Frustrated Lewis Pair-Catalysed Functionalisation of Alkenes with Iodoperfluoroalkanes

and

Gold-Catalysed Desymmetrisation of 1,4-Diynes

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Michael Spittler
aus Castrop-Rauxel

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aus dem Institut für Organische und Makromolekulare Chemie
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Berichterstatter:

1. Prof. Dr. Constantin Czekelius

2. PD Dr. Klaus Schaper

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Preface

This doctoral thesis is composed of two major parts. The first part focuses on Frustrated Lewis Pair catalysis, the second one describes a total synthesis of mesembrine.

Part I, "Frustrated Lewis Pair-Catalysed Functionalisation of Alkenes with Iodoperfluoroalkanes", focuses on FLP-catalysis. In this context, an unpublished part will be presented. Additionally, published work on the reaction mechanism of FLP-catalysed iodoperfluoroalkylations is presented. It is attached and can be cited as "Spittler, M., Helmecke, L. and Czekelius, C., Mechanistic Insights into FLP-Catalyzed Iodoperfluoroalkylations. *Eur. J. Org. Chem.* **2018**, DOI: 10.1002/ejoc.201800866".[1] The results of this publication will be summarised together with the unpublished work. As FLPs were the major topic of this doctoral dissertation, a comprehensive introduction will be given as well.

Part II, "Gold-Catalysed Desymmetrisation of 1,4-Diynes", covers a published total synthesis of (+)-mesembrine. This total synthesis is cited as "Total Synthesis of (+)-Mesembrine Applying Asymmetric Gold Catalysis, Michael Spittler, Kiril Lutsenko, Constantin Czekelius, *J. Org. Chem.* 2016, 81, 6100-6105."[2] Since no unpublished experimental data will be discussed in this context, only a brief introduction to the related topics of gold catalysis and total syntheses of mesembrine will be given. A short summary of the total synthesis can also be found in this part.

Both parts will be presented independently from each other and contain a separate list of contents. Part I, "Frustrated Lewis Pair-Catalysed Functionalisation of Alkenes with Iodoperfluoroalkanes", starts on page 3 and part II, "Gold-Catalysed Desymmetrisation of 1,4-Diynes", on page 161. From page 181 onwards the publications can be found.

Part I

Frustrated Lewis Pair-Catalysed Functionalisation of Alkenes with Iodoperfluoroalkanes

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Abbreviations

BCF	tris(pentafluorophenyl)borane
BHT	3,5-di-*tert*-butyl-4-hydroxytoluene
COSY	correlated spectroscopy
DABCO	1,4-diazabicyclo[2.2.2]octane
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
δ	chemical shift
DIPA	diisopropylamine
eq.	equivalent(s)
HSQC	heteronuclear single quantum correlation
IR	infrared spectroscopy
NHC	*N*-heterocyclic carbene
NMR	nuclear magnetic resonance
SET	single electron transfer
TBAF	tetrabutylammonium fluoride
TFA	trifluoroacetic acid
THF	tetrahydrofurane
TLC	thin layer chromatography
TEEDA	*N*,*N*,*N*′,*N*′-tetraethylethylenediamine
TMEDA	*N*,*N*,*N*',*N*'-tetramethylethylenediamine

1 Abstract

This doctoral dissertation describes work in the field of Frustrated Lewis Pair (FLP) chemistry and a total synthesis of Mesembrine.

Firstly, FLP-systems were investigated which are capable to iodoperfluoralkylate molecules bearing functional groups like amides, esters and ethers. For this purpose electronically tuned phosphanes as well as boranes were synthesised. Next, various phosphanes and solvents were screened. For an elucidation of the mechanism, kinetic studies including a treatment of catalyst degradation pathways were performed. By several test reactions radical intermediates were proven. Terminal alkynes as well as electron-poor alkenes were subjected to iodoperfluoroalkylations. Besides these FLP-catalysed reactions, an iodoperfluoroalkylation utilising solely tri-*tert*-butylphosphane under the influence of sunlight was established for 9-decen-ol, 1-octyne and phenylacetlyene.

Secondly, a total synthesis of (+)-mesembrine was condcuted starting from 4-bromoveratrole with a surprisingly challenging synthesis of a 1,4-diynamide as the key intermediate. This diynamide was successfully subjected to a gold-catalysed enantioselective desymmetrisation to build up a methylene pyrrolidine comprising a quaternary stereocentre.

2 Introduction

The introduction of this doctoral dissertation focuses on the topics perfluoroalkylation and Frustrated Lewis Pairs (FLP). Before the presentation of perfluoroalkylation methods, a short introduction to fluorinated compounds will be given.

2.1 Fluorinated Compounds

Back in 1930, commercial organo-fluorine chemistry started to emerge as alternative coolants for methyl chloride and ammonia in refrigerators. In those years, the production of dichlorodifluoromethane, one important chlorofluorocarbon (CFC), started (Figure 1). Over time other applications of fluorinated compounds as cleaning agents and blowing agents for foam products arose. A very big interest in fluorinated compounds surfaced in World War II, as U^{235} was needed for the preparation of nuclear bombs and uranium isotopes could be separated in the form of UF_6 (Figure 1). Due to the very high reactivity of UF_6 stable seals as well as greases were needed. Therefore, many fluorine-containing polymers, greases and other materials were developed during World War II and are still admired for their special properties. The most remarkable property of many fluorine-containing compounds is their high stability. However, their stability caused a lot of trouble, too. In the late 19th century the CFCs were banned and are no longer produced, as they lead to ozone layer depletion upon UV-induced homolysis.[3]

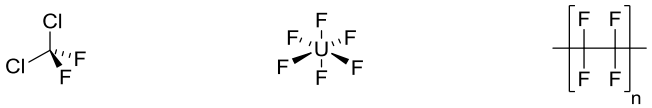


Figure 1: Structural formulas of important fluorinated compounds.

Today, fluorinated compounds play an important role in our society as they have diversified applications. For example, fluorinated compounds are widely used in the pharmaceutical chemistry, can be useful as organocatalysts,[4] and are of great use for daily appliances as helpful materials like Teflon (PTFE, Figure 1).[3] The utility of fluorinated compounds is justified by the stability of the C-F bond. With a bond energy of around 490 kJ/mol it is among the most stable conventional bonds in organic chemistry.[5]

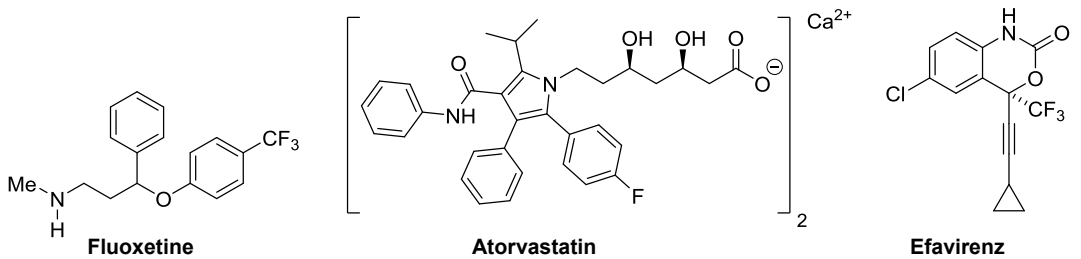


Figure 2: A selection of fluorinated drugs.

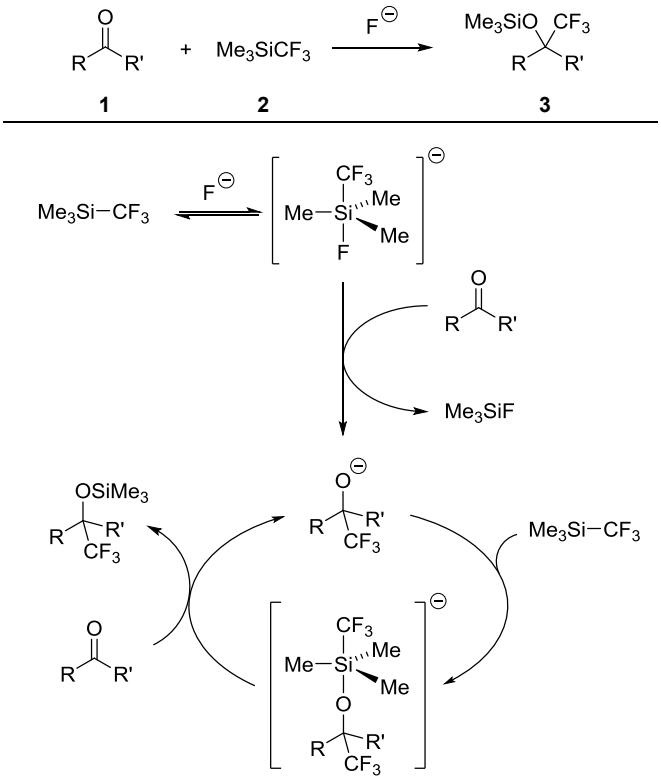
In 2008, Atorvastatin (Lipitor®, Figure 2), a cholesterol-lowering drug, was the world-wide best-selling drug with a revenue of roughly $US 5.9 billion.[6] Other well-known fluorinated drugs are the top-selling antidepressant Fluoxetine[6] and the reverse transcriptase inhibitor Efavirenz (Figure 2),[7] which is predominantly used by HIV patients. Calculations show that in 2010 20% of the administered drugs contained fluorine. Moreover, the fraction of newly approved drugs increased to around 30% within the last years.[8]

2.2 Trifluoromethylation and Perfluoroalkylation

Perfluoroalkyl groups can be used to adjust a molecule's properties towards higher lipophilicity. In many cases this increased lipophilicity allows for better pharmacokinetics, stronger binding of hydrophobic enzyme pockets, and a better blood-brain barrier penetration.[9] Therefore it does not come as a surprise that perfluoroalkylations are of great interest in synthetic chemistry. The widely diversified chemistry of perfluoroalkyl iodides[10] and fluoroalkyl radicals[11-12] was reviewed by different contributors. Neal O. Brace published an extensive series of three reviews about perfluoroalkyl iodides and their use in synthetic chemistry.[13-15] The most important perfluorinated alkyl substituent in organo-fluorine chemistry[16] is the trifluoromethyl-group.
Nucleophilic, electrophilic as well as radical trifluoromethylations will be described followed by perfluoroalkylations.

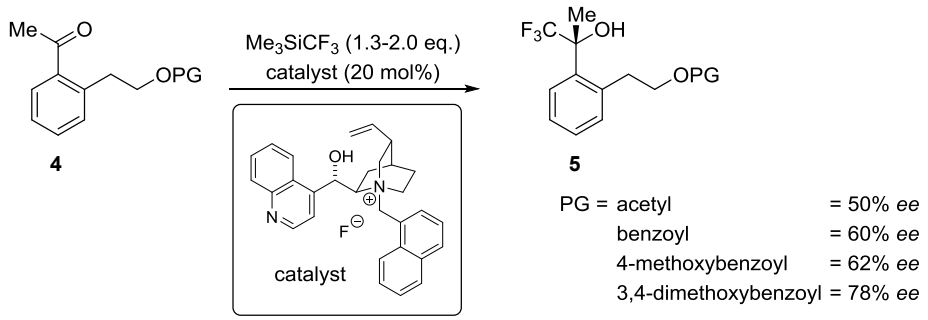
2.2.1 Nucleophilic Trifluoromethylation

For a nucleophilic trifluoromethylation a stabilised CF_3^--equivalent is needed. Without any stabilisation, free CF_3^--anions easily collapse into fluoride and a difluorocarbene. A stabilisation can be accomplished by removing electron density from the carbon atom. The mainly used approaches for this purpose are the coordination to copper and a sigma bond to silicon.[17] One of the best established nucleophilic trifluoromethylation agents is (trifluoromethyl)trimethylsilane (**1**) (Scheme 1), also called the Ruppert-Prakash reagent. It is widely used for α-trifluoromethylations of carbonyl-compounds. The scope of this transformation spans from sterically demanding aromatic and aliphatic aldehydes to ketones. Furthermore, esters, cyclic anhydrides, amides, imides and further substrates can be transformed into the corresponding trifluoromethylated compounds.[16,18] The proposed mechanism for this conversion is shown in Scheme 1. A common catalyst for this reaction is tetrabutylammonium fluoride (TBAF), serving as the source of fluoride anions to activate (trifluoromethyl)trimethylsilane (**1**) for the CF_3^--transfer (Scheme 1).



Scheme 1: Trifluoromethylation of carbonyls with Me_3SiCF_3 and a fluoride source (top), proposed mechanism (bottom).[16,18]

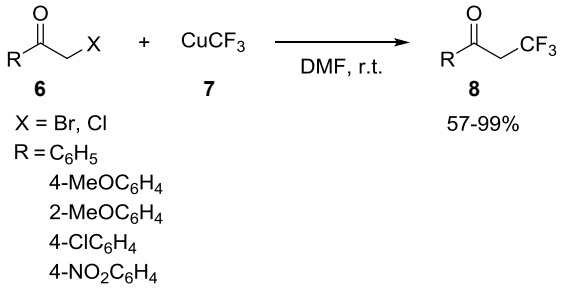
Interesting variants with other catalysts than TBAF, and enantioselective protocols have been developed.[16] In 1994, Kobayashi *et al.* were the first to present an asymmetric trifluoromethylation utilising a cinchona-derived ammonium fluoride (Scheme 2).[19] Up to this day, high enantiomeric excesses remain a challenge, as each substrate requires an adjustment of the solvent, reaction temperature and the catalyst.[16]



Scheme 2: Selected examples of asymmetric trifluoromethylation applying quaternary cinchona-derived ammonium fluorides.[19]

As already mentioned, copper proves to be a very useful transition metal with respect to perfluoroalkylations. For example, a combination of catalytic amounts of (thiophene-2-carbonyloxy)copper (CuTc) and potassium fluoride is useful for the trifluoromethylation of

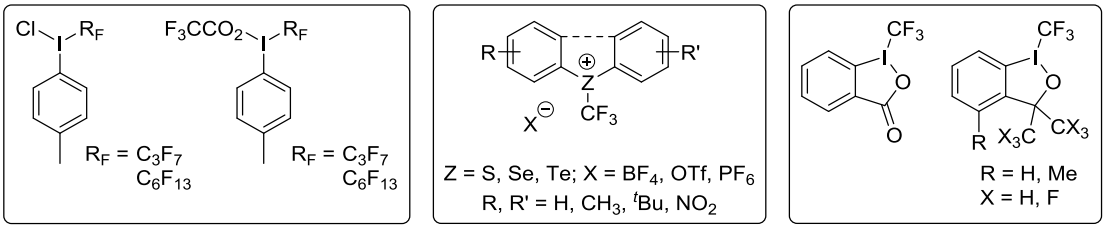
allylic and propargylic halides.[16,20] Another possibility is the trifluoromethylation of α-haloketones with $CuCF_3$ species **7** (Scheme 3).[21]



Scheme 3: Copper(I)-CF_3 as a CF_3-group transfer agent for α-haloketones.[21]

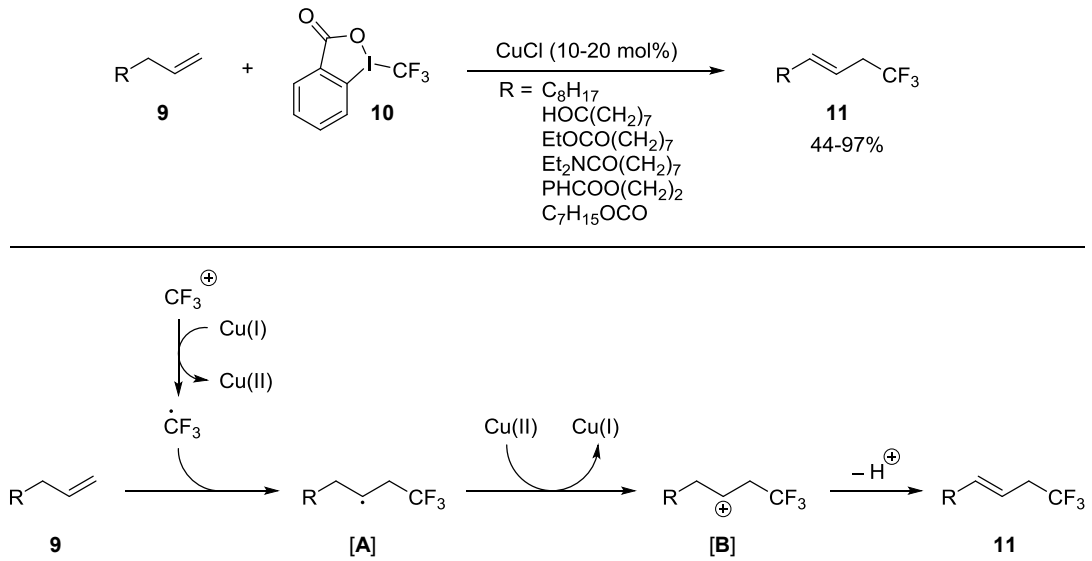
2.2.2 Electrophilic Trifluoromethylation

Since the development of the first electrophilic trifluoromethylation reagents by Yagupolskii *et al.* in 1978[22] (Scheme 4), several other electrophilic trifluoromethylation agents have been developed by Umemoto and Togni.[23-25] These are of special interest for the trifluoromethylation of late stage intermediates of multistep syntheses and therefore play an important role in synthetic chemistry.



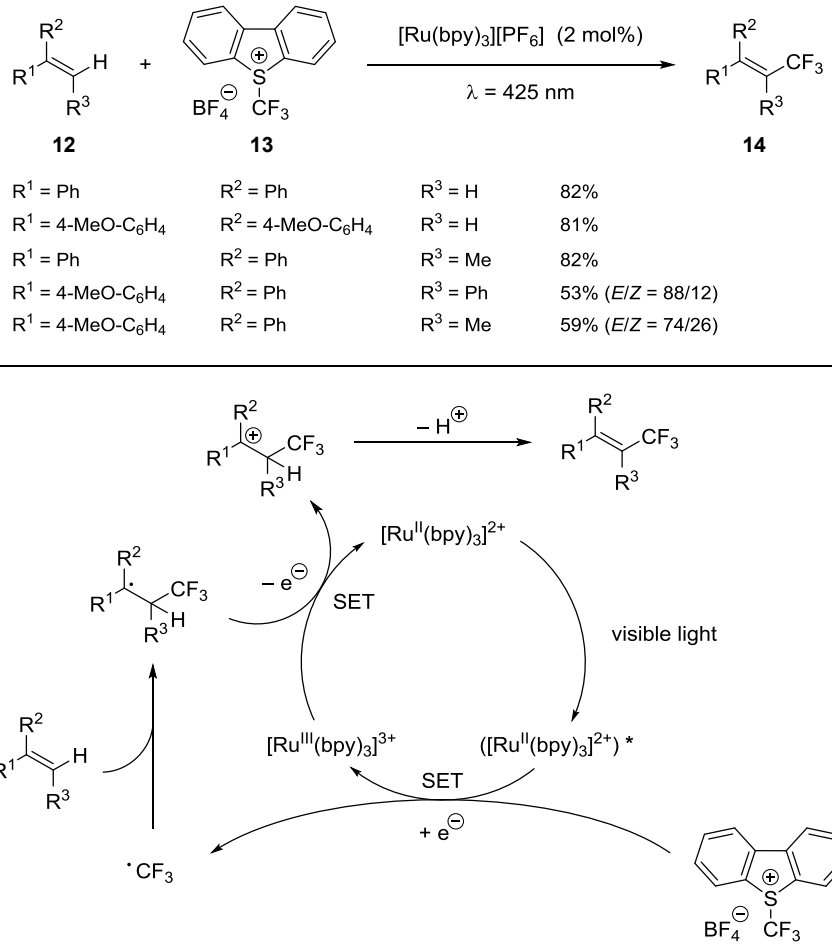
Scheme 4: Electrophilic trifluoromethylation agents.[22-25]

In Scheme 5 the use of Togni's reagent in combination with copper(I) for the trifluoromethylation of terminal electron-rich alkenes is presented. Referring to a review of Postigo *et al.*,[25] combinations of Togni's reagents and catalytic amounts of copper(I)-reagents are valuable combinations for trifluoromethylations. Recently, a single electron transfer (SET) from copper(I) to the CF_3^+-cation and the subsequent formation of a CF_3-radical was proposed. This radical attacks the alkene to form the allyl radical [**A**]. It is then oxidised by copper(II), giving the cation [**B**], which is deprotonated to give the trifluoromethylated alkene. Under the same reaction conditions electron-deficient quinones can be trifluoromethylated.[26]



Scheme 5: Trifluoromethylation of alkenes with Togni's reagent (top), proposed mechanism (bottom).[27]

Umemoto's as well as Togni's reagent can be employed under photocatalytic conditions.[25] For instance, Akita *et al.*[28] showed that Umemoto's reagent **13**, in combination with $[Ru(bpy)_3][PF_6]$ and a light source is capable of converting alkenes into the corresponding CF_3-alkenes (Scheme 6). The light source was needed to excite $[Ru(bpy)_3]^{2+}$ resulting in a SET to Umemoto's reagent under liberation of a CF_3-radical. Diphenylethenes **12** with electron-donating substituents or electron-withdrawing halogen substituents were transformed into CF_3-alkenes in good yields. Even trisubstituted alkenes were converted into the corresponding alkenes in moderate to good yields but were isolated as mixtures of the (*E*)- and (*Z*)-isomer.[28]

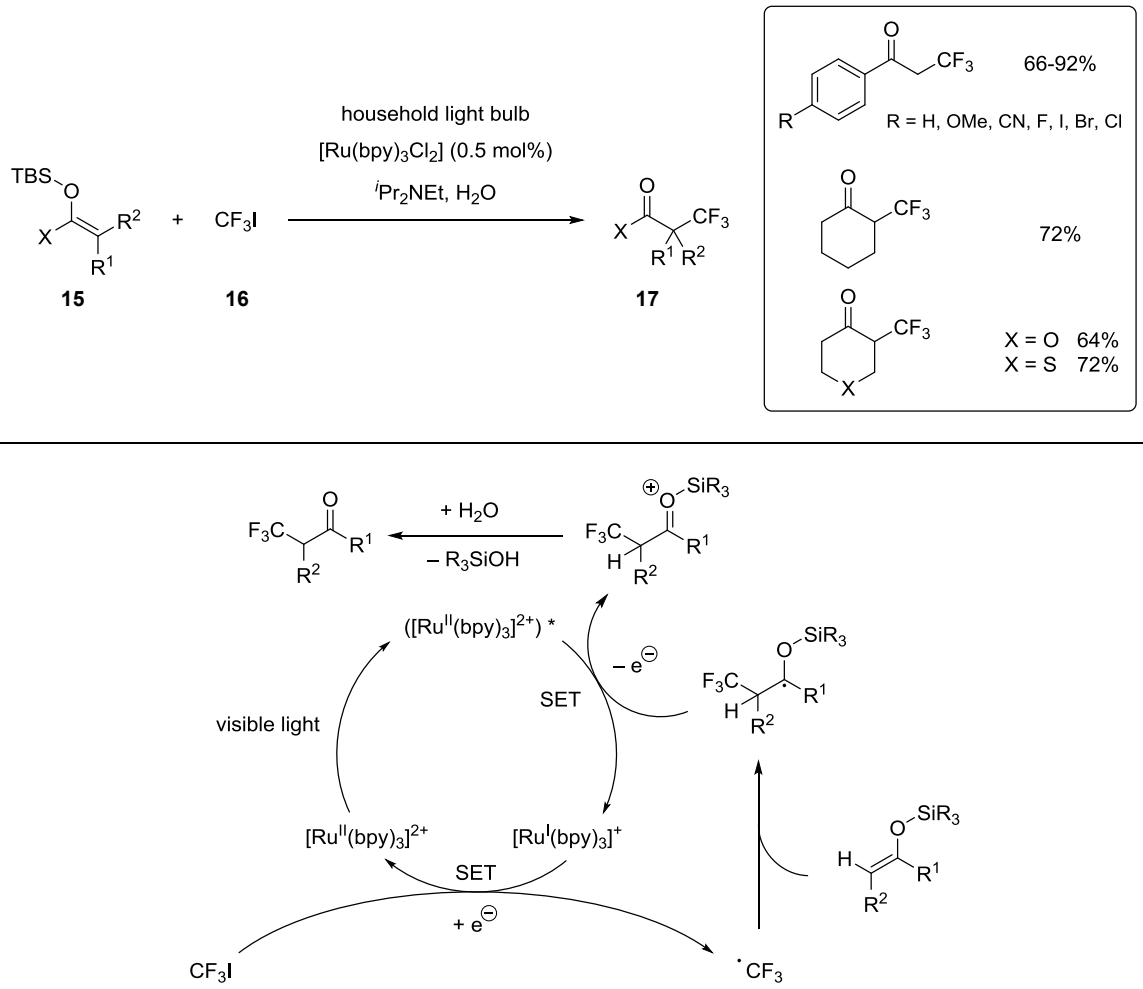


Scheme 6: Trifluoromethylation of di- and trisubstituted alkenes with Umemoto's reagent (top), proposed mechanism (bottom).[28]

Upon closer examination of the presented reactions electrophilic trifluoromethylations cannot be classified as classical electrophilic reactions, but rather as radical reactions with electrophilic radicals. As outlined in the review of Postigo *et al.*[25] a lot of controversy remains whether the CF_3^+-cation itself performs a substitution, or a single electron transfer (SET) followed by a radical reaction.

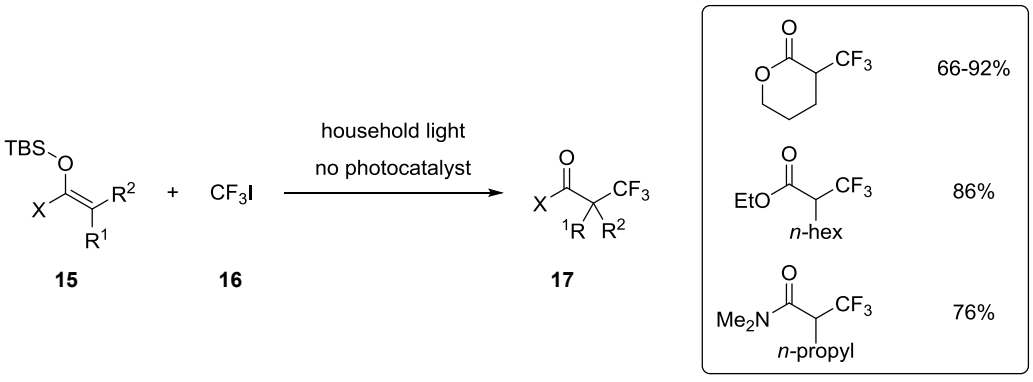
2.2.3 Radical Trifluoromethylation

The CF_3-radical is electrophilic with an energetically low-lying SOMO, thus reactions with electron-rich alkenes, bearing a high-lying HOMO, should proceed fast.[29] With these considerations in mind, MacMillan *et al.* developed a versatile method for the trifluoromethylation of aldehydes, ketones, esters and amides.[30] The first step for the α-trifluoromethylation of these carbonyl compounds is the formation of the corresponding silyl enol ether. After a SET from the exited photocatalyst to the trifluoroiodomethane, a CF_3-radical adds to the C=C double bond. The proposed mechanism involving a photoinduced activation of the catalyst followed by a SET is shown below (Scheme 7).



Scheme 7: Photomediated α-trifluoromethylation of silyl enol ethers (top), proposed mechanism (bottom).[30]

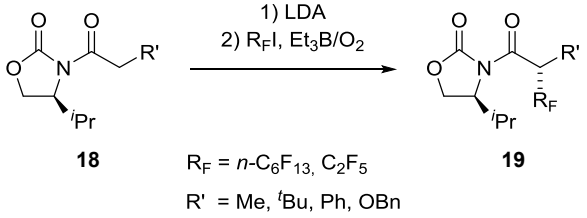
It was also possible to omit the photocatalyst for some electron-rich silyl enol ether (Scheme 8). This observation is explained by a feasible photoinduced electron transfer (PET) from the acetal to CF_3I followed by the formation of a CF_3-radical.[29]



Scheme 8: Photocatalyst-free α-trifluoromethylation of silyl enol ethers.[30]

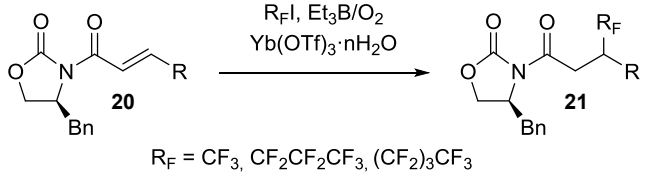
Kobayashi *et al.* were the first to diastereoselectively perfluoroalkylate lithium enolates of *N*-acyloxazolidinones **18** to α-perfluoroalkyl carboximides **19** with 55-93% *de* (Scheme 9).[31] They used the well-known chiral Evans auxiliaries, a valuable tool, which was presented in 1981,[32] in

combination with perfluoroalkyl iodides and triethylborane plus oxygen to start the radical chain reaction.



Scheme 9: Diastereoselective radical perfluoroalkylation of *N*-acyloxazolidinones.[31]

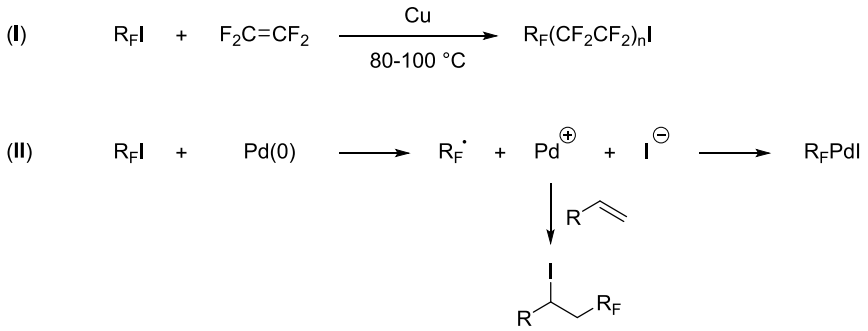
A similar method was developed for the conjugate hydrofluoroalkylation of α,β-unsaturated acyloxazolidinones **20**.[33] For the hydrofluoroalkylation of these acyloxazolidinones, perfluoroalkyl iodides were employed under radical conditions in the presence of ytterbium triflate hydrate (Scheme 10). By subsequent transformations of the obtained products unnatural fluorinated amino acids were obtained.[33]



Scheme 10: Conjugate perfluoroalkylation of acyloxazolidinones.[33]

2.2.4 Perfluoroalkylations

Many metals – e.g. Cu, Fe, Ni, Mg, Pd – or transition metal complexes – e.g. $Pd(PPh_3)_4$, $RhCl(PPh_3)_3$, $IrH(CO)(PPh_3)_3$ – can initiate the addition of perfluoroalkyl iodides to alkenes or alkynes.[34] These metals and transition metal complexes likely act as a single electron donor. For example, copper helps to make the telomerisation of tetrafluoroethylene with perfluoroalkyl iodides more efficient regarding the product distribution, reaction temperatures and reaction time [Scheme 11, (**I**)].

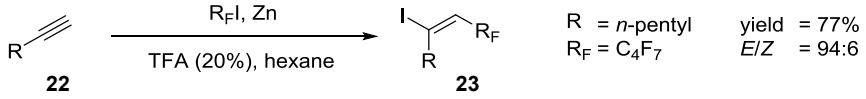


Scheme 11: (**I**) Telomerisation of tetrafluoroethylene, (**II**) Pd-catalysed iodoperfluoroalkylation of alkenes.[34]

$Pd(PPh_3)_4$ proved to be an efficient mediator for iodoperfluoroalkylations of alkenes and alkynes. Working solvent-free at room temperature gave the corresponding adduct within 0.5-1 h

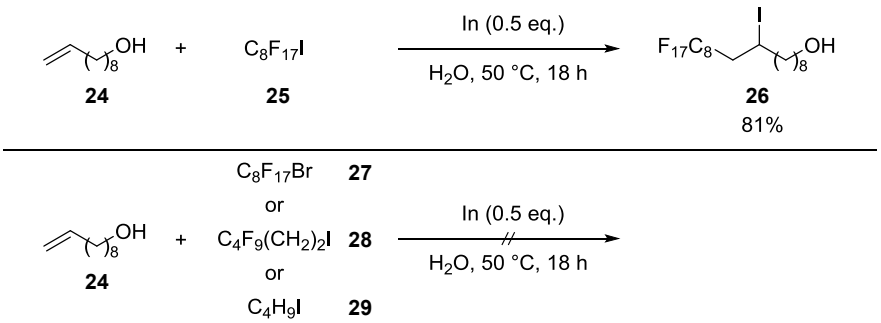
[Scheme 11, (**II**)].[34] Interestingly, the order of the addition of the reactants is very important in this case. By mixing $Pd(PPh_3)_4$ and a perfluoroalkyl iodide, R_FPdI is formed which is inert to alkenes. However, after premixing an alkene and Pd before the addition of a perfluoroalkyl iodide high yields of the iodoperfluoroalkylation product are obtained.

Perfluoroalkyl vinyl iodides **23** are most commonly synthesised via a radical addition to terminal alkynes. For example Ramachandran *et al.*[9] used a combination of zinc and trifluoroacetic acid (TFA) to conduct the reaction with high yields and high stereoselectivity (Scheme 12).



Scheme 12: Radical iodoperfluoroalkylation of terminal alkynes utilising zinc and TFA.[9]

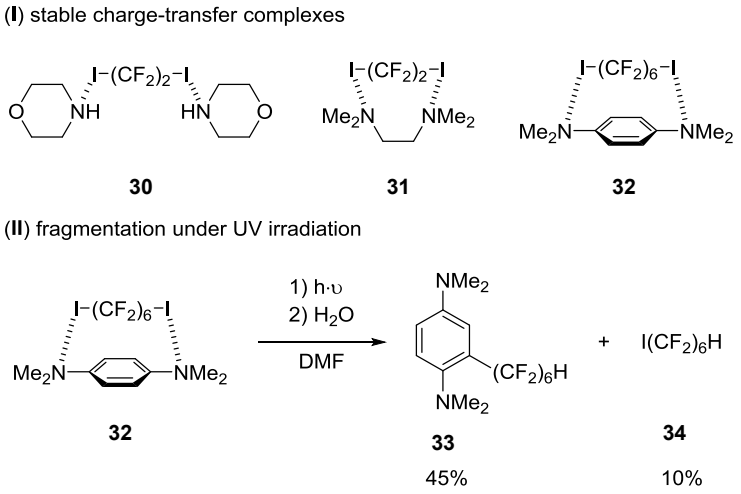
These perfluoroalkyl vinyl iodides **23** can be used for a palladium-catalysed cross-coupling. Ramachandran *et al.* successfully surveyed Negishi, Sonogashira as well as Suzuki couplings.[9] Another interesting example is an iodoperfluoroalkylation of 9-decenol (**24**) in water initiated by indium (Scheme 13). Kanamori and Takagi[35] optimised the reaction and observed the best yields with a twofold excess of the perfluoroalkyl iodide and 0.5 equivalents indium.



Scheme 13: Indium-mediated iodoperfluoroalkylations of 9-decenol.[35]

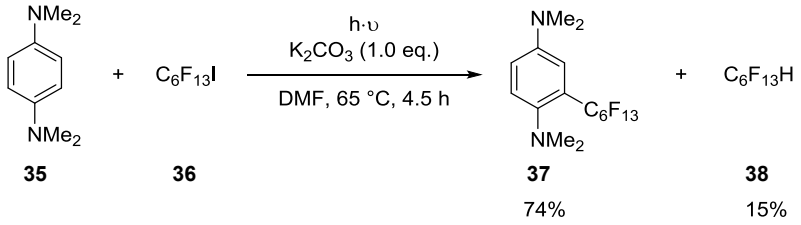
They observed no reaction at all once they substituted perfluorooctyl iodide (**25**) by perfluorooctyl bromide (**27**), 1-iodo-1H,1H,2H,2H-nonafluorohexane (**28**) or 1-iodobutane (**29**). Hence, only perfluoroalkyl iodides seem to be suitable substrates.

Besides metal-initiated reactions, Chen presented photo-induced electron-transfer reactions.[36] In this context he describes crystalline charge-transfer complexes between perfluoroalkyl iodides and amines (Scheme 14). Under irradiation with a mercury lamp, diamine complex **32** fragments to diamine **33** and not into its starting materials.



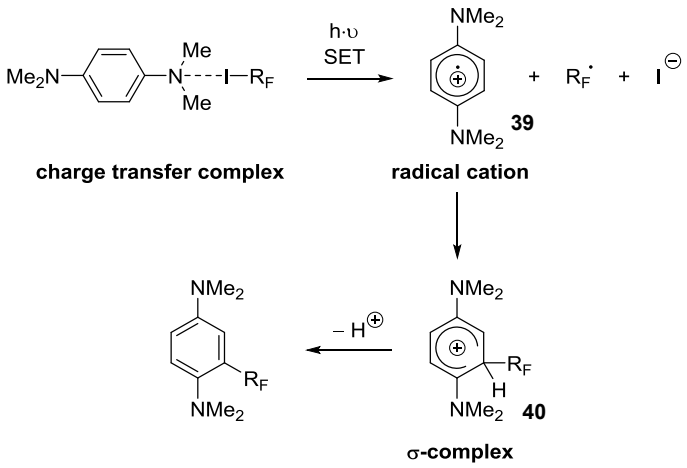
Scheme 14: (**I**) Complexes of α,ω-diiodoperfluoroalkanes and diamines, (**II**) photomediated fragmentation of an charge-transfer complex.[36]

This interesting reactivity led to further tests. No stable complexes between perfluoroalkyl iodides and diamines can be obtained, but perfluoroalkyl iodides reacted readily with aromatic diamine **35** under irradiation (Scheme 15).



Scheme 15: Photomediated $S_{RN}Ar$ at an aromatic diamine.[36]

Chen conducted diverse experiments to elucidate the mechanism (Scheme 16). As a start reaction a SET from the diamine to the perfluoroalkyl iodide is proposed, which results in the formation of radical cation **39** and a perfluoroalkyl radical. Chen reasons that aromatic amines are known as electron donors and perfluoroalkyl iodides as electron acceptors. This consideration manifests in an upfield shift of the $-CF_2I$-moiety in α,ω-diiodoperfluoroalkane-diamine complexes (Scheme 14). Further evidence was obtained throughout EPR measurements, since they were able to observe radical cation **39** (Scheme 16) by irradiating diamine **35** in the presence of perfluoroalkyl iodide **36** (Scheme 15). The formed perfluoroalkyl radical then performs a substitution at the aromatic ring yielding a σ-complex. After a deprotonation the final product is obtained.[36]

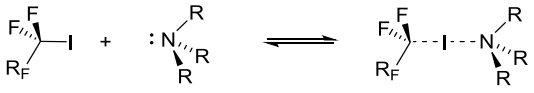


Scheme 16: Mechanistic proposal for the radical aromatic substitution at an aromatic diamine.[36]

Chen presents many more reactions involving perfluoroalkyl iodides in his review[34] and rises one interesting question within the conclusion. Many different initiators are used for iodoperfluoroalkylations, but nearly all are based on the formation of a perfluoroalkyl radical $R_F^{\bullet}$. However, a huge difference between the reaction systems regarding their substrate scope and selectivity are observed. This observation implies an incomplete understanding of these reaction systems.

2.2.4.1 Activation of Perfluoroalkyl Iodides by Lewis Bases

The following subchapter will focus on Lewis base-mediated perfluoroalkylations, starting with recent work by Chen *et al.*,[37] who conducted photochemical perfluoroalkylations utilising an amine additive in THF as the solvent. Perfluoroalkyl iodides can form halogen bond adducts with Lewis bases. The amine can use its lone pair electrons to interact with the σ*-orbital located between carbon and iodine (Scheme 17).



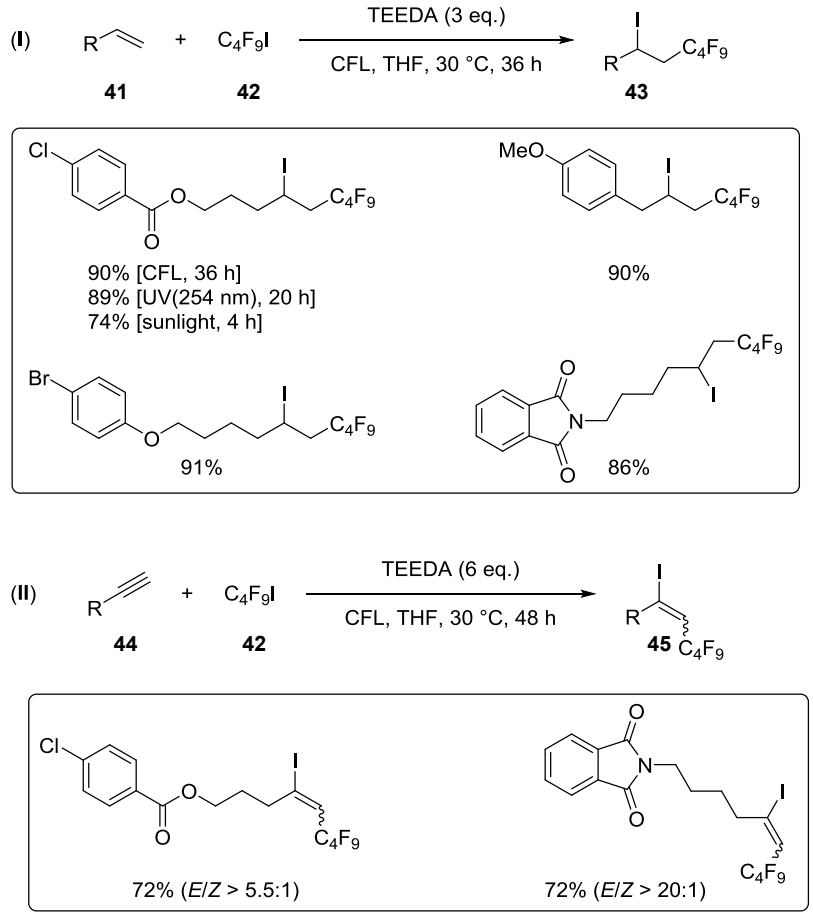
Scheme 17: Adduct formation between a perfluoroalkyl iodide and an amine.

This interaction results in an upfield shift of the ^{19}F-NMR-signal of the $-CF_2I$ moiety. By conducting a Job's plot analysis, Chen *et al.* determined binding constants (K_a) between $C_{10}F_{21}I$ and four Lewis bases. The results are summarised in the following table (Table 1).

Table 1: Binding constants (K_a) between Lewis bases and $C_{10}F_{21}I$ (1:1 adduct) in $CDCl_3$.[37]

Lewis base	binding constant K_a
NEt_3	0.42 M^{-1}
TEEDA	1.1 M^{-1}
THF	0.28 M^{-1}
Dioxane	0.17 M^{-1}

N,*N*,*N*',*N*'-Tetraethylethane-1,2-diamine (TEEDA) has the highest binding constant and showed the best results throughout their reaction optimisation. Under optimised conditions, using TEEDA, they were able to perfluoroalkylate alkenes and alkynes efficiently (selected examples in Scheme 18). As a light source UV-lamps, compact fluorescent lamps (CFL) and even just sunlight were used. For their substrate screening a CFL was used.

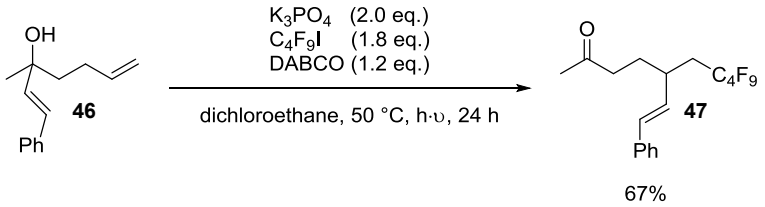


Scheme 18: Photomediated iodoperfluoroalkylation reactions of alkenes (**I**) and alkynes (**II**).[37]

Besides the depicted alkenes, further functionalised alkenes like a cholesterol derivative and quinine were functionalised in good yields. To sum up their observations good functional group tolerance was observed, allowing iodoperfluoroalkylations of esters, ethers and even alcohols.

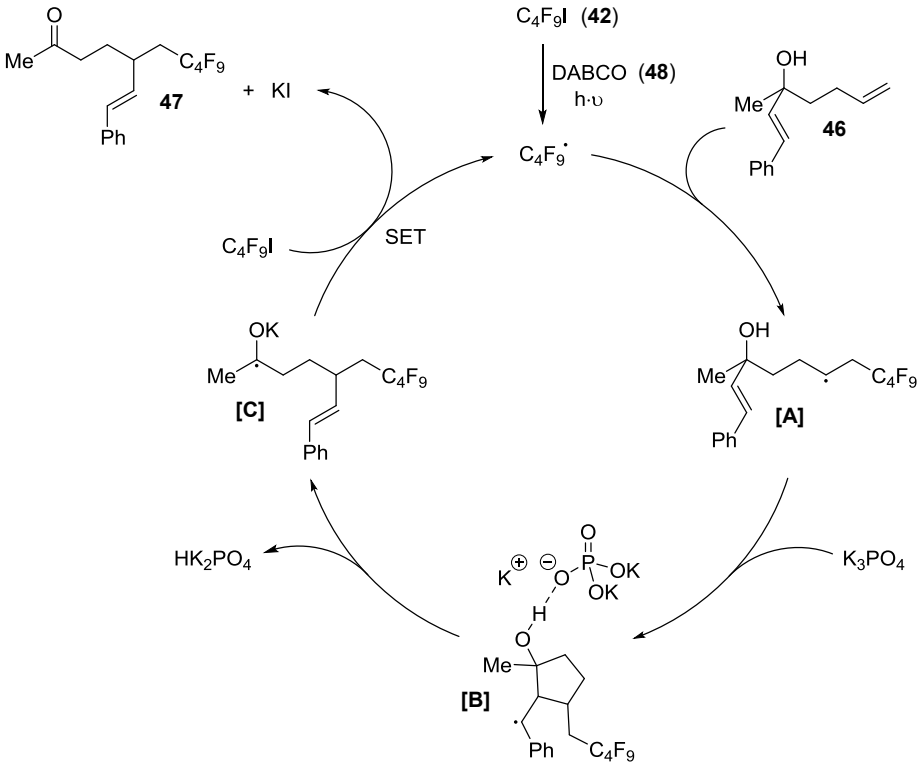
Another example for an activation of perfluoroalkyl iodides by amines was published by Studer *et al.*[38] They investigated an alkene 1,2-difunctionalisation by radical alkenyl migration. At

the beginning, they used lithium hexamethyldisilazide for the deprotonation of alcohol **46**, followed by an addition of DABCO (**48**) and nonafluoro-1-iodobutane (**42**) to initiate an 1,4-alkenyl migration (Scheme 19). After irradiating for 18 hours (Philips Master HPI-T Plus, 400 W) at 50 °C, they obtained 1,4-alkenyl migration product **47** in 34% yield with complete *E*-selectivity.



Scheme 19: Photomediated alkene functionalisation followed by an 1,4-alkenyl migration.[38]

They tested several inorganic bases (e.g. LiOH, NaOH, Li_3PO_4) and amines (e.g. TMEDA, DBU), but the initial conditions proved to be best (Scheme 19). With these optimised conditions they were able to convert several similar substrates. Their mechanistical proposal is shown in Scheme 20.

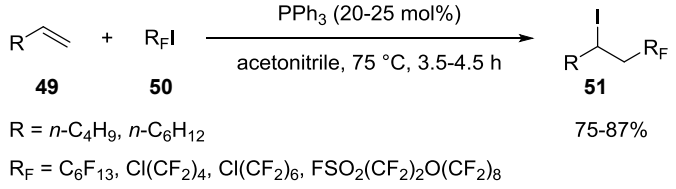


Scheme 20: Proposed mechanism of the iodoperfluoroalkylation and consecutive 1,4-alkenyl migration.[38]

The initiation of this reaction is described as a homolytic C−I-bond cleavage mediated by visible light, which is possible due to a halogen-bond complex between C_4F_9I (**42**) and DABCO (**48**). A perfluoroalkyl radical attacks alkene **46** under formation of radical [**A**], which can cyclise under formation of radical intermediate [**B**]. Studer *et al.* suggest an interaction between K_3PO_4 at this

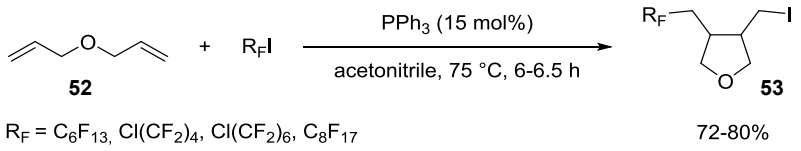
stage, which activates the C−C-bond towards homolytic cleavage to form intermediate [**C**]. In a final step, this ketyl radical can reduce C_4F_9I and thereby form ketone **47** and sustain a catalytic cycle.

A detailed screening of the literature revealed two examples for phosphane-catalysed iodoperfluoroalkylations. In 1990, Huang and Zhang[39] described a iodoperfluoroalkylation of electron-rich alkenes in the presence of substoichiometric amounts of PPh_3 (Scheme 21, Scheme 22). This iodoperfluoroalkylation proceeded quite efficiently and resulted in yields ranging from 75-87%. They used a twofold excess of the alkene with respect to R_FI in all cases.



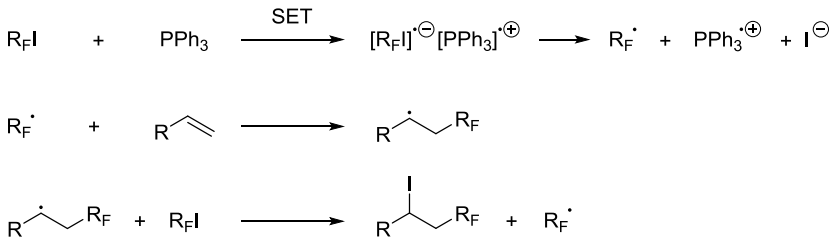
Scheme 21: Iodoperfluoroalkylation of linear, terminal alkenes utilising PPh_3.[39]

To elucidate the mechanism of this reaction, diallyl (**52**) ether was tested (Scheme 22). Since the formation of a tetrahydrofurane derivative **53** was observed, a free radical pathway is probable. This rationale was further supported by a completely suppressed reaction in the presence of 10 mol% hydroquinone.



Scheme 22: Iodoperfluoroalkylation of diallyl ether utilising PPh_3.[39]

Taken these results into account, they formulated a possible mechanism involving free radicals and a SET by triphenylphosphane (Scheme 23).

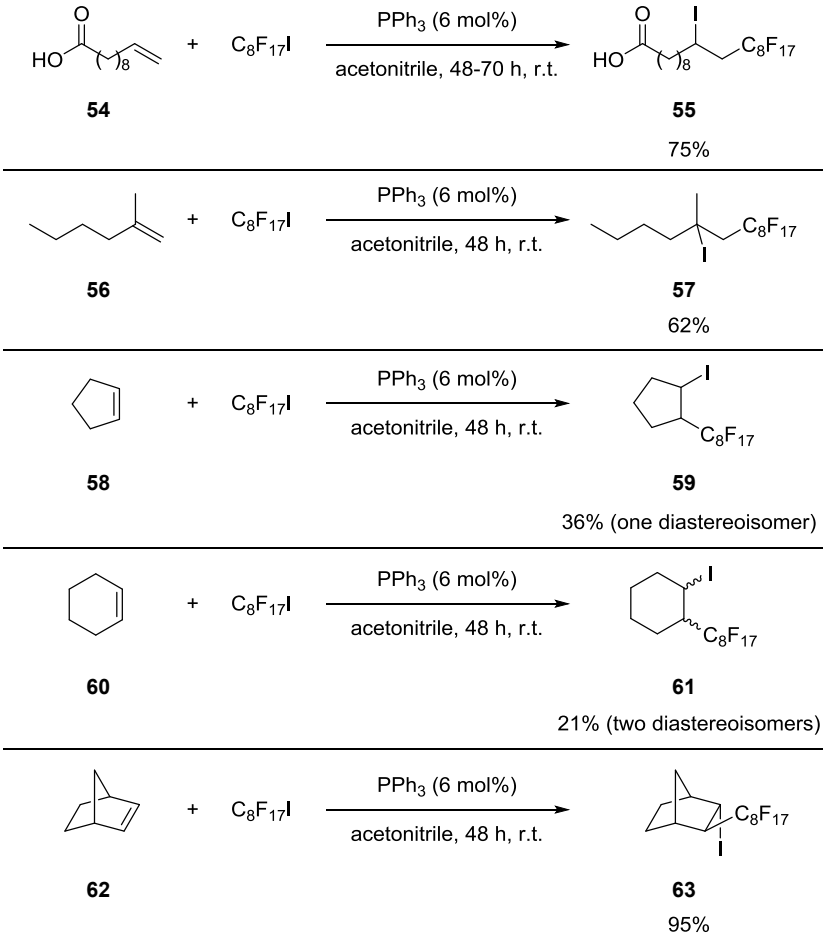


Scheme 23: Proposed mechanism for the iodoperfluoroalkylation of alkenes utilising PPh_3.[39]

Besides triphenylphosphane, they tested triethylphosphite, tri-*n*-butylphosphane tris(diethylamino)phosphane, triphenylarsine, various amines and hydroxylamine. Triethylphosphite, tri-*n*-butylphosphane as well as hydroxylamine worked comparable to PPh_3. Tris(diethylamino)phosphane caused a reduction of the perfluoroalkyl iodides to R_FH,

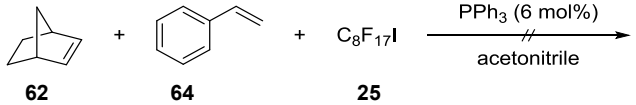
triphenylarsine initiated the reaction only very slowly, and a use of amines resulted in complex product mixtures.

The second example for a phosphane-catalysed iodoperfluoroalkylation was published in 2002 by Moreno-Mañas *et al.*[40] Based on observations throughout a prior publication, they tested a iodoperfluoroalkylation with $RuH_2(PPh_3)_4$ and PPh_3 itself parallelly. To their surprise, PPh_3 alone catalysed the reaction quite efficiently for 10-undecanoic acid (**54**), norbornene (**62**) as well as 2-methylhex-1-ene (**56**) (Scheme 24). In contrast, cyclopentene (**58**) and -hexene (**60**) gave low yields.



Scheme 24: PPh_3-mediated iodoperfluoroalkylation of alkenes.[40]

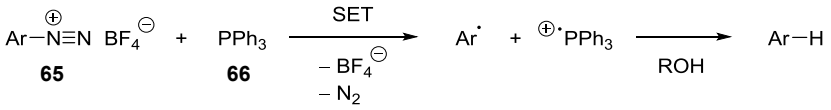
Interestingly, they did not observe any conversion of neither styrene nor 1,3-cylcohexadiene. Their rationale for this finding is a too high stability of the formed benzylic or allylic radical. Additionally, styrene (**64**) inhibits the conversion of norbornene (**62**) (Scheme 25).



Scheme 25: Inhibition of the iodoperfluoroalkylation of norbornene by styrene.[40]

Moreno-Mañas *et al.*[40] describe the reaction mechanism similar to Huang and Zhang: A SET from phosphane to perfluoroalkyl iodide, followed by a free radical chain mechanism.

Triphenylphosphane can act as an electron donor. This was shown for a fragmentation of arenediazonium salts **65**, mediated by triphenylphosphane (**66**) as well as trialkyl phosphites (Scheme 26).[41]



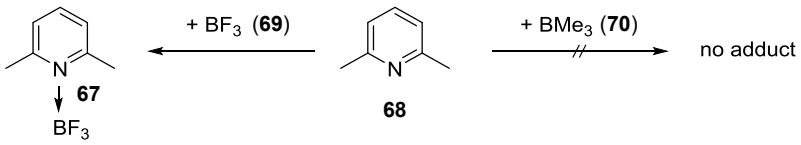
Scheme 26: SET of triphenylphosphane to arenediazonium salts.[41]

To avoid a photomediated cleavage of the diazonium salt this reaction was conducted in the dark. Nevertheless, a fast reaction towards the benzene derivative was observed. Since the reaction does not proceed without a phosphane or phosphite under these conditions, and oxygen inhibits the reaction, Yasui *et al.* concluded that a SET has to take place. Further evidence was obtained by EPR spectroscopy which showed the decisive radical cations.[41]

2.3 Frustrated Lewis Pairs (FLPs)

In 1923 Gilbert Newton Lewis established the concept of Lewis acids and Lewis bases.[42] His concept implies, that Lewis acids are substances, which "[...] employ a lone pair from another molecule in completing the stable group of one of its own atoms".[42] Further on, a Lewis base is a substance, which "[...] has a lone pair of electrons which may be used to complete the stable group of another atom."[42] Stable adducts between a Lewis acid and a base can be formed by an interaction of the lowest unoccupied molecular orbital of the Lewis acid with the highest occupied molecular orbital of the Lewis base.[43]

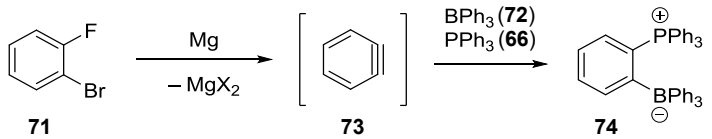
Almost 20 years later in 1942 Brown observed that not all Lewis acids and bases can form stable adducts.[44] For example, boron trifluoride (**69**) (BF_3) is able to form a stable adduct **67** with 2,6-lutidine (**68**), but trimethyl borane (**70**) (BMe_3) is not (Scheme 27).



Scheme 27: Reactions of 2,6-lutidine with BF_3 and BMe_3.[44]

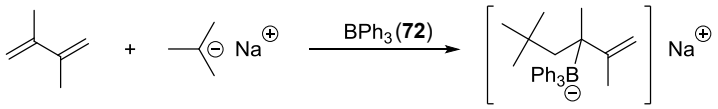
Thus, the strength of a Lewis base is not an exclusive limitation for the formation of Lewis pairs. Steric effects play an important role, too. Another example in this context is the formation of adducts between trimethylborane and amines. Triethylamine (Et_3N) is a stronger base compared to trimethylamine (Me_3N). However, the adduct between Et_3N and trimethylborane (BMe_3) is less stable compared to the adduct between Me_3N and BMe_3.[44]

Long before the definition of FLPs, in 1959 Wittig and Benz[45] reported a cooperative addition of triphenylborane (**72**) and triphenylphosphane (**66**) to cyclohexa-1,3-dien-5-yne (**73**) under formation of phosphonium borate **74** as a side product besides an adduct of triphenylborane and triphenylphosphane (Scheme 28).



Scheme 28: Synthesis of betaine **74** starting with 1-bromo-2-fluorobenzene (**71**).[45]

Another observation went mostly unregarded in 1966, when Tochtermann observed a reaction between 2,3-dimethylbutadiene (**75**), a trityl anion **76** and triphenylborane (**72**) resulting in 1,2-adduct **77** (Scheme 29).[45]

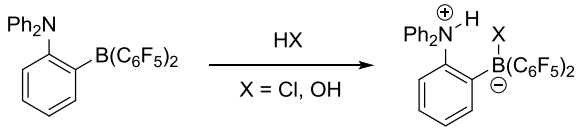


75 **76** **77**

Scheme 29: Synthesis of an ate-complex starting from 2,3-butadiene.[46]

However, an expected polymerisation did not occur.[46] Tochtermann reasoned that the trityl anion and triphenylborane cannot form an adduct due to their steric demand. The observed reactivity was explained by a π-complex between the borane and the double bond. Thereby, the alkene is activated for an attack of the trityl anion. By this attack ate-complex **77** is obtained. It is noteworthy that Tochtermann called combinations of sterically demanding Lewis acids and bases an "antagonistic pair" which is similar to the now used term Frustrated Lewis Pairs.[46]

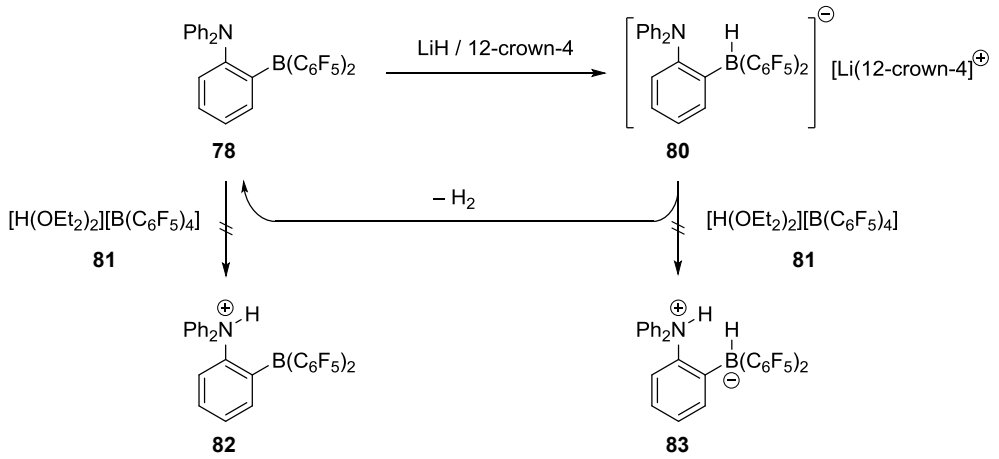
Many years later in 2003, Roesler and Piers *et al.*[47] were at the edge of establishing the field of Frustrated Lewis Pairs. They synthesised amino borane **78** with the idea of a molecular hydrogen storage and were able to cleave H_2O as well as HCl heterolytically under formation of ammonium borate **79** (Scheme 30).



78 **79**

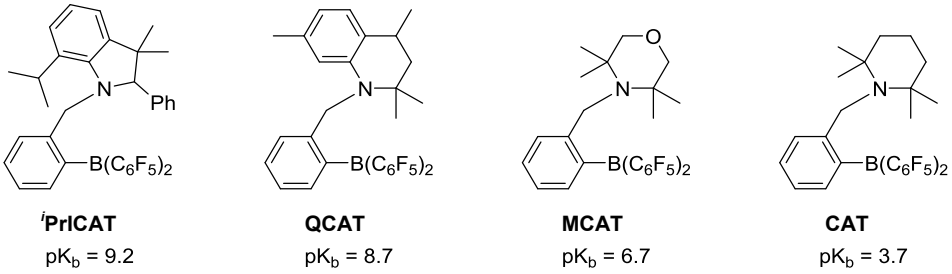
Scheme 30: Ammonium borate formation starting from amino borane **78**.[47]

To synthesise a dihydrogen adduct starting from amino borane **78**, they reacted amino borane **78** with lithium hydride and obtained borate **80** (Scheme 31). Then they tried to synthesise the dihydrogen adduct **83** using Jutzi's acid **81**, but observed a recovery of the amino borane and concomitant H_2 release. Roesler and Piers *et al.* identified the low basicity of the amino borane as the major problem. The low basicity results from a delocalisation to the aromatic rings as well as an electron-withdrawing effect of the borane moiety and is demonstrated by the fact that amino borane **78** cannot be protonated by Jutzi's acid **81**.[47]



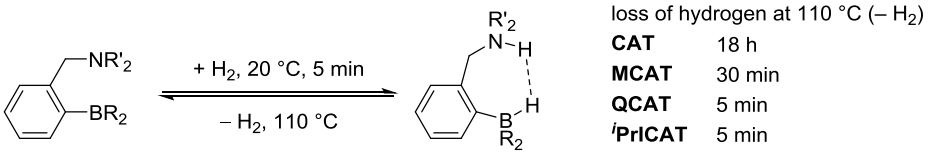
Scheme 31: Synthetic route for the formation of dihydrogen adduct **83** starting with aminoborane **78**.[47]

In the course of their final remarks, Roesler and Piers *et al.* suggest to increase the basicity of the nitrogen centre to obtain the dihydrogen adduct. This idea was taken up by Repo *et al.*, who published a "revision of Piers' *ansa*-aminoborane"[48] in 2012 containing the successful formation of a dihydrogen complex starting from an amino borane. As a start, they synthesised different amino boranes and determined their pK_b values (Scheme 32).[49]



Scheme 32: Selected amino boranes (top) and the corresponding pK_b values (bottom).[49]

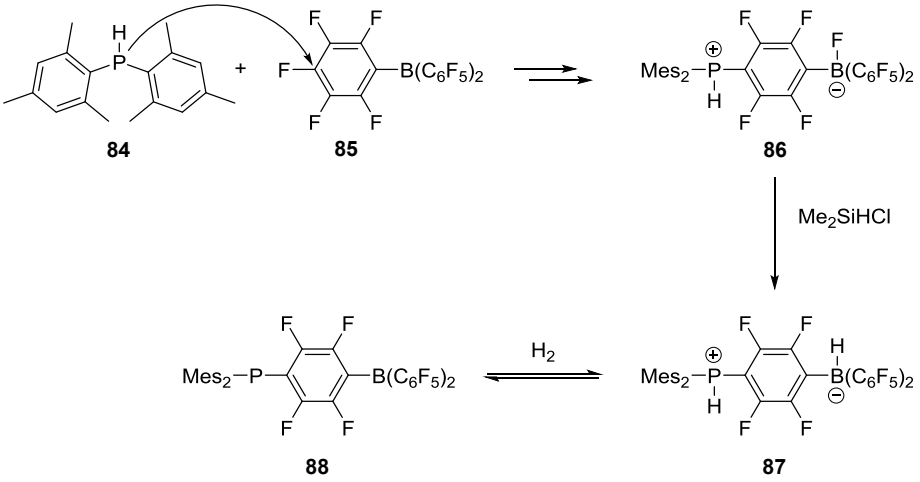
Hydrogen could be activated by all of these amino boranes in a reversible fashion. The release of hydrogen took longest for most basic **CAT** and only short for the less basic variants (Scheme 33). Besides the heterolytic cleavage of hydrogen they were also able to hydrogenate imines with catalytic amounts of the amino boranes.



Scheme 33: Reversible hydrogen activation of amino boranes.[49]

However, the first to report a reversible metal-free hydrogen activation were Stephan *et al.* in 2006.[50] They observed a reaction between dimesitylphosphane (**84**) and tris(pentafluorophenyl)borane (**85**), which did not result in a formation of a Lewis adduct, but in betaine **86** (Scheme 34). The formation of betaine **86** is explained by a nucleophilic attack of

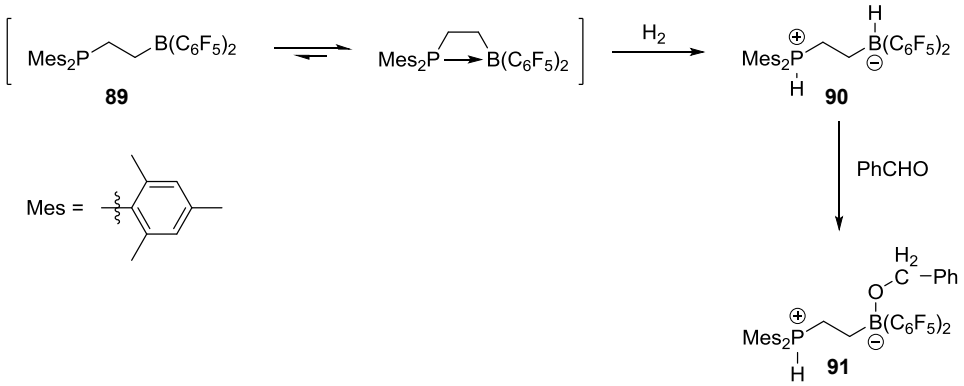
dimesitylphosphane at the *para*-position of a pentafluorophenyl ring of $B(C_6F_5)_3$ and a subsequent transfer of the fluorine atom to the boron atom. Betaine **86** reacts rapidly with dimethylchlorosilane to dihydrogen adduct **87**, which releases H_2 upon heating above 100 °C. Gratifyingly, the dihydrogen adduct can be regained by reacting phosphinoborane **88** with H_2 at 25 °C. As a result, this molecule was the first metal-free system, which was able to cleave hydrogen heterolytically and reversibly.



Scheme 34: Reaction between dimesitylphosphane **84** and tris(pentafluorophenyl)borane **85** under formation of the first metal-free hydrogenation catalyst.[50]

In 2007 Stephan *et al.*[51] called those systems consisting of sterically demanding phosphane donors and Lewis acids "Frustrated Lewis Pairs" (FLP). These FLPs have an unquenched Lewis acidity as well as basicity, which can result in an activation of small molecules.

After these discoveries, the field of FLPs developed rapidly. For example Erker's group published their first intramolecular ethylene bridged phosphinoborane **89** in 2007 (Scheme 35), which was able to cleave hydrogen heterolytically and act as a hydride transfer agent for benzaldehyde.[52]



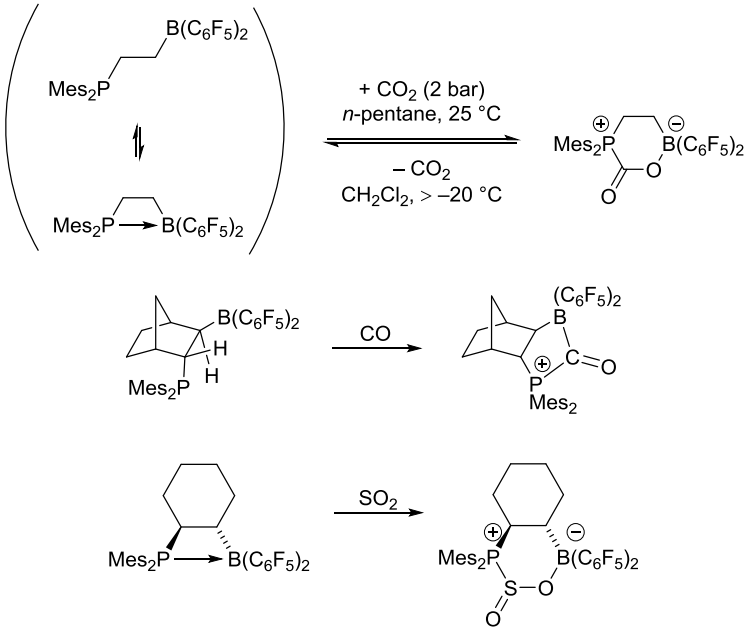
Scheme 35: Heterolytic cleavage of hydrogen by an intramolecular phosphane-/borane-system and a consecutive reaction with benzaldehyde.[52]

2.3.1 Frustrated Lewis Pair Catalysis

The number of applications for frustrated Lewis pairs in catalysis grew strongly within the last ten years. Several reviews[53-56] give an overview over these applications and selected examples are presented in this chapter.

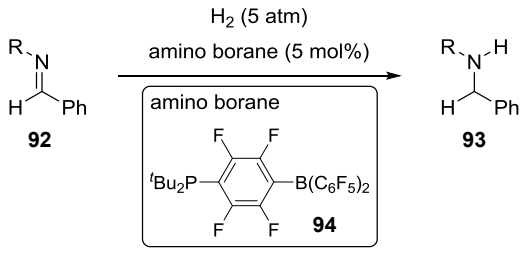
2.3.1.1 Activation of Small Molecules

Erker's group published many intramolecular frustrated Lewis pairs, which are for example capable of reversibly binding carbon dioxide,[57] carbon monoxide[58] and sulphur dioxide[55] (Scheme 36, top to bottom).



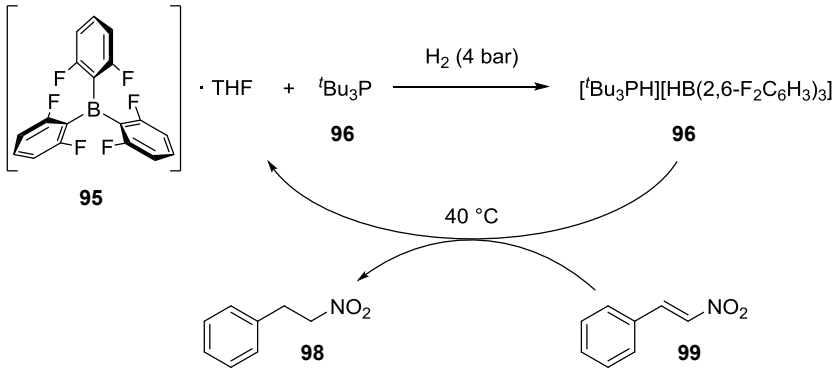
Scheme 36: Activation of small molecules like CO and SO_2 by intramolecular FLPs.[55,57-58]

The best studied topics in connection with FLPs are the activation of hydrogen[56,59-64] and the catalytic hydrogenations.[56,65-67] Accordingly, many different systems for this purpose have been developed. For example enamines, imines,[56,66-67] enones[56,65] and silyl enol ether[56] can be reduced. The first catalytic hydrogenation of imines by Stephan *et al.*[67] utilising phosphinoborane **94** is shown in Scheme 37.



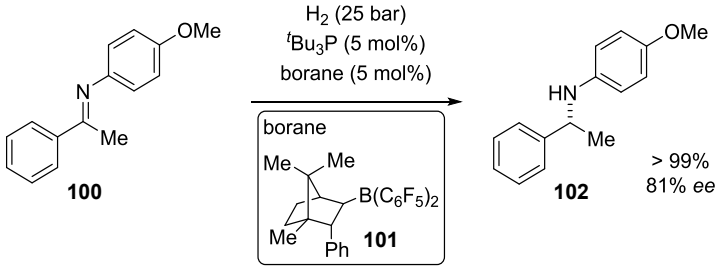
Scheme 37: First metal-free catalytic hydrogenation of imines.[67]

Molecules like esters or sulfoxides are challenging substrates for FLP-catalysed reactions, because the functional groups are eventually coordinated and activated by the FLPs. Hence, a development of FLPs with higher functional group tolerance is of great interest. In 2013, Paradies *et al.* published a method for the hydrogenation of nitroolefines and acrylates.[68] Instead of the usually utilised $B(C_6F_5)_3$, a THF-adduct of $B(2,6\text{-}F_2C_6H_3)_3$ (**95**) in combination with $^tBu_3P$ (**96**), was used (Scheme 38).



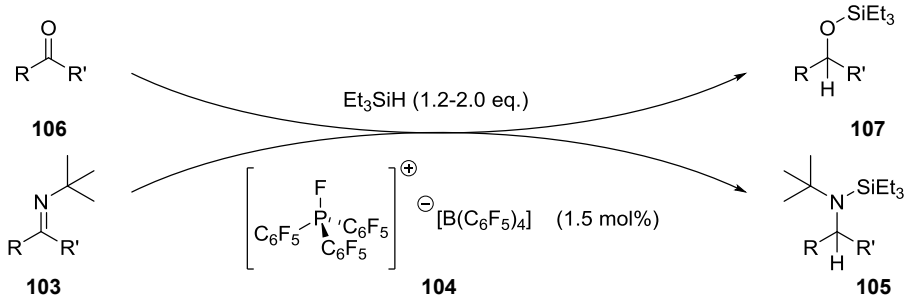
Scheme 38: FLP-catalysed hydrogenation of a nitroalkene.[68]

Even enantioselective variants of the hydrogenation reactions have been developed within the last years. In 2010 Klankermayer *et al.*[69-70] presented the first enantioselective variant of an imine reduction, using a chiral borane derived from camphor to achieve 20-83% *ee* for several substrates (Scheme 39).



Scheme 39: FLP-catalysed enantioselective reduction of imines.[69-70]

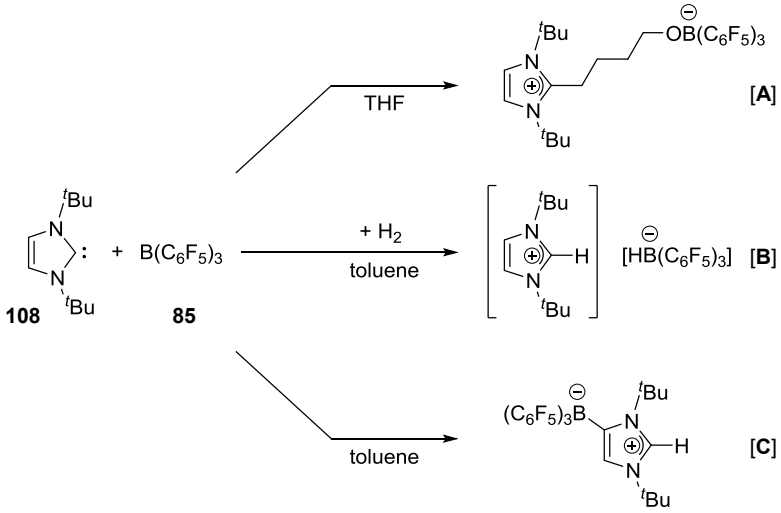
Besides the hydrogenation reactions with FLPs, interesting applications of perfluorinated ion pairs **104** (Scheme 40) have been developed. For example catalytic hydrosilylations of ketones, imines and nitriles are now possible.[71]



Scheme 40: Perfluorinated ion-pair catalysed hydrosilylation of ketones and imines.[71]

2.3.1.2 *N*-heterocyclic carbenes as Lewis Base

Besides the commonly used electron-rich phosphanes or amines, carbenes can be used as Lewis base for the activation of dihydrogen. Tamm *et al.*[72] were the first who examined carbenes and chose imidazolin-2-ylidene type carbenes (Scheme 41). They have ligand properties comparable to electron-rich organophosphanes. By mixing $B(C_6F_5)_3$ and 1,3-di-*tert*-butylimidazolin-2-ylidene (**108**) in THF they obtained the imidazolium-borate zwitterion [**A**] almost quantitatively. In order to avoid a reaction between the solvent and the FLP, they changed the solvent to toluene. A solution of carbene **108** and $B(C_6F_5)_3$ in toluene was purged with H_2 and they were able to isolate the corresponding hydrogen complex [**B**]. Hence, this FLP is able to activate dihydrogen.

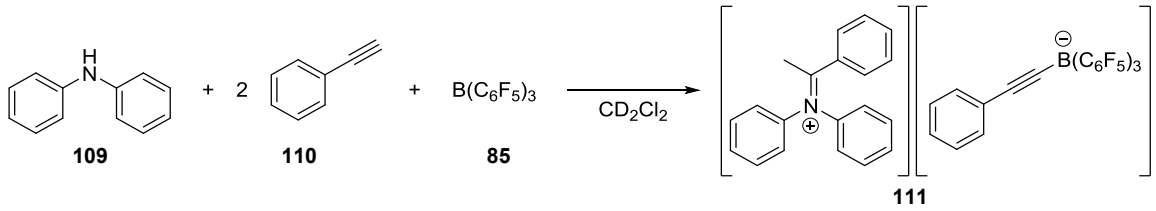


Scheme 41: Formation of different imidazolium salts starting from $B(C_6F_5)_3$ (**85**) and a NHC **108**.[72]

However, the applicability of this FLP is quite limited. Tamm *et al.*[72] observed a complete loss of catalytic activity within two hours. This observation can be explained by a quantitative formation of adduct [**C**]. In this adduct, the $B(C_6F_5)_3$ moiety was attached to the 4-position of the imidazole ring and a proton migration took place. Hence, the butylimidazolin-2-ylidenes would have to be protected in the 4- and 5-position to obtain a more robust catalytic system.

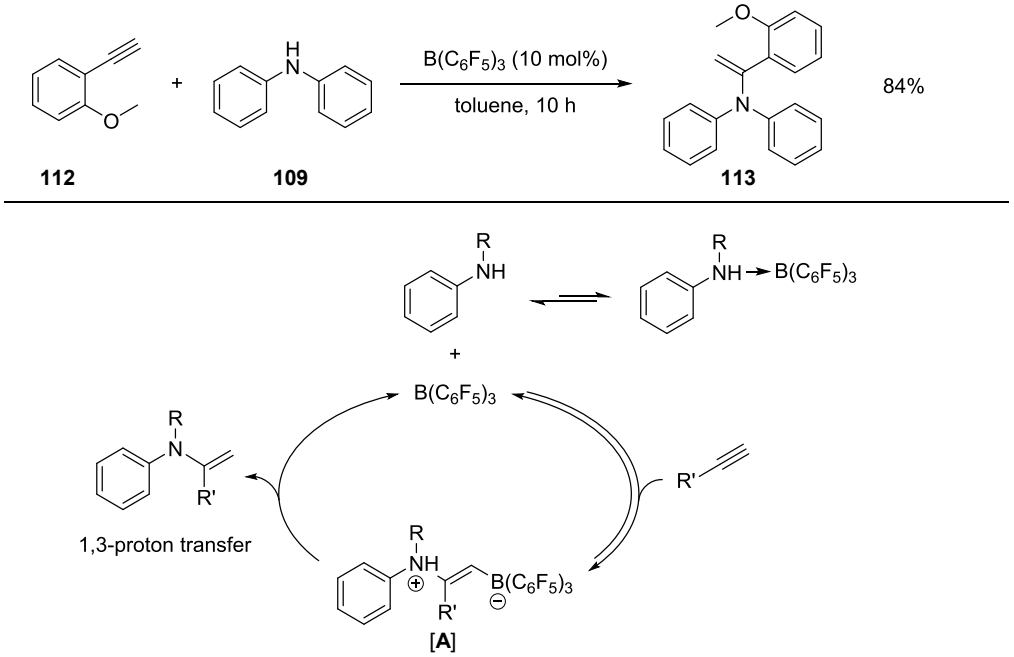
2.3.1.3 Hydroamination of Terminal Alkynes

Throughout the last years, manifold reactions involving FLPs besides the activation of small molecules were studied.[54,73] For example Stephan and Mahdi developed a metal-free hydroamination of terminal alkynes applying FLP catalysis followed by a reduction.[74] Their initial observation was the formation of $[Ph_2N{=}C(CH_3)Ph][PhC{\equiv}CB(C_6F_5)]$ **111** (Scheme 42) after mixing stoichiometric amounts of diphenylamine (**109**), phenylacetylene (**110**) and tris(pentafluorophenyl)borane (**85**).



Scheme 42: Formation of the salt $[Ph_2N{=}C(CH_3)Ph][PhC{\equiv}CB(C_6F_5)]$ starting from phenylacetylene (**110**), diphenylamine (**109**) and $B(C_6F_5)_3$ (**85**).[74]

Then, a catalytic process for the hydroamination of substituted phenylacetylides, 2-thiophenylacetylene or 9-ethynylphenanthrene with diphenylamines or isopropylphenylamine was developed (Scheme 43). For electron-poor fluorine-substituted phenylacetylides lower reaction temperatures (−30 °C instead of 25 °C) had to be applied for high yields. It is noted that the alkyne has to be added slowly, since intermediate [**A**] would otherwise deprotonate the alkyne and a catalytically inactive salt as shown in Scheme 42 would be formed.

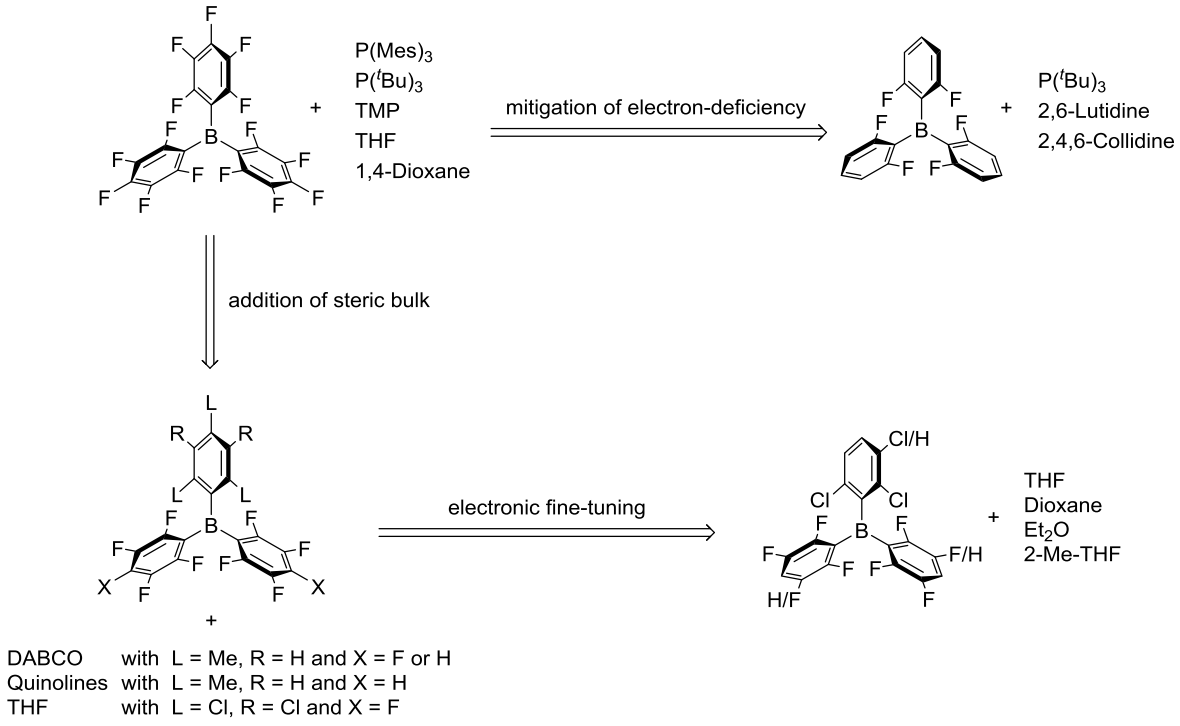


Scheme 43: Exemplary catalytic hydroamination (top), proposed mechanism (bottom).[74]

Gratifyingly, it was also possible to hydrogenate the obtained enamines in a one-pot fashion by pressurising with H_2.

2.3.1.4 Functional Group Tolerance as well as Water-stable Systems

In 2015, Pápai and Soós *et al.*[75] published a moisture-tolerant Frustrated Lewis Pair catalyst system, which was capable of a hydrogenation of aldehydes as well as ketones. For an appropriate design of the borane, different effects have to be taken into account. A borane can form a dative complex with water, resulting in a deactivation of the borane and an acidification of H_2O. In the worst case the Lewis base can deprotonate the activated H_2O molecule, resulting in the formation of a protonated Lewis base as well as a borate bearing a hydroxide anion. Another possibility is that the Lewis base enhances the bonding strength between H_2O and the borane via H-bonding interactions. Ideally the Lewis base can restore the borane by loosening the borane-water-adduct. With these reflections in mind, Pápai and Soós *et al.* designed the boranes. On the one hand efforts were made to optimise the size-exclusion design, on the other hand an electronic fine-tuning had to be performed (Scheme 44).

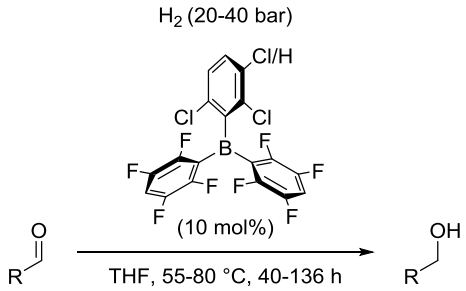


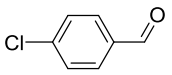
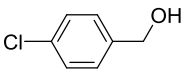
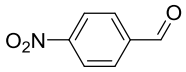
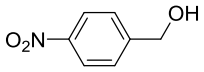
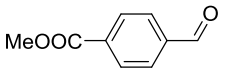
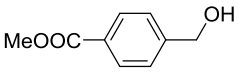
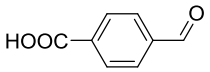
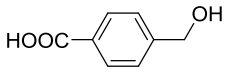
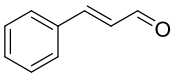
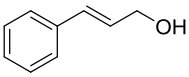
Scheme 44: Catalyst design of Pápai and Soós *et al.*[75]

An exclusive change of steric bulk by introducing a mesityl substituent as one of the aromatic rings did not result in an applicable system. Therefore, chlorine substituents were introduced. Chlorine is much bulkier than fluorine and more electron-withdrawing compared to a methyl group. However, the borane should not be too electron-deficient, either. In some cases electron-deficient boranes did not react in the desired way.

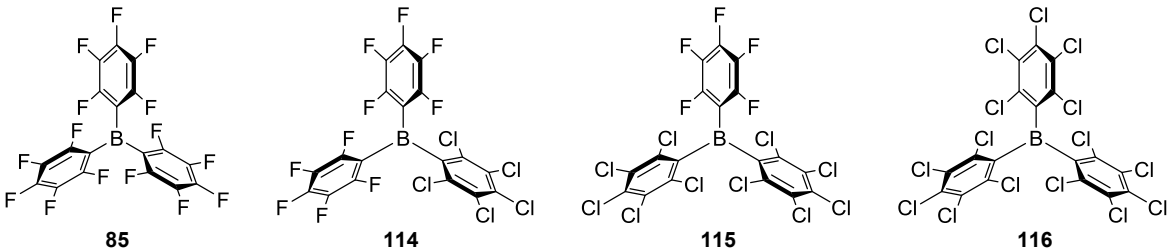
In the following table (Table 2) selected examples of a reduction of aldehydes conducted by Pápai and Soós *et al.*[75] are given, showing the utility of this catalyst system. Besides these results, Tibor Soós presented further work regarding moisture-tolerant FLP-systems.[76]

Table 2: Selected examples of FLP-catalysed reductions of aldehydes.[75]



substrate	product	conversion [%]	yield [%]
		99	93
		99	95
		99	76
		99	76
		85	60

As an alternative to three pentafluorophenyl-substituents in $B(C_6F_5)_3$, a gradual substitution with pentachlorphenyl-substituents was tested by O'Hare *et al.*[77] (Scheme 45). They concluded that C_6Cl_5-groups are more electron-withdrawing than C_6F_5-groups. Thus, the more C_6Cl_5-groups are introduced the higher the electrophilicity.

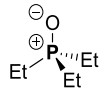


Scheme 45: Electronically tuned boranes.[77]

This tendency is counterintuitive because fluorine is the most electronegative element ($\chi_{Pauling} = 4.0$) and chlorine is nearly one unit less electronegative ($\chi_{Pauling} = 3.2$). A rationale for C_6Cl_5-groups being more electron-withdrawing can be found in a weaker π-overlap (3p-2p) of chlorine and the aromatic nucleus, compared to a strong back donation by fluorine (2p-2p).

Measurements of the Lewis acid strength with the Gutmann Beckett and Childs method revealed that $B(C_6F_5)(C_6Cl_5)_2$ (**115**) and $B(C_6Cl_5)_3$ (**116**) cannot bind *trans*-crotonaldehyde (Table 3) due to their steric bulk. Moreover, $B(C_6Cl_5)_3$ (**116**) cannot even bind Et_3PO. Anyhow, $B(C_6F_5)_2(C_6Cl_5)$ (**114**) and $B(C_6F_5)(C_6Cl_5)_2$ (**115**) clearly are weaker Lewis acids compared to $B(C_6F_5)_3$ (**85**) in view of shifts in the Gutmann Beckett method.

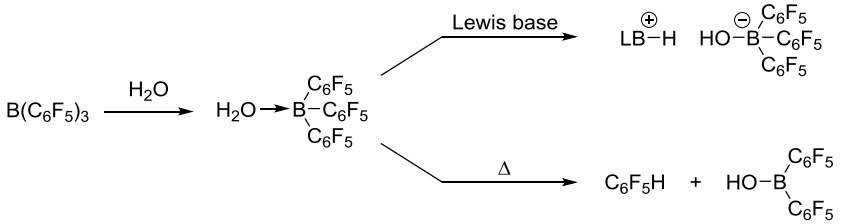
Table 3: Lewis acidity measurements by Gutmann Beckett and Childs method.[77]

Lewis acid	Gutmann Beckett method 	Childs method 
	^{31}P-NMR Δδ [ppm](1)	^{1}H-NMR Δδ [ppm](2)
$B(C_6F_5)_3$ (**85**)	33.7	1.05
$B(C_6F_5)_2(C_6Cl_5)$ (114)	32.5	0.63
$B(C_6F_5)(C_6Cl_5)_2$ (115)	31.2	–
$B(C_6Cl_5)_3$ (116)	0.0	–

(1)Change in the ^{31}P-NMR shift of triethylphosphine oxide. (2)Change in the ^{1}H-NMR shift of H^3 of *trans*-crotonaldehyde.

Another interesting observation of O'Hare *et al.*[77] is that $B(C_6F_5)_2(C_6Cl_5)$ (**114**) binds H_2O only reversibly and coordinated water can be removed under vacuum or in the presence of molecular sieves. Furthermore, $B(C_6Cl_5)_3$ (**116**) can be refluxed in a mixture of toluene and water for several days without any decomposition. Hence, $B(C_6F_5)_2(C_6Cl_5)$ (**114**), $B(C_6F_5)(C_6Cl_5)_2$ (**115**) and $B(C_6Cl_5)_3$ (**116**) might be interesting Lewis acids due to their water tolerance.

Besides a use of alternative boranes, Ashley *et al.*[78] developed a reaction system using the most prominent Lewis acid in FLP chemistry namely $B(C_6F_5)_3$. First of all, they discussed the deactivation modes of $B(C_6F_5)_3$ by H_2O (Scheme 46). On the one hand, a Lewis base can mediate a deprotonation of H_2O resulting in the formation of a borate (Scheme 46, top). On the other hand, $B(C_6F_5)_3$ can be hydrolysed when heated up (Scheme 46, bottom). Both paths result in irreversible deactivation of the borane.

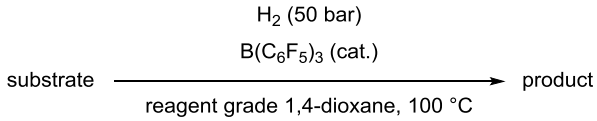


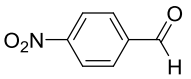
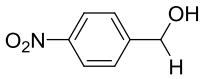
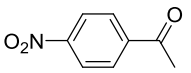
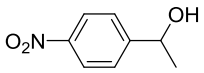
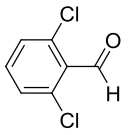
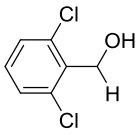
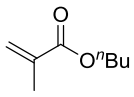
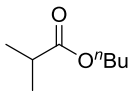
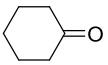
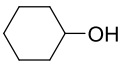
Scheme 46: Deactivation modes of $B(C_6F_5)_3$ by H_2O.[78]

However, Ashley *et al.* found that a combination of $B(C_6F_5)_3$ and 1,4-dioxane as a solvent as well as mild Lewis base can be used for an efficient catalytic hydrogenation of ketones (Table 4) even in the presence of water. They reason that the major deactivation pathway for $B(C_6F_5)_3$ in the

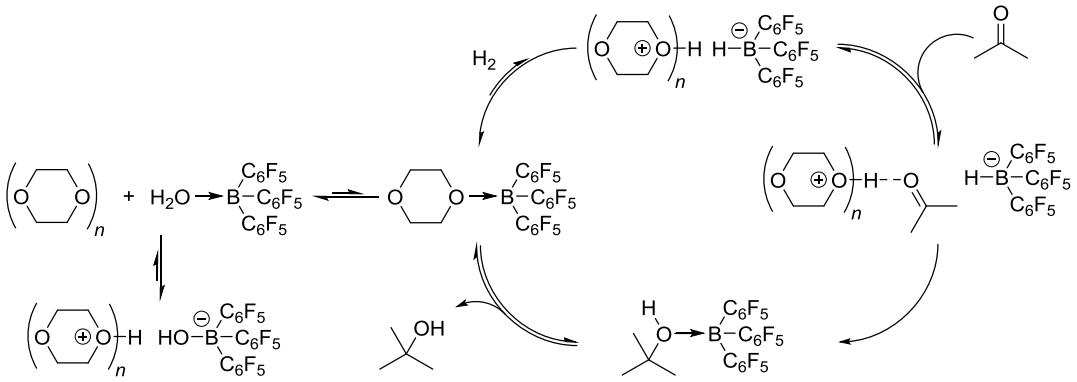
presence of H_2O is the borate formation (Scheme 46). This process can be prevented by avoiding relatively strong bases.[78]

Table 4: Catalytic hydrogenation of ketones using $B(C_6F_5)_3$ in 1,4-dioxane.[78]



substrate	product	$B(C_6F_5)_3$ [mol%]	t [h]	conv. [%]
		10	17	>99
		10	17	>99
		5	17	>99
		2.5	21	48
		5	18	0

They were able to hydrogenate several substrates like aromatic ketones or a Michael system. As observed before, cyclohexanone is a challenging substrate and cannot be hydrogenated under the applied conditions. The mechanism of this reaction is believed to follow the one proposed for anhydrous conditions, but with an off-cycle resting state (Scheme 47).



Scheme 47: Mechanistical proposal for an FLP-catalysed hydrogenation mediated by $B(C_6F_5)_3$ (**85**) and 1,4-dioxane.[78]

Closely related to these observations are preceding publications by Ashley *et al.*[79] and Stephan *et al.*,[80-81] showing that a combination of $B(C_6F_5)_3$ and ethereal solvents can be used for catalytic hydrogenation.

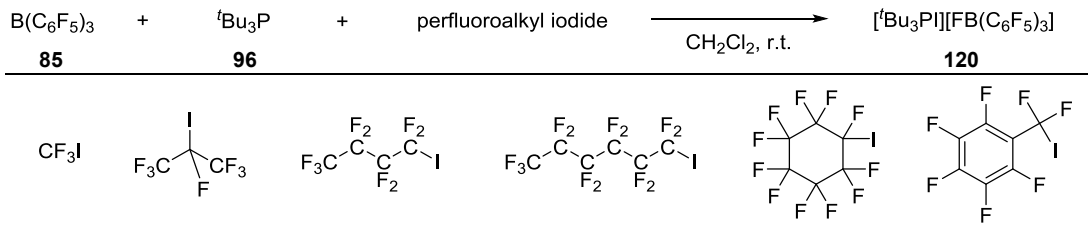
3 State of Knowledge - Activation of Perfluoroalkyl Iodides

In the Czekelius group the activation of perfluoroalkyl iodides by frustrated Lewis pairs was investigated and established.[82] Since these results are the fundamental basis to this thesis they are presented in detail.

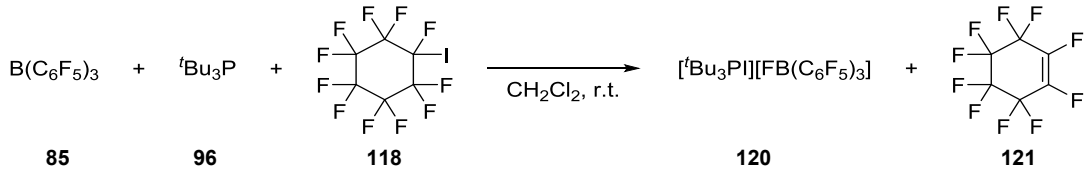
3.1 Synthesis of Iodophosphonium Fluoroborates

One of the first observation was the formation of [^{t}Bu$_3$PI][FB(C$_6$F$_5$)$_3$] (**120**) when mixing perfluoroalkyl iodides with ^{t}Bu$_3$P (**96**) and B(C$_6$F$_5$)$_3$ (**85**). This iodophosphonium fluoroborate was isolated as the sole product in yields ranging from 54-85% (Table 5). Its structure was confirmed by NMR and crystal structure analysis.[5,83]

Table 5: Synthesis of the iodophosphonium fluoroborate [^{t}Bu$_3$PI][FB(C$_6$F$_5$)$_3$] (**120**) (top), perfluoroalkyl iodide, reaction times and yields (bottom).[82]

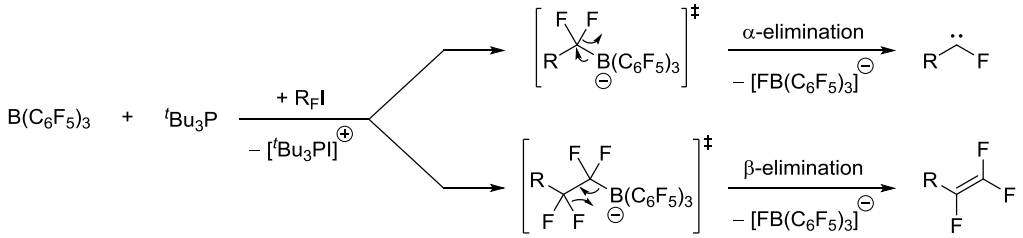


The resulting organic second products were difficult to identify, but in the case of undecafluoro-6-iodocyclohexane (**118**) the NMR-spectra showed the formation of perfluorocyclohex-1-ene (**121**) (Scheme 48).



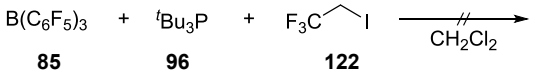
Scheme 48: Formation of perfluorocyclohex-1-ene (**121**) starting from undecafluoro-6-iodocyclohexane (**118**).[82]

This observation indicates a formal β-elimination process (Scheme 49) for this perfluoroalkyl iodide. A β-elimination process however, is not possible for perfluoroalkyl iodides like CF$_3$I (**16**) or perfluorobenzyl iodide (**119**) due to an absence of β-fluoride atoms. Nevertheless, the formation of [^{t}Bu$_3$PI][FB(C$_6$F$_5$)$_3$] (**120**) was observed. As a consequence, an α-elimination might take place, concomitant with the formation of a perfluorocarbene (Scheme 49).



Scheme 49: Mechanistic proposals for the formation of [^{t}Bu$_3$PI][FB(C$_6$F$_5$)$_3$] by an α- or β-elimination process.[82]

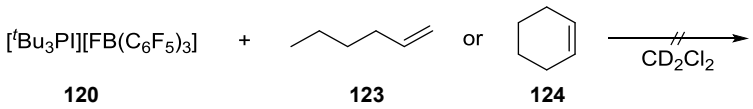
To evaluate the limitations of this reaction, B(C$_6$F$_5$)$_3$ and ^{t}Bu$_3$P were reacted with trifluoro-2-iodoethane (**122**), but no reaction occurred (Scheme 50). This observation can presumably be explained by the weaker polarisation of the C-I-bond in trifluoro-2-iodoethane.



Scheme 50: Reaction of trifluoro-2-iodoethane (**122**) with B(C$_6$F$_5$)$_3$ (**85**) and ^{t}Bu$_3$P (**96**).[82]

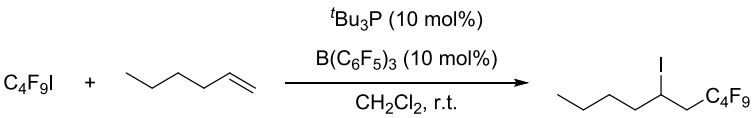
3.2 Catalytic Activation of Perfluoroalkyl Iodides

The previous experiments suggested that the combination of B(C$_6$F$_5$)$_3$ and ^{t}Bu$_3$P is capable to activate the C-I bond and may mediate the addition of a perfluoroiodoalkane to an alkene. However, phosphonium borate [^{t}Bu$_3$PI][FB(C$_6$F$_5$)$_3$] (**120**) did not react with hex-1-ene (**123**) or cyclohexene (**124**) (Scheme 51). Thus, the salt does not seem to be able to transfer neither the fluoride nor the iodonium ion.



Scheme 51: Reaction between [^{t}Bu$_3$PI][FB(C$_6$F$_5$)$_3$] (**120**) and alkenes.[82]

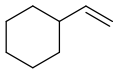
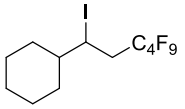
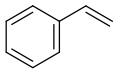
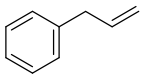
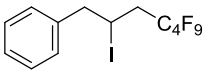
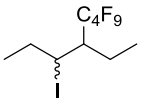
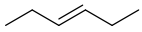
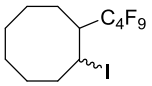
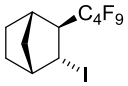
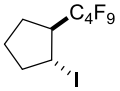
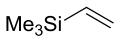
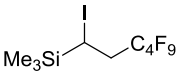
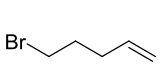
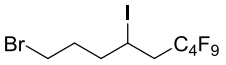
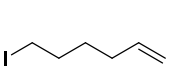
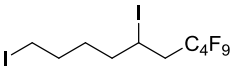
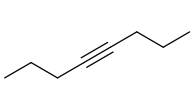
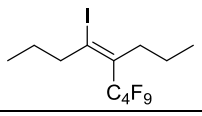
As an alternative, a potential transfer of perfluoroalkyl iodides to alkenes with catalytic amounts of B(C$_6$F$_5$)$_3$ and ^{t}Bu$_3$P was investigated (Scheme 52). As a surprise, when nonafluoro-1-iodobutane (**42**) was reacted in the presence of hex-1-ene (**123**) and catalytic amounts of B(C$_6$F$_5$)$_3$ as well as ^{t}Bu$_3$P, the perfluoroiodoalkane **125** was formed in 73% yield (Scheme 52).



Scheme 52: FLP-catalysed iodoperfluoroalkylation of 1-hexene (**123**) with nonafluoro-1-iodobutane (**42**).[82]

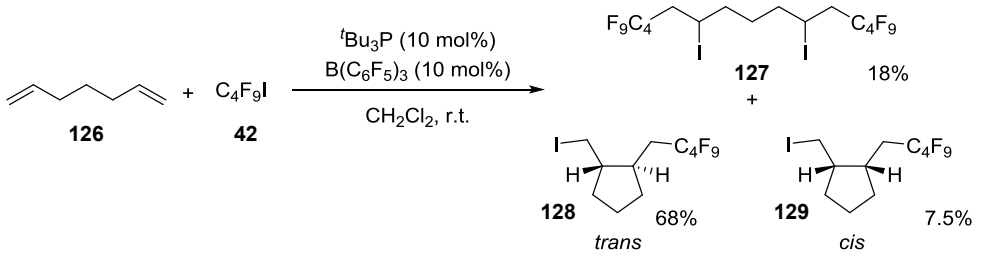
With the promising result at hand, several substrates were tested and successfully converted under the same conditions (Table 6).

Table 6: FLP-catalysed synthesis of perfluoroiodoalkanes/-alkenes.[82]

educt	product	reaction time [h]	isolated yield [%]
		12	95
	no reaction	12	-
		40	56
		22	33
	no reaction	24	-
		12	55
		12	37
		20	54
		12	81
		17	56
		24	84
		24	18

The following observations can be derived from Table 6. First of all, the reaction seems to be sensitive to steric demand. For example (*E*)-3-hexene does not react at all, but (*Z*)-3-hexene gives 33% of the iodoperfluoroalkylation product. Secondly, all successfully converted alkenes are relatively electron-rich. Thirdly, the perfluorobutyl substituent always adds at the terminal position.

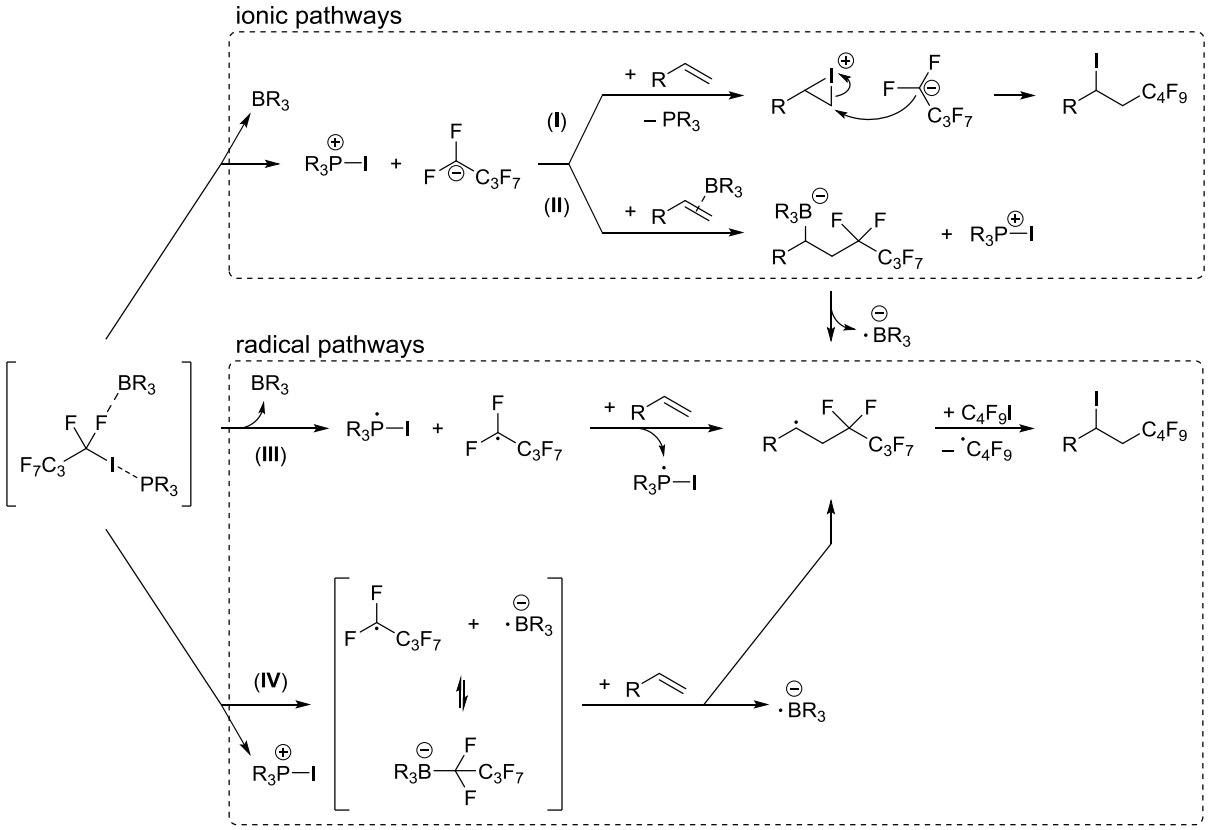
In order to understand more about the iodoperfluoroalkylation, control reactions were carried out. It was demonstrated that both the borane and phosphane need to be present for a successful conversion, since no reaction occurred with solely the borane or the phosphane. In the ^{11}B- and ^{1}H-NMR-spectrum no evidence for the formation of a π-complex between $B(C_6F_5)_3$ and 1-hexene was found, while the phosphane seems to weaken the C-I bond by halide interactions. This was indicated by a change in shift in both the ^{19}F- and ^{31}P-NMR-spectrum of a mixture of perfluoroalkyl iodide and $^{t}Bu_3P$. To obtain more decisive evidence regarding the mechanism, additional experiments for a verification of radical intermediates were conducted. First of all, Czekelius *et al.* observed no conversion of styrene (Table 6), which could be explained by radical quenching. Secondly, an addition of 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) to a reaction mixture had no impact on the conversion rate. However, BHT might be an unsuitable radical scavenger, thus this observation is not conclusive. Thirdly, throughout EPR measurements radical intermediates could not be proven. Still, an indication of radical intermediates was obtained by an iodoperfluoroalkylation of 1,6-heptadiene (**126**) (Scheme 53). The formation of cyclopentane derivatives **128** as well as **129** was observed which is more consistent with the assumption of a radical pathway.



Scheme 53: Iodoperfluoroalkylation of 1,6-heptadiene (**126**).[82]

Since Czekelius *et al.* could prove neither a radical nor an ionic mechanism, they proposed four different mechanistic rationales for the activation of perfluoroalkyl iodides (Scheme 54) involving either ionic or radical intermediates. The ionic pathways involve a heterolytic cleavage of the C−I-bond under formation of an iodophosphonium cation and a perfluoroalkyl anion. Then, an iodonium ion could be formed with the alkene [Scheme 54, (**I**)] and a nucleophilic attack at the less hindered position would follow. Another possibility would be a borane-mediated activation of the alkene for a nucleophilic attack by the perfluoroalkyl anion [Scheme 54, (**II**)] with a subsequent radical cleavage of the B−C-bond. However, this process would be unlikely due to the stability of such borates. The radical pathway (**III**) would include a radical cleavage of the C−I-bond, forming a radical phosphane-iodine adduct and a perfluoroalkyl radical, which can then attack the alkene. As a last proposal, the formation of a perfluoroalkyl borate was suggested,

which could then cleave heterolytically [Scheme 54, (**IV**)] and the perfluoroalkyl radical could perform a radical addition to the alkene.



Scheme 54: Mechanistic rationales for the FLP-catalysed iodoperfluoroalkylation.[82]

4 Research Question

In 2016, Czekelius *et al.*[82] presented an iodoperfluoroalkylation of unfunctionalised, electron-rich alkenes utilising the most prominent combination in FLP-chemistry: $B(C_6F_5)_3$ and its counterpart $^tBu_3P$. Since only unfunctionalised alkenes could be converted, one of the major tasks of this thesis is the expansion of the substrate scope. $B(C_6F_5)_3$ is prone to form stable adducts or even react with heteroatom bearing molecules. Therefore, alternative boranes have to be synthesised (Figure 3). Besides these Lewis acids, alternative phosphanes will be synthesised, which were successfully used in FLP-catalysed hydrogenations.[84] Both the boranes and the phosphanes will be probed for their catalytic potency.

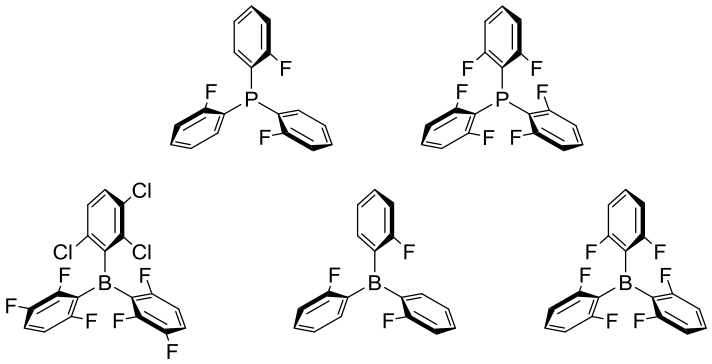


Figure 3: Electronically tuned phosphanes and boranes.

To test the functional group tolerance, commercially available or readily synthesizeable educts should be tested (Figure 4). In this context, ethers, aliphatic and aromatic esters, amines, as well as amides and alcohols will be examined (Figure 4). For these substrates the synthesised boranes and phosphanes will be probed.

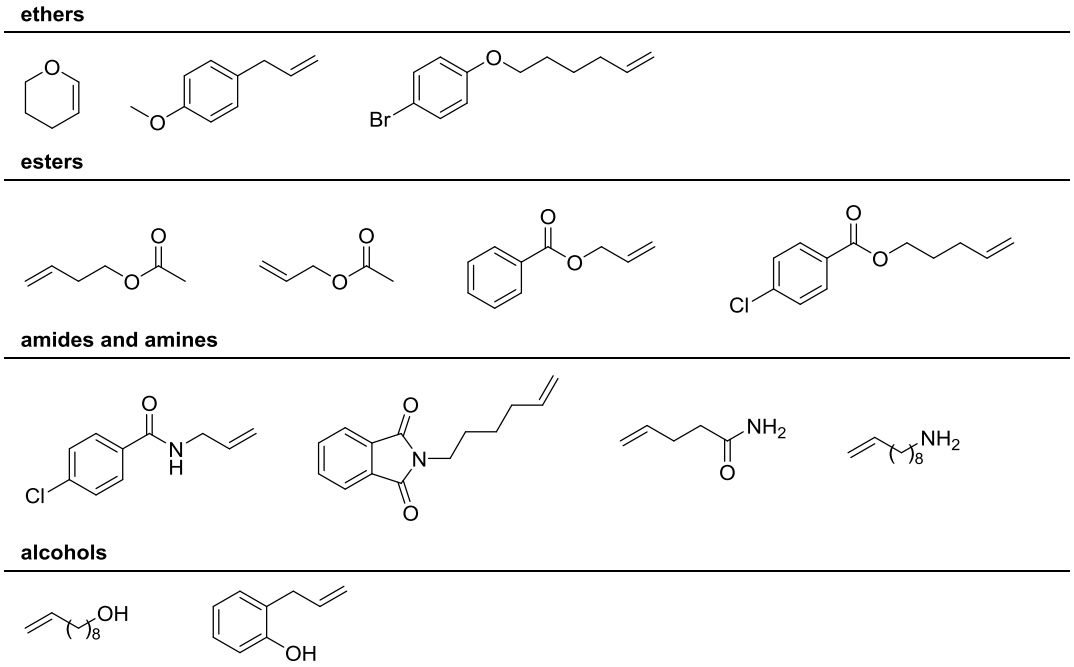


Figure 4: Selected examples of substrates for the test of the functional group tolerance.

Besides electron-rich alkenes, Czekelius *et al.*[82] were also able to iodoperfluoroalkylate the internal alkyne 4-octyne. To continue this study, terminal and internal alkynes (Figure 5) will be tested. An iodoperfluoroalkylation of terminal alkynes is of great interest, as this motive can be found in many reaction sequences.

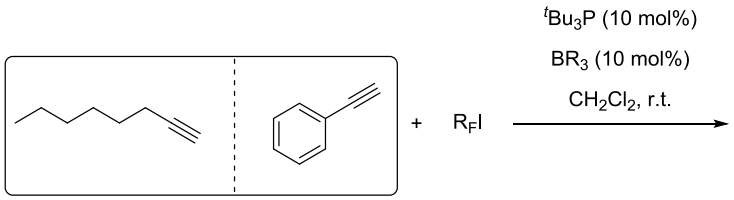


Figure 5: FLP-catalysed iodoperfluoroalkylation of exemplary alkynes.

Alkenes containing electron-deficient double bonds are challenging substrates for iodoperfluoroalkylation since perfluoroalkyl radicals are electrophilic and only react readily with electron-rich double bonds. Therefore, this substance-class will be examined and a successful iodoperfluoroalkylation of electron-deficient alkenes (Figure 6) would lead to implications regarding the reaction mechanism.

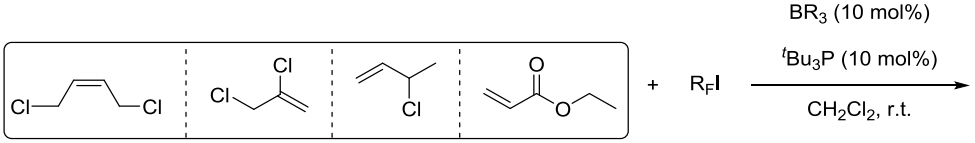
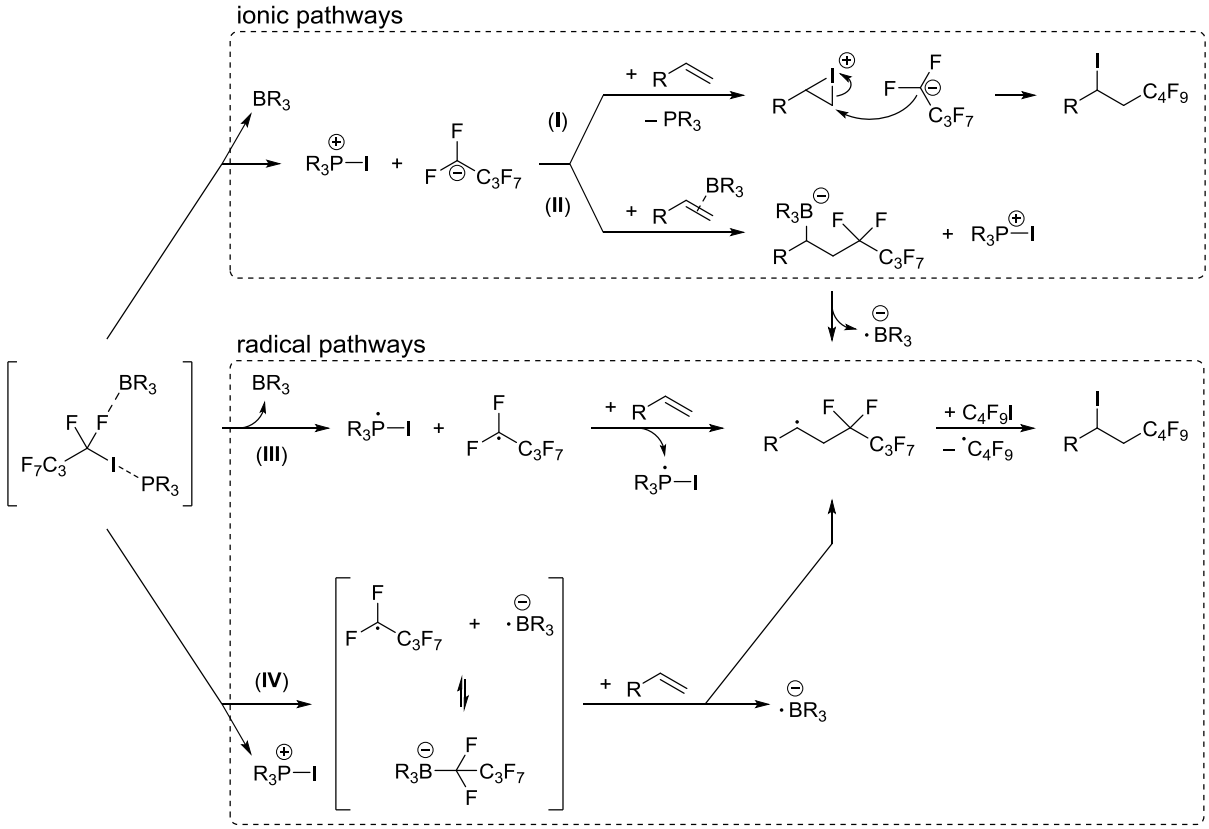


Figure 6: FLP-catalysed iodoperfluoroalkylation of exemplary electron-deficient alkenes.

Czekelius *et al.*[82] started with mechanistic studies which resulted in first indications for a radical mechanism (Scheme 55). However, they could not rule out an ionic mechanism. Since an FLP-catalysed iodoperfluoroalkylation was unknown in the literature before, a thorough examination of the mechanism will be conducted. For example, an iodoperfluoroalkylation in the presence of styrene as well as 1,4-hexadiene should be performed to obtain new evidence for a radical mechanism. An absent iodoperfluoroalkylation would give new hints for a radical process. Along with these test reactions, kinetic investigations will be conducted to understand more about the role of each compound involved in the reaction.



Scheme 55: Mechanistical proposals for the FLP-catalysed iodoperfluoroalkylation by Czekelius *et al.*[82]

5 Results and Discussion

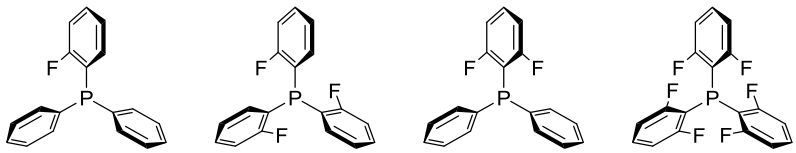
The chapter "Results and Discussion" is divided into two main parts. Firstly, syntheses of electronically tuned phosphanes and boranes are described. Secondly, iodoperfluoroalkylations of alkenes as well as alkynes are presented.

5.1 Syntheses of Electronically Tuned Phosphanes and Boranes

To overcome the limitations regarding the functional group tolerance of the FLP-catalysed iodoperfluoroalkylation, electronically tuned phosphanes, as well as boranes, were synthesised. These syntheses are described in the following chapter. At the beginning of each subchapter, a short literature review regarding established strategies is provided.

5.1.1 Syntheses of Electronically Tuned Phosphanes

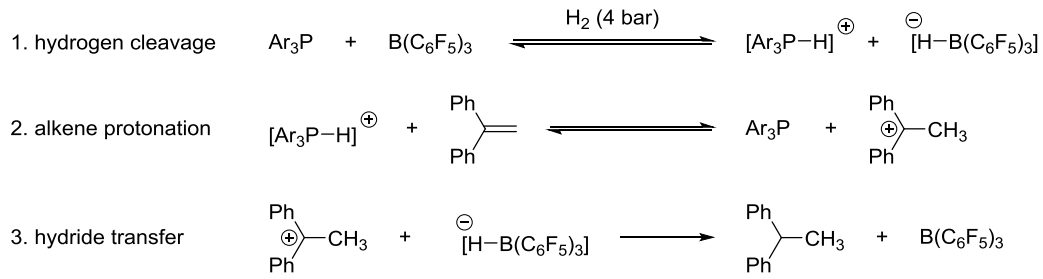
In 2013 Paradies *et al.* published a study regarding electronic effects of triarylphosphanes in FLP-catalysed hydrogenations.[84] Their approach to understand the reactivity of triarylphosphanes is mainly based on the pK_a of the respective hydrophosphonium salts $[R_3PH]^+$. Additionally, they also assessed the Lewis basicity of the triarylphosphane R_3P. As expected, the pK_a drops when more fluorine substituents are integrated into the triarylphosphane (Scheme 56).



pK_a	6.11	3.03	5.16	0.7

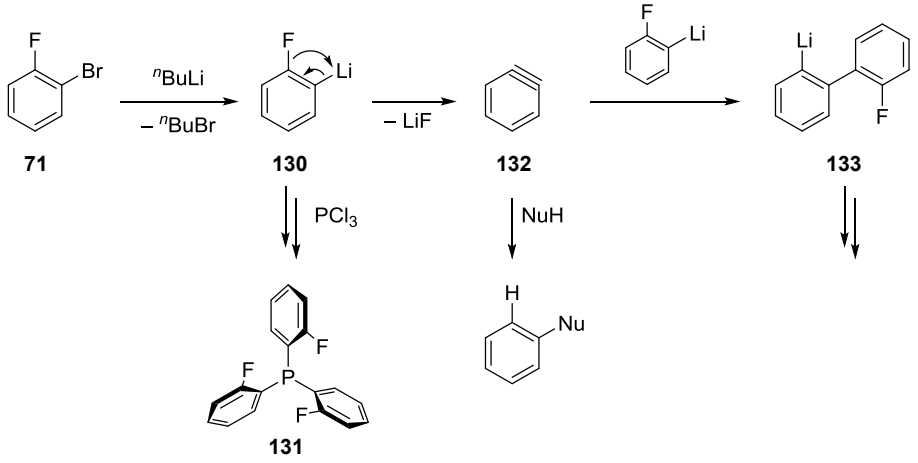
Scheme 56: Electron-deficient phosphanes and pK_a values of the respective hydrophosphonium salts $[R_3PH]^+$.[84]

Based on various observations they proposed a mechanism for the FLP-catalysed hydrogenation (Scheme 57). In a first step, hydrogen is cleaved heterolytically. They showed that this equilibrium is strongly influenced by the pK_a of the hydrophosphonium salt $[R_3PH]^+$. As a rule of thumb a higher pK_a results in easier hydrogen splitting. In the second step, $[R_3PH]^+$ acts as a Brønsted-acid, protonating the alkene. In this case, lower pK_a result in more efficient protonation of the alkene. As a result, a certain balance between acidity and basicity has to be established. The third and last step is the hydride transfer, which depends on the $[H{-}B(C_6F_5)]^-$ concentration.



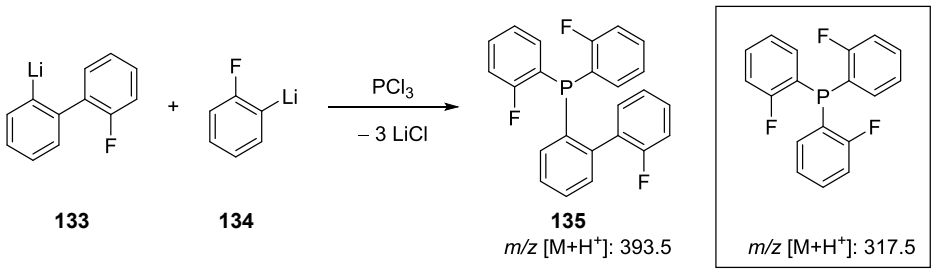
Scheme 57: Proposed mechanism for the FLP-catalysed hydrogenation of alkenes.[84]

Inspired by this work, electronically tuned phosphanes were synthesised. The synthesis of tris(2-fluorophenyl)phosphane (**131**) was conducted according to a procedure by Scheffler *et al.*[85] and it proved to be challenging. During the lithiation of 1-bromo-2-fluorobenzene (**71**), a white solid precipitated, which could either be the lithiated species itself or lithium fluoride. If lithium fluoride had formed, an elimination would have taken place (Scheme 58) resulting in the formation of benzyne (**132**). Benzyne is a very reactive molecule, preferentially reacting with nucleophiles.



Scheme 58: Lithiation of 1-bromo-2-fluorobenzene (**71**), the formation of desired tris(2-fluorophenyl)phosphane (**131**) and side reactions.

Throughout the addition of phosphorus trichloride, a dark brown colouration was observed. This colouration indicates the formation of side products, which was confirmed by TLC-control showing a complex product mixture. Nevertheless, the brown colouration is in line with observations of Scheffler *et al.*[85] By three subsequent recrystallisations from ethanol the purity could be increased to > 95%. However, it could not be further improved by column chromatography and another sublimation. Since the yield was very low at this point, no further attempts to purify the product were conducted. A mass spectrum of the obtained amorphous material showed two main signals at m/z = 317.5 and m/z = 393.5. The mass peak m/z = 317.5 can be assigned to the desired product and the other peak might be the result of a reaction of biaryl **133** with phosphorous trichloride.

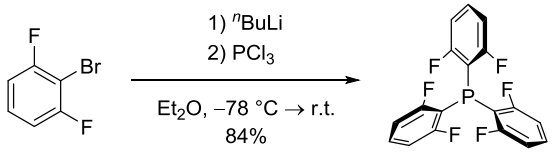


Scheme 59: Formation of phosphane **135** and the respective molecular mass.

The presence of phosphane **135** matches the observations in ^{31}P- and ^{19}F-NMR-spectra, showing signals with comprehensible shifts and multiplicities. As shown in Scheme 58, phosphane **135** can be formed after benzyne formation.

The synthesis was repeated and a recrystallisation from ethanol was possible directly after the extraction. However, the obtained material was impure and column chromatography had to be performed. Throughout this purification it was observed that tris(2-fluorophenyl)phosphane is poorly soluble in mixtures of *n*-hexane and EtOAc containing more than 90% *n*-hexane. Separations with such eluent-mixtures were not efficient due to a very slow elution. After several tests, a mixture of cyclohexane and CH_2Cl_2 (95:5) was used in combination with a long column to obtain pure product. The yield of 13% is low compared to the yield of Scheffler *et al.*, who obtained 60%.[85] Possibly, the reaction has to be conducted at lower temperatures than −78 °C to avoid elimination of lithium fluoride and the consecutive benzyne formation.

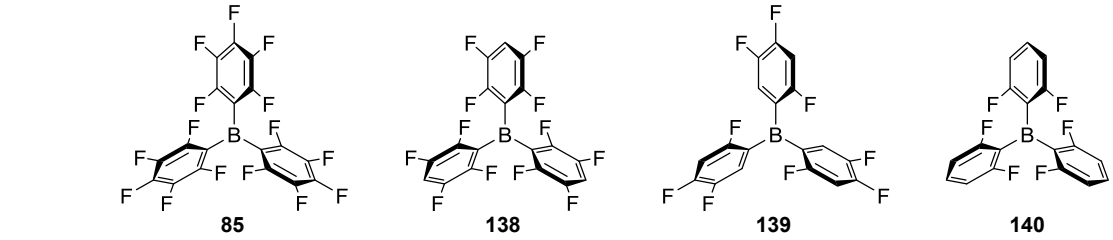
Fortunately, the synthesis of tris(2,6-difluorophenyl)phosphane (**137**) (Scheme 60) proceeded without any problems. A procedure of Stuart *et al.*[86] was only slightly changed and adapted. Instead of diluting *n*-butyllithium before the addition, a direct dropwise addition was performed. The obtained yield of 84% is comparable to the yield of 87% obtained by Stuart *et al.*



Scheme 60: Synthesis of tris(2,6-difluorophenyl)phosphane (**137**).

5.1.2 Synthesis of Electronically Tuned Boranes

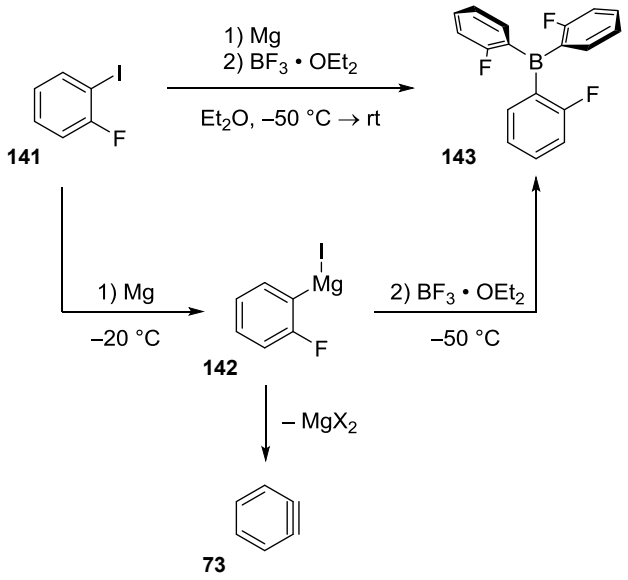
Besides electronically tuned phosphanes, electronically tuned boranes were synthesised. As described earlier, FLP-based systems were used even in water-containing solvents. The tuning of the Lewis acidity was described by Alcarazo *et al.*,[87] Berionni *et al.*[88] and Paradies *et al.*[89] In the following scheme selected examples of Lewis acidities for arylboranes are described.



Scheme 61: Lewis acidities of selected boranes.[87,90]

5.1.2.1 Tris(2-fluorophenyl)borane

For the synthesis of tris(2-fluorophenyl)borane (**143**) ($B(2\text{-}FC_6H_4)_3$) only one protocol by Naumann *et al.*[91] is available in the literature. Unfortunately, this protocol states a yield of just 12% for $B(2\text{-}FC_6H_4)_3$ (**143**). This low yield can be understood considering the problems throughout the synthesis of tris(2-fluorophenyl)phosphane. Metallated aromatic rings with a fluoride substituent in *ortho*-position are very unstable and tend to eliminate metal fluorides with concomitant benzyne formation.



Scheme 62: Synthesis of tris(2-fluorophenyl)borane (**143**) via a Grignard reagent and benzyne (**73**) formation as a side reaction.

The formation of the Grignard reagent **142** with magnesium at −20 °C proceeded as good as described (Scheme 62). Nevertheless, a two-phase system was unexpectedly formed during the reaction. By removal of all volatiles a yellowish foam was obtained, which was then sublimated. The sublimation did not result in an isolation of pure product. A yellow/brownish resin resublimated at the cooling finger, which was removed twice in a N_2 counterflow. Later, the sublimation was cancelled, since a resublimation in the cooling trap was observed. A control by a

^{19}F-NMR spectroscopy of the crude product showed a mixture of various substances (Figure 7, experiment 1). Further attempts to isolate a clean product for this experiment were unsuccessful. Two subsequent attempts to synthesise the desired borane resulted in complex product mixtures (Figure 7, experiment 2 and 3). In the second attempt ^{i}PrMgCl was used for the generation of the Grignard reagent, but no clean product was observed. The third attempt, using magnesium for the preparation of the Grignard reagent, was unsuccessful, as well.

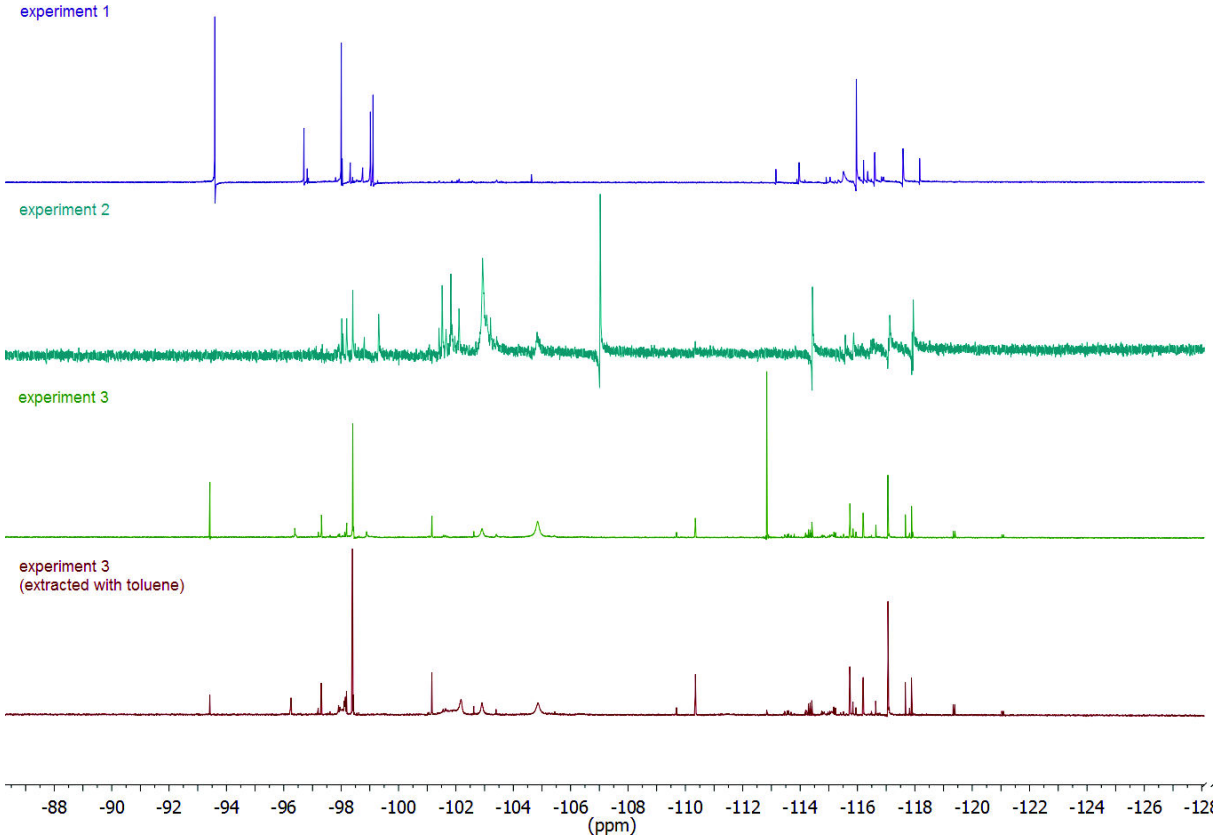
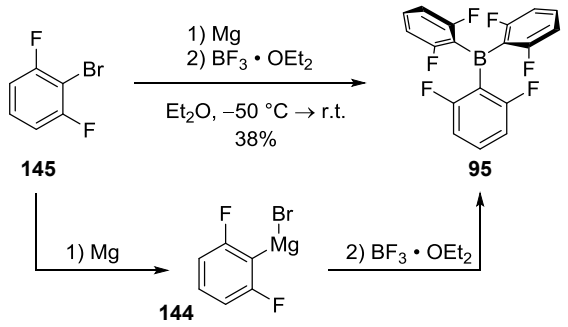


Figure 7: Stacked ^{19}F-NMR-spectra from crude products of the tris(2-fluorophenyl)borane (**143**) syntheses.

Since a successful preparation of $B(2\text{-}FC_6H_4)_3$ (**143**) seemed improbable at this point, the synthesis was not repeated.

5.1.2.2 Tris(2,6-difluorophenyl)borane

The synthesis of tris(2,6-difluorophenyl)borane (**95**) was conducted according to a protocol of Berionni *et al.*[88] They used magnesium to generate the respective Grignard reagent of 1-bromo-2,6-difluorobenzene (**145**), which was exposed to $BF_3 \cdot OEt_2$ to obtain the desired borane (Scheme 63). Unfortunately, 1-bromo-2,6-difluorobenzene (**145**) did not react with active magnesium. Its activity was controlled by an addition of 1,2-dibromoethane, which reacted readily.



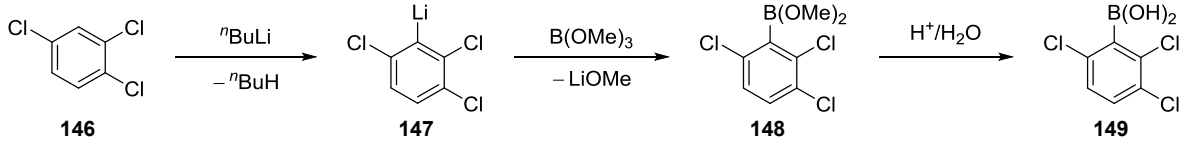
Scheme 63: Synthesis of tris(2,6-difluorophenyl)borane (**95**) via a Grignard reagent.

