Anionic Phospho-Fries Rearrangements for the Synthesis of Planar-Chiral Ferrocenes and their Application in (atropselective) Suzuki-Miyaura Reactions

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Bibliographical Description and Abstract

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Technische Universität Chemnitz, Faculty of Natural Sciences
Dissertation 2017, 328 Pages, 161 Figures, 42 Tables

The present Ph D thesis describes the synthesis and characterization of novel planar-chiral 1,2-*P*,*O*-ferrocenes and their application in the Pd-catalyzed Suzuki-Miyaura reaction. It was especially focused on the development of a new synthetic pathway to this type of substitution pattern by applying the anionic phospho-Fries rearrangement in ferrocene chemistry.
Starting from hydroxy ferrocene, a high diversity of Fc–O–P-type (Fc = (η^5-C_5H_5)(η^5-C_5H_4)) compounds were synthesized, whereby the electronic properties of the phosphorus fragments were varied. The anionic phospho-Fries rearrangement successfully occurred subsequent to an *ortho*-lithiation with a non-nucleophilic base giving the 1,2-*P*,*O*-ferrocenes in up to quantitative yields. The usage of *chiral pool*-based alcohols for the synthesis of chiral ferrocenyl phosphates allowed a diastereoselective proceeding, giving single isomers in up to 95 % *de*. Temperature-dependent investigations of mixed ferrocenyl-, phenyl- and *N*-heterocyclic-phosphates revealed a limitation of ferrocenyl-based rearrangements per reaction step, contrary to phenyls.
1,2-*P*,*O*-ferrocenyl phosphonates could successfully be converted into phosphines by applying Stelzer *P*,*C* cross-coupling reactions on ferrocenes for the first time. Their usage as ligands for *C*,*C* cross-coupling reactions was confirmed by the synthesis of sterically hindered biaryls in high yields at 70 °C with a low catalyst loading of 1 mol-% Pd.
Functionalization of the 1,2-*P*,*O*-structural motif could be achieved by applying nucleophilic aromatic substitution reactions (S_NAr) as an alternative pathway for the synthesis of ferrocenyl aryl ethers. Subsequent to a Fries rearrangement sterically-demanding 1,3-di-*ortho*-substituted aryloxy ferrocenes could be obtained. Multi S_NAr reactions of hydroxyferrocenes at polyfluorinated arenes gave up to penta-ferrocenyl-functionalized aryl ethers, whose electrochemical properties were investigated.
The reaction of CH_2-enlarged ferrocenylmethanols gave α-ferrocenylcarbenium ions instead of phosphates, while treating them with chlorophosphates. Enantiopure 2-P(S)Ph_2-substituted derivatives of these ions underwent a subsequent intermolecular "S^{2-}" migration, resulting in thioethers, for example (S_p,S_p)-(2-(P(S)Ph_2)FcCH_2)$_2$S, in a unique mechanism. Instead, the presence of electronrich arenes gave electrophilic aromatic substituted benzenes bearing chiral ferrocenylmethyl backbones. These type of ligands gave biaryls with up to 26 % *ee*.

Keywords: *Ferrocene, Planar Chirality, Fries Rearrangement, Suzuki-Miyaura Reaction, Chiral Pool, Phosphate, Phosphonate, Phosphine, Biaryl Coupling, Electrochemistry, Single-Crystal X-Ray Diffraction Analysis, Ether Formation*

"*Die Wissenschaft fängt eigentlich erst da an interessant zu werden, wo sie aufhört.*"

Justus von Liebig
(1803–1873, deutscher Chemiker)

Die vorliegende Dissertation wurde im Zeitraum von Oktober 2012 bis April 2017 unter Anleitung von Herrn Professor Dr. Heinrich Lang an der Professur Anorganische Chemie der Technischen Universität Chemnitz durchgeführt.

Herrn Professor Dr. Lang
danke ich für die Bereitstellung optimaler Bedingungen, für die gewährten Freiheiten bei der Bearbeitung dieses Themas, sein stetes Interesse am Fortgang dieser Arbeit sowie das mir entgegengebrachte Vertrauen.

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Abbreviations

Ac	Acetyl
equiv.	Equivalent
calcd	calculated
Bn	Benzyl
Boc	*tert*-Butyloxycarbonyl
Bu	(*n*-)Butyl
CCD	Charge-Coupled Device
Cp	Cyclopentadienyl
CSD	Cambridge Structural Database
Cy	Cyclohexyl
dba	Dibenzylideneacetone
DCC	*N*,*N*'-Dicyclohexylcarbodiimide
de	diastereomeric excess
dr	diastereomeric ratio
dioxane	1,4-Dioxane
DFT	Density functional theory
DMAP	4-*N*,*N*-Dimethylaminopyridine
DME	1,2-Dimethoxyethane
DMF	*N*,*N*-Dimethylformamide
dppf	1,1'-Bis(diphenylphosphino)ferrocene
EA	Elemental analysis
ee	enantiomeric excess
er	enantiomeric ratio
Et	Ethyl
Fc	Ferrocenyl, Fe(η^5-C_5H_5)(η^5-C_5H_4)
Fur	Furyl
GC	Gas chromatography
GC-MS	Gas chromatgraphy with mass spectrometry-coupling
HPLC	High-performance liquid chromatography
HRMS	High-resolution mass spectrometry
i	*iso* or *ipso*
IUPAC	International Union of Pure and Applied Chemistry
IVCT	Intervalence Charge Transfer
LDA	Lithium diisopropylamide
LMCT	Ligand-to-metal Charge Transfer
m	*meta*
Me	Methyl

Mp.	Melting point
MTBE	Methyl-*tert*-butyl ether
n	*normal*
NIR	Near-infrared
NMP	*N*-Methyl-2-pyrrolidone
Nu	Nucleophile
o	*ortho*
ORTEP	Oak Ridge Thermal Ellipsoid Plot
OTTLE	Optically Transparent Thin Layer Electrochemical
p	*para*
Pin	Pinacolate
Ph	Phenyl
ppm	parts per million
Pr	Propyl
rel.	relative
sec	*secondary*
tert	*tertiary*
THF	Tetrahydrofuran
THP	Tetrahydropyran
TMEDA	*N*,*N*,*N*',*N*'-Tetramethylethylenediamine
TMP	2,2,6,6-Tetramethylpiperidine
TMS	Trimethylsilyl
Tol	Tolyl
Ts	Tosyl
UV	Ultraviolet
UV/Vis	Ultraviolet and visible
VE	Valence electron

NMR	Nuclear Magnetic Resonance
br	broad
COSY	Correlated Spectroscopy
d	Doublet
HMBC	Heteronuclear Multiple Bond Correlation
m	Multiplet
pt	Pseudotriplet
q	Quartet
s	Singlet
sept	Septet
t	Triplet
TMS	Tetramethylsilane

Preamble

The results obtained within this Ph D thesis have been published in international leading peer-reviewed journals.

(**1**) M. Korb, D. Schaarschmidt, H. Lang, *Organometallics* **2014**, *33*, 2099–2108.
(**2**) M. Korb, H. Lang, *Organometallics* **2014**, *33*, 6643–6659.
(**3**) M. Korb, P. J. Swarts, D. Miesel, A. Hildebrandt, J. C. Swarts, H. Lang, *Organometallics* **2016**, *35*, 1287–1300.
(**4**) M. Korb, H. Lang, *Inorg. Chem. Commun.* **2016**, *72*, 30–32.
(**5**) M. Korb, H. Lang, *Eur. J. Inorg. Chem.* **2017**, *2017*, 2099–2108.
(**6**) M. Korb, S. W. Lehrich, H. Lang, *J. Org. Chem.* **2017**, *82*, 3102–3124.
(**7**) M. Korb, J. Mahrholdt, H. Lang, *Eur. J. Inorg. Chem.*, *accepted*, DOI-number 10.1002/ejic.201700645.

The original abstracts of the listed publications are attached in appendixes **A**–**G**. The respective manuscripts were created under the supervision of Prof. Dr. Heinrich Lang. Parts of this work have been presented at scientific conferences in the form of talks or posters, which are summarized in appendix **J**.

The original manuscripts were separated into different sections of changed order to ensure a better comprehension by combining content-related work, by avoiding overlaps and duplication. An exception is Section 3.2.5, which contains unpublished work. Formats and writing were unified and may differ from the original, journal-related style.

The contribution of co-authors includes discussion and content-related consideration (**1**), (spectro-)electrochemical measurements and expertise for their evaluation (**3**,**6**) and synthetic support as part of a Bachelor thesis (**7**).

The contents of publications (**1**), (**2**), (**4**) and (**6**) are combined in Section 3.1, which is subdivided into 3.1.1 (**1**), 3.1.2 (**2**) and 3.1.3 (**4**,**6**). Sections 3.1.4 and 3.1.5 contain content from all four publications.

Section 3.2 combines the content of publications (**3**) (3.2.1 and 3.2.2) and (**6**) (3.2.3 and 3.2.4). Solely part 3.2.5 contains unpublished work. The content of (**7**) can be found in 3.3 and 3.4.

1 Introduction

The declared purpose of becoming a greenhouse gas neutral nation until 2050 by the German government requires a reduction of green house gas emission by 80 to 95 % with respect to 1990.[1] This means one ton of CO_2-equivalents per person in 2050. One decisive factor therefore, is the reduction of fossil energy sources like crude oil, coal and natural gas. Chemical processes, which use these carbon sources as starting materials for bulk and fine chemicals, need to increase the efficiency for their synthetic procedures. Thus, reaction steps and times, required energy and by-products have to be reduced, while increasing the yield of the desired products. Catalytic reactions, and especially *C*,*C* coupling reactions, turned out to play a key-role within this optimization process. Nowadays, already 80 % of all chemical products required at lease one catalytic transformation, generating a turnover of 3 trillion US-Dollar.[2] Thus, catalysis plays an important role within each persons life for example by using fuels or by consuming fruits and vegetables, which were grown by using agrochemicals. Furthermore, drugs (*e.g.* Ibuprofen as an analgesic), perfumes and flavors are prominent examples for everyday products derived by catalytic processes.[3]
In general, catalysts or catalytic systems are compounds or systems that increase the speed of a reaction by lowering the activation barrier for the desired product. Thus, less energy is required, since the temperature for the reaction can commonly be reduced. They are not degenerated and can be applied for several runs, enabling the synthesis of huge amounts of the product, while using low quantities of catalyst. A skillful design of the catalytic systems also enhances the formation of single products by avoiding the formation of by-products. Catalysis is part of the "green-chemistry" approach, due to their waste preventing, atom-economic and energy efficient proceeding and by reducing protection group strategies to a minimum.

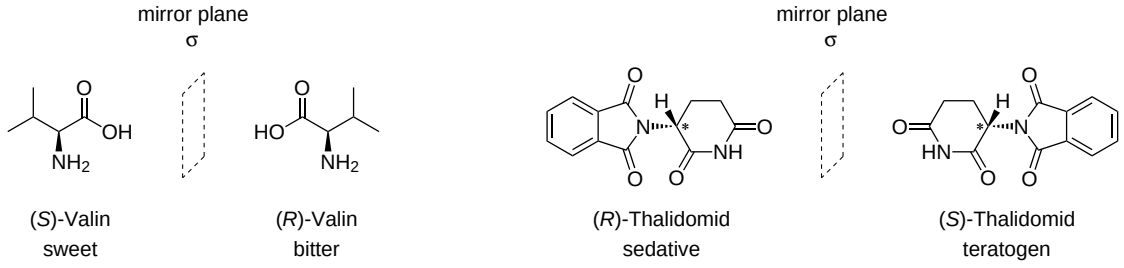


Figure 1.1 (*R*)-/(*S*)-Valine (left) with their natural taste and both enantiomers of Thalidomide (right) with their physiological effect.

Catalysis also plays an important role for the synthesis of pharmaceuticals and natural products.[4] They are moreover discovered by isolating them from plants or bacteria as stereochemically pure substances. In combination with biological processes in humans, which are based on chiral genetic material and enzymes, enantiomers can cause different effects for each isomer. For example, the olfactory perception of the two isomers of carvon differs between

mint (the (*S*)-isomer) and caraway (the (*R*)-isomer). The (–)-isomer of menthol has a three times more intense smell than the (+)-derivative.[5] The amino acid valine differs in its taste between sweet for the essential proteinogenic *L*-form, and bitter in case of the *D*-from (Figure 1.1). An unpleasant and sustainable defining example was the usage of Contergan® since 1957. Initially invented as a sedative, it readily showed up to act against morning nausea. Unfortunately, the usage by pregnant women resulted in disabled children, due to the teratogenic properties of the (*S*)-isomer of Thalidomid (Figure 1.1). Further investigations revealed that this incident would not have been obviated by treatment with the enantiopure (*R*)-drug, since both isomers racemize in the blood plasme within minutes.[6] Nevertheless, aggravated standards, regarding pharmacological and toxicological activity, were established in the USA and the EU in 1992. Since then, both enantiomers have to be examined separately in clinical tests. This resulted in an increase of enantiopure drugs. A further advantage of avoiding the inactive isomer is the lowering of the costs. In 2004, more than 50 % of the 10 most-sold drugs were sold enantiopure.[7]

The production of enantiopure products requires a more efficient synthetic procedure. The resolution of racemic mixtures might be sufficient for lab scale applications or for their clinical investigations, whereas in industrial processes a huge amount of waste would be generated. As a key-step, asymmetric homogeneous catalysis plays the most important role, since only low amounts of chiral substances are required. The initial chiral information is easily available from *chiral pool* based substances. They can be isolated stereopure and are commercially available. The improvements within the field of catalytic *C*,*C* cross-coupling catalysis enables the formation of complex molecules by using low amounts of a metal source, which lowers the price. Nevertheless, most of the catalysts are optimized for single processes or substrates and still degrade too fast. As a goal, the German society of catalysis announced a program for robust, predictable and efficient catalytic systems and their complete mechanistic comprehension.[7] A key-role is the design and development of stable, well-defined ligands, whereas the costs and effort for their synthesis must not be neglected.

The task of this Ph D thesis is the synthesis of planar-chiral 1,2-*P*,*O*-functionalized ferrocenes by anionic phospho-Fries rearrangements. This reaction has not yet been described for organometallic systems and thus, requires basic investigation regarding reaction conditions and substrate scope. The suitability of the respective 1,2-*P*,*O*-phosphines in for catalytic transformations shall be investigated for the (atropselective) synthesis of hindered biaryls by Suzuki-Miyaura *C*,*C* cross-coupling reactions.

Hereinafter, the principles of *C*,*C* coupling reactions are explained, whereas the synthesis of biaryls is paramount. The special features of ferrocenes as a three-dimensional backbone are discussed regarding reactivity and chirality. The synthesis of planar-chiral derivatives and especially the 1,2-*P*,*O*-substitution pattern will be focused, whereby *chiral pool* substances shall be used for establishing the planar-chirality. For a better comprehension of the anionic Fries rearrangement, its mechanism will be explained and successful proceedings shall be examined for estimating the structure and electronic properties of suitable organometallic starting materials.

2 State of Knowledge

2.1 Transition Metal Catalyzed *C,C* Cross-Coupling Reactions

The field of transition metal catalyzed *C,C* cross-coupling reactions has been discovered in the 1970s as a labor curiosity. Within the recent decades they have become an indispensable component in chemistry. They also evolved from the laboratory to the industrial scale synthesis of, *e.g.*, agro-, pharmaceutical- and fine chemicals.[8] Thus, their discoverers Akira Suzuki, Ei-ichi Negishi and Richard F. Heck were awarded with the Nobel Prize in 2010 "*for palladium-catalyzed cross couplings in organic synthesis*", which underscores the high importance of this type of reaction.[9,10]

Cross-coupling reactions are characterized by the formation of a covalent bond between two different reactions partners (Figure 2.1). One of them is an organic electrophilic aryl, alkyl, and vinyl (pseudo-)halide R–X. As the nucleophilic coupling partner, metal- or non-metal-functionalized alkyl, allyl, aryl, alkenyl, and alkinyl compounds R'–M are used. Both are reacted in the presence of catalytic amounts of a transition metal complex, whereas Pd is most commonly used.[11] The generated organo-palladium compounds are comparably stable towards oxygen and moisture, and tolerate a wide range of functional groups,[11] which makes them suitable for the synthesis of natural products and therein reduces the required protective groups.[4] The systems are robust and can easily be scaled up, making them attractive for industrial applications.[8]

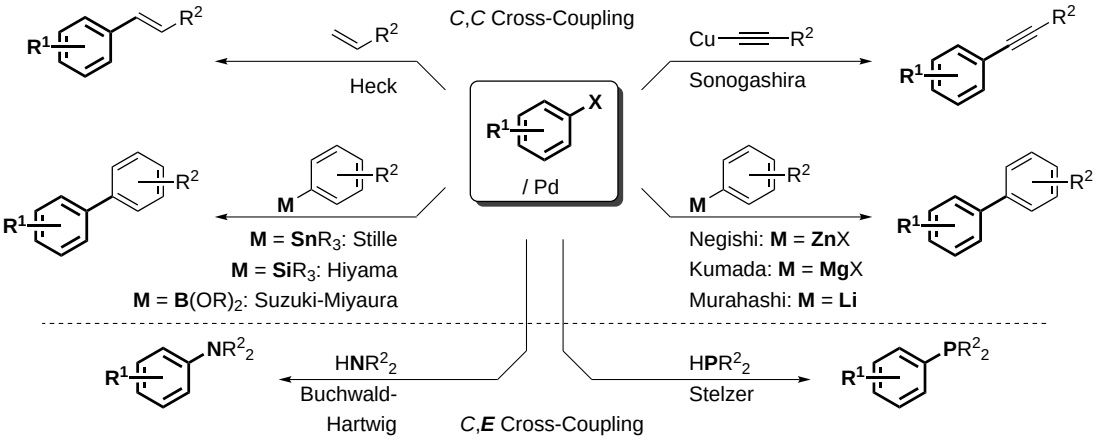


Figure 2.1 Selected Pd-catalyzed *C,C*[12] and *C,E*[13–15] ($E = N$, P) cross-coupling reactions starting from aryl halides.
R, R^1, R^2 = H or a singly bounded organic fragment; X = halogen or suitable leaving group.

The most important *C,C* cross-coupling reactions are the Kumada, Murahashi, Sonogashira, Negishi, Suzuki-Miyaura, Stille and Hiyama ractions (Figure 2.1).[11] The Heck reaction also gives *C,C* coupled products, whereby the mechanism differs. Thus, the C–C bond is formed

prior to the reductive elimination in an olefin-insertion step. Besides the C,C also C,N and C,P cross-coupling reactions have to be mentioned as important transition metal catalyzed reactions (Figure 2.1).[13–15]

2.2 Suzuki-Miyaura Reaction

As the most convenient C,C cross-coupling reaction, the Suzuki-Miyaura reaction has to be attributed. It has first been described in 1979 by N. Miyaura, K. Yamada and A. Suzuki[16] and uses, for example, aryl, alkyl and alkinyl boron compounds as the nucleophilic reaction partner. As electrophiles, allyl, benzyl, alkyl and aryl halides are most commonly used. The most important substrate combination is the synthesis of biaryls. Especially the synthesis of natural products, which can be used as active substances in drugs, is of high importance (Figure 2.2).[11,17–20]

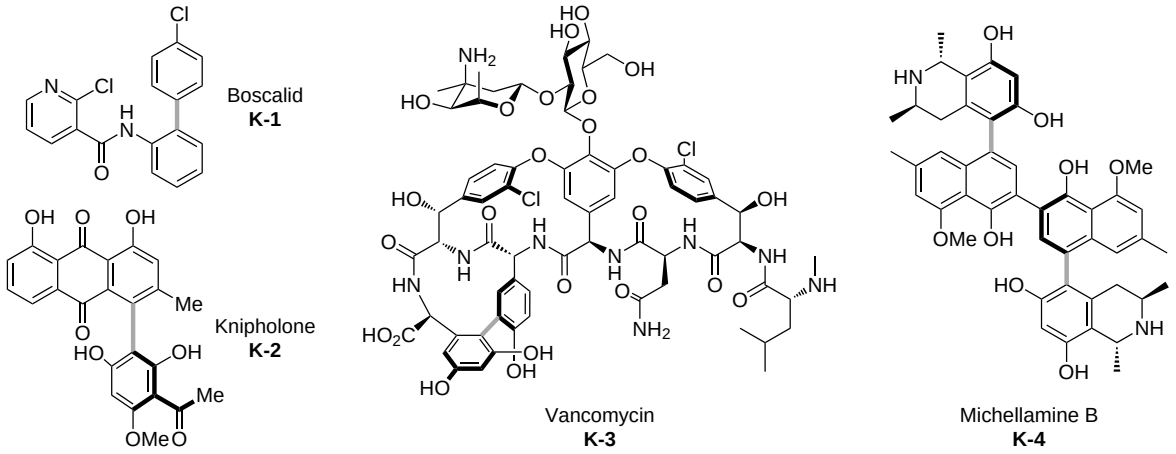


Figure 2.2 Natural products bearing biaryl axes (light grey bonds).[11,17–20]

The fungicide Boscalid (**K-1**) is produced in a more than 1000 tons per year by the BASF AG.[11,18] Knipholone (**K-2**) was successfully tested as an anti-malaria and anti-cancer drug.[19] Vancomycin (**K-3**) is used as a 3^{rd} line glycopeptide antibioticum against multi resistend bacteria,[20] and Michellamine B (**K-4**) has been found to efficiently treat HIV (Figure 2.2).[17,21]

The variety of structural motifs and functional groups, which are tolerated in Suzuki-Miyaura reactions, is exemplarily shown by the synthesis of Losartan **K-8** (Figure 2.3)[22] The coupling exclusively occurs at the bromine substituent of **K-5**, whereas the more strongly bonded chlorine atom is not attacked. Subsequent removal of the trityl protective group from **K-7** gives Losartan (**K-8**) in high yield.[23] Losartan was initially developed by DuPont® in 1986 and is sold since 1995 as the first AT_1-antagonist by a joint venture of DuPont® and Merck under the name Cozaar® for the treatment of high blood pressure and diabetes.[24] The synthetic strategy evolved, whereas a biaryl coupling has always been a decisive step.[23] The separate synthesis of the two different building blocks **K-5** and **K-6** and their final combination simplifies the overall effort, which is impressively demonstrated by this example.

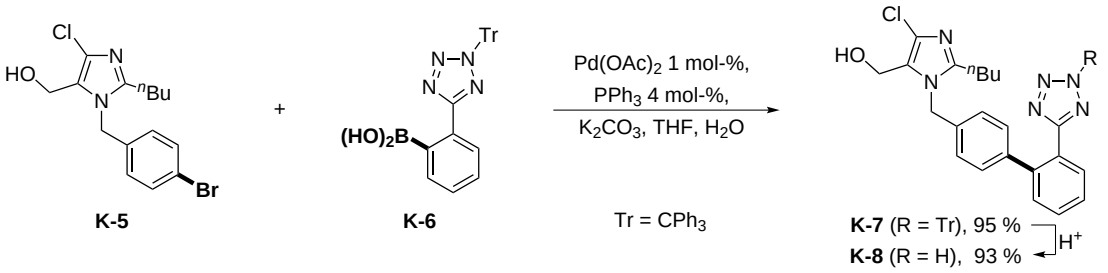


Figure 2.3 *C*,*C* Cross-coupling step within the synthesis of the drug Losartan **K-8** for lowering the blood pressure.[22]

The most important organo-boron compounds for Suzuki-Miyaura couplings are boronic acids (Figures 2.1 and 2.3). Their ester or amide derivatives can also be applied and are accessible from the boronic acids.[25] The boron functionality can, for example, be introduced by a hydroboration reaction of terminal alkynes with boranes (Figure 2.4).[26] *C*,*C* Cross-coupling or C–H activation reactions of arenes with dialkyl boronates become increasingly popular.[11,27] However, the most important strategy is the conversion of lithio-[28] or magnesio-arenes,[29] in a transmetalation type process. This can most easily be achieved by a lithium-halogene exchange of aryl halides with an organolithium reagent and reaction with BX_3 (X = halogenes) as the electrophile. Subsequent acid-catalyzed hydrolysis gives the respective boronic acids.[28]

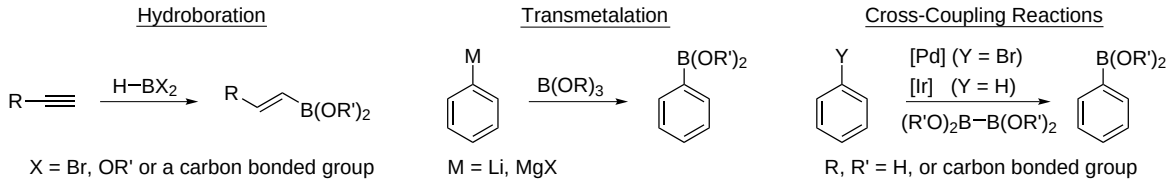


Figure 2.4 Synthetic methodologies for the synthesis of boronic acids and esters.[11,26–29]

The advantage of the Suzuki-Miyaura reaction compared to the other types of *C*,*C* cross-couplings (Figure 2.1) is the stability of the nucleophilic organo-boron reagents towards air and moisture, their thermal stability and low toxicity. Thus, they are commercially available and can easily be stored. Besides the *C*,*C* coupled product, borates are formed as the only by-product, which can easily be separated by an aqueous work-up procedure. However, the usage of stoichiometric amounts of a base is required for the activation of the boronic acid, due to their low nucleophilicity.[30,31]

2.2.1 Catalytic Cycle

The catalytic cycle of the Suzuki-Miyaura reaction starts with the oxidative addition of the organic electrophile R–X at a Pd(0) species, followed by the transmetalation of the boronic acid or a boronate. Finally, the reductive elimination releases the *C*,*C*-coupled product R–R' and regenerates the Pd(0) species as the active catalyst (Figure 2.5).[11] *Cis*-/*trans*-isomerizations have been omitted for clarity.

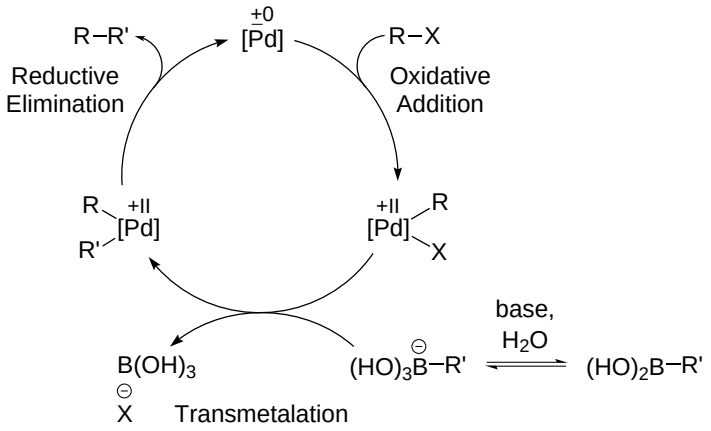


Figure 2.5 Catalytic cycle of the Suzuki-Miyaura reaction.[11]

The catalytically active 12 or 14 VE Pd(0) species is generated *in situ* from a Pd-precatalyst (Figure 2.6).[11] In case of the 18 VE Pd(0) complex $Pd(PPh_3)_4$ the phosphino ligands dissociate step-wisely. This equilibrium is influenced by the concentration of the phosphino ligands, whereby an excess decreases the catalytic activity. Another common Pd(0) source is the 16 VE Pd(0) complex $Pd_2(dba)_3$ (dba = dibenzylideneacetone). The dissociation of the weakly-bonded η^2-bonded alkenes proceeds irreversibly, which requires the addition of further donor molecules. Thus, $Pd_2(dba)_3$ is predominantly used if the stabilizing properties of new ligands within catalytic reactions shall be investigated, since no competing equilibrium with the starting ligands occurs.
If Pd(II) complexes, for example $Pd(OAc)_2$ or $PdCl_2(PPh_3)_2$, are used as precatalysts, a they initially have to be reduced. If phosphines are present, the inter- or intramolecular attack of nucleophiles, such as OAc^- or OH^-, results in the formation of phosphine oxides as the driving force (Figure 2.6).[32] Thus, higher amounts of the potential ligands are required, since their consumption has to be considered. Furthermore, in a transmetalation-type process the boronic acid $ArB(OH)_2$ can replace anionic-bonded groups. A subsequent reductive elimination releases a homo-coupled product and the active catalyst.[11,33]

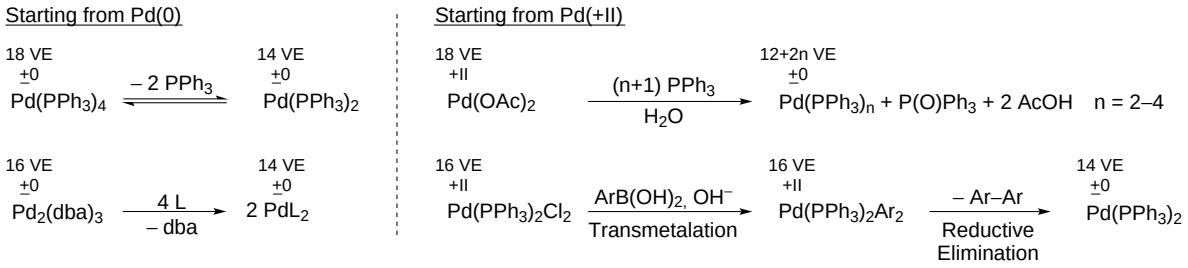


Figure 2.6 Generation of the catalytically active 14 VE Pd(0) species.
L = two-electron donor; dba = dibenzylideneacetone; PPh_3 is representative for any suitable phosphine.

Besides phosphines also N-heterocyclic carbenes (= NHC's) are widely used in catalysis as strong ligands (Figure 2.9).[34]

Oxidative Addition

The most important step of the catalytic cycle for all cross-coupling reactions is the oxidative addition of the arylhalide to a coordinative and electronically unsaturated Pd(0) complex. In organometallic chemistry four pathways are known, which include a synchron/consecutive, a S_N2, an ionic, and a radical mechanism.[11,33] Within the oxidative addition the number of valence electrons, ligands, and the oxidation state are increased by 2 for mononuclear complexes.[11,33]

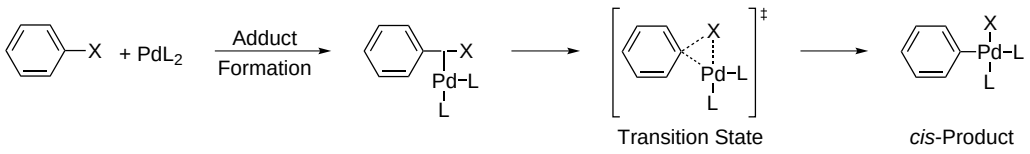


Figure 2.7 Synchron/consecutive oxidative oxidation mechanism.[11,33]
X = halogenes, OTf; L = singly-binding two-electron donor.

The underlying mechanism within a reaction depends on the polarity of the C–X bond, the type and electronic properties of X (X = halogene, OTf) and on the chemical environment of the Pd atom.[35] For Suzuki-Miyaura reactions, moreover a synchron/consecutive mechanism is considered (Figure 2.7). Results from DFT calculations reveal, that the S_N2 pathway is only passed for a few particular substrates.[35,36] The synchron pathway is induced by an adduct formation of the 12/14 VE Pd(0) species with the aromatic π-system and the C–X bond.[37] The donation of electron density from the Pd atom into the LUMO of the C–X bond weakens, and finally breaks the bond. This includes a three-membered transition state, giving a *cis*-Pd(II) complex (Figure 2.7). It also explains, why the rate of the oxidative addition strongly depends on the C–X bond strength is facilitated from Cl<Br<I. For X = Cl, the oxidative addition is the rate determing step, whereas for X = Br and I the activation barrier can be exceeded by the transmetalation process.[11]
The *cis*-complexes readily isomerize into their respective *trans*-derivatives as shown by Casado und Espinet.[38] They investigated the oxidative addition of a fluorinated iodo-arene with $Pd(PPh_3)_4$.

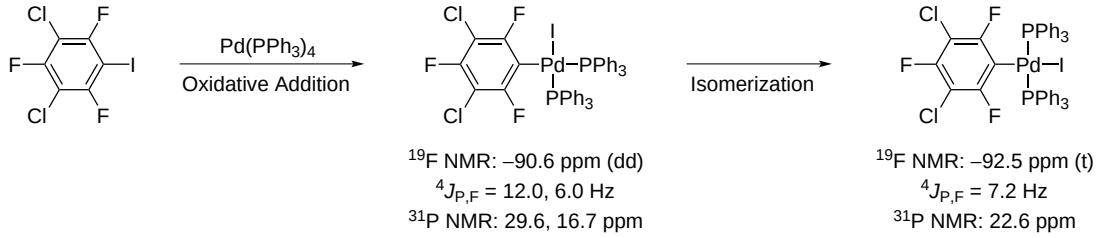


Figure 2.8 Investigation of the oxidative addition and isomerization of a fluorinated aryl iodide at $Pd(PPh_3)_4$.[38]

The progress of the reaction was monitored by ^{19}F and ^{31}P NMR spectroscopy (Figure 2.8). They showed that the *cis*-Pd(II) complex was exclusively formed at 25 °C after one hour in THF. Slow isomerization takes place at 60 °C, and after 5 h a 1:2 mixture of the *cis*-/*trans*-

complexes was detected. The reversed *trans*-*cis*-isomerization did not occur, ascribing the *trans*-complex to be thermodynamically stable. The initial formation of the *cis*-derivative is thus only compatible with the synchron mechanism.
As mentioned before, organic bromides, iodides and triflates were the preferred substrates for Suzuki-Miyaura reactions until the end of the 1990s. They could be converted within a few hours, whereas the respective chloroarenes turned out to be unreactive. However, the usage of chloro-substituted educts was highly requested, since a huge substrate scope is commercially available, and for lower prices, as compared to the higher bromo and iodo derivatives.

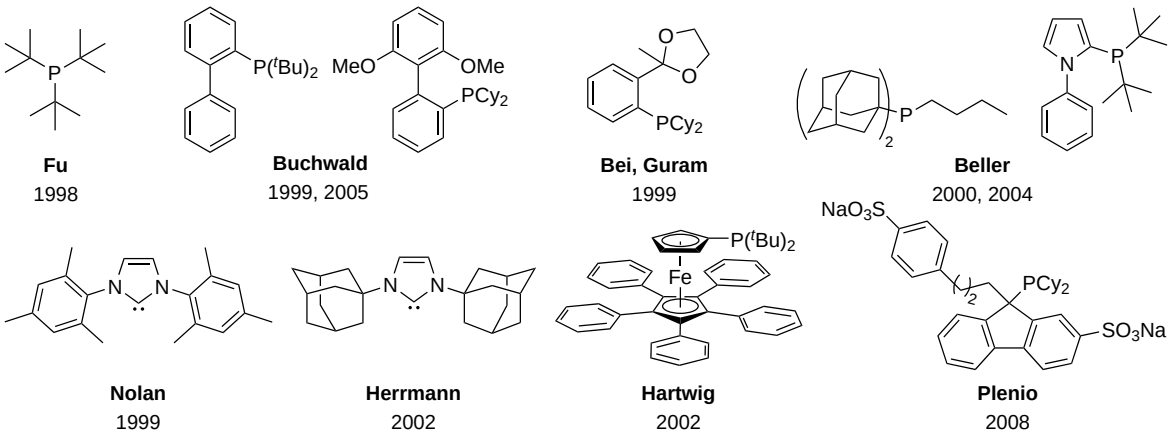


Figure 2.9 Common literature reported compounds that enable an efficient conversion of chloroarenes within Suzuki-Miyaura reactions.[39–47]

The first ligand system for a successful coupling of chloroarenes was published in 1998 by the group of Fu[39] and has rapidly been extended by Buchwald,[40,41] Bei and Guram,[42] and Nolan[43] in the same year. A few years later the groups of Beller,[44] Herrmann,[45] Hartwig[46] and Plenio[47] also contributed within this field (Figure 2.9). They are all characterized by an increased steric demand and σ-donor strength.[48] A special feature for Buchwalds biaryls is a stabilization of the catalytically active Pd species by the aromatic π-system.[41] Nowadays, even deactivated chloroarenes can be coupled at 25 °C with a low catalyst loading of 0.01 mol %.

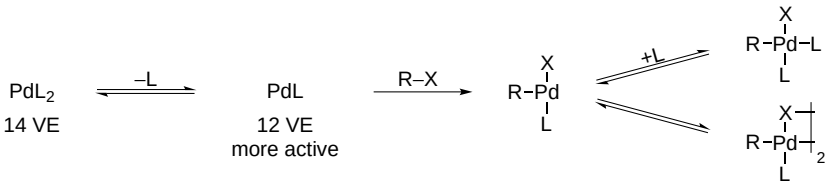


Figure 2.10 Oxidative addition of R–X to a 12 VE mono-phosphino Pd complex.
X = halogene; L = two-electron donor; R = singly-binding organic substituent.

The sterically demanding phosphines force the formation of a 12 VE mono-phosphino-Pd(0) complex (Figure 2.10). The equilibrium is shifted from the PdL_2 to the PdL species, while reducing the ligand concentration.[49] This allowed the isolation of a *T*-shaped complex, formed within the oxidative addition.[50] Besides the steric demand of the phosphine ligands, also *non*-classical C–H hydrogen bridge-bonds stabilize this unsaturated complexes, which has

been proven not only by singly-crystal X-ray diffraction analysis.[50] The presence of PdL as the catalytically more active species is further supported by an optimized Pd/L ratio of 1:1.5 for L = P(^{t}Bu)$_3$.[39] In similarity, a Pd(dba)$_2$/L mixture with L = P(1-Adamantyl)(^{t}Bu)$_2$ reacts faster in an oxidative addition reaction than the prepared PdL$_2$ complex.[50] The lower activation barrier for the oxidative addition of PdL compared to PdL$_2$ was proven by calculations.[33] The interaction of hetero-atoms and aromatic π-systems with the active catalyst further stabilize these systems.[48]

As shown in Figure 2.8 the oxidative addition process is followed by a *cis-trans*-isomerization, if non-chelating ligands, such as PPh$_3$, are used. This can proceed *via* three different mechanisms (Figure 2.11).

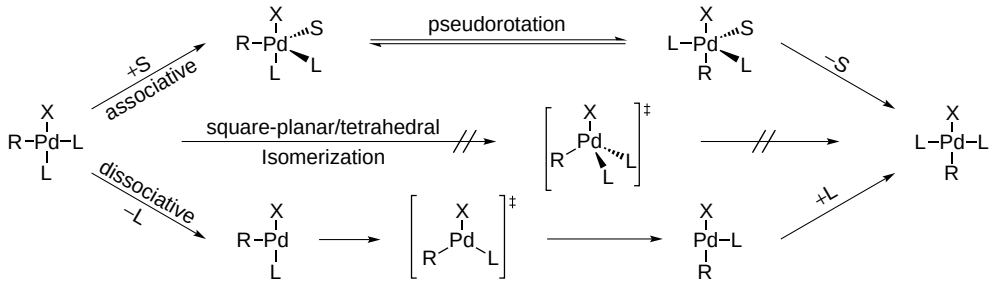


Figure 2.11 Possible reaction pathways for the *cis-*/*trans*-isomerization of PdL$_2$(R)(X).[33,38,51]
X = halogene; L = two-electron donor; R = singly-binding organic substituent; S = solvent or L.

