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„Synthesis of and transition metal catalysis by novel asymmetric phosphorous linked diferrocene ligand prototypes“

verfasst von / submitted by

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„Throughout the centuries
there have been men
who took first steps
down new roads
armed with nothing
but their vision“

- Alisa Zinov’yevna Rosenbaum

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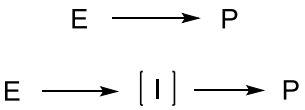
1. Introduction

1. 1. Catalysis

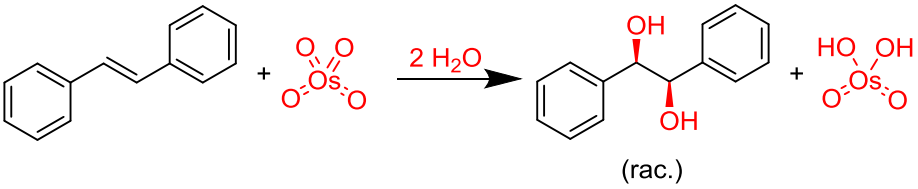
In most basic terms, preparative chemistry is the scientific field investigating chemical reactions, i.e. observing, scrutinizing and utilizing the change of atom connectivity or molecular configurations at unchanging atom connectivity.

In the dawn of chemical science, chemical reactions were thought of being mere stoichiometric transformations of one or more educts into one or more products, forming at times isolable intermediates. Scheme 1 presents this simple paradigm abstracted.

Scheme 2 shows one concrete example: OsO_4 dihydroxylates *E*-stilbene – the educts –, forming an organoosmate ester – the intermediate, not shown – which is hydrolyzed yielding 1,2-diphenyl-1,2-dihydroxyethane and $OsO_2(OH)_2$ – the products.

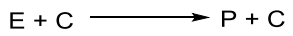


Scheme 1: Abstract chemical equations of a stoichiometric chemical reaction (above) and a stoichiometric reaction proceeding via an intermediate (below).



Scheme 2: Example of a stoichiometric reaction.

However, in the 19th century it was discovered that chemical reactions are not limited to mere stoichiometric transformations. In countless instances, a chemical reaction requires the presence of an additive which is restored after the reaction is completed on the molecular level – a catalyst. Scheme 3 shows the abstracted catalytic chemical reaction.



Scheme 3: Abstract chemical equation of a catalytic chemical reaction. While the “C” component seems superfluous, simple E→P does not belong to the set of observable chemical reactions in this instance.

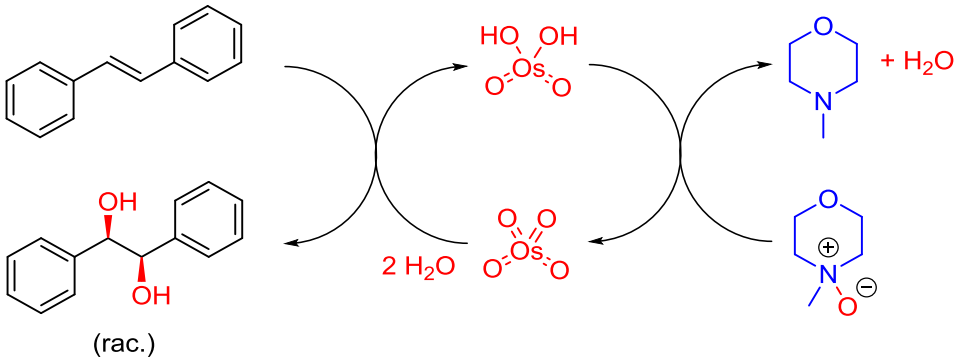
Controlling chemical reactivities via catalysts established an entirely new paradigm of reaction engineering. Not only do many reactions not – or only very slowly and/or unselectively – proceed without a catalyst, chemists would be limited by reactivities inherent to the starting materials and intermediates in synthesis design, whereas usage of catalysts allows for transformations entirely impossible by functional group chemistry of the starting materials alone.

To some degree, this problem could be overcome without catalysis by using chemical additives in a stoichiometric ratio. Yet, one of the intrinsic advantages of catalysts is not being necessary equivalently to the starting material. Depending on the reaction rate desired, a small amount of catalyst will suffice. This, in turn, is one of the major economical motivations to utilize the paradigm of catalysis when performing synthetic tasks.

Depending on whether or not educt(s) and catalyst are in the same phase – usually both in solution – or forming different phases – usually a solid catalyst phase and starting materials forming solutions, liquids or gases – a given instance of catalysis is classified either as

- Homogeneous catalysis
- Heterogeneous catalysis

Scheme 4 presents an example. Just as in scheme 2, OsO_4 dihydroxylates *E*-stilbene, forming 1,2-diphenyl-1,2-dihydroxyethane. But resulting $OsO_2(OH)_2$ is regenerated to OsO_4 by an equivalent of NMO, hence it is no longer necessary to use stoichiometric amounts of OsO_4, which is both expensive and toxic contrary to NMO [1].



Scheme 4: Concrete example of a catalytic reaction.

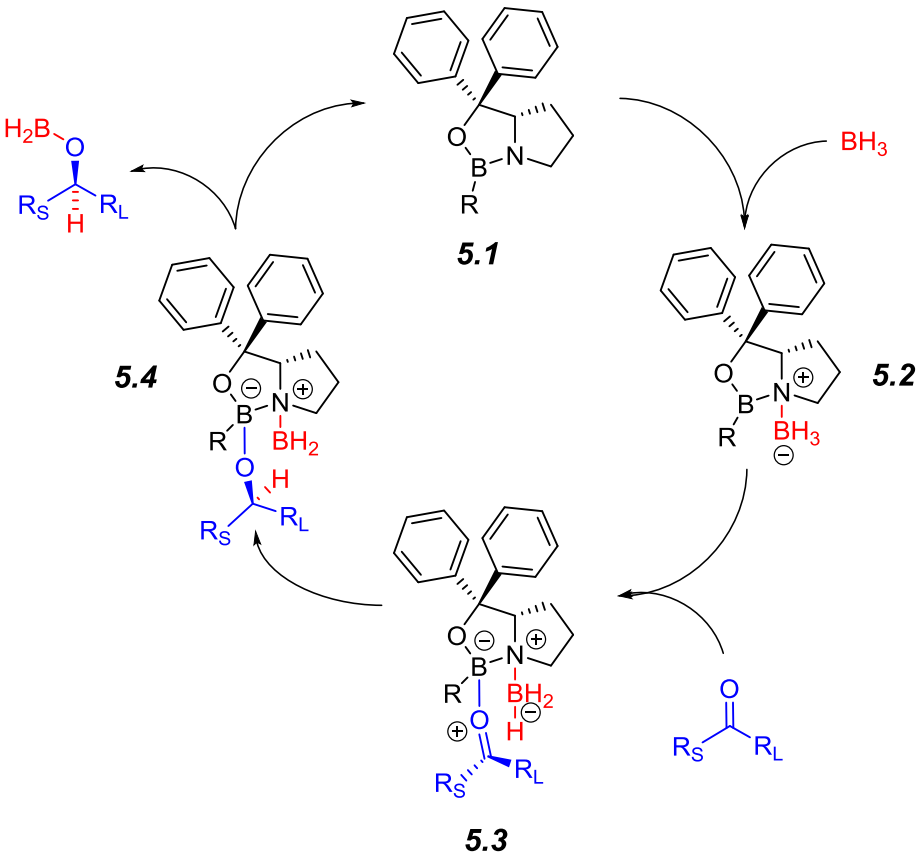
Designing catalysts for a desired chemical transformation allows for a lot of control in said transformation. Scheme 5 demonstrates some of the key virtues of catalysis. Oxazaborolidine 5.1 catalyzes the enantioselective reduction of ketones to alcohols using BH_3 [2].

In the first step, BH_3 interacts with the lone pair of tertiary amine in 5.1 forming a dative bond. This demonstrates the catalytic property of activating previously rather inert compounds.

In the second step, the ketone, possessing one rather large and one rather small substituent denoted as R_L and R_S, respectively, coordinates the now rather cationically polarized oxazaborolidine B using a lone pair. The proline-like structure of the catalyst forces an orientation of the large carbonyl substituent away from the propylene bridge.

In the third step, hydride bound to B is thus only able to attack one of the two possible carbonyl sites. This demonstrates the regio-, stereo- and/or enantioselectivity possible by catalytic control of a chemical reaction.

In the final step, the reduced starting material is released, usually in excellent yield and enantioselectivity while the catalyst re-enters the catalytic cycle. At the end of the reaction, the oxazaborolidine can be recovered, demonstrating the atom economy often – though not always – coming with catalysis.

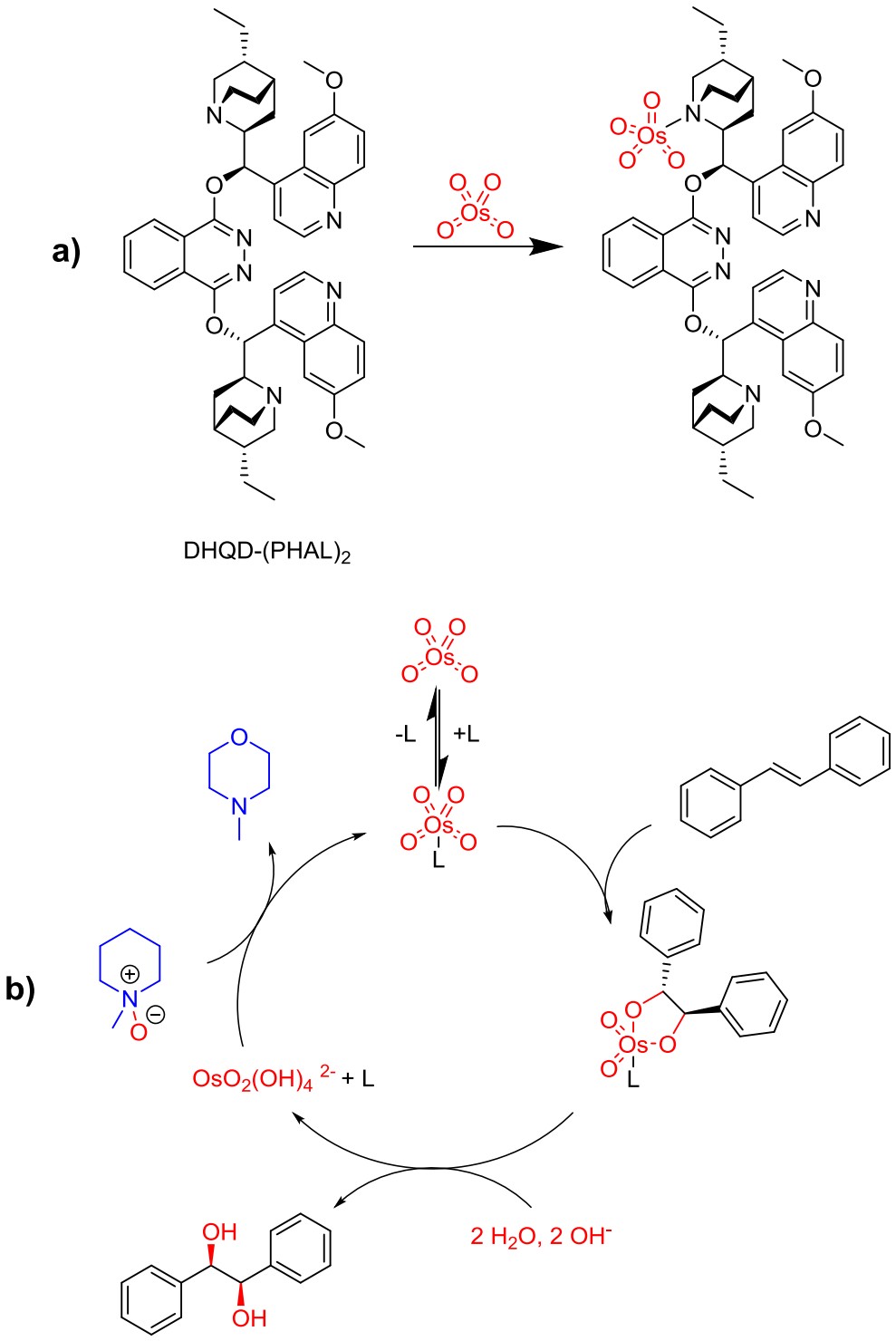


Scheme 5: Key merits of catalysis, demonstrated by ketone reduction using the CBS catalyst.

In order to achieve these key virtues as exhibited by the CBS reduction, an entire part of organic synthesis is dedicated to the design of ligands such as the oxazaborolidine shown above. This process is usually cumbersome and as to yet still relies heavily on trial-and-error methodology.

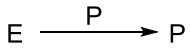
Returning to the example of dihydroxylation of *E*-stilbene, scheme 6 presents a chiral, usually enantiopure compound known as Dihydroquinidine Di(2,3-dihydro-1,4-Phthalazinedione) [$(DHQD)_2$-PHAL] which serves as a ligand (a). This compound is added to the starting materials of the catalytic Os(VIII)-based dihydroxylation (b).

In the initiation step, OsO_4 coordinates one of the trialkylamine N's. This osmium-complex is more reactive than the OsO_4 all by itself and the reaction now works enantioselectively.



Scheme 6: Top: Formation of a coordination compound of $(DHQD)_2$-PHAL and OsO_4. Bottom: Catalytic cycle started by said complex. [3]

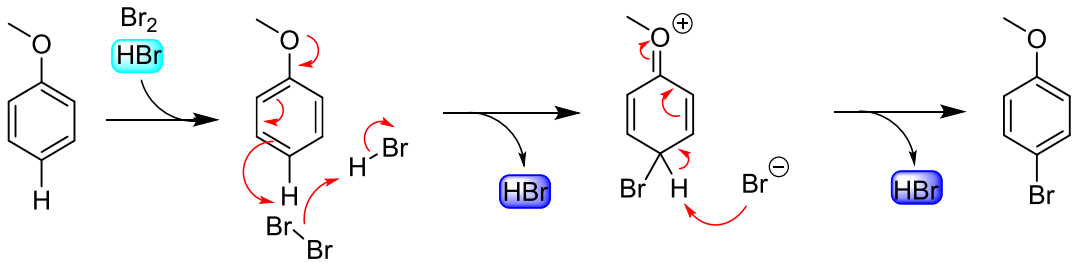
Beyond the paradigm of simple catalysis, more complex and more interesting abstract reaction schemes are conceivable. For example, what if the reaction is catalyzed, not by an extra additive, but by its own product? In this case, autocatalysis is achieved. Scheme 7 presents the generalized equation.



Scheme 7: Abstract equations of autocatalytically driven chemical reactions. A product molecule catalyzes the transformation of a set of educts into a set of products.

One example investigated is presented in scheme 8: The S_EAr-type bromination of anisole using Br_2 catalyzed by a cat. amount of HBr which is required to activate Br_2 for the S_EAr attack on anisole. This step creates an equivalent of HBr. In the consecutive step, Br^- abstracts a proton from the Wheland complex to restore aromaticity, creating the desired brominated aromatic product as well as one extra equivalent of HBr.

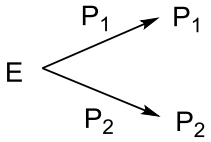
Thus, after every molecular reaction, the amount of bronsted acid increases, hence increasing the reaction rate of the remaining anisole by more bronsted acid being available [4]



Scheme 8: Autocatalytic bromination of anisole.

The autocatalytic chain reaction-like transformation is not limited to being driven by the side product as shown in the rather simple example above. Depending on the chemical reaction, the autocatalyst could also be the more sophisticated organic product molecule.

An interesting special case of autocatalysis involves two or more possible products, in which each product catalyzes its own formation as depicted in Scheme 9.

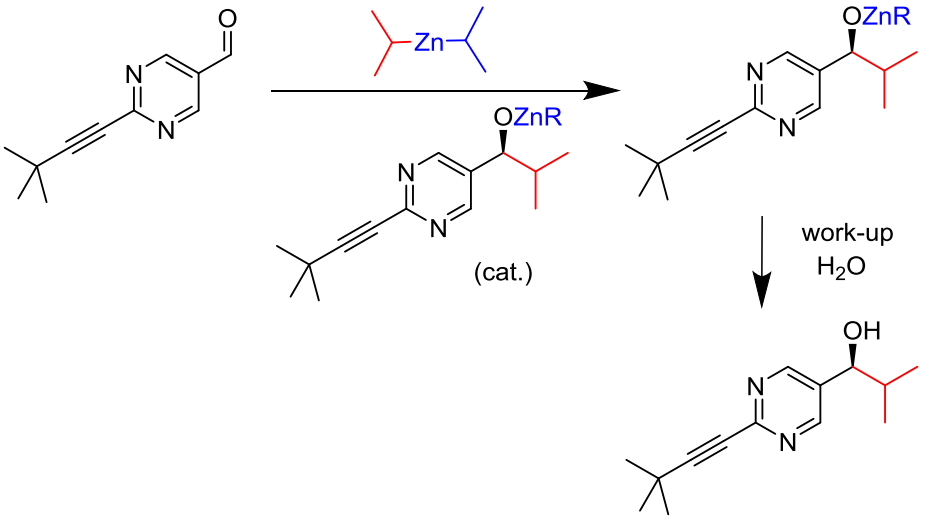


Scheme 9: Abstract equation of an autoamplified chemical reaction. Two possible products catalyze their own formation each.

As to yet, only few instances of this interesting type of self-selecting chemical transformations are known. Usually it has been found that the transformation of some prochiral molecule – a carbonyl compound, for instance – is autocatalyzed by its chiral product – the corresponding secondary or tertiary alcohol –, where each enantiomer catalyzes the formation of itself including the same configuration. If each enantiomer catalyzes the formation of itself but possessing the opposite configuration, a perfect racemate would result by auto-balancing.

For example, the group of Soai *et al.* found that the addition of organozinc compounds to pyrimidine-5-carbaldehydes results in good e.e. if cat. amounts of the resulting alcohol with far smaller e.e. have been present.

Scheme 10 presents the principles of this transformation. Zn(II) mediated alkylation of pyrimidine-5-carbaldehydes results in a chiral alkoxy Zn intermediate. This intermediate is a more active alkylation agent than the initial dialkyl Zn and has been shown to catalyze the formation of the alkylation product of the same configuration. A small e.e. in either configured carbalkoxy Zn compound hence yields a greater e.e. in products [5].



Scheme 10: Zn(II) mediated alkylation of pyrimidine-5-carbaldehydes.

One must consider that organometallic compounds form numerous equilibria, usually between aggregates with solvent molecules or other electron pair donating molecules in in solution. Often, the compound of interest of study is not the monomer, but one of a number of dimers, trimers, tetramers, hexamers,... It is suspected that the catalytically active species cannot be the monomer due to the observed excellent enantioinduction, but a dimer or tetramer in solution [6].

Fig. 1 demonstrates the power of automultiplication of the Soai reaction in a concrete example. Carrying out the uncatalyzed Soai reaction once, a racemate not perfectly equal on the molecular level of pyrimidinecarbalcohols results, favoring slightly the (S)-enantiomer. A slight excess of the (R)-enantiomer instead would have been equally probable.

Using this racemate as a catalyst in a subsequent alkylation run, an e.e. of 57% is achieved, caused by a statistical excess of (S)-carbalcohol produced in run one. Using the alcohol produced in run two for run three, an e.e. of 99% was produced. By run four, enantiomer (S) was multiplied by a factor of 630,000 while enantiomer (R) was not even multiplied by a factor of 1,000 [5].

This finding points out an interesting novel way of creating asymmetry into preparative chemistry, for example for creating enantioselectivity *ex nihilo* in a synthetic route towards a product molecule or for forming asymmetric catalysts passing on asymmetric information.

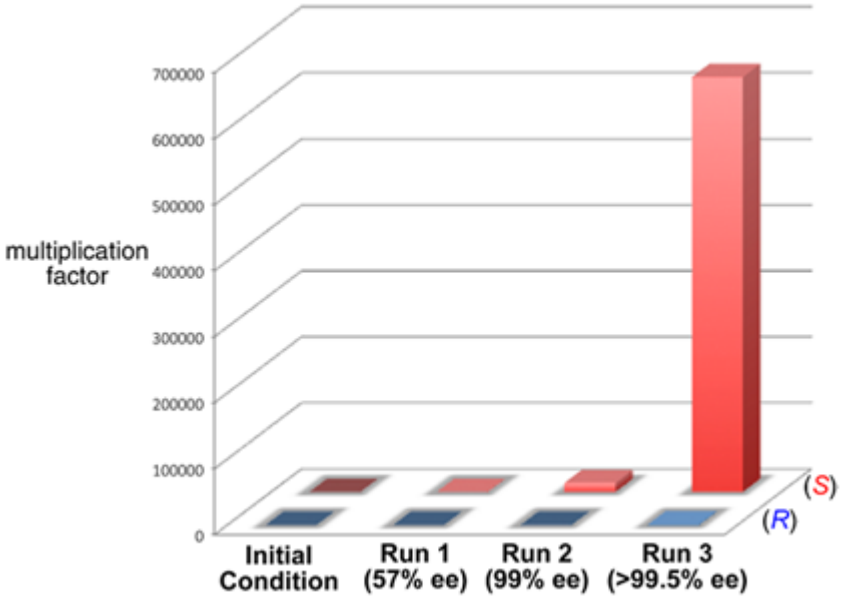


Fig. 1: Multiplication factor of both enantiomers at different subsequent runs. This figure was taken directly from ref [5].

1. 2. Chirality

Chirality is a property intrinsic to several geometric objects. An object is called chiral if all properties are equal except for the mirrored image, which is not superimposable.

One simple example often used includes idealized hands, which are mirror images of each other, identical in every aspect except they cannot be superimposed congruently. In chemistry, many molecules exhibit this property as well. Chart 1 summarizes sorts of chirality encountered in chemistry.

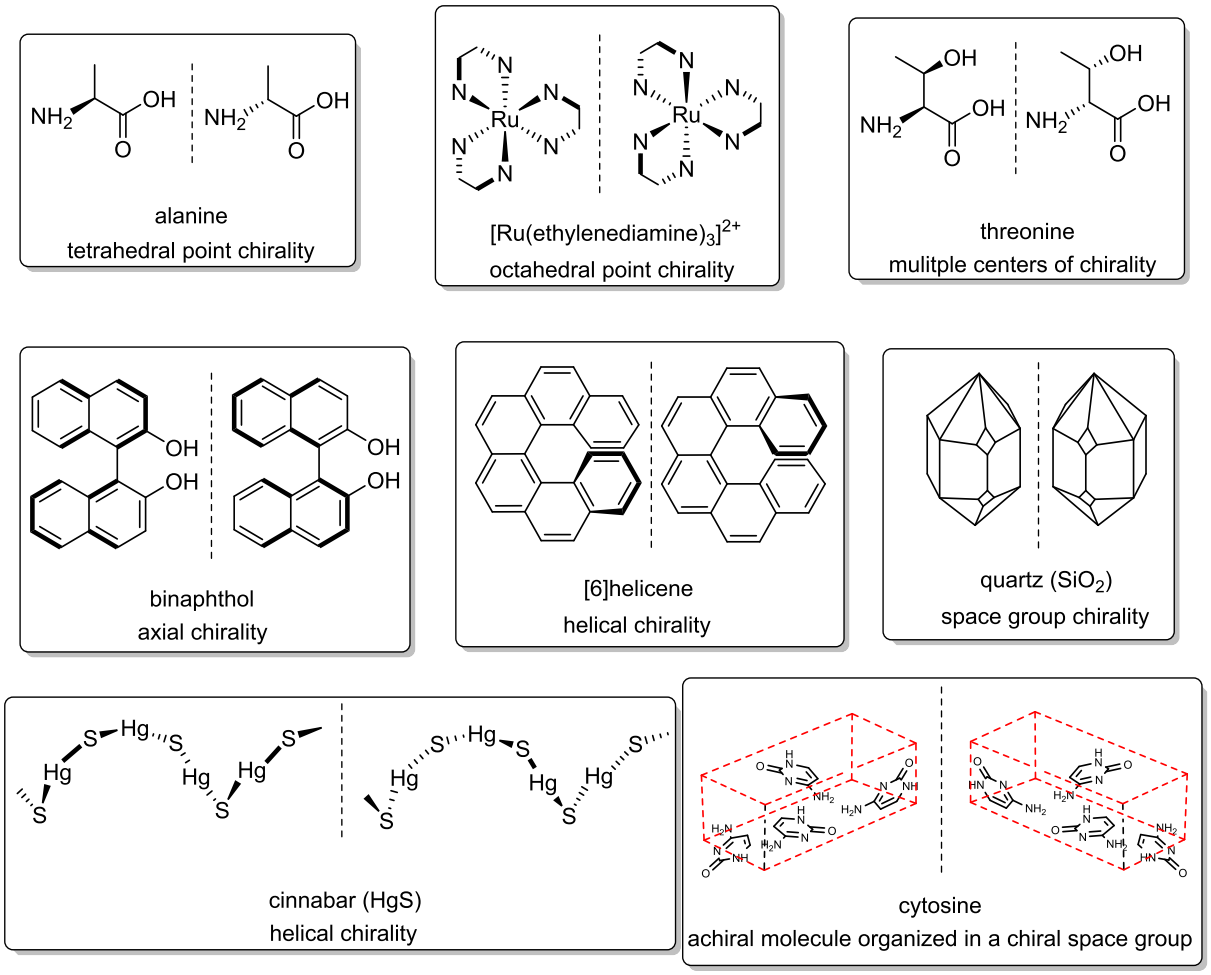


Chart 1: Different instances of chirality demonstrated by pairs of enantiomers.

All by itself, chirality is not a relevant property in a molecule. Since chemical composition, connectivity and internuclear distances of two enantiomers are exactly equal, so are molecular energy and every physico-chemical parameter.

Chirality comes into play only if interacting with another chiral electromagnetic field, for instance circularly polarized light or another enantiomeric molecule.

One example of this behavior of centers of chirality meeting is observed in the field of polymer science: In atactic polypropylene, configuration of the tertiary carbon varies statistically. In isotactic polypropylene, however, all methyl side chains show the same configuration except for a few statistical errors.

Hence, on a molecular level, there is no order in the former polymer due to the randomness of methyl side chain orientation but self-organized helical order in the latter. On a macroscopic level at normal conditions, the former polymer forms a technically uninteresting viscous oil or rubber, the latter forms a partially crystalline solid which is commercially valueable.

Due to similar reasons of forming qualitatively better interactions, it is often observed that crystallizing mixtures with a low e.e. leads to some enantiomeric enrichment of the purified product, for example in $NaClO_3$ crystallization, crystallization of amino acid mixtures from solution or leucine sublimation.

Also, the vast majority of biomolecules consists of chiral molecules, most of the others being achiral. Only very few biochemical substances exist as racemates in nature with only very few exceptions such as endiandric acid.

Just as in the example of polypropylene, biomacromolecules such as enzymes would not possess a well-defined structure required for their tasks in living organisms if their building blocks would be *rac.* Hence, enzymes consist of enantiopure chiral monomers, as does the majority of molecules produced by biocatalytic processes.

Therefore it is obvious that chiral organic molecules such as pesticides, drugs or food additives must be produced enantioselectively if they interact with organisms. *Rac.* mixtures are in almost all cases inacceptable, particularly as drugs. While one enantiomer might exhibit the desired effect, the other will, at best, be inactive or affect the organism harmfully.

A well-known tragic example is the Contergan scandal. The drug thalidomide was marketed as a racemate. Whereas one enantiomer worked as a drug and showed no side effects, the other turned out to be teratogenic, causing limb deformations and organ deficiencies to the fetus.

Yielding enantiomerically pure products is therefore an eminent task in synthetic chemistry. This is not a trivial undertaking since enantiomers are identical in almost

all regards. Hence special methods have to be employed in order to not yield both enantiomers in statistically equal amounts.

A product can be enantiomerically pure if its precursor has been enantiomerically pure. This is called substrate control of the chemical reaction. However, substrate control only bends the question of enantio-induction to the starting material. The starting material may stem from an organism and hence be enantiopure, or it has been gained from a non-enantiopure compound.

A compound can be obtained in enantiomerically pure form even if its percursor is prochiral or racemic, i.e. *rac.* Scheme 11 summarizes preparative strategies.

In the case of optical resolution (a), a racemate reacts with an enantiopure additive, be it covalently or non-covalently, for example by salt formation. This way two products are formed which are no longer enantiomers, but diastereomers. These no longer exhibit identical physico-chemical properties and can be separated by fractional crystallization or chiral column chromatography. The chiral additive is removed and can be reused.

However, if only one enantiomer is desired, this method intrinsically turns at least 50% of the starting material into waste. In some instances, re-racemization of the undesired enantiomer can increase the yield of the desired one at the cost of iterating the optical resolution procedure.

Kinetic optical resolution is closely related. A pair of enantiomers reacts with another chiral compound in different reaction rates, usually by means of asymmetric catalysis described below, transforming one enantiomer faster than the other. Stopping the reaction at the right point, the two former enantiomers are now two different compounds to be separated by differences in physico-chemical properties. However, both enantiomers will be transformed eventually since solely the kinetic reaction rates differ, but not the reaction enthalpies.

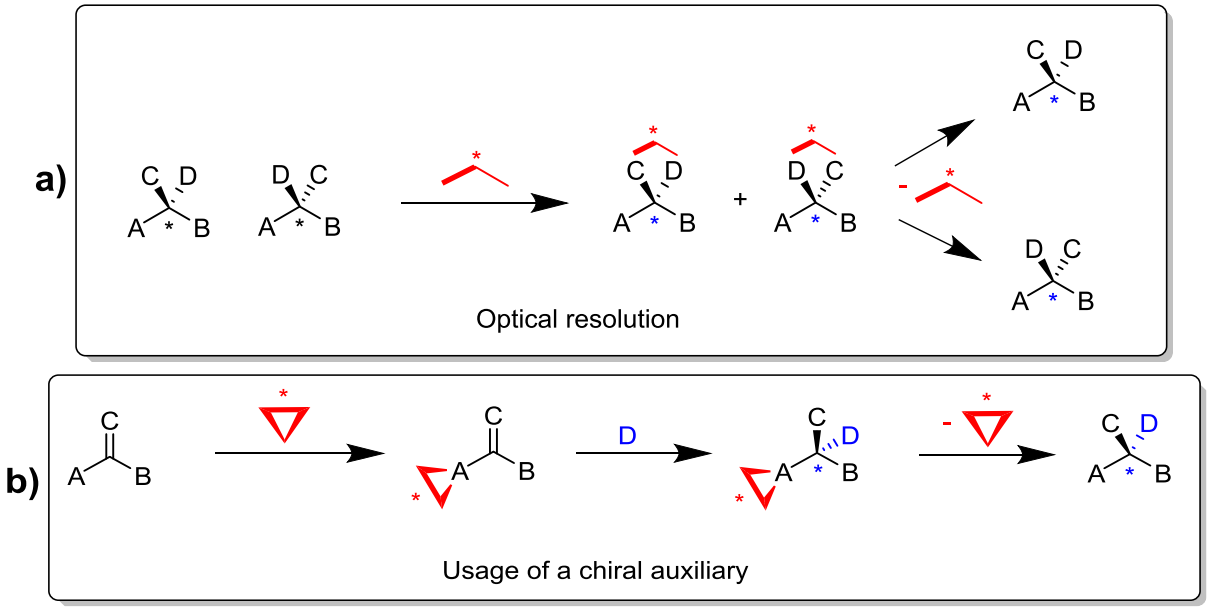
Instead, the synthesis can be designed starting from a prochiral starting material. Similar to optical resolution, the prochiral substrate reacts stoichiometrically with an enantiopure auxiliary (b). The resulting compound is thus enantiopure. In a subsequent reaction, a diastereomer is produced hence circumventing the statistically equal formation of enantiomers. After conversion of the starting material, the chiral auxiliary is removed and sometimes can be recovered.

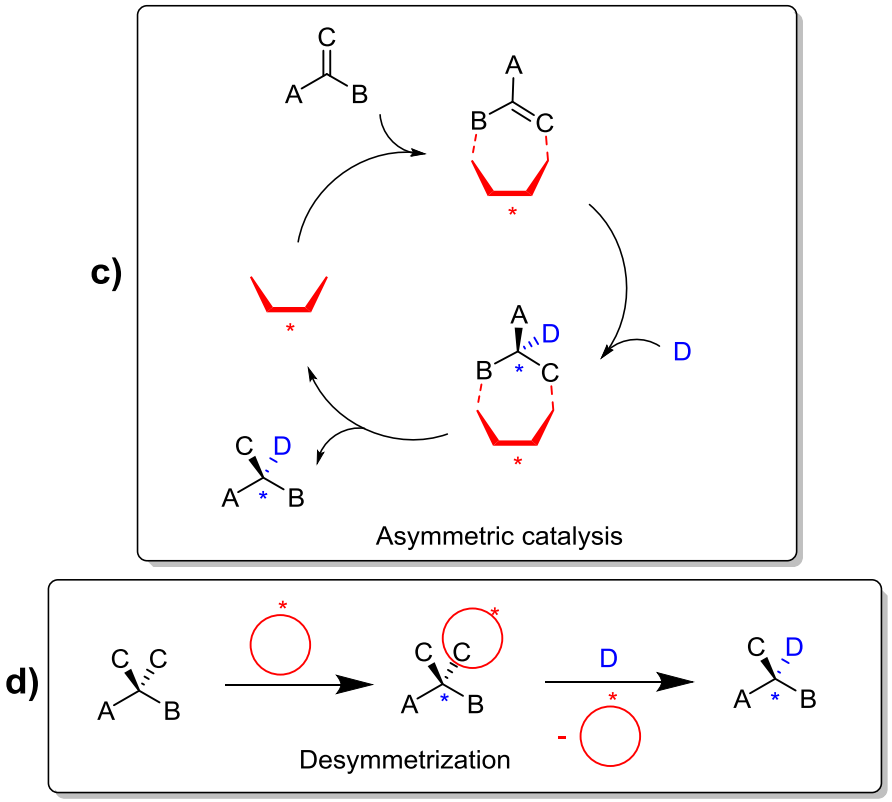
This method ideally wastes none of the starting material in contrast to enantiomer separation. However, it introduces two extra synthetic steps – binding and cleaving the auxiliary – and it requires a stoichiometric amount of the chiral auxiliary which may be very impractical for industrial-scale applications.

Instead, the usage of the auxiliary can be engineered into a catalytic process. In the case of asymmetric catalysis (c), the prochiral starting material intermediarily binds to the enantiopure catalyst, usually hence activating the achiral starting material for the follow-up reaction which produces a diastereomer just as in the chiral auxiliary method.

In the final step, the now chiral, enantiopure product is released and the asymmetric catalyst re-enters the catalytic cycle. The sheer practicality of this method turned asymmetric catalysis into one of the most researched fields in organic chemistry in the last decades.

Desymmetrization uses starting materials that contain enantiotopic atoms or groups (d). A chiral auxiliary or catalyst reacts with one of them preferentially since the two possible products are diastereomers. A subsequent reaction removes the auxiliary during introduction of substituent D.





Scheme 11: Different pathways to produce enantiopure molecules.

If both the starting material and the reagent/auxiliary/catalyst used are enantiopure compounds, two cases may occur. The molecules involved are either matched, that is they interact comparatively well with each other, or mismatched, meaning if either one of the two molecules involved was of the opposite configuration, the interaction would be less hindered as it is and the reaction would take place faster.

1. 3. Organometallic catalysis

The field of organometallic chemistry comprises primarily the study of C-metal bonds as well as the study of interactions between organic molecules and metals in a wider sense. Sometimes, the C-metal bonded species is of interest as a product.

In many instances, though, chemists are more interested in intermediary C-metal bonds in catalysis. Usage of transition metals has been demonstrated to enable chemical reactivities hard to implement or even entirely impossible to facilitate in the field of classical, main group element organic synthesis.

One of the distinct advantages of organometallic chemistry is the metal being the decisive reactive center. These centers can be fine-tuned by careful choice of the coordinating ligands. Thus electron densities, reactive orbitals and their shapes can be designed. This way it is possible to exert a lot of control in various transformations over reactivities, chemo-, regio-, stereo- and enantioselectivites.

Scheme 12 presents a selection of such transformations. Cu and Au cations are known to show a strong affinity to electron-rich C-C double or triple bonds. In such a way activated olefins or alkynes may react far more readily with nucleophiles.

The Diels-Alder reaction pictured (a) does not take place at the low temperature necessary to avoid sigmatropic proton shifts in cyclopentadiene. Hence a catalyst is necessary. In this case the LUMO of the dienophile is energetically lowered enough due to electron withdrawing Cu(II) bound to the ethylene π-orbitals for the HOMO of the diene to react with it, hence performing the reaction [7].

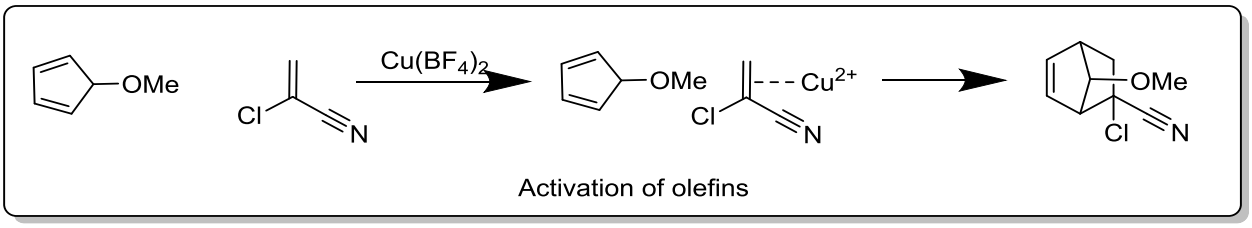
Inversely, binding of metals to multiple C-C bonds may stabilize labile bonds. For example, even anti-aromatic cyclobutadiene (b) – normally not to be observed above – 196 °C – is stable if bound to a metal in a diolefin complex. Woodward-Hoffmann rules no longer apply to orbital symmetries changed by metal coordination. This compound was used, for example, in pericyclic reaction to synthesize cubane [8].

Also aryne species (c), normally occurring solely as high-energy intermediates hard to isolate can be stabilized in complexes, stored and used as aryne synthons [9]. Bennett *et al.* even discovered an 1,4-diaryne species (d), stabilized in a binuclear Ni diphosphine complex [10].

Complementarily, proper choice of ligands can favor unusual oxidation states in metals (e), such as Ag(II) [11], Fe(IV) [12] and Mn(-I) [13] which in turn may present interesting properties to be exploited in chemical reaction design.

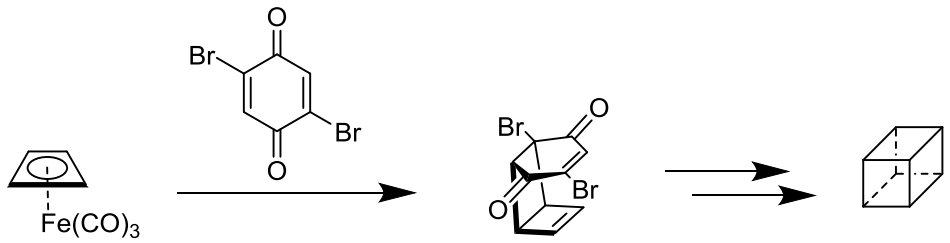
Even umpolung can be achieved by transition metal chemistry (f). For example, the enzyme cytochrome P-450 contains a catalytic Fe-porphyrine center. O bound to this iron center exhibits a comparatively electrophilic, „oxen“-like chemistry. This can be observed in hydroxylase-type enzymes which are capable of inserting O in unactivated C-H bonds and react even with negatively charged C atoms, as seen in the biosynthesis of cortisone [14].

(a)



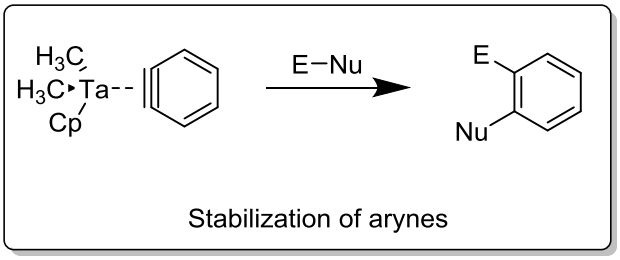
Activation of olefins

(b)



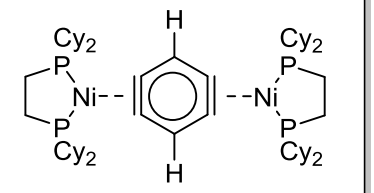
Stabilization of anti-aromatic cyclobutadiene

(c)

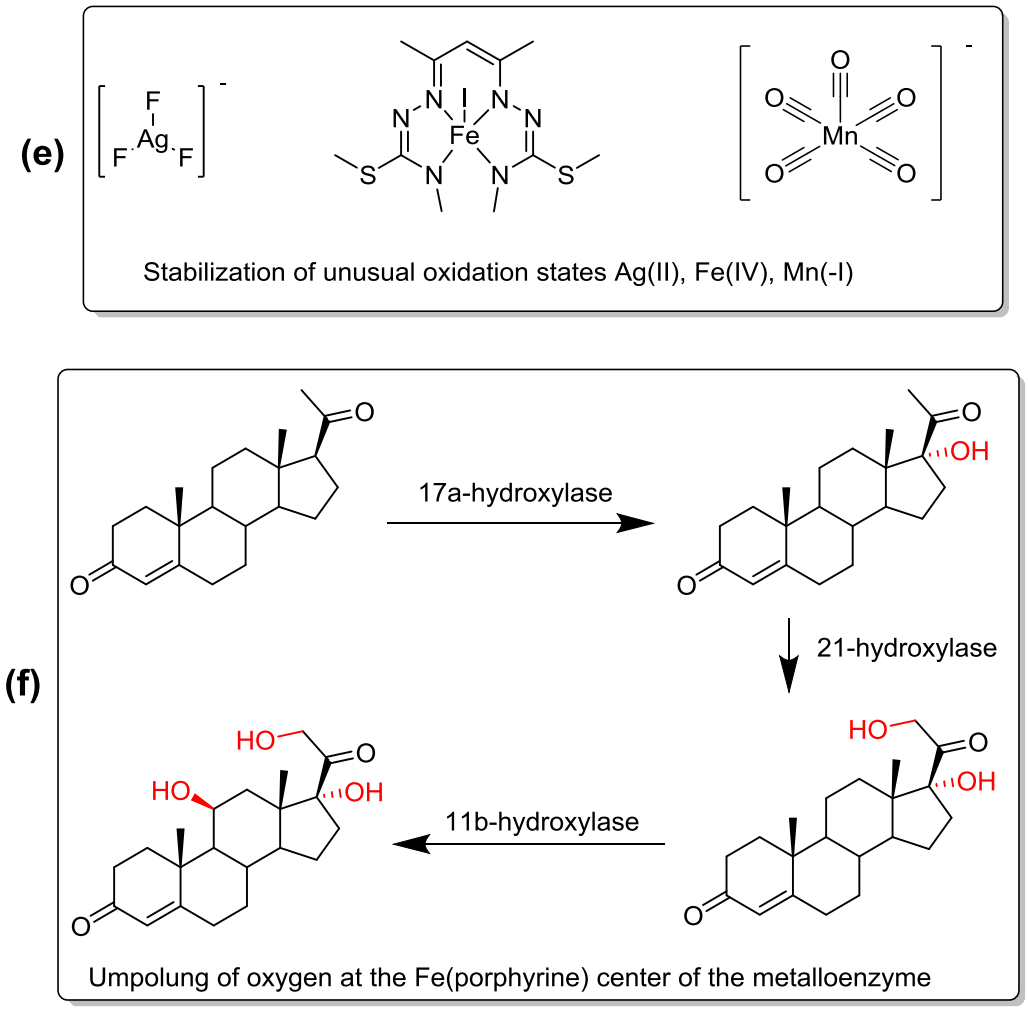


Stabilization of arynes

(d)



Stabilization of 1,4-diaryne



Scheme 12: Selected examples of how metal coordination compounds influence traditional organic chemistry.

Organometallic compounds and their reactivities have been used in order to engineer catalytic transformations barely or not at all possible in classical organic chemistry. Scheme 13 presents a selection of examples.

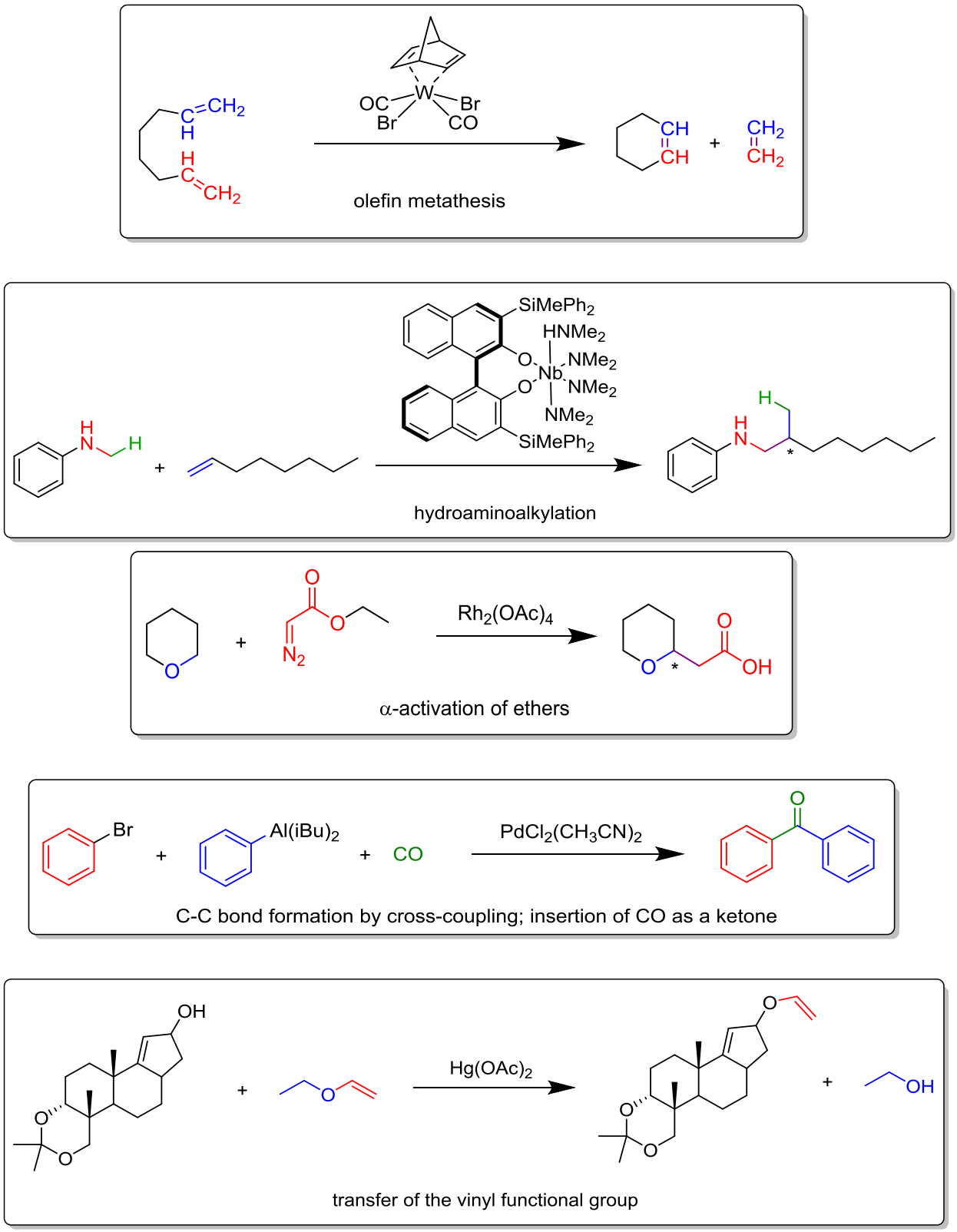
In olefin metathesis, two olefins exchange their olefinic C's and substituents [15]. This transformation is impossible to conduct in one step without a catalytically active metal.

In hydroaminoalkylation, the more reactive N-H bond of a secondary amine is kept intact whereas the vicinal C-H is activated contrary to chemical intuition [16].

Otherwise inert functional groups such as ethers can also be C-H activated [17].

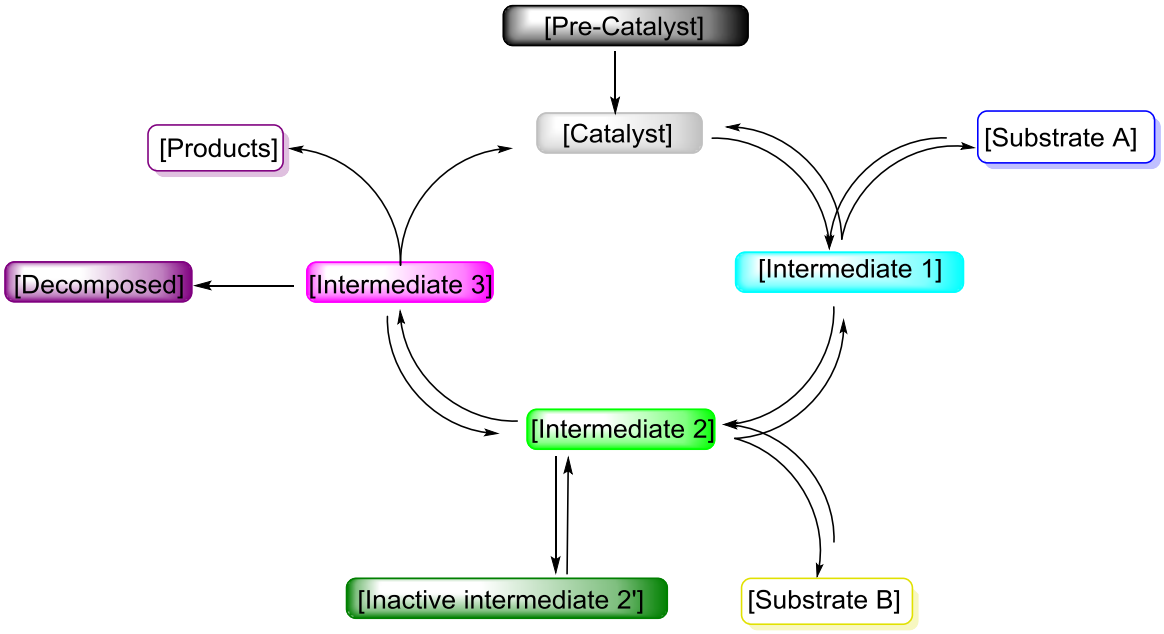
Using metal centers, a nucleophilic and electrophilic carbon center are bound to the metal and after insertion of coordinated CO release a diarylketone. [18].

Also, the vinylation of allylalcohols with ethylvinylether in the presence of $Hg(OAc)_2$ was reported to proceed without isomerization [19].



Scheme 13: Transition metal catalyzed transformations of organic molecules, engineered by chemists

Scheme 14 depicts an abstracted catalytic cycle demonstrating common reactions as well as side reactions encountered in transition metal catalysis. Usually, a stable precursor is first activated *in situ*, for example by dissociation of a ligand, yielding the active catalyst, for example with a free coordination site. The active catalyst reacts with substrates A and B, usually by way of reversible equilibria. Often equilibria with inactive species are formed. Usually, one step is irreversible and rate-determining.

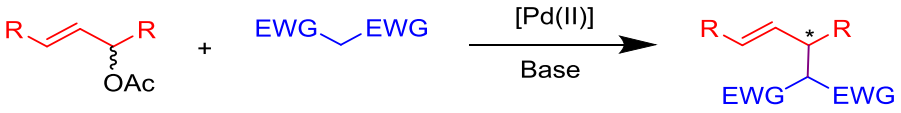


Scheme 14: General transition metal catalytic cycle.

1. 3. 1. Allylic alkylation

The allylic alkylation serves as an example for a transition metal-catalyzed reaction. A Pd(II)-catalyzed C-C bond forming reaction takes place between an allylic substrate possessing an anionic leaving group such as acetate substituted in an allylic position and an carbanion, for instance malonate (Scheme 15).

If the substitution proceeds at a chiral center and thus a non-racemic product is produced, usually in the presence of a chiral Pd-catalyst this reaction is called an asymmetric allylic alkylation. This asymmetric reaction has become one of the major benchmarking reactions for testing enantioinductive capabilities of novel asymmetric ligands able to coordinate Pd(II).



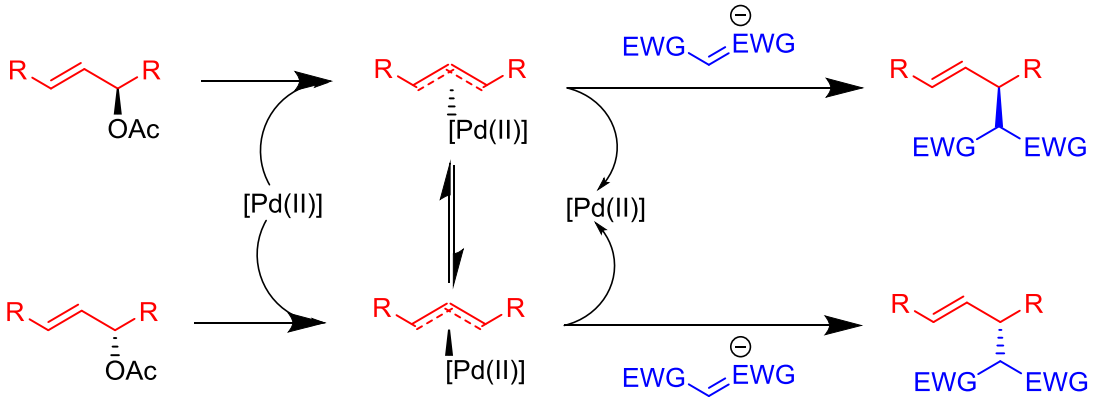
Scheme 15: Allylic alkylation catalyzed by Pd(II). For R ≠ H, a new stereocenter is formed.

Scheme 16 shows the mechanism. A *rac.* mixture of an allylacetate reacts with complex [Pd(II)], cleaving AcO^- and forming an η^3–allyl-Pd complex.

The now formed coordination compound will equilibrate the binding site of the allyl moiety to Pd in a rapid, non rate-determining equilibrium. Depending on the other ligands bound to Pd(II), these two possible complexes will occur in a certain ratio, ideally favoring one of those.

The allyl ligand then undergoes nucleophilic attack forming the product and restoring the reactive catalyst [Pd(II)]. This attack proceeds from the outer sphere for soft nucleophiles such als malonate but from the inner sphere for hard nucleophiles such as organolithium or Grignard reagents.

A mixture of enantiomers is being formed, the ratio depending on the individual reactivities of the two allyl complexes. The initial ratio of allylic acetate enantiomers does not matter due to the rapid re-equilibration step of the intermediary Pd-allyl complex. Yet one starting material enantiomers – the matched one – will react faster than the other enantiomer.



Scheme 16: Mechanism of the allylic alkylation. Note that [Pd(II)] already includes a ligand bound to the metal center.

To demonstrate the potential of this chemical reaction, chart 2 presents some arbitrarily chosen compounds possibly accessible by (asymmetric) allylic alkylation.

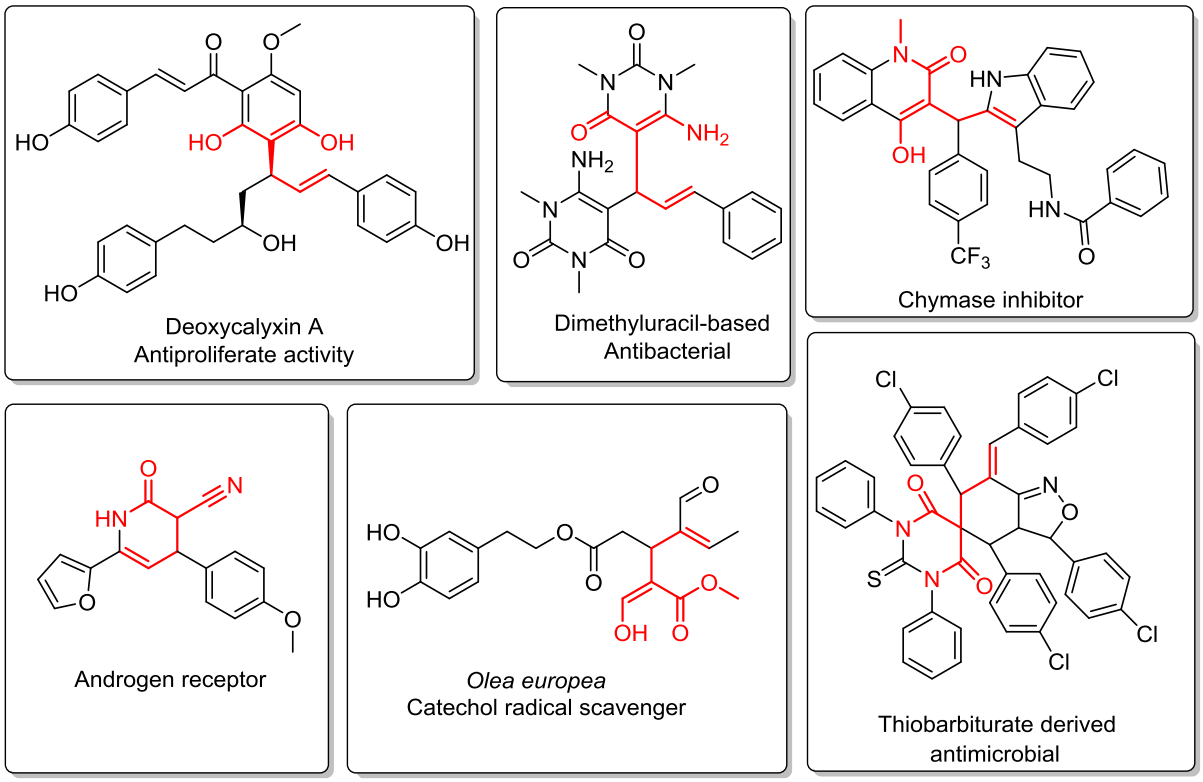
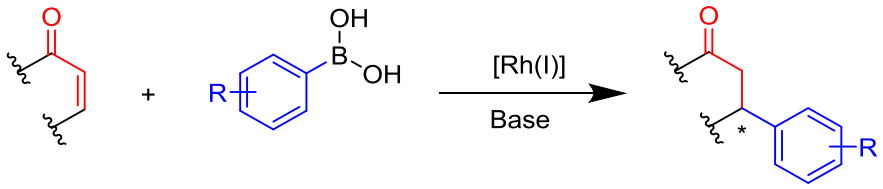


Chart 2: Selection of biologically relevant molecules bearing an allylic active methylene moiety (marked red)

1. 3. 2. 1,4-Addition to enones

1,4-Addition of aryls to enones is a Rh(I)-catalyzed chemical reaction forming a C-C bond between an aryl nucleophile functionalized with a boronic acid functional group and the β-C of an enone, forming a 3-arylketone structure. Scheme 17 describes the chemical transformation.

Depending on the starting material and the ligand(s) bound to Rh(I), 1,4-arylation may form chiral compounds. The latter reaction is called asymmetric 1,4-arylation of enones. This reaction is performed regularly to determine enantioinductive capabilities of novel ligands, particularly chelate ligands intended to coordinate Rh(I) with diene moieties [20] or a phosphine olefin ligand [21] [22].



Scheme 17: 1,4-Arylation of enones catalyzed by Rh(I). Depending on the enone, a new stereocenter is formed.

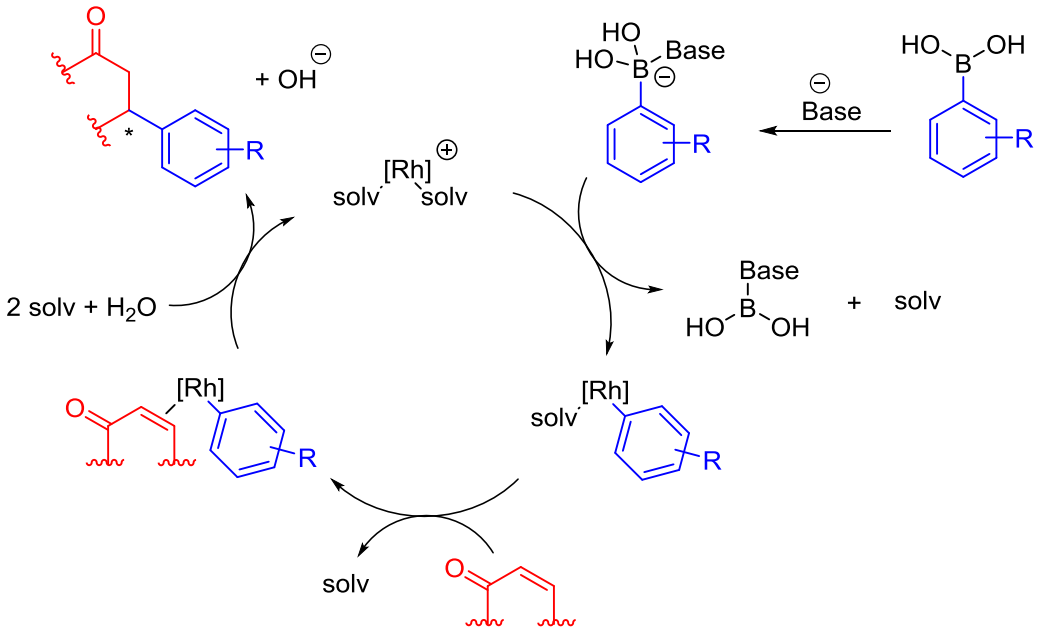
Scheme 18 depicts the suggested mechanism for the asymmetric 1,4-arylation of enones [23]. The cationic complex $[Rh(I)]^+$ is stabilized by solvent molecules, for instance by dioxane.

The arylboronic acid is nucleophilically attacked by a base, for example OH^-, forming a boronate anion. Said anion coordinates $[Rh(I)]^+$ by replacing one solvent molecule and cleaving the boronic acid functional group off as a mineral boronic acid, yielding a neutral Rh complex.

This complex forms a bond with the olefin functional group of the enone. Depending on the geometry of the enone and the other Rh ligand(s), the aryl ligand and the enone ligand will arrange accordingly.

This Rh(I) complex undergoes C-C bond formation, most plausibly by 1,2-migratory insertion of the enone double bond between aryl and [Rh]. Depending on the enone and the other Rh ligand(s), either site of the enone may be more accessible and thus more reactive.

The catalyst is then probably renewed by protonolysis of the newly formed C-Rh σ-bond.



Scheme 18: Mechanism of the 1,4-arylation. Note that [Rh(I)] already includes a ligand bound to the metal center.

Chart 3 presents some compounds hypothetically synthesizable by (asymmetric) 1,4-arylation of enones.

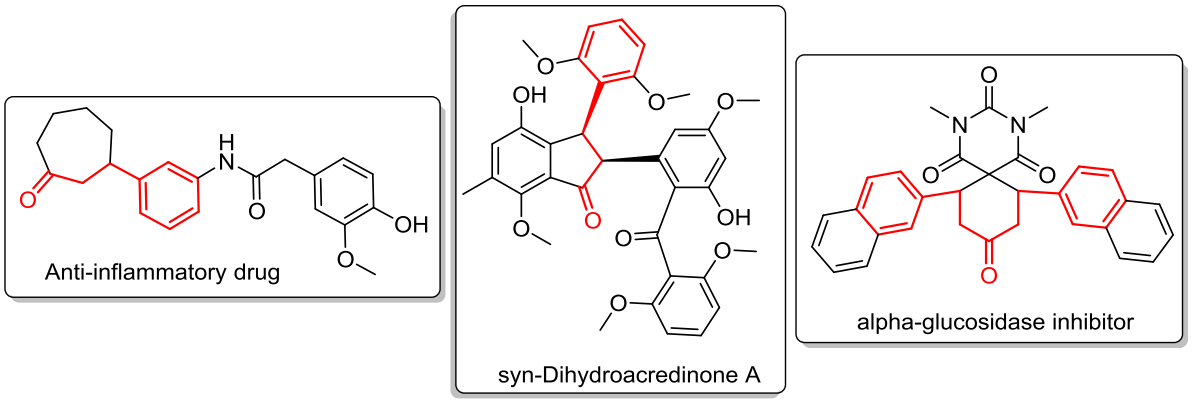


Chart 3: Selection of biologically relevant molecules bearing a β-arylketone moiety (marked red)

1. 4. Metallocenes

Metallocenes form a subgroup of organometallic compounds. They are defined by one metal center being coordinated by two Cp rings as cyclic η^5-ligands. Depending on the metal, these compounds either serve as catalysts, for example various titanocenes and zirconocenes, or as stable building blocks for organic compounds, the most important example being ferrocene.

In the case of ferrocene, the metal is iron. Hence, ferrocene is stable in agreement to the 18-electron rule (covalent model: 8 electrons [Fe(II)] + 2•5 electrons [Cp, L_2X]; ionic model: 6 electrons [Fe^{2+}] + 2•6 electrons [Cp^-, L_2X_2]). Furthermore, due to the negative charge of the Cp ring, it is aromatic according to Hückel due to possessing 6 π-electrons.

Ferrocene was first synthesized by pumping a solution of Cp dimer through an iron pipe. The orange substance being formed was discarded. The compound was discovered later by accident as a remarkably stable unknown substance when attempting to couple two Cp rings to fulvalene, using Fe(III) as an oxidant.

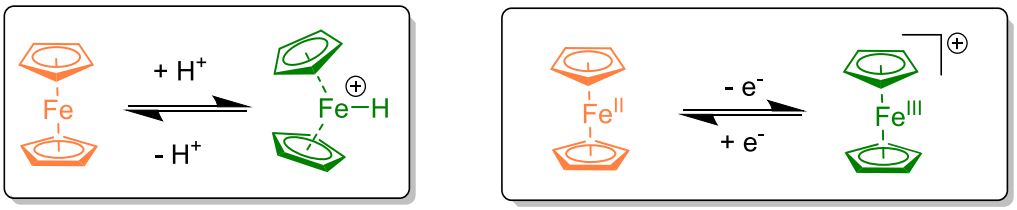
Hence, the first structure proposal for the resulting orange powder $C_{10}H_{10}Fe$ was planar with iron bridging both Cp rings by being bound to a single C atom each. Wilkinson and Fischer independently found out about the actual sandwich structure of the compound shown in fig. 2.

Iron is located in the center between two parallel Cp rings and all C's as well as H's, all C-C bonds as well as all C-H bonds being equal. This discovery and the subsequent synthesis of ferrocene analogs containing other central metals was awarded with the Nobel prize for chemistry in 1973.

Fig. 2: Left-hand side: Sandwich structure of $C_{10}H_{10}Fe$ (ferrocene) represented by a Lewis diagram. Right-hand side: Ferrocene structure constructed from Fourier-transformed X-ray diffractograms in 1955. The figure was taken directly from ref. [24].

Contrary to the majority of organometallic compounds, ferrocene is stable enough to be handled without any protective atmosphere. It is inert to moisture, stable to air at normal conditions and even at heating at 110 °C [25]. In its very nature, ferrocene is an electron rich aromatic compound, hence it can act as a bronsted base and as a reductant as shown in scheme 19.

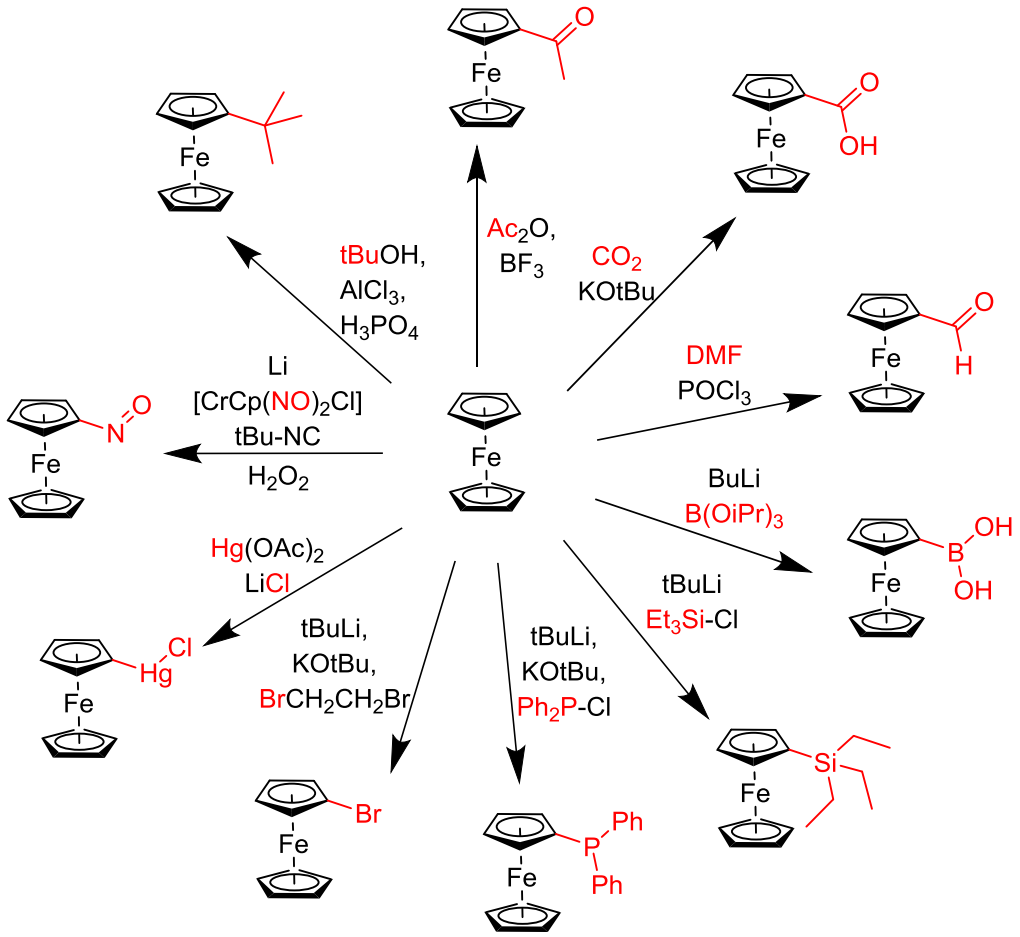
Ferrocene reacts only with very strong bronsted acids, is stable to bases, stable to basic reagents, reduction and still rather stable to many strong oxidative reagents such as H_2O_2 [26] and O_3 [27], but the iron center can be reversibly oxidized to Fe(III) electrochemically creating a less stable species prone to dissociating its Cp ligands. This electrochemical reaction has been used as a calibration reaction at + 400 mV against standard hydrogen electrode.



Scheme 19: Left-hand side: ferrocene acting as a bronsted base; right-hand side: ferrocene acting as a reductant

In fact, ferrocene is stable enough as an organometallic moiety to serve as a building block in organic synthesis. The Cp rings can be modified widely to incorporate ferrocenes in organic compounds.

Scheme 20 presents several examples demonstrating how ferrocene derivatives exhibit a chemical reactivity comparable to that of an electron-rich aromat: Lewis acid catalyzed Friedel-Crafts acylation [28], basic carboxylation [29], Vilsmeyer-Haack formylation [30] which is very selective for electron-rich aromatic systems, C-H lithiation followed up by an boronic acid [31], silyl [32], phosphine [33], and bromine [33] electrophilic substitution, metalation exemplified by mercuration [34], nitrosylation [35] using a transition metal complex and Lewis acid catalyzed Friedel-Crafts alkylation [36].



Scheme 20: Ferrocene CH substitution chemistry, closely related to electron-rich arene chemistry.

Ferrocene and its derivatives such as those pictured in chart 4 have found different practical applications. Ferrocene is added to petrol as an anti-knocking agent. Polymerization of vinylferrocene produces a polystyrol-analogous polymer with interesting electrochemical properties. This polymer is being used directly or as a copolymer in various electrical and redox applications.

Ferrocifenes form a ferrocene-based class of cytotoxic anti-tumor drugs. Ferrocifene mode of action works by stabilizing radicals and thus damage DNA in its immediate surroundings, ideally in cancerous cells. Possessing an estrogen lead structure, Ferrocifenes are used in breast cancer treatment.

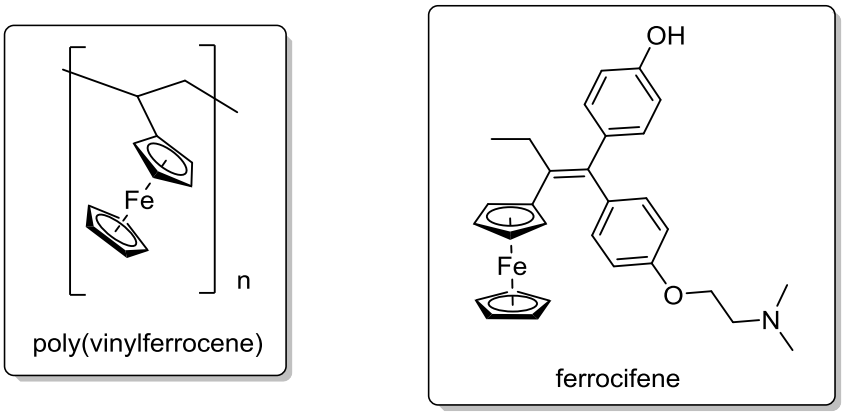


Chart 4: Commercially synthesized ferrocene derivatives.

Beyond that, ferrocene has found widespread usage as a key structural motif in chiral ligands for homogeneous catalysts, both in academic research and in industrial-scale applications. The reason for this is a powerful property of 1,2- or 1,3-substituted ferrocenes called planar chirality.

Fig. 3 presents enantiomers of a chiral di-substituted ferrocene. If ferrocene is 1,2- or 1,3-di-substituted at the same ring, the mirror-image is no longer superimposable with the original molecule. Hence those two compounds are enantiomers, all other physico-chemical properties being equal. Since the substituted ferrocene cannot invert the binding site of the Cp ring site η^5-coordinated to the metal center, the enantiomers are separable.

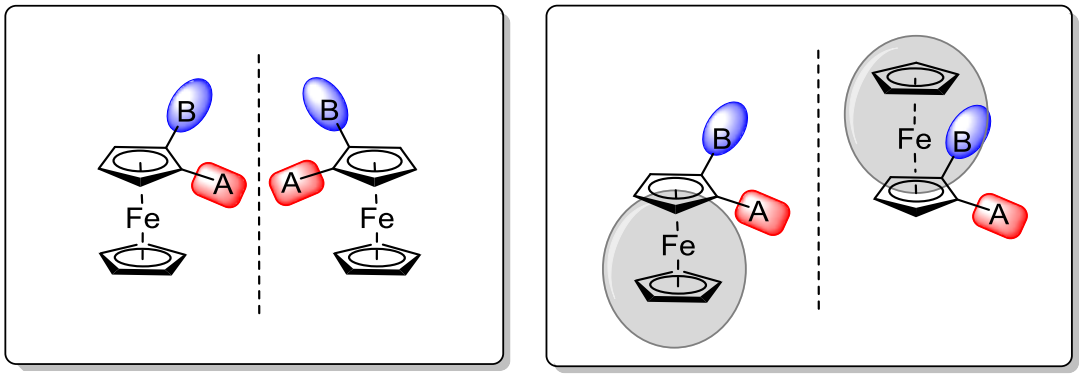
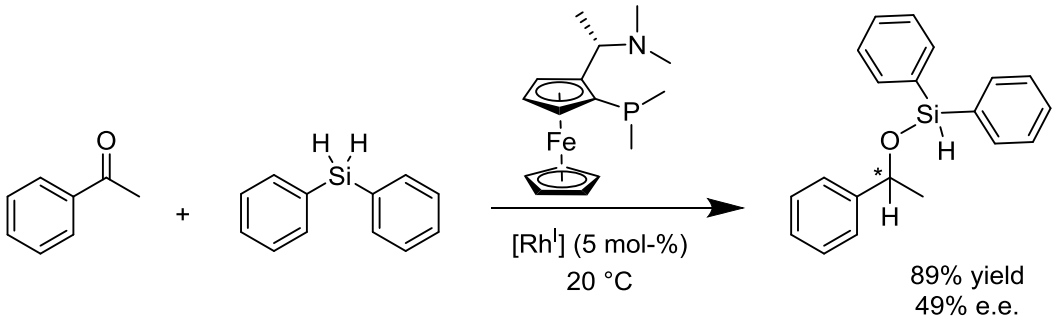


Fig. 3: Left-hand diagram: Planar chiral enantiomers of di-substituted ferrocenes, produced by mirroring. Right-hand diagram: Difference of space occupation by enantiomers when aligning the arylic substituents, demonstrating its enantioinductive capabilities.

The first group to use non-racemic ferrocenes as ligands in transition metal catalysis, Hayashi *et al.*, performed Rh(I)-catalyzed hydrosilylations of ketones followed by hydrolysis to afford asymmetric alcohols achieving good yields and moderate e.e. (Scheme 21) Various bidentate chelating ferrocenes have been tested [37].

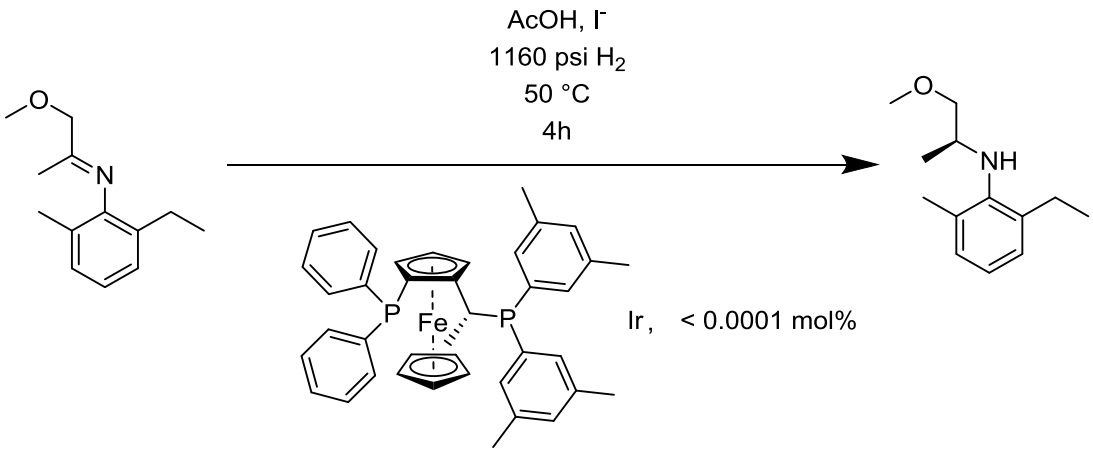


Scheme 21: 1,2-hydrosilylation of acetophenone using diphenylsilane performed by Hayashi *et al*. [37]

Ever since, ferrocene moieties became popular as structural motifs in ligands and have been employed widely. Several vastly different derivatives have been developed and tested including ansa-ferrocene ligands [38]. Nowadays, ferrocene-based transition metal catalysts are utilized in key steps even in industrial-scale processes.

Scheme 22 presents the asymmetry inducing step in the commercial synthesis of the pesticide Metolachlor. A prochiral imine is reduced by H_2, catalyzed by Ir coordinated by a diphosphineferrocene containing phosphine groups with different steric and electronic features known as Xyliphos [39].

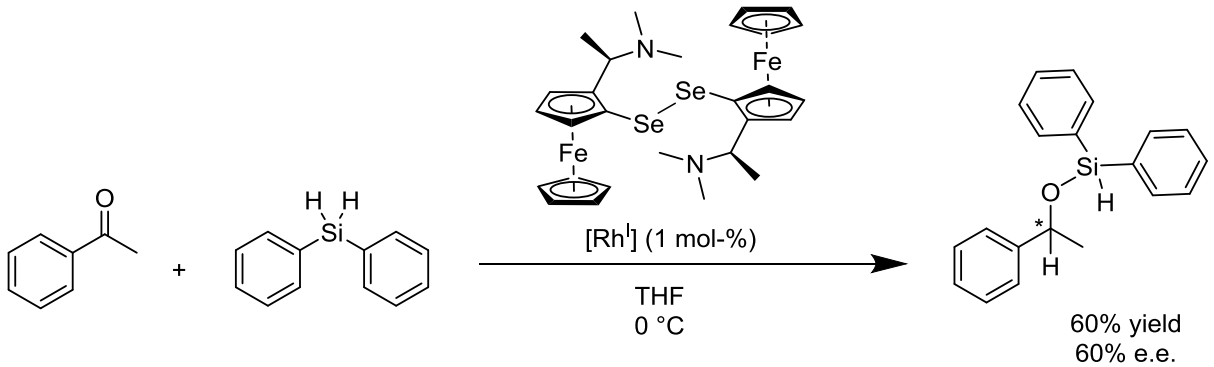
While yielding an e.e. of merely 79%, the catalyst performs the hydrogenation reaction rapidly and efficiently (> 7,000,000 TON, > 2,000,000 h^{-1} TOF, just 0.07 kg Xyliphos per 10,000 kg sec. amine product). To date, more than 10,000 tons hydrogenated product are produced per year this way.



Scheme 22: Asymmetric hydrogenation of an imine to yield an enantiopure precursor of metolachlor. [39]

While ferrocene ligands are successful in various areas of organic synthesis, it is obvious that enantioinductive molecules including two or more ferrocene moieties proximate to the catalytic center present a potentially greater potential to induce asymmetry. As to yet, these structures are comparatively rare and only a couple of them have been tested in chemical catalysis, summarized below.

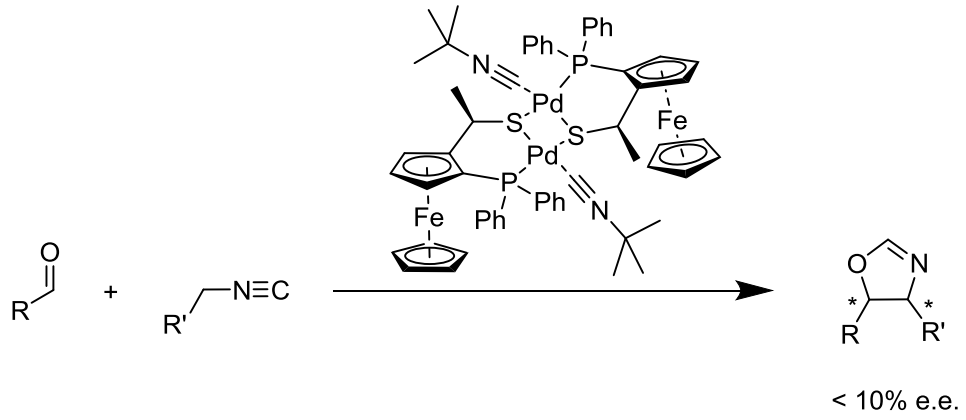
In 1996, Uemura *et al*. tested dichalcogene-bridged diferrocene compounds based on Ugi's amine coordinating Rh or Ir in hydrosilylation. After hydrolyzation, secondary alcohols were achieving moderate to good e.e. (Scheme 23) The diselenide-bridged ligand turned out to perform best. [40]



Scheme 23: Rh(I)-catalyzed 1,2-hydrosilylation of acetophenone using diphenylsilane performed by Uemura *et al*. [40]

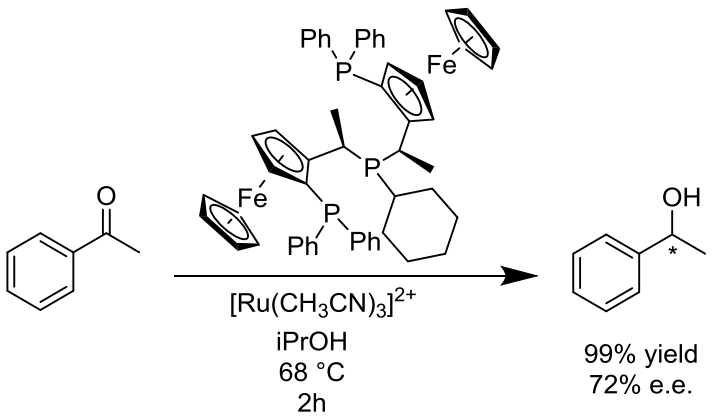
In the same year, Albinati *et al.* investigated a bidentate PS-ligand obtained from Ugi's amine, producing a diferrocene bound coordinatively as a di-Pd isonitrile

complex. This kind of coordination complexes are able to facilitate aldol additions and follow-up dihydrooxazole cyclizations of an aldehyde and an isonitrile. (Scheme 24) The group tested the dimerically bridged catalyst only to find out that while the aldol addition takes place, the catalytic species does not transfer its enantiomeric information well. [41]



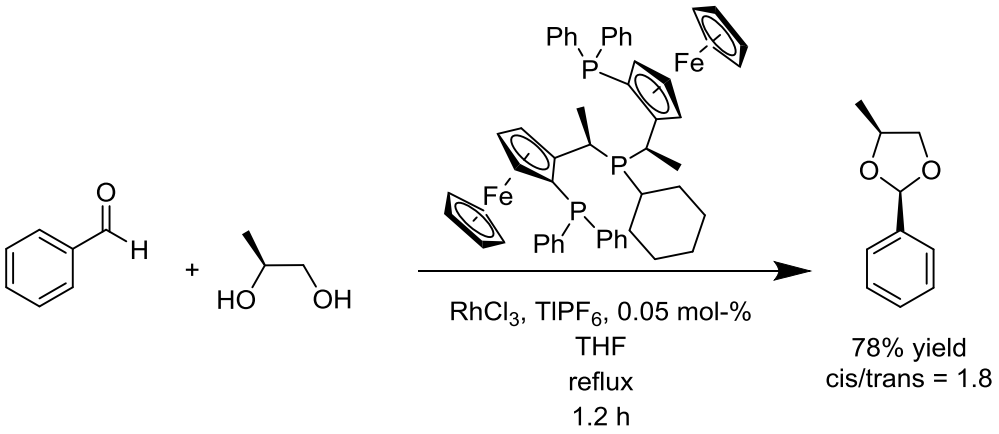
Scheme 24: Pd-catalyzed aldol addition and subsequent dihydrooxazole cyclization of an aldehyde and an isocyanide carried out by Albinati *et al*. [41]

Togni *et al*. reported a diferrocenetriphosphine compound based on Ugi's amine baptized pigiphos. In 1997, they tested a Ru(II)-catalyzed transfer hydrogenation of acetophenone, yielding 1-phenylethanol with up to 72% e.e. (Scheme 25) The excellent yield and the good e.e. achieved were encouraging considering this was the first application of the tridentate Pigiphos ligand [42].



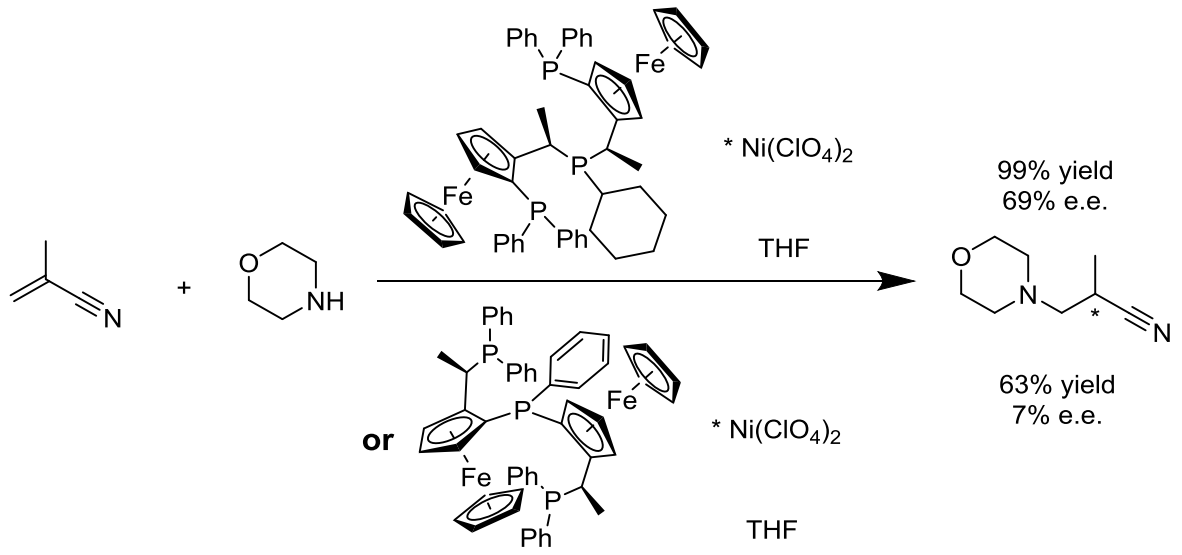
Scheme 25: Ru(II)-catalyzed H transfer from iPrOH to acetophenone forming 1-phenylethanol carried out by Togni *et al*. [42]

The same group worked in 1998 with chiral lewis acids using pigiphos as an asymmetric ligand attempting to engineer diastereo- and enantioselective acetalization procedures using benzaldehyde and different diols. (Scheme 26) While in most cases the yield of cyclic acetals was good, a lack of diastereoselectivity was reported [43].



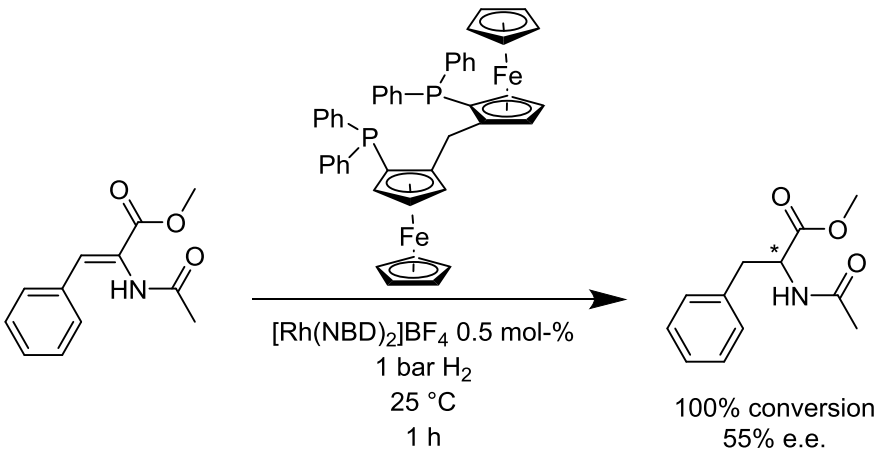
Scheme 26: Rh(III)-catalyzed acetalization of benzaldehyde and 1,2-dihydroxypropane performed by Togni *et al*. [43]

Togni *et al.* used pigiphos and other tridentate asymmetric ligands such as the similar gipiphos ligand family in 2004 to drive Ni(II)-catalyzed hydroamination of activated (EWG substituted) olefins, achieving both good yields and good e.e. (Scheme 27) The group found these catalysts perform equally well in ionic liquids, in which the reaction does not have to be carried out under inert conditions. [44]



Scheme 27: Ni(II)-catalyzed hydroamination of nitrile-substituted olefins with morpholine. [44]

Weissensteiner *et al.* synthesized C-linked diferrocene ligands in 2006 to perform Rh-catalyzed hydrogenations using H_2 (Scheme 28). The researchers achieved e.e. up to 55% for trisubstituted olefins, but only 15% e.e. and less for geminal substituted olefins and C=O-bonds [45] .



Scheme 28: Rh-catalyzed olefin reduction by H_2 performed by Weissensteiner *et al*. [45]

By a well-known paradigm in homogeneous asymmetric catalysis, rigid catalyst structures produce greater e.e. and overall less side products than unrestricted ones.

A rigid structure cannot vary its geometry too much, hence it will keep the geometry it was designed for most or all of the time. For a flexible structure the opposite is true. The ligand is able to adopt non-reactive conformations at times, slowing the process

down, or even conformations catalyzing the formation of other, undesired products such as the undesired enantiomer. While some exceptions to the rule are known, this principle generally holds true.

As for cyclized diferrocene compounds – diferrocenyl cycles – there are only a few examples as to date and most of them do not concern application in catalysis. Chart 5 summarizes these diferrocenyl cycles sorted by inventor and year of publication.

The first such diferrocenyl cycle ever was a biferrocene *o,o'*-bridged by phenylphosphineoxide synthesized by Mathey *et al.* in 1974 [46]. In 1976, Atwood and Shoemaker found a diferrocene alane species occurring after a rearrangement of a ferrocenedialane substituted each ring [47]. Schlögl *et al.* produced the first C-only bridged diferrocenyl cycle in 1977, yielding both *cis*- and *trans*-isomers [48].

In 1991, Köhler *et al.* synthesized *cis*- and *trans* diferrocenes bridged by a norbornane scaffold to measure iron-iron interaction of the ferrocene cores via cyclic voltammetry. For this synthesis, the group started with the di-Cp norbornane scaffold and produced the ferrocene moiety in a follow-up reaction [49]. In a similar fashion, they produced a cyclic diferrocene bridged by two silyl groups [50].

Ogawa, Sato *et al.* discovered an *o,o'*-bis(dithio)-bridged diferrocene in 2002 by oxidizing ferrocene-1,2-dithiostannate using I_2 [51]. Snieckus et al. accidentally produced an azepanone diferrocene cycle when attempting an esterification of a biferrocene precursor [52].

Gaede *et al.* produced novel cyclized diferrocenes among other organometallic coordination complexes in 2004 in order to study metal-metal communication by cyclovoltammetry [53].