Alcarazo *et al.*[87] reported a yield of 59% of tris(2,6-difluorophenyl)borane (**95**) using ^{i}PrMgCl instead of magnesium for the Grignard formation. With this method a smooth conversion seemed to take place, resulting in a white product after removal of the solvents. Nevertheless, the crude product could not be cleaned up satisfyingly; neither by two sublimations nor by a recrystallisation. Superimposed ^{19}F-NMR-spectra show nearly no change in the relative peak intensity. As the purity of the product was only about 90% at this point, and since only little material remained, no further tests for a purification process were conducted. Instead, the experiment was repeated.

In the course of another attempt to synthesise $B(2,6\text{-}F_2C_6H_3)_3$ (**95**) the protocol was slightly changed to improve the yield. Instead of directly adding $BF_3 \cdot OEt_2$ via a syringe, it was dissolved in THF, cooled with an acetone/dry ice bath and then cannulated to the solution of Grignard reagent. Instead of a sublimation from the crude product, an extraction with toluene followed by a sublimation was performed. Both the ^{1}H- and the ^{19}F-NMR-spectrum of the resulting grey solid indicated a purity of about 80%. By three subsequent sublimations and a recrystallisation from boiling *n*-hexane white needles (purity ≥96%) were obtained (yield = 38%).

5.1.2.3 Water-Stable Boranes

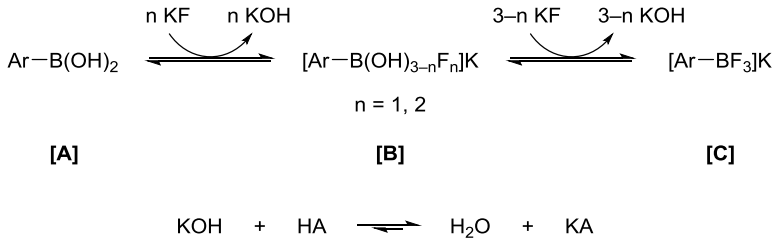
As a first step in the synthesis sequence towards a water-stable borane, (2,3,6-trichlorophenyl)boronic acid (**149**) should be synthesised following a protocol of Soós *et al.*[75] Starting from an aromatic system, a lithiated nucleophile **147** was generated, which was reacted with trimethyl borate to dimethyl boronate **148**. This boronate was then hydrolysed to obtain boronic acid **149** (Scheme 64).



Scheme 64: Synthesis of boronic acid **149** beginning with a lithiation of 1,2,4-trichlorobenzene (**146**).

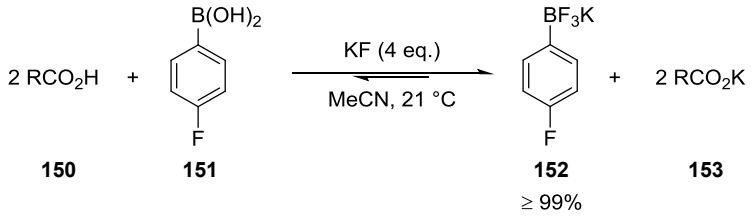
The reaction proceeded without unexpected difficulties throughout all experiments. Two major problems of this protocol are the formation of a hardly intermixable suspension which forms in the course of the *n*-butyllithium addition (Scheme 64), and the removal of the solvent which was unexpectedly time-consuming in all cases. Throughout some examinations, the crude product had to be filtered off and washed with *n*-hexane to remove a yellowish impurity. However, an analytically pure product was obtained in every case. The yields ranged from 42 up to 80% with a tendency towards a yield between 70-80%. This yield is comparable to the yield of 63% described in the literature.[75]

The most common method for the synthesis of trifluoroborates from boronic acids utilises KHF_2 in methanol. This method by Vedejs *et al.*[92] was analysed and successfully optimised by Lennox and Lloyd-Jones.[93] Vedejs *et al.* were not able to apply KF as the fluorine source. An analysis with ^{19}F-NMR-spectroscopy by Lennox and Lloyd-Jones revealed that mixed salts [**B**] are formed with KF, but not the desired trifluoroborate [**C**] (Scheme 65).



Scheme 65: Equilibria of aromatic boronic acids with potassium fluoride and potassium hydroxide.[93]

They reasoned that the addition of carboxylic acids should drive the equilibria towards trifluoroborate [**C**]. As expected, they could drive the conversion to up to 99% by adding 30 equivalents of acetic acid or with two equivalents of tartaric acid (Scheme 66).

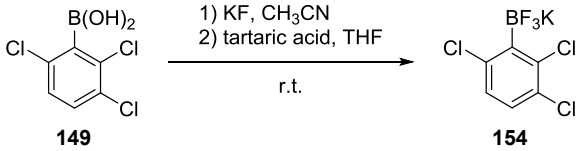


Scheme 66: Conversion of boronic acid **151** with potassium fluoride and a carboxylic acid.

Further tests lead to a simple and facile reaction procedure: The boronic acid is dissolved in acetonitrile and aqueous potassium fluoride is added followed by a solution of tartaric acid in THF. Potassium bitartrate precipitates together with residues of KF and the product can be gained by simple filtration. Besides the simple reaction procedure, an etching of the glassware by HF_2^- is avoided.

The protocol of Lennox and Lloyd-Jones[93] was tested once for (2,3,6-trichlorophenyl)boronic acid (**149**) (Scheme 67). During the reaction no problems emerged, but the yielded product was

impure. On the one hand, the ^{19}F-NMR-spectrum showed around 5% of an impurity. On the other hand, the ^{1}H-NMR-spectrum clearly indicated the presence of around 8% educt and roughly 6% of another aromatic compound – potentially resulting from an intermediate of the transformation (Scheme 65). Obviously, the reaction was incomplete and therefore longer reaction times or a higher excess of KF should be considered for a retry of this experiment.

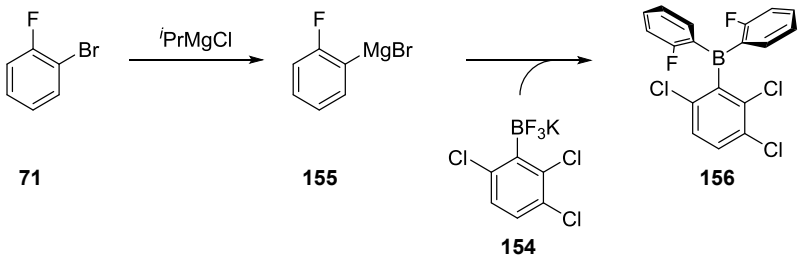


149 **154**

Scheme 67: Conversion of (2,3,6-trichlorophenyl)boronic acid (**149**) to potassium (2,3,6-trichlorophenyl)trifluoroborate (**154**).

Since this etching-free method did not give pure fluoroborate, the classical method using KHF_2 in methanol was conducted. A protocol by Soós *et al.*[75] proved to be reliable and gave potassium (2,3,6-trichlorophenyl)trifluoroborate (**154**) in yields above 90% throughout several syntheses. One disadvantage of this protocol is the fact that all used glassware was etched severely.

With potassium (2,3,6-trichlorophenyl)trifluoroborate (**154**) at hand, the synthesis of a water-stable borane was tested. For this purpose, 1-bromo-2-fluorobenzene (**71**) was reacted with a solution of ^{i}PrMgCl to obtain Grignard reagent **155** (Scheme 68). TLC controls of inertly taken samples indicated no formation of side products even after warming up to 0 °C. Only the educt and a single product were observed. This product might be fluorobenzene, resulting from a hydrolysis of the Grignard reagent. Directly after transferring the Grignard reagents solution into a potassium (2,3,6-trichlorophenyl)trifluoroborate suspension, a dark brown solid precipitated. Over night the reaction solution was allowed to warm to r.t. and a TLC control revealed the formation of several products, of which one seemed to be predominant.



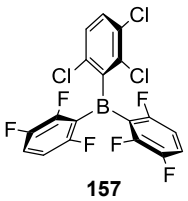
71 **155** **154** **156**

Scheme 68: Unsuccessful synthesis of bis(2-fluorophenyl)(2,3,6-trichlorophenyl)borane (**156**).

Workup was conducted under open bench conditions and in the end, a brown resin (filtrate) as well as minor amounts of a white solid (residue) were obtained. Both raw products show a mixture of several compounds. According to the ^{1}H-NMR-spectrum the filtrate contains a 1:1-mixture of aromatic and aliphatic compounds. In the ^{19}F-NMR-spectrum thirteen signals were observed. A ^{1}H-NMR-spectrum of the residue shows mainly toluene and minor amounts of

other organic compounds. The ^{19}F-NMR-spectrum shows only traces of an unknown fluorinated compound. To sum things up, the synthesis of bis(2-fluorophenyl)(2,3,6-trichlorophenyl)borane (**156**) was not successful. For following reactions, the formation of Grignard reagent **155** should be monitored via TLC and NMR. Furthermore, Grignard reagent **155** and trifluoroborate **154** might be combined at lower temperatures to avoid side reactions.

The synthesis of (2,3,6-trichlorophenyl)bis(2,3,6-trifluorophenyl)borane (**157**) was conducted as described by Soós and Pápai *et al.*,[75] only the workup was carried out differently. To obtain high quality material, sublimations were conducted. The yield of 49% was comparable to the yield described in the literature.



157

Figure 8: (2,3,6-Trichlorophenyl)bis(2,3,6-trifluorophenyl)borane (**157**).

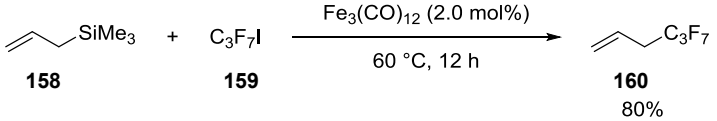
Additional borane syntheses were conducted by Lukas Heynck (Czekelius group) as part of his master thesis.[94]

5.2 FLP-Catalysed Iodoperfluoroalkylations

As described in the chapter "State of Knowledge - Activation of Perfluoroalkyl Iodides", Czekelius *et al.* developed a method to activate perfluoroalkyl iodides for an iodoperfluoroalkylation of alkenes as well as an internal alkyne. One of the major tasks of this thesis was to expand the substrate scope of this catalytic system. This chapter starts with investigations of the iodoperfluoroalkylation of alkenes and alkynes. Secondly, tests specifically addressing functional group tolerance are presented.

5.2.1 Allyltrimethylsilane

Allylsilanes are valuable reagents for the introduction of allyl moieties. For example, Fuchikami and Ojima[95] investigated a reaction between allylsilanes and polyfluoroalkanes. They were able to allylate different polyfluoroalkanes in the presence of triiron dodecacarbonyl [$Fe_3(CO)_{12}$] or triruthenium dodecacarbonyl [$Ru_3(CO)_{12}$] (Scheme 69).

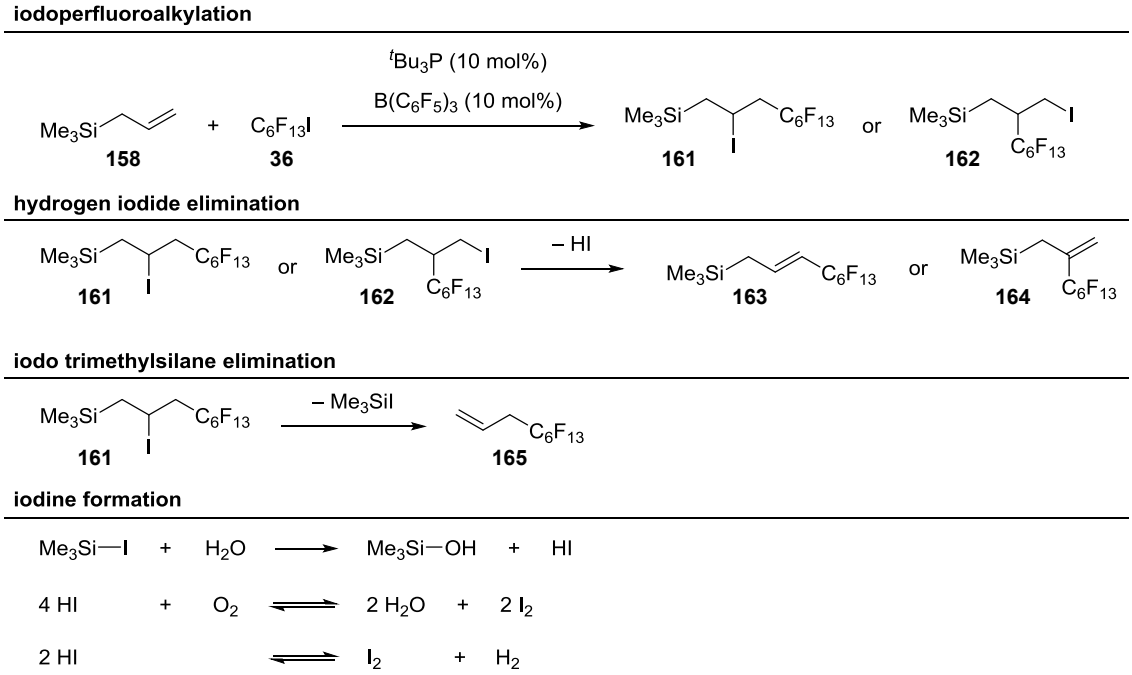


158 **159** **160**
80%

Scheme 69: Selected example of an allylation of a perfluoroalkyl iodide catalysed by $Fe_3(CO)_{12}$.[95]

They state that they "[...] found that the reaction of polyfluoroalkyl iodides or bromides with allyltrimethylsilane catalyzed by $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$ gave 3-polyfluoroalkylprop-1-ene exclusively in high yields."[95] However, they did not isolate iodoperfluoroalkylation products.

With the motivation to iodoperfluoroalkylate allyltrimethylsilane (**158**) it was converted utilising standard reaction conditions with $B(C_6F_5)_3/{}^tBu_3P$ as catalysts. In the course of a first test, a TLC-control indicated a complete conversion within three days. The observed product seemed to decompose on SiO_2 plates. As a result, neutral Al_2O_3 was used for column chromatography. After the removal of the solvent, only minor amounts of a transparent liquid were isolated. Most probable, the applied pressure of 10 mbar for the complete removal of the solvents was too low, causing severe losses in the course of the solvent removal. Interestingly, the obtained product turned pink after dissolving in $CDCl_3$. Presumably, hydrogen iodide or trimethylsilyl iodide is eliminated catalysed by protons in $CDCl_3$ (Scheme 70). Subsequently, iodine is formed explaining the pink discolouration (Scheme 70). As a consequence acidic conditions should be avoided throughout workup.



Scheme 70: Functionalisation of allyltrimethylsilane (**158**), subsequent elimination and the formation of iodine.

The ^1H- and ^{19}F-NMR-spectra of the mentioned NMR sample indicate a mixture of products. Signals of a trimethylsilyl group were present, suggesting the presence of a trimethylsilyl moiety inside the product. After six days the same sample was measured once more and the spectrum changed severely (Figure 9). Signals at shifts around 3-4.5 ppm vanished and new signals at > 5 ppm arose (Figure 9). This change is in line with an elimination process accompanied by alkene formation (Scheme 70).

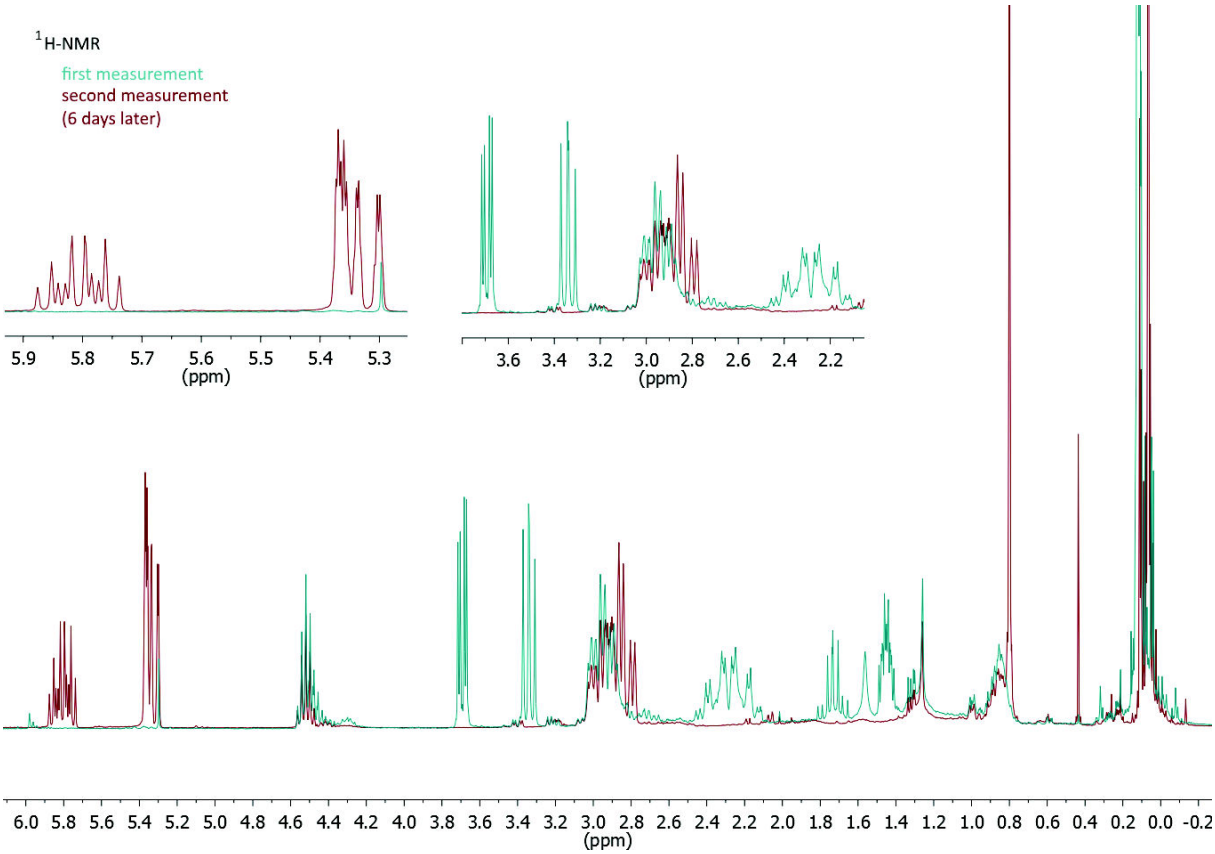
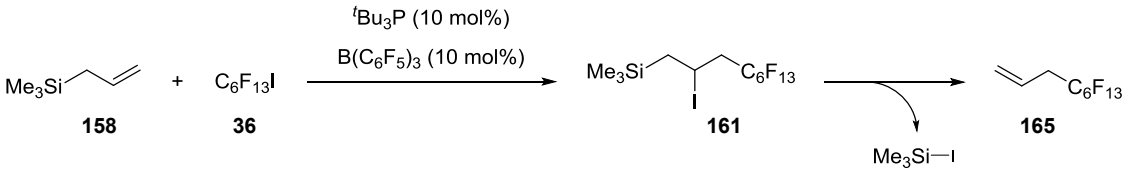


Figure 9: Superimposed ^{1}H-NMR-spectra of iodoperfluoroalkylated allyltrimethylsilane (**158**) before and after storing it in $CDCl_3$.

The conversion of allyltrimethylsilane was repeated in a Teflon-insert screw cap vial. A control by NMR spectroscopy after four days indicated a complete conversion to the potential elimination product **165** (Scheme 71). As soon as the vial was opened, white smoke escaped. Consequently, a compound like trimethylsilyliodide might have been formed which caused smoke formation.

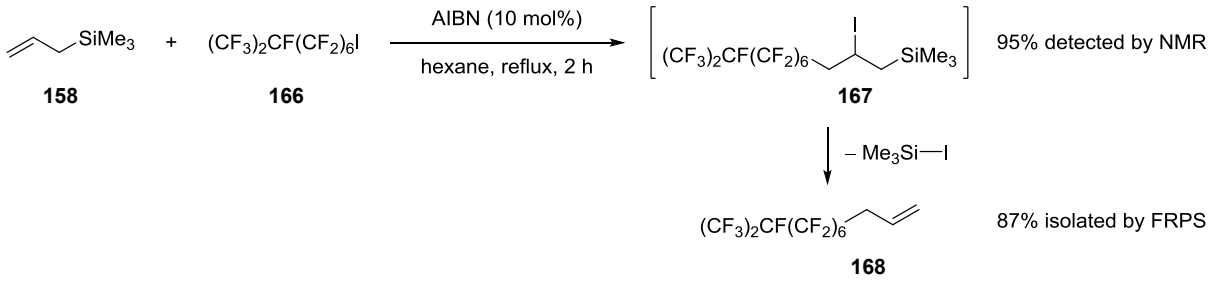


Scheme 71: Iodoperfluoroalkylation of allyltrimethylsilane (**158**) and the subsequent elimination of trimethylsilyliodide.

Again, column chromatography on neutral Al_2O_3 (Brockmann III) was utilised to isolate a product. However, no clean product could be obtained. The product was highly volatile and seemed to decompose quickly. After one week at r.t. in a closed round-bottom flask, nearly 50% of the mass was lost and a purple gas had developed. The remaining purple liquid was dissolved in *n*-pentane, filtered over basic Al_2O_3 and concentrated by evaporation. Only a minor amount of an impure compound was obtained. Besides the described experiments, several additional attempts to isolate a pure product were conducted without success.

Consequently, the isolation of clean iodoperfluoroalkylation product seems to be challenging. Obviously, it is quite unstable as well as volatile and side products can be hardly separated by column chromatography. Even a fractional distillation seems inconvenient due to thermal stress. No further attempts to isolate the product were performed, but a conversion was monitored in an NMR-tube.

As Curran and Ryu *et al.*[96] were able to observe iodoperfluoroalkylation product **167** only by NMR and could not isolate it, they obviously had to tackle a similar problem. Utilising fluorous reverse-phase silica (FRPS), they could isolate the respective elimination product **168**. Unfortunately they did not provide spectral data for the iodoperfluoroalkylation product **167** of allyltrimethylsilane.



Scheme 72: Radical iodoperfluoroalkylation of allyltrimethylsilane (**158**) and a subsequent elimination.[96]

In the case at hand, the attempt to monitor the reaction via NMR measurements was successful, as well. Several spectra were measured after reaction times ranging from 23 min up to 267 h. For the measurements the reaction solution was prepared inside the glovebox. The first spectrum after 23 min clearly indicated the formation of a new product. It is assumed, that the perfluoroalkyl chain will be added at the terminal position. Looking at the assignment of the detected signals (Figure 10), the assumption of a terminal addition can be confirmed. As expected for a terminal addition, a new signal at δ = 4.0 – 4.5 ppm is observed. In contrast, for an internal addition a new signal at δ = 3.0 – 3.5 ppm would be assumed. The remaining signals at δ = 2.9 ppm and δ = 1.8 ppm as well as their pattern fit the expectations, too. Due to ^{1}H-^{19}F-coupling and the presence of diastereotopic protons, complex coupling patterns are observed.

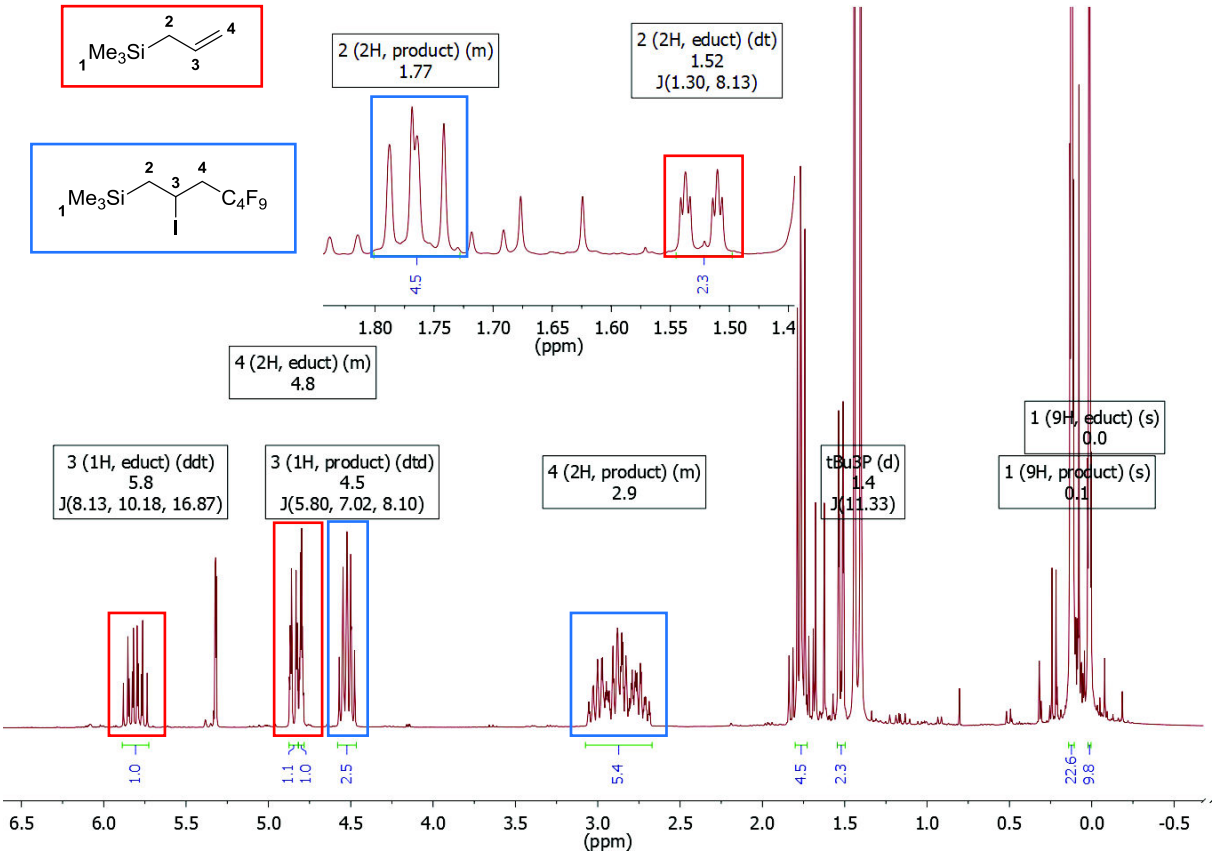


Figure 10: ^{1}H-NMR-spectrum of the iodoperfluoroalkylation of allyltrimethylsilane (**158**) after 23 min reaction time and an assignment of the signals.

In former experiments the formation of perfluoroalkylated allyltrimethylsilane was proposed, but no clean spectrum could be obtained. The spectrum measured after 2.5 hours shows nearly exclusively perfluoroalkylated allyltrimethylsilane (Figure 11). After this complete conversion, the expected elimination process was observed. Spectral data of the allylated nonafluoro-1-iodobutane are in accordance to values in the literature.[97] For a better overview, the results are summarised in the following table.

Table 7: Reaction progress of the iodoperfluoroalkylation of allyltrimethylsilane.

reaction time	allyltrimethylsilane	perfluoroalkylation product	elimination product
23 min	30%	70%	–
2.5 h	7%	93%	–
3.5 h	4%	96%	–
27 h	–	83%	17%
100 h	–	35%	65%
267 h	–	7%	93%
after workup	0%	0%	99%

The calculated values are not precise, since they only project a molar ratio of chosen ^{1}H-NMR-signals. As already mentioned, small amounts of side products were observed which were not considered for the calculations. For allyltrimethylsilane a signal at 4.83 ppm, for perfluoroalkylated product a signal at 4.52 ppm. and for the elimination product a signal at 5.82 ppm was chosen for the determination of the conversion.

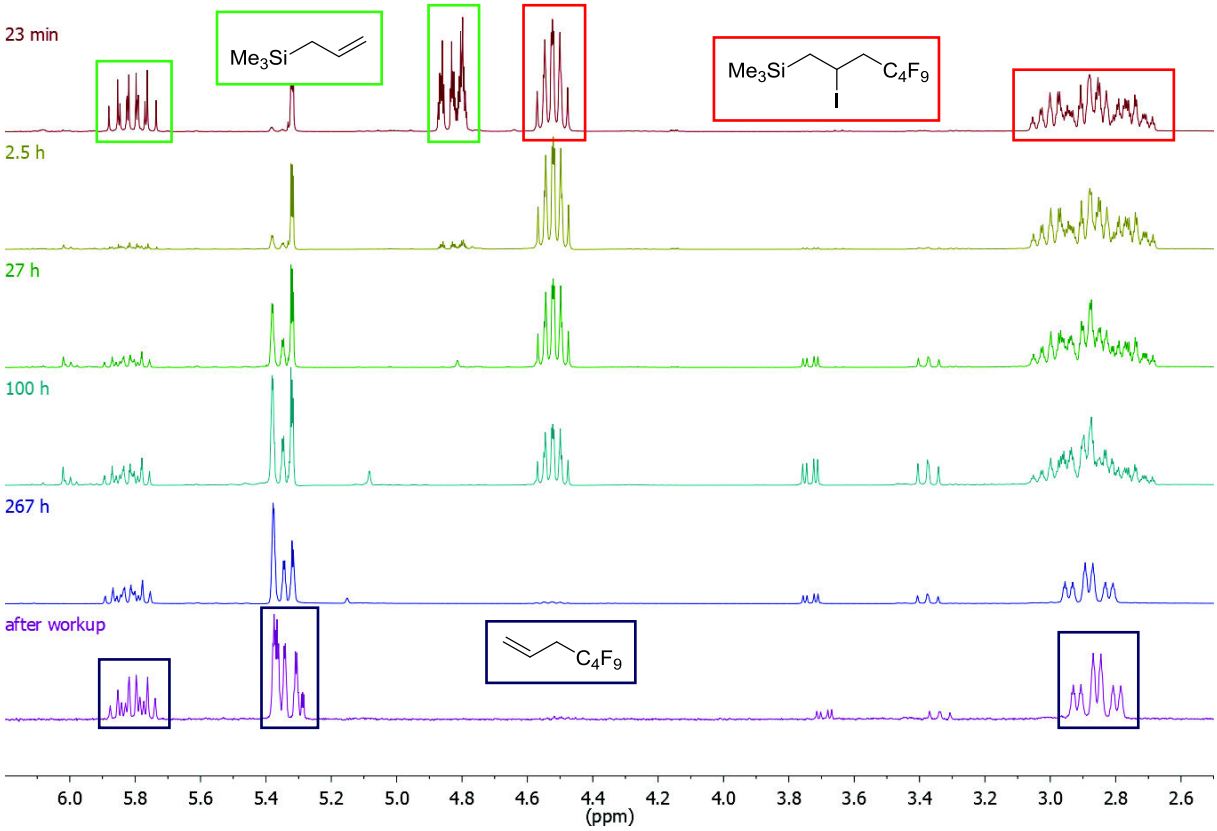


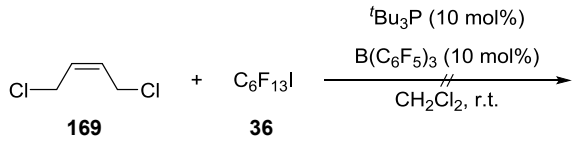
Figure 11: Stacked ^{1}H-NMR-spectra of the FLP-catalysed iodoperfluoroalkylation of allyltrimethylsilane (**158**) and an assignment of the signals.

To sum this chapter up, allyltrimethylsilane was was iodoperfluoroalkylated successfully, but could not be isolated due to a relative fast elimination process of trimethylsilyliodide.

5.2.2 Electron-Poor Alkenes

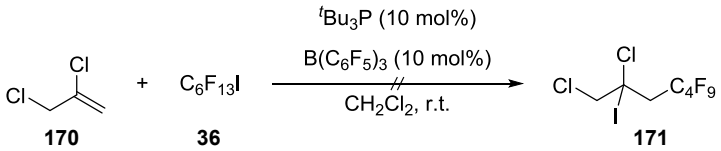
As described, unsubstituted aliphatic alkenes are electron-rich and can be iodoperfluoroalkylated promoted by FLPs. To evaluate the activity for a functionalisation of electron-poor alkenes, a standard FLP-system, consisting of $B(C_6F_5)_3$ and $^{t}Bu_3P$, was tested. Additionally, a variation of the borane was probed in one case.

Firstly, the attempts to iodoperfluoroalkylate three different chlorinated alkenes are presented. As a first educt, *cis*-1,4-dichloro-2-butene (**169**) was chosen. After five days stirring under inert conditions, a conversion could be observed neither in the ^{1}H- nor in the ^{19}F-NMR-spectrum (Scheme 73). A repetition of this experiment confirmed this observation.



Scheme 73: Unsuccessful FLP-catalysed iodoperfluoroalkylation of *cis*-1,4-dichloro-2-butene (**169**).

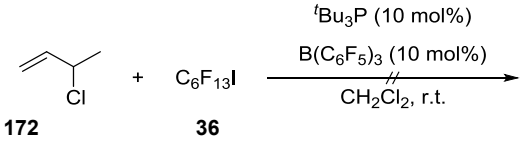
As a second electron-poor alkene, 2,3-dichloro-1-propene (**170**) was chosen. A first control by NMR spectroscopy after 27 hours indicated the formation of minor amounts of a new product. A ^{1}H-NMR-spectrum showed a triplet at 3.13 ppm which could hint at the presence of iodoperfluoroalkylation product **171** (Scheme 74). Furthermore, new signals in the ^{19}F-NMR-spectrum support this assumption.



Scheme 74: FLP-catalysed iodoperfluoroalkylation of 2,3-dichloro-1-propene (**170**).

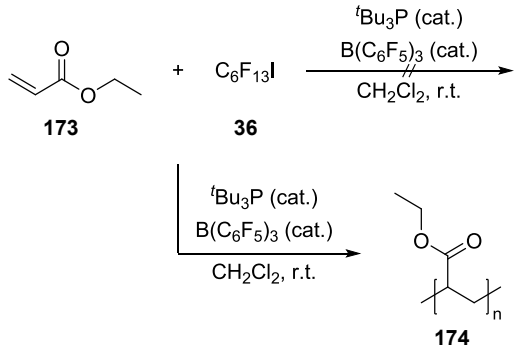
Another control by NMR spectroscopy after 19 days indicated nearly no further conversion and a TLC-control showed one weak band, thus workup was conducted. For this purpose filtration with basic aluminium oxide in a glass pipette (Brockmann III) was conducted. Only 13.3 mg of a transparent liquid were obtained which could not be identified as the desired product. In view of both ^{1}H- and ^{19}F-NMR-spectra, mainly educt and solvent seems to be present. Two repetition experiments were performed, resulting in similar observations. One of these two experiments was conducted in an amber glass screw-cap vial and the other one in a translucent vial. Both experiments showed the same triplet in ^{1}H-NMR-spectra as well as the same new signals in ^{19}F-NMR-spectra. As before, a conversion of around 10% was observed, which did not increase within ten days. Since 10 mol% of the catalysts were used, a stoichiometric reaction might be a reasonable rationale. No further efforts were made to isolate the potential product, but the use of stoichiometric amounts of catalyst and an adjusted workup might lead to an isolation of the unknown product.

As the last chlorinated alkene, 3-chlorobut-1-ene (**172**) was tested (Scheme 75). A reaction control by NMR after 98 hours indicated no conversion at all. To verify this result, a repetition of the reaction was conducted and again no conversion was observed after four days.



Scheme 75: Unsuccessful FLP-catalysed iodoperfluoroalkylation of 3-chlorobut-1-ene (**172**).

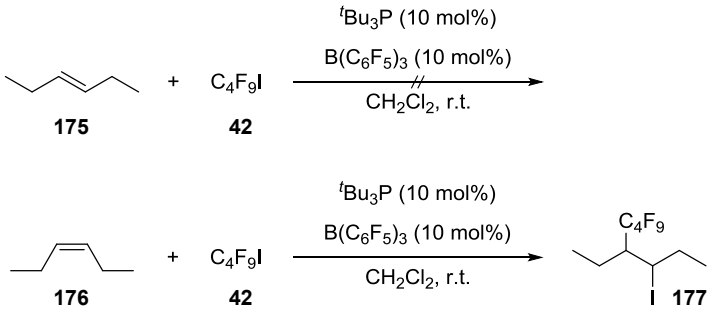
No literature reference for the iodoperfluoralkylation of the described chlorinated alkenes can be found. Consequently, these alkenes might be intrinsically unsuitable for iodoperfluoroalkylations. Since ester moieties are tolerated under certain conditions, ethyl acrylate (**173**) was tested as a challenging substrate. Besides its ester functionality it is also an α,β-unsaturated carbonyl compound, hence an electron-deficient alkene.



Scheme 76: Unsuccessful iodoperfluoroalkylation of ethyl acrylate (**173**) and a potential polymerisation as a plausible side reaction.

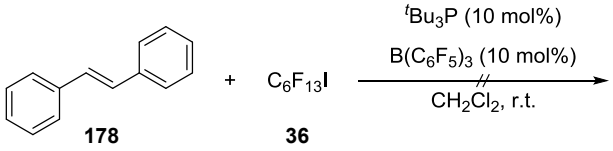
The iodoperfluoroalkylation was tested with $B(C_6F_5)_3$ as the catalyst, but no iodoperfluoroalkylation was observed after four days reaction time (Scheme 76). Anyhow, the ^{1}H-NMR-spectrum indicated a complete conversion of ethyl acrylate. No more signals of the enone moiety were observed, but new signals in the aliphatic range. This observation strongly indicated a polymerisation of ethyl acrylate (**172**) to (poly)ethyl acrylate (**174**). The conversion in presence of $B(C_6F_5)_3$ was tested once more in the presence of 4 Å molecular sieve, but no iodoperfluoroalkylation was detected. Again, a polymerisation was indicated.

Czekelius *et al.*[82] observed no conversion of (*E*)-3-hexene (**175**), but could convert the corresponding (*Z*)-3-hexene (**176**) successfully (Scheme 77). Hence, *E*-configured alkenes seem to be unsuitable for this reaction system and might be generally problematic for iodoperfluoroalkylations. For example, no successful conversion of (*Z*)-3-hexene (**176**) can be found in the literature.



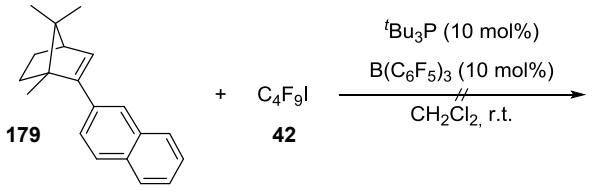
Scheme 77: Iodoperfluoroalkylation of (*E*)-3-hexene (**175**) and of (*Z*)-3-hexene (**176**).

As another example for an (*E*)-alkene, (*E*)-stilbene (**178**) was chosen. No conversion was observed after 77 h (Scheme 78). This result is not surprising in the light of the absence of a conversion of styrene in earlier experiments.



Scheme 78: Unsuccessful iodoperfluoroalkylation of (*E*)-stilbene (**179**).

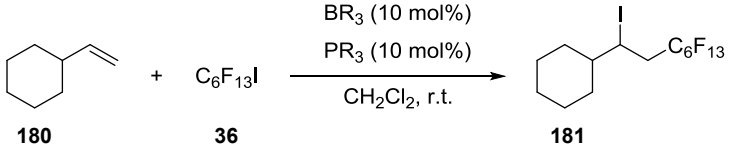
Since camphor derivative **179** was accessible due to another ongoing synthesis, it was tested with the standard catalysts, as well. No conversion was observed within seven days reaction time.



Scheme 79: Unsuccessful iodoperfluoroalkylation of camphor derivative **179.**

5.2.3 Screening of Phosphanes

The largest part of the phosphane screening is presented in the attached publication.[1] The final screening was conducted by Lucas Helmecke (Czekelius group). Preceding screenings with $^{t}Bu_3P$, $^{n}Bu_3P$, PCy_3, $PMes_3$, P(*o*-tol)$_3$ and $P(C_6F_5)_3$ will not be presented but showed the same tendencies as in the final screening. The presented test reactions were conducted under slightly varying conditions. All screenings were conducted with vinylcyclohexane (**180**) (Scheme 80) and variations refer only to concentrations and batch sizes. For detailed information see the experimental section.



Scheme 80: Screening system; iodoperfluoroalkylation of vinylcyclohexane.

The synthesised electron-deficient phosphanes tris(2-fluorophenyl)phosphane ($P(2\text{-}FC_6H_4)_3$) as well as tris(2,6-difluorophenyl)phosphane ($P(2,6\text{-}F_2C_6H_3)_3$) showed no considerable catalytic activity in combination with $B(C_6F_5)_3$.

Table 8: Screening of phosphanes in combination with $B(C_6F_5)_3$ for the iodoperfluoroalkylation.

borane	[mol%]	phosphane	[mol%]	reaction time [h]	conversion [%]
$B(C_6F_5)_3$	10.1	$P(2,6\text{-}F_2C_6H_3)_3$	10.0	93	–[(1)]
$B(C_6F_5)_3$	10.9	$P(2\text{-}FC_6H_4)_3$	9.79	116	–[(2)]

[(1)]Vinylcyclohexane (56.4 mg, 0.512 mmol), tridecafluoro-1-iodohexane (227 mg, 0.509 mmol), CH_2Cl_2 (2.5 ml).
[(2)]Vinylcyclohexane (80.5 mg, 0.730 mmol), tridecafluoro-1-iodohexane (330 mg, 0.740 mmol), CH_2Cl_2 (2.1 ml).

Table 9 shows a screening of different phosphanes in combination with $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$. In contrast to $B(C_6F_5)_3$, tricyclohexyl- and tris(pentafluorophenyl)phosphane are tolerated as the phosphane. However, the reaction seems to be slowed down, since nearly no progress of conversion was observed for PCy_3 and $P(C_6F_5)_3$ from 24 until 124 hours reaction time. Additionally, the observed conversions are comparably low with around 15% for PCy_3 and roughly 25% for $P(C_6F_5)_3$. With $^tBu_3P$ the reaction proceeds smoothly and reached a conversion of around 95% after 12 days. With trimesitylphosphane (Mes_3P) no reaction progress was observed within 92 hours, possibly due to steric hindrance.

Table 9: Screening of phosphanes in combination with $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ for the iodoperfluoroalkylation.

borane [mol%]	phosphane	[mol%]	reaction time [h]	conversion [%]	
				^{1}H-NMR	^{19}F-NMR
10.1	$^tBu_3P$	10.5	24	18	18
			124	41	43
			290	95	97
9.82	Cy_3P	10.6	24	20	20
			125	24	27
9.94	$(C_6F_5)_3P$	10.3	24	13	12
			125	15	14
9.91	Mes_3P	10.1	92	–	–

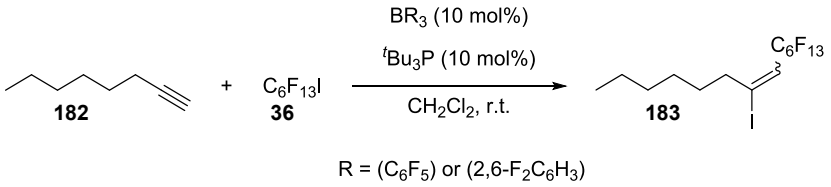
Vinylcyclohexane (80.5 mg, 0.730 mmol), nonafluoro-1-iodobutane (251 mg, 0.726 mmol), CH_2Cl_2 (2.1 ml).

The observed slow reaction in the presence of $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$, combined with different phosphanes, might be explained by a photomediated reaction which is currently investigated by Lucas Helmecke (Czekelius group).

5.2.4 Alkynes

Czekelius *et al.* were able to show that the internal alkyne 4-octyne can be iodoperfluoroalkylated with a combination of $B(C_6F_5)_3$ and $^tBu_3P$.[82] As the next step, a conversion of terminal alkynes was investigated. First of all, 1-octyne (**182**) was selected to be iodoperfluoroalkylated with tridecafluoro-1-iodohexane (**36**). For the test reactions $B(C_6F_5)_3$ or $B(2,6\text{-}F_2C_6H_3)_3$ in combination

with $^{t}Bu_3P$ were selected. The reactions were conducted in a 10 ml round-bottom flask sealed with a rubber septum.



Scheme 81: Iodoperfluoroalkylation of 1-octyne (**182**) with different boranes.

A control by NMR spectroscopy after two days indicated a conversion below 10% with $B(C_6F_5)_3$ and of around 30% with $B(2,6\text{-}F_2C_6H_3)_3$. Accordingly, tris(2,6-difluorophenyl)borane seems to be the better suitable Lewis acid compared to $B(C_6F_5)_3$. A TLC-control indicated the formation of a major product and several side products with low retention factors. For workup, a filtration over aluminium oxide was performed and a transparent liquid was obtained. For both test reactions, ^{1}H- and ^{19}F-NMR-spectra indicate a relatively pure product and no educt after this filtration. The newly formed triplet at 6.21 ppm (Figure 12) fits a terminal addition of the perfluoroalkyl-fragment. Furthermore, the presence of another triplet at 5.92 ppm could hint at the formation of a second stereoisomer.

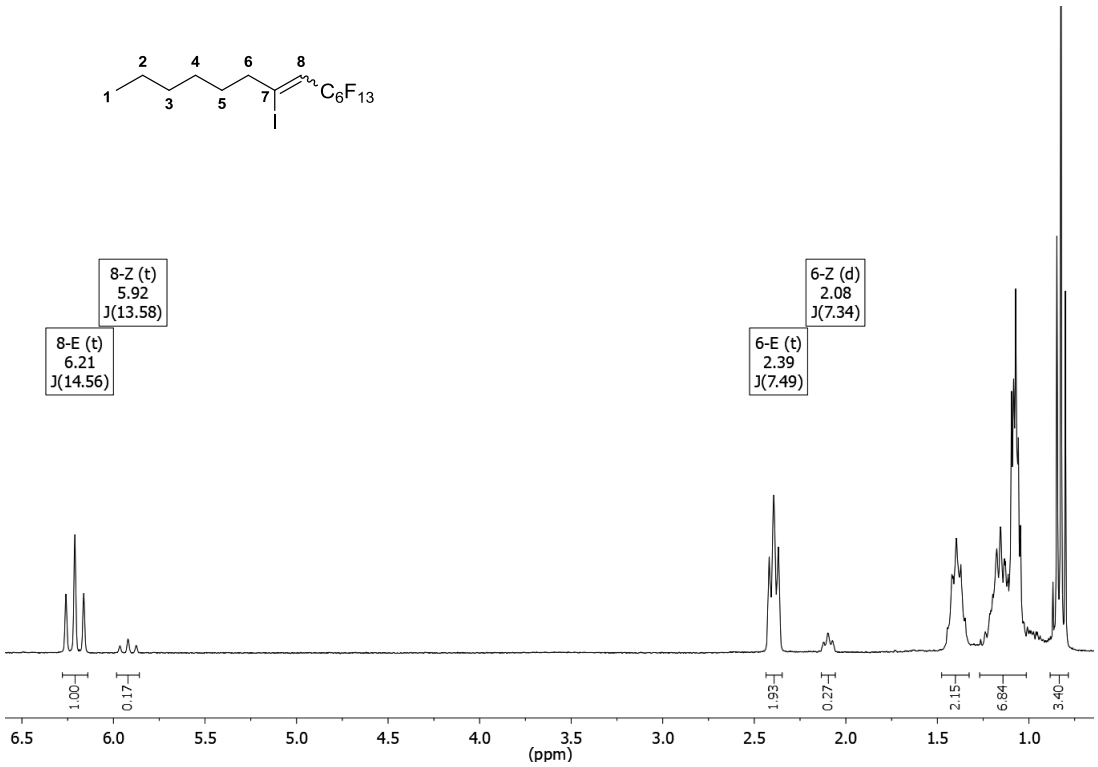


Figure 12: ^{1}H-NMR-spectrum of the crude product of the iodoperfluoroalkylation of 1-octyne (**182**).

Raw products were combined and purified by column chromatography on SiO_2. In the course of the purification, most probably a mixture of the (*E*)- and (*Z*)-isomer was isolated. Another purification gave the main product in its pure form. By comparison to data presented in the

literature, this molecule was identified as the (*E*)-isomer (Figure 13). In contrast, the (*Z*)-isomer could not be isolated in pure form and no comparison spectrum was found in the literature.

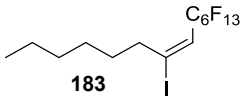


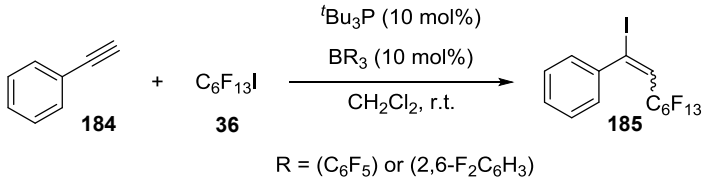
Figure 13: (*E*)-1,1,1,2,2,3,3,4,4-Nonafluoro-6-iodo-5-dodecene (**183**).

The iodoperfluoroalkylation of 1-octyne (**182**) was repeated under slightly different conditions with both $B(C_6F_5)_3$ and $B(2,6\text{-}F_2C_6H_3)_3$. Reaction solutions were stirred inside the glovebox in amber screw-top vials and samples were taken inside the glovebox. After one day and four days a sample was withdrawn inside the glovebox and filled up with $CDCl_3$ outside the glovebox. With $B(C_6F_5)_3$ only insignificant conversions were observed in the ^{1}H- and ^{19}F-NMR-spectrum. The samples with $B(2,6\text{-}F_2C_6H_3)_3$ however, showed a conversion of 40% in the ^{1}H-NMR-spectrum and of around 50% in the ^{19}F-NMR-spectrum. Additionally, the ^{19}F-NMR-spectrum clearly indicated the formation of side products. Surprisingly, another sample after four days showed a conversion of 33-40% for $B(2,6\text{-}F_2C_6H_3)_3$ and another sample after six days only 10%. A reflection of the potential reason for this observation resulted in the consideration that the reaction might proceed or even just start in the NMR-tube under the influence of light. The reason for this chain of thought is that the sample which was taken after one day was measured with a delay of 49 hours, the one taken after four days after 18 hours and the last one within one hour. Thus, despite the advancing reaction time, the yield only seemed to be dependent on the gap between the sample withdrawal and measurement. To assure this assumption is correct, another sample was taken inside the glovebox after 12 days. To avoid a photomediated reaction, another sample was filled up with C_6D_6 directly inside the glovebox and was measured directly. Both the ^{1}H- and the ^{19}F-NMR-spectrum showed no conversion, substantiating the assumption of a light sensitive reaction system.

Then both reaction solutions were transferred into a translucent vial. After another eight days, samples were taken once more and they were filled up with C_6D_6 directly inside the glovebox. Again, no conversion could be detected with $B(C_6F_5)_3$. In contrast, the reaction proceeded slowly with $B(2,6\text{-}F_2C_6H_3)_3$/^{t}Bu$_3$P inside a translucent vial. After eight days a conversion of 50-65% and after 27 days a conversion of 63-80% were indicated by the NMR-spectra. Because of this promising conversion, a purification by column chromatography was carried out and four different products were isolated. Gratifyingly, the (*E*)-stereoisomer was isolated in pure form (30%). Furthermore, a mixture of the stereoisomers (14%, *E*:*Z* = 1.0:0.42) was isolated. Another side product showing signals at −111 and −112 ppm in a ratio of 2:1 in the ^{19}F-NMR-spectrum

was isolated as in previous experiments. Several further tests to iodoperfluoroalkylate 1-octyne with a FLP catalyst system were conducted, but no efficient protocol could be established.

Parallely to 1-octyne, an iodoperfluoroalkylation of phenylacetylene (**184**) was tested. As described before, $B(C_6F_5)_3$ and $B(2,6\text{-}F_2C_6H_3)_3$ in combination with $^tBu_3P$ were probed (Scheme 82). Throughout the preparation of the reaction solutions, a strong brown-reddish colour of the solution containing $B(C_6F_5)_3$ and a yellowish solution with $B(2,6\text{-}F_2C_6H_3)_3$ were observed.



Scheme 82: Iodoperfluoroalkylation of phenylacetylene (**184**) utilising two different boranes.

A first control by NMR spectroscopy after one day showed nearly no conversion for $B(2,6\text{-}F_2C_6H_3)_3$ and a conversion of below 10% for $B(C_6F_5)_3$. For this estimation of conversions, a singlet at 3.07 ppm of phenylacetylene and a triplet at 6.59 ppm of the potential product **185** as well as all available signals in the ^{19}F-NMR-spectra were taken into account. The second measurement after 14 days showed a completely different picture. With $B(C_6F_5)_3$, the NMR-spectra indicated a conversion of 25-30%. In contrast, with $B(2,6\text{-}F_2C_6H_3)_3$, a conversion of around 80% was indicated in both the ^{1}H- and ^{19}F-NMR-spectrum. However, side product formation can be observed in the ^{19}F-NMR-spectrum, thus a conversion cannot be estimated reliably. This side product formation was confirmed by TLC, indicating the formation of various compounds. Both crude products were worked up by column chromatography.

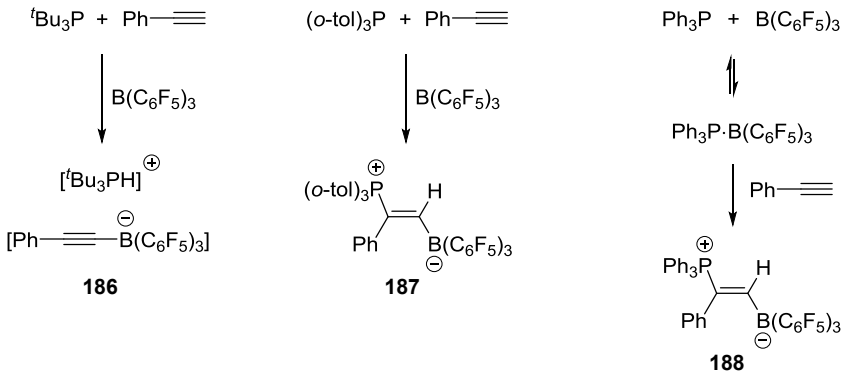
In the case of $B(2,6\text{-}F_2C_6H_3)_3$, clean (*E*)-iodoperfluoroalkylation product **185** was isolated in 20% yield, but also four side products. The first two side products were eluted as mixture fractions and NMR-spectra show signals which are similar to the iodoperfluoroalkylation product **185**. Minor amounts of the third and fourth side product were isolated, too. Spectra of the side products were not conclusive and showed an aromatic compound as well as a $B(2,6\text{-}F_2C_6H_3)_3$ derivative or other fluorinated compounds. To summarise the purification, only 20% clean potential (*Z*)-**185** were isolated, whereas a conversion of 63-80% was assumed.

To sum up the iodoperfluoroalkylation of phenylacetylene, a nearly complete conversion was assumed, but only minor amounts of the products were obtained. Even though ^{1}H-NMR-spectra indicated a clean reaction, TLC-controls showed the formation of several products. Thus, an assessment of conversion by NMR is not a reliable tool. Several further tests to iodoperfluoroalkylate phenylacetylene with a FLP catalyst system were conducted, but no

efficient protocol could be established. The formation of side products as well as a huge gap between calculated conversions and the isolated yields could not be prevented.

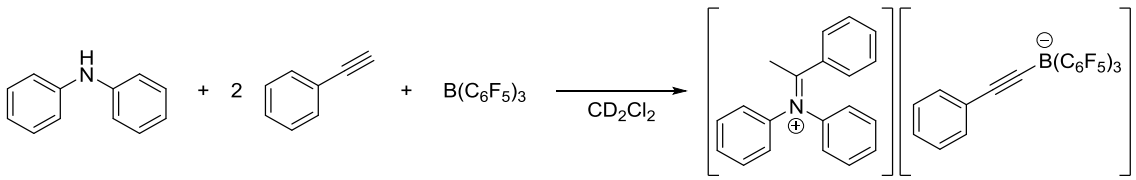
Interestingly, when phenylacetylene was added to solid $B(C_6F_5)_3$ and $^tBu_3P$ smoke formation as well as a reddish colouration were observed. The succession of the addition of $B(C_6F_5)_3$, $^tBu_3P$ and phenylacetylene seems to be important, as different colourations are observed depending on the order of additions. When $B(C_6F_5)_3$ and $^tBu_3P$ were dissolved in CH_2Cl_2 before phenylacetylene was added, the solution only had a slightly yellowish colour. By directly adding phenylacetylene to $B(C_6F_5)_3$ and $^tBu_3P$ a reddish colouration is observed. Hence, a reaction seems to take place when phenylacetylene is directly added to the undissolved catalyst. Therefore, $B(C_6F_5)_3$ and $^tBu_3P$ should be dissolved before the addition of phenylacetylene. Taking all observations into account, several variations of this iodoperfluoroalkylation were tested, but no efficient protocol could be established.

A rationale for the unsatisfactory conversion of terminal alkynes can be found in the literature. In 2009, Dureen and Stephan[98] observed the formation of a salt derived from phenylacetylene, $^tBu_3P$ and $B(C_6F_5)_3$. They added $B(C_6F_5)_3$ to a precooled solution (−35 °C) of phenylacetylene and $^tBu_3P$ or other phosphanes in toluene and shook until $B(C_6F_5)_3$ was completely dissolved and a yellowish oil separated from the solution. This oil was isolated, dried to obtain a solid and recrystallised to afford the salt $[^tBu_3PH][PhC{\equiv}CB(C_6F_5)]$ **186** (Scheme 83) in 82% yield. In contrast to $^tBu_3P$, with $(o\text{-tol})_3P$ or Ph_3P zwitterionic *E*-configured species (**187**, **188**, Scheme 83) were formed.



Scheme 83: Reaction of phenylacetylene with different phosphanes and $B(C_6F_5)_3$.[98]

Consequently, the formation of $[^tBu_3PH][PhC{\equiv}CB(C_6F_5)]$ **186** seems to be a fast and efficient process. With that in mind, it is questionable, whether an efficient iodoperfluoroalkylation of phenylacetylene can be conducted in the presence of $^tBu_3P/B(C_6F_5)_3$. In this context, Stephan and Mahdi developed a metal-free hydroamination of terminal alkynes (Scheme 84).[99]

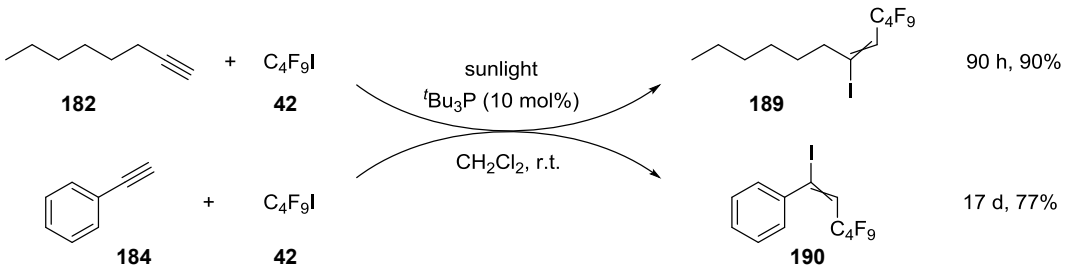


Scheme 84: Formation of the salt $[Ph_2N{=}C(CH_3)Ph][PhC{\equiv}CB(C_6F_5)]$.[99]

They noted that the alkyne has to be added slowly, since a catalytically inactive salt as shown in Scheme 84 is formed otherwise. Hence, phenylacetylene might be added in small portions to a solution of ^{t}Bu$_3$P, B(C$_6$F$_5$)$_3$ and tridecafluoro-1-iodohexane to achieve higher conversions.

As mentioned earlier, Chen *et al.* published a "Halogen-Bond-Promoted Photoactivation of Perfluoroalkyl Iodides"[37] in 2017. On the basis of this new publication and, as mentioned earlier, the assumption of a photochemical process as the driver behind the reaction, a photochemical process with ^{t}Bu$_3$P as the initiator was tested.

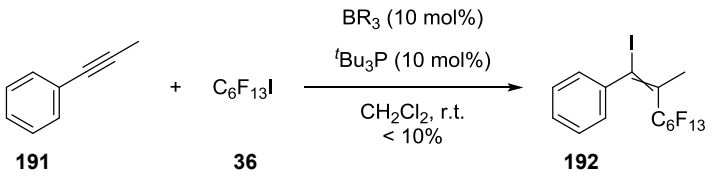
1-Octyne (**182**) and phenylacetylene (**184**) could be converted to the corresponding iodoperfluoroalkylation products in the presence of solely ^{t}Bu$_3$P under the influence of sunlight (Scheme 85). Phenylacetylene (**184**) reacted quite slowly with a conversion of 37-47% after 90 h and of 86-87% after 17 days. In contrast, 1-octyne (**182**) reacted relatively fast and showed a conversion of 90% within 90 h.



Scheme 85: Photomediated iodoperfluoroalkylation of 1-octyne (**182**) and phenylacetylene (**184**).

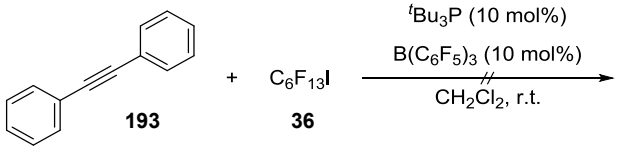
In contrast to the use of a combination of ^{t}Bu$_3$P and a borane, no side products were observed with solely ^{t}Bu$_3$P. Furthermore, relatively high yields of around 96% for 1-octyne (**182**) and 77% for phenylacetylene (**184**) (mixtures of diastereoisomers) were obtained. As a consequence, Lucas Helmecke started to investigate a photomediated variation of this iodoperfluoroalkylation.

At last, two internal alkynes were examined. The conversion of 1-phenyl-1-propyne (**191**) was tested with B(C$_6$F$_5$)$_3$ and B(2,6-F$_2$C$_6$H$_3$)$_3$. With B(2,6-F$_2$C$_6$H$_3$)$_3$ no conversion was observed within 70 hours, but with B(C$_6$F$_5$)$_3$ a conversion of 10-13%. A purification by column chromatography yielded around 8.8% of a perfluoroalkylation product, which is likely a mixture of the (*E*)- and (*Z*)-isomer (95:5). Due to this low yield, no thorough analysis was conducted.



Scheme 86: Iodoperfluoroalkylation of 1-phenyl-1-propyne (**191**).

As a last alkyne, diphenylacetylene was tested, but no conversion could be detected within 77 hours reaction time (Scheme 87).



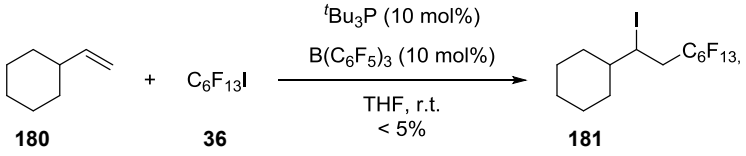
Scheme 87: Unsuccessful iodoperfluoroalkylation of diphenylacetylene (**193**).

Consequently, the tested internal alkynes are no suitable substrates for a combination of a borane and a phosphane. However, for a successful iodoperfluoroalkylation of alkynes solely $^{t}Bu_3P$ in combination with a light source can be used.

5.2.5 Functional Group Tolerance in FLP-Catalysed Iodoperfluoroalkylations

One of the most important parts of this thesis is the development of FLP-based reaction systems which can iodoperfluoroalkylate substrates bearing functional groups. At the beginning of this examination, some substrates were tested extensively to develop solutions to overcome limitations regarding the functional group tolerance. Tests of several other substrates, which are outlined towards the end of the chapter, were not as extensive.

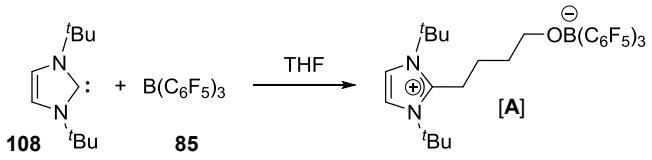
Before the exploration of new substrates, a transformation of vinylcyclohexane (**180**), which is known to be high yielding in CH_2Cl_2, was conducted in tetrahydrofurane (THF) as the solvent (Scheme 88).



Scheme 88: Iodoperfluoroalkylation of vinylcyclohexane (**180**) in THF.

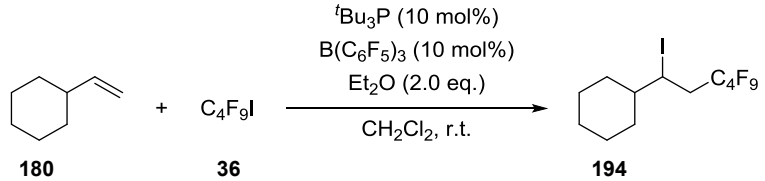
A yield of only 3.7% was obtained after one day reaction time. This experiment was one of the early experiments and even this yield of 3.7% might have been obtained only due to the fact, that catalyst and substrates were all added into one vial before the addition of THF. As discussed throughout the introduction, a combination of NHC **108** and $B(C_6F_5)_3$ (**85**) reacts with THF under formation of betaine [**A**] (Scheme 89). A similar reaction could also take place with a

combination of $B(C_6F_5)_3$ and $^tBu_3P$. $B(C_6F_5)_3$ can coordinate the oxygen in the ring and $^tBu_3P$ would then open the ring by a nucleophilic attack. Thereby, the catalysts would be deactivated.



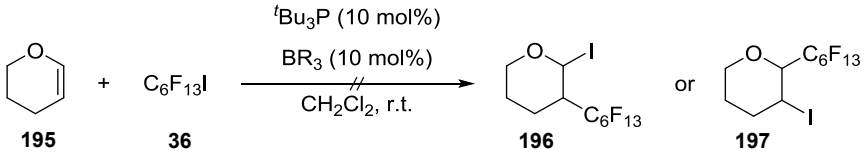
Scheme 89: Ring opening of THF by a combination of an NHC (**108**) and $B(C_6F_5)_3$ (**85**).

Another experiment was conducted to test the influence of Et_2O on the reaction rate (Scheme 90). After 53 hours a control by NMR spectroscopy showed a conversion of 61-67% with $B(C_6F_5)_3$ as the borane. Hence, the reaction seems to be slowed down massively, since without Et_2O a conversion of above 90% was observed within 24 hours.



Scheme 90: Iodoperfluoroalkylation of vinylcyclohexane (**180**) in the presence of Et_2O.

Since ethers do not seem to inhibit the reaction completely, a functionalisation of 3,4-dihydro-2*H*-pyrane (**195**) was examined (Scheme 91). As a start, the iodoperfluoroalkylation was tested with $C_6F_{13}I$ catalysed by $B(2,6\text{-}F_2C_6H_3)_3$ and $^tBu_3P$. No conversion was observed within two days, but the reaction solution was coloured green.



Scheme 91: Iodoperfluoroalkylation of 3,4-dihydro-2*H*-pyrane (**195**).

Since the formation of a stable adduct between 3,4-dihydro-2*H*-pyrane (**195**) and the borane is a probable explanation for this colouration, an absent conversion can be understood. One approach to avoid this irreversible adduct formation is the addition of stoichiometric amounts of other ethers like tetrahydrofurane (THF) and diethylether (Et_2O). Consequently, an addition of these two ethers was tested in combination with $B(C_6F_5)_3$. THF (1.8 eq.) was added finally and a dark green solution was observed as before. After stirring for two days, a brown colouration of the solution was observed and no conversion was detected by NMR spectroscopy. Next, the procedure was slightly changed and Et_2O (1.8 eq.) instead of THF was added before $B(C_6F_5)_3$. This time, a yellow-orange coloured solution was obtained, which turned dark green within

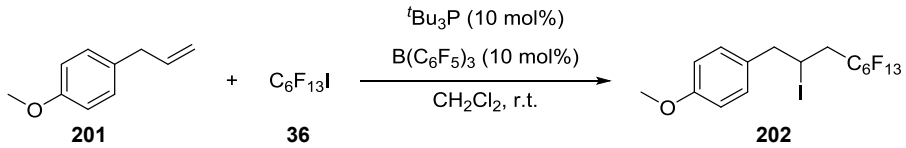
10 minutes. This colouration turned into red-brown within two days and a control by NMR spectroscopy indicated a minor conversion to an unknown product. Thus, the reaction solution was worked up. In the course of the workup, no product could be isolated. The experiment was repeated with 8 eq. Et_2O whereby a control by NMR spectroscopy after six days showed minor new signals. Again, no product could be obtained. No further attempts to perfluoroalkylate 3,4-dihydro-2*H*-pyrane (**195**) were conducted.

3,4-Dihydro-2*H*-pyrane (**195**) might be a special substrate, but a glance at the literature reveals that some protocols are closely related to iodoperfluoroalkylations. For example a hydroperfluoroalkylation of 3,4-dihydro-2*H*-pyrane[100] as well as a areneselenolate-mediated perfluoroalkyl-sulfenylation[101] (Scheme 92) are described in the literature.

Scheme 92: A hydroperfluoroalkylation (top) and an areneselenolate-mediated perfluoroalkyl-sulfenylation (bottom) of 3,4-dihydro-2*H*-pyrane (**195**).

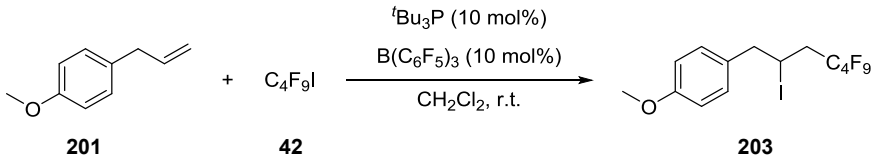
Especially the hydroperfluoroalkylation seems to be closely related to iodoperfluoroalkylations, as a radical chain reaction with perfluoroalkyl radicals as intermediates is proposed.

Since the presence of Et_2O was tolerated throughout an iodoperfluoroalkylation and allylbenzene was successfully converted by Czekelius *et al.*,[82] closely related 4-allylanisole (**201**) was chosen as a substrate. It was reacted under standard conditions utilising $^tBu_3P/B(C_6F_5)_3$ (Scheme 93).



Scheme 93: Iodoperfluoroalkylation of 4-allylanisole (**201**).

After two days, a ^{1}H-NMR-spectrum showed a conversion of 30% and a ^{19}F-NMR-spectrum a conversion of around 50%. A purification by column chromatography was challenging and had to be repeated three times. Several solvent mixtures were tested and with cyclohexane:acetone = 98.7:1.3 in combination with a long column pure product was isolated in a yield of 18%. However, besides the pure product, diverse mixture fractions were obtained. The iodoperfluoroalkylation was repeated with nonafluoro-1-iodobutane (**42**) instead of tridecafluoro-1-iodohexane (**36**) (Scheme 94).

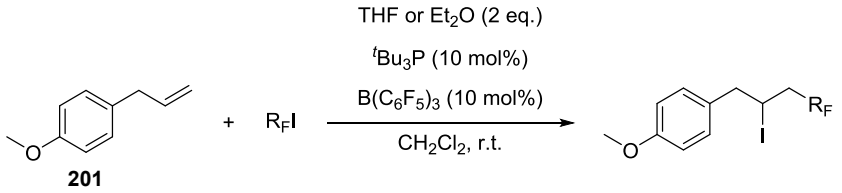


201 **42** **203**

Scheme 94: Iodoperfluoroalkylation of 4-allylanisole (**201**) with nonafluoro-1-iodobutane (**42**).

In this case, the reaction solution was stirred inside the glovebox and samples were also taken inside the glovebox. After three days, a conversion of around 33% was indicated in the ^{1}H-NMR-spectrum, but the ^{19}F-NMR-spectrum showed a conversion of around 60%. A following spectrum eight days later showed a comparable result. After withdrawal of this sample, the reaction solution was transferred into a translucent vial in order to examine the light sensitivity of the system. Another sample after overall 17 days showed no further conversion, thus VIS radiation might not influence the reaction progress or the catalytic species was inactive at this stage. As before, the purification process was very challenging. However, 28% of pure product was obtained, which is in line with the conversion observed in the ^{1}H-NMR-spectra. The high discrepancy between ^{1}H- and ^{19}F-NMR-spectra might be partly explained by a relaxation delay (D_1) of only one second. Increasing the relaxation delay to 10 seconds can improve the integration accuracy drastically, which was shown in later experiments.

As for 3,4-dihydro-2*H*-pyrane, a variation using two equivalents of THF as well as Et_2O was performed (Scheme 95). Within three days reaction time, no conversion was detected at all in the presence of THF. Next, a variation with two equivalents of Et_2O was probed. In contrast to THF, Et_2O did not inhibit the reaction completely. After five days a conversion of 19-25% was observed. Then, a conversion of 29-37% was detected after 14 days. Compared to the reaction in absence of Et_2O the reaction rate seems to be lowered massively, since without Et_2O a conversion of 30% was observed after two days. This observation might be explained by the presence of 20 ppm of BHT in Et_2O, which can quench radicals.



Scheme 95: Iodoperfluoroalkylation of 4-allylanisole (**201**) in the presence of ethers.

To investigate alternative Lewis acids, $B(2,6\text{-}F_2C_6H_3)_3$ and (2,3,6-trichlorophenyl)bis(2,3,6-trifluorophenyl)borane ($B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$) were used. After two days a conversion of around 5% was observed with $B(2,6\text{-}F_2C_6H_3)_3$, which increased to roughly 13% after 16 days. A repetition of this reaction with a new batch of $B(2,6\text{-}F_2C_6H_3)_3$ inside the glovebox showed an insignificant conversion of only 4-5% within 11 days reaction time. With $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ no conversion at all was observed within three days.
The following table gives an overview over the presented results.

Table 10: Summary of the iodoperfluoroalkylations of 4-allylanisole (**201**) using varied conditions.

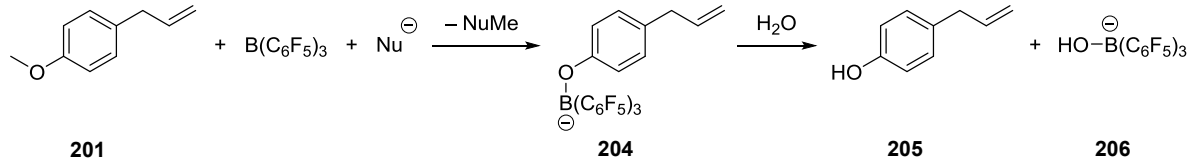
borane	R_FI	ether additive	reaction time [d]	conversion [%][(1)]	yield [%]
$B(C_6F_5)_3$	$C_6F_{13}I$	–	2	30	18[(2)]
$B(C_6F_5)_3$	C_4F_9I	–	3	33	28
$B(C_6F_5)_3$	C_4F_9I	THF (2 eq.)	3	–	–
$B(C_6F_5)_3$	$C_6F_{13}I$	Et_2O (2 eq.)	14	29	21[(2)]
$B(2,6\text{-}F_2C_6H_3)_3$	$C_6F_{13}I$	–	16	13	–
$B(2,6\text{-}F_2C_6H_3)_3$[(3)]	$C_6F_{13}I$	–	11	5	–
$B(2,3,6\text{-}Cl_3C_6H_2)$ $(2,3,6\text{-}F_3C_6H_2)_2$[(3)]	C_4F_9I	–	3	–	–

[(1)]Calculated based on the ^{1}H-NMR-spectrum. [(2)]Additional product was obtained as mixture fractions. [(3)]Stirring and sample withdrawal carried out inside the glovebox.

To increase the yield of the iodoperfluoroalkylation product an use of around 40 mol% $^tBu_3P/B(C_6F_5)_3$ was tested. However, samples after one and five days reaction time showed a conversion of only 50%. After eight days reaction time around 10 mol% additional catalyst mixture was added. Four days later, a conversion of 68-75% was detected. As a result, increasing

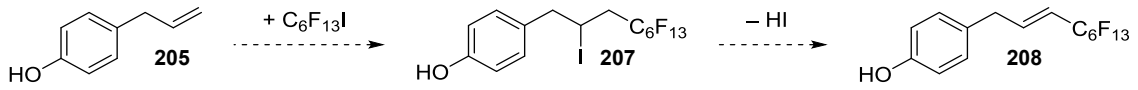
the catalyst loading at the start does not seem to be a reasonable method to increase the yield. However, a stepwise addition of the catalysts might be reasonable.

To investigate, whether $B(C_6F_5)_3$ is deactivated by formation of borate **204** (Scheme 96), the workup of this reaction solution was adapted. As a first step, a hydrolysis with 1 M HCl was conducted. Under these conditions, putative borate **204** should hydrolyse under liberation of 4-allylphenol (**205**).



Scheme 96: Presumed demethylation of 4-allylanisole (**201**) mediated by $B(C_6F_5)_3$ (**85**).

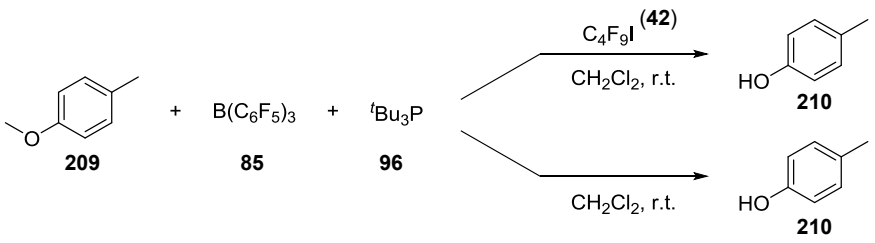
TLC-controls indicated the presence of two components with low retention factors, which were isolated as a mixture throughout the purification process. In this product mixture no methyl group ($–CH_3$) was detected and an IR-spectrum showed the diagnostic OH stretch at 3350 cm^{-1}. Both observations support the assumption of a demethylation of allylanisole. The ^{19}F-NMR-spectrum indicates the presence of a mixture of two similar iodoperfluoroalkylation products.



Scheme 97: Presumed side products forming throughout the iodoperfluoroalkylation of 4-allylanisole (**201**).

Another attempt to purify the side products on neutral Al_2O_3 failed, even though TLC controls indicated one clean fraction. Eventually phenol derivative **207** and elimination product **208** were isolated as a mixture, explaining the presence of alkene protons, but also the typical signals for iodoperfluoroalkylation products. IR-spectra of both the seemingly clean fractions and the mixture fractions showed an OH stretch. No further attempts to isolate the side products were carried out.

To obtain additional support for a demethylation of anisole derivatives, 4-methylanisole (**209**) was subjected to stoichiometric amounts of $B(C_6F_5)_3$ as well as $^tBu_3P$ (Scheme 98) twice. In one case, C_4F_9I (1 eq.) was added along with $B(C_6F_5)_3/^tBu_3P$ (Scheme 98).

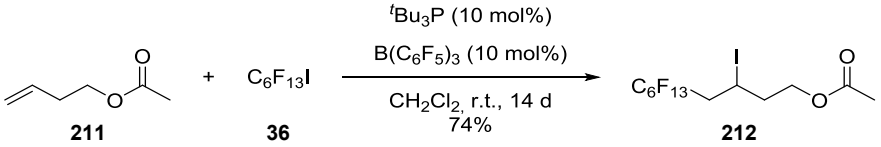


Scheme 98: Demethylation of 4-methylanisole (**209**) in the presence or absence of C_4F_9I (**42**) mediated by a Lewis acid and/or base.

In both cases, the signals of $B(C_6F_5)_3$ shift to higher field in the ^{19}F-NMR-spectrum and two separate singlets for the methyl group are detected in the ^{1}H-NMR-spectrum. With C_4F_9I present, two signal sets of $B(C_6F_5)_3$ were observed. Since controls by NMR spectroscopy were not conclusive, TLC controls were conducted. These TLCs showed a dominant new spot for both solutions. By column chromatography, an odorous compound was isolated, which was identified as 4-methylphenol (**210**).[102] As a consequence, $B(C_6F_5)_3/^tBu_3P$ seems to be able to demethylate anisole derivatives and the deactivation of $B(C_6F_5)_3$ in the manner of a borate formation seems plausible.

To accelerate the reaction, this iodoperfluoroalkylation was also tested at 60 °C in a sealed flask. However, after five and 11 days, respectively, the reaction controls showed conversions of only around 25-34%. The addition of additional catalyst (5 mol%) increased the conversion to around 46-65%. As concluded before, a stepwise addition of catalyst might be a reasonable measure to achieve high yields. This stepwise addition was probed throughout one of the last attempts to achieve higher yields. A solution of around 35 mol% $B(C_6F_5)_3$ and $^tBu_3P$ was added to the substrates via a dropping funnel within four hours under inert conditions. Directly after the addition a conversion of around 30% was detected and after stirring for one day a conversion of only 41% was observed. Due to this lack of positive outcome, the reaction solution was discarded. As a result, a continuous addition of the catalysts was unsuccessful and no further attempts for the iodoperfluoroalkylation of 4-allylanisole were performed.

To find out whether an ester group inhibits the FLP-catalysed iodoperfluoroalkylation, 3-butenyl acetate (**211**) was chosen as an exemplary substrate. 3-Butenyl acetate (**211**) is both a terminal and electron-neutral alkene, thus the limiting factor should be the ester functionality. Interestingly, no iodoperfluoroalkylation of 3-butenyl acetate was found in the literature.



Scheme 99: Iodoperfluoroalkylation of 3-butenyl acetate (**211**).

Gratifyingly, a reaction control after five days indicated a conversion of around 13% and after 14 days a complete conversion was indicated by the ^{19}F-NMR-spectrum. The corresponding ^{1}H-NMR-spectrum also showed a nearly complete conversion of 85%. After a longer search for an appropriate eluent (cyclohexane:CH_2Cl_2 = 65:35), iodoperfluoroalkylation product **212** could be isolated in pure form in a yield of 74%. Its structure was confirmed by 2D-NMR-spectra.

Reaction kinetics can be used to elucidate the reaction mechanism. If the reaction was zeroth order an invariable rate constant would be expected. By reviewing the observed conversions of

13% after five days and a quantitative reaction after 14 days, a zeroth order kinetic can be ruled out. In the course of a repetition experiment the reaction rate was monitored more closely. In the following table (Table 11) the conversions are listed.

Table 11: Conversions of 3-butenyl acetate (**211**) at r.t., influence of light exposure.

reaction time	conversion [%]	
	^{1}H-NMR	^{19}F-NMR
44 h	<5	<5
6 d[(1)]	14	10
12 d	50	50
21 d	80	90
35 d	≥95	≥95

[(1)]The reaction solution was stirred inside an amber glass vial for the first six days. Then the solution was transferred to a translucent vial.

Since a correlation to light exposure was expected, the reaction solution was transferred into a translucent vial after six days. However, the conversion did not seem to proceed faster than before. Throughout the repetition, a conversion of 50% was observed after 12 days in relation to a conversion of 85% after 14 days during the previous experiment in an amber glass vial. The yield of 76% after the reaction was comparable, as well. Hence, the reaction does not seem to proceed faster under light exposure.

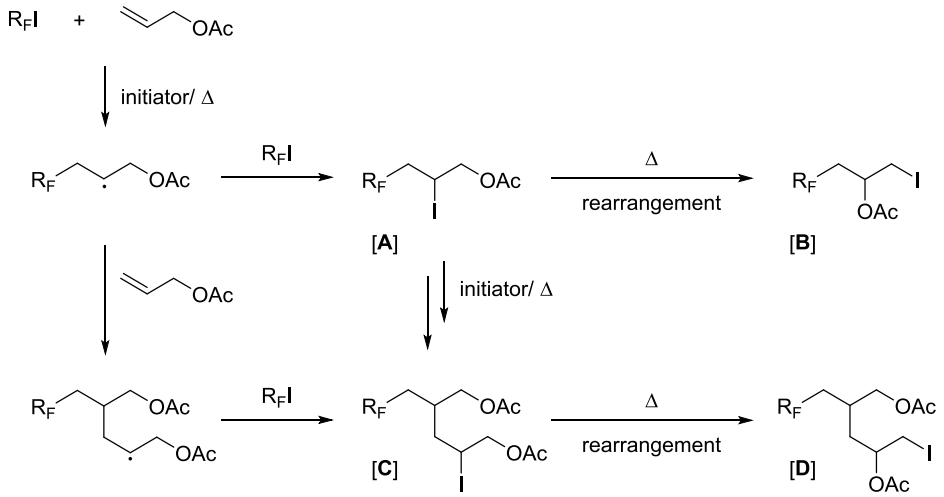
To speed up the reaction, it was conducted at 60 °C in a sealed flask. The results of three controls by NMR spectroscopy are summarised in the following table (Table 12). Samples were taken inertly in an N_2-counterflow.

Table 12: Conversions of 3-butenyl acetate (**211**) at an elevated temperature of 60 °C.

reaction time	conversion [%]	
	^{1}H-NMR	^{19}F-NMR
24 h	65	83
69 h	79	88
134 h	79	86

As expected, the reaction proceeds much faster at elevated temperatures. The incomplete conversion might be explained by catalyst decomposition at 60 °C. Additionally, a huge difference between the conversion calculated on the basis of singlets in ^{1}H-NMR-spectra and the ^{19}F-NMR-spectra was observed. A possible explanation might be the formation of side products. In both the ^{1}H- and the ^{19}F-NMR-spectra unassigned peaks were observed. As a possible explanation, homolytic cleavage of the RCF_2−I bond might take place at 60 °C, followed by radical reactions. However, after workup a high yield of 69% was obtained.

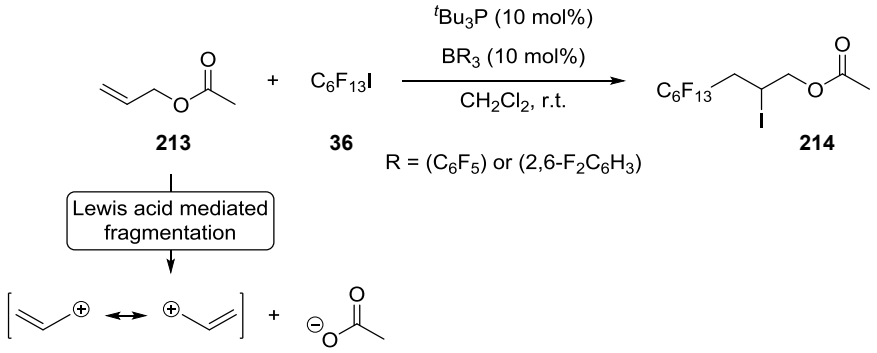
Following 3-butenyl acetate, allyl acetate (**213**) was tested as a substrate. Regarding its reactivity, allyl acetate is completely different compared to 3-butenyl acetate. Allyl acetate and its derivatives are a common source for allyl groups and are often used in palladium-catalysed reactions.[103] The reason for its use is that the allyl moiety can be cleaved off easily giving an allyl cation and an acetate fragment. Even though an iodoperfluoroalkylation of allyl acetate could be challenging, Améduri *et al.*[104] described a high yielding radical iodoperfluoroalkylation of allyl acetate. They used different organic peroxides and analysed the resulting product mixture. In Scheme 100 the iodoperfluoroalkylation as well as potential side reactions are described.



Scheme 100: Radical iodoperfluoroalkylation of allyl acetate (**213**) and potential side reactions.[104]

As an example, a reaction with dibenzoylperoxide as initiator, nonafluoro-1-iodobutane and a starting temperature of 80 °C gave 90% of monoadduct [**A**], 2.5% of diadduct [**C**] and 2.5% of rearrangement product [**D**].

An iodoperfluoroalkylation of allyl acetate (**213**) utilising 10 mol% $^{t}Bu_3P/B(C_6F_5)_3$ might be inhibited by the cleavage of allyl acetate into an allyl cation and acetate (Scheme 101).



Scheme 101: Iodoperfluoroalkylation of allyl acetate (**213**) and a potential Lewis acid-mediated fragmentation into acetate and an allyl cation.

Reaction controls by NMR spectroscopy after five and 13 days indicated a conversion of around 15-20%. A purification by column chromatography was conducted on silica gel and 14% of the

iodoperfluoroalkylation allyl acetate **214** was obtained. Obviously, the reaction did not proceed after the first control by NMR spectroscopy. A probable explanation might be the mentioned cleavage of allyl acetate and a subsequent borate formation.

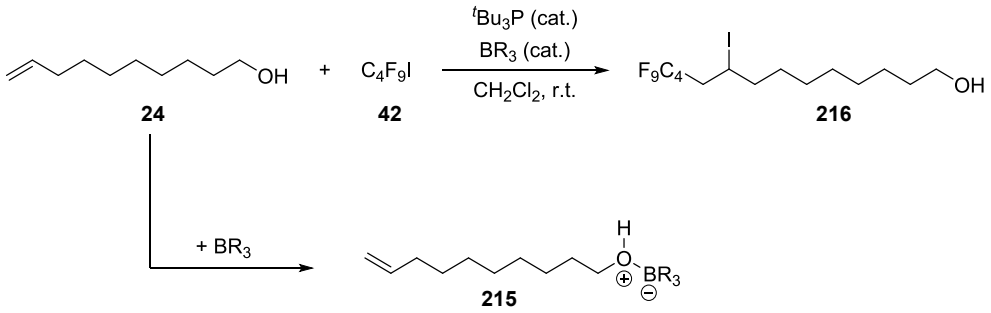
The functionalisation of allyl acetate was repeated with $B(C_6F_5)_3$ as well as $B(2,6\text{-}F_2C_6H_3)_3$. In the following table (Table 13) the results are presented.

Table 13: Conversions for the iodoperfluoroalkylation of allyl acetate (**213**) using $B(C_6F_5)_3$ (left) and $B(2,6\text{-}F_2C_6H_3)_3$ (right).

borane	$B(C_6F_5)_3$		$B(2,6\text{-}F_2C_6H_3)_3$	
	conversion [%]		conversion [%]	
reaction time [d]	^{1}H-NMR	^{19}F-NMR	^{1}H-NMR	^{19}F-NMR
3	<5	<5	–	–
7	8	10	–	–
18	25	35	–	–
25	29	43	–	–

The reaction seems to proceed very slowly with $B(C_6F_5)_3$, but not at all with $B(2,6\text{-}F_2C_6H_3)_3$. The gap between the conversions calculated based on ^{1}H- and ^{19}F-NMR-spectra can be explained by a relaxation time (D_1) of only one second for the ^{19}F-NMR-spectra. This short relaxation delay causes a distortion of the integrals due to different relaxation times of educt and product. According to former observations, the conversions calculated based on ^{1}H-NMR-spectra are more reliable. This assumption is supported by an isolated yield of 25% with $B(C_6F_5)_3/{}^t\text{Bu}_3\text{P}$ compared to a conversion of 29% based on the ^{1}H-NMR-spectrum (Table 13).

As a very challenging substrate, the aliphatic alcohol 9-decen-1-ol (**24**) was tested. First of all, ${}^t\text{Bu}_3\text{P}/B(C_6F_5)_3$ was tested in the presence of molecular sieves. No reaction could be detected within 75 hours. One probable explanation is the formation of a borate **215**, which is catalytically inactive (Scheme 102).



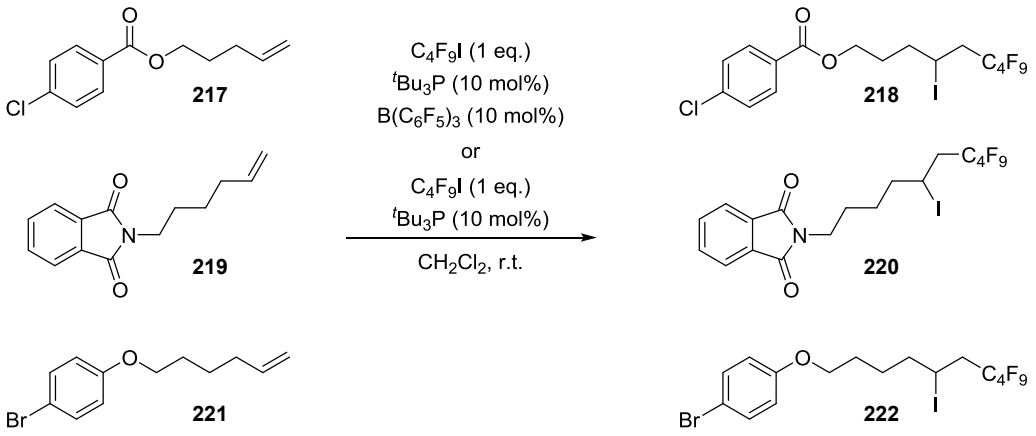
Scheme 102: Iodoperfluoroalkylation of 9-decen-1-ol (**24**) with nonafluoro-1-iodobutane (**42**).

As a second alternative, $B(2,6\text{-}F_2C_6H_3)_3$ was tested, but no reaction was detected within 44 hours, either. Then, sterically demanding $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ was probed. At room

temperature a slow reaction was observed. After 18 hours, a conversion of around 10% was detected. Another reaction control after 14 days showed a conversion of 12-20%. By column chromatography a mixture of product and educt was obtained. A yield of around 16% was calculated. The same reaction was conducted using $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ at 60 °C. After 24 hours, a conversion of 57-78% was detected. Stirring at room temperature for four days did not change the detected conversion. A purification by column chromatography yielded 38% pure product and 12% product as a mixture fraction, thus leading to a total yield of 50%.

The following substrates were not examined as thorough as the substrates described before as their iodoperfluoroalkylation is either known in the literature or a conversion was not possible at all. In the literature,[37] high yielding iodoperfluoroalkylation for the aromatic ester pent-4-en-1-yl 4-chlorobenzoate (**217**), the phthalimide derivative 2-(hex-5-en-1-yl)isoindoline-1,3-dione (**219**) as well as the aromatic ether 1-bromo-4-(hex-5-en-1-yloxy)benzene (**221**) are described. In this case, reactions using $^t Bu_3P/B(C_6F_5)_3$ and solely $^t Bu_3P$ were tested (Scheme 103).

Since pent-4-en-1-yl 4-chlorobenzoate (**217**) is a benzoic acid derivative, which bears an electron-deficient carbonyl function, and is additionally substituted by an electron-withdrawing chlorine substituent in *para*-position, only a weak interaction between $B(C_6F_5)_3$ and the carbonyl function is expected. This weak interaction is reflected in a complete conversion within 24 h using a combination of $^t Bu_3P$ and $B(C_6F_5)_3$. After workup, 87% of the iodoperfluoroalkylated benzoate **218** was isolated. With solely $^t Bu_3P$, a conversion of only around 30% was detected. As alternative boranes, $B(2,3,6\text{-}Cl_3C_6H_2)_2(2,3,6\text{-}F_3C_6H_2)$ and $B(2,6\text{-}F_2C_6H_3)_3$ were tested. Both boranes proved to be unsuitable choices, as the reaction proceeds very slowly with both of them. After 27 h reaction time, a conversion of around 20% was detected with $B(2,3,6\text{-}Cl_3C_6H_2)_2(2,3,6\text{-}F_3C_6H_2)$ and a minor conversion of ≤10% with $B(2,6\text{-}F_2C_6H_3)_3$. Even after 12 days, the conversion only increased to around 30% and roughly 19%, respectively.



Scheme 103: Iodoperfluoroalkylation of an aromatic ester, a phthalimide derivative as well as an aromatic ether.

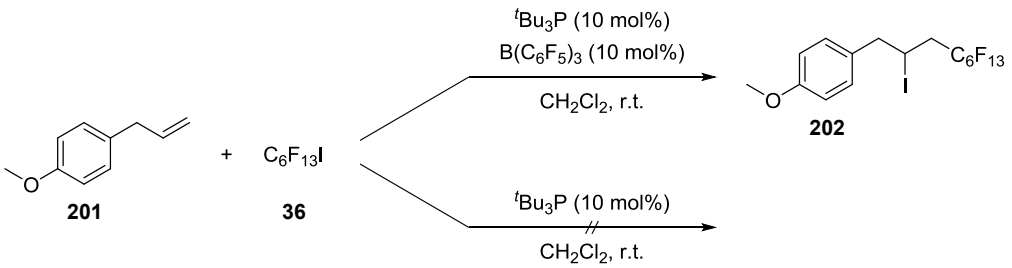
When phthalimide derivative 2-(hex-5-en-1-yl)isoindoline-1,3-dione (**219**) was reacted with 10 mol% ^{t}Bu$_3$P, a conversion of around 28-37% was observed. As a combination of ^{t}Bu$_3$P and B(C$_6$F$_5$)$_3$ showed a higher conversion this reaction solution was worked up. Again, column chromatography was quite challenging. However, after several purifications pure iodoperfluoroalkylated phthalimide **220** was isolated in a yield of 58%. In the case of 1-bromo-4-(hex-5-en-1-yloxy)benzene (**221**), the reaction did not proceed at all with solely ^{t}Bu$_3$P, but showed complete conversion with ^{t}Bu$_3$P/B(C$_6$F$_5$)$_3$ within 24 hours. This is another example for the need of B(C$_6$F$_5$)$_3$ for a successful iodoperfluoroalkylation.

Purifications of iodoperfluoroalkylated products by normal phase column chromatography are typically challenging. The alkene and the respective iodoperfluoroalkylation product have similar adsorption properties on silica gel. Consequently, several separations have to be conducted and therby yields decrease. The described results are summarised in the following table (Table 14).

Table 14: Summary of the iodoperfluoroalkylations using ^{t}Bu$_3$P/B(C$_6$F$_5$)$_3$ (10 mol%) or ^{t}Bu$_3$P (10 mol%).

substrate	borane	reaction time [h]	conversion [%]		isolated yield [%]
			^{1}H-NMR	^{19}F-NMR	
pent-4-en-1-yl 4-chlorobenzoate (**217**)	–	24	≈30	≈28	–
	B(C$_6$F$_5$)$_3$	24	≥95	≥95	87
2-(hex-5-en-1-yl)isoindoline-1,3-dione (**219**)	–	24	–	37	–
	B(C$_6$F$_5$)$_3$	24	67	72	58
1-bromo-4-(hex-5-en-1-yloxy)benzene (**221**)	–	71	≤10	≤10	–
	B(C$_6$F$_5$)$_3$	24	≥90	≥95	80

In the context of these results, the conversion of 4-allylanisole (**201**) was repeated under standardised conditions with B(C$_6$F$_5$)$_3$/^{t}Bu$_3$P and solely ^{t}Bu$_3$P (Scheme 104). Chen *et al.*[37] described a yield of 90% with their optimised conditions for this aromatic ether (see chapter 2.2.4.1).

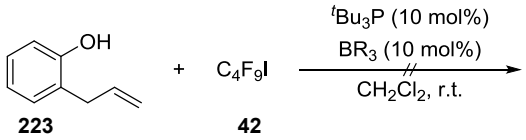


Scheme 104: Iodoperfluoroalkylation of 4-allylanisole (**201**) in the presence and absence of B(C$_6$F$_5$)$_3$.

Surprisingly, with solely ^{t}Bu$_3$P no conversion was observed at all after seven days reaction time. In contrast, a conversion of 43-46% was observed after 24 h and seven days. As described earlier,

throughout an extensive treatment regarding the iodoperfluoroalkylation of 4-allylanisole (**201**), $B(C_6F_5)_3$ might be deactivated by borate formation explaining the low yields.

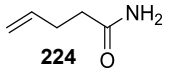
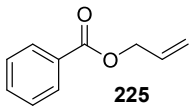
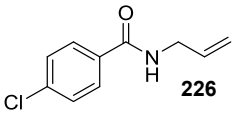
To test whether phenol groups are tolerated or not 2-allylphenol (**223**) was tested in a reaction with $B(C_6F_5)_3$ and $B(2,6\text{-}F_2C_6H_3)_3$ in combination with ^{t}Bu$_3$P. Both of the reactions resulted in the formation of an iodoperfluoroalkylation product.



Scheme 105: Iodoperfluoroalkylation of 2-allylphenol (**223**) using $B(C_6F_5)_3$ and $B(2,6\text{-}F_2C_6H_3)_3$ as the borane.

Since an aromatic ester was converted quantitatively, allyl benzoate (**225**) as well as *N*-allyl-4-chlorobenzamide (**226**) were tested. This aromatic ester as well as the aromatic amide are both allyl systems and might be challenging substrates. In the literature, no iodoperfluoroalkylation can be found for either of them. The same holds true for vinylogous enamide pent-4-enamide (**224**). All three substrates could not be converted successfully (Table 15), but pure educts were observed.

Table 15: Unsuccessful iodoperfluoroalkylations utilising a combination of $B(C_6F_5)_3$ and ^{t}Bu$_3$P.

substrate	reaction time [h]	observations	
		^{1}H-NMR	^{19}F-NMR
 **224**	24	pure educt	pure educt, $B(C_6F_5)_3$ decomposition
 **225**	24	pure educt	pure educt, $B(C_6F_5)_3$ decomposition
 **226**	24	pure educt	pure educt, $B(C_6F_5)_3$ decomposition

Alkene (1.0 eq.), C_4F_9I (70.0 µL, 0.407 mmol, 0.96-1.0 eq), ^{t}Bu$_3$P (9.8-10 mol%), $B(C_6F_5)_3$ (10-13 mol%) in CH_2Cl_2 (1.2 ml). Amber glass vial.

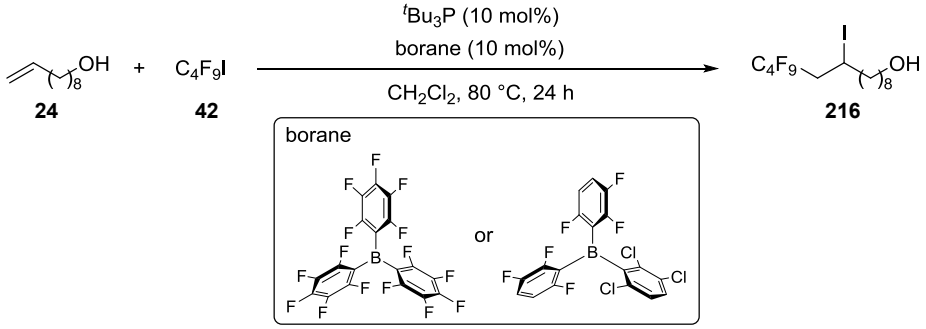
Besides the presented results, Lukas Heynck (Czekelius group) screened additional substrates as part of his master thesis.[94]

5.2.5.1 High Temperature Reaction - Optimisation of the Reaction Conditions

An unsatisfying reaction progress is usually overcome by an increase of the reaction temperature, higher catalyst loadings or a modification of the catalyst. As described earlier, an elevated reaction temperature of 60 °C was successfully tested for 9-decenol (**24**) as well as 3-butenyl acetate (**211**). For 4-allylanisole (**201**) elevated temperatures were not advantageous.

In this chapter, elevated reaction temperatures will be examined in more detail. With all previous results regarding iodoperfluoroalkylations in mind, a reaction at 80 °C in CH_2Cl_2 was considered reasonable. Even though CH_2Cl_2 is low boiling and a pressure tube has to be used, CH_2Cl_2 was chosen as it proved to be the best solvent for this iodoperfluoroalkylation (see attached publication[1]).

9-Decen-1-ol (**24**) could not be converted with $B(C_6F_5)_3/^tBu_3P$ at room temperature, but was successfully iodoperfluoroalkylated in the presence of $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2/^tBu_3P$ at 60 °C. Under optimised conditions at 80 °C inside a pressure tube, a reaction in the presence of $B(C_6F_5)_3/^tBu_3P$ and $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2/^tBu_3P$ was reexamined for 9-decen-1-ol. In both cases, conversions of around 70-80% were observed. This result was quite surprising since $B(C_6F_5)_3$ should be deactivated in the presence of 9-decen-1-ol. Consequently, this observation evoked the thought of a photochemical process with $^tBu_3P$ itself.



Scheme 106: Iodoperfluoroalkylation of 9-decen-1-ol (**24**) using different boranes.

As a first test of this assumption of a photomediated reaction, conversions of procedures utilising solely $^tBu_3P$, $B(C_6F_5)_3/^tBu_3P$ as well as $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2/^tBu_3P$ were compared after three hours reaction time (Table 16).

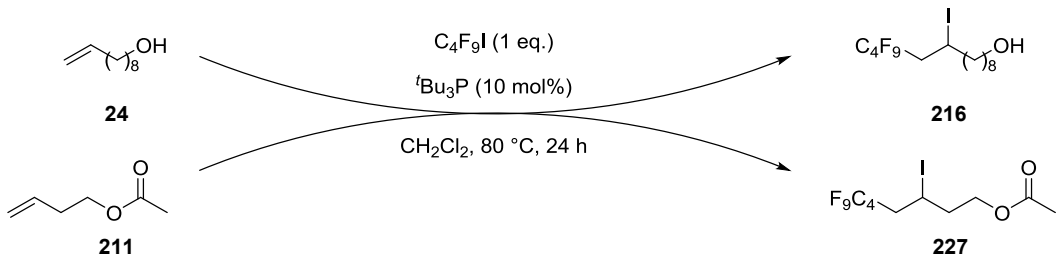
Table 16: Comparison of different catalyst combinations for the iodoperfluoroalkylation of 9-decen-1-ol (**24**).

borane	reaction time [h]	conversion [%]	
		^{1}H-NMR	^{19}F-NMR
–	3	55	59
$B(C_6F_5)_3$	3	30	31
$B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$	3	68	71

9-Decen-1-ol (1 eq.), C_4F_9I (1 eq.), $^tBu_3P$ (10 mol%), if applicable BR_3 (10 mol%), CH_2Cl_2, 80 °C.

Obviously, the reaction proceeds even slower in the presence of $B(C_6F_5)_3$, but seems to be accelerated by chemically more resistant $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ to a certain extend. However, the iodoperfluoroalkylation still works well even without the presence of a borane.

The procedure utilising solely $^tBu_3P$ as a catalyst was repeated with 9-decen-1-ol (**24**) as well as 3-butenyl acetate (**211**) in the pressure tube at 80 °C for 24 h (Scheme 107).



Scheme 107: Photomediated iodoperfluoroalkylations of 9-decen-1-ol (**24**) and 3-butenyl acetate (**211**).

Both reactions proceeded smoothly, showing a conversion of 76-81% for 9-decen-1-ol (**24**) and even of 82-89% for 3-butenyl acetate (**211**). Thus, it can be concluded that this photochemical process is quite efficient. To exemplify that the observed reactivity is really based on a photochemical process three additional test reactions were conducted including one reaction in the dark (Table 17). As a reference point $^{t}Bu_3P$ was utilised as a catalyst at 80 °C in a translucent pressure tube. After three hours a conversion of 61-72% was detected. Interestingly, the reaction solution was coloured yellow temporarily. Next, the reaction was conducted at room temperature. Surprisingly, an even higher conversion of 82% was observed. Presumably, the catalytic species is deactivated quite fast at 80 °C resulting in lower yields.

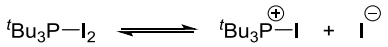
Table 17: Test experiments regarding a photomediated iodoperfluoroalkylation of of 9-decen-1-ol (**24**).

T [°C]	reaction time [h]	conversion [%]	
		^{1}H-NMR	^{19}F-NMR
80	3	61	72
25	3	82	82
	27	90	93
80[(2)]	3	–[(1)]	20
	27	25	24

[(1)]Conversions were calculated on the basis of spectra of the reaction solution. Conversions ≤20% cannot be integrated reasonably in the ^{1}H-NMR-spectra. [(2)]Exclusion of light.

To verify a photochemical reaction, the reaction was conducted under exclusion of light at 80 °C. Under these conditions a minor conversion of around 20% was detected, which might be caused by poor light exclusion or a thermal reaction.

To sum the results up, a photochemical process does seem to take place and the observed yellow colouration might be an indication for the formation of a photoactive species. Interestingly, a mixture of tri-*tert*-butylphosphane and iodine is described as a yellow solution in the literature (Scheme 108).[83]



Scheme 108: Adduct between tri-*tert*-butylphosphane and iodine.

The question arose whether an adduct between $^{t}Bu_3P$ and I_2 is a feasible option or not. Commercially available nonafluoro-1-iodobutane (C_4F_9I) is coloured violet and has to be filtered over Al_2O_3 or decolourised, e.g. with a sulfite followed by a distillation, to obtain iodine free material. C_4F_9I can easily form iodine in the presence of oxygen, or when it is stored in translucent containers. For this work C_4F_9I was filtered over basic Al_2O_3 and then stored inside the glovebox. No colouration was observed even after storing it inside the glovebox for several months. However, iodine might have been formed throughout the reactions. As a first test, one of the yellow reaction solutions was mixed with a sodium sulfite solution. The colouration vanished immediately, indicating the presence of iodine. As the next step a spectroscopic analysis of the reaction solution was conducted. First, an UV VIS spectrum of a mixture of $^{t}Bu_3P$ and I_2 as well as solely I_2 was measured. A solution of iodine in CH_2Cl_2 is purple and has its absorption maximum at 506 nm (Figure 14). However, the spectrum changes drastically when I_2 is mixed with $^{t}Bu_3P$. A mixture of $^{t}Bu_3P$ and I_2 (0.5 eq.) has local maxima at 276 nm as well as 321 nm and the yellow colouration can be explained by a tailing into the VIS range. Measuring a reaction solution containing $^{t}Bu_3P$, 9-decen-1-ol, C_4F_9I and the iodoperfluoroalkylation product of 9-decen-1-ol (conversion of 56-59%) showed an almost identical spectrum compared to a mixture of $^{t}Bu_3P$ and I_2 (Figure 14).

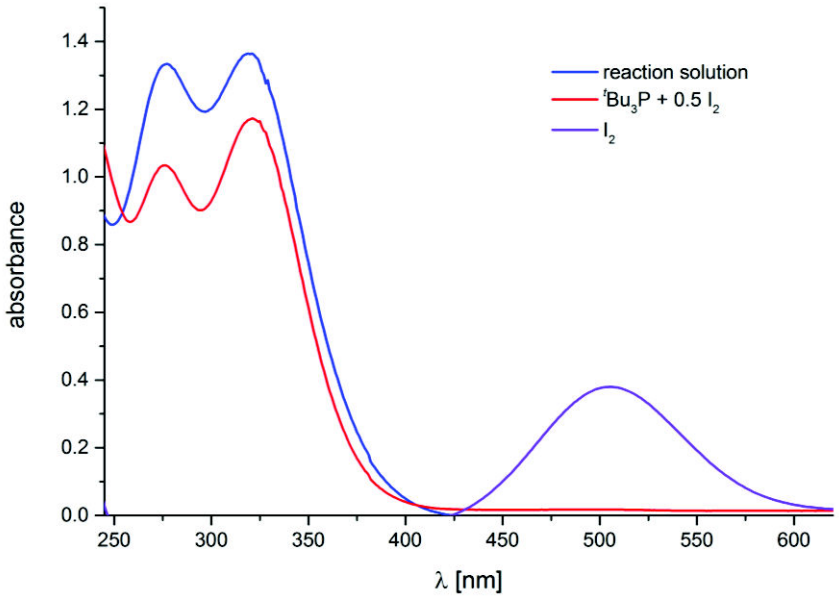


Figure 14: UV VIS spectra of a reaction solution of an iodoperfluoroalkylation of 9-decen-1-ol, a mixture of $^{t}Bu_3P$ and I_2 and solely I_2.

To assure that the $^{t}Bu_3P{-}I_2$ adduct is the observed species, solely C_4F_9I, $^{t}Bu_3P$ mixed with C_4F_9I and also $^{t}Bu_3P$ mixed with 9-decen-1-ol were measured (Figure 15). C_4F_9I has its absorption maximum at 270 nm, which is in line with a gas phase absorption spectrum.[105] This absorption band results from a transition of a non-binding electron of iodine to the σ* orbital of the C−I

bond. An excitation in this band results in a cleavage of the C−I bond giving an alkyl radical and iodine. As expected, mixtures of C_4F_9I or 9-decen-1-ol with $^tBu_3P$ do not show absorption band in the VIS range.

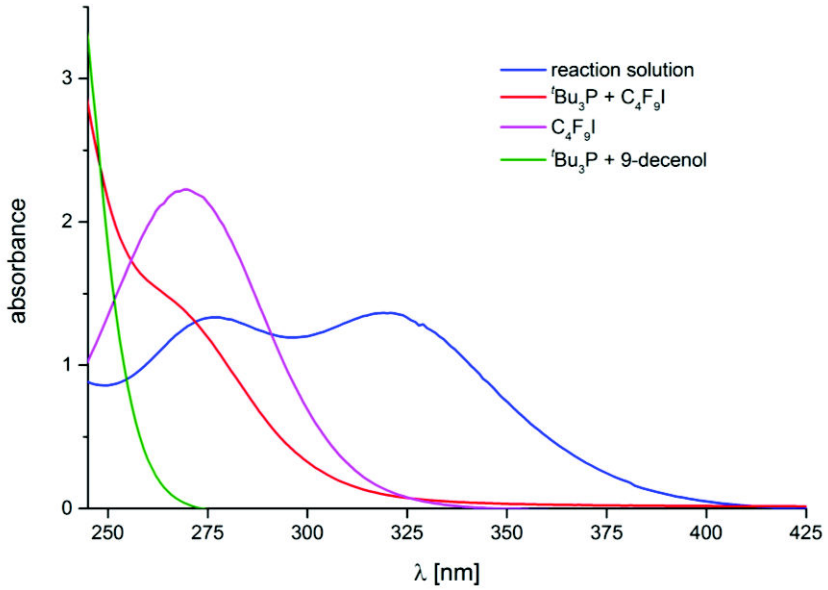


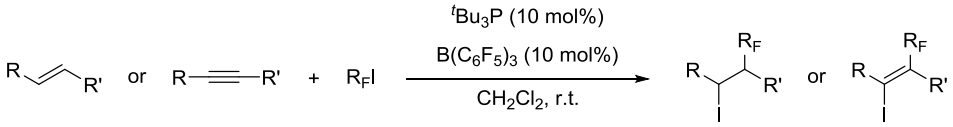
Figure 15: UV VIS spectra of a reaction solution of an iodoperfluoroalkylation of 9-decen-1-ol, C_4F_9I solely, $^tBu_3P$ mixed with C_4F_9I and $^tBu_3P$ mixed with 9-decen-1-ol.

As the next logical step, a potential reaction acceleration by iodine was probed. Two reaction mixtures containing 9-decen-1-ol, C_4F_9I and $^tBu_3P$ (10 mol%) were prepared and to one of them iodine (9.5 mol%) was added. A control by NMR spectroscopy after four hours revealed a lower conversion with additional iodine (≈30%) compared to a reaction without extra iodine (55-63%). Hence, a $^tBu_3P{-}I_2$ adduct as the photoactive species is no convenient explanation. Instead, the presence of iodine obviously lowers the reaction rate and the formation of the $^tBu_3P{-}I_2$ adduct might even be a major path for a deactivation of the catalyst. Further thorough investigations will be conducted in the near future by Lucas Helmecke.

At last, toluene as well as THF were tested as alternative solvents since they are higher boiling and thereby pressure vessels could be avoided. In toluene no iodoperfluoroalkylation and in THF a conversion of around 24% was observed. This result was surpring, since for the FLP-mediated iodoperfluoroalkylation the use of only small portions of THF resulted in a complete inhibition of the reaction.

6 Summary

The major objectives of this thesis were the expansion of the substrate scope and the elucidation of the mechanism of a frustrated Lewis pair-catalysed (FLP) iodoperfluoroalkylation of alkenes and alkynes (Scheme 109).



Scheme 109: FLP-catalysed iodoperfluoroalkylation of alkenes and alkynes.

At the start of this work, electronically tuned boranes and phosphanes (Figure 16) were synthesised with the aim of understanding more about the FLP-catalysed iodoperfluoroalkylation.

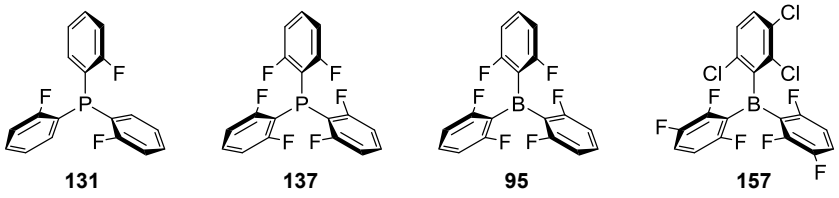
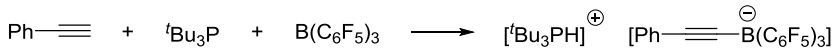


Figure 16: Synthesised electronically tuned boranes as well as phosphanes.

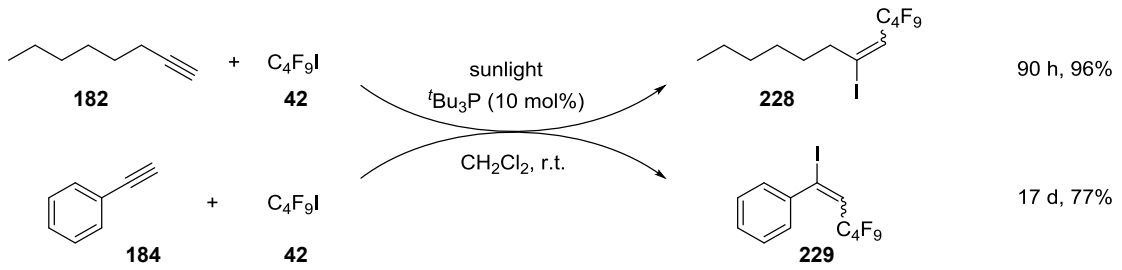
In the course of the investigations, ^{t}Bu$_3$P proved to be the only active phosphane. Electron-poor phosphanes like P(2,6-F$_2$C$_6$H$_3$)$_3$ showed to be unsuitable Lewis bases. A contrary trend was observed for the Lewis acid. B(C$_6$F$_5$)$_3$, the most commonly used borane in FLP-chemistry, showed high catalytic activity. However, less electron-deficient boranes could not be used as Lewis acid.

Since an internal alkyne was successfully iodoperfluoroalkylated by Czekelius *et al.*,[82] terminal alkynes were subjected to ^{t}Bu$_3$P/B(C$_6$F$_5$)$_3$. Unsatisfyingly, no efficient protocol could be established. The reactions were slow and low yielding. A plausible explanation for this observation is a known catalyst deactivation by the formation of an alkynylborate (Scheme 110).



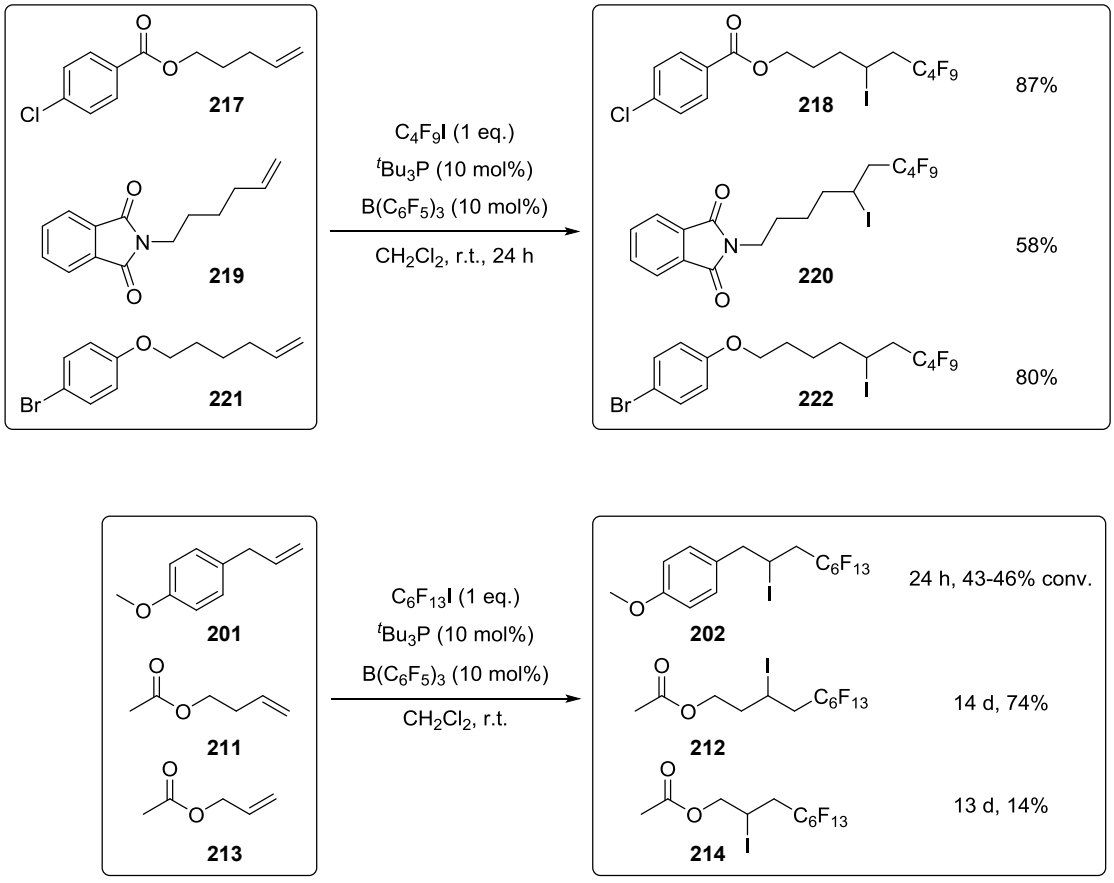
Scheme 110: Catalyst deactivation by alkynylborate formation.[98]

Over the course of the iodoperfluoroalkylation of alkynes strong evidence for a photomediated process was obtained. This photomediated reactivity was successfully shown by an iodoperfluoroalkylation of 1-octyne (**182**) as well as phenylacetylene (**184**) in the presence of solely ^{t}Bu$_3$P and sunlight as a light source (Scheme 111).



Scheme 111: Photomediated iodoperfluoroalkylation of terminal alkynes; respective reaction times and yields.

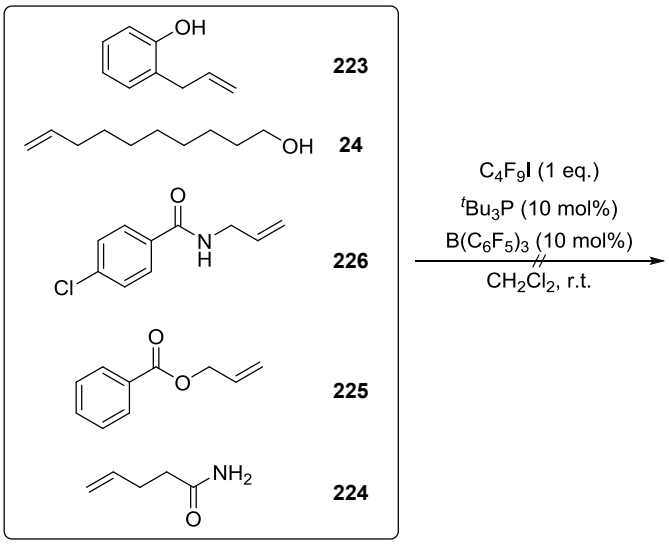
One major goal was to improve the functional group tolerance of this FLP-catalysed iodoperfluoroalkylation. As already mentioned, FLPs, with the exception of ^{t}Bu$_3$P/B(C$_6$F$_5$)$_3$, were not suitable for iodoperfluoroalkylations. Gratifyingly, aliphatic as well as aromatic esters, aromatic ethers and a phthalimide were successfully iodoperfluoroalkylated (Scheme 112). However, aliphatic esters reacted very slowly and 4-allylanisole (**201**) showed to be a challenging substrate for this FLP-system, as it is demethylated, leading to a deactivation of the borane.



Scheme 112: Iodoperfluoroalkylation of heteroatom functionalised alkenes.

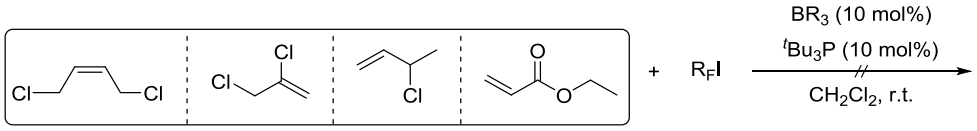
Apart from these successful iodoperfluoroalkylations other heteroatom-functionalised alkenes could not be converted at all (Scheme 112). For example, 9-decenol (**24**) can most probably form a borate with B(C$_6$F$_5$)$_3$ and thereby might terminate the reaction. Furthermore, allyl-systems could

not be converted. They seem to be fairly incompatible with iodoperfluoroalkylations in general, as only few examples of iodoperfluoroalkylated allyl-systems are known in the literature.



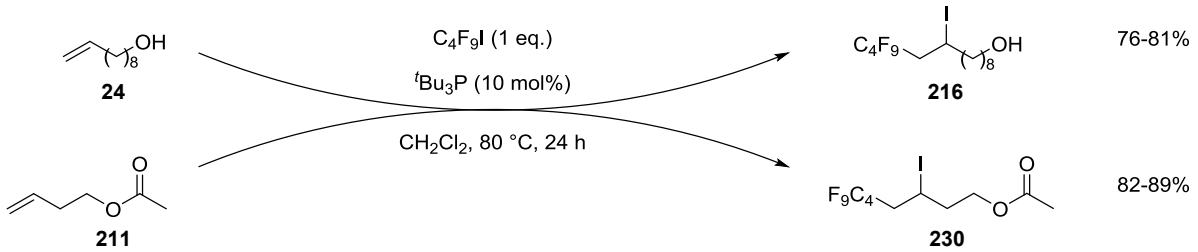
Scheme 113: Unsuccessful iodoperfluoroalkylations of alkenes containing either acid protons or an allyl-system.

Alongside of heteroatom functionalised alkenes, electron deficient alkenes were tested but could not be converted. Since perfluoroalkyl radicals are very electrophilic, the observed absent iodoperfluoroalkylation is plausible (Scheme 114).



Scheme 114: Electron-deficient alkenes tested under standard FLP-catalysis conditions.

Throughout an optimisation of the FLP-catalysed iodoperfluoroalkylation of 9-decen-1-ol (**24**) and 3-butenyl acetate (**211**), an efficient protocol using solely a phosphane, was developed (Scheme 115). No significant reaction acceleration was observed by adding a borane.



Scheme 115: Photomediated iodoperfluoroalkylations of 9-decen-1-ol (**24**) and 3-butenyl acetate (**211**) and the respective conversions.

Since the reactions were conducted in translucent test tubes, a photomediated process was presumed. This assumption was confirmed by a reaction under the exclusion of light. Interestingly, a yellow colouration was observed in the course of iodoperfluoroalkylations mediated by $^{t}Bu_3P$. This suggested the formation of a species which can absorb irradiation in the

visual light range. Thereby, the sunlight-mediated reaction acceleration could be explained. Gratifyingly, it was possible to prove that a complex of ^{t}Bu$_3$P and iodine causes this colouration (Figure 17).

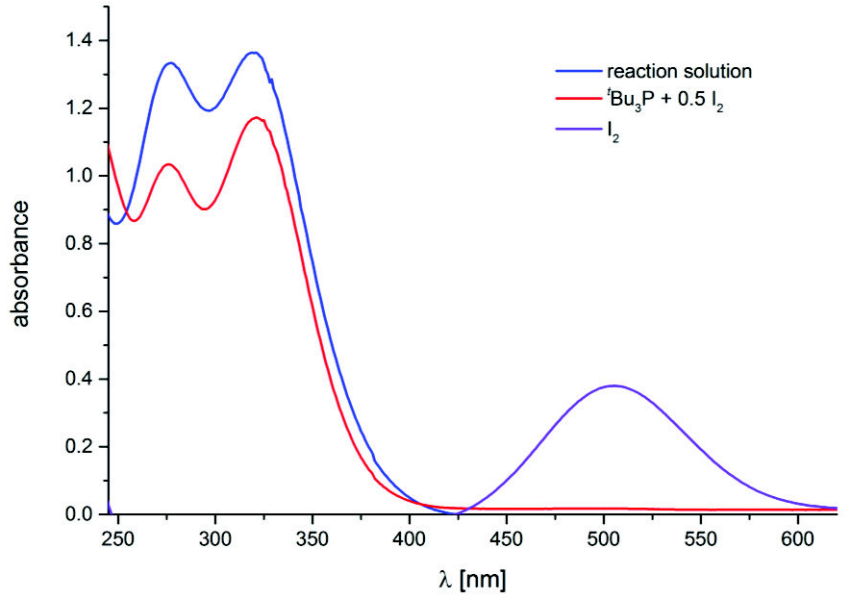
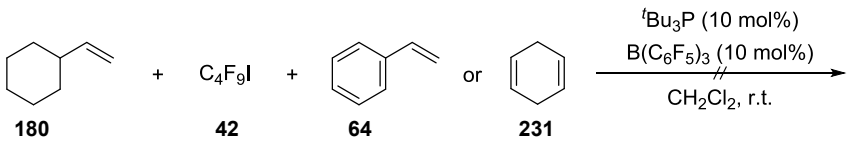


Figure 17: UV-VIS-spectra of the reaction solution of an iodoperfluoroalkylation of 9-decenol with ^{t}Bu$_3$P, a mixture of ^{t}Bu$_3$P with I_2 as well as solely I_2.

However, it was not possible to show that this complex of ^{t}Bu$_3$P and I_2 is relevant to the catalytic cycle. Additional iodine did not increase the reaction rate but instead slowed the reaction down.

In summary it can be stated that the functional group tolerance was expanded and its limitations were understood. Several strategies to overcome a limited substrate scope in the context of FLP-catalysed hydrogenations were not successful for the examined iodoperfluoroalkylation. In the course of the experiments a protocol using solely ^{t}Bu$_3$P was established for heteroatom functionalised alkenes and two unfunctionalised alkynes. These first promising results might arouse interest in the development of a photomediated iodoperfluoroalkylation.

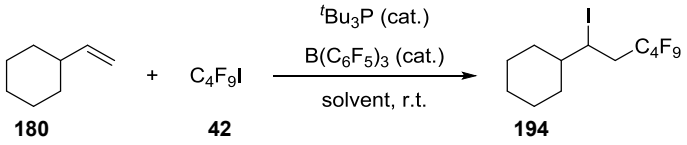
For the elucidation of the reaction mechanism several test reactions to discriminate between radical or ionic pathways and kinetic investigations were conducted. To prove the presence of radical intermediates, iodoperfluoroalkylations of vinylcyclohexane in the presence of styrene or 1,4-cyclohexadiene were conducted. In both experiments no iodoperfluoroalkylation was observed, indicating radical trapping (Scheme 116).



Scheme 116: Absent iodoperfluoroalkylation of vinylcyclohexane (**180**) in the presence of styrene (**64**) or 1,4-cyclohexadiene (**231**).

Several other observations implied the presence of radical intermediates making the presence of radicals highly probable.

The iodoperfluoroalkylation of vinylcyclohexane (**180**) was used as a test reaction for a solvent and a phosphane screening (Scheme 117). ^{t}Bu$_3$P (**96**) proved to be the only suitable phosphane. Dichloromethane was found to be the best performing solvent in this reaction.



Scheme 117: Iodoperfluoroalkylation of vinylcyclohexane (**180**).

Kinetic investigations revealed that ^{t}Bu$_3$P is involved in a fast initial process, which is causing a strong offset (Figure 18). However, the reaction rates were nearly identical after this fast initial reaction despite of varying ^{t}Bu$_3$P concentrations (Figure 18).

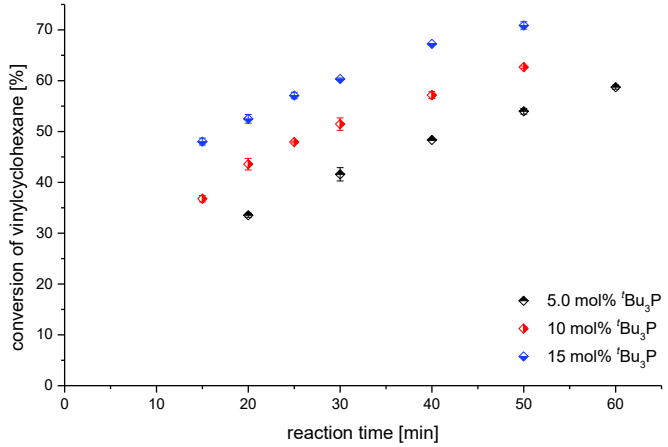
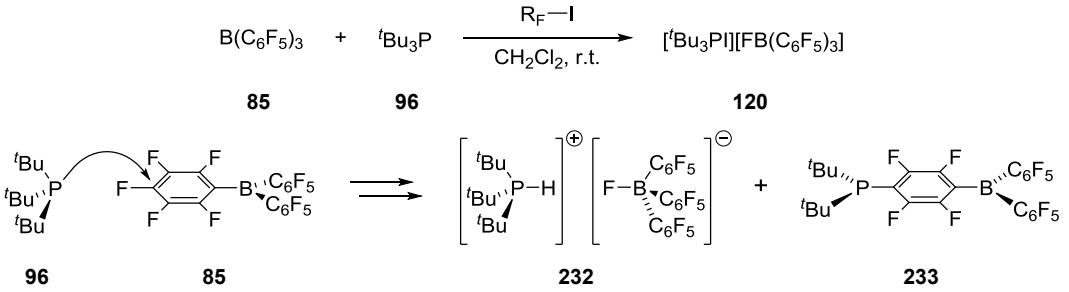


Figure 18: Kinetic investigation; influence of differing start concentrations of ^{t}Bu$_3$P.

Calculations suggested a first order dependence for C_4F_9I and showed a slight increase of the reaction rate with increasing $B(C_6F_5)_3$ concentrations. In contrast, an excess of the alkene decreases the reaction rate. Different deactivation modes of the FLP were probed. On the one hand, a fluoroborate **120** can be formed, which is catalytically inactive (Scheme 118). On the other hand, ^{t}Bu$_3$P can attack $B(C_6F_5)_3$ nucleophilicly. By a consecutive fluoride transfer and deprotonation of one *tert*-butyl group, a hydrophosphonium salt **232** and phosphinoborane **233** are formed.



Scheme 118: Deactivation modes for the FLP-system; fluoroborate **120** formation (top), phosphino borane **233** and concomitant hydrophosphonium salt **232** formation (bottom).

It was shown that the phosphinoborane formation is quite slow and does not influence the reaction rate. The fluoroborate formation however, is relatively fast. As a result, $^{t}Bu_3P$, $B(C_6F_5)_3$ and C_4F_9I should not be premixed before the start of the reaction. More detailed information regarding mechanistic considerations are described in the attached publication "Mechanistic Insights into FLP-Catalyzed Iodoperfluoroalkylations".[1]

7 Experimental Section

Chemicals, Glassware and Reactors

All syntheses involving air- and moisture-sensitive compounds were carried out inside a glove box (Vacuum Atmospheres Company, OMNI-LAB) under N_2 atmosphere (Air Liquide ALPHAGAZ™ 5.0). Glassware was dried for 2 hours at 120 °C and cooled down in *vacuo*. The used solvents were purchased purely or purified and/or dried by conventional methods. To dry dimethyl sulfoxide, *N*,*N*-dimethylformamide as well as triethylamine 4 Å molecular sieve and to dry methanol 3 Å molecular sieve was used. Dichloromethane, toluene, *n*-pentane, tetrahydrofurane and diethylether were dried with a solvent purification system (MBraun, MB SPS 800). Reagents were purchased from abcr, Acros, Fluorochem, J & K scientific, Sigma Aldrich, TCI or VWR Chemicals. For Grignard reactions magnesium turnings (purum, for Grignard reactions, ≥ 99.5%) were activated by stirring with 1 M hydrochloric acid for 1 min. They were subsequently washed with water, ethanol and finally Et_2O. The solvent was decanted off after each washing step. To dry the activiated magnesium turnings a rotary evaporator and then a high vacuum pump was used.

Software

The shown structural formulas were prepared with ChemDraw Professional 16.0 from CambridgeSoft. The evaluation of NMR-spectra was carried out with MestReNova (version 8.0.1) from Mestrelab Research. For the analysis of the kinetic data, OriginPro (version 9.0) and Microsoft Excel 2010 were used.

Thin layer chromatography

Reactions were monitored by thin-layer chromatography (TLC) using Macherey-Nagel silica gel plates ALUGRAM® Xtra SIL G/UV_{254} (0.20 mm thickness) and visualised by UV light or staining reagents if necessary. As staining reagents self-prepared potassium permanganate solution ($KMnO_4$ (3.0 g), K_2CO_3 (20 g), NaOH (5.0 ml, 5.0 w%), H_2O (300 ml)) or cerium molybdophosphoric acid (molybdophosphoric acid (0.5 g), H_2O (250 ml), conc. H_2SO_4 (16 ml), Cer(IV)sulphate (2.0 g)) were used.

Preparative column chromatography

Purifications via column chromatography were carried out on silica gel from Fisher Scientific (Acros Organics, highly purified, particle diameter 40-60 µm, pore diameter 60 Å) or Macherey-Nagel (0.04- 0.063 mm, pore diameter 60 Å) or neutral and basic aluminium oxide from Macherey Nagel or VWR (particle diameter 50-200 µm). The solvent mixtures were made from distilled (cyclohexane, *n*-hexane, *n*-pentane, acetone, CH_2Cl_2 and ethyl acetate) or pure solvents.

GC

GC measurements were conducted with a Perkin Elmer Clarus 500 GC without an autosampler equipped with a SUPELCO SLB-5ms column (30 m x 0.25 mm x 0.25 μm).

NMR-spectroscopy

^{1}H-, ^{11}B-, ^{13}C, ^{19}F-, ^{31}P-NMR spectra were recorded on Bruker Avance III 300 and 600. Chemical shifts are reported in parts per million (ppm). ^{1}H-NMR shifts are reported in reference to the corresponding solvent. ^{19}F-NMR shifts were reported in ppm and referenced to $CFCl_3$ in C_6D_6 and ^{31}P-NMR to H_3PO_4 in D_2O (internally or externally). Coupling constants (*J*) are reported in Hertz (Hz). The attributions of the chemical shifts were determined by means of COSY, HSQC, HMQC and DEPT experiments. If not described differently the NMR-spectra were measured at 298 K. For inert additions to an NMR sample outsight the glovebox, a Kontes® NMR tube sealing manifold was used.

IR- and UV-VIS-spectroscopy

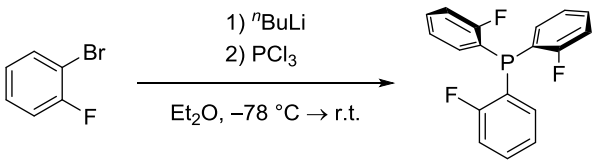
IR-spectra were measured as thin films on a NaCl single crystal with a JASCO FT/IR-6200.
UV-VIS-spectra were measured on a Perkin Elmer Lamda 2 UV VIS spectrometer in Hellma cuvettes (10 x 10 mm, Suprasil quartz glass).

Mass spectrometry and elemental analysis

High resolution mass spectra (HRMS) were measured with a *Bruker Daltonics* UHR-QTOF maXis 4G. Elemental analysss were measured on an *elementar* Vario Micro Cube.

