 (2xdd, *J* = 15.9, 8.4 Hz, 1H, *cis*/*trans*), 5.24 (qd, *J* = 4.9, 1.6 Hz, 1H, *trans*), 5.07 (dddd, *J* = 11.8, 6.6, 3.3, 1.2 Hz, 1H, *cis*), 4.80–4.55 (m, 1H, *cis*/*trans*), 2.29–2.06 (m, 1H, *cis*/*trans*), 1.84 (dt, *J* = 14.3, 11.7 Hz, 1H, *cis*/*trans*), 1.46 (d, *J* = 6.3 Hz, 3H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 149.0 (*cis*/*trans*), 135.4 (*cis*/*trans*), 133.7 (*cis*), 133.3 (*trans*), 128.8 (*cis*), 128.6 (*trans*), 126.8 (*cis*), 125.1 (*trans*), 125.0 (*cis*), 79.0 (*cis*), 76.4 (*trans*), 75.1 (*cis*), 72.5 (*trans*), 35.4 (*cis*), 33.2

(*trans*), 21.2 (*cis*), 20.9 (*trans*). **HRMS** (EI) calcd. for $[C_{13}H_{14}O_3]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 218.0937, found 218.0942.

(*E*)-4-Phenyl-6-styryl-1,3-dioxan-2-one (136c)



cis



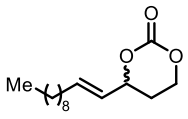
trans

According to **General Procedure D**: 1,5-diphenylpent-3-en-1-yl (4-methoxybenzyl) carbonate (0.40 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (10 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 37 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 64% (20:10 *cis*/*trans*). Separated between EtOAc (20 mL) and H_2O (20 mL).Extracted with EtOAc (2x 20 mL), washed with H_2O (3x 20 mL) and dried over $MgSO_4$. Eluting with PE/DCM 1:1.

Isolated yield 0.12 g (0.44 mmol, 44%) as a mixture of diastereomers (32:10 *cis*/*trans*).

TLC: R_f = 0.12 (1:1 PE/DCM). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3064, 3030, 2922, 2855, 1748, 1599, 1495, 1454, 1245, 1208, 1103, 969, 757, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.48–7.27 (m, 10H, *cis*/*trans*), 6.76 (2xdd, *J* = 15.4, 1.3 Hz, 1H, *cis*/*trans*), 6.22 (2xdd, *J* = 16.0, 6.0 Hz, 1H, *cis*/*trans*), 5.64 (dd, *J* = 7.2, 4.6 Hz, 1H, *trans*), 5.54 (dd, *J* = 11.8, 3.0 Hz, 1H, *cis*), 5.26 (dddd, *J* = 11.4, 6.6, 3.3, 1.3 Hz, 1H, *cis*), 5.20–5.13 (m, 1H, *trans*), 2.52–2.10 (m, 2H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.8 (*cis*/*trans*), 137.8 (*trans*), 137.5 (*cis*), 135.4 (*cis*), 135.3 (*trans*), 134.0 (*cis*), 133.7 (*trans*), 129.1 (*cis*/*trans*), 129.0 (*cis*/*trans*), 128.9 (*cis*), 128.8 (*trans*), 128.8 (*cis*), 128.7 (*trans*), 126.8 (*cis*), 126.8 (*trans*), 125.7 (*cis*), 125.4 (*trans*), 124.7 (*cis*/*trans*), 79.7 (*cis*), 79.1 (*cis*), 77.3 (*trans*), 76.2 (*trans*), 36.0 (*cis*), 34.0 (*trans*). **HRMS** (ESI) calcd. for $[C_{18}H_{16}NaO_3]^+$ $(M+Na)^+$: m/z = 303.0992, found 303.0994.

(*E*)-4-(Undec-1-en-1-yl)-1,3-dioxan-2-one (136d)



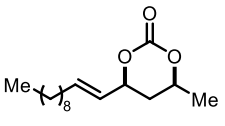
According to **General Procedure D**: (*E*)-4-methoxybenzyl tetradec-3-en-1-yl carbonate (0.45 g, 1.2 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (29 mg, 60 µmol, 5 mol%), diphenyldiselenide (19 mg, 60 µmol, 5 mol%), phenylsilane (0.15 mL, 1.2 mmol, 1.0 equiv) and 4Å molar sieves (12 mg) were dissolved in MeCN (12 mL, 0.1 M). Reaction time 72 h. 1,3,5-Trimethoxybenzene (0.11 g, 0.66 mmol, 0.50 equiv) were added. NMR analysis resulted in 41%. Separated between EtOAc (20 mL) and H_2O (20 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (2x 20 mL) and dried over $MgSO_4$. Eluting with PE/DCM 7:3.

Isolated yield 63 mg (0.25 mmol, 21%).

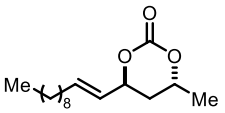
TLC: R_f = 0.08 (PE/DCM 7:3). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2926, 2855, 1752, 1409, 1245, 1193, 1111, 973, 768. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.85 (dtd, *J* = 15.0, 6.8, 1.1 Hz, 1H), 5.50 (ddt,

J = 15.4, 6.5, 1.5 Hz, 1H), 4.91 (ddd, *J* = 9.8, 6.5, 3.8 Hz, 1H), 4.53–4.30 (m, 2H), 2.24–1.90 (m, 4H), 1.26 (s, 14H), 0.99–0.78 (m, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 148.7, 136.6, 126.0, 79.3, 66.4, 32.1, 31.9, 29.5, 29.5, 29.3, 29.1, 28.7, 27.5, 22.7, 14.1. **HRMS** (APCI) calcd. for $[C_{15}H_{27}O_3]^+$ $(M+H)^+$: m/z = 255.1955, found 255.1955.

(*E*)-4-Methyl-6-(undec-1-en-1-yl)-1,3-dioxan-2-one (136e)



cis



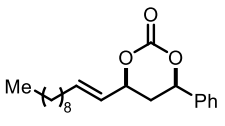
trans

According to **General Procedure D**: 4-methoxybenzyl pentadec-4-en-2-yl carbonate (0.35 g, 0.91 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (22 mg, 45 µmol, 5 mol%), diphenyldiselenide (14 mg, 46 µmol, 5 mol%), phenylsilane (0.11 mL, 0.89 mmol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 37 h. 1,1’,2,2’-Tetrachloroethane (47 µL, 0.45 mmol, 0.50 equiv) were added. NMR analysis resulted in 65% (34:10 *cis*/*trans*). Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc,(3x 30 mL) washed with H_2O (2x 30 mL) and dried over $MgSO_4$. Eluting with PE/Et_2O 2:1.

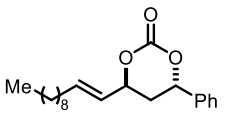
Isolated yield 94 mg (0.35 mmol, 39%) as a mixture of diastereomers (34:10 *cis*/*trans*).

TLC: R_f = 0.12 (PE/Et_2O 2:1). **IR** (ATR): ṽ [cm^{-1}] = 2926, 2855, 1744, 1461, 1394, 1238, 1197, 1122, 1036, 969, 768. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.93–5.75 (m, 1H, *cis*/*trans*), 5.46 (ddt, *J* = 15.4, 7.1, 1.6 Hz, 1H, *cis*/*trans*), 4.99 (m, 1H, A), 4.83 (ddd, *J* = 10.9, 7.0, 3.2 Hz, 1H, *cis*), 4.58 (dtq, *J* = 12.5, 6.3, 2.9 Hz, 1H, *cis*/*trans*), 2.17–1.94 (m, 3H, *cis*/*trans*), 1.73 (dt, *J* = 14.4, 11.7 Hz, 1H, *cis*/*trans*), 1.42 (d, *J* = 6.2 Hz, 3H, *cis*/*trans*), 1.26 (s, 14H, *cis*/*trans*), 0.94–0.81 (m, 3H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ [ppm] = 149.2 (*cis*/*trans*), 136.6 (*cis*/*trans*), 126.3 (*cis*/*trans*), 79.4 (*cis*/*trans*), 75.0 (*cis*/*trans*), 35.4 (*cis*/*trans*), 32.1 (*cis*/*trans*), 31.9 (*cis*/*trans*), 29.5 (*cis*/*trans*), 29.5 (*cis*/*trans*), 29.3 (*cis*/*trans*), 29.1 (*cis*/*trans*), 28.7 (*cis*/*trans*), 22.7 (*cis*/*trans*), 21.2 (*cis*/*trans*), 14.1 (*cis*/*trans*). **HRMS** (APCI) calcd. for $[C_{16}H_{29}O_3]^+$ $(M+H)^+$ m/z = 269.2111, found 269.2116.

(*E*)-4-Phenyl-6-(undec-1-en-1-yl)-1,3-dioxan-2-one (136f)



cis



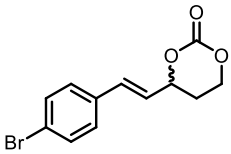
trans

According to **General Procedure D**: 4-methoxybenzyl (1-phenyltetradec-3-en-1-yl) carbonate (0.45 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (25 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 51 µmol, 5 mol%), phenylsilane (0.12 mL, 0.10 µmol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 39 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 57% (62:10 *cis*/*trans*). Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/DCM 1:1.

Isolated yield 0.12 g (0.38 mmol, 38%) as a mixture of diastereomers (64:10 *cis*/*trans*).

TLC: R_f = 0.12 (PE/DCM 1:1). **IR** (ATR): ṽ [cm^{-1}] = 2926, 2855, 1752, 1457, 1372, 1238, 1208, 1103, 760, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.50–7.30 (m, 5H, *cis*/*trans*), 5.90 (dt, *J* = 15.3, 6.7 Hz, 1H, *cis*/*trans*), 5.64–5.41 (m, 2H, *cis*/*trans*), 5.02 (ddd, *J* = 10.7, 7.0, 2.9 Hz, 1H, *cis*/*trans*), 2.34 (dt, *J* = 14.6, 3.0 Hz, 1H, *cis*/*trans*), 2.15–2.00 (m, 3H, *cis*/*trans*), 1.26 (s, 14H, *cis*/*trans*), 0.96–0.77 (m, 3H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 149.0 (*cis*/*trans*), 137.8 (*trans*), 136.9 (*cis*), 129.0 (*trans*), 128.9 (*cis*), 126.0 (*trans*), 125.7 (*cis*), 79.7 (*cis*/*trans*), 79.5 (*cis*/*trans*), 36.1 (*cis*/*trans*), 32.1 (*cis*/*trans*), 31.9 (*cis*/*trans*), 29.5 (*cis*/*trans*), 29.5 (*cis*/*trans*), 29.3 (*cis*/*trans*), 29.1 (*cis*/*trans*), 28.7 (*cis*/*trans*), 22.7 (*cis*/*trans*), 14.1 (*cis*/*trans*). **HRMS** (APCI) calcd. for $[C_{21}H_{34}NO_3]^+$ $(M+NH_4)^+$, m/z = 348.2533, found 348.2533.

(*E*)-4-(4-Bromostyryl)-1,3-dioxan-2-one (136g)

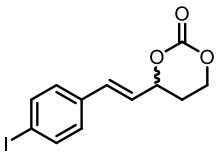


According to **General Procedure D**: 5-(4-bromophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (0.40 g, 0.98 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (15 mg, 49 µmol, 5 mol%), phenylsilane (0.12 mL, 0.98 mmol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 39 h. 1,1’,2,2’-Tetrachloroethane (52 µL, 0.49 mmol, 0.50 equiv) were added. NMR analysis resulted in 36%. Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (2x 30 mL), brine (1x 20 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 3:2.

Isolated yield 85 mg (0.30 mmol, 31%).

TLC: R_f = 0.12 (PE/EtOAc 3:2). **IR** (ATR): ṽ [cm^{-1}] = 3474, 3030, 2922, 2855, 1748, 1487, 1405, 1245, 1219, 1111, 1010. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.47 (dt, *J* = 6.6, 2.2 Hz, 2H), 7.32–7.21 (m, 2H), 6.68 (dd, *J* = 16.0, 1.3 Hz, 1H), 6.18 (dd, *J* = 15.9, 6.1 Hz, 1H), 5.14 (dddd, *J* = 10.1, 5.8, 4.0, 1.4 Hz, 1H), 4.57–4.38 (m, 2H), 2.27 (dq, *J* = 14.4, 4.0 Hz, 1H), 2.12 (dtd, *J* = 14.5, 9.3, 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.3, 134.3, 132.5, 132.0, 128.3, 125.5, 122.6, 78.8, 66.4, 27.5. **HRMS** (EI) calcd. for $[C_{12}H_{11}BrO_3]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 281.9886, found 281.9878.

(*E*)-4-(4-Iodostyryl)-1,3-dioxan-2-one (136h)



According to **General Procedure D**: 5-(4-iodophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (0.45 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 166 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis

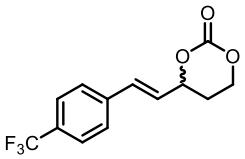
resulted in 23%. Separated between EtOAc (25 mL) and H_2O (25 mL). Extracted with EtOAc (2x 25 mL), washed with H_2O (3x 25 mL) and dried over $MgSO_4$. Eluting with PE/Et_2O 1:3.

Isolated yield 26 mg.

*Precise yield could not be determined as irremovable residues from the eluent remained.

TLC: R_f = 0.06 (PE/Et_2O 1:3). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2960, 2930, 1744, 1484, 1405, 1249, 1219, 1115, 1062, 969, 910, 809, 731. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.75–7.62 (m, 2H), 7.17–7.08 (m, 2H), 6.67 (d, *J* = 16.2 Hz, 1H), 6.19 (dd, *J* = 15.9, 6.0 Hz, 1H), 5.20–5.05 (m, 1H), 4.58–4.37 (m, 2H), 2.27 (dq, *J* = 14.6, 4.0 Hz, 1H), 2.21–2.02 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.3, 137.9, 134.8, 132.6, 128.4, 125.6, 94.2, 78.7, 66.4, 27.5. **HRMS** (ESI) calcd. for $[C_{12}H_{11}ClNaO_3]^+$ $(M+Na)^+$: m/z = 352.9645, found 352.9643.

(*E*)-4-(4-(Trifluoromethyl)styryl)-1,3-dioxan-2-one) (136j)

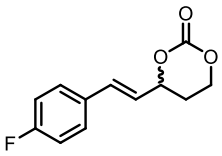


According to **General Procedure D**: (5-(4-(trifluoromethyl)phenyl)pent-3-en-1-yl) carbonate (0.40 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (25 mg, 51 µmol, 5 mol%), diphenyldiselenide (16 mg, 51 µmol, 5 mol%), phenylsilane (0.13 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 60 h. 1,1’,2,2’-Tetrachloroethane (54 µL, 0.51 mmol, 0.50 equiv) were added. NMR analysis resulted in 68%. Eluting with PE/EtOAc 7:3.

Isolated yield 0.19 g (0.69 mmol, 68%).

TLC: R_f = 0.06 (PE/EtOAc 7:3). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2981, 2922, 1744, 1617, 1408, 1326, 1248, 1218, 1162, 1107, 1066, 1017, 972, 823, 767. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.60 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 6.84–6.73 (m, 1H), 6.29 (dd, *J* = 16.0, 5.8 Hz, 1H), 5.18 (dddd, *J* = 9.6, 5.6, 4.0, 1.4 Hz, 1H), 4.57–4.40 (m, 2H), 2.30 (dq, *J* = 14.4, 4.0 Hz, 1H), 2.14 (dtd, *J* = 14.6, 9.3, 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.2, 138.8, 132.1, 127.4, 127.0, 125.7 (q, *J* = 3.8 Hz, C-F), 122.6, 78.5, 77.2, 66.4, 27.5. **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 63.2 (s). **HRMS** (ESI) calcd. for $[C_{13}H_{15}F_3NO_3]^+$ $(M+NH_4)^+$: m/z = 290.0999, found 290.1002.

(*E*)-4-(4-Fluorostyryl)-1,3-dioxan-2-one (136k)



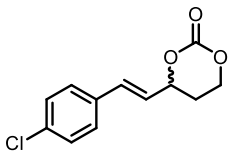
According to **General Procedure D**: 5-(4-fluorophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (0.35 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.13 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (10 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 39 h. 1,1’,2,2’-Tetrachloroethane (54 µL, 0.51 mmol, 0.50 equiv) were added. NMR analysis

resulted in 54%. Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (2x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 3:2.

Isolated yield 0.10 g (0.47 mmol, 46%).

TLC: R_f = 0.30 (PE/EtOAc 3:2). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3474, 2922, 2859, 1752, 1510, 1409, 1226, 1159, 1111, 828. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.43–7.32 (m, 2H), 7.15–6.98 (m, 2H), 6.70 (d, *J* = 15.8 Hz, 1H), 6.11 (dd, *J* = 15.9, 6.2 Hz, 1H), 5.14 (dt, *J* = 9.8, 4.9 Hz, 1H), 4.58–4.34 (m, 2H), 2.27 (dq, *J* = 14.5, 4.0 Hz, 1H), 2.22–2.02 (m, 1H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 161.2, 132.6, 131.5, 128.5 (d, *J* = 8.1 Hz, C-F), 125.9, 124.5, 115.8 (d, *J* = 21.7 Hz, C-F), 78.9, 66.4, 27.6. **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 113.2 (s). **HRMS** (EI) calcd. for $[C_{12}H_{11}FO_3]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 222.0687, found 222.0683.

(*E*)-4-(4-Chlorostyryl)-1,3-dioxan-2-one (136l)

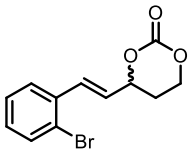


According to **General Procedure D**: 5-(4-chlorophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (0.36 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (10 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 74 h. 1,1’,2,2’-Tetrachloroethane (52 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 27%. Separated between EtOAc (25 mL) and H_2O (25 mL). Extracted with EtOAc (2x 25 mL), washed with H_2O (3x 25 mL) and dried over $MgSO_4$. Eluting with PE/Et_2O 1:3.

Isolated yield 44 mg (0.18 mmol, 18%).

TLC: R_f = 0.06 (PE/EtOAc 1:3). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2926, 2855, 1748, 1491, 1409, 1249, 1219, 1111, 1047, 969, 813, 768. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.32 (s, 4H), 6.70 (dd, *J* = 16.0, 1.3 Hz, 1H), 6.17 (dd, *J* = 15.9, 6.1 Hz, 1H), 5.14 (ddt, *J* = 10.7, 6.5, 3.2 Hz, 1H), 4.58–4.38 (m, 2H), 2.35–2.19 (m, 1H), 2.13 (ddt, *J* = 14.3, 9.2, 4.6 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.3, 134.4, 133.8, 132.5, 129.0, 128.0, 125.4, 78.8, 66.4, 27.5. **HRMS** (ESI) calcd. for $[C_{12}H_{11}ClNaO_3]^+$ $(M+Na)^+$: m/z = 261.0289, found 261.0289.

(*E*)-4-(2-Bromostyryl)-1,3-dioxan-2-one (136m)

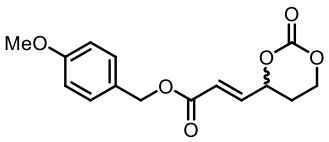


According to **General Procedure D**: 5-(2-bromophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (0.41 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 51 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (10 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 85 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 41%. Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (2x 20 mL), brine (1x 20 mL) and dried over Na_2SO_4. Eluting with PE/Et_2O 1:3.

Isolated yield 80 mg (0.28 mmol, 28%).

TLC: R_f = 0.04 (PE/Et_2O 1:3). **IR** (ATR): ṽ [cm^{-1}] = 3470, 3060, 2922, 1737, 1469, 1435, 1405, 1245, 1215, 1189, 1111, 1047, 965, 753. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.54 (ddd, *J* = 18.3, 7.9, 1.5 Hz, 2H), 7.30 (tdd, *J* = 7.8, 1.3, 0.6 Hz, 1H), 7.23–7.10 (m, 1H), 7.07 (dt, *J* = 15.9, 0.7 Hz, 1H), 6.15 (dd, *J* = 15.9, 6.5 Hz, 1H), 5.19 (dddd, *J* = 9.3, 6.4, 4.0, 1.3 Hz, 1H), 4.60–4.38 (m, 2H), 2.39–2.06 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.3, 135.4, 133.1, 132.8, 129.9, 127.9, 127.7, 127.3, 124.0, 78.9, 66.5, 27.5. **HRMS** (ESI) calcd. for $[C_{12}H_{11}BrNaO_3]^+$ $(M+Na)^+$: m/z = 304.9784, found 304.9781.

4-Methoxybenzyl (*E*)-3-(2-oxo-1,3-dioxan-4-yl)acrylate (136n)



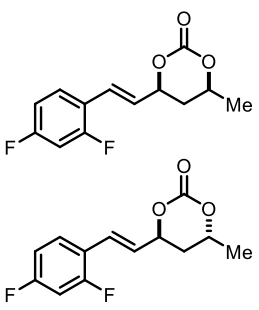
According to **General Procedure D**: *tert*-butyl-6-((((4-methoxybenzyl)oxy)carbonyl)oxy)hex-3-enoate (0.35 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 49 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 mmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 46 h. 1,3,5-Trimethoxybenzene (84 mg, 0.50 µmol, 0.50 equiv) were added. NMR analysis resulted in 44%. Separated between EtOAc (30 mL) and H_2O (30 mL).Extracted with EtOAc (2x 25 mL), washed with brine (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/Et_2O 1:2.

Isolated yield 0.11 g (0.38 mmol, 38%).

*The NMR yield corresponds to the product being a *tert*-butyl-ester. Transesterification occurred during the workup.

TLC: R_f = 0.12 (1:2 PE/Et_2O). **IR** (ATR): ṽ [cm^{-1}] = 2963, 2840, 1748, 1517, 1245, 1163, 1111, 1029, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.47 (dd, *J* = 5.7, 1.5 Hz, 1H), 7.37–7.29 (m, 2H), 6.95-6.81 (m, 2H), 6.11 (dd, *J* = 5.7, 2.0 Hz, 1H), 5.16 (ddt, *J* = 8.3, 4.8, 1.8 Hz, 1H), 5.10 (s, 2H), 4.36-4.27 (m, 2H), 3.81 (s, 3H), 2.27–2.11 (m, 1H), 1.96 (ddt, *J* = 14.7, 8.2, 5.1 Hz, 1H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 181.5, 160.0, 155.7, 154.8, 130.4, 127.1, 121.8, 114.0, 80.0, 69.8, 63.5, 55.3, 32.6. **HRMS** (ESI) calcd. for $[C_{15}H_{20}NO_6]^+$ $(M+NH_4)^+$: m/z = 310.1285, found 310.1288.

(*E*)-4-(2,4-Difluorostyryl)-6-methyl-1,3-dioxan-2-one (136o)



cis

trans

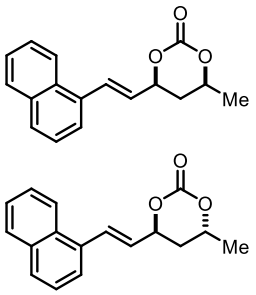
According to **General Procedure D**: 6-(2,4-difluorophenyl)hex-4-en-2-yl (4-methoxybenzyl) carbonate (0.38 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (25 mg, 51 µmol, 5 mol%), diphenyldiselenide (16 mg, 52 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (9.9 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 61 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.51 mmol, 0.50 equiv) were added. NMR

analysis resulted in 70% (18:10 *cis*/*trans*). Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (2x 20 mL), brine (1x 20 mL) and dried over Na_2SO_4. Eluting with PE/Et_2O 1:2.

Isolated yield 0.16 g (0.62 mmol, 62%) as a mixture of diastereomers (25:10 *cis*/*trans*).

TLC: R_f = 0.12 (PE/Et_2O 1:2). **IR** (ATR): ṽ [cm^{-1}] = 3440, 2982, 2937, 1737, 1614, 1502, 1431, 1394, 1275, 1238, 1197, 1141, 1092, 969, 850, 813, 768, 731. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.41 (td, *J* = 8.4, 6.4 Hz, 1H, *cis*/*trans*), 6.94–6.70 (m, 3H), 6.23 (2xdd, *J* = 16.1, 5.9 Hz, 1H, *cis*/*trans*), 5.23 (d, *J* = 5.4 Hz, 1H, *trans*), 5.07 (ddd, *J* = 10.6, 6.7, 3.3 Hz, 1H, *cis*), 4.77–4.58 (m, 1H, *cis*/*trans*), 2.31–2.06 (m, 1H, *cis*/*trans*), 1.84 (dt, *J* = 13.8, 11.6 Hz, 1H, *cis*/*trans*), 1.51–1.41 (m, 3H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.8 (*cis*), 148.7 (*trans*), 128.9 (dd, *J* = 9.6, 5.0 Hz, C-F, *cis*/*trans*), 127.4 (dd, *J* = 5.6, 2.2 Hz, C-F, *cis*/*trans*), 125.5 (*cis*/*trans*), 111.8 (dt, *J* = 21.3, 1.9 Hz, C-F, *cis*/*trans*), 104.3 (t, *J* = 25.7 Hz, C-F, *cis*/*trans*), 78.9 (*cis*/*trans*), 77.2 (*cis*), 76.3 (*trans*), 75.1 (*cis*), 72.5 (*trans*), 35.3 (*cis*), 33.1 (*trans*), 21.2 (*cis*), 20.9 (*trans*). **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 109.6 (d, *J* = 8.0 Hz, *cis*), - 109.7 (d, *J* = 8.1 Hz, *trans*), - 112.8 (d, *J* = 8.1 Hz, *trans*), - 113.3 (d, *J* = 8.0 Hz, *cis*). **HRMS** (ESI) calcd. for $[C_{13}H_{12}F_2NaO_3]^+$ $(M+Na)^+$: m/z = 277.0647, found 277.0649.

(*E*)-4-Methyl-6-(2-(naphthalen-1-yl)vinyl)-1,3-dioxan-2-one (136p)



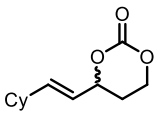
According to **General Procedure D**: 4-methoxybenzyl (6-(naphthalen-1-yl)hex-4-en-2-yl) carbonate (0.39 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 0.10 mmol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 39 h. 1,1’,2,2’-Tetrachloroethane (52 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 40% (23:10 *cis*/*trans*). Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/Et_2O 1:2.

Isolated yield 84 mg (0.31 mmol, 32%) as a mixture of diastereomers (23:10 *cis*/*trans*).

TLC: R_f = 0.12 (PE/Et_2O 1:2). **IR** (ATR): ṽ [cm^{-1}] = 3056, 2974, 2933, 1748, 1513, 1394 1245, 1197, 1137, 1103, 775. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 8.12–8.02 (m, 1H, *cis*/*trans*), 7.94–7.79 (m, 2H, *cis*/*trans*), 7.63–7.41 (m, 5H, *cis*/*trans*), 6.22 (dd, *J* = 15.8, 5.9 Hz, 1H, *cis*/*trans*), 5.35 (td, *J* = 5.2, 1.6 Hz, 1H, *trans*), 5.19 (dddd, *J* = 11.1, 6.6, 3.3, 1.2 Hz, 1H, *cis*), 4.83–4.74 (m, 1H, *trans*), 4.70 (ddd, *J* = 11.7, 6.2, 2.8 Hz, 1H. *cis*), 2.37–2.12 (m, 1H, *cis*/*trans*), 1.91 (dt, *J* = 14.3, 11.7 Hz, 1H, *cis*/*trans*), 1.49 (2xd, *J* = 6.3 Hz, 3H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 149.0 (*cis*/*trans*), 133.6 (*cis*/*trans*), 133.2 (*cis*/*trans*), 131.1 (*trans*), 131.1 (*cis*), 130.9 (*trans*), 128.9 (*cis*/*trans*), 128.7 (*cis*), 128.4 (*trans*), 128.2 (*cis*), 126.5 (*trans*), 126.4 (*cis*), 126.1 (*trans*), 126.0 (*cis*), 125.6 (*cis*), 125.5 (*trans*), 124.3 (*cis*), 124.1 (*trans*), 123.6 (*trans*), 123.5 (*cis*),

79.0 (*cis*), 76.5 (*trans*), 75.2 (*cis*), 72.6 (*trans*), 35.5 (*cis*), 33.3 (*trans*), 21.3 (*cis*), 20.9 (*trans*). **HRMS** (ESI) calcd. for $[C_{17}H_{17}O_3]^+$ $(M+H)^+$: m/z = 269.1172, found 269.1175.

(*E*)-4-(2-cyclohexylvinyl)-1,3-dioxan-2-one (136q)

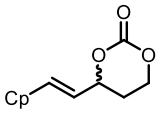


According to **General Procedure D**: 5-cyclohexylpent-3-en-1-yl (4-methoxybenzyl) carbonate (0.33 g, 0.99 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (15 mg, 49 µmol, 5 mol%), phenylsilane (0.12 mL, 0.99 mmol, 1.0 equiv) and 4Å molar sieves (10 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 67 h. 1,1’,2,2’-Tetrachloroethane (52 µL, 0.49 mmol, 0.50 equiv) were added. NMR analysis resulted in 44%. Separated between EtOAc (25 mL) and H_2O (25 mL). Extracted with EtOAc (2x 25 mL), washed with H_2O (2x 25 mL) and dried over $MgSO_4$. Eluting with PE/Et_2O 1:2.

Isolated yield 44 mg (0.21 mmol, 21%).

TLC: R_f = 0.10 (1:2 PE/Et_2O). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2926, 2855, 1752, 1480, 1405, 1245, 1193, 1111, 969, 768. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.80 (ddd, *J* = 15.6, 6.6, 1.1 Hz, 1H), 5.44 (ddd, *J* = 15.5, 6.6, 1.3 Hz, 1H), 4.96–4.82 (m, 1H), 4.51–4.31 (m, 2H), 2.14 (dq, *J* = 14.5, 4.0 Hz, 1H), 2.08-1.93 (m, 2H), 1.78–1.59 (m, 4H), 1.38–0.97 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.8, 142.0, 123.6, 79.5, 66.4, 40.3, 32.4, 32.4, 27.6, 26.0, 25.9. **HRMS** (APCI) calcd. for $[C_{12}H_{19}O_3]^+$ $(M+H)^+$: m/z = 211.1329, found 211.1329.

(*E*)-4-(2-Cyclopentylvinyl)-1,3-dioxan-2-one (136r)

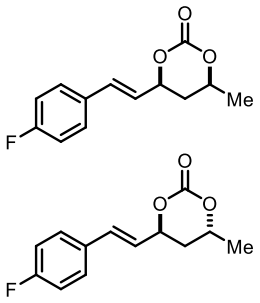


According to **General Procedure D**: 5-cyclopentylpent-3-en-1-yl (4-methoxybenzyl) carbonate (0.32 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (10 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 67 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 41%. Separated between EtOAc (25 mL) and H_2O (25 mL). Extracted with EtOAc (2x 25 mL), washed with H_2O (2x 25 mL) and dried over $MgSO_4$. Eluting with PE/Et_2O 1:2.

Isolated yield 40 mg (0.21 mmol, 20%).

TLC: R_f = 0.12 (PE/Et_2O 1:2). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2952, 2870, 1752, 1405, 1245, 1193, 1111, 973, 768. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.83 (ddd, *J* = 15.4, 7.6, 1.1 Hz, 1H), 5.48 (ddd, *J* = 15.4, 6.6, 1.1 Hz, 1H), 4.91 (dddd, *J* = 9.1, 6.6, 4.0, 1.1 Hz, 1H), 4.52–4.30 (m, 2H), 2.57–2.37 (m, 1H), 2.15 (dq, *J* = 14.5, 4.0 Hz, 1H), 2.01 (dtd, *J* = 14.5, 9.4, 5.1 Hz, 1H), 1.88–1.47 (m, 6H), 1.40–1.18 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.8, 140.9, 124.1, 79.4, 66.4, 42.8, 32.8, 32.7, 27.5, 25.1. **HRMS** (APCI) calcd. for $[C_{11}H_{17}O_3]^+$ $(M+H)^+$: m/z = 197.1172, found 197.1173.

(*E*)-4-(4-Fluorostyryl)-6-methyl-1,3-dioxan-2-one (136s)

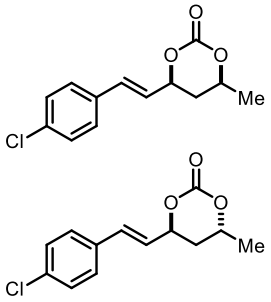


According to **General Procedure D**: 6-(4-fluorophenyl)hex-4-en-2-yl (4-methoxybenzyl) carbonate (0.33 g, 0.91 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (22 mg, 45 µmol, 5 mol%), diphenyldiselenide (14 mg, 45 µmol, 5 mol%), phenylsilane (0.11 mL, 0.89 mmol, 0.98 equiv) and 4Å molar sieves (10 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 39 h. 1,1’,2,2’-Tetrachloroethane (48 µL, 0.45 mmol, 0.50 equiv) were added. NMR analysis resulted in 55% (26:10 *cis*/*trans*). Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/DCM 1:3.

Isolated yield 0.55 g (0.23 mmol, 25%) as a mixture of diastereomers (19:10 *cis*/*trans*)

TLC: R_f = 0.12 (PE/DCM 1:3). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2982, 2933, 1741, 1662, 1603, 1510, 1446, 1394, 1301, 1226, 1197, 1141, 1096, 969, 857, 826, 768. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.43-7.30 (m, 2H, *cis*/*trans*), 7.04 (t, *J* = 8.7 Hz, 2H, *cis*/*trans*), 6.69 (2xd, *J* = 15.5 Hz, 1H, *cis*/*trans*), 6.09 (2xdd, *J* = 15.9, 6.7 Hz, 1H, *cis*/*trans*), 5.24 (t, *J* = 5.3 Hz, 1H, *trans*), 5.06 (ddd, *J* = 10.8, 6.7, 3.4 Hz, 1H, *cis*), 4.79–4.57 (m, 1H, *cis*/*trans*), 2.28–2.06 (m, 1H, *cis*/*trans*), 1.84 (dt, *J* = 14.3, 11.7 Hz, 1H, *cis*/*trans*), 1.47 (dd, *J* = 6.3, 0.9 Hz, 3H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 164.1 (*cis*/*trans*), 161.6 (*cis*/*trans*), 148.9 (*cis*), 148.8 (*trans*), 132.5 (*cis*), 132.2 (*trans*), 128.4 (d, *J* = 8.2 Hz, C-F, *cis*), 128.4 (d, *J* = 8.2 Hz, C-F, *trans*), 124.8 (d, *J* = 2.4 Hz, C-F, *trans*), 124.8 (d, *J* = 2.2 Hz, C-F, *cis*), 115.8 (d, *J* = 21.7 Hz, C-F, *cis*/*trans*), 78.9 (*cis*), 76.3 (*trans*), 75.1 (*cis*), 72.5 (*trans*), 35.4 (*cis*), 33.2 (*trans*), 21.2 (*cis*), 20.8 (*trans*). **^{19}F NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 113.2 (m, C-F). **HRMS** (APCI) calcd. for $[C_{13}H_{17}FNO_3]^+$ $(M+NH_4)^+$: m/z = 254.1187, found 254.1191.

(*E*)-4-(4-Chlorostyryl)-6-methyl-1,3-dioxan-2-one (136t)

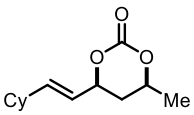


According to **General Procedure D**: 6-(4-chlorophenyl)hex-4-en-2-yl (4-methoxybenzyl) carbonate (0.38 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (25 mg, 51 µmol, 5 mol%), diphenyldiselenide (16 mg, 52 µmol, 5 mol%), phenylsilane (0.12 mL, 0.99 mmol, 1.0 equiv) and 4Å molar sieves (12 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 40 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 65% (20:10 *cis*/*trans*). Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (2x 20 mL) and dried over Na_2SO_4. Eluting with PE/Et_2O 2:3.

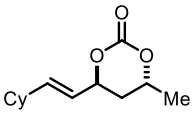
Isolated yield 0.11 g (0.44 mmol, 43%) as a mixture of diastereomers (22:10 *cis*/*trans*).

TLC: R_f = 0.10 (PE/Et_2O 1:3). **IR** (ATR): ṽ [cm^{-1}] = 2982, 2933, 1744, 1491, 1394, 1238, 1197, 1141, 1096, 969, 731. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.32 (s, 4H, *cis*/*trans*), 6.68 (2xdd, *J* = 15.9, 3.9 Hz, 1H, *cis*/*trans*), 6.15 (2xdd, *J* = 15.9, 7.2 Hz, 1H, *cis*/*trans*), 5.23 (d, *J* = 5.2 Hz, 1H, *trans*), 5.14–4.98 (m, 1H, *cis*), 4.77–4.57 (m, 1H, *cis*/*trans*), 2.27–2.08 (m, 1H, *cis*/*trans*), 1.84 (dt, *J* = 14.3, 11.7 Hz, 1H, *cis*/*trans*), 1.47 (d, *J* = 6.3 Hz, 3H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.8 (*cis*/*trans*), 133.9 (*cis*/*trans*), 132.3 (*cis*/*trans*), 129.0 (*cis*/*trans*), 128.0 (*cis*), 127.9 (*trans*), 125.8 (*trans*), 125.6 (*cis*), 78.7 (*cis*), 77.2 (*cis*/*trans*), 76.1 (*trans*), 75.0 (*cis*), 72.5 (*trans*), 35.4 (*cis*), 33.1 (*trans*), 21.2 (*cis*), 20.9 (*trans*). **HRMS** (ESI) calcd. for $[C_{13}H_{13}ClNaO_3]^+$ $(M+Na)^+$: m/z = 275.0445, found 275.0444.

(*E*)-4-(2-Cyclohexylvinyl)-6-methyl-1,3-dioxan-2-one (136u)



cis



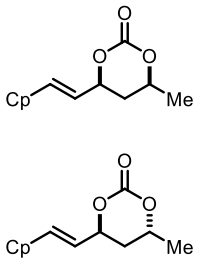
trans

According to **General Procedure D**: 6-cyclohexylhex-4-en-2-yl (4-methoxybenzyl) carbonate (0.35 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 38 h. 1,1’,2,2’-Tetrachloroethane (52 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 74% (37:10 *cis*/*trans*). Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 30 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/Et_2O 2:1.

Isolated yield 0.13 g (0.60 mmol, 60%) as a mixture of diastereomers (36:10 *cis*/*trans*).

TLC: R_f = 0.12 (PE/Et_2O 2:1). **IR** (ATR): ṽ [cm^{-1}] = 2981, 2922, 2851, 1741, 1450, 1394, 1241, 1197, 1096, 1029, 969, 768. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.78 (dd, *J* = 15.5, 6.6 Hz, 1H, *cis*/*trans*), 5.49–5.36 (m, 1H, *cis*/*trans*), 4.99 (d, *J* = 5.2 Hz, 1H, *trans*), 4.83 (ddd, *J* = 10.8, 6.9, 3.1 Hz, 1H, *cis*), 4.71–4.50 (m, 1H, *cis*/*trans*), 2.14–1.92 (m, 2H, *cis*/*trans*), 1.81–1.56 (m, 6H, *cis*/*trans*), 1.42 (2xd, *J* = 6.3 Hz, 3H, *cis*/*trans*), 1.36–0.98 (m, 5H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 149.2 (*cis*/*trans*), 141.9 (*cis*), 141.3 (*trans*), 123.9 (*cis*), 123.7 (*trans*), 79.6 (*cis*/*trans*), 75.0 (*cis*), 72.3 (*trans*), 40.2 (*cis*/*trans*), 35.5 (*cis*), 33.2 (*trans*), 32.5 (*cis*), 32.4 (*cis*/*trans*), 32.4 (*trans*), 26.0 (*trans*), 25.9 (*cis*), 21.2 (*cis*), 20.9 (*trans*). **HRMS** (APCI) calcd. for $[C_{13}H_{21}O_3]^+$ $(M+H)^+$: m/z = 215.1485, found 215.1485.

(*E*)-4-(2-Cyclopentylvinyl)-6-methyl-1,3-dioxan-2-one (136v)

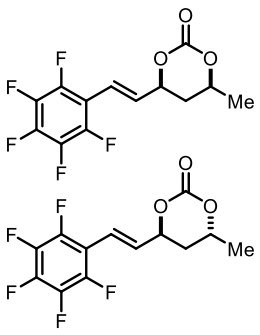


According to **General Procedure D**: 6-cyclopentylhex-4-en-2-yl (4-methoxybenzyl) carbonate (0.33 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (25 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 39 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 65% (33:10 *cis*/*trans*). Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (2x 30 mL) and dried over $MgSO_4$. Eluting with PE/Et_2O 2:1.

Isolated yield 0.11 g (0.51 mmol, 51%) as a mixture of diastereomers (33:10 *cis*/*trans*).

TLC: R_f = 0.12 (PE/Et_2O 2:1). **IR** (ATR): ṽ [cm^{-1}] = 2948, 2870, 1737, 1454, 1394, 1238, 1193, 1133, 1092, 1034, 969, 891, 768, 734. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.89–5.73 (m, 1H, *cis*/*trans*), 5.54–5.37 (m, 1H, *cis*/*trans*), 4.99 (q, *J* = 5.2 Hz, 1H, *trans*), 4.83 (dddd, *J* = 11.4, 7.0, 3.2, 0.9 Hz, 1H, *cis*), 4.58 (dqd, *J* = 12.4, 6.3, 2.9 Hz, 1H, *cis*/*trans*), 2.45 (qt, *J* = 8.1, 6.8 Hz, 1H, *cis*/*trans*), 2.10 (dt, *J* = 14.3, 3.0 Hz, 1H, *cis*/*trans*), 1.88–1.47 (m, 7H, *cis*/*trans*), 1.42 (d, *J* = 6.3 Hz, 3H, *cis*/*trans*), 1.39–1.17 (m, 2H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 149.2 (*cis*/*trans*), 140.9 (*cis*), 140.2 (*trans*), 124.4 (*cis*), 124.2 (*trans*), 79.4 (*cis*/*trans*), 75.0 (*cis*), 72.4 (*trans*), 42.8 (*cis*/*trans*), 35.4 (*cis*/*trans*), 33.2 (*trans*), 32.7 (*cis*), 25.1 (*cis*/*trans*), 21.2 (*cis*), 20.9 (*trans*). **HRMS** (APCI) calcd. for $[C_{12}H_{19}O_3]^+$ $(M+H)^+$: m/z = 211.1329, found 211.1329.

(*E*)-4-Methyl-6-(2-(perfluorophenyl)vinyl)-1,3-dioxan-2-on (136x)

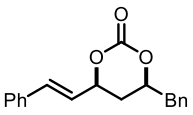


According to **General Procedure D**: 4-methoxybenzyl (6-(perfluorophenyl)hex-4-en-2-yl) carbonate (0.43 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 41 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 64% (20:10 *cis*/*trans*). Separated between EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (3x 30 mL) and dried over $MgSO_4$. Eluting with PE/DCM 1:2. Isolated yield 0.15 g (0.49 mmol, 49%) as a mixture of diastereomers (20:10 *cis*/*trans*).

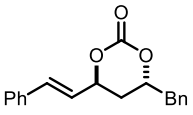
TLC: R_f = 0.10 (PE/DCM 1:2). **IR** (ATR): ṽ [cm^{-1}] = 2986, 2937, 1737, 1655, 1521, 1495, 1379, 1293, 1241, 1193, 1133, 1103, 1040, 999, 962, 850, 813, 764, 697. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 6.69 (2xdd, *J* = 16.3, 6.4 Hz, 1H, *cis*/*trans*), 6.61–6.46 (m, 1H, *cis*/*trans*), 5.26 (q, *J* = 4.9 Hz, 1H, *trans*), 5.10 (dt, *J* = 12.0, 4.3 Hz, 1H, *cis*), 4.77–4.59 (m, 1H, *cis*/*trans*), 2.33–2.07 (m, 1H, *cis*/*trans*), 1.84 (dt, *J* = 14.3, 11.7 Hz, 1H, *cis*/*trans*), 1.48 (2xd, *J* = 6.3 Hz, 3H, *cis*/*trans*).

^{13}C NMR (101 MHz, Chloroform-*d*): δ [ppm] = 148.3 (*cis*), 148.2 (*trans*), 146.1 (m, C-F, *cis*), 143.6 (m, C-F, *trans*), 141.8 (m, C-F, *trans*), 139.1 (m, C-F, *cis*/*trans*), 136.4 (m, C-F, *cis*), 134.4 (*trans*), 133.8 (*cis*), 117.3 (*trans*), 117.2 (*cis*), 110.5 (*cis*), 110.3 (*trans*), 78.2 (*cis*), 75.8 (*trans*), 75.1 (*cis*), 72.5 (*trans*), 35.0 (*cis*), 32.8 (*trans*), 21.1 (*cis*), 20.7 (*trans*). **^{19}F NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 142.5 (dd, *J* = 21.7, 9.1 Hz, F-F, *cis*/*trans*), - 154.6 (t, *J* = 20.1 Hz, F-F, *cis*/*trans*), - 162.6 (m, F-F, *cis*/*trans*). **HRMS** (APCI) calcd. for $[C_{13}H_{10}F_5O_3]^+$ $(M+H)^+$: m/z = 309.0545, found 309.0547.

(*E*)-4-Benzyl-6-styryl-1,3-dioxan-2-one (136y)



cis



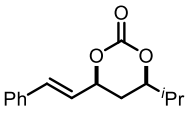
trans

According to **General Procedure D**: 1,6-diphenylhex-4-en-2-yl (4-methoxybenzyl) carbonate (0.42 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (25 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 mmol, 1.0 equiv) and 4Å molar sieves (10 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 39 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 55% (25:10 *cis*/*trans*). Separated between EtOAc (20 mL) and H_2O (20 mL). Extracted with EtOAc (2x 20 mL), washed with H_2O (2x 20 mL) and dried over $MgSO_4$. Eluting with PE/Et_2O 3:2.

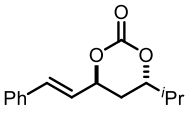
Isolated yield 0.10 g (0.35 mmol, 35%) as a mixture of diastereomers (26:10 *cis*/*trans*).

TLC: R_f = 0.08 (PE/Et_2O 3:2). **IR** (ATR): ṽ [cm^{-1}] = 3064, 3030, 2930, 1744, 1603, 1495, 1454, 1394, 1241, 1211, 1170, 1100, 1029, 969, 753, 701. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.49–7.09 (m, 10H, *cis*/*trans*), 6.78–6.59 (m, 1H, *cis*/*trans*), 6.24–6.01 (m, 1H, *cis*/*trans*), 5.26–5.15 (m, 1H, *trans*), 5.01 (dddd, *J* = 11.3, 6.7, 3.2, 1.2 Hz, 1H, *cis*), 4.86–4.61 (m, 1H, *cis*/*trans*), 3.28–3.08 (m, 1H, *cis*/*trans*), 2.94 (dt, *J* = 13.9, 7.2 Hz, 1H, *cis*/*trans*), 2.22–1.94 (m, 1H, *cis*/*trans*), 1.81 (dt, *J* = 14.3, 11.7 Hz, 1H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 148.7 (*cis*/*trans*), 135.4 (*cis*/*trans*), 135.0 (*cis*/*trans*), 133.7 (*cis*/*trans*), 129.6 (*trans*), 129.5 (*cis*), 128.8 (*trans*), 128.8 (*cis*), 128.7 (*cis*), 128.6 (*trans*), 127.3 (*cis*/*trans*), 126.8 (*cis*/*trans*), 124.9 (*cis*/*trans*), 79.0 (*cis*), 79.0 (*trans*), 41.5 (*cis*), 41.1 (*trans*), 33.0 (*cis*), 30.7 (*trans*). **HRMS** (ESI) calcd. for $[C_{19}H_{18}NaO_3]^+$ $(M+Na)^+$: m/z = 317.1148, found 317.1149.

(*E*)-4-Isopropyl-6-styryl-1,3-dioxan-2-one (136z)



cis



trans

According to **General Procedure D**: 4-methoxybenzyl (2-methyl-7-phenylhept-5-en-3-yl) carbonate (0.37 g, 1.0 mmol, 1.0 equiv), 2,4,6-tris(4-methoxyphenylpyrylium tetrafluoroborate (24 mg, 50 µmol, 5 mol%), diphenyldiselenide (16 mg, 50 µmol, 5 mol%), phenylsilane (0.12 mL, 1.0 µmol, 1.0 equiv) and 4Å molar sieves (11 mg) were dissolved in MeCN (10 mL, 0.1 M). Reaction time 38 h. 1,1’,2,2’-Tetrachloroethane (53 µL, 0.50 mmol, 0.50 equiv) were added. NMR analysis resulted in 61% (27:10 *cis*/*trans*). Separated between

EtOAc (30 mL) and H_2O (30 mL). Extracted with EtOAc (3x 20 mL), washed with H_2O (2x 30 mL) and dried over $MgSO_4$. Eluting with PE/EtOAc 9:1 and PE/DCM 1.5:1 (DCM with 1V% MeOH).

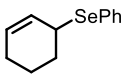
Isolated yield 58 mg (0.24 mmol, 24%) as a mixture of diastereomers (34:10 *cis*/*trans*).

TLC: R_f = 0.12 (PE/EtOAc 9:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3060, 3027, 2967, 2933, 1737, 1603, 1513 1489, 1390, 1230, 1189, 1096, 969, 850, 813, 749, 693. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.48-7.21 (m, 5H, *cis*/*trans*), 6.72 (dd, *J* = 16.0, 7.9 Hz, 1H, *cis*/*trans*), 6.18 (dd, *J* = 15.9, 5.9 Hz, 1H, *cis*/*trans*), 5.29–5.20 (m, 1H, *trans*), 5.11–4.99 (m, 1H, *cis*), 4.27 (dtd, *J* = 7.6, 6.8, 3.2 Hz, 1H, *cis*/*trans*), 2.38–1.74 (m, 2+1H, *cis*/*trans*), 1.11–0.93 (m, 6H, *cis*/*trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 149.3 (*cis*/*trans*), 135.5 (*cis*/*trans*), 133.5 (*cis*), 133.3 (*trans*), 128.8 (*cis*), 128.6 (*trans*), 126.8 (*cis*), 125.2 (*trans*), 83.3 (*cis*), 80.4 (*trans*), 78.9 (*cis*), 76.5 (*trans*), 32.5 (*cis*), 32.2 (*trans*), 30.8 (*cis*), 28.9 (*trans*), 17.7 (*trans*), 17.5 (*cis*). **HRMS** (EI) calcd. for $[C_{15}H_{18}O_3]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 246.1250, found 246.1244.

6.3 Project “synthesis of 2-methylenepentan-1-ones”

6.3.1. Synthesis of starting materials

Cyclohex-2-en-1-yl(phenyl)selane

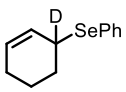


A N_2 flushed Schlenk flask was equipped with diphenyldiselenide (3.9 g, 13 mmol, 0.99 equiv) and diluted with a 1:1 volumetric mixture of THF and EtOH (124 mL, 0.1 M). The solution was cooled to 0 °C and $NaBH_4$ (0.94 g, 25 mmol, 2.0 equiv) was added. Upon nearly complete loss of the initial yellow/orange color, 3-bromocyclohexene (2.0 g, 13 mmol, 1.0 equiv) was added dropwise and the mixture was stirred for 1 h. After quenching with 1.0 M NaOH (40 mL) and sat. $NaHCO_3$ (40 mL), the organic phase was extracted with *n*-pentane (4x 30 ml), washed with brine (1x 50 mL) and dried over $MgSO_4$. Purification by column chromatography (*n*-pentane) resulted in 2.9 g (12 mmol, 98%) of cyclohex-2-en-1-yl(phenyl)selane as a yellowish oil.

*Majority of analytical data obtained in an independent project.[231]

TLC: R_f = 0.58 (*n*-pentane). **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.65–7.51 (m, 2H), 7.33-7.21 (m, 3H), 5.91–5.82 (m, 1H), 5.81–5.72 (m, 1H), 3.98 (tdd, *J* = 4.6, 2.8, 1.7 Hz, 1H), 2.20–1.82 (m, 5H), 1.73–1.55 (m, 1H).

(Cyclohex-2-en-1-yl-1-d)(phenyl)selane (167)



A dried Schlenk flask was equipped with dry THF (120 mL, 0.1 M) and cooled to - 78°C in an acetone/dry ice bath. A 2.0 M solution of LDA in THF (7.5 mL, 15 mmol, 1.3 equiv) and a 1.6 M solution of KO^{t}Bu in THF (9.5 mL, 15 mmol, 1.1 equiv) was added and the combined mixture stirred for 30 min at - 78°C. A this temperature cyclohex-2-en-1-yl(phenyl)selane (2.9 g, 12 mmol, 1.0 equiv) was added and the red solution was quenched with D_2O (8.0 mL,

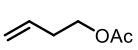
0.40 mol, 30 equiv) after 1 h. The organic phase was washed with brine (2x 50 mL) and dried over $MgSO_4$. Purification by column chromatography (*n*-pentane) resulted in 2.1 g (9.0 mmol, 75%) of (cyclohex-2-en-1-yl-1-d)(phenyl)selane (25% remained undeuterated).

*Majority of analytical data obtained in an independent project.[231]

*traces of $(PhSe)_2$ remained as side product.

TLC: R_f = 0.58 (*n*-pentane). **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.63–7.52 (m, 2H), 7.35–7.21 (m, 3H), 5.91–5.83 (m, 1H), 5.81–5.73 (m, 1H), 3.98 (td, *J* = 4.5, 2.5 Hz, 25% H, 75% D), 2.14–1.81 (m, 5H), 1.72–1.57 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 134.1, 131.5, 130.7, 129.8 (d, *J* = 5.5 Hz, C-D), 129.2, 129.0, 127.7 (d, *J* = 8.6 Hz, C-D), 41.2, 29.4 (d, *J* = 14.3 Hz, C-D), 24.9, 19.6 (d, *J* = 4.7 Hz, C-D). **^{2}H NMR** (61 MHz, Chloroform + traces of Chloroform-*d*): δ [ppm] = 4.0 (s, 1D). **HRMS** (EI) calcd. for $[C_{12}H_{13}DSe]^+$ $(M)^{+\cdot}$: m/z = 239.0323, found 239.0325.

But-3-en-1-yl acetate

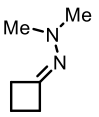


A round flask was equipped with but-3-en-1-ol (5.0 g, 69 mmol, 1.0 equiv), 4-DMAP (0.44 g, 3.6 mmol, 5 mol%) and diluted with DCM (77 mL, 0.9 M). To the solution was added Ac_2O (7.5 mL, 79 mmol, 1.1 equiv) and the mixture was stirred at r.t. for 21 h. Sat. $NaHCO_3$ was added until gas evaporation ceased and the organic phase was extracted with DCM (2x 50 mL). After drying over $MgSO_4$ and concentration, 6.0 g (53 mmol, 76%) of but-3-en-1-yl acetate were obtained as a colorless oil.

*analytical data are in accordance with cited literature which also served as reaction template.[279]

IR (ATR): ṽ [cm^{-1}] = 2970, 1736, 1435, 1634, 1230, 1039, 909, 730. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.78 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.19–5.01 (m, 2H), 4.11 (t, *J* = 6.8 Hz, 2H), 2.38 (qt, *J* = 6.8, 1.4 Hz, 2H), 2.04 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 171.1, 134.0, 117.2, 63.5, 33.0, 20.9. **HRMS** (EI) calcd. for $[C_6H_{11}O_2]^+$ $(M+H)^+$: m/z = 115.0754, found 115.0754.

2-Cyclobutylidene-1,1-dimethylhydrazine (188)



A N_2 flushed Schlenk flask was equipped with cyclobutanone (2.9 g, 42 mmol, 1.0 equiv) and 1,1-dimethylhydrazine (3.8 mL, 50 mmol, 1.2 equiv) and the mixture was refluxed at 70 °C under N_2 for 44 h. The reaction was allowed to cool down and diluted with Et_2O. The organic phase was washed with water (2x 10 mL), dried over $MgSO_4$ and concentrated to obtain 2.6 g (23 mmol, 56%) of 2-cyclobutylidene-1,1-dimethylhydrazine as a yellow oil.

*analytical data are in accordance with cited literature which also served as reaction template.[237]

IR (ATR): ṽ [cm^{-1}] = 3436, 3227, 2955, 2862, 2821, 2780, 1736, 1666, 1446, 1371, 1021. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 3.02–2.82 (m, 4H), 2.55 (s, 5H), 1.95 (tt, *J* = 8.6, 7.5 Hz, 2H).**^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 160.6, 46.9, 35.4, 35.2, 14.4. **HRMS** (EI) calcd. for $[C_6H_{12}N_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 112.1000, found 112.0995.

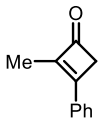
2-Benzylcyclobutan-1-one (179a)

A dried Schlenk flask was equipped with 2-cyclobutylidene-1,1-dimethylhydrazine (1.1 g, 9.5 mmol, 1.0 equiv) diluted with dry THF (23 mL, 0.4 M) and cooled to - 78°C. To the solution was added a ^{n}BuLi solution (2.4 M in *n*-hexane) (4.4 mL, 11 mmol, 1.1 equiv) and stirred at - 78°C for 1 h. Benzylbromide (1.3 mL, 11 mmol, 1.2 equiv) was added dropwise and the reaction stirred for 15 min at - 78°C and then allowed to warm up overnight. After a reaction time of 19 h, the reaction was quenched by the addition of 1 M HCl and stirred for an additional hour. The organic phase was extracted with Et_2O (2x 20 mL), dried over $MgSO_4$ and concentrated. Purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) resulted in 0.82 g (5.1 mmol, 54%) of 2-benzylcyclobutan-1-one as a colorless oil.

*analytical data are in accordance with cited literature which also served as reaction template.[237]

TLC: R_f = 0.58 (PE/Et_2O 3:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063, 3026, 2996, 2995, 2922, 1774, 1498, 1453, 1080, 741, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.40–7.08 (m, 5H), 3.60 (ddddd, *J* = 11.5, 8.4, 7.4, 5.5, 2.7 Hz, 1H), 3.19–2.94 (m, 2H), 2.96–2.72 (m, 2H), 2.16 (dtd, *J* = 11.2, 10.2, 5.2 Hz, 1H), 1.75 (ddt, *J* = 11.2, 9.7, 7.7 Hz, 1H).**^{13}C NMR** (100 MHz, Chloroform-*d*): δ [ppm] = 210.9, 138.9, 128.7, 128.5, 126.3, 61.2, 44.5, 35.2, 16.6. **HRMS** (EI) calcd. for $[C_6H_{12}N_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 112.1000, found 112.0995.

2-Methyl-3-phenylcyclobut-2-en-1-one (201)



A 2-neck round flask was equipped with *N*,*N*-dimethylpropionamide (2.5 g, 25 mmol, 1.0 equiv) and diluted with DCM (50 mL, 0.5 M). To the solution was added 2-fluoro-pyridine (2.6 mL, 30 mmol, 1.2 equiv) and phenylacetylene (3.3 mL, 30 mmol, 1.2 equiv). Tf_2O (4.6 mL, 28 mmol, 1.1 equiv) was added dropwise and after complete addition, the mixture was refluxed for 23 h.

Subsequently, the solution was cooled to 0 °C and the reaction was quenched by the addition of 1.0 M NaOH aq. (55 mL, 55 mmol, 2.2 equiv) and the reaction was stirred at that temperature for 5 h.

After neutralization by the addition of 1.0 M HCl aq., the organic phase was extracted with DCM (1x 50 mL), washed with water (1x 100 mL), sat. Na_2CO_3 (2x 100 mL) and brine (1x 100 mL), dried over $MgSO_4$ and concentrated.

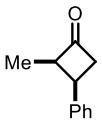
The orange concentrate was diluted with EtOH (100 mL, 0.3 M) and a 1.6 w% solution of KO^{t}Bu in THF (4.8 mL, 7.7 mmol, 0.31 equiv) was added and the reaction was stirred at r.t. for 18 h.

The reaction was quenched by the addition of sat. NH_4Cl and water, the organic phase extracted with DCM (1x 100mL), washed with water (2x 100 mL) and brine (1x 100 mL), dried over $MgSO_4$ and concentrated. Purification by automated column chromatography (PE to PE/Et_2O 99:1 to 85:15) resulted in 1.4 g (9.1 mmol, 36%) of 2-methyl-3-phenylcyclobut-2-en-1-one as a yellow precipitate.

*analytical data are in accordance with cited literature which also served as reaction template.[246]

MP: = 63.8°C. **TLC:** R_f = 0.28 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3056, 2948, 2914, 1748, 1617, 1446, 1345, 1066, 1013, 767, 693. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.64–7.54 (m, 2H), 7.59–7.41 (m, 3H), 3.46 (q, *J* = 2.3 Hz, 2H), 2.01 (t, *J* = 2.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 190.0, 163.5, 141.0, 132.8, 130.9, 129.2, 129.0, 48.2, 9.4. **HRMS** (EI) calcd. for $[C_{11}H_{10}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 158.0732, found 158.0729.

(*cis*)-2-Methyl-3-phenylcyclobutan-1-one (182l-*cis*)



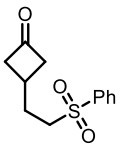
A round flask was equipped with 2-methyl-3-phenylcyclobut-2-en-1-one (0.31 g, 1.9 mmol, 1.0 equiv), Pd (10 wt%) on activated charcoal (21 mg, 0.20 mmol, 10 mol%) and both diluted with EtOAc (10 mL, 0.2 M). The flask was purged with H_2 gas (via balloon) for 5 min, the system was closed and then stirred for 6 h at r.t. After completion, the mixture was filtered over Celite, rinsed with EtOAc and concentrated. Purification by column chromatography (PE to PE/Et_2O 50:1 to 9:1) resulted in 0.22 g (1.4 mmol, 72%) of (*cis*)-2-methyl-3-phenylcyclobutan-1-one as a colorless oil.

*analytical data are in accordance with cited literature which also served as reaction template.[246]

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.28 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3063, 3030, 2970, 2929, 1774, 1602, 1494, 1453, 1397, 1133, 1095, 1054, 764, 738, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.30 (m, 2H), 7.30–7.20 (m, 1H), 7.20–7.15 (m, 2H), 3.78 (td, *J* = 9.9, 5.1 Hz, 1H), 3.75–3.63 (m, 1H), 3.51 (ddd, *J* = 17.6, 9.6, 3.8 Hz, 1H), 3.21 (ddd, *J* = 17.7, 5.1, 2.1 Hz, 1H), 0.78 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 211.1, 139.6, 128.5, 127.9, 126.7, 58.9, 50.0, 33.3, 10.1. **HRMS** (EI) calcd. for $[C_{11}H_{12}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 160.0888, found 160.0885.

3-(2-(Phenylsulfonyl)ethyl)cyclobutan-1-one (199a)



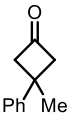
A round flask was equipped with 1,3-dioxoisoindolin-2-yl 3-oxocyclobutane-1-carboxylate (1.5 g, 5.8 mmol, 1.0 equiv), Hantzsch-Ester (2.2 g, 8.7 mmol, 1.5 equiv), $Ir(ppy)_3$ (39 mg, 59 µmol, 1 mol%) and (vinylsulfonyl)benzene (1.9 g, 12 mmol, 2.0 equiv) and diluted with *N,N*-dimethylacetamide (20 mL 0.3 M). The solution was degassed with N_2 for 30 min and then irradiated at 448 nm (700 mA) at 19 °C for 2 h. The reaction was terminated by the addition of sat. $NaHCO_3$, the organic phase extracted with Et_2O (2x 50 mL), washed with sat. $NaHCO_3$ (2x 50 mL) and brine (1x 100 mL) and dried over $MgSO_4$. After concentration and purification by automated column chromatography (*n*-hexane/Et_2O 95:5 to 20:80), 0.38 g (1.6 mmol, 27%) of 3-(2-(phenylsulfonyl)ethyl)cyclobutan-1-one were obtained as a yellow oil.

*The product was synthesized using an adapted procedure developed by Dr. Tao Lei based on the following procedure.[244]

TLC: R_f = 0.26 (PE/Et_2O 1:3). **IR** (ATR): ṽ [cm^{-1}] = 3063, 2922, 1774, 1446, 1386, 1304, 1144, 1088, 805, 741, 689. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 8.02–7.84 (m, 2H), 7.75–7.62 (m, 1H), 7.66-7.53 (m, 2H), 3.27–3.00 (m, 4H), 2.79–2.59 (m, 2H), 2.48 (dtdd, *J* = 14.7, 8.7, 7.3, 6.0 Hz, 1H),

2.13-1.96 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 205.8, 139.0, 133.9, 129.4, 128.0, 55.0, 52.4, 29.0, 22.8. **HRMS** (ESI) calcd. for $[C_{12}H_{18}NO_3S]^{+\cdot}$ $(M+NH_4)^{+\cdot}$: m/z = 256.1002, found 256.1006.

3-Methyl-3-phenylcyclobutan-1-one (182a)



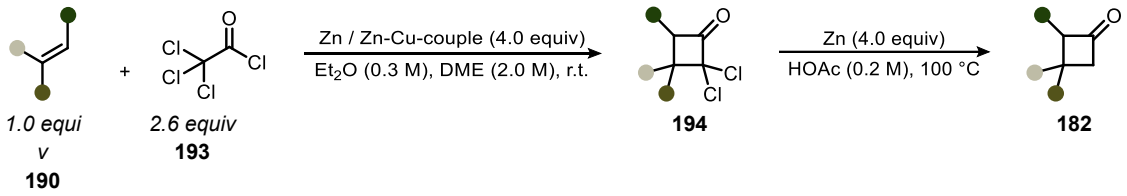
A round flask was equipped with *N*,*N*’-dimethylacetamide (2.0 g, 23 mmol, 1.0 equiv), diluted with 1,2-dichloromethane (23 mL, 1.0 M) and cooled to - 15 °C. To the cooled solution was added Tf_2O (4.2 mL, 26 mmol, 1.1 equiv) and the suspension was stirred for 15 min at this temperature. Afterwards, prop-1-en-2-ylbenzene (3.0 mL, 23 mmol, 1.0 equiv) and 2,4,6-collidine (3.0 mL, 23 mmol, 0.99 equiv) were added simultaneously, resulting in an orange-red slurry. The reaction was allowed to warm up and then refluxed at 90 °C over night. The reaction was quenched with water, further refluxed for 17 h and the organic phase then extracted with DCM (3x 25 mL) and washed with water (4x 100 mL) and brine (1x 100 mL), dried over $MgSO_4$ and concentrated. Purification by column chromatography (PE to PE/EtOAc 99:1 to 50:1) resulted in 0.52 g (3.3 mmol, 14%) of 3-methyl-3-phenylcyclobutan-1-one as a yellowish oil.

*The product was synthesized using the following procedure.[238]

*analytical data are in accordance with cited literature.[280]

TLC: R_f = 0.10 (PE/EtOAc 99:1). **IR** (ATR): ṽ [cm^{-1}] = 3060, 3026, 2959, 2922, 2870, 1781, 1498, 1446, 1379, 1304, 1185, 1140, 1080, 1028, 764, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.45–7.20 (m, 5H), 3.54–3.42 (m, 2H), 3.18–3.06 (m, 2H), 1.61 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 206.7, 148.3, 128.6, 126.3, 125.6, 59.3, 34.0, 31.1. **HRMS** (ESI) calcd. for $[C_{11}H_{13}O]^+$ $(M+H)^+$: m/z = 161.0961, found 161.0960.

General Procedure E: *SET* mediated [2+2] cycloaddition reaction[239]



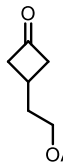
1.0 equiv **190** + *2.6 equiv* **193** → **194** → **182**

Scheme 118: Reaction procedure for the [2+2] cycloaddition using Zn/Zn-Cu couple.

A round flask was equipped with the respective alkene (1.0 equiv) and diluted with 1,2-dimethoxyethane (DME) (2.0 M) and Et_2O (0.3 M). The solution was cooled to 0 °C and Zn or Zn-Cu-couple (4.0 equiv) was added. To the cooled solution was added trichloroacetyl chloride (2.6 equiv) dropwise and the reaction was allowed to warm up and stirred until complete conversion. The reaction was filtered, rinsed with Et_2O, washed with water and brine, dried and concentrated and used without further purification.

The crude material was diluted with HOAc (0.2 M), Zn (4.0 equiv) was added portion wise and the reaction refluxed at 100 °C until completion. The slurry was filtered into a beaker containing water and rinsed with Et_2O or DCM. $NaHCO_3$ sat. aq. was added and the organic phase was washed with water, $NaHCO_3$ sat. aq. and brine, dried and concentrated. After purification by column chromatography the desired cyclobutanones were obtained.

2-(3-Oxocyclobutyl)ethyl acetate (182e)



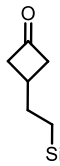
According to **General Procedure E**: but-3-en-1-yl acetate (3.1 g, 27 mmol, 1.0 equiv) was diluted with Et_2O (90 mL, 0.3 M) and 1,2-dimethoxyethane (14 mL, 2.0 M). To the cooled solution was added Zn-Cu-couple (14 g, 0.21 mol, 7.9 equiv) and trichloroacetyl chloride (8.0 mL, 72 mmol, 2.7 equiv). The reaction was stirred for 67 h, filtered and rinsed with Et_2O and concentrated, affording 2-(2,2-dichloro-3-oxocyclobutyl)ethyl acetate which was used without further purification.

Crude 2-(2,2-dichloro-3-oxocyclobutyl)ethyl acetate (27 mmol) was diluted with HOAc (185 mL, 0.1 M) and Zn (8.9 g, 0.14 mol, 5.1 equiv) was added. After refluxing for 21 h, the reaction was filtered, rinsed with EtOAc and washed with water (1x 100 mL) and sat. $NaHCO_3$ (3x 100 mL). After drying over $MgSO_4$ and concentration, 1.5 g (9.8 mmol, 37%) of 2-(3-oxocyclobutyl)ethyl acetate were obtained as a brownish oil.

*analytical data are in accordance with cited literature.[281]

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2959, 1781, 1733, 1435, 1367, 1230, 1174, 1110, 1043, 969. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 4.11 (t, *J* = 6.4 Hz, 2H), 3.28–3.10 (m, 2H), 2.84–2.67 (m, 2H), 2.58–2.36 (m, 1H), 2.05 (s, 3H), 1.93 (dt, *J* = 7.6, 6.4 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 207.4, 171.1, 63.2, 52.6, 34.9, 21.2, 20.9. **HRMS** (APCI) calcd. for $[C_8H_{16}NO_3]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 174.1125, found 174.1125.

3-(2-(Trimethylsilyl)ethyl)cyclobutan-1-one (182f)



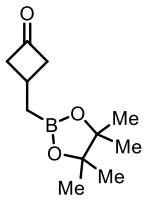
According to **General Procedure E**: but-3-en-1-yltrimethylsilane (3.0 g, 24 mmol, 1.0 equiv) was diluted with Et_2O (78 mL, 0.3 M) and 1,2-dimethoxyethane (12 mL, 2.0 M). To the cooled solution was added Zn (6.2 g, 94 mmol, 4.0 equiv) and trichloroacetyl chloride (6.8 mL, 61 mmol, 2.6 equiv). The reaction was stirred for 67 h, filtered and rinsed with Et_2O. Washing with water (3x 100 mL) and brine (1x 100 mL), drying over $MgSO_4$ and concentration, afforded crude 2,2-dichloro-3-(2-(trimethylsilyl)ethyl)cyclobutan-1-one which was used without further purification.

Crude 2,2-dichloro-3-(2-(trimethylsilyl)ethyl)cyclobutan-1-one (24 mmol) was diluted with HOAc (100 mL, 0.2 M) and Zn (7.7 g, 0.12 mmol, 5.0 equiv) was added. After refluxing for 23 h, the reaction was filtered, rinsed with Et_2O and washed with water (3x 100 mL) and brine (1x 50 mL). After

drying over $MgSO_4$ and concentration, 3.0 g (18 mmol, 74%) of 3-(2-(trimethylsilyl)ethyl)cyclobutan-1-one were obtained as a brownish oil.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2955, 2911, 1781, 1248, 909, 861, 734. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 3.20–3.02 (m, 2H), 2.72–2.54 (m, 2H), 2.32 (ttt, *J* = 8.7, 7.4, 6.0 Hz, 1H), 1.63–1.47 (m, 2H), 0.58–0.43 (m, 2H), 0.00 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 210.6, 53.8, 32.4, 28.6, 16.9, 0.0. **HRMS** (APCI) calcd. for $[C_8H_{15}SiO]^{+\cdot}$ $(M\text{-}CH_3)^{+\cdot}$: m/z = 155.0887, found 155.0887.

3-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutan-1-one (182h)

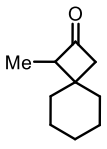


According to **General Procedure E**: 2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.82 g, 4.9 mmol, 1.0 equiv) was diluted with Et_2O (16 mL, 0.3 M) and 1,2-dimethoxyethane (2.0 mL, 2.0 M). To the cooled solution was added Zn (1.4 g, 21 mmol, 4.2 equiv) and trichloroacetyl chloride (1.5 mL, 14 mmol, 2.8 equiv). The reaction was stirred for 93 h, filtered and rinsed with Et_2O. Washing with water (3x 20 m), drying over $MgSO_4$ and concentration, afforded crude 2,2-dichloro-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutan-1-one which was used without further purification.

Crude 2,2-dichloro-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutan-1-one (4.9 mmol) was diluted with HOAc (25 mL, 0.3 M) and Zn (1.6 g, 24 mmol, 5.0 equiv) was added. After refluxing for 16 h, the reaction was filtered, rinsed with Et_2O and washed with water (3x 50 mL) and extracted with Et_2O (1x 50 mL). After drying over $MgSO_4$, concentration and purification by column chromatography (PE to PE/Et_2O 30:1 to 3:1), 57 mg (0.27 mmol, 6%) of 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutan-1-one were obtained as a yellowish oil.

TLC: R_f = 0.46 (PE/Et_2O 3:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2978, 2933, 1781, 1371, 1319, 1215, 1144, 969, 846. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 3.27–3.09 (m, 2H), 2.79–2.63 (m, 2H), 2.67–2.48 (m, 1H), 1.23 (s, 12H), 1.17 (d, *J* = 7.2 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 209.2, 83.3, 77.2, 54.5, 24.8, 20.0. **^{11}B NMR** (128 MHz, Chloroform-*d*): δ [ppm] = 33.2. **HRMS** (EI) calcd. for $[C_{11}H_{19}BO_3]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 210.1427, found 210.1427.

1-Methylspiro[3.5]nonan-2-one (182j)

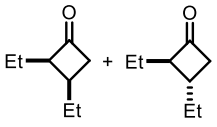


According to **General Procedure E**: ethylidenecyclohexane (2.0 g, 18 mmol, 1.0 equiv) was diluted with Et_2O (62 mL, 0.3 M) and 1,2-dimethoxyethane (9.5 mL, 1.9 M). To the cooled solution was added Zn-Cu-couple (9.4 g, 0.14 mol, 7.9 equiv) and trichloroacetyl chloride (5.4 mL, 48 mmol, 2.7 equiv). The reaction was stirred for 45 h, filtered and rinsed with Et_2O. Washing with water (3x 100 mL) and brine (1x 100 mL), extracted with Et_2O (1x 50 mL) drying over $MgSO_4$ and concentration, afforded crude 1,1-dichloro-3-methylspiro[3.5]nonan-2-one which was used without further purification.

Crude 1,1-dichloro-3-methylspiro[3.5]nonan-2-one (18 mmol) was diluted with HOAc (90 mL, 0.2 M) and Zn (6.0 g, 92 mmol, 5.0 equiv) was added. After refluxing for 17 h, the reaction was filtered, rinsed with Et_2O, washed with water (3x 100 mL), brine (1x 100 mL) and extracted with Et_2O (1x 50 mL). After drying over $MgSO_4$, concentration and purification by column chromatography (PE to PE/Et_2O 50:1 to 30:1), 1.2 g (7.9 mmol, 43%) of 1-methylspiro[3.5]nonan-2-one were obtained as a colorless oil.

TLC: R_f = 0.56 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2922, 2851, 1774, 1446, 1185, 1036, 905. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 2.87 (qdd, *J* = 7.4, 2.9, 1.9 Hz, 1H), 2.77–2.57 (m, 2H), 1.72–1.55 (m, 5H), 1.49–1.17 (m, 5H), 1.03 (d, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 211.4, 62.5, 54.9, 39.1, 33.8, 31.3, 25.8, 24.3, 23.2, 7.7. **HRMS** (EI) calcd. for $[C_{10}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 152.1201, found 152.1197.

2,3-Diethylcyclobutan-1-one (182k)



cis *trans*

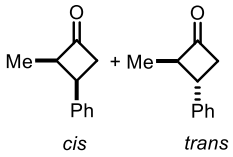
According to **General Procedure E**: a *cis/*trans-mixture of hex-3-ene (3.0 g, 36 mmol, 1.0 equiv) was diluted with Et_2O (100 mL, 0.4 M) and 1,2-dimethoxyethane (15 mL, 2.4 M). To the cooled solution was added Zn (9.3 g, 0.14 mmol, 4.0 equiv) and trichloroacetyl chloride (10 mL, 90 mmol, 2.5 equiv). The reaction was stirred for 71 h, filtered and rinsed with Et_2O. Washing with water (3x 100 mL) and brine (1x 100 mL), drying over $MgSO_4$ and concentration, afforded crude 2,2-dichloro-3,4-diethylcyclobutan-1-one, which was used without further purification.

Crude 2,2-dichloro-3,4-diethylcyclobutan-1-one (36 mmol) was diluted with HOAc (150 mL, 0.2 M) and Zn (12 g, 0.18 mol, 5.0 equiv) was added. After refluxing for 21 h, the reaction was filtered, rinsed with Et_2O, washed with water (3x 100 mL) and sat. $NaHCO_3$ (2x 50 mL). After drying over $MgSO_4$, concentration and purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1), 2.0 g (15 mmol, 43%) of 2,3-diethylcyclobutan-1-one were obtained as a colorless oil (39:10 *trans/cis*).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.42 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2963, 2929, 1774, 1491, 734.**^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 3.23–3.04 (m, 1H, *cis*), 2.99 (ddd, *J* = 17.4, 8.6, 2.8 Hz, 1H, *trans*), 2.75 (dtd, *J* = 13.0, 6.6, 3.0 Hz, 1H, *trans*), 2.63–2.50 (m, 1H, *trans*), 2.48 (ddd, *J* = 16.9, 4.7, 2.4 Hz, 1H, *cis*), 2.35 (ddq, *J* = 9.5, 6.8, 4.8 Hz, 1H, *cis*), 1.94 (tq, *J* = 13.8, 7.0 Hz, 1H, *trans*), 1.77–1.41 (m, 4H, *cis/trans*), 1.32–1.13 (m, 1H, *cis*), 1.04–0.87 (m, 6H, *cis/trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 211.9 (*cis*), 211.4 (*trans*), 66.7 (*trans*), 63.5 (*cis*), 49.8 (*cis*), 49.5 (*trans*), 32.5 (*trans*), 29.5 (*trans*), 29.4 (*cis*), 23.0 (*cis*), 22.3 (*trans*), 17.7 (*cis*), 12.8 (*cis*), 12.5 (*trans*), 12.4 (*cis*), 11.7 (*trans*). **HRMS** (EI) calcd. for $[C_8H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 126.1045, found 126.1036.

2-Methyl-3-phenylcyclobutan-1-one (182l)



According to **General Procedure E**: (*Z*)-prop-1-en-1-ylbenzene (2.0 g, 17 mmol, 1.0 equiv) was diluted with Et_2O (56 mL, 0.3 M) and 1,2-dimethoxyethane (8.0 mL, 2.0 M). To the cooled solution was added Zn (4.5 g, 68 mmol, 4.0 equiv) and trichloroacetyl chloride (5.0 mL, 45 mmol, 2.6 equiv). The reaction was stirred for 67 h, filtered and rinsed with Et_2O. Washing with water (3x 100 m) and brine (1x 100 mL), drying over $MgSO_4$ and concentration, afforded 2,2-dichloro-4-methyl-3-phenylcyclobutan-1-one which was used without further purification.

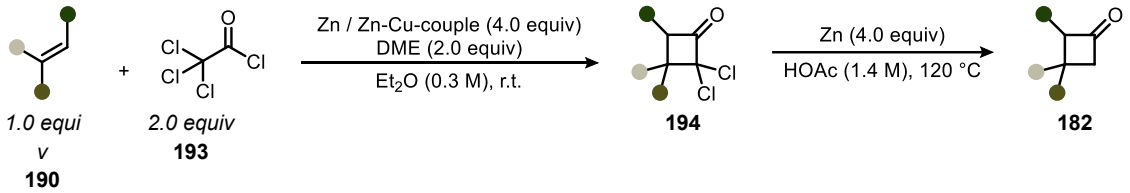
Crude 2,2-dichloro-4-methyl-3-phenylcyclobutan-1-one (17 mmol) was diluted with HOAc (85 mL, 0.3 M) and Zn (5.6 g, 85 mmol, 5.0 equiv) was added. After refluxing for 22 h, the reaction was filtered, rinsed with Et_2O and washed with water (3x 100 mL) and sat. $NaHCO_3$ (1x 100 mL) and extracted with Et_2O (2x 50 mL). After drying over $MgSO_4$, concentration and purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1 and PE to PE/toluene 50:1 to 10:1), 0.45 g (2.8 mmol, 16%) of 2-methyl-3-phenylcyclobutan-1-one were obtained as a yellowish oil (52:10 *trans*/*cis*).

*analysis of configuration was done by 2D NMR experiments.

*analytical data are in accordance with cited literature.[282]

TLC: R_f = 0.24 (toluene). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063, 3030, 2967, 2929, 1781, 1602, 1498, 1453, 1401, 1144**,** 1032, 738, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.45–7.13 (m, 5H *cis*/*trans*), 3.86-3.64 (m, 2H, *cis*), 3.61–3.42 (m, 2H, *cis*), 3.46–3.09 (m, 4H, *trans*), 1.30 (d, *J* = 7.1 Hz, 3H, *trans*), 0.78 (d, *J* = 7.3 Hz, 3H, *cis*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 211.1 (*cis*), 209.2 (*trans*), 142.9 (*trans*), 128.7 (*trans*), 128.5 (*cis*), 127.9 (*cis*), 126.8 (*trans*), 126.7 (*cis*), 126.5 (*trans*), 62.8 (*trans*), 58.9 (*cis*), 51.6 (*trans*), 50.0 (*cis*), 37.8 (*trans*), 33.3 (*cis*), 13.3 (*trans*), 10.1 (*cis*). **HRMS** (APCI) calcd. for $[C_{11}H_{16}NO]^+$ $(M+NH_4)^+$: m/z = 178.1226, found 178.1226.

General Procedure E’: Adapted *SET* mediated [2+2] cycloaddition reaction[242]



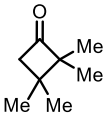
Scheme 119: Adapted reaction procedure for the [2+2] cycloaddition using Zn-Cu couple.

A dried Schlenk was equipped with the respective alkene (1.0 equiv) and diluted with dry Et_2O (0.7 M). To the solution was added Zn-Cu-couple (4.0 equiv) and the suspension was cooled to 0 °C. In a separate Schlenk flask was prepared a solution of trichloroacetyl chloride (2.0 equiv) and 1,2-dimethoxyethane (DME) (2.0 equiv) in dry Et_2O (4.2 M). The second solution was added dropwise to the Zn suspension and the reaction mixture was stirred at rt until complete conversion. The

suspension was filtered over Celite, rinsed with Et_2O, washed with water, sat. $NaHCO_3$ and brine and dried. After concentration, the crude material was used without further purification.

The crude material was diluted with HOAc (1.4 M), Zn (4.0 equiv) was added portion wise and the reaction refluxed at 120 °C until completion. The slurry was filtered over Celite into a beaker containing water and rinsed with DCM. Sat. $NaHCO_3$ was added and the organic phase was washed with water, sat. $NaHCO_3$ and brine, dried and concentrated. After purification by column chromatography the desired cyclobutanones were obtained.

2,2,3,3-Tetramethylcyclobutan-1-one (182b)



According to **General Procedure E’:** 2,3-dimethylbut-2-ene (2.1 g, 24 mmol, 1.0 equiv) was diluted with dry Et_2O (35 mL, 0.7 M) and Zn-Cu-couple (6.4 g, 98 mmol, 4.0 equiv) was added. A mixture of 1,2-dimethoxyethane (4.5 g, 50 mmol, 2.1 equiv) and trichloroacetyl chloride (5.6 mL, 50 mmol, 2.1 equiv) in dry Et_2O (10 mL, 4.8 M) was added dropwise. After a reaction time of 67 h, the suspension was filtered, rinsed with Et_2O, washed with water (1x 100 mL), sat. $NaHCO_3$ (5x 100 mL) and brine (1x 100 mL) and extracted with Et_2O (1x 50 mL). Drying over $MgSO_4$ and concentration afforded crude 2,2-dichloro-3,3,4,4-tetramethylcyclobutan-1-one which was used without further purifications.

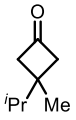
Alternative second step:[243]

Crude 2,2-dichloro-3,3,4,4-tetramethylcyclobutan-1-one (24 mmol) was diluted with MeOH (61 mL, 0.4 M) and Zn (8.0 g, 0.12 mol, 5.0 equiv) was added. NH_4Cl (6.5 g, 0.12 mol, 5.0 equiv) was added portion wise and the suspension was stirred for 23 h. The reaction was filtered into a beaker containing water, rinsed with MeOH and DCM and washed with water (3x 100 mL) and extracted with DCM (2x 50 mL). After drying over $MgSO_4$, concentration and purification by column chromatography (PE to PE/Et_2O 50:1 to 30:1), 0.50 g (3.9 mmol, 16%) of 2,2,3,3-tetramethylcyclobutan-1-one were obtained as a colorless oil.

*analytical data are in accordance with cited literature[283]

TLC: R_f = 0.44 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2959, 2926, 2855, 1736, 1453, 1401, 1297, 1256, 1129. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 2.79 (s, 2H), 1.18 (s, 6H), 1.08 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 215.3, 61.7, 56.6, 31.8, 24.3, 19.2. **HRMS** (EI) calcd. for $[C_8H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 126.1045, found 126.1037.

3-Isopropyl-3-methylcyclobutan-1-one (182c)



According to **General Procedure E’:** 2,3-dimethylbut-1-ene (2.0 g, 24 mmol, 1.0 equiv) was diluted with dry Et_2O (35 mL, 0.7 M) and Zn-Cu-coupled (6.3 g, 98 mmol, 4.0 equiv) was added. A mixture of 1,2-dimethoxyethane (4.3 g, 47 mmol, 2.0 equiv) and trichloroacetyl chloride (5.4 mL, 48 mmol, 2.0 equiv) in dry Et_2O (10 mL, 4.8 M) was added dropwise. After a reaction time of 21 h, the suspension was filtered, rinsed with Et_2O, washed with water (2x 100 mL),

sat. $NaHCO_3$ (5x 100 mL) and brine (1x 100 mL) and extracted with Et_2O (1x 100 mL). Drying over $MgSO_4$ and concentration afforded crude 2,2-dichloro-3-isopropyl-3-methylcyclobutan-1-one which was used without further purifications.

Crude 2,2-dichloro-3-isopropyl-3-methylcyclobutan-1-one (22 mmol) was diluted with HOAc (36 mL, 0.6 M) and Zn (5.7 g, 87 mmol, 4.0 equiv) was added. After refluxing for 18 h, the reaction was filtered, rinsed with DCM and washed with sat. $NaHCO_3$ (3x 100 mL), brine (1x 100 mL) and extracted with DCM (1x 50 mL). After drying over $MgSO_4$, concentration and purification by column chromatography (PE to PE/Et_2O 50:1 to 30:1), 0.72 g (5.7 mmol, 24%) of 3-isopropyl-3-methylcyclobutan-1-one were obtained as a colorless oil.

TLC: R_f = 0.58 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2963, 2877, 2255, 1774, 1464, 1189, 1107, 909, 730. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 2.91–2.76 (m, 2H), 2.70–2.54 (m, 2H), 1.80 (hept, *J* = 6.8 Hz, 1H), 1.17 (d, *J* = 0.5 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 208.5, 57.5, 37.0, 33.1, 20.2, 17.7. **HRMS** (EI) calcd. for $[C_8H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 126.1045, found 126.1039.

3-Benzylcyclobutan-1-one (182d)

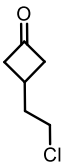
According to **General Procedure E’:** allylbenzene (3.0 g, 25 mmol, 1.0 equiv) was diluted with dry Et_2O (35 mL, 0.7 M) and Zn (6.7 g, 0.10 mol, 4.0 equiv) was added. A mixture of 1,2-dimethoxyethane (4.6 g, 51 mmol, 2.0 equiv) and trichloroacetyl chloride (6.0 mL, 54 mmol, 2.1 equiv) in dry Et_2O (10 mL, 5.0 M) was added dropwise. After a reaction time of 68 h, the suspension was filtered, rinsed with Et_2O, washed with water (1x 100 mL), sat. $NaHCO_3$ (4x 100 mL) and brine (1x 100 mL). Drying over $MgSO_4$ and concentration afforded crude 3-benzyl-2,2-dichlorocyclobutan-1-one which was used without further purifications.

Crude 3-benzyl-2,2-dichlorocyclobutan-1-one (24 mmol) was diluted with HOAc (26 mL, 1.0 M) and Zn (6.3 g, 96 mmol, 4.0 equiv) was added. After refluxing for 16 h, the reaction was filtered, rinsed with DCM and washed with water (1x 100 mL), sat. $NaHCO_3$ (2x 100 mL) and brine (1x 100 mL). After drying over $MgSO_4$, concentration and purification by automated flash column chromatography (PE to PE/Et_2O 99:1 to 90:10), 1.9 g (12 mmol, 47%) of 3-benzylcyclobutan-1-one were obtained as a colorless oil.

*analytical data are in accordance with cited literature.[284]

TLC: R_f = 0.34 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063, 3026, 2914, 2851, 1774, 1498, 1379, 1099, 738, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.37–7.28 (m, 2H), 7.27–7.15 (m, 3H), 3.22-3.05 (m, 2H), 2.91 (d, *J* = 7.1Hz, 2H), 2.86–2.65 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 207.8, 140.0, 128.6, 128.6, 126.4, 52.3, 41.9, 25.0. **HRMS** (EI) calcd. for $[C_{11}H_{12}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 160.0888, found 160.0884.

3-(2-Chloroethyl)cyclobutan-1-one (182g)



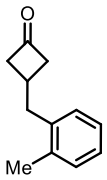
According to **General Procedure E’:** 4-chlorobut-1-ene (3.1 g, 34 mmol, 1.0 equiv) was diluted with dry Et_2O (50 mL, 0.7 M) and Zn-Cu-coupled (9.0 g, 0.14 mol, 4.0 equiv) was added. A mixture of 1,2-dimethoxyethane (6.4 g, 71 mmol, 2.1 equiv) and trichloroacetyl chloride (7.8 mL, 70 mmol, 2.0 equiv) in dry Et_2O (15 mL, 4.8 M) was added dropwise. After a reaction time of 17 h, the suspension was filtered, rinsed with Et_2O, washed with water (2x 100 mL), sat. $NaHCO_3$ (5x 100 mL) and brine (1x 100 mL) and extracted with Et_2O (1x 50 mL). Drying over $MgSO_4$ and concentration afforded crude 2,2-dichloro-3-(2-chloroethyl)cyclobutan-1-one which was used without further purifications.

Crude 2,2-dichloro-3-(2-chloroethyl)cyclobutan-1-one (34 mmol) was diluted with HOAc (56 mL, 0.6 M) and Zn (8.8 g, 0.14 mol, 4.0 equiv) was added. After refluxing for 2 h, the reaction was filtered, rinsed with DCM and washed with sat. $NaHCO_3$ (2x 100 mL) and water (2x 100 mL). After drying over $MgSO_4$, concentration and purification by column chromatography (PE to PE/Et_2O 30:1 to 10:1), 1.3 g (9.7 mmol, 28%) of 3-(2-chloroethyl)cyclobutan-1-one were obtained as a colorless oil.

*analytical data are in accordance with cited literature.[285]

TLC: R_f = 0.32 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2959, 2922, 1777, 1386, 1289, 1103, 723. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 3.57 (t, *J* = 6.5 Hz, 2H), 3.30–3.12 (m, 2H), 2.83–2.66 (m, 2H), 2.70-2.50 (m, 1H), 2.07 (dt, *J* = 7.5, 6.5 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 206.9, 52.4, 43.3, 38.6, 21.8. **HRMS** (EI) calcd. for $[C_6H_9ClO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 132.0342, found 132.0335.

3-(2-Methylbenzyl)cyclobutan-1-one (182i)

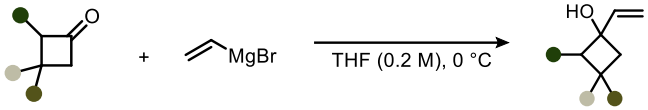


According to **General Procedure E’:** 1-allyl-2-methylbenzene (0.98 g, 7.4 mmol, 1.0 equiv) was diluted with dry Et_2O (11 mL, 0.7 M) and Zn (2.0 g, 30 mmol, 4.1 equiv) was added. A mixture of 1,2-dimethoxyethane (1.4 g, 16 mmol, 2.1 equiv) and trichloroacetyl chloride (1.7 mL, 15 mmol, 2.1 equiv) in dry Et_2O (4.0 mL, 4.0 M) was added dropwise. After a reaction time of 17 h, the suspension was filtered, rinsed with Et_2O, washed with water (1x 50 mL), sat. $NaHCO_3$ (5x 50 mL) and brine (1x 50 mL) and extracted with Et_2O (1x 50 mL). Drying over $MgSO_4$ and concentration afforded crude 2,2-dichloro-3-(2-methylbenzyl)cyclobutan-1-one which was used without further purifications.

Crude 2,2-dichloro-3-(2-methylbenzyl)cyclobutan-1-one (6.1 mmol) was diluted with HOAc (10 mL, 0.6 M) and Zn (1.6 g, 24 mmol, 4.0 equiv) was added. After refluxing for 19 h, the reaction was filtered, rinsed with DCM and washed with sat. $NaHCO_3$ (3x 50 mL) and water (1x 50 mL). After drying over $MgSO_4$, concentration and purification by column chromatography (PE to PE/Et_2O 100:1 to 30:1), 0.37 g (2.1 mmol, 35%) of 3-(2-methylbenzyl)cyclobutan-1-one were obtained as a colorless oil.

TLC: R_f = 0.28 (PE/Et_2O 30:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3019, 2918, 2862, 1774, 1490, 1457, 1382, 1103, 741. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.24–7.05 (m, 4H), 3.28–3.07 (m, 2H), 2.91 (d, *J* = 7.0 Hz, 2H), 2.90–2.68 (m, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 207.9, 138.1, 136.1, 130.4, 128.6, 126.5, 126.1, 52.5, 39.1, 23.5, 19.5. **HRMS** (EI) calcd. for $[C_{12}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 174.1045, found 174.1042.

General Procedure F: Grignard reaction[248]

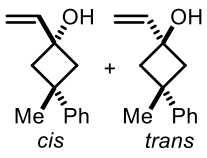


182 *1.0-1.5 equiv* **202** **174**

Scheme 120: Reaction equation for the Grignard reaction.

A Schlenk flask was equipped with the respective cyclobutanone (1.0 equiv) and diluted with dry THF (0.2 M). The solution was cooled to 0 °C and a solution of vinyl magnesium bromide (1.0 M in THF, 1.1-1.5 equiv) was added dropwise. The reaction was allowed to warm up and quenched with sat. NH_4Cl upon completion. The organic phase was extracted with Et_2O and washed with water and brine, dried and concentrated. Purification by column chromatography resulted in the corresponding vinylic cyclobutanols (as mixtures of diastereomers).

3-Methyl-3-phenyl-1-vinylcyclobutan-1-ol (174a)



According to **General Procedure F**: 3-methyl-3-phenylcyclobutan-1-one (1.5 g, 9.3 mmol, 1.0 equiv) was diluted in dry THF (46 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (13 mL, 13 mmol, 1.4 equiv) for 4 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with brine (2x 100 mL), extracted with Et_2O (1x 20 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE/EtOAc 50:1) 1.2 g (6.2 mmol, 66%) of 3-methyl-3-phenyl-1-vinylcyclobutan-1-ol were obtained as a yellowish oil (14:10 *trans*/*cis*).

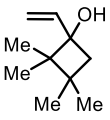
*analysis of configuration was done by 2D NMR experiments.

*analytical data are in accordance with cited literature.[250]

TLC: R_f = 0.08 (PE/EtOAc 50:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3336, 2970, 2929, 1494, 1420, 1267, 1177, 1058, 1028, 991, 916, 764, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.32 (dddd, *J* = 7.8, 7.0, 2.8, 1.3 Hz, 2H, *cis*/*trans*), 7.27–7.11 (m, 3H, *cis*/*trans*), 6.24 (dd, *J* = 17.2, 10.6 Hz, 1H, *cis*), 5.90 (dd, *J* = 17.2, 10.6 Hz, 1H, *trans*), 5.42–5.13 (m, 2H, *cis*), 5.18–4.87 (m, 2H, *trans*), 2.80–2.67 (m, 2H, *trans*), 2.70-2.52 (m, 4H, *cis*), 2.44–2.28 (m, 2H, *trans*), 1.59 (s, 3H, *trans*), 1.41 (s, 3H, *cis*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 152.1 (*cis*), 151.0 (*trans*), 144.3 (*trans*), 143.9 (*cis*), 128.3 (*cis*), 128.2 (*trans*), 125.4 (*cis*), 125.4 (*cis*), 125.3 (*trans*), 125.1 (*trans*), 112.7 (*cis*),

111.0 (*trans*), 71.2 (*trans*), 70.4 (*cis*), 48.1 (*cis*), 47.7 (*trans*), 35.6 (*cis*), 33.7 (*cis*), 33.5 (*trans*), 31.4 (*trans*). **HRMS** (EI) calcd. for $[C_{13}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 188.1201, found 188.1195.

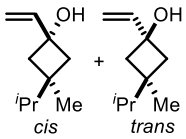
2,2,3,3-Tetramethyl-1-vinylcyclobutan-1-ol (174b)



According to **General Procedure F**: 2,2,3,3-tetramethylcyclobutan-1-one (0.32 g, 2.5 mmol, 1.0 equiv) was diluted in dry THF (13 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (3.4 mL, 3.4 mmol, 1.3 equiv) for 17 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was extracted with Et_2O (2x 25 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE to PE/Et_2O 30:1) 0.23 g (1.5 mmol, 59%) of 2,2,3,3-tetramethyl-1-vinylcyclobutan-1-ol were obtained as a colorless oil.

TLC: R_f = 0.42 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3444, 2952, 2870, 1740, 1453, 1416, 1371, 1215, 1140, 1114, 998, 920. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 6.07 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.31–5.00 (m, 2H), 2.15 (d, *J* = 12.3 Hz, 1H), 1.75 (d, *J* = 12.3 Hz, 1H), 1.15 (s, 3H), 1.00 (s, 3H), 0.96 (s, 3H), 0.91 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 141.8, 112.9, 45.8, 44.8, 34.1, 25.9, 24.9, 22.1, 19.0. **HRMS** (EI) calcd. for $[C_{10}H_{18}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 154.1358, found 154.1351.

3-Isopropyl-3-methyl-1-vinylcyclobutan-1-ol (174c)

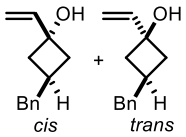


According to **General Procedure F**: 3-isopropyl-3-methylcyclobutan-1-one (0.48 g, 3.8 mmol, 1.0 equiv) was diluted in dry THF (19 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (5.0 mL, 5.0 mmol, 1.3 equiv) for 25 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was extracted with Et_2O (2x 25 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE/Et_2O 10:1) 0.24 g (1.6 mmol, 41%) of 3-isopropyl-3-methyl-1-vinylcyclobutan-1-ol obtained as a colorless oil (19:10 *trans*/*cis*).

*analytical data are in accordance with cited literature.[250]

TLC: R_f = 0.28 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3347, 2959, 2929, 2873, 1464, 1420, 1367, 1252, 1192, 1032, 991, 916. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 6.13 (dd, *J* = 17.3, 10.6 Hz, 1H, *cis*), 6.02 (dd, *J* = 17.2, 10.6 Hz, 1H, *trans*), 5.29–4.95 (m, 2H, *trans*/*cis*), 2.16–1.94 (m, 2H, *trans/cis*), 1.88-1.73 (m, 2H, *trans*/*cis* + 1H *cis*), 1.59 (hept, *J* = 6.8 Hz, 1H, *trans*), 1.13 (s, 3H, *trans*), 0.93 (s, 3H, *cis*), 0.78 (dd, *J* = 9.2, 6.8 Hz, 6H, *trans*/*cis*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 145.3 (*trans*), 144.9 (*cis*), 111.6 (*cis*), 110.8 (*trans*), 70.3 (*trans*), 69.4 (*cis*), 46.6 (*cis*), 46.3 (*trans*), 39.0 (*cis*), 37.5 (*trans*), 33.9 (*trans*), 32.3 (*cis*), 21.2 (*trans*), 19.9 (*cis*), 16.5 (*trans*), 16.3 (*cis*). **HRMS** (EI) calcd. for $[C_{10}H_{18}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 154.1358, found 154.1346.

3-Benzyl-1-vinylcyclobutan-1-ol (174d)

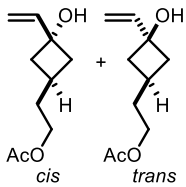


According to **General Procedure F**: 3-benzylcyclobutan-1-one (1.5 g, 9.5 mmol, 1.0 equiv) was diluted in dry THF (30 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (12 mL, 12 mmol, 1.3 equiv) for 17 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 100 mL), extracted with Et_2O (1x 100 mL) and dried with $MgSO_4$. After concentration and purification by automated column chromatography (PE to PE/Et_2O 99:1 to 75:25) 1.1 g (5.7 mmol, 60%) of 3-benzyl-1-vinylcyclobutan-1-ol were obtained as a yellowish oil (37:10 *trans*/*cis*).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.46 (PE/Et_2O 3:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3336, 3026, 2967, 2929, 1494, 1453, 1423, 1244, 1162, 1028, 916, 760, 723, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.29–7.20 (m, 2H, *cis*/*trans*), 7.19–7.13 (m, 1H, *cis*/*trans*), 7.13–7.08 (m, 2H, *cis*/*trans*), 6.04 (m, 1H, *cis*/*trans*), 5.19 (m, 1H, *cis*/*trans*), 5.03 (m, 1H, *cis*/*trans*), 2.83–2.75 (m, 1H, *cis*), 2.73 (d, *J* = 7.4 Hz, 2H, *trans*), 2.69 (d, *J* = 8.2 Hz, 2H, *cis*), 2.37–2.28 (m, 2H, *trans*), 2.20–2.13 (m, 2H, *cis*), 2.13–2.02 (m, 1H, *trans*), 2.00-1.93 (m, 2H, *cis*), 1.89 (ddt, *J* = 11.8, 9.4, 2.4 Hz, 2H, *trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.4 (*cis*), 142.5 (*trans*), 140.7 (*cis*), 140.7 (*trans*), 128.5 (*cis*), 128.5 (*trans*), 128.3 (*cis*), 128.3 (*trans*), 125.9 (*trans*), 125.9 (*cis*), 111.8 (*cis*), 111.4 (*trans*), 73.9 (*cis*), 71.4 (*trans*), 43.1 (*trans*), 42.5 (*cis*), 42.0 (*trans*), 40.8 (*cis*), 29.2 (*cis*), 26.7 (*trans*). **HRMS** (EI) calcd. for $[C_{13}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 188.1199, found 188.1201.

2-(3-Hydroxy-3-vinylcyclobutyl)ethyl acetate (174e)

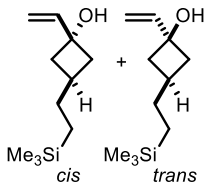


According to **General Procedure F**: 2-(3-oxocyclobutyl)ethyl acetate (1.3 g, 8.5 mmol, 1.0 equiv) was diluted in dry THF (50 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (9.5 mL, 9.5 mmol, 1.1 equiv) for 4 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (2x 100 mL), extracted with Et_2O (2x 50 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE to PE/EtOAc 9:1) 0.83 g (4.5 mmol, 53%) of 2-(3-hydroxy-3-vinylcyclobutyl)ethyl acetate were obtained as a yellowish oil (46:10 *cis*/*trans*).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.2 (PE/EtOAc 4:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3414, 2967, 2929, 1736, 1364, 1233, 1036, 916. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 6.11 (dd, *J* = 17.3, 10.6 Hz, 1H, *cis*), 6.01 (dd, *J* = 17.4, 10.7 Hz, 1H, *trans*), 5.34–4.96 (m, 2H, *cis*/*trans*), 4.01 (td, *J* = 6.6, 2.6 Hz, 2H, *cis*/*trans*), 2.56 (dt, *J* = 16.2, 8.2 Hz, 1H, *trans*), 2.46–2.31 (m, 2H, *cis*), 2.30–2.14 (m, 2H, *trans*), 2.03 (s, 3H, *cis*/*trans*), 2.00-1.67 (m, 5H *cis* + 2H *trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 171.2 (*cis/trans*), 144.2 (*trans*), 142.4 (*cis*), 111.8 (*trans*), 111.5 (*cis*), 77.2 (*trans*), 74.2 (*trans*), 71.6 (*cis*), 63.1 (*cis*), 42.0 (*cis/trans*), 40.8 (*trans*), 35.7 (*cis*), 35.2 (*trans*), 25.2 (*trans*), 22.5 (*cis*), 21.0 (*cis*). **HRMS** (APCI) calcd. for $[C_{10}H_{17}O_3]^+$ $(M+H)^+$: m/z = 185.1172, found 185.1170.

3-(2-(Trimethylsilyl)ethyl)-1-vinylcyclobutan-1-ol (174f)

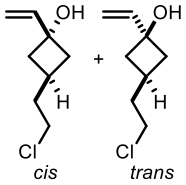


According to **General Procedure F**: 3-(2-(trimethylsilyl)ethyl)cyclobutan-1-one (1.6 g, 9.5 mmol, 1.0 equiv) was diluted in dry THF (47 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (14 mL, 14 mmol, 1.5 equiv) for 2 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (2x 100 mL), extracted with Et_2O (2x 50 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE to PE/Et_2O 30:1 to 4:1) 1.4 g (6.9 mmol, 74%) of 3-(2-(trimethylsilyl)ethyl)-1-vinylcyclobutan-1-ol were obtained as a yellowish oil (35:10 *cis*/*trans*).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.2 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3336, 2955, 2914, 1248, 861. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 6.13 (dd, *J* = 17.3, 10.7 Hz, 1H, *cis*), 6.07–5.95 (m, 1H, *trans*), 5.38–4.95 (m, 2H, *cis/trans*), 2.44–2.25 (m, 2H, *cis*), 2.24–2.09 (m, 2H, *trans*), 1.90–1.74 (m, 2H, *trans*), 1.79–1.65 (m, 4H *cis* + 1H *trans*), 1.49–1.29 (m, 1H *cis* + 1H *trans*), 0.46–0.32 (m, 2H, *cis*), - 0.03 (s, 9H, *cis/trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 146.4 (*trans*), 144.7 (*cis*), 113.1 (*trans*), 112.7 (*cis*), 75.6 (*trans*), 72.9 (*cis*), 43.6 (*cis*), 42.4 (*trans*), 33.1 (*trans*), 32.6 (*cis*), 32.6 (*trans*), 29.8 (*cis*), 15.6 (*cis*), 0.0 (*cis/trans*). **HRMS** (EI) calcd. for $[C_{10}H_{19}OSi]^{+\cdot}$ $(M\text{-}CH_3)^{+\cdot}$: m/z = 183.1200, found 183.1201.

3-(2-Chloroethyl)-1-vinylcyclobutan-1-ol (174g)

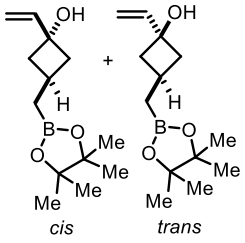


According to **General Procedure F**: 3-(2-chloroethyl)cyclobutan-1-one (0.94 g, 7.1 mmol, 1.0 equiv) was diluted in dry THF (35 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (9.2 mL, 9.2 mmol, 1.3 equiv) for 4 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 25 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE to PE/Et_2O 10:1 to 3:1) 0.36 g (2.2 mmol, 31%) of 3-(2-chloroethyl)-1-vinylcyclobutan-1-ol were obtained as a yellowish oil (16:1 *trans*/*cis*).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.6 (PE/Et_2O 1:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3339, 2967, 2929, 1293, 1244, 1162, 1036, 991, 920, 719. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 6.12 (dd, *J* = 17.3, 10.7 Hz, 1H, *trans*), 6.02 (dd, *J* = 17.3, 10.6 Hz, 1H, *cis*), 5.35–4.97 (m, 2H, *trans*/*cis*), 3.47 (t, *J* = 6.6 Hz, 2H, *trans*/*cis*), 2.47–2.35 (m, 2H, *trans*/*cis*), 2.11–1.94 (m, 1H, *trans*/*cis*), 1.98–1.88 (m, 2H, *trans*/*cis*), 1.83 (ddt, *J* = 11.6, 9.1, 2.4 Hz, 2H, *trans*/*cis*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.1 (*cis*), 142.3 (*trans*), 112.0 (*cis*), 111.6 (*trans*), 77.2 (*cis*), 71.6 (*trans*), 43.1 (*trans*), 41.7 (*trans*), 40.6 (*cis*), 39.6 (*trans*), 39.3 (*cis*), 39.2 (*cis*), 25.9 (*cis*), 23.0 (*trans*). **HRMS** (EI) calcd. for $[C_8H_{12}ClO]^{+\cdot}$ $(M\text{-}H)^{+\cdot}$: m/z = 159.0571, found 159.0576.

3-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-vinylcyclobutan-1-ol (174h)

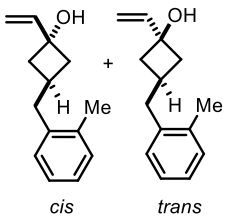


According to **General Procedure F**: 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutan-1-one (1.1 g, 5.0 mmol, 1.0 equiv) was diluted in dry THF (25 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (5.6 mL, 5.6 mmol, 1.1 equiv) for 4 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 20 mL), extracted with Et_2O (1x 20 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE to PE/Et_2O 10:1 to 3:1) 0.30 g (1.3 mmol, 25%) of 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-vinylcyclobutan-1-ol were obtained as a colorless oil (40:10 *trans*/*cis*).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.38 (PE/Et_2O 1:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3429, 2978, 2929, 1371, 1315, 1237, 1144, 916, 849. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 6.12 (dd, *J* = 17.2, 10.6 Hz, 1H, *trans*), 6.08–5.93 (m, 1H, *cis*), 5.25 (dd, *J* = 17.3, 1.3 Hz, 1H, *trans*), 5.16 (dd, *J* = 17.3, 1.3 Hz, 1H, *cis*), 5.05 (dd, *J* = 10.7, 1.2 Hz, 1H, *trans*), 5.00 (dd, *J* = 10.6, 1.2 Hz, 1H, *cis*), 2.69 (hept, *J* = 8.2 Hz, 1H, *cis*), 2.43 (ddt, *J* = 9.7, 4.8, 2.5 Hz, 2H, *trans*), 2.31–2.18 (m, 2H, *cis*), 2.02 (dq, *J* = 16.2, 8.2 Hz, 1H, *trans*), 1.95–1.84 (m, 2H, *cis*), 1.81 (td, *J* = 9.3, 2.8 Hz, 2H, *trans*), 1.23 (s, 12H, *trans*/*cis*), 1.01 (d, *J* = 7.4 Hz, 2H, *trans*), 0.96 (d, *J* = 7.9 Hz, 2H, *cis*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.6 (*trans*), 142.8 (*trans*/*cis*), 140.2 (*cis*), 113.4 (*trans*), 111.3 (*trans*/*cis*), 110.9 (*cis*), 83.0 (*trans*), 77.2 (*cis*), 74.1 (*cis*), 71.3 (*trans*), 44.5 (*trans*/*cis*), 43.3 (*trans*), 42.4 (*cis*), 27.5 (*cis*), 24.8 (*trans*), 24.5 (*cis*), 21.1 (*trans*). **^{11}B NMR** (128 MHz, Chloroform-*d*): δ [ppm] = 33.2. **HRMS** (EI) calcd. for $[C_{13}H_{23}BO_3]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 238.1740, found 238.1751.

3-(2-Methylbenzyl)-1-vinylcyclobutan-1-ol (174i)



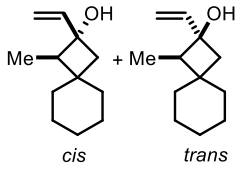
According to **General Procedure F**: 3-(2-methylbenzyl)cyclobutan-1-one (0.37 g, 2.1 mmol, 1.0 equiv) was diluted in dry THF (11 mL, 0.3 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (2.8 mL, 2.8 mmol, 1.3 equiv) for 2 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 20 mL), extracted with Et_2O (1x 20 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE to PE/Et_2O 10:1) 0.24 g (1.2 mmol, 56%) of 3-(2-methylbenzyl)-1-vinylcyclobutan-1-ol were obtained as a yellowish oil (38:10 *trans*/*cis*).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.42 (PE/Et_2O 3:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3339, 2967, 2929, 2858, 1490, 1457, 1423, 1379, 1244, 1162, 1129, 991, 916, 738. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 6.12 (dd, *J* = 17.2, 10.6 Hz, 1H, *trans*), 6.07 (dd, *J* = 17.3, 10.6 Hz, 1H, *cis*), 5.26 (dd, *J* = 17.3, 1.1 Hz, 1H, *trans*), 5.21 (dd, *J* = 17.3, 1.2 Hz, 1H, *cis*), 5.08 (dd, *J* = 10.7, 1.1 Hz, 1H, *trans*), 5.06 (dd, *J* = 10.6, 1.2 Hz, 1H, *cis*), 2.84 (qd, *J* = 8.1, 7.0 Hz, 1H, *cis*), 2.78 (d, *J* = 7.2 Hz, 2H, *trans*), 2.72 (d, *J* = 7.7 Hz, 2H, *cis*),

2.44–2.33 (m, 2H, *trans*), 2.30 (s, 3H, *trans/cis*), 2.28–2.18 (m, 2H, *cis*), 2.21–2.06 (m, 1H, *trans*), 2.08–1.96 (m, 2H, *cis*), 1.94 (ddt, *J* = 11.8, 9.4, 2.4 Hz, 2H, *trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.4 (*cis*), 142.5 (*trans*), 138.8 (*trans*), 136.0 (*cis*), 135.9 (*trans*), 130.2 (*trans*), 130.1 (*cis*), 128.7 (*trans*), 128.6 (*cis*), 126.0 (*trans*), 126.0 (*cis*), 125.8 (*cis*), 125.8 (*trans*), 111.8 (*cis*), 111.5 (*trans*), 110.0 (*cis*), 74.0 (*cis*), 71.5 (*trans*), 42.1 (*trans*), 40.9 (*cis*), 40.0 (*trans*), 39.6 (*cis*), 27.7 (*cis*), 25.2 (*trans*), 19.5 (*trans*), 19.5 (*cis*). **HRMS** (EI) calcd. for $[C_{14}H_{18}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 202.1358, found 202.1359.

1-Methyl-2-vinylspiro[3.5]nonan-2-ol (174j)

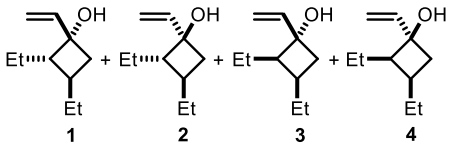


According to **General Procedure F**: 1-methylspiro[3.5]nonan-2-one (1.0 g, 6.7 mmol, 1.0 equiv) was diluted in dry THF (22 mL, 0.3 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (10 mL, 10 mmol, 1.5 equiv) for 21 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 30 mL), extracted with Et_2O (2x 30 mL) and dried with $MgSO_4$. After concentration 0.93 g (5.1 mmol, 77%) of 1-methyl-2-vinylspiro[3.5]nonan-2-ol were obtained as a yellowish oil (10:1 *trans*/*cis*).

*analysis of configuration was done by 2D NMR experiments.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3421, 2992, 2851, 1446, 1233, 1170, 991, 916. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.98 (dd, *J* = 17.3, 10.6 Hz, 1H, *trans*), 5.82 (dd, *J* = 17.3, 10.7 Hz, 1H, *cis*), 5.28–4.92 (m, 2H, *trans*/*cis*), 2.05 (q, *J* = 7.3 Hz, 1H, *trans*/*cis*), 1.98–1.75 (m, 3H, *trans*/*cis*), 1.64–1.42 (m, 4H, *trans*/*cis*), 1.45–1.28 (m, 3H, *trans*/*cis*), 1.32–1.07 (m, 1H, *trans*/*cis*), 0.93 (d, *J* = 7.4 Hz, 3H, *trans*/*cis*). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 145.5 (*trans*), 110.7 (*trans*), 73.7 (*trans*), 47.8 (*trans*), 44.4 (*trans*), 40.2 (*trans*), 36.4 (*trans*), 32.7 (*trans*), 26.2 (*trans*), 23.4 (*trans*), 22.4 (*trans*), 7.3 (*trans*). **HRMS** (EI) calcd. for $[C_{12}H_{20}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 180.1514, found 180.1510.

2,3-Diethyl-1-vinylcyclobutan-1-ol (174k)



According to **General Procedure F**: 2,3-diethylcyclobutan-1-one (1.1 g, 9.0 mmol, 1.0 equiv) was diluted in dry THF (45 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (13 mL, 13 mmol, 1.5 equiv) for 2 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 50 mL), extracted with Et_2O (1x 50 mL) and dried with $MgSO_4$. After concentration 0.55 g (3.6 mmol, 40%) of 2,3-diethyl-1-vinylcyclobutan-1-ol were obtained as a colorless oil (103:29:16:10 1/4/2/3).

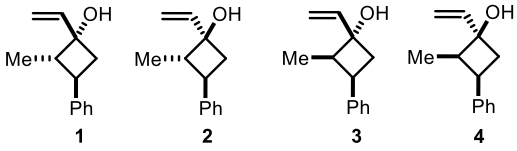
*analysis of configuration was done by 2D NMR experiments. The major isomer 1 was declared by the absence of the respective NOESY coupling. Furthermore, we anticipated that the Grignard reagent would end up preferably on the other side compared to the adjacent ethyl group to avoid steric tension. Based on this dominant stereoselectivity of the Grignard

reaction, 4 was chosen as the second major isomer. The third most isomers is then anticipated to be number 2 as the *trans* relation between the two ethyl groups was the dominant configuration in the starting material.

*In the ^{13}C NMR spectra the third signal set is hypothesized to be the 2, isomer 3 is not observed.

IR (ATR): ṽ [cm^{-1}] = 3451, 2959, 2929, 2877, 1461, 991, 916, 734. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 6.05 (dd, *J* = 17.3, 10.6 Hz, 1H, all isomers), 5.36–4.90 (m, 2H, all isomers), 2.35–1.21 (m, 8H, all isomers), 0.96–0.75 (m, 6H, all isomers). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 145.3 (**1**), 144.8 (**4**), 140.2 (**2**), 112.3 (**2**), 110.9 (**1**), 110.3 (**4**), 77.2 (**4**), 75.0 (**1**), 74.5 (**2**), 56.6 (**2**), 52.3 (**1**), 48.8 (**4**), 40.0 (**2**), 39.2 (**4**), 38.8 (**1**), 37.9 (**1**), 34.2 (**2**), 32.1 (**4**), 29.5 (**2**), 29.2 (**1**), 23.6 (**4**), 23.6 (**2**), 22.0 (**1**), 17.4 (**4**), 13.4 (**4**), 12.3 (**1**), 12.1 (**2**), 11.9 (**4**), 11.7 (**1**). **HRMS** (EI) calcd. for $[C_{10}H_{18}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 154.1358, found 154.1350.

2-Methyl-3-phenyl-1-vinylcyclobutan-1-ol (174l)



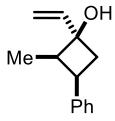
According to **General Procedure F**: 2-methyl-3-phenylcyclobutan-1-one (0.45 g, 2.8 mmol, 1.0 equiv) was diluted in dry THF (12 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (4.5 mL, 4.5 mmol, 1.6 equiv) for 3 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 15 mL), extracted with Et_2O (1x 15 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE to PE/Et_2O 50:1 to 1:1) 0.28 g (4.5 mmol, 53%) of 2-methyl-3-phenyl-1-vinylcyclobutan-1-ol were obtained as a colorless oil (356:95:45:10 1/4/2/3).

* analysis of configuration was done by 2D NMR experiments. The major isomer 1 was declared by the absence of the respective NOESY coupling. Furthermore, we anticipated that the Grignard reagent would end up preferably on the other side compared to the adjacent methyl group to avoid steric tension. Based on this dominant stereoselectivity of the Grignard reaction, 4 was chosen as the second major isomer. The third most isomers is then anticipated to be number 2 as the *trans* relation between the methyl and the phenyl group was the dominant configuration in the starting material.

*In the ^{13}C NMR spectra the third signal set is hypothesized to be the 2, isomer 3 is not entirely observed.

TLC: R_f = 0.32 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3421, 2970, 2926, 1498, 1453, 946, 920, 749, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.36–7.27 (m, 2H, all isomers), 7.26–7.13 (m, 3H, all isomers), 6.30 (dd, *J* = 17.3, 10.7 Hz, 1H, **4**), 6.14 (dd, *J* = 17.3, 10.8 Hz, 1H, **2**), 6.02 (ddd, *J* = 17.3, 10.7, 0.9 Hz, 1H, **1**+**3**), 5.45–5.04 (m, 2H, all isomers), 3.40 (q, *J* = 8.8 Hz, 1H, all but **1**), 3.32 (q, *J* = 9.4 Hz, 1H, **1**), 2.79 (pd, *J* = 7.6, 3.4 Hz, 1H, all but **1**), 2.70–2.45 (m, 2H, all but **1**), 2.49–2.32 (m, 2H, **1**), 2.31-2.18 (m, 1H, **1**), 1.11 (dd, *J* = 6.8, 1.0 Hz, 3H, **1**+**3**), 1.03 (dd, *J* = 6.7, 0.9 Hz, 3H, **2**), 0.79 (dd, *J* = 7.4, 1.0 Hz, 3H, **4**). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.2 (**2**), 143.5 (**1**), 143.2 (**4**), 140.2 (**3**), 139.4 (**3**), 128.4 (**4**), 128.4 (**1**), 128.0 (**2**), 128.0 (**2**), 126.8 (**4**), 126.5 (**1**), 126.2 (**4**), 126.1 (**1**), 125.9 (**2**), 113.4 (**4**), 112.2 (**1**), 111.5 (**2**), 77.2 (**2**), 75.3 (**1**), 72.2 (**4**), 51.4 (**4**), 47.2 (**1**), 44.3 (**2**), 42.4 (**1**), 41.2 (**4**), 40.1 (**1**), 38.7 (**4**), 36.9 (**2**), 34.0 (**2**), 14.2 (**4**), 12.2 (**1**), 10.0 (**2**). **HRMS** (EI) calcd. for $[C_{13}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 188.1201, found 188.1199.

(*cis*)-2-Methyl-3-phenyl-1-vinylcyclobutan-1-ol (174l-*cis*)

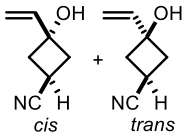


According to **General Procedure F**: (*cis*)-2-methyl-3-phenylcyclobutan-1-one (0.35 g, 2.2 mmol, 1.0 equiv) was diluted in dry THF (8.0 mL, 0.3 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (2.8 mL, 2.8 mmol, 1.3 equiv) for 3 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 20 mL), extracted with Et_2O (1x 20 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE/Et_2O 50:1 to 10:1) 0.31 g (1.7 mmol, 77%) of (*cis*)-2-methyl-3-phenylcyclobutan-1-one were obtained as a colorless oil.

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.38 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3365, 2967, 2929, 1640, 1602, 1494, 1453, 1252, 1222, 1144, 1069, 995, 916, 752, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.25 (m, 2H), 7.26–7.11 (m, 3H), 6.30 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.39 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.17 (dd, *J* = 10.7, 1.1 Hz, 1H), 3.40 (dt, *J* = 10.3, 8.4 Hz, 1H), 2.79 (dqd, *J* = 8.6, 7.5, 3.3 Hz, 1H), 2.67–2.42 (m, 2H), 0.78 (d, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 143.2, 140.2, 128.0, 128.0, 125.9, 111.4, 72.1, 44.3, 36.9, 33.9, 10.0. **HRMS** (EI) calcd. for $[C_{13}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 188.1201, found 188.1191.

3-Hydroxy-3-vinylcyclobutane-1-carbonitrile (174m)



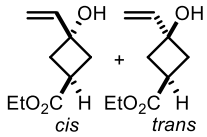
According to **General Procedure F**: 3-oxocyclobutane-1-carbonitrile (1.0 g, 11 mmol, 1.0 equiv) was diluted in dry THF (50 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (11 mL, 11 mmol, 1.0 equiv) for 19 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (2x 100 mL), extracted with Et_2O (1x 50 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE/EtOAc 30:1 to 1:1) 0.52 g (4.2 mmol, 40%) of 3-hydroxy-3-vinylcyclobutane-1-carbonitrile were obtained as a colorless oil (13:1 *trans*/*cis*).

*analysis of configuration was done by 2D NMR experiments.

*analytical data are in accordance with cited literature.[286]

TLC: R_f = 0.36 (PE/Et_2O 1:1). **IR** (ATR): ṽ [cm^{-1}] = 3406, 2996, 2952, 2240, 1643, 1423, 1241, 1118, 995, 924. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 6.18–5.94 (m, 1H, *trans/cis*), 5.37–5.15 (m, 2H, *trans/cis*), 3.27 (tt, *J* = 9.1, 7.4 Hz, 1H, *cis*), 2.75–2.47 (m, 5H *trans* + 4H *cis*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 141.5 (*cis*), 139.6 (*trans*), 122.4 (*cis*), 121.8 (*trans*), 113.9 (*cis*), 113.8 (*trans*), 74.3 (*cis*), 72.0 (*trans*), 40.4 (*trans*), 39.7 (*cis*), 15.5 (*cis*), 13.2 (*trans*). **HRMS** (APCI) calcd. for $[C_7H_8NO]^{+\cdot}$ $(M\text{-}H)^{+\cdot}$: m/z = 122.0600, found 122.0598.

Ethyl 3-hydroxy-3-vinylcyclobutane-1-carboxylate (174n)

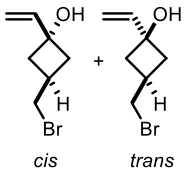


According to **General Procedure F**: ethyl 3-oxocyclobutane-1-carboxylate (1.1 g, 7.8 mmol, 1.0 equiv) was diluted in dry THF (40 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (8.5 mL, 8.5 mmol, 1.1 equiv) for 17 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (3x 100 mL), extracted with Et_2O (1x 50 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE/EtOAc 30:1 to 1:1) 0.41 g (2.4 mmol, 31%) of ethyl 3-hydroxy-3-vinylcyclobutane-1-carboxylate were obtained as a colorless oil (66:10 *trans*/*cis*).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.52 (PE/Et_2O 1:1). **IR** (ATR): ṽ [cm^{-1}] = 3410, 2985, 2944, 1714, 1375, 1349, 1237, 1189, 1110, 1036, 991, 920, 910. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 6.17–5.98 (m, 1H, *trans/cis*), 5.44–5.01 (m, 2H, *trans/cis*), 4.15 (q, *J* = 7.1 Hz, 2H, *trans/cis*), 3.28 (tt, *J* = 9.3, 7.7 Hz, 1H, *cis*), 2.72 (ddd, *J* = 16.7, 8.8, 7.7 Hz, 1H, *trans*), 2.51 (ddt, *J* = 12.0, 6.8, 2.4 Hz, 2H, *trans/cis*), 2.38 (dddd, *J* = 21.9, 9.0, 4.0, 2.2 Hz, 2H, *trans/cis*), 1.26 (td, *J* = 7.1, 2.8 Hz, 3H, *trans/cis*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 175.5 (*trans*), 175.3 (*cis*), 142.8 (*cis*), 141.3 (*trans*), 112.5 (*trans*), 112.4 (*cis*), 73.8 (*cis*), 71.5 (*trans*), 60.8 (*trans*), 60.6 (*cis*), 39.5 (*trans*), 38.4 (*cis*), 31.1 (*cis*), 29.1 (*trans*), 14.2 (*cis*), 14.2 (*trans*). **HRMS** (EI) calcd. for $[C_7H_9O_3]^{+\cdot}$ $(M-(CH_2-CH_3))^{+\cdot}$: m/z = 141.0546, found 141.0544.

3-(Bromomethyl)-1-vinylcyclobutan-1-ol (174o)

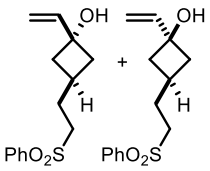


According to **General Procedure F**: 3-(bromomethyl)cyclobutan-1-one (0.97 g, 5.9 mmol, 1.0 equiv) was diluted in dry THF (20 mL, 0.3 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (6.5 mL, 6.5 mmol, 1.1 equiv) for 2 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 20 mL) and dried with $MgSO_4$. After concentration and purification by automated column chromatography (*n*-hexane to *n*-hexane/Et_2O 95:5 to 80:20) 0.32 g (1.7 mmol, 29%) of 3-(bromomethyl)-1-vinylcyclobutan-1-ol were obtained as a colorless oil (59:10 *cis*/*trans*).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.21 (*n*-hexane/Et_2O 3:1). **IR** (ATR): ṽ [cm^{-1}] = 3336, 2978, 2933, 1640, 1423, 1244, 1162, 1048, 991, 920. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 6.09 (dd, *J* = 17.3, 10.6 Hz, 1H, *cis*), 6.03 (dd, *J* = 17.3, 10.6 Hz, 1H, *trans*), 5.35–4.99 (m, 2H, *cis*), 5.26–5.03 (m, 2H, *trans*), 3.48 (d, *J* = 7.2 Hz, 2H, *cis*), 3.45 (d, *J* = 7.4 Hz, 2H, *trans*), 2.97–2.80 (m, 1H, *trans*), 2.48–2.36 (m, 2H, *cis*), 2.37–2.19 (m, 1H *cis* + 2H *trans*), 2.10–1.99 (m, 2H, *trans*), 1.98–1.85 (m, 2H, *cis*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 143.5 (*trans*), 142.0 (*cis*), 112.5 (*trans*), 112.1 (*cis*), 72.7 (*trans*), 70.3 (*cis*), 41.1 (*cis*), 39.9 (*trans*), 38.9 (*cis*), 38.8 (*trans*), 30.2 (*trans*), 27.8 (*cis*). **HRMS** (EI) calcd. for $[C_7H_{10}BrO]^{+\cdot}$ $(M-H)^{+\cdot}$: m/z = 188.9910, found 188.9910.

3-(2-(Phenylsulfonyl)ethyl)-1-vinylcyclobutan-1-ol (174p)

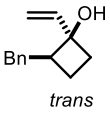


According to **General Procedure F**: 3-(2-(phenylsulfonyl)ethyl)cyclobutan-1-one (0.78 g, 3.3 mmol, 1.0 equiv) was diluted in dry THF (10 mL, 0.3 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (4.4 mL, 4.4 mmol, 1.4 equiv) for 2 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 20 mL) and dried with $MgSO_4$. After concentration and purification by automated column chromatography (*n*-hexane/Et_2O 90:10 to 25:75) 0.41 g (1.6 mmol, 47%) of 3-(2-(phenylsulfonyl)ethyl)-1-vinylcyclobutan-1-ol were obtained as a colorless oil (39:10 *cis*/*trans*).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.34 (PE/Et_2O 1:3). **IR** (ATR): ṽ [cm^{-1}] = 3483, 2967, 2929, 1446, 1304, 1144, 1088, 998, 924, 738, 689. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.94–7.87 (m, 2H, *cis*/*trans*), 7.71–7.62 (m, 1H, *cis*/*trans*), 7.62–7.53 (m, 2H, *cis*/*trans*), 6.05 (dd, *J* = 17.3, 10.6 Hz, 1H, *cis*), 5.96 (dd, *J* = 17.3, 10.6 Hz, 1H, *trans*), 5.30–4.96 (m, 2H, *cis*/*trans*), 3.07–2.89 (m, 2H, *cis*/*trans*), 2.47 (dt, *J* = 16.1, 8.1 Hz, 1H, *trans*), 2.41–2.26 (m, 2H, *cis*/*trans*), 2.23–2.12 (m, 2H, *trans*), 1.97–1.66 (m, 5H, *cis* + 2H, *trans*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 143.7 (*trans*), 142.1 (*cis*), 139.1 (*trans*), 133.7 (*cis*), 129.3 (*cis*/*trans*), 128.0 (*cis*/*trans*), 112.2 (*trans*), 111.9 (*cis*), 71.1 (*cis*), 68.2 (*trans*), 54.5 (*trans*), 54.3 (*cis*), 41.4 (*cis*), 40.4 (*trans*), 29.6 (*cis*), 29.1 (*trans*), 26.8 (*trans*), 24.0 (*cis*). **HRMS** (ESI) calcd. for $[C_{14}H_{22}NO_3S]^+$ $(M+NH_4)^+$: m/z = 284.1315, found 284.1316.

trans-2-Benzyl-1-vinylcyclobutan-1-ol (174q)



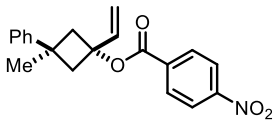
According to **General Procedure F**: 2-benzylcyclobutan-1-one (0.63 g, 4.0 mmol, 1.0 equiv) was diluted in dry THF (20 mL, 0.2 M) and reacted with vinylmagnesium bromide (1.0 M in THF) (4.4 mL, 4.4 mmol, 1.1 equiv) for 2 h. The reaction was quenched with sat. NH_4Cl and water, the organic phase was washed with water (1x 20 mL) and dried with $MgSO_4$. After concentration and purification by column chromatography (PE to PE/Et_2O 30:1 to 10:1) 0.41 g (2.2 mmol, 56%) of *trans*-2-benzyl-1-vinylcyclobutan-1-ol were obtained as a colorless oil.

*configuration in accordance with known literature.[248]

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.32 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3559, 3421, 3063, 3026, 2981, 2940, 2858, 1453, 991, 916, 730, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.33–7.20 (m, 2H), 7.24–7.12 (m, 3H), 6.03 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.24–4.95 (m, 2H), 2.93 (dd, *J* = 13.7, 6.4 Hz, 1H), 2.75 (dd, *J* = 13.7, 9.2 Hz, 1H), 2.71–2.49 (m, 1H), 2.25–1.98 (m, 2H), 1.95–1.71 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 143.7, 140.6, 128.8, 128.3, 125.8, 111.2, 45.8, 35.4, 32.7, 21.0. **HRMS** (EI) calcd. for $[C_{13}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 188.1201, found 188.1190.

(*cis*)-3-Methyl-3-phenyl-1-vinylcyclobutyl 4-nitrobenzoate (176-*cis*)



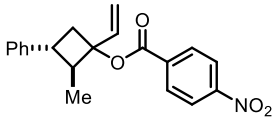
A round flask was equipped with 3-methyl-3-phenyl-1-vinylcyclobutan-1-ol (0.22 g, 1.2 mmol, 1.0 equiv) and diluted with DCM (30 mL, 0.04 M). The solution was cooled to 0 °C and 4-DMAP (29 mg, 0.24 mmol, 20 mol%) and NEt_3 (0.5 mL, 3.6 mmol, 3.0 equiv) were added and the solution stirred for 5 min at 0 °C. 4-Nitrobenzoyl chloride (0.49 g, 2.7 mmol, 2.2 equiv) was added, the solution allowed to warm up to r.t. and stirred for a total time of 24 h before being quenched by the addition of water. The organic phase was extracted with DCM (1x 25 mL) washed with water (1x 25 mL) and dried over $MgSO_4$. The crude material was purified by precipitation from *n*-hexane and small amounts of DCM in the freezer. Filtration resulted in 0.19 g (0.57 mmol, 48%) of (1r,3r)-3-methyl-3-phenyl-1-vinylcyclobutyl 4-nitrobenzoate as a beige precipitate.

*The product was synthesized using the following procedure.[232]

*analysis of configuration was done by 2D NMR experiments.

MP = 113.8°C. **IR** (ATR): ṽ [cm^{-1}] = 3123, 2952, 1722, 1606, 1520, 1349, 1304, 1166, 1103. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 8.35–8.29 (m, 2H), 8.28–8.23 (m, 2H), 7.38–7.32 (m, 2H), 7.29-7.16 (m, 3H), 6.05 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.12–5.00 (m, 2H), 3.14–3.00 (m, 2H), 2.85–2.73 (m, 2H), 1.53 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 163.3, 150.6, 149.6, 138.9, 136.3, 130.7, 128.4, 125.7, 125.3, 123.6, 114.5, 79.6, 46.1, 36.7, 33.7. **HRMS** (ESI) calcd. for $[C_{20}H_{19}NNaO_4]^+$ $(M+Na)^+$: m/z = 360.1206, found 360.1206.

(*trans*)-2-methyl-3-phenyl-1-vinylcyclobutyl 4-nitrobenzoate



A round flask was equipped with 2-methyl-3-phenyl-1-vinylcyclobutan-1-ol (0.74 g, 5.8 mmol, 1.0 equiv) and diluted with DCM (100 mL, 0.04 M). The solution was cooled to 0 °C and 4-DMAP (0.15 g, 1.2 mmol, 20 mol%) and NEt_3 (2.5 mL, 18 mmol, 3.1 equiv) were added and the solution stirred for 5 min at 0 °C. 4-Nitrobenzoyl chloride (2.2 g, 12 mmol, 2.0 equiv) was added, the solution allowed to warm up to r.t. and stirred for a total time of 21 h before being quenched by the addition of water. The organic phase was extracted with DCM (1x 50 mL) washed with water (2x 100 mL) and dried over $MgSO_4$. The crude material was purified by column chromatography (PE to PE/Et_2O 30:1 to 3:1) and subsequently precipitated from *n*-hexane and small amounts of DCM in the freezer. Filtration resulted in 0.26 g (0.77 mmol, 13%) of (*trans*)-2-methyl-3-phenyl-1-vinylcyclobutyl 4-nitrobenzoate as a white precipitate.

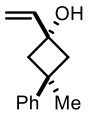
*The product was synthesized using the following procedure.[232]

*analysis of configuration was done by 2D NMR experiments.

MP = 117.8°C. **TLC:** R_f = 0.76 (PE/Et_2O 3:1). **IR** (ATR): ṽ [cm^{-1}] = 3116, 3086, 3026, 2974, 2929, 2870, 1722, 1606, 1524, 1349, 1289, 1103, 838, 715. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 8.38–8.22 (m, 4H), 7.40–7.29 (m, 2H), 7.29–7.19 (m, 3H), 6.24 (dd, *J* = 17.5, 10.9 Hz, 1H), 5.32–5.15 (m, 2H), 3.29 (q, *J* = 9.4 Hz, 1H), 3.00 (ddd, *J* = 13.2, 8.6, 0.8 Hz, 1H), 2.70 (dq,

J = 9.6, 6.9 Hz, 1H), 2.64–2.55 (m, 1H), 1.38 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 163.5, 150.6, 143.1, 138.7, 136.5, 130.6, 128.5, 126.5, 123.6, 114.7, 84.5, 77.2, 48.7, 42.2, 37.2, 13.3. **HRMS** (ESI) calcd. for $[C_{20}H_{19}NNaO_4]^+$ $(M+Na)^+$: m/z = 360.1206, found 360.1206.

(*cis*)-3-Methyl-3-phenyl-1-vinylcyclobutan-1-ol (174a-*cis*)



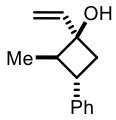
A round flask was equipped with (*cis*)-3-methyl-3-phenyl-1-vinylcyclobutyl 4-nitrobenzoate (65 mg, 0.19 mmol, 1.0 equiv) and diluted with MeOH (6.5 mL, 0.03 M). To the solution was added $LiOHxH_2O$ (9.7 mg, 0.23 mmol, 1.2 equiv) and the mixture was stirred at r.t. for 19 h. The reaction was quenched by the addition of water and the organic phase was extracted with EtOAc (1x 10 mL), washed with brine (1x 20 mL) and brine (1x 40 mL) and dried over $MgSO_4$. After purification by column chromatography (PE/EtOAc 50:1), 24 mg (0.13 mmol, 65%) of (*cis*)-3-methyl-3-phenyl-1-vinylcyclobutan-1-ol were obtained as a colorless oil.

*The product was synthesized using the following procedure.[233]

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.08 (PE/EtOAc 50:1). **IR** (ATR): ṽ [cm^{-1}] = 3362, 3026, 2955, 2929, 2862, 1494, 1446, 1267, 1177, 1058, 1028, 995, 954, 916, 760, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.37–7.28 (m, 2H), 7.25–7.14 (m, 3H), 5.91 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.12 (dd, *J* = 17.3, 1.2 Hz, 1H), 4.93 (dd, *J* = 10.6, 1.2 Hz, 1H), 2.79–2.68 (m, 2H), 2.43–2.32 (m, 2H), 1.60 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 151.0, 144.3, 128.3, 125.4, 125.4, 111.1, 71.3, 47.8, 35.6, 33.5. **HRMS** (EI) calcd. for $[C_{13}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 188.1201, found 188.1198.

(*trans*)-2-methyl-3-phenyl-1-vinylcyclobutan-1-ol (174l-*trans*)



A round flask was equipped with (*trans*)-2-methyl-3-phenyl-1-vinylcyclobutyl 4-nitrobenzoate (0.27 g, 0.81 mmol, 1.0 equiv) and diluted with MeOH (25 mL, 0.03 M). To the solution was added $LiOHxH_2O$ (43 mg, 1.0 mmol, 1.3 equiv) and the mixture was stirred at r.t. for 66 h. The reaction was quenched by the addition of water and the organic phase was extracted with Et_2O (1x 40 mL), washed with water (1x 40 mL) and brine (1x 40 mL) and dried over $MgSO_4$. After purification by column chromatography (PE to PE/Et_2O 10:1), 0.13 g (0.67 mmol, 83%) of (*trans*)-2-methyl-3-phenyl-1-vinylcyclobutan-1-ol were obtained as a colorless oil.

*The product was synthesized using the following procedure.[233]

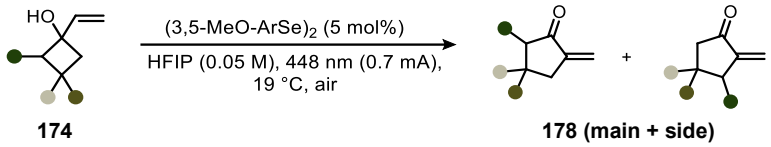
*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.38 (PE/Et_2O 3:1). **IR** (ATR): ṽ [cm^{-1}] = 3429, 3026, 2974, 2926, 1736, 1602, 1498, 1453, 1416, 1371, 1215, 991, 946, 920, 749, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.32 (t, *J* = 7.5 Hz, 2H), 7.21 (dd, *J* = 12.0, 7.3 Hz, 3H), 6.02 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.24 (dt, *J* = 17.3, 1.0 Hz, 1H), 5.09 (dt, *J* = 10.7, 1.0 Hz, 1H), 3.33 (q, *J* = 9.4 Hz, 1H), 2.45 (dt, *J* = 9.7, 6.9 Hz, 1H), 2.38 (dd, *J* = 12.0, 8.4 Hz, 1H), 2.26 (dd, *J* = 11.8, 10.0 Hz, 1H), 1.12 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR**

(101 MHz, Chloroform-*d*): δ [ppm] = 144.2, 143.5, 128.4, 126.5, 126.1, 112.2, 75.3, 47.2, 42.4, 40.1, 12.2. **HRMS** (EI) calcd. for $[C_{13}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 188.1201, found 188.1198.

6.3.2. Synthesis of 2-methylenecyclopentan-1-ones

General Procedure G: Selenium-π-acid catalyzed ring expansion reaction

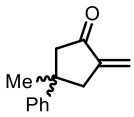


174 **178 (main + side)**

Scheme 121: Reaction equation for the selenium-π-acid catalyzed ring expansion reaction.

A photovial was equipped with the corresponding vinylic cyclobutanol (0.5 mmol, 1.0 equiv), 1,2-bis(3,5-dimethoxyphenyl)diselane (5 mol%) and both diluted with HFIP (0.05 M). The photovial was closed with a screw cap, cannulas were added to allow for air exchange and the vial was placed in the water-cooled (19 °C) irradiation setup. The mixture was irradiated (448 nm, 0.7 mA) for the given amount of time and consecutively the solvent removed under reduced pressure. 1,3-dinitrobenzene (0.50 equiv) was added (unless otherwise noted) as internal standard and the crude reaction mixture dissolved in 2.0 mL of $CDCl_3$. After determination of the NMR Yield, the NMR sample was added back with $CHCl_3$ and again concentrated. Purification by column chromatography resulted in the respective 2-methylenecyclopentan-1-ones.

4-Methyl-2-methylene-4-phenylcyclopentan-1-one (178a)

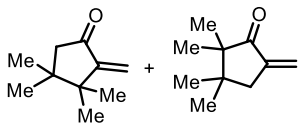


According to **General Procedure G:** 3-methyl-3-phenyl-1-vinylcyclobutan-1-ol (94 mg, 0.50 mmol, 1.0 equiv) and $(3,5\text{-MeO-ArSe})_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 11 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 97% product formation and purification by column chromatography (PE to PE/EtOAc 99:1 to 19:1) resulted in 79 mg (0.43 mmol, 85%) of 4-methyl-2-methylene-4-phenylcyclopentan-1-one as a colorless oil.

*analytical data are in accordance with cited literature.[287]

TLC: R_f = 0.34 (PE/EtOAc 19:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3086, 3060, 3030, 2959, 2907, 1729, 1643, 1408, 1267, 1144, 943, 767, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.38–7.32 (m, 2H), 7.33–7.19 (m, 3H), 6.10 (ddd, *J* = 3.1, 2.0, 1.0 Hz, 1H), 5.41 (ddd, *J* = 2.8, 1.8, 1.0 Hz, 1H), 3.07–2.91 (m, 2H), 2.76 (dd, *J* = 17.4, 0.9 Hz, 1H), 2.64 (dd, *J* = 17.4, 1.6 Hz, 1H), 1.34 (d, *J* = 0.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 205.3, 148.2, 144.2, 128.6, 126.4, 125.4, 118.3, 52.1, 43.6, 41.1, 30.0. **HRMS** (EI) calcd. for $[C_{13}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 186.1045, found 186.1044.

3,3,4,4-tetramethyl-2-methylenecyclopentan-1-one and 2,2,3,3-tetramethyl-5-methylenecyclopentan-1-one (178b)



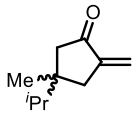
main side

According to **General Procedure G:** 2,2,3,3-tetramethyl-1-vinylcyclobutan-1-ol (92 mg, 0.50 mmol, 1.0 equiv) and (3,5-MeO-ArSe)$_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 11 h, 1,3-dinitrobenzene (43 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 91% main product and 9% side product formation and purification by column chromatography (PE to PE/EtOAc 50:1 to 9:1) resulted in 70 mg (0.46 mmol, 91%) of 3,3,4,4-tetramethyl-2-methylenecyclopentan-1-one and 2,2,3,3-tetramethyl-5-methylenecyclopentan-1-one (97:10 mixture).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.38 and 0.26 (PE/EtOAc 19:1). **IR** (ATR): ṽ [cm^{-1}] = 2967, 2873, 1725, 1640, 1464, 1394, 1293, 1215, 1166, 1080, 935. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 6.06 (t, *J* = 1.3 Hz, 1H, side), 5.98 (d, *J* = 0.8 Hz, 1H, main), 5.32 (td, *J* = 2.3, 1.3 Hz, 1H, side), 5.17 (d, *J* = 0.8 Hz, 1H, main), 2.43 (t, *J* = 2.5 Hz, 2H, side), 2.24 (s, 2H, main), 1.08 (d, *J* = 0.7 Hz, 6H, main), 0.97 (s, 6H, main), 0.95 (s, 6H, side), 0.93 (s, 6H, side). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 206.7 (main), 155.6 (main), 118.3 (side), 115.6 (main), 50.9 (main), 45.2 (main), 41.7 (side), 38.5 (main), 38.3 (side), 24.0 (side), 23.8 (main), 23.7 (main), 19.3 (side). **HRMS** (EI) calcd. for $[C_{10}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 152.1201, found 153.1192.

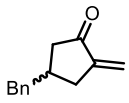
4-Isopropyl-4-methyl-2-methylenecyclopentan-1-one (178c)



According to **General Procedure G:** 3-isopropyl-3-methyl-1-vinylcyclobutan-1-ol (78 mg, 0.51 mmol, 1.0 equiv) and (3,5-MeO-ArSe)$_2$ (11 mg, 26 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 9 h, 1,3-dinitrobenzene (43 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 95% product formation and purification by column chromatography (PE to PE/EtOAc 50:1 to 9:1) resulted in 68 mg (0.50 mmol, 88%) of 4-isopropyl-4-methyl-2-methylenecyclopentan-1-one as a colorless oil.

TLC: R_f = 0.32 (PE/EtOAc 19:1). **IR** (ATR): ṽ [cm^{-1}] = 2959, 2877, 1729, 1643, 1464, 1408, 1379, 1248, 1151, 1103, 935. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.99 (td, *J* = 2.6, 1.2 Hz, 1H), 5.29 (td, *J* = 2.3, 1.2 Hz, 1H), 2.47 (t, *J* = 2.5 Hz, 2H), 2.19 (d, *J* = 1.2 Hz, 2H), 1.63 (hept, *J* = 6.8 Hz, 1H), 0.90 (dd, *J* = 6.8, 2.7 Hz, 6H), 0.86 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 206.8, 145.2, 117.5, 51.8, 42.6, 40.1, 37.8, 20.1, 18.2, 17.4. **HRMS** (EI) calcd. for $[C_{10}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 152.1201, found 152.1192.

4-Benzyl-2-methylenecyclopentan-1-one (178d)

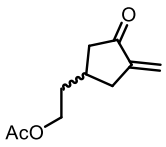


According to **General Procedure G:** 3-benzyl-1-vinylcyclobutan-1-ol (94 mg, 0.50 mmol, 1.0 equiv) and (3,5-MeO-ArSe)$_2$ (11 mg, 25 µmol, 5 mol%) were diluted

with HFIP (10 mL, 0.05 M). After a reaction time of 11 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 97% product formation and purification by column chromatography (PE to PE/toluene 30:1 to 1:1 to toluene and a second column with toluene) resulted in 73 mg (0.39 mmol, 78%) of 4-benzyl-2-methylenecyclopentan-1-one as a yellow oil.

TLC: R_f = 0.32 (toluene). **IR** (ATR): ṽ [cm^{-1}] = 3063, 3026, 2914, 2851, 1725, 1643, 1494, 1453, 1405, 1256, 1144, 1107, 939, 752, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.37–7.18 (m, 3H), 7.21-7.13 (m, 2H), 5.98 (td, *J* = 2.6, 1.1 Hz, 1H), 5.29 (td, *J* = 2.3, 1.1 Hz, 1H), 2.83–2.63 (m, 3H), 2.55-2.31 (m, 3H), 2.21–2.06 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 206.1, 144.5, 139.7, 128.9, 128.5, 126.3, 117.3, 44.8, 41.5, 36.0, 35.3. **HRMS** (EI) calcd. for $[C_{13}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 186.1045, found 186.1035.

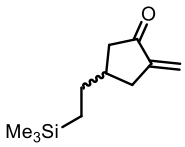
2-(3-Methylene-4-oxocyclopentyl)ethyl acetate (178e)



According to **General Procedure G:** 2-(3-hydroxy-3-vinylcyclobutyl)ethyl acetate (92 mg, 0.50 mmol, 1.0 equiv) and $(3,5\text{-MeO-ArSe})_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 11 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in quant. product formation and purification by column chromatography (PE to PE/Et_2O 10:1 to 2:1) resulted in 72 mg (0.40 mmol, 79%) of 2-(3-methylene-4-oxocyclopentyl)ethyl acetate as a yellowish oil.

TLC: R_f = 0.18 (PE/Et_2O 3:1). **IR** (ATR): ṽ [cm^{-1}] = 2955, 2907, 1736, 1643, 1237, 1043. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.98 (ddd, *J* = 3.0, 2.1, 1.1 Hz, 1H), 5.31 (ddd, *J* = 2.9, 1.8, 1.1 Hz, 1H), 4.13 (t, *J* = 6.5 Hz, 2H), 2.98–2.79 (m, 1H), 2.66–2.47 (m, 1H), 2.42–2.13 (m, 2H), 2.14–1.98 (m, 3H), 1.78 (q, *J* = 6.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 205.7, 171.0, 144.3, 117.3, 62.7, 44.9, 36.3, 34.4, 30.9, 20.9. **HRMS** (APCI) calcd. for $[C_{10}H_{18}NO_3]^+$ $(M+NH_4)^+$: m/z = 200.1281, found 200.1282.

2-Methylene-4-(2-(trimethylsilyl)ethyl)cyclopentan-1-one (178f)

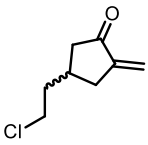


According to **General Procedure G:** 3-(2-(trimethylsilyl)ethyl)-1-vinylcyclobutan-1-ol (0.1 g, 0.50 mmol, 1.0 equiv) and $(3,5\text{-MeO-ArSe})_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 9 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 91% product formation and purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) resulted in 81 mg (0.41 mmol, 82%) of 2-methylene-4-(2-(trimethylsilyl)ethyl)cyclopentan-1-one as a colorless oil.

TLC: R_f = 0.46 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 2952, 2907, 1729, 1643, 1248, 861. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 5.95 (ddd, *J* = 3.2, 2.2, 1.2 Hz, 1H), 5.33–5.16 (m, 1H), 2.92–2.74 (m, 1H), 2.61–2.42 (m, 1H), 2.27 (ddt, *J* = 16.3, 8.2, 2.9 Hz, 1H), 2.19–1.94 (m, 2H), 1.50–

1.32 (m, 2H), 0.65–0.39 (m, 2H), - 0.02 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 208.6, 146.9, 118.6, 46.7, 38.5, 37.9, 31.8, 16.2, 0.0. **HRMS** (EI) calcd. for $[C_{10}H_{17}OSi]^{+\cdot}$ $(M\text{-}CH_3)^{+\cdot}$: m/z = 181.1043, found 181.1047.