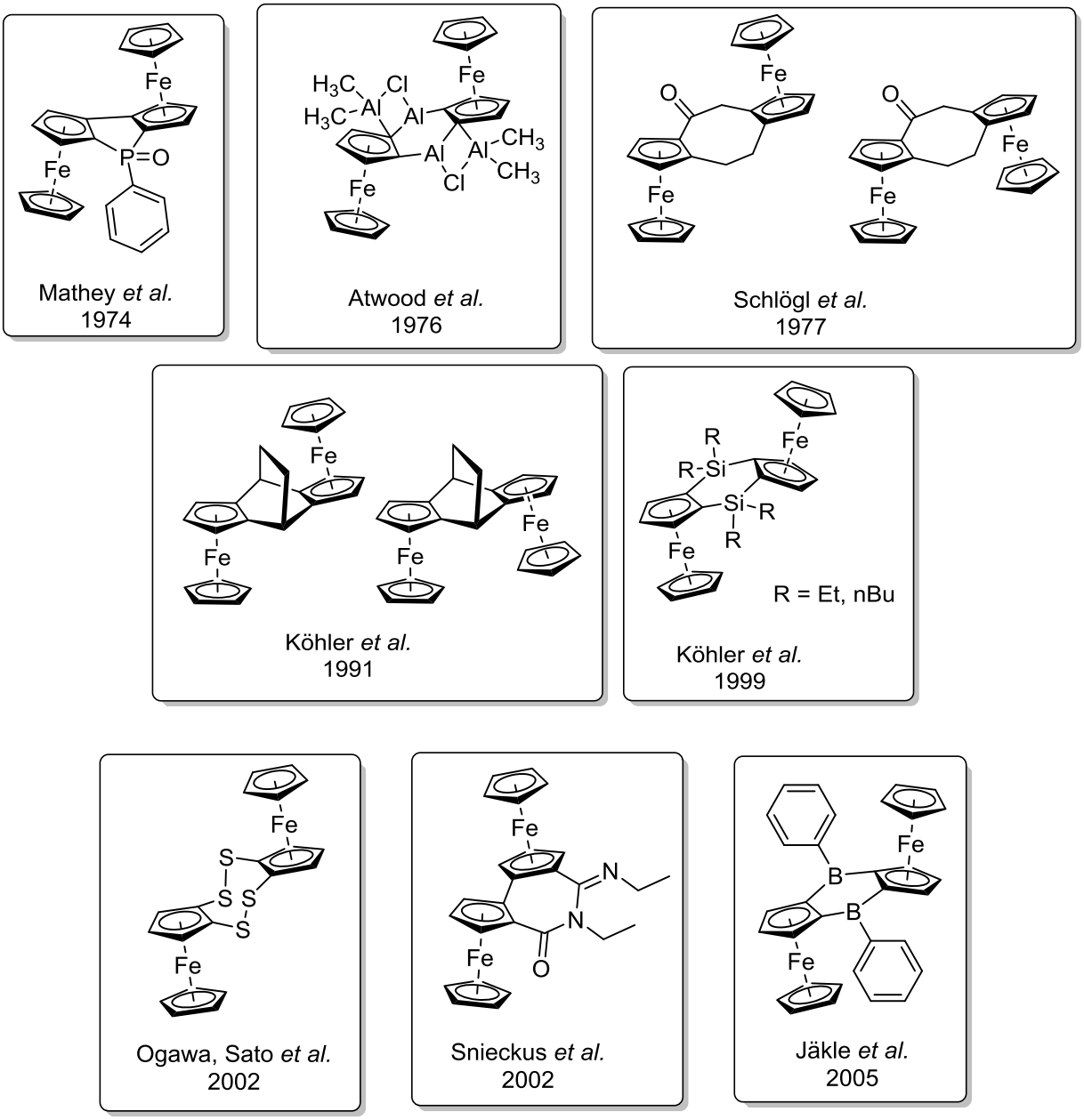
Jäkle *et al.* synthesized in 2005 the first dibora diferrocene cycle [54].

Santi et al. synthesized a biferrocene *o,o'*-linked by a *Z*-olefin in 2007. To produce this compound they started from the planar di-Cp precursor and finally attached the FeCp moiety [55].

In 2008, Jäkle et al. in course of their work on dibora diferrocenes synthesized B-mesyl- and B-pentafluorophenyl derivatives to investigate these new compounds by cyclic voltammetry [56]. In 2012, they produced the corresponding dimethoxy- and dihydroxydiboradiferrocenes and observed reversible polycondensation of the bis(boronic) acid [57], followed up in 2015 by synthesis and redox behavior

investigation of biferrocenes linked at the o position by one Sn or one B substituent [58].

The most recent contribution by the group of Jäkle concerns an *o,o'*-P,Sn and an *o,o'*-P,B linked diferrocenyl cycle and their Rh complexes. Particularly the latter diferrocenyl cycle presents an interesting molecule since it contains both a Lewis acid and a Lewis base [59]



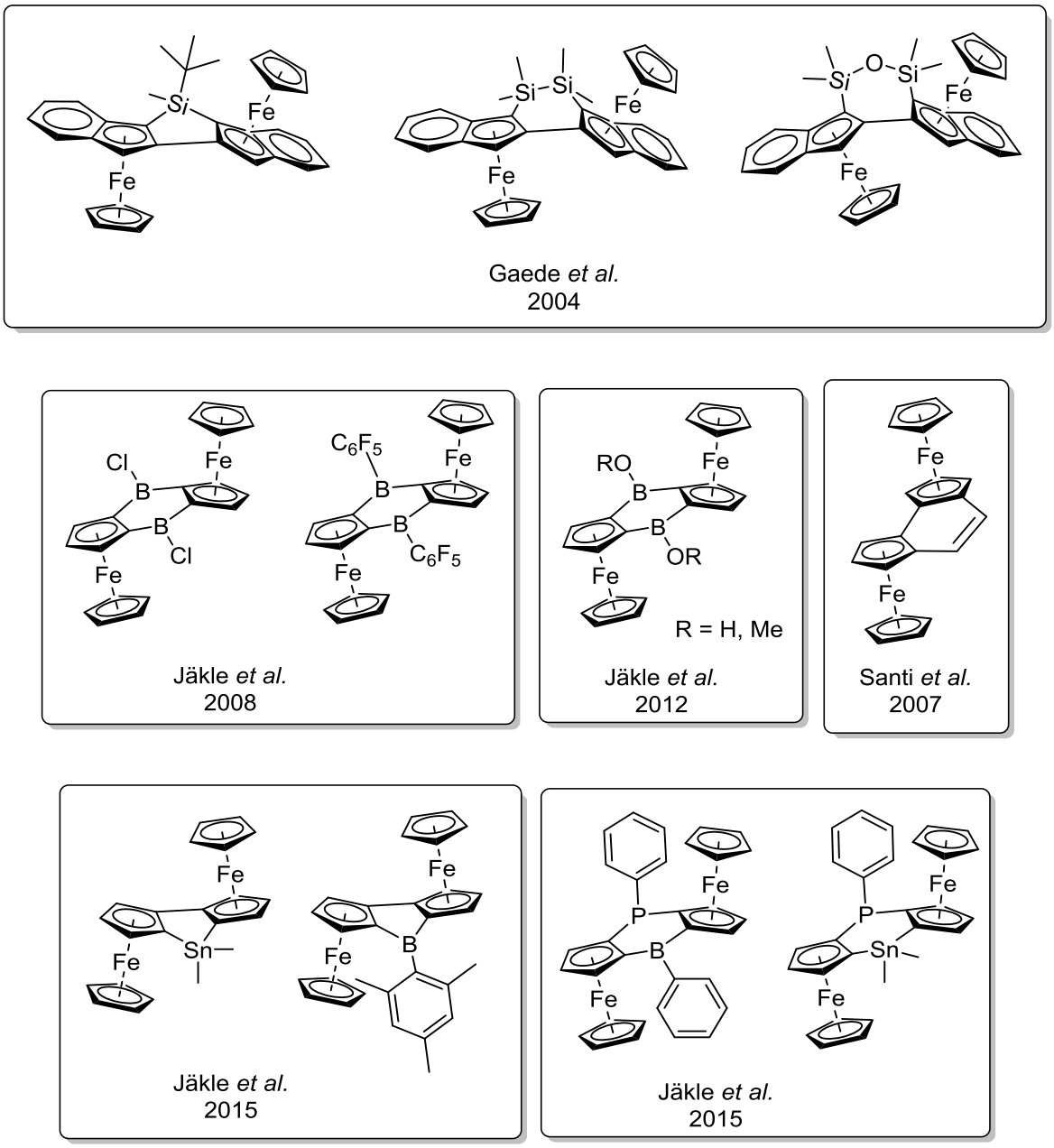
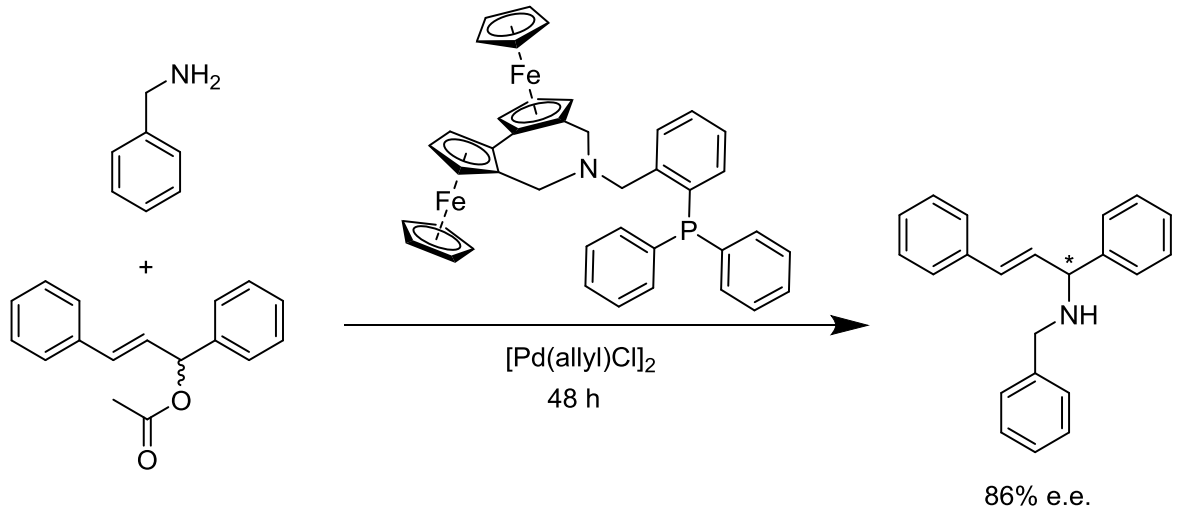


Chart 5: Summary of diferrocenyl cycles not used in catalysis as to date of this writing.

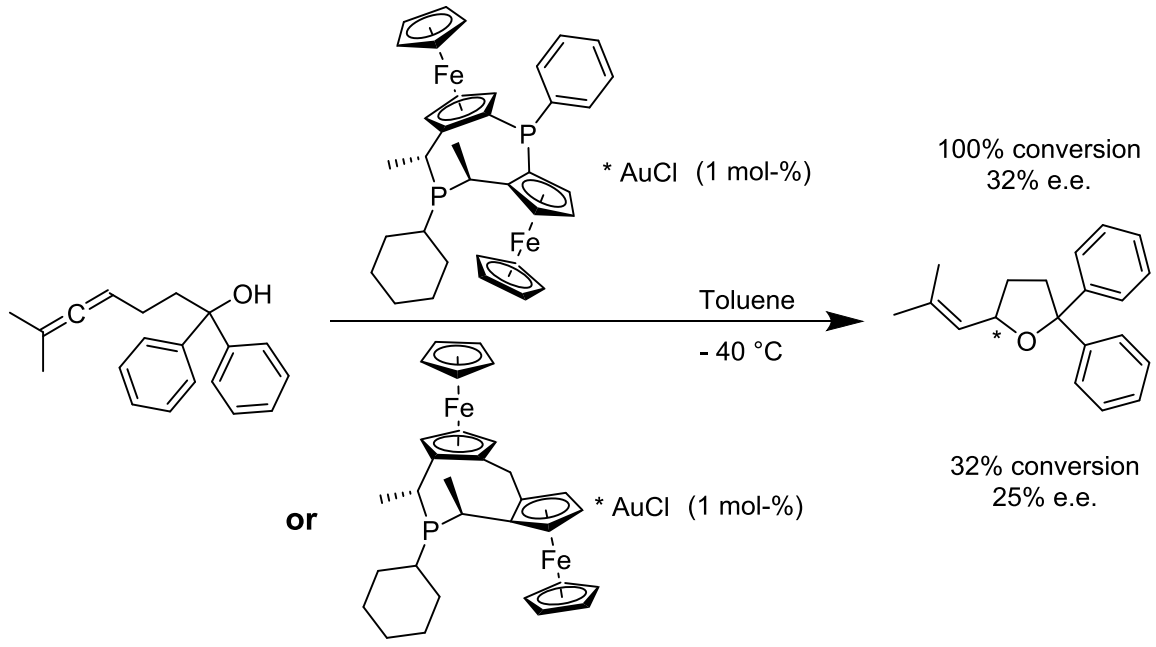
To date only two publications utilizing diferrocenyl cycles in catalysis have been published.

Widhalm, Weissensteiner *et al.* synthesized various biferrocenylazepines substituted by groups containing phosphines in 2002 (Scheme 29) which were tested in various Pd(II)-catalyzed asymmetric allylic substitutions and up to 86% e.e. have been obtained [60].



Scheme 29: Pd(II)-catalyzed asymmetric allyl amination with a diferrocenoazepine ligand [60]

Togni *et al*. tested two novel cyclic diferrocene compounds based on Ugi's amine in 2012, one bridged by two P atoms and another bridged by one P and one C atom forming eight-membered rings (Scheme 30). These were used in Au(I)-mediated hydroalkoxylation cyclizations of allenes achieving varying conversions and e.e. up to 32% [61].

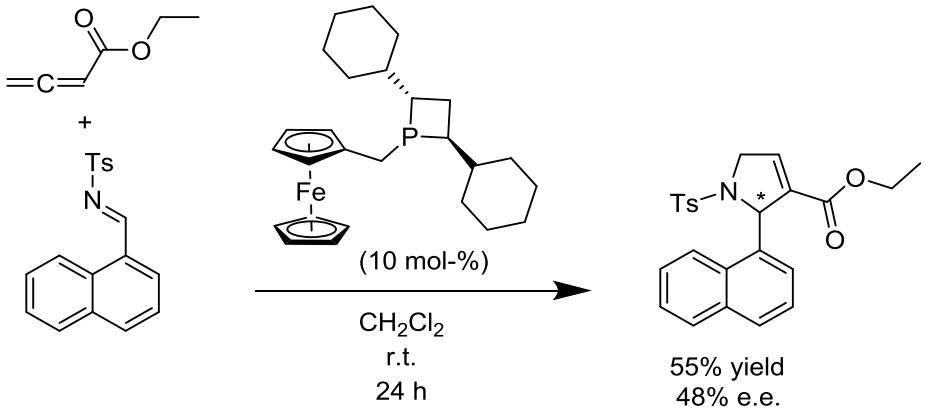


Scheme 30: Au(I)-catalyzed intramolecular hydroalkoxylation of allenes [61]

Aside from application in transition metal catalysis, ferrocene derivatives have started to be applied in organocatalysis as well. Since ferrocene-P bonds are rather stable,

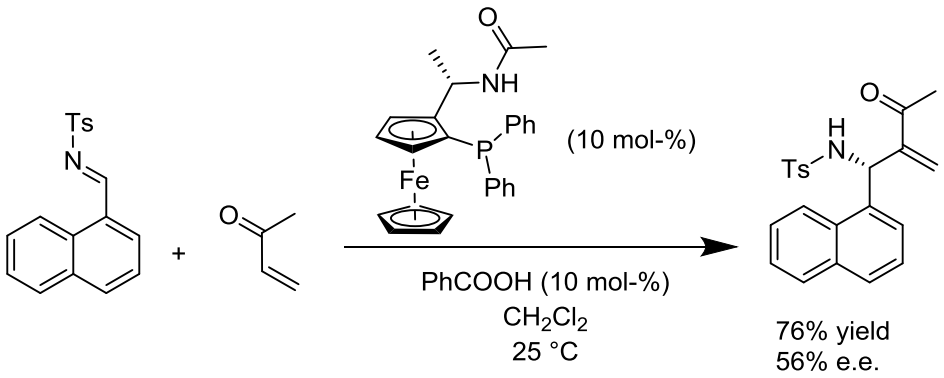
and P(III) directly attached to the ferrocene ring is also stabilized against oxidation this trend is not surprising [62].

For instance, Martinetti *et al.* tested various P(III) ligands in 2007 for the Lu cyclization of an electron poor allene and a tosylimine, including also ferrocenes containing a phosphetane moiety (Scheme 31). While induced e.e. have been moderate, phosphetanes lacking a ferrocene moiety turned out to be far less effective [63].



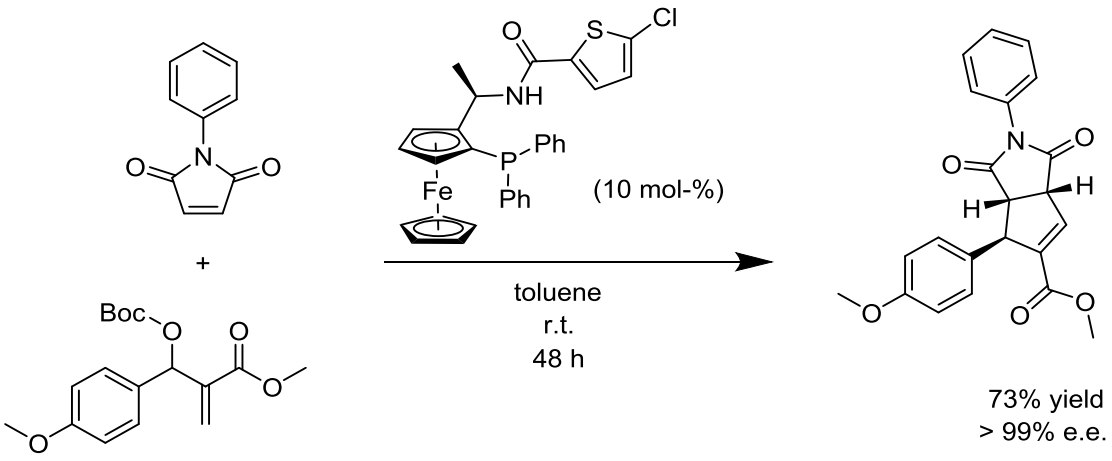
Scheme 31: P(III)-catalyzed Lu cyclization using a ferrocene organocatalyst [63]

Focusing entirely on organocatalysts containing ferrocene moieties, Zhong *et al.* tested a number of different monoferrocenylphosphine derivatives in 2015 as catalysts for the Morita-Baylis-Hillman reaction of tosylimines and methylvinylketone (Scheme 32). The most efficient catalyst turned out to be *N*-acylated PPFA [64].



Scheme 32: P(III)-catalyzed Morita-Baylis-Hillman reaction of a tosylimine and methylvinylketone [64]

Zhong followed up this project by investigating the P(III)-catalyzed 2,3-dipolar cycloaddition of Morita-Baylis-Hillman products and maleimides in 2016 (Scheme 33), achieving high e.e. and good yields using more complex acylated PPFA ligands [65].



Scheme 33: P(III)-catalyzed 2,3-dipolar cycloaddition of a Morita-Baylis-Hillman product and maleimide [65]

2. Aims of the thesis

Considering the extended area influenced through the presence of a planar chiral ferrocene, one can envision the increased potential when mounting two functionalized ferrocene units at the catalytic center.

While there are multiple hypothetical ways of connecting these two units, this project is limited to using Ph-substituted P as a linker. Triaryl substitution significantly slows down oxidation of P(III) and facilitates handling of products. P(III)-containing ligands can be used as:

- Metal-coordinating ligands
- Organocatalysts
- P-based auxiliaries

As has been pointed out in the introductory section, the exploration of diferrocenyl cycles in catalysis has only just begun. Fig. 4 lines out the desired structure for this project at the left-hand side. Two ferrocene units are coupled via P(III) or P(V) atoms.

For this geometry a quadrant rule may be valid. The target structural motif can be imaginarily divided by two planes passing through P and center of X: One coplanar to the diferrocenyl cycle, the other being perpendicular to it. The intended 3D structure blocks diagonal quadrants.

The idea of blocking diagonal quadrants in order to control the asymmetric induction of this chiral molecule can be compared to one of the most efficient Ziegler-Natta catalysts for isotactic propylene polymerization, shown at the right-hand side in fig. 4. Note the structural similarities of this ansa-zirconocene, blocking two diagonal quadrants, the conformation stabilized both by the catalytic center (Zr) and another bridging element ($SiMe_2$).

In order to freeze this conformation, these ferrocenes may be bridged at the *o,o'*-positions, denoted as X in the diagram below.

Particularly chiral ligands with high symmetry C_n or D_n are favored as the number of substrate complexes and corresponding parallel reaction paths is reduced.

A C_2 axis is often included in a catalyst design in order to limit the number of alternative and undesired reaction pathways. The schematic target motif does include a pseudo C_2-axis passing through P and backbone variable X. If the Ph and

the Q derivatives of P were not equal, it would be an actual C_2 axis. While this means the overall symmetry group of the target motif is just C_1, this decision allows for two identical ferrocene synthons to be coupled in retrosynthesis.

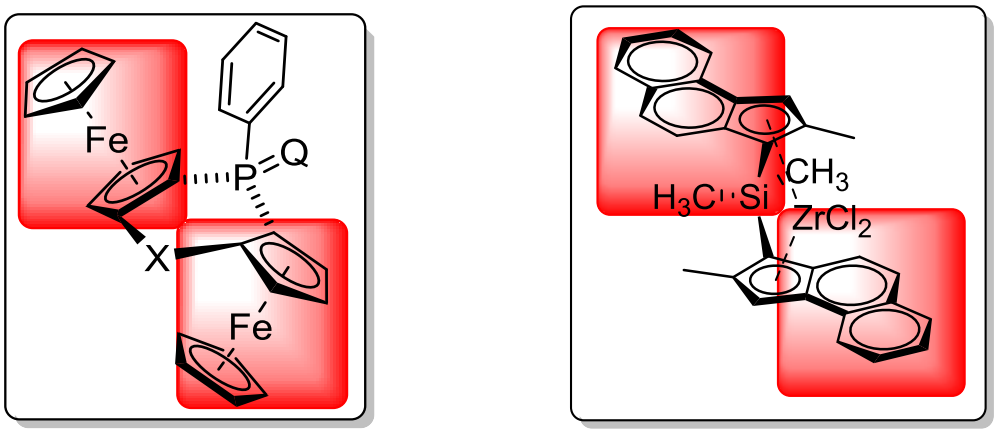


Fig. 4: Left-hand side: Desired structural motif. Right-hand side: One of the most efficient Ziegler-Natta catalysts.

Since there is an overall lack of protocols to synthesize the structural motif presented above, the first aim of this thesis is to devise a synthetic route starting from unsubstituted ferrocene, including one enantioinductive step, leading probably to noncyclic diferrocene intermediates first and this will be followed up by a cyclization as final step.

In order to produce different testable prototypes, the group denoted ‚X' should comprise various bridges with 2-4 atoms, such as C, but also group V and VI elements. These heteroatoms may serve to

a) produce bidentate ligands for kinetic stability of transition metal complexes or

b) to offer an alternative center of reaction, if P at the other side is not reactive.

Since there is little known about the more subtle detailed chemistry intrinsic to this kind of compounds and the scope of this thesis being limited, at least protocols for stable precursors for future diferrocenyl cycles should be established and documented.

Asymmetric cycles and stable precursors are to be tested preliminarily if a promising compound is produced in satisfactory quantity to demonstrate its enantioinductive

potential. This can be done in well-documented benchmarking reactions of transition metal catalysis such as asymmetric allylic alkylation and asymmetric 1,4-arylation of enones presented in the introductory section.

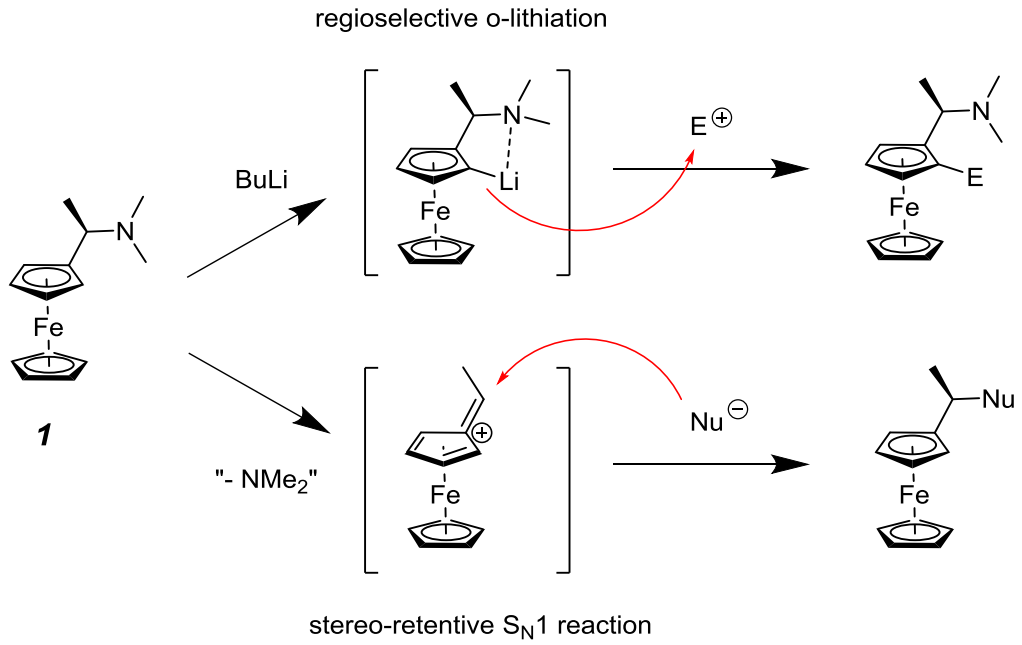
3. Results

3. 1. Synthesis of Ugi's amine from ferrocene

There are many ways available to synthesize planar chiral ferrocene derivatives [66]. In this case, Ugi's amine ***1*** was prepared as an enantiopure precursor for more complex asymmetric ferrocene containing compounds.

In fact, Ugi's amine played and still plays an important role in introducing chirality in ferrocene derivatives. Many modern asymmetric ligand structures are based on Ugi's amine. This popular chiral precursor can be further modified in two ways as demonstrated in scheme 34:

- Stereoselective *o*-lithiation and subsequent reaction with an electrophile [67]
- Stereoretentive S_N1 displacement of the dimethylamine moiety by a nucleophile [68].



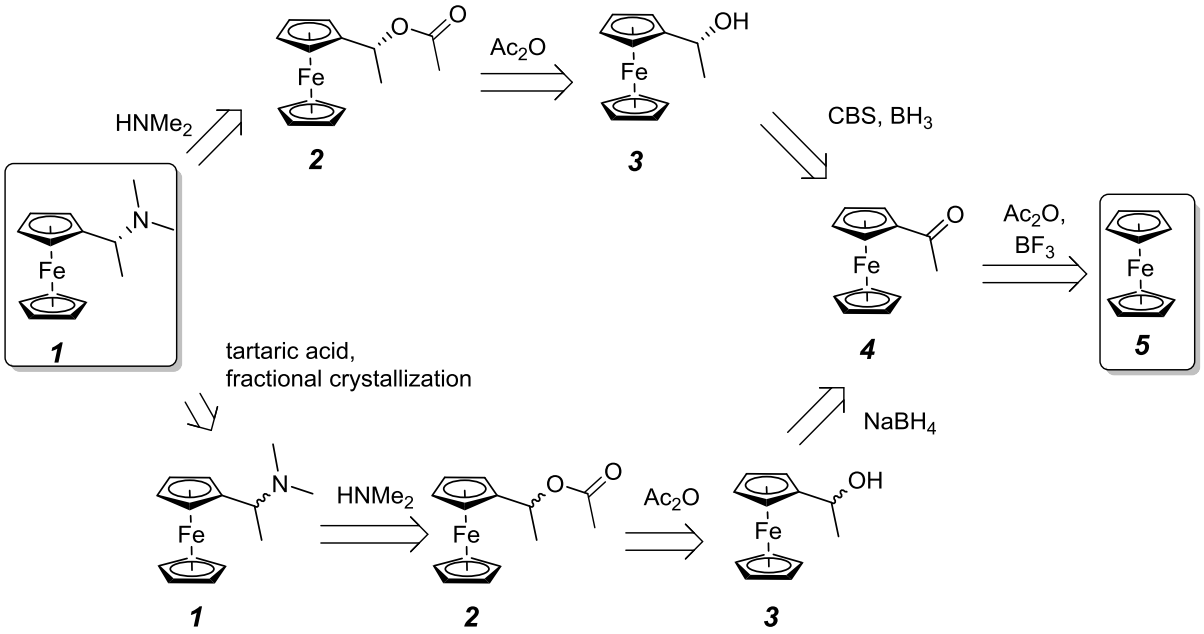
Scheme 34: Ugi's amine ***1*** as a chiral precursor for more complex chiral ferrocene derivatives

Two synthetic routes are used in literature to synthesize enantiopure Ugi's amine ***1*** from ferrocene, summed up by scheme 35.

The first route yields Ugi's amine ***1*** by stereo-retentive substitution of an appropiate leaving group such as acetate ***2*** which is prepared by esterification of the enantiopure hydroxy precursor ***3***. This precursor ***3***, in turn, can be produced by

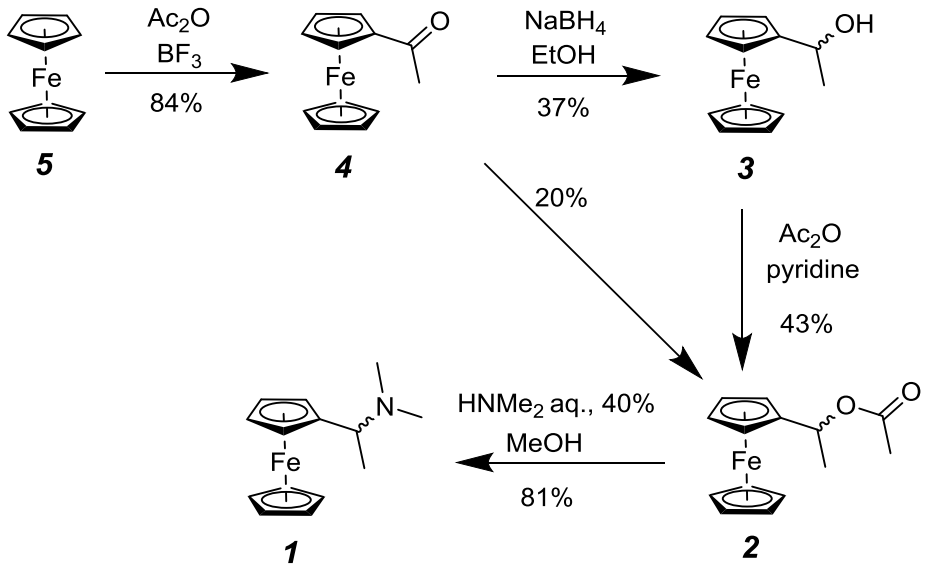
asymmetric reduction of acetylferrocene ***4*** for example by BH_3/CBS catalyst [69] (colloquially referred to as CBS catalyst) or a hydride source – such as formic acid – and a chiral catalyst [70].

The alternative route, used in this project, was based on enantiopure ***1*** obtained by optical resolution rather than asymmetric catalysis. Fractional co-crystallization of *rac.* ***1*** and enantiopure tartaric acid affords enantiopure Ugi's amine ***1***. The required racemate may be synthesized from acetylferrocene ***4*** by the same way, only the reduction needs not be asymmetric. Acetylferrocene ***4*** can be synthesized from ferrocene ***5*** by Friedel-Crafts acylation using Ac_2O. [71] [72]



Scheme 35: Retrosynthetic analysis of enantiopure Ugi's amine.

Scheme 36 summarizes the synthesis of amine ***1*** as performed in this project. Ferrocene ***5*** was functionalized by Friedel-Crafts acylation using Ac_2O, $BF_3 \cdot Et_2O$ and the crude material was purified by recrystallization from *n*-heptane [28] yielding 84% of acetylferrocene.

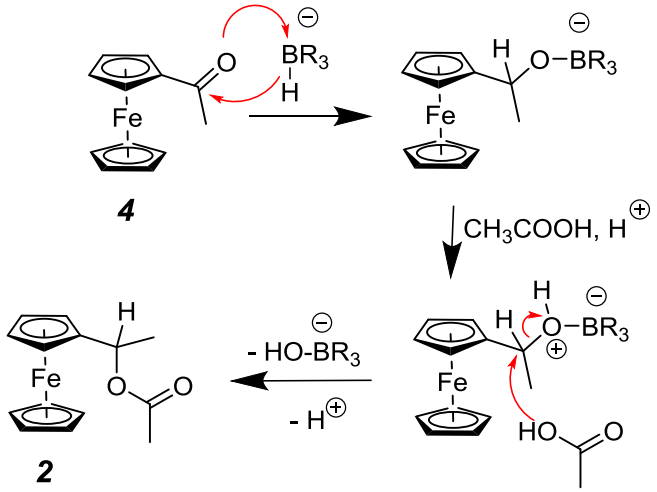


Scheme 36: Synthesis of *rac.* Ugi-amine.

Acetylferrocene ***4*** was reduced to alcohol ***3*** using $NaBH_4$ in EtOH for 24 h. The resulting intermediary boronic ester was quenched with AcOH. Alternatively, asymmetric carbonyl reduction protocols using the CBS catalyst and BH_3 have been published [73].

Curiously, beside 37% yield of the expected hydroxy compound ***3***, 20% of the *O*-acetylated product ***2*** was formed as well and isolated by column chromatography. Obviously the modified work-up procedure using AcOH instead of a mineral acid such as HCl lead to the one-pot ester formation.

Scheme 37 presents a plausible mechanism. The intermediarily formed ferrocenylethoxyboronic acid ester is protonated by AcOH, then attacked nucleophilically by AcO^-. The strong affinity of B and O drives the bond forming reaction.



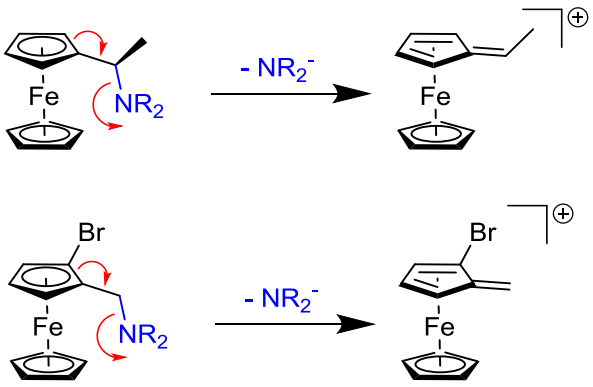
Scheme 37: Proposed mechanism of how acetate ***2*** forms from acetylferrocene ***4*** and $NaBH_4$, worked up with Ac_2O.

Alcohol ***3*** was *O*-acetylated by Ac_2O in pyridine for 24 h [68]. Even though complete conversion of alcohol ***3*** to ester ***2*** could be demonstrated by TLC testing, about half of the esterificated product ***2*** as regained as alcohol ***3*** after preparative chromatography on SiO_2. This is attributed to an instability of the acetic ester ***2*** in the acidic environment of SiO_2.

Ugi's amine ***1*** was synthesized by S_N1 displacement of the acetoxy moiety in ***2*** by 40% aq. Me_2NH in MeOH over the course of 2 d in 81% yield [68]

Ferrocene derivatives show an interesting behavior when nucleophilically replacing a leaving group in quasi-benzylic position by S_N1 mechanism. An intermediary carbenium cation stabilized by and conjugated with the vicinal Cp moiety is formed after the leaving group dissociates. The not involved CpFe residue blocks one of the two possible attacking sites of the nucleophile, forcing it to approach the ferrocenyl carbenium from the same site the leaving group departed. Hence the configuration of the substrate molecule is retained despite of the S_N1 nature of the reaction [68].

In fact, this relatively stable, fulvene-like carbenium cation is observed as a fragment in several HRMS at later points of this project. Scheme 38 shows the formation of these cations from 1-aminoethylferrocenes and *o*-bromoferrocenemethylamines.



Scheme 38: Fulvene-like ferrocenylmethyl cations observed in HRMS throughout this project

3. 2. α-Substituted Di(ferrocenylethylene) compounds

3. 2. 1. P(III) and P(V)-linked diferrocenes

Starting from enantiopure amine ***1***, synthetic routes leading up to asymmetric diferrocenes and, subsequently, diferrocenyl cycles had to be devised. Scheme 39 sums up the retrosynthetic analysis.

For the desired diferrocenyl cycles, one must discriminate between P-linked diferrocenes bridged either by all-C backbones or by backbones containing a heteroatom such as N or O, or even an entire functional group, such as urea for instance.

The hetero atom (or group) ***I*** including diferrocenyl cycles could be synthesized by direct acid catalyzed nucleophilic substitution of the diamine functional groups of a diaminediferrocene precursor ***IV***. Diamine ***IV*** in turn could be produced from coupling of two *o*-lithiated amines ***V*** with Cl_2PPh. If necessary, the phosphine atom may be protected for subsequent transformation, for example by oxidation or boranation.

Alternatively, ***IV*** could be activated for cyclization as acetate ***III*** or by methylation of the two diamine functional groups leading to a bis(trimethylammonium) di-iodide ***II***. These intermediates can then be transformed by nucleophilic displacement of the acetoxy- or trimethylammonium group to ***I***.

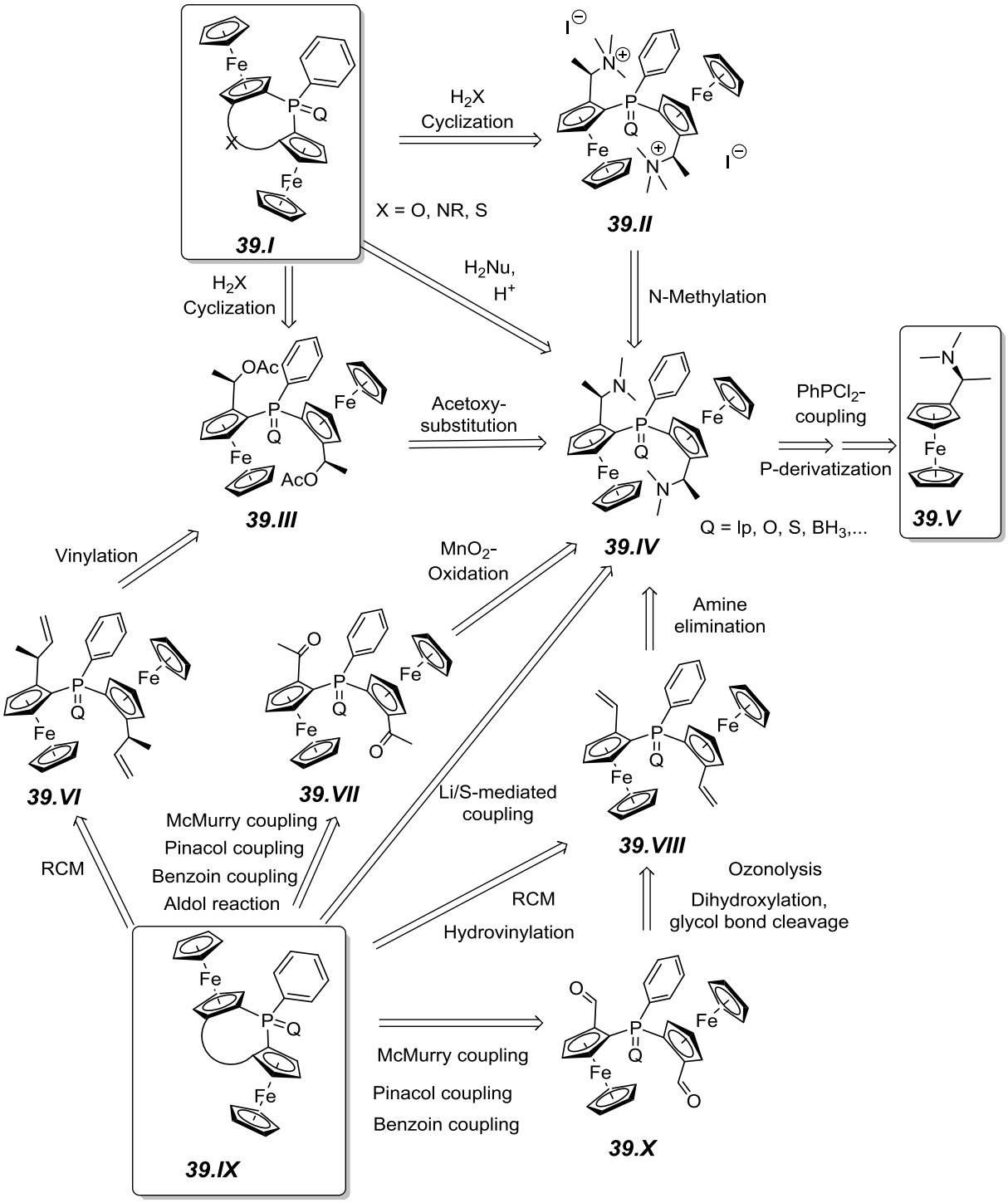
The all-C backbone diferrocenyl cycle ***IX*** could be synthesized by various means of coupling: By RCM or hydrovinylation of a diolefin precursor ***VI*** / ***VIII*** or by one of various carbonyl coupling protocols: McMurry coupling, Pinacol coupling, Benzoin coupling or, if a α-CH bond is available, intramolecular aldol reaction.

Alternatively, a protocol describes a direct benzylic dimerization of the Ph analogue of amine ***1*** utilizing Li and S [74] which may be modified to cyclize diaminophosphine ***IV***.

Diolefin precursors can be produced in two ways: either by twofold elimination of dimethylamine ***IV*** or by nucleophilic vinyl substitution at the diacetate ***III*** to give ***VI***.

Carbonyl precursors ***VII*** / ***X*** are available either by ozonolysis or dihydroxylation followed by glycol cleavage using olefin precursor ***VI*** or ***VIII***. Alternatively, diaminophosphine ***IV*** can be oxidized at the quasi-benzylic position using MnO_2 or by substitution of amine/acetate leaving groups of ***II***, ***III*** or ***IV*** with a thiol lacking a α-H

followed up by oxidation of the resulting thioether then a Pummerer rearrangement yielding dicarbonyl ***VII***.



Scheme 39: Retrosynthetic analysis: Formation of P-linked diferrocenes from amine ***39.V*** and cyclization of P-linked diferrocenes.

Scheme 41 summarizes the coupling and derivatization of the enantiopure starting material. In preexperiments amine ***1*** was lithiated with *n*-BuLi in dry Et_2O and reacted

with various electrophiles including $ClPPh_2$ [75], $B(OMe)_3$ [76] and Me_3SiCl [75] according to published literature.

After successful synthesis of these phosphine-, silyl- and boronic acid derivatives, synthesis of diaminophosphine ***6*** was attempted. This compound is known by literature. Its synthesis via lithiation has been proven difficult in the past [77] when its synthesis was first performed. Later, a different protocol using lithiation was established [78].

Attempts to synthesize diaminophosphine ***6*** using 1 eq of *n*-BuLi in dry Et_2O resulted in no product formation but in observation of *n*-Bu substituted P products.

Diaminophosphine ***6*** was finally synthesized according to the protocol published by Togni *et al.* in 2012 using *tert.*-BuLi instead in Et_2O and after purification of ***1*** by vacuum distillation [61], yielding 60% of the product. As a side product, the corresponding monoferrocenylphosphite ***7***, starting material and the P-oxidized diamine ***11*** were discovered as trace impurities removed by column chromatography. Alternatively, a recent publication presents a method for producing phosphines with three different substitutes [79] which is of interest for future synthetic efforts.

Hence P was inserted between two ferrocenyl moieties. Diaminophosphine ***6*** is a potential ligand already, usable as a mono-, di- or tridentate ligand in metals, or as a P(III) organocatalyst potentially effective in asymmetric Morita-Baylis-Hillman, Rauhut-Currier and Lu reactions. On the other hand, it may be usable as an asymmetric or desymmetrizing auxiliary in phosphine-promoted chemical processes such as Appel-, Wittig-, Staudinger- or Mitsunobu reactions.

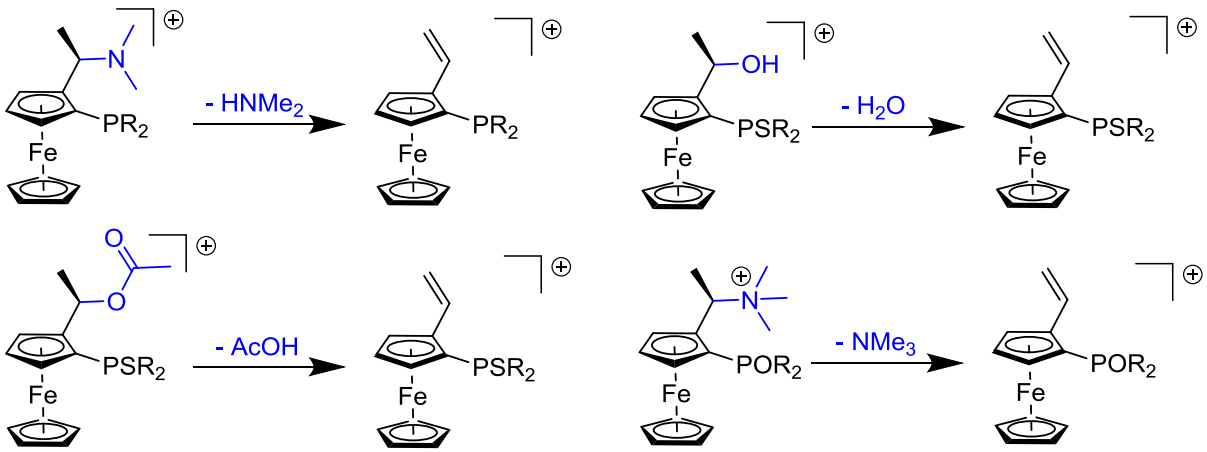
To create another interesting cyclization precursor, twofold elimination of diamine moieties was performed by heating a suspension of the starting material ***6*** in Ac_2O in analogy to a published procedure [80].

Preliminary elimination tests on *rac.* amine ***1*** heated in Ac_2O in ambient atmosphere pointed out the necessity to perform this reaction in an inert atmosphere as most of the starting material decomposed for the most part, yielding only 22% vinylferrocene after purification by column chromatography.

Somewhat surprisingly, divinylphosphine ***8*** was gained from diaminophosphine ***6*** in up to 74% yield under this harsh reaction conditions. Throughout this project,

eliminations of hetero atom groups at the quasi-benzylic position has been observed to occur readily in ESI HRMS as summarized in scheme 40.

However, it turned out to be vital to keep a high temperature throughout the twofold elimination reaction as acetoxy- and hydroxy substituents such as monovinylmonoacetatephosphine ***9*** and monovinylmonohydroxyphosphine ***10*** have been found instead of the dimethylamine groups if the reaction was not heated sufficiently or stopped too early. Visually, the twofold elimination is complete if the original orange suspension turned to a black, almost non-transparent color.



Scheme 40: Elimination reactions of α-heteroatom substituted ethylferrocene derivatives observed in HRMS throughout this project

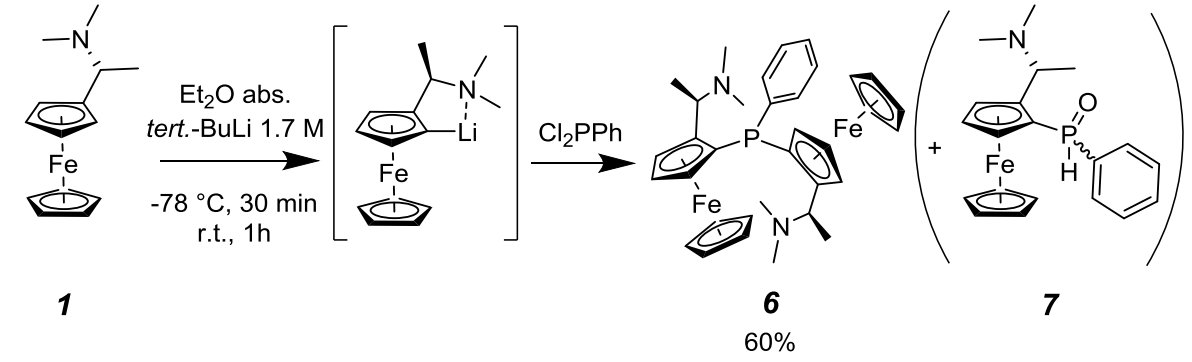
Diaminophosphine ***6*** and divinylphosphine ***8*** were oxidized quantitatively to the corresponding phosphineoxides ***11*** and ***12*** by H_2O_2 in MeOH at r.t. under standard conditions [26]. The reaction was observed to proceed more readily for diaminophosphine ***6*** as it forms a homogeneous solution contrary to divinylphosphine ***8***. Phosphineoxides generally can be reduced back to phosphines by AlH_3 or $HSiCl_3$ [81].

Analogously, ***6***and ***8*** were heated with sulfur in toluene for 4 h under Ar [77] to give phosphinesulfides ***13*** and ***14*** in quantitative yield.

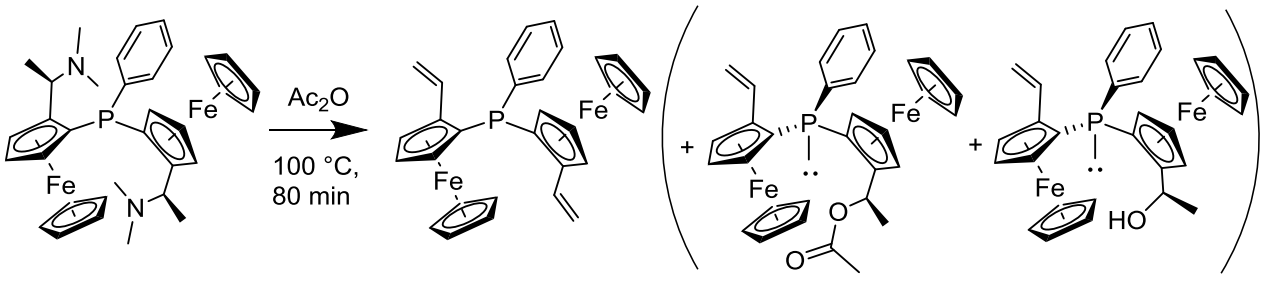
The progress of this reaction could not be tracked since phosphine starting material and phosphinesulfide product showed the same retention in TLC. Phosphinesulfides generally can be reduced to phosphines using Raney Ni and H_2 or by sulfide transfer to $P(OMe)_3$ or $P(NMe_2)_3$ [82].

While seeming like an arbitrary decision at this point in the project, sulfidation of phosphines turned out to be a brilliant decision in retrospect. Phosphinesulfides proved stable against any reaction condition employed during this project, phosphinesulfides eluate far more easily in column chromatography than their phosphineoxide analogs, readily form easy-to-handle solids in many cases and even crystals pure enough for X-ray crystallography could be obtained in some cases.

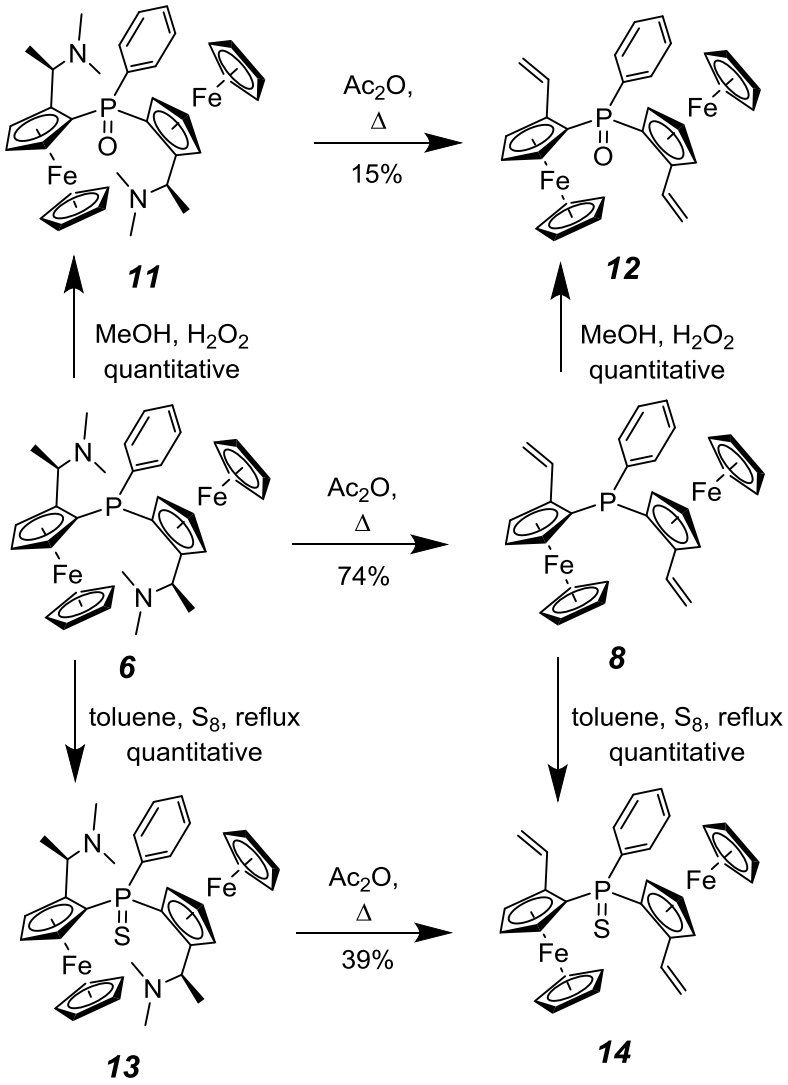
When performing elimination of diaminophosphine ***6*** and derivatization of divinylphosphine ***8*** in this order, compounds ***12*** and ***14*** were gained in good yields of up to 74%. However, when reversing the order and attempting derivatization first, then twofold elimination of diaminophosphineoxide ***11*** and sulfide ***13***, the yields of divinylphosphineoxide ***12*** and sulfide ***14*** were only 15% and 39%, respectively.



1 ***6*** 60% ***7***



6 ***8*** 74% ***9*** ***10***



Scheme 41: Synthesis of P-bridged Ugi's amine, twofold elimination, and P(V) derivatives

Fig. 5 and 6 show the NMR spectra recorded from diaminophosphines ***6***, ***11***, ***13*** or divinylphosphines ***8***, ***12***, ***14*** and divinylphosphinoborane complex ***58*** synthesized at a later point of the project (see section 3.4.). Overall, the spectra of analogous compounds containing different phosphine functional groups are similar to each other.

Nuclei chemically proximate to the P atom are generally shifted towards downfield following a trend P=S > P=O > P: in agreement with ^{31}P-NMR shifts ($Fc_2PhP{=}S$ ~ 40 ppm, $Fc_2PhP{=}O$ ~ 30 ppm, Fc_2PhP: ~ -45 ppm). From this it can be speculated that a strong -I/-M behavior of the R3P=S is operating and thus an overall EWG nature of this functional group can be concluded.

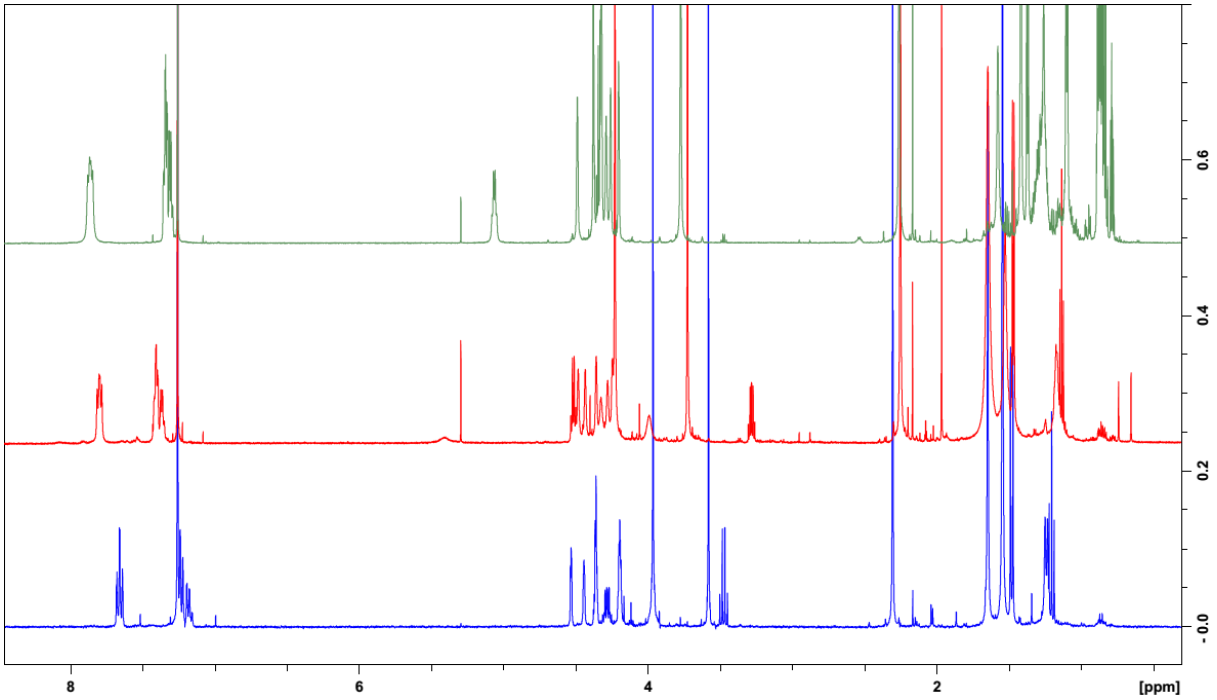
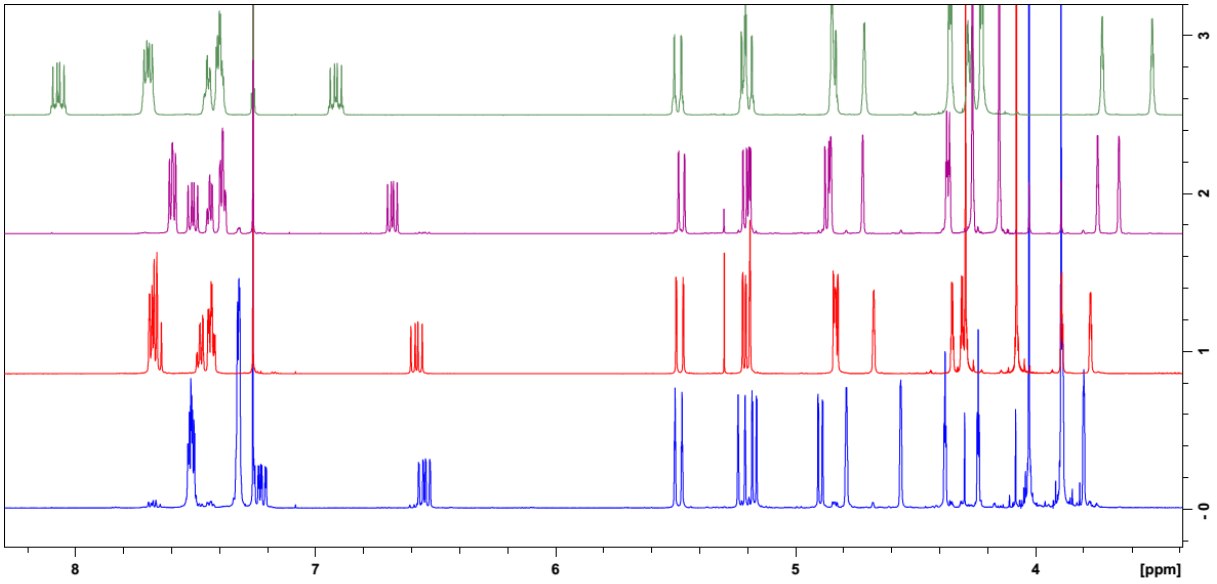


Fig. 5: ^{1}H-NMR spectra of diaminophosphine ***6*** (blue line), diaminophosphineoxide ***11*** (red line) and diaminophosphinesulfide ***13*** (green line)



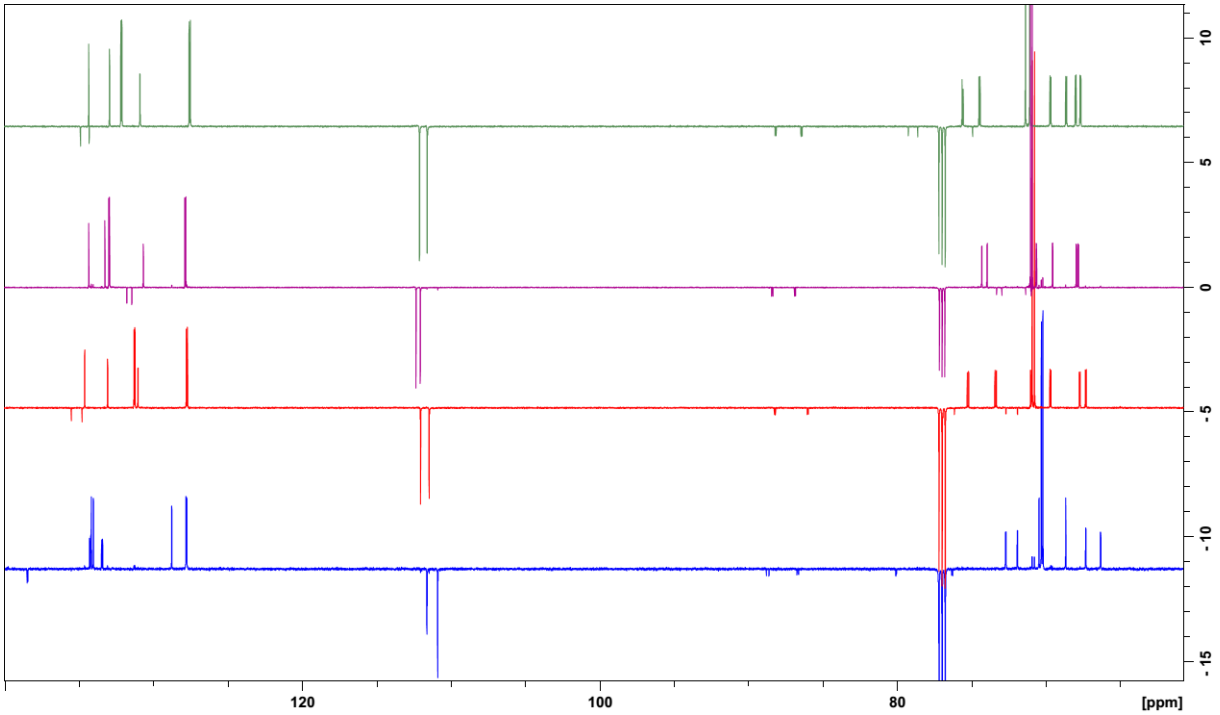


Fig. 6: ^{1}H-NMR (above) and ^{13}C-NMR (below) spectra of divinylphosphine ***8*** (blue line), divinylphosphineoxide ***12*** (red line), divinylphosphinoborane ***58*** and divinylphosphinesulfide ***14*** (green line)

All of the diferrocene derivatives synthesized to this point are chiral and potential ligands capable of coordinating metal centers as a chelate and fencing them chirally.

Hence, these compounds have been tested for asymmetric induction in two transition metal catalyzed benchmarking reactions: Pd(II)-catalyzed asymmetric allylic alkylation and Rh(I)-catalyzed asymmetric 1,4-arylation of enones. The results are presented in more detail in section 3.5.

While moderate enantioinduction was observed, it became clear that the unrestrained diferrocenylphosphines have to be made more rigid best by cyclization to produce more reliable asymmetric inductors.

When looking at diaminophosphines ***6***, ***11***, ***13*** and divinylphosphines ***8***, ***12***, ***14*** produced in scheme 41 above, there are in principle two ways of cyclization: Either via connecting side chains or via twofold CH functionalization ortho to P.

Regarding the latter, Togni *et al.* inserted a carbonyl group by a Friedel-Crafts like reaction using diethylcarbonate. Subsequent reduction of the ketone by $LiAlH_4$ produced a methylene bridged diferrocenyl cycle [61].

For this project, the former possibility of transforming the side chains was chosen.

The reactivity of diaminophosphine ***6*** was investigated by derivatization reactions with BH_3 [83] and MeI [84] according to literature. Scheme 42 sums up the findings. While the starting material provides three atoms offering lone pairs, both reactions showed only single-site reactivity of the starting material.

Methylation of diaminophosphine ***6*** by MeI in dry MeCN and subsequent precipitation by Et_2O addition yielded the phosphonium salt ***16*** quantitatively as confirmed by ^{31}P-NMR and HRMS.

Boranation of diaminophosphine ***6*** by BH_3 • THF in THF abs. in an inert atmosphere, on the other hand, preferentially yielded 45% of the aminoborane ***15*** along with traces of the expected phosphinoborane ***17*** contrary to chemical intuition. Also, only one of the two amine groups has been boranated.

In order to distinguish the two ferrocene substituents, a Re/Si nomenclature was employed for the purposes of this project. Fig. 7 shows an example. Employing the Newman projection, phosphorous and its other three substituents determine the site of the ferrocene unit in question according to Cahn-Ingold-Prelog rules. This system was constructed in analogy to Re/Si carbonyl sites in relation to an attacking nucleophile.

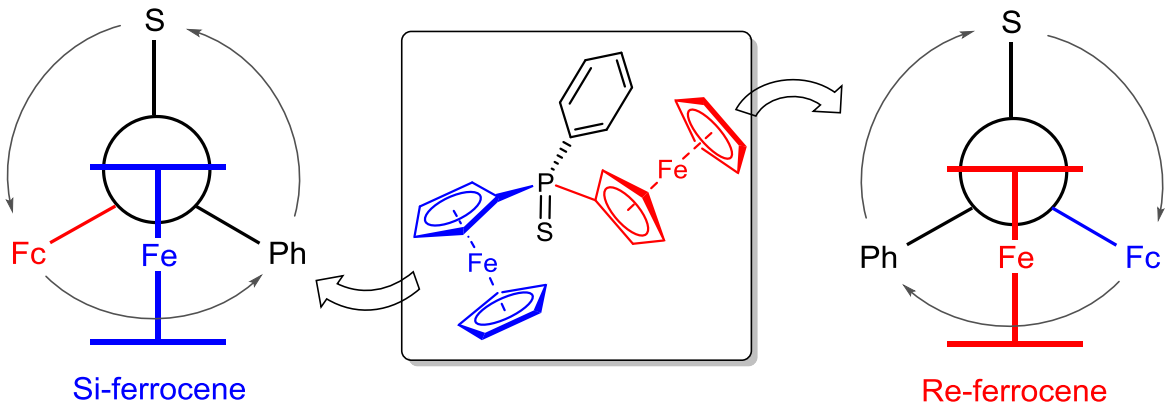


Fig. 7: Illustration of the Re/Si nomenclature applied to diferrocenylphenylphosphinesulfide

The site of boranation could be preliminary determined to be the ferrocene substituted to the Re-site. This could be deduced by comparison with spectra of asymmetric compounds synthesized at a later point in the project. If amine ***1*** of the

opposite configuration had been used as starting material, the more reactive site would be the Si-ferrocene side chain.

Fig. 8 presents crystal structures of diaminophosphine ***6***. Employing Re/Si nomenclature, it becomes obvious that the unreactive Si-site is shielded by the phenyl ring. The reactive Re-site, on the other hand, is located at the lone pair site of the phosphorous and hence more accessible.

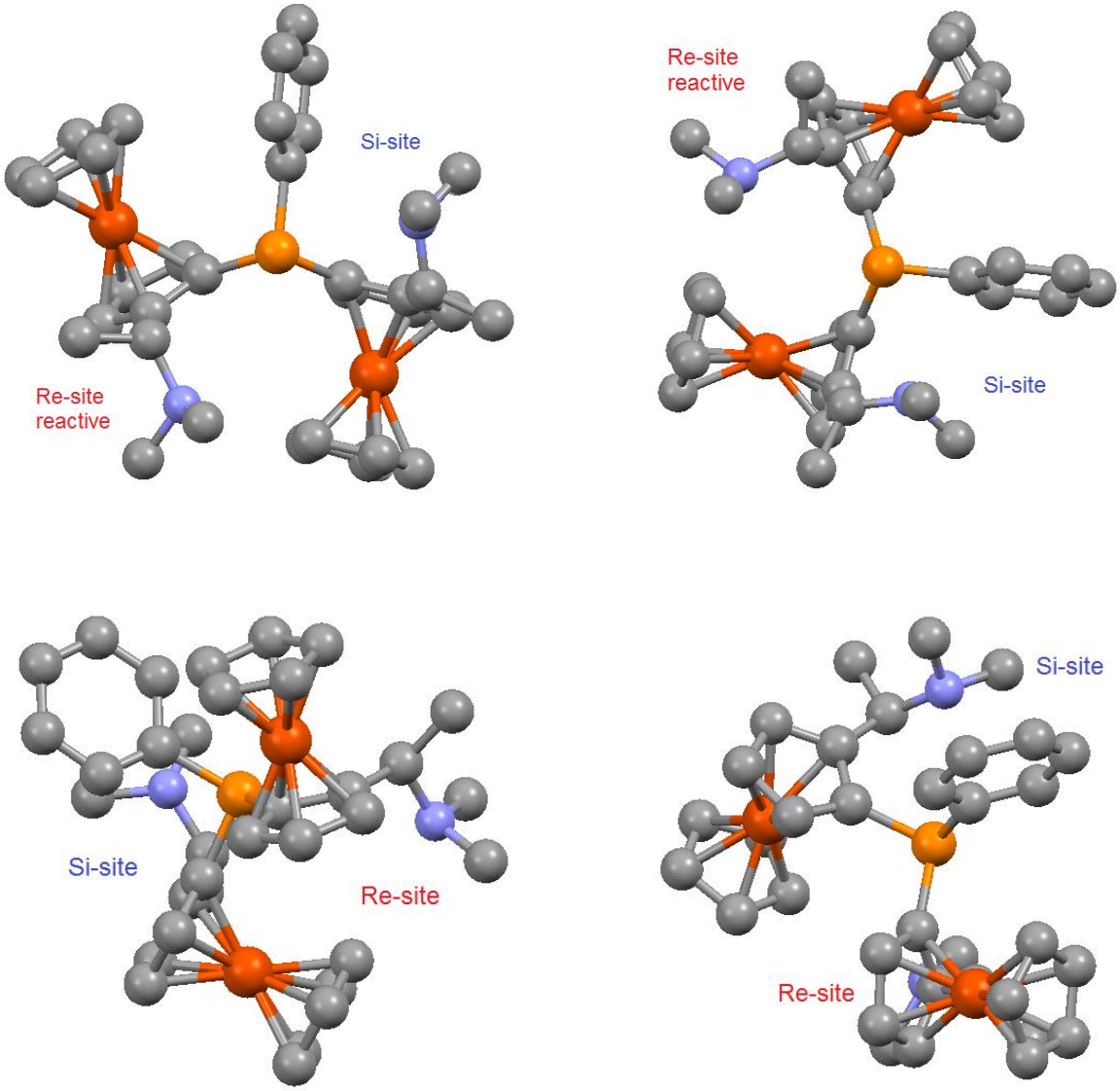
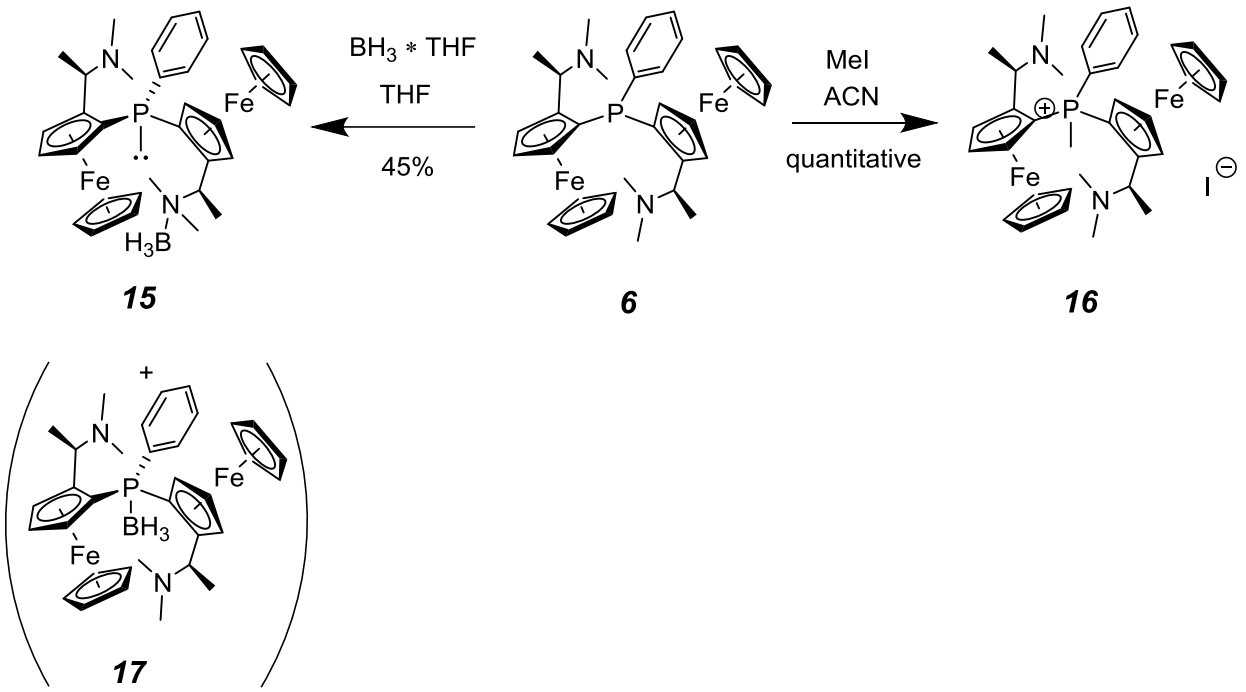


Fig. 8: Re- and Si-sites of diaminophosphine ***6*** presented by an X-ray recording performed by Togni *et al.*

While this synthetic branch was not pursued due to the limited scope of this project, this method of desymmetrization allows for a variety of interesting chemical transformations diversifying the two ferrocenyl moieties. Some of the many

possibilities of how to transform ferrocenylethylamines are highlighted in the following subsections in more detail. BH_3 bound to phosphines can be removed by BH_3 exchange to better acceptors, usually secondary amines such as Cy_2NH in MeOH under reflux [83].



Scheme 42: Chemoselectivities of methylation and boranation of diaminophosphine ***6***

3. 2. 2. Cyclization of di(vinylferrocene) phosphines

Divinylphosphines ***8***, ***12*** and ***14*** were tested for cyclization to produce a chemically and conformationally stable all-C backbone diferrocenyl cycle. One option immediately obvious for this kind of starting material seemed olefin RCM.

3. 2. 2. a. Olefin RCM

An olefin RCM is not always compatible with a given starting material due to the sterically demanding catalyst scaffolds. However, several publications point out that olefin metathesis point out that olefin metathesis works for allylferrocenes [85] [86] [87] [88] and even vinylferrocenes [89] [90] employing Grubbs or Schrock-type catalysts. RCM of the diphenyl analogues has been successfully carried out in published literature [91].

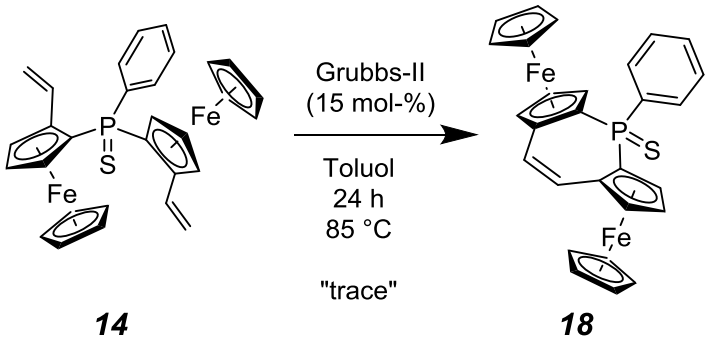
In case of the divinyl starting material ***8***, P-coordination to the Ru(II) metal center may be a concern, as amines are known to coordinate to Ru thus blocking catalyst activity. A number of exceptions is known [92] [93]:

- Quaternary/protonated amines
- EWG substituted amines such as amides and carbamates
- Amines β-substituted with an EWG
- N bound to a quaternary C
- Sterically crowded tertiary amines
- Arylic amines
- Alkoxyamines
- Aminoboranes

However, for divinylphosphineoxide ***12*** and phosphinesulfide ***14*** this should not be a concern.

Disappointingly, using divinylphosphine ***8***, phosphineoxide ***12*** and phosphinesulfide ***14***, 10 mol-% of Grubbs 1st or 2nd generation catalysts, dry DCM or toluene as solvents and r.t. or 90 °C in a flame-dried Schlenck tube under Ar no cyclized product was found after 24 h of reaction. Instead, starting material has been recovered. Employing a syringe pump to add the catalyst in a more controlled manner did not improve results.

As scheme 43 sums up, merely for divinylphosphinesulfide ***14*** a trace of the expected RCM product was detected by HRMS in one experiment. Since non-fragmenting mass spectroscopy such as ESI employed throughout this project does not provide constitutional information it cannot be definitely confirmed that the cycle ***18*** has formed.



14 ***18***

Scheme 43: Attempted RCM of divinylphosphinesulfide ***14***. Only traces could be found by HRMS analysis of the crude mixture.

The lack of reactivity can be rationalized from the crystal structure of divinylphosphinesulfide ***14*** shown in fig. 9 below. The targeted vinyl groups are sterically blocked by the ferrocene moieties. If the solid state conformation is also representative for the preferred conformations of this molecule in solution, the vinyl moieties are pointing away from each other and an intramolecular RCM is disfavored.

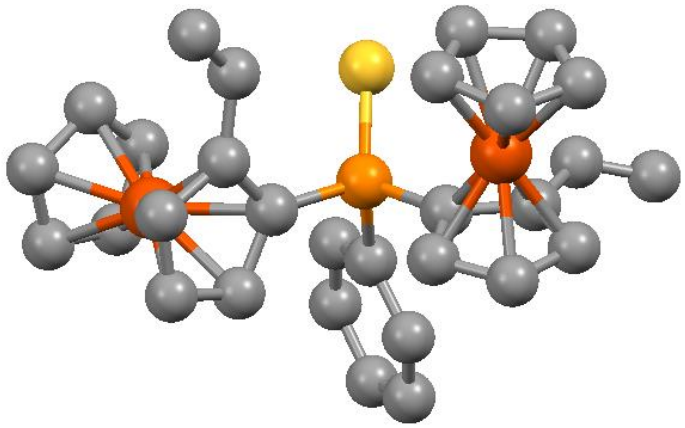
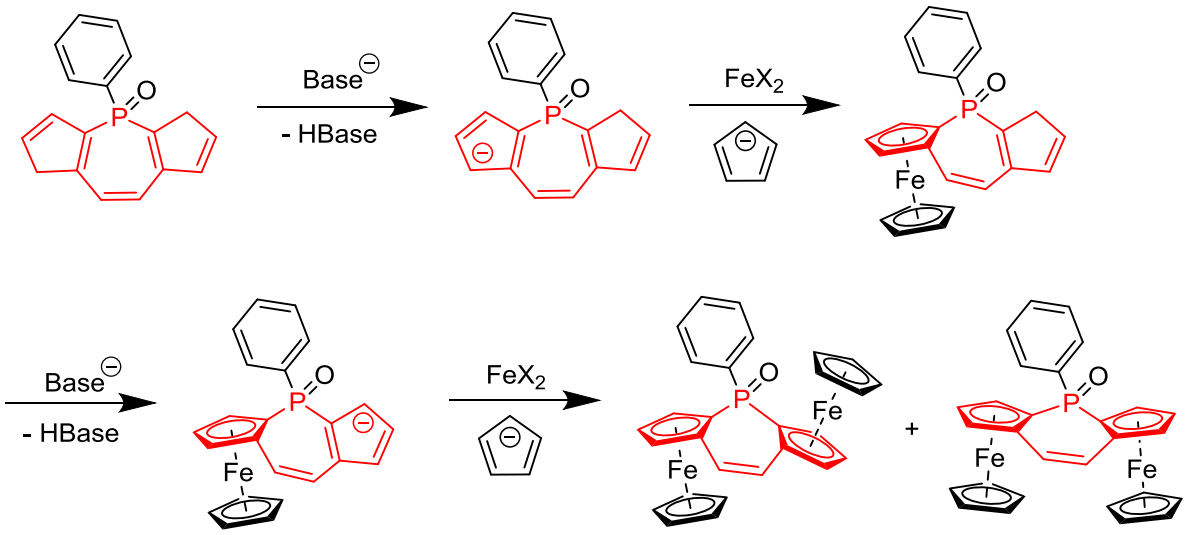


Fig. 9: Three-dimensional structure of divinylphosphinesulfide ***14*** based on X-ray crystallography.

From this it was concluded that diferrocenyl cycles of type ***18*** are not accessible in any meaningful yield by the chosen synthetic route. However, such compounds may still be available by taking an entirely different preparative approach presented in scheme 44.

Instead of starting with complete ferrocene moieties, one could start from the planar biscyclopentadiene system and complete the ferrocene units subsequently, perhaps

ending up with a *cis*/*trans* diferrocene mixture. This approach was successfully implemented by other groups working on similar diferrocenyl cycles [49] [50] [55].



Scheme 44: Proposed alternative synthesis of *Z*-1,2-ethylene bridged diferrocenylphosphines starting from the planar polycyclic core of the target molecule.

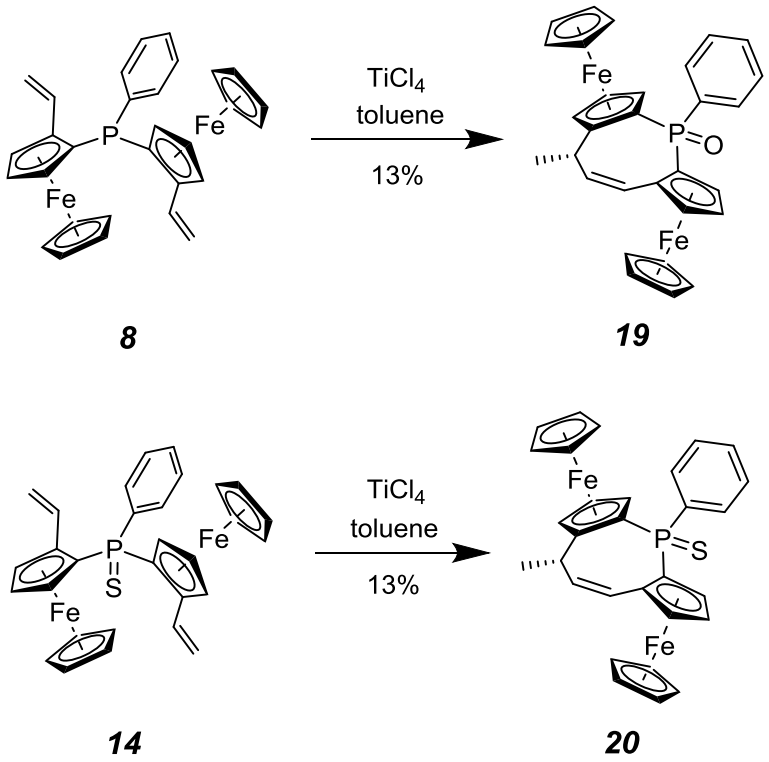
3. 2. 2. b. Divinyl coupling by hydrovinylation

An alternative coupling method of divinyl compounds uses hydrovinylation, in which one olefin group is activated and reacts with the other olefin moiety.

Inspired by radically driven *E*/*Z*-isomerizations and polymerizations of olefins, divinylphosphine ***8*** and phosphineoxide ***12*** were each heated in toluene under reflux in an inert atmosphere with a cat. amount of AIBN as radical starter. However, only starting material and, in case of ***8***, some P-oxidized product was recovered.

Alternatively, hydrovinylation was observed to work acid catalyzed for vinylferrocenes [48] [94] [95] [96]. Furthermore, it has been observed as an undesired reaction in an intended $TiCl_4$-promoted cyclization of a similar starting compound [80].

Scheme 45 summarizes the hydrovinylation cyclization experiments performed on divinylphosphine ***8*** and divinylphosphinesulfide ***14*** using 3 eq. of $TiCl_4$ in dry toluene. It was possible to yield 13% of both propylene-bridged diferrocenyl cycles ***19*** and ***20***, the former being isolated as a pure compound and characterized. Curiously, the harsh acidic environment lead to a quantitative oxidation of the phosphorous atom despite inert conditions applied.

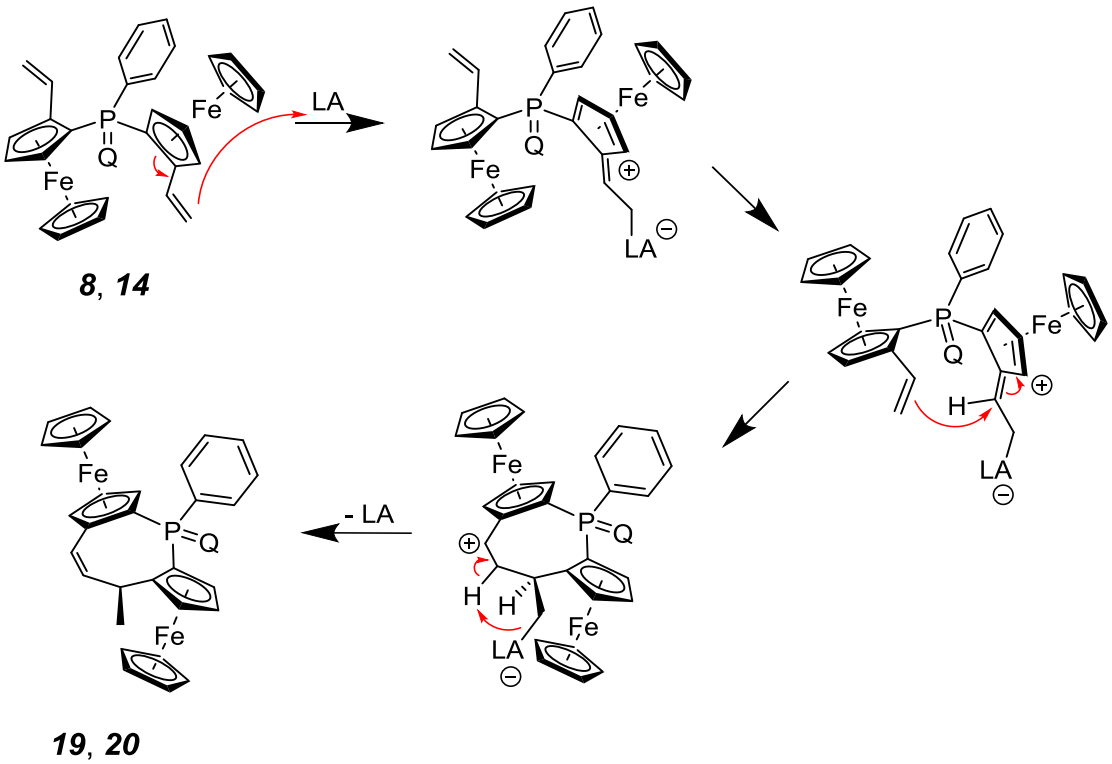


Scheme 45: $TiCl_4$ mediated intramolecular hydrovinylations. Note how P(III) is completely oxidized to P(V) oxide in the process.

Based on these findings, a reasonable mechanism was formulated as presented in scheme 46. The Ti(IV)-based Lewis acid electrophilically attacks a vinyl moiety at the terminal C, inducing a fulvene-like carbenium cation stabilized by its quasi-benzylic position. This activated olefin is nucleophilically attacked by the more electron-rich other vinyl group.

Concerning the regioselectivity, the attacking vinyl will form the C-C bond with its terminal C to locate the cationic charge quasi-benzylically. Concerning the stereoselectivity, the attacking vinyl will approach the cationic vinyl from the side not blocked by the sterically demanding CpFe-substituent. This prediction is based on information discovered about the retentive S_N1 reaction of ferrocenyl-substituted C atoms [68].

The positive charge located on the newly formed diferrocenyl cycle is depleted by elimination of a proton and formation of an olefin. Simultaneously or at another point in time, the Ti-C bond is cleaved by protonolysis.



Scheme 46: Hypothetical reaction mechanism of the intramolecular hydrovinylation of divinyldiferrocenes with $TiCl_4$ as a Lewis acid (LA).

Many methods are available for carbonyl-carbonyl coupling such as Pinacol or McMurry coupling [97] or oxidation, ester formation and consecutive acyloin condensation or imide formation. Due to time limitation of the project, this synthetic route was not investigated.

3. 2. 3. Cyclization of di(ferrocenylethylamine) phosphines

Other than relying on divinylphosphines, diaminophosphine compounds ***6***, ***11*** and ***13*** were used in ring closing steps. According to retrosynthetic consideration these precursors can be expected to form cycles incorporating hetero atoms, producing potential bidental ligands.

3. 2. 3. a. Non-activated dimethylamines

Due to the simplicity of the experiments, cyclization of ***6*** by direct reaction with bidentate nucleophiles was attempted first.

Diaminophosphine ***6*** was stirred either with 1 eq of NaHS • H_2O or 1 eq of $BnNH_2$ in a mixture of MeCN and DCM for 6 d, then in DMF for 60 h at r.t. and for 7 h at 100 °C under Ar. Product formation was not observed in any case and starting materials were regained by column chromatography.

Hence other avenues of activating the stable dimethylamine functional groups had to be taken; in published literature, methods to transform ferrocenylmethylamines belong mostly to one of four processes:

- Nucleophilic substitution of the quasi-benzylic amine catalyzed by AcOH; this method is used almost exclusively for mono- or di-substituted phosphanes R_2PH and RPH_2 as nucleophiles. For example, Togni *et al* used this route of cyclization for diaminophosphine ***6*** [61]. While interesting in case of more sophisticated nucleophiles, such as diphosphanes, this approach fails for most other nucleophiles and was hence not attempted. This is explained in more detail in section 3.3.
- Oxidation of the aminomethylene group by MnO_2 to a carbonyl.
- Displacement of the amine by an acetoxy group employing Ac_2O
- Alkylation of the tertiary amine forming an ammonium salt as a leaving group for subsequent nucleophilic substitutions.

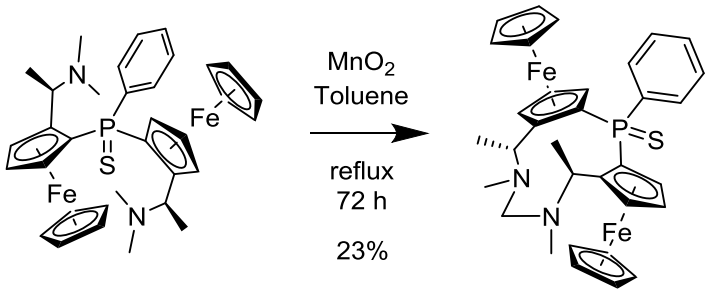
3. 2. 3. b. Mn(IV)-mediated oxidation

Diamino compounds ***6***, ***11*** and ***13*** may be starting materials for synthetically valuable corresponding bis(methylketones). These in turn could undergo a variety of coupling reactions as pointed out in the retrosynthetic analysis shown in scheme 39. This oxidation of aminomethylferrocenes can be performed using activated MnO_2 as a oxidant [98].

In case of diaminophosphine ***6***, starting material was recovered even after 72 h of continuous heating of the suspension in toluene at reflux. Diaminophosphineoxide ***11*** decomposed completely in the process.

For phosphinesulfide ***13***, 23% of a single product ***21*** was discovered (Scheme 47). After thorough study of NMR and mass spectra, the product was determined to possess an unexpected formaldehydeaminal diferrocenyl cycle structure.

The ring closing might have been formed by the radical nature of the MnO_2 oxidation process [99]. Only one instance of regioselective MnO_2-mediated oxidation of a C bound to a quasi-benzylically substituted N has been reported in literature [100].



13 ***21***

Scheme 47: MnO_2-mediated oxidation of diaminophosphinesulfide ***13*** resulting in an unexpected macrocyclic aminal ***21*** after a formal loss of methane.

It can thus be concluded that diferrocenyldiamines are too stable and/or too sterically hindered for this oxidation method. Other homogenous oxidation protocols of quasi-benzylic C's such as using $KMnO_4$ as an oxidant have not been carried out.

3. 2. 3. c. Acetoxy substitution

Dimethylamino groups can be replaced by acetoxy substituents which are far more reactive leaving groups. It has been observed in the twofold elimination of diaminophosphine ***6*** that such acetoxy derivatives are intermediates in the formation of divinyl compound ***8***.