During the associative pathway a further donor molecule, which can be an additional ligand, halide or solvent molecule, binds to the Pd(II) complex, resulting in an 18 VE trigonal pyramidal coordination. Within this molecular geometry, the axial and equatorial positions can isomerize for example by a pseudorotation process, giving the *trans*-complex after release of a ligand. Within the dissociative pathway, the ligand is initially released, giving a *T*-shaped trigonal complex. After a *Y*-shaped transition state, the *trans*-addition of the ligand gives the isomerized complex. The third path proceeds without changing the coordination number by a tetrahedral transition. However, quantum chemical calculations revealed that the activation barrier for the square-planar/tetrahedral reordering is too high.[33,51] Kinetic investigations supported the proceeding by an associative or dissociative mechanism.[38]

Transmetalation

Within the transmetalation process, the second organic group is transferred from the organoboron compound to the Pd(II) complex. The designation of this step is similar in all mentioned Pd-catalyzed *C,C* cross-coupling reactions (Figure 2.1) but misleading in case of the Suzuki-Miyaura reaction, since boron is not classified as a classic metal. Thus, the term metathesis might also be used. As mentioned before, this requires stoichiometric amounts of base. As shown for the synthesis of Losartan (Figure 2.3) moreover inorganic bases, *e.g.* carbonates or phosphates, are added. Solely quaternary borates, such as sodium tetraphenyl borate[52] (**A**, Figure 2.4), and boronates[53] (**B**, Figure 2.4) can be converted without the

need for additional amounts of a base. However, it could also be shown that hydroxy palladate complexes rapidly undergo a transmetalation reaction with boronic acids in the absence of an additional base (**C**, Figure 2.4).[54] This leads to the question if the transmetalation proceeds *via* an hydroxy palladate (Path **A**, Figure 2.13) or an boronate mechanism (Path **B**, Figure 2.13).

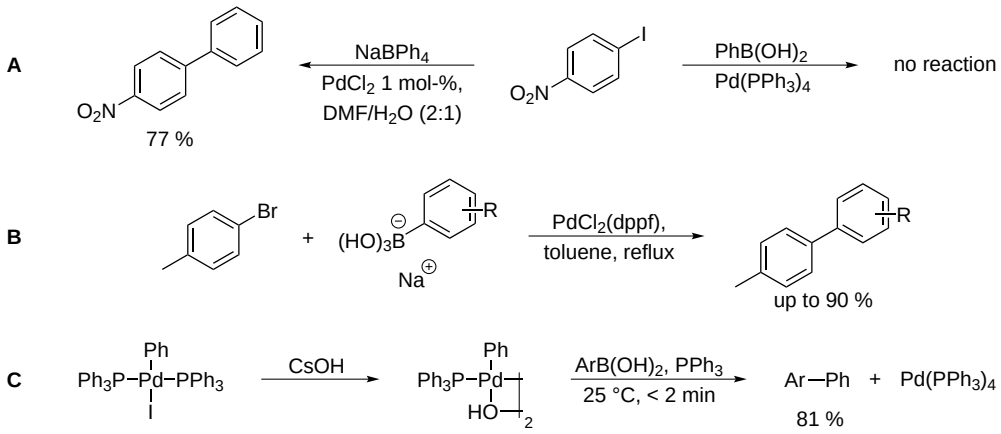


Figure 2.12 Transmetalation in the Suzuki-Miyaura reaction without additional amounts of base.[52–54]

Kinetic investigations in which the rate constants of both paths could be determined, revealed that the hydroxy palladate pathway is approximately 10^4-times faster than the boronate one.[55] It should be noted that the kinetic properties were determined for reactions of aryl boronic acids/esters with aryl halides (X = Cl, Br, I) in aqueous DMF, acetone or THF with PPh_3 or PCy_3 as ligands in the presence of carbonate bases. While changing the reaction conditions, the rate constants and the preference of the hydroxy palladate pathway may also no longer be relevant.[55] Nevertheless, the hydroxy palladate and the boronate pathway led to the formation of a zwitterionic species, which passes a 4-membered transition state and released the transmetalated complex. The $B(OH)_3$ species is complexed by the halide. The transmetalation can also occur from the respective *cis*-configured complex, which has been omitted for clarity in Figure 2.13. A *cis-trans*-isomerization during this step does not occur, due to the concerted mechanism.

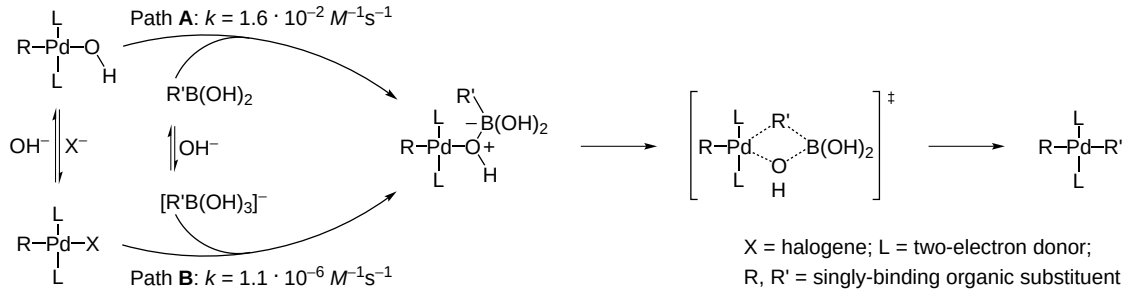


Figure 2.13 The two reaction pathways for the transmetalation process in the Suzuki-Miyaura reaction.[55]

Reductive Elimination

The catalytic cycle of the Suzuki-Miyaura reaction (Figure 2.5) is finalized by the reductive elimination process. Therein, the C–C bond formation takes place and the catalytically active Pd(0)-species is regenerated. The reductive elimation proceeds reversed compared to the oxidative addition process. This requires a *cis*-configured complex to reach the three-membered transision state (Figure 2.7). In case of a diaryl-Pd(II)-species this can readily occur without the dissociation of a ligand.[30] Based on quantum chemical calculations, the isomerization requires an activation barrier of only 25–50 kJ/mol[33] In contrast to the oxidative addition, where associative and dissociative pathways can be passed (Figure 2.11), the reductive elimination exclusively proceeds dissociatively.[51]
The reaction rate of the reductive elimination depends on the chemical environment of the Pd(II)-species. Electron-poor and sterically demanding ligands (L) accelerate the process. In case of the reactive ligands R and R', electron-rich derivatives are easier reductively eliminated, due to a weaker Pd–C bond.[56] Kinetic investigations of the reductive elimination of Pd(II) complexes could not be performed, since they are too instable and readily eliminate the product. Thus, the respective Pt complexes $PtL_2(C_6H_4R)(C_6H_4R')$ were examined. As expected, the reductive elimination of the electron-rich R, R' = NMe_2 derivatives proceeds faster than for the CF_3 complexes. Notably, an electronically inverse ligand system with R = NMe_2 and R' = CF_3 further accelerates the reaction.[56]

2.2.2 Synthesis of Sterically Hindered Biaryls

Within their first results in 1981, Suzuki and Miyaura investigated the reaction of 2-bromotoluene and 2-bromomesitylene with phenylboronic acid (Figure 2.14).[57] They observed that the yield of the mono-*ortho*-substituted biaryl exceeded those for the di-substituted derivative, even at higher temperatures and longer reaction times. The synthesis of tri-functionalized biaryls can be achieved, if stronger bases, for example $Ba(OH)_2$, K_3PO_4, and Cs_2CO_3, are used.[58]

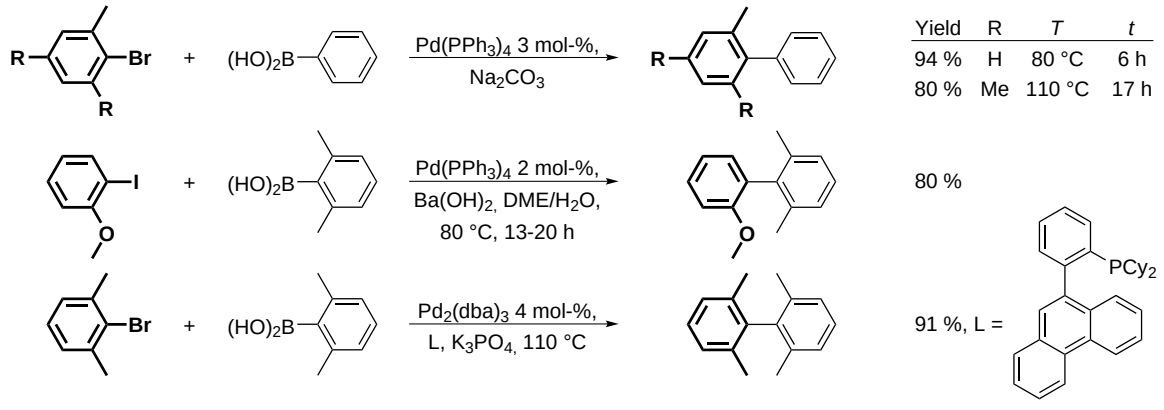


Figure 2.14 Synthesis of mono-,[57] di-,[57] tri-[58] and tetra-*ortho*-substituted biaryls.[59]

The most challenging task is the synthesis of tetra-*ortho*-substituted biaryls, whereby the simple change of the reaction conditions is not sufficient. The steric demand of the aryl halide and

the boronic acid complicates the oxidative addition and the transmetalation process. In similarity to the conversion of chloro- compared to bromo- or iodo-arenes, sterically demanding and electronically modified ligands are required (Figures 2.9 and 2.14).[59] As a prerequisite for a succesful coupling of tetra-*ortho*-substituted biaryls within Suzuki-Miyaura *C,C* cross-coupling reactions stericically demanding phosphines (Hoshi and Hagiwara,[60] Hor,[61] Ackermann,[62] Tang,[63] Kwong,[64] and Qiu[65]) N-heterocyclic carbenes (Dorta,[66] Tu,[67] Glorius,[68] Schmidt,[69] Willans,[70] Nolan[71]) or amides (Jin[72]) are required as complex ligands for palladium (Figure 2.15).

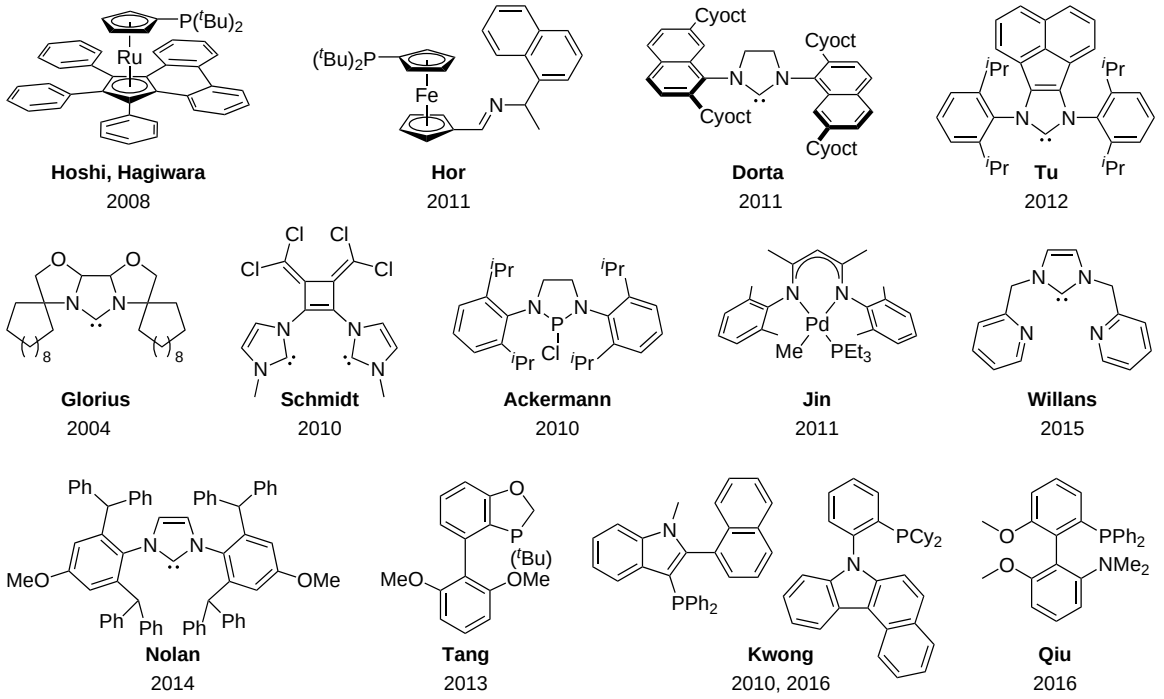


Figure 2.15 Prominent compounds applied in the synthesis of tetra-*ortho*-substituted biaryls.[60–72]

Besides the shown examples for the synthesis of tetra-*ortho* biaryls, the number of compounds that facilitate the synthesis of tri-substituted derivatives is also rising. Therefore, also phosphines are predominantly applied.[73–75]

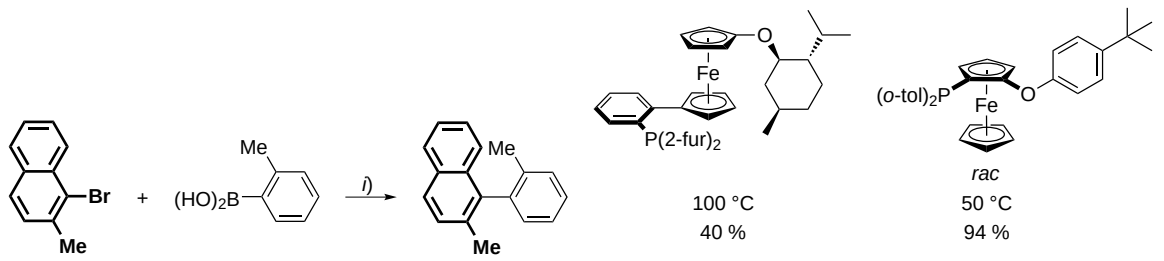


Figure 2.16 Comparison of the 1,1'- and a 1,2-*P*,*O*-substitution pattern within the synthesis of tri-*ortho*-substituted biaryls.[74]
Reaction conditions: *i*) aryl halide (1.0 mmol), boronic acid (1.5 mmol), K_3PO_4 (3.0 mmol), toluene (2 mL), $Pd_2(dba)_3$ (0.05 mol-%), phosphine (0.2 mol-%), 24 h.

Of high interest, within the field of tri-*ortho*-substituted biaryls, is the increase of the catalytic

activity by lowering the temperature and catalyst concentration.[76] The estimation of the activity is very complex and depends, *inter alia*, on the substitution pattern as shown for a 1,1'- and 1,2-substituted system (Figure 2.16).[74] Both molecules allow for a lowering of the Pd-concentration to 0.1 mol-%, whereas the spatial proximity of both donor atoms further stabilizes the catalytically active Pd species and gives the biaryl in higher yield at even lower temperatures.

2.2.3 Atropselective Biaryl Couplings

The rising number of *ortho*-substituents was not only necessary for a better classification of the increasing number of catalytically more active ligands, and for a better understanding of the mechanism of the coupling reaction. The steric demand of the *ortho*-substituents also affects the rotation of both phenyls around the biaryl C–C bond.

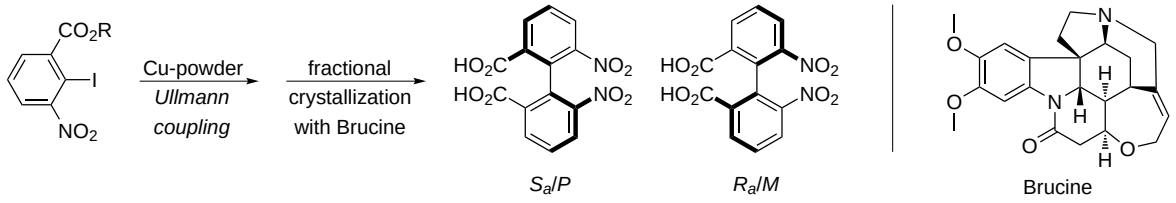


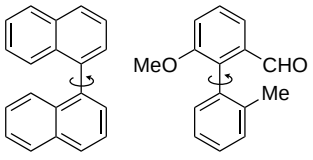
Figure 2.17 Separation of both isomers of 6,6'-dinitrobiphenyl-2,2'-dicarboxylic acid by racemic resolution with Brucine, as a first example of atropisomerism.[77]

The phenomena of a hindered rotation around the biaryl axis has first been observed by Christie and Kenner in 1922, who separated both isomers of 6,6'-dinitrobiphenyl-2,2'-dicarboxylic acid by racemic resolution with Brucine (2,3-dimethoxystrychnine) (Figure 2.17).[77] Both isomers solely differed by their optical activity, and thus Christie and Kenner postulated a new type of axial chirality, which is based on a steric hinderance of the rotation around the biaryl axis. In 1933, this type of chirality was described as atropisomerism by Kuhn,[78] who also received a Nobel Prize in 1938 "*for his work on carotenoids and vitamins*".[79] Atropisomers can be recognized as physically separable, if the half life time ($t_{1/2}$) of the racemization exceed 1000 s (16.7 min) at a given temperature.[80] The half life times ($t_{1/2}$) were determined by a time-dependent measurement of the loss of optical activity, which were found to be first order.[81]

Thus, a long half life time is required while working with stereopure biaryls. The stability towards racemization is improved, if the number and the steric demand of the *ortho*-substituents is increased. While di-substituted **K-9** racemizes within one hour below 50 °C,[82] tri- (**K-10** and **K-11**) and tetra-substituted derivatives (**K-12**) achieve half life times of minimum 3, and up to > 200 h at > 120 °C.[81–83] In Addition the steric demand and size of the backbone affects $t_{1/2}$, although it does not contribute to the properties of the *ortho*-groups. However, the lower flexibility of the biaryls enhances $t_{1/2}$ from 3 h (**K-10**) to 12 h (**K-11c**) for equally substituted *ortho*-positions. Increasing the size of the *ortho*-bonded group from, for example, OMe (**K-11a**) to Me (**K-11f**), or from CHO (**K-11a**) to CH_2OH (**K-11b**), also stabilizes the biaryl towards racemization, illustrated by the enhanced activation barrier (ΔG) (Figure

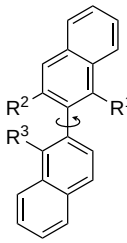
2.18).[84] Stirring of **K-9** and **K-12** in different solvents revealed a strong dependency on the polarity. Increasing the polarity shortens $t_{1/2}$ from 69 to 15 min for **K-9** and from 4.5 h to 60 min for **K-12**.

However, if the *ortho*-substituents are connected to each other and involve the biaryl axis in a cyclic structure, a flattening of both aryls can occur, which reduces the activation barrier. Thus, tetra-*ortho*-substituted biaryls lactams equilibrate at ambient temperature within seconds.[80] While working with hydroxy-functionalized biaryls, for example BINOL (**K-12**), the usage of even weakly acidic media (1.2 *M* HCl in dioxane/water) can result in the protonation of one of the aromatic ring systems. The connection of the biaryl axis to the formed sp^3-carbon allows for a rapid rotation and racemizes **K-12** within 24 h at 100 °C.[82]



K-9 **K-10**

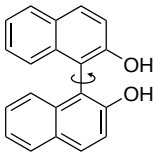
Solvent	C_6H_6	DMF	toluene
ΔG KJ/mol	100.7	98.5	125
θ in °C	44 °C	50 °C	110 °C
$t_{1/2}$	69 min	15 min	176 min



K-11a–f

	ΔG KJ/mol	$t_{1/2}$ in h	R^1	R^2	R^3
a	101[a)]	17.0	CHO	OMe	OMe
b	130	3.6	CH_2OH	OMe	OMe
c	134	12.1	CHO	OMe	Me
d	130	4.8	CN	OMe	Me
e	134	13.2	CONHMe	OMe	Me
f	143	206.5	Me	Me	CHO

θ = 121 °C, in tetrachlorethene; a) 25 °C.



K-12

$C_{10}H_{10}$	OPh_2
155.5	158
195 °C	220
4.5 h	60 min

Figure 2.18 Racemization times of di-, tri-, and tetra-*ortho*-substituted biaryls.[81–83]

Besides a racemic resolution, stereoselective couplings and desymmetrization reactions became a focus of attention.[85] Especially atrop-diastereo- and enantioselective Suzuki-Miyaura *C,C* couplings are discussed herein, whereas numerous couplings with other transition metals are known.[80] The post-functionalization of racemic biaryls has been reviewed recently.[80]

Atrop-Diastereoselective Couplings

A diastereoselective proceeding can be achieved by using aryl halides bearing a stereogenic center in close proximity to the position where the coupling occurs.[85]

The group of Buchwald showed that *ortho*-donors take part within the catalytic cycle by coordinating to the Pd species (Figure 2.19).[40,86] Using (*R*)-**K-13** revealed the formation of an oxo-palladacycle **K-14**. The configuration of biaryl (*R,P*)-**K-15**, which is established within the transmetalation process, depends on the configuration of the methyl group and its steric interaction with the MOM-group (= methoxymethyl) and the ligand **K-16**.[40,85,86] Replacing the MOM by the steric more demanding TES (= triethylsilyl) group further increases the *de*.[85]

The approach of *ortho*-directing donors has been extended, whereby non-acidic instead of hydroxy-groups were chosen. A well understood example is the coupling of the β-methoxy sulfoxide (R,R^S)-**K-17** with 2-methoxynaphthylboronic acid, giving the biaryl (R,R^S)-**K-18** in >98 % *de* and 99 % yield (Figure 2.20)[87] The presence of the two stereo centers is decisive for the complete control of the configuration. Thus, removal of the *S*-stereogenic center by converting it into a sulfon gives biaryl (*R*)-**K-19** with only 70 % *de*. Even more

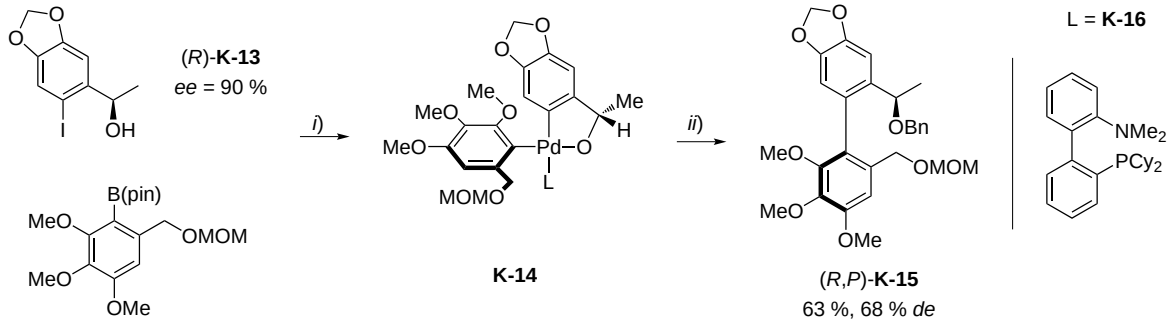


Figure 2.19 Diastereoselective Suzuki-Miyaura reaction *via* an oxa-palladacycle.[40,85,86]
Reaction conditions: *i*) $Pd(OAc)_2$ (5 mol-%), L (10 mol-%), dioxane/water (9:1), $Ba(OH)_2$, 100 °C; *ii*) NaH, BnBr, THF, 25 °C, 4 h. MOM = methoxymethyl; pin = pinacol, Bn = benzyl.

important is the relative configuration of both stereocenters towards each other. Inverting the configuration of the methoxy group also inverts the configuration of the biaryl axis in biaryl (S,R^S)-**K-20**, whereas the *de* drops to 10 % (Figure 2.20).[87]

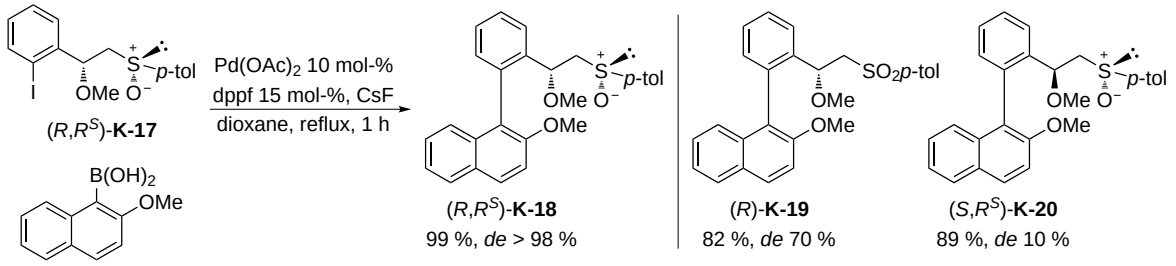


Figure 2.20 Influence of the number and relative configuration of stereocenters on a diastereoselective Suzuki-Miyaura reaction.[87]

These results were used for the synthesis of a axial chiral thioether (M)-**K-24**. When sulfoxid (R^S)-**K-21** was coupled with the N-functionalized boronic ester **K-22** biaryl (R^S,M)-**K-23** could be obtained with 90 % *de* (Figure 2.21).[88] Subsequent removal of the boc group and reduction of the sulfoxide gave (M)-**K-24**.

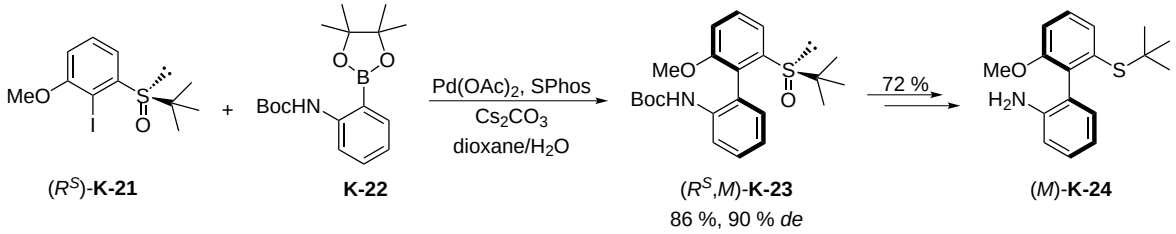


Figure 2.21 Diastereoselective Suzuki-Miyaura reaction with a chiral sulfoxide.[88]
SPhos = 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl; boc = *tert*-butyloxycarbonyl.

That also donor atoms, which are not in spatial proximity to the reaction center, influence the diastereoselective proceeding, could be shown be the coupling of boronic ester **K-25** with aryl halides **K-26a**,**b** (Figure 2.22). Using the innocent TIPS (= tri*iso*propylsilyl) group a *de* of only 11 % could be detected in the product **K-27a**.[89] Increasing the donor abilities by replacing the TIPS by a phosphinyl-bearing group (**K-26b**) enhances the *de* to

>98 % in **K-27b**, due to a coordination of the phosphorus to palladium during the catalytic cycle. [21,40,86,90]

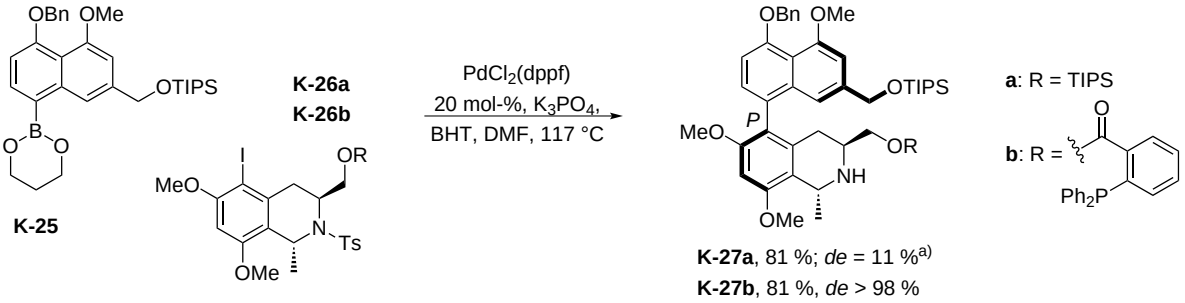


Figure 2.22 Diastereoselective Suzuki-Miyaura reaction with intramolecular stereoinduction by a phosphine. [21,40,86,89,90]
a) $Pd(PPh_3)_4$, 96 °C; TIPS = tri*iso*propylsilyl, BHT = 2,6-di-*tert*-butyl-4-methylphenol.

Another approach, besides the usage of chiral donor groups, was introduced by Uemura *et al.* by complexing the aryl halide with a tricarbonylchromium fragment (Figure 2.23). [91] This approach combines several advantages. The organometallic group reduces the electron density and accelerates the oxidative addition of the aryl halide and hence, smoother reaction conditions can be applied. The planar benzene core is converted into an three-dimensional backbone, bearing a steric demanding group at one site, which allows for the introduction of planar chirality. The $Cr(CO)_3$ fragment is sensitive towards oxidation and can thus easily be removed.

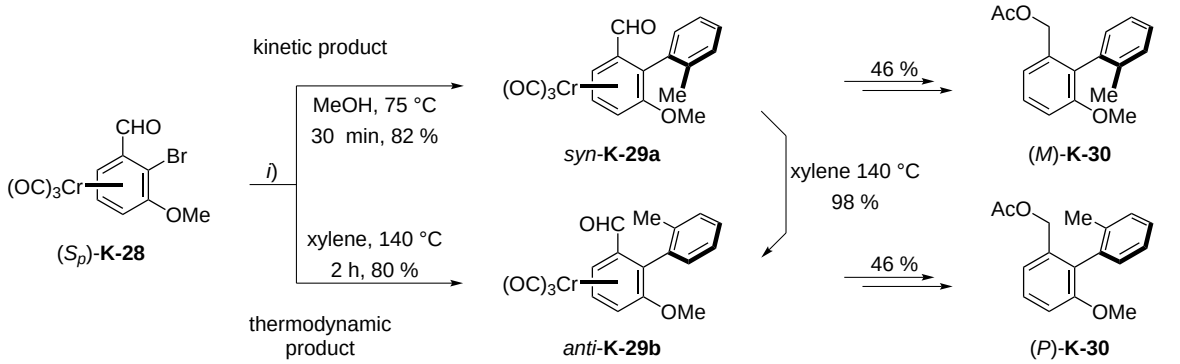


Figure 2.23 Planar-chiral tricarbonylchromium complexes within diastereoselective Suzuki-Miyaura reactions. [91]
Reaction conditions: *i*) 2-tolylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3.

Reacting planar-chiral **K-28** with *o*-tolylboronic acid gave biaryl K-29 within <2 h (Figure 2.23). The relative configuration depended on the reaction temperature and gave the kinetic product *syn*-**K29a** at 75 °C. Changing the steric demands by interchanging the CHO with the Me substituent inverts the relative configuration. [4] The thermodynamic product *anti*-**K29b**, where steric interactions by the methyl group and the $Cr(CO)_3$ fragment are avoided, can either be achieved by performing the reaction, or stirring of *syn*-**K29a** at 140 °C in xylene. Post-functionalization and removal of the protective $Cr(CO)_3$ fragment gave each biaryl (*M*)/(*P*)**K-30** enantiomerically pure and they could be used as key intermediates for

the synthesis of (–)-Steganone.[91,92]

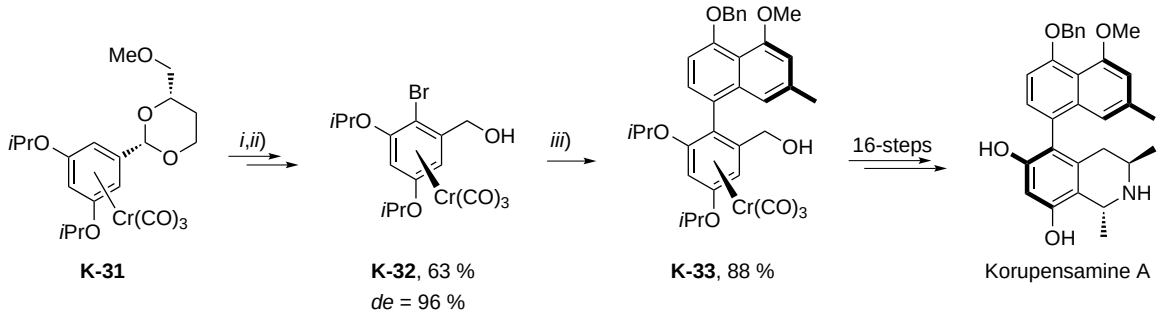
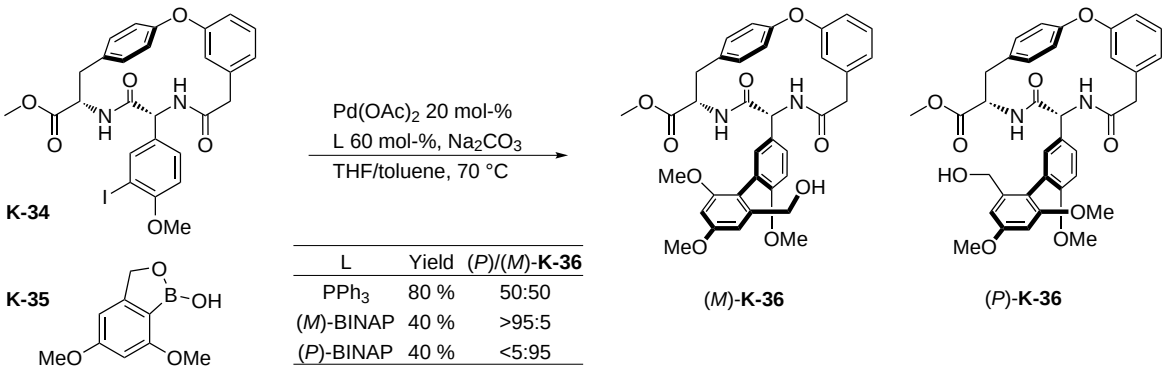


Figure 2.24 Diastereoselective Suzuki-Miyaura reaction with a $Cr(CO)_3$-functionalized aryl halide.[92]
Reaction conditions: *i*) BuLi, Et_2O, –78 °C, $C_2Br_2F_4$, $TiCl_4$, 64 % based on **K-31**; *ii*) $NaBH_4$, $MeOH/CH_2Cl_2$ (2:1), 0 °C, 99 %; *iii*) $Pd(PPh_3)_4$ 5 mol-%, 1 *M* aq. Na_2CO_3/MeOH (1:10), 75 °C, 30 min, the $B(OH)_2$ derivat of the naphthyl fragment was used as the boronic acid

The introduction of planar chirality at the tricarbonylchromium complex was achieved by diastereoselective *ortho*-lithiation with a chiral *ortho*-directing acetal (Figure 2.24).[92] Subsequent bromination gave **K-32** diastereomerically pure. Applying **K-32** in Suzuki-Miyaura reactions at low temperatures (75 °C) gave the kinetically favored *syn*-complex **K-33**, similar to the reaction shown in Figure 2.23. Enantiomerically pure **K-33** was a key-intermediate for the synthesis of Korupensamine A, which was obtained as the desired (P)-derivative by post-functionalization and removal of the $Cr(CO)_3$ fragment without changing the configuration of the biaryl axis (Figure 2.24).[92]



L	Yield	(*P*)/(*M*)-**K-36**
PPh_3	80 %	50:50
(*M*)-BINAP	40 %	>95:5
(*P*)-BINAP	40 %	<5:95

Figure 2.25 Suzuki-Miyaura reaction as a part of the total synthesis of Vancomycin.[93]
BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene

The presence of chiral backbones bearing donor atoms does not inevitably result in a high diastereoselectivity as shown for the synthesis of the glycopeptide Vancomycin.[93] When the chiral aryl halide **K-34** was reacted with **K-35** and PPh_3 as a non-chiral ligand within a Suzuki-Miyaura reaction, the biaryl **K-36** was obtained as a racemic mixture of both atropisomers (Figure 2.25).[93] However, both isomers were separated from each other by column chromatography and were enantiomerically pure. Applying the chiral (*P*)- and (*M*)-isomers of BINAP as ligands for the Suzuki-Miyaura coupling, instead of PPh_3, gave only one diastereomer in a high isomeric purity of $> 90\,\%$ *de*).[93]. However, the interaction of the

BINAP ligand and the chiral backbone of **K-34** gave each isomer with only 40 % yield. The usage of BINAP for an atropselective proceeding ascribes this as an atrop-enantioselective reactions, since the chiral information of the chiral backbone in **K-34** is negligible.

Atrop-Enantioselective Couplings

In 2000 the first examples of atrop-enantioselective Suzuki-Miyaura reactions, that require the chiral information in only catalytic amounts, were published by Cammidge and Buchwald.[94,95] They performed the reaction of 2-tolylboronic acid with phosphonate **K-37** in the presence of the chiral biaryl-based phosphine (*P*)-**K-40** and obtained the coupling product **K-38** with 87 % and high yield (98 %) (Figure 2.26). It is remarkable that solely 0.24–6 mol-% of the ligand (*P*)-**K-40** and 0.2–3 mol-% of the palladium source were used. Replacing of all methyl by ethyl groups in the substrates further increased the *ee* to 92 %. The phosphonate moiety inn **K-38** could easily be converted to phosphine **K-39**, giving a catalytic access to enantiomerically pure phosphines, which can be used as ligands in catalysis.[95]

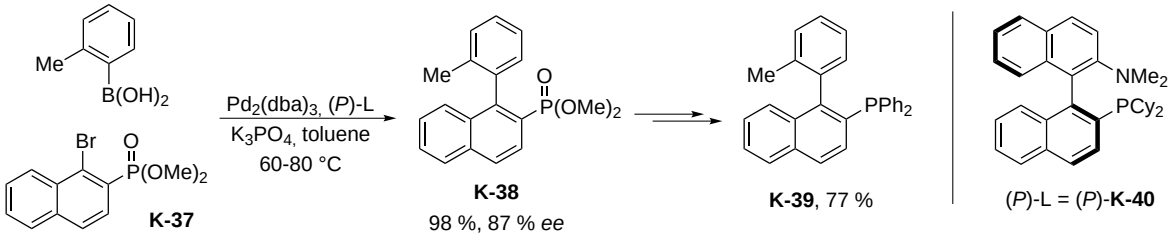


Figure 2.26 Enantioselective Suzuki-Miyaura reaction with subsequent conversion into an axial-chiral phosphine.[95]

Other stereopure molecules, which have been tested in different stereoselective reactions, were applied for the atrop-enantioselective synthesis of biaryls with high *ee* as shown by the groups of Lassaletta,[96] Uozumi,[97] Lin,[98] Qiu,[99,100] Iwasawa,[101] Tang,[102] Zhang[103] and Kündig[104] (Figure 2.27).