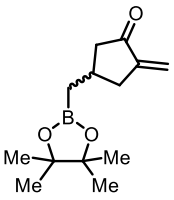
4-(2-Chloroethyl)-2-methylenecyclopentan-1-one (178g)



According to **General Procedure G:** 3-(2-chloroethyl)-1-vinylcyclobutan-1-ol (81 mg, 0.50 mmol, 1.0 equiv) and $(3,5\text{-MeO-ArSe})_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 9 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 96% product formation and purification by column chromatography (PE to PE/DCM 4:1 to 1:1) resulted in 52 mg (0.33 mmol, 66%) of 4-(2-chloroethyl)-2-methylenecyclopentan-1-one as a colorless oil.

TLC: R_f = 0.28 (PE/DCM 1:1). **IR** (ATR): ṽ [cm^{-1}] = 2955, 2926, 1736, 1453, 1401. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 6.00 (ddd, *J* = 3.2, 2.1, 1.1 Hz, 1H), 5.33 (dq, *J* = 2.9, 1.1 Hz, 1H), 3.59 (td, *J* = 6.7, 1.4 Hz, 2H), 2.99–2.83 (m, 1H), 2.64–2.53 (m, 1H), 2.53–2.38 (m, 1H), 2.38–2.25 (m, 1H), 2.05 (dd, *J* = 17.5, 8.9 Hz, 1H), 1.92 (q, *J* = 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 205.4, 144.1, 117.6, 44.4, 42.8, 38.2, 35.9, 31.2. **HRMS** (EI) calcd. for $[C_8H_{11}ClO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 158.0498, found 158.0483.

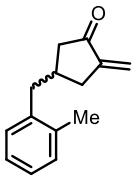
2-Methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclopentan-1-one (178h)



According to **General Procedure G:** 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-vinylcyclobutan-1-ol (0.12 g, 0.50 mmol, 1.0 equiv) and $(3,5\text{-MeO-ArSe})_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 11 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 96% product formation and purification by column chromatography (toluene to toluene/Et_2O 50:1 to 10:1) resulted in 67 mg (0.28 mmol, 57%) of 2-methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclopentan-1-one as a yellow oil.

TLC: R_f = 0.38 (toluene/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 2978, 2933, 1729, 1643, 1371, 1319, 1252, 1140, 1103, 969, 846. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 5.94 (dt, *J* = 3.1, 1.5 Hz, 1H), 5.26 (dt, *J* = 2.8, 1.4 Hz, 1H), 2.97–2.76 (m, 1H), 2.70–2.48 (m, 1H), 2.45–2.16 (m, 2H), 2.02 (dd, *J* = 17.6, 9.0 Hz, 1H), 1.24 (d, *J* = 1.2 Hz, 12H), 0.96 (dd, *J* = 7.1, 2.2 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 207.0, 145.3, 116.6, 83.2, 47.0, 38.8, 30.0, 24.8, 24.8i. **^{11}B NMR** (128 MHz, Chloroform-*d*): δ [ppm] = 33.2. **HRMS** (EI) calcd. for $[C_{13}H_{21}BO_3]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 236.1584, found 236.1585.

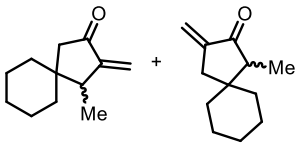
4-(2-Methylbenzyl)-2-methylenecyclopentan-1-one (178i)



According to **General Procedure G:** 3-(2-methylbenzyl)-1-vinylcyclobutan-1-ol (0.10 g, 0.50 mmol, 1.0 equiv) and (3,5-MeO-ArSe)$_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 12 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 94% product formation and purification by column chromatography (toluene) resulted in 48 mg (0.24 mmol, 48%) of 4-(2-methylbenzyl)-2-methylenecyclopentan-1-one as a yellow oil.

TLC: R_f = 0.28 (toluene). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2948, 1722, 1640, 1494, 1457, 1405, 1256, 1140, 1103, 741. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.20–7.04 (m, 4H), 6.00 (td, *J* = 2.5, 1.2 Hz, 1H), 5.30 (td, *J* = 2.2, 1.1 Hz, 1H), 2.85–2.61 (m, 3H), 2.58–2.33 (m, 3H), 2.31 (s, 3H), 2.25–2.06 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 206.1, 144.5, 137.9, 136.0, 130.4, 129.5, 126.4, 125.9, 117.4, 45.0, 38.6, 36.1, 34.0, 19.5. **HRMS** (EI) calcd. for $[C_{14}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 200.1201, found 200.1193.

4-Methyl-3-methylenespiro[4.5]decan-2-one and 1-methyl-3-methylenespiro[4.5]decan-2-one (178j)

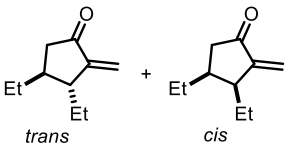


According to **General Procedure G:** 1-methyl-2-vinylspiro[3.5]nonan-2-ol (92 mg, 0.51 mmol, 1.0 equiv) and (3,5-MeO-ArSe)$_2$ (11 mg, 26 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 10 h, 1,3-dinitrobenzene (43 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 75% main product formation and 4% side product formation and purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) resulted in 63 mg (0.36 mmol, 70%) of 4-methyl-3-methylenespiro[4.5]decan-2-one and 1-methyl-3-methylenespiro[4.5]decan-2-one as a yellowish oil (22:1 mixture).

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.58 and 0.46 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 2929, 2855, 1725, 1643, 1453, 1394, 1233, 931. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 6.07 (dd, *J* = 3.2, 0.9 Hz, 1H, side), 5.99 (dd, *J* = 3.0, 1.0 Hz, 1H, anti), 5.27 (dt, *J* = 2.9, 1.5 Hz, 1H, side), 5.16 (dd, *J* = 2.8, 1.0 Hz, 1H, main), 2.55 (d, *J* = 17.9 Hz, 1H, main/side), 2.49 (dq, *J* = 6.9, 3.4 Hz, 1H, main/side), 2.02 (dd, *J* = 17.9, 1.5 Hz, 1H, main/side), 1.70–1.49 (m, 4H, main/side), 1.42–1.12 (m, 6H, main/side), 1.10 (d, *J* = 6.9 Hz, 3H, main), 1.00 (d, *J* = 7.1 Hz, 3H, side). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 207.0 (side), 206.6 (main), 150.3 (main), 117.3 (side), 116.1 (main), 49.2 (side), 48.0 (main), 46.5 (main), 46.1 (side), 40.2 (main), 39.2 (side), 36.9 (side), 36.6 (main), 30.7 (side), 29.4 (main), 26.0 (main), 23.8 (side), 23.3 (main), 22.5 (side), 22.1 (main), 21.3 (side), 20.5 (side), 12.5 (main), 8.7 (side). **HRMS** (EI) calcd. for $[C_{12}H_{18}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 178.1358, found 178.1347.

3,4-Diethyl-2-methylenecyclopentan-1-one (178k)



According to **General Procedure G:** 2,3-diethyl-1-vinylcyclobutanol (isomeric mixture) (78 mg, 0.51 mmol, 1.0 equiv) and $(3,5\text{-MeO-ArSe})_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 9 h, 1,3-dinitrobenzene (43 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 80% product formation (35/10 ratio of diastereomers) and purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) resulted in 34 mg (0.22 mmol, 44%) of 3,4-diethyl-2-methylenecyclopentan-1-one as a mixture of diastereomers (38:10 *trans*/*cis*)

*analysis of configuration was done by 2D NMR experiments.

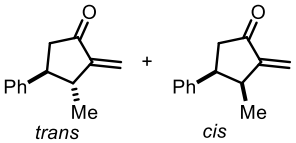
TLC: R_f = 0.56 and 0.48 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 2963, 2929, 1729, 1640, 1461, 1408, 1103, 939. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 6.03 (dd, *J* = 2.6, 1.1 Hz, 1H, *trans*), 5.99 (dd, *J* = 2.4, 1.2 Hz, 1H, *cis*), 5.24 (dd, *J* = 2.3, 1.1 Hz, 1H, *trans*), 5.18 (dd, *J* = 2.2, 1.2 Hz, 1H, *cis*), 2.69–2.57 (m, 1H, *cis*), 2.54 (ddd, *J* = 18.4, 7.8, 0.8 Hz, 1H, *trans*), 2.40 (tq, *J* = 6.2, 2.5 Hz, 1H, *trans*), 2.37–2.27 (m, 1H, *cis*), 2.26–2.09 (m, 2H, *cis*), 2.10–1.94 (m, 1H, *trans*), 1.84 (ddt, *J* = 14.3, 8.1, 5.9 Hz, 1H, *trans*), 1.76–1.33 (m, 3H, *trans/cis*), 1.36–1.17 (m, 1H, *trans*), 1.21–1.01 (m, 1H, *cis*), 1.03–0.84 (m, 6H, *trans/cis*). **^{13}C NMR** (101 MHz, Chloroform-*d*): [ppm] = 207.2 (*cis*), 207.1 (*trans*), 148.8 (*cis*), 148.5 (*trans*), 117.3 (*trans*), 116.5 (*cis*), 48.1 (*trans*), 46.5 (*cis*), 43.0 (*trans*), 42.3 (*trans*), 39.4 (*cis*), 38.1 (*cis*), 27.8 (*trans*), 25.6 (*trans*), 21.8 (*cis*), 20.3 (*cis*), 12.0 (*cis*), 11.9 (*trans*), 11.5 (*cis*), 10.8 (*trans*). **HRMS** (EI) calcd. for $[C_{10}H_{17}O]^+$ $(M+H)^+$: m/z = 153.1274, found 153.1272.

3-Methyl-2-methylene-4-phenylcyclopentan-1-one (178l-main) and *cis*-2-methyl-5-methylene-3-phenylcyclopentan-1-one (178l-side)

According to **General Procedure G:** 2-methyl-3-phenyl-1-vinylcyclobutan-1-ol (isomeric mixture) (94 mg, 0.50 mmol, 1.0 equiv) and $(3,5\text{-MeO-ArSe})_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 9 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 92% (74% *cis* + 18% *trans*) main- and 5.0% (cis/trans n.d.) side product formation and purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) resulted in 67 mg (0.36 mmol, 72%) of 3-methyl-2-methylene-4-phenylcyclopentan-1-one as a yellowish oil (47:10 *trans*/*cis*) and 2.8 mg of *cis*-2-methyl-5-methylene-3-phenylcyclopentan-1-one.

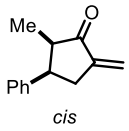
*analysis of configuration was done by 2D NMR experiments.

*anti / syn was analyzed based on 2D NMR and the configuration of the starting material.



TLC: R_f = 0.36 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3030, 2963, 1725, 1640, 1453, 1241, 760, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.41-7.32 (m, 2H, *trans*), 7.28 (dq, *J* = 5.1, 1.7 Hz, 3H, *trans*), 7.25–7.21 (m, 2H, *cis*), 7.04 (dd, *J* = 7.1, 1.8 Hz, 3H, *cis*), 6.14–6.07 (m,

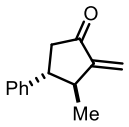
1H, *trans/cis*), 5.31–5.24 (m, 1H, *trans*), 5.24 (dd, *J* = 2.6, 0.8 Hz, 1H, *cis*), 3.55 (q, *J* = 7.3 Hz, 1H, *cis*), 3.20 (ddt, *J* = 11.2, 6.9, 3.4 Hz, 1H, *cis*), 2.87–2.77 (m, 2H, *trans*), 2.77–2.70 (m, 1H, *trans*), 2.61–2.47 (m, 1H, *trans*), 2.17 (s, 2H, *cis*), 1.16 (d, *J* = 6.0 Hz, 3H, *trans*), 0.85 (d, *J* = 7.0 Hz, 3H, *cis*). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 212.2 (*cis*), 205.3 (*trans*), 150.2 (*trans*), 149.6 (*cis*), 141.6 (*trans*), 128.7 (*trans*), 128.4 (*cis*), 127.8 (*cis*), 127.3 (*trans*), 127.0 (*trans*), 126.7 (*cis*), 117.1 (*cis*), 116.4 (*trans*), 48.4 (*trans*), 46.1 (*trans*), 44.1 (*trans*), 43.4 (*cis*), 43.0 (*cis*), 41.1 (*cis*), 16.1 (*trans*), 15.5 (*cis*). **HRMS** (EI) calcd. for $[C_{13}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 186.1045, found 186.1040.



cis

TLC: R_f = 0.42 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3030, 2967, 2929, 2873, 1725, 1643, 1453, 1021, 946, 760, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.41–7.32 (m, 2H), 7.32–7.23 (m, 3H), 6.14–6.06 (m, 1H), 5.37 (dt, *J* = 2.9, 1.4 Hz, 1H), 3.08–2.93 (m, 1H), 2.81 (td, *J* = 11.5, 6.3 Hz, 1H), 2.70 (ddt, *J* = 15.6, 11.5, 3.1 Hz, 1H), 2.44 (dq, *J* = 11.6, 6.8 Hz, 1H), 1.10 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 206.9, 144.2, 142.1, 128.8, 127.2, 127.0, 117.4, 51.3, 48.2, 37.0, 12.4. **HRMS** (EI) calcd. for $[C_{13}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 186.1045, found 186.1037.

(*trans*)-3-Methyl-2-methylene-4-phenylcyclopentan-1-one (178l-*trans*)



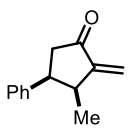
According to **General Procedure G:** (*trans*)-2-methyl-3-phenyl-1-vinylcyclobutan-1-ol (96 mg, 0.51 mmol, 1.0 equiv) and $(3,5\text{-MeO-ArSe})_2$ (11 mg, 26 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 12 h, 1,3-dinitrobenzene (43 mg, 0.26 mmol, 0.50 equiv) was added. NMR analysis resulted in 98% product formation and purification by automated column chromatography (PE to PE/Et_2O 99:1 to 85:15) resulted in 75 mg (0.40 mmol, 79%) of (*trans*)-3-methyl-2-methylene-4-phenylcyclopentan-1-one as a colorless oil.

*analytical data are in accordance with cited literature.[288]

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.3 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3086, 3030, 2963, 2899, 2877, 1725, 1640, 1453, 1405, 1241, 1125, 931, 760, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.39–7.32 (m, 2H), 7.29-7.22 (m, 3H), 6.10 (dd, *J* = 3.0, 0.8 Hz, 1H), 5.29–5.21 (m, 1H), 2.87–2.70 (m, 3H), 2.60–2.46 (m, 1H), 1.15 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 205.3, 150.2, 141.6, 128.7, 127.3, 127.0, 116.4, 48.4, 46.1, 44.1, 16.1. **HRMS** (EI) calcd. for $[C_{13}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 186.1045, found 186.1040.

(*cis*)-3-Methyl-2-methylene-4-phenylcyclopentan-1-one (178l-*cis*)



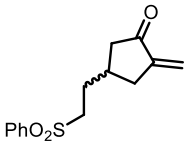
According to **General Procedure G:** (*cis*)-2-methyl-3-phenyl-1-vinylcyclobutan-1-ol (95 mg, 0.50 mmol, 1.0 equiv) and $(3,5\text{-MeO-ArSe})_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 12 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 94% product formation and

purification by column chromatography (PE to PE/Et_2O 30:1 to 10:1) resulted in 58 mg (0.31 mmol, 62%) of (*cis*)-3-methyl-2-methylene-4-phenylcyclopentan-1-one as a colorless oil.

*analysis of configuration was done by 2D NMR experiments.

TLC: R_f = 0.28 (PE/Et_2O 10:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3030, 2967, 2929, 1722, 1640, 1498, 1453, 1401, 1237, 1129, 1095, 935, 756, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.36–7.16 (m, 3H), 7.13-6.96 (m, 2H), 6.18–6.03 (m, 1H), 5.24 (dd, *J* = 2.6, 0.9 Hz, 1H), 3.55 (td, *J* = 7.4, 5.9 Hz, 1H), 3.20 (dtdd, *J* = 9.7, 7.0, 4.9, 2.7 Hz, 1H), 2.84–2.58 (m, 2H), 0.85 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 206.6, 149.6, 140.8, 128.4, 127.8, 126.7, 117.1, 43.4, 43.0, 41.1, 15.5. **HRMS** (EI) calcd. for $[C_{13}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 186.1045, found 186.1041.

2-Methylene-4-(2-(phenylsulfonyl)ethyl)cyclopentan-1-one (178p)

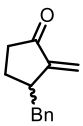


According to **General Procedure G:** 3-(2-(phenylsulfonyl)ethyl)-1-vinylcyclobutan-1-ol (0.13 g, 0.50 mmol, 1.0 equiv) and (3,5-MeO-ArSe)$_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 13 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 57% product formation and purification by automated column chromatography (DCM to DCM/MeCN 99:1 to 95:5) resulted in 62 mg of 2-methylene-4-(2-(phenylsulfonyl)ethyl)cyclopentan-1-one as a yellow oil.

* only 61% conversion obtained after 13 h of reaction time.

TLC: R_f = 0.38 (DCM/MeCN 50:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063, 1722, 1640, 1446, 1304, 1148, 1088, 734, 689. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.97–7.86 (m, 2H), 7.75–7.62 (m, 1H), 7.66–7.53 (m, 2H), 5.98 (ddd, *J* = 3.0, 2.1, 0.9 Hz, 1H), 5.31 (tt, *J* = 1.8, 0.9 Hz, 1H), 3.23–3.05 (m, 2H), 2.94–2.75 (m, 1H), 2.51 (ddd, *J* = 17.5, 6.6, 1.2 Hz, 1H), 2.36–2.14 (m, 2H), 2.03–1.81 (m, 2H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 204.7, 143.6, 138.9, 133.9, 129.4, 128.0, 118.0, 54.5, 44.4, 36.0, 32.6, 28.4. **HRMS** (ESI) calcd. for $[C_{14}H_{20}NO_3S]^+$ $(M+NH_4)^+$: m/z = 282.1158, found 282.1160.

3-Benzyl-2-methylenecyclopentan-1-one (178q)



According to **General Procedure G:** 2-benzyl-1-vinylcyclobutan-1-ol (94 mg, 0.50 mmol, 1.0 equiv) and (3,5-MeO-ArSe)$_2$ (11 mg, 25 µmol, 5 mol%) were diluted with HFIP (10 mL, 0.05 M). After a reaction time of 9 h, 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added. NMR analysis resulted in 95% product formation and purification by column chromatography (PE to PE/DCM 3:1) resulted in 65 mg (0.35 mmol, 70%) of 3-benzyl-2-methylenecyclopentan-1-one as a yellowish oil.

*analysis of configuration was done by 2D NMR experiments.

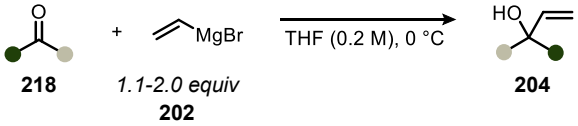
TLC: R_f = 0.20 (PE/DCM 1:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3063, 3026, 2967, 2926, 1722, 1636, 1494, 1453, 1408, 1263, 1177, 1095, 1028, 943, 846, 812, 745, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*):

δ [ppm] = 7.31 (dd, *J* = 8.0, 6.6 Hz, 2H), 7.26–7.17 (m, 3H), 6.05 (d, *J* = 2.5 Hz, 1H), 5.20 (dd, *J* = 2.4, 0.8 Hz, 1H), 3.13–2.96 (m, 2H), 2.73-2.54 (m, 1H), 2.37 (ddd, *J* = 18.5, 8.5, 4.9 Hz, 1H), 2.25 (dt, *J* = 18.3, 8.8 Hz, 1H), 2.08–1.94 (m, 1H), 1.66–1.51 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 207.2, 148.4, 139.4, 129.0, 128.5, 126.4, 117.2, 42.6, 40.6, 37.0, 26.2. **HRMS** (APCI) calcd. for $[C_{13}H_{14}O_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 187.1117, found 187.1116.

6.4 Project “1,2-aryl migration reaction”

6.4.1. Synthesis of starting materials

General Procedure H: Grignard reaction[248]

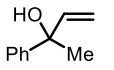


218 *1.1-2.0 equiv* **202** **204**

Scheme 122: Reaction equation for the Grignard reaction

A Schlenk flask was equipped with the respective ketone (1.0 equiv) and diluted with dry THF (0.3 M). The solution was cooled to 0 °C and a solution of vinyl magnesium bromide (1.0 M in THF, 1.1-2.0 equiv) was added dropwise. The reaction was allowed to warm up and quenched with NH_4Cl sat. aq. upon completion. The organic phase was extracted with Et_2O and washed with water and brine, dried and concentrated. Purification by column chromatography resulted in the corresponding allylic alcohols.

2-Phenylbut-3-en-2-ol (204a)



According to **General Procedure H**: acetophenone (1.1 g, 9.5 mmol, 1.0 equiv) was diluted in dry THF (30 mL, 0.3 M) and reacted with vinylmagnesium bromide (19 mL, 19 mmol, 2.0 equiv). After a reaction time of 1 h, the reaction was quenched, the organic phase extracted with Et_2O (2x 25 mL), washed with brine (1x 25 mL), dried over $MgSO_4$ and concentrated. Purification by column chromatography (PE/EtOAc 30:1) yielded 0.70 g (4.7 mmol, 50%) of 2-phenylbut-3-en-2-ol as a colorless oil.

*analytical data are in accordance with cited literature.[289]

TLC: R_f = 0.12 (PE/EtOAc 30:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3388, 3060, 2981, 1446, 1066, 995, 924, 767, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.51–7.44 (m, 2H), 7.40–7.32 (m, 2H), 7.32–7.20 (m, 1H), 6.18 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.31 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.15 (dd, *J* = 10.6, 1.1 Hz, 1H), 1.66 (s, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 146.4, 144.9, 128.3, 127.0, 125.2, 112.4, 74.8, 29.4. **HRMS** (EI) calcd. for $[C_{10}H_{12}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 148.0888, found 148.0878.

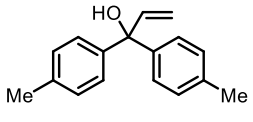
1,1-Diphenylprop-2-en-1-ol (204b)

According to **General Procedure H**: benzophenone (1.0 g, 5.5 mmol, 1.0 equiv) was diluted in dry THF (18 mL, 0.3 M) and reacted with vinylmagnesium bromide (11 mL, 11 mmol, 2.0 equiv). After a reaction time of 1 h, the reaction was quenched, the organic phase extracted with Et_2O (1x 20 mL), washed with brine (1x 20 mL), dried over $MgSO_4$ and concentrated to yield 1.0 g (4.8 mmol, 87%) of 1,1-diphenylprop-2-en-1-ol as a colorless oil.

*analytical data are in accordance with cited literature.[290]

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3555, 3451, 3086, 3060, 3026, 1490, 1446, 1408, 1334, 1170, 1028, 998, 972, 760, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.41–7.37 (m, 4H), 7.36–7.30 (m, 4H), 7.31–7.22 (m, 2H), 6.60–6.44 (m, 1H), 5.43–5.25 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 145.8, 143.5, 128.2, 127.3, 126.9, 114.0, 79.4. **HRMS** (EI) calcd. for $[C_{15}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 210.1045, found 210.1045.

1,1-di-*p*-Tolylprop-2-en-1-ol (204c)

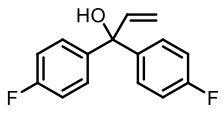


According to **General Procedure H**: di-*p*-tolylmethanone (1.0 g, 4.8 mmol, 1.0 equiv) was diluted in dry THF (16 mL, 0.3 M) and reacted with vinylmagnesium bromide (7.5 mL, 7.5 mmol,1.6 equiv). After a reaction time of 3 h, the reaction was quenched, the organic phase extracted with Et_2O (1x 60 mL), dried over $MgSO_4$ and concentrated to yield 1.0 g (4.2 mmol, 87%) of 1,1-di-p-tolylprop-2-en-1-ol as a yellowish oil.

*analytical data are in accordance with cited literature.[291]

IR (ATR): v [cm^{-1}] = 3548, 3455, 3022, 2922, 2866, 1509, 1408, 1319, 1181, 1107, 1021, 995, 913, 812, 790. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.32–7.21 (m, 4H), 7.16–7.04 (m, 4H), 6.48 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.40–5.22 (m, 2H), 2.33 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 143.8, 143.1, 136.9, 128.8, 126.8, 113.5, 79.1, 21.0.**HRMS** (EI) calcd. for $[C_{17}H_1O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 238.1358, found 238.1352.

1,1-bis(4-Fluorophenyl)prop-2-en-1-ol (204d)

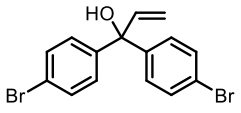


According to **General Procedure H**: bis(4-fluorophenyl)methanone (1.6 g, 7.1 mmol, 1.0 equiv) was diluted in dry THF (24 mL, 0.3 M) and reacted with vinylmagnesium bromide (14 mL, 14 mmol, 2.0 equiv). After a reaction time of 19 h, the reaction was quenched, the organic phase washed with water (3x 20 mL), dried over $MgSO_4$ and concentrated to yield 1.6 g (6.3 mmol, 89%) of 1,1-bis(4-fluorophenyl)prop-2-en-1-ol as a brownish oil.

*analytical data are in accordance with cited literature.[292]

IR (ATR): ṽ [cm^{-1}] = 3585, 3447, 1602, 1505, 1226, 1159, 1013, 931, 834. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.40–7.26 (m, 4H), 7.01 (ddt, *J* = 8.8, 6.7, 2.6 Hz, 4H), 6.55–6.34 (m, 1H), 5.45–5.17 (m, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 163.3, 160.8, 143.2, 141.4, 141.3, 128.7, 128.6, 115.1, 114.9, 114.5, 78.7. **^{19}F NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 115.7 (tt, *J* = 8.5, 5.3 Hz). **HRMS** (EI) calcd. for $[C_{15}H_{12}F_2O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 246.0856, found 246.0855.

1,1-bis(4-Bromophenyl)prop-2-en-1-ol (204e)

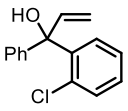


According to **General Procedure H**: bis(4-bromophenyl)methanone (1.5 g, 4.4 mmol, 1.0 equiv) was diluted in dry THF (15 mL, 0.3 M) and reacted with vinylmagnesium bromide (5.8 mL, 5.8 mmol, 1.3 equiv). After a reaction time of 15 h, the reaction was quenched, the organic phase washed with brine (1x 25 mL), dried over $MgSO_4$ and concentrated. Purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) yielded 1.3 g (3.6 mmol, 83%) of 1,1-bis(4-bromophenyl)prop-2-en-1-ol as a colorless oil.

*analytical data are in accordance with cited literature.[291]

TLC: R_f = 0.32 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3567, 3447, 3086, 1483, 1394, 1010, 976, 820. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.50–7.39 (m, 4H), 7.29–7.14 (m, 4H), 6.41 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.45–5.20 (m, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.3, 142.5, 131.4, 128.6, 121.7, 115.1, 78.8. **HRMS** (EI) calcd. for $[C_{15}H_{12}Br_2O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 365.9255, found 365.9241.

1-(2-Chlorophenyl)-1-phenylprop-2-en-1-ol (204f)

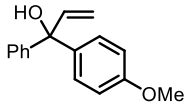


According to **General Procedure H**: (2-chlorophenyl)(phenyl)methanone (2.0 g, 9.2 mmol, 1.0 equiv) was diluted in dry THF (31 mL, 0.3 M) and reacted with vinylmagnesium bromide (14 mL, 14 mmol, 1.5 equiv). After a reaction time of 19 h, the reaction was quenched, the organic phase extracted with Et_2O (1x 50 mL), washed with water (1x 50 mL), dried over $MgSO_4$ and concentrated to yield 1.9 g (7.7 mmol, 83%) of 1-(2-chlorophenyl)-1-phenylprop-2-en-1-ol as a colorless oil.

*analytical data are in accordance with cited literature.[293]

IR (ATR): ṽ [cm^{-1}] = 3597, 3451, 3063, 3030, 1446, 1326, 1039, 1002, 924, 760, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.78–7.63 (m, 1H), 7.38–7.22 (m, 9H), 6.60 (ddd, *J* = 17.0, 10.8, 1.2 Hz, 1H), 5.45–5.27 (m, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 145.0, 142.4, 141.4, 132.6, 131.3, 129.2, 129.0, 128.3, 127.4, 126.7, 126.5, 115.0, 79.6. **HRMS** (EI) calcd. for $[C_{15}H_{13}ClO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 244.0655, found 244.0644.

1-(4-Methoxyphenyl)-1-phenylprop-2-en-1-ol (204g)

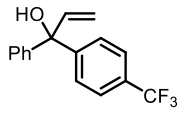


According to **General Procedure H**: (4-methoxyphenyl)(phenyl)methanone (1.3 g, 6.0 mmol, 1.0 equiv) was diluted in dry THF (20 mL, 0.3 M) and reacted with vinylmagnesium bromide (9.0 mL, 9.0 mmol, 1.5 equiv). After a reaction time of 19 h, the reaction was quenched, the organic phase extracted with Et_2O (2x 50 mL), washed with water (1x 100 mL), dried over $MgSO_4$ and concentrated to yield 1.4 g (5.8 mmol, 96%) of 1-(4-methoxyphenyl)-1-phenylprop-2-en-1-ol as a yellowish oil.

*analytical data are in accordance with cited literature.[291]

IR (ATR): ṽ [cm^{-1}] = 3473, 3060, 3026, 2836, 1610, 1509, 1248, 1177, 1032, 831, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.44–7.20 (m, 9H), 6.92–6.79 (m, 2H), 6.49 (dd, *J* = 16.9, 10.7 Hz, 1H), 5.39–5.23 (m, 2H), 3.80 (s, 3H). **^{13}C NMR** (75 MHz, Chloroform-*d*): δ [ppm] = 158.8, 145.9, 143.7, 138.1, 128.3, 128.1, 127.2, 126.8, 113.7, 113.5, 79.1, 55.3. **HRMS** (EI) calcd. for $[C_{16}H_{16}O_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 240.1150, found 240.1145.

1-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (204h)

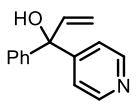


According to **General Procedure H**: phenyl(4-(trifluoromethyl)phenyl)methanone (1.5 g, 6.0 mmol, 1.0 equiv) was diluted in dry THF (20 mL, 0.3 M) and reacted with vinylmagnesium bromide (7.8 mL, 7.8 mmol, 1.3 equiv). After a reaction time of 2 h, the reaction was quenched, the organic phase washed with brine (2x 50 mL), dried over $MgSO_4$ and concentrated. Purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) yielded 0.55 g (2.0 mmol, 33%) of 1-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol as a colorless oil.

*analytical data are in accordance with cited literature.[291]

TLC: R_f = 0.36 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3552, 3455, 3063, 3030, 1326, 1166, 1125, 1069, 1017, 838, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.62–7.55 (m, 2H), 7.56–7.48 (m, 2H), 7.41–7.25 (m, 5H), 6.50 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.42–5.27 (m, 2H).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 149.5, 145.1, 142.7, 128.4, 127.7, 127.1, 126.8, 125.0(q, *J* = 3.7 Hz, C-F), 114.9, 79.1, 77.3. **^{19}F NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 63.0. **HRMS** (EI) calcd. for $[C_{16}H_{13}F_3O_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 278.0918, found 278.0912.

1-Phenyl-1-(pyridin-4-yl)prop-2-en-1-ol (204i)

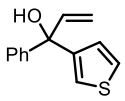


According to **General Procedure H**: phenyl(pyridin-4-yl)methanone (1.5 g, 8.2 mmol, 1.0 equiv) was diluted in dry THF (27 mL, 0.3 M) and reacted with vinylmagnesium bromide (12 mL, 12 mmol, 1.5 equiv). After a reaction time of 19 h, the reaction was quenched, the organic phase extracted with Et_2O (1x 20 mL), washed with water (1x 20 mL), dried over $MgSO_4$ and concentrated. Purification by column chromatography (PE/Et_2O 1:1 to Et_2O) yielded 0.15 g (0.71 mmol, 9%) of 1-phenyl-1-(pyridin-4-yl)prop-2-en-1-ol as a white precipitate.

*analytical data are in accordance with cited literature.[291]

MP = 133.5°C. **TLC:** R_f = 0.38 (Et_2O). **IR** (ATR): ṽ [cm^{-1}] = 3145, 3086, 3063, 2795, 1599, 1446, 1412, 1002, 928, 820, 767. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 8.53 (d, *J* = 5.4 Hz, 2H), 7.44–7.28 (m, 7H), 6.47 (dd, *J* = 17.1, 10.6 Hz, 1H), 5.49–5.28 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 155.4, 148.7, 144.4, 141.9, 128.6, 128.1, 126.9, 121.9, 115.7, 78.7. **HRMS** (ESI) calcd. for $[C_{14}H_{14}NO]^+$ $(M+H)^+$: m/z = 212.1070, found 212.1071.

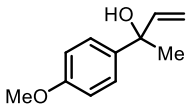
1-Phenyl-1-(thiophen-2-yl)prop-2-en-1-ol (204j)



According to **General Procedure H**: phenyl(thiophen-2-yl)methanone (1.5 g, 8.0 mmol, 1.0 equiv) was diluted in dry THF (28 mL, 0.3 M) and reacted with vinylmagnesium bromide (12 mL, 12 mmol, 1.5 equiv). After a reaction time of 20 h, the reaction was quenched, the organic phase extracted with Et_2O (1x 20 mL), washed with water (1x 20 mL), dried over $MgSO_4$ and concentrated to yield 1.2 g (5.4 mmol, 67%) of 1-phenyl-1-(thiophen-2-yl)prop-2-en-1-ol as a yellowish oil.

IR (ATR): ṽ [cm^{-1}] = 3533, 3429, 3060, 3026, 1446, 1233, 928, 834, 760, 693. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.58–7.45 (m, 3H), 7.42–7.26 (m, 5H), 6.96 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.89 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.51 (dd, *J* = 17.0, 10.5 Hz, 1H), 5.50–5.24 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 151.0, 145.0, 143.0, 128.1, 127.6, 126.6, 126.3, 125.6, 125.5, 114.1, 77.5. **HRMS** (EI) calcd. for $[C_{13}H_{12}OS]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 216.0609, found 216.0606.

2-(4-Methoxyphenyl)but-3-en-2-ol (204k)

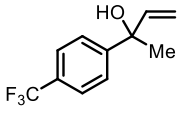


According to **General Procedure H**: 1-(4-methoxyphenyl)ethan-1-one (1.5 g, 10 mmol, 1.0 equiv) was diluted in dry THF (34 mL, 0.2 M) and reacted with vinylmagnesium bromide (15 mL, 15 mmol, 1.5 equiv). After a reaction time of 69 h, the reaction was quenched, the organic phase extracted with Et_2O (1x 20 mL), washed with water (1x 20 mL), dried over $MgSO_4$ and concentrated. Purification by column chromatography (PE/Et_2O 10:1 to 3:1) yielded 0.90 g (5.1 mmol, 51%) of 2-(4-methoxyphenyl)but-3-en-2-ol as a colorless oil.

*analytical data are in accordance with cited literature.[294]

TLC: R_f = 0.67 (PE/Et_2O 1:1). **IR** (ATR): ṽ [cm^{-1}] = 3447, 2978, 2937, 2836, 1610, 1513, 1300, 1248, 1177, 1032, 920, 831. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.50–7.28 (m, 2H), 6.95–6.77 (m, 2H), 6.16 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.28 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.13 (dd, *J* = 10.6, 1.1 Hz, 1H), 3.80 (s, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 158.6, 145.0, 138.6, 126.4, 113.5, 112.0, 74.4, 55.3, 29.3. **HRMS** (EI) calcd. for $[C_{11}H_{14}O_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 178.0994, found 178.0983.

2-(4-(Trifluoromethyl)phenyl)but-3-en-2-ol (204l)

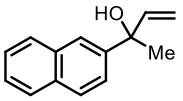


According to **General Procedure H**: 1-(4-(trifluoromethyl)phenyl)ethan-1-one (1.6 g, 8.5 mmol, 1.0 equiv) was diluted in dry THF (28 mL, 0.3 M) and reacted with vinylmagnesium bromide (11 mL, 11 mmol, 1.3 equiv). After a reaction time of 18 h, the reaction was quenched, the organic phase washed with water (1x 50 mL), dried over $MgSO_4$ and concentrated. Purification by automated column chromatography (*n*-hexane to *n*-hexane /toluene 50:50 to toluene and *n*-hexane to *n*-hexane/Et_2O 99:1 to 80:20) yielded 0.92 g (4.3 mmol, 50%) of 2-(4-(trifluoromethyl)phenyl)but-3-en-2-ol as a colorless oil.

*analytical data are in accordance with cited literature.[295]

TLC: R_f = 0.46 (PE/Et_2O 3:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3384, 2985, 1617, 1412, 1326, 1162, 1121, 1073, 1013, 924, 842. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.59 (s, 4H), 6.15 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.31 (dd, *J* = 17.3, 0.9 Hz, 1H), 5.19 (dd, *J* = 10.6, 0.8 Hz, 1H), 1.67 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 150.3, 144.1, 129.2 (q, *J* = 32.3 Hz, C-F), 125.5, 125.1 (q, *J* = 3.8 Hz, C-F), 122.8, 113.2, 74.6, 29.4. **^{19}F NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 63.0. **HRMS** (EI) calcd. for $[C_{11}H_{11}F_3O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 216.0762, found 216.0754.

2-(Naphthalen-2-yl)but-3-en-2-ol (204m)

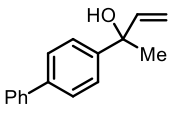


According to **General Procedure H**: 1-(Naphthalen-2-yl)ethan-1-one (1.5 g, 8.8 mmol, 1.0 equiv) was diluted in dry THF (29 mL, 0.3 M) and reacted with vinylmagnesium bromide (12 mL, 12 mmol, 1.3 equiv). After a reaction time of 18 h, the reaction was quenched, the organic phase extracted with Et_2O (1x 20 mL), washed with water (1x 20 mL), dried over $MgSO_4$ and concentrated. Purification by column chromatography (PE to PE/Et_2O 10:1 to 3:1 and then PE/Et_2O 10:1) yielded 0.70 g (3.5 mmol, 40%) of 2-(naphthalen-2-yl)but-3-en-2-ol as a yellowish oil.

*analytical data are in accordance with cited literature.[296]

TLC: R_f = 0.44 (PE/Et_2O 3:1). **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3399, 3056, 2978, 1599, 1505, 1371, 1125, 924, 857, 820, 749. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.95 (d, *J* = 2.0 Hz, 1H), 7.91–7.78 (m, 3H), 7.57 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.55–7.41 (m, 2H), 6.26 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.36 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.20 (dd, *J* = 10.6, 1.1 Hz, 1H), 1.76 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.7, 143.7, 133.2, 132.5, 128.2, 127.9, 127.5, 126.1, 125.9, 124.1, 123.4, 112.8, 74.9, 29.3. **HRMS** (EI) calcd. for $[C_{14}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 198.1045, found 198.1033.

2-([1,1'-Biphenyl]-4-yl)but-3-en-2-ol (204n)

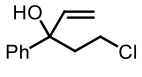


According to **General Procedure H**: 1-([1,1'-biphenyl]-4-yl)ethan-1-one (1.5 g, 7.6 mmol, 1.0 equiv) was diluted in dry THF (26 mL, 0.3 M) and reacted with vinylmagnesium bromide (12 mL, 12 mmol, 1.6 equiv). After a reaction time of 18 h, the reaction was quenched, the organic phase extracted with Et_2O (2x 30 mL), dried over $MgSO_4$

and concentrated to yield 1.7 g (7.5 mmol, 97%) of 2-([1,1'-biphenyl]-4-yl)but-3-en-2-ol as a yellowish oil.

IR (ATR): ṽ [cm^{-1}] = 3399, 3030, 2978, 1487, 1073, 1006, 920, 838, 767, 734, 697. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.65–7.49 (m, 6H), 7.50–7.38 (m, 2H), 7.41–7.28 (m, 1H), 6.32–6.11 (m, 1H), 5.35 (dd, *J* = 17.3, 1.1 Hz, 1H), 5.18 (dd, *J* = 10.6, 1.2 Hz, 1H), 1.71 (d, *J* = 1.9 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 145.5, 144.8, 140.8, 139.9, 128.8, 127.3, 127.1, 127.0, 125.7, 112.4, 74.7, 29.4. **HRMS** (EI) calcd. for $[C_{16}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 224.1201, found 224.1198.

5-Chloro-3-phenylpent-1-en-3-ol (204o)

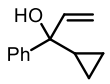


According to **General Procedure H**: 3-chloro-1-phenylpropan-1-one (1.6 g, 9.2 mmol, 1.0 equiv) was diluted in dry THF (30 mL, 0.3 M) and reacted with vinylmagnesium bromide (13 mL, 13 mmol, 1.4 equiv). After a reaction time of 19 h, the reaction was quenched, the organic phase washed with water (3x 50 mL), dried over $MgSO_4$ and concentrated to yield 1.3 g (6.6 mmol, 72%) of 5-chloro-3-phenylpent-1-en-3-ol as a yellowish oil.

*analytical data are in accordance with cited literature.[297]

IR (ATR): ṽ [cm^{-1}] = 3552, 3444, 3086, 3060, 3026, 2967, 1446, 1051, 991, 924, 767, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.47–7.33 (m, 5H), 7.34–7.22 (m, 1H), 6.18 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.35 (dd, *J* = 17.2, 0.8 Hz, 1H), 5.23 (dd, *J* = 10.7, 0.8 Hz, 1H), 3.60 (td, *J* = 10.5, 5.7 Hz, 1H), 3.42 (td, *J* = 10.5, 5.6 Hz, 1H), 2.56–2.27 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.3, 143.1, 128.5, 127.3, 125.1, 113.6, 76.5, 44.6, 40.2. **HRMS** (EI) calcd. for $[C_{11}H_{13}ClO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 196.0655, found 196.0647.

1-Cyclopropyl-1-phenylprop-2-en-1-ol (204p)

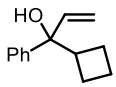


According to **General Procedure H**: cyclopropyl(phenyl)methanone (2.1 g, 15 mmol, 1.0 equiv) was diluted in dry THF (45 mL, 0.3 M) and reacted with vinylmagnesium bromide (22 mL, 22 mmol, 1.5 equiv). After a reaction time of 2 h, the reaction was quenched, the organic phase extracted with Et_2O (1x 40 mL), washed with water (1x 40 mL), dried over $MgSO_4$ and concentrated to yield 1.6 g (9.2 mmol, 63%) of 1-cyclopropyl-1-phenylprop-2-en-1-ol as a yellowish oil.

*analytical data are in accordance with cited literature.[298]

IR (ATR): ṽ [cm^{-1}] = 3451, 3086, 3011, 1490, 1446, 1408, 1025, 987, 916, 760, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.61–7.50 (m, 2H), 7.41–7.31 (m, 2H), 7.28 (s, 1H), 6.03 (dd, *J* = 17.2, 10.6 Hz, 1H), 5.38 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.19 (dd, *J* = 10.6, 1.4 Hz, 1H), 1.36 (ddt, *J* = 8.4, 7.3, 5.6 Hz, 1H), 0.66–0.54 (m, 1H), 0.54–0.41 (m, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 143.7, 140.3, 126.1, 125.1, 123.9, 111.8, 73.9, 19.2, 0.0, -1.3. **HRMS** (EI) calcd. for $[C_{12}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 174.1045, found 174.1039.

1-Cyclobutyl-1-phenylprop-2-en-1-ol (204q)

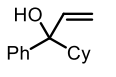


According to **General Procedure H**: cyclobutyl(phenyl)methanone (1.6 g, 9.8 mmol, 1.0 equiv) was diluted in dry THF (32 mL, 0.3 M) and reacted with vinylmagnesium bromide (14 mL, 14 mmol, 1.4 equiv). After a reaction time of 18 h, the reaction was quenched, the organic phase extracted with Et_2O (1x 40 mL), dried over $MgSO_4$ and concentrated to yield 1.2 g (6.5 mmol, 66%) of 1-cyclobutyl-1-phenylprop-2-en-1-ol as a yellowish oil.

*analytical data are in accordance with cited literature.[299]

IR (ATR): ṽ [cm^{-1}] = 3570, 3466, 2978, 2940, 2862, 1446, 991, 916, 752, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.47–7.40 (m, 2H), 7.37–7.29 (m, 2H), 7.29–7.17 (m, 1H), 6.12 (dd, *J* = 17.3, 10.7 Hz, 1H), 5.28 (dd, *J* = 17.3, 1.2 Hz, 1H), 5.16 (dd, *J* = 10.7, 1.2 Hz, 1H), 3.06–2.81 (m, 1H), 2.15-1.58 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 144.6, 142.3, 128.1, 126.8, 125.6, 113.1, 44.0, 22.7, 22.2, 16.9. **HRMS** (EI) calcd. for $[C_{13}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 188.1201, found 188.1202.

1-Cyclohexyl-1-phenylprop-2-en-1-ol (204r)

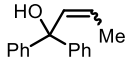


According to **General Procedure H**: cyclohexyl(phenyl)methanone (2.0 g, 11 mmol, 1.0 equiv) was diluted in dry THF (34 mL, 0.3 M) and reacted with vinylmagnesium bromide (16 mL, 16 mmol, 1.5 equiv). After a reaction time of 2 h, the reaction was quenched, the organic phase washed with water (3x 30 mL), extracted with Et_2O (2x 30 mL), dried over $MgSO_4$ and concentrated to yield 2.0 g (9.1 mmol, 86%) of 1-cyclohexyl-1-phenylprop-2-en-1-ol as a yellowish oil.

*analytical data are in accordance with cited literature.[293]

IR (ATR): ṽ [cm^{-1}] = 3481, 3086, 3060, 3026, 2929, 2855, 1740, 1446, 976, 920, 764, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.46–7.39 (m, 2H), 7.38–7.29 (m, 2H), 7.26–7.16 (m, 1H), 6.30 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.31 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.18 (dd, *J* = 10.8, 1.2 Hz, 1H), 1.88–1.53 (m, 4H), 1.51–1.40 (m, 2H), 1.30–0.89 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 145.6, 143.3, 128.1, 126.5, 125.5, 112.5, 79.2, 47.7, 27.2, 26.8, 26.7, 26.6, 26.5. **HRMS** (EI) calcd. for $[C_{15}H_{20}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 216.1514, found 216.1505.

1,1-Diphenylbut-2-en-1-ol (204s)



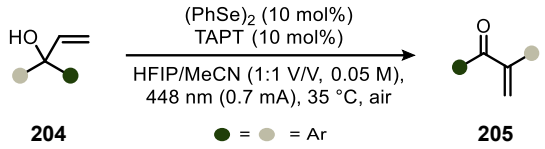
According to **General Procedure H**: benzophenone (1.0 g, 5.5 mmol, 1.0 equiv) was diluted in dry THF (19 mL, 0.3 M) and reacted with propinylmagnesium bromide (0.5 M in THF) (22 mL, 11 mmol, 2.0 equiv). After a reaction time of 3 h, the reaction was quenched, the organic phase extracted with Et_2O (2x 50 mL), dried over $MgSO_4$ and concentrated. Purification by column chromatography (PE to PE/EtOAc 99:1 to 50:1) yielded 0.58 g (2.6 mmol, 47%) of 1,1-diphenylbut-2-en-1-ol as a colorless oil (16:10 *E/Z*).

*analytical data are in accordance with cited literature.[300]

TLC: R_f = 0.12 (PE/EtOAc 99:1). **IR** (ATR): ṽ [cm^{-1}] = 3555, 3455, 3060, 3026, 2963, 1490, 1446, 1375, 1330, 1166, 976, 760, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.58–7.09 (m, 10H, *E/Z*), 6.21-6.06 (m, 1H, *E/Z*), 5.81 (dq, *J* = 11.6, 7.2 Hz, 1H, *Z*), 5.64 (dq, *J* = 15.5, 6.6 Hz, 1H, *E*), 1.79 (dd, *J* = 6.6, 1.6 Hz, 3H, *E*), 1.57 (dd, *J* = 7.1, 1.9 Hz, 3H, *Z*).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 147.6 (*Z*), 146.5 (*E*), 137.0 (*E*), 136.9 (*Z*), 129.2 (*Z*), 128.2 (*E*), 128.1 (*E*), 127.1 (*Z*), 126.9 (*E*), 126.9 (*Z*), 126.4 (*E*), 126.0 (*Z*), 79.1 (*E*), 79.0 (*Z*), 17.8 (*E*), 14.8 (*Z*). **HRMS** (EI) calcd. for $[C_{16}H_{16}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 224.1201, found 224.1193.

6.4.2. Synthesis of the biarylic α,β-unsaturated ketones

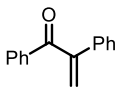
General Procedure I: Selenium-π-acid photoredox catalyzed reaction for biarylated substrates:



Scheme 123: Procedure for the selenium-π-acid photoredox dualcatalyzed synthesis of bi-arylated α,β-unsaturated ketones **205**.

A photovial was equipped with the corresponding vinylic alcohol (0.50 mmol, 1.0 equiv), $(PhSe)_2$ (10 mol%) and TAPT (10 mol%) and both diluted with a 1:1 volumetric mixture of HFIP and MeCN (0.05 M). The photovial was closed with a screw cap, cannulas were added to allow for air exchange and the vial was placed in the heated (35 °C) irradiation setup. The mixture was irradiated (448 nm, 0.7 mA) for the given amount of time and consecutively the solvent removed under reduced pressure. 1,3-dinitrobenzene (0.50 equiv) was added (unless otherwise noted) as internal standard and the crude reaction mixture dissolved in 2.0 mL of $CDCl_3$. After determination of the NMR Yield, the NMR sample was added back with $CHCl_3$ and again concentrated. Purification by column chromatography resulted in the respective prop-2-en-1-ones.

1,2-Diphenylprop-2-en-1-one (205b)



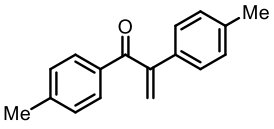
According to **General Procedure I:** 1,1-diphenylprop-2-en-1-ol (0.11 g, 0.50 mmol, 1.0 equiv), $(PhSe)_2$ (16 mg, 50 µmol, 10 mol%), TAPT (24 mg, 50 µmol, 10 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 12 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 72% product formation. Purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) resulted in 63 mg (0.30 mmol, 60%) of 1,2-diphenylprop-2-en-1-one as a yellowish oil (inseparable benzophenone remains as a 16% impurity).

*analytical data are in accordance with cited literature.[301]

*in a single case, the signals of remaining impurities were compared with performed NMR analysis of the initial ketones used in the synthesis of the vinylic alcohols used in this transformation. Based on this result, all subsequent impurities of further reactions were anticipated to be of analogue origin.

TLC: R_f = 0.36 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3060, 3030, 1666, 1595, 1446, 1334, 1278, 1215, 980, 775, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.95–7.87 (m, 2H), 7.63–7.51 (m, 1H), 7.48-7.39 (m, 4H), 7.40–7.28 (m, 3H), 6.07 (s, 1H), 5.65 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 197.6, 148.3, 137.1, 133.1, 130.1, 130.0, 128.6, 128.4, 128.4, 127.1, 120.9. **HRMS** (EI) calcd. for $[C_{15}H_{10}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 208.0888, found 208.0881.

1,2-di-*p*-Tolylprop-2-en-1-one (205c)



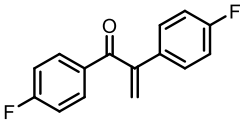
According to **General Procedure I:** 1,1-di-p-tolylprop-2-en-1-ol (0.12 g, 0.50 mmol, 1.0 equiv), $(PhSe)_2$ (16 mg, 50 µmol, 10 mol%), TAPT (24 mg, 50 µmol, 10 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 12 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 50% product formation. Purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) resulted in 49 mg (0.21 mmol, 41%) of 1,2-di-*p*-tolylprop-2-en-1-one as a yellowish oil (inseparable di-*p*-tolylmethanone remains as a 16% impurity).

*analytical data are in accordance with cited literature.[302]

*in a single case, the signals of remaining impurities were compared with performed NMR analysis of the initial ketones used in the synthesis of the vinylic alcohols used in this transformation. Based on this result, all subsequent impurities of further reactions were anticipated to be of analogue origin.

TLC: R_f = 0.42 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3030, 2922, 1662, 1606, 1513, 1222, 1177, 980, 823, 771. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.82 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.98 (s, 1H), 5.54 (s, 1H), 2.40 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 197.5, 148.3, 144.0, 138.3, 134.5, 134.3, 130.2, 129.3, 129.1, 128.9, 126.8, 119.0, 21.7, 21.2. **HRMS** (APCI) calcd. for $[C_{17}H_{17}O]^+$ $(M+H)^+$: m/z = 237.1274, found 237.1275.

1,2-bis(4-Fluorophenyl)prop-2-en-1-one (205d)

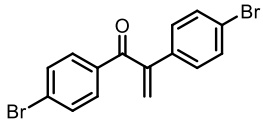


According to **General Procedure I:** 1,1-bis(4-fluorophenyl)prop-2-en-1-ol (0.12 g, 0.50 mmol, 1.0 equiv), $(PhSe)_2$ (16 mg, 50 µmol, 10 mol%), TAPT (24 mg, 50 µmol, 10 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 12 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 64% product formation. Purification by column chromatography (PE to PE/acetone/DCM 80:1:2) resulted in 63 mg (0.26 mmol, 52%) of 1,2-bis(4-fluorophenyl)prop-2-en-1-one as a yellowish oil (inseparable bis(4-fluorophenyl)methanone remains as a 12% impurity).

*in a single case, the signals of remaining impurities were compared with performed NMR analysis of the initial ketones used in the synthesis of the vinylic alcohols used in this transformation. Based on this result, all subsequent impurities of further reactions were anticipated to be of analogue origin.

TLC: R_f = 0.42 (PE/acetone/DCM 40:1:1). **IR** (ATR): ṽ [cm^{-1}] = 3075, 1662, 1599, 1505, 1230, 1155, 842. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.98–7.88 (m, 2H), 7.46–7.35 (m, 2H), 7.17–7.06 (m, 2H), 7.10–6.99 (m, 2H), 6.03 (s, 1H), 5.62 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 195.7, 167.1, 164.3 (d, *J* = 42.3 Hz, C-F), 161.7, 147.0, 133.3 (d, *J* = 3.0 Hz, C-F), 132.9 (d, *J* = 3.4 Hz, C-F), 132.6 (d, *J* = 9.4 Hz, C-F), 128.8 (d, *J* = 8.2 Hz, C-F), 120.9 (d, *J* = 1.6 Hz, C-F), 115.7 (d, *J* = 21.8 Hz, C-F). **^{19}F NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 105.1 (tt, *J* = 8.4, 5.5 Hz), - 106.3, - 113.47 (tt, *J* = 8.5, 5.3 Hz). **HRMS** (EI) calcd. for $[C_{15}H_{10}F_2O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 244.0700, found 244.0691.

1,2-bis(4-Bromophenyl)prop-2-en-1-one (205e)

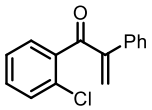


According to **General Procedure I:** 1,1-bis(4-bromophenyl)prop-2-en-1-ol (0.19 g, 0.51 mmol, 1.0 equiv), $(PhSe)_2$ (16 mg, 50 µmol, 10 mol%), TAPT (25 mg, 50 µmol, 10 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 10 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 49% product formation. Purification by automated column chromatography (*n*-hexane to *n*-hexane/Et_2O 99:1 to 95:5) resulted in 83 mg (0.23 mmol, 45%) of 11,2-bis(4-bromophenyl)prop-2-en-1-one as a red oil.

*analytical data are in accordance with cited literature.[303]

TLC: R_f = 0.52 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3090, 1662, 1584, 1487, 1394, 1319, 1211, 1174, 1073, 1010, 980, 834, 797. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.77–7.70 (m, 2H), 7.63–7.54 (m, 2H), 7.52–7.45 (m, 2H), 7.33–7.22 (m, 2H), 6.09 (s, 1H), 5.68 (s, 1H).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 195.9, 146.8, 135.6, 135.6, 131.9, 131.4, 128.7, 128.5, 122.9, 122.2, 77.2. **HRMS** (EI) calcd. for $[C_{15}H_{10}Br_2O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 363.9098, found 363.9096.

1-(2-Chlorophenyl)-2-phenylprop-2-en-1-one (205f-1)

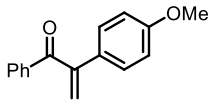


According to **General Procedure I:** 1-(2-chlorophenyl)-1-phenylprop-2-en-1-ol (0.12 g, 0.50 mmol, 1.0 equiv), $(PhSe)_2$ (16 mg, 50 µmol, 10 mol%), TAPT (25 mg, 50 µmol, 10 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 11 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 70% product formation. Purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) resulted in 58 mg (0.24 mmol, 48%) of 1-(2-chlorophenyl)-2-phenylprop-2-en-1-one as a yellowish oil.

*structural analysis was performed by 2D NMR in C_6D_6.

TLC: R_f = 0.48 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3056, 2926, 2847, 1703, 1669, 1591, 1490, 1435, 1356, 1233, 1125, 1066, 1036, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.52–7.30 (m, 9H), 6.23 (s, 1H), 5.81 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 196.4, 148.8, 138.9, 136.2, 131.5, 131.2, 130.1, 129.4, 129.3, 128.5, 128.4, 128.3, 126.6. **HRMS** (EI) calcd. for $[C_{15}H_{11}ClO]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 242.0498, found 242.0488.

2-(4-Methoxyphenyl)-1-phenylprop-2-en-1-one (205g-2)



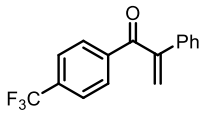
According to **General Procedure I:** 1-(4-methoxyphenyl)-1-phenylprop-2-en-1-ol (0.12 g, 0.51 mmol, 1.0 equiv), $(PhSe)_2$ (16 mg, 51 µmol, 10 mol%), TAPT (25 mg, 51 µmol, 10 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 10 h concentrated and 1,3-dinitrobenzene (43 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 25% product formation. Purification by column chromatography (PE to PE/Et_2O 30:1 to 10:1) resulted in 27 mg (0.12 mmol, 23%) of 2-(4-methoxyphenyl)-1-phenylprop-2-en-1-one as a yellowish oil.

*structural analysis was performed by 2D NMR.

*analytical data are in accordance with cited literature.[304]

TLC: R_f = 0.32 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3063, 3004, 2959, 2933, 2840, 1669, 1606, 1513, 1289, 1252, 1215, 1177, 1032, 838. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 7.95–7.86 (m, 2H), 7.61–7.50 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.98 (s, 1H), 5.53 (s, 1H), 3.81 (s, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 197.9, 159.8, 147.7, 133.0, 130.0, 129.5, 128.4, 128.3, 119.0, 114.0, 77.2, 55.3. **HRMS** (APCI) calcd. for $[C_{16}H_{15}O_2]^+$ $(M+H)^+$: m/z = 239.1067, found 239.1069.

2-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (205h-1)



According to **General Procedure I:** 1-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (0.14 g, 0.50 mmol, 1.0 equiv), $(PhSe)_2$ (16 mg, 50 µmol, 10 mol%), TAPT (25 mg, 50 µmol, 10 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 10 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 61% product formation. Purification by column chromatography (PE to PE/Et_2O 50:1 to 30:1) resulted in 61 mg (0.22 mmol, 44%) of 2-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one as a yellowish oil (inseparable phenyl(4-(trifluoromethyl)phenyl)methanone remains as a 12% impurity).

*structural analysis was performed by 2D NMR.

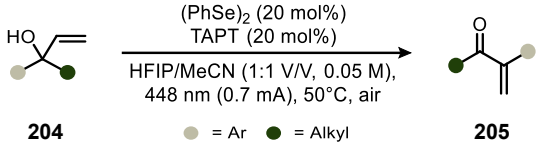
*analytical data are in accordance with cited literature.[305]

*in a single case, the signals of remaining impurities were compared with performed NMR analysis of the initial ketones used in the synthesis of the vinylic alcohols used in this transformation. Based on this result, all subsequent impurities of further reactions were anticipated to be of analogue origin.

TLC: R_f = 0.56 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3063, 1669, 1323, 1170, 1129, 1066, 984, 700. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ [ppm] = 8.02–7.95 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.45–7.32 (m, 5H), 6.14 (s, 1H), 5.71 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 196.3, 147.9, 140.0, 136.5, 130.1, 130.1, 128.7, 128.5, 127.1, 125.4 (q, *J* = 3.8 Hz, C-F), 122.6. **^{19}F NMR** (376 MHz, Chloroform-*d*): δ [ppm] = - 63.5, - 63.6 .**HRMS** (EI) calcd. for $[C_{13}H_{11}F_3O_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 276.0762, found 276.0752.

6.4.3. Synthesis of the aryl-alkyl substituted α,β-unsaturated ketones

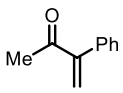
General Procedure J: Selenium-π-acid photoredox catalyzed reaction for aryl-alkyl substrates:



Scheme 124: Procedure for the selenium-π-acid photoredox dualcatalyzed synthesis of aryl-alkyl substituted α,β-unsaturated ketones **205**.

A photovial was equipped with the corresponding vinylic alcohol (0.50 mmol, 1.0 equiv), $(PhSe)_2$ (20 mol%) and TAPT (20 mol%) and both diluted with a 1:1 volumetric mixture of HFIP and MeCN (0.05 M). The photovial was closed with a screw cap, cannulas were added to allow for air exchange and the vial was placed in the heated (50 °C) irradiation setup. The mixture was irradiated (448 nm, 0.7 mA) for the given amount of time and consecutively the solvent removed under reduced pressure. 1,3-dinitrobenzene (0.50 equiv) was added (unless otherwise noted) as internal standard and the crude reaction mixture dissolved in 2.0 mL of $CDCl_3$. After determination of the NMR Yield, the NMR sample was added back with $CHCl_3$ and again concentrated. Purification by column chromatography resulted in the respective prop-2-en-1-ones.

3-Phenylbut-3-en-2-one (205a)



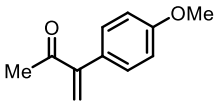
According to **General Procedure J:** 2-phenylbut-3-en-2-ol (75 mg, 0.51 mmol, 1.0 equiv), $(PhSe)_2$ (32 mg, 0.10 mmol, 20 mol%), TAPT (49 mg, 0.10 mmol, 20 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 11 h concentrated and 1,3-dinitrobenzene (43 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 57% product formation. Purification by column chromatography (PE to PE/acetone/DCM 40:1:1) resulted in 27 mg (0.18 mmol, 36%) of 3-phenylbut-3-en-2-one as a yellowish oil (inseparable acetophenone remains as a 6% impurity).

*analytical data are in accordance with cited literature.[306]

*in a single case, the signals of remaining impurities were compared with performed NMR analysis of the initial ketones used in the synthesis of the vinylic alcohols used in this transformation. Based on this result, all subsequent impurities of further reactions were anticipated to be of analogue origin.

TLC: R_f = 0.24 (PE/acetone/DCM 40:1:1). **IR** (ATR): ṽ [cm^{-1}] = 3056, 3026, 2926, 1684, 1360, 1170, 775, 704. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.41–7.25 (m, 5H), 6.18 (d, *J* = 0.6 Hz, 1H), 5.97 (d, *J* = 0.6 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 199.4, 149.5, 137.0, 128.5, 128.2, 128.1, 125.8, 27.4. **HRMS** (APCI) calcd. for $[C_{10}H_{11}O]^+$ $(M+H)^+$: m/z = 174.0804, found 174.0805.

3-(4-Methoxyphenyl)but-3-en-2-one (205k)



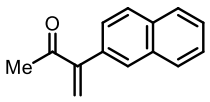
According to **General Procedure J:** 2-(4-methoxyphenyl)but-3-en-2-ol (90 mg, 0.51 mmol, 1.0 equiv), $(PhSe)_2$ (32 mg, 0.10 mmol, 20 mol%), TAPT (49 mg, 0.10 mmol, 20 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 10 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 27% product formation. Purification by column chromatography (PE/Et_2O 30:1 to 3:1) resulted in 9.8 mg (0.15 mmol, 11%) of 3-(4-methoxyphenyl)but-3-en-2-one as a yellowish oil (inseparable 1-(4-methoxyphenyl)ethan-1-one remains as a 25% impurity).

*analytical data are in accordance with cited literature.[304]

*in a single case, the signals of remaining impurities were compared with performed NMR analysis of the initial ketones used in the synthesis of the vinylic alcohols used in this transformation. Based on this result, all subsequent impurities of further reactions were anticipated to be of analogue origin.

TLC: R_f = 0.36 (PE/Et_2O 3:1). **IR** (ATR): ṽ [cm^{-1}] = 3444, 2937, 2840, 1673, 1599, 1513, 1252, 1170, 1028, 834. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.33–7.22 (m, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.11 (d, *J* = 0.6 Hz, 1H), 5.95 (d, *J* = 0.6 Hz, 1H), 3.84 (s, 3H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 199.9, 159.6, 148.9, 130.6, 129.7, 124.6, 113.6, 55.3, 27.5. **HRMS** (EI) calcd. for $[C_{11}H_{12}O_2]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 176.0829, found 176.0837.

3-(Naphthalen-2-yl)but-3-en-2-one (205m)



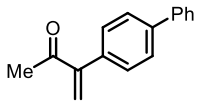
According to **General Procedure J:** 2-(naphthalen-2-yl)but-3-en-2-ol (99 mg, 0.50 mmol, 1.0 equiv), $(PhSe)_2$ (31 mg, 0.10 mmol, 20 mol%), TAPT (49 mg, 0.10 mmol, 20 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 10 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 29% product formation. Purification by automated column chromatography (toluene and *n*-hexane to *n*-hexane/Et_2O 99:1 to 90:10) resulted in 15 mg (75 µmol, 15%) of 3-(naphthalen-2-yl)but-3-en-2-one as a yellowish oil (inseparable 1-(naphthalen-2-yl)ethan-1-one remains as a 37% impurity).

*analytical data are in accordance with cited literature.[307]

*in a single case, the signals of remaining impurities were compared with performed NMR analysis of the initial ketones used in the synthesis of the vinylic alcohols used in this transformation. Based on this result, all subsequent impurities of further reactions were anticipated to be of analogue origin.

TLC: R_f = 0.20 (toluene). **IR** (ATR): ṽ [cm^{-1}] = 3056, 1677, 1628, 1360, 1230, 1192, 1159, 1129, 861, 623, 752. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.89–7.76 (m, 3H), 7.67–7.50 (m, 1H), 7.49 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.42 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.25 (d, *J* = 0.5 Hz, 1H), 6.08 (d, *J* = 0.6 Hz, 1H), 2.49 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 199.6, 149.6, 134.5, 133.1, 133.0, 128.2, 127.7, 127.6, 126.3, 126.2, 126.0, 27.6. **HRMS** (EI) calcd. for $[C_{14}H_{12}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 196.0888, found 196.0886.

3-([1,1'-Biphenyl]-4-yl)but-3-en-2-one (205n)



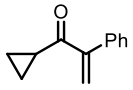
According to **General Procedure J:** 2-([1,1'-biphenyl]-4-yl)but-3-en-2-ol (0.11 g, 0.50 mmol, 1.0 equiv), $(PhSe)_2$ (31 mg, 0.10 mmol, 20 mol%), TAPT (49 mg, 0.10 mmol, 20 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 10 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 47% product formation. Purification by column chromatography (PE to PE/toluene 10:1 to 1:1 to toluene) resulted in 43 mg (0.20 mmol, 39%) of 3-([1,1'-biphenyl]-4-yl)but-3-en-2-one as a yellowish oil (inseparable 1-([1,1'-biphenyl]-4-yl)ethan-1-one remains as a 14% impurity).

*analytical data are in accordance with cited literature.[308]

*in a single case, the signals of remaining impurities were compared with performed NMR analysis of the initial ketones used in the synthesis of the vinylic alcohols used in this transformation. Based on this result, all subsequent impurities of further reactions were anticipated to be of analogue origin.

TLC: R_f = 0.32 (toluene). **IR** (ATR): ṽ [cm^{-1}] = 3056, 3030, 2926, 1669, 1602, 1487, 1401, 1360, 1323, 1267, 1080, 950, 842, 771, 697. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.66–7.53 (m, 4H), 7.51-7.30 (m, 5H), 6.21 (d, *J* = 0.5 Hz, 1H), 6.05 (d, *J* = 0.5 Hz, 1H), 2.49 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 199.9, 159.6, 148.9, 130.6, 129.7, 124.6, 113.6, 55.3, 27.5. **HRMS** (APCI) calcd. for $[C_{16}H_{15}O]^+$ $(M+H)^+$: m/z = 223.1117, found 223.1117.

1-Cyclopropyl-2-phenylprop-2-en-1-one (205p)

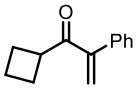


According to **General Procedure J:** 1-cyclopropyl-1-phenylprop-2-en-1-ol (88 mg, 0.50 mmol, 1.0 equiv), $(PhSe)_2$ (31 mg, 0.10 mmol, 20 mol%), TAPT (49 mg, 0.10 mmol, 20 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 18 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 38% product formation. Purification by column chromatography (PE to PE/Et_2O 50:1 to 10:1) resulted in 24 mg (0.14 mmol, 28%) of 1-cyclopropyl-2-phenylprop-2-en-1-one as a yellowish oil (inseparable cyclopropyl(phenyl)methanone remains as a 25% impurity).

*in a single case, the signals of remaining impurities were compared with performed NMR analysis of the initial ketones used in the synthesis of the vinylic alcohols used in this transformation. Based on this result, all subsequent impurities of further reactions were anticipated to be of analogue origin.

TLC: R_f = 0.52 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 3060, 3011, 1669, 1386, 1043, 1013, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.42–7.29 (m, 5H), 6.14 (d, *J* = 0.9 Hz, 1H), 5.85 (d, *J* = 0.8 Hz, 1H), 2.27 (tt, *J* = 7.8, 4.6 Hz, 1H), 1.24–1.13 (m, 2H), 1.02–0.89 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 202.5, 150.1, 137.3, 132.7, 128.3, 128.2, 123.0, 19.0, 12.2. **HRMS** (EI) calcd. for $[C_{12}H_{12}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 172.0888, found 172.0881.

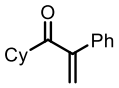
1-Cyclobutyl-2-phenylprop-2-en-1-one (205q)



According to **General Procedure J:** 1-cyclobutyl-1-phenylprop-2-en-1-ol (94 mg, 0.50 mmol, 1.0 equiv), $(PhSe)_2$ (31 mg, 0.10 mmol, 20 mol%), TAPT (49 mg, 0.10 mmol, 20 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 10 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 70% product formation. Purification by automated column chromatography (PE to PE/Et_2O 99:1 to 90:10) resulted in 29 mg (0.15 mmol, 31%) of 1-cyclobutyl-2-phenylprop-2-en-1-one as a yellowish oil.

TLC: R_f = 0.38 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 2981, 2944, 2866, 1677, 1494, 1356, 1140, 984, 775, 700. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.43–7.24 (m, 5H), 6.02 (d, *J* = 0.8 Hz, 1H), 5.88 (d, *J* = 0.8 Hz, 1H), 3.76 (pd, *J* = 8.7, 1.1 Hz, 1H), 2.48–2.26 (m, 2H), 2.21–2.07 (m, 2H), 2.06–1.93 (m, 1H), 1.91-1.73 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 202.8, 148.1, 137.4, 128.3, 128.2, 128.0, 124.4, 42.8, 25.2, 17.9. **HRMS** (EI) calcd. for $[C_{13}H_{14}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 186.1045, found 186.1044.

1-Cyclohexyl-2-phenylprop-2-en-1-one (205r)



According to **General Procedure J:** 1-cyclohexyl-1-phenylprop-2-en-1-ol (0.11 g, 0.50 mmol, 1.0 equiv), $(PhSe)_2$ (31 mg, 0.10 mmol, 20 mol%), TAPT (49 mg, 0.10 mmol, 20 mol%) and dissolved in a 1:1 mixture of HFIP/MeCN (10 mL, 0.05 M). The reaction was irradiated for 11 h concentrated and 1,3-dinitrobenzene (42 mg, 0.25 mmol, 0.50 equiv) was added as internal standard and NMR analysis resulted in 84% product formation. Purification by column chromatography (PE to PE/Et_2O 50:1) resulted in 36 mg (0.17 mmol, 33%) of 1-cyclohexyl-2-phenylprop-2-en-1-one as a yellowish oil.

*analytical data are in accordance with cited literature.[309]

TLC: R_f = 0.52 (PE/Et_2O 10:1). **IR** (ATR): ṽ [cm^{-1}] = 2929, 2855, 1677, 995, 909, 775, 730. **^{1}H NMR** (300 MHz, Chloroform-*d*): δ [ppm] = 7.48–7.15 (m, 5H), 5.95 (s, 1H), 5.84 (s, 1H), 2.92 (tt, *J* = 11.4, 3.4 Hz, 1H), 1.98–1.56 (m, 5H), 1.53–1.09 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ [ppm] = 206.4, 149.3, 137.5, 128.3, 128.1, 128.0, 122.2, 46.9, 29.0, 25.9, 25.7. **HRMS** (EI) calcd. for $[C_{15}H_{18}O]^{+\cdot}$ $(M)^{+\cdot}$: m/z = 214.1358, found 214.1350.

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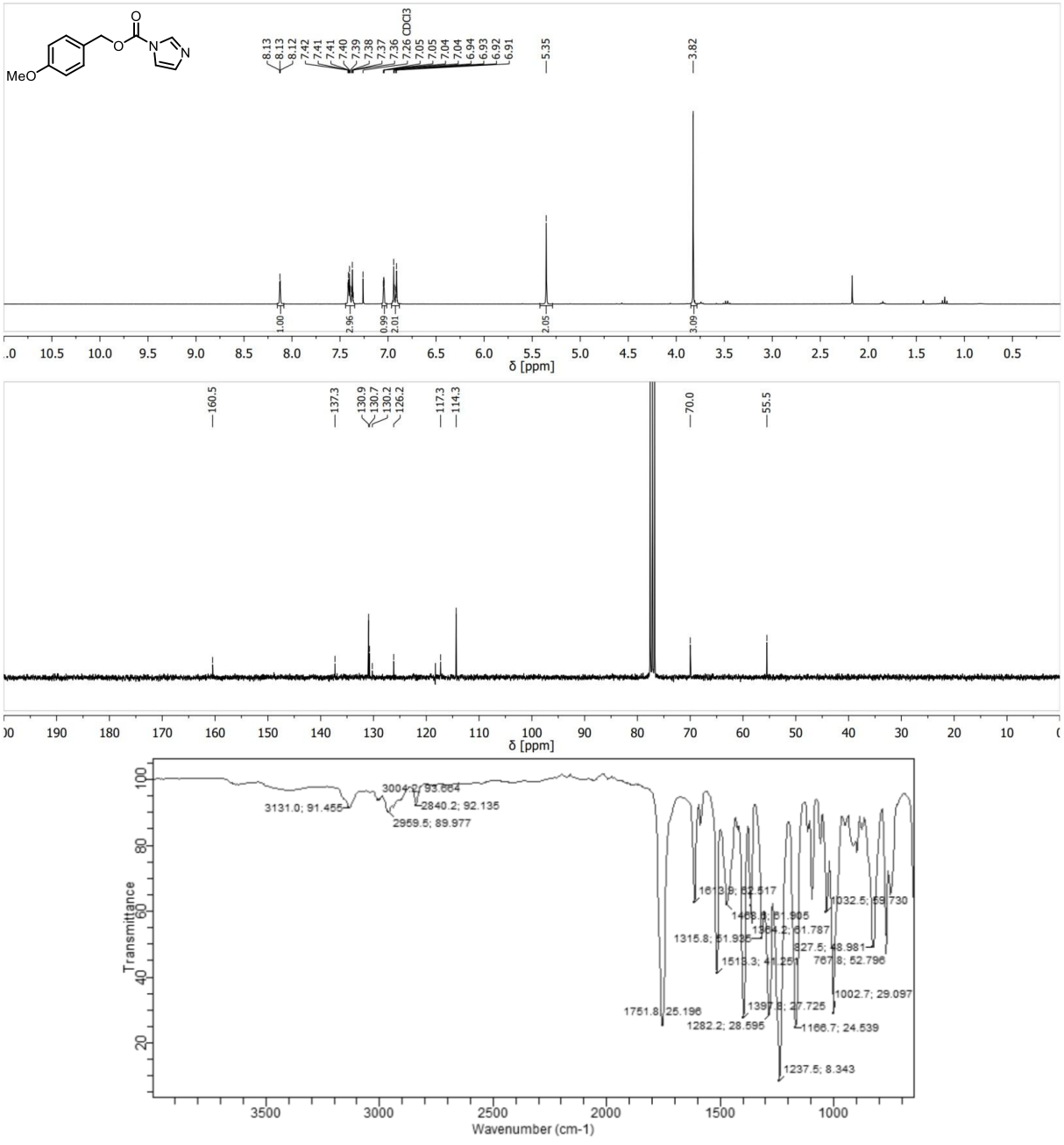
8 Appendix

8.1 Spectra of project “1,3-dioxan-2-ones” – starting materials

4-Methoxybenzyl 1*H*-imidazole-1-carboxylate (143)

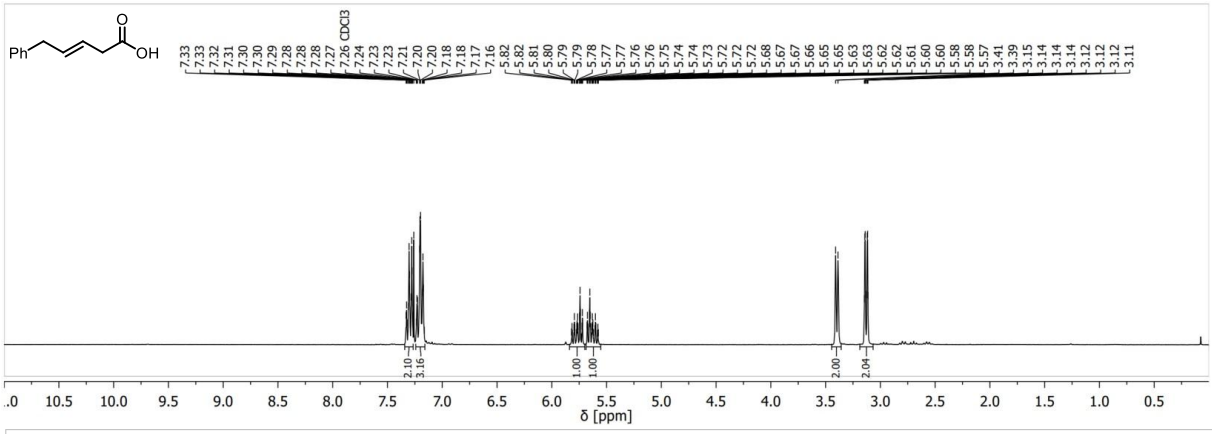
^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**

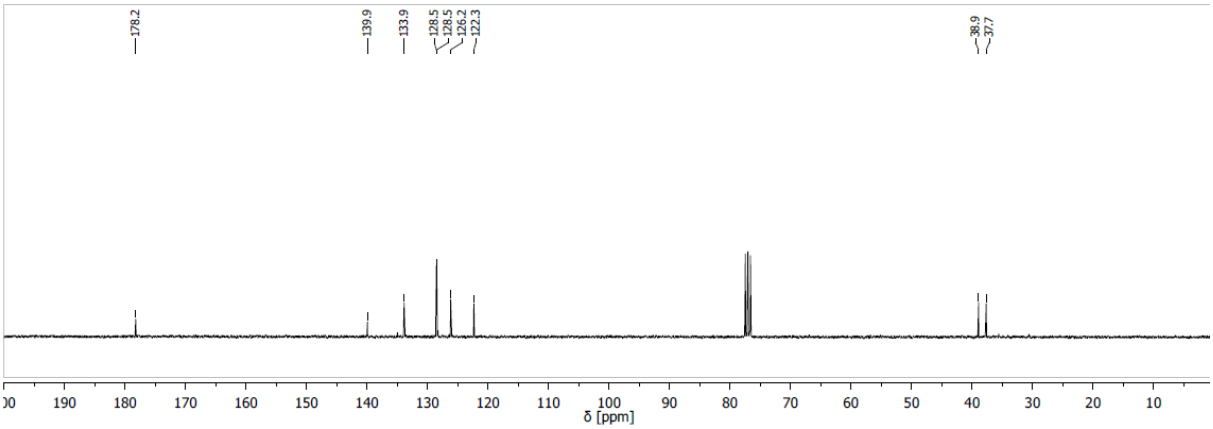


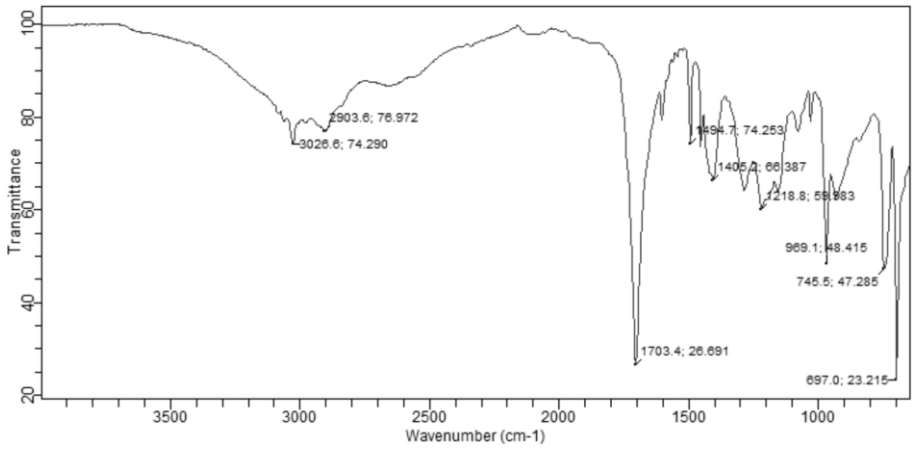
Spectra of project “1,3-dioxan-2-ones” – starting materials

(*E*)-5-Phenylpent-3-enoic acid

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



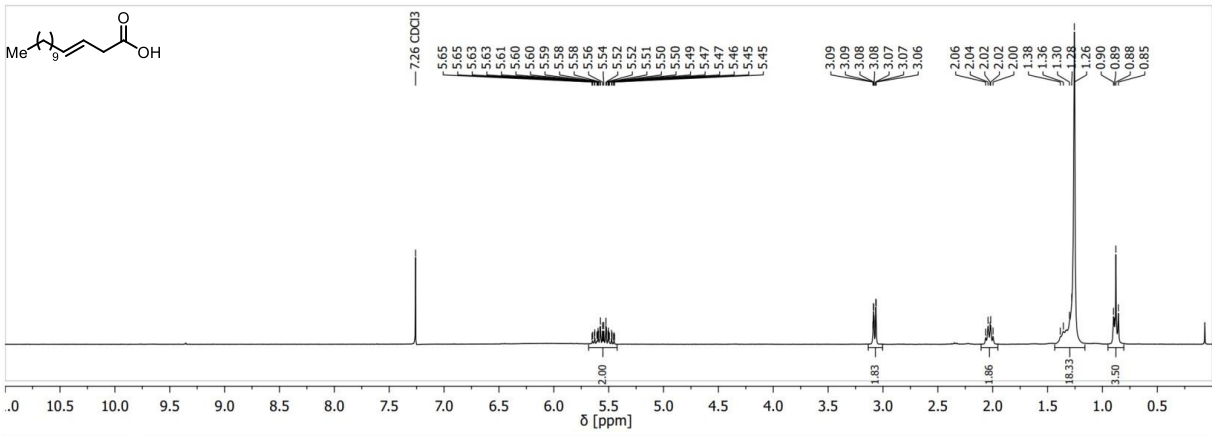


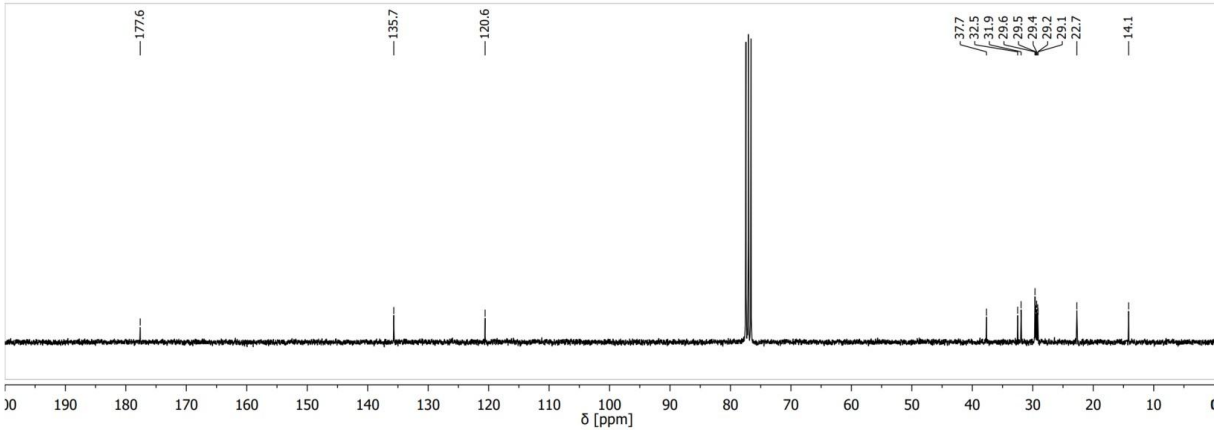


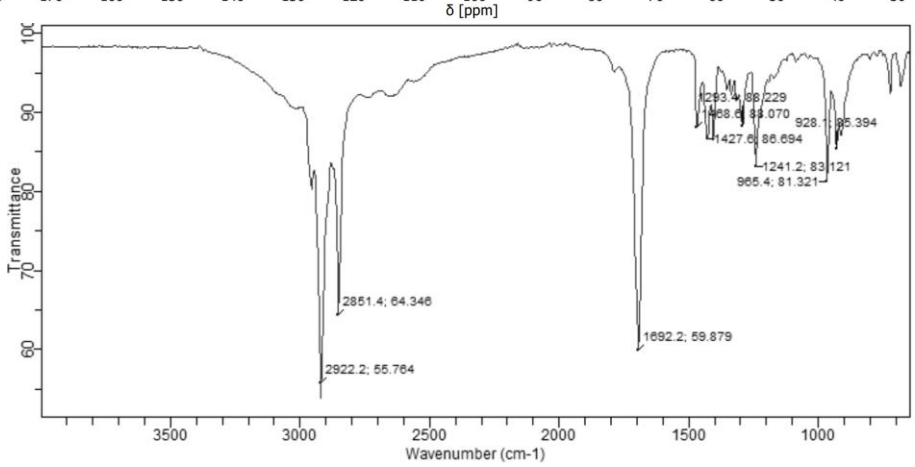
Spectra of project “1,3-dioxan-2-ones” – starting materials

(*E*)-Tetradec-3-enoic acid

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-d**, IR**



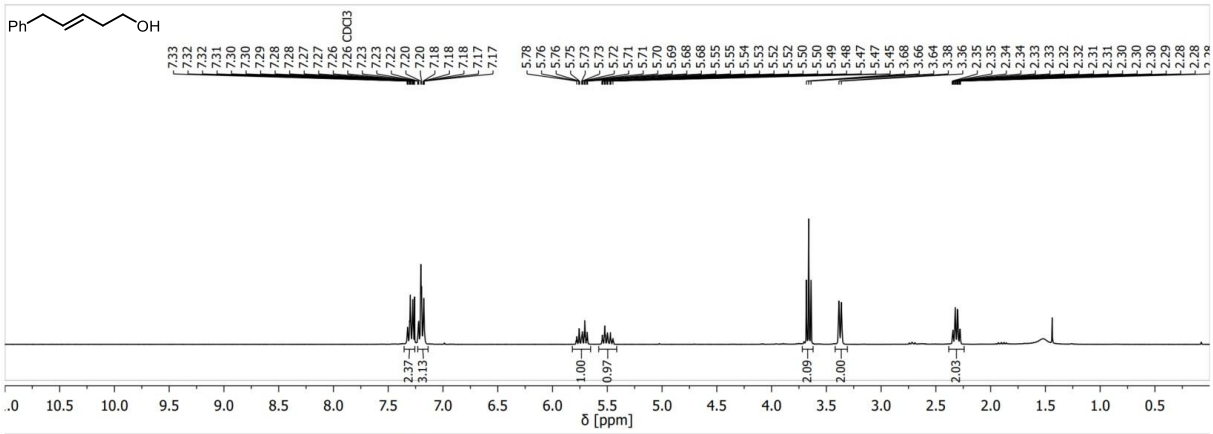


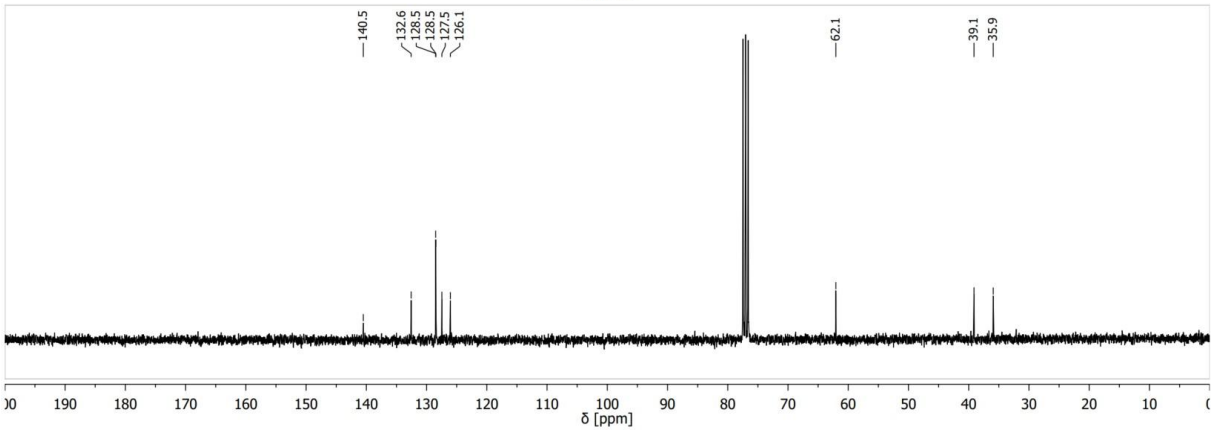


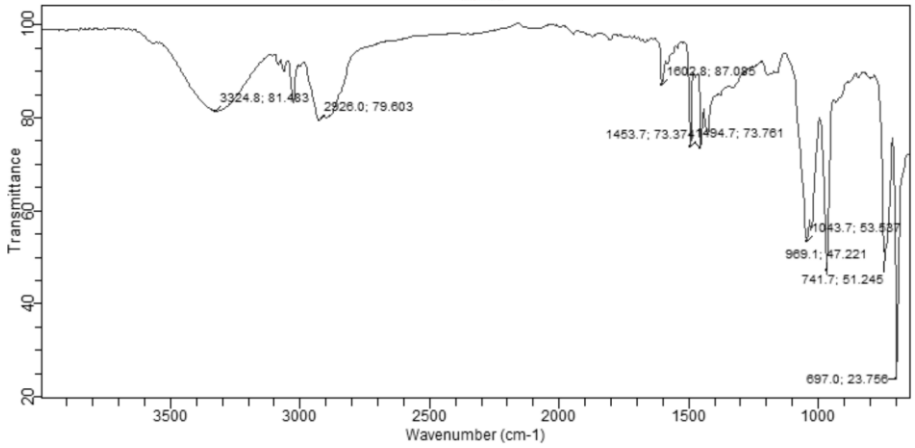
Spectra of project “1,3-dioxan-2-ones” – starting materials

(*E*)-5-Phenylpent-3-en-1-ol (147a)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



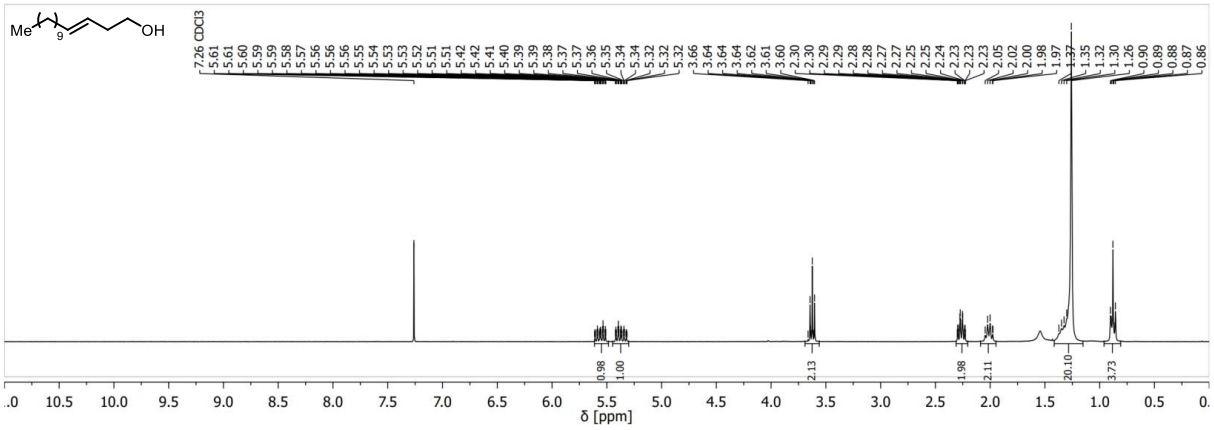


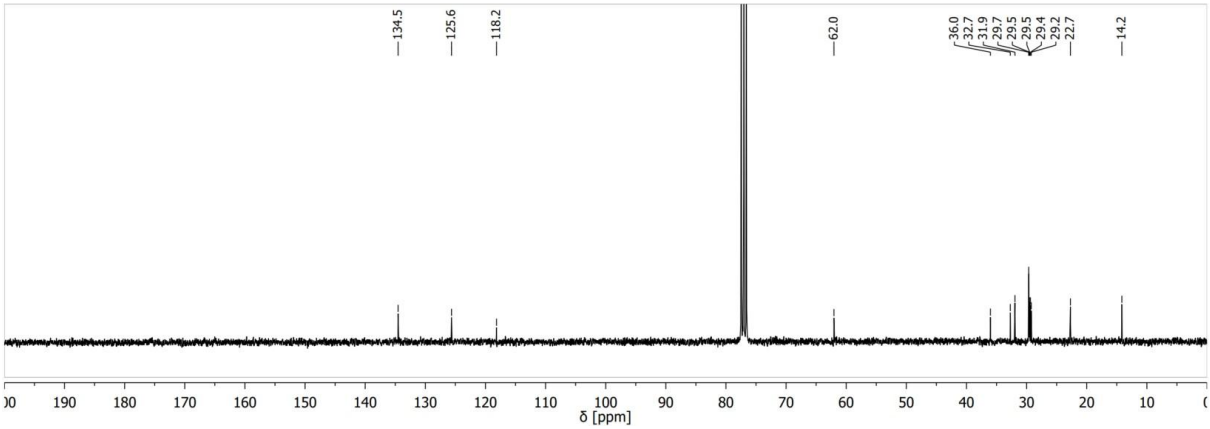


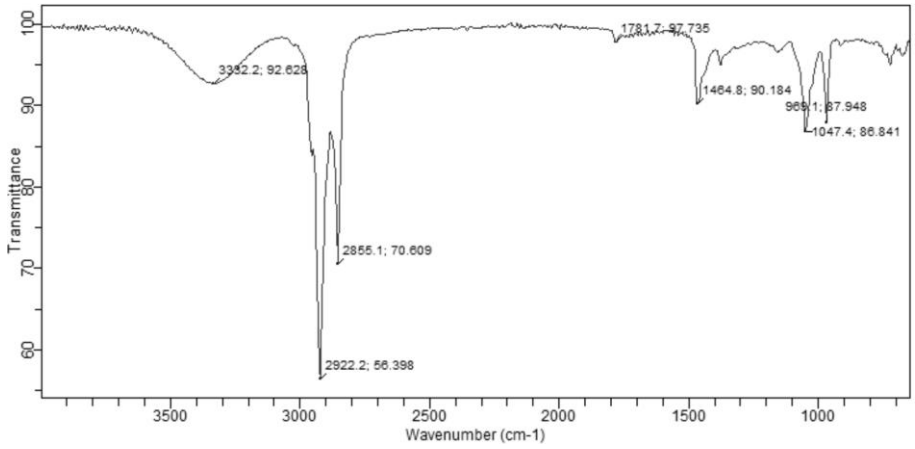
Spectra of project “1,3-dioxan-2-ones” – starting materials

(*E*)-Tetradec-3-en-1-ol (147b)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



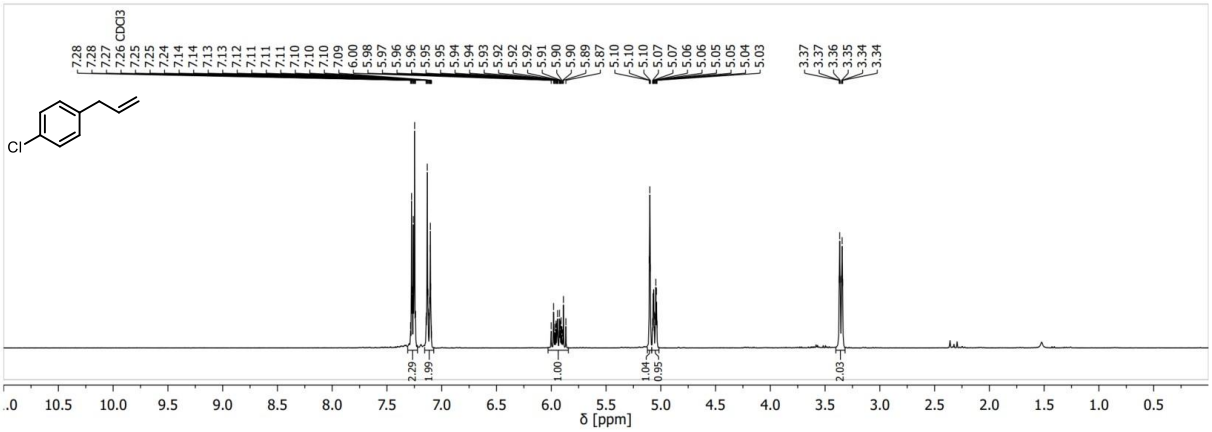


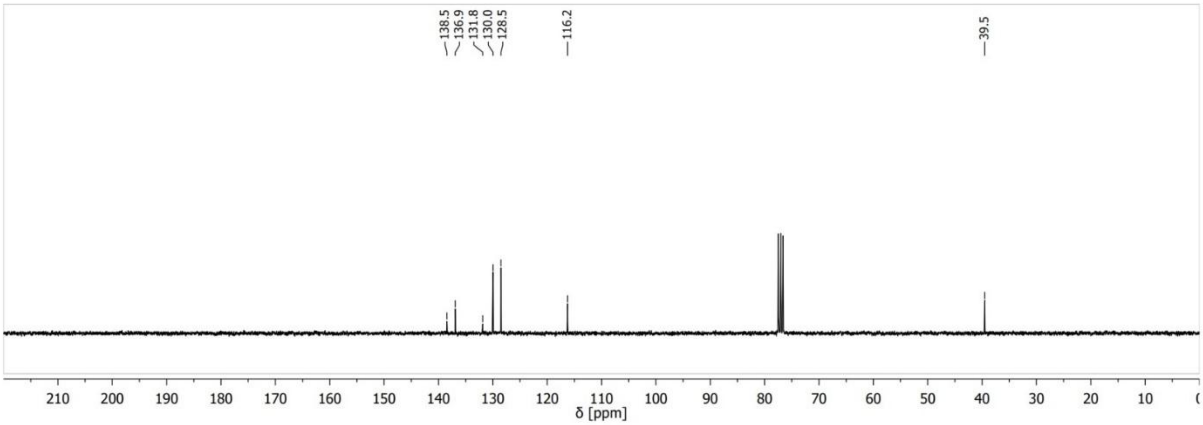


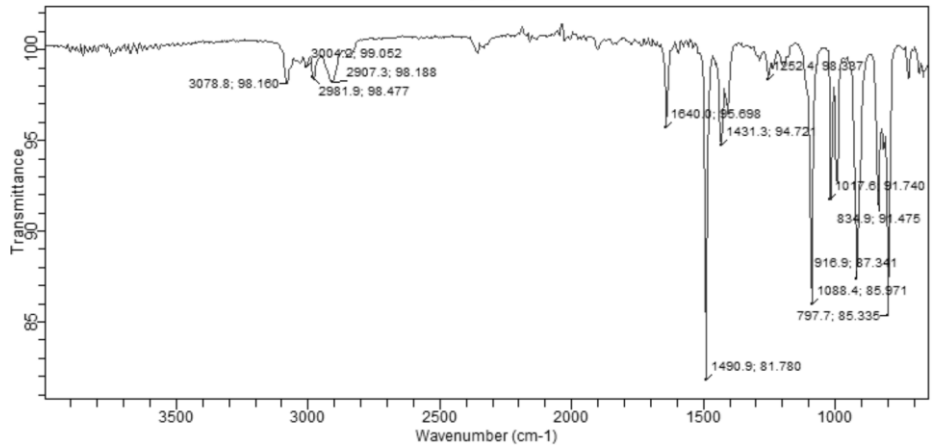
Spectra of project “1,3-dioxan-2-ones” – starting materials

1-Allyl-4-chlorobenzene (153a)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



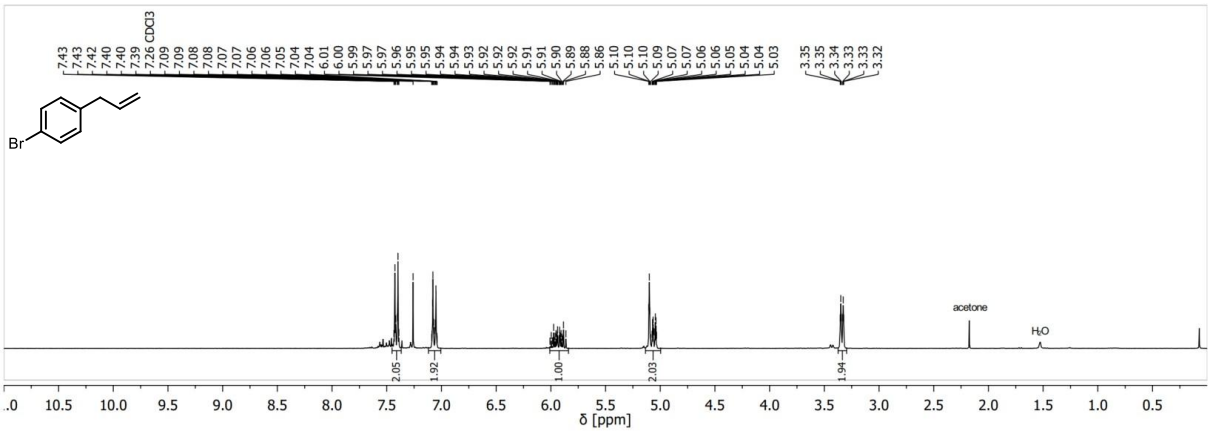


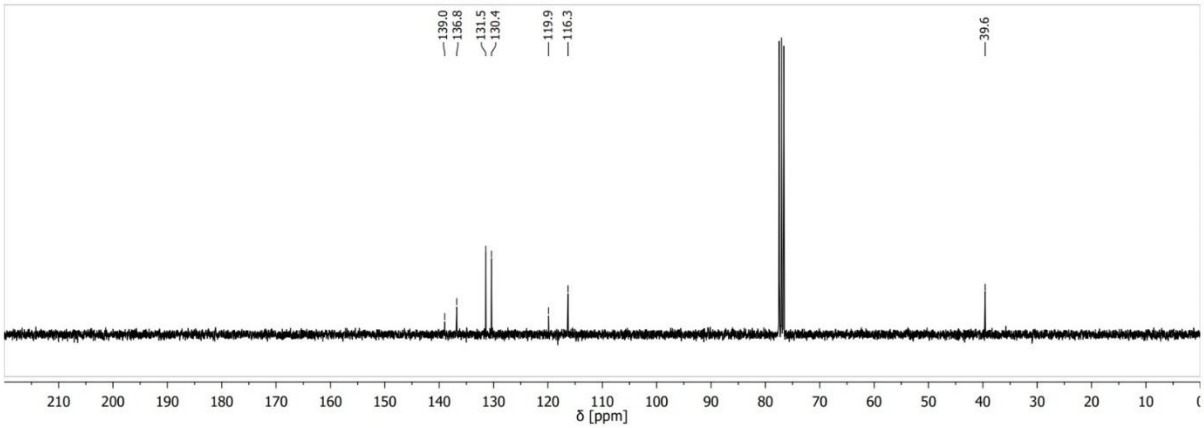


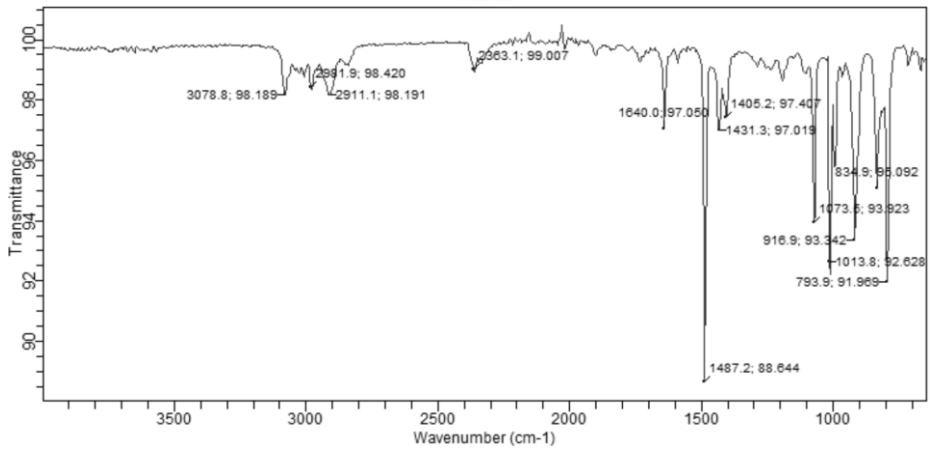
Spectra of project “1,3-dioxan-2-ones” – starting materials

1-Allyl-4-bromobenzene (153b)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**

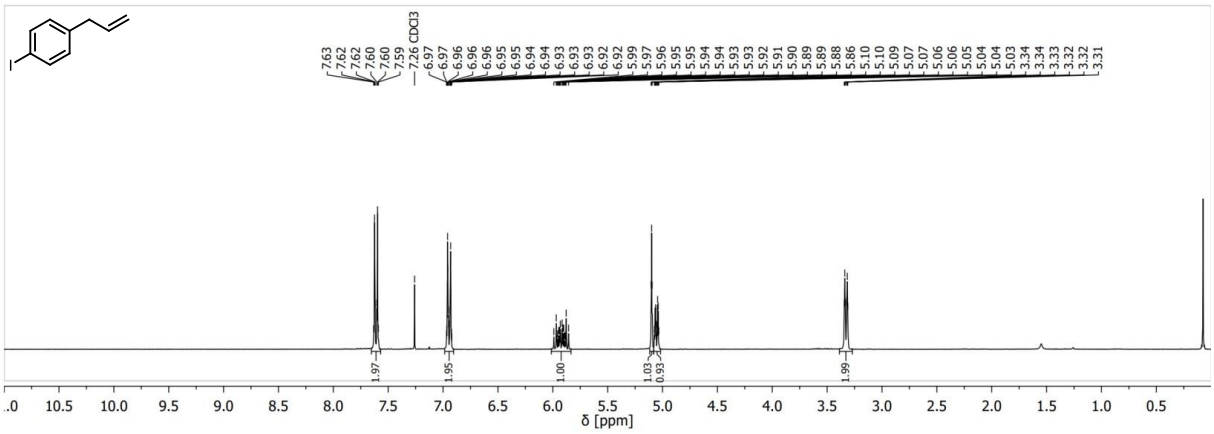


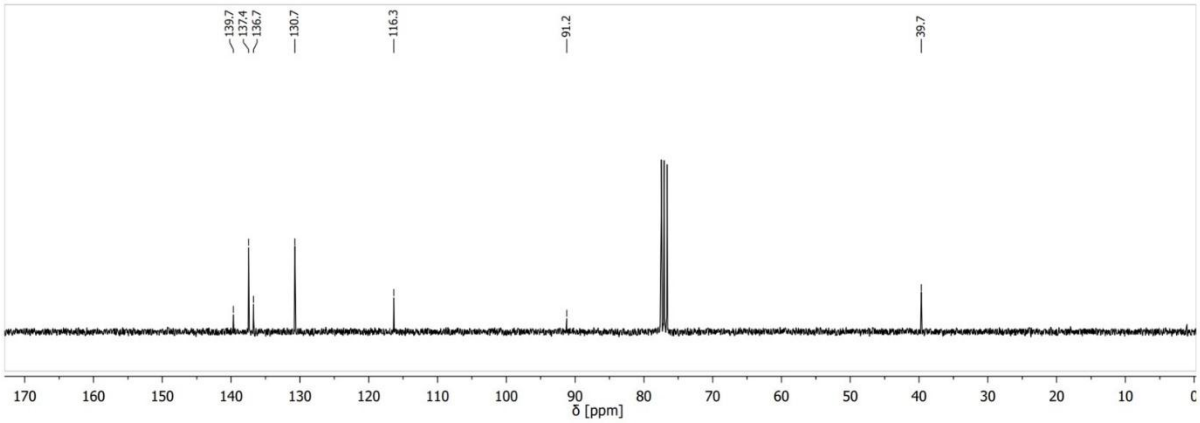


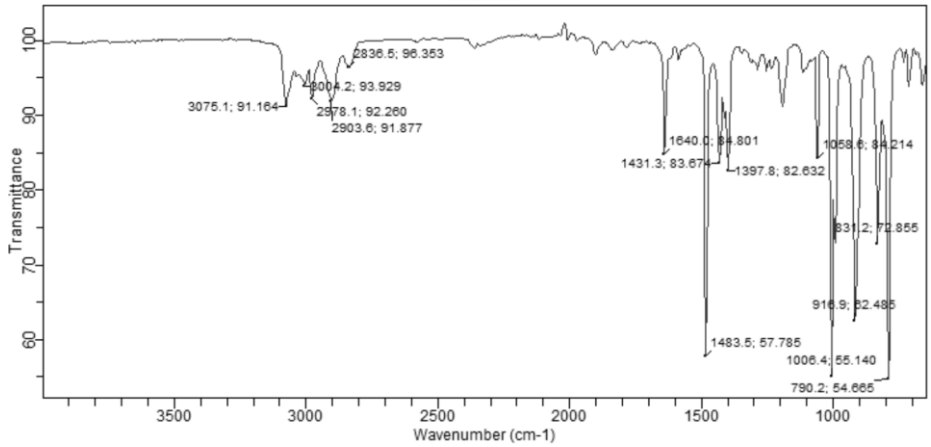


1-Allyl-4-iodobenzene (153c)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



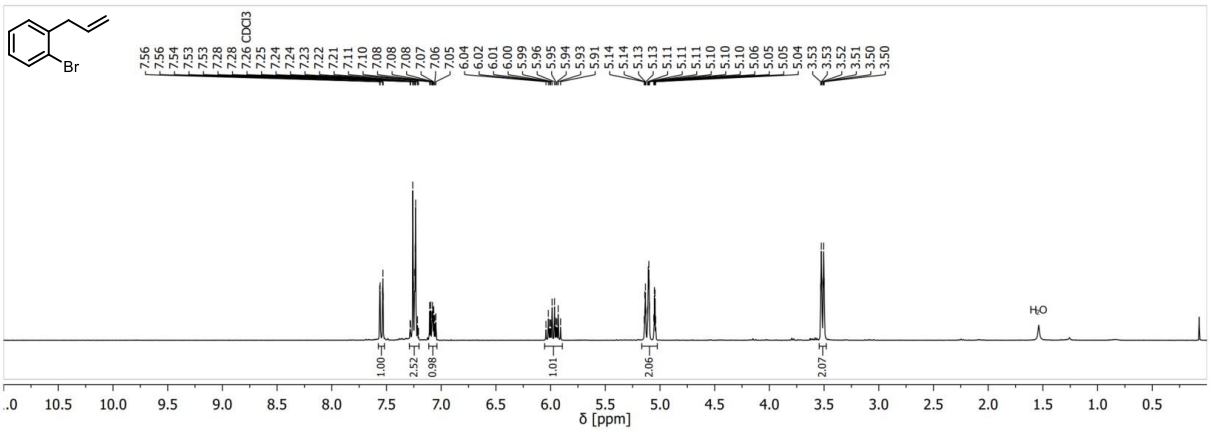


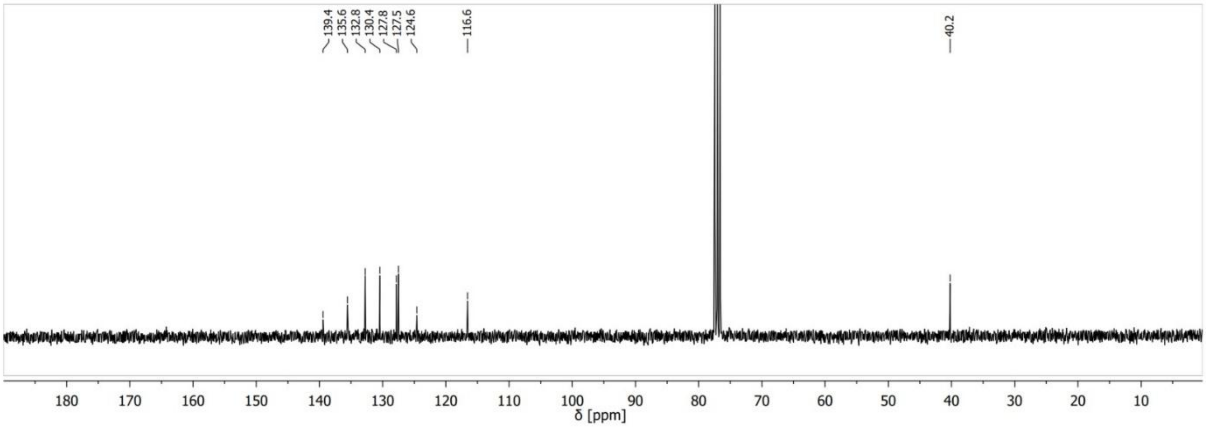


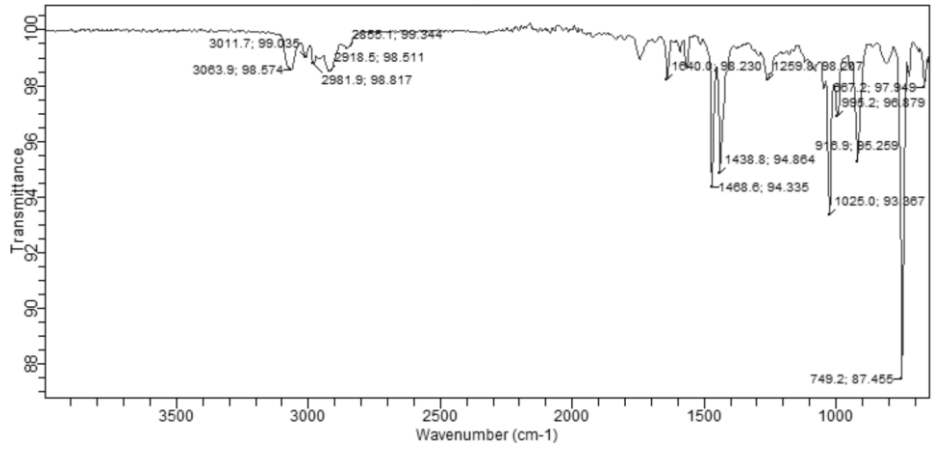
Spectra of project “1,3-dioxan-2-ones” – starting materials

1-Allyl-2-bromobenzene (153d)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



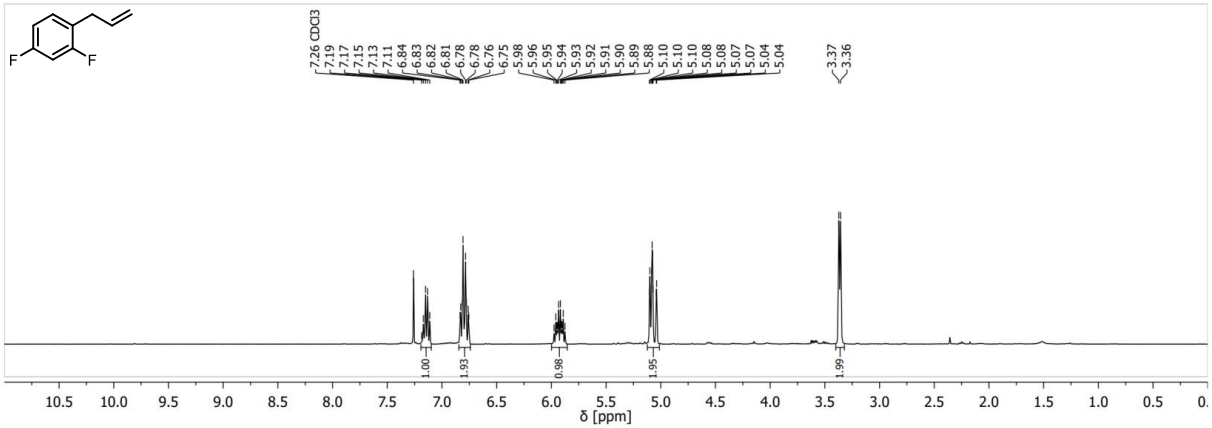


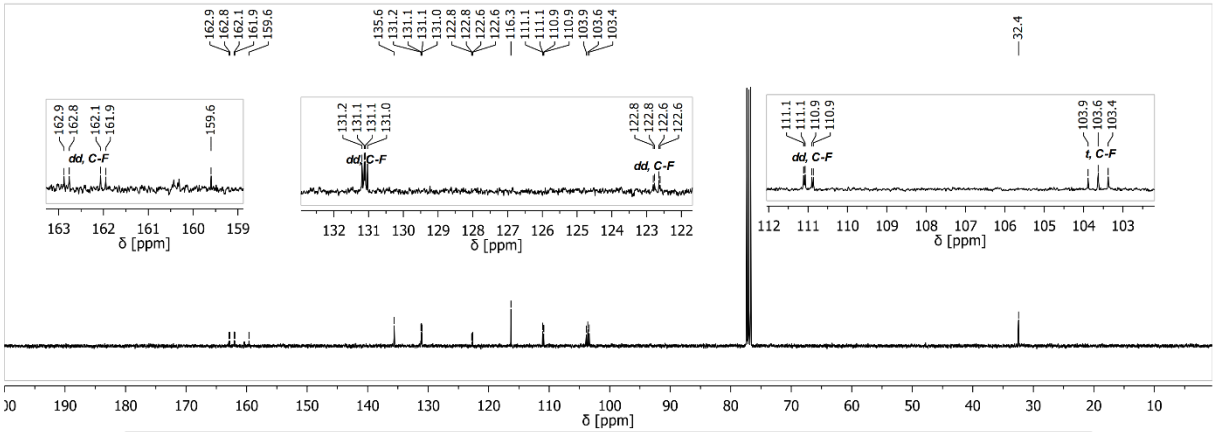


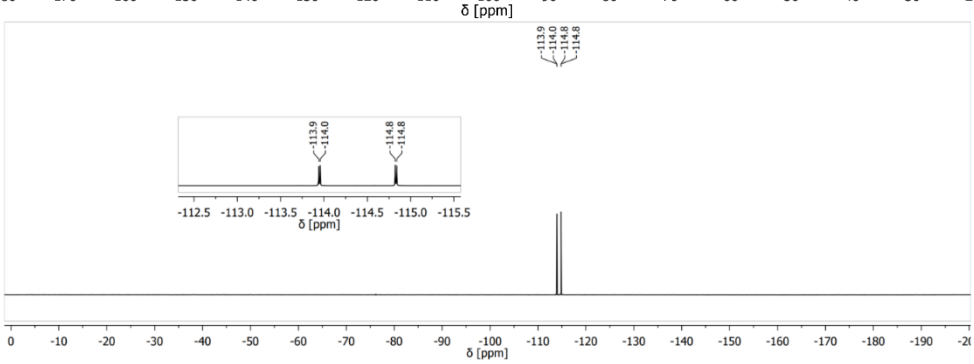
Spectra of project “1,3-dioxan-2-ones” – starting materials

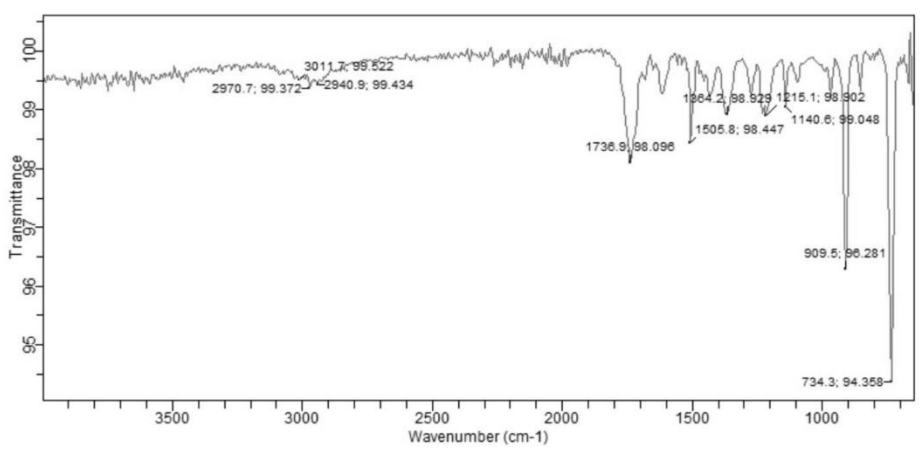
1-Allyl-2,4-difluorobenzene (153e)

^{1}H NMR (400 MHz), **^{13}C NMR** (101 MHz), **^{19}F{^{1}H} NMR** (376 MHz): Chloroform-*d*, **IR**





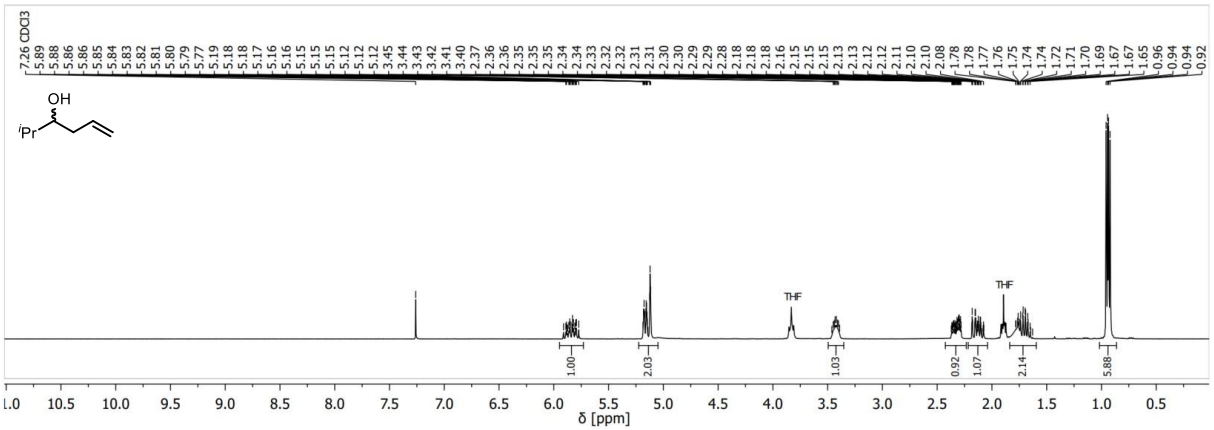




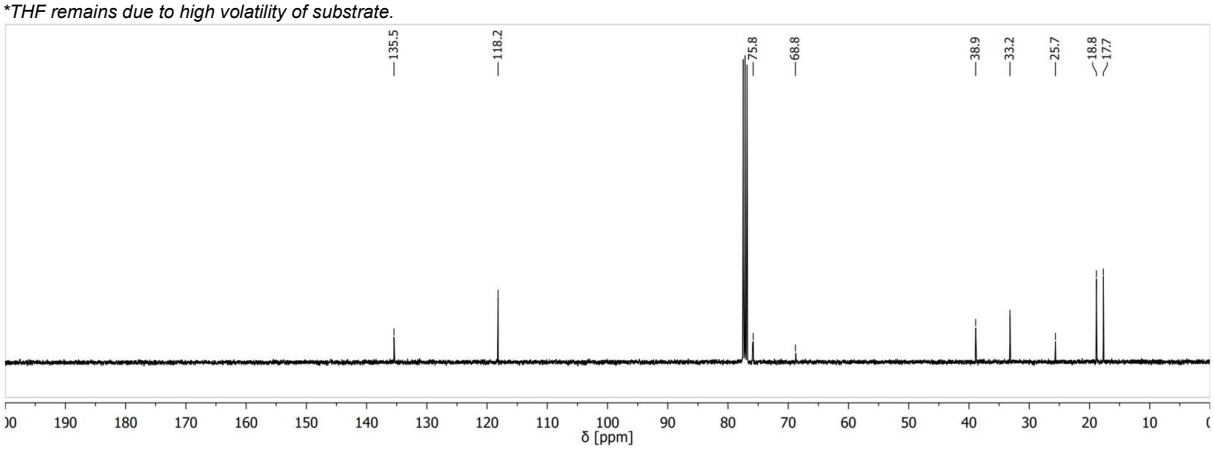
Spectra of project “1,3-dioxan-2-ones” – starting materials

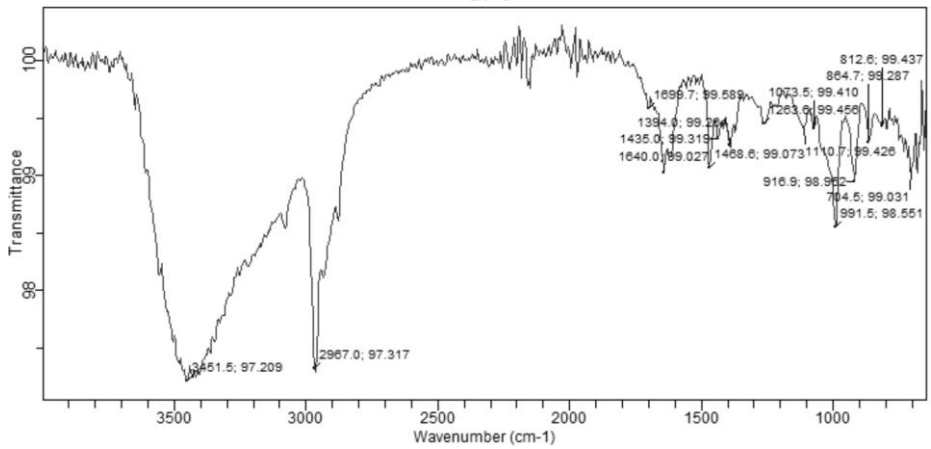
2-Methylhex-5-en-3-ol (152a)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



**THF remains due to high volatility of substrate.*

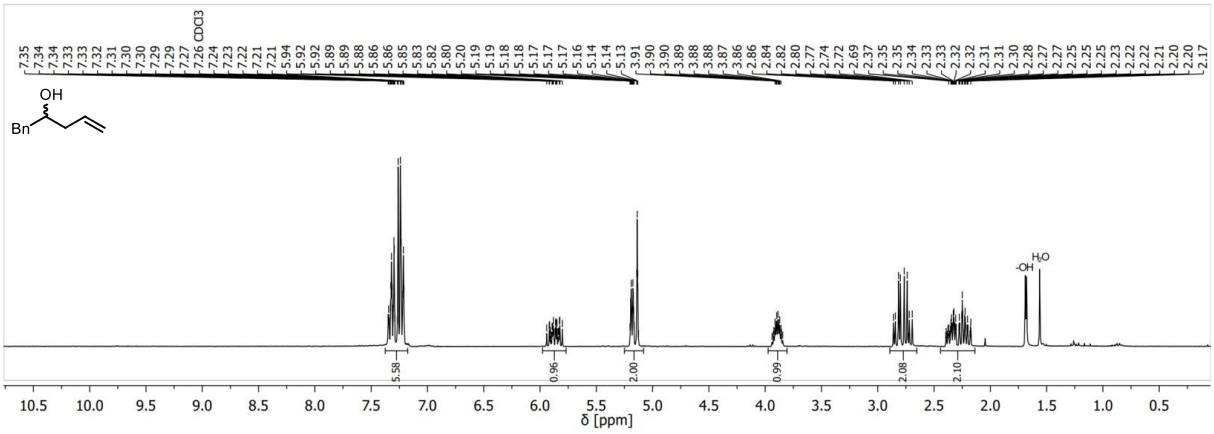


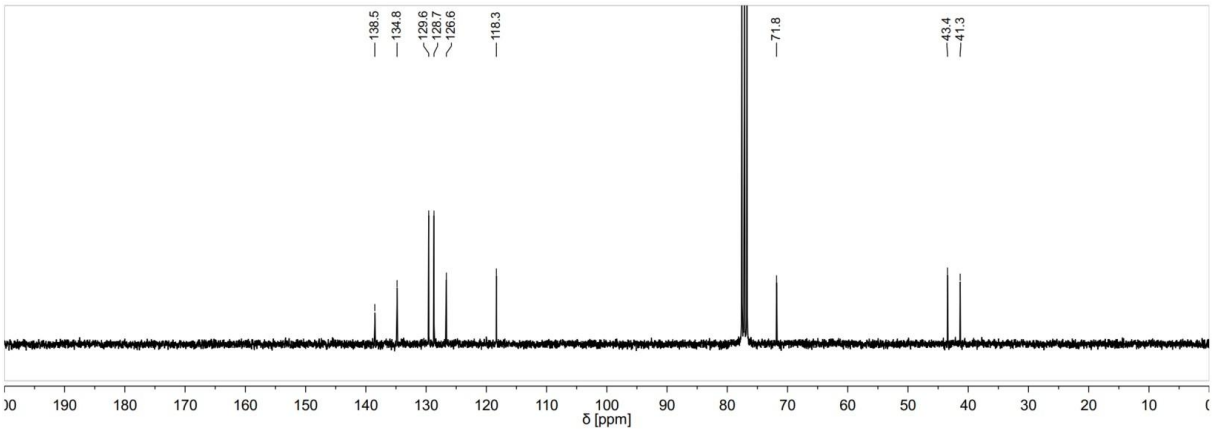


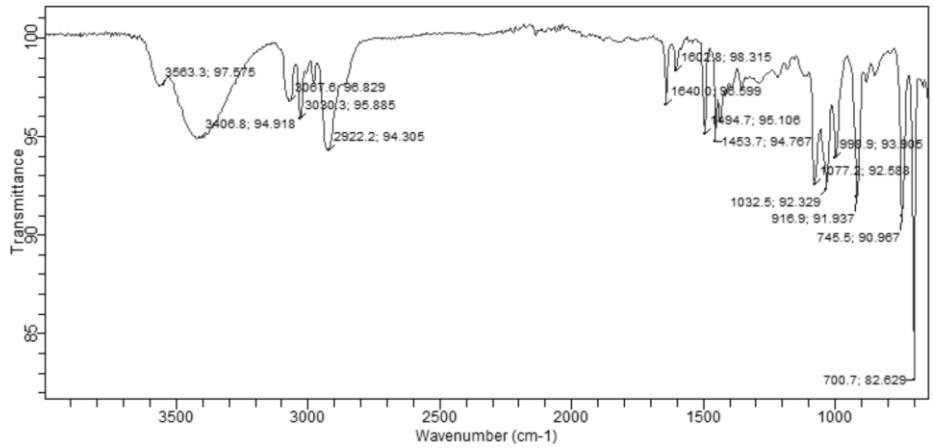
Spectra of project “1,3-dioxan-2-ones” – starting materials

1-Phenylpent-4-en-2-ol (152b)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



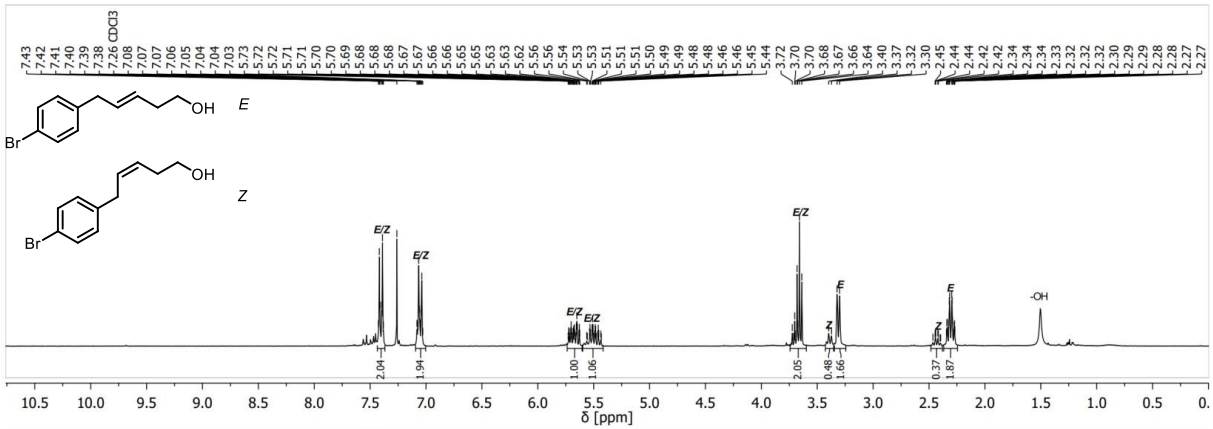


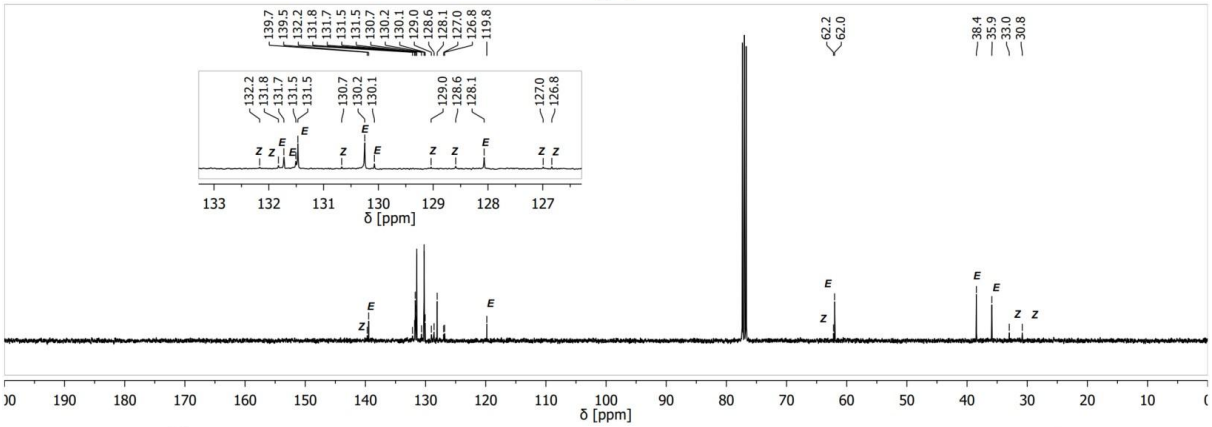


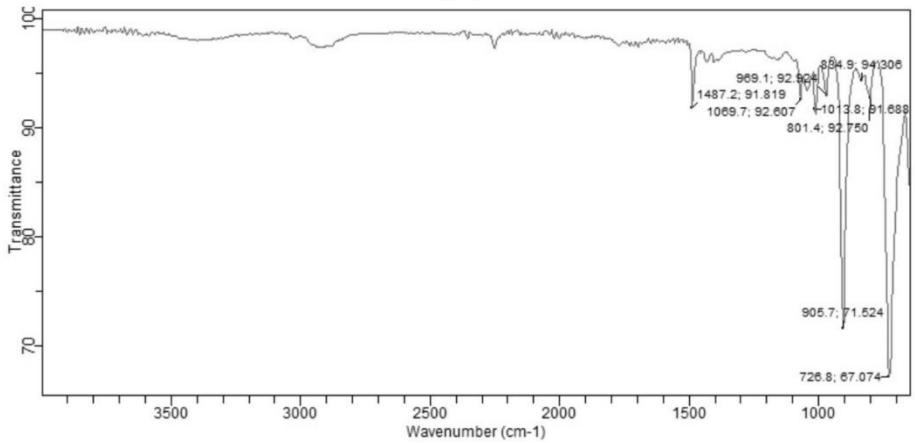
Spectra of project “1,3-dioxan-2-ones” – starting materials

5-(4-Bromophenyl)pent-3-en-1-ol (142a)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

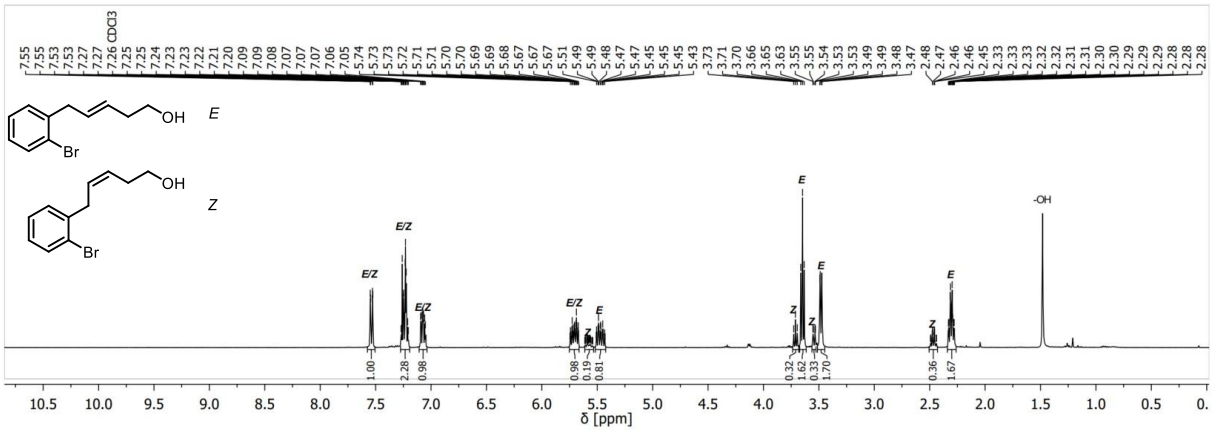


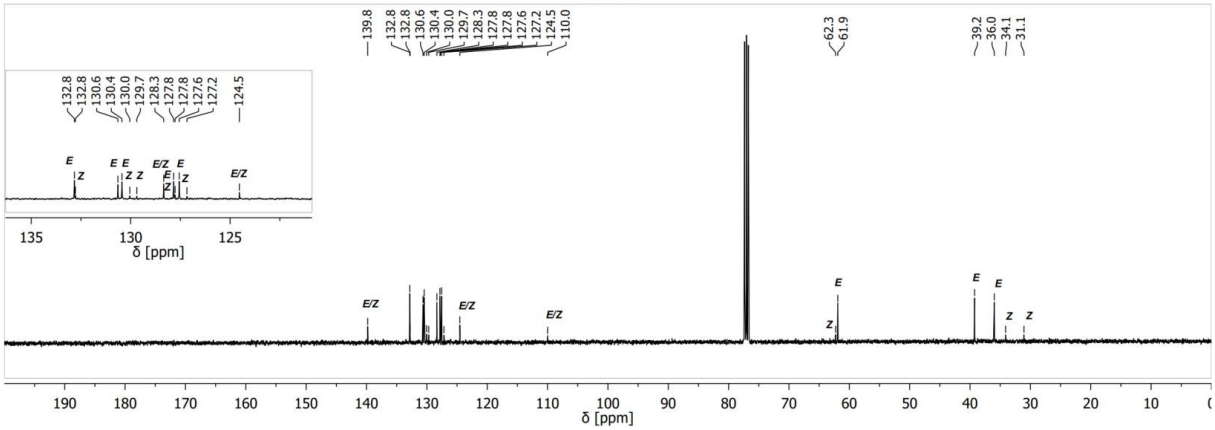


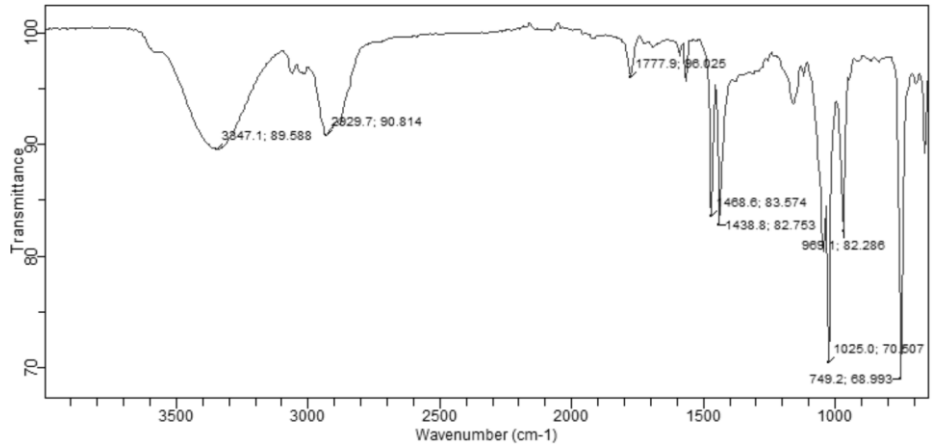


5-(2-Bromophenyl)pent-3-en-1-ol (142b)

^{1}H NMR (400 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



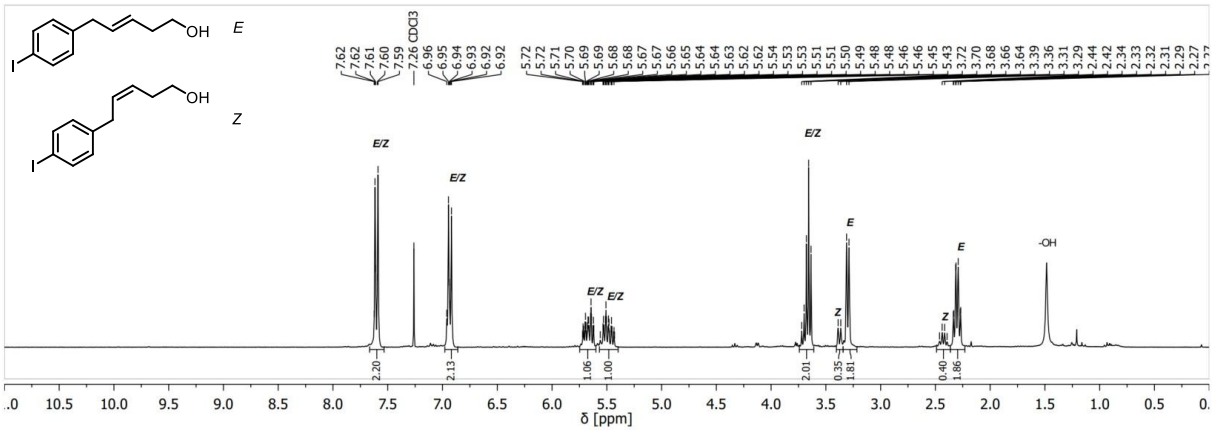


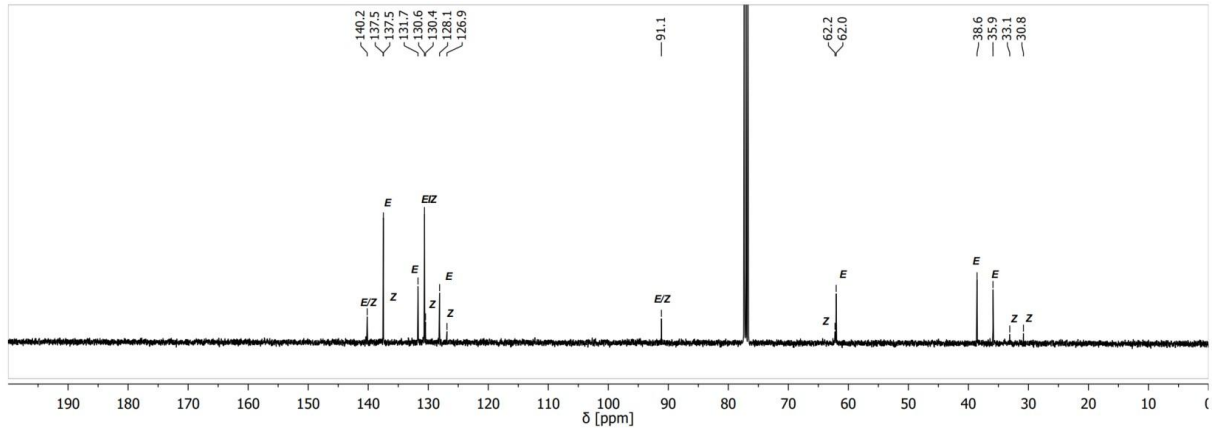


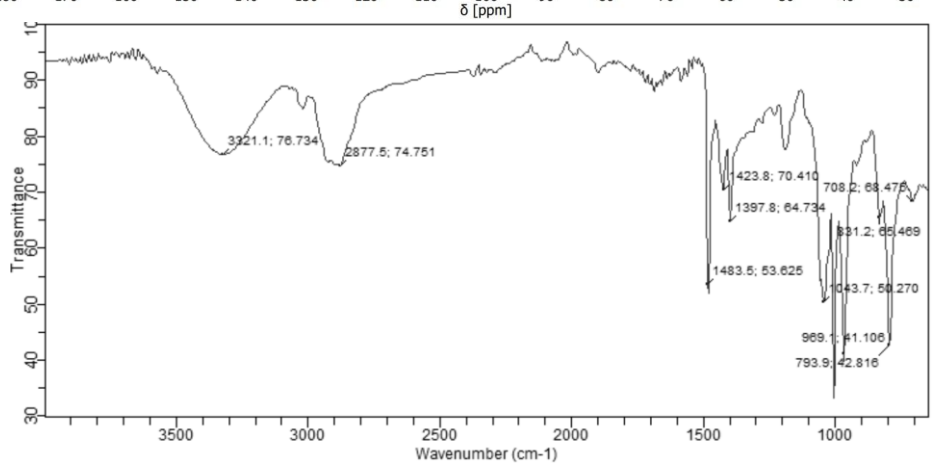
Spectra of project “1,3-dioxan-2-ones” – starting materials

5-(4-Iodophenyl)pent-3-en-1-ol (142c)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

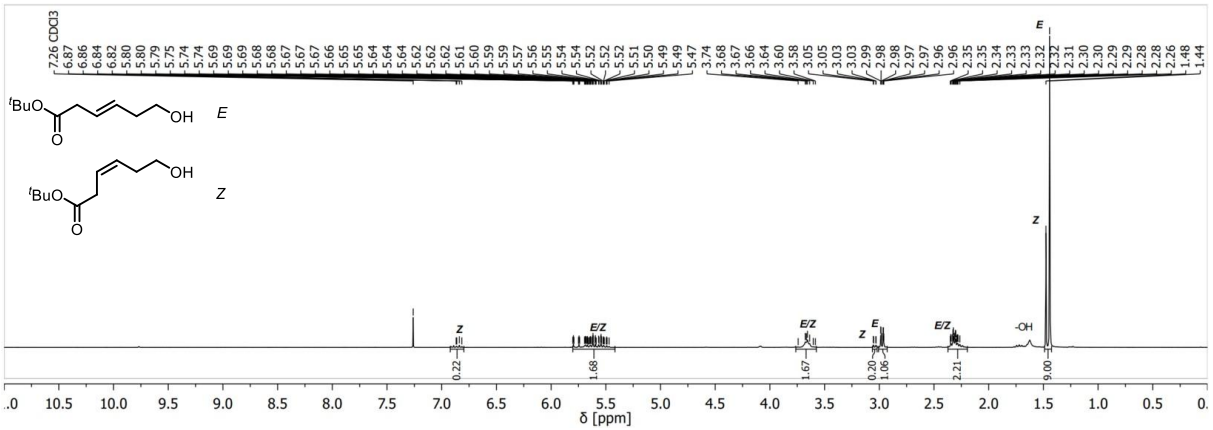


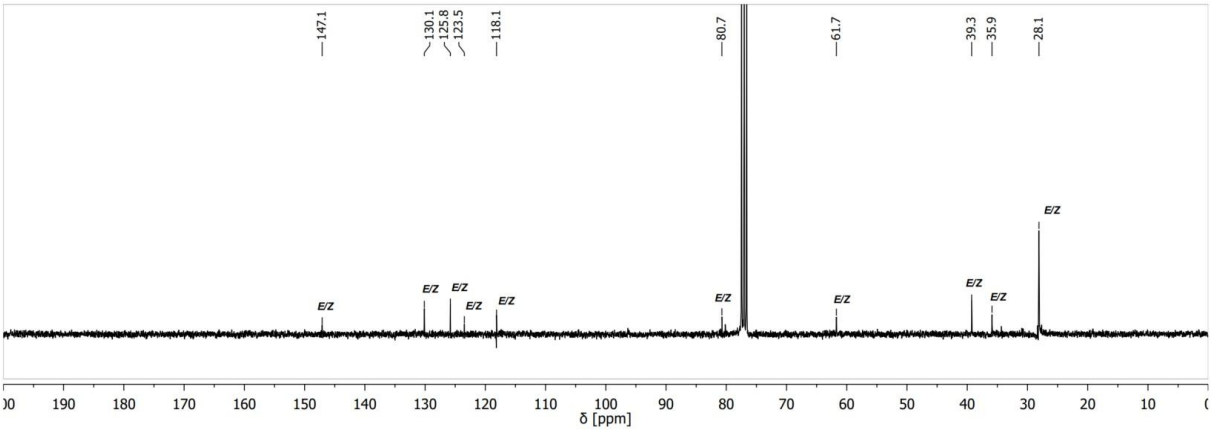


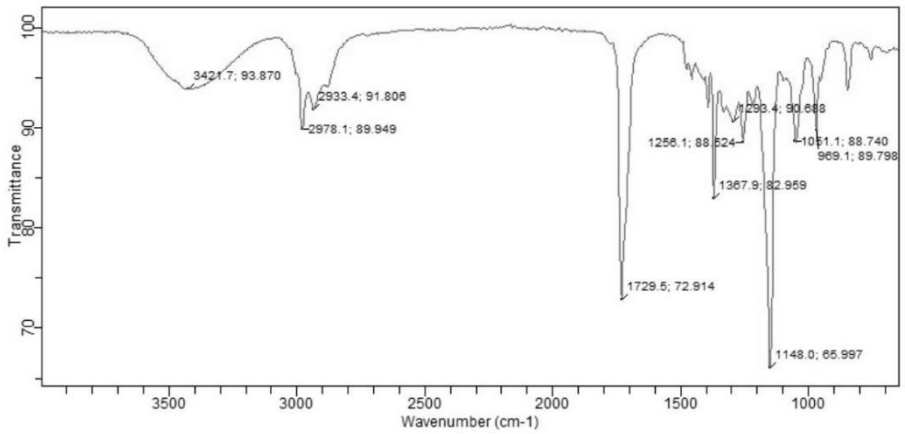


tert-Butyl 6-hydroxyhex-3-enoate (142d)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



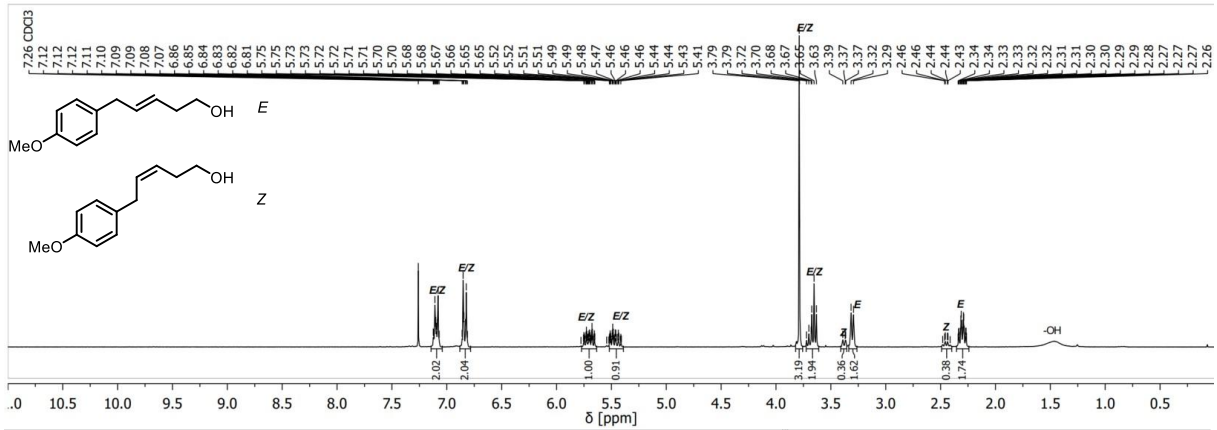


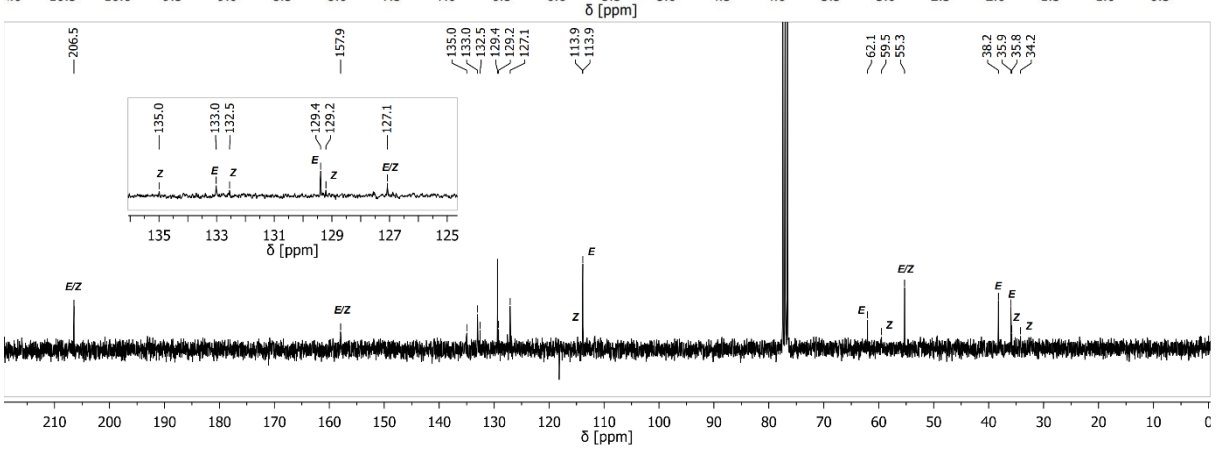


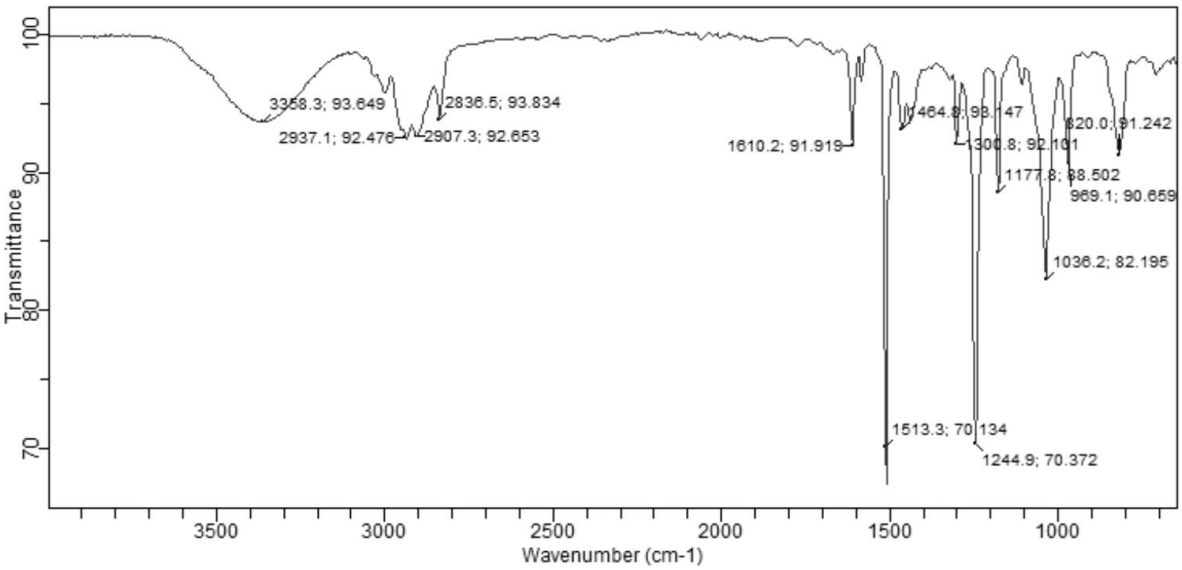
Spectra of project “1,3-dioxan-2-ones” – starting materials