7.1 Electronically Tuned Phosphanes and Boranes

7.1.1 Tris(2-fluorophenyl)phosphane



The synthesis of tris(2-fluorophenyl)phosphane was conducted similar to a literature-known procedure.[85]

EXPERIMENT 7.1.1-A **MS 126**

The synthesis of tris(2-fluorophenyl)phosphane was conducted similar to a literature-known procedure.[85] 1-Bromo-2-fluorobenzene (4.55 ml, 7.28 g, 41.6 mmol, 3.20 eq.) was dissolved in dry Et_2O (33 ml, 1.3 M) and cooled to − 85 °C with a cryostat. *n*-Butyllithium (16.6 ml, 2.5 M in hexane, 42 mmol, 3.2 eq.) was dissolved in dry Et_2O (64 ml, 0.5 M) and cooled to − 78 °C. The *n*-butyllithium solution was canulated dropwise into the solution of bromofluorobenzene within

30 min. During the addition a white solid started to preticipate. Phosphorus trichloride (1.14 ml, 1.79 g, 13.0 mmol, 1.00 eq.) was dissolved in dry Et_2O (40 ml, 0.3 M), cooled to − 78 °C and transferred to the reaction solution via cannula dropwise within 35 min. At the start of the addition a smoke formation and shortly afterwards a colour change was observed. Throughout the addition the solution turned into a brown suspension. The suspension was stirred at −78 °C for 10 min and was then warmed up to − 20 °C within 3 h. The reaction mixture was washed with a mixture of desalinated water and brine (1:1, 2 x 50 ml) as well as desalinated water (3 x 50 ml). The aqueous phase was extracted with EtOAc (3 x 50 ml) and the organic layer was washed with brine (1 x 30 ml). A TLC-control indicated a complete extraction. The combined organic phases were dried with Na_2SO_4, filtered, concentrated and dried in *vacuo*. A yellowish liquid (5.24 g) was obtained. By adding ethanol (3 ml) and *n*-hexane no crystallisation could be induced. After removal of the solvents *n*-hexane was added, resulting in a crystallisation of white crystalls, which slowly dissolved in the residual liquid. Purification by column chromatography on SiO_2 (*n*-hexane:EtOAc = 97:3) yielded miscellaneous mixture fractions. A yellowish, partly white crystalline material (2.24 g) was obtained. It was recrystallised from ethanol (16 ml). The resulting white amorphous material (1.06 g) was collected on a filter, washed with ice-cooled ethanol (11 ml) and dried in *vacuo*. Another recrystallisation from ethanol (8 ml) was conducted. The recrystallisation was repeated three times and the purity could only be increased up to 95%. Another purification by column chromatography on SiO_2 (hexane:EtOAc = 97:3) yielded mixture fractions. During the purification a crystallisation of the raw product on the column was observed. By another recrystallisation of the obtained product from *n*-hexane and EtOAc (15:1, 13 ml) the purity could not be increased. By sublimation of a recrystallised product at 120-130 °C and $5 \cdot 10^{-2}$ mbar a white powder was obtained. The purity could not increased by this measure.

A yield cannot be given in a reasonable fashion.

REPETITION OF EXPERIMENT 7.1.1-A **MS 131**

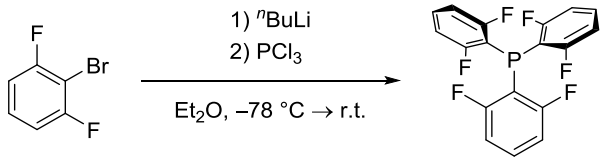
1-Bromo-2-fluorobenzene (4.00 g, 22.9 mmol, 3.0 eq.) was dissolved in dry Et_2O (36 ml, 0.6 M) and cooled to −78 °C with an acetone/dry ice bath. *n*-Butyllithium (9.1 ml, 2.5 M in hexane, 23 mmol, 3.0 eq.) was added dropwise within 11 min and after a short time a white solid started to precipitate. Because of poor mixing the suspension was slightly shaken in the cooling bath. In another flask phosphorus trichloride (0.67 ml, 1.1 g, 7.6 mmol, 1.0 eq.) was dissolved in dry Et_2O (12 ml, 0.6 M). After the addition of some drops to the fluorobenzene solution a brown colouration was observed. The fluorobenzene solution was diluted with dry Et_2O (9 ml) and shaken in the cooling bath to improve the mixing. PCl_3 was added via syringe, making the suspension mixable and causing a brown colouration. After 2 h stirring at −78 °C a yellowish

suspension was obtained, which was allowed to warm to r.t. over night. The reaction mixture was washed with a mixture of desalinated water and brine (1:1, 1 x 60 ml) as well as desalinated water (3 x 30 ml). The aqueous phase was extracted with Et_2O (3 x 30 ml) and the organic layer was washed with brine (3 x 25 ml). A TLC-control indicated a complete extraction. The combined organic phases were dried with $MgSO_4$, filtered, concentrated and dried in *vacuo*. A yellowish, partly crystalline substance (2.37 g) was obtained. After recrystallisation from ethanol (9 ml) only minor amounts precipitated. The solid was filtered off with a frit and white solid precipitated instantly in the filtrate. This solid was also collected on the same frit and the product was washed with ice-cooled ethanol (15 ml). After drying the product in *vacuo* a control by NMR spectroscopy indicated a rather pure product. The filtrate was concentrated giving a solid material (2.1 g). Purification by column chromatography on SiO_2 (hexane:EtOAc = 97:3) of the material obtained from the filtrate yielded miscellaneous mixture fractions, of which the product containing ones were combined, concentrated, adsorbed on celite and purified with a flash chromatography system on SiO_2 (*n*-hexane:EtOAc = 95:5 → 90:10). Again, only mixture fractions were obtained and the product containing fractions were combined, concentrated and dried in *vacuo*. The white crystalline material (0.60 g) was purified by column chromatography (cyclohexane:CH_2Cl_2 = 95:5 → cyclohexane:CH_2Cl_2:EtOAc = 93:7:1) on a long column. The product was obtained as white crystalls (314 mg) and the side products were discarded.

yield (316.26 g·mol^{-1}): 0.31 g (0.99 mmol, 13%)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 3H), 7.16 – 7.04 (m, 6H), 7.03 – 6.93 (m, 3H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ −103.3 (d, J = 56.8 Hz). **^{31}P-NMR** (121 MHz, $CDCl_3$) δ −42.5 (q, J = 56.9 Hz). Analytic data are consistent with the literature-known data.[85,106]

7.1.2 Tris(2,6-difluorophenyl)phosphane



The synthesis of tris(2,6-difluorophenyl)phosphane was conducted similar to a literature-known procedure.[86]

EXPERIMENT 7.1.2-A **MS 129**

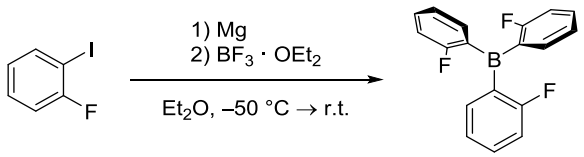
1-Bromo-2,6-difluorobenzene (1.53 g, 7.93 mmol, 3 eq.) was dissolved in dry Et_2O (14 ml, 0.5 M) and cooled to −78 °C with an acetone/dry ice bath. *n*-Butyllithium (3.2 ml, 2.5 M in hexane, 7.9 mmol, 3.0 eq.) was added dropwise within 13 min to the cooled solution and it was stirred for 2 h at this temperature. In another flask a solution of phosphorus trichloride (0.23 ml, 2.6 mmol,

1.0 eq.) in Et_2O (13 ml, 0.2 M) was prepared, which was then added to the other solution within 22 min. It was allowed to warm to r.t. over night, resulting in the precipitation of a white solid. A TLC-control indicated a complete conversion of the educt and the formation of one main product. The reaction was quenched by addition of NH_4Cl-solution (10 w%, 35 ml) and the phases were separated. The organic phase was washed with NH_4Cl-solution (10 w%, 10 ml) and desalinated water (2 x 10 ml). The combined aqueous phases were extracted with Et_2O (3 x 10 ml). A TLC-control indicated a complete extraction. The combined organic phases were washed with saturated NH_4Cl-solution (10 ml) and then dried with $MgSO_4$. After filtering, the solvent was removed to obtain a white crude product (1.24 g). Purification by column chromatography on SiO_2 (*n*-hexane:EtOAc = 98:2) yielded the product as a white crystalline material and minor amounts of side products.

yield (370.23 g·mol^{-1}): 0.821 g (2.22 mmol, 84%)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 3H), 6.92 – 6.79 (m, 6H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ −101.0 (d, J = 39.2 Hz). **^{31}P-NMR** (121 MHz, $CDCl_3$) δ −78.4 (sept, J = 39.3 Hz). Analytic data are consistent with the literature-known data.[86]

7.1.3 Tris(2-fluorophenyl)borane



The synthesis of tris(2-fluorophenyl)borane was conducted similar to a literature-known procedure.[91]

EXPERIMENT 7.1.3-A **MS 133**

Magnesium turnings (0.416 g. 17.1 mmol, 3.00 eq., activated) were stirred in an oven-dried *Schlenk* flask over night and then suspended in Et_2O (4 ml, 4 M). The suspension was cooled to −20 °C with a cryostat. 1-Iodo-2-fluorobenzene (3.81 g, 17.1 mmol, 3 eq.) was dissolved in dry Et_2O (6 ml, 3 M) and a small portion was added to the cooled magnesium suspension. An iodine crystal and dibromoethane (0.05 ml) were added. Within 1 h a cloudy suspension developed and the rest of the iodofluorobenzene solution was added dropwise. After stirring at −20 °C for 20 min nearly the complete magnesium was consumed. The yellowish solution was allowed to warm up to −6 °C within 1 h and the whole magnesium was consumed. After cooling to −50 °C, $BF_3 \cdot OEt_2$ (0.72 ml, 5.7 mmol, 1.0 eq.) was added dropwise via syringe. It was stirred at −50 °C for another hour, then it was allowed to warm up to 0 °C over night. A yellowish two-phase system developed and the volatiles were removed utilising a secondary cold trap. The resulting yellowish foam was transferred into a sublimation apparatus inside the glovebox. A sublimation

(120 °C, $3 \cdot 10^{-3}$ mbar) yielded a yellow/brownish fluid. The sublimation was cancelled due to product in the cooling trap. A control by NMR spectroscopy was conducted, the crude product was extracted with toluene (3 x 10 ml), filtered with a syringe filter and thereby transferred into another *Schlenk* flask. All volatiles were removed with a secondary cooling trap and the product was recrystallised interly with dry *n*-hexane (4 ml). Minor amounts (< 10 mg) of a yellowish solid precipiated, which were filtered off under standard conditions and washed with *n*-hexane. The yellow solid turned black as it was dissolved in $CDCl_3$. The filtrate was concentrated and analysed by NMR spectroscopy.

No product was obtained.

EXPERIMENT 7.1.3-B **MS 135**

1-Bromo-2-fluorobenzene (1.97 ml, 3.15 g, 18.0 mmol, 3 eq.) was dissolved in dry Et_2O (60 ml, 0.3 M) in a three-neck round-bottom flask and cooled to −40 °C with a cryostat. The temperature was measured with an internal thermometer. A solution of ^{i}PrMgCl (9.0 ml, 2.0 M in THF, 18 mmol, 3.0 eq.) was added dropwise within 25 min and the temperature did not exceed −39 °C. The solution was warmed up to 0 °C within 1.5 h and stirred at this temperature over night. The resulting white suspension was cooled to −50 °C and $BF_3 \cdot OEt_2$ (0.76 ml, 6.0 mmol, 1.0 eq.) was added dropwise. No rise in temperature was observed. The suspension was slowly warmed up to 0 °C within 3 h, stirred at this temperature for 30 min and then another 30 min at r.t. A mixture of a white and brown solid precipitated. Most of the solvent was evaporated and the resulting sirup was extracted with dry toluene (3 x 10 ml). The toluene extracts were filtered with a syringe filter and all volatiles were removed. An NMR analysis of the crude product was conducted. It was then refluxed for 4 h in dry *n*-hexane (30 ml), cooled to 40 °C, filtered with a *Schlenk* frit and rinsed with dry *n*-hexane (4 ml). A yellow solid and traces of a white substance remained in the flask. After removal of all volatiles from the filtrate a yellow oil was obtained. No crystallisation took place by cooling with an icebath. An NMR control of the crude product was conducted.

No product was obtained.

EXPERIMENT 7.1.3-C **MS 138**

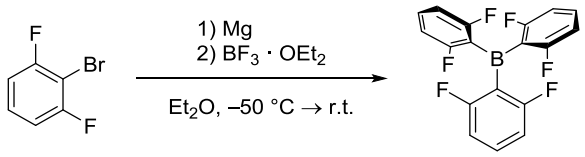
Magnesium turnings (0.972 g. 41.1 mmol, 3.00 eq., activated) were stirred in an oven-dried *Schlenk* flask for 2 h and then suspended in Et_2O (9.8 ml, 4.1 M). Dibromoethane (0.1 ml, 1 mmol) was added causing blistering and the precipitation of a highly dispersed white solid. The suspension was cooled to −24 °C with a cryostat. 1-Iodo-2-fluorobenzene (8.88 g, 40.0 mmol, 3 eq.) was dissolved in dry Et_2O (25 ml, 1.6 M) and then added dropwise to the cooled magnesium suspension. After stirring for 2 h at −20 °C nearly all magnesium was consumed. $BF_3 \cdot OEt_2$ (1.69 ml, 13.3 mmol, 1.00 eq.) was dissolved in dry Et_2O (40 ml), cooled with an

ice bath and then slowly cannulated to the Grignard reagent. At the start of the addition the solution became foggy, becoming greyer throughout the addition and towards the end a grey and green dispersion was present. The emulsion was allowed to warm up to 0 °C over night and seemed to be poorly mixed, thus the cooling bath was removed and it was shaken. Two yellow phases developed after a better mixing and no solid was present. Most of the solvent was evaporated, then dry *n*-hexane (91 ml) was added and the suspension was refluxed for 5 h inertly. A yellowish solid stayed undissolved and the solution was filtered using a Schlenk frit. The filtrate is a dark yellow solution with minor amounts of a yellow resin. The solvent was removed inertly and small parts of the crude product seemed to sublimate. A sample for an NMR measurement was taken inertly. The crude product was dissolved in dry toluene (25 ml) and filtered using a Schlenk frit. Toluene (4 ml) was used for afterwashing and an orange-red fluid was obtained. The solvent was removed inertly, yielding a dark organe-red resin. An control by NMR spectroscopy was conducted.

The flask was opened and wet *n*-hexane was added. A suspension containing a yellow solid was formed. After filtering off the solid the yellow solid turned into a black resin within 5 min.

No product was obtained.

7.1.4 Tris(2,6-difluorophenyl)borane



The synthesis of tris(2,6-difluorophenyl)borane was conducted similar to a literature-known procedures.[87-88]

EXPERIMENT 7.1.4-A **MS 130**

Magnesium turnings (0.219 g. 9.00 mmol, 2.98 eq., activated) were suspended in Et_2O (6 ml, 1.5 M) and cooled to −20 °C with a cryostat. 1-Bromo-2,6-difluorobenzene (1.75 g, 9.07 mmol, 3 eq.) was dissolved in dry Et_2O (5 ml, 2 M) and then parts of it were slowly added to the cooled magnesium suspension. As no reaction occurred, dibromoethane (0.05 ml) was added, resulting in a cloudy suspension. Further bromodifluorobenzene was added and no reaction occurred. The suspension was slowly warmed up to −10 °C over 1 h. An iodine crystall was added and the resulting colourated solution turned transparent nearly immediately. Further efforts were made to start the reaction, but it could not be initiated.

EXPERIMENT 7.1.4-A **MS 130W**

1-Bromo-2,6-difluorobenzene (1.75 g, 9.07 mmol, 3.0 eq.) was dissolved in dry THF (90 ml, 0.1 M) and cooled to −20 °C with a cryostat. A solution of ^{i}PrMgCl (4.5 ml, 2.0 M in THF,

9.0 mmol, 3.0 eq.) was added dropwise. After stirring for 25 min at this temperature, the solution was warmed up with an ice bath and stirred for 1 h at 0 °C. Then the reaction solution was cooled to −50 °C with a cryostat and $BF_3 \cdot OEt_2$ (0.38 ml, 3.0 mmol, 1.0 eq.) was added dropwise via syringe. The solution was allowed to warm up to 0 °C very slowly over night. Removal of the solvent and all volatiles with a secondary cold trap generated a white foam. The substance was transferred into a sublimation apparatus inside the glovebox and was then sublimated (120 °C → 160 °C, $3 \cdot 10^{-3}$ mbar). A white crystalline powder (616 mg) was obtained, which was analysed by NMR. The product was sublimated again (120 °C, $3 \cdot 10^{-3}$ mbar) and the resulting white powder was analysed by NMR. An inert recrystallisation from dry *n*-hexane (14.5 ml) yielded white needles. The supernatant fluid was removed, the crystals were washed with *n*-hexane (2 x 1.5 ml) and then dried. The solid (270 mg) was analysed by NMR.

A yield cannot be given in a reasonable fashion.

EXPERIMENT 7.1.4-B **MS 140**

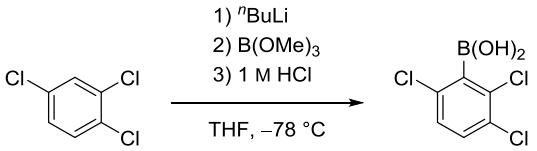
1-Bromo-2,6-difluorobenzene (5.21 g, 27.0 mmol, 3 eq.) was dissolved in dry THF (200 ml) and cooled to −25 °C with a cryostat. A solution of ^{i}PrMgCl (13.5 ml, 2.0 M in THF, 27 mmol, 3.0 eq.) was added dropwise within 23 min. After stirring at −25 °C for 30 min, the solution was stirred at 0 °C for 1 h. The resulting grey/brownish solution was cooled to −50 °C. In another flask $BF_3 \cdot OEt_2$ (1.14 ml, 9.00 mmol, 1.00 eq.) was dissolved in dry THF (36 ml), cooled with an acetone/dry ice bath and then slowly cannulated into the other solution. The resulting clear solution was stirred at −50 °C for 1 h, then the solution was allowed to reach r.t. within 1 h. By removal of all volatiles with a secondary cold trap a white and partly grey substance was obtained. By extraction with toluene (1 x 16 ml, 1 x 12 ml, 1 x 8 ml) and subsequent filtration via syringe filter, a clear yellowish solution was obtained. A white residue (< 1 g) remained behind. By removal of all volatiles with a secondary cold trap a grey solid was obtained. The substance was transferred into a sublimation apparatus inside the glovebox and then sublimated (120 °C, $3 \cdot 10^{-3}$ mbar). Only small amounts of a white crystalline powder (149 mg) were obtained, since nearly all material fell back into the sublimation apparatus. The crude product was sublimated again and a white powder obtained (0.690 g) was obtained. A third sublimation yielded also a white powder (0.77 g). Both sublimates were combined and inertly recrystallised from boiling *n*-hexane (34.8 ml). Inert filtration with a Schlenk frit, rinsing with *n*-hexane (3 ml) of the collected needle shaped crystalls and drying in high vacuum yieled white needles (1.19 g).

yield (350.07 g·mol^{-1}): 1.2 g (3.4 mmol, 38%, purity ≥ 96%)

^{1}H-NMR (300 MHz, CD_2Cl_2) δ 7.60 – 7.42 (m, 1H), 6.95 – 6.85 (m, 2H). **^{19}F-NMR** (282 MHz, CD_2Cl_2) δ −99.8. Analytic data are consistent with literature-known values.[88]

7.1.5 (2,3,6-Trichlorophenyl)bis(2,3,6-trifluorophenyl)borane

7.1.5.1 (2,3,6-trichlorophenyl)boronic acid



The synthesis of (2,3,6-trichlorophenyl)boronic acid was conducted several times according to literature-known procedure with yields ranging from 42-80%.[75] One exemplary execution is described.

EXPERIMENT 7.1.5-A **MS 318**

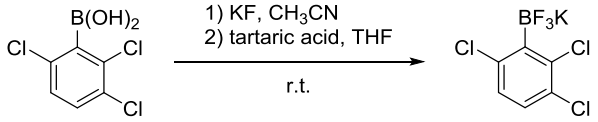
1,2,4-trichlorobenzene (5.30 g, 24.0 mmol, 1.00 eq.) was dissolved in dry THF (31 ml, 0.7 M) and cooled to −78 °C. *n*-Butyllithium (32.1 ml, 2.49 M in hexane, 32.1 mmol, 1.10 eq.) was added to the cooled solution dropwise. After the addition of around 9 ml *n*-butyllithium solution a suspension was formed and the *n*-butyllithium addition was continued very slowly. After 2 h stirring at −78 °C, trimethyl borate (7.0 ml, 63 mmol, 2.1 eq.) was added dropwise via syringe and a clear solution was obtained. The solution was allowed to warm up over night, resulting in a white suspension. The supension was cooled with an ice bath and hydrochloric acid (1 M, 40 ml) was added. After stirring at r.t. for 2 h the phases were separated and the aqueous phase was extracted with Et_2O (3 x 20 ml). The combined organic phases were washed with brine (3 x 15 ml) and then dried with Na_2SO_4. The drying agent was filtered off and the solvents were removed thoroughly (60 °C, 13 mbar) at a rotary evaporator. A partly wet, white solid (6.7 g) was obtained, which washed on a frit with *n*-hexane (2 x 10 ml) and then dried at a rotary evaporator (45 °C, 15 mbar). A white solid was obtained.

yield (225.26 g·mol^{-1}): 5.23 g (23.2 mmol, 80%)

m.p. = 152-154 °C (lit. 149-150 °C)

^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.72 (s, 2H), 7.57 (d, J = 8.6 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H). **^{11}B-NMR** (96 MHz, DMSO-d_6) δ 27.6. Analytic data are consistent with literature-known values.[75]

7.1.5.2 Potassium (2,3,6-trichlorophenyl)trifluoroborate

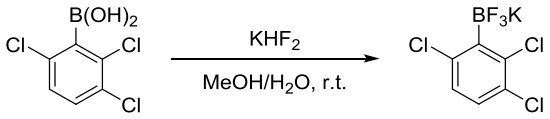


EXPERIMENT 7.1.5-B **MS 149**

(2,3,6-Trichlorophenyl)boronic acid (0.451 g, 2.00 mmol, 1.00 eq.) was dissolved in acetonitrile (8.0 ml, 0.25 M). A solution of potassium fluoride (0.465 g, 8.00 mmol, 4.00 eq.) in desalinated water (0.8 ml, 10 M) and L-(+)-tartaric acid (0.615 g, 4.10 mmol, 2.05 eq.) in THF (3.0 ml, 1.4 M) was prepared. The potassium fluoride solution was added to the educt solution and stirred at r.t. until a clear solution was formed after 10 min. Addition of L-(+)-tartaric acid solution caused immediate precipitate of a white solid. This solid was filtered off and washed with acetonitrile (3 x 6 ml). After removal of the solvent in *vacuo* the product was obtained as a white solid in impure form.

yield (287.34 g·mol^{-1}): 0.49 g (1.7 mmol, 85%, impure)

The synthesis of potassium (2,3,6-trichlorophenyl)trifluoroborate was conducted several times according to literature-known procedure[75] with yields above 90%. One exemplary execution is described.

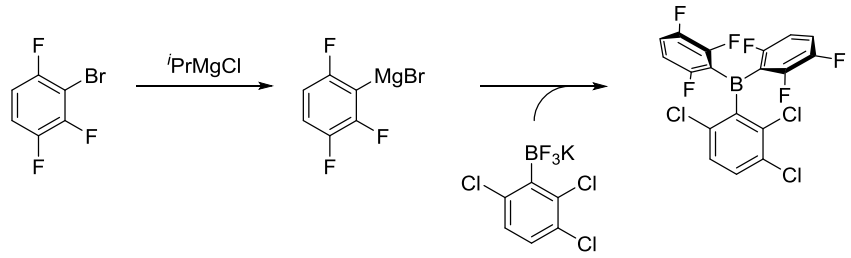


EXPERIMENT 7.1.5-C **MS 320**

(2,3,6-Trichlorophenyl)boronic acid (4.39 g, 19.5 mmol, 1.00 eq.) was dissolved in methanol (30 ml, 0.65 M). A solution of potassium hydrogen difluoride (6.09 g, 78.0 mmol, 4.00 eq.) in desalinated water (22 ml, 3.5 M) was added to the educt solution, resulting in the precipitation of a white solid and a noticeable temperature rise. After stirring over night, acetone (30 ml) was added and nearly all solid was dissolved. The suspension was filtered and the residue was washed with acetone (3 x 8 ml). After a thorough removal of the solvent at a rotary evaporator (60 °C, 7 mbar) a white solid was obtained, which was dissolved in acetone (35 ml). Small amounts of a white solid stayed undissolved and the yellow solution was filtered. The solvent was removed thoroughly (60 °C, 13 mbar) once more and the resulting yellowish solid was washed with *n*-hexane (3 x 15 ml) on a frit. The pure white powder (5.45 g) was dried in a vacuum oven at 70 °C and 7 mbar for 24 h.

yield (287.34 g·mol^{-1}): 5.42 g (18.9 mmol, 97%)

^{1}H-NMR (300 MHz, DMSO-d_6) δ 7.28 (d, J = 8.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H). **^{19}F-NMR** (282 MHz, DMSO-d_6) −132.5 (dd, J = 88.5, 40.6 Hz). **^{11}B-NMR** (96 MHz, DMSO-d_6) δ 1.8 (q, J = 46.3 Hz). Analytic data are consistent with literature-known values.[75]



7.1.5.3 (2,3,6-Trichlorophenyl)bis(2,3,6-trifluorophenyl)borane

The synthesis of (2,3,6-trichlorophenyl)bis(2,3,6-trifluorophenyl)borane was conducted according to literature-known procedure.[75]

EXPERIMENT 7.1.5-D **MS 194W**

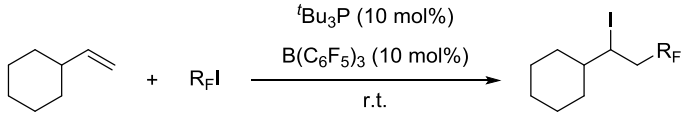
1-Bromo-2,3,6-trifluorobenzene (2.30 g, 10.9 mmol, 2.3 eq.) was dissolved in dry THF (31 ml, 0.35 M) and cooled to −24 °C. Within 8 min ^{i}PrMgCl (5.5 ml, 2.0 M in THF, 11 mmol, 2.3 eq.) was added, resulting in a yellowish solution. The solution was warmed to 0 °C with an icebath, stirred at this temperature for 30 min and then for 1 h at rt. Potassium (2,3,6-trichlorophenyl)trifluoroborate (1.36 g, 4.74 mmol, 1.00 eq.) was suspended in dry THF (1.4 ml, 1.4 M). The Grignard solution as well as the fluoroborate suspension was cooled to 0 °C with an icebath and the Grignard solution was transferred within 12 min. After 40 min the icebath was removed and the solution was stirred at r.t. for 15 h. Volatiles were removed inertly and then the solid was dried (75 °C, 12 mbar) with a rotary evaporator. The resulting yellow-orange foam was extracted with toluene (3 x 15 ml). Volatiles were removed and the solid was dried (75 °C, 13 mbar), yielding a yellow-orange resin (1.9 g). *n*-Pentane (2.5 ml) was added, resulting in no precipitation. After storage in the refrigenerator for 2 d, a white solid precipitated, which was filtered off. The crystals were washed with icecooled *n*-pentane (3 x 1.5 ml) and dried. Two subsequent sublimations (120 °C, 1·10^{-2} mbar) yielded the product as amorphous crystals.

yield (453.40 g·mol^{-1}): 1.05 g (2.31 mmol, 49%)

^{1}H-NMR (300 MHz, C_6D_6) δ 6.73 (d, J = 8.6 Hz, 1H), 6.59 (d, J = 8.6 Hz, 1H), 6.44 (qd, J = 9.2, 5.2 Hz, 2H), 6.16 – 6.02 (m, 2H). **^{19}F-NMR** (282 MHz, C_6D_6) δ −103.1 (d, J = 15.8 Hz), −122.7 (d, J = 21.8 Hz), −142.2 (dd, J = 21.8, 15.7 Hz). Analytic data are consistent with literature-known values.[75]

7.2 Functional Group Tolerance in FLP-Catalysed Iodoperfluoroalkylations

7.2.1 Vinylcyclohexane



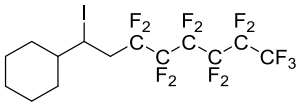
EXPERIMENT 7.2.1-A **MS 134**

$B(C_6F_5)_3$ (42 mg, 0.082 mmol, 0.098 eq.), $^tBu_3P$ (17 mg, 0.084 mmol, 0.10 eq.), vinylcyclohexane (92.2 mg, 0.837 mmol, 1 eq.) and tridecafluoro-1-iodohexane (452 mg, 1.01 mmol, 1.21 eq.) were weighed out into a screw-top vial and then dissolved in THF (1.6 ml). The resulting brownish solution was stirred sealed with a Teflon-insert screw cap. After 1 d stirring at r.t. Most of the solvent was evaporated and the product was isolated as a transparent liquid by column chromatography (*n*-hexane).

yield (556.15 g·mol^{-1}): 17.4 mg (0.0313 mmol, 3.7%)

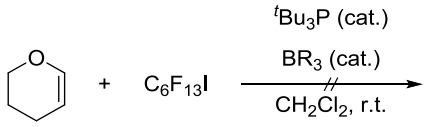
EXPERIMENT 7.2.1-B **MS 202**

$^tBu_3P$ (15.9 mg, 0.0786 mmol, 10.8 mol%) as well as $B(C_6F_5)_3$ (35.9 mg, 0.0701 mmol, 9.61 mol%) were weighed out into a vial and dissolved in CH_2Cl_2 (2.1 ml, 0.35 M). Et_2O (0.15 ml, 0.11 g, 1.4 mmol, 2.0 eq.), vinylcyclohexane (100 µl, 80.5 mg, 0.730 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (125 µL, 251 mg, 0.726 mmol, 0.995 eq.) were added via Hamilton syringe. The solution was stirred sealed with a Teflon-insert screw cap inside the glovebox. After stirring for 53 h, a sample was taken for a control by NMR spectroscopy. A conversion of 61-67% was observed.



^{1}H-NMR (300 MHz, C_6D_6) δ [ppm] 4.06 (−CHI−, td, J = 6.6, 3.1 Hz, 1H), 2.77 – 2.41 (−CH_2−R_F, m, 2H), 1.58 – 1.38 (Cy, m, 3H), 1.37 – 1.22 (Cy, m, 2H), 1.14 – 0.80 (Cy, m, 5H), 0.51 – 0.40 (Cy, m, 1H). **^{19}F-NMR** (282 MHz, C_6D_6) δ [ppm] −81.0 (tt, J = 10.0, 2.5 Hz, 3F), −112.1 – −114.8 (m, 2F), −121.5 – −121.9 (m, 2F), −122.6 – −123.0 (m, 2F), −123.3 – −123.6 (m, 2F), −126.0 – −126.3 (m, 2F). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] 44.5, 44.5, 39.3 (−$H_2CCF_2R_F$, t, $^2J_{CF}$ = 20.7 Hz), 33.6, 29.9, 29.7, 26.2, 25.9, 25.8. **IR** (film on NaCl), $\tilde{\nu}$ [cm^{-1}] 2931, 2857, 1452, 1365, 1239, 1145, 1070, 845, 813, 734, 700, 661, 526. **Elemental analysis** for $C_{14}H_{14}F_{13}I$, calculated: C = 30.24%, H = 2.54%, measured: C = 30.27%, H = 2.51%.

7.2.2 3,4-Dihydro-2*H*-pyrane



EXPERIMENT 7.2.2-A **MS 139**

^{t}Bu$_3$P (28 mg, 0.14 mmol, 0.18 eq.) as well as B(2,6-$F_2C_6H_3)_3$ (41 mg, 0.080 mmol, 0.089 eq.) were weighed out into a screw-top vial and dissolved in small amounts CH_2Cl_2, resulting a brownish solution. 3,4-Dihydro-2*H*-pyrane (67 mg, 0.80 mmol, 1 eq.) and tridecafluoro-1-iodohexane (0.36 g, 0.80 mmol, 1.0 eq.) were added and then dissolved in CH_2Cl_2 (1 ml, 0.8 M). The solution was stirred sealed inside the glovebox. After 2 d stirring at r.t., the vial was removed from the glovebox and a sample for NMR measurements was taken from the green solution. A minor conversion was indicated.

EXPERIMENT 7.2.2-B **MS 142 A**

^{t}Bu$_3$P (19 mg, 0.094 mmol, 0.11 eq.), 3,4-dihydro-2*H*-pyrane (74 mg, 0.88 mmol, 1 eq.), $C_6F_{13}I$ (0.37 g, 0.82 mmol, 0.94 eq.) as well as $B(C_6F_5)_3$ (43 mg, 0.084 mmol, 0.095 eq.) were weighed out into a 10 ml round-bottom flask and then dissolved in CH_2Cl_2 (2 ml, 0.4 M), resulting in a dark green solution. Dry THF (0.12 g, 1.6 mmol, 1.8 eq.) was added. The dark green solution was stirred sealed with a rubber septum. After 2 d stirring at r.t., a sample for NMR measurements was taken from the brown solution. No conversion was indicated.

EXPERIMENT 7.2.2-C **MS 142 B**

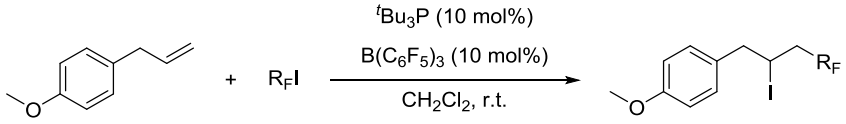
^{t}Bu$_3$P (19 mg, 0.094 mmol, 0.11 eq.), 3,4-dihydro-2*H*-pyrane (74 mg, 0.88 mmol, 1 eq.), tridecafluoro-1-iodohexane (0.36 g, 0.80 mmol, 0.91 eq.), dry Et_2O (0.12 g, 1.6 mmol, 1.8 eq.) and $B(C_6F_5)_3$ (43 mg, 0.084 mmol, 0.095 eq.) were weighed out into a 10 ml round-bottom flask and then dissolved in CH_2Cl_2 (2 ml, 0.4 M). The resulting yellow-orange solution was stirred sealed with a rubber septum and turned dark green within 10 min. After 2 d stirring at r.t., a sample for NMR measurements was taken from the red-brown solution. A minor conversion was indicated. The solution was diluted with *n*-pentane (3 ml) and the brownish liquid was not dissolved. The liquid was filtered with a glass pipette filled with basic aluminium oxide, holding the brownish liquid back. *n*-Pentane (2.5 ml) was used for afterwashing and the resulting solution was concentrated at a maximum of 650 mbar. A colourless liquid (76 mg) was obtained which was analysed by NMR spectroscopy. This analysis showed no iodoperfluoroalkylation product.

EXPERIMENT 7.2.2-D **MS 146**

^{t}Bu$_3$P (36 mg, 0.18 mmol, 22 mol%), 3,4-dihydro-2*H*-pyrane (67 mg, 0.80 mmol, 1.0 eq.), tridecafluoro-1-iodohexane (0.36 g, 0.80 mmol, 1.0 eq.), dry Et_2O (0.48 g, 6.4 mmol, 8.1 eq.) and

$B(C_6F_5)_3$ (82 mg, 0.16 mmol, 20 mol%) were weighed out into a 10 ml round-bottom flask and then dissolved in CH_2Cl_2 (2 ml, 0.4 M). The resulting yellow-orange solution was sealed with a rubber septum, unloaded from the glovebox and was stirred under N_2 atmosphere. The solution turned green within 30 min. After 2 d stirring at r.t. a sample for NMR measurements was taken. A purification by column chromatography on SiO_2 (*n*-hexane:EtOAc = 97:3) was conducted after 11 d. Silica gel was deactivated with Et_3N containing eluent. Minor amounts of two products were obtained (3.3 mg; 19.8 mg) which were analysed by NMR. This analysis showed no iodoperfluoroalkylation product.

7.2.3 4-Allylanisole



EXPERIMENT 7.2.3-A **MS 148**

^{t}Bu$_3$P (16 mg, 0.079 mmol, 9.5 mol%), 4-allylanisole (123 mg, 0.830 mmol, 1.00 eq.), tridecafluoro-1-iodohexane (357 mg, 0.801 mmol, 0.965 eq.) and $B(C_6F_5)_3$ (43 mg, 0.084 mmol, 10 mol%) were weighed out into a 10 ml round-bottom flask and then dissolved in CH_2Cl_2 (2 ml, 0.4 M). After the addition of $B(C_6F_5)_3$ the solution turned yellow and 1 d later a brown colouration was observed. It was stirred at r.t. sealed with a rubber septum. After 2 d a sample for NMR measurements was taken with a N_2-flushed syringe. After 6 d most of the solvent was evaporated and by column chromatography (eluent = cyclohexane, then cyclohexane:CH_2Cl_2 = 95:5 and finally cyclohexane: CH_2Cl_2 = 90:10) mixture fractions were yielded. Another purification (cyclohexane:acetone = 98.7:1.3) yielded pure product (93.6 mg) as well as a mixture of educt and product (70.9 mg).

yield (594.15 g·mol^{-1}): 90.3 mg (0.152 mmol, 18%)

EXPERIMENT 7.2.3-B **MS 166 A**

^{t}Bu$_3$P (16.7 mg, 0.0825 mmol, 10.0 mol%), $B(C_6F_5)_3$ (40.5 mg, 0.0791 mmol, 9.61 mol%), 4-allylanisole (122 mg, 0.823 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (282 mg, 0.815 mmol, 0.990 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2.5 ml, 0.3 M). After 3 d stirring at r.t. a sample for NMR measurements was taken inside the glovebox. This sample was filled up with $CDCl_3$ outside the glovebox. After 11 d and 17 d, respectively, a control by NMR spectroscopy was taken inside the glovebox and was directly filled up with C_6D_6. Also after 11 d the reaction yellow-orange solution was transferred into a transparent screw top vial. Workup after 19 d by column chromatography (*n*-pentane:acetone = 98.8:1.2) yielded only mixture fractions (0.18 g) and clean educt. Another purification

(*n*-pentane:acetone = 99:1) on the same column was unsuccessful, giving only mixture fractions (0.18 g). A third purification (*n*-pentane:acetone = 99:1) on a longer column gave clean product (40.4 mg) and mixture fractions (95.6 mg). A fourth purification (cyclohexane:acetone = 99:1) gave additional clean product (74.0 mg).

yield (494.14 g·mol^{-1}): 114 mg (0.232 mmol, 28%)

EXPERIMENT 7.2.3-C **MS 166 B**

^{t}Bu$_3$P (16.6 mg, 0.0820 mmol, 9.97 mol%), B(C$_6$F$_5$)$_3$ (40.8 mg, 0.0797 mmol, 9.68 mol%), 4-allylanisole (122 mg, 0.823 mmol, 1.00 eq.), nonafluoro-1-iodobutane (279 mg, 0.807 mmol, 0.980 eq.) and THF (130 mg, 1.80 mmol, 2.19 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2.5 ml). After 3 d stirring at r.t. a sample for NMR measurements was taken inside the glovebox. This sample was filled up with $CDCl_3$ outside the glovebox. Then, after 5 d the reaction solution was unloaded from the glovebox and desalinated water (5 µL, 0.3 mmol, 0.3 eq.) was added in an N_2-counterflow. One day later a sample for NMR measurements was taken and the reaction solution was discarded. No conversion was observed.

EXPERIMENT 7.2.3-D **MS 159**

^{t}Bu$_3$P (16.6 mg, 0.0820 mmol, 10.1 mol%), B(C$_6$F$_5$)$_3$ (41.2 mg, 0.0805 mmol, 9.89 mol%), 4-allylanisole (121 mg, 0.814 mmol, 1.00 eq.), tridecafluoro-1-iodohexane (368 mg, 0.825 mmol, 1.01 eq.) and Et_2O (119 mg, 1.61 mmol, 1.97 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2 ml). After 5 and 14 d stirring at r.t. a sample for NMR measurements was taken in N_2-counterflow. Workup after 56 d by column chromatography on SiO_2 (*n*-pentane:acetone = 99:1 → 98.5:1.5) yielded mixture fractions (98.6 mg) and clean product (103 mg).

yield (594.15 g·mol^{-1}): 103 mg (0.173 mmol, 21%)

EXPERIMENT 7.2.3-E **MS 151**

^{t}Bu$_3$P (16 mg, 0.079 mmol, 9.9 mol%), B(2,6-F$_2$C$_6$H$_3$)$_3$ (28 mg, 0.080 mmol, 10 mol%), 4-allylanisole (118 mg, 0.796 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (354 mg, 0.794 mmol, 0.997 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2 ml). After 2 and 16 d stirring at r.t., respectively, samples for NMR measurements were taken in N_2-counterflow. No conversion was observed.

EXPERIMENT 7.2.3-F **MS 171 A**

^{t}Bu$_3$P (33.9 mg, 0.168 mmol, 8.75 mol%), B(C$_6$F$_5$)$_3$ (85.7 mg, 0.167 mmol, 8.70 mol%), 4-allylanisole (285 mg, 1.92 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (804 mg, 1.80 mmol, 0.938 eq.) were weighed into a vial and then dissolved in CH_2Cl_2 (5.0 ml). The solution was transferred into a sealed flask and heated up to 60 °C with an oil-bath. After stirring for 5 and

11 d, respectively, samples for a control by NMR spectroscopy were taken inertly. After 29 d a solution of ^{t}Bu$_3$P (15.7 mg, 0.0776 mmol, 4.04 mol%) and B(C$_6$F$_5$)$_3$ (47.8 mg, 0.0934 mmol, 4.86 mol%) in CH_2Cl_2 (1.0 ml) was added. Eleven days later another sample was taken. A conversion of 46-65% was observed.

EXPERIMENT 7.2.3-G **MS 171 C**

^{t}Bu$_3$P (16.2 mg, 0.0801 mmol, 9.65 mol%), B(2,6-F$_2$C$_6$H$_3$)$_3$ (27.5 mg, 0.0786 mmol, 9.47 mol%), 4-allylanisole (123 mg, 0.830 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (377 mg, 0.845 mmol, 1.02 eq.) were weighed out into a transparent screw-top vial and then dissolved in CH_2Cl_2 (2.5 ml). After 6 and 11 d, respectively, stirring at r.t. samples for a control by NMR spectroscopy was taken inside the glovebox. No conversion was observed.

EXPERIMENT 7.2.3-H **MS 175**

^{t}Bu$_3$P (64.3 mg, 0.318 mmol, 38.9 mol%) as well as B(C$_6$F$_5$)$_3$ (168 mg, 0.328 mmol, 40.2 mol%) were weighed out into amber glass screw-top vial and dissolved in CH_2Cl_2 (2.5 ml). 4-Allylanisole (121 mg, 0.816 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (394 mg, 0.884 mmol, 1.08 eq.) were added via syringe. After 1, 5 and 12 d, respectively, stirring at r.t. samples for a control by NMR spectroscopy were taken inside the glovebox. After 8 d a solution of ^{t}Bu$_3$P (22.5 mg, 0.111 mmol, 13.6 mol%) as well as B(C$_6$F$_5$)$_3$ (47.5 mg, 0.0928 mmol, 11.4 mol%) in CH_2Cl_2 (0.5 ml) was added inside the glovebox. After 26 d hydrochloric acid (1 ml, 1 M) was added and the emulsion was stirred for 10 min. An extraction with EtOAc (2 x 3 ml) was conducted, the organic layer was washed with brine (3 ml) and then dried with Na_2SO_4. A purification by column chromatography (*n*-pentane:acetone = 97:3) yielded a mixture of educt and product as well as unidentified side products (124 mg). Another purification on neutral Al_2O_3 (Brockmann I) yielded impure side products.

A corrected yield was calculated based on the ^{1}H-NMR-spectrum.

yield (594.15 g·mol^{-1}): 0.18 g (0.30 mmol, 37%)

EXPERIMENT 7.2.3-I **MS 185**

A solution of ^{t}Bu$_3$P (69.3 mg, 0.345 mmol, 34.3 mol%) as well as B(C$_6$F$_5$)$_3$ (181 mg, 0.354 mmol, 35.2 mol%) in CH_2Cl_2 (3.0 ml) was prepared inside the glovebox. A solution of 4-allylanisole (149 mg, 1.01 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (453 mg, 1.02 mmol, 1.01 eq.) in CH_2Cl_2 (1.0 ml) was prepared inside the glovebox and transferred into a 25 ml Schlenk flask. The catalyst solution was added dropwise within 4 h via an oven-dried dropping funnel. The temperature was kept between 15-20 °C. Directly after the complete addition and after 23 h samples for NMR measurements were taken. A conversion of 41-55% conversion was observed for the later sample.

EXPERIMENT 7.2.3-J **MS 207**

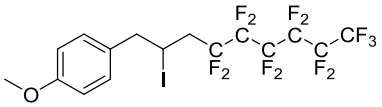
^{t}Bu$_3$P (14.6 mg, 0.0722 mmol, 10.6 mol%) and (2,3,6-trichlorophenyl)bis(2,3,6-trifluorophenyl)borane (33.4 mg, 0.0737 mmol, 10.3 mol%) were weighed out into a vial and then dissolved in CH_2Cl_2 (0.8 ml). 4-Allylanisole (106 mg, 0.715 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (269 mg, 0.778 mmol, 1.09 eq.) were weighed out into an amber glass screw-top vial, dissolved in CH_2Cl_2 (0.5 ml) and the catalyst solution was added. The vial was rinsed with CH_2Cl_2 (0.8 ml, overall 2.1 ml). After 6 d stirring at r.t. a sample for NMR measurements was taken inside the glovebox. No conversion was observed.

EXPERIMENT 7.2.3-K **MS 257 A**

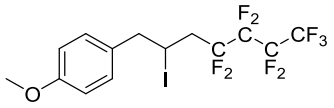
^{t}Bu$_3$P (14.9 mg, 0.0736 mmol, 10.1 mol%) and B(C_6F_5)$_3$ (39.2 mg, 0.0766 mmol, 10.5 mol%) were weighed out into a vial and then dissolved in CH_2Cl_2 (0.6 ml). 4-Allylanisole (108 mg, 0.729 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (320 mg, 0.718 mmol, 0.985 eq.) were weighed out into an amber glass screw-top vial, dissolved in CH_2Cl_2 (1.5 ml, overall 2.1 ml) and the catalyst solution was added. After stirring at r.t. inside the glovebox for 24 h and 7 d, respectively, samples for NMR measurements were withdrawn. A conversion of 43-46% was observed for the later sample.

EXPERIMENT 7.2.3-L **MS 257 B**

Analogous to experiment 7.2.4-a, ^{t}Bu$_3$P (14.8 mg, 0.0732 mmol, 9.95 mol%), 4-allylanisole (109 mg, 0.735 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (378 mg, 0.848 mmol, 1.15 eq.) were reacted. No conversion was observed.



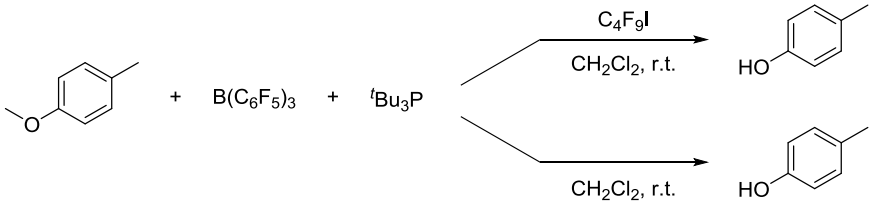
^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm] 7.16 – 7.09 (Ar−H, m, 2H), 6.92 – 6.85 (Ar−H, m, 2H), 4.43 (−CHI−, dq, J = 8.4, 6.4 Hz, 1H), 3.81 (−OMe, s, 3H), 3.28 – 3.10 (Ar−CH_2−, m, 2H), 2.99 – 2.76 (−CH_2−R_F, m, 2H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ [ppm] −80.9 (tt, J = 10.1, 2.6 Hz, 3F), −111.4 – −114.5 (m, 2F), −121.6 – −122.1 (m, 2F), −122.7 – −123.2 (m, 2F), −123.4 – −123.9 (m, 2F), −126.0 – −126.5 (m, 2F). **^{13}C NMR** (75 MHz, $CDCl_3$) δ [ppm] 159.0, 130.8, 130.2, 114.1, 55.4, 46.4, 40.8 (−$H_2C$$CF_2R_F$, t, $^2J_{CF}$ = 21.0 Hz), 20.4. **IR** (film on NaCl), $\tilde{\nu}$ [cm^{-1}] 3003, 2956, 2937, 2838, 1613, 1585, 1514, 1467, 1442, 1363, 1247, 1145, 1038, 840, 811, 734, 698, 657, 518. **Elemental analysis** for $C_{16}H_{12}F_{13}IO$, calculated: C = 32.34%, H = 2.04%, measured: C = 30.60%, H = 2.10%.



^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm] 7.18 – 7.07 (Ar−H, m, 2H), 6.94 – 6.82 (Ar−H, m, 2H), 4.43 (−CHI−,dq, *J* = 8.4, 6.4 Hz, 1H), 3.81 (−OMe, s, 3H), 3.28 – 3.08 (Ar−CH_2−, m, 2H), 3.01 – 2.73 (−CH_2−R_F, m, 2H). **^{19}F-NMR** (282 MHz, CDCl3) δ [ppm] −81.1 (tt, *J* = 9.7, 3.2 Hz, 3F), −111.6 – −114.7 (m, 2F), −124.5 – −124.7 (m), −125.8 – −126.0 (m, 2F). **^{13}C NMR** (75 MHz, $CDCl_3$) δ [ppm] 159.0, 130.8, 130.2, 114.1, 55.4, 46.4, 40.6 (−$H_2C$$CF_2R_F$, t, $^{2}J_{CF}$ = 20.9 Hz), 20.3. **IR** (film on NaCl), $\tilde{\nu}$ [cm^{-1}] 2838, 1613, 1585, 1514, 1467, 1442, 1351, 1246, 1135, 1037, 881, 832, 726, 518. ***m/z*** calculated for $C_{14}H_{13}F_9IO$ [M + H^+]: 494.9862, found: 494.9857.

This substance has been described in former publications,[37] but due to one missing signal at 100.1 ppm in the ^{13}C-NMR-spectrum and variations of multiplicities in the ^{1}H- as well as ^{19}F-NMR-spectra, a thorough examination was conducted.

7.2.4 4-Methylanisole



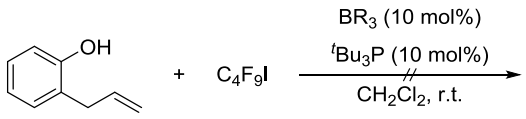
EXPERIMENT 7.2.4-A **MS 275 A**

$^{t}Bu_3P$ (72.3 mg, 0.357 mmol, 0.999 eq.) as well as $B(C_6F_5)_3$ (182 mg, 0.355 mmol, 0.994 eq.) were weighed out into an amber glass screw-cap vial and dissolved in CH_2Cl_2 (1.0 ml). 4-Methylanisole (43.7 mg, 0.358 mmol, 1.00 eq.) was weighed out into a vial, dissolved in CH_2Cl_2 (1.0 ml) and transferred to the catalyst solution. After 2 d and 13 d samples for a control by NMR spectroscopy was withdrawn. After 14 d desalinated water (0.05 ml) was added. Purification by column chromatography on SiO_2 (*n*-pentane:Et_2O = 84:16) yielded an odorous compound which was identified as 4-methylphenol.

EXPERIMENT 7.2.4-B **MS 275 B**

Analogous to experiment 7.2.4-a $^{t}Bu_3P$ (72.5 mg, 0.358 mmol, 0.992 eq.), $B(C_6F_5)_3$ (183 mg, 0.357 mmol, 0.990 eq.), 4-methylanisole (44.1 mg, 0.361 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (182 mg, 0.355 mmol, 0.994 eq.) were reacted. After 2 d and 13 d samples for a control by NMR spectroscopy was withdrawn. After 14 d desalinated water (0.05 ml) was added. Purification by column chromatography on SiO_2 (*n*-pentane:Et_2O = 84:16) yielded an odorous compound which was identified as 4-methylphenol.

7.2.5 2-Allyphenol



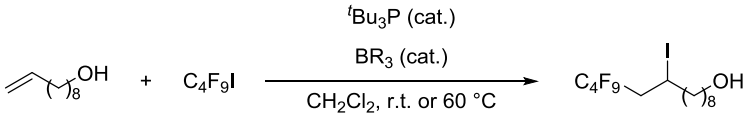
EXPERIMENT 7.2.5-A **MS 210 A**

^{t}Bu$_3$P (15.1 mg, 0.0746 mmol, 9.72 mol%) as well as B(C_6F_5)$_3$ (37.4 mg, 0.0504 mmol, 9.52 mol%) were weighed out into a vial and dissolved in CH_2Cl_2 (0.8 ml). 2-Allylphenol (103 mg, 0.768 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (292 mg, 0.844 mmol, 1.10 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (0.5 ml). Catalyst solution was transferred and the vial was rinsed with CH_2Cl_2 (0.8 ml, overall 2.1 ml). After 98 h a sample for NMR measurements was taken outside the glovebox. No conversion was observed.

EXPERIMENT 7.2.5-B **MS 210 B**

Analogous to experiment 7.2.5-b ^{t}Bu$_3$P (14.6 mg, 0.0722 mmol, 9.22 mol%); B(2,6-$F_2C_6H_3$)$_3$ (27.1 mg, 0.0774 mmol, 9.89 mol%), 2-allylphenol (105 mg, 0.783 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (294 mg, 0.850 mmol, 1.09 eq.) were reacted. After 98 h a sample for NMR measurements was taken outside the glovebox. No converson was observed.

7.2.6 9-Decen-1-ol



EXPERIMENT 7.2.6-A **MS 203 A**

^{t}Bu$_3$P (15.2 mg, 0.751 mmol, 9.93 mol%) as well as B(C_6F_5)$_3$ (37.1 mg, 0.0725 mmol, 9.58 mol%) were weighed out into an amber glass screw-cap vial, 4 Å molecular sieve (106 mg) and CH_2Cl_2 (1.0 ml) was added. 9-Decen-1-ol (119 mg, 0.757 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (340 mg, 0.983 mmol, 1.30 eq.) were weighed out into a vial, dissolved in CH_2Cl_2 and transferred into the catalyst solution (2.1 ml overall). After 75 h a sample for NMR measurements was taken inside the glovebox. No conversion was observed.

EXPERIMENT 7.2.6-B **MS 211 A**

^{t}Bu$_3$P (15.2 mg, 0.0751 mmol, 10.3 mol%) as well as B(2,6-$F_2C_6H_3$)$_3$ (26.4 mg, 0.0754 mmol, 10.3 mol%) were weighed out into a vial and dissolved in CH_2Cl_2 (0.8 ml). 9-Decen-1-ol (115 mg, 0.731 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (275 mg, 0.795 mmol, 1.09 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (0.5 ml). Catalyst solution was transferred and the vial was rinsed with CH_2Cl_2 (0.8 ml, overall 2.1 ml). After 44 h a sample for NMR measurements was taken inside the glovebox. No conversion was observed.

EXPERIMENT 7.2.6-C **MS 211 B**

Analogous to experiment 7.2.6-b $^{t}Bu_3P$ (15.1 mg, 0.0746 mmol, 9.95 mol%), $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ (36.2 mg, 0.0798 mmol, 10.6 mol%), 9-decen-1-ol (118 mg, 0.750 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (268 mg, 0.775 mmol, 1.03 eq.) were reacted. After 18 h and 14 d, respectively, samples for NMR measurements were taken inside the glovebox. A purification by column chromatography (CH_2Cl_2:MeOH = 99:1) yielded a mixture of educt and product. A corrected yield was calculated.

yield (502.20 g·mol^{-1}) 60 mg(0.12 mmol, 16%)

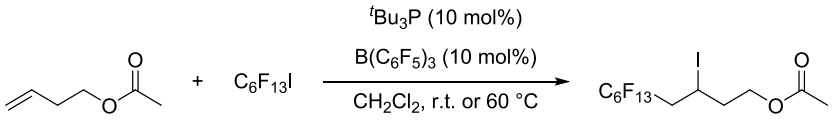
EXPERIMENT 7.2.6-D **MS 211 C**

$^{t}Bu_3P$ (29.1 mg, 0.144 mmol, 9.88 mol%), $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ (32.5 mg, 0.0717 mmol, 4.92 mol%), 9-decen-1-ol (229 mg, 1.46 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (502 mg, 1.45 mmol, 0.997 eq.) were weighed out into a vial, dissolved in CH_2Cl_2 (4.2 ml) and transferred into a sealed flask. After stirring at 60 °C for 24 h, a sample for NMR measurements was taken outside the glovebox under inert conditions. The solution was stirred at r.t. for additional 5 d. A purification by column chromatography (CH_2Cl_2:MeOH = 100:0.5) yielded mainly pure product (280 mg, 0.556 mmol, 38%) as well as a mixture of educt and product (corrected yield: 90 mg, 0.18 mmol, 12%).

yield (502.20 g·mol^{-1}) 0.37 g(0.74 mmol, 50%)

^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm] 4.28 – 4.14 (m, 1H), 3.54 (t, J = 6.6 Hz, 2H), 2.96 – 2.53 (m, 2H), 1.80 – 1.57 (m, 2H), 1.54 – 1.38 (m, 4H), 1.36 – 1.14 (m, 11H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ [ppm] −81.06 (tt, J = 9.7, 3.3 Hz, 3F), −111.35 – −115.53 (m, 2F), −124.44 – −124.72 (m, 2F), −125.74 – −126.09 (m, 2F). **^{13}C NMR** (75 MHz, $CDCl_3$) δ [ppm] 63.1, 41.7 ($-H_2CCF_2R_F$, t, $^{2}J_{CF}$ = 20.8 Hz), 40.4, 32.9, 29.7, 29.4, 29.4, 28.5, 25.8, 20.9. Analytic data are consistent with the literature-known data.[35]

7.2.7 3-Butenyl acetate



EXPERIMENT 7.2.7-A **MS 158**

$^{t}Bu_3P$ (16.2 mg, 0.0801 mmol, 10.0 mol%), $B(C_6F_5)_3$ (41.7 mg, 0.0814 mmol, 10.2 mol%), 3-butenyl acetate (91.4 mg, 0.801 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (357 mg, 0.801 mmol, 1.00 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2 ml). The resulting solution was stirred at r.t. sealed with a Teflon-insert screw cap. After 5 d and 14 d, respectively, samples for controls by NMR spectroscopy were taken outside

the glovebox under N_2 counterflow. After 34 d most of the solvent was evaporated and by column chromatography on SiO_2 (cyclohexane:CH_2Cl_2 = 65:35) pure product was yielded.

yield (560.09 g·mol^{-1}): 331 mg (0.591 mmol, 74%)

EXPERIMENT 7.2.7-B **MS 158W A**

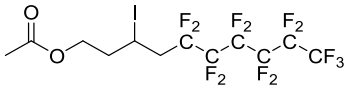
^{t}Bu$_3$P (16.7 mg, 0.0825 mmol, 10.5 mol%), B(C_6F_5)$_3$ (40.9 mg, 0.0799 mmol, 10.2 mol%), 3-butenyl acetate (89.9 mg, 0.786 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (357 mg, 0.801 mmol, 1.02 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2.5 ml). The resulting solution was stirred at r.t. sealed with a Teflon-insert screw cap inside the glovebox. After 44 h and 6 d, respectively, samples for controls by NMR spectroscopy were taken inside the glovebox. The reaction solution was then transferred into a transparent screw-top vial. After 12 d, 21 d and 35 d, respectively, samples for controls by NMR spectroscopy were taken inside the glovebox. Most of the solvent was evaporated and by column chromatography on SiO_2 (cyclohexane:CH_2Cl_2 = 65:35) pure product was yielded.

yield (560.09 g·mol^{-1}): 333 mg (0.595 mmol, 76%)

EXPERIMENT 7.2.7-C **MS 158W B**

^{t}Bu$_3$P (33.7 mg, 0.167 mmol, 10.3 mol%), B(C_6F_5)$_3$ (83.5 mg, 0.163 mmol, 10.1 mol%), 3-butenyl acetate (184 mg, 1.61 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (726 mg, 1.63 mmol, 1.01 eq.) were weighed out into a screw-top vial and then dissolved in CH_2Cl_2 (5 ml). The resulting solution was transfered into a 50 ml sealed flask and heated to 60 °C with an oil bath. After 24 h, 69 h and 134 h, respectively, samples for a control by NMR spectroscopy were taken in N_2-counterflow. Most of the solvent was evaporated and by column chromatography on SiO_2 (cyclohexane:CH_2Cl_2 = 65:35) slightly impure product was yielded.

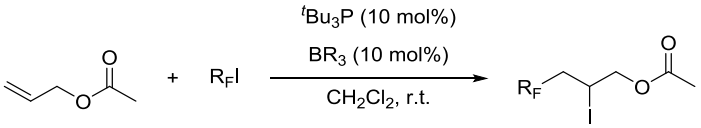
yield (560.09 g·mol^{-1}): 0.67 g (1.2 mmol, 74%)



^{1}H-NMR (600 MHz, $CDCl_3$) δ [ppm] 4.45 – 4.36 (−CH_2CO_2−, m, 1H), 4.35 – 4.27 (−CHI−, m, 1H), 4.21 – 4.10 (−CH_2CO_2−, m, 1H), 3.03 – 2.90 (R_FCH_2−, m, 1H), 2.90 – 2.76 (R_FCH_2−, m, 1H), 2.22 – 2.14 (−CH_2CH_2−, m, 1H), 2.14 – 2.07 (−CH_2CH_2−, m, 1H), 2.08 – 2.02 (−CH_3, m, 3H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ [ppm] −80.8 (tt, J = 10.1, 2.6 Hz, 3F), −110.9 – −115.1 (m, 2F), −121.6 – −122.0 (m, 2F), −122.7 – −123.1 (m, 2F), −123.5 – −123.9 (m, 2F), −126.0 – −126.4 (m, 2F). **^{13}C NMR** (151 MHz, $CDCl_3$) δ [ppm] 170.8, 119.7, 118.0, 116.3, 112.7, 111.1, 108.7, 64.2, 42.0 (−$H_2CCF_2R_F$, t, $^2J_{CF}$ = 20.8 Hz), 39.0, 20.9, 15.3. **IR** (film on NaCl), $\tilde{\nu}$ [cm^{-1}]

2962, 1747, 1433, 1366, 1237, 1042, 845, 812, 733, 699, 657, 606, 553, 530. ***m/z*** calculated for $C_{12}H_{11}F_{13}IO_2$ [M + H$^+$] = 560.9591, found 560.9593.

7.2.8 Allyl acetate



EXPERIMENT 7.2.8-A **MS 167**

^{t}Bu$_3$P (16.7 mg, 0.0825 mmol, 9.18 mol%), B(C$_6$F$_5$)$_3$ (41.0 mg, 0.0801 mmol, 8.91 mol%), allyl acetate (90.0 mg, 0.899 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (405 mg, 908 mmol, 1.01 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2.5 ml, 0.4 M). After 5 d and 13 d, respectively, samples for a control by NMR spectroscopy were taken in N_2-counterflow. Most of the solvent was evaporated and by column chromatography (*n*-pentane:CH_2Cl_2 = 80:20) pure product was yielded.

yield (546.07 g·mol^{-1}): 74.5 mg (0.136 mmol, 15%)

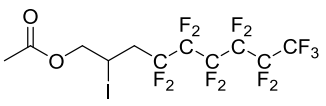
EXPERIMENT 7.2.8-B **MS 173 A**

^{t}Bu$_3$P (16.4 mg, 0.0811 mmol, 9.66 mol%), B(C$_6$F$_5$)$_3$ (42.2 mg, 0.0824 mmol, 9.82 mol%), nonafluoro-1-iodobutane (282 mg, 0.815 mmol, 0.972 eq.) and allyl acetate (84.0 mg, 0.839 mmol, 1.00 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2.5 ml, 0.3 M). After 3, 7, 18 and 25 d, respectively, samples for a control by NMR spectroscopy were taken inside the glovebox. After 35 d, most of the solvent was removed and by column chromatography on SiO_2 (*n*-pentane:CH_2Cl_2 = 80:20) pure product was yielded.

yield (446.05 g·mol^{-1}): 92.2 mg (0.207 mmol, 25%)

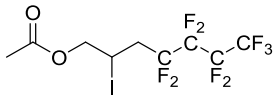
EXPERIMENT 7.2.8-C **MS 173 B**

^{t}Bu$_3$P (17.1 mg, 0.0845 mmol, 10.9 mol%), B(2,6-F$_2$C$_6$H$_3$)$_3$ (28.1 mg, 0.0803 mmol, 10.4 mol%), nonafluoro-1-iodobutane (293 mg, 0.847 mmol, 1.10 eq.) and allyl acetate (77.4 mg, 0.773 mmol, 1.00 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2.5 ml, 0.3 M). After 3, 7, 18 and 25 d, respectively, samples for a control by NMR spectroscopy were taken inside the glovebox. No conversion was detected.



^{1}H-NMR (300 MHz, C_6D_6) δ [ppm] 4.03 – 3.79 (−CHI− + R_FCH_2−, m, 3H), 2.61 –2.26 (−CH_2CO_2−, m, 2H), 1.57 (−CH_3, s, 3H). **^{19}F-NMR** (282 MHz, C_6D_6) δ [ppm] −81.1 (tt, *J* = 10.0, 2.5 Hz, 3F), −112.2 – −114.6 (m, 2F), −121.7 – −122.0 (m, 2F), −122.7 – −123.1 (m, 2F),

−123.4 – −123.7 (m, 2F), −126.1 – −126.4 (m, 2F). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] 169.1, 128.1, 68.4, 38.1 (−H_2*C*CF_2R_F, t, $^2J_{CF}$ = 21.4 Hz), 20.0, 12.1. **IR** (film on NaCl), $\tilde{\nu}$ [cm^{-1}] 2958,1749, 1433, 1364, 1238, 1145, 1047, 977, 734, 708, 698, 658. ***m/z*** calculated for $C_{11}H_8F_{13}INaO_2$ [M + Na$^+$] = 568.9254, found 568.9256.



^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm] 3.98 – 3.79 (−CHI− + R_FCH_2−, m, 3H), 2.57 – 2.22 (−CH_2CO_2−, m, 2H), 1.56 (−CH_3, s, 3H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ [ppm] −81.0 – −81.3 (m, 3F), −112.4 – −114.8 (m, 2F), −124.2 – −124.5 (m, 2F), −125.7 – −126.1 (m, 2F). **^{13}C NMR** (75 MHz, C_6D_6) δ [ppm] 169.1, 68.4, 37.9 (−H_2*C*CF_2R_F, t, $^2J_{CF}$ = 21.2 Hz), 20.0, 12.0. **IR** (film on NaCl), $\tilde{\nu}$ [cm^{-1}] 2958, 1750, 1432, 1382, 1356, 1233, 1135, 1043, 1026, 881, 739, 725. ***m/z*** calculated for $C_9H_8F_9INaO_2$ [M + Na$^+$] = 468.9318, found 468.9316.

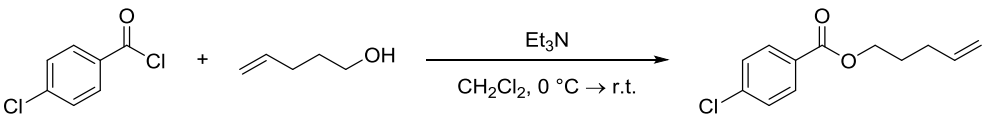
STANDARD PROCEDURE A

Inside the glovebox, ^{t}Bu$_3$P and if applicable $B(C_6F_5)_3$ were weighed into a glass vial and then dissolved in CH_2Cl_2 (1.7 ml). The alkene as well as C_4F_9I were weighed into an amber glass screw-cap vial and were then dissolved in CH_2Cl_2 (0.40 ml). The catalyst solution was transferred to the alkene. The resulting solution was sealed with a Teflon insert screw cap and stirred at r.t.

STANDARD PROCEDURE B

Inside the glovebox, ^{t}Bu$_3$P and if applicable $B(C_6F_5)_3$ were weighed into a glass vial and then dissolved in CH_2Cl_2 (0.9 ml). The alkene was weighed into another glass vial, which was placed inside an amber glass screw-cap vial. The catalyst solution was transferred to the alkene and C_4F_9I was added via Hamilton syringe. The resulting solution was sealed with a Teflon insert screw cap and stirred at r.t.

7.2.9 Pent-4-en-1-yl 4-chlorobenzoate



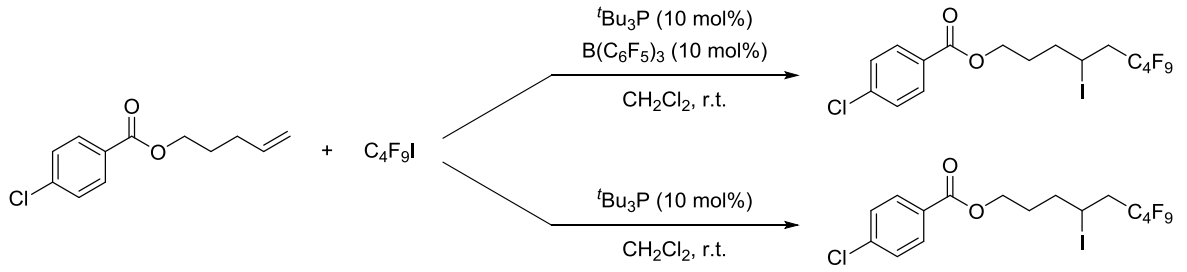
EXPERIMENT 7.2.9-A **MS 220**

The synthesis of pent-4-en-1-yl 4-chlorobenzoate was conducted similar to a literature-known procedure.[37] A solution of 4-chlorobenzoyl chloride (3.50 g, 20.0 mmol, 1.00 eq.) in CH_2Cl_2 (30 ml) was cooled with an ice bath. Pent-4-en-1-ol (1.72 g, 20.0 mmol, 1.00 eq.) was added in one portion, followed by dropwise addition of Et_3N (4.2 ml, 30 mmol, 1.5 eq.). The cooling bath was removed and the white suspension was stirred at r.t. for 20 h. After addition of desalinated

water (15 ml) and brine (1 ml), phases were separated. The organic layer was washed with brine (2 x 10 ml) and then dried with Na_2SO_4. After removal of all volatiles, purification by column chromatography on SiO_2 (*n*-hexane:EtOAc = 98:2) yielded pure product.

yield (224.68 g·mol^{-1}) 4.02 g (17.9 mmol, 89%)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.45 – 7.38 (m, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.13 – 4.95 (m, 2H), 4.33 (t, *J* = 6.6 Hz, 2H), 2.29 – 2.13 (m, 2H), 1.97 – 1.77 (m, 2H). Analytic data are consistent with literature-known values.[111]



EXPERIMENT 7.2.9-B **MS 259 A**

Following STANDARD PROCEDURE A, ^{t}Bu$_3$P (14.6 mg, 0.0722 mmol, 9.83 mol%), $B(C_6F_5)_3$ (37.3 mg, 0.0729 mmol, 9.92 mol%), pent-4-en-1-yl 4-chlorobenzoate (165 mg, 0.734 mmol, 1.00 eq.) and C_4F_9I (256 mg, 0.740 mmol, 1.01 eq.) were reacted. After 24 h the reaction was quenched by additon of desalinated water (10 µl) and a sample was withdrawn for a control by NMR spectroscopy. Purification by column chromatography on SiO_2 (*n*-pentane:Et_2O = 98:2) yielded pure iodoperfluoroalkylation product.

yield (570.62 g·mol^{-1}) 364 mg (0.638 mmol, 87%)

EXPERIMENT 7.2.9-C **MS 259 B**

Following STANDARD PROCEDURE A, ^{t}Bu$_3$P (14.8 mg, 0.0732 mmol, 9.96 mol%), pent-4-en-1-yl 4-chlorobenzoate (165 mg, 0.734 mmol, 1.00 eq.) and C_4F_9I (263 mg, 0.760 mmol, 1.04 eq.) were reacted. After 24 h the reaction was quenched by additon of desalinated water (10 µl) and a sample was withdrawn for a control by NMR spectroscopy. A conversion of ≈ 30% was observed.

EXPERIMENT 7.2.9-D **MS 232 A**

Analogous to STANDARD PROCEDURE A, ^{t}Bu$_3$P (10.0 mg, 0.0494 mmol, 10.0 mol%), $B(2,3,6\text{-}Cl_3C_6H_2)_2(2,3,6\text{-}F_3C_6H_2)$ (23.8 mg, 0.0525 mmol, 10.6 mol%), pent-4-en-1-yl 4-chlorobenzoate (111 mg, 0.494 mmol, 1.00 eq.) and C_4F_9I (171 mg, 0.494 mmol, 1.00 eq.) were reacted in CH_2Cl_2 (1.4 ml). After 27 h and 12 d a sample was withdrawn for a control by NMR spectroscopy. Purification by column chromatography on SiO_2 (*n*-pentane:Et_2O = 98.3:1.7)

yielded pure iodoperfluoroalkylation product (37.8 mg) as well as educt (67.2 mg, 0.299 mmol, 61%).

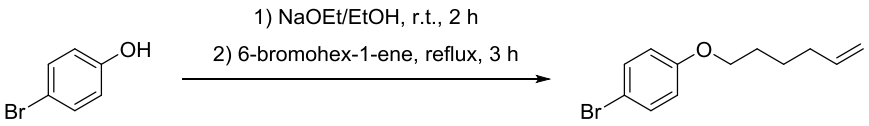
yield (570.62 g·mol^{-1}) 37.8 mg (0.0662 mmol, 13%)

EXPERIMENT 7.2.9-E **MS 232 B**

Analogous to STANDARD PROCEDURE A, $^{t}Bu_3P$ (10.3 mg, 0.0509 mmol, 10.3 mol%), $B(2,6\text{-}F_2C_6H_3)_3$ (18.2 mg, 0.0520 mmol, 10.5 mol%), pent-4-en-1-yl 4-chlorobenzoate (111 mg, 0.494 mmol, 1.00 eq.) and C_4F_9I (186 mg, 0.538 mmol, 1.09 eq.) were reacted in CH_2Cl_2 (1.4 ml). After 27 h and 12 d, respectively, a sample was withdrawn for a control by NMR spectroscopy. A conversion of ≈ 19% was observed for the later sample.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.47 – 7.38 (m, 2H), 4.46 – 4.32 (m, 3H), 3.09 – 2.69 (m, 2H), 2.14 – 1.84 (m, 3H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ −81.1 (tt, J = 9.7, 3.3 Hz), −111.1 – −112.4 (m), −114.4 – −115.5 (m), −124.4 – −124.8 (m), −125.7 – −126.2 (m). Analytic data are consistent with literature-known values.[37]

7.2.10 1-Bromo-4-(hex-5-en-1-yloxy)benzene

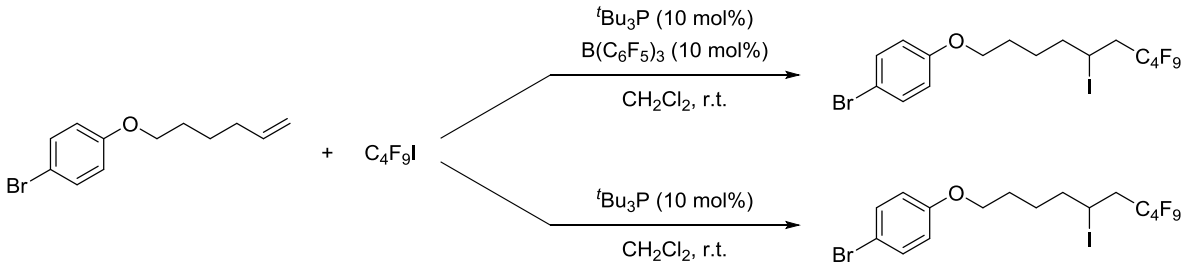


EXPERIMENT 7.2.10-A **MS 225**

The synthesis of pent-4-en-1-yl 4-chlorobenzoate was conducted similar to a literature-known procedure.[37] Sodium (0.76 g, 33 mmol, 1.5 eq.) was dissolved in dry EtOH (20 ml) and then 4-bromophenol (3.8 g, 22 mmol, 1.0 eq.) was added. After stirring at r.t. for 2 h, 6-bromohex-1-ene (45 w%, mixture with $HCBr_3$, 3.9 g, 24 mmol, 1.1 eq.) was added and the solution was refluxed for 3 h. After stirring for additional 14 h at r.t. the yellow suspension was filtered and all volatiles were removed. The solid was dissolved in EtOAc (50 ml) and the resulting organic phase was washed with a mixture of desalinated water and brine (4:1, 25 ml) as well as solely brine (5 ml). It was dried with Na_2SO_4. After removal of all volatiles, purification by column chromatography on SiO_2 (*n*-hexane → *n*-hexane:EtOAc = 97:3) gave pure product.

yield (255.16 g·mol^{-1}) 3.60 g (14 mmol, 64%)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 6.82 – 6.72 (m, 2H), 5.83 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.09 – 4.93 (m, 2H), 3.93 (t, J = 6.4 Hz, 2H), 2.19 – 2.06 (m, 2H), 1.86 – 1.71 (m, 2H), 1.63 – 1.49 (m, 2H). Analytic data are consistent with literature-known values.[37]



EXPERIMENT 7.2.10-B **MS 351**

Following STANDARD PROCEDURE A, $^{t}Bu_3P$ (14.9 mg, 0.0736 mmol, 10 mol%), $B(C_6F_5)_3$ (37.4 mg, 0.0738 mmol, 10 mol%), 1-bromo-4-(hex-5-en-1-yloxy)benzene (186 mg, 0.729 mmol, 1.00 eq.) and C_4F_9I (251 mg, 0.726 mmol, 0.996 eq.) were reacted. After 24 a sample was withdrawn for a control by NMR spectroscopy outside the glovebox. Purification by column chromatography on SiO_2 (*n*-hexane:EtOAc = 99:1, twofold *n*-pentane:Et_2O = 99:1) yielded pure iodoperfluoroalkylation product.

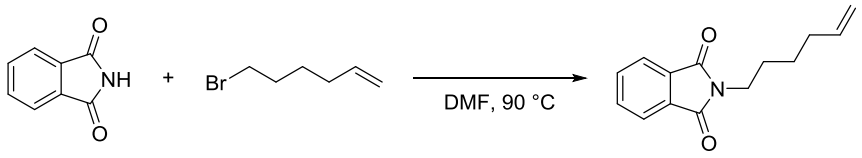
yield (601.09 g·mol^{-1}) 349 mg (0.581 mmol, 80%)

EXPERIMENT 7.2.10-C **MS 260 B**

Following STANDARD PROCEDURE A, $^{t}Bu_3P$ (14.7 mg, 0.0727 mmol, 9.86 mol%), 1-bromo-4-(hex-5-en-1-yloxy)benzene (188 mg, 0.737 mmol, 1.00 eq.) and C_4F_9I (257 mg, 0.743 mmol, 1.010 eq.) were reacted. After 3 d a sample for a control by NMR spectroscopy was withdrawn outside the glovebox. A conversion < 10% was observed.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 2H), 6.81 – 6.73 (m, 2H), 4.35 (tt, *J* = 8.2, 5.3 Hz, 1H), 3.95 (t, *J* = 6.0 Hz, 2H), 3.07 – 2.66 (m, 2H), 1.98 – 1.68 (m, 5H), 1.68 – 1.54 (m, 1H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ −81.0 (tt, *J* = 9.6, 3.3 Hz), −111.2 – −113.0 (m), −113.6 – −116.1 (m), −124.3 – −124.8 (m), −125.7 – −126.1 (m). Analytic data are consistent with literature-known values.[37]

7.2.11 2-(Hex-5-en-1-yl)isoindoline-1,3-dione



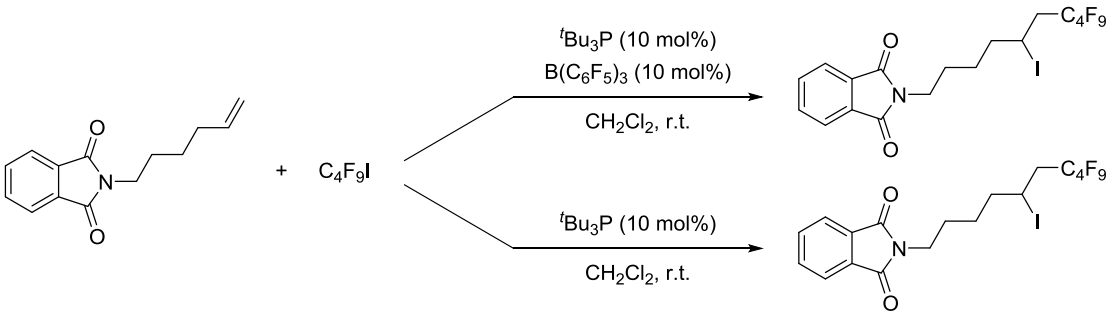
EXPERIMENT 7.2.11-A **MS 333**

The synthesis of 2-(hex-5-en-1-yl)isoindoline-1,3-dione was conducted similar to a literature-known procedure.[37] 6-Bromohexene (3.45 g, 21.2 mmol, 1.00 eq.) was dissolved in dry DMF (23 ml). Phthalimide potassium salt (4.34 g, 23.4 mmol, 1.11 eq.) was added in N_2 counterflow and the solution was heated to 90 °C for 21 h. The reaction solution was rinsed into desalinated water (75 ml), followed by afterwashing with CH_2Cl_2 (50 ml). The phases were separated and the

aqueous phase was extracted with CH_2Cl_2 (1 x 50 ml, 2 x 30 ml). Combined organic layers were washed with aq. KOH (0.2 M, 100 ml) as well as a mixture of brine and desalinated water (1:1, 50 ml) and then dried with Na_2SO_4. After removal of all volatiles, purification by column chromatography on SiO_2 (*n*-hexane:EtOAc = 90:10) yielded pure product.

yield (229.28 g·mol^{-1}) 3.08 g (13.4 mmol, 63%)

^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.72 – 7.64 (m, 2H), 5.75 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.98 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.95 – 4.88 (m, 1H), 3.67 (t, *J* = 7.3 Hz, 2H), 2.12 – 2.02 (m, 2H), 1.72 – 1.62 (m, 2H), 1.47 – 1.37 (m, 2H). Analytic data are consistent with literature-known values.[112]



EXPERIMENT 7.2.11-B **MS 341 A**

Following STANDARD PROCEDURE B, ^{t}Bu$_3$P (8.3 mg, 0.041 mmol, 10 mol%), $B(C_6F_5)_3$ (20.7 mg, 0.040 mmol, 9.89 mol%), 2-(hex-5-en-1-yl)isoindoline-1,3-dione (93.5 mg, 0.408 mmol, 1.00 eq.) and C_4F_9I (70.0 µl, 0.407 mmol, 0.997 eq.) were reacted. After 24 a sample was withdrawn for a control by NMR spectroscopy outside the glovebox. Purification by column chromatography on SiO_2 (*n*-hexane:EtOAc = 93:7) yielded pure iodoperfluoroalkylation product (135 mg).

yield (575.21 g·mol^{-1}) 135 mg (0.235 mmol, 58%)

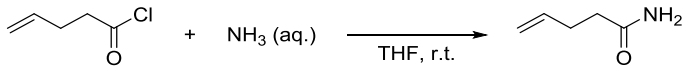
EXPERIMENT 7.2.11-C **MS 341 B**

Following STANDARD PROCEDURE B, ^{t}Bu$_3$P (8.3 mg, 0.041 mmol, 10 mol%), 2-(hex-5-en-1-yl)isoindoline-1,3-dione (93.3 mg, 0.407 mmol, 1.00 eq.) and C_4F_9I (70.0 µl, 0.407 mmol, 1.00 eq.) were reacted. After 24 a sample for a control by NMR spectroscopy was withdrawn outside the glovebox. A conversion of 28-37% was observed.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.77 (m, 2H), 7.77 – 7.67 (m, 2H), 4.30 (tt, *J* = 8.1, 5.3 Hz, 1H), 3.71 (t, *J* = 7.1 Hz, 2H), 3.06 – 2.64 (m, 1H), 1.93 – 1.57 (m, 3H), 1.53 – 1.40 (m, 1H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ −81.01 (tt, *J* = 9.7, 3.3 Hz), −111.01 – −112.75 (m), −114.04 – −115.89 (m), −124.23 – −124.79 (m), −125.40 – −126.64 (m).

Analytic data are consistent with literature-known values.[37]

7.2.12 Pent-4-enamide

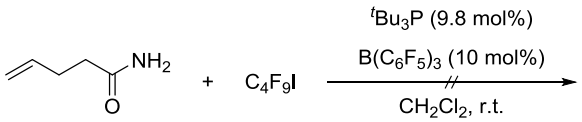


EXPERIMENT 7.2.12-A **MS 316**

The synthesis of pent-4-enamide was conducted similar to a literature-known procedure.[113] A mixture of THF (64 ml) and aqueous ammonia (63 ml, 25 w%, 0.82 mol, 26 eq.) was cooled with an ice bath. To this solution pent-4-enoyl chloride (3.70 g, 31.2 mmol, 1.00 eq.) was added and the cooling bath was removed afterwards. The resulting two phase system was stirred vigorously for 18 h. THF was removed by at a rotary evaporator, giving a single-phase system, which was diluted with desalinated water (20 ml) and then extracted with EtOAc (3 x 60 ml). The organic phase was washed with brine (50 ml). Due to an incomplete extraction (TLC), the combined aqueous layers were extracted with EtOAc (2 x 40 ml) once more. After removal of all volatiles from the combined aqueous layers, the resulting solid was diluted in desalinated water (60 ml) and then an extraction with EtOAc (3 x 30 ml) was conducted. Combined organic layers were washed with brine (30 ml) and then dried with $MgSO_4$. After removal of all volatiles, the white residue was dissolved in EtOAc (50 ml), the resulting suspension washed with brine (15 ml) and then $MgSO_4$ was used to dry the organic phase. After removal of all volatiles, a white solid was obtained.

yield (99.13 g·mol^{-1})	2.76 g (27.8 mmol, 89%)

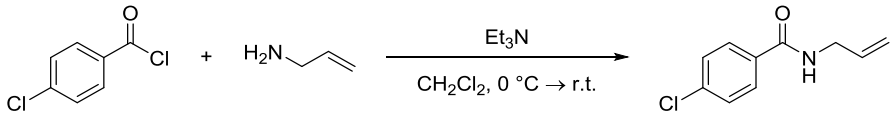
^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.85 (ddt, *J* = 17.2, 10.2, 6.3 Hz, 1H), 5.59 (s, 2H), 5.10 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.06 – 5.01 (m, 1H), 2.47 – 2.29 (m, 4H). Analytic data are consistent with literature-known values.[114]



EXPERIMENT 7.2.12-B **MS 321**

Inside the glovebox, ^{t}Bu$_3$P (8.4 mg, 0.042 mmol, 9.8 mol%), $B(C_6F_5)_3$ (22.6 mg, 0.044 mmol, 10 mol%) as well as pent-4-enamide (42.1 mg, 0.407 mmol, 1.00 eq.) were weighed into a glass vial and dissolved in CH_2Cl_2 (1.2 ml). The vial was put into an amber glass screw-cap vial and nonafluoro-1-iodobutane (70.0 µl, 0.408 mmol, 0.958 eq.) was added with a syringe. After stirring for 24 h, a sample for NMR measurements was taken outside the glovebox. No conversion was observed.

7.2.13 *N*-Allyl-4-chlorobenzamide

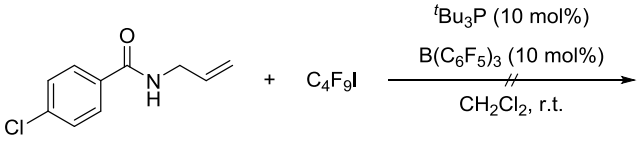


EXPERIMENT 7.2.13-A **MS 261**

The synthesis of *N*-allyl-4-chlorobenzamide was conducted similar to a literature-known procedure. 4-Chlorobenzoyl chloride (2.6 ml, 20 mmol, 1.0 eq) was dissolved in dry CH_2Cl_2 (15 ml) and was cooled with an ice bath. Prop-2-en-1-amine (1.4 ml, 19 mmol, 0.93 eq.) and Et_3N (2.8 ml, 20 mmol, 1.0 eq.) were dissolved in CH_2Cl_2 (2.0 ml) in a separate flask. This solution was added to the cooled 4-chlorobenzoyl chloride solution dropwise within 5 min. The cooling bath was removed afterwards. After 21 h the reaction was quenched by addition of desalinated water (15 ml). Phases were separated and the organic phase was extracted with CH_2Cl_2 (15 ml). Combined organic phases were washed with brine (5 ml) and then dried with Na_2SO_4. After removal of all volatiles, the product was isolated by column chromatography on SiO_2 (*n*-hexane:EtOAc = 78:22) in pure form.

yield (195.65 g·mol^{-1}) 3.50 g (17.9 mmol, 94%)

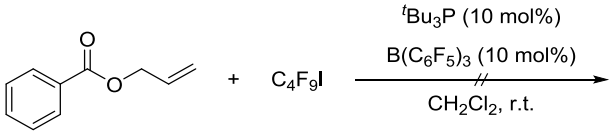
^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.72 (m, 2H), 7.40 (m, 2H), 6.25 (bs, 1H), 5.93 (ddt, *J* = 17.1, 10.2, 5.7 Hz, 1H), 5.25 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.19 (dq, *J* = 10.2, 1.4 Hz, 1H), 4.07 (tt, *J* = 5.7, 1.6 Hz, 2H). Analytic data are consistent with literature-known values.[115]



EXPERIMENT 7.2.13-B **MS 323**

Inside the glovebox, ^{t}Bu$_3$P (8.3 mg, 0.041 mmol, 10 mol%), B(C_6F_5)$_3$ (26.5 mg, 0.052 mmol, 13 mol%) as well as *N*-allyl-4-chlorobenzamide (79.7 mg, 0.407 mmol, 1.00 eq.) were weighed into a glass vial and dissolved in CH_2Cl_2 (1.2 ml). The vial was put into an amber glass screw-cap vial and nonafluoro-1-iodobutane (70.0 µl, 0.408 mmol, 1.01 eq.) was added with a syringe. After stirring for 24 h, a sample for NMR measurements was taken outside the glovebox. No conversion was observed.

7.2.14 Allyl benzoat



EXPERIMENT 7.2.14-A **MS 326**

Inside the glovebox, ^{t}Bu$_3$P (8.6 mg, 0.043 mmol, 10 mol%), B(C_6F_5)$_3$ (21.1 mg, 0.041 mmol, 10 mol%) as well as allyl benzoate (66.1 mg, 0.408 mmol, 1.00 eq.) were weighed into a glass vial and dissolved in CH_2Cl_2 (1.2 ml). The vial was put into an amber glass screw-cap vial and nonafluoro-1-iodobutane (70.0 µl, 0.408 mmol, 1.00 eq.) was added with a syringe. After stirring for 24 h, a sample for NMR measurements was taken outside the glovebox. No conversion was observed.

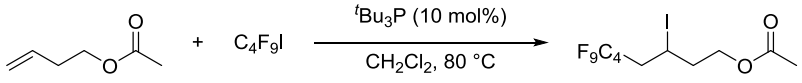
7.3 High Temperature Reactions

For the following experiments, Ace pressure tubes (L x O.D. = 102 × 25.4 mm) with a front seal (FETFE®) were used. Tests regarding the buildup of pressure at elevated temperatures showed pressures below 4 bar at 100 °C with 3 ml CH_2Cl_2 in a 20 ml pressure reactor.

STANDARD PROCEDURE C

^{t}Bu$_3$P and if appropriate BR_3 were weighed into a glass vial and then dissolved in CH_2Cl_2 (1.0 ml) inside the glovebox. An alkene was weighed into a separate vial, dissolved in CH_2Cl_2 (1.0 ml) and then transferred into a pressure tube followed by the catalyst solution. C_4F_9I (85.0 µL, 0.494 mmol, 0.997 eq.) was added with a Hamilton syringe directly into the pressure tube. Outside the glovebox the reaction solution was heated to 80 °C in an oil bath. After 24 h the reaction solution was cooled with an ice bath and a sample for NMR measurements was withdrawn.

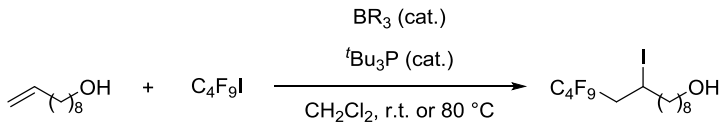
7.3.1 3-Butenyl acetate



EXPERIMENT 7.3.1-A **MS 337 B**

According to STANDARD PROCEDURE C, ^{t}Bu$_3$P (10.2 mg, 0.050 mmol, 10 mol%), 3-butenyl acetate (56.7 mg, 0.497 mmol, 1.00 eq.) and C_4F_9I (0.995 eq.) were reacted. A conversion of 82-89% was observed.

7.3.2 9-Decen-1-ol



EXPERIMENT 7.3.2-A **MS 336 B**

According to STANDARD PROCEDURE C, ^{t}Bu$_3$P (10.1 mg, 0.050 mmol, 10 mol%), B(C$_6$F$_5$)$_3$ (26.1 mg, 0.051 mmol, 10 mol%), 9-decen-1-ol (77.4 mg, 0.495 mmol, 1.00 eq.) and C$_4$F$_9$I (0.997 eq.) were reacted. A conversion of 70-78% was observed.

EXPERIMENT 7.3.2-B **MS 336 A**

According to STANDARD PROCEDURE C, ^{t}Bu$_3$P (10.1 mg, 0.050 mmol, 10 mol%), B(2,3,6-Cl$_3$C$_6$H$_2$)(2,3,6-F$_3$C$_6$H$_2$)$_2$ (23.0 mg, 0.051 mmol, 10 mol%), 9-decen-1-ol (77.6 mg, 0.497 mmol, 1.00 eq.) and C$_4$F$_9$I (0.995 eq.) were reacted. A conversion of 68-78% was observed.

EXPERIMENT 7.3.2-C **MS 337 A**

According to STANDARD PROCEDURE C, ^{t}Bu$_3$P (10.2 mg, 0.050 mmol, 10 mol%), 9-decen-1-ol (77.6 mg, 0.497 mmol, 1.00 eq.) and C$_4$F$_9$I (0.994 eq.) were reacted. A conversion of 76-81% was observed.

EXPERIMENT 7.3.2-D **MS 338 A**

Analogous to STANDARD PROCEDURE C, ^{t}Bu$_3$P (10.3 mg, 0.0509 mmol, 10 mol%), 9-decen-1-ol (77.2 mg, 0.494 mmol, 1.00 eq.) and C$_4$F$_9$I.(1.00 eq.) were reacted. After 3 h the reaction solution was cooled with an ice bath and a sample for NMR measurements was withdrawn. A conversion of 55-59% was observed.

EXPERIMENT 7.3.2-E **MS 338 B**

Analogous to STANDARD PROCEDURE C, ^{t}Bu$_3$P (10.2 mg, 0.0504 mmol, 10 mol%), B(C$_6$F$_5$)$_3$ (25.5 mg, 0.0498 mmol, 10 mol%), 9-decen-1-ol (77.5 mg, 0.498 mmol, 1.00 eq.) and C$_4$F$_9$I (0.996 eq.) were reacted. After 3 h the reaction solution was cooled with an ice bath and a sample for NMR measurements was withdrawn. A conversion of 30-31% was observed.

EXPERIMENT 7.3.2-F **MS 338 C**

Analogous to STANDARD PROCEDURE C, ^{t}Bu$_3$P (10.1 mg, 0.0499 mmol, 10 mol%), B(2,3,6-Cl$_3$C$_6$H$_2$)(2,3,6-F$_3$C$_6$H$_2$)$_2$ (23.4 mg, 0.0516 mmol, 10 mol%), 9-decen-1-ol (77.5 mg, 0.497 mmol, 1.00 eq.) and C$_4$F$_9$I (0.996 eq.) were reacted. After 3 h the reaction solution was cooled with an ice bath and a sample for NMR measurements was withdrawn. A conversion of 68-71% was observed.

EXPERIMENT 7.3.2-G **MS 343 A**

Similar to STANDARD PROCEDURE C, $^{t}Bu_3P$ (10.3 mg, 0.051 mmol, 10 mol%), 9-decen-1-ol (77.4 mg, 0.495 mmol, 1.00 eq.) and C_4F_9I (0.997 eq.) were reacted. The solution was coloured yellow temporarily within the first hour. After 3 h the reaction solution was cooled with an ice bath and a sample for NMR measurements was withdrawn. A conversion of 61-72% was observed.

EXPERIMENT 7.3.2-H **MS 343 B**

$^{t}Bu_3P$ (10.3 mg, 0.051 mmol, 10 mol%) and 9-decen-1-ol (77.5 mg, 0.496 mmol, 1.00 eq.) were weighed into separate vials inside the glovebox, dissolved in CH_2Cl_2 (1.0 ml each, overall 2.0 ml) and transferred into a pressure tube. C_4F_9I (85.0 µL, 0.494 mmol, 0.996 eq.) was added with a Hamilton syringe. Outside the glovebox the reaction solution was stirred at room temperature. The solution was coloured yellow. After 3 and 27 h, respectively, a sample for NMR measurements was withdrawn. A conversion of 82% was observed for the later sample. The yellow reaction solution was mixed with a saturated Na_2SO_3 solution and the colouration vanished immediately.

EXPERIMENT 7.3.2-I **MS 343 C**

$^{t}Bu_3P$ (10.3 mg, 0.051 mmol, 10 mol%) and 9-decen-1-ol (77.4 mg, 0.495 mmol, 1.00 eq.) were weighed into separate vials inside the glovebox, dissolved in CH_2Cl_2 (1.0 ml each, overall 2.0 ml) and transferred into a pressure tube under exclusion of light. Additionally, the tube was covered in aluminium foil. C_4F_9I (85.0 µL, 0.494 mmol, 0.997 eq.) was added with a Hamilton syringe under red light. Outside the glovebox the reaction solution was heated to 80 °C in an oil bath positioned in a darkened fume hood. After 3 and 27 h, respectively, the reaction solution was cooled with an icebath and a sample for NMR measurements was withdrawn under red light. A conversion of 24-30% was observed for the later sample.

EXPERIMENT 7.3.2-J **MS 348 A**

$^{t}Bu_3P$ (8:4 mg, 0.042 mmol, 10 mol%) and 9-decen-1-ol (63.4 mg, 0.406 mmol, 1.00 eq.) were weighed into a translucent screw cap vial and dissolved in CH_2Cl_2 (1.2 ml) inside the glovebox. C_4F_9I (70.0 µL, 0.407 mmol, 1.00 eq.) was added with a Hamilton syringe. A sample for NMR measurements was withdrawn after 4 h. A conversion of 55-63% was observed.

EXPERIMENT 7.3.2-K **MS 348 B**

$^{t}Bu_3P$ (8:6 mg, 0.043 mmol, 10 mol%) and 9-decen-1-ol (63.8 mg, 0.408 mmol, 1.00 eq.) were weighed into a translucent screw cap vial and dissolved in CH_2Cl_2 (1.2 ml) inside the glovebox. C_4F_9I (70.0 µL, 0.407 mmol, 0.996 eq.) was added with a Hamilton syringe. Outside the glove

iodine (9.8 mg, 0.039 mmol, 9.5 mol%) was added under N_2. A sample for NMR measurements was withdrawn after 4 h. A conversion of 20-30% was observed.

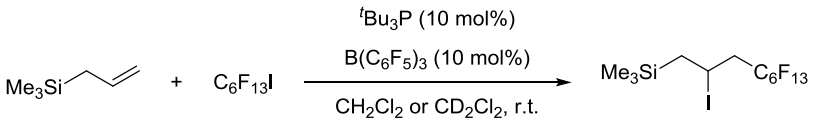
EXPERIMENT 7.3.2-L **MS 339 A**

Analogous to STANDARD PROCEDURE C, ^{t}Bu$_3$P (10.2 mg, 0.0504 mmol, 10 mol%), 9-decen-1-ol (77.0 mg, 0.493 mmol, 1.00 eq.) and C_4F_9I (1.00 eq.) were reacted in toluene instead of CH_2Cl_2. The temperature of the oil bath was increased to 100 °C. After 3 h the reaction solution was cooled with an ice bath and a sample for NMR measurements was withdrawn. No conversion was observed.

EXPERIMENT 7.3.2-M **MS 339 B**

Analogous to STANDARD PROCEDURE C, ^{t}Bu$_3$P (10.2 mg, 0.0504 mmol, 10 mol%), 9-decen-1-ol (77.5 mg, 0.498 mmol, 1.00 eq.) and C_4F_9I (0.996 eq.) were reacted in THF instead of CH_2Cl_2. The temperature of the oil bath was decreased to 60 °C. After 3 h the reaction solution was cooled with an ice bath and a sample for NMR measurements was withdrawn. A conversion of 24% was observed.

7.4 Allyltrimethylsilane



EXPERIMENT 7.3.2-A **MS 128**

$B(C_6F_5)_3$ (41 mg, 0.080 mmol, 0.10 eq.), ^{t}Bu$_3$P (16 mg, 0.080 mmol, 0.10 eq.), allyltrimethylsilane (90.2 mg, 0.789 mmol, 1 eq.) and tridecafluoro-1-iodohexane (406 mg, 0.910 mmol, 1.15 eq.) were weighed out into a screw-top vial and then dissolved in CH_2Cl_2 (1.1 ml). The resulting brownish solution was stirred sealed with a Teflon-insert screw cap. After 3 d stirring at r.t. a TLC-control indicated a complete conversion and the product was isolated as a transparent liquid (96.4 mg) by column chromatography (*n*-hexane:CH_2Cl_2 = 96:4) on neutral aluminium oxide (Brockmann III). The product decomposed in $CDCl_3$.

A yield cannot be given in a reasonable fashion.

EXPERIMENT 7.3.2-B **MS 132W**

^{t}Bu$_3$P (17 mg, 0.084 mmol, 10 mol%), $B(C_6F_5)_3$ (42 mg, 0.081 mmol, 10 mol%) allyltrimethylsilane (92.8 mg, 0.812 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (394 mg, 0.884 mmol, 1.09 eq.) were weighed out into an amber glass screw-top vial, dissolved in CH_2Cl_2 (2 ml) and the vial was sealed with a Telfon cap. After 4 d stirring at r.t. the vial was opened for TLC-controls. White smoke exited the opened vial. A sample for NMR measurements was taken.

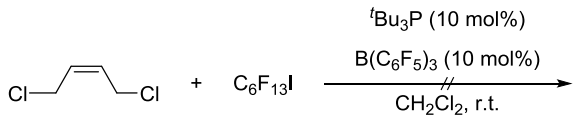
Column chromatography (*n*-pentane:CH_2Cl_2 = 98.5:1.5) on neutral aluminium oxide (Brockmann III) was used for product isolation. A volatile, transparent liquid (243 mg) was obtained, which decomposed under release of a purple gas within one week and lost half of its mass (116 mg). The remaining violet liquid was filtered over basic aluminium oxide (Brockmann I) and volatiles were removed in *vacuo* (51.8 mg). No iodoperfluoroalkylation product was isolated.

EXPERIMENT 7.3.2-C **MS 164 A**

^{t}Bu$_3$P (10.0 mg, 0.0494 mmol, 10.3 mol%), B(C_6F_5)$_3$ (25.5 mg, 0.0498 mmol, 10.4 mol%) allyltrimethylsilane (55.0 mg, 0.481 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (174 mg, 0.503 mmol, 1.05 eq.) were weighed out into a transparent screw-top vial, dissolved in CD_2Cl_2 (0.7 mL, 0.7 M) and the yellow solution was transferred into an NMR-tube. The NMR-tube was sealed with a PE cap and insulating tape. Several NMR measurements were conducted starting after 23 min, ending after 11 d. Afterwards, the reddish solution was filtered twice over basic aluminium oxide (Brockmann I), which was wetted with $CDCl_3$. A control by NMR spectroscopy showed a complete conversion.

7.5 Sterically Hindered and Electron-Deficient Substrates

7.5.1.1 *cis*-1,4-Dichloro-2-butene



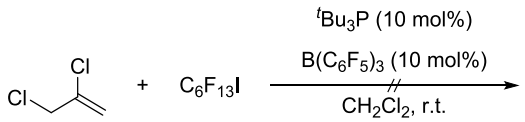
EXPERIMENT 7.3.2-A **MS 155**

^{t}Bu$_3$P (23 mg, 0.11 mmol, 13 mol%), *cis*-1,4-dichloro-2-butene (106 mg, 0.848 mmol, 1.00 eq.), tridecafluoro-1-iodohexane (372 mg, 0.834 mmol, 0.983 eq.) and B(C_6F_5)$_3$ (41 mg, 0.080 mmol, 9.4 mol%), were weighed out into a screw-top vial and then dissolved in CH_2Cl_2 (2 ml, 0.4 M). The resulting solution was stirred at r.t. sealed with a Teflon-insert screw cap. After 1 d and 5 d, respectively, samples for controls by NMR spectroscopy were taken outside the glovebox under N_2 counterflow. No conversion was detected.

EXPERIMENT 7.3.2-B **MS 155W**

^{t}Bu$_3$P (16 mg, 0.81 mmol, 9.8 mol%), *cis*-1,4-dichloro-2-butene (103 mg, 0.824 mmol, 1.00 eq.), tridecafluoro-1-iodohexane (361 mg, 0.810 mmol, 0.982 eq.) and B(C_6F_5)$_3$ (41 mg, 0.080 mmol, 9.7 mol%), were weighed out into a screw-top vial and then dissolved in CH_2Cl_2 (2 ml, 0.4 M). The resulting solution was stirred at r.t. sealed with a Teflon-insert screw cap. After 51 h a sample for NMR measurements was taken inside the glovebox. No conversion was detected.

7.5.1.2 2,3-Dichlor-1-propene



EXPERIMENT 7.3.2-C **MS 161**

^{t}Bu$_3$P (16 mg, 0.080 mmol, 10 mol%), B(C_6F_5)$_3$ (41 mg, 0.080 mmol, 10 mol%), 2,3-dichloro-1-propene (87.6 mg, 0.789 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (357 mg, 0.801 mmol, 1.01 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2 ml, 0.4 M). The resulting solution was stirred at r.t. sealed with a Teflon-insert screw cap. After 27 h and 19 d samples for controls by NMR spectroscopy were taken outside the glovebox under N_2 counterflow. Next to a TLC-control, the yellowish reaction solution was diluted with *n*-pentane (2 ml) and then filtered with a basic aluminium oxide filled glas pipette (Brockmann III). Afterwashing with *n*-pentane (8 ml) was followed by a removal of solvent in *vacuo*. No iodoperfluoroalkylation product was isolated.

A yield cannot be calculated in a reasonable fashion.

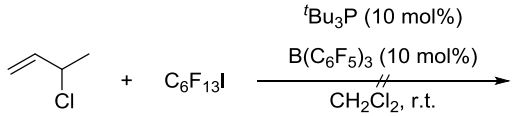
EXPERIMENT 7.3.2-D **MS 161W**

Analogous to ^{t}Bu$_3$P (16.9 mg, 0.0835 mmol, 10.6 mol%), B(C_6F_5)$_3$ (41.2 mg, 0.0805 mmol, 10.2 mol%), 2,3-dichloro-1-propene (87.4 mg, 0.788 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (359 mg, 0.805 mmol, 1.02 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2.5 ml, 0.3 M). The resulting solution was stirred at r.t. sealed with a Teflon-insert screw cap. After 7 d and 10 d, respectively, samples for NMR measurements were taken outside the glovebox under N_2 counterflow. A minor conversion was observed.

EXPERIMENT 7.3.2-E **MS 161W W**

^{t}Bu$_3$P (17.0 mg, 0.0840 mmol, 10.7 mol%), B(C_6F_5)$_3$ (42.1 mg, 0.0822 mmol, 10.5 mol%), 2,3-dichloro-1-propene (87.0 mg, 0.784 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (397 mg, 0.890 mmol, 1.14 eq.) were weighed out into a translucent screw-top vial and then dissolved in CH_2Cl_2 (2.5 ml). The resulting solution was stirred at r.t. sealed with a Teflon-insert screw cap. After 8 d a sample for NMR measurements was taken outside the glovebox under N_2 counterflow. A minor conversion was observed. The yellow-orange reaction solution was discarded afterwards.

7.5.1.3 3-Chlorobut-1-ene



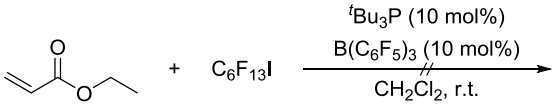
EXPERIMENT 7.3.2-F **MS 176 A**

^{t}Bu$_3$P (16.3 mg, 0.0806 mmol, 9.86 mol%) as well as B(C_6F_5)$_3$ (42.8 mg, 0.0836 mmol, 10.2 mol%) were weighed out into a vial and dissolved in CH_2Cl_2 (0.8 ml). Tridecafluoro-1-iodohexane (368 mg, 0.825 mmol, 1.01 eq.) and 3-chlorobut-1-ene (74.0 mg, 0.817 mmol, 1.00 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (0.8 ml). Catalyst solution was transferred and the vial was rinsed with CH_2Cl_2 (0.9 ml, overall 2.5 ml). After 98 h a sample for NMR measurements was taken inside the glovebox. No conversion was observed.

EXPERIMENT 7.3.2-G **MS 176W**

Analogous to experiment 7.3.2-f ^{t}Bu$_3$P (16.6 mg, 0.0820 mmol, 10.6 mol%), B(C_6F_5)$_3$ (42.8 mg, 0.0836 mmol, 10.8 mol%), tridecafluoro-1-iodohexane (360 mg, 0.807 mmol, 1.04 eq.) and 3-chlorobut-1-ene (70.1 mg, 0.774 mmol, 1.00 eq.) were reacted. A sample for NMR measurements was withdrawn after 96 h outside the glovebox. No conversion was observed.

7.5.1.4 Ethyl acrylate



EXPERIMENT 7.3.2-H **MS 183 A**

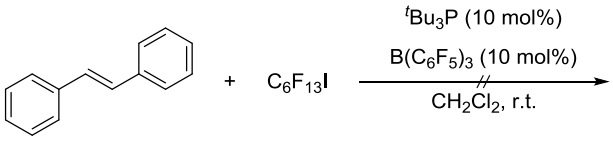
^{t}Bu$_3$P (10.2 mg, 0.0504 mmol, 9.71 mol%) as well as B(C_6F_5)$_3$ (25.8 mg, 0.0504 mmol, 9.71 mol%) were weighed out into a vial and dissolved in CH_2Cl_2 (0.5 ml). Ethyl acrylate (52.0 mg, 0.519 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (229 mg, 0.514 mmol, 0.989 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (0.5 ml). Catalyst solution was transferred and the vial was rinsed with CH_2Cl_2 (0.5 ml, overall 1.5 ml). After 96 h a sample for NMR measurements was taken outside the glovebox. No iodoperfluoroalkylation was detected.

EXPERIMENT 7.3.2-I **MS 192 B**

^{t}Bu$_3$P (10.2 mg, 0.0504 mmol, 9.31 mol%) as well as B(C_6F_5)$_3$ (26.2 mg, 0.0512 mmol, 9.46 mol%) were weighed out into a vial and dissolved in CH_2Cl_2 (0.8 ml). Ethyl acrylate (54.2 mg, 0.541 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (236 mg, 0.529 mmol, 0.978 eq.) were weighed out into an amber glass screw-top vial and dissolved in CH_2Cl_2 (0.3 ml). 4 Å molecular sieve (120 mg) was added to this solution. Catalyst solution was transferred and the vial was

rinsed with CH_2Cl_2 (0.4 ml, overall 1.5 ml). After 8 d a sample for NMR measurements was taken outside the glovebox. No iodoperfluoroalkylation was detected.

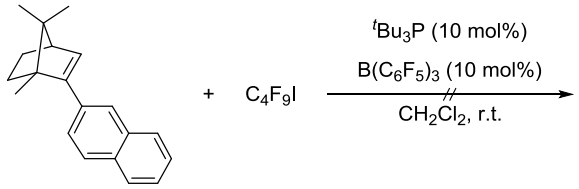
7.5.1.5 (*E*)-Stilbene



EXPERIMENT 7.3.2-J **MS 186**

^{t}Bu$_3$P (10.1 mg, 0.0499 mmol, 9.84 mol%) as well as B(C_6F_5)$_3$ (26.8 mg, 0.0523 mmol, 10.3 mol%) were weighed out into a vial and dissolved in CH_2Cl_2. (*E*)-Stilbene (91.4 mg, 0.507 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (238 mg, 0.534 mmol, 1.05 eq.) were weighed out into an amber glass screw-top vial and dissolved in CH_2Cl_2 (overall 2 ml). The catalyst solution was transferred to the substrate solution and stirred for 77 h at r.t. sealed with a Teflon-insert screw cap inside the glovebox. A sample was taken for a control by NMR spectroscopy. No conversion was detected.

7.5.1.6 2-((1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)naphthalene

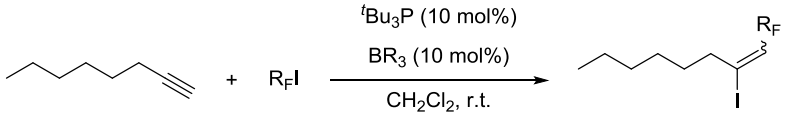


EXPERIMENT 7.3.2-K **MS 218**

B(C_6F_5)$_3$ (26.7 mg, 0.0522 mmol, 10.1 mol%), ^{t}Bu$_3$P (10.1 mg, 0.0499 mmol, 9.69 mol%) as well as (1*R*,4*R*)-1,7,7-trimethyl-2-(2-naphthyl)bicyclo[2.2.1]hept-2-en (135 mg, 0.515 mmol, 1.00 eq.) were weighed out in an amber glass screw-top vial, nonafluor-1-iodobutane (189 mg, 0.546 mmol, 1.06 eq.) was added via syringe and then all compounds were dissolved in CH_2Cl_2 (2.0 ml). After 50 h stirring inside the glovebox a sample for NMR measurements was taken inside the glovebox. After 7 d another sample was taken outside the glovebox. No conversion was detected.

7.6 Alkynes

7.6.1 1-Octyne



EXPERIMENT 7.6.1-A **MS 143 A**

^{t}Bu$_3$P (17 mg, 0.084 mmol, 10 mol%), 1-octyne (88 mg, 0.80 mmol, 1.0 eq.), tridecafluoro-1-iodohexane (0.36 g, 0.81 mmol, 1.0 eq.) and B(C_6F_5)$_3$ (42 mg, 0.082 mmol, 0.10 eq.) were weighed out into a 10 ml round-bottom flask and then dissolved in CH_2Cl_2 (2 ml, 0.4 M). It was stirred sealed with a rubber septum for 2 d and a control by NMR spectroscopy was conducted. After 8 d the solvent was evaporated completely and after 10 d the suspension was diluted with *n*-pentane (1 ml), causing a yellow substance to precipitate. A TLC-control was conducted. The liquid was filtered with a glass pipette filled with small amounts of basic aluminium oxide and *n*-pentane (4 x 1 ml) was used for afterwashing. The resulting solution was concentrated at a maximum of 400 mbar. A clear, transparent liquid was obtained (160 mg).

A yield cannot be calculated in a reasonable fashion.

EXPERIMENT 7.6.1-B **MS 143 B**

^{t}Bu$_3$P (16 mg, 0.079 mmol, 9.2 mol%), 1-octyne (95 mg, 0.86 mmol, 1.0 eq.), tridecafluoro-1-iodohexane (0.36 g, 0.81 mmol, 0.94 eq.) and B(2,6-$F_2C_6H_3$)$_3$ (29 mg, 0.083 mmol, 0.092 eq.) were weighed out into a 10 ml round-bottom flask and then dissolved in CH_2Cl_2 (2 ml). It was stirred sealed with a rubber septum for 2 d and a control by NMR spectroscopy was conducted. After 8 d the solvent was evaporated completely and after 10 d the suspension was diluted with *n*-pentane (1 ml), causing a yellow substance to precipitate. A TLC-control was conducted. The liquid was filtered with a glass pipette filled with small amounts of basic aluminium oxide and *n*-pentane (4 x 1 ml) was used for afterwashing. The resulting solution was concentrated at a maximum of 400 mbar. A clear, transparent liquid was obtained (252 mg).

The raw products of experiment 7.6.1-a and experiment 7.6.1-b were combined and purified applying column chromatography on SiO_2 with *n*-pentane as the eluent. The product was obtained as presumably *E*/*Z*-mixture fractions (296 mg, *E*/*Z* = 1.00:0.17) and a side product (37 mg). Another purification on SiO_2 (*n*-pentane) gave analytically pure *E*-isomer (84.6 mg) and a mixture of isomers (118 mg).

A yield cannot be calculated in a reasonable fashion.

EXPERIMENT 7.6.1-C **MS 165 A**

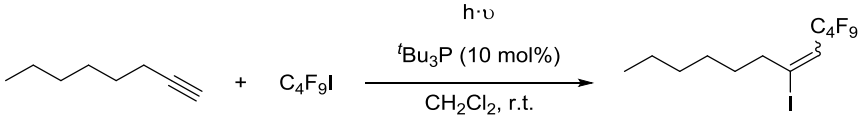
^{t}Bu$_3$P (16.8 mg, 0.0830 mmol, 10.5 mol%), B(C$_6$F$_5$)$_3$ (41.0 mg, 0.0801 mmol, 10.1 mol%), 1-octyne (87.0 mg, 0.789 mmol, 1.00 eq.) and nonofluoro-1-iodobutane (291 mg, 0.841 mmol, 1.07 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2.5 ml, 0.3 M). It was stirred at r.t. sealed with a Teflon-insert screw cap inside the glovebox. After 1 and 4 d, respectively, samples for a control by NMR spectroscopy were withdrawn inside the glovebox, which were filled up with $CDCl_3$ outside the glovebox. After 12 d another NMR-control was conducted, but the sample was directly filled up with C_6D_6 inside the glovebox. Afterwards the reaction solution was filled into a transparent vial and the intensively yellow solution stirred for another 8 d before a control by NMR spectroscopy was conducted.

EXPERIMENT 7.6.1-D **MS 165 B**

^{t}Bu$_3$P (16.8 mg, 0.0830 mmol, 10.5 mol%), B(2,6-F$_2$C$_6$H$_3$)$_3$ (27.7 mg, 0.0791 mmol, 10.0 mol%), 1-octyne (86.9 mg, 0.789 mmol, 1.00 eq.) and nonofluoro-1-iodobutane (300 mg, 0.867 mmol, 1.10 eq.) were weighed out into an amber glass screw-top vial and then dissolved in CH_2Cl_2 (2.5 mL,). It was stirred at r.t. sealed with a Teflon-insert screw cap inside the glovebox. After 1, 4 and 6 d, respectively, samples for a control by NMR spectroscopy were withdrawn inside the glovebox, which were filled up with $CDCl_3$ outside the glovebox. After 12 d another NMR-control was conducted, but the sample was directly filled up with C_6D_6 inside the glovebox. Afterwards the reaction solution was filled into a transparent vial and the slightly yellowish solution stirred for another 8 d before a control by NMR spectroscopy was conducted. After overall 32 d a last sample was withdrawn. Purification applying column chromatography on SiO_2 (*n*-pentane) yielded pure product (110 mg), presumably *E*/*Z*-mixture fractions (48.9 mg) and two side products (3.2 and 12.3 mg).

yield *E*-isomer (465.13 g·mol^{-1}): 110 mg (0.236 mmol, 30%)

yield *E*/*Z*-mixture (465.13 g·mol^{-1}) 48.9 mg (0.107 mmol, 14%, (*E*):(*Z*) = 1.0:0.42)

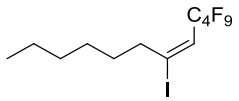


EXPERIMENT 7.6.1-E **MS 230**

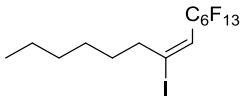
^{t}Bu$_3$P (14.4 mg, 0.0712 mmol, 10.5 mol%) was weighed out into a translucent screw-top vial and then dissolved in CH_2Cl_2 (2.1 ml). 1-Octyne (100 µL, 0.678 mmol, 1.00 eq.) as well as nonafluoro-1-iodobutane (120 µL, 0.697 mmol, 1.03 eq.) were added via Hamilton syringe. The solution was stirred at r.t. sealed with a Teflon-insert screw cap outside the glovebox. After 90 h a sample for

NMR measurements was taken outside the glovebox in N_2-counterflow. Column chromatography (*n*-pentane) on SiO_2 was used to isolate a mixture of products (296 mg).

yield (456.13 g·mol^{-1}): 296 mg (0.649 mmol, 96%, mixture of isomers ≈91:9)

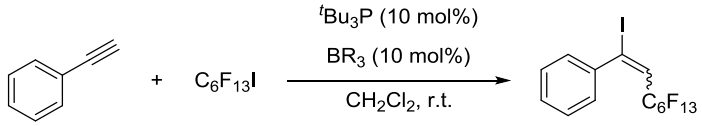


^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.32 (t, *J* = 14.5 Hz, 1H), 2.63 (t, *J* = 7.4 Hz, 3H), 1.57 (ddt, J = 11.7, 9.3, 4.8 Hz, 2H), 1.40 – 1.24 (m, *J* = 4.6 Hz, 6H), 0.95 – 0.85 (m, 3H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ −80.9 - −81.5 (m, 3F), −105.4 - −106.0 (m, 2F), −124.1 - −124.5 (m, 2F), −125.7 - −126.1 (m, 2F). Analytic data are consistent with literature-known values.[107-108]



^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.32 (t, *J* = 14.5 Hz, 1H), 2.63 (t, *J* = 7.5 Hz, 2H), 1.66 – 1.46 (m, 2H), 1.47 – 1.19 (m, 6H), 0.97 – 0.82 (m, 3H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ −80.8 (tt, *J* = 9.9, 2.5 Hz, 3F), −105.3 - −105.6 (m, 2F), −121.5 - −121.9 (m, 2F), −122.7 - −123.0 (m, 2F), −123.1 - −123.5 (m, 2F), −126.0 - −126.4 (m, 2F). Analytic data are consistent with literature-known values.[109]

7.6.2 Phenylacetylene



EXPERIMENT 7.6.2-A **MS 153 A**

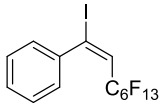
^{t}Bu$_3$P (16 mg, 0.079 mmol, 10 mol%), $B(C_6F_5)_3$ (40.4 mg, 0.0789 mmol, 10 mol%), phenylacetylene (82.0 mg, 0.783 mmol, 1.00 eq.) as well as tridecafluoro-1-iodohexane (0.366 g, 0.821 mmol, 1.05 eq.) were weighed out into amber glass screw-top vial and then dissolved in CH_2Cl_2 (2 ml). The brownish solution was stirred at r.t. sealed with a Teflon-insert screw cap. After 1 d and 14 d, respectively, samples for NMR measurements were taken outside the glovebox in an N_2-counterflow. After 23 d column chromatography (*n*-pentane:CH_2Cl_2 = 98:2) on SiO_2 was used to isolate two products (48.5 mg and 5.5 mg). The major compound was identified as the iodoperfluoroalkylation product.

yield (548.09 g·mol^{-1}): 48.5 mg (0.0885 mmol, 10%)

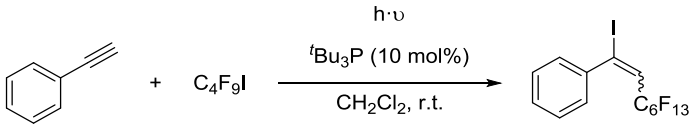
EXPERIMENT 7.6.2-B **MS 153 B**

Analogous to experiment 7.6.2-a, $^{t}Bu_3P$ (16 mg, 0.079 mmol, 9.3 mol%), $B(2,6\text{-}F_2C_6H_3)_3$ (27 mg, 0.078 mmol, 9.2 mol%), phenylacetylene (86.5 mg, 0.847 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (0.393 g, 0.881 mmol, 1.04 eq.) were reacted. The solution turned yellowish. After 17 d column chromatography (cyclohexane) on SiO_2 was used for workup. Besides the desired product (92.6 mg), several side-products were isolated.

yield (548.09 g·mol^{-1}): 92.6 mg (0.169 mmol, 20%)



^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 6.60 (t, J = 13.4 Hz, 1H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ −80.7 – −81.0 (m), −105.1 – −105.4 (m), −121.5 – −122.0 (m), −122.7 – −123.1 (m), −126.0 – −126.4 (m). Analytic data are consistent with literature-known values.[110]



EXPERIMENT 7.6.2-C **MS 229**

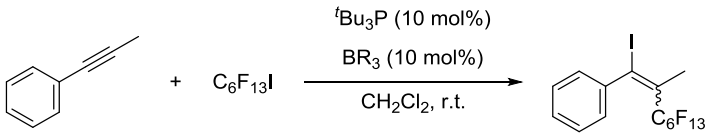
$^{t}Bu_3P$ (14.0 mg, 0.0692 mmol, 9.47 mol%), phenylacetylene (74.7 mg, 0.731 mmol, 1.00 eq.) as well as nonafluoro-1-iodobutane (290 mg, 0.838 mmol, 1.15 eq.) were weighed out into a translucent screw-top vial and then dissolved in CH_2Cl_2 (2.1 ml). The solution was stirred at r.t. sealed with a Teflon-insert screw cap outside the glovebox. After 90 h and 17 d a sample was taken outside the glovebox in N_2-counterflow. Column chromatography (*n*-pentane) on SiO_2 was used to isolate a mixture of products (257 mg) and minor amounts of side products (97.2 mg).

yield (448.07 g·mol^{-1}): 0.25 g (0.56 mmol, 77%, mixture of isomers ≈95:5)

The yield was corrected due to minor *n*-pentane impurities.

^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 6.59 (t, J = 13.6 Hz, 1H). **^{19}F-NMR** (282 MHz, $CDCl_3$) δ −81.0 (tt, J = 9.4, 2.8 Hz), −105.4 – −105.5 (m), −109.1 – −109.3 (m), −123.7 – −123.9 (m), −125.8 – −125.9 (m). Analytic data are consistent with literature-known values.[110]

7.6.3 1-Phenyl-1-propyne



EXPERIMENT 7.6.3-A **MS 180 A**

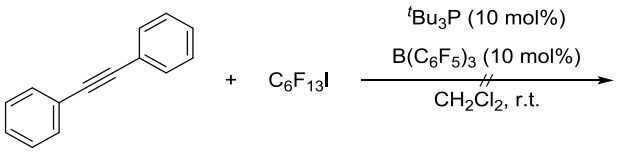
^{t}Bu$_3$P (17.4 mg, 0.0860 mmol, 12.8 mol%) and B(C_6F_5)$_3$ (40.7 mg, 0.0795 mmol, 11.9 mol%) were weighed out into a vial and dissolved in CH_2Cl_2 (1.5 ml). 1-Phenyl-1-propyne (77.9 mg, 0.671 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (341 mg, 0.765 mmol, 1.14 eq.) were weighed out in an amber glass screw-top vial and dissolved in CH_2Cl_2. Catalyst solution was transferred and the vial was rinsed with CH_2Cl_2 (overall 2.5 ml). The solution was stirred at r.t. inside the glovebox and after 70 h a sample was taken not inertly outside the glovebox. Most of the solvent was evaporated and a purification by column chromatography (*n*-pentane) yielded a mixture of isomers (38.7 mg).

yield (M = 562.11 g·mol^{-1}) 0.0387 g (0.0688 mmol, 8.8%)

EXPERIMENT 7.6.3-B **MS 180 B**

Analogous to experiment 7.6.3-a ^{t}Bu$_3$P (16.4 mg, 0.0811 mmol, 11.9 mol%), B(2,6-$F_2C_6H_5$)$_3$ (32.9 mg, 0.0940 mmol, 13.8 mol%), 1-phenyl-1-propyne (79.1 mg, 0.681 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (353 mg, 0.792 mmol, 1.16 eq.) were reacted. The solution was stirred at r.t. inside the glovebox and after 70 h a sample was taken not inertly outside the glovebox. No conversion was observed.

7.6.4 Diphenylacetylene

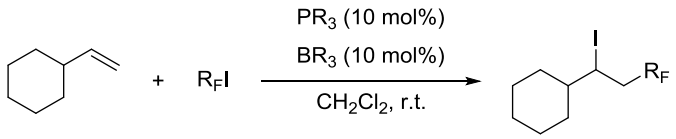


EXPERIMENT 7.6.4-A **MS 187**

B(C_6F_5)$_3$ (26.0 mg, 0.0508 mmol, 10.2 mol%) and ^{t}Bu$_3$P (10.3 mg, 0.0509 mmol, 10.2 mol%) were weighed out into a vial and dissolved in CH_2Cl_2. Diphenylacetylene (88.7 mg, 0.498 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (223 mg, 0.500 mmol, 1.00 eq.) were weighed out in an amber glass screw-top vial and dissolved in CH_2Cl_2 (overall 2 ml). Catalyst solution was transferred to the substrate solution and stirred for 77 h at r.t. sealed with a Teflon-insert screw cap inside the glovebox. A sample was taken for a control by NMR spectroscopy. No conversion was observed.

7.7 Phosphane Screening

7.7.1 Screening of Alternative Phosphanes



STANDARD PROCEDURE D

Phosphane (PR_3) as well as borane (BR_3) were weighed out in an amber glass screw-top vial and dissolved in CH_2Cl_2 (2.5 ml) inside the glovebox. Vinylcyclohexane (70.0 µL, 56.4 mg, 0.512 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (110 µL, 227 mg, 0.509 mmol, 0.994 eq.) were added via Hamilton syringe, the vial was sealed with a Teflon-insert screw cap and the solution is stirred inside the glovebox.

EXPERIMENT 7.7.1-A **MS 188 A**

According to STANDARD PROCEDURE D, tris(2,6-difluorophenyl)phosphane ($P(2,6\text{-}F_2C_6H_3)_3$, 19.0 mg, 0.0513 mmol, 10.0 mol%) and $B(C_6F_5)_3$ (26.4 mg, 0.0516 mmol, 10.1 mol%) were used as catalysts. After 93 h a sample for NMR measurements was taken outside the glovebox. No conversion was observed. No conversion was observed.

EXPERIMENT 7.7.1-B **MS 188 B**

According to STANDARD PROCEDURE D, tris(2,6-difluorophenyl)phosphane ($(2,6\text{-}F_2C_6H_3)_3P$, 19.0 mg, 0.0513 mmol, 10.0 mol%) and BPh_3 (12.9 mg, 0.0533 mmol, 10.4 mol%) were used as catalysts. After 93 h a sample for NMR measurements was taken outside the glovebox. No conversion was observed.

STANDARD PROCEDURE E

Phosphane (PR_3) as well as borane (BR_3) were weighed out in an amber glass screw-top vial and dissolved in CH_2Cl_2 (2.1 ml) inside the glovebox. Vinylcyclohexane (100 µL, 80.5 mg, 0.730 mmol, 1.00 eq.) and tridecafluoro-1-iodohexane (160 µL, 330 mg, 0.740 mmol, 1.01 eq.) were added via Hamilton syringe, the vial is sealed with a Teflon-insert screw cap and the solution is stirred inside the glovebox.

EXPERIMENT 7.7.1-C **MS 195 C**

According to STANDARD PROCEDURE E, tri(2-fluorophenyl)phosphane (22.6 mg, 0.0715 mmol, 9.79 mol%), $B(C_6F_5)_3$ (40.9 mg, 0.0799 mmol, 10.9 mol%), vinylcyclohexane and tridecafluoro-1-iodohexane were reacted. After 5 d a sample for NMR measurements was taken outside the glovebox. No conversion was observed.

STANDARD PROCEDURE F

Phosphane (PR_3) as well as borane (BR_3) were weighed out in an amber glass screw-top vial and dissolved in CH_2Cl_2 (2.1 ml) inside the glovebox. Vinylcyclohexane (100 µL, 80.5 mg, 0.730 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (125 µL, 251 mg, 0.726 mmol, 0.995 eq.) were added via Hamilton syringe, the vial was sealed with a Teflon-insert screw cap and the solution was stirred inside the glovebox.

EXPERIMENT 7.7.1-D **MS 209 C**

According to STANDARD PROCEDURE F, Mes_3P (28.6 mg, 0.0736 mmol, 10.1 mol%), $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ (32.8 mg, 0.0723 mmol, 9.91 mol%), vinylcyclohexane and nonafluoro-1-iodobutane were reacted. After 92 h a sample for NMR measurements was taken outside the glovebox. No conversion was observed.

EXPERIMENT 7.7.1-E **MS 204 A**

According to STANDARD PROCEDURE F, $^tBu_3P$ (15.5 mg, 0.0766 mmol, 10.5 mol%), $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ (33.5 mg, 0.0739 mmol, 10.1 mol%), vinylcyclohexane and nonafluoro-1-iodobutane were reacted. After 24 and 124 h, respectively, a sample for NMR measurements was taken inside the glovebox and another sample after 12 d outside the glovebox. A conversion of 41-43% was observed.

EXPERIMENT 7.7.1-F **MS 204 B**

According to STANDARD PROCEDURE F, Cy_3P (21.6 mg, 0.0770 mmol, 10.6 mol%), $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ (32.5 mg, 0.0717 mmol, 9.82 mol%), vinylcyclohexane and nonafluoro-1-iodobutane were reacted. After 24 h a sample for NMR measurements was taken inside the glovebox and another sample after 125 h outside the glovebox. A conversion of 24-27% was observed.

EXPERIMENT 7.7.1-G **MS 204 C**

According to STANDARD PROCEDURE F, $(C_6F_5)_3P$ (40.2 mg, 0.0755 mmol, 10.3 mol%), $B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ (32.9 mg, 0.0726 mmol, 9.94 mol%), vinylcyclohexane and nonafluoro-1-iodobutane were reacted. After 24 h a sample for NMR measurements was taken inside the glovebox and another sample after 125 h outside the glovebox. A conversion of 14-15% was observed.

7.8 UV-VIS-Measurements

The following solutions were measured on a Perkin Elmer Lamda 2 UV VIS spectrometer in Hellma cuvettes (10 x 10 mm, Suprasil quartz glass). All spectra but the one of I_2 were measure in dried and degassed CH_2Cl_2. The spectrum of I_2 was measured in untreated p.a. CH_2Cl_2.

1) Nonafluoro-1-iodobutane

C_4F_9I (39.6 mg, 0.114 mmol) was dissolved in CH_2Cl_2 (2.00 ml) inside the glovebox in a volumetric flask. This solution was diluted in a volumetric flask (800 µL in 5.00 ml). The following concentration was present: $[C_4F_9I] = 9.0 \cdot 10^{-3}$ M.

2) Tri-*tert*-butylphosphane and 9-decen-1-ol

$^t Bu_3P$ (8.5 mg, 0.041 mmol) and 9-decenol (6.3 mg, 0.040 mmol) were dissolved in CH_2Cl_2 (1.00 ml) in a volumetric flask inside the glovebox. This solution was diluted in a volumetric flask (500 µL in 5.00 ml). The following concentration was present: $[^t Bu_3P] = 4.2 \cdot 10^{-3}$ M, [9-decenol] = $4.0 \cdot 10^{-4}$ M.

3) Tri-*tert*-butylphosphane and nonafluoro-1-iodobutane

$^t Bu_3P$ (8.3 mg, 0.041 mmol) and C_4F_9I (15.1 mg, 0.044 mmol) were dissolved in CH_2Cl_2 (1.00 ml) in a volumetric flask inside the glovebox. This solution was diluted in a volumetric flask (200 µL in 5.00 ml). The following concentration was present: $[^t Bu_3P] = 1.6 \cdot 10^{-3}$ M, $[C_4F_9I] = 1.7 \cdot 10^{-3}$ M.

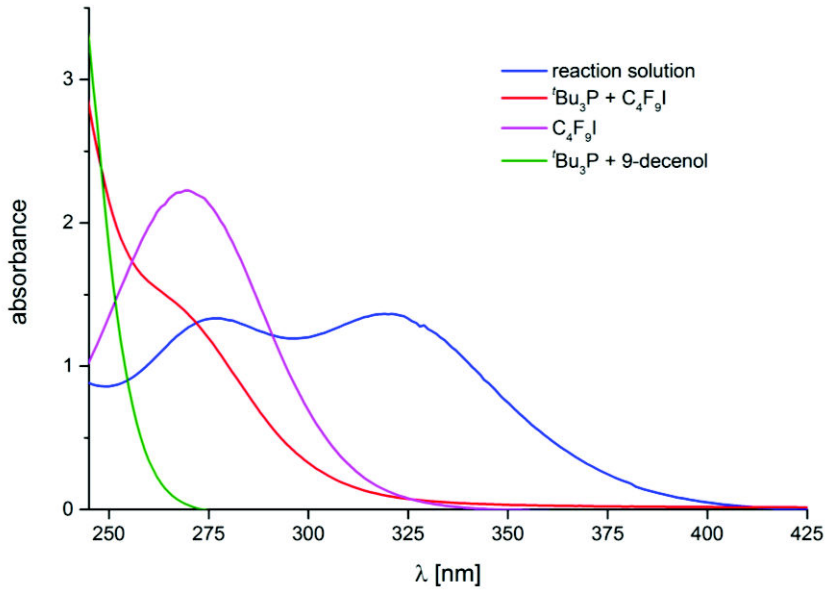


Figure 19: UV VIS spectra of a reaction solution of an iodoperfluoroalkylation of 9-decen-1-ol, solely C_4F_9I, $^t Bu_3P$ mixed with C_4F_9I and $^t Bu_3P$ mixed with 9-decen-1-ol.

4) Reaction solution of the iodoperfluoroalkylation of 9-decen-1-ol

$^t Bu_3P$ (8.6 mg, 0.043 mmol, 10 mol%) as well as 9-decen-1-ol (64.1 mg, 0.0410 mmol, 1.00 eq.) were weighed into a translucent screw-cap vial inside the glovebox and were dissolved in CH_2CL_2 (1.2 ml). C_4F_9I (70.0 µL, 0.407 mmol, 0.992 mmol) was added with a Hamilton syringe. The reaction solution was stirred inside the glovebox and was coloured yellow within 30 min. After 24 h a sample for NMR measurements (conversion of 56-59%) was withdrawn and the solution was diluted in a volumetric flask twice (125 µL in 10.00 ml, 1.0 ml in 5.0 ml). Without a consumption of $^t Bu_3P$, the following concentration would be present: $[^t Bu_3P] = 1.0 \cdot 10^{-4}$ M

The yellow reaction solution was mixed with a saturated Na_2SO_3 solution and the colouration vanished immediately.

5) Tri-*tert*-butylphosphane and iodine

^{t}Bu$_3$P (9.4 mg, 0.046 mmol) was dissolved in CH_2Cl_2 (2.0 ml) inside the glovebox. Iodine (6.1 mg, 0.024 mmol) was added and the resulting yellow solution was diluted in a volumetric flask (50 µL in 10.00 ml). The following concentrations were present: [^{t}Bu$_3$P] = $1.2 \cdot 10^{-4}$ M, [I_2] = $6.0 \cdot 10^{-4}$ M.

6) Iodine

Iodine (11 mg, 0.043 mmol) was dissolved in CH_2Cl_2 (10.00 ml, p.a.) and the resulting purple solution was diluted in a volumetric flask (1.00 ml in 10.00 ml). The following concentration was present: [I_2] = $4.3 \cdot 10^{-4}$ M.