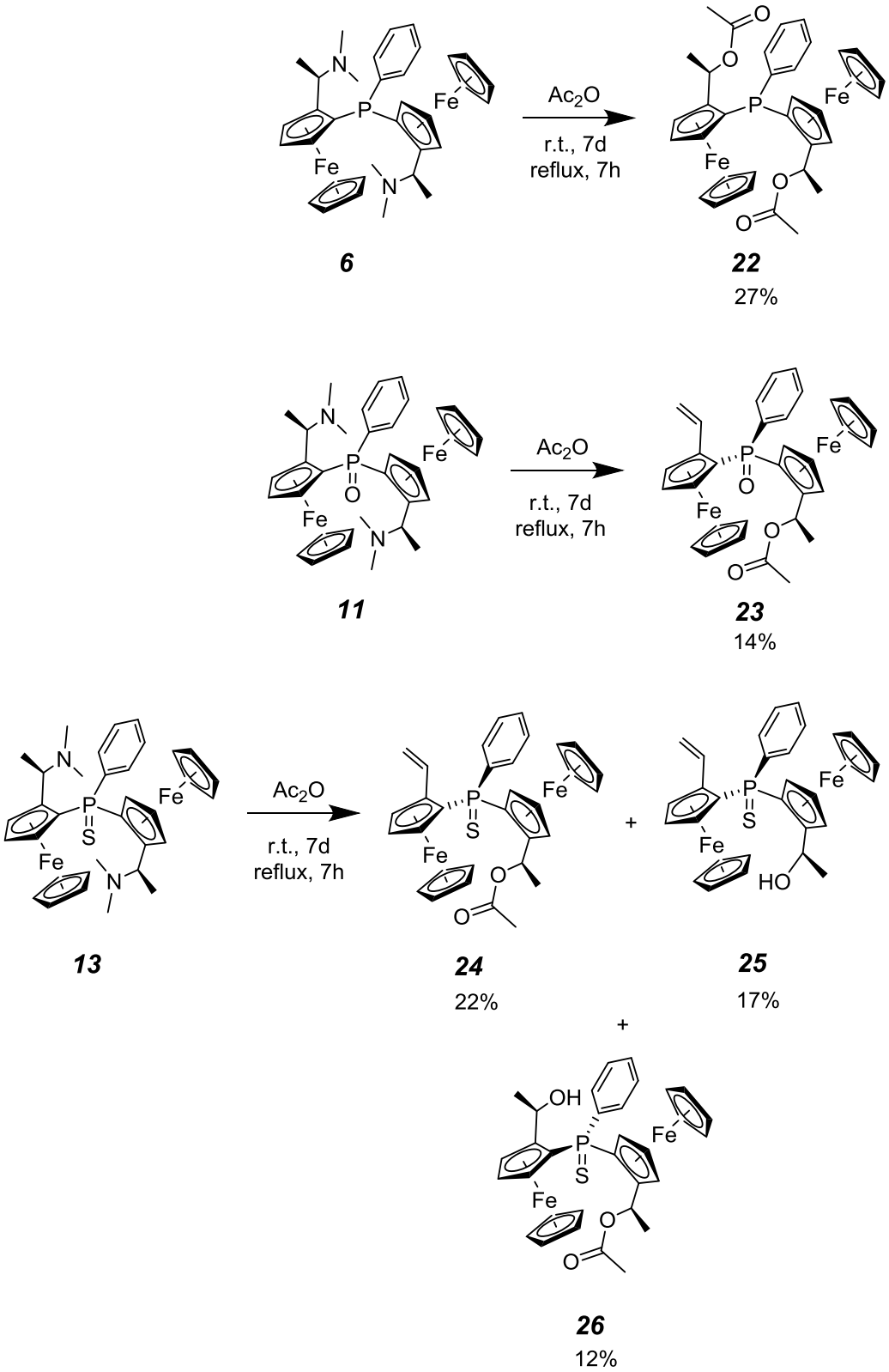
Several protocols have been developed for this chemical reaction [101] [102] [103] [104]. When attempting to synthesize the diacetoxy analogs of diaminophosphines ***6***, ***11*** and ***13*** at various temperatures (0 °C, at r.t. or reflux, in Ac_2O, in AcOH or in a mixture of Ac_2O and AcOH) at different reaction times, either no product formation was observed or mixed monoacetatemonovinyl compounds and small amounts of the intended diacetates not useful for cyclization attempts.

Therefore the plan of using diacetates as precursors for diferrocenyl cycles was abandoned. Instead, the non-symmetric products observed might form a great starting point for an extensive ligand library of di- or tridentate ligands. The resulting acetoxy substituents can be replaced by many heteroatom nucleophiles containing

O, N, P or S. Hence the synthesis of a multitude of mixed dimethylamine-, acetoxy-, hydroxy- and vinyl substituted diferrocene compounds was attempted.

Diamines ***6***, ***11*** and ***13*** were stirred for 7 d at r.t. and 7 h at about 100 °C under Ar. At this stage TLC tests showed several products in each reaction entry. Separation of the formed half to a dozen products yielded several mixtures as well as some pure products most of which crystallized effortlessly.

Scheme 48 summarizes the identified products. The cumbersome and time-consuming purification of the remaining mixtures was abandoned at this point due to not addressing the intended goal of this project.



Scheme 48: Acetoxylation of diaminophosphine ***6***, diaminophosphineoxide ***11*** and diaminophosphinesulfide ***13***. The scheme depicts only pure, isolated products. Several other species have been detected which could not be purified sufficiently for structure elucidation.

In four cases, structures could be confirmed by X-ray structure analysis, summarized in fig. 10.

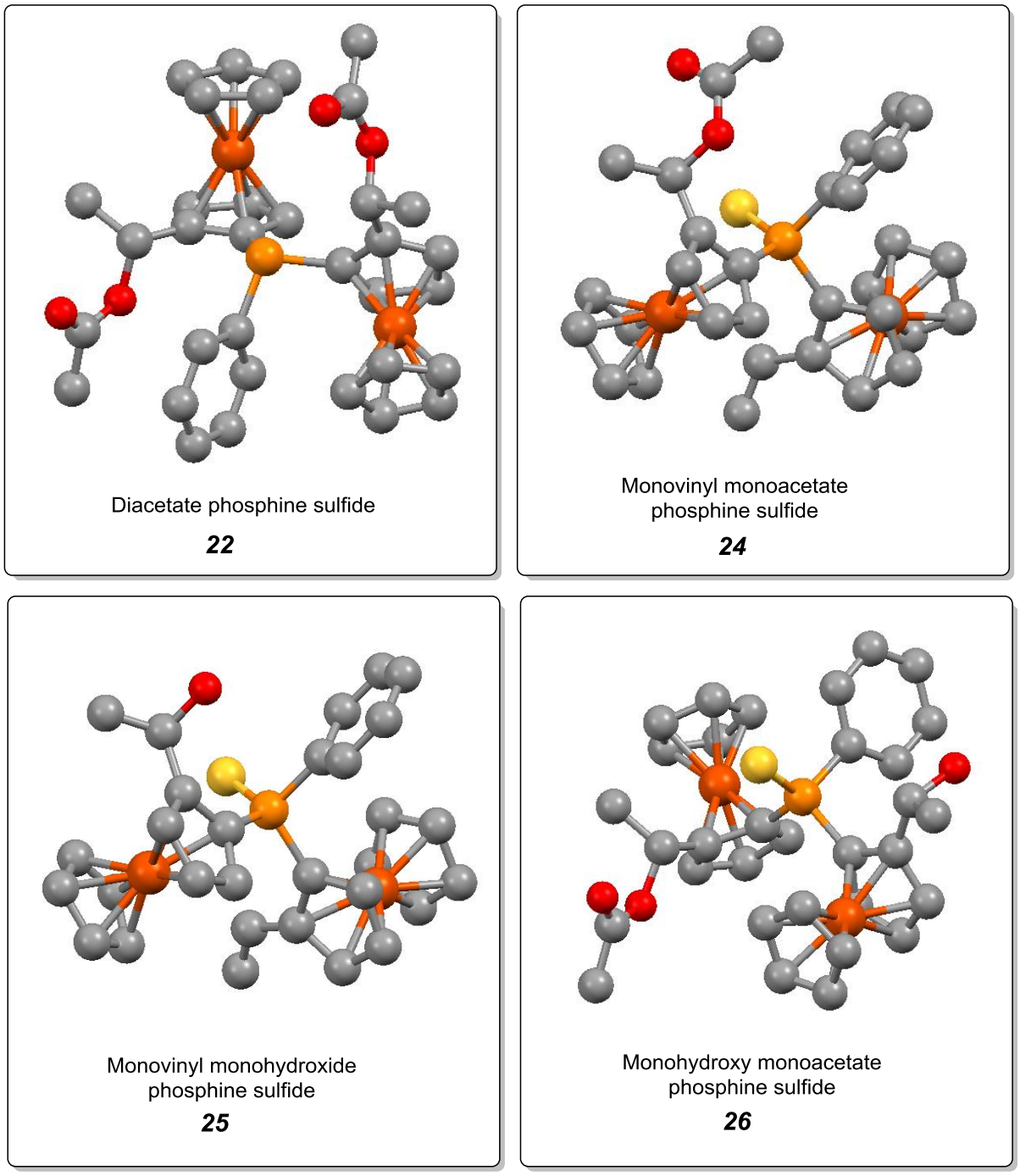


Fig. 10: Three-dimensional molecular structures obtained by X-ray crystallography.

Fig. 11 below compares the NMR spectra of monovinylmonoacetates ***9***, ***23*** and ***24***, demonstrating not unexpected pronounced similarities.

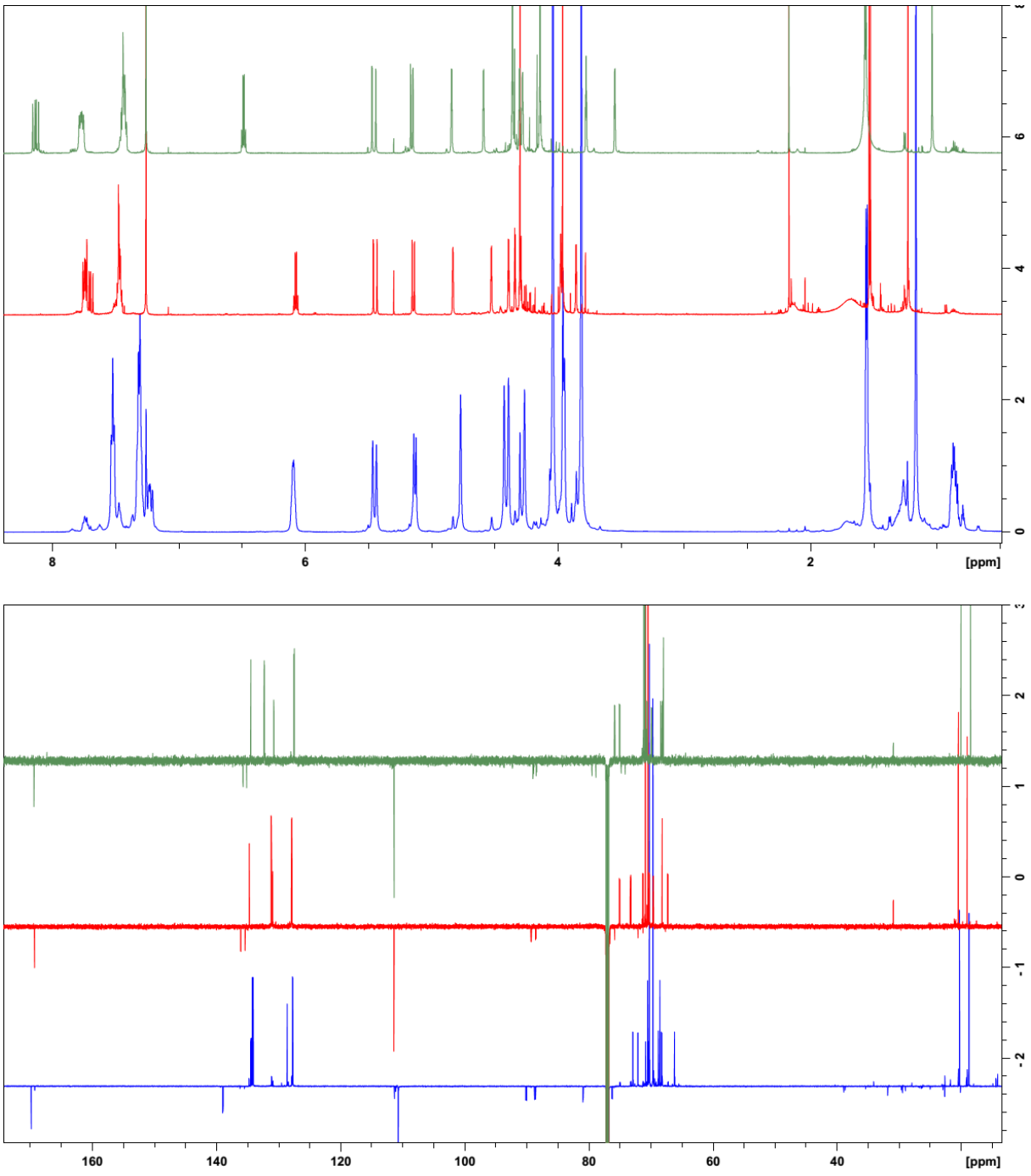


Fig. 11: ^{1}H-NMR (above) and ^{13}C-NMR (below) spectra of monovinylmonoacetatephosphine ***9*** (blue line), phosphineoxide ***23*** (red line) and phosphinesulfide ***24*** (green line)

One peculiar signal first occurring in ^{1}H-NMR spectra of divinylphosphines ***8***, ***12*** and ***14*** in fig. 6 and recurring in these spectra is a vinyl proton chemically shifted far downfield typical for phenylic protons and even beyond.

Complementary X-ray diffraction experiments of monovinylmonoacetatephosphinesulfide ***24*** shown in fig. 12 allowed for the identification of the proton in question. This proton is the internal vinyl H of the

ferrocene moiety bound to the Re site of the diferrocenylphosphine compounds in respect to the other three P substituents. The reason for this downfield shift could be conjectured to be caused by an interaction with the spatially proximate S – internuclear distance = 2.862 - 2.873 Å measured by X-ray crystallography –, perhaps in conjunction with the vinylogous α-acidic position regarding the phosphinesulfide functional group.

This isolated proton signal would make an excellent monitor proton in any future kinetic experiments involving mono- or divinylferrocene compounds of this class.

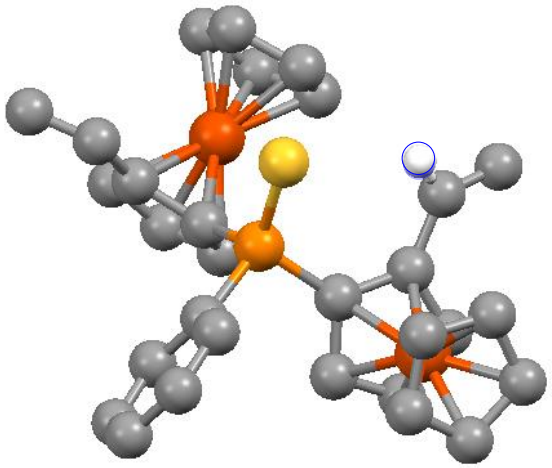


Fig. 12: X-ray structure of divinylphosphinesulfide ***14***. The strongly shifted vinyl proton is marked blue.

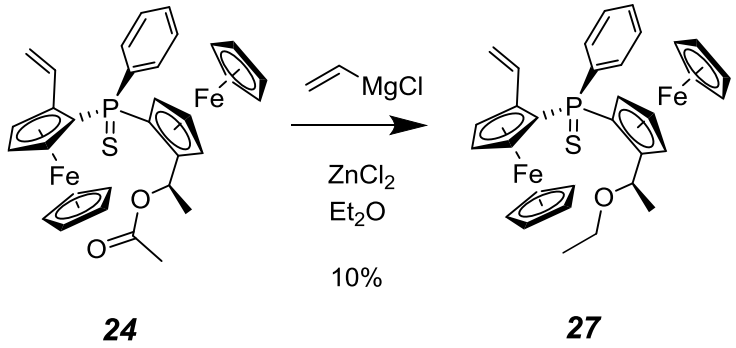
This down-field proton was observed in every mono-elimination of this class of diferrocenylphosphine compounds. The absolute configuration of monovinylmonoacetatephosphinesulfide ***24*** being elucidated by X-ray diffractometry, it can be conjectured preliminarily that the Re-site of the diferrocene compounds used is more reactive, indicating this site may be more accessible.

This also nicely agrees with the fact that the diaminophosphine ***6*** is more reactive at the Re-site ferrocene. This allows for a greater control in designing future asymmetric compounds.

The products obtained by acetoxy substitution may still be synthetically useful. One publication reporting the synthesis of all-C bridged ansa-ferrocenes presents a C-C bond forming reaction promoted by $ZnCl_2$. An acetate leaving group is substituted with a vinyl group added as vinyl MgCl at the quasi-benzylic C [105].

Hence, diolefins may be synthesized from monovinylmonoacetatephosphine ***9***, diacetatephosphine ***22***, monovinylmonoacetatephosphineoxide ***23*** or monovinylmonoacetatephosphinesulfide ***24*** available for RCM due to the larger ring or else available for hydrovinylation.

Reaction of either diferrocenyl compound ***9***, ***22*** or ***23*** with a suspension formed by $ZnCl_2$ and vinyl MgCl in dry Et_2O under Ar yielded no desired product but returned starting material or divinyl compounds resulting from AcOH being eliminated. Solely attempted vinyl substitution of monovinylmonoacetatephosphinesulfide ***24*** yielded 10% of an unexpected compound suggested as the corresponding ethoxyether ***27*** shown in scheme 49.



Scheme 49: Unexpected ethoxylation of monovinylmonoacetatephosphinesulfide ***24***

3. 2. 3. d. Ammonium iodide salt formation

Since diaminophosphine ***6*** yielded no usable ammonium salt, ammonium iodide salts of phosphineoxide ***11*** and sulfide ***13*** were next investigated. According to published literature MeI was added to a solution of ***11*** or ***13*** in dry MeCN/DCM followed by addition of Et_2O [25].

Instead of the anticipated diammonium salts, only single methylation was observed in both cases by HRMS despite of employing a large excess of MeI. However, in published literature, cases of bidentate nucleophiles replacing a dimethylammonium group connecting two C's have been studied [60] [106].

This kind of reactions could conceivably take place in the following way. In a first step, the nucleophile displaces the ammonium group on C number one. In the subsequent step, the now monodentate nucleophile displaces dimethylamine – formerly dimethylammonium – on C number two intramolecularly. Overall, this way

bidentate nucleophile bridges can displace dimethylammonium bridges in a one-pot reaction.

This situation is similar for monoammonium salts ***32*** and ***33***. Hence these compounds might work as well in cyclization despite earlier findings of dimethylamines being inert to simple intermolecular nucleophilic displacement. The salts produced were used without further purification despite NMR and MS data being ambiguous about the purity of the salts.

Cyclizations were attempted using diaminophosphineoxide salt ***32*** and sulfide salt ***33*** both with 1 eq of NaHS • H_2O as a source of S in water [106] and with 1 eq of $BnNH_2$ as a source of N in MeCN [60] using established ammonium substitution procedures.

After 3 h of heating under Ar, the four intended cyclized products were detected in the crude mixture by HRMS. However, after purification by column chromatography on SiO_2, none of the diferrocenyl cycles was recovered. Instead, monovinylmonohydroxyphosphines and monovinylmono(diamine)phosphines were isolated as decomposition products. While these compounds are still interesting as asymmetric precursors, the cyclization procedure had to be adapted to keep the intended diferrocenyl cycles intact.

Thus, ammonium iodide salts ***32*** and ***33*** and either 1 eq of NaHS • H_2O or 1 eq of $BnNH_2$ were dissolved in DMF and heated in a microwave oven for better efficiency. The crude mixture was purified by column chromatography using the non acidic sorbens Al_2O_3 instead of SiO_2, yielding hetero atom containing diferrocenyl cycles ***29***, ***30***, ***35*** and ***36*** as pure products albeit in poor yields of 11%, 12%, 14% and 15%, respectively. Scheme 50 pictures the reactions carried out.

Also, in case of the benzylic amine diferrocenyl cycles, the cleaved products containing a vinyl group at the Re-site ferrocene and a side chain bearing a benzylic amine were isolated and characterized. In case of the phosphinesulfide, crystals formed and the structure was determined by X-ray crystallography (fig. 13). A distance between the two phenyl rings of about 4.40 Å was found.

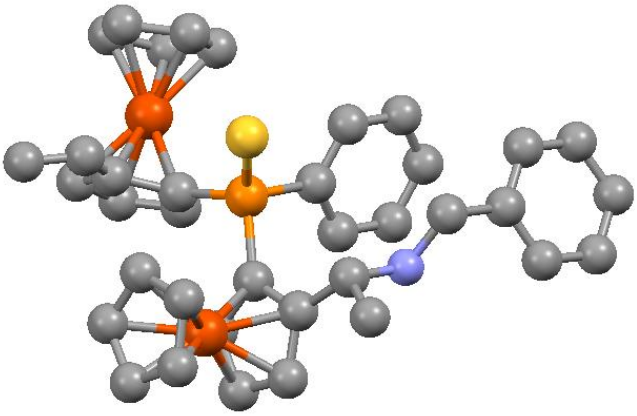


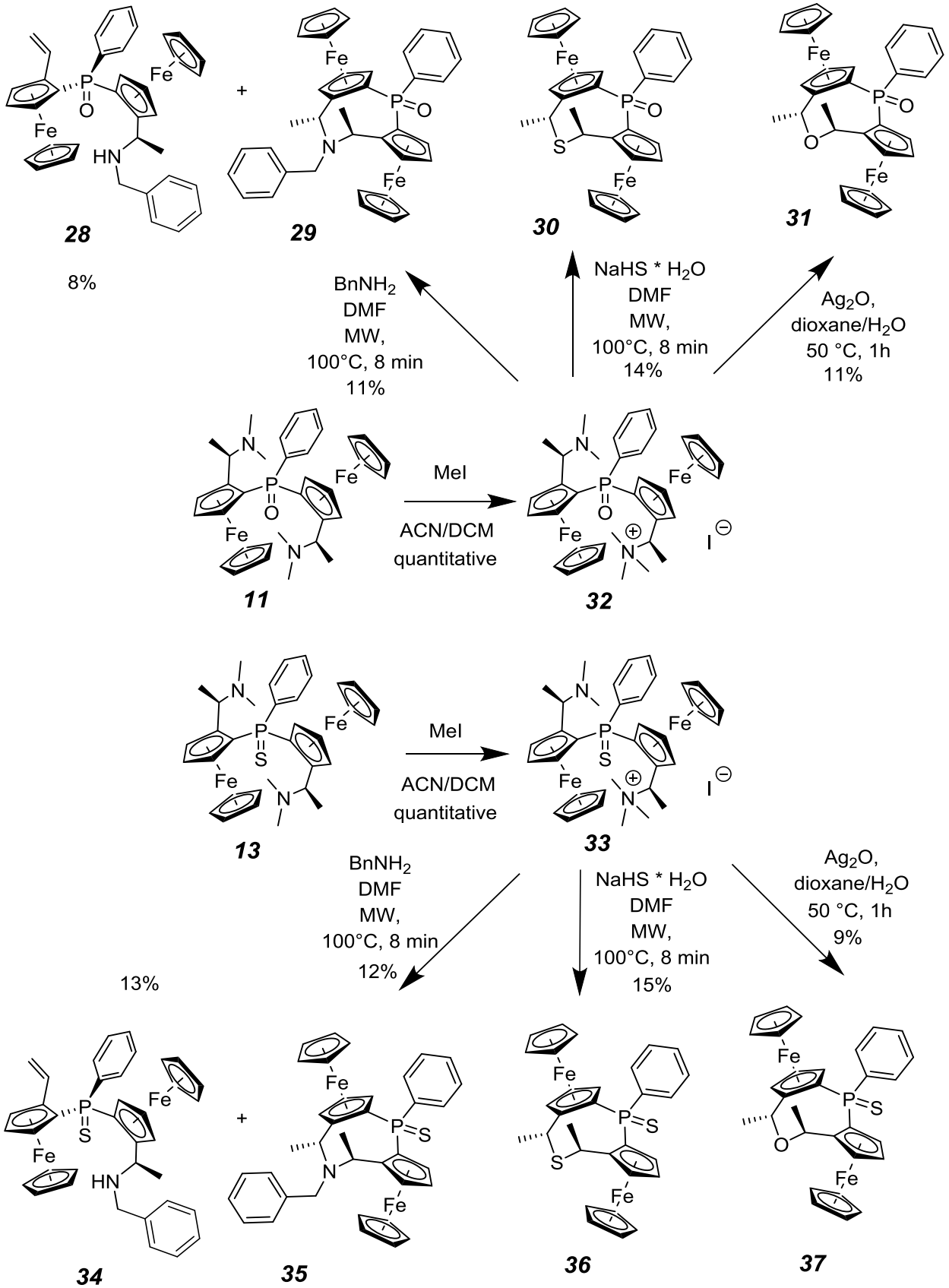
Fig. 13: X-ray structure of phosphinesulfide ***34***.

Hence the first amine containing diferrocenyl cycle prototypes ***29*** and ***35*** have been prepared. S containing diferrocenyl cycle prototypes ***30*** and ***36*** may be used either as a sulfide or, after mono-S-oxidation, as a sulfoxide as a ligand in transition metal catalysis, as an organocatalyst or as an asymmetric auxiliary in reactions dependent on sulfides or sulfoxides such as asymmetric Corey-Chaikovsky oxiranations / cyclopropanantions.

Since boranation of diaminophosphine ***6*** as well as mono elimination showed a strong regioselective preference for the Re-site ferrocene side chain, it is interesting as to whether methylation of diaminophosphineoxide ***11*** and diaminophosphinesulfide ***13*** shows the same Re-site regioselectivity.

Since the NMR spectra recorded of the salts in CD_2Cl_2 could not be interpreted, Hoffmann elimination using Ag_2O and warming to 50 °C for 1 h was carried out for both ammonium iodide salts ***32*** and ***33*** according to published procedure [107] in a water/dioxane mixture. The expected monovinylmono(diamine)phosphines may be used to determine the regioselectivity of methylation.

Surprisingly, in both cases the *O*-bridged diferrocenyl cycles ***31*** and ***37*** were formed instead of the anticipated mono-elimination products in yields of 11% and 9%, respectively. Apparently, the reaction of the ammonium salts with water was faster than the AgI formation driven salt metathesis from I^- to OH^- followed by amine elimination. These findings are summed up in scheme 50. Fig. 14 presents the ^{1}H-NMR and ^{13}C-NMR spectra recorded of the six novel diferrocenyl cycles.



Scheme 50: Mono-methylation of diaminophosphineoxide ***11*** and diaminophosphinesulfide ***13***. Cyclization of the resulting ammonium iodide salts forming ethers ***31*** and ***37***, benzylic amines ***29*** and ***35*** as well as thioethers ***30*** and ***36***.

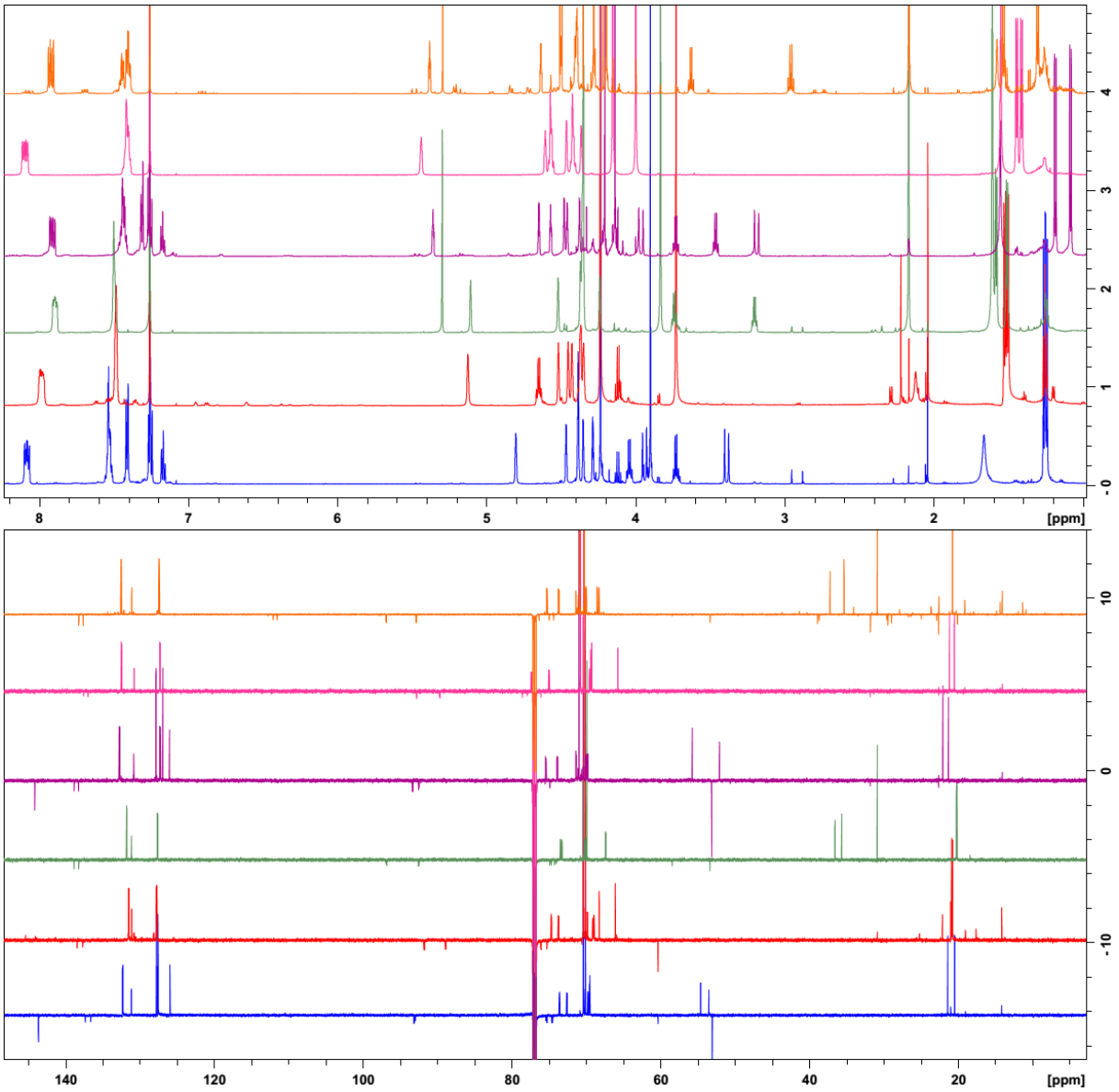


Fig. 14: ^{1}H-NMR (above) and ^{13}C-NMR (below) spectra of benzylic aminephosphineoxide ***29*** (blue line), etherphosphineoxide ***31*** (red line), thioetherphosphineoxide ***30*** (green line), benzylic aminephosphinesulfide ***35*** (purple line), etherphosphinesulfide ***37*** (pink line) and thioetherphosphinesulfide ***36*** (orange line) diferrocenyl cycles.

To summarize this section, these nine novel diferrocenyl cycles form the starting point for more specialized projects in future investigations of this class of compounds. There is a lot of screening left to do regarding the variability of ferrocene side chains, other phosphine substituents than Ph, other bidentate nucleophiles to be inserted in the backbone.

One of the most important questions left unanswered is variability of diferrocenyl cycles when carrying out a mono-lithiation ortho to P on one of the two ferrocene

building blocks. This way a great variety of functional groups may be introduced such as boronic acid, halogenides, sulfides, alkyl-, acyl-, aryl-, formyl-, silyl-, vinyl-, alkynyl-, nitryl-, nitrosyl-, phosphine and carboxyl groups, all of whom introduce greater asymmetry and/or other functional groups forming chelates in combination with phosphine.

Despite this promising outlook, these diferrocenyl cycles based on amine ***1*** suffer a crucial weakness. Elimination of the hetero atom bound to the ethyl side chain occurs easily and could not be supressed.

Therefore, structures analogous to those presented here but not prone to the above side reaction had to be devised. Two options pictured in chart 6 are:

a) Omitting the α-methyl groups

b) placing the hetero atom at C2 instead of C1 at ethylferrocene structural element thusly disfavoring elimination.

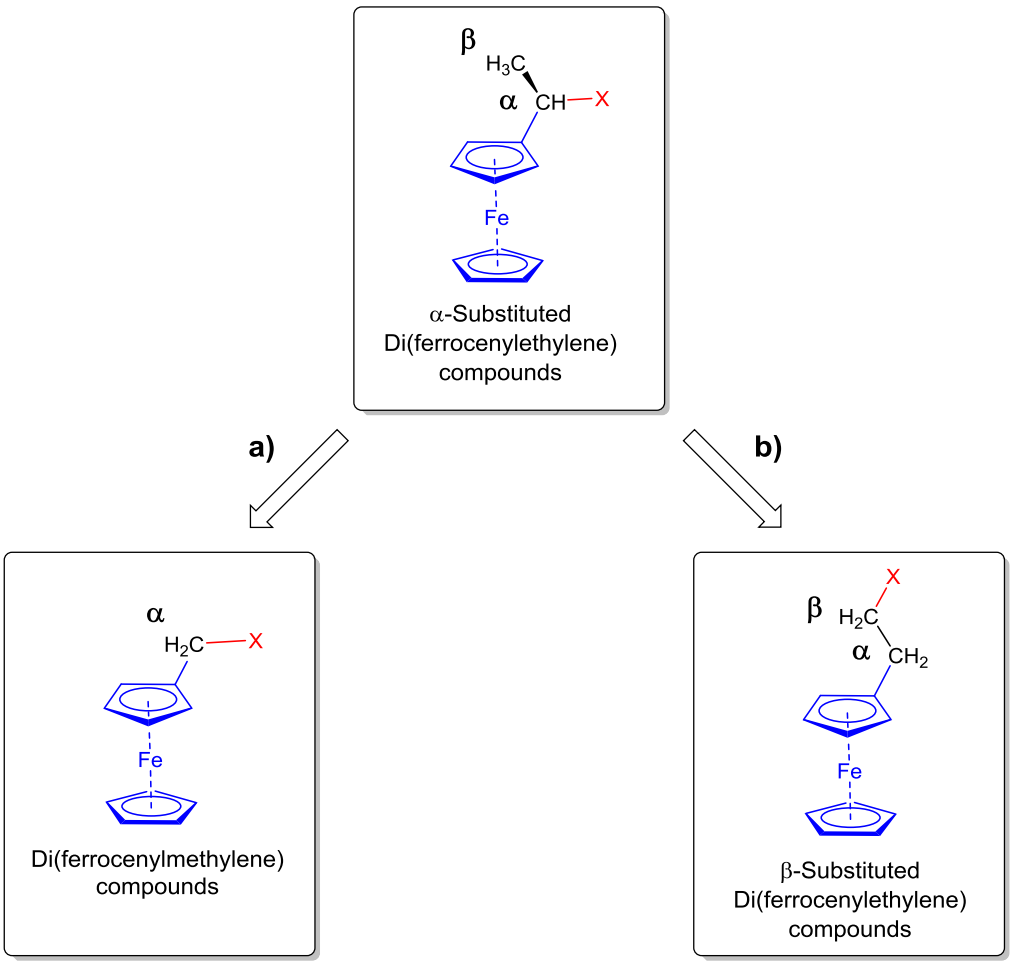


Chart 6: Changes in the design of the side chain substitution to disfavor heteroatom elimination

3. 3. Di(ferrocenylmethylene) compounds

While heteroatom containing diferrocenyl cycles ***29***, ***30***, ***31***, ***35***, ***36*** and ***37*** are promising prototypes for future synthesis and modification, previous synthetic experience pointed to lability inherent to the molecular structure used.

One way immediately obvious to solve this problem is to use unsubstituted CH_2 groups instead. This requires an enantiopure, chiral ferrocene precursor other than Ugi's amine. Scheme 51 presents a retrosynthetic analysis.

In order to synthesize a hetero atom containing diferrocenyl cycle ***VIII***, there are in general two major pathways: Either cyclizing a P-linked diferrocene precursor or a backbone linked one.

The intermediate ***XI*** may be synthesized by coupling of two ortho-lithiated ferrocenes ***VII*** with Cl_2PPh. The resulting diamine ***XI*** may be substituted by protonation catalyzed nucleophilic substitution. Else a leaving group may be created either by acetoxy substitution or by alkylation of the tertiary amine groups yielding either a diacetoxy precursor ***X*** or a diammonium precursor ***IX***.

On the other hand, the backbone-bridged diferrocenyl compound ***II*** could be produced in a similar fashion from using an already 2-brominated ferrocenemethylamine ***III*** bearing a chiral auxiliary. This synthesis can either be carried out by acid catalyzed nucleophilic substitution or by creating a suitable leaving group as mentioned above.

A number of chiral auxiliaries have been developed for the ferrocenylmethyl moiety. One possible auxiliary carrying chiral information is *N*-ephedrine as described by the group of Weissensteiner *et al.* [25]

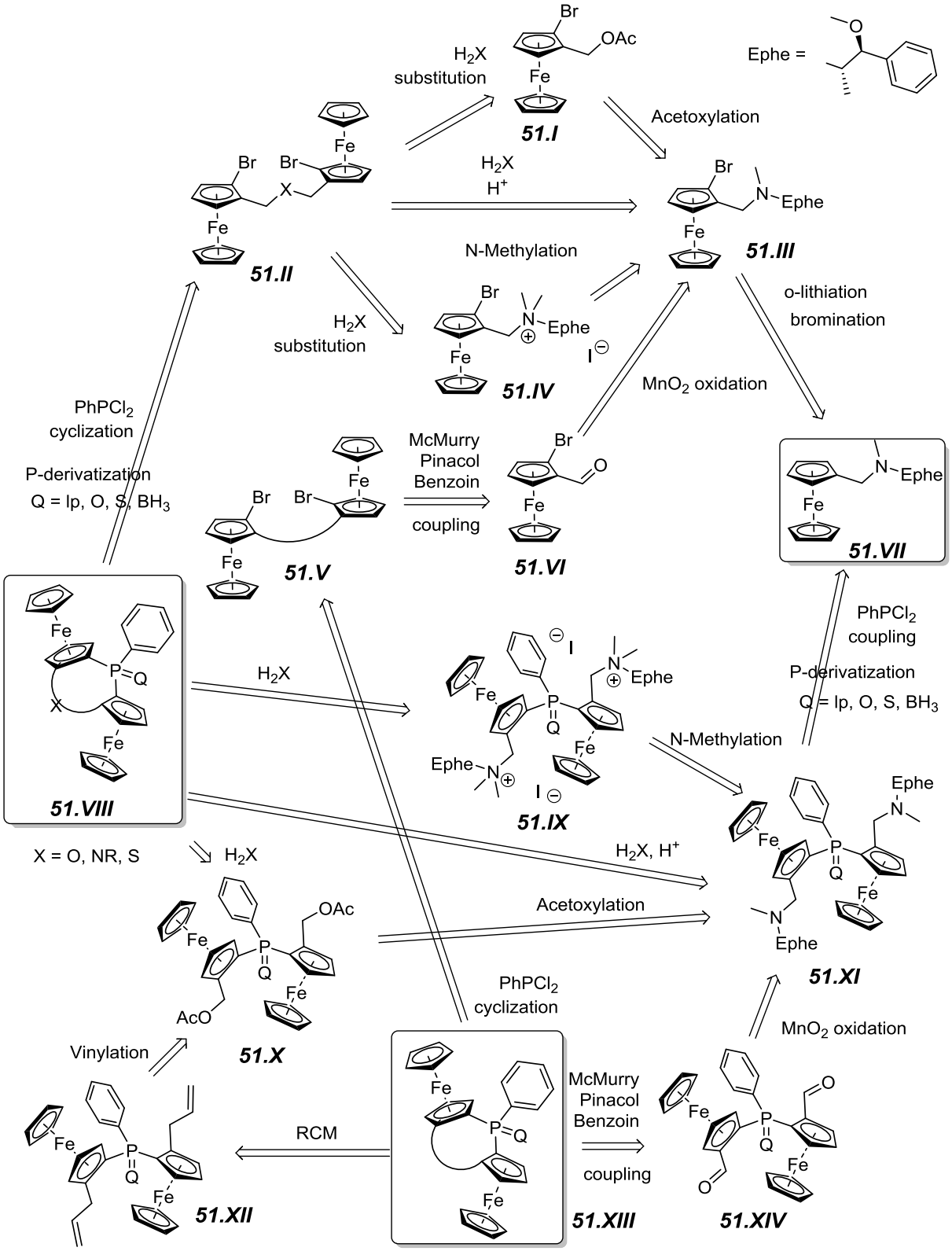
Other than Ugi's amine ***1*** which introduces centrochirality still persisting when replacing the amino group, enantioselective *o*-lithiation followed up by bromination is necessary for this molecule to direct future lithiations after removal of the ephedrine auxiliary.

The synthesis of a diferrocenyl cycle ***XIII*** containing an all-C backbone raises a similar question. Either the all-C backbone linked diferrocene ***V*** has to be synthesized, then cyclized or a P-linked diferrocene precursor ***XII*** / ***XIV*** is produced first, then the carbon-bridge is inserted.

In case of the former, the C-bridged bis-ortho brominated precursor ***V*** could be produced from ***V*** using various suitable olefin coupling protocols such as McMurry, Pinacol or Benzoin coupling. This compound ***VI*** may be available by MnO_2 mediated oxidation of the *o*-brominated amine precursor ***III***.

One possible P-linked diferrocene precursor ***XII*** bears two allyl functional groups to be closed by olefin RCM. This precursor may be available from the diacetoxy intermediate ***X*** by vinylation.

Another possible P-linked diferrocene precursor ***XIV*** carries two aldehyde groups to be coupled by various protocols. Molecule ***XIV*** in turn may be available by MnO_2 mediated oxidation of the P-linked diamine precursor ***XI*** or, as described above, by ammonium/acetate nucleophilic substitution of ***IX***, ***X*** or ***XI*** followed up by S oxidation and pummerer rearrangement.



Scheme 51: Retrosynthetic analysis: Formation of cyclized P-linked diferrocenes starting from ferrocenemethylephedrine ***51.VII***, corresponding to ***42***.

3. 3. 1. “Bridge-first” approach

Bridge-first linkage of methylferrocene was attempted first, enabling the introduction of various hetero atoms or entire functional groups in order to yield diferrocenyl cycles at the end of the synthetic route.

Scheme 52 presents the synthesis of N- and S linked di(ferrocenylmethylene) compounds. *N*-Ferrocenylmethylephedrine ***42*** was regioselectively *o*-lithiated in dry *n*-pentane using *tert.*-BuLi then brominated according to published literature [25] yielding 86% of *o*-bromo derivative ***43***.

Instead of using 1,2-dibromotetrafluoroethane as an electrophile, which is a liquid at normal conditions, a dry THF solution of solid 1,2-dibromotetrachloroethane was employed since the former bromination agent is classified as a CFC and hence no longer commercially available.

1-Bromo-2-aminomethylferrocene ***43*** was activated by quaternation with MeI in dry MeCN to give 81% of compound ***44*** which precipitated upon adding Et_2O [25].

Connecting of two molecules ***44*** to N was attempted using 0.5 eq $BnNH_2$ as a bidentate nucleophile. Heating a solution of both reagents in benzene in an autoclave similar as described in the literature for $HNMe_2$ substitution of the same starting material ***44*** [25] resulted in decomposition of the starting material.

Thus the procedure was modified and ***44*** and 0.5 eq of $BnNH_2$ were were heated in benzene/DMF using a microwave oven. The desired diferrocenylamine ***46*** was isolated in 65% yield.

Repetition with an excess of $BnNH_2$ (10 eq) yielded secondary amine ***45*** in 90%. Monoferrocenylamine ***45*** was reacted with another eq of ***44*** to produce diferrocenylbenzylic amine ***46*** in better overall yield than the one-pot reaction. (87% over 2 steps vs. 65%).

Applying the same procedure for ammonium iodide salt ***44*** and 0.5 eq of $NaHS \bullet H_2O$ yielded diferrocenylthioether ***47*** albeit in poor yield (25%). Furthermore, one equivalent of hydrolyzed product ***48*** was isolated as a side product.

Interestingly, hydrolysis products of ammonium iodide salt ***44*** have not been detected during synthesis of benzylic amine derivatives ***45*** and ***46*** to the same extent. This raises the question as to whether initial sulfide substitution of the ammonium group

turns the molecule more prone to hydrolyzation the same way NaI is added as a catalyst in nucleophilic substitution reactions.

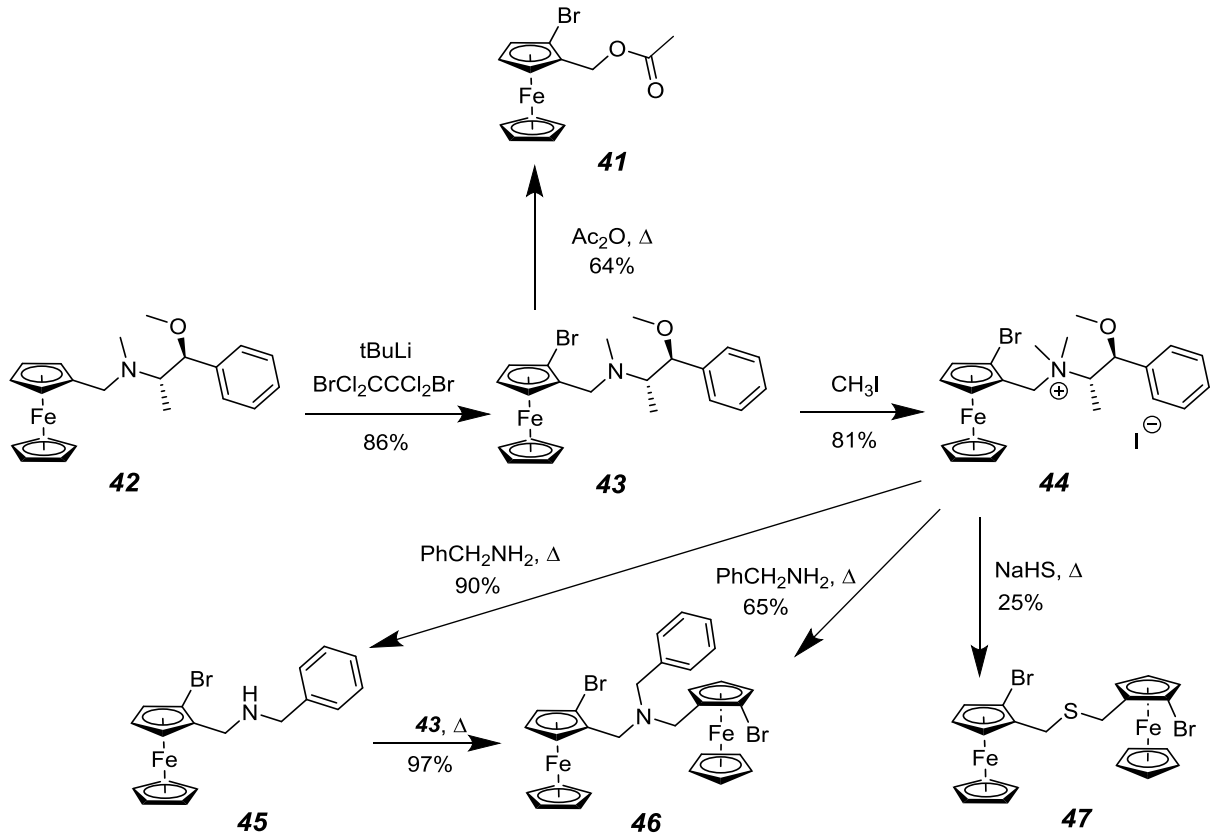
While still interesting as a chiral compound, it is clear that this procedure of synthesizing thioether ***47*** is to be optimized by using a dry source of sulfide in future synthesis.

Attempting the same optimization as in the benzylic amine analogue ***46***, ammonium iodide salt ***44*** and an excess of NaHS • H_2O were dissolved in a benzene/DMF mixture and heated in a microwave oven.

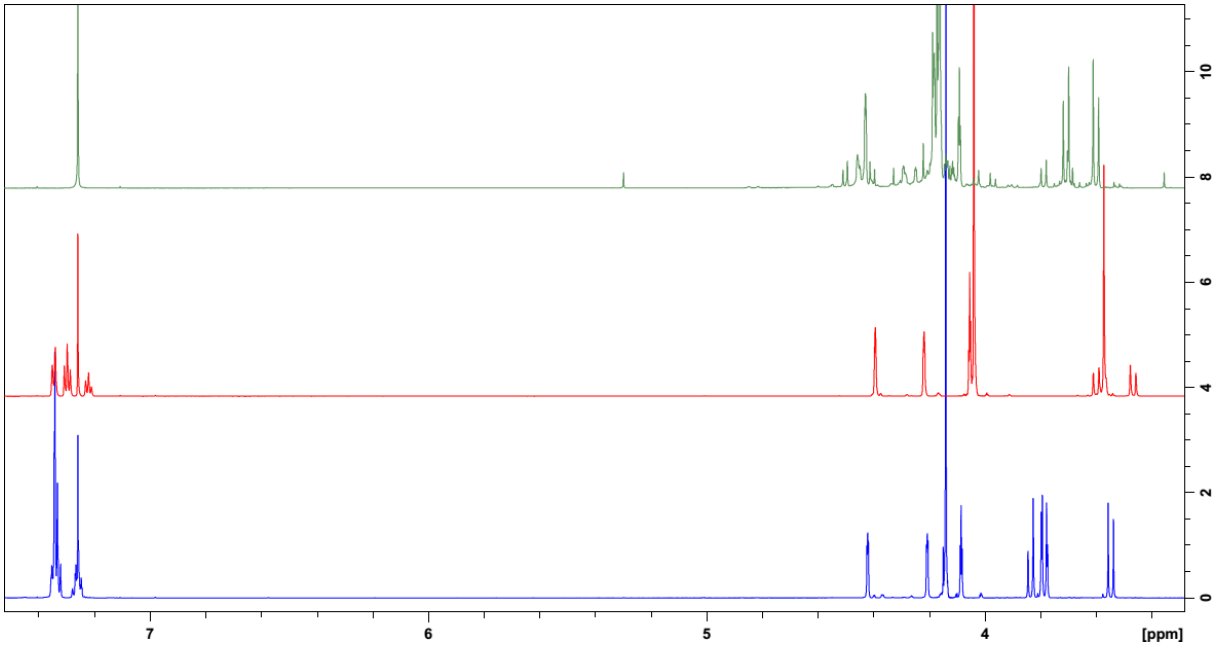
The expected thiol was not detected. Instead, a compound with formula $C_{18}H_{24}FeNO_2$ calculated from HRMS was isolated. Its structure was not elucidated. Curiously, only few ferrocene derivatives of the common motif Fc-CH_2-SH are being published in literature.

Circumventing ammonium salts as starting materials for nucleophilic substitutions, *o*-bromoamine ***43*** was turned into the corresponding acetate with Ac_2O. Contrary to published literature [108], precursor ***43*** suspended in Ac_2O was heated using a microwave oven instead of an oil bath yielding 64% of planar chiral acetoxyferrocene ***41***.

Subsequent reactions of acetoxy compound ***41*** with either an excess or 0.5 eq of NaHS • H_2O dissolved in benzene and DMF and heated by microwave irradiation resulted neither in the expected ferrocenylmethylenethiol nor in the diferrocenylthioether ***47*** Instead *o*-bromoferrocenealcohol ***48*** was isolated.



Scheme 52: Synthesis of N- and S-bridged methylferrocenes.



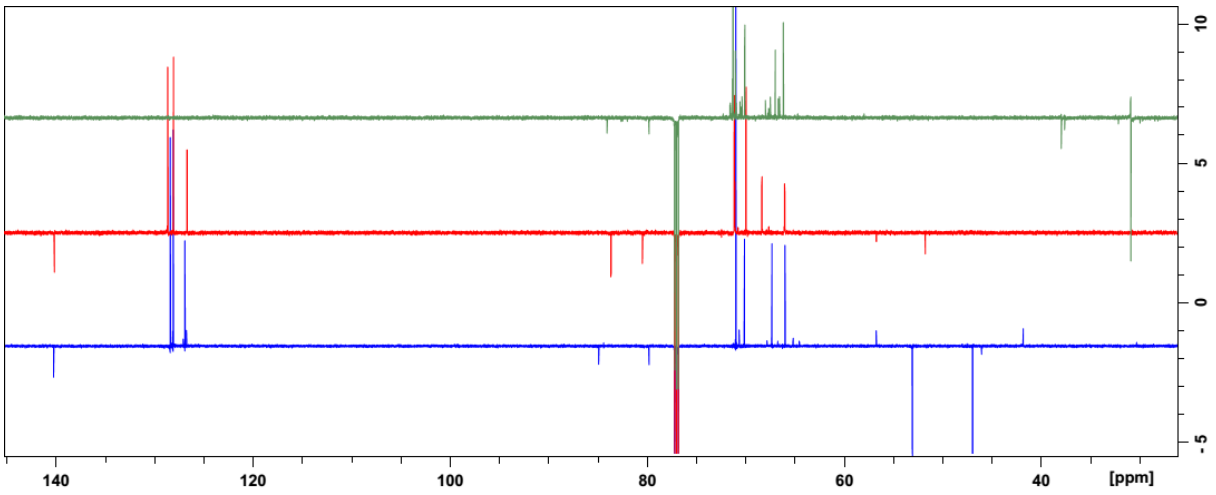


Fig. 15: ^{1}H-NMR (above) and ^{13}C-NMR (below) spectra of monoferrocenylbenzylic amine ***45*** (blue line), diferrocenylbenzylic amine ***46*** (red line) and diferrocenylthioether ***47*** (green line).

Subsequent cyclization of diferrocene compounds ***46*** and ***47*** bridged by N and S containing links would result in di(normethyl) analogs of diferrocenyl cycles described in section 3.2. With sufficient quantity of diferrocenylbenzylic amine compound ***46*** in hand, cyclization by metalation and subsequent coupling to Cl_2PPh was attempted.

Lithium bromo exchange was carried out by three different methods: Lithiation of ***46*** by 2 eq of *n*-BuLi in dry Et_2O as well as formation of a di-Grignard compound either by direct metalation using 3 eq of Mg flakes in THF or by transmetalation in THF using 2 eq of iPrMgCl.

No product was detected in either of the three trials described above. Hence, cyclization attempts of diferrocenylbenzylic amine ***46*** and diferrocenylthioether ***47*** have been abandoned.

However, these compounds could still be interesting for future asymmetric ligand design. Replacing the Br substituents in diferrocenylbenzylic amine ***46*** with atoms or functional groups capable of Lewis acid coordination yields a hypothetical tridentate planar chiral compounds with structural similarities to Pigiphos described by Togni *et al.* as well as published Mg ligands promoting hydroamination described by Hultzsch *et al.* [109].

Other than that, the synthetic route derived in this section opens up the possibility of introducing three different substituents bound to the N center.

3. 3. 2. “Phosphine-first” approach

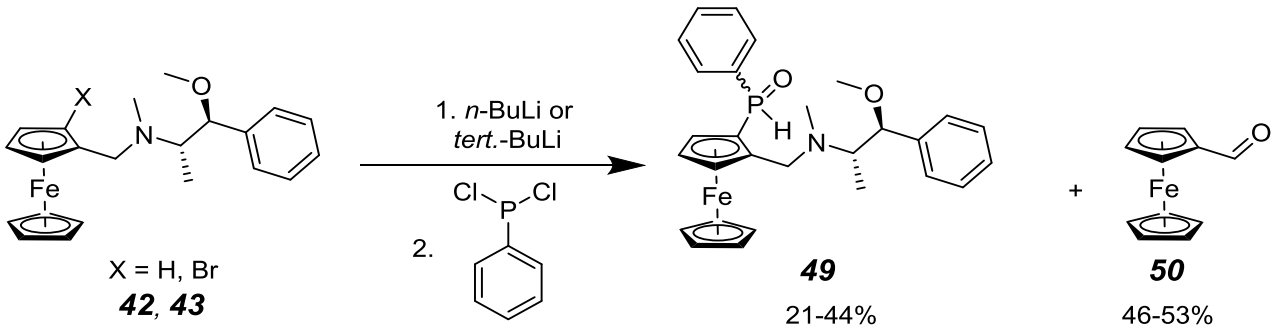
The strategy of obtaining diferrocenylphosphine cycles was hence changed to the more familiar route starting with coupling of two ferrocenyl subgroups via metalation, followed by reaction with bidentate electrophile Cl_2PPh. In a second step a bridge connecting C2 and C2’ of opposing Cp rings is introduced.

Scheme 53 presents step one of this synthetic route. *N*-ephedrineferrocenylmethylamine ***42*** was metalated by *tert.*-BuLi in *n*-pentane or in Et_2O and reacted with Cl_2PPh applying similar conditions as published by Weissensteiner *et al.* [25] and Togni *et al.* [61].

In both cases, several products were formed. The major ones have been isolated and identified as being the same for both procedures: unreacted starting material ***42***, phosphineoxide ***49*** (21-44%) and phosphinic acid and its ethylester formed by oxidation, both resulting from just one lithiated ferrocene reacting with Cl_2PPh and subsequent aq. work-up. Furthermore, ferrocenecarbaldehyde ***50*** was formed despite the harshly basic/reductive reaction conditions.

Repeating the reaction using 2-bromoferrocene ***43*** as a starting material instead as well as *tert.*-BuLi in dry Et_2O in a procedure adapted from literature [25] gave the exact same results.

While of no interest for the intended synthetic aim, similar phosphites have been used very successfully already in asymmetric catalysis [110]. The observed phosphite ***49*** may serve as a central precursor for a future family of asymmetric ligands.



Scheme 53: Summarized *o*-lithiation reactions of ferrocenylmethylephedrine followed up by an electrophilic attack by Cl_2PPh.

It was thus necessary to adapt the retrosynthetic analysis presented in scheme 51. The attempted twofold coupling of lithiated ferrocenes to Cl_2PPh most likely failed due to the steric demand of the bulky ephedrine auxiliary. Synthesis of a diferrocenylphosphine is hence more probable to succeed if the large amine substituent is replaced by a small one prior to metalation.

Scheme 54 below presents the synthetic path chosen and carried out. Ammonium iodide salt ***44*** described in section 3.3.1. was suspended in benzene and 50 eq of 40% aq. Me_2NH solution and heated for 16 h in an autoclave according to a procedure developed by Weissensteiner *et al.* [25]. Subsequent work-up and purification yielded 85% of 1-Bromo-2-(dimethyl)aminomethylferrocene ***51***.

Halogen exchange of an enantiopure, planar chiral intermediate ***51*** using 1.1 eq of iPrMgCl in THF or 1.5 eq of Mg flakes in THF abs. failed to yield the Grignard reagent.

In the latter case, a yellow solid readily dissolvable in water was formed. HRMS revealed a mixture consisting mostly of starting material as well as a compound with HRMS of 464.0076 not identified as to date of this writing.

Using Li in place of Mg, metalation with *n*-BuLi in dry Et_2O took place which was followed by reaction with Cl_2PPh [25]. In this case the desired diaminophosphine ***53*** was obtained as a brown oil in 59% yield together with minor amounts of *N,N*-dimethylaminomethylferrocene ***54***.

Diaminophosphine ***53*** being a novel, purely planar chiral molecule is interesting as a catalyst all by itself already since the dimethyl analogue diaminophosphine ***6*** performs well as an enantioinductive structure as described in section 3.5. in detail.

When comparing diamine ***53*** to diamine ***6*** synthesized in section 3.2., it would be interesting as to whether the amine moieties show an equally distinct Re/Si ferrocene side chain regiochemistry or – lacking methyl side chains – both functional groups react with comparable ease, for example in *N*-boranation.

However, for this project, diaminophosphine ***53*** prepared was used for subsequent cyclization experiments. MnO_2 driven dicarbaldehyde synthesis was ruled out as it did not work for the dimethyl analogs ***6***, ***11*** and ***13*** as described in section 3.2.

Acid catalyzed nucleophilic substitution and acetoxy substitution of the dimethylamine moieties by Ac_2O seemed far more interesting for this class of

diferrocenes since the concern of elimination occurring in the side chain can be ruled out.

Diaminophosphine ***53*** and $BnNH_2$ were suspended in AcOH and heated for 3 h in analogy to published procedure for similar substitution of an amine by a pyrazole moiety [111]. Disappointingly, no conversion of starting material was observedn either by TLC testing nor after isolation and characterization.

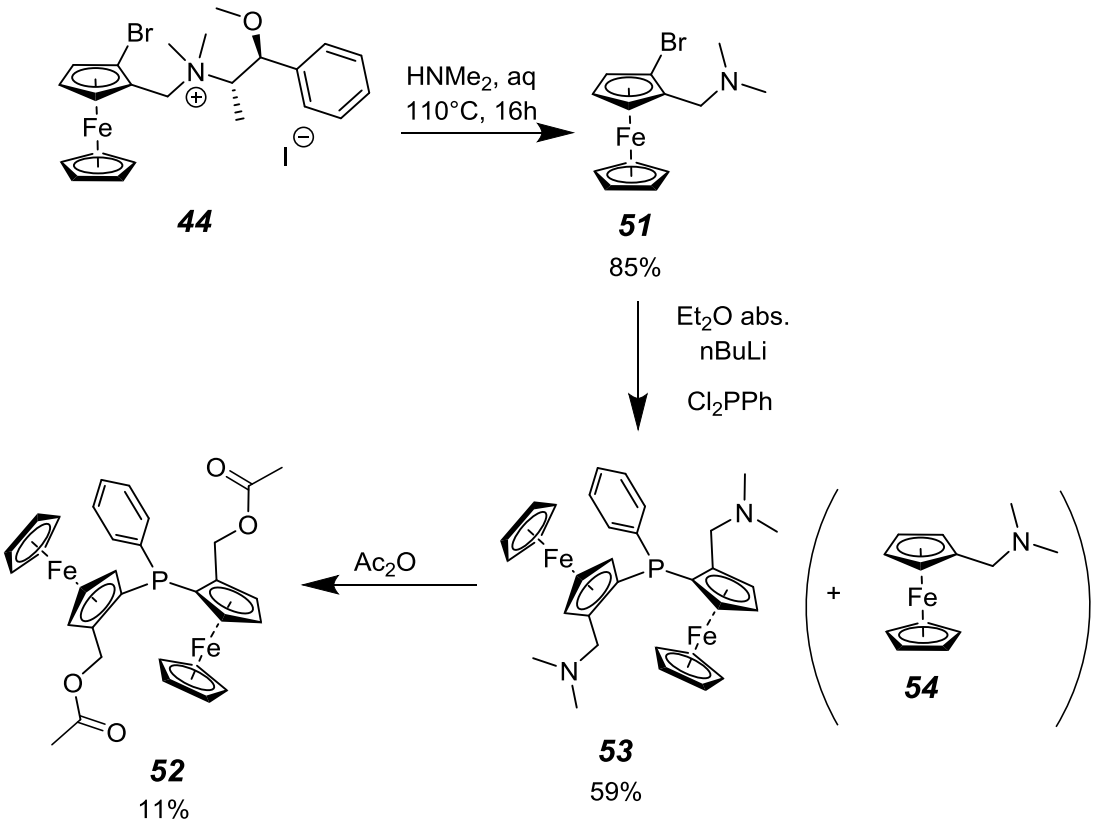
This type of substitution reaction was used almost exclusively for phosphane nucleophiles (see for example [61]). This can be rationalized: While phosphanes are better nucleophiles than the corresponding amines, they are far inferior bronsted bases ($pK_b(NH_3)$ ~ 4.8; $pK_b(PH_3)$ ~ 27) and hence are not protonated by the acidic chemical environment of AcOH, retaining their nucleophilic abilities, while amines mostly are protonated and thus deactivated as ammonium compounds.

However, N-C bonds may still be formed by this type of procedures if more than one N is prsent in the intended nucleophile and not all of them are protonated, just as in the case of using pyrazole.

Next, diaminophosphine ***53*** was transformed into the corresponding diacetoxyphosphine ***52*** by heating a suspension of the starting material in Ac_2O in analogy to published literature [25]. While diacetoxyphosphine ***52*** was isolated as a pure product, the yield was poor using this procedure (11%).

Preliminary cyclization tests of diacetoxyphosphine ***52*** with 1 eq of $BnNH_2$ in DMF failed. Neither stirring at r.t. nor heating in a microwave oven at 100 °C afforded the desired cycle.

After chromatography of the reaction mixture, starting materials as well as P-oxidized substrate were isolated, pointing to the need for triarylphosphine protection – such as P=S and/or using an inert atmosphere microwave oven. It is possible that the diacetate might not be sufficiently reactiveand should be replaced by better leaving groups.



Scheme 54: Synthesis of diacetoxyphosphine ***52***

3. 4. β-Substituted Di(ferrocenylethylene) compounds

Other than cycles and precursors with and without appended methyl groups described in sections 3.2. and 3.3., diferrocenyl macrocycles (nine-membered or larger rings) could be conceivably produced from divinylphosphines ***8***, ***12*** or ***14*** described in section 3.2. Terminally substituted ethyl side chains can be expected to be less prone to elimination. Scheme 55 sums up the retrosynthetic analysis carried out.

Diferrocenyl macrocycles ***I*** containing a hetero atom X in their backbone can be synthesized from a diferrocene bearing acetoxy- (***IV***) or any other leaving groups ***II*** at the termini of the ethyl side chains. These intermediates, in turn, are available from a di-primary diol ***V***.

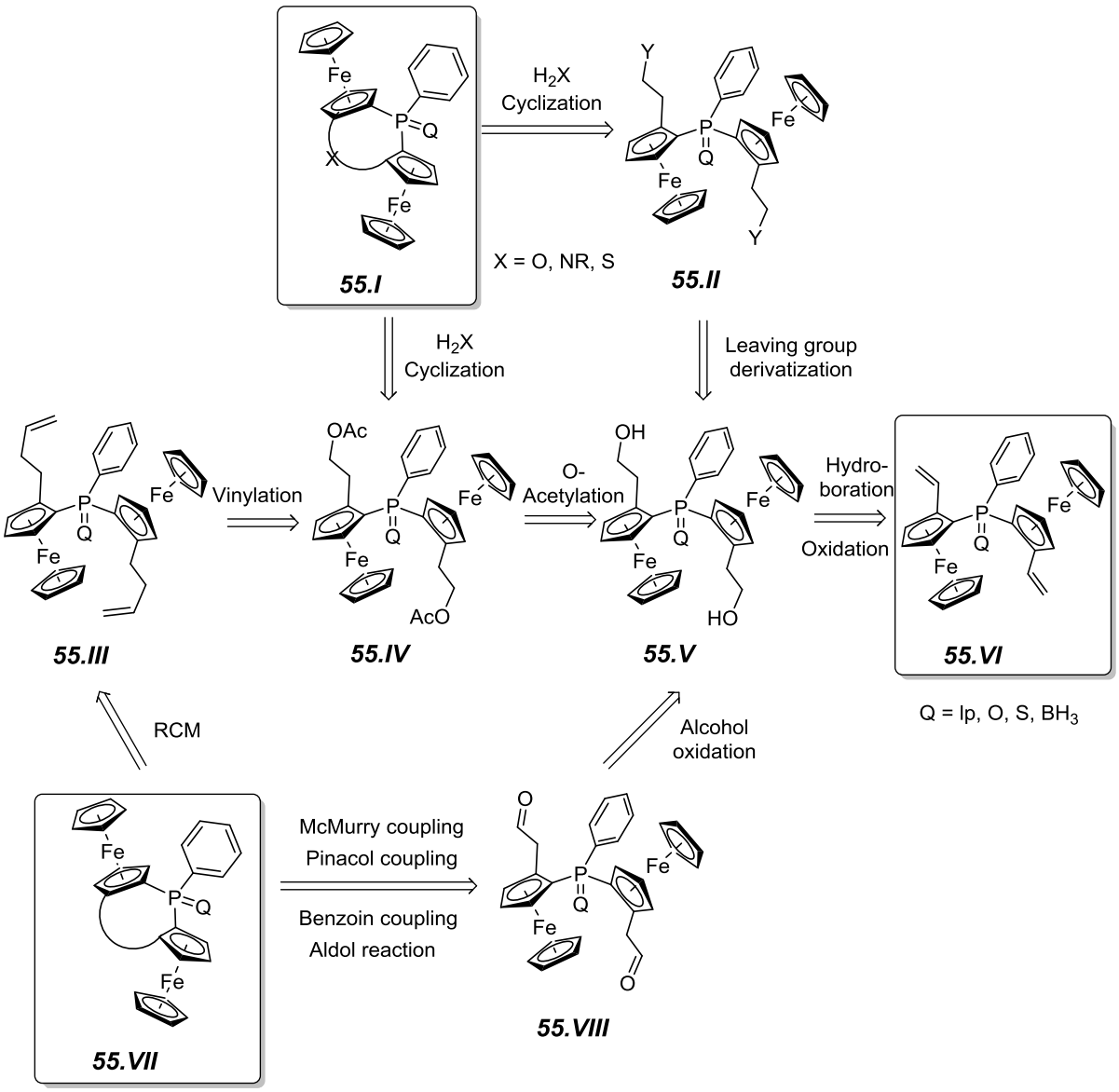
This dihydroxy compound ***V*** can be synthesized from known divinyl precursor ***VI*** by double *anti*-Markovnikov addition, for example by hydroboration and oxidative work-up.

All-carbon diferrocenyl macrocycles ***VII*** could conceivably be produced either by olefin RCM or hydrovinylation of a diolefin precursor ***III*** produced from a diacetoxy precursor ***IV*** by vinyl substitution.

Alternatively, such macrocycles are available from a dicarbonyl precursor ***VIII*** by carbonyl coupling reactions such as McMurry coupling, Pinacol coupling, Benzoin coupling or aldol reaction.

Also, carbonyl precursor ***VIII*** could be transformed into a terminal diolefin followed up by RCM to yield macrocycle ***VII***. Dialdehyde ***VIII*** can possibly be synthesized by a selective oxidation reaction of the dihydroxy precursor ***V*** such as Swern or Dess-Martin oxidation.

As to yet, only a few published procedures to obtain the structural motif Fc-CH_2-CH_2-Q exist.



Scheme 55: Retrosynthetic analysis of macrocyclic P-linked diferrocenes from divinylphosphines.

Scheme 56 presents reactions carried out to gain a di-primary diol. Divinylphosphine ***8*** was treated with BH_3 • THF complex in THF followed up by basic H_2O_2 mediated oxidation in an adapted published procedure [112].

Performing the reaction with a damaged BH_3 • THF reagent about one tenth of the expected concentration, 20% yield of divinylphosphinoborane ***58*** as well as divinylphosphineoxide ***12*** were produced accidentally.

Repeating the experiment with excess BH_3 • THF, the product discovered was a mixture of two diols in overall 54% yield; in both cases one borane is attached to the P. However, it turned out that the product consisted of both the di-primary diol ***55*** as well as a diol containing primary and secondary hydroxyl groups (***56***) in an approximate 1:1 ratio. Hence unsubstituted BH_3 is sufficiently regioselective. What's

remarkable about this reaction is that only one of the two vinyl groups reacts Markovnikov-unselectively.

Comparing the NMR spectrum of the isolated mixture to the spectra of other asymmetric compounds, the terminal hydroxyethyl side chain has been found to be substituted to the Si-ferrocene compared to the three other residues of P. The Re-ferrocene hydroxyethyl side chain was 50% internally and 50% terminally substituted. This supports the finding of diaminophosphine ***6*** boranation and mono-elimination regioselectivity in section 3.2.

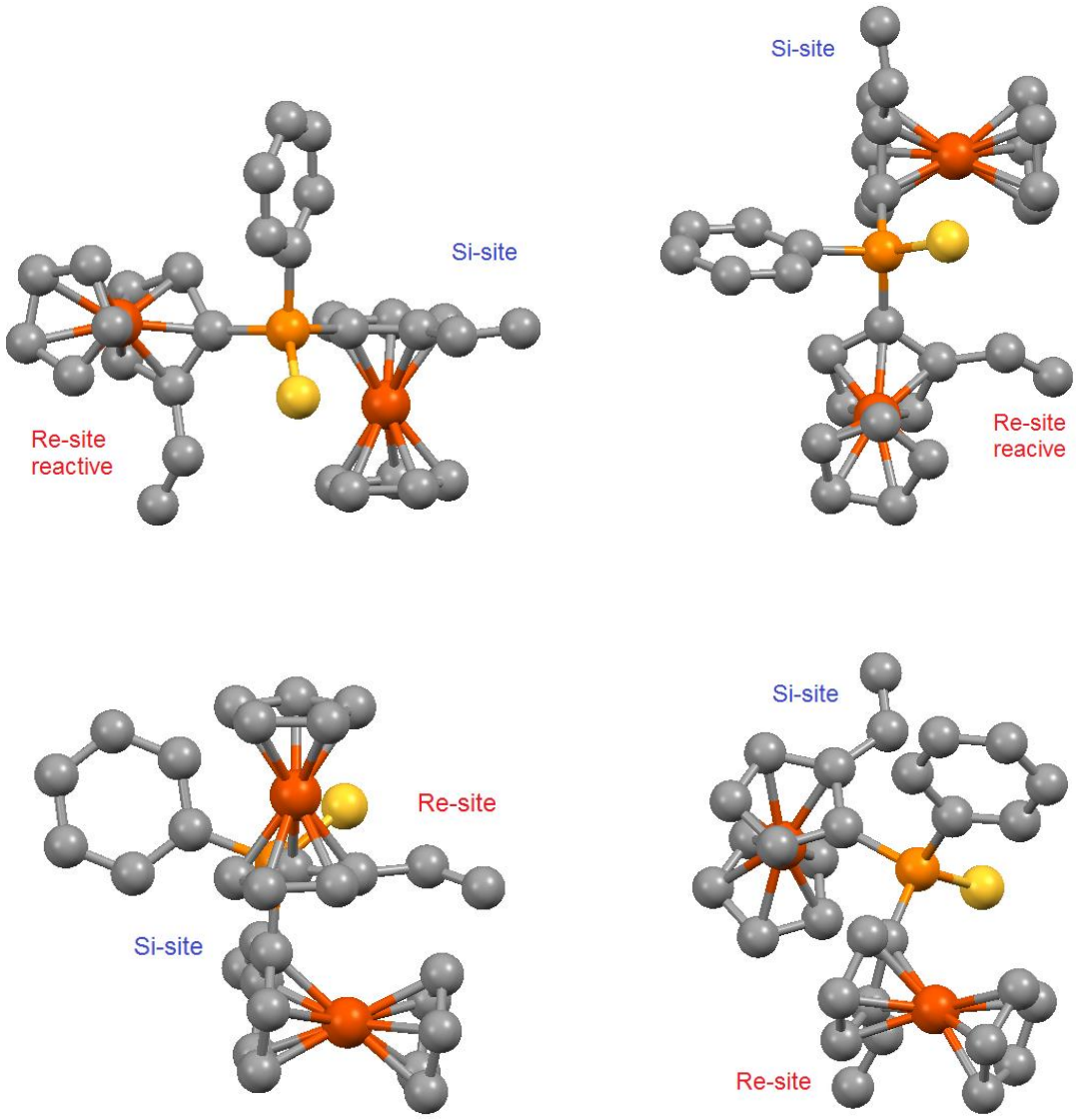


Fig. 16: Re- and Si-sites presented by an X-ray recording of divinylphosphinesulfide ***14***

Since this mixture turned out to be inseparable by column chromatography, these compounds were no longer of interest for this project.

To improve *anti*-Markovnikov regioselectivity, the sterically demanding borane reagent 9-BBN was used in THF instead of BH_3. Work-up using KOAc and H_2O_2 in adaptation of an established protocol [113] resulted in exclusive formation of di-primary diol ***57*** in 25% yield.

However, despite of using an excess of 9-BBN, the P center was oxidized during work-up. This resulted in the chromatographic purification of dihydroxyphosphineoxide ***57*** requiring very polar solvents and lead to rather long eluation times and solvents being wasted.

Curiously, ESI HRMS of the purified product revealed tiny amounts of a side product carrying the mass of the intended product plus one cyclooctene equivalent which raises the question as to how this mass came about (fig. 17). It cannot be explained by 9-BBN complexing since the mass of the B is missing. It can be conjectured that the octene ring system was transferred to either a vinyl group or a hetero atom via a quaternary B intermediate in a Matteson-similar rearrangement.

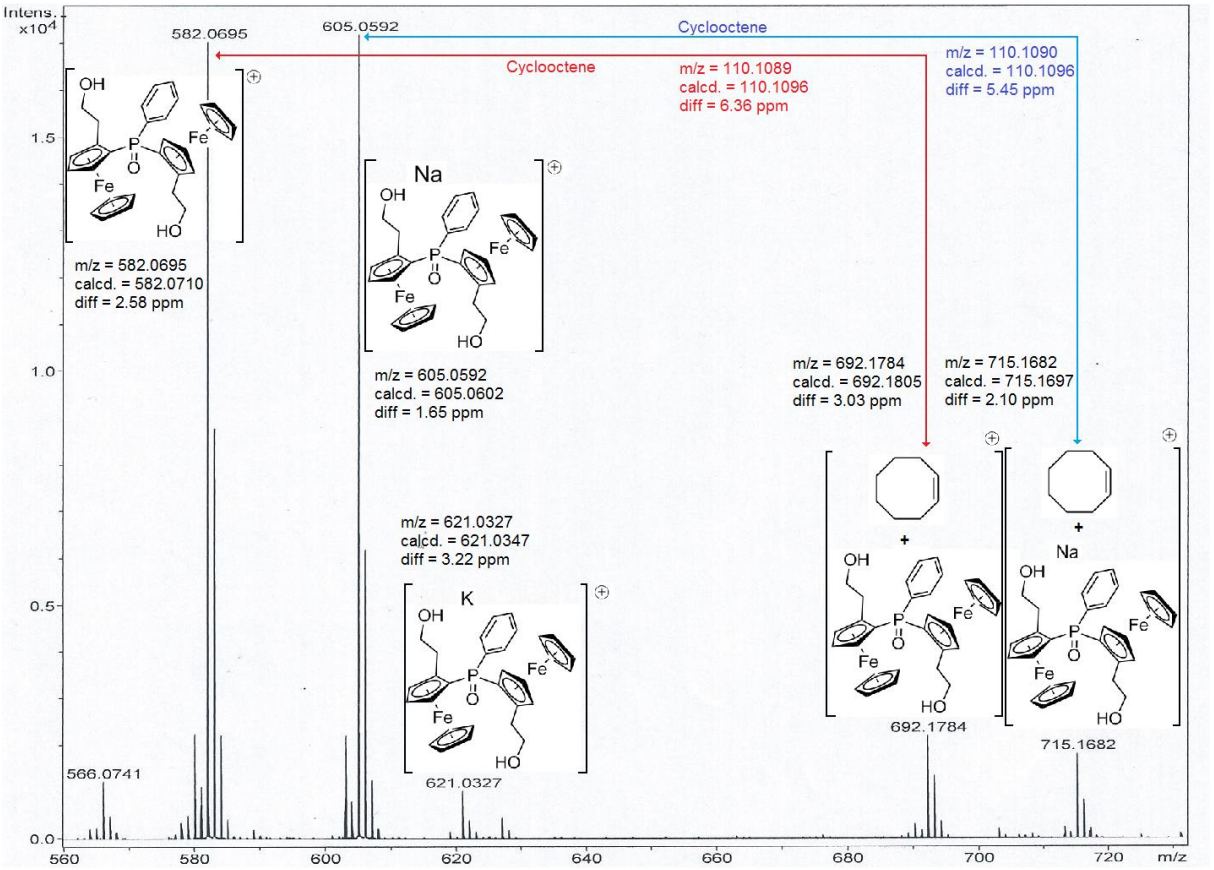
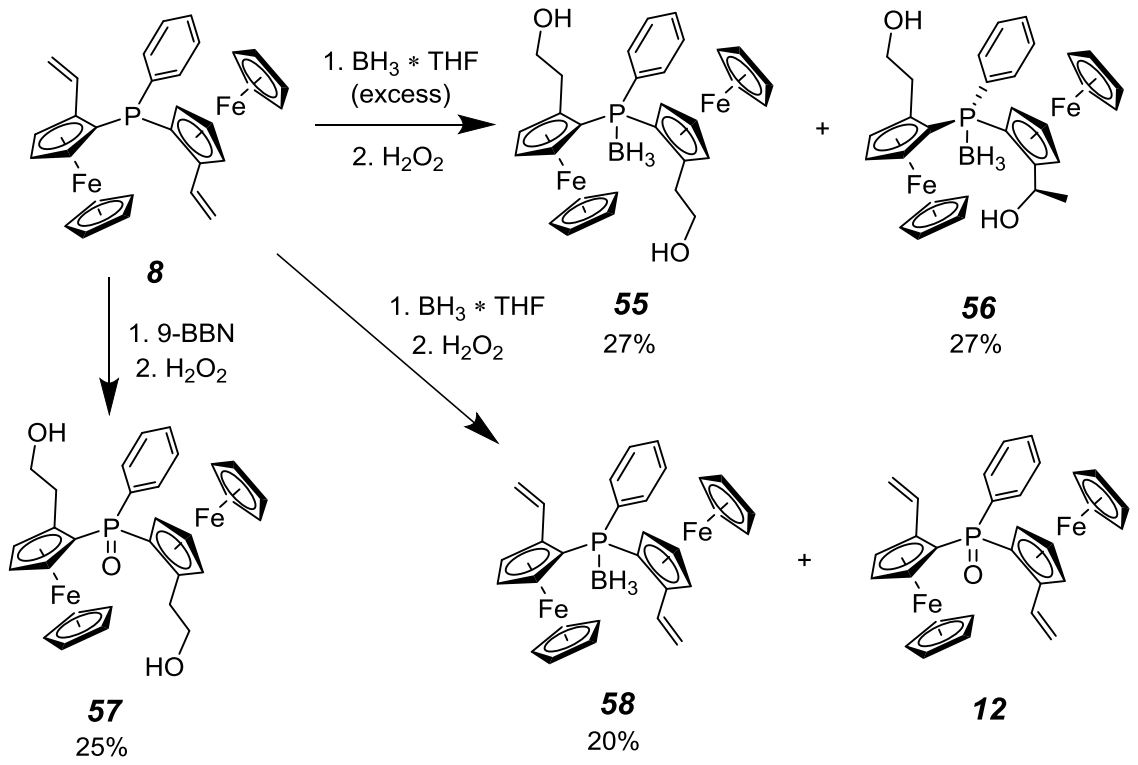


Fig. 17: HRMS of dihydroxyphosphineoxide ***57***. Ions both of $[\mathbf{57}]^+$ and $[\mathbf{57} + Na]^+$ have been detected as well as either mass plus the mass of cyclooctene, albeit in lower abundance.



Scheme 56: Synthesis of P boranes and dihydroxy compounds using BH_3 or 9-BBN

To circumvent the problem of diol phosphineoxide polarity, 9-BBN terminal hydroxylation was carried out on divinylphosphinesulfide ***14*** instead, described in scheme 57. The procedure reliably yielded di-terminal diol phosphinesulfide ***59*** in 60% yield as a compound easily purified by column chromatography. Both monovinylmonohydroxyphosphinesulfides ***62*** and ***63*** have been discovered as side products.

Hypothetically, another compound easy to purify might have been achieved by protecting the P atom of divinylphosphine ***8*** in a first step by 1 eq of BH_3, then adding an excess of 9-BBN before oxidizing the two C-B bonds by H_2O_2 synthesized.

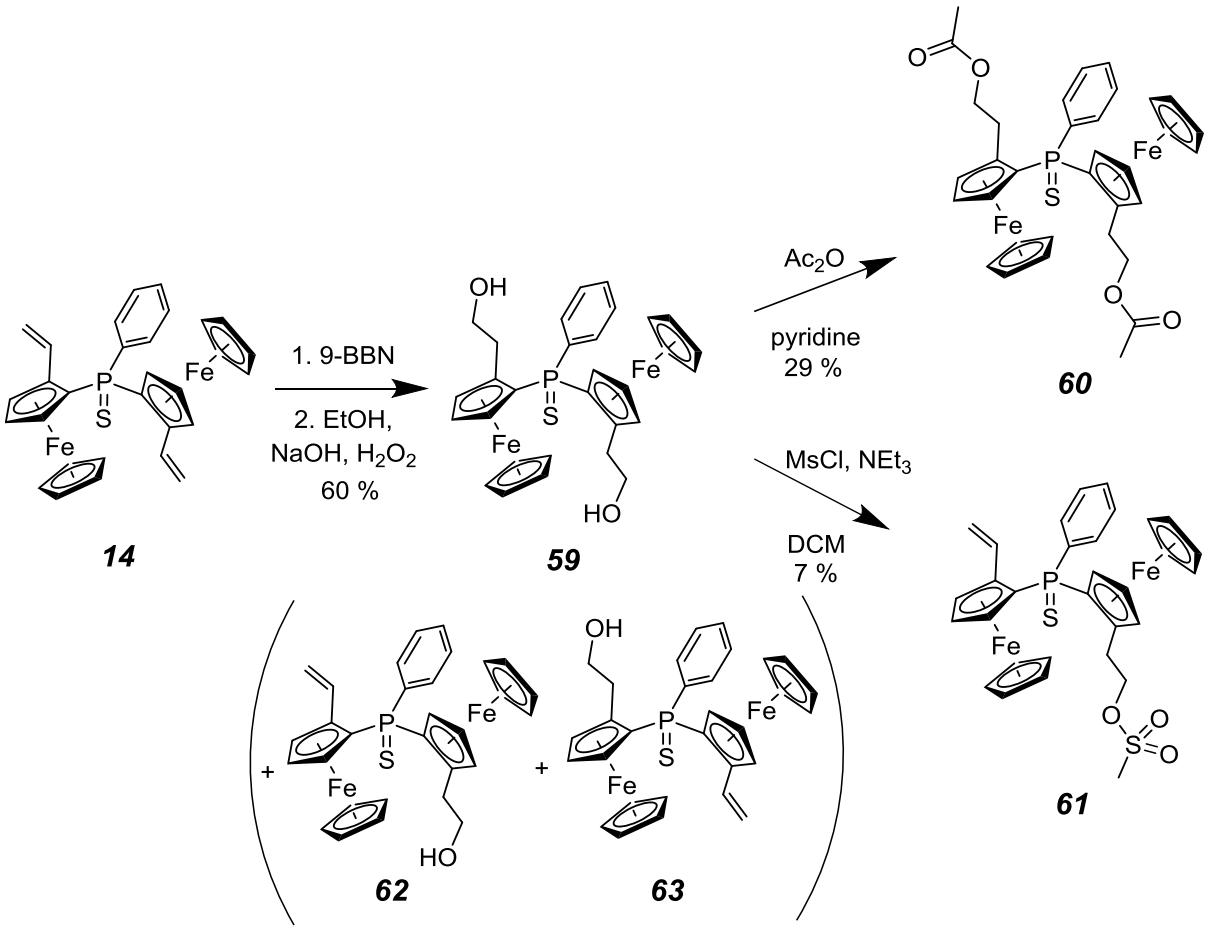
Diol phosphinesulfide ***59***, being inert to most cyclization reactions had to be activated for further usage. This could be done by three basic transformations:

- Hydroxide oxidation to aldehydes, ketones, carboxylic acids or esters
- Derivatization, for example by esterification or acetalization
- Turning the hydroxide into a good leaving group and subsequent substitution.

For this project the latter option was chosen.

Reaction of di-primary diol phosphinesulfide ***59*** with MsCl in DCM catalyzed by Et_3N [114] yielded 7% of one product ***61***. Unfortunately, this compound, while planarly asymmetric, bears one vinyl and one mesyl group not interesting for cyclizations similar to previous acetoxylation attempts.

Reaction of diol phosphinesulfide ***59*** with Ac_2O in pyridine both as a solvent and nucleophilic catalyst [68] yielded the desired diacetatephosphinesulfide ***60*** as sole product in only 29%.



Scheme 57: Synthesis of diacetoxyphosphinesulfide ***60*** from divinylphosphinesulfide ***14***.

Attempts of producing a diferrocenyl macrocycle by uncatalyzed reaction of diacetatephosphinesulfide ***60*** with 1 eq of $BnNH_2$ in DMF – either at r.t. or by microwave heating – did not convert the starting material.

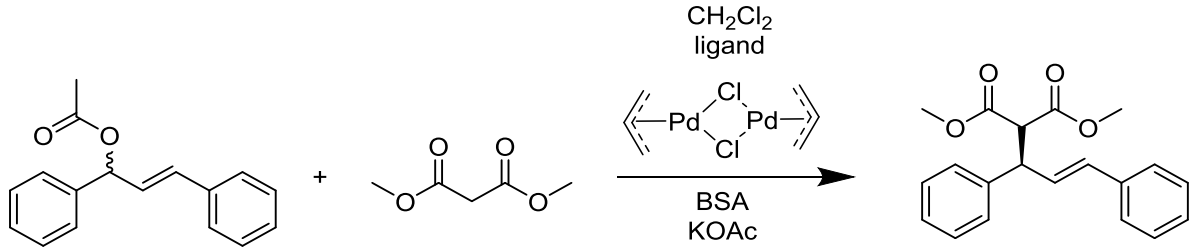
3. 5. Catalysis

Different non-cyclized diferrocenylphosphine compounds described in section 3.2. have been tested with regards to their asymmetry inducing capabilities, which can be done best by using them as ligands in well-studied catalytic reactions.

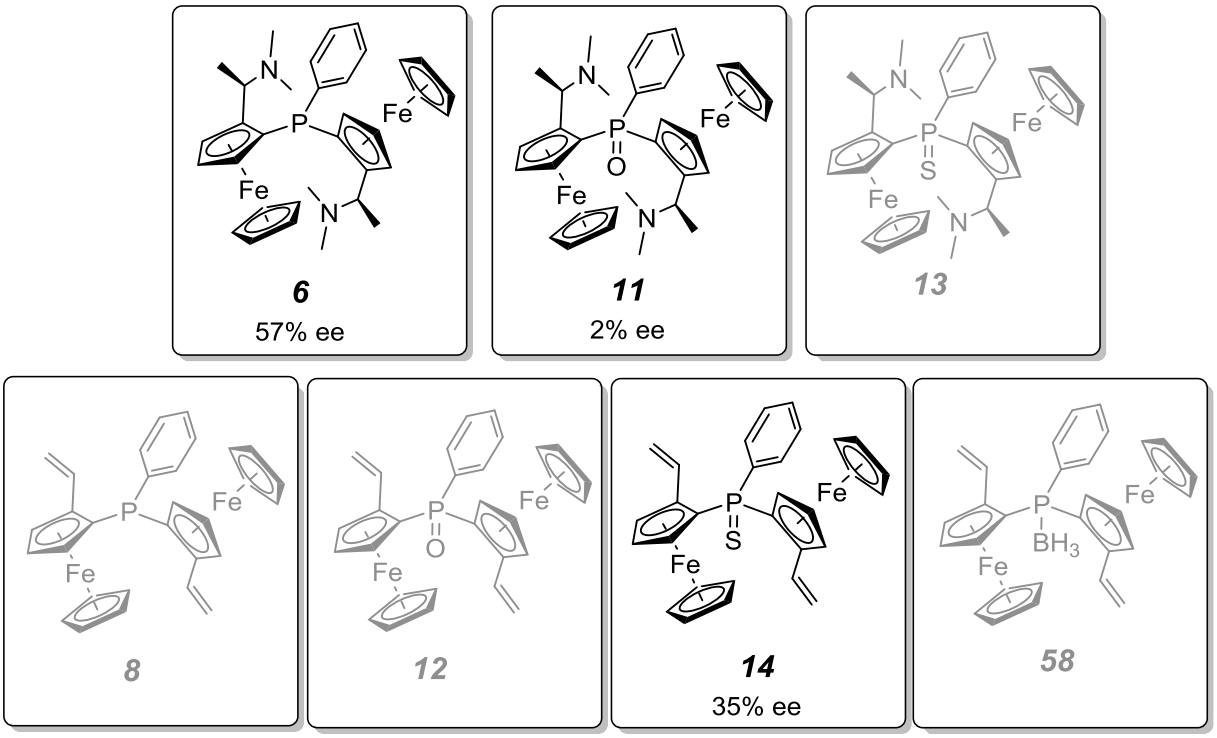
3. 5. 1. Asymmetric allylic alkylation

Pd(II)-catalyzed asymmetric allylic alkylation is one of the most frequently performed benchmarking reactions. The theoretical background of this chemical reaction is explained in section 1.3.1. A considerable number of studies have been performed using ferrocene-based ligands [69] [115] [116] hence there exists a great comparability of results.

Scheme 58 describes the test reaction performed, the compounds used as ligands and the e.e. of ***66*** produced by each. The protocol used was published by Widhalm *et al.* [117], alkylating 1,3-diphenylallylacetate in dry DCM with dimethylmalonate deprotonated by *N*,*O*-Bis(trimethylsilyl)acetamide (BSA) and a catalytic amount of KOAc. The procedure was modified to carry out the catalysis for 48 h until complete conversion of starting material was observed.



64 ***65*** ***66***



Scheme 58: Top: Pd(II)-catalyzed asymmetric allylic alkylation. Bottom: Ligands tested in asymmetric allylic alkylation.

Solely diaminophosphine ***6***, diaminophosphineoxide ***11*** and divinylphosphinesulfide ***14*** produced product ***66*** in any significant extent. Little or no conversion was observed using the other potential ligands.

Diaminophosphineoxide ligand ***11*** produced merely a racemate of ***66*** (2% e.e. measured; $\Delta\Delta G^{\ddagger} < 0.1$ kJ/mol). Hence while it coordinates and activates Pd(II) for the allylic alkylation reaction, the enantioinductive part of the scaffold is probably spatially too distant from the catalytic center for steric interaction.