5-(4-Methoxyphenyl)pent-3-en-1-ol (142e)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**

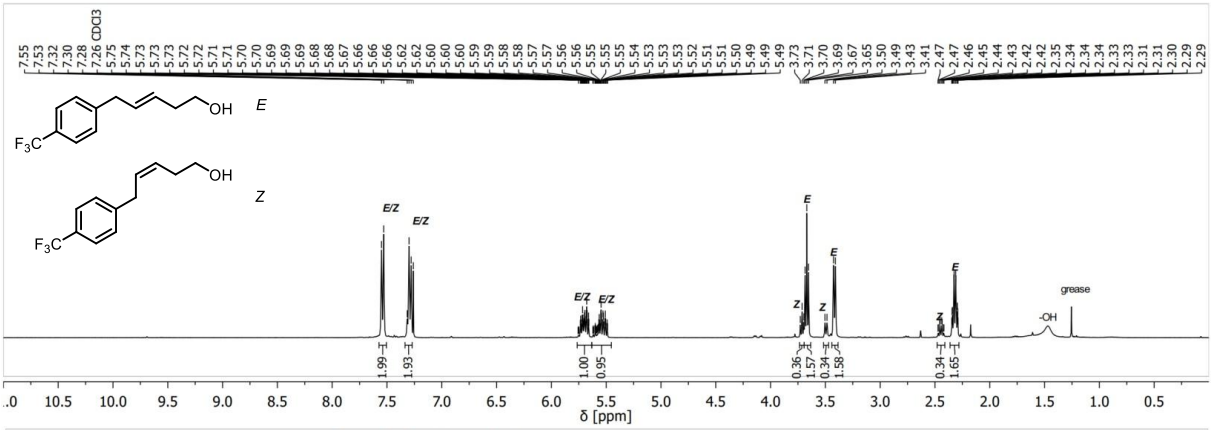


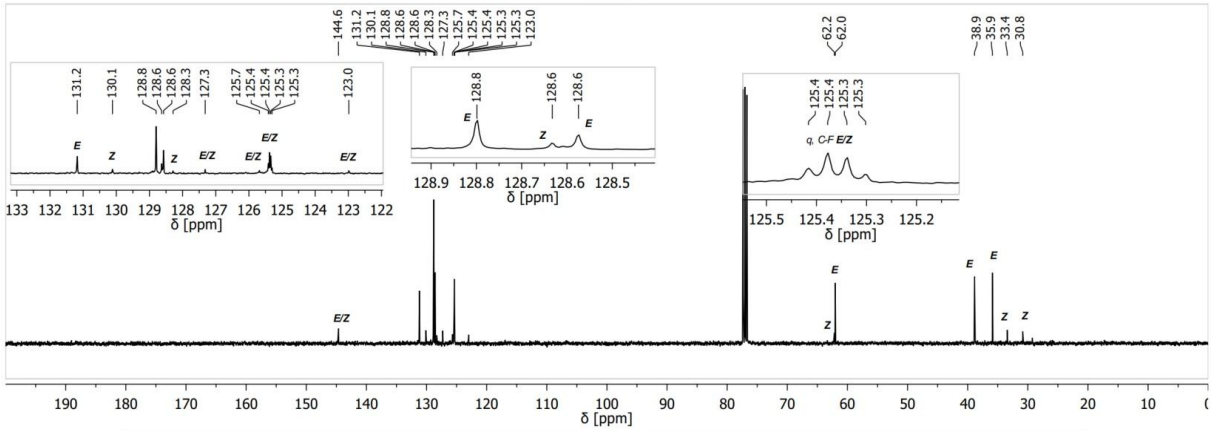


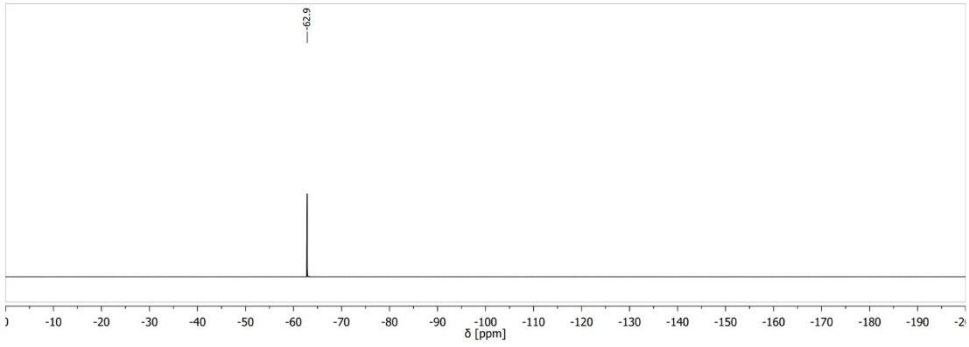


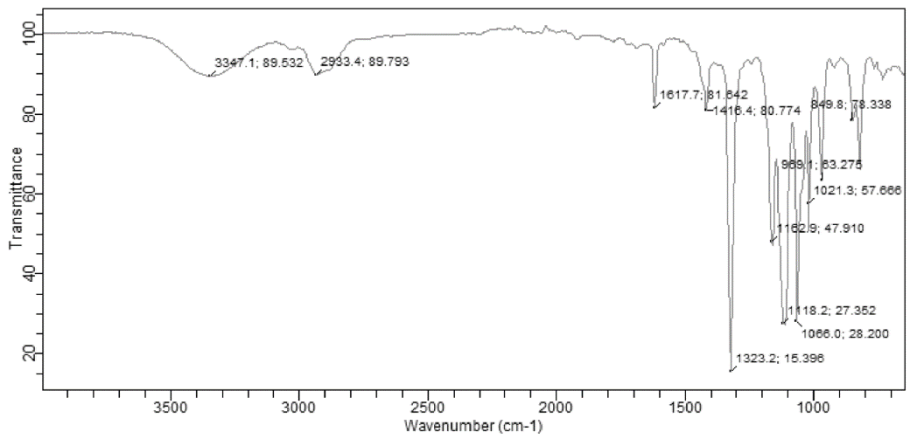
5-(4-(Trifluoromethyl)phenyl)pent-3-en-1-ol (142f)

^{1}H NMR (400 MHz), **^{13}C NMR** (101 MHz), **^{19}F{^{1}H} NMR** (376 MHz): Chloroform-*d*, **IR**



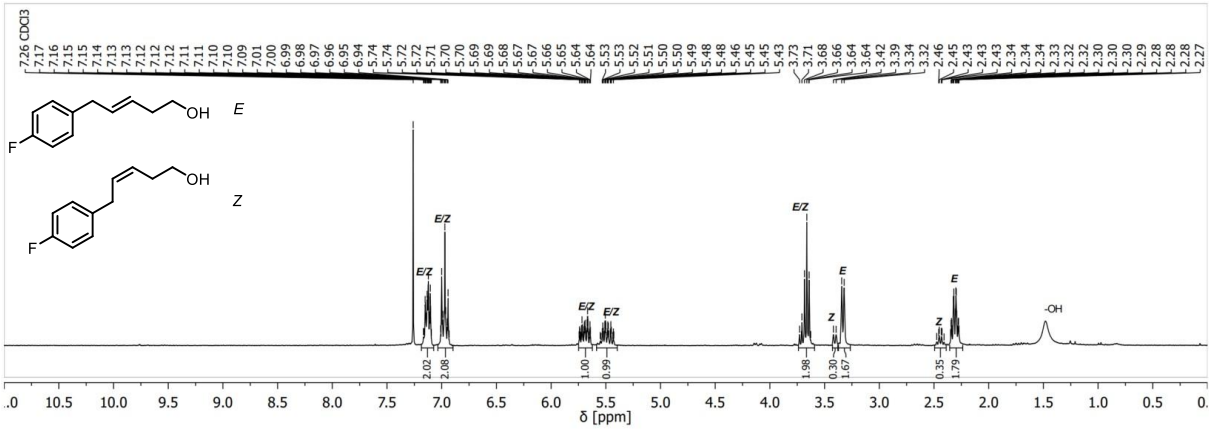


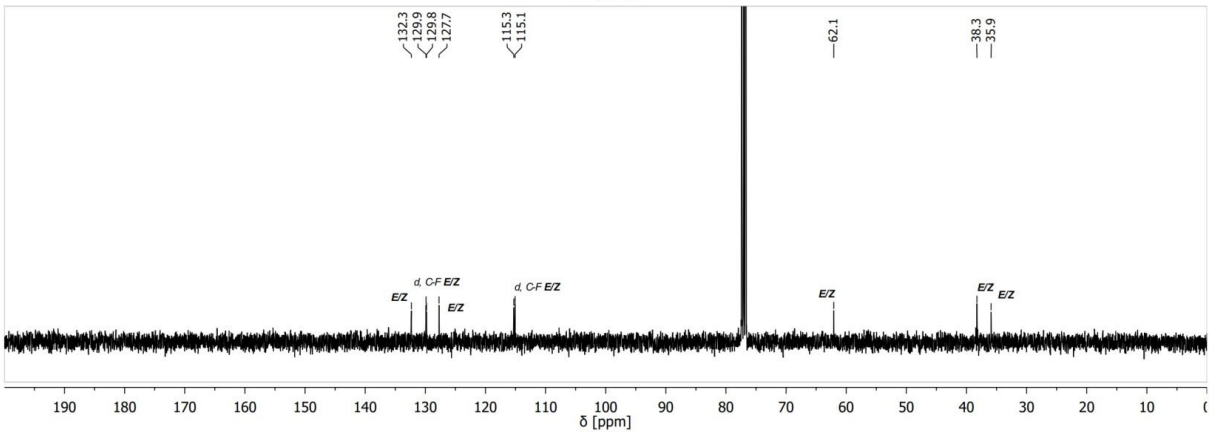


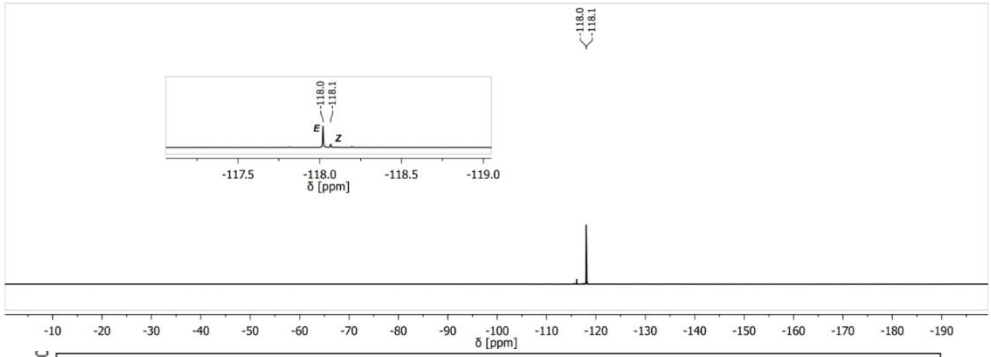


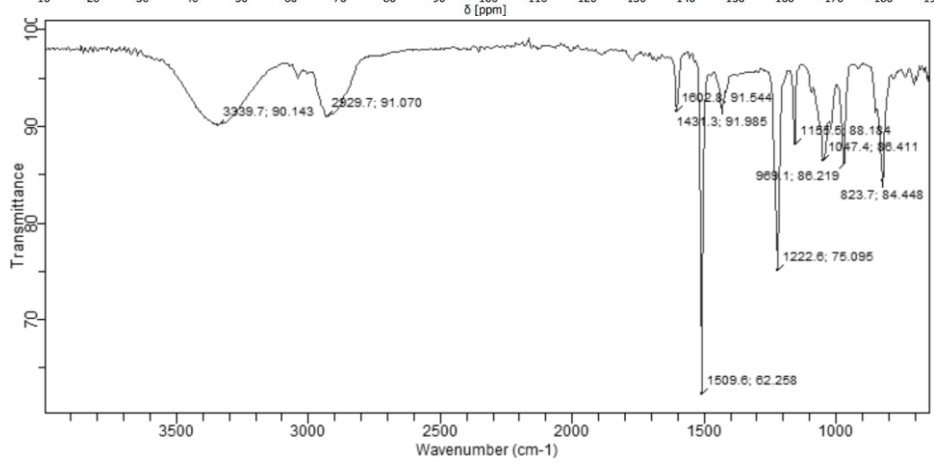
5-(4-Fluorophenyl)pent-3-en-1-ol (142g)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz), **^{19}F{^{1}H} NMR** (376 MHz): Chloroform-*d*, **IR**



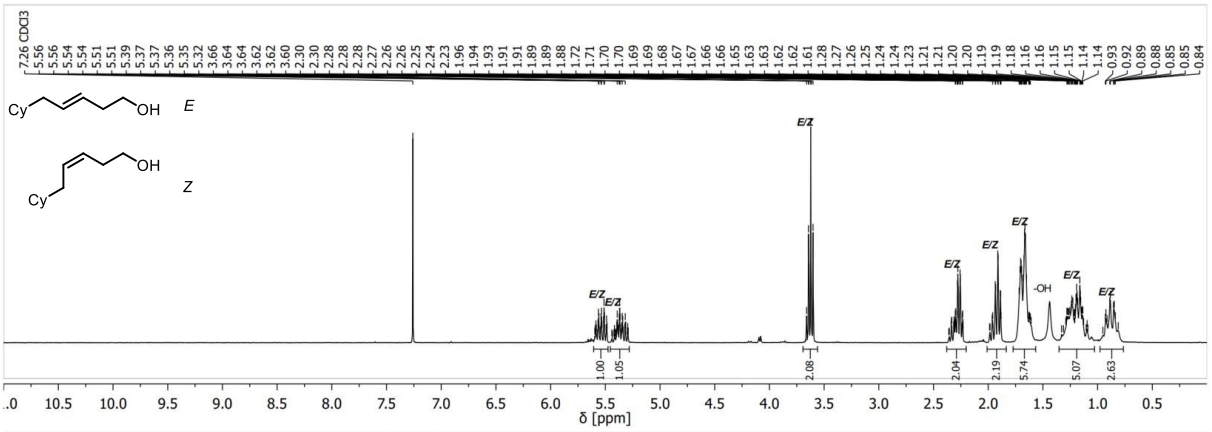


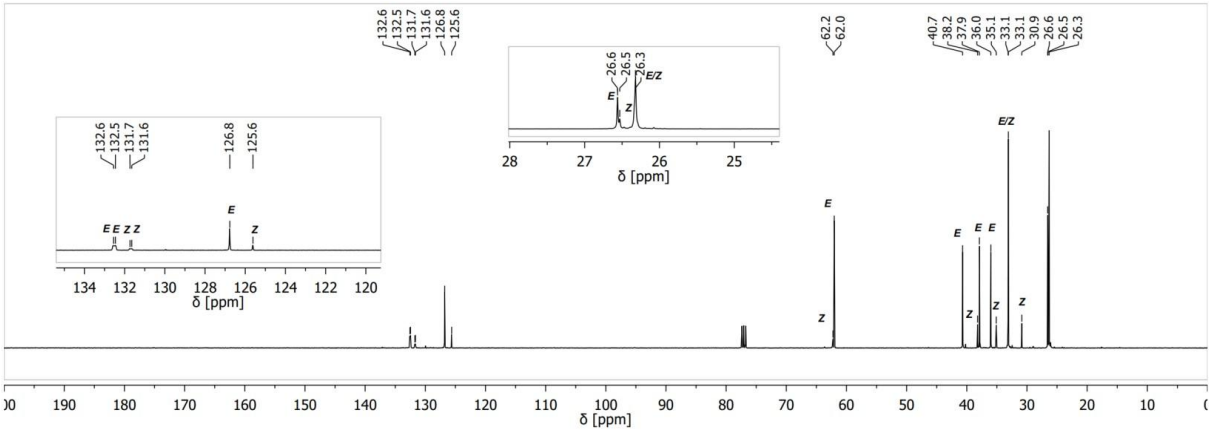


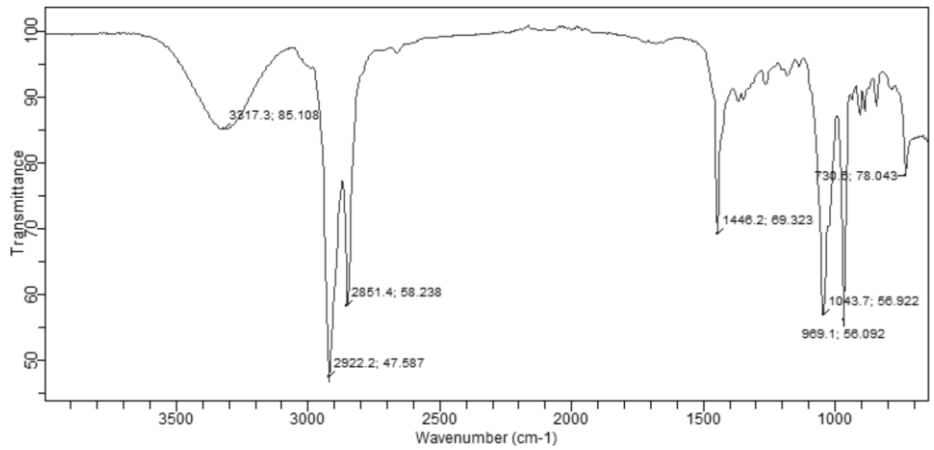


5-Cyclohexylpent-3-en-1-ol (142h)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

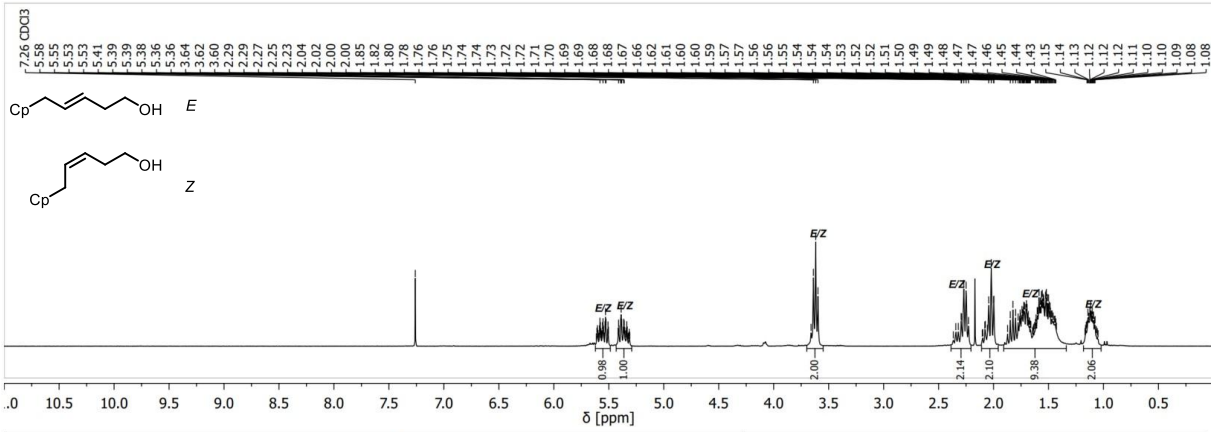


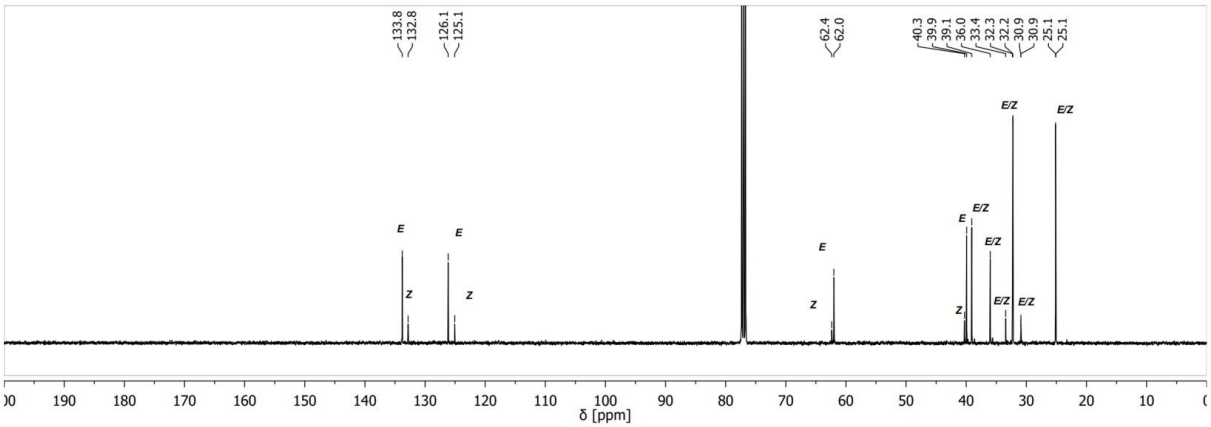


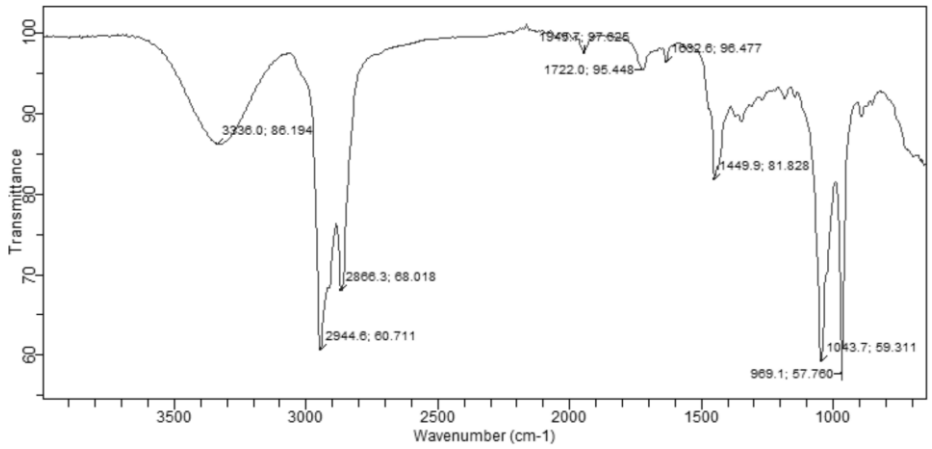


5-Cyclopentylpent-3-en-1-ol (142i)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

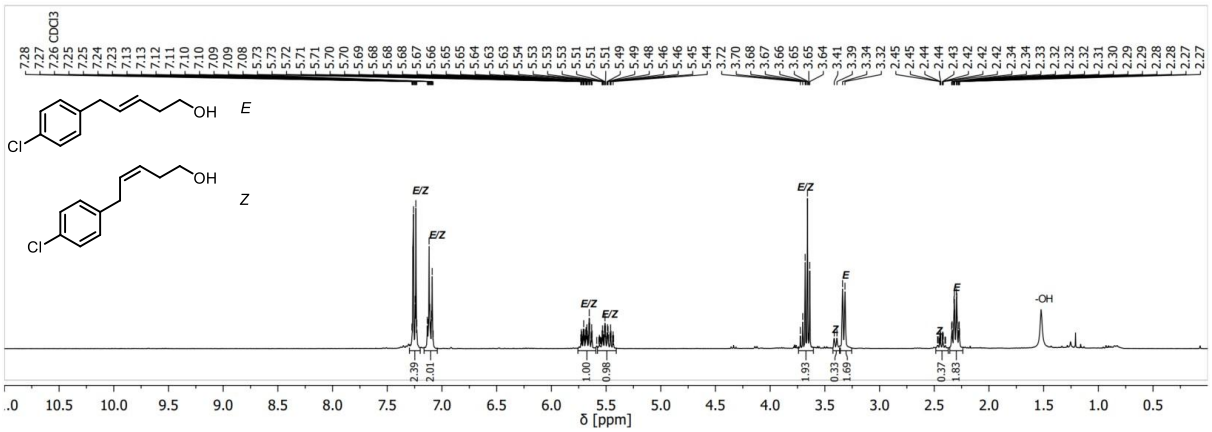


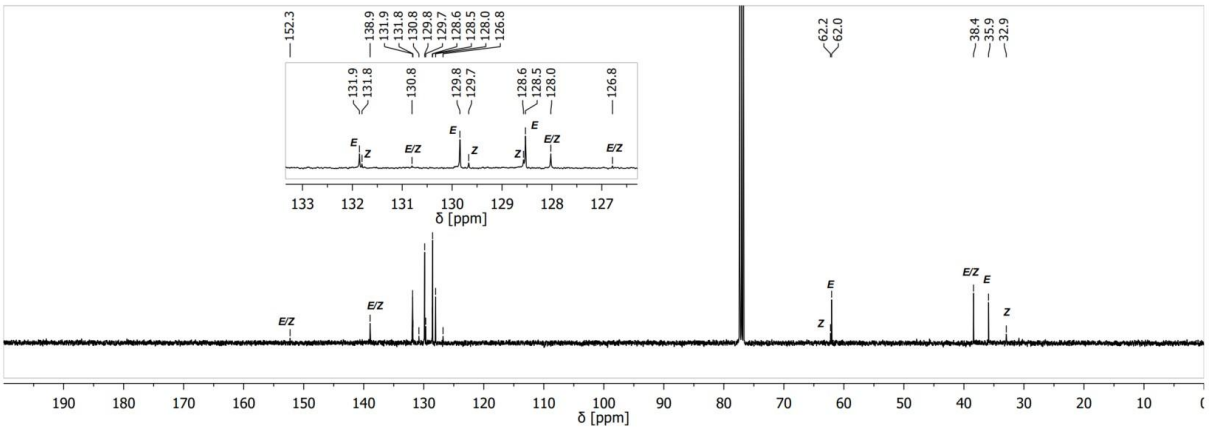


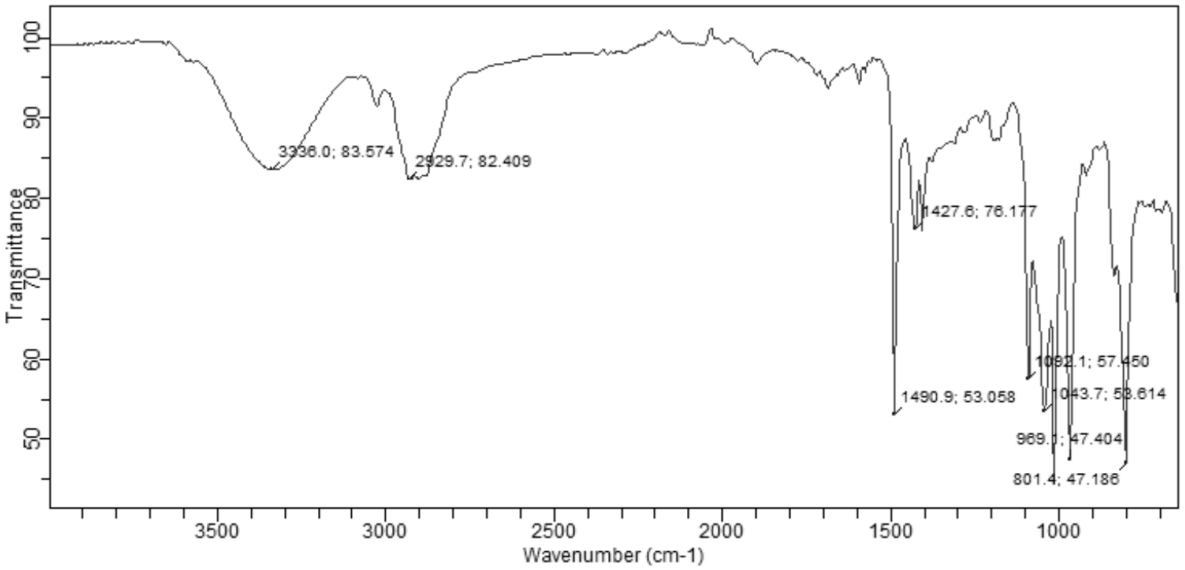


5-(4-Chlorophenyl)pent-3-en-1-ol (142j)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

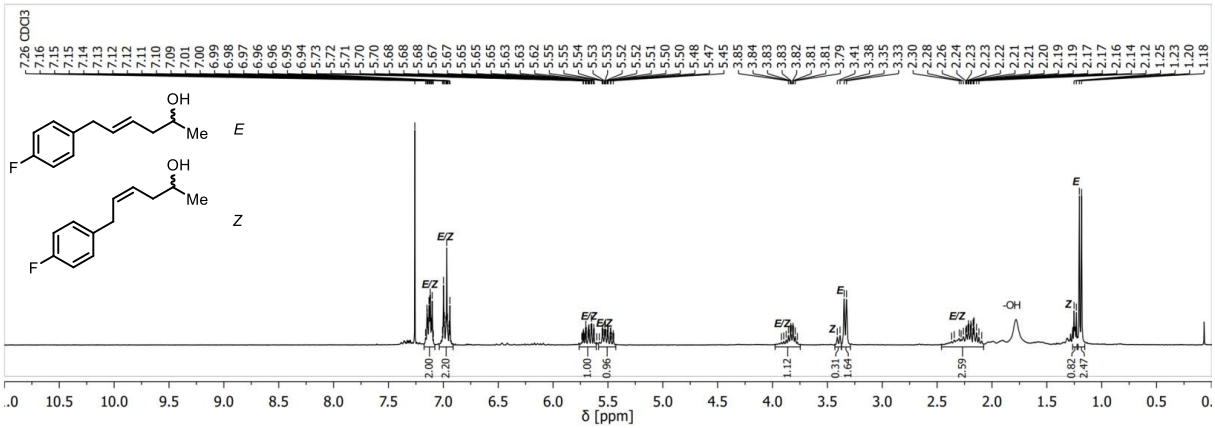


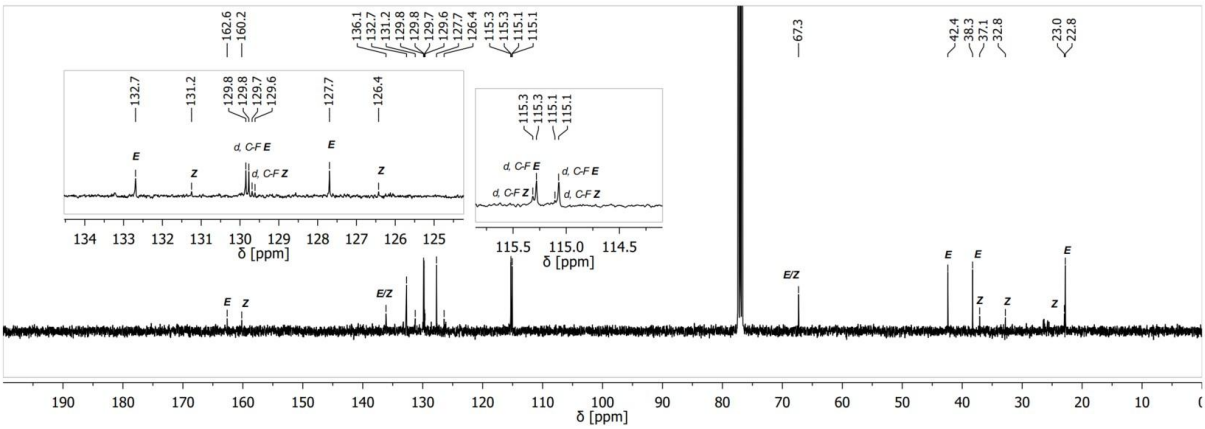


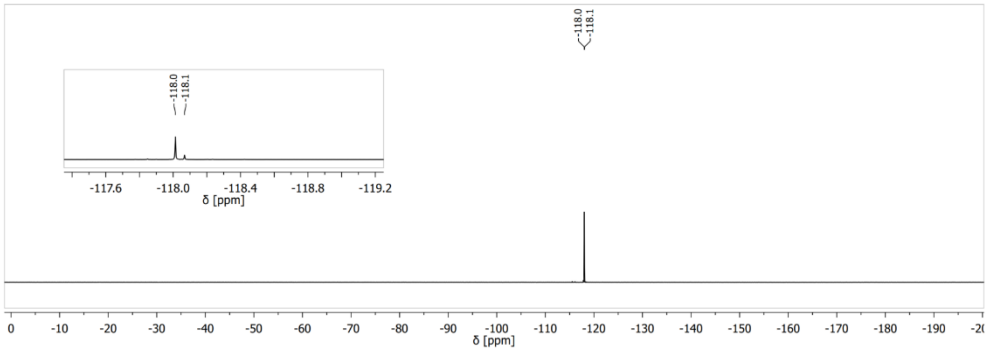


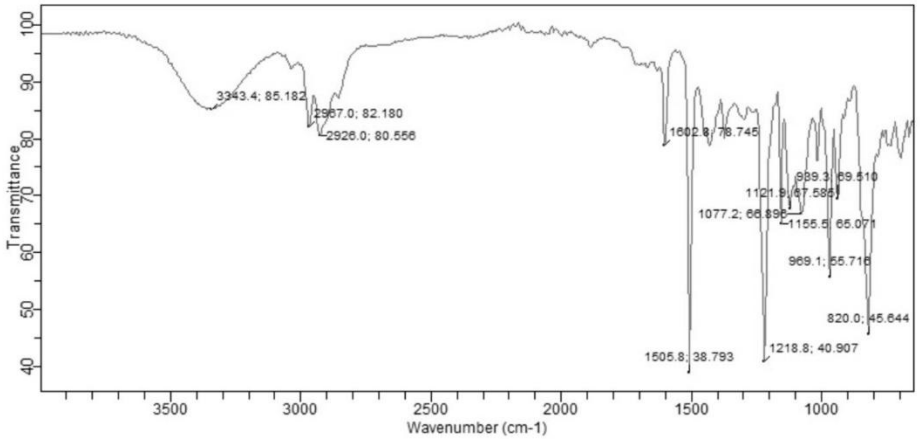
6-(4-Fluorophenyl)hex-4-en-2-ol (142k)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz) **^{19}F{^{1}H} NMR** (376 MHz): Chloroform-*d*, **IR**



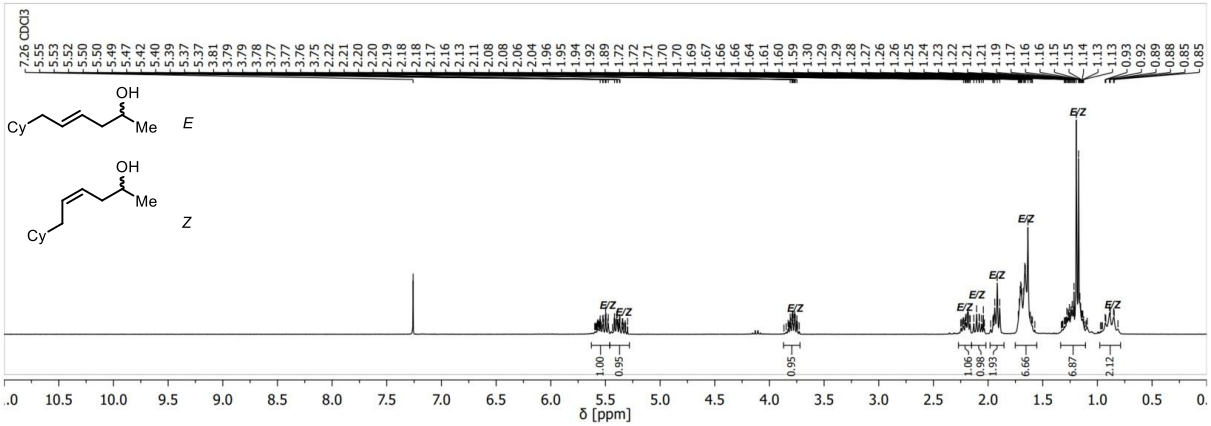


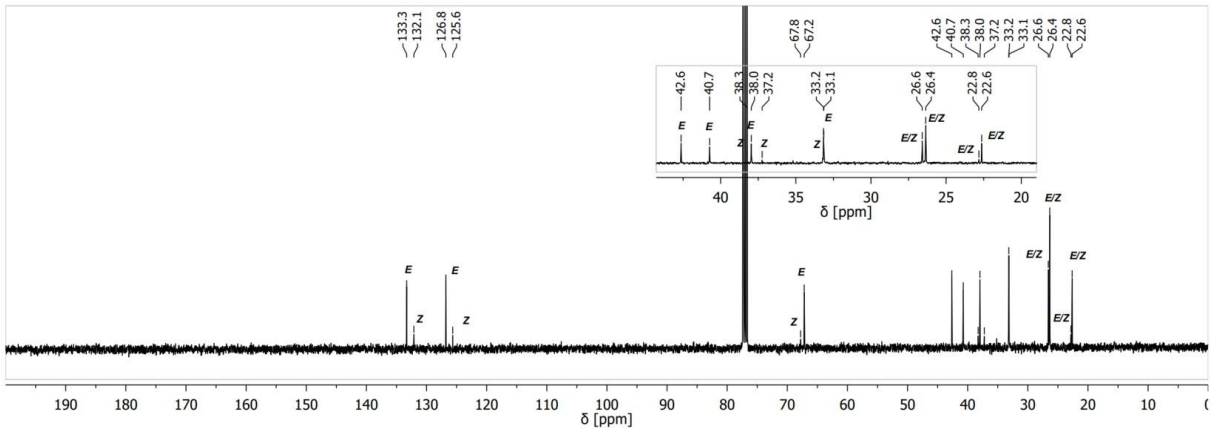


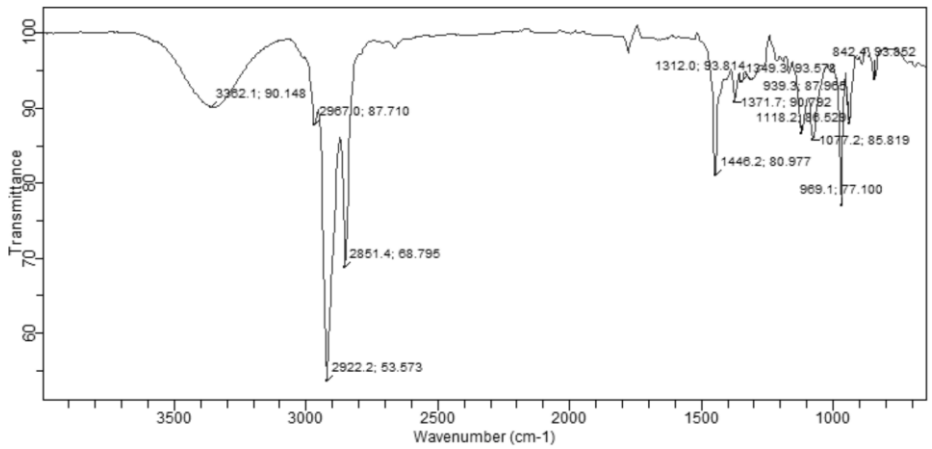


6-Cyclohexylhex-4-en-2-ol (142l)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



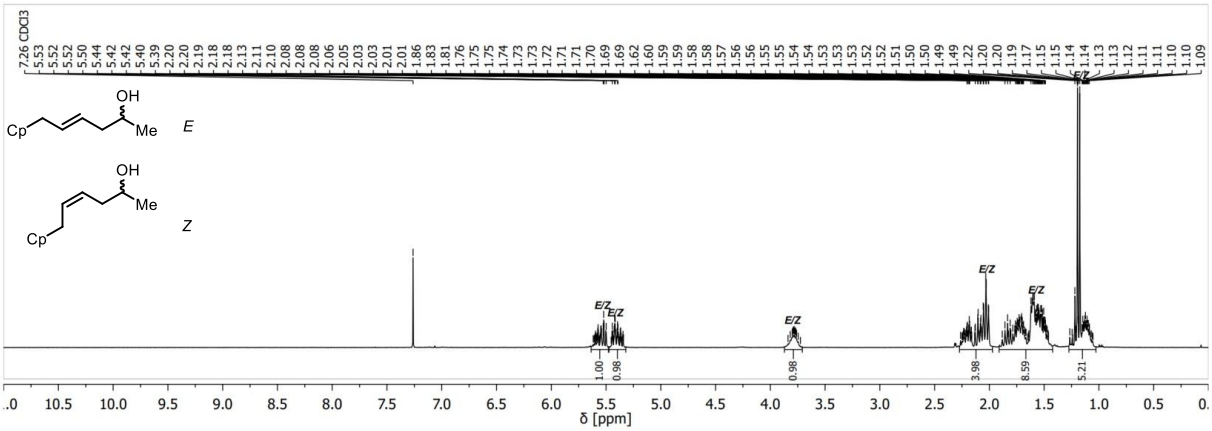


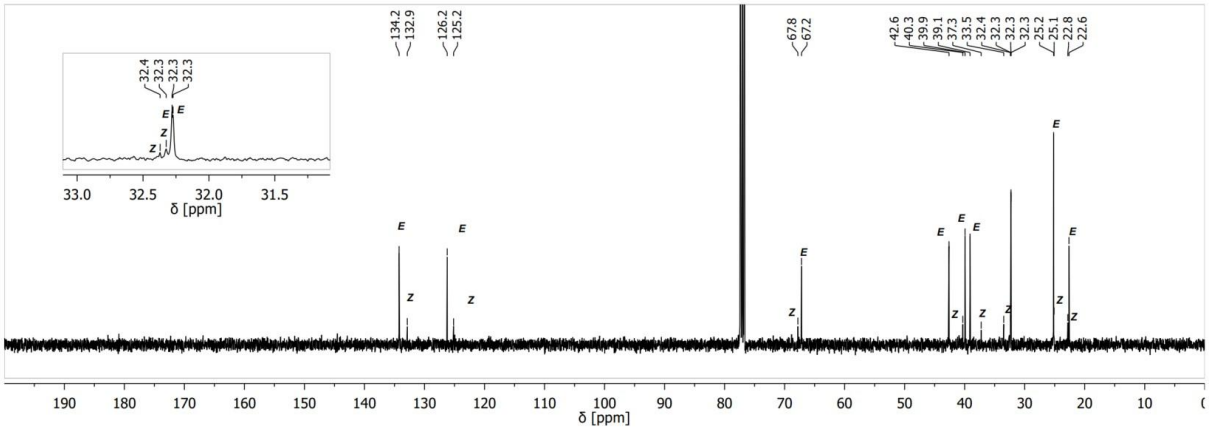


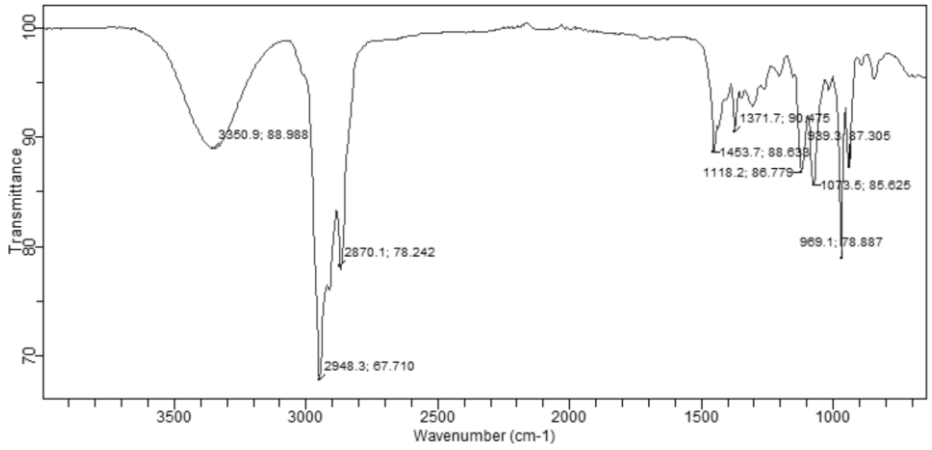
Spectra of project “1,3-dioxan-2-ones” – starting materials

6-Cyclopentylhex-4-en-2-ol (142m)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



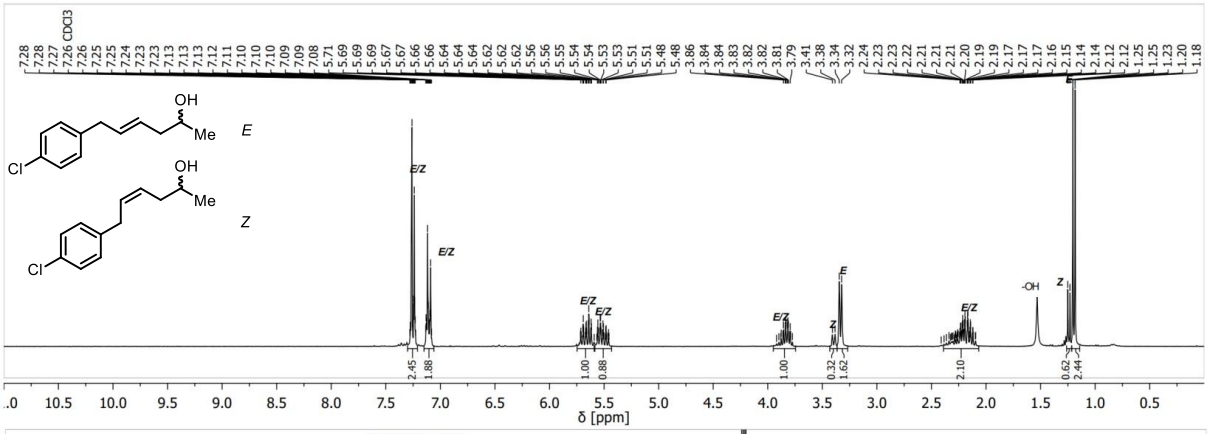


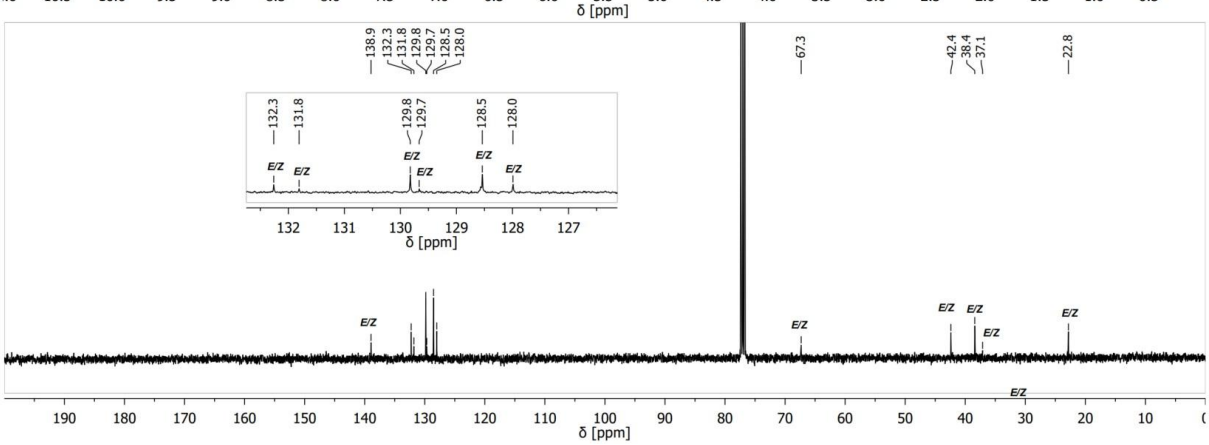


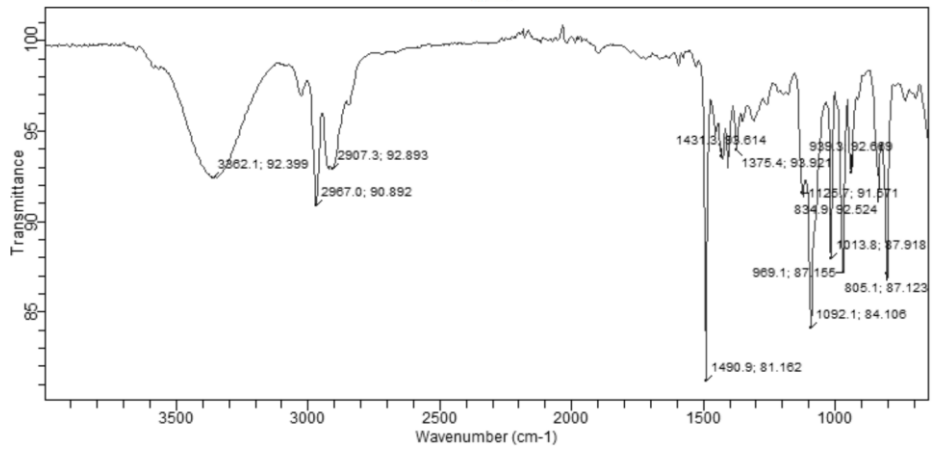
Spectra of project “1,3-dioxan-2-ones” – starting materials

6-(4-Chlorophenyl)hex-4-en-2-ol (142n)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

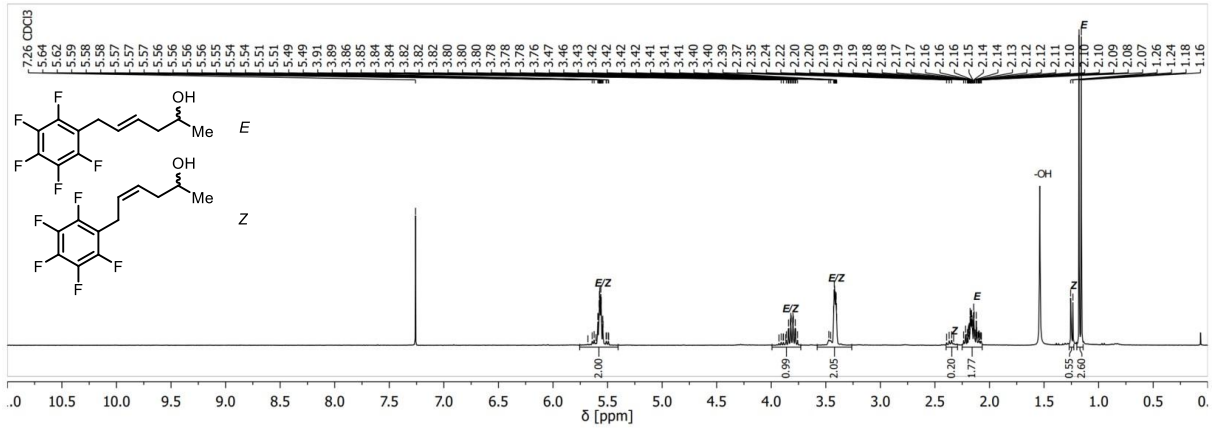


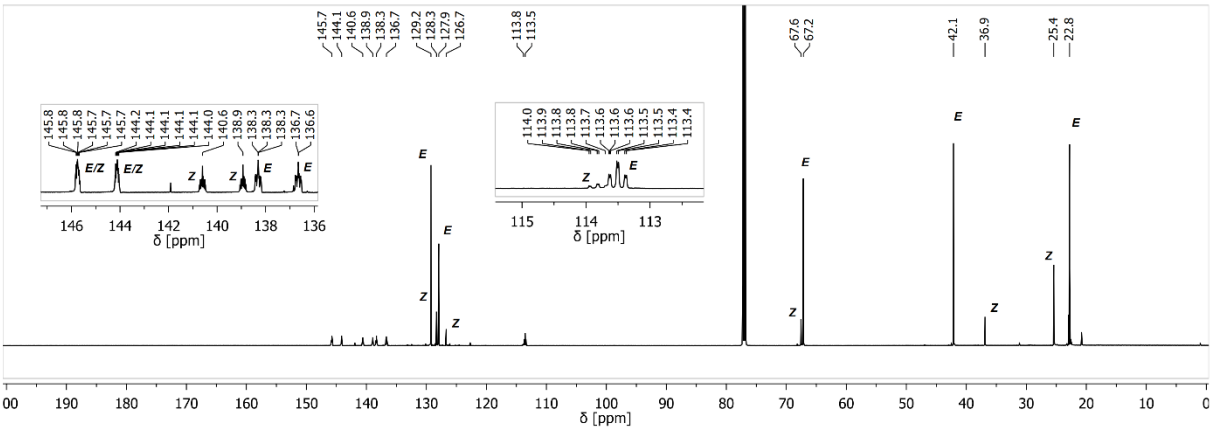


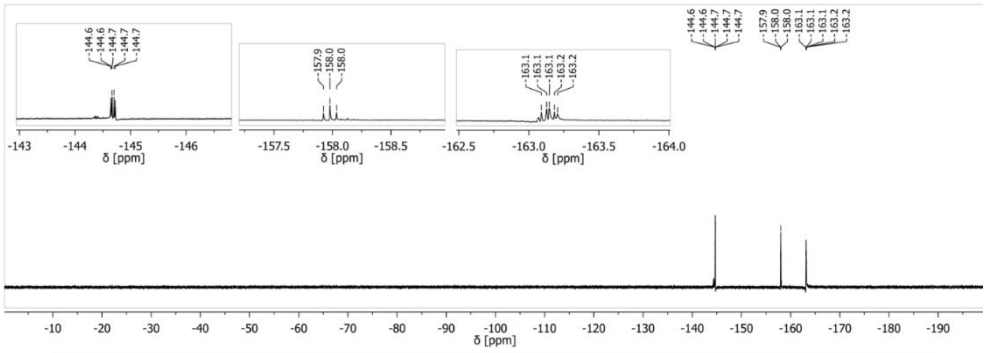


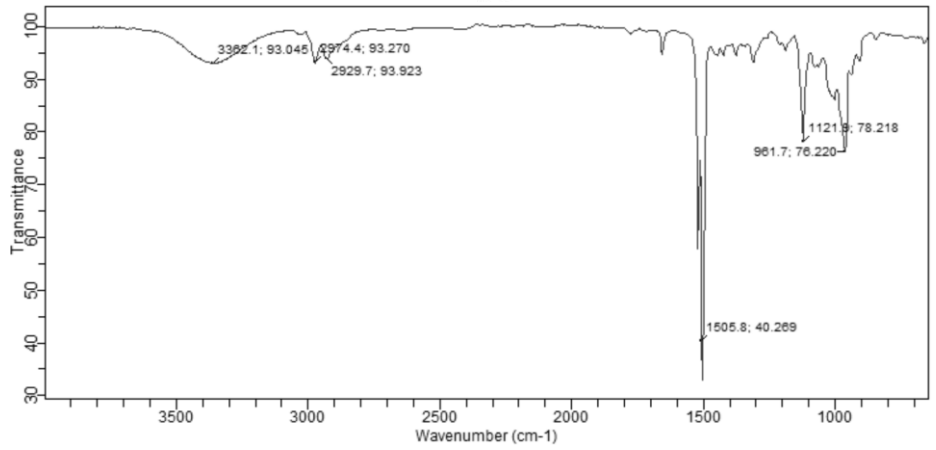
6-(Perfluorophenyl)hex-4-en-2-ol (142o)

^{1}H NMR (300 MHz), **^{13}C NMR** (151 MHz), **^{19}F{^{1}H} NMR** (376 MHz): Chloroform-*d*, **IR**



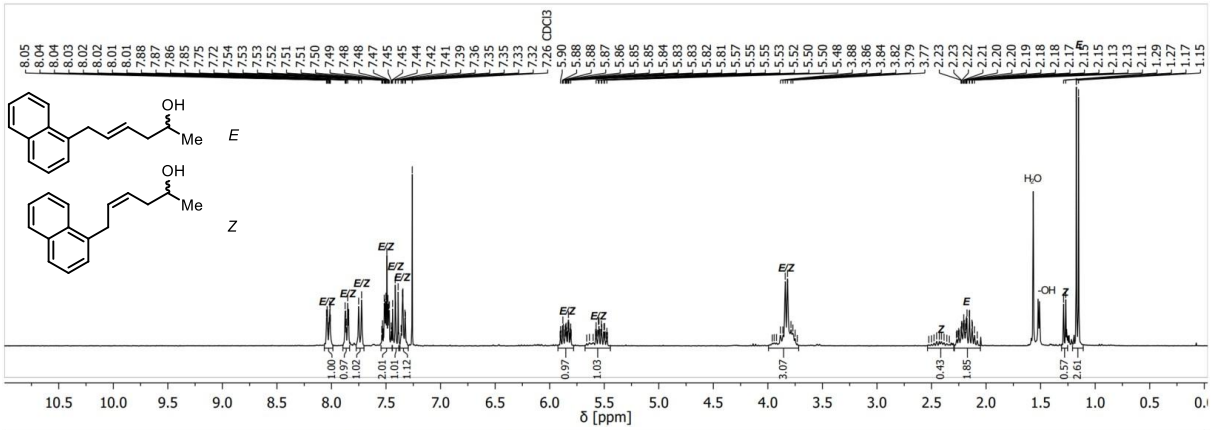


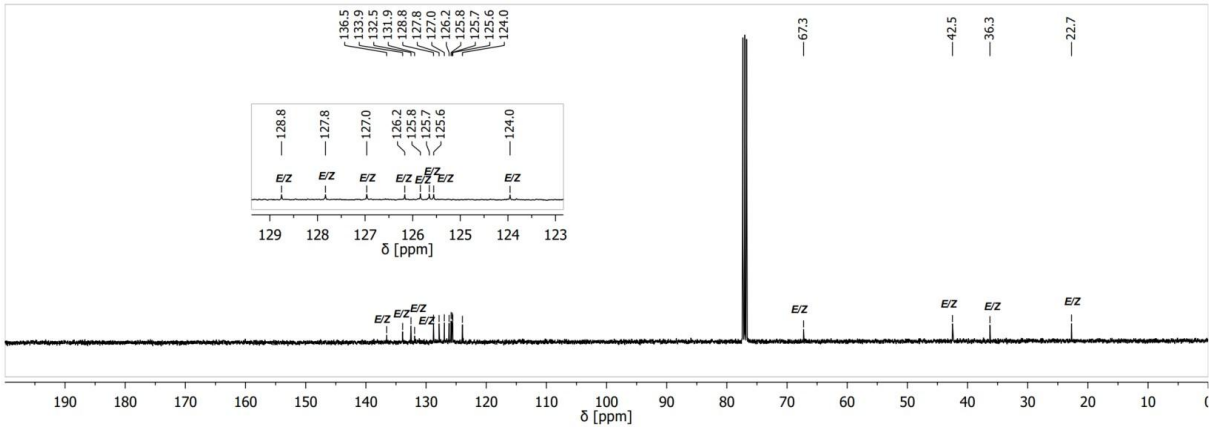


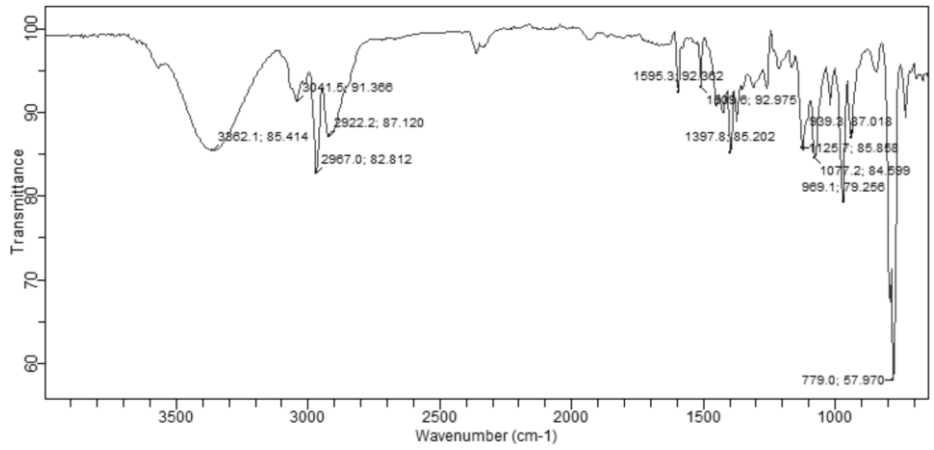


6-(Naphthalen-1-yl)hex-4-en-2-ol (142p)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

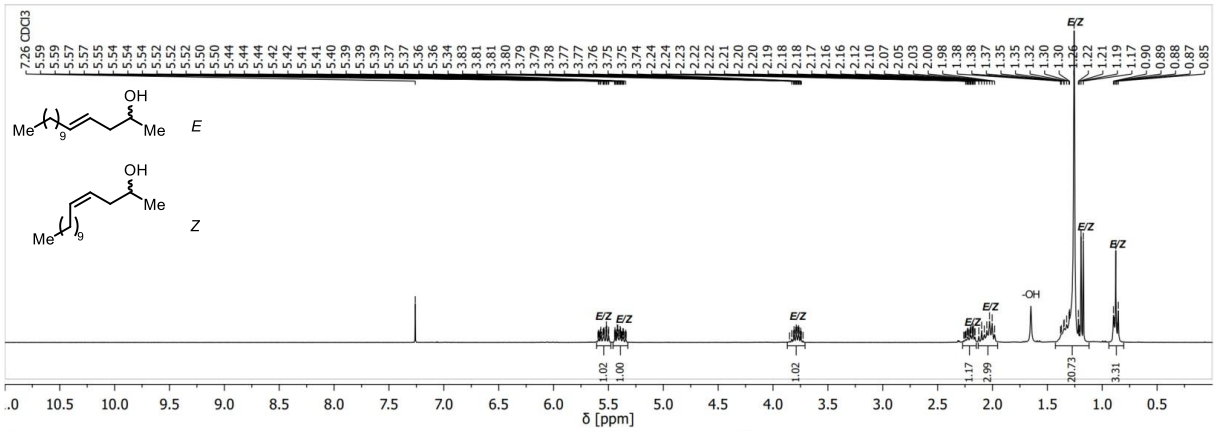


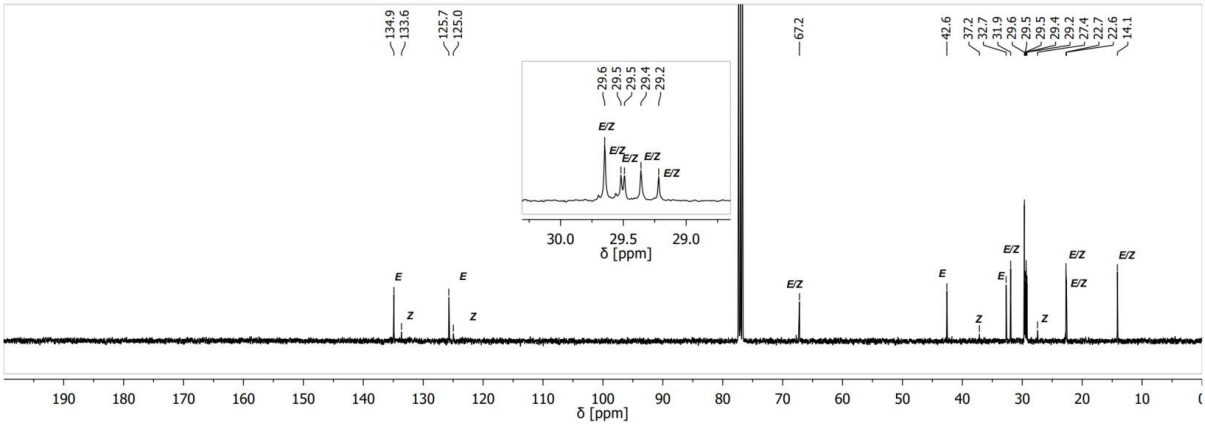


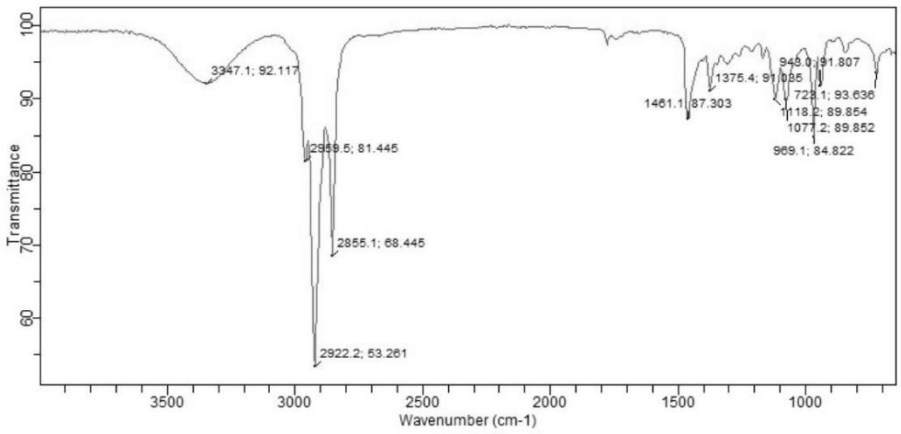


Pentadec-4-en-2-ol (142q)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



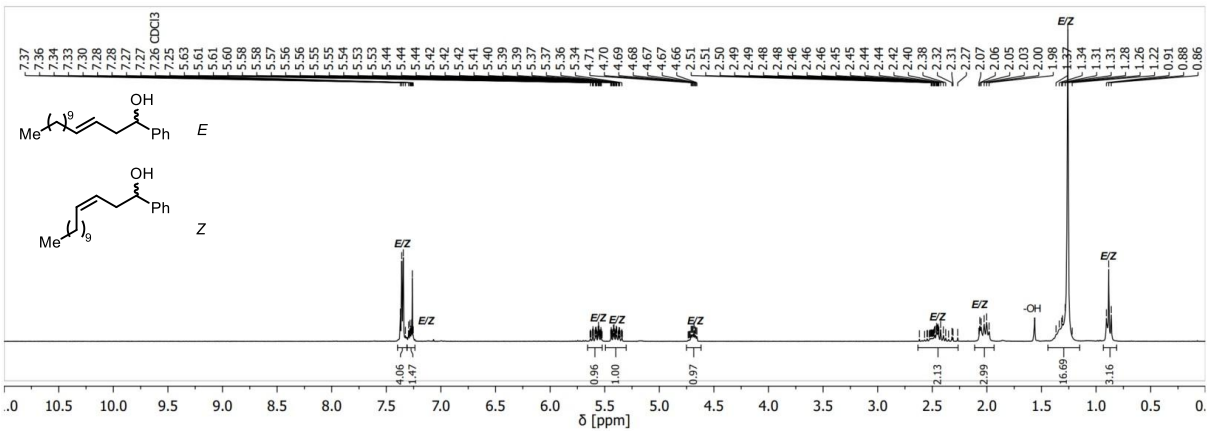


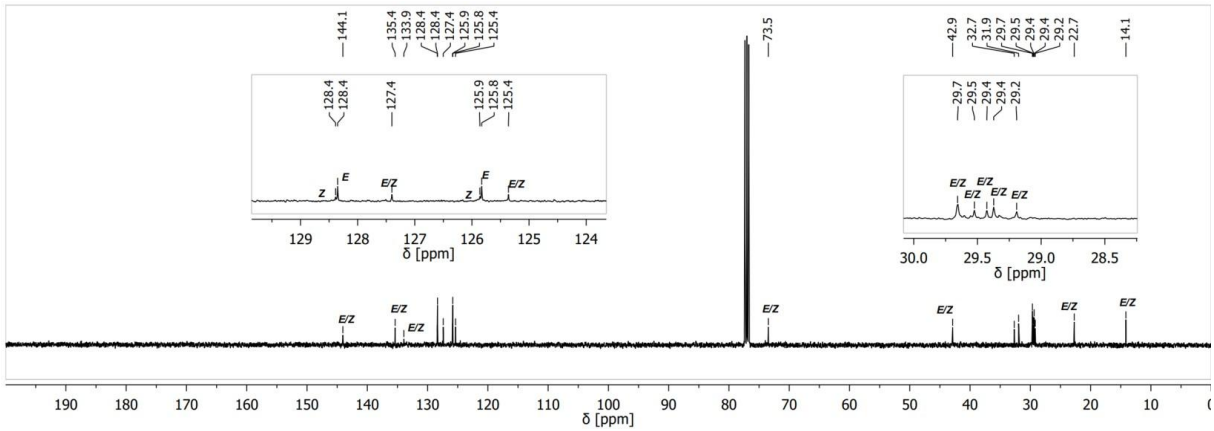


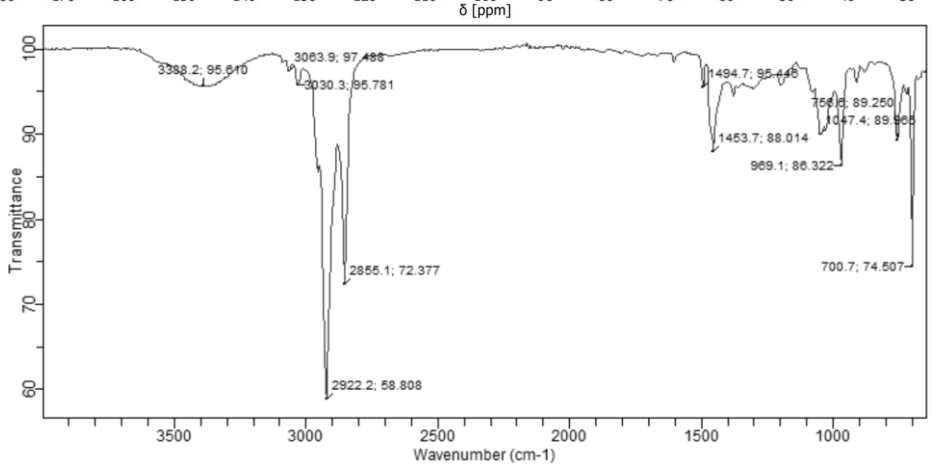
Spectra of project “1,3-dioxan-2-ones” – starting materials

1-Phenyltetradec-3-en-1-ol (142r)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d,* **IR**

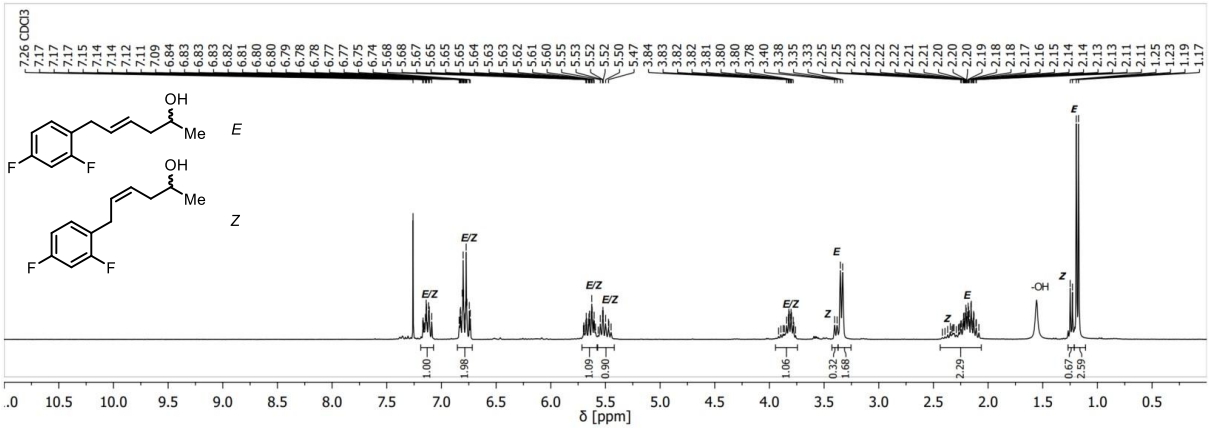


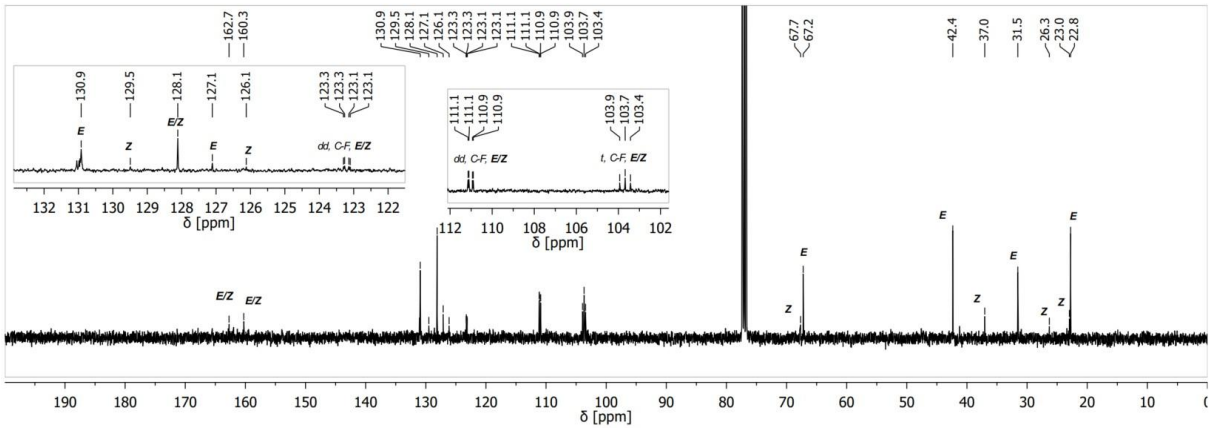


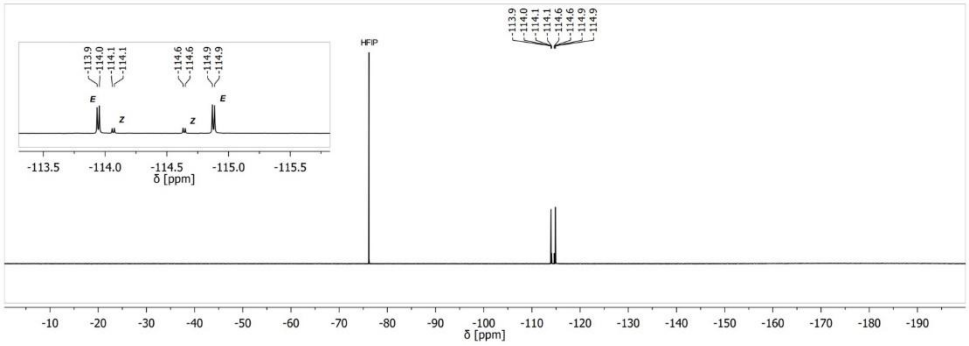


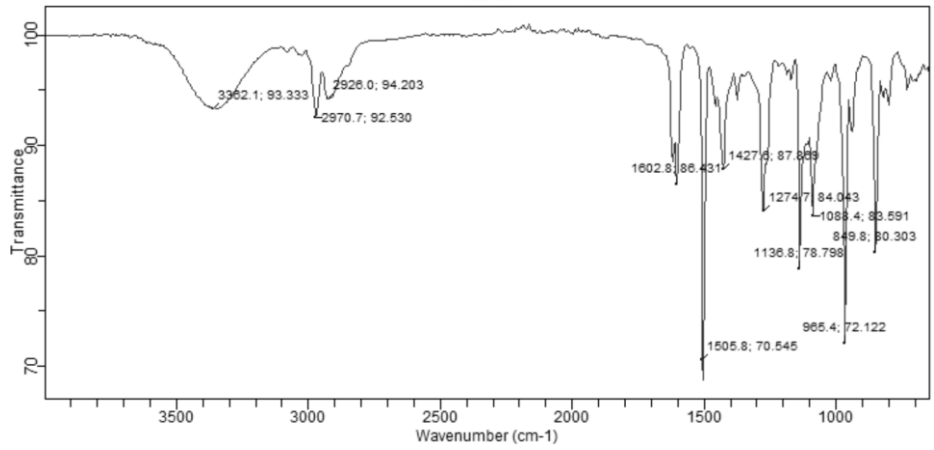
6-(2,4-Difluorophenyl)hex-4-en-2-ol (142s)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz), **^{19}F{^{1}H} NMR** (376 MHz): Chloroform-*d*, **IR**



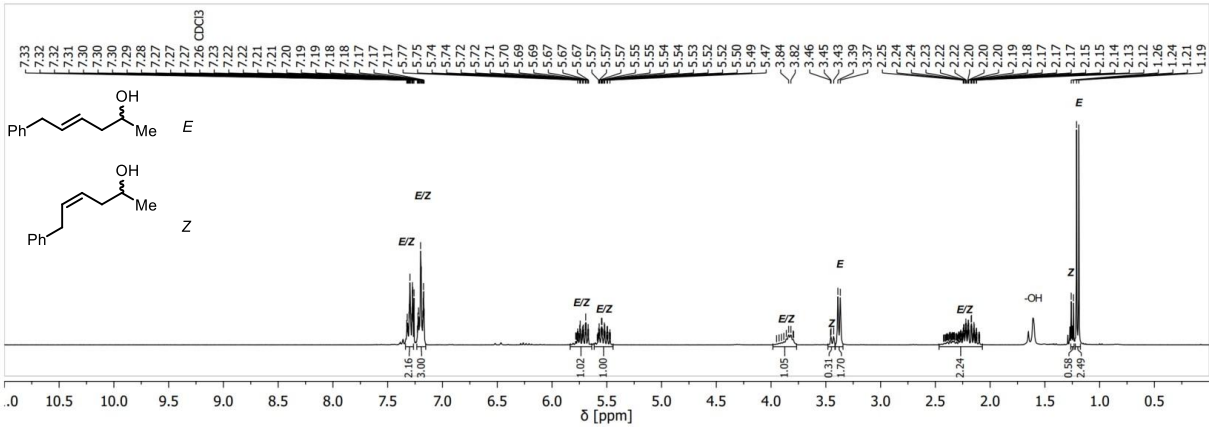


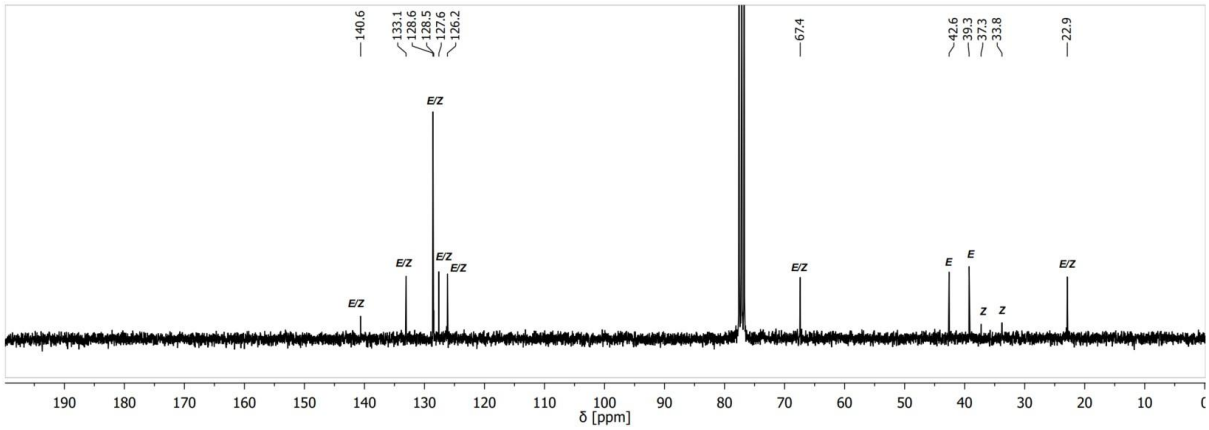


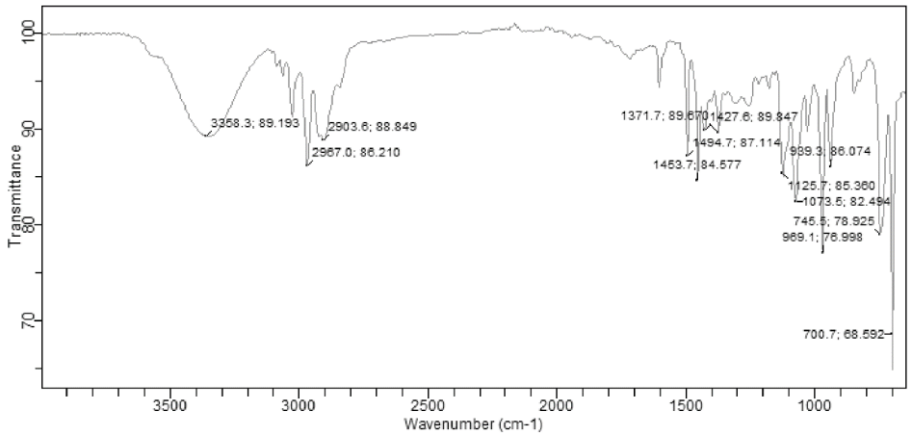


6-Phenylhex-4-en-2-ol (142t)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



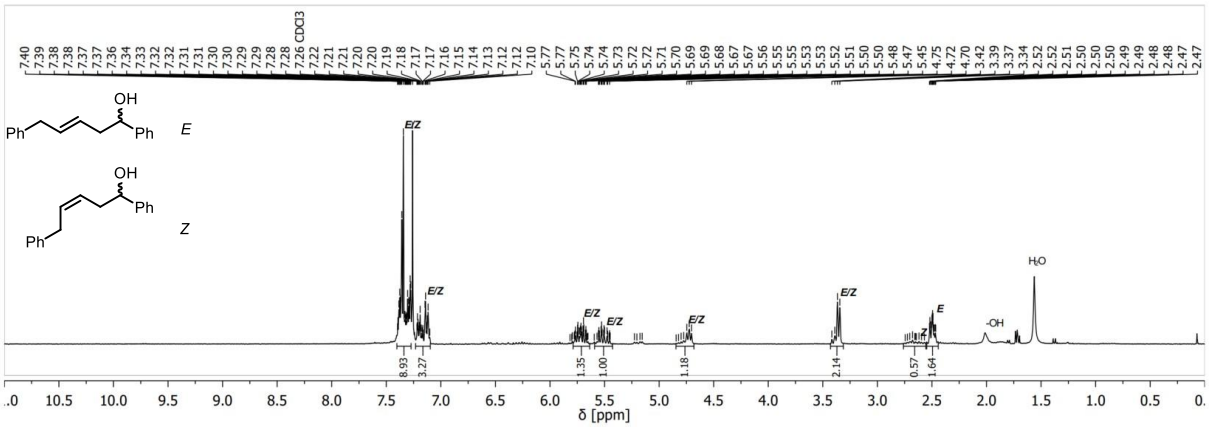


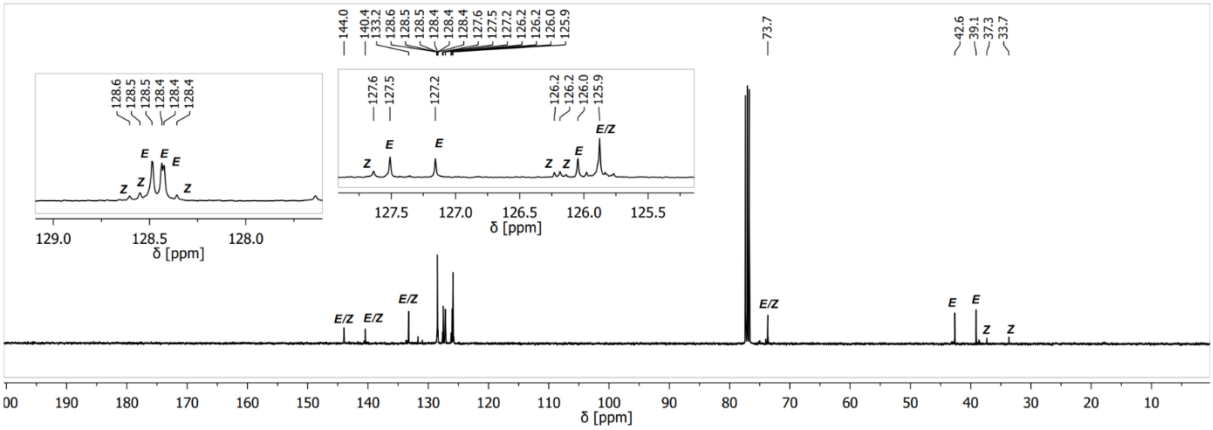


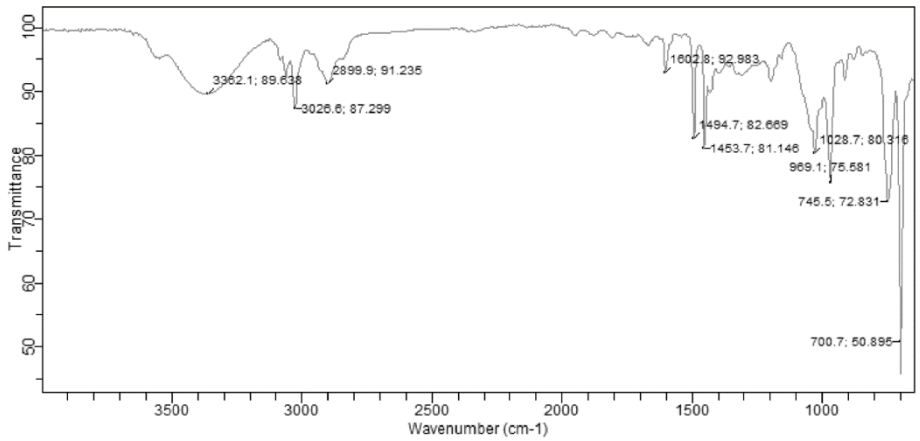
Spectra of project “1,3-dioxan-2-ones” – starting materials

1,5-Diphenylpent-3-en-1-ol (142u)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d,* **IR**



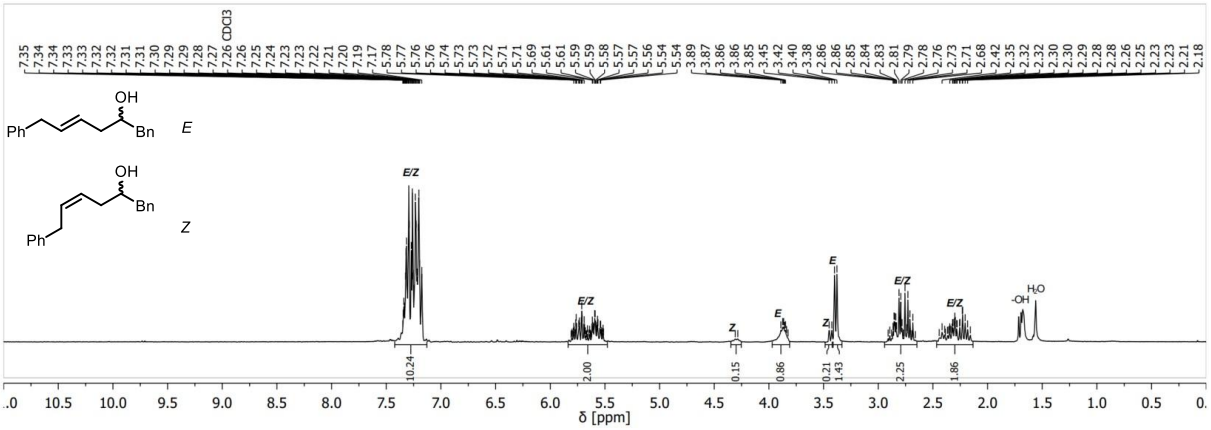


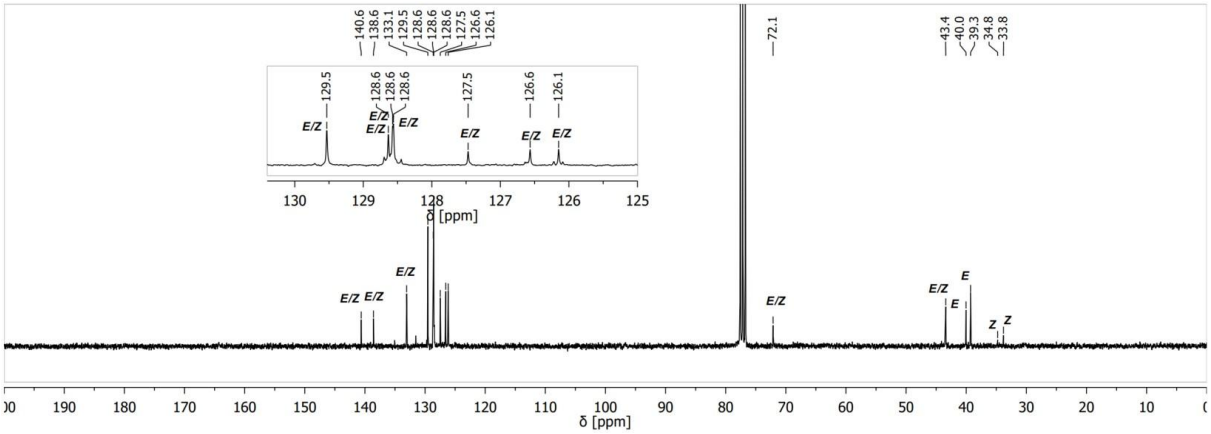


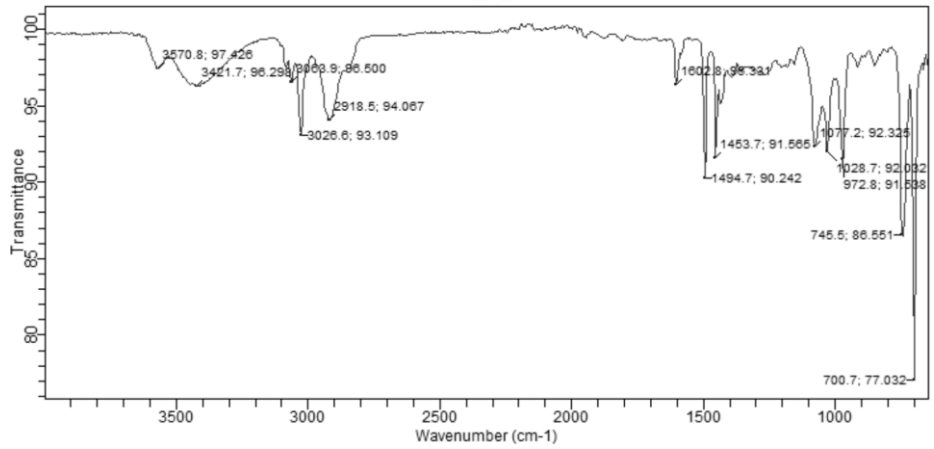
Spectra of project “1,3-dioxan-2-ones” – starting materials

1,6-Diphenylhex-4-en-2-ol (142v)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



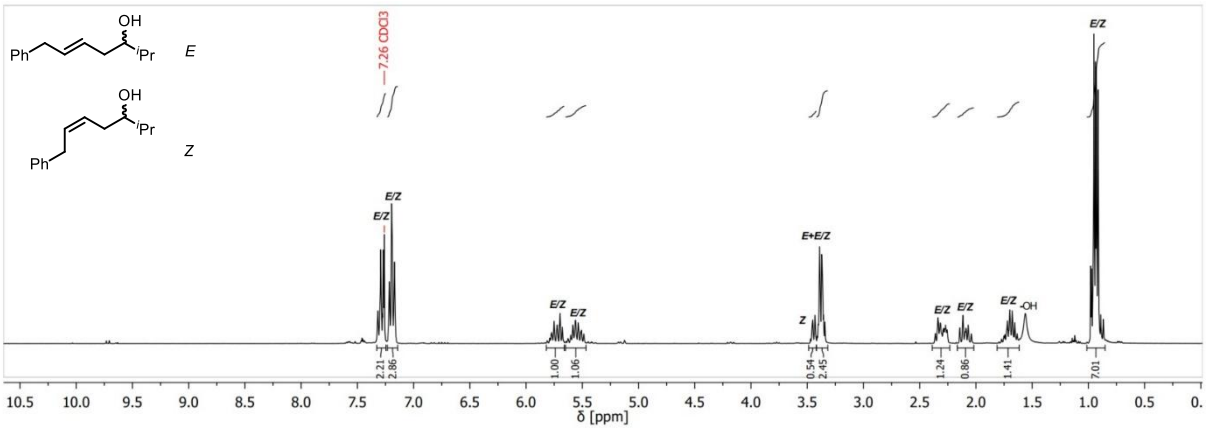


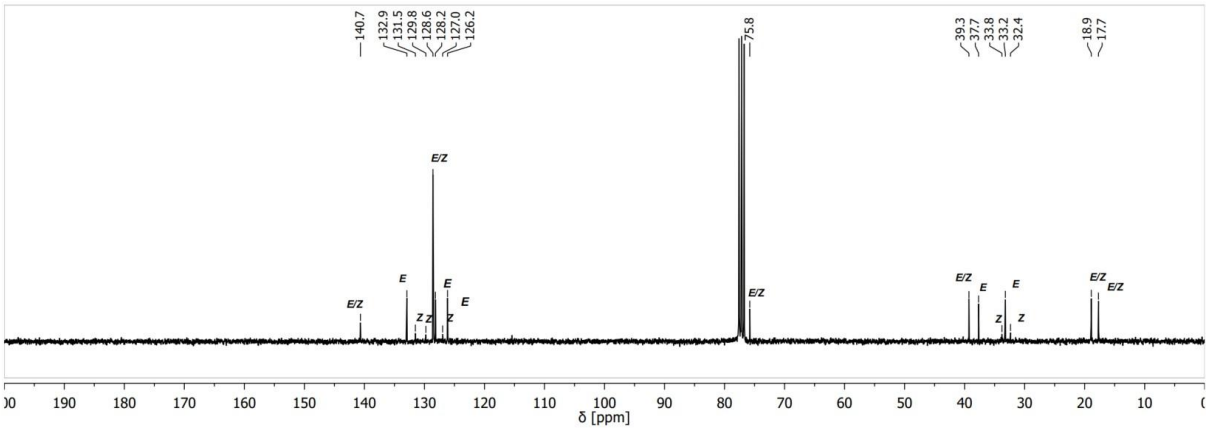


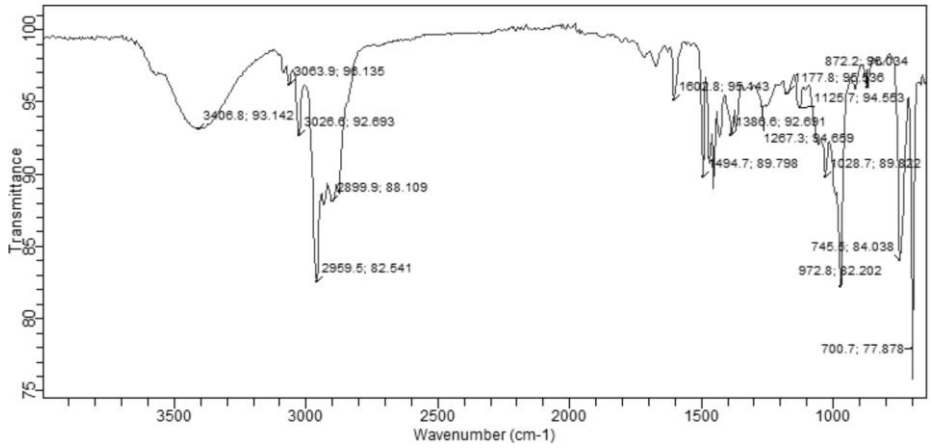
Spectra of project “1,3-dioxan-2-ones” – starting materials

2-Methyl-7-phenylhept-5-en-3-ol (142w)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



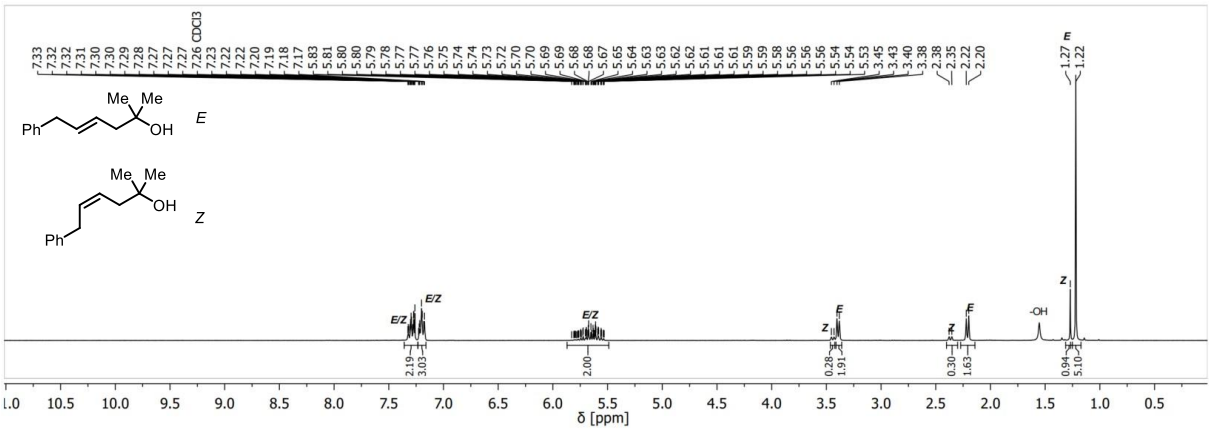


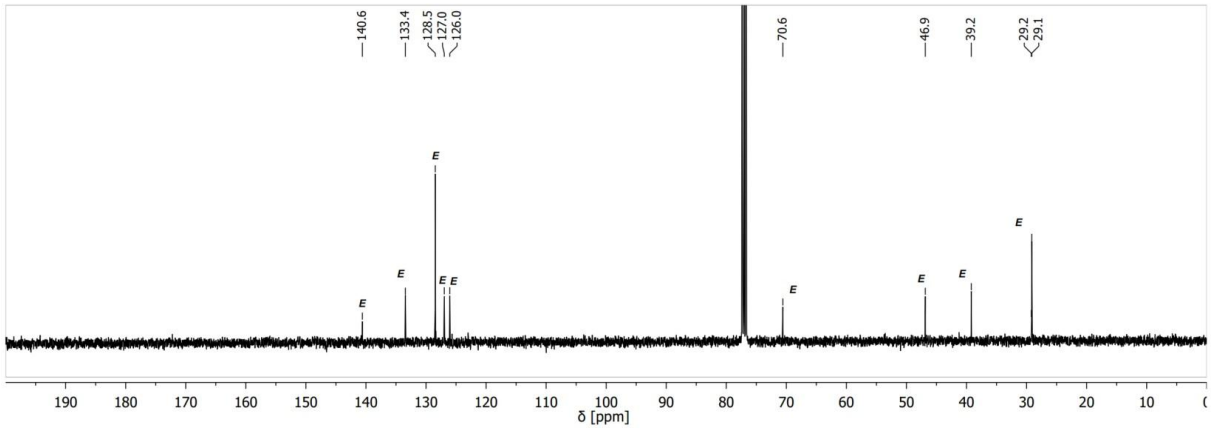


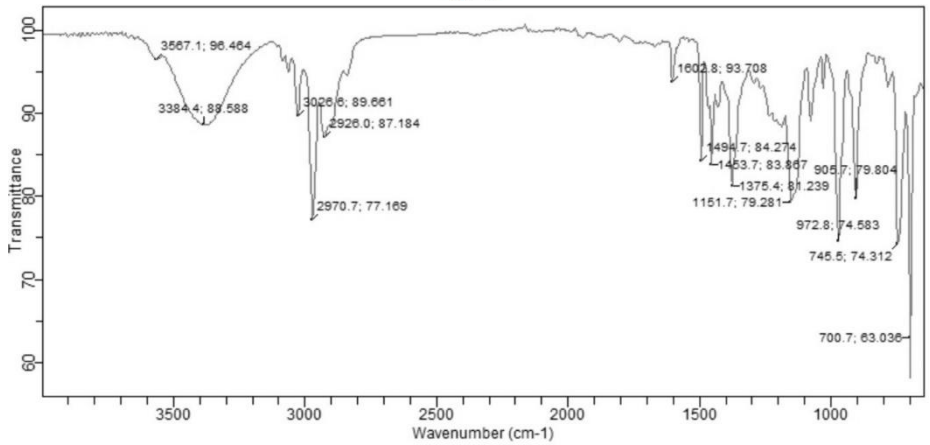
Spectra of project “1,3-dioxan-2-ones” – starting materials

2-Methyl-6-phenylhex-4-en-2-ol (142x)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d,* **IR**



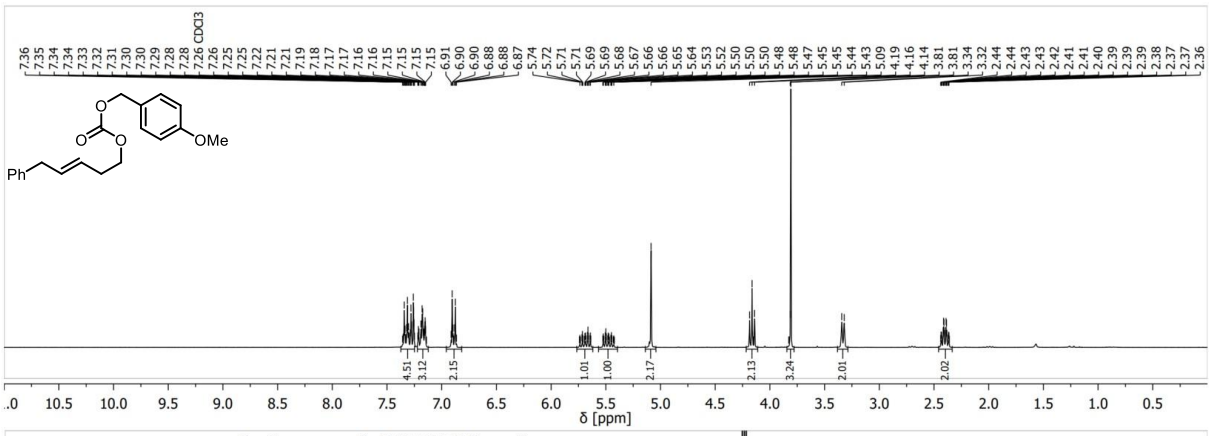


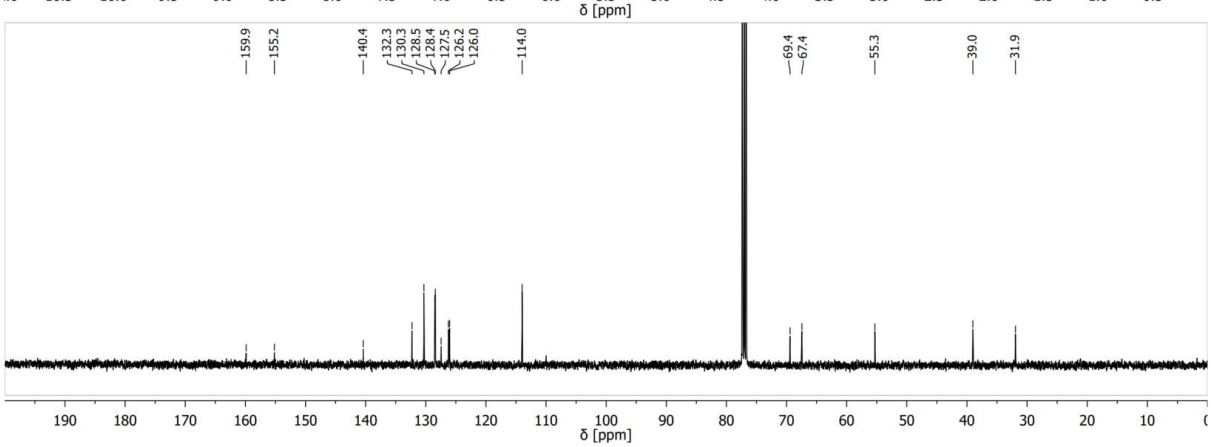


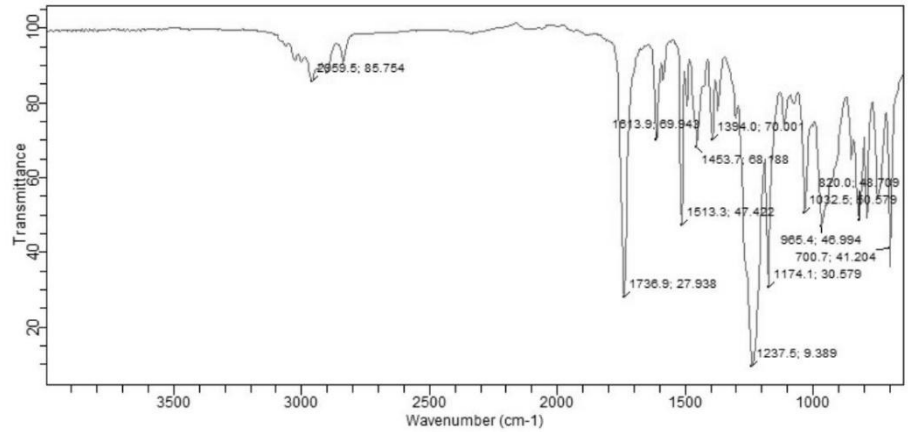
Spectra of project “1,3-dioxan-2-ones” – starting materials

(*E*)-4-Methoxybenzyl (5-phenylpent-3-en-1-yl) carbonate (135a)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



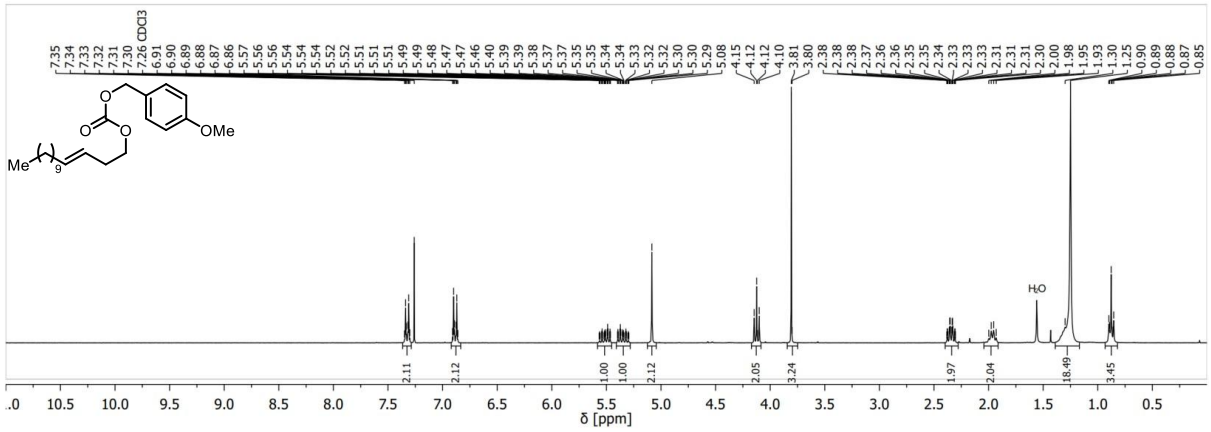


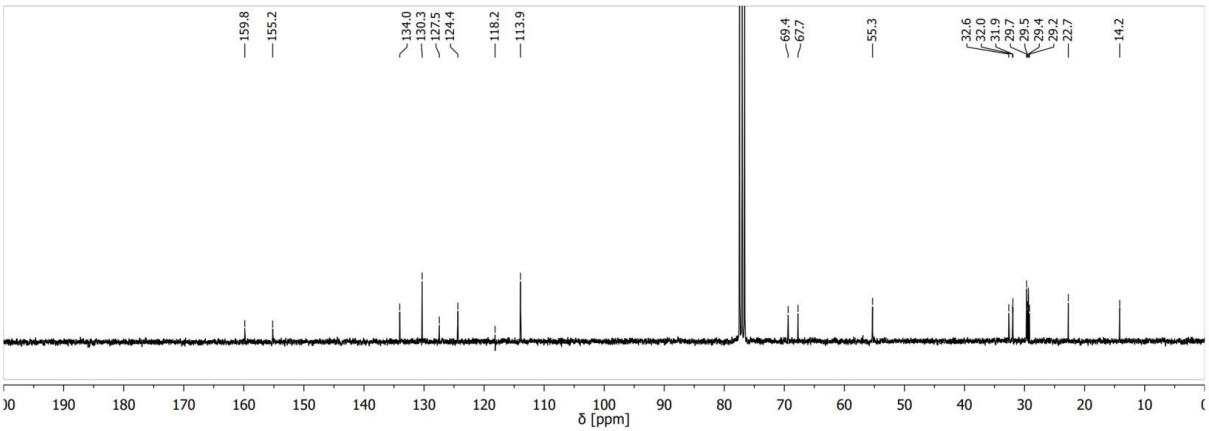


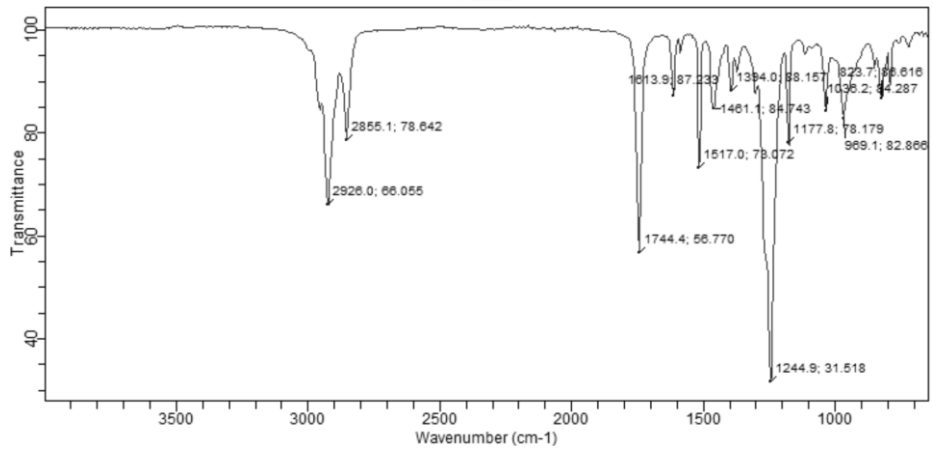
Spectra of project “1,3-dioxan-2-ones” – starting materials

(*E*)-4-Methoxybenzyl tetradec-3-en-1-yl carbonate (135d)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**

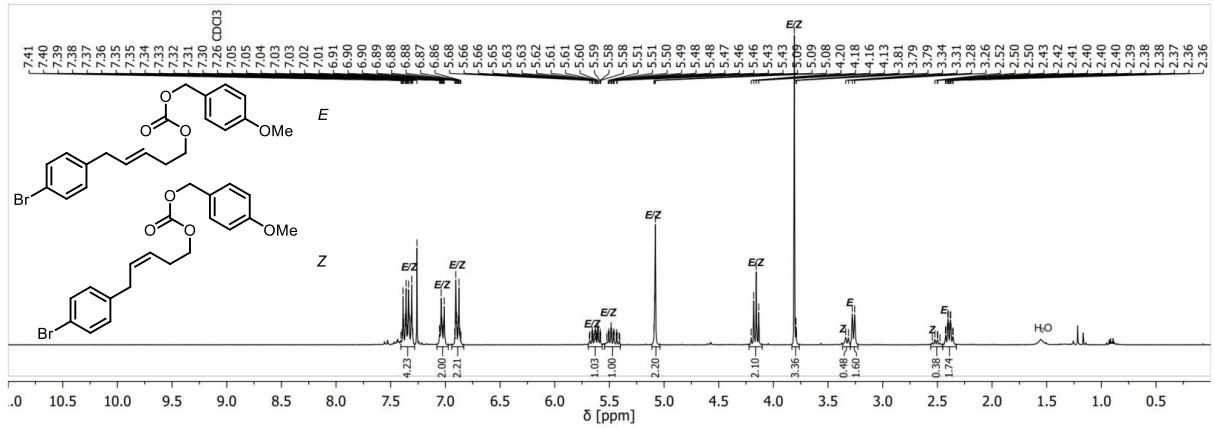


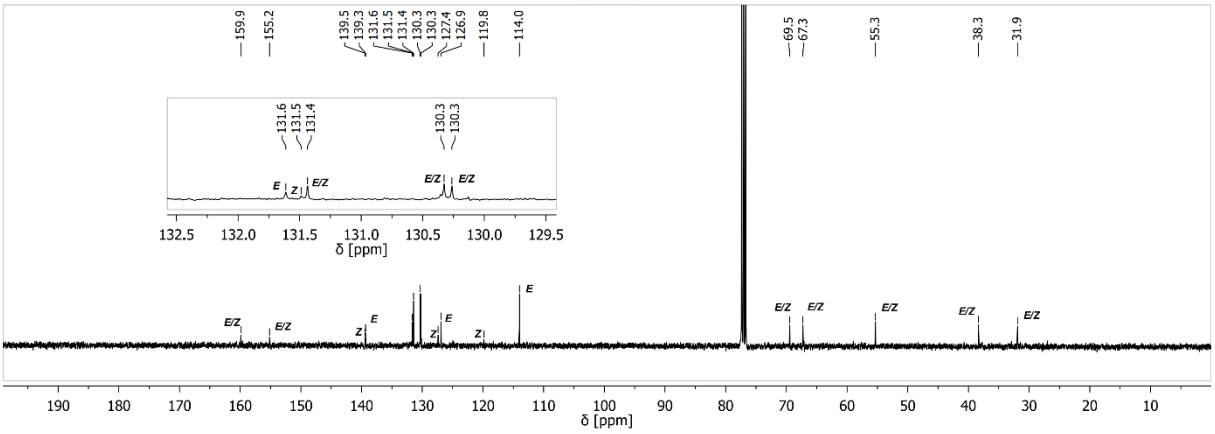


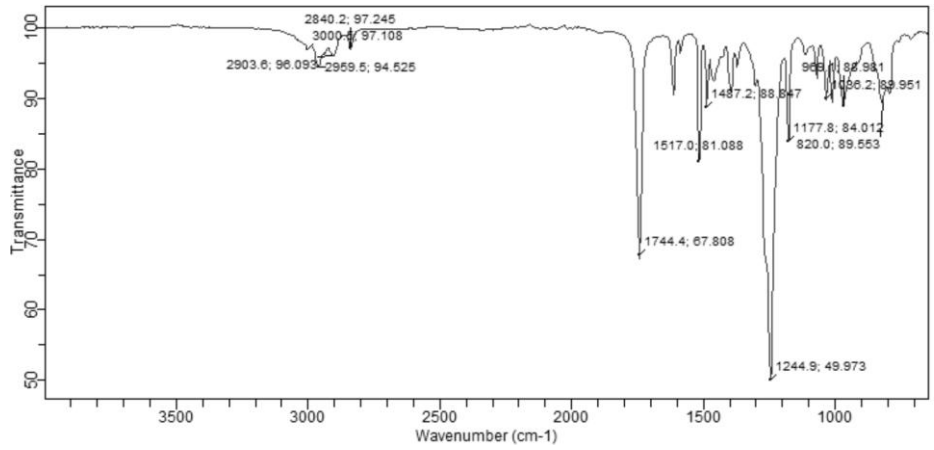


5-(4-Bromophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (135g)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



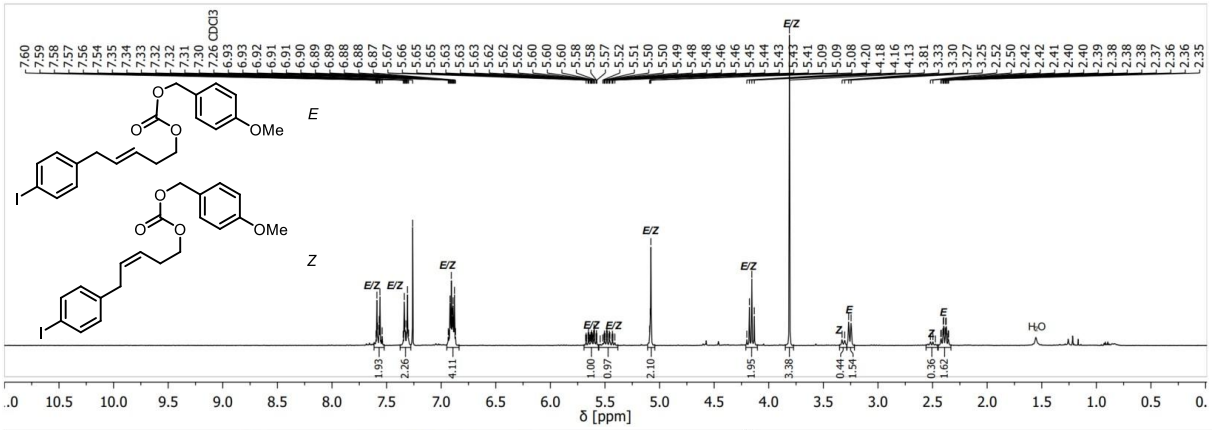


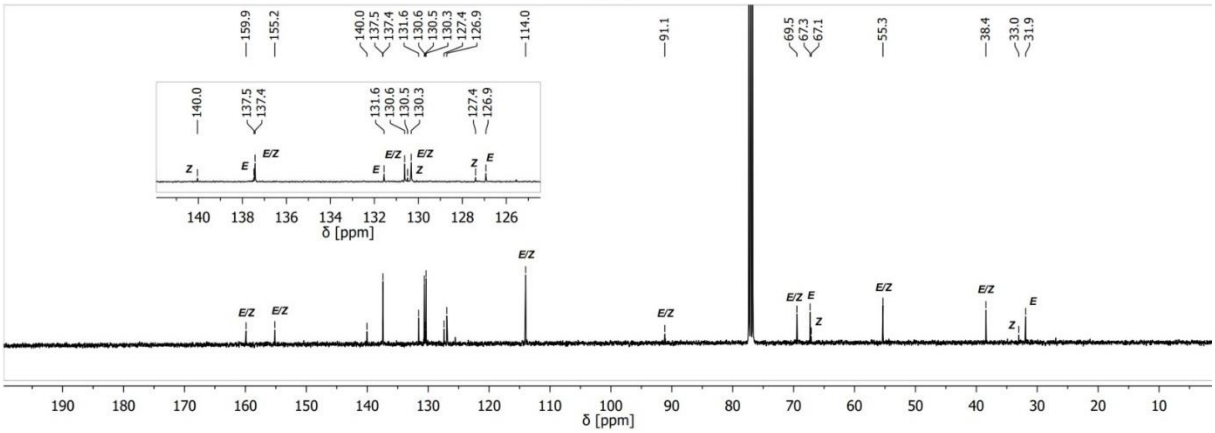


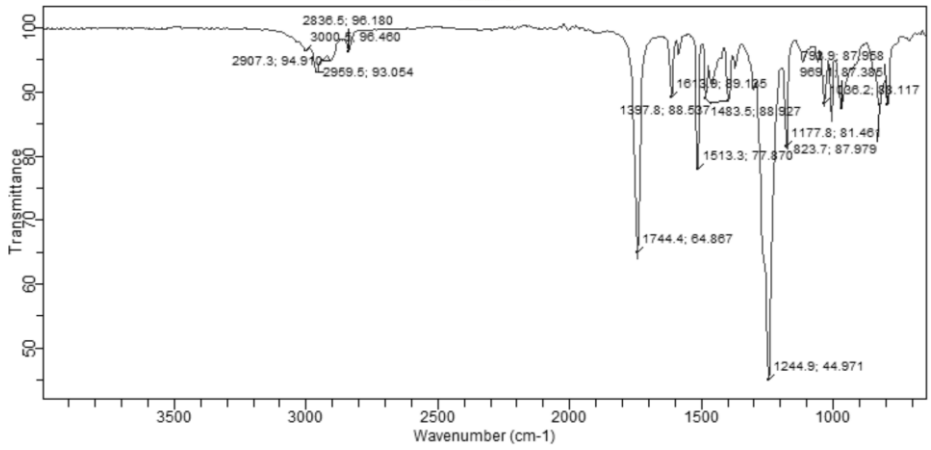
Spectra of project “1,3-dioxan-2-ones” – starting materials

5-(4-Iodophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (135h)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

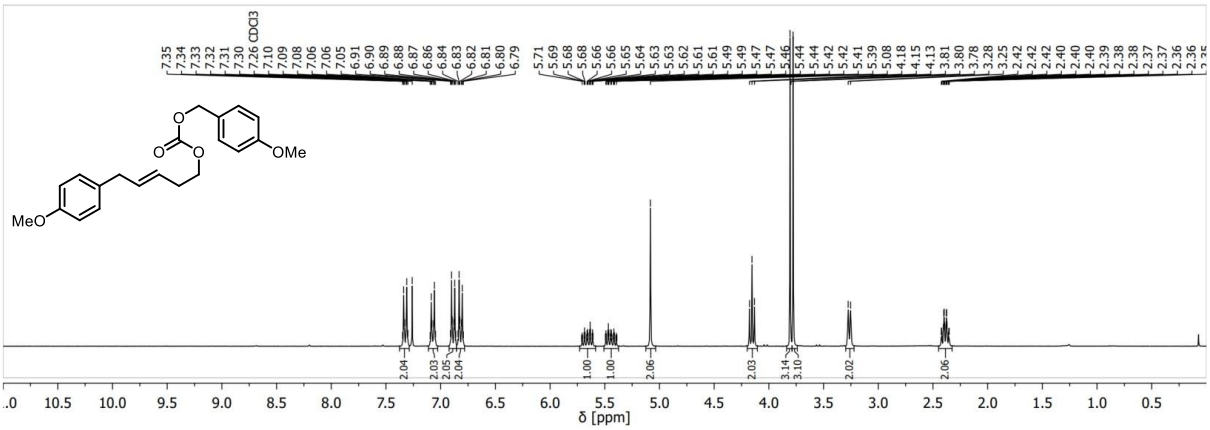


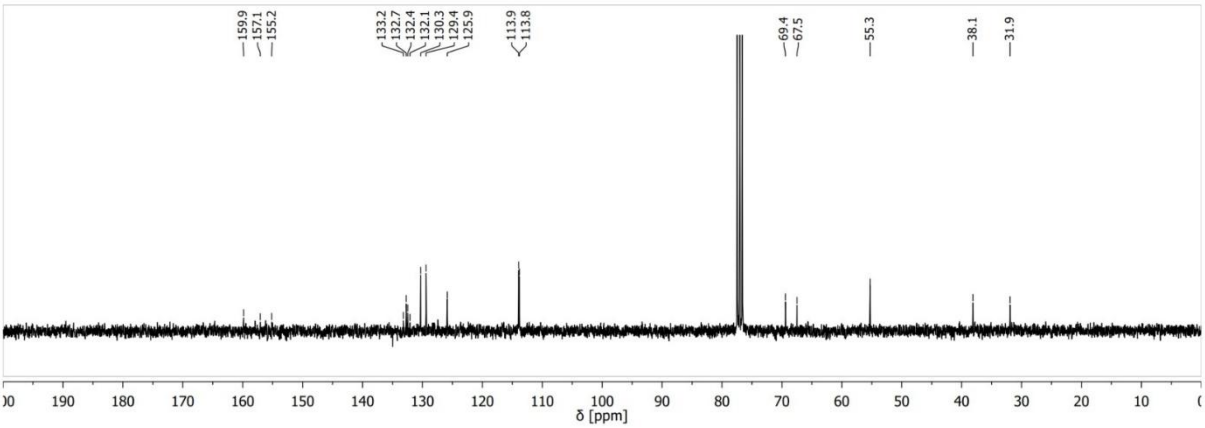


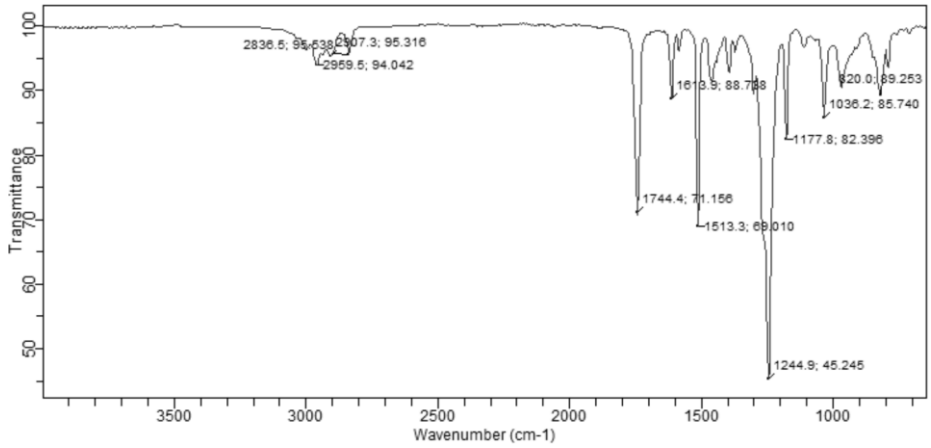


(*E*)-4-Methoxybenzyl (5-(4-methoxyphenyl)pent-3-en-1-yl) carbonate (135i)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



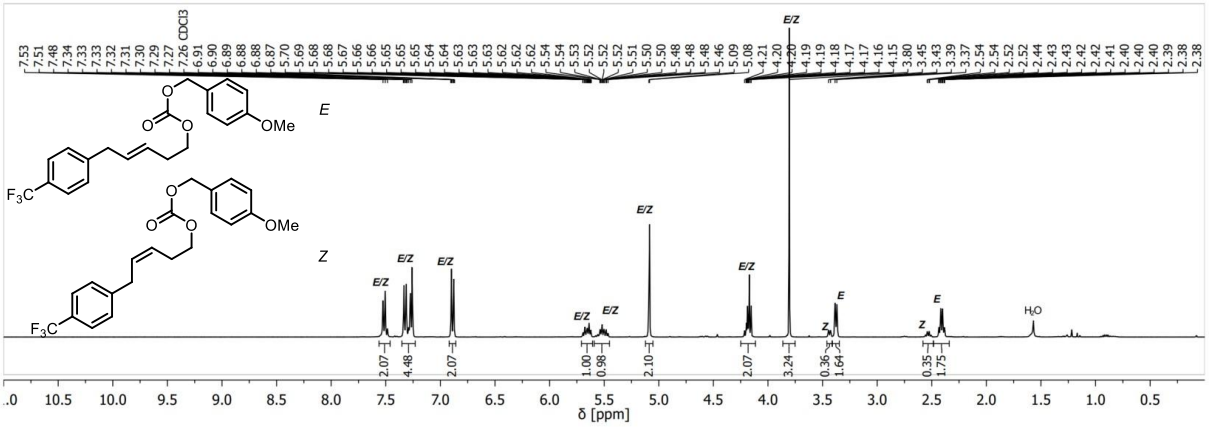


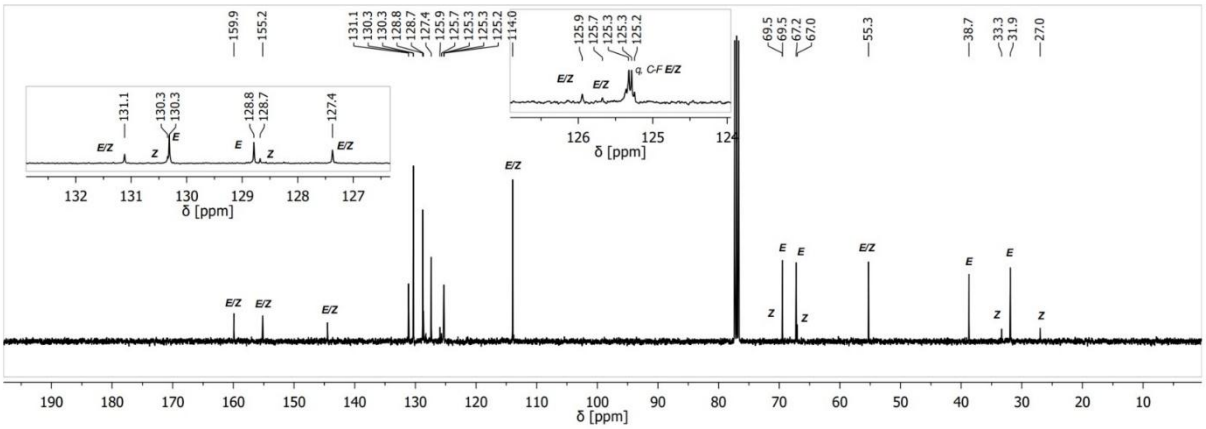


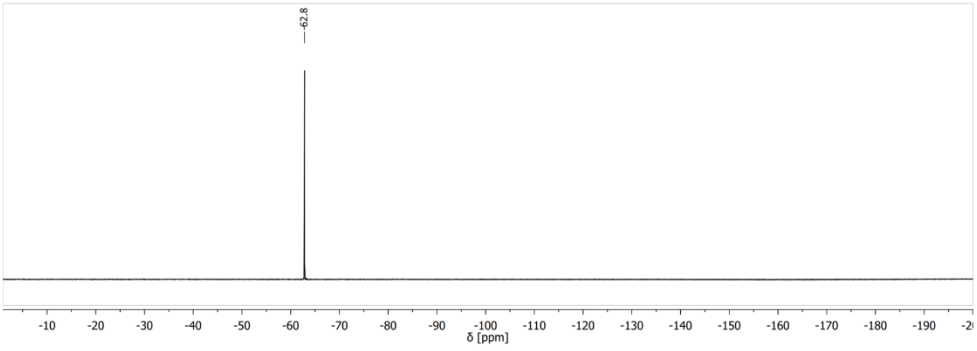
Spectra of project “1,3-dioxan-2-ones” – starting materials

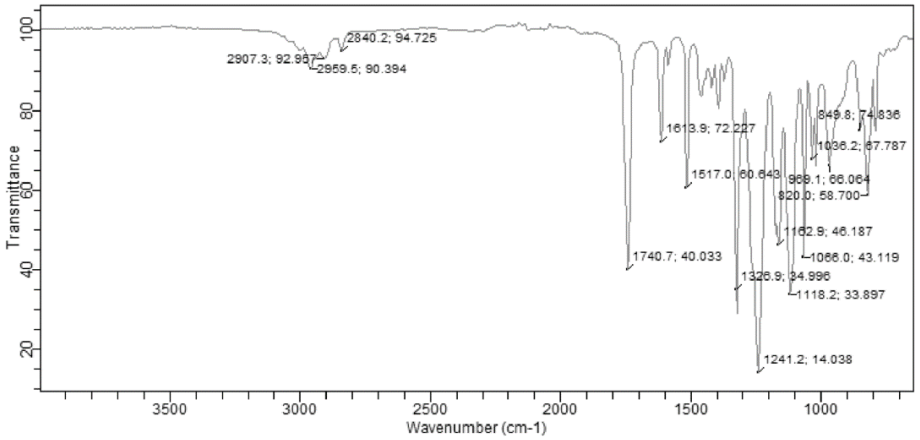
4-Methoxybenzyl (5-(4-(trifluoromethyl)phenyl)pent-3-en-1-yl) carbonate (135j)

^{1}H NMR (400 MHz), **^{13}C NMR** (101 MHz) **^{19}F{^{1}H} NMR** (376 MHz) : Chloroform-*d*, **IR**





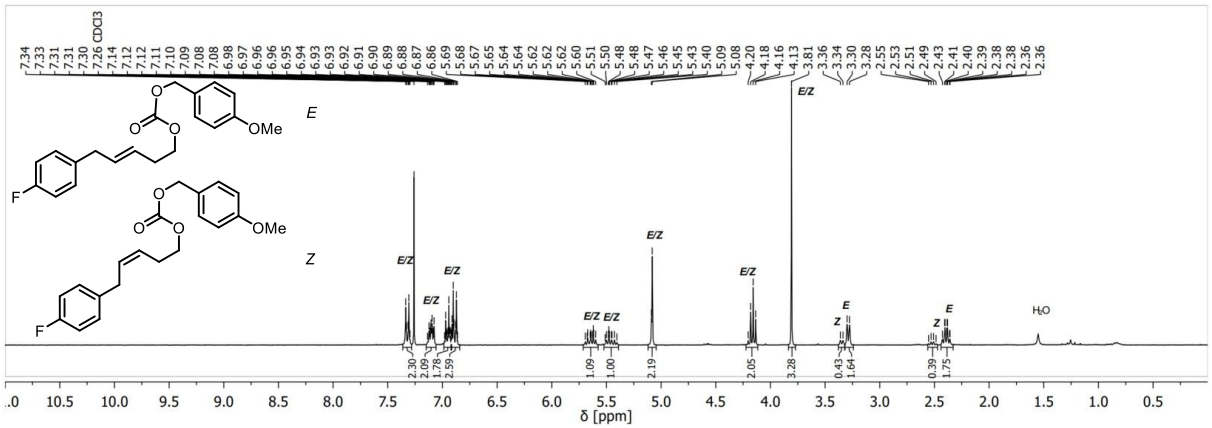


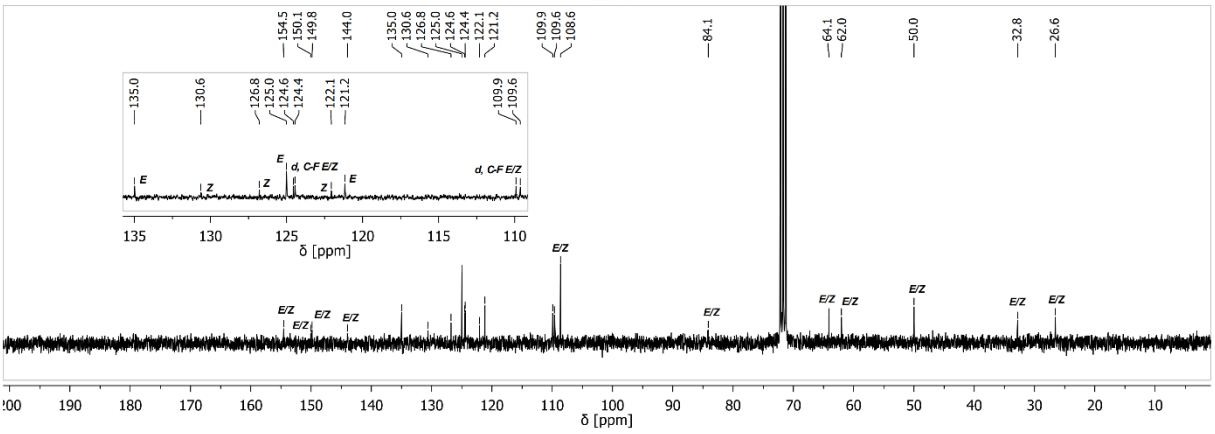


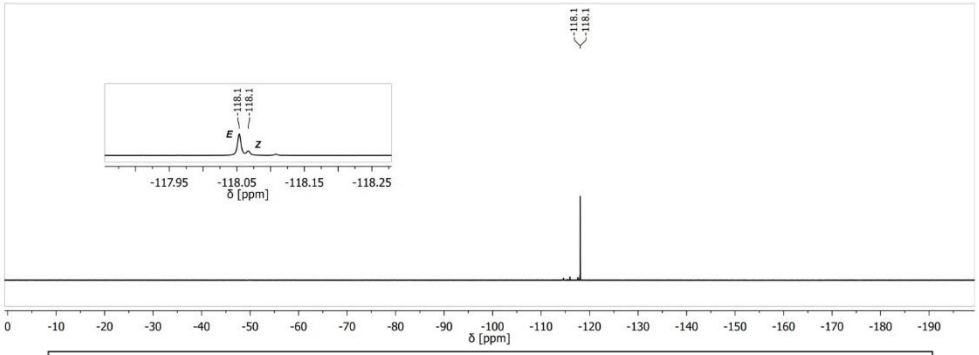
Spectra of project “1,3-dioxan-2-ones” – starting materials

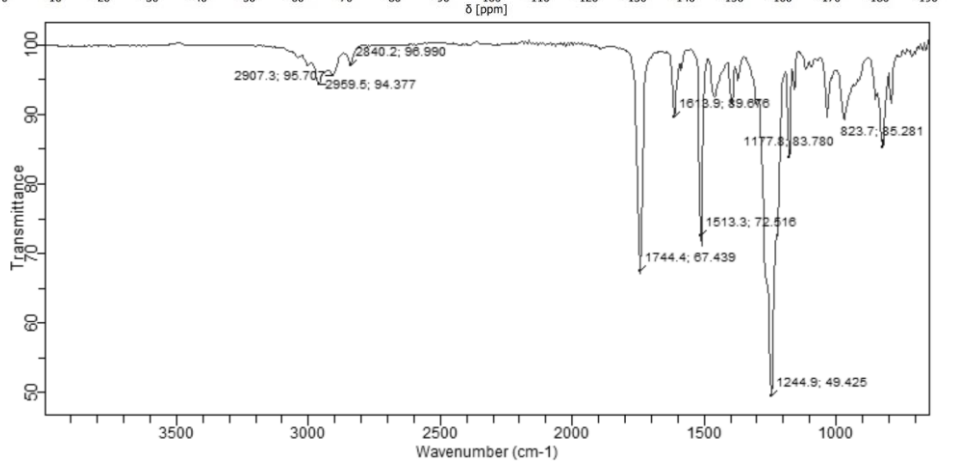
5-(4-Fluorophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (135k)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz), **^{19}F{^{1}H} NMR** (376 MHz): Chloroform-*d*, **IR**



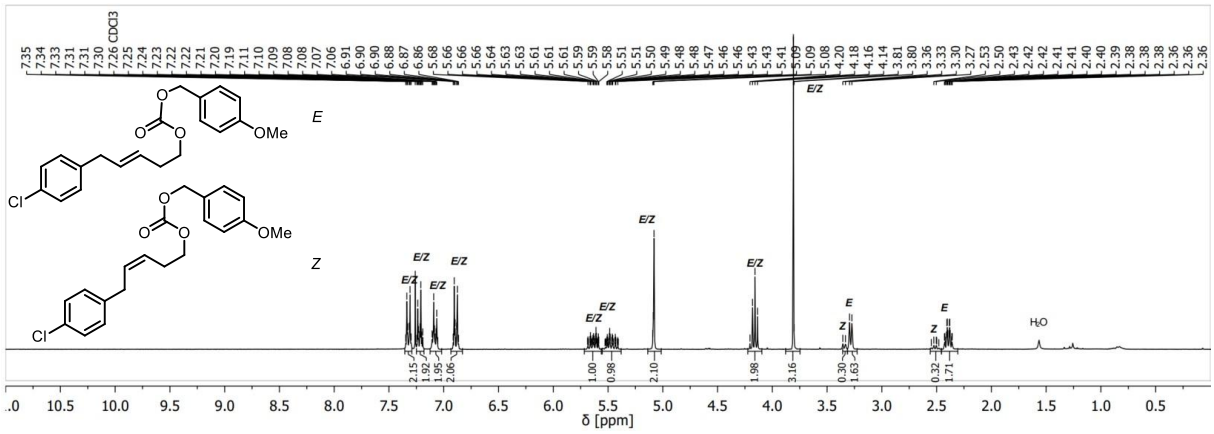


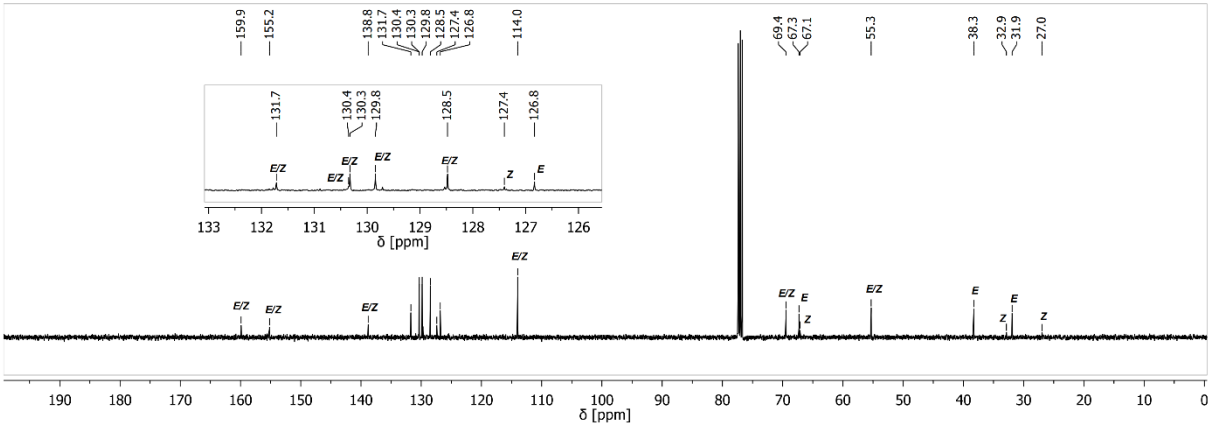


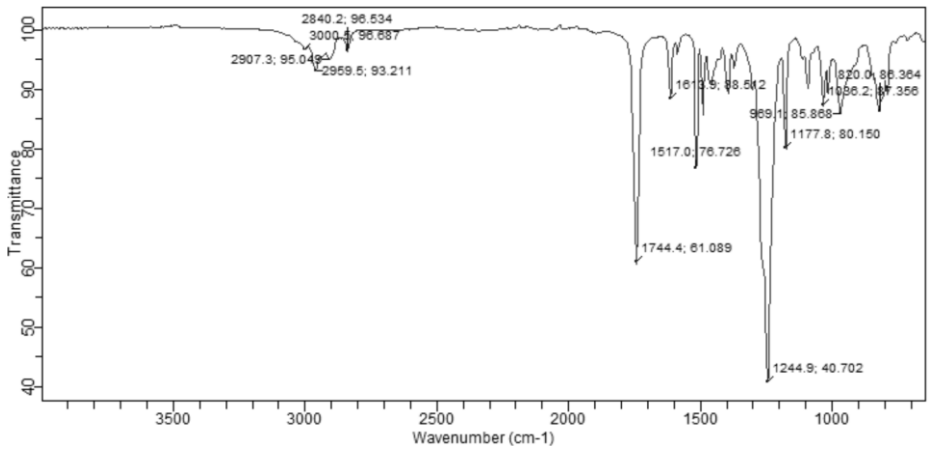


5-(4-Chlorophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (135l)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

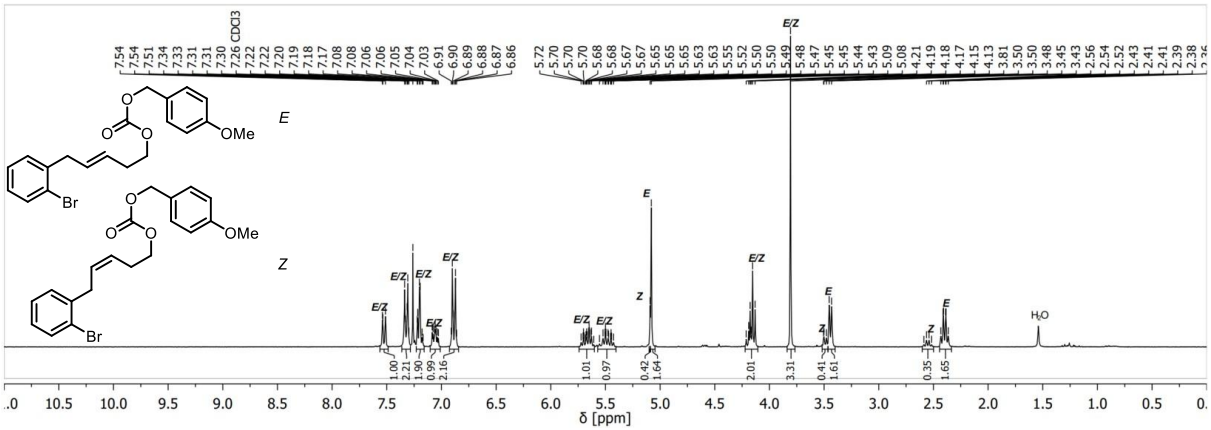


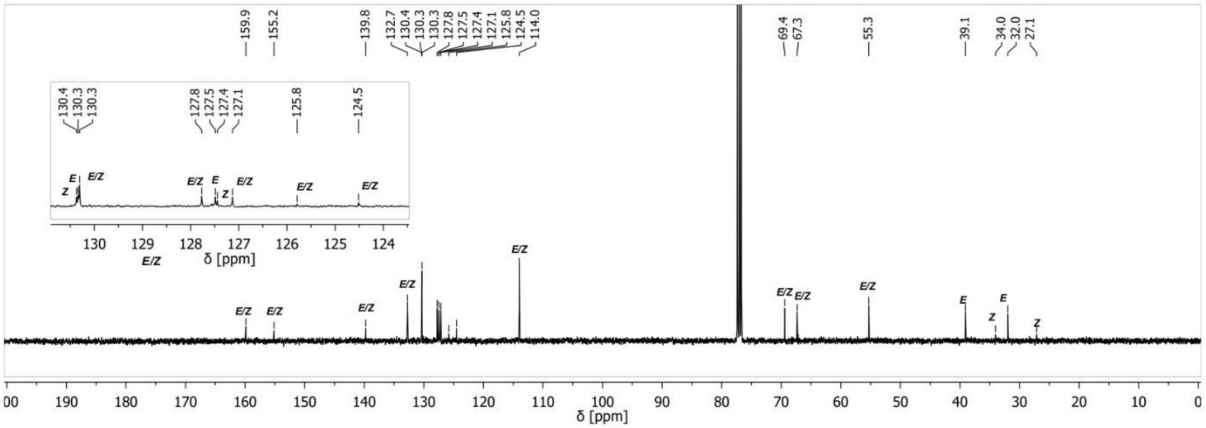


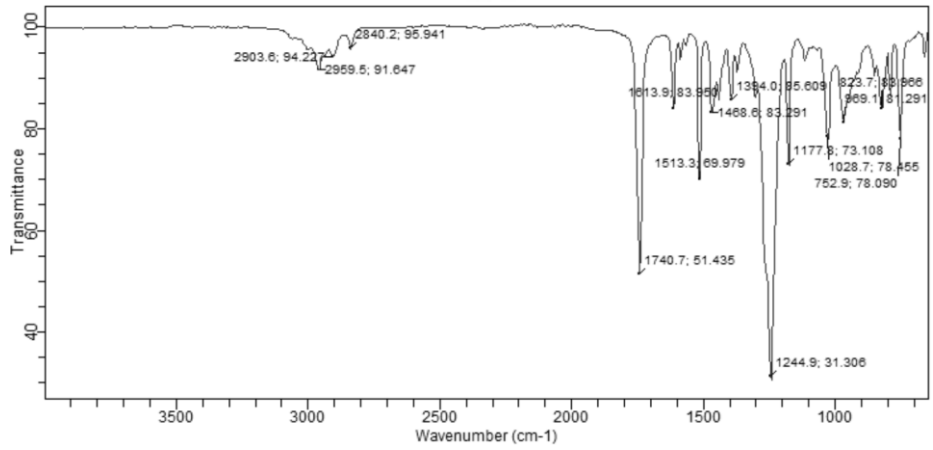


5-(2-Bromophenyl)pent-3-en-1-yl (4-methoxybenzyl) carbonate (135m)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



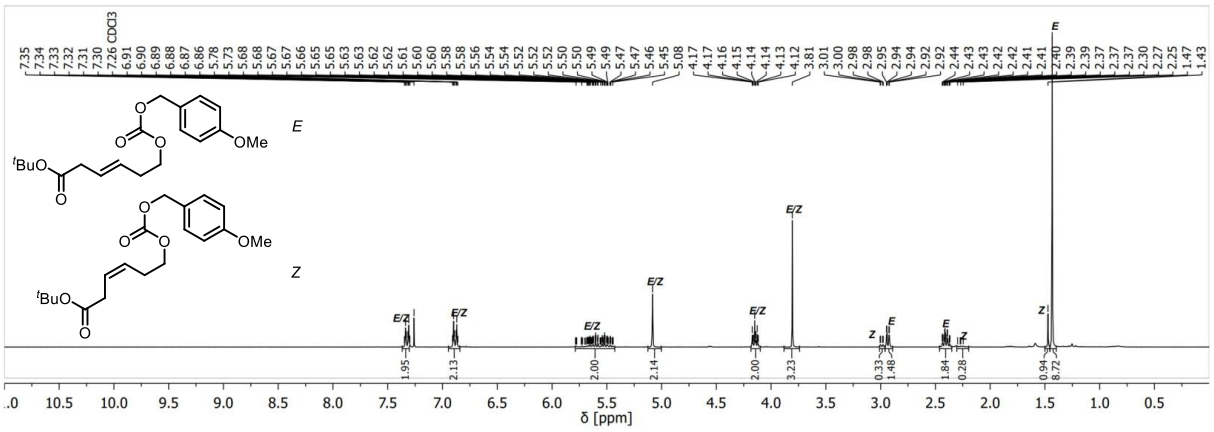


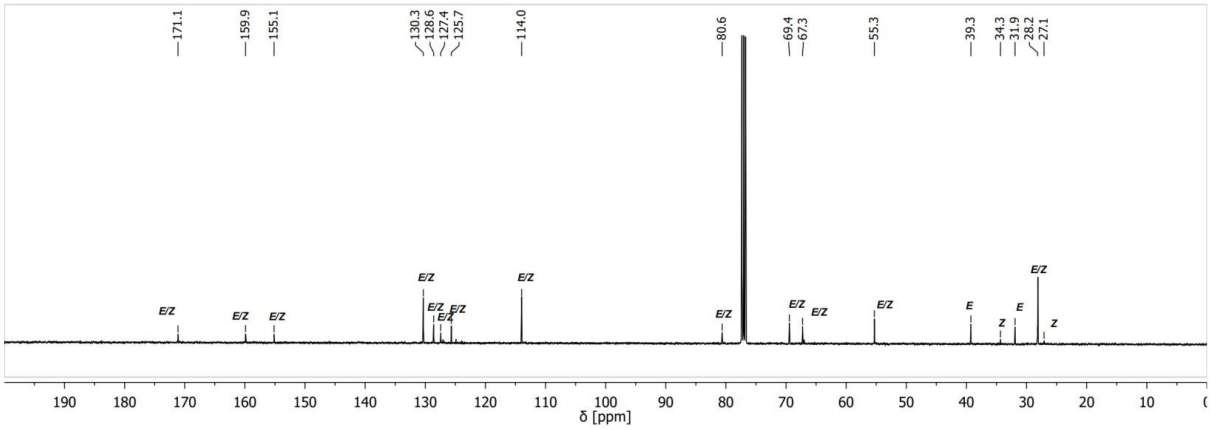


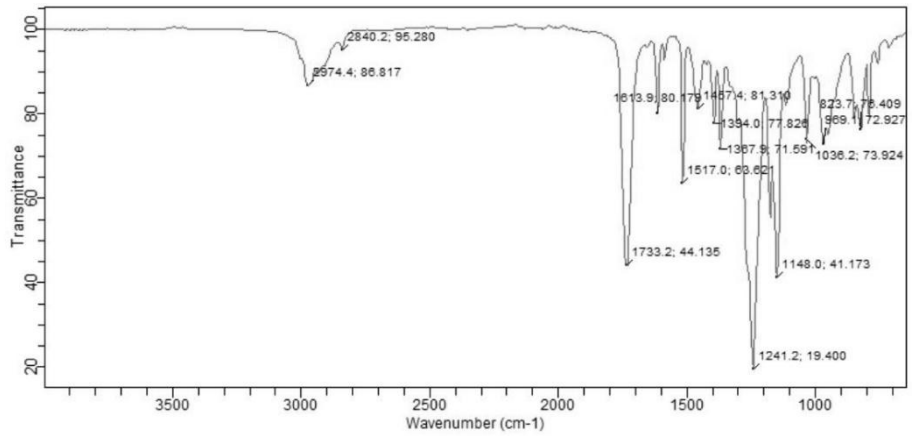
Spectra of project “1,3-dioxan-2-ones” – starting materials

tert-Butyl-6-((((4-Methoxybenzyl)oxy)carbonyl)oxy)hex-3-enoate (135n)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