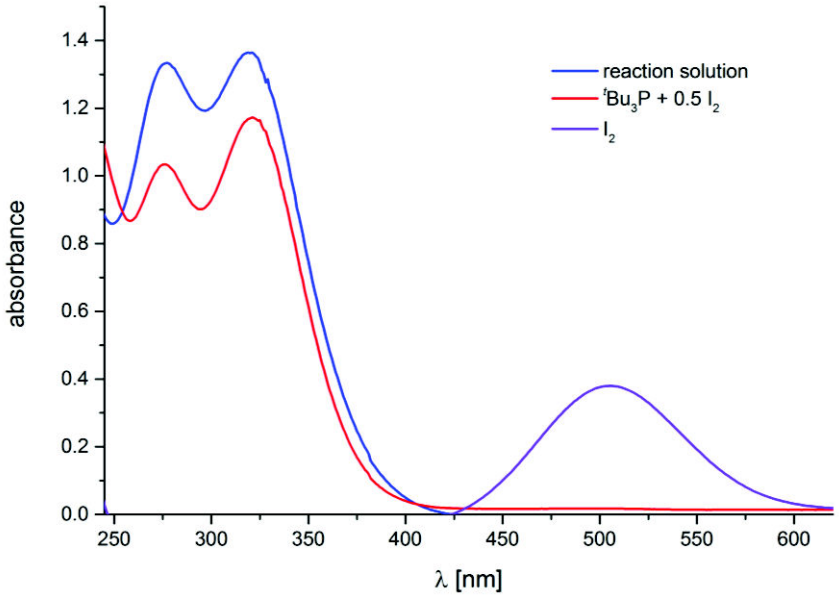
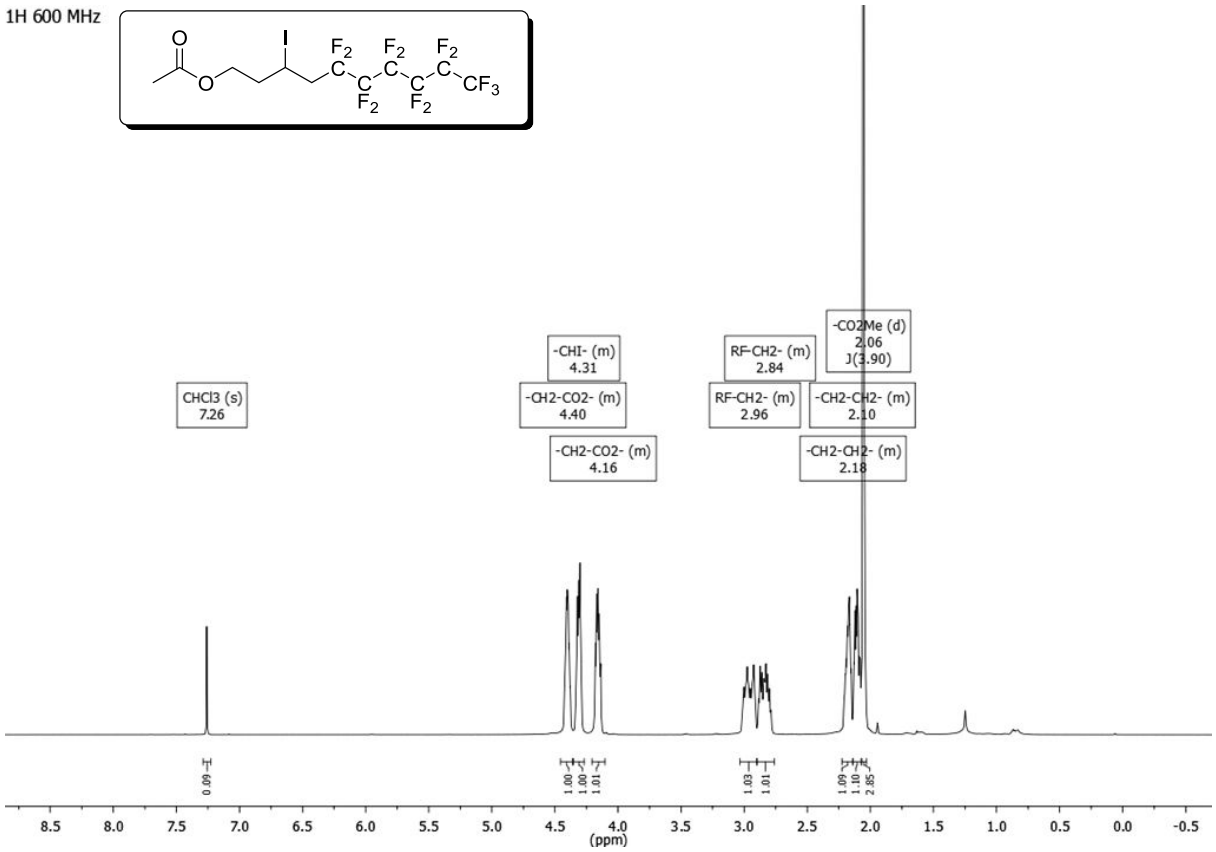
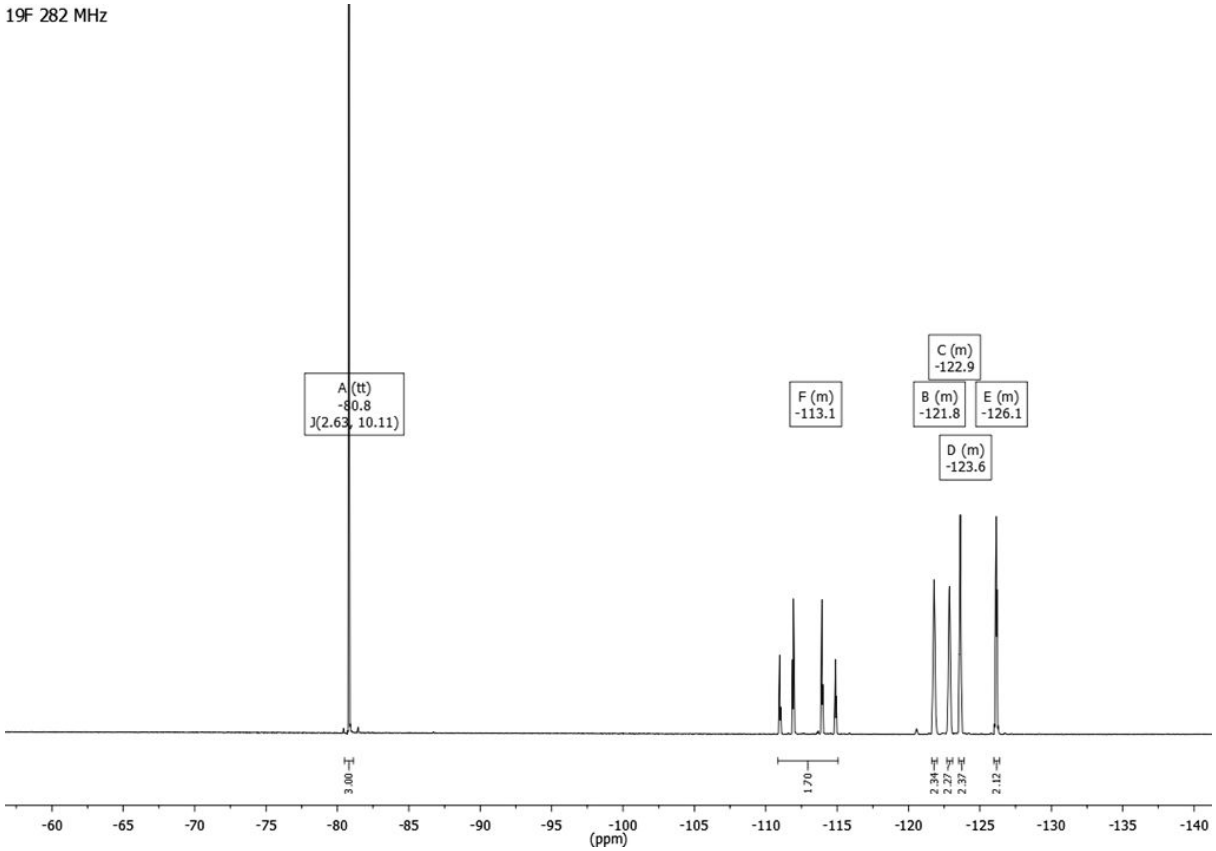


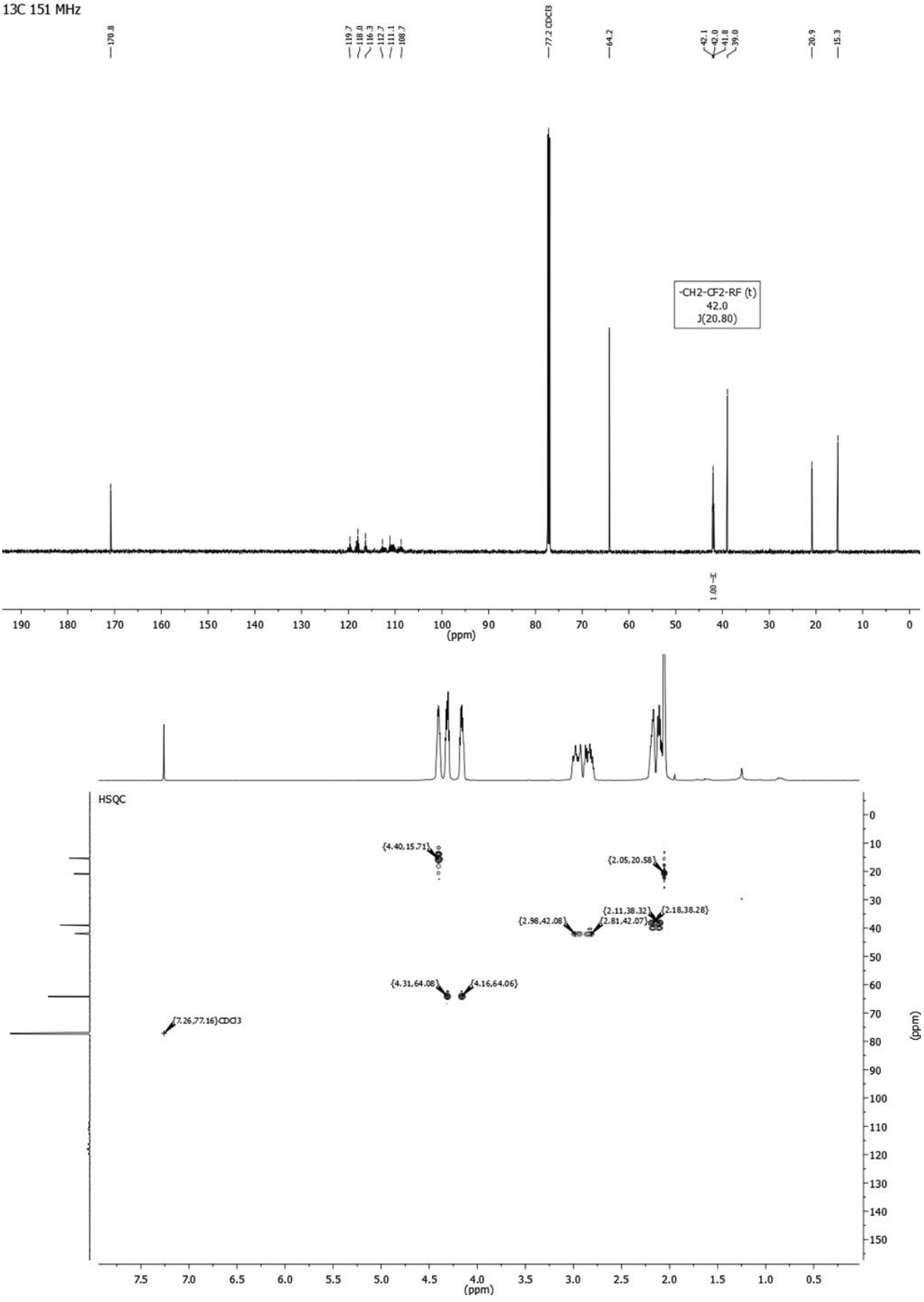
Figure 20: UV-VIS-spectra of the reaction solution of an iodoperfluoroalkylation of 9-decenol with ^{t}Bu$_3$P, a mixture of ^{t}Bu$_3$P with I_2 as well as solely I_2.

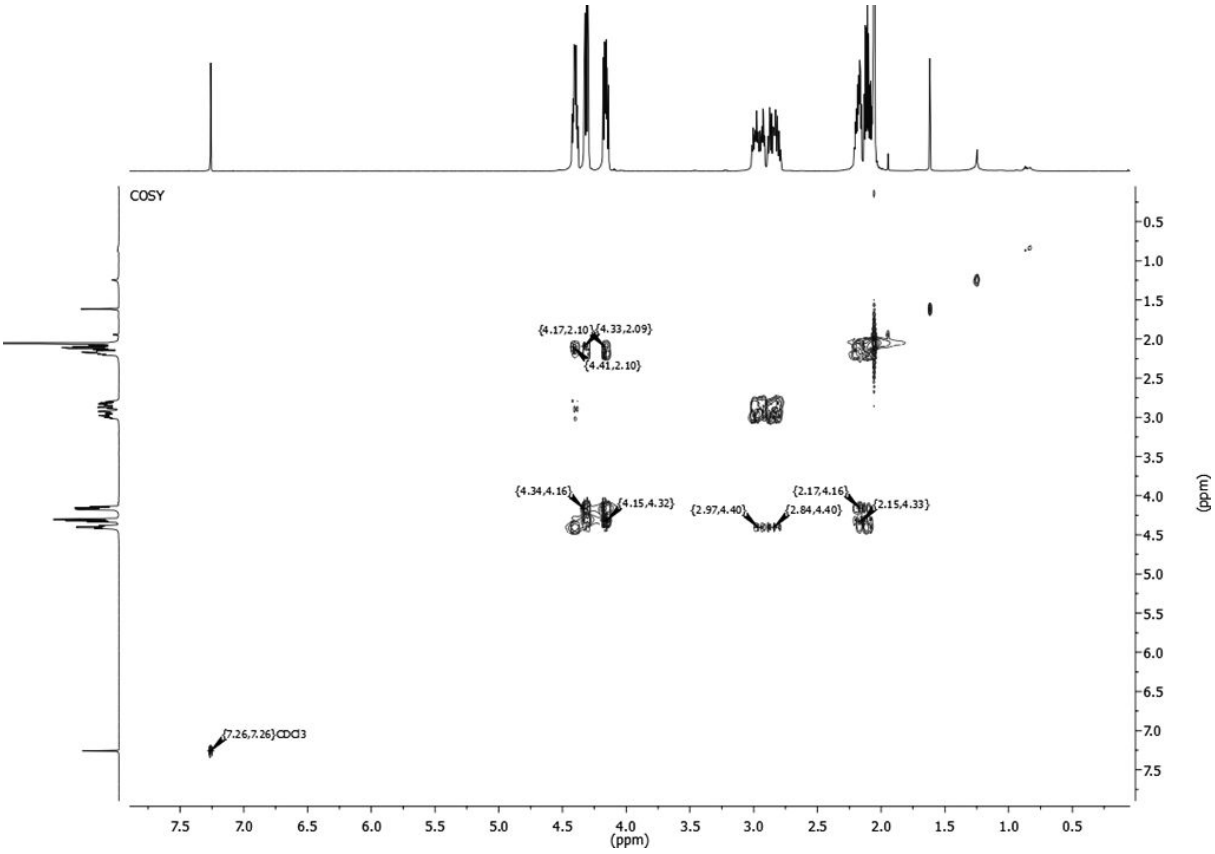
8 Spectral Data

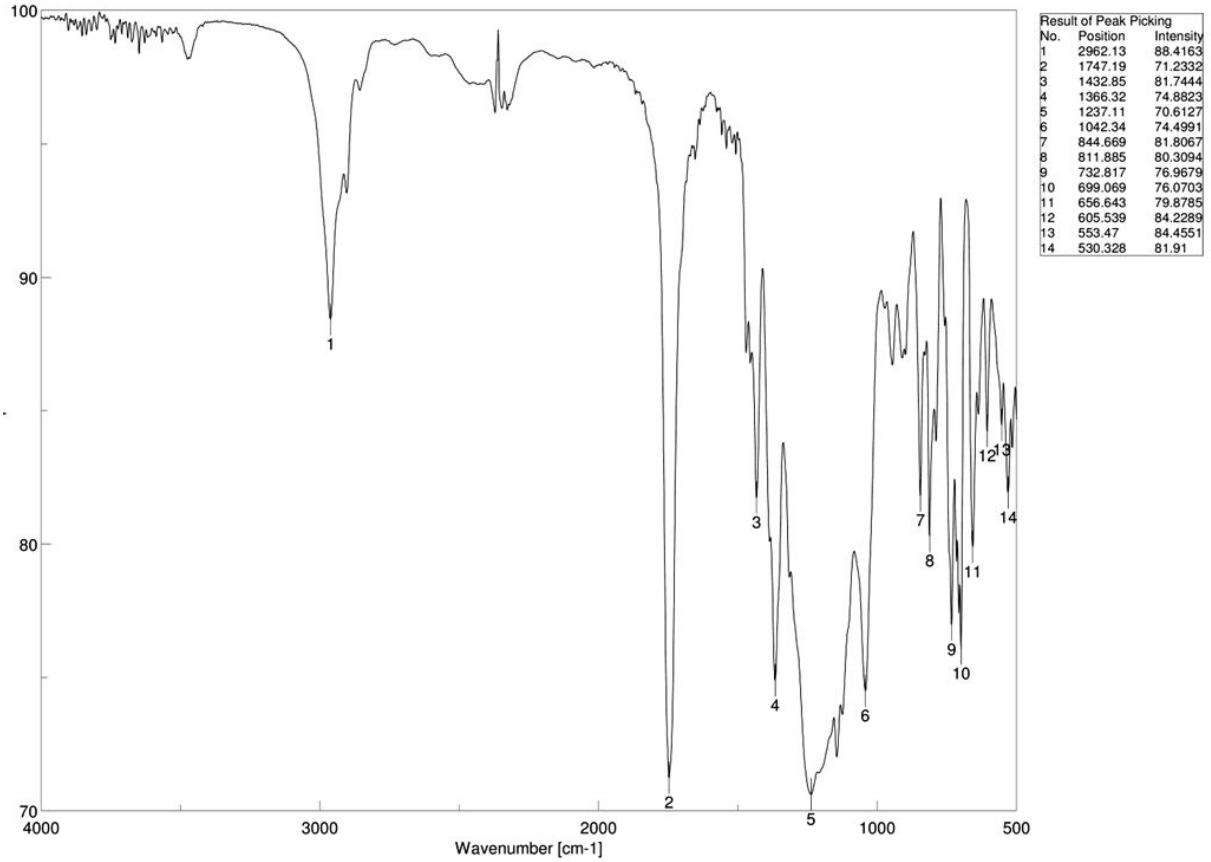
8.1 5,5,6,6,7,7,8,8,8-Nonafluoro-3-iodooctyl acetate





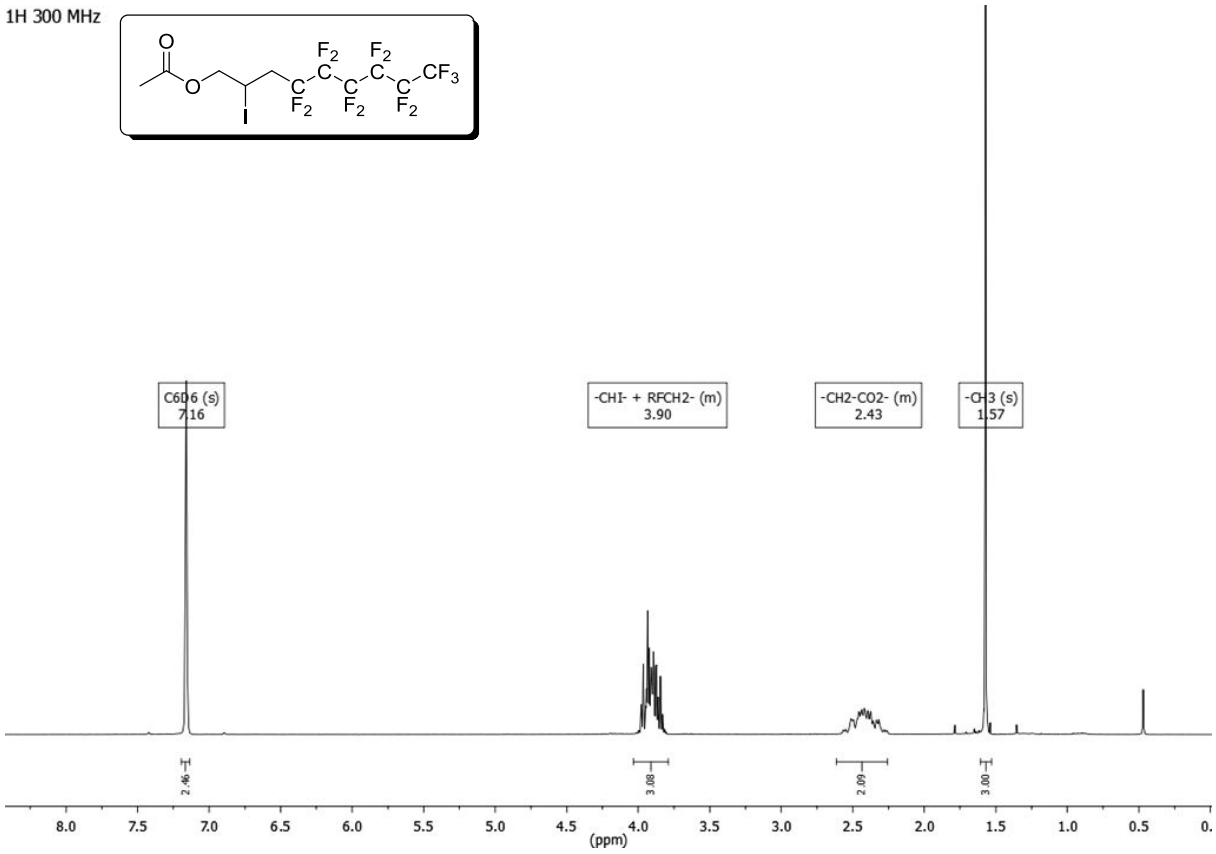

13C 151 MHz
170.8
119.7
118.0
116.3
112.7
111.1
108.7
77.2 CDCl3
64.2
42.1
42.0
41.8
39.0
20.9
15.3
-CH2-CF2-RF (t)
42.0
J(20.80)
1.00
(ppm)
HSQC
{4.40,15.71}
{2.05,20.58}
{2.11,38.32}
{2.18,38.28}
{2.98,42.08}
{2.81,42.07}
{4.31,64.08}
{4.16,64.06}
{7.26,77.16}CDCl3
(ppm)
(ppm)

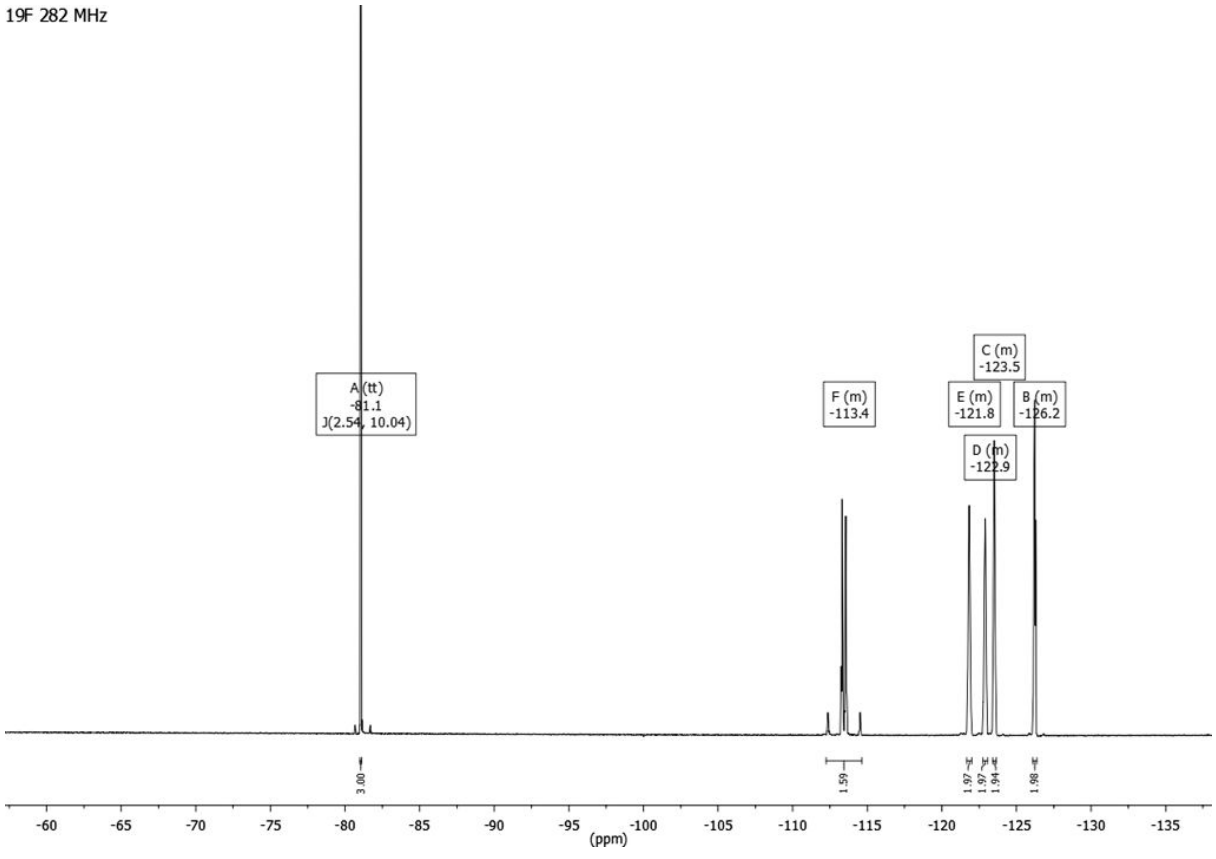


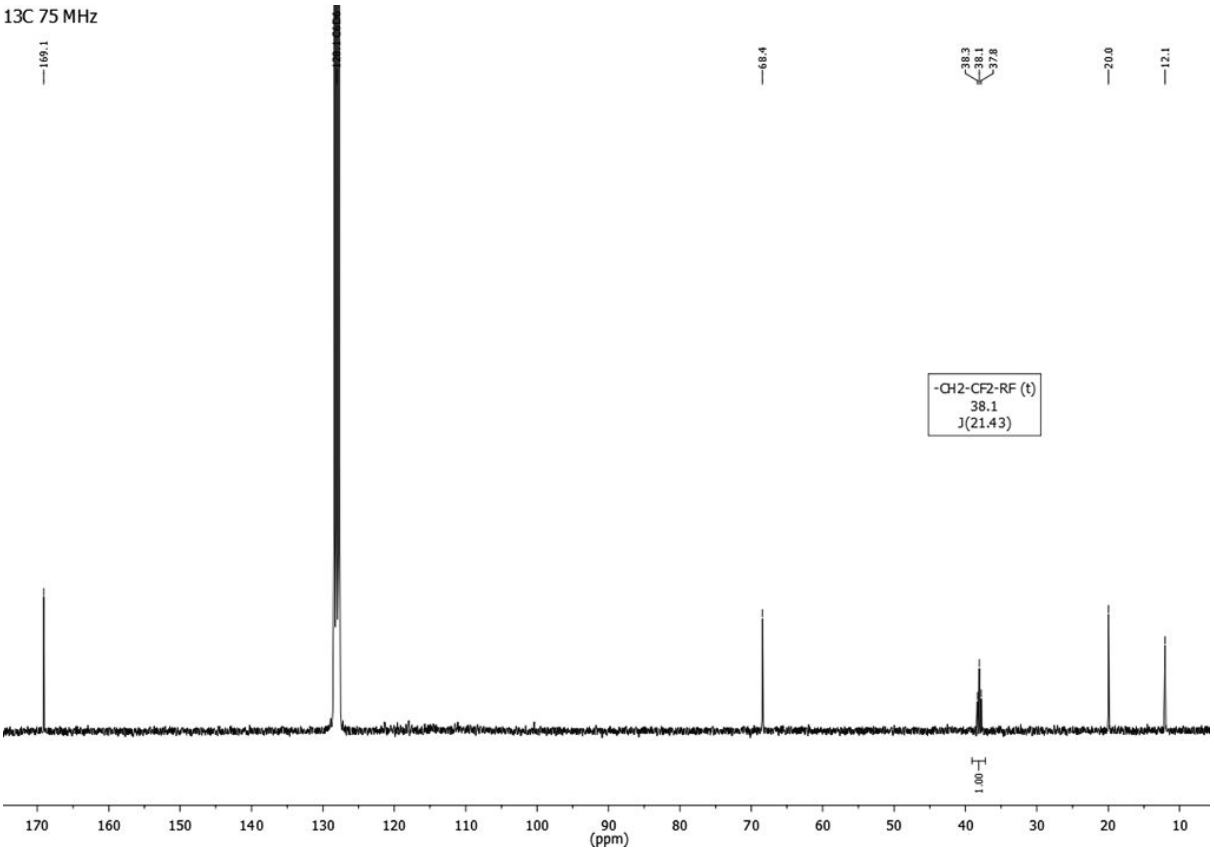


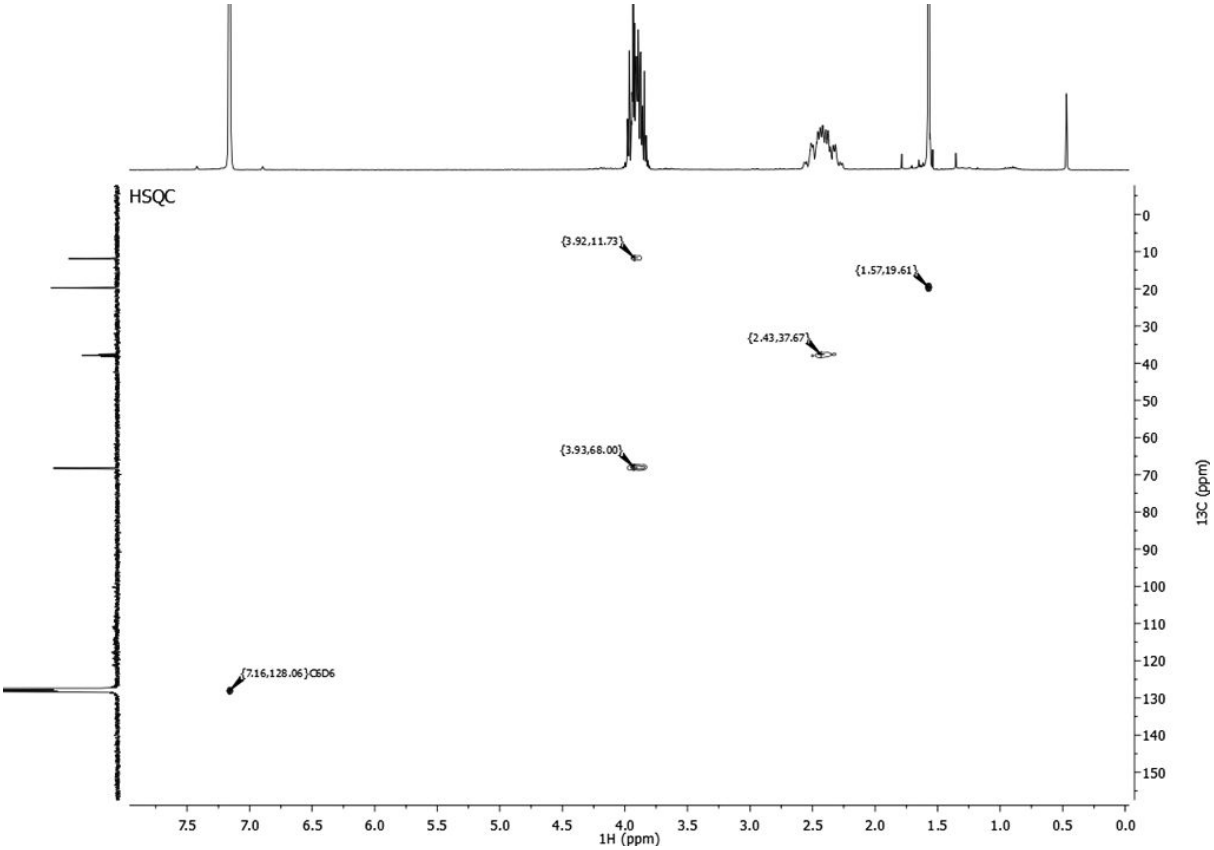
Result of Peak Picking		
No.	Position	Intensity
1	2962.13	88.4163
2	1747.19	71.2332
3	1432.85	81.7444
4	1366.32	74.8823
5	1237.11	70.6127
6	1042.34	74.4991
7	844.669	81.8067
8	811.885	80.3094
9	732.817	76.9679
10	699.069	76.0703
11	656.643	79.8785
12	605.539	84.2289
13	553.47	84.4551
14	530.328	81.91

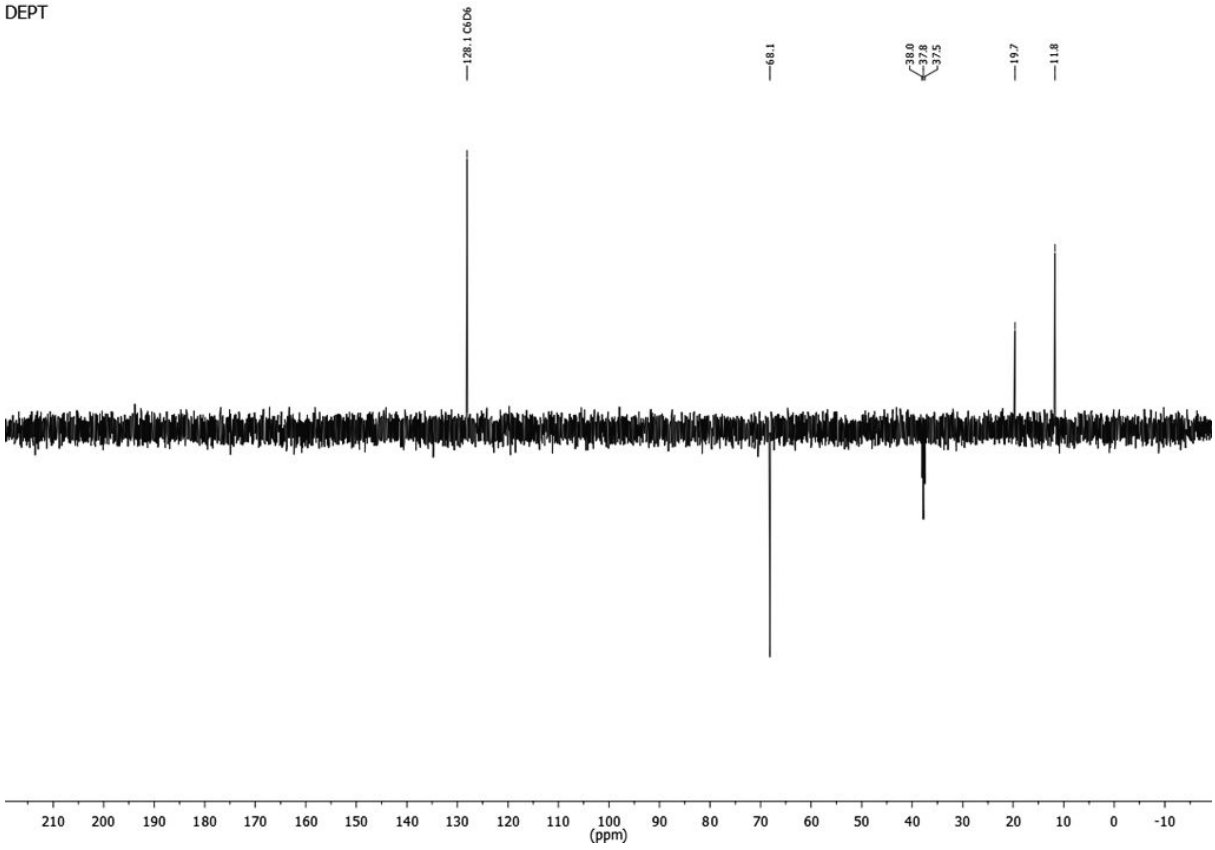
8.2 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-2-iodononyl acetate

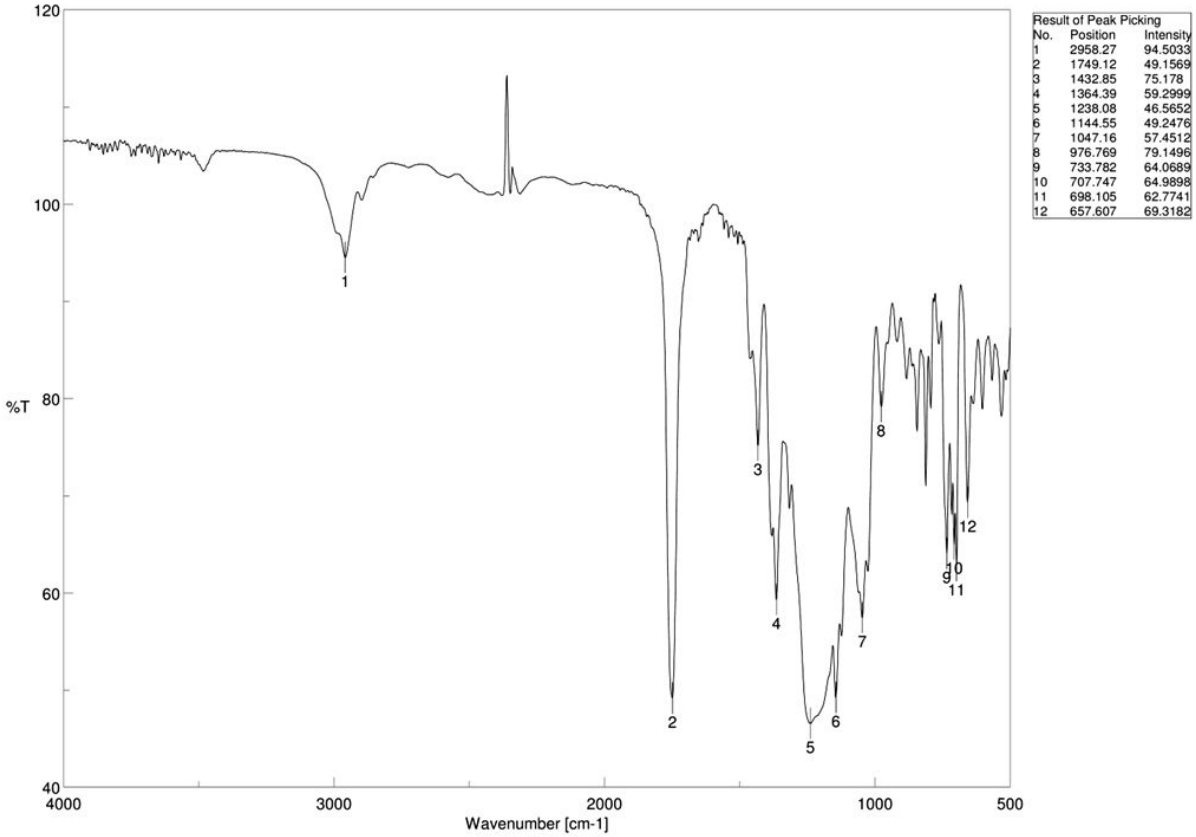





13C 75 MHz
169.1
68.4
38.3
38.1
37.8
20.0
12.1
-CH2-CF2-RF (t)
38.1
J(21.43)
1.00
(ppm)


HSQC
{3.92,11.73}
{1.57,19.61}
{2.43,37.67}
{3.93,68.00}
{7.16,128.06}C6D6
13C (ppm)
1H (ppm)



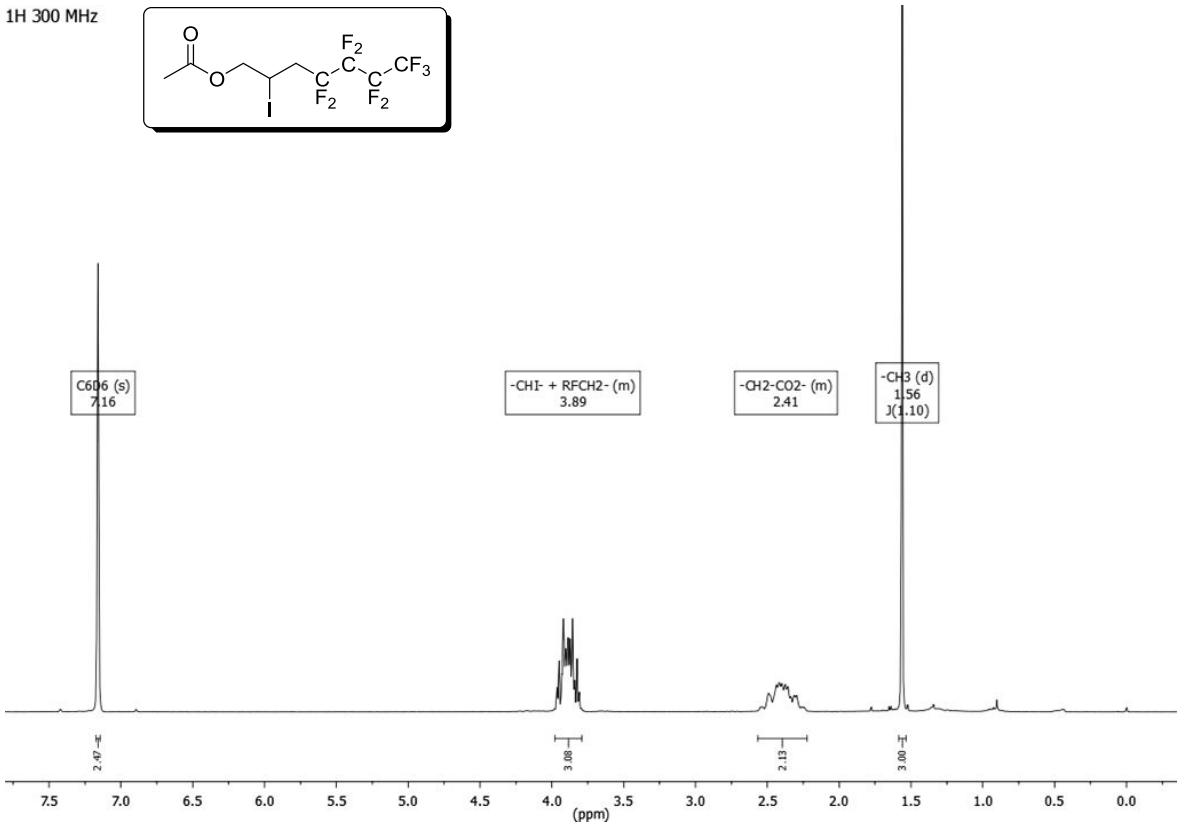


Result of Peak Picking

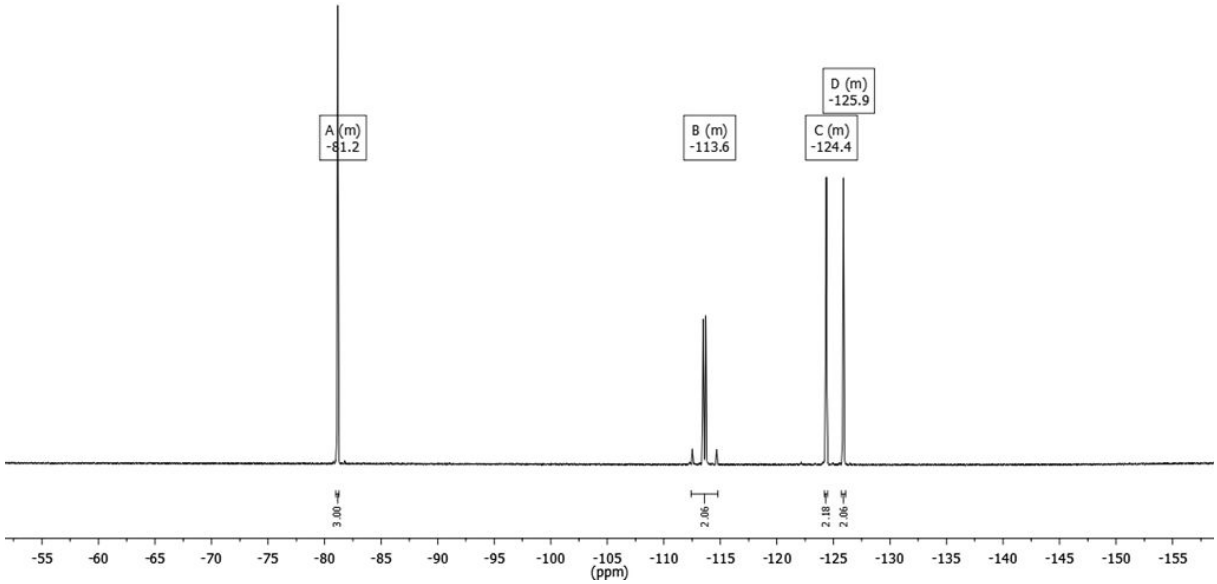
No.	Position	Intensity
1	2958.27	94.5033
2	1749.12	49.1569
3	1432.85	75.178
4	1364.39	59.2999
5	1238.08	46.5652
6	1144.55	49.2476
7	1047.16	57.4512
8	976.769	79.1496
9	733.782	64.0689
10	707.747	64.9898
11	698.105	62.7741
12	657.607	69.3182

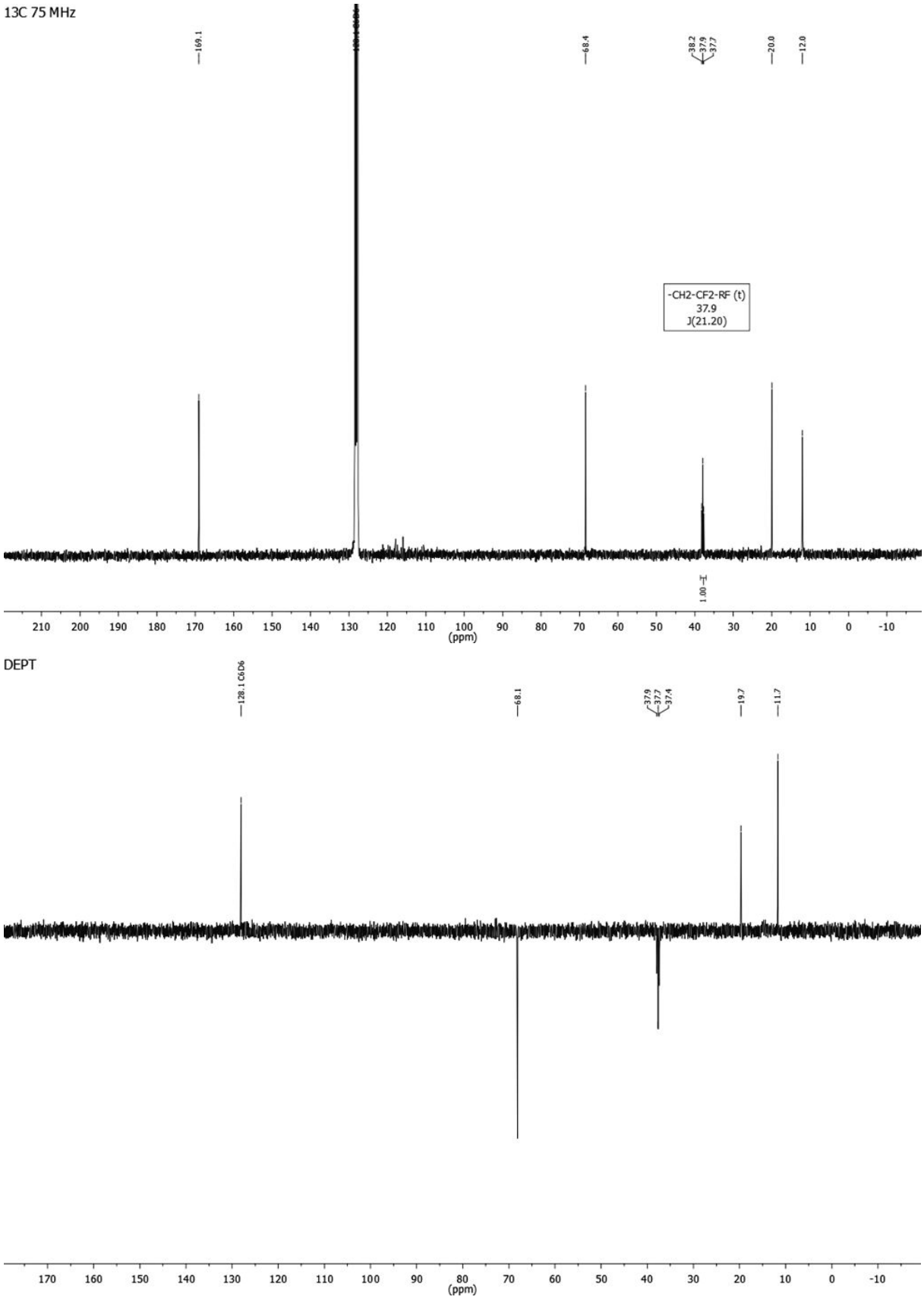
8.3 4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptyl acetate

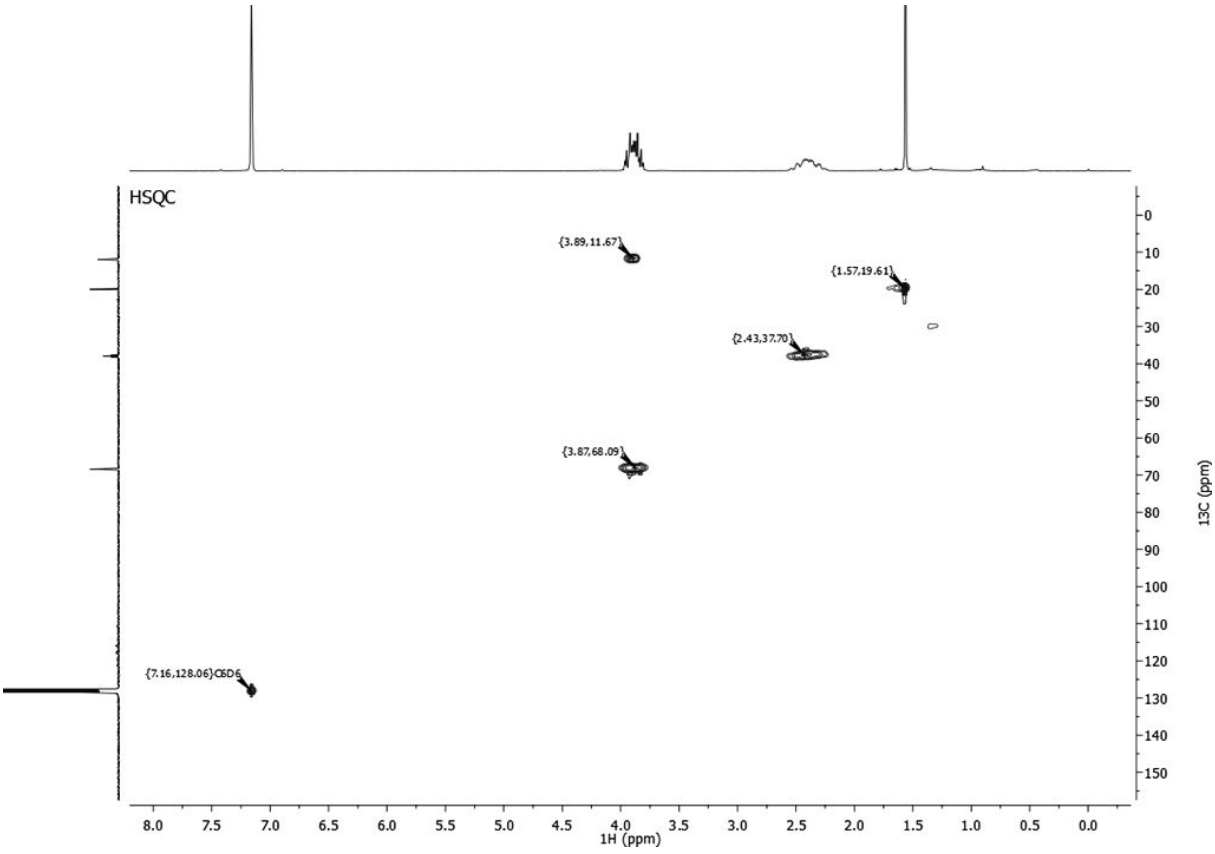
1H 300 MHz

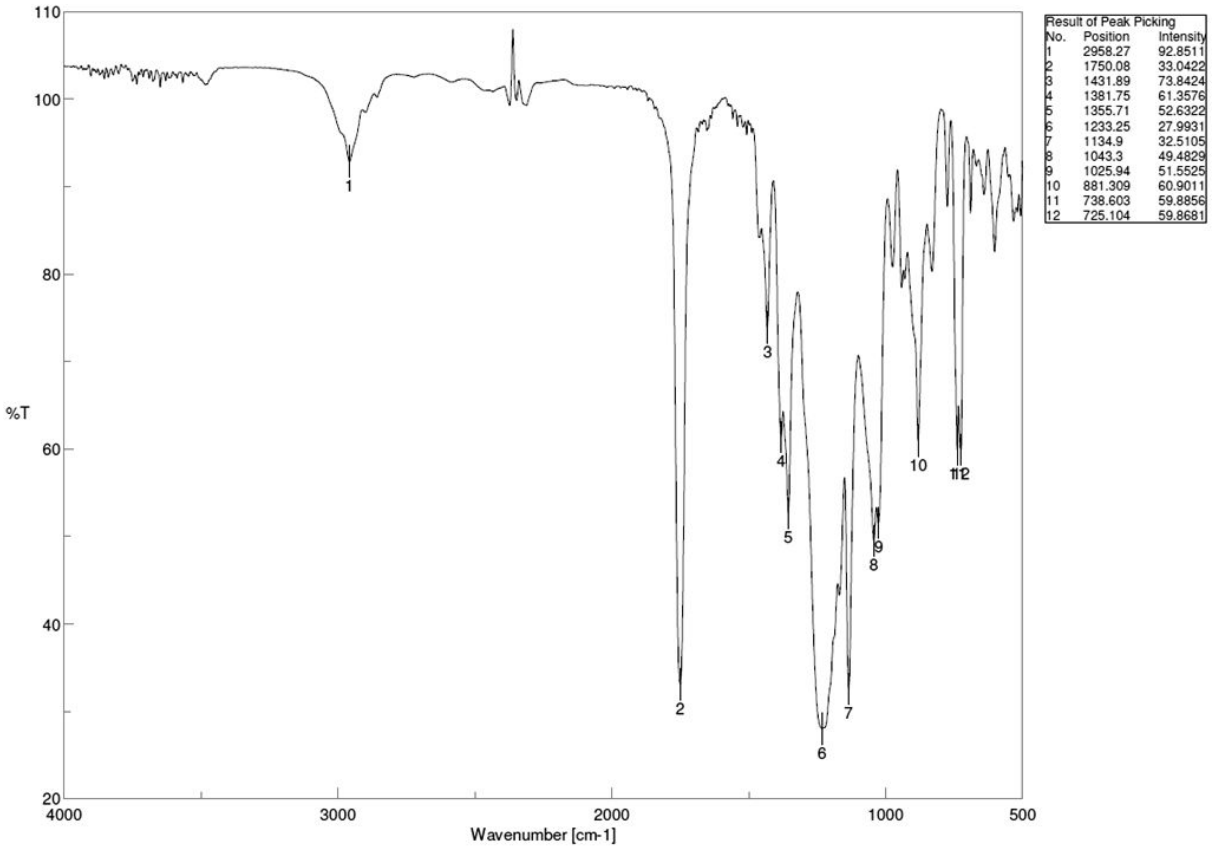


19F 282 MHz




13C 75 MHz
169.1
68.4
38.2
37.9
37.7
20.0
12.0
-CH2-CF2-RF (t)
37.9
J(21.20)
1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)
DEPT
128.1 C6D6
68.1
37.9
37.7
37.4
19.7
11.7
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)





Result of Peak Picking

No.	Position	Intensity
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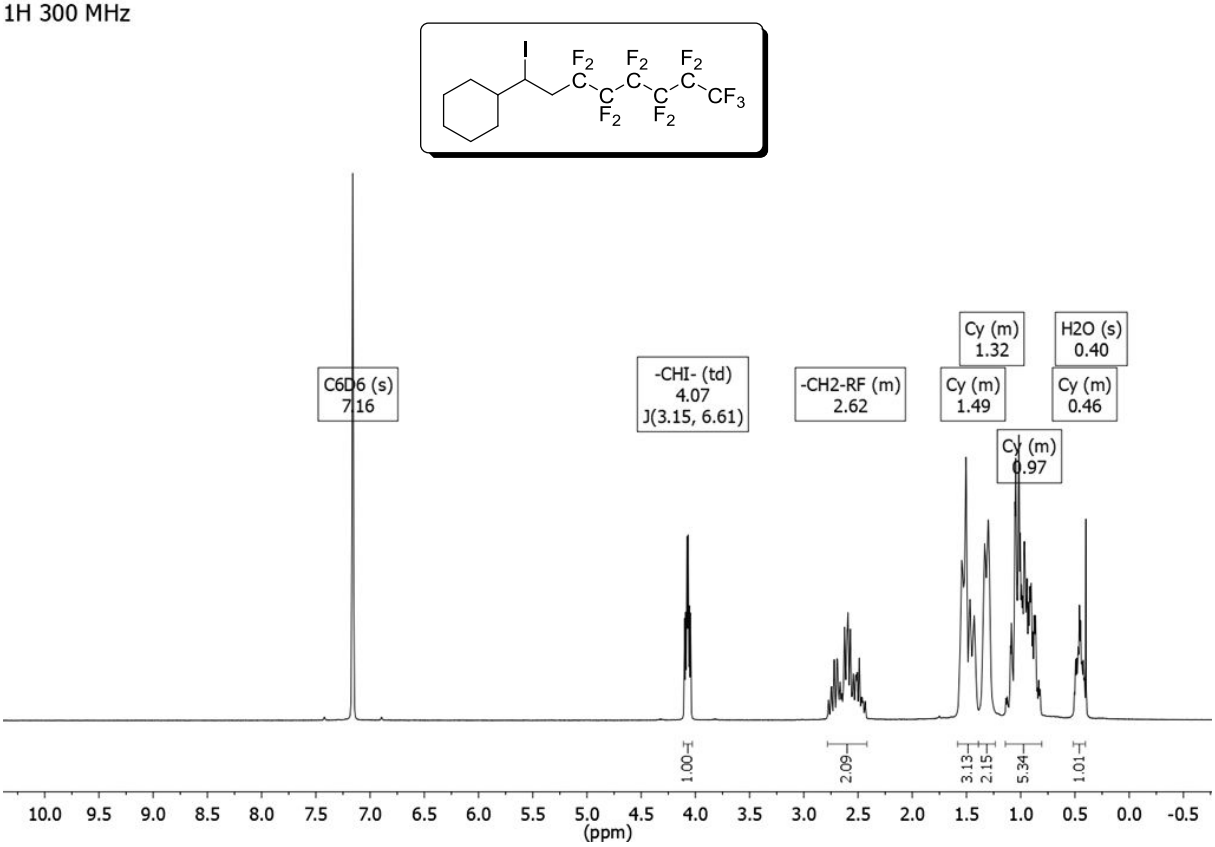
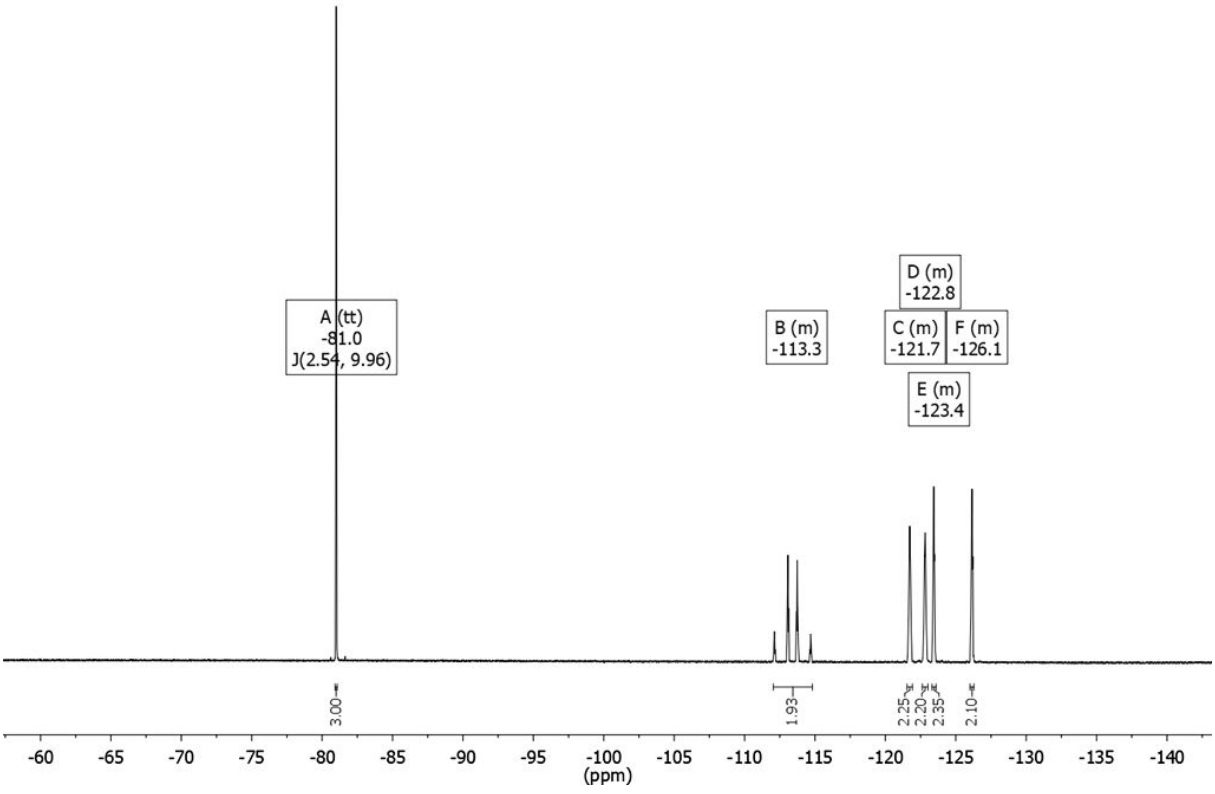
2	1750.08	33.0422
3	1431.89	73.8424
4	1381.75	61.3576
5	1355.71	52.6322
6	1233.25	27.9931
7	1134.9	32.5105
8	1043.3	49.4829
9	1025.94	51.5525
10	881.309	60.9011
11	738.603	59.8856
12	725.104	59.8681

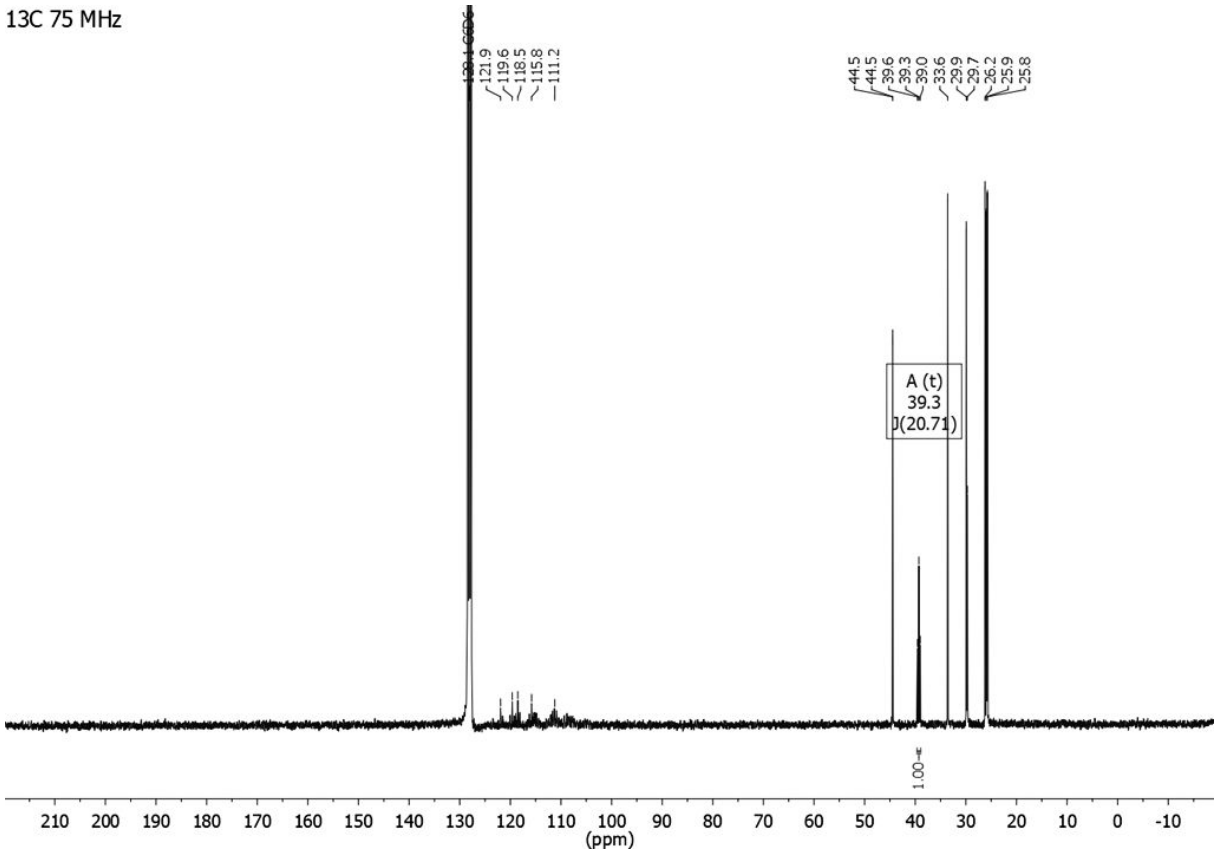
8.4 (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooctyl)cyclohexane

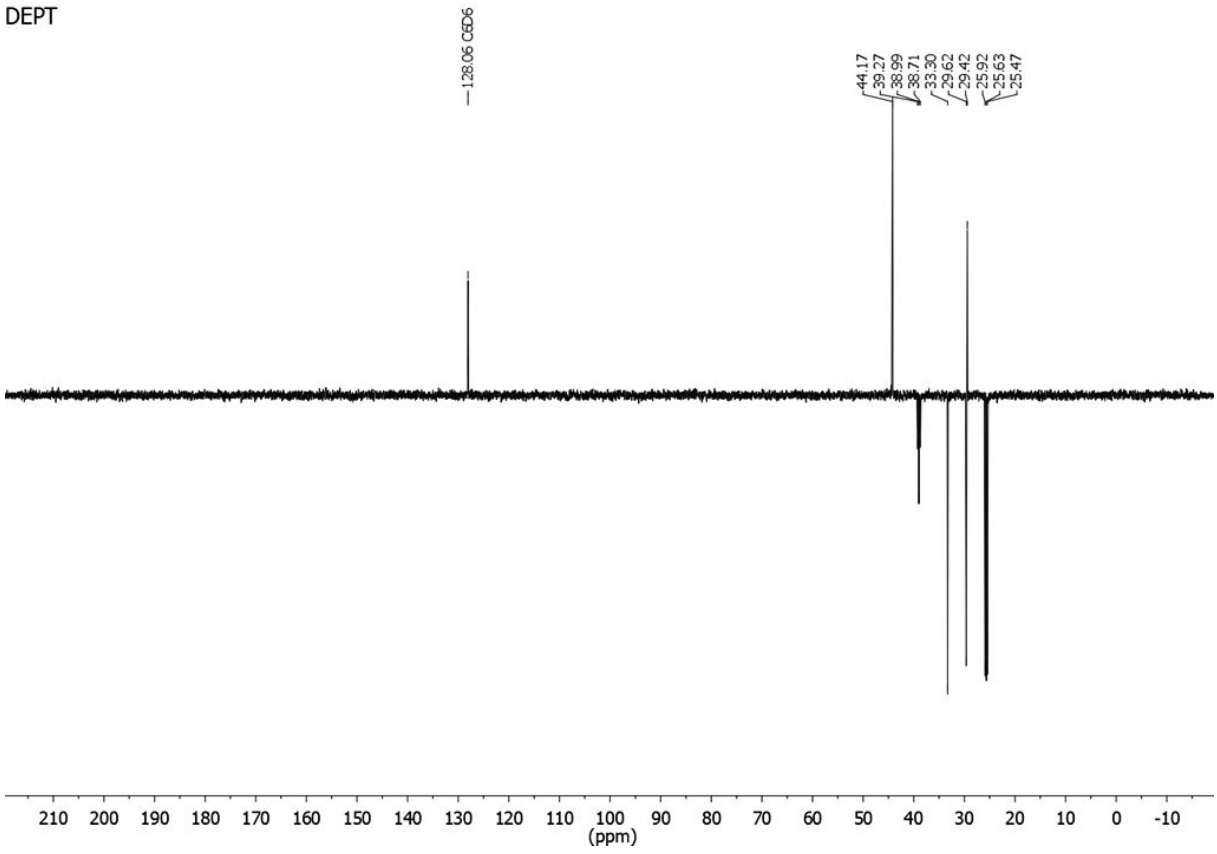
1H 300 MHz

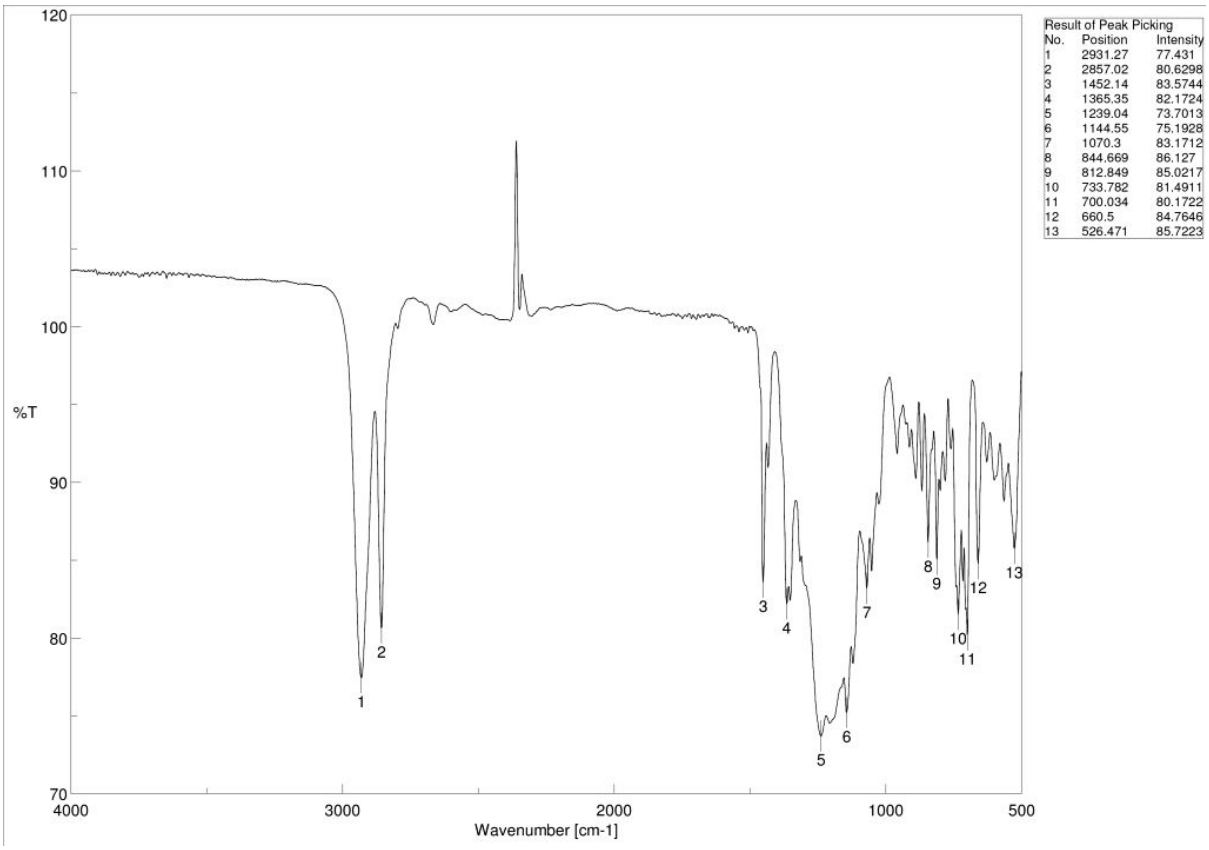


19F 282 MHz




13C 75 MHz
121.9
119.6
118.5
115.8
111.2
44.5
44.5
39.6
39.3
39.0
33.6
29.9
29.7
26.2
25.9
25.8
A (t)
39.3
J(20.71)
1.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)


DEPT
128.06 C6D6
44.17
39.27
38.99
38.71
33.30
29.62
29.42
25.92
25.63
25.47
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)



Result of Peak Picking

No.	Position	Intensity
1	2931.27	77.431
2	2857.02	80.6298
3	1452.14	83.5744
4	1365.35	82.1724
5	1239.04	73.7013
6	1144.55	75.1928
7	1070.3	83.1712
8	844.669	86.127
9	812.849	85.0217
10	733.782	81.4911
11	700.034	80.1722
12	660.5	84.7646
13	526.471	85.7223

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Part II

Gold-Catalysed Desymmetrisation of 1,4-Diynes

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Abbreviations

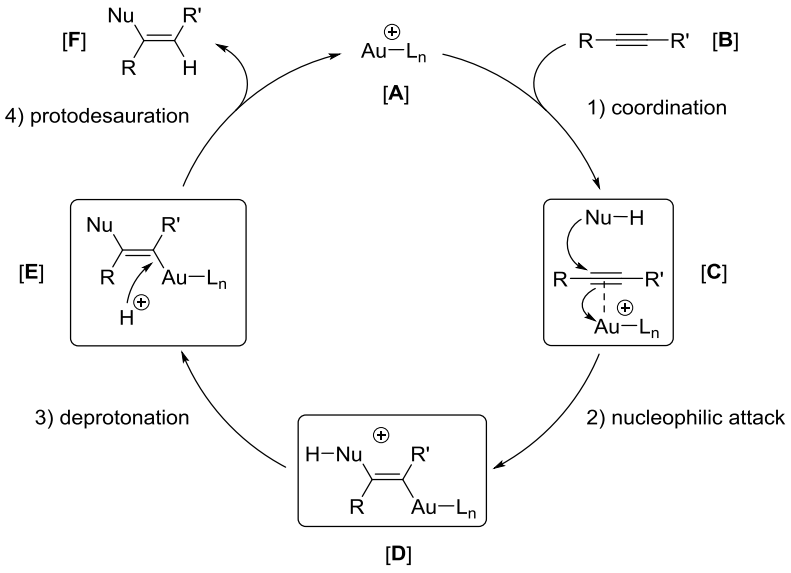
BINOL	1,1'-bi-2-naphthol
BIPHEP	2,2'-bis(diphenylphosphino)biphenyl
Boc	*tert*-butyloxycarbonyl
BPE	1,2-bis(phosphino)ethane
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEAD	diethyl azodicarboxylate
δ	chemical shift
DIAD	diisopropyl azodicarboxylate
DIPA	diisopropylamine
DMAP	4-dimethylaminopyridine
eq.	equivalent(s)
LDA	lithium diisopropylamide
NHC	*N*-heterocyclic carbene
Pd/C	palladium on carbon
PMHS	polymethylhydrosiloxane
TFA	trifluoroacetic acid
TLC	thin layer chromatography
TriP	3,3'-bis(2,4,6-triisopropylphenyl)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate
XantPhos	4,5-bis(diphenylphosphino)-9,9-dimethylxanthene

1 Introduction

1.1 Gold Catalysis

For a long time gold was seen as an inert and catalytically inactive metal. As outlined in a review by Hutchings and Hashmi,[1] only little research was done on gold compounds as a catalyst or reactive species until the 21st century. In 2003, only 9000 publications dealing with gold catalysis were available. Of these 9000 publications, only about 100 dealt with homogeneous gold catalysts.[2] Considering the fact that the first homogenous gold catalysis system was discovered back in 1976,[3] the slow appearance of gold-catalysis research seems surprising. However, since the turn of the millennium gold catalysis developed into a very useful tool for activating C−C multiple bonds towards *O*-, *N*- or *C*-nucleophiles.[4-5] Therefore, today manifold variations of gold-catalysed transformations are known in the literature.[2,6-9]

Even though miscellaneous variations of gold-catalysed reactions are known, the mechanism is similar for most of them. The mechanism of a gold-catalysed functionalisation of C-C multiple bonds will be exemplified for an alkyne (Scheme 1). The mechanism for the functionalisation of allenes and alkenes is equivalent to the presented mechanism.



Scheme 1: Catalytic cycle for the gold-catalysed functionalisation of alkynes.[10]

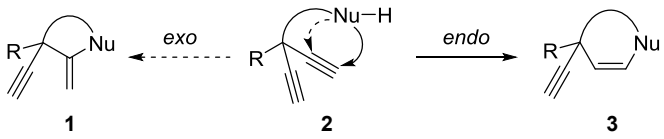
First, a gold(I)-species [**A**] coordinates the alkyne [**B**] (Scheme 1). By the formation of a linear gold(I)-complex [**C**], the alkyne is activated for an intra- or intermolecular nucleophilic attack and forms an intermediate [**D**]. Thirdly, a deprotonation to an intermediate [**E**] takes place. In the fourth and last step the so-called protodesauration occurs releasing the desired product [**F**] and the gold(I)-catalyst. More detailed mechanistic considerations can be found in two publications by Hashmi.[11-12]

1.2 Gold-Catalysed Desymmetrisations and An Enantioselctive Variation

A desymmetrisation of 1,4-diynes by Czekelius *et al.*[5,13-15] lays the foundation for the synthesis of mesembrine described in this thesis. Therefore, the developement of this desymmetrisation is described extensively. At first, a desymmetrisation was developed,[5,13] followed by an enantioselective variant.[14-15]

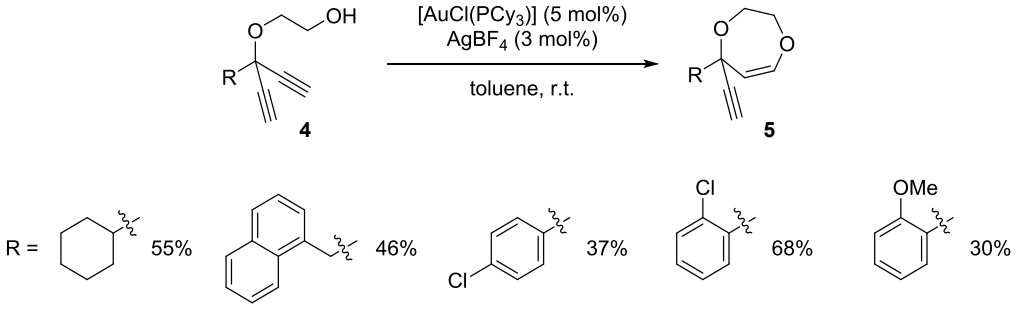
1.2.1 Gold-Catalysed Desymmetrisation

3,3-Disubstituted 1,4-diynes **2** are of interest in the context of natural product synthesis as they can be used as building blocks for heterocycles. In this context gold catalysis can be a useful tool. Gold-catalysed intramolecular cyclisations predominantly proceed in *exo*-fashion.[13] However, 3,3-disubstituted 1,4-diynes **2** can potentially cyclise in an *endo-dig*-cyclisation (Scheme 2), too.



Scheme 2: Intramolecular *endo*- or *exo*-cyclisation of 1,4-diynes **2**.[13]

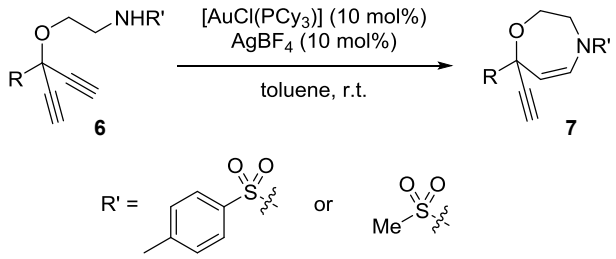
This *endo-dig*-cyclisation is of great interest for the formation of seven-membered heterocycles, as not many possibilities for their formation are known in the literature.[13] To construct seven-membered heterocycles, 3,3-disubstituted 1,4-diynols **4** were synthesised by a reaction of esters with the corresponding alkynylides followed by an *O*-alkylation. With a cationic gold-phosphane complex as the catalyst (Scheme 3) the 1,4-diynols **4** showed high *endo*-selectivity and many different seven-membered heterocycles **5** were afforded. The substrate scope embraces aromatic substituents, *ortho*- or *para*- substituted benzenes as well as aliphatic substituents (Scheme 3). Thus, a versatile method for the formation of dioxepines was developed.



Scheme 3: Cyclisation of 1,4-diynols **4** to dioxepines **5** (top), selected examples with yields (bottom).[13]

To expand the scope of this method other substrates were tested. 1,4-Diynesulfonamides **6** were successfully cyclised to tetrahydrooxazepines **7** (Scheme 4), but the catalyst loading had to be increased and the yields were low (≤ 36%).

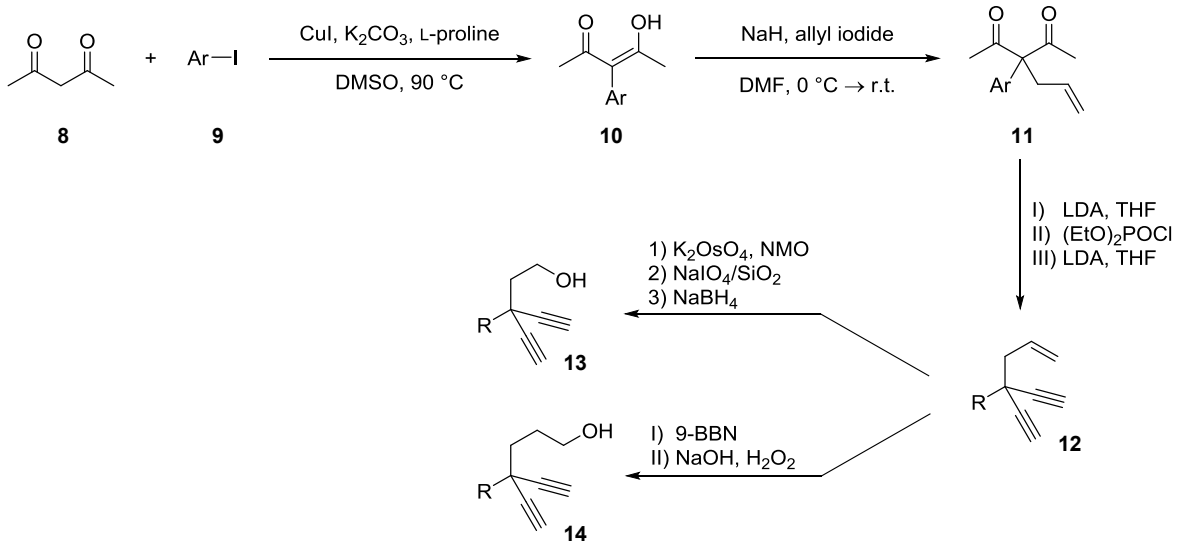
These low yields were explained by catalyst degradation. In contrast to 1,4-diynesulfonamides **6**, primary amines as well as carboxamides were no suitable substrates.



Scheme 4: Cyclisation of 1,4-diyneamides **6** to tetrahydrooxazepines **7**.[13]

In a subsequent publication by Czekelius *et al.*,[5] the substrate scope was expanded to 3-hydroxyethyl-1,4-diynes **13** as well as 3-hydroxypropyl-1,4-diynes **14** (Scheme 5). For these diynes no general synthetic pathway was known at this point of time. Thus, they developed a synthetic route starting from acetylacetone (**8**) which was arylated with aryl iodides **9** mediated by copper. The resulting 3-aryl-acetylacetones **10** were alkylated with allyl iodide and subsequently diketone **11** was transformed into 1,4-diyne **12** via an enolphosphate. The next steps depend on the molecule of interest.

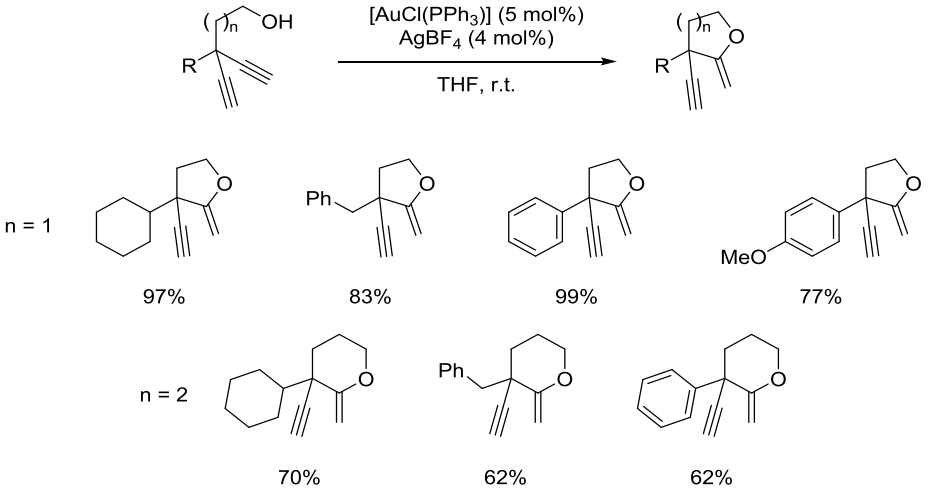
For 3-hydroxyethyl-1,4-diynes **13** a sequence of Upjohn dihydroxylation, diol cleavage and a reduction of the aldehyde with $NaBH_4$ can be applied. 3-Hydroxypropyl-1,4-diynes **14** can be synthesised by hydroboration followed by workup with $NaOH/H_2O_2$. The later described total synthesis of (+)-mesembrine was partly based upon this pathway (Scheme 5).



Scheme 5: Synthesis of 3-hydroxyethyl-1,4-diynes **13** as well as 3-hydroxypropyl-1,4-diynes **14**.[5]

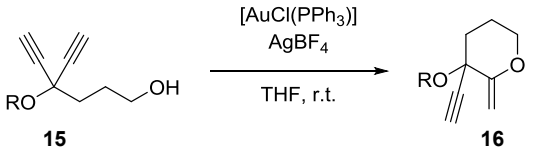
Applying former reaction conditions to 3-hydroxyethyl-1,4-diynes **13**, utilising $[AuCl(PCy_3)]/AgBF_4$ in toluene, resulted in poor conversions. However, changing the solvent to THF and the gold salt to $[AuCl(PPh_3)]$ resulted in an efficient system (Scheme 6). Interestingly, a

complete *exo*-selectivity was observed. This changed selectivity might be explained by a change regarding the linker length. 3-Hydroxyethyl-1,4-diynes **13** have a chain length of three atoms and the previously used 1,4-diynes had a chain length of four atoms (Scheme 3, Scheme 4). However, since 3-hydroxypropyl-1,4-diynes **14** also cyclise exclusively in *exo*-fashion, the length of the chain cannot be the decisive factor.



Scheme 6: Cyclisation of 3-hydroxyethyl- (top, n = 1) as well as 3-hydroxypropyl-1,4-diynes (bottom, n = 2).[5]

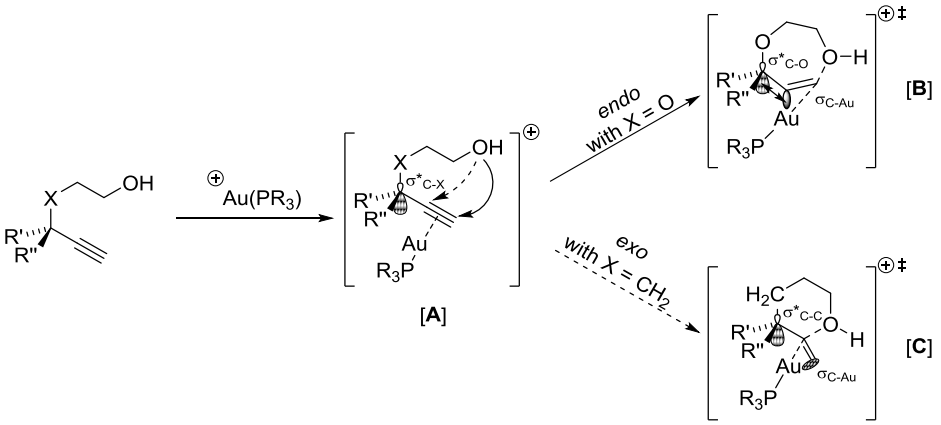
As a second potential explanation, the electron withdrawing effect of the alkoxy substituent in the 3-position was under suspicion to cause the selectivity reversal. To examine this assumption, 3-alkoxysubstituted 1,4-diyne **15** was synthesised and cyclised (Scheme 7). As it cyclised to *exo*-cyclisation product **16**, the electron-withdrawing effect of the substituent in 3-position alone cannot guide the regioselectivity.



Scheme 7: Cyclisation of an 3-alkoxy substituted 3-hydroxypropyl-1,4-diyne.[5]

Since further experiments showed that a solvent effect can be ruled out as the reason for the reversal of selectivity as well, stereoelectronic effects were taken into consideration. To identify potential stereoelectronic interactions, the mechanism and the presumed transition states have to be evaluated. The first step of the gold-catalysed intramolecular cyclisation is the coordination of a gold(I)-species at the alkyne (Scheme 8, [**A**]). After the coordination the intramolecular attack can take place, resulting in either an *endo*- or an *exo*-transition state. A closer evaluation of the two transition state geometries revealed a potential interaction between the σ^*(C−O)- and the σ(C−Au)-orbital (Scheme 8, [**B**]) for molecules with an alkoxy bridge. This stabilising interaction

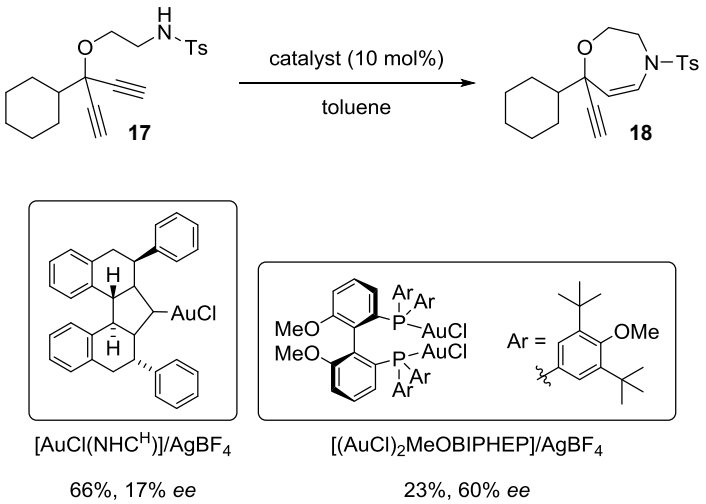
is presumably the reason for the *endo*-selectivity of compounds with intramolecular nucleophiles, which are connected by an alkoxy bridge. For molecules with an alkyl bridge the σ^*(C−C)-orbital (Scheme 8, [**C**]) is energetically too high to interact with the σ(C−Au)-orbital. Thus, the *endo* transition state might not be favoured and an *exo*-cyclisation takes place.



Scheme 8: Stereoelectronical explanation for the observed *endo*-/*exo*-selectivity.[5]

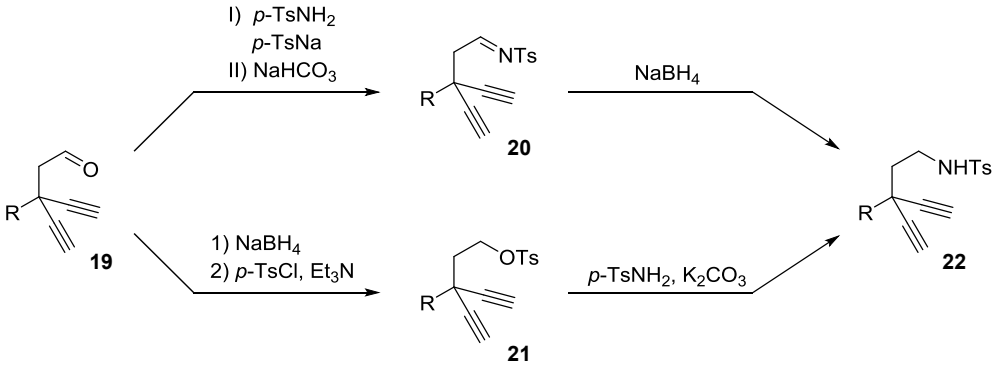
1.2.2 Gold-Catalysed Enantioselective Desymmetrisation

Since a catalytic desymmetrisation of 3,3-disubstituted 1,4-diynes was successfully developed, an asymmetric desymmetrisation was investigated as the next logical step. This investigation was already started before by Czekelius *et al.*[13] They were able to achieve first promising results, but obtained either a low yielded or a low enantiomeric excess utilising an optically pure NHC or a bidendate phosphane (Scheme 9).



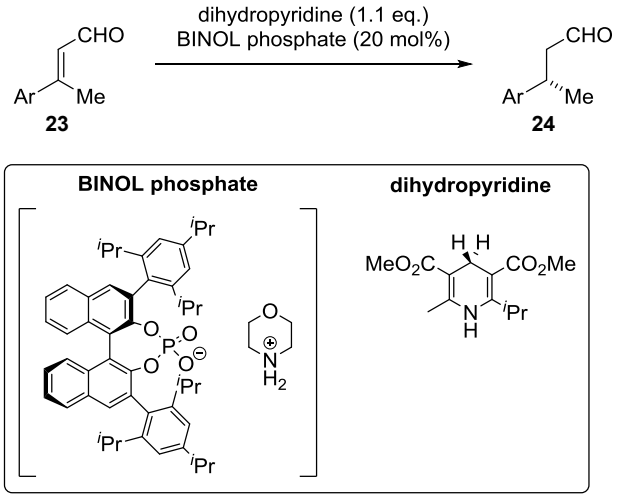
Scheme 9: Enantioselective desymmetrisation of a diynamide utilising gold catalysts.[13]

Before they started to investigate this asymmetric desymmetrisation more thoroughly, they synthesised additional diynamides **43** with tosyl imines **41** or tosylates **42** as the intermediates.[14]



Scheme 10: Synthesis of diynamides via tosyl imines or tosylates.[14]

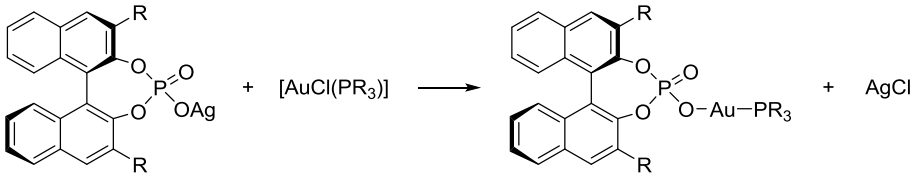
With these substrates at hand, Czekelius *et al.* probed the cyclisation with several phosphane based gold(I)-catalysts and obtained negligible enantiomeric excesses. Since a more thorough screening of chiral ligands did not seem to be promising, a new strategy had to be applied. Instead of the common phosphane or carbene ligands, optical active counterions can be used in catalytic processes. In this context, List *et al.*[16] coined the term "asymmetric counterion-directed catalysis" (ACDC). With this asymmetric counterion-directed catalysis List *et al.* were able to conduct an enantioselective counterion-mediated transfer hydrogenation at α,β-unsaturated aldehydes (Scheme 11).[16]



Scheme 11: Catalytic transfer hydrogenation of α,β-unsaturated aldehydes using an asymmetric counterion.[16]

Even before this publication, chiral counterions were known and successfully applied, as outlined in a review by *Lacour et al.*[17] For example, in 2004 Akiyama[18] published an enantioselective Mannich-type reaction with a phosphate as the chiral counterion

Inspired by this work, Czekelius *et al.* chose 1,1'-bi-2-napthol (BINOL) phosphates as a chiral counterion. Initially, several 3,3'-substituted BINOL phosphate gold(I)-complexes **27** were tested, which were prepared from gold(I)-precursors **47** and silver BINOL phosphates **46** (Equation 1).



25 **26** **27**

Equation 1: Preparation of gold catalysts from a gold(I)-precursor and a silver 3,3'-substituted BINOL phosphate.

Four factors were varied to optimise the cyclisation: Substituents in 3,3'-position, the ligand of gold(I), the solvent and the reaction temperature. The best results were observed with triisopropylphenyl-substituents in 3,3'-position (TriP, Figure 1), ^{t}Bu$_3$P as the ligand of gold(I), $CHCl_3$ as the solvent and reaction temperatures of −55 °C.

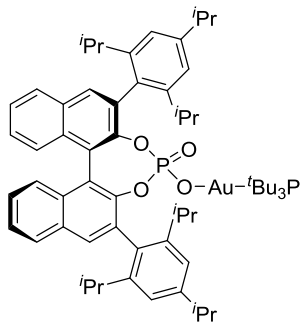
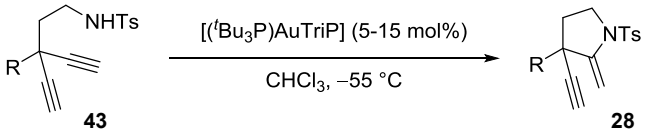


Figure 1: [(^{t}Bu$_3$P)AuTriP] TriP = 3,3'-(triisopropylphenyl)binol phosphate.

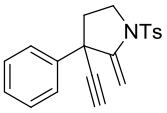
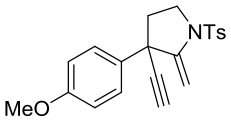
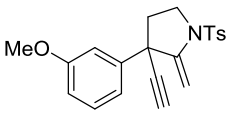
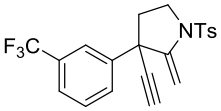
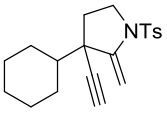
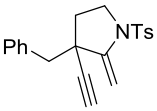
Since the reaction was most efficient in non-polar solvents at low temperatures, the formation of a contact ion pair between the gold(I)-alkyne complex with the chiral phosphate is feasible. The formation of such contact ion pair might be the reason for the observed good enantioselectivities.

With these optimised conditions, the substrate scope was evaluated (for selected examples see Table 1). Aromatic substituents as well as aliphatic substituent at the 1,4-diyneamide **43** were tolerated. However, aliphatic substituents require a higher catalyst loading (15 mol%) and longer reaction times.

Table 1: Gold-catalysed asymmetric desymmetrisation of diynamides, selected examples.[14]



43 **28**

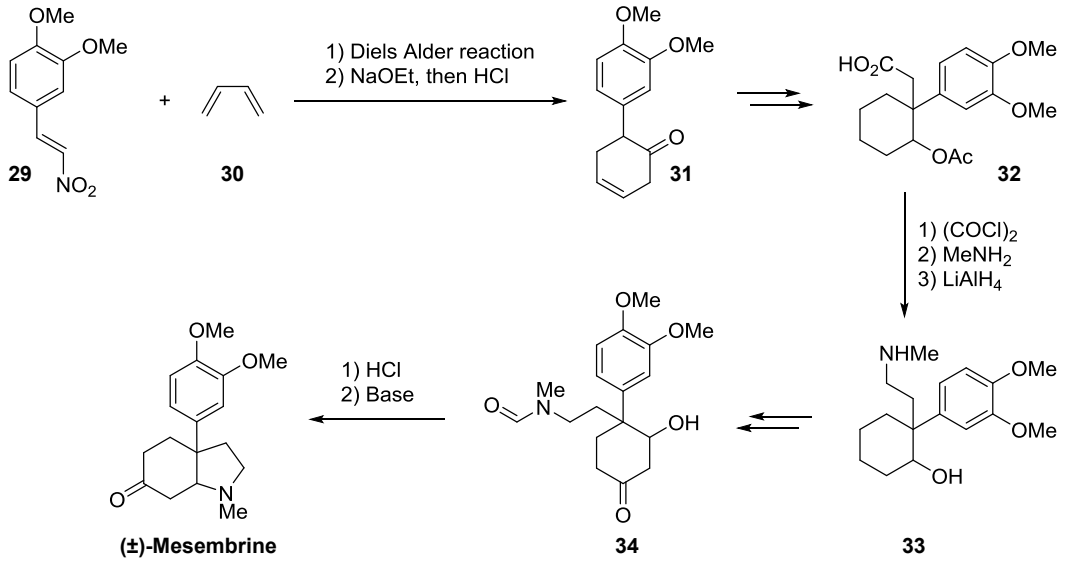
product	reaction time	yield [%]	*ee* [%]
	22 h	99	92
	21 h	93	82
	24 h	94	77
	24 h	87	81
	7 d	47	77
	7 d	53	64

1.3 Construction of a Quaternary Stereocentre − Total Syntheses of Mesembrine

A large number of mesembrine total syntheses are known in literature. A recently published review of total syntheses of mesembrine by Czekelius[19] and a review from 2010 of Zhao *et al.*[20] provide an overview of these total syntheses. Within this chapter, the first total synthesis of (±)-mesembrine, (+)-mesembrine as well as (−)-mesembrine are described. Additionally, the most recent total synthesis is presented.

The first total synthesis of mesembrine was published in 1965 by Shamma and Rodriguez (Scheme 12).[21-22] They began with nitrostyrene derivate **29** and synthesised mesembrine in 21 steps. As a start reaction, *cis*-1,3-butadiene (**30**) was reacted with styrene derivate **29** in a Diels-Alder-reaction to introduce the six-membered ring. The resulting nitro compound was

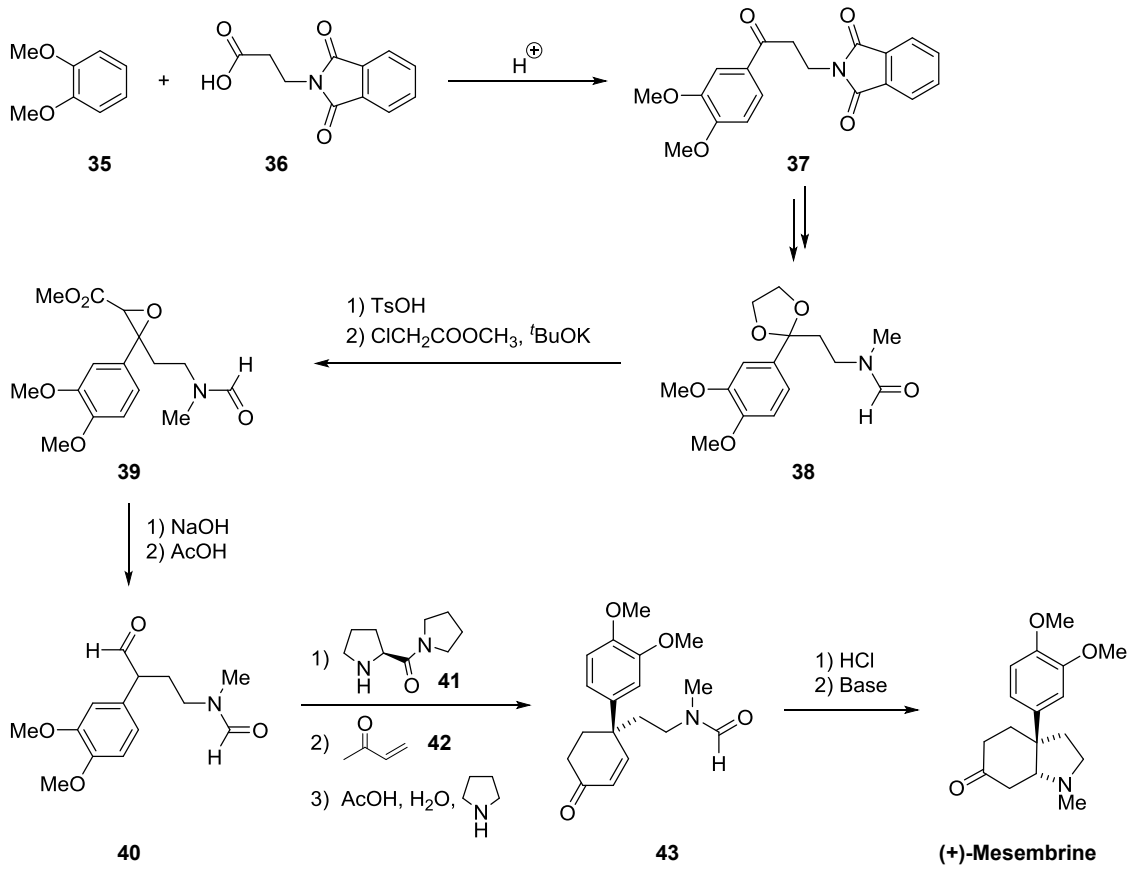
transformed to ketone **31** in a Nef-reaction. Acid **32** was obtained by a palladium-catalysed reduction, the introduction of an allyl moiety and a subsequent oxidation sequence.



Scheme 12: Total Synthesis of (±)-mesembrine by Shamma and Rodriguez.[21-22]

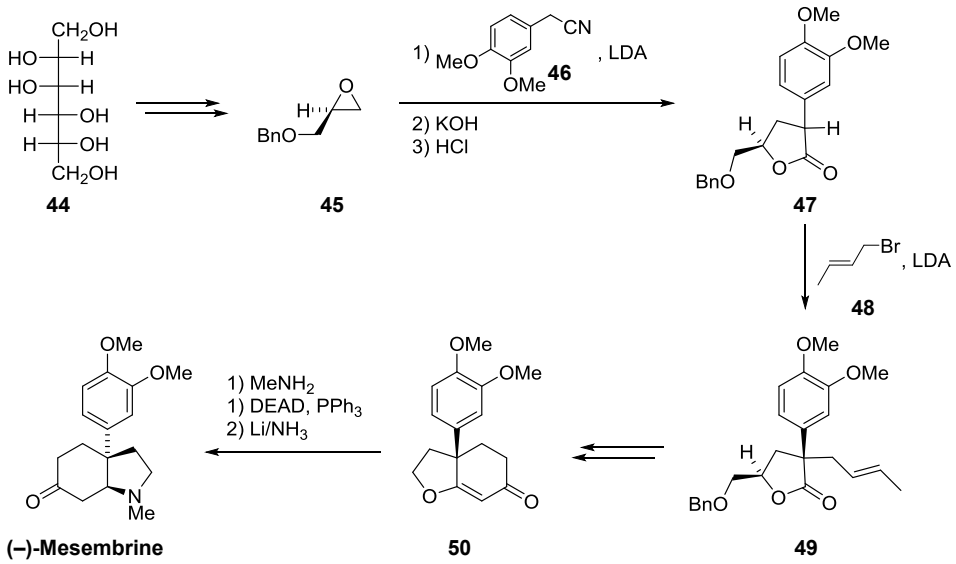
Besides the already established six-membered ring, a pyrrolidine ring had to be built up. For this purpose, acid **32** was transformed into an aminoalcohol **33**. Next, the molecule had to be prepared for a repositioning of the oxygen at the six-membered ring. For this purpose the amine was protected and a long sequence of redox-processes and one α-bromination was necessary to obtain β-hydroxyketone **34**. With this molecule at hand, an acid mediated elimination as well as a deprotection of the amine was conducted. After basification, racemic (±)-mesembrine was successfully obtained (Scheme 12).

The first asymmetric total synthesis of (+)-mesembrine was conducted by Yamada *et al.*[23] in 1971. They used an auxiliary-controlled reaction to introduce the chiral information. As a starting point they chose 1,2-dimethoxybenzene (**35**), which was condensed with phthalimide **36**. The resulting ketone **37** was transformed to the protected amine **38**. A modified Darzens reaction, which is a useful tool to generate α,β-epoxyesters, was conducted to obtain epoxide **39**. Next, a saponification gave aldehyde **40**, which was used for the enantioselective ring closure. For this purpose, (*S*)-1-prolylpyrrolidine (**41**) was introduced at first. The six-membered ring and thereby the quaternary carbon centre was then synthesised using a Robinson annulation with methyl vinyl ketone (**42**). By an intramolecular attack of the amine at the Michael system **43**, (+)-mesembrine was formed. However, this material was a mixture of isomers as its optical purity was only of about 26% *ee*.



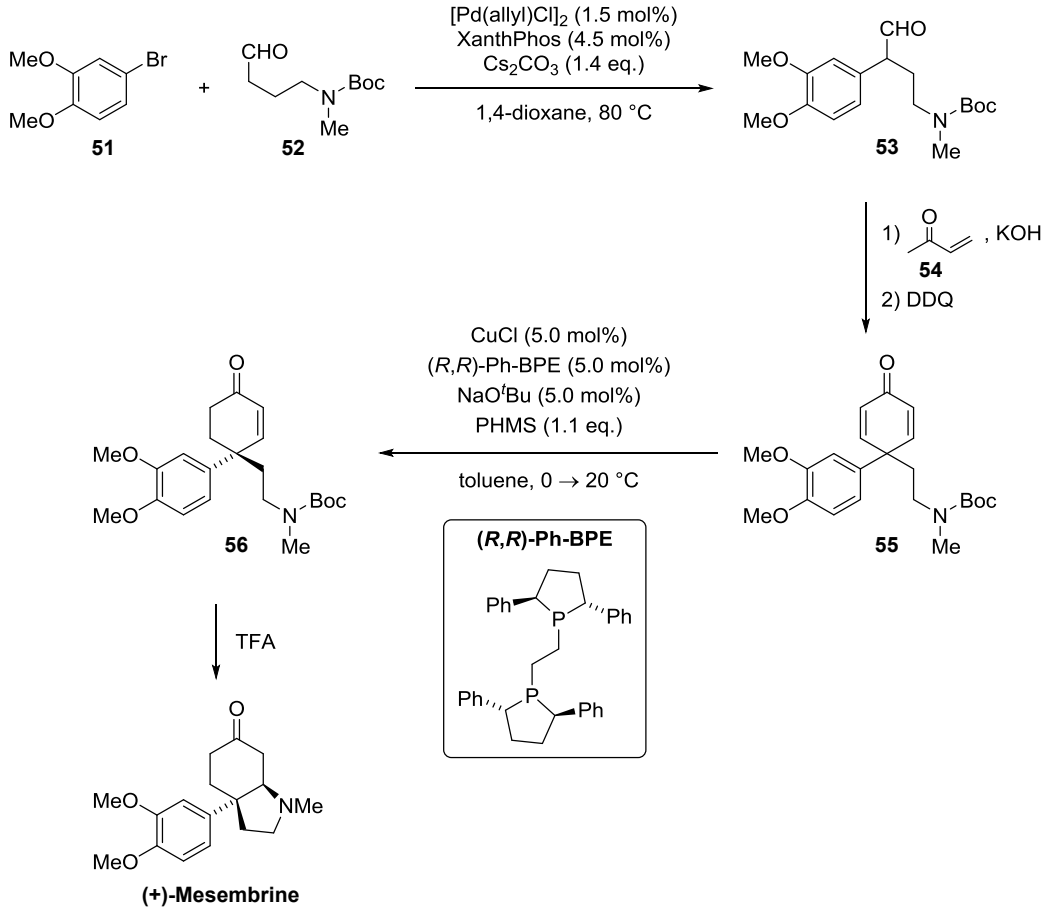
Scheme 13: Total Synthesis of (+)-mesembrine by Yamada *et al.*[23]

As (+)-mesembrine is not the naturally occurring isomer, the first synthesis of the (−)-mesembrine is described in this chapter. Takano *et al.*[24] used (D)-mannitol (**44**) as a chiral template for their synthesis (Scheme 14). By a multistep procedure enantiomerically pure glycidol **45** was synthesised starting from (D)-mannitol (**44**). This epoxide was regioselectively opened with 3,4-dimethoxybenzylcyanide (**46**), followed by a hydrolysis of the cyanide and an acid-mediated formation of cyclic ester **47**. This lactone had to be converted into a pyrrolidine ring later in this sequence. As one key step the quaternary stereocentre was built by a nucleophilic substitution at (*E*)-1-bromobut-2-ene (**48**). The stereocentre originating from (D)-mannitol controls the stereochemistry at the quaternary carbon in lactone **49** rendering it a substrate-controlled reaction. A removal of the side chain in 4-position at the lactone ring was followed by the formation of the cyclohexenone **50**. Lastly, the tetrahydrofurane ring was converted to a pyrrolidine ring by ring opening with methylamine and a subsequent Mitsunobu reaction for ring closure. A Birch reduction led to the final enantiomerically pure product (−)-mesembrine.



Scheme 14: Total synthesis of (−)-mesembrine by Takano *et al.*[24]

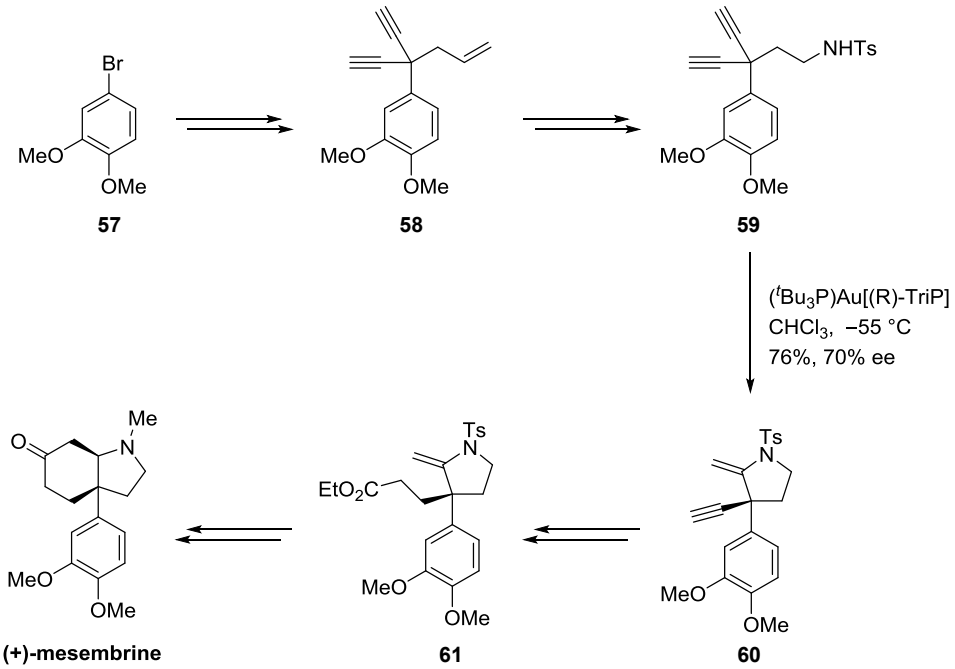
Lastly, the most recent total synthesis of mesembrine is presented. The key step of this synthesis by Shen *et al.*[25] is a copper catalysed desymmetrisation (Scheme 15). They started the synthesis by a Pd-catalysed α-arylation of aldehyde **52** with 4-bromo-1,2-dimethoxybenzene (**51**). With the resulting aldehyde **53** at hand they conducted a Robinson annulation to establish a cyclohexanone ring, which was dehydrogenated with DDQ to obtain dienone **55**. This dienone was the key intermediate, as it was used to show the utility of their copper-catalysed desymmetrisation. For this desymmetrisation they used a copper(I) source, a bisphosphinoethane ((*R*,*R*)-Ph-BPE), NaO^{t}Bu and a hydrosilane. With a yield of 82% and 97% enantiomeric excess the cyclohexanone **56** was obtained. A removal of the Boc-protecting group by TFA was the last step to afford (+)-mesembrine.



Scheme 15: Most recent total synthesis of (+)-mesembrine by Shen *et al.*[25]

2 Summary

The total synthesis of (+)-mesembrine was condcuted starting from 4-bromoveratrole (**57**) (Scheme 16). Ene-1,4-diyne **58** was synthesised in three steps utilising an Ullmann-type coupling in the first step. Surprisingly, the synthesis of 1,4-diynamide **59**, the key intermediate, was challenging. In the end, diynamide **59** was synthesised by a Mitsunobu reaction with Boc-protected *p*-toluenesulfonamide. This diynamide was successfully subjected to a gold-catalysed enantioselective desymmetrisation to build up a methylene pyrrolidine **60**, incorporating a quaternary stereocentre. After this key step, a six-membered ring was build up. For this purpose, ester **61** was synthesised by a carboxylation of the alkynylide and a subsequent hydrogenation. Gratifiyingly, the removal of the tosyl group was directly followed by an intramolecular cylisation. With this material at hand, (+)-mesembrine was obtained in four steps. More detailed information regarding this toal synthesis are described in the attached publication "Total Synthesis of (+)-Mesembrine Applying Asymmetric Gold Catalysis."[26]



Scheme 16: Total synthesis of (+)-mesembrine, key intermediates and a descriptions of the key step.

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Mechanistic Insights into FLP-Catalyzed Iodoperfluoroalkylations

The publication "Spittler, M., Helmecke, L. and Czekelius, C., Mechanistic Insights into FLP-Catalyzed Iodoperfluoroalkylations. *Eur. J. Org. Chem.* **2019**, 458-468." is presented as one part of the dissertation. It is integrated into this thesis without any changes. Authors to this publication were Michael Spittler, Lucas Helmecke and Constantin Czekelius. Experimental contributors were Michael Spittler and Lucas Helmecke. The major experimental part was contributed by Michael Spittler (75%) and a lower part by Lucas Helmecke (25%).

- Michael Spittler contributed the solvent screening, the kinetic investigation (inter alia a variation of the concentration of C_4F_9I, $^tBu_3P$, $B(C_6F_5)_3$ and the alkene) as well as the related calculations, the elucidation of side reactions involving $^tBu_3P$ and $B(C_6F_5)_3$ alone and in combination with C_4F_9I, the isolation of $[^tBu_3PR][FB(C_6F_5)_3]$ (R = H or I) and related test reactions, test reaction involving styrene, 1,4-cyclohexadiene and tributyltin hydride.
- Lucas Helmecke contributed the phosphane screening including the determination of NMR-shifts as well as test reactions, the synthesis of pent-4-en-1-ylcyclopropane as well as two connected test reactions, test reactions involving 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).
- The manuscript was mainly prepared by Michael Spittler involving the preparation of all chapters, its conceptualisation and literature search. Lucas Helmecke contributed a first draft of the introduction and a paragraph regarding the phosphane screening, the synthesis of pent-4-en-1-ylcyclopropane as well as 6-bromohexene, a description of the test reactions with 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) as well as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and a statement about the a photochemical test reaction regarding styrene. Additionally, he contributed to the literature search and correction process. Constantin Czekelius was strongly involved in the preparation of the introduction as well as the conclusion and corrected the manuscript.
- The preparation of the supporting information was mainly conducted by Michael Spittler. Lucas Helmecke contributed data regarding the phosphane screening, the synthesis of pent-4-en-1-ylcyclopropane, 6-bromohexene, test reactions with 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO). Lucas Helmecke and Constantin Czekelius contributed to the correction process.

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Full Paper

Frustrated Lewis Pair Catalysis

SPECIAL ISSUE

Mechanistic Insights into FLP-Catalyzed Iodoperfluoroalkylations

Michael Spittler,[a] Lucas Helmecke,[a] and Constantin Czekelius*[a]

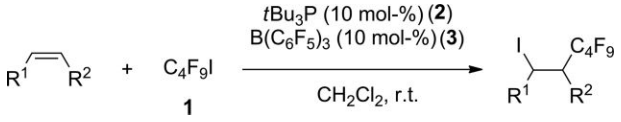
Dedicated to Professor Dr. Manfred Braun on the occasion of his 70th birthday

Abstract: The frustrated Lewis pair-catalyzed iodoperfluoroalkylation of olefins, its substrate activation mode, and catalyst degradation pathways are mechanistically investigated by kinetic measurements. The transformation most likely proceeds via coordination of the phosphane to the perfluoroalkyl iodide and involves radical intermediates.

Introduction

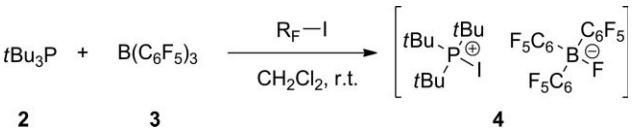
Today, fluorinated organic molecules play a key role in both science and technology.[1] Despite the negative public reputation of CFCs, which have caused a depletion of the ozone layer, the synthesis of fluorinated compounds has fostered synthetic method development[2] due to their widespread application in the fields of agrochemicals,[3] pharmaceuticals[4] and medicinal chemistry.[5] The flourishing use of fluorine is based upon its unique properties such as the high stability of the C–F bond (binding energy: 440–490 kJ/mol), its small size (1.47 Å) and its high electronegativity (4.0).[1,6] A single substitution of hydrogen by fluorine can alter the characteristics of a drug massively, for example with respect to its pharmacodynamics and pharmacokinetics.[1,6,7] Consequently, the development of selective fluorination techniques is of great importance in the pharmaceutical industry. A plethora of methods for fluorination and fluoroalkylation has been described in past years[8] involving special fluorinating reagents,[8f,9] diverse transition metal catalysts,[10] metal-free alternatives involving amines as Lewis base catalysts,[11] or photo-mediated perfluoroalkylations.[11,12] However, enantioselective methods and late stage introduction of fluorine is still a crucial goal.

In 2016, we reported the iodoperfluoroalkylation of unsaturated hydrocarbons by frustrated Lewis pairs (Scheme 1).[13] Using a catalyst system based on the seminal contributions by Piers, Stephan and Erker[14] we found that alkynes as well as terminal and internal *cis*-alkenes are perfluoroalkylated in the presence of tri-*tert*-butylphosphane (**2**) and tris(pentafluorophenyl)borane (**3**). The reaction proceeds regioselectively with iodine at the higher substituted carbon, but it is not diastereoselective in most cases. For example, the transformation of (*Z*)-3-hexene gives a mixture of the lk- and ul-isomers.



Scheme 1. FLP-catalyzed iodoperfluoroalkylation of unsaturated hydrocarbons.[13]

In the absence of alkenes the addition of various perfluoroalkyl iodides to the Lewis pair catalyst leads to the formation of the unreactive salt [*t*Bu$_3$PI][FB(C$_6$F$_5$)$_3$] (**4**) (Scheme 2). This may be explained by elimination of fluoride in either α- or β-position from an intermediately formed perfluoroalkyl borate.



Scheme 2. Salt formation of iodophosphonium fluoroborate.

These observations raised the question whether the reaction proceeds via an ionic or radical pathway. The initial results, as reported earlier, did not allow to unequivocally provide an answer. Herein, we would like to report mechanistic investigations addressing the elucidation of this reaction mechanism.

Results and Discussion

We started our investigation with a screening of the Lewis base in order to check whether tri-*tert*-butylphosphane (**2**) can be substituted. To identify potential candidates, we screened phosphanes with comparable properties regarding their steric bulk and donor strength. As a measure for bulkiness, the ligand cone angle (θ) can be utilized. *t*Bu$_3$P, which is commonly used in FLP chemistry, has a ligand cone angle of 182°,[15] which makes it one of the bulkiest phosphanes. Additionally, the Tolman elec-

[a] *Institute for Organic Chemistry and Macromolecular Chemistry, Heinrich-Heine-Universität Düsseldorf, Universitätsstr. 1, 40225 Düsseldorf, Germany*
E-mail: constantin.czekelius@hhu.de
http://www.catalysis.hhu.de/

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejoc.201800866.

tronic parameter (TEP) assesses the donor strength of the Lewis base. These properties are shown in Figure 1 for the different phosphanes screened.

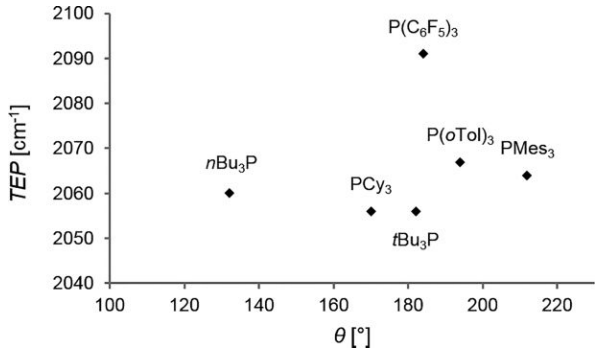


Figure 1. Tolman electronic parameter (TEP) and ligand cone angle of selected phosphanes.[15]

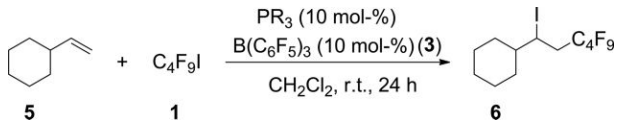
To scrutinize suitable phosphanes, which can interact with perfluoroalkyl iodides and thereby weaken the C–I-bond, NMR spectra of equimolar mixtures of phosphanes and nonafluoro-1-iodobutane (**1**) were recorded and compared to reference samples. A shift of the $-CF_2I$-moiety of the perfluoroalkyl iodide as well as the phosphane was observed only for tBu$_3$P and PCy$_3$. For nBu$_3$P only a slight shift of the $-CF_2I$-moiety was detected (Table 1).

Table 1. Mixtures of phosphanes and C_4F_9I, change in NMR shift.[a,b]

Phosphane	^{19}F $\Delta\delta$ [ppm]	^{31}P $\Delta\delta$ [ppm]
tBu$_3$P	11.5	4.5
nBu$_3$P	3.4	0
PCy$_3$	8.48	2.1
PMes$_3$	0	0
P(oTol)$_3$	0	0
P(C$_6$F$_5$)$_3$	0	0

[a] Equimolar mixture of phosphane and C_4F_9I in CH_2Cl_2. External standard $CFCl_3$ in C_6D_6. [b] For spectra, see Supporting Information.

As a test reaction the well-established iodoperfluoroalkylation of vinylcyclohexane (**5**) was chosen (Scheme 3). Only the use of tBu$_3$P led to formation of the corresponding product (>95 % conversion) while the other phosphanes did not promote the reaction at all. The unique combination of high basicity and bulkiness is apparently crucial for successful transformation of the perfluoroalkyl iodide.



Scheme 3. Iodoperfluoroalkylation of vinylcyclohexane.

Next, we investigated the influence of the solvent in detail. Surprisingly, as shown in Table 2, no conversion was observed at all in aromatic solvents such as benzene or toluene. On the other side, electron-deficient, halogenated aromatic solvents seem to be appropriate for the perfluoroalkylation. Our data do not support the assumption that the dipole moment alone is the key property in this case, as our reaction works best in CH_2Cl_2 (1.6 D) and results in lower yields when using chlorobenzene (1.7 D) or fluorobenzene (1.6 D).

Table 2. Solvent screening in the iodoperfluoroalkylation of vinylcyclohexane.[a]

Solvent	Conversion [%]		Dipole moment[16]
	^{1}H	^{19}F	[D]
[D$_6$]Benzene	0	0	0
Toluene	0	0	0.4
CH_2Cl_2	95	≥99	1.6
Chlorobenzene	32	31	1.7
1,2-Dichlorobenzene	68	72	2.5
1,3-Dichlorobenzene	49	50	1.7
Fluorobenzene	35	35	1.6
1,2-Difluorobenzene	68	72	–
1,4-Difluorobenzene	26	25	–

[a] Vinylcyclohexane (0.41 mmol), C_4F_9I (0.41 mmol), B(C$_6$F$_5$)$_3$ (10 mol-%), tBu$_3$P (10 mol-%), solvent (1.2 mL), room temp., 24 h.

One possible explanation for these results is a π-stacking effect.[17] Due to stronger electrostatic interactions, benzene and the perfluorinated phenyl rings of B(C$_6$F$_5$)$_3$ should show a stronger interaction compared to halogenated benzene derivatives.[17] This interaction possibly causes a deactivation of the Lewis acid.

To elucidate the mechanism of this perfluoroalkylation, we started kinetic investigations. Our first results were quite promising, since we observed a clean reaction without by-product formation and seemingly simple curve progressions (Figure 2). Fitting the curve assuming zeroth, first or second order kinetics, good coefficients of determination were obtained. However, zeroth and first order fits have a significant intercept. A second order fit suits the data well, implying a second order dependency of either C_4F_9I **1**, vinylcyclohexane (**5**) or a combination of them. At this point, further reactions had to be conducted to learn more about the rate determining factors.

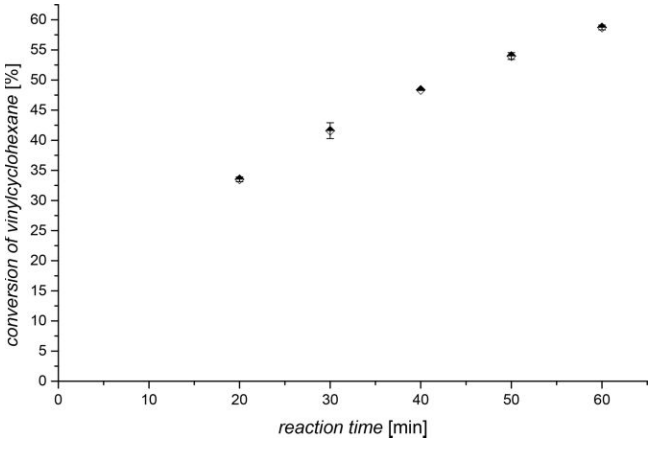


Figure 2. GC-experiments, reference procedure: vinylcyclohexane (1.0 equiv.), C_4F_9I (1.0 equiv.), tBu$_3$P (5 mol-%), B(C$_6$F$_5$)$_3$ (5 mol-%), CH_2Cl_2, 20 °C.

We envisioned that the cleavage of the C–I-bond in nonafluoro-1-iodobutane (**1**), either homo- or heterolytically, could take part in the rate-limiting step. Figure 3 depicts the strong dependency of the reaction rate on the C_4F_9I concentration.

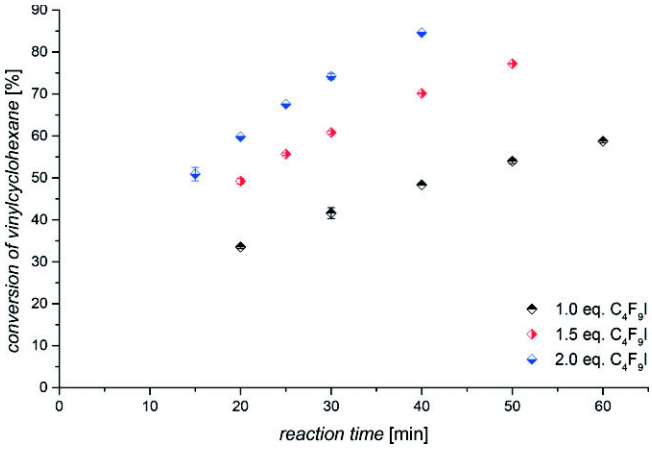


Figure 3. Influence of an excess of C_4F_9I on the reaction rate: C_4F_9I (1.0, 1.5, 2.0 equiv.), vinylcyclohexane (1.0 equiv.), tBu$_3$P (5 mol-%), $B(C_6F_5)_3$ (5 mol-%), CH_2Cl_2, 20 °C.

We calculated linear fits of a zeroth, first and second order dependence on the C_4F_9I concentration (see Supporting Information). A first order dependency fits the variation of the perfluoroalkyl iodide concentration best. For 1.0 equivalent a rate constant of $k_{1.0}$ = 0.012 min^{-1}, for 1.5 equivalents $k_{1.5}$ = 0.011 min^{-1} and for 2.0 equivalents $k_{2.0}$ = 0.010 min^{-1} was calculated. This suggests that the iodoperfluoroalkylation is first order regarding C_4F_9I. Still, a constant offset for a first order fit was observed, indicating a faster second process at the beginning of the reaction. To investigate this interesting effect further, we varied the ratio of both Lewis base and Lewis acid. To our surprise, a sharp increase regarding the offset was found by increasing the amount of tBu$_3$P (Figure 4).

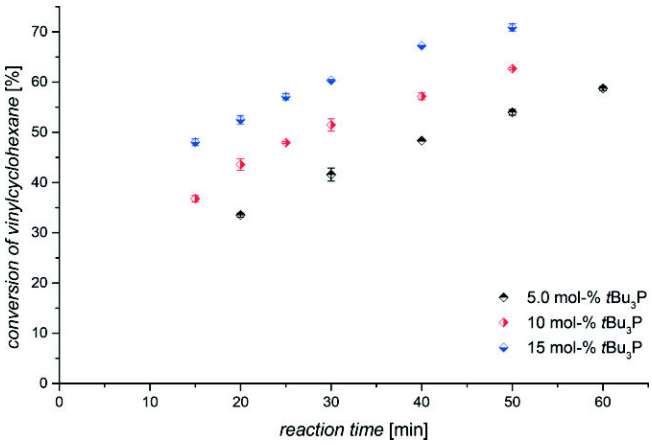


Figure 4. Influence of an excess of tBu$_3$P on the reaction rate: tBu$_3$P (5, 10 and 15 mol-%), vinylcyclohexane (1.0 equiv.), C_4F_9I (1.0 equiv.), $B(C_6F_5)_3$ (5 mol-%), CH_2Cl_2, 20 °C.

As Figure 5 shows, by tripling the amount of tBu$_3$P, the slope increases slightly from –0.012 min^{-1} to –0.017 min^{-1}, but the intercept is more than doubled from 0.18 to 0.41. Apparently, tBu$_3$P plays a key role in a fast-starting reaction, but does not seem to be determining for the subsequent reaction progress.

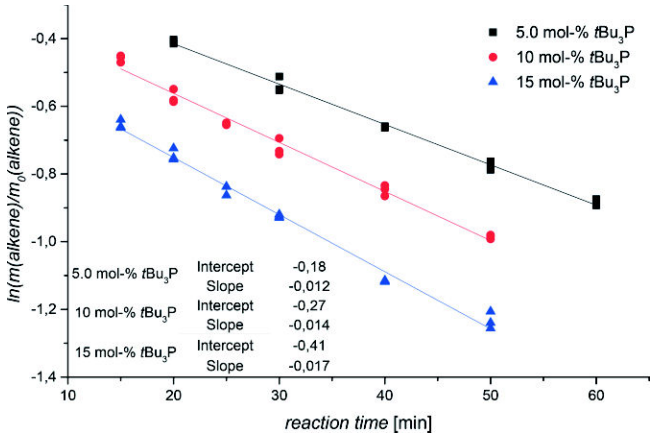


Figure 5. Calculation regarding the influence of an excess of tBu$_3$P on the reaction rate (see Supporting Information).

In order to follow the fast initial process involving free tBu$_3$P, an altered procedure using NMR analysis and 1-undecene (**13**) instead of vinylcyclohexane (**5**) was used. Herein, the first data point was obtained after 7 min reaction time (Figure 6).

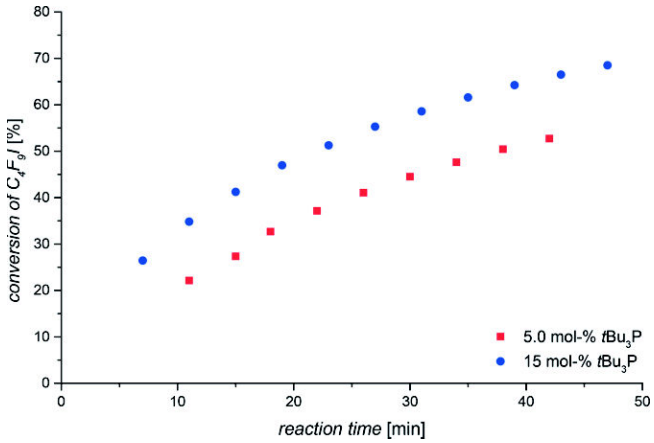


Figure 6. Influence of an excess of tBu$_3$P: tBu$_3$P (5 and 15 mol-%), 1-undecene (1.1 equiv.), C_4F_9I (1.0 equiv.), $B(C_6F_5)_3$ (10 mol-%), CH_2Cl_2, room temp.

Remarkably, 26 % conversion was detected after 7 min using 15 mol-% tBu$_3$P. The resulting change in rate constants ($k_{5.0}$ = 0.016 min^{-1}, k_{15} = 0.020 min^{-1}) is comparable to the GC-experiments (Figure 4). The same applies for the intercepts, since tripling the amount of tBu$_3$P results in an approximately doubled intercept. Throughout this experiment with an excess of tBu$_3$P, a very interesting observation were newly formed signals in the ^{19}F-NMR spectrum (Figure 7). These signals seem to arise from a $B(C_6F_5)_3$ derivative and the integral ratio relative to the $B(C_6F_5)_3$ signals did not shift over the monitoring period.

Therefore, we tested an excess of the Lewis acid $B(C_6F_5)_3$. Different potential ways for $B(C_6F_5)_3$ to activate substrates are described in literature. Stephan and co-worker[7c] documented an interaction between fluorine and $B(C_6F_5)_3$, which can result in fluoride abstraction under certain conditions giving hydrophosphonium fluoroborate **9** (Scheme 4). $B(C_6F_5)_3$ can also interact with alkenes.[18]

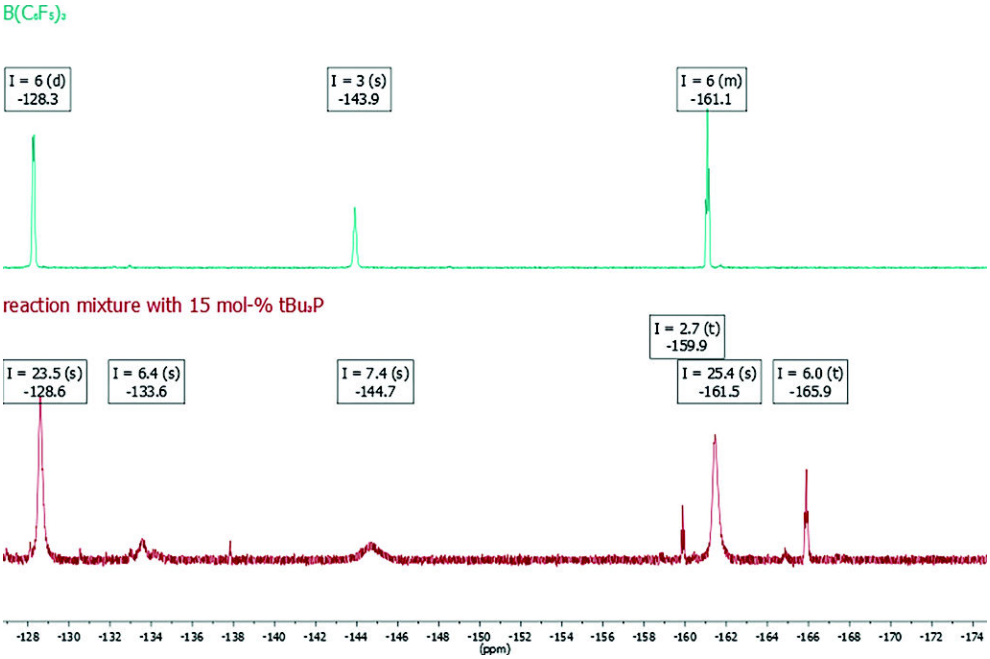
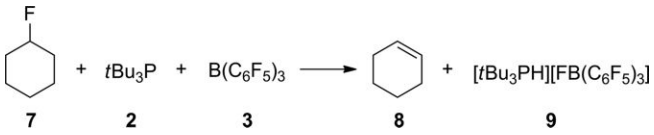


Figure 7. Comparison of ^{19}F-NMR spectra, top: $B(C_6F_5)_3$, below: reaction mixture with 15 mol-% tBu_3P.



Scheme 4. Fluoride abstraction by $B(C_6F_5)_3$.[7c]

Consequently, a variation of the concentration of this Lewis acid $B(C_6F_5)_3$ may have an effect on the reaction rate. As already mentioned, we observed formation of fluoroborate [tBu$_3$PI]-[$FB(C_6F_5)_3$] (**4**) after mixing $B(C_6F_5)_3$, tBu$_3$P and C_4F_9I (Scheme 2).[13] Higher $B(C_6F_5)_3$ ratios increased the rate constant notably without a change regarding the offset or altering the curve's progression (Figure 8). So it seems unlikely that $B(C_6F_5)_3$ is involved in the fast initial process. Assuming a first order dependency, doubling the concentration of $B(C_6F_5)_3$ should result in a doubled rate constant, but we did not observe such an effect (Table 3) and only a slight increase.

One interesting observation throughout our experiments was that premixing tBu$_3$P and $B(C_6F_5)_3$ in CH_2Cl_2 resulted in a yellow solution, whereas reaction mixtures to which $B(C_6F_5)_3$ was added last, showed no color. Solutions of both tBu$_3$P and $B(C_6F_5)_3$ alone are colorless. Piers et al.[19] reported the same observation after mixing tBu$_3$P (**2**) and $B(C_6F_5)_3$ (**3**) and concluded the formation of an addition product by a S_NAr reaction forming **12** after subsequent deprotonation and yielding [tBu$_3$PH][$FB(C_6F_5)_3$] (**9**) as by-product (Scheme 5).

We conducted iodoperfluoroalkylation reactions after premixing tBu$_3$P and $B(C_6F_5)_3$ for 33 and 61 min to assess a reaction between the Lewis pair. However, the reaction rate did not change substantially ($k_{standard}$ = 0.012 min^{-1}, k_{33min} = 0.011 min^{-1}, k_{61min} = 0.010 min^{-1}) (Figure 9).