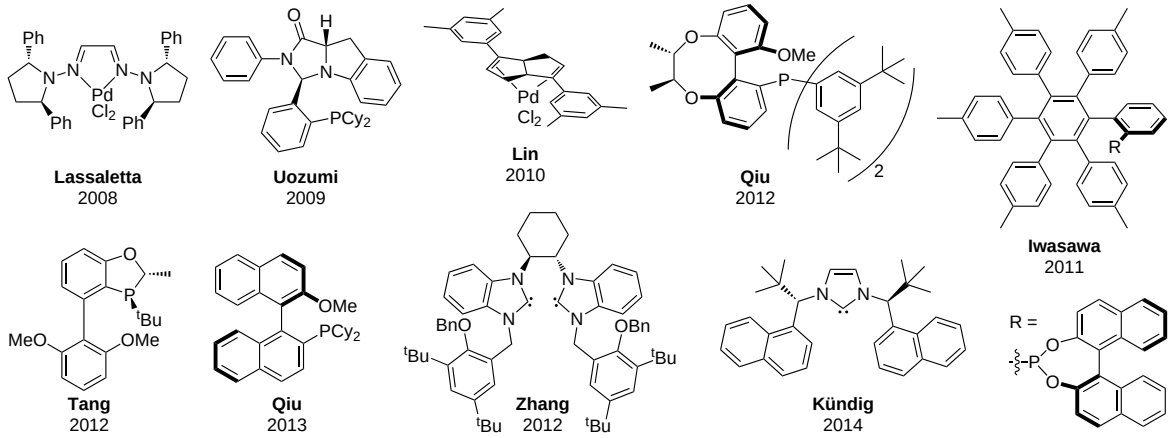


Figure 2.27 Selected compounds for atrop-enantioselective Suzuki-Miyaura reactions.[96–104]

Nevertheless, the synthesis of sterically hindered, tri- and tetra-*ortho*-substituted biaryls in

high yields is still a challenging task. They can either be obtained with low catalyst and ligand loadings within a few hours as low enantioenriched mixtures, or by enantioselective couplings that require high catalyst and ligand loadings, which can take severeal days. This discrepancy is illustrated in Figure 2.28, showing the synthesis of 2,2'-dimethyl-1,1'-binaphthyl by either a diastereopure (S_p)-1,2-ferrocene derived from Ugi's amine,[105] or by a sterically demanding 1,1'-ferrocenylimine.[61] The 1,1'-imino ferrocene is known to be an effective ligand for the synthesis of tetra-*ortho*-substituted biaryls (Figure 2.15) and gives the product with a low catalyst loading within 24 h in 98 % yield. In contrast, the planar-chiral derivative, which is required for an atrop-enantioselective proceeding, requires a 5-times higher Pd and 15-times higher phosphine loading and 72 h reaction time for at least 85 % *ee*.
Up to date only two systems showed an effective chirality transfer from the ligand to the substrate at low catalyst loadings, which were reported by the group of Dorta[106] and Tang[102] (Figure 2.27), clarifying the huge demand of research within this field.

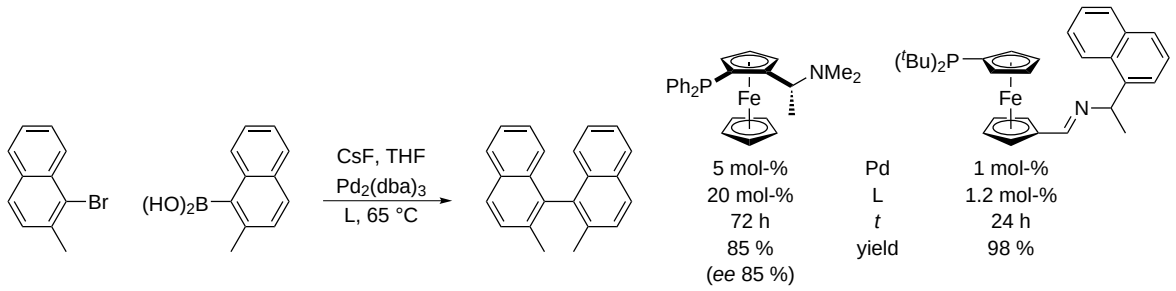


Figure 2.28 Comparison between 1,2- and 1,1'-substituted ferrocenes for atrop-enantioselective Suzuki-Miyaura reactions.[61,105]

Besides this example, further planar-chiral compounds have successfully been applied in atrop-enantioselective Suzuki-Miyaura couplings, for example, the phosphines from Johannsen[107] and Yiao[108], the N-heterocyclic carbene from Labande[109], and Duninas [2.2]paracyclophane[110] (Figure 2.29). Recently, our research group[75] and Manoury[111] contributed with ferrocenes bearing hemilabile *ortho*-vinyl- or oxygen-donors.

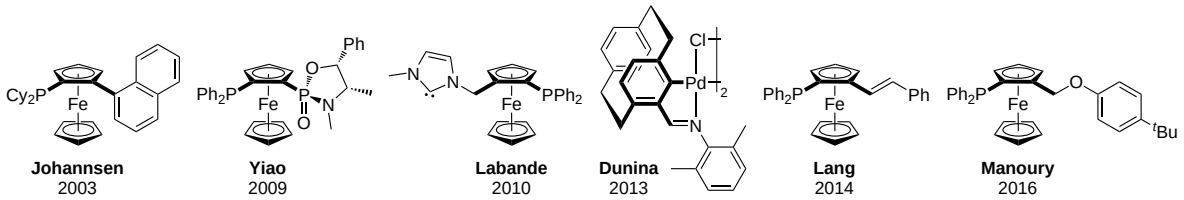


Figure 2.29 Planar-chiral compounds, which have been investigated for atrop-enantioselective Suzuki-Miyaura reactions.[75,107–111]

2.3 Planar-Chiral Ferrocenes

Ferrocene (bis(η^5-cyclopentadienyl)iron)) is probably the most prominent three-dimensionally expanded molecule for establishing planar chirality. Its first synthesis has been reported independently by Kealy & Pauson[112] and Miller *et al.*[113] and has been described as a σ-complex. R. B. Woodward proposed the name *ferrocene* based on the combination of *ferrum* and *benzene.*[114] The correction of the structure and verification of its three-dimensional nature was reported by E. O. Fischer in 1952[115], who received a Nobel Prize for this work in 1973.[79]

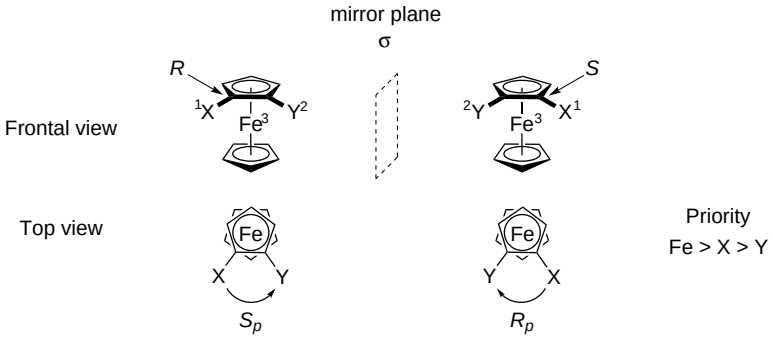


Figure 2.30 Configuration of the planar-chiral ferrocenes, determined by Cahn, Ingold and Prelog[116] (top) and Schlögl[117] (bottom).

The chemical properties have rapidly been investigated and showed a similar behavior to benzene, whereas the partial negatively charged cyclopentadienyl rings accelerate electrophilic aromatic substitution reactions by $3{\cdot}10^6$.[118] In contrast, the ferrocenyl backbone can be decomposed by strong oxidants, for example bromine and hydrogen peroxide, which complicates the synthesis of, e.g., nitroferrocene.[118]

Planar-chirality at ferrocenes occurs if two different substituents are attached in 1,2- or 1,3-position at one cyclopentadienyl ring, which therefore acts as the chirality element (Figure 2.30). The stereodescriptor can be defined by the method of Cahn, Ingold and Prelog, where the configuration of the carbon-atom, bearing the substituent with the highest priority, is determined.[116] In this case, the iron atom is assigned with the lowest priority. Another, more common method has been introduced by Schlögl, using the top view of towards the respective plane in a Newman projection.[117] The priorities of each group (Fe, X and Y) are assigned according to Cahn, Ingold and Prelog. Their clockwise arrangement gives a R_p configuration, and a descending order counterclockwise the S_p isomer. If X and Y posses a lower priority than Fe, both methods give opposed stereodescriptors.

2.3.1 Racemic Functionalization

A 1,2-functionalization can be achieved by lithiation of ferrocenes bearing *ortho*-directing groups and subsequent reaction with the desired electrophile. These *ortho*-directing substituents should contain donor atoms to stabilize the lithium ion, otherwise 1,3- and 1,1'-functionalizations occure as found for alkyl groups.[119] Due to the oxophilic properties of the

lithium ion oxygen-donors, as found in THP-ether[120] **K-41** (= tetrahydropyranyl), alcohols[121,122] of type **K-42**, acetals[123] (**K-43**), carboxylic acids[124] and amides[125] (**K-44**), sulfonic acids[126] (**K-45**), and phosphine oxides[127] (**K-46**) were investigated, but also the usage of *N*-donors[128,129] (**K-47**) is common (Figure 2.31). The application of *ortho*-directing groups in *ortho*-directed metalations has been reviewed recently.[130]

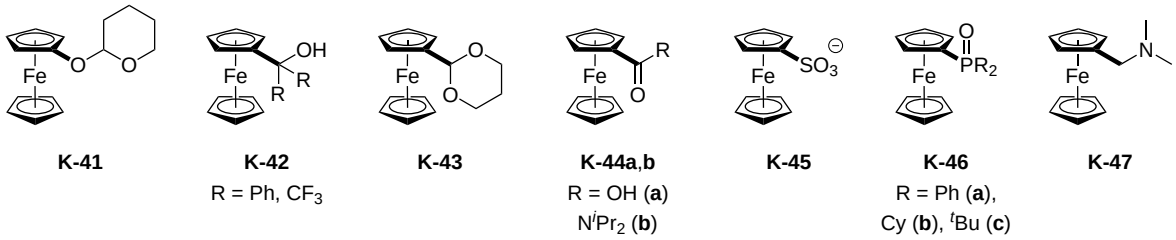


Figure 2.31 Mono-substituted ferrocenes applied in *ortho*-directed metalations.[120–129].

2.3.2 Racemic Resolution

The separation of both isomers of the formed 1,2-substituted ferrocenes can be achieved by kinetic or classic resolution, such as fractional crystallization or column chromatography. An example for a classic racemic resolution is the separation of 2-haloferrocenes **K-48**, which were obtained as a racemic mixture by *ortho*-lithiation of **K-47** and subsequent reaction with iodine (Figure 2.32).[129]

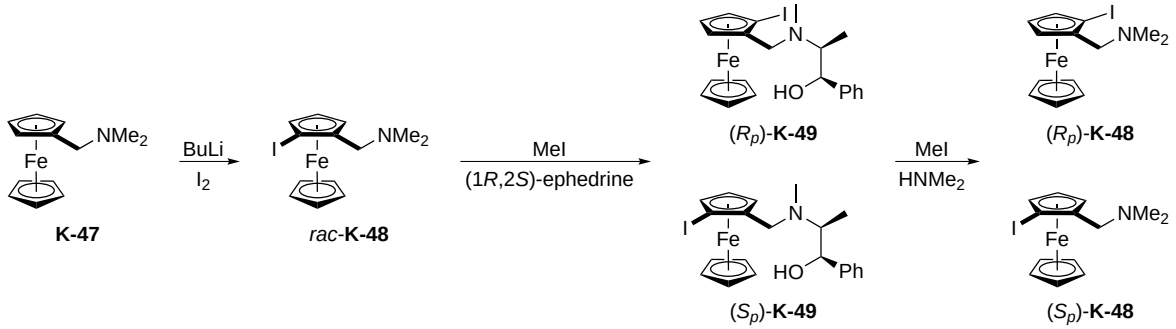


Figure 2.32 Resolution of 2-*N*,*N*-dimethylaminomethyl-1-iodoferrocene with ephedrine.[129]

Quarternization with MeI and subsequent nucleophilic substitution with the chiral auxiliary (1*R*,2*S*)-ephedrine gave both diastereomers of **K-49** in a 1:1 mixture that were separated by column chromatography. Nucleophilic substitution reaction of the methiodide of **K-49** with dimethylamine gave the (R_p)- and (S_p)-isomer of **K-48** enantiomerically pure (Figure 2.32).[129] After the separation, ephedrine is obtained as its *N*-methylated derivative and cannot be reused, which is the main disadvantage of this approach.

A similar method is illustrated by the *ortho*-functionalization of ferrocenecarboxylic acid **K-44a** with $ClPPh_2$, giving **K-50** as a racemic mixture. Racemic resolution of the acid was achieved by reaction with the diacetonide of D-glucose and column chromatographic separation of both diastereomers (Figure 2.33).[124] Hydrolysis under basic conditions gave (S_p)-**K-50** and (R_p)-**K-50** isomerically pure, as well as the chiral auxiliary.

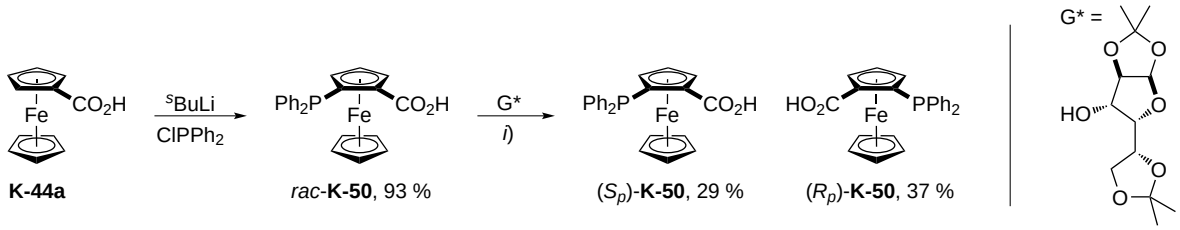


Figure 2.33 Resolution of 2-(diphenylphosphino)ferrocenecarboxylic acid by ester formation with the diacetonide of D-glucose.[124]
Reaction conditions: *i*) 1^{st} DCC, DMAP, G*; 2^{nd} KO^{t}Bu, H_2O. DCC = *N*,*N*'-dicyclohexylcarbodiimide; DMAP = 4-dimethylaminopyridine.

In recent years, kinetic resolutions of ferrocenyl derivatives have also been investigated. Compared to classic racemic resolutions, the chiral information is solely required in catalytic amounts. The first example has been reported by Thomson in 1959, who converted a cyclohaxenone-annelated ferrocene with (–)-menthhydrazid into the respective hydrazone. Kinetic resolution gave the (R_p)-isomer of the cyclohexanone.[131]

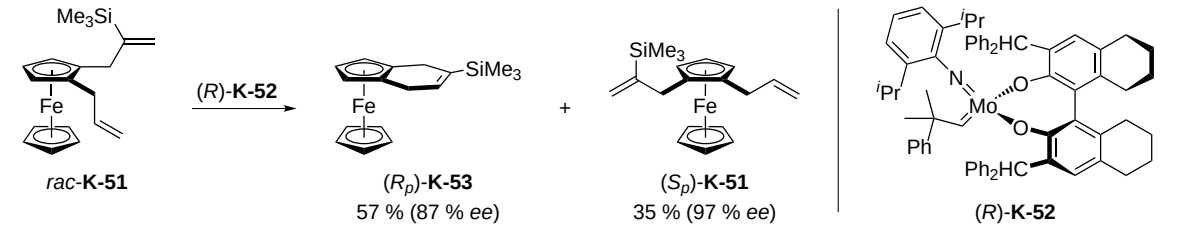


Figure 2.34 Kinetic resolution of a 1,2-diallylferrocene by ring-closing metathesis.[132]

A few years later, Ogasawara *et al.* applied a ring-closing metathesis reaction for the resolution of the 1,2-diallyl ferrocene *rac*-**K-51**.[132] Only 5 mol% of the chiral biaryl-based molybdenum carbene complex (*R*)-**K-52** were required as a catalyst, giving the cyclized product (R_p)-**K-53** and the remaining starting material (S_p)-**K-51** within 24 h at ambient temperature virtually isomerically pure (Figure 2.34).[132]

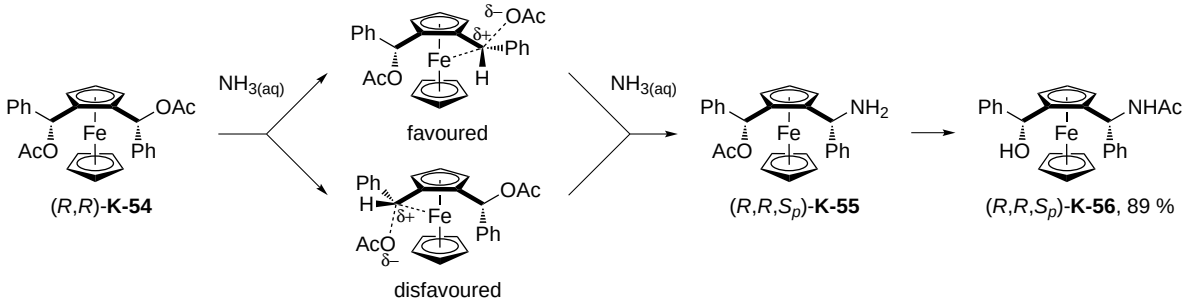


Figure 2.35 Desymmetrization of a homodisubstituted ferrocenyl acetate by amminolysis.[133]

Disadvantageous within all racemic resolution reactions is maximum yield of 50 %, which can be achieved for the desired isomer. In contrast, desymmetrization reactions are not limited to one isomer as demonstrated for the 1,2-homodisubstituted ferrocene (*R*,*R*)-**K-**

54 (Figure 2.35).[133] Ammonolysis in aqueous ammonia removes the *exo*-positioned acetate group, whereby the formed positive charge is stabilized by an interaction with the iron atom. Subsequent nucleophilic addition of NH_3 gave (R,R,S_p)-**K-56** in 89 % yield. The choice about which of the two acetates is in *exo*-position depends on the orientation of the steric demanding phenyl groups that have to be positioned away from each other. The intermediate amine (R,R,S_p)-**K-55** rapidly reacts with the present acetate anions, which could be prevented shortening of the reaction time.

2.3.3 Enantioselective Functionalization

A more efficient pathway for the synthesis of isomerically pure planar chiral ferrocenes is the stereoselective introduction of substituents, instead of a racemic formation with subsequent resolution. The first attempts were reported in 1969, where isopropylferrocene was lithiated with a BuLi/(–)-Sparteine mixture (Figure 2.36). Subsequent reaction with $ClSiMe_3$ gave a 1,3,1'-substituted ferrocene with 3 % *ee*.[134]
This method was improved 1996 by the group of Snieckus, who used **K-44b** as a more *ortho*-directing substrate, giving the huge variety of 1,2-substituted products (**K-57**) in 81–98 % *ee* (Figure 2.36).[135] Further improvement of the reaction by reducing the loading of (–)-Sparteine to 0.4 equiv was recently reported.[136]

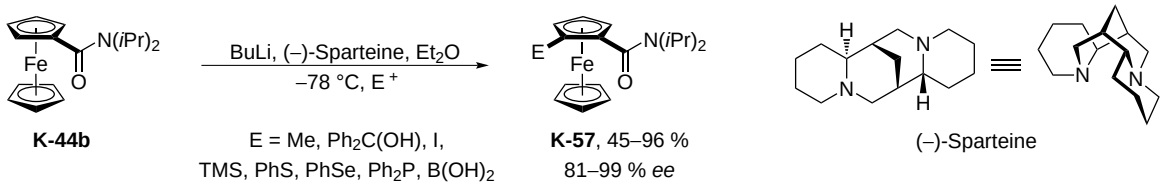


Figure 2.36 Enantioselective *ortho*-lithiation of a ferrocenecarboxamide with (–)-Sparteine.[135]

In the same year of Snieckus' approach by using (–)-Sparteine, Uemura introduced (R,R)-tetramethyl-1,2-diaminocyclohexane as a suitable additive for the successful enantioselective synthesis of 1,2-disubstituted planar-chiral ferrocenes (Figure 2.37)[137] Starting from the dimethylaminomethylferrocene **K-47** *ortho*-directed lithiation and subsequent reaction with DMF gave formylferrocene (R_p)-**K-58** in 80 % *ee*. The amount of the chiral additive could be reduced to only 0.2 equiv, by changing the base from BuLi to *i*PrLi, which enhanced the stereoselectivity of the *ortho*-lithiation to 98 %.[138]
A different approach was reported by Simpkins, who used lithium bis((*R*)-1-phenylethyl)amide (Simpkins base) as a chiral base instead of BuLi.[139] Lithiation of phosphine oxide **K-46a** with Simpkins base gave the *ortho*-substituted ferrocene **K-59** with 54 % *ee* in high yield (Figure 2.37). It should be noted that the usage of simpkins base for other substrates gave rather racemic mixtures.[139]

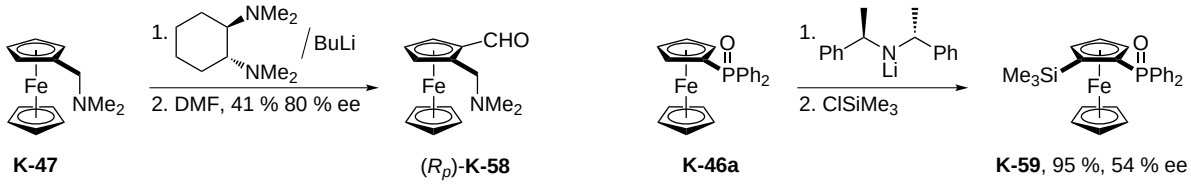


Figure 2.37 Enantioselective *ortho*-lithiation with (*R*,*R*)-*N*,*N*,*N*',*N*'-tetramethylcyclohexane-1,2-diamine[137] and *Simpkins*-base.[139]

2.3.4 Diastereoselective Functionalization

The diastereoselective functionalization is also based on *ortho*-directed lithiations and is the predominantly used approach for the synthesis of stereopure planar-chiral ferrocenes. A successful diastereoselective *ortho*-lithiation can be achieved, if the source of the chiral information is in close proximity to the ferrocenyl backbone.[130] The first example has already been reported in 1969 by using the (S)-methylpiperidine in **K-60** as the *ortho*-directing group (Figure 2.38). The ferrocenecarboxylic acid **K-61** was obtained by addition of dry ice to the lithiated species. Removal of the chiral piperidine group was achieved by quaternization of the nitrogen atom with methyl iodide and subsequent reduction, whereby the obtained ferrocene (R_p)-**K-62** exclusively shows planar-chirality.[130]

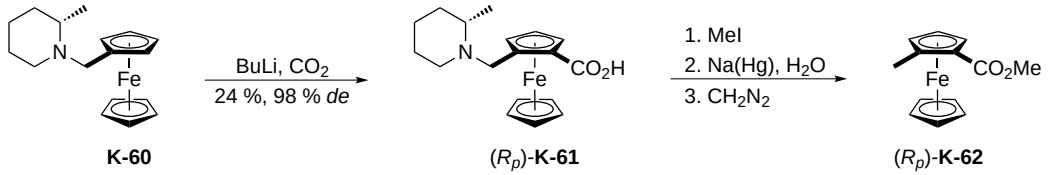


Figure 2.38 Diastereoselective *ortho*-lithiation of (*S*)-1-ferrocenylmethyl-2-methylpiperidine.[130]

Ugis doubts concerning the optical purity of the products prompted him to report an improved protocol by replacing the piperidylmethyl group in **K-60**. He introduced *N*,*N*-dimethyl-1-ferrocenylethylamine (**K-63**), whereby both isomers are accessible by resolution with tartaric acid. Amine **K-63** served as a starting point for a huge variety of related compounds and was since then known as Ugi's amine. It can readily be deprotonated with BuLi, whereby a steric repulsion of the methyl group and the ferrocenyl backbone result in excellent selectivities (Figure 2.39).[140] Treatment with an electrophile gave (R,S_p)-**K-64** in 92 % *de*, whereby the minor isomer can easily be removed by column chromatography or crystallization. The dimethylamino group can be replaced by huge variety of nucleophiles (Figure 2.39) by quaternization with methyl iodide and removal of NMe_3. The formed carbenium ion is stabilized by an interaction with the iron atom, which required *exo*-elimination of NMe_3 and *exo*-addition of the nucleophiles, respectively. Thus, the substitution proceeds under retention of the configuration, whereby the methyl group has to be directed away from the phosphine to avoid steric interactions (Figure 2.39).[130]

Diastereoselective *ortho*-directed lithiations have emerged as a straightforward approach for the synthesis of stereopure planar-chiral ferrocenes. Recently, many groups joined this field

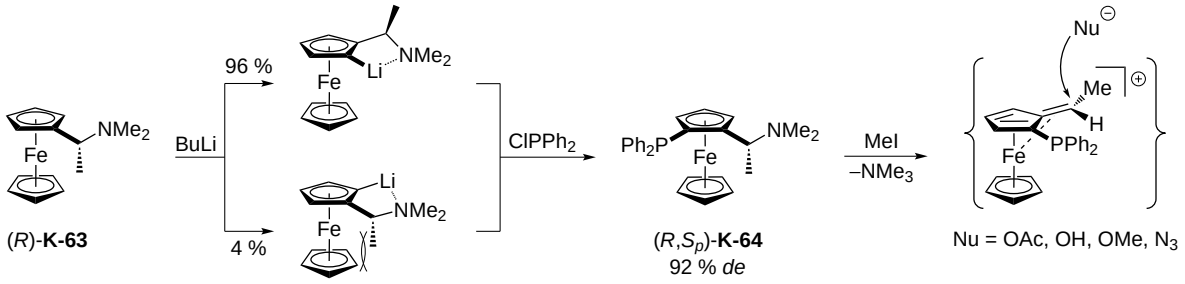


Figure 2.39 Diastereoselective *ortho*-lithiation of Ugi's amine and subsequent functionalization of the chiral auxiliary.[140]

of ferrocene chemistry and established a huge variety of different *ortho*-directing groups.[130] As shown in Figure 2.39 they can easily be functionalized, or were introduced as protecting groups and can thus be cleaved by standard reaction protocols. Figure 2.40 gives an overview of chiral *ortho*-directing functionalities and highlights the hydrogen atom, which is removed within the lithiation process. Furthermore, reagents for the functionalization or cleavage of the chiral auxiliary are given.[130]

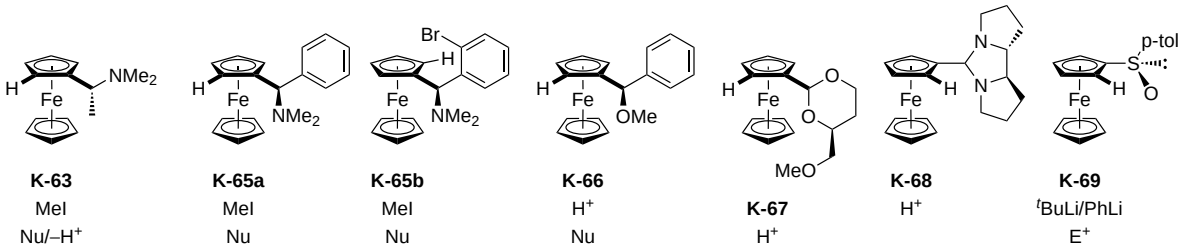


Figure 2.40 Chiral ferrocenes applied in diastereoselective *ortho*-lithiations and functionalization of the chiral auxiliary I.[140–145]

Replacing the methyl group in Ugi's amine by a phenyl group (**K-65a**) does not influence the configuration within the lithiation process. However, the introduction of an *ortho*-bromine in **K-65b** gives, upon treatment with ^{t}BuLi, a double-lithiated species. The interaction of both organolithium fragments superseded the *ortho*-directing propterties of the NMe_2 substituent, which therefore acted as the steric interacting group.[141] The phenyl substituent in **K-66** is crucial for a diastereoselective proceeding,[142,146] in contrast to **K-63** and **K-65a** where both groups gave products in high *de*. As shown in Figure 2.39, α-substituents can easily be removed by a cationic activation and subsequent reaction with an nucleophile.[130] Formylferrocene[147] is a key compound for the introduction of several different functionalities. An excellent combination of protecting and *ortho*-directing group is their conversion to chiral acetals (**K-67**)[143] and aminals (**K-68**).[144] The formyl group can smoothly be released under acidic conditions. Also non-carbon-based chiral *ortho*-directing groups were successfully applied, for example the highly versatile sulfoxide **K-69**.[145], which can easily be obtained by reaction of a commercially available menthyl-sulfinate with lithioferrocene. *Ortho*-lithiations proceed diastereomerically pure, ascribed to the donor-abilities of the oxide oxygen. The sulfoxide functionality can be removed by treatment with ^{t}BuLi or PhLi and the remaining

planar-chiral lithioferrocene is available for a subsequent reaction with an electrophile (Figure 2.40).[130]

The number of reaction steps for the synthesis of stereopure planar-chiral ferrocenes can be reduced, if the *ortho*-directing group is generated *in situ*, as shown for hemiaminal anions. They can be obtained by the reaction of 1,1'-diformylferrocene and a pyrrolidine amide **K-70**. The combination of the sterically demanding chiral backbone and the strong oxygen donor gave dilithiated ferrocenes. Addition of electrophiles and simple aqueous work-up result in tetra-substituted diformylferrocenes within one reaction step (Figure 2.41).[148] Carbonyl compounds can also be converted into chiral oxazolines (**K-71**), by reacting carboxylic acids, acid chlorides or nitriles with aminoethanols. The steric repulsion occurs between the substituent R and the organolithium derivative, which is coordinated by the nitrogen atom and thus, positioned above the ferrocenyl plane.[130,149] Hydrazones (**K-72**), which were derived from ketones and chiral hydrazines, can stabilize the lithium ion by nitrogen and oxygen donors. Their cleavage requires oxidants, such as O_3, $TiCl_3$, or VCl_2.[150] Axial-chiral binaphthyl backbones in combination with a nitrogen donor also acted as stereoselective *ortho*-directing backbones (**K-73**), enabeling diastereopure lithiations at ambient temperature. The removal of the biaryl backbone is similar to Ugi's amine.[151]

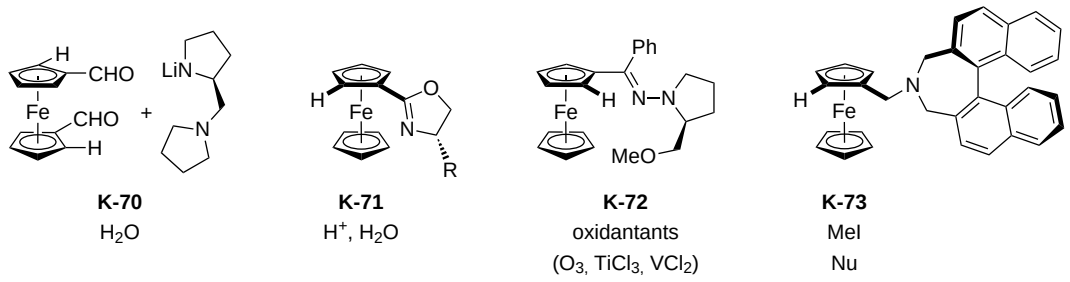


Figure 2.41 Chiral ferrocenes applied in diastereoselective *ortho*-lithiations and functionalization of the chiral auxiliary II.[148–151]

With respect to *C,C* cross-coupling reactions, in which phosphines are required as ligands, phosphorus-based *ortho*-directing groups are of special interest. Suitable *P*-chiral ferrocenes are based on phosphine oxides (**K-74**),[152] ephedrine-based phosphonates (**K-75**)[153] and BH_3-adducts of phosphoramidates (**K-76**)[154] (Figure 2.42). After their successful stereopure *ortho*-functionalization they can be converted into phosphines.[130]

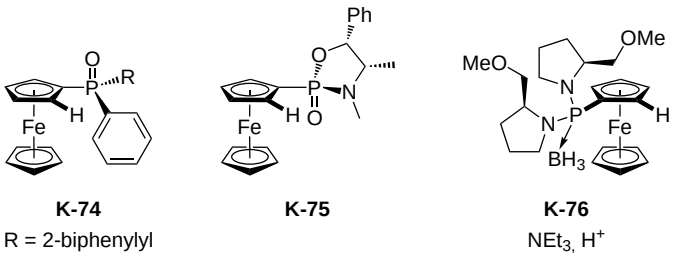


Figure 2.42 *P*-Chiral ferrocenes applied in diastereoselective *ortho*-lithiations.[152–154]

2.4 *P,O*-Substituted Ferrocenes

The *ortho*-functionalization of ferrocenes is based on carbon-, sulfur- and phosphorus-bonded *ortho*-directing groups. As electrophiles, silanes, phosphines and a huge variety of carbon-based electrophiles have been applied in the recent years. However, the usage of oxygen-based *ortho*-directing groups and electrophiles has not been mentioned within Section 2.3, although oxygen atoms have been shown to be very effective donor atoms for the stabilization of *ortho*-lithium atoms. The lack of oxygen electrophiles limits its application in this field of chemistry. Thus, the number of *P*,*O*-substituted ferrocenes as suitable ligands in catalytic reactions has sparsely been investigated. For the synthesis of 1,2-X,O-substituted ferrocenes (X = C, S, P, ...) two pathways can be applied, whereby one starts with an oxygen-functionalized ferrocene and one requires an oxygen-based electrophile. The key-step in both procedures is the formation of a direct ferrocenyl C–O bond.

2.4.1 Oxygen-Electrophiles

Up to date, two possibilities for the introduction of oxygen-bonded groups are known. A standard procedure has been reported in 1959 by Nesmeyanov by applying copper-mediated Ullmann-type couplings on iodoferrocene, giving ferrocenyl acetate in the presence of acetic acid as an air and moisture stable compound (Figure 2.43).[147] In similarity, ferrocenylboronic acid can be reacted with $Cu(OAc)_2$.[155] Both reactions were also applied on the respective 1,1'-homodisubstituted ferrocenes.[147,155] Ferrocenylacetate can be hydrolyzed to ferrocenol in deoxygenated ethanolic KOH-solutions. Hydroxyferrocene can be seen as the organometallic analogue of phenol. Ferrocenol is rapidly oxidized to a cyclopentadienone complex and decomposes within hours under atmospheric conditions in solution, and is thus generated *in situ* from ferrocenyl acetate. However, it can easily be handled in the absence of oxygen and was applied in Williamson ether syntheses, whereas sterically non-demanding substrates are preferably converted (Figure 2.43).[156] However, sterically demanding, secondary substrates could successfully be reacted by reacting the respective alcoholate in Ullmann-type couplings with iodoferrocene, in similarity to the synthesis of ferrocenyl acetate.

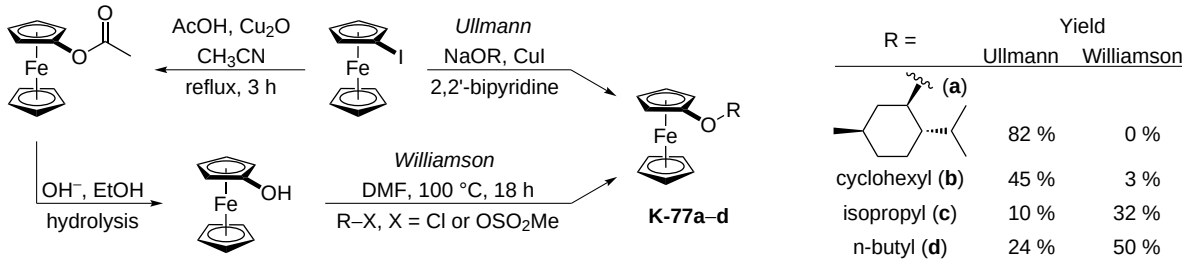


Figure 2.43 Synthesis of oxygen-functionalized ferrocenes by Ullmann-type couplings or Williamson ether synthesis.[147,156]

The yields of ferrocenyl ethers **K-77a**–**d** for both pathways show opposite trends. The high yields for sterically demanding substrates within Ullmann couplings are due to an increased nucleophilicity of secondary alcohols. Substituted phenols, which are not avail-

able for Williamson reactions, were also applied in Ullman-type couplings, whereas electron-withdrawing groups proved to be disadvantegous.[157]

A rare example of an oxygen electrophile is bis(trimethylsilyl)peroxide. It can be reacted with lithio- or 1,1'-dilithioferrocene giving the trimethylsilyl ethers in 82 and 51 % yield, respectively (Figure 2.44).[158] The hydroxy functionality can easily be released from the silylethers under basic conditions or with a fluoride source.[159] The synthesis of ferrocenol by hydrolysis of ferrocenyl acetate is very common and almost exclusively used, whereas the peroxide approach is hardly applied. This is moreover due to the handling of the peroxide, which has to be stored at <0 °C and rapidly decomposes in the presence of traces of transition metals.[160] Further applications of $(Me_3SiO)_2$ can be found besides ferrocene chemistry, by converting phosphine sulfides and selenides into oxides[161] and also induces Baeyer-Villiger oxidations.[162] Nevertheless, the successful formation of a Fc–O bond is remarkable, since the usage of peroxides usually oxidizes the ferrocenyl backbone, which my result in decomposition.

Figure 2.44 Oxygen functionalization of ferrocenes with bis(trimethylsilyl)peroxide.[158,159]

The introduction of hydroxy functionalities in *ortho*-position to a given substituent is even more challenging. In case of the peroxide approach, solely the chiral *ortho*-directing oxazoline derivative **K-71** was applied, besides its racemic derivative (Figure 2.45).[163] The 1,2-disubstituted stereopure hydroxyferrocene (S,S_p)-**K-82** was obtained in an average overall yield of 43 %, due the formation of the silylated side product **K-80**.

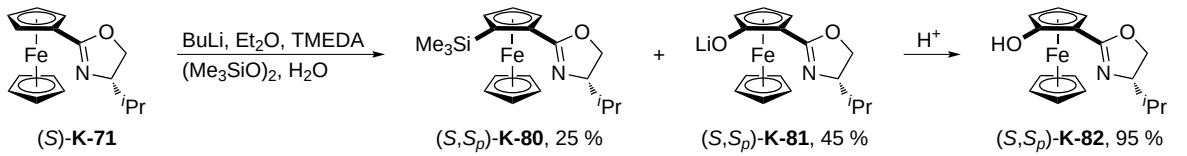


Figure 2.45 Diastereoselective oxygen functionalization of ferrocene with bis(trimethylsilyl)peroxide.[163]

In contrast, the Ullmann-type coupling is more common for the *ortho*-hydroxylation of ferrocenes, since the required iodo-substituent can easily be introduced by several methods, including diastereoselective *ortho*-directing groups, as shown in Figures 2.40 and 2.41. However, the formation of the Fc–O bond by the Ullmann-type coupling is the key-step within this procedures, and its low tolerance towards *ortho*-substituents mainly restricted a broad application. Thus, since its development in 1959,[155] the adoption to substrates bearing *ortho*-directing groups occurred first in 2008 by the group of Erker.[164] They used non-chiral (**K-43**, Figure 2.31) and *C*-chiral acetals (**K-67**, Figure 2.40) for the introduction of iodo substituents and could successfully convert them into the respective acetates **K-84** in excellent yield (Figure 2.46). Prior to the acid-catalyzed removal of the chiral auxiliary they replaced

the acyl- by a sterically demanding silyl-substituent, which is stable under basic conditions but readily releases the hydroxy group by addition of $[Bu_4N]F$. It could recently be shown that the coupling reaction tolerates acidic *N*H-functionalities and can also be applied on different carboxylic acids than acetic acid (Figure 2.43).[165] Directly nitrogen-functionalized ferrocenes also allowed the conversion of their *ortho*-iodo derivatives into acetates with up to 78 % yield for an NMe_2 group, whereas a pyrrolidine substituent decreased the yield to 33 %.[166]

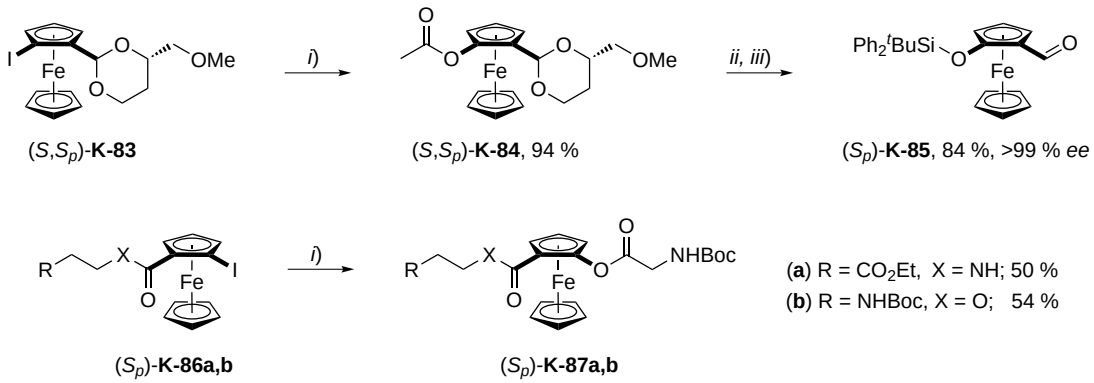


Figure 2.46 Stereoselective introduction of different carboxylic acids at *ortho*-substituted ferrocenes by Ullmann-type couplings.[164,165]
Reaction conditions: *i*) Cu_2O, MeCN, carboxylic acid, 3 h, reflux; *ii*) NaOMe, DMF, ^{t}BuPh$_2$SiCl; *iii*) *p*-TsOH, H_2O/CH_2Cl_2.