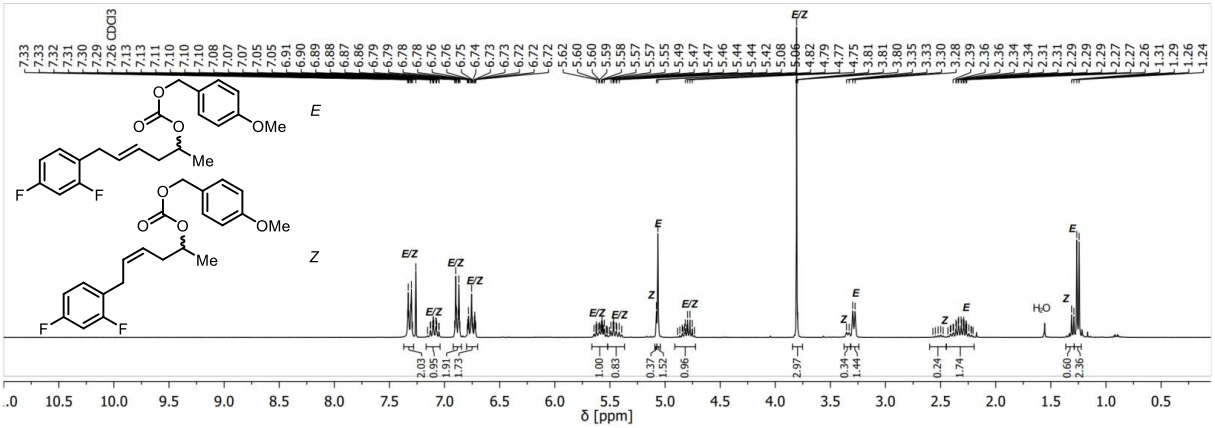


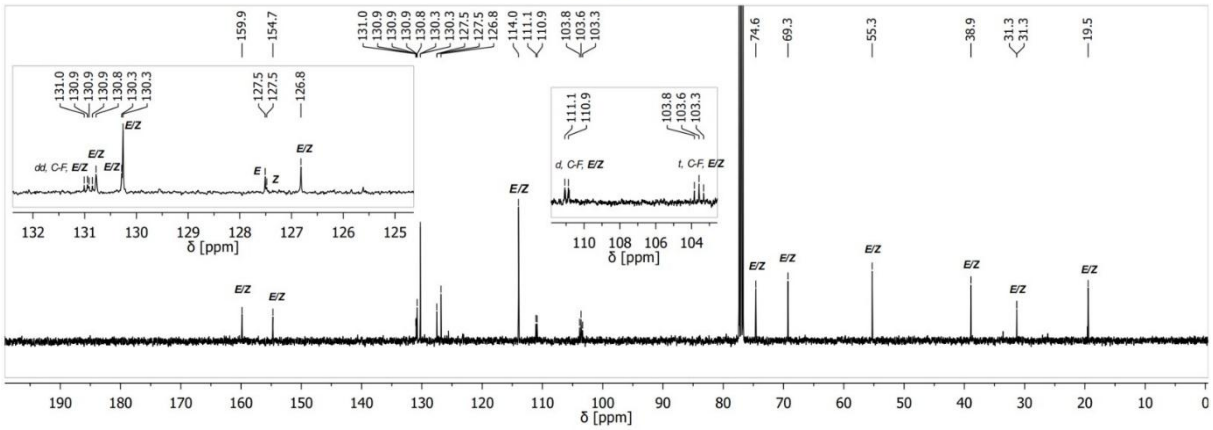


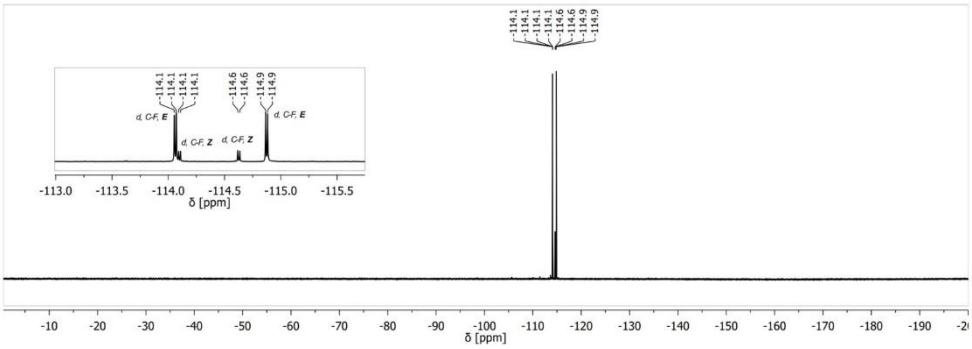


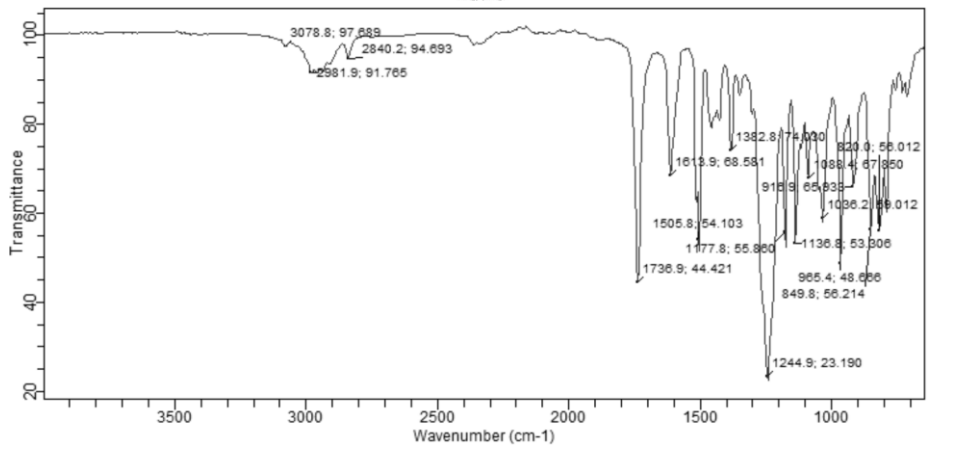
6-(2,4-Difluorophenyl)hex-4-en-2-yl (4-methoxybenzyl) carbonate (135o)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz) **^{19}F{^{1}H} NMR** (376 MHz) : Chloroform-*d*, **IR**





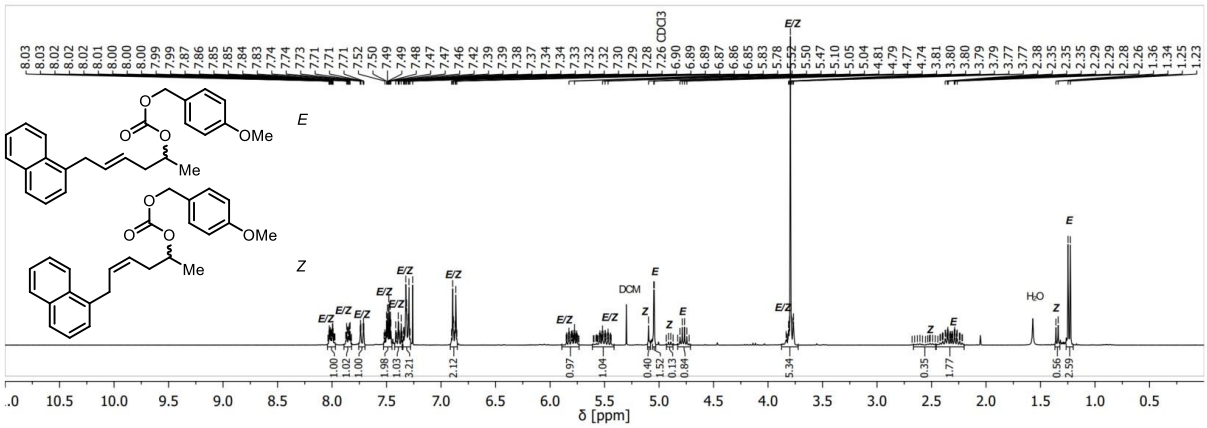




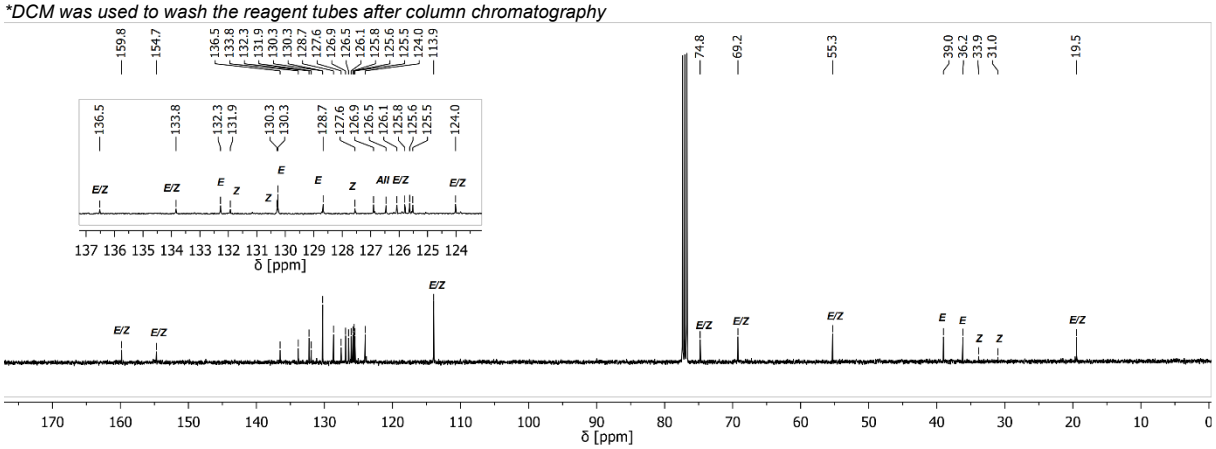
Spectra of project “1,3-dioxan-2-ones” – starting materials

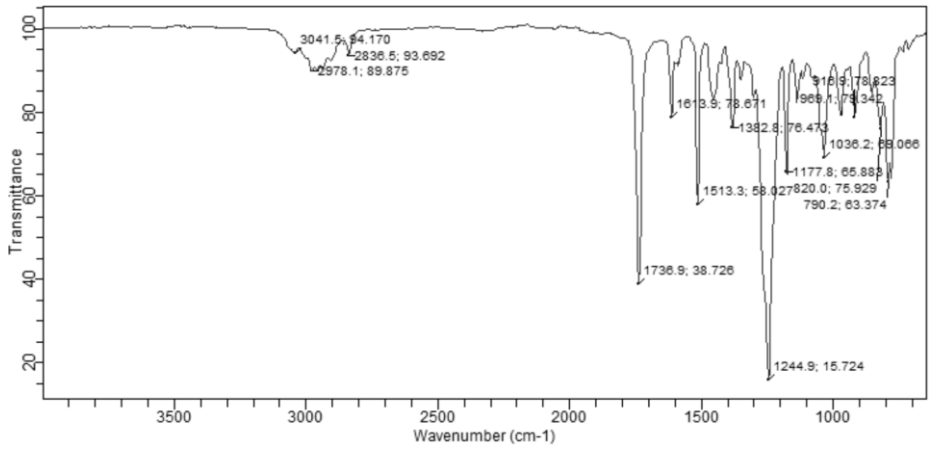
4-Methoxybenzyl (6-(naphthalen-1-yl)hex-4-en-2-yl) carbonate (135p)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



**DCM was used to wash the reagent tubes after column chromatography*

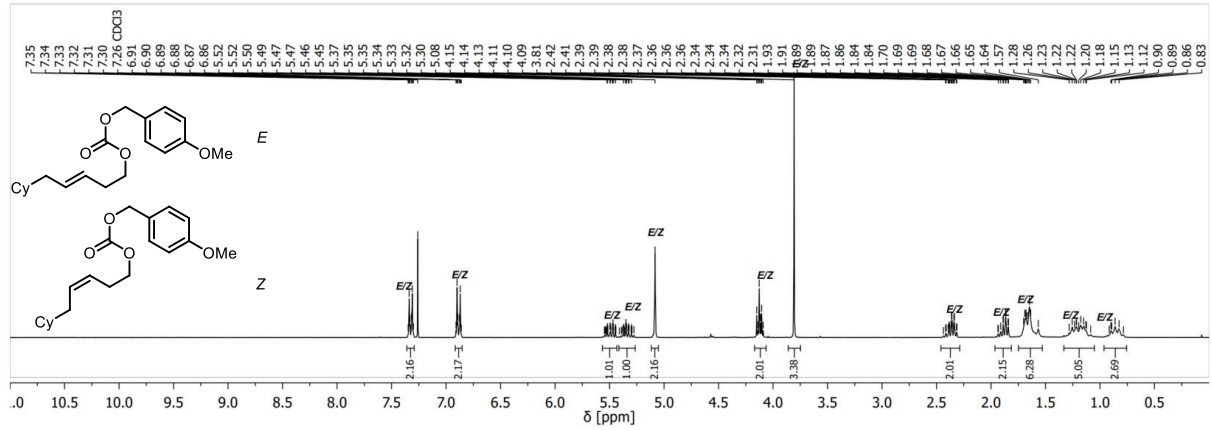


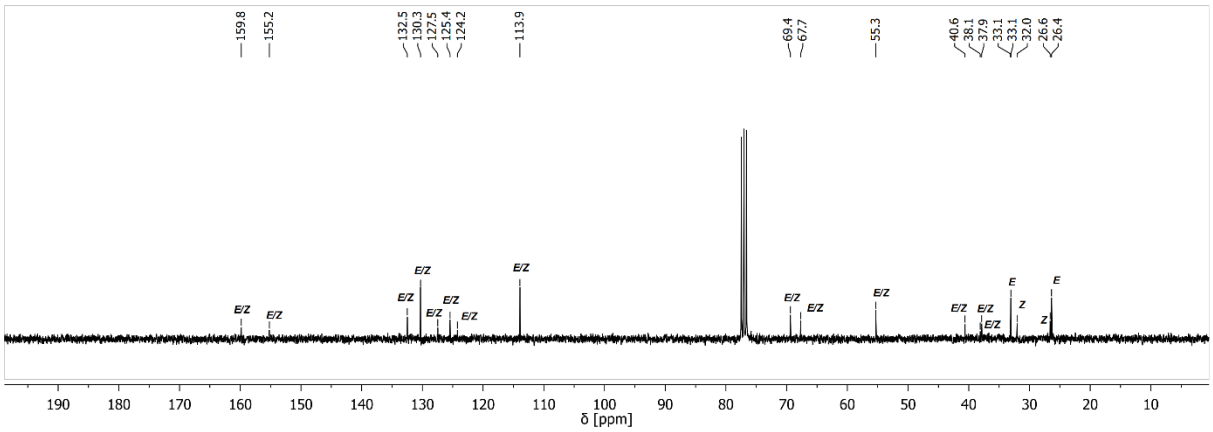


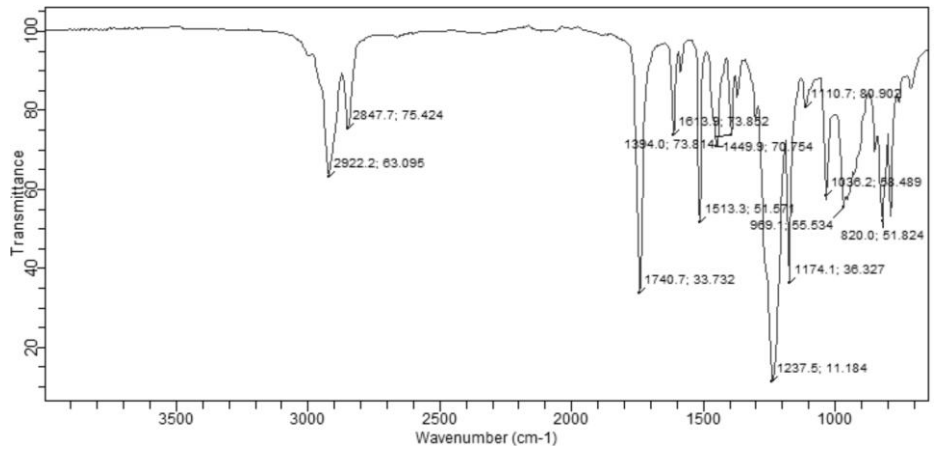
Spectra of project “1,3-dioxan-2-ones” – starting materials

5-Cyclohexylpent-3-en-1-yl (4-methoxybenzyl) carbonate (135q)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**

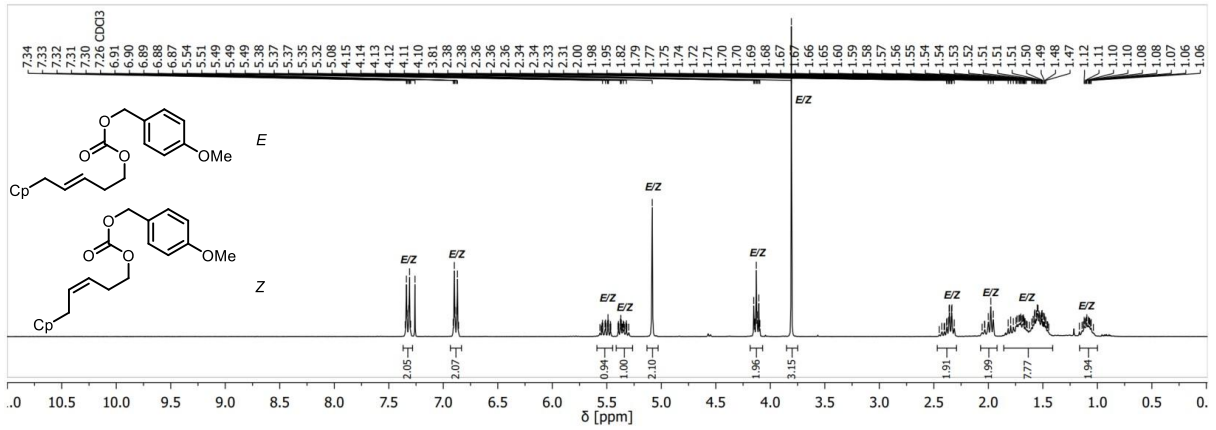


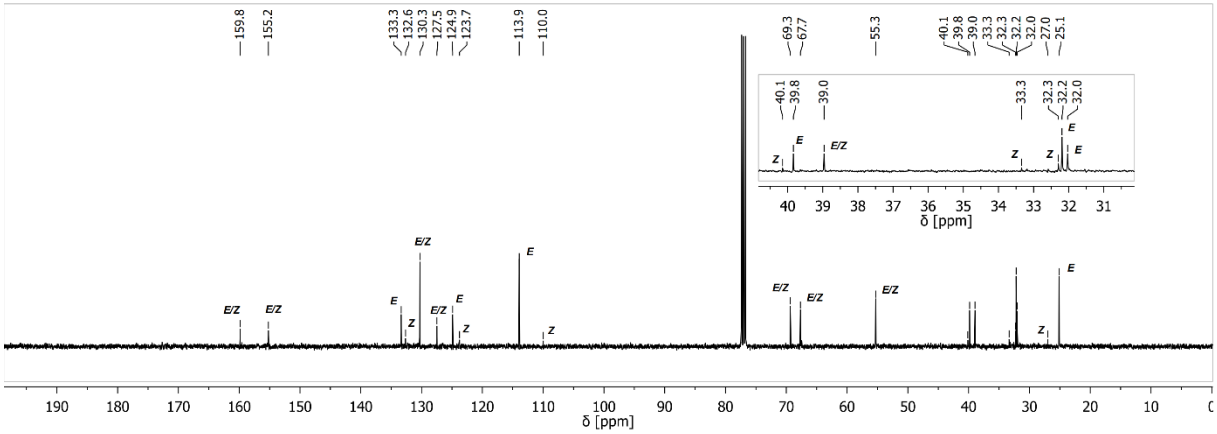


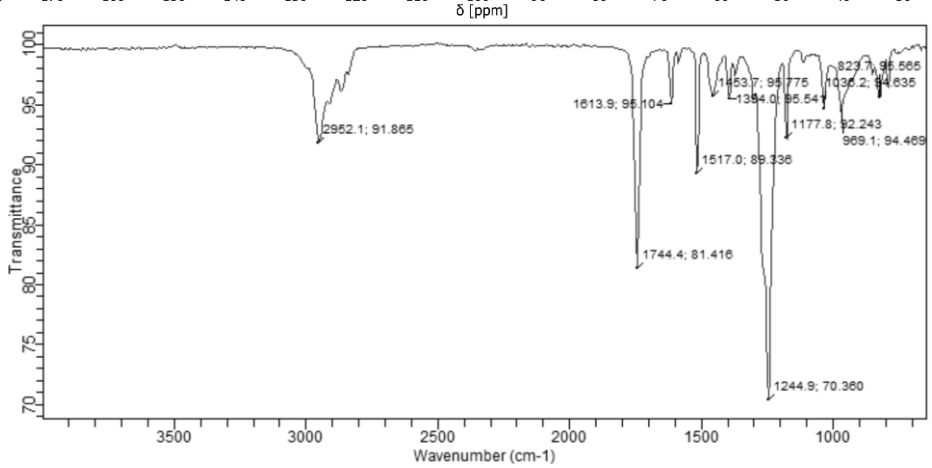


5-Cyclopentylpent-3-en-1-yl (4-methoxybenzyl) carbonate (135r)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

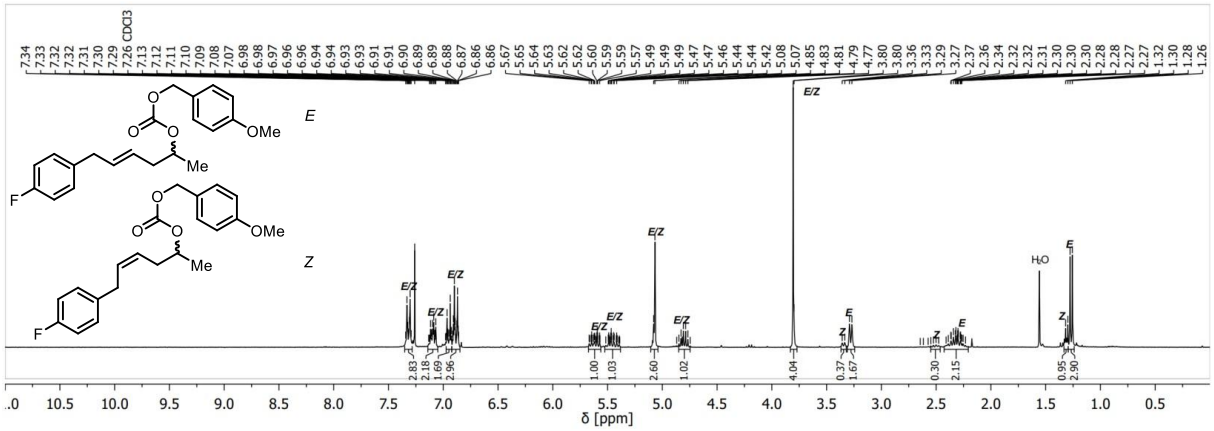


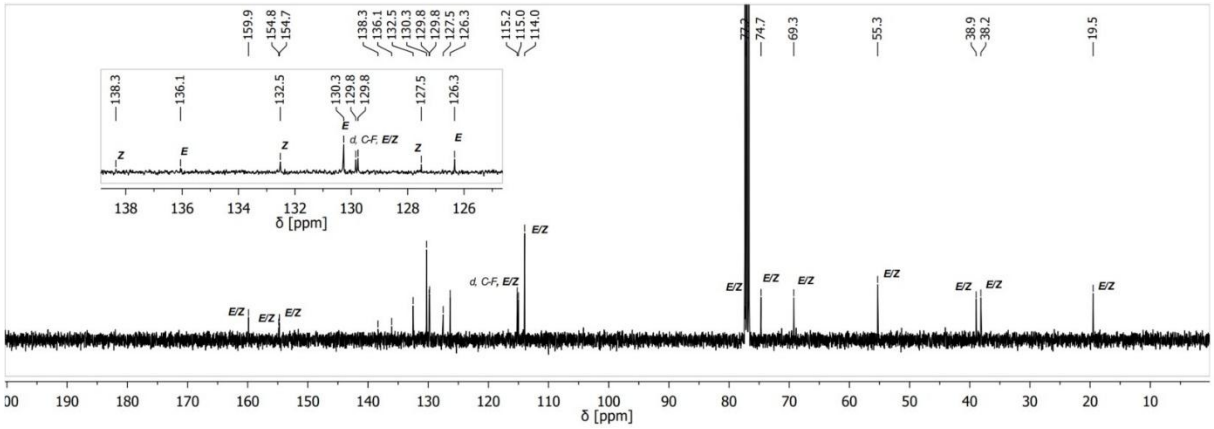


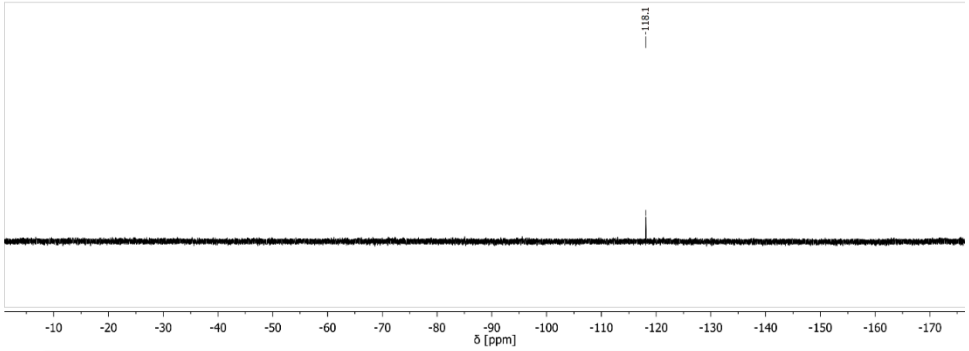


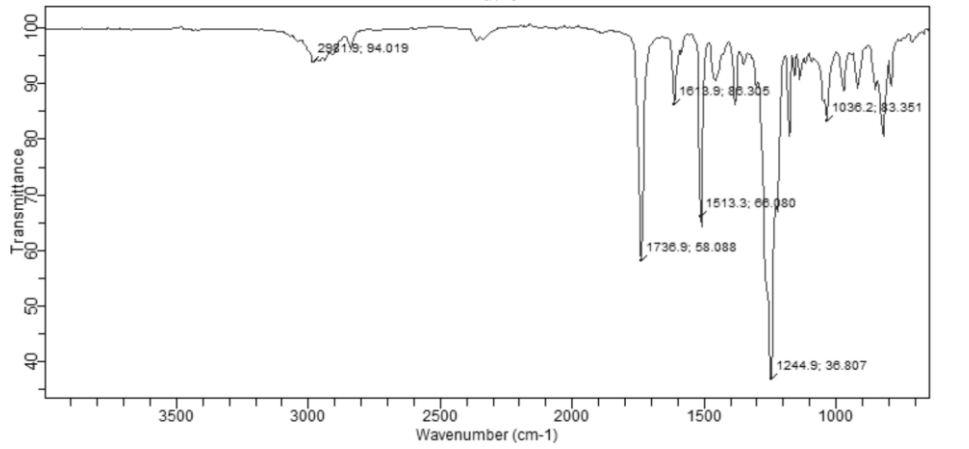
6-(4-Fluorophenyl)hex-4-en-2-yl (4-methoxybenzyl) carbonate (135s)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz), **^{19}F NMR** (376 MHz): Chloroform-*d*, **IR**



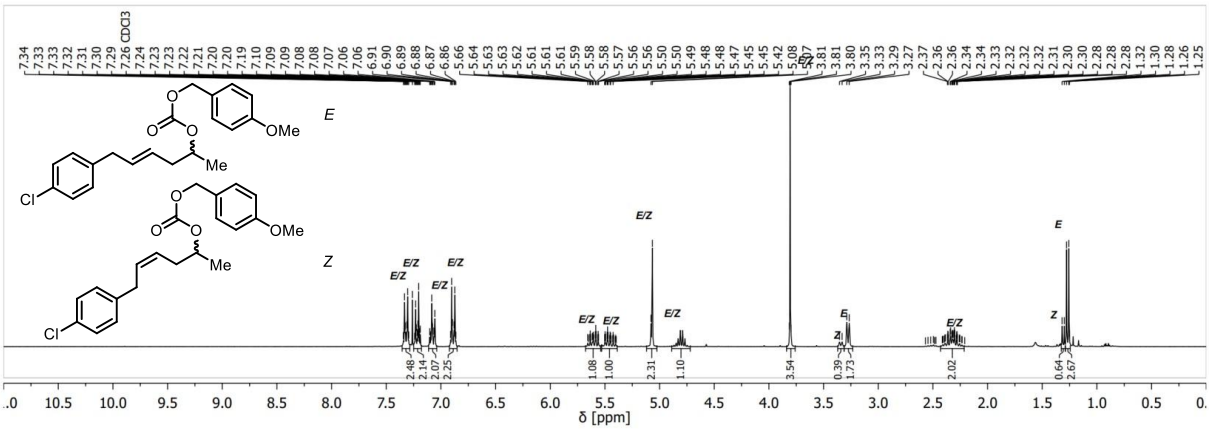


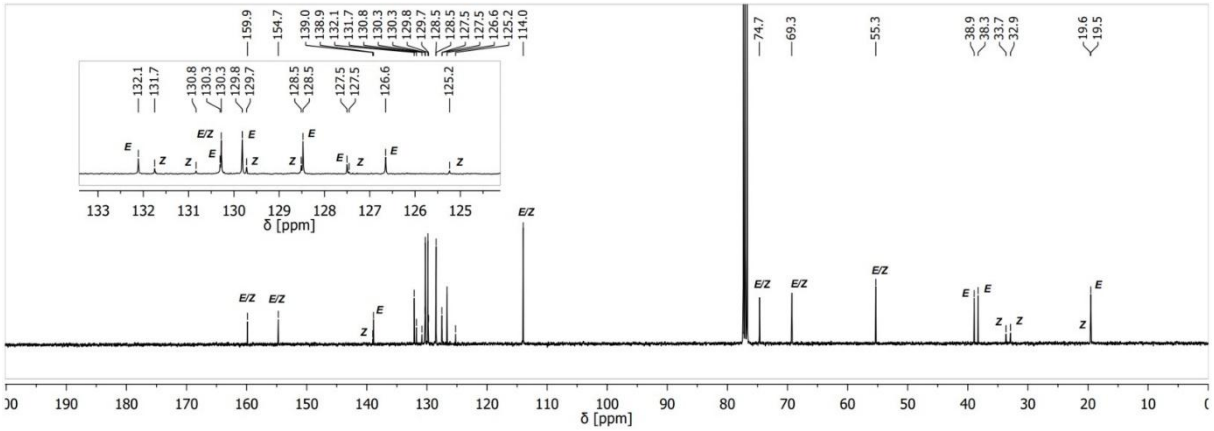


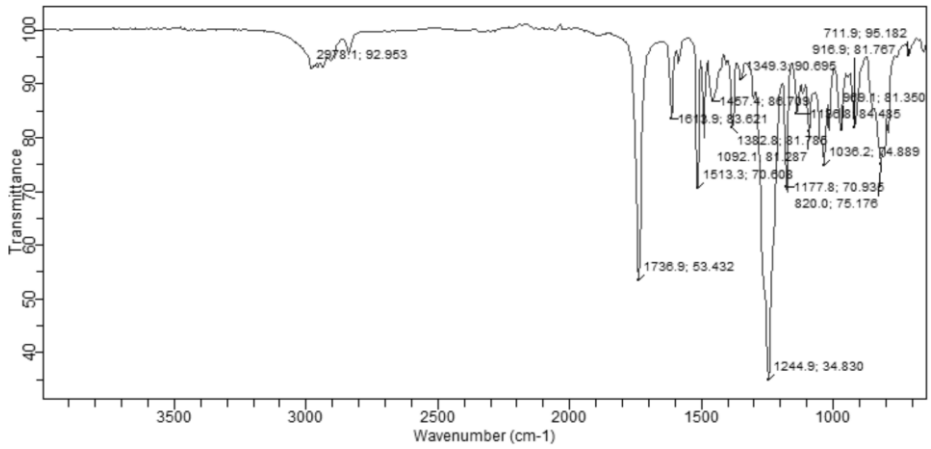


6-(4-Chlorophenyl)hex-4-en-2-yl (4-methoxybenzyl) carbonate (135t)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



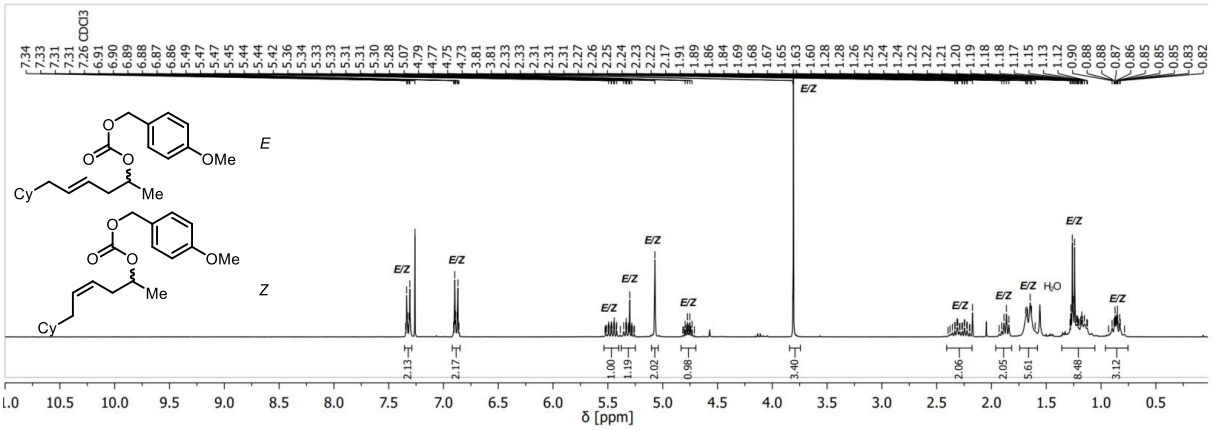


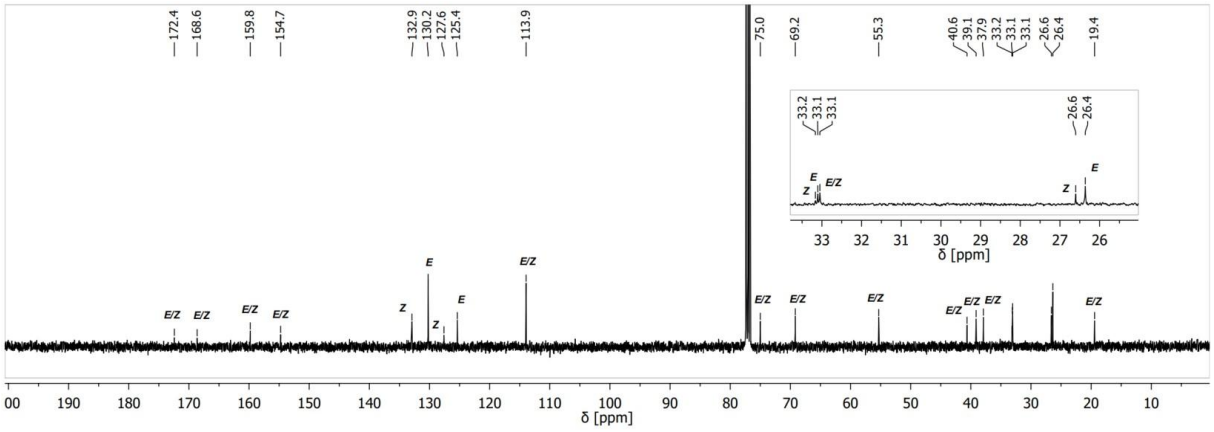


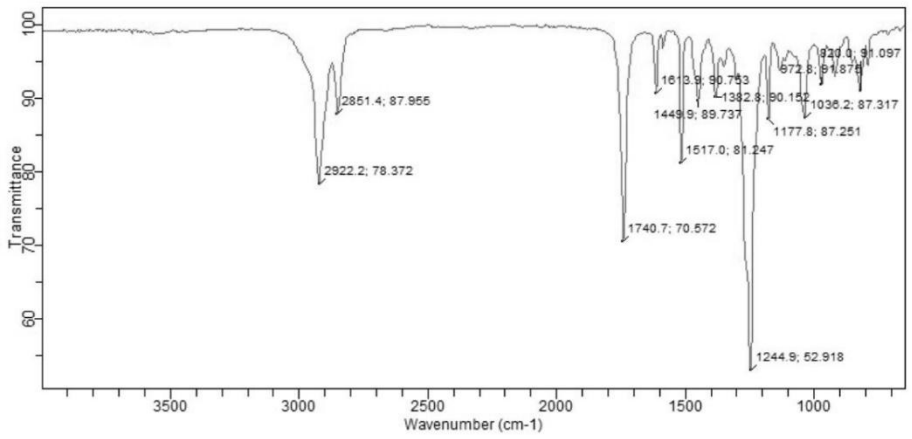
Spectra of project “1,3-dioxan-2-ones” – starting materials

6-Cyclohexylhex-4-en-2-yl (4-methoxybenzyl) carbonate (135u)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

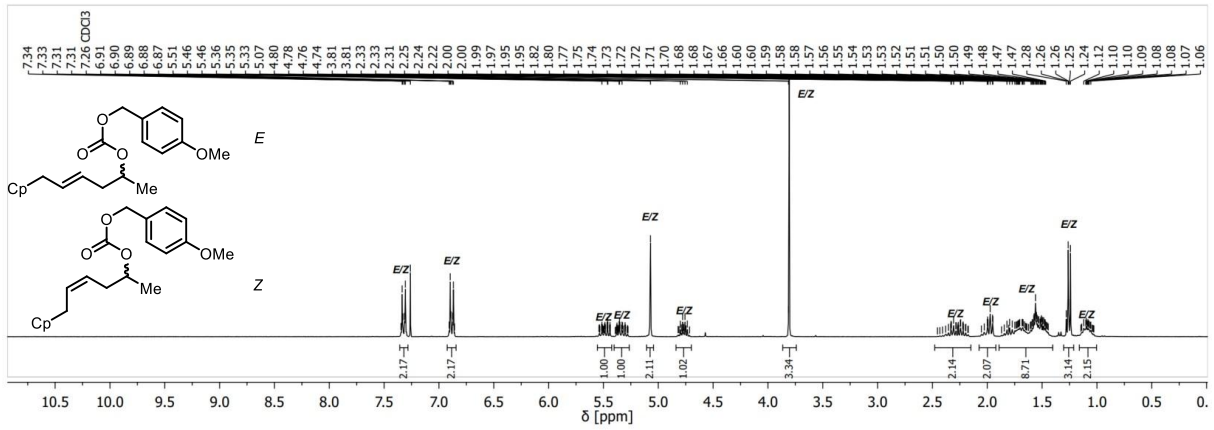


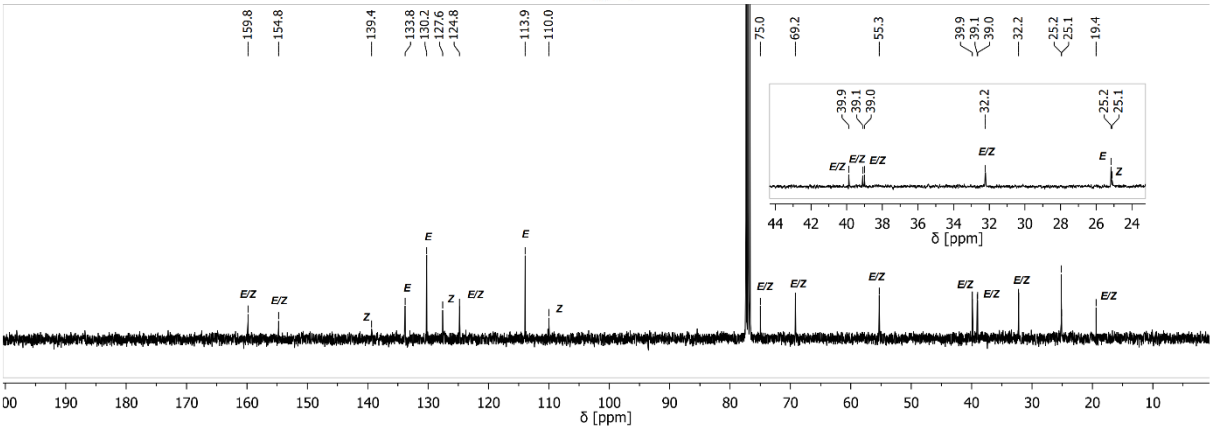


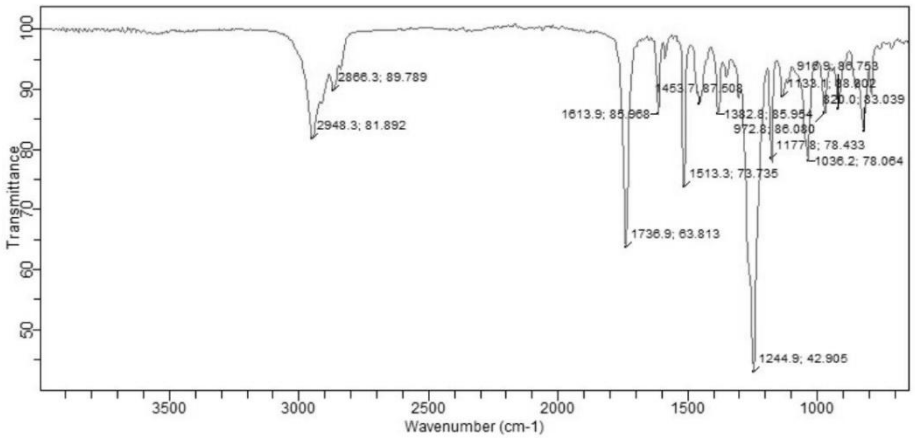


6-Cyclopentylhex-4-en-2-yl (4-methoxybenzyl) carbonate (135v)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

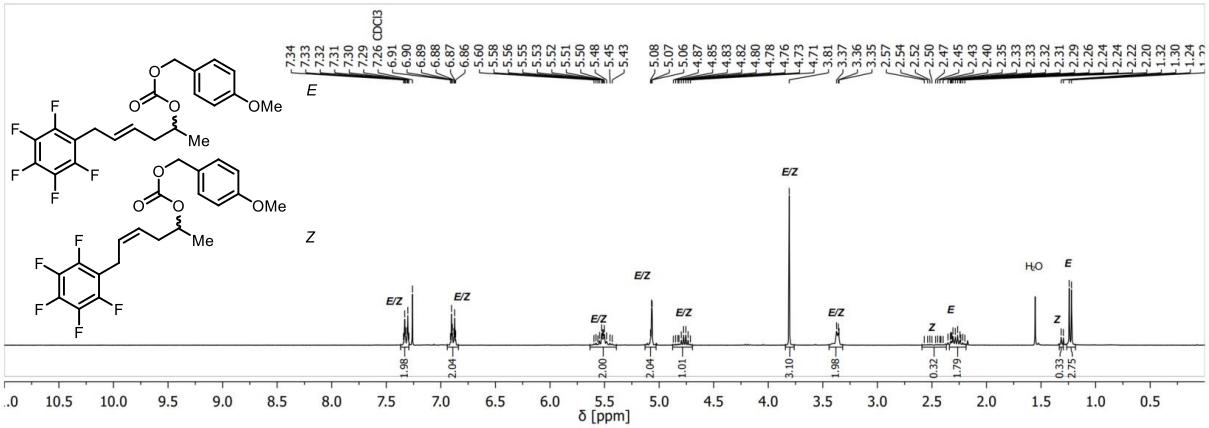


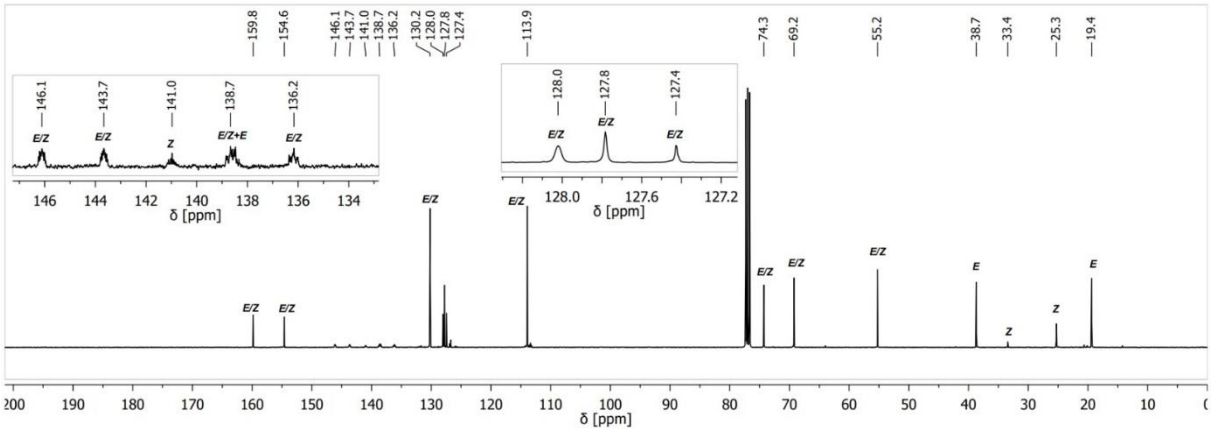


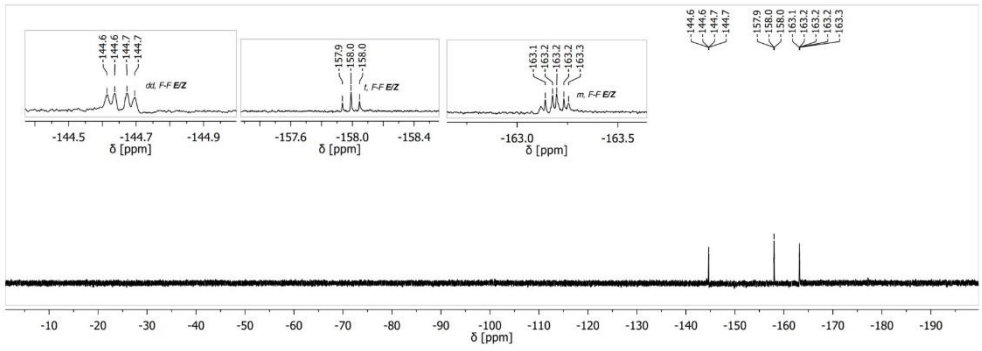


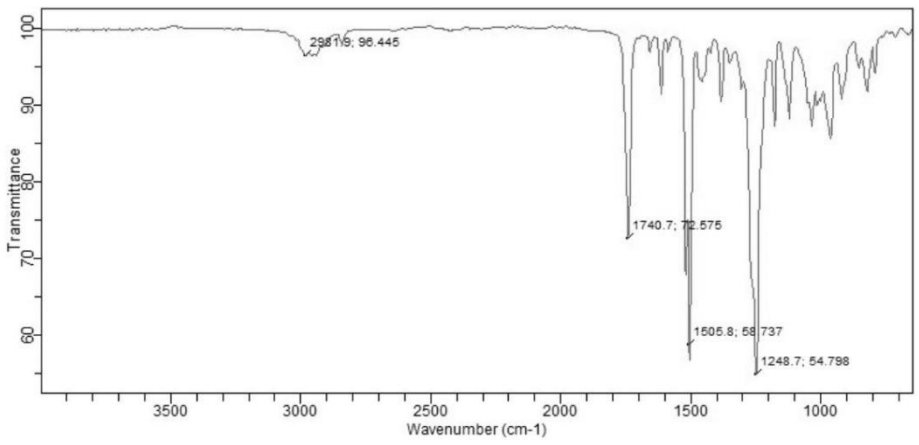
4-Methoxybenzyl (6-(perfluorophenyl)hex-4-en-2-yl) carbonate (135x)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz), **^{19}F NMR** (376 MHz): Chloroform-*d*, **IR**



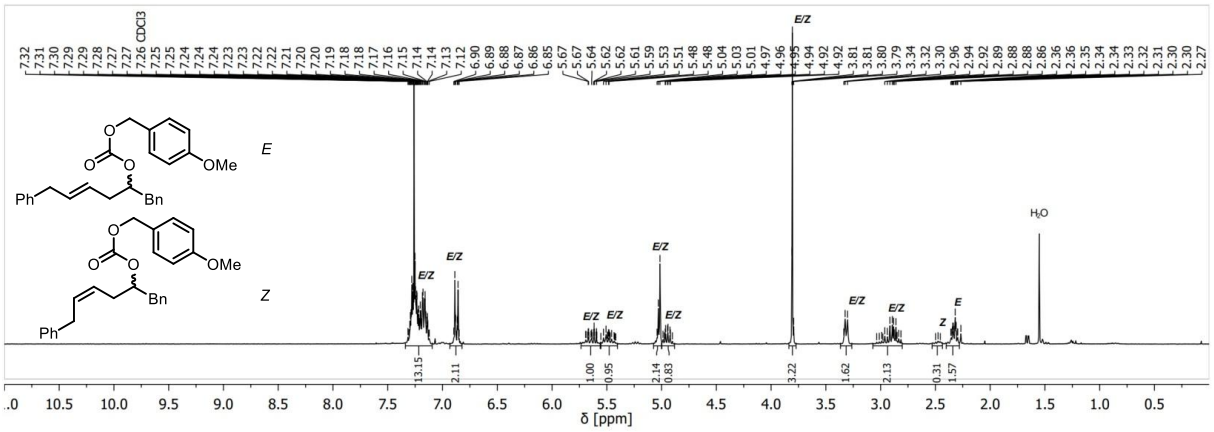


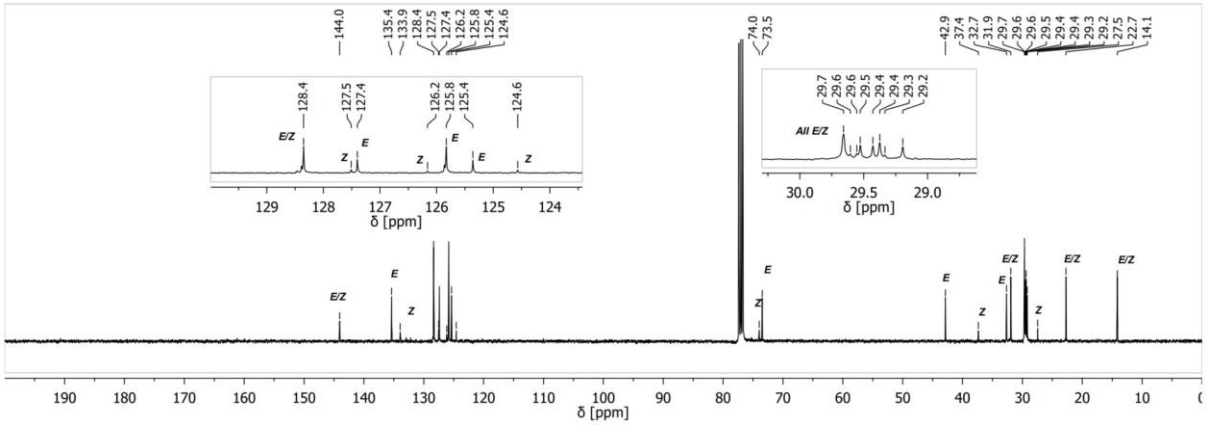


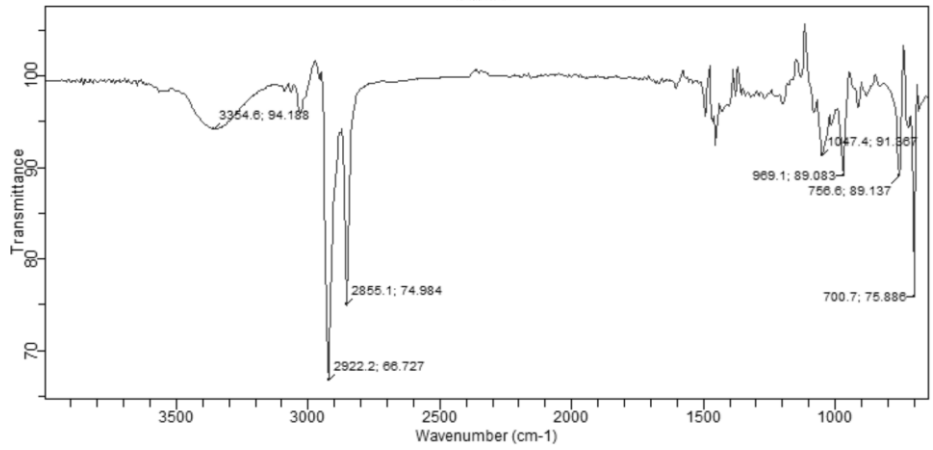


1,6-Diphenylhex-4-en-2-yl (4-methoxybenzyl) carbonate (135y)

^{1}H NMR (300 MHz), **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**

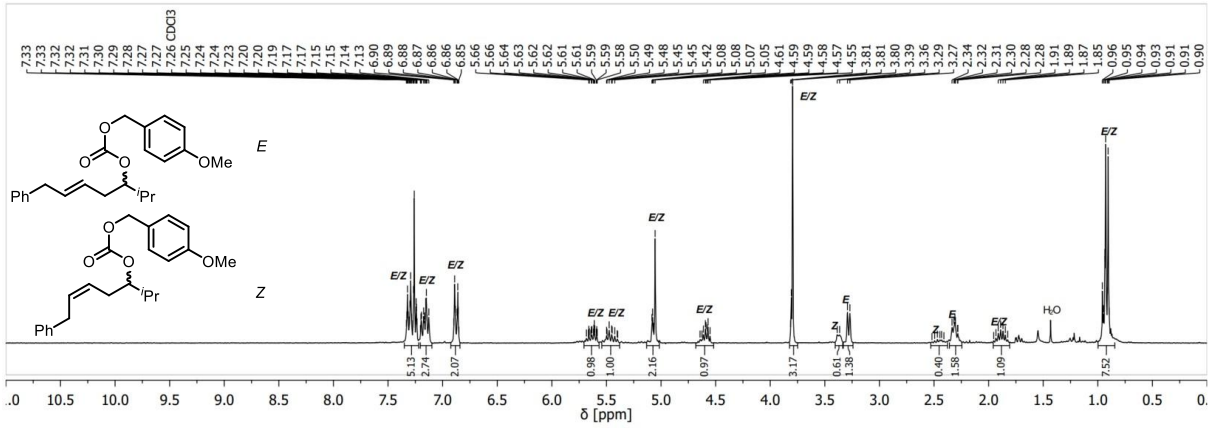


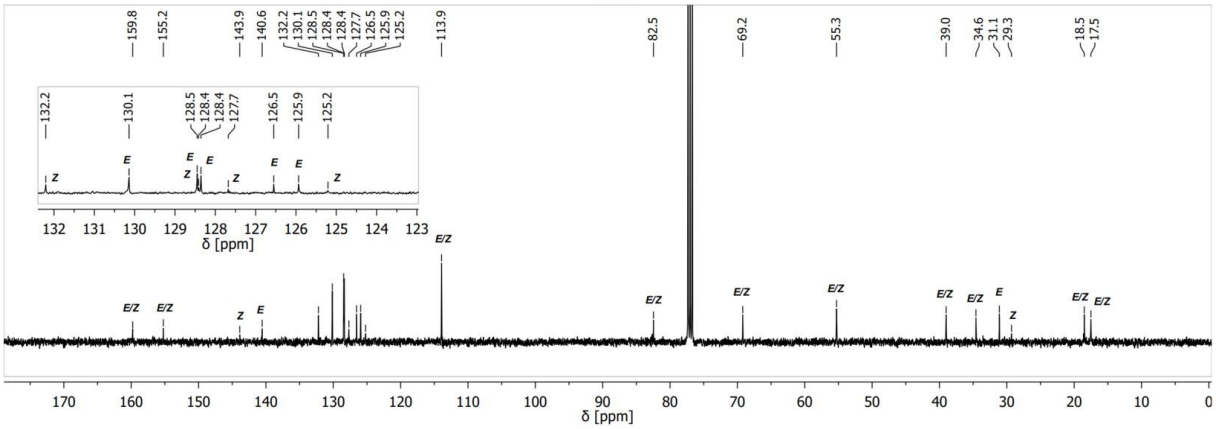


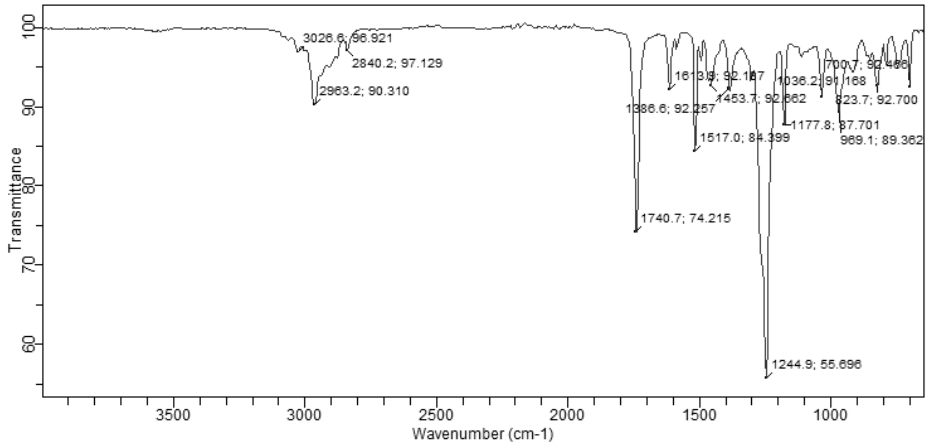


4-Methoxybenzyl (2-methyl-7-phenylhept-5-en-3-yl) carbonate (135z)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



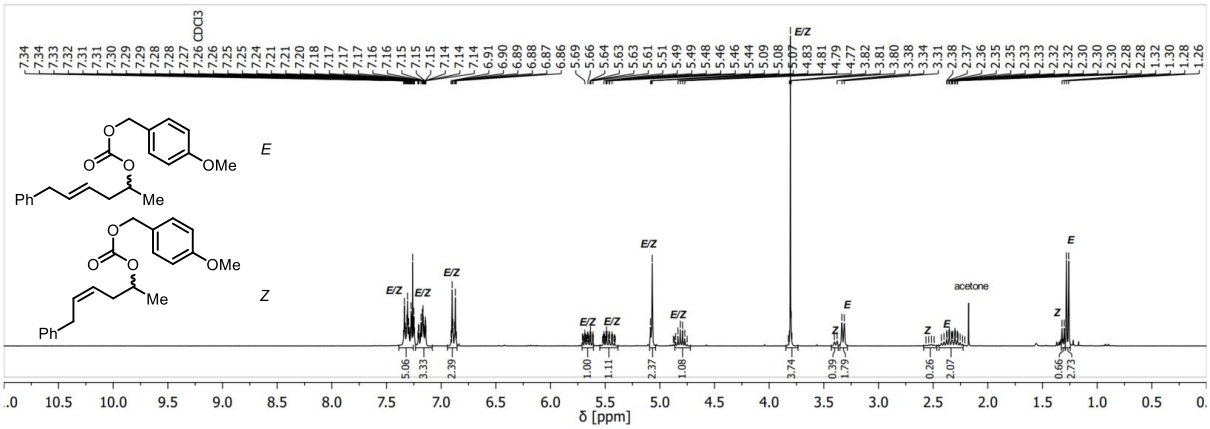


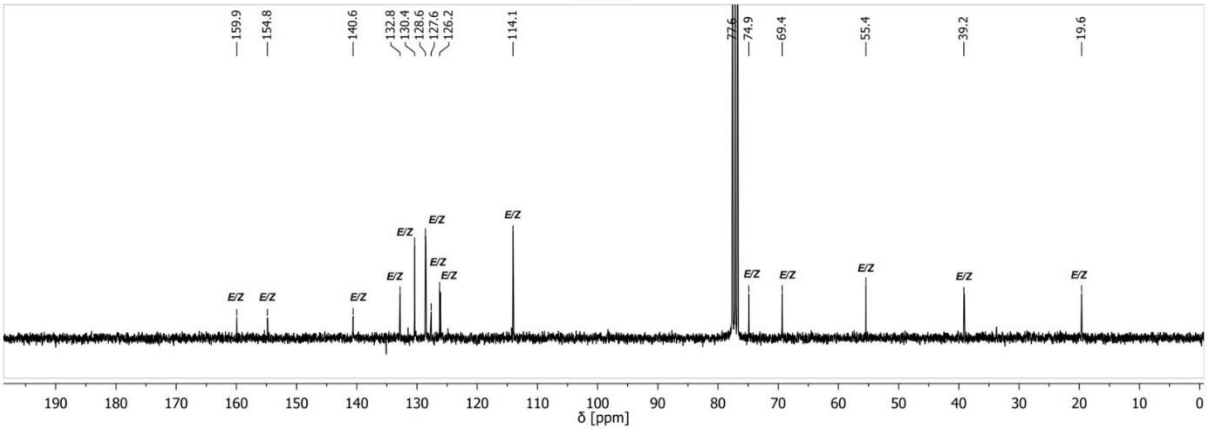


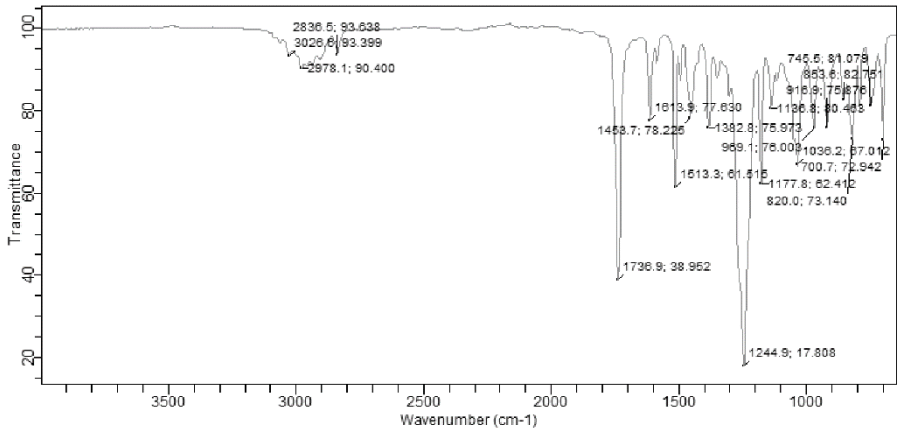
Spectra of project “1,3-dioxan-2-ones” – starting materials

4-Methoxybenzyl (6-phenylhex-4-en-2-yl) carbonate (135bb)

^{1}H NMR (300 MHz) **^{13}C NMR** (75 MHz): Chloroform-d **IR**



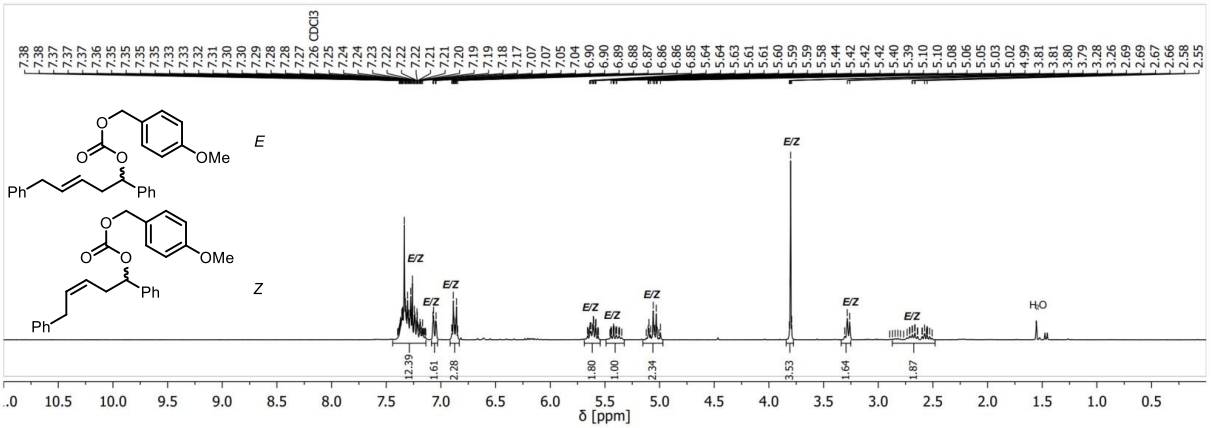


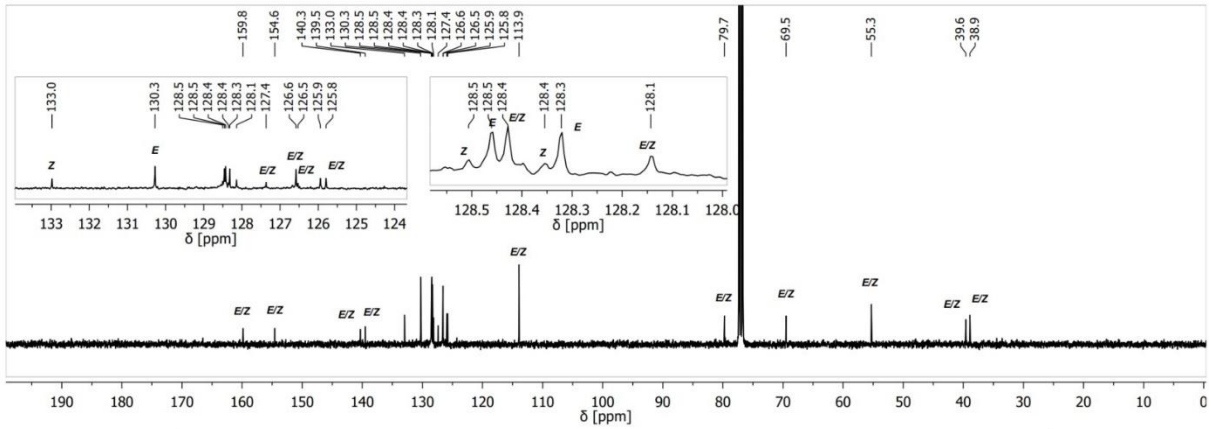


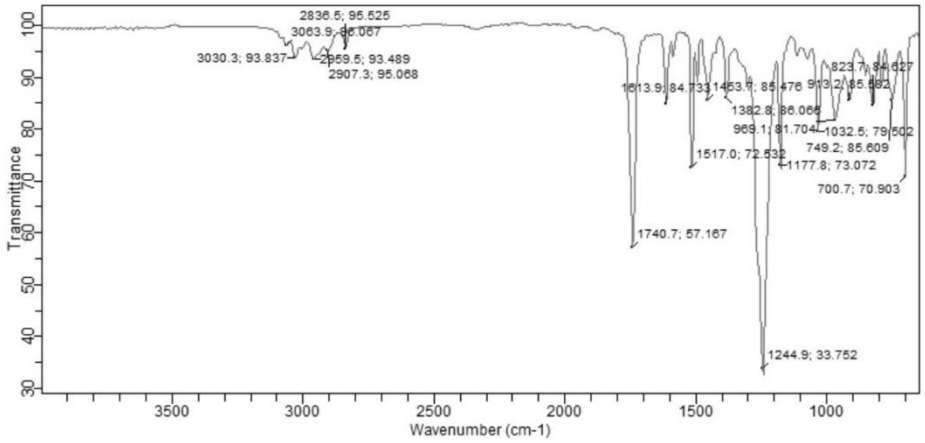
Spectra of project “1,3-dioxan-2-ones” – starting materials

1,5-Diphenylpent-3-en-1-yl (4-methoxybenzyl) carbonate (135cc)

^{1}H NMR (300 MHz) **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**

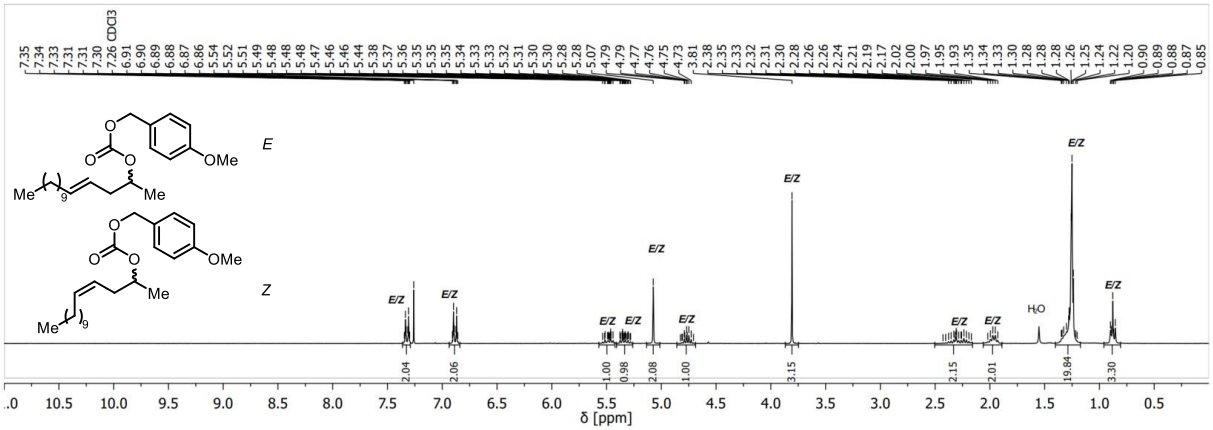


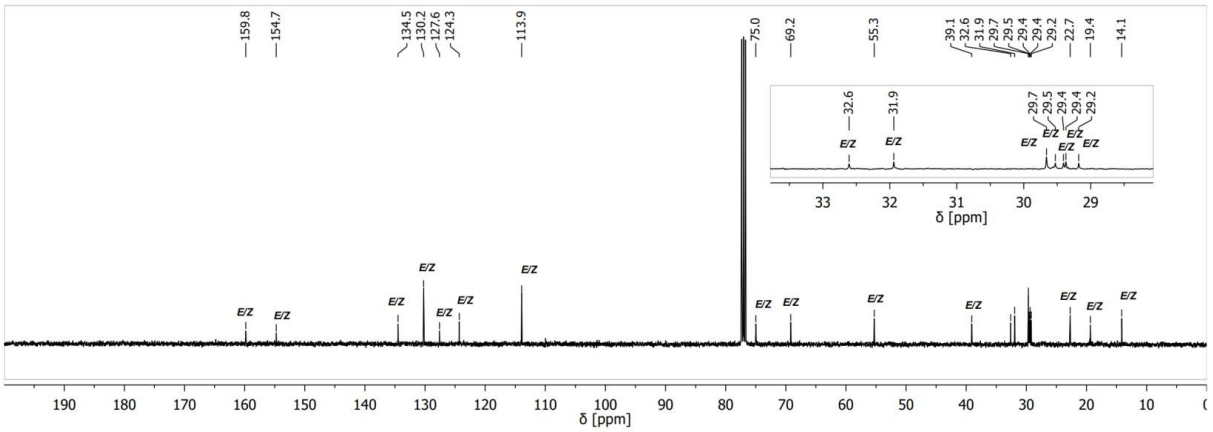


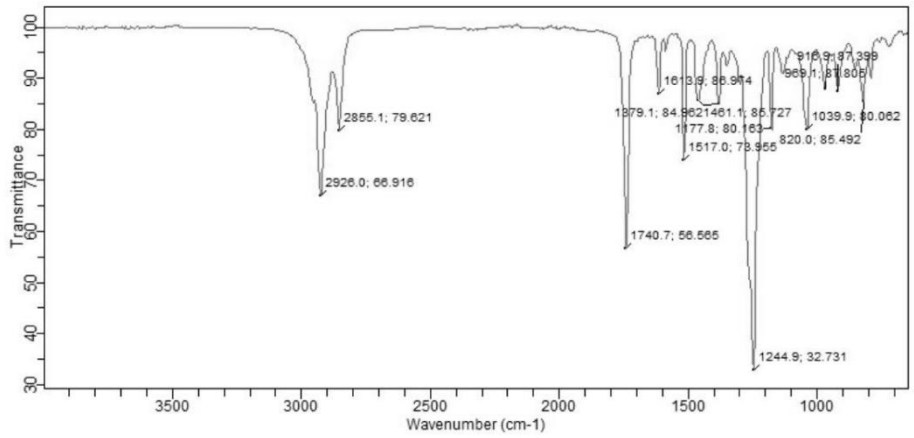


4-Methoxybenzyl pentadec-4-en-2-yl carbonate (135ee)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

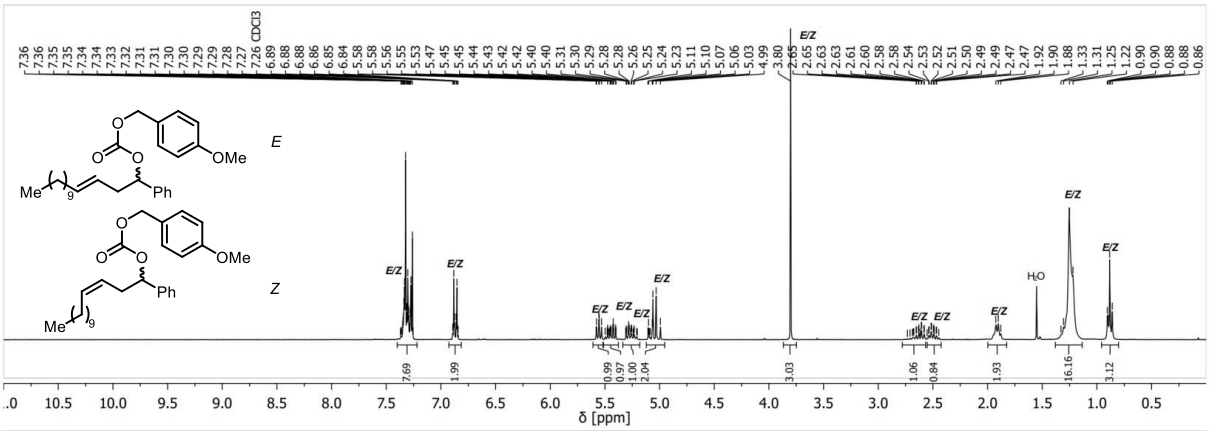


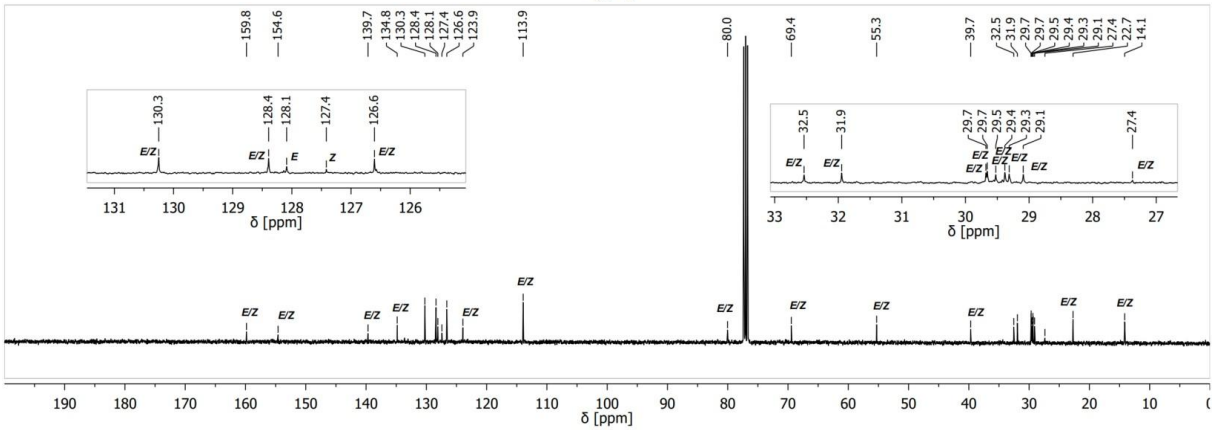


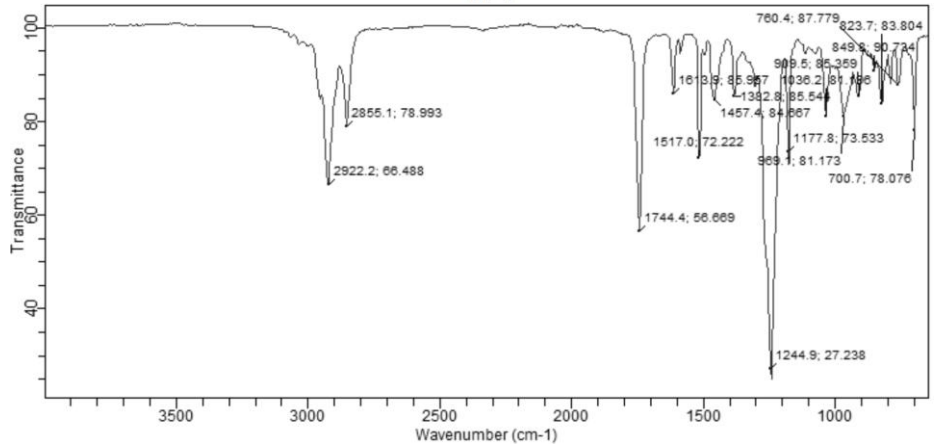


4-Methoxybenzyl (1-phenyltetradec-3-en-1-yl) carbonate (135ff)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



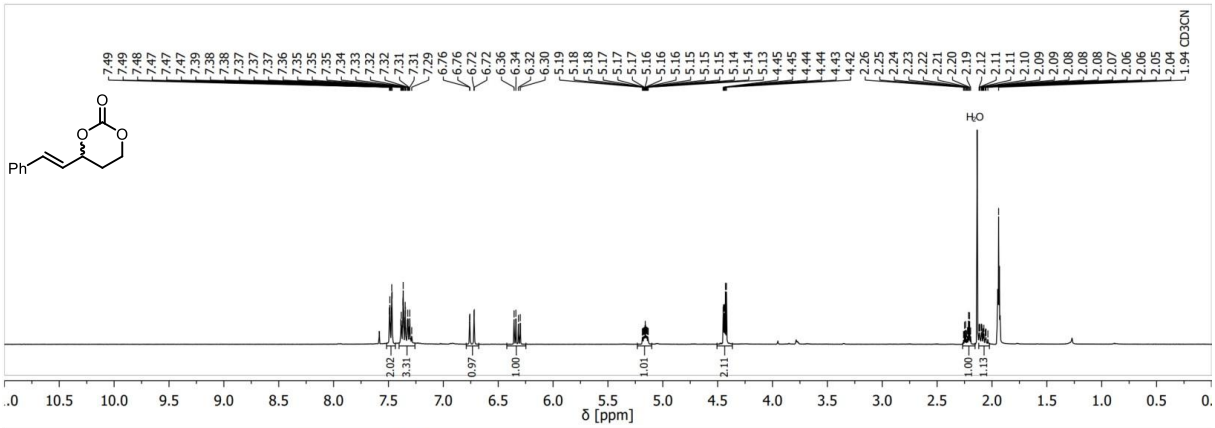


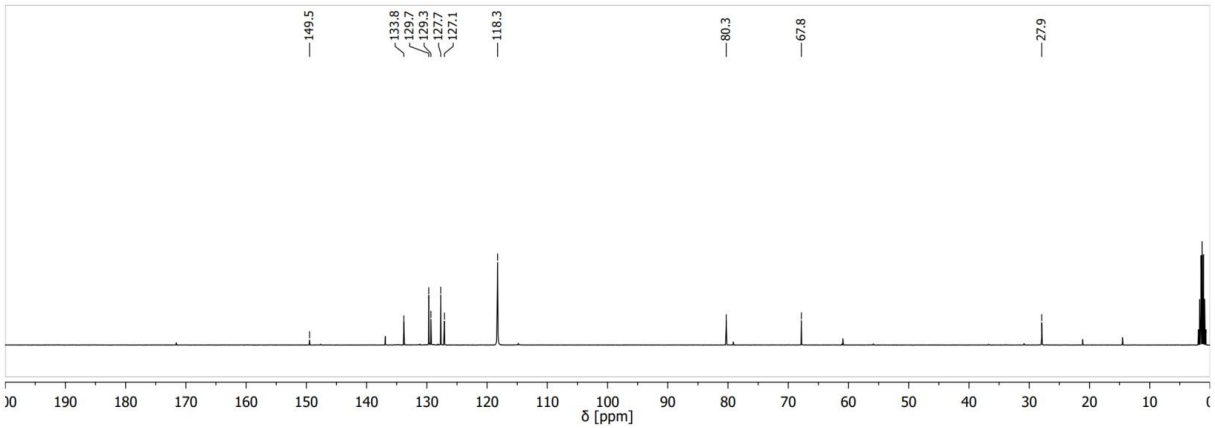


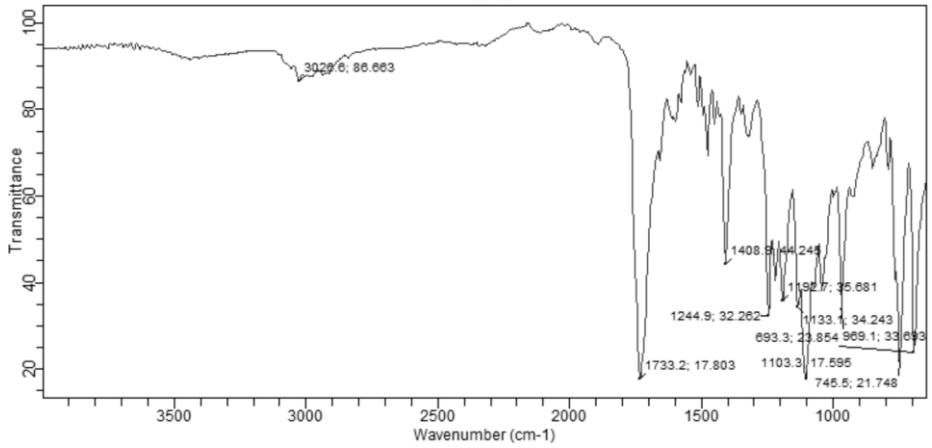
8.2 Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-Styryl-1,3-dioxan-2-one (136a)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz): MeCN-d_3**, IR**



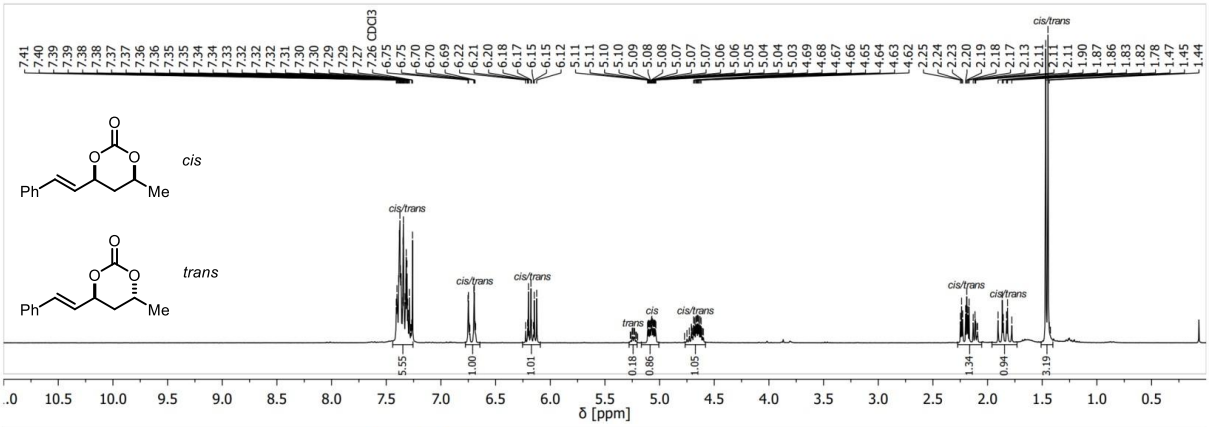


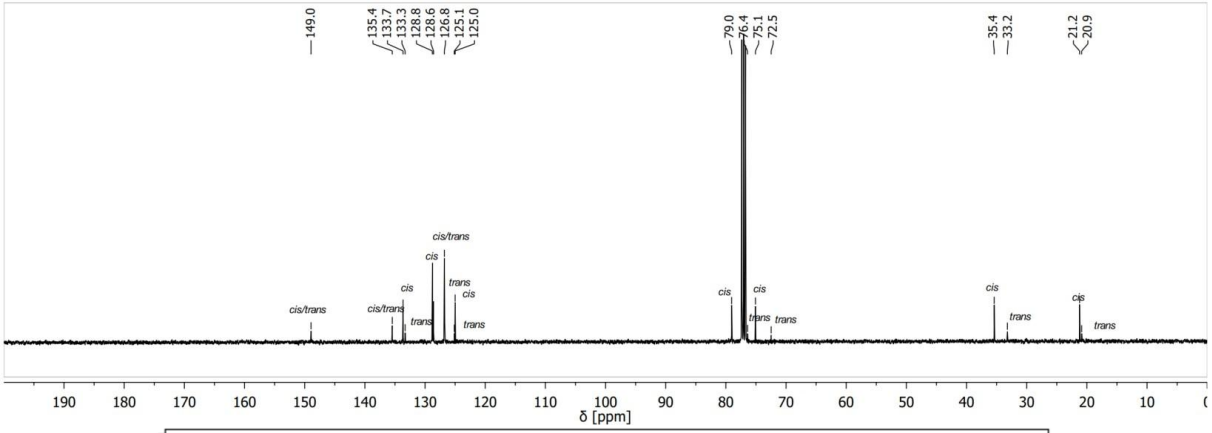


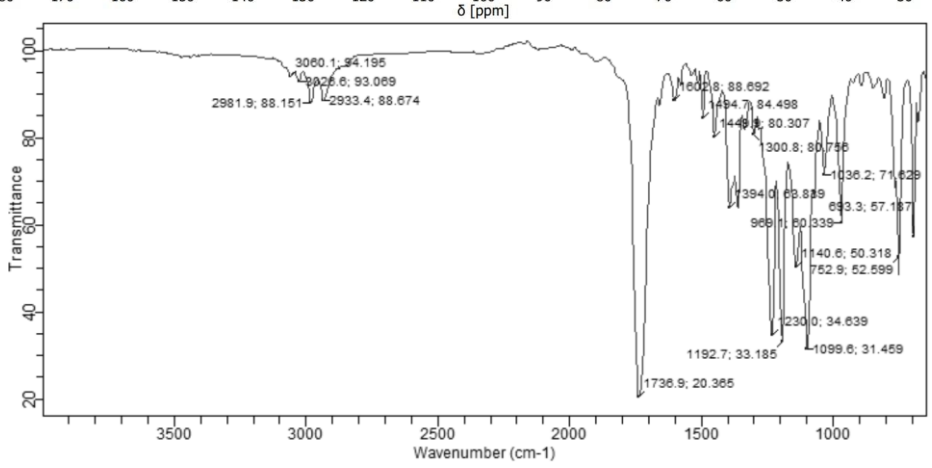
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-Methyl-6-styryl-1,3-dioxan-2-one (136b)

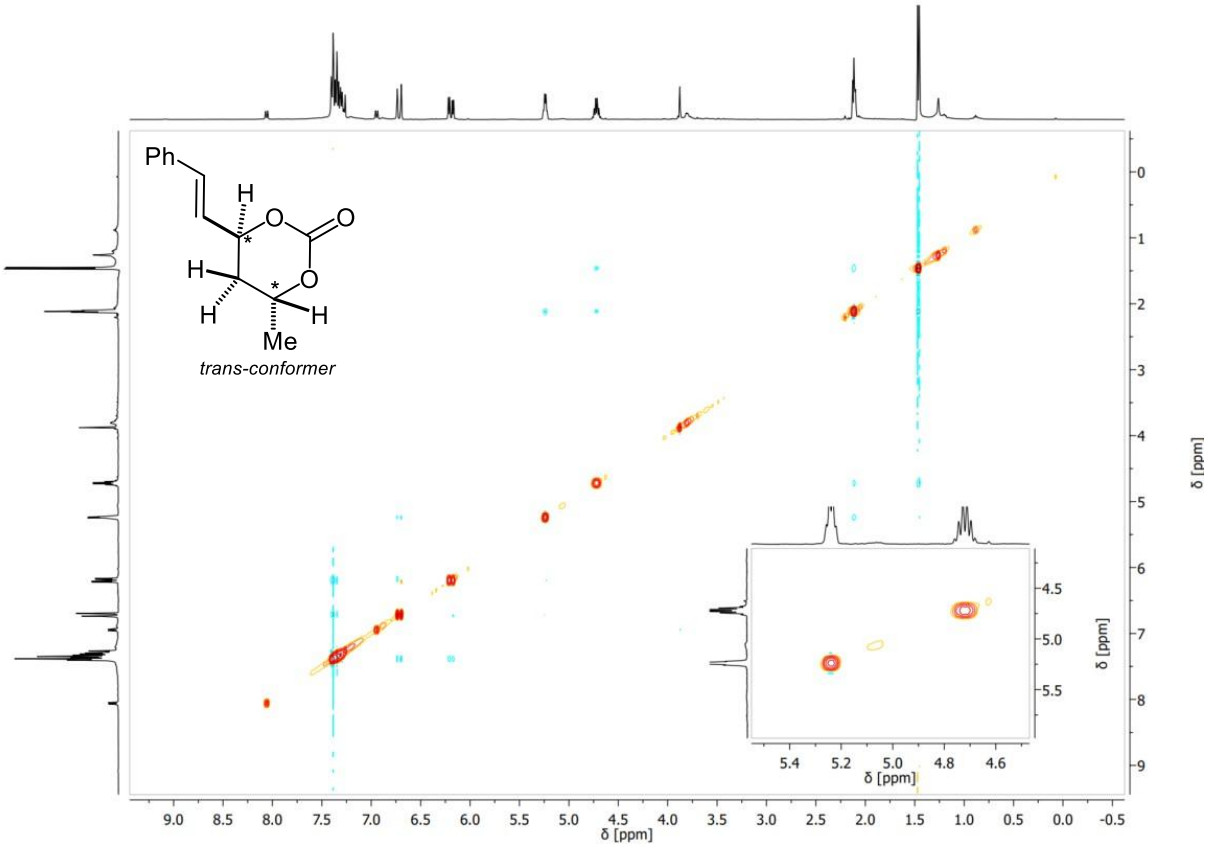
^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

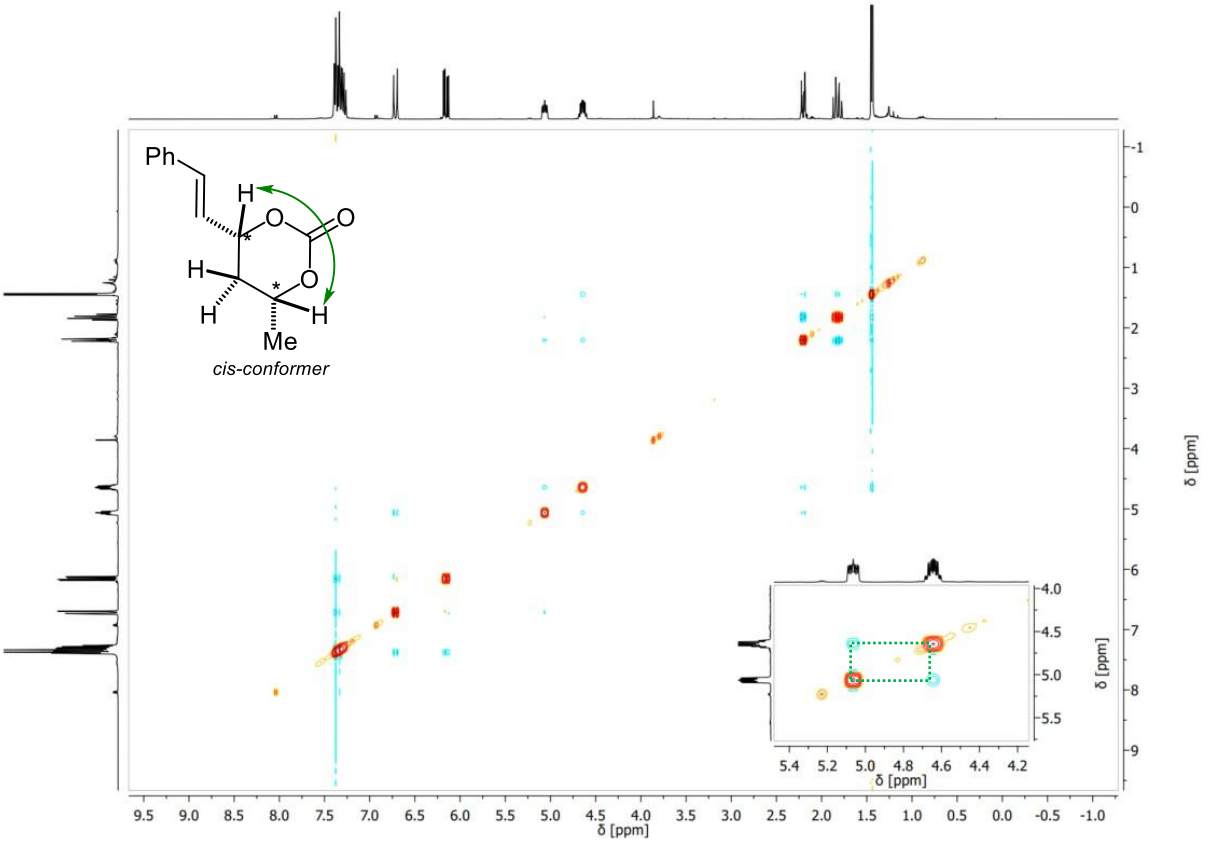






Spectra of project “1,3-dioxan-2-ones” – products

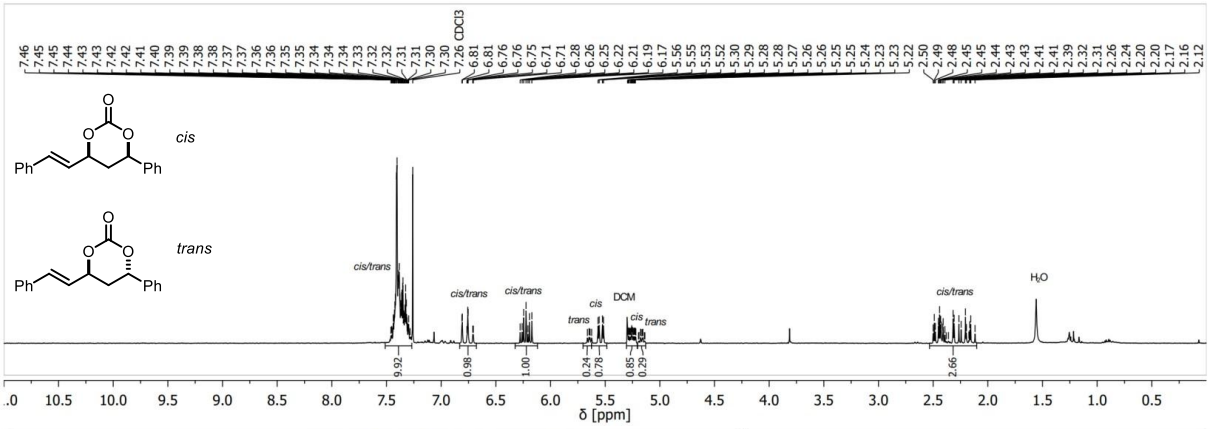


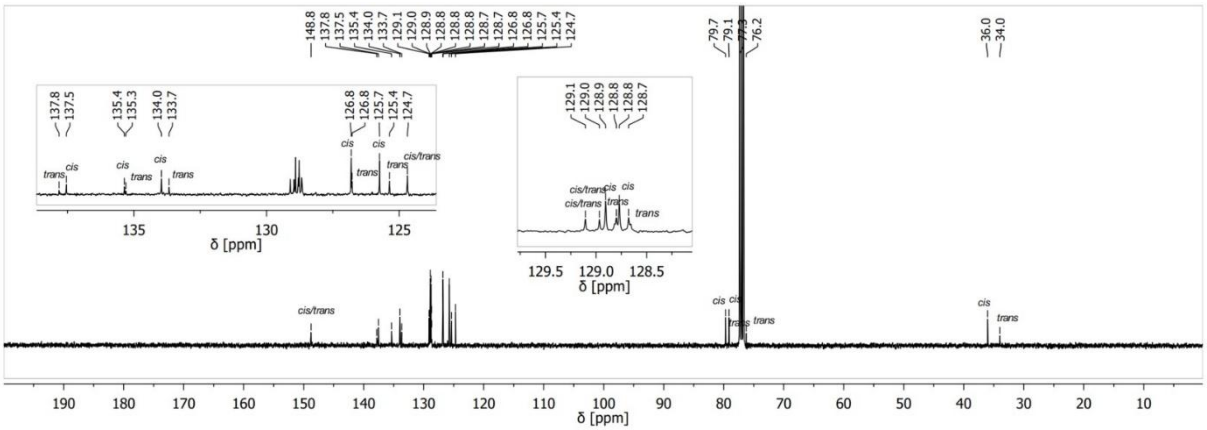


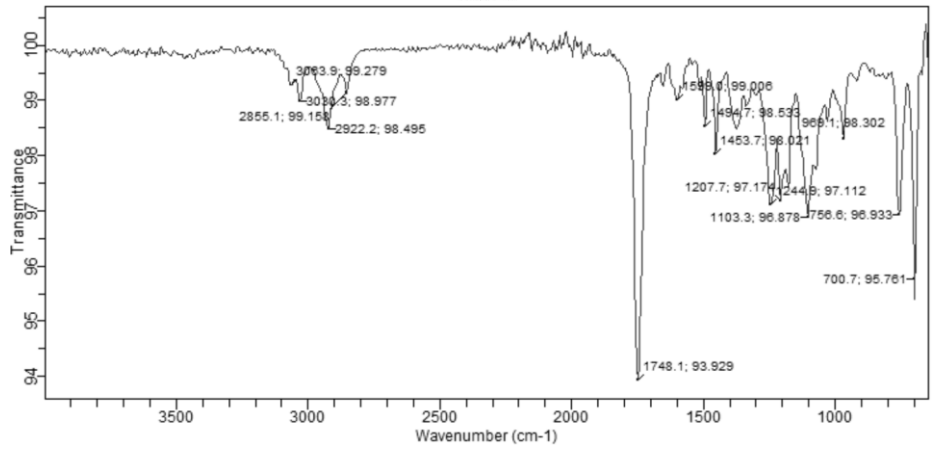
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-Phenyl-6-styryl-1,3-dioxan-2-one (136c)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



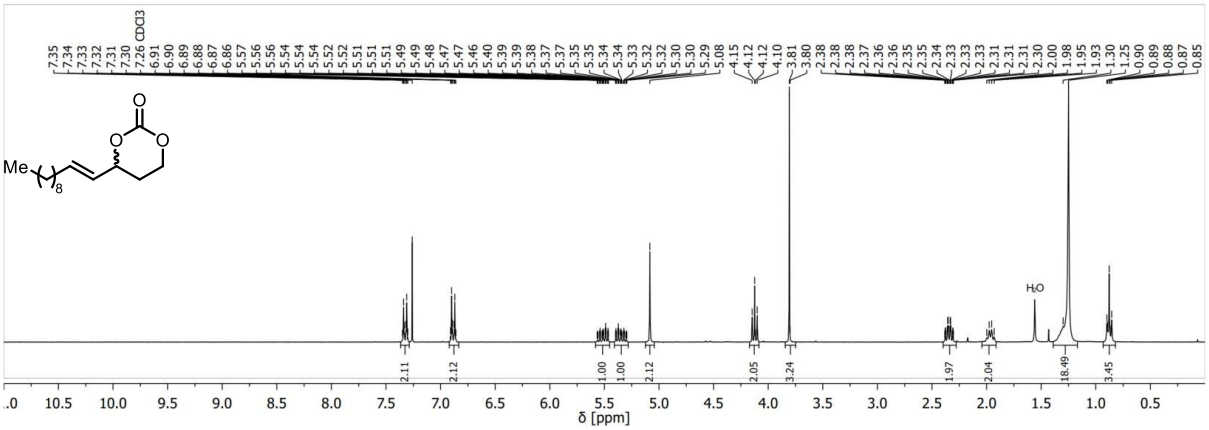


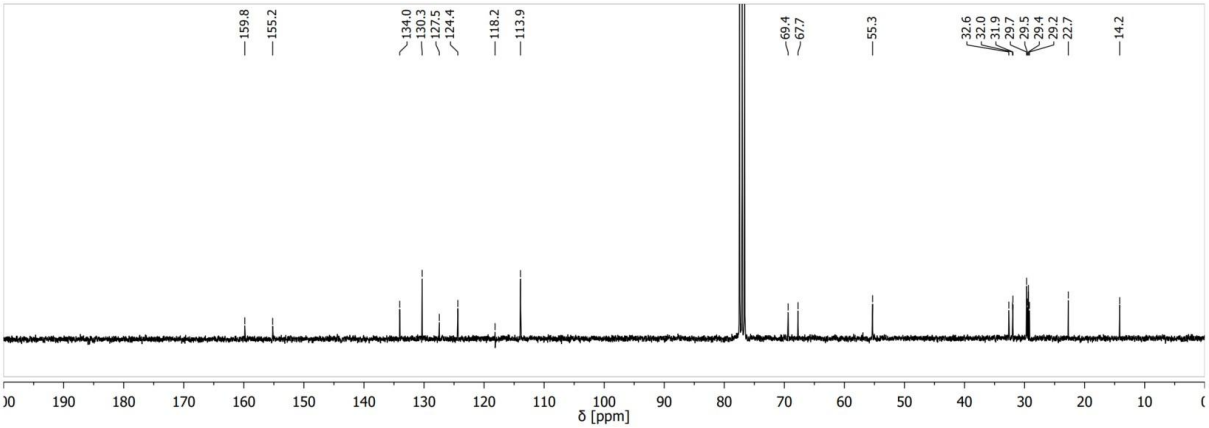


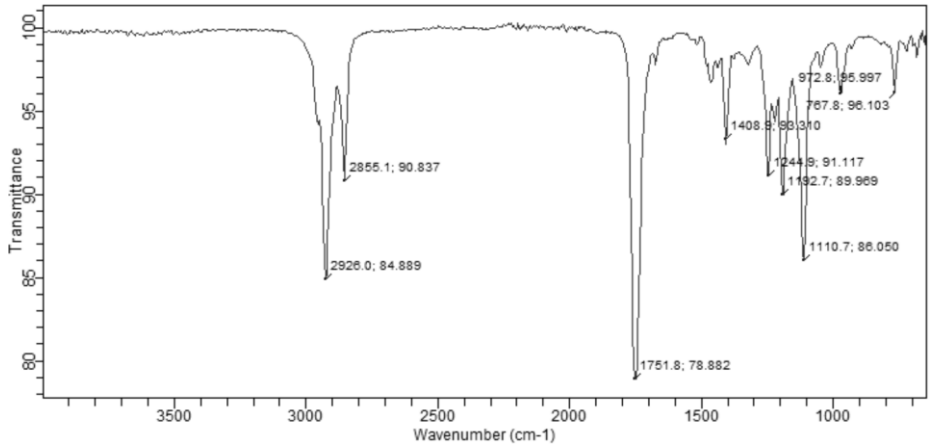
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-(Undec-1-en-1-yl)-1,3-dioxan-2-one (136d)

^{1}H NMR (300 MHz) **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



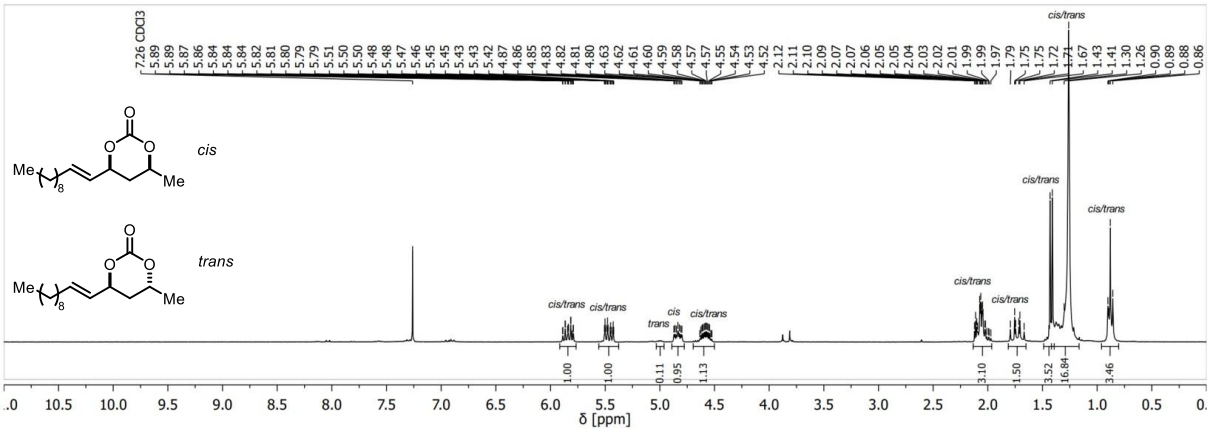


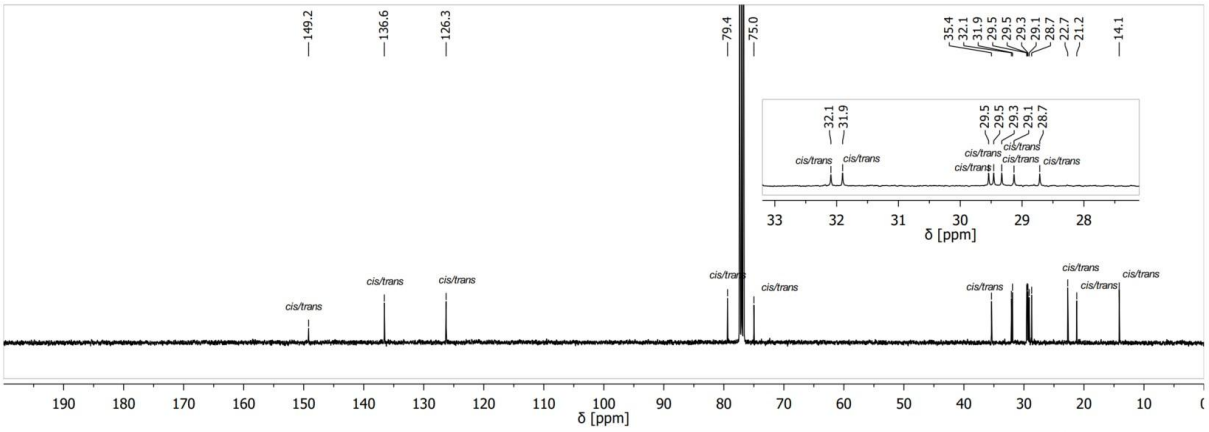


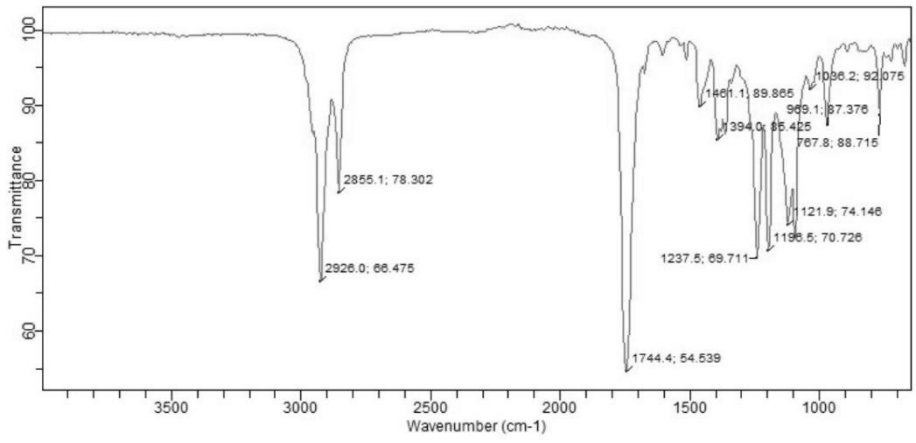
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-Methyl-6-(undec-1-en-1-yl)-1,3-dioxan-2-one (136e)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



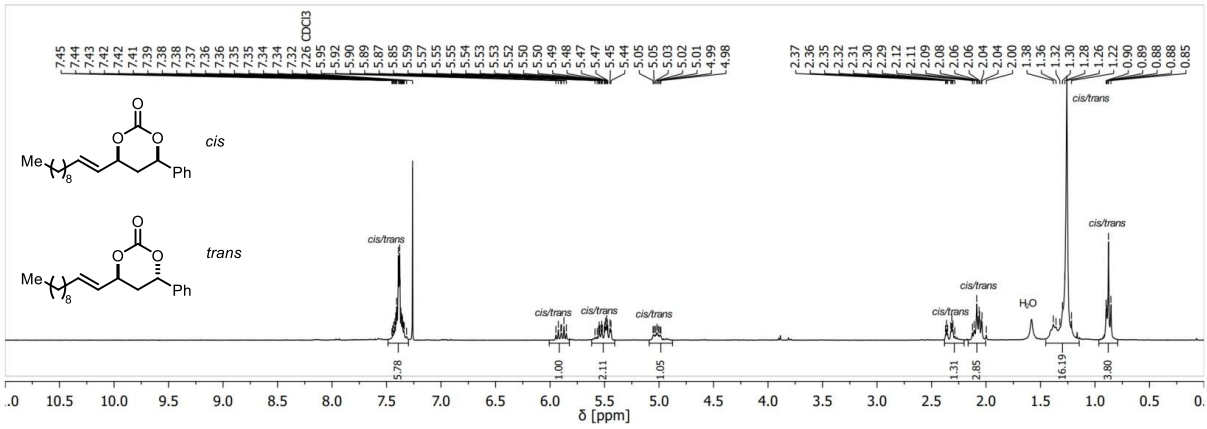


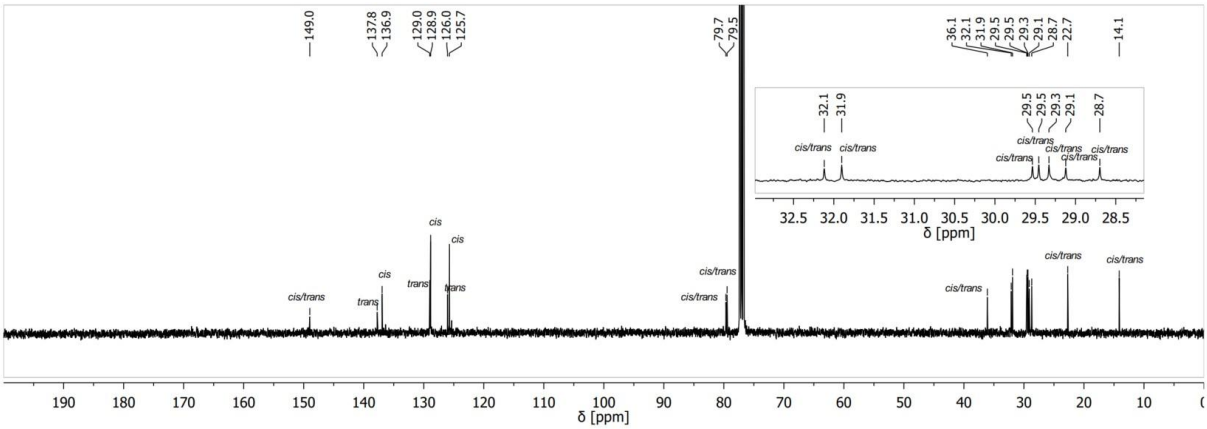


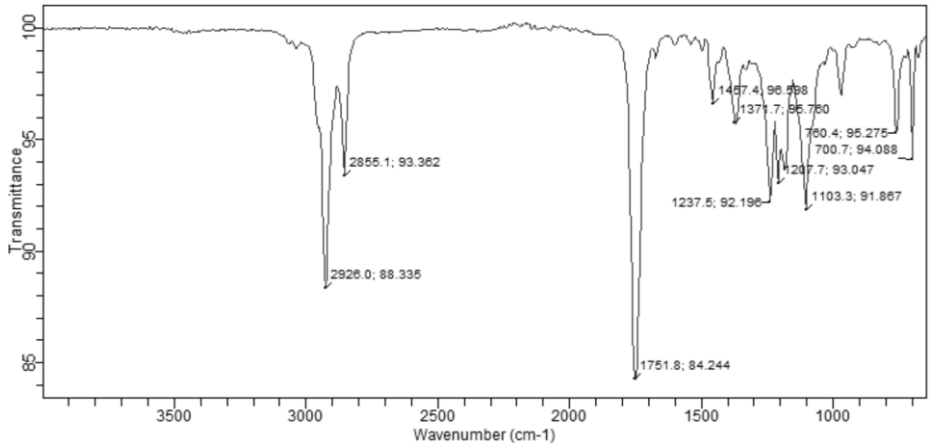
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-Phenyl-6-(undec-1-en-1-yl)-1,3-dioxan-2-one (136f)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



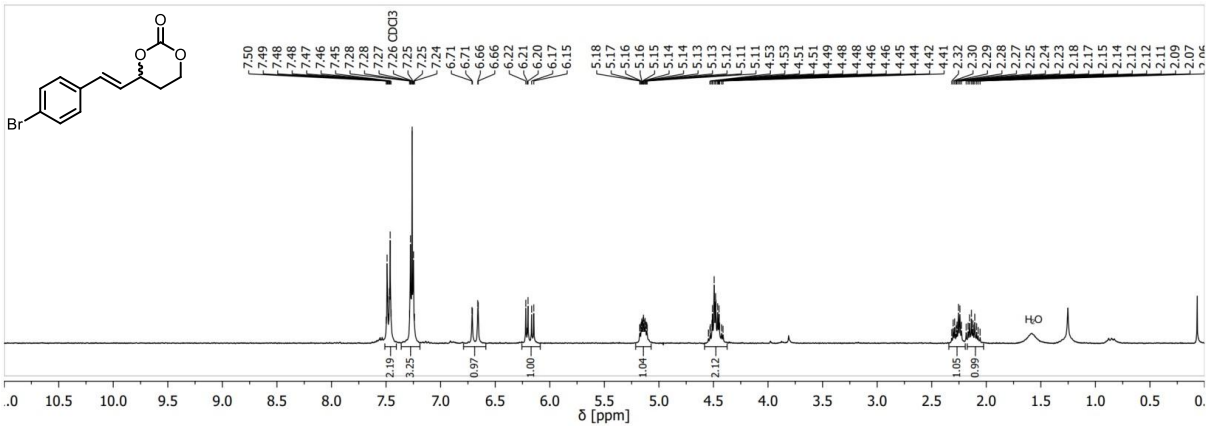


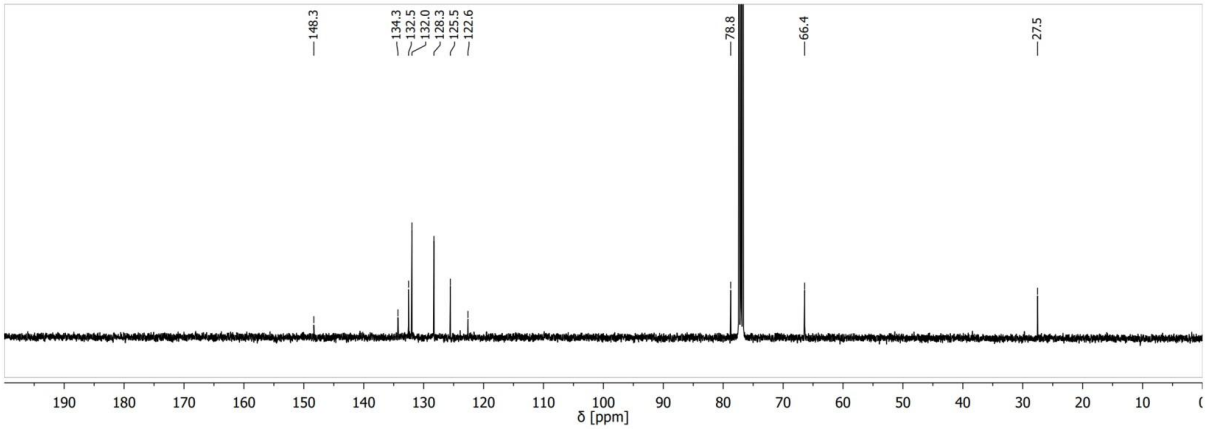


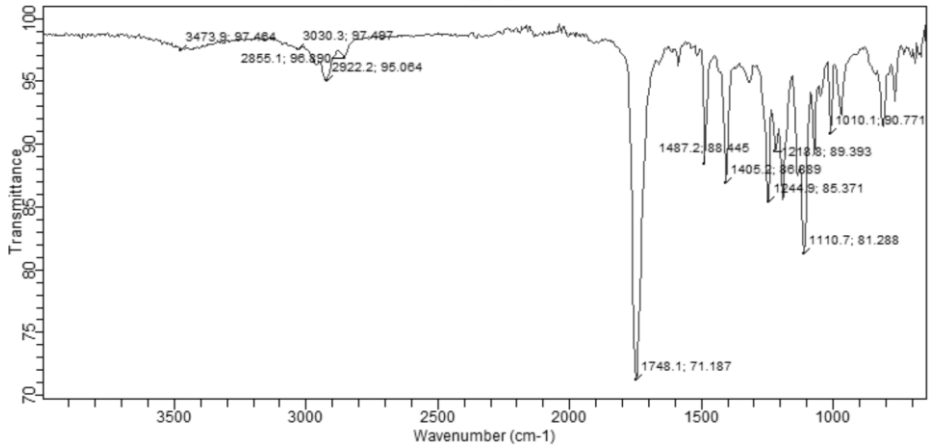
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-(4-Bromostyryl)-1,3-dioxan-2-one (136g)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



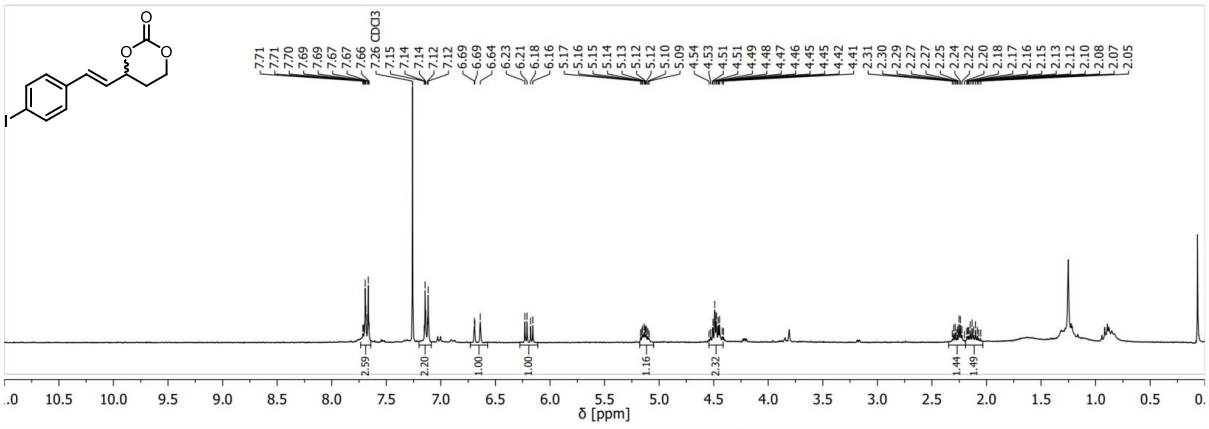


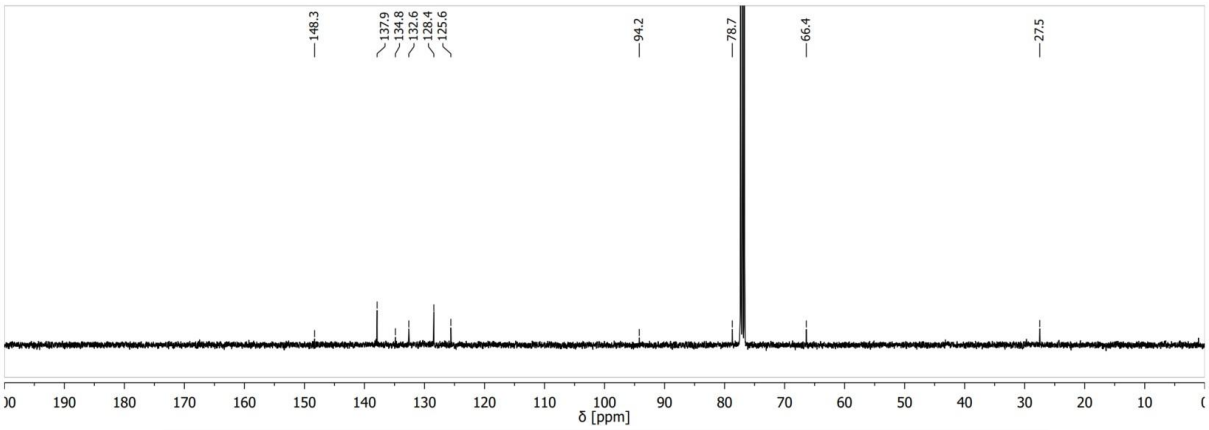


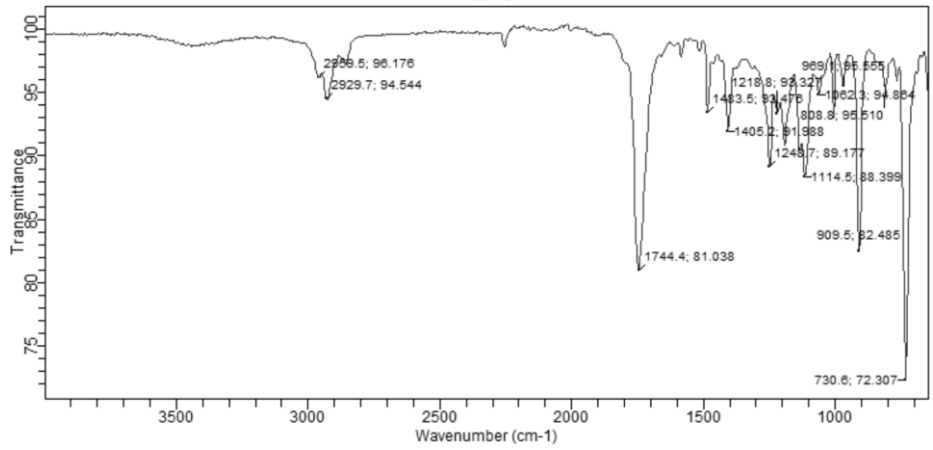
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-(4-Iodostyryl)-1,3-dioxan-2-one (136h)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



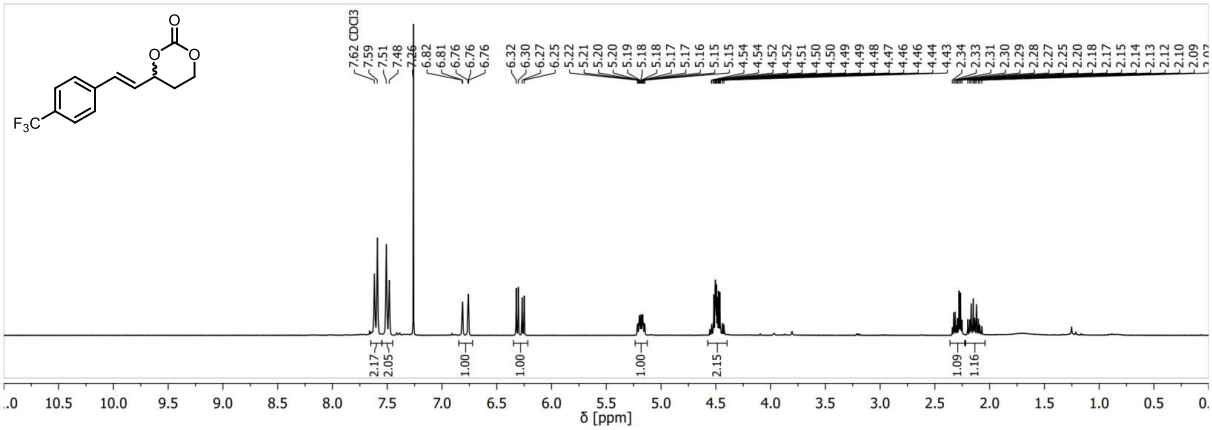


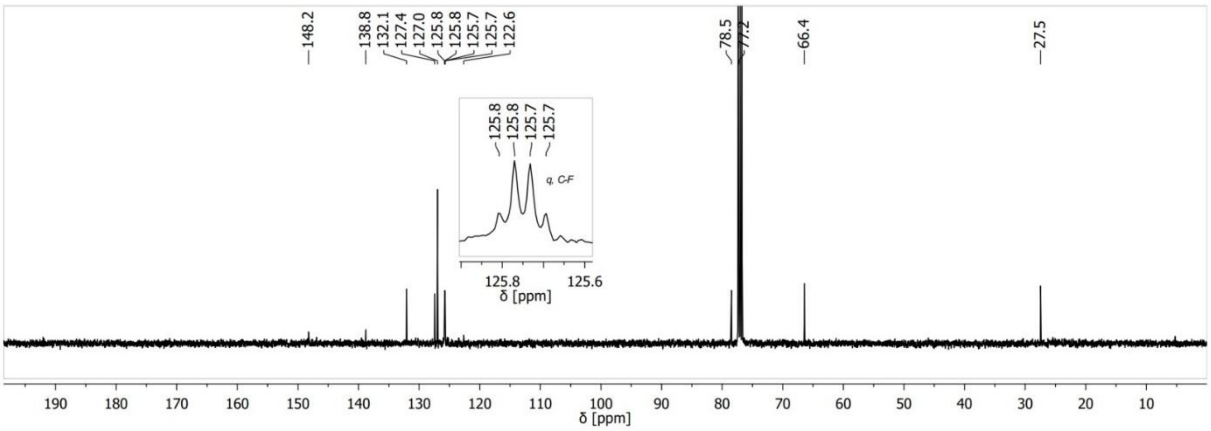


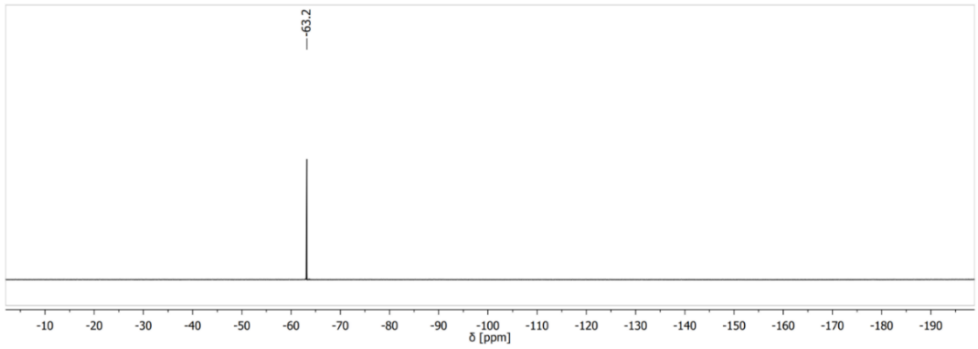
Spectra of project “1,3-dioxan-2-ones” – products

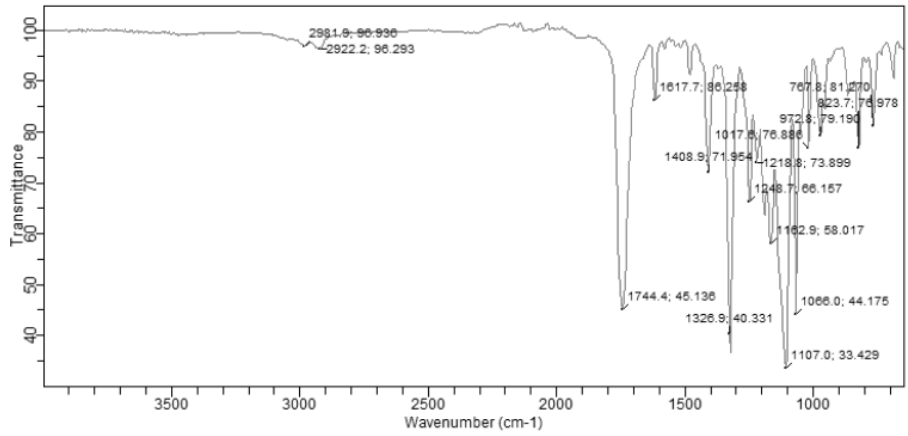
(*E*)-4-(4-(Trifluoromethyl)styryl)-1,3-dioxan-2-one (136j)

^{1}H NMR (300 MHz), **^{13}C NMR** (101 MHz), **^{19}F{^{1}H} NMR** (376 MHz): Chloroform-*d*, **IR**



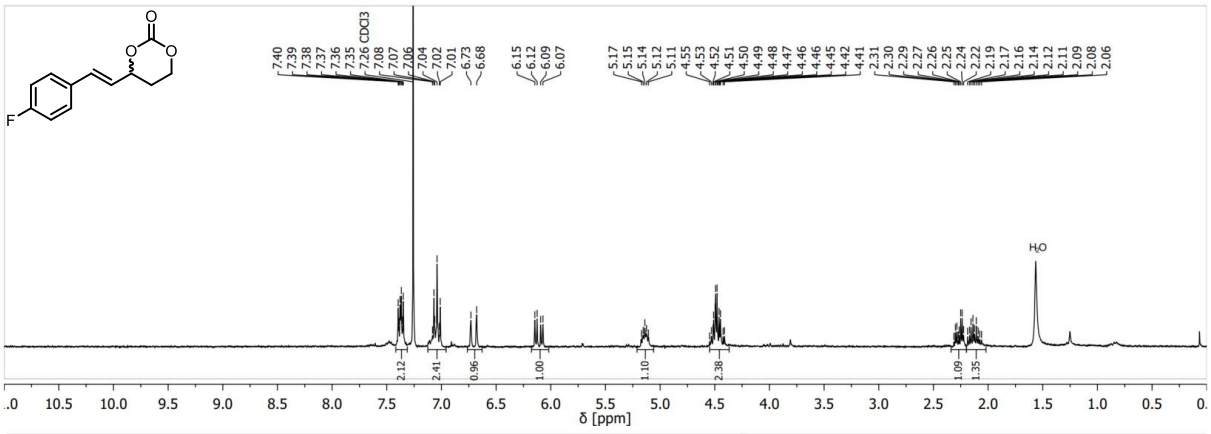


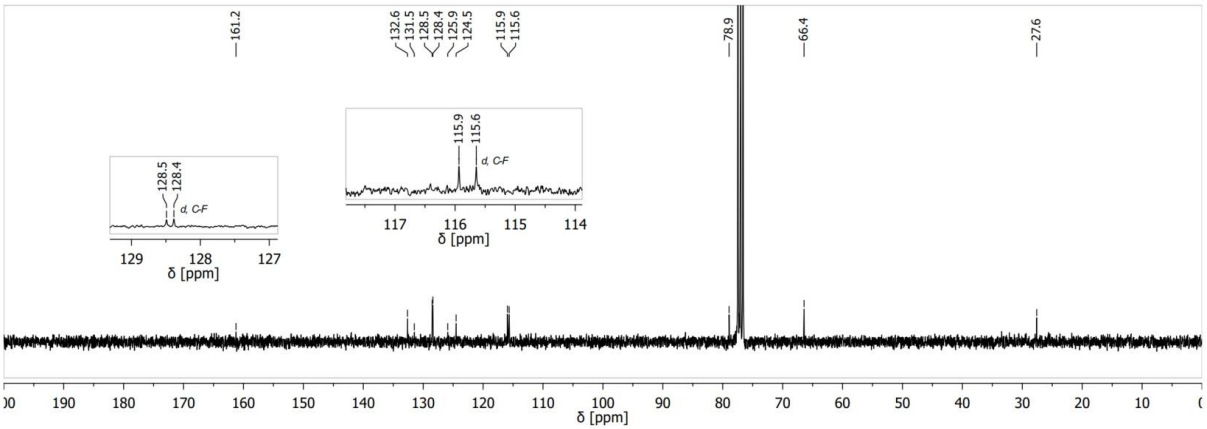


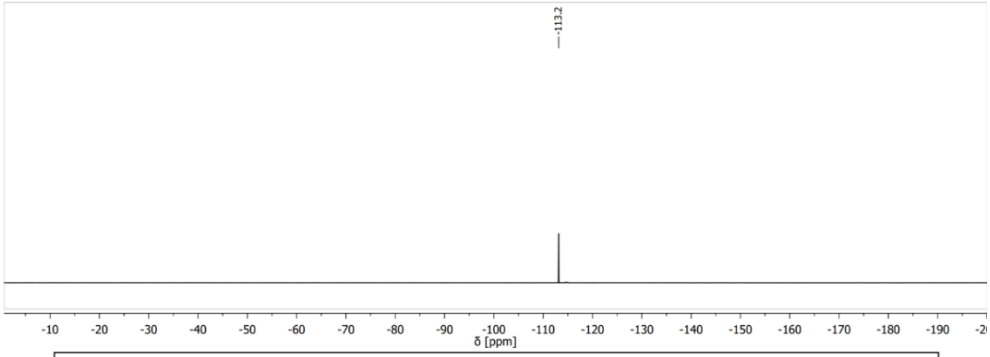


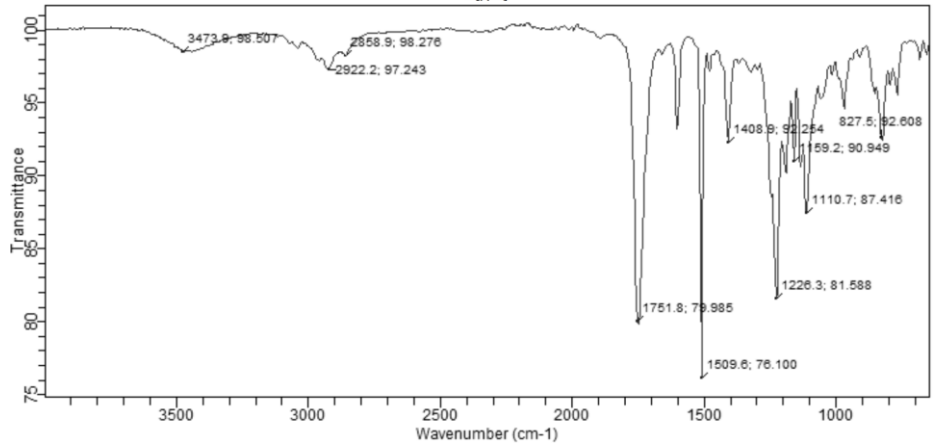
(*E*)-4-(4-Fluorostyryl)-1,3-dioxan-2-one (136k)

^{1}H NMR (300 MHz) **^{13}C NMR** (75 MHz), **^{19}F{^{1}H} NMR** (376 MHz): Chloroform-*d*, **IR**





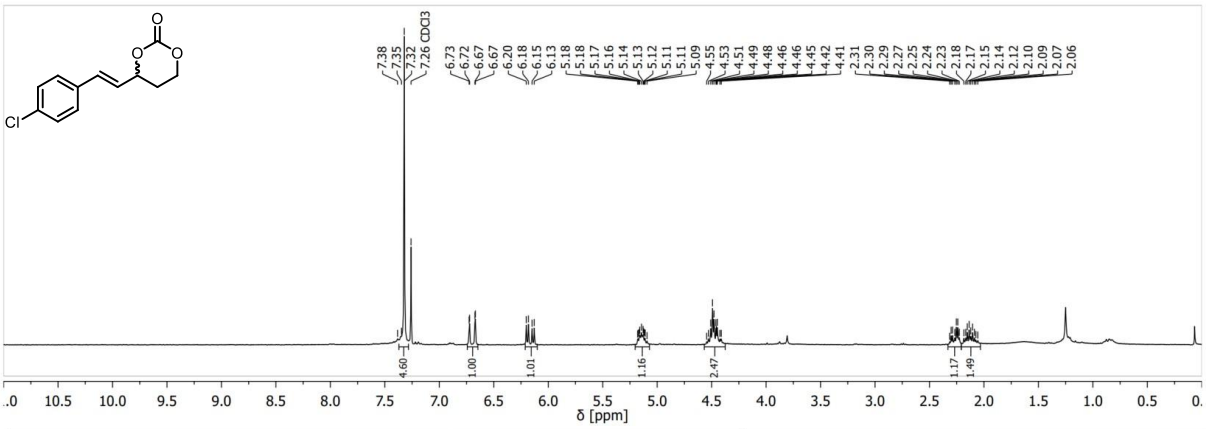


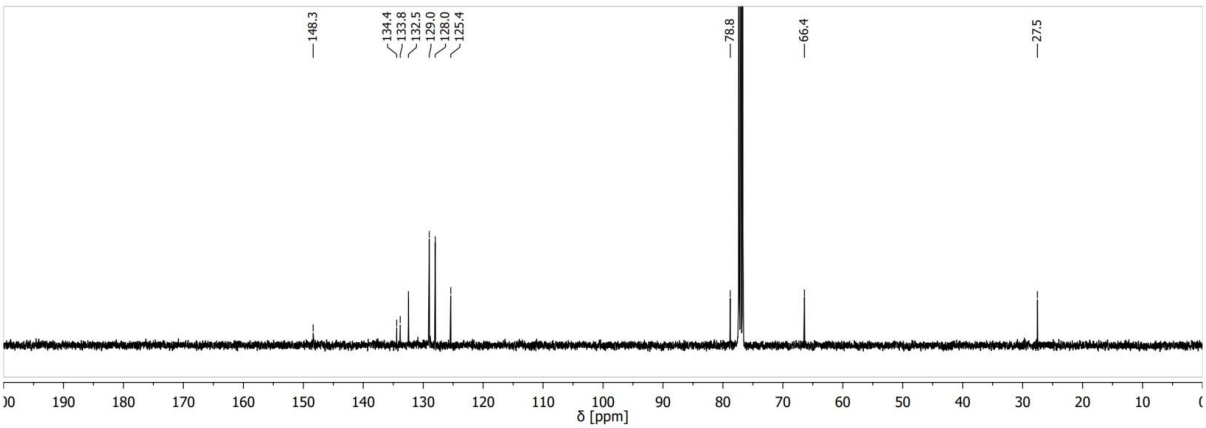


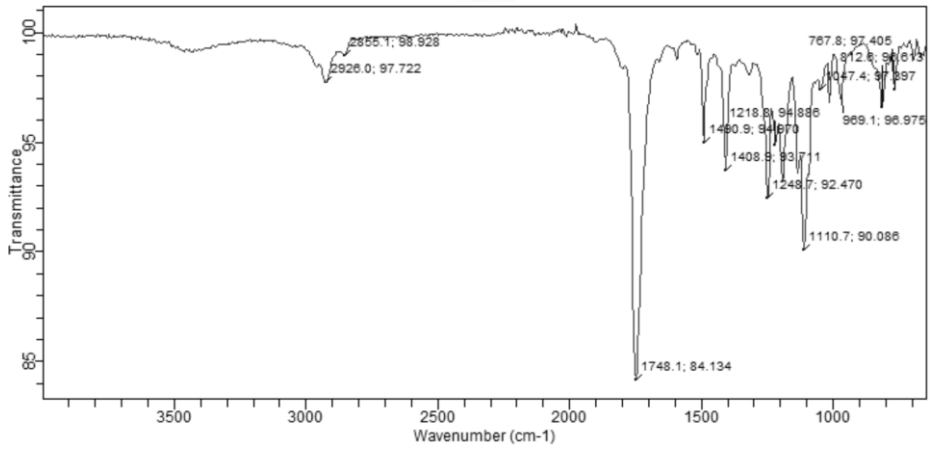
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-(4-Chlorostyryl)-1,3-dioxan-2-one (136l)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



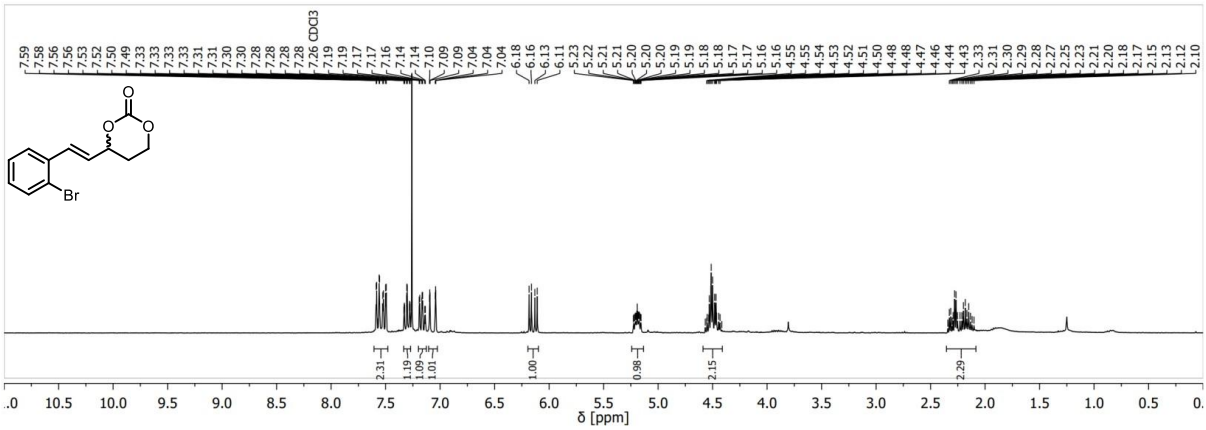


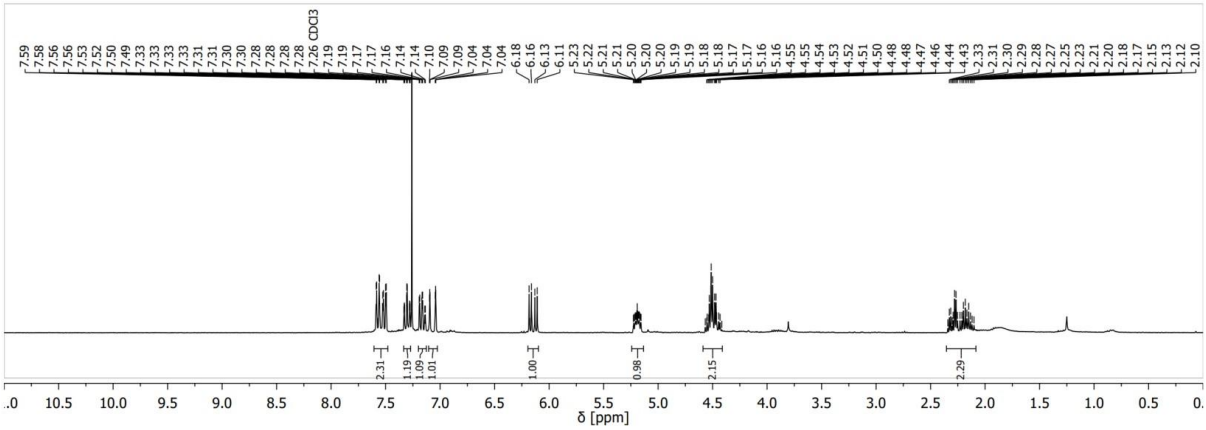


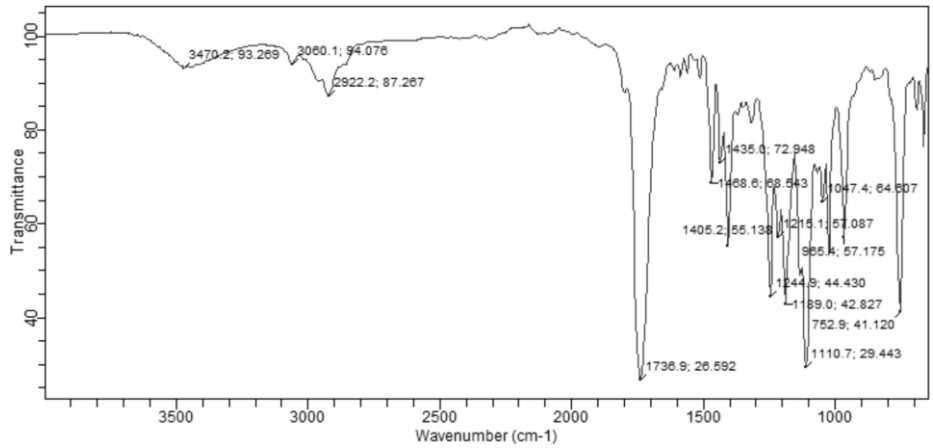
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-(2-Bromostyryl)-1,3-dioxan-2-one (136m)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

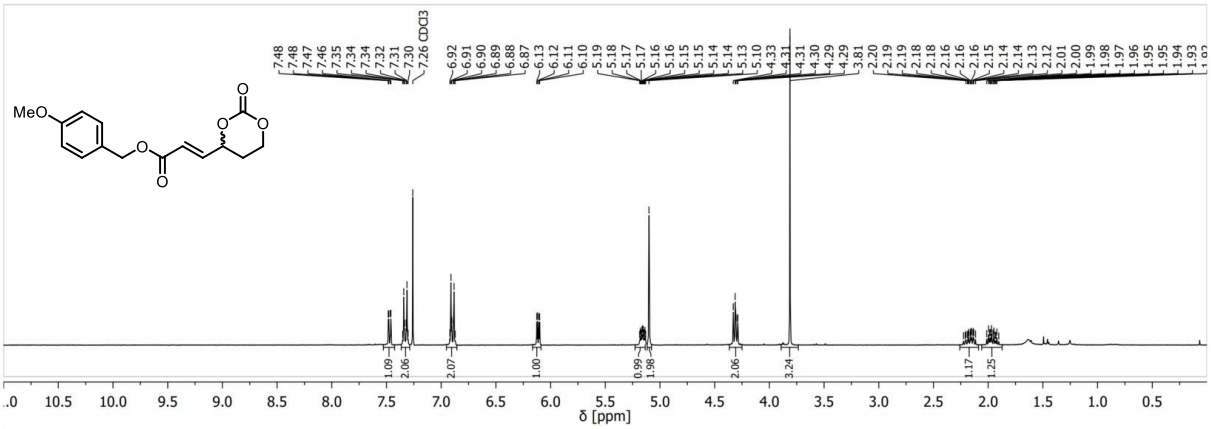


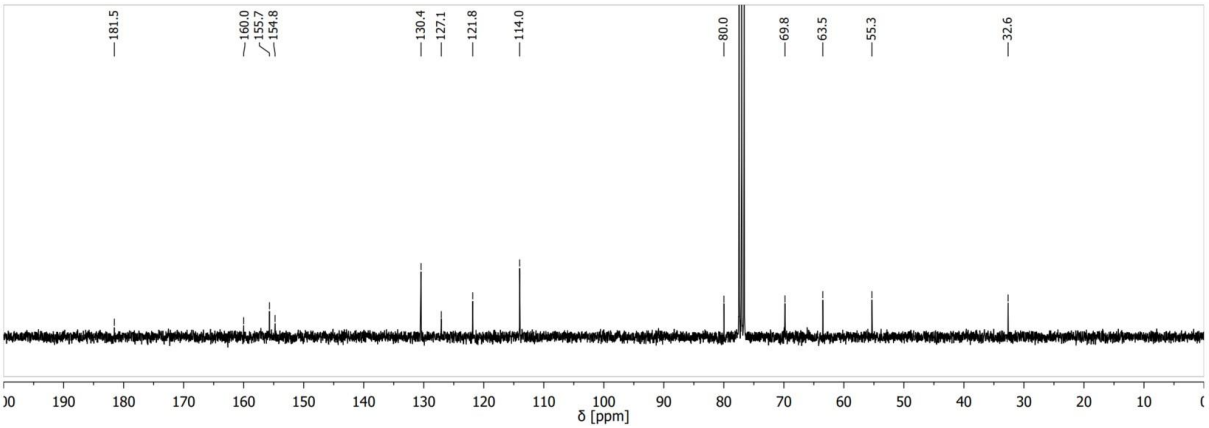


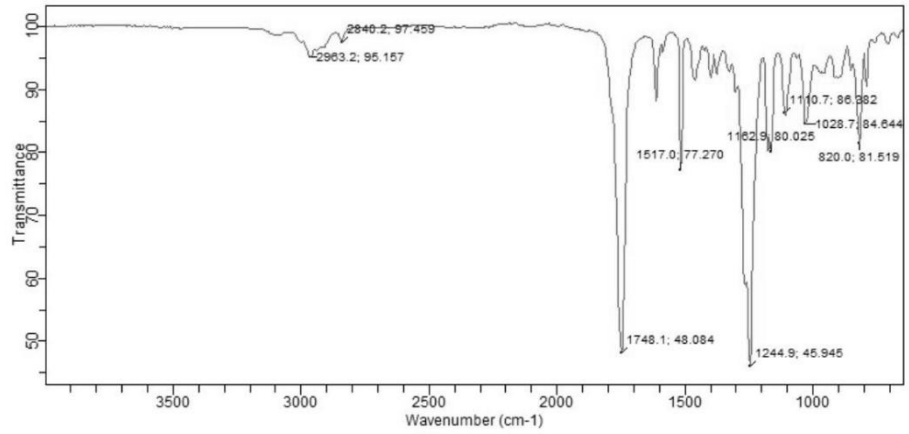


4-Methoxybenzyl (*E*)-3-(2-oxo-1,3-dioxan-4-yl)acrylate (136n)

^{1}H NMR (300 MHz) **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**

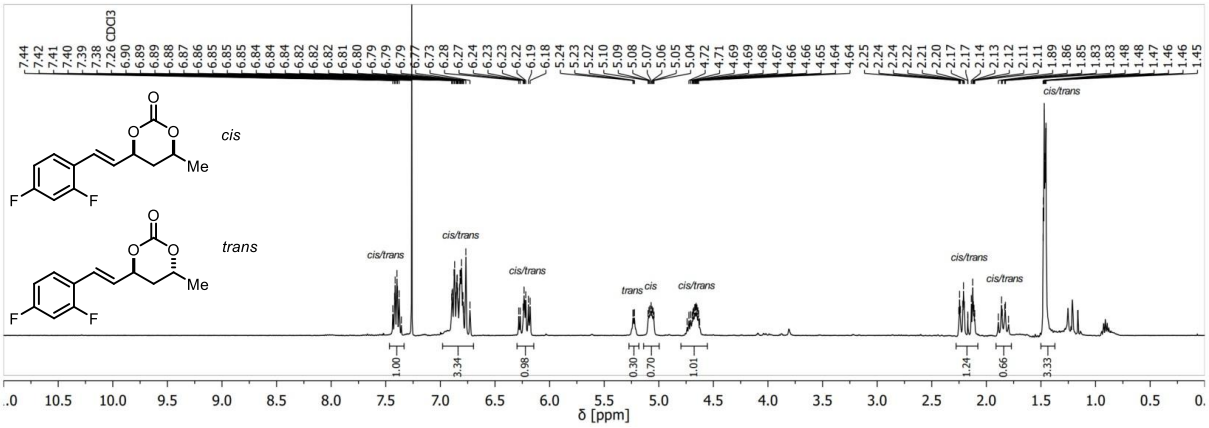


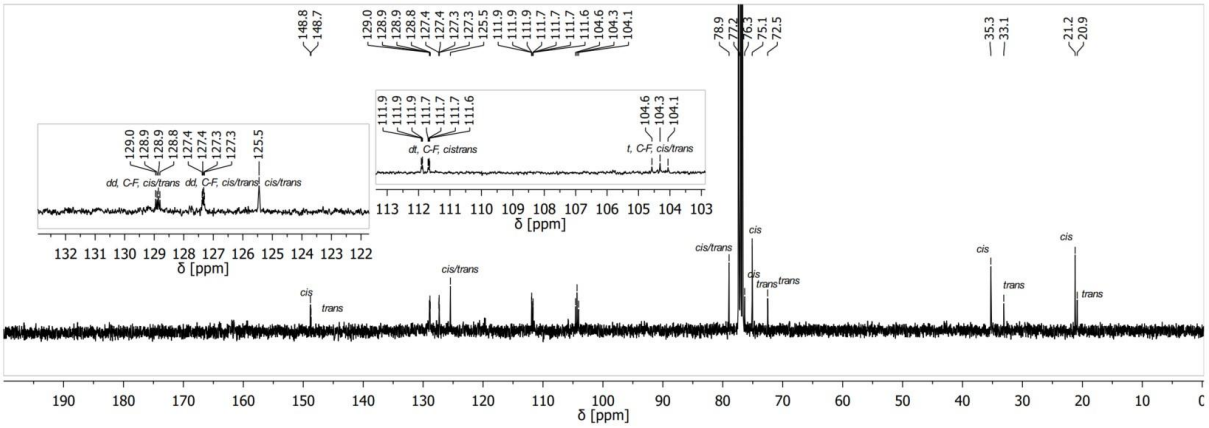


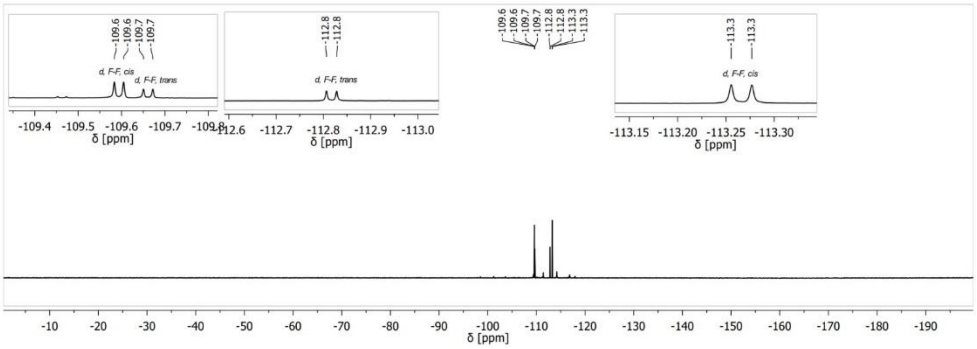


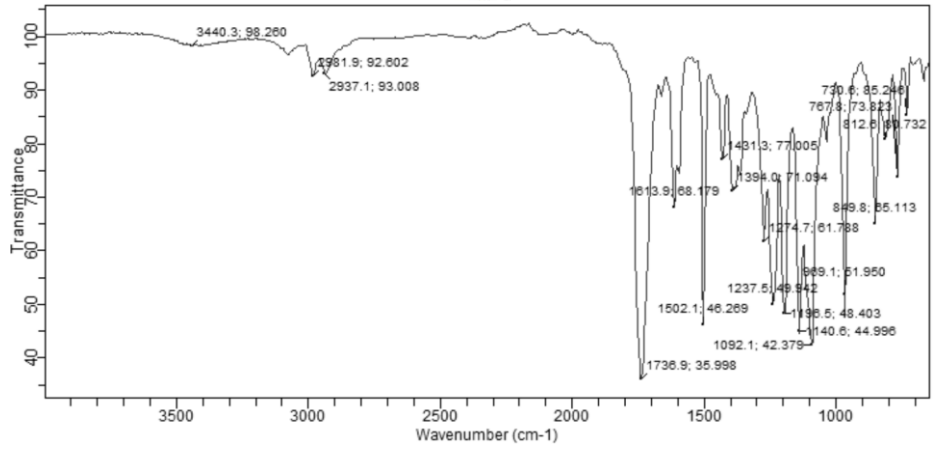
(*E*)-4-(2,4-Difluorostyryl)-6-methyl-1,3-dioxan-2-one (136o)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz), **^{19}F{^{1}H} NMR** (376 MHz): Chloroform-*d*, **IR**





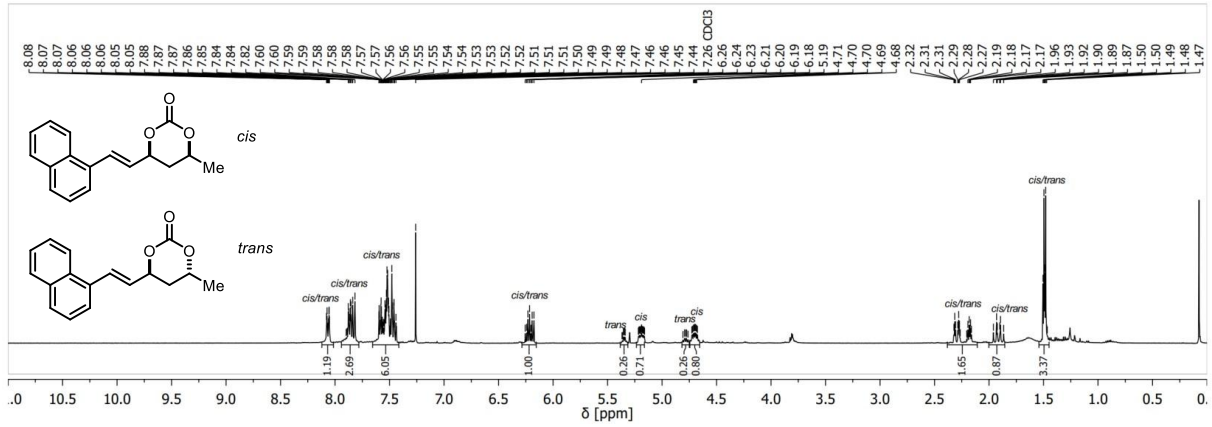


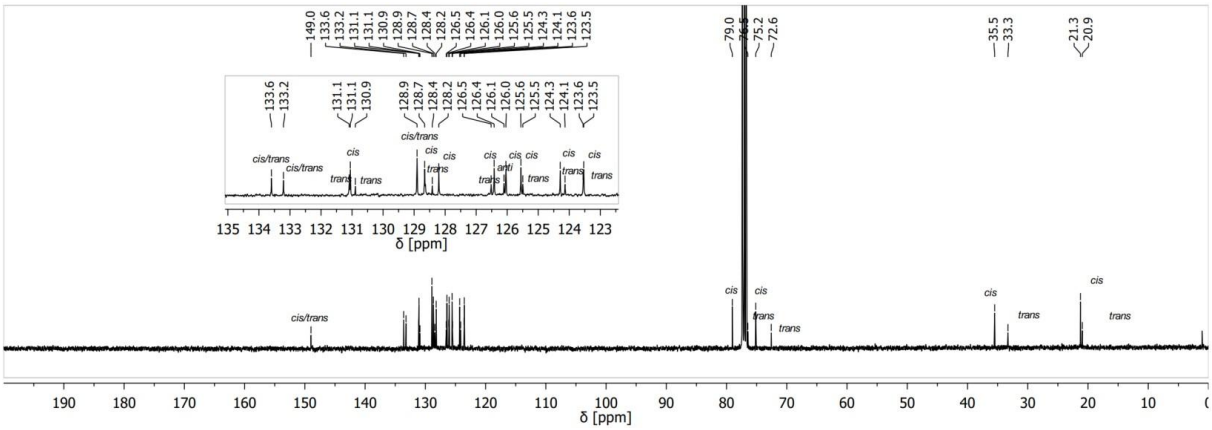


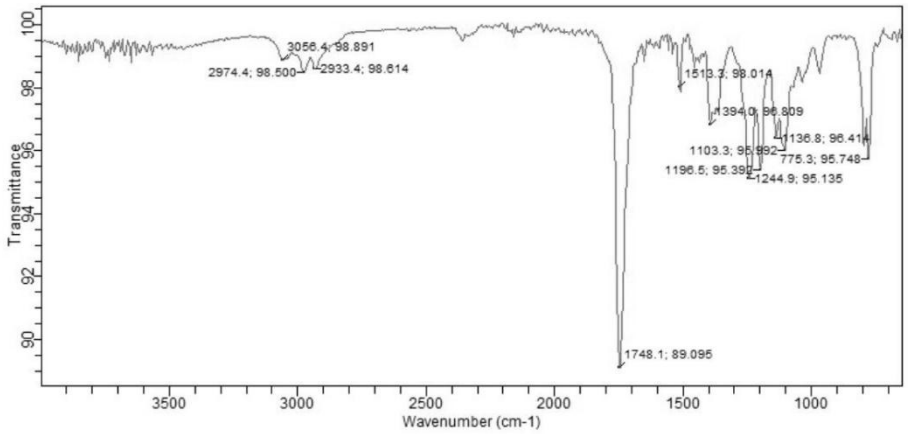
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-Methyl-6-(2-(naphthalen-1-yl)vinyl)-1,3-dioxan-2-one (136p)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