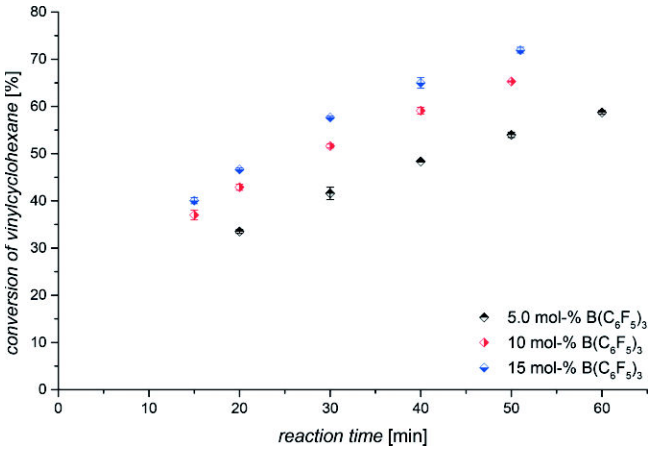


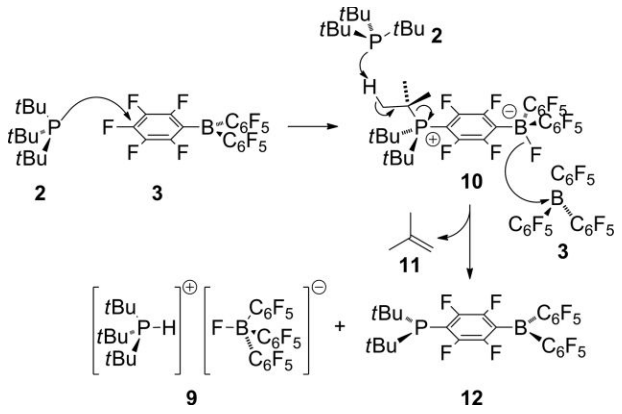
Figure 8. Influence of an excess of $B(C_6F_5)_3$ on the reaction rate: $B(C_6F_5)_3$ (5, 10 and 15 mol-%), vinylcyclohexane (1.0 equiv.), C_4F_9I (1.0 equiv.), tBu$_3$P (5 mol-%), $B(C_6F_5)_3$ (5 mol-%), CH_2Cl_2, room temp.

Table 3. GC-experiment, variation of the $B(C_6F_5)_3$ concentration.[a]

$B(C_6F_5)_3$ [mol-%]	slope [min^{-1}]	intercept
5.0	–0.012	0.18
10	–0.017	0.22
15	–0.021	0.21

[a] See Supporting Information.

To validate this observation, an analogous NMR-experiment was conducted with higher catalyst loading. tBu$_3$P and $B(C_6F_5)_3$ were premixed for 78 min. As before, only a slight drop in reaction rate was detected (k = 0.024 min^{-1} compared to k = 0.026 min^{-1}, Figure 10).



Scheme 5. Proposed mechanism for the nucleophilic aromatic substitution of tBu$_3$P at B(C$_6$F$_5$)$_3$ by Piers et al.[19]

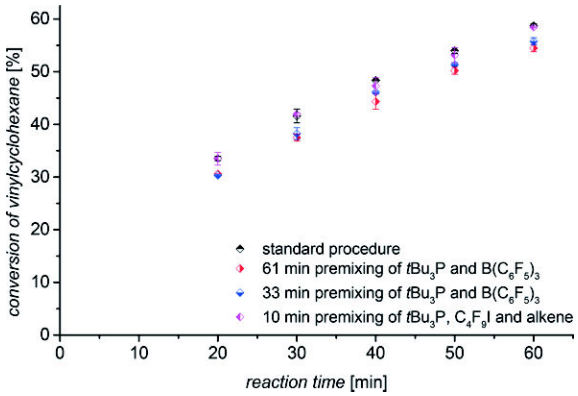


Figure 9. A comparison of different reaction procedures focusing on the premixing of tBu$_3$P and B(C$_6$F$_5$)$_3$: vinylcyclohexane (1.0 equiv.), C$_4$F$_9$I (1.0 equiv.), tBu$_3$P (5 mol-%), B(C$_6$F$_5$)$_3$ (5 mol-%), CH$_2$Cl$_2$, 20 °C.

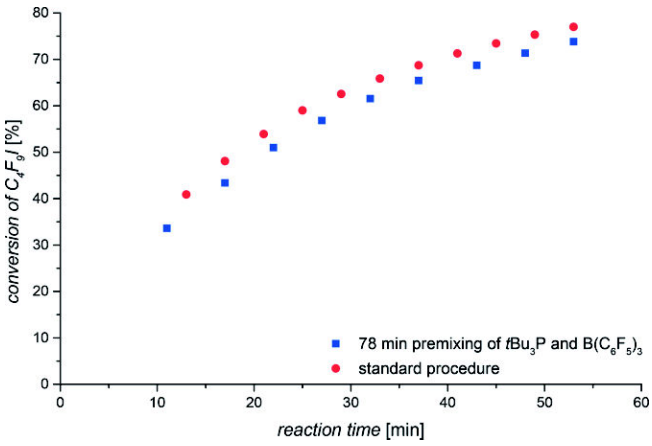


Figure 10. Iodoperfluoroalkylation after premixing of tBu$_3$P and B(C$_6$F$_5$)$_3$ for 78 min: vinylcyclohexane (1.0 equiv.) C$_4$F$_9$I (1.0 equiv.), tBu$_3$P (10 mol-%), B(C$_6$F$_5$)$_3$ (10 mol-%), CH$_2$Cl$_2$, room temp.

After premixing tBu$_3$P and B(C$_6$F$_5$)$_3$ for 78 min and subsequent addition of C$_4$F$_9$I as well, nearly no change in shift of the pentafluorophenyl-signals was detected in the ^{19}F-NMR spectrum. This supports the assumption that the reaction of tBu$_3$P and B(C$_6$F$_5$)$_3$ is slower than the perfluoroalkylation period itself. As a consequence, nucleophilic substitution of tBu$_3$P at B(C$_6$F$_5$)$_3$ does not seem to play a major role in our system.

After an extended premixing (25 hours) of tBu$_3$P and B(C$_6$F$_5$)$_3$ the reaction rate drops severely. However, the reaction still proceeds smoothly and gives 55 % conversion after 324 min (Figure 11). The first ^{19}F NMR spectrum in this kinetic investigation clearly indicated the formation of [*F*B(C$_6$F$_5$)$_3$]$^-$ on the basis of its diagnostic signal at –189 ppm. The amount of [FB(C$_6$F$_5$)$_3$]$^-$ was found to be constant within the observation period.

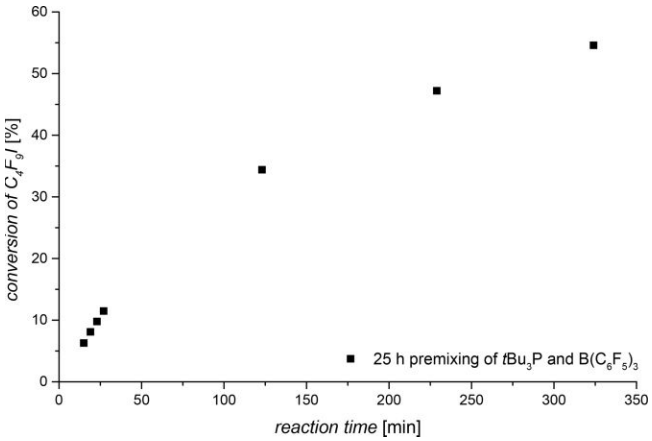


Figure 11. Reaction progress after 25 h premixing of tBu$_3$P and B(C$_6$F$_5$)$_3$.

The last component to investigate in this study was vinylcyclohexane (**5**). Since the GC method used could not be validated for an excess of this alkene (see Supporting Information), the reaction was followed by NMR (Figure 12).

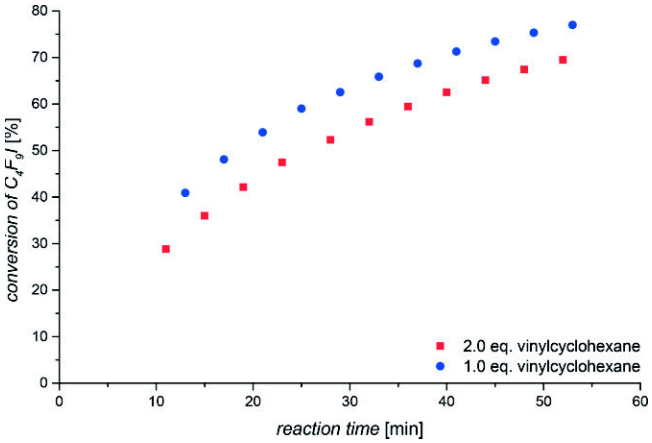


Figure 12. Influence of an excess of vinylcyclohexane: vinylcyclohexane (1.0, 2.0 equiv.) C$_4$F$_9$I (1.0 equiv.), tBu$_3$P (10 mol-%), B(C$_6$F$_5$)$_3$ (10 mol-%), CH$_2$Cl$_2$, room temp.

After linearization, a rate constant of $k_{2.0}$ = 0.022 min^{-1} was obtained for two equivalents of vinylcyclohexane (**5**), which is slightly lower than that for one equivalent ($k_{1.0}$ = 0.026 min^{-1}). We wanted to verify this observation with a linear alkene. 1-Undecene (**13**) was chosen as a high-boiling compound and we observed the same behavior (Figure 13). The rate constant also drops slightly for an excess of 1-undecene ($k_{1.1}$ = 0.015 min^{-1}, $k_{2.0}$ = 0.012 min^{-1}).

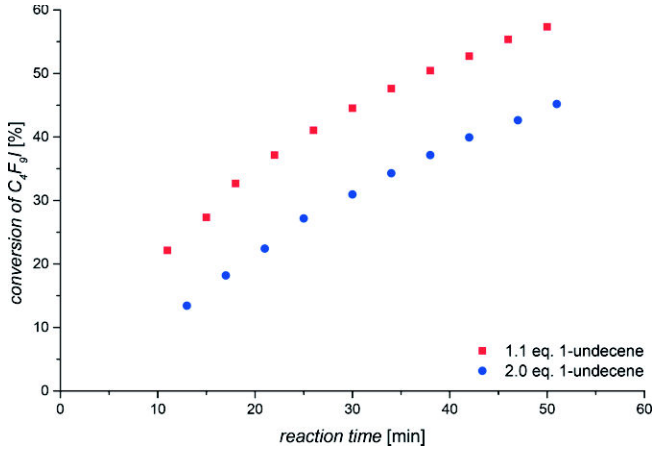


Figure 13. Influence of an excess of 1-undecene: 1-undecene (1.1, 2.0 equiv.) C_4F_9I (1.0 equiv.), tBu$_3$P (5 mol-%), B(C_6F_5)$_3$ (5 mol-%), CH_2Cl_2, room temp.

These results suggest that the alkene does not take part in the rate-limiting step. On the contrary, it slows the reaction down, presumably by its coordination to B(C_6F_5)$_3$.[18] This coordination has been proposed to potentially result in a nucleophilic attack e.g. by phosphanes forming the corresponding betaines.[18a,18b] Such process could also play a role in our reaction system, but we have no spectroscopic evidence for betaine formation.

To evaluate the loss of active catalyst by fluoroborate formation within our usual observation period, we premixed tBu$_3$P, B(C_6F_5)$_3$ and C_4F_9I and added vinylcyclohexane (**5**) after 60 min. To our surprise, this resulted in a completely different curve progression. Most noticeable, the usual offset as an indication for a fast initial process cannot be observed (Figure 14). On the contrary, the reaction showed an initial lag phase.

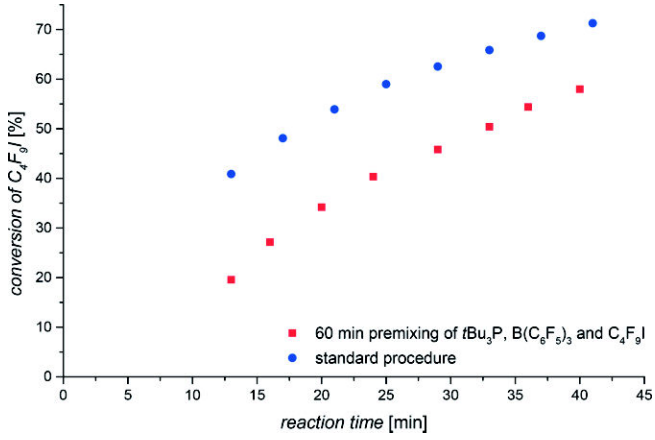


Figure 14. Reaction progress after 60 min premixing of tBu$_3$P, B(C_6F_5)$_3$ and C_4F_9I: vinylcyclohexane and C_4F_9I (1.0 equiv.), tBu$_3$P (10 mol-%), B(C_6F_5)$_3$ (10 mol-%), CH_2Cl_2, room temp.

After a short induction period, the reaction proceeds with a slightly lower rate constant (k_{60min} = 0.023 min^{-1}, $k_{standard}$ = 0.026 min^{-1}). This similar rate constant implies that the amount of catalytically active species does not seem to be reduced substantially. However, minor amounts of the diagnostic signal for [*F*B(C_6F_5)$_3$]$^-$ at –191 ppm in the ^{19}F-NMR spectra were detected. To verify an initiation phase, a similar procedure was tested in a GC-experiment (5 mol-% catalyst). tBu$_3$P, B(C_6F_5)$_3$ and C_4F_9I were mixed for 62 min before the addition of vinylcyclohexane. Like before, a lag phase is visible (Figure 15) and the rate constant drops slightly (k_{62min} = 0.0084 min^{-1}, $k_{standard}$ = 0.012 min^{-1}).

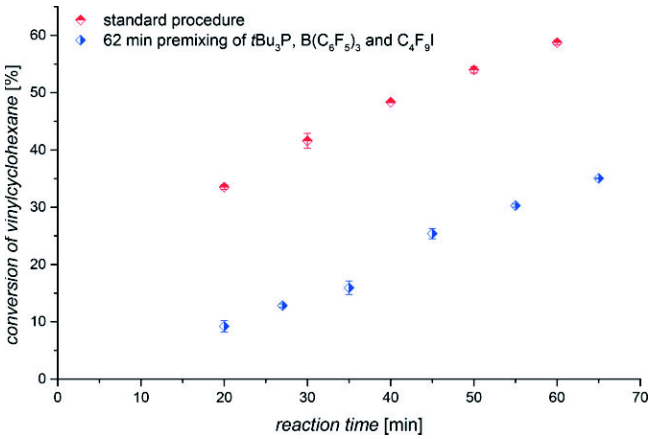


Figure 15. Reaction progress after 62 min premixing of tBu$_3$P, B(C_6F_5)$_3$ and C_4F_9I: vinylcyclohexane and C_4F_9I (1.0 equiv.), tBu$_3$P (5 mol-%), B(C_6F_5)$_3$ (5 mol-%), CH_2Cl_2, room temp.

We tried to quantify the loss of catalytically active species by salt formation. Since both [tBu$_3$PR]$^+$ (R = H or I) and [FB(C_6F_5)$_3$]$^-$ cannot be quantified via GC, NMR experiments were conducted. After mixing tBu$_3$P, B(C_6F_5)$_3$ and C_4F_9I in CD_2Cl_2, ^{19}F-NMR spectra were measured over a period of 52 min. Unexpectedly, no new ^{19}F signal for [*F*B(C_6F_5)$_3$]$^-$ was observed, but a gradual upfield shift of the original B(C_6F_5)$_3$ (Figure 16).

Most likely, a fast interchange of fluoride between [FB(C_6F_5)$_3$]$^-$ and free B(C_6F_5)$_3$ occurs. Even at –30 °C no separation into two signal sets in NMR was observed. Hence, the interchange seems to be quite fast. To validate this assumption, B(C_6F_5)$_3$ **3** and [tBu$_3$PH][FB(C_6F_5)$_3$] **9** were mixed in equimolar ratio. As assumed, only one signal set was observed (Figure 17).

On a closer look, the resulting shifts of an equimolar mixture of B(C_6F_5)$_3$ (**3**) and [tBu$_3$PH][FB(C_6F_5)$_3$] (**9**) were precisely in the middle of the original shifts. This observation opened a potential possibility to quantify salt formation. With this insight at hand, we reviewed the spectra of our NMR-experiments. For our standard procedure with 1.0 equiv. vinylcyclohexane (**5**), only a slight shift (*o*,*m*-F: –0.6 ppm, *p*-F: –1.7 ppm) of the pentafluorophenyl-signals in B(C_6F_5)$_3$ can be noticed within 53 min, implying no significant loss of catalytic species.

As an alternative cause for a shift of the pentafluorophenyl signals, a mixture of iodoperfluoroalkylation product **6** and B(C_6F_5)$_3$ (**3**) was probed. No shift was observed. Additionally, iodoperfluoroalkylation product **6** and tBu$_3$P (**2**) were mixed and no shift was detected in this case, too.

In order to test for a catalyst regeneration we probed a combination of B(C_6F_5)$_3$ and phosphonium fluoroborate salts [tBu$_3$PR][FB(C_6F_5)$_3$] (R = H or I) (Scheme 6).

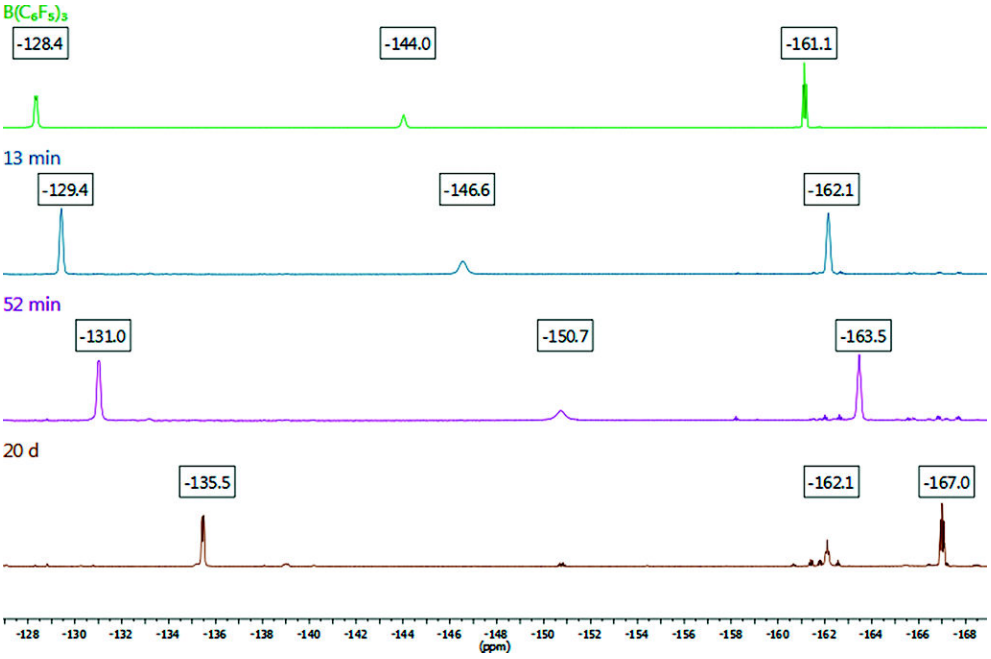


Figure 16. Comparison of ^{19}F-NMR spectra, top: $B(C_6F_5)_3$, below: reaction of tBu$_3$P, $B(C_6F_5)_3$ with C_4F_9I.

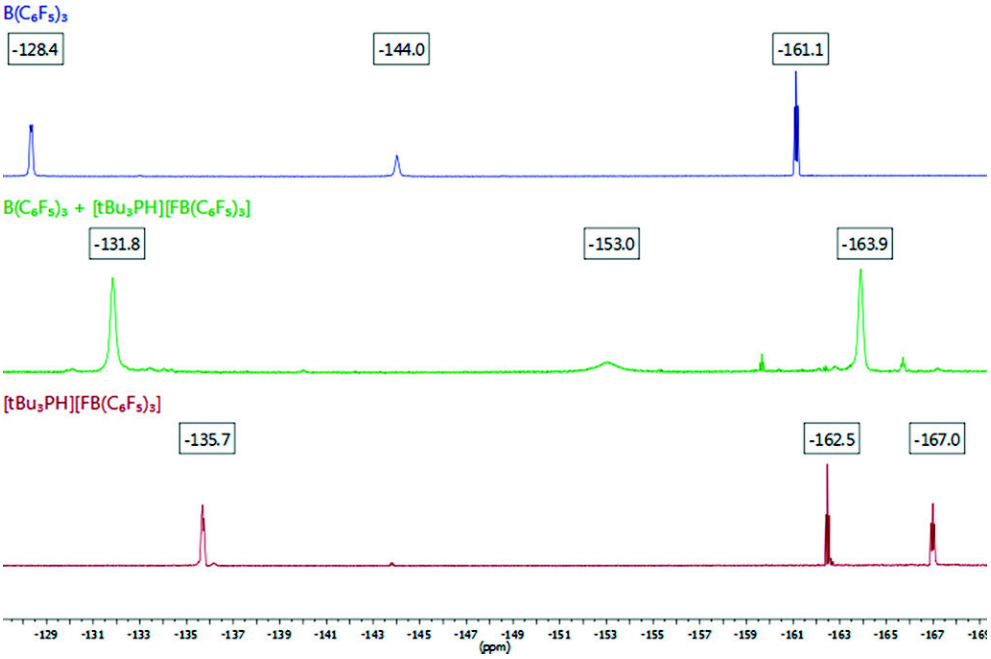
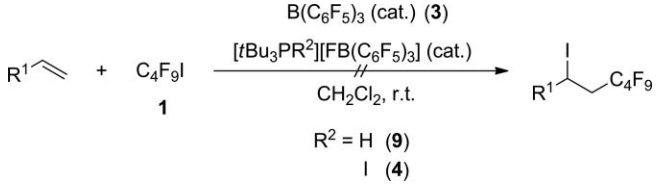


Figure 17. Comparison of ^{19}F-NMR spectra, top: $B(C_6F_5)_3$, middle: 1:1 mixture of $B(C_6F_5)_3$ and [tBu$_3$PH][FB(C_6F_5)$_3$], bottom: [tBu$_3$PH][FB(C_6F_5)$_3$].



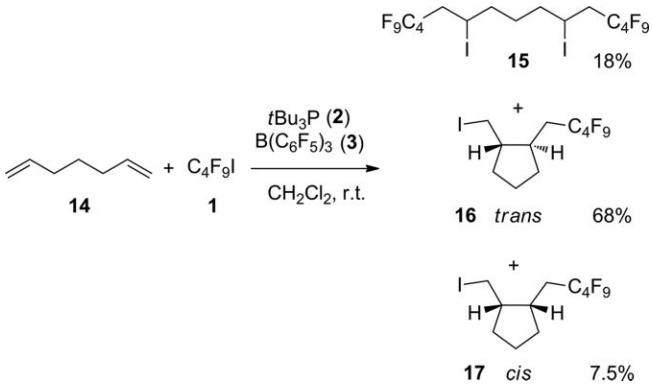
Scheme 6. Attempt to iodoperfluoroalkylate in the presence of [tBu$_3$PR]-[FB(C_6F_5)$_3$] (R = H or I) in combination with $B(C_6F_5)_3$.

With both phosphonium salts we observed no reaction at all. ^{31}P-NMR spectra showed no change of the [tBu$_3$PR]-shifts and as described before, only one signal set was observed for the pentafluorophenyl rings. Consequently, no regeneration of free tBu$_3$P occurs for a combination of the salts and $B(C_6F_5)_3$.

An alternative pathway for this perfluoroalkylation is a photochemical process. Chen et al.[11] showed that Lewis bases can promote the photochemical reaction between alkenes and perfluoroalkyl iodides via halogen-bonding. For that reason we conducted all experiments under best possible exclusion of ambient light and working under red light. To probe this photomediated pathway for our system, we conducted a GC-experiment under reference conditions but used tBu$_3$P as the only catalyst.

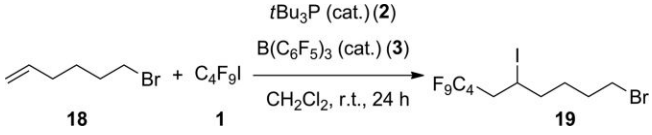
Under these conditions we detected a conversion of 3–5 % as followed by GC and NMR, which might be caused by the sample withdrawal itself. As a comparison, we tested a photochemical reaction of vinylcyclohexane (**5**) and nonafluoro-1-iodobutane (**1**) promoted by 10 mol-% tBu$_3$P (**2**) under the influence of direct sunlight. Within 24 h a conversion of about 40 % was observed.

Following kinetic investigations, we addressed the question whether the reaction mechanism involves ionic or radical intermediates. While in FLP-mediated reactions commonly ionic pathways are described, Stephan et al.[20] reported single electron transfer processes in the reaction of the aromatic phosphane Mes$_3$P and B(C$_6$F$_5$)$_3$ with tetrachloro-1,4-benzoquinone. They were able to prove the formation of the corresponding radical cation [Mes$_3$P•]$^+$. However, when aliphatic phosphane tBu$_3$P was used as Lewis base, the reaction seemed to follow an ionic pathway. We had found earlier[13] that 1,6-heptadiene (**14**) is transformed under the reaction conditions into the difunctionalized compound **15** and perfluoroalkylated cyclopentane derivatives **16** and **17** (Scheme 7). This finding is more consistent with a radical than the involvement of a primary carbocation. In the literature, the formation of cyclic products via a radical mechanism has already been described.[21]



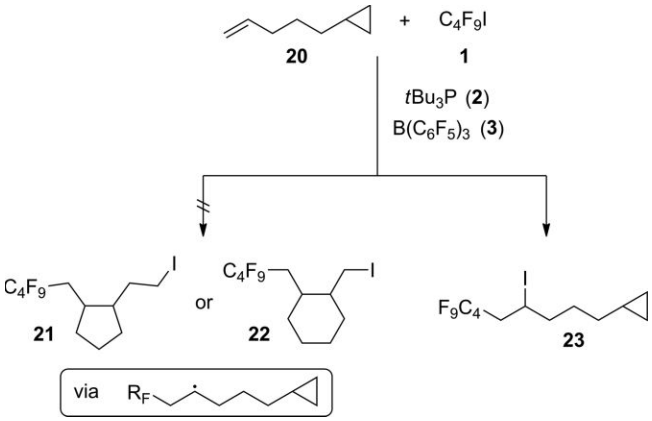
Scheme 7. Iodoperfluoroalkylation of 1,6-heptadiene.[13]

To obtain further evidence for a radical mechanism, we probed the perfluoroalkylation of two alkenes, which can cyclize under radical conditions. Studer and co-workers reported the cyclisation of 6-bromohexene (**18**) under radical conditions.[22] However, following our methodology we could only isolate the acyclic perfluoroalkylation product **19** (Scheme 8).



Scheme 8. Iodoperfluoroalkylation of vinylcyclohexane.

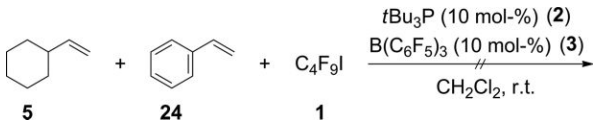
It is described in literature that the corresponding cyclic product is exclusively formed following bromine abstraction[23] and not by a terminal addition of a radical to the alkene. Subsequently, 4-penten-1-yl-cyclopropane (**20**) was synthesized and a perfluoroalkylation was conducted (Scheme 9).



Scheme 9. Iodoperfluoroalkylation of 4-penten-1-ylcyclopropane.

After an attack of a perfluoroalkyl radical at the double bond, a secondary radical would be formed, which could open the cyclopropane ring. However, we did not observe such a process. NMR spectroscopy showed acyclic iodoperfluoroalkylation product **23** of the alkene and an unimpaired cyclopropane ring.

As described before,[13] styrene (**24**) does not react under the standard conditions at all. Moreover, one equivalent of styrene inhibits the FLP-catalyzed perfluoroalkylation of vinylcyclohexane (**5**) (Scheme 10). Since styrene may quench radicals undergoing polymerization, a mixture of styrene, tBu$_3$P and C$_4$F$_9$I was irradiated at 370 nm and 254 nm, respectively, as a test reaction. No conversion or polymerization was detected. Therefore, quenching of radicals by styrene (**24**) seems to be less likely. Potentially, π-stacking[24] or coordination of boron to the alkene might quench the reaction.[18]

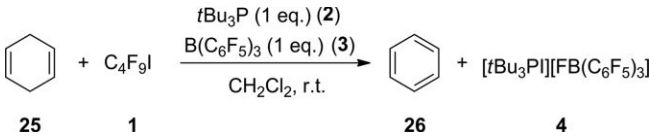


Scheme 10. Iodoperfluoroalkylation of vinylcyclohexane in the presence of styrene.

As another alternative to discriminate between radical and ionic mechanisms, 1,4-cyclohexadiene (**25**) was subjected to our catalytic system. This diene itself did not react with C$_4$F$_9$I (**1**) in presence of catalytic amounts of tBu$_3$P (**2**) and B(C$_6$F$_5$)$_3$ (**3**). As with styrene, it inhibited the conversion of vinylcyclohexane (**5**). NMR spectra show unreacted vinylcyclohexane and 1,4-cyclohexadiene (see Supporting Information).

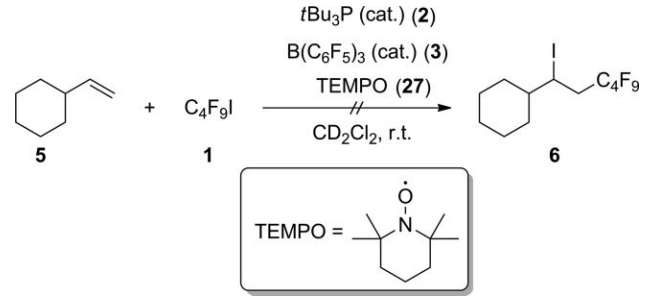
After mixing equimolar amounts of 1,4-cyclohexadiene, C$_4$F$_9$I, tBu$_3$P and B(C$_6$F$_5$)$_3$, substantial amounts (about 30 %) of benzene (**26**) were detected, suggesting the presence of radical intermediates (Scheme 11). However, no C$_4$F$_9$H (**29**) could be detected in this case. The ^{19}F-NMR spectrum shows a nearly complete consumption of C$_4$F$_9$I (**1**) and the formation of [tBu$_3$PI][FB(C$_6$F$_5$)$_3$] (**4**).

Next, we tested free radical 2,2,6,6-tetramethylpiperidine 1-oxyl (**27**, TEMPO). A perfluoroalkylation in presence of one equivalent TEMPO showed no conversion at all, the same is true for a reaction in the presence of 0.1 equivalents (Scheme 12). As an alternative procedure, TEMPO was added to an ongoing



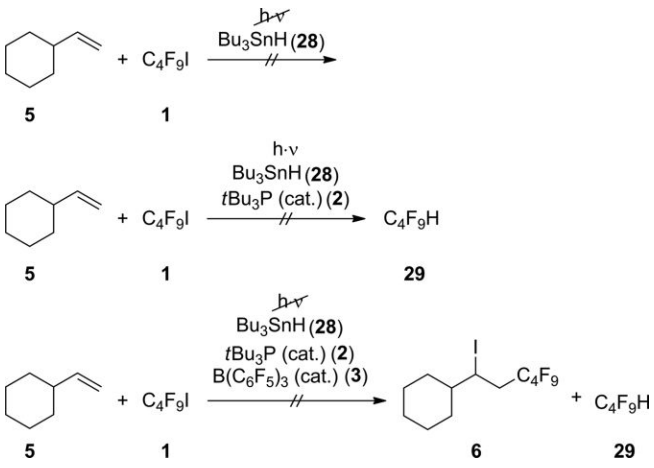
Scheme 11. Radical dehydrogenation of 1,4-cyclohexadiene in the presence of tBu$_3$P, B(C$_6$F$_5$)$_3$ and C$_4$F$_9$I.

iodoperfluoroalkylation after 20 min. Consecutive NMR-controls showed a direct stop of the reaction after the addition of TEMPO. However, B(C$_6$F$_5$)$_3$ did seem to react. ^{19}F-NMR spectra of an equimolar mixture of TEMPO and B(C$_6$F$_5$)$_3$ showed an alteration of the pentafluorophenyl-signals. Additionally, the ^{11}B-NMR spectrum indicated the presence of a tetrahedral boron center. Presumably, direct interaction between TEMPO and B(C$_6$F$_5$)$_3$ quenches the perfluoroalkylation.



Scheme 12. Attempt for an iodoperfluoroalkylation in the presence of free radical TEMPO.

Our last experiments in the context of radical reactions addressed the addition of tributyltin hydride (**28**) as a radical hydrogen donor. As a negative control, we mixed vinylcyclohexane (**5**), C$_4$F$_9$I and Bu$_3$SnH in an amber glass NMR-tube and observed no reaction (Scheme 13). When we mixed tBu$_3$P, vinylcyclohexane, C$_4$F$_9$I and Bu$_3$SnH in a transparent NMR tube, we detected the formation of C$_4$F$_9$H (**29**). This reaction is expected for a radical reaction between perfluoroalkyl-radical (·C$_4$F$_9$) and Bu$_3$SnH. Then, we conducted an experiment under standard iodoperfluoroalkylation conditions, but added Bu$_3$SnH after 20 min in the dark. Iodoperfluoroalkylation product **6**, C$_4$F$_9$H (**29**) and presumably perfluorooctane were observed.



Scheme 13. Experiments involving tributyltin hydride.

These results suggested that radicals play an important role in the FLP-catalyzed iodoperfluoroalkylation.

Conclusions

The investigated frustrated Lewis pair-catalyzed iodoperfluoroalkylation of olefins is a highly complex reaction. Our kinetic experiments suggest a first order dependence on the perfluoroalkyl iodide, which is coordinated and activated by the phosphane. The Lewis base is involved in a fast starting reaction, which slows down rapidly. An excess of the phosphane results in a strong offset, followed by reaction rates comparable to those under standard conditions. An excess of the Lewis acid also increases the reaction rate moderately, but does not alter the curve progression. The alkene does not seem to take part in a rate-limiting step. On the contrary, an excess slows down the reaction speed, presumably by coordinating to the Lewis acid.

Two potential pathways for a deactivation of the catalyst were investigated. On the one hand, tBu$_3$P, B(C$_6$F$_5$)$_3$ and the perfluoroalkyl iodide can form a iodophosphonium fluoroborate [tBu$_3$PI][FB(C$_6$F$_5$)$_3$]. On the other hand, tBu$_3$P and B(C$_6$F$_5$)$_3$ can react in a S$_N$Ar-reaction to form a phosphino borane and hydrophosphonium fluoroborate [tBu$_3$PH][FB(C$_6$F$_5$)$_3$]. Experimental evidence shows, that the latter process does not seem to play a significant role for our system. In contrast, the formation of the iodophosphonium fluoroborate can deactivate the catalyst system more readily.

This FLP-catalyzed iodoperfluoroalkylation may follow an ionic or radical pathway. Transformations in the presence of hydrogen donors such as 1,4-cyclohexadiene or tributyltin hydride suggest the occurrence of perfluoroalkyl radicals. A radical pathway is rare for FLP-catalyzed reactions and may open new synthetic potential for the activation of small molecules.

Experimental Section

General Notes: All syntheses involving air- and moisture-sensitive compounds were carried out inside a glovebox under N$_2$ atmosphere. Reagents as well as solvents were purchased from Acros, Sigma Aldrich, abcr, TCI, J & K scientific or VWR Chemicals. Solvents were dried with the solvent purification system MP-SPS 800 from M. Braun, predistilled and if necessary degassed by freeze-pump-thaw. Reactions were monitored by thin-layer chromatography (TLC) using Macherey–Nagel silica gel plates ALUGRAM® Xtra SIL G/UV$_{254}$ (0.20 mm thickness). ^{1}H-, ^{11}B-, ^{13}C, ^{19}F-, ^{31}P-NMR spectra were recorded on Bruker Avance III 300 and 600. Chemical shifts are reported in parts per million (ppm). ^{1}H-NMR shifts are reported in reference to the corresponding solvent. ^{19}F-NMR shifts were reported in ppm and referenced to CFCl$_3$ in C$_6$D$_6$ and ^{31}P-NMR to H$_3$PO$_4$ in D$_2$O. IR spectra were recorded using a Jasco FT/IR-6200 spectrometer. Samples were measured as film on a NaCl crystal. The absorption bands were given in wave numbers (cm^{-1}). Elemental analyses were measured on an Elementar Vario Micro Cube.

6-Bromohexene (18): Triphenylphosphane (11.5 g, 43.9 mmol, 1.10 equiv.) in CH$_2$Cl$_2$ (29 mL) was cooled to 0 °C. Bromine (2.30 mL,

43.9 mmol, 1.10 equiv.) was added dropwise and the solution was stirred for 2 h at room temperature. Subsequently, pyridine (4.30 mL, 53.3 mmol, 1.10 equiv.) was added dropwise to the reaction solution and the mixture was cooled to 0 °C. 5-Hexen-1-ol (4.80 mL, 39.9 mmol, 1.00 equiv.) in CH_2Cl_2 (7 mL) was added dropwise and the solution was stirred for 20 h at room temperature. After complete conversion of the alcohol, which was controlled via TLC (hexane/ethyl acetate, 90:10), pentane (20 mL) was added to the reaction solution. The reaction flask was cooled to −78 °C and the precipitate was filtered off. The clear reaction solution was concentrated and washed with hydrochloric acid (1 M, 3 × 20 mL). The aqueous phase was extracted with pentane (3 × 20 mL). The combined organic phases were washed with saturated $NaHCO_3$ (10 mL) and dried with Na_2SO_4. The solution was again concentrated and distilled at reduced pressure (61–63 °C, 45 mbar). A clear oil was obtained (3.17 g, 19.4 mmol, 49 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.88–5.72 (ddt, J = 16.9, 10.2, 6.7 Hz, 1 H, CH_2CH), 5.08–4.94 (m, 2 H, CH_2CH), 3.46–3.37 (t, J = 6.8 Hz, 2 H, CH_2Br), 2.15–2.03 (m, 2 H, CH_2CHCH_2), 1.94–1.82 (m, 2 H, CH_2CH_2Br), 1.61–1.48 (m, 2 H, $CH_2CH_2CH_2Br$) ppm.[25]

6-(*tert*-Butyldimethylsilyloxy)-1-hexene: TBDMSCl (24.5 g, 162 mmol, 1.01 equiv.) and imidazole (13.1 g, 193 mmol, 1.20 equiv.) were added to a solution of 5-hexen-1-ol (16.0 g, 160 mmol, 1.00 equiv.) in THF (80 mL). After stirring overnight desalinated water (40 mL) was added. The aqueous layer was extracted with diethyl ether (5 × 20 mL) and dried with Na_2SO_4. After evaporation of diethyl ether, the crude product was distilled under reduced pressure to obtain the desired product (99 °C, 30 mbar). (29.8 g, 139 mmol, 87 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90–5.73 (ddt, J = 16.9, 10.2, 6.7 Hz, 1 H, CH_2=CH), 5.06–4.90 (m, 2 H, CH_2=CH), 3.67–3.57 (t, J = 6.3 Hz, 2 H, CH_2OTBDMS), 2.14–1.99 (d, J = 7.1 Hz, 2 H, CH_2CH_2OTBDMS), 1.63–1.48 (m, 2 H, $CH_2CH_2CH_2$OTBDMS), 1.48–1.37 (m, 2 H, $CH_2CH_2CH_2CH_2$OTBDMS), 0.95–0.84 [s, 9 H, $OSi(CH_2)_2(CH_3)_3$], 0.09–0.01 [s, 6 H, $OSi(CH_2)_2(CH_3)_3$] ppm. IR (film on NaCl): $\tilde{\nu}$ = 3077, 2930, 1642, 1472, 1387, 1361, 1255, 1102, 910, 835, 775, 661 cm^{-1}.[26]

***tert*-Butyl(4-cyclopropylbutoxy)dimethylsilane:** Et_2Zn (1.0 M in hexane, 140 mL, 140 mmol, 2.00 equiv.) in CH_2Cl_2 (250 mL) was cooled to 0 °C and trifluoroacetic acid (11.0 mL, 142 mmol, 2.04 equiv.) in CH_2Cl_2 (250 mL) was added over 2 h. After stirring the solution for 30 min a solution of freshly distilled diiodomethane (11.3 mL, 140 mmol, 2.00 equiv.) in CH_2Cl_2 (250 mL) was added over 1 h. After stirring for another 30 min 6-(*tert*-butyldimethylsilyloxy)-1-hexene (14.9 g, 69.7 mmol) in CH_2Cl_2 (140 mL) was added. The reaction was stirred at room temperature until the alkene signals disappeared completely in the ^{1}H NMR spectra. A saturated NH_4Cl solution (200 mL) was added and the aqueous layer was extracted with diethyl ether (5 × 20 mL) and dried with Na_2SO_4. The solution was concentrated (60 mL) and used as crude product.

4-Cyclopropylbutane-1-ol: The crude product *tert*-butyl(4-cyclopropylbutoxy)dimethylsilane was added to tetra-*n*-butylammonium fluoride-trihydrate (49.1 g, 138 mmol, 1.99 equiv.) and stirred overnight. After completion, saturated NH_4Cl (150 mL) was added to the reaction and the organic phase was extracted with diethyl ether (3 × 100 mL). The combined organic phases where washed with brine (200 mL) and dried with Na_2SO_4. After evaporation (750 mbar, 40 °C) of the solvent the yellow liquid was purified by column chromatography (silica gel, pentane/diethyl ether = 3:1) to give the desired product as light yellow liquid (5.79 g, 44.5 mmol, 63 %). ^{1}H NMR (300 MHz, $CDCl_3$): 3.63 (t, J = 6.8, 2 H, CH_2OH), 1.60 (m, 2 H, CH_2CH_2OH), 1.46 (m, 2 H, $CH_2CH_2CH_2$OH), 1.23 (m, 2 H, $CH_2CH_2CH_2CH_2$OH), 0.65 (m, 1 H, $CHCH_2CH_2$); 0.39 (m, 2 H, $CHCH_2CH_2$), 0.00 (m, 2 H, $CHCH_2CH_2$) ppm.[27]

4-Cyclopropylbutanal: 4-Cyclopropylbutan-1-ol **23** (5.79 g, 44.5 mmol, 1.00 equiv.) in CH_2Cl_2 (400 mL) was cooled to 0 °C. Dess–Martin periodinane (20.7 g, 49.0 mmol, 1.10 equiv.) was added in one portion and stirred for 1 h. The reaction was then stirred for a further hour at room temperature. The reaction was diluted with cooled pentane (200 mL) and the solid was removed through a Celite pad. The product was concentrated via distillation (60 °C) and a yellow liquid was obtained. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.77 (t, J = 1.86, 1 H, HC=O), 2.46 (td, J = 7.36, 1.86, 1 H, CH_2HC=O), 1.74 (p, J = 7.36, 2 H, CH_2CH_2HC=O), 1.24 (m, 2 H, $CH_2CH_2CH_2$HC=O), 0.64 (m, 1 H, $CHCH_2CH_2$), 0.42 (m, 2 H, $CHCH_2CH_2$), 0.01 (m, 2 H, $CHCH_2CH_2$) ppm.[28]

1-(Penten-4-yl)cyclopropane (20): Methyltriphenylphosphonium bromide (24 g, 67 mmol, 1.5 equiv.) in Et_2O (220 mL) was cooled to 0 °C and *n*-butyllithium (2.5 M, 27 mL, 67 mmol, 1.5 equiv.) was added. The yellow suspension was stirred for 1 h. 4-Cyclopropylbutanal (5.8 g, 44 mmol, 1.0 equiv.) in Et_2O (45 mL) was added at 10 °C. The suspension was stirred for 1 h at room temperature and quenched with saturated NH_4Cl (150 mL). The suspension was filtered through a Celite pad and concentrated via distillation. The crude product was purified by column chromatography (silica gel, eluent: pentane) and concentrated via distillation (oil bath = 150 °C) to get a clear liquid. Finally, it was stirred over NaH and condensed under reduced pressure (0.52 g, 4.7 mmol, 10 %). 1-(Penten-4-yl)-cyclopropane **20** is very volatile and has to be stored at −20 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.82 (ddt, J = 16.9, 10.1, 6.6 Hz, 1 H, CH_2=CH); 4.97 (m, 2 H, CH_2=CH), 2.08 (m, 2 H, CH_2=$CHCH_2$), 1.51 (m, 2 H, CH_2=$CHCH_2CH_2$), 1.21 (m, 2 H, CH_2=$CHCH_2CH_2CH_2$), 0.66 (m, 1 H, $CHCH_2CH_2$), 0.40 (m, 2 H, $CHCH_2CH_2$), 0.01 (m, 2 H, $CHCH_2CH_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 139.3, 114.3, 34.4, 33.8, 29.1, 10.9, 4.52 ppm.

10-Bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane (23): tBu$_3$P (0.0153 g, 0.0756 mmol, 10 mol-%) and $B(C_6F_5)_3$ (0.0386 g, 0.0756 mmol, 10 mol-%) were weighed in an amber glass screw-top jar and dissolved in CH_2Cl_2 (2.1 mL). After addition of 6-bromohexene (**18**) (0.100 mL, 0.748 mmol, 1.00 equiv.) and nonafluoro-1-iodobutane (**1**) (0.130 mL, 0.755 mmol, 1.01 equiv.) the jar was sealed with a Teflon-insert screw cap and the solution was stirred for 68 h. After removal of the solvent the crude product was purified by column chromatography (silica gel, eluent: pentane, R_f = 0.73) to give product **23** (0.352 g, 0.692 mmol, 93 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.40–4.25 (m, 1 H, CHI), 3.51–3.36 (t, J = 6.6 Hz, 2 H, CH_2Br), 3.07–2.64 (m, 2 H, CH_2CF_2), 2.08–1.46 (m, 6 H, CHI-$CH_2CH_2CH_2$-CH_2Br) ppm. ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 42.0, 41.7, 41.4, 39.5, 33.1, 31.7, 28.5, 19.9 ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = −80.9 to −81.1 (t, J = 9.6 Hz, 3F, CF_3), −111.1to −115.5 (m, 2 F, CF_2), −124.3 to −124.8 (m, 2 F, CF_2), −125.6to −126.2 (m, 2 F, CF_2). IR (film on NaCl): $\tilde{\nu}$ = 3215, 2942, 1455, 1433, 1350, 1232, 1134, 880, 724 cm^{-1}. $C_{10}H_{11}BrF_9I$: calcd. C 23.60, H 2.18; found C 23.61, H 2.42.

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Keywords: Frustrated Lewis pairs · Perfluoroalkylation · Reaction mechanisms · Halogenation · Radicals

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SUPPORTING INFORMATION

Title: Mechanistic Insights into FLP-Catalyzed Iodoperfluoroalkylations
Author(s): Michael Spittler, Lucas Helmecke, Constantin Czekelius*

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1 General Experimental Procedures

All syntheses involving air- and moisture-sensitive compounds were carried out inside a glove box (*Vacuum Atmospheres Company* model OMNI-LAB) under N_2 atmosphere (*Air Liquide ALPHAGAZ*™ 5.0). Glassware was dried for 2 hours at 120 °C and cooled down in vacuo.

Reagents as well as solvents were purchased from Acros, Sigma Aldrich, abcr, TCI, J & K scientific or VWR Chemicals. Chemicals were used without further purification or purified according to laboratory methods.[1] Vinylcyclohexane was purified by distillation at ambient pressure after refluxing over CaH_2 for 2 h. Solvents were dried with the solvent purification system MP-SPS 800 from *M.Braun*, predistilled and if necessary degassed with freeze-pump-thaw.

Reactions were monitored by thin-layer chromatography (TLC) using *Macherey-Nagel* silica gel plates ALUGRAM® Xtra SIL G/UV_{254} (0.20 mm thickness) and visualised by UV light or staining reagents if necessary. As staining reagents self-prepared potassium permanganate solution ($KMnO_4$ (3.0 g), K_2CO_3 (20 g), NaOH (5.0 ml 5.0%), H_2O (300 ml)) or cerium molybdophosphoric acid (molybdophosphoric acid (0.5 g), H_2O (250 ml), conc. H_2SO_4 (16 ml), Ce(IV)sulphate (2.0 g)) were used. Chromatographic purification of products was performed on *Macherey-Nagel* 60 M (0.04 - 0.063 mm) silica gel.

^{1}H-, ^{11}B-, ^{13}C, ^{19}F-, ^{31}P-NMR spectra were recorded on *Bruker* Avance III 300 and 600. Chemical shifts are reported in parts per million (ppm). ^{1}H-NMR shifts are reported in reference to the corresponding solvent. ^{19}F-NMR shifts were reported in ppm and referenced to $CFCl_3$ in C_6D_6 and ^{31}P-NMR to H_3PO_4 in D_2O. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, ddd = doublet of doublet of doublet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons, and d) assignment. Coupling constants (*J*) were reported in Hertz (Hz). The attributions of the chemical shifts were determined by means of COSY, HSQC, and HMQC experiments. If not described differently the NMR-spectra were measured at 298 K. For inert additions to an NMR sample outsight the glovebox, a Kontes® NMR tube sealing manifold was used.

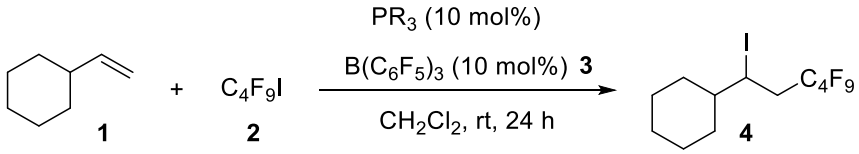
IR spectra were recorded using a *Jasco* FT/IR-6200 spectrometer. Samples were measured as film on a NaCl crystal. The absorption bands were given in wave numbers (cm^{-1}). High resolution mass spectra (HRMS) were measured with a *Bruker Daltonics* UHR-QTOF maXis 4G. Elemental analysis were measured on an *elementar* Vario Micro Cube.

Due to the volatility of 4-pentenyl-1-cyclopropane it was obtained as mixture with solvent and small amounts of impurities, whereby an elemental analysis was not possible.

Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$[2] and [$^tBu_3PI$][$FB(C_6F_5)_3$][3] were synthesised according to a literature procedure. GC setup and experiments are described in the respective chapter.

2 Screenings

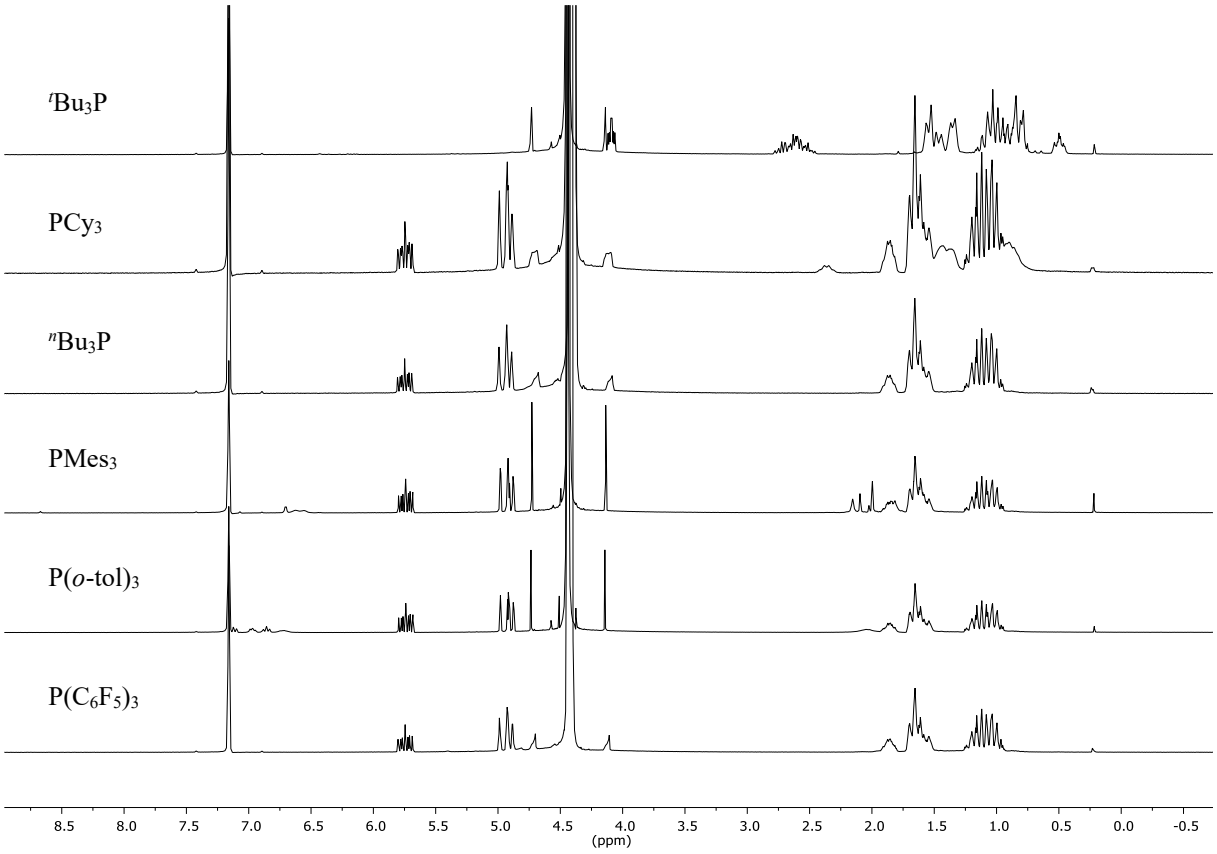
2.1 Phosphane screening



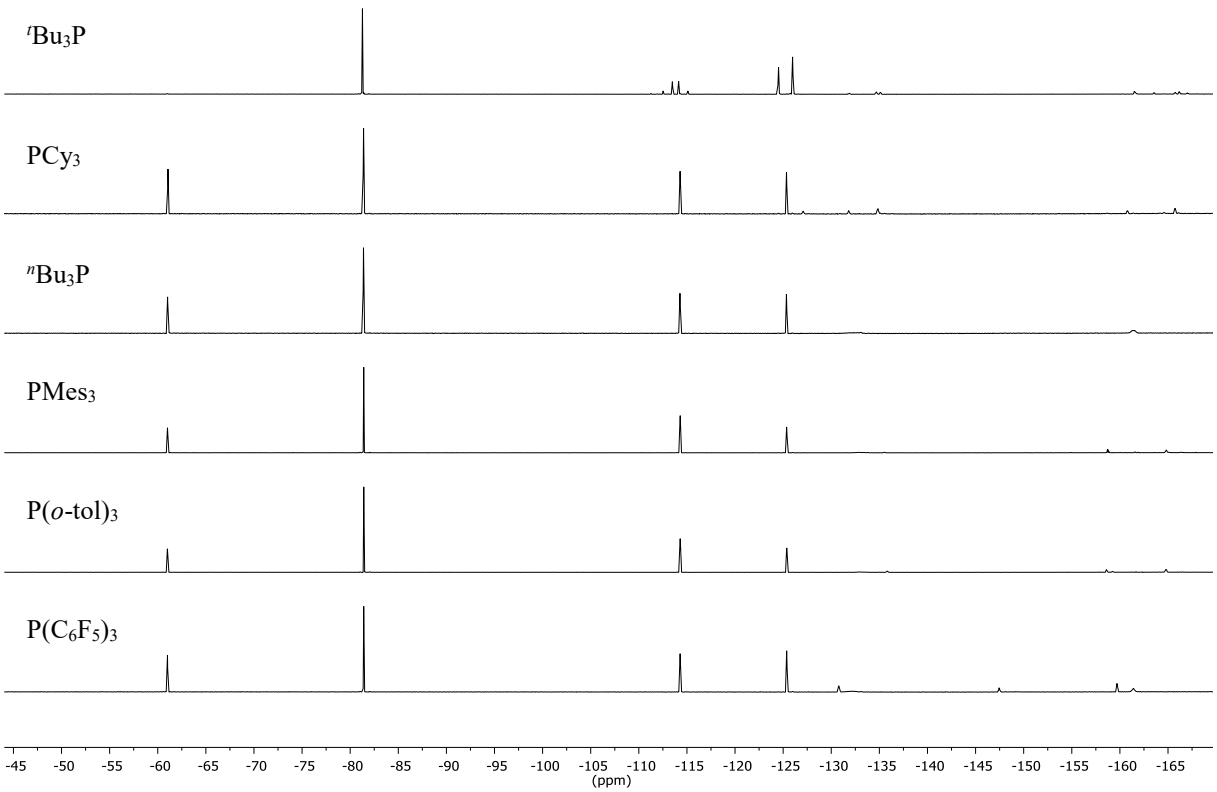
Phosphane (10 mol%) and tris(pentafluorophenyl)borane (**2**) (10 mol%) were weighed into a small glass vial and dissolved in CH_2Cl_2 (1.2 ml). After placing the glass vial in an amber glass screw-top jar vinylcyclohexane (**1**) (56 µl, 0.41 mmol, 1.0 eq.) was added. Under light exclusion using red light, nonafluoro-1-iodobutane (**2**) (70 µl, 0.41 mmol, 1.0 eq.) was added and the jar was sealed with a Teflon-insert screw cap. After stirring for 24 h conversion was determined *via* ^{1}H- and ^{19}F-NMR-spectroscopy (Table 1).

Table 1: Phosphane screening, calculated conversions.

		conversion [%]	
		^{1}H-NMR	^{19}F-NMR
Tri-*tert*-butylphosphane	$^tBu_3P$	≥95%	≥95%
Tricyclohexylphosphane	PCy_3	–	–
Tri-*n*-butylphosphane	$^nBu_3P$	–	–
Trimesitylphosphane	$PMes_3$	–	–
Tri(*o*-tolyl)phosphane	$P(o\text{-tol})_3$	–	–
Tris(pentafluorophenyl)phosphane	$P(C_6F_5)_3$	–	–



NMR-spectrum 1: ^{1}H-NMR-spectra (300 MHz, C_6D_6) of reaction solution after 24 h in CH_2Cl_2.



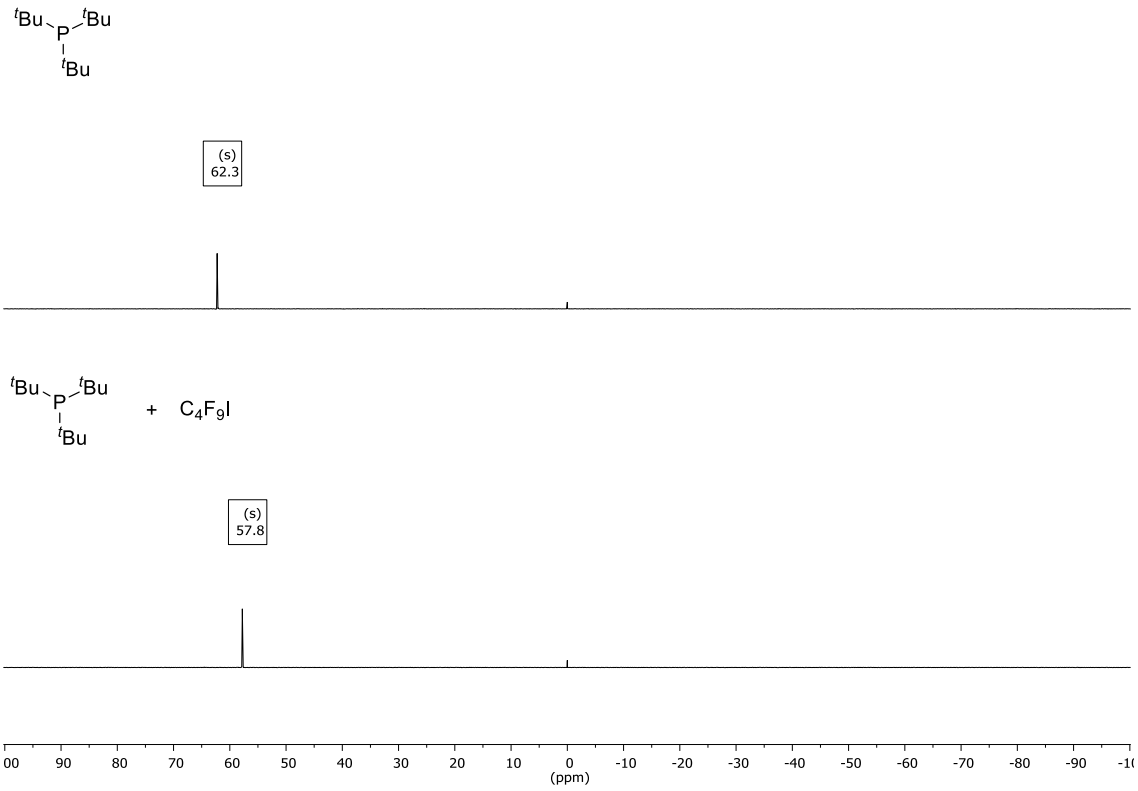
NMR-spectrum 2: ^{19}F-NMR-spectra (282 MHz, C_6D_6) of reaction solution after 24 h in CH_2Cl_2.

2.2 Determination of the NMR-shifts of the phosphanes in the presence of nonafluoro-1-iodobutane

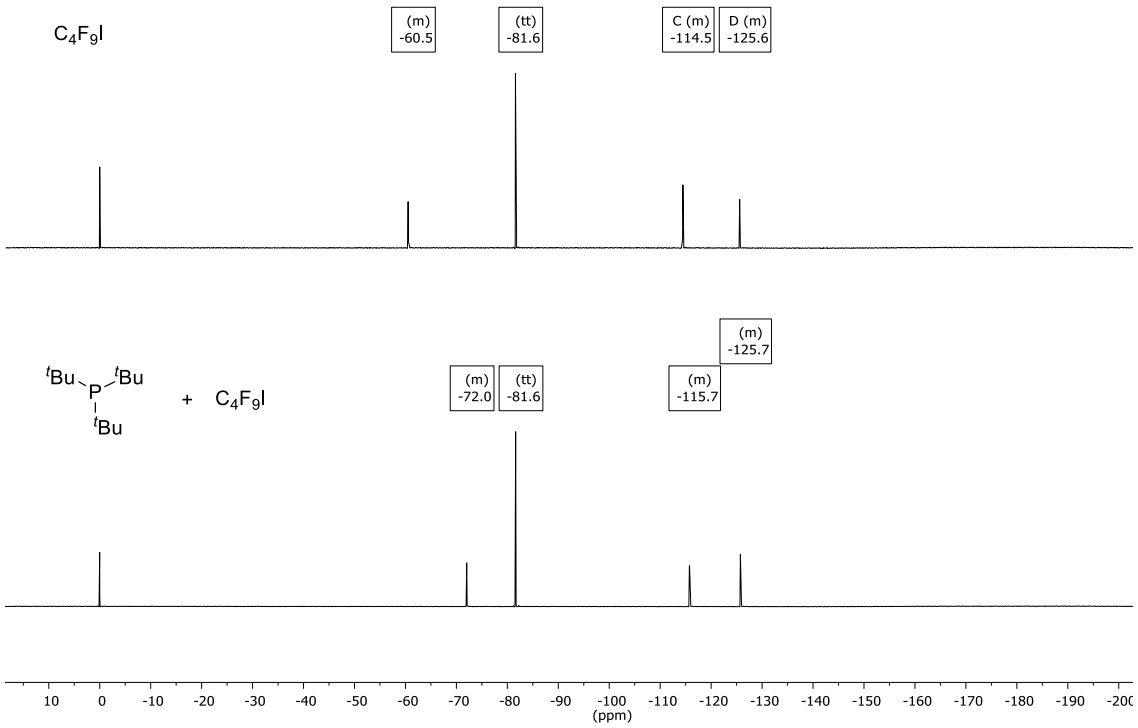
The individual phosphane was weighed into a small glass vial, dissolved in CH_2Cl_2 (0.5 ml) and transferred into a Young valve NMR tube equipped with H_3PO_4 in D_2O and $CFCl_3$ in C_6D_6 as external standards. After measuring ^{31}P-NMR-spectra, nonafluoro-1-iodobutane (**2**) was added inside the glovebox and the ^{31}P-NMR- as well as ^{19}F-NMR-spectra were measured (Table 2).

Table 2: Shifts of the different phosphanes without and with nonafluoro-1-iodobutane and the corresponding Tolman electronic parameter as well as ligand cone angle.[4]

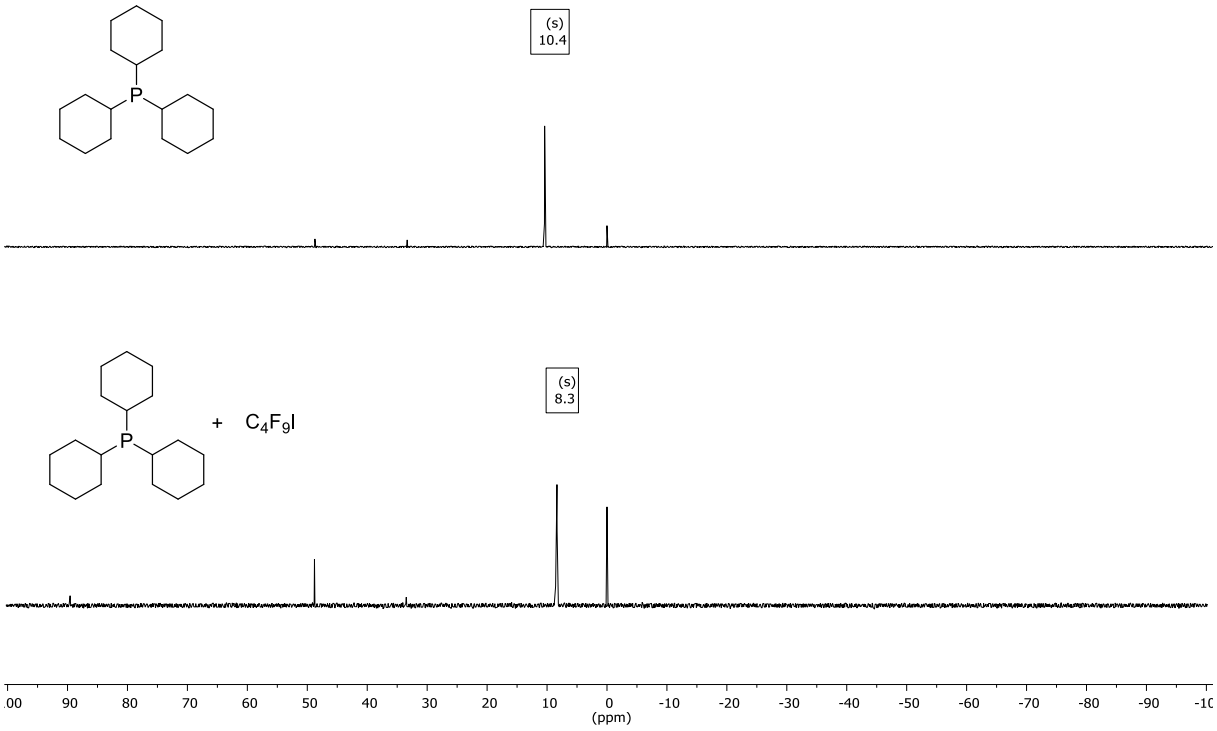
					Δδ			
		^{31}P-NMR without C_4F_9I [ppm]	^{31}P-NMR with C_4F_9I [ppm]	^{19}F-NMR [ppm]	^{31}P-NMR [ppm]	^{19}F-NMR [ppm]	ν (CO)[4] [cm^{-1}]	θ[4] [degree]
Nonafluoro-1-iodobutane				–60.5 –81.6 –114.5 –125.6				
Tri-*tert*-butylphosphane	$^{t}Bu_3P$	62.3	57.8	–72.0 –81.6 –115.7 –125.7	4.48	11.5 0.01 1.25 0.10	2056.1	182
Tricyclohexylphosphane	PCy_3	10.4	8.34	–69.0 –81.6 –115.5 –125.7	2.06	8.48 0.01 1.04 0.10	2056.4	170
Tri-*n*-butylphosphane	$^{n}Bu_3P$	–31.4	–31.4	–63.9 –81.6 –114.9 –125.7	–	3.40 0.02 0.40 0.06	2060.3	132
Trimesitylphosphane	$PMes_3$	–36.9	–36.9	–60.6 –81.6 –114.5 –125.6	–	0.06 0.00 0.02 0.01	2064.1	212
Tri(*o*-tolyl)phosphane	$P(o\text{-tol})_3$	–30.4	–30.4	–60.6 –81.6 –114.5 –125.6	–	0.11 0.01 0.04 0.01	2066.6	194
Tris(pentafluorophenyl)phosphane	$(C_6F_5)_3P$	–74.7	–74.7	–60.6 –81.7 –114.5 –125.7	–	0.10 0.10 0.01 0.05	2090.9	184



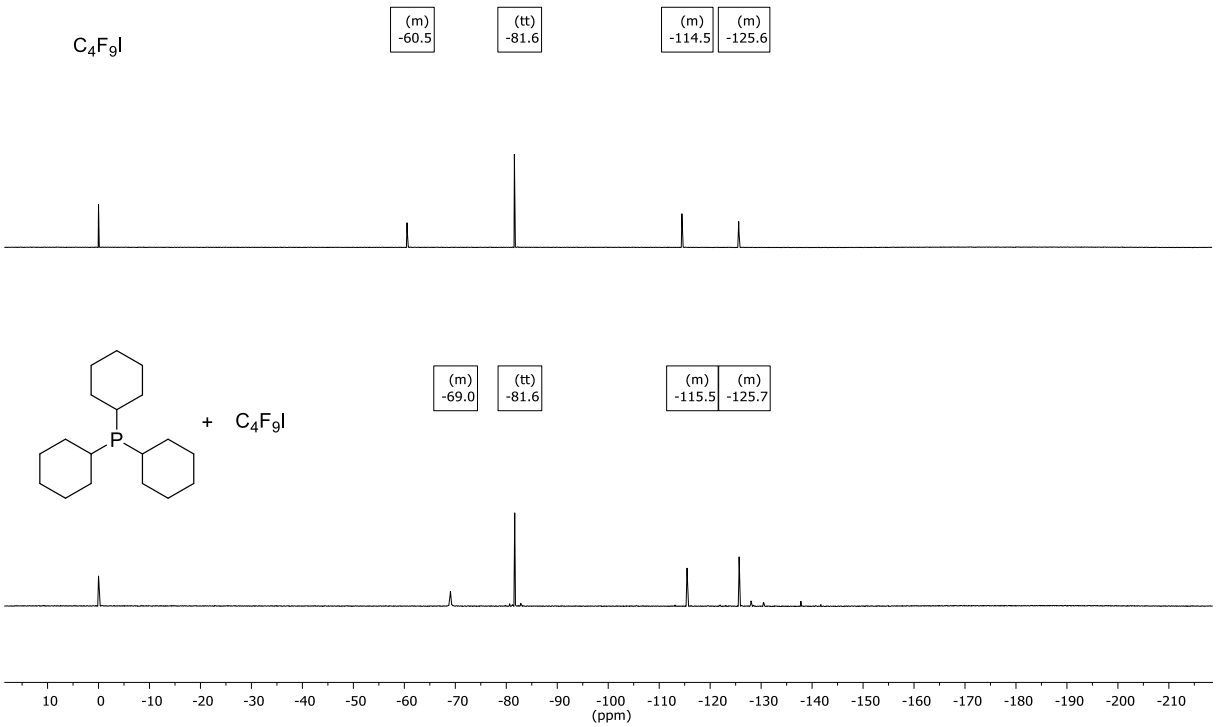
NMR-spectrum 3: ^{31}P-NMR-spectra (121 MHz, D_2O) in CH_2Cl_2.



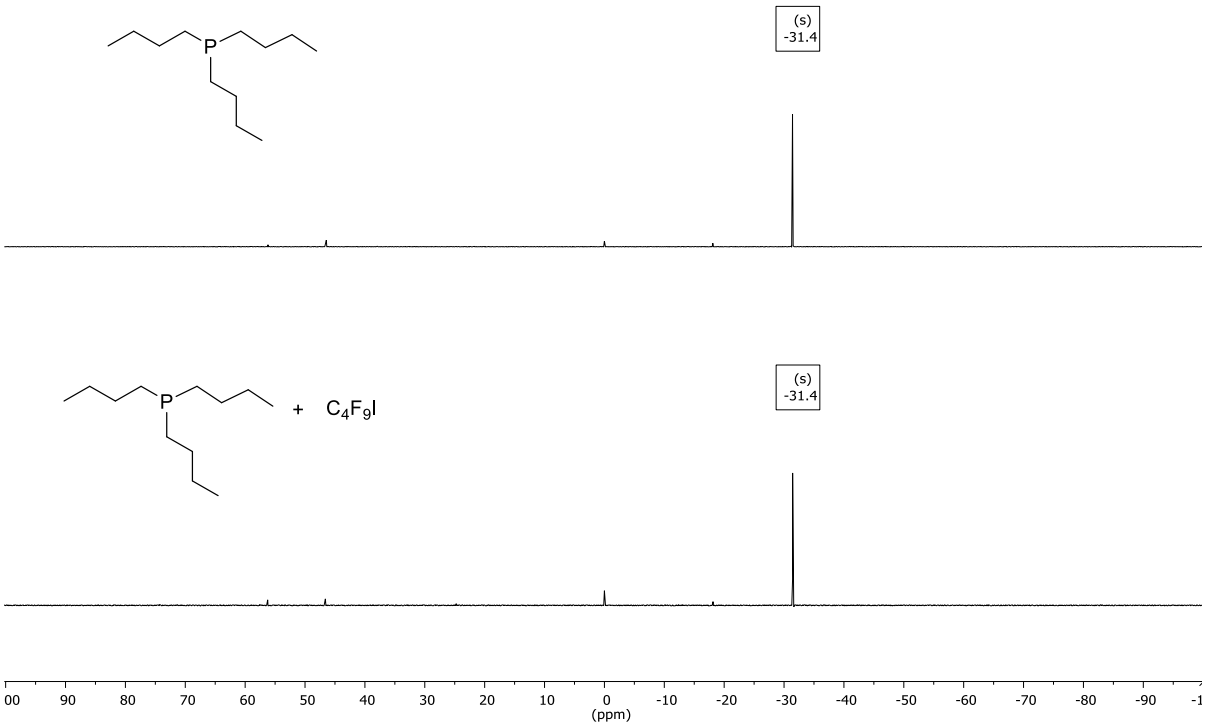
NMR-spectrum 4: ^{19}F-NMR-spectra (282 MHz, C_6D_6) in CH_2Cl_2.



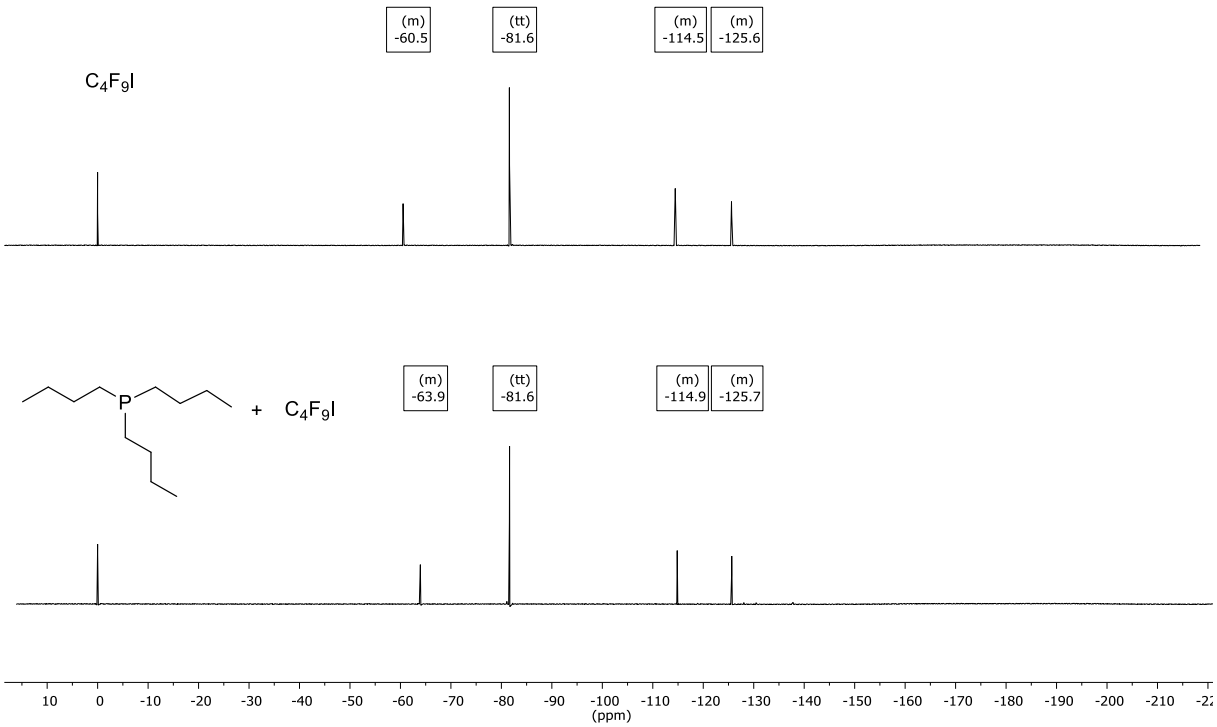
NMR-spectrum 5: ^{31}P-NMR-spectra (121 MHz, D_2O) in CH_2Cl_2.



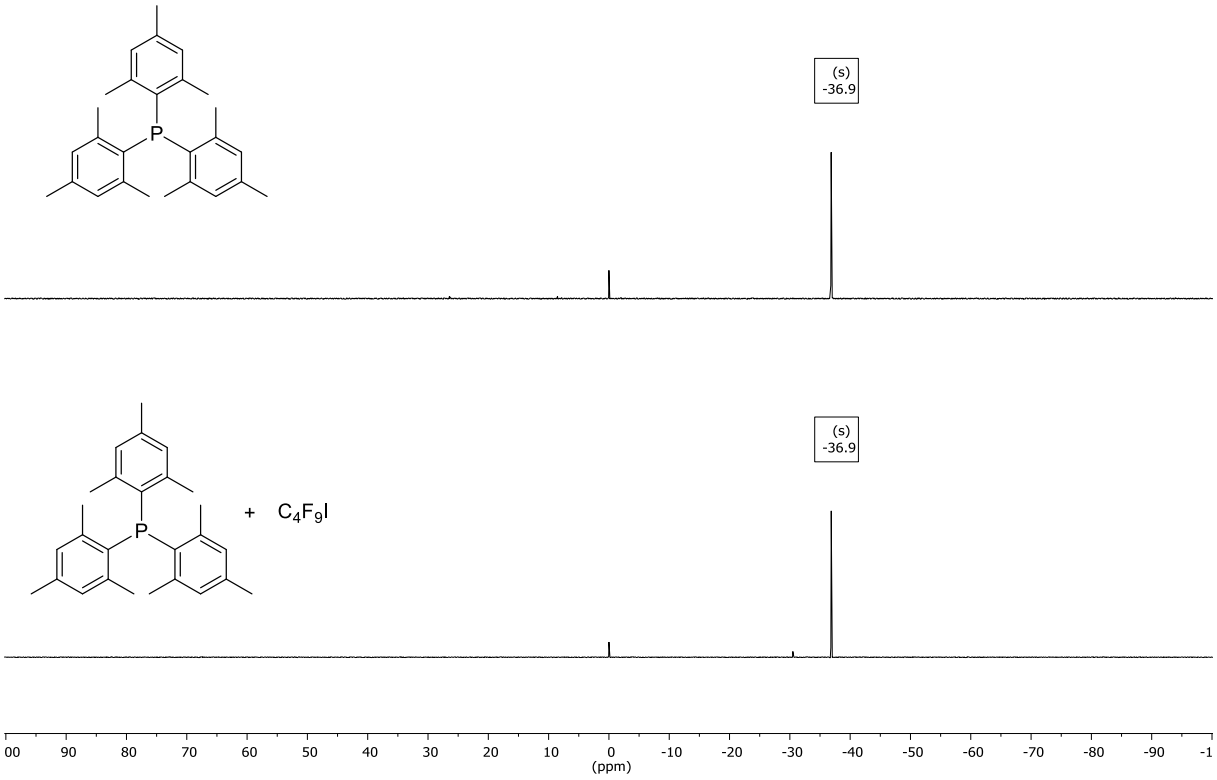
NMR-spectrum 6: ^{19}F-NMR-spectra (282 MHz, C_6D_6) in CH_2Cl_2.



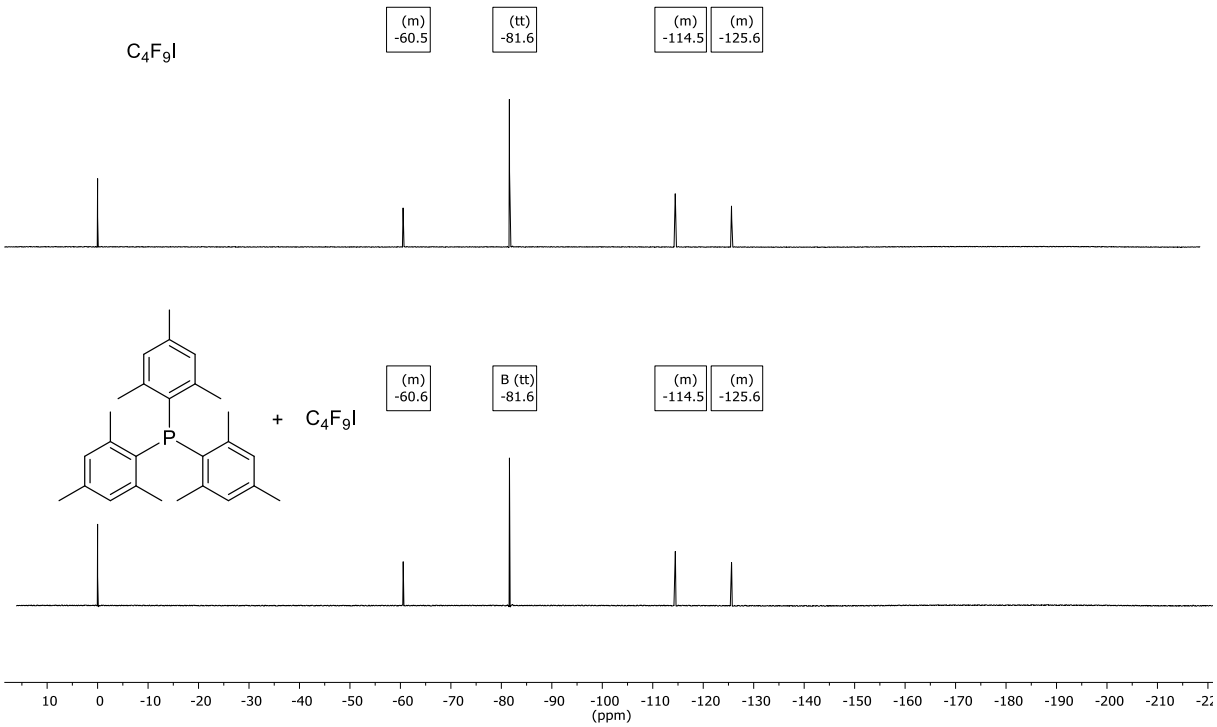
NMR-spectrum 7: ^{31}P-NMR-spectra (121 MHz, D_2O) in CH_2Cl_2.



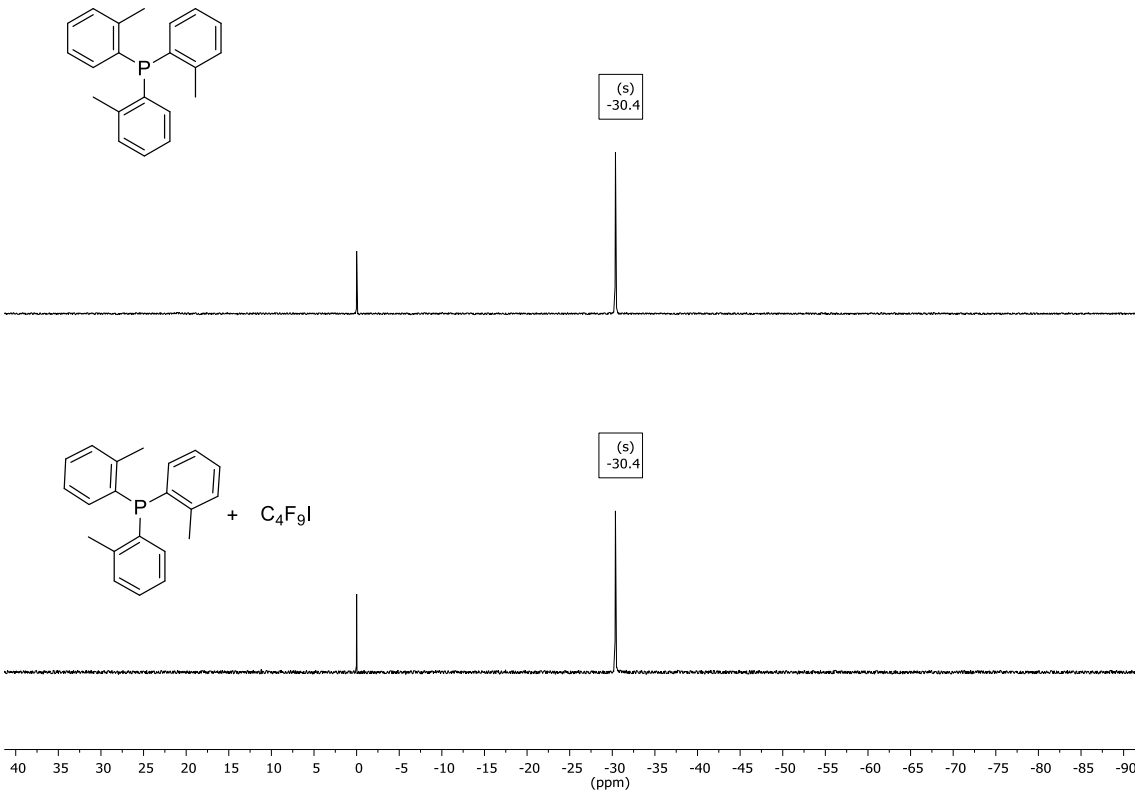
NMR-spectrum 8: ^{19}F-NMR-spectra (282 MHz, C_6D_6) in CH_2Cl_2.



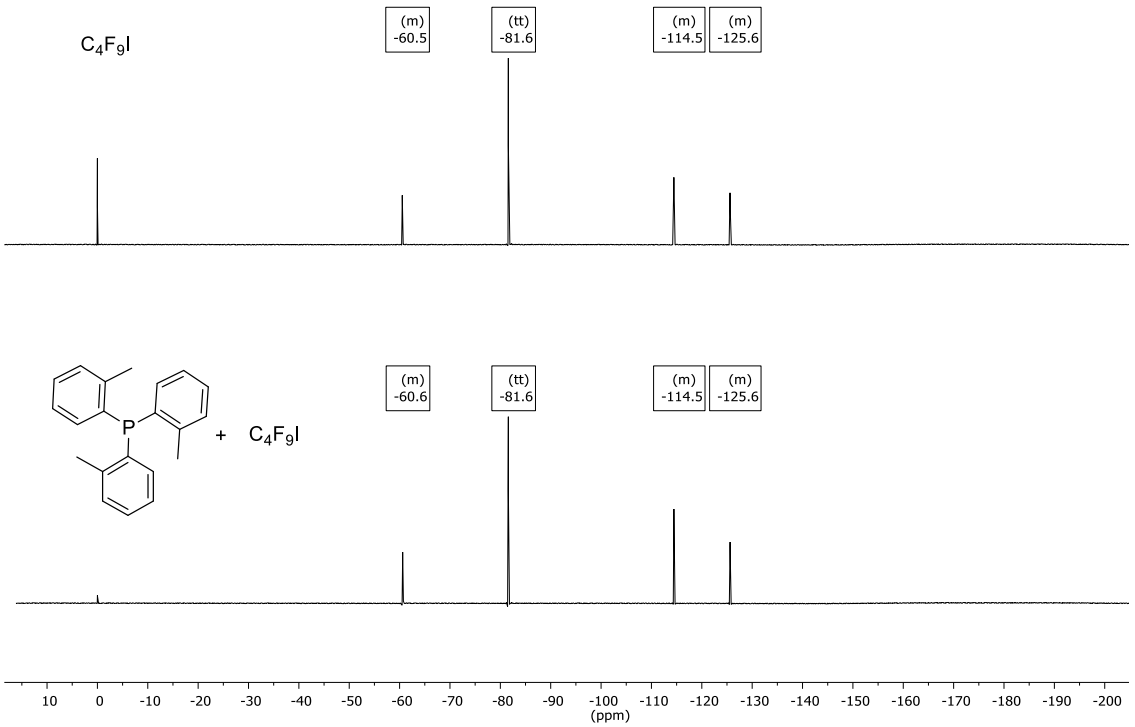
NMR-spectrum 9: ^{31}P-NMR-spectra (121 MHz, D_2O) in CH_2Cl_2.



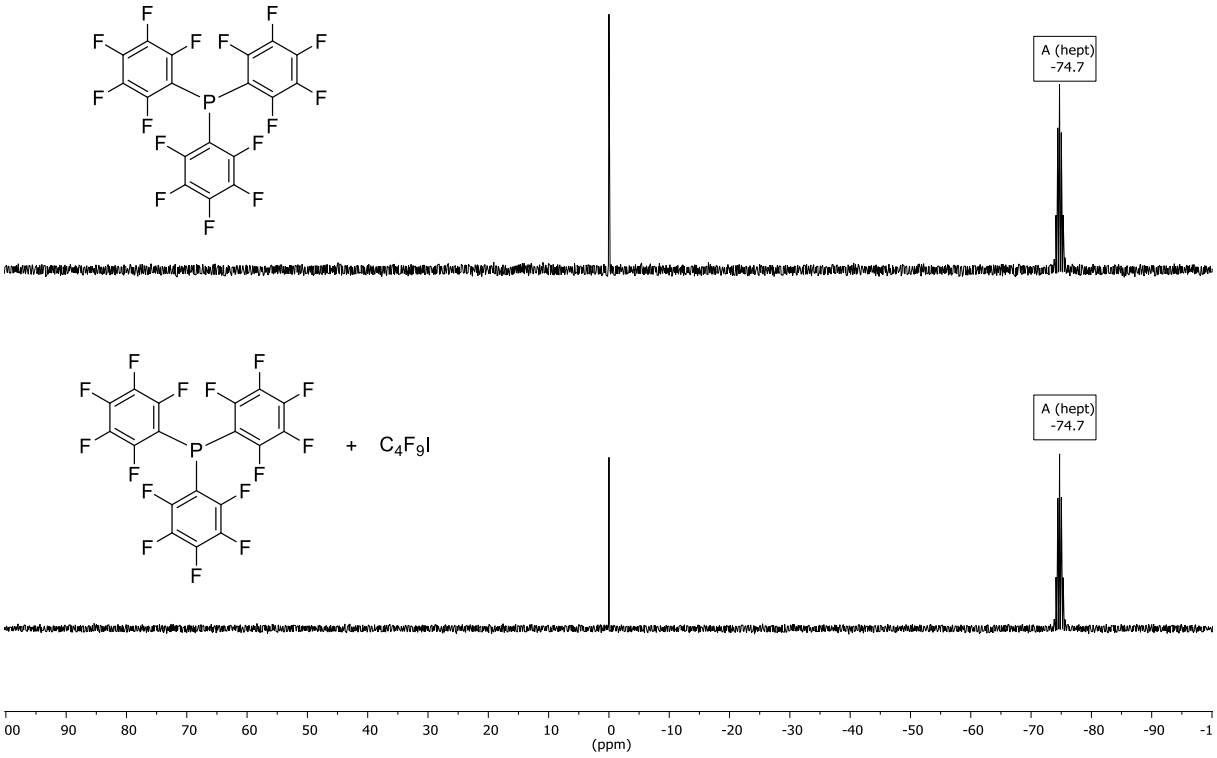
NMR-spectrum 10: ^{19}F-NMR-spectra (282 MHz, C_6D_6) in CH_2Cl_2.



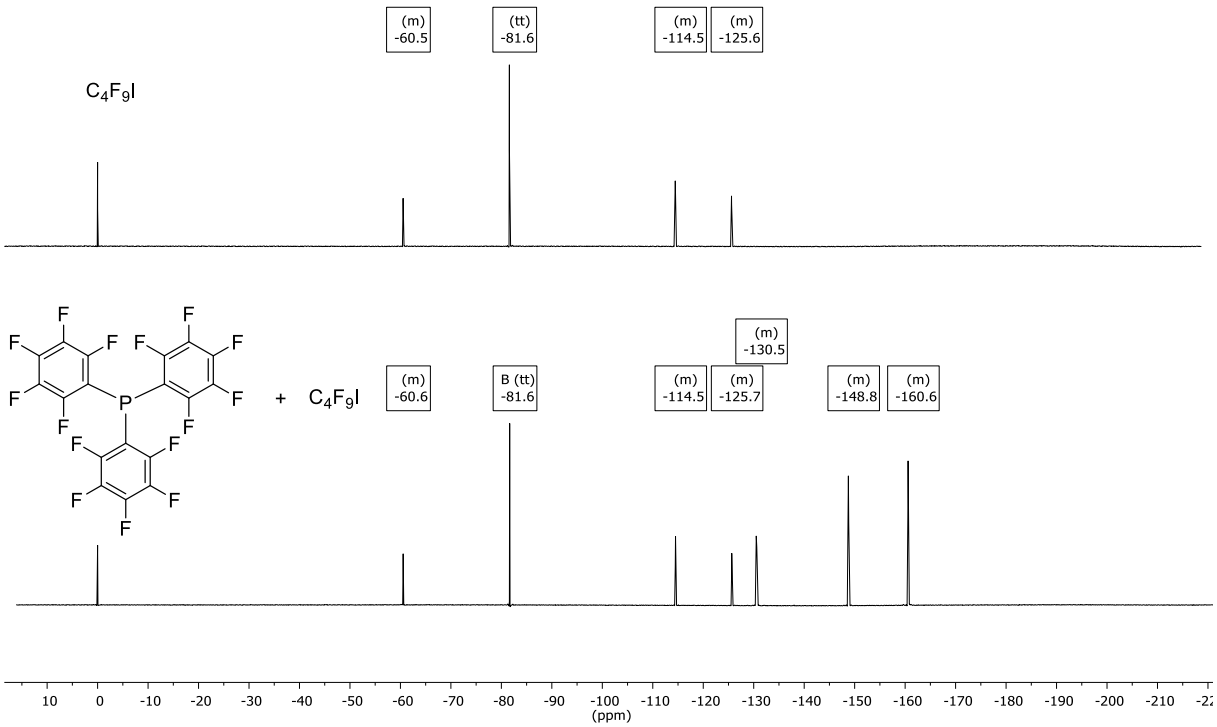
NMR-spectrum 11: ^{31}P-NMR-spectra (121 MHz, D_2O) in CH_2Cl_2.



NMR-spectrum 12: ^{19}F-NMR-spectra (282 MHz, C_6D_6) in CH_2Cl_2.

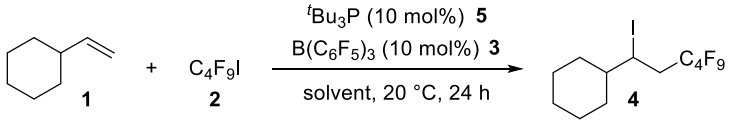


NMR-spectrum 13: ^{31}P-NMR-spectra (121 MHz, D_2O) in CH_2Cl_2.



NMR-spectrum 14: ^{19}F-NMR-spectra (282 MHz, C_6D_6) in CH_2Cl_2.

2.3 Solvent screening



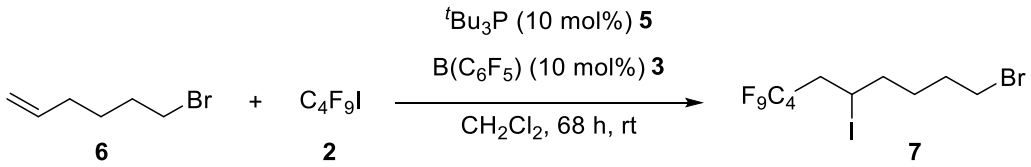
$^{t}Bu_3P$ (**5**) (10 mol%) and $B(C_6F_5)_3$ (**3**) (10 mol%) were weighed into a small glass vial and dissolved in the denoted solvent (1.2 ml). After placing the glass vial in an amber glass screw-top jar, vinylcyclohexane (**1**) (56 µl, 0.41 mmol, 1.0 eq.) was added. Under light exclusion using red light nonafluoro-1-iodobutane (**2**) (70 µl, 0.41 mmol, 1.0 eq.) was added and the jar was sealed with a Teflon-insert screw cap. After stirring for 24 h at 20 °C, a sample was taken (0.10 ml) and diluted with C_6D_6 (0.50 ml). Conversion was determined *via* ^{1}H- and ^{19}F-NMR-spectroscopy (Table 3).

Table 3: Overview of the result of the solvent screening.

	conversion [%]		dipole moment
	^{1}H-NMR	^{19}F-NMR	[debye][5]
benzene-d_6	–	–	0
toluene	–	–	0.4
CH_2Cl_2	95	≥99	1.6
chlorobenzene	32	31	1.7
1,2-dichlorobenzene	68	72	2.5
1,3-dichlorobenzene	49	50	1.7
fluorobenzene	35	35	1.6
1,2-difluorobenzene	68	72	–
1,4-difluorobenzene	26	25	–

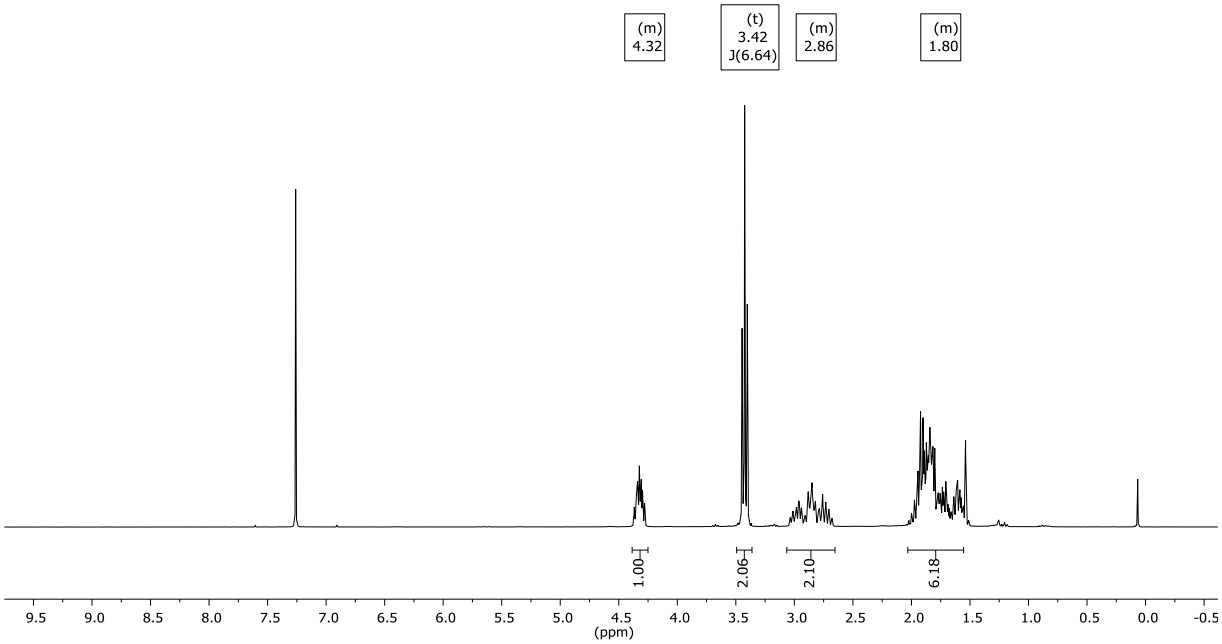
3 Iodoperfluoroalkylation reactions

3.1 Reaction of 6-bromohexene with nonafluoro-1-iodobutane

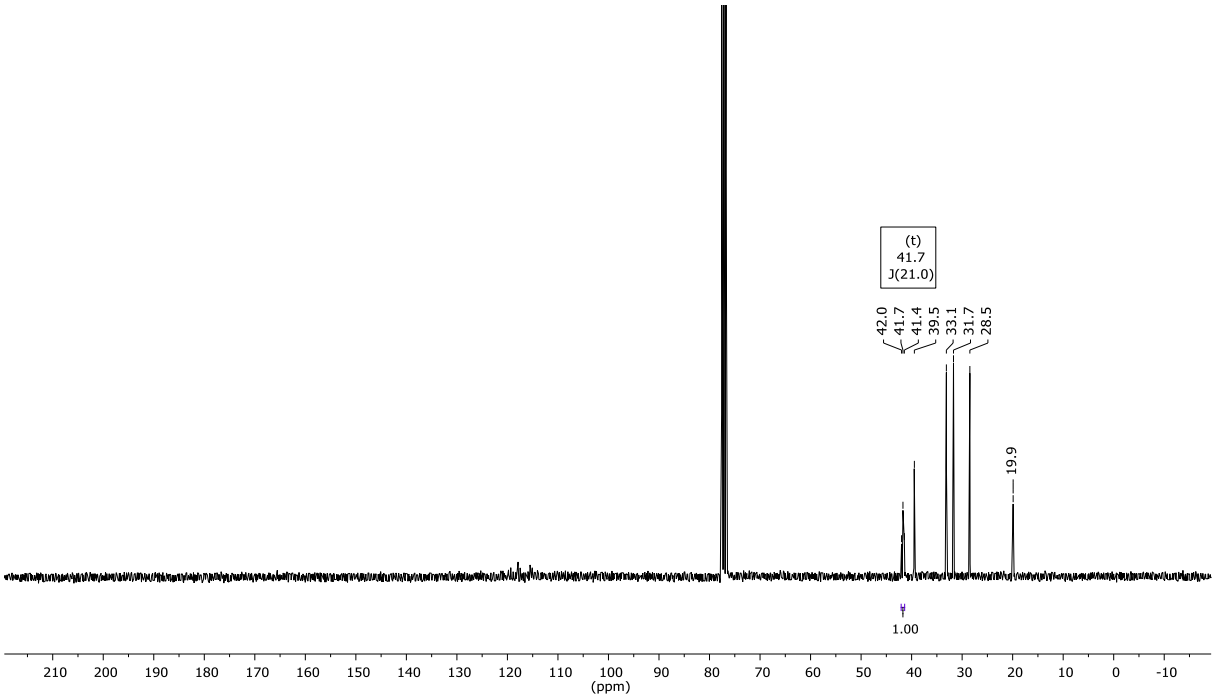


^{t}Bu$_3$P (**5**) (0.0153 g, 0.0756 mmol, 10 mol%) and B(C$_6$F$_5$)$_3$ (**3**) (0.0386 g, 0.0756 mmol, 10 mol%) were weighed in an amber glass screw-top jar and dissolved in CH_2Cl_2 (2.1 ml). After addition of 6-bromohexene (**6**) (100 µl, 0.748 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (130 µl, 0.755 mmol, 1.01 eq.) the jar was sealed with a Teflon-insert screw cap and the solution was stirred for 68 h. After removal of the solvent the crude product was purified by column chromatography (silica gel, eluent: pentane, $R_f = 0.73$) to give product **7** (0.352 g, 0.692 mmol, 93%).

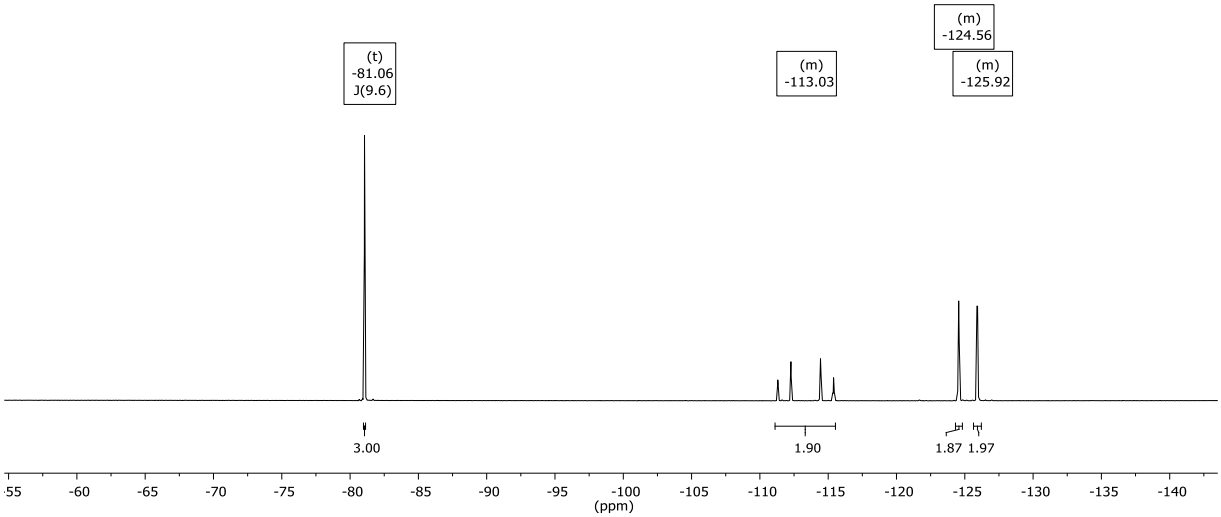
^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm] 4.40 - 4.25 (m, 1H, C*H*I), 3.51 - 3.36 (t, J = 6.6 Hz, 2H, C*H*$_2$Br), 3.07 - 2.64 (m, 2H, C*H*$_2$CF$_2$), 2.08 - 1.46 (m, 6H, CHI-C*H*$_2$C*H*$_2$C*H*$_2$-CH$_2$Br). **^{13}C{^{1}H}-NMR** (75.5 MHz, $CDCl_3$) δ [ppm] 41.7 (−H$_2$*C*CF$_2$R$_F$, t, $^2J_{CF}$ = 21.0 Hz), 39.5, 33.1, 31.7, 28.5, 19.9. **^{19}F-NMR** (282 MHz, $CDCl_3$) δ [ppm] –80.9 - –81.1 (t, J = 9.6 Hz, 3F, CF_3), –111.1 - −115.5 (m, 2F, CF_2), –124.3 - –124.8 (m, 2F, CF_2), –125.6 - –126.2 (m, 2F, CF_2). **IR** (film on NaCl), $\tilde{\nu}$ [cm^{-1}] 3215, 2942, 1455, 1433, 1350, 1232, 1134, 880, 724. **Elemental analysis** for $C_{10}H_{11}BrF_9I$: calculated: C: 23.60 %, H: 2.18 %, measured: C: 23.61%, H: 2.42%.



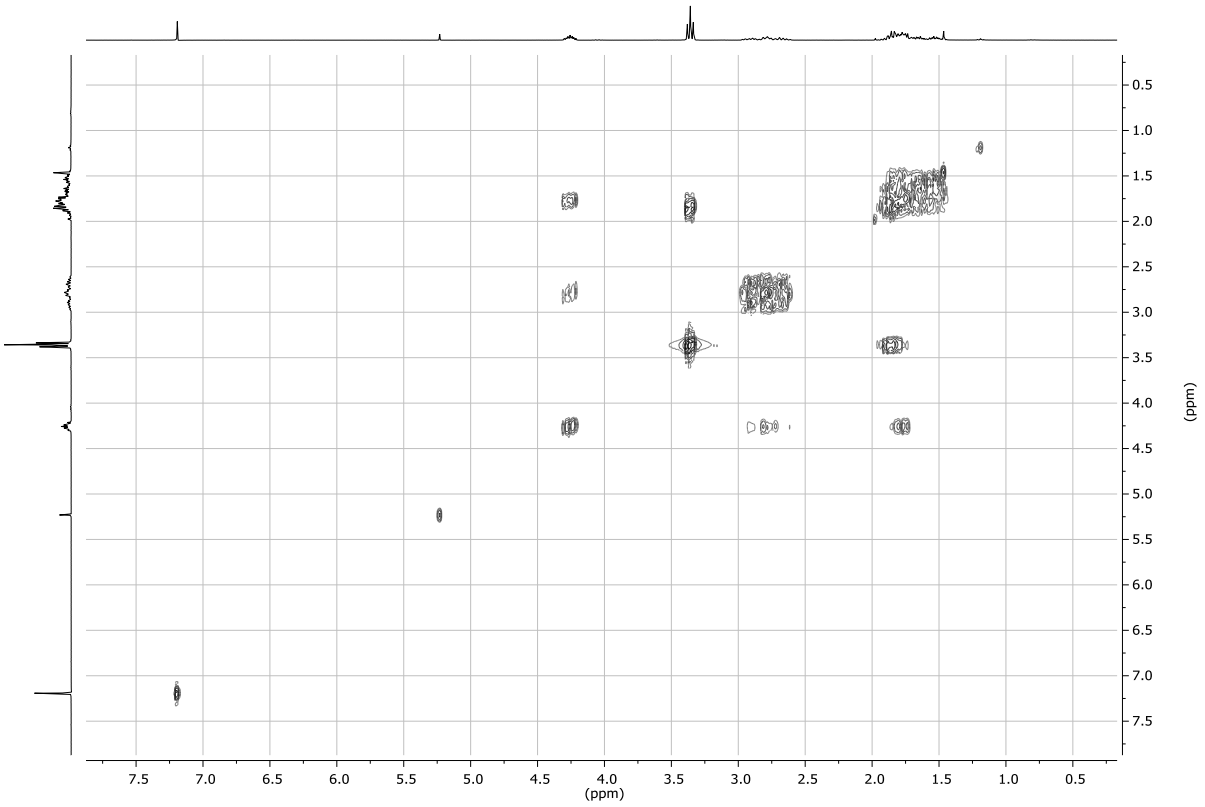
NMR-spectrum 15: ^{1}H-NMR-spectrum (300 MHz, $CDCl_3$) of 10-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane.



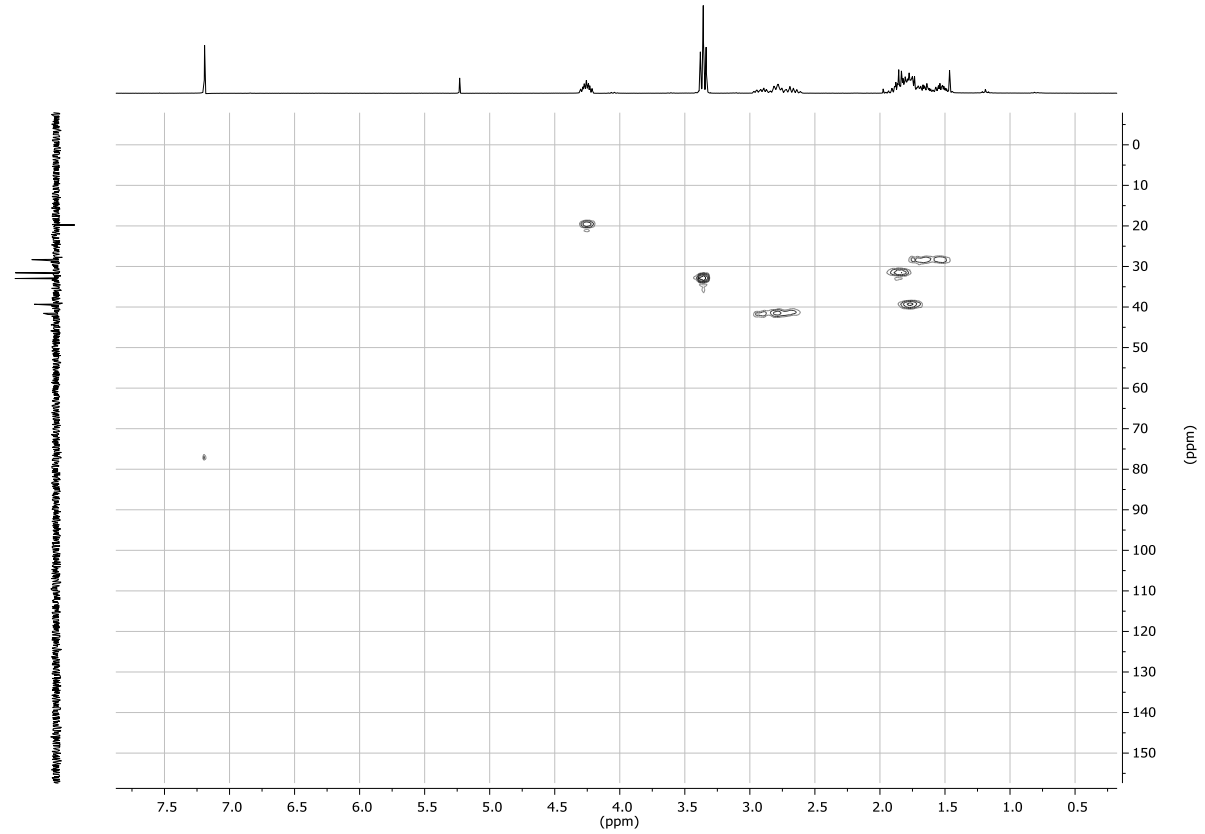
NMR-spectrum 16: ^{13}C-NMR-spectrum (75.5 MHz, $CDCl_3$) of 10-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane.



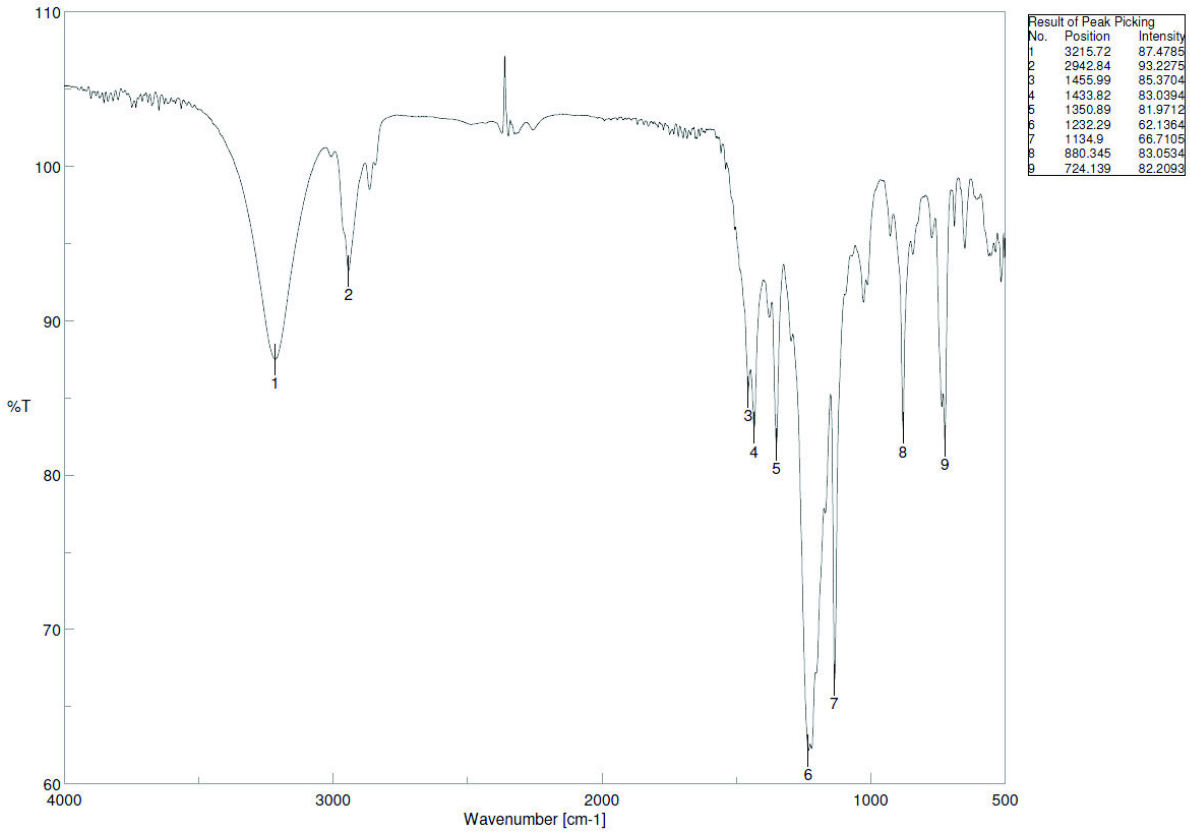
NMR-spectrum 17: ^{13}F-NMR-spectrum (282 MHz, $CDCl_3$) of 10-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane.



NMR-spectrum 18: COSY-spectrum (300 MHz, $CDCl_3$) of 10-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane.

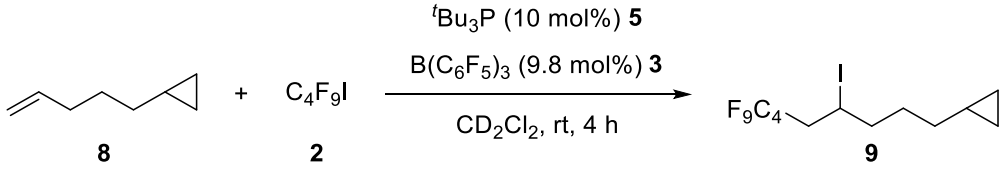


NMR-spectrum 19: HSQC-spectrum (300, 75.5 MHz, $CDCl_3$) of 10-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane.

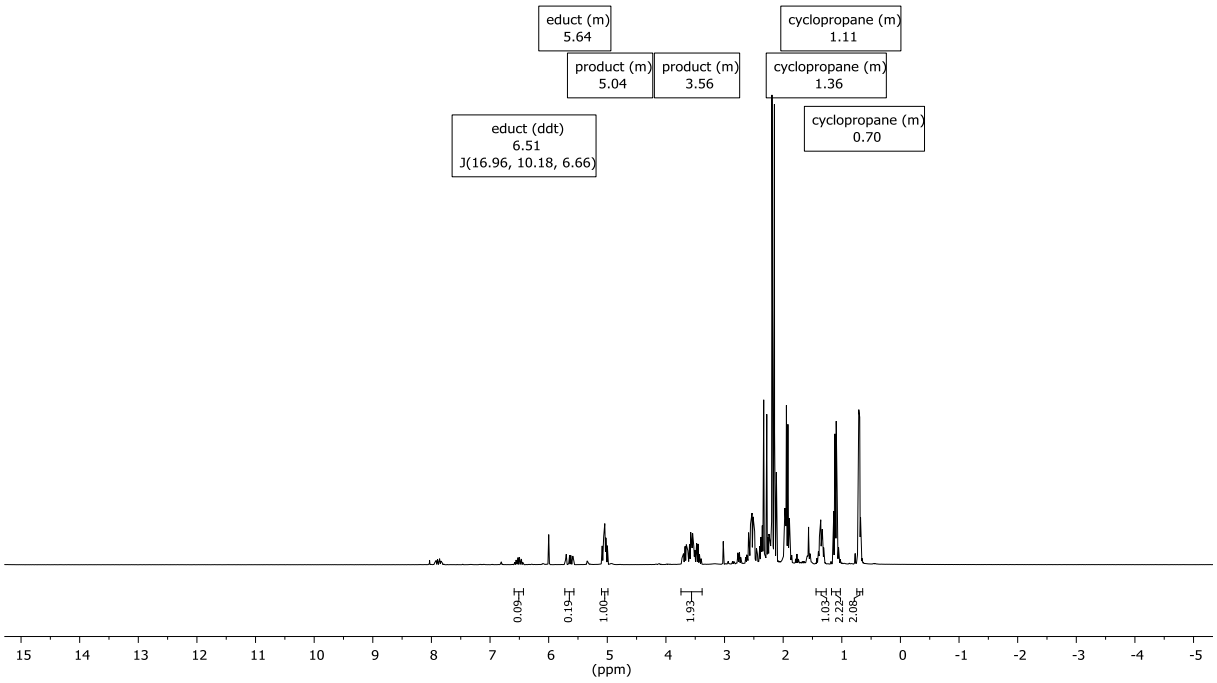


IR-spectrum (film on NaCl) 1: 10-bromo-1,1,1,2,2,3,3,4,4-nonafluoro-6-iododecane.

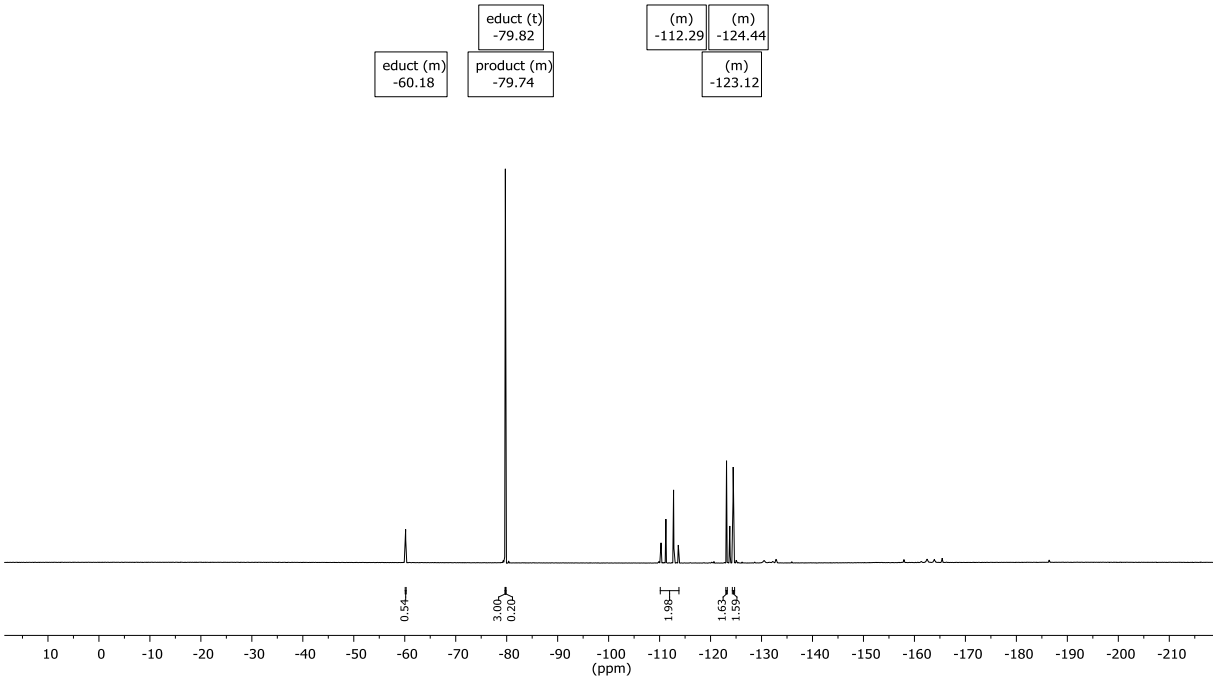
3.2 Reaction of 4-penten-1-ylcyclopropane, NMR-experiment



Inside the glovebox, $^{t}Bu_3P$ (**5**) (5.6 mg, 0.0277 mmol, 10 mol%) and $B(C_6F_5)_3$ (**3**) (13.8 mg, 0.0270 mmol, 9.8 mol%) were weighed into a small glass vial, dissolved in CD_2Cl_2 (0.6 ml) and transferred into an amber NMR tube. Outside the glovebox, 4-penten-1-ylcyclopropane (**8**) (30.3 mg, 0.275 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (35.0 µl, 0.206 mmol, 1.15 eq.) was added with a syringe under argon atmosphere. The NMR tube was sealed with a black cap, wrapped with aluminum foil and measured after 4 h.



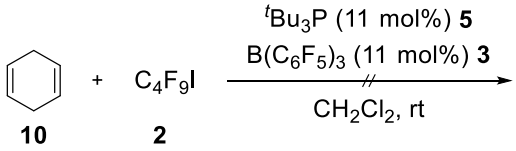
NMR-spectrum 20: ^{1}H-NMR-spectra (300 MHz, CD_2Cl_2) of the reaction with 4-penten-1-ylcyclopropane.



NMR-spectrum 21: ^{19}F-NMR-spectra (282 MHz, CD_2Cl_2) of the reaction with 4-penten-1-ylcyclopropane.

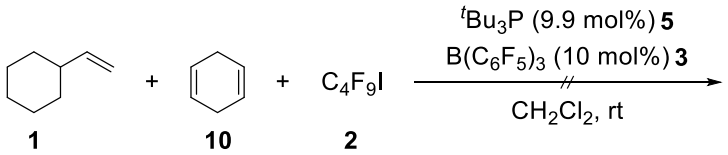
3.3 Reactions involving 1,4-cyclohexadiene

3.3.1 Iodoperfluoroalkylation of 1,4-cyclohexadiene

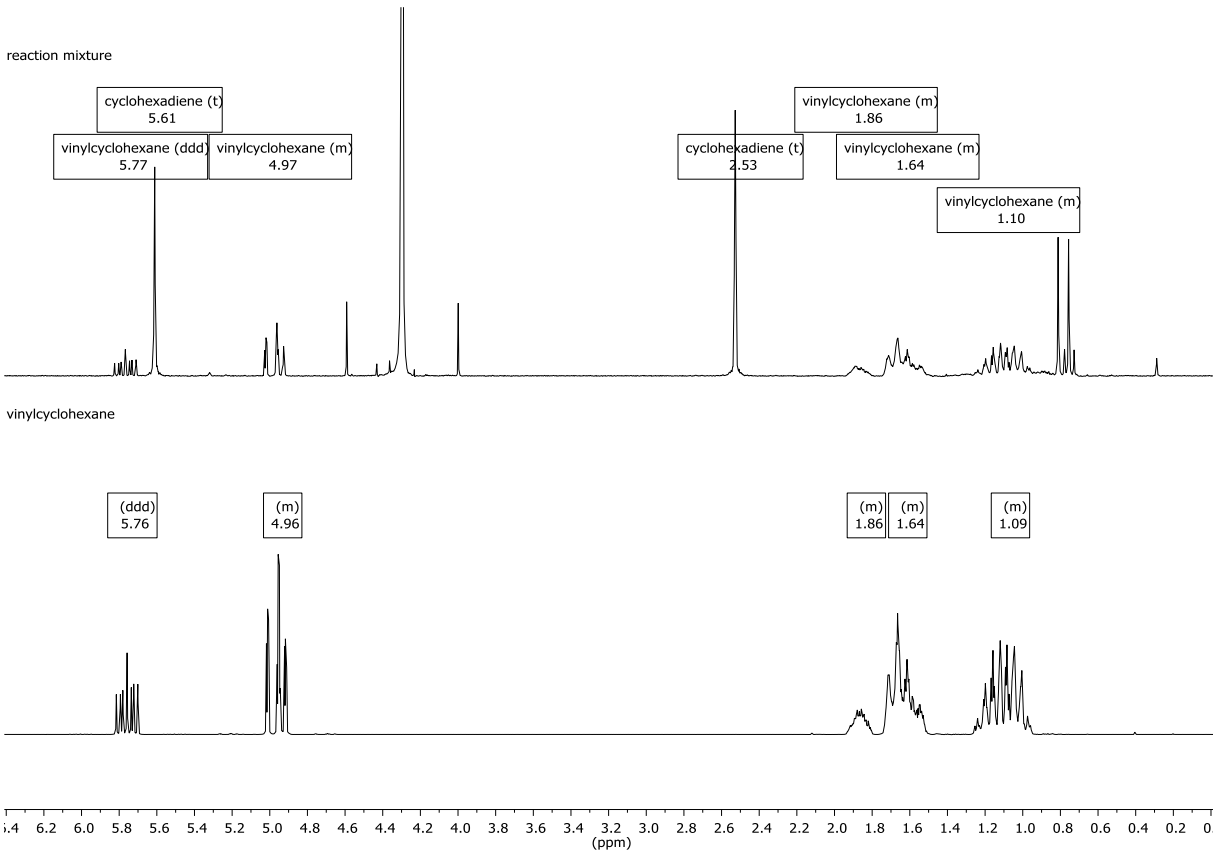


1,4-Cyclohexadiene (**10**) (56.3 mg, 0.703 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (255 mg, 0.737 mmol, 1.05 eq.) were weighed into an amber glass jar and dissolved in CH_2Cl_2 (0.5 ml). A solution of $^tBu_3P$ (**5**) (15.6 mg, 0.0771 mmol, 11 mol%) and $B(C_6F_5)_3$ (**3**) (39.4 mg, 0.0770 mmol, 11 mol%) in CH_2Cl_2 (1.6 ml) was added. The jar was sealed with a Teflon-insert screw cap. After 2 and 9 days NMR samples were withdrawn.

3.3.2 Iodoperfluoroalkylation of vinylcyclohexane in the presence of 1,4-cyclohexadiene

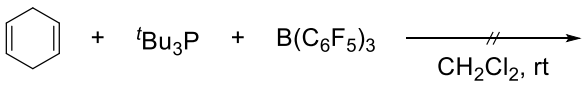


1,4-Cyclohexadiene (**10**) (56.5 mg, 0.705 mmol, 1.04 eq.) was weighed into an amber glass jar and dissolved in CH_2Cl_2 (1.0 ml). After addition of vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.), a solution of $^tBu_3P$ (**5**) (14.6 mg, 0.0722 mmol, 9.9 mol%) and $B(C_6F_5)_3$ (**3**) (37.6 mg, 0.0734 mmol, 10 mol%) in CH_2Cl_2 (1.1 ml) was added. The jar was sealed with a Teflon-insert screw cap. After 1 and 8 days NMR samples were withdrawn.



NMR-spectrum 22: Stacked ^{1}H-NMR-spectra (300 MHz, C_6D_6) of the reaction solution after 24 h (top) and vinylcyclohexane (bottom).

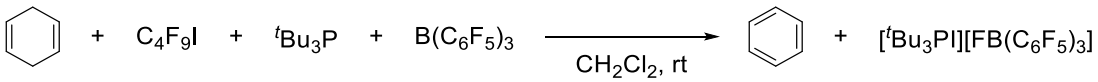
3.3.3 Stoichiometric reaction of 1,4-cyclohexadiene, ^{t}Bu$_3$P and B(C$_6$F$_5$)$_3$



10 **5** **3**

^{t}Bu$_3$P (**5**) (53.9 mg, 0.266 mmol, 1.0 eq.) and B(C$_6$F$_5$)$_3$ (**3**) (133 mg, 0.260 mmol, 0.98 eq.) were weighed into an amber glass jar and dissolved in CH_2Cl_2 (1.0 ml). 1,4-Cyclohexadiene (**10**) (21 mg, 0.26 mmol, 1.0 eq.) was added and the jar was sealed with a Teflon-insert screw cap. After 6 and 13 days NMR samples were withdrawn.

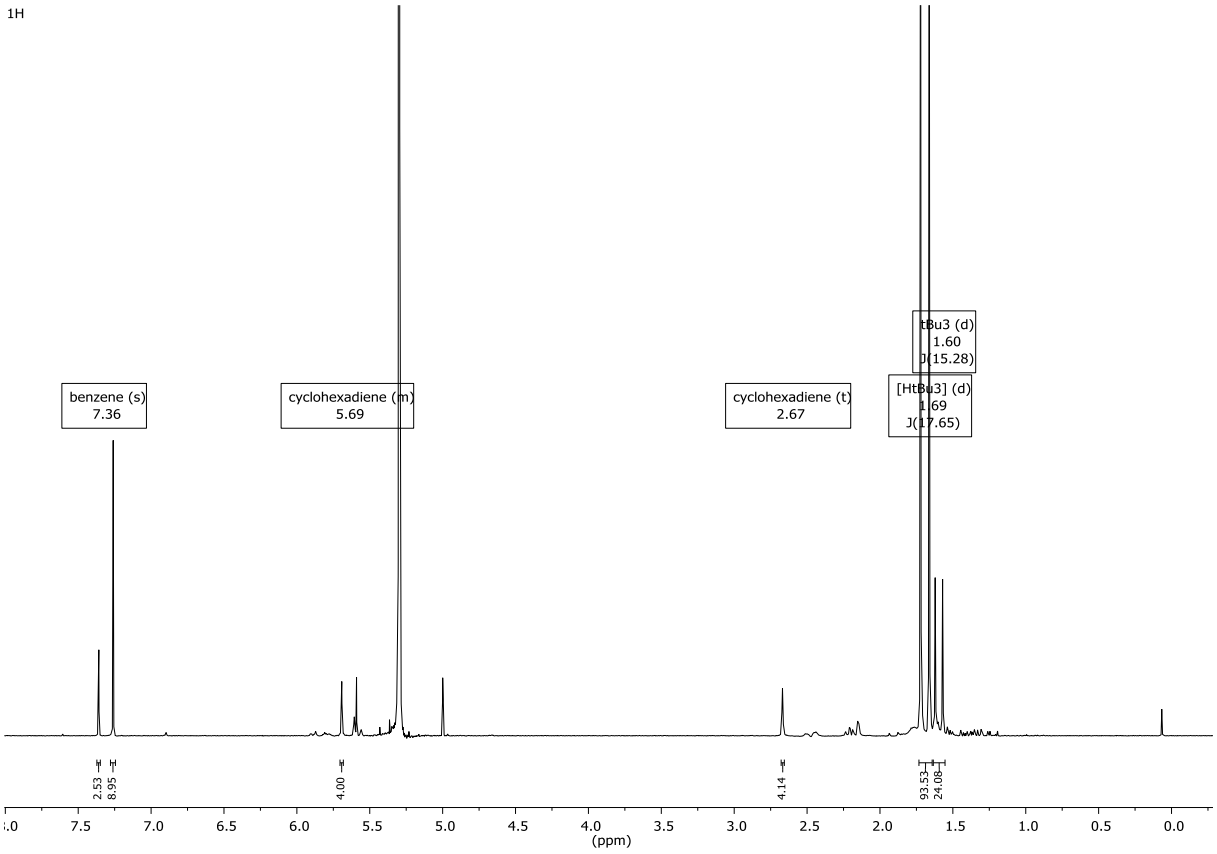
3.3.4 Stoichiometric reaction of 1,4-cyclohexadiene, ^{t}Bu$_3$P, B(C$_6$F$_5$)$_3$ and C$_4$F$_9$I



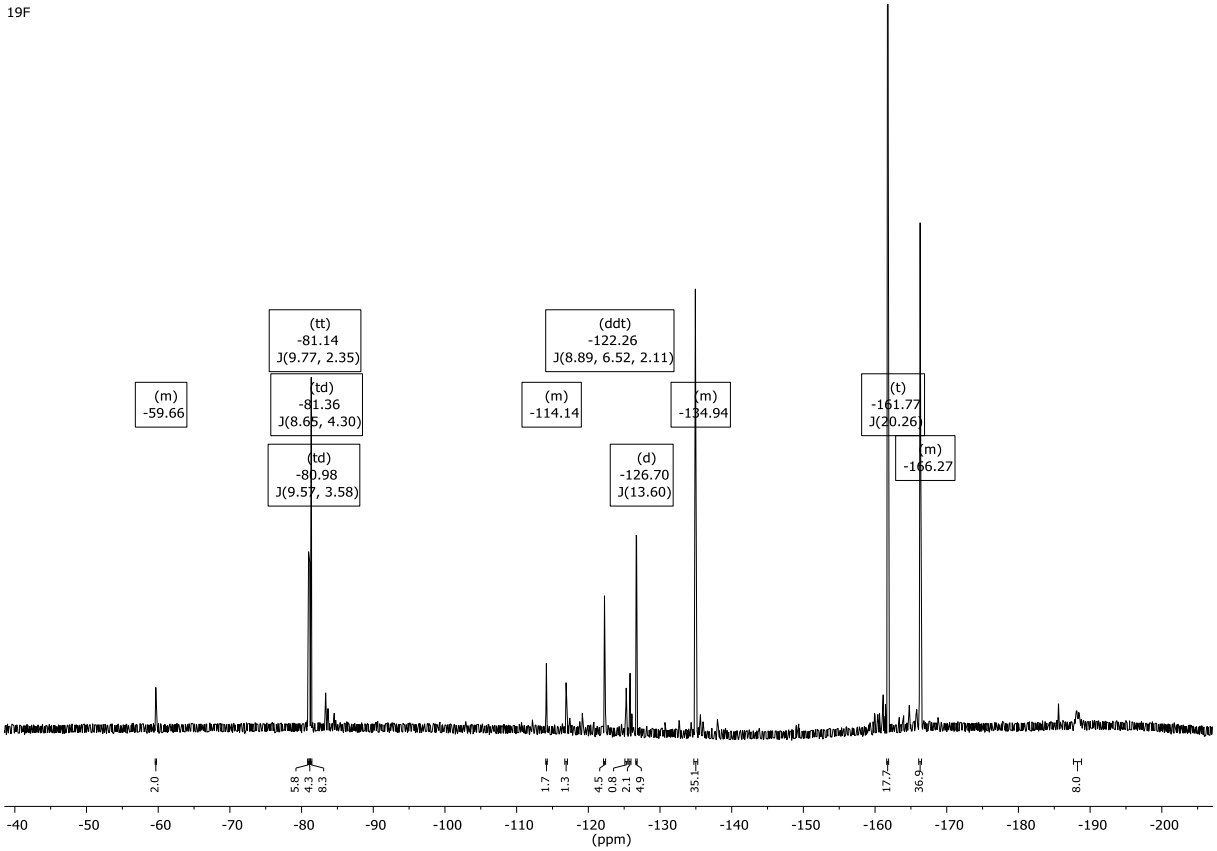
10 **2** **5** **3** **11** **12**

^{t}Bu$_3$P (**5**) (137 mg, 0.265 mmol, 1.0 eq.) and B(C$_6$F$_5$)$_3$ (**3**) (53.6 mg, 0.268 mmol, 0.98 eq.) were weighed into an amber glass jar and dissolved in CH_2Cl_2 (1.0 ml). 1,4-Cyclohexadiene (**10**) (25 µl, 0.26 mmol, 1.0 eq.) and nonafluoro-1-iodobutane (**2**) (45 µl, 0.26 mmol, 1.0 eq.) were added and the jar was sealed with a Teflon-insert screw cap. After 13 days an NMR samples was withdrawn.

By column chromatography, undefined fluorinated products were obtained.



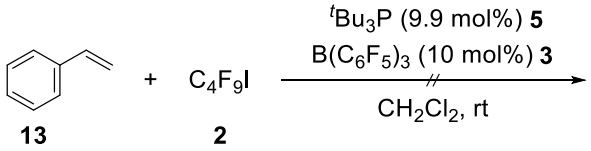
NMR-spectrum 23: ^{1}H-NMR-spectrum (300 MHz, $CDCl_3$) after 13 days reaction time.



NMR-spectrum 24: ^{19}F-NMR-spectrum (282 MHz, $CDCl_3$) after 13 days reaction time.