Divinylphosphinesulfide ***14***, offering $R_3P{=}S$ and two vinyl functional groups for coordination, produces a fair but insufficient enantioinduction of 35% e.e. This corresponds to an energy difference $\Delta\Delta G^{\ddagger}$ of 1.8 kJ/mol of the two diastereomeric transition states according to Eyring's equation, pointing out the need to constrain the probably very variable conformation space of the molecule. However, it remains interesting as to how exactly this molecule binds to Pd(II), being the only divinyl ligand activating the catalytic reaction.

The greatest enantioinduction observed for asymmetric allylic alkylation was achieved by using diaminophosphine ***6***. At a r.t. of 21 °C, the energy difference $\Delta\Delta G^{\ddagger}$ of the two diastereomeric transition states is 3.2 kJ/mol. Therefore future attempts at

creating a non-cyclized diferrocene system similar to those treated in this project should use its structure as a role model. In literature, a rather similar compound named Pigiphos has been devised by Togni *et al*. [42] [43] [44].

These findings, however, cannot be used to disregard the usage of the other inactive compounds as ligands, for all this result means is that they do not bind to Pd(II) in a sufficient extent. Hence, another catalytic test system was employed to complement the informations gained from asymmetric allylic alkylation.

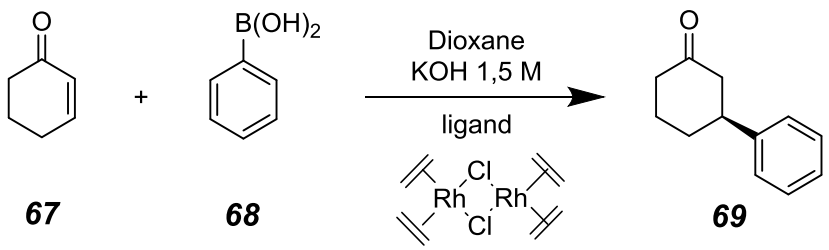
3. 5. 2. Asymmetric 1,4-addition to enones

Another important benchmark reaction is the Rh(I)-catalyzed 1,4-arylation of enones. The mechanism of this reaction is explained in more detail in section 1.3.2. The catalytic reaction was performed according to a procedure published by Hayashi *et al* [118], forming the catalytic coordination complex in situ. Alternative procedures working with the isolated Rh complexes are also known [119].

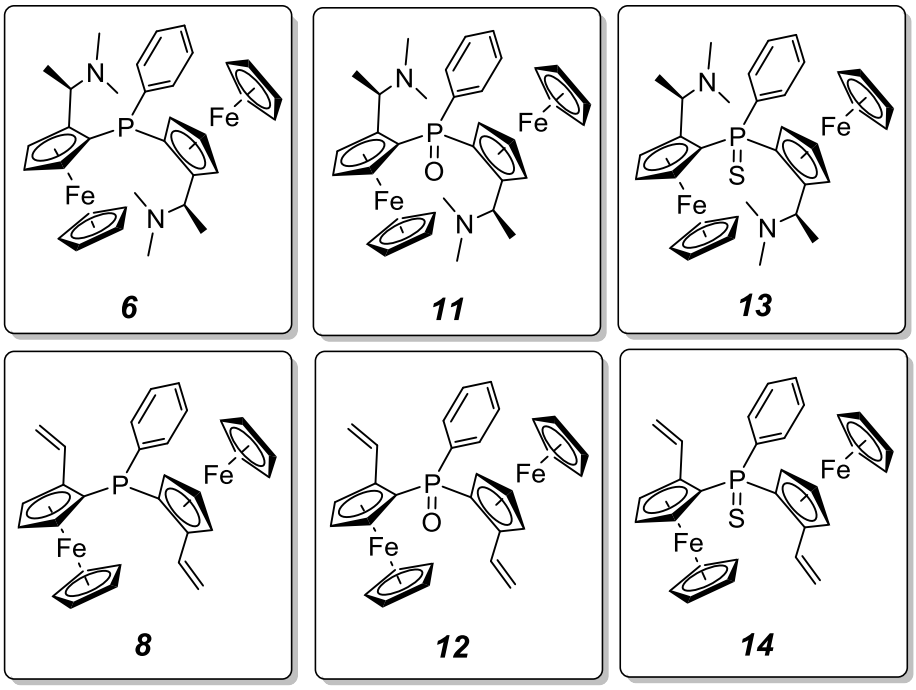
Scheme 59 sums up the reactions performed as well as the compounds used as ligands. The catalytically active complex was formed from $[Rh(ethylene)_2Cl]_2$ and the individual ligand in dioxane and water, before phenylboronic acid ***68*** and cyclohexenone ***67*** were added to form 3-phenylcyclohexane ***69*** asymmetrically.

Stirring the reaction mixture at room temperature lead to no observable product formation. Heating the reaction mixture at about 50 °C for 24 h caused formation of ***69*** in all cases (crude ^{1}H-NMR). Yet, only submilligram amount of ***69*** could be recovered after work-up.

These amounts were insufficient to determine enantiomeric ratios reliably by chiral HPLC.



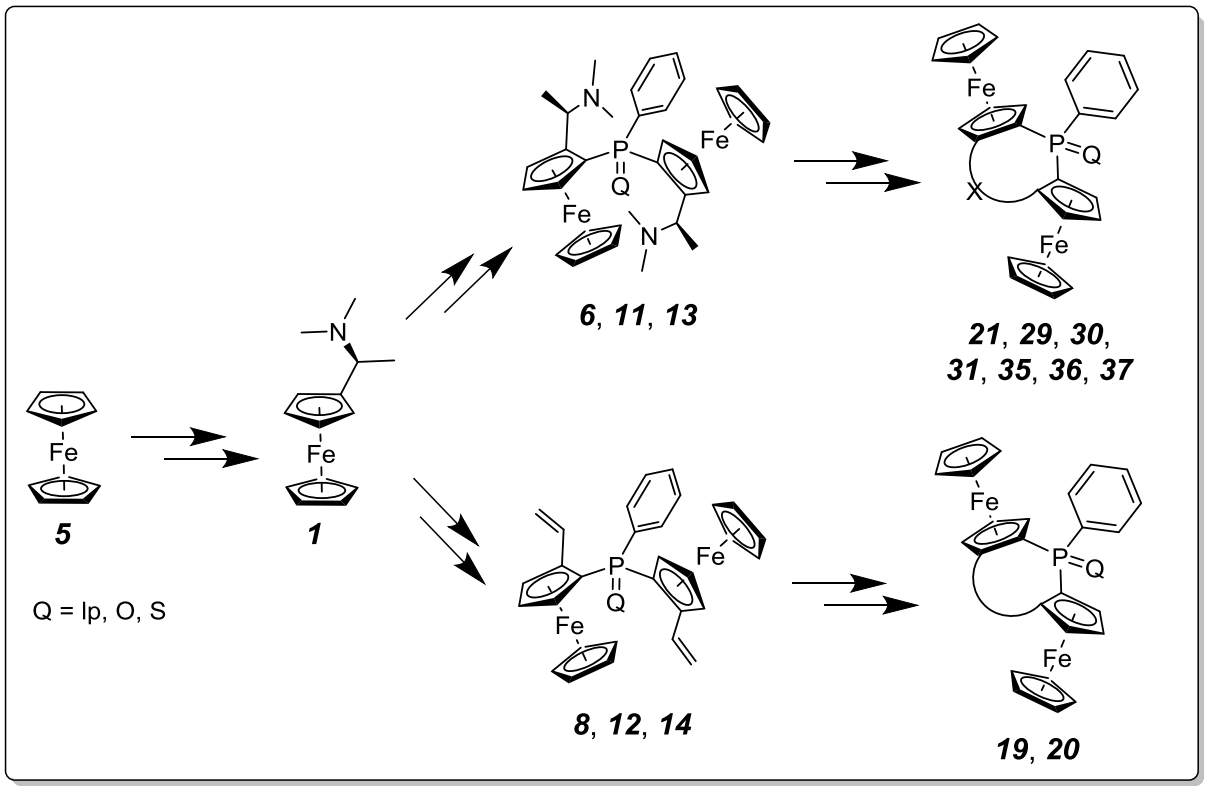
67 ***68*** ***69***



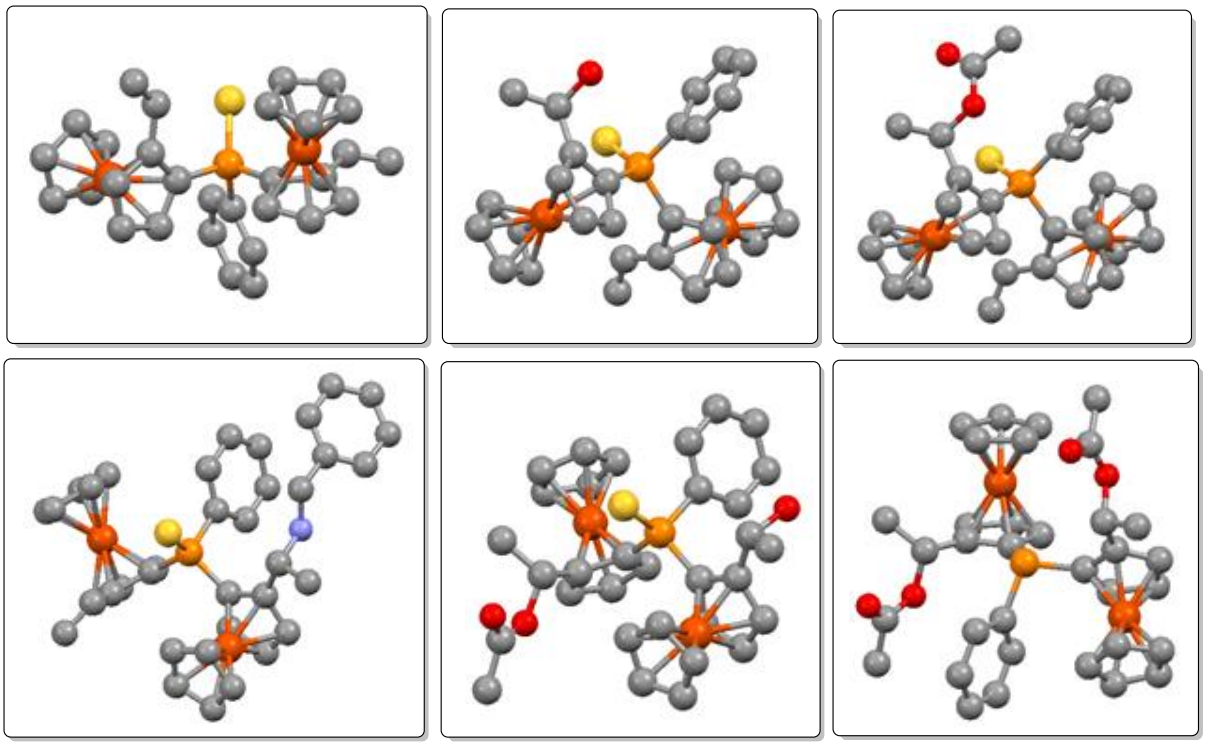
Scheme 59: Top: Rh-catalyzed asymmetric 1,4-arylation of enones. Bottom: Ligands tested in asymmetric 1,4-arylation.

4. Conclusions and Outlook

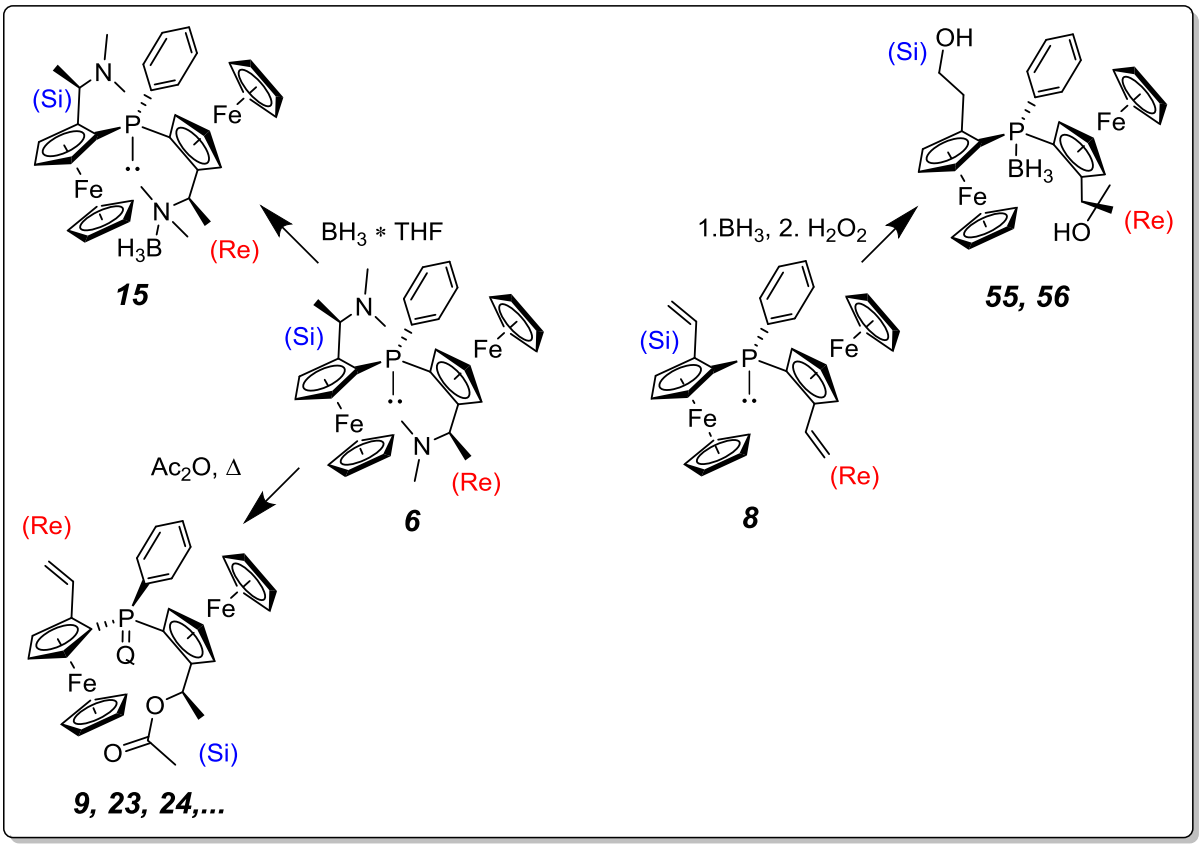
Starting with ferrocene, a synthetic route was successfully devised via Ugi's amine as a chiral precursor to produce diferrocenylphosphines, phosphineoxides and phosphinesulfides.



From some of the intermediates ***14***, ***22***, ***24***, ***25***, ***26*** and ***34*** crystal structures were determined, shedding light on the 3D structure of diferrocenes.

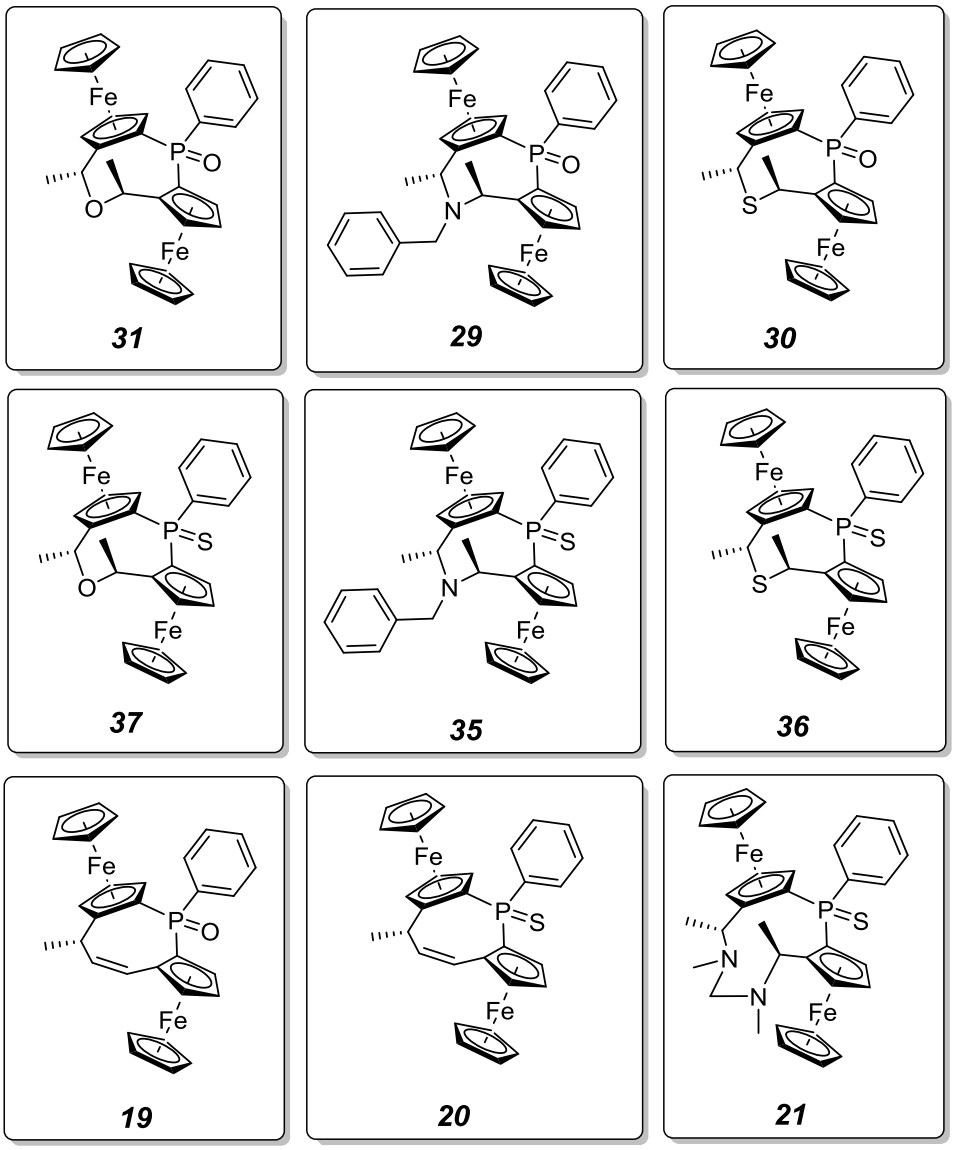


In symmetrical diferrocenylphosphine compounds Fc_2PhP, a distinctly different reactivity of ferrocene subunits was observed. Employing Re/Si site nomenclature by determining configuration of the other three P-substituents it was found the Re-ferrocene reacts more readily than the Si one.

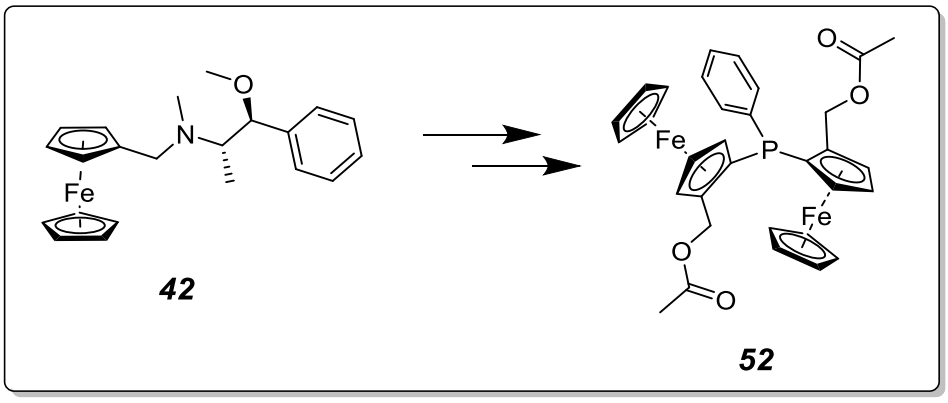


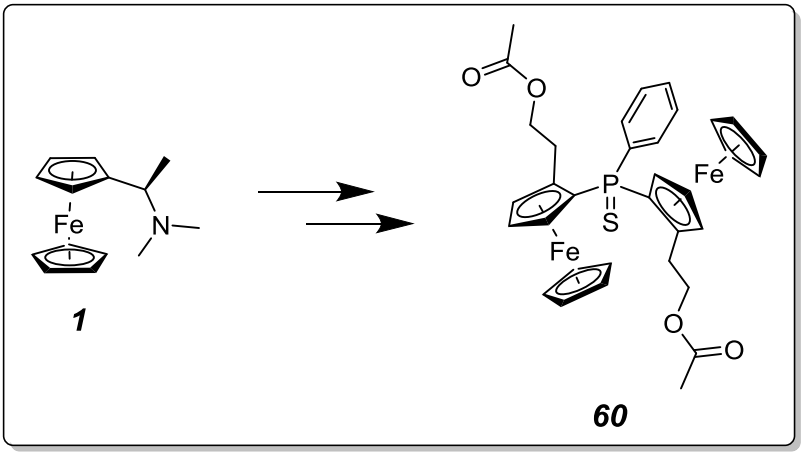
Seven diferrocenyl compounds ***6***, ***8***, ***11***, ***12***, ***13***, ***14*** and ***58*** have been put to test in the asymmetric allylic alkylation, affording low to moderate e.e. ranging from 2-57%, providing information of how to design more successful uncyclized diferrocene ligands in future projects.

Nine new diferrocenyl cycles ***19***, ***20***, ***21***, ***29***, ***30***, ***31***, ***35***, ***36*** and ***37***, were prepared and characterized. These prototypes adhere to the structural motif desired at the beginning of this work, containing C-, N-, O-, S- and one aminal backbone. Although yields are still low at the present stage, optimization steps will provide this conceptually new group of rigid phosphine ligands in reasonable amounts to be tested in catalysis in more detail.

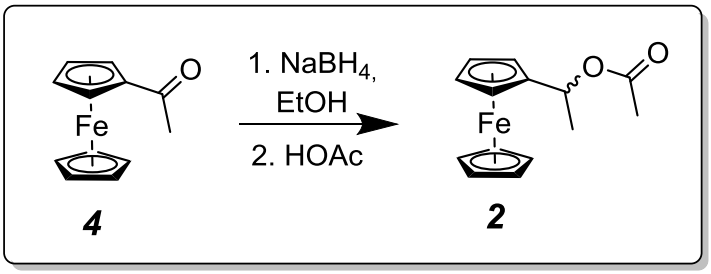


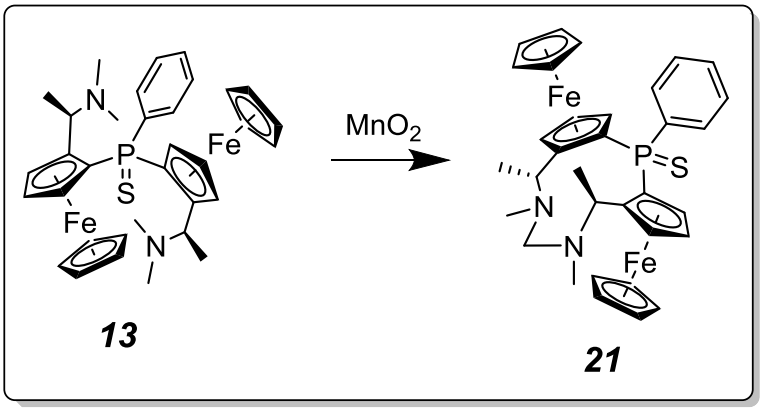
Two new reaction routes towards other types of diferrocenyl cycles have been established: One starting from aminomethylferrocene *N*-substituted with a chiral *o*-directing auxiliary and one starting from Ugi's amine, both leading to diferrocenylphosphine with two *O*-acetylgroups in the side chain. These new compounds may serve as key intermediates for future cyclization attempts.

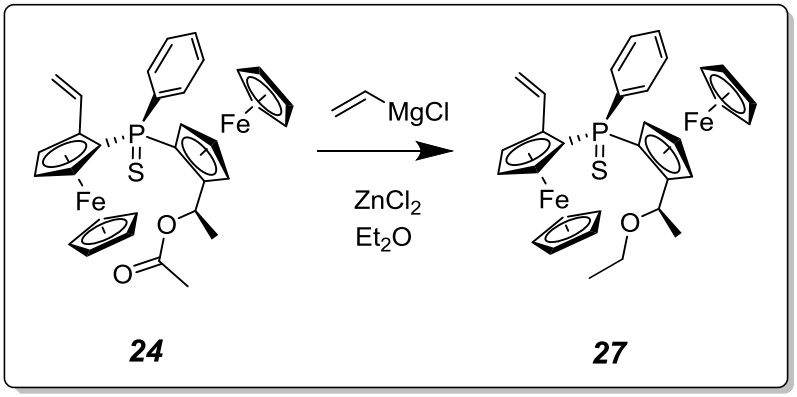




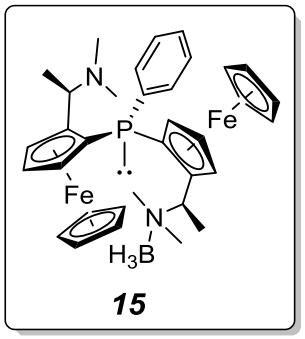
Several unexpected reactions have been observed, including the exclusive boranation of one amino group in ***6*** without affecting the phosphine over boranation of P; incorporation of an octene ring in a diferrocenyl molecule in an as to yet not elucidated way; one-pot reduction/*O*-acetylation of acetylferrocene when working up with AcOH; formation of cyclic aminal ***21*** via alkylation of N mediated by MnO_2 oxidation of ***13***; and ethoxy-substitution of an acetate by $ZnCl_2$ and vinyl MgCl in dry Et_2O.



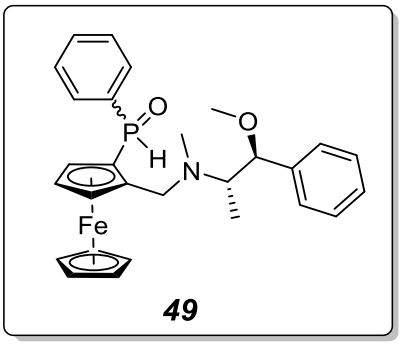




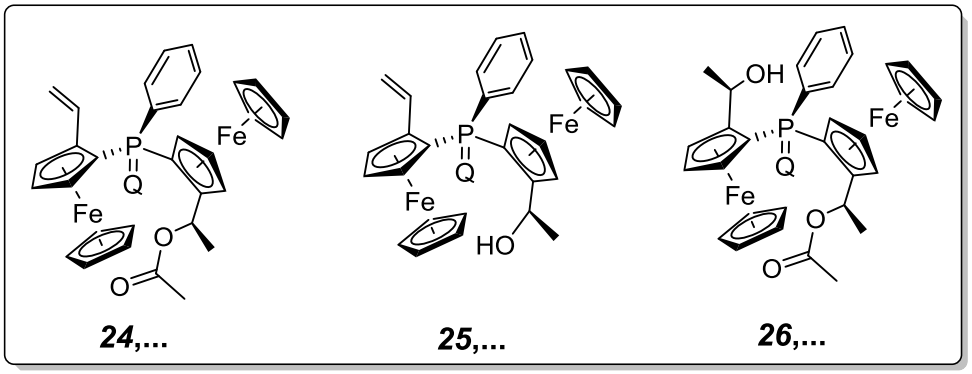
While exploring synthetic routes, interesting intermediates and side products have been discovered, showing potential as precursors for alternative ferrocene-based asymmetric ligands: Diaminophosphinomonoborane ***15***, phosphite ***49***, monovinyl compounds ***24***, ***25*** and ***26*** as well as their analogs, bromoferrocene ***45*** and diferrocenes ***46*** and ***47***, secondary/primary dihydroxydiferrocene ***56*** as well as monovinylmonomesylcompound ***61***.



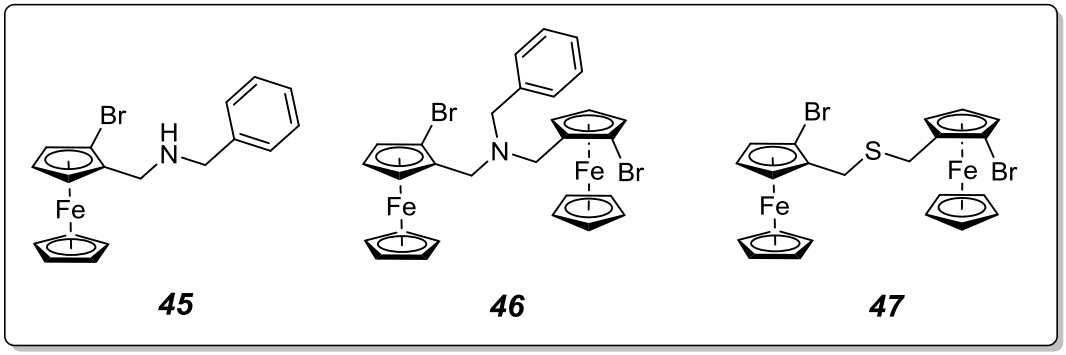
15



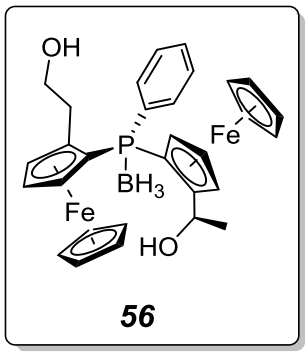
49



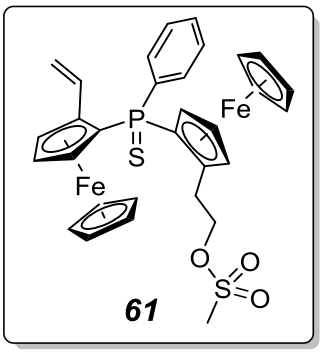
24,... ***25,...*** ***26,...***



45 ***46*** ***47***



56



61

Throughout this project, P sulfide proved to be a particularly useful functional group under all performed conditions. It proved stable, was easily purified by column chromatography and forms in most cases crystalline solids and yielded five out of the six recorded crystal structures.

Perhaps most important to the reaction development chemist, many of the novel chemical reactivities – the only working olefin RCM, the MnO_2-mediated aminoalkylation, the ethoxylation described in section 3.2. – have been observed solely for the phosphinesulfide derivative, clearly pointing out the potential of the as to yet rarely used phosphinesulfide functional group in reaction discovery.

5. Experimental part

5. 1. General experimental part

Abs. THF was dried by distillation from sodium benzophenonketyl under Ar. Et_2O and *n*-pentane were dried by distillation over $LiAlH_4$, MeCN and DCM by distillation from CaH_2 in ambient atmosphere.

Reaction progress was monitored by TLC, SiO_2 or Al_2O_3 sheets with F_{254} fluorescent indicator.

Preparative column chromatography was carried out by an Biotage Isolera One automated flash chromatography instrument using self-packed columns containing either SiO_2 – Macherey-Nagel silica gel 60M (particle size 40-63 µm) – or Al_2O_3 – Merck aluminum oxide 90 standardized (activation grade II-III).

Melting points were measured on a Reichelt Thermovar Kofler apparatus, uncorrected.

HPLC analysis was performed on an Agilent Technologies 1200 series system using a Chiralcel OD-H chiral column.

Routine NMR spectra were recorded on a 400 MHz Bruker AVIII 400 spectrometer operating at 400.27 MHz (^{1}H), 100.66 MHz (^{13}C) and 162.04 MHz (^{31}P) with autosampler. ^{1}H-NMR spectra, ^{13}C{^{1}H}-NMR spectra and 2D spectra used for substance characterization were recorded either on a 600 MHz Bruker AVIII 600 spectrometer operating at 600.25 MHz (^{1}H) and 150.95 MHz (^{13}C) or on a Bruker AVIII 700 spectrometer at 700.40 MHz (^{1}H) and 176.13 MHz (^{13}C).

^{13}C{^{1}H}-NMR spectra were recorded in J-modulated mode. NMR chemical shifts are referenced to non-deuterated $CHCl_3$ residual shifts: At 7.26 ppm for ^{1}H-NMR, at 77.00 ppm to $CDCl_3$ for ^{13}C-NMR and at 0.00 ppm to 85% H_3PO_4 for ^{31}P-NMR.

Coupling patterns in ^{1}H-NMR and ^{13}C{^{1}H}-NMR spectra are denoted using standard abbreviations s (singlet), d (duplet), t (triplet), q (quartet), m (multiplet) and p (pseudo). For ^{13}C{^{1}H}-NMR spectra carbon resonances were identified as C_q, CH, CH_2 and CH_3.

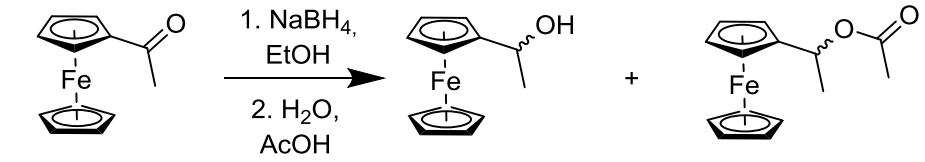
HRMS were recorded by a Bruker Maxis ESI oa-RTOF mass spectrometer equipped with a quadrupole analyzer ion guide.

5. 2. Specific experimental part

In this section, experimental procedures newly developed or modified from published procedures are presented. Spectral data are given only for new compounds.

5. 2. 1. Synthesis of Ugi's amine from ferrocene

Synthesis of *rac.* 1-(1-Hydroxyethyl)ferrocene and 1-(1-Acetoxyethyl)ferrocene



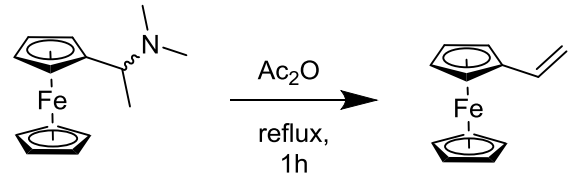
4
$C_{12}H_{12}FeO$
228,072 g/mol

3
$C_{12}H_{14}FeO$
230,088 g/mol
37%

2
$C_{14}H_{16}FeO_2$
272,125 g/mol
20%

Procedure: Acetylferrocene ***4*** (8.250 g, 36.17 mmol) was suspended in 120 mL of EtOH abs. under Ar. $NaBH_4$ (0.567 g, 14.99 mmol, 0.41 eq) was added and the red solution was stirred at 28°C for 18 h. A crude ^{1}H-NMR spectrum was recorded and a second crop of $NaBH_4$ (0.856 g, 22.63 mmol, 0.63 eq) was added to the only partially reacted mixture. After 6 h of stirring the solvent was removed under reduced pressure and the residue was dissolved in 100 mL of water and 100 mL of EtOAc. AcOH was added until no more gas evolved (ca. 15 mL), the organic layer was separated and the aq. layer was extracted three times with 80 mL of EtOAc. The combined organic extracts were washed with 100 mL of water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the black viscous residue was dried. The crude product was purified by column chromatography (SiO_2; 5→40% EtOAc in *n*-heptane), yielding 37% of alcohol ***3*** (3.047 g) as an orange solid and 20% of acetate ***2*** (1.933 g) as a yellow solid.

Synthesis of Vinylferrocene from Ugi's amine



1
$C_{14}H_{19}FeN$
257,158 g/mol

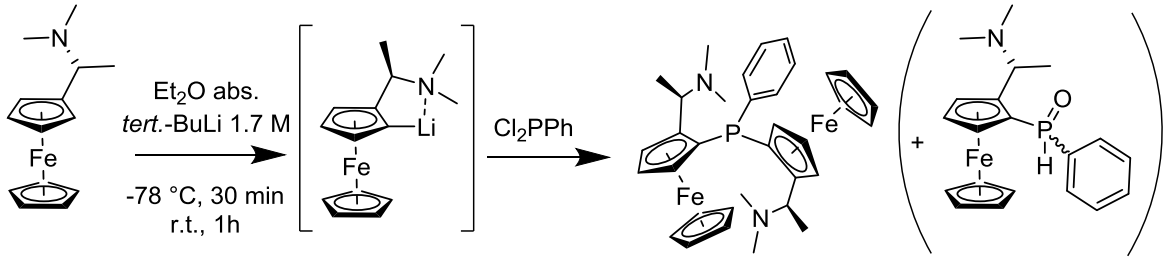
$C_{12}H_{12}Fe$
212,073 g/mol
22%

Procedure: [80] *Rac.* amine ***1*** (660 mg, 2.57 mmol) was dissolved in 4 mL of Ac_2O and stirred for 1 h at 100 °C in ambient atmosphere, the color of the solution changing from clear orange to murky brown. The suspension was cooled to r.t. and Ac_2O was removed under reduced pressure. The viscous black residue was filtered through paper and the residue washed after with 15 mL of Ac_2O. The resulting suspension was dried under reduced pressure and the solid brown residue was purified via column chromatography (SiO_2, 5→40% EtOAc in *n*-heptane), yielding 22% of vinylferrocene (119 mg) as orange crystals.

5. 2. 2. α-Substituted di(ferrocenylethylene) compounds

5. 2. 2. 1. P(III) and P(V) linked diferrocenes

Synthesis of 1,1‘‘-(Phenylphosphinidene)bis[(2*S*)-2-[(1*R*)-1-(dimethylamino)-ethyl]]ferrocene



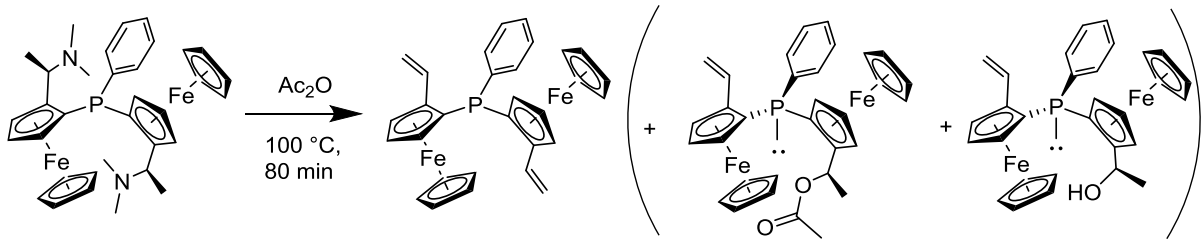
1
$C_{14}H_{19}FeN$
257,158 g/mol

6
$C_{34}H_{41}Fe_2N_2P$
620,380 g/mol
60%

7
$C_{20}H_{24}FeNOP$
381,237 g/mol

Procedure: [61] Amine ***1*** (5.165 g, 20.08 mmol) was dissolved in 50 mL of dry Et_2O in a flame-dried Schlenck tube under Ar. The orange solution was degassed three times, then cooled to -78 °C and *tert.*-BuLi solution (1.7 M in *n*-pentane; 12 mL, 20.4 mmol, 1.02 eq) was added slowly. The solution was stirred for 30 min at this temperature, warmed to r.t., and stirred for 1 h. The deep red solution was cooled to -78 °C and Cl_2PPh (1.4 mL, 10.32 mmol, 0.51 eq) was added dropwise. The resulting solution was stirred while warming up to r.t. overnight. Water (60 mL) was added to the orange suspension, followed by DCM to dissolve residual solid material. The aq. layer was separated, the organic layer was washed three times with 60 mL of water then three times with 60 mL of brine. The reddish organic fraction was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The orange solid was purified via column chromatography (SiO_2; 66% Et_2O, 33% *n*-heptane, 1% Et_3N) yielding 60% of diaminophosphine ***6*** (3.743 g) as a red crystalline solid.

Synthesis of 1,1‘‘-(Phenylphosphinidene)di[(2*S*)-2-vinyl]ferrocene



6
$C_{34}H_{41}Fe_2N_2P$
620,380 g/mol

8
$C_{30}H_{27}Fe_2P$
530,210 g/mol
74%

9
$C_{32}H_{31}Fe_2O_2P$
590,262 g/mol

10
$C_{30}H_{29}Fe_2OP$
548,225 g/mol

Procedure: [80] Diaminophosphine ***6*** (760 mg, 1.26 mmol) was suspended in 6.3 mL of Ac_2O in a flame-dried Schlenck tube under Ar. The orange solution was degassed three times, then stirred and heated to about 100 °C (oil bath temperature ~120 °C) for 80 min while the starting material dissolved and the color of the solution changed gradually from orange via red to black. The mixture was cooled to r.t. and Ac_2O was removed under reduced pressure. The black residue was dried and purified by column chromatography (SiO_2; 0→10% EtOAc in *n*-heptane) yielding 74% of divinylphosphine ***8*** (481 mg) as an orange-to-reddish crystalline solid.

Divinyl compound ***8***:

M.p.: 168-169 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.54-7.50 (m, 2H); 7.34-7.30 (m, 3H); 7.23 (ddd, *J* = 17.8, 10.8, 2.7 Hz, 1H); 6.54 (ddd, *J* = 17.5, 10.9, 1.4 Hz, 1H); 5.49 (dt, *J* = 17.6, 1.5 Hz, 1H); 5.22 (dt, *J* = 17.5, 1.3 Hz, 1H); 5.17 (dd, *J* = 10.8, 1.4 Hz, 1H); 4.90 (dd, *J* = 10.8, 1.4 Hz, 1H); 4.79 (m, 1H); 4.56 (m, 1H); 4.38 (pt, *J* = 2.6 Hz, 1H); 4.24 (pt, *J* = 2.5 Hz, 1H); 4.03 (s, 5H); 3.89 (s, 5H); 3.89 (m, 1H); 3.80 (m, 1H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 138.48 (d, J_{CP} = 8.1 Hz, C_q); 134.27 (d, J_{CP} = 13.4 Hz, CH); 134.12 (d, J_{CP} = 21.6 Hz, CH); 133.47 (d, J_{CP} = 9.4 Hz, CH); 127.80 (d, J_{CP} = 7.9 Hz,); 111.63 (d, J_{CP} = 1.8 Hz, CH_2); 110.91 (CH_2); 88.72 (d, J_{CP} = 24.7 Hz, C_q); 86.70 (d, J_{CP} = 18.2 Hz, C_q); 80.09 (d, J_{CP} = 6.2 Hz, C_q); 76.32 (d, J_{CP} = 9.6 Hz, C_q); 72.72 (d, J_{CP} = 5.6 Hz, CH); 71.94 (d, J_{CP} = 2.9 Hz, CH); 70.87 (d, J_{CP} = 23.4 Hz,

CH); 70.32 (CH); 70.22 (CH); 68.69 (CH); 67.34 (d, J_{CP} = 2.2 Hz, CH); 66.34 (d, J_{CP} = 3.6 Hz, CH) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = -41.89 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{27}Fe_2P$; $[M]^+$ 530.0549, found: 530.0548; $[M+H]^+$ 531.0627, found: 531.0616; $[M+Na]^+$ 553.0447, found: 553.0445.

Acetate ***9***:

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.52 (pt, *J* = 7.2 Hz, 2H); 7.35-7.28 (m, 3H); 7.23 (dd, *J* = 17.0, 10.6 Hz, 1H); 6.10 (m, 1H); 5.45 (d, *J* = 17.7 Hz, 1H); 5.13 (d, *J* = 10.8 Hz, 1H); 4.77 (m, 1H); 4.43 (m, 1H); 4.39 (m, 1H); 4.27(m, 1H); 4.04 (s, 5H); 3.96 (m, 1H); 3.95 (m, 1H); 3.81 (s, 5H); 1.56 (d, *J* = 6.3 Hz, 3H); 1.17 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 169.85 (C_q); 138.95 (d, J_{CP} = 8.3 Hz, C_q); 134.43 (d, J_{CP} = 13.7 Hz, CH); 134.14 (d, J_{CP} = 22.0 Hz, CH); 128.59 (CH); 127.71 (d, J_{CP} = 7.9 Hz, CH); 110.72 (CH_2); 90.08 (d, J_{CP} = 22.2 Hz, C_q); 88.67 (d, J_{CP} = 26.2 Hz, C_q); 80.91 (d, J_{CP} = 8.3 Hz, C_q); 76.25 (d, J_{CP} = 10.8 Hz, C_q); 72.90 (d, J_{CP} = 5.7 Hz, CH); 72.08 (d, J_{CP} = 4.0 Hz, CH); 70.51 (CH); 70.24 (CH); 69.67 (CH); 68.80 (d, J_{CP} = 3.2 Hz, CH); 68.54 (CH); 68.28 (d, J_{CP} = 8.9 Hz, CH); 66.19 (d, J_{CP} = 3.9 Hz, CH); 20.26 (CH_3); 18.74 (CH_3) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = -45.17 (s) ppm.

HRMS: m/z calculated for M = $C_{32}H_{31}Fe_2O_2P$; $[M+O+Na]^+$ 629.0607, found 629.0590.

Alcohol ***10***:

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.65-7.60 (m, 2H); 7.40-7.35 (m, 3H); 7.21 (ddd, *J* = 17.5, 10.8, 2.4 Hz, 1H); 5.49 (d, *J* = 17.5 Hz, 1H); 5.17 (pd, *J* = 10.9 Hz, 1H); 4.87 (m, 1H); 4.80 (m, 1H); 4.41 (m, 1H); 4.34 (m, 1H); 4.19 (pt, *J* = 2.3 Hz, 1H); 4.07 (s, 5H); 4.03 (s, 1H); 3.86 (s, 5H); 3.83 (m, 1H); 1.38 (d, *J* = 6.5 Hz, 3H); 1.10 (s, 1H) ppm.

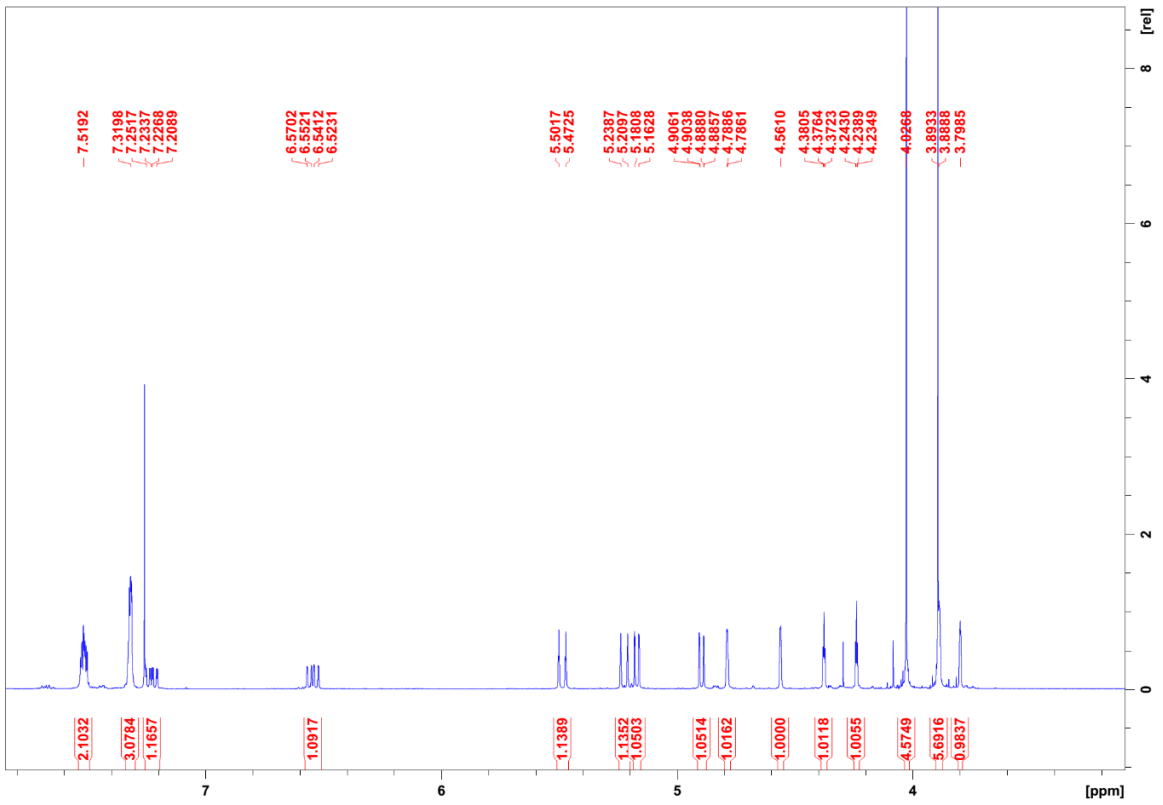
^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 139.36 (d, J_{CP} = 8.2 Hz, C_q); 134.27 (d, J_{CP} = 22.1 Hz, CH); 134.11 (d, J_{CP} = 13.7 Hz, CH); 129.52 (CH); 128.41 (d, J_{CP} = 8.0 Hz, CH); 111.13 (CH_2); 94.96 (d, J_{CP} = 18.9 Hz, C_q); 88.96 (d, J_{CP} = 26.0 Hz, C_q); 79.83

(d, J_{CP} = 6.1 Hz, C_q); 75.04 (d, J_{CP} = 10.1 Hz, C_q); 72.58 (d, J_{CP} = 5.7 Hz, CH); 71.30 (d, J_{CP} = 3.2 Hz, CH); 70.67 (CH); 70.18 (CH); 69.56 (CH); 68.45 (d, J_{CP} = 3.3 Hz, CH); 68.12 (CH); 66.54 (d, J_{CP} = 4.0 Hz, CH); 65.48 (d, J_{CP} = 6.9 Hz, CH); 21.74 (CH_3) ppm.

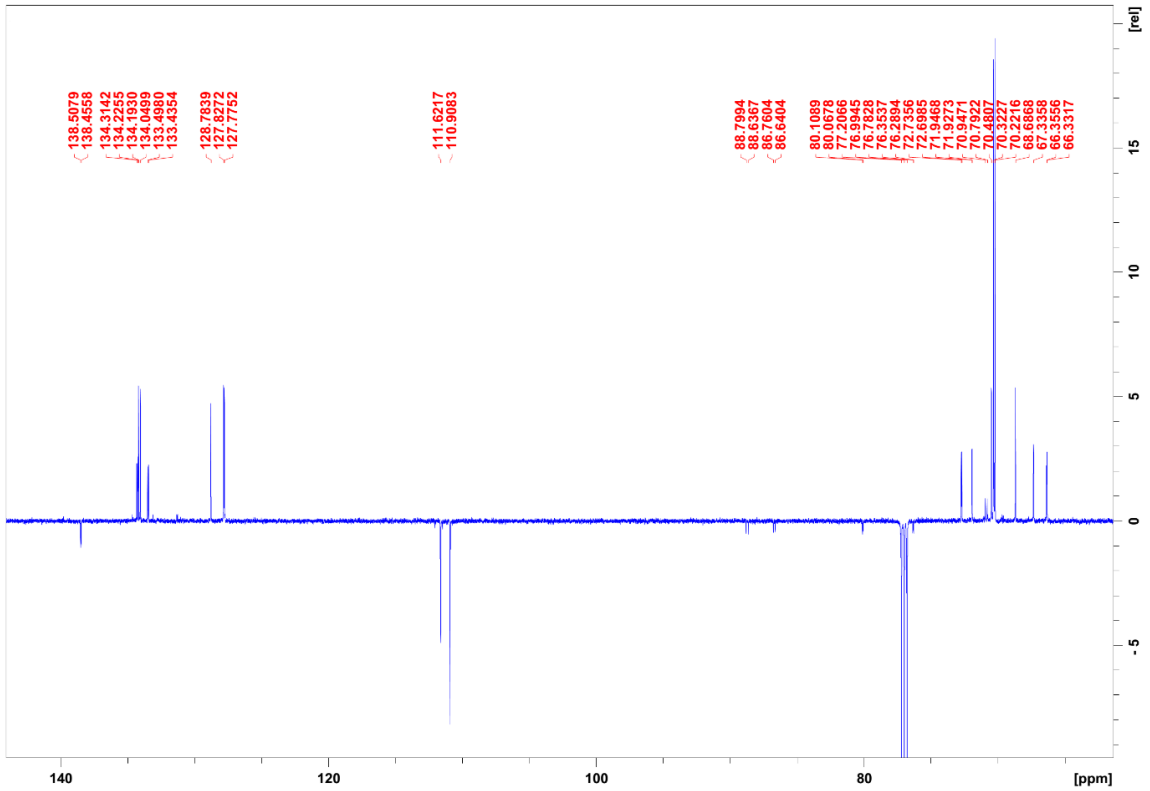
^{31}P-NMR (400 MHz, $CDCl_3$) δ = -42.86 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{29}Fe_2OP$; $[M+H]^+$ 549.0733, found: 549.0711; $[M+Na]^+$ 571.0553, found: 571.0539.

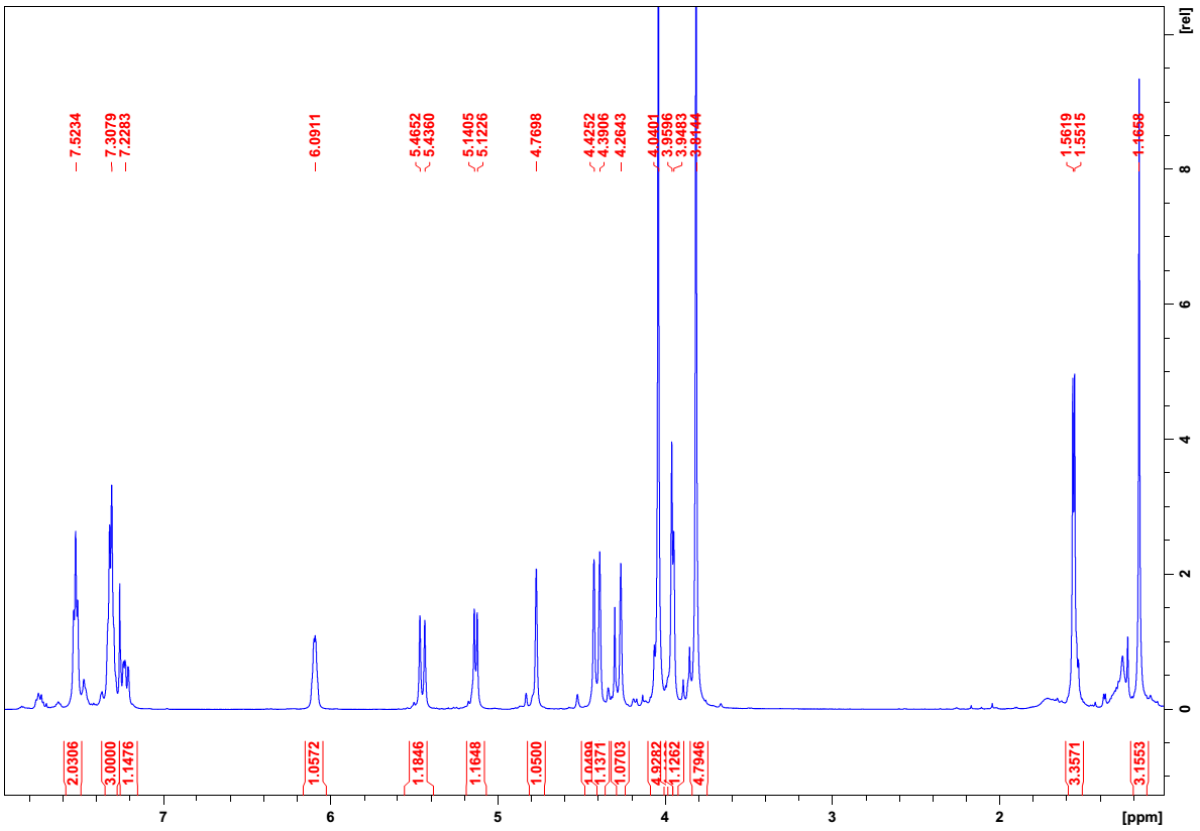
^{1}H-NMR (Divinylphosphine ***8***):



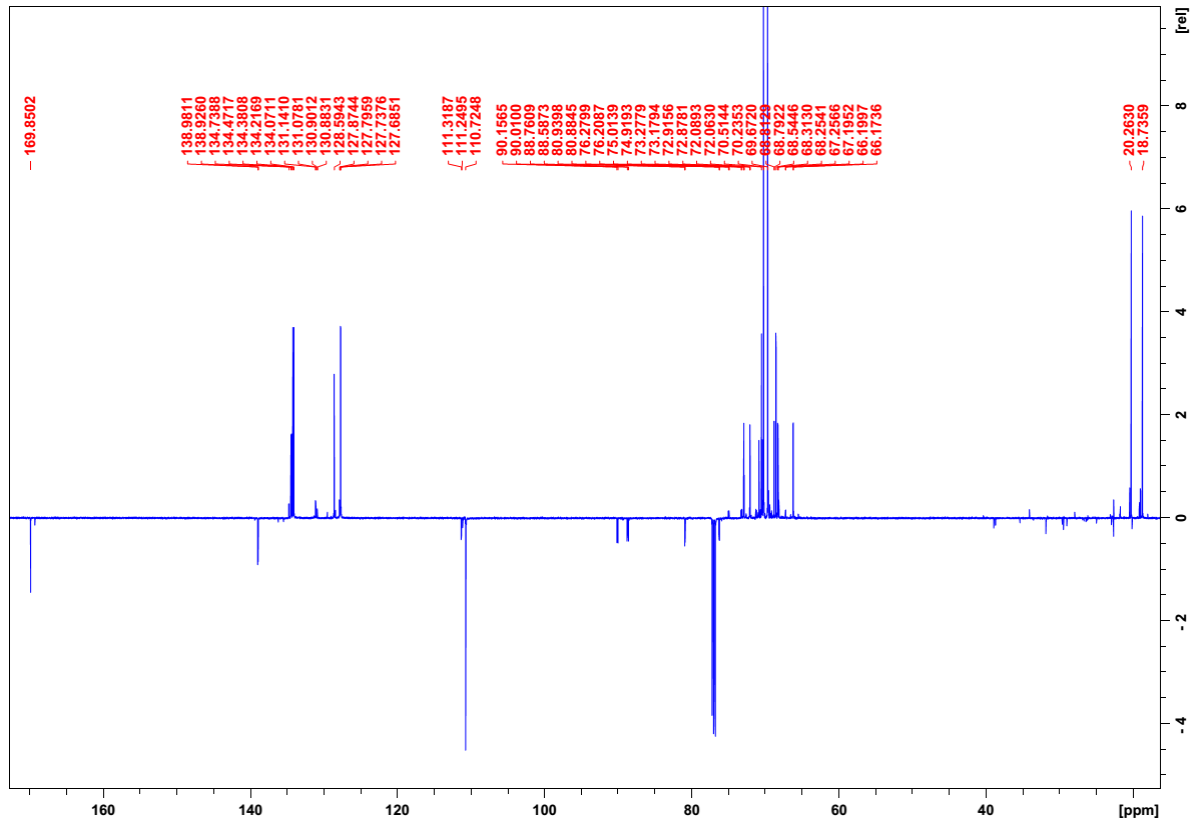
^{13}C{^{1}H}-NMR (Divinylphosphine ***8***):



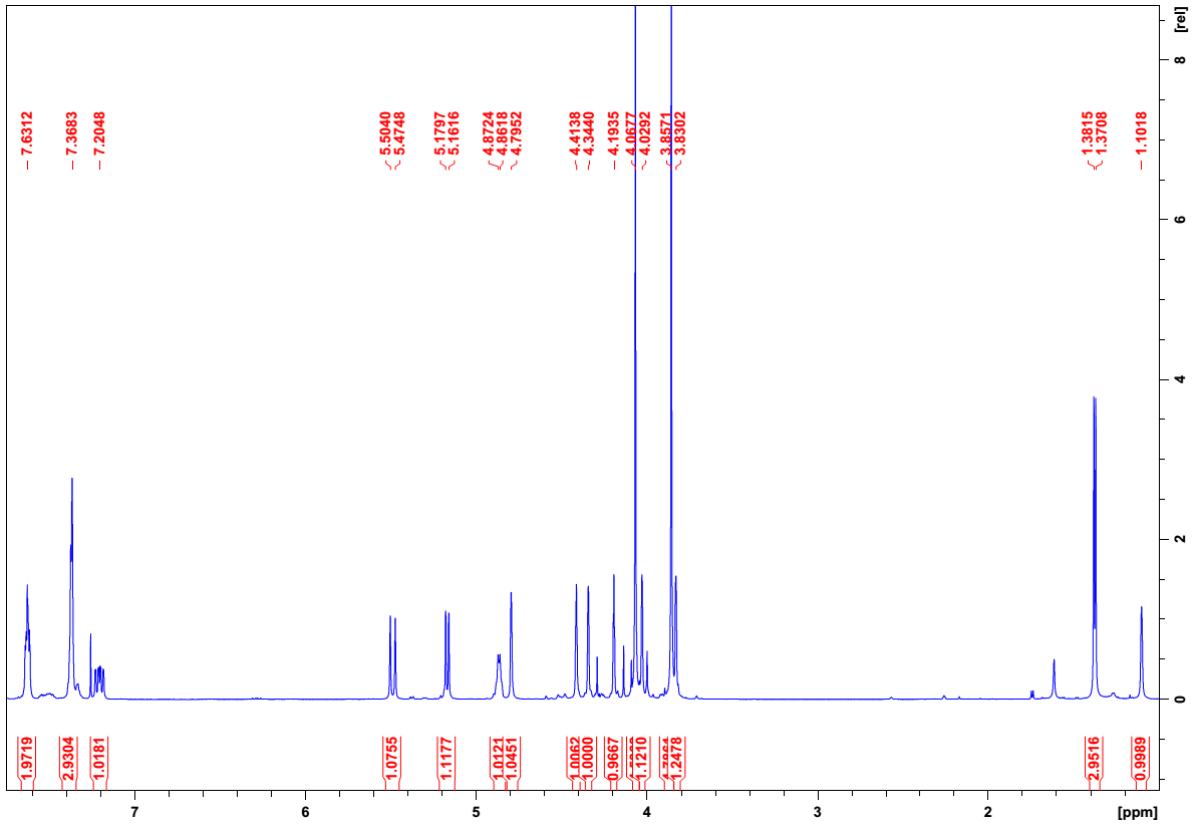
^{1}H-NMR (Acetate ***9***):



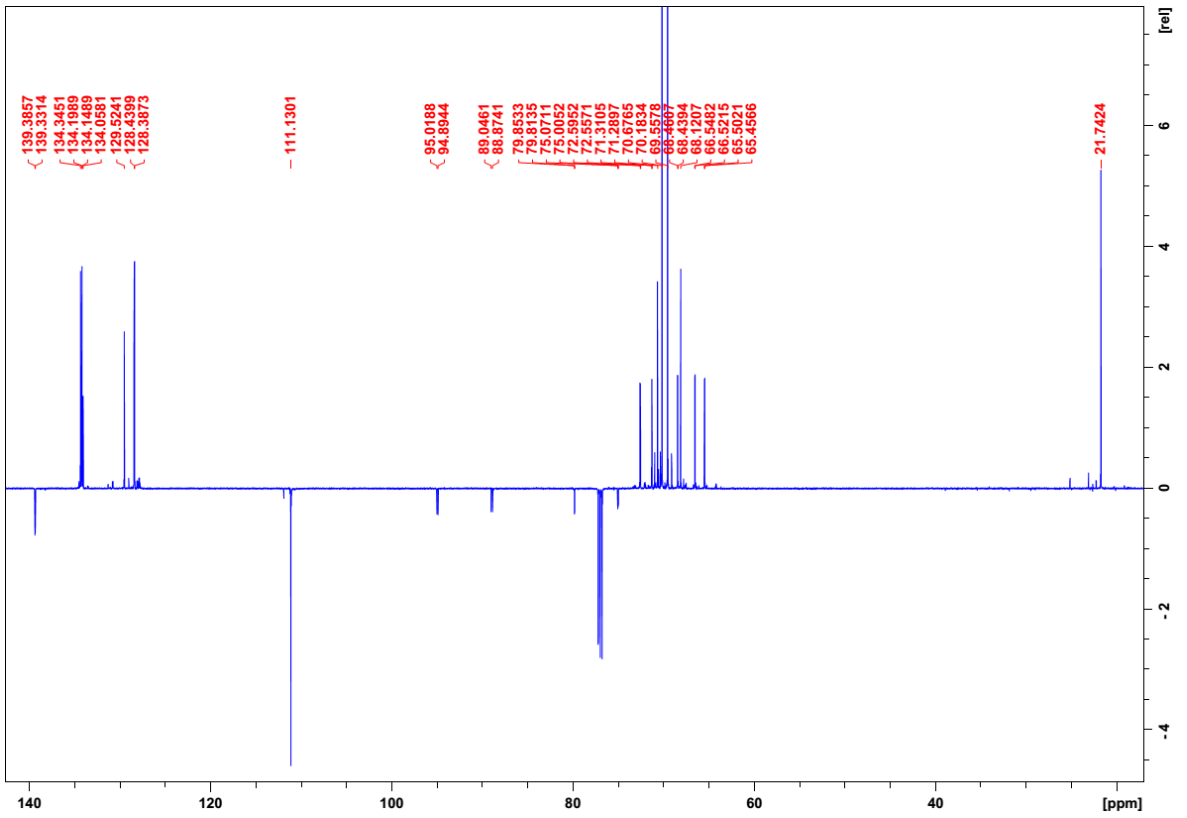
^{13}C{^{1}H}-NMR (Acetate ***9***):



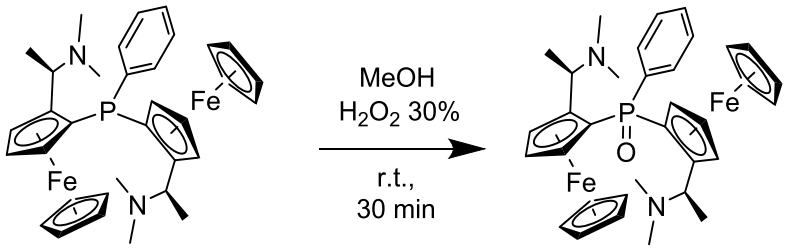
^{1}H-NMR (Alcohol ***10***):



^{13}C{^{1}H}-NMR (Alcohol ***10***):



Synthesis of 1,1''-(Phenylphosphinideneoxide)bis[(2*S*)-2-[(1*R*)-1-(dimethylamino)-ethyl]]ferrocene



6
$C_{34}H_{41}Fe_2N_2P$
620,380 g/mol

11
$C_{34}H_{41}Fe_2N_2OP$
636,379 g/mol
100%

Procedure: [26] Diaminophosphine ***6*** (630 mg, 1.02 mmol) was dissolved in 8.0 mL of MeOH and cooled an ice bath. Aq. H_2O_2 (30%; 210 µL, 1.85 mmol, 1.82 eq) was added to the orange solution. The solution was warmed to r.t. and stirred for 40 min. The reaction mixture was quenched by adding 10% aq. $NaHSO_3$. A sat. aq. solution of $NaHCO_3$ was added to the suspension until a pH of 7 was reached. The aq. suspension was extracted three times with 8 mL of DCM. The combined organic fractions were dried over $MgSO_4$ and the solvent was removed under reduced pressure yielding diaminophosphineoxide ***11*** quantitatively (647 mg) as an orange solid. The highly polar product was pure enough not to require further purification.

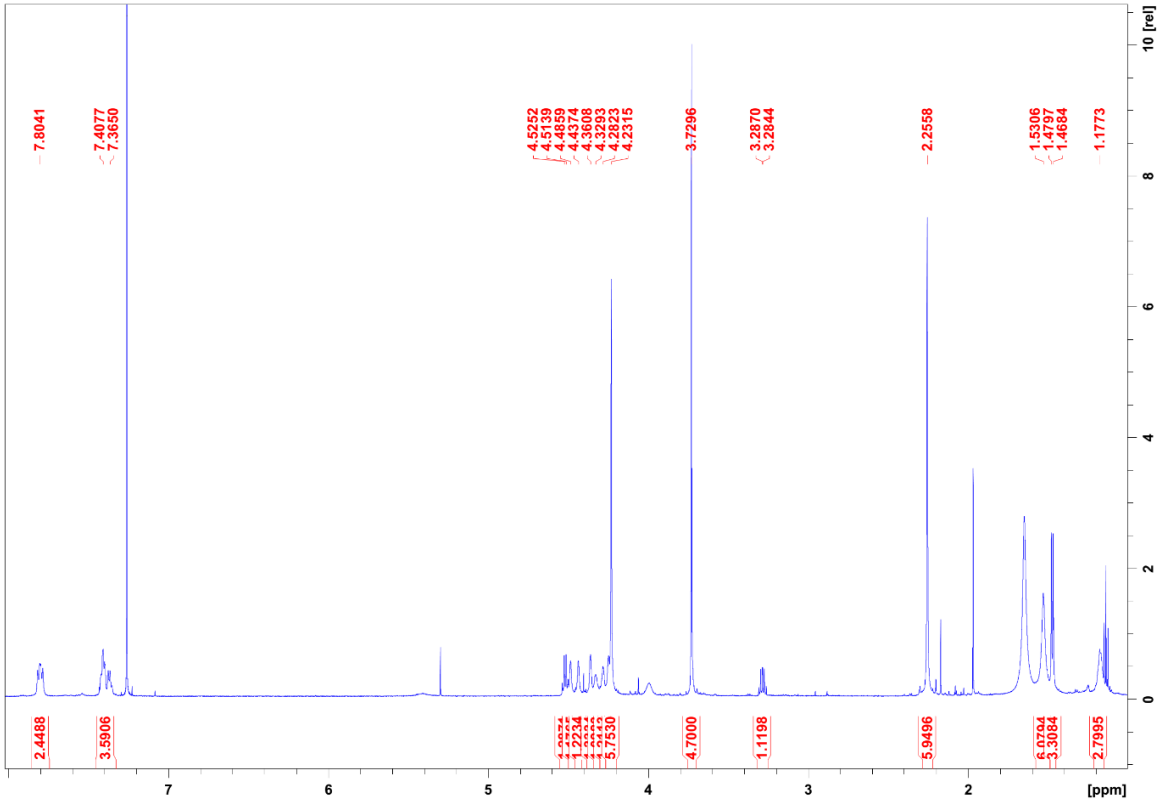
^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.80 (dd, *J* = 11.4, 8.0 Hz, 2H); 7.43-7.35 (m, 3H); 4.52 (q, *J* = 6.8 Hz, 1H); 4.49 (m, 1H); 4.44 (m, 1H); 4.36 (m, 1H); 4.33 (m, 1H); 4.28 (m, 1H); 4.25 (m, 1H); 4.23 (s, 5H); 3.73 (s, 5H); 3.31-3.26 (m, 1H); 2.26 (s, 6H); 1.53 (s, 6H); 1.47 (d, *J* = 6.8 Hz, 3H); 1.21-1.15 (m, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 130.07 (d, J_{CP} = 9.2 Hz, CH); 129.44 (CH); 127.20 (CH); 89.90 (C_q); 85.23 (C_q); 75.14 (C_q); 73.60 (CH); 71.89 (CH); 71.25 (C_q); 71.72 (d, J_{CP} = 14.9 Hz, CH); 70.34 (CH); 70.20 (CH); 69.59 (d, J_{CP} = 9.8 Hz, CH); 69.32 (CH); 67.91 (CH); 55.17 (CH); 40.97 (CH_3); 34.66 (CH); 14.93 (CH_3); 13.05 (CH_3); 13.04 (CH_3) ppm.

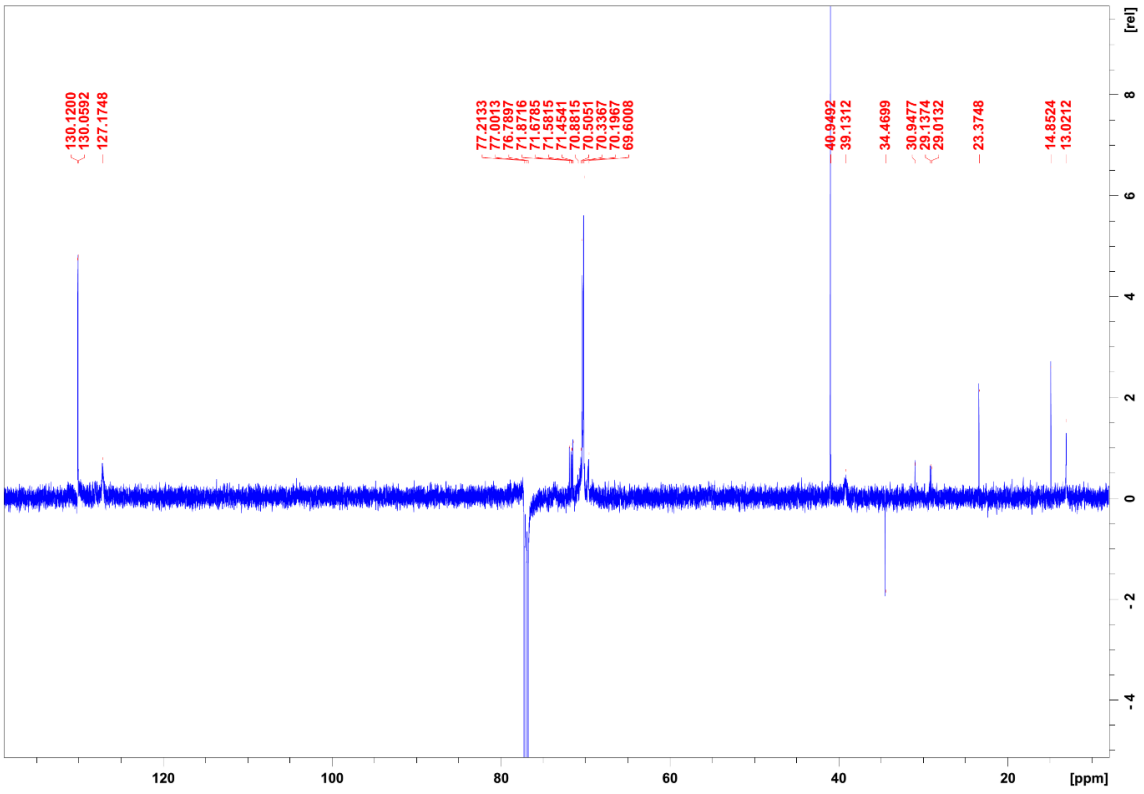
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 29.59 (s) ppm.

HRMS: m/z calculated for M = $C_{34}H_{41}Fe_2N_2OP$; $[M+H]^+$ 637.1734, found: 637.1726.

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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71.6735
71.5845
71.4541
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14.8524
13.0212
[rel]
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6
4
2
0
-2
-4
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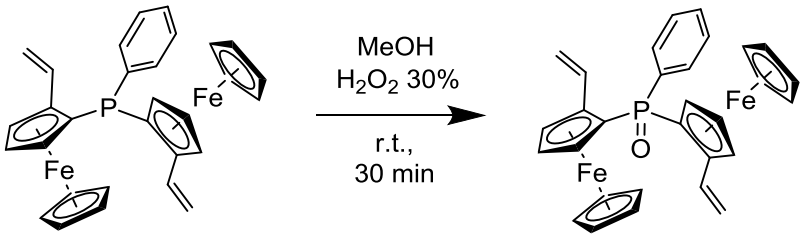
80
60
40
20
[ppm]

Synthesis of 1,1''-(Phenylphosphinideneoxide)di[(2*S*)-2-vinyl]ferrocene



8
$C_{30}H_{27}Fe_2P$
530,210 g/mol

12
$C_{30}H_{27}Fe_2OP$
546,209 g/mol
99%

Procedure: [26] Divinylphosphine ***8*** (196 mg, 0.37 mmol) was suspended in 3.2 mL of MeOH and cooled in an ice bath. Aq. H_2O_2 (30%; 90 µL, 0.80 mmol, 2.15 eq) was added to the mixture. The suspension was warmed to r.t. and stirred for 1 h. The reaction mixture was quenched by adding 10% aq. $NaHSO_3$. The aq. suspension was extracted two times with 4 mL of DCM. The combined organic fractions were washed with 4 mL of volume of water and dried over $MgSO_4$. The solvent was removed under reduced pressure. The product was purified by column chromatography (SiO_2; 0→40% EtOAc in *n*-heptane) yielding divinylphosphineoxide ***12*** quantitatively (201 mg) as an orange-to-reddish solid.

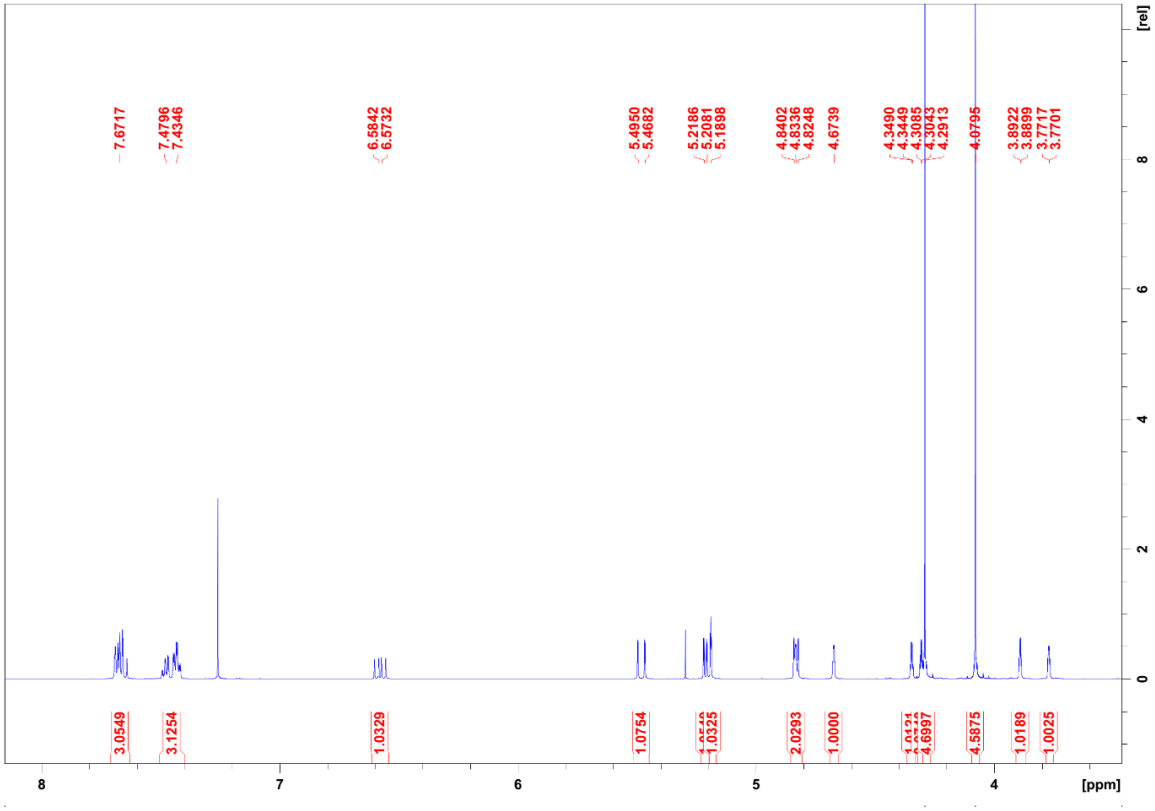
^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.70-7.64 (m, 3H); 7.50-7.41 (m, 3H); 6.58 (dd, *J* = 17.5, 10.9 Hz, 1H); 5.48 (dd, *J* = 17.7, 1.7 Hz, 1H); 5.21 (dd, *J* = 7.9, 1.6 Hz, 1H); 5.19 (pt, *J* = 1.4 Hz, 1H); 4.83 (m, 1H); 4.83 (dd, *J* = 10.8, 1.6 Hz, 1H); 4.67 (m, 1H); 4.35 (m, 1H); 4.31 (m, 1H); 4.29 (s, 5H); 4.08 (s, 5H); 3.89 (m, 1H); 3.77 (m, 1H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 135.17 (d, J_{CP} = 108.9 Hz, C_q); 134.61 (CH); 133.10 (CH); 131.29 (d, J_{CP} = 9.5 Hz, CH); 131.06 (d, J_{CP} = 2.6 Hz, CH); 127.79 (CH); 112.06 (CH_2); 111.48 (CH_2); 88.23 (d, J = 10.3 Hz, C_q); 86.03 (d, J_{CP} = 10.9 Hz, C_q); 75.26 (d, J_{CP} = 14.6 Hz, CH); 73.40 (d, J_{CP} = 15.3 Hz, CH); 72.70 (C_q); 71.93 (C_q); 71.02 (d, J_{CP} = 11.4 Hz, CH); 70.94 (CH); 70.79 (CH); 69.72 (d, J_{CP} = 11.4 Hz, CH); 67.74 (d, J_{CP} = 9.4 Hz, CH); 67.34 (d, J_{CP} = 9.3 Hz, CH) ppm; 2 C_q not found.

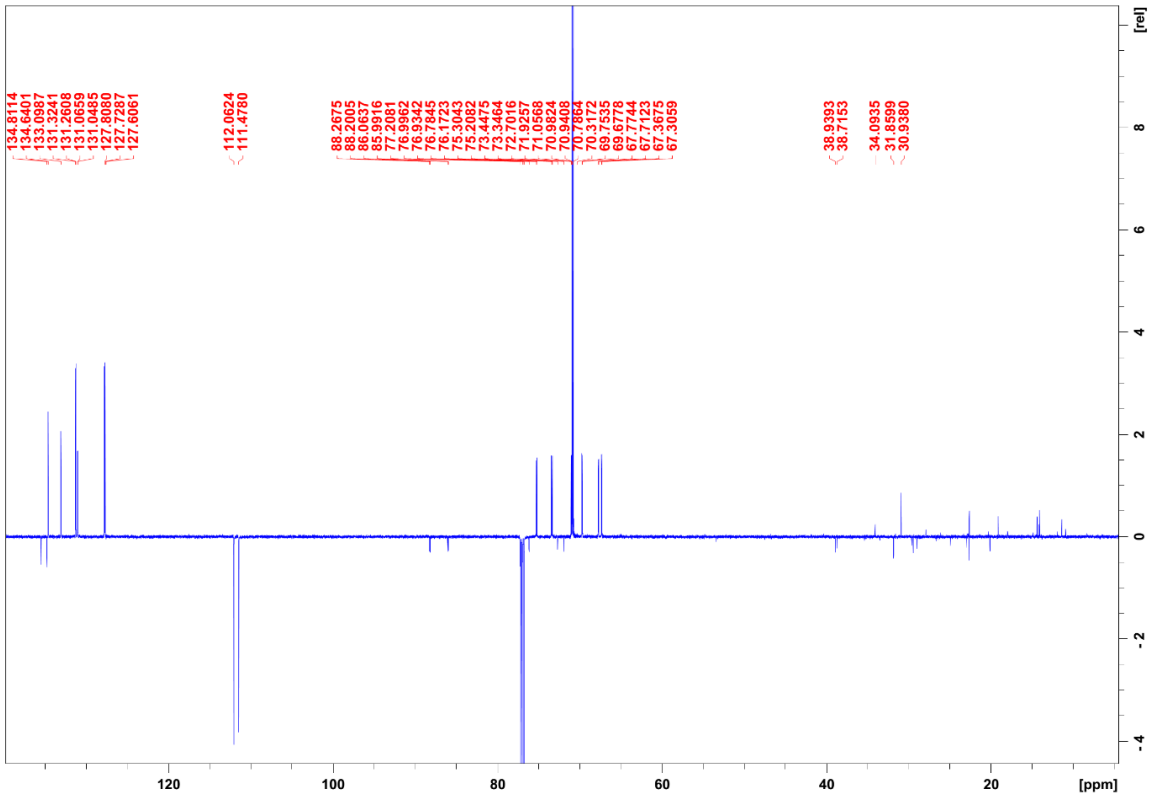
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 30.48 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{27}Fe_2OP$; $[M]^+$ 546.0498, found: 546.0498; $[M+H]^+$ 547.0577, found: 547.0560; $[M+Na]^+$ 569.0396, found: 569.0394; $[2M+Na]^+$ 1115.0894, found: 1115.0885.

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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88.2675
88.2005
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77.2081
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75.3043
73.4092
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70.9824
70.9408
70.7864
70.3172
69.7535
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31.8599
30.9380
[rel]
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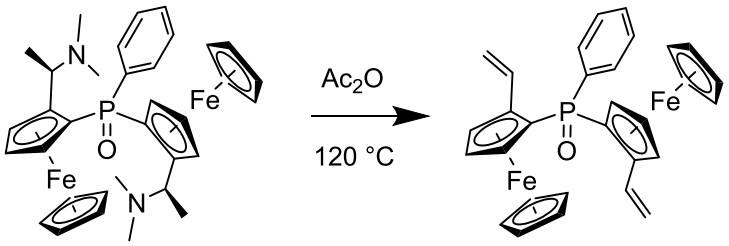
4
2
0
-2
-4
120
100
80
60
40
20
[ppm]

Synthesis of 1,1‘‘-(Phenylphosphinideneoxide)di[(2*S*)-2-vinyl]ferrocene

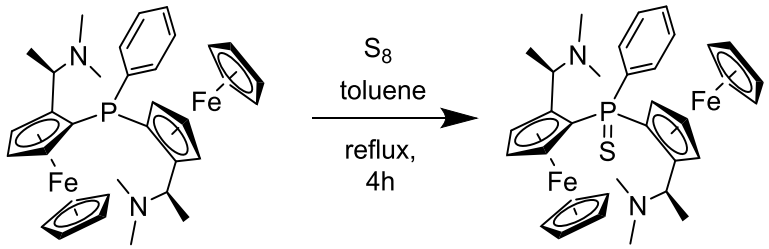


11
$C_{34}H_{41}Fe_2N_2OP$
636,379 g/mol

12
$C_{30}H_{27}Fe_2PO$
546,209 g/mol
15%

Procedure: [80] Diaminophosphineoxide ***11*** (130 mg, 0.20 mmol) was suspended in 1 mL of Ac_2O in a flame-dried Schlenck tube under Ar. The orange solution was degassed three times, then stirred and heated (oil bath temperature 120 °C) until the initial orange suspension turned to black. The mixture was cooled to r.t. and Ac_2O was removed under reduced pressure. The residue was purified via column chromatography (SiO_2; 0→95% EtOAc in *n*-heptane) yielding 15% of divinylphosphineoxide ***12*** (17 mg) as an orange solid.

Synthesis of 1,1‘‘-(Phenylphosphinidenesulfide)bis[(2*S*)-2-[(1*R*)-1-(dimethylamino)-ethyl]]ferrocene



6
$C_{34}H_{41}Fe_2N_2P$
620,380 g/mol

13
$C_{34}H_{41}Fe_2N_2PS$
652,440 g/mol
100%

Procedure: [77] Diaminophosphine ***6*** (315 mg, 0.51 mmol) and sulfur (100 mg, 3.12 mmol, 6.14 eq) were dissolved in 4 mL of toluene in a flame-dried Schlenck tube under Ar. The solution was degassed three times, then stirred and heated under reflux for 4 h, then cooled to r.t. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2; 1.5% Et_3N in Et_2O) yielding diaminophosphinesulfide ***13*** quantitatively (331 mg) as an orange oil.

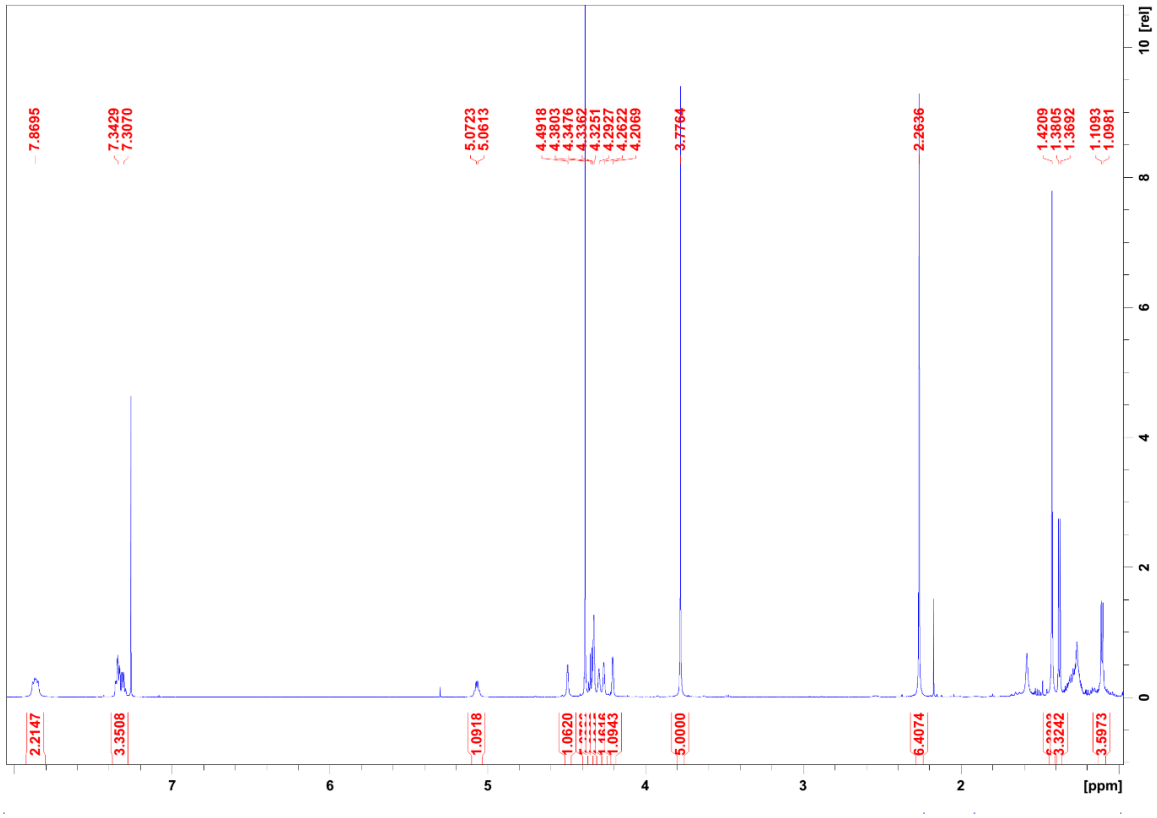
^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.87 (dd, *J* = 12.8, 7.6 Hz, 2H); 7.37-7.29 (m, 3H); 5.07 (q, *J* = 6.7 Hz, 1H); 4.49 (m, 1H); 4.38 (s, 5H); 4.34 (q, *J* = 6.8 Hz, 1H); 4.32 (m, 2H); 4.29 (m, 1H); 4.26 (m, 1H); 4.21 (m, 1H); 3.78 (s, 5H); 2.26 (s, 6H); 1.42 (s, 6H); 1.38 (d, *J* = 6.8 Hz, 3H); 1.10 (d, *J* = 6.7 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 138.19 (d, J_{CP} = 91.5 Hz, C_q); 131.17 (d, J_{CP} = 10.2 Hz, CH); 129.14 (d, J_{CP} = 2.5 Hz, CH); 126.47 (d, J_{CP} = 12.3 Hz, CH); 98.11 (d, J_{CP} = 11.8 Hz, C_q); 93.84 (d, J_{CP} = 11.4 Hz, C_q); 79.18 (d, J_{CP} = 96.6 Hz, C_q); 74.37 (d, J_{CP} = 11.6 Hz, CH); 74.07 (d, J_{CP} = 11.6 Hz, CH); 72.27 (d, J_{CP} = 94.20 Hz, C_q); 70.87 (CH); 70.59 (d, J_{CP} = 9.6 Hz, CH); 70.47 (CH); 70.44 (d, J_{CP} = 9.4 Hz, CH); 68.64 (d, J_{CP} = 9.7 Hz, CH); 66.57 (d, J_{CP} = 10.5 Hz, CH); 54.91 (CH); 53.67 (CH); 40.35 (CH_3); 38.55 (CH_3); 10.97 (CH_3); 8.95 (CH_3) ppm.

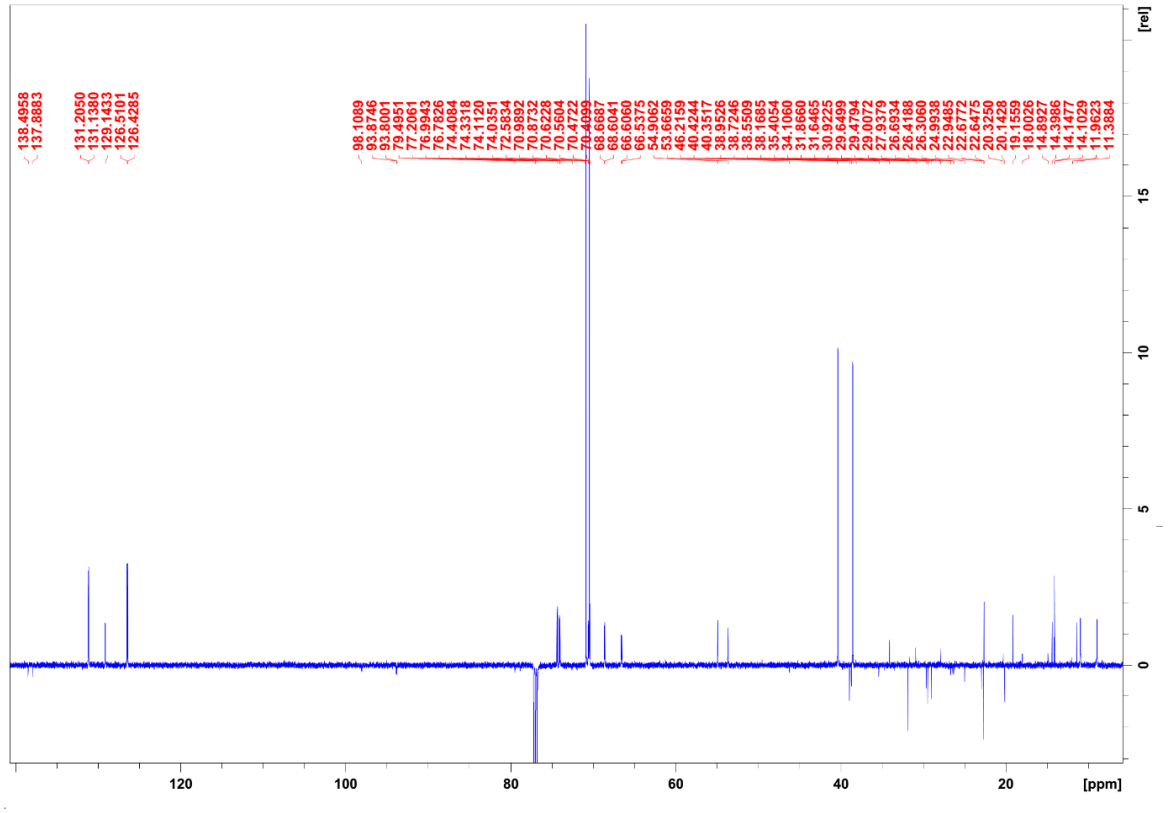
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 40.55 (s) ppm.