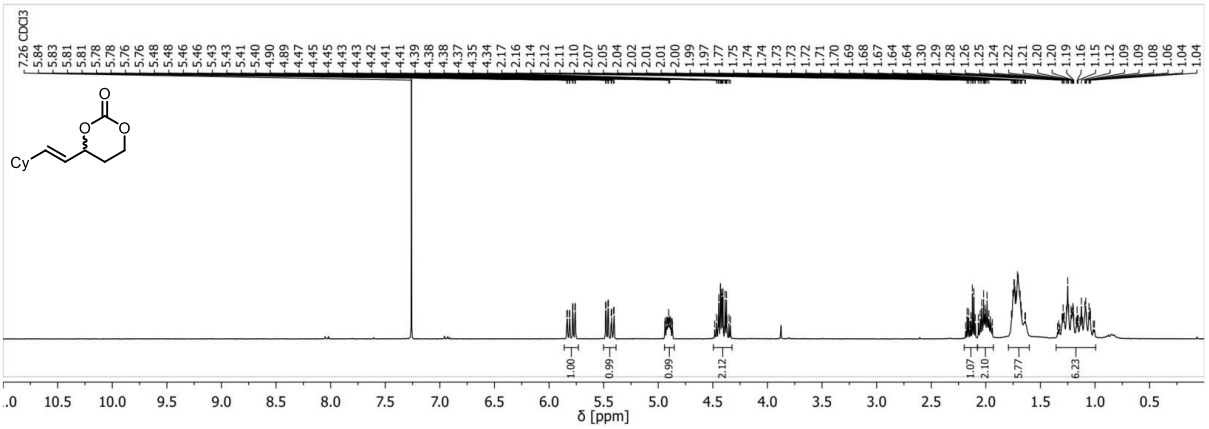


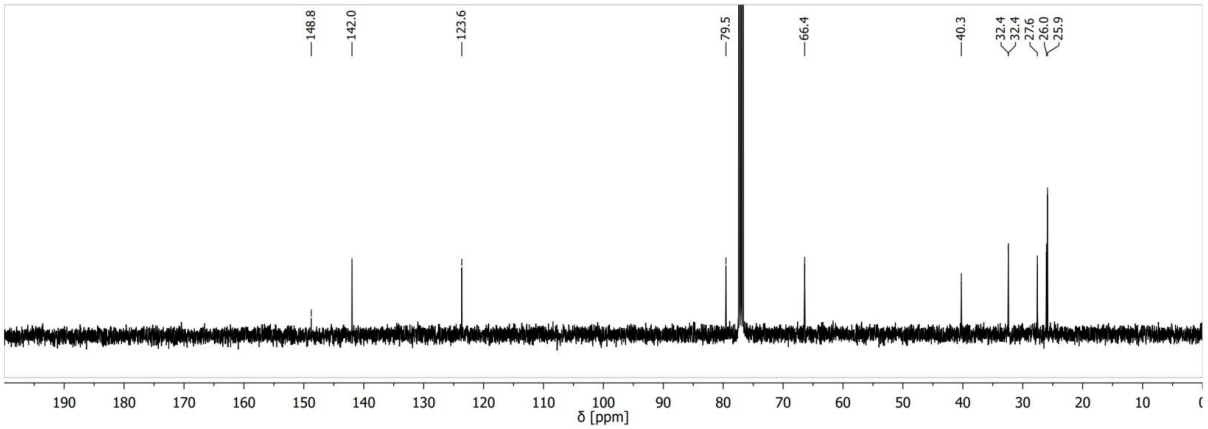


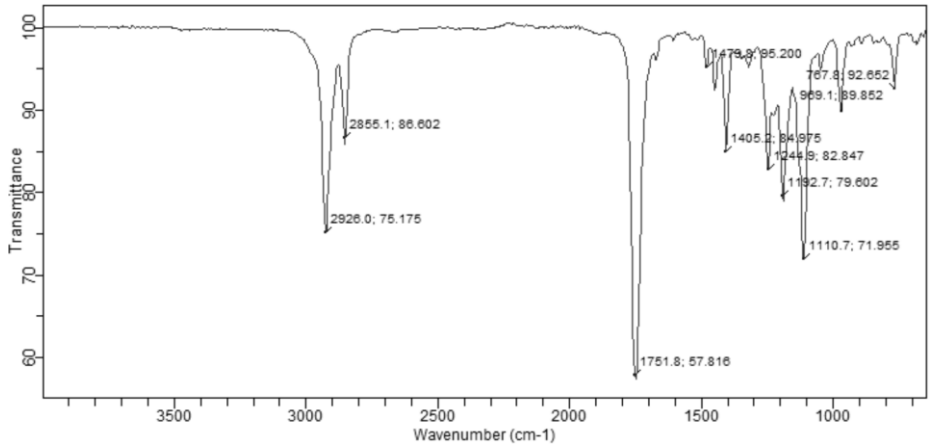
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-(2-Cyclohexylvinyl)-1,3-dioxan-2-one (136q)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



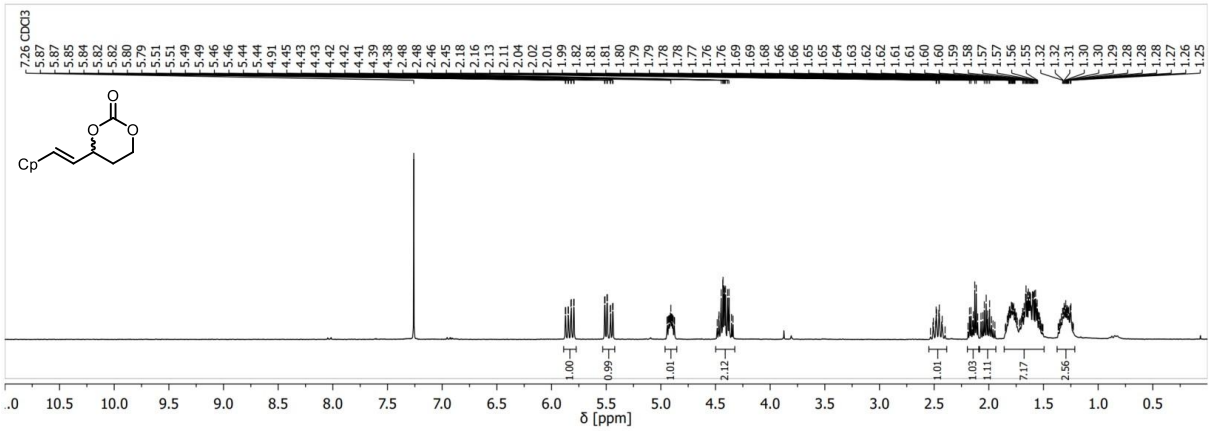


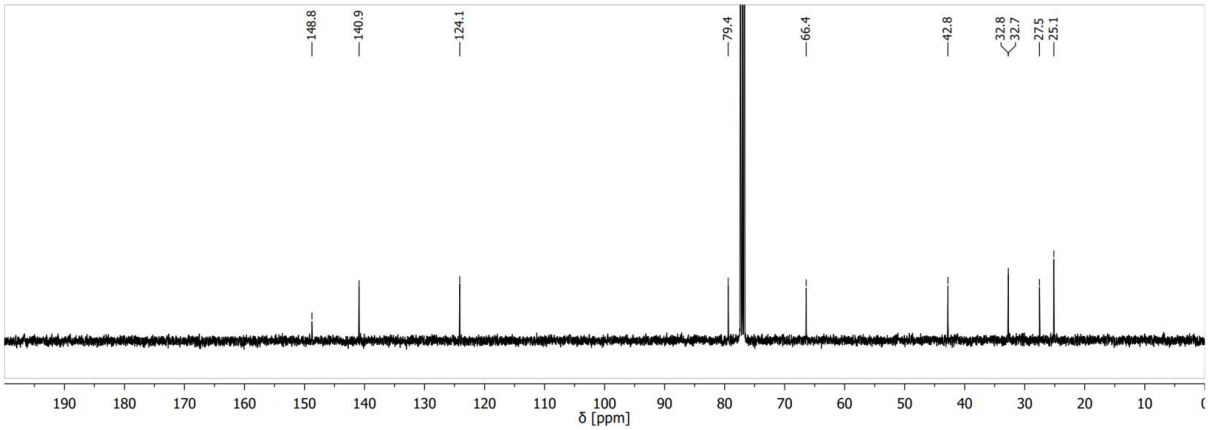


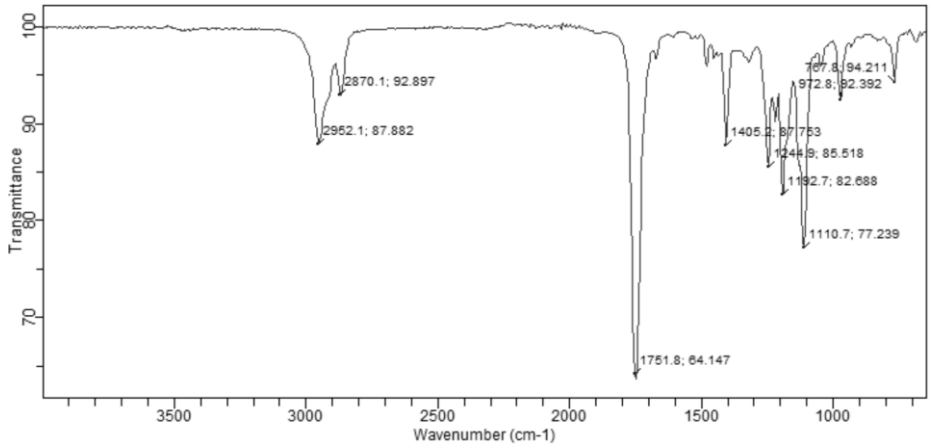
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-(2-Cyclopentylvinyl)-1,3-dioxan-2-one (136r)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

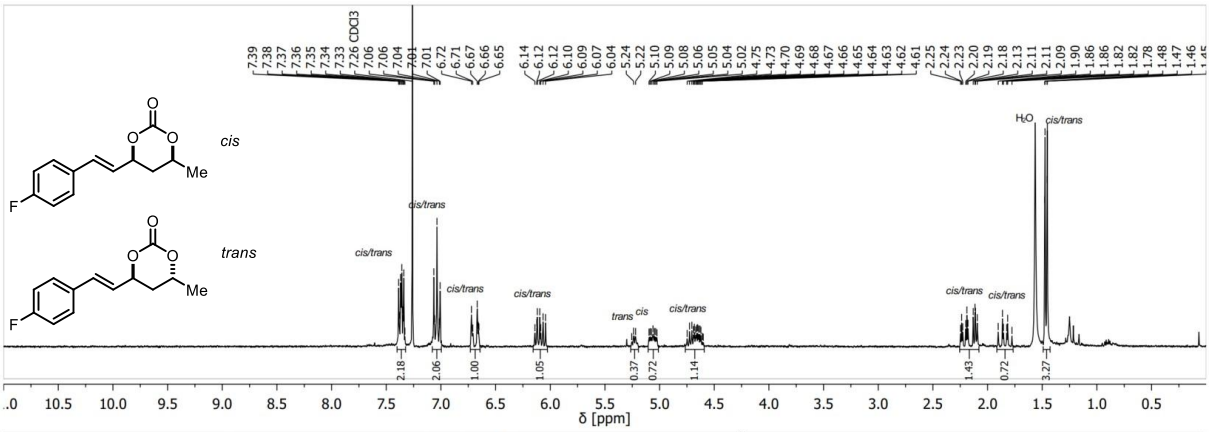


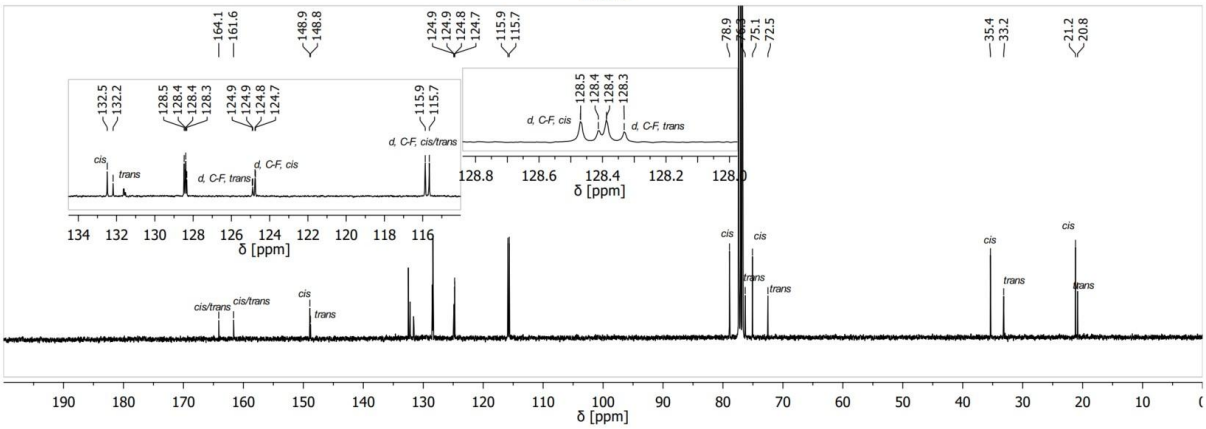


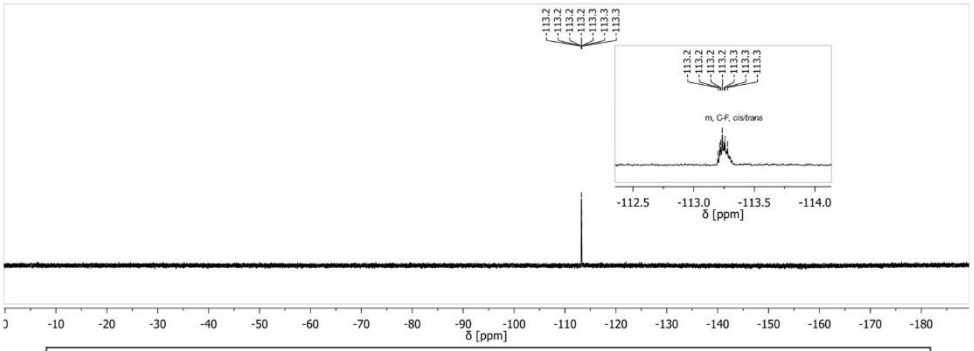


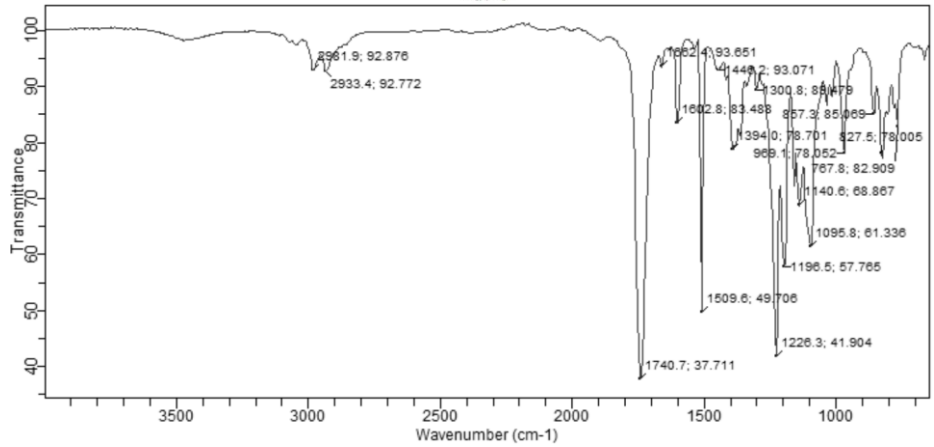
(*E*)-4-(4-Fluorostyryl)-6-methyl-1,3-dioxan-2-one (136s)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz), **^{19}F NMR** (376 MHz): Chloroform-*d*, **IR**





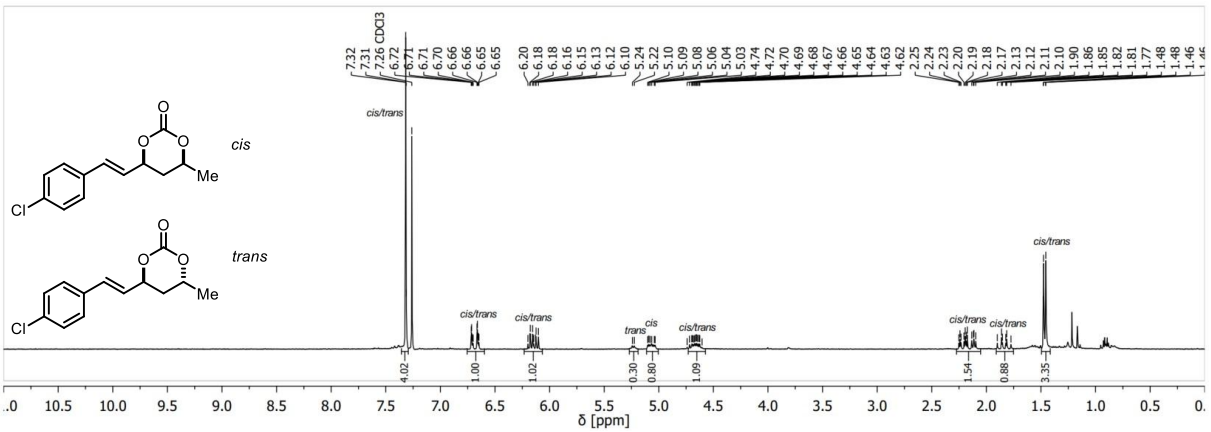


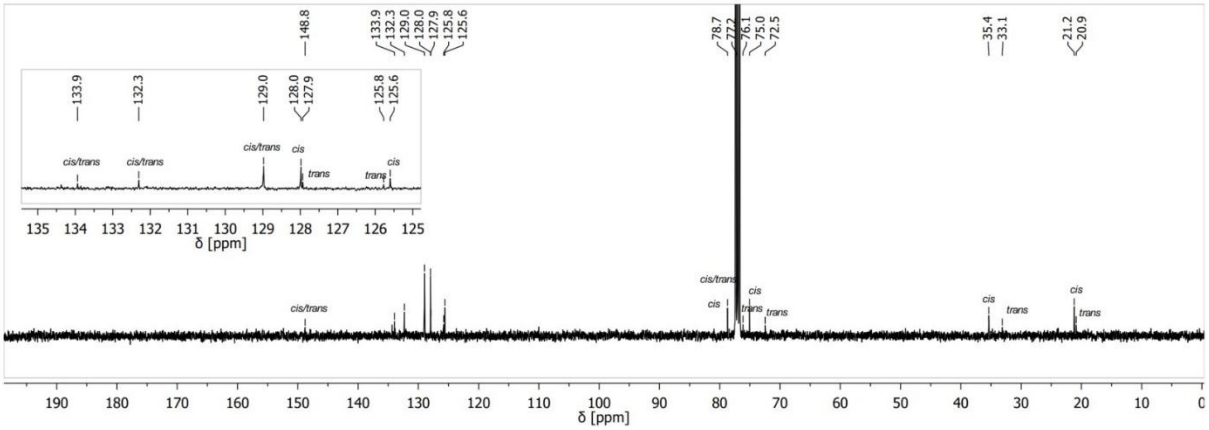


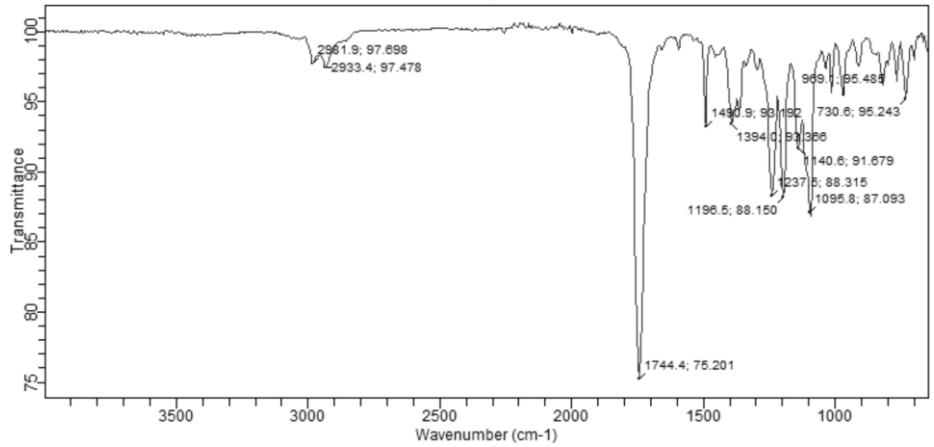
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-(4-Chlorostyryl)-6-methyl-1,3-dioxan-2-one (136t)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



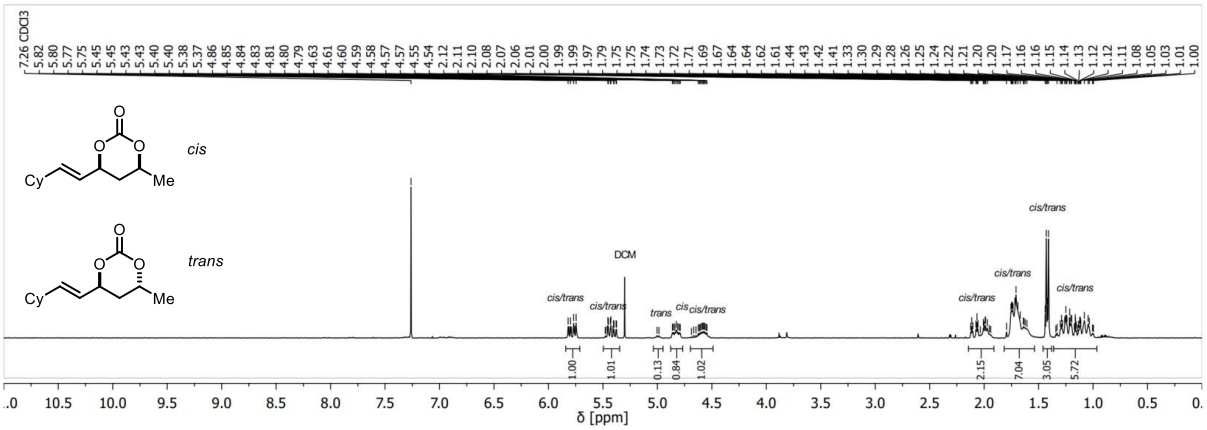


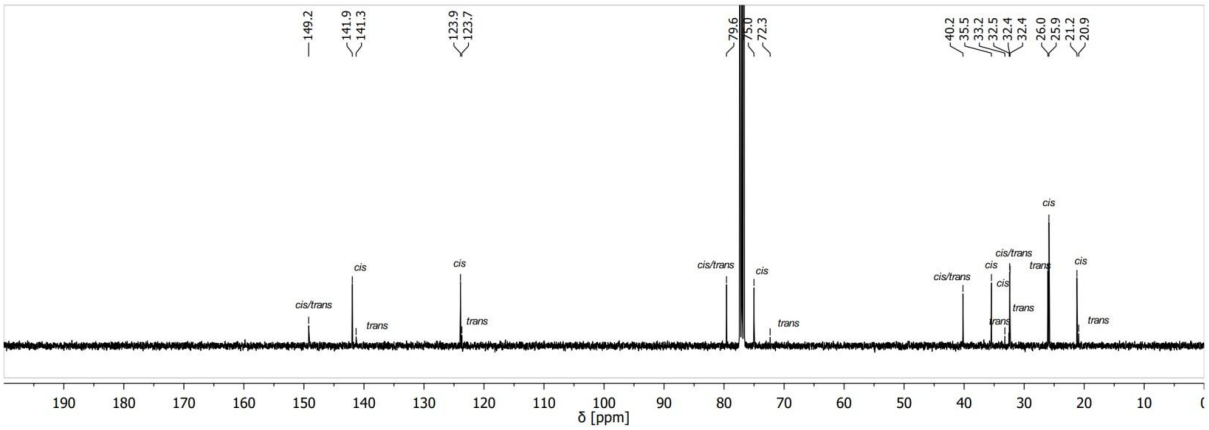


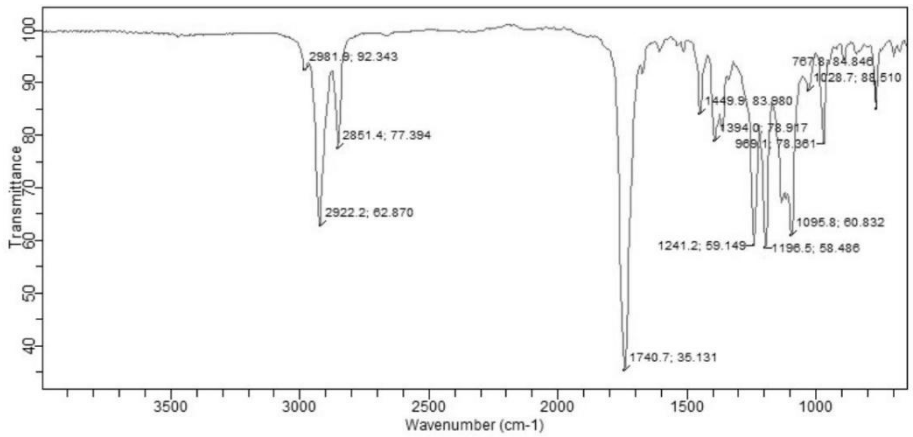
Spectra of project “1,3-dioxan-2-ones” – products

(*E*)-4-(2-Cyclohexylvinyl)-6-methyl-1,3-dioxan-2-one (136u)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

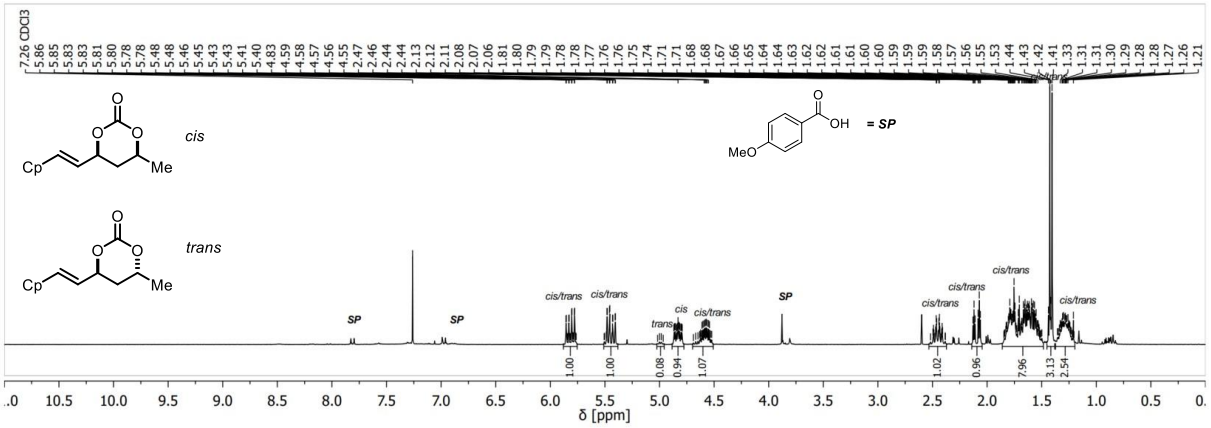


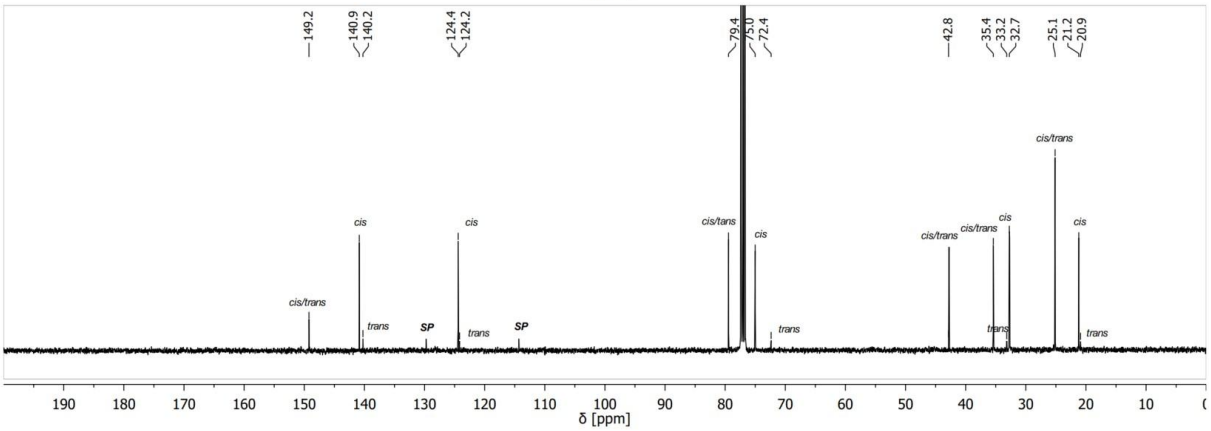


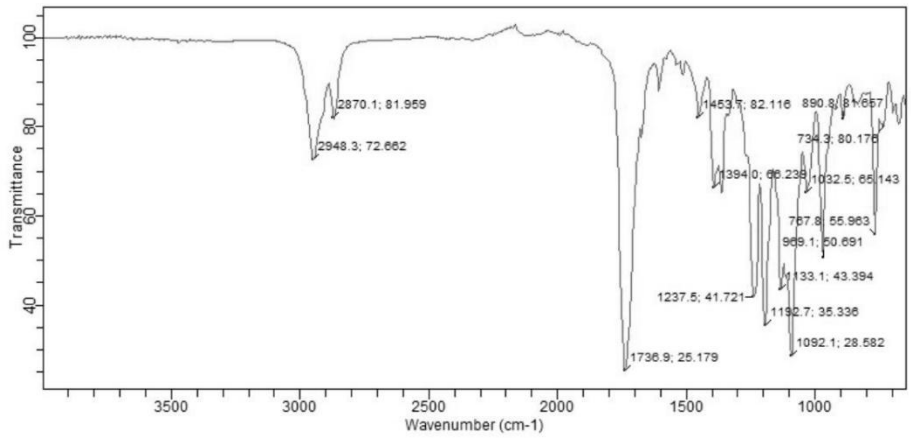


(*E*)-4-(2-Cyclopentylvinyl)-6-methyl-1,3-dioxan-2-one (< 5% SP) (136v)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

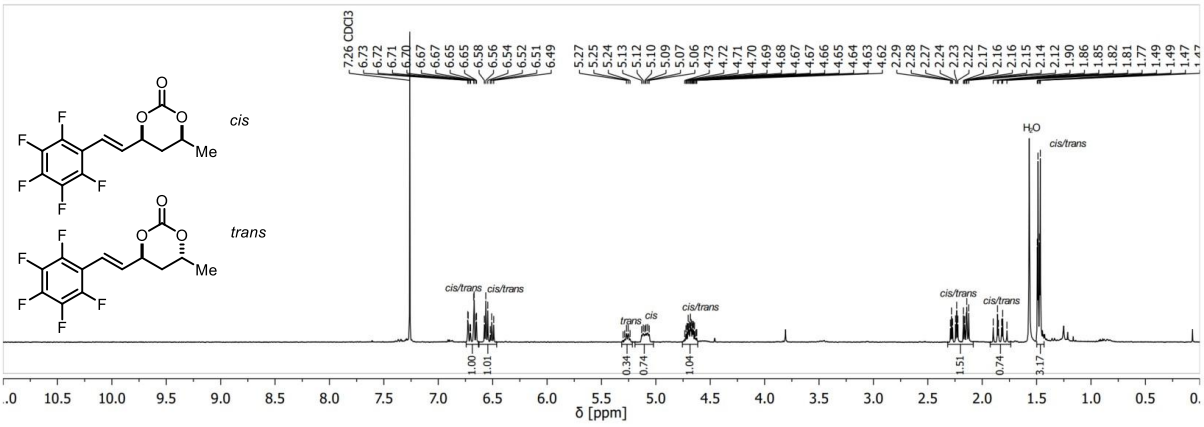


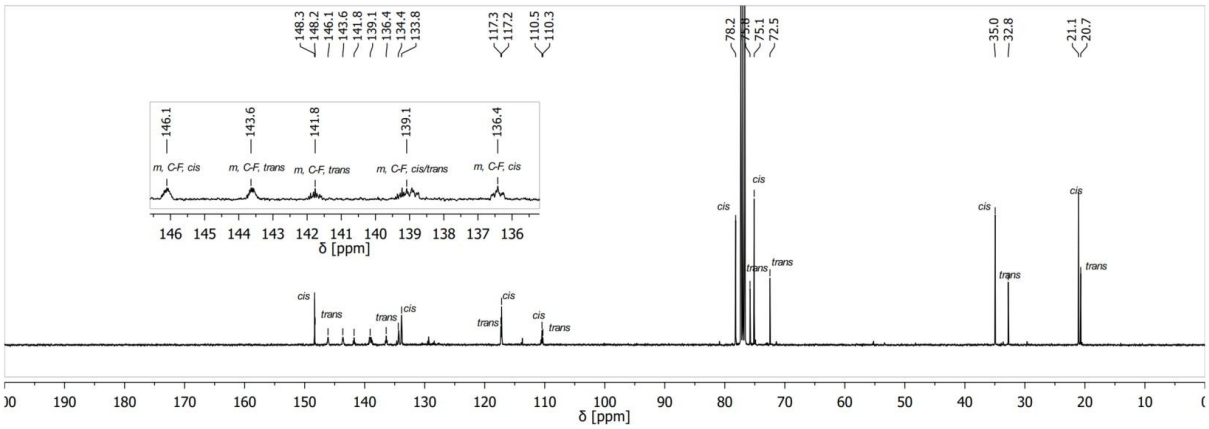


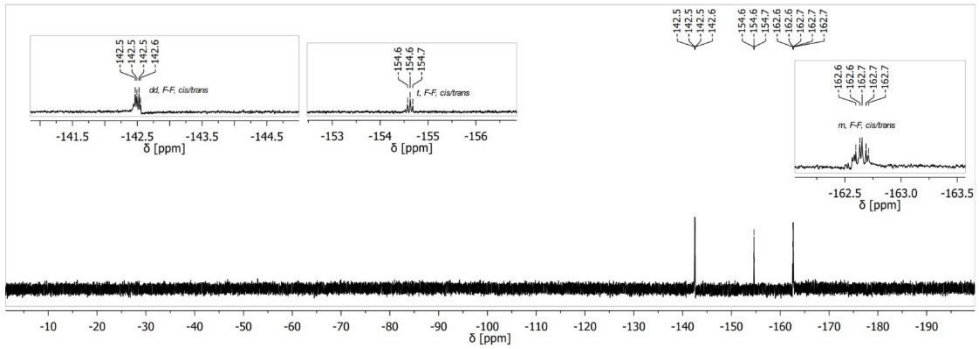


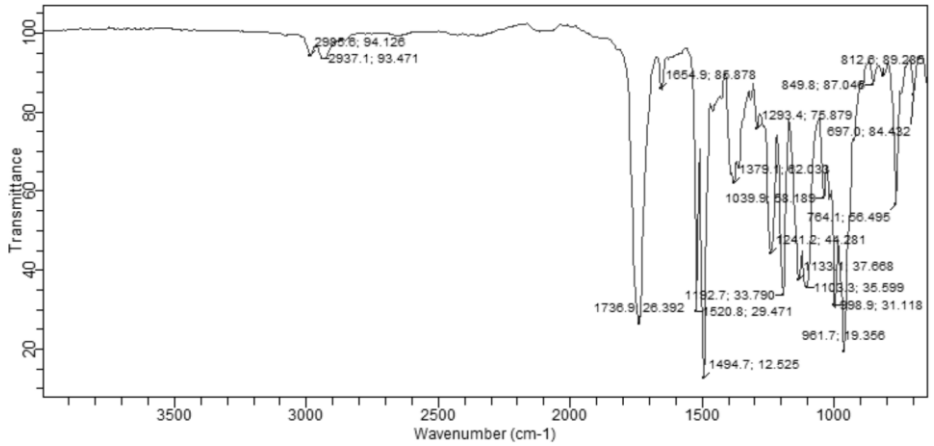
(*E*)-4-Methyl-6-(2-(perfluorophenyl)vinyl)-1,3-dioxan-2-one (136x)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz), **^{19}F NMR** (376 MHz): Chloroform-*d*, **IR**





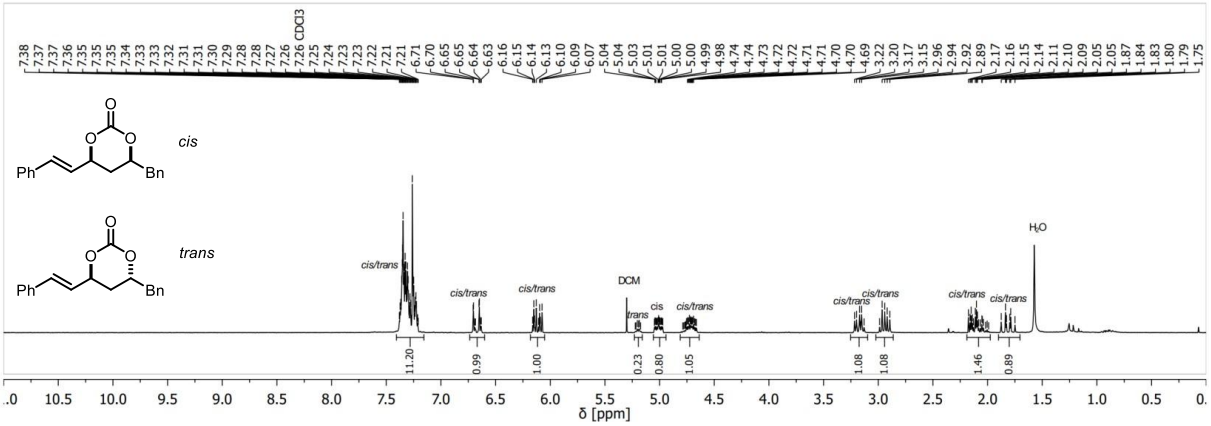




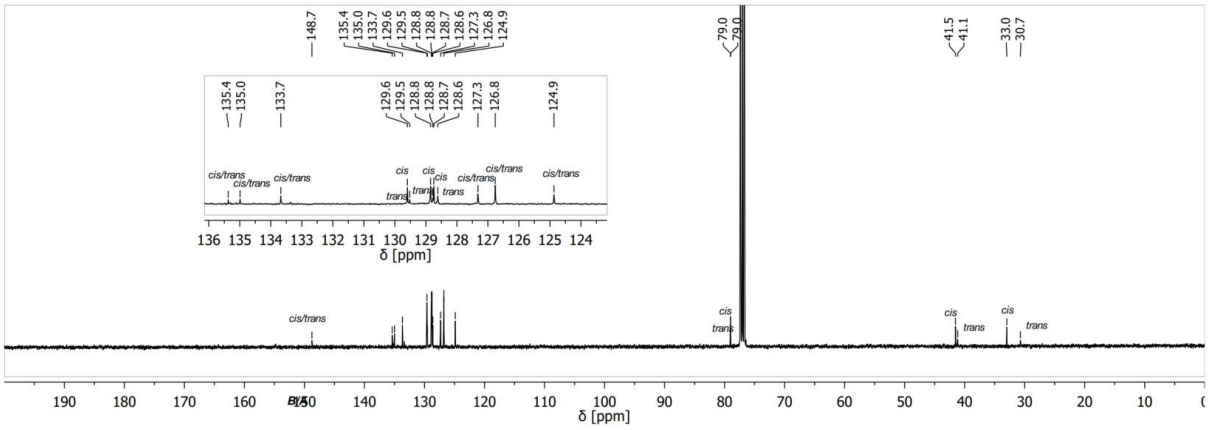
Spectra of project “1,3-dioxan-2-ones” – products

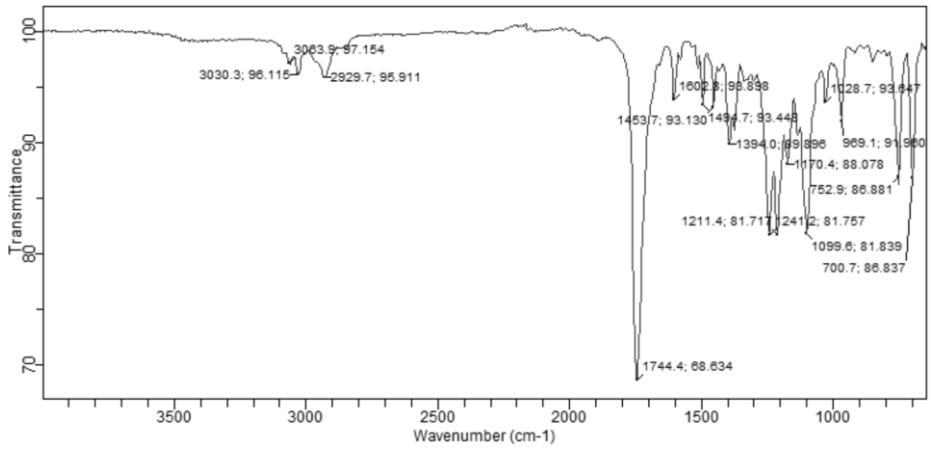
(*E*)-4-Benzyl-6-styryl-1,3-dioxan-2-one (136y)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



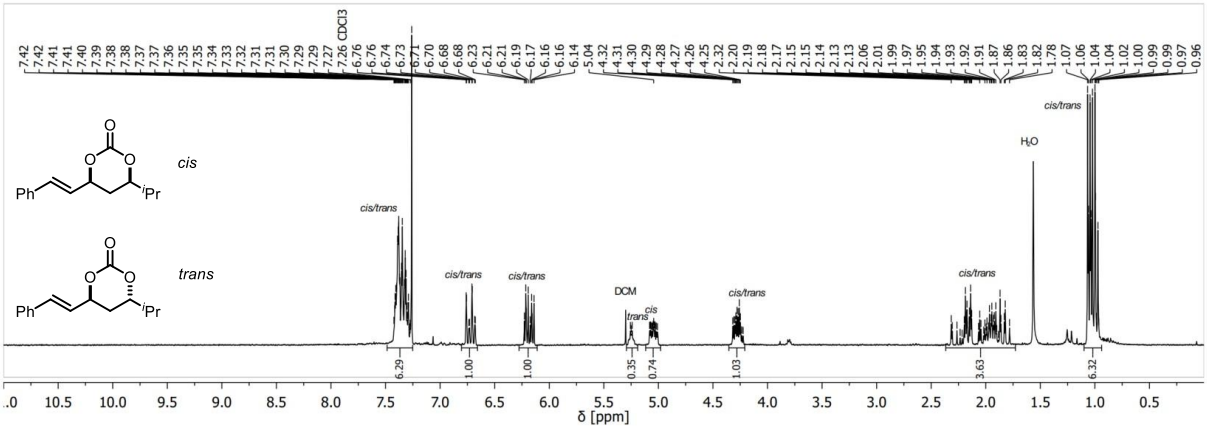
*DCM was used to wash the reagent tube after column chromatography

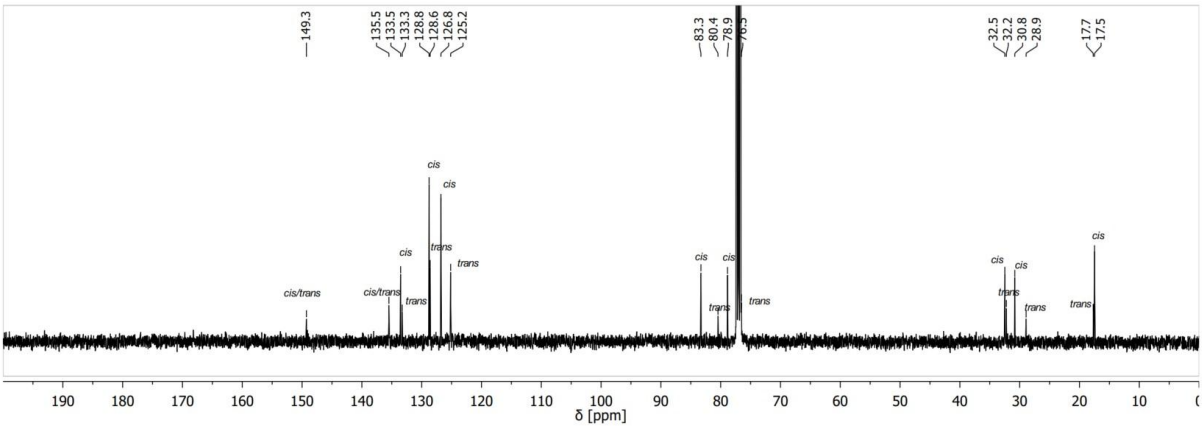


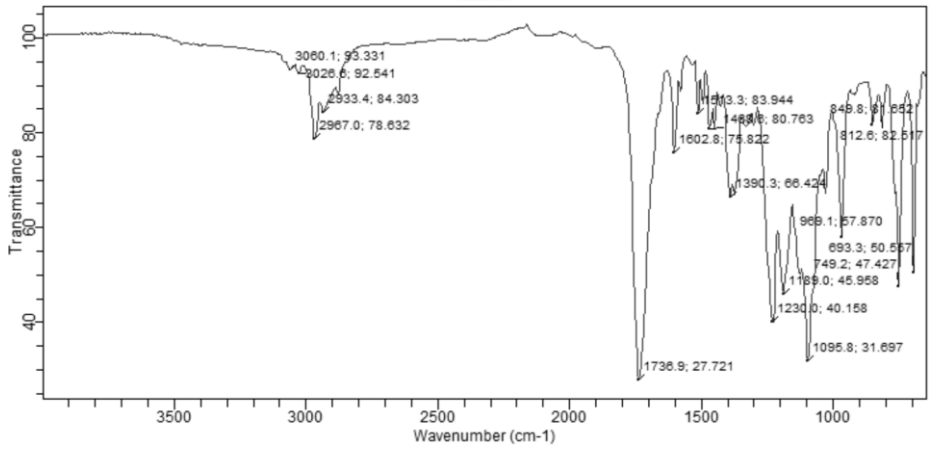


(*E*)-4-Isopropyl-6-styryl-1,3-dioxan-2-one (136z)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



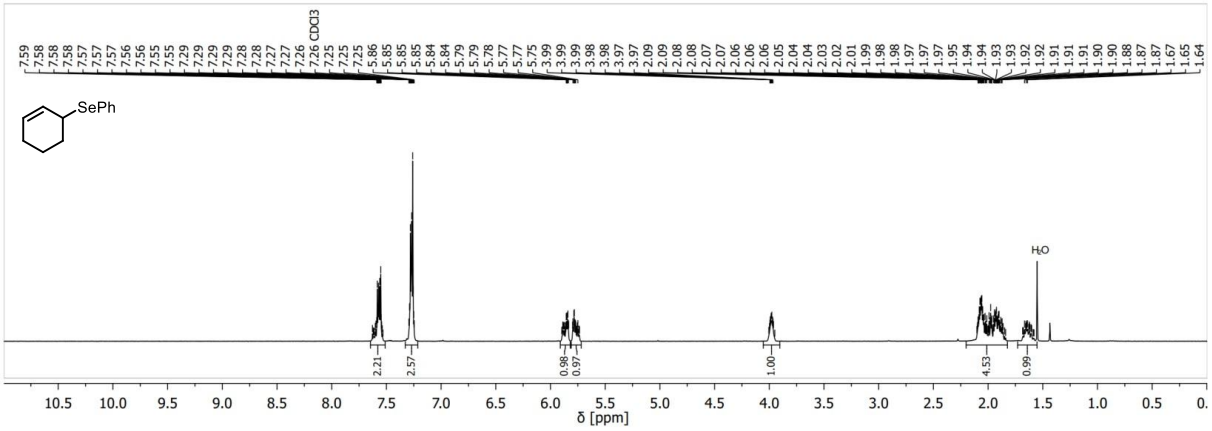




8.3 Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

Cyclohex-2-en-1-yl(phenyl)selane

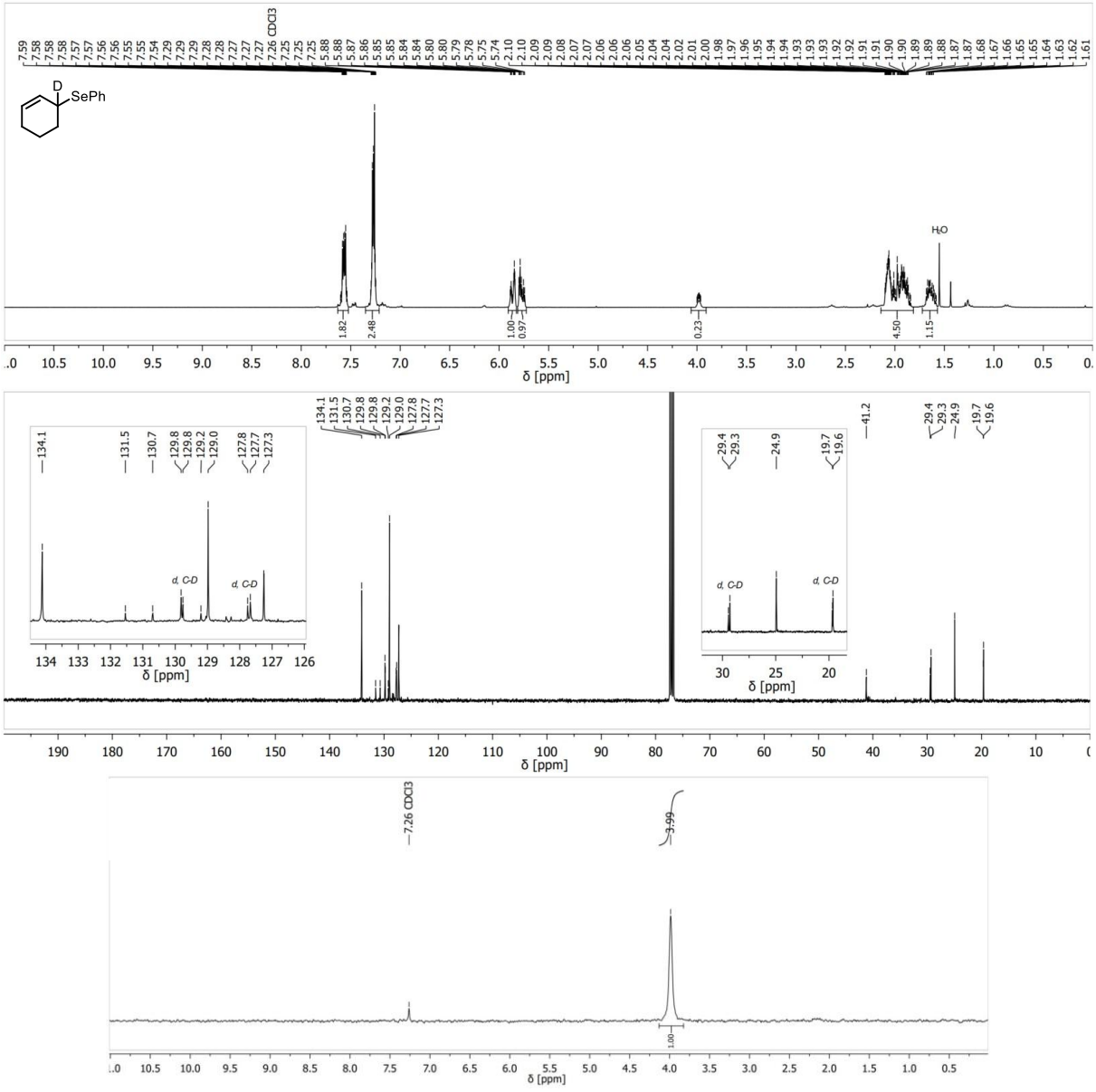
^{1}H NMR (300 MHz): Chloroform-*d*, **IR**



Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

Cyclohex-2-en-1-yl(phenyl)selane (167)

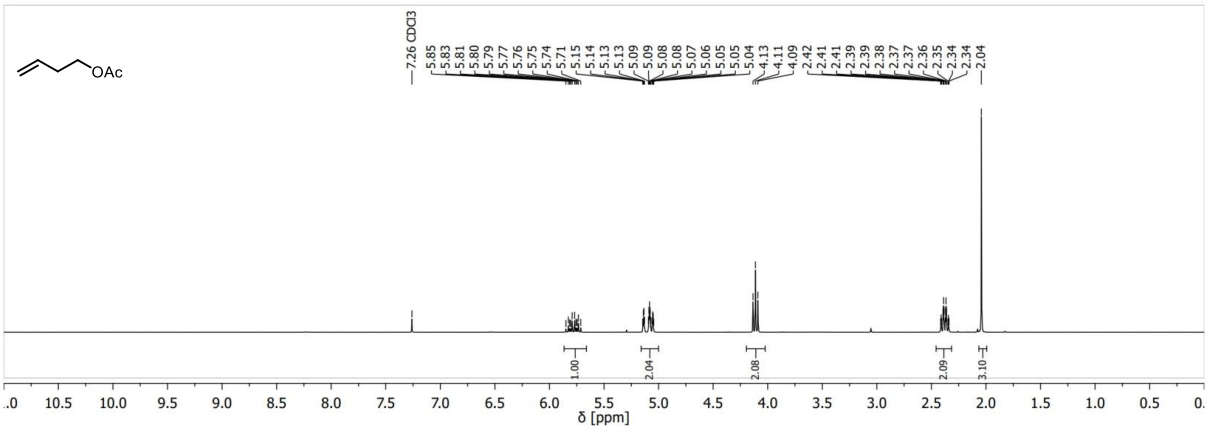
^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **^{2}H NMR** (61 MHz): Chloroform-*d*, **IR**

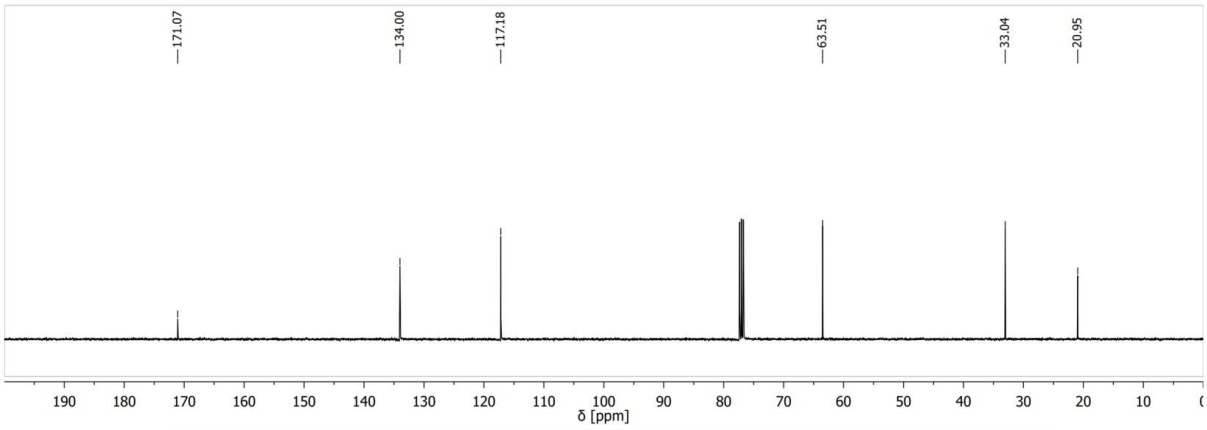


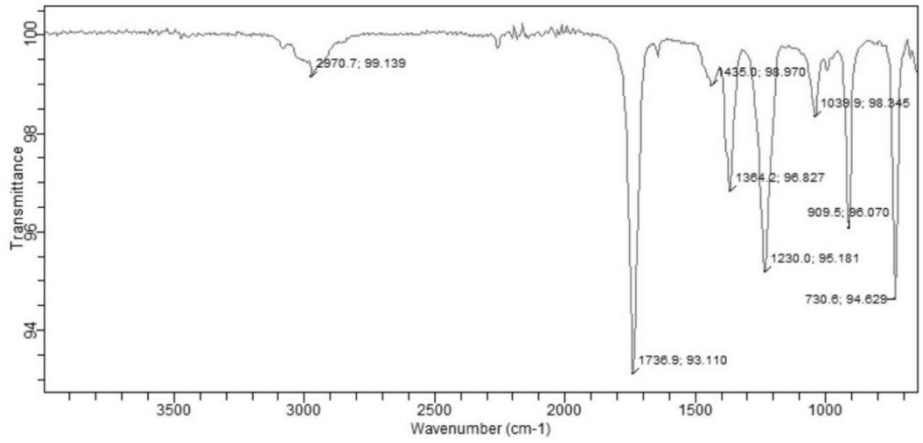
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

But-3-en-1-yl acetate

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



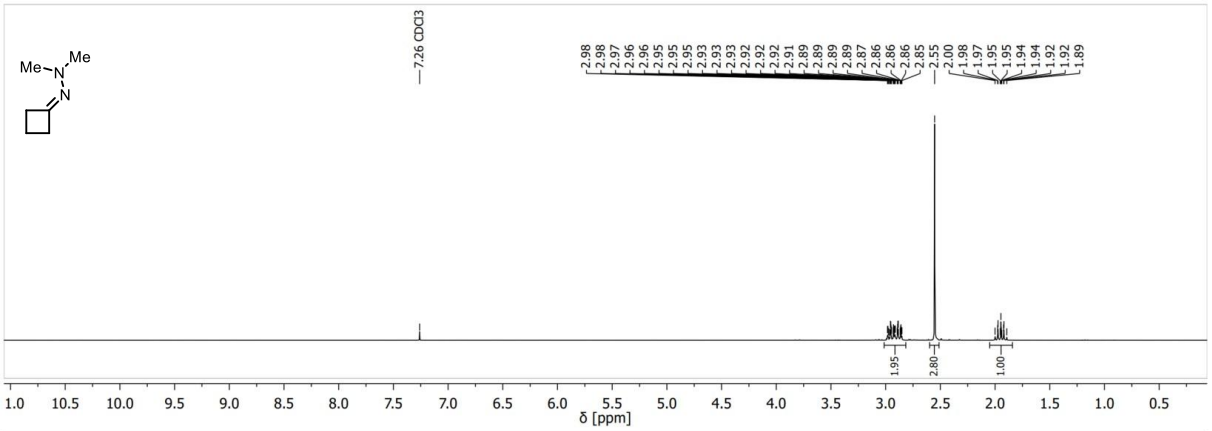


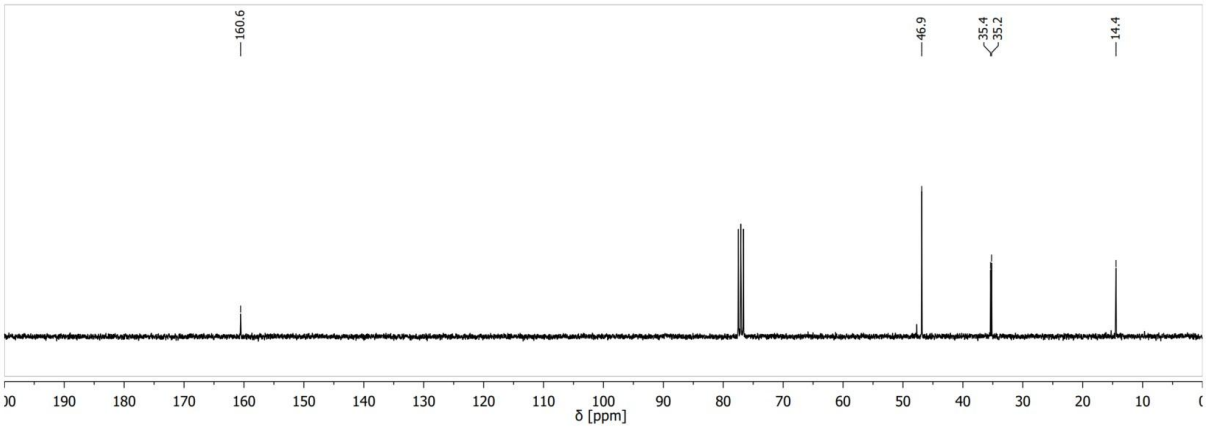


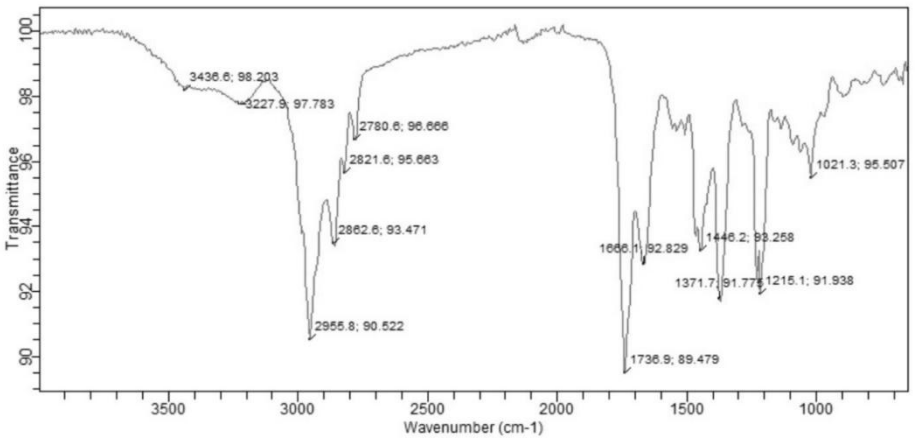
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2-Cyclobutylidene-1,1-dimethylhydrazine (188)

^{1}H NMR (300 MHz) **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



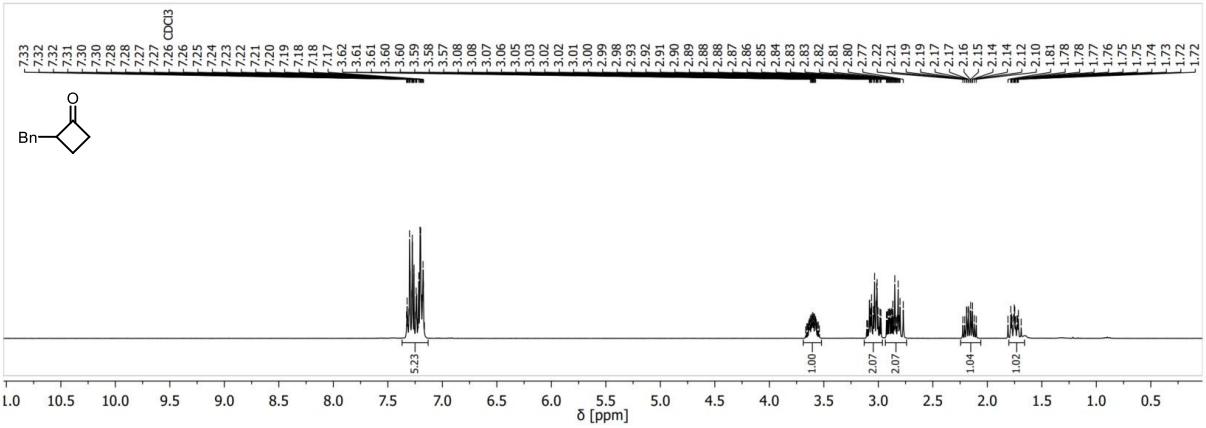


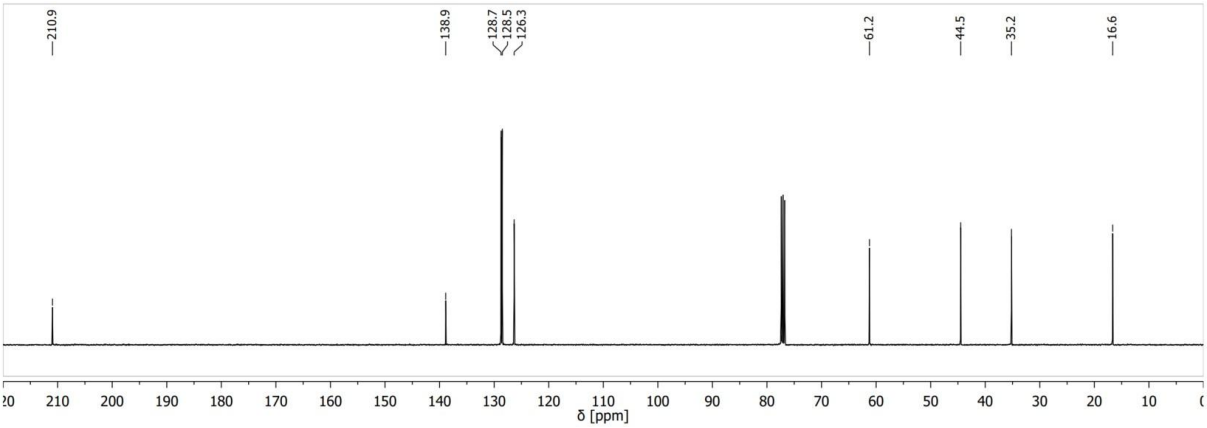


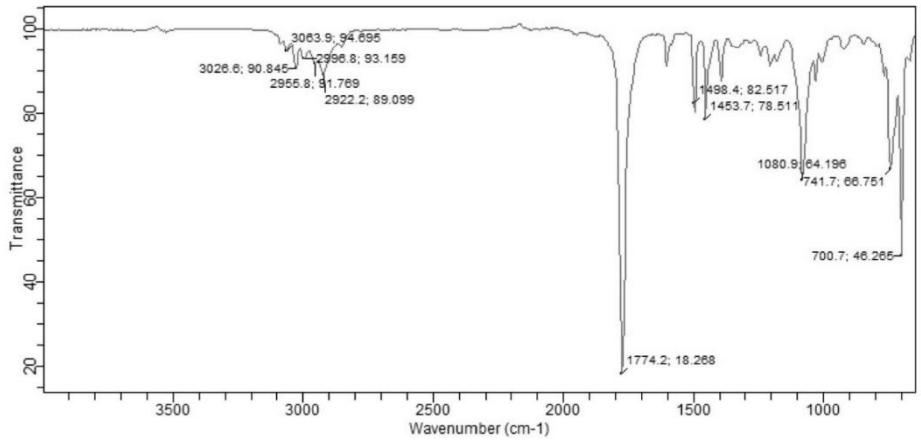
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2-Benzylcyclobutan-1-one (179a)

^{1}H NMR (300 MHz) **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



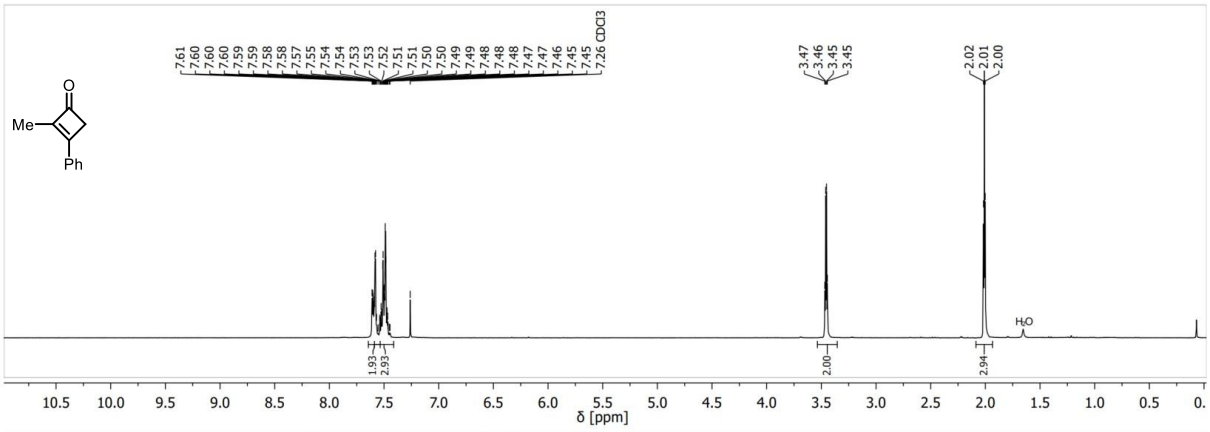


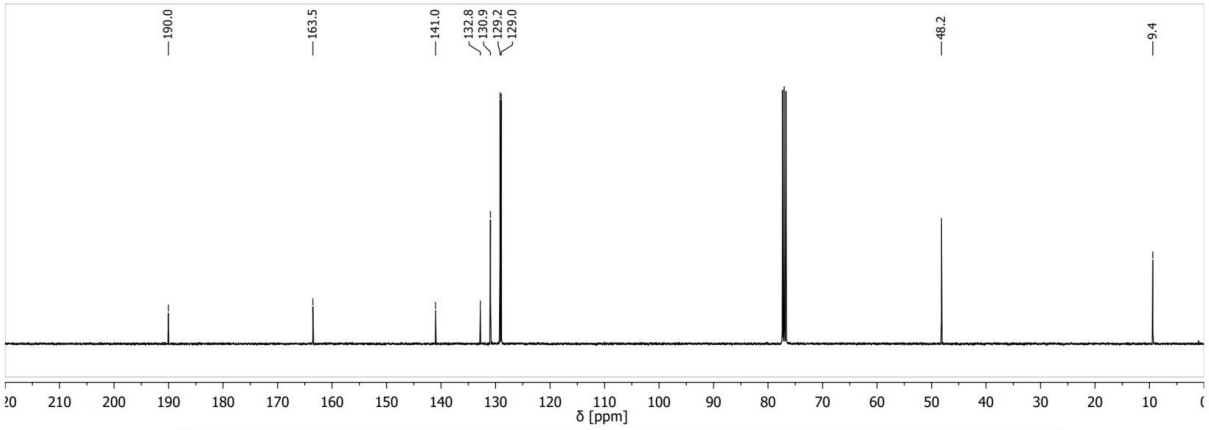


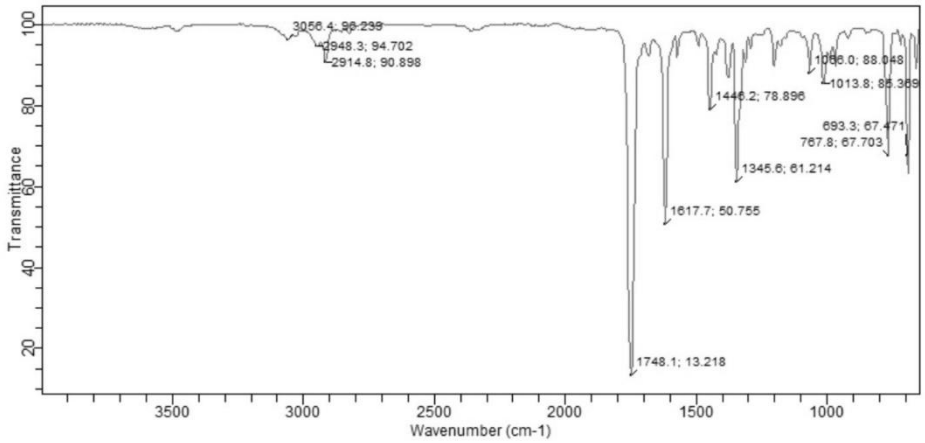
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2-Methyl-3-phenylcyclobut-2-en-1-one (201)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



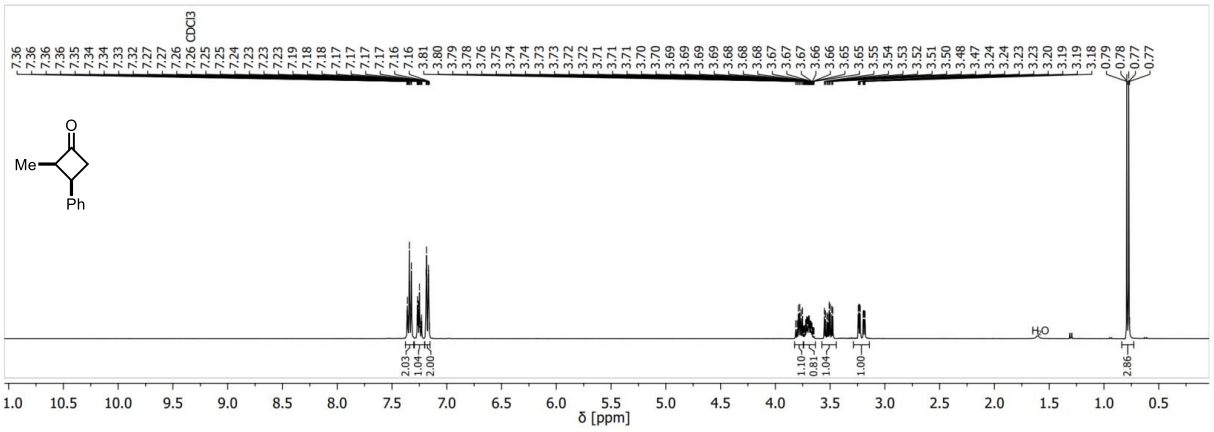


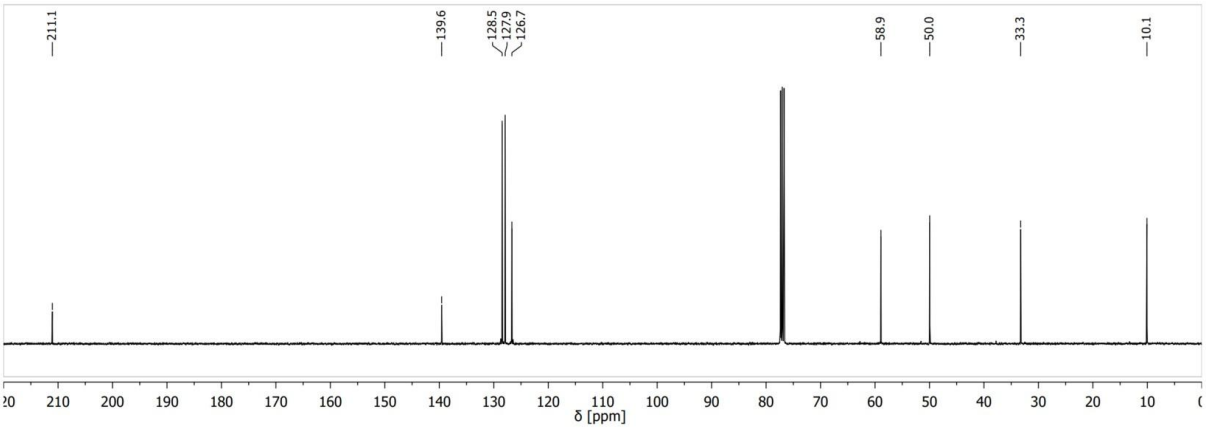


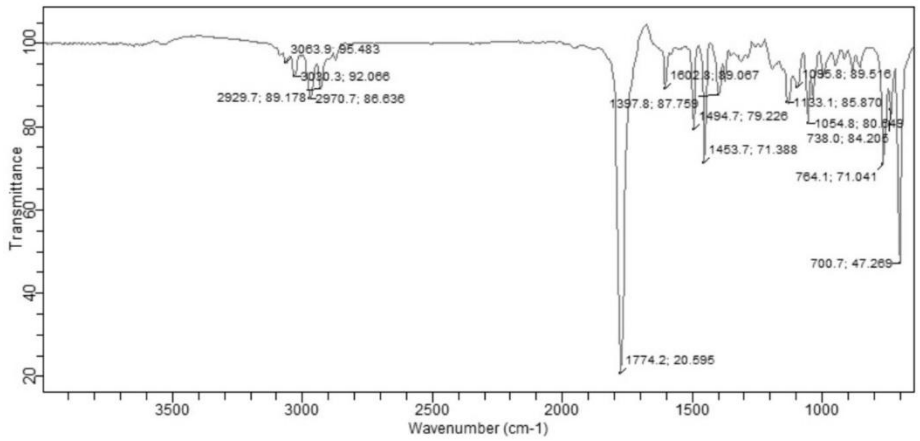
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

(*cis*)-2-Methyl-3-phenylcyclobutan-1-one (182l-*cis*)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz), **NOESY** (400 MHz): Chloroform-*d*, **IR**

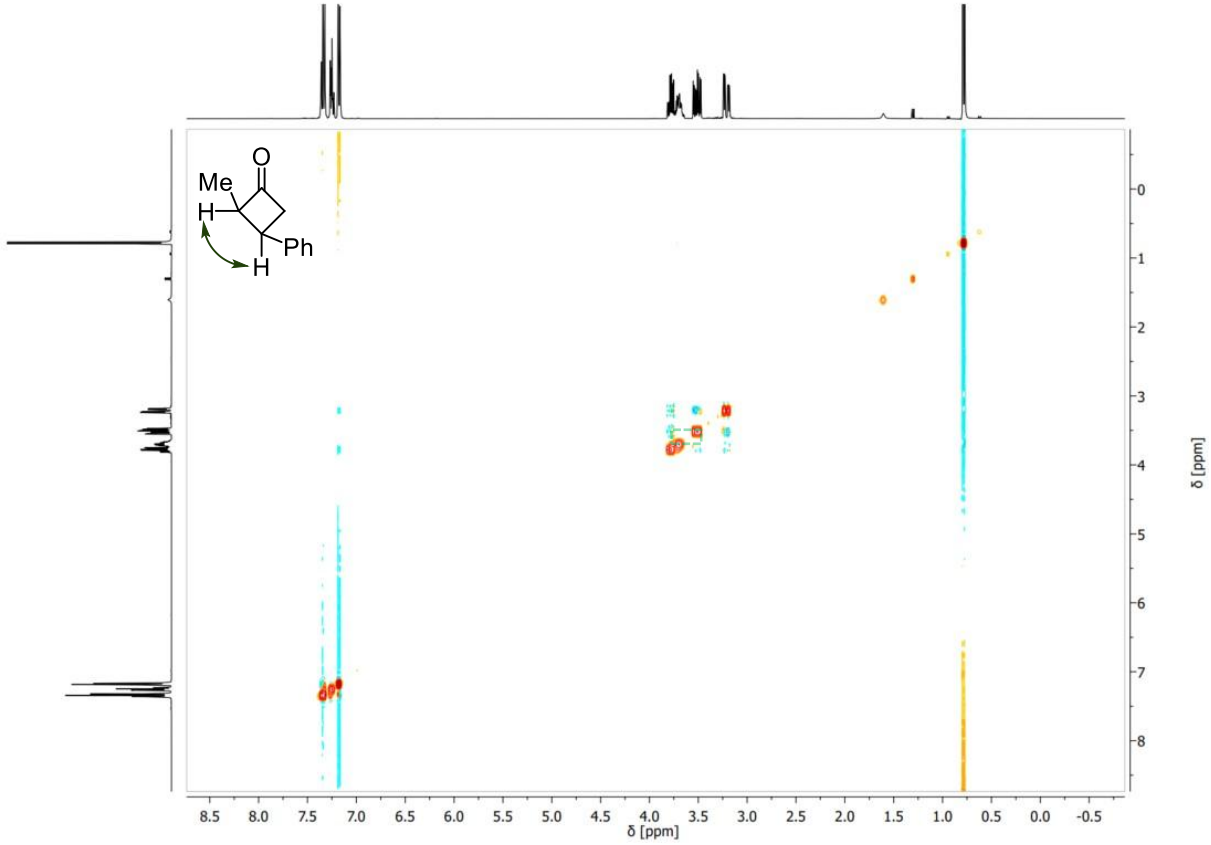






8 Appendix

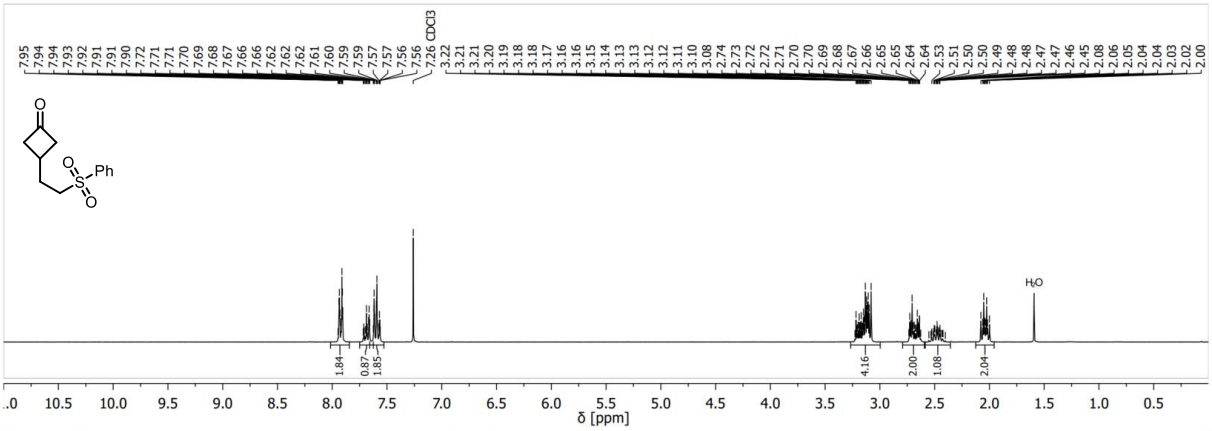
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

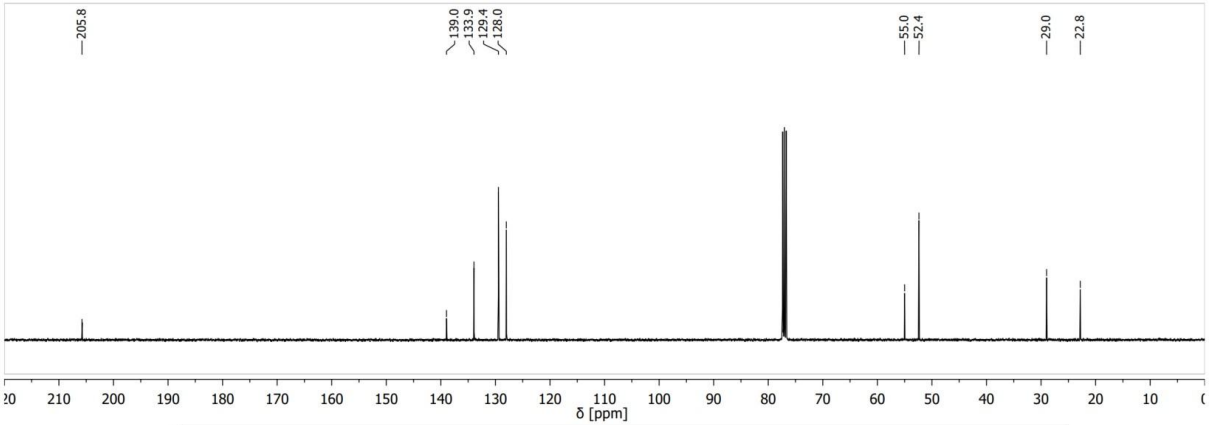


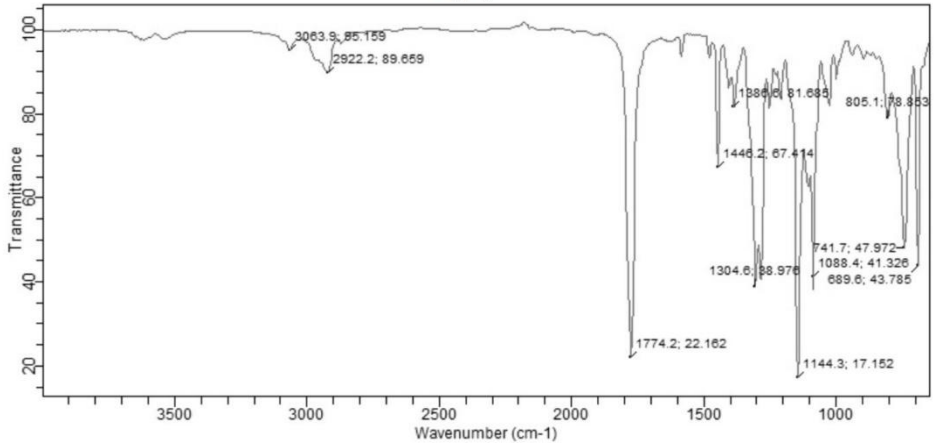
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-(2-(Phenylsulfonyl)ethyl)cyclobutan-1-one (199a)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



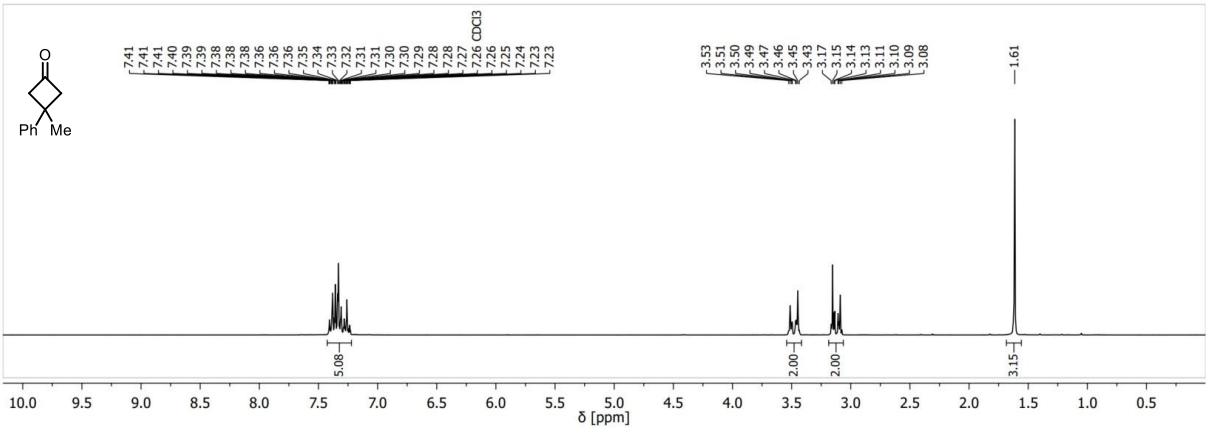


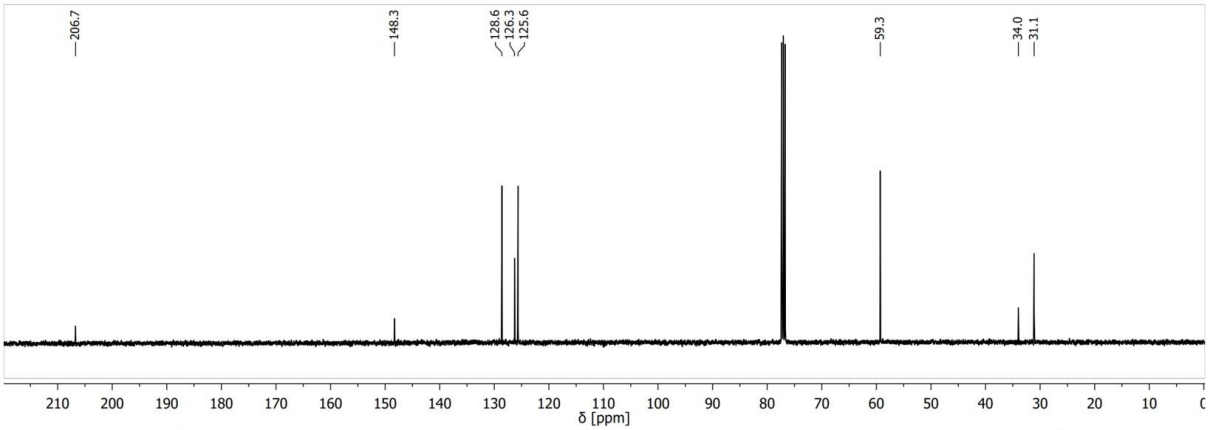


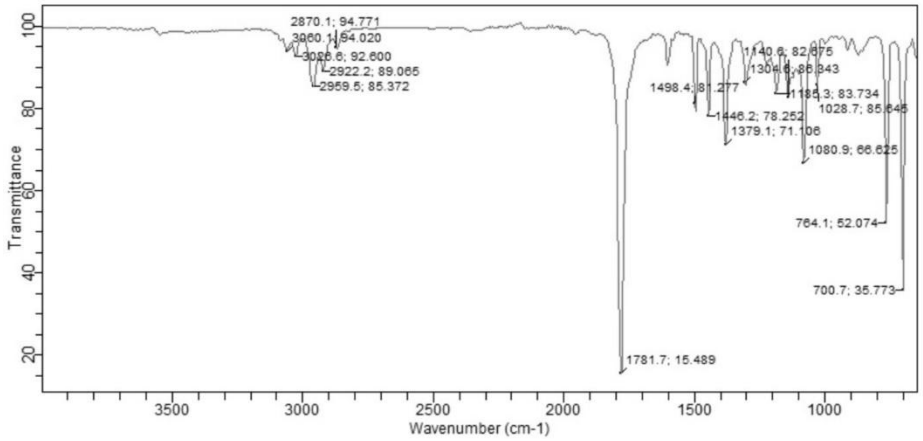
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-Methyl-3-phenylcyclobutan-1-one (182a)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



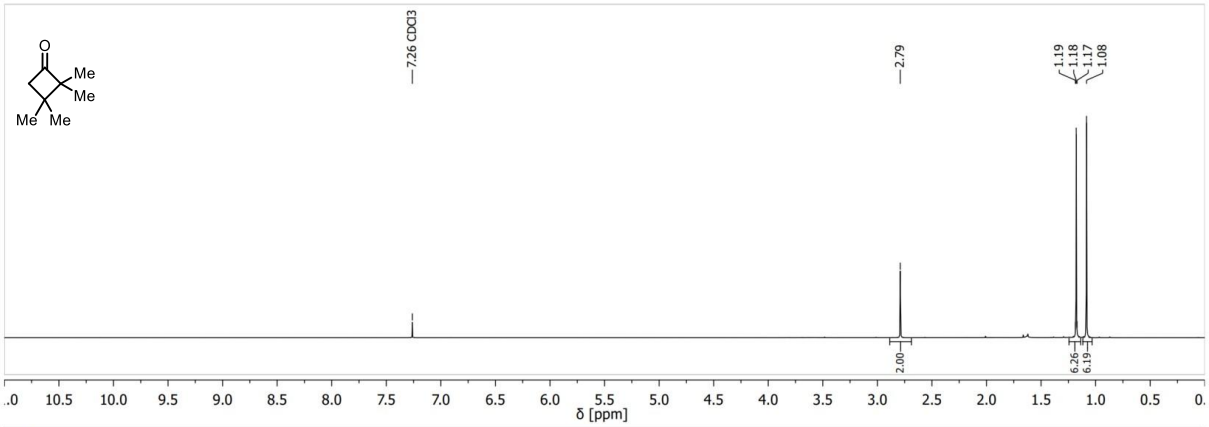


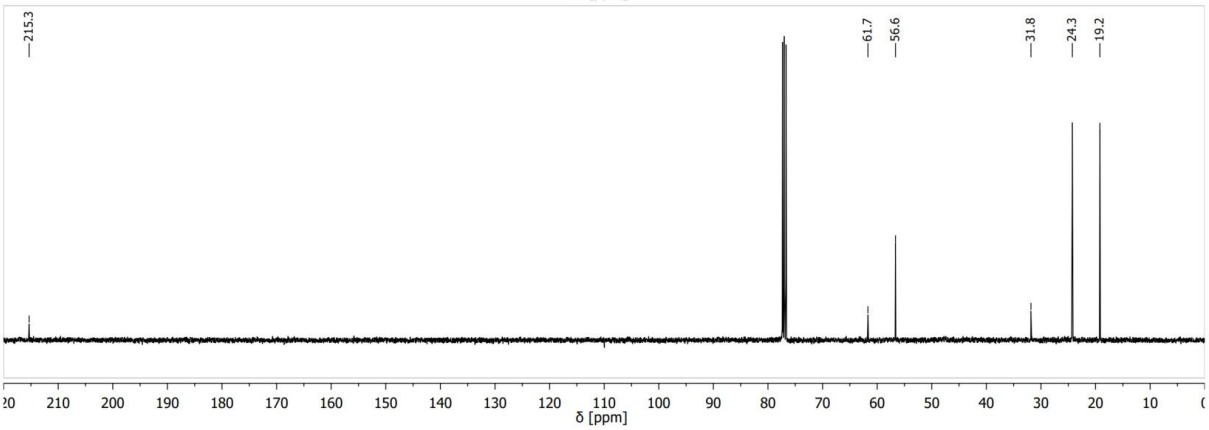


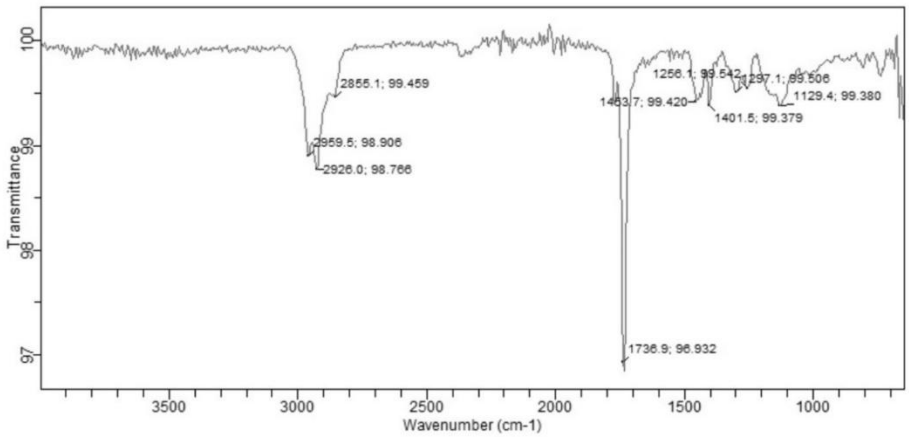
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2,2,3,3-Tetramethylcyclobutan-1-one (182b)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



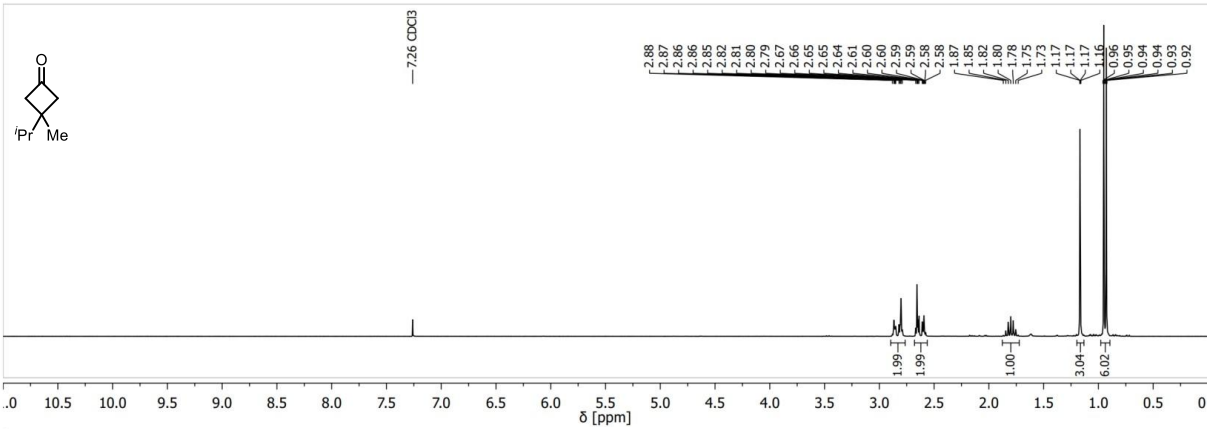


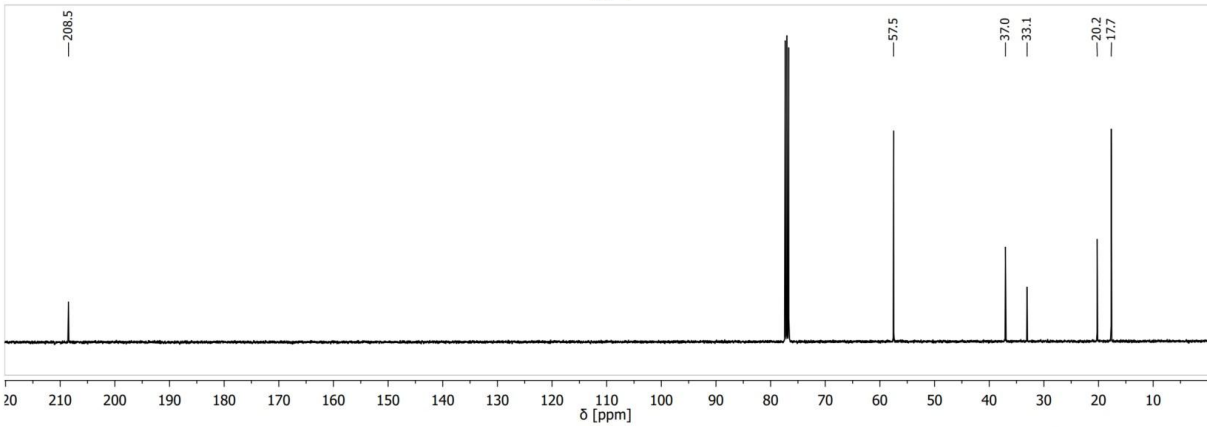


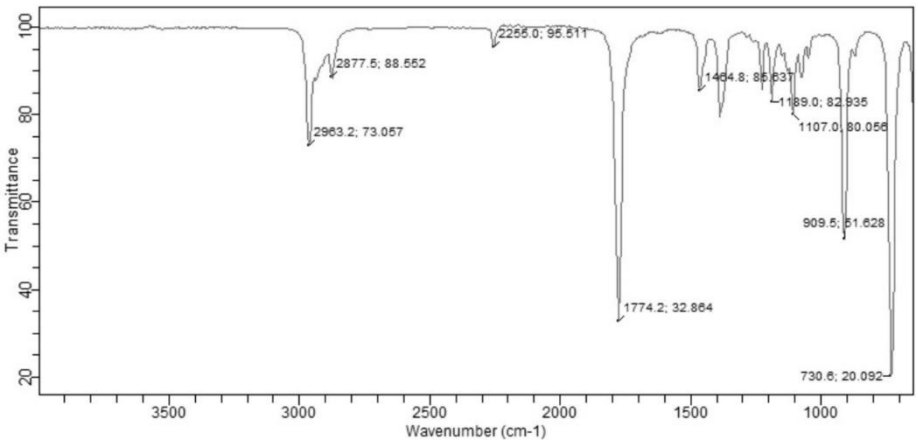
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-Isopropyl-3-methylcyclobutan-1-one (182c)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



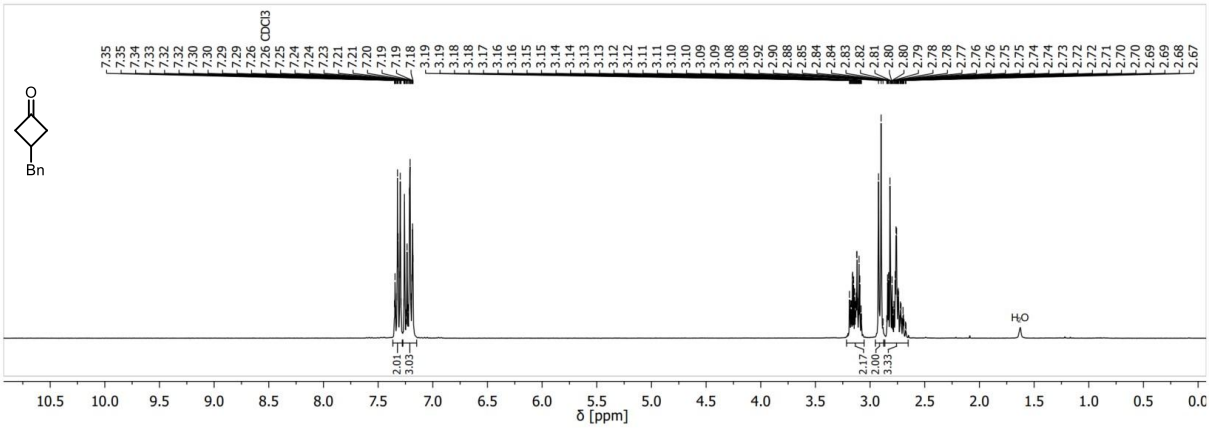


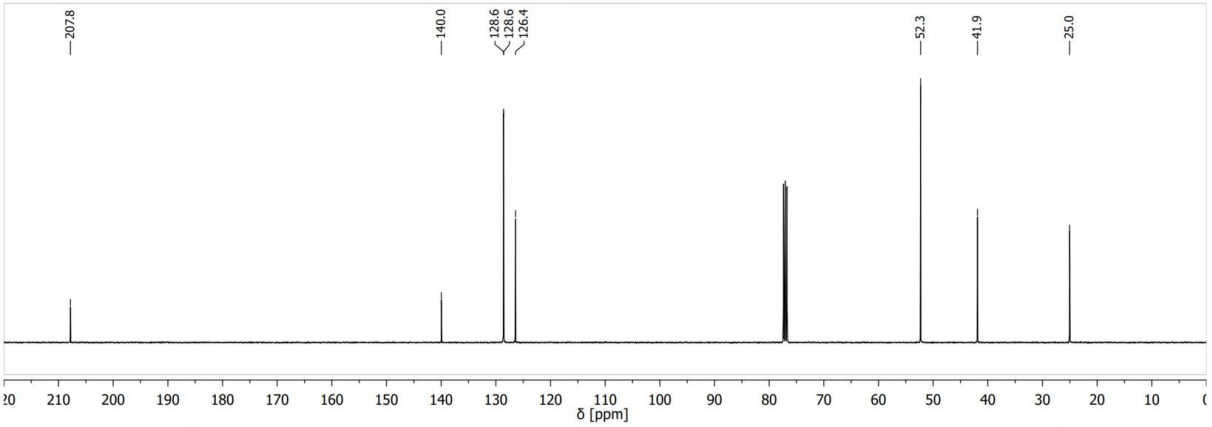


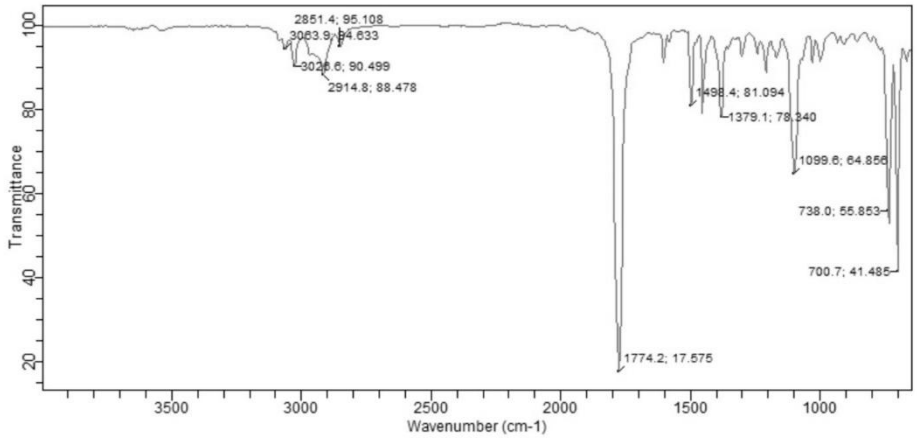
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-Benzylcyclobutan-1-one (182d)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



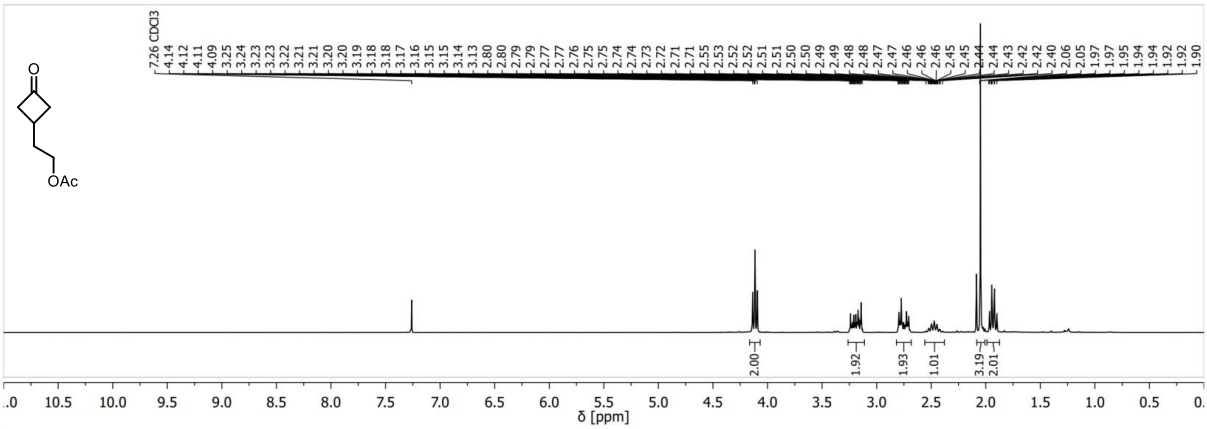


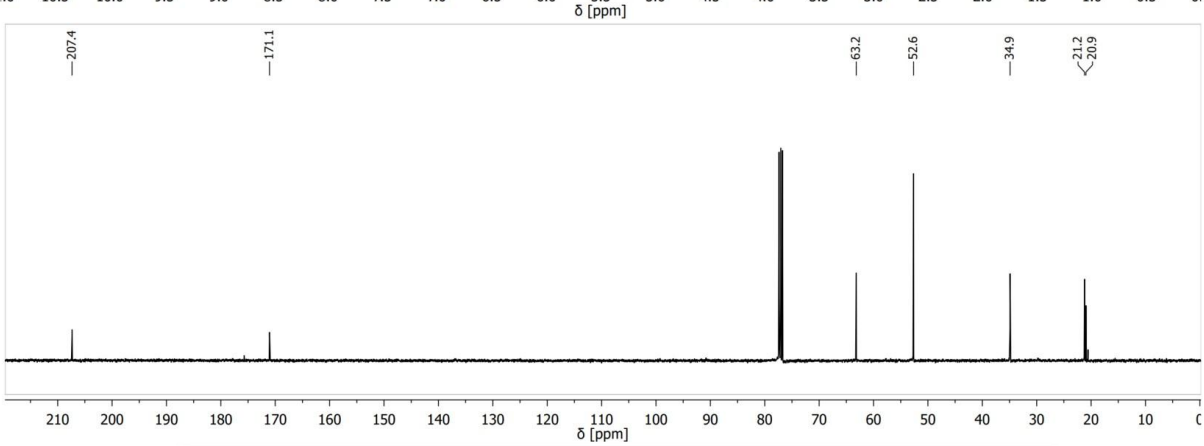


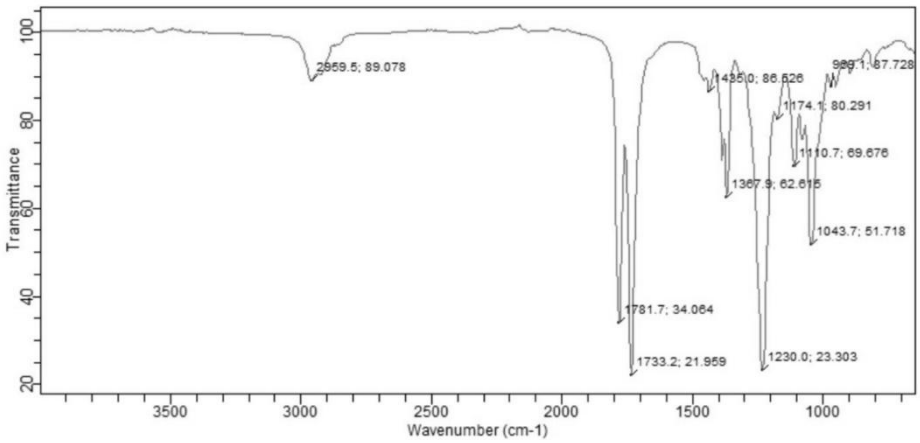
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2-(3-Oxocyclobutyl)ethyl acetate (182e)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



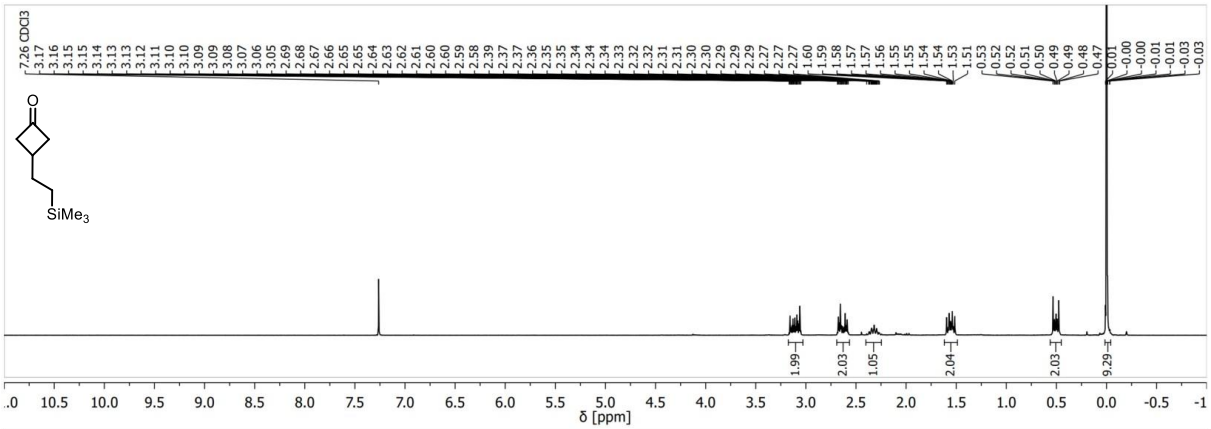


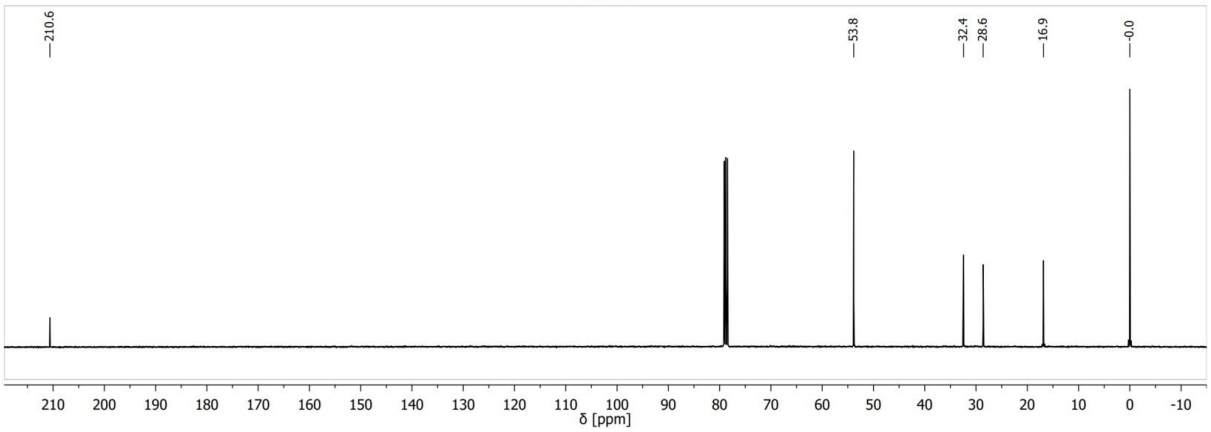


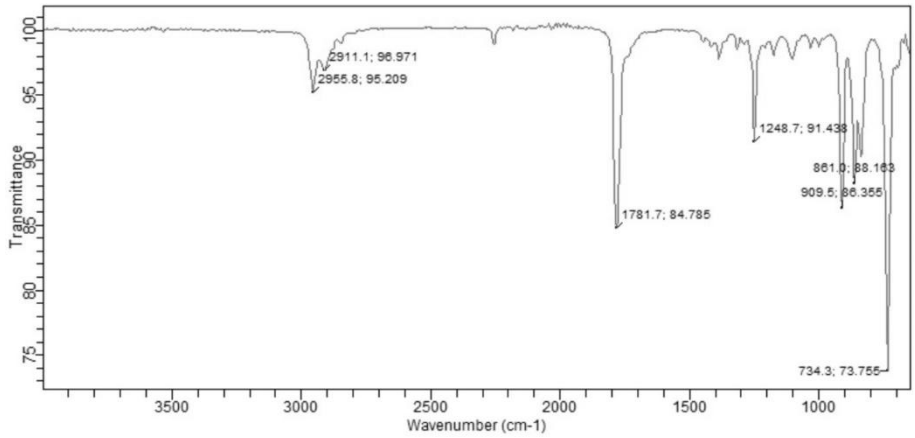
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-(2-(Trimethylsilyl)ethyl)cyclobutan-1-one (182f)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



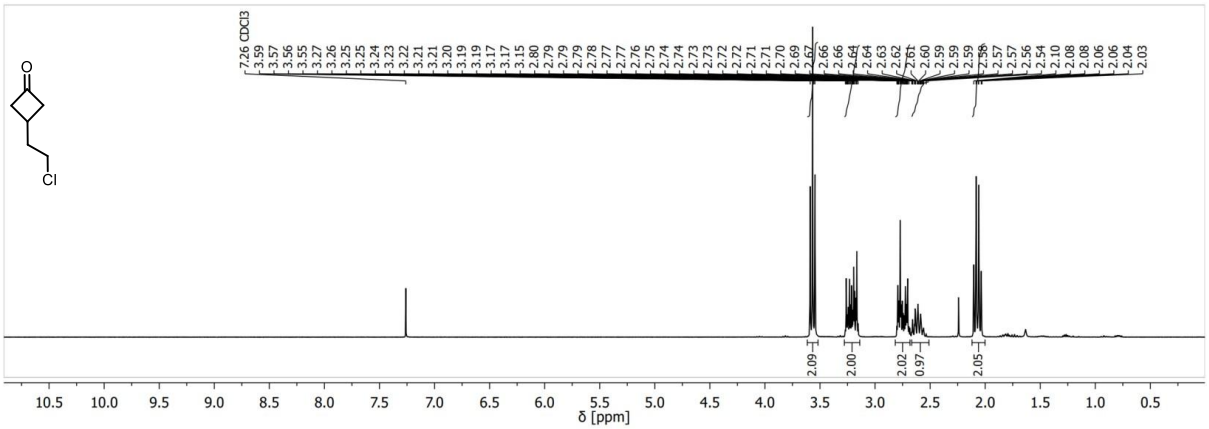


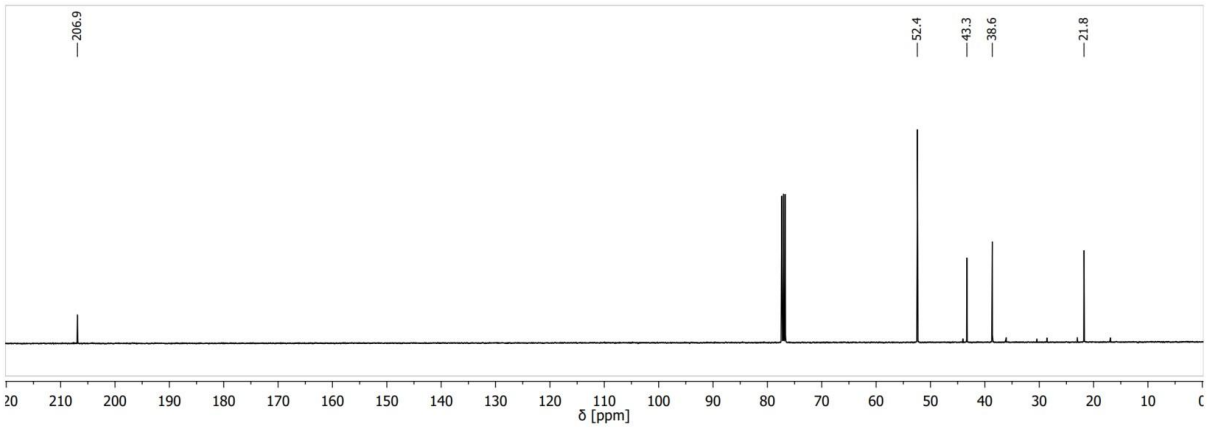


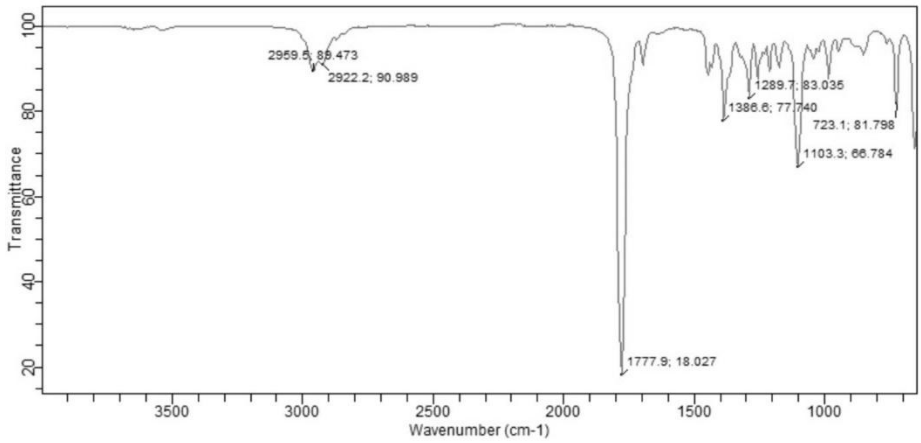
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-(2-Chloroethyl)cyclobutan-1-one (182g)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



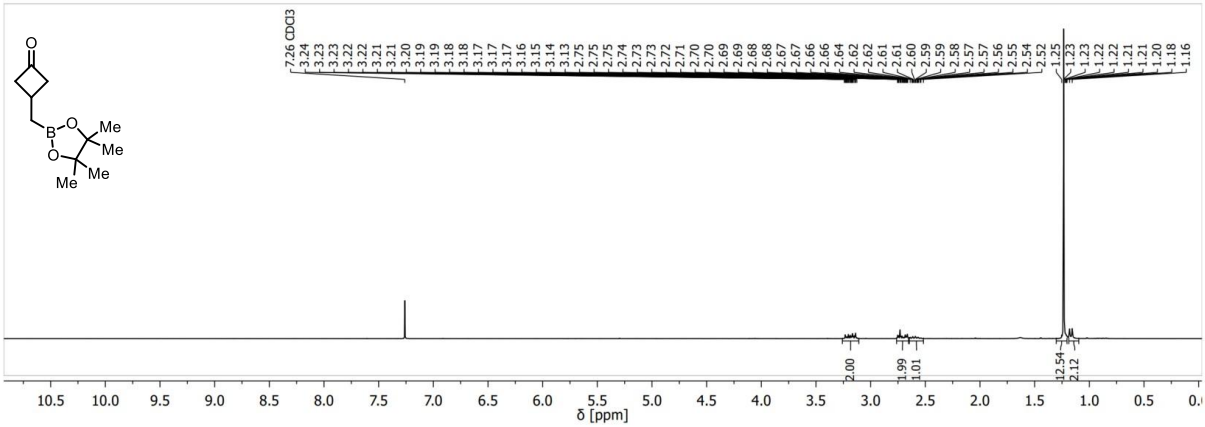


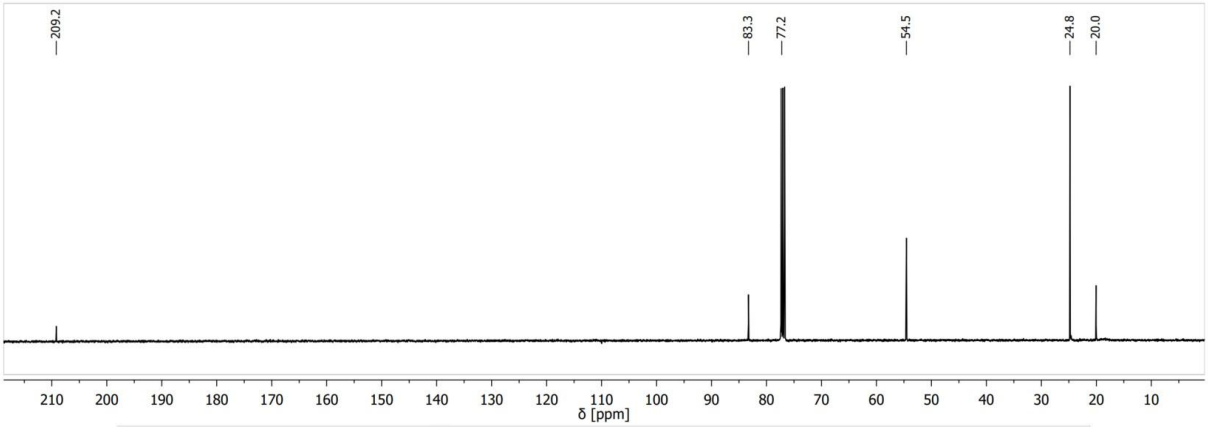


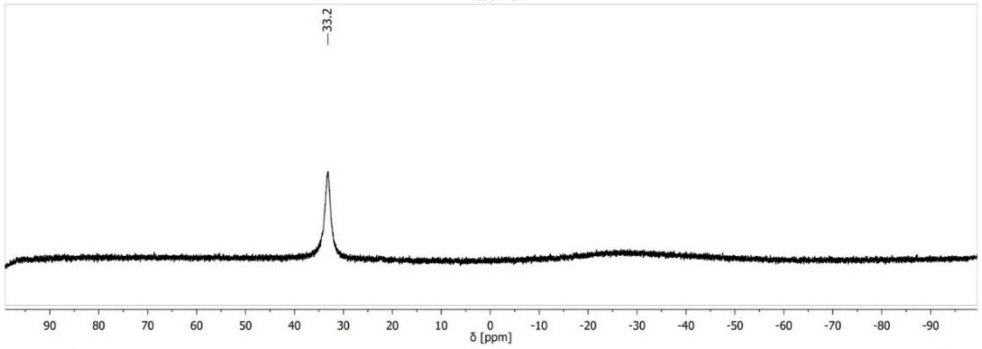
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

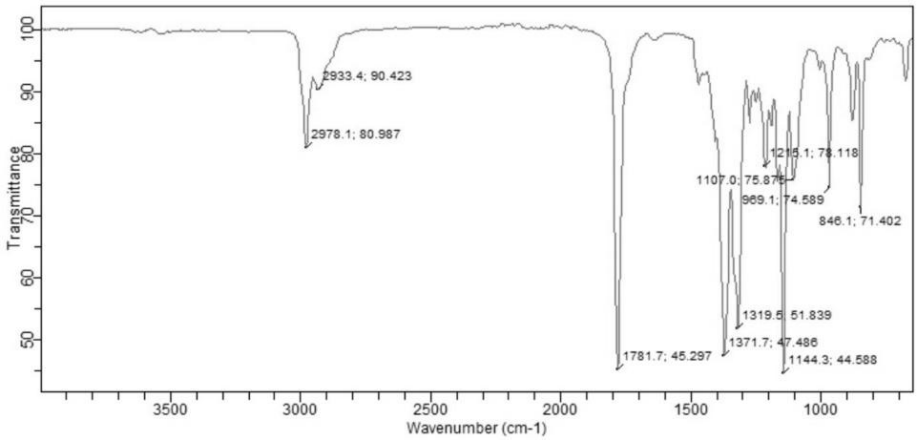
3-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutan-1-one (182h)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz), **^{11}B NMR** (128 MHz): Chloroform-*d*, **IR**





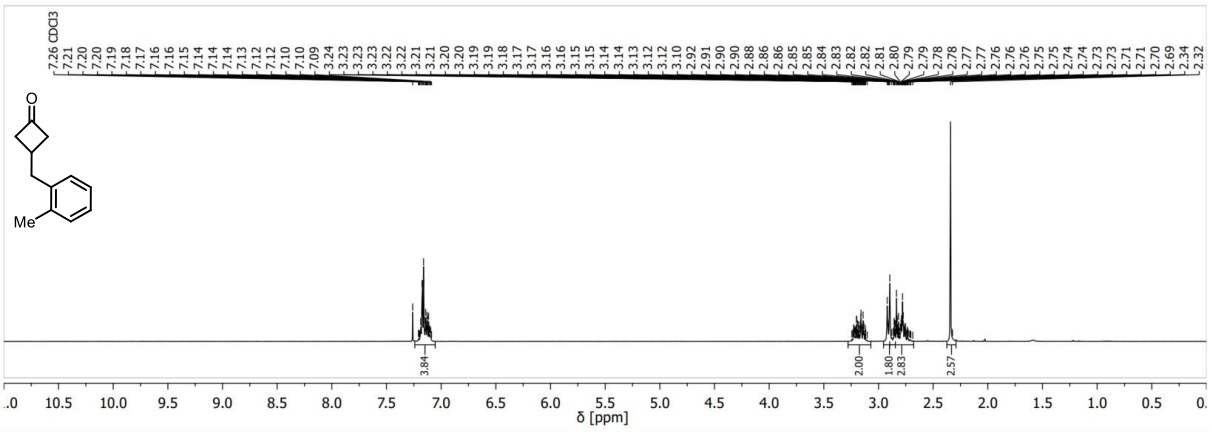


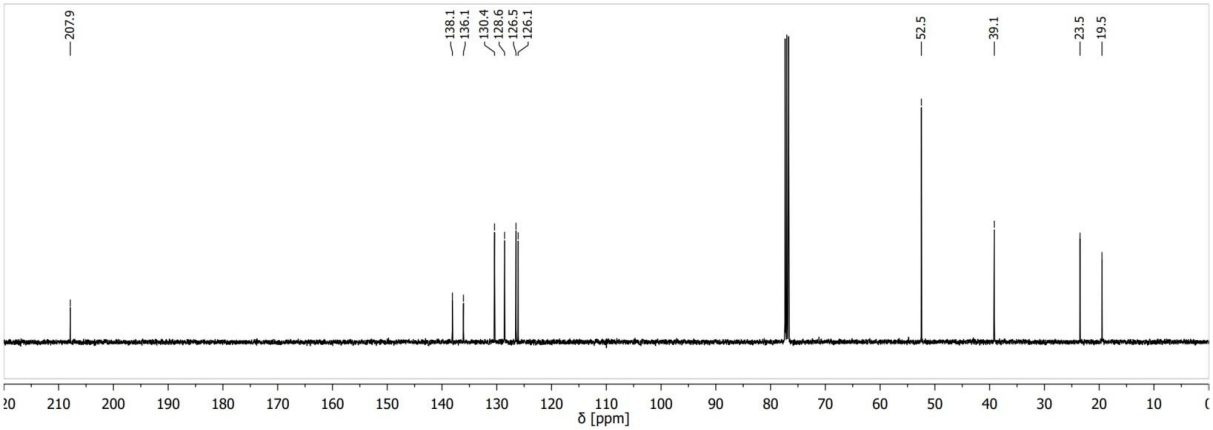


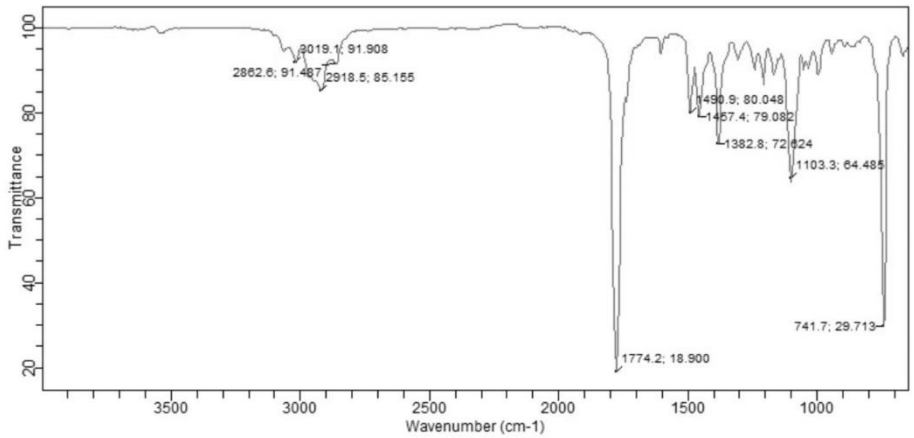
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-(2-Methylbenzyl)cyclobutan-1-one (182i)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



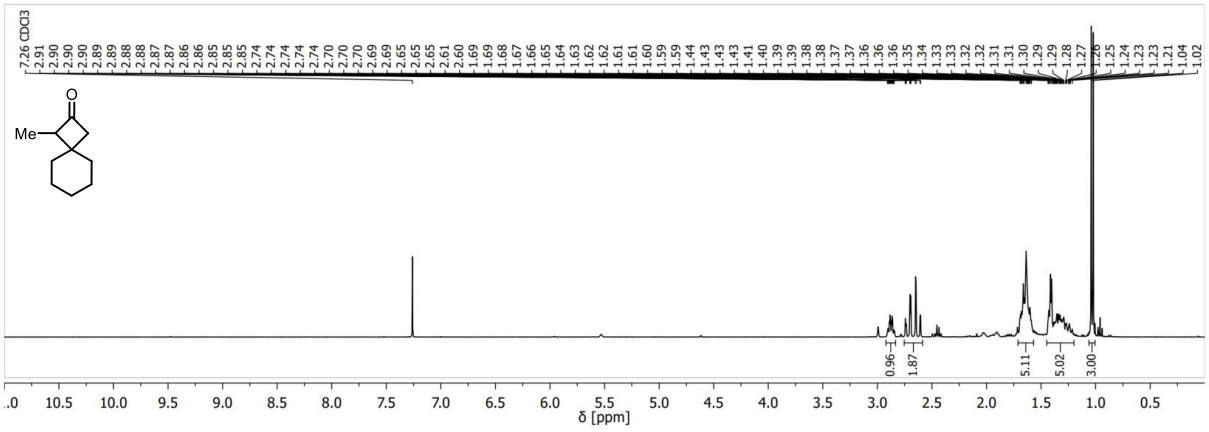


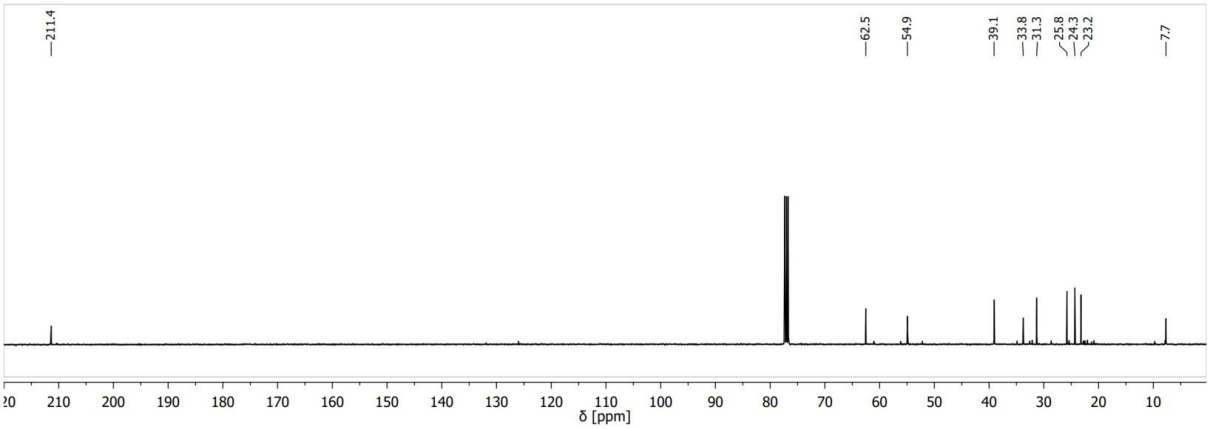


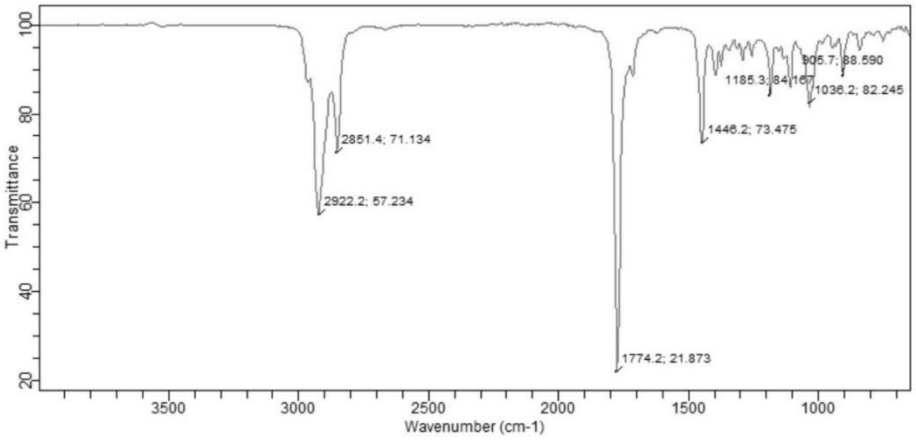
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

1-Methylspiro[3.5]nonan-2-one (182j)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



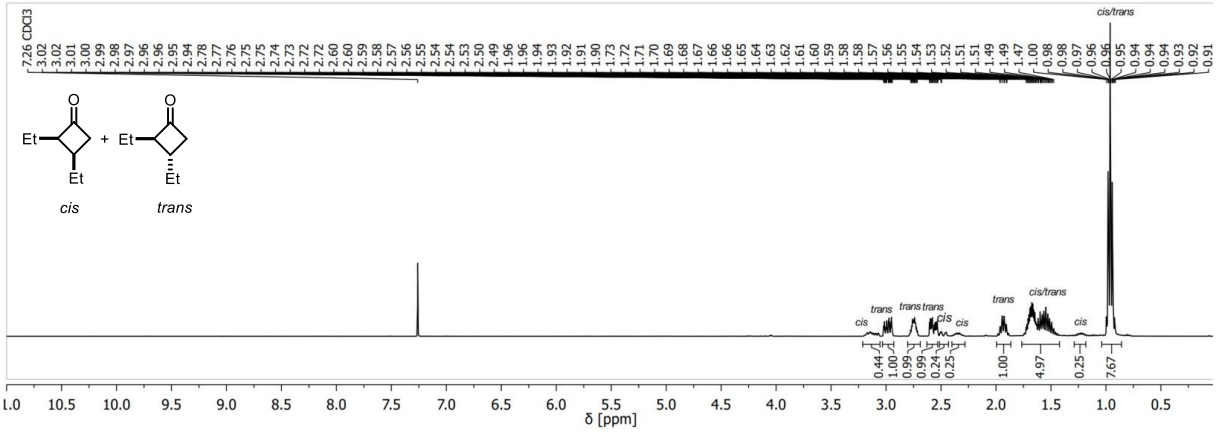


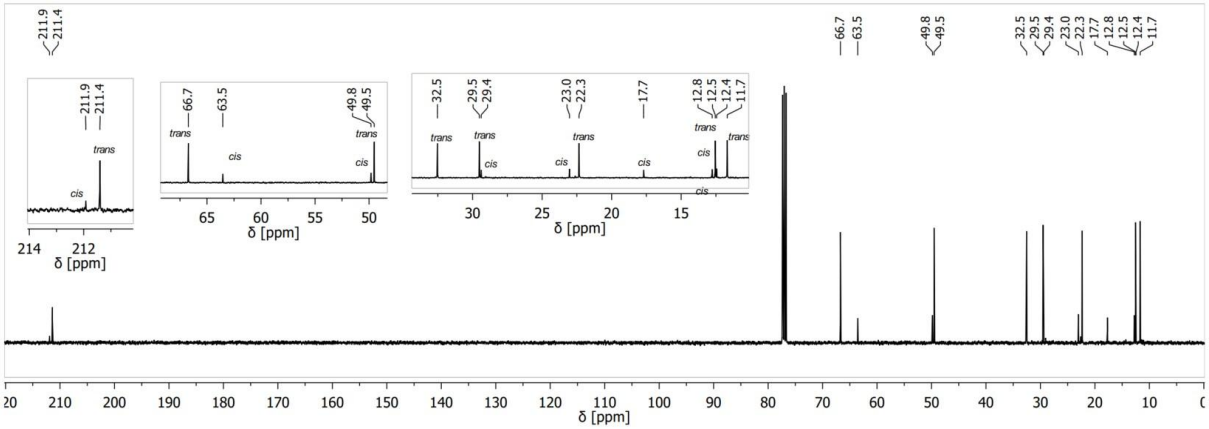


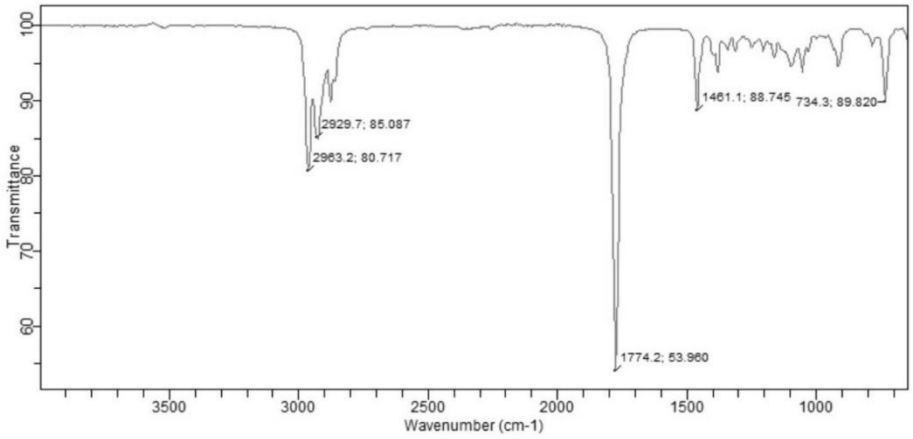
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2,3-Diethylcyclobutan-1-one (182k)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

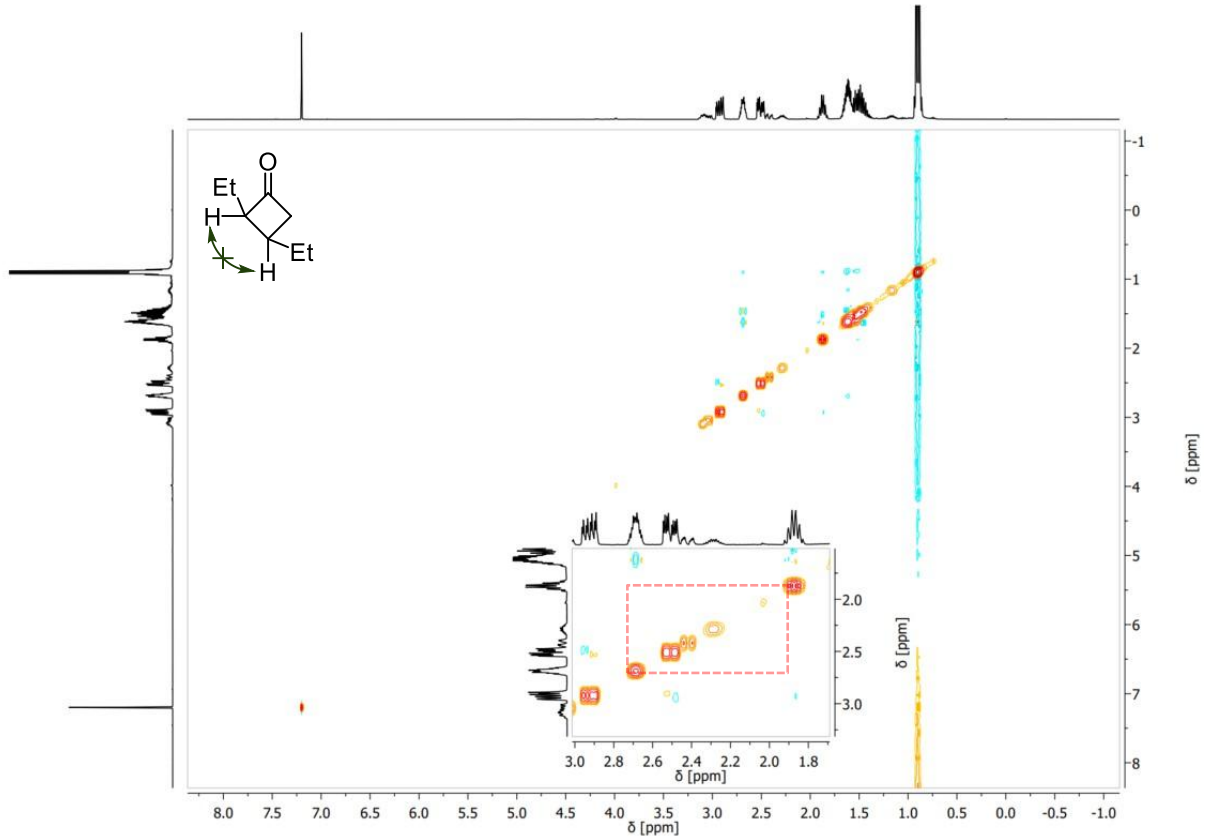






8 Appendix

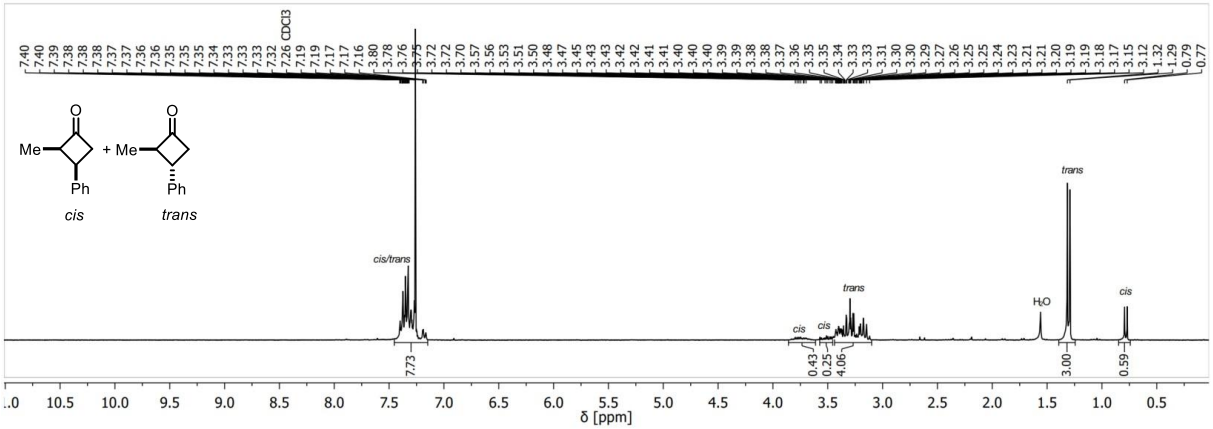
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

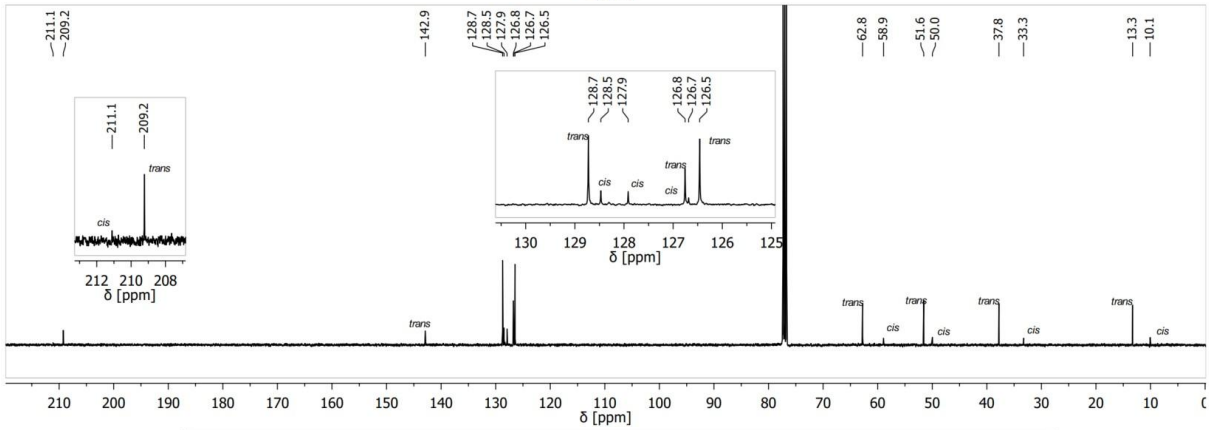


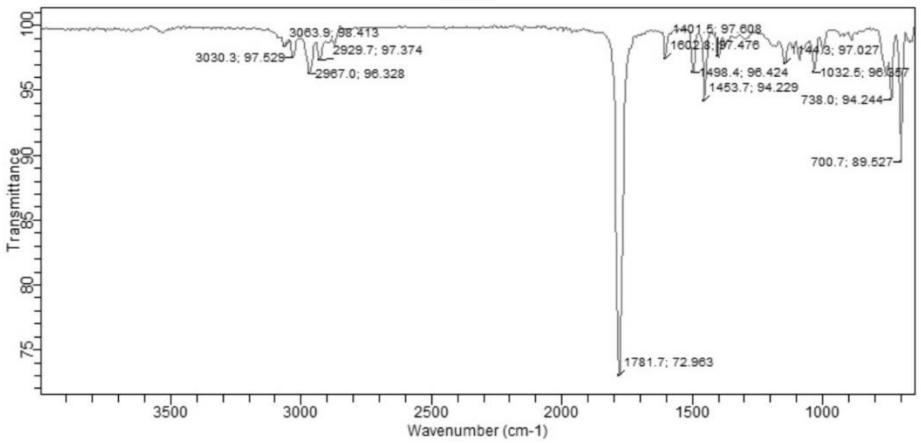
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2-Methyl-3-phenylcyclobutan-1-one (182l)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz), **NOESY** (400 MHz): Chloroform-*d*, **IR**

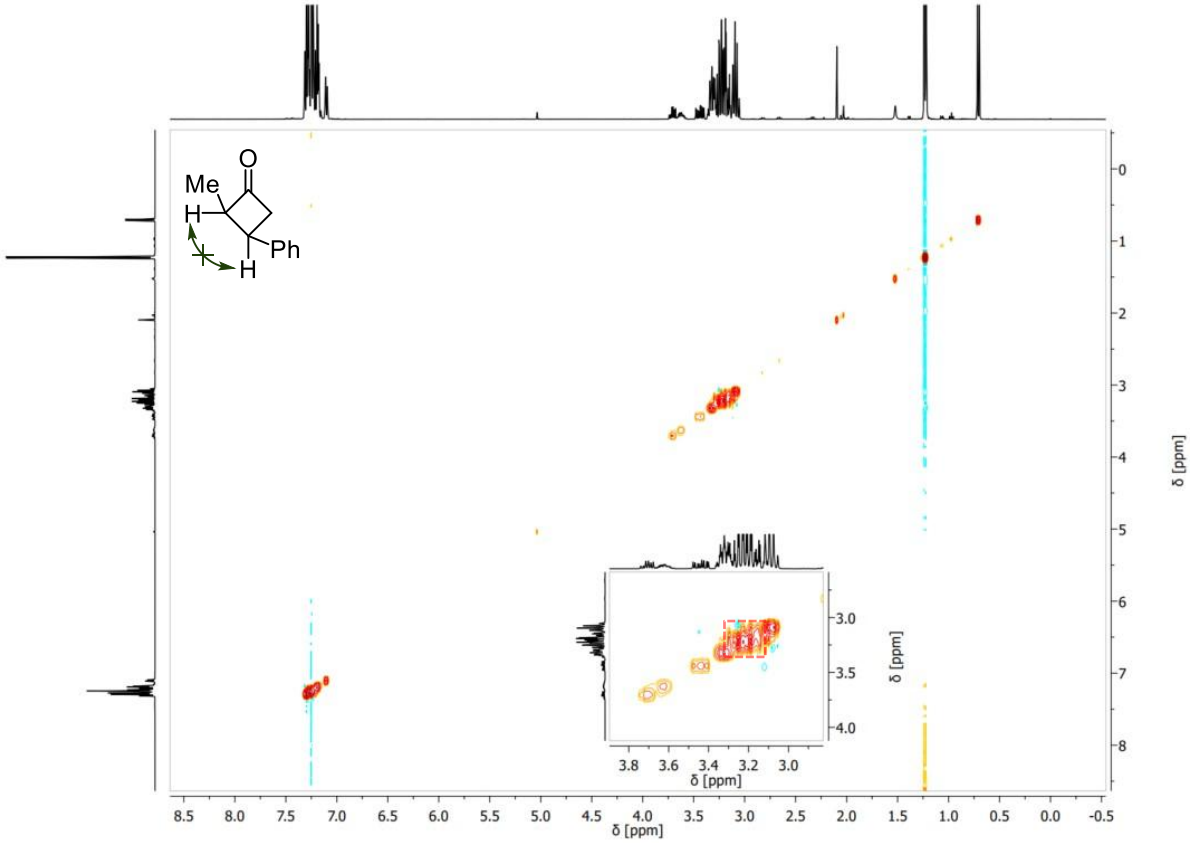






8 Appendix

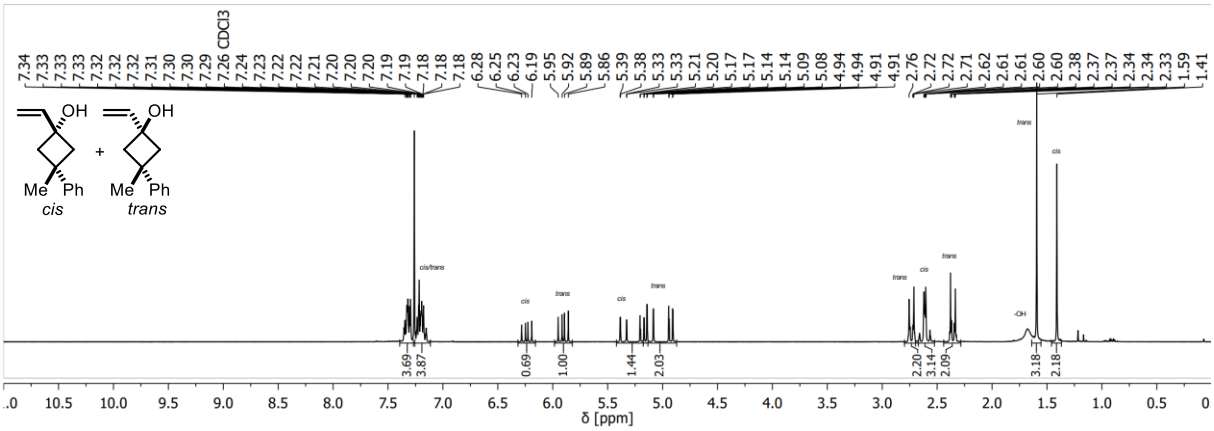
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

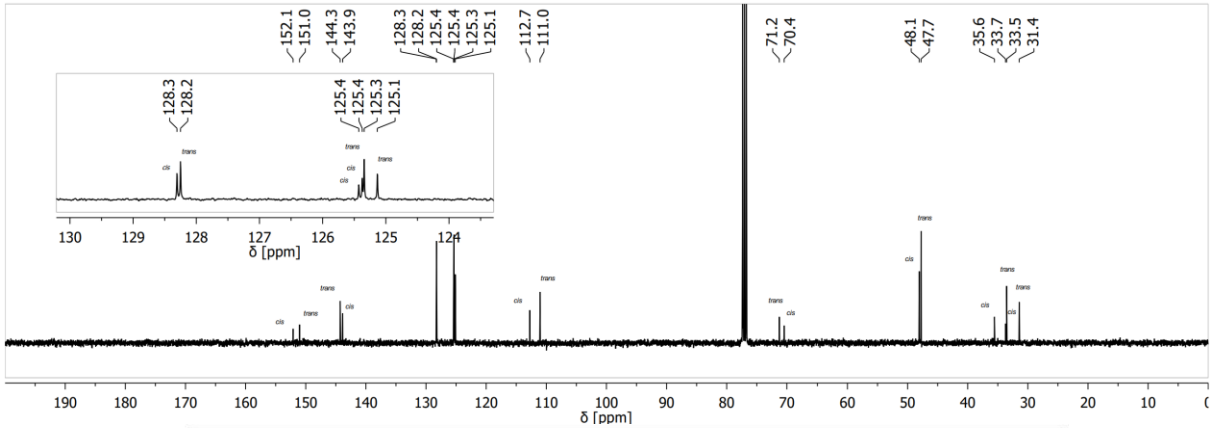


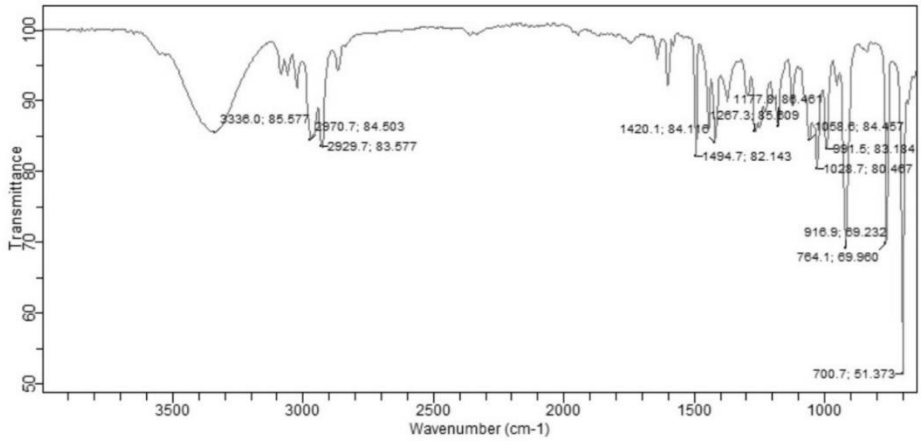
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-Methyl-3-phenyl-1-vinylcyclobutan-1-ol (174a)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