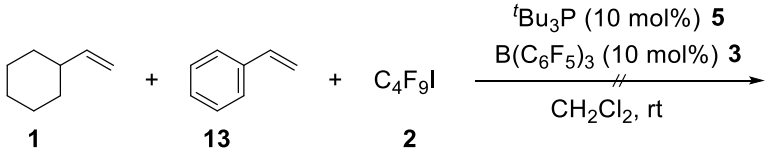
3.4 Reactions involving styrene

3.4.1 Iodoperfluoroalkylation of styrene

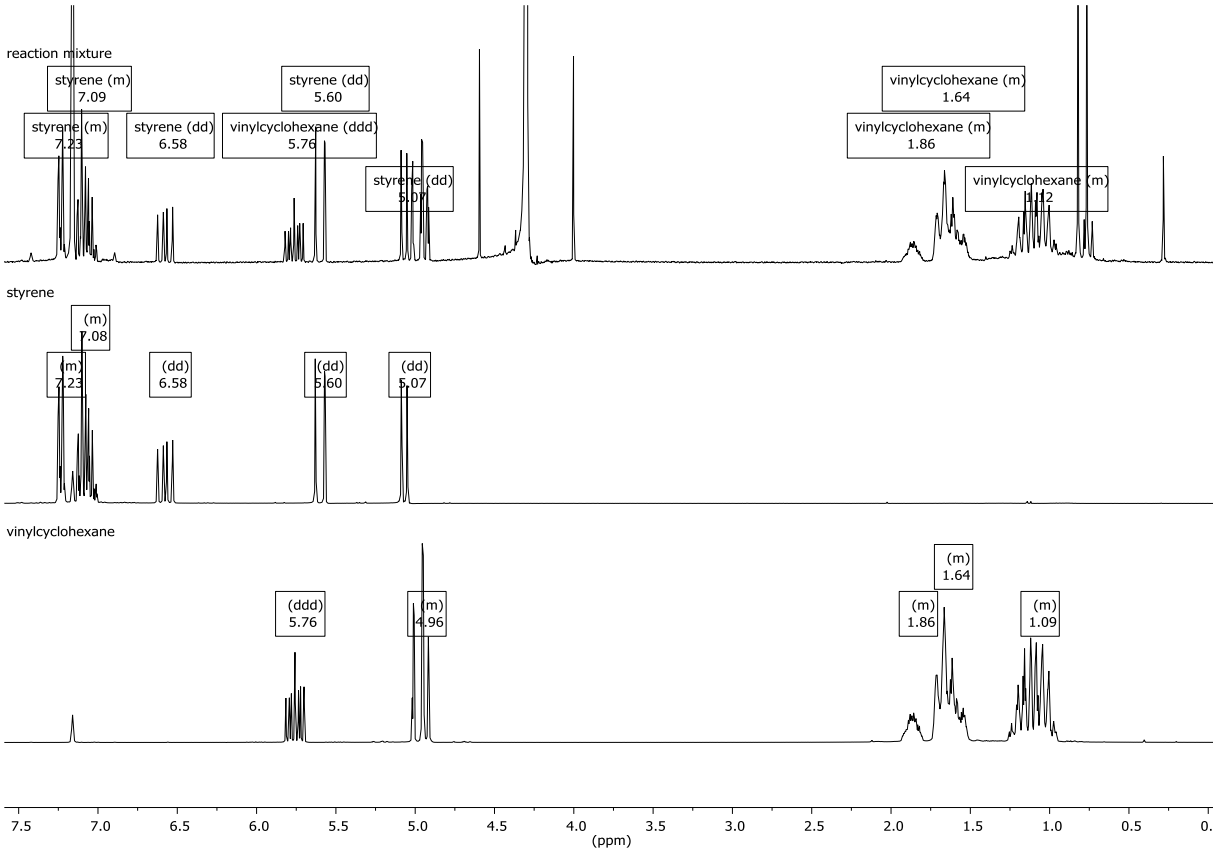


Freshly distilled styrene (**13**) (77.6 mg, 0.745 mmol, 1.00 eq.) was weighed into an amber glass jar and dissolved in CH_2Cl_2 (0.5 ml). Nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.974 eq.) as well as a solution of $^tBu_3P$ (**5**) (14.9 mg, 0.0736 mmol, 9.9 mol%) and $B(C_6F_5)_3$ (**3**) (39.0 mg, 0.0762 mmol, 10 mol%) in CH_2Cl_2 (1.6 ml) was added. The jar was sealed with a Teflon-insert screw cap. After 1 and 9 days NMR samples were withdrawn.

3.4.2 Iodoperfluoroalkylation of vinylcyclohexane in the presence of styrene

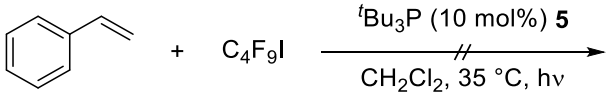


Freshly distilled styrene (**13**) (76.0 mg, 0.730 mmol, 1.00 eq.) was weighed into an amber glass jar and dissolved in CH_2Cl_2 (0.5 ml). Vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.) as well as a solution of $^tBu_3P$ (**5**) (14.7 mg, 0.0727 mmol, 10 mol%) and $B(C_6F_5)_3$ (**3**) (38.5 mg, 0.0752 mmol, 10 mol%) in CH_2Cl_2 (1.6 ml) was added. The jar was sealed with a Teflon-insert screw cap. After 1 and 9 days NMR samples were withdrawn.



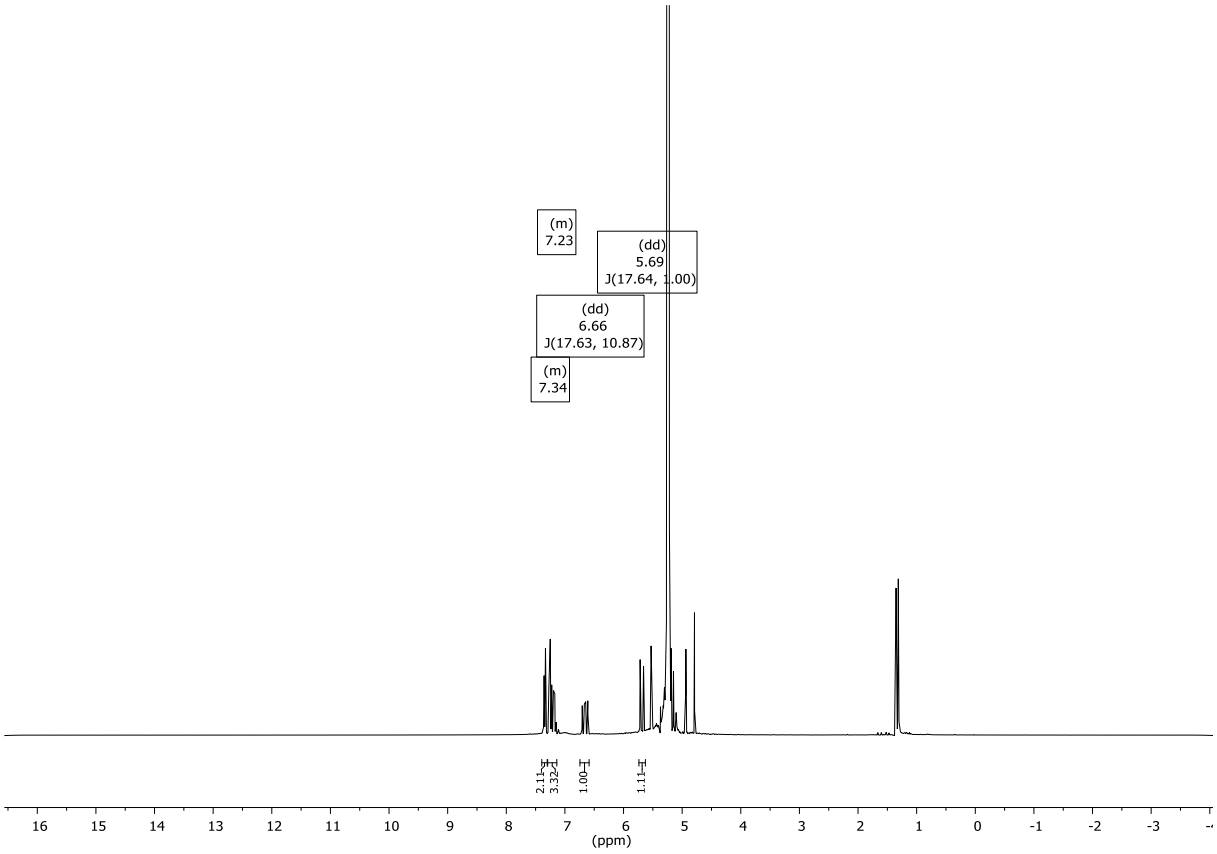
NMR-spectrum 25: Stacked ^{1}H-NMR-spectra (300 MHz, C_6D_6) of the reaction solution after 24 h (top), styrene (middle) and vinylcyclohexane (bottom).

3.4.3 Test reaction for a styrene polymerisation

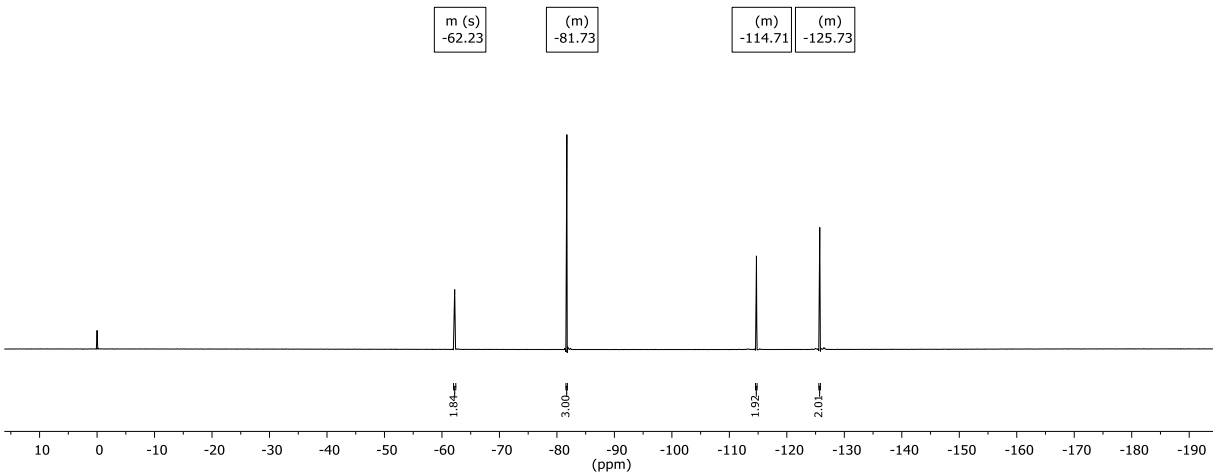


13 **2**

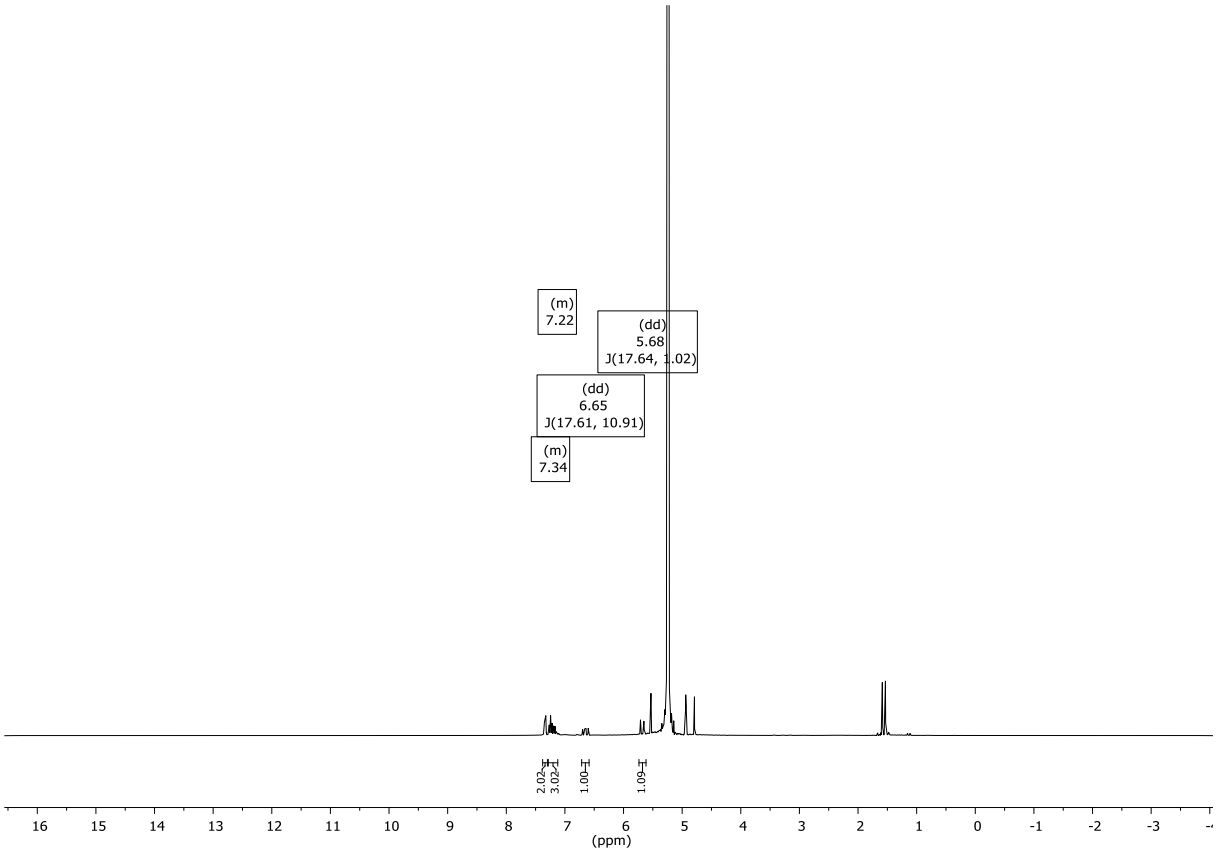
$^{t}Bu_3P$ (**5**) (3.7 mg, 0.018 mmol, 10 mol%) was weighed into a small glass vial, dissolved in CH_2Cl_2 (0.5 ml) and styrene (**13**) (70.4 mg, 0.177 mmol, 1.00 eq.) was added. The solution was transferred into a Young valve NMR tube. Under light exclusion using red light nonafluoro-1-iodobutane (**2**) (35.0 µl, 0.206 mmol, 1.15 eq.) was added. The Young valve NMR tube was sealed and irradiated for 2 h (blue LED (370 nm). After the first NMR spectra measurement the sample was irradiated for further 2 h (254 nm).



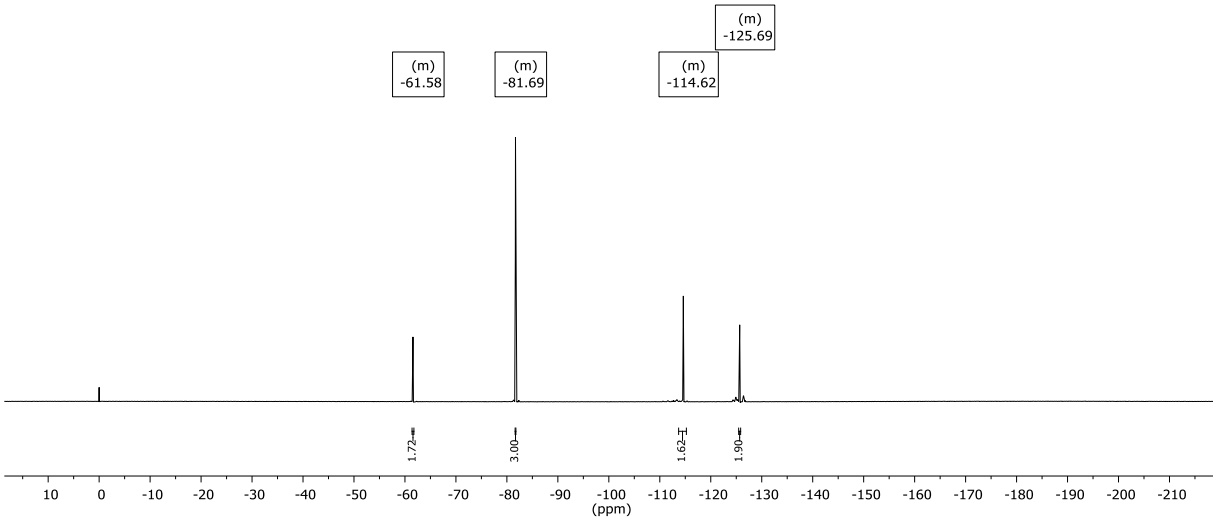
NMR-spectrum 26: ^{1}H-NMR-spectra (300 MHz, D_2O) in CH_2Cl_2 after irradiation (370 nm).



NMR-spectrum 27: ^{19}F-NMR-spectra (282 MHz, D_2O) in CH_2Cl_2 after irradiation (370 nm).



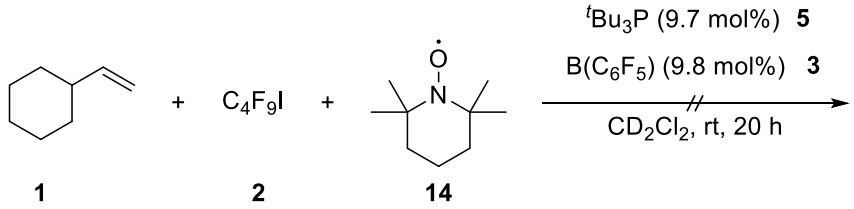
NMR-spectrum 28: ^{1}H-NMR-spectra (300 MHz, D_2O) in CH_2Cl_2 after irradiation (254 nm).



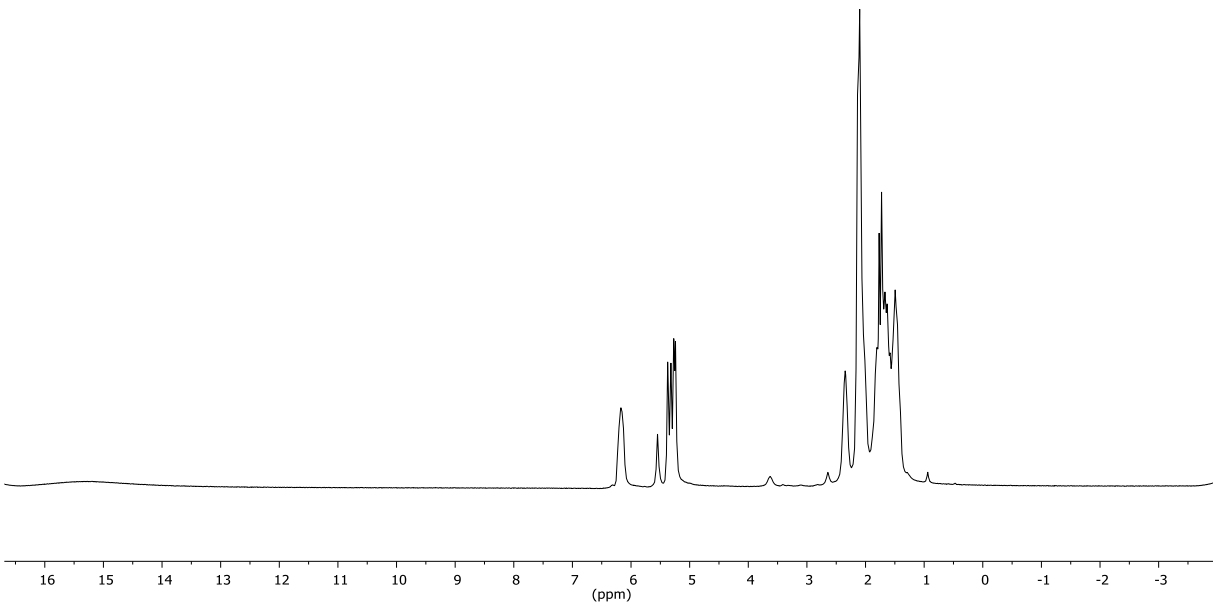
NMR-spectrum 29: ^{19}F-NMR-spectra (282 MHz, D_2O) in CH_2Cl_2 after irradiation (254 nm).

3.5 Reaction in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)

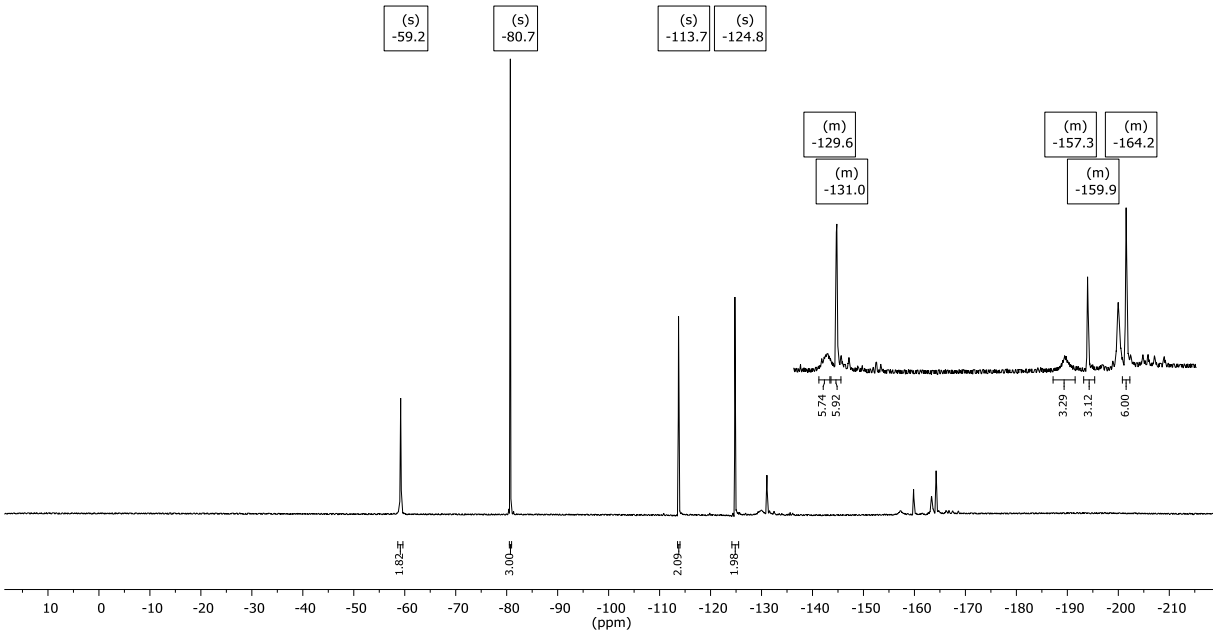
3.5.1 Equimolar amounts of TEMPO



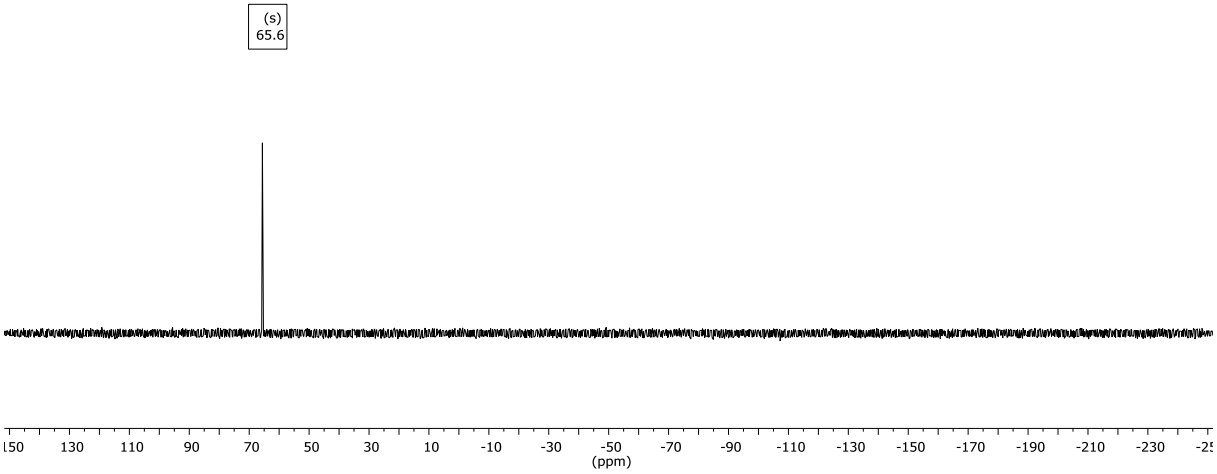
^{t}Bu$_3$P (**5**) (3.5 mg, 0.017 mmol, 9.7 mol%) and B(C_6F_5)$_3$ (**3**) (9.0 mg, 0.018 mmol, 9.7 mol%) were weighed into a small glass vial, dissolved in CD_2Cl_2 (0.3 ml) and vinylcyclohexane (**1**) (25.0 µl, 0.179 mmol, 1.00 eq.) was added. The solution was transferred into a Young valve NMR tube. Separately TEMPO (**14**) (31.0 mg, 0.198 mmol, 1.10 eq.) was weighed in another glass vial, dissolved in CD_2Cl_2 (0.2 ml) and transferred into the same Young valve NMR tube. Under light exclusion using red light nonafluoro-1-iodobutane (**2**) (35.0 µl, 0.206 mmol, 1.15 eq.) was added. The Young valve NMR tube was sealed and an NMR measurement was conducted after 20 h.



NMR-spectrum 30: ^{1}H-NMR-spectra (300 MHz, CD_2Cl_2) of the reaction with 1.10 eq. TEMPO.



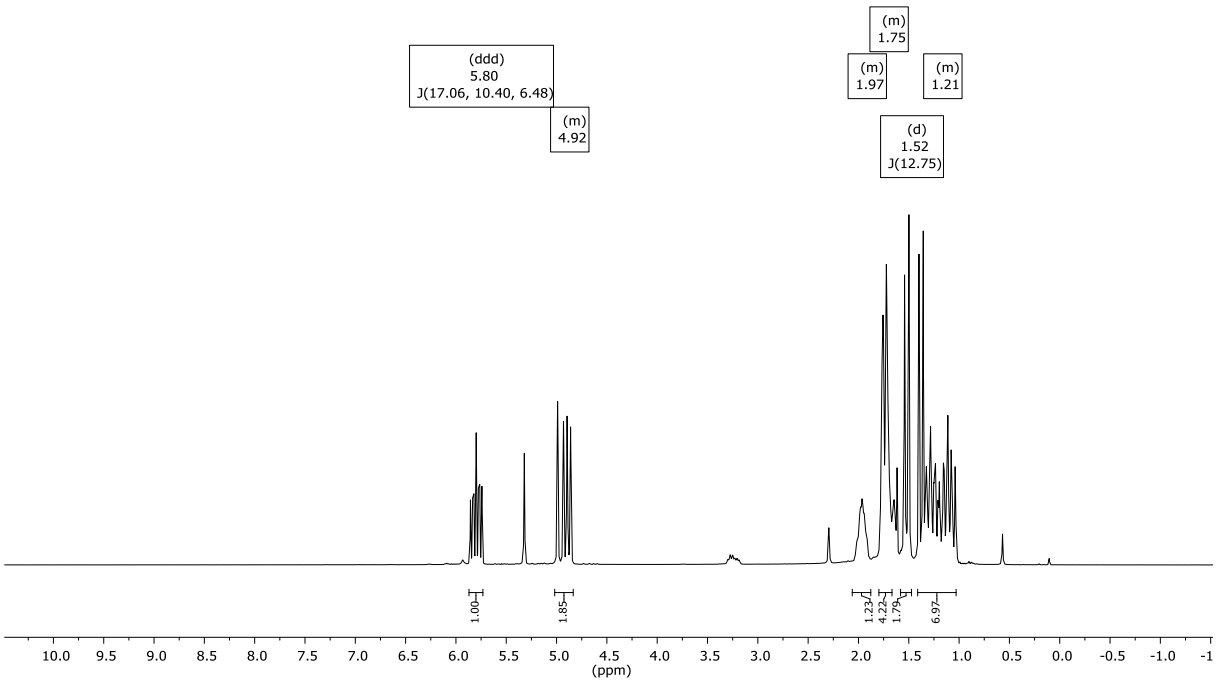
NMR-spectrum 31: ^{19}F-NMR-spectra (282 MHz, CD_2Cl_2) of the reaction with 1.10 eq. TEMPO.



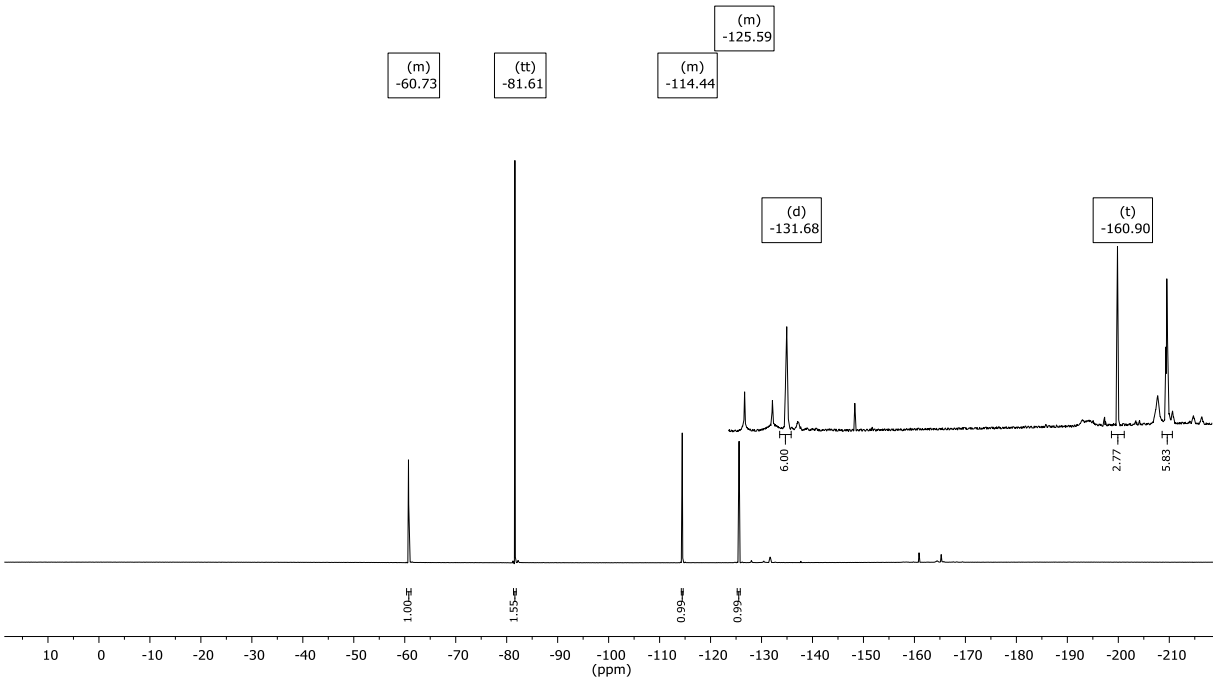
NMR-spectrum 32: ^{31}P-NMR-spectra (121 MHz, CD_2Cl_2) of the reaction with 1.10 eq. TEMPO.

3.5.2 12.8 mol% TEMPO

$^{t}Bu_3P$ (**5**) (3.6 mg, 0.018 mmol, 9.9 mol%) and $B(C_6F_5)_3$ (**3**) (9.2 mg, 0.018 mmol, 10 mol%) were weighed into a small glass vial, dissolved in CD_2Cl_2 (0.2 ml) and vinylcyclohexane (**1**) (25.0 µl, 0.179 mmol, 1.00 eq.) was added. The solution was transferred into a Young valve NMR tube. Separately TEMPO (**14**) (3.6 mg, 0.023 mmol, 13 mol%) was weighed in another glass vial, dissolved in CD_2Cl_2 (0.2 ml) and transferred into the same Young valve NMR tube. Under light exclusion using red light nonafluoro-1-iodobutane (**2**) (35.0 µl, 0.206 mmol, 1.15 eq.) was added. The Young valve NMR tube was sealed and the solution was measured after 24 h.

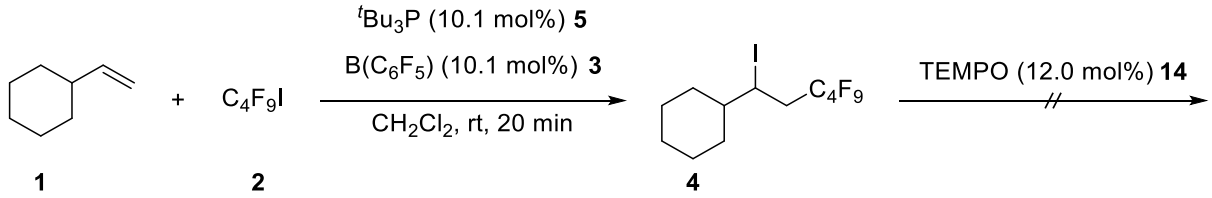


NMR-spectrum 33: ^{1}H-NMR-spectra (300 MHz, CD_2Cl_2) of the reaction with TEMPO, 12.8 mol%.

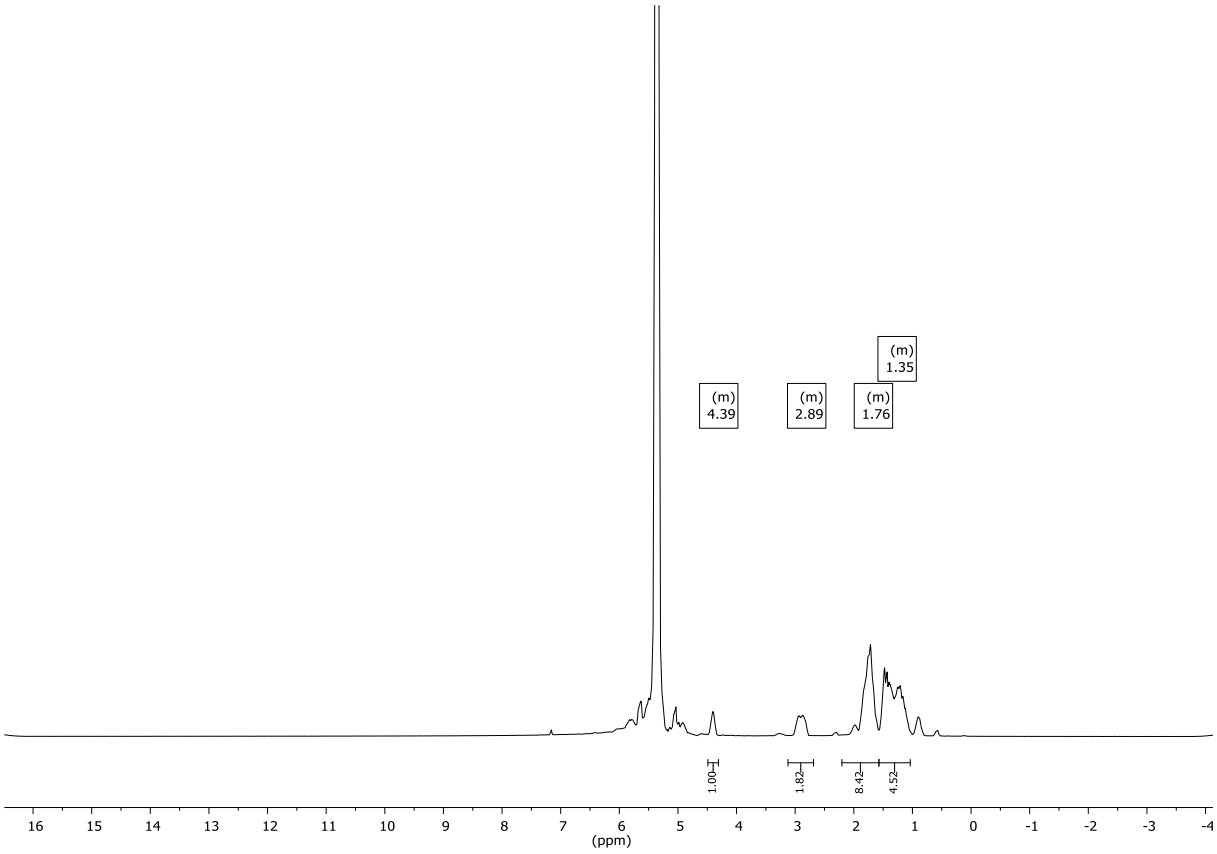


NMR-spectrum 34: ^{19}F-NMR-spectra (282 MHz, CD_2Cl_2) of the reaction with TEMPO, 12.8 mol%.

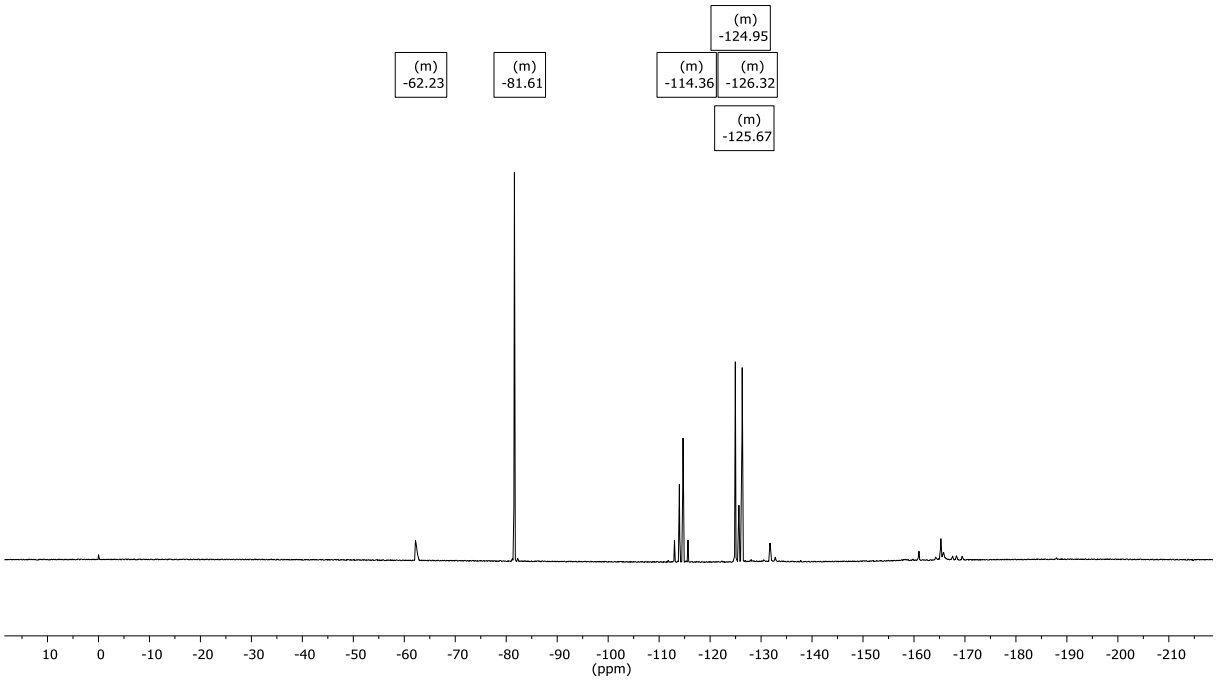
3.5.3 Delayed addition of TEMPO



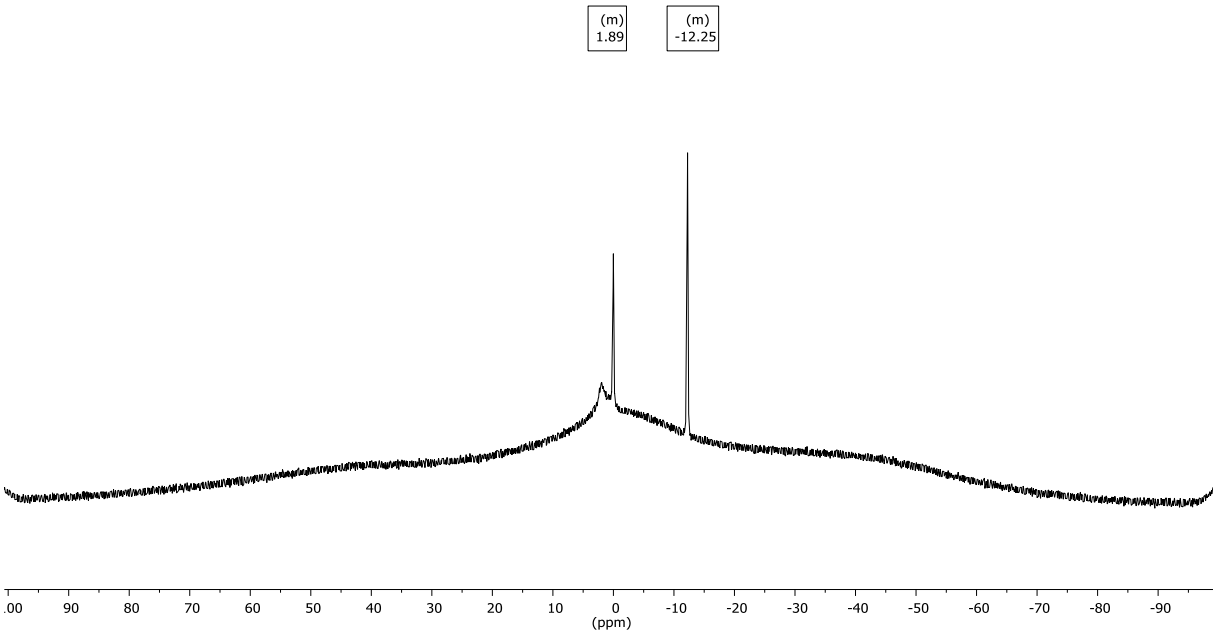
^{t}Bu$_3$P (**5**) (3.6 mg, 0.018 mmol, 10 mol%) and B(C_6F_5)$_3$ (**3**) (9.1 mg, 0.018 mmol, 10 mol%) were weighed into a small glass vial, dissolved in CH_2Cl_2 (0.45 ml). Under light exclusion using red light vinylcyclohexane (**1**) (24.0 µl, 0.175 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (30.0 µl, 0.175 mmol, 1.00 eq.) were added and stirred for 20 min. The solution was transferred into an amber NMR tube. Separately weighed TEMPO (**14**) (3.3 mg, 0.021 mmol, 12 mol%) was dissolved in CH_2Cl_2 (0.1 ml) and transferred into the same amber NMR tube. The NMR tube was sealed and the solution was measured after 1 h.



NMR-spectrum 35: ^{1}H-NMR-spectra (300 MHz, C_6D_6) in CH_2Cl_2 of the reaction with subsequent addition of TEMPO.

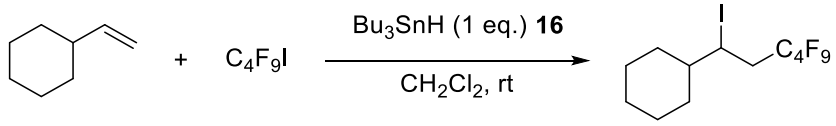


NMR-spectrum 36: ^{19}F-NMR-spectra (282 MHz, C_6D_6) in CH_2Cl_2 of the reaction with subsequent addition of TEMPO.



NMR-spectrum 37: ^{11}B-NMR-spectrum (282 MHz, C_6D_6) in CH_2Cl_2 of the reaction with subsequent addition of TEMPO.

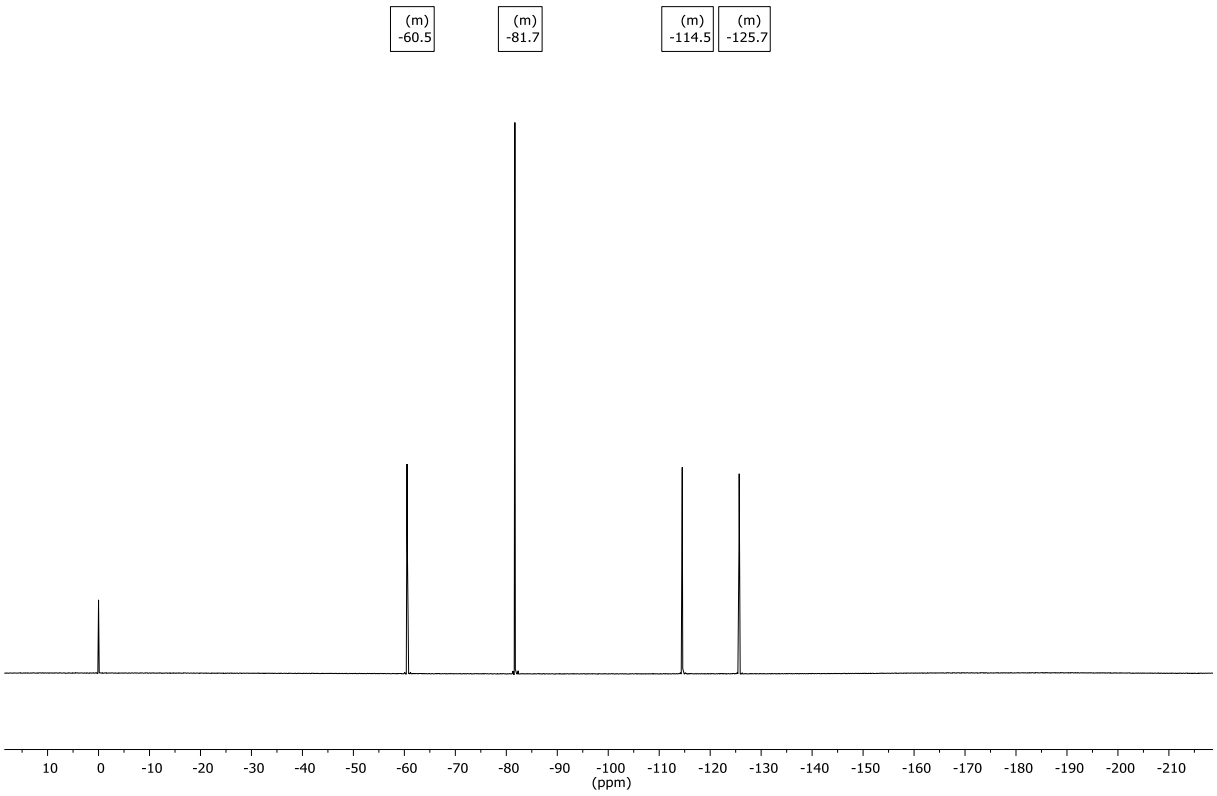
3.6 Reactions involving tributyltin hydride



1 **2** **4**

3.6.1 Control reaction with vinylcyclohexane and nonafluoro-1-iodobutane

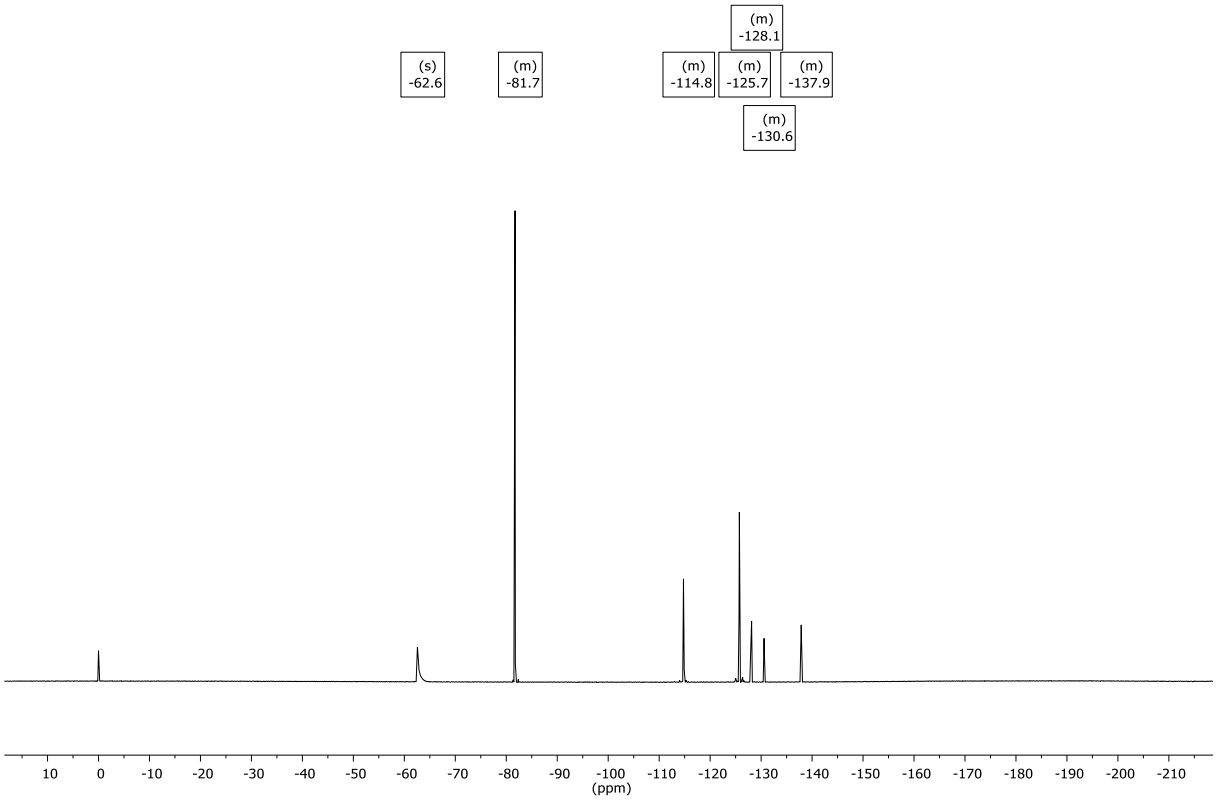
Under light exclusion using red light, vinylcyclohexane (**1**) (25.0 µl, 0.183 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (32.0 µl, 0.186 mmol, 1.02 eq.) were injected into an amber glass NMR-tube, equipped with $CFCl_3$ in C_6D_6 as an external standard. The reactants were dissolved in CH_2Cl_2 (0.80 ml). Outside the glovebox, tributyltin hydride (**16**) (20 µl, 0.076 mmol, 0.42 eq.) was added under inert conditions.



NMR-spectrum 38: ^{19}F-NMR-spectrum (282 MHz, C_6D_6) in CH_2Cl_2 of the reaction solution after 1.5 h.

3.6.2 Control reaction with ^{t}Bu$_3$P, vinylcyclohexane and nonafluoro-1-iodobutane

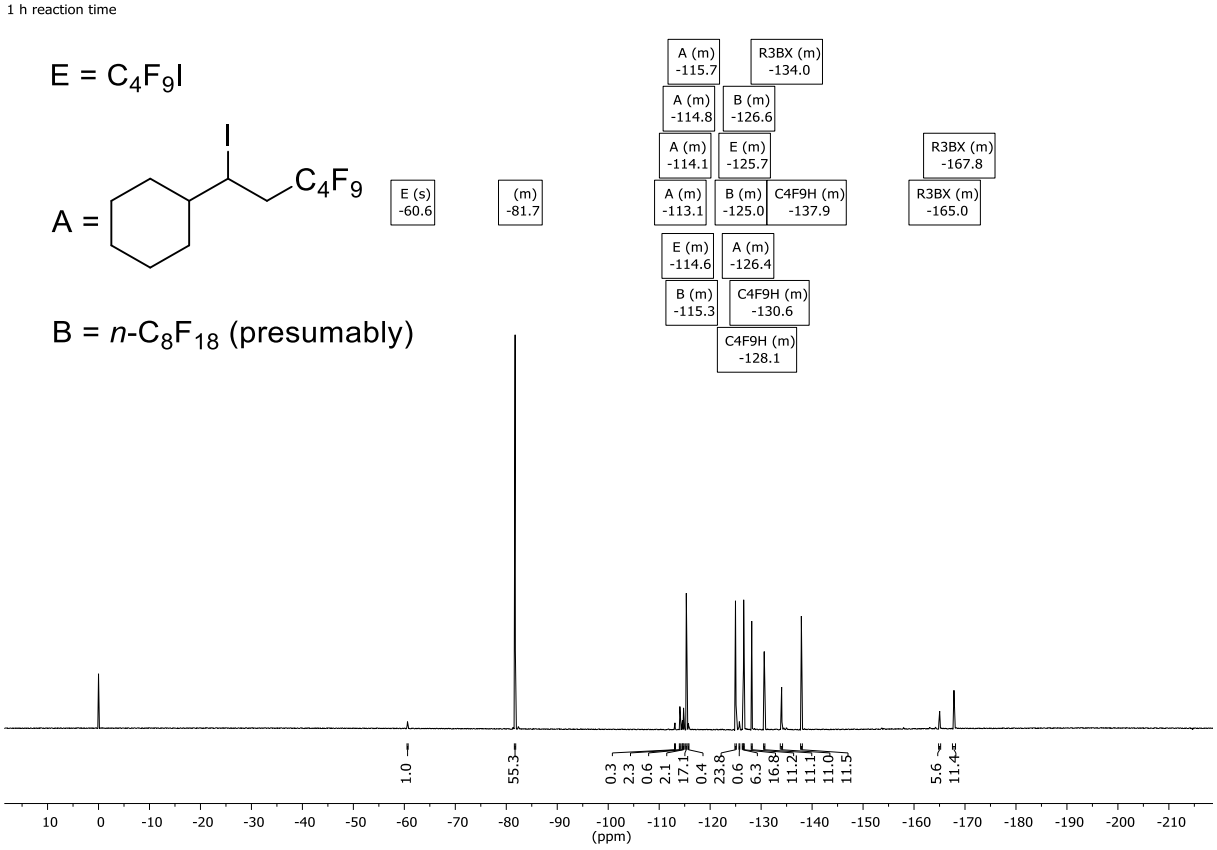
Vinylcyclohexane (**1**) (25.0 µl, 0.183 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (32.0 µl, 0.186 mmol, 1.02 eq.) were added to a solution of ^{t}Bu$_3$P (**5**) (3.8 mg, 0.019 mmol, 10 mol%) in CH_2Cl_2 (0.55 ml) in transparent NMR-tube, equipped with $CFCl_3$ in C_6D_6 as an external standard. Outside the glovebox, tributyltin hydride (**16**) (50 µl, 0.076 mmol, 0.42 eq.) was added under inert conditions.



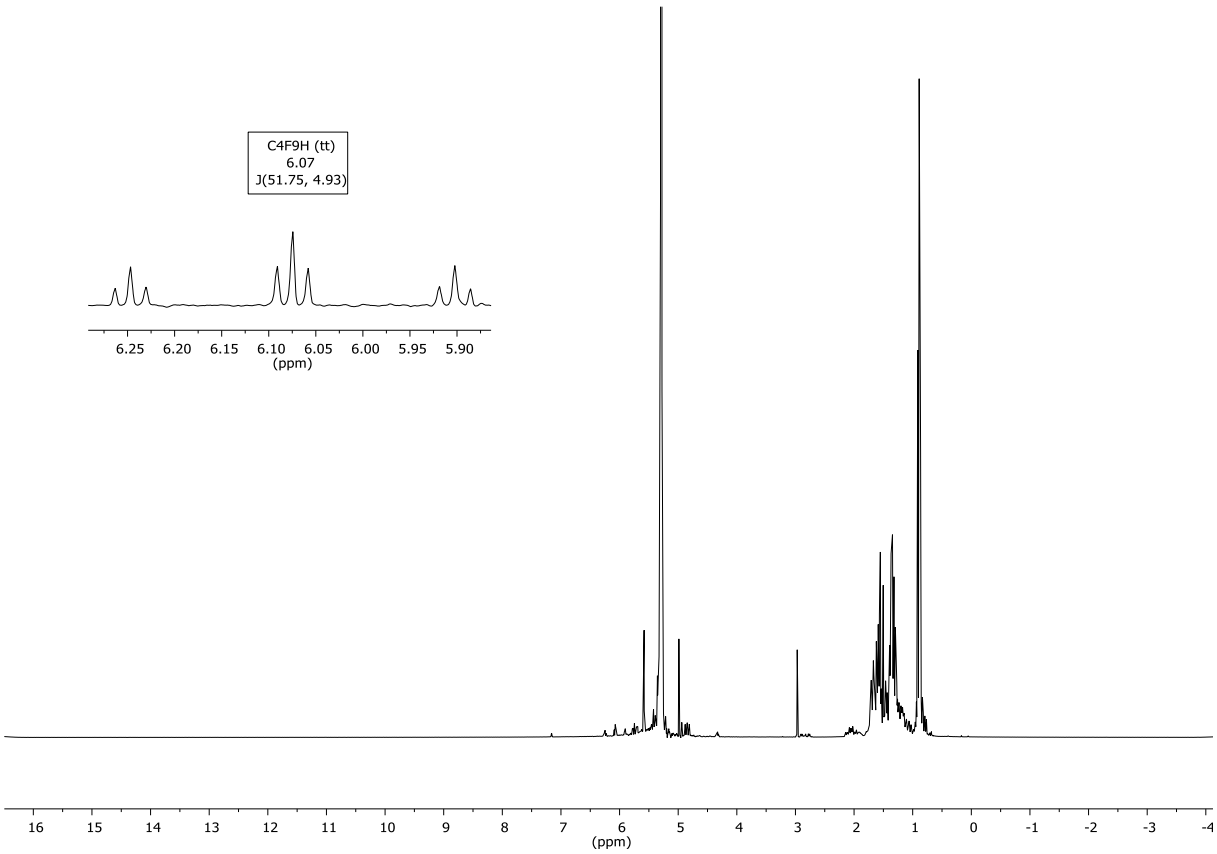
NMR-spectrum 39: ^{19}F-NMR-spectrum (282 MHz, C_6D_6) in CH_2Cl_2 of the reaction solution after 1 h. Reference for C_4F_9H.[6]

3.6.3 Reaction in the presence of ^{t}Bu$_3$P, B(C$_6$F$_5$)$_3$, vinylcyclohexane and nonafluoro-1-iodobutane

Under light exclusion using red light, vinylcyclohexane (**1**) (25.0 µl, 0.183 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (32.0 µl, 0.186 mmol, 1.02 eq.) were added to a solution of ^{t}Bu$_3$P (**5**) (3.6 mg, 0.018 mmol, 9.7 mol%) in combination with B(C_6F_5)$_3$ (**3**) (9.3 mg, 0.018 mmol, 9.9 mol%) in CH_2Cl_2 (0.55 ml) in transparent NMR-tube, equipped with $CFCl_3$ in C_6D_6 as an external standard. Outside the glovebox, tributyltin hydride (**16**) (50 µl, 0.076 mmol, 0.42 eq.) was added under inert conditions.



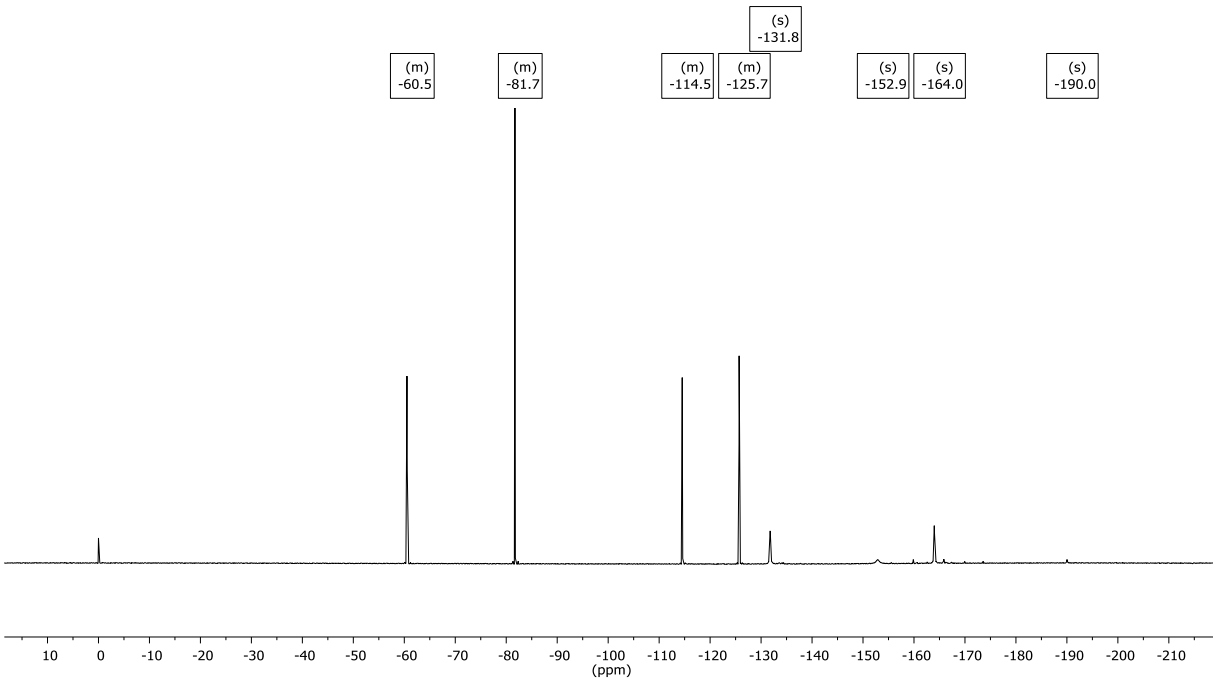
NMR-spectrum 40: ^{19}F-NMR-spectrum (282 MHz, C_6D_6) in CH_2Cl_2 of the reaction solution after 1 h. Reference for C_4F_9H.[6]



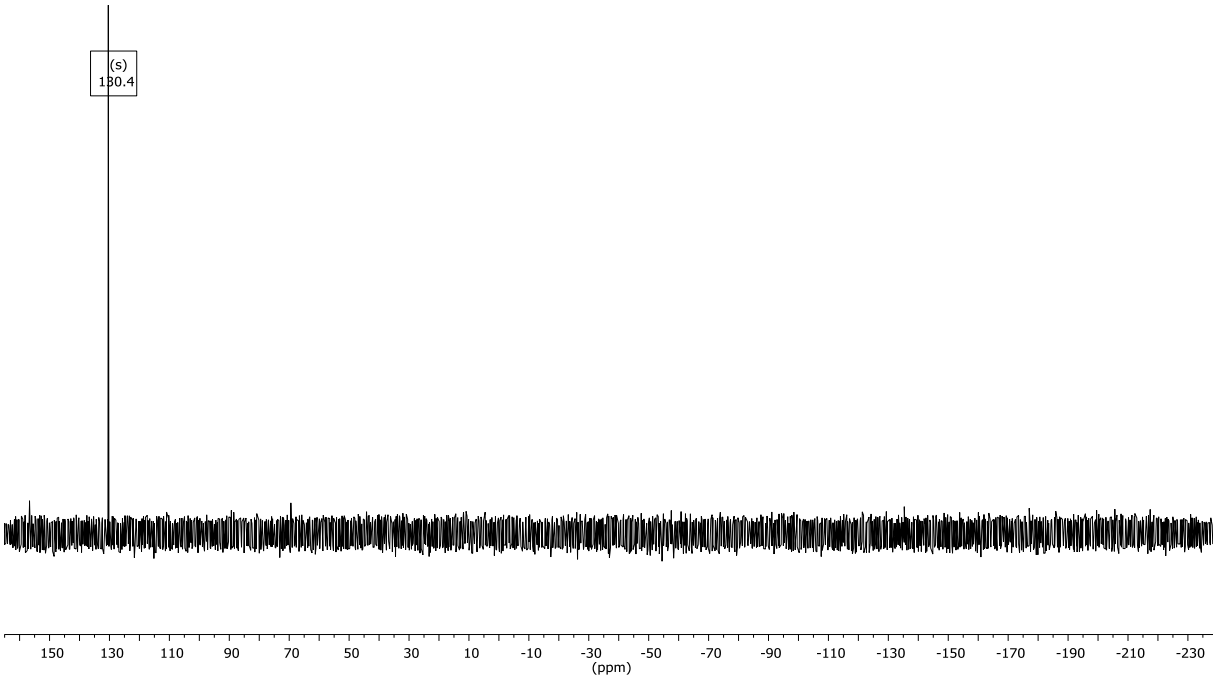
NMR-spectrum 41: ^{1}H-NMR-spectrum (300 MHz, C_6D_6) in CH_2Cl_2 of the reaction solution after 7 h. Reference for C_4F_9H.[6]

3.7 Reaction in the presence of [^{t}Bu$_3$PI][FB(C$_6$F$_5$)$_3$] and B(C$_6$F$_5$)$_3$

[^{t}Bu$_3$PI][FB(C$_6$F$_5$)$_3$] (**12**) (13.2 mg, 0.015 mmol, 8.4 mol%) and B(C$_6$F$_5$)$_3$ (**3**) (9.2 mg, 0.018 mmol, 9.8 mol%) were weighed into a glass vial and dissolved in CH_2Cl_2 (0.80 ml). Under light exclusion using red light, vinylcyclohexane (**1**) (25.0 µl, 0.183 mmol, 1.00 eq.) as well as nonafluoro-1-iodobutane (**2**) (32.0 µl, 0.186 mmol, 1.02 eq.) were added. The solution was transferred into a Young valve NMR tube equipped with $CFCl_3$ in C_6D_6 as an external standard.



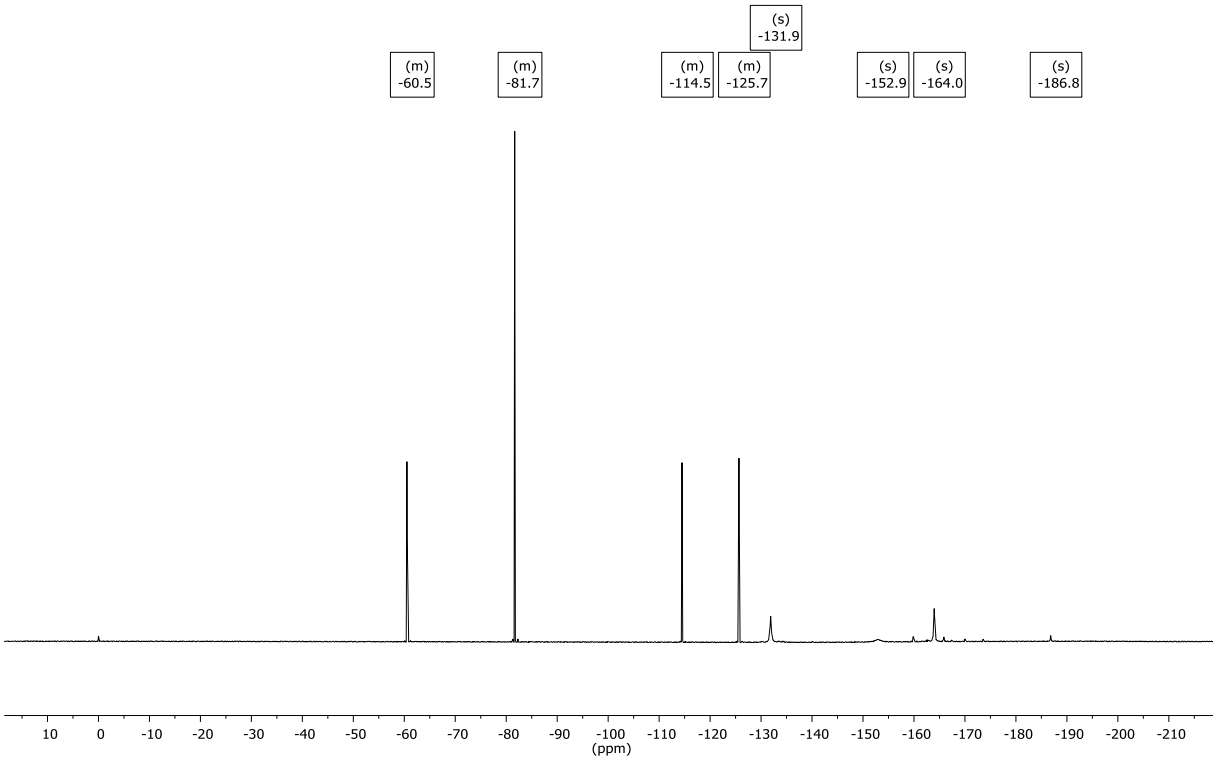
NMR-spectrum 42: ^{19}F-NMR-spectrum (282 MHz, C$_6$D$_6$) in CH_2Cl_2, iodoperfluoroalkylation in the presence of [^{t}Bu$_3$PI][FB(C$_6$F$_5$)$_3$] and B(C$_6$F$_5$)$_3$, 7.5 h reaction time.



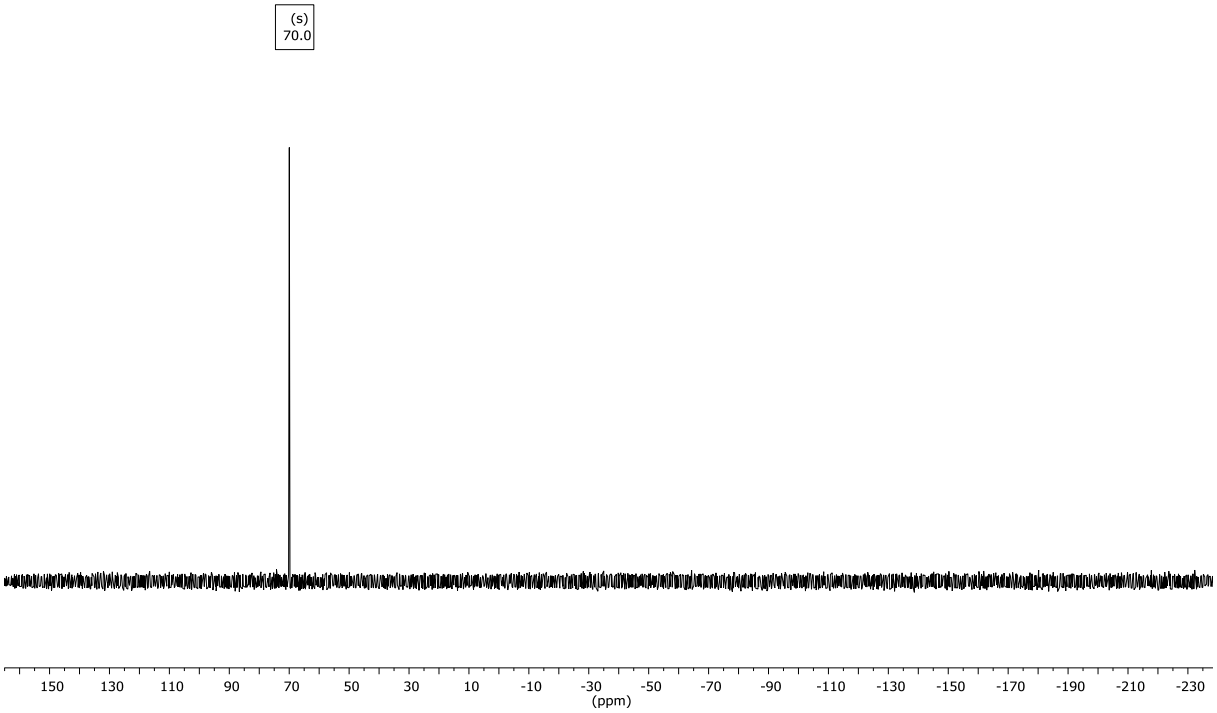
NMR-spectrum 43: ^{31}P-NMR-spectrum (121 MHz, C_6D_6) in CH_2Cl_2, iodoperfluoroalkylation in the presence of [^{t}Bu$_3$PI][FB(C_6F_5)$_3$] and B(C_6F_5)$_3$, 7.5 h reaction time.

3.8 Reaction in the presence of [^{t}Bu$_3$PH][FB(C_6F_5)$_3$] and B(C_6F_5)$_3$

[^{t}Bu$_3$PH][FB(C_6F_5)$_3$] (**17**) (10.1 mg, 0.014 mmol, 10 mol%) and B(C_6F_5)$_3$ (**3**) (7.4 mg, 0.014 mmol, 11 mol%) were weighed into a glass vial, dissolved in CH_2Cl_2 (0.40 ml) and transferred into an amber glass NMR tube equipped with $CFCl_3$ in C_6D_6 as an external standard. Under light exclusion using red light, a solution of 1-undecene (**18**) (20.8 mg, 0.135 mmol, 1.00 eq.) as well as nonafluoro-1-iodobutane (**2**) (46.6 mg, 0.135 mmol, 0.999 eq.) in CH_2Cl_2 (0.40 ml) was added.

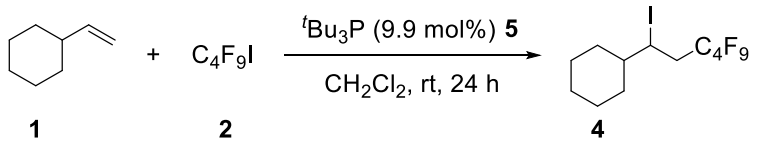


NMR-spectrum 44: ^{19}F-NMR-spectrum (282 MHz, C_6D_6) in CH_2Cl_2, iodoperfluoroalkylation in the presence of [^{t}Bu$_3$PH][FB(C$_6$F$_5$)$_3$] and B(C$_6$F$_5$)$_3$, 27 h reaction time.



NMR-spectrum 45: ^{31}P-NMR-spectrum (121 MHz, C_6D_6) in CH_2Cl_2, iodoperfluoroalkylation in the presence of [^{t}Bu$_3$PH][FB(C$_6$F$_5$)$_3$] and B(C$_6$F$_5$)$_3$, 27 h reaction time.

3.9 $^{t}Bu_3P$ mediated photochemical background reaction



3.9.1 Reaction under light exclusion

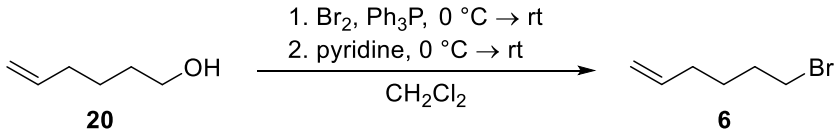
Inside the glovebox, $^{t}Bu_3P$ (**5**) (7.3 mg, 0.036 mmol, 9.9 mol%) was weighed into a glass vial, dissolved in CH_2Cl_2 (0.60 ml) and transferred into a pointed flask. All following work steps were conducted under red light and best possible light exclusion. A round-bottom flask, enwrapped with aluminium foil, was filled with *n*-decane (**19**) (40.0 µl), vinylcyclohexane (**1**) (40.3 mg. 0.365 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (131 mg, 0.378 mmol, 1.03 eq.) dissolved in CH_2Cl_2 (0.70 ml). Outside the glovebox, the $^{t}Bu_3P$ solution was transferred into the educt solution. After stirring for 64 minutes, aqueous H_2O_2 (30%, 0.10 ml) was added to quench the reaction. A sample was withdrawn for both NMR and GC measurements.

3.9.2 Reaction under irradiation

Inside the glovebox, $^{t}Bu_3P$ (**5**) (14.8 mg, 0.0736 mmol, 10 mol%) was weighed into a transparent glass jar, dissolved in CH_2Cl_2 (2.5 ml) and vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.) as well as nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.995 eq.) were added. After 24 h an NMR-sample was withdrawn.

4 Radical clock synthesis

4.1 Synthesis of 6-bromohexene



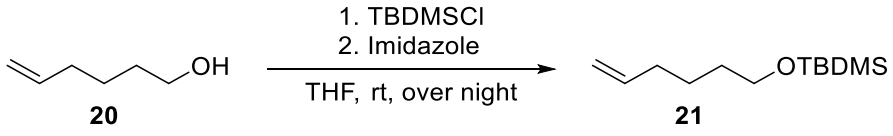
Triphenylphosphane (11.5 g, 43.9 mmol, 1.10 eq.) in CH_2Cl_2 (29 ml) was cooled to 0 °C. Bromine (2.30 ml, 43.9 mmol, 1.10 eq.) was added dropwise and the solution was stirred for 2 h at room temperature. Subsequently, pyridine (4.30 ml, 43.9 mmol, 1.10 eq.) was added dropwise to the reaction solution and the mixture was cooled again to 0 °C. 5-Hexen-1-ol (**20**) (4.80 ml, 39.9 mmol, 1.00 eq.) in CH_2Cl_2 (7 ml) was added dropwise and the solution was stirred for 20 h at room temperature. After complete conversion of the alcohol, which was controlled *via* TLC (hexane: ethyl acetate 90:10), pentane (20 ml) was added to the reaction solution. The reaction flask was cooled to −78°C and the precipitate was filtered off. The clear reaction solution was concentrated and washed with hydrochloric acid (1 M, 3 x 20 ml). The aqueous phase was extracted with pentane (3 x 20 ml). The combined organic phases were washed with saturated $NaHCO_3$ (10 ml) and dried over Na_2SO_4. The solution was again concentrated and distillated at reduced pressure (61-63 °C, 45 mbar). A clear oil was obtained (3.17 g, 19.4 mmol, 49%).

^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm] 5.88 – 5.72 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, CH_2CH), 5.08 – 4.94 (m, 2H, CH_2CH), 3.46 – 3.37 (t, *J* = 6.8 Hz, 2H, CH_2Br), 2.15 – 2.03 (m, 2H, CH_2CHCH_2), 1.94 – 1.82 (m, 2H, CH_2CH_2Br), 1.61 – 1.48 (m, 2H, $CH_2CH_2CH_2Br$).

Spectroscopic data are consistent with literature values.[7]

4.2 1-(Penten-4-yl)cyclopropane

4.2.1 Synthesis of 6-(*tert*-butyldimethylsilyloxy)-1-hexene

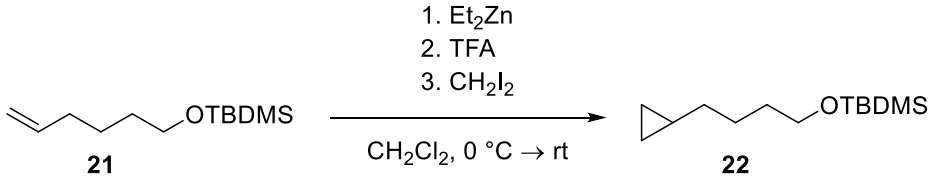


To a solution of 5-hexen-1-ol (**20**) (16.0 g, 160 mmol, 1.00 eq.) in THF (80 ml), TBDMSCl (24.5 g, 162 mmol, 1.01 eq.) and imidazole (13.1 g, 193 mmol, 1.20 eq.) were added. After stirring overnight desalinated water (40 ml) was added and the aqueous layer was extracted with diethyl ether (5 x 20 ml) and dried over Na_2SO_4. After evaporation of diethyl ether, the crude product was distilled under reduced pressure to obtain the desired product **21** (130 °C, 99 °C, 30 mbar). (29.8 g, 139 mmol, 87 %).

^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm] 5.90 – 5.73 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H, CH_2=C*H*), 5.06 – 4.90 (m, 2H, C*H*$_2$=CH), 3.67 - 3.57 (t, *J* = 6.3 Hz, 2H, C*H*$_2$OTBDMS), 2.14 – 1.99 (d, *J* = 7.1 Hz, 2H, C*H*$_2$CH$_2$OTBDMS), 1.63 – 1.48 (m, 2H, C*H*$_2$CH$_2$CH$_2$OTBDMS), 1.48 – 1.37 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$OTBDMS), 0.95 – 0.84 (s, 9H, OSi(CH$_2$)$_2$(C*H*$_3$)$_3$), 0.09 – 0.01 (s, 6H, OSi(C*H*$_2$)$_2$(CH$_3$)$_3$). **IR** (film on NaCl), $\tilde{\nu}$ [cm^{-1}] 3077, 2930, 1642, 1472, 1387, 1361, 1255, 1102, 910, 835, 775, 661.

Spectroscopic data are consistent with literature values.[8]

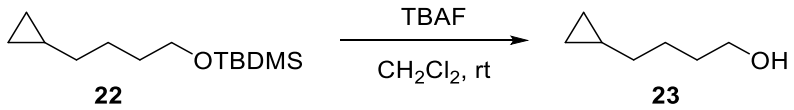
4.2.2 Synthesis of *tert*-butyl(4-cyclopropylbutoxy)dimethylsilane



21 **22**

Et_2Zn (1.0 M in hexane, 140 ml, 140 mmol, 2.00 eq.) in CH_2Cl_2 (250 ml) was cooled to 0 °C and trifluoroacetic acid (11.0 ml, 142 mmol, 2.04 eq.) in CH_2Cl_2 (250 ml) was added over 2 h. After stirring the solution for 30 min a solution of freshly distilled diiodomethane (11.3 ml, 140 mmol, 2.00 eq.) in CH_2Cl_2 (250 ml) was added over 1 h. After stirring for another 30 min 6-(*tert*-butyldimethylsilyloxy)-1-hexene (**21**) (14.9 g, 69.7 mmol) in CH_2Cl_2 (140 ml) was added. The reaction solution was stirred at rt until a complete consumption of the alkene was detected by NMR-spectroscopy. A saturated NH_4Cl solution (200 ml) was added and the aqueous layer was extracted with diethyl ether (5 x 20 ml) and dried over Na_2SO_4. The solution was concentrated (60 ml) and used as crude product for the next reaction.

4.2.3 Synthesis of 4-cyclopropylbutane-1-ol



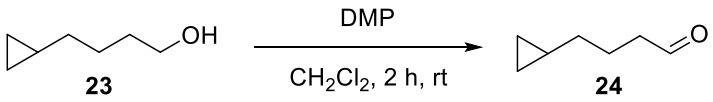
22 **23**

The crude product **22** of **4.2.2** was added to tetra-*n*-butylammonium fluoride -trihydrate (49.1 g, 138 mmol, 1.99 eq.) and stirred overnight. After completion, saturated NH_4Cl (150 ml) was added to the reaction and the organic phase was extracted with diethyl ether (3 x 100 ml). The combined organic phases where washed with brine (200 ml) and dried over Na_2SO_4. After evaporation (750 mbar, 40 °C) of the solvent the yellow liquid was purified by column chromatography (silica gel, pentane:diethyl ether = 3:1) to give the desired product as light yellow liquid (5.79 g, 44.5 mmol, 63 %).

^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm] 3.63 (t, *J* = 6.8, 2H, C*H*$_2$OH), 1.60 (m, 2H, C*H*$_2$CH$_2$OH), 1.46 (m, 2H, C*H*$_2$CH$_2$CH$_2$OH), 1.23 (m, 2H, C*H*$_2$CH$_2$CH$_2$CH$_2$OH), 0.65 (m, 1H, C*H*CH$_2$CH$_2$); 0.39 (m, 2H, CHCH$_2$C*H*$_2$), 0.00 (m, 2H, CHC*H*$_2$CH$_2$).

Spectroscopic data are consistent with literature values.[9]

4.2.4 4-Cyclopropylbutanal

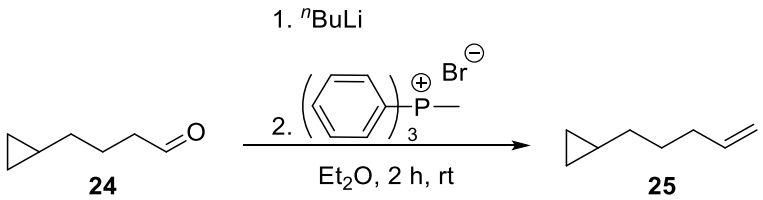


4-Cyclopropylbutan-1-ol (**23**) (5.79 g, 44.5 mmol, 1.00 eq.) in CH_2Cl_2 (400 ml) was cooled to 0 °C. Dess-Martin periodinane (20.7 g, 49.0 mmol, 1.10 eq.) was added in one portion and stirred for 1 h. The reaction was then stirred for a further hour at room temperature. The reaction was diluted with cooled pentane (200 ml) and the solid was removed through a celite pad. The product was concentrated *via* distillation (60 °C) and a yellow liquid was obtained.

^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm] 9.77 (t, *J* =1.86, 1H, *H*C=O), 2.46 (td, *J* = 7.36, 1.86, 1H, C*H*$_2$HC=O), 1.74 (p, *J* = 7.36, 2H; C*H*$_2$CH$_2$HC=O), 1.24 (m, 2H, C*H*$_2$CH$_2$CH$_2$HC=O), 0.64 (m, 1H, C*H*CH$_2$CH$_2$), 0.42 (m, 2H, CHC*H*$_2$CH$_2$), 0.01 (m, 2H, CHCH$_2$C*H*$_2$).

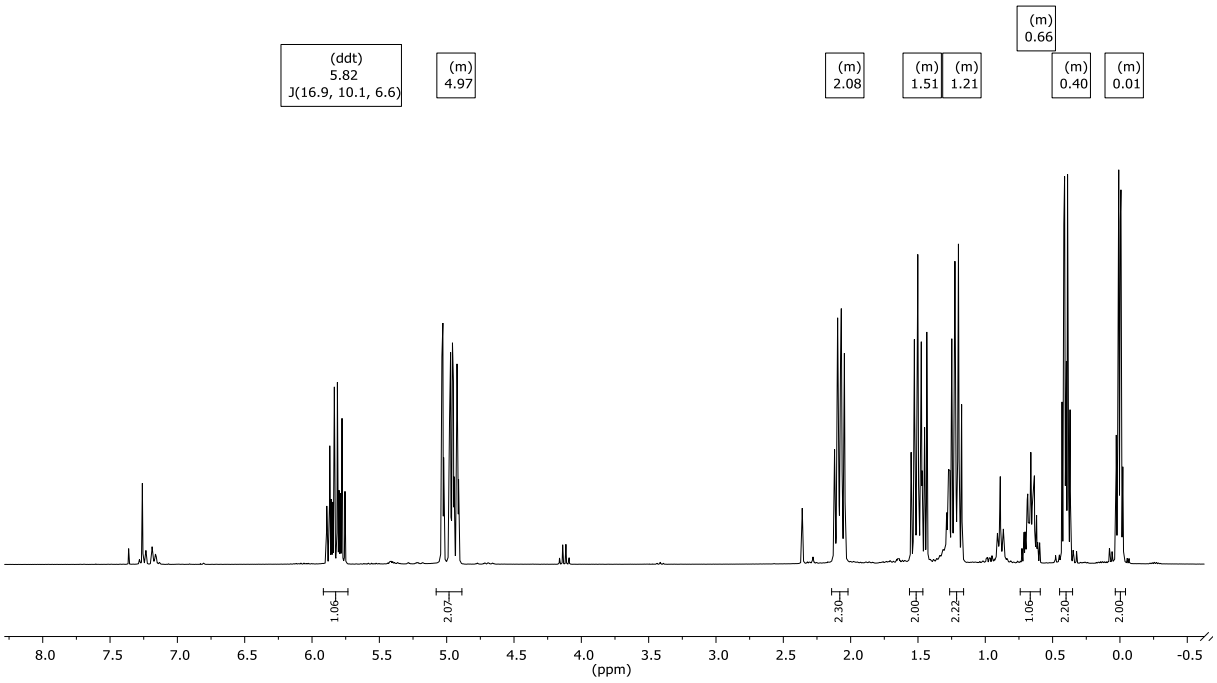
Spectroscopic data are consistent with literature values.[10]

4.2.5 1-(Penten-4-yl)cyclopropane

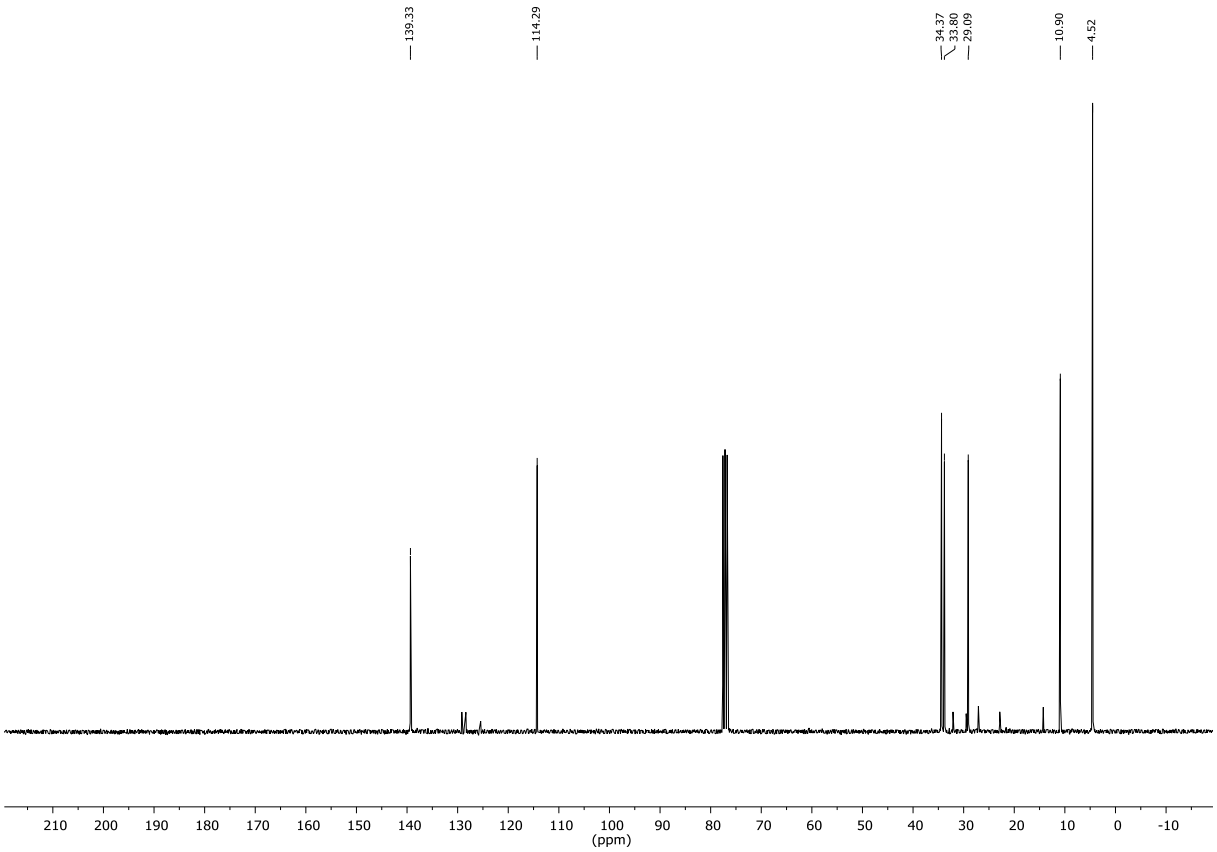


Methyltriphenylphosphonium bromide (23.9 g, 66.8 mmol, 1.50 eq.) in Et_2O (220 ml) was cooled to 0 °C and *n*-butyllithium (2.50 M, 26.8 ml, 66.7 mmol, 1.50 eq.) was added. The yellow suspension was stirred for 1 h. 4-Cyclopropylbutanal (**24**) (5.8 g, 44 mmol, 1.0 eq.) in Et_2O (45 ml) was added at 10 °C. The suspension was stirred for 1 h at room temperature and quenched with saturated NH_4Cl (150 ml). The suspension was filtered through a celite pad and concentrated *via* distillation. The crude product was purified by column chromatography (silica gel, eluent: pentane) and concentrated *via* distillation (oil bath = 150 °C) to get a clear liquid. Finally, it was stirred over NaH and condensed under reduced pressure (0.516 g, 4.68 mmol, 10 %). 1-(Penten-4-yl)cyclopropane (**25**) is very volatile and has to be stored at −20 °C.

^{1}H-NMR (300 MHz, $CDCl_3$) δ [ppm] 5.82 (ddt, J = 16.9, 10.1, 6.6, 1H, CH_2=C*H*); 4.97 (m, 2H, C*H*$_2$=CH), 2.08 (m, 2H, CH$_2$=CHC*H*$_2$), 1.51 (m, 2H, CH$_2$=CHCH$_2$C*H*$_2$), 1.21 (m, 2H, CH$_2$=CHCH$_2$CH$_2$C*H*$_2$), 0.66 (m, 1H, C*H*CH$_2$CH$_2$), 0.40 (m, 2H, CHCH$_2$C*H*$_2$), 0.01 (m, 2H, CHC*H*$_2$CH$_2$). **^{13}C{^{1}H}-NMR** (75.5 MHz, $CDCl_3$) δ [ppm] 139.3, 114.3, 34.4, 33.8, 29.1, 10.9, 4.52.



NMR-spectrum 46: ^{1}H-NMR-spectrum (300 MHz, $CDCl_3$) of 1-(penten-4-yl)cyclopropane.



NMR-spectrum 47: ^{13}C-NMR-spectrum (75.5 MHz, $CDCl_3$) of 1-(penten-4-yl)cyclopropane.

5 [^{t}Bu$_3$PI][FB(C$_6$F$_5$)$_3$] formation, NMR-experiments

5.1 Room temperature measurement

Inside the glovebox, ^{t}Bu$_3$P (**5**) (8.2 mg, 0.041 mmol, 0.28 eq.) and B(C$_6$F$_5$)$_3$ (**3**) (22 mg, 0.042 mmol, 0.29 eq.) were weighed into a glass, dissolved in CD_2Cl_2 (overall 0.62 ml) and transferred into a Young valve NMR tube. Fluorobenzene (10 µl, 0.11 mmol) was added as an internal standard, followed by addition of nonafluoro-1-iodobutane (**2**) (50 mg, 0.14 mmol, 1.0 eq.). The NMR tube was sealed and NMR-measurements were conducted.

5.2 Low temperature measurement

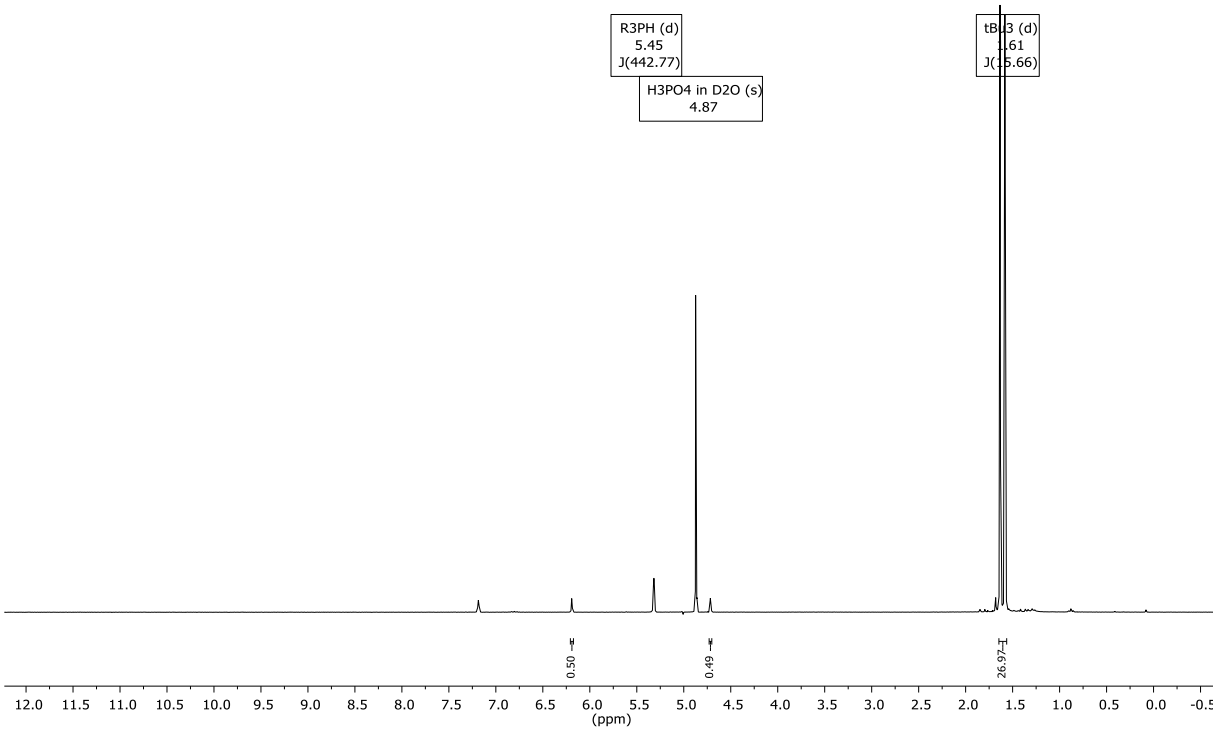
Inside the glovebox, ^{t}Bu$_3$P (**5**) (7.5 mg, 0.037 mmol, 0.26 eq.) was dissolved in CD_2Cl_2 and transferred into a Young valve NMR tube, which was filled with trifluoromethylcyclohexane (3.5 µl, 0.025 mmol) as internal standard. A solution B(C$_6$F$_5$)$_3$ (**3**) (19 mg, 0.036 mmol, 0.25 eq.) in combination with nonafluoro-1-iodobutane (**2**) (50 mg, 0.15 mmol, 1.0 eq.) was added. Several spectra were measured at 25 °C up to −30 °C.

6 Synthesis of [^{t}Bu$_3$PH][FB(C$_6$F$_5$)$_3$]

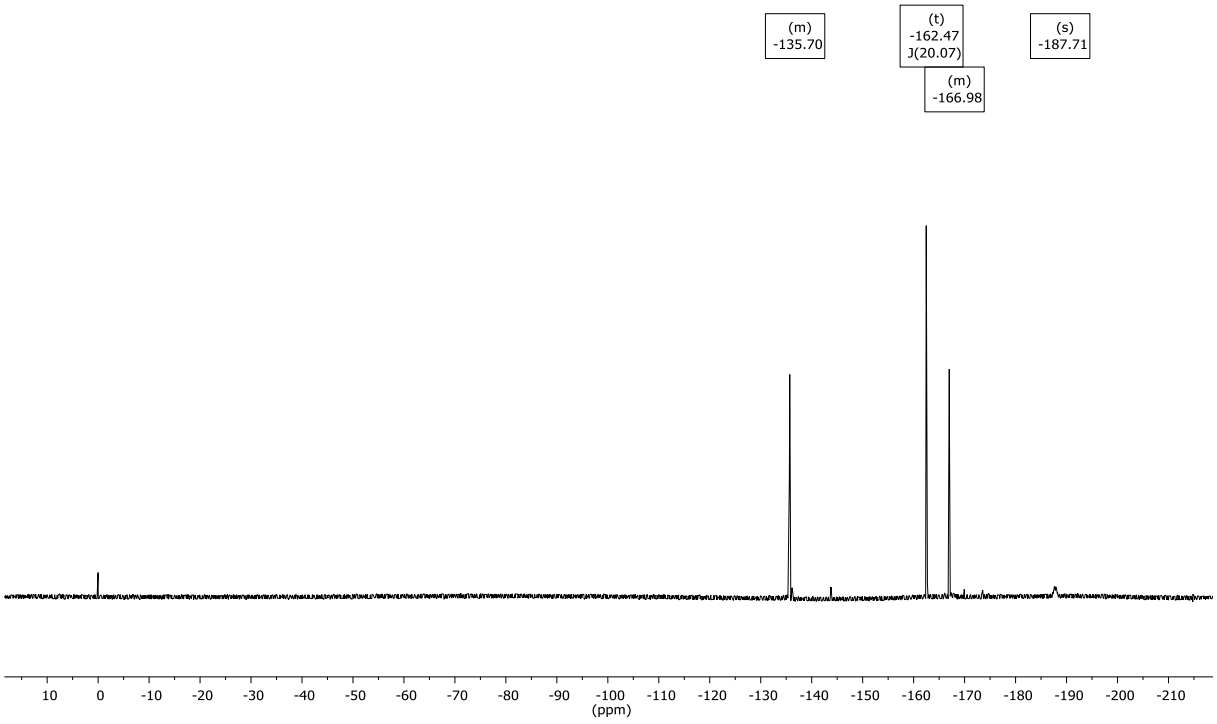
^{t}Bu$_3$P (**5**) (198 mg, 0.979 mmol, 1.00 eq.) and B(C$_6$F$_5$)$_3$ (**3**) (538 mg, 1.05 mmol, 1.07 eq.) were dissolved in toluene (20 ml) in a transparent screw-cap jar. After 2 d the reaction solution was transferred into a reactor bomb and heated up to 100 °C for 5 d. The resulting two-phase system was transferred into a flask and layered with pentane. After 1 d at −20 °C crystals (95.3 mg) were obtained.

^{1}H-NMR (300 MHz, CD_2Cl_2) δ [ppm] 5.45 (d, *J* = 443 Hz, 1H), 1.61 (d, *J* = 15.7 Hz, 27H). **^{19}F-NMR** (282 MHz, CD_2Cl_2) δ [ppm] −135.4 - −135.9 (m), −162.5 (t, *J* = 20.1 Hz), −166.8 - −167.3 (m), −187.7. ^{31}P NMR (121 MHz, CD_2Cl_2) δ [ppm] 56.69. **^{11}B NMR** (96 MHz, CD_2Cl_2) δ [ppm] −0.50 (d, *J* = 71.2 Hz).

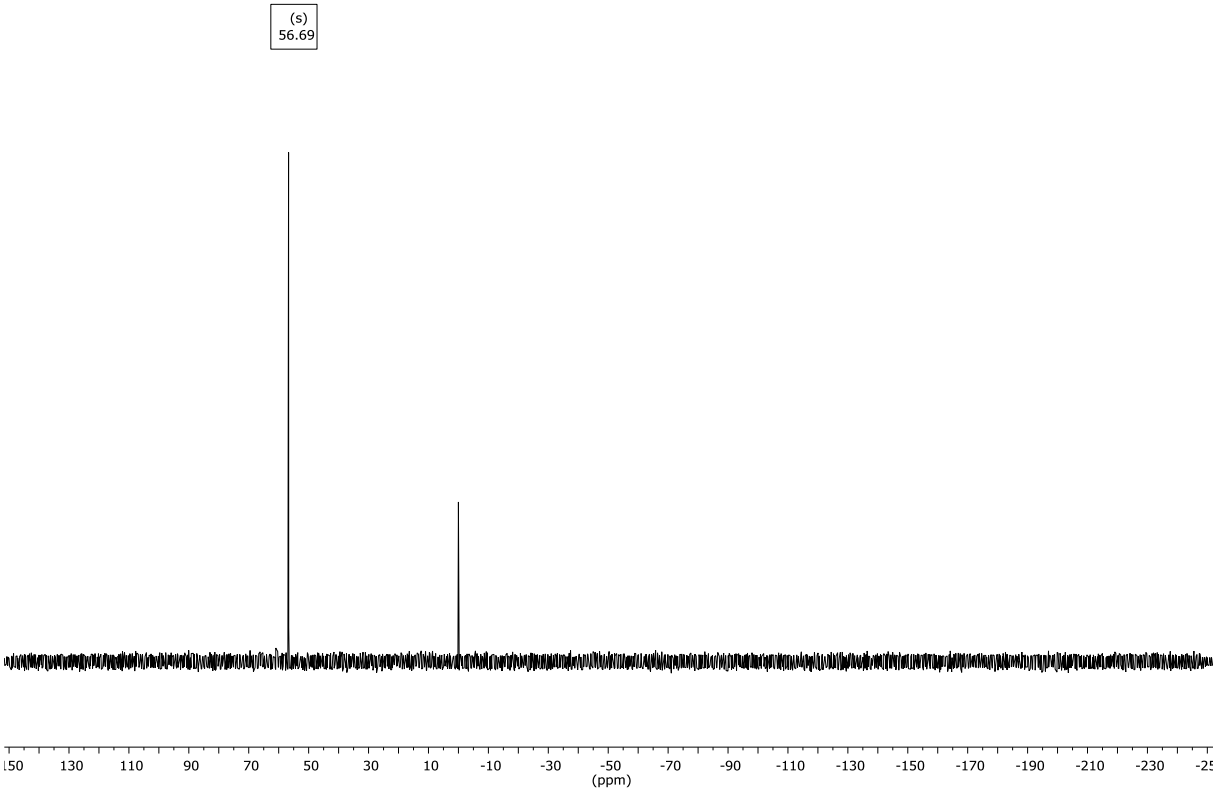
Piers et al.[11] described slightly different shifts for [^{t}Bu$_3$PH][FB(C$_6$F$_5$)$_3$] (**17**). However, ^{1}H- and ^{31}P-NMR-spectra show the determining signals for [^{t}Bu$_3$PH]$^+$ and ^{19}F- as well as ^{11}B-NMR-spectra show the determining signals for [FB(C$_6$F$_5$)$_3$]$^-$.



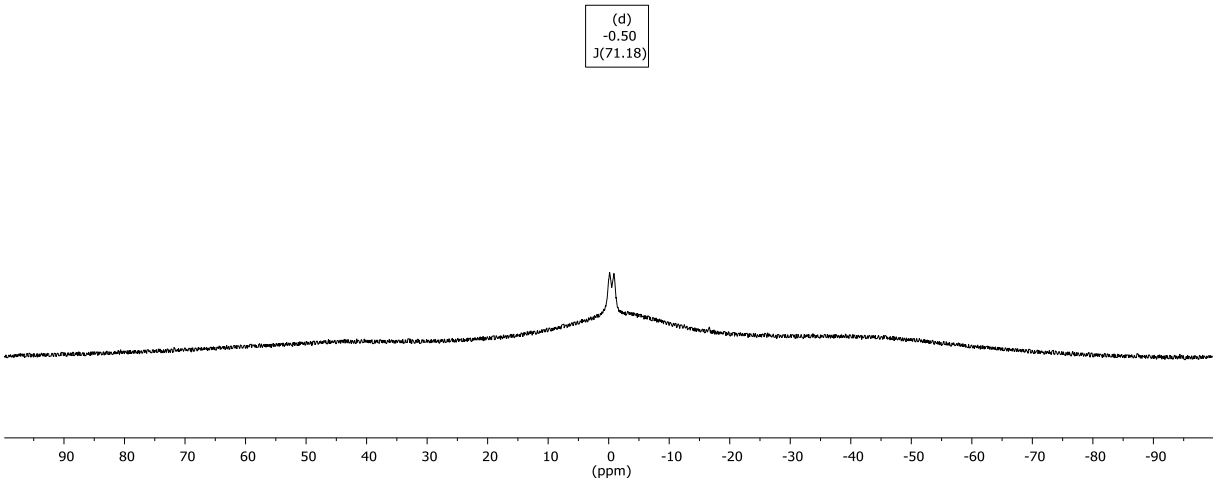
NMR-spectrum 48: ^{1}H-NMR-spectrum (300 MHz, CD_2Cl_2) of [^{t}Bu$_3$PH][FB(C_6F_5)$_3$].



NMR-spectrum 49: ^{19}F-NMR-spectrum (282 MHz, CD_2Cl_2) of [^{t}Bu$_3$PH][FB(C_6F_5)$_3$].



NMR-spectrum 50: ^{31}P-NMR-spectrum (121 MHz, CD_2Cl_2) of [^{t}Bu$_3$PH][FB(C_6F_5)$_3$].



NMR-spectrum 51: ^{11}B-NMR-spectrum (96 MHz, CD_2Cl_2) of [^{t}Bu$_3$PH][FB(C_6F_5)$_3$].

7 GC-experiments

Preface

To monitor the reaction progress, we used *n*-decane (TCI, purity ≥99.5%, product number: S0282, stored over 4 Å molecular sieve) as an internal standard. For the calibration curve, we prepared solutions of vinylcyclohexane (**1**) and *n*-decane (**19**) in CH_2Cl_2 in volumetric flasks inside the glovebox. GC measurements were conducted with a Perkin Elmer Clarus 500 GC without an autosampler equipped with a SUPELCO SLB-5ms column (30 m x 0.25 mm x 0.25 µm).

We validated our GC method in a range of about 15 - 90% conversion, because of higher standard deviations outside this range. As a result, we could not measure data for an excess of vinylcyclohexane (**1**) and had to use NMR measurements. These higher standard deviations apart from our calibration range can be understood in the light of a substantial boiling point difference between vinylcyclohexane (b.p. = 128 °C) and *n*-decane (b.p. = 174 °C), resulting in mass discrimination by the split stream.

Standard procedure A for GC experiments

A 10 ml round-bottom flask was wrapped in aluminum foil and then equipped with a Teflon stir bar (6 x 2 mm) as well as *n*-decane (**19**) (80.0 µl) as internal standard. ^{t}Bu$_3$P (**5**) and $B(C_6F_5)_3$ (**3**) were weighed into separate glass vials. After these first preparations, all work steps were conducted under red light and best possible light exclusion. ^{t}Bu$_3$P (**5**) was dissolved, transferred into the round-bottom flask and the vial was rinsed twice (in total 1.3 ml CH_2Cl_2). Vinylcyclohexane (**1**) as well as nonafluoro-1-iodobutane (**2**) were added. One minute after adding C_4F_9I, a solution of freshly dissolved $B(C_6F_5)_3$ (**3**) was added and the vial was rinsed twice (in total 1.3 ml CH_2Cl_2). The flask was sealed with a rubber septum and then unloaded from the glovebox. It was attached to an N_2 stream and stirred at 20 °C (thermostat). Samples were withdrawn as follows: A 1.0 ml syringe (Braun) was flushed with N_2 at a separate flask three times, then 0.10 ml of the reaction solution were withdrawn and diluted with 0.10 ml CH_2Cl_2 (saturated with water). This solution was used for injection into the GC.

Table 4: Calibration curve for vinylcyclohexane with *n*-decane as internal standard.

c(vinylcyclohexane) [mg·ml^{-1}]	c(*n*-decane) [mg·ml^{-1}]	c(V)/c(D)	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	area(V)/area(D)
29.8	25.6	1.17	23719	20258	1.17
			24777	21176	1.17
			19991	17224	1.16
			22081	19054	1.16
			33018	27379	1.21
			32540	27473	1.18
24.2	25.6	0.945	20462	20064	1.02
			22055	22322	0.99
			19807	19843	1.00
			20709	20565	1.01
			11616	12086	0.96
18.1	25.6	0.709	8542	16889	0.506
			10845	21615	0.502
			5197	10812	0.481
			10151	20200	0.503
			10353	20386	0.508
12.1	25.6	0.473	8542	16889	0.506
			10845	21615	0.502
			5197	10812	0.481
			10151	20200	0.503
			10353	20386	0.508
4.03	25.6	0.158	3308	20089	0.165
			3303	19792	0.167
			3218	19732	0.163
			1860	11827	0.157
			3117	18840	0.165

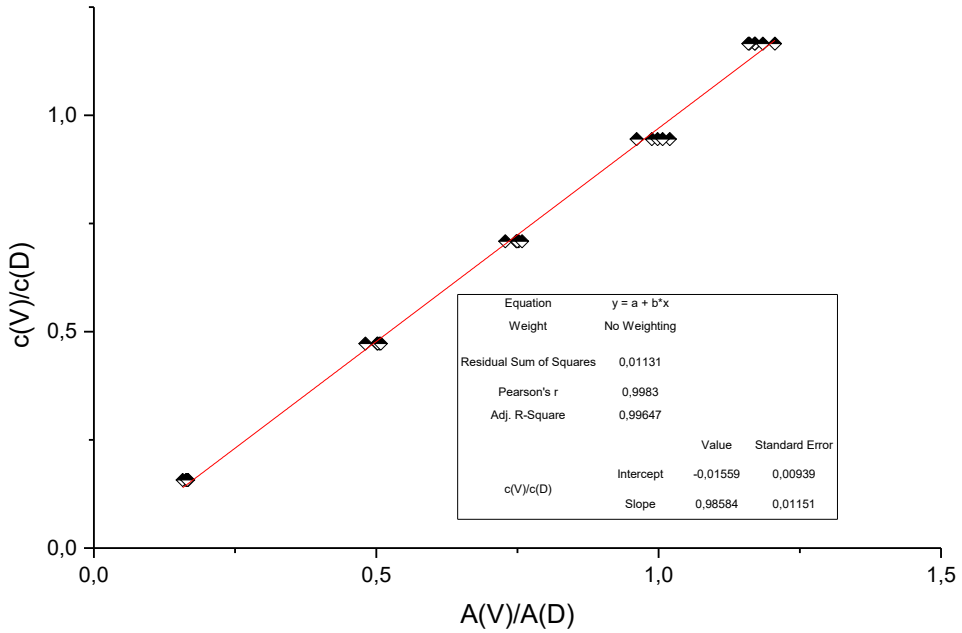


Figure 1: Calibration curve for vinylcyclohexane.

The following datasets contain calculated values. The mass of vinylcyclohexane is calculated with the following equation:

$$\mathrm{m(V)} = (0{,}98584 \cdot \mathrm{A(V)(A(D)} - 0{,}01559) \cdot \mathrm{m(D)}$$

Subsequently, the conversion is calculated as follows:

$$\mathrm{conversion} = (\mathrm{m_0(V)} - \mathrm{m(V)})/\mathrm{m_0(V)}$$

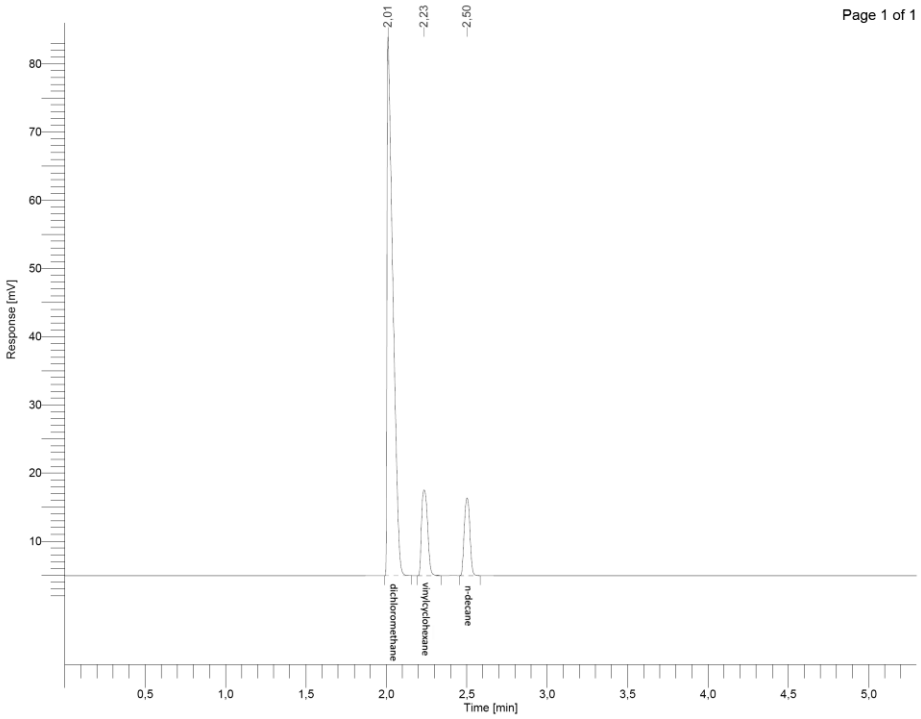


Figure 2: Exemplary chromatogram of the calibration.

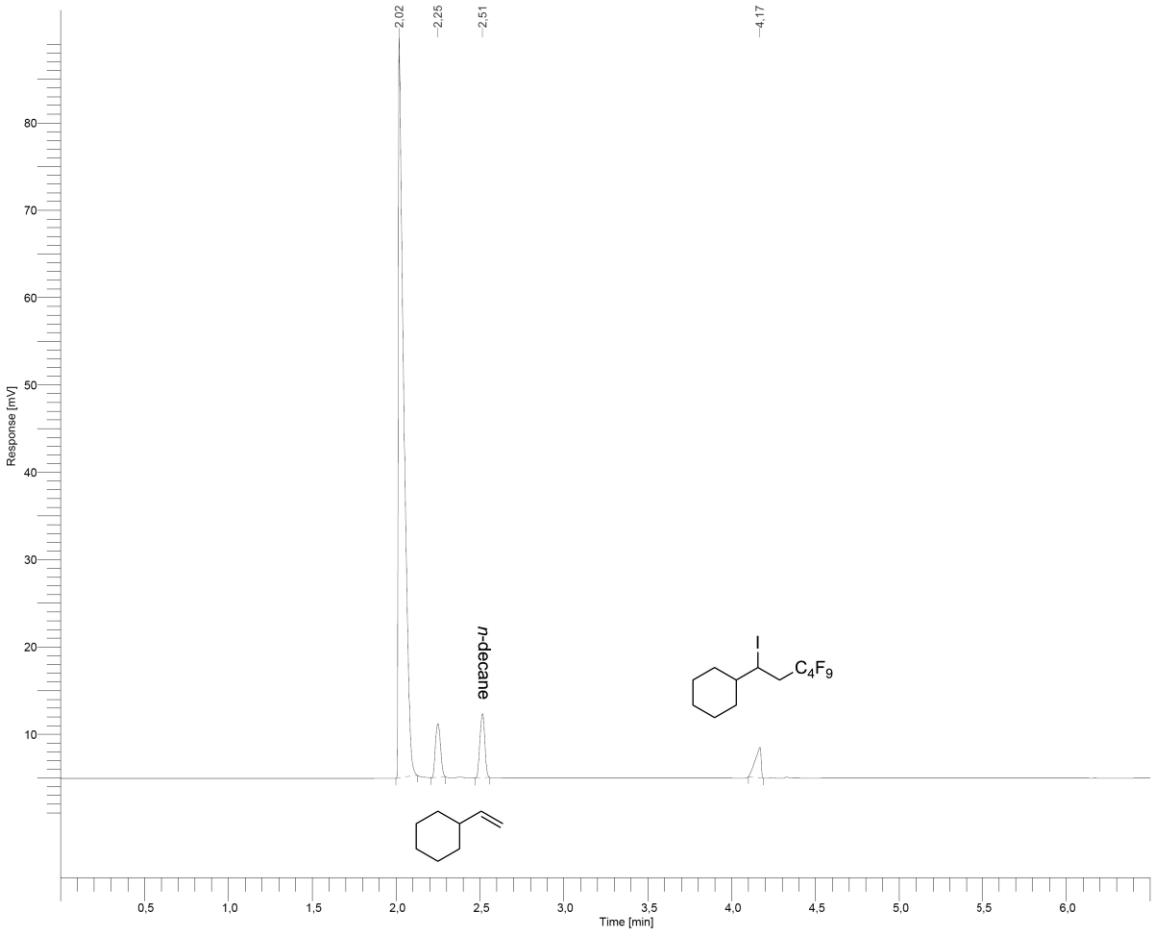


Figure 3: Exemplary chromatogram of a reaction solution.

7.1 GC-experiment, standard conditions

$^{t}Bu_3P$ (**5**) (7.5 mg, 0.037 mmol, 5.0 mol%), vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.), nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.) and $B(C_6F_5)_3$ (**3**) (18.7 mg, 0.0365 mmol, 5.0 mol%) were reacted as described in Standard procedure A for GC experiments.

Table 5: Standard conditions.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V_0)[a]	ln([V]/[V_0])[a]
20	14089	14830	0.950	53.8	33	0.67	-0.403
20	15586	16463	0.947	53.6	33	0.67	-0.407
20	15914	16944	0.939	53.2	34	0.66	-0.415
30	17161	20105	0.854	48.2	40	0.60	-0.512
30	12145	14755	0.823	46.5	42	0.58	-0.549
30	12310	14998	0.821	46.3	42	0.58	-0.552
40	10447	14134	0.739	41.6	48	0.52	-0.659
40	10817	14655	0.738	41.6	48	0.52	-0.661
40	11384	15463	0.736	41.5	48	0.52	-0.663
50	9730	14576	0.668	37.5	53	0.47	-0.763
50	9073	13916	0.652	36.6	55	0.45	-0.787
50	9639	14644	0.658	37.0	54	0.46	-0.778
60	9054	15329	0.591	33.1	59	0.41	-0.889
60	8843	15023	0.589	33.0	59	0.41	-0.892
60	9621	16060	0.599	33.6	58	0.42	-0.874

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane.

Table 6: Basis for depicted graphs, standard conditions.

Δt [min]	average conversion [%]	standard deviation [%]
20	34	0.40
30	42	1.31
40	48	0.11
50	54	0.56
60	59	0.40

7.2 GC-experiments, 10 mol% $^{t}Bu_3P$

$^{t}Bu_3P$ (**5**) (14.8 mg, 0.0732 mmol, 10 mol%), vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.), nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.) and $B(C_6F_5)_3$ (**3**) (18.6 mg, 0.0363 mmol, 5.0 mol%) were reacted as described in Standard procedure A for GC experiments.

Table 7: Standard procedure, 10 mol% $^{t}Bu_3P$.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V_0)[a]	ln([V]/[V_0])[a]
15	12930	14535	0.890	50.3	38	0.62	-0.470
15	16766	18496	0.906	51.3	36	0.64	-0.451
15	15529	17195	0.903	51.1	37	0.63	-0.455
20	14601	17740	0.823	46.5	42	0.58	-0.549
20	12729	16041	0.794	44.8	44	0.56	-0.587
20	12308	15436	0.797	45.0	44	0.56	-0.582
25	11059	14895	0.742	41.8	48	0.52	-0.655
25	11534	15450	0.747	42.1	48	0.52	-0.649
25	11938	16089	0.742	41.8	48	0.52	-0.655
30	14415	20194	0.714	40.2	50	0.50	-0.695
30	11905	17463	0.682	38.3	52	0.48	-0.742
30	13381	19449	0.688	38.7	52	0.48	-0.732
40	9306	15394	0.605	33.9	58	0.42	-0.865
40	12123	19455	0.623	35.0	57	0.43	-0.834
40	12210	19805	0.617	34.6	57	0.43	-0.845
50	8912	16491	0.540	30.2	62	0.38	-0.980
50	8707	16167	0.539	30.1	63	0.37	-0.984
50	8739	16354	0.534	29.9	63	0.37	-0.992

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane.

Table 8: Basis for depicted graphs, standard procedure, 10 mol% $^{t}Bu_3P$.

Δt [min]	average conversion [%]	standard deviation [%]
15	37	0.64
20	44	1.15
25	48	0.18
30	51	1.22
40	57	0.67
60	59	0.40

7.3 GC-experiments, 15 mol% $^{t}Bu_3P$

$^{t}Bu_3P$ (**5**) (22.2 mg, 0.110 mmol, 15 mol%), vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.), nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.) and $B(C_6F_5)_3$ (**3**) (18.8 mg, 0.0367 mmol, 5.0 mol%) were reacted as described in Standard procedure A for GC experiments.

Table 9: Standard procedure, 15 mol% $^{t}Bu_3P$.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V_0)[a]	ln([V]/[V_0])[a]
15	11378	15412	0.738	41.6	48	0.52	-0.660
15	11473	15589	0.736	41.5	48	0.52	-0.663
15	15038	19956	0.754	42.5	47	0.53	-0.639
20	10695	15919	0.672	37.8	53	0.47	-0.757
20	10442	15479	0.675	37.9	53	0.47	-0.753
20	13653	19683	0.694	39.0	52	0.48	-0.724
25	9388	15499	0.606	34.0	58	0.42	-0.863
25	12908	20787	0.621	34.8	57	0.43	-0.837
25	13226	21298	0.621	34.8	57	0.43	-0.837
30	10794	18831	0.573	32.1	60	0.40	-0.920
30	11291	19813	0.570	31.9	60	0.40	-0.926
30	10472	18441	0.568	31.8	61	0.39	-0.929
40	7243	15265	0.474	26.4	67	0.33	-1.115
40	7664	16163	0.474	26.4	67	0.33	-1.115
40	7695	16278	0.473	26.3	67	0.33	-1.118
50	6787	16133	0.421	23.3	71	0.29	-1.239
50	6382	15412	0.414	22.9	72	0.28	-1.256
50	8808	20279	0.434	24.1	70	0.30	-1.206

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane.

Table 10: Basis for depicted graphs, standard procedure, 15 mol% $^{t}Bu_3P$.

Δt [min]	average conversion [%]	standard deviation [%]
15	48	0.68
20	52	0.85
25	57	0.63
30	60	0.19
40	67	0.07
50	71	0.74

7.4 GC-experiments, 1.5 eq. C_4F_9I

$^tBu_3P$ (**5**) (7.5 mg, 0.037 mmol, 5.1 mol%), vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.), nonafluoro-1-iodobutane (**2**) (190 µl, 1.10 mmol, 1.51 eq.) and $B(C_6F_5)_3$ (**3**) (18.6 mg, 0.0363 mmol, 5.0 mol%) were reacted as described in Standard procedure A for GC experiments.

Table 11: Standard procedure, 1.5 eq. C_4F_9I.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V_0)[a]	ln([V]/[V_0])[a]
20	10270	14013	0.733	41.3	49	0.51	-0.668
20	10538	14437	0.730	41.1	49	0.51	-0.672
20	9530	13326	0.715	40.3	50	0.50	-0.693
25	8883	13878	0.640	35.9	55	0.45	-0.806
25	9775	15399	0.635	35.6	56	0.44	-0.815
25	9673	15298	0.632	35.5	56	0.44	-0.819
30	8051	14152	0.569	31.8	60	0.40	-0.927
30	7863	13916	0.565	31.6	61	0.39	-0.934
30	7423	13316	0.557	31.2	61	0.39	-0.948
40	6199	14268	0.434	24.1	70	0.30	-1.206
40	6632	15350	0.432	24.0	70	0.30	-1.212
40	6902	15915	0.434	24.1	70	0.30	-1.208
50	4822	14400	0.335	18.4	77	0.23	-1.478
50	4947	14856	0.333	18.3	77	0.23	-1.483

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane.

Table 12: Basis for depicted graphs, standard conditions, 1.5 eq. C_4F_9I.

Δt [min]	average conversion [%]	standard deviation [%]
20	49	0.68
25	56	0.28
30	61	0.42
40	70	0.09
50	77	0.09

7.5 GC-experiments, 2.0 eq. C_4F_9I

$^tBu_3P$ (**5**) (7.4 mg, 0.037 mmol, 5.0 mol%), vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.), nonafluoro-1-iodobutane (**2**) (250 µl, 1.45 mmol, 1.99 eq.) and $B(C_6F_5)_3$ (**3**) (18.8 mg, 0.0367 mmol, 5.0 mol%) were reacted as described in Standard procedure A for GC experiments.

Table 13: Standard procedure, 2.0 eq. C_4F_9I.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V_0)[a]	ln([V]/[V_0])[a]
15	9771	14076	0.694	39.1	51	0.49	-0.723
15	12372	16999	0.728	41.0	49	0.51	-0.675
15	9887	14430	0.685	38.5	52	0.48	-0.737
20	7906	13714	0.576	32.3	60	0.40	-0.914
20	8186	14117	0.580	32.5	60	0.40	-0.908
20	7985	13812	0.578	32.4	60	0.40	-0.911
25	6902	14681	0.470	26.2	68	0.32	-1.124
25	7287	15551	0.469	26.1	68	0.32	-1.128
25	7232	15434	0.469	26.1	68	0.32	-1.128
30	5425	14484	0.375	20.7	74	0.26	-1.360
30	7436	19157	0.388	21.4	73	0.27	-1.323
30	5578	15175	0.368	20.3	75	0.25	-1.380
40	3887	16675	0.233	12.5	84	0.16	-1.862
40	4224	18451	0.229	12.3	85	0.15	-1.881
40	5224	22534	0.232	12.4	85	0.15	-1.868

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane.

Table 14: Basis for depicted graphs, standard procedure, 2.0 eq. C_4F_9I.

Δt [min]	average conversion [%]	standard deviation [%]
15	51	1.61
20	60	0.12
25	68	0.06
30	74	0.75
40	85	0.15

7.6 GC-experiments, 10 mol% $B(C_6F_5)_3$

$^tBu_3P$ (**5**) (7.5 mg, 0.037 mmol, 5.1 mol%), vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.), nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.) and $B(C_6F_5)_3$ (**3**) (37.5 mg, 0.0732 mmol, 10 mol%) were reacted as described in Standard procedure A for GC experiments.

Table 15: Standard procedure, 10 mol% $B(C_6F_5)_3$.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V_0)[a]	ln([V]/[V_0])[a]
15	12208	13865	0.880	49.8	38	0.62	-0.481
15	13745	15145	0.908	51.3	36	0.64	-0.450
15	13598	15074	0.902	51.0	37	0.63	-0.456
20	11615	14433	0.805	45.4	44	0.56	-0.572
20	12293	14946	0.822	46.4	42	0.58	-0.550
20	12299	15076	0.816	46.1	43	0.57	-0.558
30	13200	18880	0.699	39.3	51	0.49	-0.716
30	10082	14629	0.689	38.8	52	0.48	-0.731
30	10212	14831	0.689	38.7	52	0.48	-0.732
40	10542	17605	0.599	33.6	58	0.42	-0.875
40	9378	16046	0.584	32.7	59	0.41	-0.900
40	9227	15929	0.579	32.4	60	0.40	-0.909
50	7400	14797	0.500	27.9	65	0.35	-1.060
50	8122	16157	0.503	28.0	65	0.35	-1.055
50	7847	15682	0.500	27.9	65	0.35	-1.060

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane.

Table 16: Basis for depicted graphs, standard procedure, 10 mol% $B(C_6F_5)_3$.

Δt [min]	average conversion [%]	standard deviation [%]
15	37	1.02
20	43	0.64
30	52	0.43
40	59	0.72
50	65	0.10

7.7 GC-experiments, 15 mol% $B(C_6F_5)_3$

$^tBu_3P$ (**5**) (7.5 mg, 0.037 mmol, 5.1 mol%), vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.), nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.) and $B(C_6F_5)_3$ (**3**) (56.1 mg, 0.110 mmol, 15 mol%) were reacted as described in Standard procedure A for GC experiments.

Table 17: Standard procedure, 15 mol% $B(C_6F_5)_3$.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V_0)[a]	ln([V]/[V_0])[a]
15	13787	15999	0.862	48.7	39	0.61	-0.503
15	12653	14765	0.857	48.4	40	0.60	-0.508
15	13288	15743	0.844	47.7	41	0.59	-0.524
20	11702	15277	0.766	43.2	46	0.54	-0.623
20	11178	14668	0.762	43.0	47	0.53	-0.628
20	12047	15906	0.757	42.7	47	0.53	-0.634
30	9442	15414	0.613	34.4	57	0.43	-0.851
30	9344	15414	0.606	34.0	58	0.42	-0.862
30	9572	15808	0.606	34.0	58	0.42	-0.863
40	9377	17941	0.523	29.2	64	0.36	-1.015
40	7311	14858	0.492	27.4	66	0.34	-1.077
40	9465	18876	0.501	28.0	65	0.35	-1.058
51	6167	15145	0.407	22.5	72	0.28	-1.273
51	6161	15393	0.400	22.1	73	0.27	-1.291
51	7387	17686	0.418	23.1	71	0.29	-1.247

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane.

Table 18: Basis for depicted graphs, standard procedure, 15 mol% $B(C_6F_5)_3$.

Δt [min]	average conversion [%]	standard deviation [%]
15	40	0.65
20	47	0.31
30	58	0.28
40	65	1.12
51	72	0.63

7.8 GC-experiment, 33 min premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$

Analogous to Standard procedure A for GC experiments, $^{t}Bu_3P$ (**5**) (7.4 mg, 0.037 mmol, 5.0 mol%) as well as $B(C_6F_5)_3$ (**3**) (18.5 mg, 0.361 mmol, 4.9 mol%) were dissolved in CH_2Cl_2 (1.0 ml + 0.5 ml for rinsing) and filled into a pointed flask. After 33 min this solution was added to a solution of vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.) in CH_2Cl_2 (1.0 ml) outside the glovebox.

Table 19: Varied procedure, 33 min premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V$_0$)[a]	ln([V]/[V$_0$])[a]
20	15646	15848	0.987	55.9	31	0.69	-0.364
20	15870	16021	0.991	56.1	30	0.70	-0.361
20	16158	16285	0.992	56.2	30	0.70	-0.359
30	13508	15629	0.864	48.8	39	0.61	-0.500
30	15121	16887	0.895	50.6	37	0.63	-0.463
30	13056	14871	0.878	49.6	38	0.62	-0.484
40	13833	17912	0.772	43.6	46	0.54	-0.614
40	13741	17930	0.766	43.2	46	0.54	-0.622
40	14774	19187	0.770	43.4	46	0.54	-0.617
50	12489	17902	0.698	39.3	51	0.49	-0.718
50	14860	21306	0.697	39.2	51	0.49	-0.718
50	15125	21829	0.693	39.0	52	0.48	-0.725
60	10742	16659	0.645	36.2	55	0.45	-0.799
60	11091	17560	0.632	35.5	56	0.44	-0.820
60	10970	17520	0.626	35.1	56	0.44	-0.829

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane.

Table 20: Basis for depicted graphs, varied procedure, 33 min premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$.

Δt [min]	average conversion [%]	standard deviation [%]
20	30	0.18
30	38	1.12
40	46	0.21
50	51	0.19
60	56	0.69

7.9 GC-experiment, 61 min premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$

Analogous to Standard procedure A for GC experiments, $^{t}Bu_3P$ (**5**) (7.4 mg, 0.037 mmol, 5.0 mol%) as well as $B(C_6F_5)_3$ (**3**) (18.6 mg, 0.363 mmol, 5.0 mol%) were premixed and stirred for 61 min inside the glovebox. Vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.) and nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.) were added inside the glovebox.

Table 21: Varied procedure, 61 min premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V_0)[a]	ln([V]/[V_0])[a]
20	15428	15646	0.986	55.9	31	0.69	-0.365
20	14717	14914	0.987	55.9	31	0.69	-0.365
20	15067	15274	0.986	55.9	31	0.69	-0.365
30	12891	14320	0.900	50.9	37	0.63	-0.458
30	12696	14374	0.883	49.9	38	0.62	-0.477
30	13229	14929	0.886	50.1	38	0.62	-0.474
40	15683	19208	0.816	46.1	43	0.57	-0.558
40	12518	15854	0.790	44.5	45	0.55	-0.592
40	12041	15500	0.777	43.8	46	0.54	-0.608
50	11819	16350	0.723	40.7	49	0.51	-0.682
50	11429	16197	0.706	39.7	51	0.49	-0.707
50	11593	16374	0.708	39.9	50	0.50	-0.703
60	10787	16278	0.663	37.2	54	0.46	-0.771
60	9816	15237	0.644	36.2	55	0.45	-0.800
60	10025	15432	0.650	36.5	55	0.45	-0.791

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane.

Table 22: Basis for depicted graphs, varied procedure, 61 min premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$.

Δt [min]	average conversion [%]	standard deviation [%]
20	31	0.03
30	37	0.65
40	44	1.45
50	50	0.67
60	54	0.68

7.10 GC-experiment, 10 min premixing of $^{t}Bu_3P$, C_4F_9I and alkene

Analogous to Standard procedure A for GC experiments, to a solution of $^{t}Bu_3P$ (**5**) (7.5 mg, 0.037 mmol, 5.1 mol%) in CH_2Cl_2 (1.3 ml), vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.) as well as nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.) were added. After 10 min a solution of $B(C_6F_5)_3$ (**3**) (18.8 mg, 0.367 mmol, 5.0 mol%) was added inside the glovebox.

Table 23: Varied procedure, 10 min premixing of $^{t}Bu_3P$, C_4F_9I and alkene.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V_0)[a]	ln([V]/[V_0])[a]
20	12998	13773	0.944	53.4	34	0.66	-0.410
20	13803	14834	0.930	52.7	35	0.65	-0.424
20	18937	19641	0.964	54.6	32	0.68	-0.388
30	12199	14739	0.828	46.7	42	0.58	-0.544
30	13098	15764	0.831	46.9	42	0.58	-0.540
30	12603	15287	0.824	46.6	42	0.58	-0.548
40	13742	17735	0.775	43.7	46	0.54	-0.611
40	10479	14336	0.731	41.2	49	0.51	-0.670
40	14717	19571	0.752	42.4	47	0.53	-0.642
50	11826	17048	0.694	39.0	52	0.48	-0.724
50	9412	14276	0.659	37.0	54	0.46	-0.776
50	9995	15156	0.659	37.1	54	0.46	-0.776
60	8321	14001	0.594	33.3	59	0.41	-0.883
60	9206	15392	0.598	33.5	58	0.42	-0.876
60	9114	15267	0.597	33.5	58	0.42	-0.878

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane.

Table 24: Basis for depicted graphs, varied procedure, 10 min premixing of $^{t}Bu_3P$, C_4F_9I and alkene.

Δt [min]	average conversion [%]	standard deviation [%]
20	33	1.21
30	42	0.23
40	47	1.57
50	53	1.42
60	58	0.14

7.11 GC-experiment, 62 min premixing of $^{t}Bu_3P$, $B(C_6F_5)_3$ and C_4F_9I

Analogous to Standard procedure A for GC experiments, a solution of $^{t}Bu_3P$ (**5**) (7.4 mg, 0.037 mmol, 5.0 mol%), $B(C_6F_5)_3$ (**3**) (18.6 mg, 0.363 mmol, 5.0 mol%) and nonafluoro-1-iodobutane (**2**) (125 µl, 0.726 mmol, 0.994 eq.) in CH_2Cl_2 (2.5 ml) was stirred for 62 min inside the glovebox. Vinylcyclohexane (**1**) (100 µl, 0.730 mmol, 1.00 eq.) was added.

Table 25: Varied procedure, 62 min premixing of $^{t}Bu_3P$, $B(C_6F_5)_3$ and C_4F_9I.

reaction time [min]	area(vinylcyclohexane) [µV·s]	area(*n*-decane) [µV·s]	A(V)/A(D)[a]	m(V)[a] [mg]	conversion[a] [%]	m(V)/m(V_0)[a]	ln([V]/[V_0])[a,b]
20	17206	13523	1.272	72.3	10	0.90	–
20	18466	14204	1.300	73.9	8	0.92	–
20	18917	14744	1.283	73.0	9	0.91	–
27	16049	13050	1.230	69.9	13	0.87	–
27	17178	13877	1.238	70.4	13	0.87	–
27	18167	14690	1.237	70.3	13	0.87	–
35	16877	14392	1.173	66.6	17	0.83	-0.190
35	20751	17227	1.205	68.4	15	0.85	-0.162
35	21488	17966	1.196	67.9	16	0.84	-0.169
45	13383	12794	1.046	59.3	26	0.74	-0.305
45	15209	14198	1.071	60.8	25	0.75	-0.281
45	15103	14251	1.060	60.1	25	0.75	-0.292
55	14656	14736	0.995	56.4	30	0.70	-0.357
55	15867	16034	0.990	56.1	30	0.70	-0.362
55	15772	15971	0.988	55.9	31	0.69	-0.364
65	12288	13306	0.923	52.3	35	0.65	-0.432
65	13273	14348	0.925	52.3	35	0.65	-0.430
65	13407	14512	0.924	52.3	35	0.65	-0.432

[a] Calculated values; V = vinylcyclohexane, D = *n*-decane. [b] Several data points were not used for further calculations, since they are not within the calibration range.

Table 26: Basis for depicted graphs, varied procedure, 62 min premixing of $^{t}Bu_3P$, $B(C_6F_5)_3$ and C_4F_9I.

Δt [min]	average conversion [%]	standard deviation [%]
20	9	1.00
27	13	0.31
35	16	1.18
45	25	0.90
55	30	0.26
65	35	0.06

8 NMR-experiments

Preface to NMR-experiments

At first we used trifluoromethylcyclohexane as an internal standard, but this seemed to result in an interference with our catalytic system. Hence, we were forced to perform this reaction without an internal standard, but used an external standard ($CFCl_3$ in C_6D_6) for signal referencing. We chose CH_2Cl_2 as the solvent after tests in CD_2Cl_2 due to a better comparability to our GC experiments and doubts regarding a constant quality of CD_2Cl_2.

Subsequent datasets show a first data point after 10 - 13 minutes. This time gap is caused by 1) a preparation inside the glovebox, resulting in a gap between addition $B(C_6F_5)_3$ (**3**) and introduction into the NMR 2) automated insertion into the NMR spectrometer (contrary to manually).

Standard procedure B

Inside the glovebox, $^tBu_3P$ (**5**) was dissolved in CH_2Cl_2 and transferred into a Young valve NMR tube, which was enwrapped in aluminium foil and equipped with $CFCl_3$ in C_6D_6 as an external standard. Under red light, vinylcyclohexane (**1**) followed by nonafluoro-1-iodobutane (**2**) was injected directly into the NMR tube. About one minute later, a solution of $B(C_6F_5)_3$ (**3**) in CH_2Cl_2 was added. Overall 0.90 ml CH_2Cl_2 were used. The tube was sealed with a Young valve and NMR-measurements were conducted.

For the kinetic analysis, ^{19}F-NMR-spectra (relaxation delay = 8 s) were analysed. Four signals, two of educt and product each, were used for the calculation of its substance amount fraction. The signal of the internal standard was set to an integral of 1.0.

8.1 NMR-experiment, standard procedure

$^{t}Bu_3P$ (**5**) (3.6 mg, 0.018 mmol, 10 mol%), vinylcyclohexane (**1**) (24.0 µl, 0.175 mmol, 1.00 eq.), nonafluoro-1-iodobutane (**2**) (30.0 µl, 0.174 mmol, 0.994 eq.) and $B(C_6F_5)_3$ (**3**) (9.0 mg, 0.018 mmol, 10 mol%) were reacted as described in Standard procedure B.