Remarkable results were reported by the group of Butenschön, who lithiated methoxyferrocene **K-88** in *ortho*-position (**K-89**) and subsequently converted it to the first 1,2-dioxygen-functionalized ferrocene **K-90** (Figure 2.47).[167] They also used 1,2-diiodoferrocene **K-91**, which allowed for two Ullmann-couplings and successfully gave 1,2-diacetylated **K-92** in 88 %.

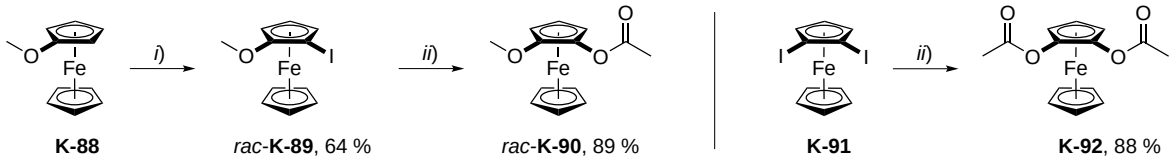


Figure 2.47 Acetylation of 1-iodo-2-methoxy and 1,2-diiodoferrocene by Ullamnn-type couplings.[167]
Reaction conditions: *i*) BuLi, KO^{t}Bu, THF, –78 °C, I_2; *ii*) HOAc, Cu_2O, MeCN, 3 h, reflux.

The functionalization of ferrocenes with oxygen-based substituents in the presence of *ortho*-directing groups is still a challenging task. The remarkable results by using bis(trimethylsilyl)peroxide and applying Ullmann couplings may not distract that besides the shown examples no further research has been published.

2.4.2 Introduction of Phosphorus by Oxygen-Based *ortho*-Directing Groups

Phosphorus-based reagents are widely used as electrophiles for the reaction with lithiated species. Thus, a promising strategy for the synthesis of *P,O*-substituted ferrocenes is the

reaction of *ortho*-lithiated oxygen-functionalized ferrocenes. Extensive research was published by Schaarschmidt as a member of the research group of Lang within a recent Ph D thesis.[76] As shown in Section 2.4.1, aromatic and aliphatic ferrocenylether are easily accessible.[156,157] The *ortho*-directing properties of ferrocenyl ether **K-93** were investigated by treatment with BuLi in different amounts and subsequent reaction with $ClPPh_2$ (Figure 2.48).[73] Applying a **K-93**/BuLi ratio of 1:1 gave **K-94** as the main product besides **K-95**–**97**. Changing to 1:2 gave **K-95** instead. Compounds **K-96** and **K-97** could not be separated from each other. The multiple lithiations that occur already at low BuLi ratios ascribing the ether functionality to be a rather weak *ortho*-directing group.

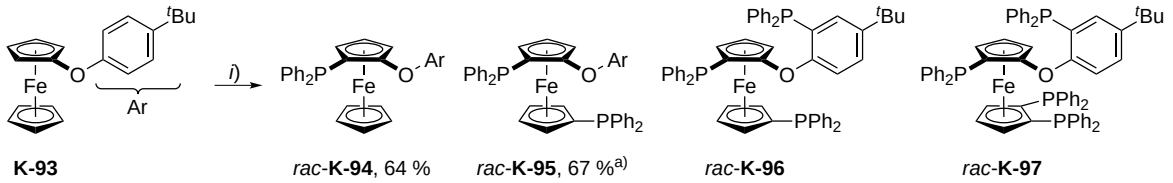


Figure 2.48 Lithiation behavior of ferrocenylether **K-93** and subsequent reaction with $ClPPh_2$.[73]
Reaction conditions: *i*) 1^{st} BuLi (1 equiv), TMEDA, hexane, 25 °C, 12 h; 2^{nd} –78 °C, $ClPPh_2$, 1 h; a) 2 equiv of BuLi.

Switching from the phenyl ($ClPPh_2$) to the cyclohexyl chlorophosphine $ClPCy_2$, as a stronger σ-donor, gave mixtures of single- and multi-substituted products, which could not be separated from each other.[73] This problem was circumvented by reacting the mixture of lithioferrocenes, derived from **K-93**, with $ClSn(Bu)_3$. Compound **K-98** could be separated by column chromatography and successfully be converted to phosphine **K-99** (Figure 2.49).[73] Nevertheless, the huge amount of side products in the first reaction step gave **K-99** in a poor overall yield of 21 %.

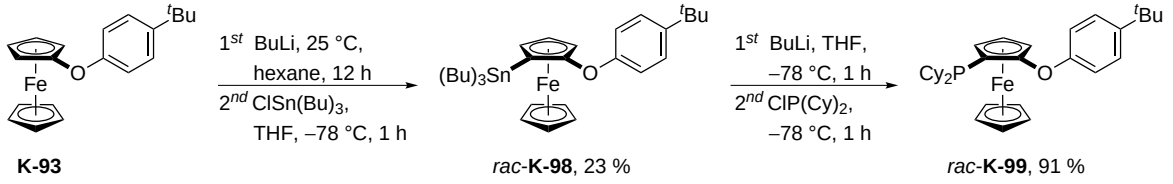


Figure 2.49 Synthesis of a 1,2-*P*,*O*-substituted ferrocene by a two-step process by using $ClSn(Bu)_3$.[73]

The diastereoselective lithiation was investigated by using the menthyl-functionalized ferrocenylether **K-77a** (Figure 2.50). A diastereomeric ratio (*dr*) of 1.6:1 for the 1,2-*P*,*O* product revealed a weak influence of the chiral menthyl group towards the lithiation process. Nevertheless, the absence of TMEDA clarified the weak *ortho*-stabilization of lithiated species by ether functionalities and resulted in the formation of a dimeric structure, which explains the the exclusive formation of the 1,1'-derivative (Figure 2.50).[76]
The competition between a lithiation in 2- and 1'-position was avoided by a double lithiation in the presence of TMEDA or (–)-Sparteine (Figure 2.51). While increasing the steric demand gradually within the series menthyl<borneyl<fenchyl enhances the *de* accordingly

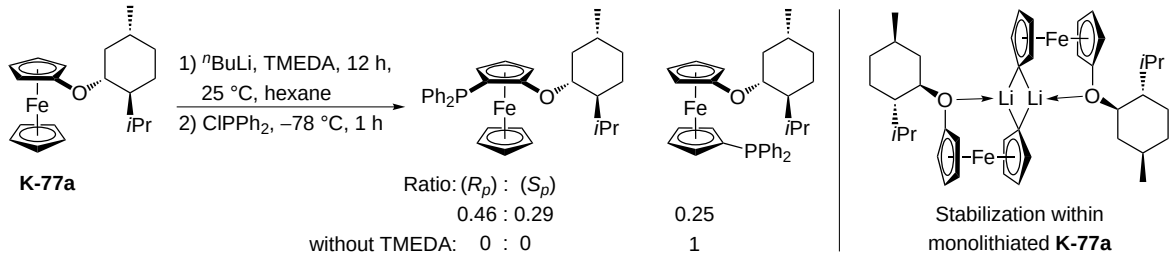


Figure 2.50 1,2- and 1,1'-Functionalization of ferrocenylmenthylether by a dimeric lithiated species.[73]

by 20<70<80 %.[76] The replacement of TMEDA (65 % *de*) by the chiral amine (80 % *de*) resulted in a positive interaction of both chiral groups for the fenchyl (**K-77e**) and the borneyl ether **K-77f**, contrary to the menthyl derivative **K-77a** where a decrease from 26 % to 20 % *de* was observed.[76] The effective chirality transfer in case of the borneyl and fenchyl substituents is due to the steric demand and bicyclic backbone and the presence of three methyl groups in close proximity to the oxygen donor atom.[168]

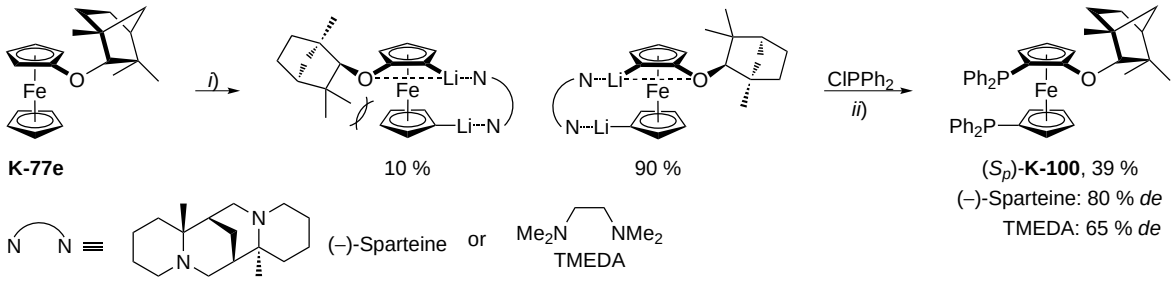


Figure 2.51 Diastereoselective 2,1'-dilithiation of fenchylferrocenylether **K-77e**.[76]
Reaction conditions: *i*) BuLi, (–)-Sparteine or TMEDA, hexane, 25 °C, 12 h; *ii*) $ClPPh_2$, –78 °C to 25 °C, 12 h.

1,1'-Dilithiated ferrocenes can be converted into [1]ferrocenophanes, which allowed for more diverse substitution pattern. Addition of Cl_2PPh to the dilithiated species of borneyl ether **K-77f** gave [1]phosphaferrocenophane **K-101** (Figure 2.52).[76] The strained ring was opened by subsequent addition of PhLi, whereas the Li ion was positioned in 2-position, due to the stabilization by the oxygen atom.

The diastereomeric excess of the *ortho*-lithiation is not influenced by the ferrocenophane formation and remains at 70 %.

The regioselectivity for the position of the phosphorus substituents can be inverted by using [1]sila- instead of [1]phosphaferrocenophanes. They are also derived from 1,1'-dilithiated ferrocenes, *e.g.* derived from **K-77e**, by reation with Cl_2SiMe_2. The treatment of [1]silaferrocenophane **K-104** with organolithium compounds exclusively ring-opened with the lithium ion positioned *ortho* towards the ether functionality. Thus, the subsequent addition of the phosphorus electrophile moreover gave the respective 1,2-*P,O* ferrocene (S_p)-**K-105** as a single isomer after crystallization (Figure 2.53). However, the overall process is rather ineffective and gave the products in less than 7 % yield, due to a polymerization of the strained [1]silaferrocene **K-104**. The silyl-substituent acts as an "place holder" for H^+ or further elec-

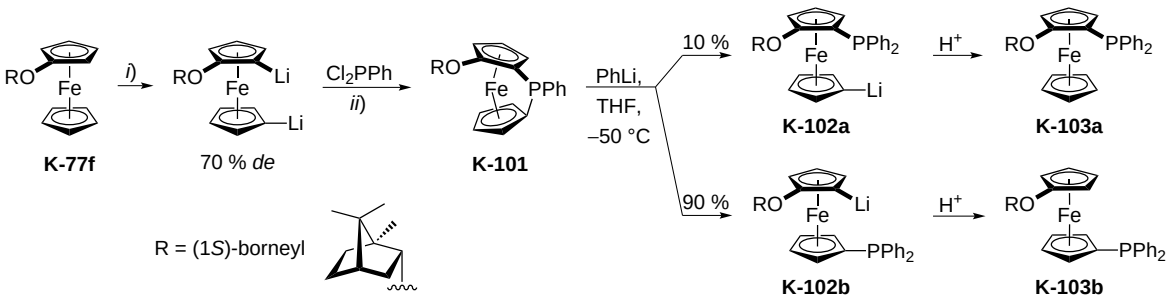


Figure 2.52 Synthesis and ring opening of [1]phosphaferrocenophane **K-101**.[76]
Reaction conditions: *i*) BuLi, (–)-Sparteine (2 equiv), hexane, 25 °C, 12 h; *ii*) Cl_2PPh, –78 °C to 25 °C, 12 h. The overall yield of **K-103a**,**b** is 36 %. (R_p)-**K103a** is formed as the main diastereomer.

trophiles. Nevertheless, it does neither positively, nor negatively influence the performance of the respective ligand within *C*,*C* cross-coupling reactions.[76]

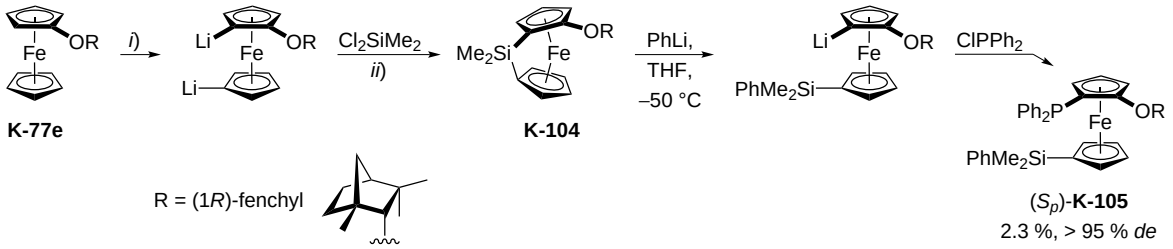


Figure 2.53 Synthesis and ring opening of [1]silaferrocenophane **K-104** to 1,2-*P*,*O*-substituted ferrocenes.[76]
Reaction conditions: *i*) BuLi, (–)-Sparteine (2 equiv), hexane, 25 °C, 12 h; *ii*) Cl_2SiMe_2, –78 °C to 25 °C, 12 h.

Although 1,2-*P*,*O*-substituted ferrocenes could be obtained in the past, a high-yielding regio- and stereoselective synthetic strategy is still pending.

2.5 Fries Rearrangements

The Fries rearrangement is a 1,3-O→C migration at aromatic compounds named after Karl Fries, who published his first examples in 1908.[169] He reacted phenolic esters in the presence of a Lewis acid to acyl phenoles (Figure 2.54). The reaction is induced by the coordination of the Lewis acid to either the ketone or the phenolic oxygen, or in acidic media,[170] respectively. The activated ester splits off an acylium carbocation, which undergoes an electrophilic aromatic substitution reaction (S_EAr) with the aromatic backbone. Based on the electron density in *ortho*- and *para*-position the acyl group can be substitutet in 2- (1,3-O→C) and 4-position (1,5-O→C), respectively. Besides this cationic version, Fries rearrangements can proceed *via* radical/photo-induced mechanisms,[171] first reported 1960 by Anderson and Reese,[172] and anionic pathways. Photo-induction results in a homolytic O–C bond cleavage of the ester-functionality. The formed acyl radical recombines in 2-/4-position with the aromatic backbone, similar to the cationic proceeding (Figure 2.54).

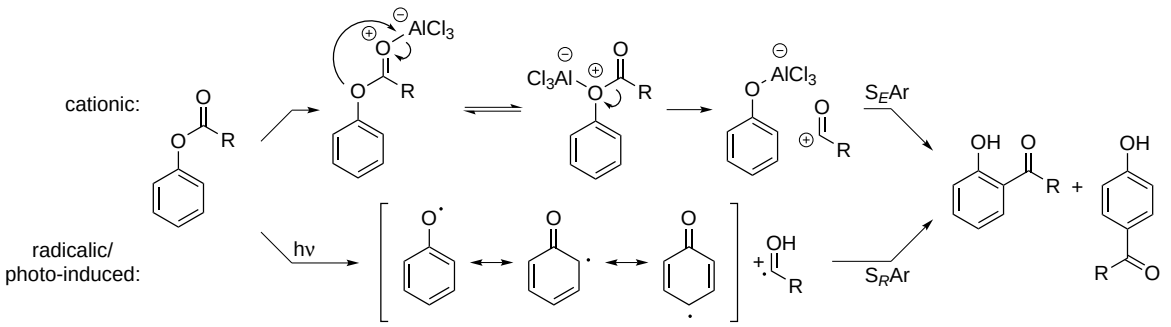


Figure 2.54 Cationic and radicalic Fries rearrangements.[169,171,172]

2.5.1 Anionic Fries Rearrangements at Non-Organometallics

The anionic Fries rearrangement is induced by an *ortho*-lithiation and subsequent intramolecular 1,3-O→C migration (Figure 2.55), which combines several advantages compared to cationic and radicalic proceedings.

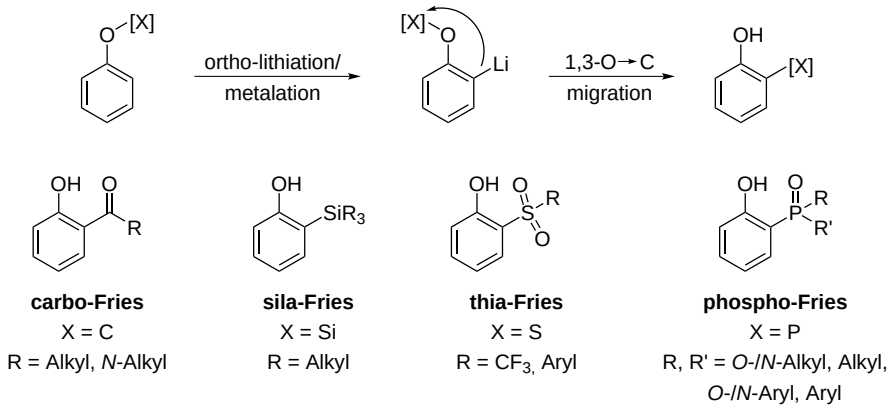


Figure 2.55 Different types of anionic Fries rearrangements depending on the rearranging group.[169,173–176]

As shown in the previous Sections, *ortho*-lithiations can be performed at low or ambient temperatures, whereas the activation with Lewis acids requires harsh reaction conditions, and photo-excitation affects the whole molecule. Furthermore, the regioselective lithiation exclusively results in the formation of 1,2-substituted products, since the migrating group rearranges by an intramolecular mechanism and is not released during the process.
Besides the initially reported carbo-Fries rearrangements,[169,172,177] also heteroatom-based versions with X = Si (sila-),[173] S (thia-)[174,175] and P (phospho-)[176] were explored, whereas the names are derived from the binding atom of the migrating groups (Figure 2.55). It should be noted that anionic carbo-Fries rearrangements of *N*,*N*-dialkyl carbamates have also been described as Snieckus rearrangements,[178,179] although Snieckus himself described this type of reaction as anionic *ortho*-Fries.[180]

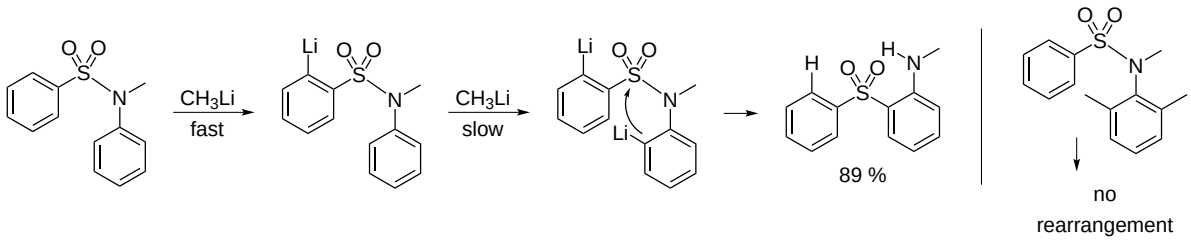


Figure 2.56 Double lithiation within thia-Fries rearrangements at phenylsulfonamides.[181]

It should be noted that recently 1,3-N→C migrations where described as Fries rearrangements,[171] which consequently needs to consider S→C versions within this topic. Electron-withdrawing substituents at the migrating groups accelerate the lithiation, and facilitate the rearrangement by ensuring a nucleophilic addition at the bonded atom. For S-based rearrangements sulfones are applied, which also stabilize hydroxy functionalities in the formed product towards tautomerization by forming intramolecular hydrogen bridge bonds.[175] It could also be shown that, although bearing the less acidic hydrogens, rearrangements exclusively occurred in the *ortho*-position of the *N*-based aromatic (Figure 2.56).[181] This has to be considered by choosing the appropriate amount of base and the addition of electrophiles.

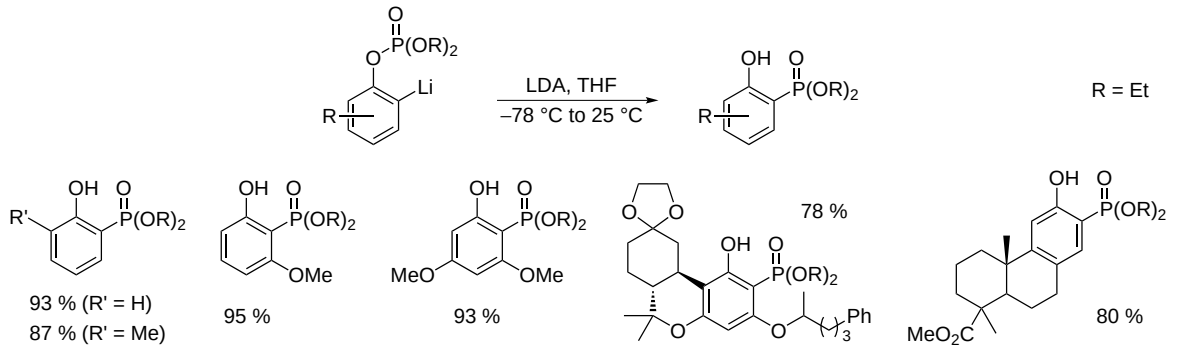


Figure 2.57 Anionic phospho-Fries rearrangements at phenyl phosphates and natural products.[176,182]

The first phospho-version of the Fries rearrangement has been accidantely been discovered by Melvin in 1981.[182] He converted substituted phenols with diethyl phosphate into the

respective phosphoric esters. Treatment with LDA at –78 °C gave the 1,2-*P*,*O*-substituted *ortho*-hydroxy phosphonates (Figure 2.57). The reaction tolerates several substitution pattern and can be adopted to natural products, where no loss of chiral information at the backbone is observed within the products. Rearrangements at chiral BINOL backbones also proceed under maintenance of the axial-chiral information.[183] The progress of the anionic phospho-Fries rearrangement (*apFr*) was nicely reviewed by Taylor and Watson in 2004.[176] Changing from monoaryl- to di- and triaryl phosphoric esters allows for two and three consecutive rearrangements within one reaction step at the same molecule, as shown for the conversion of triphenyl phosphate into its phosphine oxide (Figure 2.58).[176] This behavior is unique, compared to the carbo-, thia-, and sila-versions.

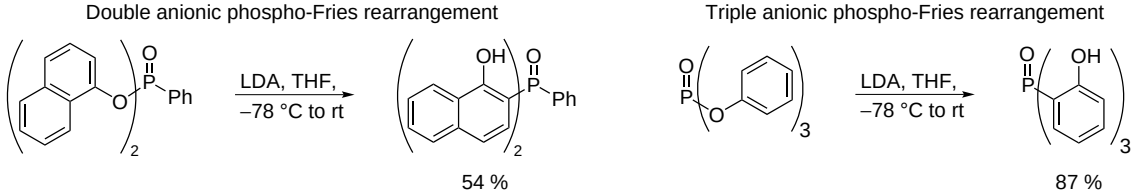


Figure 2.58 Simultaneous double and triple anionic phospho-Fries rearrangements at diaryl phosphonates and triaryl phosphates.[176,184–190]

Using phosphorus-chiral groups gave the rearrangement products with retention of configuration at the phosphorus atom, which unambiguously confirms the intramolecular proceeding. By applying the *apFr* to phosphorus-chiral groups it could unambiguously be proven that the anionic version of the Fries rearrangement proceeds by an intramolecular mechanism and does not release the migrating group (Figure 2.59). The reaction proceeded under retention of configuration at the phosphorus atom, which suggests a 5-coordinated transition state caused by a *syn* addition/elimination mechanism, which was proven by single crystal X-ray diffraction analysis.[191,192]

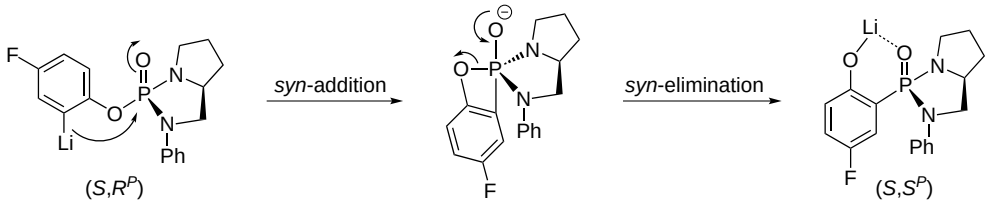


Figure 2.59 Retention of configuration at *P*-chiral substituents within anionic phospho-Fries rearrangements.[191,192]

The regioselectivity of Fries rearrangements at phenyl-based compounds is accompanied with the selectivity of the lithiation process and thus, depends on the steric demand of *ortho*-/*meta*-substituents, electronic effects or selective metalations induced by halogen-metal exchange.[176,184]

2.5.2 Anionic Fries Rearrangements at Organometallics

Accidentally discovered in 1990, the sila-version was the first example of an anionic Fries rearrangement that proceeded at organometallic compounds.[173] Attempts to introduce a dimethylallyl group by lithiation of the tricarbonylchromium complex **K-106** resulted in the migration of the silyl protecting group, which gave **K-108** instead (Figure 2.60). Tricarbonylchromium fragments act as electron-withdrawing groups and are usually introduced to facilitate deprotonation reactions at low temperatures, which explains the low yield of **K-108**.

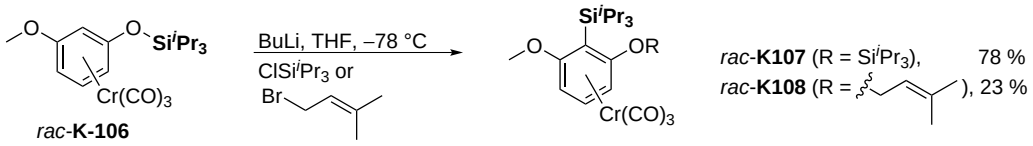


Figure 2.60 Anionic sila-Fries rearrangement at tricarbonylchromium complex **K-106**.[173]

The group of Butenschön, who also explored the anionic thia-Fries rearrangement at $Cr(CO)_3$ complexes,[193] showed that anionic Fries rearrangements also proceed at ferrocenyl-based triflates (Figure 2.61).[167,194] Although deprotonation reactions at the electron-rich ferrocenyl backbones are decelerated, and their C_5-ring geometry enlarges the distance to the *ortho*-substituents, the 1,2-*S*,*O* rearranged products **K-111a**–**c** were obtained in virtually quantitative yields. The usage of **K-111c**, where triflic anhydride was used as an electrophile, allowed for a subsequent anionic Fries rearrangement to the 1,3-di-*ortho*-substituted ferrocene **K-112** (Figure 2.61).[194]

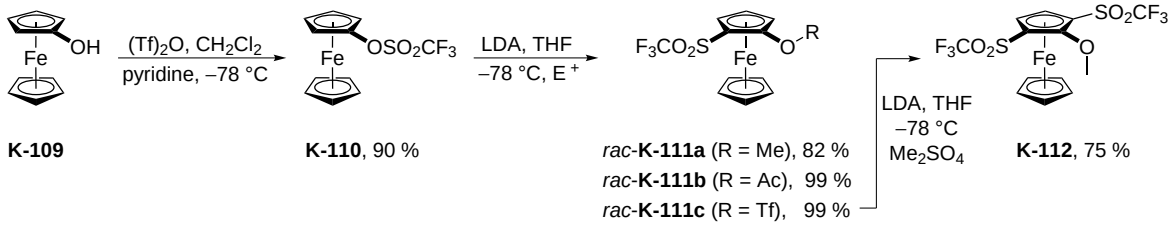


Figure 2.61 Anionic thia-Fries rearrangements for the synthesis of *ortho*- and 1,3-di-*ortho*-substituted ferrocenes.[194]

Consecutive rearrangements within one reaction step were observed, when 1,1'-functionalized **K-113** was applied (Figure 2.62). The rearrangement exclusively gave the *meso*-isomers, which was explained by a step-wise proceeding and a stereoinduction after the first process towards the hitherto non-rearranged cyclopentadienyl ring.[167]

The respective phospho-Fries version has, with exception of the results described herein, not been reported for ferrocenyl-based compounds or further organometallics. However, examples for non-classic 1,3-S→C migrations of phosphoryl fragments have been reported, which should be considered due to their similar mechanism. Based on mercaptoferrocene **K-113**, which is more stable towards oxidation than the respective hydroxy derivative, *S*-ferrocenyl phosphate **K-114** could be converted to the 1,2-S,P-ferrocenes **K-115** (Figure 2.63).[195]

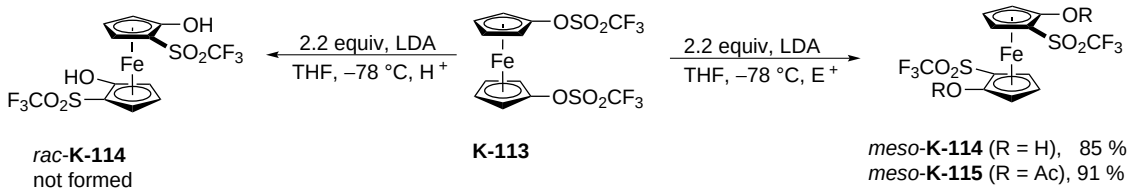


Figure 2.62 Anionic thia-Fries rearrangements at 1,1'-disubstituted ferrocenes for the synthesis of 1,1',2,2'-*S*,*O*-derivatives.[194]

Investigations with *P*-chiral groups showed retention of the configuration at the phosphorus atom (Figure 2.59). Replacement of phenyl by ferrocenyl-based backbones allows for diastereoselective rearrangements of the migrating groups. The chiral functionalization with (*R*,*R*)-diaminocyclohexane in **K-116** gave the 1,3-S→C-rearranged product **K-117** as a single diastereomer (Figure 2.64).

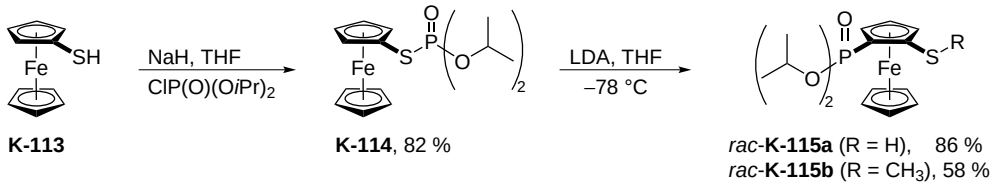


Figure 2.63 Anionic phospho-1,3-S→C rearrangements by starting from mercaptoferrocene.[195]

The successful investigations of anionic thia- and sila-Fries rearrangements and 1,3-S→C migrations of phosphosphorus-based groups at a ferrocenyl backbone let to the conclusion that the respective anionic phospho-Fries version may also be practicable and efficiently yield the desired 1,2-*P*,*O*-substituted ferrocenes. However, the lithiation and rearrangement process is influenced by several parameters, which can cause side reactions.

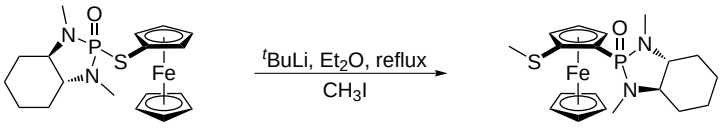


Figure 2.64 Diastereoselective anionic phospho-1,3-S→C rearrangement to 1,2-*S*,*P*-substituted (*R*,*R*,*S*$_p$)-**K-117**.[195]

They are summarized in Figure 2.65 to illustrate the complexity of the system. The succesful formation of an anionic phospho-Fries rearranged product **E** (Figure 2.65) requires a negative charge in *ortho*-position **B**, which is typically introduced by lithiation/deprotonation or halogene-metal exchange from **A**. However, this process competes with a nucleophilic attack at the phosphorus atom, resulting in a cleavage of the migration group (**F**). Thus, bases such as non-nucleophilic, steric demanding amides are preferably applied. Furthermore, a strict temperature regime has to be maintained. A successful Fries rearrangement also requires an intramolecular addition at the binding atom. Otherwise, the *ortho*-lithiated species is

protonated upon an aqueous work-up, indicating an unsuccessful lithiation. Addition of an electrophile, *e.g.* Me_2SO_4 can verify a successful lithiation by giving the *ortho*-methylated species **C** (Figure 2.65).[196]

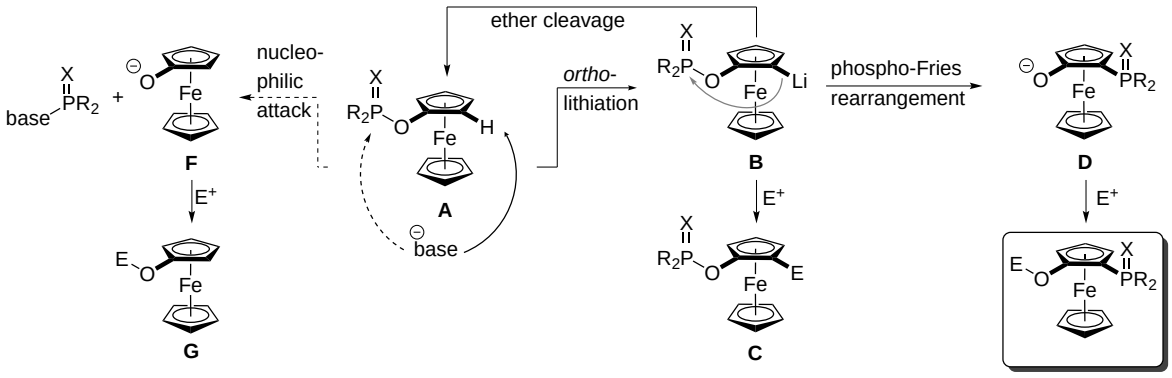


Figure 2.65 Possible side reactions within anionic phospho-Fries rearrangements.[196]

2.5.3 Anionic Homo-Fries Rearrangements

Homo-Fries Rearrangements at Non-Organometallics

The homologation of the O→C migration from 1,3 to 1,4 O→C by insertion of a carbon fragment is designated as an anionic homo-Fries rearrangement. This type of reaction is sparsely investigated, but was an essential step for the synthesis of a cyclo-*Mumbaistatin* derivative **K-120** (Figure 2.66), which is used as a target for drugs against type-2 diabetes mellitus and for brain tumor investigations.[197] The reaction is induced by an metal-halogen exchange at **K-118**. After the 1,4-O→C migration of the ester functionality, the benzylic alcoholate underwent a subsequent intramolecular cyclization, whereas a nucleophilic attack at the established keto-carbonyl carbon atom occurred. The thus formed hemiacetal anion consecutively *trans*-esterificates and forms the final spiroacetal **K-120** in a diastereomeric ratio (*dr*) of 13:1. Removal of protective groups gives the cyclo-*Mumbaistatin* derivative *rac*-**K-120**.

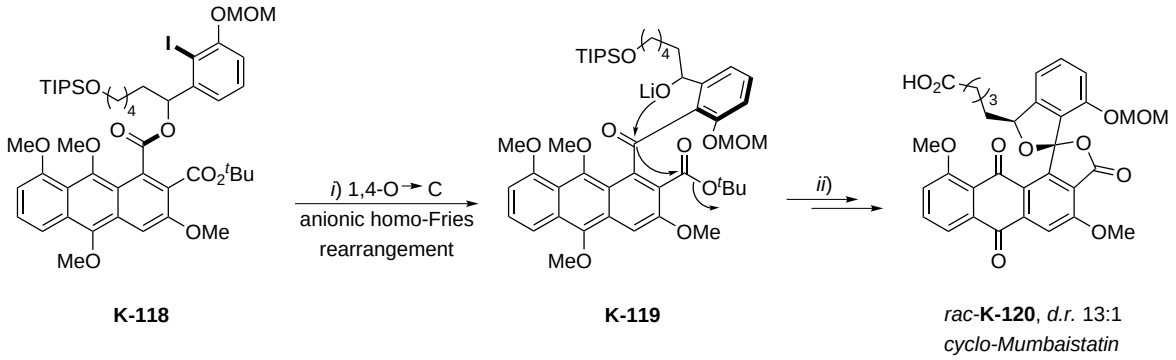


Figure 2.66 Anionic homo-Fries rearrangement for the synthesis of cyclo-*Mumbaistatin* **K-120**.[197]
Reaction conditions: *i*) ^{i}PrMgCl·LiCl, THF, –15 °C for 1.5 h, then 50 °C, 2 h, 76 %. *ii*) Jones reagent ($CrO_3 \cdot H_2SO_4$), 0 °C, 30 min, 59 %.

The 1,4-homo-Fries rearrangement occurs if other rearrangements are suppressed (Figure 2.67).[179] Lithiation of benzylcarbamate **K-121a** was attempted to occur in the benzylic position, which was prevented by the electron-rich butyl group. Thus, lihtiation at the phenyl ring occurred and gave **K-122** after an anionic homo-Fries rearrangement. Replacement of the butyl group by a hydrogen atom in **K-121b** allowed the lithiation in the benzylic position to the 1,2-O→C rearranged product **K-123**.

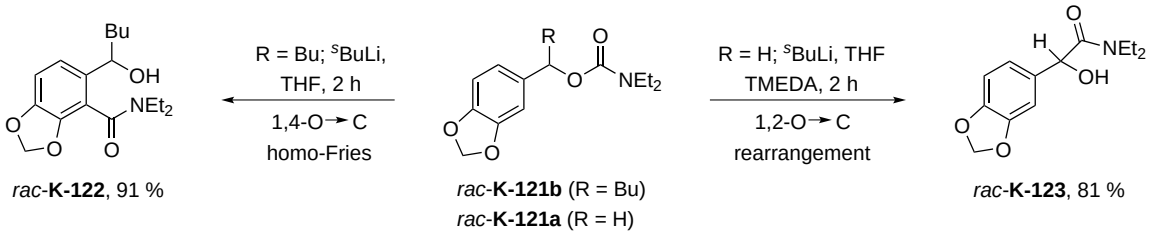


Figure 2.67 Anionic homo-Fries rearrangement and 1,2-O→C migration.[179]

For *ortho*-cresyl derivatives **K-124** an inverse proceeding of an anionic homo-phospho-Fries rearrangement was observed, where the migration occurred from the aromatic to a benzylic position in **K-125** (Figure 2.68), contrary to Figures 2.66 and 2.67.[198] Lithiation exclusively occurred in the benzylic position, probably due to a complexation of the lithiated species by both phosphato-substituents. Lithiation at the phenyl core required a halogen-metal exchanged of the brominated species **K-124b**, which induced the respective 1,3-migration and gave **K-126** quantitatively.