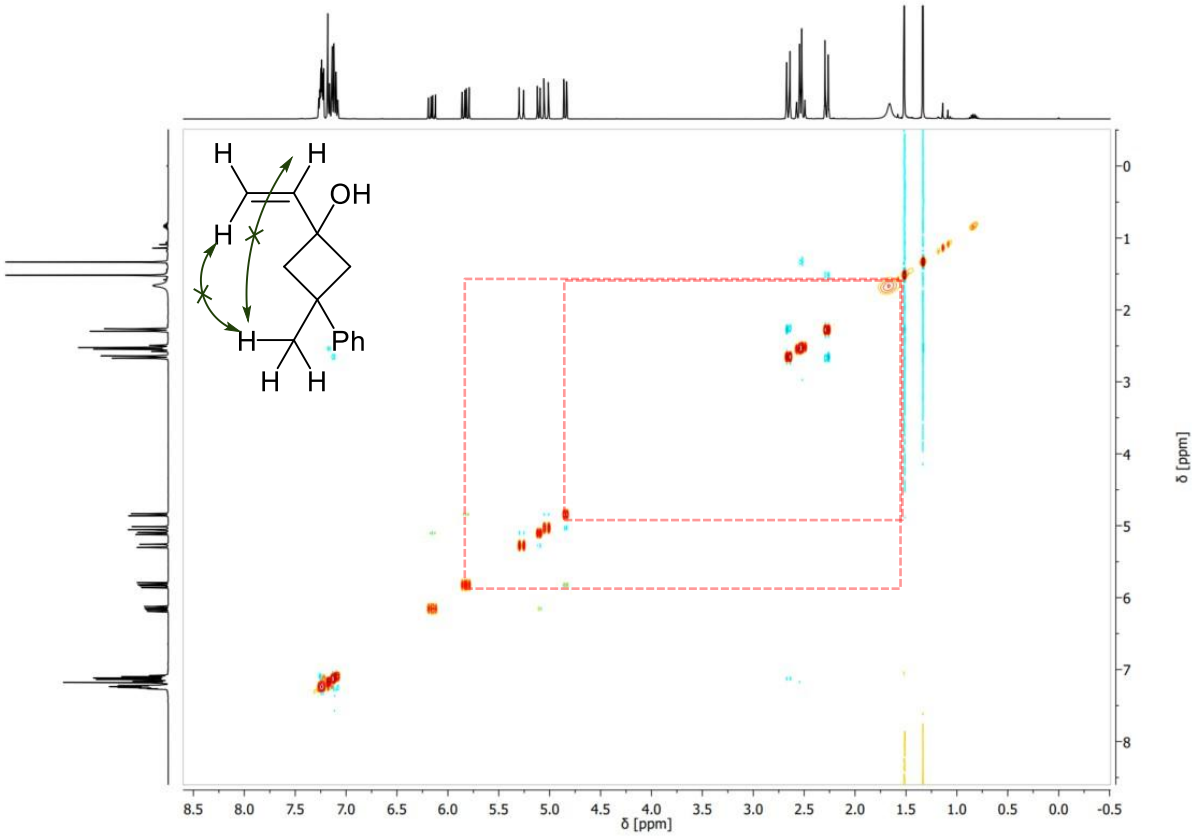






8 Appendix

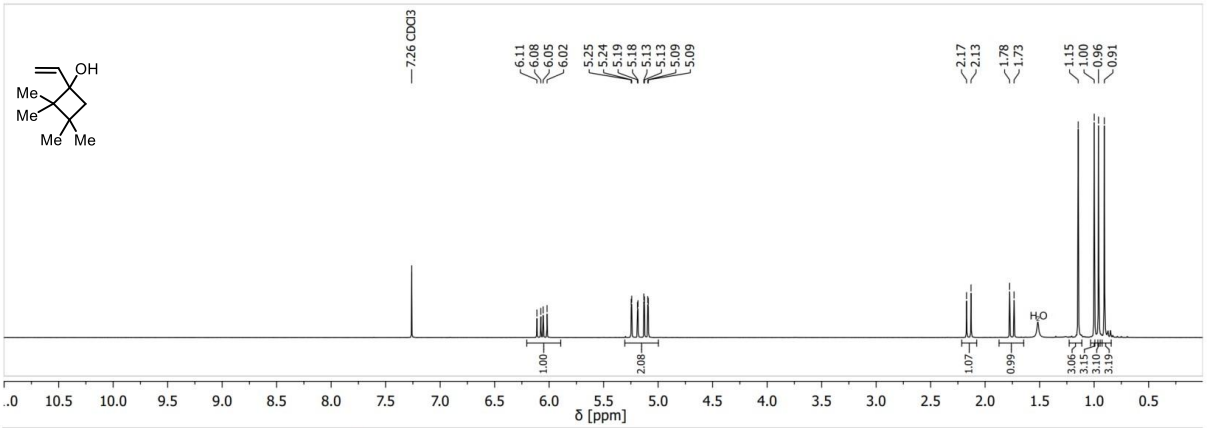
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

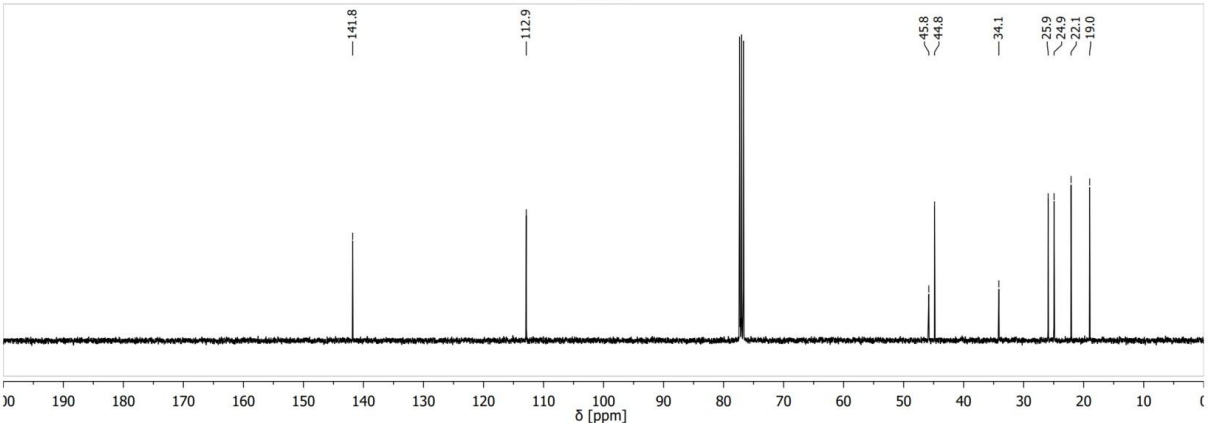


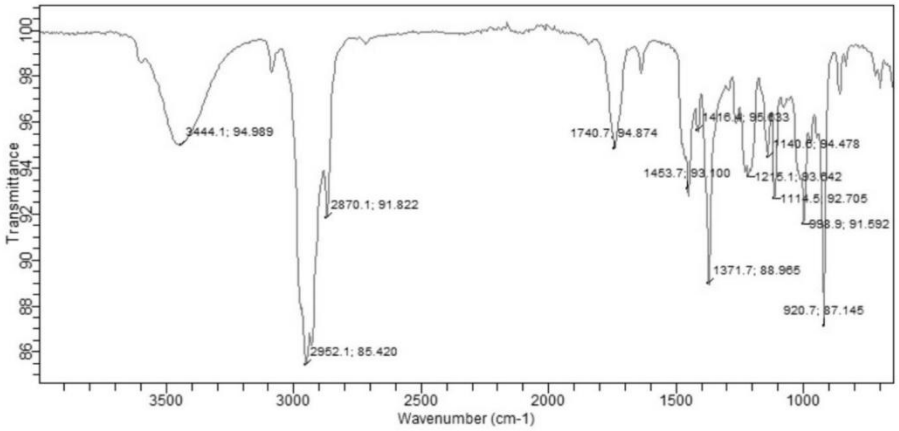
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2,2,3,3-Tetramethyl-1-vinylcyclobutan-1-ol (174b)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



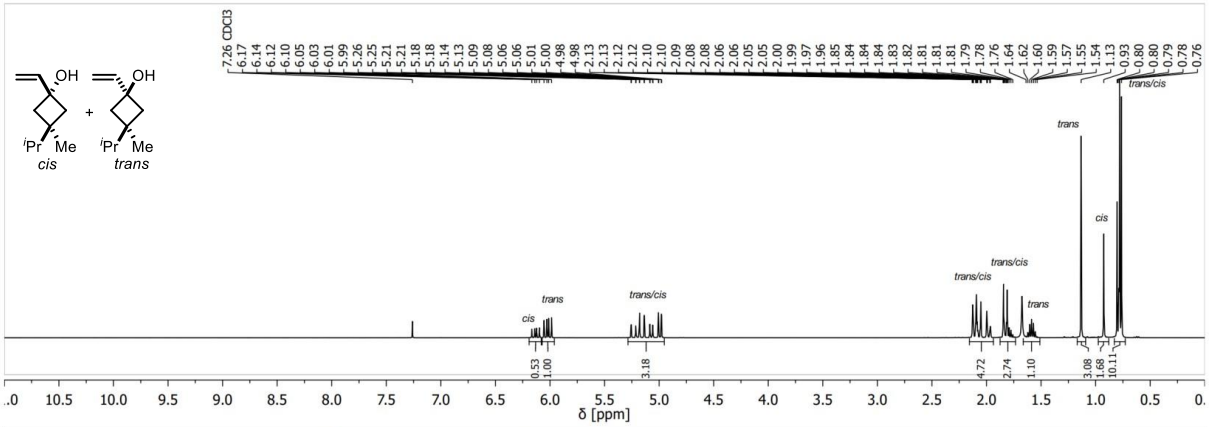


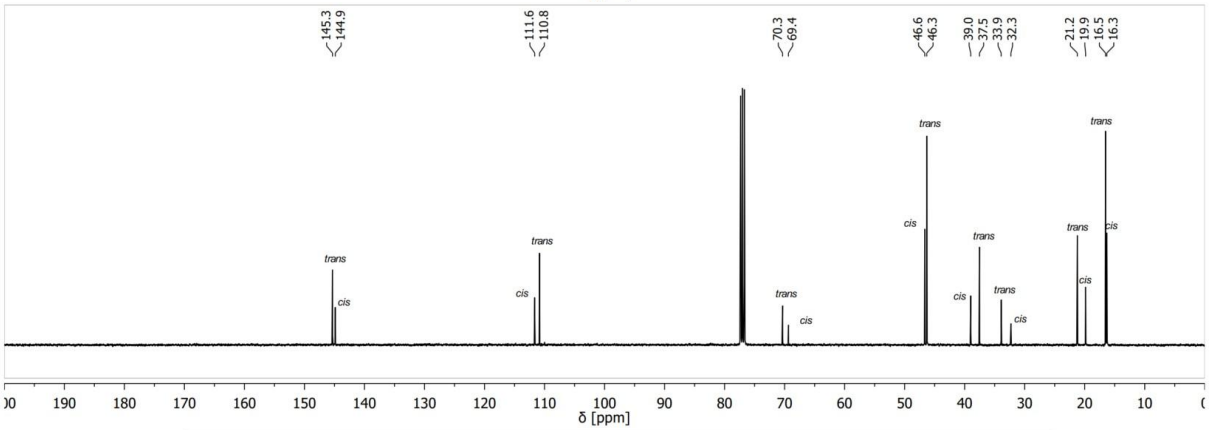


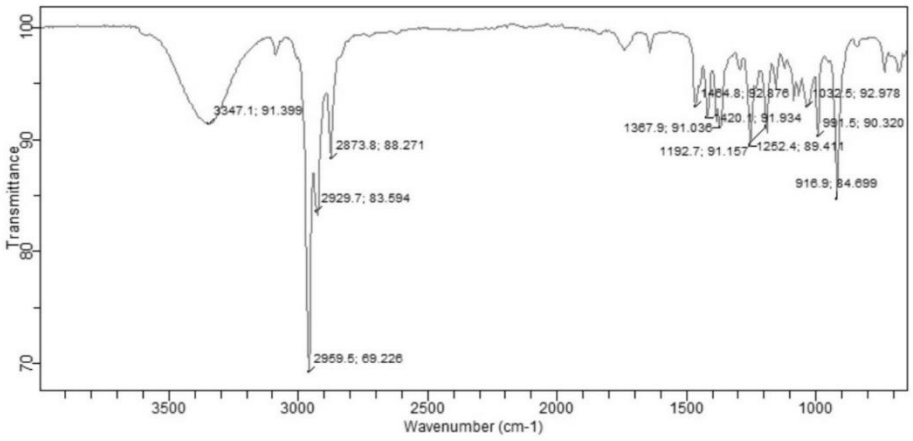
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-Isopropyl-3-methyl-1-vinylcyclobutan-1-ol (174c)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

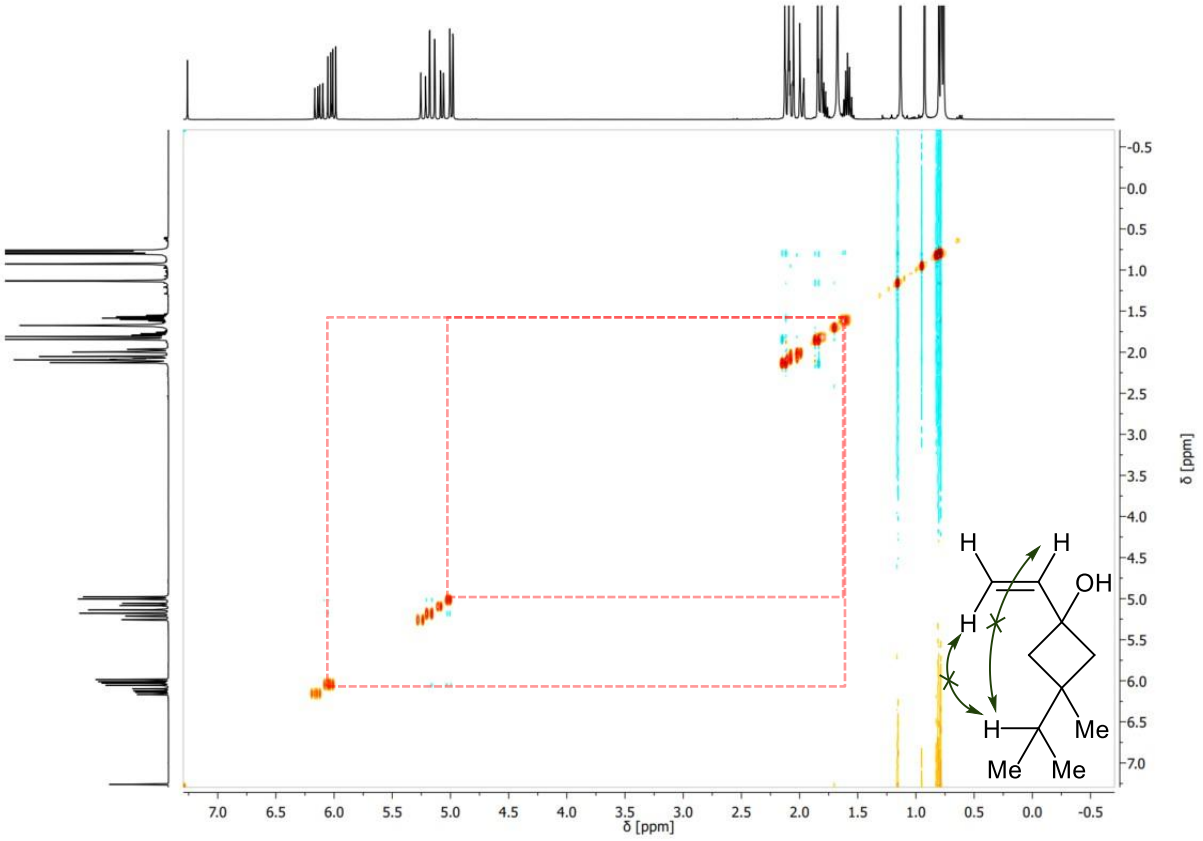






8 Appendix

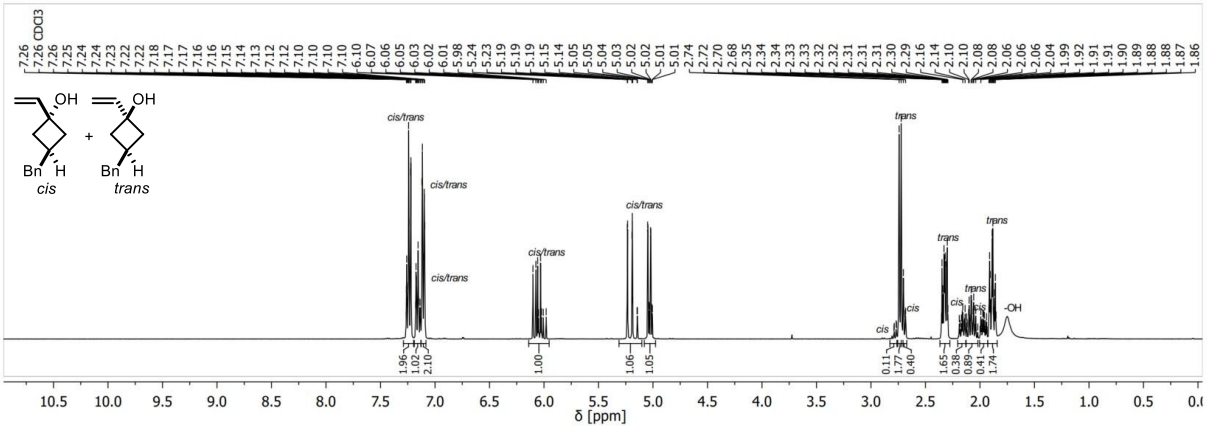
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

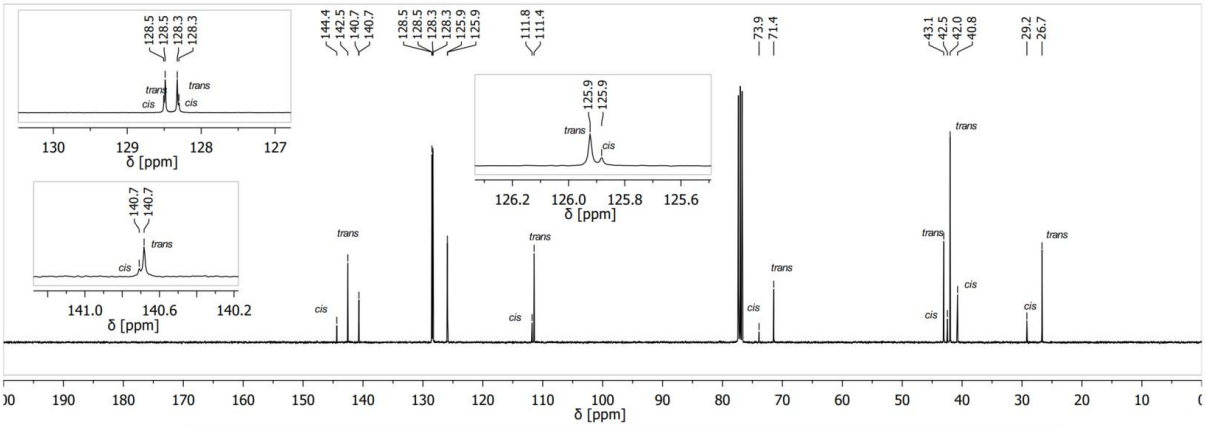


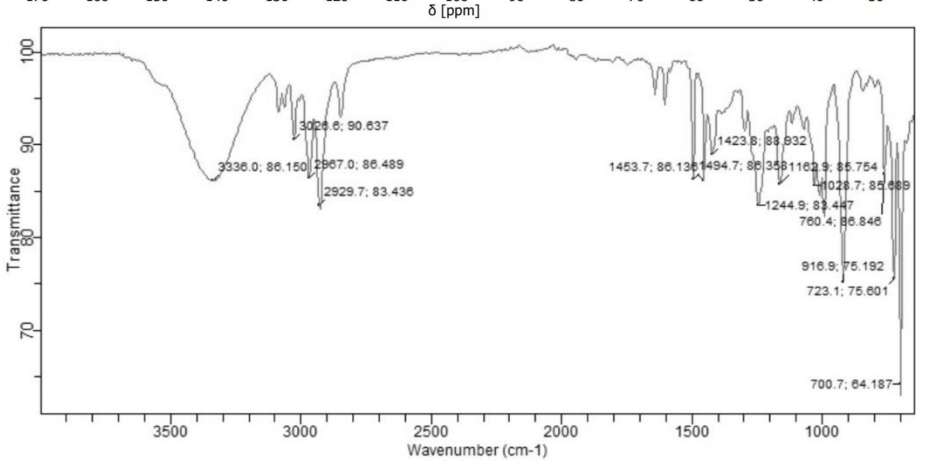
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-Benzyl-1-vinylcyclobutan-1-ol (174d)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

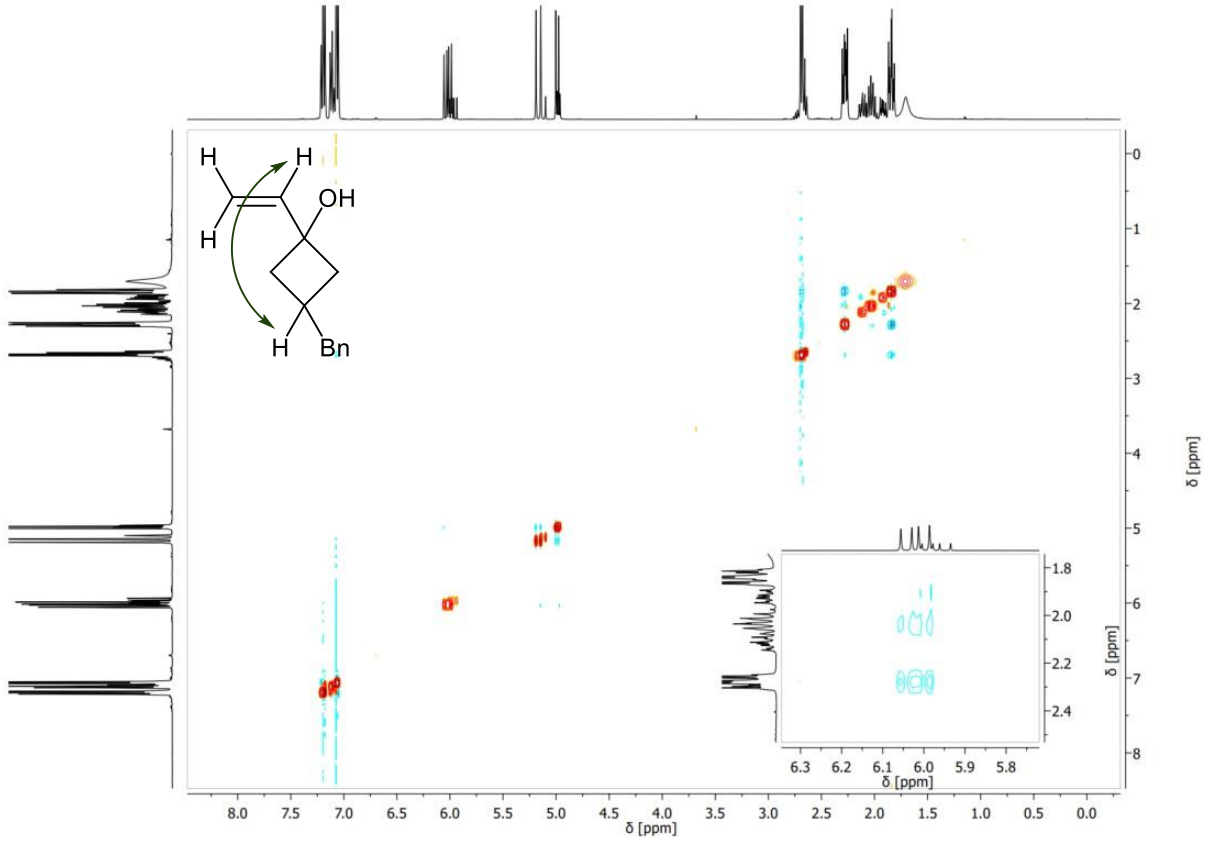






8 Appendix

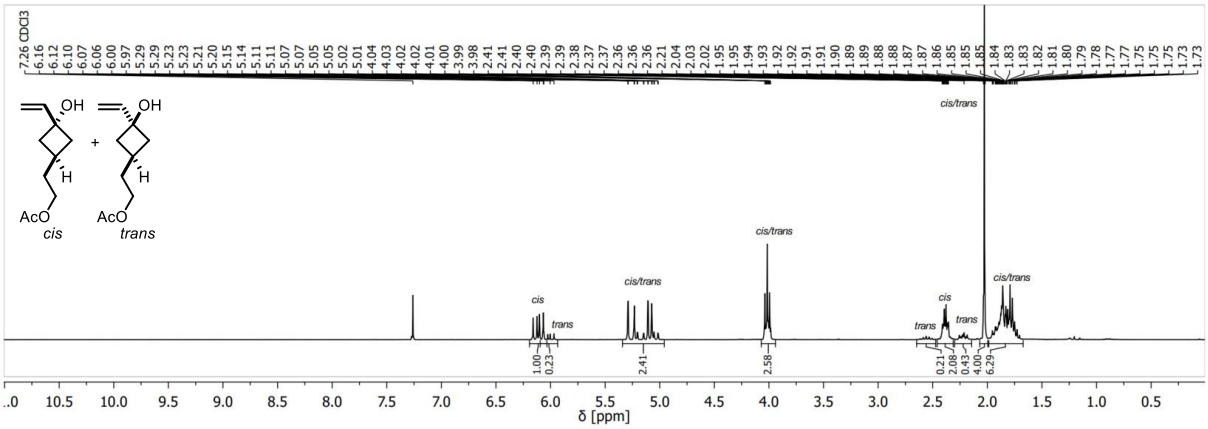
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

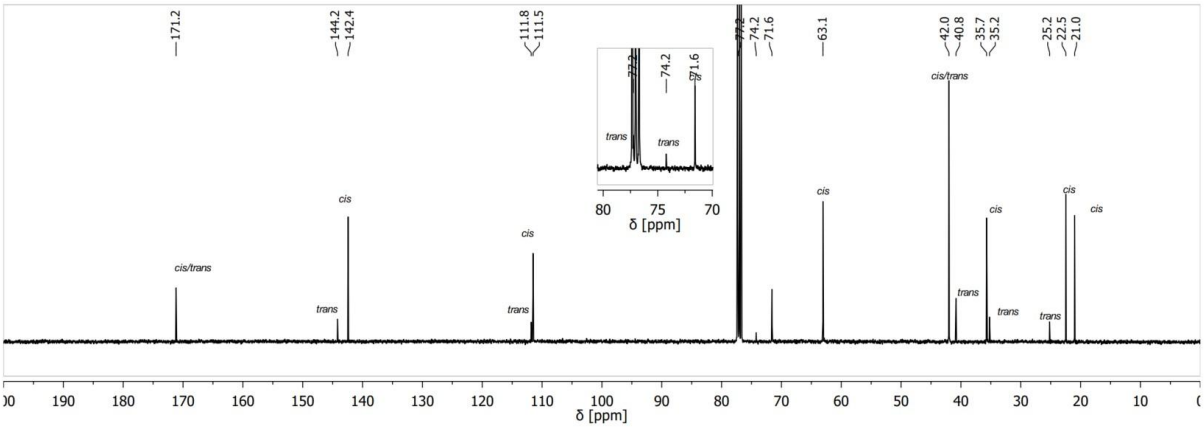


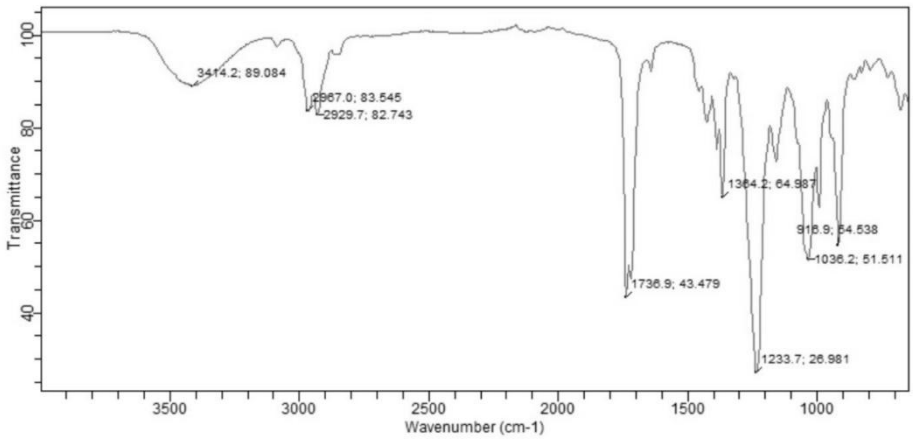
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2-(3-Hydroxy-3-vinylcyclobutyl)ethyl acetate (174e)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

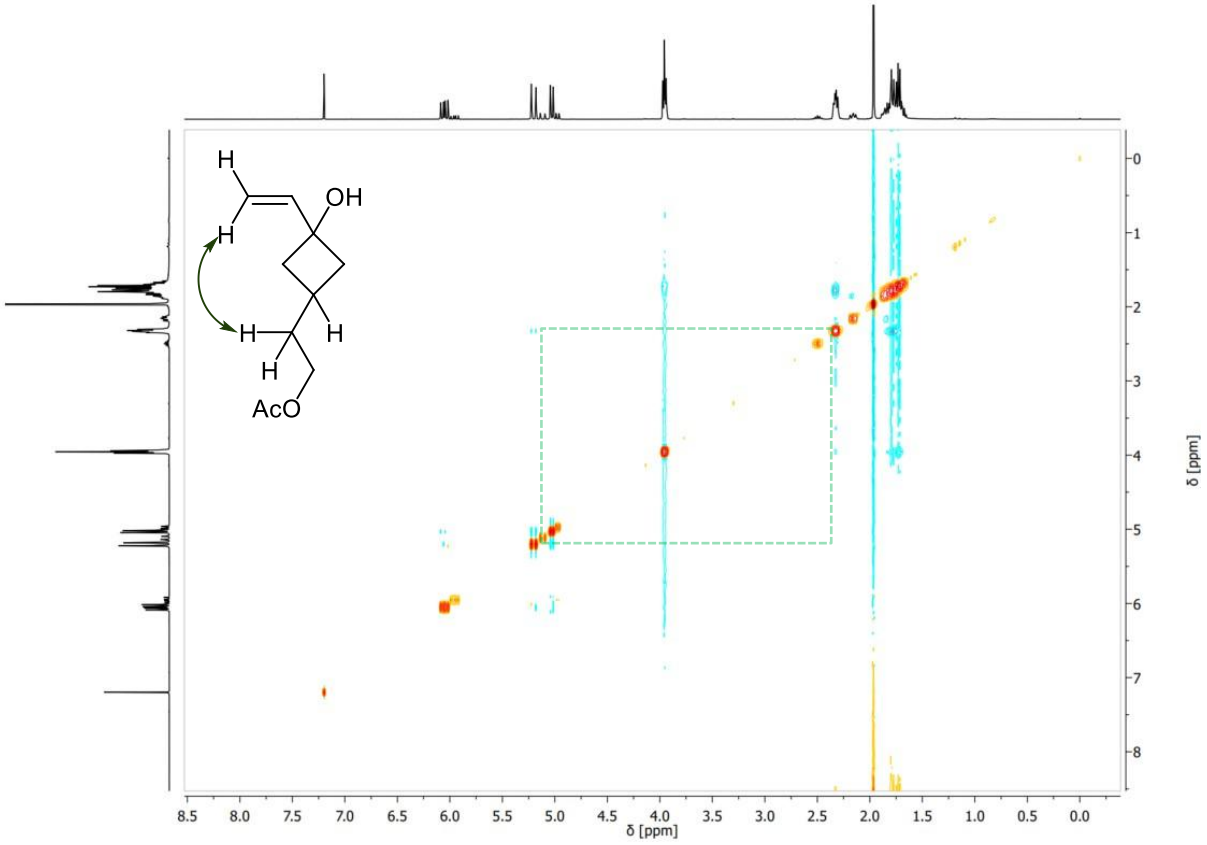






8 Appendix

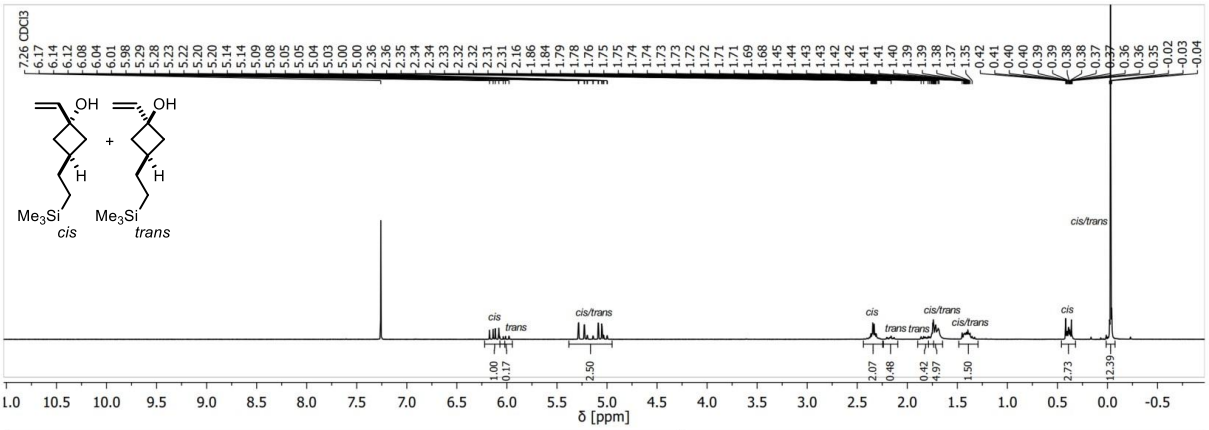
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

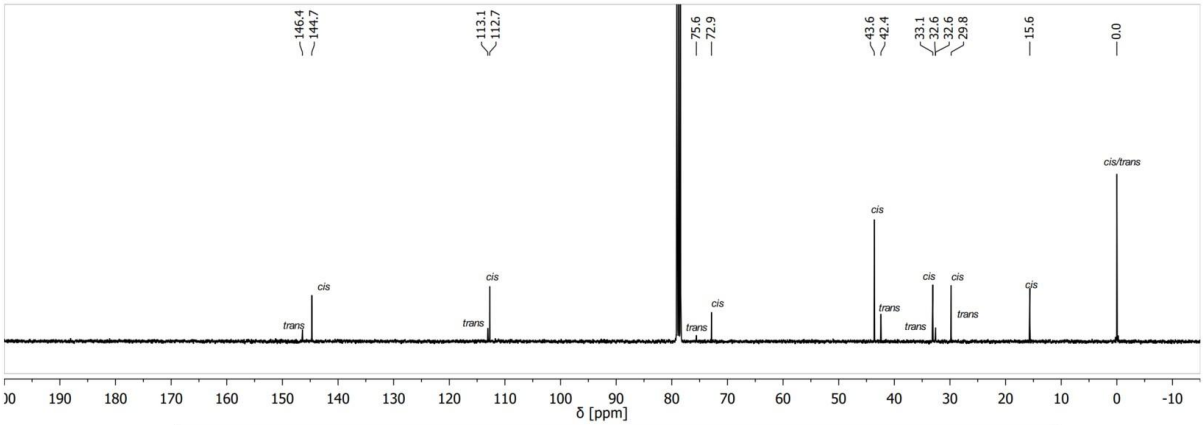


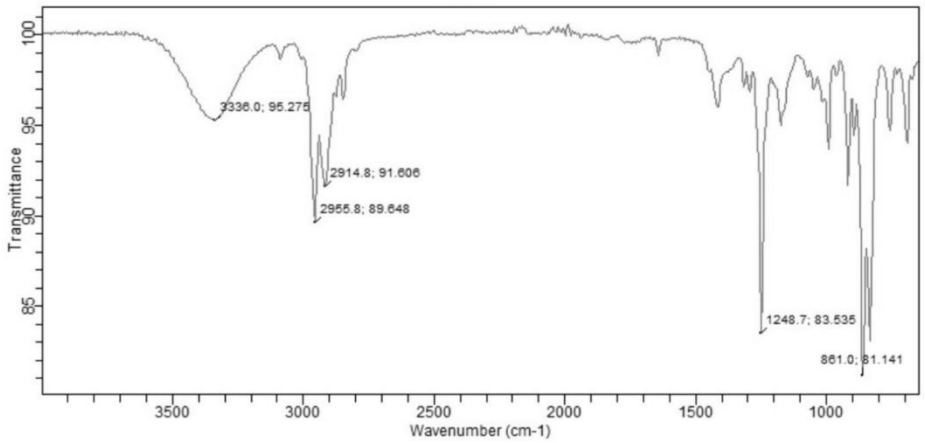
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-(2-(Trimethylsilyl)ethyl)-1-vinylcyclobutan-1-ol (174f)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

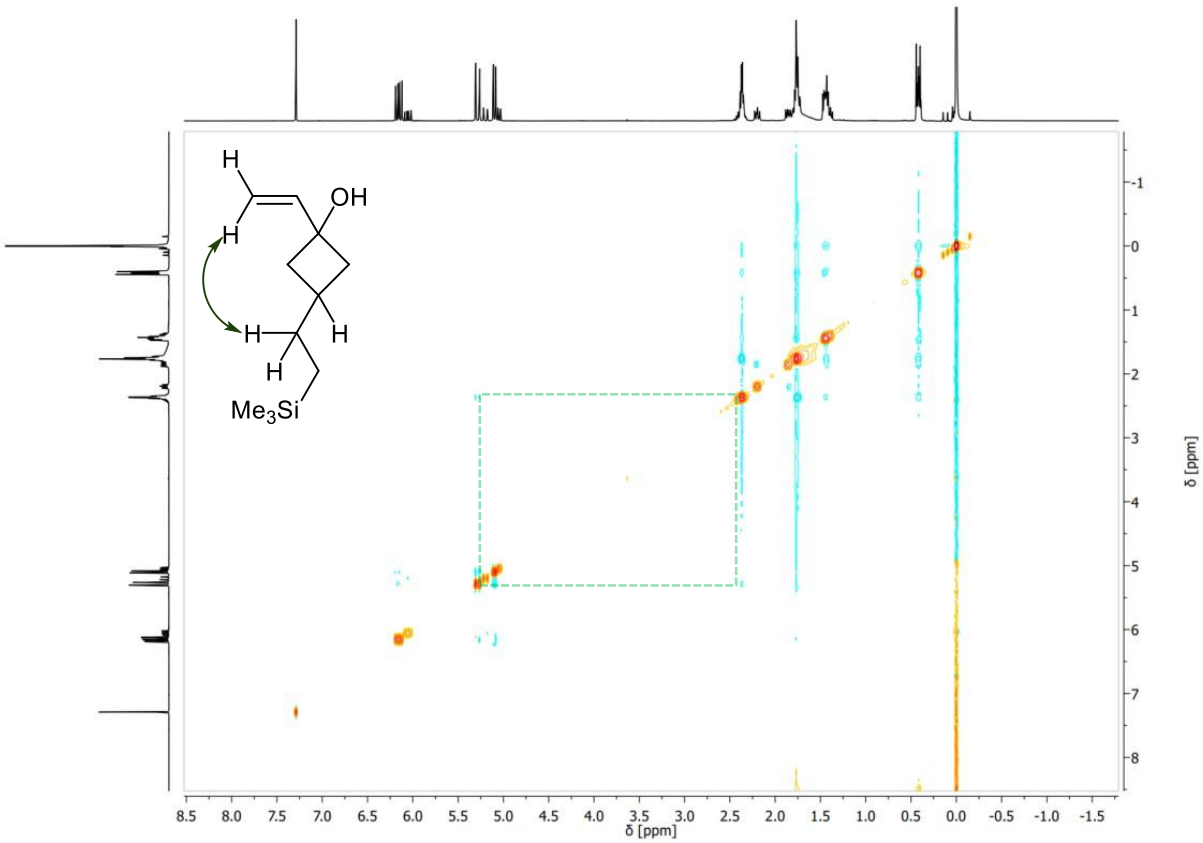






8 Appendix

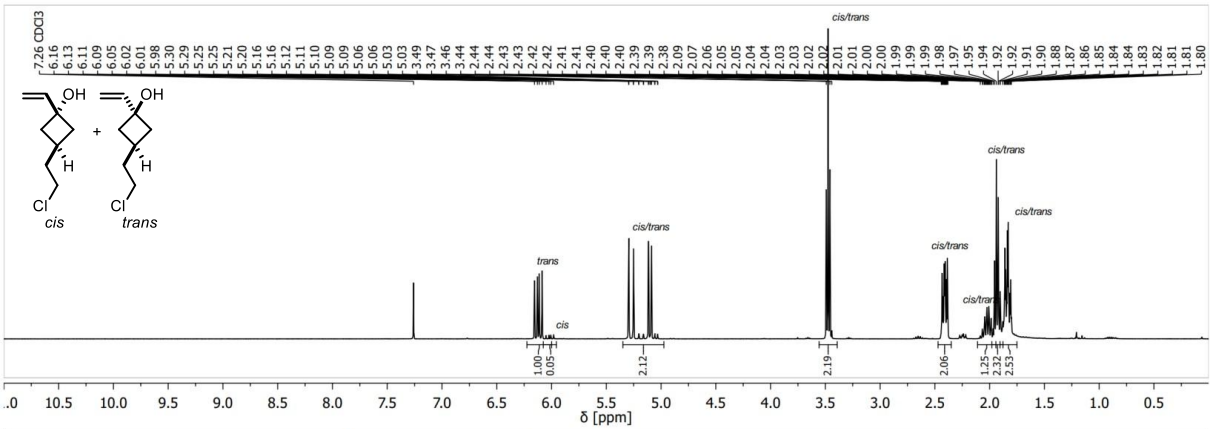
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

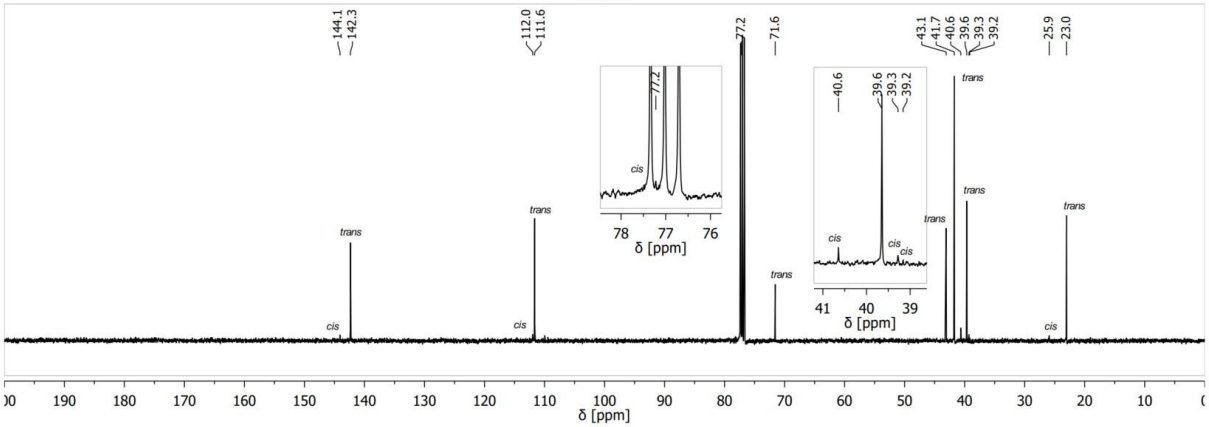


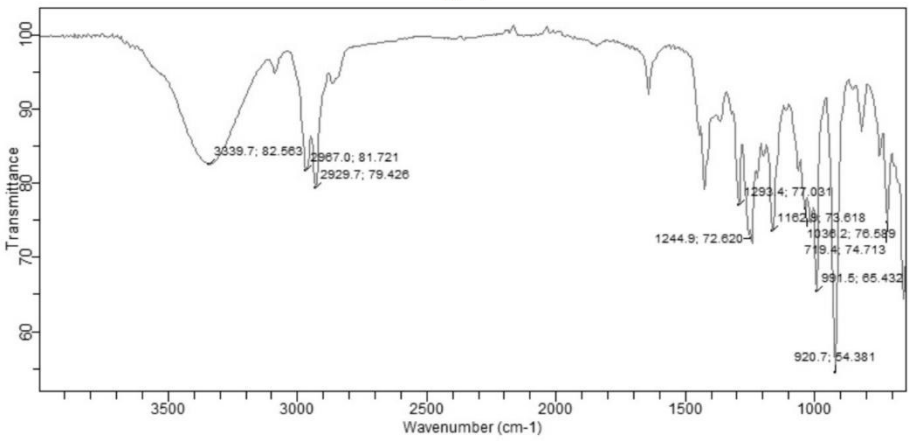
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-(2-Chloroethyl)-1-vinylcyclobutan-1-ol (174g)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

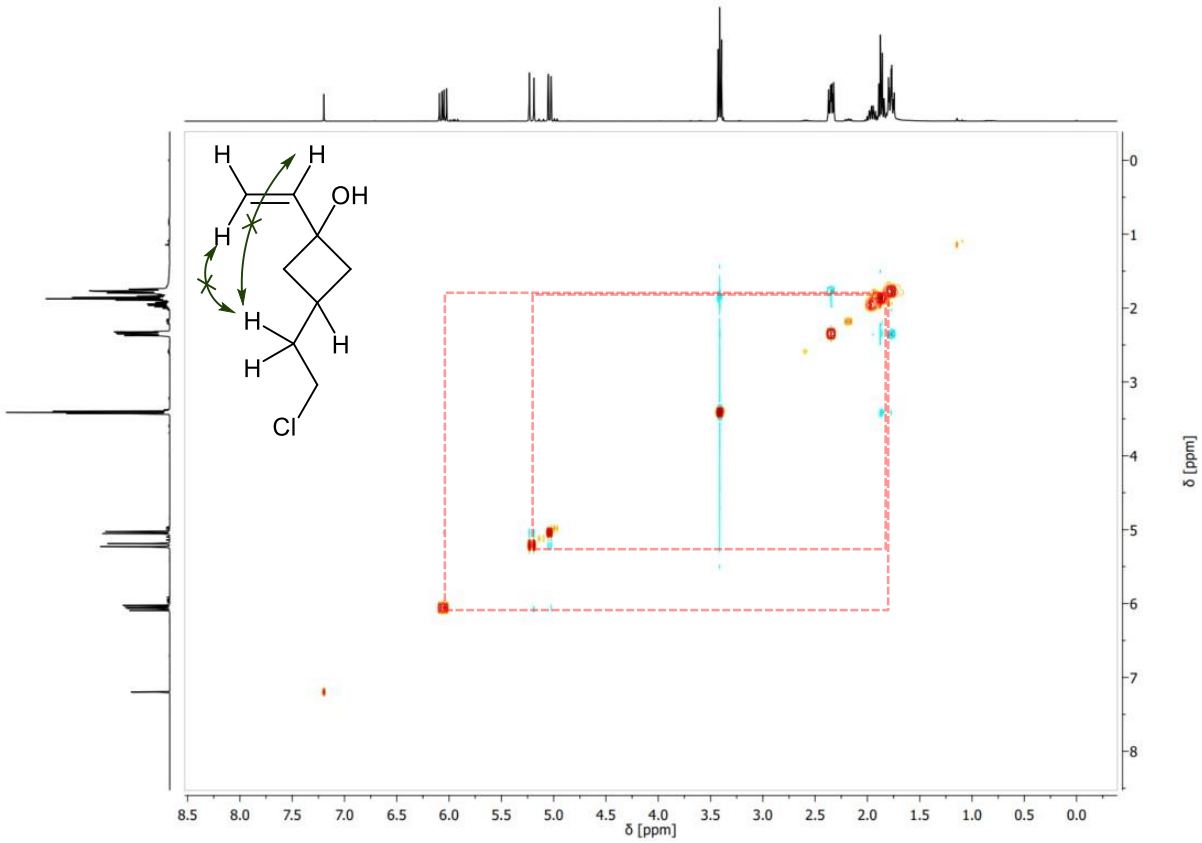






8 Appendix

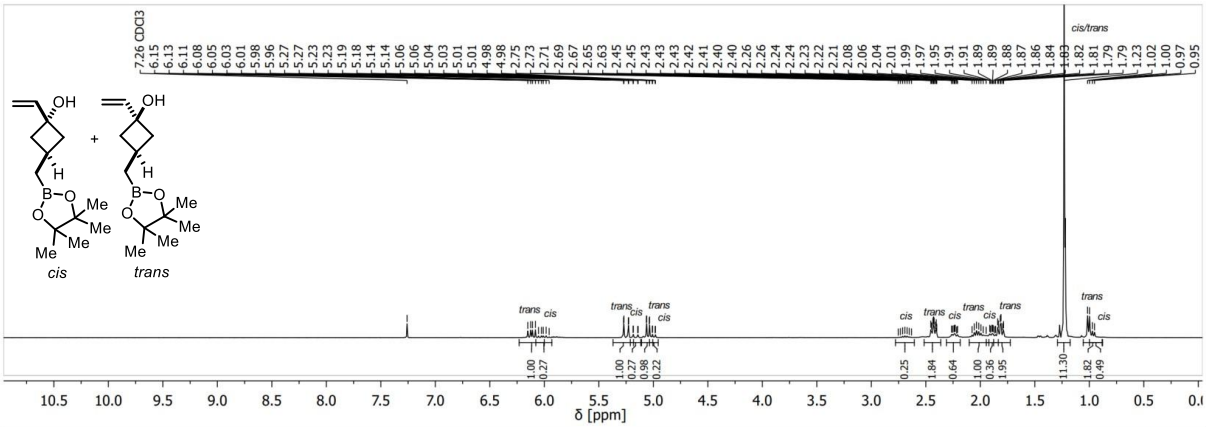
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

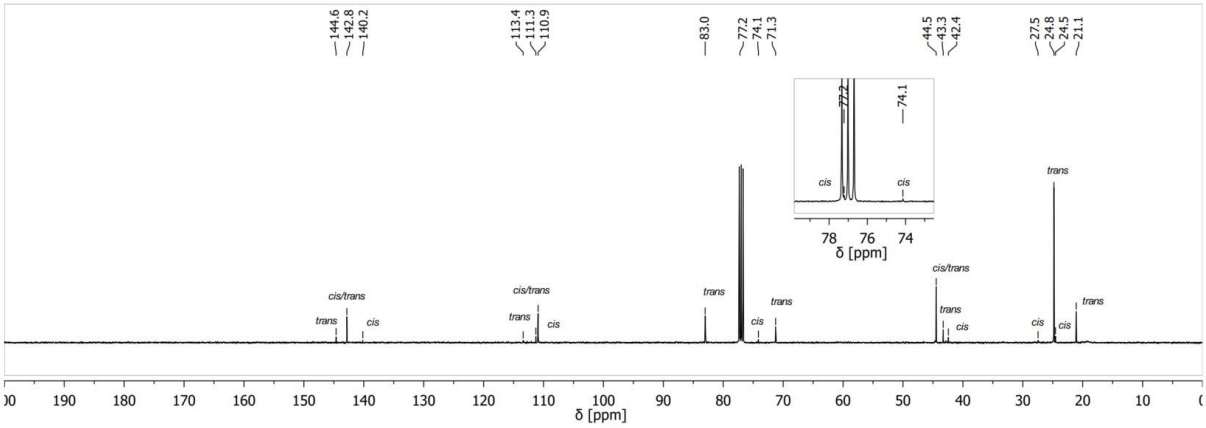


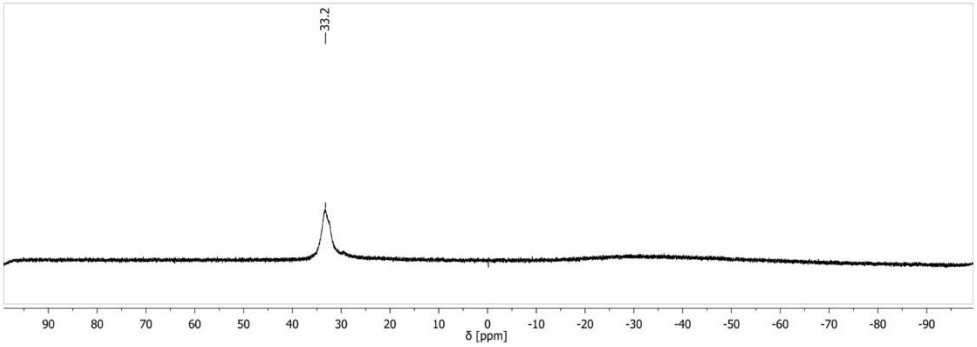
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

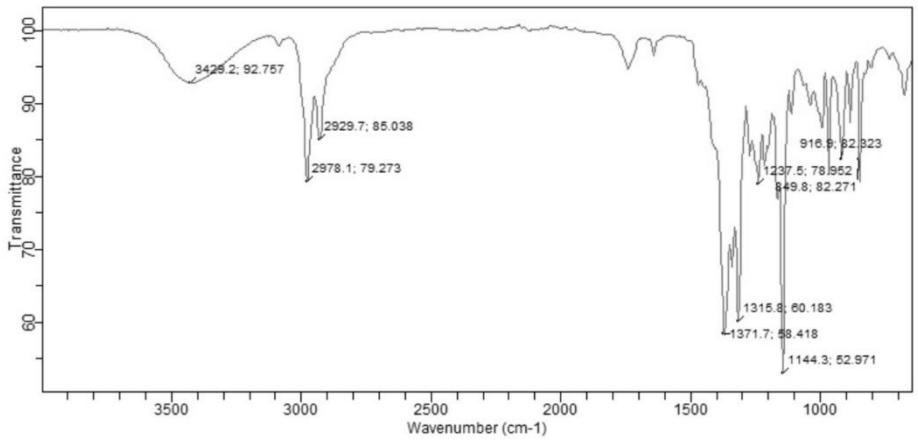
3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-vinylcyclobutan-1-ol (174h)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **^{11}B NMR** (128 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

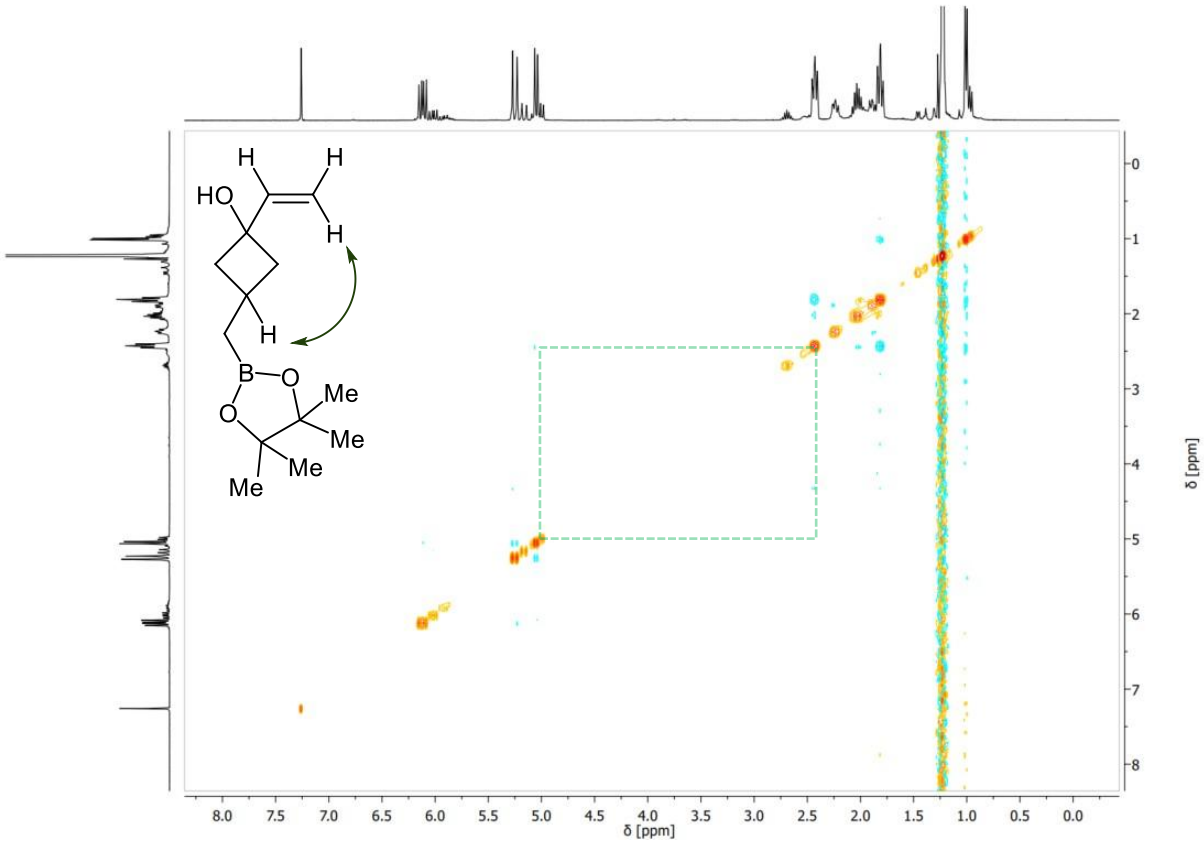








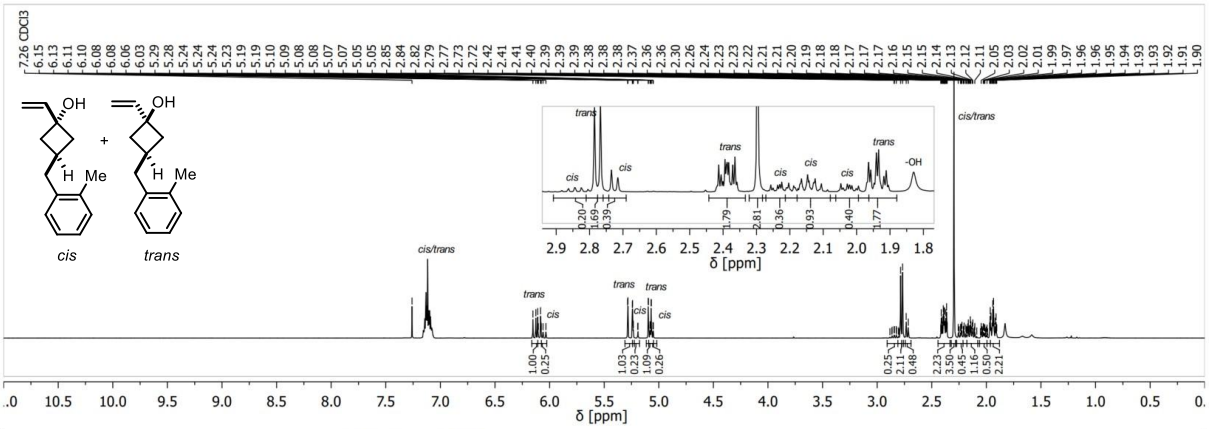
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

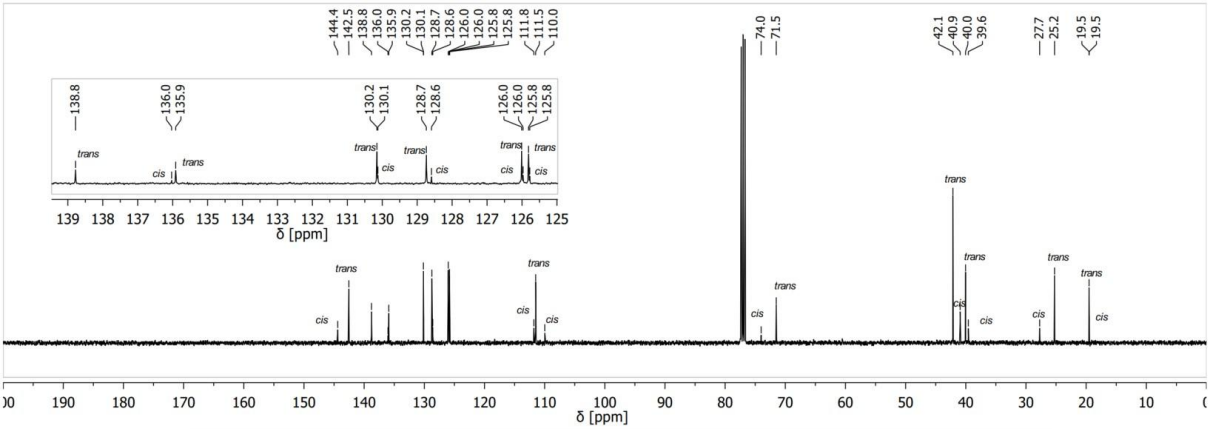


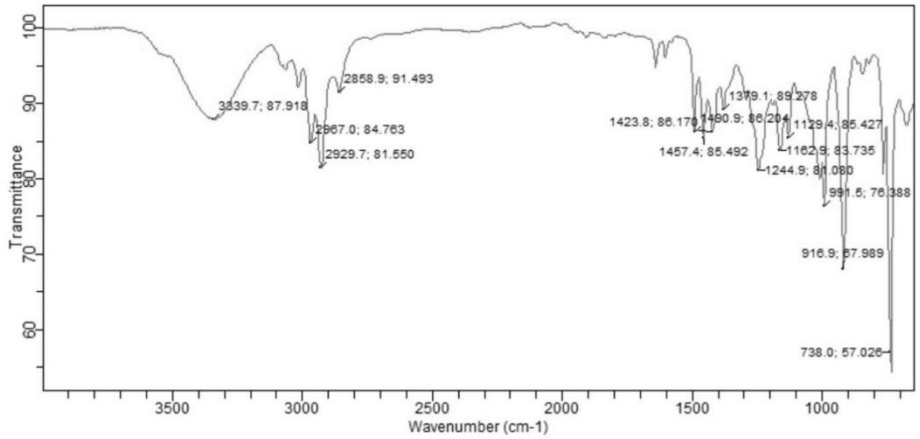
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-(2-Methylbenzyl)-1-vinylcyclobutan-1-ol (174i)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

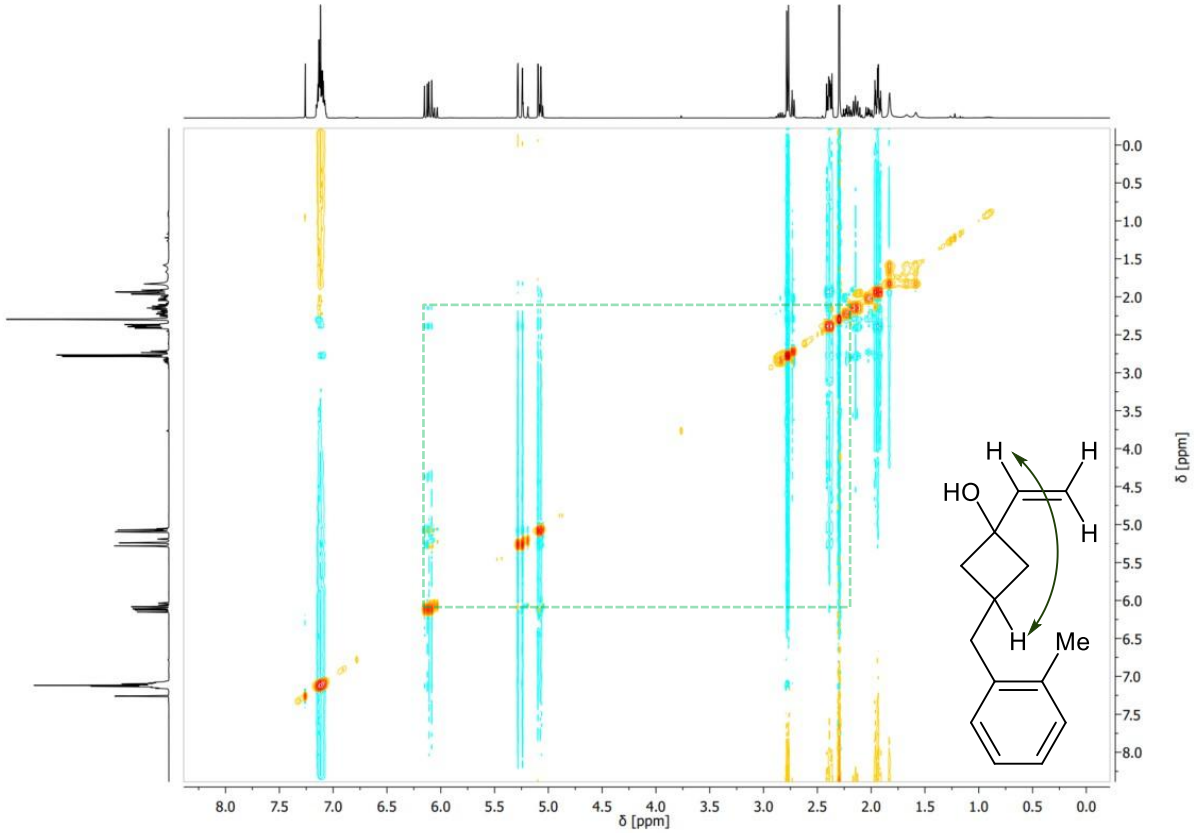






8 Appendix

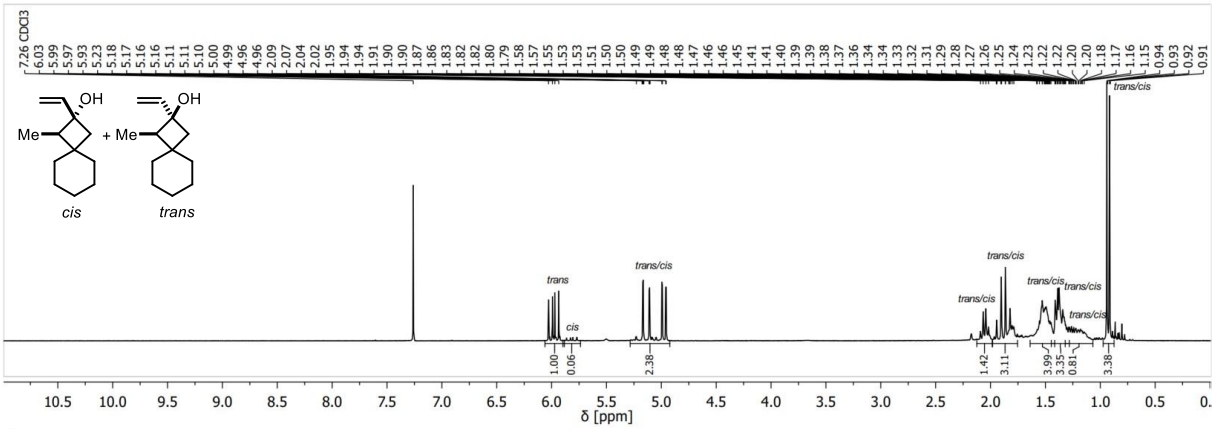
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

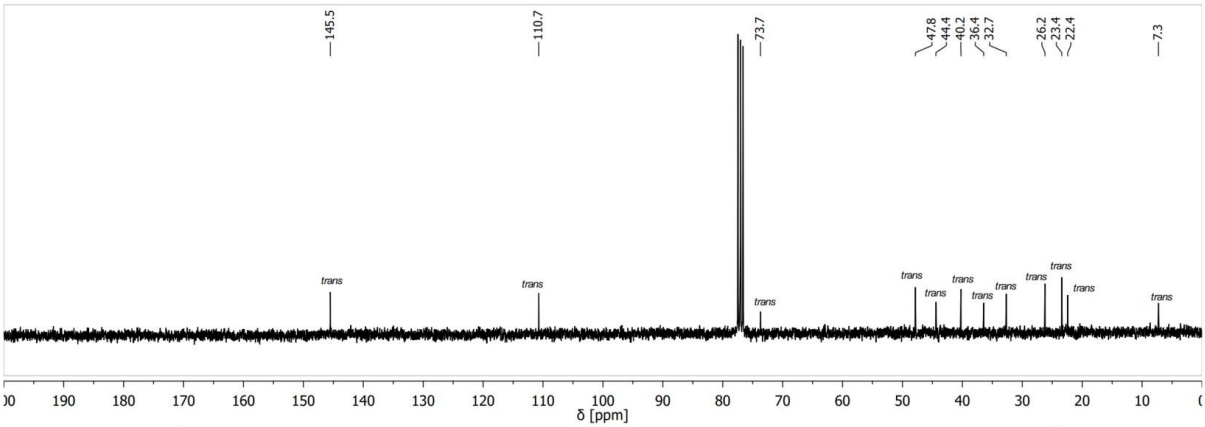


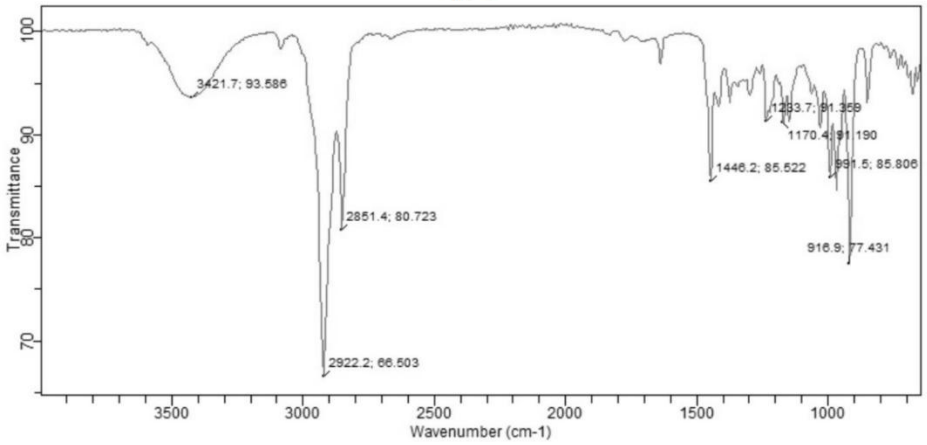
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

1-Methyl-2-vinylspiro[3.5]nonan-2-ol (174j)

^{1}H NMR (300 MHz) **^{13}C NMR** (75 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

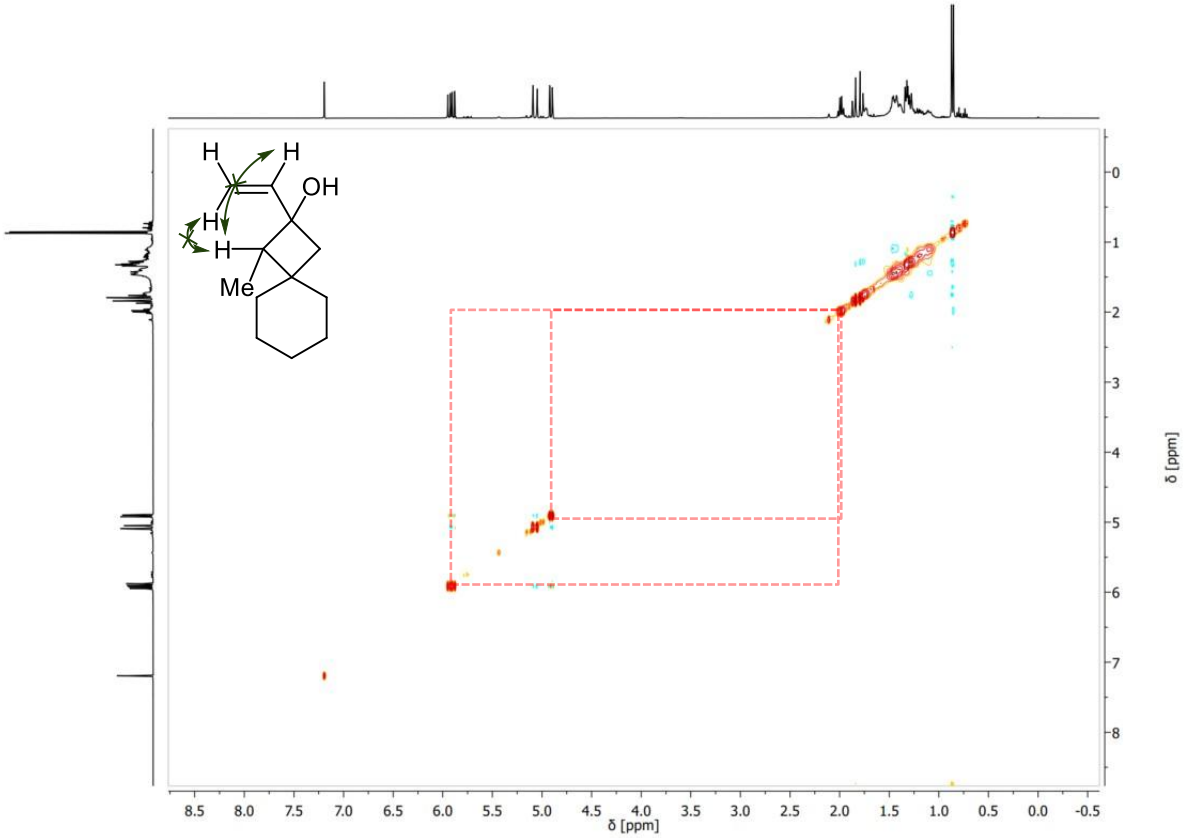






8 Appendix

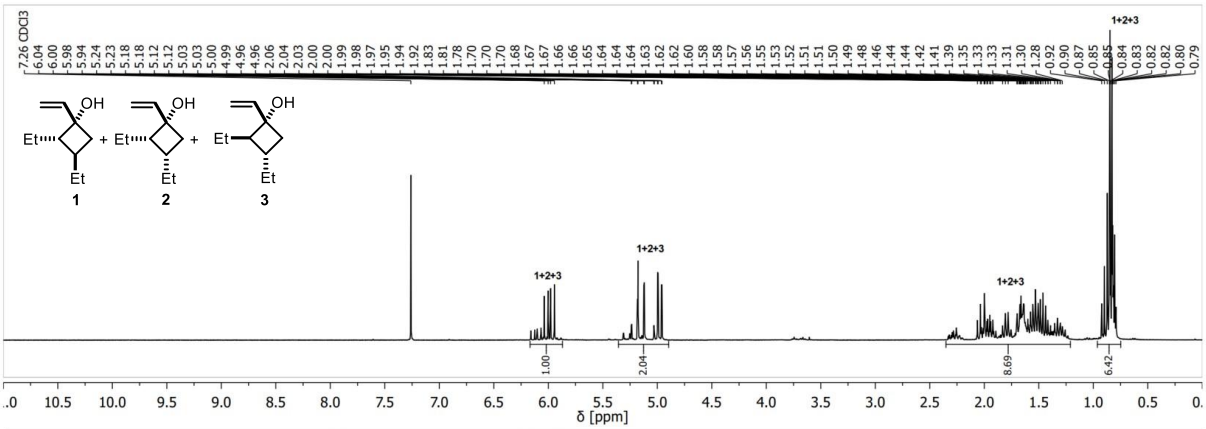
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

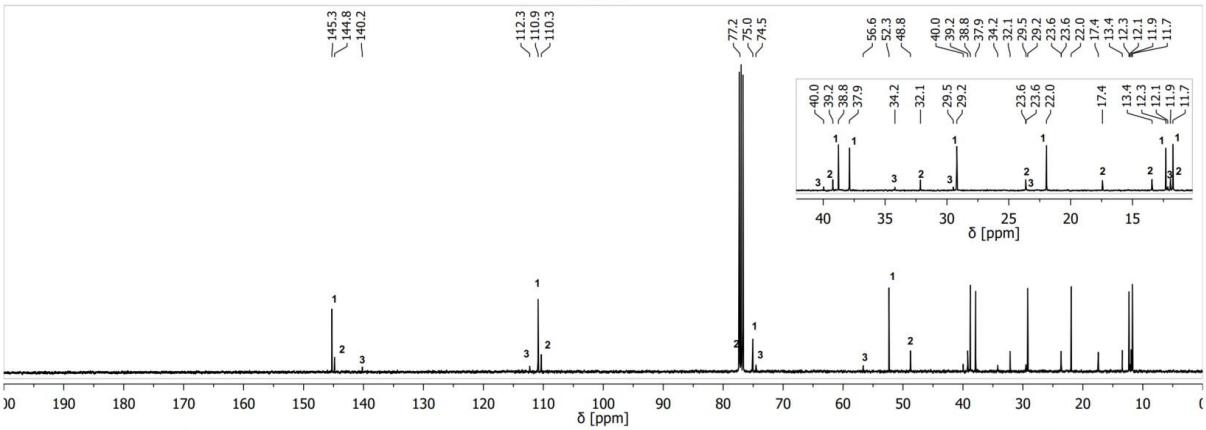


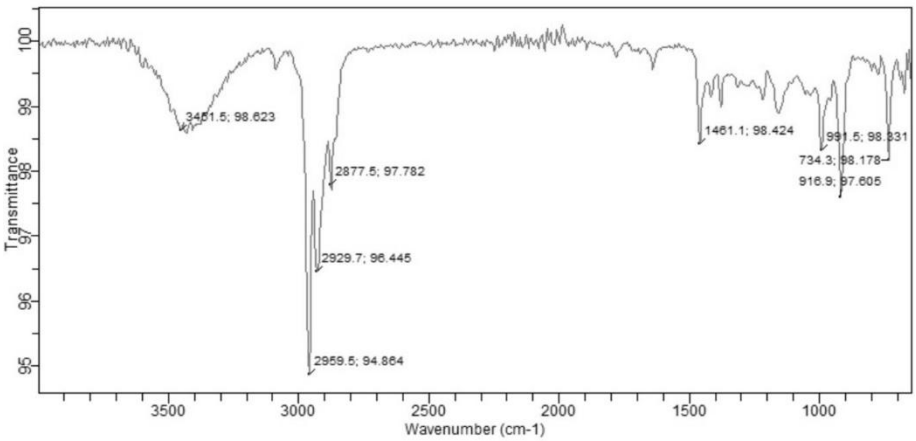
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2,3-Diethyl-1-vinylcyclobutan-1-ol (174k)

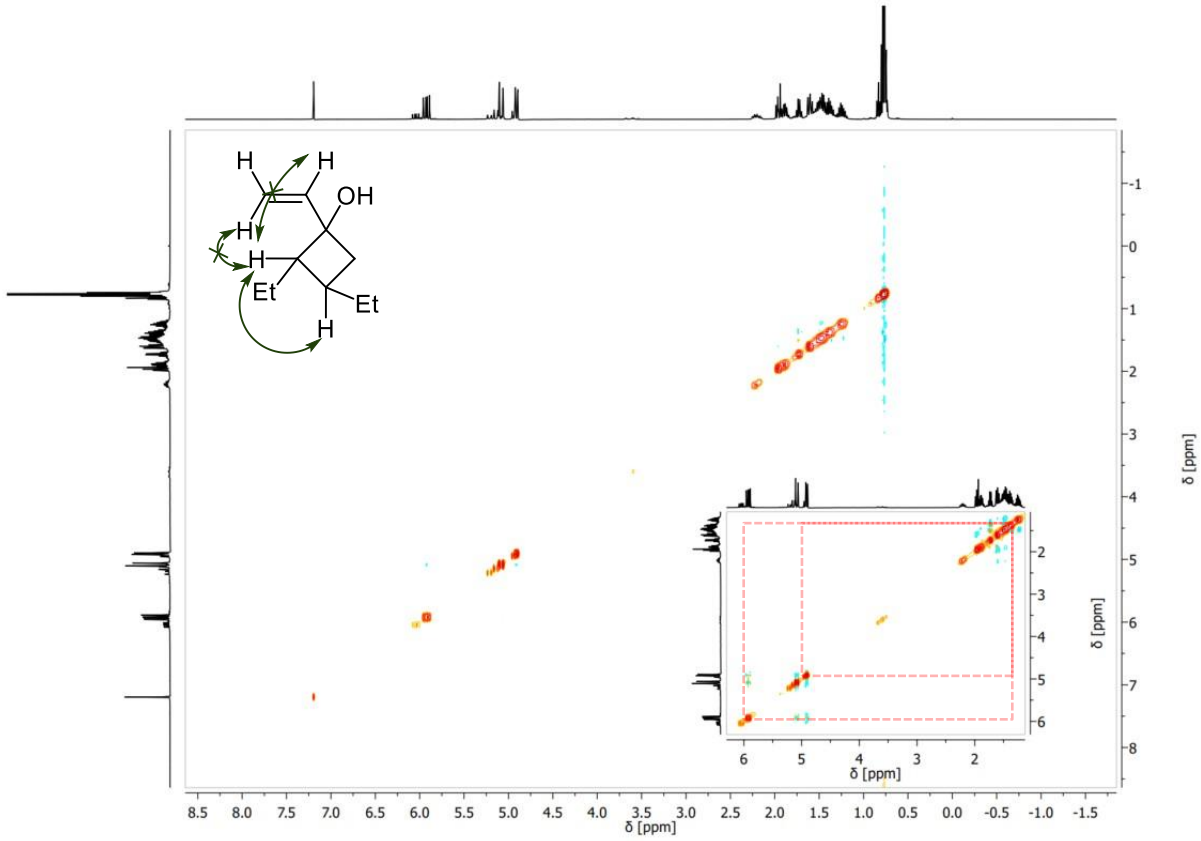
^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**







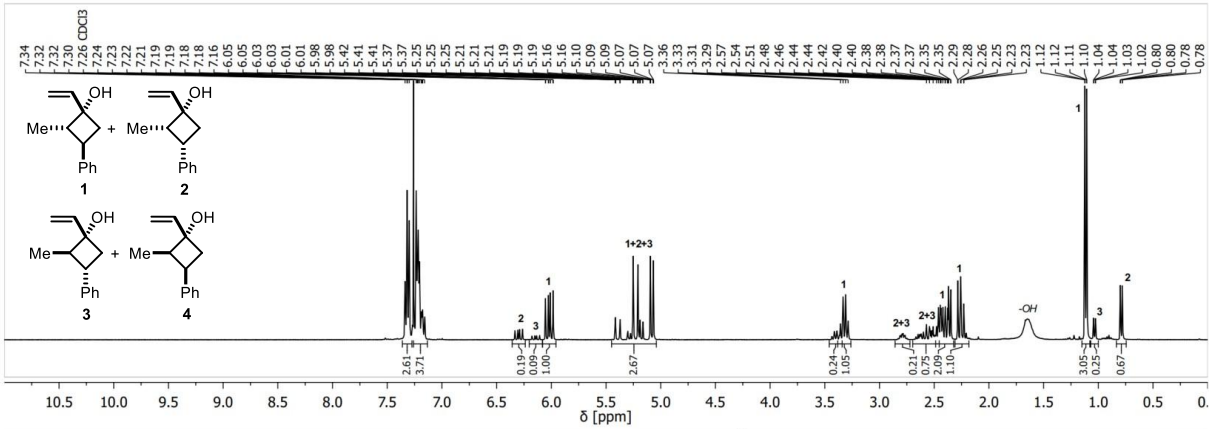
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

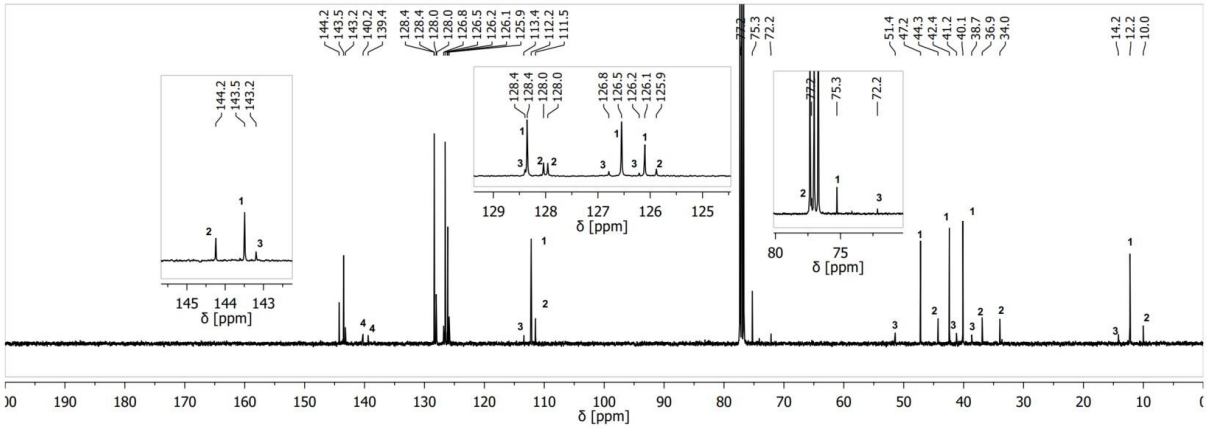


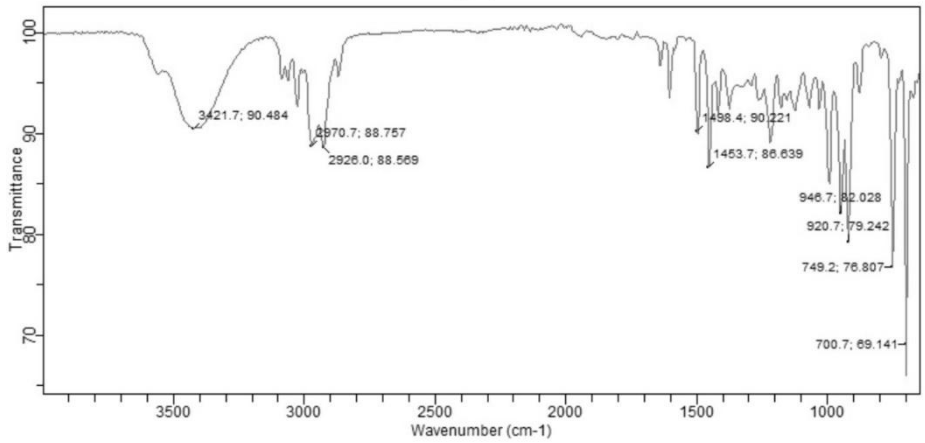
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

2-Methyl-3-phenyl-1-vinylcyclobutan-1-ol (174l)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

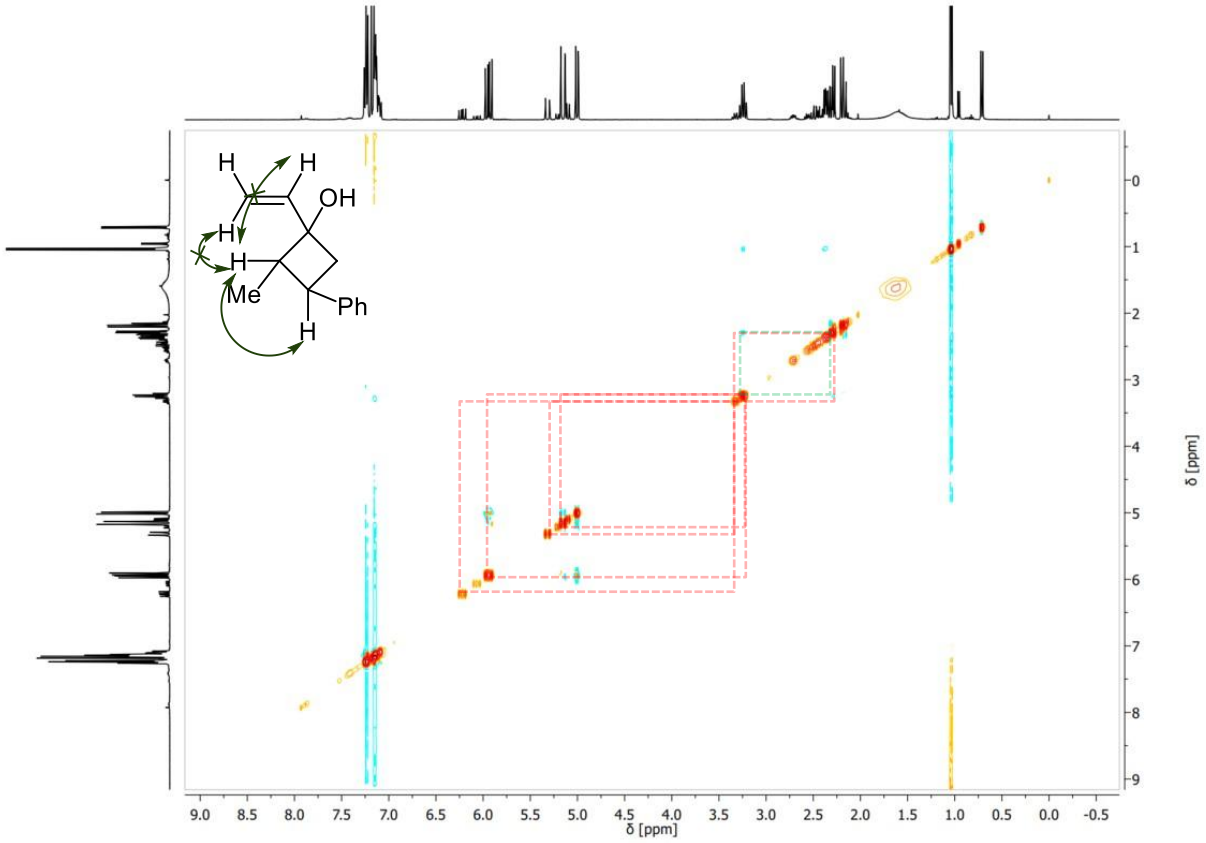






8 Appendix

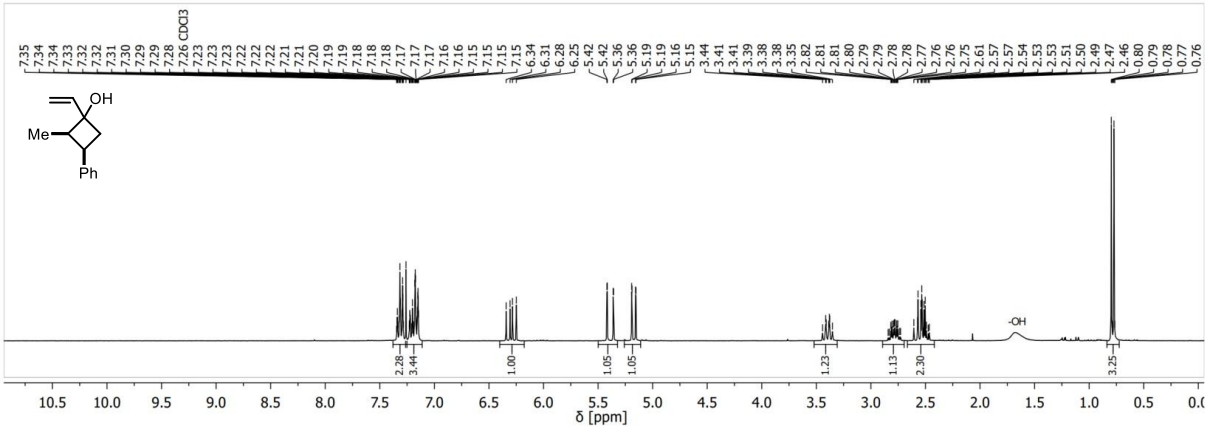
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

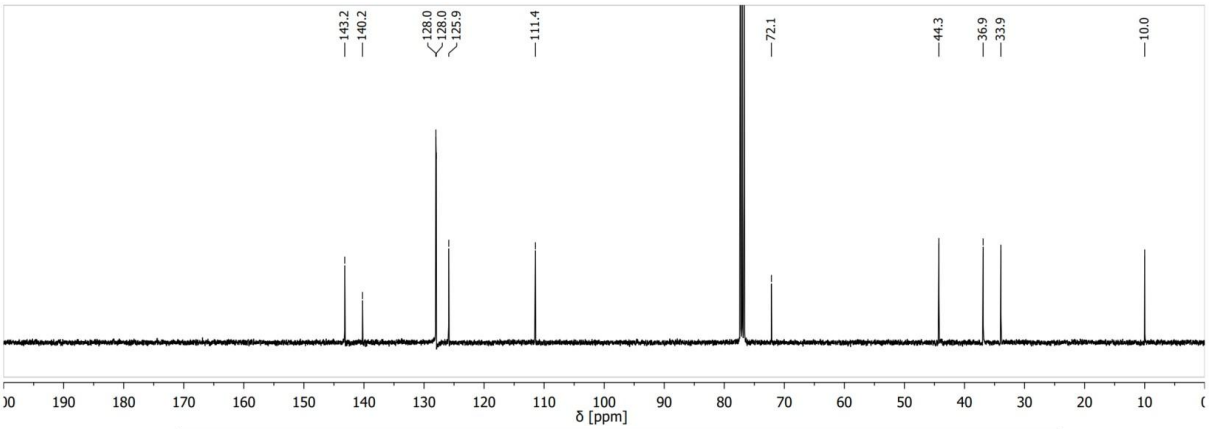


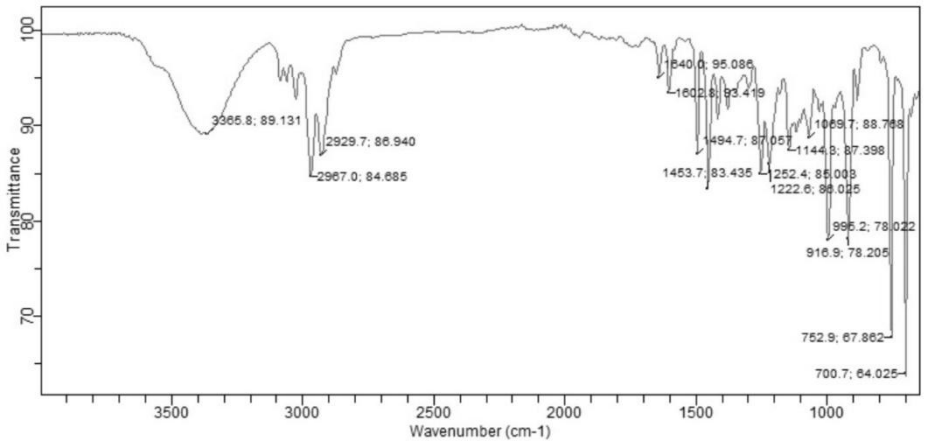
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

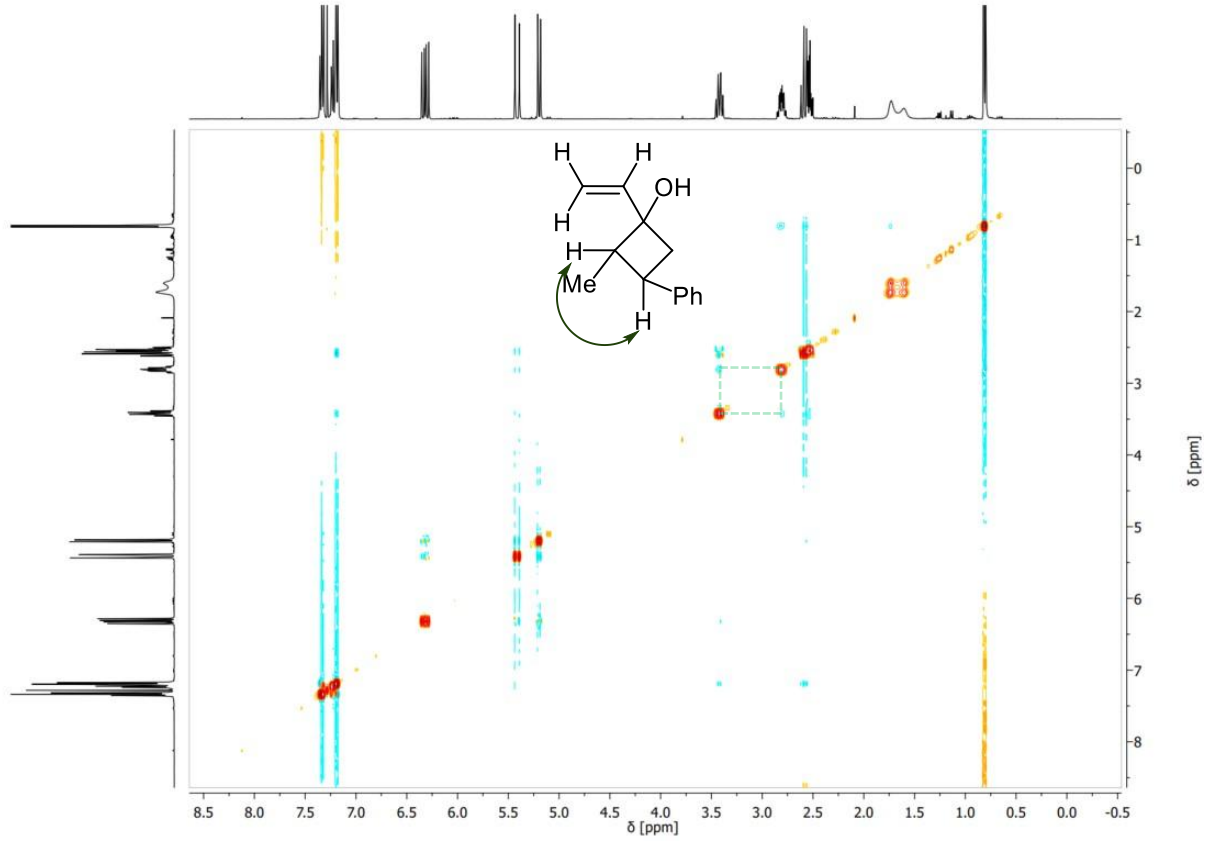
(*cis*)-2-Methyl-3-phenyl-1-vinylcyclobutan-1-ol (174l-*cis*)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**





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H
OH
H
H
Me
Ph
H
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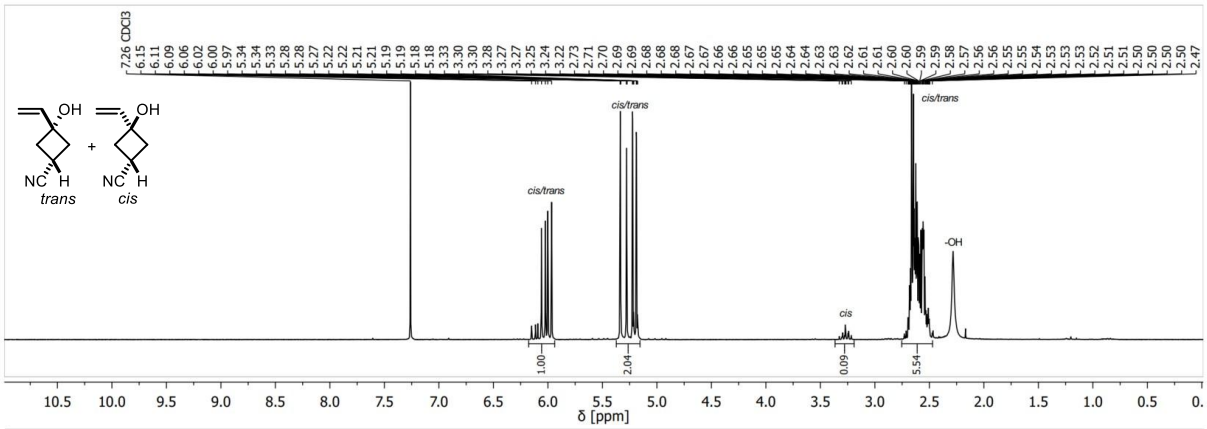
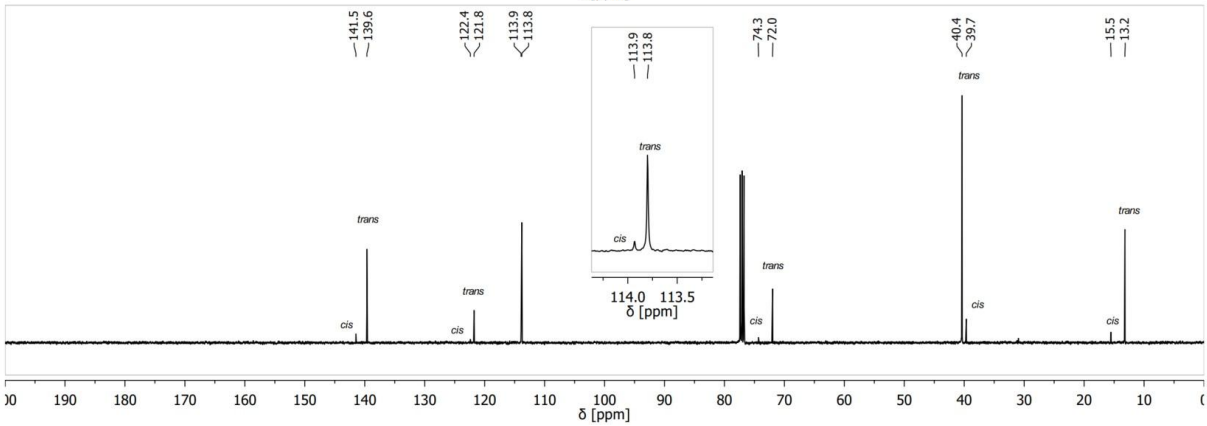
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ [ppm]
0
1
2
3
4
5
6
7
8
δ [ppm]

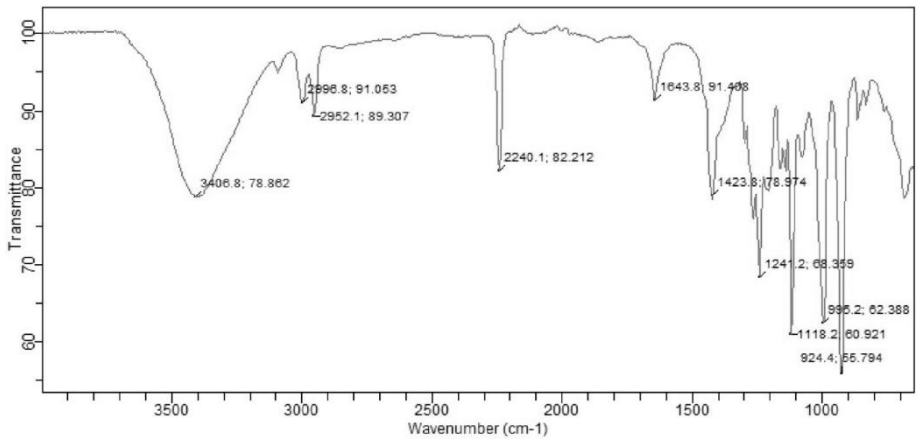
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-Hydroxy-3-vinylcyclobutane-1-carbonitrile (174m)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

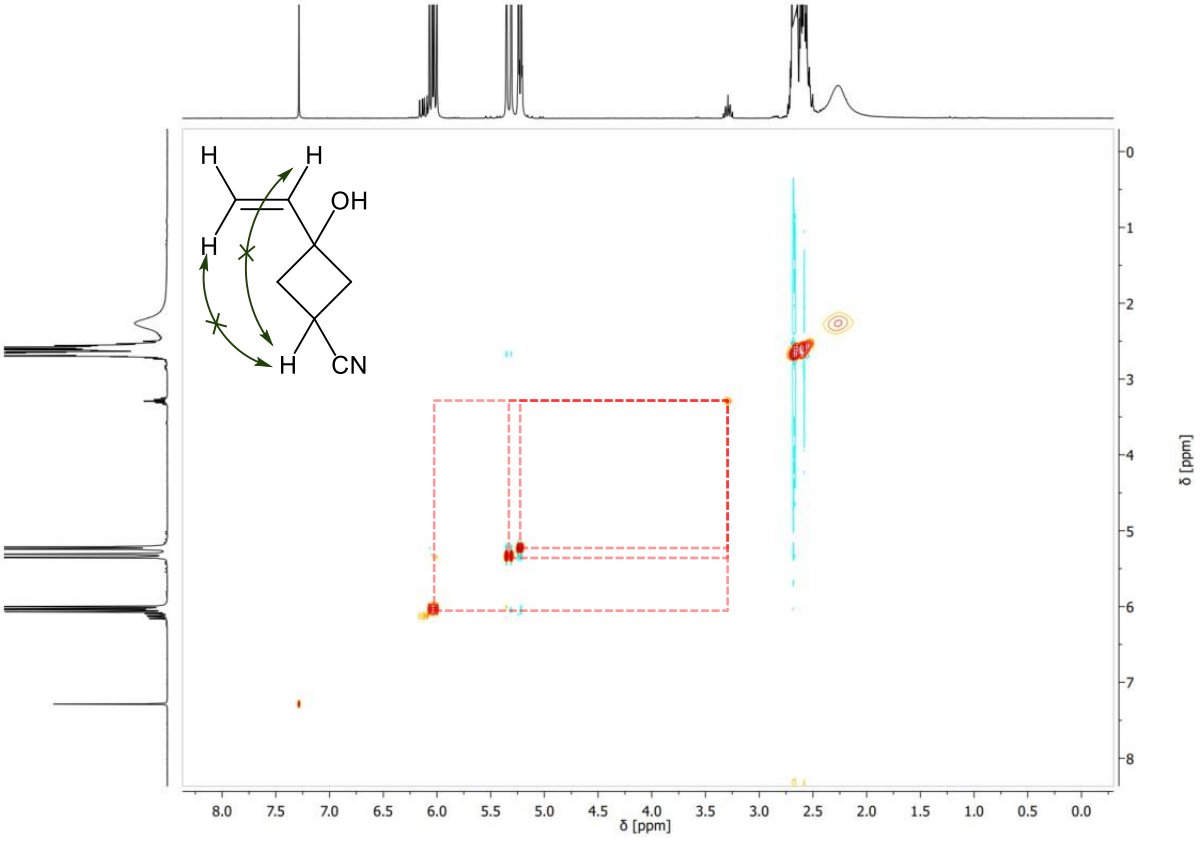






8 Appendix

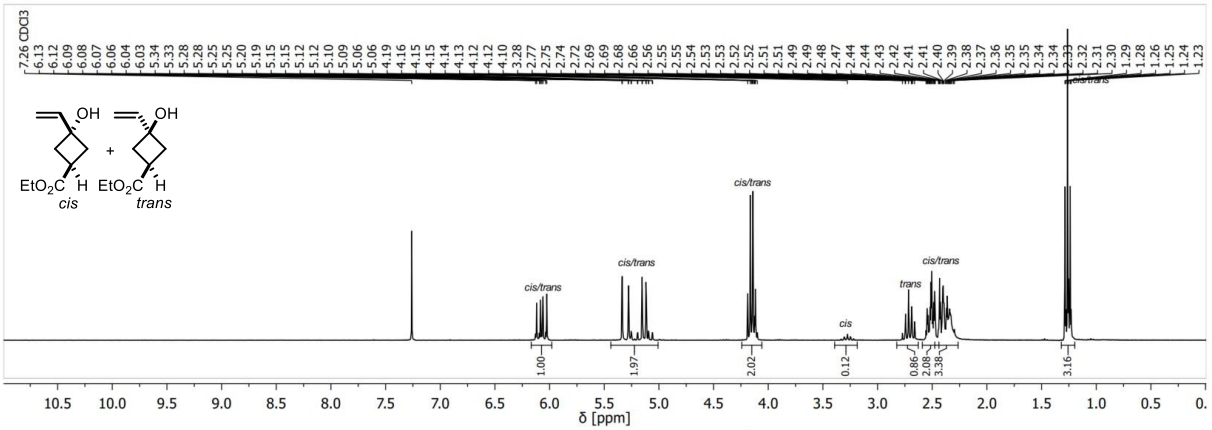
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

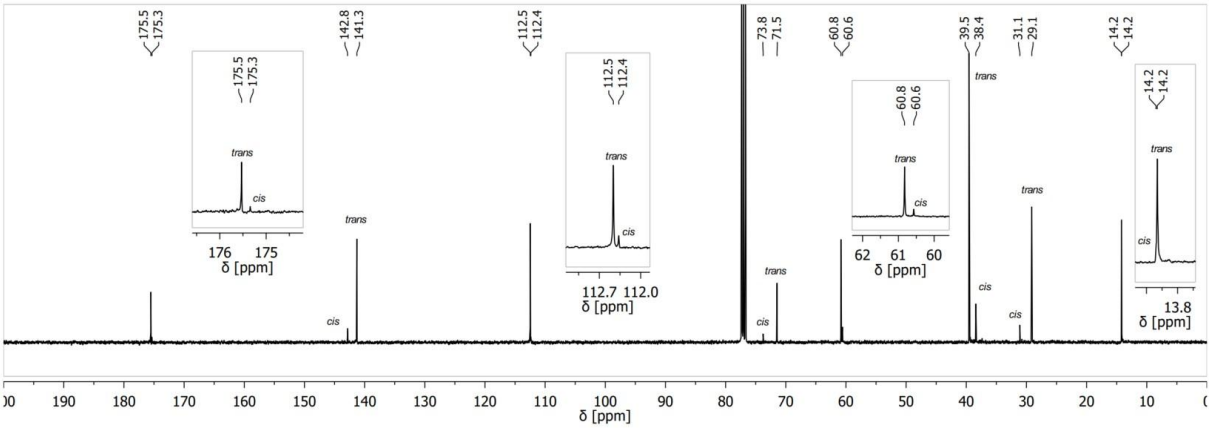


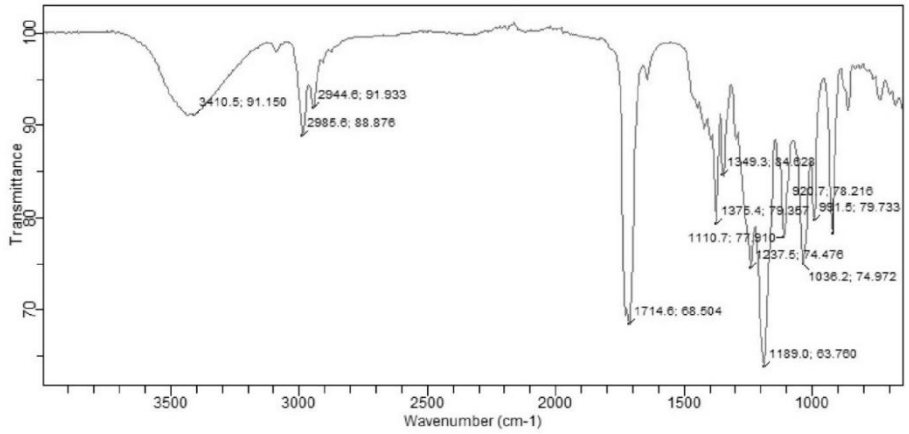
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

Ethyl 3-hydroxy-3-vinylcyclobutane-1-carboxylate (174n)

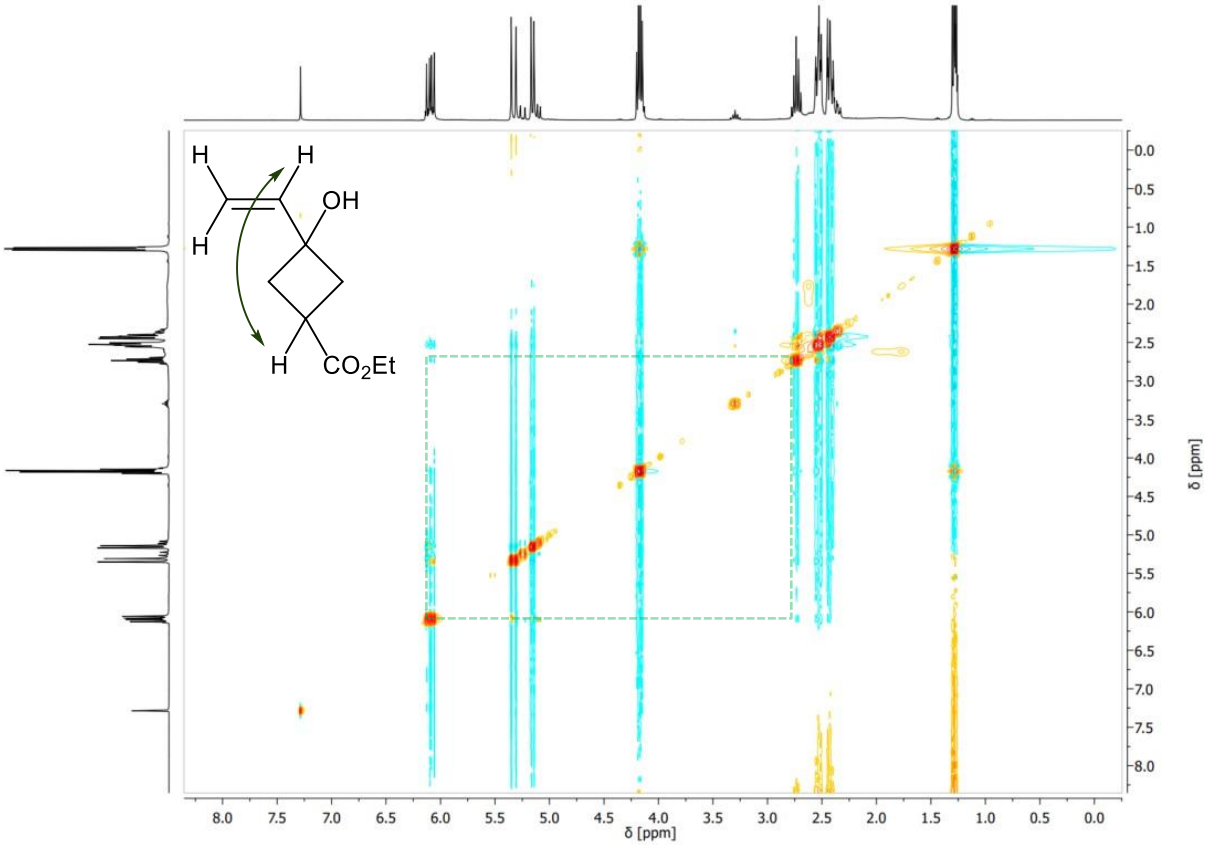
^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**







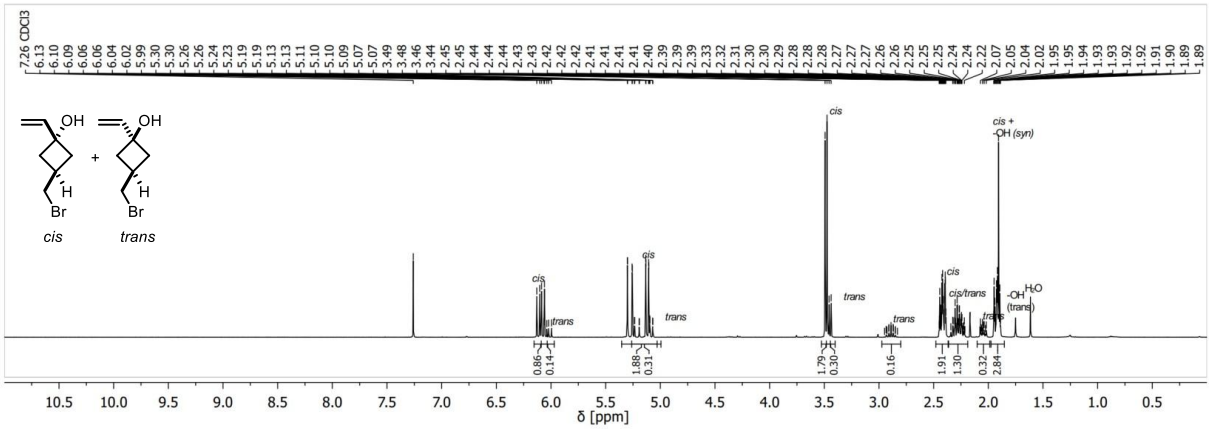
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

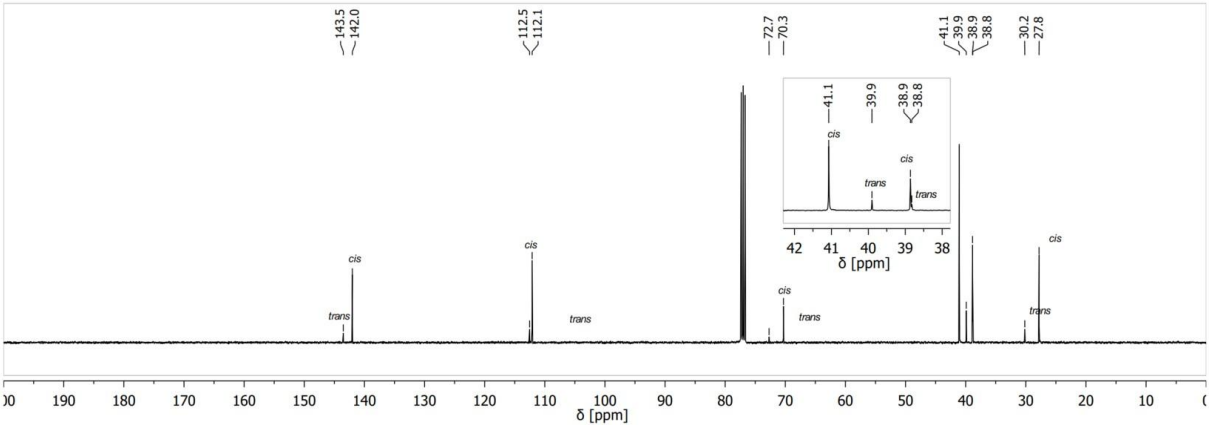


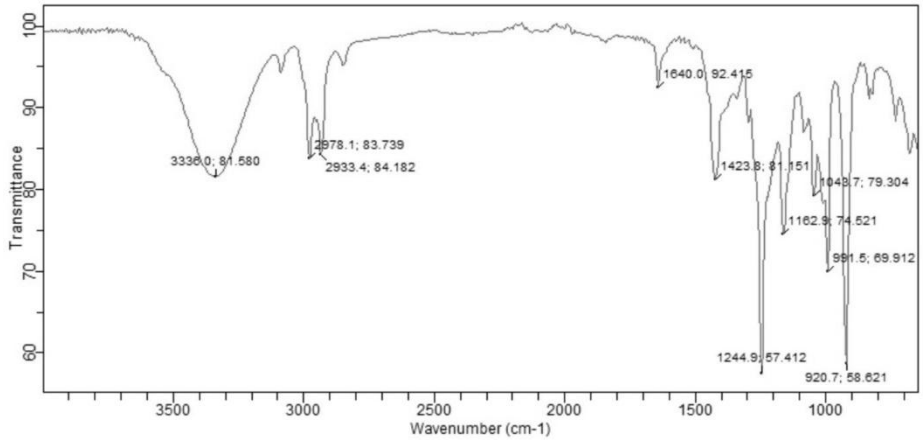
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-(Bromomethyl)-1-vinylcyclobutan-1-ol (174o)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

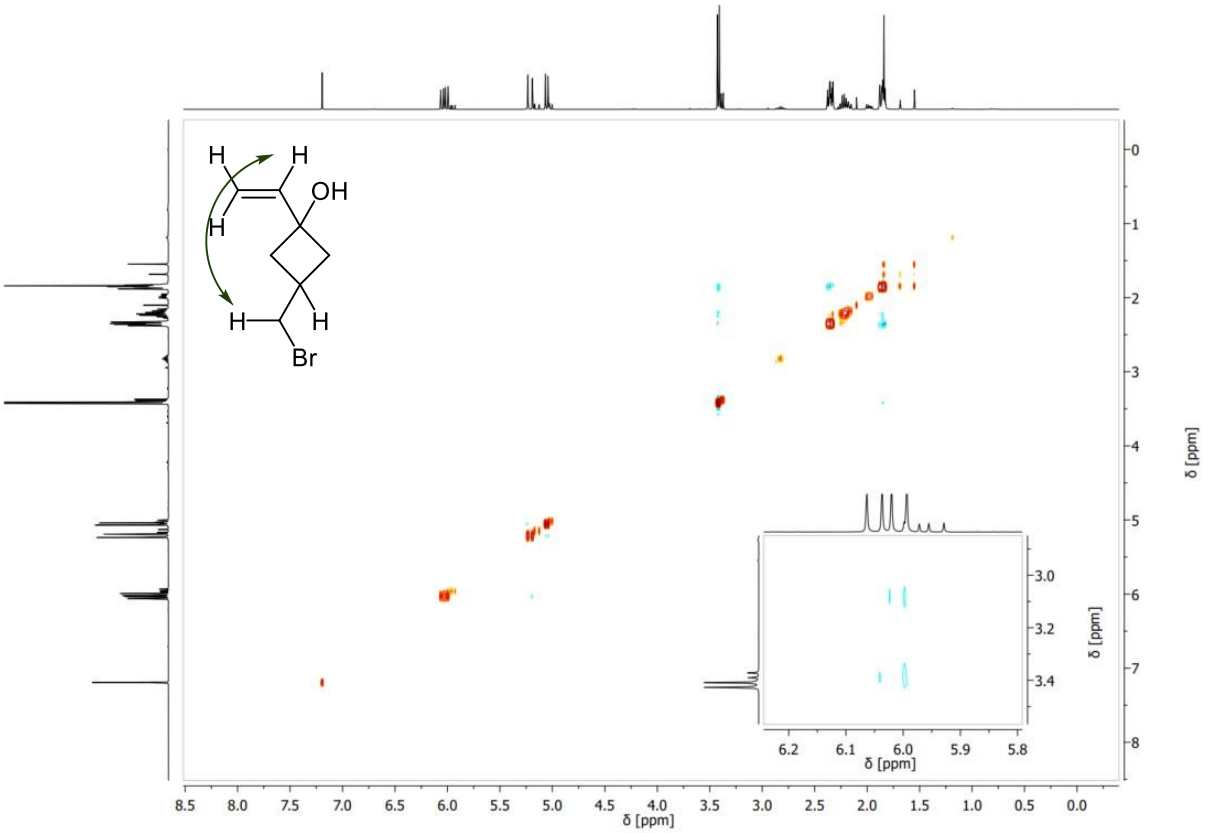






8 Appendix

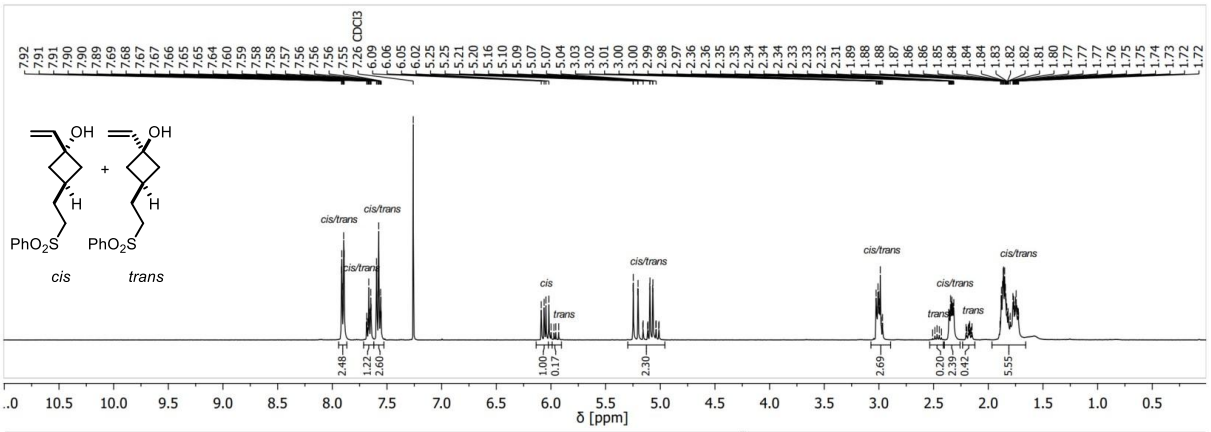
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

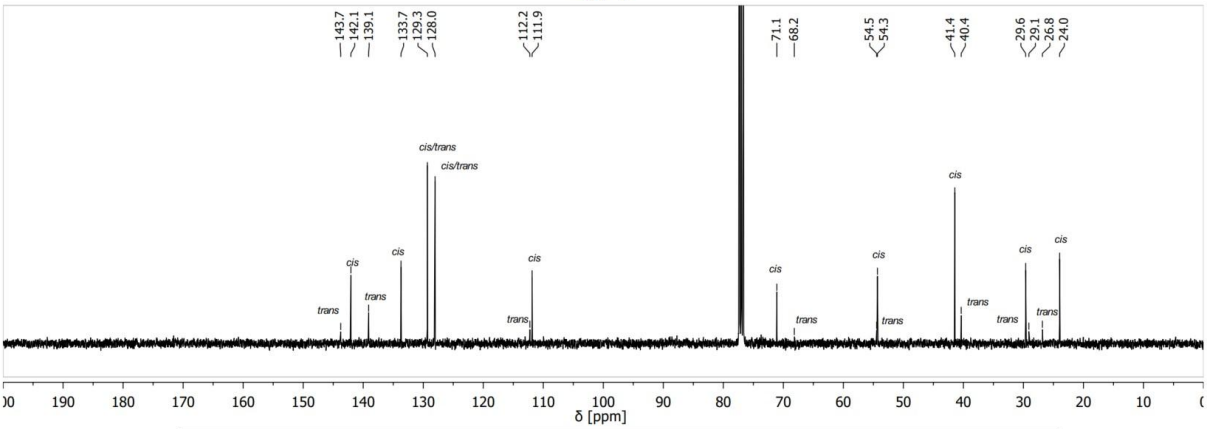


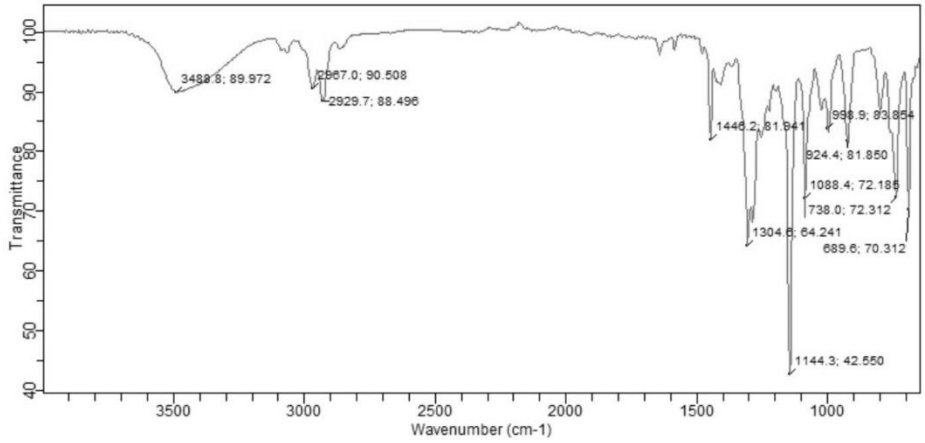
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

3-(2-(Phenylsulfonyl)ethyl)-1-vinylcyclobutan-1-ol (174p)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

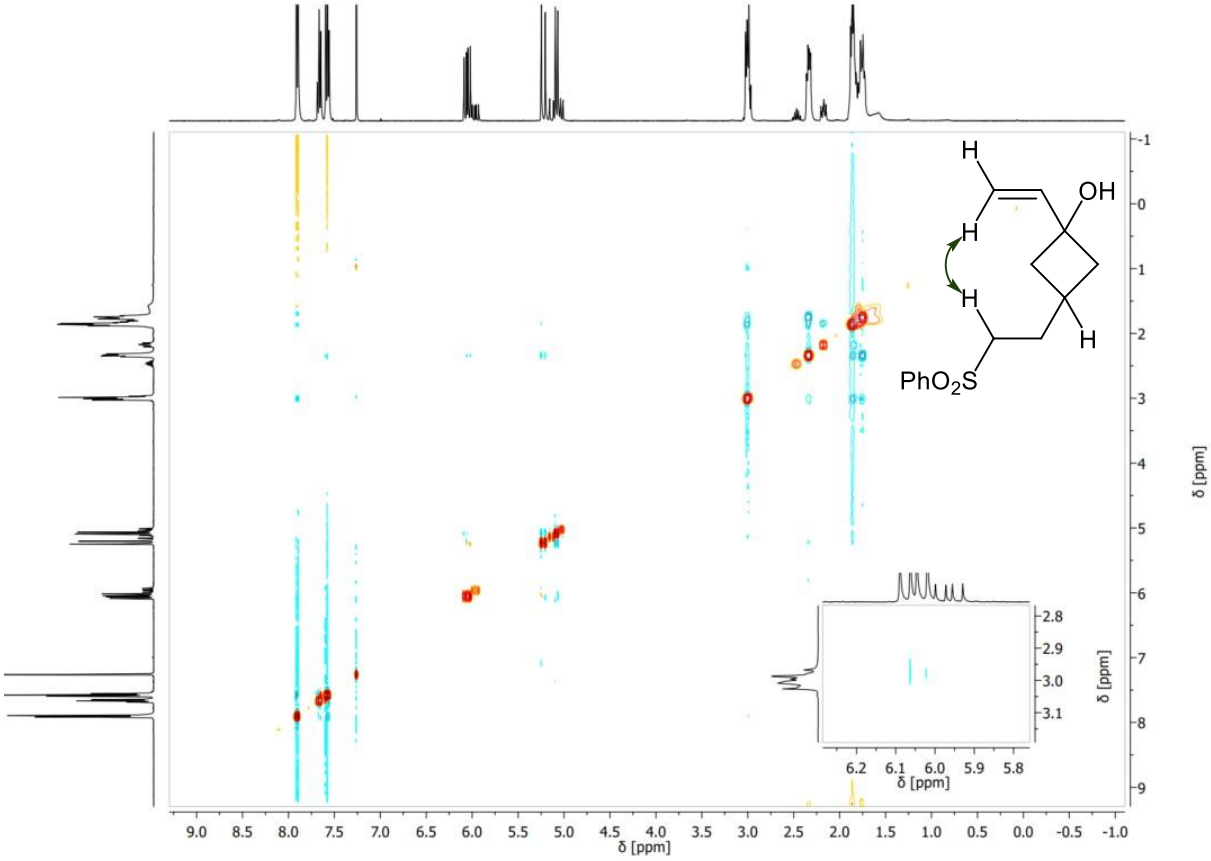






8 Appendix

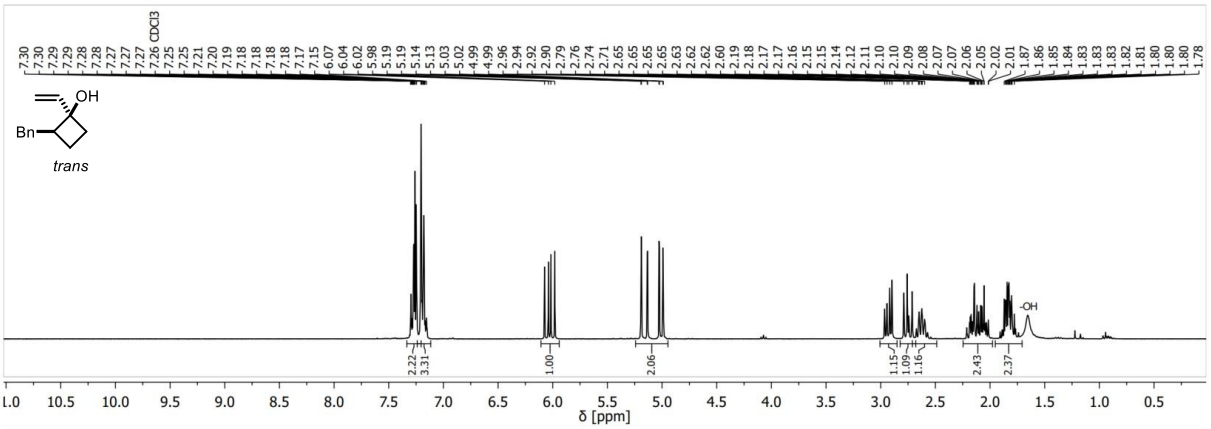
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

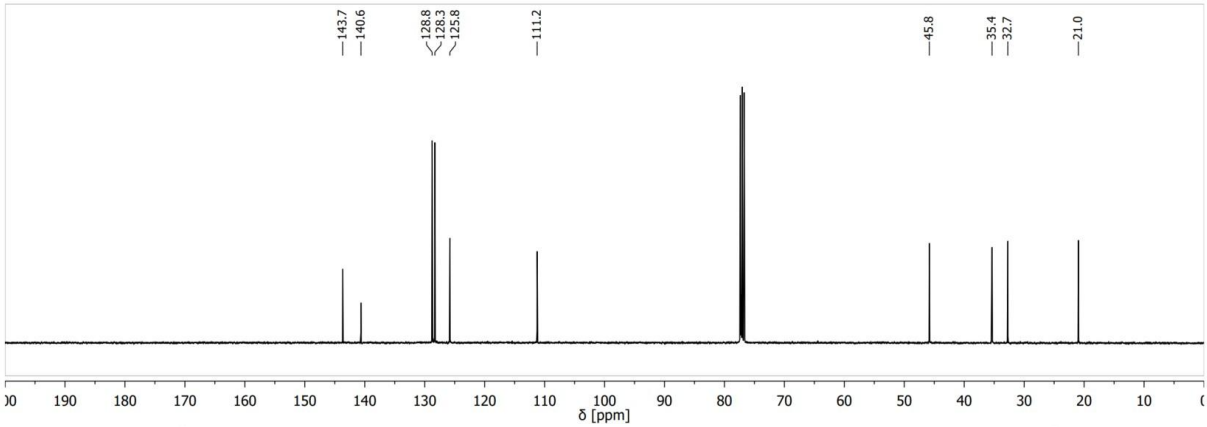


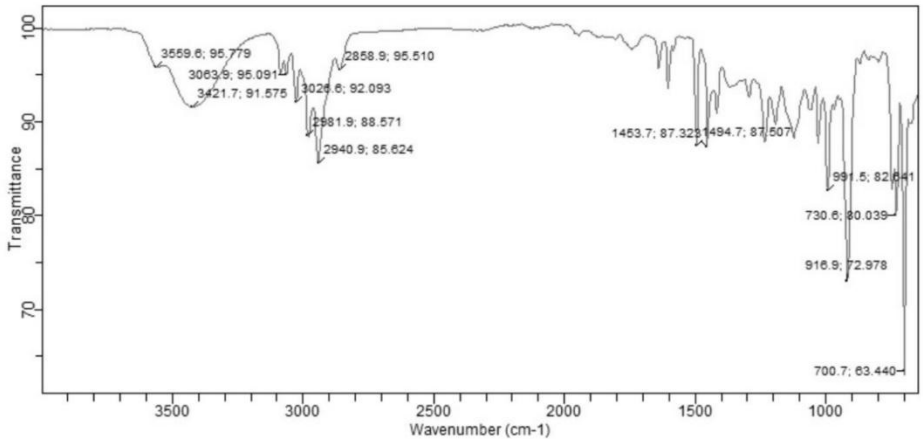
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

trans-2-Benzyl-1-vinylcyclobutan-1-ol (174q)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

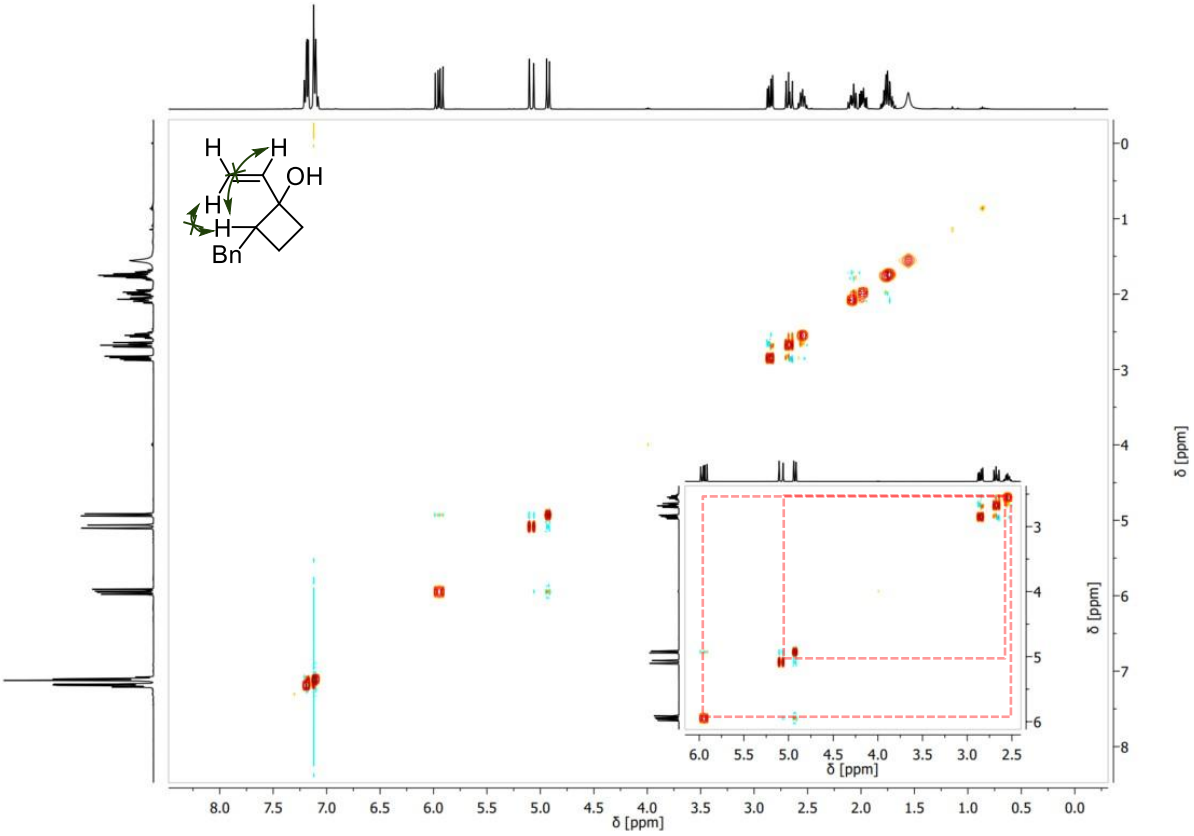






8 Appendix

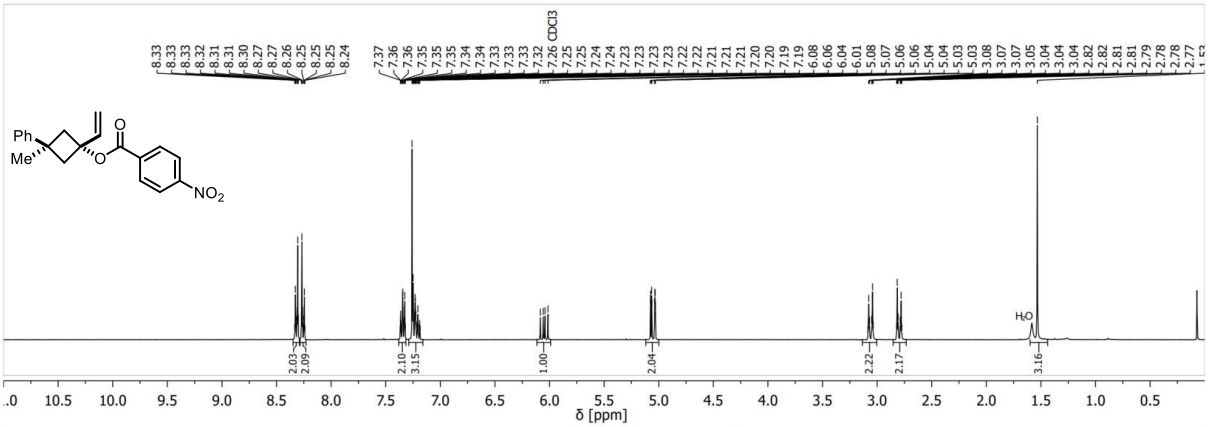
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

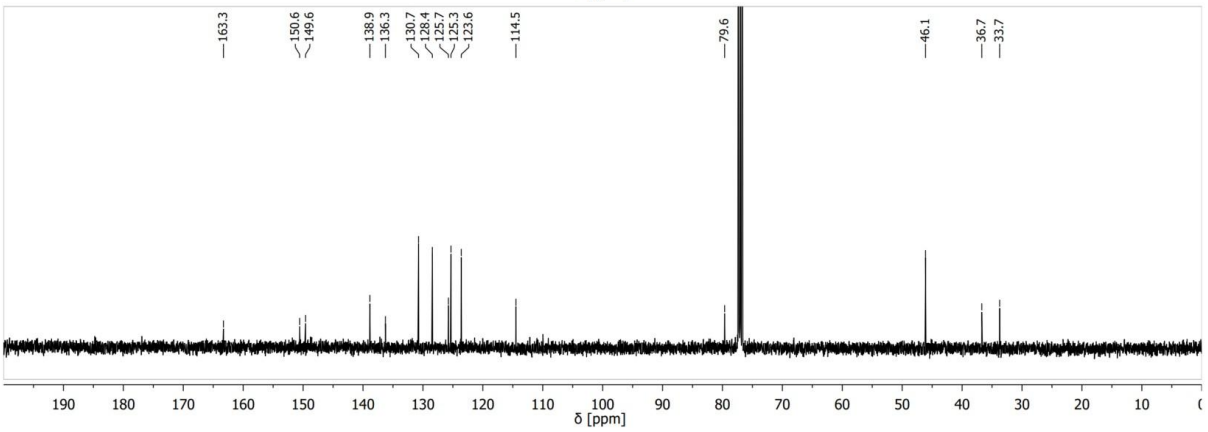


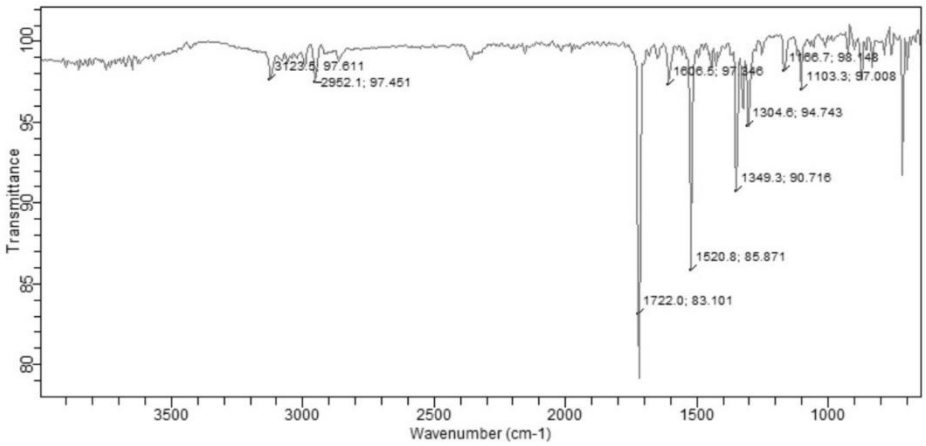
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

(*cis*)-3-Methyl-3-phenyl-1-vinylcyclobutyl 4-nitrobenzoate (176-*cis*)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

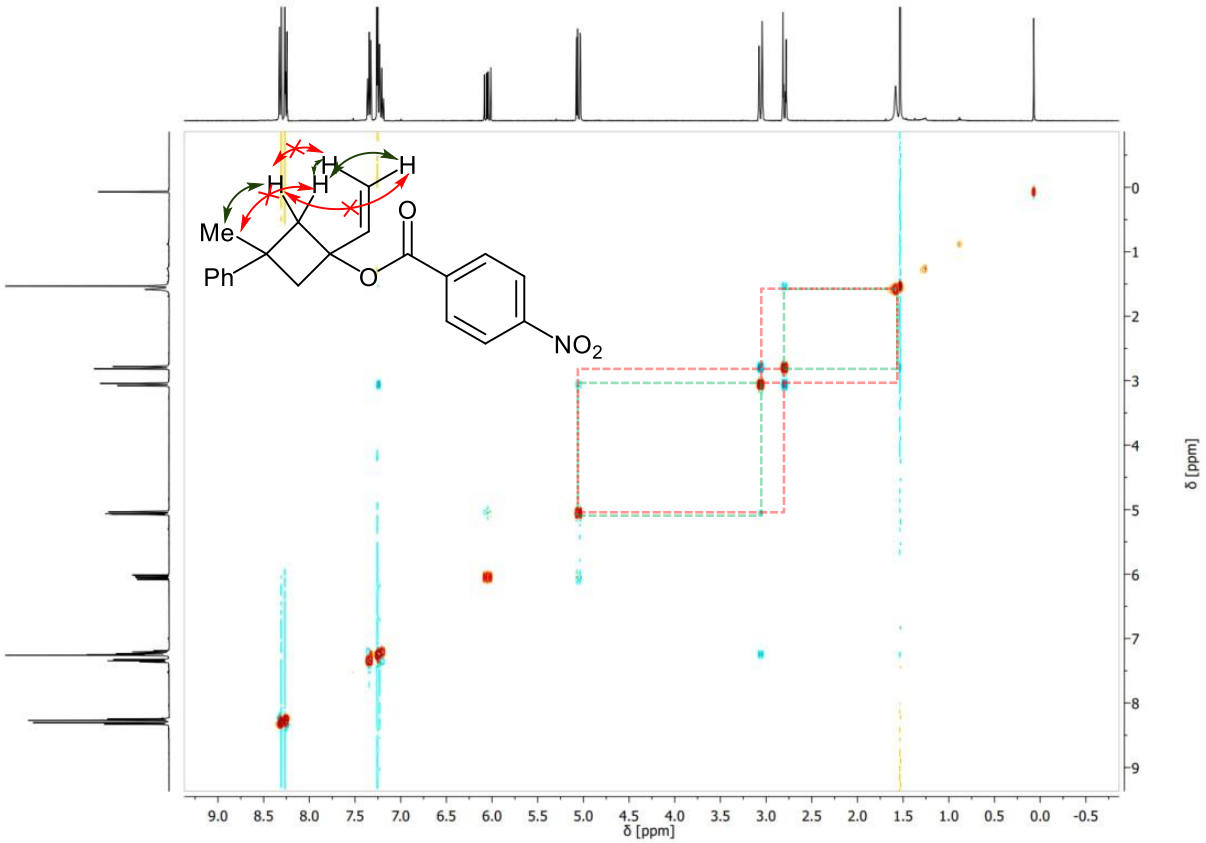






8 Appendix

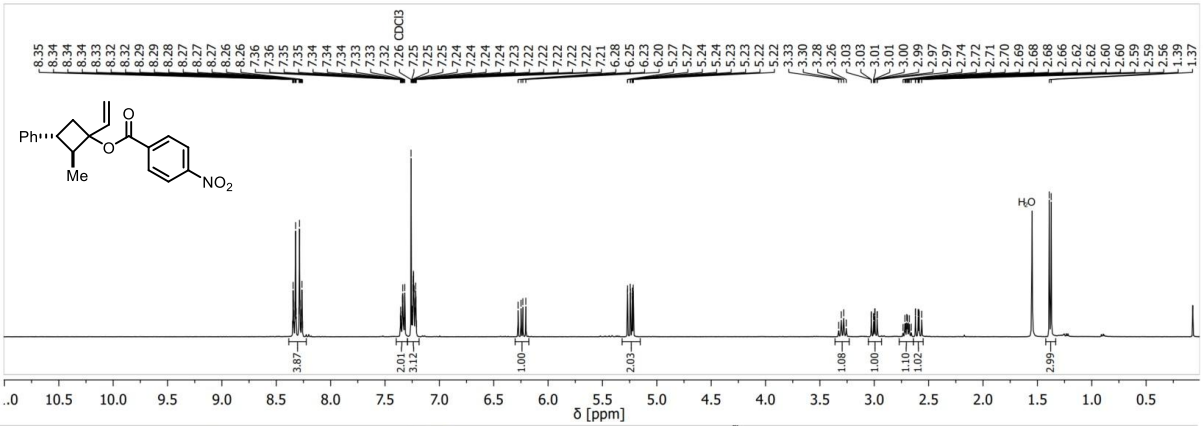
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

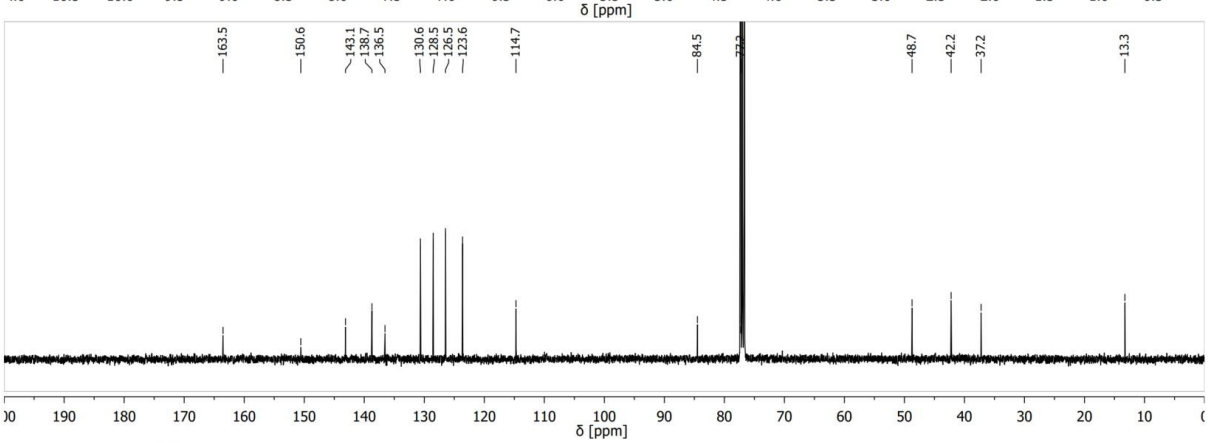


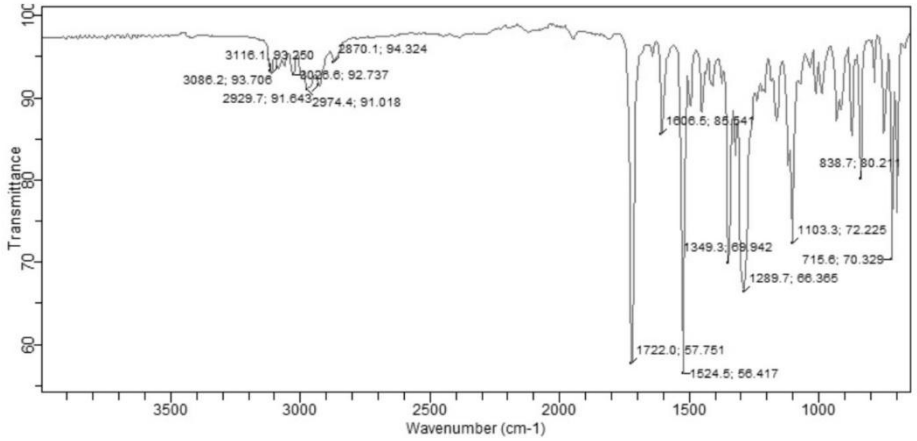
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

(*trans*)-2-Methyl-3-phenyl-1-vinylcyclobutyl 4-nitrobenzoate

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

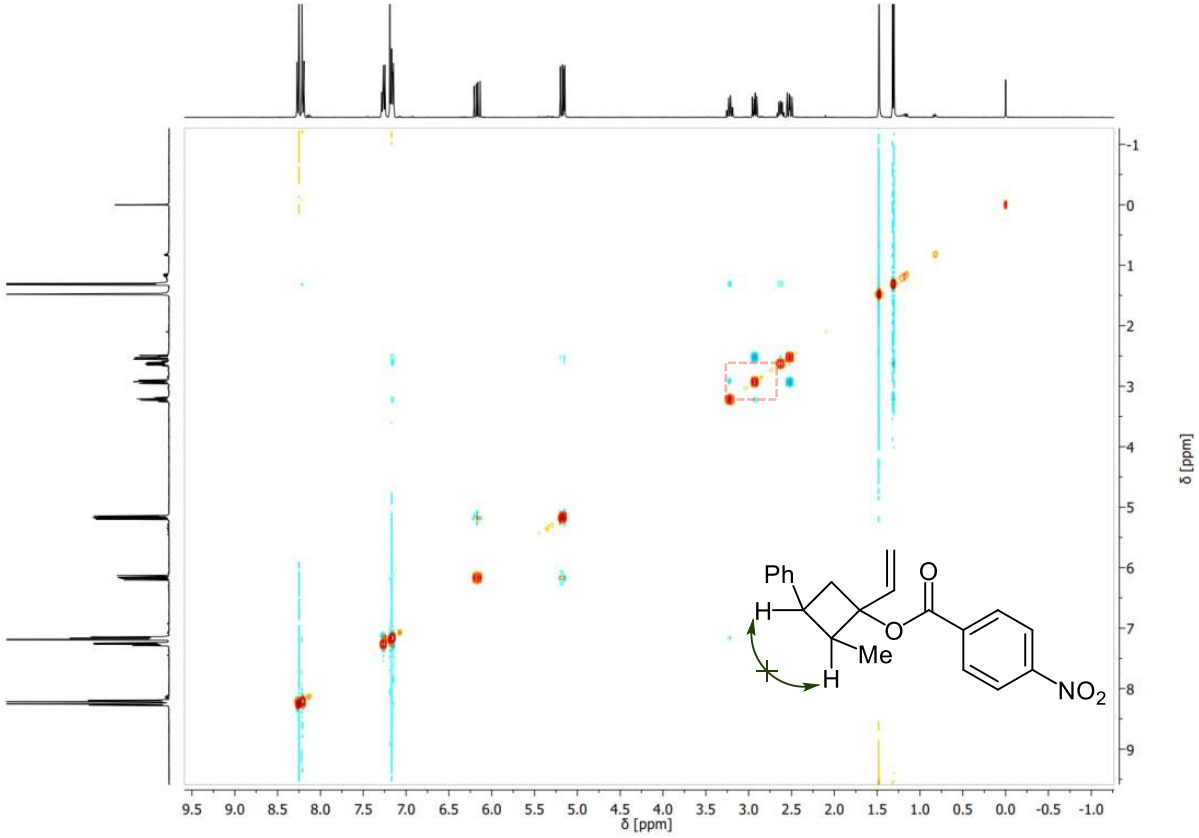






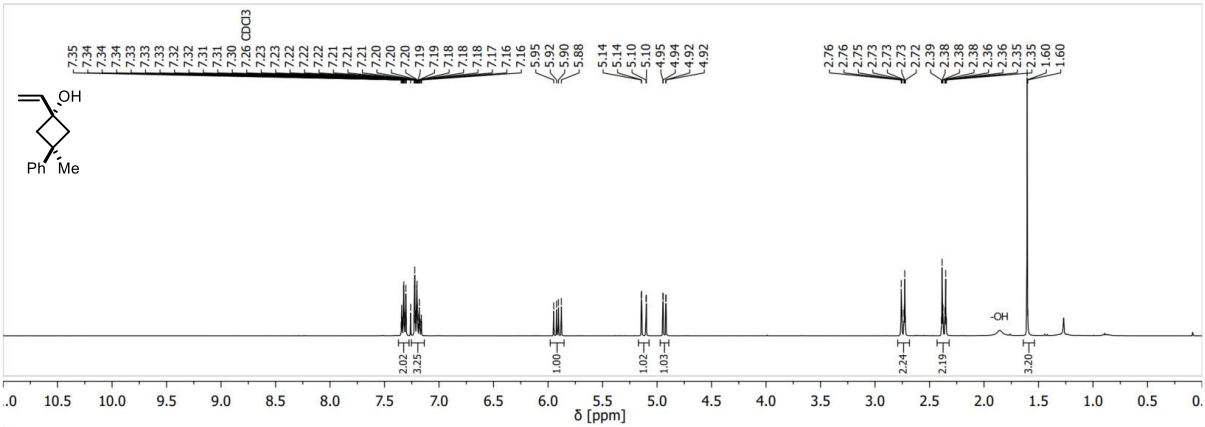
8 Appendix

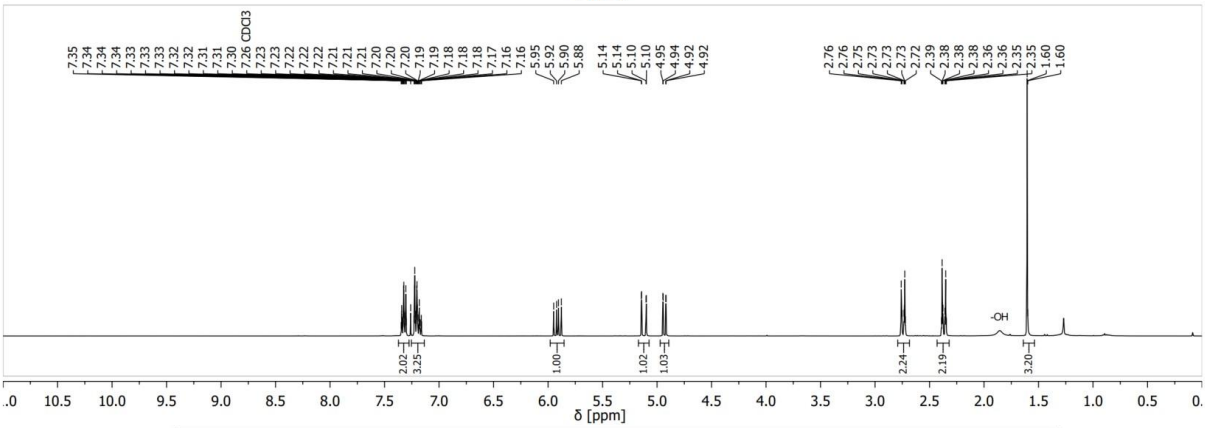
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