Table 27: Standard procedure, 1.0 equivalents of vinylcyclohexane.

shift [ppm]	0 (ES)	−62.3 (E)[a]	−124.9 (P)[b]	−125.6 (E)[a]	−126.2 (P)[b]	Δt [min]	χ(product)[c]	χ(educt)[c]	ln(χ(educt))[c]
	1	7.95	5.44	7.64	5.34	13	0.409	0.591	-0.526
	1	6.97	6.43	6.75	6.28	17	0.481	0.519	-0.656
	1	6.25	7.27	6.04	7.10	21	0.539	0.461	-0.774
	1	5.70	7.99	5.24	7.75	25	0.590	0.410	-0.891
	1	5.11	8.49	4.95	8.30	29	0.625	0.375	-0.982
integral	1	4.67	8.92	4.49	8.75	33	0.659	0.341	-1.075
	1	4.32	9.42	4.15	9.18	37	0.687	0.313	-1.162
	1	4.00	9.82	3.83	9.61	41	0.713	0.287	-1.247
	1	3.67	10.01	3.51	9.84	45	0.734	0.266	-1.326
	1	3.43	10.40	3.29	10.10	49	0.753	0.247	-1.399
	1	3.20	10.56	3.04	10.33	53	0.770	0.230	-1.470

[a] Educt signal C_4F_9I. [b] Product signal, $C_{12}H_{14}F_9I$. [c] Calculated values.

8.2 NMR-experiment, 2.0 eq. vinylcyclohexane

^{t}Bu$_3$P (**5**) (3.6 mg, 0.018 mmol, 10 mol%), vinylcyclohexane (**1**) (38.6 mg, 0.351 mmol, 2.01 eq.), nonafluoro-1-iodobutane (**2**) (30.0 µl, 0.174 mmol, 1.00 eq.) and B(C_6F_5)$_3$ (**3**) (9.0 mg, 0.018 mmol, 10 mol%) were reacted as described in Standard procedure B.

Table 28: Standard procedure, 2.0 equivalents of vinylcyclohexane.

shift [ppm]	0 (ES)	−62.3 (E)[a]	−124.9 (P)[b]	−125.6 (E)[a]	−126.2 (P)[b]	Δt [min]	χ(product)[c]	χ(educt)[c]	ln(χ(educt))[c]
integral	1	14.29	5.93	14.54	5.75	11	0.288	0.712	-0.340
	1	13.51	7.69	13.58	7.54	15	0.360	0.640	-0.446
	1	11.84	8.76	11.95	8.57	19	0.421	0.579	-0.547
	1	11.05	10.20	11.31	9.99	23	0.475	0.525	-0.643
	1	10.12	11.26	10.33	11.15	28	0.523	0.477	-0.740
	1	9.29	12.26	9.60	11.94	32	0.562	0.438	-0.825
	1	8.55	12.94	8.87	12.61	36	0.595	0.405	-0.903
	1	8.08	13.91	8.39	13.55	40	0.625	0.375	-0.981
	1	7.18	13.90	7.51	13.53	44	0.651	0.349	-1.053
	1	7.04	15.11	7.38	14.74	48	0.674	0.326	-1.122
	1	6.61	15.65	6.95	15.23	52	0.695	0.305	-1.187
	1	6.25	16.07	6.42	15.55	56	0.714	0.286	-1.252

[a] Educt signal, C_4F_9I. [b] Product signal, $C_{12}H_{14}F_9I$. [c] Calculated values.

8.3 NMR-experiment, 78 min premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$

Analogous to Standard procedure B, $^{t}Bu_3P$ (**5**) (3.7 mg, 0.018 mmol, 10 mol%) and $B(C_6F_5)_3$ (**3**) (9.0 mg, 0.018 mmol, 10 mol%) were weighed into a glass vial, dissolved in CH_2Cl_2 (0.80 ml) and transferred into an NMR tube. After 78 min vinylcyclohexane (**1**) (24.0 µl, 0.175 mmol, 1.00 eq.) as well as nonafluoro-1-iodobutane (**2**) (30.0 µl, 0.174 mmol, 0.994 eq.) were injected, it was rinsed with CH_2Cl_2 (0.10 ml) and NMR measurements were conducted.

Table 29: Varied procedure, 78 min premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$.

shift [ppm]	0 (ES)	−62.3 (E)[a]	−124.9 (P)[b]	−125.6 (E)[a]	−126.2 (P)[b]	Δt [min]	χ(product)[c]	χ(educt)[c]	ln(χ(educt))[c]
	1	9.14	4.58	8.91	4.56	11	0.336	0.664	-0.410
	1	7.74	5.92	7.49	5.75	17	0.434	0.566	-0.569
	1	6.79	7.03	6.59	6.89	22	0.510	0.490	-0.713
	1	6.06	7.92	5.88	7.79	27	0.568	0.432	-0.840
integral	1	5.41	8.63	5.24	8.41	32	0.615	0.385	-0.956
	1	4.91	9.24	4.73	9.02	37	0.654	0.346	-1.063
	1	4.50	9.81	4.32	9.57	43	0.687	0.313	-1.162
	1	4.07	10.05	3.90	9.80	48	0.714	0.286	-1.250
	1	3.73	10.43	3.57	10.15	53	0.738	0.262	-1.340

[a] Educt signal, C_4F_9I. [b] Product signal, $C_{12}H_{14}F_9I$. [c] Calculated values.

8.4 NMR-experiment, 25 h premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$.

Analogous to Standard procedure B, $^{t}Bu_3P$ (**5**) (3.6 mg, 0.018 mmol, 10 mol%) and $B(C_6F_5)_3$ (**3**) (8.9 mg, 0.017 mmol, 9.9 mol%) were weighed into a glass vial, dissolved in CD_2Cl_2 (0.45 ml) and transferred into an NMR tube. The NMR tube was sealed with a Young valve and an NMR measurement was conducted. After 25 h nonafluoro-1-iodobutane (**2**) (30.0 µl, 0.174 mmol, 0.994 eq.) as well as vinylcyclohexane (**1**) (24.0 µl, 0.175 mmol, 1.00 eq.) were injected, it was rinsed with CD_2Cl_2 (0.45 ml) and NMR measurements were conducted.

Table 30: Varied procedure, 25 h premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$.

shift [ppm]	−62.3 (E)[a]	−124.9 (P)[b]	−125.6 (E)[a]	−126.2 (P)[b]	Δt [min]	χ(product)[c]	χ(educt)[c]	ln(χ(educt))[c]
	6.00	0.41	5.77	0.38	15	0.063	0.937	-0.065
	6.00	0.52	5.81	0.52	19	0.081	0.919	-0.084
	6.00	0.65	5.81	0.63	23	0.098	0.902	-0.103
integral	6.00	0.75	5.81	0.78	27	0.115	0.885	-0.122
	6.00	3.11	5.79	3.07	123	0.344	0.656	-0.421
	6.00	5.38	5.78	5.15	229	0.472	0.528	-0.639
	6.00	7.21	5.76	6.93	324	0.546	0.454	-0.790

[a] Educt signal, C_4F_9I. [b] Product signal, $C_{12}H_{14}F_9I$. [c] Calculated values.

8.5 NMR-experiment, 60 min premixing of $^{t}Bu_3P$, $B(C_6F_5)_3$ and C_4F_9I

Analogous to Standard procedure B, $^{t}Bu_3P$ (**5**) (3.6 mg, 0.018 mmol, 10 mol%) and $B(C_6F_5)_3$ (**3**) (8.9 mg, 0.017 mmol, 9.9 mol%) were weighed into a glass vial, dissolved in CH_2Cl_2 (0.80 ml) and transferred into an NMR tube. Nonafluoro-1-iodobutane (**2**) (30.0 µl, 0.174 mmol, 0.994 eq.) was injected directly into the NMR tube and the tube was sealed with a Young valve. After 60 min, vinylcyclohexane (**1**) (24.0 µl, 0.175 mmol, 1.00 eq.) was injected, it was rinsed with CH_2Cl_2 (0.10 ml) and NMR measurements were conducted.

Table 31: Varied procedure, 60 min premixing of $^{t}Bu_3P$, $B(C_6F_5)_3$ and C_4F_9I.

shift [ppm]	0 (ES)	−62.3 (E)[a]	−124.9 (P)[b]	−125.6 (E)[a]	−126.2 (P)[b]	Δt [min]	χ(product)[c]	χ(educt)[c]	ln(χ(educt))[c]
integral	1	14.66	3.54	14.26	3.49	13	0.196	0.804	-0.218
	1	13.47	4.98	13.11	4.92	16	0.271	0.729	-0.317
	1	12.33	6.42	12.02	6.23	20	0.342	0.658	-0.418
	1	11.10	7.46	10.82	7.36	24	0.403	0.597	-0.516
	1	10.27	8.64	9.95	8.46	29	0.458	0.542	-0.613
	1	9.39	9.46	9.08	9.30	33	0.504	0.496	-0.701
	1	8.67	10.28	8.40	10.07	36	0.544	0.456	-0.785
	1	8.15	11.22	7.89	10.90	40	0.580	0.420	-0.867

[a] Educt signal, C_4F_9I. [b] Product signal, $C_{12}H_{14}F_9I$. [c] Calculated values.

Standard procedure C

Inside the glovebox, $^{t}Bu_3P$ (**5**) was dissolved in CH_2Cl_2 (0.80 ml) and one half (0.40 ml) of this solution was transferred into an NMR tube, which was enwrapped in aluminium foil and equipped with $CFCl_3$ in C_6D_6 as an external standard. Under red light, nonafluoro-1-iodobutane (**2**) was injected directly into the NMR tube. About one minute later, a solution of $B(C_6F_5)_3$ (**3**) mixed with 1-undecene (**18**) in CH_2Cl_2 was added. Overall 0.90 ml CH_2Cl_2 were injected into the NMR tube. The tube was sealed with a Young valve and NMR-measurements were conducted.

For the kinetic analysis, ^{19}F-NMR-spectra (relaxation delay = 8 s) were analysed. Four signals, two of educt and product each, were used for the calculation of its substance amount fraction.

8.6 NMR-experiment, 1.1 eq. 1-undecene

$^{t}Bu_3P$ (**5**) (1.8 mg, 0.0089 mmol, 5.1 mol%), 1-undecene (**18**) (29.8 mg, 0.193 mmol, 1.11 eq.), nonafluoro-1-iodobutane (**2**) (30.0 µl, 0.174 mmol, 1.00 eq.) and $B(C_6F_5)_3$ (**3**) (4.5 mg, 0.0088 mmol, 5.1 mol%) were reacted as described in Standard procedure C.

Table 32: Standard procedure, 1.1 equivalents of 1-undecene.

shift [ppm]	0 (ES)	−62.3 (E)[a]	−124.1 (P)[b]	−125.7 (E)[a]	−126.4 (P)[b]	Δt [min]	χ(product)[c]	χ(educt)[c]	ln(χ(educt))[c]
	1	188.31	52.21	183.28	53.48	11	0.221	0.779	-0.250
	1	162.51	60.84	157.21	59.46	15	0.273	0.727	-0.319
	1	154.76	73.44	149.61	74.23	18	0.327	0.673	-0.396
	1	141.75	82.84	137.51	82.17	22	0.371	0.629	-0.464
	1	139.04	96.15	134.54	94.38	26	0.411	0.589	-0.529
integral	1	127.75	101.30	123.59	100.37	30	0.445	0.555	-0.589
	1	114.06	103.07	109.76	100.35	34	0.476	0.524	-0.647
	1	119.14	120.53	115.29	117.99	38	0.504	0.496	-0.702
	1	109.27	120.76	105.03	118.13	42	0.527	0.473	-0.749
	1	104.54	126.68	98.91	125.53	46	0.554	0.446	-0.806
	1	97.25	129.27	93.95	127.74	50	0.573	0.427	-0.852

[a] Educt signal, C_4F_9I. [b] Product signal, $C_{12}H_{14}F_9I$. [c] Calculated values.

8.7 NMR-experiment, 2.0 eq. 1-undecene

$^{t}Bu_3P$ (**5**) (1.8 mg, 0.0086 mmol, 5.0 mol%), 1-undecene (**18**) (54.1 mg, 0.351 mmol, 2.02 eq.), nonafluoro-1-iodobutane (**2**) (30.0 µl, 0.174 mmol, 1.00 eq.) and $B(C_6F_5)_3$ (**3**) (4.5 mg, 0.0088 mmol, 5.1 mol%) were reacted as described in Standard procedure C.

Table 33: Standard procedure, 2.0 equivalents of 1-undecene.

shift [ppm]	0 (ES)	−62.3 (E)[a]	−124.1 (P)[b]	−125.7 (E)[a]	−126.4 (P)[b]	Δt [min]	χ(product)[c]	χ(educt)[c]	ln(χ(educt))[c]
integral	1	11.87	1.82	11.48	1.80	13	0.134	0.866	-0.144
	1	10.44	2.28	10.11	2.29	17	0.182	0.818	-0.201
	1	10.29	3.00	9.92	2.84	21	0.224	0.776	-0.254
	1	9.77	3.57	9.48	3.61	25	0.272	0.728	-0.317
	1	9.05	4.03	8.74	3.94	30	0.309	0.691	-0.370
	1	8.74	4.48	8.45	4.49	34	0.343	0.657	-0.420
	1	8.24	4.92	7.97	4.66	38	0.371	0.629	-0.464
	1	8.18	5.38	7.92	5.32	42	0.399	0.601	-0.510
	1	7.67	5.66	7.44	5.57	47	0.426	0.574	-0.556
	1	7.46	6.10	7.21	5.99	51	0.452	0.548	-0.601

[a] Educt signal, C_4F_9I. [b] Product signal, $C_{12}H_{14}F_9I$. [c] Calculated values.

8.8 NMR-experiment, 1.1 eq. 1-undecene, 15 mol% $^{t}Bu_3P$

Analogous to Standard procedure C, $^{t}Bu_3P$ (**5**) (5.3 mg, 0.026 mmol, 15 mol%) was dissolved in CH_2Cl_2 (0.50 ml) and transferred into a pointed bottom flask. $B(C_6F_5)_3$ (**3**) (4.5 mg, 0.0088 mmol, 5.1 mol%) and 1-undecene (**18**) (30.1 mg, 0.195 mmol, 1.12 eq.) were dissolved in CH_2Cl_2 and transferred into an amber glass NMR tube. Nonafluoro-1-iodobutane (**2**) (30.0 µl, 0.174 mmol, 1.00 eq.) was added. Outside the glovebox, the $^{t}Bu_3P$ solution was added inertly under argon. NMR measurements were conducted.

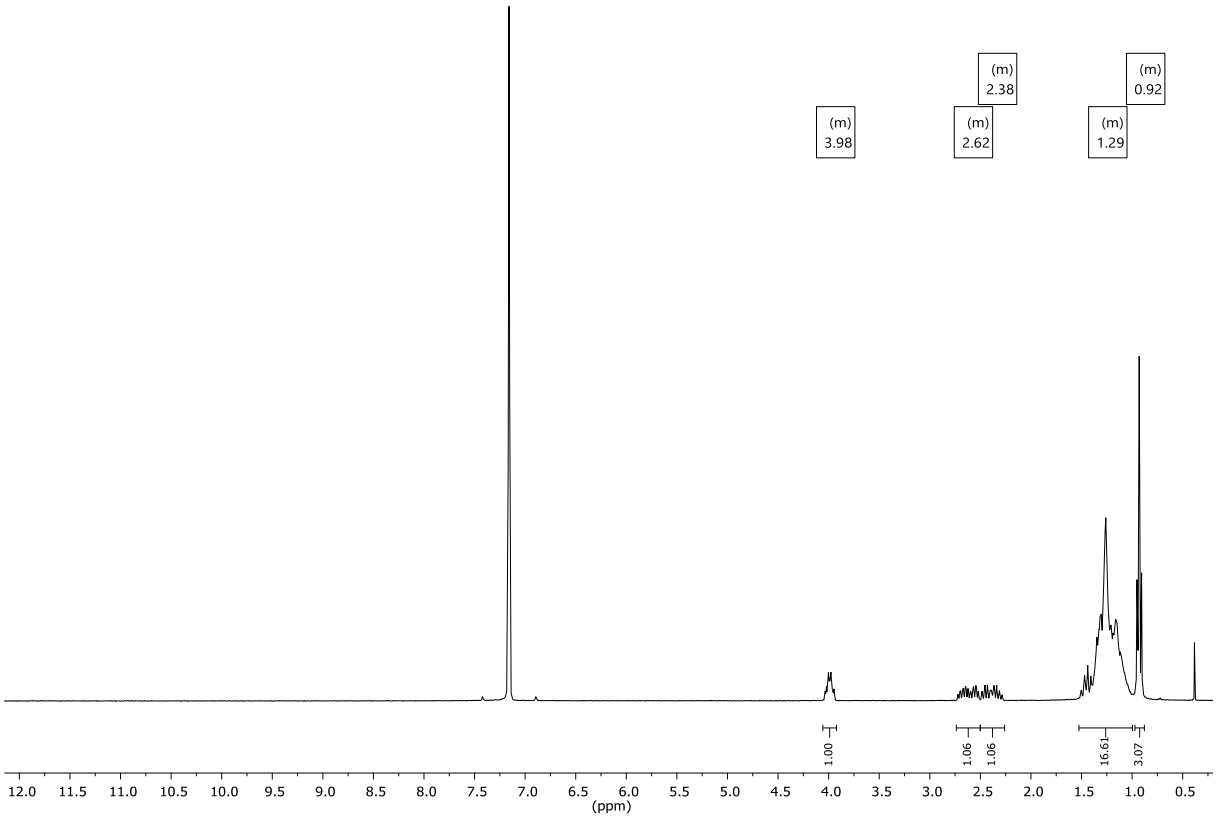
Table 34: Varied procedure, 1.1 eq. 1-undecene, 15 mol% $^{t}Bu_3P$.

shift [ppm]	0 (ES)	−62.3 (E)[a]	−124.1 (P)[b]	−125.7 (E)[a]	−126.4 (P)[b]	Δt [min]	χ(product)[c]	χ(educt)[c]	ln(χ(educt))[c]
	1	144.67	52.70	148.79	52.78	7	0.264	0.736	-0.307
	1	142.17	77.68	146.52	76.44	11	0.348	0.652	-0.428
	1	121.82	88.10	127.28	86.60	15	0.412	0.588	-0.531
	1	112.52	102.89	117.42	100.67	19	0.470	0.530	-0.634
	1	104.25	114.05	109.79	110.96	23	0.512	0.488	-0.718
	1	95.58	122.86	102.43	121.85	27	0.553	0.447	-0.805
integral	1	87.31	128.89	93.02	126.21	31	0.586	0.414	-0.882
	1	77.23	130.81	84.47	128.35	35	0.616	0.384	-0.957
	1	77.34	147.11	84.90	144.21	39	0.642	0.358	-1.028
	1	70.17	147.27	77.14	145.03	43	0.665	0.335	-1.093
	1	69.22	160.21	76.47	156.70	47	0.685	0.315	-1.155
	1	61.59	157.65	68.42	153.58	51	0.705	0.295	-1.222
	1	61.53	169.36	69.04	167.42	55	0.721	0.279	-1.275

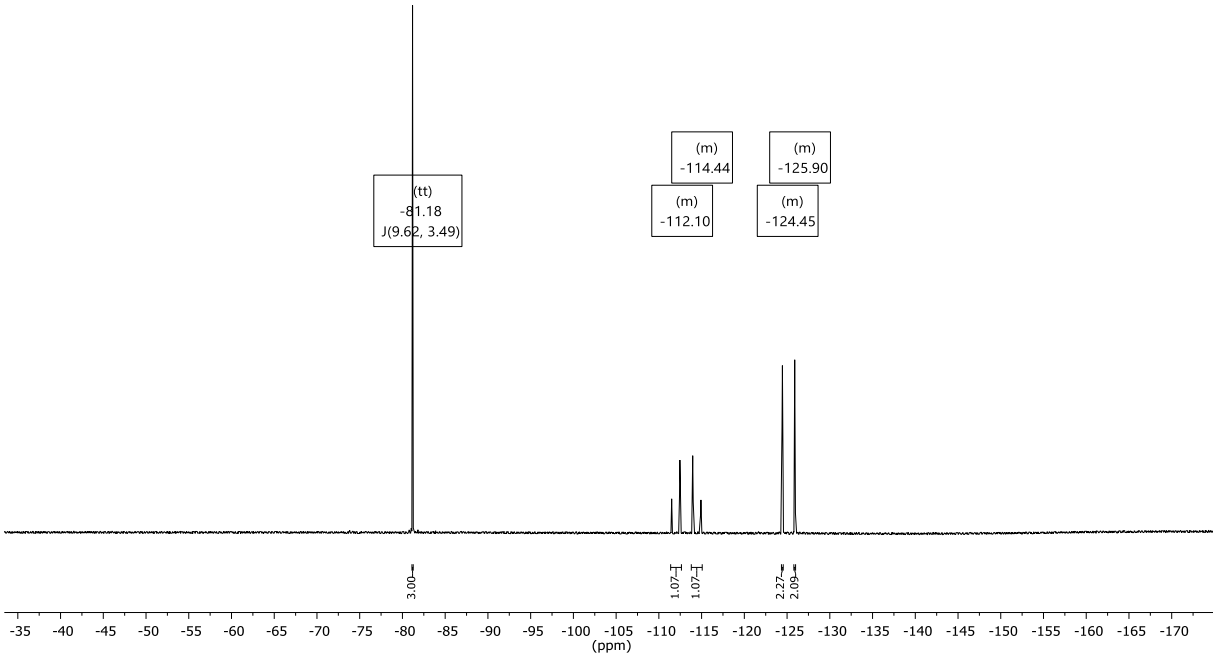
[a] Educt signal, C_4F_9I. [b] Product signal, $C_{12}H_{14}F_9I$. [c] Calculated values.

Spectroscopic data for iodoperfluoroalkylation product of 1-undecene (1,1,1,2,2,3,3,4,4-nonafluoro-6-iodopentadecane) (**26**) are as follows:

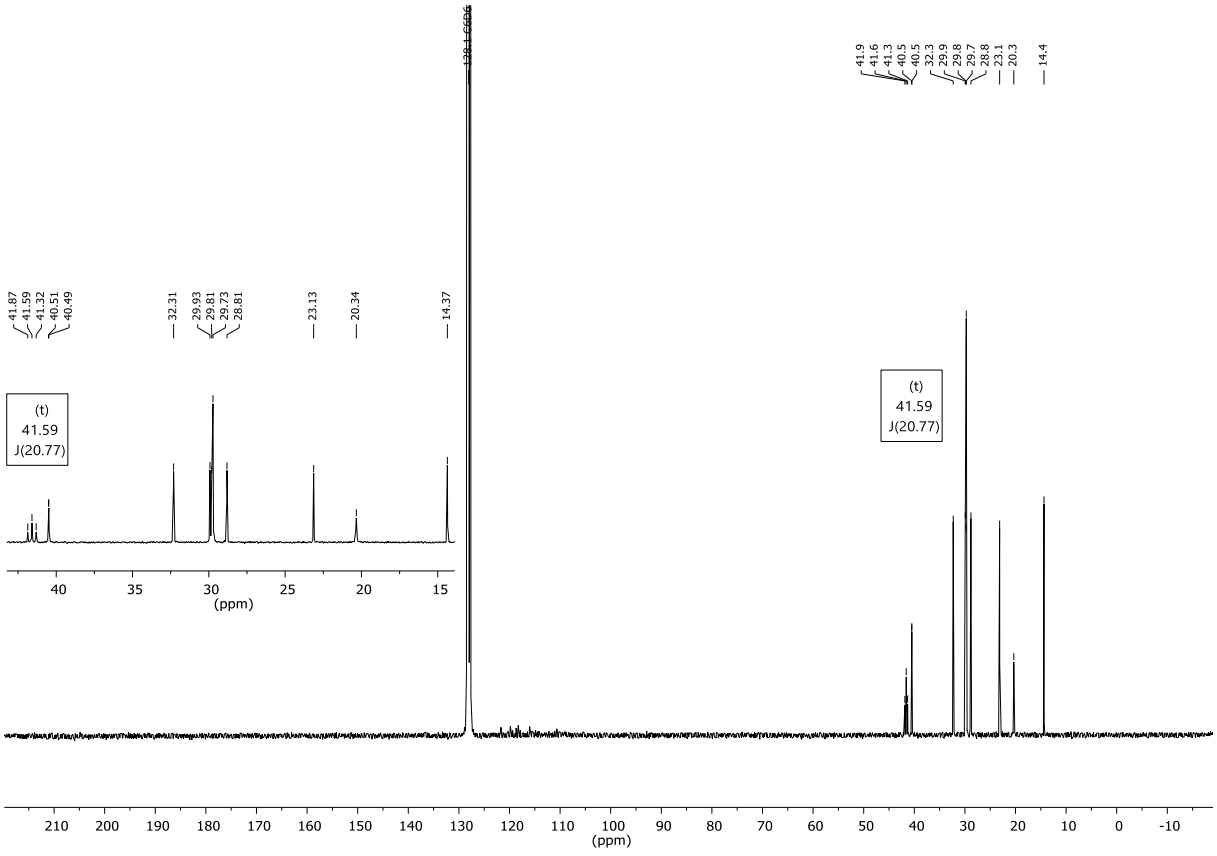
^{1}H-NMR (300 MHz, C_6D_6) δ [ppm] 4.07 - 3.91 (m, 1H), 2.76 - 2.48 (m, 1H), 2.52 - 2.25 (m, 1H), 1.53 - 1.00 (m, 17H), 0.99 - 0.87 (m, 2H).**^{19}F-NMR** (282 MHz, C_6D_6) δ [ppm] −81.2 (tt, J = 9.6, 3.5 Hz), −111.4 - −112.7 (m), −113.8 - −115.0 (m), −124.3 - −124.6 (m), −125.8 - −126.0 (m). **^{13}C-NMR** (75 MHz, C_6D_6) δ [ppm] 41.6 ($-H_2CCF_2R_F$, t, $^{2}J_{CF}$ = 20.8 Hz), 40.51, 40.49, 32.31, 29.93, 29.81, 29.73, 28.81, 23.13, 20.34, 14.37. **IR** (film on NaCl), $\tilde{\nu}$ [cm^{-1}] 2927, 2857, 1467, 1351, 1235, 1136, 1016, 880, 724, 553.



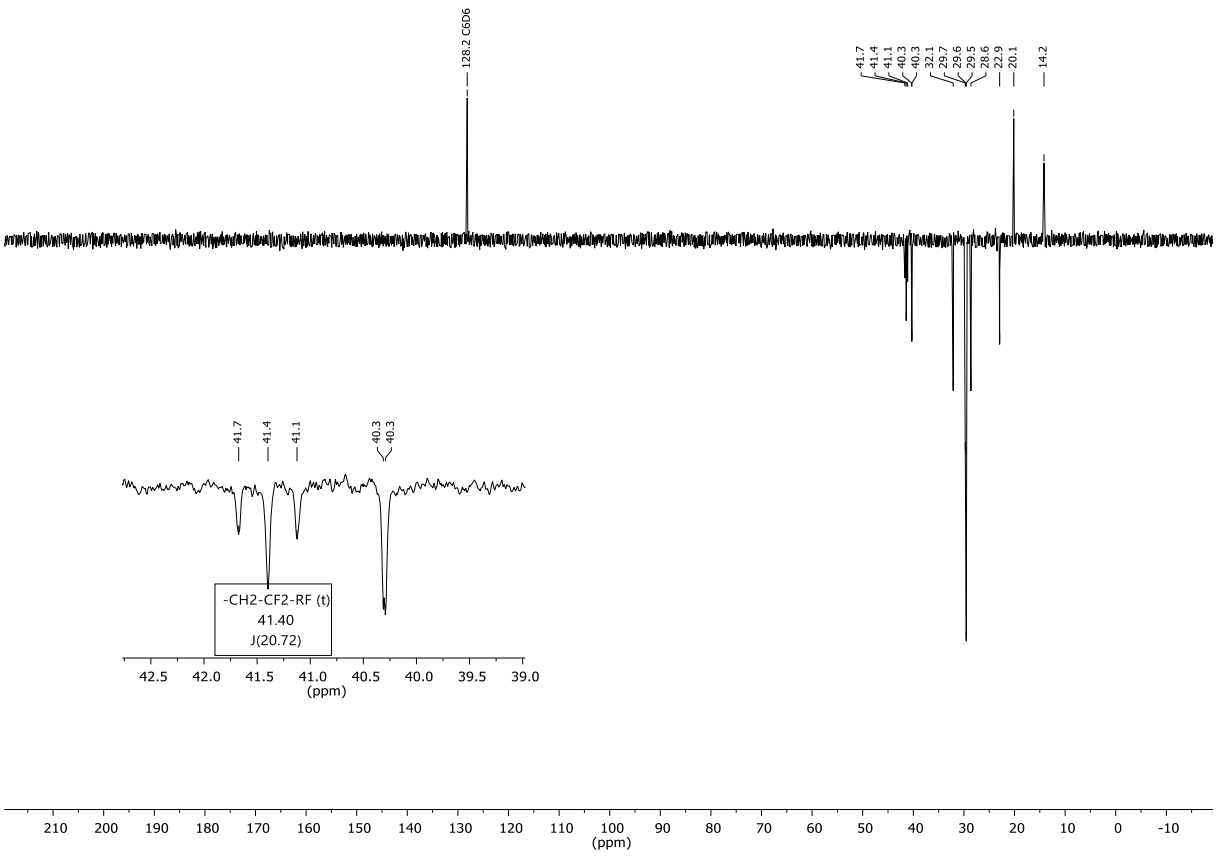
NMR-spectrum 52: ^{1}H (300 MHz, C_6D_6) of 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodopentadecane.



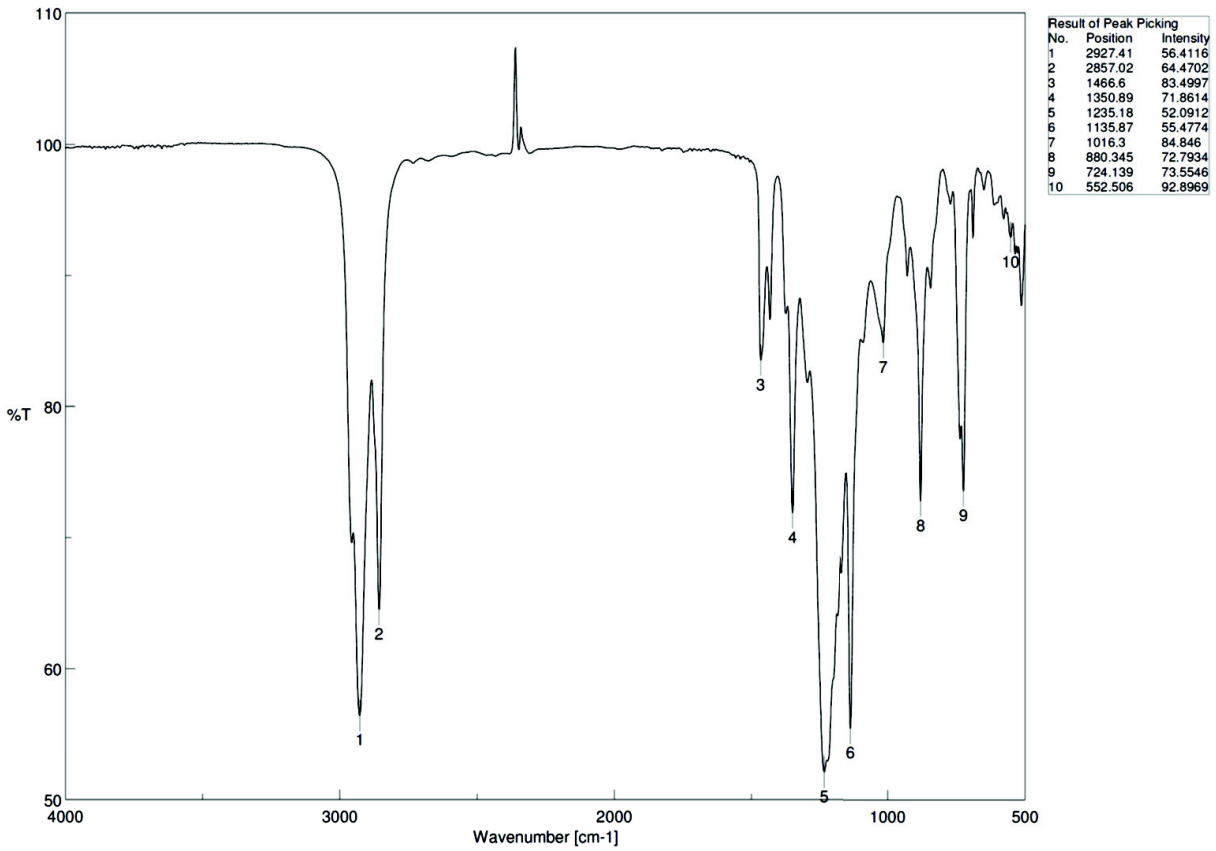
NMR-spectrum 53: ^{19}F (282 MHz, C_6D_6) of 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodopentadecane.



NMR-spectrum 54: ^{13}C (75 MHz, C_6D_6) of 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodopentadecane.



NMR-spectrum 55: DEPT (75 MHz, C_6D_6) of 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodopentadecane.



IR-spectrum (film on NaCl) 2: 1,1,1,2,2,3,3,4,4-nonafluoro-6-iodopentadecane.

8.9 Calculations

For our calculations we used the presented values

To examine zeroth order behaviour, we used the corresponding integrated rate law.

$$[A]_t = [A]_0 - k \cdot t \quad \text{or} \quad [A]_t - [A]_0 = -k \cdot t$$

To examine first order behaviour, we used the corresponding integrated rate law.

$$\frac{[A]_t}{[A]_0} = e^{-k \cdot t} \quad \text{or} \quad \ln\left(\frac{[A]_t}{[A]_0}\right) = -k \cdot t$$

To examine second order behaviour, we used the corresponding integrated rate law.

$$\frac{1}{[A]_0} - \frac{1}{[A]_t} = -k \cdot t$$

Throughout GC experiments we measured the conversion of vinylcyclohexane, hence we had to extrapolate from the values calculated for vinylcyclohexane to nonafluoro-1-iodobutane concentrations. For this purpose, the consumed amount of substance of vinylcyclohexane was offset with the initial amount of nonafluoro-1-iodobutane. For a better comparability, similar time spans should be incorporated.

8.9.1 GC experiment, different fits for standard curve

Table 35: Calculated values for the depicted fits.

reaction time [min]	$[C_4F_9I]_0$ [mol/l]	$[C_4F_9I]$ [mol/l]	$[C_4F_9I]-[C_4F_9I]_0$ [mol/l]	$\ln([C_4F_9I]/[C_4F_9I]_0)$	$1/[C_4F_9I]_0-1/[C_4F_9I]$ [l/mol]
20	0.25893	0.17201	-0.08692	-0.40901	-1.95156
20	0.25893	0.17139	-0.08754	-0.41261	-1.97256
20	0.25893	0.16998	-0.08895	-0.42086	-2.02089
30	0.25893	0.15394	-0.10499	-0.52	-2.63399
30	0.25893	0.14823	-0.1107	-0.55777	-2.88403
30	0.25893	0.1478	-0.11113	-0.56072	-2.90399
40	0.25893	0.1325	-0.12643	-0.66995	-3.68488
40	0.25893	0.13231	-0.12662	-0.6714	-3.69588
40	0.25893	0.13196	-0.12698	-0.6741	-3.71627
50	0.25893	0.11909	-0.13984	-0.77667	-4.53489
50	0.25893	0.11618	-0.14275	-0.80144	-4.74546
50	0.25893	0.11735	-0.14158	-0.79143	-4.65974
60	0.25893	0.10469	-0.15424	-0.90558	-5.6902
60	0.25893	0.10431	-0.15462	-0.90919	-5.72476
60	0.25893	0.10627	-0.15267	-0.89063	-5.5484

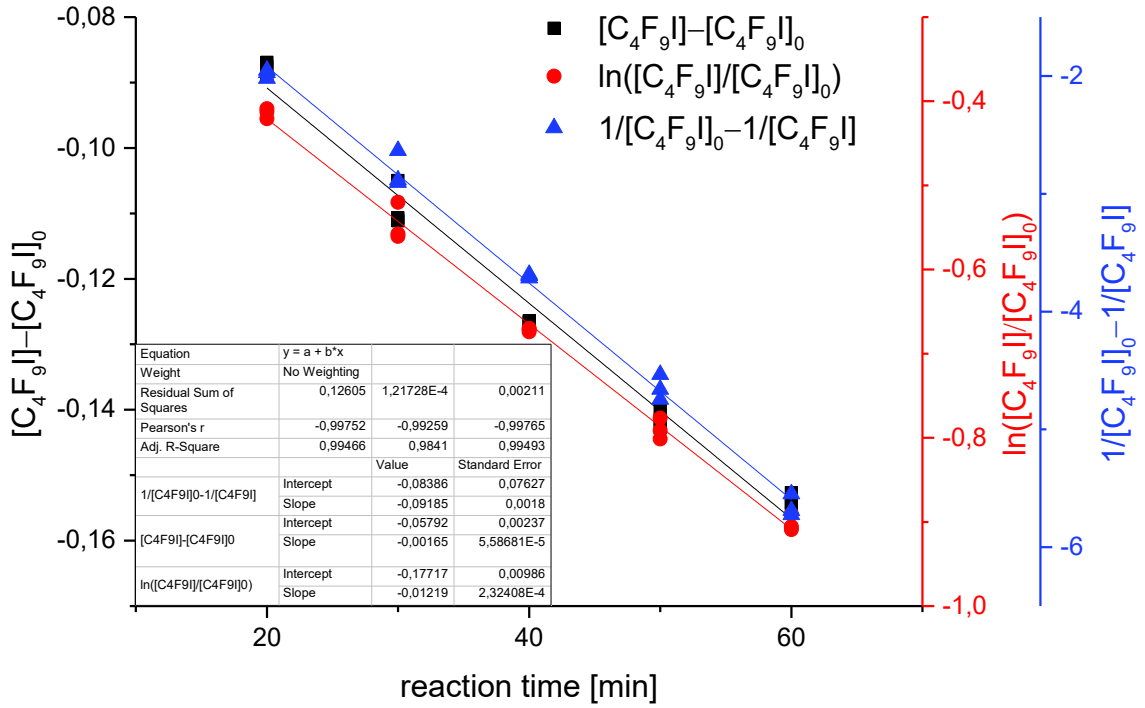
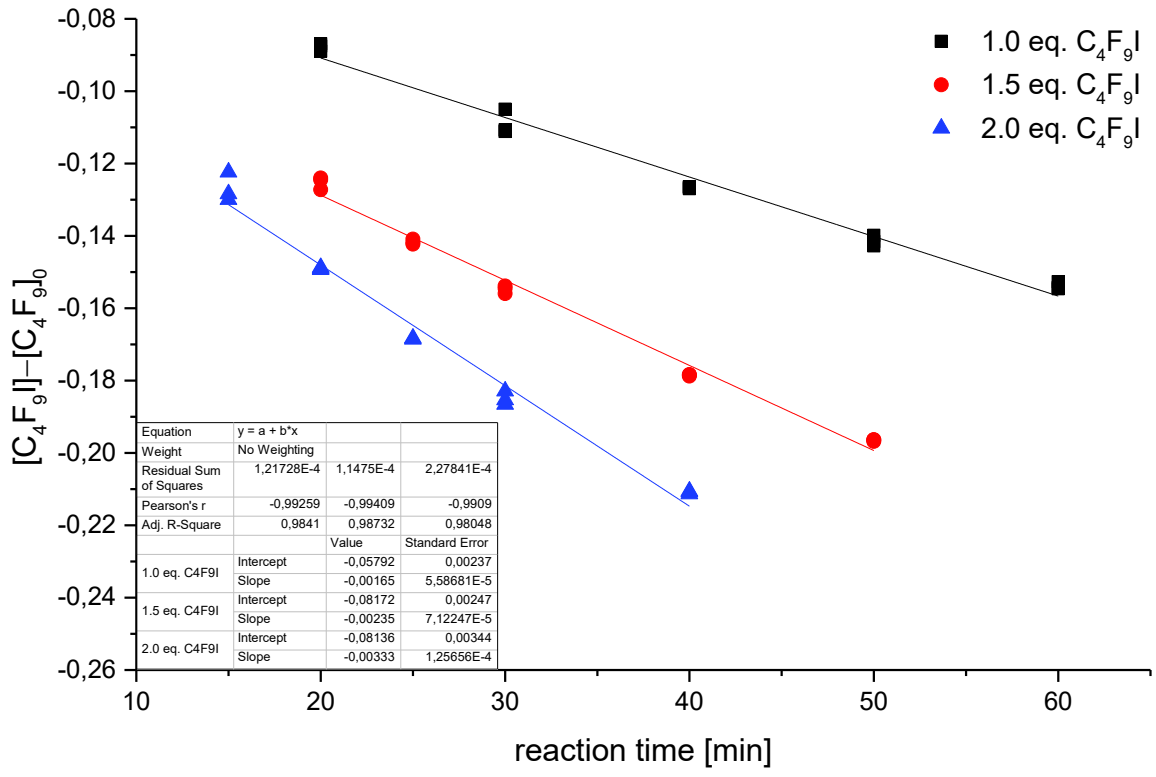


Figure 4: GC experiment, zeroth, first and second order fit for standard curve.

8.9.2 GC-experiments, variation of C_4F_9I

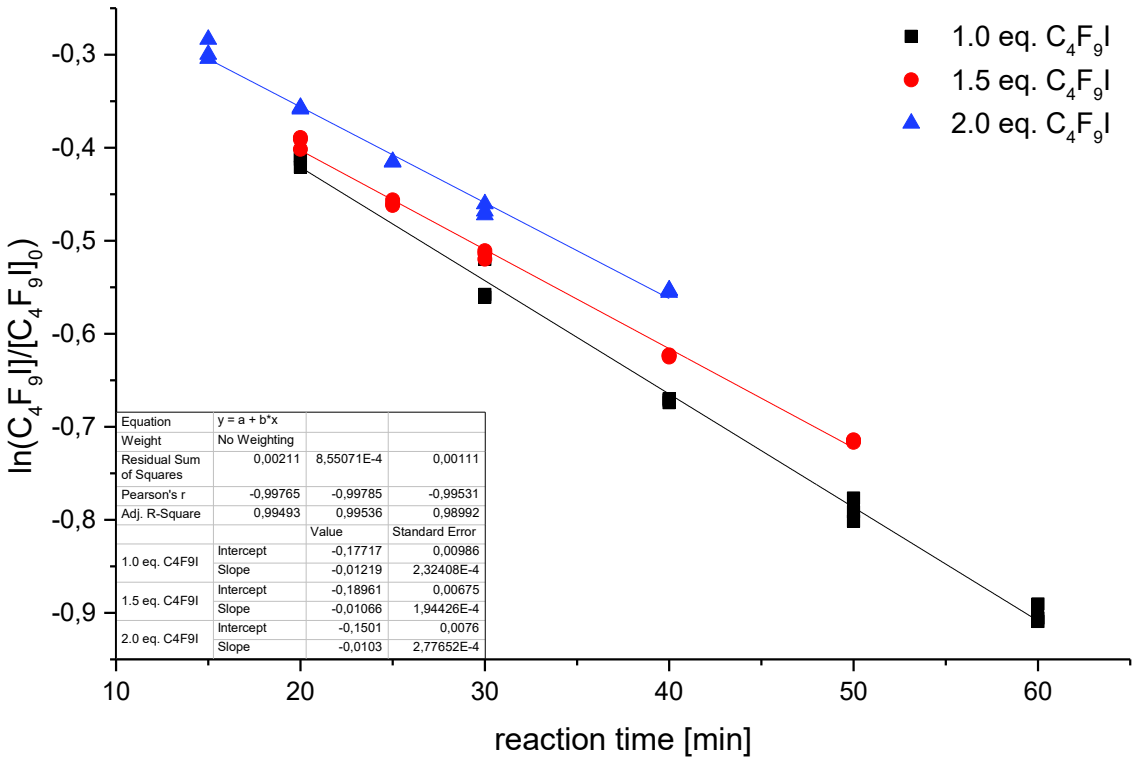
Table 36: Calculated values for a zeroth, first and second order fit.

reaction time [min]	$[C_4F_9I]_0$ [mol/l]	$[C_4F_9I]$ [mol/l]	$[C_4F_9I]-[C_4F_9I]_0$ [mol/l]	$\ln([C_4F_9I]/[C_4F_9I]_0)$	$1/[C_4F_9I]_0-1/[C_4F_9I]$ [l/mol]
1.0 eq. C_4F_9I					
20	0.25893	0.17201	-0.08692	-0.40901	-1.95156
20	0.25893	0.17139	-0.08754	-0.41261	-1.97256
20	0.25893	0.16998	-0.08895	-0.42086	-2.02089
30	0.25893	0.15394	-0.10499	-0.52	-2.63399
30	0.25893	0.14823	-0.1107	-0.55777	-2.88403
30	0.25893	0.1478	-0.11113	-0.56072	-2.90399
40	0.25893	0.1325	-0.12643	-0.66995	-3.68488
40	0.25893	0.13231	-0.12662	-0.6714	-3.69588
40	0.25893	0.13196	-0.12698	-0.6741	-3.71627
50	0.25893	0.11909	-0.13984	-0.77667	-4.53489
50	0.25893	0.11618	-0.14275	-0.80144	-4.74546
50	0.25893	0.11735	-0.14158	-0.79143	-4.65974
60	0.25893	0.10469	-0.15424	-0.90558	-5.6902
60	0.25893	0.10431	-0.15462	-0.90919	-5.72476
60	0.25893	0.10627	-0.15267	-0.89063	-5.5484
1.5 eq. C_4F_9I					
20	0.38466	0.26067	-0.12399	-0.38911	-1.23659
20	0.38466	0.26013	-0.12453	-0.39118	-1.24454
20	0.38466	0.25744	-0.12722	-0.40158	-1.28474
25	0.38466	0.24377	-0.14089	-0.45612	-1.50247
25	0.38466	0.24281	-0.14185	-0.46009	-1.51876
25	0.38466	0.24236	-0.1423	-0.46194	-1.52642
30	0.38466	0.23082	-0.15385	-0.51074	-1.73276
30	0.38466	0.23011	-0.15455	-0.51379	-1.746
30	0.38466	0.22873	-0.15593	-0.51981	-1.77223
40	0.38466	0.20635	-0.17832	-0.62281	-2.24654
40	0.38466	0.20591	-0.17876	-0.62495	-2.2569
40	0.38466	0.2062	-0.17846	-0.62351	-2.24992
50	0.38466	0.18834	-0.19632	-0.71413	-2.70991
50	0.38466	0.18821	-0.19645	-0.71479	-2.71342
50	0.38466	0.18787	-0.19679	-0.71659	-2.72302
2.0 eq. C_4F_9I					
15	0.49577	0.36741	-0.12836	-0.29963	-0.70469
15	0.49577	0.37341	-0.12236	-0.28344	-0.66096
15	0.49577	0.36581	-0.12996	-0.30401	-0.71662
20	0.49577	0.34643	-0.14934	-0.35843	-0.86953
20	0.49577	0.34703	-0.14874	-0.3567	-0.86452
20	0.49577	0.34672	-0.14905	-0.3576	-0.86711
25	0.49577	0.32746	-0.16831	-0.41473	-1.0367
25	0.49577	0.32719	-0.16858	-0.41557	-1.03927
25	0.49577	0.32719	-0.16858	-0.41558	-1.03929
30	0.49577	0.31042	-0.18535	-0.46818	-1.20436
30	0.49577	0.31285	-0.18292	-0.46039	-1.17937
30	0.49577	0.30918	-0.18659	-0.47219	-1.21732
40	0.49577	0.2852	-0.21057	-0.55292	-1.48924
40	0.49577	0.28446	-0.21131	-0.55553	-1.49841
40	0.49577	0.28497	-0.2108	-0.55372	-1.49204



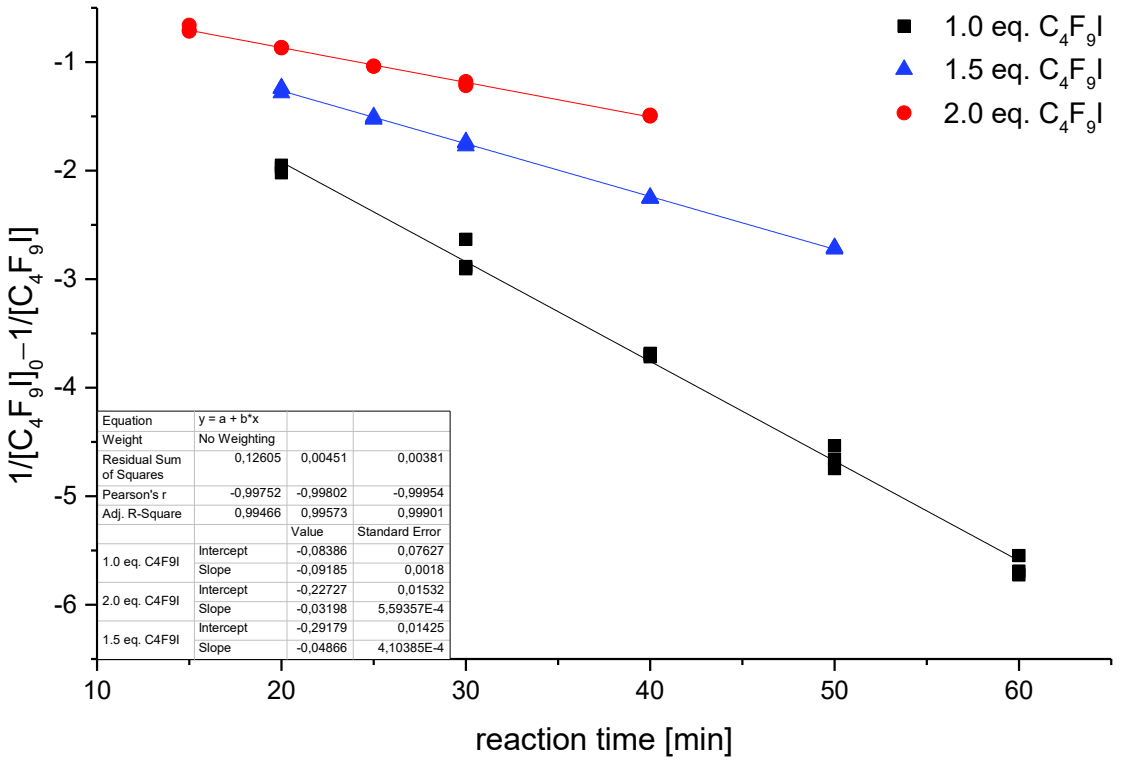
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1,21728E-4	1,1475E-4	2,27841E-4
Pearson's r	-0,99259	-0,99409	-0,9909
Adj. R-Square	0,9841	0,98732	0,98048
		Value	Standard Error
1.0 eq. C4F9I	Intercept	-0,05792	0,00237
	Slope	-0,00165	5,58681E-5
1.5 eq. C4F9I	Intercept	-0,08172	0,00247
	Slope	-0,00235	7,12247E-5
2.0 eq. C4F9I	Intercept	-0,08136	0,00344
	Slope	-0,00333	1,25656E-4

Figure 5: GC experiment, zeroth order fit for a variation of C_4F_9I.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,00211	8,55071E-4	0,00111
Pearson's r	-0,99765	-0,99785	-0,99531
Adj. R-Square	0,99493	0,99536	0,98992
		Value	Standard Error
1.0 eq. C4F9I	Intercept	-0,17717	0,00986
	Slope	-0,01219	2,32408E-4
1.5 eq. C4F9I	Intercept	-0,18961	0,00675
	Slope	-0,01066	1,94426E-4
2.0 eq. C4F9I	Intercept	-0,1501	0,0076
	Slope	-0,0103	2,77652E-4

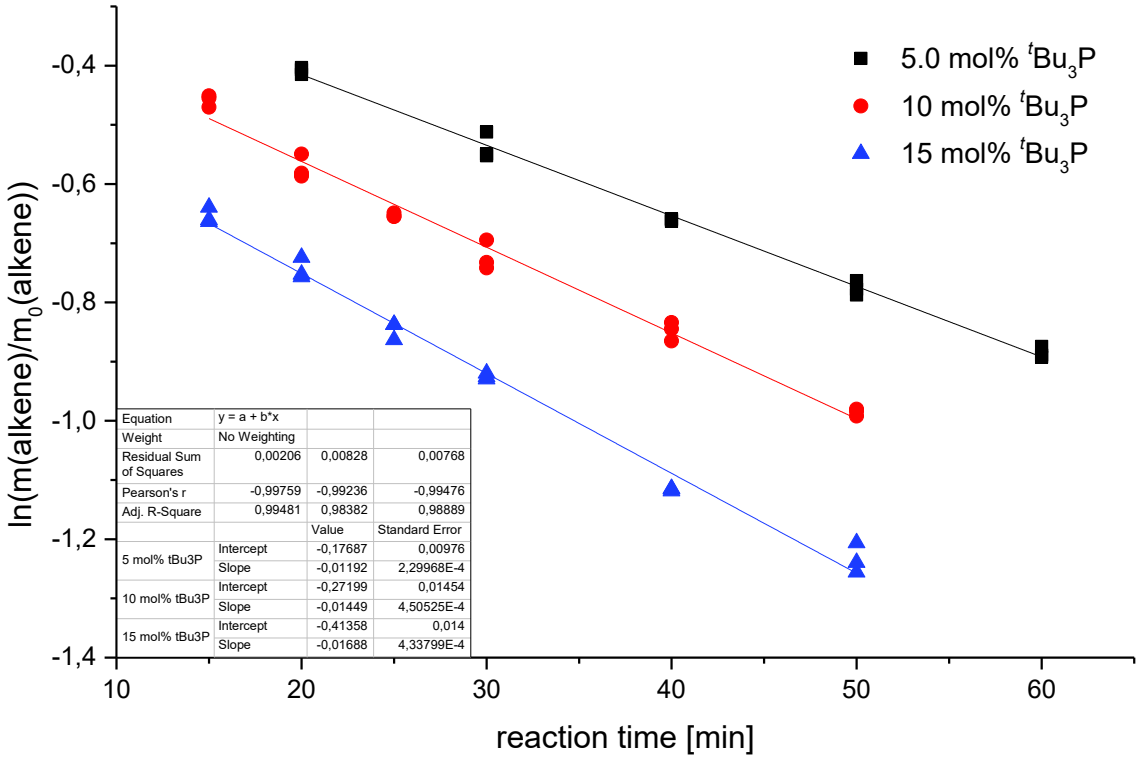
Figure 6: GC experiment, first order fit for a variation of C_4F_9I.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,12605	0,00451	0,00381
Pearson's r	-0,99752	-0,99802	-0,99954
Adj. R-Square	0,99466	0,99573	0,99901
		Value	Standard Error
1.0 eq. C4F9I	Intercept	-0,08386	0,07627
	Slope	-0,09185	0,0018
2.0 eq. C4F9I	Intercept	-0,22727	0,01532
	Slope	-0,03198	5,59357E-4
1.5 eq. C4F9I	Intercept	-0,29179	0,01425
	Slope	-0,04866	4,10385E-4

Figure 7: GC experiment, second order fit for a variation of C_4F_9I.

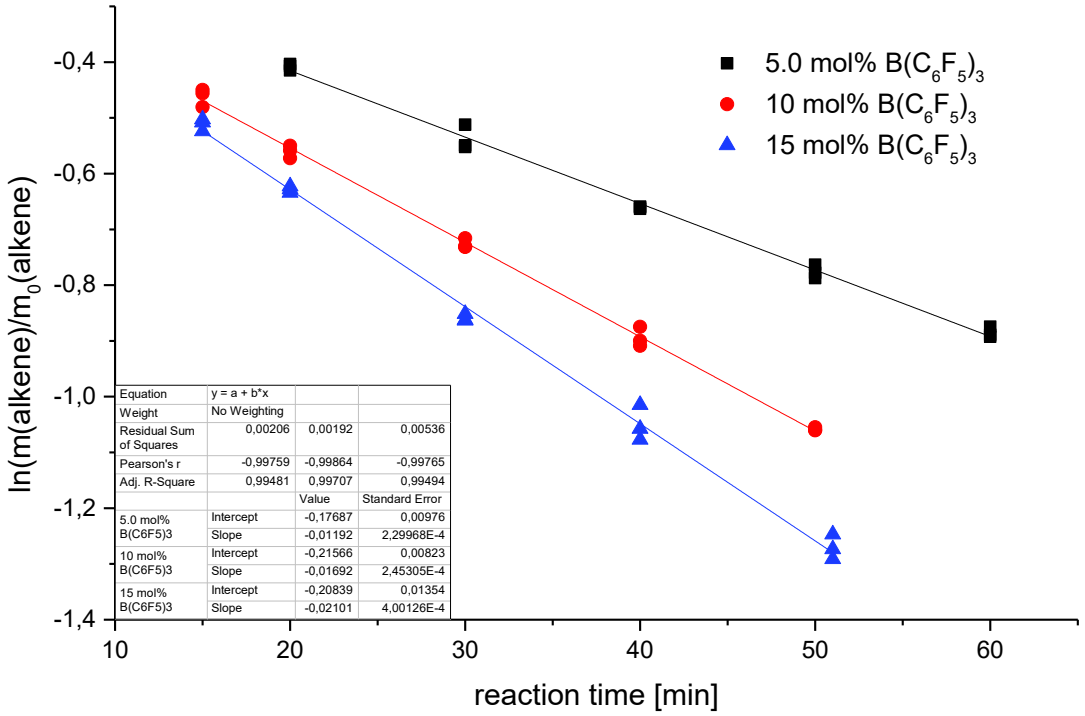
8.9.3 GC-experiments, variation of $^tBu_3P$



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,00206	0,00828	0,00768
Pearson's r	-0,99759	-0,99236	-0,99476
Adj. R-Square	0,99481	0,98382	0,98889
		Value	Standard Error
5 mol% tBu3P	Intercept	-0,17687	0,00976
	Slope	-0,01192	2,29968E-4
10 mol% tBu3P	Intercept	-0,27199	0,01454
	Slope	-0,01449	4,50525E-4
15 mol% tBu3P	Intercept	-0,41358	0,014
	Slope	-0,01688	4,33799E-4

Figure 8: GC experiment, first order fit for a variation of $^tBu_3P$.

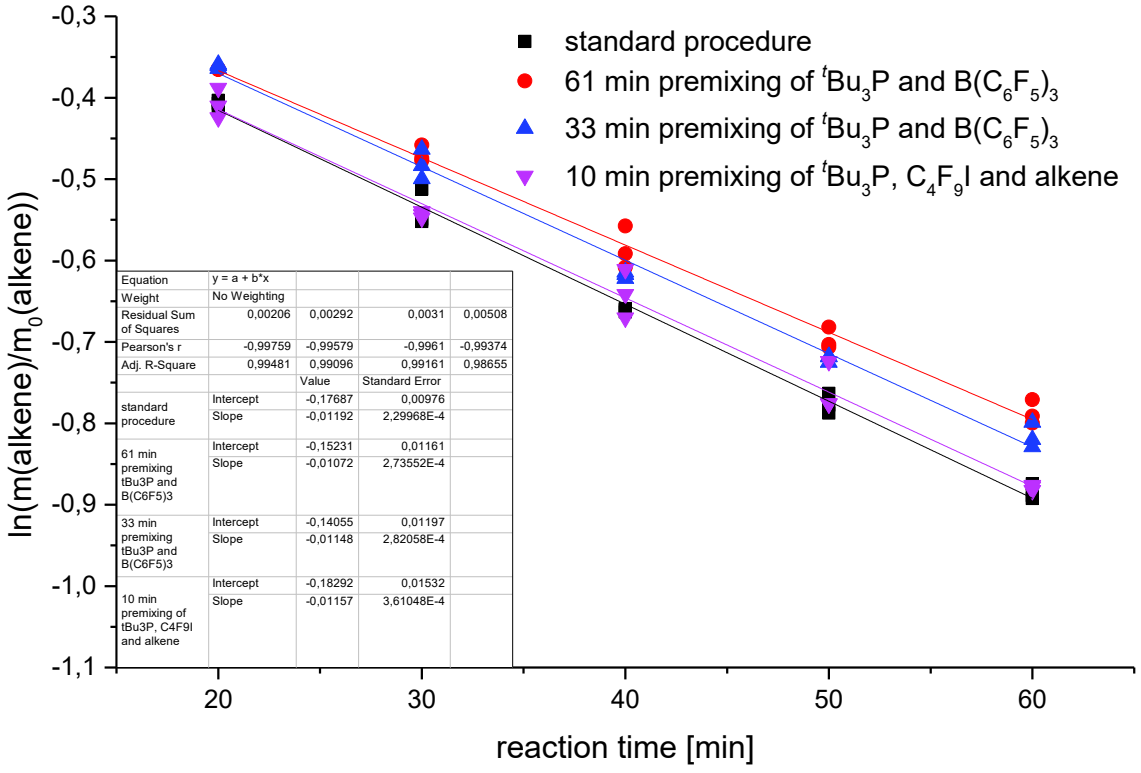
8.9.4 GC-experiments, variation of $B(C_6F_5)_3$



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,00206	0,00192	0,00536
Pearson's r	-0,99759	-0,99864	-0,99765
Adj. R-Square	0,99481	0,99707	0,99494
		Value	Standard Error
5.0 mol% B(C6F5)3	Intercept	-0,17687	0,00976
	Slope	-0,01192	2,29968E-4
10 mol% B(C6F5)3	Intercept	-0,21566	0,00823
	Slope	-0,01692	2,45305E-4
15 mol% B(C6F5)3	Intercept	-0,20839	0,01354
	Slope	-0,02101	4,00126E-4

Figure 9: GC experiment, first order fit for a variation of $B(C_6F_5)_3$.

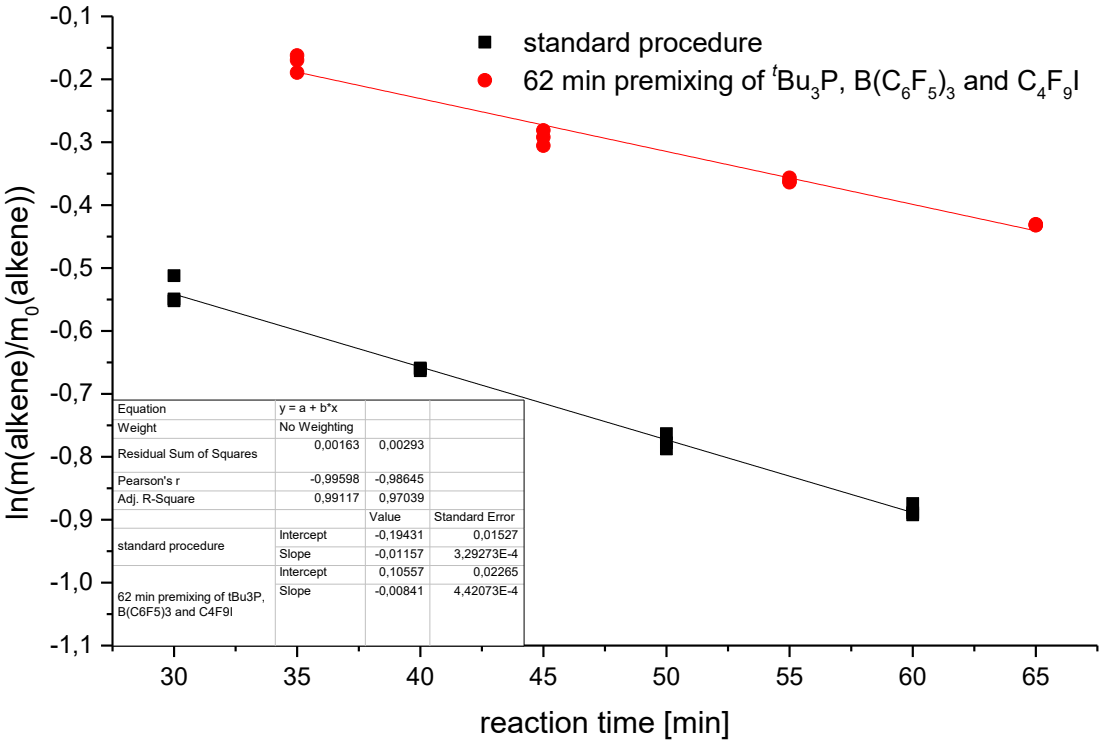
8.9.5 GC-experiments, varied procedures



Equation	y = a + b*x			
Weight	No Weighting			
Residual Sum of Squares	0,00206	0,00292	0,0031	0,00508
Pearson's r	-0,99759	-0,99579	-0,9961	-0,99374
Adj. R-Square	0,99481	0,99096	0,99161	0,98655
		Value	Standard Error	
standard procedure	Intercept	-0,17687	0,00976	
	Slope	-0,01192	2,29968E-4	
61 min premixing tBu3P and B(C6F5)3	Intercept	-0,15231	0,01161	
	Slope	-0,01072	2,73552E-4	
33 min premixing tBu3P and B(C6F5)3	Intercept	-0,14055	0,01197	
	Slope	-0,01148	2,82058E-4	
10 min premixing of tBu3P, C4F9I and alkene	Intercept	-0,18292	0,01532	
	Slope	-0,01157	3,61048E-4	

Figure 10: GC experiment, first order fit for a variation of $B(C_6F_5)_3$.

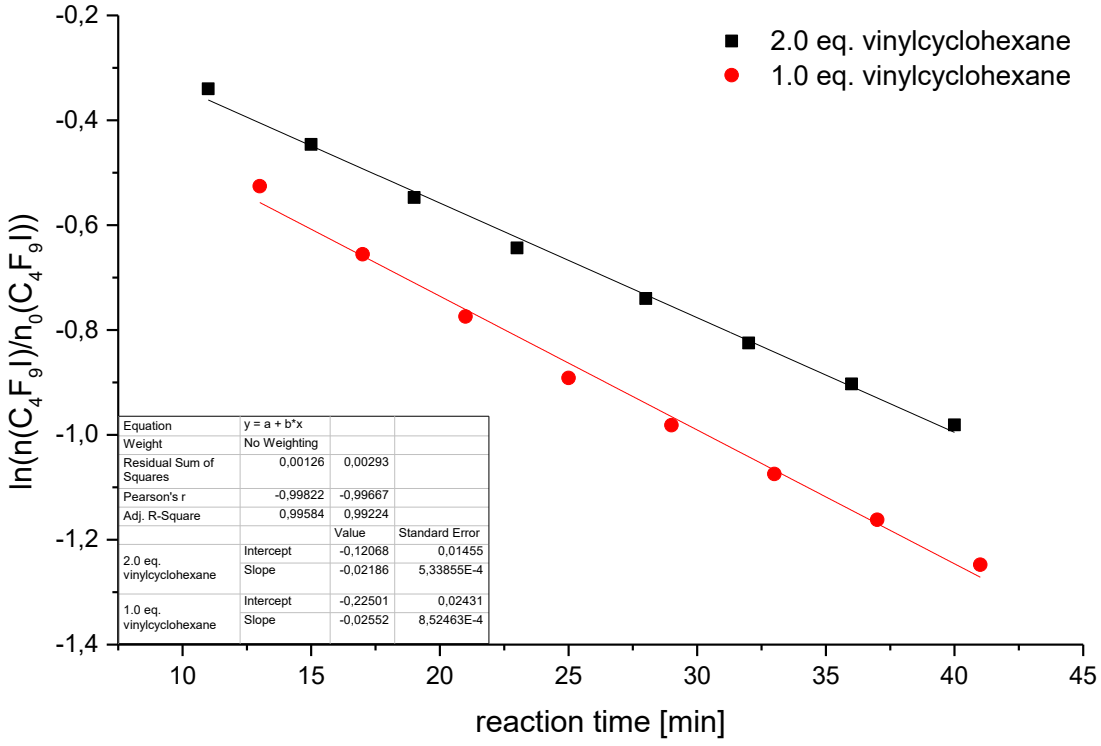
8.9.6 GC-experiments, 62 min premixing of $^{t}Bu_3P$, $B(C_6F_5)_3$ and C_4F_9I



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,00163	0,00293	
Pearson's r	-0,99598	-0,98645	
Adj. R-Square	0,99117	0,97039	
		Value	Standard Error
standard procedure	Intercept	-0,19431	0,01527
	Slope	-0,01157	3,29273E-4
62 min premixing of tBu3P, B(C6F5)3 and C4F9I	Intercept	0,10557	0,02265
	Slope	-0,00841	4,42073E-4

Figure 11: GC experiment, 62 min premixing of $^{t}Bu_3P$, $B(C_6F_5)_3$ and C_4F_9I.

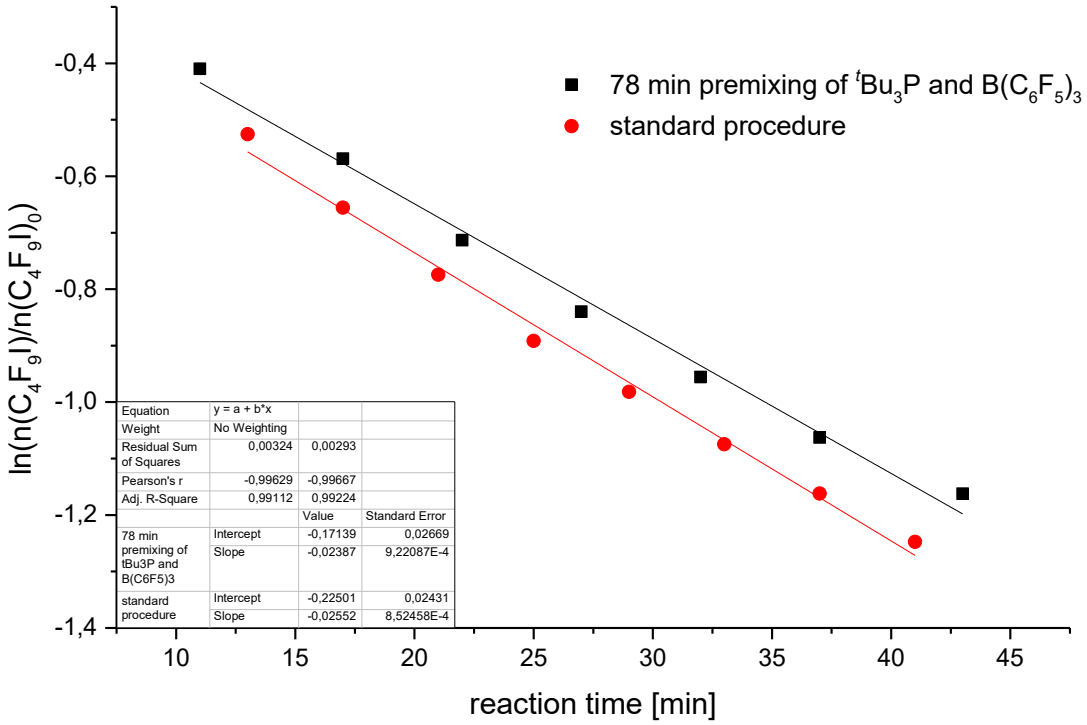
8.9.7 NMR-experiments, variation of vinylcyclohexane



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,00126	0,00293	
Pearson's r	-0,99822	-0,99667	
Adj. R-Square	0,99584	0,99224	
		Value	Standard Error
2.0 eq. vinylcyclohexane	Intercept	-0,12068	0,01455
	Slope	-0,02186	5,33855E-4
1.0 eq. vinylcyclohexane	Intercept	-0,22501	0,02431
	Slope	-0,02552	8,52463E-4

Figure 12: NMR-experiments, variation of vinylcyclohexane, C_4F_9I fit.

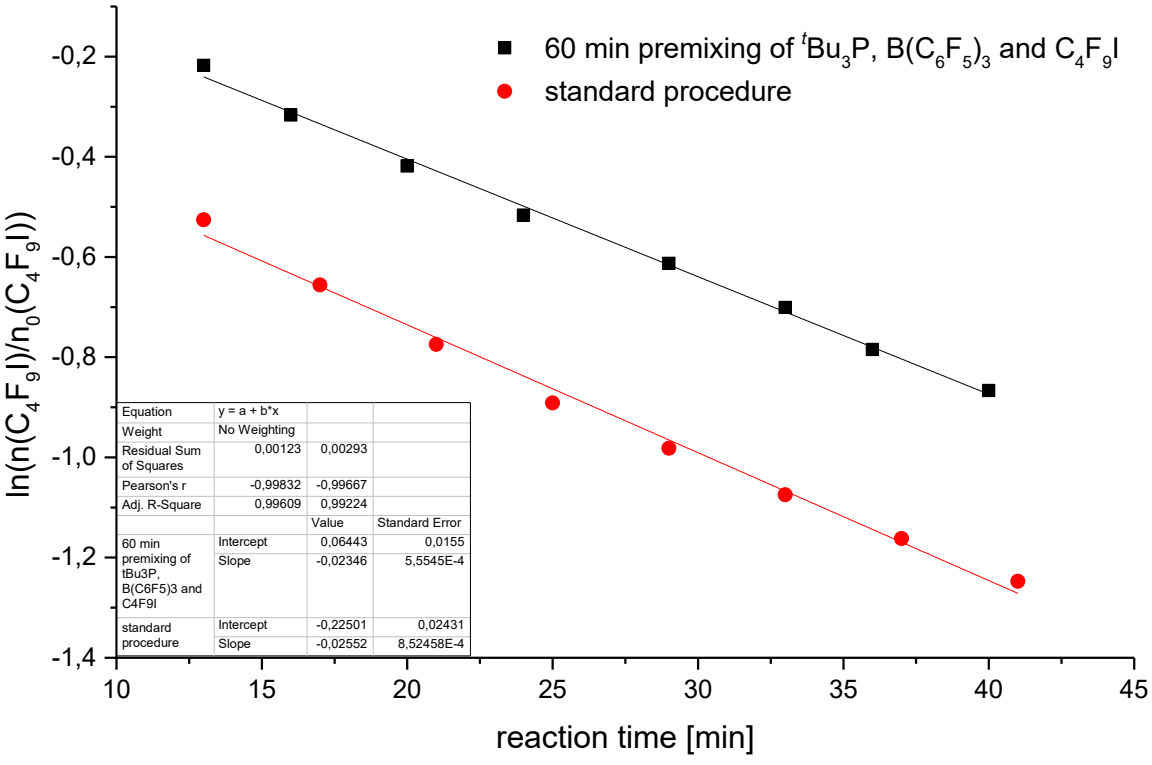
8.9.8 NMR-experiments, 78 min premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,00324	0,00293	
Pearson's r	-0,99629	-0,99667	
Adj. R-Square	0,99112	0,99224	
		Value	Standard Error
78 min premixing of tBu3P and B(C6F5)3	Intercept	-0,17139	0,02669
	Slope	-0,02387	9,22087E-4
standard procedure	Intercept	-0,22501	0,02431
	Slope	-0,02552	8,52458E-4

Figure 13: NMR-experiments, 78 min premixing of $^{t}Bu_3P$ and $B(C_6F_5)_3$. Substrate: vinylcyclohexane.

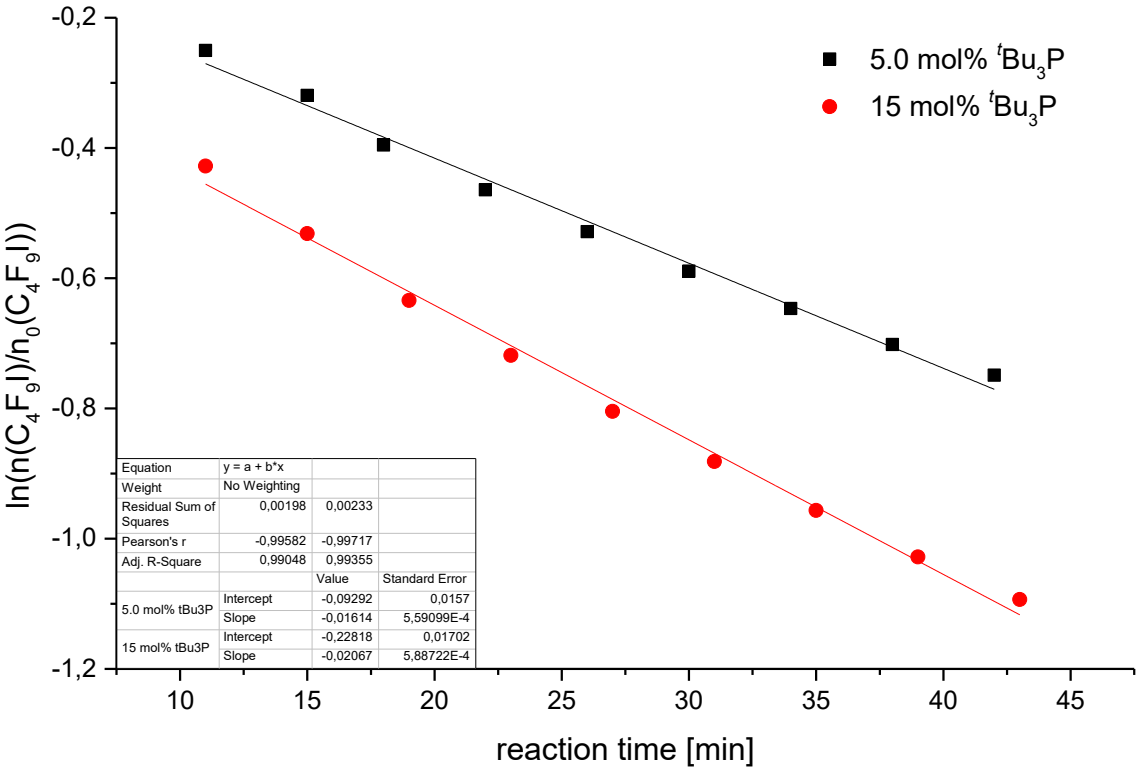
8.9.9 NMR-experiments, 60 min premixing of $^{t}Bu_3P$, $B(C_6F_5)_3$ and C_4F_9I



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,00123	0,00293	
Pearson's r	-0,99832	-0,99667	
Adj. R-Square	0,99609	0,99224	
		Value	Standard Error
60 min premixing of tBu3P, B(C6F5)3 and C4F9I	Intercept	0,06443	0,0155
	Slope	-0,02346	5,5545E-4
standard procedure	Intercept	-0,22501	0,02431
	Slope	-0,02552	8,52458E-4

Figure 14: NMR-experiments, 60 min premixing of $^{t}Bu_3P$, $B(C_6F_5)_3$ and C_4F_9I. Substrate: vinylcyclohexane.

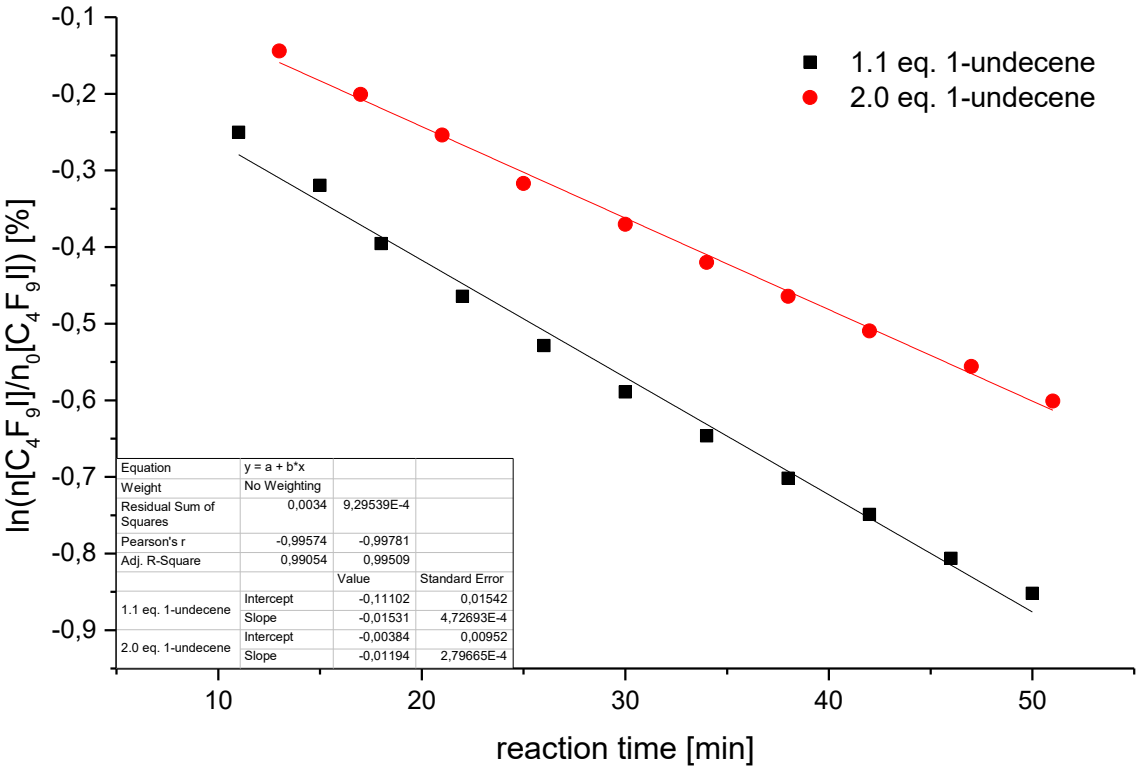
8.9.10 NMR-experiments, variation of $^{t}Bu_3P$



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,00198	0,00233	
Pearson's r	-0,99582	-0,99717	
Adj. R-Square	0,99048	0,99355	
		Value	Standard Error
5.0 mol% tBu3P	Intercept	-0,09292	0,0157
	Slope	-0,01614	5,59099E-4
15 mol% tBu3P	Intercept	-0,22818	0,01702
	Slope	-0,02067	5,88722E-4

Figure 15: NMR-experiments, variation of $^{t}Bu_3P$. Substrate: vinylcyclohexane.

8.9.11 NMR-experiments, variation of 1-undecene

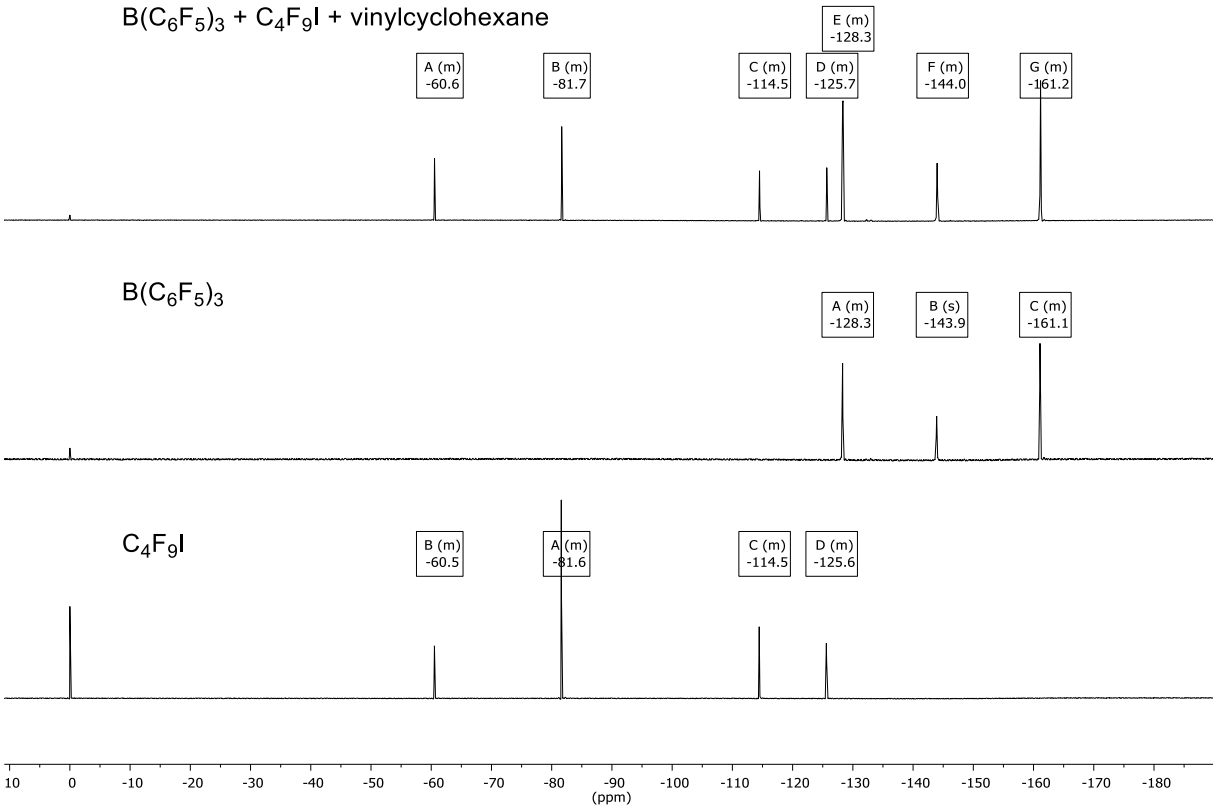


Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0,0034	9,29539E-4	
Pearson's r	-0,99574	-0,99781	
Adj. R-Square	0,99054	0,99509	
		Value	Standard Error
1.1 eq. 1-undecene	Intercept	-0,11102	0,01542
	Slope	-0,01531	4,72693E-4
2.0 eq. 1-undecene	Intercept	-0,00384	0,00952
	Slope	-0,01194	2,79665E-4

Figure 16: NMR-experiments, variation of 1-undecene.

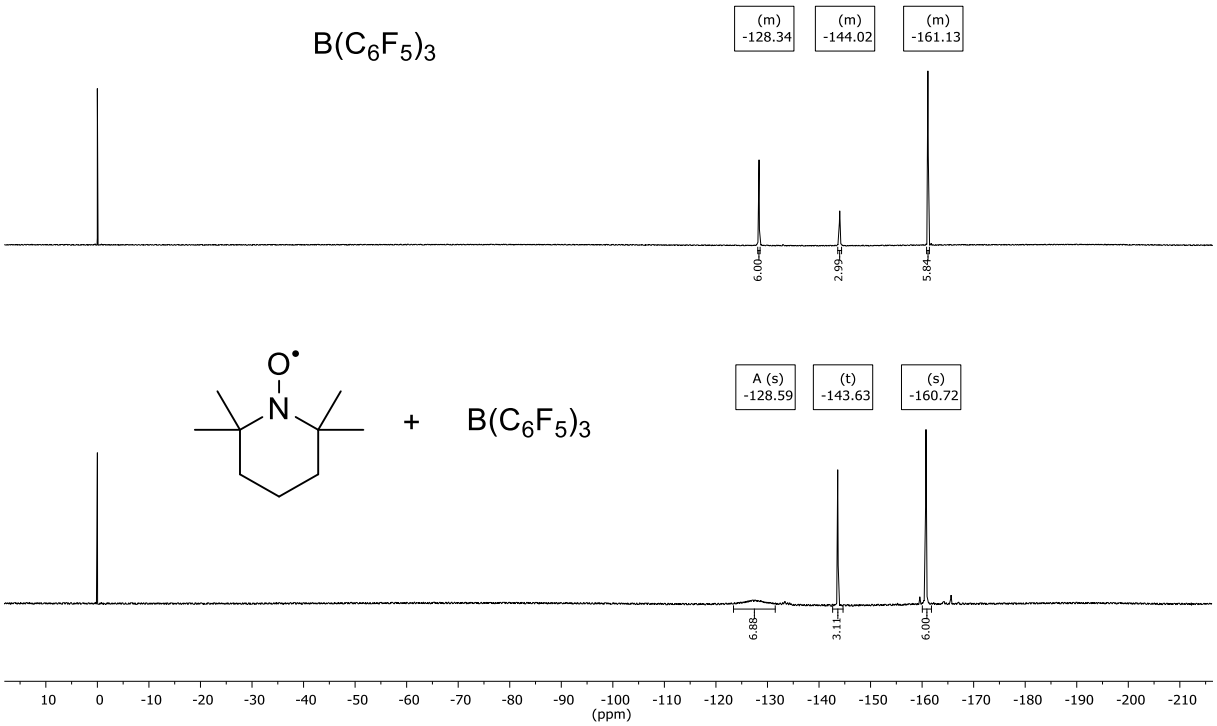
9 NMR examination of substance mixtures

9.1 $B(C_6F_5)_3$, C_4F_9I and vinylcyclohexane



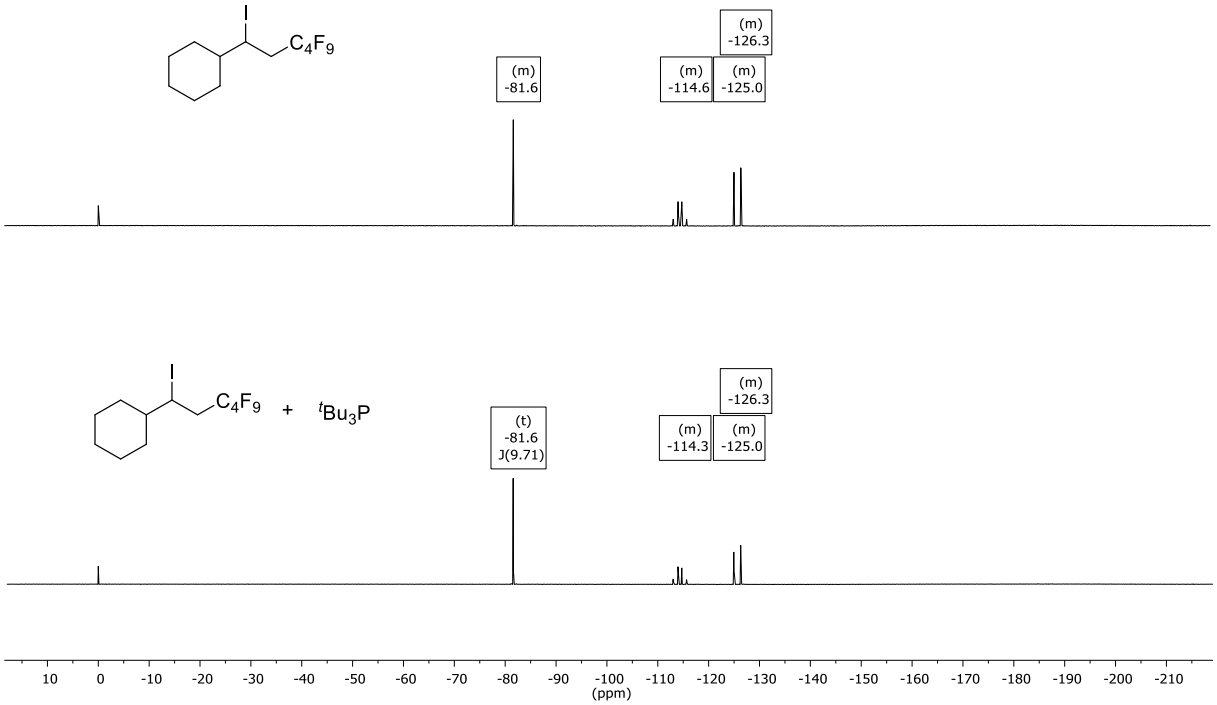
NMR-spectrum 56: ^{17}F-NMR-spectra (282 MHz in CH_2Cl_2, C_6D_6) of a mixture of $B(C_6F_5)_3$, C_4F_9I and vinylcyclohexane.

9.2 $B(C_6F_5)_3$ and 2,2,6,6-Tetramethyl-1-piperidinyloxy

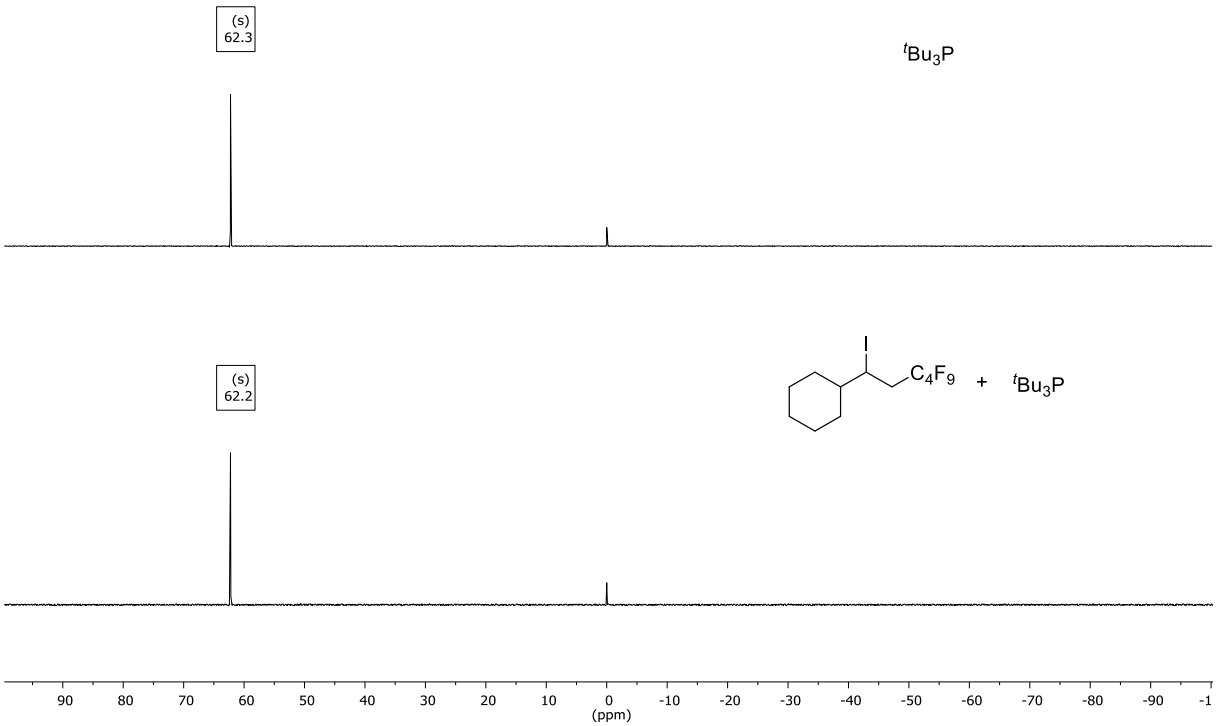


NMR-spectrum 57: ^{19}F-NMR-spectra (282 MHz, CD_2Cl_2) of $B(C_6F_5)_3$ (top), $B(C_6F_5)_3$ and TEMPO (bottom).

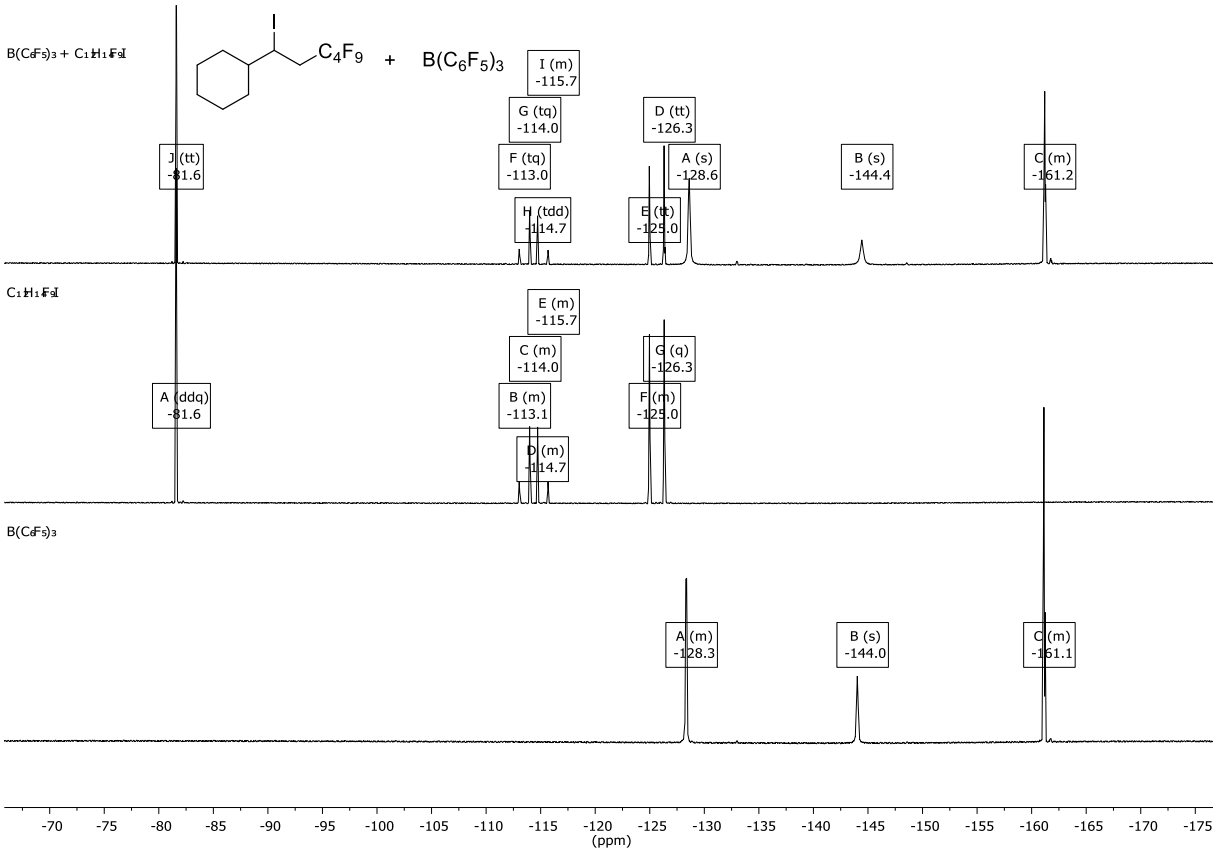
9.3 $^{t}Bu_3P$ and (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)cyclohexane



NMR-spectrum 58: ^{19}F-NMR-spectra (282 MHz, C_6D_6) in CH_2Cl_2.

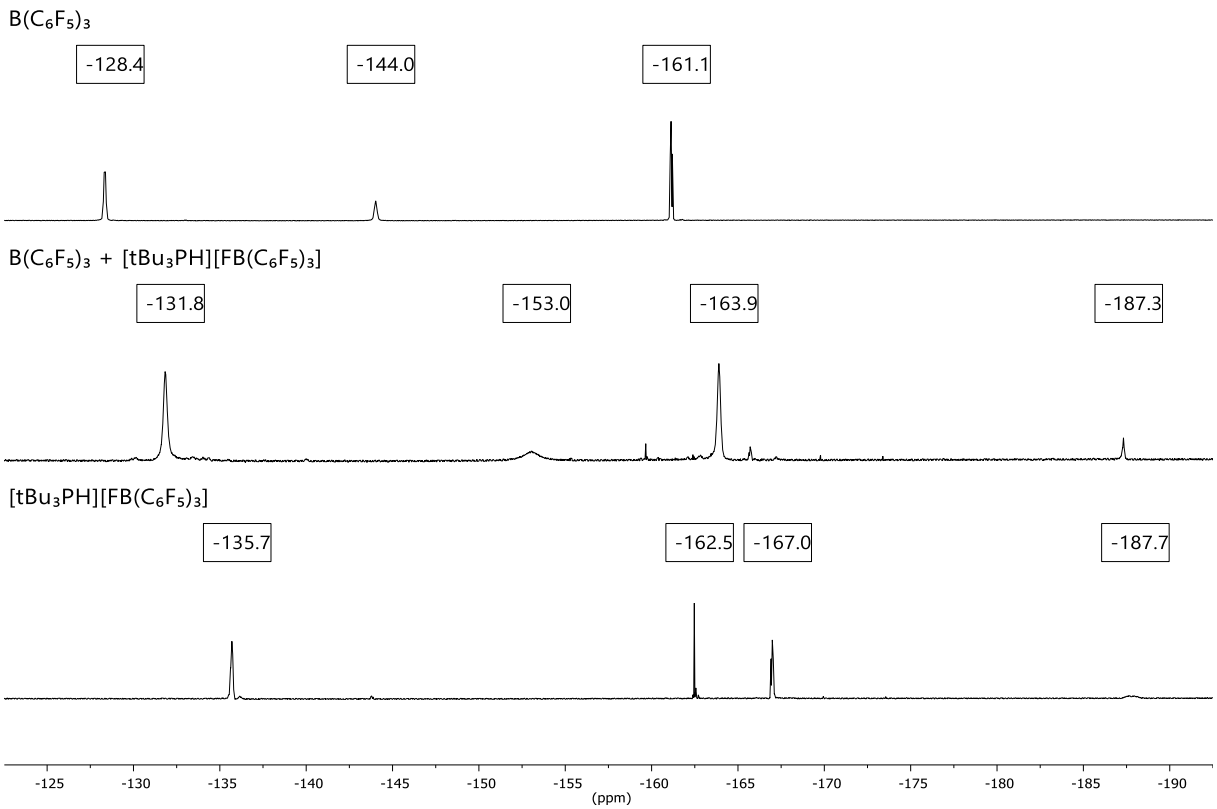


NMR-spectrum 59: ^{31}P-NMR-spectra (121 MHz, D_2O,) in CH_2Cl_2.



NMR-spectrum 60: ^{19}F-NMR-spectra (282 MHz, C_6D_6) in CH_2Cl_2.

9.4 $B(C_6F_5)_3$ and [^{t}Bu$_3$PH][FB(C_6F_5)$_3$]



NMR-spectrum 61: ^{19}F-NMR-spectra (282 MHz, C_6D_6) in CH_2Cl_2.

10 Literature

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Total Synthesis of (+)-Mesembrine Applying Asymmetric Gold Catalysis

The publication "Spittler, M., Lutsenko, K. and Czekelius, C., Total Synthesis of (+)-Mesembrine Applying Asymmetric Gold Catalysis, *J. Org. Chem.,* **2016**, 81, 6100-6105." is presented as part of the dissertation. It is integrated into this thesis without any changes. Authors to this publication were Michael Spittler and Constantin Czekelius. Experimental contributors were Michael Spittler and Kiril Lutsenko. The major part was contributed by Michael Spittler (75%) and a lower part by Kiril Lutsenko (25%).

- Experimental work was mainly conducted by Michael Spittler. Kiril Lutsenko conducted the synthesis of 3-(3,4-dimethoxyphenyl)-3-ethynylpent-4-ynal and subsequently tested the synthesis of *N*-(3-(3,4-dimethoxyphenyl)-3-ethynylpent-4-yn-1-yl)-4-methylbenzenesulfonamide. A protocol for the synthesis of this sulfonamide could not be established.
- Experimental work by Kiril Lutsenko was conducted in the context of his master thesis "Studien zur Totalsynthese von Mesembrin", September 2014, Heinrich-Heine-University, Düsseldorf, Germany.
- Parts of the experimental work of Michael Spittler were conducted in the context of his master thesis "Studien zur Totalsynthese von Indol-Alkaloiden durch 1,4-Diin-Cyclisierung", March 2015, Heinrich-Heine-University, Düsseldorf, Germany. The synthesis of 3-(3,4-dimethoxyphenyl)-3-ethynylpent-4-ynal and minor amounts of *N*-(3-(3,4-dimethoxyphenyl)-3-ethynylpent-4-yn-1-yl)-4-methylbenzenesulfonamide was conducted in this context. However, no sufficiently efficient protocol for the synthesis of this sulfonamide was established in the course of his master thesis. This challenge and the following key steps of the total synthesis were accomplished as one part of the doctoral dissertation.
- The manuscript was prepared by Michael Spittler involving the preparation of all chapters, its conceptualisation and literature search. Constantin Czekelius as well as Kiril Lutsenko corrected the manuscript.
- The preparation of the supporting information was conducted by Michael Spittler. Constantin Czekelius as well as Kiril Lutsenko corrected the supporting information.
- Work by Maria Baumann addressing the preparation of *N*-(3-(3,4-dimethoxyphenyl)-3-ethynylpent-4-yn-1-yl)-4-methylbenzenesulfonamide did not meet the requirements for an authorship.

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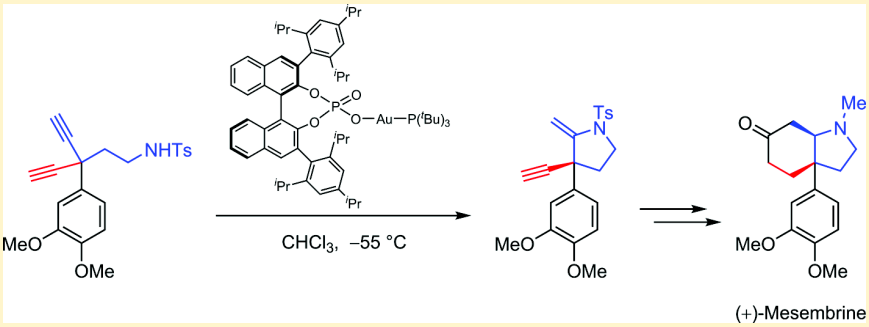
Total Synthesis of (+)-Mesembrine Applying Asymmetric Gold Catalysis

Michael Spittler, Kiril Lutsenko, and Constantin Czekelius*

Institute for Organic Chemistry and Macromolecular Chemistry, Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany

Supporting Information



ABSTRACT: The total synthesis of enantiomerically pure (+)-mesembrine is described. The central pyrrolidine moiety incorporating a quaternary, all-carbon-substituted stereocenter was constructed employing an asymmetric gold-catalyzed cycloisomerization of a 1,4-diynamide.

(−)-Mesembrine is a naturally occurring alkaloid including a pyrrolidine substructure, which was originally isolated from the succulent plant *Sceletium tortuosum*. This plant is also known as *kanna* and has been used as a stimulant by South African natives.[1] In 1957, Bodendorf and Krieger[1a] published the first accurate structural elucidation of mesembrine, and three years later Popelak et al.[2] determined its absolute configuration (Figure 1).

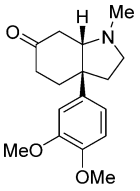


Figure 1. (−)-Mesembrine, a naturally occurring alkaloid.

Shamma and Rodriguez were the first to report a total synthesis of racemic mesembrine in 1965.[3] In 1971, Yamada and co-workers chose a chiral auxiliary-controlled approach to perform the first synthesis of enantiomerically enriched, non-natural (+)-mesembrine.[4] Ten years later, the group of Takano published the ex-chiral-pool total synthesis of the naturally occurring (−)-mesembrine starting from D-mannitol.[5] The first total synthesis of enantiopure (+)-mesembrine was performed by the Meyers group, following a reagent-controlled strategy.[6] Since then, over 40 syntheses have been published, rendering mesembrine one of the calibration standards for the application of new stereoselective methodology in the context of total synthesis.[7] In particular, the quaternary, all-carbon substituted stereocenter poses a challenge since methods for its preparation are limited in number.[8]

Within the last two decades, gold-catalyzed reactions have evolved as a remarkable field of research and today various transformations of alkenes, alkynes and allenes via carbophilic Lewis activation are well-established.[9] Employing chiral catalysts enantioselective protocols have been developed which also found application in total synthesis.[10] Recently, we have reported the desymmetrization of 1,4-diynols and 1,4-diynamides by gold-catalyzed cycloisomerization leading to heterocyclic products such as dihydro-dioxepines, tetrahydro-oxazepines, methylene tetrahydrofurans and methylene pyrrolidines.[11] While catalysts with chiral phosphine or carbene ligands gave no satisfying enantioselectivities, optically active phosphate counter-anions derived from 3,3′-disubstituted BINOL[12] were successfully employed. The cycloisomerization of diynamides **1** led to methylene pyrrolidines **3** in enantioselectivities up to 92% *ee* (eq 1).

Given the new access to pyrrolidines with a quaternary stereocenter in 3-position we became interested in exemplifying our gold-catalyzed asymmetric desymmetrization for heterocyclic natural product synthesis and chose mesembrine as a target molecule. We reasoned that not only mesembrine but also other alkaloids such as spirooxindoles or aspidospermines

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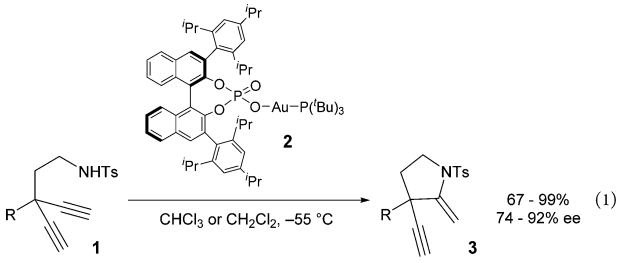
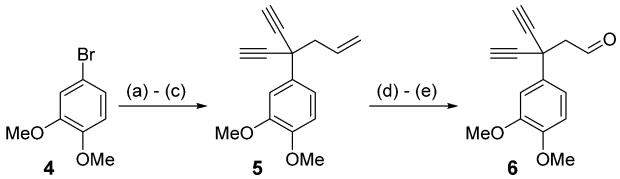


are accessible via the new route. Herein, we report the implementation of the enantioselective, gold-catalyzed diyne cycloisomerization as a key step for the total synthesis of (+)-mesembrine or related alkaloids including a pyrrolidine substructure.

Starting from commercially available 4-bromoveratrole (**4**) an Ullmann-type cross-coupling reaction with acetylacetone was performed (Scheme 1).[11b,13] Copper(I) iodide was used as

Scheme 1. Preparation of Diynal 6[a]

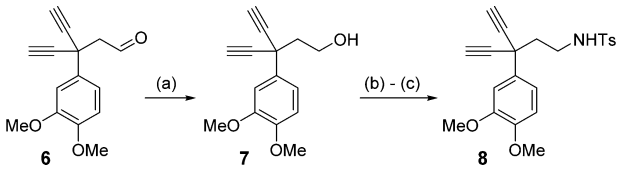


[a](a) $MeCOCH_2COMe$, CuI, L-proline, K_2CO_3, DMSO, 90 °C, 43%; (b) allyl iodide, NaH, DMF, 74%; (c) LDA, $ClPO(OEt)_2$, −78 °C, 77%; (d) K_2OsO_4, NMO, $^tBuOH/H_2O$, 83%; (e) $NaIO_4$, silica gel, 97%.

the catalyst and the coupling product was obtained in 43% yield. The resulting diketone was *C*-selectively allylated and then transformed into ene-1,4-diyne **5** via the corresponding enol phosphate ester using a modified protocol by Negishi.[14] The alkene moiety was chemoselectively dihydroxylated in an Upjohn reaction and the resulting glycol was cleaved using sodium periodate on silica gel to give aldehyde **6**.[15]

The transformation of aldehyde **6** to diynamide **8** was surprisingly challenging (Scheme 2). Following the protocol

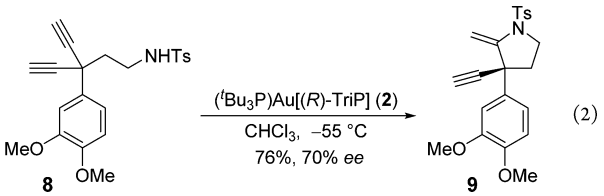
Scheme 2. Preparation of 1,4-Diynamide 8[a]



[a](a) $NaBH_4$, MeOH, 73%; (b) *p*-TsNHBoc, PPh_3, DEAD, THF, 94%; (c) TFA, CH_2Cl_2, 93%.

developed earlier we first investigated the formation of a *N*-tosylimine followed by a reduction.[11c,16] However, condensation with *p*-tosylamide and precipitation of the *p*-toluenesulfinate adduct, which was found successful for related compounds, gave no satisfying results. The reductive amination of aldehyde **6** with different ammonium salts in the presence of $NaBH_3CN$ or via a reduction of the corresponding oxime gave the desired diynamide **8** in a maximum yield of only 30%. Therefore, we considered the nucleophilic substitution of alcohol **7** as an alternative approach. For this purpose, aldehyde **6** was reduced with sodium borohydride (Scheme 2). The nucleophilic displacement of the tosylate derived from alcohol **7** with *p*-tosylamide was not productive, however. Furthermore, the employment of other *N*-nucleophiles such as ammonia or sodium azide at elevated temperatures resulted in a non-selective ring-closure. We were pleased to find that the desired product **8** could be efficiently prepared by a Mitsunobu-type reaction with Boc-*p*-tosylamide[17,18] followed by acid-mediated deprotection of the Boc group. This two-step procedure provided diynamide **8** in 87% yield.

At this point the stage was set for the gold-catalyzed, enantioselective desymmetrization which was carried out under the previously optimized conditions.[11] In former studies it was observed that both the solvent and the reaction temperature are critical parameters for the selectivity of the reaction. The enantioselectivity was found to be highest in noncoordinating chlorinated solvents such as chloroform or dichloromethane and severely decreased in a coordinating solvent like THF. Furthermore, running the reaction at low temperatures significantly improved the enantiomeric excess. Presumably, one carbon−carbon triple bond is activated by coordination of the cationic gold complex, which forms a contact ion pair with the chiral phosphate.[19] Upon this activation the amide nucleophile can attack the alkyne moiety to form methylene pyrrolidine **9**. The enantioselective cycloisomerization gave methylene pyrrolidine **9** in 76% yield and 70% *ee* after stirring for 19 h at −55 °C (eq 2).



It was shown earlier that the enantiomeric excess of related pyrrolidine compounds could be improved by recrystallization (e.g., from *n*-hexane). However, in the case of product **9** recrystallization attempts from various solvents did not significantly increase the enantiomeric excess. Therefore, we decided to proceed with the synthetic sequence since recrystallization of a later intermediate was known to result in enantiomerically pure material.[7a] Methylene pyrrolidine **9** was transformed into the corresponding unsaturated ester by treatment of the acetylide with methyl chloroformate (Scheme 3). The subsequent conjugate reduction was performed by catalytic hydrogenation using palladium on carbon at 85 bar. Ester **10** was formed in 98% yield without concomitant reduction of the enamide moiety or the aromatic substituent. In contrast, reduction using Stryker's reagent gave mixtures of the desired ester **10** and the partially reduced alkenoic ester.

Gratifyingly, deprotection of the *p*-tosyl protecting group with sodium naphthalenide directly resulted in the formation of the bicyclic hexahydro-6*H*-indol-6-one **11** in a yield of 87%.[20] Vinylogous amide **11** was converted into the *N*-Boc-protected derivative, recrystallized from *n*-hexane/Et_2O to increase the enantiomeric excess to >99% and then transformed into the *N*-methylation product **12**.[7a] For the conjugate reduction of **12**, lithium in liquid ammonia was used and (+)-mesembrine was obtained in 77% yield.[7a,21] ^1H NMR, ^{13}C NMR data[7a] and the

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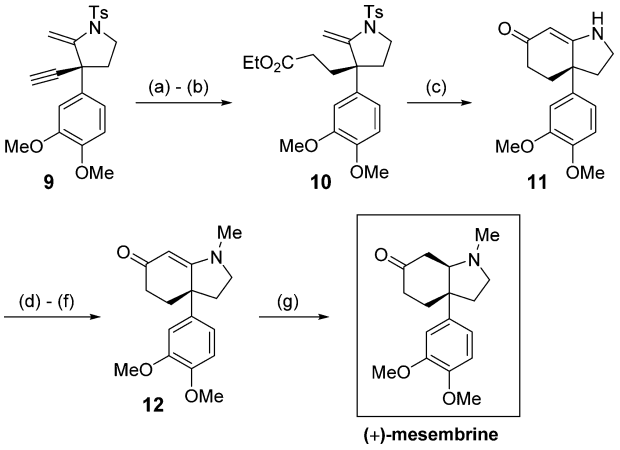
Scheme 3. Total Synthesis of (+)-Mesembrine[a]



[a](a) $ClCO_2Et$, ^nBuLi, 98%; (b) 85 bar H_2, Pd/C, 98%; (c) $NaC_{10}H_8$, THF, − 78 °C, 87%; (d) Boc_2O, DMAP, Et_3N, 91%; (e) recrystallization from *n*-hexane/Et_2O; (f) 1. $(CF_3)_2CHOH$, MW, 120 °C, 40 min; 2. NaH, MeI, THF, 97%; (g) Li/NH_3 (liq.), ^{t}BuOH, −78 °C, 77%.

optical rotation $[\alpha]_D^{23}$ = +56 (*c* = 0.37, MeOH) are in line with literature values.[6,7t]

In summary, we have demonstrated the applicability of asymmetric gold catalysis for the total synthesis of (+)-mesembrine. We have shown that pyrrolidine natural products incorporating a quaternary stereocenter, a challenging but also common structural motif, are accessible by an asymmetric 1,4-diynamide cycloisomerization. Using this general method not only mesembrine, but also various related natural products like spirooxindole or aspidospermine alkaloids could be synthesized.

EXPERIMENTAL SECTION

General Methods. All reagents used were purchased or purified to reagent grade. Solvents were dried by common laboratory techniques. Reactions were monitored with thin-layer chromatography. For reactions requiring an inert atmosphere the glassware was dried at 120 °C and standard Schlenk techniques were employed. For column chromatography silica gel 60 or aluminum oxide were used. Silica gel was deactivated by conditioning with the respective eluent and 1% (v/v) triethylamine. For reactions under microwave irradiation the CEM Discover SP-D microwave was used with 100 W. The enantiomeric excess was determined using a HPLC system equipped with a DAICEL CHIRALPAK IA or DAICEL CHIRALPAK IC column. ^{1}H and ^{13}C NMR-spectra were recorded at 600 and 300 or 151 and 75 MHz, respectively. IR-spectra were measured as thin films on a NaCl single crystal. High resolution mass spectra (HRMS) were measured with a Q-TOF spectrometer.

*3-Ethynyl-3-(3,4-dimethoxyphenyl)hex-1-ene-5-yne (**5**).* Under N_2 atmosphere, dry diisopropylamine (5.5 g, 54 mmol, 2.4 equiv) was dissolved in dry THF (135 mL, 0.4 M). At −78 °C *n*-butyllithium (1.6 M in hexane, 31 mL, 49 mmol, 2.2 equiv) was added dropwise. The solution was stirred at −78 °C for 30 min, warmed up to rt and stirred for 30 min. A solution of allylated product **14** (6.2 g, 23 mmol, 1 equiv) in THF (45 mL, 0.5 M), which was cooled in an ice bath, was transferred into the LDA-solution via cannula. After stirring for 1 h at −78 °C, diethyl chlorophosphate (7.3 g, 42 mmol, 2.1 equiv) was added via a nitrogen-flushed syringe. The solution was stirred at −78 °C for 2.5 h and then allowed to warm to rt. It was cooled to −78 °C again and in another flask dry diisopropylamine (9.7 g, 96 mmol, 4.8 equiv) was dissolved in dry THF (430 mL, 0.25 M). At−78 °C *n*-butyllithium (1.6 M in hexane, 55 mL, 88 mmol, 4.4 equiv) was added dropwise. The solution was stirred at −78 °C for 30 min, warmed up to rt and stirred for 30 min. It was cooled again to −78 °C and to this solution the enol phosphate ester solution was added via cannula. The solution was stirred in the acetone/dry ice bath and allowed to warm to rt overnight. The reaction was quenched with a mixture of dist. water and brine (2:1) after 20 h reaction time. The aqueous phase was extracted with diethyl ether and the organic phase was washed with brine. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash chromatography (eluent = *n*-hexane:EtOAc = 5:1) gave a viscous oil (4.2 g, 17 mmol, 77%). R_f = 0.44 (*n*-hexane:EtOAc = 3:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 7.24−7.17 (m, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 5.86 (ddt, *J* = 17.4, 10.3, 7.1 Hz, 1H), 5.19−4.95 (m, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 2.69 (dt, *J* = 7.1, 1.1 Hz, 2H), 2.53 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 148.8, 148.5, 133.1, 132.9, 119.1, 118.7, 110.9, 110.0, 84.3, 72.2, 56.0, 50.2, 39.8. IR (film), $\tilde{\nu}$ [cm^{-1}] 3289, 3078, 3003, 2955, 2936, 2912, 2836, 1516, 1264, 1236, 1144, 1028, 649. HRMS (ESI) *m*/*z* calculated for $C_{16}H_{17}O_2$ $[M + H]^+$ 241.1223, found 241.1223.

*3-(3,4-Dimethoxyphenyl)-3-ethynyl-pent-4-ynal (**6**).* To a vigorously stirred solution of diol **15** (2.79 g, 10.2 mmol, 1 equiv) in dry dichloromethane (100 mL, 0.1 M) $NaIO_4$ adsorbed on silica gel (21.6 g; 0.613 mmol·g^{-1}, 13.2 mmol, 1.30 equiv) was added. After complete conversion the silica gel was filtered off and the residue was washed with dichloromethane. The filtrate was evaporated and the residue dried in vacuo. A yellowish, viscous product was obtained (2.39 g, 9.85 mmol, 97%). No further purification was necessary. R_f = 0.87 (*n*-hexane:EtOAc = 1:1). mp = 61−64 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 9.85 (t, *J* = 2.6 Hz, 1H), 7.22 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.18 (d, *J* = 2.3 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.89 (d, *J* = 2.7 Hz, 2H), 2.65 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 199.6, 149.2, 148.9, 131.7, 118.4, 111.2, 109.5, 82.8, 73.7, 56.7, 56.1, 35.7. IR (film), $\tilde{\nu}$ [cm^{-1}] 3284, 3004, 2961, 2937, 2912, 2838, 2744, 1726, 1517, 1262, 1146, 1026, 666. HRMS (ESI) *m*/*z* calculated for $C_{15}H_{15}O_3$ $[M + H]^+$ 243.1016, found 243.1011.

*3-(3,4-Dimethoxyphenyl)-3-ethynyl-pent-4-yn-1-ol (**7**).* Under nitrogen atmosphere aldehyde **6** (0.205 g, 0.845 mmol, 1 equiv) was dissolved in dry methanol (8.5 mL, 0.1 M) and cooled to 0 °C. $NaBH_4$ (64.0 mg, 1.69 mmol, 2.00 equiv) was added. After complete conversion within 15 min the reaction was quenched with dist. water and hydrochloric acid (1 M) was added until pH = 2 was reached. The solution was stirred for 30 min and then neutralized with sodium hydroxide solution. Brine was added and the aqueous phase was extracted with EtOAc. The organic phase was washed with brine and dried over Na_2SO_4. The product was purified by column chromatography over silica gel (eluent = *n*-hexane:EtOAc:CH_2Cl_2 = 62:28:10). The alcohol **7** was obtained as a white solid (0.150 g, 0.614 mmol, 73%). R_f = 0.45 (*n*-hexane:EtOAc = 1:1). mp = 78−79 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 7.29−7.16 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 3.97−3.85 (m, 8H), 2.57 (s, 2H), 2.26 (t, *J* = 6.4 Hz, 2H), 1.77 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 149.0, 148.6, 133.2, 118.4, 111.0, 109.6, 84.3, 77.2, 72.5, 60.4, 56.0, 48.0, 37.8. IR (film), $\tilde{\nu}$ [cm^{-1}] 3499, 3393, 3287, 3005, 2960, 2935, 2837, 1516, 1261, 1145, 1027, 651. HRMS (ESI) *m*/*z* calculated for $C_{15}H_{17}O_3$ $[M + H]^+$ 245.1172, found 245.1171.

*N-(4-Toluenesulfonyl)-(3-(3,4-dimethoxyphenyl)-3-ethynyl-pent-4-yn-1-amine (**8**).* To a solution of protected sulfonamide **17** (0.134 g, 0.270 mmol, 1 equiv) in dichloromethane (3 mL, 0.1 M) was added trifluoroacetic acid (0.56 mL, 7.3 mmol, 27 equiv). After stirring for 7 h at rt, a saturated $NaHCO_3$ solution was added dropwise until the gas evolution ceased and pH = 8 was reached. The aqueous phase was extracted with dichloromethane and the organic phase was dried over Na_2SO_4. The drying agent was filtered off, the solution was concentrated and the residue dried in vacuo giving a brownish solid (0.998 g, 0.251 mmol, 93%). No further purification was necessary. R_f = 0.54 (*n*-hexane:EtOAc = 1:1). mp = 117−120 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 7.73−7.66 (m, 2H), 7.33−7.27 (m, 2H), 7.13 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.09 (d, *J* = 2.2 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 4.69 (s, 1H), 3.87 (s, 6H), 3.23 (ddd, *J* = 8.1, 7.1, 6.2 Hz, 2H2.53 (s, 2H), 2.43 (s, 3H), 2.18−2.09 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 149.0, 148.7, 143.5, 137.0, 132.5, 129.8,

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127.2, 118.4, 111.0, 109.5, 83.6, 72.9, 56.1, 56.0, 44.9, 40.4, 38.1, 21.6. IR (film), $\tilde{\nu}$ [cm^{-1}] 3285, 3003, 2960, 2937, 2838, 1597, 1515, 1260, 1160, 661. HRMS (ESI) m/z calculated for $C_{22}H_{24}NO_4S$ $[M + H]^+$ 398.1421, found 398.1419.

*(S)-3-(3,4-Dimethoxyphenyl)-3-ethynyl-2-methylene-1-(4-toluene-sulfonyl)-pyrrolidine (**9**).* Under N_2 atmosphere, diynamide **8** (0.435 g, 1.10 mmol, 1 equiv) was dissolved in dry $CHCl_3$ (5.5 mL, 0.2 M). At −55 °C, freshly prepared (*R*)-TriPAu(P^tBu_3) (**2**) (56 mg, 0.049 mmol, 4.4 mol %) in dry $CHCl_3$ (5.5 mL, 0.01 M) was added and the solution stirred for 19 h at −55 °C. The reaction was quenched by adding triethylamine (50 μL, 0.36 mmol) and the solvent was evaporated. Purification by flash chromatography on deactivated silica gel (*n*-hexane:EtOAc:CH_2Cl_2 = 65:11:24) gave a colorless solid (0.334 g, 0.840 mmol, 76%, 70% *ee*). The product was combined with material from earlier experiments and recrystallized from *n*-hexane/CH_2Cl_2 (3:1) giving pyrrolidine **9** with an enantiomeric excess of 68% *ee*. $[\alpha]_D^{20}$ = +87 $mL{\cdot}g^{-1}{\cdot}dm^{-1}$ (*c* = 0.58; 68% *ee*, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (DAICEL CHIRALPAK IC, 4.6 × 250 mm, eluent = *n*-hexane:isopropanol = 55:45, 0.63 $mL{\cdot}min^{-1}$, λ = 254 nm) t_R (major) = 25.8 min, t_R (minor) = 33.0 min). R_f = 0.50 (*n*-hexane:EtOAc = 6:4). mp = 143−145 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 7.80−7.72 (m, 2H), 7.32−7.26 (m, 2H), 6.89 (d, *J* = 2.2 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 5.34 (d, *J* = 1.7 Hz, 1H), 4.32 (d, *J* = 1.7 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.77 (dd, *J* = 7.1, 5.8 Hz, 2H), 2.43 (s, 3H), 2.27 (tt, *J* = 12.2, 5.8 Hz, 2H), 2.10 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ [ppm] = 148.8, 148.8, 148.5, 144.1, 134.0, 132.1, 129.4, 127.9, 119.5, 110.7, 110.6, 94.0, 84.4, 77.2, 73.4, 56.0, 50.8, 48.2, 38.9, 21.7. IR (film), $\tilde{\nu}$ [cm^{-1}] 3283, 2956, 2935, 2837, 1646, 1518, 1259, 1167, 659. HRMS (ESI) m/z calculated for $C_{22}H_{24}NO_4S$ $[M + H]^+$ 398.1421, found 398.1423.

*(R)-Methyl 3-(3-(3,4-dimethoxyphenyl)-2-methylene-1-(4-toluenesulfonyl)-pyrrolidin-3-yl)propanoate (**10**).* Ester **18** (0.121 g, 0.266 mmol) was dissolved in a mixture of THF:MeOH (1:1, 2.8 mL, 0.1 M) and Pd/C (12.1 mg, 10 w%) was added under inert conditions. The reaction was carried out in an autoclave at 85 bar hydrogen pressure for 18.5 h. Pd/C was filtered off by filtration through a Celite pad and the solvent was removed to obtain a viscous white product (0.12 g, 0.26 mmol, 98%). No further purification was necessary. R_f = 0.35 (*n*-hexane:EtOAc = 6:4). $[\alpha]_D^{20}$ = +17 $mL{\cdot}g^{-1}{\cdot}dm^{-1}$ (*c* = 0.42; 67.9% *ee*, $CHCl_3$). ^{1}H NMR (300 MHz, C_6D_6) δ = 7.52−7.46 (m, 2H), 6.62−6.55 (m, 2H), 6.37 (d, *J* = 2.1 Hz, 1H), 6.29−6.16 (m, 2H), 5.71 (d, *J* = 1.4 Hz, 1H), 4.36 (d, *J* = 1.4 Hz, 1H), 3.61 (ddd, *J* = 9.7, 7.6, 2.3 Hz, 1H), 3.37 (s, 3H), 3.25 (d, *J* = 13.4 Hz, 7H), 2.10−1.98 (m, 1H), 1.96 (s, 3H), 1.95−1.82 (m, 3H), 1.76 (ddd, *J* = 12.6, 5.8, 2.0 Hz, 1H), 1.27 (ddd, *J* = 12.7, 10.1, 7.7 Hz, 1H). ^{13}C NMR (75 MHz, C_6D_6) δ [ppm] = 173.0, 150.3, 149.7, 148.9, 143.5, 135.0, 132.5, 127.6, 118.5, 111.2, 111.1, 92.1, 55.4, 55.1, 51.1, 48.0, 34.5, 32.0, 30.0, 21.2. IR (film), $\tilde{\nu}$ [cm^{-1}] 2953, 2926, 2854, 1735, 1519, 1342, 1166, 661. HRMS (ESI) m/z calculated for $C_{24}H_{30}NO_6S$ $[M + H]^+$ 460.1788, found 460.1789.

*(R)-3a-(3,4-Dimethoxyphenyl)-1,2,3,3a,4,5-hexahydro-6H-indol-6-one (**11**).*[7g] Under inert conditions pyrrolidine **10** (0.167 g, 0.363 mmol, 1 equiv) was dissolved in dry THF (2 mL, 0.2 M). In another flask napthalene (0.335 g, 2.61 mmol, 7.19 equiv) was dissolved in THF (3 mL, 0.9 M) and sodium (50 mg, 2.2 mmol, 6.1 equiv) was added. The educt solution was cooled to −78 °C and the $NaC_{10}H_8$ solution was added dropwise until a slight green coloring persisted (1.6 mL $NaC_{10}H_8$ solution, ≈3 equiv). The reaction was quenched with sat. $NaHCO_3$ solution and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine and the solvent was removed. Purification by column chromatography (eluent = CH_2Cl_2:MeOH = 97:3) on neutral aluminum oxide (Brockmann III) yielded the product as a white solid (86.4 mg, 0.316 mmol, 87%). R_f = 0.10 (CH_2Cl_2:MeOH = 20:1). $[\alpha]_D^{20}$ = +155 $mL{\cdot}g^{-1}{\cdot}dm^{-1}$ (*c* = 0.505; 67.9% *ee*, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 7.07 (s, 1H, −N*H*−), 6.90−6.81 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 5.38 (s, 1H, =C*H*—CO—), 3.83 (s, 3H), 3.82 (s, 3H), 3.40 (ddd, *J* = 10.4, 8.1, 2.1 Hz, 1H, −NH−CH_2−CH_2−), 3.15 (tdd, *J* = 10.8, 5.9, 3.5 Hz, 1H, −NH−CH_2−CH_2−), 2.47−2.19 (m, 2H, −CO−CH_2−CH_2−), 2.19−1.79 (m, 4H, −NH−CH_2−CH_2− + −CO−CH_2−CH_2−). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 197.1, 173.5, 148.9, 148.1, 133.3, 119.6, 111.0, 110.2, 94.8, 56.1, 55.9, 51.5, 45.1, 40.2, 36.0, 33.5. IR (film), $\tilde{\nu}$ [cm^{-1}] 3183, 2939, 2872, 1575, 1514, 1264, 1219, 1026, 753. HRMS (ESI) m/z calculated for $C_{16}H_{20}NO_3$ $[M + H]^+$ 274.1438, found 274.1439.

*(R)-3a-(3,4-Dimethoxyphenyl)-1-methyl-1,2,3,3a,4,5-hexahydro-6H-indol-6-one (**12**).*[7a] Boc-protected pyrrolidine **19** (43.4 mg, 0.116 mmol, 1 equiv) was dissolved in $(CF_3)_2CHOH$ (1 mL) and heated to 115 °C for 40 min by microwave irradiation. The solvent was removed on a rotary evaporator and the crude product was dissolved in dry THF (1.3 mL, 0.09 M). It was added at 0 °C to a suspension of sodium hydride (60% in mineral oil, 5.6 mg, 0.14 mmol, 1.2 equiv) in THF (1 mL). After 15 min the cooling bath was removed and methyl iodide (9.0 μL, 0.14 mmol, 1.2 equiv) was added via syringe. Due to an incomplete conversion methyl iodide (8.0 μL, 0.13 mmol, 1.1 equiv) and sodium hydride (60 wt % in mineral oil, 5.6 mg, 0.14 mmol, 1.2 equiv) were added. After quenching by addition of a mixture of dist. water and brine, the aqueous phase was extracted with EtOAc. Combined organic phases were washed with brine and dried over Na_2SO_4. Purification by column chromatography on deactivated silica gel (eluent = CH_2Cl_2:MeOH = 95:5) yielded the product as a slightly yellowish material (32.3 mg, 0.112 mmol, 97%). R_f = 0.46 (CH_2Cl_2:MeOH = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 6.81−6.72 (m, 3H), 5.19 (s, 1H), 3.85 (d, *J* = 1.1 Hz, 6H), 3.33−3.23 (m, 2H), 2.96 (s, 3H), 2.44−2.34 (m, 1H), 2.31−2.22 (m, 1H), 2.20−2.01 (m, 3H), 2.01−1.82 (m, 1H).

*3-(3,4-Dimethoxyphenyl)pentane-2,4-dione (**13**).*[11b,13] Under N_2 atmosphere, copper(I) iodide (2.00 g, 10.5 mmol, 0.100 equiv), D/L-proline (2.42 g, 21.0 mmol, 0.200 equiv) and potassium carbonate (58.0 g, 420 mmol, 4.00 equiv) were suspended in dry DMSO (420 mL, 0.25 m). After addition of 4-bromo-1,2-dimethoxybenzene (22.8 g, 105 mmol, 1 equiv) and acetyl acetone (31.5 g, 200 mmol, 3.00 equiv), the mixture was stirred for 41 h at 90 °C. The dark green solution was cooled to 0 °C and slowly poured into HCl (1 M) while vigorously stirring. The layers were separated and the aqueous layer extracted with EtOAc. The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography (eluent = *n*-hexane:EtOAc = 5:1). Recrystallization from *n*-hexane yielded white crystals (10.8 g, 45.8 mmol, 43%). R_f = 0.27 (*n*-hexane:EtOAc = 5:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 6.86 (d, *J* = 8.1 Hz, 1H), 6.70 (dd, *J* = 8.1 Hz, 2.0 Hz, 1H), 6.66 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 1.89 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ [ppm] = 191.2, 149.1, 148.5, 129.5, 123.5, 115.0, 114.1, 111.4, 77.2, 77.2, 56.0, 55.9, 24.2. IR (film), $\tilde{\nu}$ [cm^{-1}] 3006, 2952, 2929, 2831, 1587, 1521, 1454, 1252, 1137, 1021. HRMS (ESI) m/z calculated for $C_{13}H_{17}O_4$ $[M + H]^+$ 237.1121, found 237.1120.

*3-Allyl-3-(3,4-dimethoxyphenyl)pentane-2,4-dione (**14**).* Under N_2 atmosphere, dione **13** (13.0 g, 55.0 mmol, 1 equiv) was dissolved in dry DMF (220 mL, 0.25 M). The solution was cooled to 0 °C and sodium hydride (60% in mineral oil, 2.3 g, 58 mmol, 1.1 equiv) was added in portions. After stirring for 1 h at 0 °C and 1 h at rt the solution was cooled to 0 °C. Allyl iodide (5.5 mL, 61 mmol, 1.1 equiv) was added via syringe, the solution was allowed to warm to rt and it was stirred for 3 h. Cold water was added and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. Purification by flash chromatography (eluent = *n*-hexane:EtOAc = 4:1) gave a white solid (11.3 g, 40.7 mmol, 74%). R_f = 0.24 (*n*-hexane:EtOAc = 4:1). mp = 95−96 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 6.86 (d, *J* = 8.4 Hz, 1H), 6.79 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.72 (d, *J* = 2.2 Hz, 1H), 5.69 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.16−5.02 (m, 2H), 3.87 (s, 3H), 3.84 (s, 3H), 3.02 (dt, *J* = 7.0, 1.4 Hz, 2H), 2.10 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 206.1, 149.2, 148.9, 133.7, 129.2, 120.7, 118.6, 111.4, 111.2, 74.2, 56.1, 56.0, 37.7, 28.0. IR (film), $\tilde{\nu}$ [cm^{-1}] 3379, 3082, 3006, 2968, 2937, 2838, 1705, 1519, 1150, 1024, 928, 766. HRMS (ESI) m/z calculated for $C_{16}H_{21}O_4$ $[M + H]^+$ 277.1435, found 277.1434.

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*3-Ethynyl-3-(3,4-dimethoxyphenyl)-hex-5-yn-1,2-diol (**15**).* Diyne **5** (2.95 g, 12.3 mmol, 1 equiv) was dissolved in a mixture of *tert*-butanol and water (24.5 mL, 1:1, 0.5 M). *N*-Methylmorpholine *N*-oxide (3.02 g, 25.8 mmol, 2.10 equiv) as well as potassium osmate dihydrate (67.8 mg, 0.184 mmol, 1.49 mol %) were added in portions, resulting in a brown solution. After 66 h *tert*-butanol was evaporated under reduced pressure and hydrochloric acid (1 M) was added until pH = 1 was reached. The aqueous phase was extracted with EtOAc. The organic phase was washed with brine and dried over Na_2SO_4. The crude product was purified via column chromatography over silica (eluent = *n*-hexane:EtOAc = 1:3), yielding a yellowish substance (2.79 g, 10.2 mmol, 83%). R_f = 0.12 (*n*-hexane:EtOAc = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 7.42 (dd, J = 8.7, 2.6 Hz, 1H), 7.19 (d, J = 2.3 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 4.17 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.66−3.41 (m, 2H), 2.75 (d, J = 2.9 Hz, 1H), 2.63 (s, 1H), (s, 1H), 2.21 (dd, J = 14.2, 7.9 Hz, 1H), 2.04 (dd, J = 14.2, 2.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 149.1, 148.8, 133.1, 118.4, 111.1, 109.6, 84.7, 84.0, 73.1, 73.0, 70.2, 66.7, 56.1, 49.4, 38.1. IR (film), $\tilde{\nu}$ [cm^{-1}] 3398, 3286, 3003, 2935, 2838, 1593, 1516, 1261, 1145, 1026, 648. HRMS (ESI) m/z calculated for $C_{16}H_{19}O_4$ $[M + H]^+$ 275.1278, found 275.1278.

*tert-Butyl-4-toluenesulfonyl-carbamate (**16**).*[22] Under nitrogen atmosphere 4-methylbenzenesulfonamide (15.8 g, 92.2 mmol, 1 equiv) and *N*,*N*-dimethyl-4-aminopyridine (0.563 g, 4.61 mmol, 5.00 mol %) were dissolved in dry dichloromethane (190 mL, 0.5 M). Dry triethylamine (14.1 mL, 101 mmol, 1.10 equiv) as well as di-*tert*-butyl dicarbonate (21.7 mL, 101 mmol, 1.10 equiv) were added. After 30 min the solution was concentrated and the crude product was dissolved in EtOAc. It was washed with hydrochlorid acid (1 M), dist. water as well as brine. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure to give a white powder. The product was recrystallized from a mixture of diethyl ether and *n*-hexane (1:1). The crystals were washed with ice cold *n*-hexane and vacuum-dried to obtain white crystals (21.6 g, 79.6 mmol, 86%). mp = 119 °C (lit.[22] mp = 117−119 °C).^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 7.93−7.86 (m, 2H), 7.45 (s, 1H), 7.38−7.31 (m, 2H), 2.44 (s, 3H), 1.38 (s, 9H).