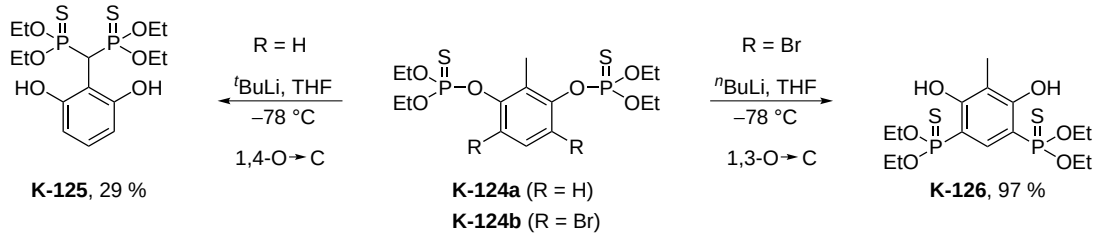
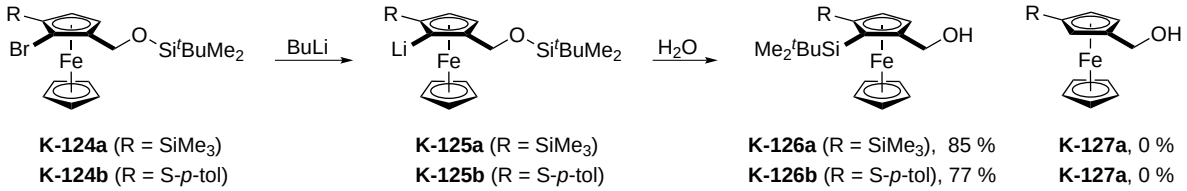


Figure 2.68 Benzylic homo-phospho-Fries *vs* phenylic *ortho*-phospho-Fries rearrangement.[198]

Homo-Fries Rearrangements at Organometallics

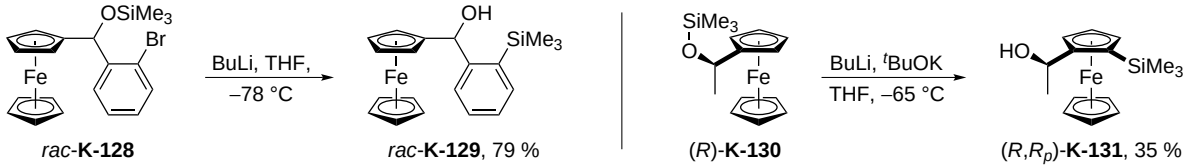
Anionic homo-Fries rearrangements at organometallics have solely been reported as sila-versions. It should be kept in mind that in case of sila derivatives, the proceeding of 1,3-migrations at aromatics are classified as Fries rearrangements, whereas the respective 1,4-homo-Fries modifications could also be considered as *retro*-Brook rearrangements.[199,200] Within the synthesis of the 1,3-disubstituted ferrocene **K-127** the place holding bromine atom in **K-124** should be exchanged by a lithium atom (**K-125**; Figure 2.69).[201] Subsequent 1,4-O→C anionic homo-sila-Fries rearrangement of the hydroxy protective group occurred, resulting in the 1,2,3-trisubstituted **K-126** prior to protonation.[201]



K-124a (R = $SiMe_3$) **K-125a** (R = $SiMe_3$) **K-126a** (R = $SiMe_3$), 85 % **K-127a**, 0 %
K-124b (R = S-*p*-tol) **K-125b** (R = S-*p*-tol) **K-126b** (R = S-*p*-tol), 77 % **K-127a**, 0 %

Figure 2.69 Anionic homo-sila-Fries rearrangement for the synthesis of 1,2,3-trisubstituted **K-126**.[201]

The presence of two electronically different aromatics allows for miscellaneous 1,4-O→C migrations. The regioselectivity towards the phenyl ring was ensured by a halogene-metal-exchange at **K-128** (Figure 2.70).[199] A lithium exchange between the phenyl and ferrocenyl groups was not observed. Treatment of a non-brominated derivative of **K-128** with BuLi, moreover, resulted in the cleavage of the silyl group, whereas 9 % of a product derived from a lithiation at the ferrocenyl backbone could be isolated. Diastereoselective anionic homo-sila-Fries rearrangement towards the ferrocenyl backbone could be achieved by replacing the phenyl by a methyl group, giving **K-131**.



rac-**K-128** *rac*-**K-129**, 79 % (*R*)-**K-130** (*R*,R_p)-**K-131**, 35 %

Figure 2.70 Regioselective anionic homo-sila-Fries rearrangement towards either phenyl or ferrocenyl substituents.[199]

With regard to the synthesis of 1,2-*P*,*O*-substituted ferrocenes, the anionic phospho-Fries rearrangement might be the most suitable synthesis strategy, due to its regioselective, intramolecular proceeding. The presence of the oxygen and phosphorus containing fragments within the starting materials does not require for further electrophiles and should thus prevent a 1'-functionalization, which is the main reason for the lack of knowledge within this field of ferrocene chemistry.

3 Theoretical Part

3.1 Anionic Phospho-Fries Rearrangements

As described in the previous chapter, the most frequent synthetic methodology relies on the *ortho*-directed metalation of single-substituted ferrocenes followed by the addition of an electrophile (Figure 3.1).[130] Just a few of these *ortho*-directing groups contain a heteroatom directly bonded to ferrocene, thus limiting the diversity of accessible ferrocenes carrying two heteroatoms in 1,2-positions. The synthesis of 1,2-*P*,*O*-substituted ferrocenes can be realized by *ortho*-directed metalation starting either from ferrocenyl ethers (Figure 3.1, path **A**) or ferrocenyl phosphine oxides (path **B**). The first path suffers from the formation of several byproducts due to di- and polymetalation of ferrocenyl aryl ethers, requiring an elaborate purification,[73,74] while for the respective alkyl derivatives lithiation occurs almost exclusively at the heretofore unsubstituted cyclopentadienyl ring.[73,74,120,167] The small number of oxygen electrophiles not affecting the ferrocene backbone or the questionable success of an Ullman-type coupling limits the use of ferrocenyl phosphine oxides[127,202] as starting materials for this approach, which has therefore not been realized yet. In contrast, intramolecular transformations, *e.g.* anionic hetero-Fries or Fries-like rearrangements, would allow the straightforward synthesis of such metallocenes; however, the scope of this reaction has been scarcely explored, as there are only three reports in ferrocene chemistry so far.[167,194,195] In principle, it should be possible to access 1,2-*P*,*O*-substituted ferrocenes exerting an *apFr* (Figure 3.1, path **C**), circumventing difficulties in the synthesis of these molecules via the *ortho*-directed metalation of ferrocenyl ethers.

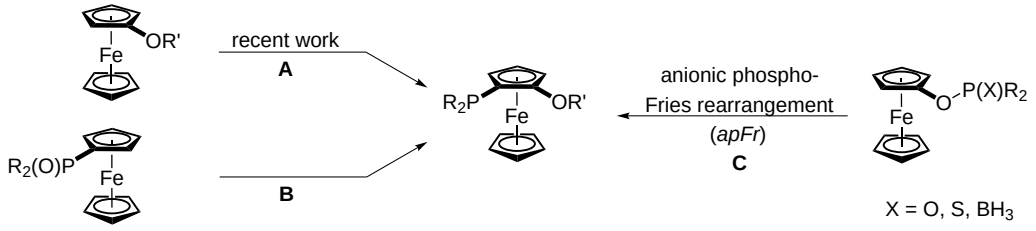


Figure 3.1 Different pathways for the synthesis of 1,2-*P*,*O*-substituted ferrocenes.

3.1.1 Suitable Starting Materials and Limitations

Oxygen-substituted ferrocenyl derivatives are most easily be obtained by reacting ferrocenol (**5**)[147] with electrophiles. The organometallic analogue of phenol is obtained by a four-step synthesis starting from ferrocene (**1**), which is converted to the stannyl-derivative **2** and reacted with iodine giving **3** (Figure 3.2).[147] A Cu(I)-mediated coupling in the presence of acetic acid results in the air and moisture stable acetate **4**. Final alkaline hydrolysis gives ferrocenol **5**, which gets oxidized rapidly under atmospheric conditions.[147] Thus, it was prepared under oxygen-free conditions and subsequently used for further reactions.

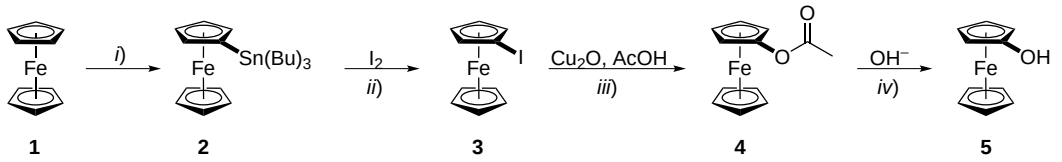


Figure 3.2 Synthesis of ferrocenol (**5**) starting from ferrocene.
Reaction conditions: *i*) ^{t}BuLi, 1 : 1 hexane/THF, 0 °C, ClSn(Bu); *ii*) I_2, CH_2Cl_2; *iii*) AcOH, Cu_2O, CH_3CN, reflux, 3 h; *iv*) KOHaq, EtOH/H_2O, reflux, 20 min, HClaq.

The ferrocenolato P(III) and P(V) compounds **6**–**15** were synthesized starting from ferrocenol (**5**) (Figure 3.3), which was reacted with the respective chlorophosphorus derivatives in the presence of triethylamine or BuLi (Figure 3.3). The ferrocenolato P(III) compounds were additionally either treated with BH_3·THF (**8**, **12** and **15**) or oxidized using H_2O_2 (**9**) or elemental sulfur (**7**, **10** and **13**), respectively. Except for the less electrophilic thio (**7**) and nitrogen containing derivatives (**12**, **14** and **15**), the products can typically be isolated in good to excellent yields. For the synthesis of phosphoramidate **14** the usage of BuLi is required for the deprotonation of **5**, otherwise no conversion was observed.

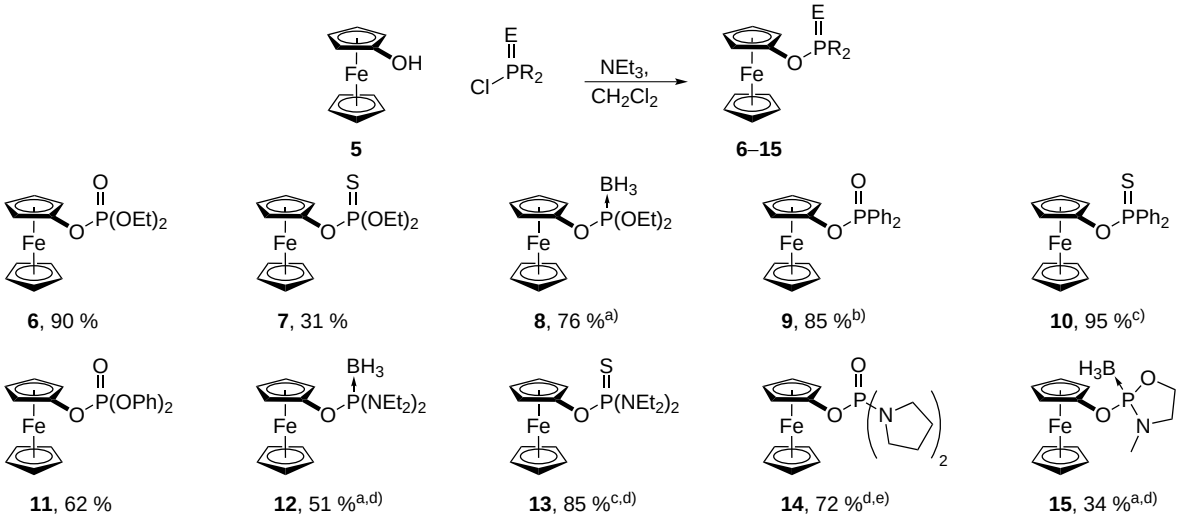
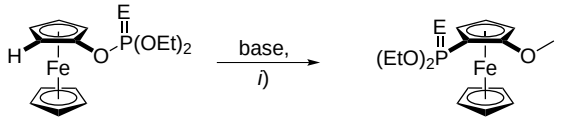


Figure 3.3 Reaction of ferrocenol (**5**) with different phosphorus electrophiles to afford **6**–**15**.
Reaction conditions: NEt_3, CH_2Cl_2, ambient temperature. Yields are based on **5**. a) BH_3·THF was added; b) H_2O_2 was added; c) S_8 was added; d) THF was used as the solvent; e) BuLi was used instead of NEt_3.

When a solution of phosphate **6** in tetrahydrofuran was treated at temperatures below –40 °C for 4 h with 2 equiv of freshly prepared LDA (lithium diisopropylamide) with subsequent addition of excess dimethyl sulfate, almost all starting material could be recovered, strongly indicating that no *ortho*-directed lithiation took place. At –30 °C, however, disubstituted ferrocene **16** could be isolated in 94 % yield as the only product (Figure 3.4).
The absences of phosphate **6** and an *ortho*-methylated ferrocene (**C**, Figure 2.65) indicate that the rate of the *apFr* is sufficiently high under these conditions.[176,187,188,198,203,204] Replacement of the P=O oxygen atom by a BH_3 protecting group decreases the yield for ferrocene **18** to 37 % (Figure 3.4). The recovery of only 31 % of the starting material may be due to

partial decomposition during the reaction. Thiophosphate **7** gives under these conditions only recovered starting material. If the stronger base ^{s}BuLi is used at –30 °C, however, thiophosphonate **17** can be isolated in 50 % yield (Figure 3.4). Running this reaction at 0 °C decreases the yield to 11 % (35 % recovered starting material). Replacement of LDA by the Simpkins base (+)-bis[(*R*)-1-phenylethyl]amine in the rearrangement of **6** resulted in a very low enantioenrichment (<5 % *ee*) of phosphonate **16**, as evinced by chiral HPLC (Experimental Section). This is in accordance with other *ortho*-directed lithiations at ferrocene, where a mere change of the base without further adoptions of the reaction conditions had only a small effect.[194,205]

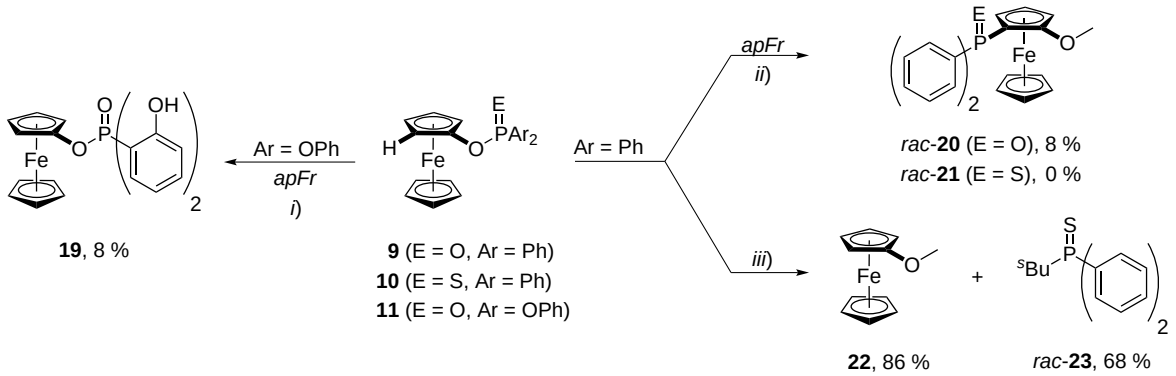


6 (E = O)
7 (E = S)
8 (E = BH_3)

rac-**16** (E = O), 94 %
rac-**17** (E = S), 50 %[a)]
rac-**18** (E = BH_3), 37 %

Figure 3.4 *ApFr* of phosphate **6**, thiophosphate **7** and borane adduct **8**.
Reaction conditions: LDA, THF, –30 °C, 4 h, Me_2SO_4 or MeI; a) ^{s}BuLi was used instead of LDA. Yields are based on **6**–**8**.

Replacing the ethoxy (**6**) by phenoxy substituents in ferrocenyl phosphonate **11** opens two different reaction pathways, as an *apFr* can take place at ferrocene and at the benzene rings (Figure 3.5). When phosphate **11** was treated with LDA at –40 °C, a double phospho-Fries rearrangement was observed at the two benzene moieties, and phosphinate **19** could be isolated in 8 % yield. Although further products were formed, as evinced by $^{31}P\{^{1}H\}$ NMR spectroscopy, no additional compound could be either isolated in pure form or identified. Based on this results, further investigations were performed (Section 3.1.3). Likewise, phosphinate **9** gave a complex product mixture when similar reaction conditions were applied (Figure 3.5), from which desired phosphine oxide **20** was isolated in 8 % yield. However, for this transformation partial nucleophilic attack of the base occurred at the phosphorus atoms, which results in the formation of ferrocenyl methyl ether (**22**; 16 %).



19, 8 %

9 (E = O, Ar = Ph)
10 (E = S, Ar = Ph)
11 (E = O, Ar = OPh)

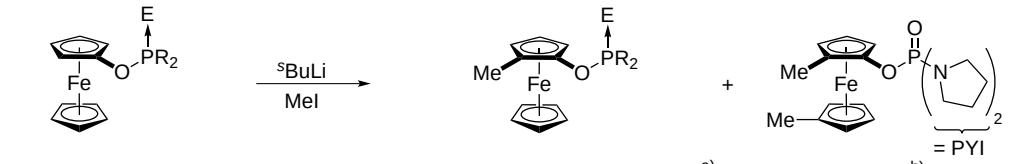
rac-**20** (E = O), 8 %
rac-**21** (E = S), 0 %

22, 86 %

rac-**23**, 68 %

Figure 3.5 *ApFr* of phosphinates **9** and **10**, and phosphate **11**.
Reaction conditions: *i*) LDA, THF, –40 °C, 4 h, MeI; *ii*) like *i*) at –30 °C; *iii*) ^{s}BuLi, –30 °C, 4 h, MeI. Yields are based on **9**–**11**.

In the case of the corresponding thiophosphinate **10**, LDA turned out to be a too weak base, as the starting material could be recovered completely. The stronger base ^{s}BuLi exclusively resulted in nucleophilic attack at the phosphorus atom, and hence only ferrocenyl methyl ether (**22**) and *sec*-butyldiphenylphosphane sulfide (**23**) were formed (Figure 3.5). The identity of**15** and **23** has *inter alia* been proven by single-crystal X-ray diffraction analysis (Figure 3.17).



12 (E = BH_3, R = NEt_2)
13 (E = S, R = NEt_2)
14 (E = O, R = PYI)

rac-**24** (E = BH_3, R = NEt_2), 64 %[a]
rac-**25** (E = S, R = NEt_2), 85 %[a]
rac-**26** (E = O, R = PYI), 64 %[b]
48 %[c]

rac-**27**, 3 %[b]
31 %[c]

Figure 3.6 Reaction of phosphoramidates **12**–**14** with ^{s}BuLi to afford *ortho*-methylated **24**–**27**.
Reaction conditions: a) THF, $\leq$ –10 °C, 3.5 h; b) hexane, ambient temperature, 18 h; c) Et_2O, $\leq$ –30 °C, 4 h. Yields are based on **12**–**14**.

Treatment of *N*-containing **12**–**15** with LDA and MeI did not result in the lithiation of these species and hence $> 80\%$ of the starting material could be recovered. The high basicity of the ferrocenyl backbone is caused by an increased electron density, due to the electron-donating *N*-bonded substituents, as it could be confirmed by electrochemical investigations (Table 3.8). Replacing LDA by the stronger base ^{s}BuLi allowed the synthesis of the *ortho*-methylated derivatives **24**–**27** (starting from **12**–**14**) (Figure 3.6).

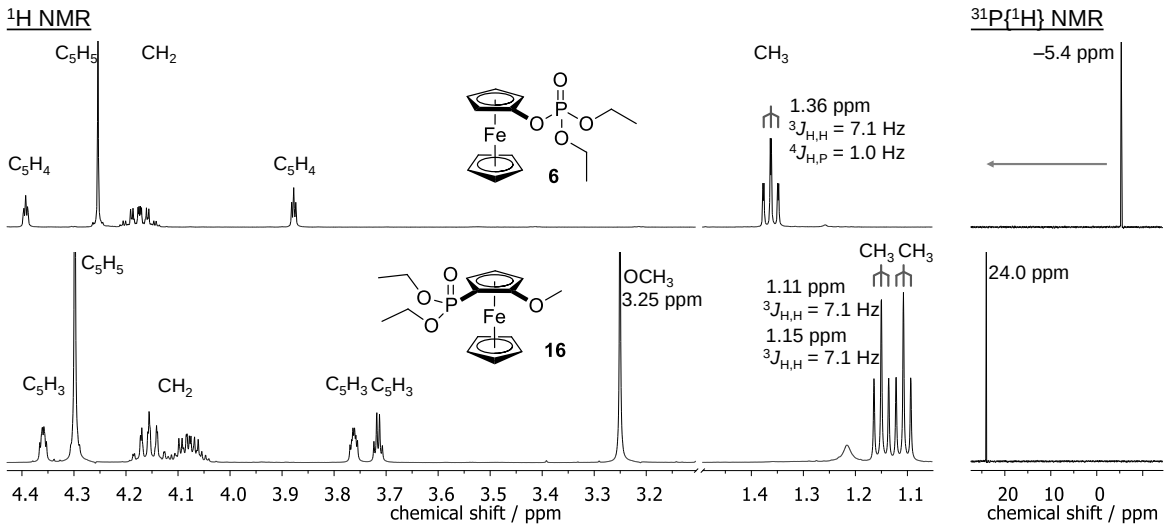


Figure 3.7 Comparison of selected parts of the ^{1}H (left) and ^{31}P{^{1}H} NMR spectra (right) of **6** (top) and its *apFr* product **16** (bottom).
Measurement conditions: 25 °C, $CDCl_3$ (**6** and ^{31}P{^{1}H} NMR of **16**) or C_6D_6 (^{1}H NMR of **16**).

Within these reactions, lithiation occurred in *ortho*-position, whereby the lithium ion is sta-

bilized by the oxygen atom of the ferrocenyl entity. An involvement of the P→E moiety is possible for E = O and S, however, in case of the borane adduct **25** (E = BH_3) it failed. Nevertheless, the *ortho*-methylated species **24**–**27** could not be separated from their starting materials **12**–**15**, due to their similar properties within the column chromatographic workup. However, they could be identified by inter alia ^{1}H and $^{13}C^{1}H$ NMR spectroscopy and are highlighted in Figure 3.7 and 3.8.

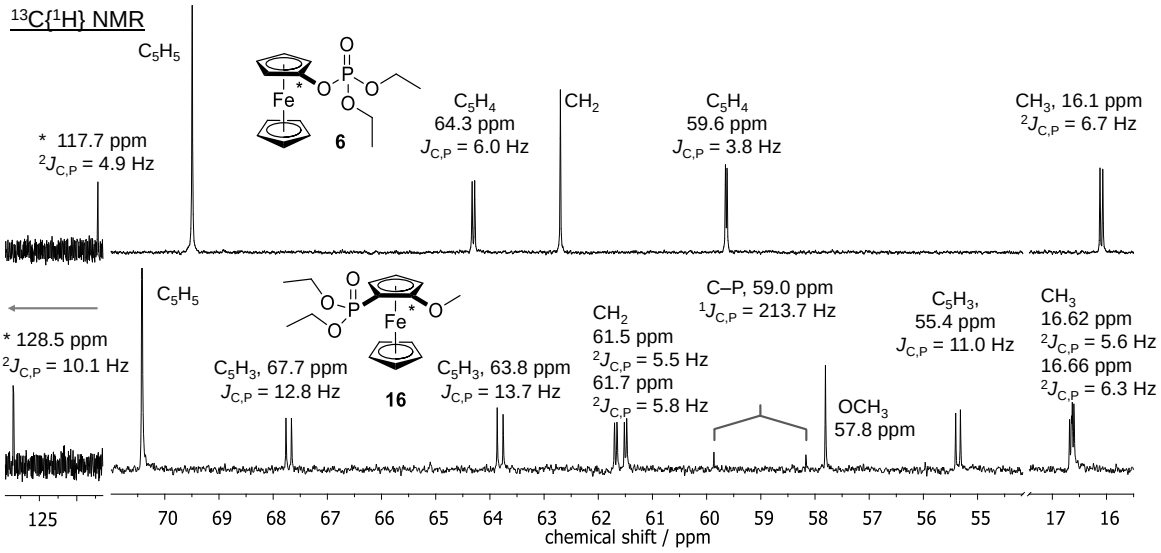


Figure 3.8 Comparison of selected parts of the $^{13}C\{^{1}H\}$ NMR spectra of **6** (top) and its *apFr* product **16** (bottom).
Measurement conditions: 25 °C, $CDCl_3$ (**6** and the left part of the $^{13}C\{^{1}H\}$ NMR of **16**) or C_6D_6 (right part of the $^{13}C\{^{1}H\}$ NMR of **16**).

The lithiation behavior strongly depends on the solvent applied, as it could be shown for pyrrolidine containing **14**. Thus, running the reaction in hexane gave **26** in a mixture along with **14** and **27** of ratio 1 : 0.24 :< 0.05, whereas in diethyl ether a ratio of 1 : 0.06 : 0.65 is characteristic, due to the increased reactivity of ^{s}BuLi. The methyl group should be substituted in *ortho*-position to the oxygen atom (1,2-subsitution), due to a stabilization of the lithium ion, as found for derivatives possessing a Fc–P bond.[206,207] To the best of our knowledge, 1,3-disubstituted products can merely be obtained by multiple step lithiations including reactions with electrophiles,[208] or were formed in a negligible yield compared to the 1,2-main product.[209] Hence, a 1,3-substitution pattern is rather expected for electrophilic aromatic substitution reactions and not for lithiation reactions as depicted in Figure 3.6.[210] The distinction between *apFr*-derived, *e.g.* **16**–**18**, and *non*-rearranged-methylated products **24**–**27** could be unambiguously proven using NMR spectroscopy. For *apFr*-derived products, on the one hand, the resonance in the $^{31}P^{1}H$ NMR spectra are shifted downfield from –5.4 (**6**), 63.8 (**7**), and 128.2 ppm (**8**) to 36.4 (**16**), 89.6 (**17**), and 135.4 ppm (**18**), respectively. Additionally, a singlet for the methoxy groups was observed at ∼ 3.5 ppm (**16**–**18**) in the ^{1}H NMR spectra (Figure 3.7). Due to the established planar chirality at ferrocene the two ethoxy moieties become diastereotopic, resulting in a doubling of all their resonances in ^{1}H and $^{13}C^{1}H$ NMR spectra, respectively (Figure 3.7).

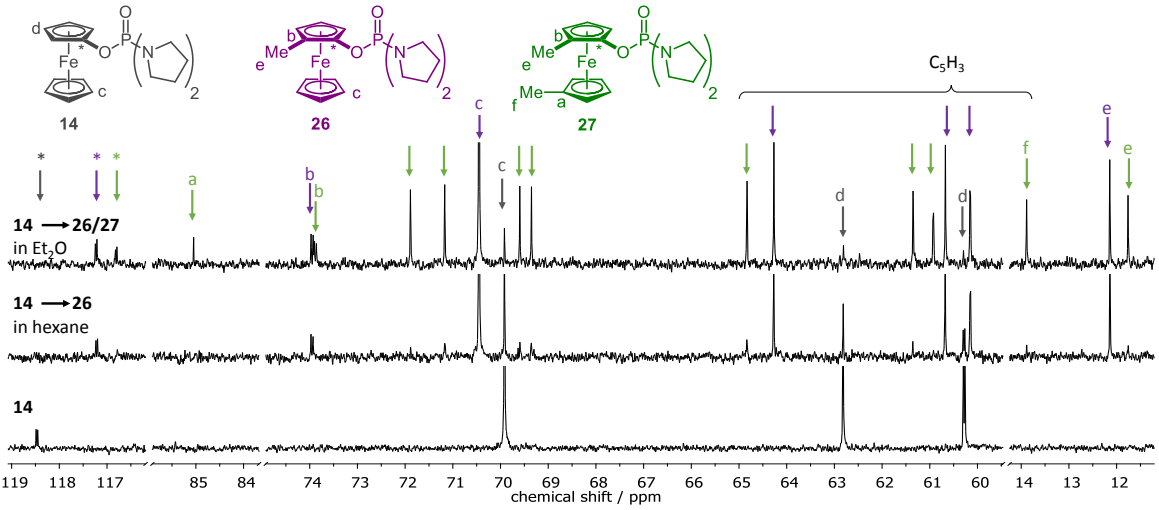


Figure 3.9 Comparison of selected parts of the $^{13}C\{^1H\}$ NMR spectra of **14** (bottom) and its methylated derivatives **26** (middle) and **27** (top). Measurement conditions: 25 °C, C_6D_6

The C–P *ipso*-carbon atom gives a doublet in the $^{13}C^1H$ NMR spectra at 59.2 ppm with a large $^1J_{C,P}$ coupling constant of 213 Hz (**16**), in agreement with the values for similar compounds (Figure 3.8).[211] While the *apFr* occurred, a singlet for the methoxy groups could be observed at ∼58 ppm and the attached *ipso*-carbon is shifted downfield from 118 (**6**) to 129 ppm (**16**). The presence of the phosphorus atom attache at the cyclopentadienyl increased the $J_{C,P}$ couplings from 4–7 to 11–14 Hz (Figure 3.8).
For methylated ferrocenes **24**–**27**, where no *apFr* occurred, the methylation could be identified besides the presence of starting material (18 % of **12** for **24**, 7 % of **13** for **25**, and 6 % of **14** for **26** and **27**, Figure 3.9). The methyl groups were observed at ∼2 ppm in the ^1H and at ∼12 ppm in the $^{13}C\{^1H\}$ NMR spectra, which are characteristic, *e.g.*, for methylferrocene.[212] The CH_3-bonded *ipso*-carbons of the cyclopentadienyls showed resonances between 74 and 75 ppm. For the 2,1'-functionalized ferrocene **27** the additional methyl group in 1'-position was observed at 13.9 ppm. The respective *ipso*-carbon of the cyclopentadienyls occurred at 85.0 ppm. The ^{11}B NMR values for the borane adducts **12**, **15** and **24** slightly differ between the $(NEt_2)_2$-functionalized compounds **12** and **24** with –39.5 ppm and the cyclic 2-aminoethanol containing species **15** (–42.6 ppm). The appropriate signals appear as doublets with a $^1J_{B,P}$ coupling constant of ∼90 Hz.

3.1.2 Chiral Pool derived Ferrocenyl Phosphates

The *apFr* of a *non*-chiral ferrocenyl phosphate (**6**) in the presence of a chiral base did not result in an enantiomerically enriched rearrangement product (Section 3.1.1).[137,194,205,213] Therefore, a diastereoselective procedure is needed, with the chiral information present in the starting phosphates. The known procedures for the synthesis of (chiral) chlorophosphates are based on the reaction of the respective alcohols in the presence of a base, such as triethylamine or pyridine, and subsequent filtration and distillation of the product mixture.[214,215] Thus,

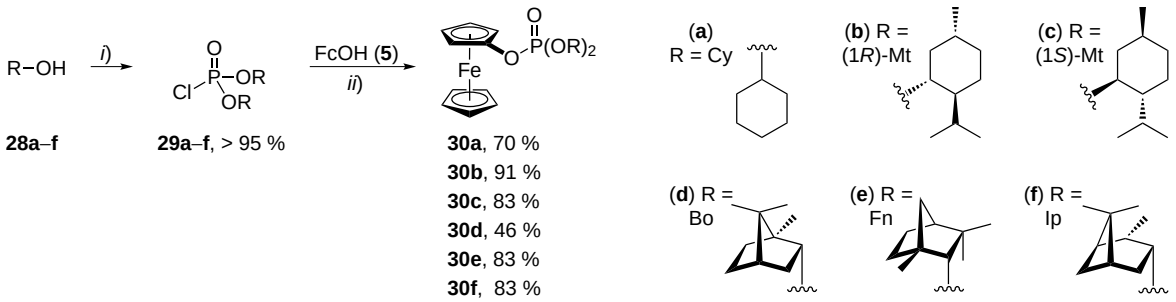


Figure 3.10 Synthesis of chiral pool derived dialkylchlorophosphates **29a**–**f** and their conversion to ferrocenyl phosphates **30a**–**f**.
Reaction conditions: *i*) Et_2O, BuLi, $POCl_3$ (0.5 equiv); *ii*) Et_2O, **5**, BuLi, –30 °C, **29a**–**f**. Yields are based on **5**.

the applied purification process results in a lower yield of the (di)chlorophosphates and high amounts of ammonium salts.

Thus, the reported procedure were amended into a straightforward, high-yielding synthetic protocol including lithiation of cyclohexyl (**28a**, Cy), (1*R*)-menthyl (**28b**, (1*R*)-Mt), (1*S*)-menthyl (**28c**, (1*S*)-Mt), (1*S*)-borneyl (**28d**, Bo), (1*R*)-α-fenchyl (**28e**, Fn) and (1*S*)-isopinocampheyl alcohols (**28f**, Ip) in diethyl ether as the solvent at 0 °C and subsequent addition of $POCl_3$ (Figure 3.10).

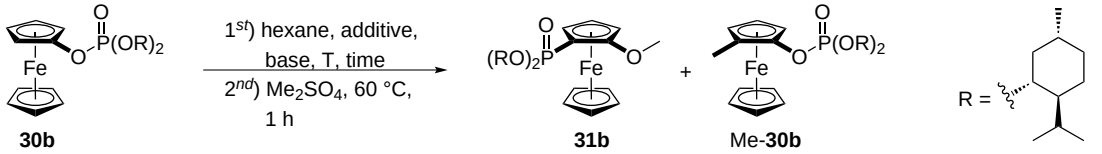
After removal of any lithium salt by simple filtration over Celite, the respective chlorophosphates **29a**–**f** were obtained in quantitative yields without the need for further purification (Experimental Section). Conversion of **29a**–**f** to the ferrocenyl phosphates **30a**–**f** was realized by the deprotonation of ferrocenol (**5**) using BuLi and subsequent treatment **5**-Li with the chlorophosphates **29a**–**f** (Figure 3.10). After the appropriate workup, ferrocenes **30a**–**f** could be isolated in good to excellent yields.

However, the *apFr* of **30a**–**f** does not proceed under the reaction conditions which we have reported recently for short-chain diethyl phosphate (Section 3.1.1). Low yields obtained in the temperature range from –30 to 0 °C and the beginning of ether cleavage at higher temperatures prompted us to use nonpolar instead of polar solvents. The required activity of the lithium base can be enabled by addition of a diamine such as TMEDA (tetramethylethylenediamine) or the chiral (–)-Sparteine (=(–)-Spart) (Table 3.1).

Using the optimized reaction conditions (hexane, diamine, base, ambient temperature, 18 h) from Table 3.1, the desired rearrangement products could be obtained in good to quantitative yields (Table 3.2). It should be noted that the sterically more demanding aliphatic substituents, in comparison to ethyl groups, stabilize all phosphates as well as all further products toward hydrolysis and, hence, these compounds can be handled in air and moisture for several weeks without a notable rate of decomposition.

The kinetically controlled lithiation of ferrocenyl phosphates **30a**–**f** resulted in a diastereomeric excess during the *apFr* that depends on the demand of the aliphatic substituents (Table 3.1). Therefore, the fenchyl derivative **31e** exhibits with 80 % the highest *de*, due to the three methyl groups located closer to the oxygen-bonded carbon in comparison with the other chiral pool alcohols. The *de* of the rearrangement products **31a**–**f** can easily be

Table 3.1 Optimization of the reaction conditions for the *apFr* of *chiral pool* derived ferrocenyl phosphate **30b**.



Entry	Base	equiv	T / °C	Additive	Solvent (time / h)	Yield / %[a] **30b**	**31b**	Me-**30b**
1	LDA	3	–20	–	THF (4)	60	19	–
2	LDA	1.3	–5	–	THF (4)	38	15	–
3	LDA	3	0	–	THF (4)	50	–	–
4	^{s}BuLi	1	0	–	Et_2O (2)	7	–	22
5	LDA[b]	2	–10	–	THF (3)	71	–	24
6	^{s}BuLi	2	0	–	Et_2O (3)	–	40	–
7	LDA	2	–78 to 25	TMEDA	hexane (18)	–	63	–
8	^{s}BuLi	2	25	–	TBME[c](4)	91	–	–
9	LDA	2	25	TMEDA	hexane (18)	–	99[d]	–
10	LiTMP	2	25	TMEDA	hexane (18)	–	99[d]	–

[a] The yields were determined from $^{31}P\{^1H\}$ and ^1H NMR spectra of the mixture.
[b] 2 *M* solution in Et_2O.
[c] *tert*-butyl methyl ether.
[d] Isolated yields.

obtained by the integration of fitted signals in the $^{31}P\{^1H\}$ NMR spectra (Table 3.2) and is further influenced by the required diamine and the base. Instead of LDA the use of the sterically more demanding base LiTMP (=lithium tetramethyl piperidide) resulted in an increase of the *de* for **31e** from 0.72 (LDA) to 0.80 (LiTMP).

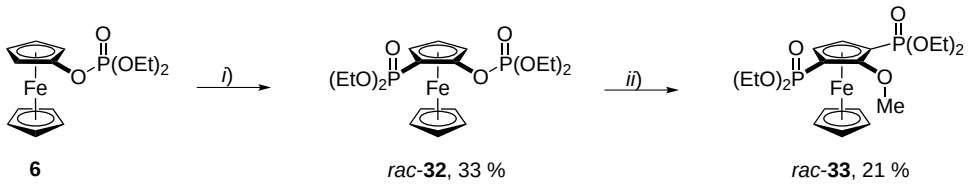
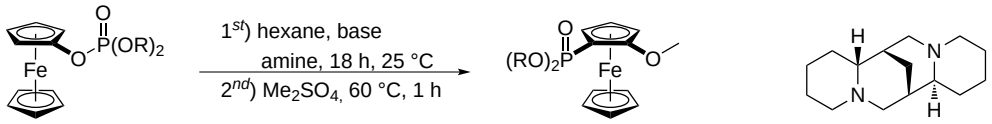


Figure 3.11 Conversion of **6** to *ortho*-phosphonato ferrocenyl phosphate *rac*-**32** and consecutive *apFr*.
Reaction conditions: *i*) LDA, THF, –20 °C, 4 h, $ClP(O)(OEt)_2$. Yield based on **6**; *ii*) LDA, THF, –30 °C, 4 h, MeI. Yield based on *rac*-**32**.

Recrystallization of **31e** further improved the *de* to 90 %, which confirms the fenchyl substituent to be the most appropriate for establishing diastereomerically enriched products. However, when the diamine from the achiral TMEDA is changed to the chiral (–)-Sparteine, no further positive influence on the *de* of **31e** was observed. Interestingly, when (–)-Sparteine is used for the rearrangement of the (1*R*)- and (1*S*)-menthyl phosphates **30b**,**c**, a double stereo differentiation is not detectable, due to an enhanced **de** for both of the phosphonates **31b**,**c** (Table 3.2). However, a mismatch situation occurred for **31d**–**f**, in which (–)-Sparteine is not beneficial for the stereoselectivity.

Table 3.2 Optimization of the diastereoselective proceeding for the *apFr* of *chiral pool* derived ferrocenyl phosphates **30a**–**f**.