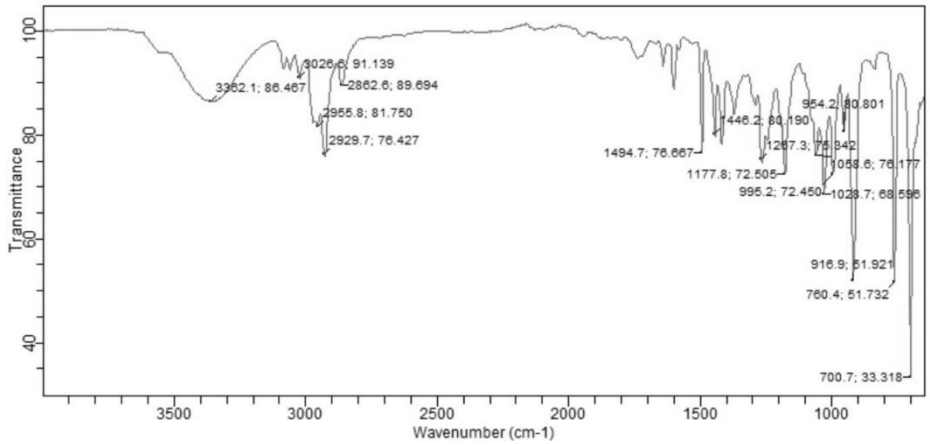


(*cis*)-3-Methyl-3-phenyl-1-vinylcyclobutan-1-ol (174a-*cis*)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

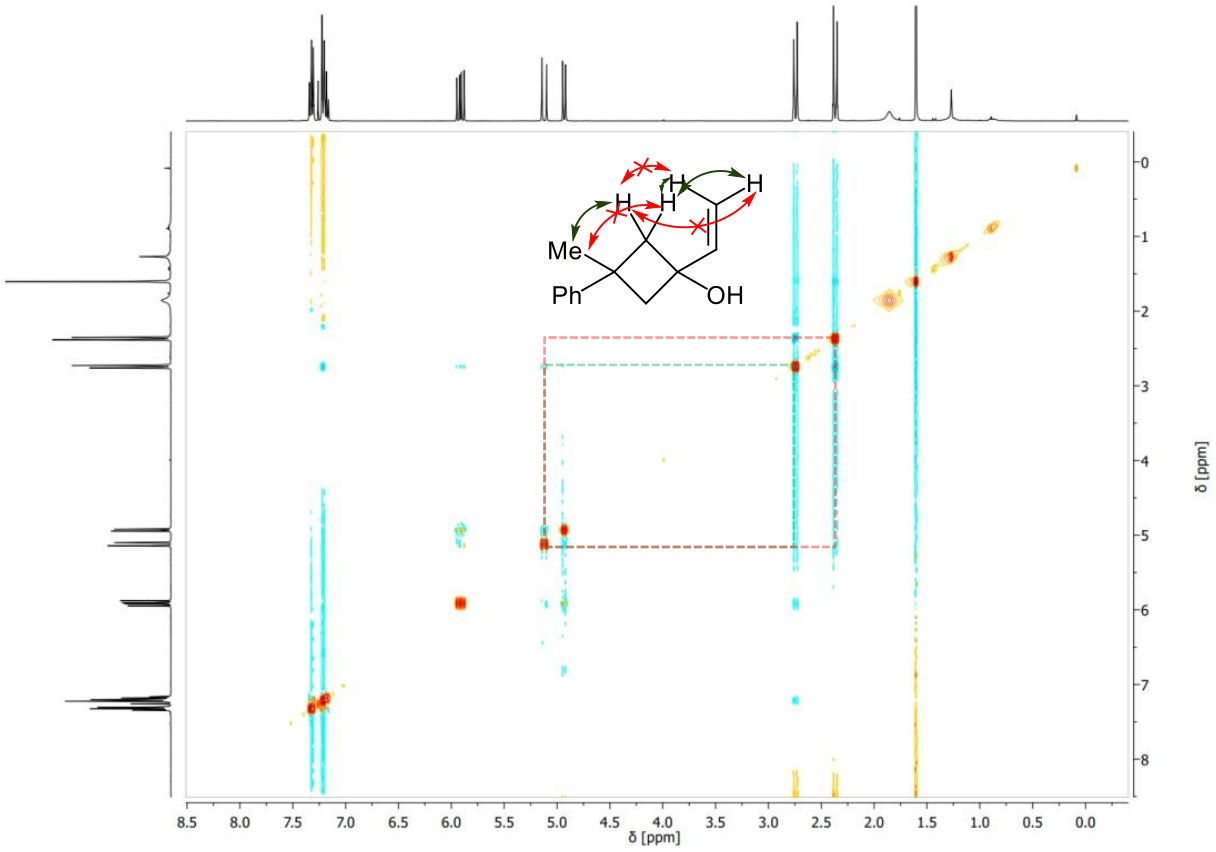






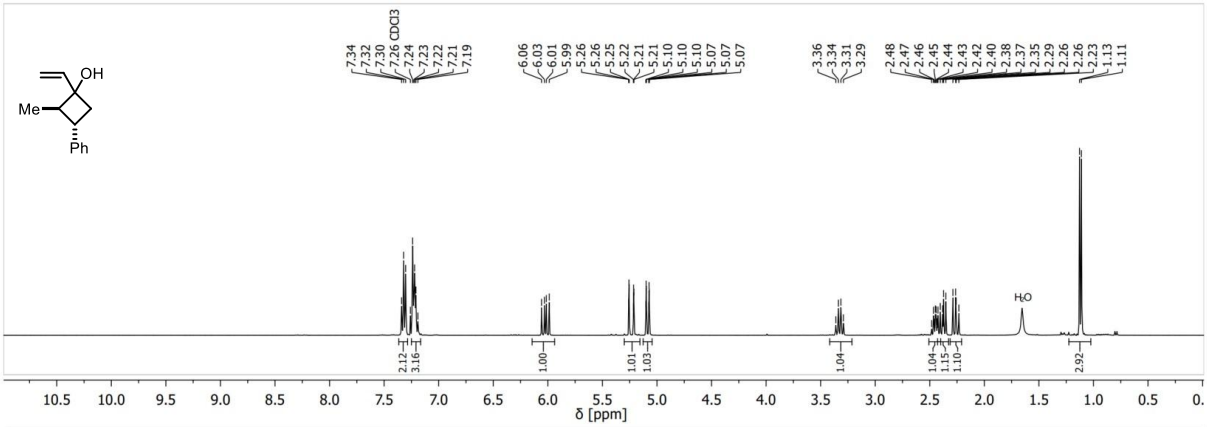
8 Appendix

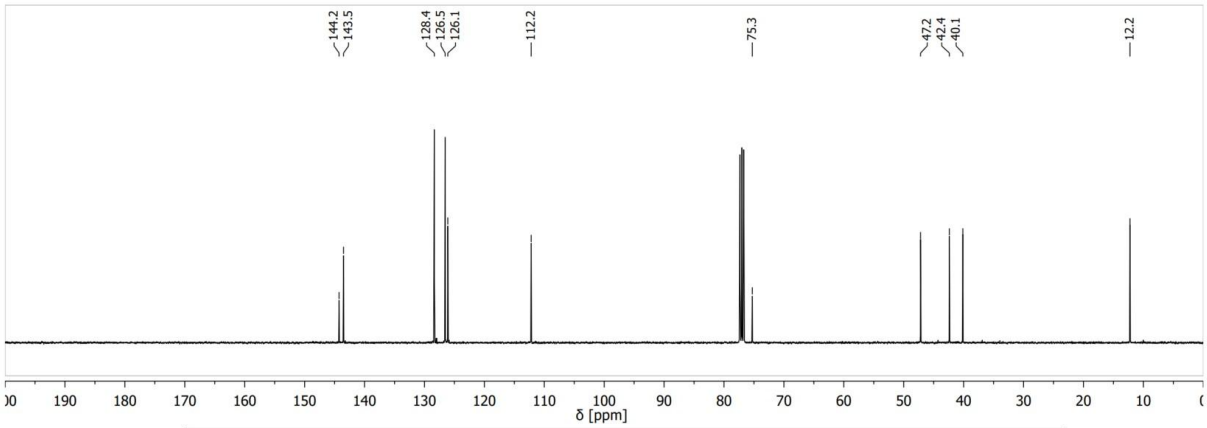
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

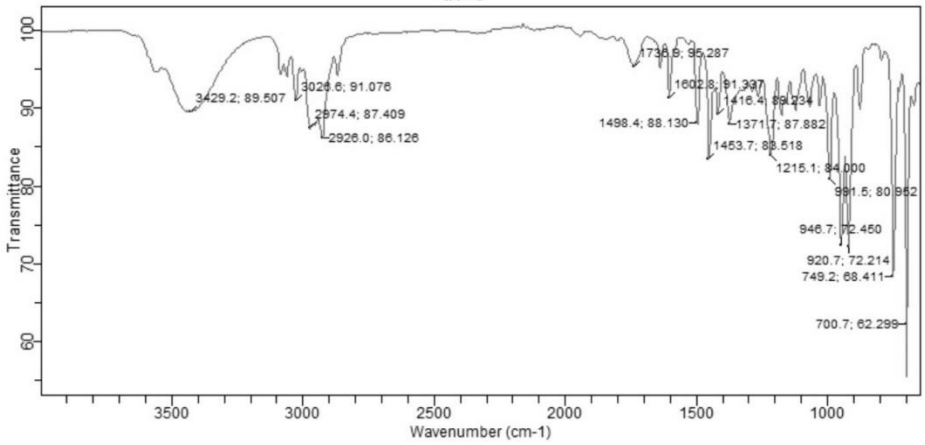


(*trans*)-2-Methyl-3-phenyl-1-vinylcyclobutan-1-ol (174l-*trans*)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

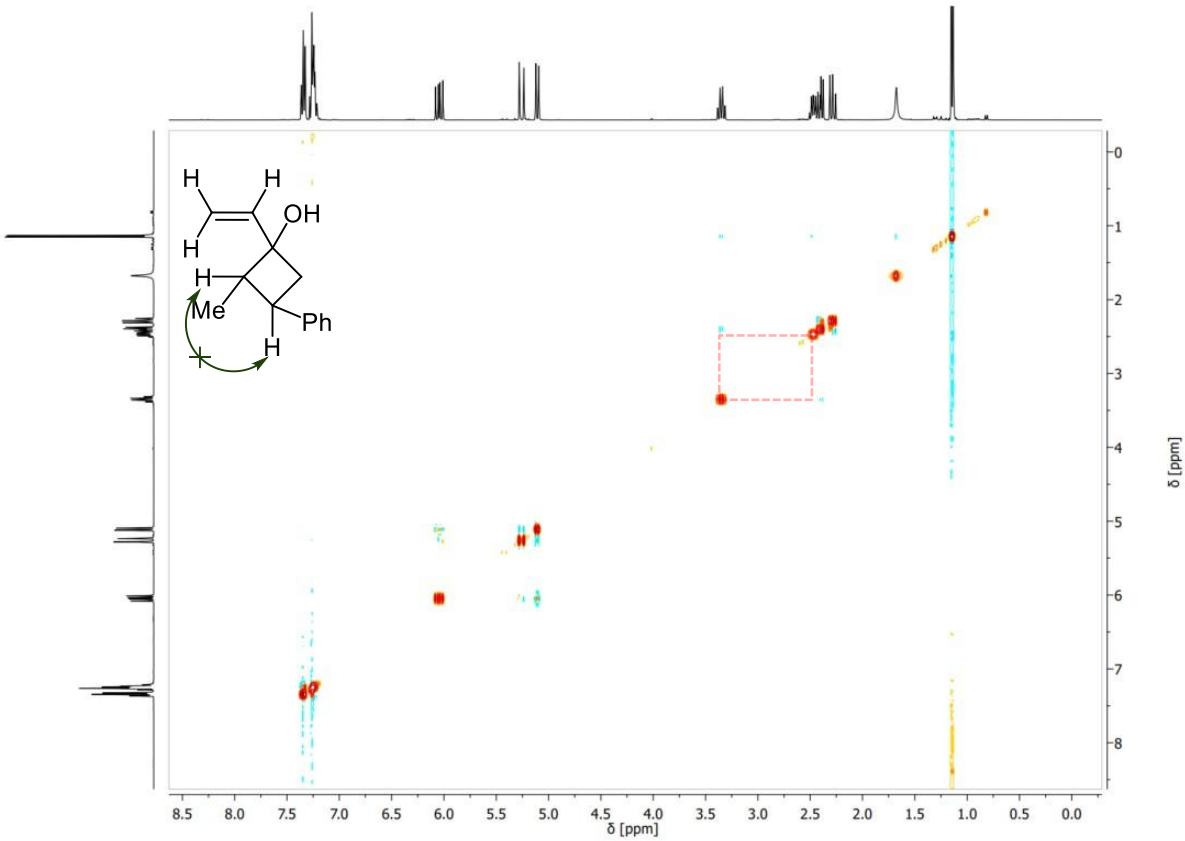






8 Appendix

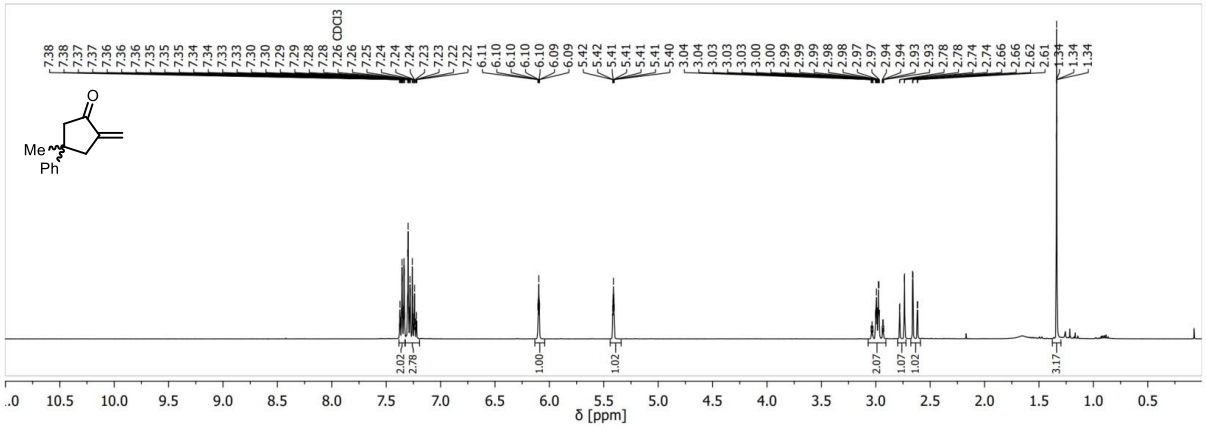
Spectra of project “2-methylenecyclopentan-1-ones” – starting materials

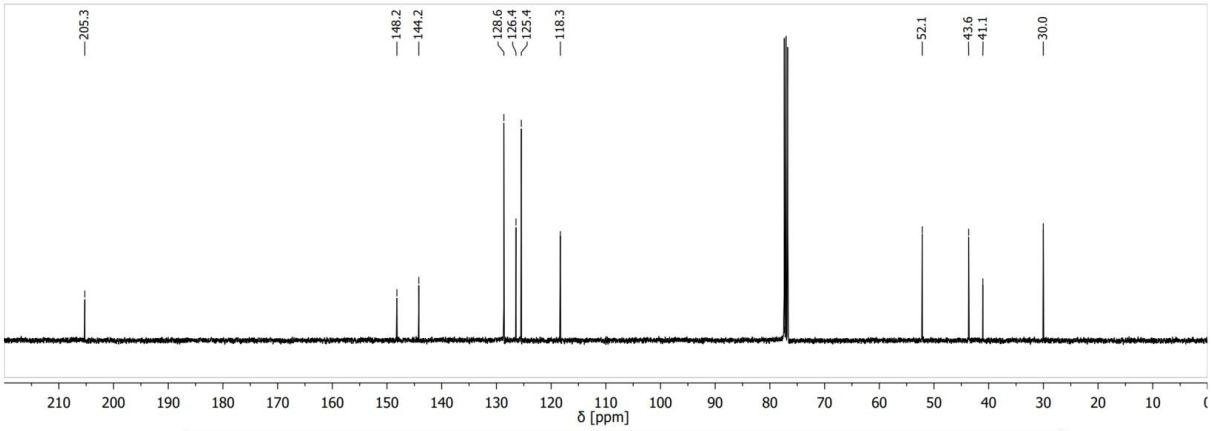


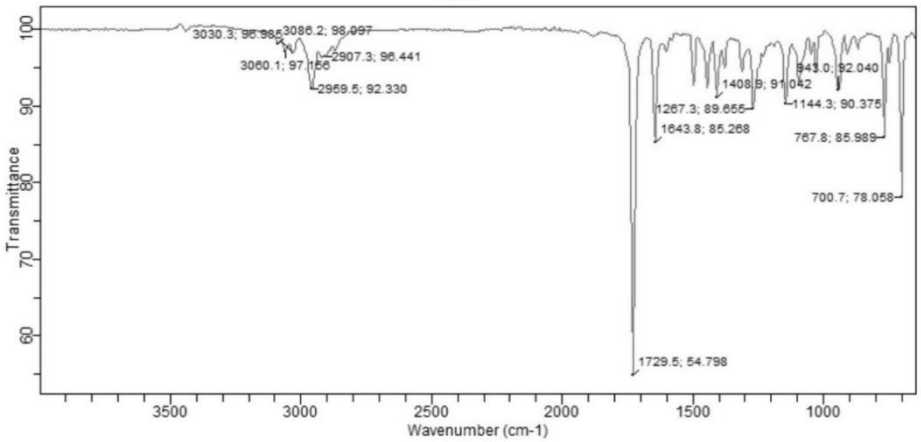
8.4 Spectra of project “2-methylenecyclopentan-1ones” – products

4-Methyl-2-methylene-4-phenylcyclopentan-1-one (178a)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



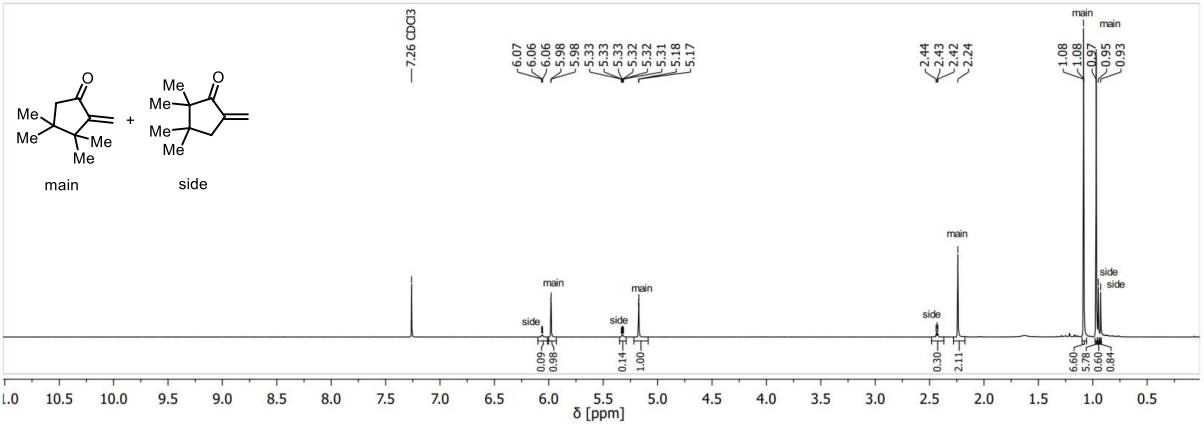


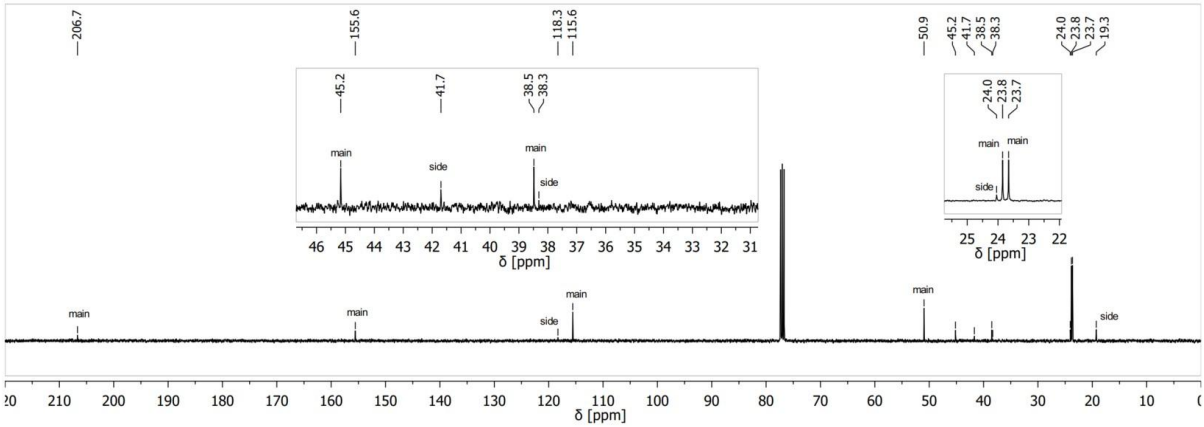


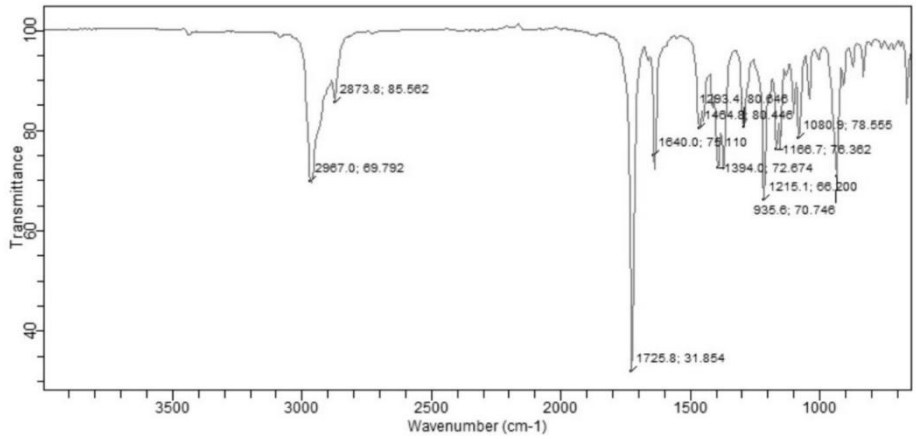
Spectra of project “2-methylenecyclopentan-1ones” – products

3,3,4,4-tetramethyl-2-methylenecyclopentan-1-one and 2,2,3,3-tetramethyl-5-methylenecyclopentan-1-one (178b)

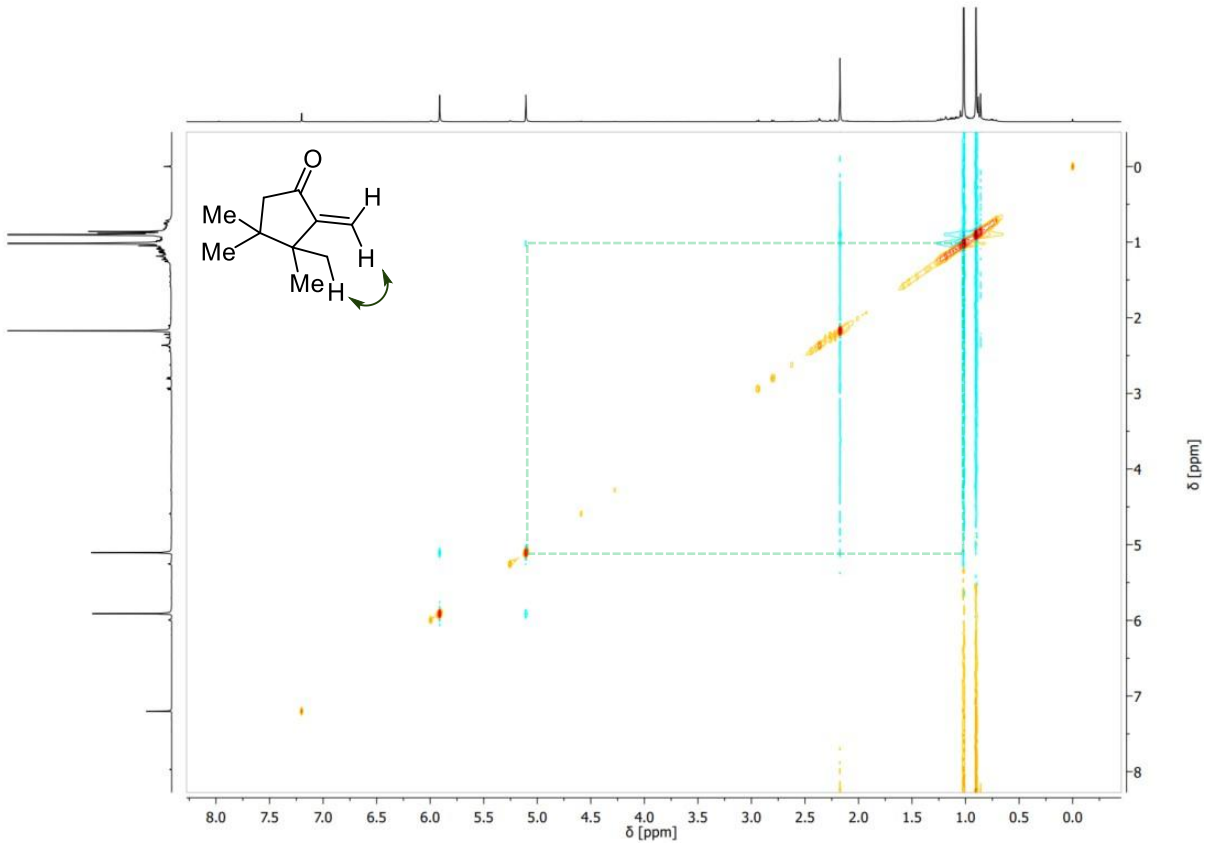
^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz)**:** Chloroform-*d*, **IR**







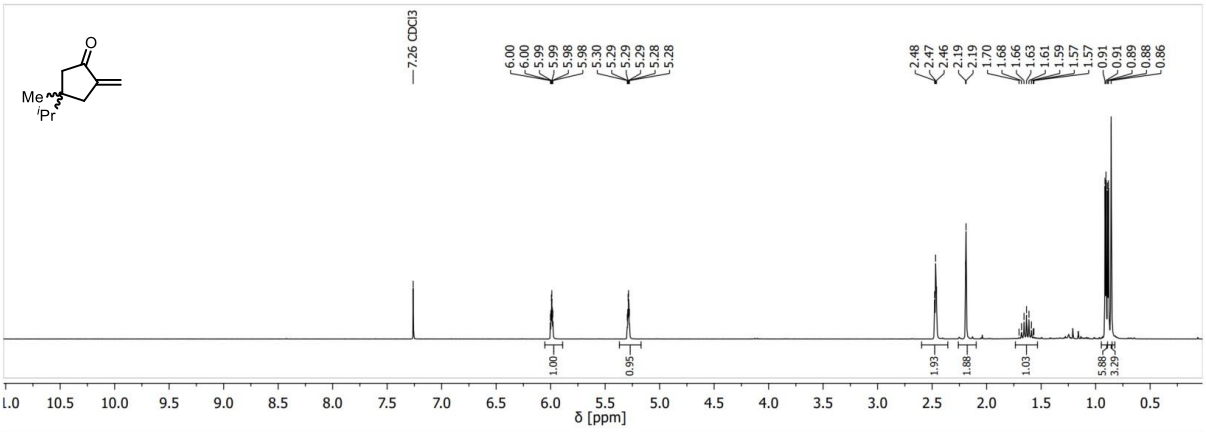
Spectra of project “2-methylenecyclopentan-1ones” – products

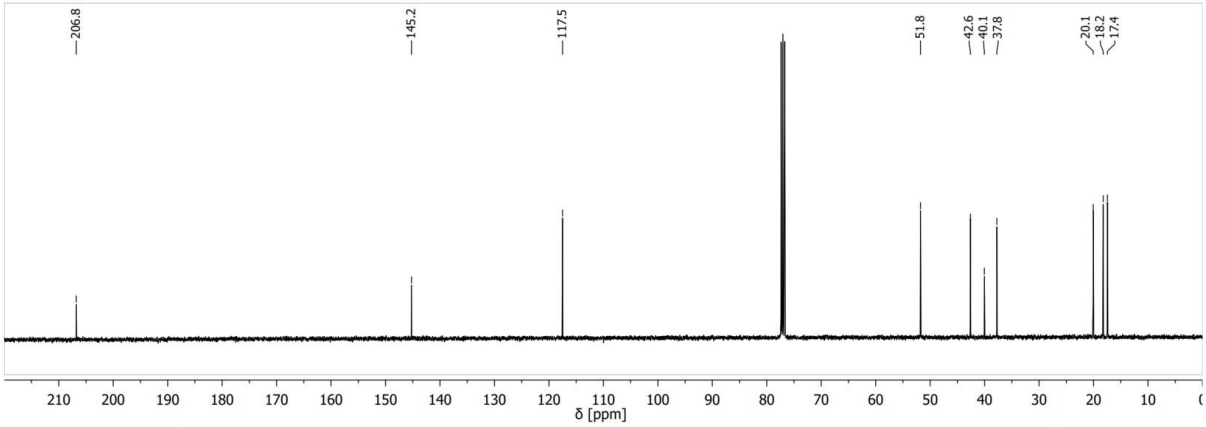


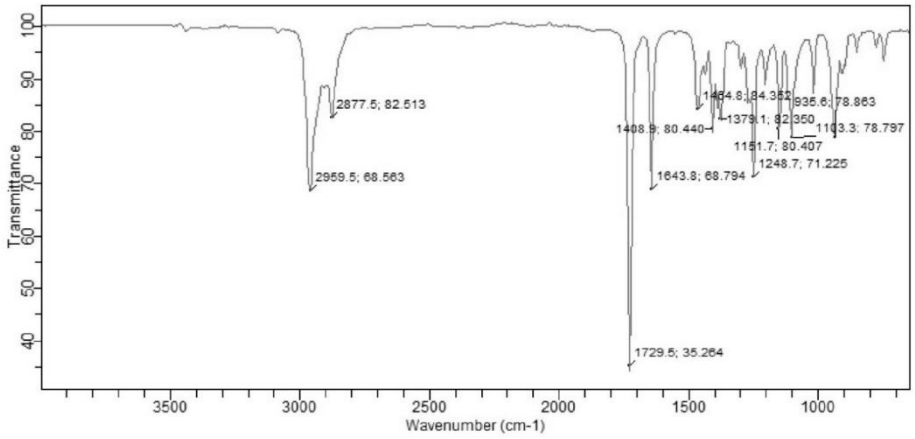
Spectra of project “2-methylenecyclopentan-1ones” – products

4-Isopropyl-4-methyl-2-methylenecyclopentan-1-one (178c)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



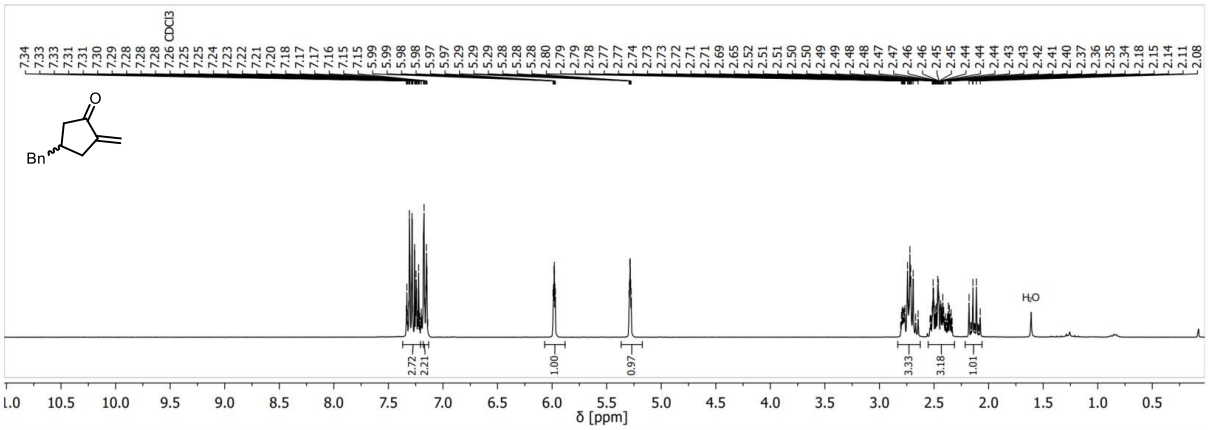


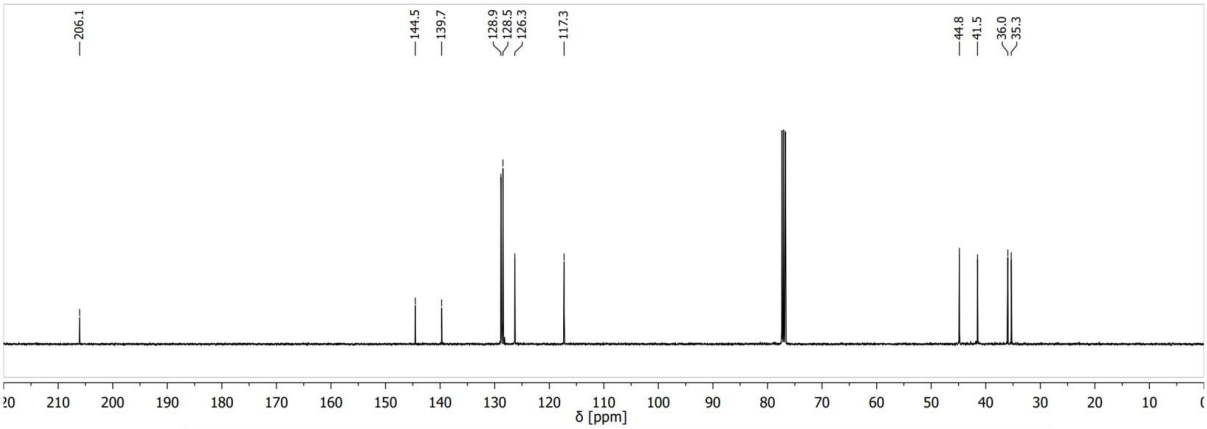


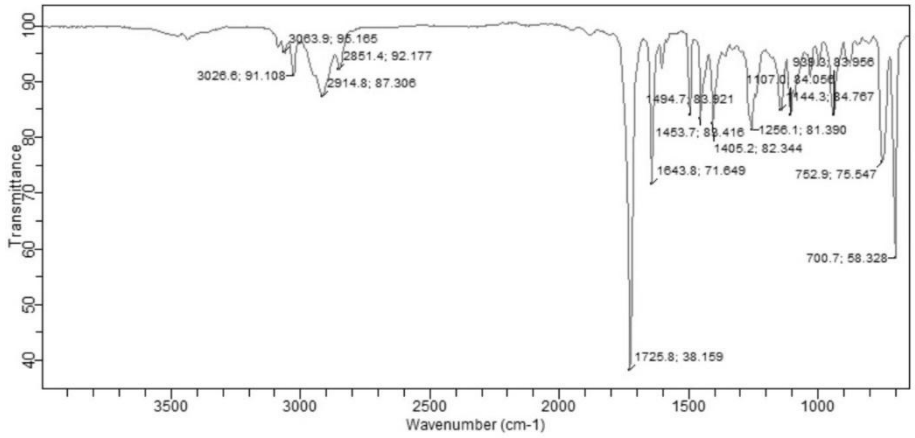
Spectra of project “2-methylenecyclopentan-1ones” – products

4-Benzyl-2-methylenecyclopentan-1-one (178d)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

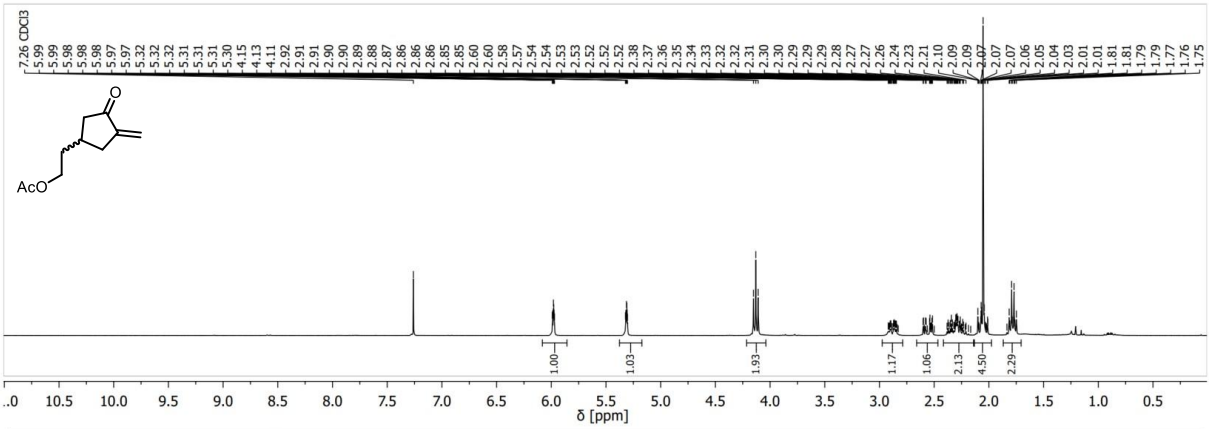


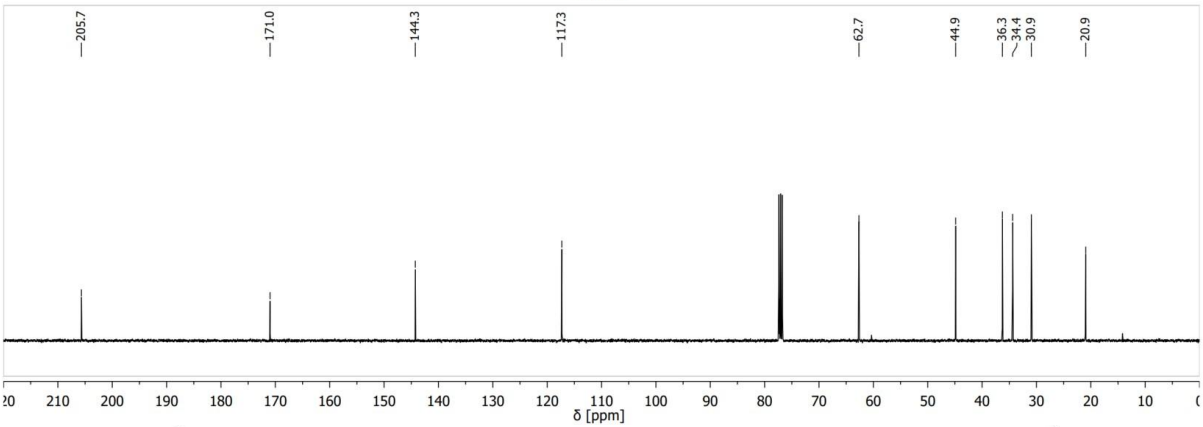


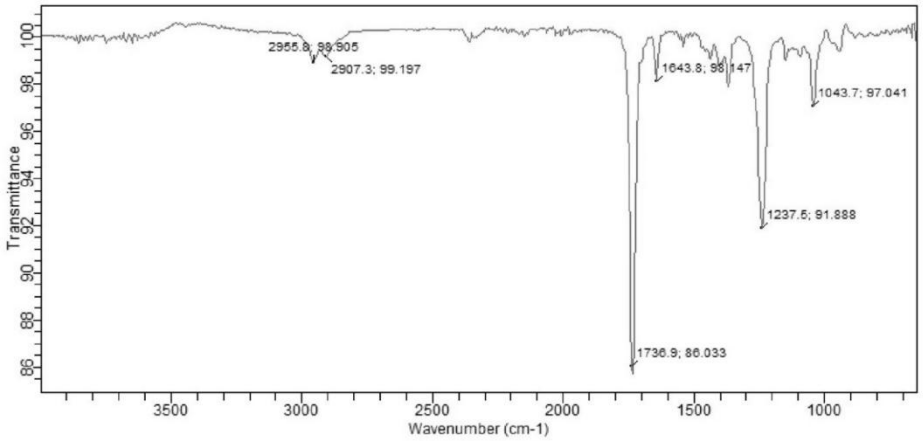


2-(3-Methylene-4-oxocyclopentyl)ethyl acetate (178e)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



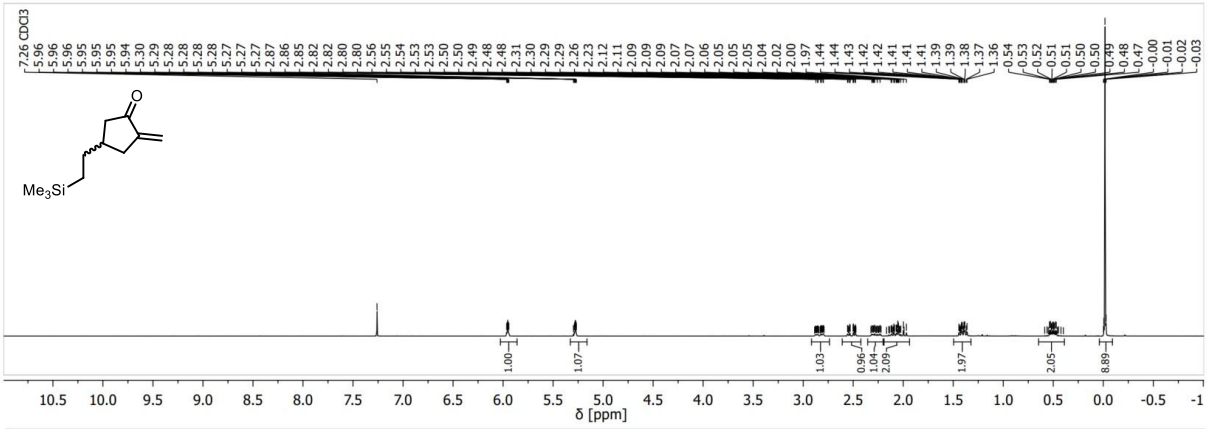


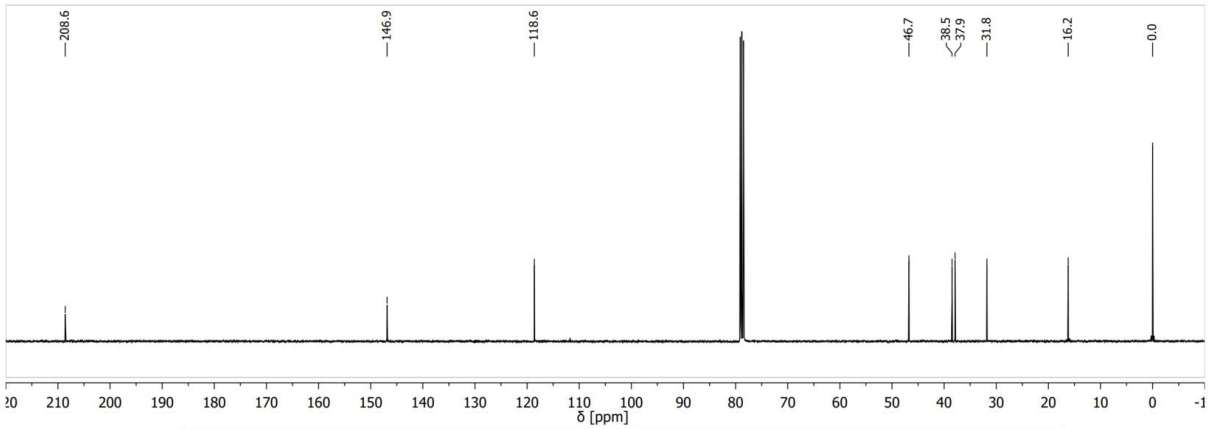


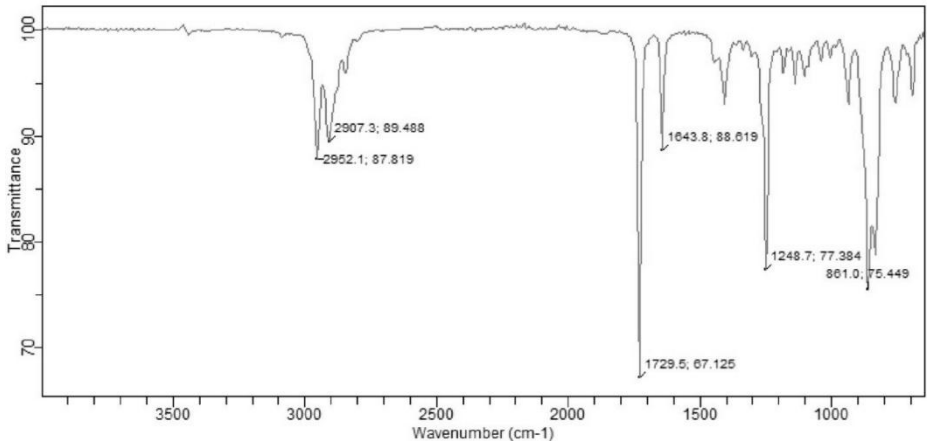
Spectra of project “2-methylenecyclopentan-1ones” – products

2-Methylene-4-(2-(trimethylsilyl)ethyl)cyclopentan-1-one (178f)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**

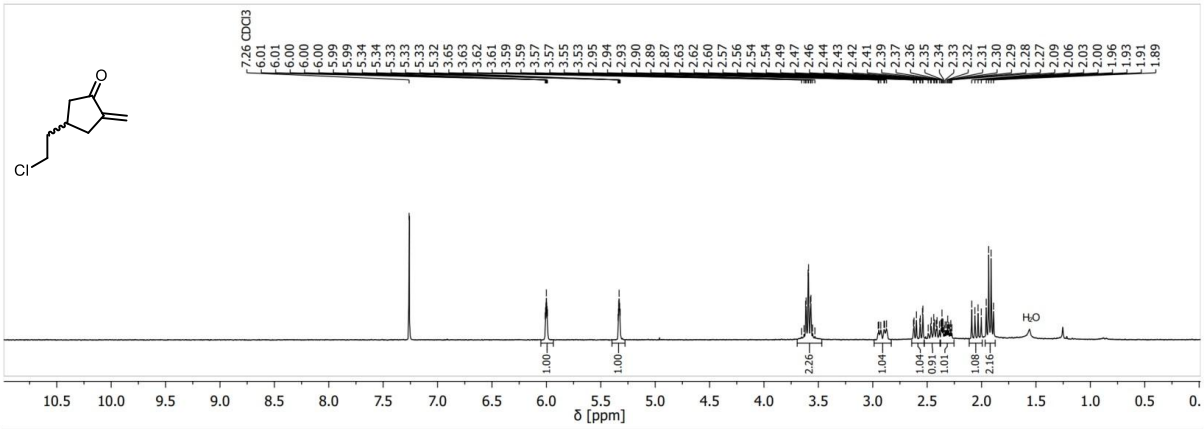


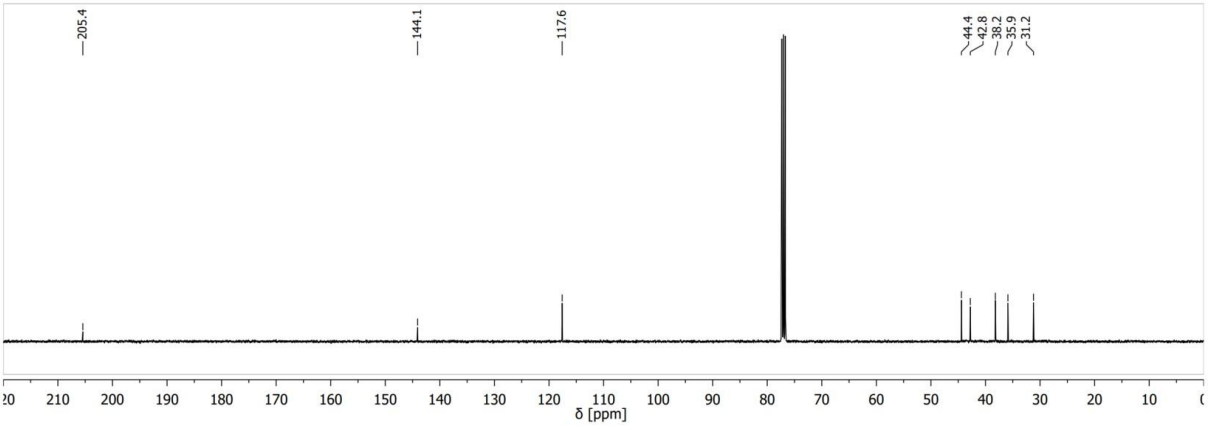


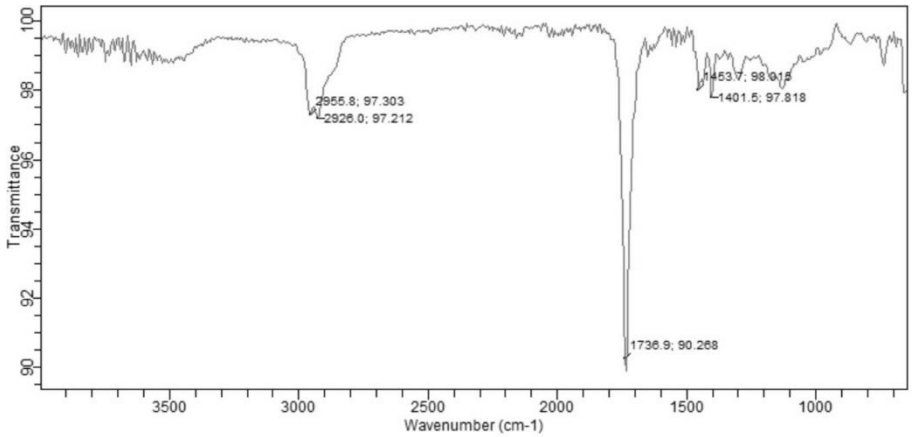


4-(2-Chloroethyl)-2-methylenecyclopentan-1-one (178g)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



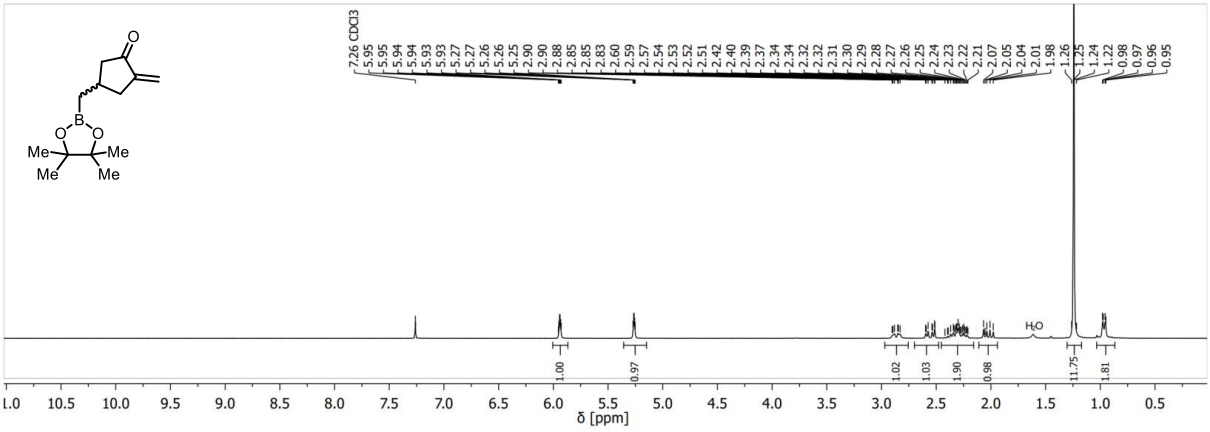


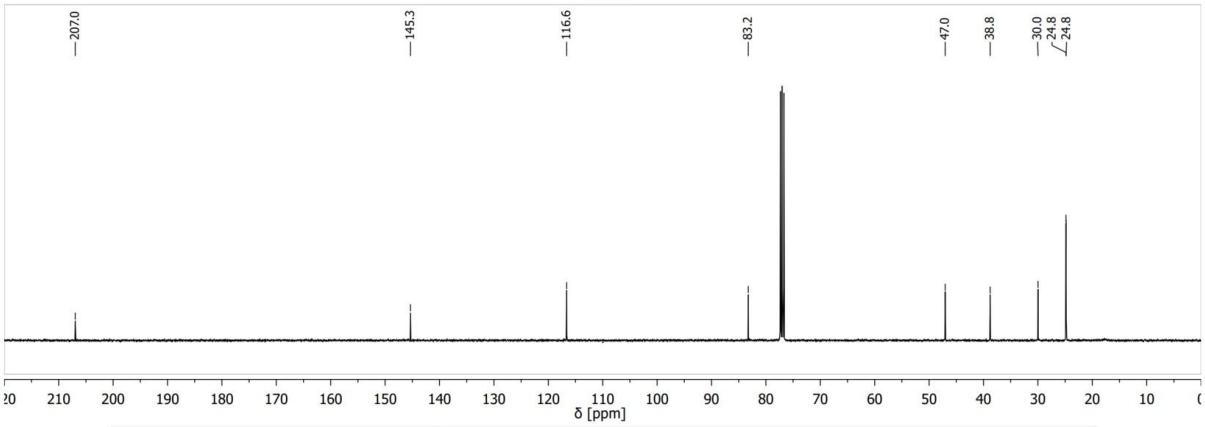


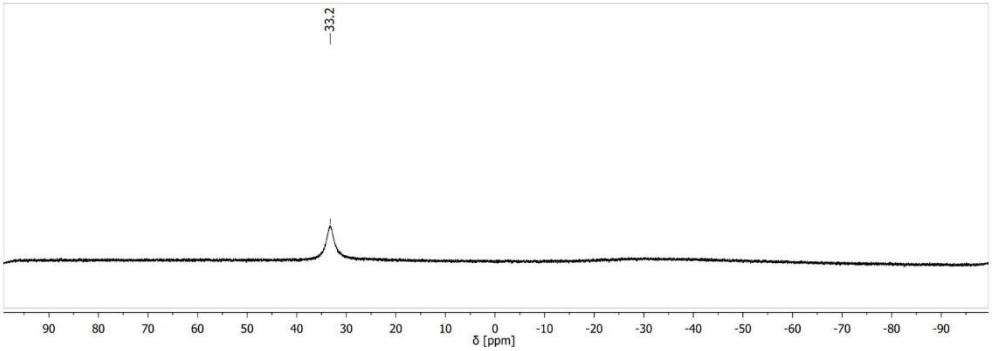
Spectra of project “2-methylenecyclopentan-1ones” – products

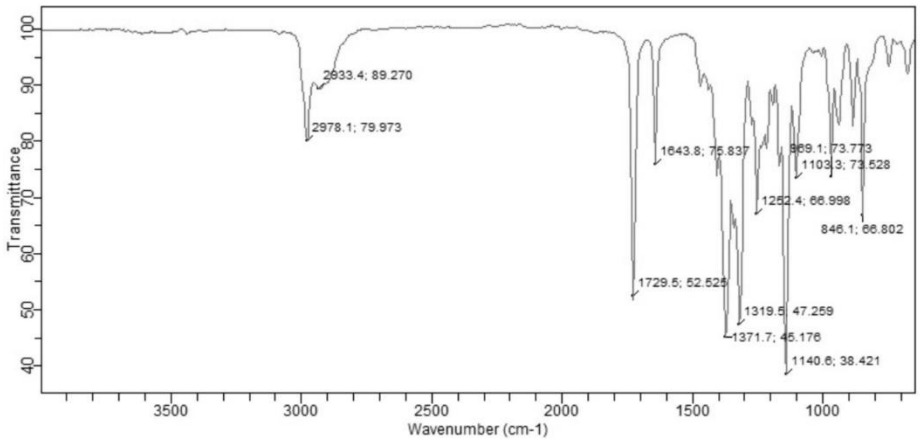
2-Methylene-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclopentan-1-one (178h)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **^{11}B NMR** (128 MHz): Chloroform-*d*, **IR**





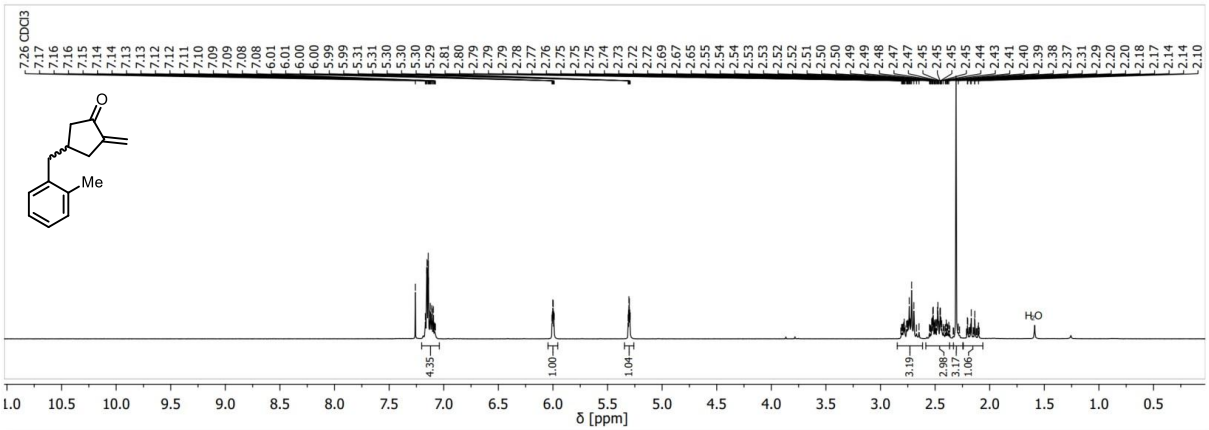


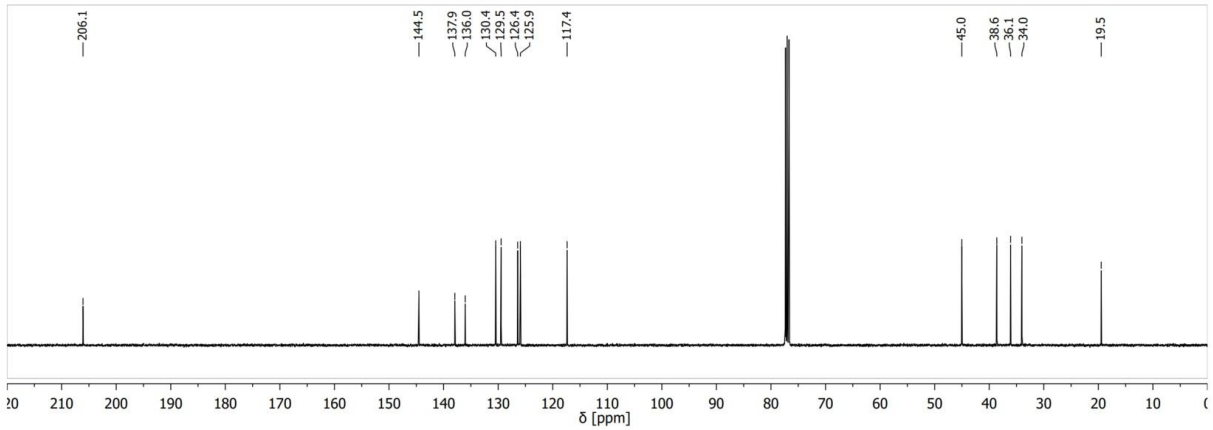


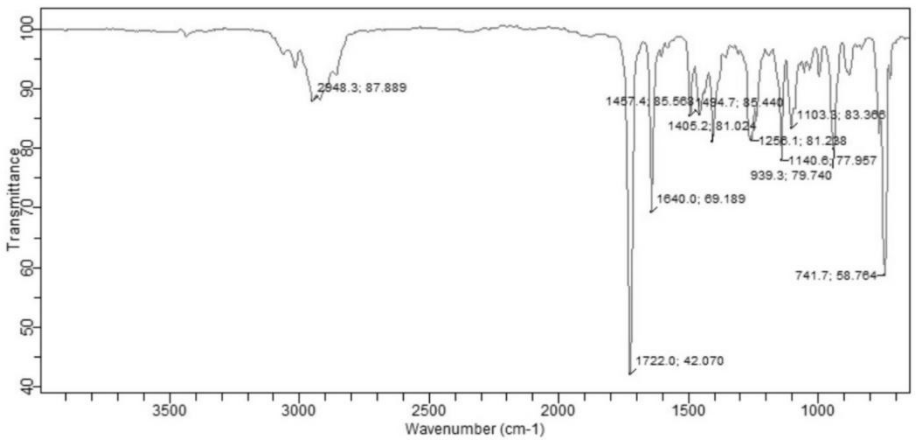
Spectra of project “2-methylenecyclopentan-1ones” – products

4-(2-Methylbenzyl)-2-methylenecyclopentan-1-one (178i)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



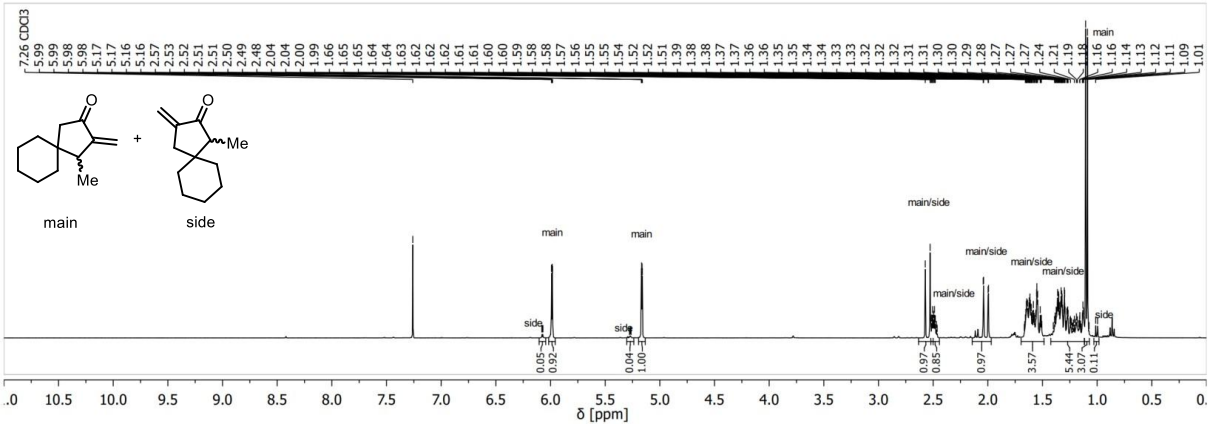


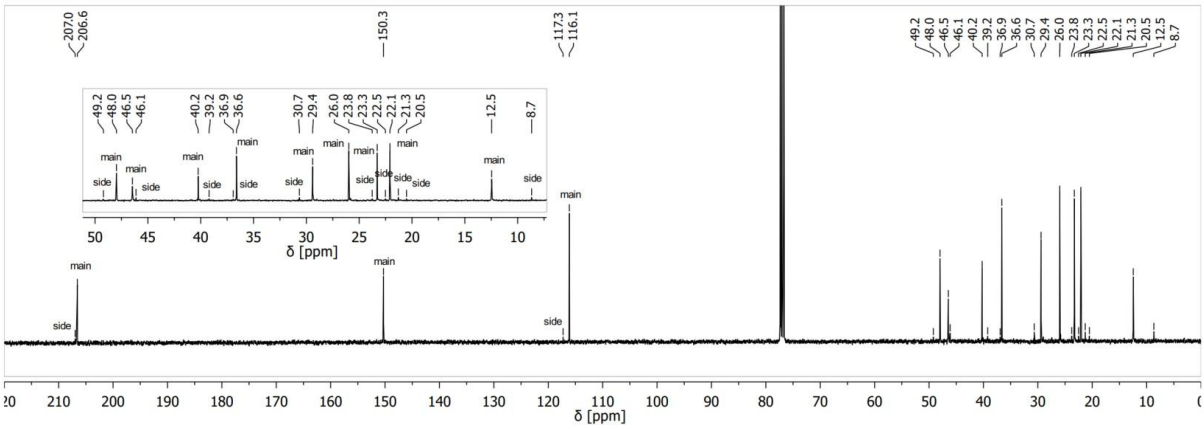


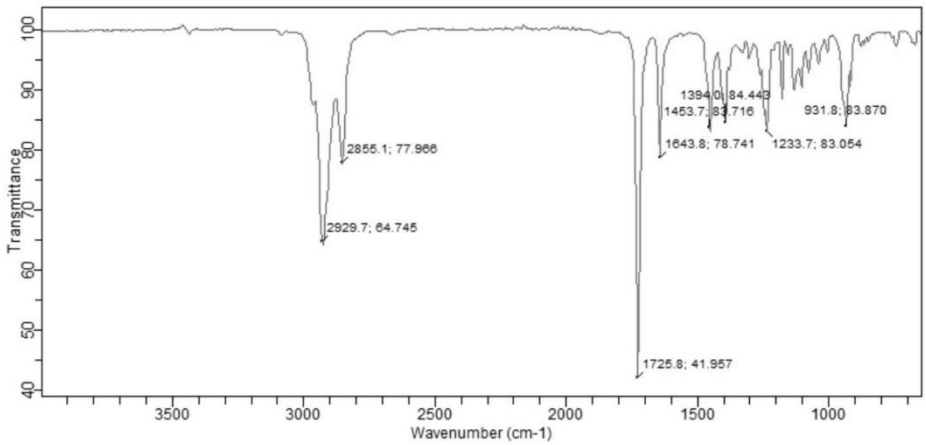
Spectra of project “2-methylenecyclopentan-1ones” – products

4-Methyl-3-methylenespiro[4.5]decan-2-one and 1-methyl-3-methyl-enespiro[4.5]decan-2-one (178j)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **HSQC**, **HMBC** (400 MHz/101 MHz): Chloroform-*d*, **IR**

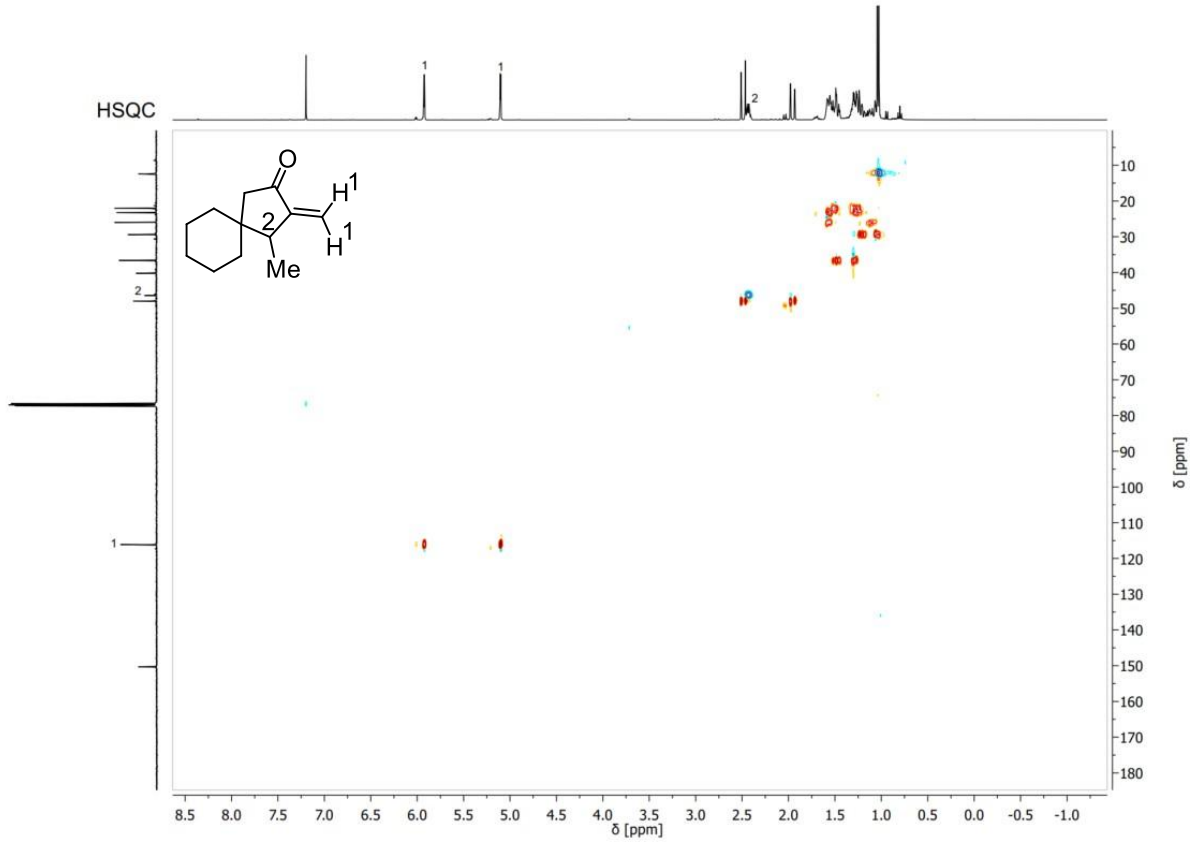


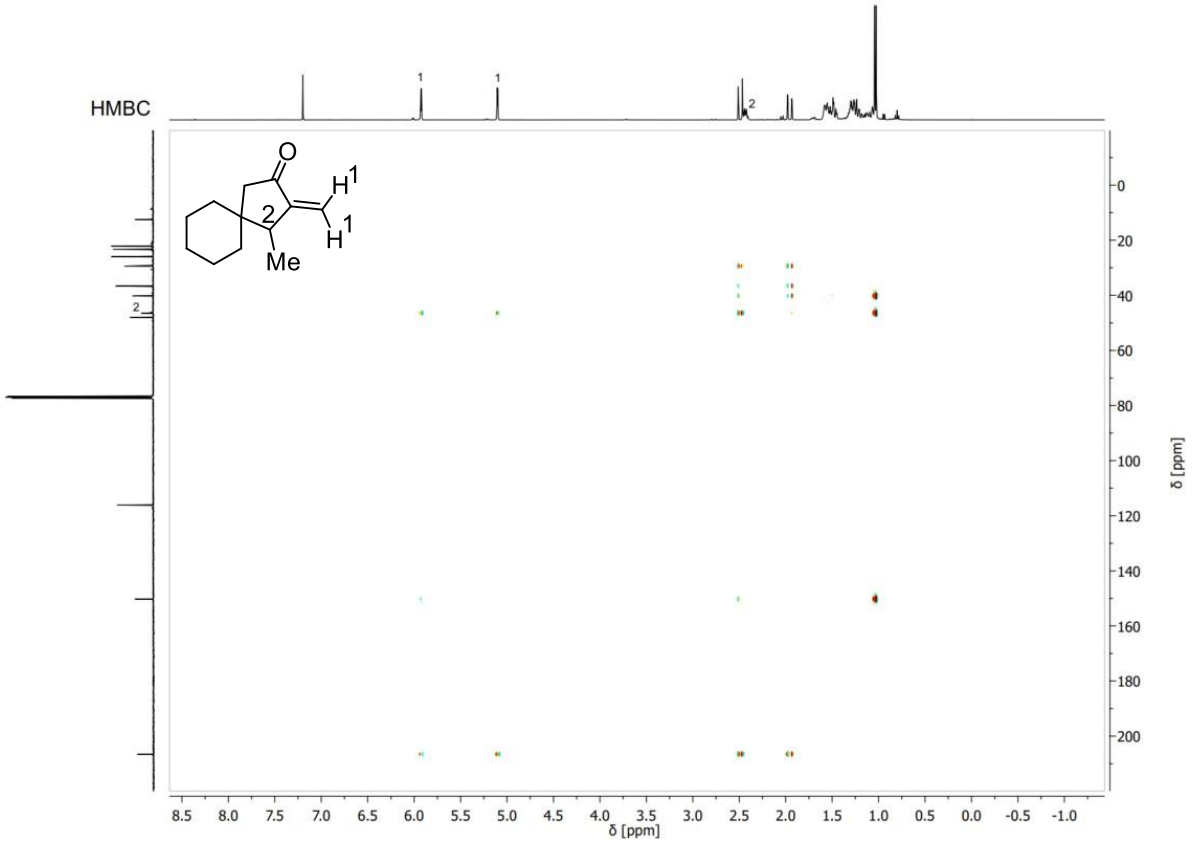




8 Appendix

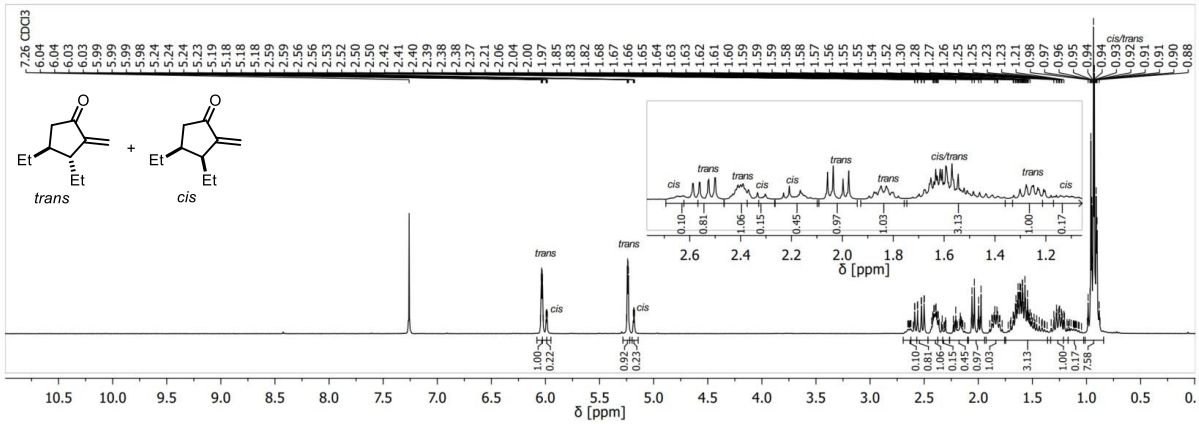
Spectra of project “2-methylenecyclopentan-1ones” – products

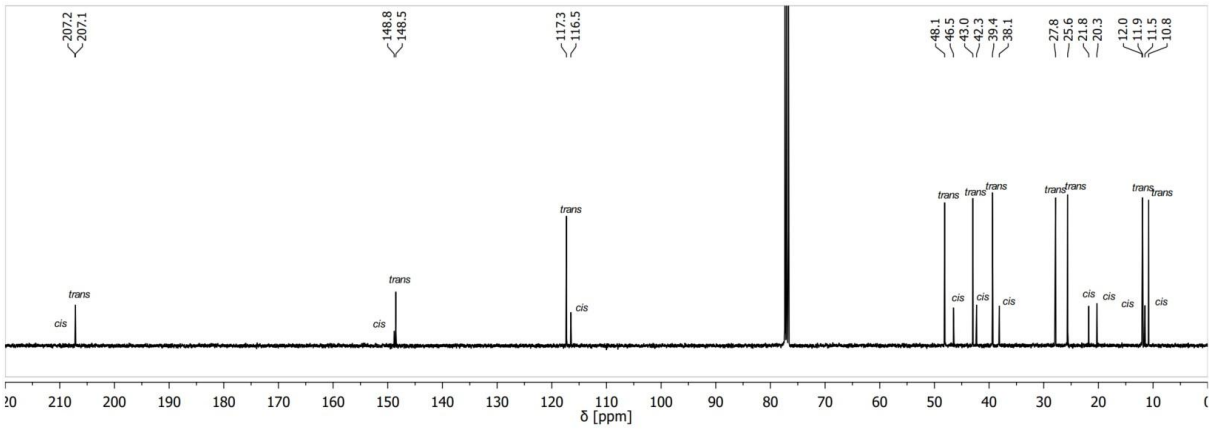


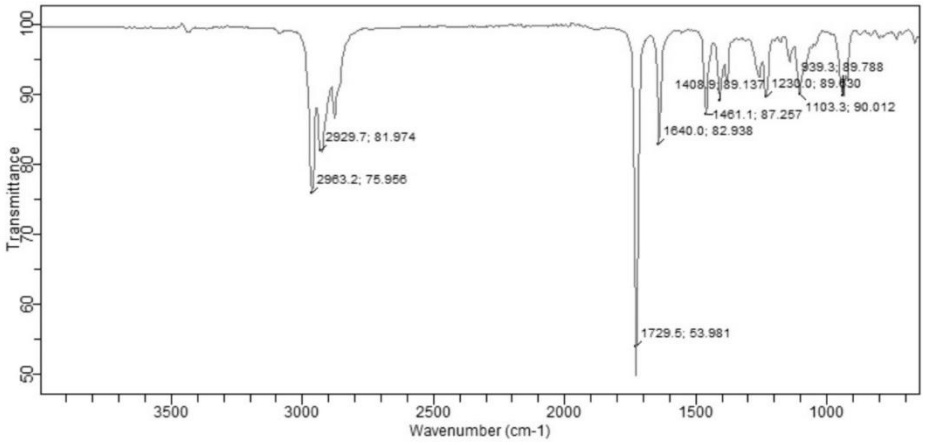


3,4-Diethyl-2-methylenecyclopentan-1-one (178k)

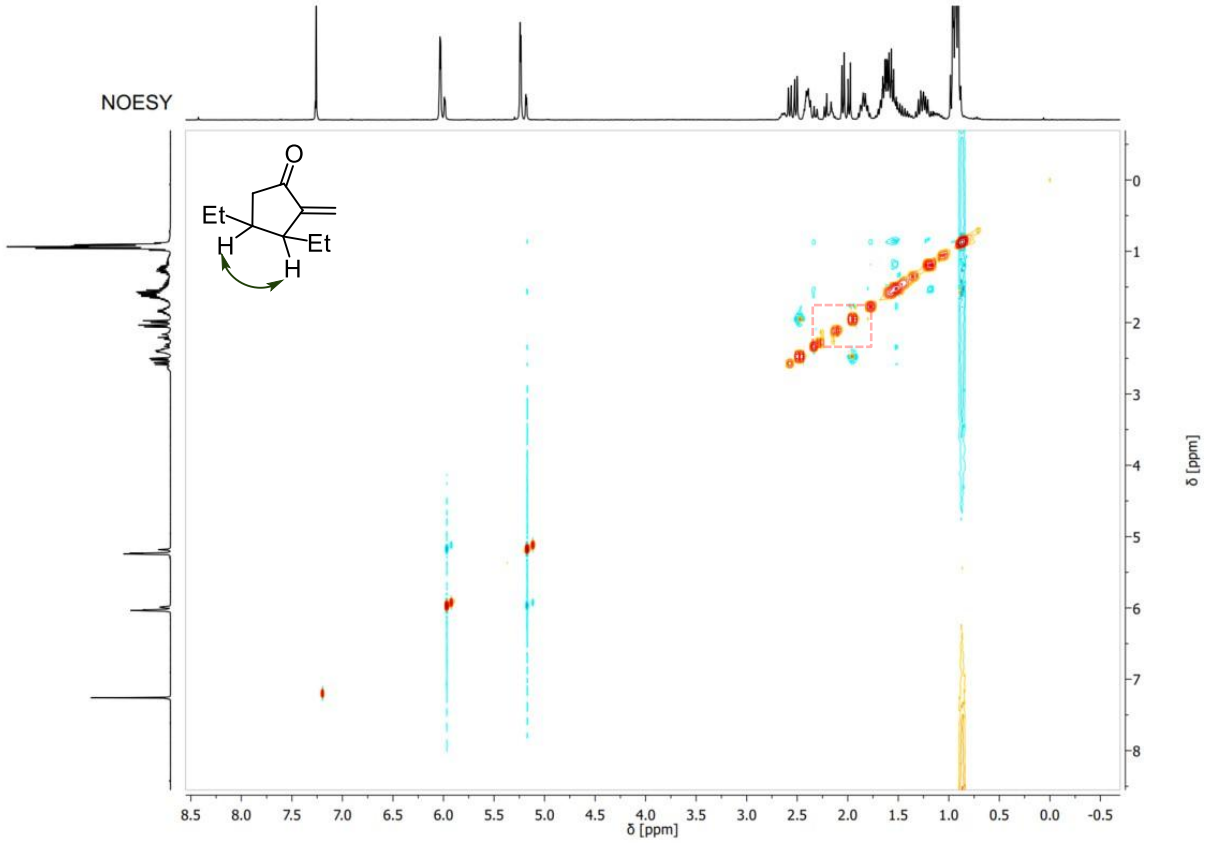
^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz)**, HSQC**, **HMBC** (400 MHz/101 MHz): Chloroform-*d*, **IR**

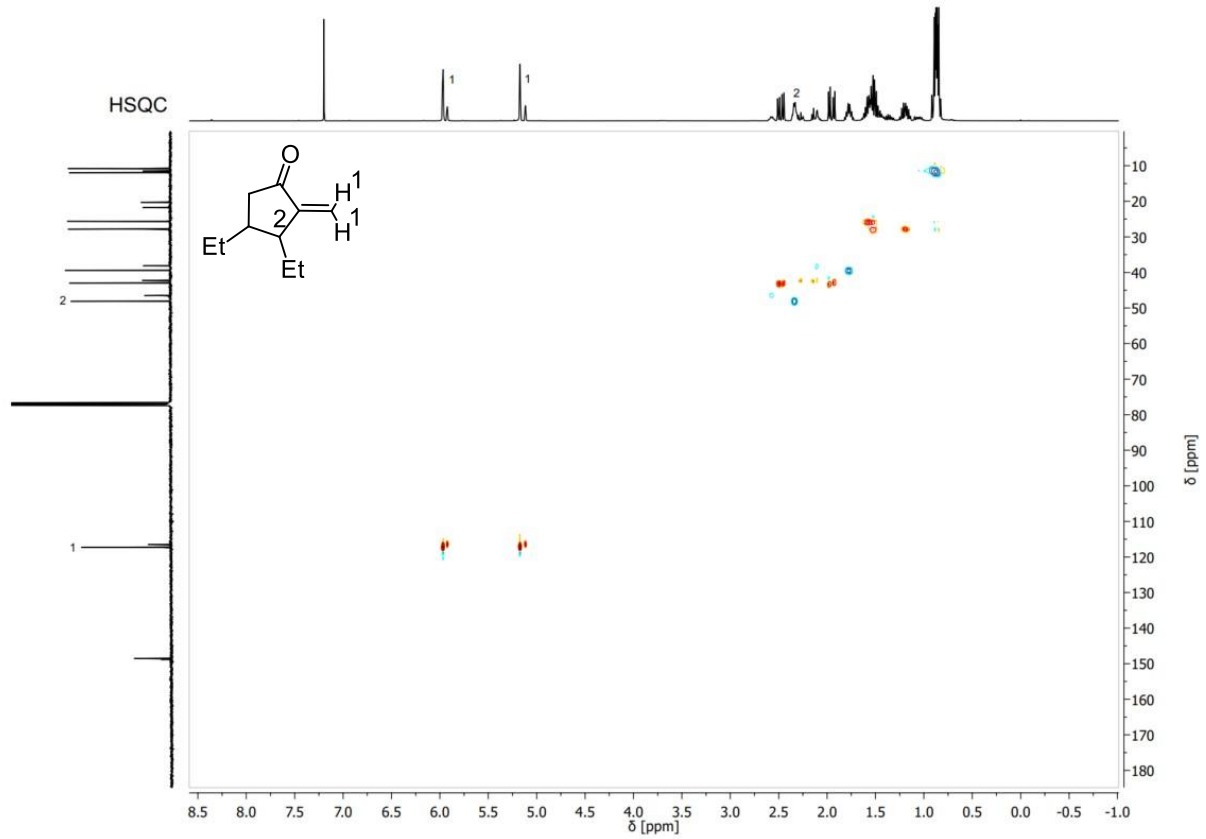






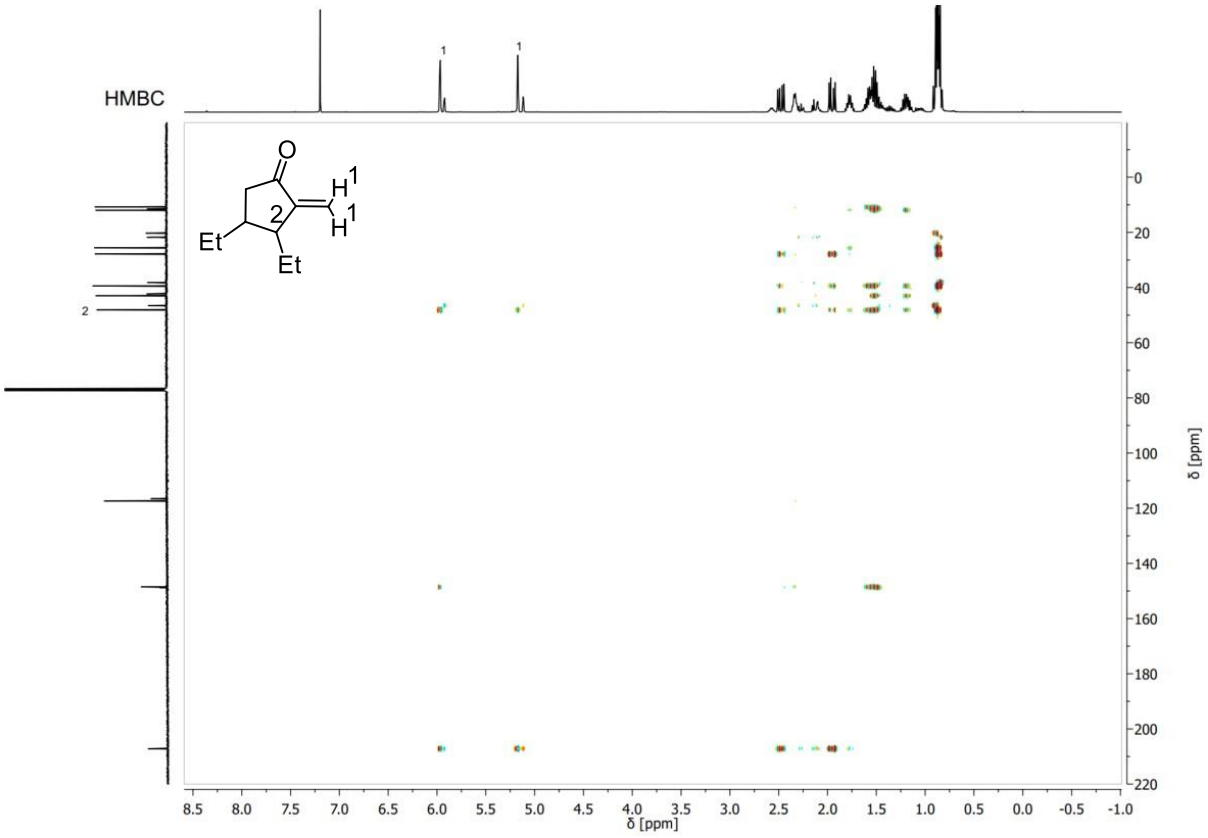
Spectra of project “2-methylenecyclopentan-1ones” – products





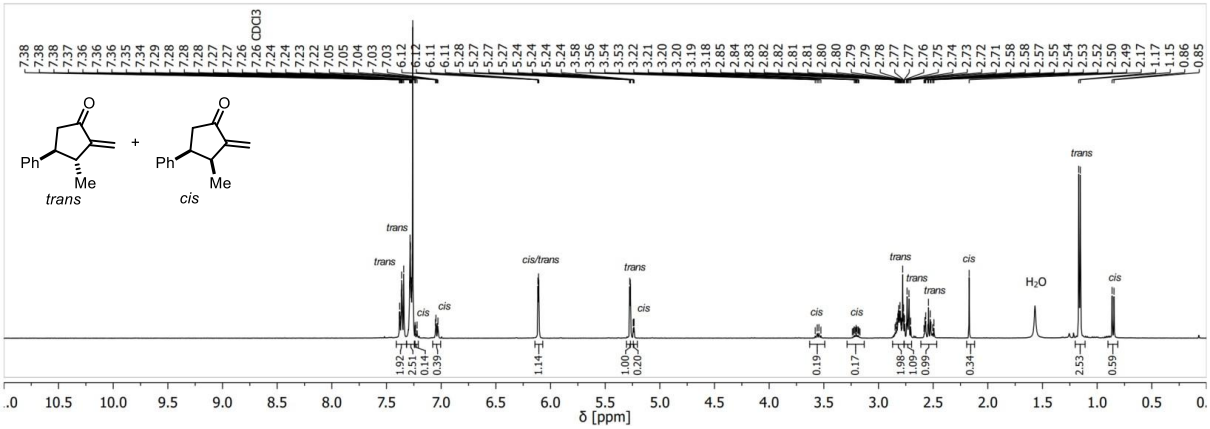
8 Appendix

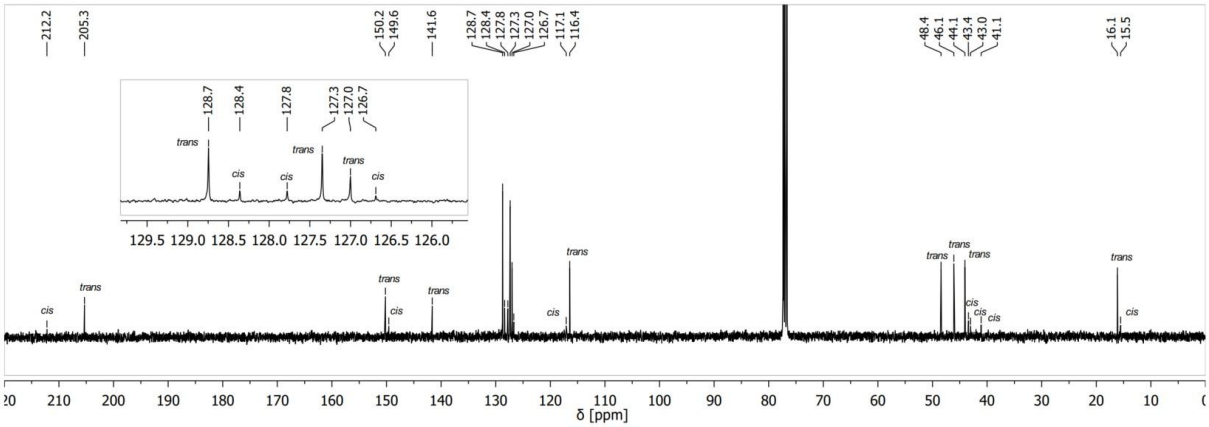
Spectra of project “2-methylenecyclopentan-1ones” – products

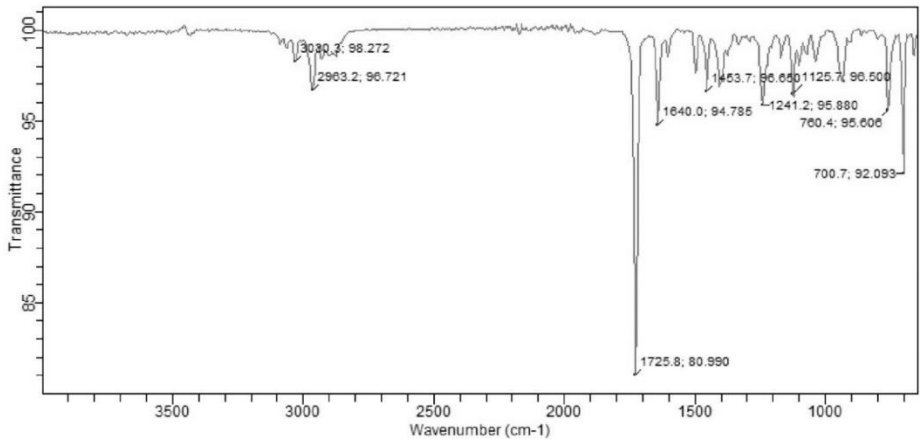


3-Methyl-2-methylene-4-phenylcyclopentan-1-one (178l-main)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

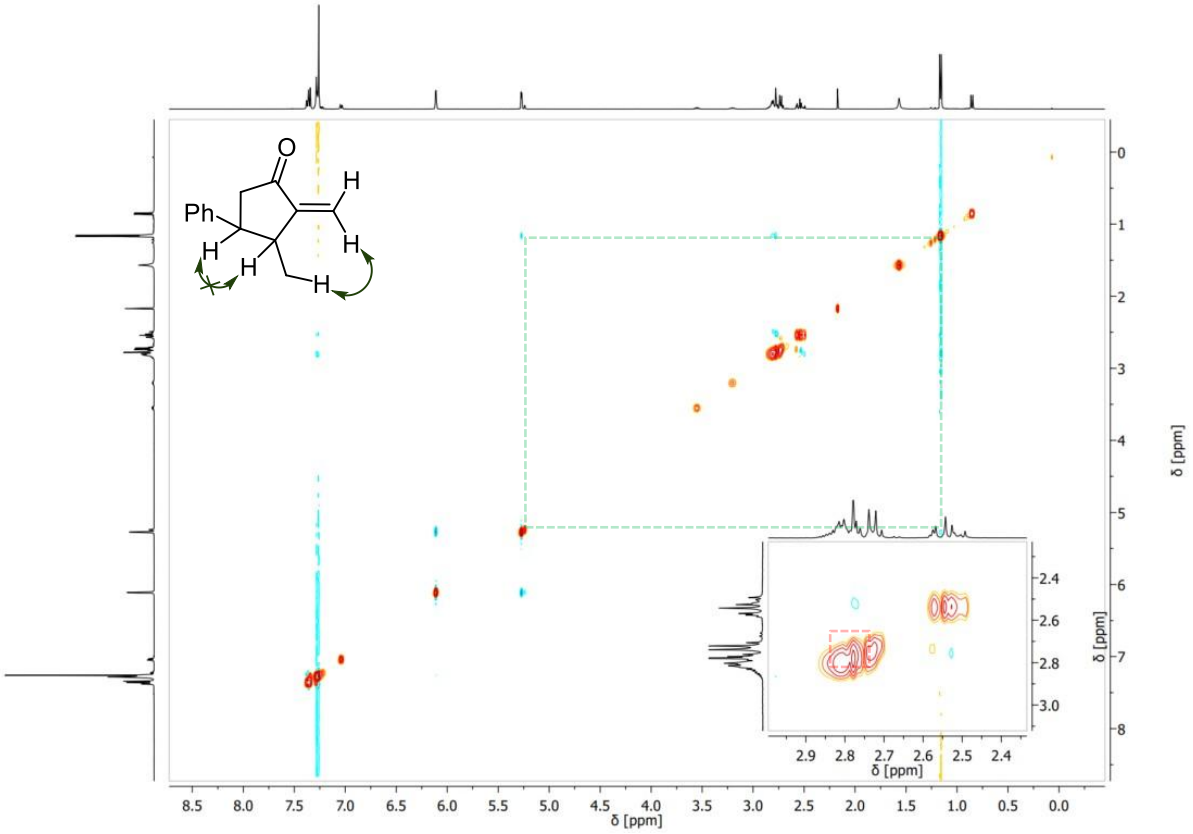






8 Appendix

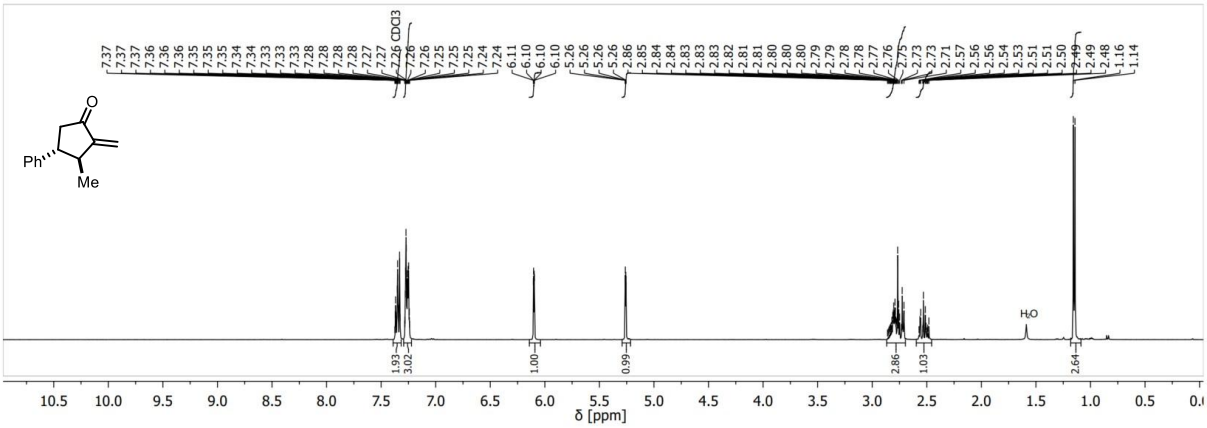
Spectra of project “2-methylenecyclopentan-1ones” – products

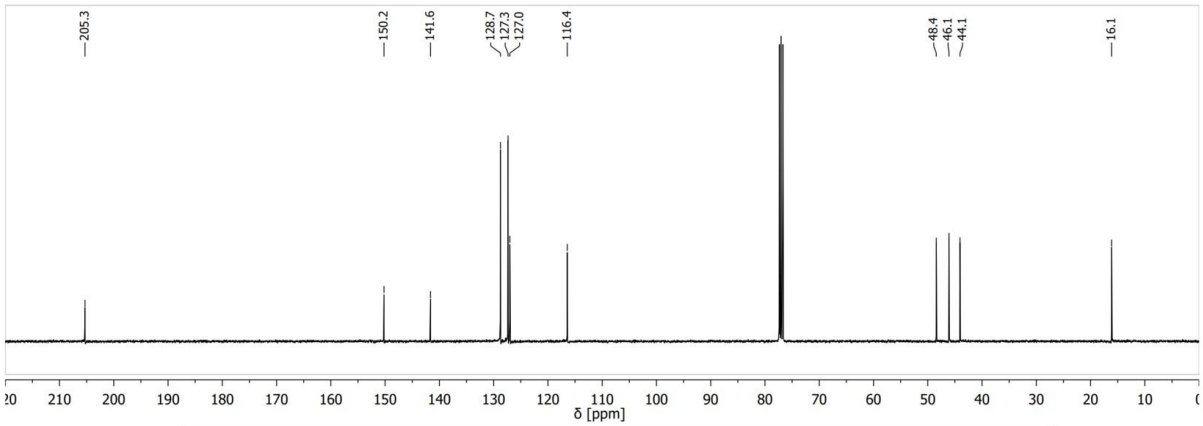


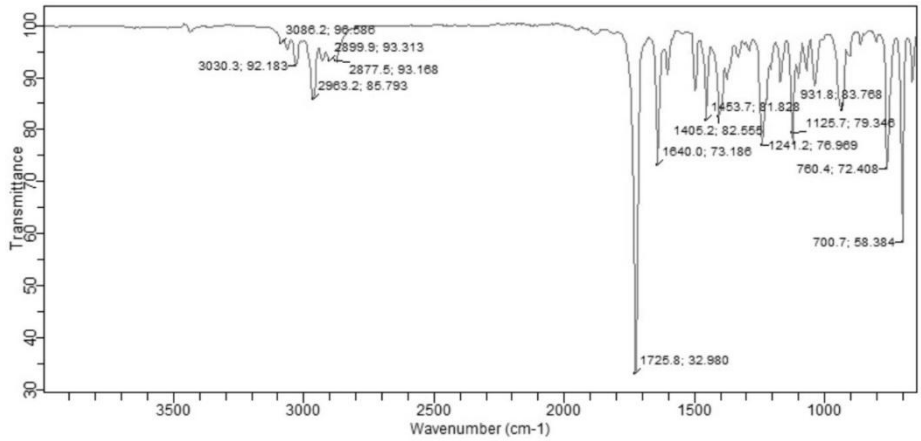
Spectra of project “2-methylenecyclopentan-1ones” – products

(*trans*)-3-Methyl-2-methylene-4-phenylcyclopentan-1-one (178l-*trans*)

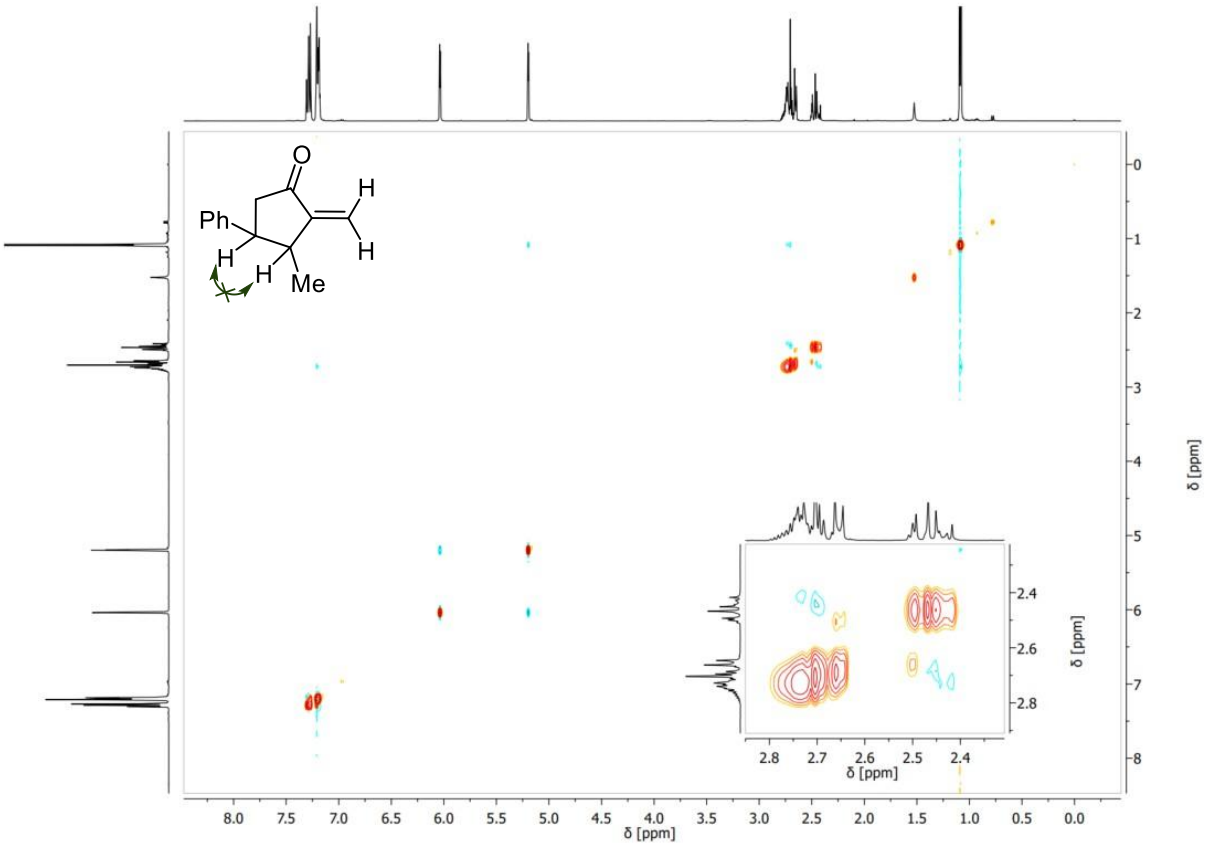
^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**





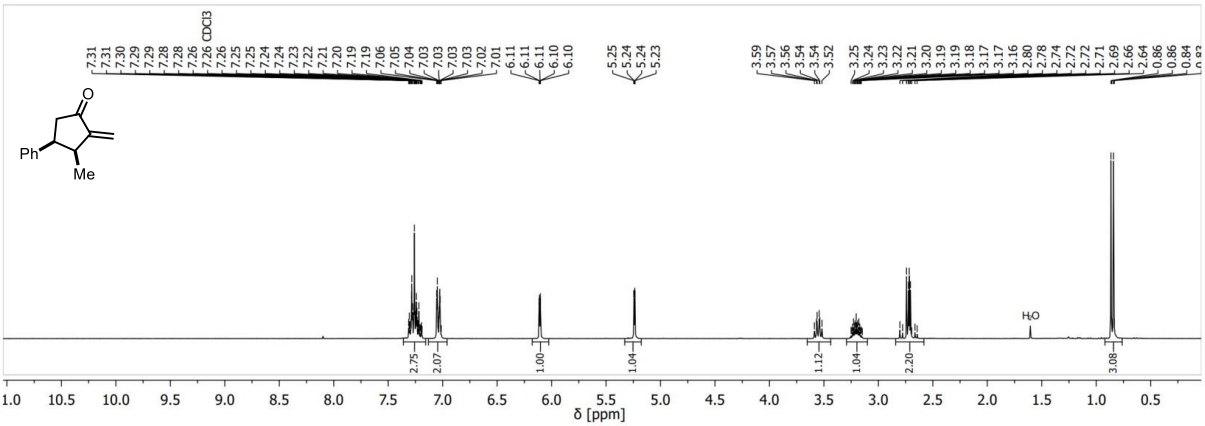


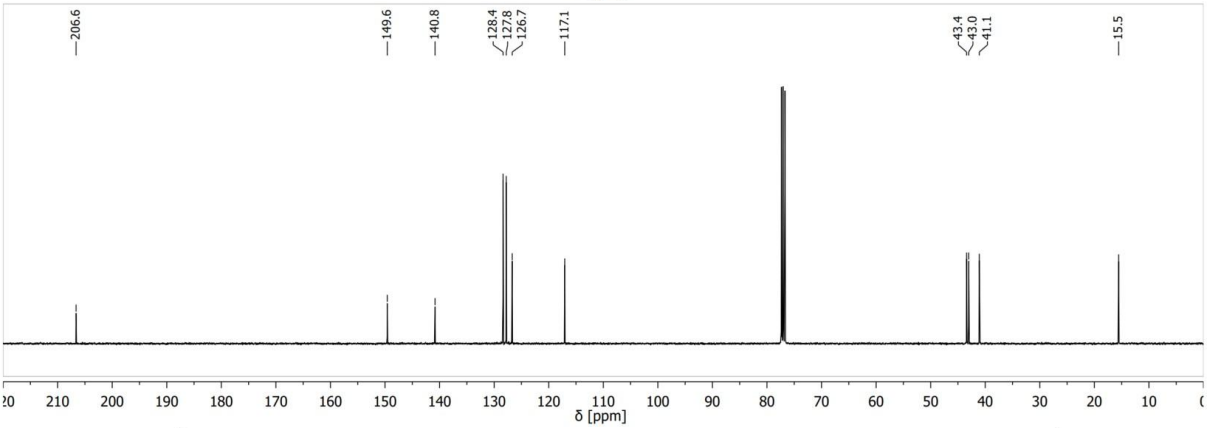
Spectra of project “2-methylenecyclopentan-1ones” – products

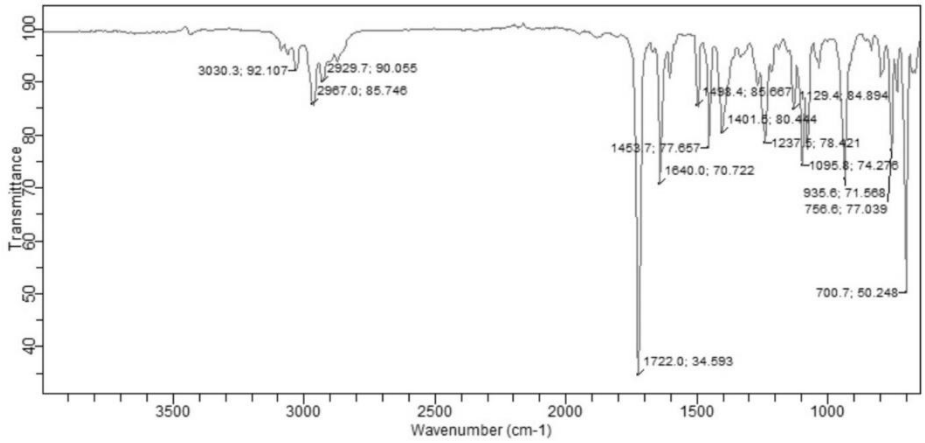


(*cis*)-3-Methyl-2-methylene-4-phenylcyclopentan-1-one (178l-*cis*)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

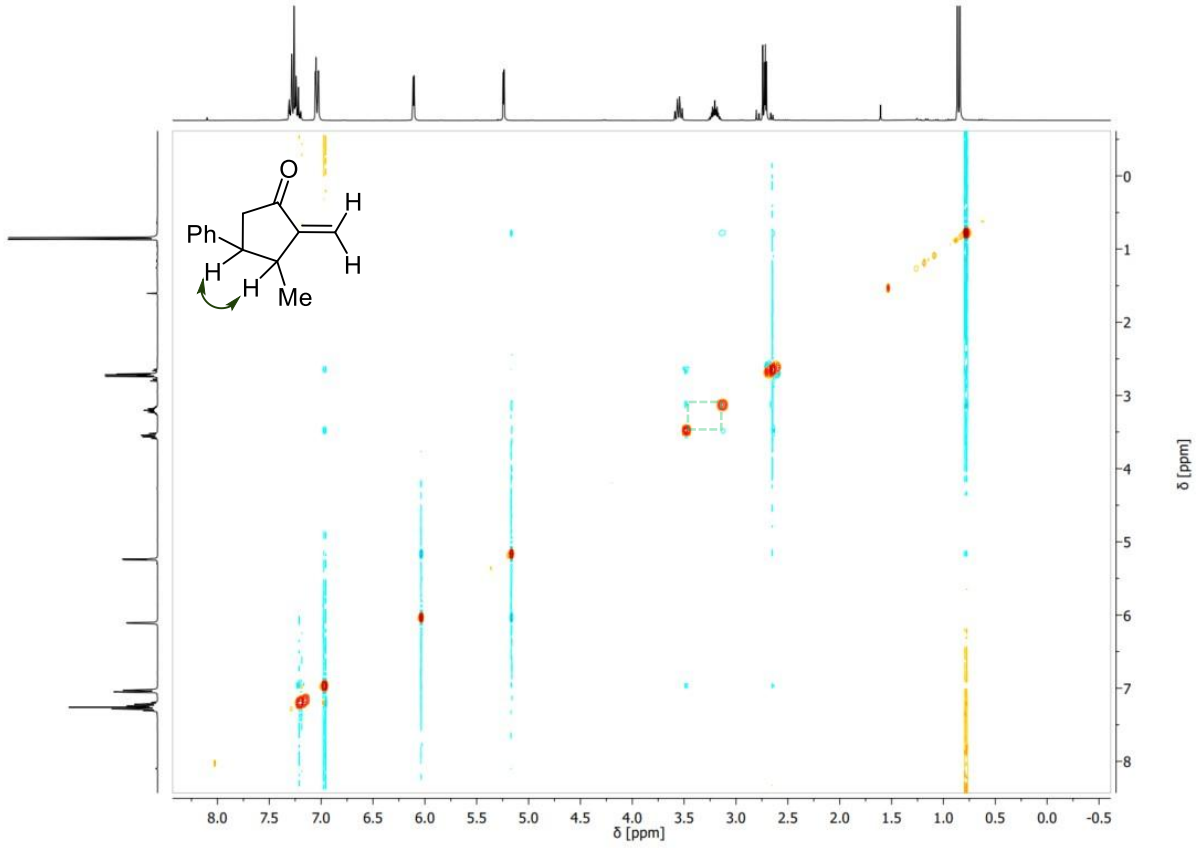






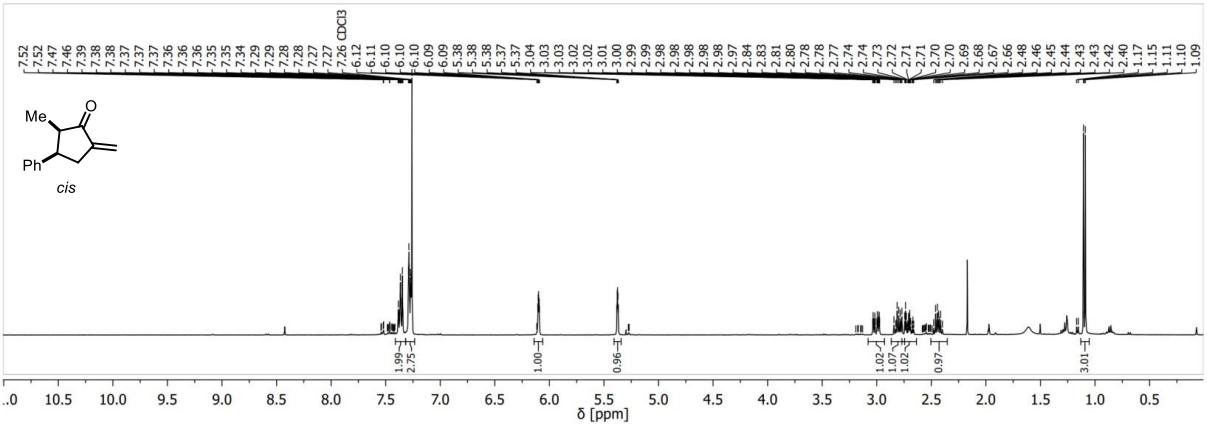
8 Appendix

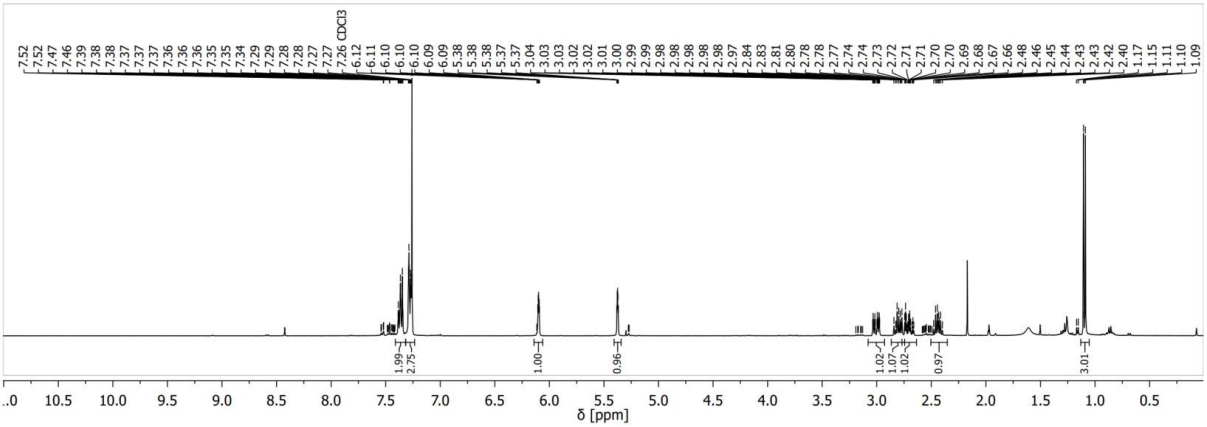
Spectra of project “2-methylenecyclopentan-1ones” – products

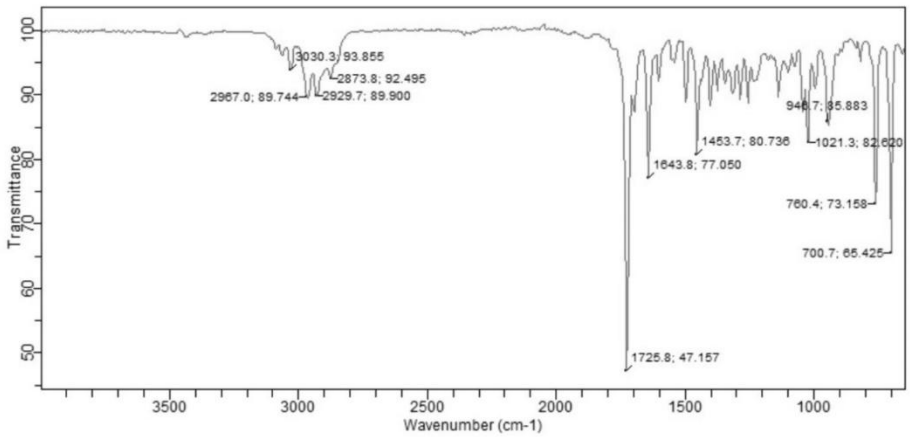


cis-2-Methyl-5-methylene-3-phenylcyclopentan-1-one (178l-side)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

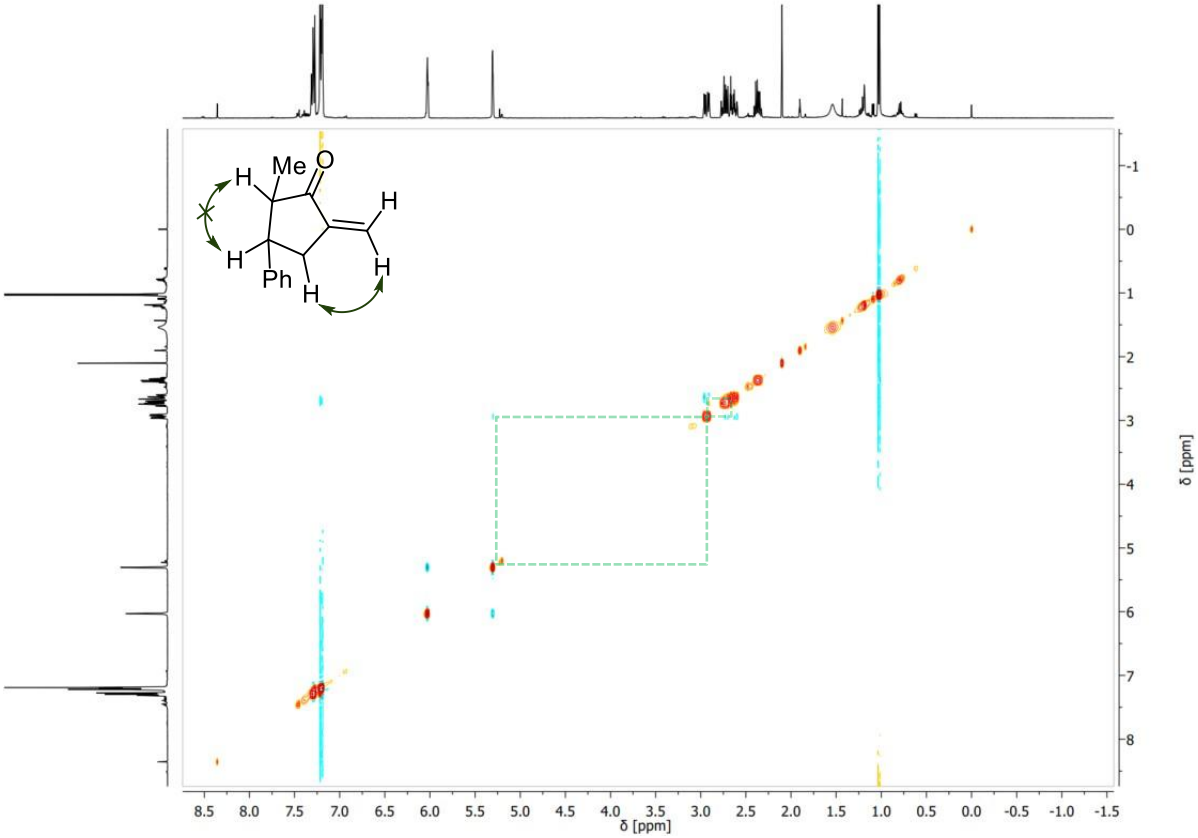






8 Appendix

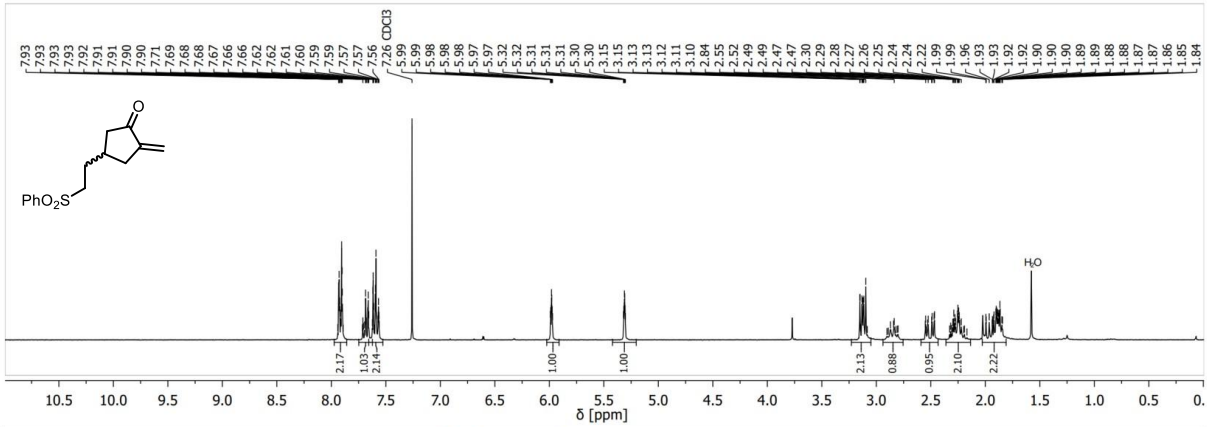
Spectra of project “2-methylenecyclopentan-1ones” – products

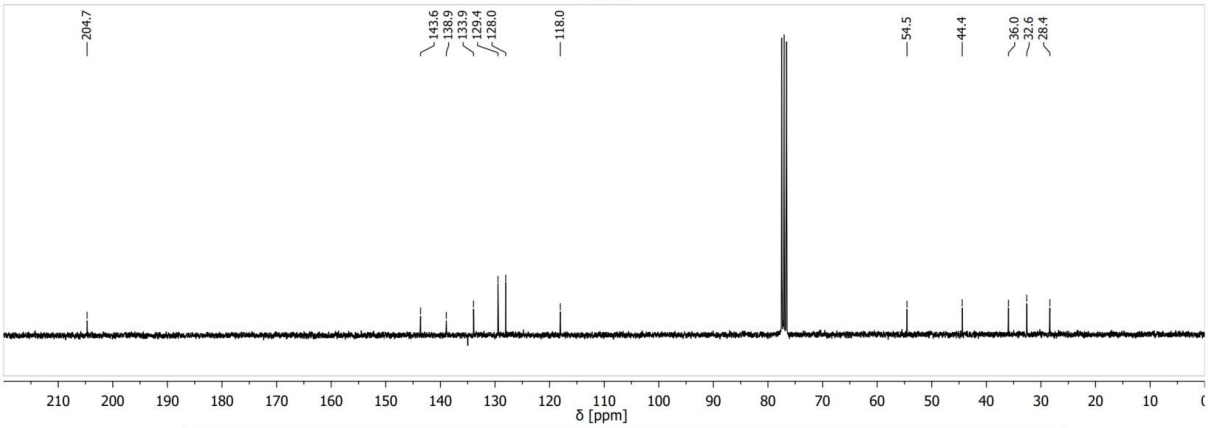


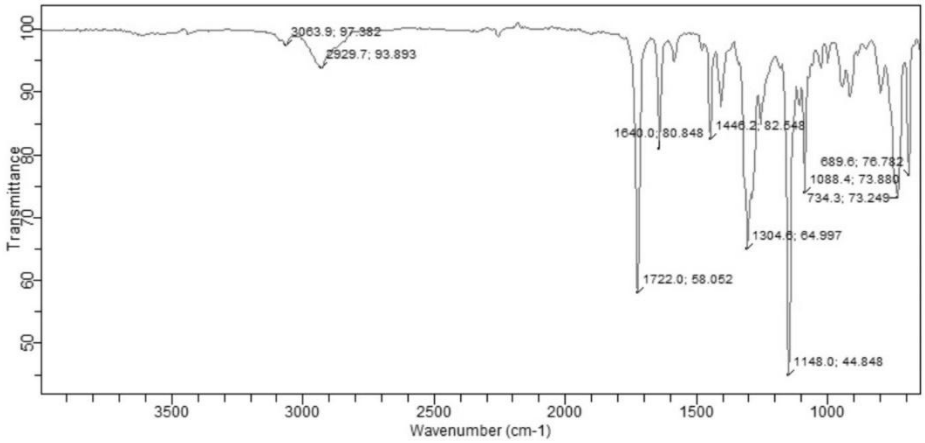
Spectra of project “2-methylenecyclopentan-1ones” – products

2-Methylene-4-(2-(phenylsulfonyl)ethyl)cyclopentan-1-one (178p)

^{1}H NMR (300 MHz) **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**

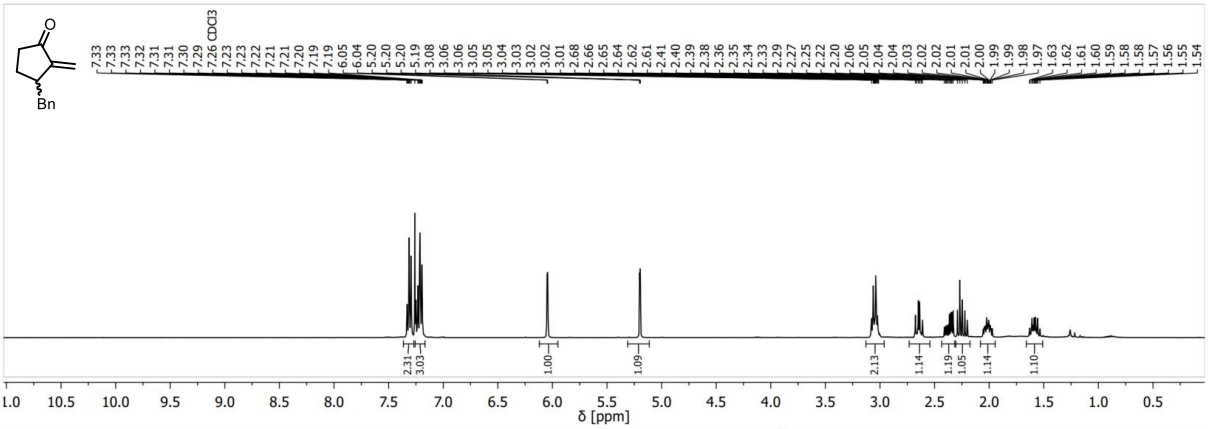


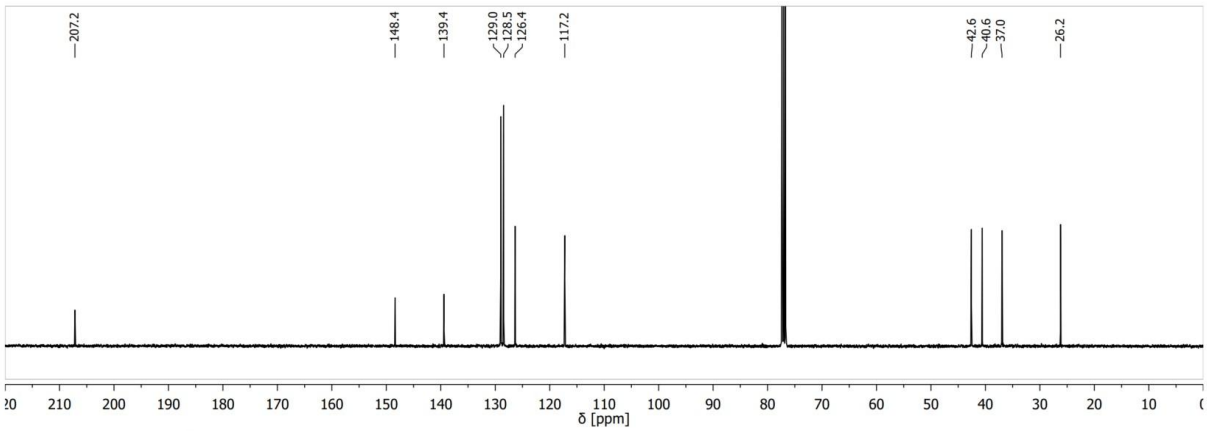


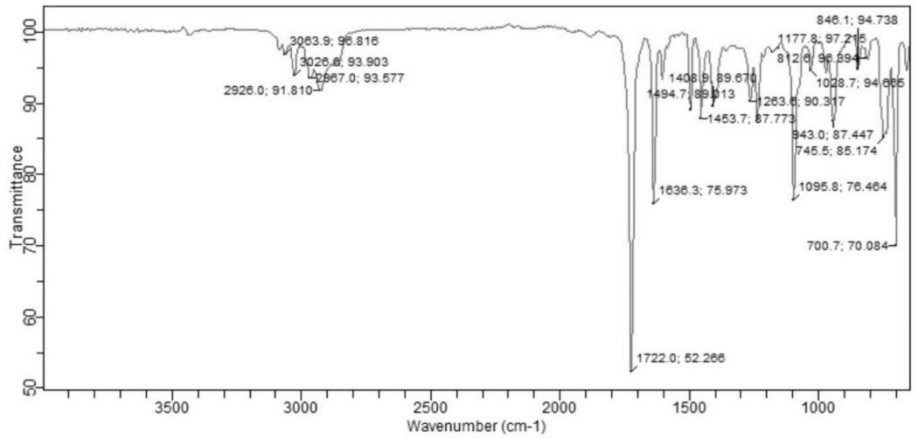


3-Benzyl-2-methylenecyclopentan-1-one (178q)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

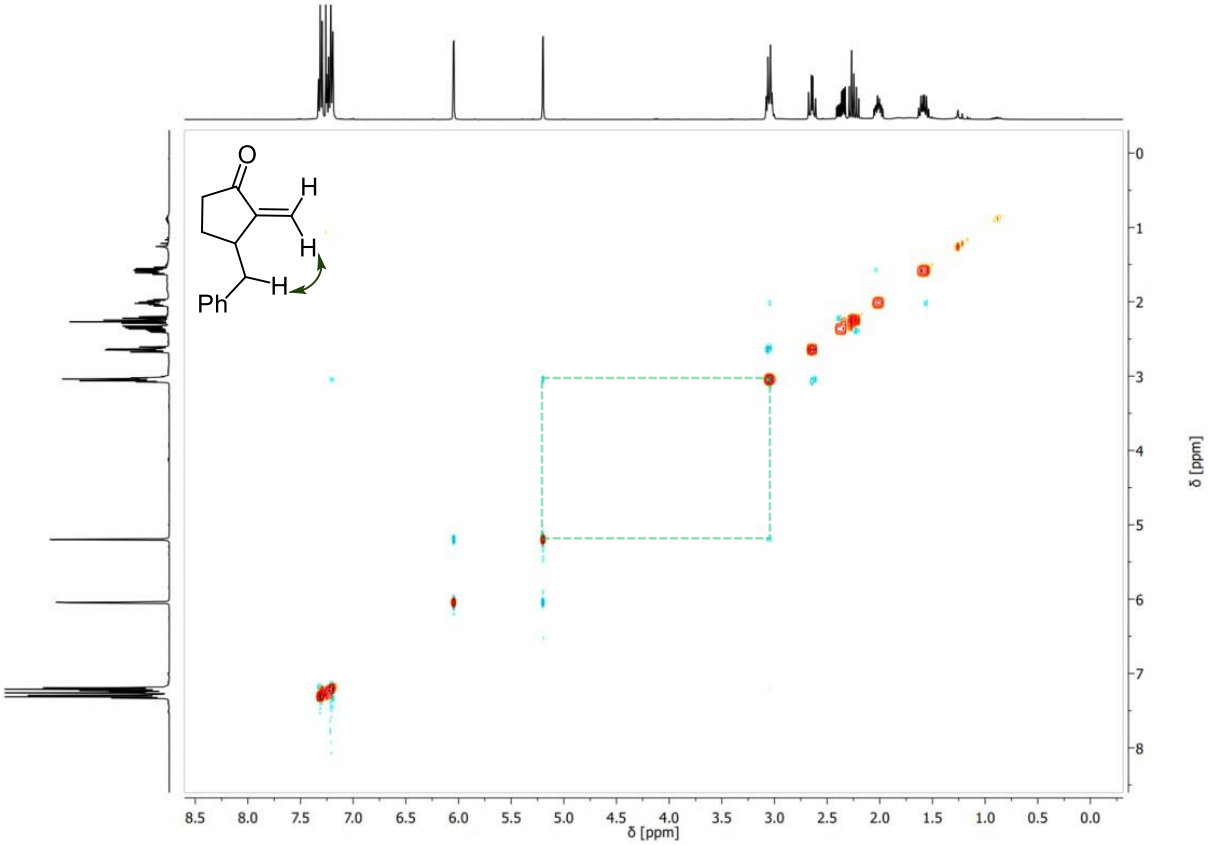






8 Appendix

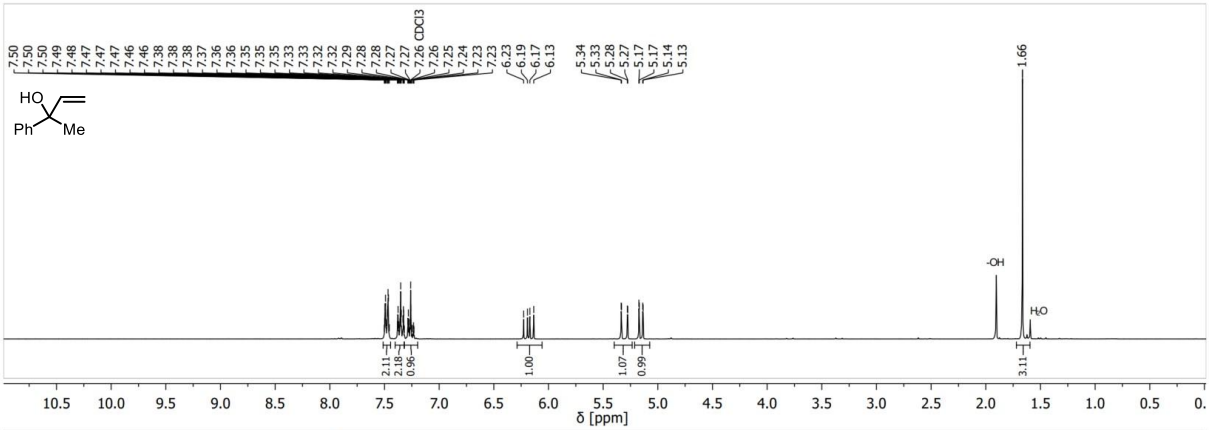
Spectra of project “2-methylenecyclopentan-1ones” – products

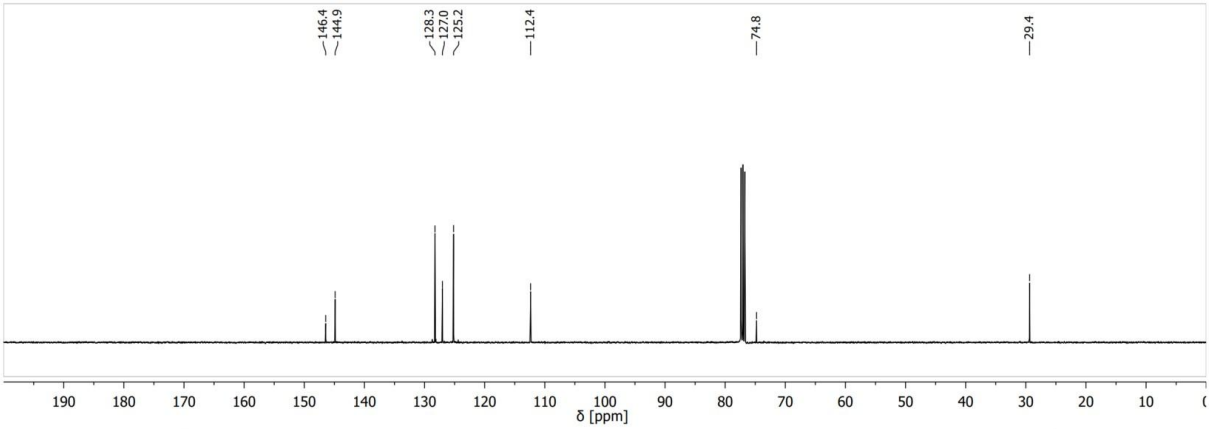


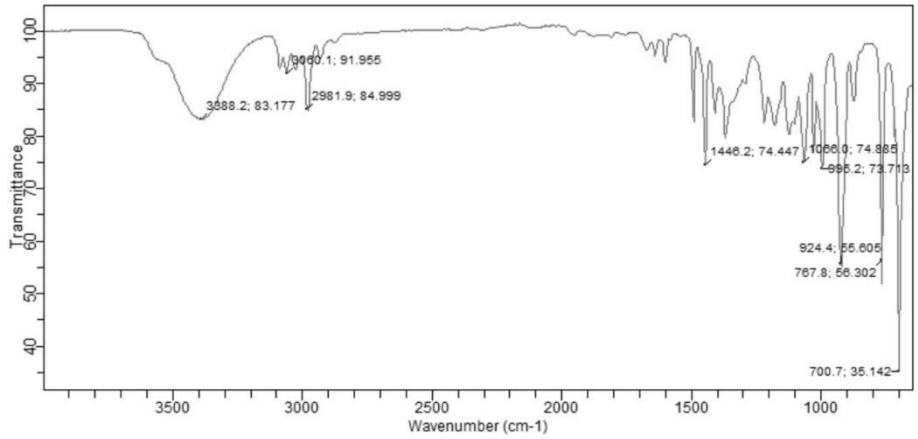
8.5 Spectra of project “1,2-aryl migration” – starting materials

2-Phenylbut-3-en-2-ol (204a)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



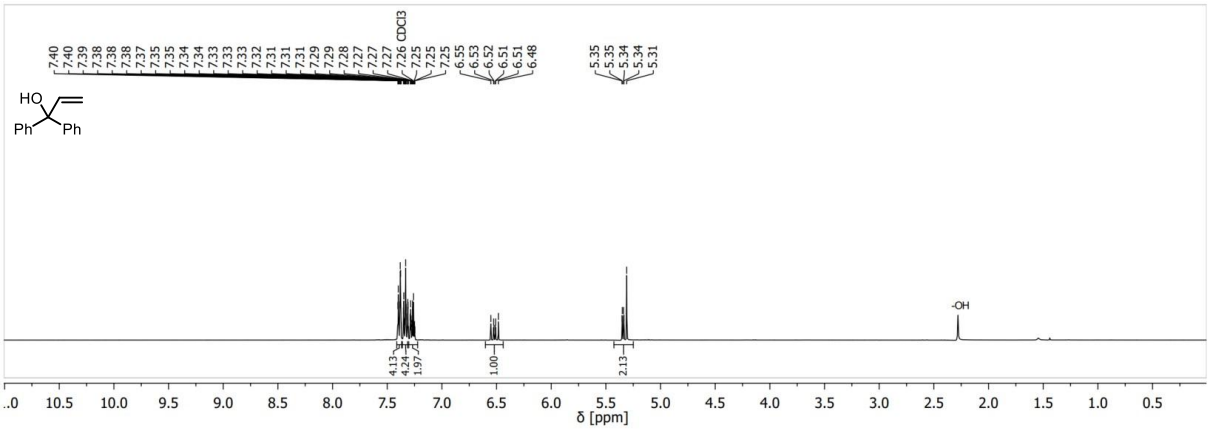


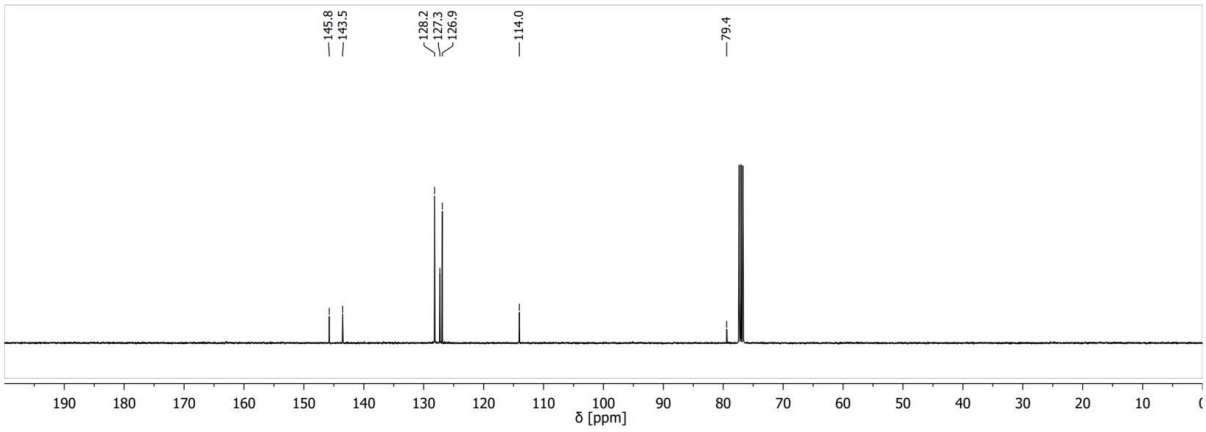


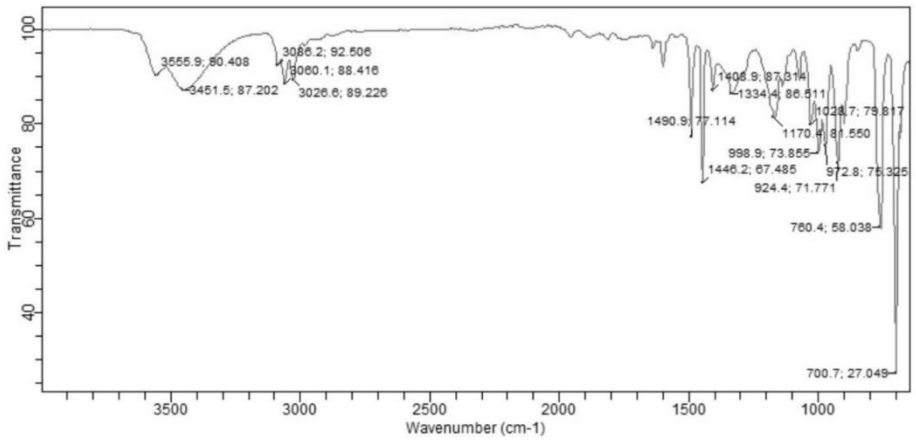
Spectra of project “1,2-aryl migration” – starting materials

1,1-Diphenylprop-2-en-1-ol (204b)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



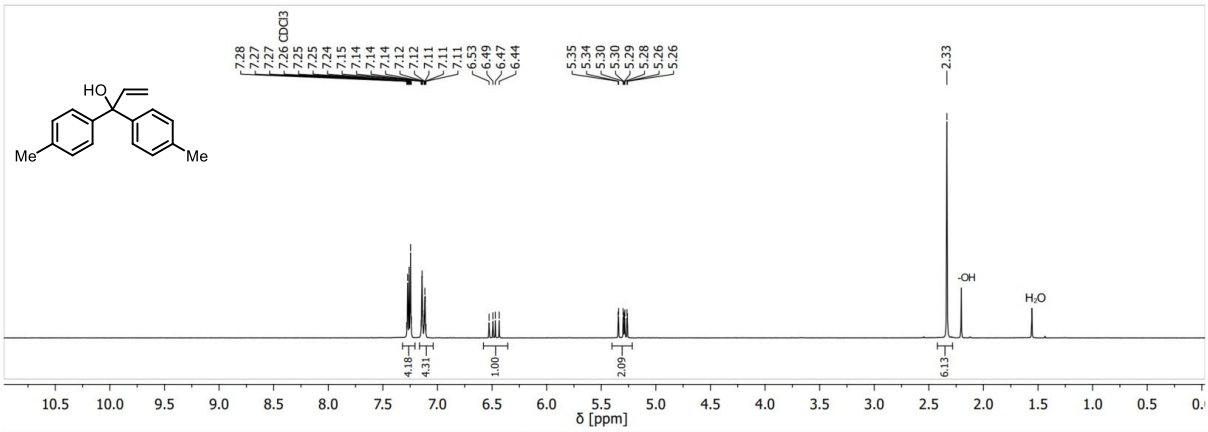


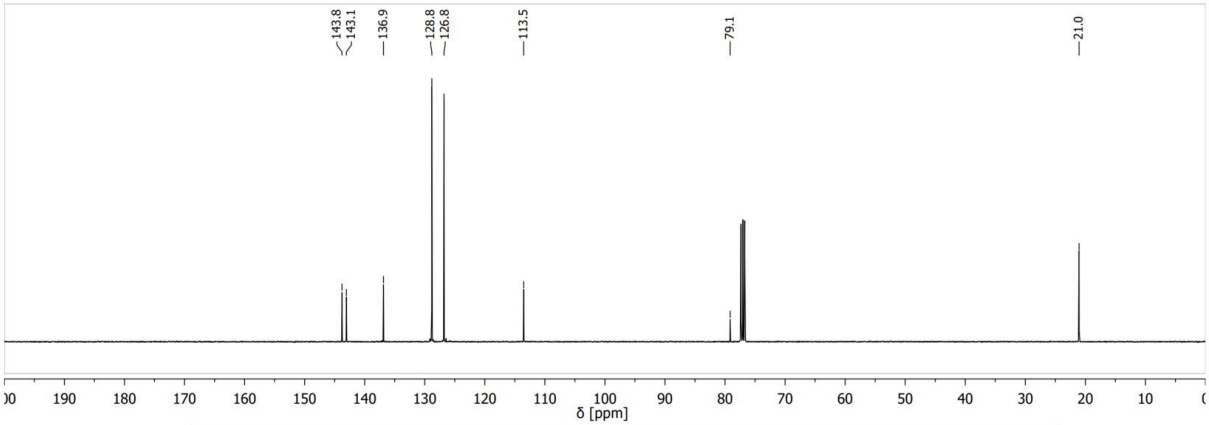


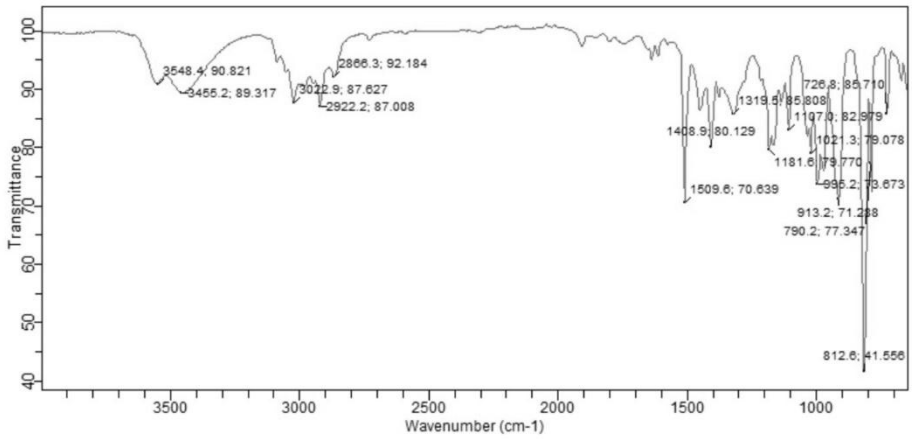
Spectra of project “1,2-aryl migration” – starting materials

1,1-di-*p*-Tolylprop-2-en-1-ol (204c)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



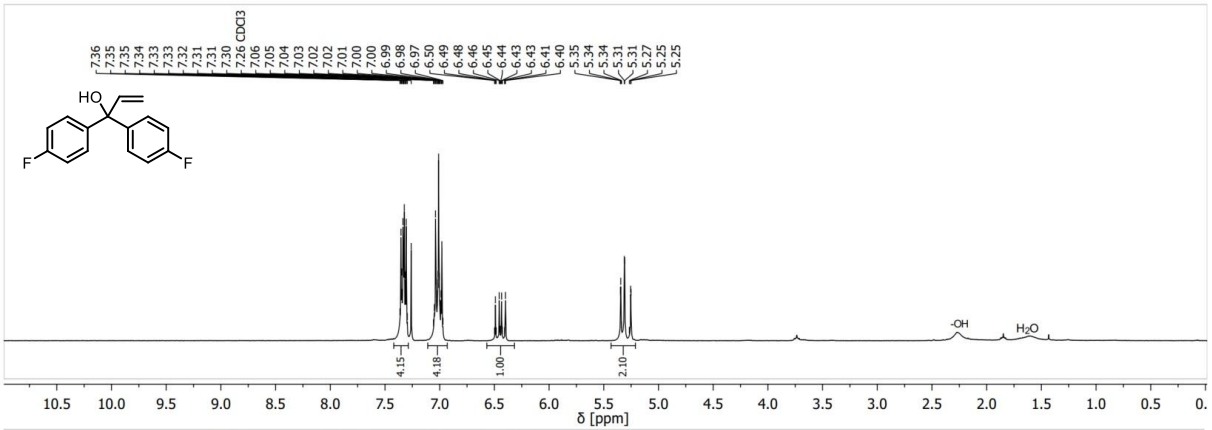


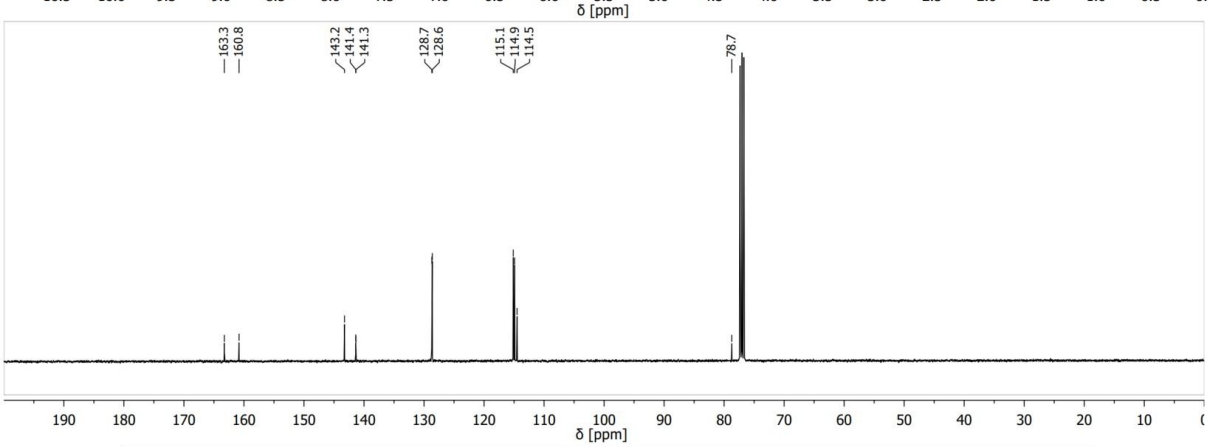


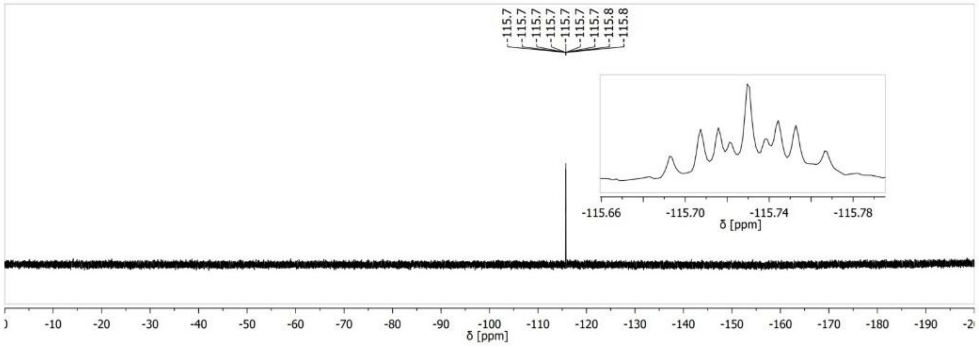
Spectra of project “1,2-aryl migration” – starting materials

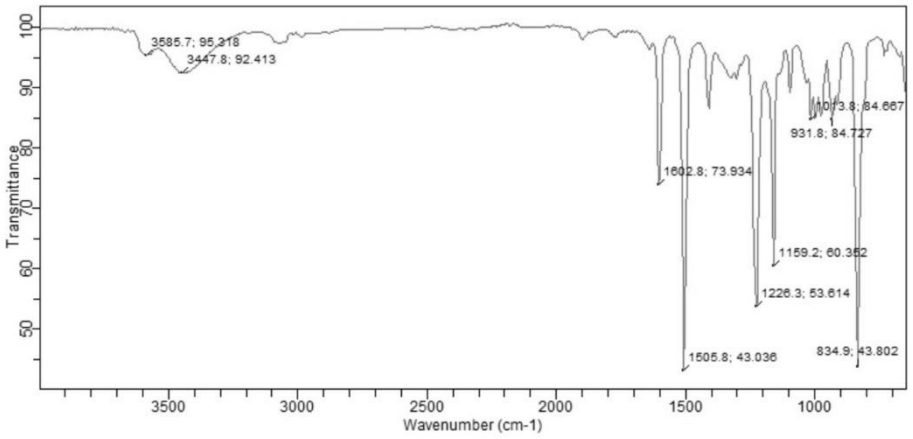
1,1-bis(4-Fluorophenyl)prop-2-en-1-ol (204d)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **^{19}F NMR** (376 MHz): Chloroform-*d*, **IR**