HRMS: m/z calculated for M = $C_{34}H_{41}Fe_2N_2PS$; $[M+H]^+$ 653.1505, found: 653.1507.

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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76.7826
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70.8732
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70.5604
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29.4794
29.0072
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26.3060
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22.8465
22.6472
22.6475
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14.1029
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11.3884
[rel]
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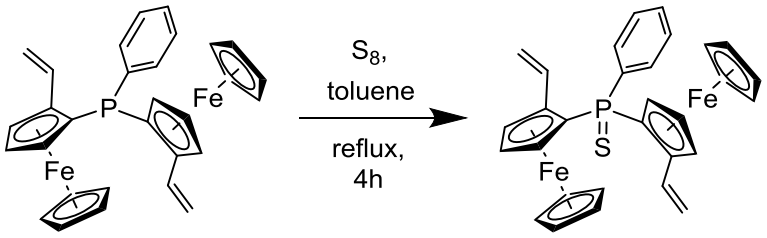
40
20
[ppm]

Synthesis of 1,1''-(Phenylphosphinidenesulfide)di[(2*S*)-2-vinyl]ferrocene



8
$C_{30}H_{27}Fe_2P$
530,210 g/mol

14
$C_{30}H_{27}Fe_2PS$
562,270 g/mol
100%

Procedure: [77] Divinylphosphine ***8*** (240 mg, 0.45 mmol) and sulfur (92 mg, 2.87 mmol, 6.34 eq) were dissolved in 3.6 mL of toluene in a flame-dried Schlenck tube under Ar. The solution was degassed three times, then stirred and heated under reflux for 4 h, then cooled to r.t. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2; 0→10% EtOAc in *n*-heptane) yielding divinylphosphinesulfide ***14*** quantitatively (255 mg) as orange crystals.

M.p.: 191-192 °C (decomposition).

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.11-8.04 (m, 1H); 7.73-7.67 (m, 2H); 7.47-7.37 (m, 3H); 6.95-6.88 (m, 1H); 5.52-5.46 (m, 1H); 5.24-5.17 (m, 1H); 5.21 (m, 1H); 4.86-4.82 (m, 2H); 4.71 (m, 1H); 4.36 (s, 5H); 4.28 (m, 1H); 4.26 (m, 1H); 4.23 (s, 5H); 3.72 (m, 1H); 3.51 (m, 1H) ppm.

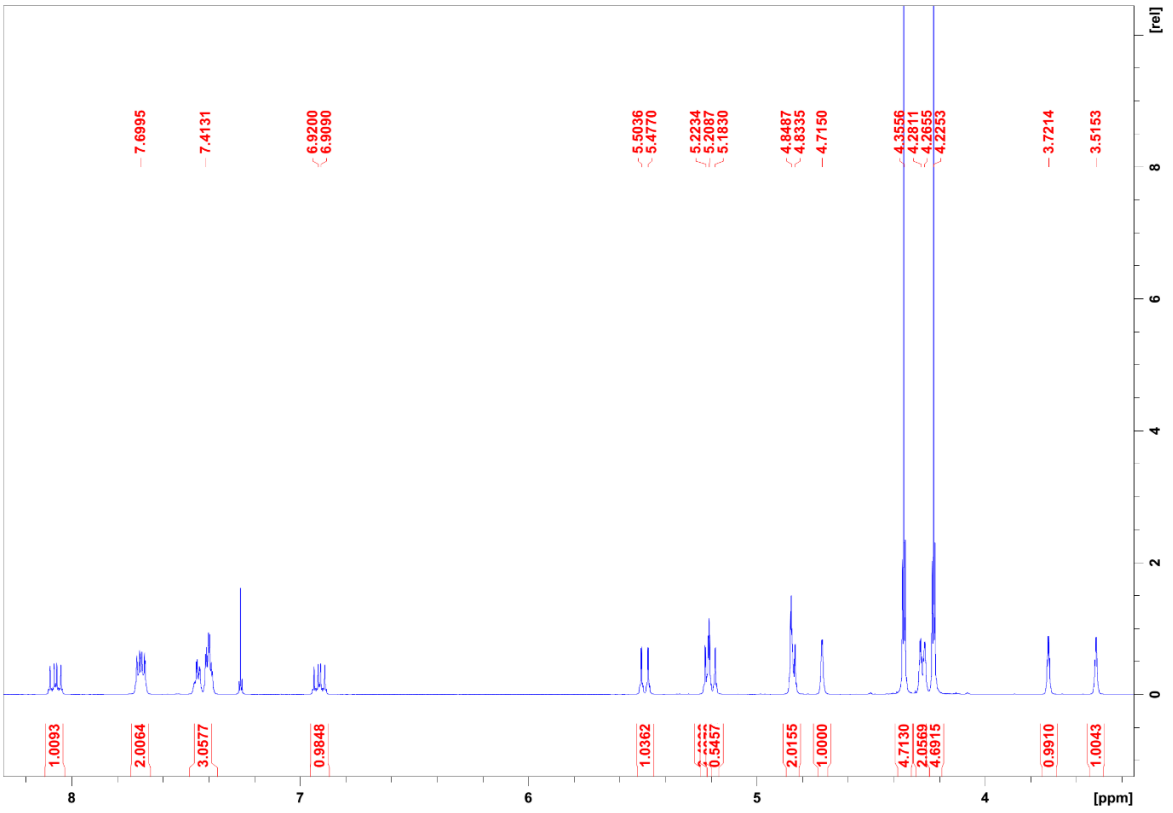
^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 134.63 (d, J_{CP} = 87.8 Hz, C_q); 134.37 (CH); 132.97 (CH); 132.18 (d, J_{CP} = 10.6 Hz, CH); 130.92 (d, J_{CP} = 2.9 Hz, CH); 127.58 (d, J_{CP} = 12.3 Hz, CH); 112.13 (CH_2); 111.61 (CH_2); 88.19 (d, J_{CP} = 11.6 Hz, C_q); 86.45 (d, J_{CP} = 11.5 Hz, C_q); 79.27 (C_q); 78.63 (C_q); 75.62 (d, J_{CP} = 11.8 Hz, CH); 74.48 (d, J_{CP} = 12.7 Hz, CH); 71.40 (CH); 71.10 (CH); 69.72 (d, J_{CP} = 10.4 Hz, CH); 68.66 (d, J_{CP} =10.5 Hz, CH); 68.02 (d, J_{CP} = 9.0 Hz, CH); 67.70 (d, J_{CP} = 9.1 Hz, CH) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 40.54 (s) ppm.

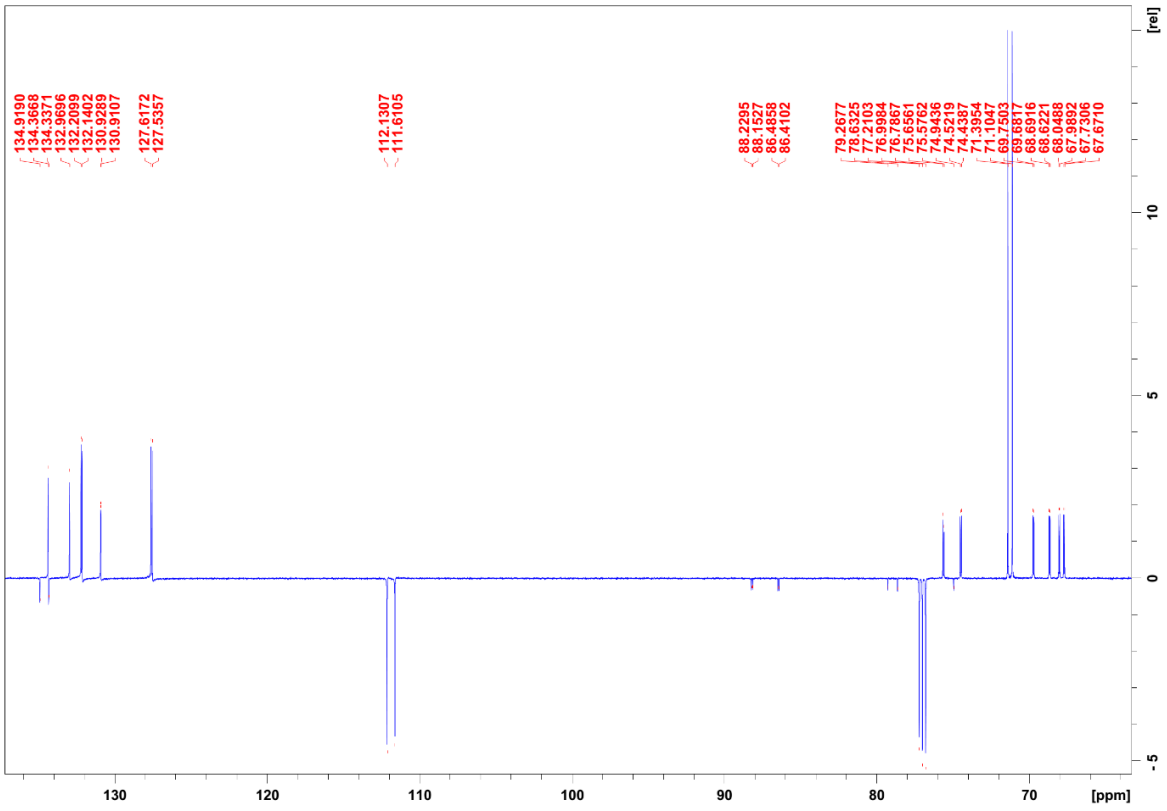
HRMS: m/z calculated for M = $C_{30}H_{27}Fe_2PS$; $[M]^+$ 562.0270, found: 562.0270; $[2M+Na]^+$ 1147.0438, found: 1147.0433.

Crystal data: monoclinic; space group $P2_1$; *a* = 8.4709 Å; *b* = 14.1401 Å; *c* = 21.031 Å; *α* = 90°; *β* = 91.88°; *γ* = 90°; *Z* = 4; *T* = -143.0 K; 32376 reflections measured; 8917 unique which were used in all calculations. The final *R1* was 0.0268 (I > 2σ(I)) and wR_2 was 0.0651 (all data).

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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74.4387
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68.6221
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67.7306
67.6710
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0
-5
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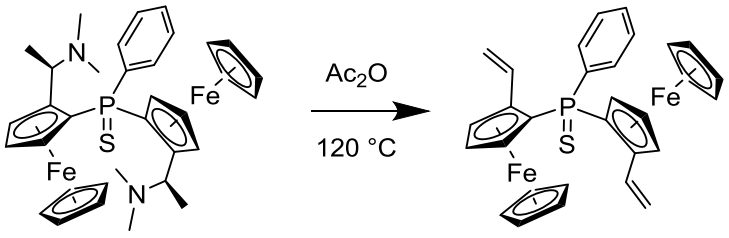
70
[ppm]

Synthesis of 1,1''-(Phenylphosphinidenesulfide)di[(2*S*)-2-vinyl]ferrocene

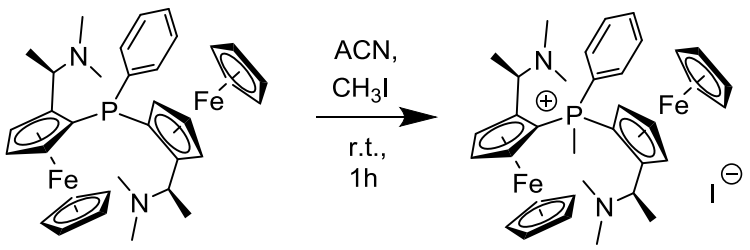


13
$C_{34}H_{41}Fe_2N_2PS$
652,440 g/mol

14
$C_{30}H_{27}Fe_2PS$
562,270 g/mol
39%

Procedure: [80] Diaminophosphinesulfide ***13*** (230 mg, 0.35 mmol) was suspended in 1.8 mL of Ac_2O in a flame-dried Schlenck tube under Ar. The orange solution was degassed three times, then stirred and heated (oil bath temperature 120 °C) until the initial orange suspension turned to a black solution via a red one. The mixture was cooled to r.t. and Ac_2O was removed under reduced pressure. The residue was purified by column chromatography (SiO_2; 0→10% EtOAc in *n*-heptane) yielding 39% of divinylphosphinesulfide ***14*** (76 mg) as an orange crystalline solid.

Synthesis of 1,1''-(Phenylmethylphosphinidenium)bis[(2*S*)-2-[(1*R*)-1-(dimethylamino)-ethyl]]ferrocene iodide



6
$C_{34}H_{41}Fe_2N_2P$
620,380 g/mol

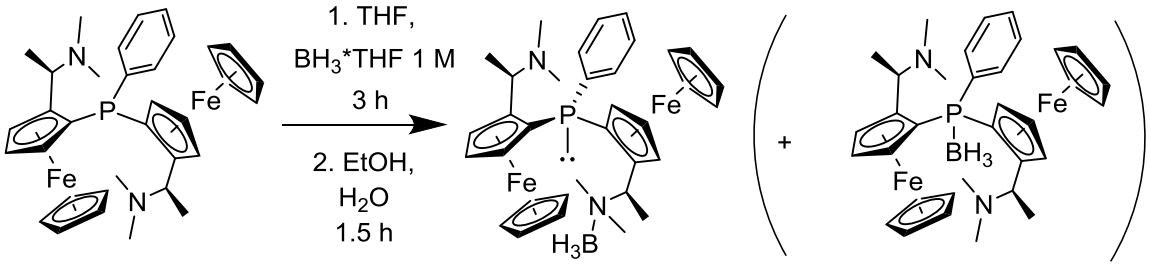
16
$C_{35}H_{44}Fe_2IN_2P$
762,319 g/mol
100%

Procedure: [84] In a flame-dried Schlenck tube, diaminophosphine ***6*** (99 mg, 0.16 mmol) was dissolved in 0.8 mL of dry MeCN under Ar. The solution was degassed three times, MeI (135 µL, 2.17 mmol, 13.6 eq) was added and the solution was stirred for 1 h at r.t. The volatiles of the suspension were removed under reduced pressure, yielding 122 mg of a yellow solid consisting mostly of the P-methylated diaminophosphine ***16***.

^{31}P-NMR (400 MHz, CD_2Cl_2) δ = 26.63 (s) ppm

HRMS: m/z calculated for M = $C_{35}H_{44}Fe_2N_2P$; $[M]^+$ 635.1935, found: 635.1926;

Synthesis of 1,1‘‘-(Phenylphosphinidene)[(2*S*)-2-[(1*R*)-1-(dimethylamino)-ethyl]]ferrocene[(2*S*)-2-[(1*R*)-1-(-N-borane-dimethylamino)-ethyl]]ferrocene



6
$C_{34}H_{41}Fe_2N_2P$
620,380 g/mol

15
$C_{34}H_{44}BFe_2N_2P$
634,214 g/mol
45%

17
$C_{34}H_{44}BFe_2N_2P$
634,214 g/mol

Procedure: [83] Diaminophosphine ***6*** (87 mg, 0.14 mmol) was dissolved in THF abs. in a flame-dried Schlenck tube under Ar. The solution was degassed three times, then BH_3 • THF (1 M; 0.3 mL, 0.3 mmol, 2.14 eq) was added at r.t. and the orange solution was stirred for 3 h. Then 3 mL of EtOH and 3 mL of water were added and the reaction mixture was stirred for another 90 min. The solution was extracted with DCM, the organic layer was washed with brine and sat. aq. $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→75% (Et_2O + 1.5% Et_3N) in *n*-heptane) yielding 45% of N-boranated diaminophosphine ***15*** (40 mg) as a brightly orange solid as well as traces of P-boranated diaminophosphine ***17***.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.89-7.86 (m, 2H); 7.35-7.30 (m, 2H); 7.30-7.27 (m, 1H); 4.75 (dd, *J* = 2.5, 1.2 Hz, 1H); 4.63 (dd, *J* = 2.5, 0.9 Hz, 1H); 4.63-4.57 (m, 1H); 4.45 (m, 1H); 4.43 (m, 1H); 4.41-4.37 (m, 1H); 4.38-4.35 (m, 2H); 3.84 (s, 5H); 3.56 (s, 5H); 2.34 (s, 6H); 2.15 (s, 3H); 1.98 (s, 3H); 1.87 (d, *J* = 7.0 Hz, 3H); 1.81-1.55 (m, 3H); 1.43 (d, *J* = 6.9 Hz, 3H) ppm.

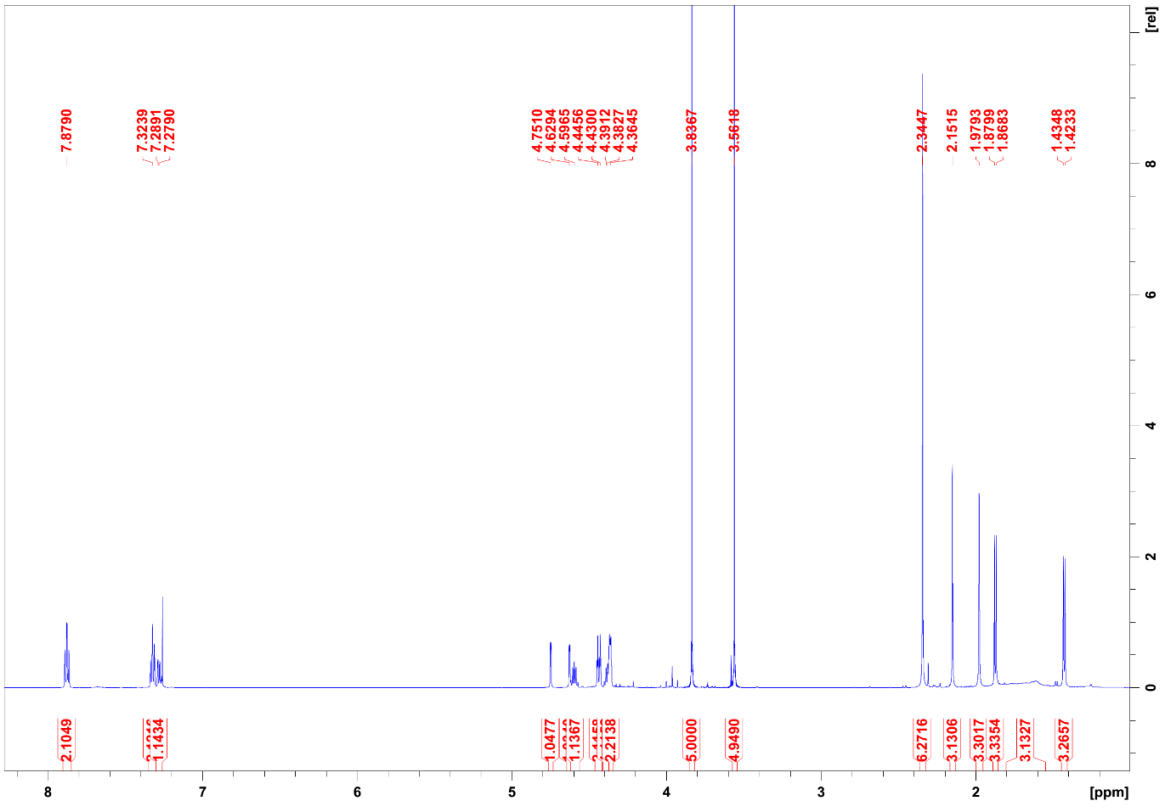
^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 140.89 (d, J_{CP} = 5.9 Hz, C_q); 134.55 (d, J_{CP} = 24.9 Hz, CH); 128.78 (d, J_{CP} = 1.1 Hz, CH); 127.88 (d, J_{CP} = 9.3 Hz, CH); 98.47 (d, J_{CP} = 34.4 Hz, C_q); 92.07 (d, J_{CP} = 31.9 Hz, C_q); 80.92 (d, J_{CP} = 15.7 Hz, C_q); 79.01

(d, J_{CP} = 12.4 Hz, C_q); 71.47 (d, J_{CP} = 6.1 Hz, CH); 71.09 (d, J_{CP} = 4.6 Hz, CH); 70.48 (CH); 69.66 (CH); 69.51 (CH); 68.83 (d, J_{CP} = 4.4 Hz, CH); 68.67 (CH); 67.28 (d, J_{CP} = 5.9 Hz, CH); 62.74 (d, J_{CP} = 14.3 Hz, CH); 55.81 (d, J_{CP} = 14.0 Hz, CH); 52.79 (d, J_{CP} = 7.5 Hz, CH_3); 44.16 (d, J_{CP} = 2.0 Hz, CH_3); 40.64 (CH_3); 19.14 (CH_3); 10.36 (CH_3) ppm.

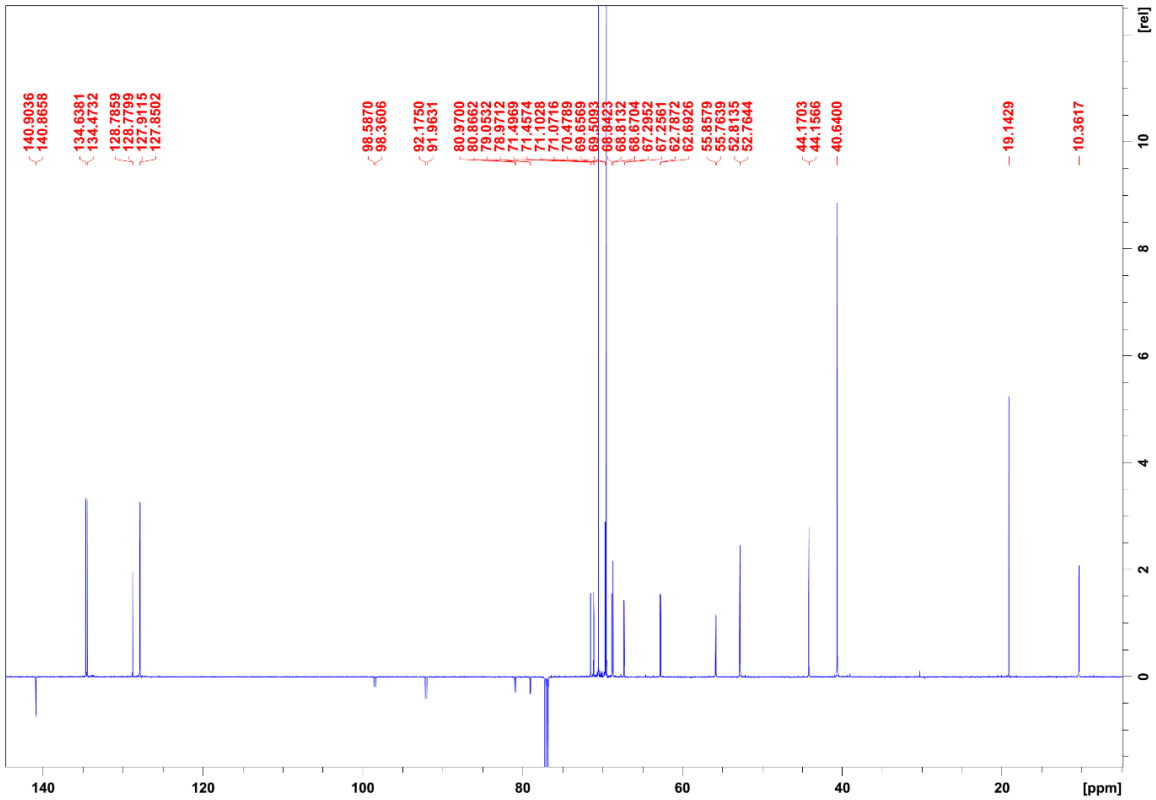
^{31}P-NMR (400 MHz, $CDCl_3$) δ = -48.48 (s) ppm.

HRMS: m/z calculated for M = $C_{34}H_{44}BFe_2N_2P$; $[M+H]^+$ 635.2112, found: 635.2100.

^{1}H-NMR:



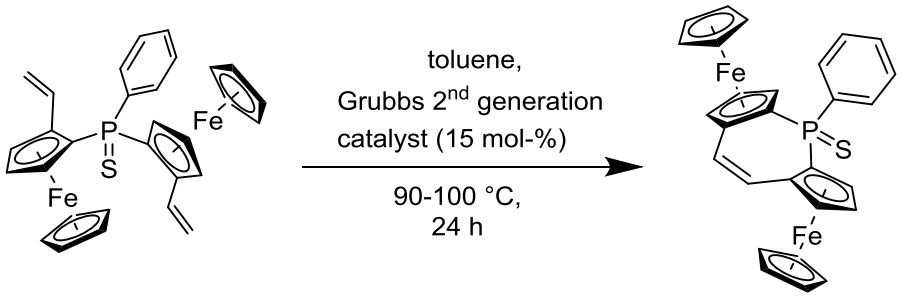
$^{13}C\{^{1}H\}$-NMR:


140.9036
140.8658
134.6381
134.4732
128.7859
128.7799
127.9115
127.8502
98.5870
98.3606
92.1750
91.9631
80.9700
80.8662
79.9532
78.3772
71.4969
71.4574
71.1028
71.0716
70.4789
69.6569
69.5093
68.8423
68.8132
68.6704
67.2952
67.2561
62.7872
62.6926
55.8579
55.7639
52.8135
52.7644
44.1703
44.1566
40.6400
19.1429
10.3617
[rel]
[ppm]

5. 2. 2. 2. Cyclization of di(vinylferrocene) phosphines

5. 2. 2. 2. a. Olefin RCM

Attempted metathesis of 1,1‘‘-(Phenylphosphinidenesulfide)di[(2*S*)-2-vinyl]ferrocene



14
$C_{30}H_{27}Fe_2PS$
562,270 g/mol

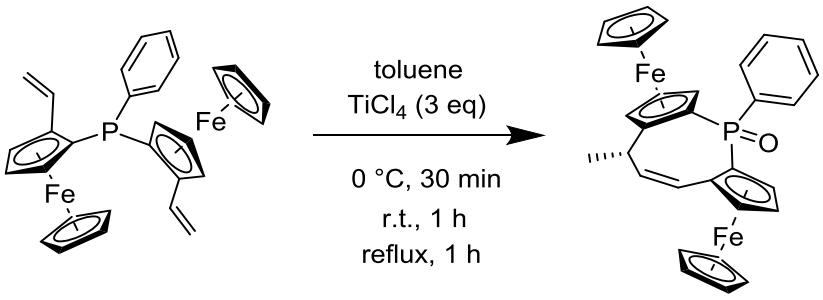
18
$C_{28}H_{23}Fe_2PS$
534,216 g/mol

Procedure: Divinylphosphinesulfide ***14*** (51 mg, 0.09 mmol) was dissolved in 1 mL of dry toluene in a flame-dried Schlenck tube under Ar. The orange solution was degassed three times, then 2nd generation Grubbs catalyst (12.1 mg, 0.014 mmol, 15 mol-%) was added to the solution. The reaction mixture was heated to 85 °C and stirred for 24 h. About 10% of the starting material transformed into a mixture other compounds. The reaction was stopped and the solvent was removed under reduced pressure. The starting material was regained and the novel compound mixture was isolated by column chromatography (SiO_2; 8% EtOAc in *n*-heptane) containing traces of the intended RCM product ***18*** according to HRMS findings.

HRMS: m/z calculated for M = $C_{28}H_{23}Fe_2PS$; $[M]^+$ 533.9957, found: 533.9953; $[M+Na]^+$ 556.9855, found: 556.9850.

5. 2. 2. 2. b. Divinyl coupling by hydrovinylation

Synthesis of (2*S*,4*R*,8*S*)-4-Methyl-1-phenyl-diferroceno-5-*Z*-ethylene-1-phosphinoxide



8
$C_{30}H_{27}Fe_2P$
530,210 g/mol

19
$C_{30}H_{27}Fe_2OP$
546,209 g/mol
13%

Procedure: [80] Divinylphosphine ***8*** (52 mg, 0.10 mmol) was dissolved in 3 mL of toluene in a flame-dried Schlenck tube under Ar. The orange solution was degassed three times and cooled in an ice bath. $TiCl_4$ (33 µL, 0.30 mmol, 3.0 eq) was added to the solution. The resulting dark green suspension was stirred at 0 °C for 30 min, warmed to r.t., stirred for 1 h, heated to reflux and stirred for 1 h. The green suspension was cooled to r.t. Sat. aq. $NaHCO_3$ (3 mL) was added upon which the color of the suspension turned back to orange. The reaction mixture was filtered through SiO_2 and washed after with EtOAc. The resulting solution was washed with 3 mL of water and brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, 40→100% EtOAc in *n*-heptane) yielding 13% of phosphineoxide diferrocenyl cycle ***19*** (7 mg) as a glassy yellow solid.

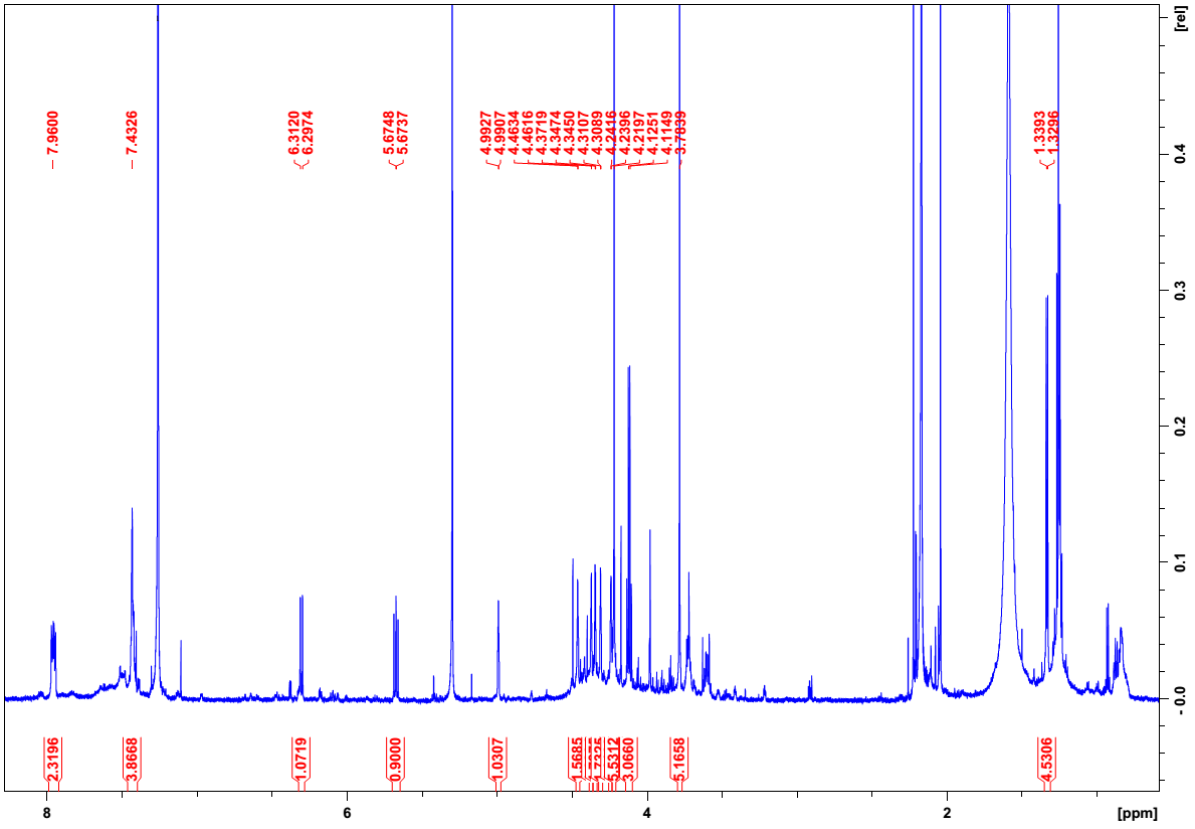
^{1}H-NMR (700 MHz, $CDCl_3$) δ = 7.98-7.94 (m, 2H); 7.45-7.40 (m, 3H); 6.30 (d, *J* = 10.3 Hz, 1H); 5.67 (dd, *J* = 10.2, 9.3 Hz, 1H); 4.99 (m, 1H); 4.46 (m, 1H); 4.37 (m, 1H); 4.35 (m, 1H); 4.31 (m, 1H); 4.24 (m, 1H); 4.23 (m, 1H); 4.22 (s, 5H); 3.78 (s, 5H); 1.33 (d, *J* = 6.8 Hz, 3H) ppm.

$^{13}C\{^{1}H\}$-NMR (700 MHz, $CDCl_3$) δ = 141.33 (CH); 131.37 (d, J_{CP} = 10.2 Hz, CH); 130.76 (d, J_{CP} = 2.3 Hz, CH); 127.51 (d, J_{CP} = 12.2 Hz, CH); 125.52 (CH); 95.71 (C_q); 84.63 (C_q); 74.56 (d, J_{CP} = 11.7 Hz, CH); 72.25 (d, J_{CP} = 13.0 Hz, CH); 72.23 (d, J_{CP} = 10.0 Hz, CH); 70.38 (CH); 70.30 (CH); 69.93 (d, J_{CP} = 9.9 Hz, CH); 69.40 (d, J_{CP} = 11.2 Hz, CH); 68.76 (d, J_{CP} = 10.2 Hz, CH); 32.32 (CH); 21.35 (CH_3) ppm; 4 C_q not found.

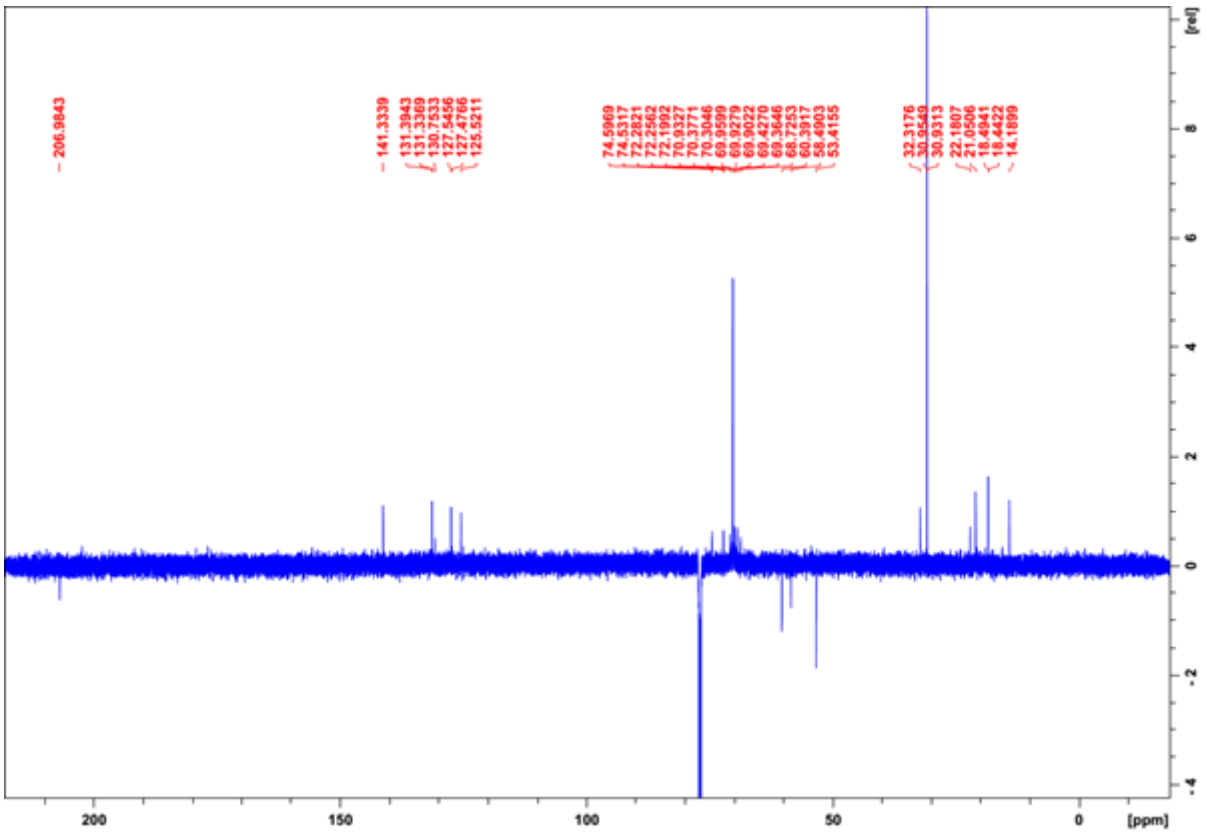
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 29.84 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{27}Fe_2OP$; $[M+H]^+$ 547.0577, found: 547.0564.

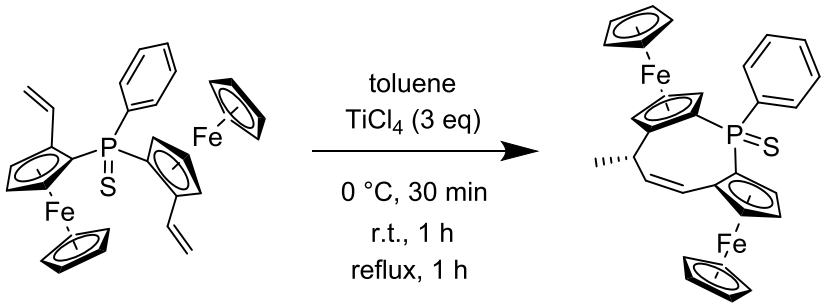
^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR:


206.9843
141.3339
131.3943
131.3369
130.7533
127.5456
127.4766
125.5211
74.5969
74.5317
72.2821
72.2562
72.1992
70.9327
70.3771
70.3046
69.9599
69.9279
69.9022
69.4270
69.3046
68.7253
60.3917
58.4903
53.4155
32.3176
30.9549
30.9313
22.1807
21.0506
18.4941
18.4422
14.1899
[rel]
8
6
4
2
0
-2
-4
200
150
100
50
0
[ppm]

Synthesis of (2*S*,4*R*,8*S*)-4-Methyl-1-phenyl-diferroceno-5-*Z*-ethylene-1-phosphinsulfide



14
$C_{30}H_{27}Fe_2PS$
562,270 g/mol

20
$C_{30}H_{27}Fe_2PS$
562,270 g/mol
13%

Procedure: [80] Divinylphosphinesulfide ***14*** (50 mg, 0.09 mmol) was dissolved in 3 mL of toluene in a flame-dried Schlenck tube under Ar. The orange solution was degassed three times and cooled in an ice bath. $TiCl_4$ (33 µL, 0.30 mmol, 3.4 eq) was added to the solution. The resulting dark green suspension was stirred at 0 °C for 30 min, warmed to r.t., stirred for 1 h, heated to reflux and stirred for 1 h. The green suspension was cooled to r.t. Sat. aq. $NaHCO_3$ (3 mL) was added upon which the suspension turned back to orange. The reaction mixture was filtered through SiO_2 and washed after with EtOAc. The resulting solution was washed with 3 mL of water and 3 mL of brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, 0→100% EtOAc in *n*-heptane) yielding 13% of impure phosphinesulfide diferrocenyl cycle ***20*** (7 mg) as a yellow solid.

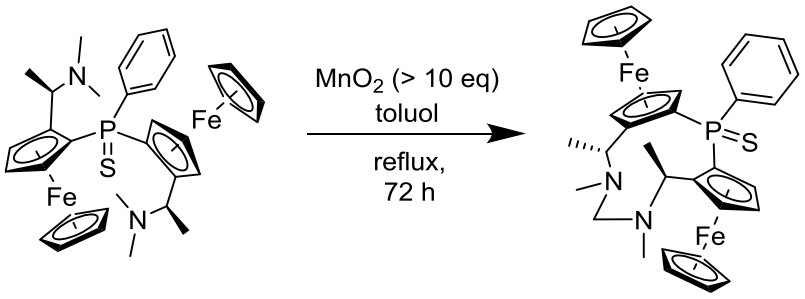
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 40.57 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{27}Fe_2PS$; $[M]^+$ 562.0270, found: 562.0245; $[2M]^+$ 1124.0540, found: 1124.0484.

5. 2. 2. 3. Cyclization of di(ferrocenylethylamine) phosphines

5. 2. 2. 3. a. Mn(IV)-mediated oxidation

Synthesis of Formaldehyde-1,1''-(Phenylphosphinidenesulfide)bis[(2*S*)-2-[(1*R*)-1-(methylamino)-ethyl]]ferrocene-aminal



13
$C_{34}H_{41}Fe_2N_2PS$
652,440 g/mol

21
$C_{33}H_{37}Fe_2N_2PS$
636,397 g/mol
23%

Procedure: [98] Diaminophosphinesulfide ***13*** (57 mg, 0.09 mmol) and MnO_2 (96 mg, 1.10 mmol, 12.7 eq) were suspended in 1.5 mL of toluene in a flame-dried Schlenck tube under Ar. The suspension was degassed three times, then heated to reflux for 72 h. The reaction mixture was cooled to r.t. and the black solid was filtered off. The remaining orange solution was washed with 2 mL of water and 2 mL of brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2, 0→100% (Et_2O + 1.5% Et_3N) in *n*-heptane) yielding 23% of aminaldiferrocenyl cycle ***21*** (13 mg) as an orange solid.

^{1}H-NMR (700 MHz, $CDCl_3$) δ = 7.66 (s, 2H); 7.42 (tq, *J* = 7.6, 1.3 Hz, 1H); 7.38-7.33 (m, 2H); 5.19 (m, 1H); 4.81 (m, 1H); 4.68 (m, 1H); 4.56 (s, 5H); 4.46 (m, 1H); 4.44 (m, 1H); 4.36 (m, 1H); 4.35 (s, 5H); 3.05 (d, *J* = 12.3 Hz, 1H); 2.84 (d, *J* = 12.3 Hz, 1H); 2.83 (q, *J* = 6.9 Hz, 1H); 2.33 (q, *J* = 6.8 Hz, 1H); 2.13 (s, 3H); 1.94 (s, 3H) ppm.

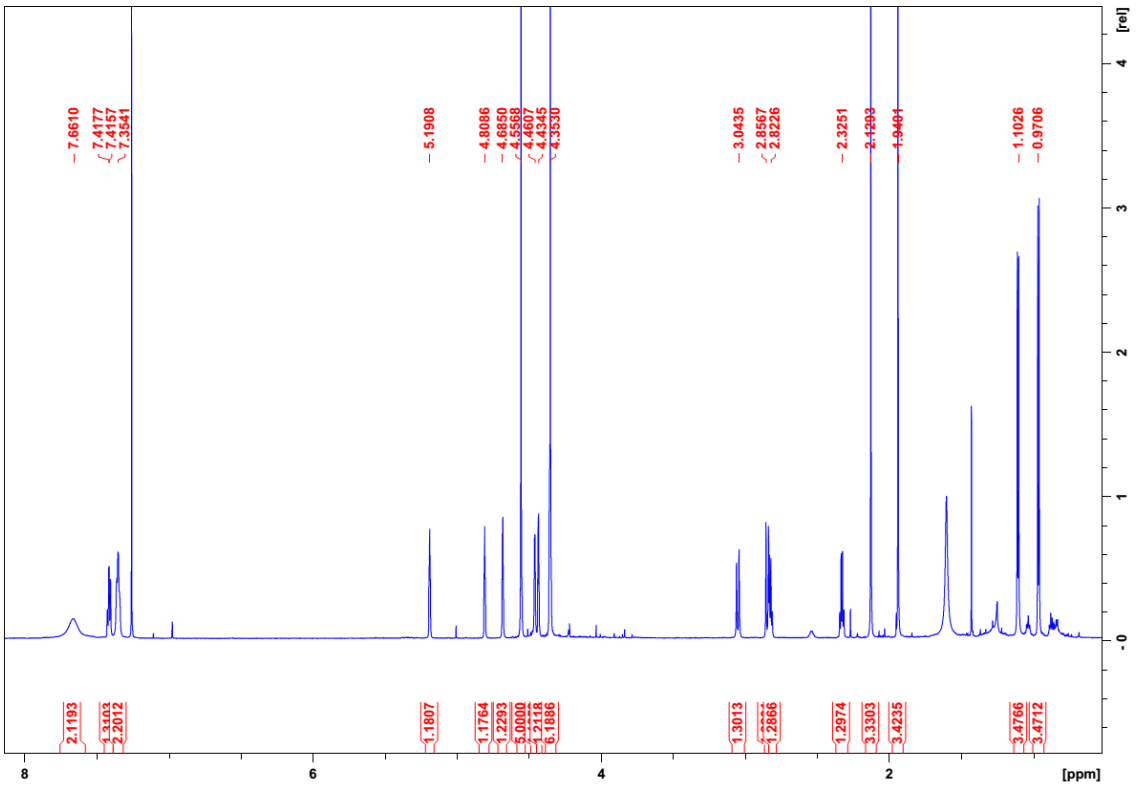
^{13}C{^{1}H}-NMR (700 MHz, $CDCl_3$) δ = 137.55 (d, J_{CP} = 90.1 Hz, C_q); 132.36 (d, J_{CP} = 10.9 Hz, CH); 130.82 (d, J_{CP} = 2.9 Hz, CH); 127.42 (d, J_{CP} = 12.6 Hz, CH); 97.55 (d,

J_{CP} = 10.7 Hz, C_q); 93.72 (d, J_{CP} = 8.3 Hz, C_q); 78.31 (d, J_{CP} = 96.3 Hz, C_q); 77.67 (d, J_{CP} = 92.0 Hz, C_q); 77.61 (CH_2); 76.28 (d, J_{CP} = 15.4 Hz, CH); 72.81 (d, J_{CP} = 17.1 Hz, CH); 71.60 (CH); 70.82 (CH); 69.85 (d, J_{CP} = 8.2 Hz, CH); 69.78 (d, J_{CP} = 11.8 Hz, CH); 69.63 (d, J_{CP} = 9.4 Hz, CH); 69.15 (d, J_{CP} = 11.7 Hz, CH); 55.93 (CH); 50.18 (CH); 40.73 (CH_3); 34.54 (CH_3); 23.12 (CH_3); 10.53 (CH_3) ppm.

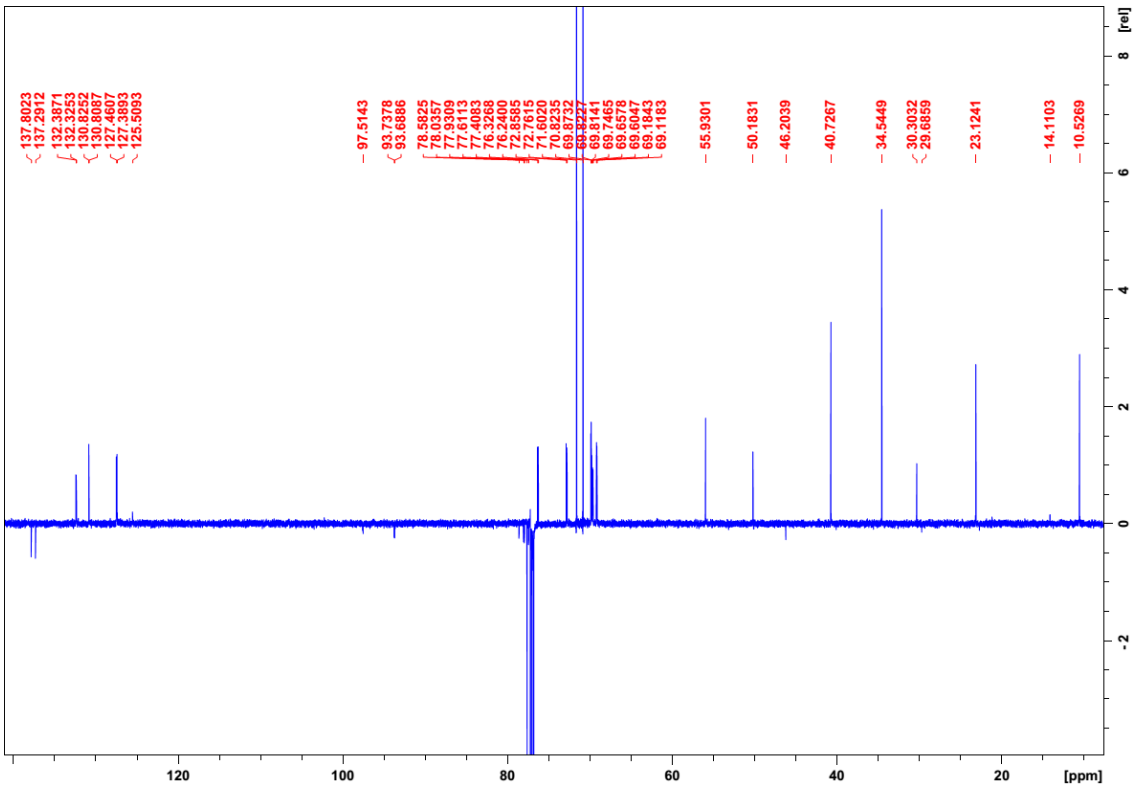
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 54.44 (s) ppm.

HRMS: m/z calculated for M = $C_{33}H_{37}Fe_2N_2PS$; $[M+H]^+$ 637.1192, found: 637.1174.

^{1}H-NMR:

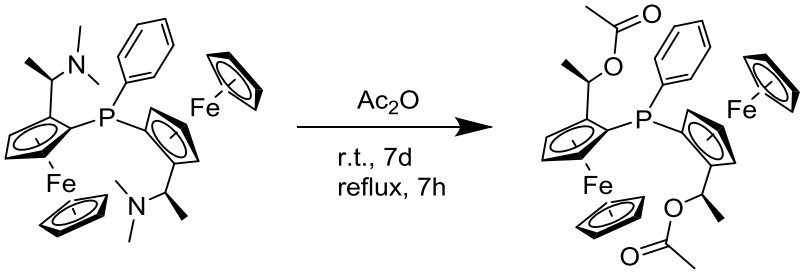


$^{13}C\{^{1}H\}$-NMR:


137.8023
137.2912
132.3871
132.3253
130.8252
130.8097
127.4607
127.3893
125.5093
97.5143
93.7378
93.6886
78.5825
78.0357
77.9309
77.6113
77.4083
76.3268
76.2400
72.8585
72.7615
71.6020
70.8235
69.8732
69.8227
69.8141
69.7465
69.6578
69.6047
69.1843
69.1183
55.9301
50.1831
46.2039
40.7267
34.5449
30.3032
29.6859
23.1241
14.1103
10.5269
[rel]
8
6
4
2
0
-2
120
100
80
60
40
20
[ppm]

5. 2. 2. 3. b. Acetoxy substitution

Synthesis of 1,1‘‘-(Phenylphosphinidene)bis[(2*S*)-2-[(1*R*)-1-(acetoxy)-ethyl]]ferrocene



6
$C_{34}H_{41}Fe_2N_2P$
620,380 g/mol

22
$C_{34}H_{35}Fe_2O_4P$
650,314 g/mol
27%

Procedure: Diaminophosphine ***6*** (619 mg, 1.00 mmol) was suspended in 1 mL of Ac_2O in a flame-dried Schlenck tube under Ar. The suspension was degassed three times and stirred for 7 d at r.t., then for 7 h at 100 °C until a multitude of products was detected in the red solution via TLC. Ac_2O was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→100% EtOAc in *n*-heptane) yielding several mixed fractions as well as 27% of pure diacetatephosphine ***22*** (177 mg) as reddish crystals.

M.p.: 155-156 °C.

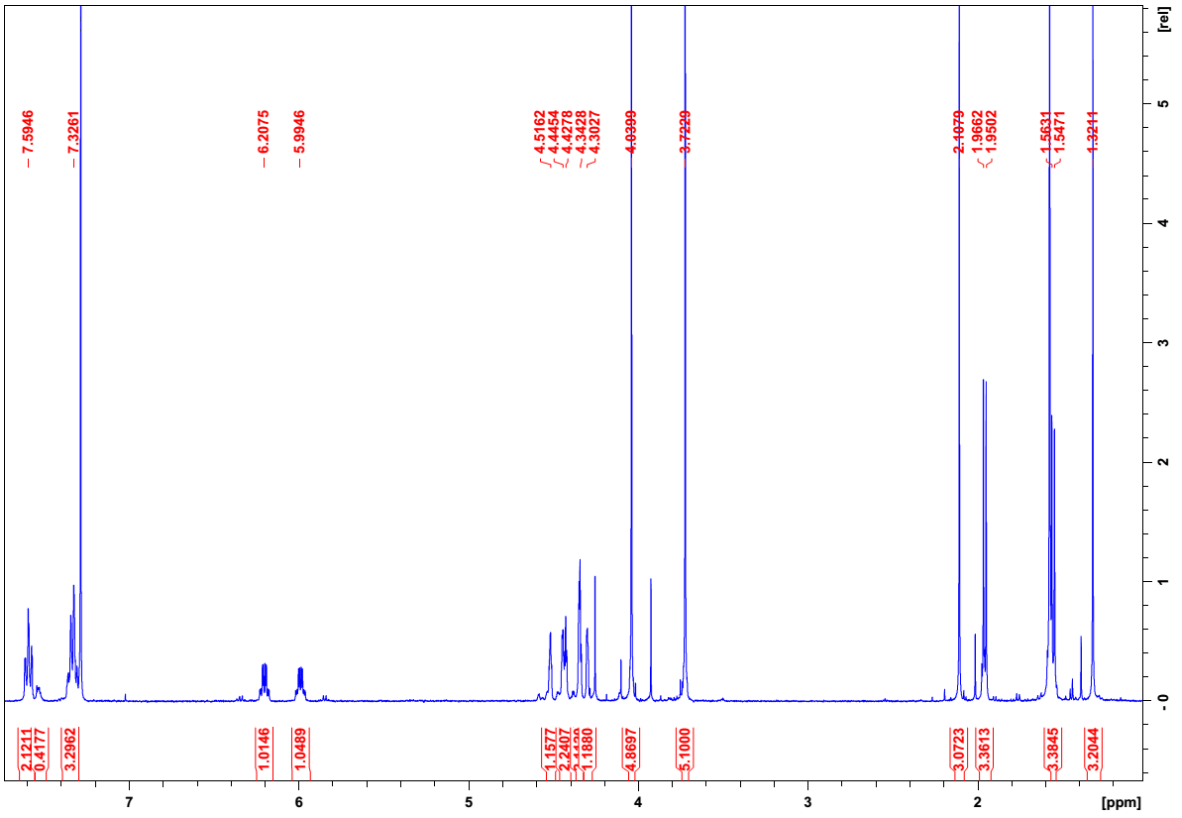
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.62-7.56 (m, 2H); 7.37-7.30 (m, 3H); 6.20 (dt, *J* = 2.50, 6.4 Hz, 1H); 5.99 (dt, *J* = 2.9, 6.4 Hz, 1H); 4.52 (m, 1H); 4.45 (m, 1H); 4.43 (pt, *J* = 2.5 Hz, 1H); 4.35 (m, 1H); 4.34 (m, 1H); 4.30 (m, 1H); 4.04 (s, 5H); 3.72 (s, 5H); 2.11 (s, 3H); 1.96 (d, *J* = 6.4 Hz, 3H); 1.56 (d, *J* = 6.4 Hz, 3H); 1.32 (s, 3H) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = -44.57 (s) ppm.

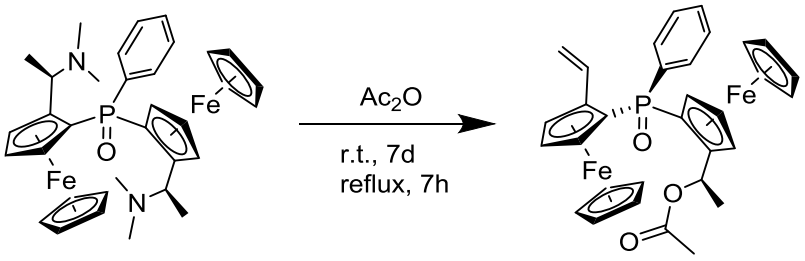
HRMS: m/z calculated for M = $C_{34}H_{35}Fe_2O_4P$; $[M+Na]^+$ 673.0869, found: 673.0877.

Crystal data: orthorhombic; space group $P2_12_12_1$; a = 7.631(2) Å; b = 10.877(2) Å; c = 36.025(8) Å; α = 90°; β = 90°; γ = 90°; V = 2990.2(12) Å^3; Z = 4; D_{calc} = 1.444 g/cm^3; T = 130.00 K; μ(MoK$_\alpha$) = 1.061 mm^{-1}; 46099 reflections measured (4.374° ≤ 2Θ ≤ 50.706°); 5441 unique (R_{int} = 0.1501, R_{sigma} = 0.1046) which were used in all calculations. The final $R1$ was 0.0653 (I > 2σ(I)) and wR_2 was 0.1220 (all data).

^{1}H-NMR:



Attempted synthesis of 1,1''-(Phenylphosphinideneoxide)bis[(2*S*)-2-[(1*R*)-1-(acetoxy)-ethyl]]ferrocene



11
$C_{34}H_{41}Fe_2N_2OP$
636,379 g/mol

23
$C_{32}H_{31}Fe_2O_3P$
606,261 g/mol
14%

Procedure: Diaminophosphineoxide ***11*** (630 mg, 0.99 mmol) was suspended in 1 mL of Ac_2O in a flame-dried Schlenck tube under Ar. The suspension was degassed three times and stirred for 7 d at r.t., then for 7 h at 100 °C until a multitude of products was detected in the red solution via TLC. Ac_2O was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 20→100% EtOAc in *n*-heptane) yielding several mixed fractions as well as 14% of pure monovinylmonoacetatephosphineoxide ***23*** (86 mg) as an orange solid.

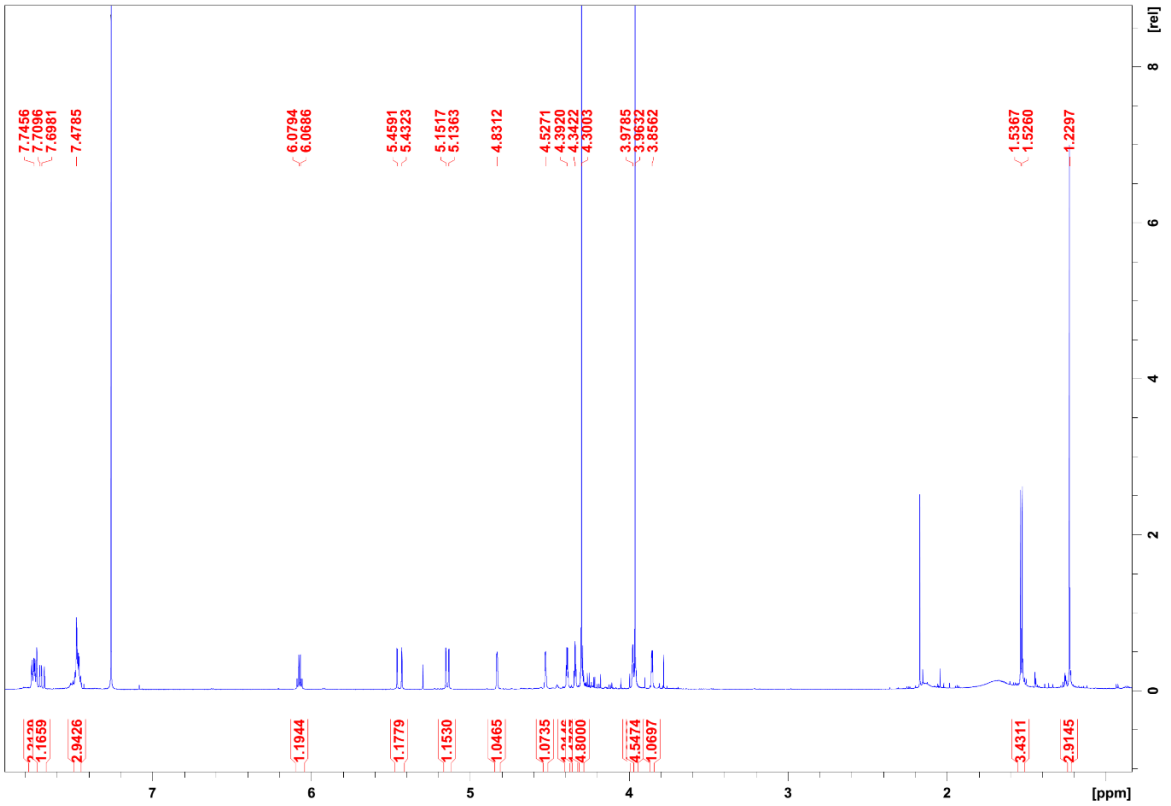
^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.75 (m, 2H); 7.70 (dd, *J* = 17.8, 10.9 Hz, 1H); 7.50-7.45, (m, 3H); 6.07 (q, *J* = 6.4 Hz, 1H); 5.45 (dd, *J* = 17.7, 1.6 Hz, 1H); 5.14 (dd, *J* = 10.8, 1.6 Hz, 1H); 4.83 (m, 1H); 4.53 (m, 1H); 4.39 (dd, *J* = 4.8, 2.3 Hz, 1H); 4.34 (dd, *J* = 4.8, 2.3 Hz, 1H); 4.30 (s, 5H); 3.98 (m, 1H); 3.97 (s, 5H); 3.86 (m, 1H); 1.53 (d, *J* = 6.4 Hz, 3H); 1.23 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 169.32 (C_q); 135.73 (d, J_{CP} = 109.2 Hz, C_q); 134.70 (CH); 131.16 (d, J_{CP} = 9.6 Hz, CH); 130.95 (d, J_{CP} = 2.8 Hz, CH); 127.87 (d, J_{CP} = 12.1 Hz, CH); 111.40 (CH_2); 89.30 (d, J_{CP} = 10.9 Hz, C_q); 88.54 (d, J_{CP} = 10.1 Hz, C_q); 75.83 (C_q); 75.03 (d, J_{CP} = 14.4 Hz, CH); 73.28 (d, J_{CP} = 15.1 Hz, CH); 72.06 (C_q); 71.25 (d, J_{CP} = 11.0 Hz, CH); 70.88 (CH); 70.45 (CH); 70.25 (d, J_{CP} = 9.2 Hz, CH); 69.62 (d, J_{CP} = 11.2 Hz, CH); 68.19 (CH); 67.29 (d, J_{CP} = 9.4 Hz, CH); 20.46 (CH_3); 19.02 (CH_3) ppm.

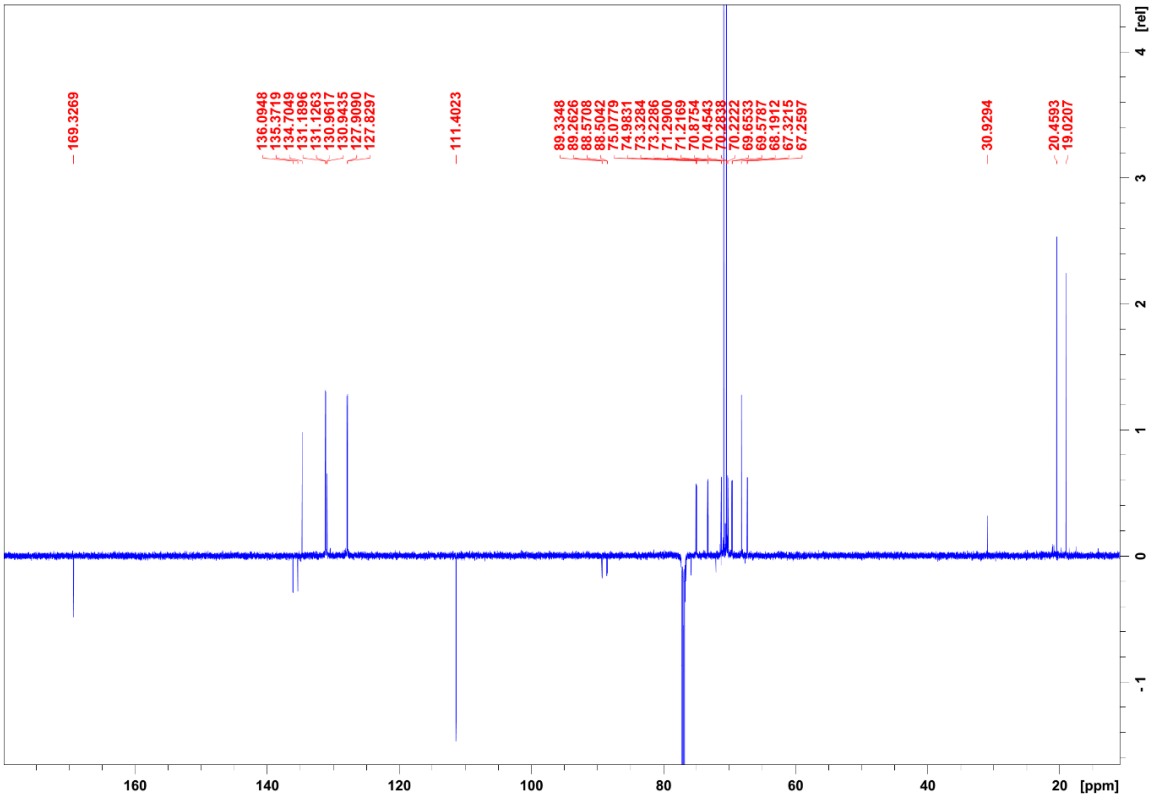
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 30.59 ppm.

HRMS: m/z calculated for M = $C_{32}H_{31}Fe_2O_3P$; $[M+Na]^+$ 629.0607, found: 629.0614; $[2M+Na]^+$ 1235.1317, found: 1235.1324.

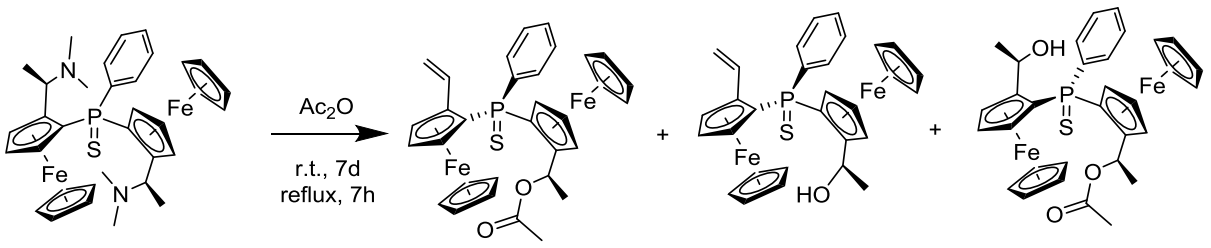
^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR:


169.3269
136.0948
135.3719
134.7049
131.1896
131.1263
130.9617
130.9435
127.9060
127.8297
111.4023
89.3348
89.2626
88.5708
88.5042
75.0779
74.9831
73.3284
73.2286
71.2900
71.2169
70.8754
70.4543
70.4233
70.4222
69.6533
69.5787
68.1912
67.3215
67.2597
30.9294
20.4593
19.0207
[rel]
[ppm]

Attempted synthesis of 1,1''-(Phenylphosphinidenesulfide)bis[(2*S*)-2-[(1*R*)-1-(acetoxy)-ethyl]]ferrocene



13
$C_{34}H_{41}Fe_2N_2PS$
652,440 g/mol

24
$C_{32}H_{31}Fe_2O_2PS$
622,322 g/mol
22%

25
$C_{30}H_{29}Fe_2OPS$
580,285 g/mol
17%

26
$C_{32}H_{33}Fe_2O_3PS$
640,337 g/mol
12%

Procedure: Diaminophosphinesulfide ***13*** (653 mg, 1.00 mmol) was suspended in 1 mL of Ac_2O in a flame-dried Schlenck tube under Ar. The suspension was degassed three times and stirred for 7 d at r.t., then for 7 h at 100 °C until a multitude of products was detected in the red solution via TLC. Ac_2O was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→100% EtOAc in *n*-heptane) yielding several mixed fractions as well as 22% of pure monovinylmonoacetatephosphinesulfide ***24*** (135 mg), 17% of pure monovinylmonohydroxyphosphinesulfide ***25*** (99 mg) and 12% of pure monohydroxymonoacetatephosphinesulfide ***26*** (74 mg) as orange crystals.

Monovinylmonoacetate ***24***:

M.p.: 177-178 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.13 (dd, *J* = 17.7, 10.8 Hz, 1H); 7.77 (dd, *J* = 13.3, 7.4 Hz, 2H); 7.47-7.41 (m, 3H); 6.49 (q, *J* = 6.4 Hz, 1H); 5.46 (dd, *J* = 17.7, 1.7 Hz; 1H); 5.16 (dd, *J* = 10.8, 1.6 Hz, 1H); 4.84 (m, 1H); 4.59 (m, 1H); 4.36 (s, 5H); 4.30 (m, 1H); 4.28 (m, 1H); 4.14 (s, 5H); 3.78 (m, 1H); 3.54 (m, 1H); 1.57 (d, *J* = 6.5 Hz, 3H); 1.04 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 169.39 (C_q); 135.44 (d, J_{CP} = 88.3 Hz, C_q); 134.47 (CH); 132.29 (d, J_{CP} = 10.5 Hz, CH); 130.77 (d, J_{CP} = 2.8 Hz, CH); 127.49 (d, J_{CP} = 12.2 Hz, CH); 111.38 (CH_2); 88.95 (d, J_{CP} = 12.1 Hz, C_q); 88.43 (d, J_{CP} = 12.0 Hz, C_q); 79.19 (d, J_{CP} = 95.2 Hz, C_q); 75.84 (d, J_{CP} = 11.4 Hz, CH); 75.03 (d, J_{CP} =

12.0 Hz, CH); 74.46 (d, J_{CP} = 95.1 Hz, C_q); 71.15 (CH); 70.94 (CH); 70.60 (d, J_{CP} = 9.0 Hz, CH); 69.88 (d, J_{CP} = 10.2 Hz, CH); 68.40 (d, J_{CP} = 10.3 Hz, CH); 68.14 (d, J_{CP} = 8.9 Hz, CH); 67.99 (CH); 20.03 (CH_3); 18.49 (CH_3) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 39.14 (s) ppm.

HRMS: m/z calculated for M = $C_{32}H_{31}Fe_2O_2PS$; $[M]^+$ 622.0481, found: 622.0462; $[M+Na]^+$ 645.0379, found: 645.0358; $[M+K]^+$ 661.0118, found: 661.0104.

Crystal data: orthorhombic; space group $P2_12_12_1$; *a* = 7.4923(3) Å; *b* = 12.0133(4) Å; *c* = 31.7580(10) Å; *α* = 90°; *β* = 90°; *γ* = 90°; *V* = 2858.45(17) Å^3; *Z* = 4; D_{calc} = 1.446 g/cm^3; *T* = 100.0 K; μ($MoK_α$) = 1.172 mm^{-1}; 52739 reflections measured (5.128° ≤ 2Θ ≤ 60.048°); 8330 unique (R_{int} = 0.0620, R_{sigma} = 0.0432) which were used in all calculations. The final *R1* was 0.0321 (I > 2σ(I)) and wR_2 was 0.0615 (all data).

Monovinylmonoalcohol ***25***:

M.p.: 205-206 °C (decomposition).

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.10 (dd, *J* = 17.6, 10.8 Hz, 1H); 7.87-7.81 (m, 2H); 7.51-7.42 (m, 3H); 5.49 (dd, *J* = 17.6, 1.6 Hz; 1H); 5.23-5.17 (m, 1H); 5.20 (dd, *J* = 10.8, 1.7 Hz, 1H); 4.88 (m, 1H); 4.49 (m, 1H); 4.34 (s, 5H); 4.33 (m, 1H); 4.24 (m, 1H); 4.17 (s, 5H); 3.77 (m, 1H); 3.71 (m, 1H); 2.41 (d, *J* = 5.3 Hz; 1H); 1.26 (d, *J* = 6.6 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 135.30 (d, J_{CP} = 87.1 Hz, C_q); 134.25 (CH); 132.10 (d, J_{CP} = 10.3 Hz, CH); 131.38 (d, J_{CP} = 2.8 Hz, CH); 127.96 (d, J_{CP} = 12.1 Hz, CH); 111.74 (CH_2); 94.90 (d, J_{CP} = 12.3 Hz, C_q); 88.43 (d, J_{CP} = 11.8 Hz, C_q); 78.56 (d, J_{CP} = 95.4 Hz, C_q); 75.05 (d, J_{CP} = 12.0 Hz, CH); 74.97 (d, J_{CP} = 12.6 Hz, CH); 73.48 (d, J_{CP} = 96.0 Hz, C_q); 71.22 (CH); 71.00 (d, J_{CP} = 9.7 Hz, CH); 70.72 (CH); 70.10 (d, J_{CP} = 10.4 Hz, CH); 68.38 (d, J_{CP} = 9.1 Hz, CH); 68.04 (d, J_{CP} = 10.5 Hz, CH); 64.38 (CH); 21.91 (CH_3) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 40.52 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{29}Fe_2OPS$; $[M]^+$ 580.0376, found: 580.0360; $[M+Na]^+$ 603.0273, found: 603.0273; $[M+K]^+$ 619.0013, found: 619.0018.

Crystal data: orthorhombic; space group $P2_12_12_1$; a = 7.5285(3) Å; b = 17.6463(7) Å; c = 39.3333(15) Å; α = 90°; β = 90°; γ = 90°; V = 5225.4(4) Å^3; Z = 8; D_{calc} = 1.475 g/cm^3; T = 130.0 K; μ(MoK$_\alpha$) = 1.273 mm^{-1}; 28853 reflections measured (2.07° ≤ 2Θ ≤ 50.7°); 9547 unique (R_{int} = 0.0412, R_{sigma} = 0.0414) which were used in all calculations. The final *R1* was 0.0455 (I > 2σ(I)) and wR_2 was 0.1093 (all data).

Monoacetatemonoalcohol ***26***:

M.p.: 174-175 °C.

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.20-8.14 (m, 2H); 7.57-7.54 (m, 3H); 6.60 (q, J = 6.3 Hz, 1H); 4.93 (m, 1H); 4.67 (m, 2H); 4.49 (m, 1H); 4.38 (m, 1H); 4.34 (m, 1H); 4.11 (s, 5H); 4.10 (s, 5H); 1.90 (s, 3H); 1.83 (d, J = 6.3 Hz, 3H); 1.63 (m, 1H); 1.43 (dd, J = 19.2, 6.4 Hz, 1H); 1.40 (d, J = 6.6 Hz, 3H) ppm.

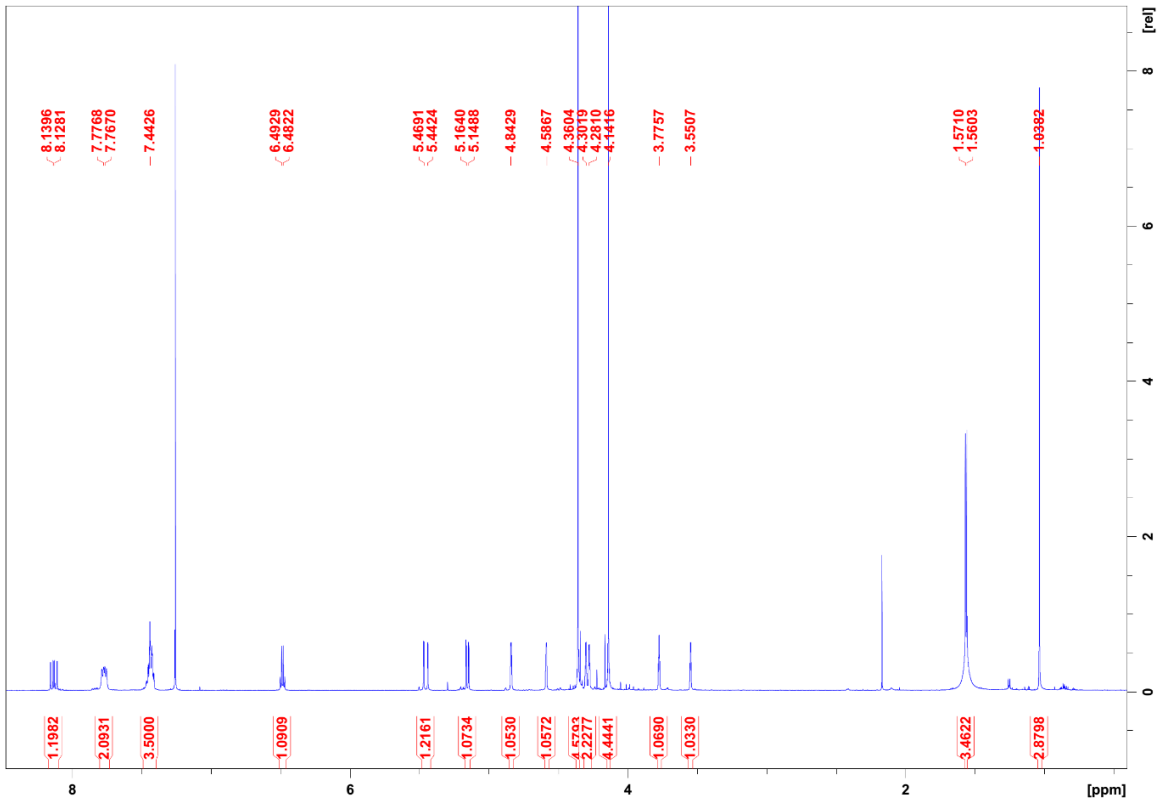
^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 169.70 (C_q); 135.42 (d, J_{CP} = 87.3 Hz, C_q); 132.21 (d, J_{CP} = 10.5 Hz, CH); 131.47 (d, J_{CP} = 2.9 Hz, CH); 127.88 (d, J_{CP} = 12.2 Hz, CH); 93.49 (d, J_{CP} = 11.8 Hz, C_q); 93.47 (d, J_{CP} = 13.5 Hz, C_q); 75.85 (d, J_{CP} = 13.4 Hz, CH); 74.53 (C_q); 73.91 (C_q); 71.53 (d, J_{CP} = 9.3 Hz, CH); 70.93 (CH); 70.60 (d, J_{CP} = 60.4 Hz, CH); 70.58 (CH); 70.27 (d, J_{CP} = 9.3 Hz, CH); 69.48 (d, J_{CP} = 10.1 Hz, CH); 68.87 (CH); 68.56 (d, J_{CP} = 10.9 Hz, CH); 64.20 (CH); 22.37 (CH_3); 22.23 (CH_3); 21.80 (CH_3) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 39.12 (s) ppm.

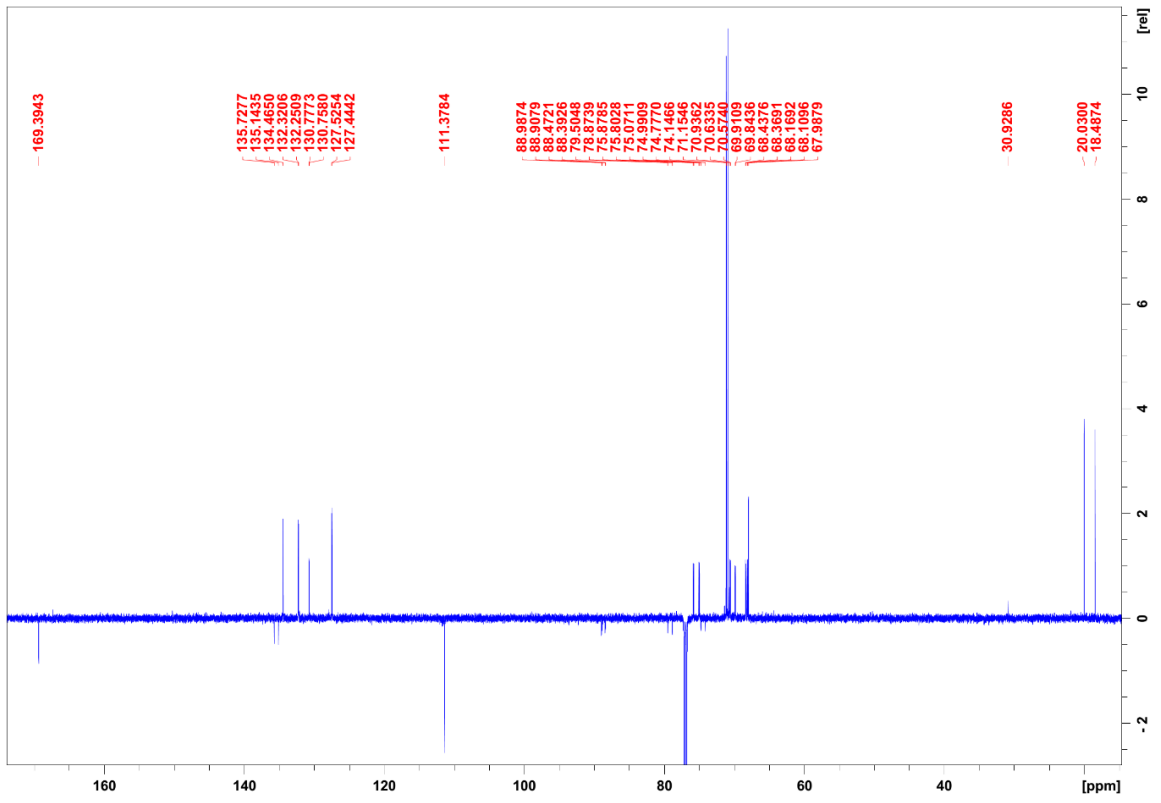
HRMS: m/z calculated for M = $C_{32}H_{33}Fe_2O_3PS$; $[M]^+$ 640.0587, found: 640.0566; $[M+Na]^+$ 663.0485, found: 663.0463.

Crystal data: orthorhombic; space group $P2_12_12_1$; a = 7.8204(11) Å; b = 17.835(3) Å; c = 20.394(2) Å; α = 90°; β = 90°; γ = 90°; V = 2844.5(7) Å^3; Z = 4; D_{calc} = 1.495 g/cm^3; T = 130.0 K; μ(MoK$_\alpha$) = 1.182 mm^{-1}; 35430 reflections measured (4.568° ≤ 2Θ ≤ 51.028°); 5258 unique (R_{int} = 0.1671, R_{sigma} = 0.1253) which were used in all calculations. The final *R1* was 0.0540 (I > 2σ(I)) and wR_2 was 0.0928 (all data).

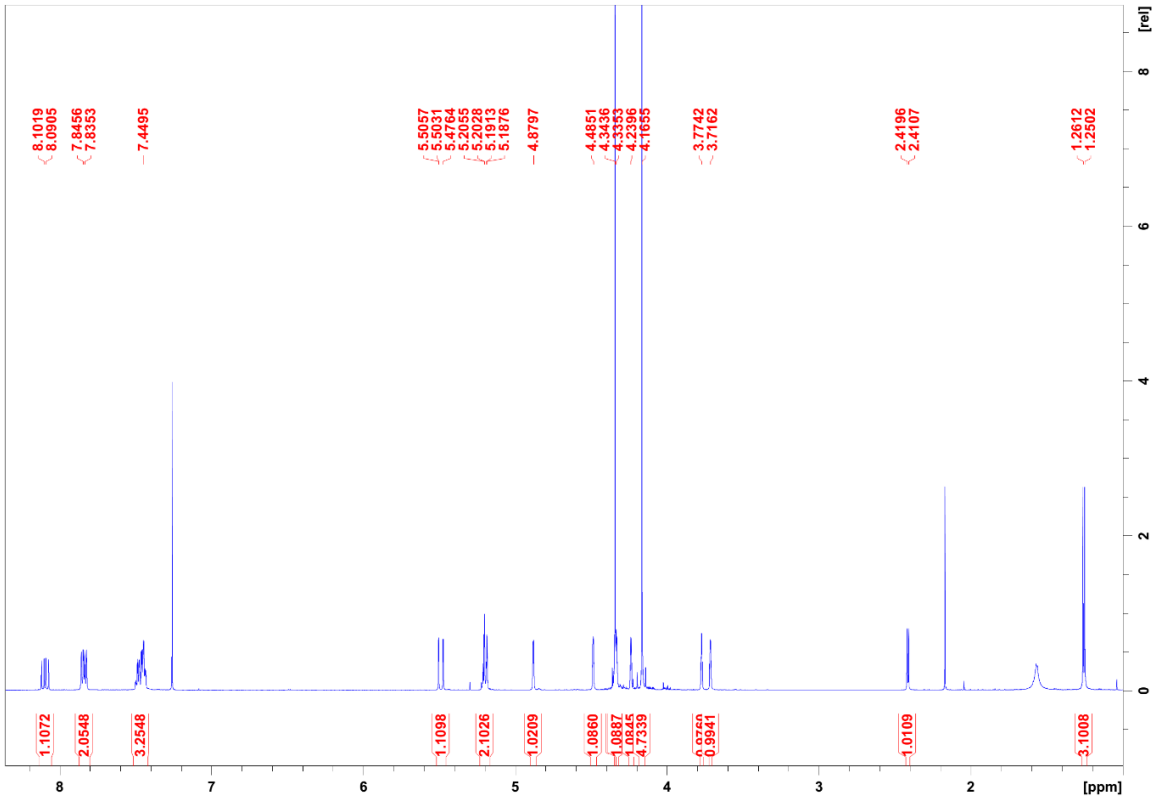
^{1}H-NMR (Acetate ***24***):



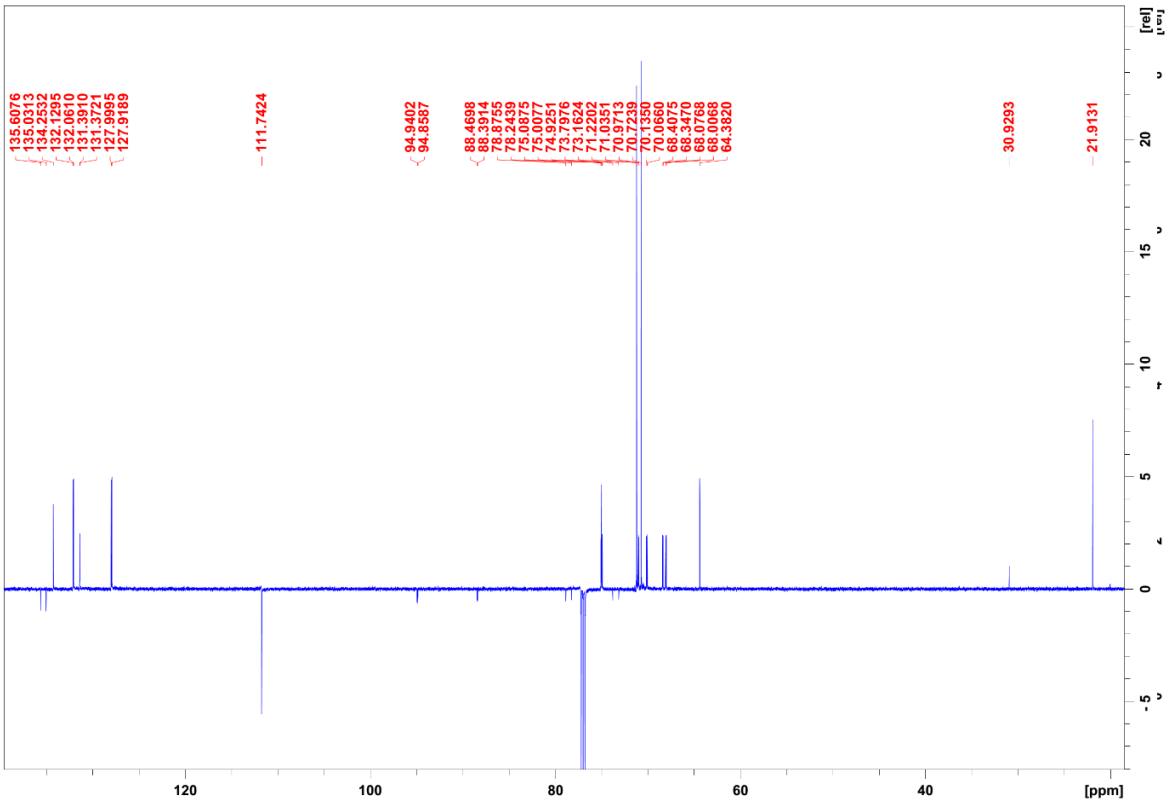
^{13}C{^{1}H}-NMR (Acetate ***24***)



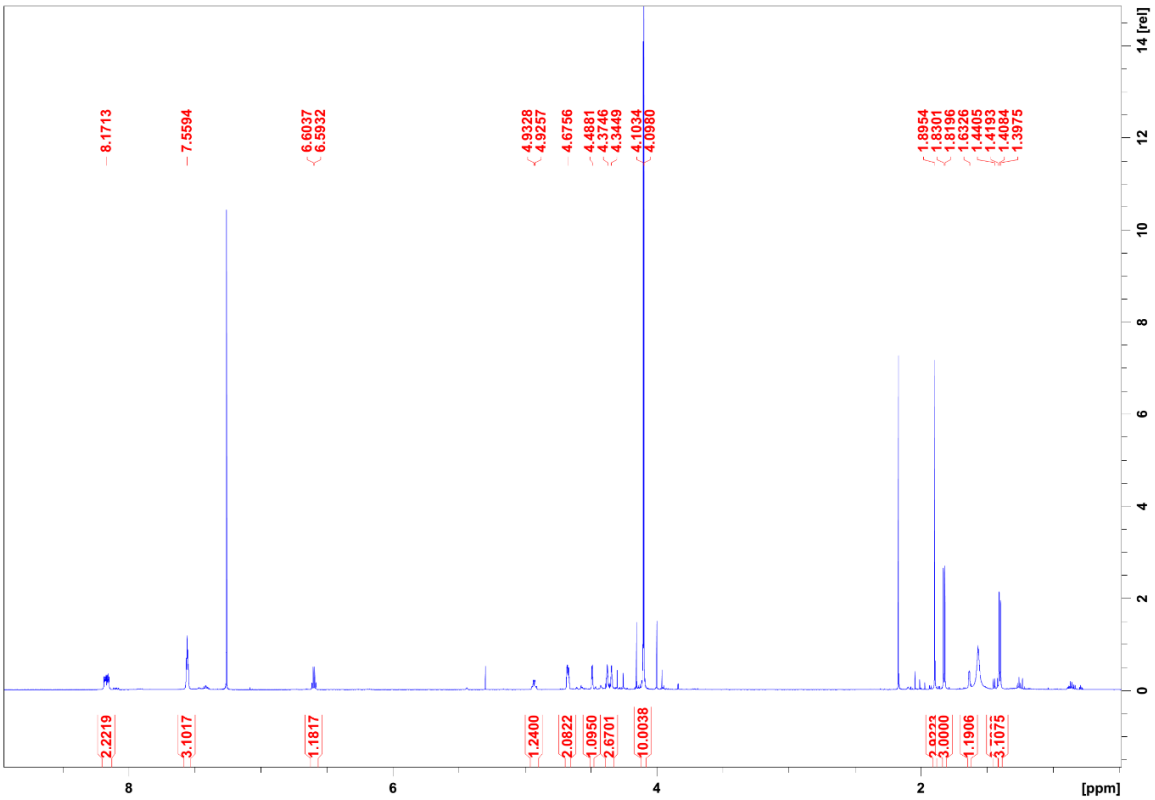
^{1}H-NMR (Alcohol ***25***):



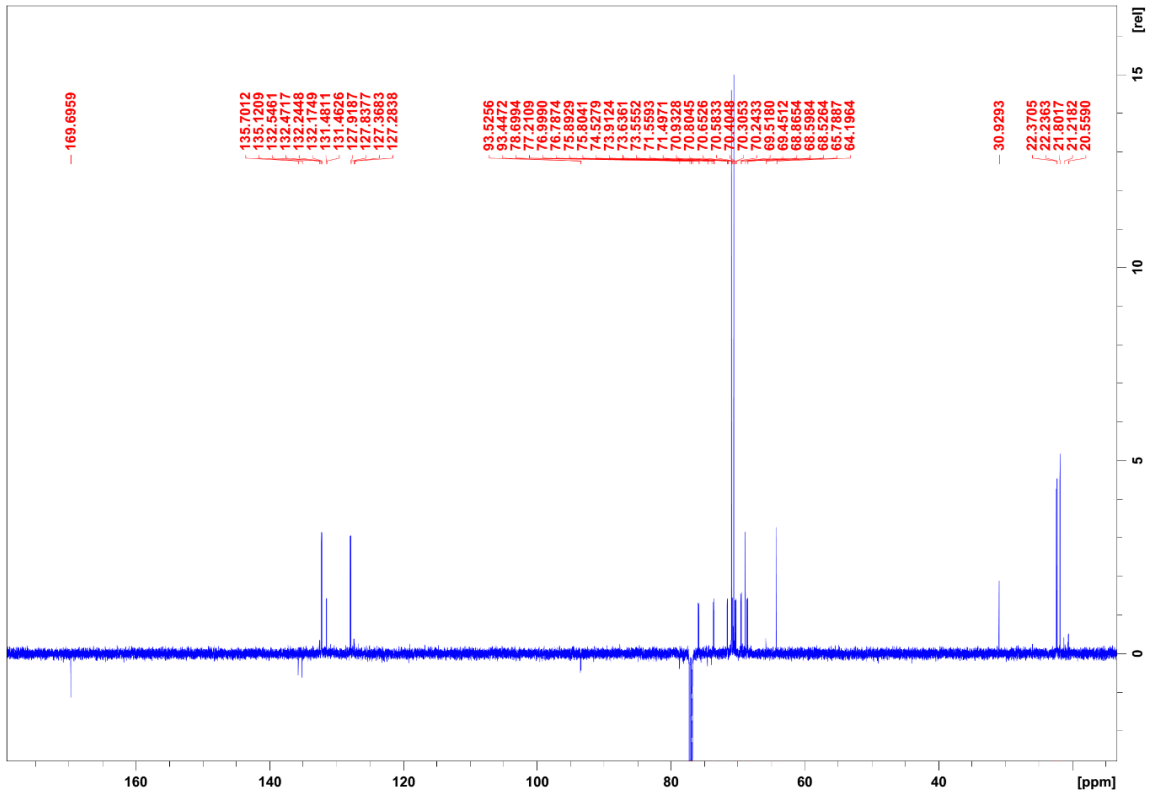
^{13}C{^{1}H}-NMR (Alcohol ***25***):



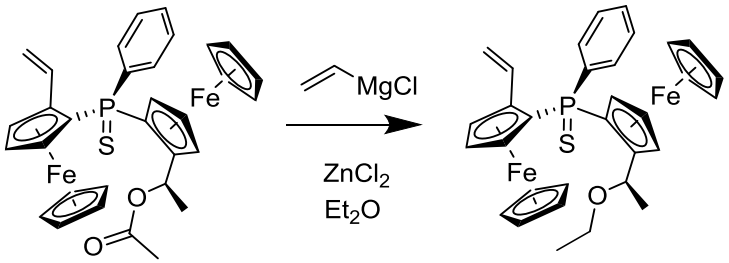
^{1}H-NMR (Hydroxyacetate ***26***):



^{13}C{^{1}H}-NMR (Hydroxyacetate ***26***):



Attempted nucleophilic vinyl substitution of monovinylmonoacetatephosphinesulfide *24*



24
$C_{32}H_{31}Fe_2O_2PS$
622,322 g/mol

27
$C_{32}H_{33}Fe_2OPS$
608,339 g/mol
10%

Procedure: [105] In a flame-dried Schlenck tube, 4.5 mL of dry Et_2O was degassed three times, cooled in an ice bath and $ZnCl_2$ (1 M in Et_2O, 0.75 mL, 0.75 mmol, 5.17 eq) and vinyl MgCl (1.6 M in THF, 0.25 mL, 0.40 mmol, 2.76 eq) were added under Ar in this order. The resulting white suspension was stirred for 1 h at 0 °C, then cooled to -78 °C. In a separate flame-dried Schlenck tube, monovinylmonoacetatephosphinesulfide ***24*** (90 mg, 0.145 mmol) was dissolved in 8 mL of dry Et_2O under Ar. The solution was degassed three times and cooled to -78 °C, then transferred to the other Schlenck tube via teflon cannula. The resulting reaction mixture was stirred and allowed to warm up to r.t. overnight. To the suspension, 14 mL of sat. aq. $NaHCO_3$ was added. The biphasic mixture was separated and the organic layer was washed with 14 mL of water and 14 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2; 0→100% EtOAc in *n*-heptane) yielding 10% of an orange solid product preliminarily identified as ***27*** (9 mg).