30a–f **31a–f**

Entry	Educt	R	Base	Amine	Yield[a]	*de*[b]
1	**30a**	cyclohexyl (Cy)	LDA	TMEDA	70 %	–
2	**30b**	(1*R*)-Mt (**b**)	LDA	TMEDA	99 %	0.29
3	**30b**		LDA	(–)-Spart	99 %	0.40
4	**30b**		LiTMP	(–)-Spart	99 %	0.00
5	**30c**	(1*S*)-Mt (**c**)	LDA	TMEDA	90 %	0.24
6	**30c**		LDA	(–)-Spart	99 %	0.38
7	**30c**		LiTMP	TMEDA	87 %	0.37
8	**30c**		LiTMP	(–)-Spart	89 %	0.00
9	**30d**	Bo (**d**)	LDA	TMEDA	80 %	0.38
10	**30d**		LDA	(–)-Spart	99 %	0.32
11	**30e**	Fn (**e**)	LDA	TMEDA	29 %	0.72
12	**30e**		LDA	(–)-Spart	79 %	0.58
13	**30e**		LiTMP	TMEDA	65 %	0.80
14	**30e**					0.90[c]
15	**30f**	Ip (**f**)	LDA	TMEDA	57 %	0.40
16	**30f**		LDA	(–)-Spart	72 %	0.30
17	**30f**		LiTMP	TMEDA	58 %	0.27
18	**30f**		LiTMP	(–)-Spart	80 %	0.13

[a] Yields refer to isolated compounds with respect to the starting ferrocenyl derivative.
[b] The values are based on the integrals of fitted signals of $^{31}P\{^{1}H\}$ NMR spectra.
[c] After single recrystallization.

After the *apFr*, the resulting hydroxy functionality is not limited to react with dimethyl sulfate, which allows for two subsequent rearrangements. Subsequent addition of diethyl chlorophosphate to the intermediate of the reaction of phosphate **6** with LDA gave ferrocene **32** (Figure 3.11). Both transformations proceeded as expected; no further ferrocene compounds could be identified. The considerably lower yields in comparison to that for the synthesis of **17** (Figure 3.4) are due to the lower stabilities of **32** and **33**; partial decomposition has been observed for both compounds even after purification. It is interesting to note that the conversion of ferrocene **32** into bisphosphonate **33** clearly simplified the NMR spectra, due to the higher symmetry of the latter compound.

In contrast to the simple OEt substituents, with the sterically more demanding alkyl groups a limitation in reactivity might occur and, thus, chlorodiphenylphosphine for the synthesis of **34** and chlorophosphates **35a**–**c** have been investigated, showing good (**35a**–**c**) to acceptable (**34**) yields (Figure 3.12). A further enhancement of the *de* of the formed 1,2-*P*,*O* ferrocene was achieved by adding a chiral chlorophosphate, which was investigated during the reaction of the fenchyl derivative **31e** by adding the respective fenchyl chlorophosphate **29e** (Figure

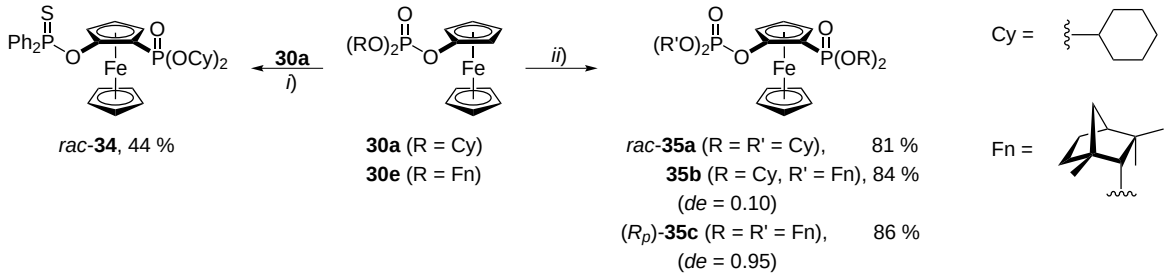


Figure 3.12 Oxygen functionalization after the *apFr* of **30a**,**e**.
Reaction conditions: *i*) LDA, hexane, TMEDA, $ClPPh_2$, S_8, 25 °C, 18 h, 60 °C, 1 h. Yield based on **30a**; *ii*) **30a**: LDA, hexane, TMEDA, **29a** for *rac*-**35a** and **29e** for **35b**, 25 °C, 18 h, 60 °C, 1 h; **30b**: LiTMP, hexane, TMEDA, **29e**, 25 °C, 18 h, 60 °C, 1 h. Yields are based on **30a** or **30e**.

3.12). The resulting 2-phosphato ferrocenyl phosphonate **35c** could be obtained with a *de* of 95 %, due to a kinetically controlled phosphate formation. With the addition of Me_2SO_4, 10 % of **31e** could be isolated with a *de* of 68 %. Reaction of nonchiral **30a** with chiral **29e** also resulted in the diastereomerically enriched phosphate **35b** (10 % *de*), revealing the chirality of the chlorophosphates to be the main reason for the kinetic phosphate formation. Single crystals of **31e** and **35c** exhibited the presence of the (R_p) diastereomer in both cases (Figure 3.19), which therefore is assumed to be the mainly formed diastereomer during the rearrangement.

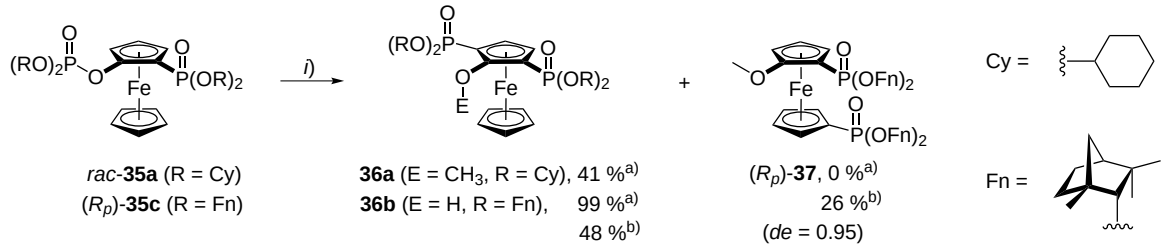


Figure 3.13 Consecutive *apFr* of *ortho*-phosphonato ferrocenyl phosphates *rac*-**35a** and (R_p)-**35c** to bis-phosphonates **36a**,**b** and the 1,1'-derivative (R_p)-**37**.
Reaction conditions: *i*) base, TMEDA, hexane, 18 h, 25 °C, Me_2SO_4, 60 °C, 1 h. Yields are based on the ferrocenyl starting material; a) LDA as the base; b) LiTMP as the base.

Similar to the diethyl derivative **32** (Figure 3.11), the 2-phosphato phosphonates **35a**,**c** can undergo a further *apFr* (Figure 3.13). Using LDA as the base, bis(phosphonates) **36a**,**b** were formed in acceptable (**36a**) to quantitative (**36b**) yields. Interestingly, the OH functionality in **36b** cannot be converted into the respective methyl ether, even using an excess of methyl sulfate at 60 °C giving a singlet for the OH functionality at 7.60 ppm in the ^1H NMR. Bis(phosphonato) hydroxyferrocene **36b** is stable toward air and moisture and is most probably stabilized by intramolecular hydrogen bridge bond formation to the phosphonato oxygen atoms.[186,216] When the base is changed from LDA to LiTMP, the increased steric demand significantly lowered the yield of **36b** from 99 to 48 %. Additionally, the formation of **37** is observed with the phosphonato substituents located at the 1,1'-positions and the *de* remaining at 95 %, based on the *de* of the starting material **35c**, which was also obtained in 11 % (95 % *de*) after the reaction. The lithiation exclusively occurred *ortho* to the phosphate

and not to the phosphonate substituent, due to the absence of any *ortho*-methylated product, which indicates a less attractive stabilization of the phosphonato in comparison to the phosphato substituent.

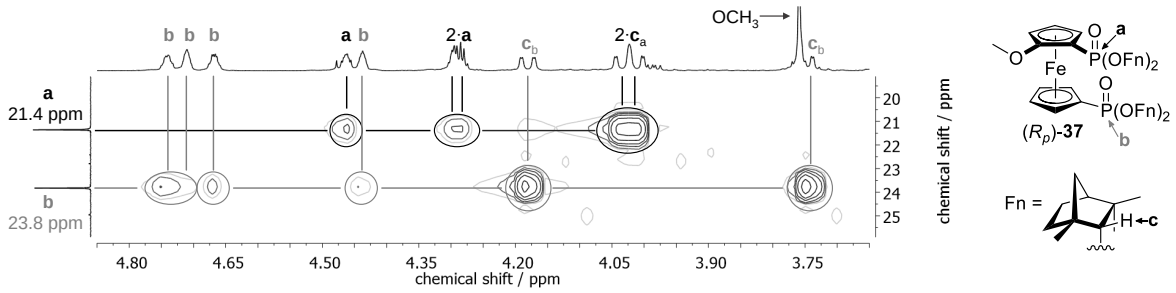
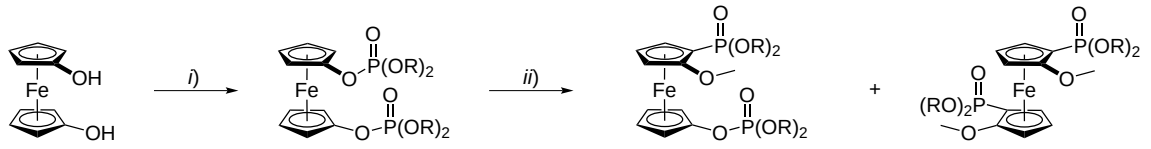


Figure 3.14 ^{1}H-^{31}P–2D NMR spectra of **37** ($CDCl_3$, 25 °C).

The verification of the 1,1'-substitution pattern in the unexpectedly formed bis(phosphonate) **37** in comparison to bis(phosphonate) **36b** (Figure 3.13) is indicated by the absence of the C_5H_5 signal in the ^{1}H and in the ^{13}C{^{1}H} NMR spectra and the appearance of the ^{31}P{^{1}H} resonances as singlets at 21.3 and 23.8 ppm, in comparison with **36b**, where doublets for both signals (21.3 and 25.8 ppm; $^{3}J_{P,P} = 3.7$ Hz) are characteristic. Additional 2D ^{1}H-^{31}P/ experiments allowed the assignment of three (21.3 ppm) and four (23.8 ppm) ^{1}H signals to the respective phosphorus resonance (Figure 3.14).



38

39a (R = Cy), 59 %
39b (R = Fn), 28 %
39c (R = Et), 60 %

40a (R = Cy), 0 %
(*R*$_p$)-**40b** (R = Fn), 18 %
de = 0.84
40c (R = Et), 0 %

41a (R = Cy), 67 %
1.3 : 1
racemic : *meso*
41b (R = Fn), 0 %
41c (R = Et), 0 %

Figure 3.15 Synthesis and *apFr* of 1,1'-functionalized ferrocenyl phosphates **39a-c** to phosphonates **40a-c** and **41a-c**.
Reaction conditions: *i*) **39a**: hexane, BuLi, **29a**, 12 h, 60 °C, 4 h; **39b**: THF, BuLi, **29e**, 12 h, 80 °C, 12 h; **39c**: CH_2Cl_2, NEt_3, $ClP(O)(OEt)_2$, –20 °C; *ii*) LDA (R = Cy), LiTMP (R = Fn), TMEDA, hexane, 25 °C, 18 h, Me_2SO_4, 50 °C, 1 h; for **39c**: LDA, THF, –30 °C, Me_2SO_4. Yields are based on the ferrocenyl starting material.

Using the 1,1'-ferrocenediol (**38**) allowed for the synthesis of bisphosphates **39a**–**c** (Figure 3.15). The low yields of up to 60 % for **39c** are due to the rapid decomposition of $Fc(OH)_2$. However, the presence of the sterically more demanding (bi)cyclic alcohols increased the stability of phosphates in **39a**,**b** compared to the ethyl derivative **39c**. However, the increased steric demand required stirring in hexane (**39a**, 4 h, 60 °C bath temperature) or THF (**39b**, 12 h, 80 °C bath temperature) to complete the reaction of both hydroxyl moieties with the chlorophosphates to **39a**,**b** (Figure 3.15). The *apFr* of cyclohexyl-substituted **39a** proceeded to the expected doublerearranged product **41a** as a mixture of both diastereomers with a *de* of 13 %. Obviously, the lithiation of the C_5H_4 cycle is influenced by the configuration established

at the first cyclopentadienyl ring. Using the reaction protocol for diastereomerically enriched fenchyl derivatives (Figure 3.2), a slight increase of the *de* (84 %) of **40b** in comparison to that for singly substituted **31e** (80 %) could be detected (Figure 3.15). Nevertheless, the rearrangement product containing phosphonates at both cyclopentadienyls (**41b**) could not be obtained for the fenchyl substituent during this reaction. This is attributed to the steric demand of the chiral fenchyl substituents or an unfavorable stabilization of the lithiated species, which prevents the rearrangement to **41b**. When the reaction conditions for ethyl phosphates (LDA, THF, –30 °C) were applied for the rearrangement of **39c** a complex mixture of several phosphorus-containing molecules was obtained, from which no product could be identified or isolated in pure form, due to their rapid decomposition.

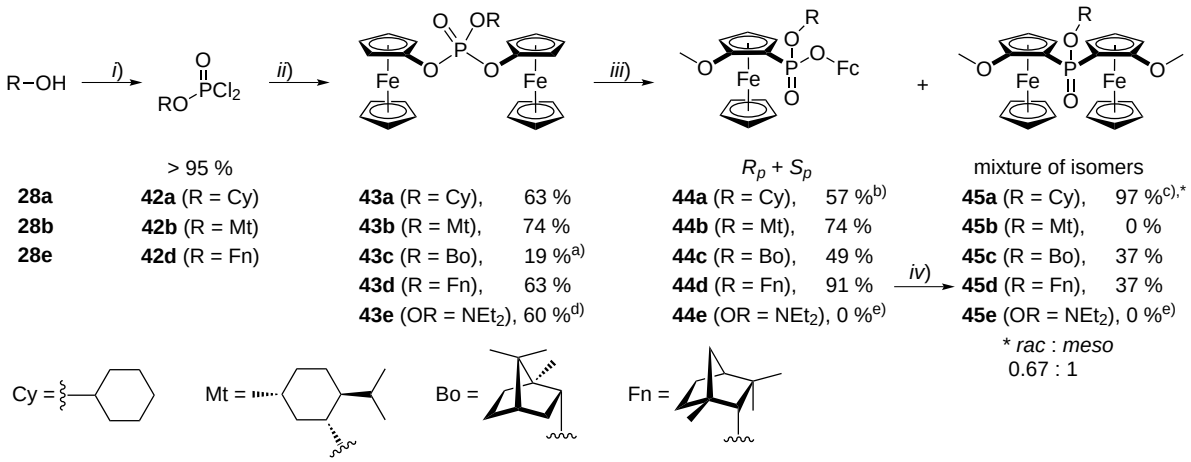


Figure 3.16 Synthesis and *apFr* of *chiral pool* diferrocenyl phosphates **43b-d**.
Reaction conditions: *i*) Et_2O, BuLi, > 3 equiv of $POCl_3$, 25 °C, 18 h; *ii*) Et_2O, BuLi, **5**, **42a**,**b**,**d**, 25 °C, 18 h. Yields are based on **5**; *iii*) hexane, TMEDA, LDA (**43a**–**c**), LiTMP (**43d**), 18 h, Me_2SO_4, 60 °C, 1 h. Yields for **44a**–**d** and **45a**–**c**are based on **43a**–**d**; *vi*) hexane, TMEDA, LDA, 18 h, Me_2SO_4, 60 °C, 1 h. The yield is based on **44d**; a) Obtained within the synthesis of **30d**; b) Using 2 equiv of LDA; c) Using > 8 equiv of LDA. d) The compound was obtained by reacting **5**, NEt_2, $ClP(NEt_2)_2$ followed by the addition ^{t}BuOOH. Yield based on **5**. e) Reaction of **43e** with LDA and MeI in THF gave the starting material.

In addition to a single *apFr* at one aryl or ferrocenyl substituent, simultaneous rearrangements are possible by replacing one alkyl by a ferrocenyl substituent. For ferrocenyls, the simultaneous formation of two planar chiral ferrocene backbones should be possible. With the chiral pool alcohols **28a**,**b**,**d**,**e** as starting materials, the dichlorophosphates **42a**,**b**,**d** were synthesized in a more simple *one-pot* approach, in comparison to literature methodologies[214] (Figure 3.16), including deprotonation of the alcohols **28a**,**b**,**d**,**e** and dropwise addition of the formed alcoholates to an excess (> 3 equiv) of $POCl_3$. After removal of all volatiles dichlorophosphates **42a**,**b**,**d** were obtained as pure colorless oils in quantitative yields, avoiding the need for further purification. The alkyl diferrocenyl phosphates **43a**–**d** are accessible by reacting **42a**–**d** with deprotonated FcOLi (**5**–Li) (Figure 3.16), whereas borneyl derivative **43c** was obtained as a side product during the synthesis of **30d**. As described in Section 3.1.1, the $^{31}P\{^1H\}$ NMR shift is a meaningful indication of a successful conversion of chlorophosphates **29** and **42** (2 to 8 ppm) to mono-ferrocenyl phosphates **30** (–4 to –7 ppm) and diferrocenyl phosphates **43** (–9 to –11 ppm). Applying phosphates **43** in

subsequent *apFr* primarily yielded the monorearranged phosphonates **44a**–**d**, as mixtures of the two possible isomers with regard to the planar chirality. For **44b**–**d** four diastereomers were formed, due to the asymmetrically substituted phosphorus atom, whereas **44a** can be obtained as a mixture of two diastereomers (45 % *de*) (Table 3.3), which indicates that the positions at the prochiral ferrocenes in the achiral phosphate are kinetically not equal. Thus, a stereoselective *apFr* is possible without a further chiral input. The second rearrangement to phosphinates **45a**–**d** is only observed in low yields. Nevertheless, when the amount of base (> 8 equiv) is increased for the nonchiral cyclohexyl-substituted **43a**, a quantitative conversion to the *meso* and the *racemic* isomers was achieved. After their separation, the *meso* product is obtained as the main diastereomer (20 % *de*). The distinction between the *racemic* (R_p,R_p/S_p,S_p) and the *meso* (R_p,S_p,R^P/R_p,S_p,S^P) is possible by comparing their NMR spectra. The pseudochiral phosphorus atom in *meso*-**45b** caused two sets of signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra, whereas for the *racemic* isomers one set of signals is observed.

Table 3.3 Integral ratios for **44a**–**d** and **45a**–**d**.[a]

	R	Area ratio of **44**[b]	*de*	Area ratio of **45**[b]	*de*
a	Cyclohexyl	1 : 0.38	0.45	–[c]	–[c]
				0.98 : 1[d,e]	0[d]
b	(1*R*)-Menthyl	0.41 : 0.29 : 1 : 0.19	–	–[f]	–
c	Borneyl	1 : 0.07 : 0.90 : 0.07	–	1 : 1	0[e]
d	Fenchyl	1 : 0.45 : 0.36 : 0.86[g]	–	1 : 0.18 : 0.06 : 0.39	–
d	Fenchyl	1 : 0.29 : 0.47 : 0.19[h]	–		
d	Fenchyl	0.64 : 1 : 0.09 : 0.50[i]	–		

[a] The reaction conditions refer to those depicted in Figure 3.16.
[b] The ratio of the integrals of fitted ^{31}P{^{1}H} NMR spectra is reported from downfield (left) to highfield (right). and ^{1}H NMR spectra of the mixture.
[c] *Racem* compound.
[d] *Meso* compound.
[e] Areas of fitted ^{1}H NMR spectra of the C_5H_5 signals were used.
[f] Not formed
[g] 2 Equiv of LiTMP were used as the base.
[h] 4 Equiv of LiTMP were used as the base.
[i] LDA was used as the base.

Attempts to obtain **45d** by a similar approach failed, resulting in an almost quantitative formation of **44d**. However, lithiation of **44d** resulted in the formation of the desired phosphinate **45d**. With regard to the stereoselectivity of the rearrangement, the decreased number of chiral substituents produced an unspecific mixture of isomers for **44b**–**d** and **45b**–**d** (Table 3.3). For **44d** the influence of the amount of the base was examined (Table 3.3), showing only a slight change in the integrals of the signals. However, when the base was changed from LiTMP to LDA a significant change of the integral of each signal in the ^{31}P{^{1}H} NMR was observed, but with none of the diastereomers formed primarily. Borneyl derivative **45c**, however, only resulted in the formation of two diastereomers instead of four, indicating a high stereoselectivity for one rearrangement. The disfavored formation of phosphinates **45a**–**d** as well as the decreased diastereoselectivity can both be explained by the fact that *apFr*, in gen-

eral, are favored for electron-poor compounds,[193,205] such as phosphates, which prevent the nucleophilic attack at the phosphorus atom, due to the higher acidity of the ferrocenyl protons. The rearrangement products **44a**–**d** are more electron rich in comparison to phosphates **43a**–**d**, due to the ferrocenyl substituent. Furthermore, the lithium ion is well stabilized by the hydroxy oxygen and the P=O moiety,[216] and a further lithiation is less desirable.
The distinction between phosphonates **44a**–**d** (19 to 22 ppm) and phosphinates **45a**–**d** (34 to 38 ppm) is also rather simple by comparing with the chemical shifts of phosphonates **31a**–**f** and **36a**–**c** (20 to 23 ppm for **31**; 20 to 26 ppm for **36**), due to the formation of up to four diastereomers. The mentioned $^{1}J_{C,P}$ coupling constant of the ferrocenyl C–P bond in Section 3.1.1, decreased from 217 Hz for phosphonates to 160 Hz for the more electron rich phosphinates **45a**–**d**.

Solid State Structures

The molecular structures of **15**, **23**, **30a**,**b**,**e**, **31e**, **35c**, **43b**,**e**, and **44a**,**c**,**d** in the solid state have been determined by single-crystal X-Ray diffraction analysis (Figures 3.17, 3.18, 3.19 and 3.20).

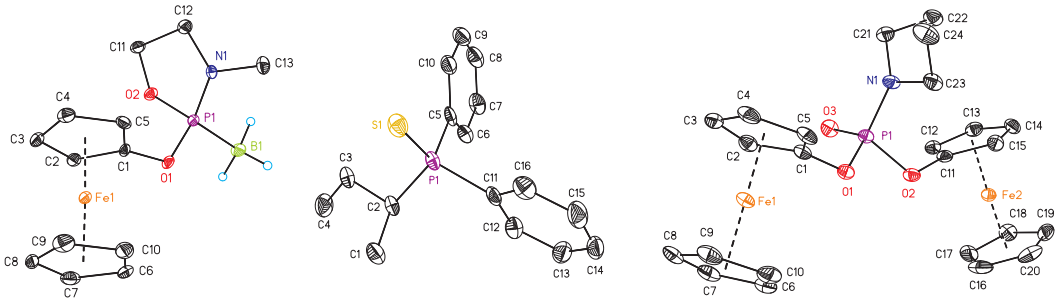


Figure 3.17 ORTEP (50 % probability level) of the molecular structures of **15** (left), **23** (middle) and **43e** (right) with the atom-numbering Scheme. All C-bonded hydrogen atoms and a second molecule in the asymmetric units of **23** have been omitted for clarity.
Selected bond lengths (Å): **15**, P–BH_3 = 1.881(5), P–N = 1.639(3); **23**, P=S = 1.9592(13); **43e**, P=O 1.463(2), P–N = 1.625(2).

Suitable crystals were obtained by different methods, *e.g.*, crystallization from hexane solutions at ambient temperature (Experimental Section). Non-chiral compounds crystallized in the centrosymmetric triclinic ($P\bar{1}$, **23**), monoclinic ($P2_1/c$, **30a** and **43a**; $C2/c$, **43e**), and orthorhombic ($Pbca$, **15**) space groups, whereas the chiral substituents lead to the chiral Sohncke space groups[217,218] $P1$ (**30e**), $P2_12_12_1$ (**30b**, **31e**), $P2_1$ (**43b**, **44c**,**d**), and $C2$ (**35c**). Compounds **23**, **30e**, **35c**, and **44c**,**d** are present with two molecules in the asymmetric unit, instead of one. Thus, the absolute configuration for **31e** and **35c** could be determined as the R_p diastereomer (Figures 3.19), whereas for **44c**,**d** a mixture of the R_p,S^P and the S_p,R^P diastereomers emerges (Figure 3.20). The methyl and further O-bonded substituents in the doubly substituted ferrocenes **31e**, **35c**, and **44a**,**c**,**d** are consequently directed away from the remaining free electron pairs in the vacant space between these two substituents. Interestingly, in cyclohexyl phosphonate **44a** an unfavorable axial conformation is observed,

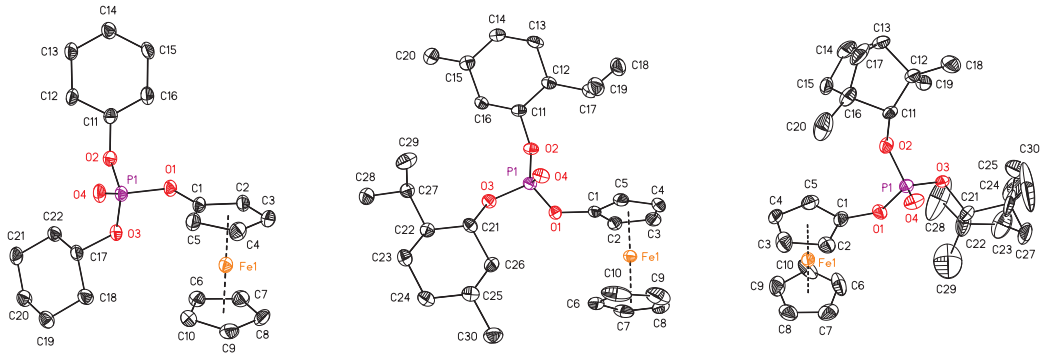


Figure 3.18 ORTEP (50 % probability level) of the molecular structures of **30a** (left), **30b** (middle) and **30e** (right) with the atom-numbering Scheme. All hydrogen atoms and a second molecule in the asymmetric unit of **30e** have been omitted for clarity.

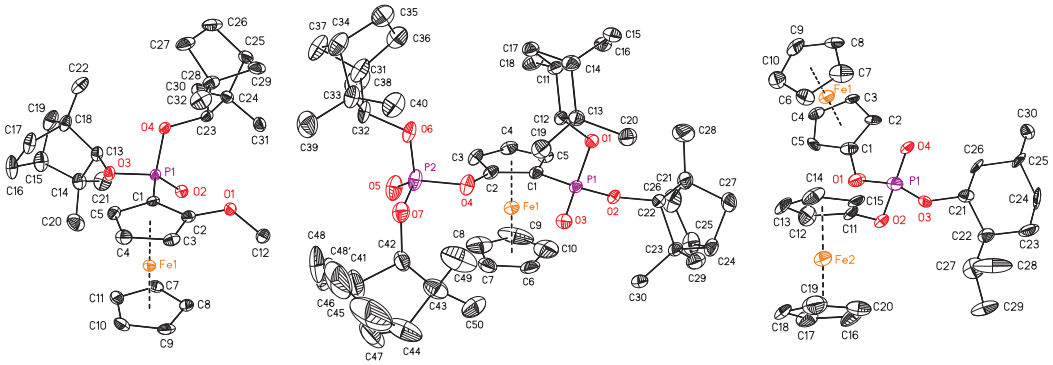


Figure 3.19 ORTEP (50 % probability level) of the molecular structures of (R_p)-**31e** (left), (R_p)-**35c** (middle) and **43b** (right) with the atom-numbering Scheme. All hydrogen atoms and a second molecule in the asymmetric units of **35c** and **43b** have been omitted for clarity.

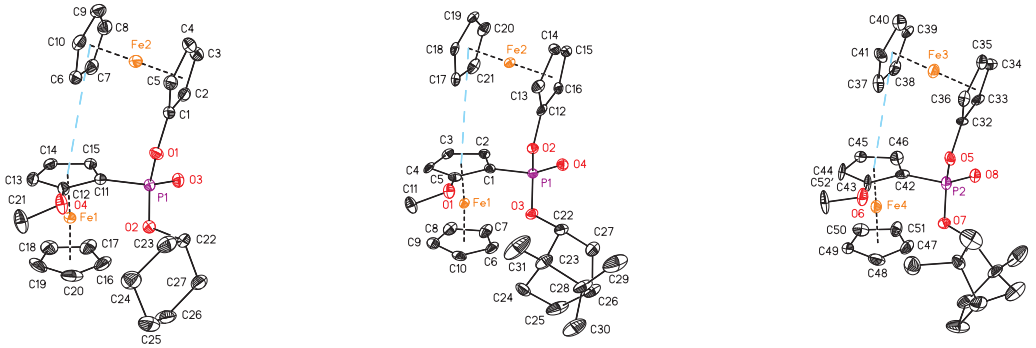


Figure 3.20 ORTEP (50 % probability level) of the molecular structures of **44a** (left), **44c** (middle) and **44d** (right) with the atom-numbering Scheme. All hydrogen atoms, a second molecule in the asymmetric units of **44c** and **44d**, two molecules of diethyl ether for **44c** have been omitted for clarity.
Intramolecular T-shaped π interaction between the centroids (Ct) of the C_5H_3 and the C_5H_5: a) Ct$\cdots$Ct, 4.5570(18) Å ; intersection, 72.6(3) °; b) Ct$\cdots$Ct, 4.556(3) and 4.572(3) Å ; intersection, 75.8(3) and 75.6(3) °; c) Ct$\cdots$Ct, 4.558(7) and 4.675(7) Å ; intersection, 75.8(7) and 72.9(7) °.

in contrast to phosphate **30a**, with the oxygen atom located in the equatorial position. In compounds **44a**,**c**,**d** strong intramolecular π contacts are present between the unsubstituted C_5H_5 and the top of the C_5H_3 rings (Figure 3.20).

3.1.3 Non-Chiral Multi-Aryl Phosphates

In addition to **11**, the ferrocenyl phosphates **47**–**50** were synthesized by reacting lithiated ferrocenol **5**-Li with $POCl_3$ or chlorophosphates $Cl_2P(O)(OR)$ (**46b**–**46e**) (Figure 3.21). The usage of BuLi as the metalation reagent, instead of widely used nitrogen bases, increased the yield, that is for **47** from 36[219,220] to 92 % and for **11** from 62 to 99 % (Figures 3.3, 3.21, Experimental Section).

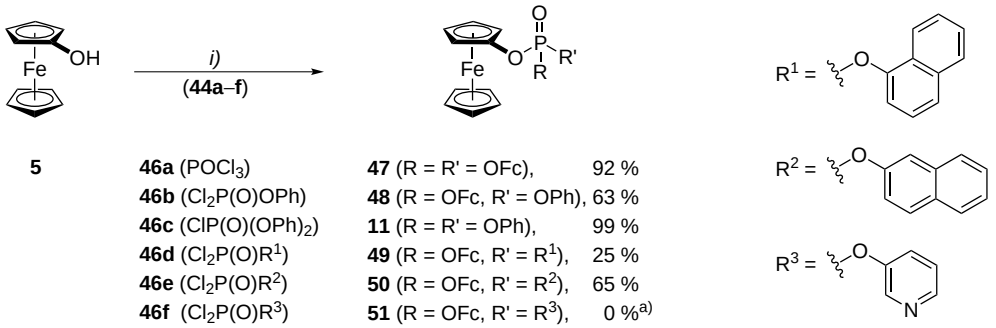


Figure 3.21 Synthesis of ferrocenyl phosphates **47**–**51**.
Reaction conditions: *i*) Et_2O (**11**,**47** and **48**)/ THF (**49**–**51**), –30 °C, BuLi, -70 °C, 0.33 equiv of **46a**, 0.5 equiv of **46b**, **46d-f** or 1 equiv of **46c**. Yields are based on **46** (**46**, **48**, **50**) or **5** (**11**, **49**). a) Instead of **51**, **47** was formed in 58 %.

However, the reaction of **5**-Li with the 3-hydroxypyridyl derivative **46f** did not result in desired phosphate **51**, but rather gave **47** in 58 (in THF) or 25 % yield (in Et_2O) showing that the solvent plays a crucial role within the appropriate reaction. Although a 2 : 1 ratio of **5**:**46f** was present, the 3-hydroxypyridyl substituent was replaced by a third nucleophilic substitution of **5**-Li. The properties of R^3 as the leaving group are due to the excellent stabilization of a negative charge within the electron-poor heterocycle. The formation of a keto-amino tautomeric structure, as possible for the 2- and 4-hydroxypyridine, is excluded, and thus, a P–N formation is rather disfavored compared to a P–O bonding of the pyridine derivative. Nevertheless, pyridyl triflates have been investigated for anionic 1,3-O→C migrations.

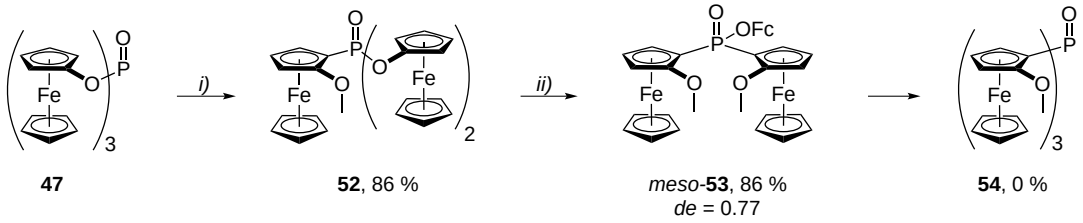


Figure 3.22 Consecutive *apFr* of triferrocenyl phosphate **47** to phosphonate **52** and phosphinate **53**.
Reaction conditions: *i*) LDA, THF, –30 °C, 3 h, Me_2SO_4. Yield based on **47**. *ii*) LDA, THF, 0 °C, 3 h, Me_2SO_4. Yield based on **52**.

The electron-withdrawing character and their different chemical structure increase their stability toward the attack of a nucleophile.[175] Treatment of $P(O)(OFc)_3$ (**47**) with LDA at various temperatures (–70 to 25 °C) resulted in the expected 1,3-O→C migration of the phosphorus fragment, which is initialized by an *ortho*-lithiation, producing **52** and **53** (Figure 3.22). After optimizing the reaction conditions for the *apFr* of **47** (Table 3.4), we obtained the highest yield for **52** of 86 % at a temperature of –30 °C. Lower temperatures reduced the conversion of **47**. Above –30 °C, partial decomposition takes place, lowering the yield. Nevertheless, the double rearranged product **53** was not formed within this reaction step, even using excess LDA (Table 3.22).

Table 3.4 Optimization of the reaction conditions for the *apFr* of triferrocenyl phosphate (**47**).[a]

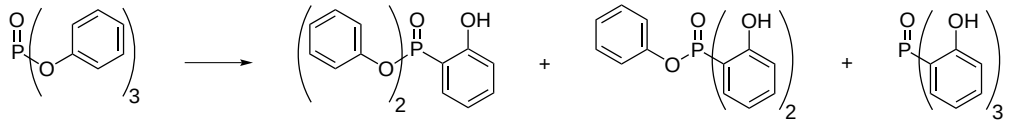
Entry	Educt	base (6 equiv)	Additive[b] (equiv)	T / °C		Yield / %[c]			
						47	**52**	**53**	**54**
1	**47**[d]	LiTMP	TMEDA	25	12 h	7	46		
2	**47**[d]	LDA	TMEDA	25	12 h	<1	7		
3	**47**	LDA		–70	2 h	17	74		
4	**47**	LDA		–30	3 h	<1	86		
5	**47**[g]	LDA	PhOLi (3)	0	4 h		59	16 (*de* 0.99)	
6	**47**[g]	LDA	PhOLi (12)	0	4 h		44	46	
7	**52**	LDA[e]		–15	3 h		66	30	
8	**52**	LDA[e]		0	4 h		<5	86 (*de* 0.77)	
9	**53**	LDA[f]		0	4 h				
10	**53**	LDA[f]		–10	3 h			86	
11	**53**	LDA[f]		50	3 h				

[a] Further reaction conditions are depicted in Figure 3.22.
[b] The equiv of the additive are equal to those of the base.
[c] The yields are based on the starting material.
[d] Hexane was used as the solvent.
[e] 4 Equivalents were used.
[f] 2 Equivalents were used.
[g] The reaction was started at –30 °C and warmed to 0 °C within 10 min.

An *apFr* of **52** by treating it with LDA gave phosphinate **53** in 86 % yield at 0 °C. The increased temperature, required for the lithiation reaction of **52**, is due to the increased electron density at the ferrocenyl backbone (*vide infra*). Phosphinate **53** was formed as a diastereomeric mixture of 0.89 : 0.11 (78 % *de*), which was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. Based on an X-ray measurement (Figure 3.29), where a similar ratio of two diastereomers (0.9 : 0.1) was observed, the mainly formed diastereomer should be assigned as the *meso*-enantiomers R_p,S_p,r^P and S_p,R_p,s^P. The *rac*-enantiomers R_p,R_p/S_p,S_p only cocrystallized in a similar ratio, and are refined as a disorder. The *meso*-isomers should give two sets of signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra; however, only one set was present. However, the formation of phosphine oxide **54** was not observed because, by the reaction of **53** with LDA at –10 °C, the starting material could be recovered in 86 % yield. In contrast, when the reaction was run at 50 °C the educt **53** was not present and probably decomposed during the course of the reaction or by a nucleophilic attack at the phosporus atom. The incomplete reaction

of ferrocenyls toward *apFr* is contrary to triphenyl phosphate **55** giving phosphine oxide **56** within one reaction step (Table 3.5).[182,184–189] Until now, the *apFr* of phenyl derivatives were warmed to 0 °C or even ambient temperature before being terminated them with HCl or H_2O.[176,182,190,221] Thus, the intermediately formed phosphonates (*e.g.*, **56**) and phosphinates (*e.g.* **57**) have not been isolated and reported yet. However, adding the scavenger, while keeping the reaction temperature at –80 °C, allowed the isolation of **56** (Table 3.5). Increasing the temperature, at which the scavenger is added, consecutively shifts the product ratio from **56** over **57** to **58** at 0 °C. The identity of **56** was verified by using single-crystal X-ray diffraction analysis (Figure 3.33). Initially, lithiation and subsequent rearrangement of **55** to form phosphonate **56** occurred at –70 °C. Gradually, increasing the temperature exceeds the activation energy for the lithiation of **56**-Li, resulting in the formation of phosphinate **57** and finally phosphine oxide **58** (Table 3.5). Thus, the number of rearrangements solely depends on the temperature required for the lithiation process, due to the absence of any *non*-rearranged but *ortho*-methylated product, derived from **55**. The amount of LDA used for the synthesis of **58** was taken from reported procedures.[182,184–188,222]
Obviously, the phenylic hydroxyl groups in **56**-Li and **57**-Li_2 do not prevent a further deprotonation by LDA. Contrary, starting at **47**, the presence of already one ferrocenylic hydroxyl group in **52**-Li, inhibits a further lithiation to **53** with even a 6 fold excess of LDA (Table 3.4). To complex the lithium ions by phenyl- instead of ferrocenyl-based hydroxyls, 12 equiv of PhOLi was added, which increased the yield of **53** from 0 to 46 % and the *de* from 0.77 to 0.99.