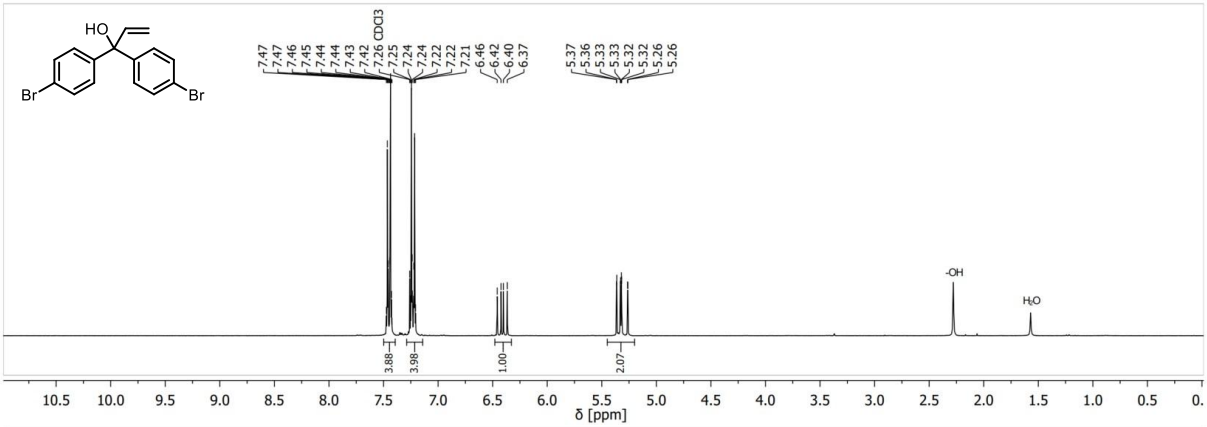


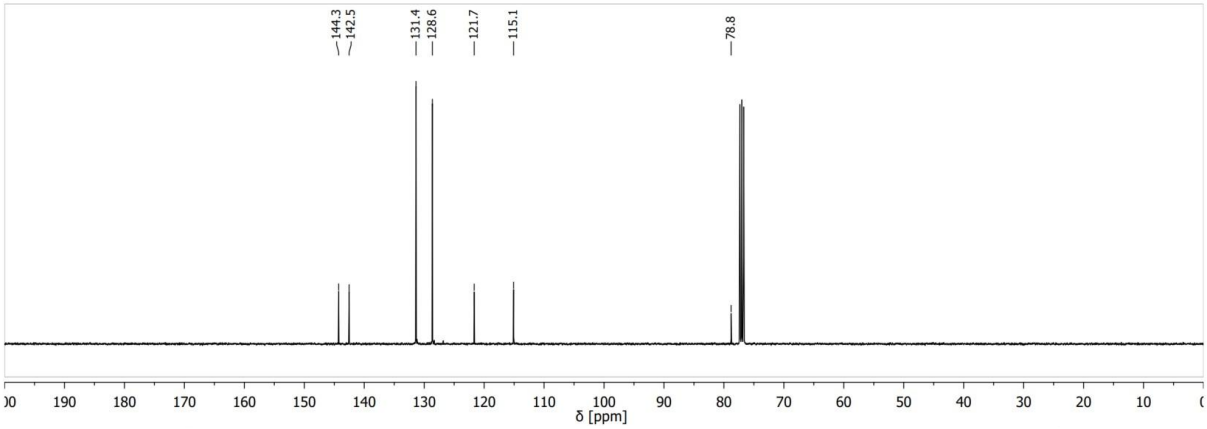


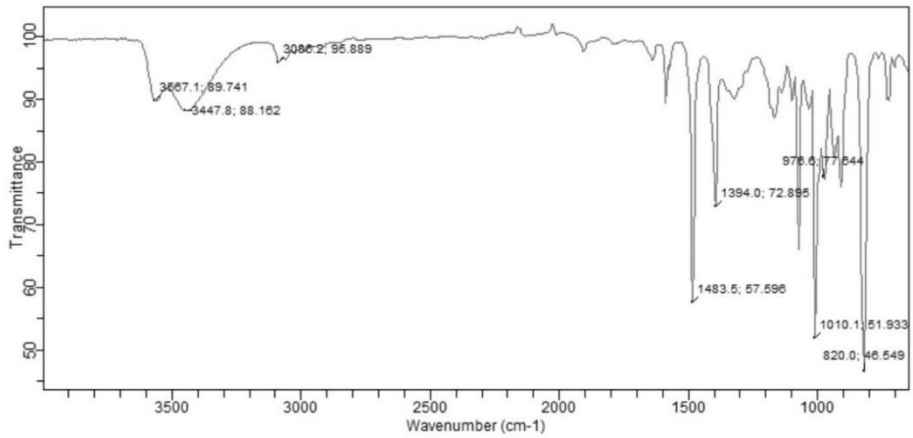
Spectra of project “1,2-aryl migration” – starting materials

1,1-bis(4-Bromophenyl)prop-2-en-1-ol (204e)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



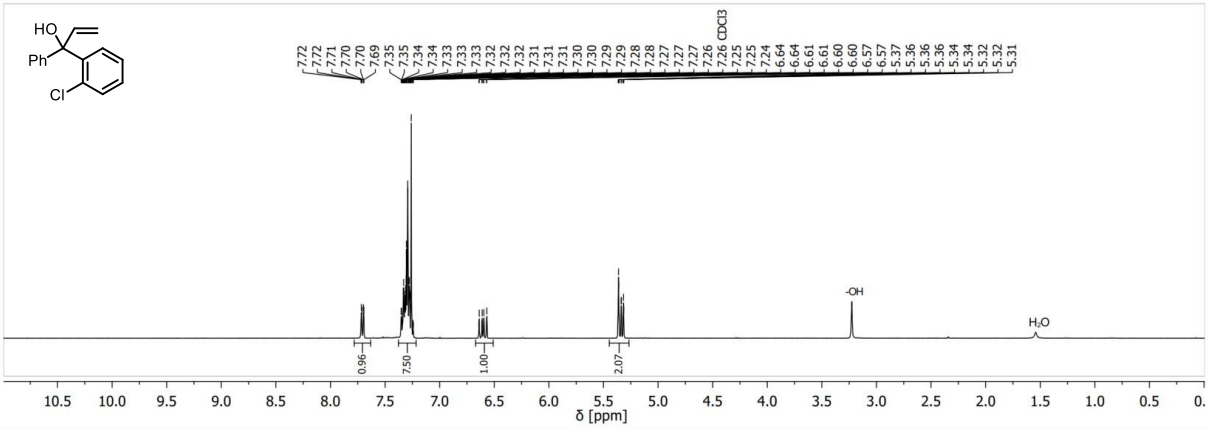


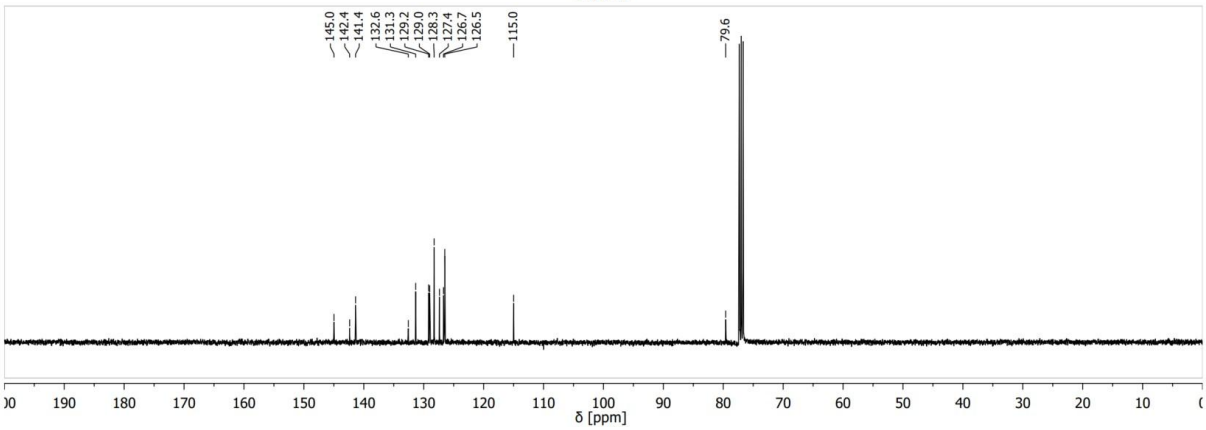


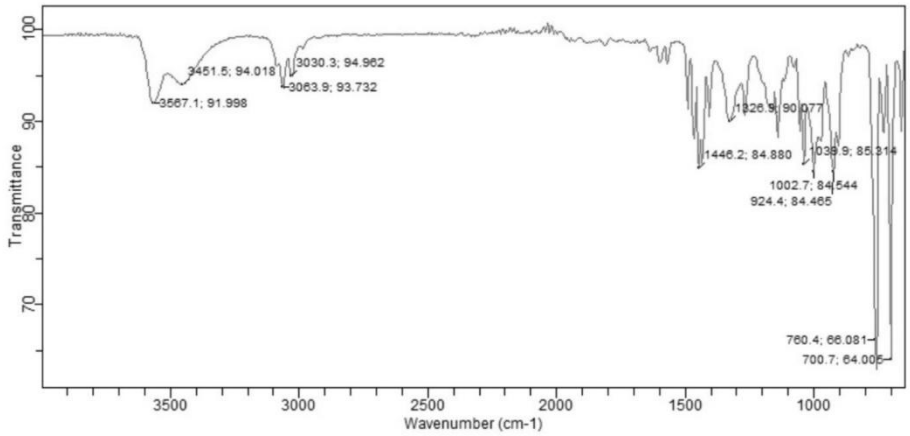
Spectra of project “1,2-aryl migration” – starting materials

1-(2-Chlorophenyl)-1-phenylprop-2-en-1-ol (204f)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



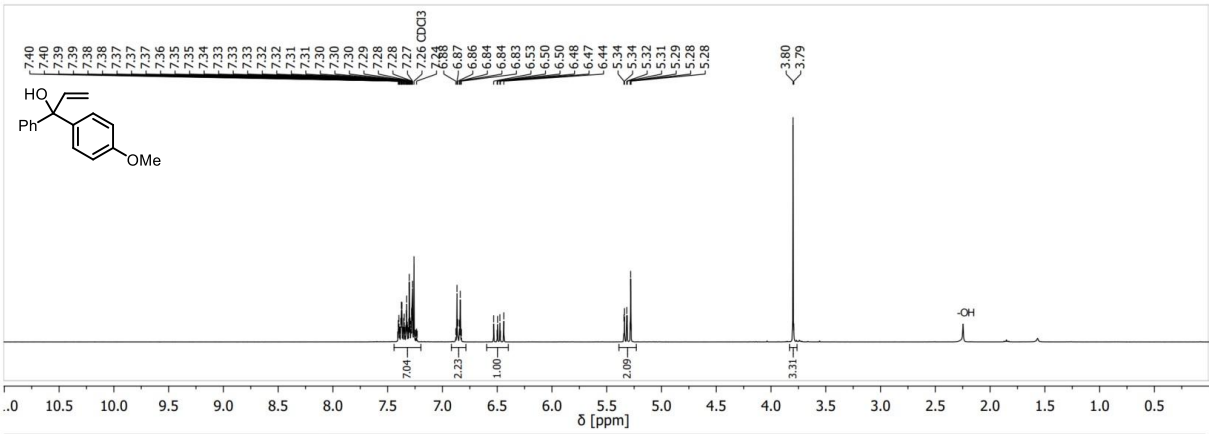


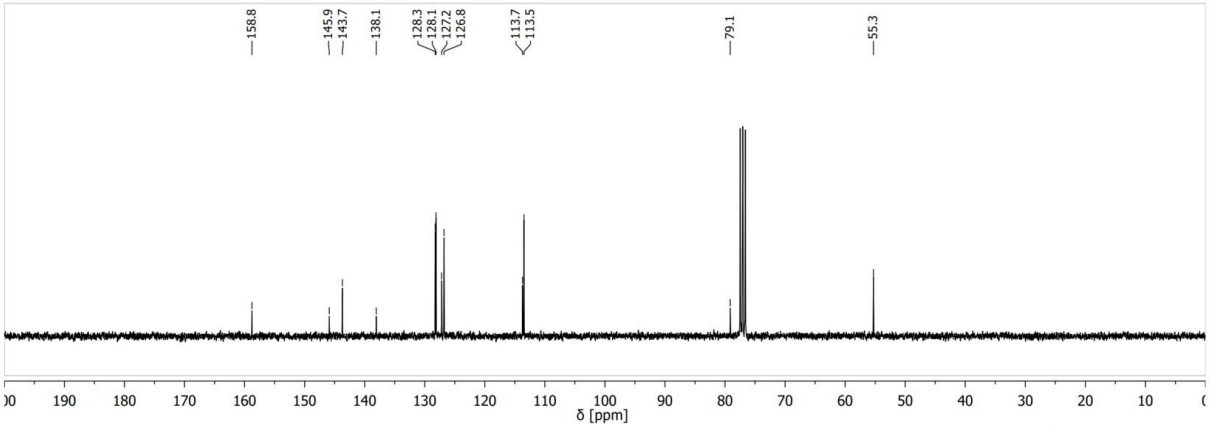


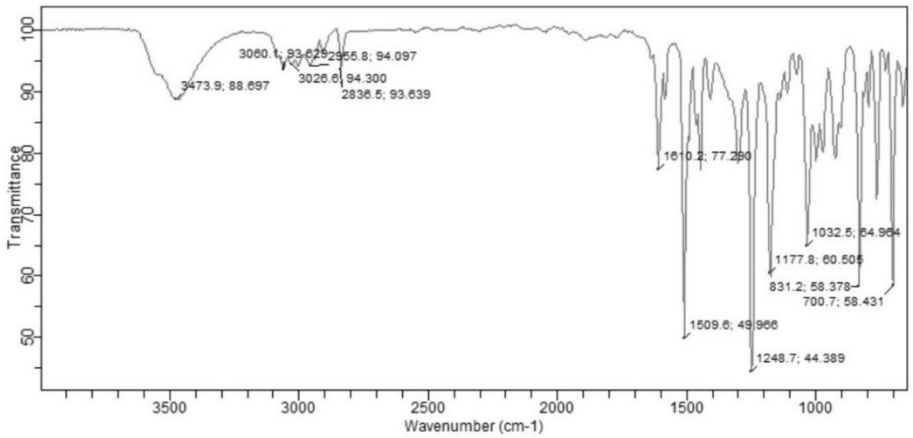
Spectra of project “1,2-aryl migration” – starting materials

1-(4-Methoxyphenyl)-1-phenylprop-2-en-1-ol (204g)

^{1}H NMR (300 MHz) **^{13}C NMR** (75 MHz): Chloroform-*d*, **IR**



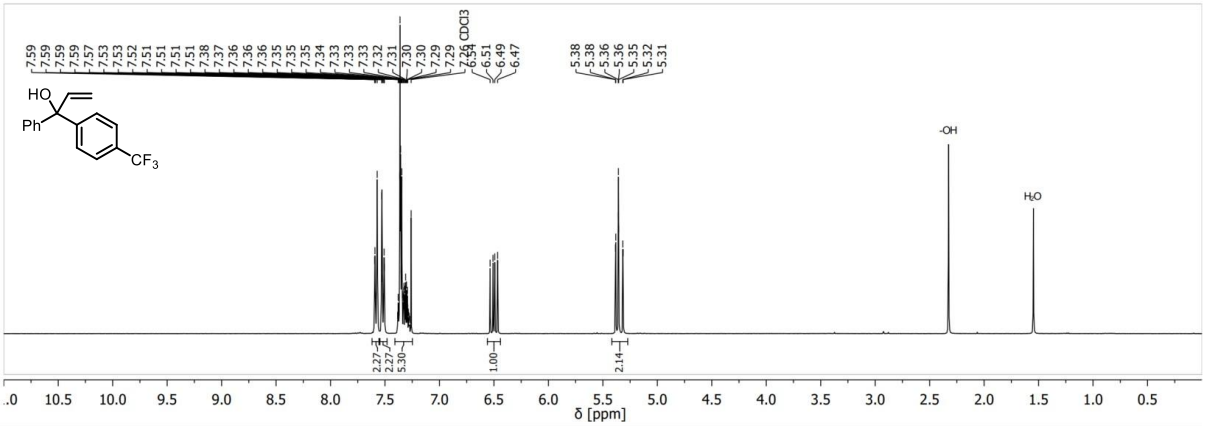


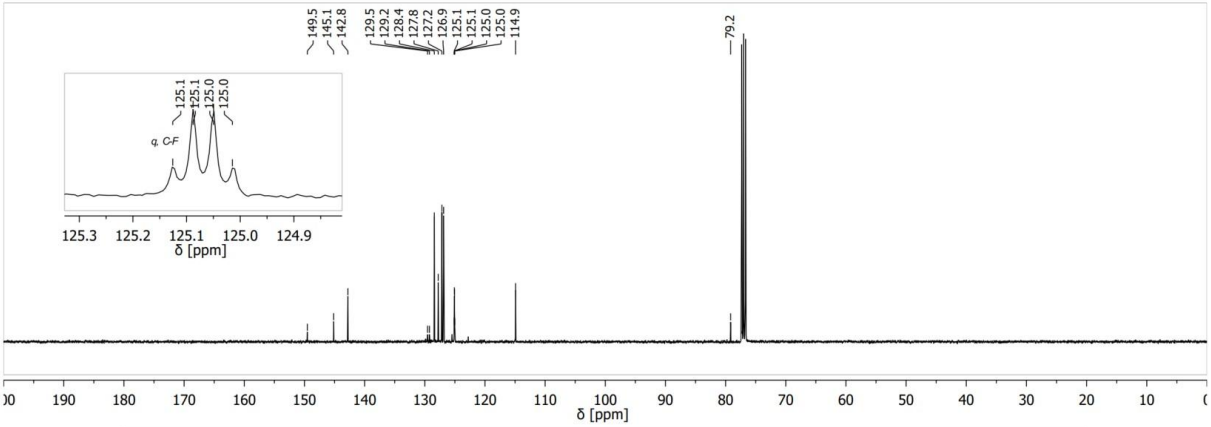


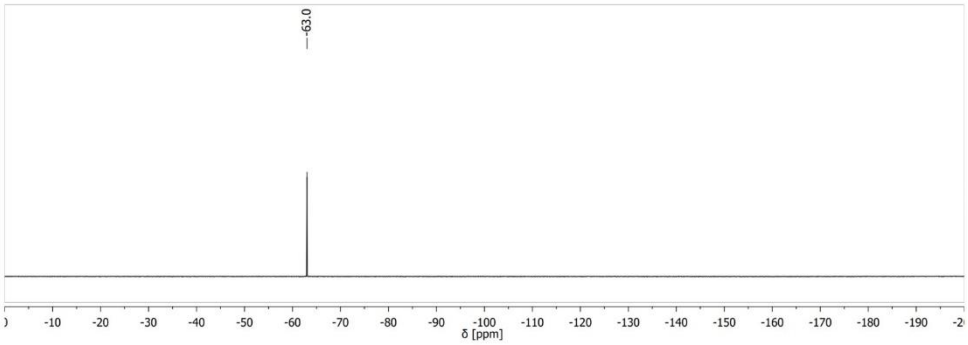
Spectra of project “1,2-aryl migration” – starting materials

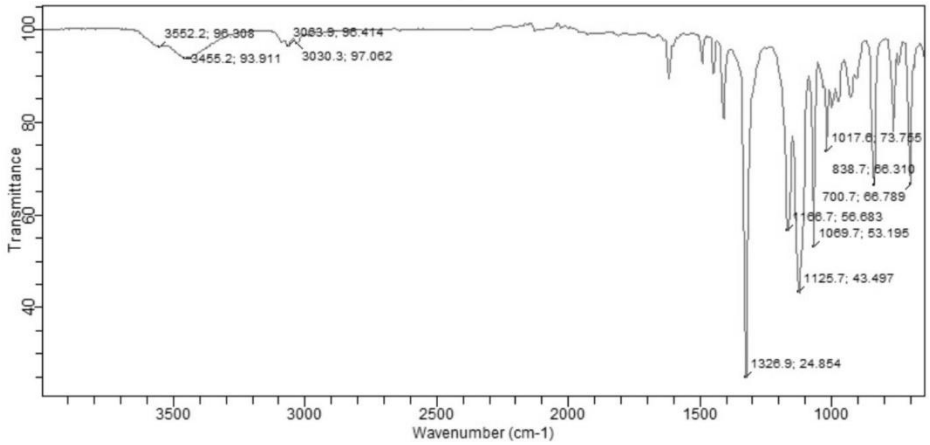
1-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (204h)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **^{19}F NMR** (376 MHz): Chloroform-*d*, **IR**





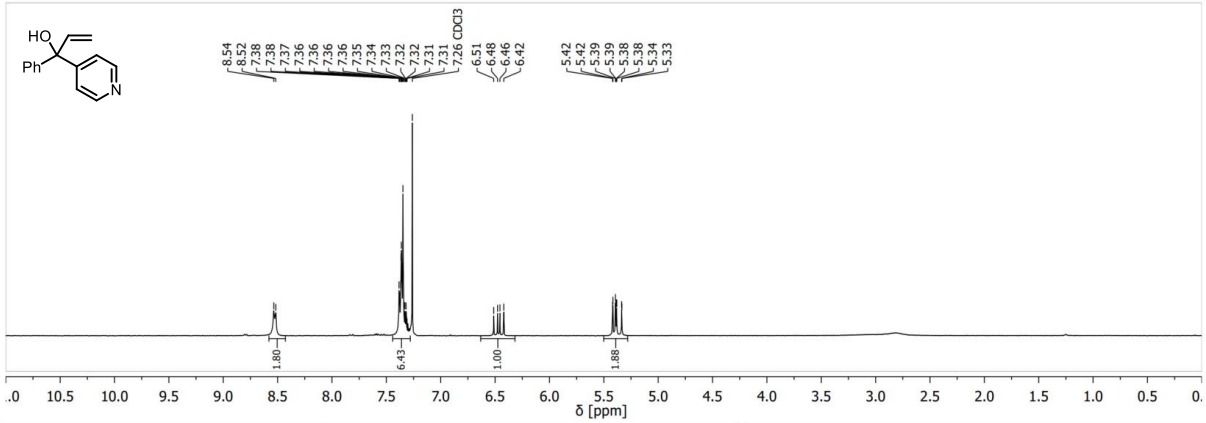


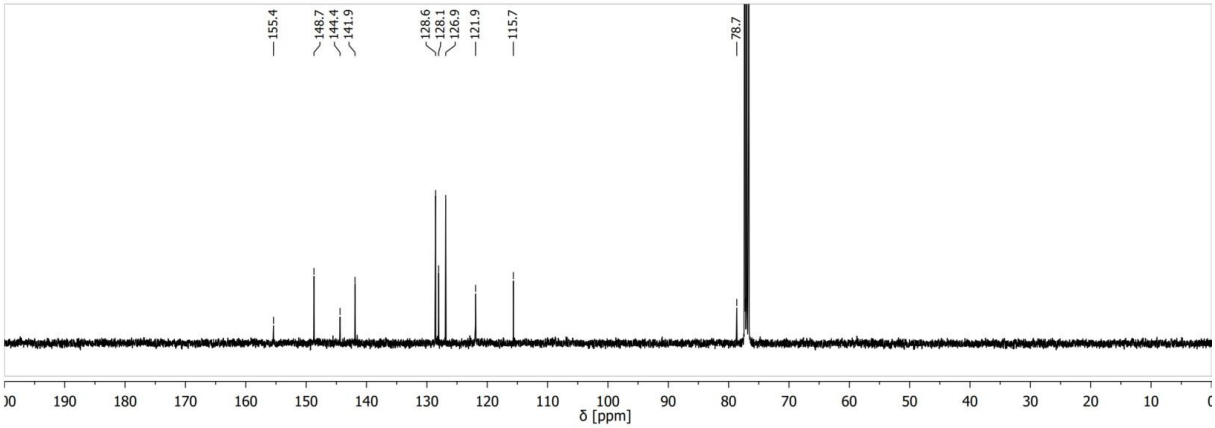


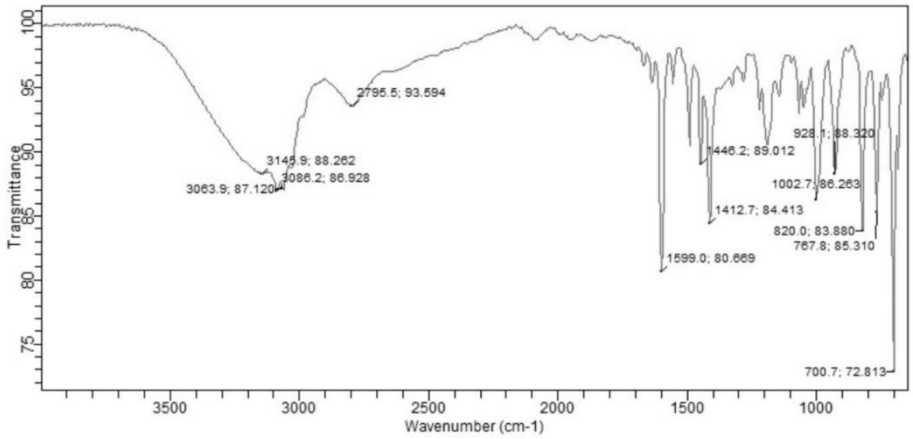
Spectra of project “1,2-aryl migration” – starting materials

1-Phenyl-1-(pyridin-4-yl)prop-2-en-1-ol (204i)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



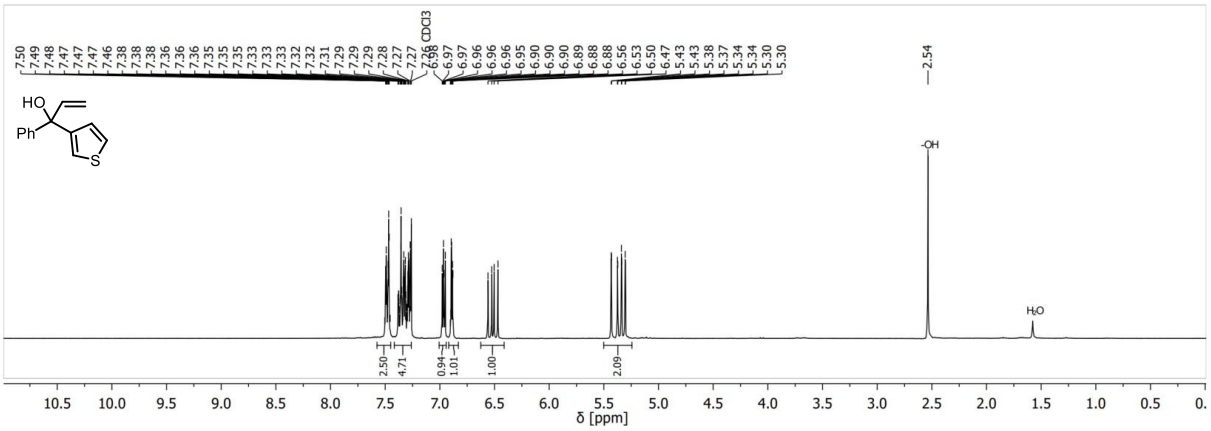


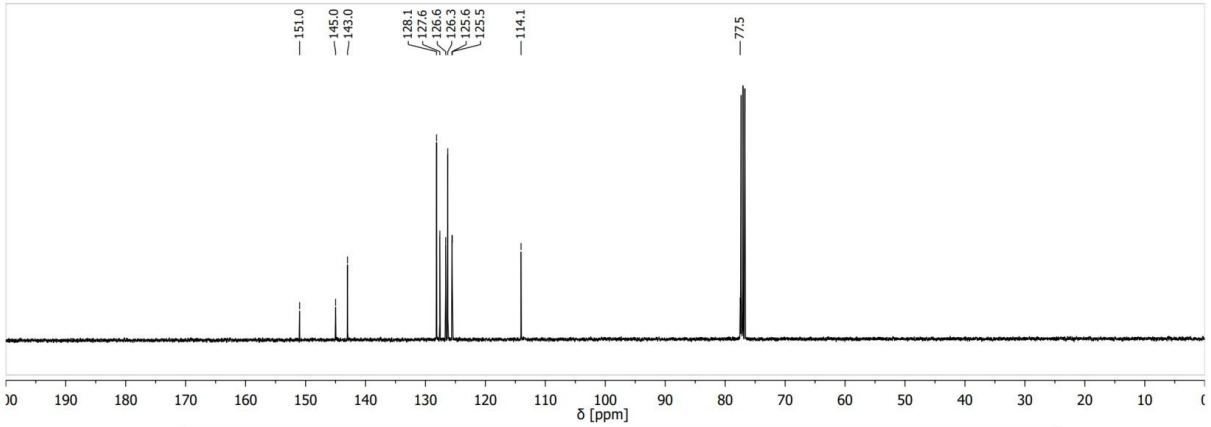


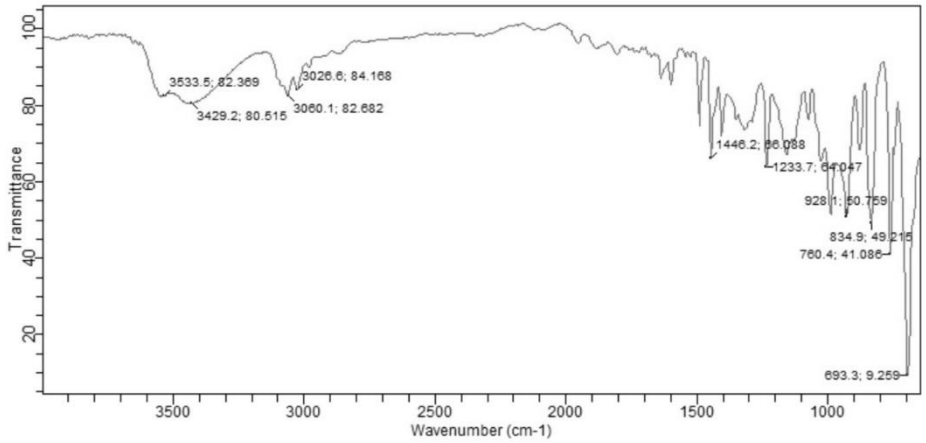
Spectra of project “1,2-aryl migration” – starting materials

1-Phenyl-1-(thiophen-2-yl)prop-2-en-1-ol (204j)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



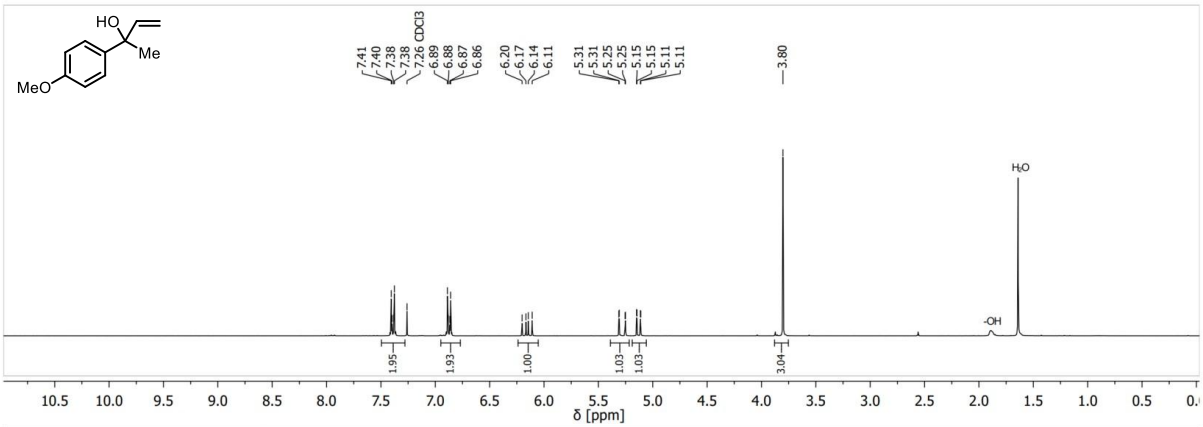


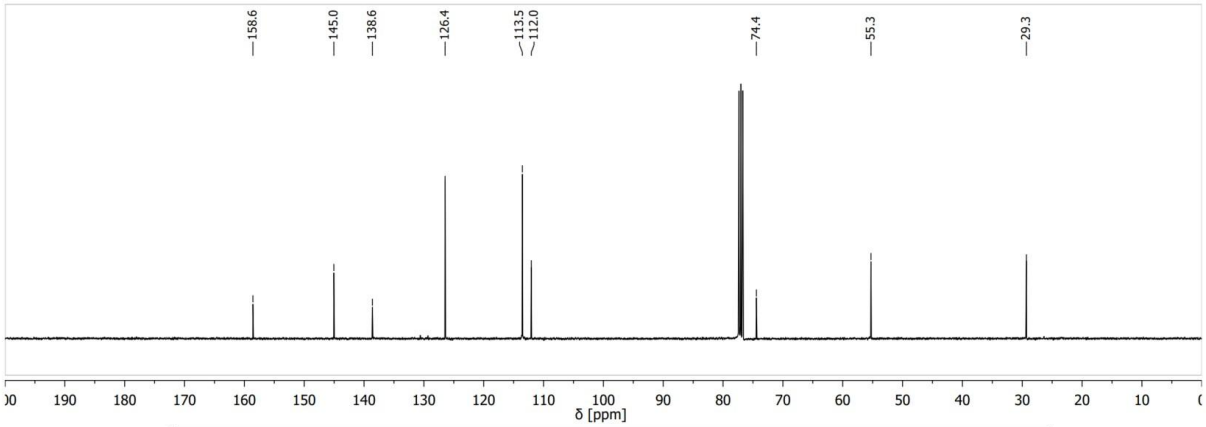


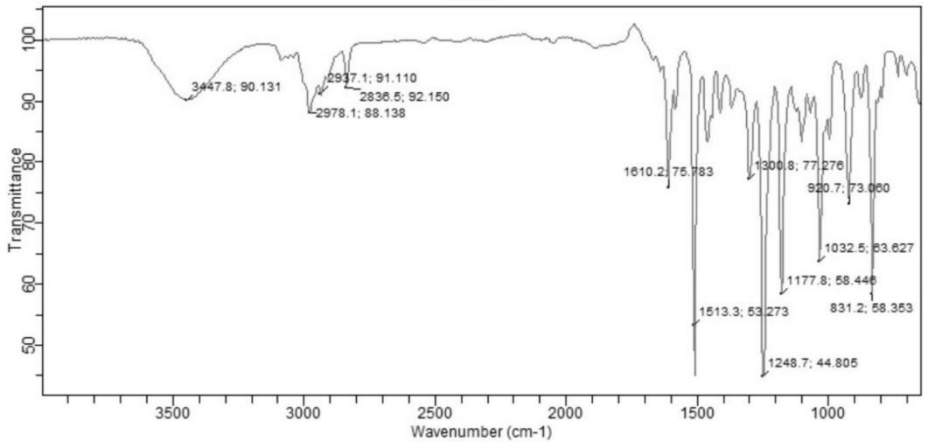
Spectra of project “1,2-aryl migration” – starting materials

2-(4-Methoxyphenyl)but-3-en-2-ol (204k)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



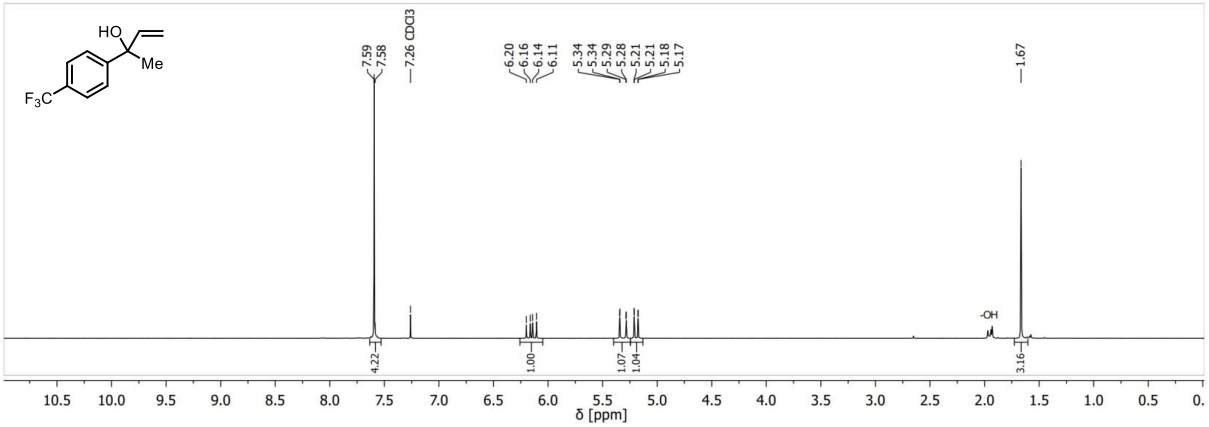


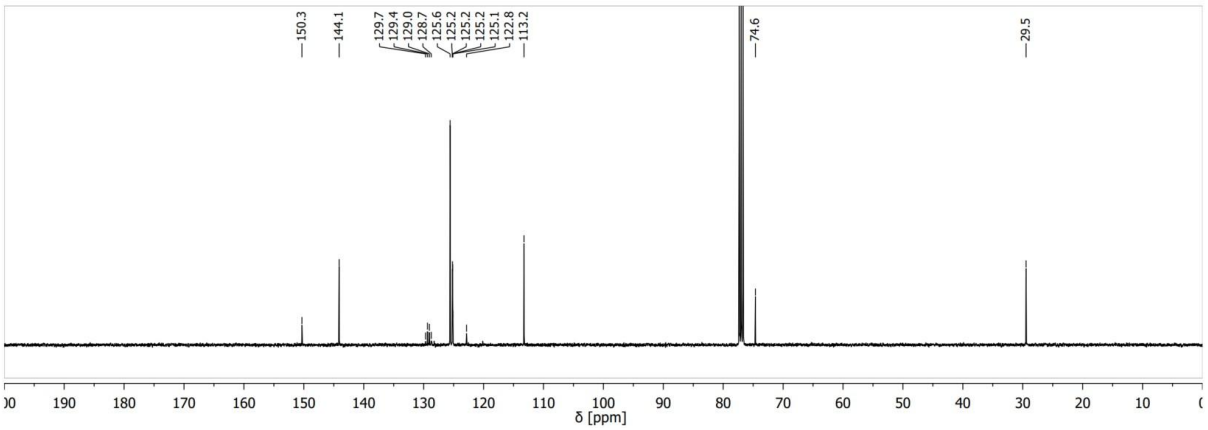


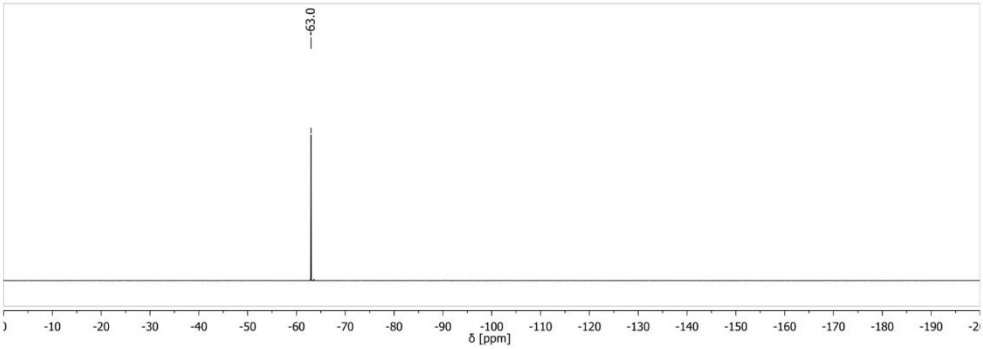
Spectra of project “1,2-aryl migration” – starting materials

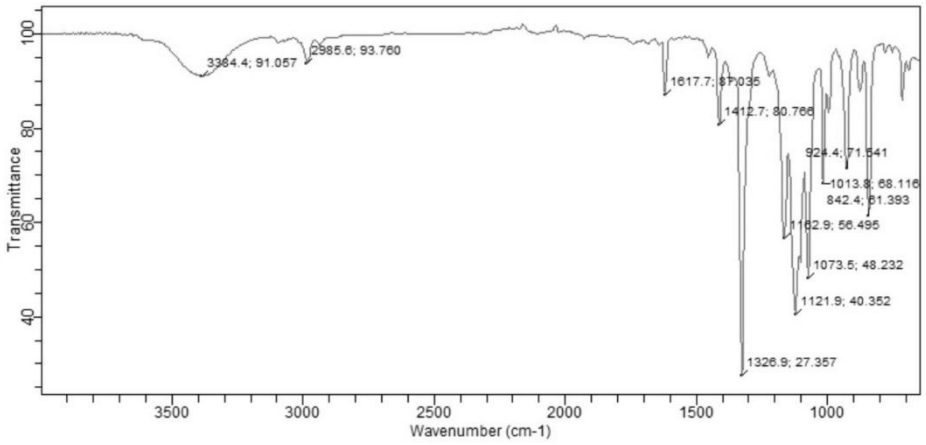
2-(4-(Trifluoromethyl)phenyl)but-3-en-2-ol (204l)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz) **^{19}F NMR** (376 MHz): Chloroform-*d*, **IR**





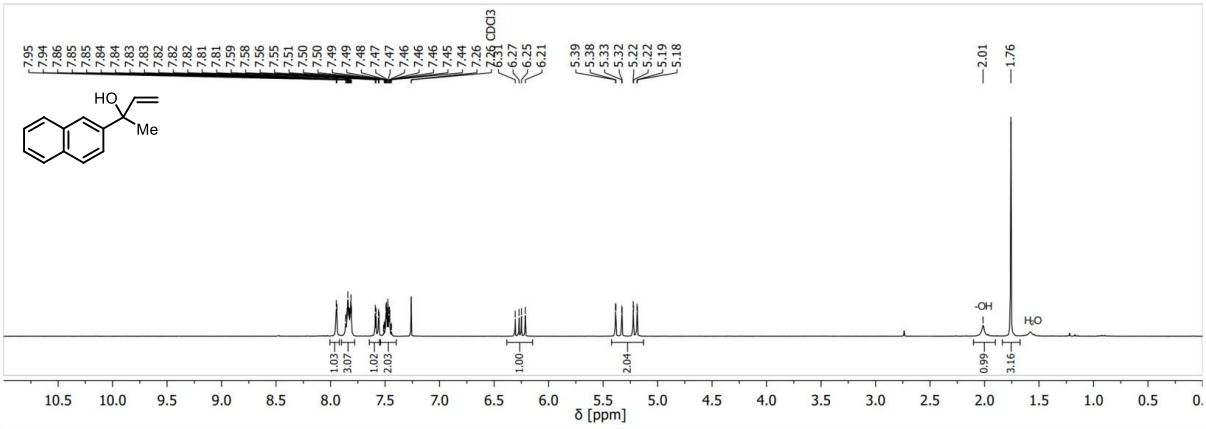


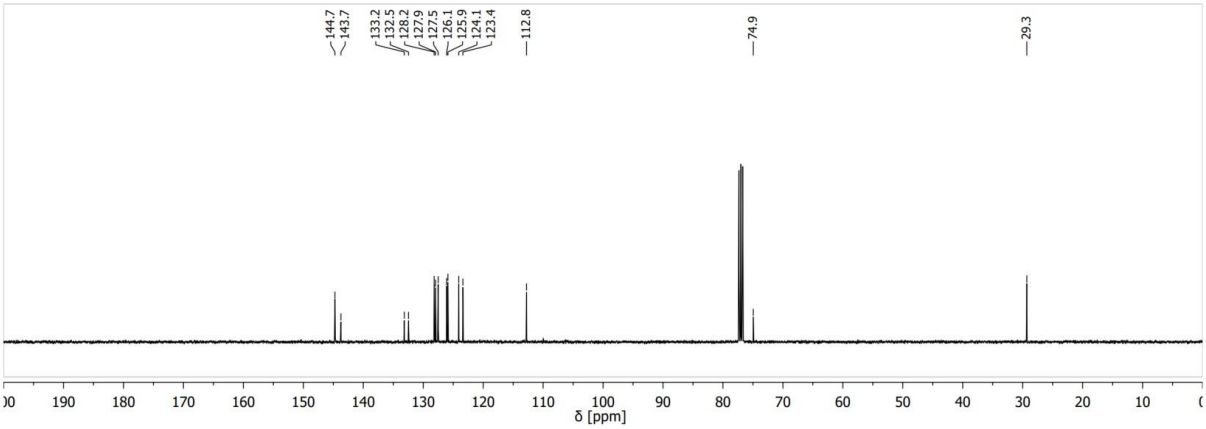


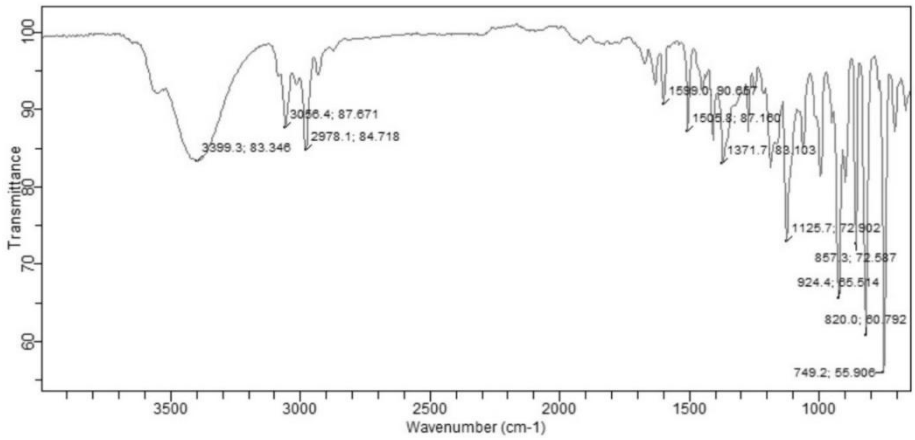
Spectra of project “1,2-aryl migration” – starting materials

2-(Naphthalen-2-yl)but-3-en-2-ol (204m)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



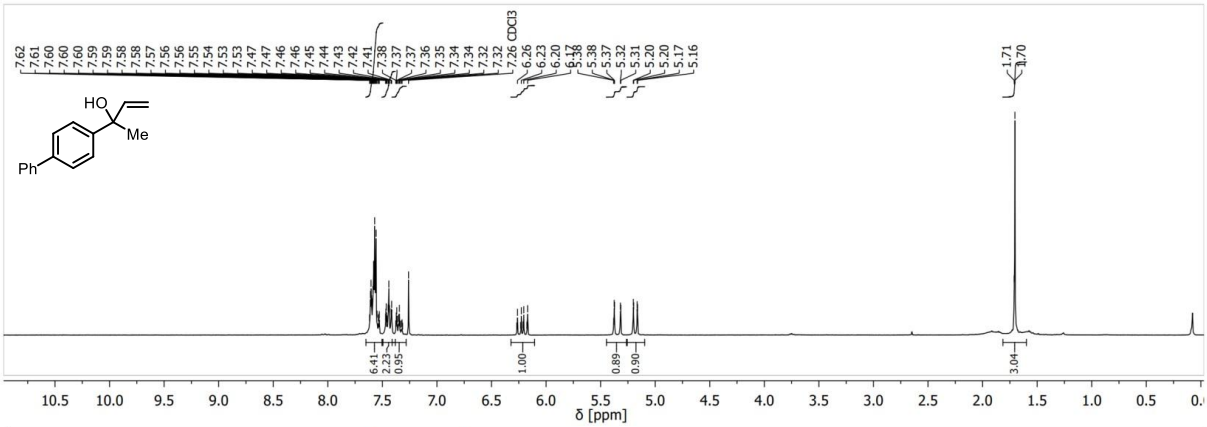


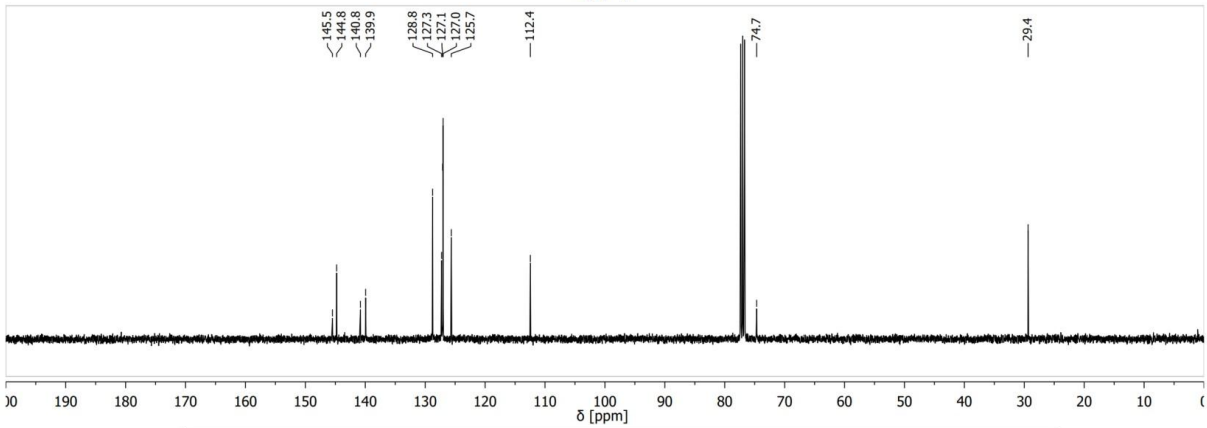


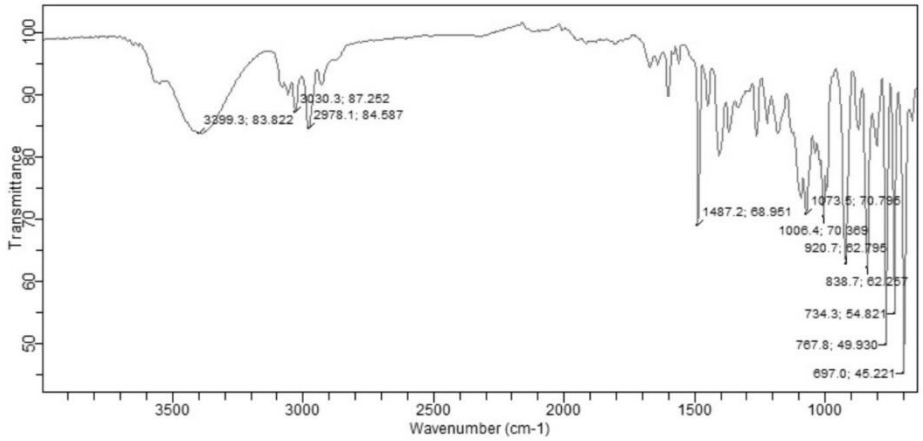
Spectra of project “1,2-aryl migration” – starting materials

2-([1,1'-Biphenyl]-4-yl)but-3-en-2-ol (204n)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



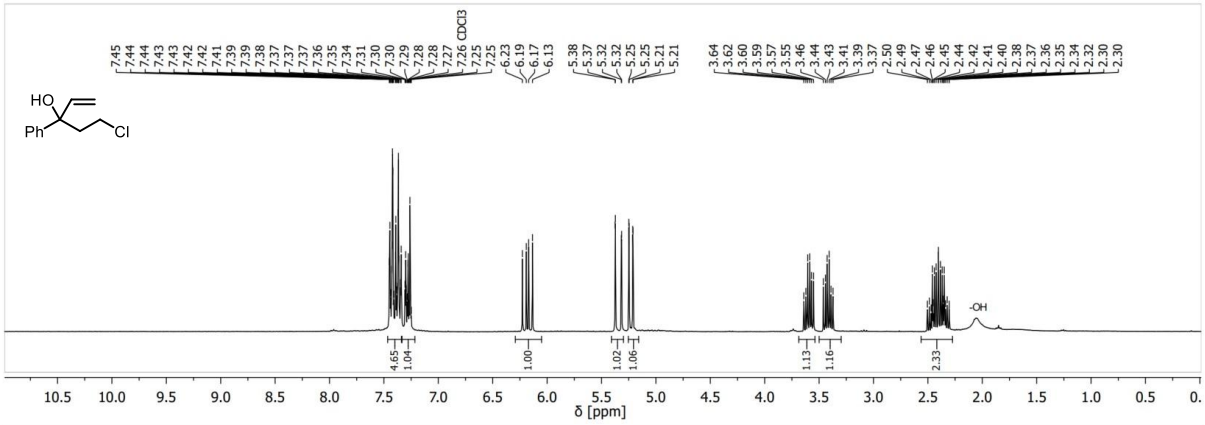


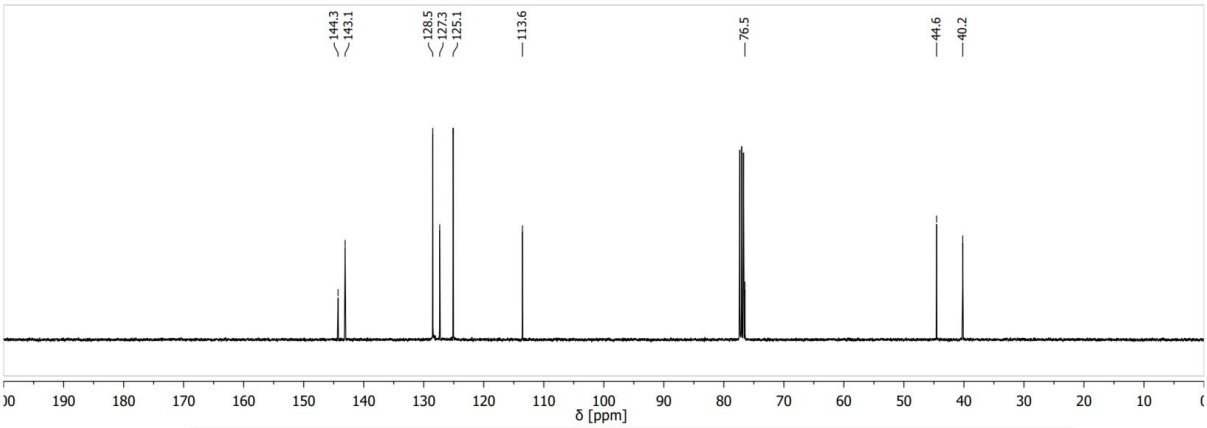


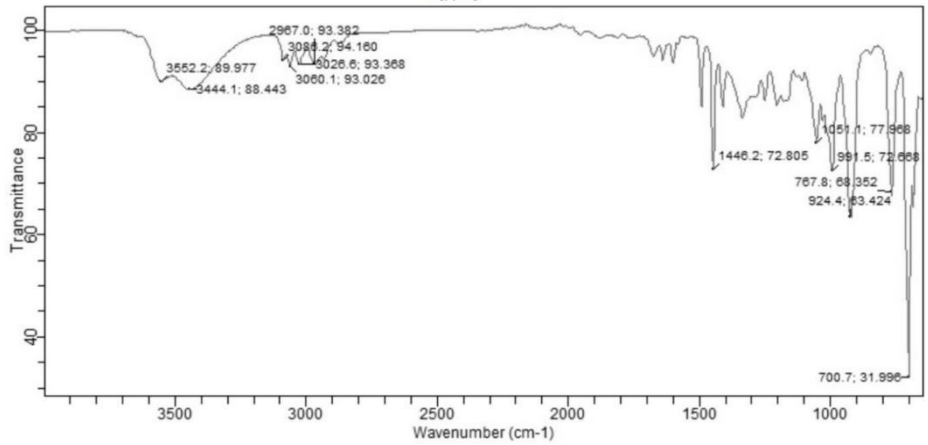
Spectra of project “1,2-aryl migration” – starting materials

5-Chloro-3-phenylpent-1-en-3-ol (204o)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



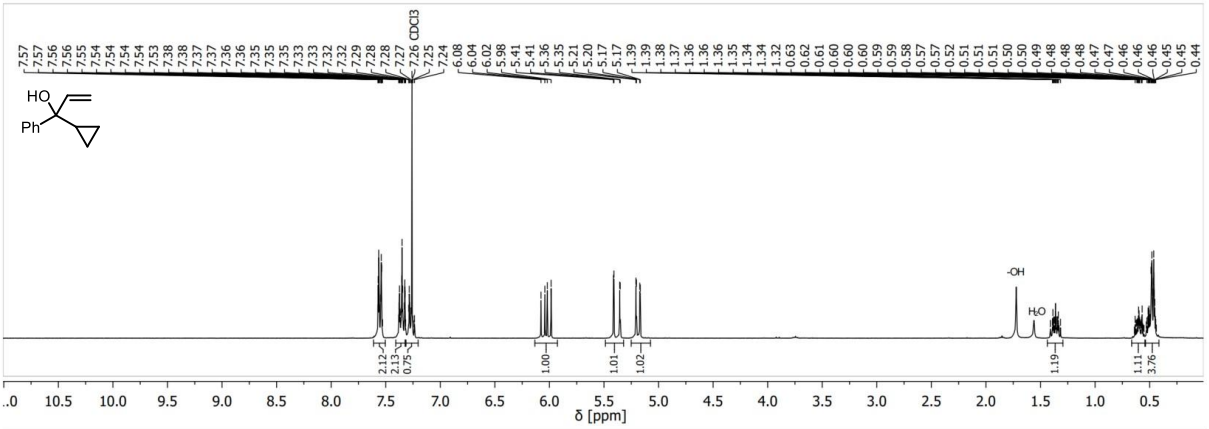


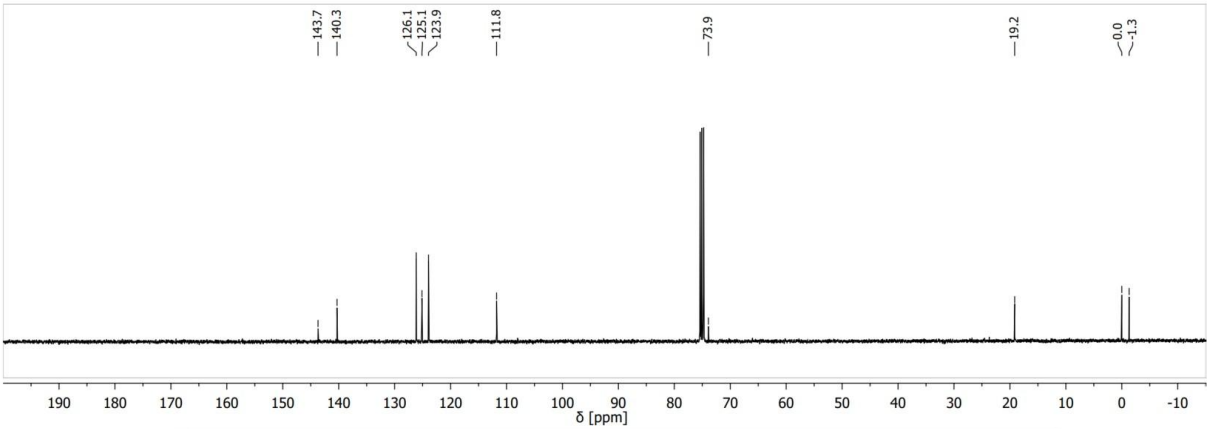


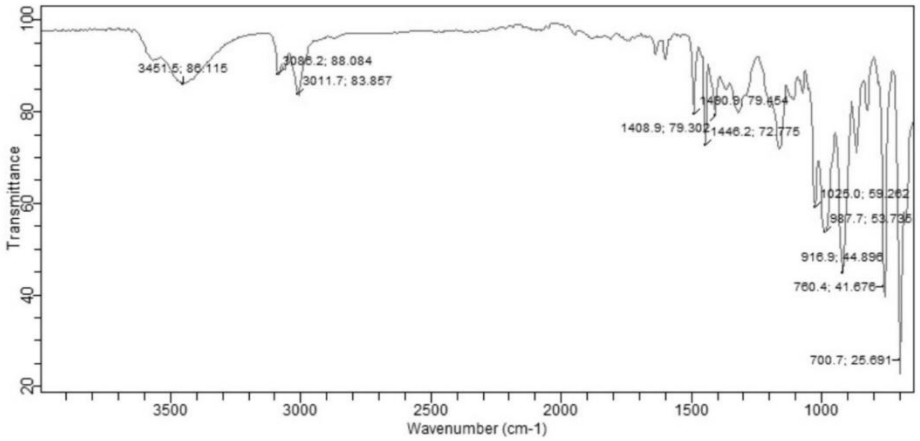
Spectra of project “1,2-aryl migration” – starting materials

1-Cyclopropyl-1-phenylprop-2-en-1-ol (204p)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



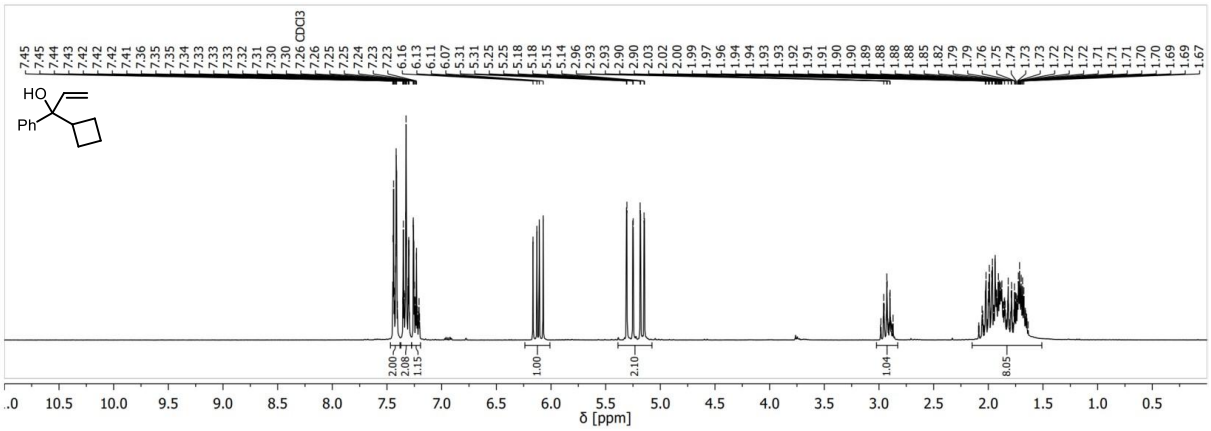


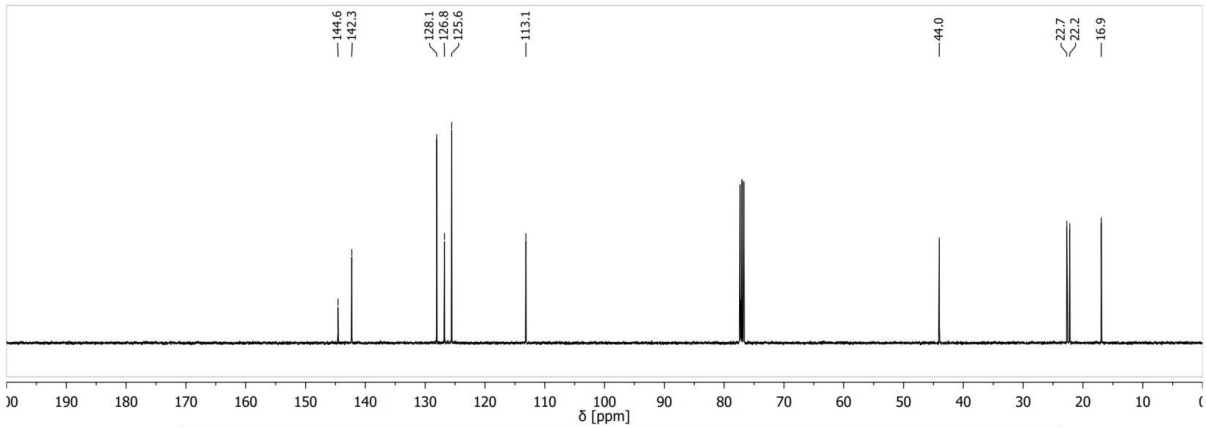


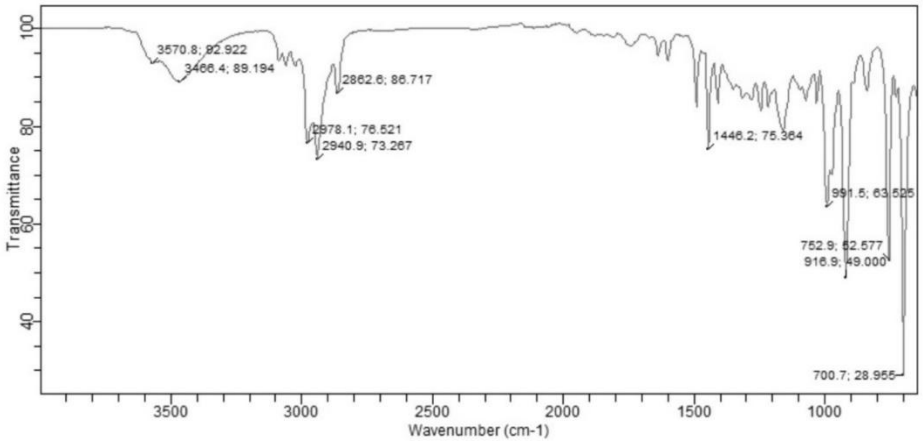
Spectra of project “1,2-aryl migration” – starting materials

1-Cyclobutyl-1-phenylprop-2-en-1-ol (204q)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



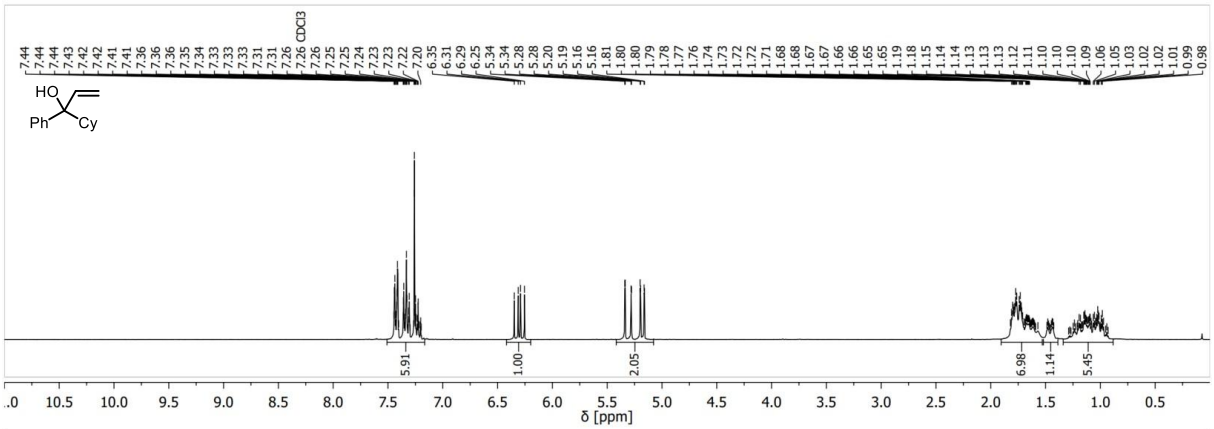


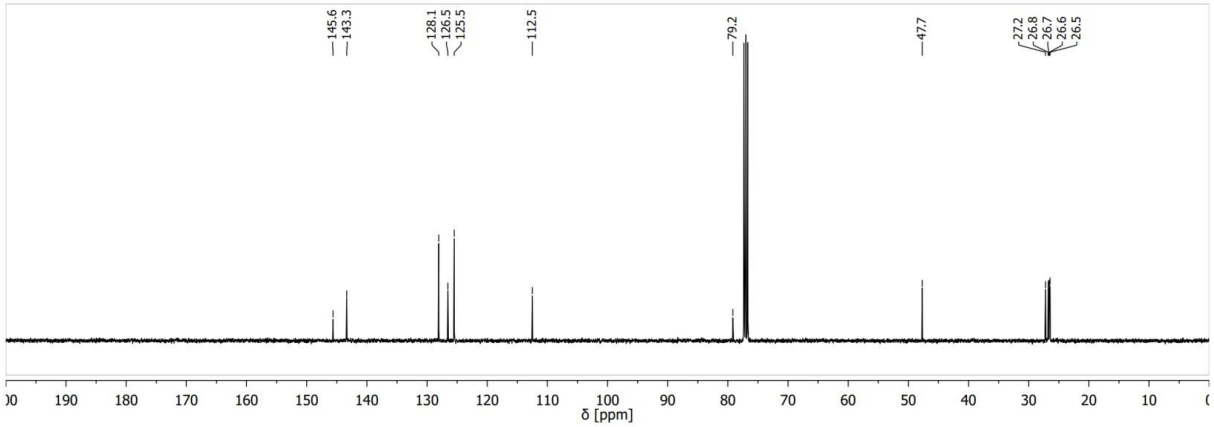


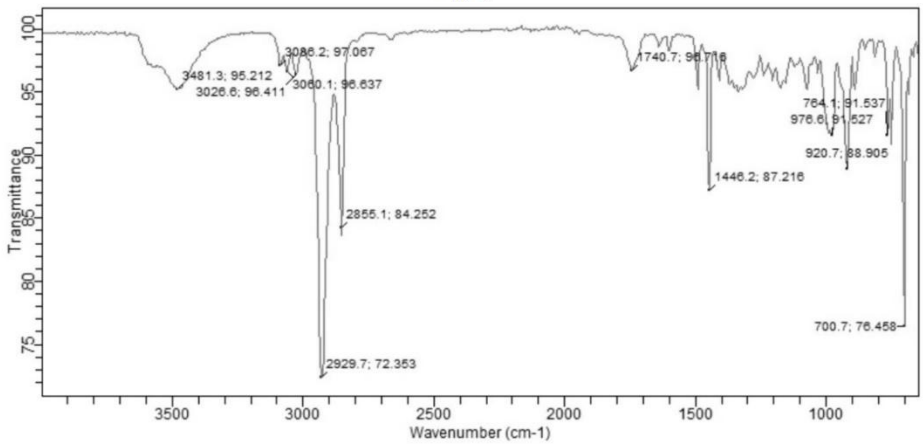
Spectra of project “1,2-aryl migration” – starting materials

1-Cyclohexyl-1-phenylprop-2-en-1-ol (204r)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



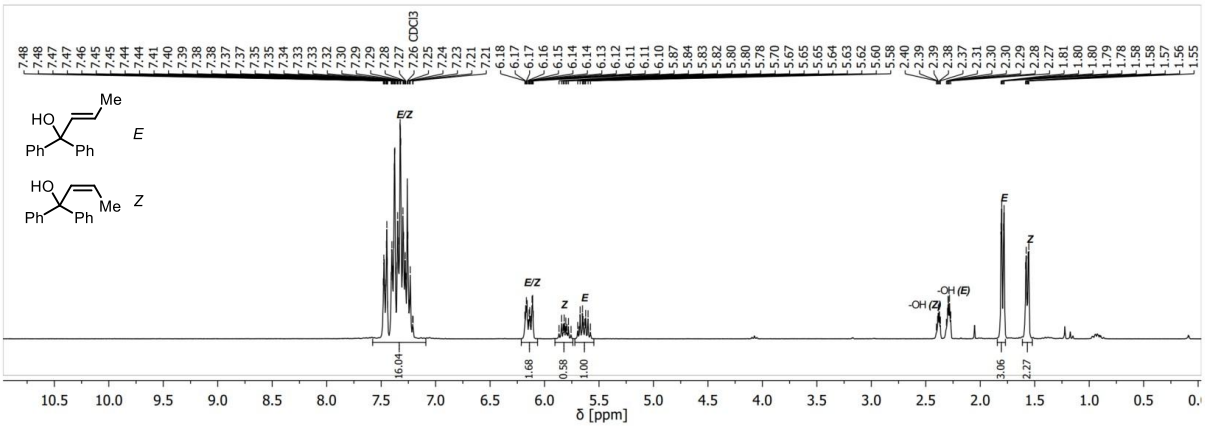


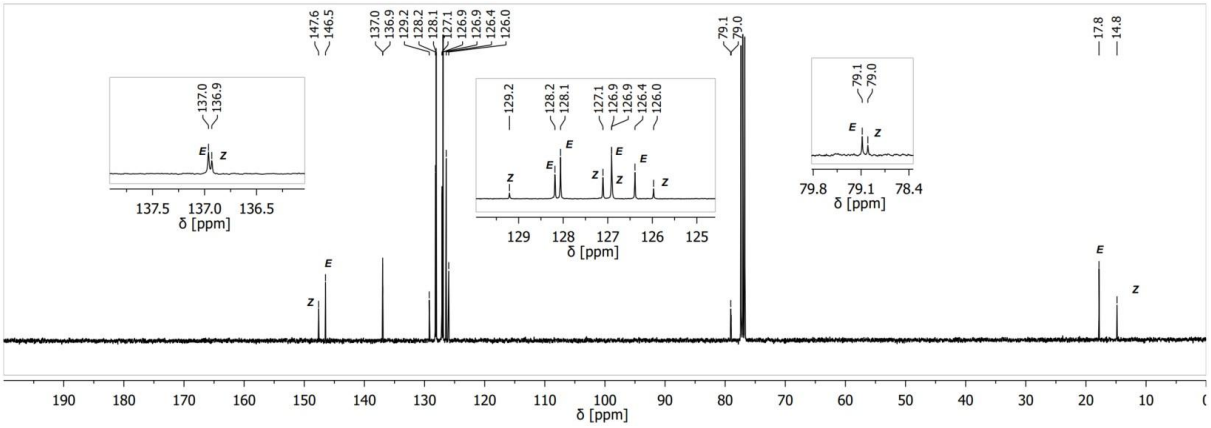


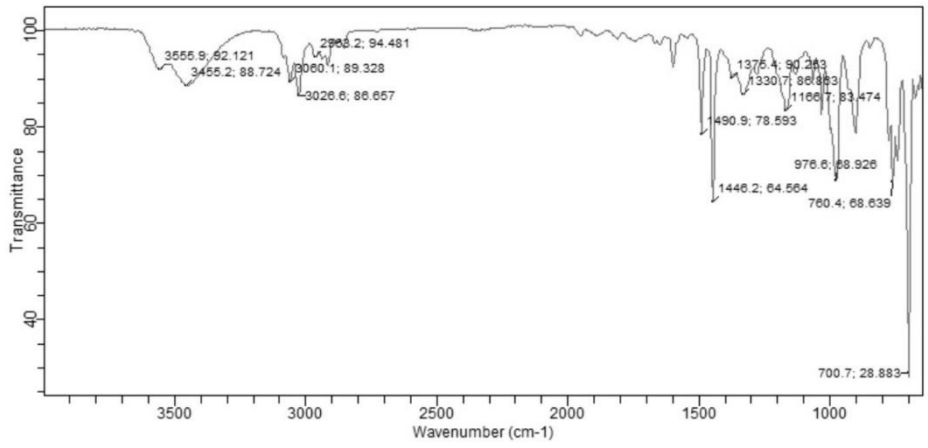
Spectra of project “1,2-aryl migration” – starting materials

1,1-Diphenylbut-2-en-1-ol (204s)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



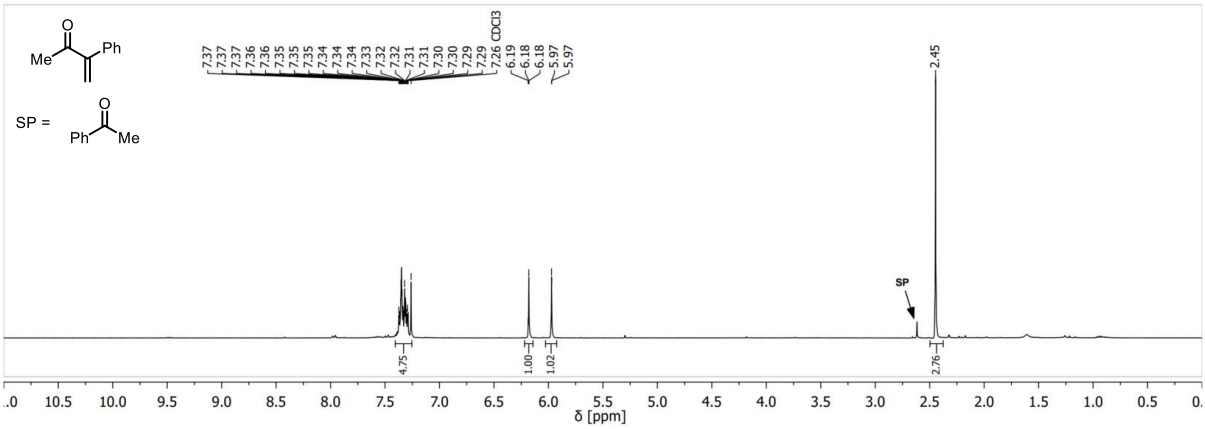


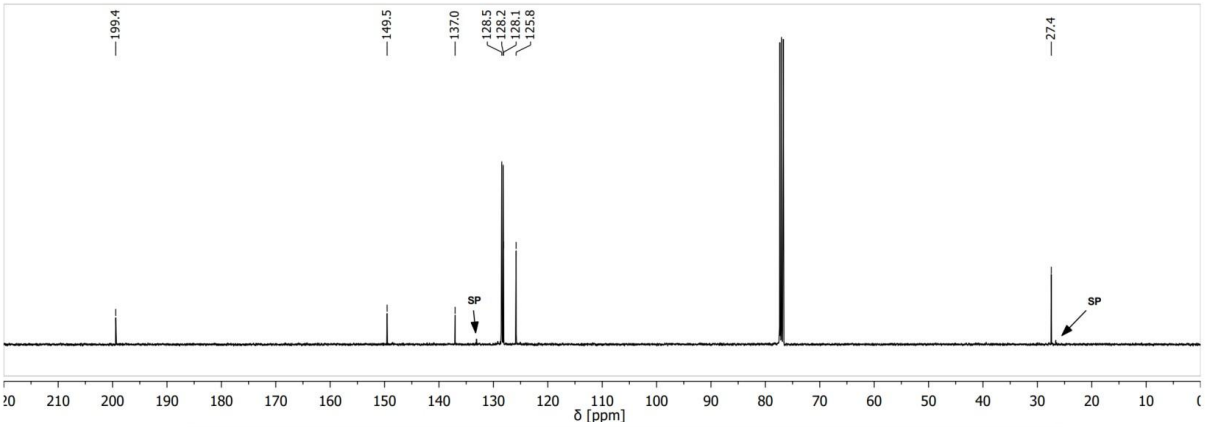


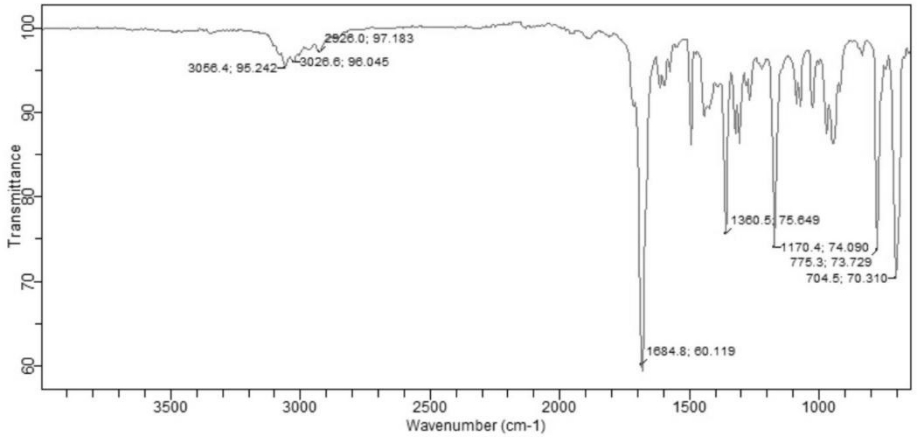
8.6 Spectra of project “1,2-aryl migration” – products

3-Phenylbut-3-en-2-one (205a)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



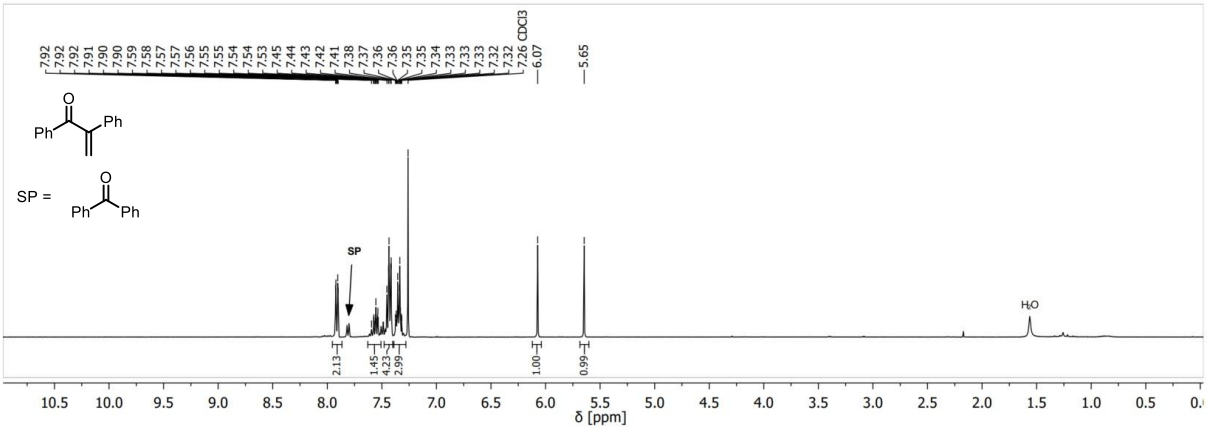


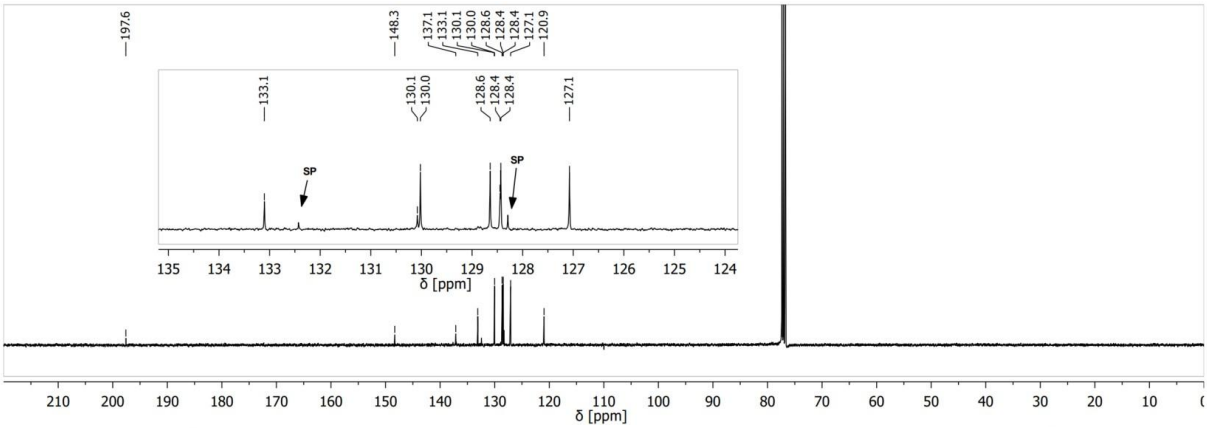


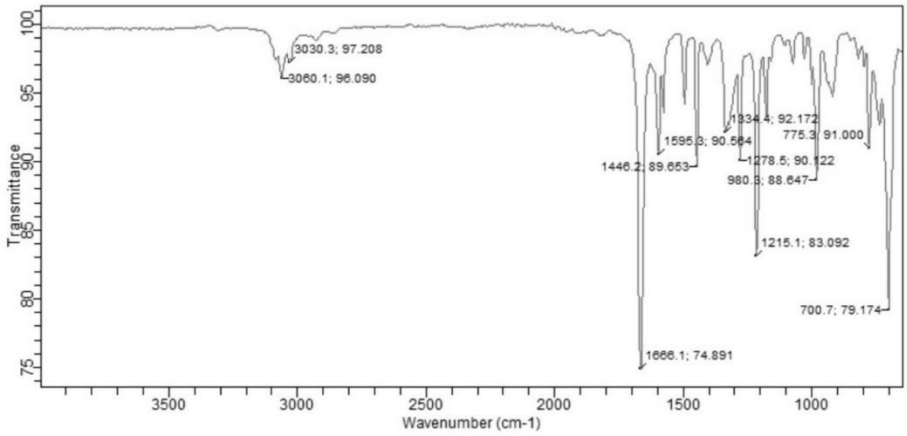
Spectra of project “1,2-aryl migration” – products

1,2-Diphenylprop-2-en-1-one (205b)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



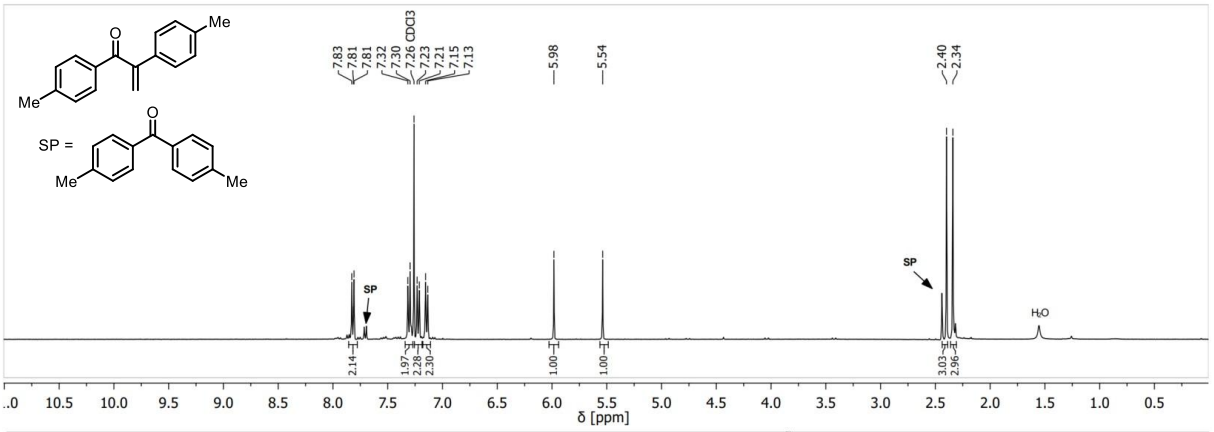


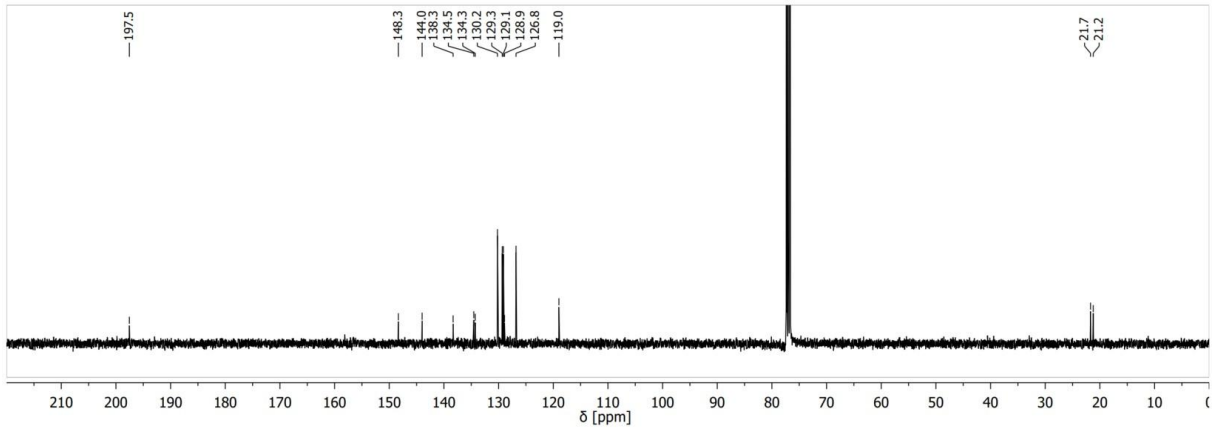


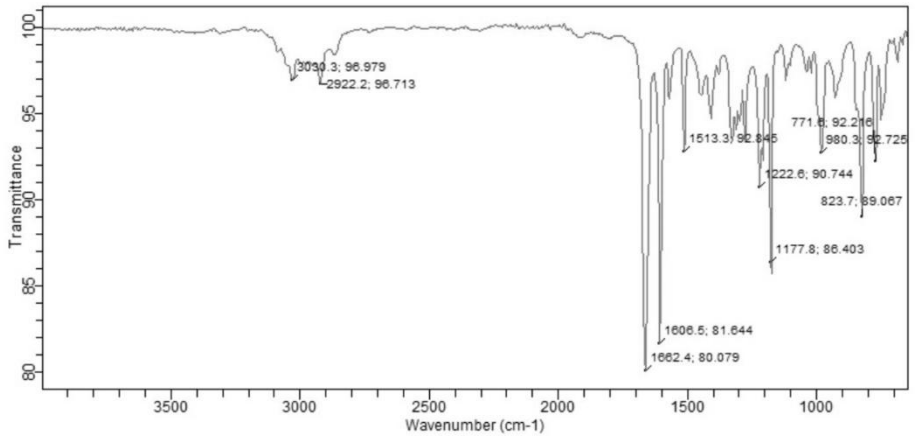
Spectra of project “1,2-aryl migration” – products

1,2-di-*p*-Tolylprop-2-en-1-one (205c)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



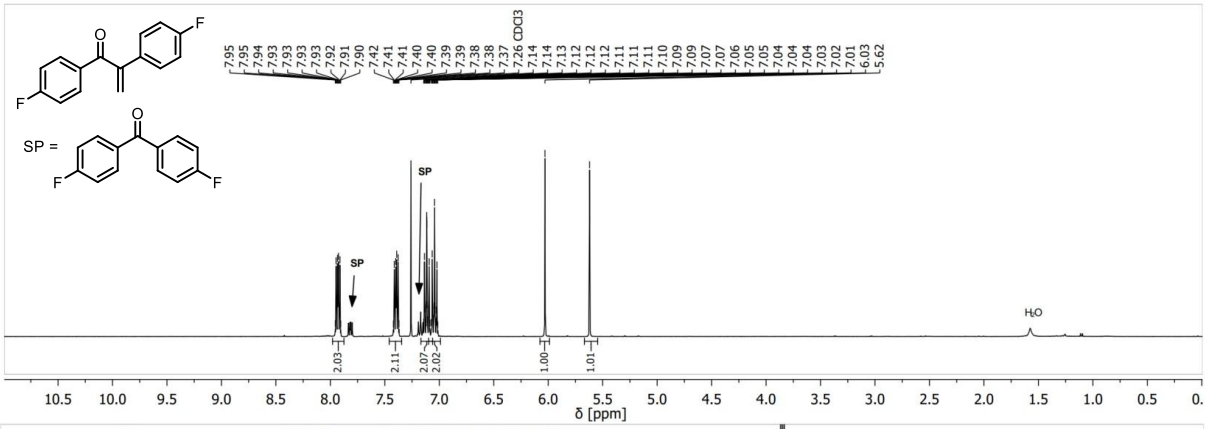


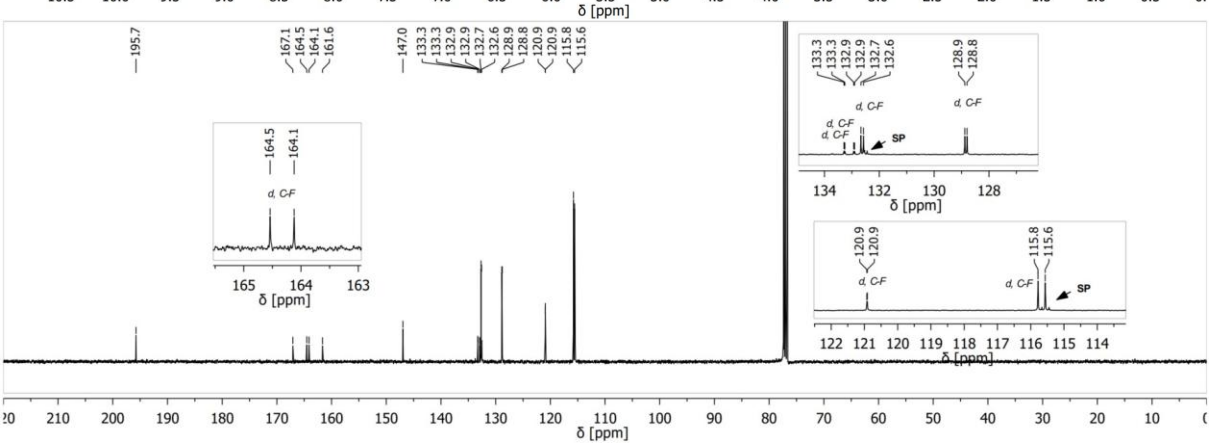


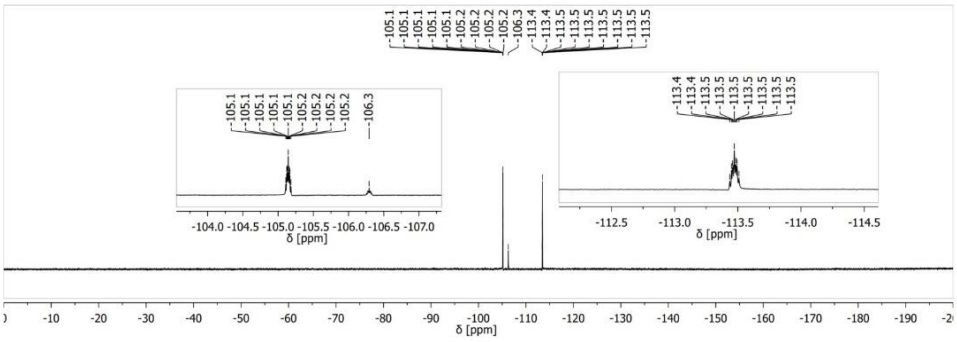
Spectra of project “1,2-aryl migration” – products

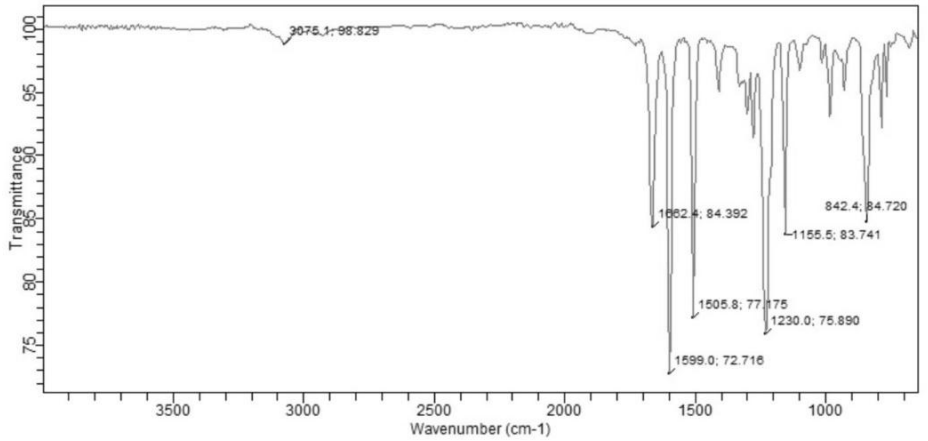
1,2-bis(4-Fluorophenyl)prop-2-en-1-one (205d)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **^{19}F NMR** (376 MHz): Chloroform-*d*, **IR**





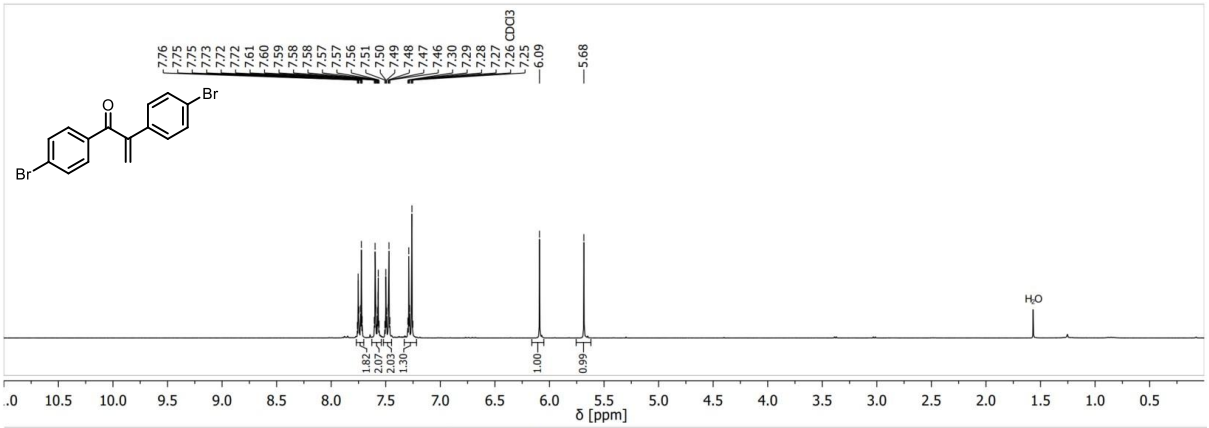


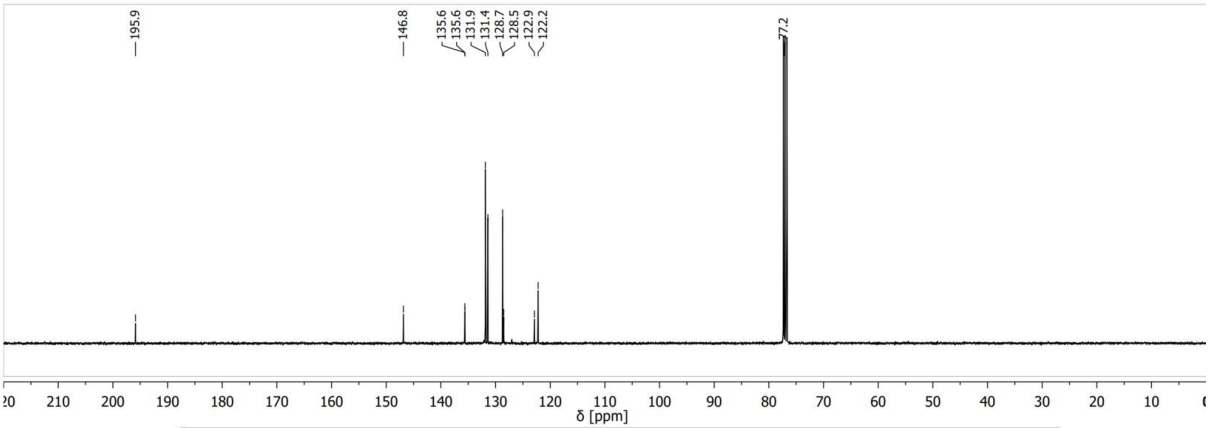


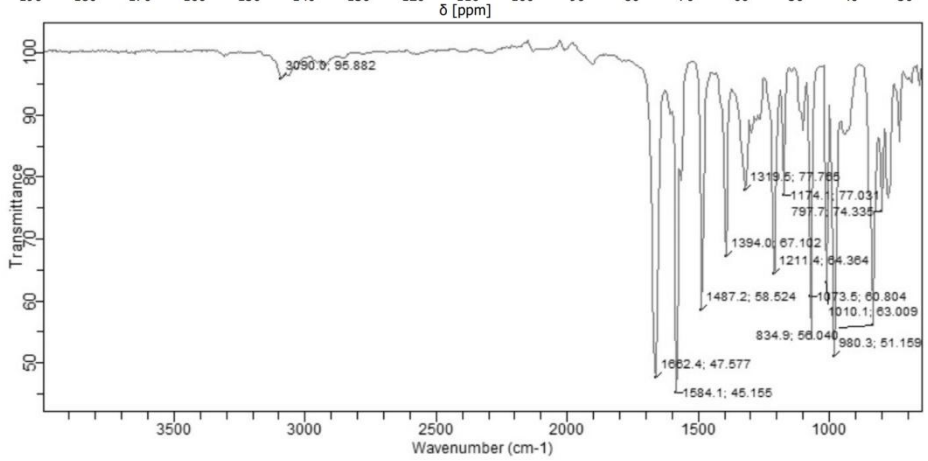
Spectra of project “1,2-aryl migration” – products

1,2-bis(4-Bromophenyl)prop-2-en-1-one (205e)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



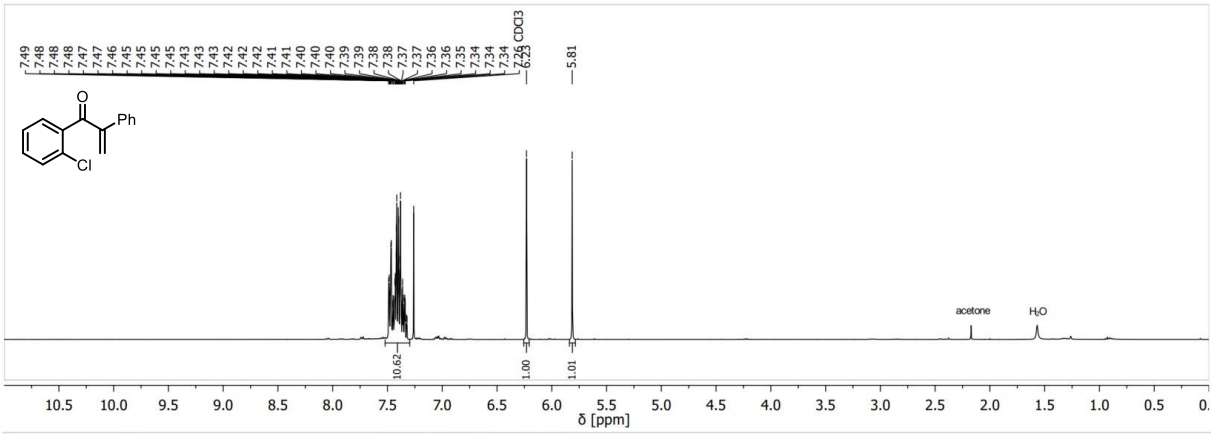


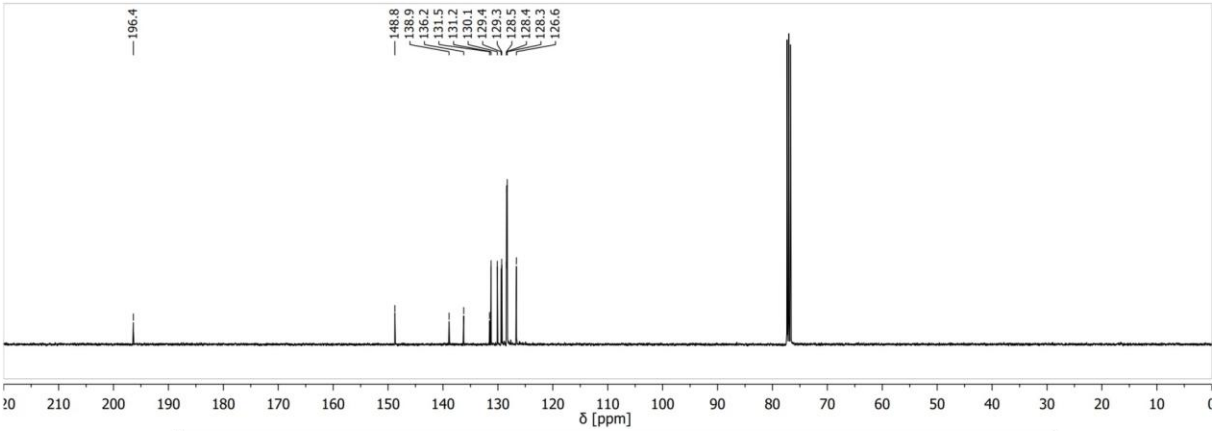


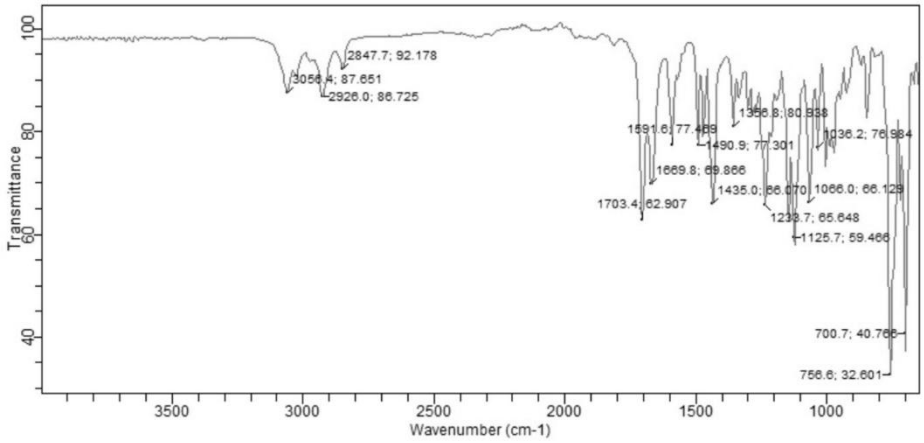
Spectra of project “1,2-aryl migration” – products

1-(2-Chlorophenyl)-2-phenylprop-2-en-1-one (205f-1)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz, C_6D_6): Chloroform-*d*, **IR**

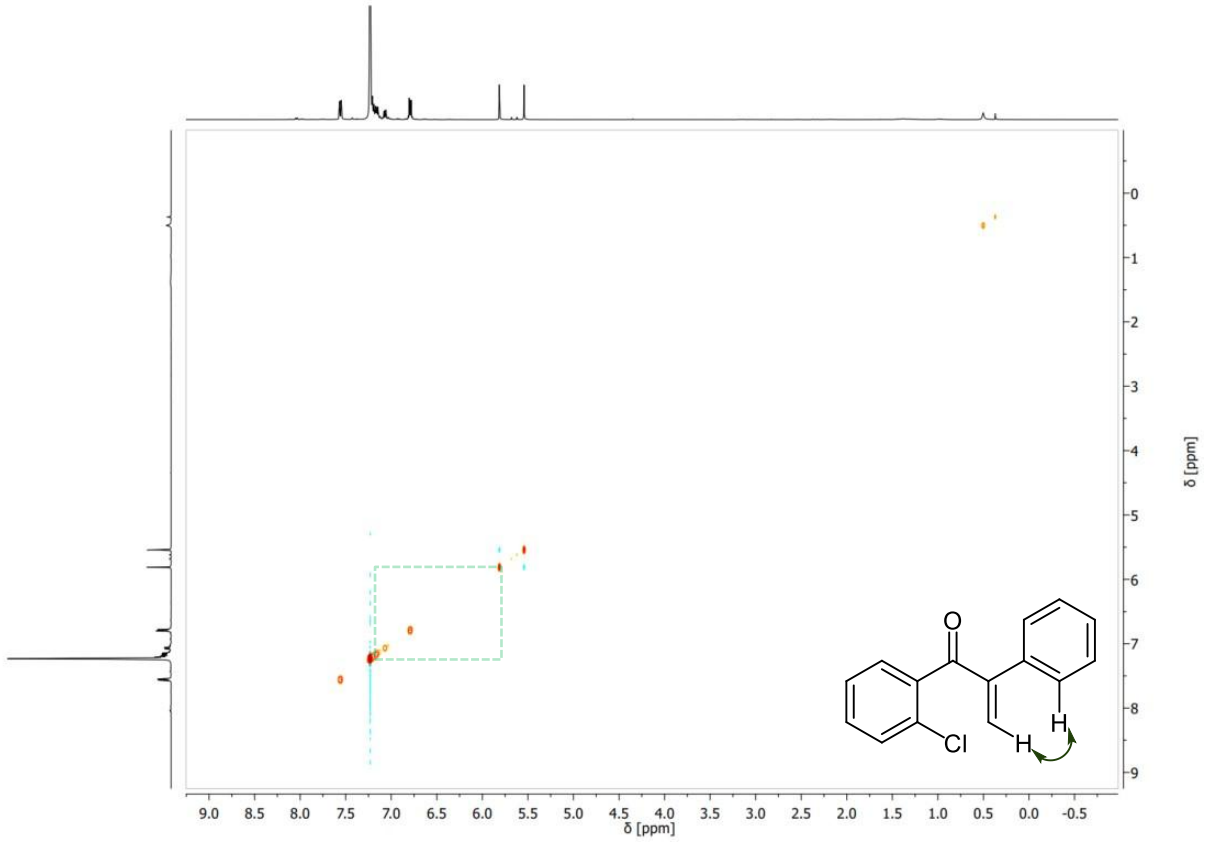






8 Appendix

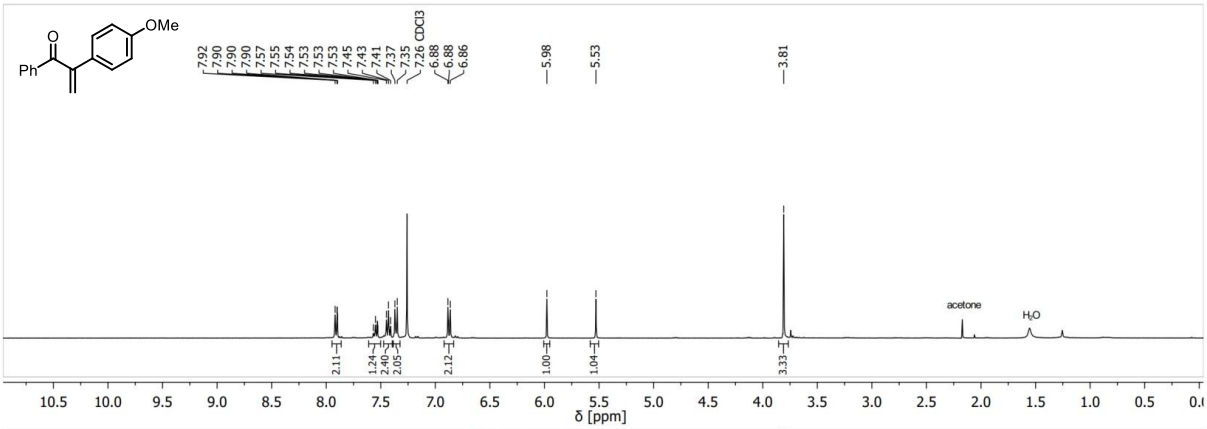
Spectra of project “1,2-aryl migration” – products

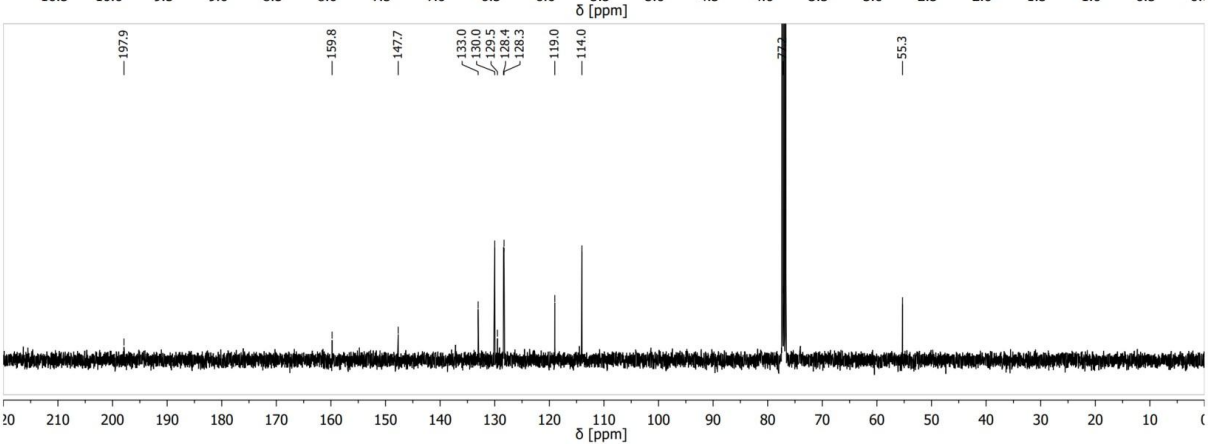


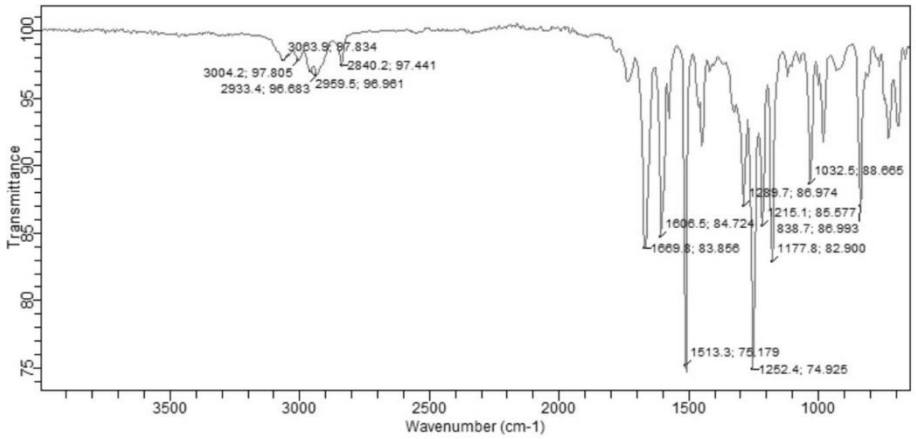
Spectra of project “1,2-aryl migration” – products

2-(4-Methoxyphenyl)-1-phenylprop-2-en-1-one (205g-2)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**

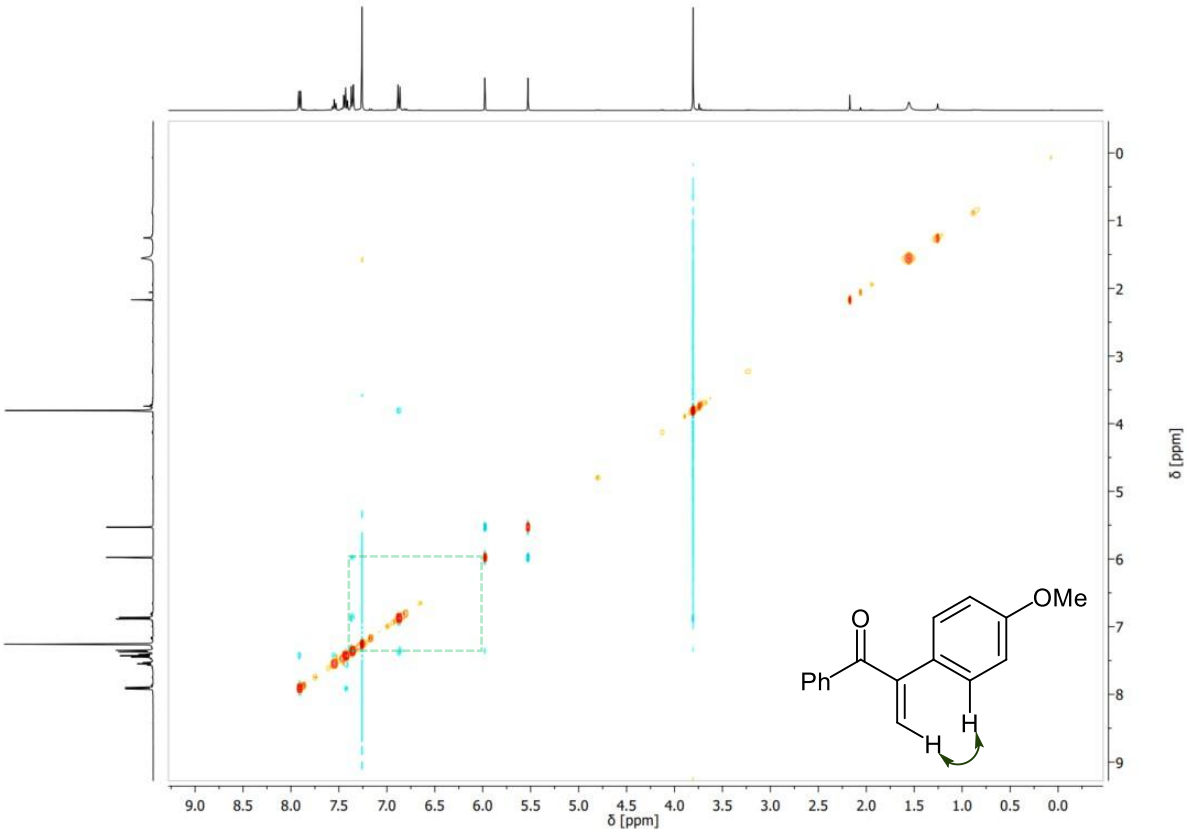






8 Appendix

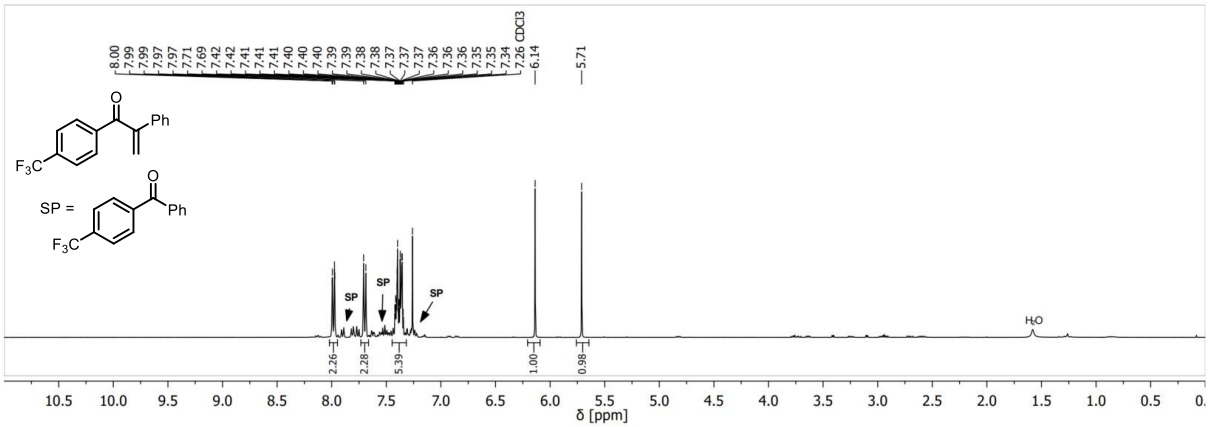
Spectra of project “1,2-aryl migration” – products

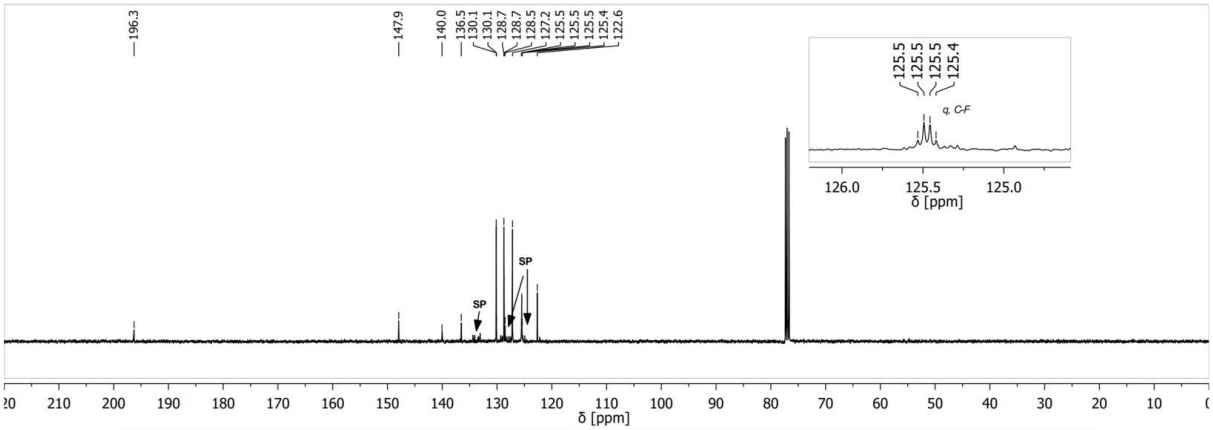


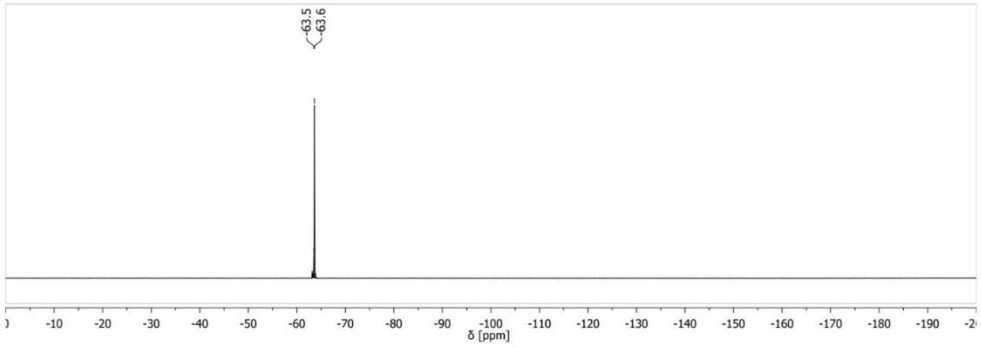
Spectra of project “1,2-aryl migration” – products

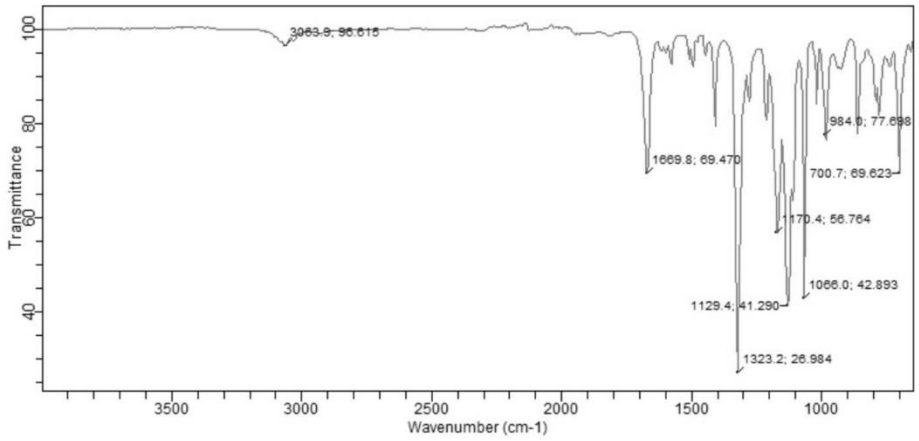
2-Phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (205h-1)

^{1}H NMR (400 MHz) **^{13}C NMR** (101 MHz) **^{19}F NMR** (376 MHz) **NOESY** (400 MHz): Chloroform-*d*, **IR**



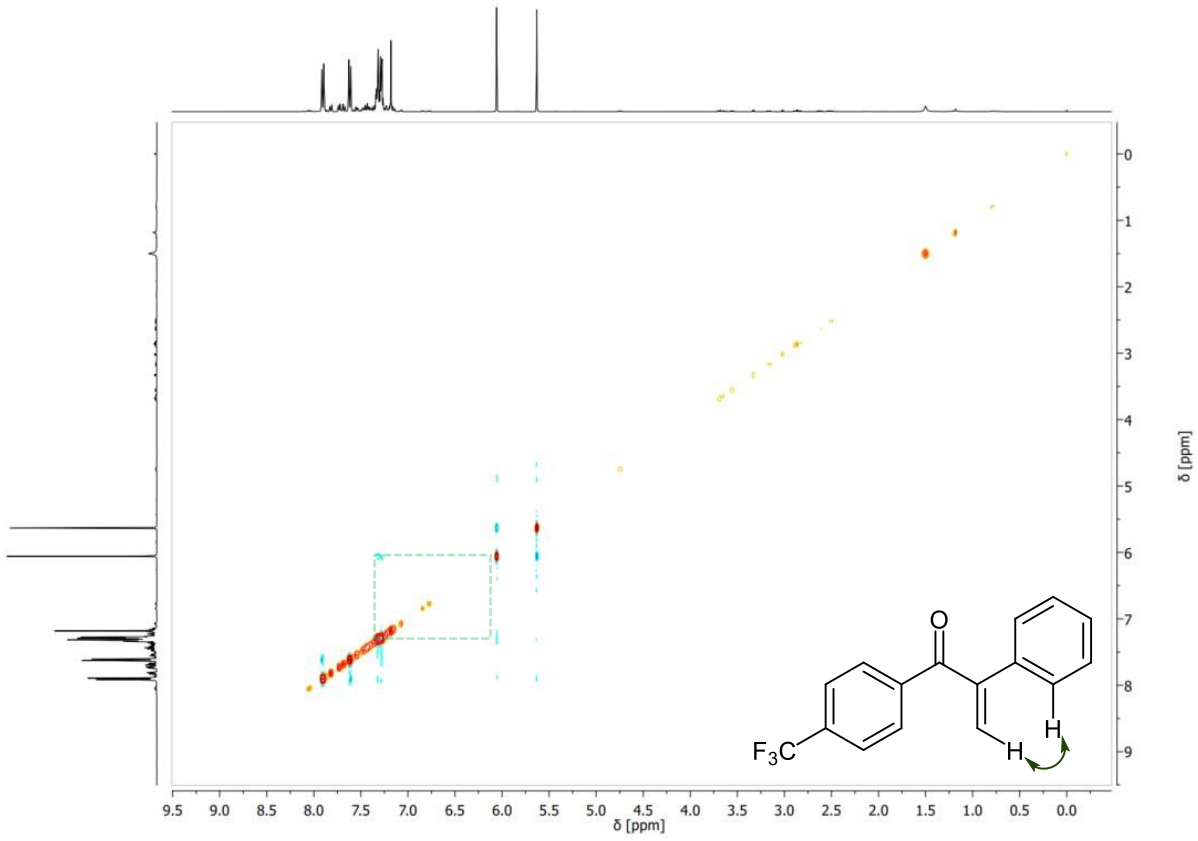






8 Appendix

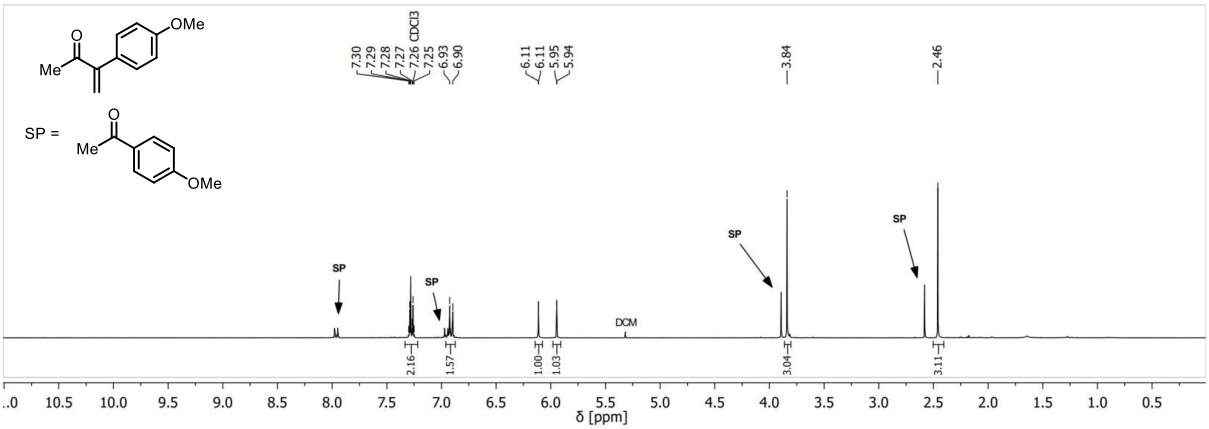
Spectra of project “1,2-aryl migration” – products

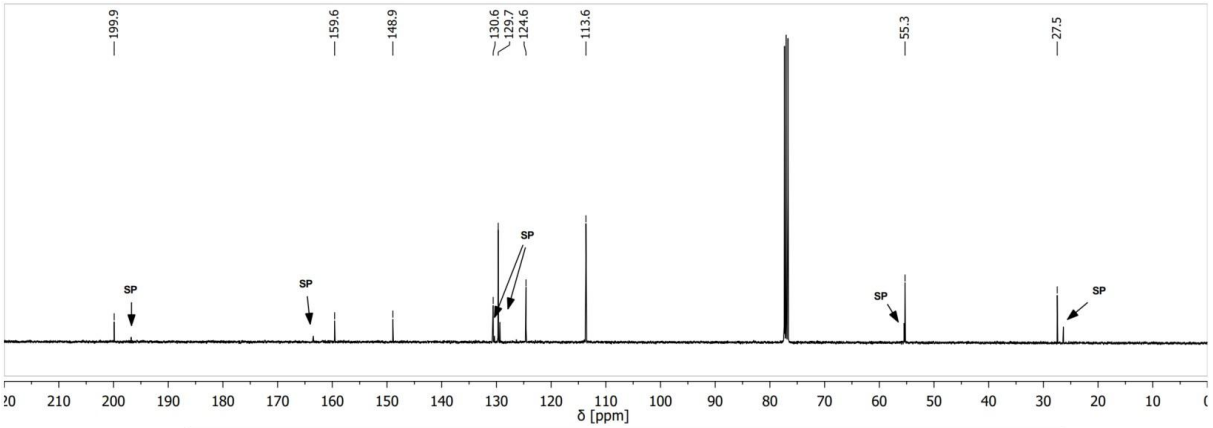


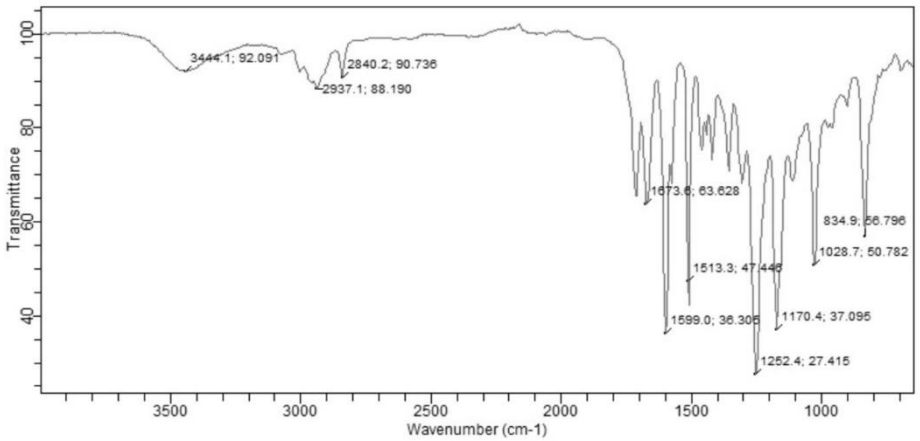
Spectra of project “1,2-aryl migration” – products

3-(4-Methoxyphenyl)but-3-en-2-one (205k)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



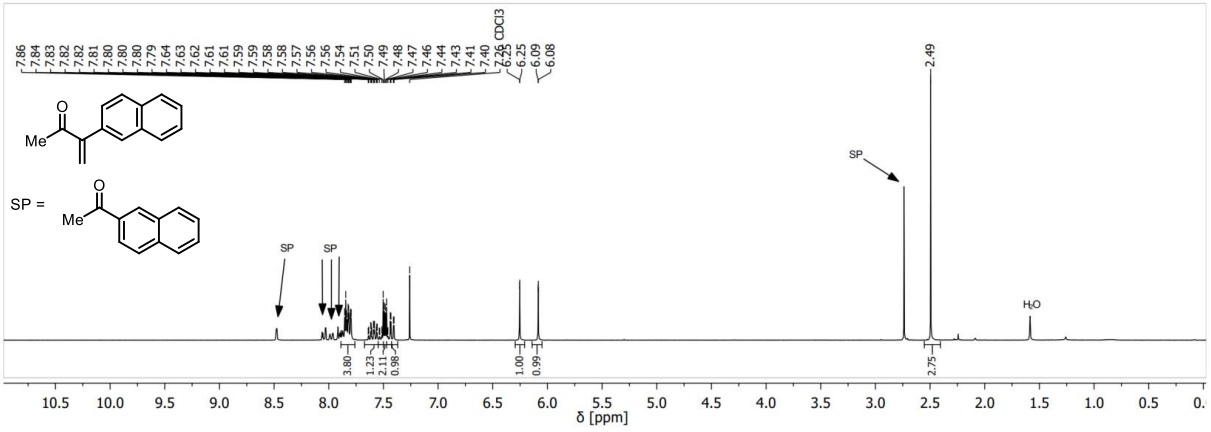


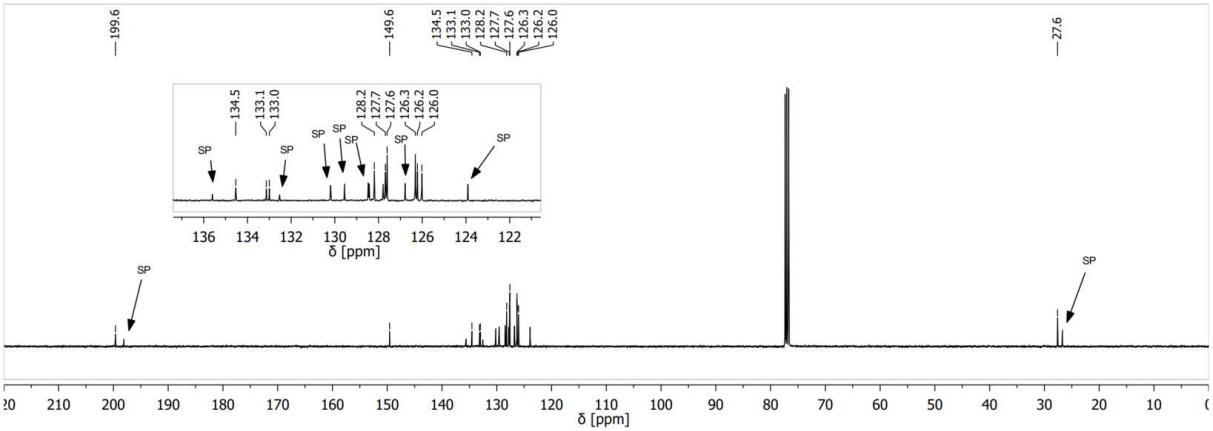


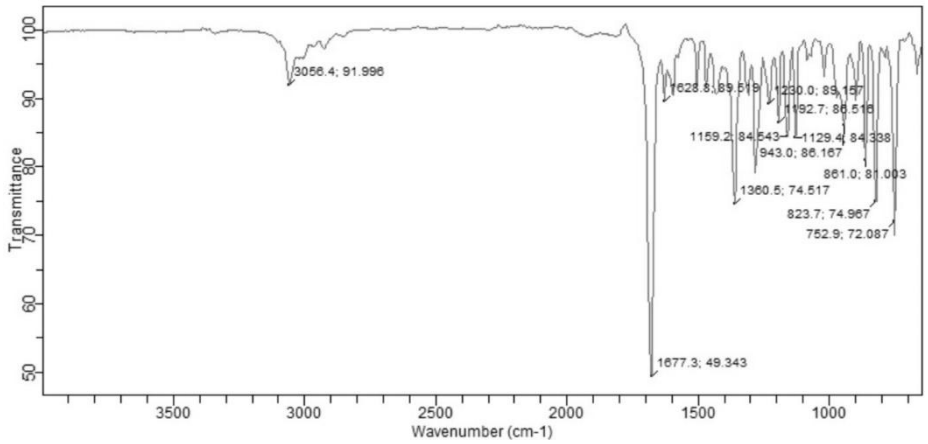
Spectra of project “1,2-aryl migration” – products

3-(Naphthalen-2-yl)but-3-en-2-one (205m)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



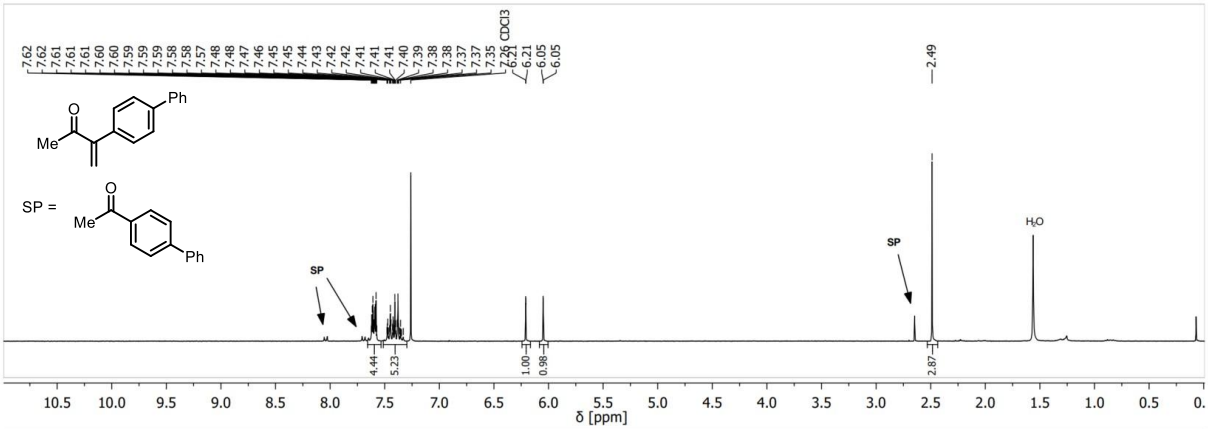


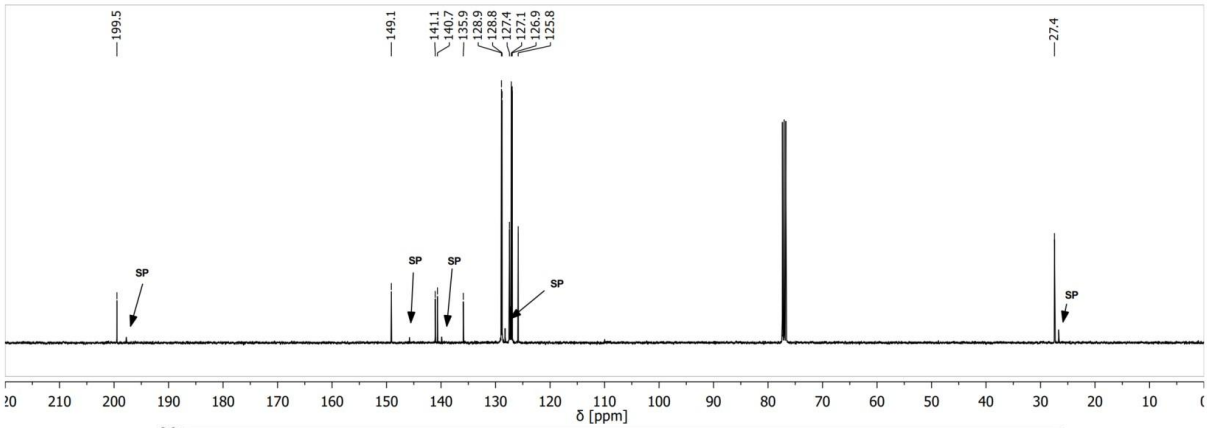


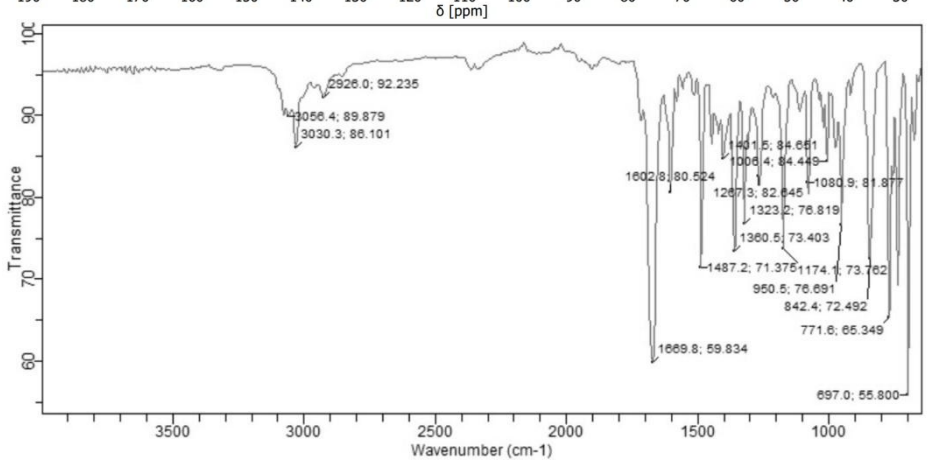
Spectra of project “1,2-aryl migration” – products

3-([1,1'-Biphenyl]-4-yl)but-3-en-2-one (205n)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



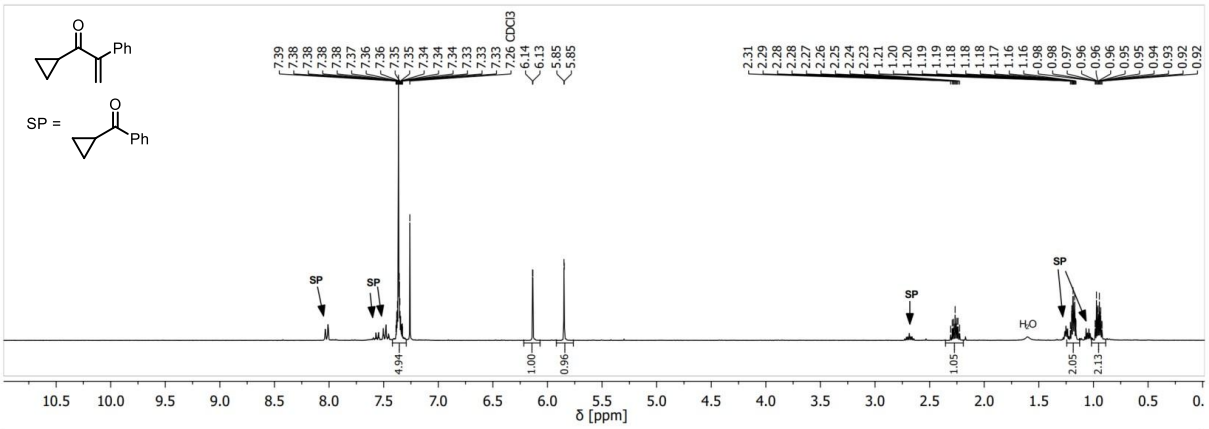


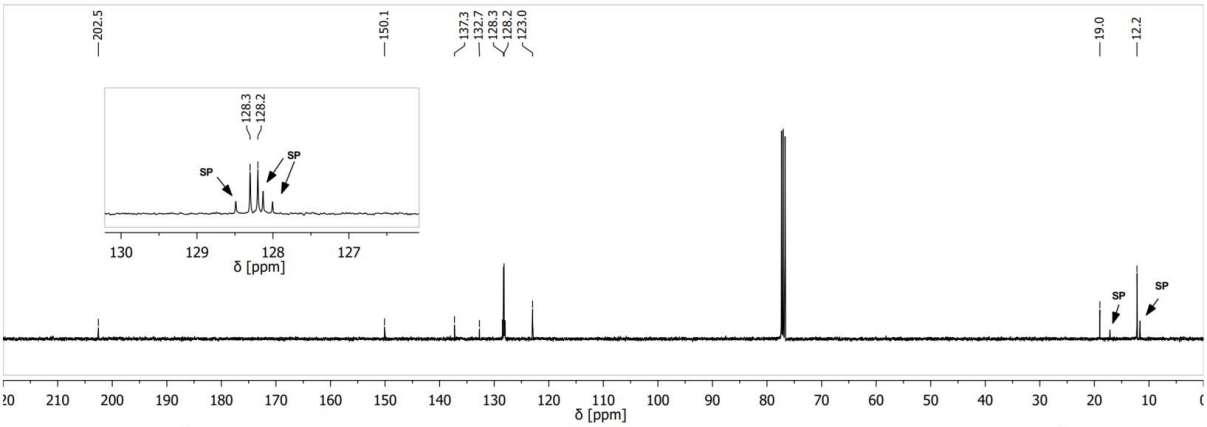


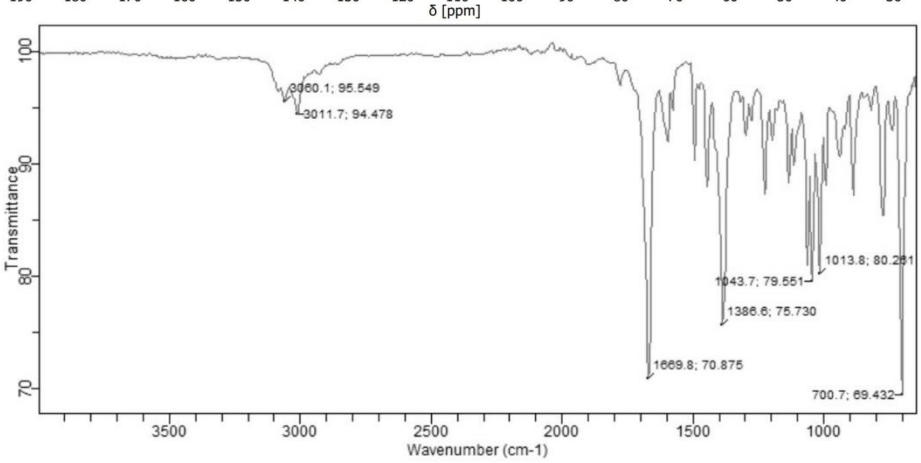
Spectra of project “1,2-aryl migration” – products

1-Cyclopropyl-2-phenylprop-2-en-1-one (205p)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



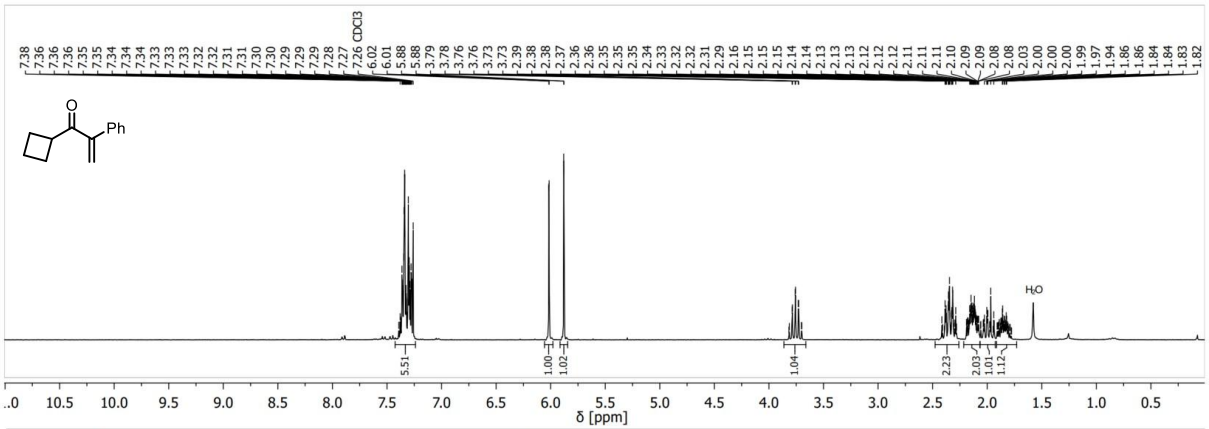


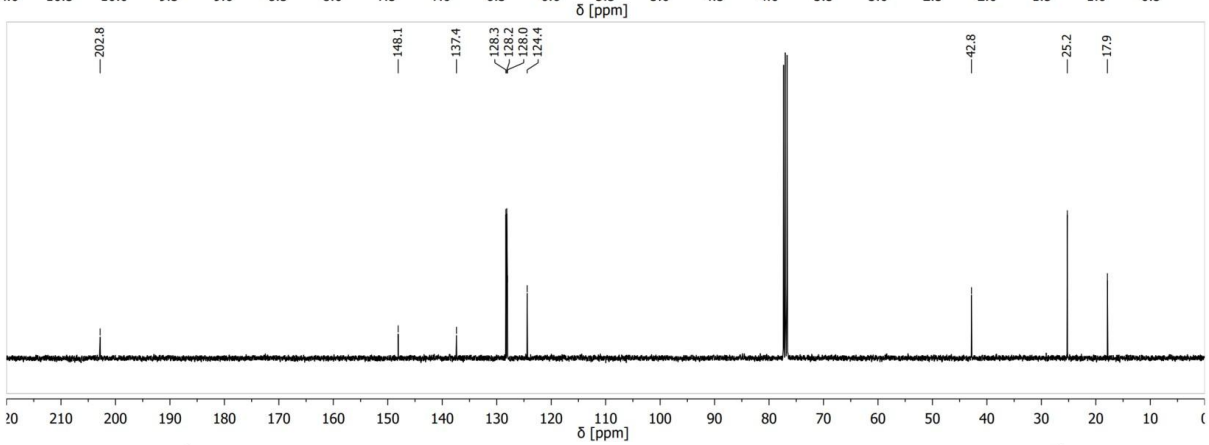


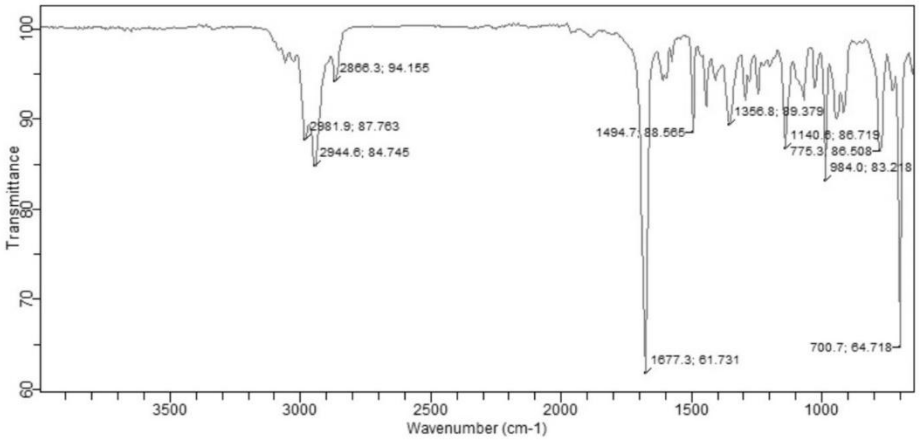
Spectra of project “1,2-aryl migration” – products

1-Cyclobutyl-2-phenylprop-2-en-1-one (205q)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**



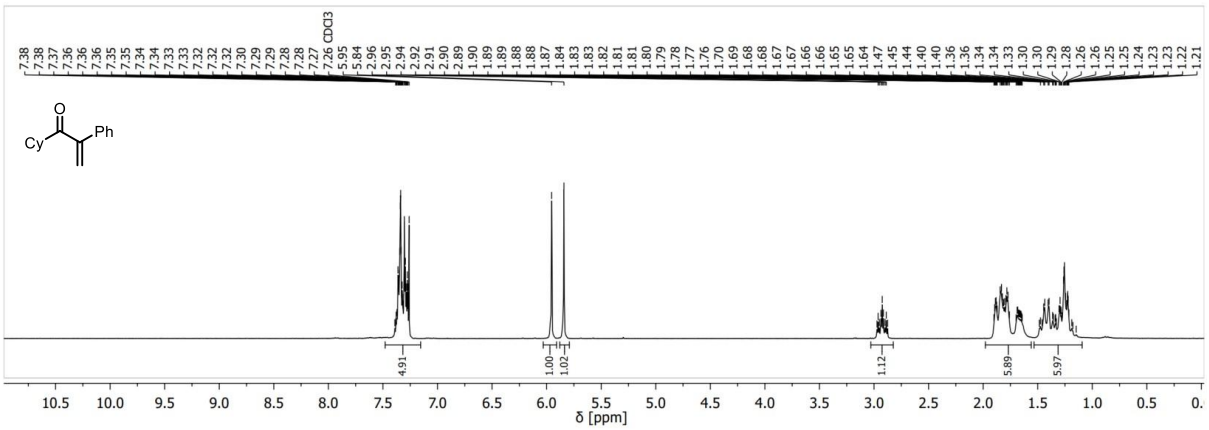


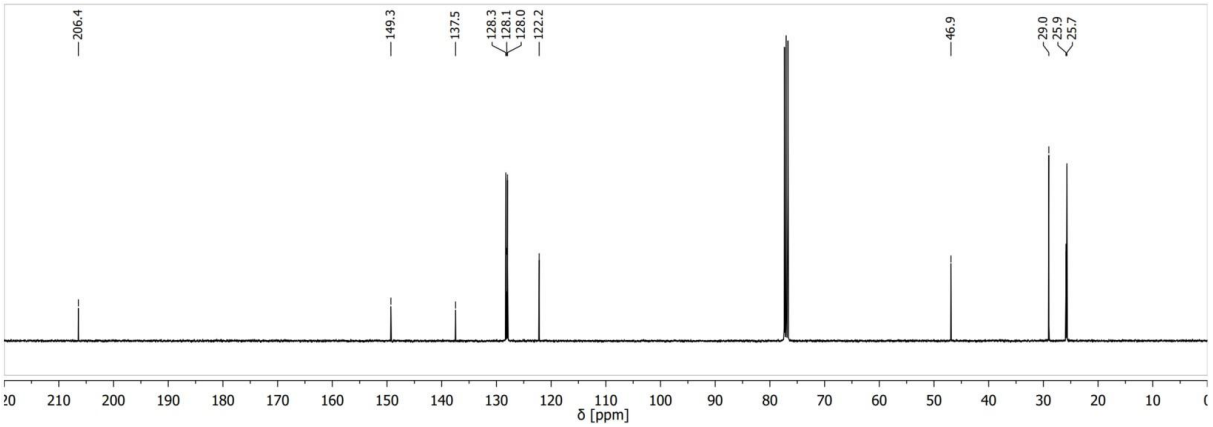


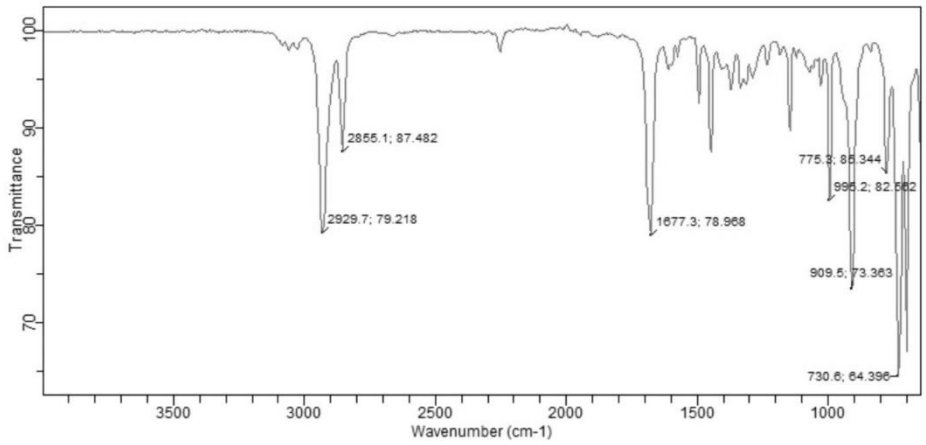
Spectra of project “1,2-aryl migration” – products

1-Cyclohexyl-2-phenylprop-2-en-1-one (205r)

^{1}H NMR (300 MHz) **^{13}C NMR** (101 MHz): Chloroform-*d*, **IR**







9 Acknowledgements

10 Declaration

With this, I declare that the presented thesis and the corresponding practical work were solely prepared by me. Furthermore, I declare that any other results that have not been obtained by myself, but that were necessary for complete presentation of each project, especially regarding explanations, were thoroughly stated as such. This declaration also extends to references taken from literature that was used throughout practical work and this concluding thesis.

Regensburg, 02. Mai 2025

Kilian Müller