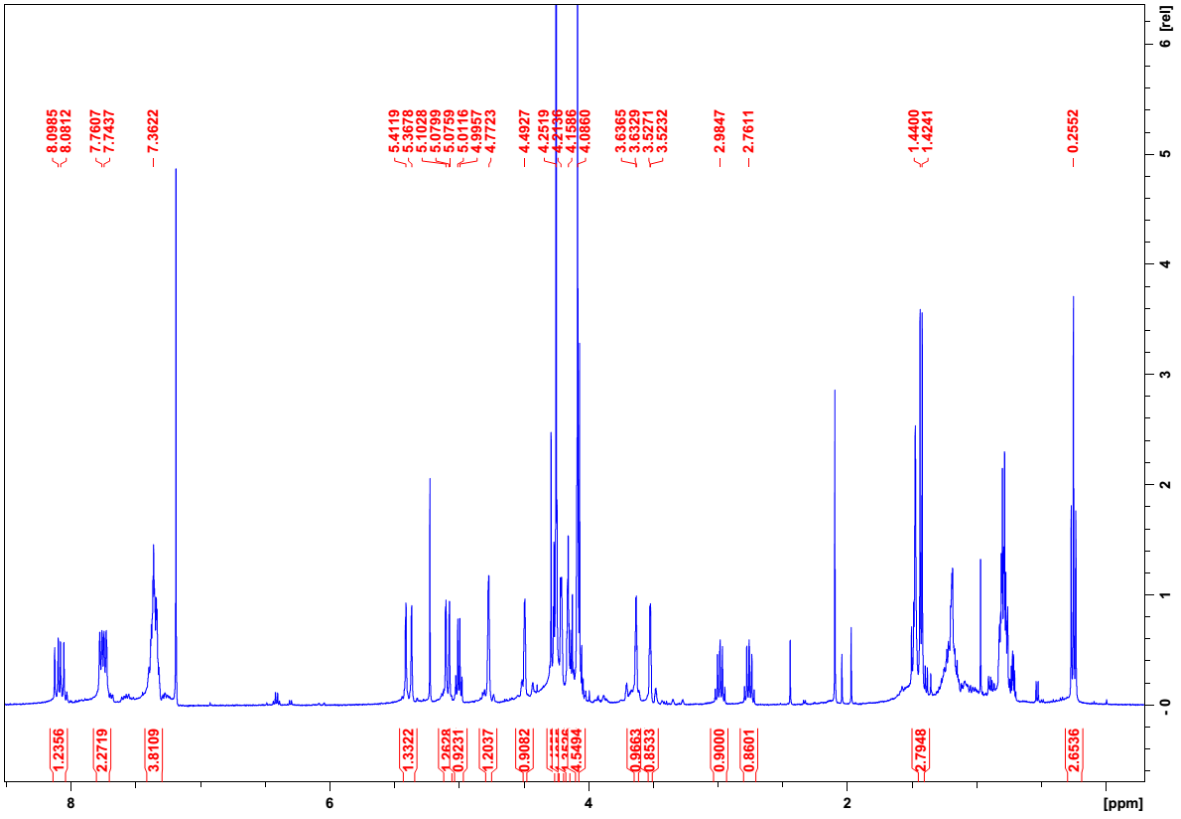
^{1}H-NMR (400 MHz, $CDCl_3$) δ = 8.09 (dd, *J* = 17.7, 10.7 Hz, 1H); 7.79-7.71 (m, 2H); 7.41-7.31 (m, 3H); 5.39 (dd, *J* = 17.7, 1.7 Hz, 1H); 5.09 (dd, *J* = 10.7, 1.7 Hz, 1H); 5.00 (q, *J* = 6.4 Hz, 1H); 4.77 (m, 1H); 4.49 (m, 1H); 4.25 (s, 5H); 4.21 (m, 1H); 4.16

(m, 1H); 4.09 (s, 5H); 3.63 (m, 1H); 3.53 (m, 1H); 2.99 (dq, *J* = 8.4, 7.1 Hz, 1H); 2.76 (dq, *J* = 8.4, 7.1 Hz, 1H); 1.43 (d, *J* = 6.4 Hz, 3H); 0.26 (t, *J* = 7.5 Hz, 3H) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 40.55 ppm.

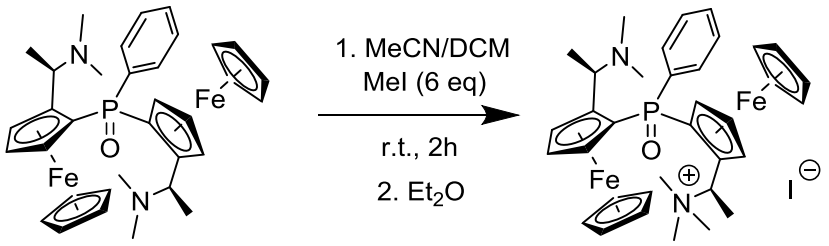
HRMS: m/z calculated for M = $C_{32}H_{33}Fe_2OPS$; $[M]^+$ 608.0689, found: 608.0674.

^{1}H-NMR:



5. 2. 2. 3. c. Ammonium iodide salt formation

Synthesis of 1,1‘‘-(Phenylphosphinideneoxide)[(2*S*)-2-[(1*R*)-1-(dimethylamino)-ethyl]]ferrocene[(2*S*)-2-[(1*R*)-1-(trimethylamino)-ethyl]]ferrocenium iodide



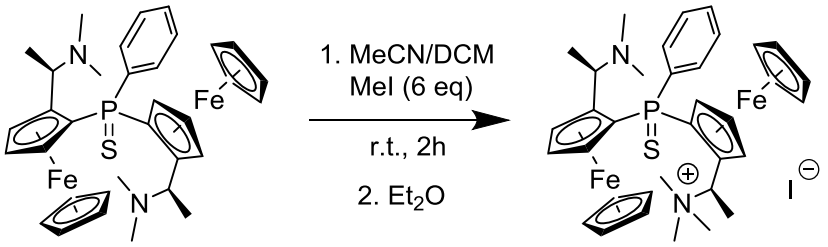
11
$C_{34}H_{41}Fe_2N_2OP$
636,379 g/mol

32
$C_{35}H_{44}Fe_2IN_2OP$
778,318 g/mol
100%

Procedure: [25] Diaminophosphineoxide ***11*** (642 mg, 1.01 mmol) was dissolved in 15 mL of dry MeCN and 15 mL of dry DCM in a flame-dried Schlenck tube under Ar. MeI (375 µL, 6.00 mmol, 5.94 eq) was added to the solution and stirred for 2 h at r.t. Precipitation of ammonium iodide salt ***32*** was started by adding 10 mL of Et_2O, yielding the salt quantitatively as an orange powder.

HRMS: m/z calculated for M = $C_{35}H_{44}Fe_2N_2OP$; $[M]^+$ 651.1885, found: 651.1868.

Synthesis of 1,1''-(Phenylphosphinidenesulfide)[(2*S*)-2-[(1*R*)-1-(dimethylamino)-ethyl]]ferrocene[(2*S*)-2-[(1*R*)-1-(trimethylamino)-ethyl]]ferrocenium iodide



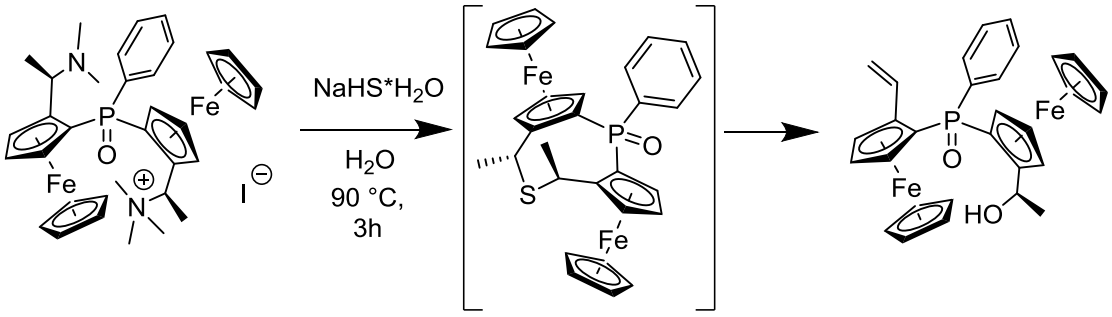
13
$C_{34}H_{41}Fe_2N_2PS$
652,440 g/mol

33
$C_{35}H_{44}Fe_2IN_2PS$
794,379 g/mol
100%

Procedure: [25] Diaminophosphinesulfide ***13*** (557 mg, 0.85 mmol) was dissolved in 13 mL of dry MeCN and 13 mL of dry DCM in a flame-dried Schlenck tube under Ar. MeI (320 µL, 5.12 mmol, 5.99 eq) was added to the solution and stirred for 2 h at r.t. Precipitation of ammonium iodide salt ***33*** was started by adding 8.5 mL of Et_2O yielding the salt quantitatively as an orange powder.

HRMS: m/z calculated for M = $C_{35}H_{44}Fe_2N_2PS$; $[M]^+$ 667.1662, found: 667.1644.

Attempted synthesis of (2*S*,4*R*,6*R*,8*S*)-4,6-Dimethyl-1-phenyl-diferroceno-5-sulfide-1-phosphineoxide



32
$C_{35}H_{44}Fe_2IN_2OP$
778,318 g/mol

30
$C_{30}H_{29}Fe_2OPS$
580,285 g/mol

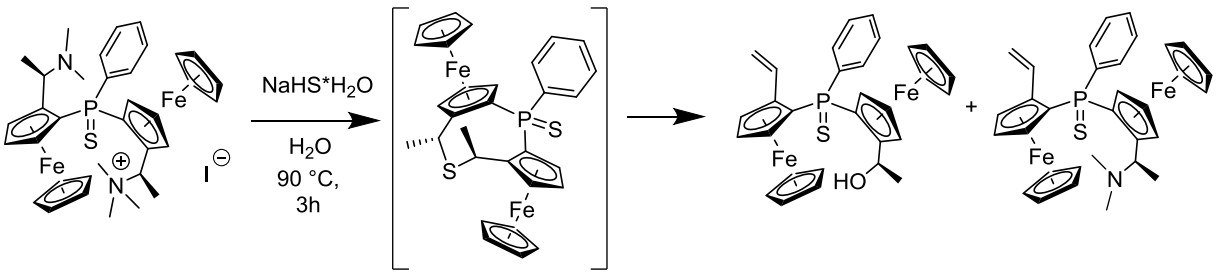
38
$C_{30}H_{29}Fe_2O_2P$
564,224 g/mol

Procedure: [106] Ammonium iodide salt ***32*** (42 mg, 0.05 mmol) and NaHS • H_2O (4 mg, 0.06 mmol, 1.0 eq) were dissolved in 1 mL of water in a Schlenck tube, degassed three times and heated to 90 °C in an oil bath for 3 h under Ar. The reaction mixture was cooled to r.t. and extracted repeatedly with small portions of Et_2O. The combined organic fractions were washed with 0.1 M aq. HCl and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The aq. mother liquor was extracted repeatedly with small portions of DCM. The combined organic fractions were washed with 0.1 M aq. HCl and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude product contained the intended product. After purification by column chromatography (SiO_2, 0→100% EtOAc in *n*-heptane), however, only alcohol ***38*** was regained.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 30.19 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{29}Fe_2O_2P$; $[M]^+$ 564.0604, found: 564.0603; $[M+Na]^+$ 587.0502, found: 587.0501; $[M+K]^+$ 603.0244, found: 603.0241.

Attempted synthesis of (2*S*,4*R*,6*R*,8*S*)-4,6-Dimethyl-1-phenyl-diferroceno-5-sulfide-1-phosphinesulfide



33
$C_{35}H_{44}Fe_2IN_2PS$
794,379 g/mol

36
$C_{30}H_{29}Fe_2PS_2$
596,346 g/mol

25
$C_{30}H_{29}Fe_2OPS$
580,285 g/mol

39
$C_{32}H_{34}Fe_2NPS$
607,355 g/mol

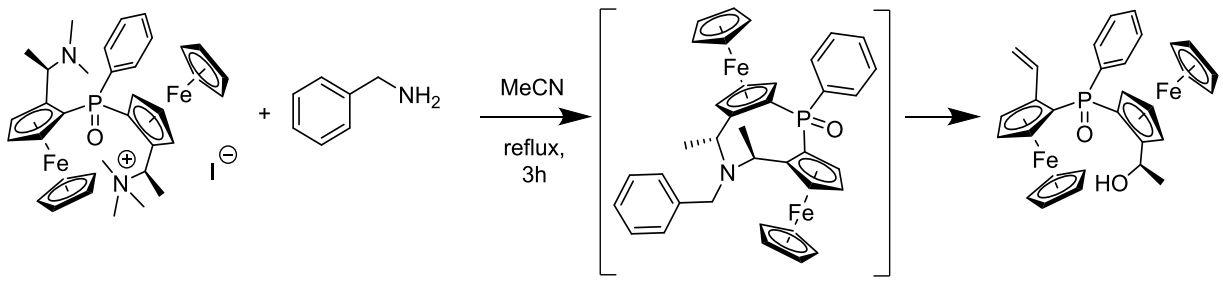
Procedure: [106] Ammonium iodide salt ***33*** (36 mg, 0.05 mmol) and NaHS • H_2O (3.5 mg, 0.05 mmol, 1.0 eq) were dissolved in 1 mL of water in a Schlenck tube, degassed three times and heated to 90 °C in an oil bath for 3 h under Ar. The reaction mixture was cooled to r.t. and extracted repeatedly with small portions of Et_2O. The combined organic fractions were washed with 0.1 M aq. HCl and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The aq. mother liquor was extracted repeatedly with small portions of DCM. The combined organic fractions were washed with 0.1 M aq. HCl and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The crude product contained the intended product. After purification by column chromatography (SiO_2, 1.5% Et_3N in Et_2O), however, only amine ***39*** and alcohol ***25*** were regained.

Amine ***39***:

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 41.91 (s) ppm.

HRMS: m/z calculated for M = $C_{32}H_{34}Fe_2NPS$; $[M+H]^+$ 608.0927, found: 608.0904.

Attempted synthesis of (2*S*,4*R*,6*R*,8*S*)-4,6-Dimethyl-5-benzyl-1-phenyl-diferroceno-5-amine-1-phosphineoxide



32
$C_{35}H_{44}Fe_2IN_2OP$
778,318 g/mol

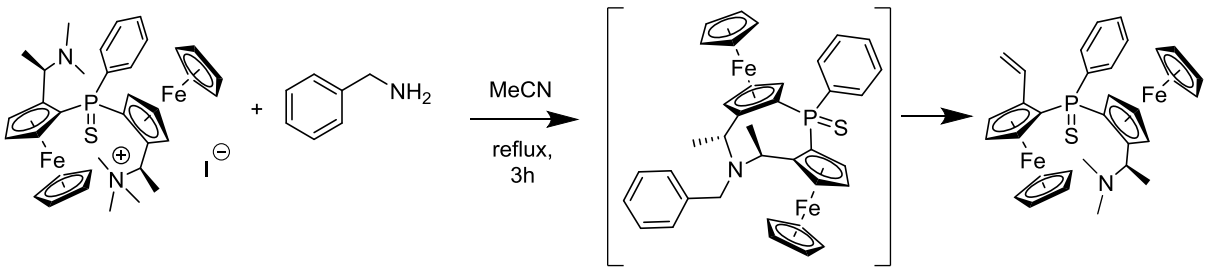
C_7H_9N
107,156 g/mol

29
$C_{37}H_{36}Fe_2NOP$
653,365 g/mol

38
$C_{30}H_{29}Fe_2O_2P$
564,224 g/mol

Procedure: [60] Ammonium iodide salt ***32*** (25 mg, 0.03 mmol) was dissolved in dry MeCN in a flame-dried Schlenck tube under Ar. A solution of $BnNH_2$ in dry MeCN (1 v-%; 350 µL, 0.03 mmol, 1.00 eq) was added. The reaction mixture was degassed three times, then heated to reflux for 3 h. The solution was cooled to r.t. and the solvent was removed under reduced pressure. The crude product contained the intended product. After purification by column chromatography (SiO_2, 60→100% (Et_2O + 1.5% Et_3N) in *n*-heptane), however, only alcohol ***38*** was regained.

Attempted synthesis of (2*S*,4*R*,6*R*,8*S*)-4,6-Dimethyl-5-benzyl-1-phenyl-diferroceno-5-amine-1-phosphinesulfide



33
$C_{35}H_{44}Fe_2IN_2PS$
794,379 g/mol

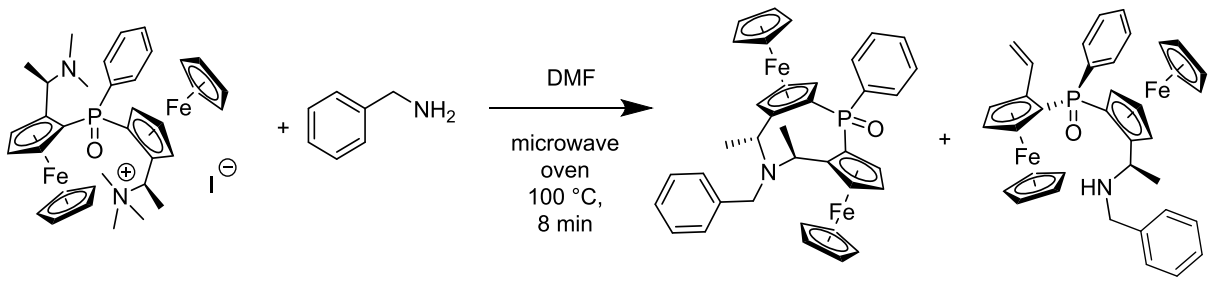
C_7H_9N
107,156 g/mol

35
$C_{37}H_{36}Fe_2NPS$
669,426 g/mol

39
$C_{32}H_{34}Fe_2NPS$
607,355 g/mol

Procedure: [60] Ammonium iodide salt ***33*** (12 mg, 0.02 mmol) was dissolved in dry MeCN in a flame-dried Schlenck tube under Ar. A solution of $BnNH_2$ in dry MeCN (1 v-%; 164 µL, 0.02 mmol, 1.0 eq) was added. The reaction mixture was degassed three times, then heated to reflux for 3 h. The solution was cooled to r.t. and the solvent was removed under reduced pressure. The crude product contained the intended product. After purification by column chromatography (SiO_2, 30→60% (Et_2O + 1.5% Et_3N) in *n*-heptane) however, only amine ***39*** was regained.

Synthesis of (2*S*,4*R*,6*R*,8*S*)-4,6-Dimethyl-5-benzyl-1-phenyl-diferroceno-5-amine-1-phosphineoxide



32
$C_{35}H_{44}Fe_2IN_2OP$
778,318 g/mol

C_7H_9N
107,156 g/mol

29
$C_{37}H_{36}Fe_2NOP$
653,365 g/mol
11%

28
$C_{37}H_{36}Fe_2NOP$
653,365 g/mol
8%

Procedure: Ammonium iodide salt ***32*** (77 mg, 0.10 mmol) and $BnNH_2$ (11 µL, 0.10 mmol, 1.0 eq) were dissolved in 8 mL of DMF and heated for 8 min at 100 °C in a microwave oven. The reaction mixture was cooled to r.t., 10 mL of DCM were added and the organic solution was washed four times with 50 mL of water each, once with 20 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Al_2O_3; 0→100% EtOAc in *n*-heptane) yielding 11% of the intended benzylic aminephosphineoxide diferrocenyl cycle ***29*** (7 mg) as a glassy orange solid as well as 8% of the sec. amine elimination product ***28*** (5 mg).

Cycle ***29***:

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.11-8.06 (m, 2H); 7.57-7.50 (m, 3H); 7.41 (d, *J* = 7.4 Hz, 2H); 7.28-7.24 (m, 2H); 7.17 (pt, *J* = 7.3 Hz, 1H); 4.80 (m, 1H); 4.47 (m, 1H); 4.39 (m, 2H); 4.35 (m, 1H); 4.29 (m, 1H); 4.24 (s, 5H); 4.04 (q, *J* = 6.8 Hz, 1H); 3,94 (d, *J* = 16.4 Hz, 1H); 3.90 (s, 5H); 3.73 (q, *J* = 6.6 Hz, 1H); 3.39 (d, *J* = 16.3 Hz, 1H); 1.26 (d, *J* = 6.5 Hz, 3H); 1.25 (d, *J* = 6.9 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 143.69 (C_q); 137.02 (d, J_{CP} = 110.2 Hz, C_q); 132.35 (d, J_{CP} = 9.38 Hz, CH); 131.20 (d, J_{CP} = 2.7 Hz, CH); 127.82 (CH); 127.63 (d, J_{CP} = 5.5 Hz, CH); 127.54 (d, J_{CP} = 6.6, CH); 126.01 (CH); 93.20 (d, J_{CP} = 13.2 Hz, C_q); 93.06 (d, J_{CP} = 13.6 Hz, C_q); 75.38 (d, J_{CP} = 22.2 Hz, C_q); 74.62 (d, J_{CP} = 18.2

Hz, C_q); 73.65 (d, J_{CP} = 11.4 Hz, CH); 72.64 (d, J_{CP} = 13.9 Hz, CH); 70.45 (CH); 70.39 (d, J_{CP} = 10.6 Hz, CH); 70.17 (CH); 69.81 (d, J_{CP} = 11.2 Hz, CH); 69.58 (d, J_{CP} = 9.6 Hz, 2 CH); 54.66 (CH); 53.55 (CH); 53.12 (CH_2); 21.44 (CH_3); 20.52 (CH_3) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 29.63 (s) ppm.

HRMS: m/z calculated for M = $C_{37}H_{36}Fe_2NOP$; $[M+H]^+$ 654.1306, found: 654.1306; $[M+Na]^+$ 676.1126, found: 676.1129.

Compound ***28***:

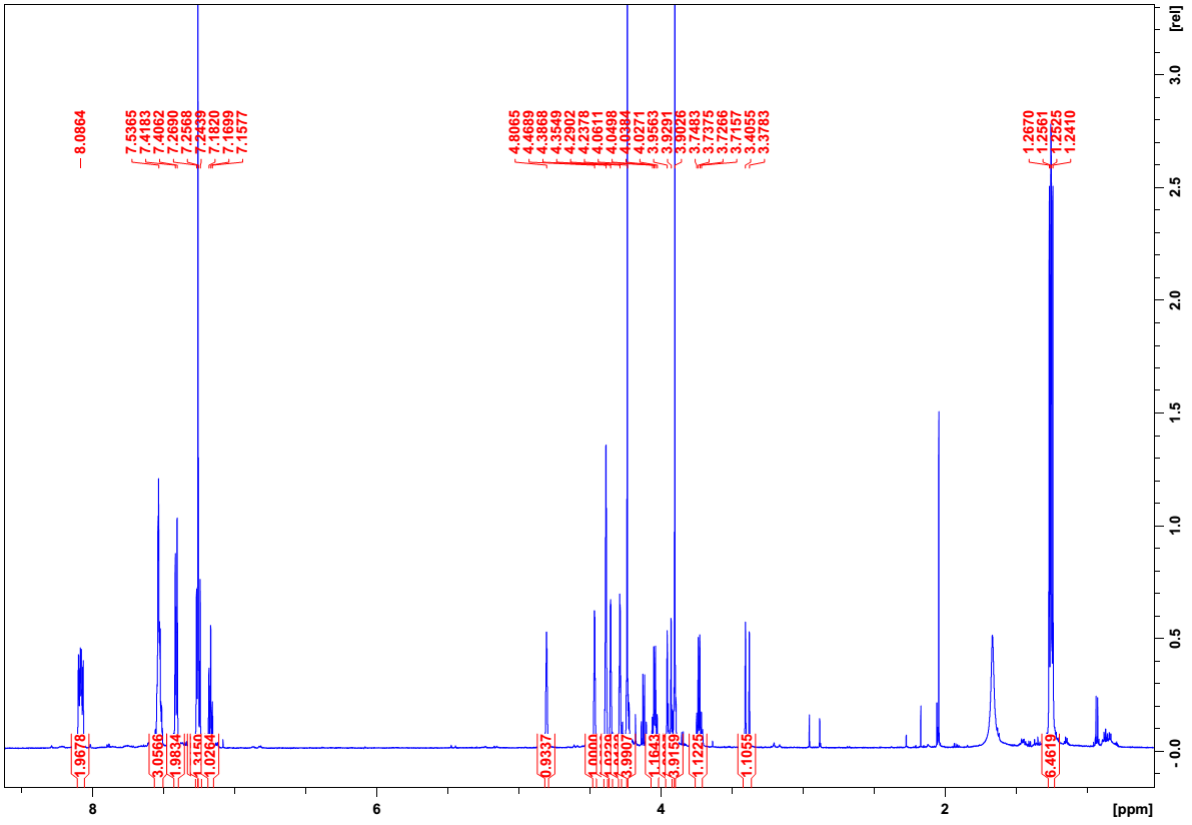
^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.80-7.69 (m, 3H); 7.55-7.34 (m, 2H); 7.33-7.27 (m, 3H); 7.16-7.10 (m, 2H); 6.84-6.80 (m, 1H); 5.46 (dd, *J* = 17.7, 1.6 Hz, 1H); 5.16 (dd, *J* = 10.8, 10.6 Hz, 1H); 4.86 (m, 1H); 4.49 (m, 1H); 4.41 (q, *J* = 2.4 Hz, 1H); 4.39 (pt, *J* = 2.0 Hz, 1H); 4.36 (m, 1H); 4.27 (s, 5H); 4.24 (s, 1H); 3.93 (s, 5H); 3.89 (d, *J* = 4.3 Hz, 1H); 3.20 (s, 2H); 1.43 (d, *J* = 6.6, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 133.52 (CH); 131.28 (CH); 130.29 (CH); 128.38 (CH); 128.26 (CH); 128.15 (CH); 127.95 (CH); 111.43 (CH_2); 90.13 (C_q); 86.08 (C_q); 71.65 (CH); 71.26 (CH); 71.17 (CH); 70.81 (CH); 70.73 (CH); 70.31 (CH); 70.28 (CH); 69.58 (CH); 67.25 (CH); 53.15 (CH_2); 20.56 (CH_3) ppm.

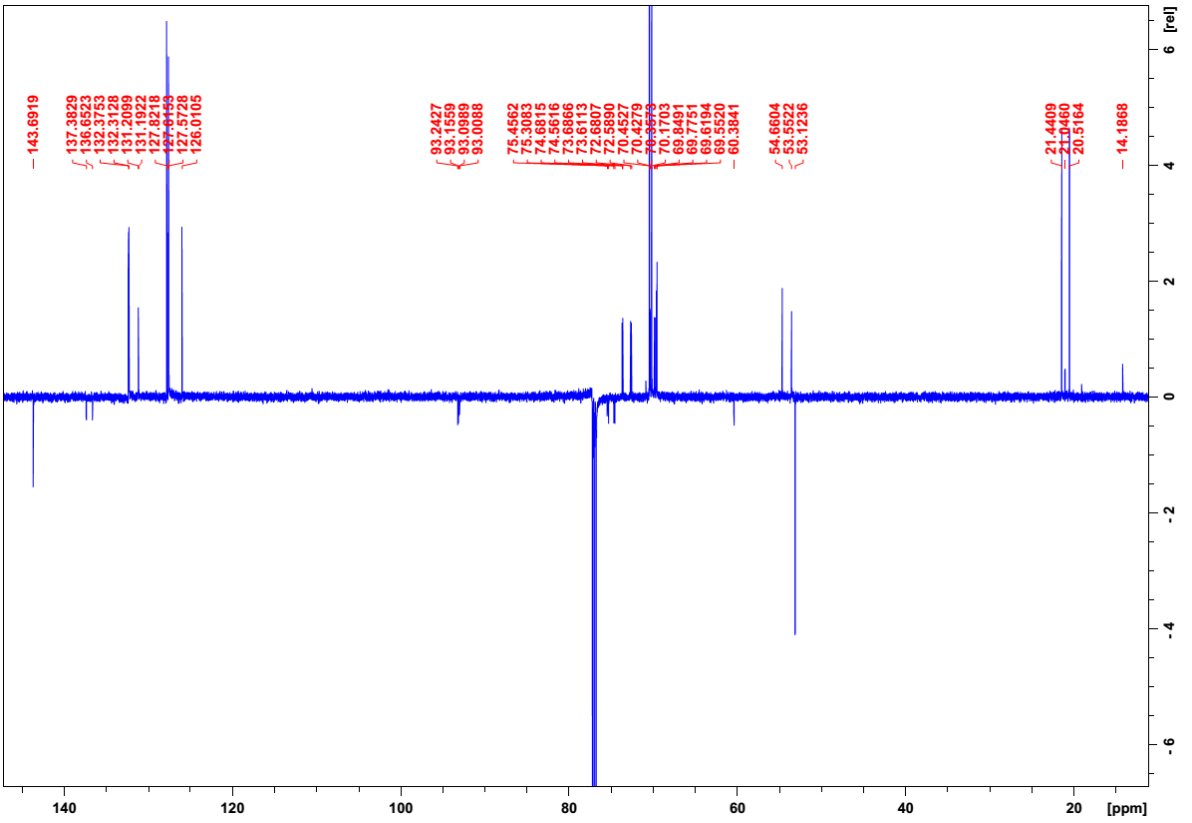
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 30.54 (s) ppm.

HRMS: m/z calculated for M = $C_{37}H_{36}Fe_2NOP$; $[M+H]^+$ 654.1306, found: 654.1314.

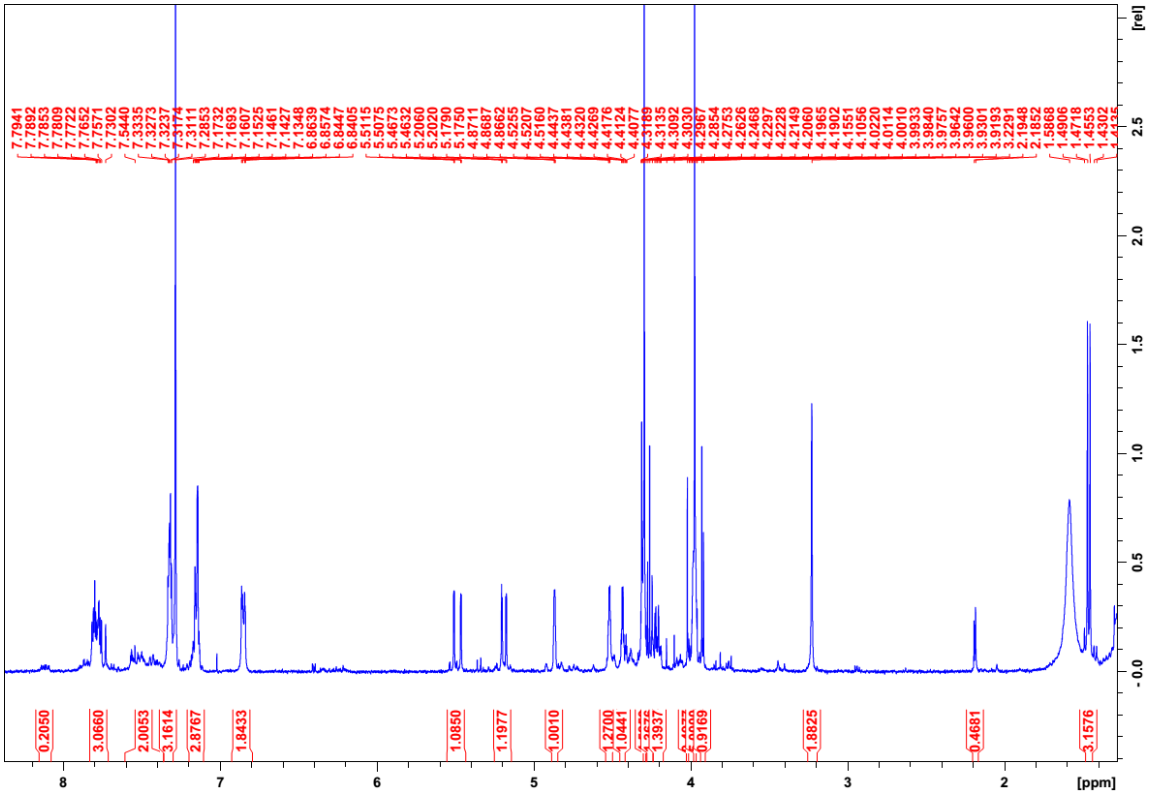
^{1}H-NMR (Diferrocenyl cycle ***29***):



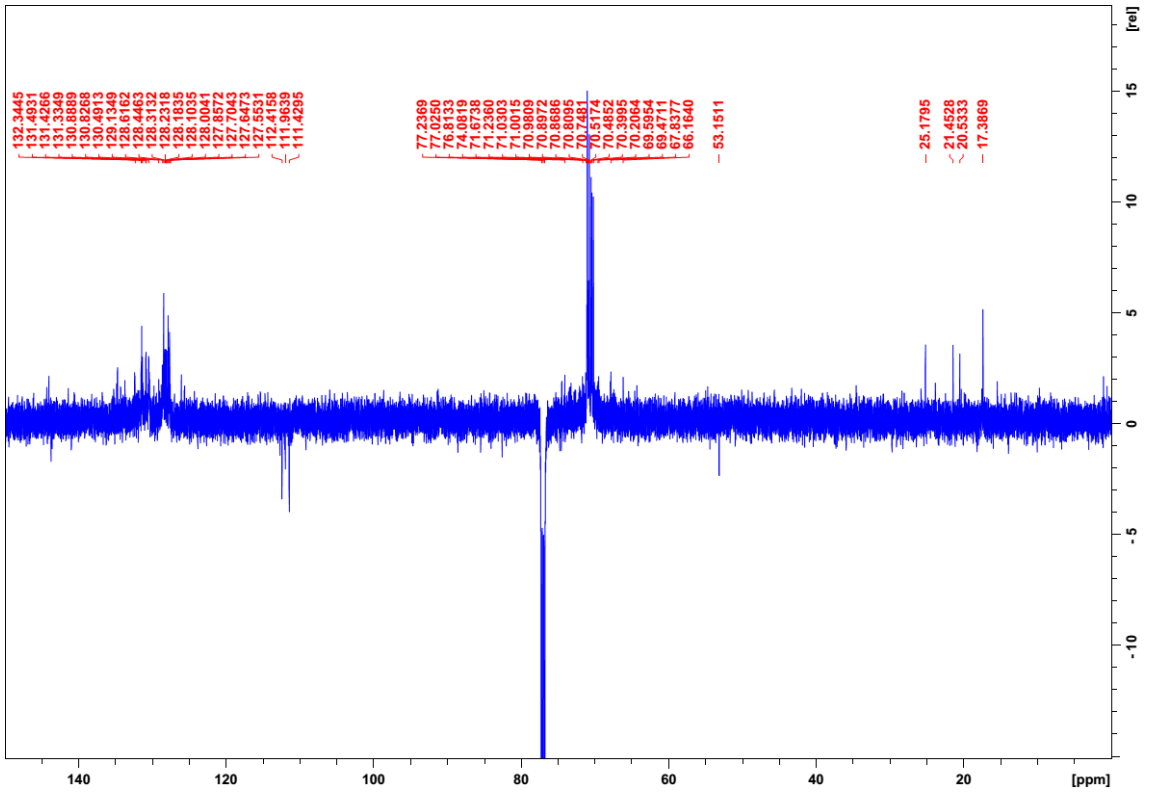
^{13}C{^{1}H}-NMR (Diferrocenyl cycle ***29***):



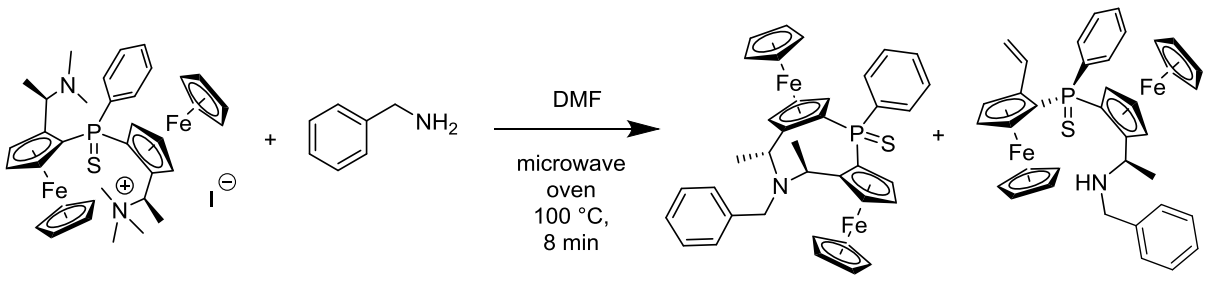
^{1}H-NMR (Secondary amine ***28***):



^{13}C{^{1}H}-NMR (Secondary amine ***28***):



Synthesis of (2*S*,4*R*,6*R*,8*S*)-4,6-Dimethyl-5-benzyl-1-phenyl-diferroceno-5-amine-1-phosphinesulfide



33
$C_{35}H_{44}Fe_2IN_2PS$
794,379 g/mol

C_7H_9N
107,156 g/mol

35
$C_{37}H_{36}Fe_2NPS$
669,426 g/mol
12%

34
$C_{37}H_{36}Fe_2NPS$
669,426 g/mol
13%

Procedure: Ammonium iodide salt ***33*** (80 mg, 0.10 mmol) and $BnNH_2$ (11 µL, 0.10 mmol, 1.00 eq) were dissolved in 8 mL of DMF and heated for 8 min at 100 °C in a microwave oven. The mixture was cooled to r.t., 10 mL of DCM were added and the organic layer was washed four times with 50 mL of water each, once with 20 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Al_2O_3; 0→100% EtOAc in *n*-heptane) yielding 12% of the intended benzylic aminephosphinesulfide diferrocenyl cycle ***35*** (8 mg) as a glassy orange solid as well as 13% of the sec. amine elimination product ***34*** (9 mg) as orange crystalline needles.

Cycle ***35***:

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.91 (ddd, *J* = 13.6, 7.8, 1.5 Hz, 2H); 7.47-7.41 (m, 3H); 7.31 (d, *J* = 7.5 Hz, 2H); 7.28-7.24 (m, 2H); 7.17 (pt, *J* = 7.2 Hz, 1H); 5.36 (m, 1H); 4.65 (dd, *J* = 4.3, 2.4 Hz, 1H); 4.57 (m, 1H); 4.48 (m, 1H); 4.46 (m, 1H); 4.38 (m, 1H); 4.21 (s, 5H); 4.14 (s, 5H); 3.98 (s, 1H); 3.73 (q, *J* = 6.9 Hz, 1H); 3.46 (q, *J* = 6.3 Hz, 1H); 3.19 (d, *J* = 16.9 Hz, 1H); 1.19 (d, *J* = 7.0 Hz, 3H); 1.09 (d, *J* = 6.4 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 144.18 (C_q); 138.58 (d, J_{CP} = 89.2 Hz, C_q); 132.79 (d, J_{CP} = 11.3 Hz, CH); 130.88 (d, J_{CP} = 3.0 Hz, CH); 127.88 (CH); 127.32 (d, J_{CP} = 12.4 Hz, CH); 127.00 (CH); 126.05 (CH); 93.39 (d, J_{CP} = 11.1 Hz, C_q); 92.56 (d, J_{CP} = 12.1 Hz, C_q); 75.55 (C_q); 75.47 (d, J_{CP} = 15.6 Hz, CH); 74.93 (C_q); 73.93 (d, J_{CP}

= 15.0 Hz, CH); 71.41 (d, J_{CP} = 9.7 Hz, CH); 71.01 (CH); 70.35 (CH); 70.07 (d, J_{CP} = 11.5 Hz, CH); 69.96 (d, J_{CP} = 9.1 Hz, CH); 69.85 (d, J_{CP} = 11.4 Hz, CH); 55.79 (CH); 53.18 (CH_2); 52.14 (CH); 22.12 (CH_3); 21.35 (CH_3) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 43.41 (s) ppm.

HRMS: m/z calculated for M = $C_{37}H_{36}Fe_2NPS$; $[M+H]^+$ 670.1078, found: 670.1068.

Compound ***34***:

M.p.: 179-180 °C (decomposition).

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.82 (dd, *J* = 12.7, 6.5 Hz, 2H); 7.29-7.23 (m, 3H); 7.13-7.08 (m, 3H); 6.80-6.76 (m, 2H); 5.47 (dd, *J* = 17.7, 1.6 Hz, 1H); 5.17 (dd, *J* = 10.8, 1.6 Hz, 1H); 4.86 (m, 1H); 4.62 (q, *J* = 6.7 Hz, 1H); 4.56 (m, 1H); 4.33 (s, 5H); 4.30 (m, 1H); 4.24 (dd, *J* = 4.1, 2.6 Hz, 1H); 4.12 (s, 5H); 3.77 (m, 1H); 3.67 (m, 1H); 3.21 (dd, *J* = 23.6, 12.8 Hz, 2H); 1.45 (d, *J* = 6.6 Hz, 3H) ppm.

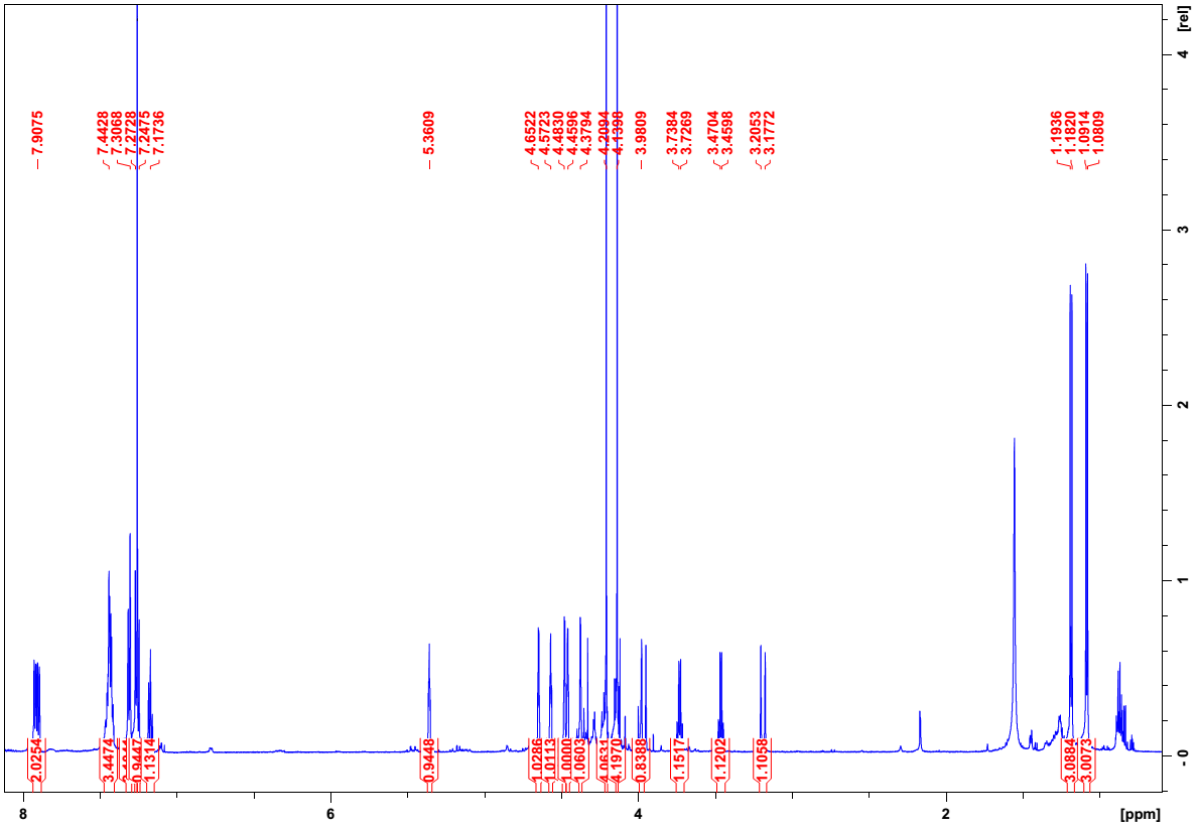
^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 140.46 (C_q); 135.15 (d, J_{CP} = 86.3 Hz, C_q); 134.47 (CH); 131.80 (d, J_{CP} = 10.2 Hz, CH); 131.14 (d, J_{CP} = 2.9 Hz, CH); 127.85 (CH); 127.82 (d, J_{CP} = 11.4 Hz, CH); 127.78 (CH); 126.14 (CH); 111.48 (CH_2); 95.12 (d, J_{CP} = 12.7 Hz, C_q); 88.55 (d, J_{CP} = 12.0 Hz, C_q); 77.91 (d, J_{CP} = 95.5 Hz, C_q); 75.03 (d, J_{CP} = 12.2 Hz, CH); 74.42 (d, J_{CP} = 12.1 Hz, CH); 73.98 (d, J_{CP} = 95.4 Hz, 1 C_q); 71.15 (CH); 71.10 (d, J_{CP} = 10.1 Hz, CH); 70.67 (CH); 69.97 (d, J_{CP} = 10.2 Hz, CH); 68.22 (d, J_{CP} = 9.1 Hz, CH); 67.94 (d, J_{CP} = 10.6 Hz, CH); 50.71 (CH_2); 50.08 (CH); 19.53 (CH_3) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 39.55 (s) ppm.

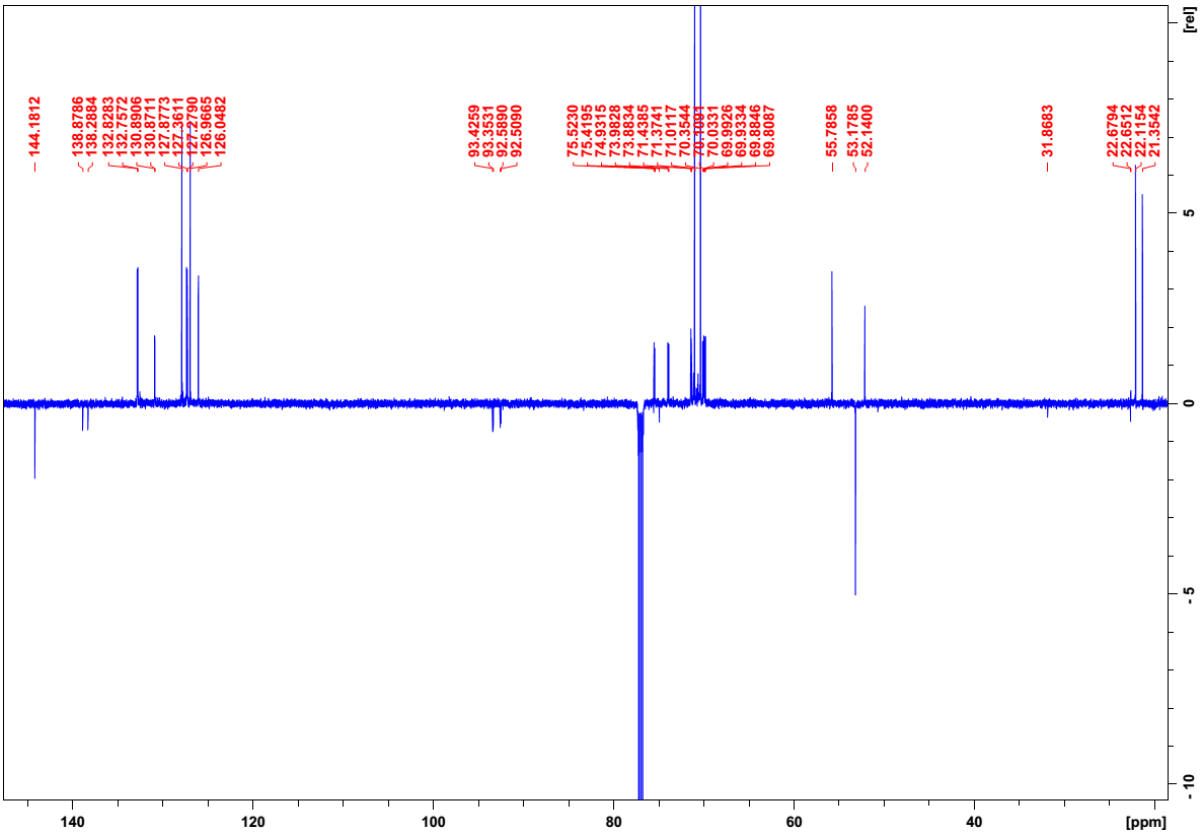
HRMS: m/z calculated for M = $C_{37}H_{36}Fe_2NPS$; $[M+H]^+$ 670.1078, found: 670.1075.

Crystal data: orthorhombic; space group $P2_12_12_1$; *a* = 12.3578 Å; *b* = 14.4342 Å; *c* = 17.4796 Å; *α* = 90°; *β* = 90°; *γ* = 90°; *Z* = 4; *T* = -143.15 K; 39094 reflections measured; 7062 unique which were used in all calculations. The final *R1* was 0.0614 ($I > 2\sigma(I)$) and wR_2 was 0.0906 (all data).

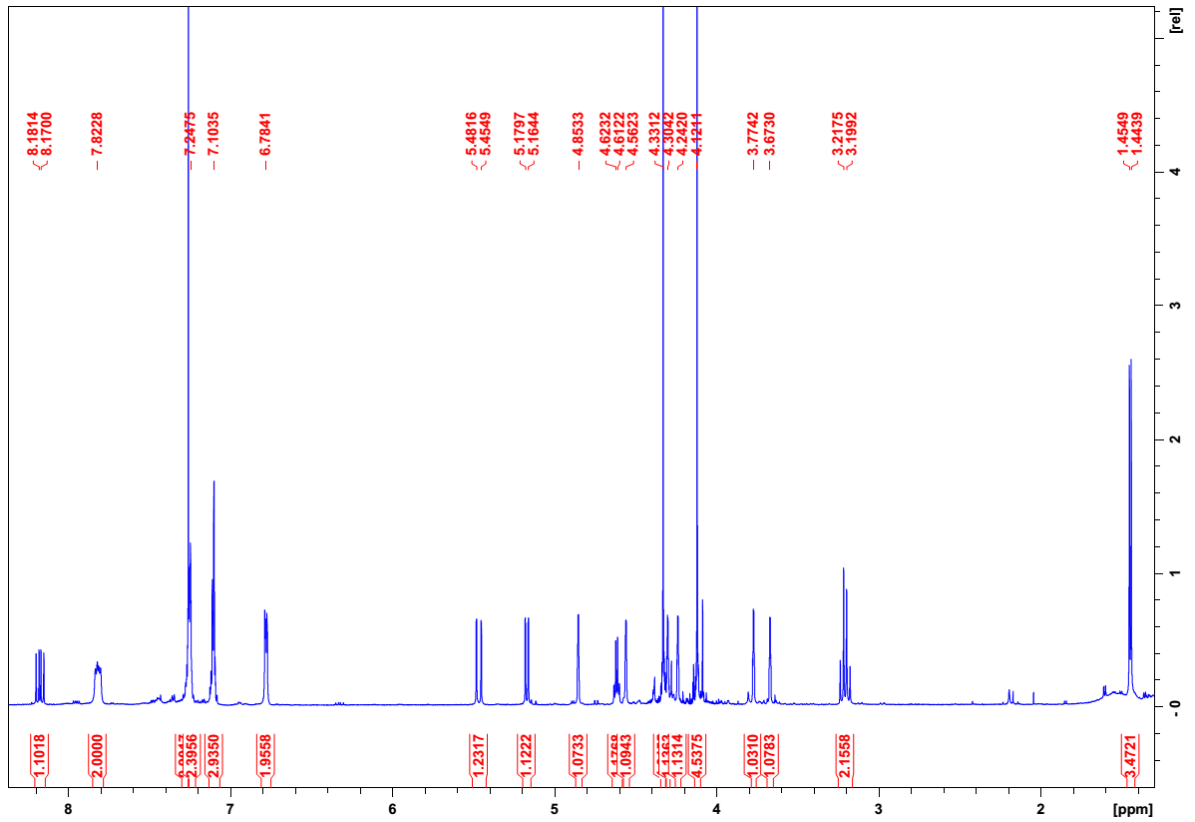
^{1}H-NMR (Diferrocenyl cycle ***35***):



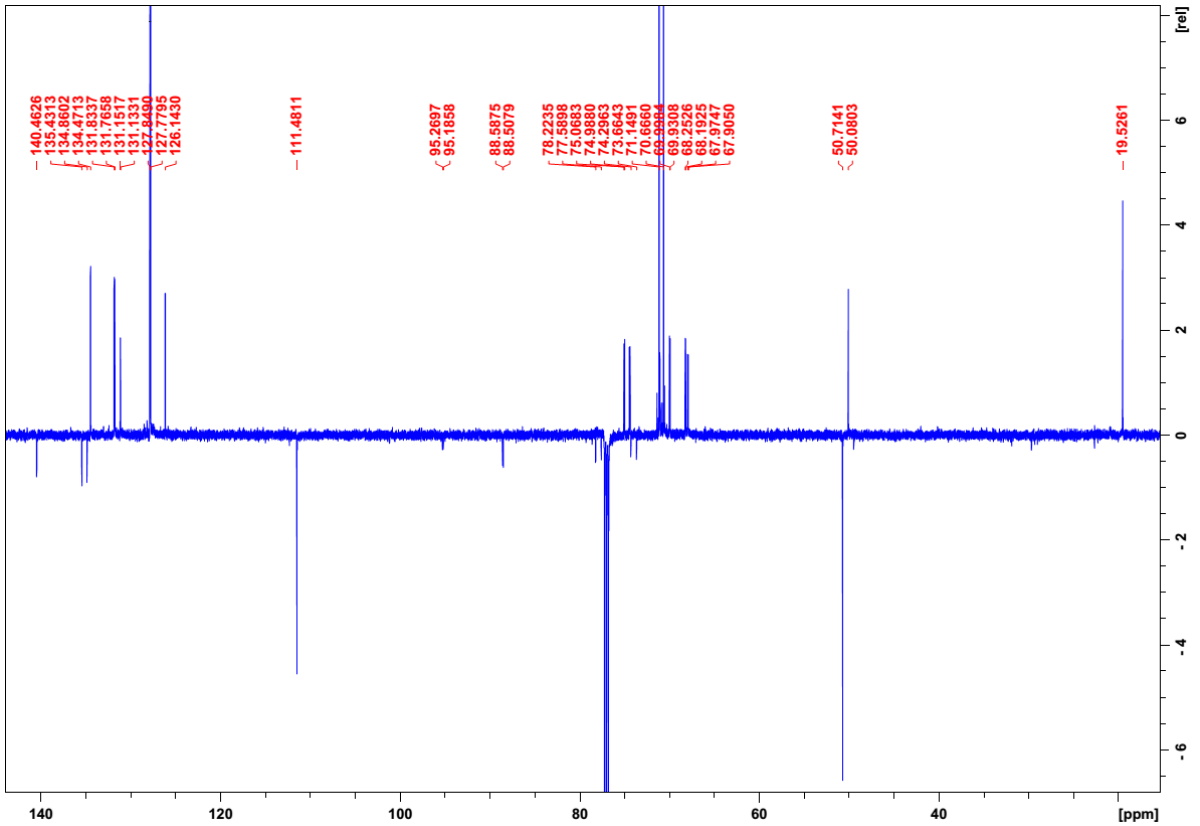
^{13}C{^{1}H}-NMR (Diferrocenyl cycle ***35***):



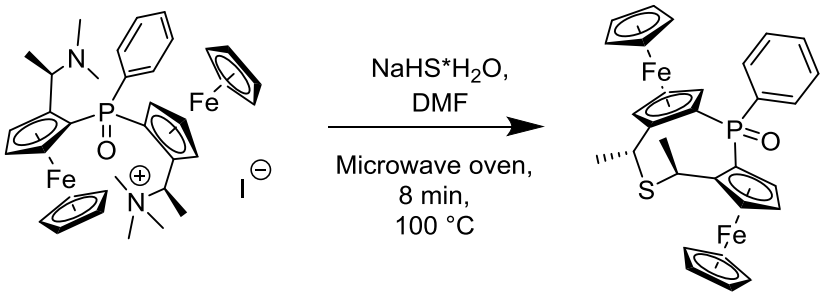
^{1}H-NMR (Secondary amine ***34***):



^{13}C{^{1}H}-NMR (Secondary amine ***34***):



Synthesis of (2*S*,4*R*,6*R*,8*S*)-4,6-Dimethyl-1-phenyl-diferroceno-5-sulfide-1-phosphineoxide



32
$C_{35}H_{44}Fe_2IN_2OP$
778,318 g/mol

30
$C_{30}H_{29}Fe_2OPS$
580,285 g/mol
14%

Procedure: Ammonium iodide salt ***32*** (75 mg, 0.10 mmol) and NaHS • H_2O (7.5 mg, 0.10 mmol, 1.0 eq) were dissolved in 8 mL of DMF and heated for 8 min at 100 °C in a microwave oven. The mixture was cooled to r.t., 10 mL of DCM were added and the organic layer was washed four times with 50 mL of water each, once with 20 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Al_2O_3; 0→100% EtOAc in *n*-heptane) yielding 14% of the intended sulfidephosphineoxide diferrocenyl cycle ***30*** (8 mg) as a glassy orange solid.

^{1}H-NMR (700 MHz, $CDCl_3$) δ = 7.92-7.85 (m, 2H); 7.52-7.48 (m, 3H); 5.30 (s, 1H); 5.11 (s, 1H); 4.52 (s, 1H); 4.37 (s, 1H); 4.36 (s, 1H); 4.35 (s, 5H); 4.24 (s, 1H); 3.83 (s, 5H); 3.74 (q, *J* = 6.9 Hz, 1H); 3.21 (q, *J* = 7.1 Hz, 1H); 1.58 (d, *J* = 7.2 Hz, 3H); 1.51 (d, *J* = 7.0 Hz, 3H) ppm.

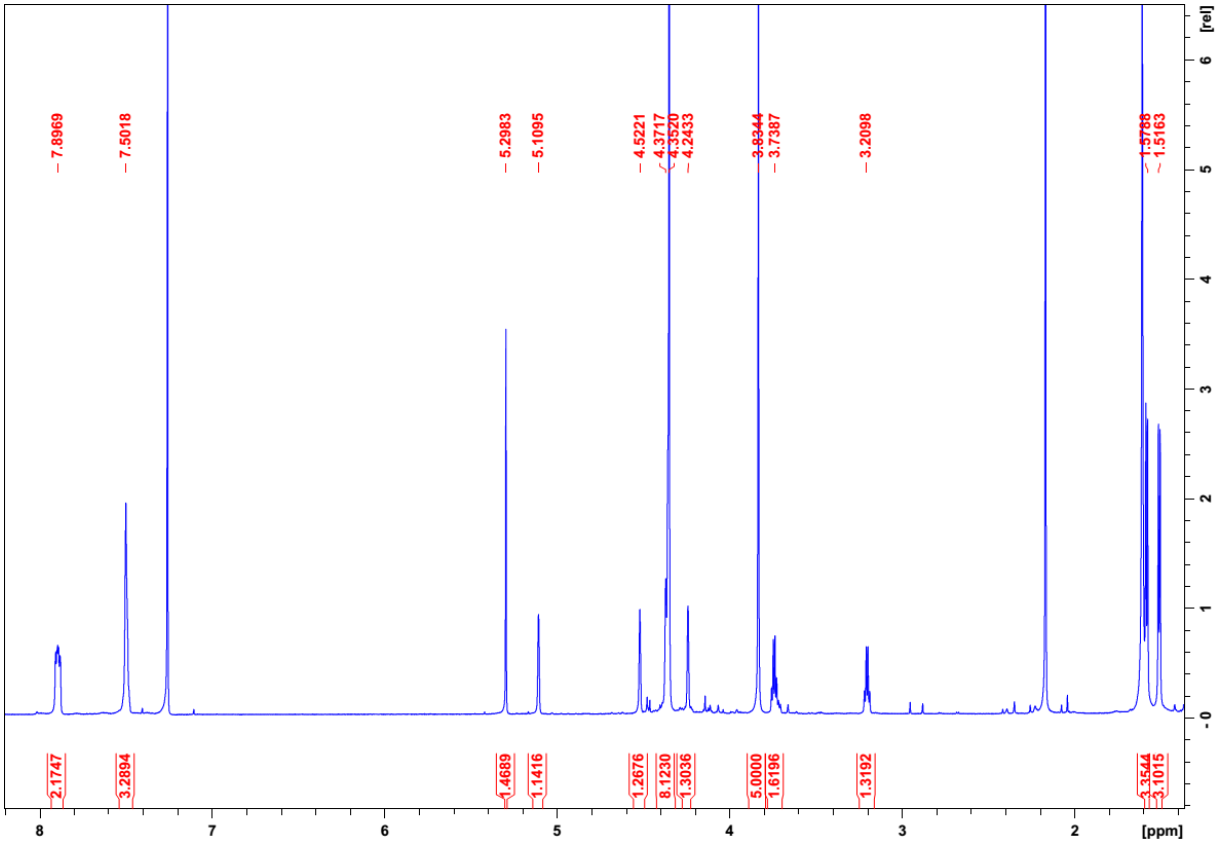
^{13}C{^{1}H}-NMR (700 MHz, $CDCl_3$) δ = 138.59 (d, J_{CP} = 111.7 Hz, C_q); 131.81 (d, J_{CP} = 9.8 Hz, CH); 131.17 (d, J_{CP} = 2.7 Hz, CH); 127.66 (d, J_{CP} = 12.1 Hz, CH); 96.88 (d, J_{CP} = 13.2 Hz, C_q); 92.56 (d, J_{CP} = 13.8 Hz, C_q); 74.83 (d, J_{CP} = 37.5 Hz, C_q); 74.20 (d, J_{CP} = 42.9 Hz, C_q); 73.50 (d, J_{CP} = 10.7 Hz, CH); 73.32 (d, J_{CP} = 13.8 Hz, CH); 70.36 (CH); 70.32 (d, J_{CP} = 11.8 Hz, CH); 70.11 (d, J_{CP} = 10.1 Hz, CH); 69.95 (CH);

67.45 (d, J_{CP} = 9.6 Hz, CH); 67.43 (d, J_{CP} = 10.0 Hz, CH); 36.62 (CH); 35.71 (CH); 20.28 (CH_3); 20.20 (CH_3) ppm.

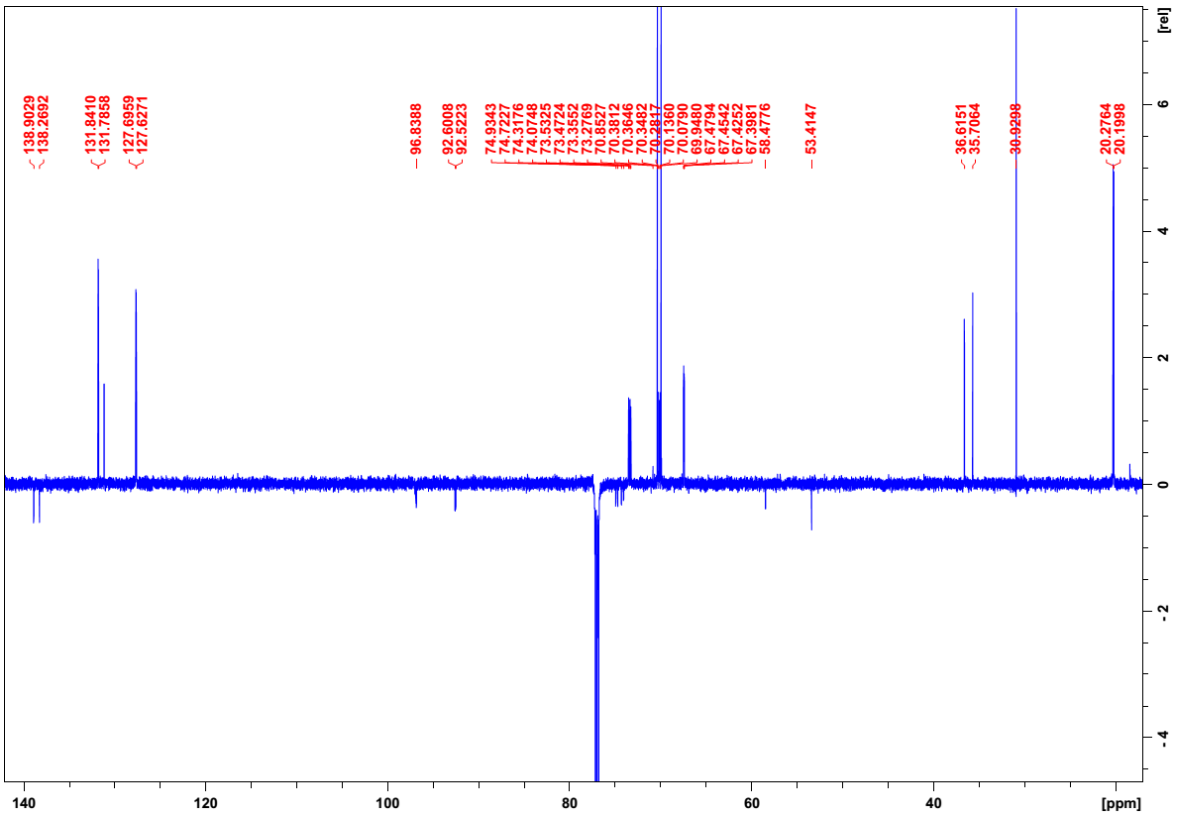
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 29.47 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{29}Fe_2OPS$; $[M]^+$ 580.0376, found: 580.0369.

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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131.8410
131.7858
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127.6271
96.8388
92.6008
92.5223
74.9343
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74.3176
74.0748
73.5325
73.4724
73.3552
73.2769
70.8527
70.3812
70.3646
70.3482
70.2817
70.1360
70.0790
69.9480
67.4794
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20.2764
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6
4
2
0
-2
-4
140
120
100
80
60
40
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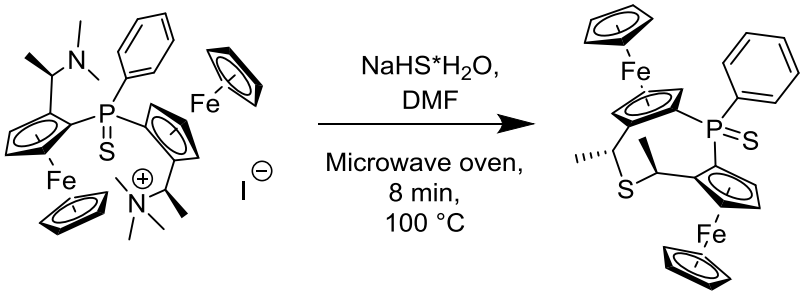
Synthesis of (2*S*,4*R*,6*R*,8*S*)-4,6-Dimethyl-1-phenyl-diferroceno-5-sulfide-1-phosphinesulfide



33
$C_{35}H_{44}Fe_2IN_2PS$
794,379 g/mol

36
$C_{30}H_{29}Fe_2PS_2$
596,346 g/mol
15%

Procedure: Ammonium iodide salt ***33*** (80 mg, 0.10 mmol) and NaHS • H_2O (8 mg, 0.11 mmol, 1.1 eq) were dissolved in 8 mL of DMF and heated for 8 min at 100 °C in a microwave oven. The mixture was cooled to r.t., 10 mL of DCM were added and the organic layer was washed four times with 50 mL of water each, once with 20 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (Al_2O_3; 0→100% EtOAc in *n*-heptane) yielding 15% of the intended sulfidephosphinesulfide diferrocenyl cycle ***36*** (9 mg) as a glassy orange solid.

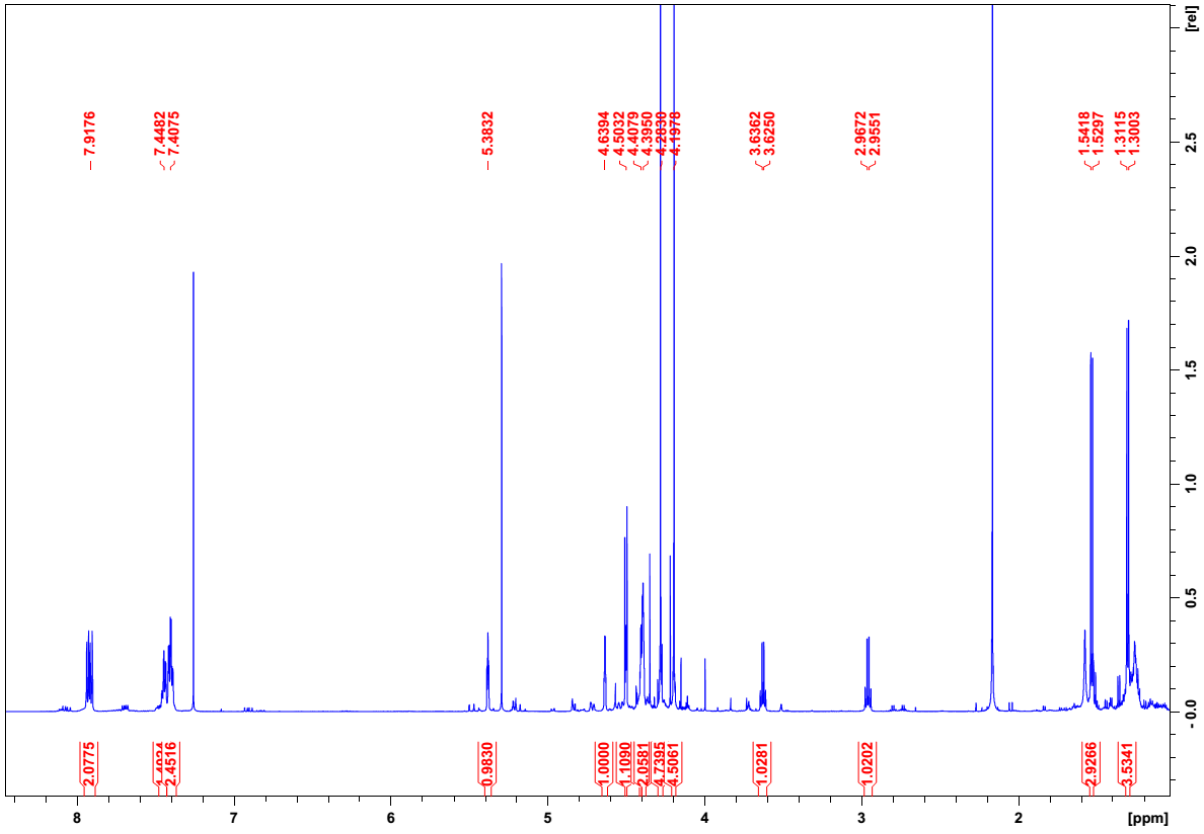
^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.95-7.90 (m, 2H); 7.47-7.43 (m, 1H); 7.43-7.38 (m, 2H); 5.38 (m, 1H); 4.64 (q, *J* = 2.2 Hz, 1H); 4.50 (m, 1H); 4.42-4.40 (m, 1H); 4.40-4.38 (m, 2H); 4.28 (s, 5H); 4.20 (s, 5H); 3.63 (q, *J* = 6.8 Hz, 1H); 2.96 (q, *J* = 7.3 Hz, 1H); 1.54 (d, *J* = 7.3 Hz, 3H); 1.31 (d, *J* = 6.8 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 137.96 (d, J_{CP} = 88.8 Hz, C_q); 132.57 (d, J_{CP} = 11.0 Hz, CH); 131.13 (d, J_{CP} = 3.1 Hz, CH); 127.45 (d, J_{CP} = 12.5 Hz, CH); 96.94 (d, J_{CP} = 11.0 Hz, C_q); 92.90 (d, J_{CP} = 10.6 Hz, C_q); 75.32 (d, J_{CP} = 15.6 Hz, CH); 75.02 (C_q); 74.42 (C_q); 73.75 (d, J_{CP} = 15.0 Hz, CH); 70.91 (CH); 70.29 (CH); 70.22 (d, J_{CP} = 11.5 Hz, CH); 70.05 (d, J_{CP} = 11.5 Hz, CH); 68.58 (d, J_{CP} = 8.6 Hz, CH); 68.34 (d, J_{CP} = 9.1 Hz, CH); 37.27 (CH); 35.39 (CH); 20.82 (CH_3); 20.79 (CH_3) ppm.

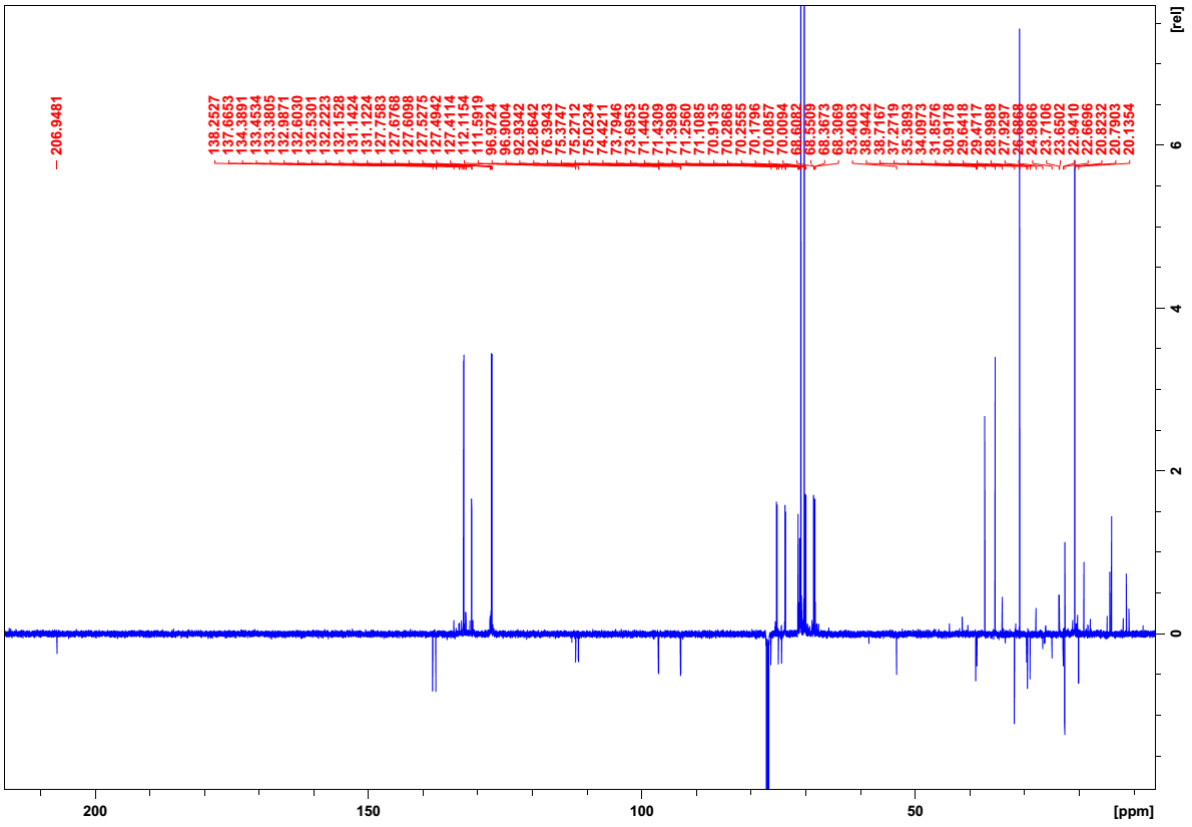
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 42.92 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{29}Fe_2PS_2$; $[M]^+$ 596.0147, found: 596.0141.

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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134.3891
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131.1424
131.1224
127.7583
127.6768
127.6098
127.5275
127.4942
127.4114
112.1154
111.5919
96.9724
96.9004
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74.4211
73.7946
73.6953
71.4405
71.4309
71.3989
71.2360
71.1085
70.9135
70.2868
70.2555
70.1796
70.0857
70.0094
69.6902
68.5509
68.3673
68.3069
53.4443
38.7442
38.7167
37.2719
35.3893
34.0973
31.8576
30.9176
29.6418
29.4717
28.9988
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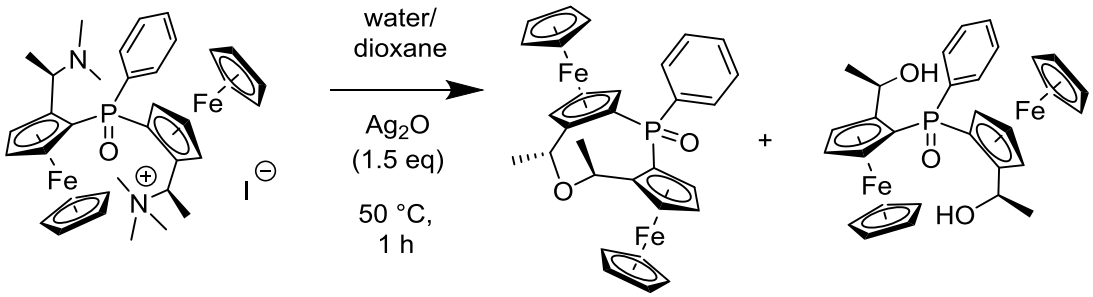
24.9866
23.7106
23.6502
22.9410
22.6696
20.8232
20.7903
20.1354
[rel]
6
4
2
0
200
150
100
50
[ppm]

Synthesis of (2*S*,4*R*,6*R*,8*S*)-4,6-Dimethyl-1-phenyl-diferroceno-5-oxide-1-phosphineoxide



32
$C_{35}H_{44}Fe_2IN_2OP$
778,318 g/mol

31
$C_{30}H_{29}Fe_2O_2P$
564,224 g/mol
11%

40
$C_{30}H_{31}Fe_2O_3P$
582,238 g/mol
6%

Procedure: [107] Ammonium iodide salt ***32*** (87 mg, 0.11 mmol) was dissolved in 1.5 mL of water and 1 mL of dioxane. The solution was warmed to 50 °C and Ag_2O (19 mg, 0.08 mmol, 1.5 eq) was added. The resulting suspension was stirred for 1 h. After complete conversion of the ammonium iodide salt ***32*** the mixture was cooled to r.t. The solid waste was removed by filtration and the solution was extracted three times with an 3 mL of DCM each, the combined organic fractions were washed with 10 mL of water and 10 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 75→100% EtOAc in *n*-heptane) yielding 11% of phosphineoxidediferrocenylether cycle ***31*** (7 mg) as a glassy orange solid and 6% of dihydroxyphosphineoxide side product ***40*** (4 mg).

Cycle ***31***:

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.02-7.95 (m, 2H); 7.51-7.47 (m, 3H); 5.13 (s, 1H); 4.65 (q, *J* = 6.5 Hz, 1H); 4.52 (s, 1H); 4.45 (s, 1H); 4.43 (s, 1H); 4.38-4.36 (m, 1H); 4.36-4.34 (m, 1H); 4.24 (s, 5H); 4.12 (q, *J* = 7.2 Hz, 1H); 3.73 (s, 5H); 1.53 (d, *J* = 6.5 Hz, 3H); 1.51 (d, *J* = 6.4 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 138.11 (d, J_{CP} = 112.4 Hz, C_q); 131.56 (d, J_{CP} = 10.0 Hz, CH); 131.14 (d, J_{CP} = 2.6 Hz, CH); 127.79 (d, J_{CP} = 12.3 Hz, CH); 91.83 (d,

J_{CP} = 13.2 Hz, C_q); 88.93 (d, J_{CP} = 14.1 Hz, C_q); 76.12 (d, J_{CP} = 10.2 Hz, C_q); 75.32 (C_q); 74.74 (d, J_{CP} = 10.6 Hz, CH); 73.78 (d, J_{CP} = 13.5 Hz, CH); 70.44 (CH); 70.17 (d, J_{CP} = 11.1 Hz, CH); 70.16 (CH); 69.88 (d, J_{CP} = 10.2 Hz, CH); 69.15 (d, J_{CP} = 9.8 Hz, CH); 69.01 (d, J_{CP} = 10.1, CH); 68.31 (CH); 66.13 (CH); 20.93 (CH_3); 20.78 (CH_3) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 31.13 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{29}Fe_2O_2P$; $[M+Na]^+$ 587.0502, found: 587.0507; $[2M+Na]^+$ 1151.1106, found: 1151.1113.

Compound ***40***:

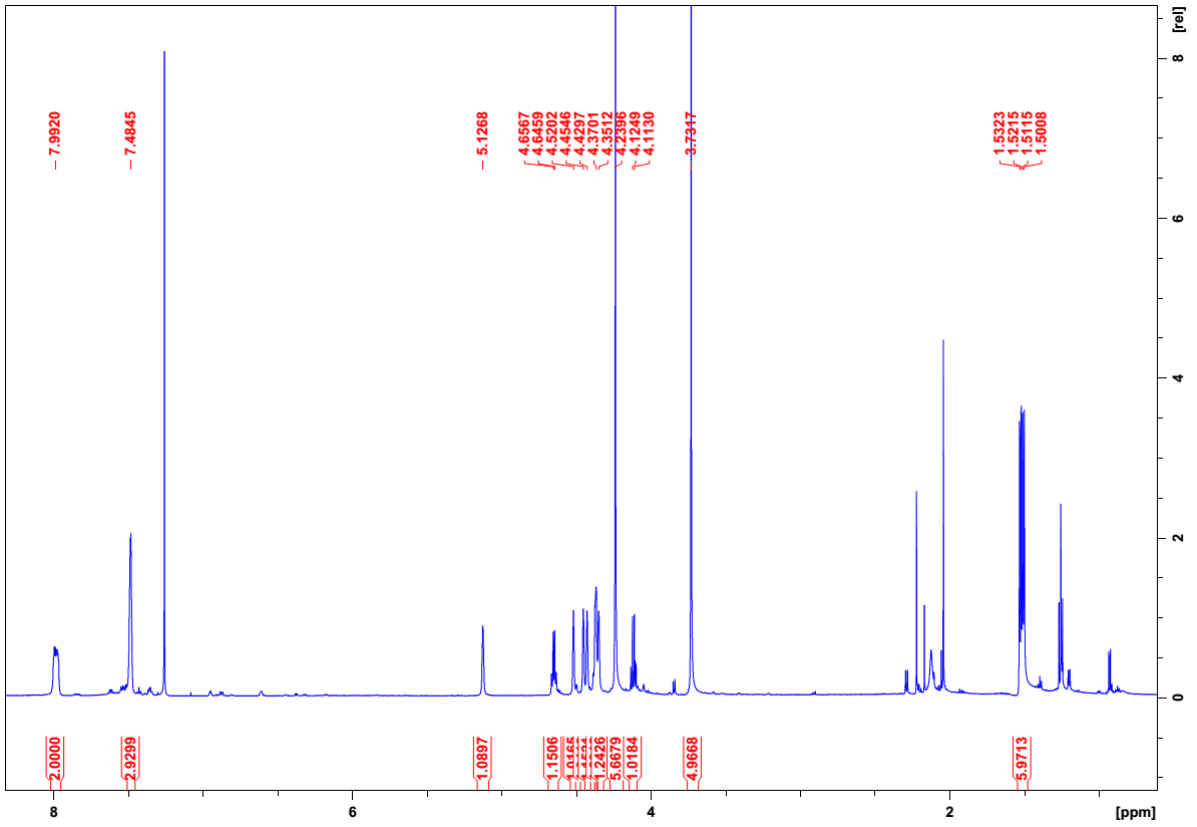
^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.95-7.90 (m, 2H); 7.55-7.50 (m, 3H); 5.93 (d, *J* = 5.4 Hz, 1H); 5.22 (m, 1H); 4.76 (m, 1H); 4.57 (d, *J* = 5.4 Hz, 1H); 4.56 (s, 1H); 4.48 (q, *J* = 2.4 Hz, 1H); 4.44 (m, 1H); 4.41 (m, 2H); 4.38 (q, *J* = 2.4 Hz, 1H); 4.17 (s, 5H); 3.75 (s, 5H); 1.64 (d, *J* = 6.7 Hz, 3H); 1.21 (d, *J* = 6.7 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 136.54 (d, J_{CP} = 110.2 Hz, C_q); 131.55 (d, J_{CP} = 2.9 Hz, CH); 129.93 (d, J_{CP} = 9.5 Hz, CH); 128.45 (d, J_{CP} = 12.1 Hz, CH); 98.73 (d, J_{CP} = 10.4 Hz, C_q); 97.57 (d, J_{CP} = 11.3 Hz, C_q); 72.64 (C_q); 71.85 (C_q); 71.75 (d, J_{CP} = 14.6 Hz, CH); 70.97 (d, J_{CP} = 15.0 Hz, CH); 70.81 (d, J_{CP} = 10.0 Hz, CH); 70.46 (CH); 70.45 (CH); 70.27 (d, J_{CP} = 11.0 Hz, CH); 69.86 (d, J_{CP} = 11.0 Hz, CH); 69.64 (d, J_{CP} = 9.8 Hz, CH); 65.35 (CH); 65.30 (CH); 22.98 (CH_3); 21.95 (CH_3) ppm.

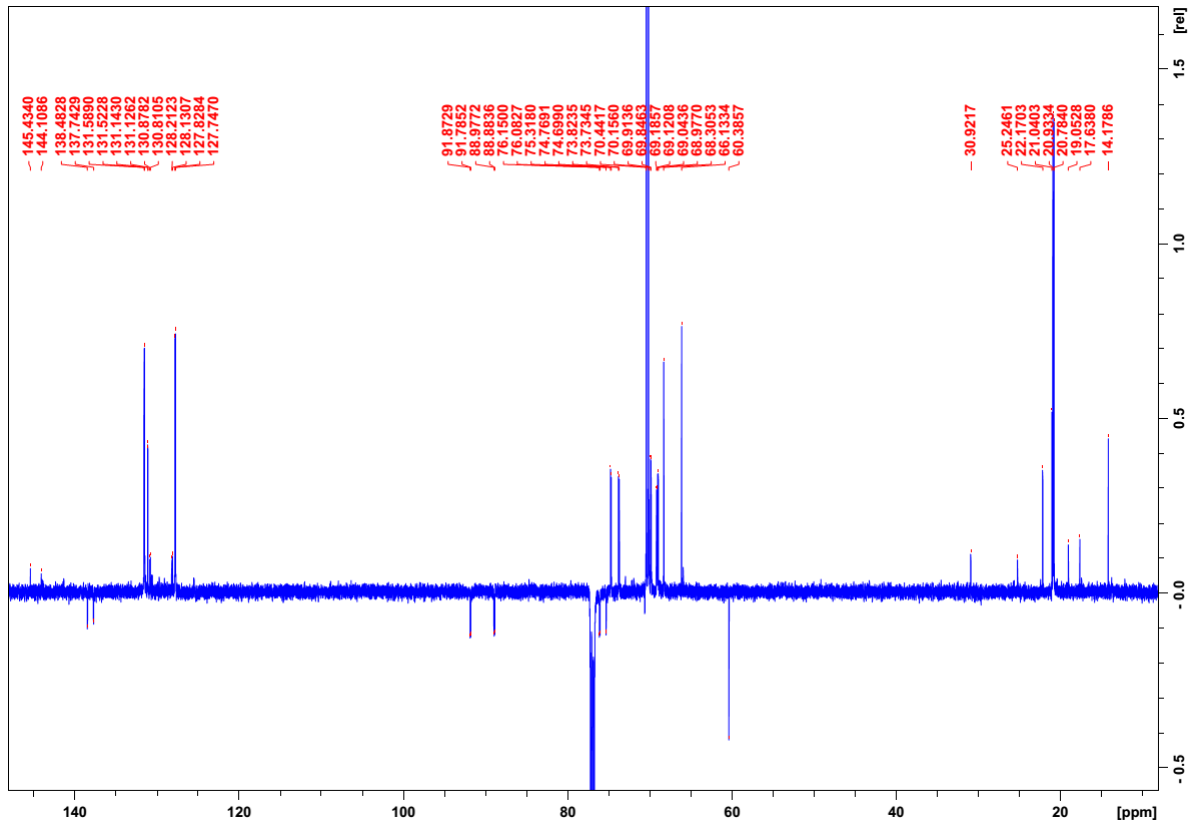
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 38.45 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{31}Fe_2O_3P$; $[M+Na]^+$ 605.0607, found: 605.0595; $[2M+Na]^+$ 1187.1317, found: 1187.1295.