Table 3.5 Temperature dependent *apFr* of triphenyl phosphate (**55**) to phosphonate (**56**), phosphinate (**57**) and phosphine oxide (**58**).[a]



55 **56** **57** **58**

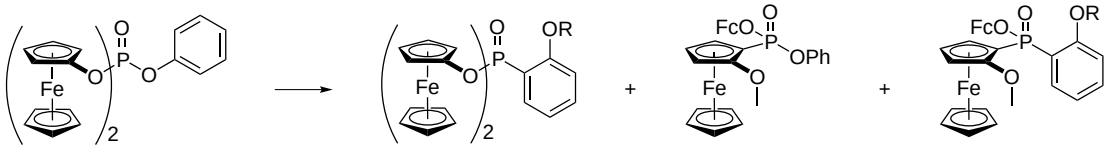
Entry	T / °C	LDA / 6 equiv	Yield / % **56**	**57**	**58**
1	–80	6	75	24	
2	–75	12	70	29	
3	–70	6	55	45	
4	–70	2	78	21	
5	0	12		9	90

[a] Reaction conditions: THF, LDA, **53**, 2 h, H^+/ H_2O. Yields are based on **55**.

However, treatment of **48** with 4 equiv of LDA at –75 °C (Table 3.6) produced only phosphonates **59** and **60** in minor yield. Increasing the reaction temperature to 0 °C resulted in a complete conversion of **48** giving **61**. Although excess dimethyl sulfate was present, compounds **59** and **61** were obtained in form of **59a**/**61a** (R = H) and as **59b**/**61b** (R = CH_3). As observed for **47** (Figure 3.22), the ferrocenyls prevent the formation of any type of phosphine oxides, within the *apFr* of **48** (Table 3.6). To examine the influence between one

(**48**) and two phenyls (**11**) on the product mixture within an *apFr*, the treatment of ferrocenyl diphenyl phosphate (**11**) has been reinvestigated (Figure 3.3). Replacing NEt_3 by BuLi as the base for the deprotonation of ferrocenol, increased the yield of **11** from 62 (Figure 3.3) to 99 %. Unmethylated **63** could recently be obtained in a yield of 8 % by running the reaction at –40 °C, due to an unsuccessful methylation by using iodomethane (Figure 3.3). Carrying out the *apFr* below –75 °C reduces the amount of unreacted starting material from 80 % for **48** to 25 % for **11**. The formation of phosphonate **62** and phosphinates **64** is observed. This reveals a positive influence of the two phenyls toward the lithiation behavior compared to **48**, where the formation of a phosphinate has not been observed. At –70 °C compound **11** was completely converted and the yields of **62** and **64** increased accordingly. Additionally, the formation of phosphinate **63** is observed. Phosphine oxide **65** could be isolated at 0 °C in a yield of 25 %.

Table 3.6 Temperature dependent *apFr* of diferrocenylphenyl phosphate (**48**) to phosphonates **59a**,**b** and **60**, and phosphinates **61a**,**b**.[a]



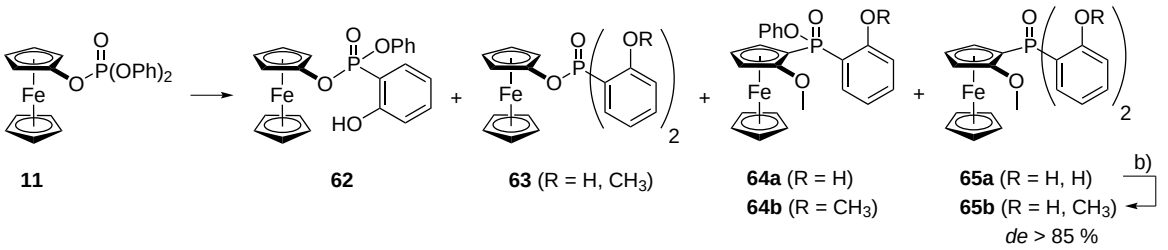
48 | **59a** (R = H), **59b** (R = CH_3) | **60** | **61a** (R = H), **61b** (R = CH_3)

Entry	T / °C	Time / h	Yield / % (**a**/**b**)			
			48	**59**	**60**	**61**
1	–75	2	80	10 (**b**)	9 (*de* 0.45)	
2	–60	4	25	27 (**a**), 13 (**b**) $\sum = 40$	29 (*de* 0.27)	
3	–35	3.5		25 (**a**), 10 (**b**) $\sum = 35$	20 (*de* 0.65)	19 (**a**), 9 (**b**) $\sum = 28$
4[b]	0	2				77 (**a**), 13 (**b**) $\sum = 90$

[a] Reaction conditions: THF, LDA (4 equiv), Me_2SO_4. Yields are based on **48**.
[b] 7 Equiv of LDA were used.

In general, the rearrangement at the phenyl rings is favored compared to that at the ferrocenyls, as clarified by the higher yields of **59** and **62** at lower temperatures, when compared to the rearrangement products **52**, **60**, and **62**–**65**. However, the formation of **60** indicates a low energy difference between lithiation at a phenyl and a ferrocenyl fragment. Furthermore, the possibility of an *ortho* lithiation is higher at the ferrocenyls, due to the presence of 4-*ortho* hydrogens in contrast to 2-*ortho* hydrogen atoms at the phenyl groups. As a consequence of the different behavior of ferrocenyl (stepwise) and phenyl groups (temperature dependent), phosphinates **61** was formed at 0 °C as the final rearranged product. In contrast, **11** gave phosphine oxide **65** at 0 °C (Table 3.7), although an excess of LDA was used.
To prevent the decomposition of oxygen-sensitive hydroxy ferrocenes,[147,167,194,223] the lithiation and rearrangement reactions were quenched by the addition of excess Me_2SO_4, result-

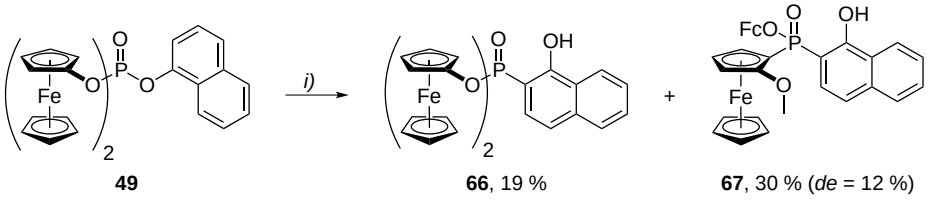
Table 3.7 Temperature dependent *apFr* of ferrocenyldiphenyl phosphate (**11**) to phosphonate **62**, phosphinates **63** and **64a**,**b**, and phosphine oxides **65a**,**b**.[a]



Entry	T	Yield / % (**a**/**b**)				
	/℃	**11**	**62**	**63**	**64**	**65**
1	–80	25	25		9 (**a**)	
2	–70		58	4	4 (**a**), 11 (**b**)	
					$\sum = 15$	
3	0			11	20 (**a**), 18 (**b**)	18 (**a**), 7 (**b**)
					$\sum = 38$	$\sum = 25$

[a] Reaction conditions: THF, LDA (8 equiv), 2 h, Me_2SO_4 (12 equiv). Yields are based on **11**.
[b] Addition of 12 equiv of Me_2SO_4.

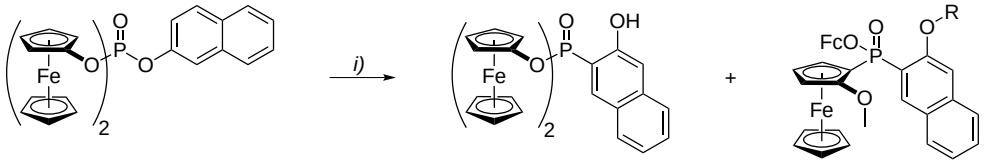
ing in the methylation of all ferrocenyl-related hydroxy functionalities. However, the *in situ* methylation of phenols is rather slow and moreover gave mixtures of the methylated and *non*-methylated derivatives **59**, **61** and **63**–**65** (Tables 3.6 and 3.7). For phosphine oxide **65**, a kinetic resolution was observed (Table 3.7). Most likely **65a** initially was formed as a racemic mixture (R_p/S_p enantiomers), due to the absence of external and internal chiral information. For **65b** (> 85 % **de**) one set of signals was observed in the $^{31}P\{^1H\}$ NMR spectra, confirming the diastereoselective proceeding. The ^1H and $^{13}C\{^1H\}$ NMR spectra showed the formation of small amounts of the respective diastereomer, which were used for calculation of the *de* by using the integrals of the OCH_3 (85 % *de*) and the OH (87 % *de*) resonances, confirming the diastereoselective process. This lets to the conclusion that the $^{31}P\{^1H\}$ NMR resonances of both diastereomers occurred isochron. The absolute configuration could be assigned to S_p,S^P/R_p,R^P by single-crystal X-ray diffraction analysis (Figure 3.30). Compound **67** is the first example of a solid-state structure of a 1-oxo-naphth-2-yl phosphinate. The differences between ferrocenyls and phenyls toward *apFr* prompted us to extend the substrate scope to condensed aromatics, which also allows us to investigate the regioselectivity of the 1,3-O→C migrations. To reduce the number of possible rearrangement products, phosphates bearing two ferrocenyls instead of one were applied. The *apFr* of 1-naphthyl derivative **49** resulted in the formation of a 1,2-substitution pattern, both at the naphthyl and at the ferrocenyl moieties, giving phosphonate **66** and phosphinate **67**, respectively, as shown in Figure 3.23. Phosphinate **67** was formed in a scalemic mixture (ratio of both diastereomers of 1 : 0.78), as it was observed for **61** (Table 3.6). Similar to triferrocenyl- (**47**) and diferrocenyl phosphate **48**, the lithiation of **49** required higher temperatures. Thus, 90 % of the starting material **49** was recovered at –70 ℃.



49 **66**, 19 % **67**, 30 % (*de* = 12 %)

Figure 3.23 Temperature-dependent *apFr* of of diferrocenyl(1-naphthyl) phosphate **49** to phosphonate **66** and phosphinate **67**.
Reaction conditions: *i*) LDA (6 equiv), THF, 0 °C, 2 h, Me_2SO_4 (8 equiv). Yields are based on **49**.

Replacement of the 1-naphthyl derivative **49** (Figure 3.23) with its 2-isomer **50** (Figure 3.24), however, allowed the *apFr* at –80 °C. Thus, phosphonate **68** reveals an increased reactivity toward the lithiation process at the 2-position of the naphthyl moiety when compared with that of the 1-substituted compound **49**. Lithiation selectively occurred at more acidic 3-position and not at the electronically richer 1-position, which is in accordance with similar rearrangements of 2-naphthyl alkyl phosphonates and phosphates, where the 2,3-substitution pattern was present in the predominantly formed products.[190,224] If the reaction temperature is increased to 0 °C, the 1,3-O→C migration occurred at both types of aromatics, resulting in **69** with a **69a**/**69b** ratio of 1 : 0.43 (Figure 3.24). Within this reaction, the phosphonate **68** could not be isolated.



50 **68**, 39 % **69a** (R = H)
69b (R = CH_3)
Σ = 63 %[a)]

Figure 3.24 Temperature-dependent *apFr* of of diferrocenyl(2-naphthyl) phosphate **50** to phosphonate **68** and phosphinate **69**.
Reaction conditions: *i*) LDA (6 equiv), THF, –80 °C, 2 h, Me_2SO_4 (8 equiv). Yields are based on **50**; a) 0 °C.

Phosphonate **70a**[219,220] was obtained by the reaction of lithiated 1,1'-ferrocenediol ($Fc(OLi)_2$; **38**-Li_2) with $POCl_3$ and subsequent addition of **5**-Li (Figure 3.27). However, **70a** was only produced in a yield of 20 %, which is attributed to the reaction protocol applied (*vide infra*, Experimental Section). Phosphate (*R*)-**70b**, possessing a chiral (*R*)-BINOL bridging backbone, was accessible by treatment of **5**-Li with chlorophosphate (*R*)-**46g** (Figure 3.25). After appropriate workup, (*R*)-**70b** could be isolated in a yield of 49 % (Figure 3.25). It was found that the addition of 2 equiv of $POCl_3$ within the synthesis of (*R*)-**46g** did not result in the formation of a bisphosphorylated BINOL. Treatment of phosphates **70a**,**b** with excess LDA (6 equiv) at –70 °C allowed *apFr* at the single substituted ferrocenyls. The formation of compounds that were lithiated at the bridging backbones of **70a**,**b** were not observed, which is in accordance with the result obtained with the phenyl derivative of **70b**.[203]

The *non*-rotatable P=O bond prevents a stabilization of the negative charge in the 3-position of the naphthyl ring. Therefore, an attack at the phosphorus atom is excluded. Phosphonate **71a** (Figure 3.25) was isolated in virtually quantitative yield. The chiral information in the backbone of **70b** resulted in a diastereoselective lithiation, owing to a preferable rotation of the P=O building block to one site of the ferrocenyl unit. After subsequent 1,3-O→C migration, phosphonate **71b** was isolated as the (R,R_p) diastereomer with a *de* of 91 %, as confirmed by single-crystal X-ray diffraction (Figure 3.32) in 57 % yield. Within this reaction, 38 % of the starting material (R)-**70b** could be recovered. Increasing the temperature to –20 °C for 2 h reduced the yield of (R,R_p)-**71b** to 37 %, whereas the *de* remained at 89 %. Most likely, the high *de* of phosphonate **71b** is due to the asymmetric BINOL group and an efficient interaction with the ferrocenyl backbone. Thus, the P=O is directed to one site of cyclopentadienyl where the lithiation occurred.

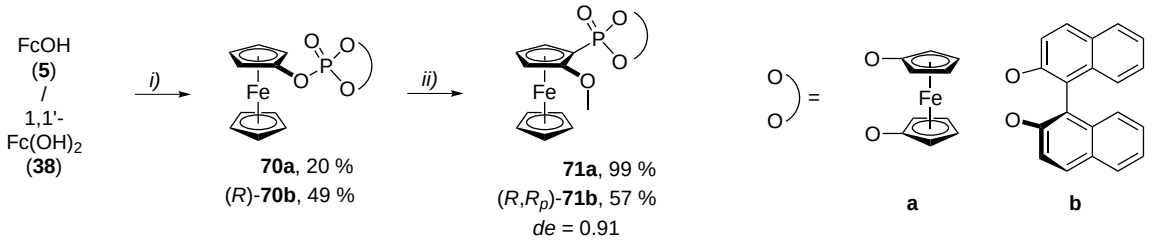


Figure 3.25 *ApFr* of phosphates **70a** and (R)-BINOL-based (R)-**70b**.
Reaction conditions: *i*) **70a**: **38**, BuLi (2 equiv), $POCl_3$, THF, **5**-Li. Yield based on **38**; **70b**: **5**, BuLi (1 equiv), Et_2O, P(O)Cl((R)-BINOL). Yield based on **5**. *ii*) LDA, THF, –10 °C (**71a**) or –70 °C (**71b**), 2 h, Me_2SO_4 Yields are based on **70a**/**b**.

To force metalation at the 1,3-dioxa[3]ferrocenophane backbone, phosphate (1R)-**72** was synthesized by reacting **38**-Li_2 with the chiral dichloro (1R)-α-fenchyl phosphate (**46h**), whereby the aliphatic substituent does not undergo lithiation reactions (Figure 3.26). The fenchyl methyl groups in the 1 and 3 positions of the bicycle enhance the stereoselectivity within such types of reactions, when compared to other chiral pool alcohols (Section 3.1.2).
Within the synthesis of (1R)-**72**, the formation of a [3,3]ferrocenophane, containing two phosphate bridged ferrocenyls, was not observed. Treatment of (1R)-**72** with the sterically demanding base LiTMP at –10 °C resulted only in the *ortho*-lithiation at both cyclopentadienyls. Subsequent addition of Me_2SO_4 gave the 1,1'-double methylated phosphate **73** (Figure 3.26). This *ansa* compound was obtained as a mixture of three *non*-separable diastereomers in a ratio of 1 : 0.25 : 0.3 (Experimental Section). Single-crystal X-ray diffraction analysis allowed the determination of the absolute configuration of one diastereomer, which could be assigned to ($1R$,R_p,S_p,s^P) containing a pseudochiral phosphorus atom (Figure 3.32). We assume that the ($1R$,R_p,S_p,s^P)-**73** isomer is the main diastereomer formed within this reaction. This can be explained by the steric hindrance of the two methyl groups at C3 at one site of the ferrocenyl backbone (Figure 3.32). Furthermore, the P=O bond is fixed at one site and favors a pseudo-*meso* lithiation. However, the absolute configuration of the other two diastereomers could not be unequivocally determined. Most likely the pseudo-*racemic* (R_p,R_p) and (S_p,S_p) isomers were formed since their ratio within the product mixture is

similar (Experimental Section). Increasing the temperature within the reaction of (1*R*)-**72** with LDA to ambient conditions did not change the *dr* of (1*R*)-**73**, whereby the amount of the recovered starting material (1*R*)-**72** increased from 0 to 6 %. This can be explained by the deprotonation and cleavage of tetrahydrofuran.[225] The addition of the methylation reagent Me_2SO_4 also resulted in an activation of the P=O bond, which favors a nucleophilic attack of water during the workup procedure and hence the cleavage of the ferrocenophane. Methylation of the thus formed 1-hydroxy moiety gave (1*R*)-**74** as a *racemic* mixture concerning the configuration of the phosphorus atom. Additionally, 20 % of 1,1'-Fc$(OMe)_2$ was isolated, indicating hydrolysis of the [3]ferrocenophane backbone of (1*R*)-**72**. The formation of the ring-opened, double-methylated compound **74** has *inter alia* been verified by the ^{1}H NMR resonances of the methyl groups. The cyclopentadienyl attached fragment occurred as a singlet at 3.37, whereas the P–O–CH_3 fragment was observed as a doublet at 3.82 ppm with a $^3J_{H,P}$ coupling constant of 8.4–11.3 Hz.

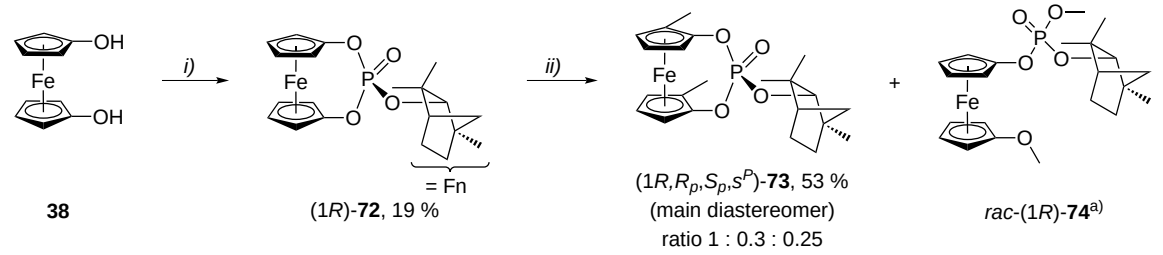


Figure 3.26 Synthesis and reaction behavior toward *apFr* of the *chiral pool*-based phosphate (1*R*)-**72**.
Reaction conditions: *i*) BuLi, $Cl_2P(O)((1\,R)-\alpha$-Fn), Et_2O. Yield based on **38**. *ii*) LiTMP, THF, –10 °C, Me_2SO_4. Yield based on **72**. a) Stirring for 18 h at ambient temperature: besides 53 % of **73**, 20 % of 1,1'-Fc$(OMe)_2$ and 10 % of **74** were formed based on **70**. *Rac*- refers to the configuration at the phosphorus atom.

The usage of ferrocene diol **38** could allow for the consecutive preparation of the superferrocenophane **77** as depicted in Figure 3.27. In this respect, **38** was metalated by using BuLi and the thus formed corresponding lithiated species gave with 2 equiv of $POCl_3$ **38**-$P_2O_2Cl_4$. It was expected that the stepwise addition of **38**-$(Li)_2$ to the latter compound should result in the formation of phosphate **77**. Instead, only 12 % of the bis[3]ferrocenophane **76** could be isolated (Figure 3.27). To investigate, if the intermediate bisphosphate **38**-$P_2O_2Cl_4$ or a mixture of the 1,3-dioxa[3]ferrocenophane **38**-POCl and $POCl_3$ was formed, **5**-Li was added instead of **38**-$(Li)_2$. After appropriate workup, **47** (42 %), **70a** (20 %) and bisphosphate **75** (11 %) could be isolated, revealing that the respective reaction mixture contained $POCl_3$, **38**-$P_2O_2Cl_4$, and **38**-POCl. The ratio of **47**/**70a**/**75** also indicated that **38**-POCl was predominantly formed (Experimental Section). Treatment of **75** with LDA at –30 °C resulted in complete decomposition of this compound by producing an insoluble residue during column chromatographic workup. In contrast, bis[3]ferrocenophane **76** gave the double rearranged bisphosphonate **78**, which was isolated in a yield of 62 % (Figure 3.27). Compared to previous results of anionic phospho-(Section 3.1) and thia-Fries[194] rearrangements, the *meso* (R_p,S_p) isomer should be exclusively formed.
The results of the reactivity of N-bonded, aliphatic Fc–O–P compounds and our previous in-

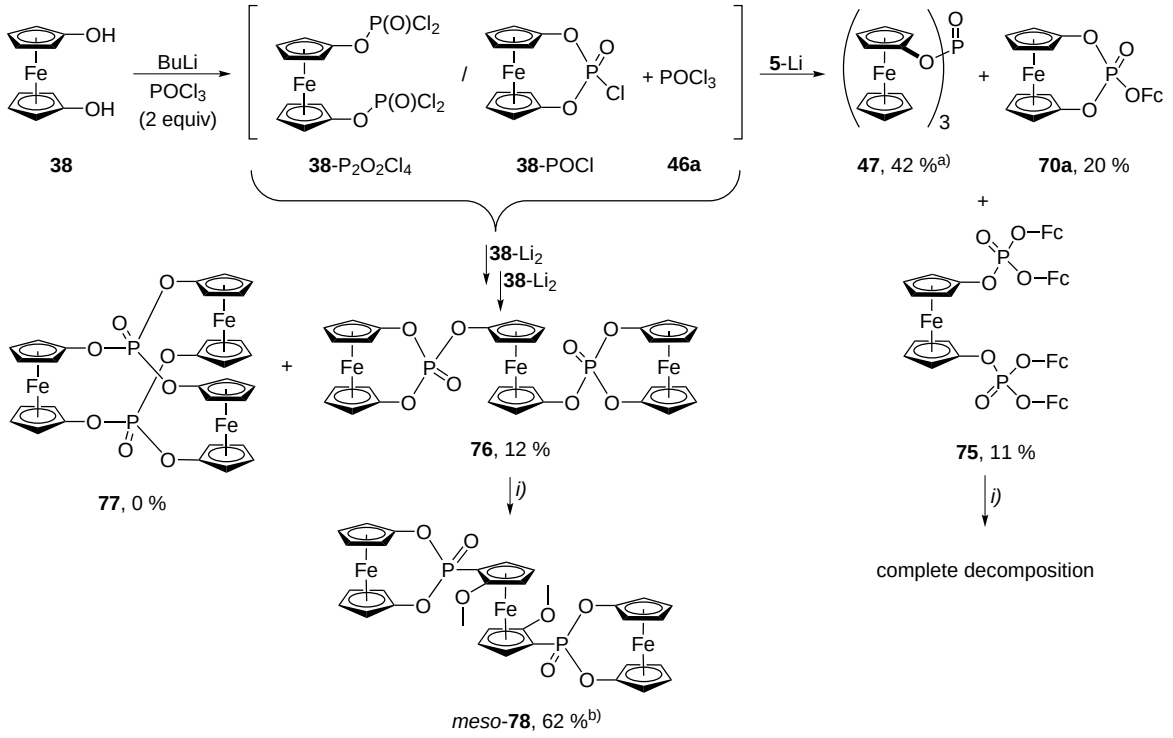
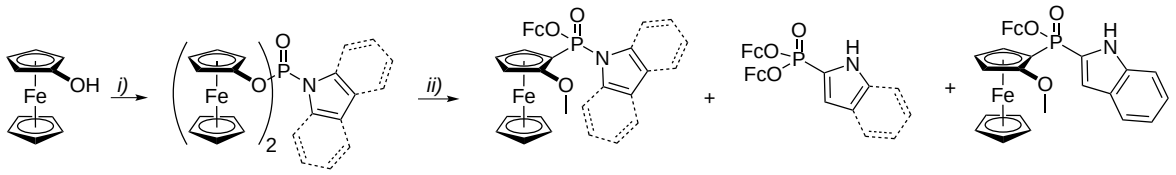


Figure 3.27 Reaction of **38** with $POCl_3$, and/or FcOLi for the synthesis of [3]ferrocenophanes **70a** and **76**, and phosphate **75**. Yields are based on **38**.
Reaction conditions: *i*) LDA (4 equiv), THF, –30 °C, 2 h Me_2SO_4 (8 equiv). a) Yield based on **5**. b) Yield based on **76**.

vestigations within this field of chemistry (Section 3.1.1) revealed that electron-withdrawing phosphorus groups increase the possibility of a lithiation and the occurrence of an *apFr*. Thus, we replaced the aliphatic by *N*-bonded nitrogen heterocycles. The lone pair of the nitrogen is rather involved in the aromatic system, which decreases the transfer of electron density to phosphorus and the ferrocenyls. Thus, their stability toward acidic media is increased.[226] Phosphonates **79**–**81** were accessible by the reaction of **5**-Li with the respective dichlorophosphonates, whereby the size of the aromatic systems increased from 1*H*-pyrrole (**79**) to 1*H*-indole (**80**) and 9*H*-carbazole (**81**, Figure 3.28). A wide range of pyrrole- and indole-based phosphonates are known, whereas carbazole derivatives are sparsely investigated.[227] This is clarified by reported procedures for the synthesis of the respective dichlorophosphates, of which only the indolyl derivative has been reported yet.[228] Treatment of lithiated carbazole with excess $POCl_3$ in tetrahydrofuran at –80 °C gave the desired dichlorophosphate (Experimental Section). In contrast, the decreased steric demand and thus the increased reactivity of lithiated pyrrole toward $POCl_3$ required a dropwise addition of pyrrole into a tetrahydrofuran solution containing >10 equiv of $POCl_3$ at –80 °C (Experimental Section). In contrast to the aliphatic derivatives **12**–**15**, the reaction of **79**–**81** with LDA followed by the addition of Me_2SO_4 gave several 1,3-O→C (**82**–**84**, **87**) anionic phospho-Fries and 1,2-N→C (**85**–**87**) rearranged products (Figure 3.28). The latter ones are the first examples of rearrangements of phosphonato moieties. Shifts at thiaphosphonates,[229] chiral phosphine oxides and sulfides[230] at pyrroles have been reported, whereas indoles have not been investigated up to

date. It should be noted that within the synthesis of the indole systems **83** and **86**, 18 % of FcOMe could also be isolated, probably due to a nucleophilic attack at the phosphorus atom, combined with the good stabilization of a negative charge at the heterocycle. The reaction of **79** even resulted in the formation of 32 % of FcOMe and 45 % of recovered starting material at –70 °C, which supports the assumption of a nucleophilic attack.



5	**79** (1*H*-pyrrol-1-yl), 44 %	**82** (1*H*-pyrrol-1-yl), 24 %[a]	**85** (1*H*-pyrrol-2-yl), 27 %	**87**, 67 %[c]
	80 (1*H*-indol-1-yl), 81 %	**83** (1*H*-indol-1-yl), 24 %	**86** (1*H*-indol-2-yl), 31 %	
	81 (9*H*-carbazol-9-yl), 27 %	**84** (9*H*-carbazol-9-yl), 56 %[b]		

Figure 3.28 Synthesis of ferrocenyl phosphonates **79-81** and their treatment with LDA causing 1,3-O→C and 1,2-N→C rearrangements for the synthesis of **82**–**87**. Reaction conditions: *i*) –30 °C, BuLi, $Cl_2P(O)(NAr)$. Yields are based on **5**. *ii*) LDA (6 equiv), THF, –40 °C, 2 h, Me_2SO_4 (8 equiv). Yields are based on **79**–**81**. a) –70 °C. b) –60 °C. c) 0 °C.

Contrary to the phenyl and naphthyl phosphates **11**, **47**–**50**, the first rearrangements occurred at the ferrocenyl substituent, resulting in the formation of phosphinates **82**–**84** (Figure 3.28). Increasing the temperature to 0 °C accelerated the rearrangements at the heterocycles, and phosphonates **85** and **86**, and phosphinate **87** could be isolated after appropriate workup. The chemical properties toward lithiation reactions could also be derived from electrochemical measurements (Table 3.8). The first rearrangement at the ferrocenyl moiety proceeded almost racemic for **82** with a *dr* of 1 : 0.89, whereas **84** occurred in a ratio of 1 : 0.28 (56 % *de*), whereby the configuration of the predominantly formed diastereomers could be assigned as R_p,S^P/S_p,R^P based on single-crystal X-ray diffraction analysis (Figure 3.35). Phosphinate **87** was formed in a ratio of 1 : 0.098 (82 % *de*). It remains unclear, whether the diastereoselective proceeding in case of **87** is caused by steric effects of the heterocycle or by a stabilization of the lithium ions by the aromatic π-system. Most of the heterocyclic phosphonates and phosphinates showed no sign of decomposition in solution, except for **82**, which rapidly decomposed due to either a nucleophilic attack at the phosphorus atom or oxidation reactions occurring at the pyrrole substituent. A mixture of $CDCl_3$ and DMSO was required for NMR investigations of compound **85**, due to its bad solubility. The structure of **85** could be verified by single-crystal X-ray diffraction analysis (Figure 3.34).

3.1.4 Characterization

NMR Spectroscopy

General features of ferrocenyl phosphates and phosphonates have already been discussed in Section 3.1.1 and 3.1.2 and are not further discussed. The OCH_3 resonances of the *apFr* species,which range between 3.5–4.0 ppm, is somewhat highfield-shifted to 2.63 ppm for the (*R*)-BINOL phosphonate **71b**. The *O*H and *N*H hydrogen resonances were observed between 9 and 12 ppm, occurring as singlets or as doublets with a $^4J_{H,P}$ coupling of $\leq$ 1 Hz

(Experimental Section). Besides the presence of the mentioned doublet ($J > 200$ Hz) of the C–P bond for ferrocenyls, the signals for phenyl related C_{Ph}–P units occurred between 100–122 ppm. The trend of the $^1J_{C,P}$ coupling constants follows the order (229–206 Hz) phosphonates > phosphinates (163–184 Hz) > phosphine oxides (111–107 Hz) for the ferrocenyl related carbons. Non-ferrocenyl related C–P couplings decrease from *N*-heterocyclic phosphonates (236–227 Hz) > non-heterocyclic phosphonates (181–190 Hz) > *N*-heterocyclic phosphinates (172 Hz) > non-heterocyclic phosphinates (132–147 Hz) > phosphine oxides (107–111 Hz). As mentioned in Section 3.1.2, the shift of the *ipso*-carbon atoms shifts from 116–119 ppm (C_{Fc}–O–P) to 126–130 ppm (C_{Fc}–O–CH_3). In contrast, the signals in 1,3-dioxa[3]ferrocenophanes **70a**, **71a**, **72**, **73**, **74** and **78** are observed at higher fields between 109–111 ppm for the C–O–P, and 129–131 ppm for the C–O–CH_3 fragments (Experimental Section). The *N*-aryl phosphonates **79**–**81**, showed similar $^{31}P\{^1H\}$ shifts ($\sim$ –11 ppm) compared to the *O*-alkyl derivatives (–15 to –17 ppm). In contrast, the *N*-alkyl substituent, occurred downfield shifted at 2.5 ppm. Phosphorus atoms that are included in 1,3-dioxa[3]ferrocenophane moieties, in general, showed downfield shifted $^{31}P\{^1H\}$ resonances compared to non-bridged derivatives. Thus, the signals for exclusively ferrocenyl containing **70a** and **76** occurred at –5.6 ppm, at –2.5 ppm for the (*R*)-BINOL derivative **70b** and at –4 to 1 ppm for the fenchyl derivatives **72** and **73**. The $^{31}P\{^1H\}$ shift accordingly changes within the series of phosphonates from *C*-bonded *N*-heterocyclic (4.0–4.5 ppm) $\leq$ *O*-/*N*-bonded *non*-bridged (14–19 ppm) < *O*-bonded [3]ferrocenophanes (30–35 ppm). Phosphinates range between 25 and 45 ppm and phosphine oxides were observed at 38–51 ppm. A trend within either the presence of an OCH_3 or OH group could be observed by comparing the **a** (OH containing) with the respective **b** derivatives (OMe instead of OH), which reveals $\Delta\sigma$ values of 4 ppm for **59**, more than 9 ppm for **61**, **64**, **69**, and 11 ppm for **65**. This is probably due to the formation of intramolecular hydrogen bridge bonds as present in the solid state (*e.g.* Figures 3.30 and 3.31), in $CDCl_3$ involving the P=O bond, which lowers the electron density at the phosphorus atom.

Solid State Structures

The molecular structures of **48**, **49**, **52**, **53**, **56**, **59a**, **65b**, **67**, **69b**, **70a**, **71b**, **73**, **76**, **80**, **81** and **84**–**86** in the solid-state have been determined by single-crystal X-ray diffraction analysis (Figures 3.29, 3.30, 3.31, 3.32, 3.33, 3.34 and 3.35).
The compounds crystallized in the centrosymmetric triclinic space group $P\bar{1}$ (**52**, **67**, **69b**, **76**, **81** and **84**), the monoclinic space groups $P2_1/n$ (**47** and **86**), $P2_1/c$ (**49**, **53**, **59a**, **65b** and **80**), $C2/c$ (**85**), and the orthorhombic space group $Pnma$ (**56**). Ferrocenes **70a**, **71b** and **73** crystallized in the *non*-centrosymmetric monoclinic space group $P21$ (**73**, abs. struct. parameter = 0.002(8)), and the orthorhombic space groups $Fdd2$ (**70a**, abs. struct. parameter = –0.01(2)) and $P2_12_12_1$ (**71b**, abs. struct. parameter = 0.012(16)). In the asymmetric unit these compounds are present with one (**48**, **49**, **52**, **53**, **59a**, **65b**, **67**, **69b**, **70a**, **71b**, **80**, **81** and **84**–**86**) two (**73**) or a half (**56** and **76**) crystallographically independent molecule(s) (Experimental Section). In phosphonate **56** a mirror plane is present in the phenyl plane including the P1, O2 and O3 atoms (Figure 3.33). The formula unit of phosphate **76**

can be calculated by the inversion through the Fe2 atom (Figure 3.33).

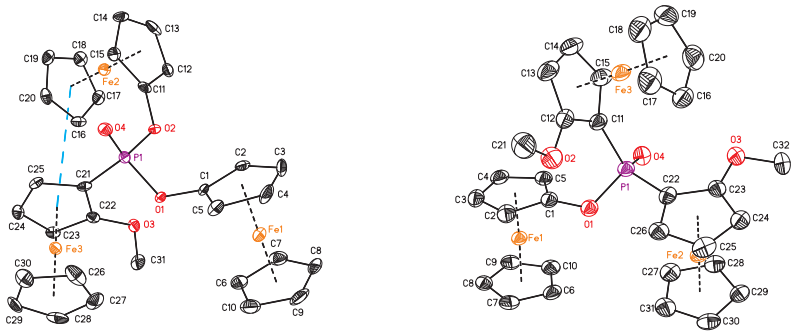


Figure 3.29 ORTEP (50 % probability level) of the molecular structures of *rac*-**52** (left) and **53** (right) with the atom-numbering Scheme. All hydrogen atoms and disordered parts of **53** (10 %) have been omitted for clarity.
Intramolecular *T*-shaped π interaction between the centroids (Ct) of the C16–C20 and C21–C25 labeled cyclopentadienyls is shown: Ct$\cdots$Ct, 4.585(3) Å; intersection, 72.6(3) °.

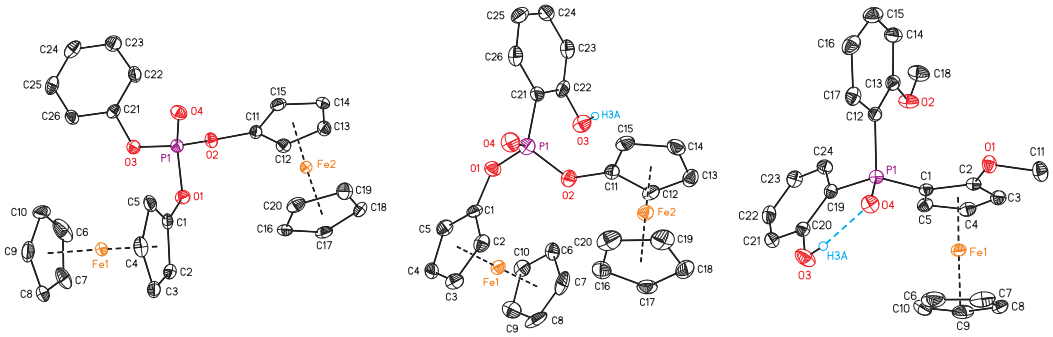


Figure 3.30 ORTEP (50 % probability level) of the molecular structures of **48** (left), **59a** (middle) and **65b** (right) with the atom-numbering Scheme. All C-bonded hydrogen atoms and the disordered C_5H_5 unit in **65b** (occupancy ratio of 0.73 : 0.27) have been omitted for clarity.
Intramolecular hydrogen bridgebond: O3$\cdots$O4, 2.597(2) Å; O3–H3A$\cdots$O4, 157 °.

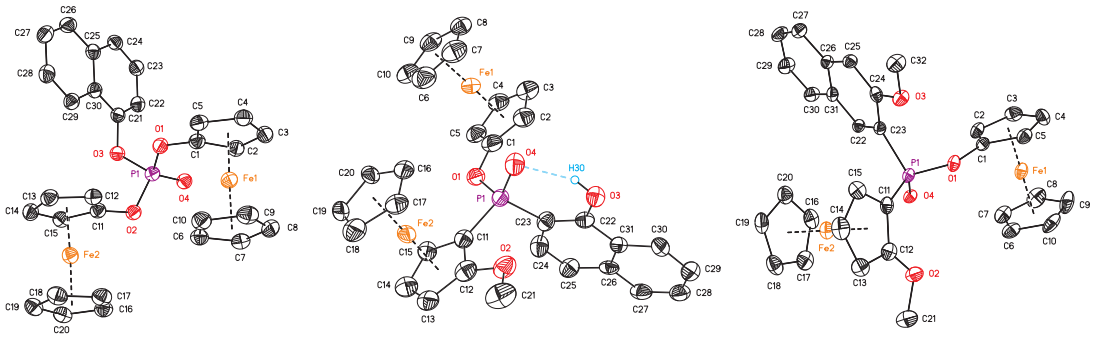


Figure 3.31 ORTEP (probability levels: 30 %, **49**; 50 %, **67** and **69b**) of the molecular structures of **49** (left), **67** (middle) and **69b** (right) with the atom-numbering Scheme. All C-bonded hydrogen atoms and the disordered parts in **67** (occupancy ratio of 0.722 : 0.278) have been omitted for clarity.
Intramolecular hydrogen bridgebond: O3$\cdots$O4, 2.624(10) Å ; O3–H3O$\cdots$O4, 153 °.