*tert-Butyl (3-(3,4-dimethoxyphenyl)-3-ethynyl-pent-4-yn-1-yl)(4-toluene-sulfonyl)carbamate (**17**).* Under N_2 atmosphere, alcohol **7** (1.51 g, 6.17 mmol, 1 equiv), triphenylphosphine (2.43 g, 9.26 mmol, 1.50 equiv) and *tert*-butyl tosylcarbamate (**16**) (1.84 g, 6.79 mmol, 1.10 equiv) were dissolved in dry THF (62 mL, 0.1 M). To this solution, diethyl azodicarboxylate (4.2 mL, 9.3 mmol, 1.5 equiv, 40 w% in toluene) was added dropwise. The solution was cooled with a water bath (15 °C). After stirring for 3 h, the solution was concentrated in vacuo. Purification by flash column chromatography over silica gel (*n*-hexane:EtOAc = 7:2) gave a white solid (2.87 g, 5.77 mmol, 94%). R_f = 0.77 (*n*-hexane:EtOAc = 1:1). mp = 129−132 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 7.78−7.72 (m, 2H), 7.33−7.23 (m, 3H), 7.24 (d, J = 2.2 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 4.12−4.02 (m, 2H), 3.93 (s, 3H), 3.88 (s, 3H), 2.59 (s, 2H), 2.47−2.38 (m, 5H), 1.33 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 150.8, 149.0, 148.7, 144.3, 137.3, 132.7, 129.4, 127.9, 118.6, 111.0, 109.7, 84.4, 83.4, 72.6, 56.1, 44.5, 44.4, 37.8, 28.0, 21.7. IR (film), $\tilde{\nu}$ [cm^{-1}] 3286, 2979, 2936, 2837, 2256, 1731, 1516, 1354, 1153, 734. HRMS (ESI) m/z calculated for $C_{27}H_{35}N_2O_6S$ $[M+NH_4]^+$ 515.2210, found 515.2211, $C_{27}H_{31}NNaO_6S$ $[M + Na]^+$ 520.1764, found 520.1763.

*(R)-Methyl 3-(3-(3,4-dimethoxyphenyl)-2-methylene-1-(4-toluene-sulfonyl)-pyrrolidin-3-yl)propiolate (**18**).* Under N_2 atmosphere, alkyne **9** (0.228 g, 0.574 mmol, 1 equiv) was dissolved in dry THF (5.7 mL). At −80 °C, *n*-butyllithium solution (1.6 M in hexane, 0.39 mL, 0.63 mmol, 1.1 equiv) was added dropwise and stirred for 20 min. Next, methyl chloroformate (88 μL, 1.2 mmol, 2.1 equiv) was added and the solution was allowed to warm to rt. After 30 min, a mixture of water, sat. $NaHCO_3$ and brine (4:1:2, 28 mL) was added, EtOAc was added and the layers were separated. The aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine (15 mL) and dried over Na_2SO_4. Purification by flash chromatography on deactivated silica gel (*n*-hexane:EtOAc:CH_2Cl_2 = 65:10:25) gave a white solid (0.255 g, 0.560 mmol, 98%). R_f = 0.29 (*n*-hexane:EtOAc:CH_2Cl_2 = 6:1:3). mp = 115−120 °C. $[\alpha]_D^{20}$ = +54 mL·g^{-1}·dm^{-1} (c = 0.49; 67.9% *ee*, $CHCl_3$). ^{1}H NMR (300 MHz, C_6D_6) δ [ppm] = 7.81−7.73 (m, 2H), 6.83−6.75 (m, 4H), 6.34 (d, J = 9.0 Hz, 1H), 5.75 (d, J = 1.6 Hz, 1H), 4.52 (d, J = 1.6 Hz, 1H), 3.53 (ddd, J = 6.8, 5.9, 2.1 Hz, 2H), 3.34 (s, 3H), 3.34 (s, 3H), 3.21 (s, 3H), 1.95 (s, 3H), 1.92−1.74 (m, 2H). ^{13}C NMR (75 MHz, C_6D_6) δ [ppm] = 153.5, 150.1, 149.9, 148.0, 144.0, 134.6, 131.0, 129.6, 127.9, 119.8, 111.7, 111.4, 94.7, 88.0, 77.3, 55.6, 55.5, 52.1, 51.1, 48.3, 37.9, 21.3. IR (film), $\tilde{\nu}$ [cm^{-1}] 3004, 2955, 2838, 2235, 1715, 1518, 1266, 1167, 751, 658. HRMS (ESI) m/z calculated for $C_{24}H_{26}NO_6S$ $[M + H]^+$ 456.1475, found 456.1479.

*(R)-tert-Butyl 3a-(3,4-dimethoxyphenyl)-6-oxo-2,3,3a,4,5,6-hexahydro-1H-indole-1-carboxylate (**19**).*[7a] Pyrrolidine **11** (0.135 g, 0.494 mmol, 1 equiv, 68% *ee*) was dissolved in dry CH_2Cl_2 (6 mL, 0.1 M). *N*,*N*-Dimethylaminopyridine (8.4 mg, 0.069 mmol, 14 mol %), triethylamine (95 μL, 0.68 mmol, 1.4 equiv) and di-*tert*-butyl dicarbonate (0.149 g, 146 μL, 0.684 mmol, 1.38 equiv) were added. After 20 min a mixture of dist. water and brine was added and the aqueous phase was extracted with CH_2Cl_2. The organic phase was washed with a mixture of dist. water and brine (1:3) and the solvent was removed. Purification by flash column chromatography (eluent = *n*-hexane:EtOAc:CH_2Cl_2 = 43:42:15) on deactivated silica gel yielded the product as a white substance (0.168 g, 0.449 mmol, 91%). The product was recrystallized from *n*-hexane and a mixture of *n*-hexane:Et_2O (2:1) in two batches, giving crystals (78.9 mg) with an *ee* > 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 6.84−6.76 (m, 3H), 6.55 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.78 (dd, J = 11.0, 8.1 Hz, 1H), 3.24 (td, J = 11.4, 5.5 Hz, 1H), 2.46−2.35 (m, 1H), 2.31 (dd, J = 12.0, 5.4 Hz, 1H), 2.26−2.14 (m, 2H), 2.13−1.92 (m, 2H), 1.54 (s, 9H). The enantiomeric excess was determined by chiral HPLC analysis (DAICEL CHIRALPAK IA, 4.6 × 250 mm, eluent = *n*-hexane:isopropanol = 82:18, 0.82 mL·min^{-1}, λ = 254 nm) t_R (major) = 13.8 min, t_R (minor) = 10.8 min.

(+)-Mesembrine.[7a,21] Enone **12** (38.6 mg, 0.134 mmol, 1 equiv) and dry *tert*-butanol (24 mg, 0.32 mmol, 2.8 equiv) were dissolved in dry THF (2 mL, 0.06 M). The solution was cooled to −78 °C and liquid ammonia (≈40 mL) was condensed into the flask. A piece of lithium (1.9 mg, 0.27 mmol, 2.0 equiv) was added and the solution was stirred for 45 min. Ammonia was evaporated and the solution was diluted with a mixture of dist. water and brine. The aqueous phase was extracted with EtOAc and the combined organic phases were washed with brine and dried over Na_2SO_4. Purification by column chromatography (eluent = CH_2Cl_2:acetone = 8:2) on neutral aluminum oxide (Brockmann III) yielded the product as a slightly yellowish substance (30.0 mg, 0.104 mmol, 77%). R_f = 0.25 (CH_2Cl_2:acetone = 6:2.5). $[\alpha]_D^{23}$ = +56 (c = 0.37, MeOH); (lit.[7t] $[\alpha]_D^{23}$ = +50.0, c = 0.53, MeOH; lit.[6] $[\alpha]$ = +58.5, c = 0.04, MeOH). ^{1}H NMR (300 MHz, $CDCl_3$) δ [ppm] = 6.93 (dd, J = 8.3, 2.3 Hz, 1H), 6.89 (d, J = 2.2 Hz, 1H), 6.84 (d, J = 8.3 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.14 (ddd, J = 9.3, 7.5, 3.1 Hz, 1H), 2.94 (t, J = 3.6 Hz, 1H), 2.60 (d, J = 3.7 Hz, 2H), 2.47−2.03 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ [ppm] = 211.5, 149.1, 147.6, 140.3, 118.0, 111.1, 110.1, 77.2, 70.5, 56.1, 56.0, 55.0, 47.6, 40.7, 40.2, 39.0, 36.4, 35.4.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00985.

Experimental details, spectral data for all new compounds and HPLC traces for compounds **9** and **19** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: constantin.czekelius@hhu.de. Fax: +49 211 81 11501.

Notes

The authors declare no competing financial interest.

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DOI: 10.1021/acs.joc.6b00985
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Supporting Information

Total Synthesis of (+)-Mesembrine Applying Asymmetric Gold Catalysis

Michael Spittler, Kiril Lutsenko, and Constantin Czekelius*
Institute for Organic Chemistry and Macromolecular Chemistry, Universität Düsseldorf, Universitätsstr. 1, D-40225 Düsseldorf, Germany

Corresponding Author

Constantin Czekelius
Fax: +49 211 81 11501
E-mail: constantin.czekelius@hhu.de

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1 General

All reagents used were purchased or purified to reagent grade. They were used without further purification unless otherwise noted. The used solvents were purchased purely or purified and/or dried by conventional methods. To dry dimethyl sulfoxide, *N*,*N*-dimethylformamide as well as triethylamine 4 Å molecular sieve and to dry methanol as well as *tert*-butanol 3 Å molecular sieve was used. To dry chloroform it was refluxed over P_2O_5 for 2 h and then distilled. It was stored over 4 Å molecular sieve as well as basic aluminium oxide under a nitrogen atmosphere in brown glass flasks. Diisopropylamine was refluxed over CaH_2 for 24 h and then distilled. It was stored over 4 Å molecular sieve under a nitrogen atmosphere. Methyl chloroformate was dried by distillation under nitrogen. Dichloromethane, tetrahydrofuran and diethylether were were dried with a Solvent Purification System. Reactions were monitored with thin-layer chromatography. To concentrate solutions under reduced pressure rotary evaporators in combination with vacuum pumps were used.

For purifications by column chromatography silica gel 60 or aluminium oxide were used. Silica gel was deactivated by conditioning with the respective eluent and 1% (v/v) triethylamine.

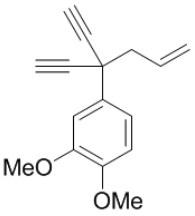
For reactions requiring an inert atmosphere the glassware was dried in a compartment dryer at 120 °C and the standard Schlenk techniques were used to work under a dry nitrogen atmosphere. For reactions under microwave irradiation the CEM Discover SP-D microwave was used with 100 W. For reactions under hydrogen pressure a Parr Instrument General Purpose Vessel made of Hastelloy C-276 with a teflon inset was used.

The enantiomeric excess was determined with a High Performance Liquid Chromatography (HPLC) system equipped with a DAICEL CHIRALPAK® IA™ (4.6 x 250 mm) or DAICEL CHIRALPAK® IC™ (4.6 x 250 mm) column. All samples were filtered with syringe filters (25 mm, 0.45 µm PTFE membrane or 13 mm, 0.2 µm PTFE membrane).

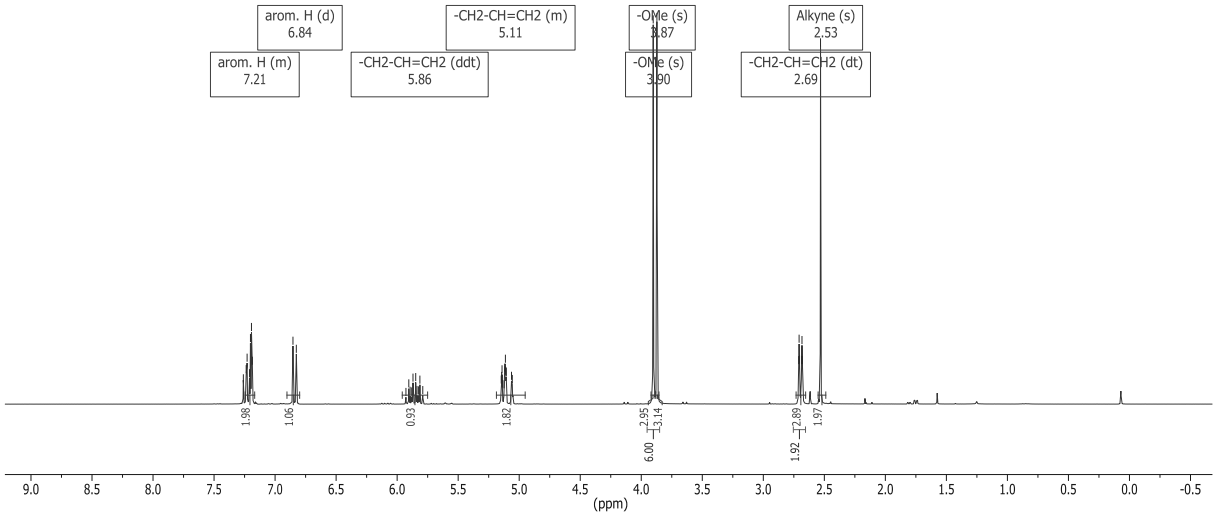
^{1}H- and ^{13}C-NMR-spectra were recorded at 600 and 300 or 151 and 75 MHz, respectively. The chemical shifts were standardised with traces of chloroform ($\delta(CHCl_3)$ = 7.26 ppm) or benzene ($\delta(C_6H_6)$ = 7.16 ppm) in ^{1}H-spectra and with the signal of deuterated chloroform ($\delta(CDCl_3)$ = 77.16 ppm) or deuterated benzene ($\delta(C_6D_6)$ = 128.06 ppm) in ^{13}C-spectra. The coupling constants *J* are given in hertz (Hz) and the chemical shifts *δ* in ppm. IR-spectra were measured as thin films on a NaCl single crystal. High resolution mass spectra (HRMS) were measured with a Q-TOF spectrometer.

2 Spectral Data

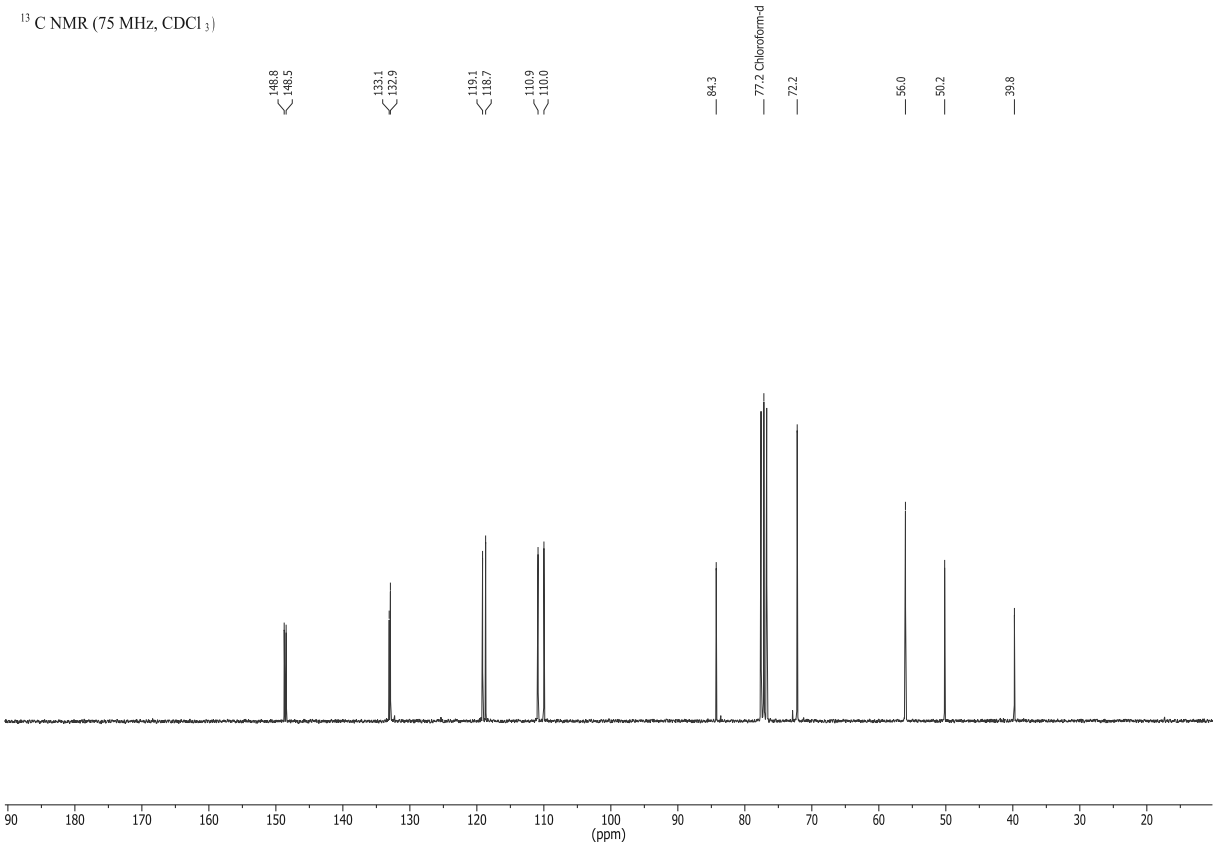
2.1 3-Ethynyl-3-(3,4-dimethoxyphenyl)hex-1-ene-5-yne (5)

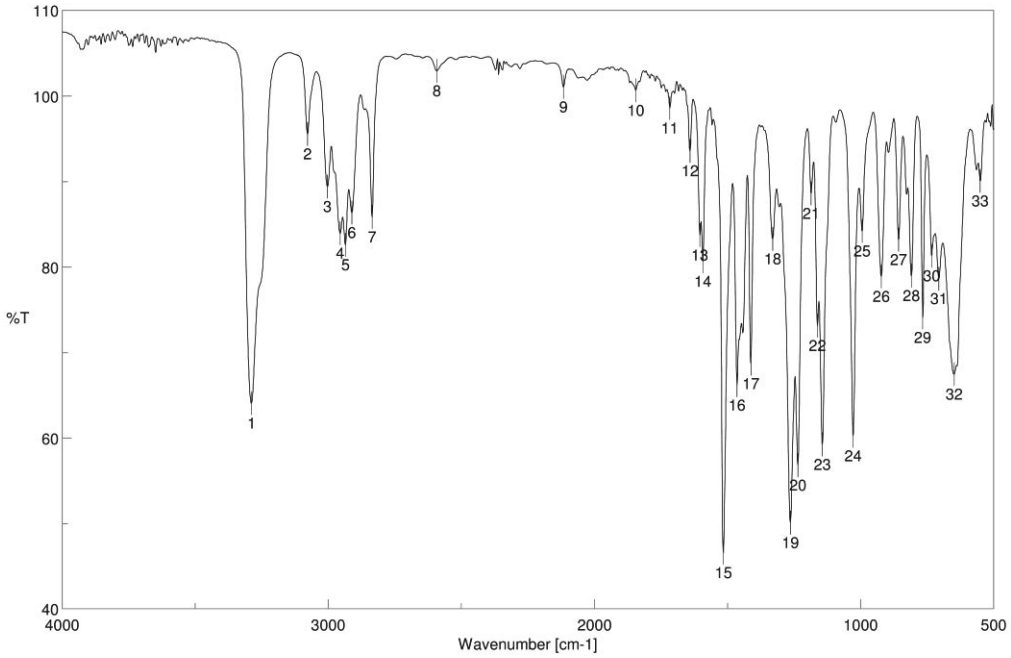


^{1}H NMR (300 MHz, $CDCl_3$)



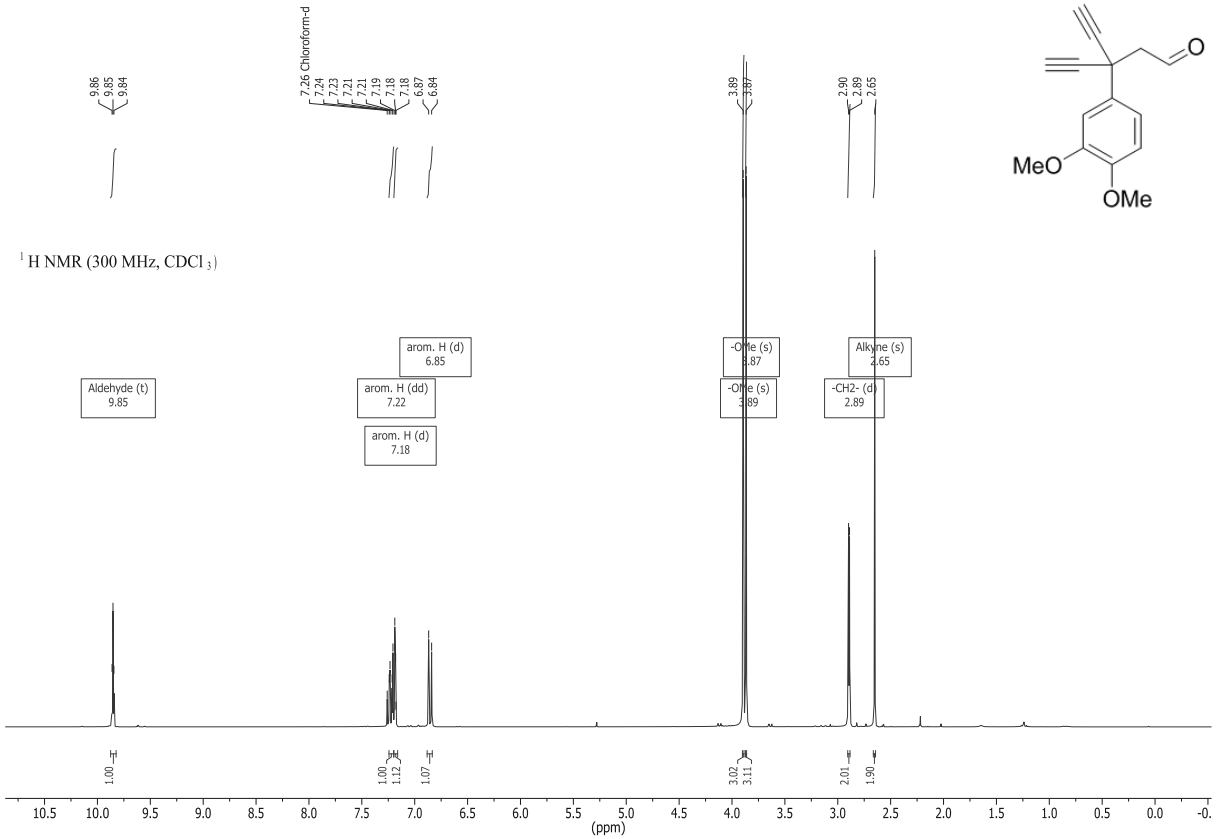
^{13}C NMR (75 MHz, $CDCl_3$)



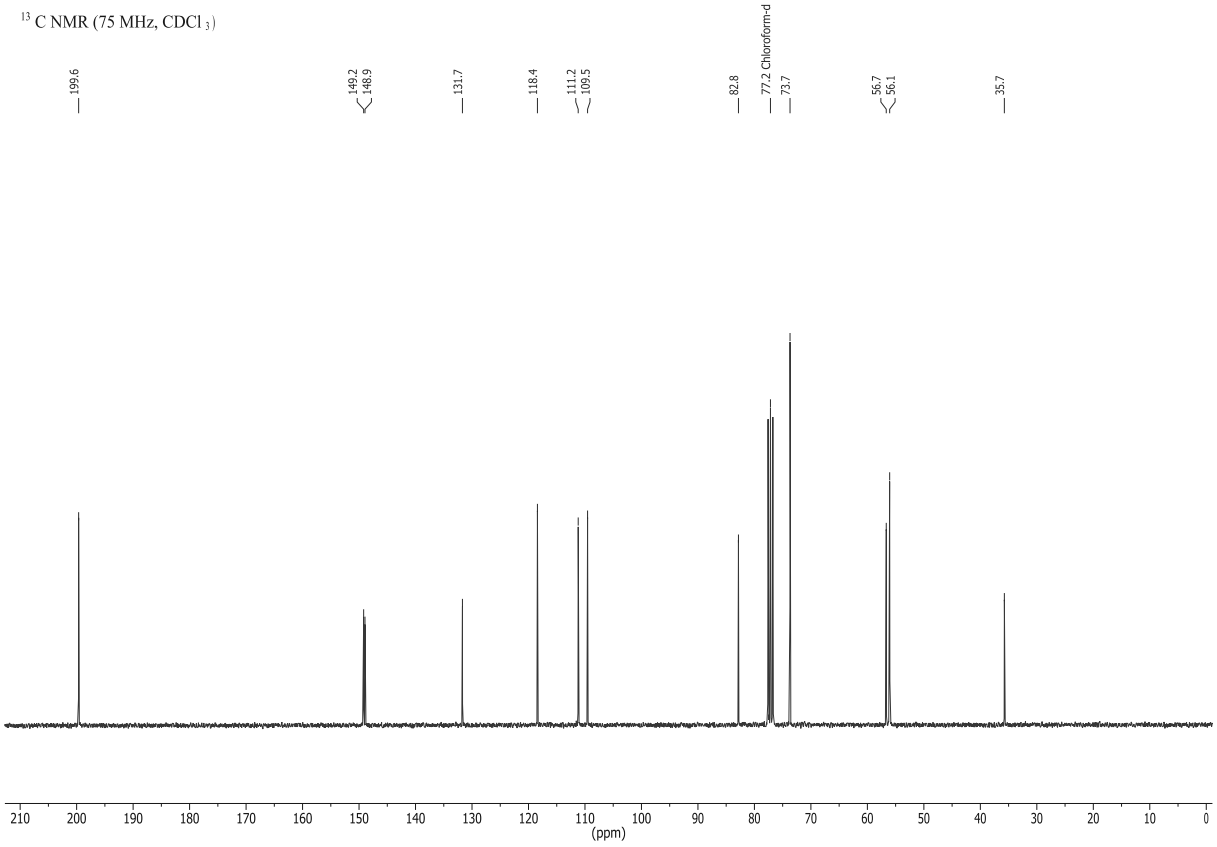


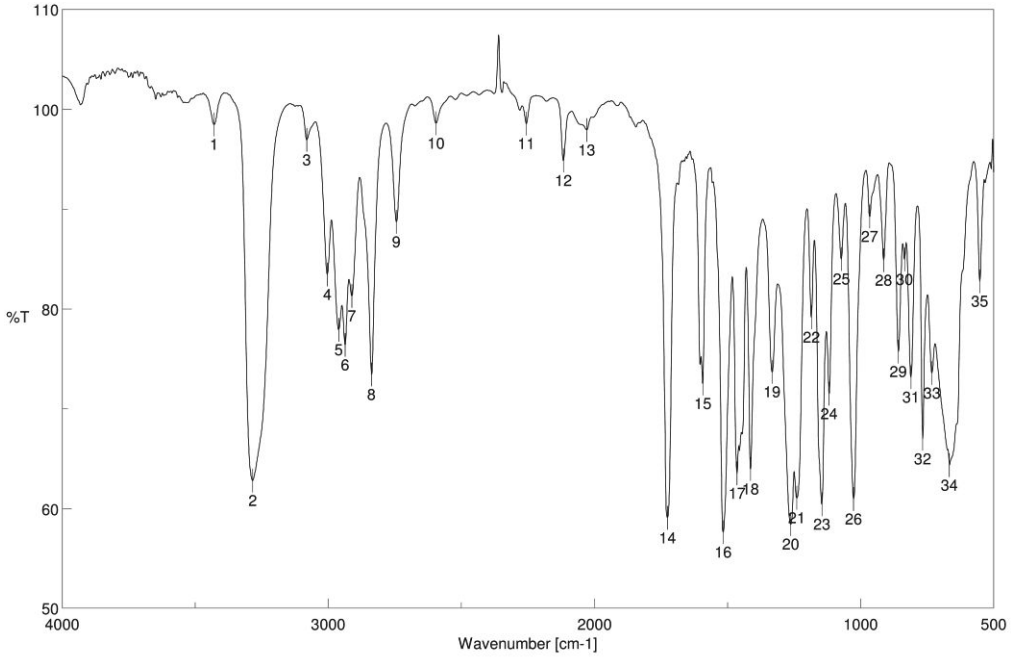
Result of Peak Picking		
No.	Position	Intensity
1	3289	64.0381
2	3077.83	95.535
3	3002.62	89.3815
4	2955.38	83.9163
5	2936.09	82.5636
6	2911.99	86.3235
7	2835.81	85.8286
8	2592.82	102.914
9	2116.49	101.037
10	1844.58	100.643
11	1716.34	98.5828
12	1641.13	93.5562
13	1603.52	83.7103
14	1592.91	80.6476
15	1515.78	46.5613
16	1463.71	66.1666
17	1412.6	68.6758
18	1330.64	83.273
19	1264.11	50.0717
20	1236.15	56.8025
21	1186.01	88.6052
22	1161.9	73.1248
23	1143.58	59.2049
24	1027.87	60.2287
25	994.125	84.1914
26	922.771	78.8497
27	857.204	83.1597
28	808.992	78.9597
29	766.566	74.0613
30	732.817	81.3086
31	705.819	78.6112
32	648.929	67.4348
33	550.577	90.0166

2.2 3-(3,4-Dimethoxyphenyl)-3-ethynyl-pent-4-ynal (6)



^{13}C NMR (75 MHz, $CDCl_3$)



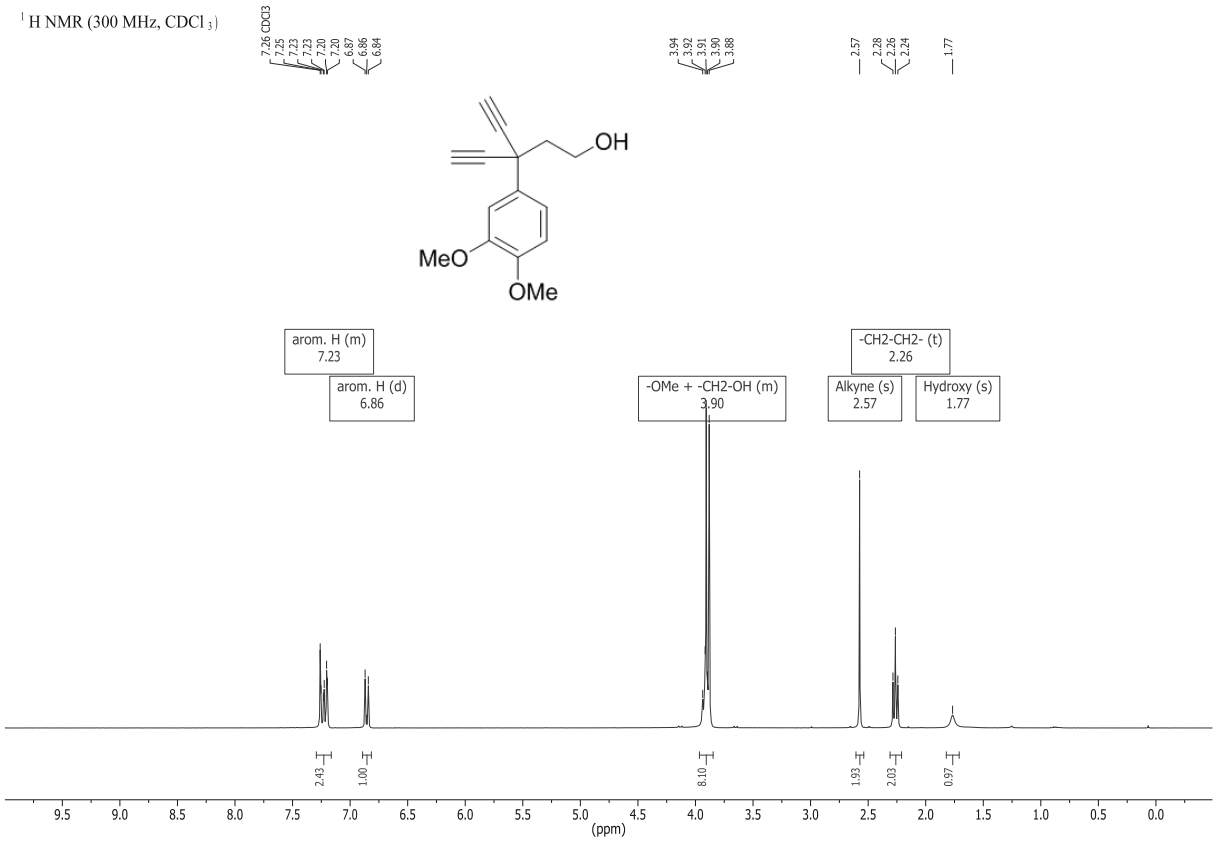


Result of Peak Picking

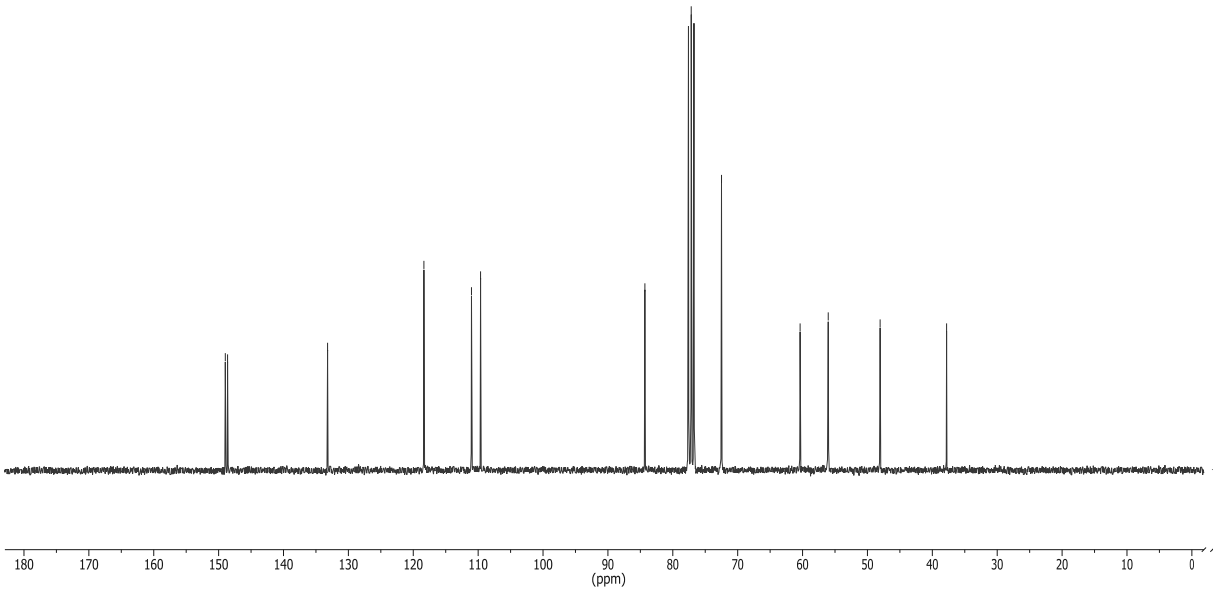
No.	Position	Intensity
1	3429.78	98.4621
2	3284.18	62.7815
3	3080.73	96.9197
4	3003.59	83.4453
5	2961.16	77.9005
6	2937.06	76.3849
7	2911.99	81.2642
8	2837.74	73.4126
9	2744.21	88.6932
10	2594.75	98.5801
11	2256.31	98.5575
12	2116.49	94.8317
13	2029.71	97.9173
14	1725.98	59.0387
15	1592.91	72.4901
16	1516.74	57.6309
17	1464.67	63.4966
18	1413.57	63.9313
19	1332.57	73.6603
20	1262.18	58.4105
21	1240	61.0261
22	1185.04	79.1143
23	1145.51	60.3877
24	1118.51	71.4946
25	1072.23	84.9747
26	1025.94	60.9197
27	966.162	89.2351
28	913.129	84.8574
29	858.168	75.7206
30	835.026	84.9191
31	810.92	73.1347
32	766.566	66.9599
33	731.853	73.5553
34	666.285	64.3212
35	551.542	82.7379

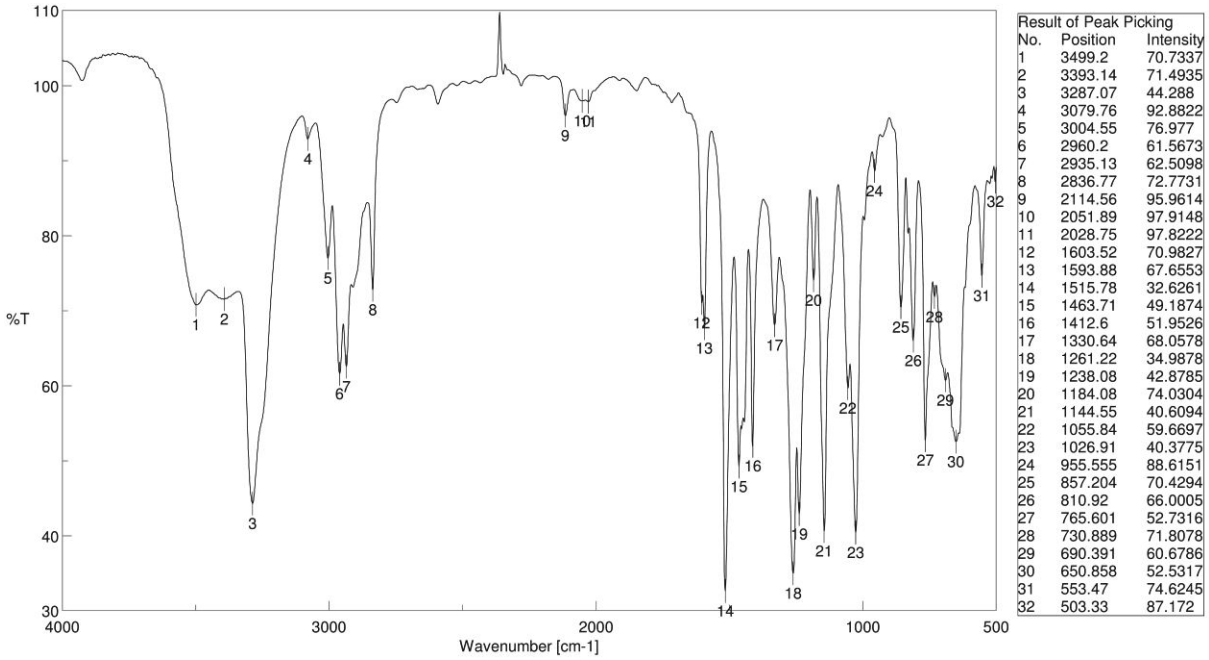
2.3 3-(3,4-Dimethoxyphenyl)-3-ethynyl-pent-4-yn-1-ol (7):

^{1}H NMR (300 MHz, $CDCl_3$)



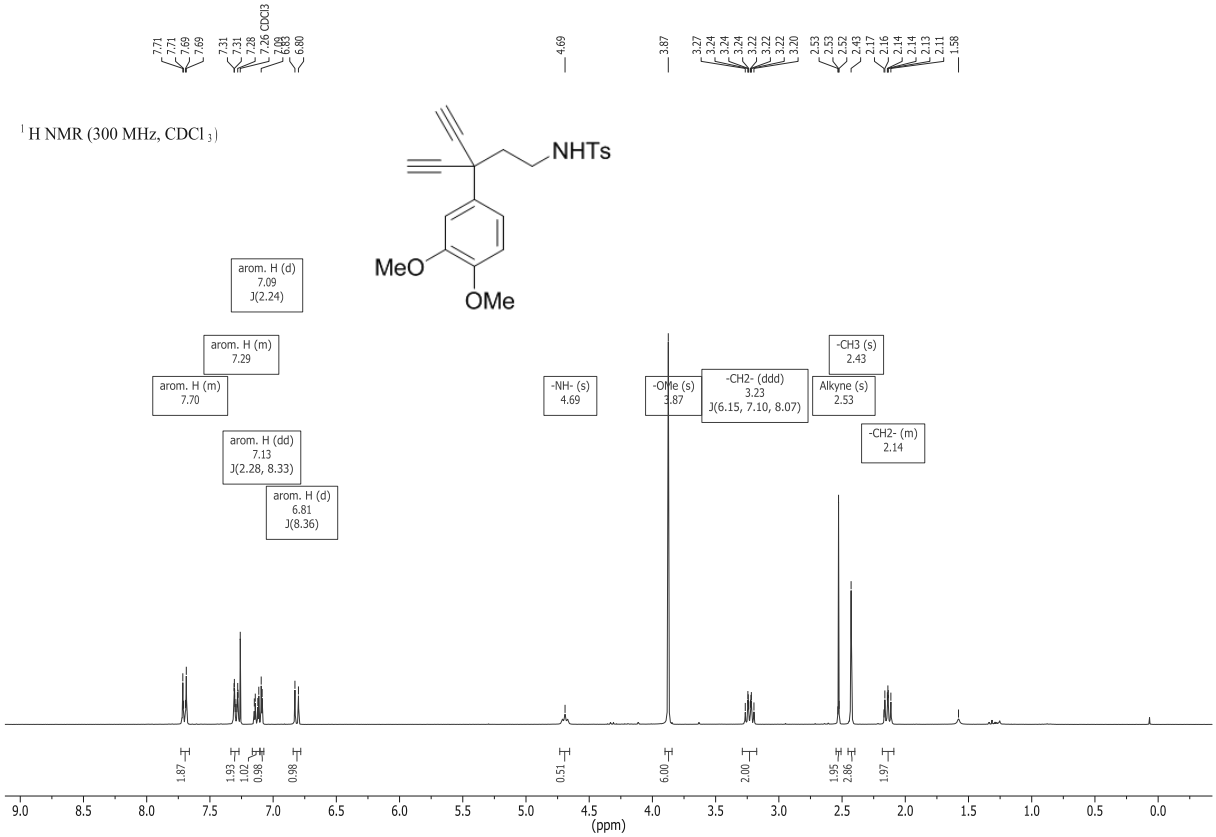
^{13}C NMR (75 MHz, $CDCl_3$)





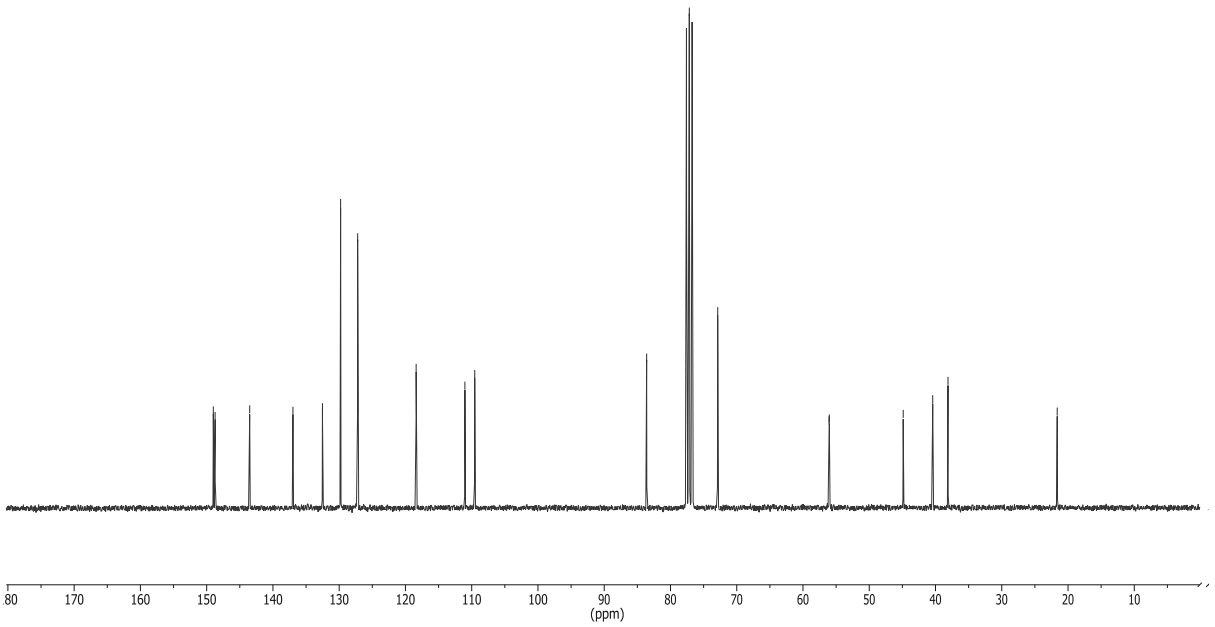
Result of Peak Picking		
No.	Position	Intensity
1	3499.2	70.7337
2	3393.14	71.4935
3	3287.07	44.288
4	3079.76	92.8822
5	3004.55	76.977
6	2960.2	61.5673
7	2935.13	62.5098
8	2836.77	72.7731
9	2114.56	95.9614
10	2051.89	97.9148
11	2028.75	97.8222
12	1603.52	70.9827
13	1593.88	67.6553
14	1515.78	32.6261
15	1463.71	49.1874
16	1412.6	51.9526
17	1330.64	68.0578
18	1261.22	34.9878
19	1238.08	42.8785
20	1184.08	74.0304
21	1144.55	40.6094
22	1055.84	59.6697
23	1026.91	40.3775
24	955.555	88.6151
25	857.204	70.4294
26	810.92	66.0005
27	765.601	52.7316
28	730.889	71.8078
29	690.391	60.6786
30	650.858	52.5317
31	553.47	74.6245
32	503.33	87.172

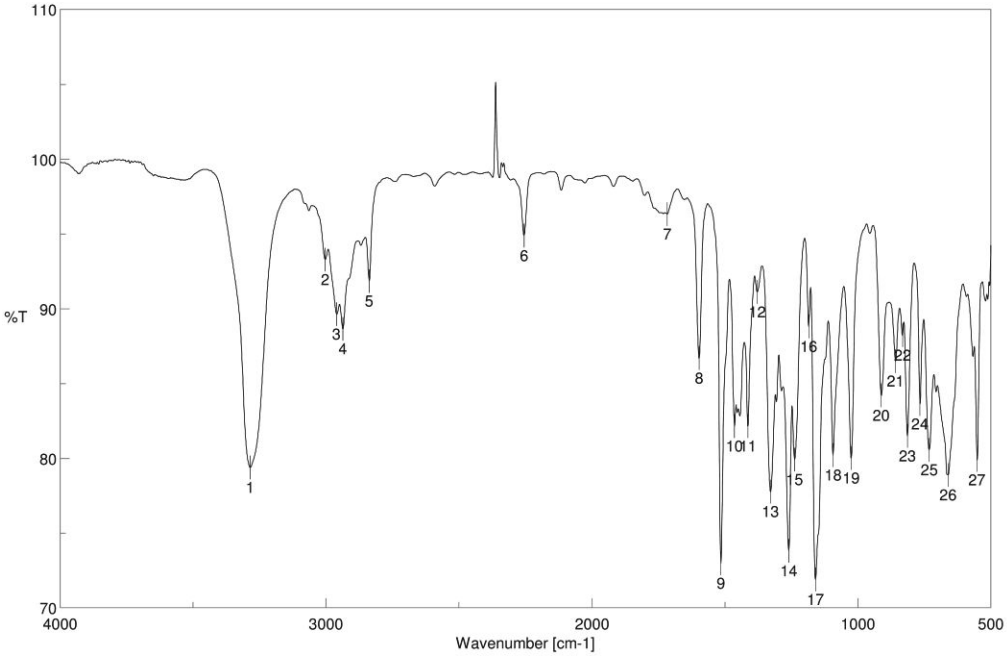
2.4 *N*-(4-Toluenesulfonyl)-(3-(3,4-dimethoxyphenyl)-3-ethynyl-pent-4-yn-1-amine (8):



149.0
148.7
143.5
137.0
132.5
129.8
127.2
118.4
111.0
109.5
83.6
77.2 CDCl3
72.9
56.1
56.0
44.9
40.4
38.1
21.6

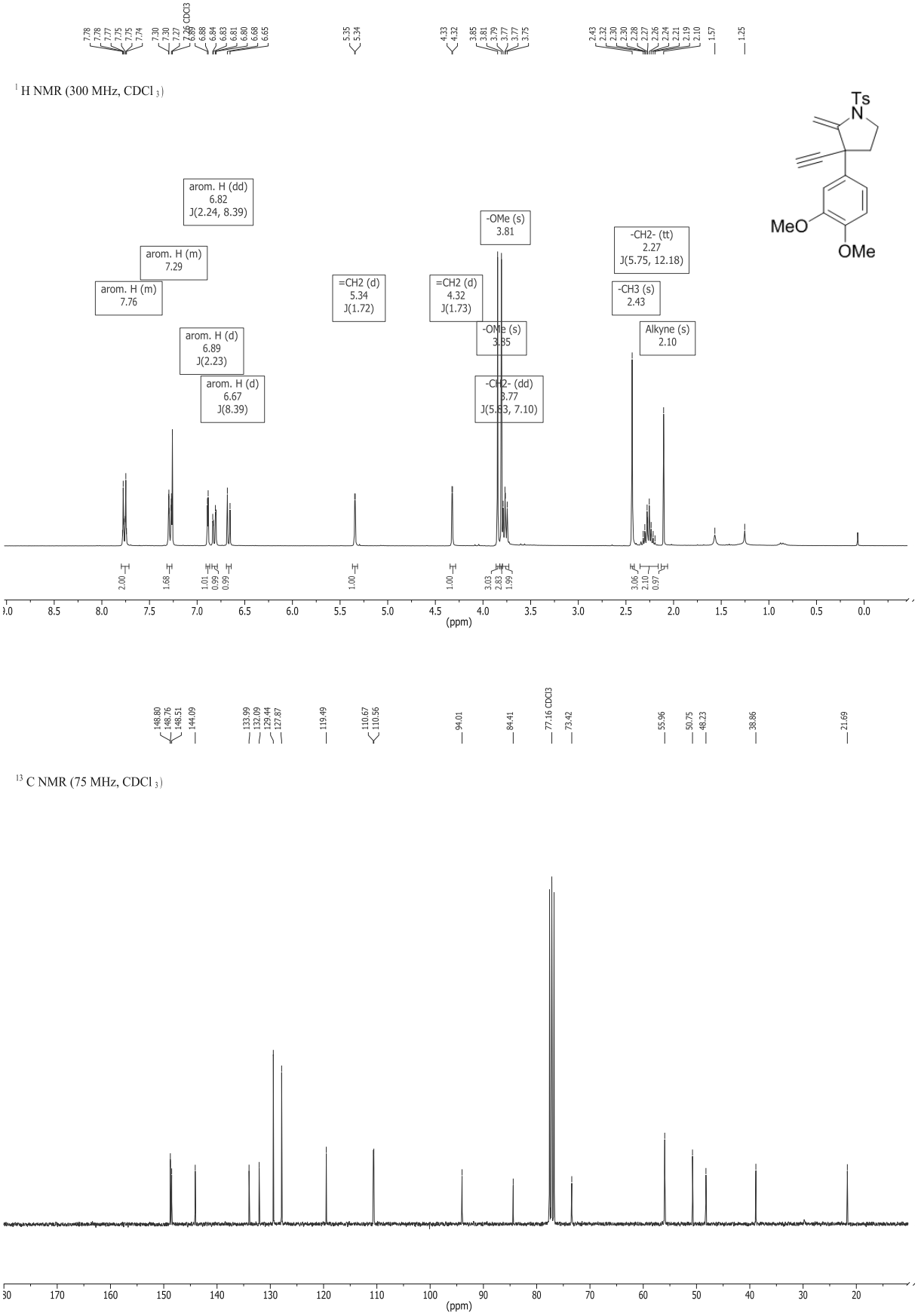
^{13}C NMR (75 MHz, $CDCl_3$)

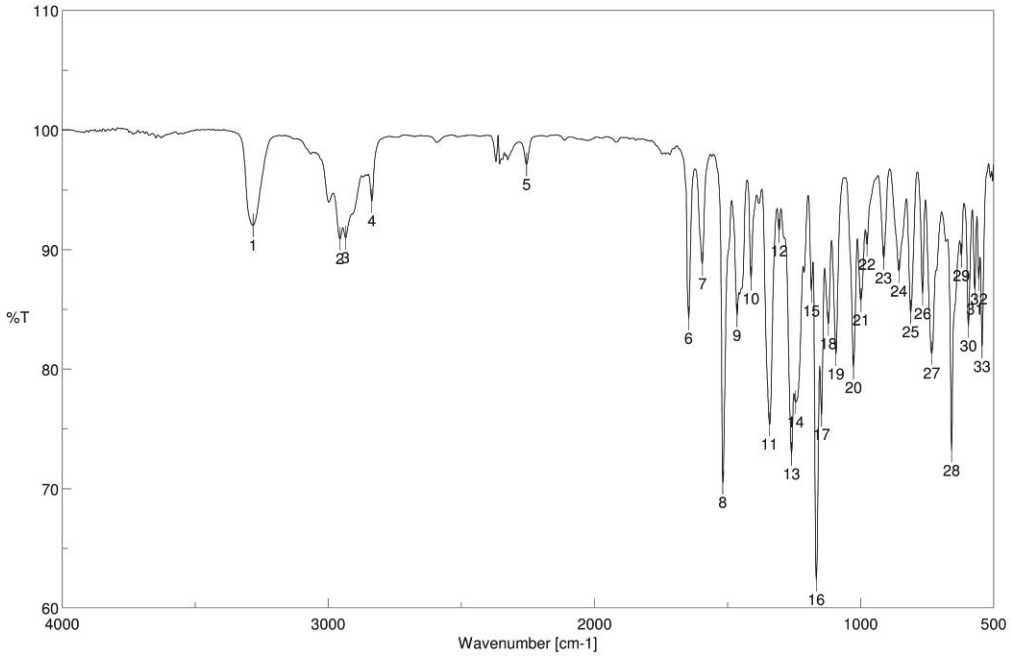




Result of Peak Picking		
No.	Position	Intensity
1	3285.14	79.3787
2	3002.62	93.2737
3	2960.2	89.6269
4	2937.06	88.6333
5	2837.74	91.8408
6	2255.34	94.8766
7	1716.34	96.3032
8	1596.77	86.6816
9	1514.81	72.9618
10	1463.71	82.1235
11	1413.57	82.1356
12	1378.85	91.0998
13	1328.71	77.7686
14	1260.25	73.7906
15	1238.08	79.9034
16	1185.04	88.8018
17	1159.97	71.8811
18	1093.44	80.2093
19	1024.98	79.997
20	912.165	84.1918
21	858.168	86.4775
22	832.133	88.2105
23	813.813	81.4861
24	766.566	83.612
25	731.853	80.5429
26	660.5	78.8569
27	551.542	79.8727

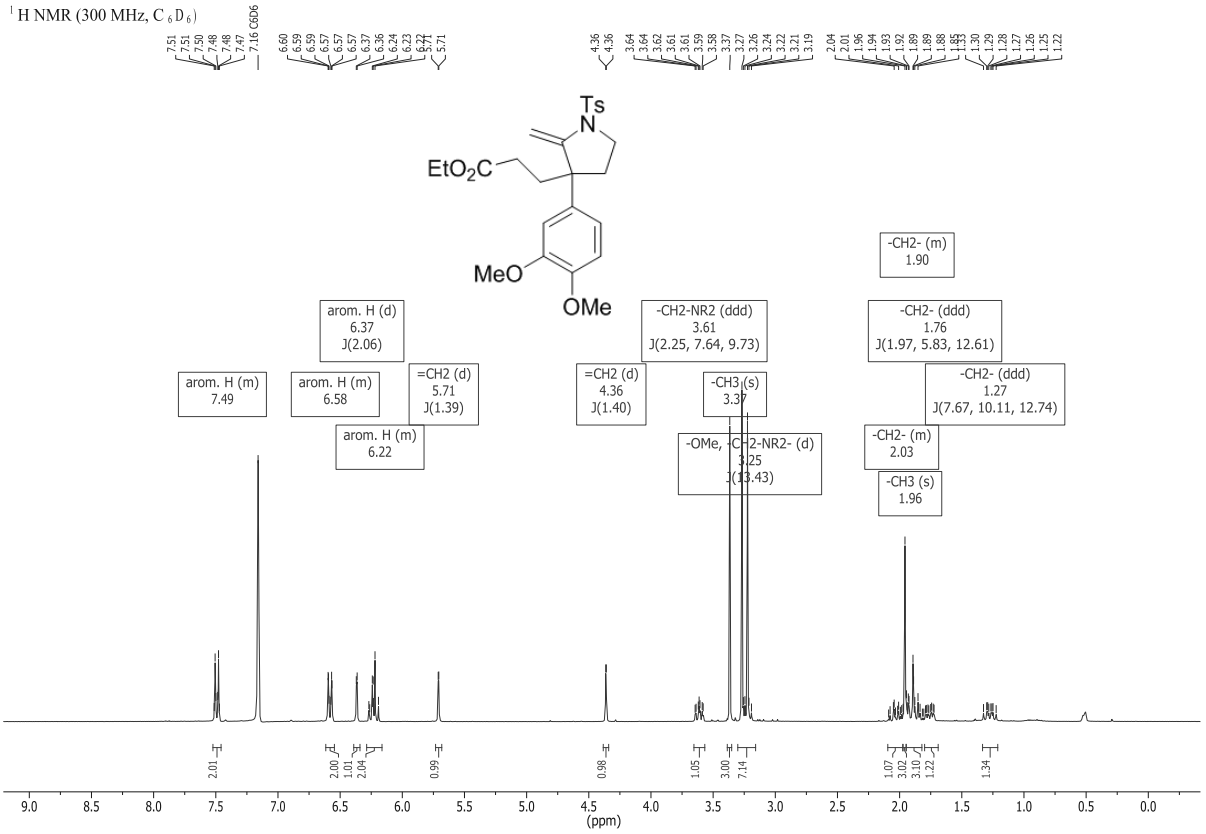
2.5 3-(3,4-Dimethoxyphenyl)-3-ethynyl-2-methylene-1-(4-toluene-sulfonyl)-pyrrolidine (9)

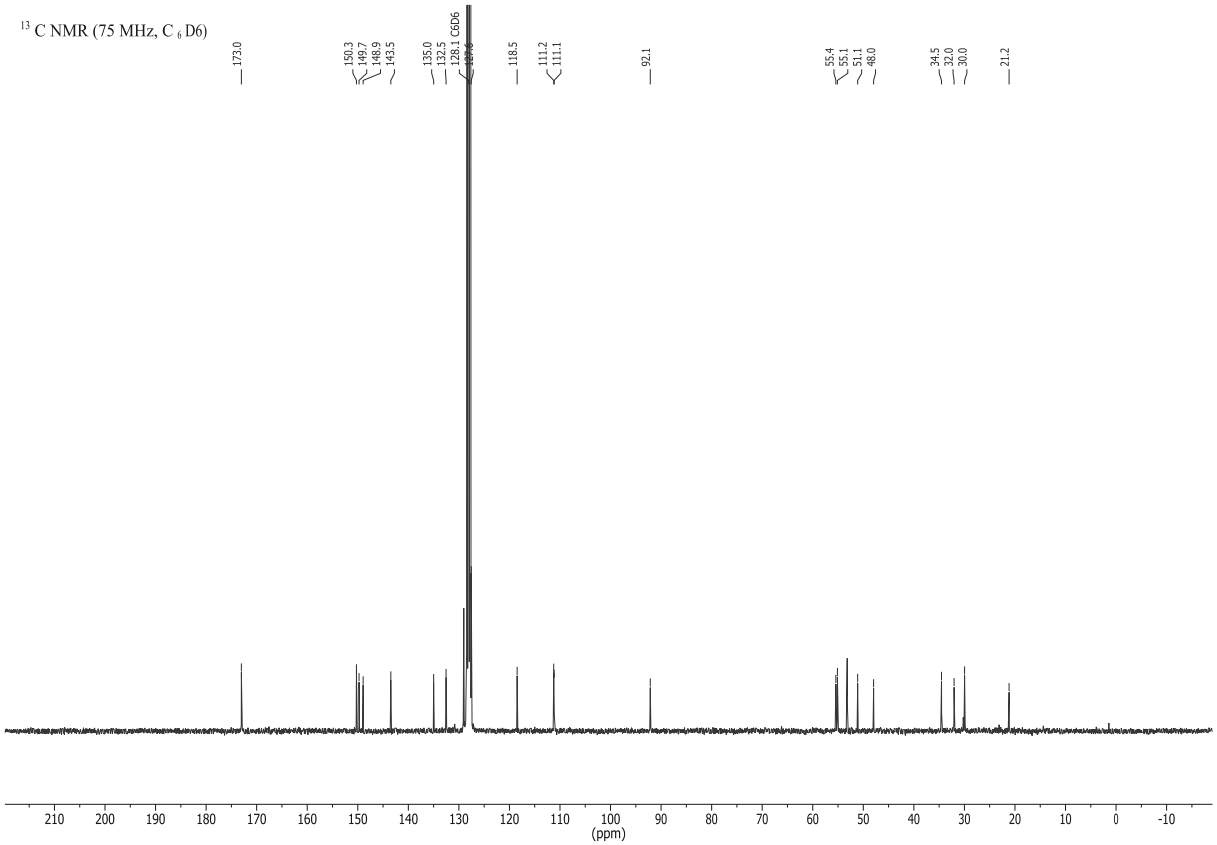


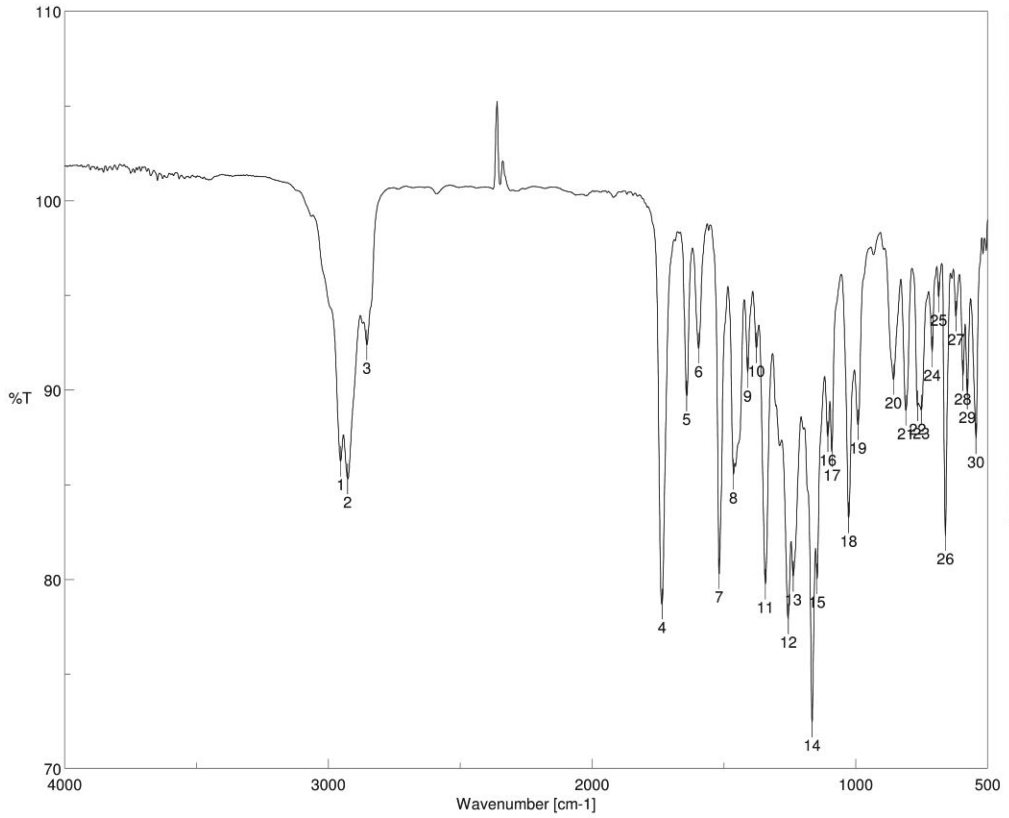


Result of Peak Picking		
No.	Position	Intensity
1	3283.21	92.0107
2	2956.34	90.8866
3	2935.13	90.9548
4	2836.77	94.0489
5	2255.34	97.0901
6	1645.95	84.2148
7	1594.84	88.7714
8	1517.7	70.5038
9	1463.71	84.4625
10	1411.64	87.5304
11	1342.21	75.3476
12	1306.54	91.5391
13	1259.29	72.8872
14	1243.86	77.1979
15	1185.04	86.5098
16	1166.72	62.3399
17	1146.47	76.1731
18	1121.4	83.7763
19	1092.48	81.2445
20	1026.91	80.0993
21	998.946	85.7532
22	975.804	90.3916
23	913.129	89.2827
24	856.239	88.1674
25	811.885	84.7428
26	767.53	86.2727
27	732.817	81.2854
28	658.571	73.1624
29	621.931	89.4587
30	594.932	83.5898
31	570.826	86.6654
32	555.398	87.5067
33	543.828	81.8589

2.6 Methyl 3-(3-(3,4-dimethoxyphenyl)-2-methylene-1-(4-toluenesulfo-nyl)-pyrrolidin-3-yl)propanoate (10):



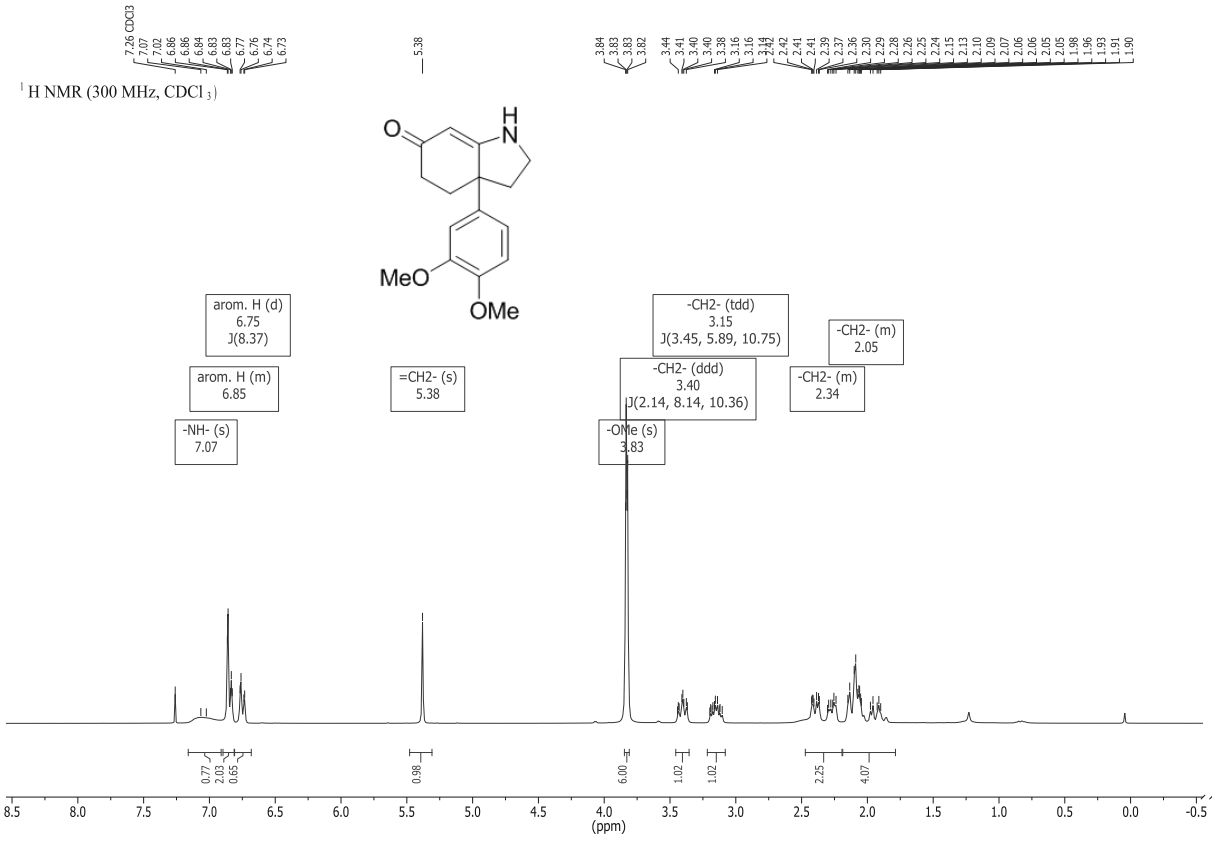


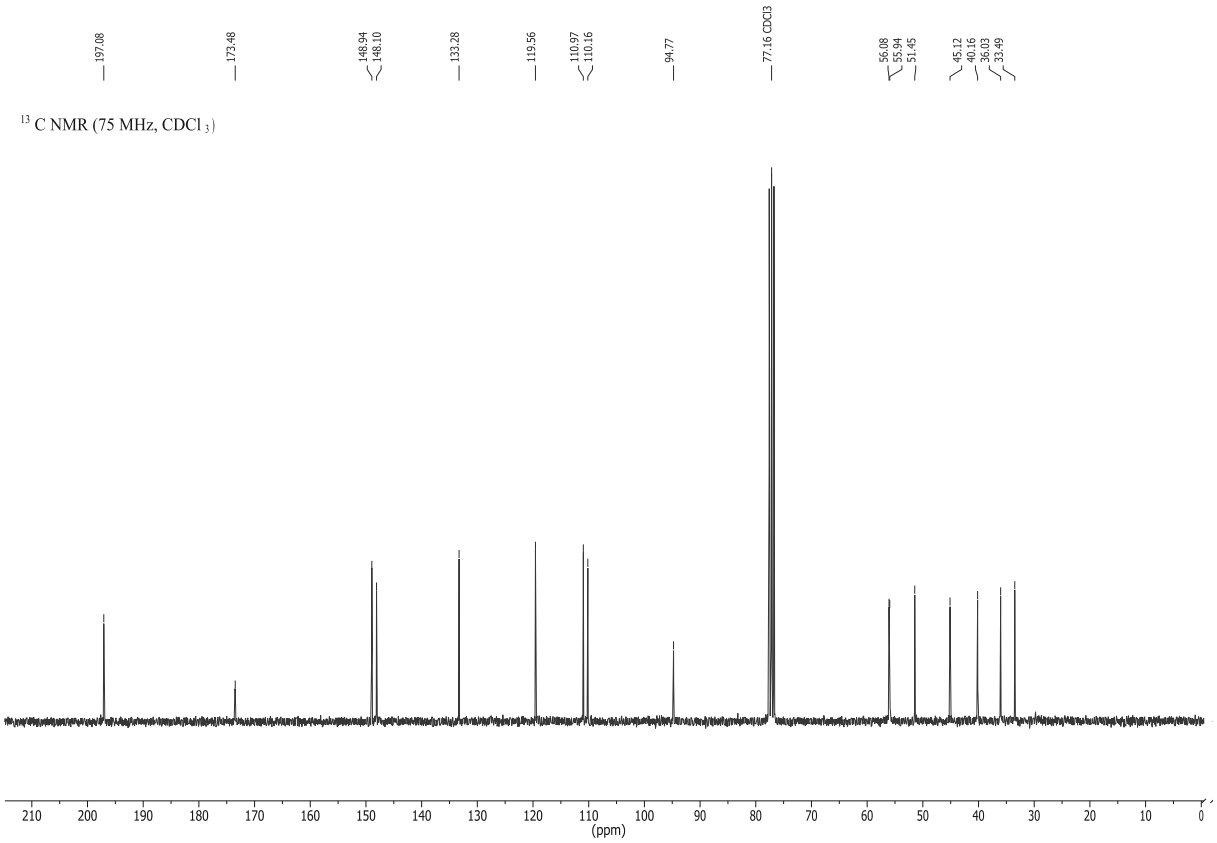


Result of Peak Picking

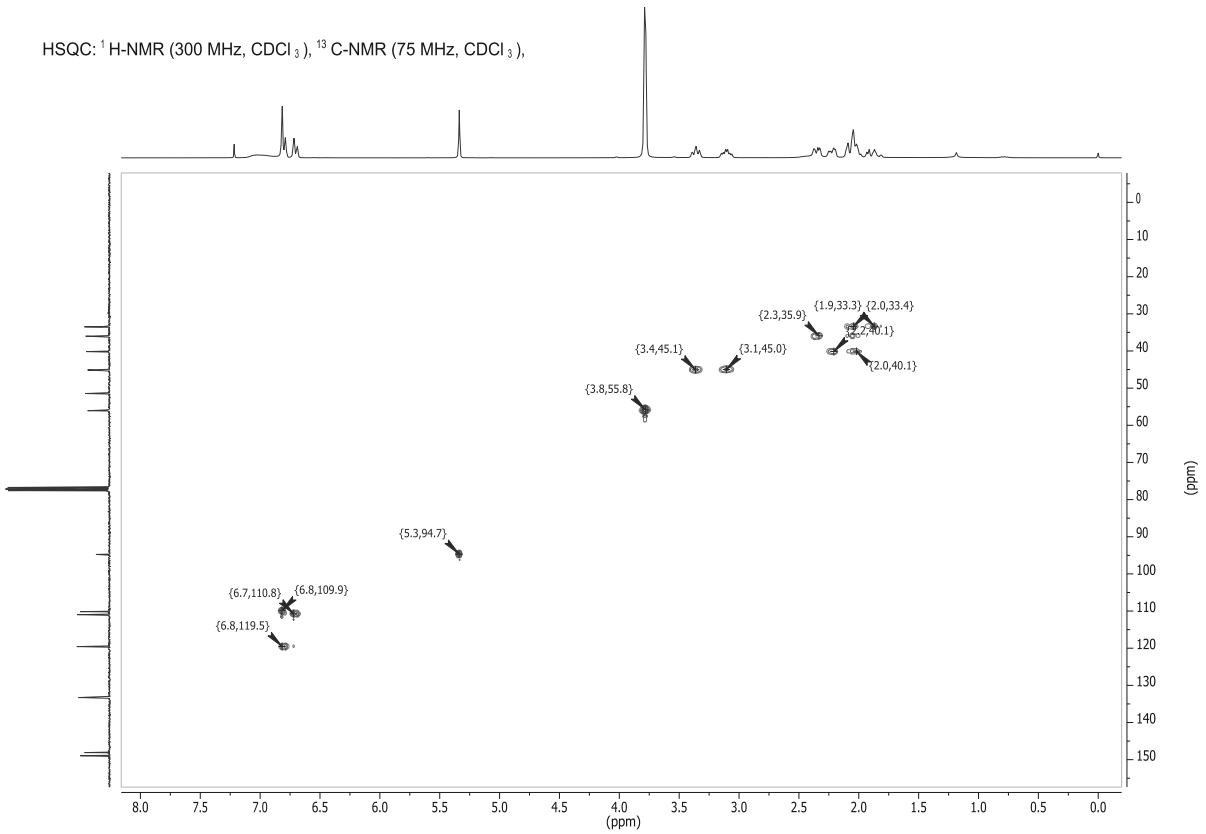
No.	Position	Intensity
1	2953.45	86.2268
2	2926.45	85.2898
3	2854.13	92.3755
4	1734.66	78.6719
5	1641.13	89.6671
6	1595.81	92.1939
7	1518.67	80.2973
8	1463.71	85.538
9	1409.71	90.8975
10	1376.93	92.2196
11	1342.21	79.7416
12	1256.4	77.9032
13	1237.11	80.1497
14	1165.76	72.4461
15	1146.47	80.008
16	1105.98	87.5187
17	1090.55	86.7304
18	1026.91	83.2321
19	991.232	88.1539
20	857.204	90.5497
21	809.956	88.9127
22	765.601	89.1619
23	752.102	88.9304
24	710.64	92.006
25	685.57	94.9172
26	660.5	82.3136
27	620.002	93.8985
28	593.968	90.7397
29	576.612	89.7804
30	543.828	87.4193

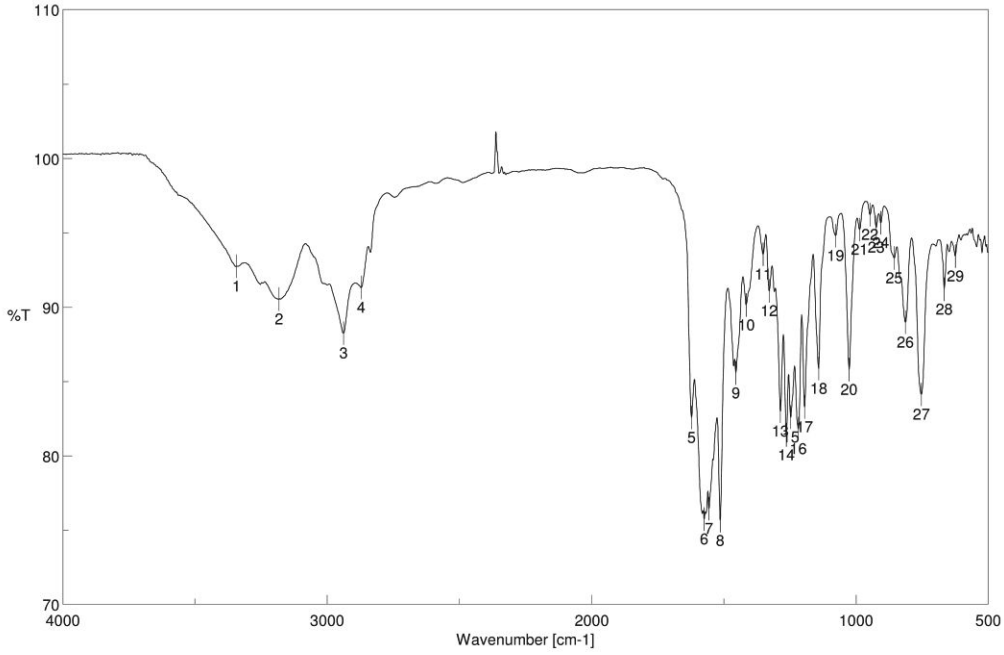
2.7 3a-(3,4-Dimethoxyphenyl)-1,2,3,3a,4,5-hexahydro-6H-indol-6-one (11):





HSQC: ^{1}H-NMR (300 MHz, $CDCl_3$), ^{13}C-NMR (75 MHz, $CDCl_3$),

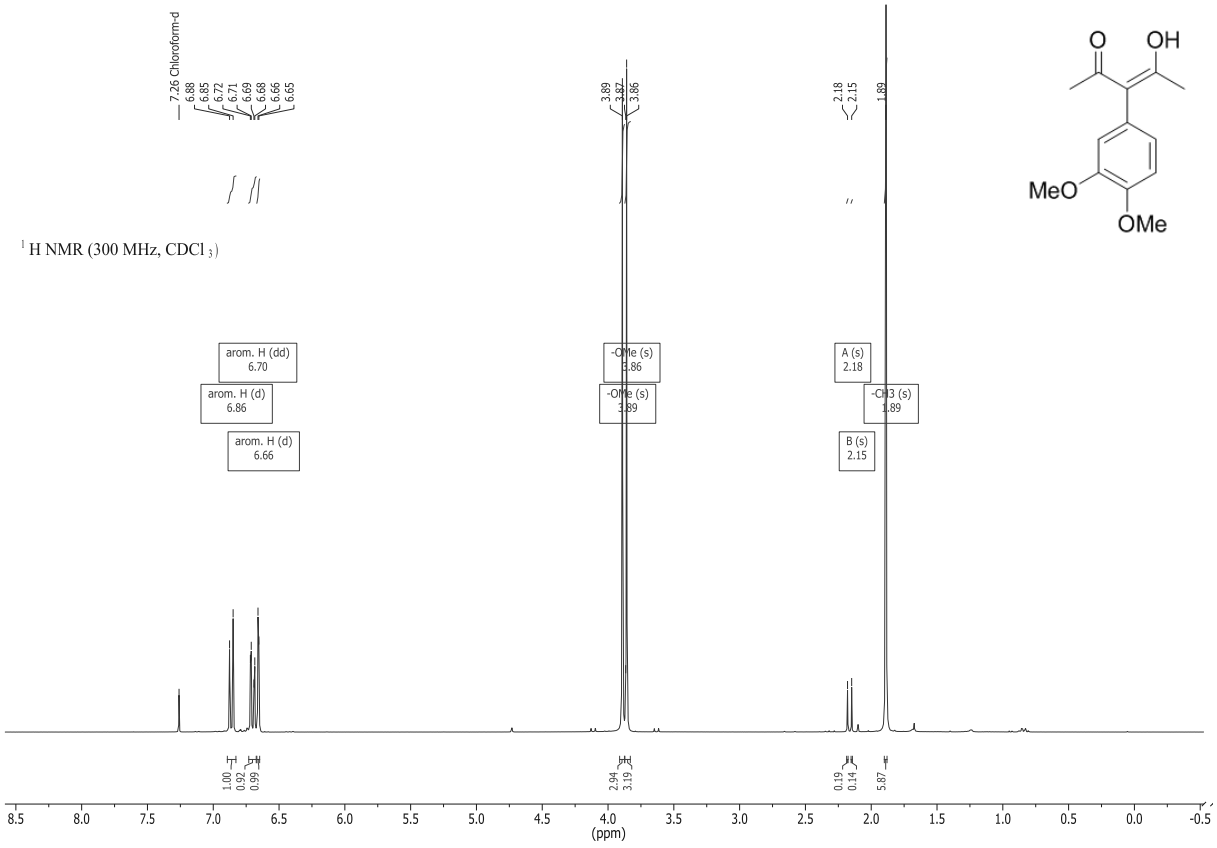


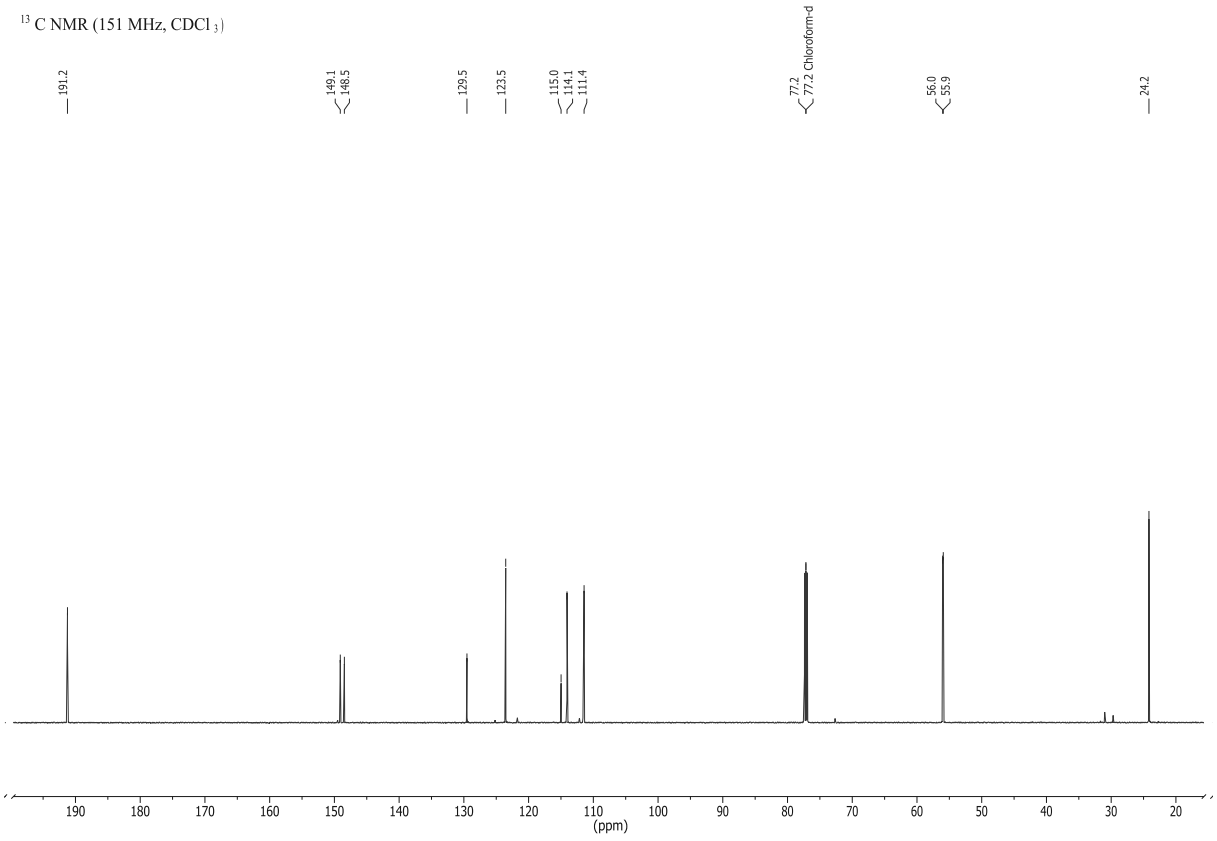


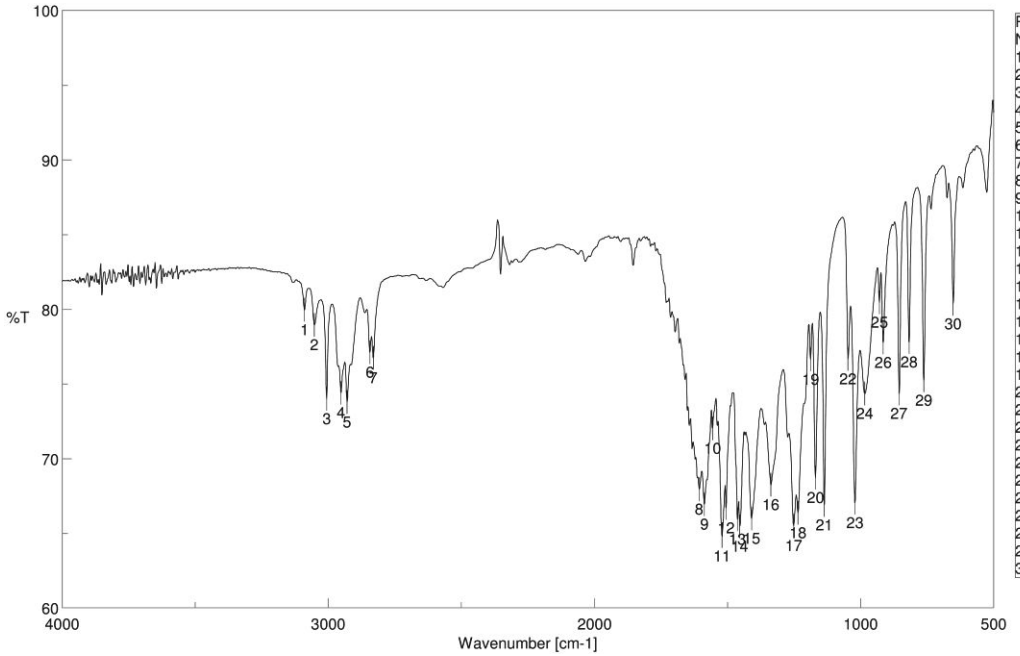
Result of Peak Picking

No.	Position	Intensity
1	3343.96	92.7288
2	3182.93	90.5276
3	2938.98	88.2292
4	2872.45	91.2964
5	1621.84	82.5541
6	1574.59	75.7234
7	1556.27	76.4252
8	1513.85	75.6386
9	1455.03	85.5456
10	1415.49	90.1378
11	1351.86	93.5402
12	1328.71	91.0853
13	1286.29	82.9966
14	1264.11	81.3771
15	1246.75	82.5769
16	1218.79	81.8171
17	1194.69	83.2742
18	1141.65	85.8493
19	1077.05	94.7981
20	1025.94	85.7864
21	986.411	95.2005
22	947.842	96.1999
23	923.736	95.3436
24	906.379	95.6557
25	856.239	93.296
26	812.849	88.968
27	753.066	84.1236
28	667.25	91.1863
29	624.823	93.4269

2.8 3-(3,4-Dimethoxyphenyl)pentane-2,4-dione (13):

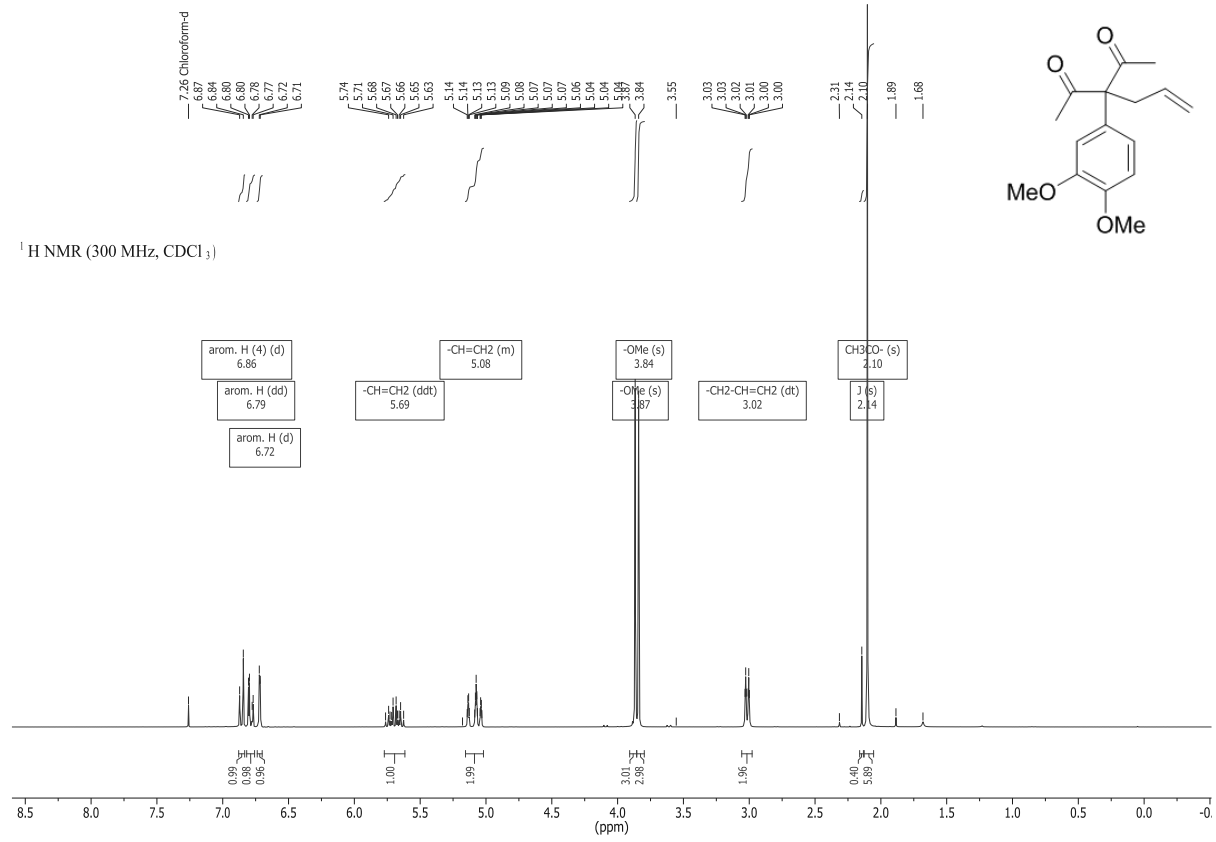




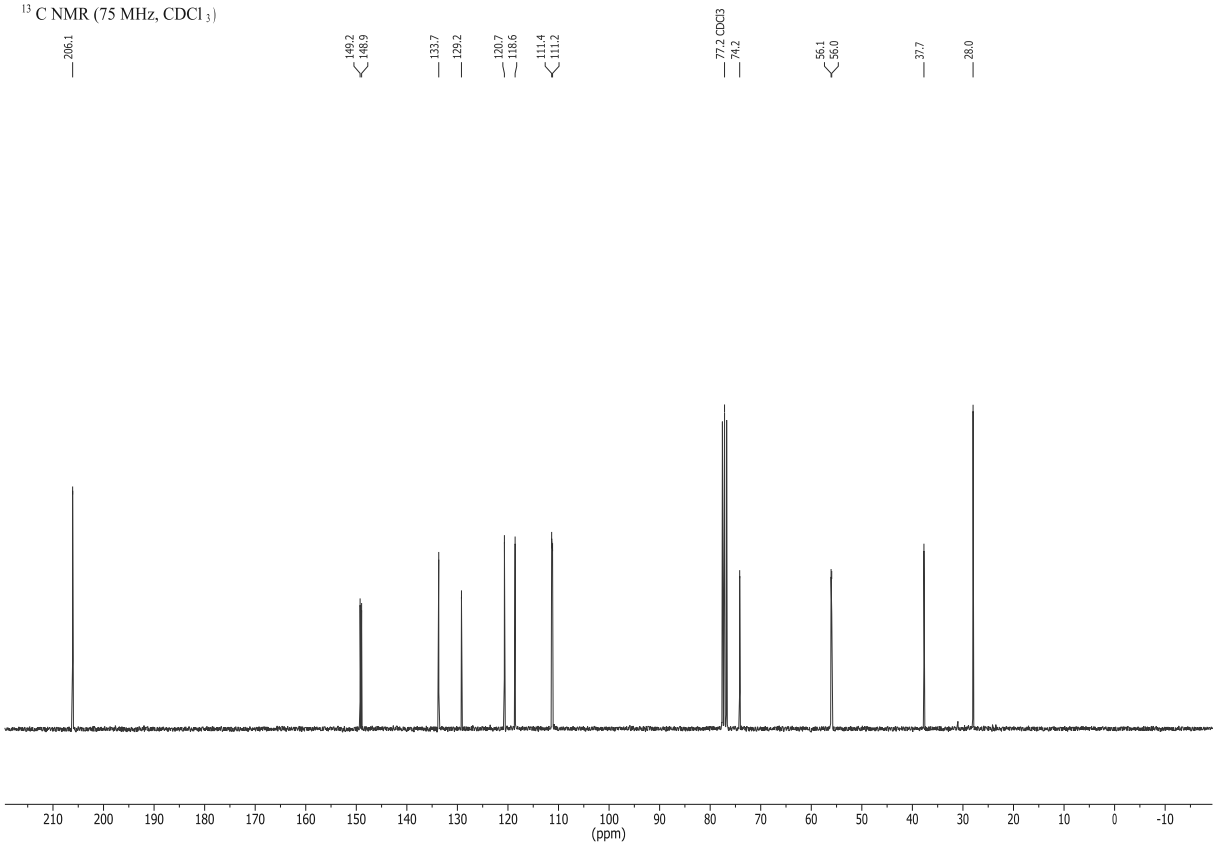


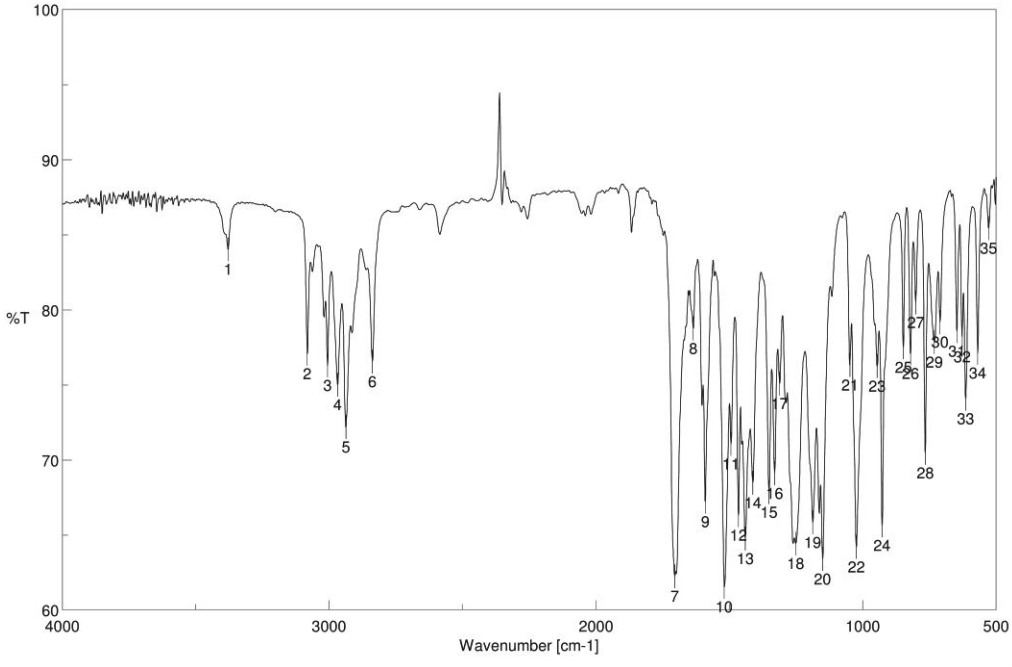
Result of Peak Picking		
No.	Position	Intensity
1	3089.4	79.9387
2	3052.76	78.9456
3	3006.48	74.0023
4	2952.48	74.4089
5	2929.34	73.7733
6	2843.52	77.1211
7	2830.99	76.7263
8	1606.41	67.9411
9	1587.13	66.9409
10	1556.27	72.0199
11	1520.6	64.7956
12	1505.17	66.6783
13	1462.74	65.9367
14	1454.06	65.4414
15	1409.71	65.9737
16	1337.39	68.2453
17	1251.58	65.5123
18	1235.18	66.3554
19	1187.94	76.6206
20	1169.62	68.7206
21	1136.83	66.8864
22	1047.16	76.6591
23	1021.12	67.023
24	984.482	74.3489
25	929.521	80.4647
26	915.058	77.7656
27	855.275	74.3412
28	817.67	77.7967
29	762.709	75.2264
30	651.822	80.3573

2.9 3-Allyl-3-(3,4-dimethoxyphenyl)pentane-2,4-dione (14):



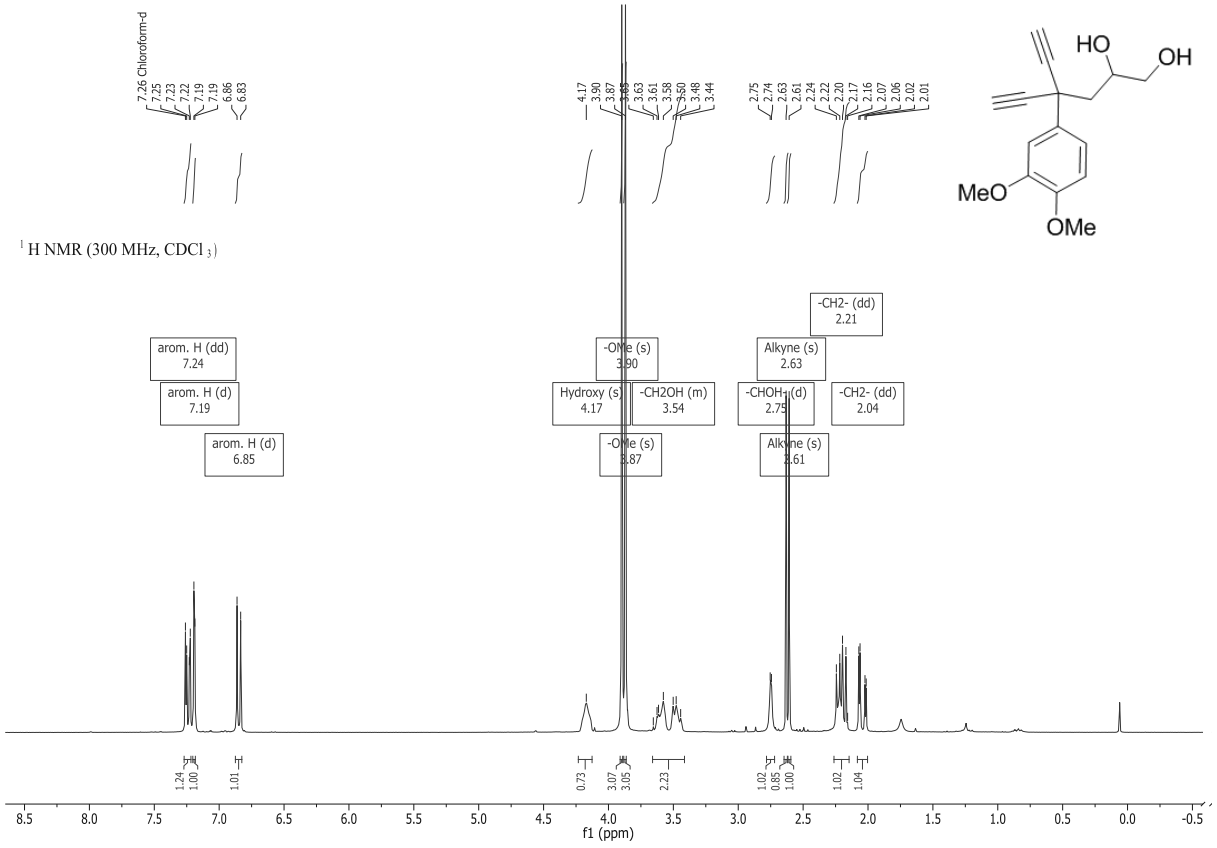
^{13}C NMR (75 MHz, $CDCl_3$)

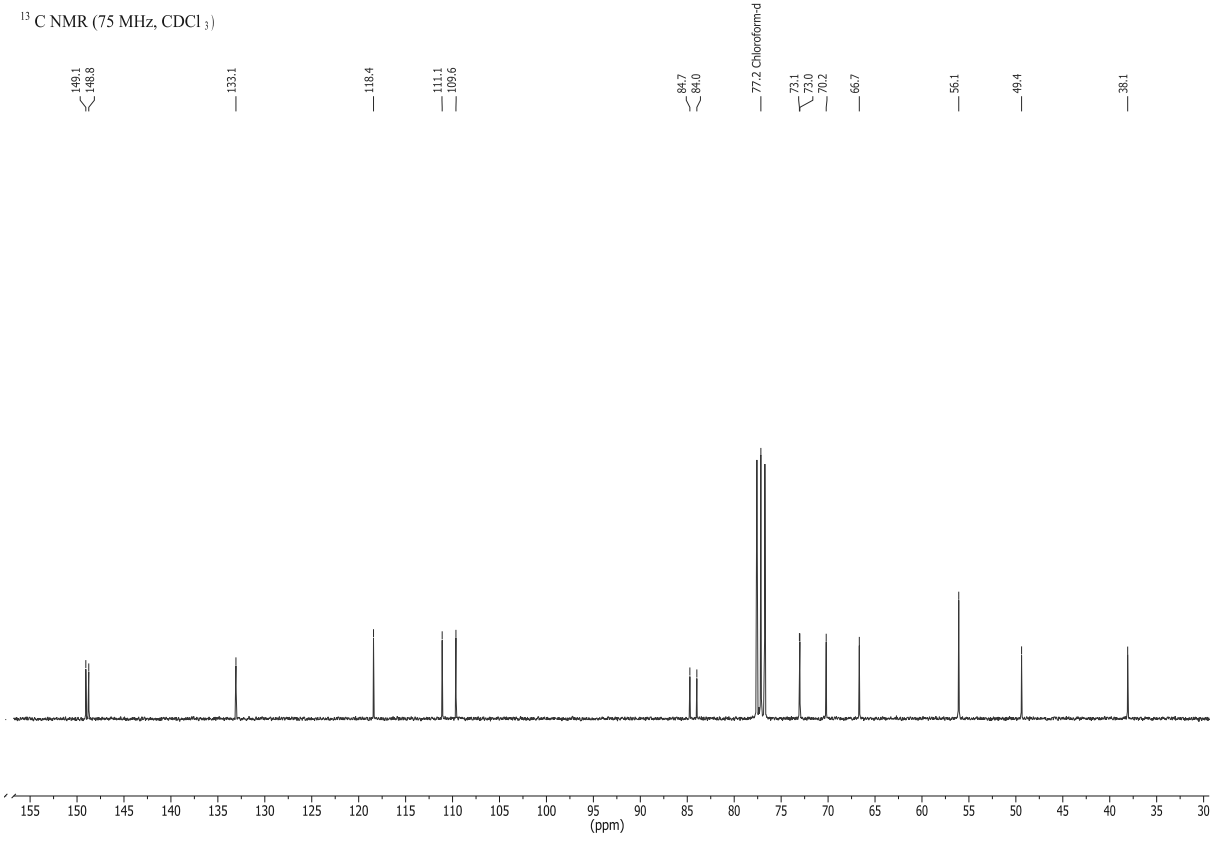


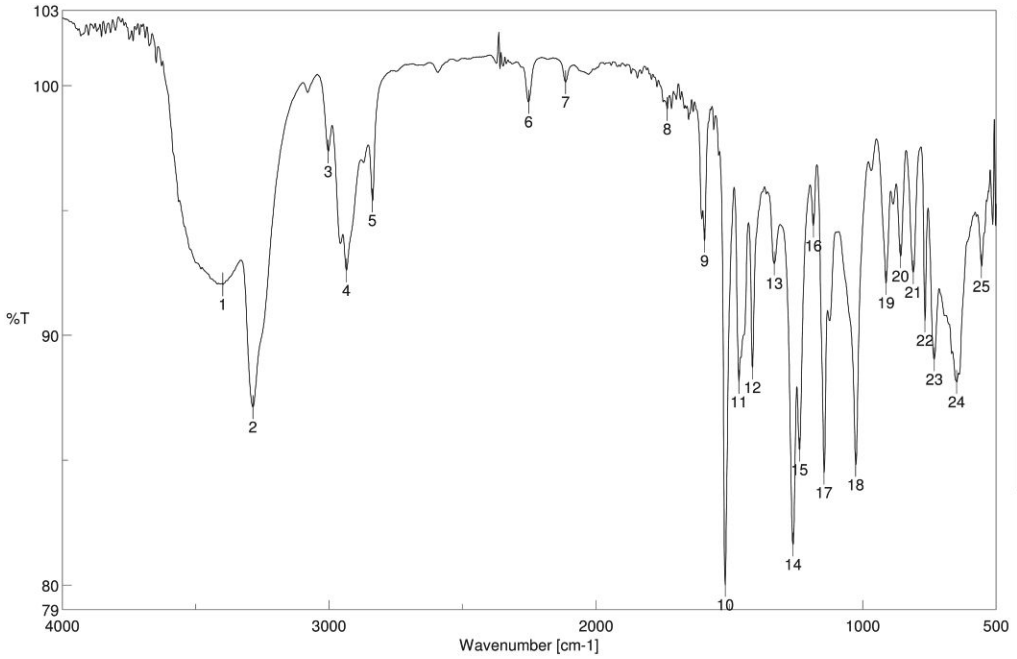


Result of Peak Picking		
No.	Position	Intensity
1	3378.67	84.0135
2	3081.69	77.0543
3	3005.52	76.294
4	2967.91	75.0107
5	2937.06	72.191
6	2837.74	76.5304
7	1704.76	62.2358
8	1635.34	78.7459
9	1590.02	67.2173
10	1518.67	61.5439
11	1493.6	71.0526
12	1465.63	66.3013
13	1440.56	64.7536
14	1411.64	68.4682
15	1350.89	67.8333
16	1329.68	69.083
17	1311.36	75.0714
18	1250.61	64.4186
19	1186.97	65.8363
20	1150.33	63.3929
21	1048.12	76.3024
22	1024.02	64.1934
23	945.913	76.2209
24	927.593	65.6302
25	847.561	77.4817
26	820.563	77.0868
27	801.278	80.4713
28	765.601	70.4515
29	730.889	77.8492
30	709.676	79.1794
31	647.001	78.5668
32	627.716	78.1867
33	614.217	74.0708
34	568.898	77.1021
35	528.4	85.4266

2.10 3-Ethynyl-3-(3,4-dimethoxyphenyl)-hex-5-yn-1,2-diol (15)

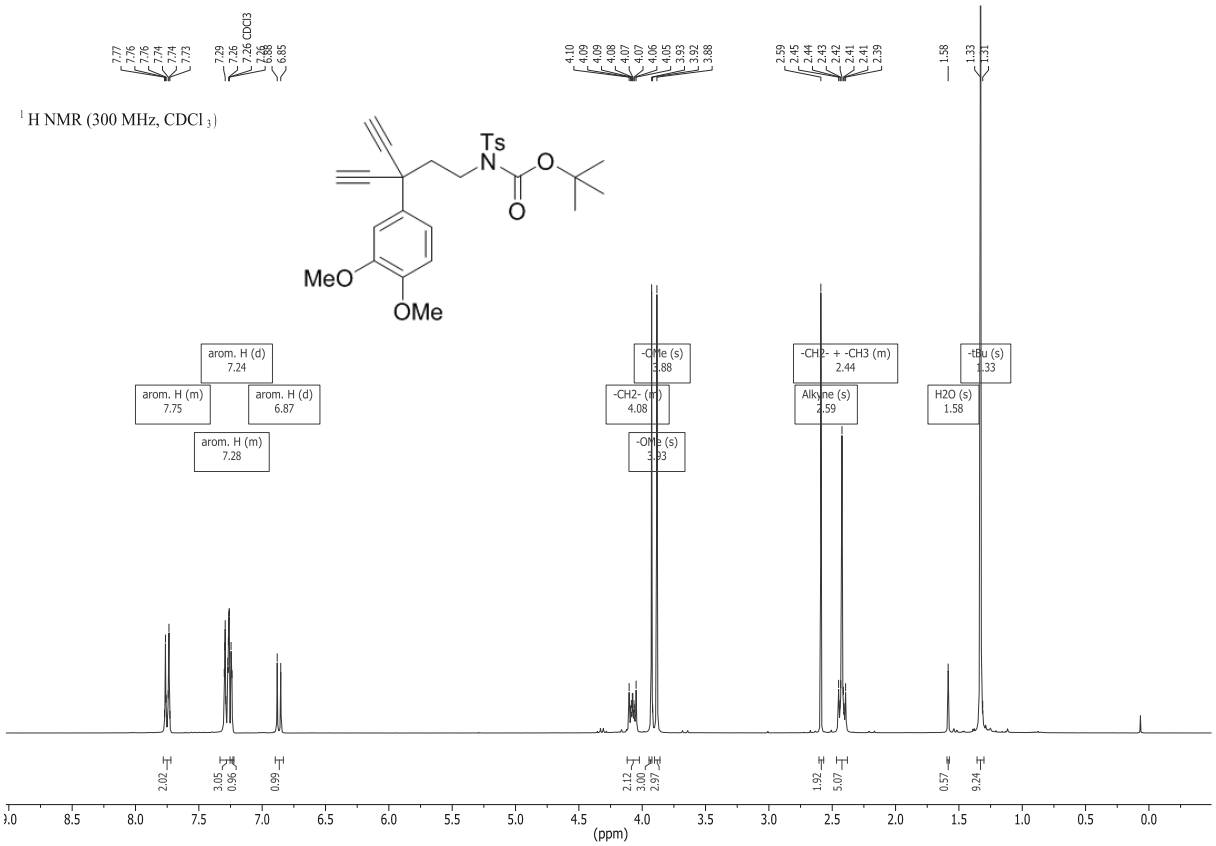


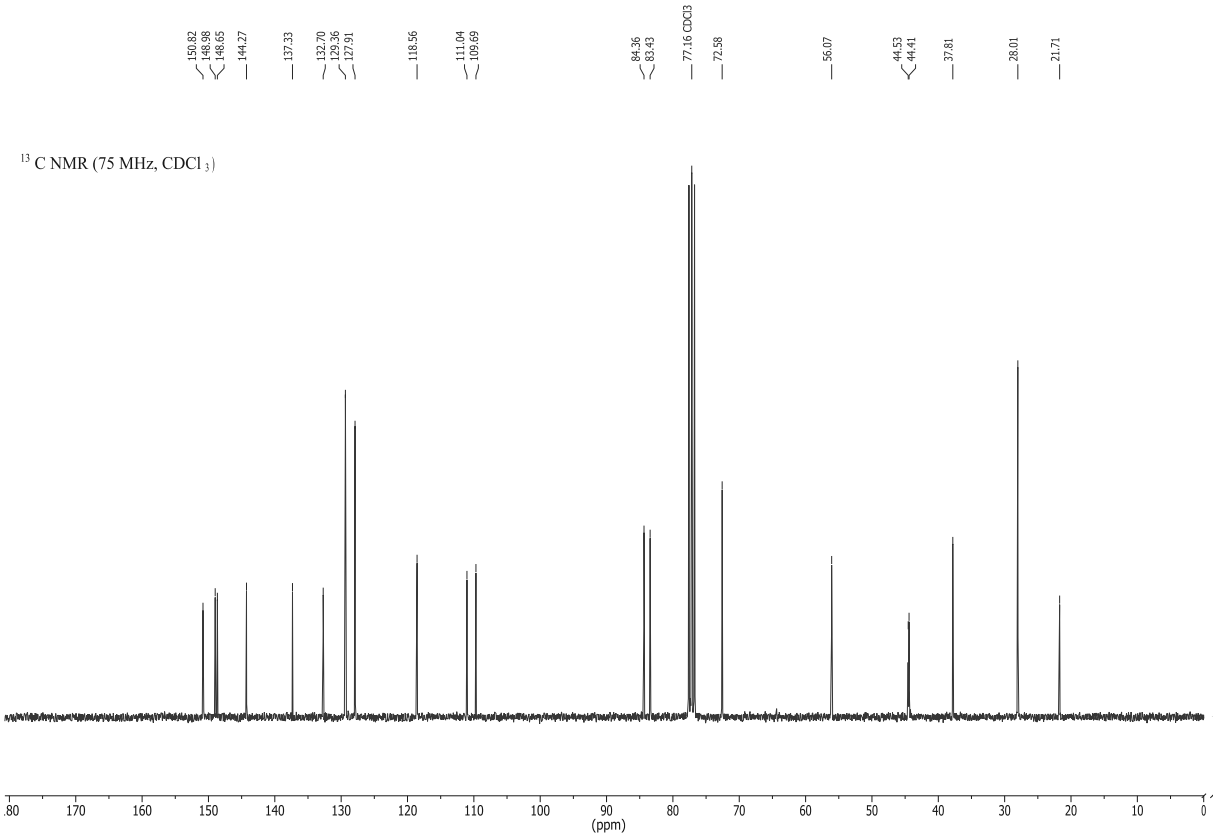


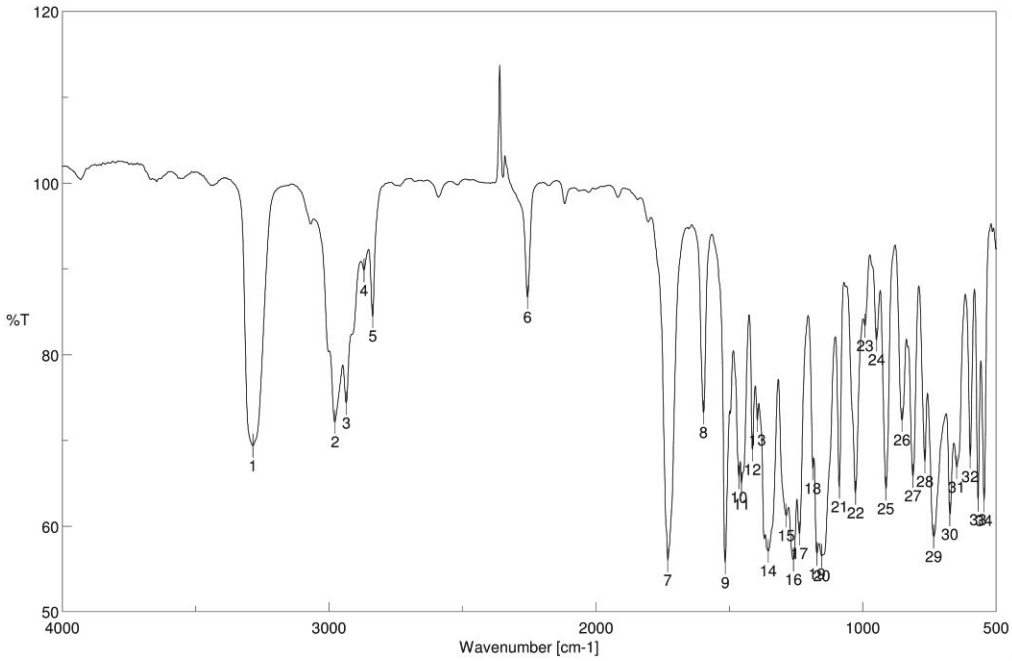


Result of Peak Picking		
No.	Position	Intensity
1	3397.96	92.028
2	3286.11	87.118
3	3002.62	97.3541
4	2935.13	92.5835
5	2837.74	95.3797
6	2252.45	99.3296
7	2113.6	100.126
8	1732.73	99.0553
9	1592.91	93.7784
10	1515.78	79.9911
11	1463.71	88.1174
12	1413.57	88.6899
13	1331.61	92.8669
14	1261.22	81.6104
15	1237.11	85.4004
16	1185.04	94.3752
17	1144.55	84.485
18	1025.94	84.7984
19	912.165	92.0897
20	858.168	93.156
21	810.92	92.5005
22	766.566	90.5808
23	731.853	89.0304
24	647.965	88.1144
25	554.434	92.7505

2.11 *tert*-Butyl (3-(3,4-dimethoxyphenyl)-3-ethynyl-pent-4-yn-1-yl) (4-toluene-sulfonyl)carbamate (17):



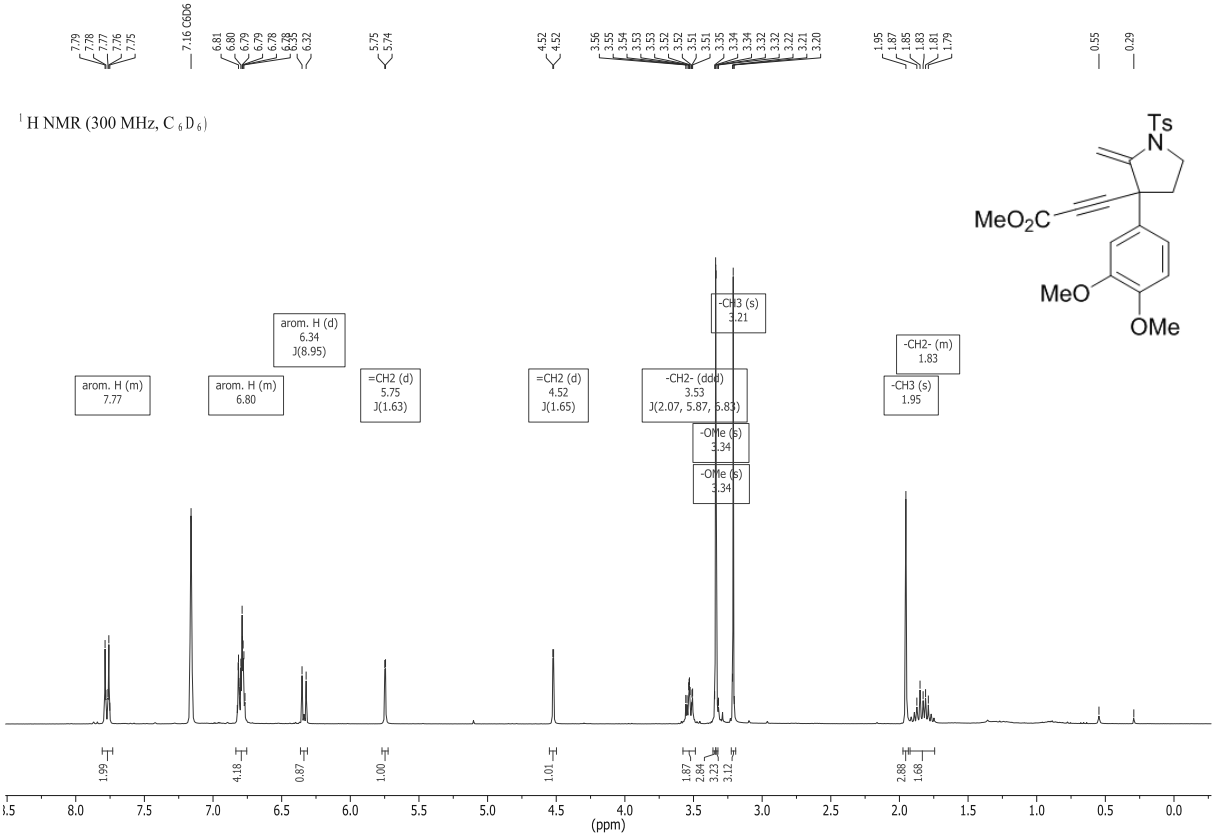




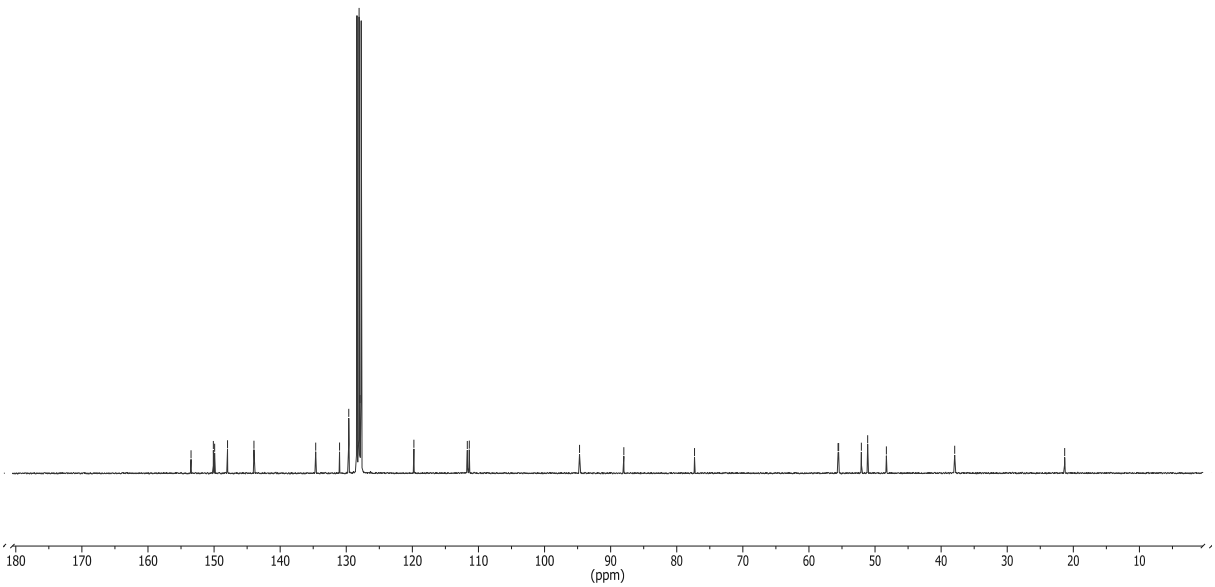
Result of Peak Picking		
No.	Position	Intensity
1	3286.11	69.3578
2	2978.52	72.1201
3	2936.09	74.3164
4	2869.56	89.7877
5	2836.77	84.4613
6	2256.31	86.675
7	1730.8	55.9921
8	1596.77	73.2031
9	1515.78	55.7109
10	1463.71	65.6602
11	1455.03	64.8716
12	1413.57	68.9175
13	1395.25	72.3311
14	1353.78	57.0692
15	1286.29	61.2076
16	1260.25	56.0482
17	1237.11	59.1207
18	1186.97	66.7128
19	1171.54	56.7452
20	1153.22	56.5158
21	1087.66	64.5413
22	1026.91	63.8312
23	991.232	83.3346
24	947.842	81.7013
25	913.129	64.329
26	853.347	72.3237
27	811.885	65.8295
28	767.53	67.4956
29	733.782	58.7586
30	673.035	61.3347
31	647.965	66.846
32	596.861	68.0604
33	567.934	63.0718
34	544.792	62.9722

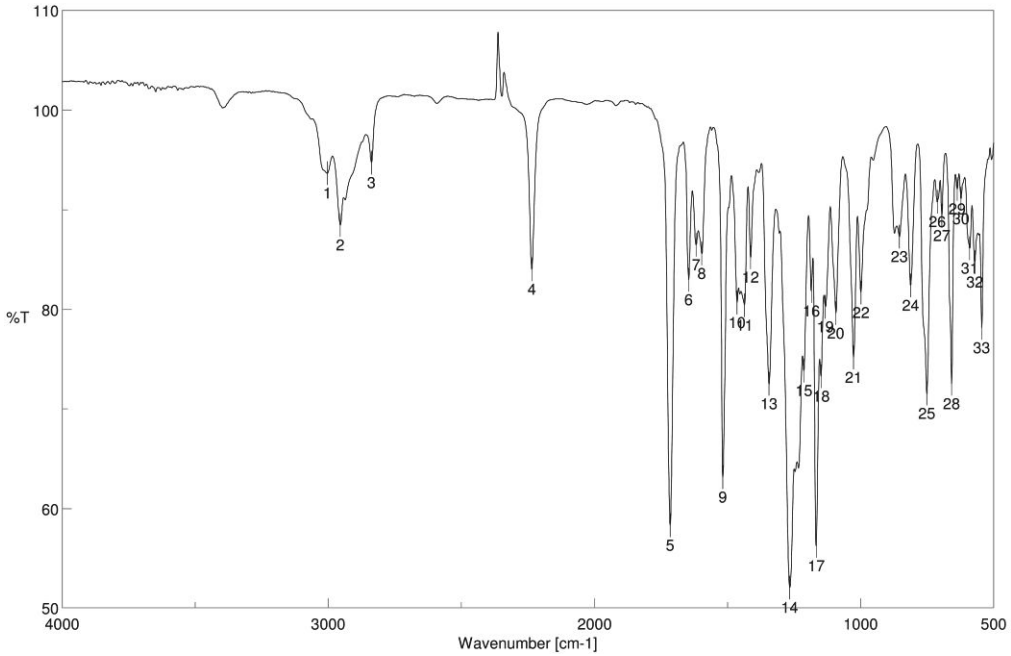
2.12 Methyl 3-(3-(3,4-dimethoxyphenyl)-2-methylene-1-(4-toluene-sulfonyl)-pyrrolidin-3-yl) propiolate (18)

^{1}H NMR (300 MHz, C_6D_6)



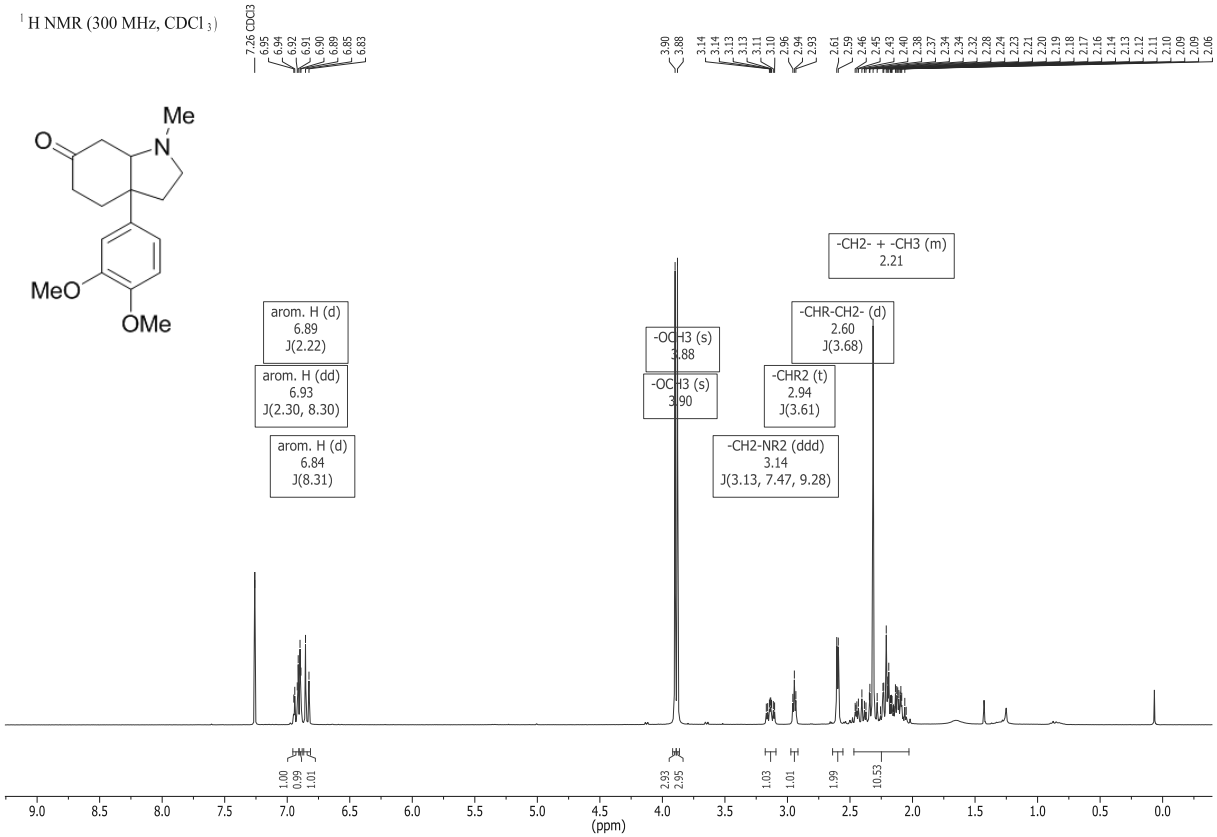
^{13}C NMR (75 MHz, C_6D_6)



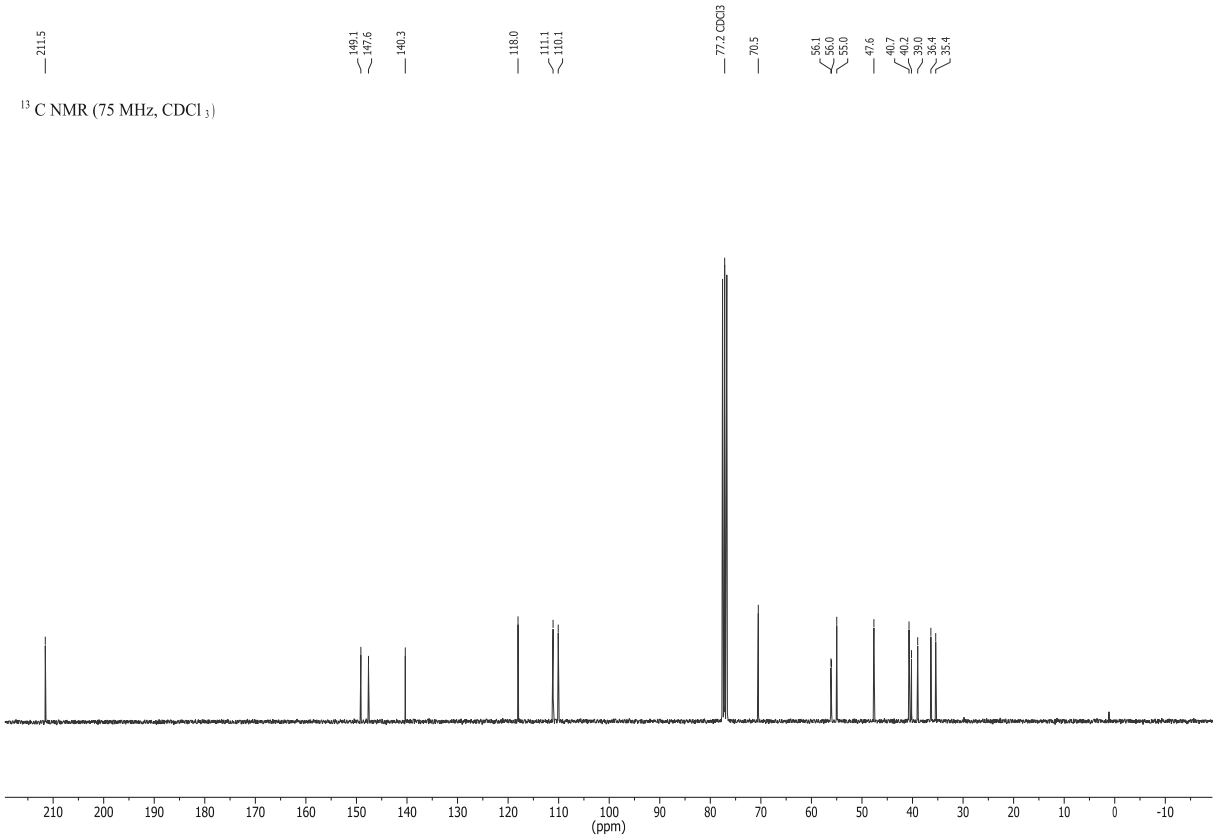


Result of Peak Picking		
No.	Position	Intensity
1	3003.59	93.6438
2	2955.38	88.451
3	2837.74	94.7021
4	2235.09	84.0014
5	1715.37	58.2776
6	1645.95	82.9433
7	1617.98	86.4634
8	1596.77	85.5656
9	1517.7	63.1098
10	1463.71	80.6221
11	1436.71	80.3832
12	1413.57	85.2131
13	1344.14	72.5064
14	1266.04	52.0286
15	1213.01	73.8288
16	1185.04	81.8123
17	1166.72	56.2237
18	1148.4	73.2565
19	1132.01	80.2179
20	1092.48	79.6036
21	1025.94	75.1502
22	998.946	81.6576
23	854.311	87.2645
24	811.885	82.3831
25	751.138	71.5059
26	711.604	90.7721
27	694.248	89.3853
28	657.607	72.4841
29	636.394	92.0597
30	622.895	91.0922
31	590.111	86.0912
32	570.826	84.7162
33	544.792	78.0983

2.13 Mesembrine



^{13}C NMR (75 MHz, $CDCl_3$)

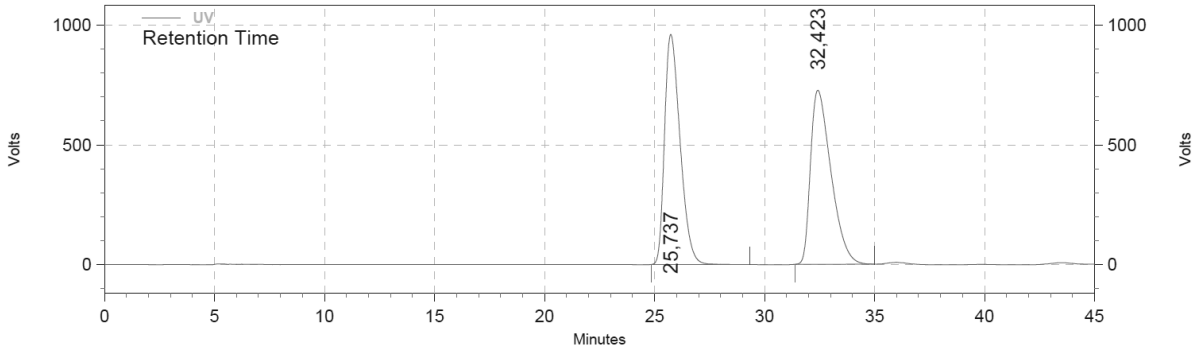


3 HPLC Traces

HPLC trace of product **9**

DAICEL CHIRALPAK® IC™, 4.6 x 250 mm

eluent = *n*-hex.:*iso*-propanol = 55:45, 0.63 mL·min^{-1}, λ = 254 nm



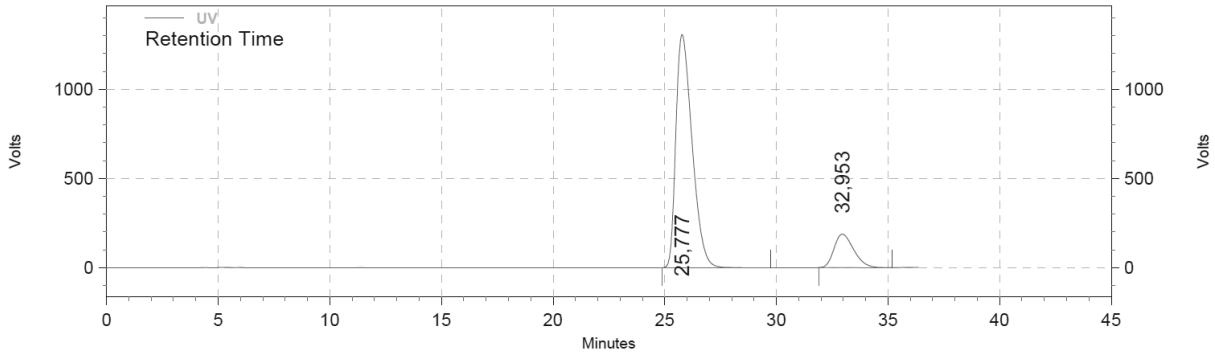
UV Results

Retention Time	Area	Area %	Height	Height %
25,737	188826944	50,11	3845201	56,94
32,423	187994478	49,89	2907935	43,06

HPLC trace of enantiomerically enriched product **9**, 70.3% *ee*

DAICEL CHIRALPAK® IC™, 4.6 x 250 mm

eluent = *n*-hexane:*iso*-propanol = 55:45, 0.63 mL·min^{-1}, λ = 254 nm)



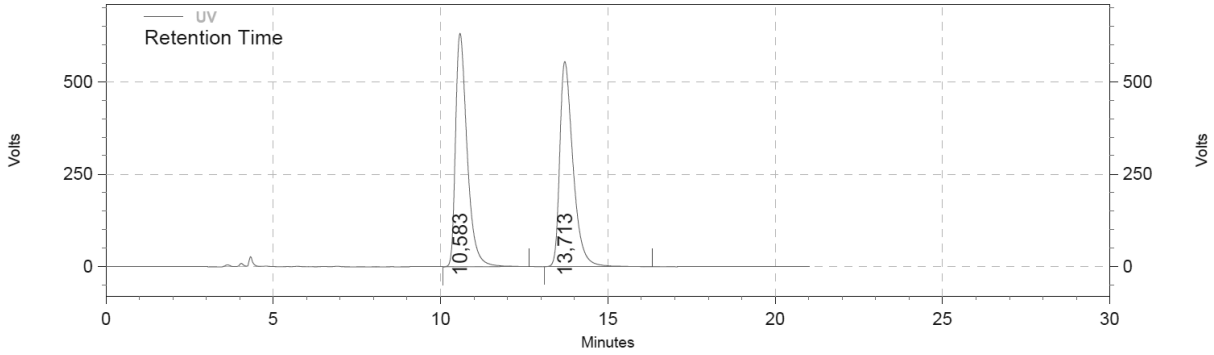
UV Results

Retention Time	Area	Area %	Height	Height %
25,777	264319899	85,15	5223409	87,42
32,953	46107305	14,85	751792	12,58

HPLC trace of racemic product **19**

DAICEL CHIRALPAK® IA™, 4.6 x 250 mm

eluent = *n*-hex.:*iso*-propanol = 82:18, 0.82 mL·min^{-1}, λ = 254 nm



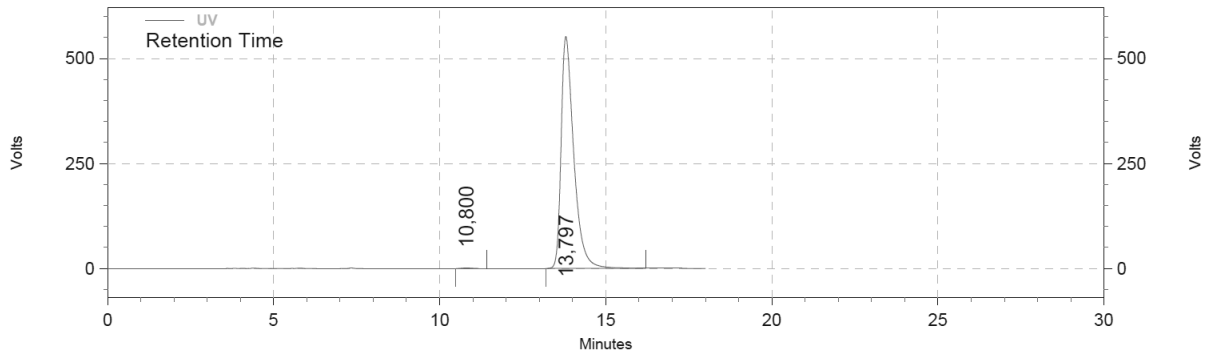
UV Results

Retention Time	Area	Area %	Height	Height %
10,583	60817370	49,91	2520216	53,22
13,713	61034366	50,09	2214825	46,78

HPLC trace of enantiomerically enriched product **19**, >99% *ee*

DAICEL CHIRALPAK® IA™, 4.6 x 250 mm

eluent = *n*-hexane:*iso*-propanol = 82:18, 0.82 mL·min^{-1}, λ = 254 nm



UV Results

Retention Time	Area	Area %	Height	Height %
10,800	100754	0,17	4387	0,20
13,797	58352340	99,83	2208040	99,80