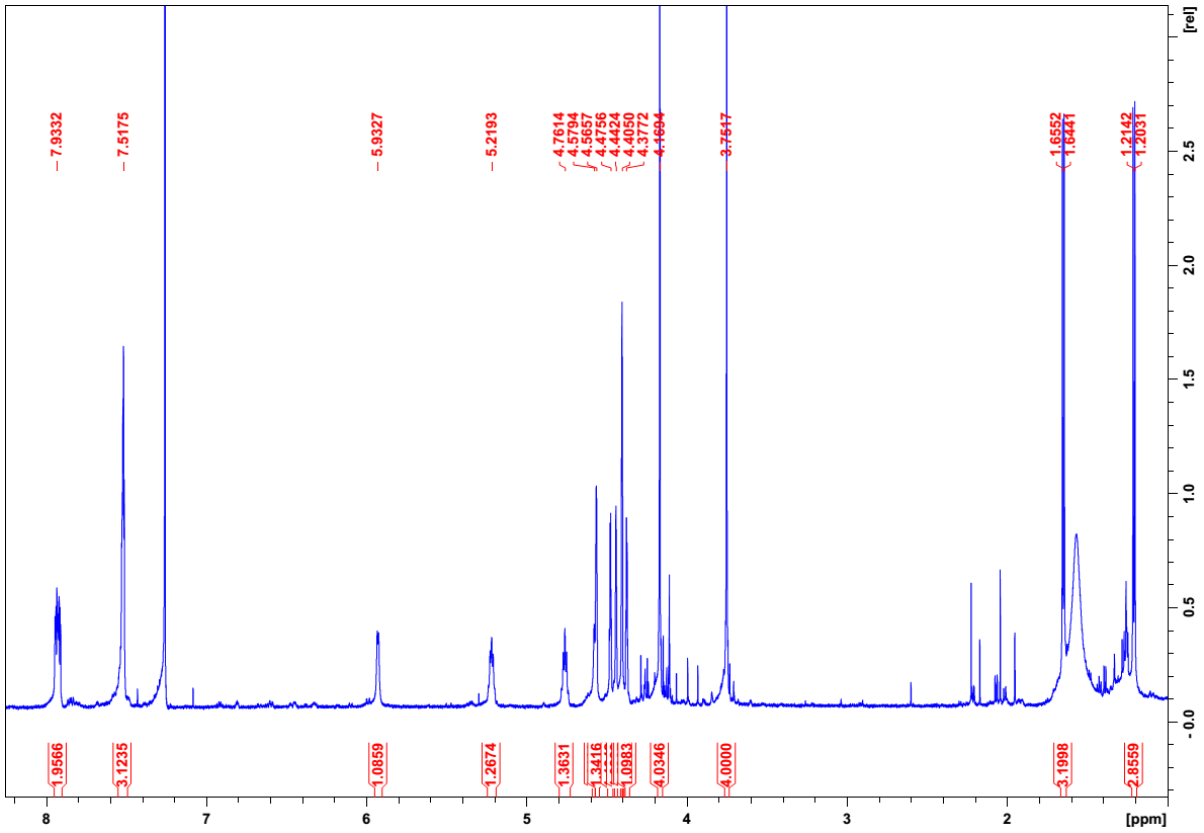
^{1}H-NMR (Diferrocenyl cycle ***31***):



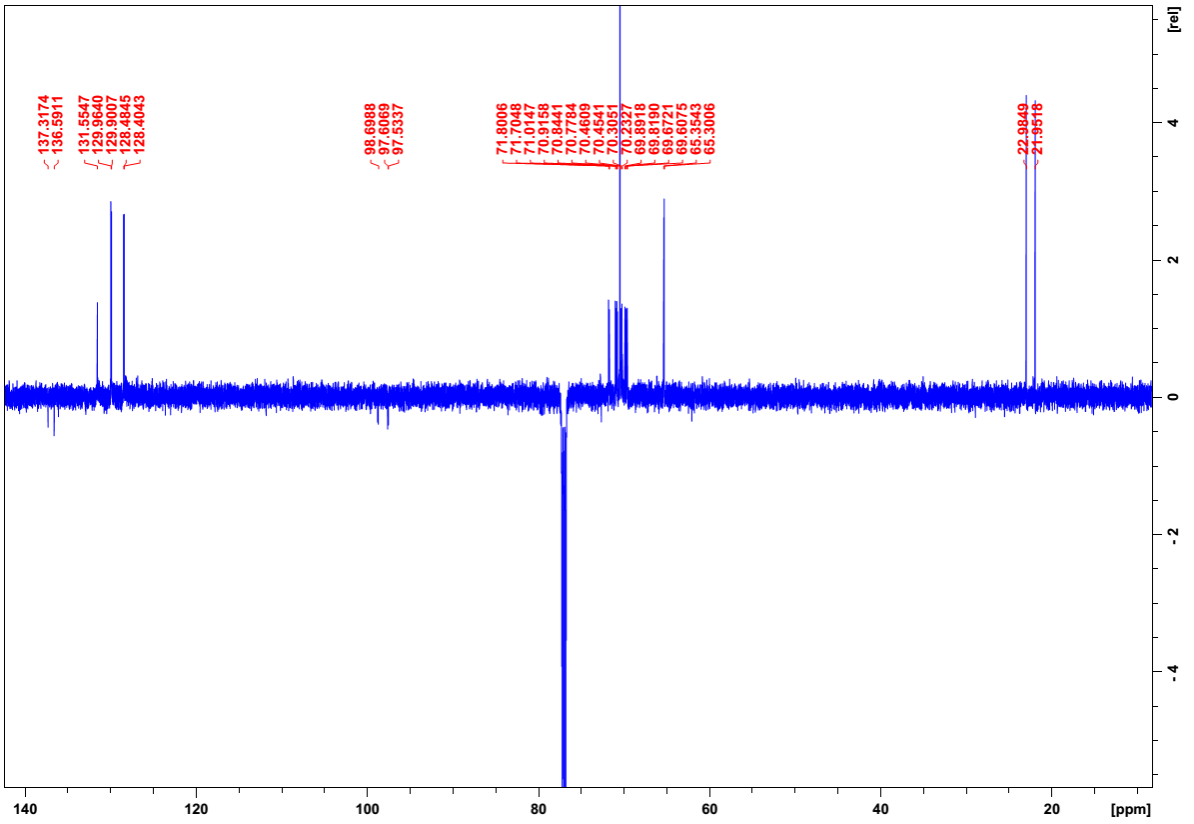
^{13}C{^{1}H}-NMR (Diferrocenyl cycle ***31***):



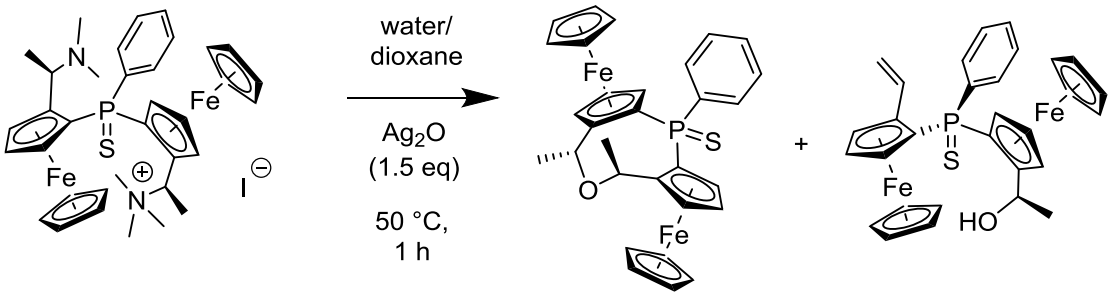
^{1}H-NMR (Diol ***40***):



^{13}C{^{1}H}-NMR (Diol ***40***):



Synthesis of (2*S*,4*R*,6*R*,8*S*)-4,6-Dimethyl-1-phenyl-diferroceno-5-oxide-1-phosphinesulfide



33
$C_{35}H_{44}Fe_2IN_2PS$
794,379 g/mol

37
$C_{30}H_{29}Fe_2OPS$
580,285 g/mol
9%

25
$C_{30}H_{29}Fe_2OPS$
580,285 g/mol
6%

Procedure: [107] Ammonium iodide salt ***33*** (87 mg, 0.11 mmol) was dissolved in 1.5 mL of water and 1 mL of dioxane. The solution was warmed to 50 °C and Ag_2O (20 mg, 0.09 mmol, 1.6 eq) was added. The resulting suspension was stirred for 1 h. After complete conversion of the ammonium iodide salt the mixture was cooled to r.t. The solid waste was removed by filtration and the solution was extracted three times with 3 mL of DCM each, the combined organic fractions were washed with 10 mL of water and 10 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 75→100% EtOAc in *n*-heptane) yielding 9% of phosphinesulfidediferrocenylether cycle ***37*** (6 mg) as a glassy orange solid and 6% of monovinylmonohydroxyphosphinesulfide side product ***25*** (4 mg).

Cycle ***37***:

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.13-8.07 (m, 2H); 7.45-7.38 (m, 3H); 5.44 (m, 1H); 4.61 (m, 1H); 4.59-4.55 (m, 2H); 4.47 (m, 1H); 4.45-4.39 (m, 2H); 4.37 (m, 1H); 4.16 (s, 5H); 4.00 (s, 5H); 1.45 (d, *J* = 6.4 Hz, 3H); 1.41 (d, *J* = 6.7 Hz, 3H) ppm.

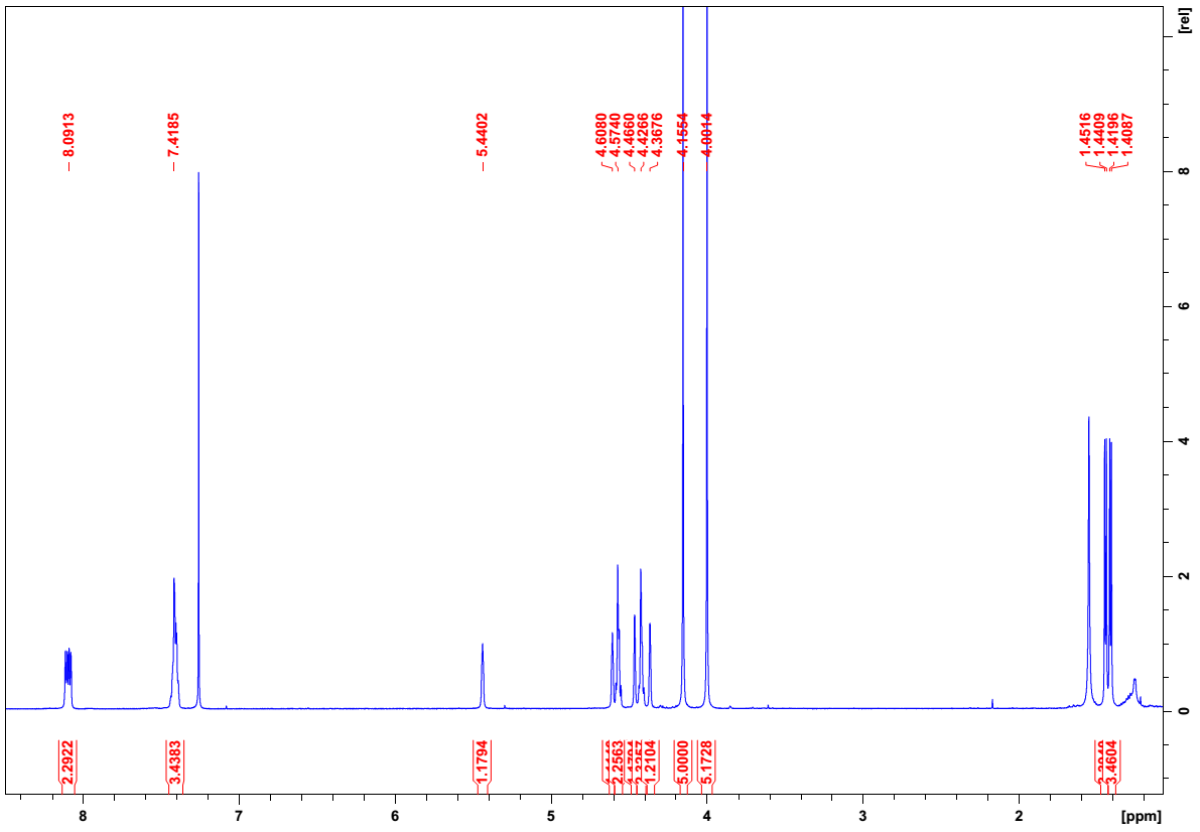
^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 137.31 (d, J_{CP} = 90.0 Hz, C_q); 132.51 (d, J_{CP} = 11.2 Hz, CH); 130.82 (d, J_{CP} = 3.0 Hz, CH); 127.33 (d, J_{CP} = 12.7 Hz, CH); 92.84 (d, J_{CP} = 9.9 Hz, C_q); 89.73 (d, J_{CP} = 10.2 Hz, C_q); 77.97 (C_q); 77.42 (d, J_{CP} = 15.5 Hz,

CH); 76.15 (C_q); 75.04 (d, J_{CP} = 15.2 Hz, CH); 70.82 (d, J_{CP} = 8.8 Hz, CH); 70.81 (CH); 70.41 (CH); 69.58 (d, J_{CP} = 11.7 Hz, CH); 69.41 (d, J_{CP} = 11.5 Hz, CH); 69.33 (d, J_{CP} = 9.0 Hz, CH); 65.79 (2 CH); 21.22 (CH_3); 20.56 (CH_3) ppm.

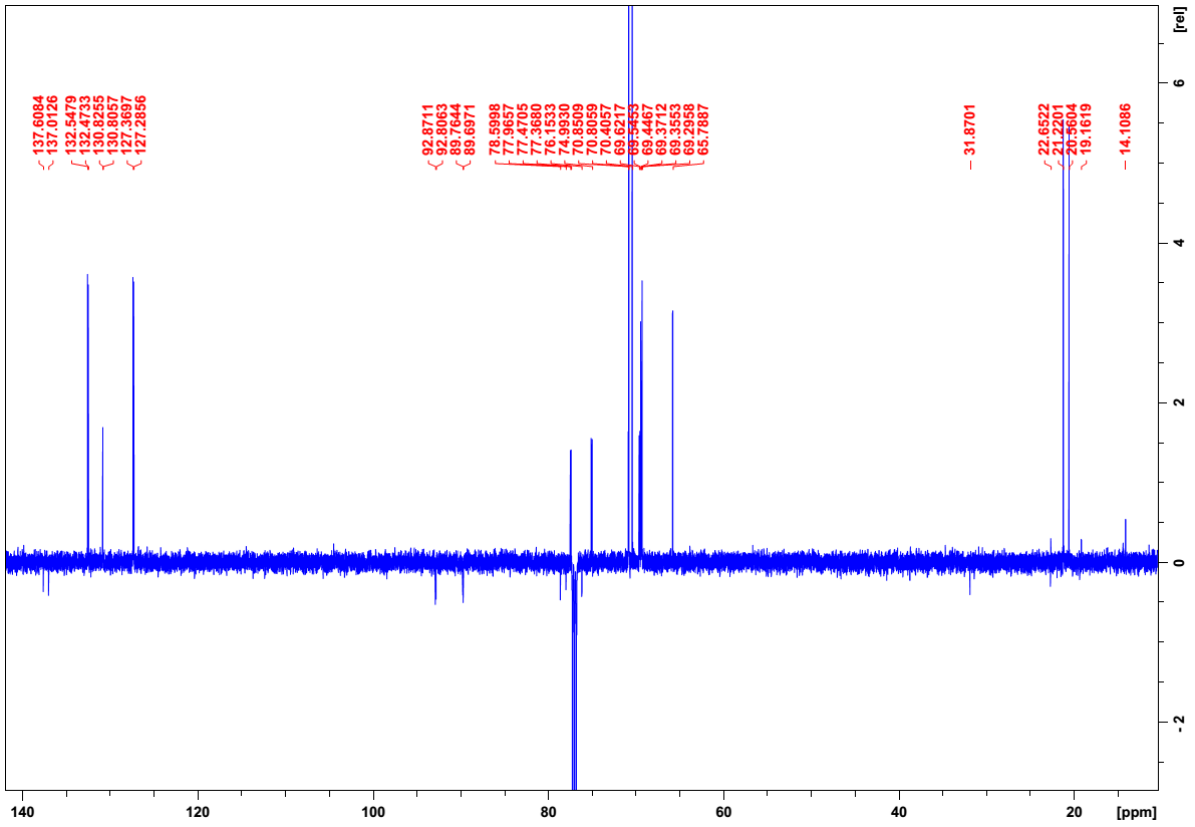
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 43.82 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{29}Fe_2OPS$; $[M+Na]^+$ 603.0273, found: 603.0279; $[2M+Na]^+$ 1183.0649, found: 1183.0662.

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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127.2856
92.8711
92.8063
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89.6971
78.5998
77.9657
77.4705
77.3680
76.1533
74.9930
70.8509
70.8059
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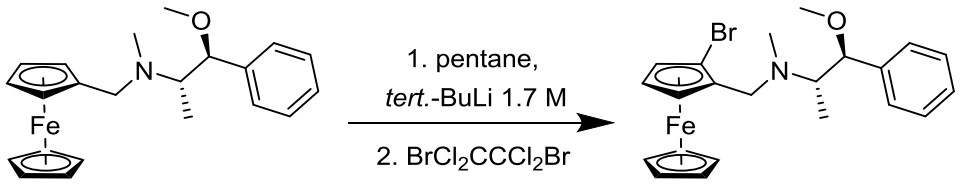
21.2201
20.5604
19.1619
14.1086
[rel]
6
4
2
0
-2
140
120
100
80
60
40
20
[ppm]

5. 2. 3. Di(ferrrocenylmethylene) compounds

5. 2. 3. 1. “Bridge-first” approach

Synthesis of *N*-(2-Bromoferrocenylmethyl)-N-methyl-1-methoxy-1-phenylprop-2-ylamine

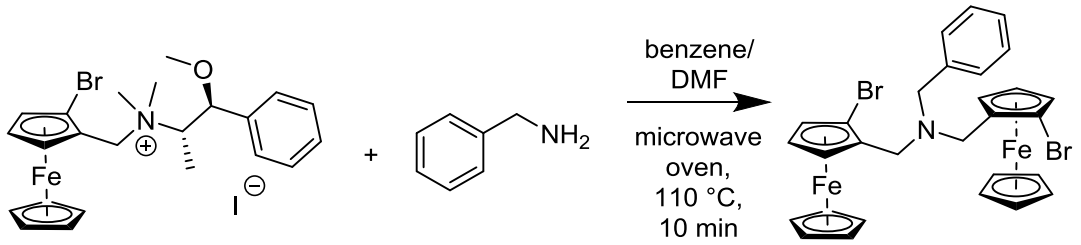


42
$C_{22}H_{27}FeNO$
377,309 g/mol

43
$C_{22}H_{26}BrFeNO$
456,205 g/mol
86%

Procedure: [25] Ferrocenylephedrine ***42*** (3.396 g, 9.00 mmol) was dissolved in 90 mL of dry *n*-pentane in a flame-dried Schlenck tube under Ar. The solution was degassed three times and cooled to -78 °C. To the suspension *tert.*-BuLi (1.7 M; 6.4 mL, 10.9 mmol, 1.2 eq) was added dropwise and the reaction mixture was stirred for 1.5 h at -78 °C, then for 2,5 h at -30 °C. The reaction mixture was cooled to -78 °C and 1,2-dibromotetrachloroethane (4.396 g, 13.50 eq, 1.5 eq) dissolved in THF abs. (13,5 mL) and degassed three times, was added dropwise. The mixture was stirred at -78°C for 20 min and allowed to warm up to r.t. overnight. To the reaction mixture 90 mL of sat. aq. $NaHCO_3$ solution were added and the organic layer was separated. The aq. layer was extracted with two times with 100 mL and once with 50 mL of Et_2O. The combined organic fractions were washed with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2; 17% (Et_2O + 1.5% Et_3N) in *n*-heptane) yielding 86% of *o*-brominated ferrocene ***43*** (3.513 g) as a dark orange oil.

Synthesis of *N,N*-Bis(2-bromoferrocenylmethyl)benzylamine



44
$C_{23}H_{29}BrFeINO$
598,145 g/mol

C_7H_9N
107,156 g/mol

46
$C_{29}H_{27}Br_2Fe_2N$
661,040 g/mol
65%

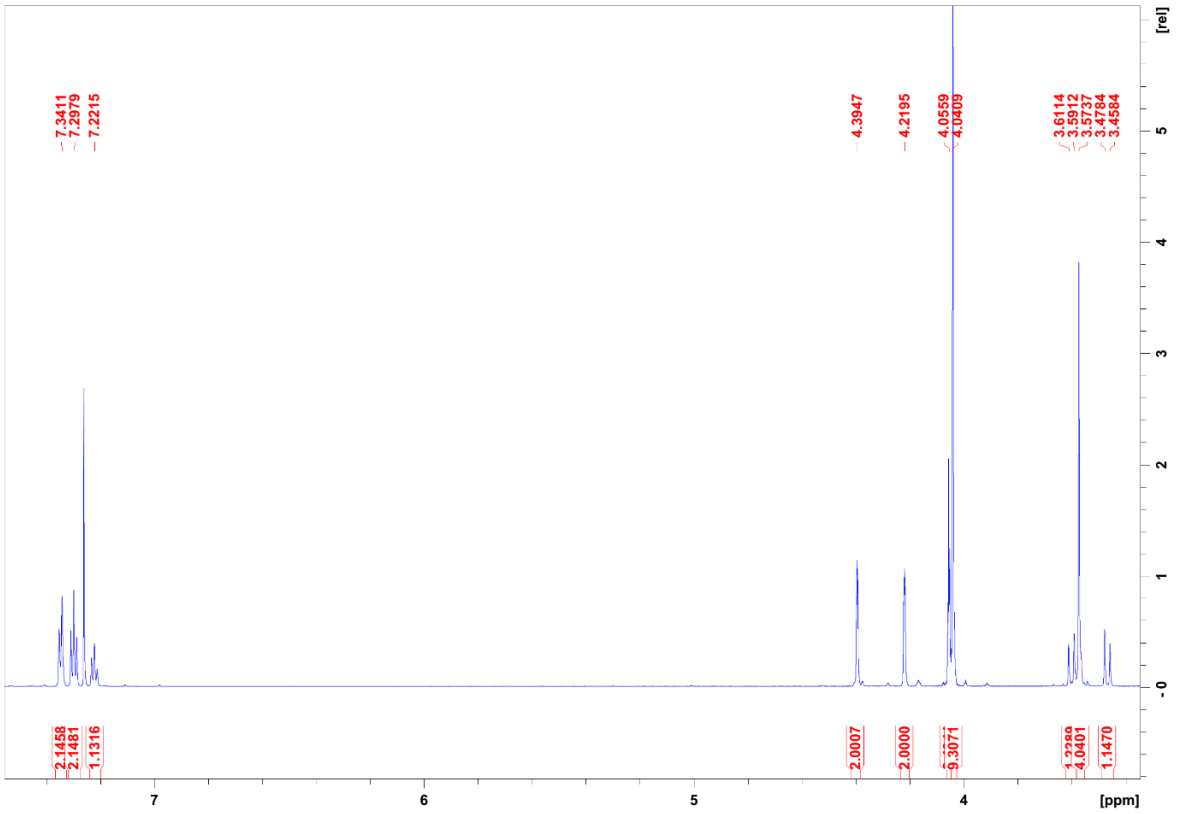
Procedure: Ammonium iodide salt ***44*** (100 mg, 0.17 mmol) was suspended in 8 mL of benzene and 2 mL of DMF in a glass tube. $BnNH_2$ (9 µL, 0.08 mmol, 0.5 eq) was added and the suspension was stirred in a microwave oven at 110°C for 10 min. The reaction mixture was cooled to r.t., volatiles were removed under reduced pressure and 25 mL of Et_2O were added. The organic mixture was washed two times with 30 mL of water, once with 30 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified via column chromatography (SiO_2; 5→15% (Et_2O + 1.5% Et_3N) in *n*-heptane) yielding 65% of diferrocenylbenzylic amine ***46*** (35.7 mg) as an orange glassy solid.

^{1}H-NMR (700 MHz, $CDCl_3$) δ = 7.35 (m, 2H); 7.30 (m, 2H); 7.22 (m, 1H); 4.40 (m, 2H); 4.22 (m, 2H); 4.06 (m, 2H); 4.04 (s, 10H); 3.60 (d, *J* = 14.2 Hz, 1H); 3.57 (s, 4H); 3.47 (d, *J* = 14.1 Hz, 1H) ppm.

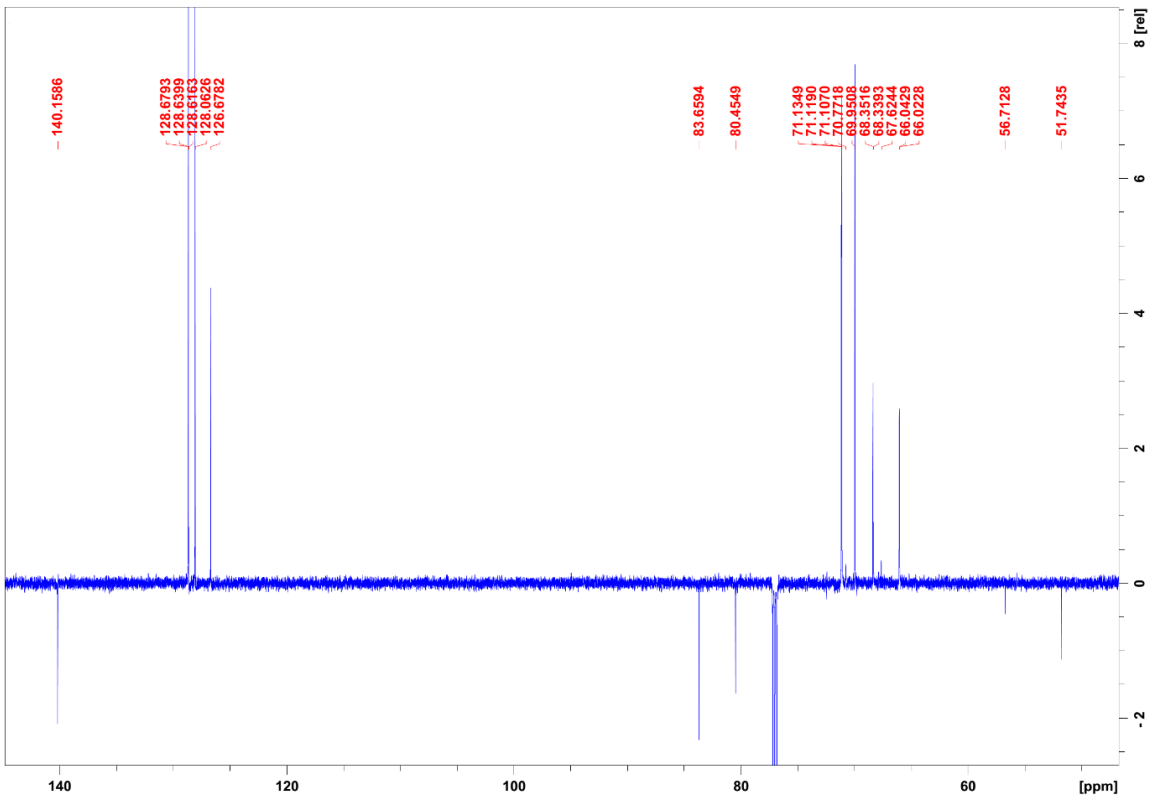
^{13}C{^{1}H}-NMR (700 MHz, $CDCl_3$) δ = 140.16 (C_q); 128.64 (CH); 128.06 (CH); 126.68 (CH); 83.66 (C_q); 80.45 (C_q); 71.12 (CH); 69.95 (CH); 68.35 (CH); 66.03 (CH); 56.71 (CH_2); 51.74 (CH_2) ppm.

HRMS: m/z calculated for M = $C_{29}H_{27}Br_2Fe_2N$; $[M]^+$ 658.9209, found: 658.9226.

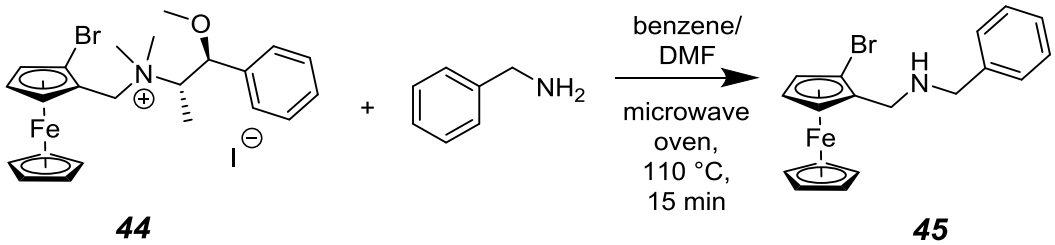
^{1}H-NMR:



^{13}C{^{1}H}-NMR:



Synthesis of *N*-(2-Bromoferrocenylmethyl)benzylamine



44
$C_{23}H_{29}BrFeINO$
598,145 g/mol

C_7H_9N
107,156 g/mol

45
$C_{18}H_{18}BrFeN$
384,098 g/mol
90%

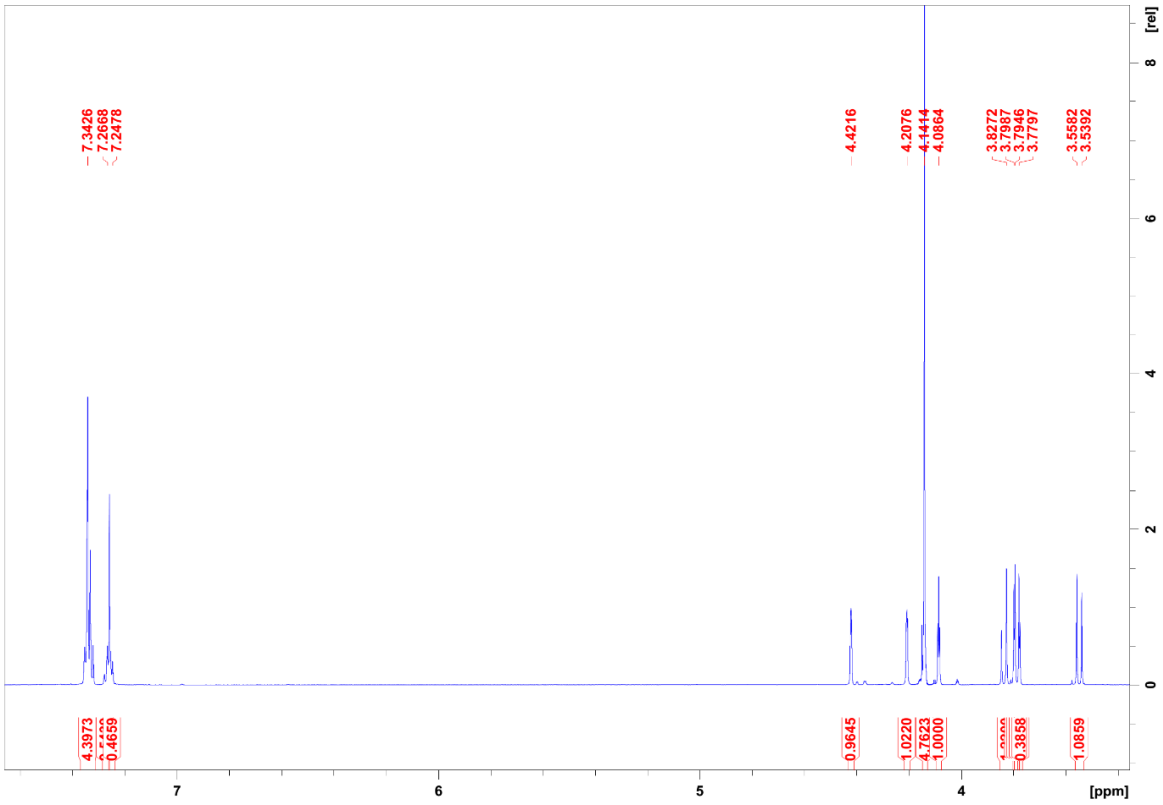
Procedure: Ammonium iodide salt ***44*** (100 mg, 0.17 mmol) was suspended in 8 mL of benzene and 1 mL of DMF in a glass tube and $BnNH_2$ (182 µL, 1.67 mmol, 10 eq) was added. The suspension was stirred in a microwave oven at 110 °C for 15 min. The reaction mixture was cooled to r.t., volatiles were removed under reduced pressure and 25 mL of Et_2O were added. The organic layer was washed two times with 30 mL of water, once with 30 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2; 10→30% (Et_2O + 1.5% Et_3N) in *n*-heptane) yielding 90% of monoferrocenylbenzylic amine ***45*** (58 mg) as a yellow oil.

^{1}H-NMR (700 MHz, $CDCl_3$) δ = 7.36-7.32 (m, 4H); 7.28-7.24 (m, 1H); 4.42 (m, 1H); 4.21 (m, 1H); 4.14 (s, 5H); 4.09 (pt, *J* = 2.5 Hz, 1H); 3.84 (d, *J* = 13.3 Hz, 1H); 3.79 (d, *J* = 13.4 Hz, 1H); 3.78 (d, *J* = 13.3 Hz, 1H); 3.55 (d, 13.4 Hz, 1H) ppm.

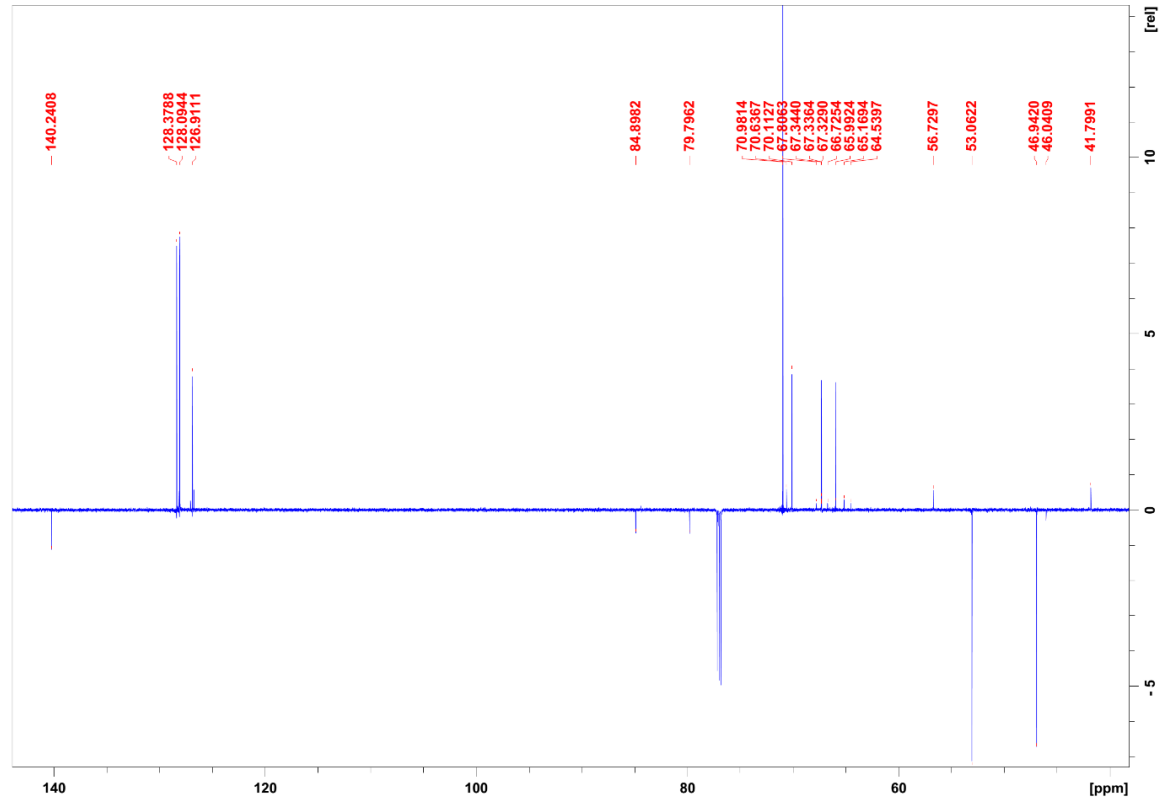
^{13}C{^{1}H}-NMR (700 MHz, $CDCl_3$) δ = 140.24 (C_q); 128.38 (CH); 128.09 (CH); 126.91 (CH); 84.90 (C_q); 79.80 (C_q); 70.98 (C_q); 70.11 (CH); 67.32 (CH); 65.98 (CH); 53.06 (CH_2); 46.94 (CH_2) ppm.

HRMS: m/z calculated for M = $C_{18}H_{18}BrFeN$; $[M]^+$ 382.9972, found: 382.9970; $[M+H]^+$ 384.0050, found: 384.0042.

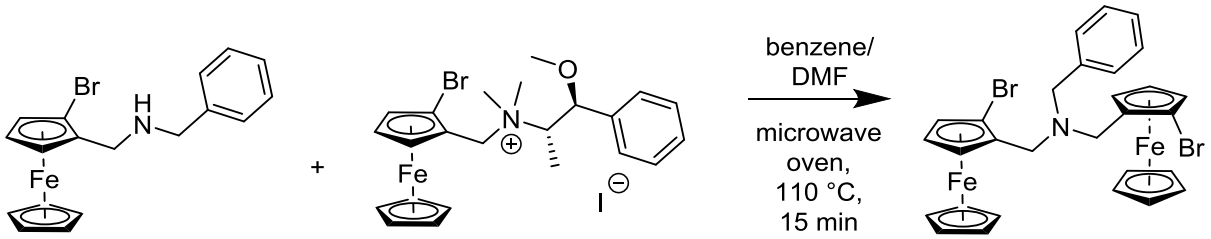
^{1}H-NMR:



^{13}C{^{1}H}-NMR:



Synthesis of *N,N*-Bis(2-bromoferrocenylmethyl)benzylamine



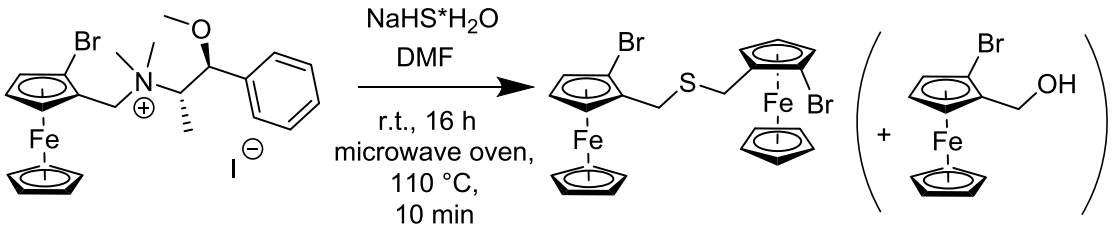
45
$C_{18}H_{18}BrFeN$
384,098 g/mol

44
$C_{23}H_{29}BrFeINO$
598,145 g/mol

46
$C_{29}H_{27}Br_2Fe_2N$
661,040 g/mol
97%

Procedure: Monoferrocenylbenzylic amine ***45*** (250 mg, 0.65 mmol) was dissolved in 8 mL of benzene and 2 mL of DMF in a glass tube. Ammonium iodide salt ***44*** (389 mg, 0.65 mmol, 1.00 eq) was added and the suspension was stirred in a microwave oven at 110 °C for 15 min. The reaction mixture was cooled to r.t., volatiles were removed under reduced pressure and 35 mL of Et_2O were added. The organic layer was washed two times with 40 mL of water, once with 40 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, 5→15% (Et_2O + 1.5% Et_3N) in *n*-heptane) yielding 97% of diferrocenylbenzylic amine ***46*** (417 mg) an orange glassy solid.

Synthesis of *S,S*-Bis(2-bromoferrocenylmethyl)thioether



44
$C_{23}H_{29}BrFeINO$
598,145 g/mol

47
$C_{22}H_{20}Br_2Fe_2S$
587,960 g/mol
25%

48
$C_{11}H_{11}BrFeO$
294,957 g/mol
25%

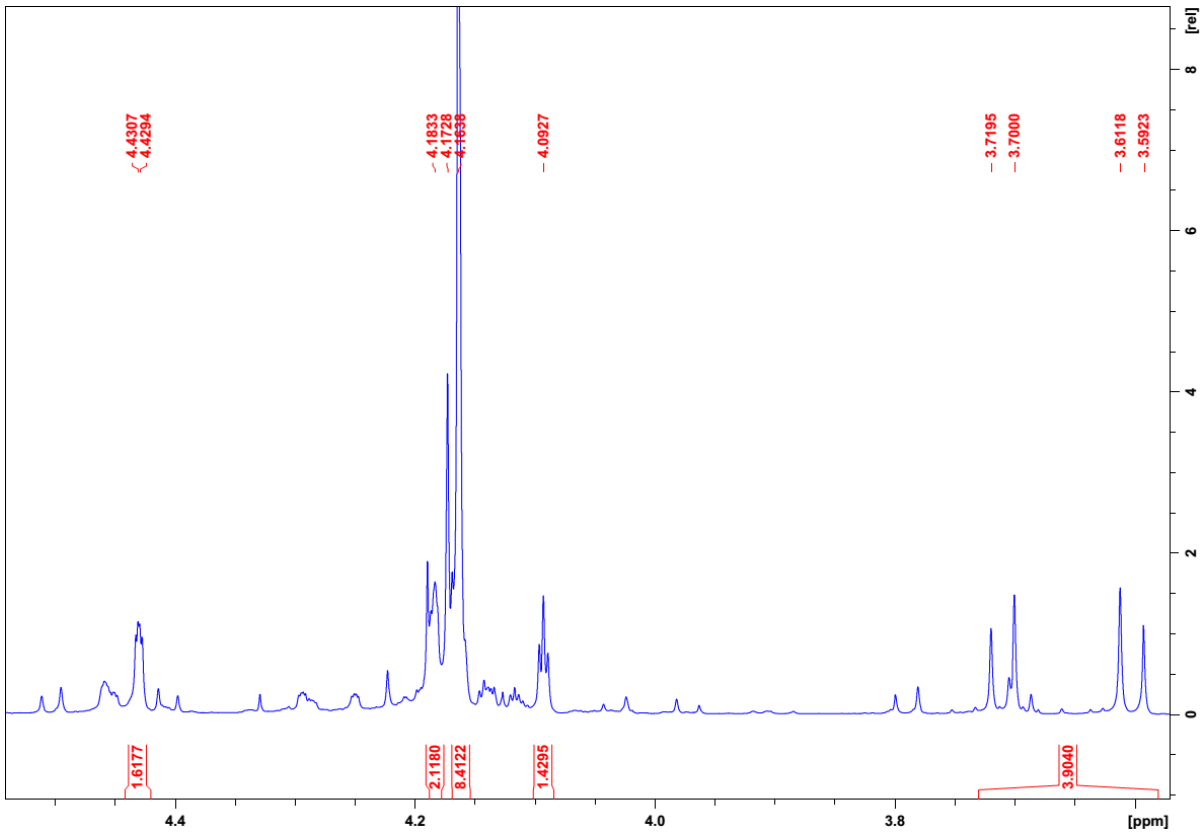
Procedure: Ammonium iodide salt ***44*** (100.0 mg, 0.167 mmol) was dissolved in 1.3 mL of DMF in a Schlenck tube and NaHS • H_2O (6.9 mg, 0.093 mmol, 0.56 eq) was added. The reaction mixture was degassed and stirred at r.t. overnight. The reaction mixture was transferred into a glass tube and 6.7 mL of DMF were added. The suspension was stirred in a microwave oven at 110°C for 10 min. The reaction mixture was cooled to r.t. and 30 mL of DCM were added. The organic layer was washed twice with 50 mL of water, once with 50 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→65% EtOAc in *n*-heptane) yielding 25% of thioether ***47*** (12.3 mg) as a yellow oil and 25% of alcohol ***48*** (12.0 mg).

^{1}H-NMR (700 MHz, $CDCl_3$) δ = 4.43 (m, 2H); 4.18 (m, 2H); 4.16 (s, 10H); 4.09 (pt, *J* = 2.6 Hz, 2H); 3.71 (d, *J* = 13.7 Hz, 2H); 3.60 (d, *J* = 13.7 Hz, 2H) ppm.

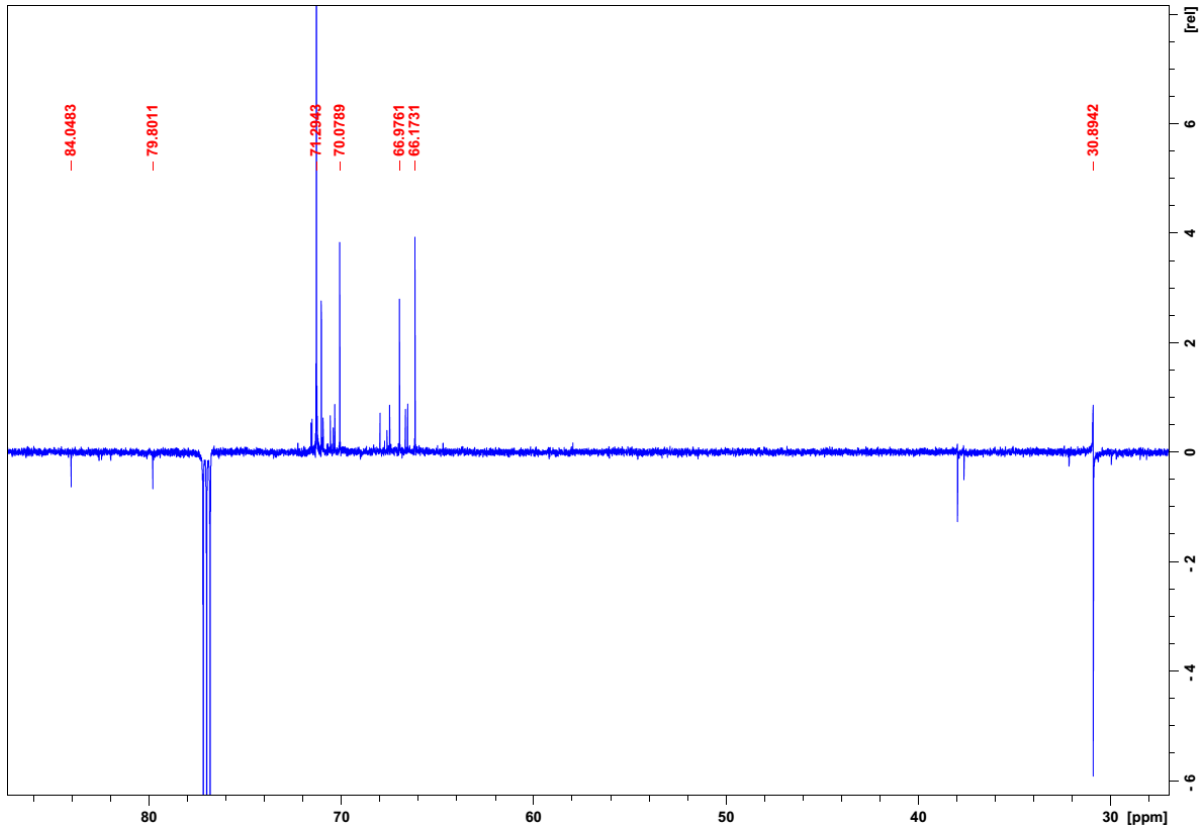
^{13}C{^{1}H}-NMR (700 MHz, $CDCl_3$) δ = 84.05 (C_q); 79.80 (C_q); 71.29 (CH); 70.08 (CH); 66.98 (CH); 66.17 (CH); 30.89 (CH_2) ppm.

HRMS: m/z calculated for M = $C_{22}H_{20}Br_2Fe_2S$; $[M]^+$ 587.8344, found: 587.8351.

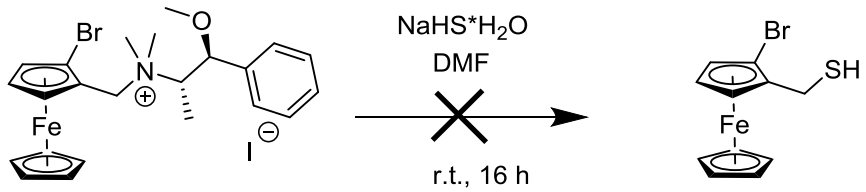
^{1}H-NMR:



^{13}C{^{1}H}-NMR:



Attempted synthesis of 1-Bromo-2-carbthiolferrocene



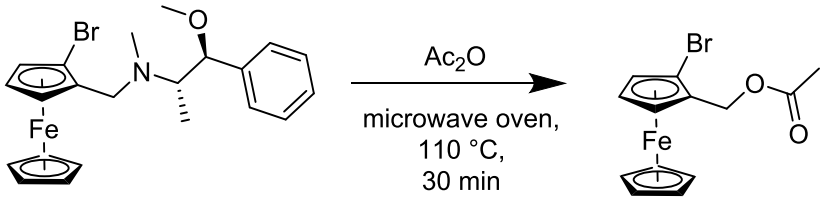
44
$C_{23}H_{29}BrFeINO$
598,145 g/mol

$C_{11}H_{11}BrFeS$
311,018 g/mol

Procedure: Ammonium iodide salt ***44*** (100 mg, 0.17 mmol) was dissolved in 1.3 mL of DMF in a Schlenck tube and NaHS • H_2O (138 mg, 1.86 mmol, 11.2 eq) was added. The reaction mixture was degassed and stirred at r.t. overnight. The reaction mixture was transferred into a glass tube and 6.7 mL of DMF were added. The suspension was stirred in a microwave oven at 110 °C for 10 min. The reaction mixture was cooled to r.t. and 100 mL of DCM were added. The organic layer was washed three times with 100 mL of water, once with 100 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified via column chromatography (SiO_2, 0→30% EtOAc in *n*-heptane) yielding a product of as to date of this writing not identified structure.

HRMS: m/z calculated for M = $C_{18}H_{24}FeNO_2$; $[M+Na]^+$ 365.1054, found: 365.1049; m/z for $[M+K]^+$ 381.0794, found: 381.0788; m/z for $[2M+Na]^+$ 707.2211, found: 707.2201; m/z for $[3M+Na]^+$ 1049.3367, found: 1049.3357; m/z for $[4M+Na]^+$ 1391.4542, found: 1391.4540.

Synthesis of 1-Bromo-2-acetoxymethylferrocene

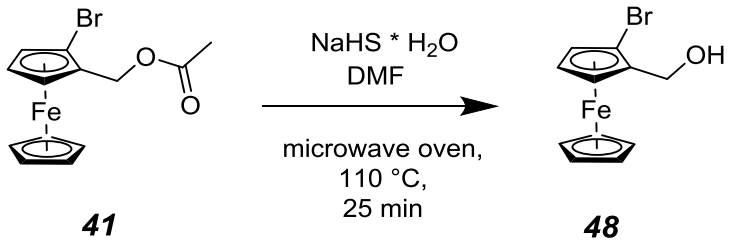


43
$C_{22}H_{26}BrFeNO$
456,205 g/mol

41
$C_{13}H_{13}BrFeO_2$
336,994 g/mol
64%

Procedure: Ferrocenemethylamine ***43*** (1.000 g, 2.192 mmol) was dissolved in 10.3 mL of Ac_2O in a glass tube. The solution was heated in a microwave oven to 110 °C for 30 min. The solvent was removed under reduced pressure. To the residue, 25 mL of DCM and 25 mL of aq. sat. $NaHCO_3$ solution were added. The aq. layer was extracted two times with 20 mL of DCM. The combined organic fractions were washed two times with 25 mL of water, once with 25 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→20% (Et_2O + 1.5% Et_3N) in *n*-heptane) yielding 64% of ferroceneacetate ***41*** (469 mg) as an orange oil.

Attempted synthesis of 1-Bromo-2-carbthiolferrocene



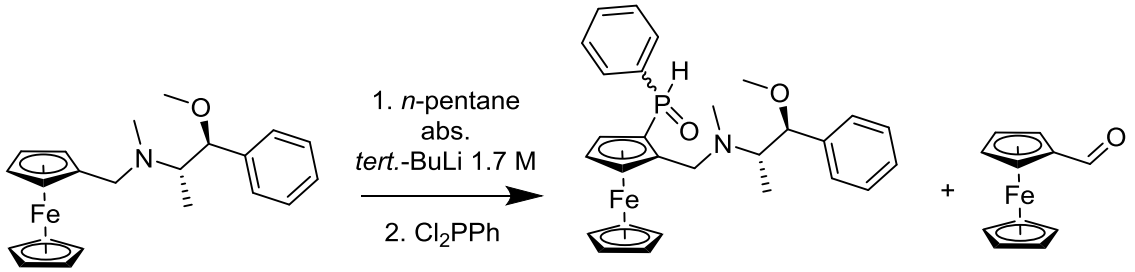
41
$C_{13}H_{13}BrFeO_2$
336,994 g/mol

48
$C_{11}H_{11}BrFeO$
294,957 g/mol
23%

Procedure: Ferrocenylmethylacetate ***41*** (68 mg, 0.20 mmol) was dissolved in 8 mL of DMF in a glass tube and NaHS • H_2O (167 mg, 2.26 mmol, 11.2 eq) was added. The solution was stirred in a microwave oven at 110°C for 25 min. The reaction mixture was cooled to r.t. and 60 mL of Et_2O were added. The organic layer was washed three times with 150 mL of water each, once with 150 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified via column chromatography (SiO_2, 0→30% EtOAc in *n*-heptane) yielding 23% of ferrocenylmethylalcohol ***48*** (14 mg) instead of the desired thiol.

5. 2. 3. 2. “Phosphine-first” approach

Attempted synthesis of 1,1‘‘-(Phenylphosphinidene)bis[N-methyl-1-methoxy-1-phenylprop-2-ylamine]N-(methyl)ferrocene



42
$C_{22}H_{27}FeNO$
377,309 g/mol

49
$C_{28}H_{32}FeNO_2P$
501,388 g/mol
44%

50
$C_{11}H_{10}FeO$
214,045 g/mol
53%

Procedure: [25] Ferrocenylmethylamine ***42*** (149 mg, 0.40 mmol) was suspended in 4 mL of dry *n*-pentane in a flame-dried Schlenck tube under Ar. The mixture was degassed, cooled to -70 °C and *tert.*-BuLi solution (1.7 M; 260 µL, 0.44 mmol, 1.12 eq) was added to the suspension. The reaction mixture was stirred for 2 h at this temperature, warmed to -30 °C and stirred for another 2.5 h. The suspension was cooled to -78 °C and Cl_2PPh (28 µL, 0.206 mmol, 0.52 eq) was added. The suspension was stirred for another 30 min at this temperature, then allowed to warm up to r.t. overnight. The reaction mixture was quenched with 4 mL of aq. sat. $NaHCO_3$ solution. The aq. layer was extracted three times with 8 mL of Et_2O each, the combined organic fractions were washed with 30 mL of water and 30 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified via column chromatography (SiO_2, 0→50% EtOAc in *n*-heptane). Due to precipitate forming, most fractions were filtrated through SiO_2, yielding various fractions of ferrocenylmethylamine starting material ***42***, 23% of ferrocenylphosphite ***49*** (45 mg; 44% yield in relation to Cl_2PPh) and 53% of ferrocenecarbaldehyde ***50*** (45 mg).

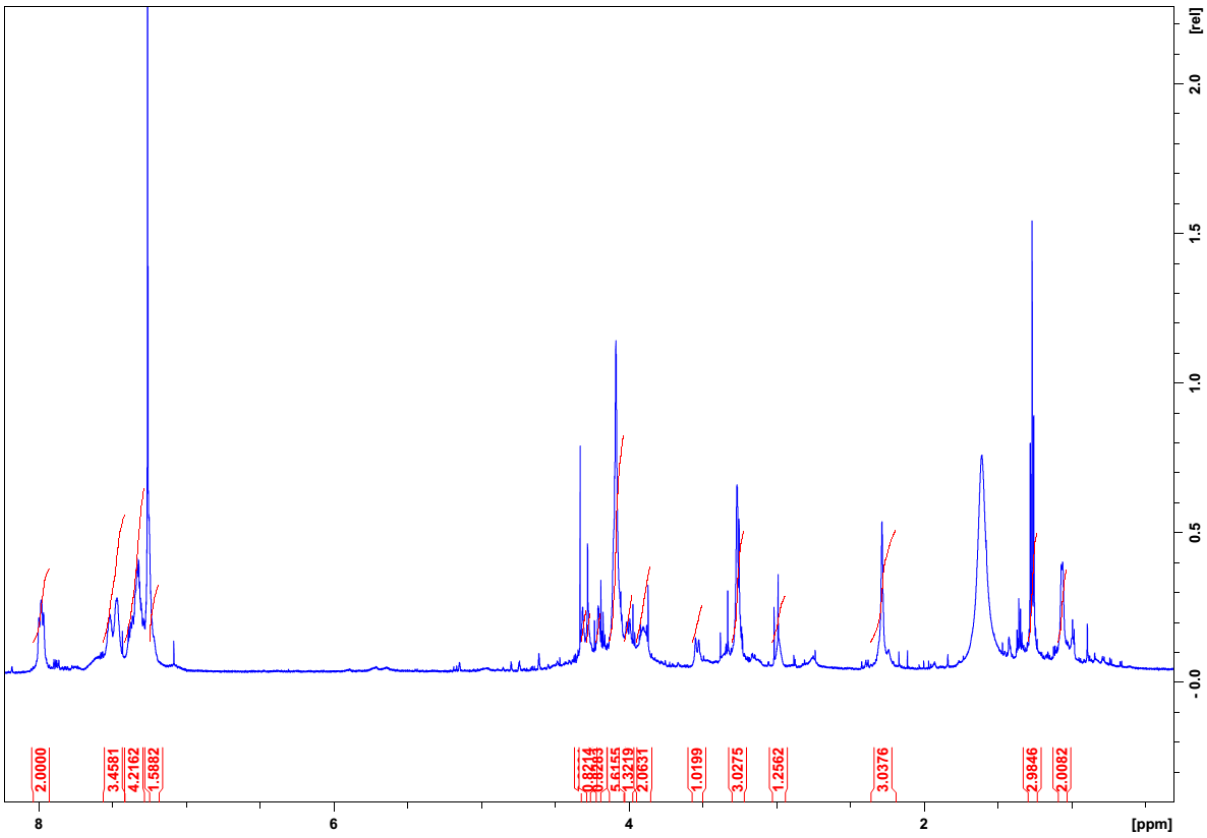
^{1}H-NMR (600 MHz, $CDCl_3$) δ = 8.02-7.93 (m, 2H); 7.56-7.42 (m, 3H); 7.42-7.28 (m, 4H); 7.25-7.21 (m, 1H); 4.31 (m, 1H); 4.28 (m, 1H); 4.21 (m, 1H); 4.09 (s, 5H); 3.90 (m, 2H); 3.54 (d, *J* = 13.2 Hz, 1H); 3.27 (s, 3H); 2.75 (s, 1H); 2.29 (s, 3H); 1.07 (d, *J* = 5.9 Hz, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 131.89 (2 CH); 131.61 (CH); 128.15 (CH); 127.98 (2 CH); 126.89 (CH); 84.78 (CH); 73.83 (d, J_{CP} = 13.0 Hz, CH); 72.74 (d, J_{CP} = 16.0 Hz, CH); 70.36 (CH); 70.04 (CH); 64.11 (CH); 56.62 (CH_3); 54.24 (CH_2); 36.17 (CH_3); 9.45 (CH_3) ppm; 4 C_q not found.

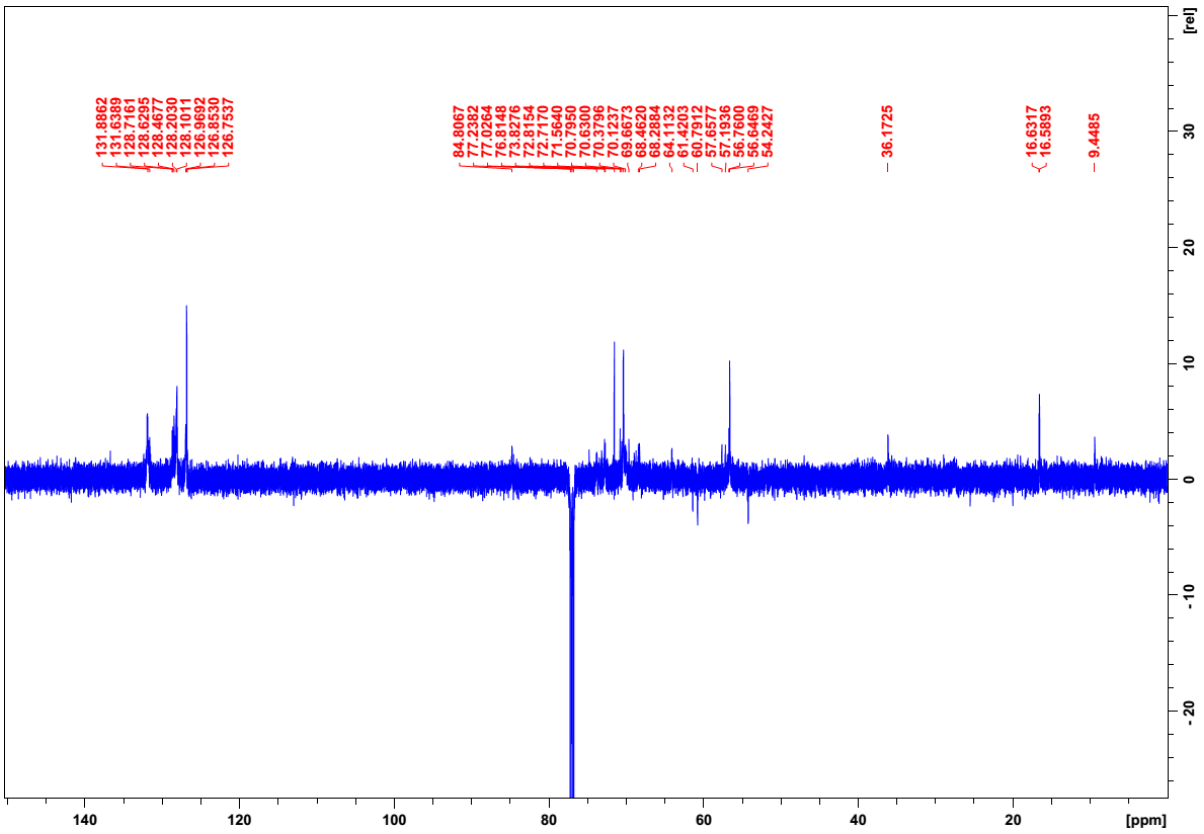
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 16.24 (s) ppm.

HRMS: m/z calculated for M = $C_{28}H_{32}FeNO_2P$; $[M-H]^-$ 500.1442, found: 500.1455; $[M+H]^+$ 502.1598, found: 502.1595.

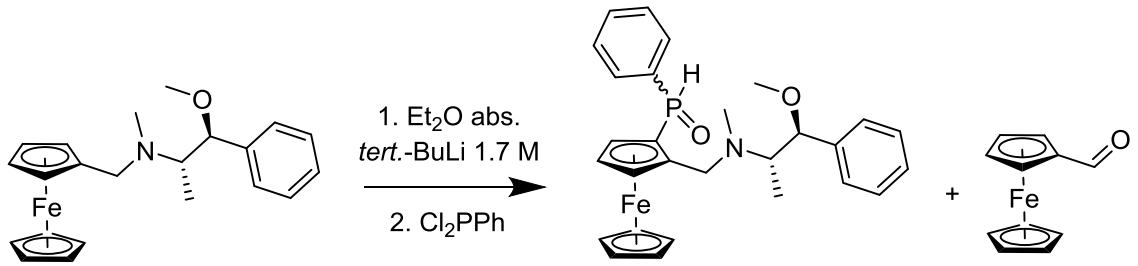
^{1}H-NMR:



^{13}C{^{1}H}-NMR:



Attempted synthesis of 1,1''-(Phenylphosphinidene)bis[N-methyl-1-methoxy-1-phenylprop-2-ylamine]N-(methyl)ferrocene



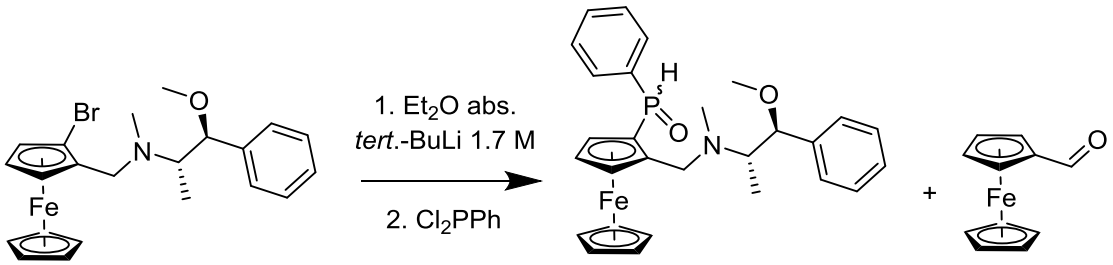
42
$C_{22}H_{27}FeNO$
377,309 g/mol

49
$C_{28}H_{32}FeNO_2P$
501,388 g/mol
21%

50
$C_{11}H_{10}FeO$
214,045 g/mol
53%

Procedure: [61] Ferrocenylmethylamine ***42*** (178 mg, 0.47 mmol) was suspended in 1 mL of dry Et_2O in a flame-dried Schlenck tube under Ar. The mixture was degassed three times, cooled to -70 °C and *tert.*-BuLi was added (1.7 M, 300 µL, 0.51 mmol, 1.08 eq). Stirring was continued for 30 min at this temperature, then the suspension was warmed to r.t. and stirring was continued for 1 h. The reaction mixture was cooled to -78 °C and Cl_2PPh (33 µL, 0.24 mmol, 0.51 eq) was added. The suspension was allowed to warm up to r.t. overnight. Water (1 mL) was added to the reaction mixture and the organic layer was washed three times with 1 mL of water, three times with 1 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→40% EtOAc in *n*-heptane). Due to precipitate forming, most fractions were filtrated through SiO_2, yielding various fractions of ferrocenylmethylamine starting material ***42***, 11% of ferrocenylphosphite ***49*** (26 mg; 21% yield in relation to Cl_2PPh) and 53% of ferrocenecarbaldehyde ***50*** (53 mg).

Attempted synthesis of 1,1''-(Phenylphosphinidene)bis[N-methyl-1-methoxy-1-phenylprop-2-ylamine]N-(methyl)ferrocene



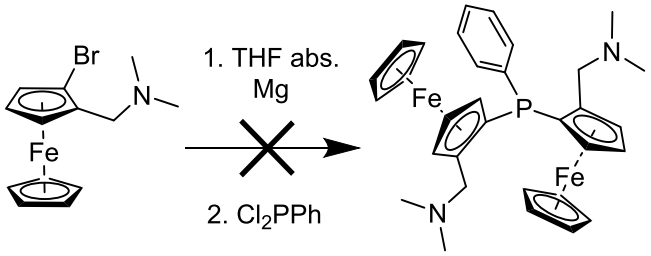
43
$C_{22}H_{26}BrFeNO$
456,205 g/mol

49
$C_{28}H_{32}FeNO_2P$
501,388 g/mol
35%

50
$C_{11}H_{10}FeO$
214,045 g/mol
46%

Procedure: [25] Ferrocenylmethylamine ***43*** (181 mg, 0.40 mmol) was suspended in 4 mL of dry Et_2O in a flame-dried Schlenck tube under Ar. The suspension was degassed three times and cooled to -40 °C. To the suspension *n*-BuLi solution (1.6 M; 260 µL, 0.42 mmol, 1.05 eq) was added and the suspension was stirred at -30 °C for 2 h. The reaction mixture was cooled to -78 °C and Cl_2PPh (28 µL, 0.21 mmol, 0.52 eq) was added to the reaction mixture and the stirred suspension was allowed to warm to r.t. overnight. To the reaction mixture with 4 mL of aq. sat. $NaHCO_3$ solution was added. The organic layer was washed with 4 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→45% EtOAc in *n*-heptane). Due to precipitate forming, most fractions were filtrated through SiO_2, yielding various fractions of ferrocenylmethylamine starting material, 18% of ferrocenylphosphite ***49*** (36 mg; 35% yield in relation to Cl_2PPh) and 46% of ferrocenecarbaldehyde ***50*** (39 mg).

Attempted synthesis of 1,1''-(Phenylphosphinidene)bis[(2*S*)-2-[(dimethylamino)-methyl]]ferrocene



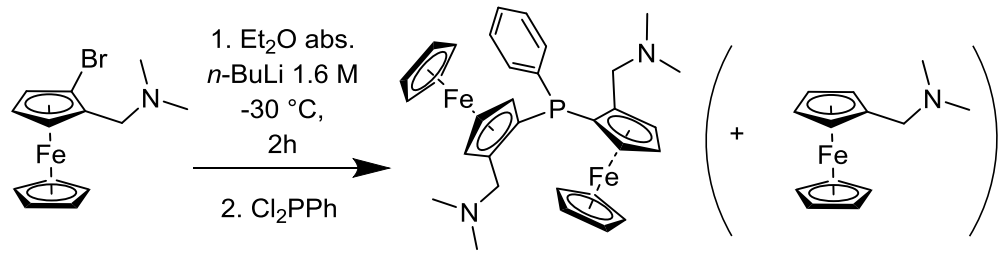
51
$C_{13}H_{16}BrFeN$
322,027 g/mol

53
$C_{32}H_{37}Fe_2N_2P$
592,326 g/mol

Procedure: Mg (30 mg, 1.2 mmol, 1.5 eq) was suspended in 1 mL of THF abs. in a flame-dried Schlenck tube under Ar. The suspension was degassed three times and ferrocenylmethylamine ***51*** (263 mg, 0.82 mmol), dissolved and degassed three times in 1 mL of THF abs., was added dropwise by syringe and heated simultaneously with a hot gun. The reaction mixture was stirred for 30 min, cooled to r.t., and transferred via teflon cannula to a degassed solution of Cl_2PPh (55 µL, 0.41 mmol, 0.50 eq) in 1 mL of THF abs. The reaction mixture was stirred at r.t. overnight. To the reaction mixture 1 mL of water and brine was added. Surprisingly, the formed product turned out to be soluble in brine. The aq. layer was extracted three times with Et_2O. The combined organic fractions were washed with aq. sat. $NaHCO_3$ solution, brine and dried over $MgSO_4$. The solvent was removed under reduced pressure an orange solid readily forming aq. solutions and not identified as to date of this writing.

HRMS: m/z found: 464.0076.

Synthesis of 1,1''-(Phenylphosphinidene)bis[(2*S*)-2-[(dimethylamino)-methyl]]ferrocene



51
$C_{13}H_{16}BrFeN$
322,027 g/mol

53
$C_{32}H_{37}Fe_2N_2P$
592,326 g/mol
59%

54
$C_{13}H_{17}FeN$
243,131 g/mol

Procedure: [25] Ferrocenylmethylamine ***51*** (1.042 g, 3.236 mmol) was dissolved in 3 mL of dry Et_2O in a flame-dried Schlenck tube under Ar. The yellow-to-orange solution was degassed three times, then cooled to -40 °C and *n*-BuLi (1.6 M; 2 mL, 3.2 mmol, 1.0 eq) was added to the reaction mixture dropwise. The solution was stirred at this temperature for 2 h, then cooled to -78 °C. Cl_2PPh (220 µL, 1.62 mmol, 0.50 eq) was added to the solution. The suspension was stirred for another 20 min at this temperature and allowed to warm to r.t. overnight. The reaction mixture was quenched with 5 mL of aq. sat. $NaHCO_3$ solution. Residues were dissolved by adding some DCM and the aq. layer was extracted twice with 10 mL of DCM each. The combined organic fractions were washed three times with 35 mL of water, three times with 35 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 65→100% (Et_2O + 1.5 Et_3N) in *n*-heptane) yielding 59% diaminophosphine ***53*** (561 mg) as a brown oil.

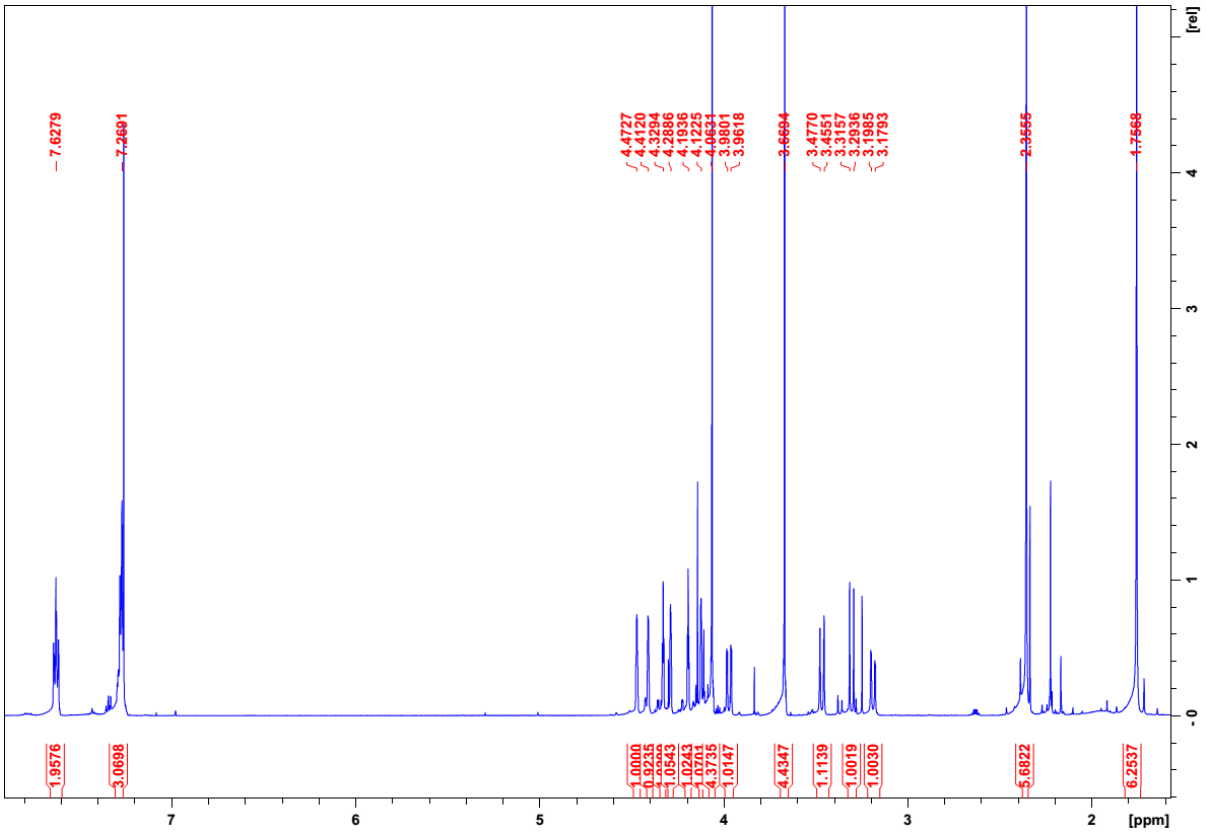
^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.65-7.61 (m, 2H); 7.31-7.26 (m, 3H); 4.47 (m, 1H); 4.41 (m, 1H); 4.33 (pt, *J* = 2.4 Hz, 1H); 4.29 (m, 1H); 4.19 (pt, *J* = 2.4 Hz, 1H); 4.12 (m, 1H); 4.06 (s, 5H); 3.97 (dd, *J* = 13.2, 2.2 Hz, 1H); 3.67 (s, 5H); 3.47 (d, *J* = 13.2 Hz, 1H); 3.30 (d, *J* = 13.3 Hz, 1H); 3.19 (dd, *J* = 13.2, 1.7 Hz, 1H); 2.36 (s, 6H); 1.76 (s, 6H) ppm.

$^{13}C\{^{1}H\}$-NMR (600 MHz, $CDCl_3$) δ = 140.57 (d, J_{CP} = 6.5 Hz, C_q); 134.38 (d, J_{CP} = 23.0 Hz, CH); 128.48 (d, J_{CP} = 0.9 Hz, CH); 127.51 (d, J_{CP} = 8.6, CH); 91.18 (d, J_{CP} = 31.5 Hz, C_q); 88.46 (d, J_{CP} = 23.0 Hz, C_q); 80.17 (d, J_{CP} = 5.9 Hz, C_q); 75.92 (d, J_{CP} = 12.9 Hz, C_q); 72.50 (d, J_{CP} = 5.4 Hz, CH); 71.71 (d, J_{CP} = 5.3 Hz, CH); 71.64 (d, J_{CP} = 3.4 Hz, CH); 70.31 (d, J_{CP} = 3.5 Hz, CH); 69.92 (CH); 69.60 (CH); 69.41 (CH); 67.99 (CH); 58.63 (d, J_{CP} = 11.2 Hz, CH_2); 57.73 (d, J_{CP} = 8.4 Hz, CH_2); 46.02 (CH_3); 44.74 (CH_3) ppm.

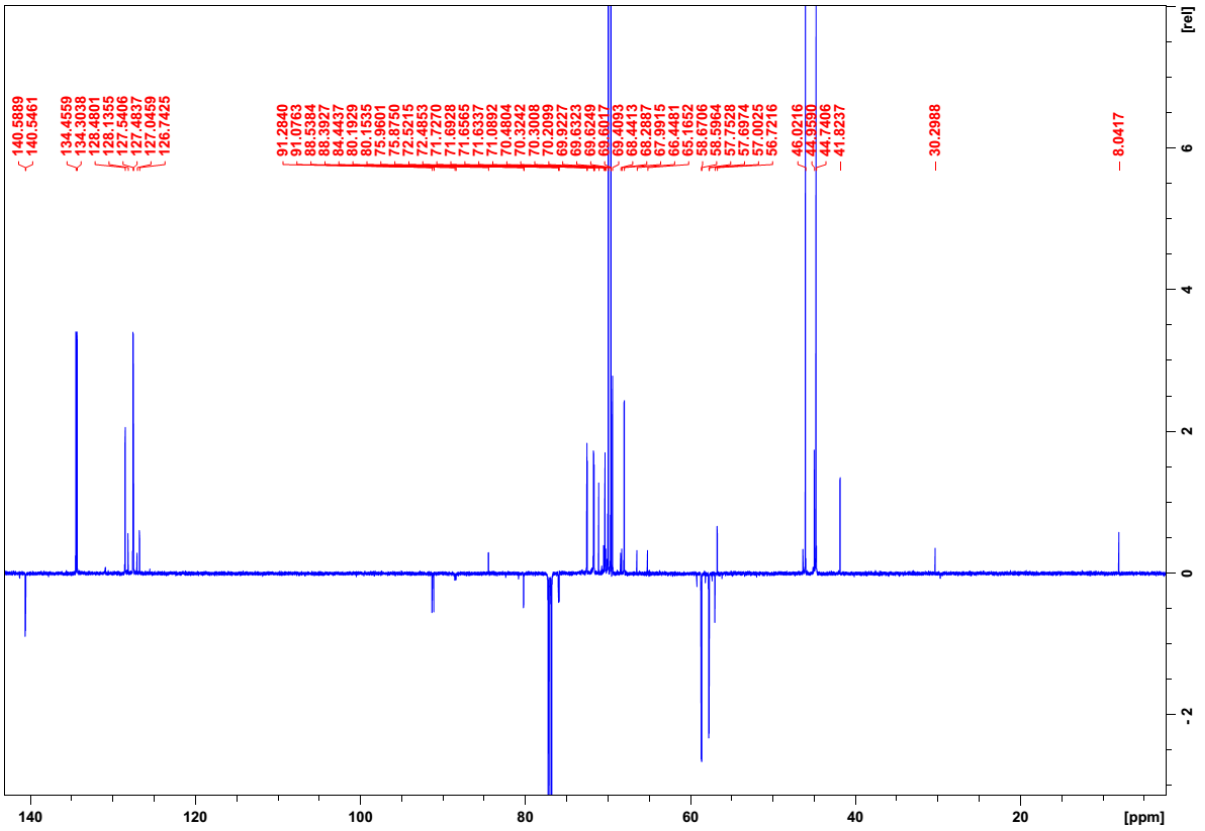
^{31}P-NMR (400 MHz, $CDCl_3$) δ = -44.15 (s) ppm.

HRMS: m/z calculated for M = $C_{32}H_{37}Fe_2N_2P$; $[M+H]^+$ 593.1471, found: 593.1457.

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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134.4559
134.3038
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128.4355
127.5406
127.4837
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126.7425
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91.0763
88.5384
88.3927
84.4437
80.1929
80.1535
75.9601
75.8750
72.5215
72.4853
71.7270
71.6928
71.6565
71.6337
71.0892
70.4804
70.3242
70.3008
70.2099
69.9227
69.6323
69.6249
69.6017
69.4093
68.4413
68.2887
67.9915
66.4481
65.1652
58.6706
58.5964
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57.0025
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44.7406
41.8237
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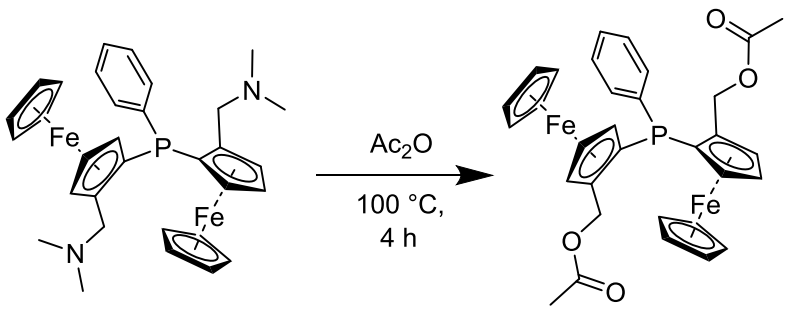
8.0417
[rel]
6
4
2
0
-2
140
120
100
80
60
40
20
[ppm]

Synthesis of 1,1''-(Phenylphosphinidene)bis[(2*S*)-2-[acetoxymethyl]]ferrocene



53
$C_{32}H_{37}Fe_2N_2P$
592,326 g/mol

52
$C_{32}H_{31}Fe_2O_4P$
622,260 g/mol
11%

Procedure: [25] Diaminophosphine ***53*** (354 mg, 0.60 mmol) was suspended in 6 mL of Ac_2O in a flame-dried Schlenck tube under Ar. The suspension was degassed three times, then heated at 100 °C for 4 h in an oil bath. Ac_2O was removed from the dark solution under reduced pressure. The residue was dissolved in DCM, washed with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 10→35% EtOAc in *n*-heptane) yielding 11% diacetatephosphine ***52*** (41 mg) as a brownish oil.

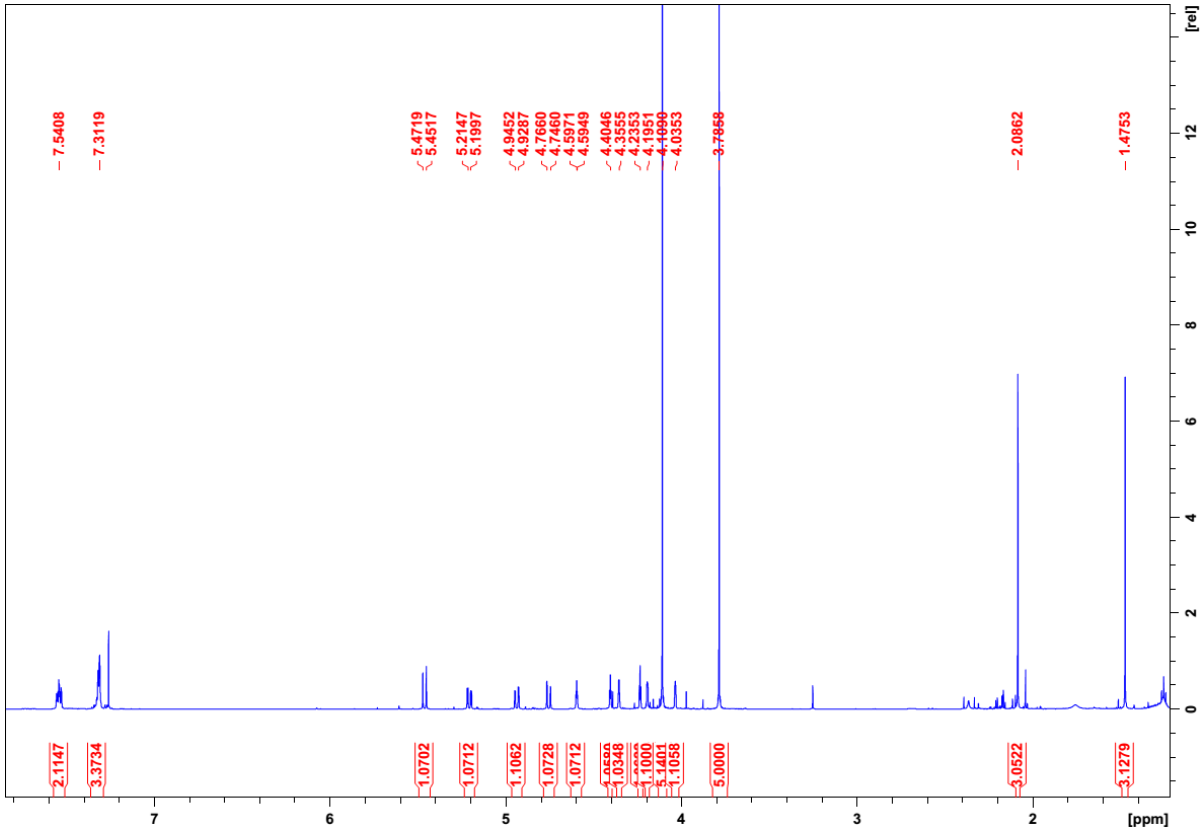
^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.56-7.52 (m, 2H); 7.36-7.30 (m, 3H); 5.46 (d, *J* = 12.1 Hz, 1H); 5.21 (dd, *J* = 12.1, 3.1 Hz, 1H); 4.94 (dd, *J* = 11.9, 2.1 Hz, 1H); 4.76 (d, *J* = 11.9 Hz, 1H); 4.60 (m, 1H); 4.40 (pt, *J* = 2.5 Hz, 1H); 4.36 (m, 1H); 4.24 (pt, *J* = 2.4 Hz, 1H); 4.19 (m, 1H); 4.11 (s, 5H); 4.04 (m, 1H); 3.79 (s, 5H); 2.09 (s, 3H); 1.48 (s, 3H) ppm.

^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 171.06 (C_q); 170.55 (C_q); 139.71 (d, J_{CP} = 7.5 Hz, C_q); 134.29 (d, J_{CP} = 23.3 Hz, CH), 128.86 (CH); 127.77 (d, J_{CP} = 8.5 Hz, CH); 87.23 (d, J_{CP} = 30.9 Hz, C_q); 83.89 (d, J_{CP} = 20.9 Hz, C_q); 81.39 (d, J_{CP} = 4.9 Hz, C_q); 76.28 (d, J_{CP} = 13.0 Hz, C_q); 72.73 (d, J_{CP} = 2.9 Hz, CH); 72.49 (d, J_{CP} = 5.5 Hz, CH); 71.93 (d, J_{CP} = 4.4 Hz, CH); 71.80 (d, J_{CP} = 3.1 Hz, CH); 71.10 (CH); 69.61 (CH); 69.59 (CH); 68.79 (CH); 61.80 (d, J_{CP} = 8.3 Hz, CH_2); 61.65 (d, J_{CP} = 13.4 Hz, CH_2); 21.27 (CH_3); 20.30 (CH_3) ppm.

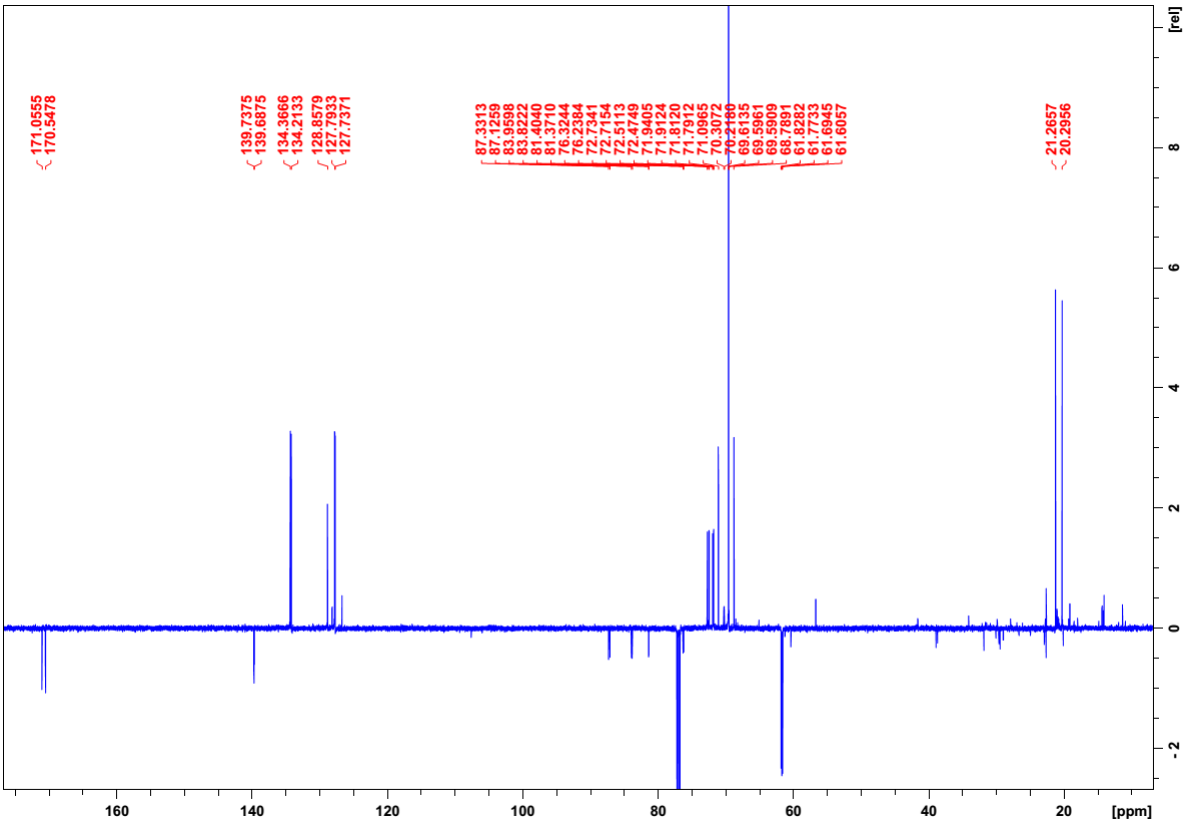
^{31}P-NMR (400 MHz, $CDCl_3$) δ = -44.03 (s) ppm.

HRMS: m/z calculated for M = $C_{32}H_{31}Fe_2O_4P$; $[M+H]^+$ 623.0737, found: 623.0722; $[M+Na]^+$ 645.0556, found: 645.0553; $[2M+Na]^+$ 1267.1215, found: 1267.1208.

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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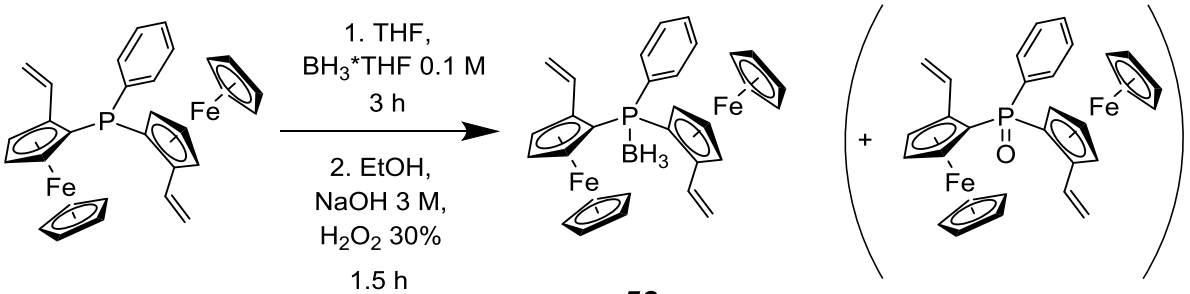
61.6057
21.2657
20.2956
[rel]
8
6
4
2
0
-2
160
140
120
100
80
60
40
20
[ppm]

5. 2. 4. β-Substituted di(ferrrocenylethylene) compounds

Synthesis of 1,1‘‘-(Phenylphosphinidene-P-borane)di[(2*S*)-2-vinyl]ferrocene



8
$C_{30}H_{27}Fe_2P$
530,210 g/mol

58
$C_{30}H_{30}BFe_2P$
544,044 g/mol
20%

12
$C_{30}H_{27}Fe_2OP$
546,209 g/mol

Procedure: [112] Divinylphosphine ***8*** (0.054 g, 0.102 mmol) was dissolved in 2 mL of THF abs. in a flame-dried Schlenck tube under Ar. The solution was degassed three times, then BH_3 • THF (~0.1 M; 0.2 mL, 0.020 mmol, 0.20 eq) was added at r.t. and the solution was stirred for 3 h. To the solution 0.7 mL of EtOH, 0.7 mL of aq. 3 M NaOH and H_2O_2 (30%; 0.25 mL, 2.44 mmol, 23.92 eq) were added in this order and stirring was continued for another 90 min. The solution was extracted with DCM, the organic layer was washed with 4 mL of brine and 4 mL of aq. sat. $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→10% EtOAc in *n*-heptane) yielding 20% P-borane divinylphosphine ***58*** (11 mg) as an orange powder.

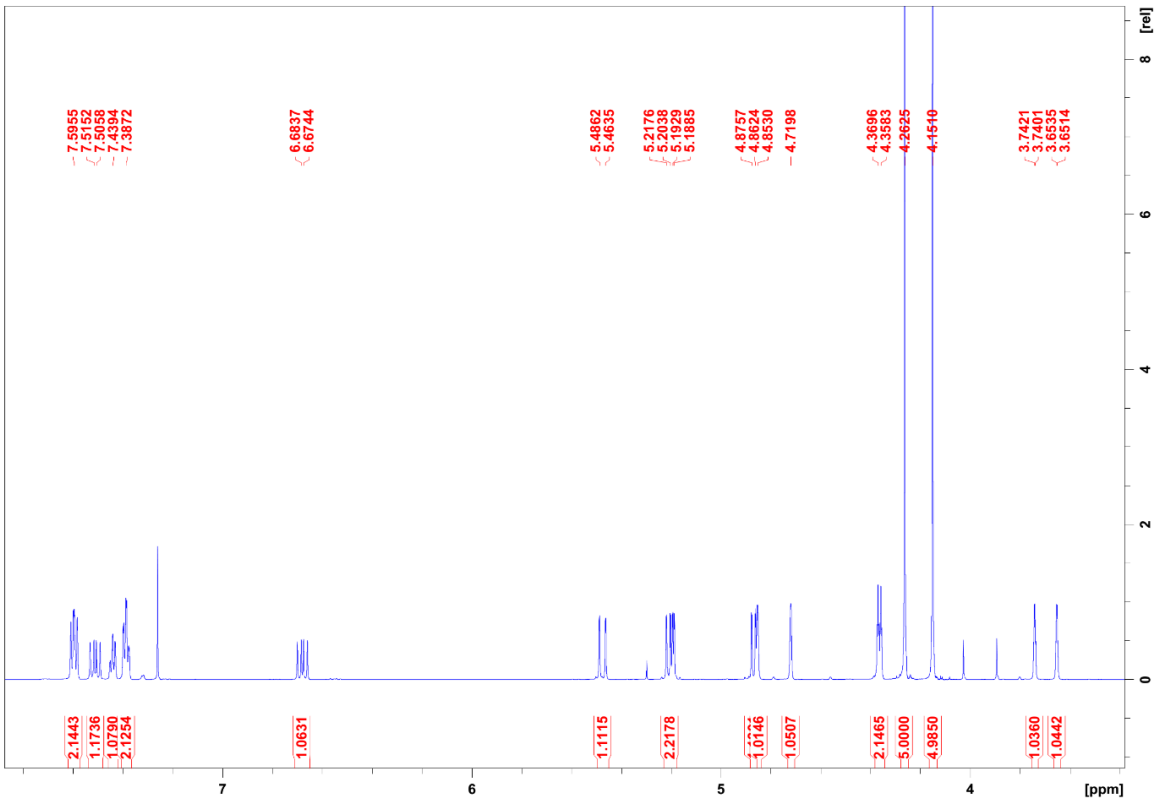
^{1}H-NMR (700 MHz, $CDCl_3$) δ = 7.62-7.57 (m, 2H); 7.51 (dd, *J* = 17.4, 10.8 Hz, 1H); 7.46-7.41 (m, 1H); 7.41-7.37 (m, 2H); 6.68 (dd, *J* = 17.3, 10.8 Hz, 1H); 5.47 (dd, *J* = 17.4, 1.4 Hz, 1H); 5.21 (dd, *J* = 17.3, 1.5 Hz, 1H); 5.20 (dd, *J* = 10.8, 1.5 Hz, 1H); 4.87 (dd, *J* = 10.8, 1.7 Hz, 1H); 4.85 (m, 1H); 4.72 (m, 1H); 4.37 (pt, *J* = 2.5 Hz, 1H); 4.36 (pt, *J* = 2.4 Hz, 1H); 4.26 (s, 5H); 4.15 (s, 5H); 3.74 (m, 1H); 3.65 (m, 1H); 2.04-1.45 (m, 3H) ppm.

$^{13}C\{^{1}H\}$-NMR (700 MHz, $CDCl_3$) δ = 134.37 (CH); 133.28 (CH); 133.00 (d, J_{CP} = 9.2 Hz, CH); 131.63 (d, J_{CP} = 58.9 Hz, C_q); 130.70 (d, J_{CP} = 2.5 Hz, CH); 127.87 (d, J_{CP} = 9.9 Hz, CH); 112.37 (CH_2); 112.08 (CH_2); 88.41 (d, J_{CP} = 14.2 Hz, C_q); 86.89 (d, J_{CP} = 11.8 Hz, C_q); 74.33 (d, J_{CP} = 5.1 Hz, CH); 73.97 (d, J_{CP} = 3.9 Hz, CH); 73.16 (d, J_{CP} = 63.4 Hz, C_q); 71.20 (d, J_{CP} = 64.6 Hz, C_q); 71.06 (CH); 70.94 (CH); 70.66 (d, J_{CP} = 6.4 Hz, CH); 69.58 (d, J_{CP} = 6.4 Hz, CH); 67.97 (d, J_{CP} = 6.6 Hz, CH); 67.84 (d, J_{CP} = 7.2 Hz, CH) ppm.

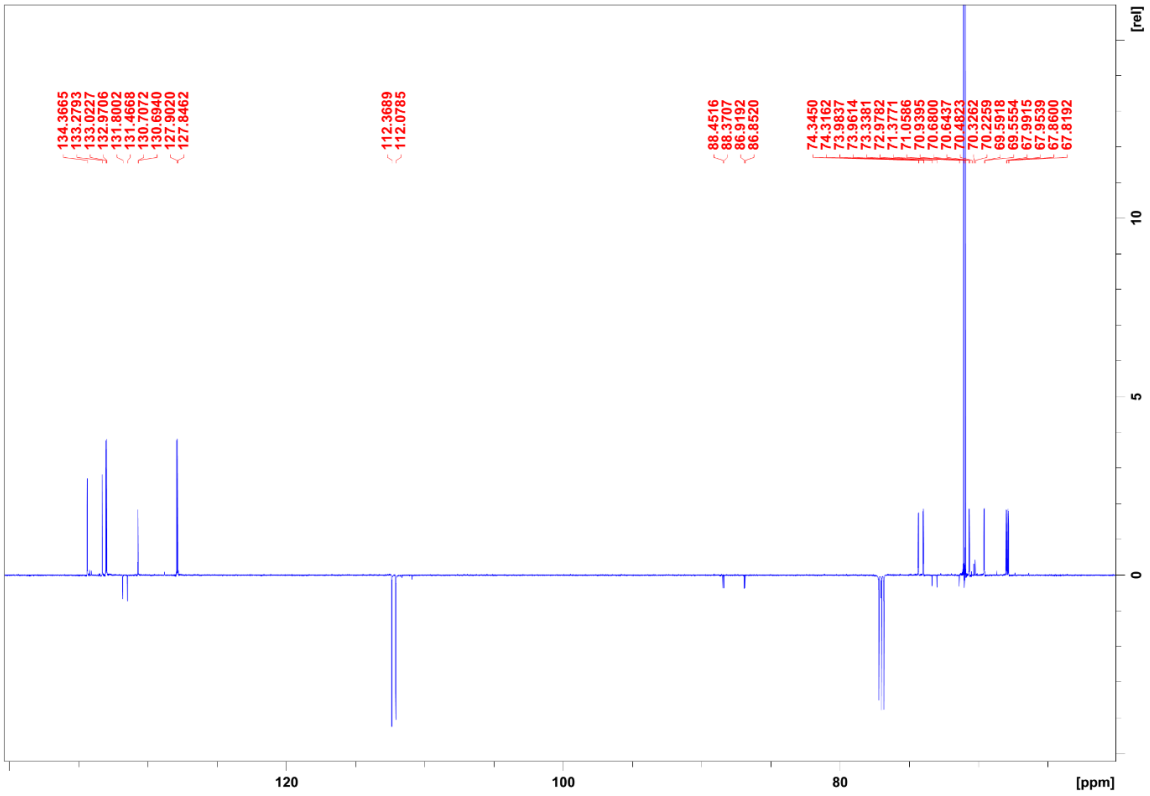
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 11.47 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{30}BFe_2P$; $[M]^+$ 544.0877, found: 544.0868; $[M+Na]^+$ 567.0775, found: 567.0767; $[M+K]^+$ 583.0514, found: 583.0512.

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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132.9706
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112.0785
88.4516
88.3707
86.9192
86.8520
74.3450
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73.9837
73.9614
73.3381
72.9782
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67.8192
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10
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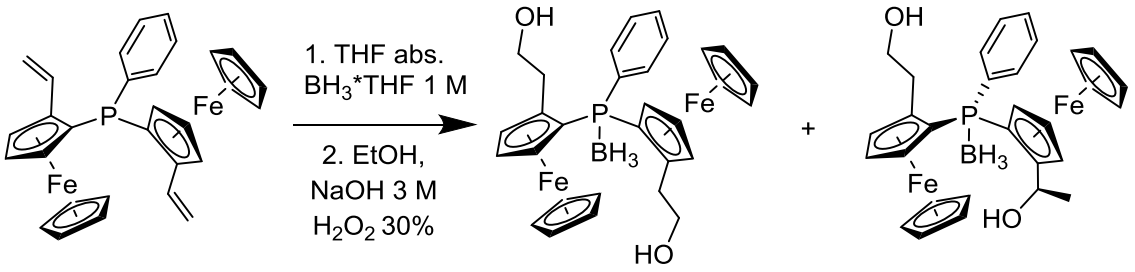
[ppm]

Synthesis of 1,1''-(Phenylphosphinidene-P-borane)di[(2*S*)-2-(-1-hydroxy-2-ethyl)]ferrocene



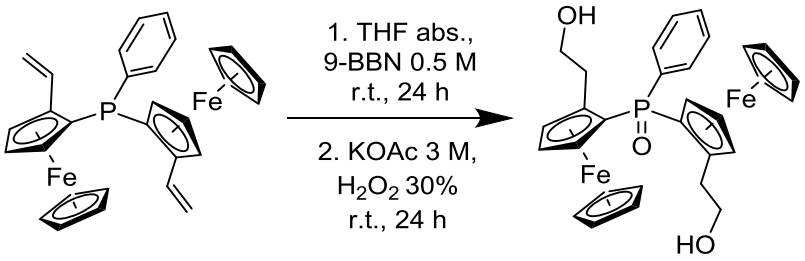
8
$C_{30}H_{27}Fe_2P$
530,210 g/mol

55
$C_{30}H_{34}BFe_2O_2P$
580,074 g/mol
27%

56
$C_{30}H_{34}BFe_2O_2P$
580,074 g/mol
27%

Procedure: [112] Divinylphosphine ***8*** (621 mg; 1.17 mmol) was dissolved in THF abs. in a flame-dried Schlenck tube under Ar. The solution was degassed three times, then BH_3 • THF (1 M; 10.5 mL, 10.50 mmol, 8.97 eq) was added to the solution at r.t. The mixture was stirred for 3 h at r.t., then 8 mL of EtOH, 8 mL of aq. 3N NaOH and H_2O_2 (30%; 6 mL, 58.8 mmol, 50.2 eq) were added in this order and the solution was stirred for another 90 min. The mixture was extracted with DCM. The organic layer was washed with brine and aq. sat. $NaHCO_3$ solution and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2; 25→50% EtOAc in *n*-heptane) yielding 54% of a 1:1 mixture of P-borane dihydroxyphosphines ***55*** and ***56*** (365 mg) as a brightly orange flaky solid.

Synthesis of 1,1''-(Phenylphosphinideneoxide)di[(2*S*)-2-(-1-hydroxy-2-ethyl)]ferrocene



8
$C_{30}H_{27}Fe_2P$
530,210 g/mol

57
$C_{30}H_{31}Fe_2O_3P$
582,239 g/mol
25%

Procedure: [113] Divinylphosphine ***8*** (56 mg, 0.11 mmol) was dissolved in 1 mL of THF abs. in a flame-dried Schlenck tube under Ar. The orange solution was degassed three times, cooled in an ice bath and 9-BBN solution (0.5 M in THF; 4 mL, 2 mmol, 19 eq) was added dropwise. The solution was stirred under Ar at r.t. for 24 h, then 0,7 mL of aq. 3 M KOAc and aq. H_2O_2 (30%; 6 mL, 59 mmol, 554 eq) were added in this order and the solution was stirred for another 24 h. The solution was extracted two times with 5 mL of DCM. The combined organic fractions were washed with 15 mL of water and 15 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was purified by column chromatography (Al_2O_3, 50→100% EtOAc in *n*-heptane, 0-20% MeOH in EtOAc) yielding 25% of dihydroxyphosphineoxide ***57*** (16 mg).

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.77-7.73 (m, 2H); 7.53-7.44 (m, 3H); 4.55 (m, 1H); 4.45 (m, 1H); 4.36 (m, 1H); 4.31 (q, *J* = 2.3 Hz, 1H); 4.30-4.26 (m, 2H); 4.28 (s, 5H); 4.11 (q, *J* = 7.2 Hz, 1H); 4.09 (m, 1H); 4.00 (m, 1H); 3.94 (s, 5H); 3.39-3.24 (m, 3H); 3.05-2.92 (m, 2H); 2.57-2.43 (m, 2H) ppm.

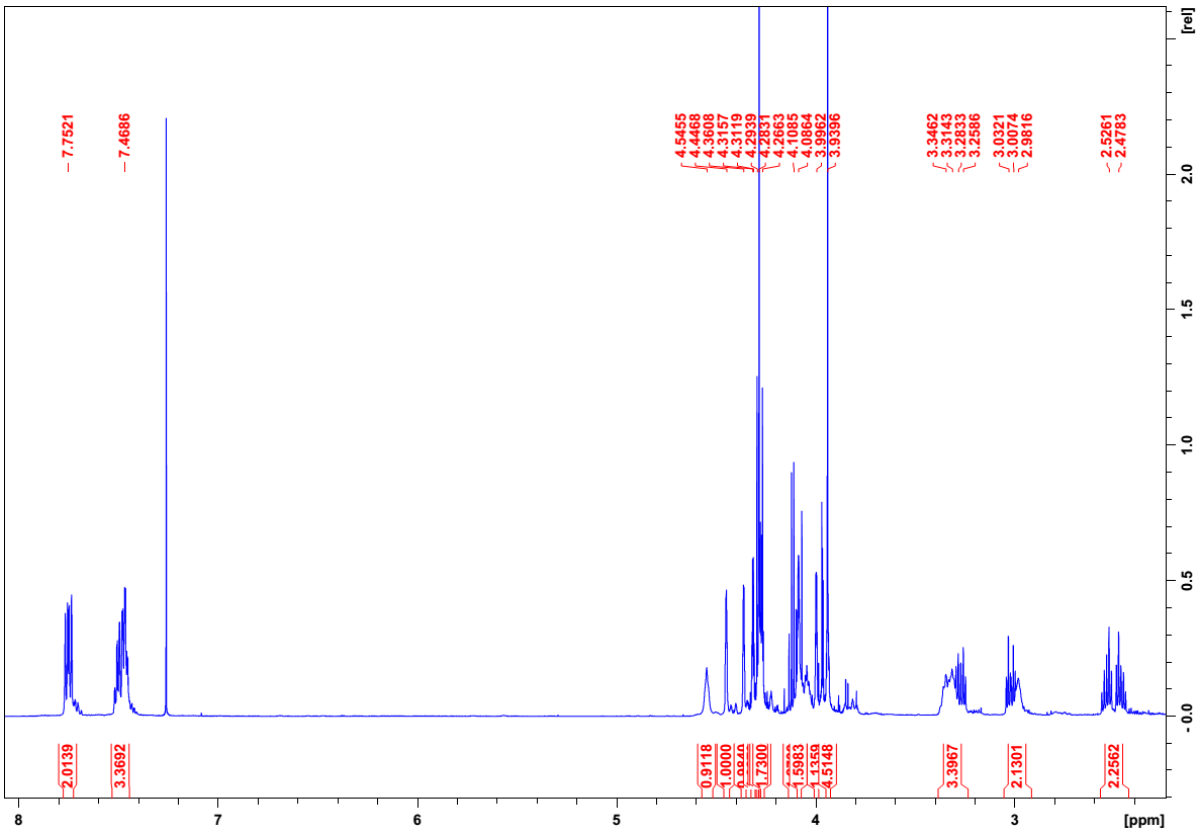
^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 135.89 (d, J_{CP} = 108.9 Hz, C_q); 131.28 (d, J_{CP} = 2.7 Hz, CH); 130.82 (d, J_{CP} = 9.6 Hz, CH); 128.05 (d, J_{CP} = 12.0 Hz, CH); 91.69 (d, J_{CP} = 10.8 Hz, C_q); 88.18 (d, J_{CP} = 11.8 Hz, C_q); 76.09 (d, J_{CP} = 115.6 Hz, C_q); 73.29 (d, J_{CP} = 15.0 Hz, CH); 72.36 (d, J_{CP} = 10.1 Hz, CH); 72.09 (d, J_{CP} = 10.2 Hz, CH);

71.25 (d, J_{CP} = 118.1 Hz, C_q); 71.24 (d, J_{CP} = 15.7 Hz, CH); 70.20 (CH); 70.11 (CH); 69.91 (d, J_{CP} = 11.0 Hz, CH); 68.98 (d, J_{CP} = 11.2 Hz, CH); 64.01 (CH_2); 62.54 (CH_2); 31.73 (CH_2); 31.10 (CH_2) ppm.

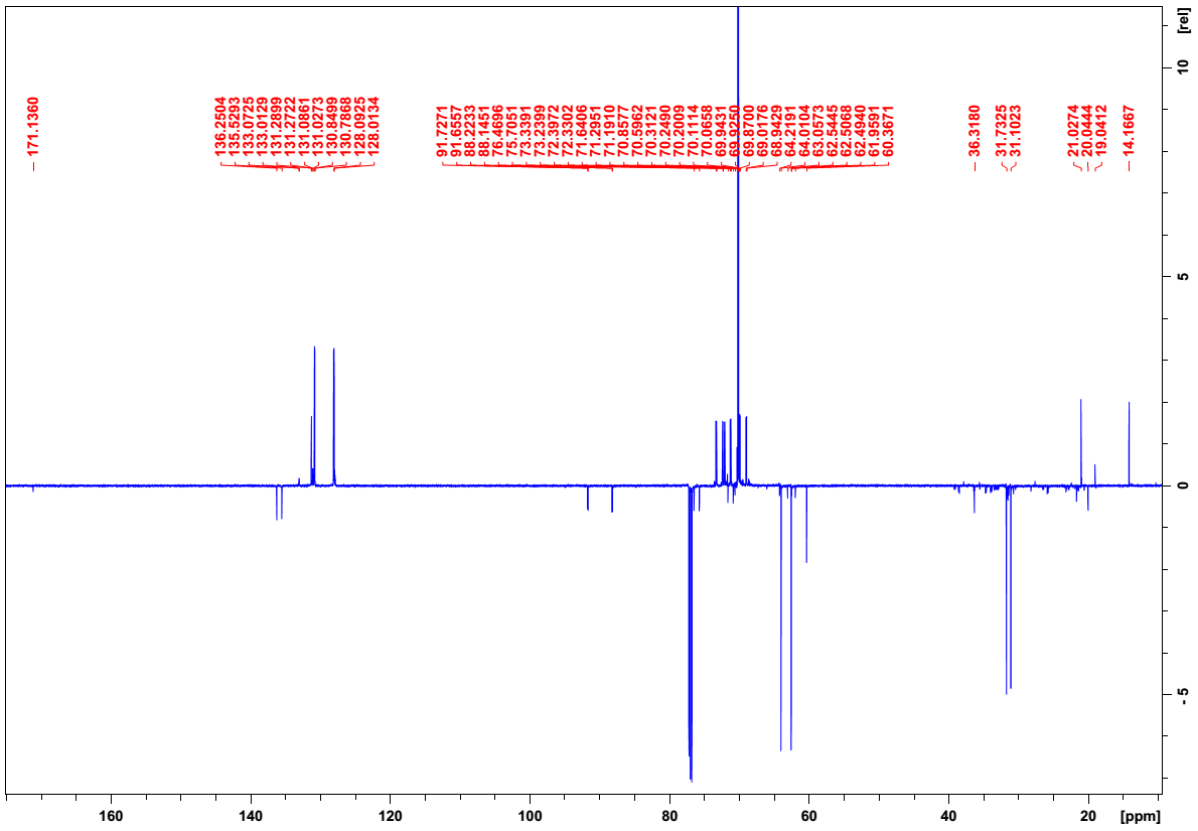
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 32.70 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{31}Fe_2O_3P$; $[M]^+$ 582.0704, found: 582.0695; $[M+Na]^+$ 605.0602, found: 605.0592; $[M+K]^+$ 621.0341, found: 621.0327.

^{1}H-NMR:



$^{13}C\{^{1}H\}$-NMR: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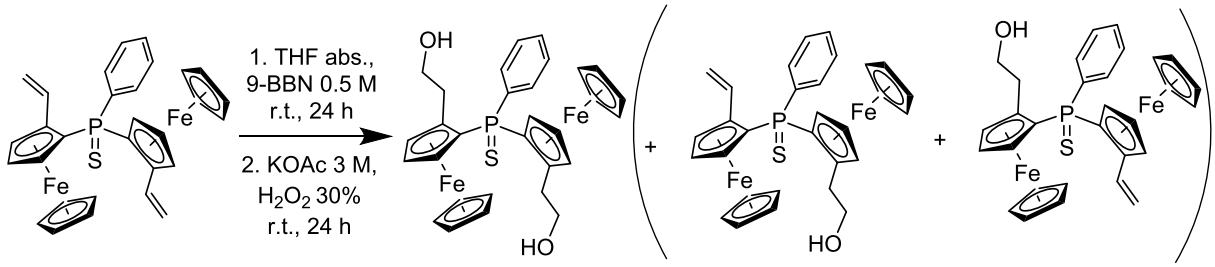
20
[ppm]

Synthesis of 1,1‘‘-(Phenylphosphinidenesulfide)di[(2*S*)-2-(-1-hydroxy-2-ethyl)]ferrocene



14	***59***	***62***	***63***
$C_{30}H_{27}Fe_2PS$	$C_{30}H_{31}Fe_2O_2PS$	$C_{30}H_{29}Fe_2OPS$	$C_{30}H_{29}Fe_2OPS$
562,270 g/mol	598,300 g/mol	580,285 g/mol	580,285 g/mol
	60%	3%	4%

Procedure: [113] Divinylphosphinesulfide ***14*** (530 mg, 0.94 mmol) was dissolved in 10 mL of THF abs. in a flame-dried Schlenck tube under Ar. The orange solution was degassed three times, cooled in an ice bath and 9-BBN solution (0.5 M in THF; 16 mL, 8 mmol, 8.5 eq) was added dropwise. The solution was stirred under Ar at r.t. for 24 h, then cooled in an ice bath, 7 mL of aq. 3 M KOAc and aq. H_2O_2 (30%; 5 mL, 49 mmol, 52 eq) were added in this order and the solution was stirred at r.t. for another 24 h. The solution was extracted two times with 12 mL of DCM. The combined organic fractions were washed with 50 mL of water and 50 mL brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was purified by column chromatography (SiO_2, 0→50% EtOAc in *n*-heptane) yielding 60% of dihydroxyphosphinesulfide ***59*** (337 mg) as an orange oil and 3% / 4% og monovinylmonohydroxyphosphinesulfides ***62*** (17 mg) and ***63*** (24 mg) as orange solids.

Diol ***59***:

^{1}H-NMR (700 MHz, $CDCl_3$) δ = 7.79 (dd, *J* = 13.0, 7.6 Hz, 2H); 7.49 (pt, *J* = 7.5 Hz, 1H); 7.44 (pt, *J* = 7.9 Hz, 2H); 4.53 (s, 1H); 4.42 (s, 1H); 4.35 (s, 5H); 4.22 (s, 1H); 4.20 (s, 1H); 4.12 (s, 5H); 4.09 (m, 2H); 3.93 (s, 1H); 3.70 (s, 1H); 3.66 (dt, *J* = 15.3, 6.5 Hz, 1H); 3.28 (m, 1H); 3.14 (m, 1H); 3.13 (m, 1H); 2.70-2.64 (m, 1H); 2.53-2.48 (m, 1H) ppm.

$^{13}C\{^{1}H\}$-NMR (700 MHz, $CDCl_3$) δ = 134.90 (d, J_{CP} = 87.1 Hz, C_q); 132.13 (d, J_{CP} = 10.4 Hz, CH); 131.11 (d, J_{CP} = 2.8 Hz, CH); 127.69 (d, J_{CP} =12.2 Hz, CH); 90.48 (d, J_{CP} = 13.0 Hz, C_q); 87.45 (d, J_{CP} = 12.7 Hz, C_q); 80.25 (d, J_{CP} = 95.7 Hz, C_q); 74.13 (d, J_{CP} = 12.8 Hz, CH); 74.04 (d, J_{CP} = 95.6 Hz, C_q); 72.99 (d, J_{CP} = 12.9 Hz, CH); 72.26 (d, J_{CP} = 9.4 Hz, CH); 71.97 (d, J_{CP} = 9.8 Hz, CH); 70.70 (CH); 70.44 (CH); 68.82 (d, J_{CP} = 10.2 Hz, CH); 67.67 (d, J_{CP} = 10.6 Hz, CH); 63.26 (CH_2); 62.07 (CH_2); 31.19 (CH_2); 30.78 (CH_2) ppm.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 40.32 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{31}Fe_2O_2PS$; $[M]^+$ 598.0481, found: 598.0479.

Alcohol ***62***:

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.76 (dd, *J* = 13.1, 7.5 Hz, 2H); 7.49-7.45 (m, 1H); 7.45-7.40 (m, 2H); 5.74-5.67 (m, 1H); 5.62-5.56 (m, 1H); 4.51 (q, *J* = 1.9 Hz, 1H); 4.34 (s, 5H); 4.31 (m, 1H); 4.17 (m, 1H); 4.14 (m, 1H); 4.13 (s, 5H); 4.12 (m, 1H); 3.84 (m, 1H); 3.84-3.79 (m, 1H); 3.63 (m, 1H); 3.21 (dt, *J* = 13.5, 6.5 Hz, 1H); 2.62-2.54 (m, 1H); 2.33-2.26 (m, 1H) ppm.

$^{13}C\{^{1}H\}$-NMR (600 MHz, $CDCl_3$) δ = 134.56 (d, J_{CP} = 87.1 Hz, C_q); 132.23 (d, J_{CP} = 10.4 Hz, CH); 130.84 (d, J_{CP} = 2.9 Hz, CH); 129.85 (d, J_{CP} = 88.8 Hz, CH); 127.57 (d, J_{CP} = 12.2 Hz, CH); 93.38 (d, J_{CP} = 12.7 Hz, C_q); 90.35 (d, J_{CP} = 12.7 Hz, C_q); 79.81 (d, J_{CP} = 96.4 Hz, C_q); 74.67 (d, J_{CP} = 95.2 Hz, C_q); 73.95 (d, J_{CP} = 13.0 Hz, CH); 72.87 (d, J_{CP} = 12.9 Hz, CH); 71.82 (d, J_{CP} = 9.8 Hz, CH); 70.47 (CH); 70.40 (CH); 70.12 (d, J_{CP} = 9.9 Hz, CH); 68.67 (d, J_{CP} = 10.2 Hz, CH); 66.89 (d, J_{CP} = 10.6 Hz, CH); 63.38 (CH_2); 30.81 (CH_2) ppm; 1 CH_2 not found.

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 40.64 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{29}Fe_2OPS$; $[M+D]^+$ 582.0517, found: 582.0520.

Alcohol ***63***:

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.76 (dd, *J* = 13.0, 7.2 Hz, 2H); 7.49-7.45 (m, 1H); 7.45-7.40 (m, 2H); 4.47 (q, *J* = 1.9 Hz, 1H); 4.40 (q, *J* = 1.8 Hz, 1H); 4.35 (s, 5H); 4.19 (m, 1H); 4.13 (s, 5H); 4.14-4.11 (m, 1H); 3.85 (dt, *J* = 1.4, 2.6 Hz, 1H); 3.63 (dd,

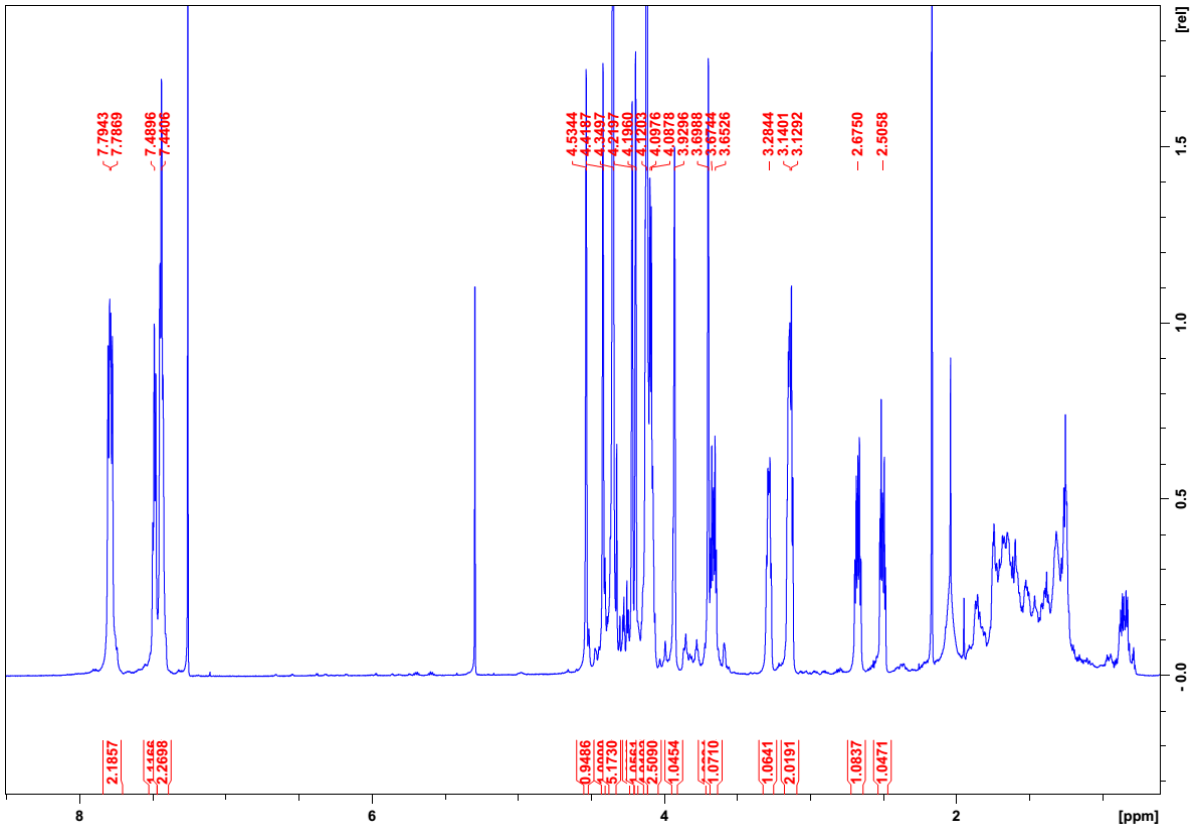
J = 15.9, 7.7 Hz, 1H); 3.58 (q, *J* = 2.1 Hz, 1H); 3.29 (ddd, *J* = 12.8, 6.9, 5.9 Hz, 1H); 3.14 (ddd, *J* = 13.8, 7.4, 6.5 Hz, 1H); 2.81 (dq, *J* = 15.9, 7.5 Hz, 1H); 2.73-2.67 (m, 1H); 2.56 (dt, 15.4, 6.1 Hz, 1H); 2.17 (s, 1H) ppm.

$^{13}C\{^{1}H\}$-NMR (600 MHz, $CDCl_3$) δ = 135.15 (d, J_{CP} = 86.7 Hz, C_q); 132.17 (d, J_{CP} = 10.4 Hz, CH); 130.95 (d, J_{CP} = 2.9 Hz, CH); 127.60 (d, J_{CP} = 12.1 Hz, CH); 95.81 (d, J_{CP} = 13.0 Hz, C_q); 87.39 (d, J_{CP} = 12.5 Hz, C_q); 80.28 (d, J_{CP} = 95.9 Hz, C_q); 74.03 (d, J_{CP} = 12.7 Hz, CH); 73.60 (d, J_{CP} = 96.0 Hz, C_q); 73.11 (d, J_{CP} = 13.1 Hz, CH); 72.19 (d, J_{CP} = 9.5 Hz, CH); 70.63 (CH); 70.43 (d, J_{CP} = 10.1 Hz, CH); 70.23 (CH); 68.17 (d, J_{CP} = 10.4 Hz, CH); 67.50 (d, J_{CP} = 10.5 Hz, CH); 62.12 (CH_2); 31.14 (CH_2) ppm; 1 CH, 1 CH_2 not found.

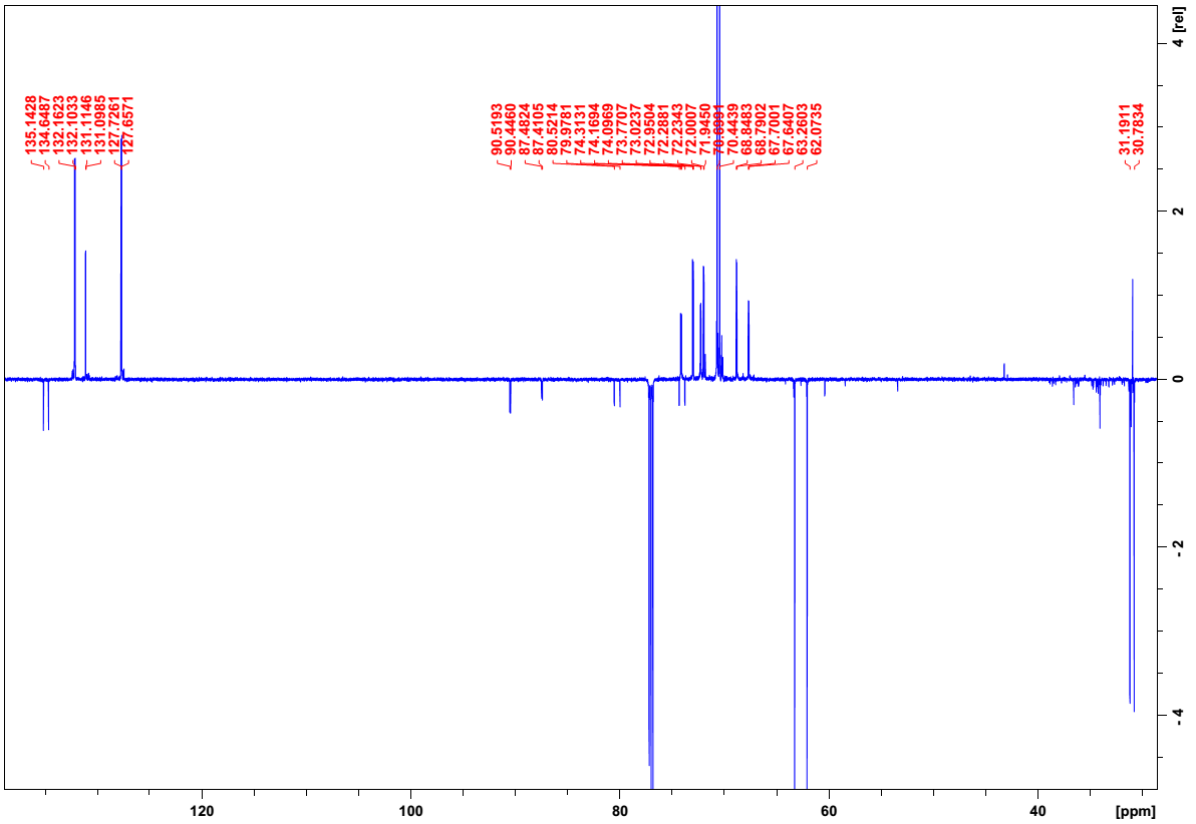
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 40.43 (s) ppm.

HRMS: m/z calculated for M = $C_{30}H_{29}Fe_2OPS$; $[M+D]^+$ 582.0517, found: 582.0518.

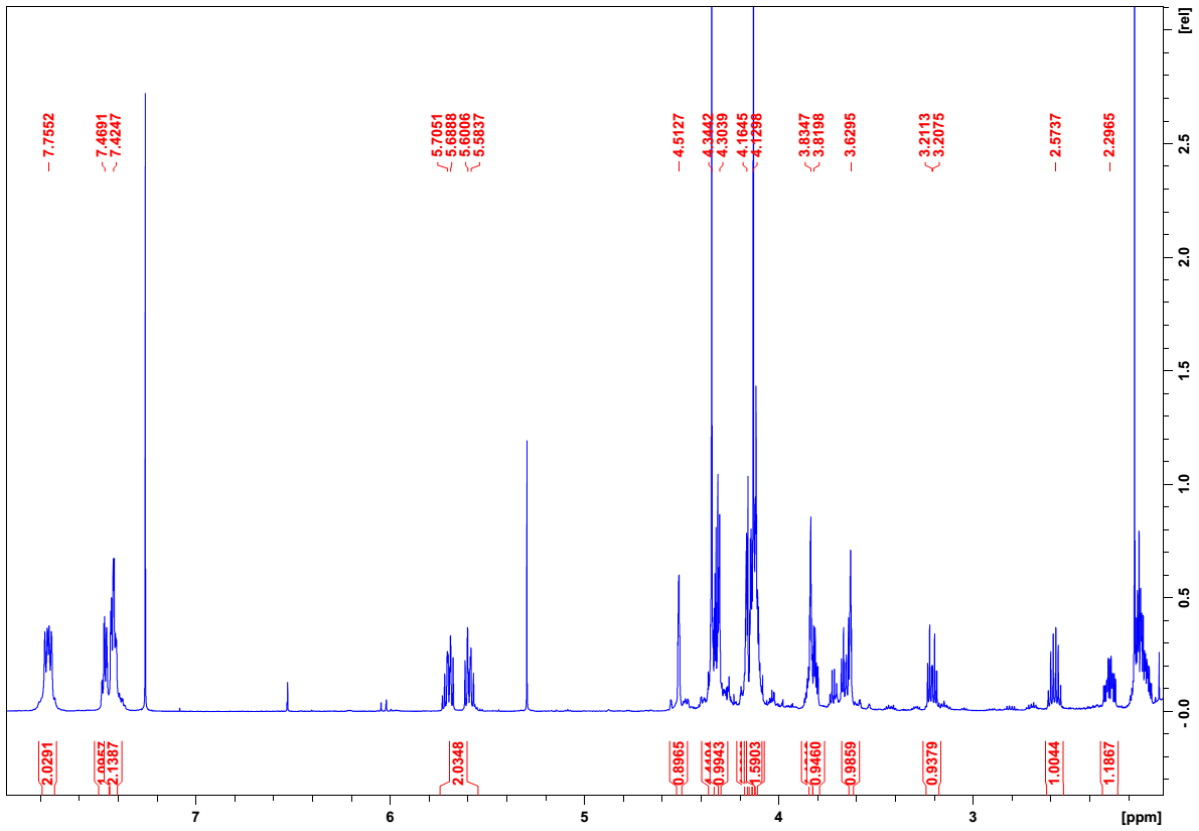
^{1}H-NMR (Diol ***59***):



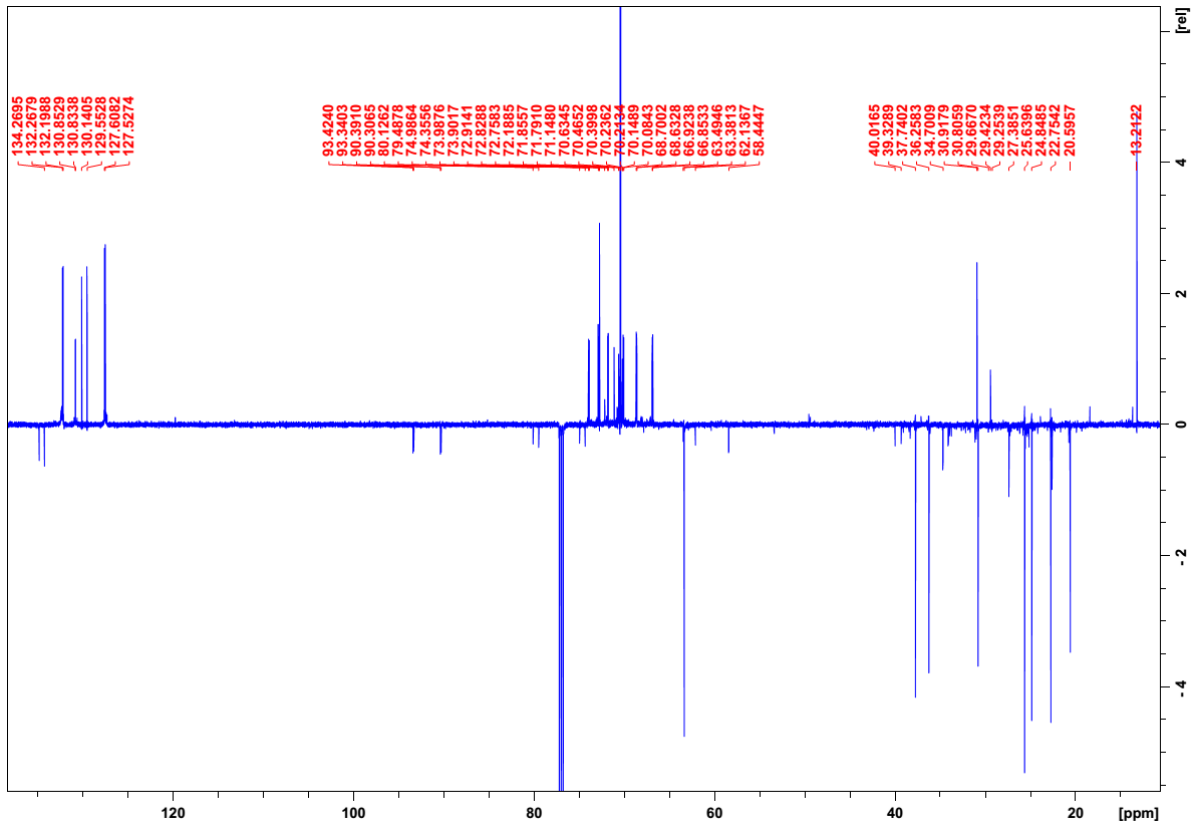
^{13}C{^{1}H}-NMR (Diol ***59***):



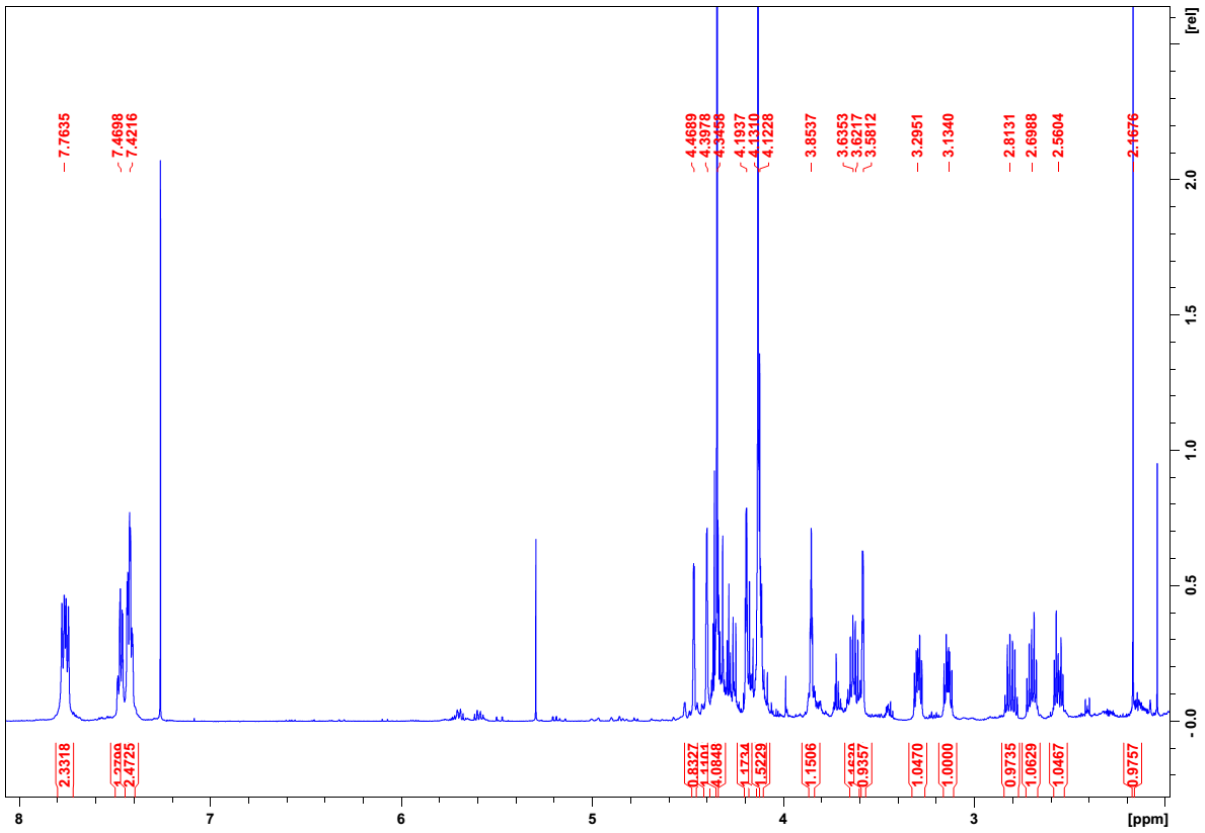
^{1}H-NMR (Alcohol ***62***):



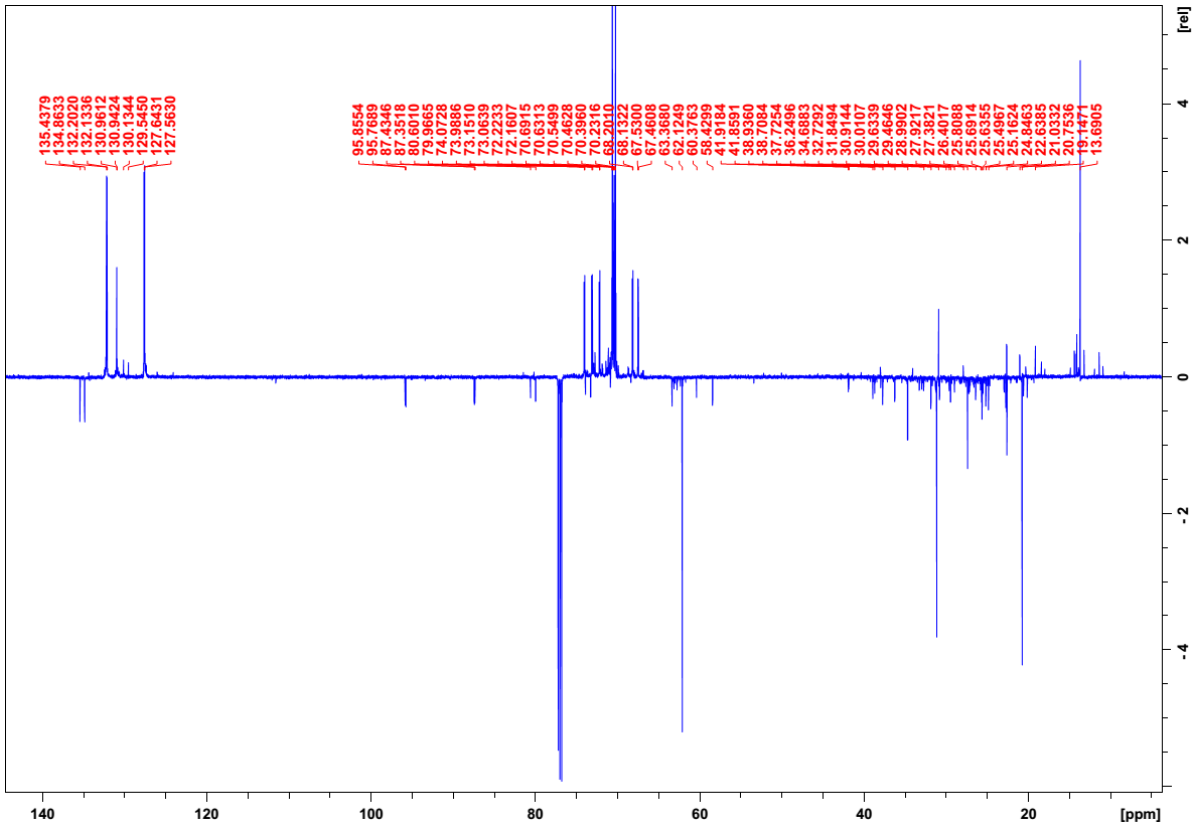
^{13}C{^{1}H}-NMR (Alcohol ***62***):



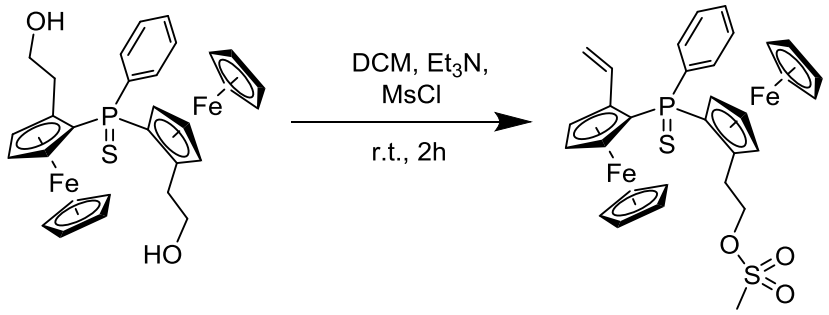
^{1}H-NMR (Alcohol ***63***):



^{13}C{^{1}H}-NMR (Alcohol ***63***):



Attempted synthesis of 1,1''-(Phenylphosphinidenesulfide)di[(2*S*)-2-(-1-mesyloxy-2-ethyl)]ferrocene



59
$C_{30}H_{31}Fe_2O_2PS$
598,300 g/mol

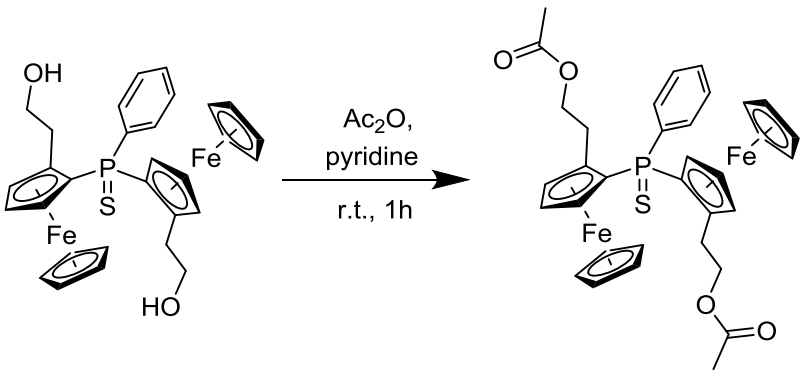
61
$C_{31}H_{31}Fe_2O_3PS_2$
658,370 g/mol
7%

Procedure: [114] Dihydroxyphosphinesulfide ***59*** (225 mg, 0.38 mmol) was dissolved in 6 mL of dry DCM and cooled in an ice bath. Et_3N (222 µL, 1.59 mmol, 4.23 eq) and MsCl (100 µL, 1.29 mmol, 3.44 eq) were added in this order and the reaction mixture was stirred at r.t. for 2 h until conversion of the diol ***59*** was complete. The reaction was quenched by adding 5 mL of water. The resulting mixture was extracted three times with DCM and the combined organic fractions were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→60% EtOAc in *n*-heptane) yielding 7% monomesylatephosphinesulfide ***61*** (18 mg).

^{31}P-NMR (400 MHz, $CDCl_3$) δ = 39.82 (s) ppm.

HRMS: m/z calculated for M = $C_{31}H_{31}Fe_2O_3PS_2$; $[M+H]^+$ 659.0229, found: 659.0235.

Synthesis of 1,1‘‘-(Phenylphosphinidenesulfide)di[(2*S*)-2-(-1-acetoxy-2-ethyl)]ferrocene



59
$C_{30}H_{31}Fe_2O_2PS$
598,300 g/mol

60
$C_{34}H_{35}Fe_2O_4PS$
682,374 g/mol
29%

Procedure: [68] Dihydroxyphosphinesulfide ***59*** (112 mg, 0.19 mmol) was dissolved in 400 µL of pyridine and Ac_2O (160 µL, 1.70 mmol, 9.09 eq) was added. After 1 h of stirring at r.t., completeness of conversion was determined. The solvent was removed under reduced pressure and the residue was dissolved in Et_2O, washed three times with 10 mL of water each, once with 10 mL of brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→25% EtOAc in *n*-heptane) yielding 29% of diacetatephosphinesulfide ***60*** (37 mg).

^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.74 (dd, *J* =13.0, 7.7 Hz, 2H); 7.51-7.47 (m, 1H); 7.43 (dt, *J* = 7.5, 12.9 Hz, 2H); 4.57-4.52 (m, 1H); 4.52-4.47 (m, 1H); 4.44 (m, 1H); 4.35 (s, 5H); 4.34 (m, 1H); 4.19 (m, 1H); 4.16 (m, 1H); 4.14 (s, 5H), 3.84 (m, 1H); 3.81 (m, 1H); 3.67 (dt, *J* = 2.3, 6.9 Hz, 1H); 3.67 (m, 1H); 3.62 (m, 1H); 3.39-3.32 (m, 1H); 2.88-2.81 (m, 1H); 2.44 (dt, *J* = 6.6, 15.2 Hz, 1H); 2.13 (s, 3H); 1.97 (s, 3H) ppm.

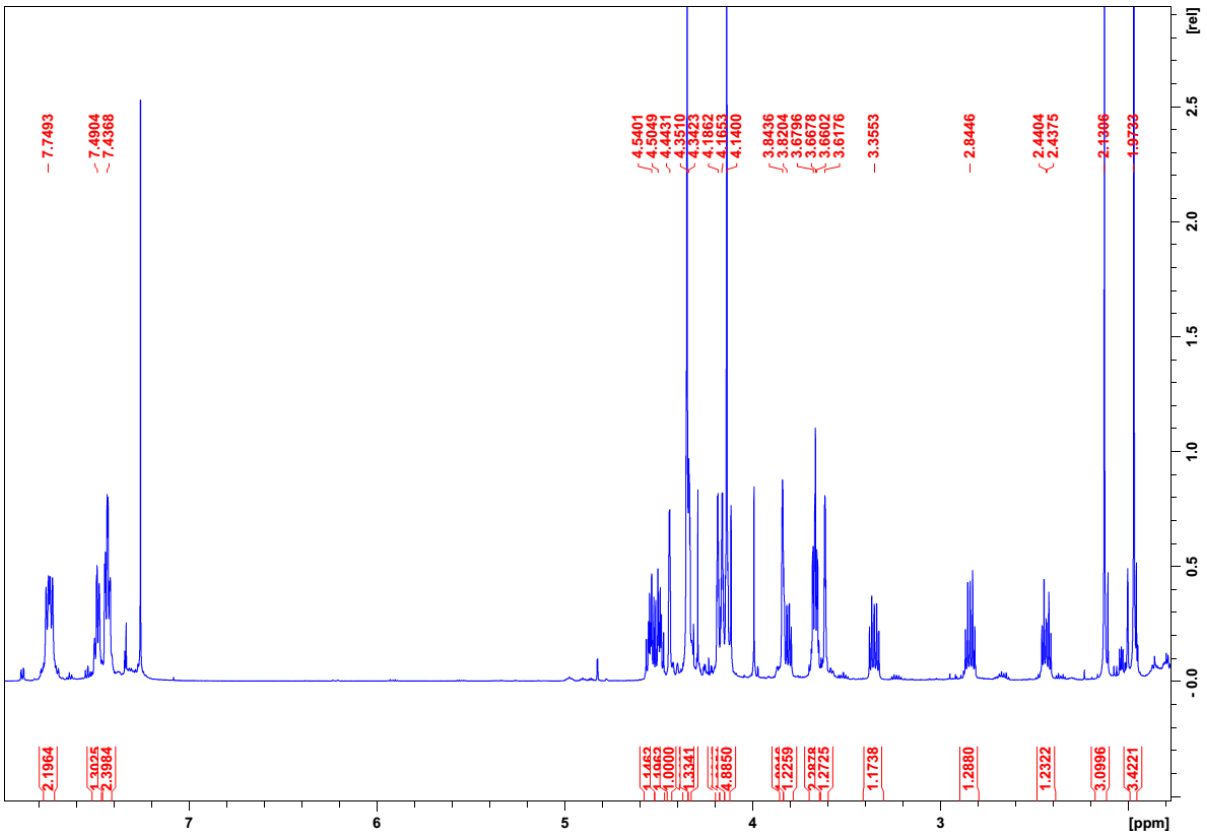
^{13}C{^{1}H}-NMR (600 MHz, $CDCl_3$) δ = 171.27 (C_q); 170.81 (C_q); 134.51 (d, J_{CP} = 87.1 Hz, C_q); 132.16 (d, J_{CP} = 10.4 Hz, CH); 131.15 (d, J_{CP} = 2.8 Hz, CH); 127.73 (d, J_{CP} = 12.2 Hz, CH); 89.38 (d, J_{CP} = 12.8 Hz, C_q); 86.74 (d, J_{CP} = 12.5 Hz, C_q); 80.59 (d, J_{CP} = 95.6 Hz, C_q); 74.07 (d, J_{CP} = 95.5 Hz, C_q); 73.94 (d, J_{CP} = 12.6 Hz, CH); 73.09 (d,

J_{CP} = 12.9 Hz, CH); 71.64 (d, J_{CP} = 9.3 Hz, CH); 71.44 (d, J_{CP} = 9.7 Hz, CH); 70.72 (CH); 70.48 (CH); 68.78 (d, J_{CP} = 10.3 Hz, CH); 67.51 (d, J_{CP} = 10.3 Hz, CH); 64.55 (CH_2); 63.53 (CH_2); 26.99 (CH_2); 26.92 (CH_2); 21.15 (CH_3); 21.00 (CH_3) ppm.

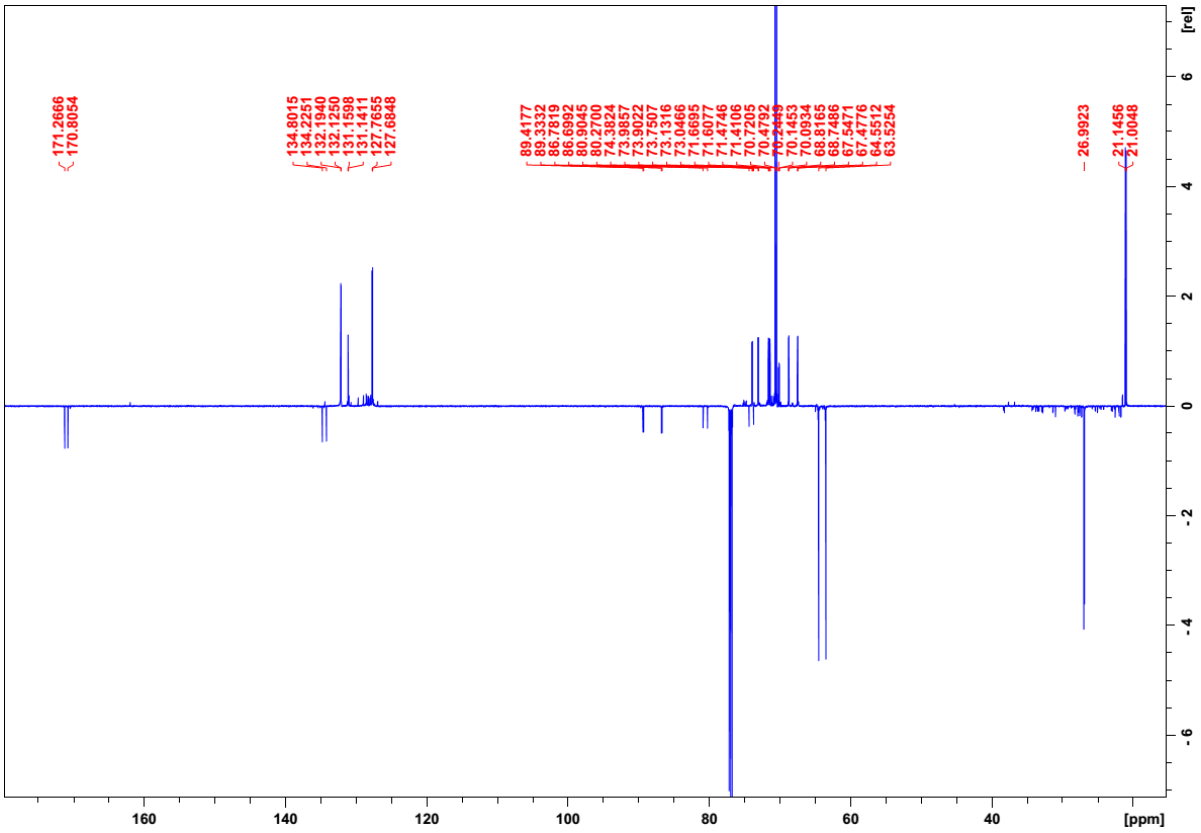
^{31}P-NMR (400 MHz, $CDCl_3$) δ = 40.13 (s) ppm.

HRMS: m/z calculated for M = $C_{34}H_{35}Fe_2O_4PS$; $[M+Na]^+$ 705.0590, found: 705.0592; $[2M+Na]^+$ 1387.1283, found: 1387.1291.

^{1}H-NMR:



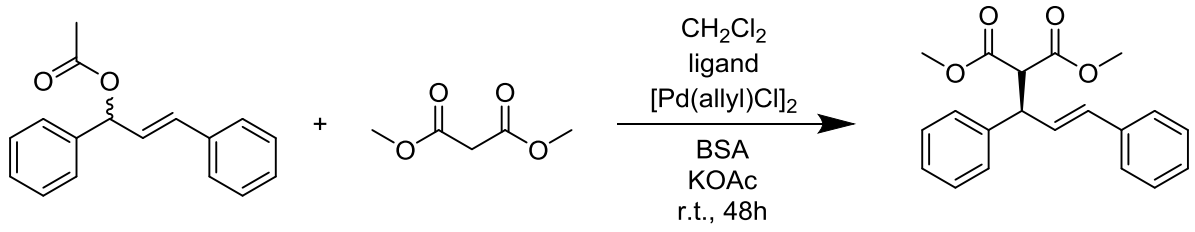
$^{13}C\{^{1}H\}$-NMR:


171.2666
170.8054
134.8015
134.2251
132.1940
132.1250
131.1598
131.1411
127.7655
127.6848
89.4177
89.3332
86.7819
86.6992
80.9045
80.2700
74.3824
73.9857
73.9022
73.7507
73.1316
73.0466
71.6695
71.6077
71.4746
71.4106
70.7205
70.4792
70.2449
70.1453
70.0934
68.8165
68.7486
67.5471
67.4776
64.5512
63.5254
26.9923
21.1456
21.0048
[rel]
[ppm]

5. 2. 5. Catalysis

5. 2. 5. 1. Asymmetric allylic alkylation

Synthesis of Dimethyl-(*E*)-2-(1,3-diphenylallyl)malonate



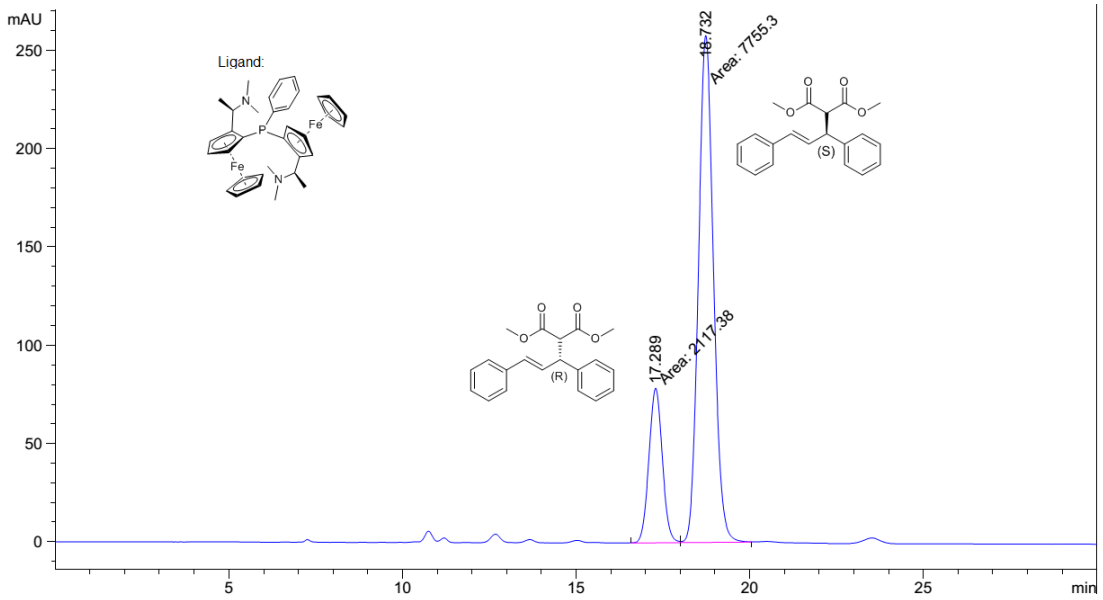
64
$C_{17}H_{16}O_2$
252,313 g/mol

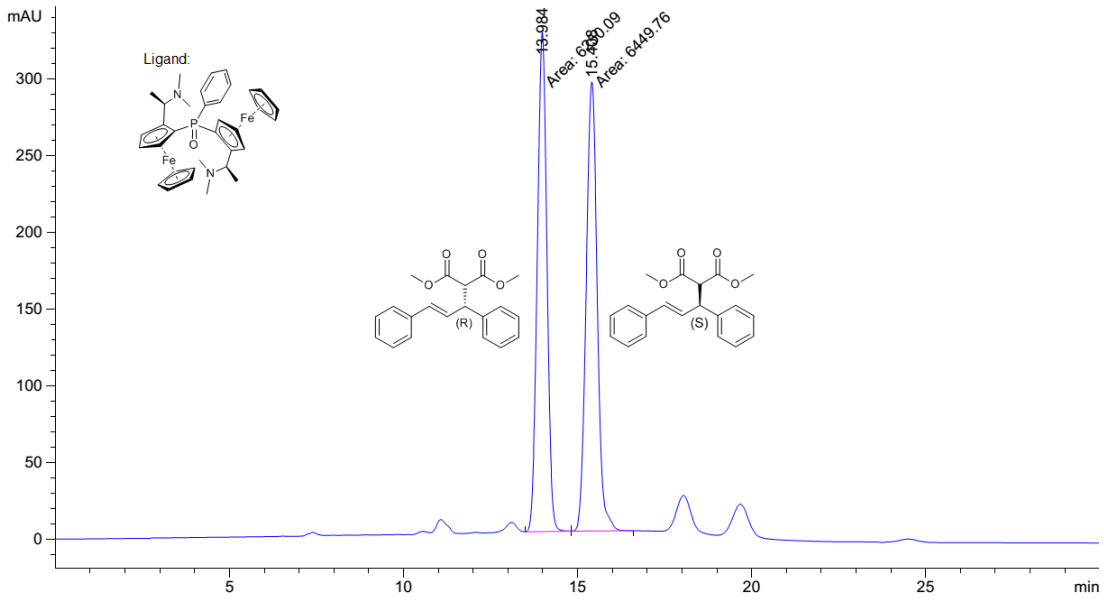
65
$C_5H_8O_4$
132,115 g/mol

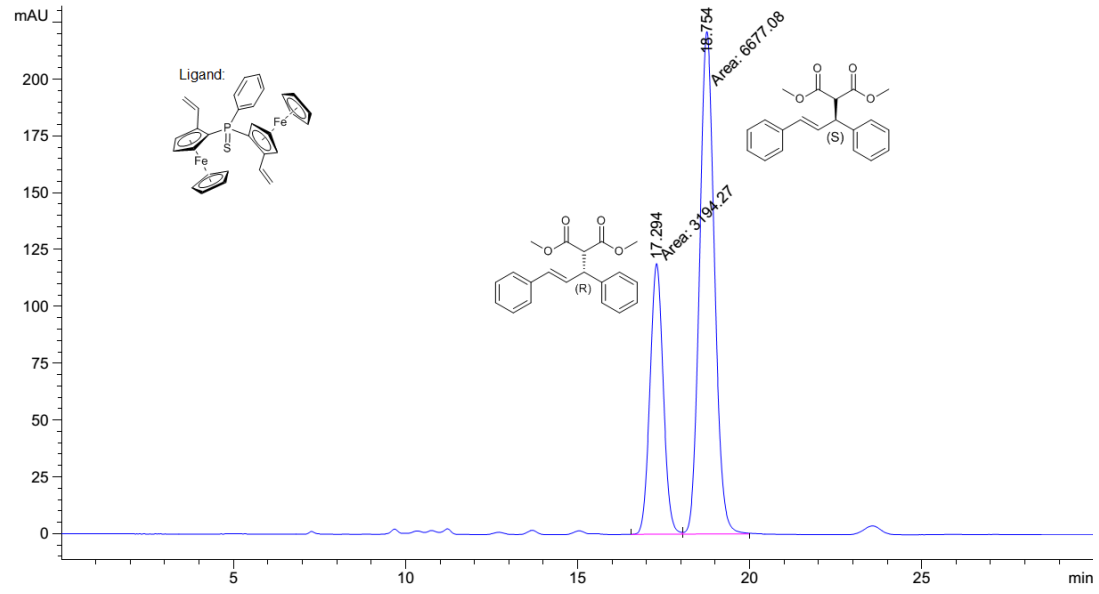
66
$C_{20}H_{20}O_4$
324,376 g/mol

Procedure: [117] In a flame-dried Schlenck tube, diferrocene ligand (0.010 mmol, 1 mol-%) and $[Pd(allyl)Cl]_2$ (1.8 mg, 0.005 mmol, 0.5 mol-%) were dissolved in 1 mL of degassed DCM in this order under Ar. The yellow solution was stirred for 20 min while it turned orange successively. To the solution, freshly distilled 1,3-diphenylallylacetate ***64*** (252 mg, 1.00 mmol), dimethylmalonate ***65*** (340 µL, 3.00 mmol, 3 eq), BSA (740 µL, 3.00 mmol, 3 eq) and a cat. amount of KOAc were added in this order. The reaction mixture was degassed once and stirred for 48 h at r.t. until the cat. conversion was completed. To the solution 15 mL of Et_2O were added. The organic layer was washed twice with sat. aq. NH_4Cl solution, dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was dried, dissolved in 2 mL of DCM and filtered through SiO_2. The e.e. of ***66*** was detected via chiral HPLC (Chiralcel OD-H, 2% iPrOH in *n*-heptane).

HPLC Analysis:

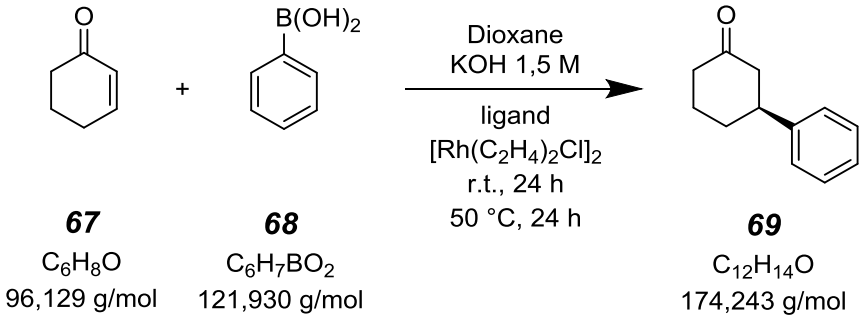






5. 2. 5. 2. Asymmetric 1,4-addition to enones

Synthesis of 3-Phenylcyclohexanone



67
C_6H_8O
96,129 g/mol

68
$C_6H_7BO_2$
121,930 g/mol

69
$C_{12}H_{14}O$
174,243 g/mol

Procedure: [118] Diferrocene ligand (11.9 µmol, 3.3 mol-%) was dissolved in 1 mL of dioxane, 120 µL of aq. 1.5 M KOH were added and the solution was stirred for 15 min. $[Rh(ethylene)_2Cl]_2$ (2.1 mg, 5.4 µmol, 1.5 mol-%) was added to the solution and stirring was continued for another 15 min. Phenylboronic acid ***68*** (86 mg, 0.72 mmol, 2 eq) and cyclohexenone ***67*** (35 µL, 0.36 mmol) were added in this order. The solution was stirred for 24 h at r.t. and for 24 h in an oil bath at 50 °C until complete starting material conversion was detected by ^{1}H-NMR. The reaction mixture was extracted twice with DCM and twice with EtOAc. The combined organic fractions were washed with water and brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2, 0→20% EtOAc in *n*-heptane). Only minuscule amounts of product ***69*** (<= 2%, 1 mg) could be isolated. These were not analyzed further.

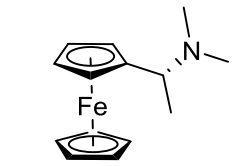
Appendix A: Abbreviations

9-BBN	9-Borabicyclo(3.3.1)nonane
abs	absolute
Ac	Acetyl
AIBN	Azobis(isobutyronitrile)
aq	aqueous [solution]
Bn	Benzyl
BSA	Bis(trimethylsilyl)acetamide
cat	catalytic [amount]
CBS	Corey-Itsuno catalyst (also known as Corey-Bakshi-Shibata catalyst)
CFC	Chlorofluorocarbon
Cp	Cyclopentadienyl
Cy	Cyclohexyl
d	day(s)
DCM	Dichloromethane
DHQD	Dihydroquinidine
DMF	Dimethylformamide
DNA	Deoxyribonucleic acid
E	Electrophile
e.e.	enantiomeric excess
ESI	electron-spray ionization
Et	Ethyl
EWG	electron-withdrawing group
Fc	Ferrocenyl
g	gram
h	hour(s)
HOMO	highest occupied molecular orbital
HRMS	High-resolution mass spectroscopy
iPr	Isopropyl (-2-propane)

L	ligand
LUMO	lowest unoccupied molecular orbital
m	meta
M	Metal
Me	Methyl
mg	milligram
min	minute(s)
mL	milliliter(s)
mmol	milli molar amount (~6.022 • 10^{20})
mol	molar amount (~6.022 • 10^{23})
µL	microliter(s)
m.p.	melting point
Ms	Mesyl (Methylsulfonyl-)
MW	Microwave oven
n-Bu	*n*-butyl (-1-butane)
nm	nanometer(s)
NMO	*N*-methyl-*N*-oxide morpholine
NMR	Nuclear magnetic resonance
Nu	Nucleophile
o	ortho
oa rTOF	orthogonally accelerating reflector time of flight [analyzator]
p	para
pH	pondus Hydrogenii
Ph	Phenyl
PHAL	2,3-dihydro-1,4-Phthalazinedione
pK_b	logarithmic acid association constant
PPFA	(2-Diphenylphosphinoferrocenyl)ethyldimethylamine
py	pyridine
rac	racemic [Mixture]
RCM	Ring-closing metathesis

tert.-Bu	*tert.*-butyl (-2-(2-methyl)-propane)
THF	Tetrahydrofurane
TLC	thin-layer chromatography
TOF	Turn-over frequency
TON	Turn-over number
Ts	Tosyl (p-methylphenylsulfonyl-)

Appendix B: Structure indices



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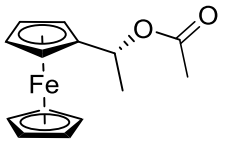

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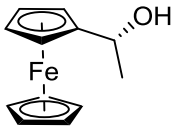

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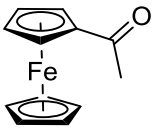

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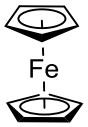

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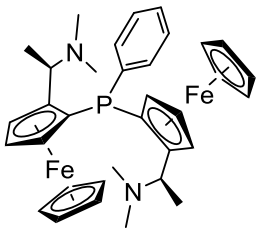

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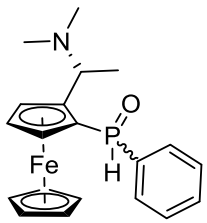

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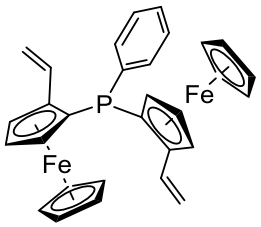

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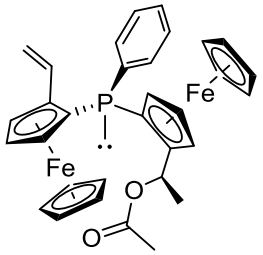

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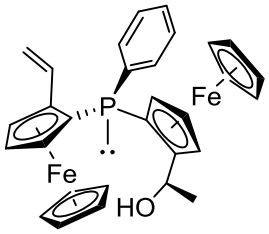

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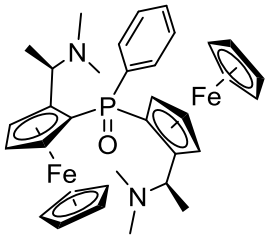

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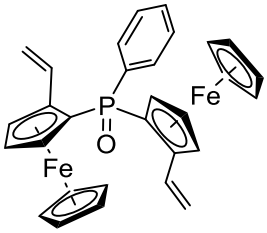

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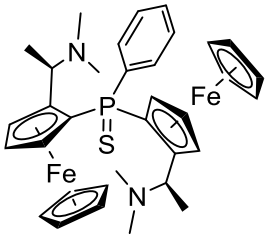

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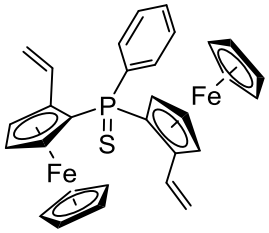

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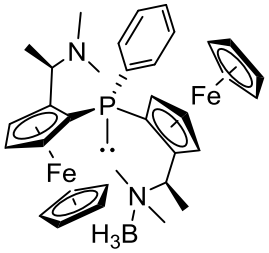

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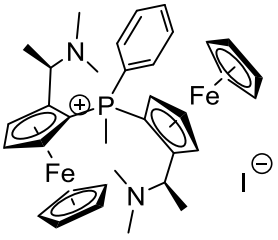

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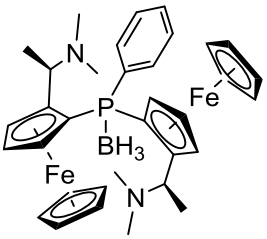

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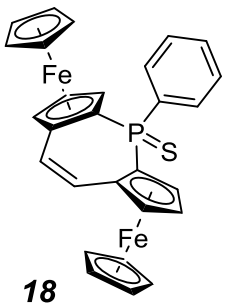

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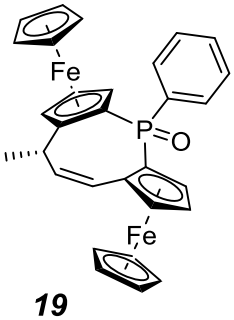

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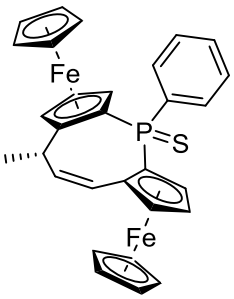

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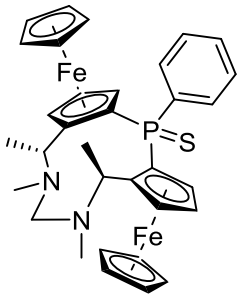

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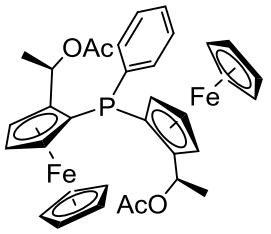

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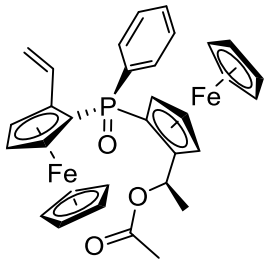

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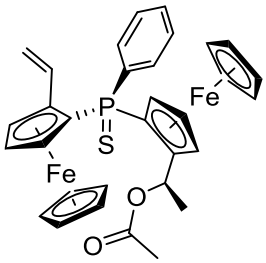

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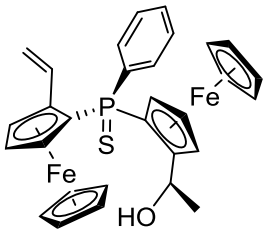

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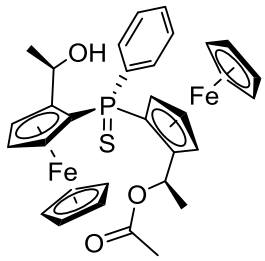

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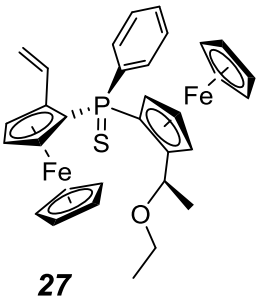

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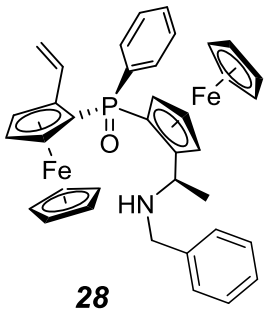

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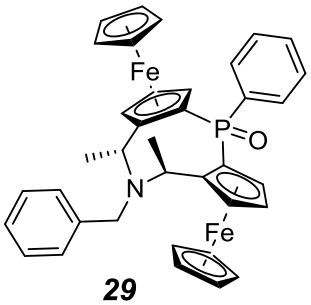

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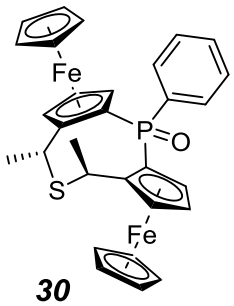

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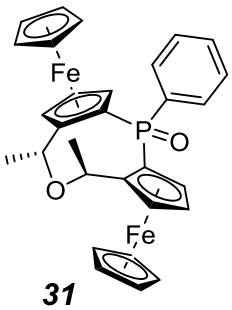

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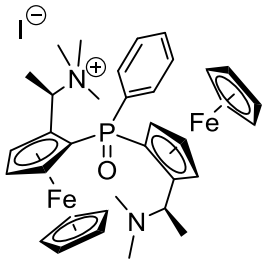

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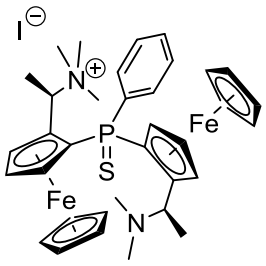

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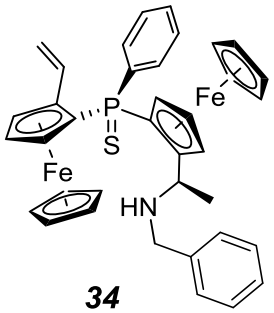

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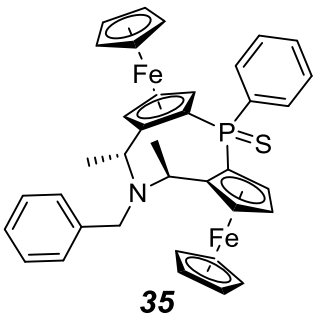

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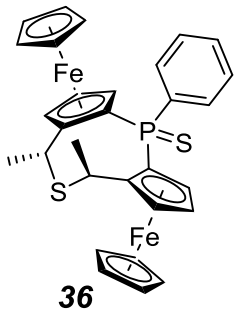

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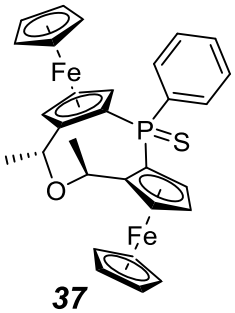

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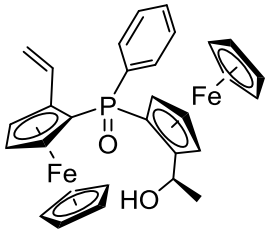

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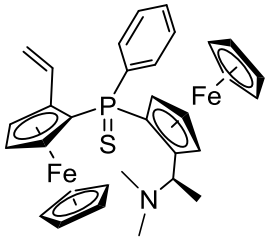

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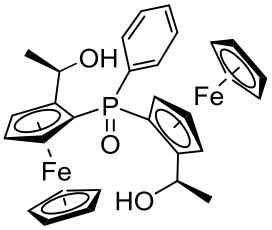

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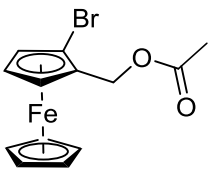

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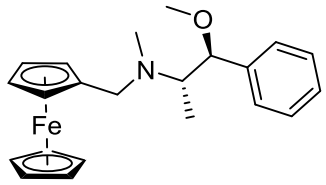

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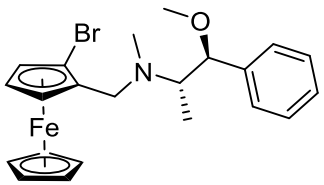

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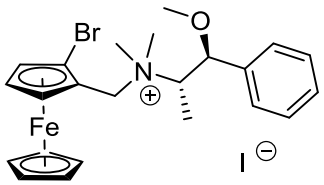

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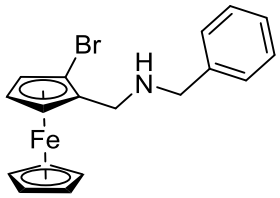

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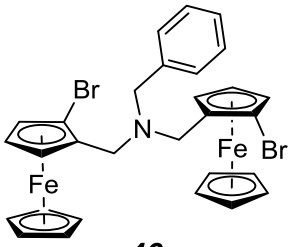

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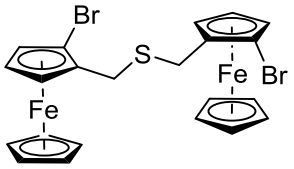

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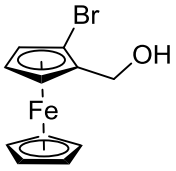

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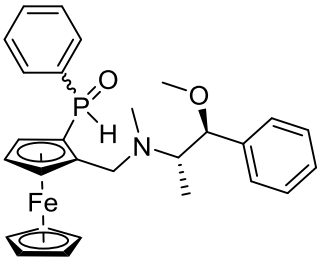

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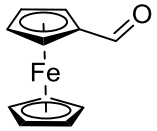

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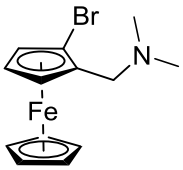

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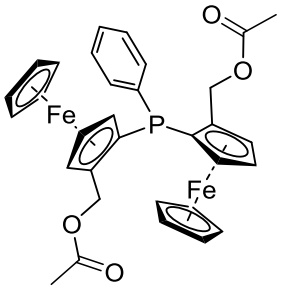

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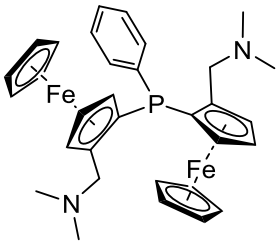

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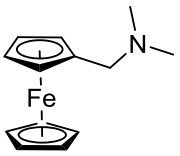

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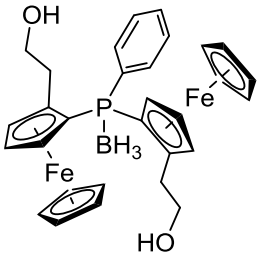

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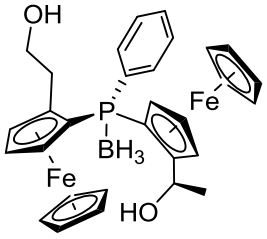

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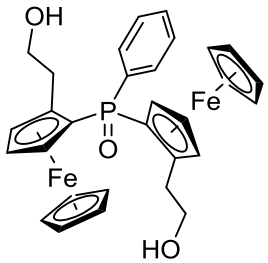

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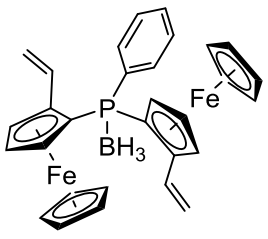

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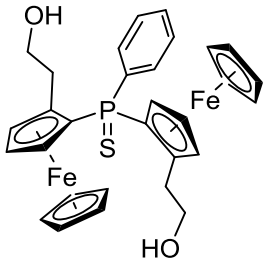

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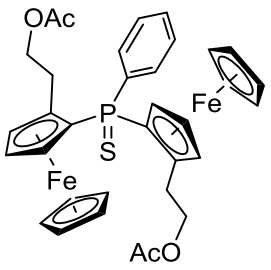

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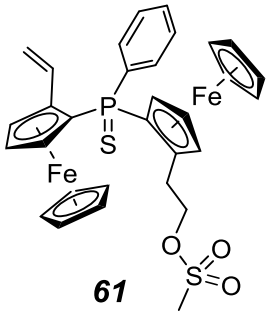

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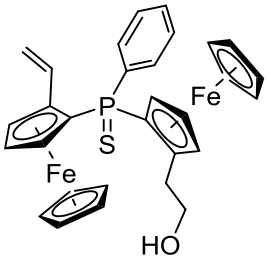

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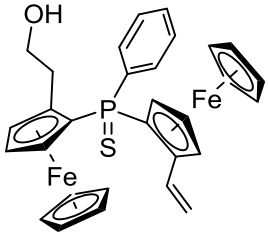

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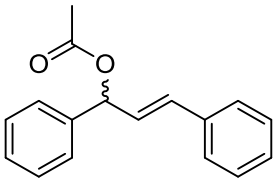

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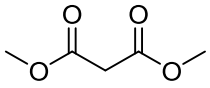

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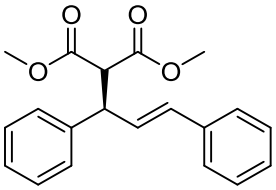

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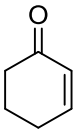

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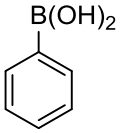

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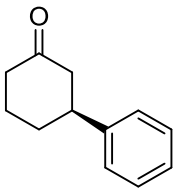

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Finally, I want to express my gratitude toward my mother Regine and my brother Gerald for being there for me the whole time, both celebrating my successes and patiently putting up with me during all of the frustrating stretches of time. Thank you for all your selfless support and kindness.

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Zusammenfassung

In Anbetracht der enormen asymmetrischen Induktionsmöglichkeiten der planaren Chiralität von Ferrocenen im Vergleich zu klassischer Centro- bzw. Axialchiralität wurden neue phosphorüberbrückte Diferrocenliganden ausgehend von Ferrocen mit Ugis Amin als chiraler Vorstufe entworfen und hergestellt, um möglichst asymmetrische chirale Reaktionsräume für homogene Katalysen über Organokatalyse oder Übergangsmetallkatalyse im Generellen zu erhalten.

Es wurden einige Strukturen in guter Ausbeute hergestellt, deren zuvor identische Ferrocenuntereinheiten starke regioselektive Unterschiede in nachfolgenden Umsetzungen zeigten und deren relative Konfigurationen zum Teil durch Röntgenstrukturanalysen bestätigt werden konnten.

Während dieses Projekts konnte wiederholt der synthetische Wert der funktionellen Gruppe Phosphinsulfid gezeigt werden. Diese Verbindungen waren einfach herzustellen und zu reinigen, oftmals kristallin und zeigten bemerkenswerte chemische Stabilität. Dank unerwarteter chemischer Reaktivitäten, die an Derivaten ohne der Gruppe nicht beobachtet wurden, und milden Methoden für die Entfernung kann Schwefel als nützliche Schutzgruppe für P(III) betrachtet werden.

Es konnte gezeigt werden, dass diese Phosphor(III)- oder (V)-überbrückten Diferrocenliganden einen enantiomeren Überschuss von bis zu 57% in einer übergangsmetallkatalysierten Testreaktion – asymmetrische allylische Alkylierung – erzeugen können, was einer Energiedifferenz der beiden konfigurationsbestimmenden Übergangszustände von 3.1 kJ/mol entspricht. Es war an dieser Stelle deutlich dass das Moleküldesign noch verbessert werden müsste.

Daher wurde versucht, die Diferrocenylphenylphosphine an den dem Phosphor benachbarten Ethyl-Seitenketten zu überbrücken um Rigidität zu erhöhen. Es konnten neun neue Ferrocen-annelierte zyklische Phosphine über verschiedene Reaktionswege erhalten werden, die jeweils mit Kohlenstoff, Sauerstoff, Stickstoff oder Schwefel überbrückt waren.

Da einige dieser Verbindungen mäßig stabil und schwierig zu reinigen waren, wurden zwei weitere Syntheserouten zu anderen, aber ähnlichen Verbindungen entwickelt, um stabilere Diferroceno-P-Zyklen zu erhalten.

Im ersten Fall geht man von Aminomethylferrocen, das einen Ephedrinsubstituenten am N trägt, aus, an dem diastereoselektive Substitution des Cp-rings durchgeführt werden kann. Der zweite Syntheseweg startet mit Ugis Amin, funktionalisiert aber den terminalen Kohlenstoff der Ethylseitenkette um Eliminierungsreaktionen zu erschweren.

Beide Routen lieferten vielversprechende phosphorüberbrückte asymmetrische Diferrocenvorstufen in akzeptablen, nicht optimierten Ausbeuten, geeignet für daran anschließende Zyklisierungsschritte.

Abstract

Considering the enormous asymmetrically inductive capabilities demonstrated by ferrocene planar chirality in comparison to both carbon and axial chiralities, novel phosphorous-linked diferrocene ligands have been designed and synthesized starting from ferrocene using Ugi's amine as an enantiopure key intermediate, planning a strongly asymmetrically inductive space for homogeneous catalysis via organocatalysis or transition metal catalysis in general.

Several structures exhibiting strong regioselectivity in subsequent synthesis for one of the previously identical ferrocene moieties over the other were obtained in good yield and relative configurations have been confirmed by X-ray analysis.

Throughout this work, the synthetic value of the phosphinesulfide functional group ($R_3P=S$) became evident. These compounds are easily prepared and purified, frequently crystalline and display remarkable chemical stability. Together with unusual chemical reactivities not observed in derivatives lacking the sulfur protecting group and mild methods for cleavage by hydrogenation sulfur may be considered a useful protecting group for P(III).

These phosphorous(III) or (V)–linked diferrocene ligands could be demonstrated to induce an enantiomeric excess up to 57% in a transition metal mediated catalytic benchmarking reaction – asymmetric allylic alkylation – corresponding to an energetic difference of 3.1 kJ/mol of the configuration determining transition states. It was clear at this point that the molecular design needed to be improved.

Thus, bridging the diferrocenylphenylphosphorous compounds at the ethyl side chains at the carbons next to the phosphorous in order to enhance rigidity was attempted. Nine novel ferrocene-annulated cyclic phosphines were synthesized via different reaction pathways containing carbon, oxygen, nitrogen or sulfur variations.

Since some of these compounds were only moderately stable and difficult to purify, two more synthetic routes have been established towards different but similar compounds in order to furnish more stable diferrocene-P-(macro)cycles.

One starts at aminomethylferrocene bearing an ephedrine moiety at the N, enabling diastereoselective substitution of the Cp ring. The second synthetic path starts at Ugi's amine but functionalizes the terminal carbon atom of the ethyl side chain in order to disfavor eliminations.

Both routes yielded promising phosphorous-linked asymmetric diferrocene precursors in acceptable, not optimized yields for useful for follow-up cyclization.