The Cp$\cdots$Cp' torsion angles in the freely rotatable ferrocenes **47**, **49**, **52**, **53**, **59a**, **65b**, **67**, **69b**, **71b**, **76**, **80**, **81** and **84**–**86** range from 0.785(5) to 14.6(14), revealing rather eclipsed

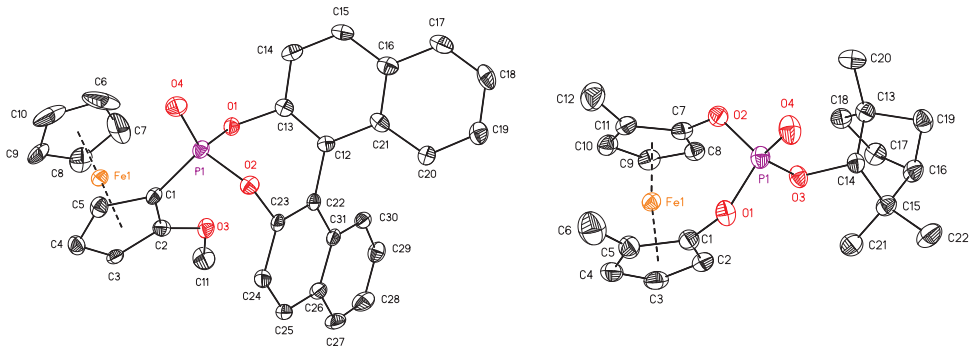


Figure 3.32 ORTEP (50 % probability level) of the molecular structures of (R,R_p)-**71b** (left) and (1R-α,R_p,S_p,s^P)-**73** (right) with the atom-numbering Scheme. All hydrogen atoms and one molecule of $CHCl_3$ in the asymmetric unit of **71b** have been omitted for clarity.

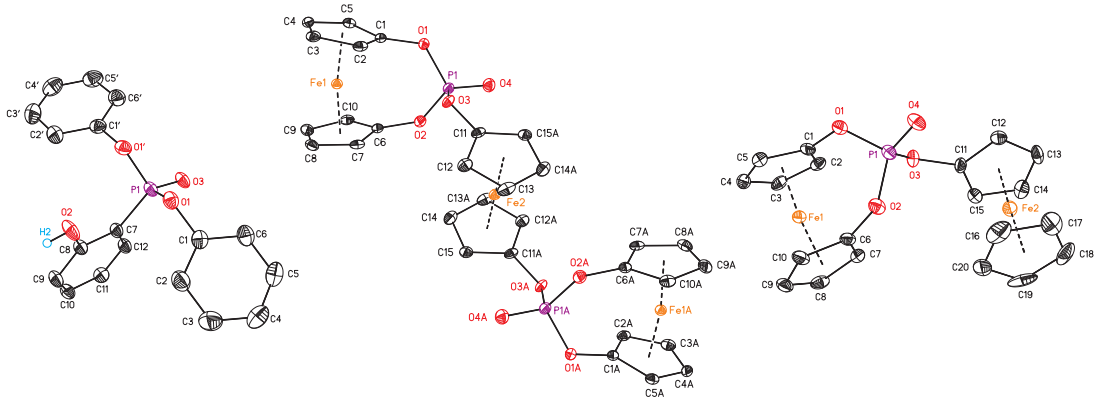


Figure 3.33 ORTEP (50 % probability level) of the molecular structures of **56** (left), **76** (middle) and **70** (right) with the atom-numbering Scheme. All C-bonded hydrogen atoms have been omitted for clarity. Symmetry operation for generating equivalent atoms ('): $x, -y+1/2, z$; (A): $-x, -y, -z+1$.

conformations, whereas the disordered part in **65b** (27.8(7) °) and one ferrocenyl in **70a** (36.1(5) °) and **76** (36.3(2) °) exhibit staggered conformations.

In rotatable-congested [3]-ferrocenophanes **70a**, **73** and **76** an eclipsed torsion angle of up to 1.1(4) °is observed, as expected. The hydroxy functionalities in **56**, **59a**, **65b** and **67** have been refined idealized with the O–H torsion derived from residual electron density (AFIX 147; **56**, **59a**, **67**) or with an idealized staggered geometry (AFIX 83; **65b**). Aromatic N-bonded hydrogen atoms haven been calculated with a constrained distance of 0.86 Å (AFIX 43). The acidic protons are involved in either intra- (**65b** and **67**) or intermolecular (**56**, **59a**, **85** and **86**) hydrogen bridge bonds. Phosphinate **67** predominantly crystallized as the S_p,S^P isomer, whereas the disordered part occurred in a R_p,R^P configuration (ratio 0.722 : 0.278). With regard to the centrosymmetric space group $P\bar{1}$ a diastereoselective crystallization of **67** took place. The other set of diastereomers (S_p,R^P/R_p,S^P), present in solution in a ratio of 1 : 0.78, was not observed. A diastereoselective crystallization process also occurred in case of phosphinate **69b**. NMR investigations (*vide supra*) revealed a ratio of both diastereomers of 1 : 0.5, whereas single crystals of **69b** appeared as a mixture of both enantiomers R_p,S^P and

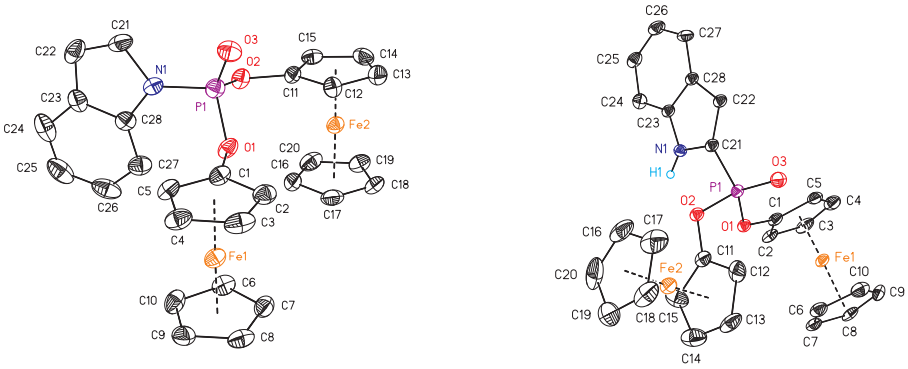


Figure 3.34 ORTEP (50 % probability level) of the molecular structures of **80** (left) and **86** (right) with the atom-numbering Scheme. All C-bonded hydrogen atoms, the disordered atoms (occupancy ratio of 0.88 : 0.12) in **86** and one disordered molecule of $CHCl_3$ in the asymmetric unit of **86** have been omitted for clarity.

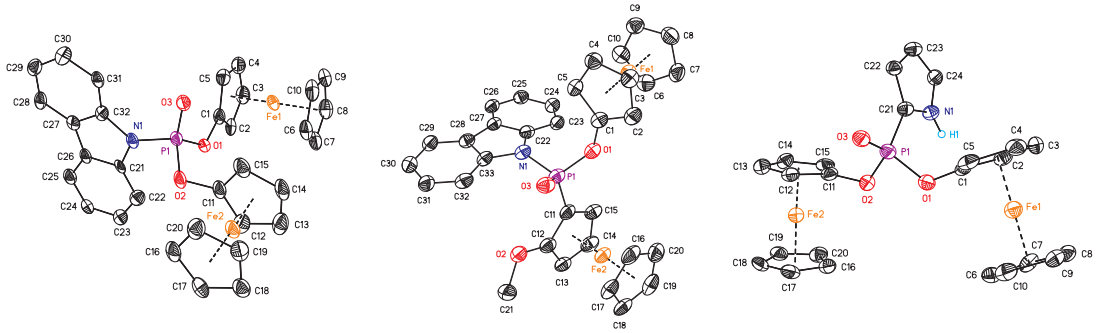


Figure 3.35 ORTEP (probability levels: 50 %, **81** and **84**; 30 %, **85**) of the molecular structures of **81** (left), **84** (middle) and **85** (right) with the atom-numbering Scheme. All C-bonded hydrogen atoms, disordered parts (occupancy ratio of 0.78 : 0.22) in **81** and one disordered packing solvent in the asymmetric unit of **84** (0.9 · CH_2Cl_2) have been omitted for clarity.

S_p,R^P, respectively, which are the most predominantly formed configurations. Phosphate **73** possesses, similar to *meso*-**53**, a pseudochiral phosphorus atom, due to the different configurations of the C_5H_3Me moieties, resulting in the (1*R*-α,R_p,S_p,s^P)-**73** isomer. We conclude that this is the predominantly formed configuration within the mixture of isomers, based on NMR investigations that showed an isomeric mixture of 1 : 0.25 : 0.3. In the carbazole derivative **84** a *dr* of 1 : 0.28 is characteristic as evidenced by NMR experiments (*vide supra*), while single crystals of the R_p,S^P- and S_p,R^P- configured molecules were obtained. Examples of triple (2-oxo)phosphine oxide structures have been reported, whereas **65b** is the first example containing three different substituents. Interestingly, the P=O bond (1.5013(15) Å) is enlarged compared to the other P(V) compounds reported herein (1.441(8)–1.477(2) Å). Ferrocene **71b** is the third example of a binaphthyl-related phosphonate, one has been reported with the same configuration at the BINOL (*R*) [231] and one as the racemic mixture. [232] The bridging of the BINOL moiety into a phosphepine structure shifts the oxygen atoms by 0.154(6) (O1) and 0.039(6) Å (O2) out of the $C_{10}H_6$ plane. However, the bending of the naphthalene entities out of their planarity is rather low (5.7(4) and 4.4(5) °). Both planes of the two

naphthyls are rotated by 54.6(2) °.

Electrochemistry

The electrochemical measurements were carried out in anhydrous dichloromethane solutions at 25 °C with a scan rate of 100 mV s^{-1} under inert conditions, containing $[N(Bu)_4][B(C_6F_5)_4]$(0.1 mmol L^{-1}) as supporting electrolyte (Experimental Section). For the measurements a three-electrode cell containing a Pt auxiliary electrode, a glassy-carbon working electrode (surface area 0.031 cm^2), and an Ag/Ag^+ (0.01 mmol L^{-1} $[AgNO_3]$) reference electrode fixed on a Luggin capillary was used. The measurement conditions are similar for all experiments performed herein, except otherwise noted. All potentials are referenced to the FcH/FcH^+ redox couple.[233]
The electrochemical behavior of the ferrocenyl phosphates **47**–**50**, **70a**,**b**, **72**, **73**, **75** and **76**, the phosphonates **52** and **71b**, the phosphinate **53** and the nitrogen-containing ferrocenyl phosphoramidates **12**–**15**, **43e**, **79**–**81** and **84** were investigated by cyclic voltammetry (CV) and square wave voltammetry (SWV) (Figure 3.36, Table 3.8).

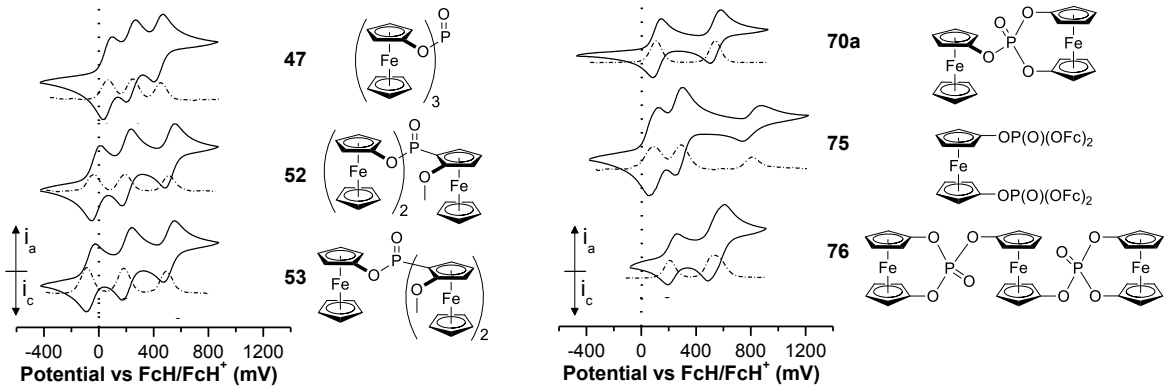


Figure 3.36 Cyclic voltammograms (solid lines) and square wave voltammograms (dotted lines) of **47**, **52**, **53**, **70a**, **75** and **76** in CH_2Cl_2 solutions (1.0 mmol L^{-1}).

The charge transfer behavior of the oxidized products of **47** and **53** were studied in an exemplary manner in more detail by *in situ* UV/Vis/NIR spectroelectrochemistry (Figure 3.37). All measured compounds, except **75** and **76**, show for each ferrocenyl moiety one well-separated reversible one electron redox event. For compound **47** with its three OFc units three separated redox processes with the first one at $E_1^{\circ\prime} = 30$ mV were found (Figure 3.36), due to the weak coordinating electrolyte $[N(Bu)_4][B(C_6F_5)_4]$, which is known to stabilize highly charged species and minimize ion pairing effects.[234,235]. However, this differs, when $[N(Bu)_4][ClO_4]$ as electrolyte was used as reported by Herberhold *et al.* There, only two reversible events were observed with a two electron step for the first and a one electron step for the second oxidation.[219] When one ferrocenyl group in **47** is replaced by an electron poorer phenyl moiety as typical in **48**, then the first redox process is shifted to a higher redox potential ($E_1^{\circ\prime} = 85$ mV) (Table 3.8), as expected. The same trend is observed for **11** in which two ferrocenyl moieties are replaced by two phenyl units ($E_1^{\circ\prime} = 106$ mV) (Table 3.8). A replacement of the phenyl group in **48** by a naphthyl moiety as characteristic for **49** or

50, however, does not have any notable influence on the first (**48** and **49**, $E_1{}^{\circ\prime} = 85\,\text{mV}$; **50**, $E_1{}^{\circ\prime} = 90\,\text{mV}$) or second redox potential (**48** and **49**, $E_1{}^{\circ\prime} = 250\,\text{mV}$; **50**, $E_1{}^{\circ\prime} = 260\,\text{mV}$). The *apFr* of **47** to **52** led to a decrease of the first redox potential, due to the more electron-donating methoxy group, which increases the electron density at the ferrocenyl (**47**, $E_1{}^{\circ\prime} = 30\,\text{mV}$; **52**, $E_1{}^{\circ\prime} = -20\,\text{mV}$). A second rearrangement to form compound **53** leads to a similar reduction of the first redox event from $E_1{}^{\circ\prime} = -20\,\text{mV}$ (**52**) to $E_1{}^{\circ\prime} = -60\,\text{mV}$ (**53**), whereas the second and third redox processes have not been influenced. The reason therefore is the lower electron-withdrawing effect of the phosphonate group in methoxy ferrocene **53**, leading to a higher electron density at the ferrocenyl moiety and as a result thereof, this compound can more easily be oxidized. *In situ* UV/Vis/NIR spectroelectrochemical measurements were additionally carried out for compounds **47** and **53**. However, no intervalence charge transfer (= IVCT) absorptions were found between 1000 and 3000 nm, as exemplarily shown for **53** in Figure 3.37. This shows that no direct electronic communication between the Fc and Fc^+ units occurs, indicating significant electrostatic interaction among the terminal Fc/Fc^+ groups as oxidation progresses.

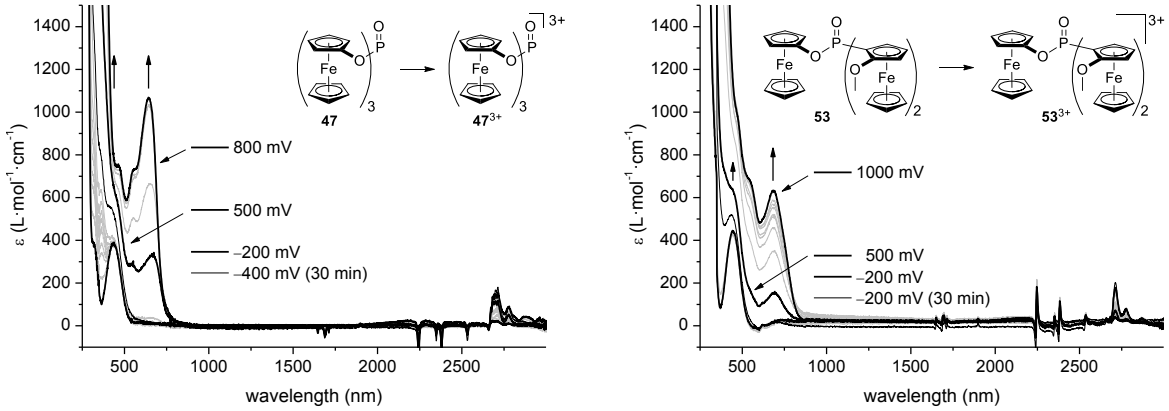


Figure 3.37 UV/Vis/NIR spectra of $P(O)(OFc)_3$ (**47**, left) and phosphinate **53** (right) at increasing potentials *vs* Ag/AgCl in CH_2Cl_2 solutions ($2.0\,\text{mmol}\,\text{L}^{-1}$) at 25 °C containing $0.1\,\text{mmol}\,\text{L}^{-1}$ of $[N(Bu)_4][B(C_6F_5)_4]$as the supporting electrolyte. Arrows indicate increasing absorptions.

Replacing the electron-rich [3]ferrocenophane group in **70a** by a chelating (*R*)-BINOL substituent in **70b**, increased the first redox potential from $E_1{}^{\circ\prime} = 110\,\text{mV}$ to $E_1{}^{\circ\prime} = 142\,\text{mV}$. A series of ferrocenophanes *inter alia* **70b** was electrochemically investigated by Herberhold using $[N(Bu)_4][ClO_4]$ as electrolyte.[219] There a lower redox separation of $\Delta E^{\circ\prime} = 300\,\text{mV}$ ($E_1{}^{\circ\prime} = 550\,\text{mV}$, $E_2{}^{\circ\prime} = 850\,\text{mV}$ vs SCE) was observed, which is attributed to the stronger coordinating character of the electrolyte (*vide supra*). Zanello *et al.* studied the redox behavior of tri- and ditellura-ferrocenophanes and described an unambiguous assignment of the molecule orbitals in the redox process.[236] The *apFr* of **70b** leading to **73b** shows a similar redox behavior. The electron-donating effect of the methoxy group to the ferrocenyl moiety in **71b** is superimposed by the electron-withdrawing effect of the phosphonate moiety.
The methyl groups in 2,2'-position in **73** shift the redox potential, in comparison to **72**, to lower values ($E_1{}^{\circ\prime} = 254\,\text{mV}$ for **73**, $E_1{}^{\circ\prime} = 302\,\text{mV}$ for **72**) due to their electron-donating

Table 3.8 Cyclic voltammetry data of ferrocenyl phosphates, phosphonates and aliphatic derivatives **11**–**15**, **43e**, **47**–**50**, **52**, **53**, **70**–**73**, **75**, **76**, **79**–**81** and **84**.[a]

Compd.	$E_1^{\circ\prime}$[b] (ΔE_p)[c]	$E_2^{\circ\prime}$[b] (ΔE_p)[c]	$E_3^{\circ\prime}$[b] (ΔE_p)[c]	$\Delta E^{\circ\prime}$[d]	Compd.	$E_1^{\circ\prime}$[b] (ΔE_p)[c]	$E_2^{\circ\prime}$[b] (ΔE_p)[c]	$\Delta E^{\circ\prime}$[d]
Phosphates and Phosphonates					Aliphatic *N*-Derivatives			
47	30(64)	235(66)	435(68)	205/200	**12**	–29(65)		
48	85(60)	250(65)	–	165	**13**	–50(62)		
11	106(60)				**14**	–63(62)		
49	85(60)	250(66)		165	**15**	62(64)		
50	90(68)	260(70)		170	**43e**	–14(74)	202(106)	216
52	–20(64)	200(62)	520(76)	220/320				
53	–60(66)	205(70)	510(80)	265/305				
[3]Ferrocenophanes					Heterocyclic *N*-Derivatives			
70a	110(62)	535(72)	–	425	**79**	100(58)	260(66)	160
70b	142(64)				**80**	95(60)	255(62)	160
71b	152(68)				**81**	90(62)	250(66)	160
72	302(64)				**84**	60(60)	290(64)	250
73	254(60)							
75	90(70)	270(60)	800(135)	180(530)				
76	225(70)	540(125)[e]		315				

[a] All potentials are given in mV vs FcH/FcH^+, with an analyte concentration of 1.0 mmol L^{-1} at 25 °C containing 0.1 mmol L^{-1} of $[N(Bu)_4][B(C_6F_5)_4]$as the supporting electrolyte.
[b] $E^{\circ\prime}$ = formal potantial.
[c] ΔE_p = difference between the anodic and cathodic peak potential.
[d] $\Delta E^{\circ\prime}$ = potential difference between the ferrocenyl-related redox processes.
[e] Broad two electron process.

effect. Compound **75**, bearing five ferrocenyls, showed three redox processes. The four OFc groups are represented by the first two redox events at $E_1^{\circ\prime}$ = 90 mV and $E_1^{\circ\prime}$ = 270 mV. Both consist of two nonseparated one-electron processes of one ferrocenyl at each phosphate fragment. The one-electron redox wave at $E_3^{\circ\prime}$ = 800 mV represents the 1,1'-substituted ferrocenyl (Table 3.8). The difference between the anodic and cathodic potential of ΔE_p = 135 mV indicates an electrochemical irreversibility of the third redox event. The redox potential at $E_3^{\circ\prime}$ = 800 mV leads to the conclusion that both phosphate groups, each bearing two oxidized ferrocenyl, exerts a high electron-withdrawing effects and therefore, for a linear increase or decrease of the redox potential.[237] Molecule **76** containing two [3]ferrocenophane motifs, compared to two ferrocenyls at the phosphorus atom (**75**), showed two redox processes: a one electron event for the non-bridged, and a redox process with a shoulder including two one-electron processes for both [3]ferrocenophanes (Figure 3.36). Electrochemical measurements of ferrocenyl phosphoramidates **79**–**81** and **84** display two reversible one-electron redox processes (Table 3.8). The nature of the *N*-heterocycle in **79**–**81** has negligible influence on the redox potential and as consequence thereof, the redox separation is with $\Delta E^{\circ\prime}$ = 160 mV identical for all three compounds. A further redox process for the *N*-heterocycle was not observed under the applied measurement conditions. The first redox process for

84 is found at $E_1^{\circ\prime}$ = 40 mV (for comparison: **81**, $E_1^{\circ\prime}$ = 90 mV), which is attributed to the electron-donating methoxy substituent. The second redox event is with $E_1^{\circ\prime}$ = 290 mV for **84** 40 mV higher than in **81**, which can be explained by the more electron-withdrawing influence of the directly to phosphorus-bonded Fc^+ moiety. Besides the importance of the electron density at the ferrocenyls for limiting a lithiation process, also the nature of the substituent is relevant. Thus, triferrocenyl phosphate **47** (30 mV, Table 3.8) underwent an *apFr*, whereas the borane adduct **15** (62 mV) showed no attack at the phosphorus atom, although it contained a ferrocenyl unit with a decreased electron density. Obviously, the strongly electron-donating cyclic *N*-alkyl group shields the phosphorus atom and thus, prevents a nucleophilic attack. Compared to *N*-aryl phosphates **79**–**81**, this is due to the electron rich *N*-alkyl substituents, enabling a better orbital overlap between the N and the P atoms. In contrast to the compounds described above, phosphoramidates **12**–**15** and **43e** did not undergo an *apFr*, although lithiation reactions were observed by using the stronger base ^{s}BuLi instead of LDA (Figure 3.6). This indicates that a higher electron density is present at the ferrocenyls in **12**–**15** and **43e**, which is verified by the lower redox potentials of up to 62 mV for the borane adduct **15**. In contrast, the aromatic derivatives and the [3]ferrocenophanes **72** and **73** are observed at higher values of 90 mV (Table 3.8). The low values for phosphonate **52** (–20 mV) and phosphinate **53** (–60 mV) are misleading, as the first redox event refers to the methoxy-substituted ferrocenyl, which is not able to undergo an *apFr*. Within the series of aliphatic ferrocenyl phosphates, the replacement of a P=O (**14**, –63 mV) by a P=S (**13**, –50 mV) and furthermore a P→BH_3 (**12**, –29 mV) group decreases the electron density at the ferrocenyl, while increasing the redox potential. This is contrary to the results obtained by *apFr* within the series of P(E)(OFc)$(OEt)_2$ with decreasing yields for E = O (94 %) > E = BH_3 (37 %) > E = S (0 %), as described in Section 3.1.1. The latter one could solely be converted by using ^{s}BuLi (50 %). Replacement of an *N*-alkyl (**14**) by a FcO moiety (**43e**) shifts the potential for the first redox event from –63 to –14 mV.

3.1.5 Conversion of 1,2-*P*,*O*-Phosphonates to Phosphines and their Application in *C*,*C* Cross-Coupling Reactions

Conversion of Phosphonates to Phosphines

The transformation of phosphonates *rac*-**16** and (R_p)-**31e** into phosphine **91**, which has been considered as auxiliary ligand for palladium in Suzuki *C*,*C* cross-couplings, was thoroughly investigated, as outlined in Figure 3.38. The attempted direct conversion of phosphonate *rac*-**16** into phosphine oxide *rac*-**20** by treatment with phenylmagnesium bromide or phenyllithium gave only unreacted starting materials. Likewise, the conversion into the dichlorophosphonate intermediate **89**[211,238] with subsequent introduction of the phenyl moieties[188,239] in a *one-pot* reaction turned out to be unsuccessful in the case of ferrocene **16**.
In contrast, reduction of this phosphonate in the presence of an excess of Li[AlH_4] and trimethylsilyl chloride followed by acidic workup under anaerobic conditions yielded phosphine **90a** quantitatively.[239,240] Successive Pd-catalyzed Stelzer *P*,*C* cross-coupling[15] was chosen for the conversion of the primary phosphine into compound **91**, as this transformation

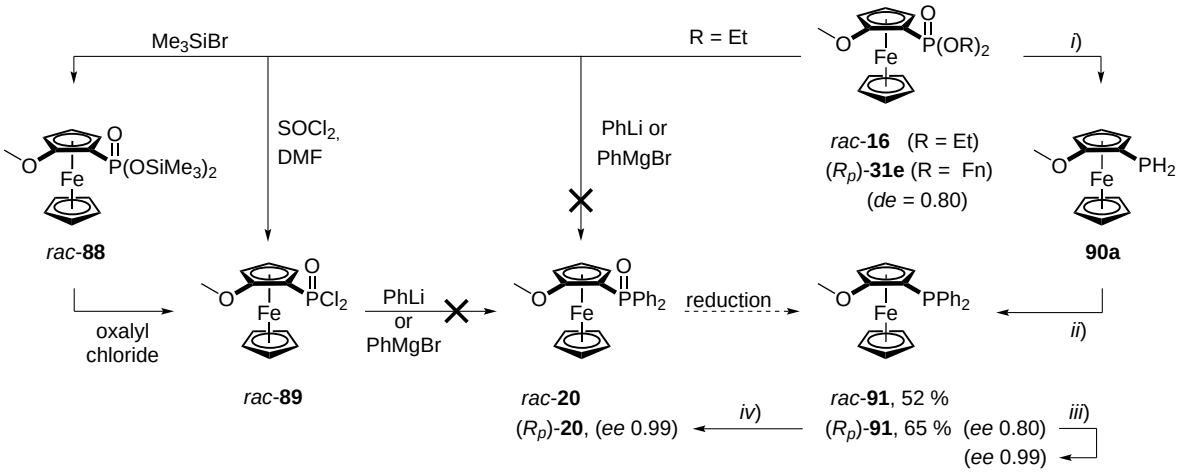
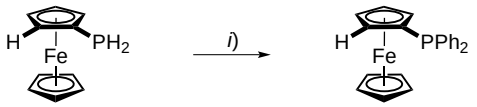


Figure 3.38 Possible Pathways for the Conversion of Phosphonate *rac*-**6** and (R_p)-**31e** into Phosphine **91**.
Reaction conditions: *i*) Li[AlH_4] (4 equiv), $ClSiMe_3$, THF, 25 °C (**6**) or 50 °C (**31e**), 12 h. *ii*) PhI (2 equiv), K_3PO_4 (2 equiv), [Pd(dppf)Cl_2] (4 mol %), toluene, 110 °C, 12 h. *iii*) crystallization from hexane; *iv*) atmospheric conditions, 2 weeks in 95/5 (*v*/*v*) hexane/^{t}BuOMe.

has, to the best of our knowledge, never been applied in ferrocene chemistry.
The phosphine **90b** is accessible in a multi gram scale from *O*,*O*-diethyl ferrocenylphosphonate, thus, we investigated **90b** instead of **16** in a test reaction to explore the reaction conditions (Table 3.9). The best results were reached using two equivalents K_3PO_4 with toluene as the solvent and [$Pd(PPh_3)_4$] giving the coupling product in 72 % (Entry 4). The usage of other bases decreases the yield dramatically.

Table 3.9 Optimization of the reaction condition for the Stelzer coupling for ferrocenyl phosphines.[a)]



90b **90c**

Entry	Base (equiv)	Solvent	Yield[b]
1	NEt_3 (4)	toluene	0 %
2	K_3PO_4 (4)	toluene	68 %
3	CsF (4)	toluene	26 %
4	K_3PO_4 (2)	toluene	72 %
5	K_3PO_4 (4)	1,4-dioxane	65 %
6	K_3PO_4 (2)	1,4-dioxane	48 %

[a] Reaction conditions: *i*) [$Pd(Ph_3)_4$] 2 mol-%, PhI (3 equiv), 110 °C.
[b] Isolated Yields.

With an increase of base also a significant amount of the corresponding phosphanoxide can be detected (up to 50 %, Entry 2). Nevertheless, it is known that phosphaneoxides can be converted to the corresponding phosphane.
Application onto 1,2-disubstituted ferrocene **90a**, however, gave ferrocenyl methyl ether (**22**)

as the only product, which was formed due to a P,C_{Cp} bond cleavage during the catalytic transformation (Figure 3.39).[241] The P,C_{Cp} bond cleavage proceeds through a P-aryl/aryl exchange at a metal complex shown in Figure 3.39. Its formation can be prevented by the use of a chelating ligand suppressing ligand scrambling as well as the absence of phenyl iodide after complete conversion of the primary and intermediately formed secondary phosphines. The utilization of 1,1'-bis(diphenylphosphino)ferrocene (dppf) as a sterically demanding, chelating ligand for palladium and avoidance of an excess of phenyl iodide circumvented this side reaction, giving access to the desired ferrocene **91** in 52 % yield (Figure 3.38). Using the enantioenriched (R_p)-**31e** under the same conditions gave (R_p)-**91** in a similar yield of 65 % and an *ee* of 99 % after single crystallization (Figure 3.38), evidenced by chiral HPLC (Experimental Section).[156]

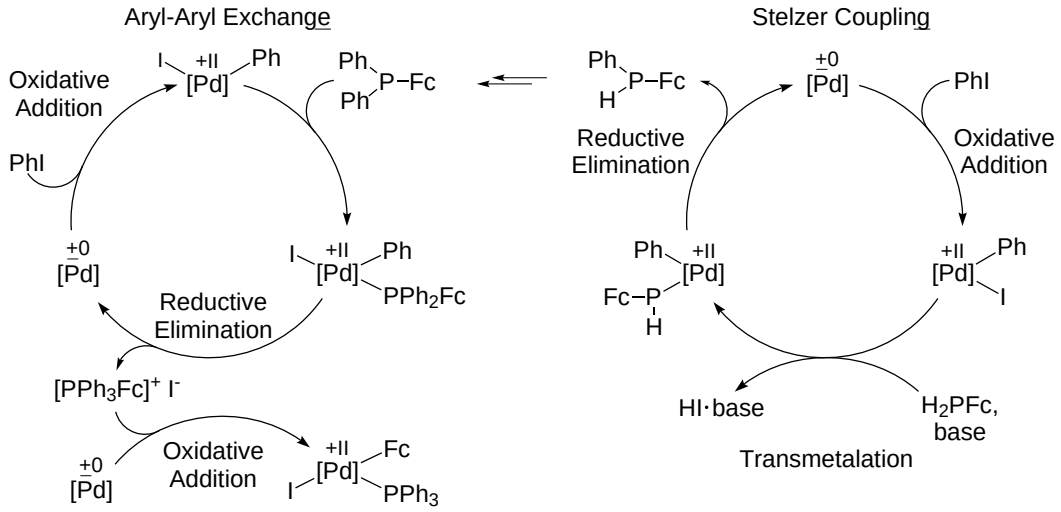


Figure 3.39 Mechanism of the Stelzer Coupling and the undesired Aryl-Aryl-Exchange. Ar = single bound aromatic group.

Single crystals of *rac*-**91** suitable for single-crystal X-ray diffraction studies were obtained by crystallization from boiling hexane, whereas (R_p)-**91** crystallized as its oxide (R_p)-**20** from the HPLC solution (5 % ^{t}BuOMe in hexane) after 2 weeks (Figure 3.38). The *racemic* derivative **91** crystallized in the centrosymmetric space group $P2_1/c$. For enantiopure (R_p)-**20** *non*-centrosymmetric $P2_12_12_1$ was present. Both were present with one molecule in the asymmetric unit. The solid-state structures unambiguously confirmed the 1,2-substitution pattern of the metallocene backbone, and the successful proceeding of the reduction and Stelzer coupling procedure. As expected, the phosphorus and oxygen atoms are both located in the plane of the cyclopentadienyl ring (**91**, rms deviation 0.0008 Å, distance of P1 –0.0010(3) Å and distance of O1 –0.079(3) Å; (P_p)-20, rms deviation 0.0075 Å, distance of P1 –0.095(7) and distance of O1 –0.091(6) Å). In both structures, the methyl group points away from the phosphorus atom. In phosphine **91**, the lone pair of the phosphorus atom is directed into the vacant space between the two substituents, which in principle should allow for a chelating complexation of a suitable transition metal, *e.g.* palladium. In the respective oxide **20**, the oxygen atom directs away from the vacant space to avoid steric and electronic interactions with the ether oxygen. The P–O bond in **20** of 1.491(2) Å is significantly enlarged

compared to those in the phosphates and phosphonates reported herein that range between 1.437(9) and 1.469(4) Å, due to the more electron rich phenyl rings.

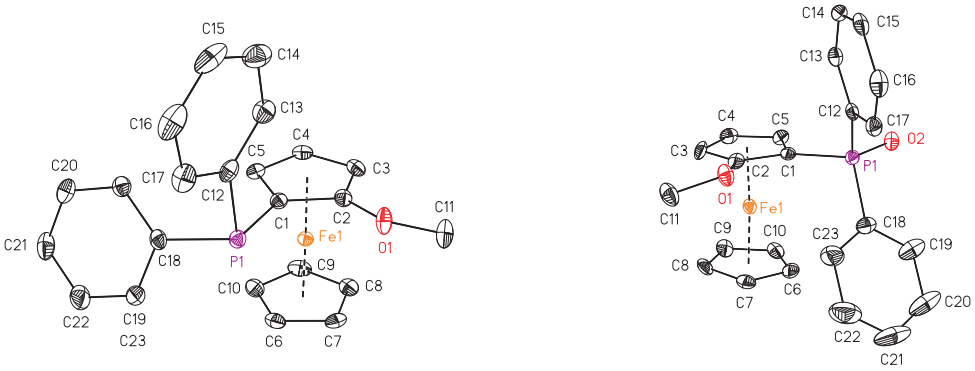


Figure 3.40 ORTEP (50 % probability level) of the molecular structures of *rac*-**91** (left) and (R_p)-**20** (right) with the atom-numbering Scheme. All hydrogen atoms have been omitted for clarity.

C,C Cross-Coupling Reactions

P,O-ferrocenes show high activities in the synthesis of sterically congested biaryls via Suzuki–Miyaura *C,C* couplings, as demonstrated recently.[73,74,130]

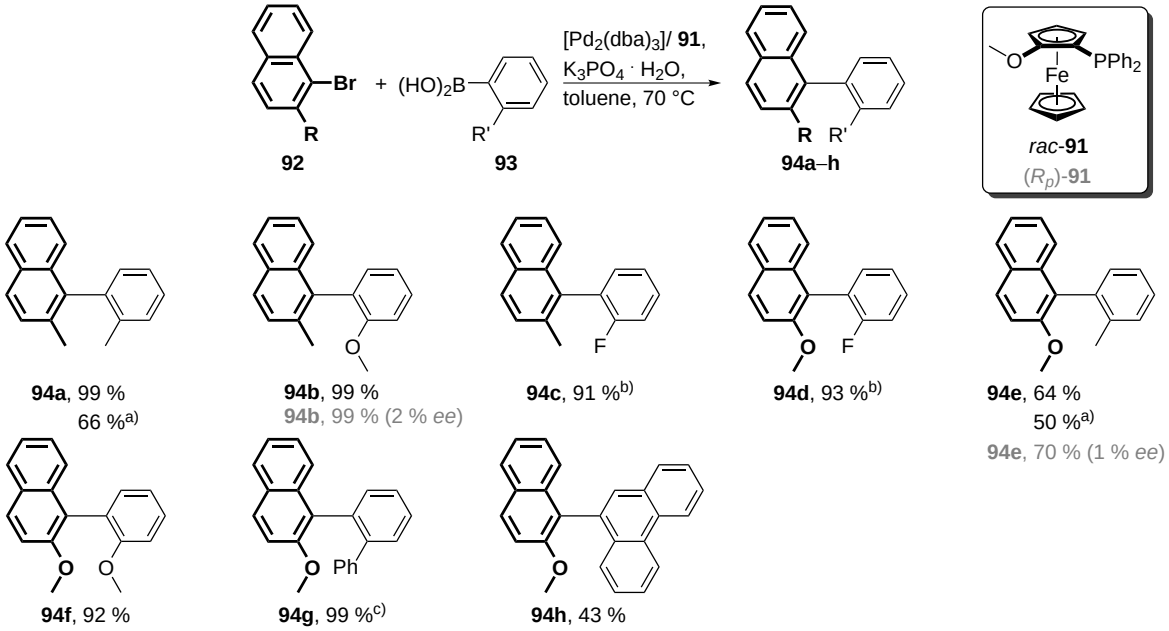


Figure 3.41 Application of phosphine *rac*- and (R_p)-**91** in the Pd-catalyzed, (atropselective) synthesis of tri-*ortho*-substituted biaryls via Suzuki-Miyaura *C,C* cross-couplings.
Reaction conditions: aryl bromide (1.0 mmol), boronic acid (1.5 mmol), $[Pd_2(dba)_3]$ 0.25 mol-%, **91** 1 mol-%, 24 h, $K_3PO_4 \cdot H_2O$ (3.0 mmol), toluene (3 mL), 70 °C. Reaction times were not optimized. Yields are based on isolated products as the average of two measurements. a) 50 °C; b) $K_3PO_4 \cdot 3\,H_2O$; c) 100 °C.

This prompted us to investigate the performance of phosphines *rac*-**91** as a ligand

in the Pd-catalyzed synthesis of *racemic* tri-*ortho*-substituted biaryls, starting from 1-bromonaphthalenes **92** and *ortho*-substituted phenylboronic acids **93** (Figure 3.41). At a catalyst concentration of 0.5 mol-% and a reaction temperature of 70 °C the respective biaryls **94a**–**h** could typically be isolated in good to excellent yields (Figure 3.41). A slightly higher temperature was required to obtain biphenyl **94g** quantitatively. For the sterically more demanding 9-phenanthryl derivative **94h** only a moderate yield of 43 % was achieved. These results are comparable with those of *P*,*O*-substituted ferrocenes described before[73,74] and exceed the performance of other (ferrocenebased) phosphines regarding reaction temperature and palladium concentration.[67,108,242] These results demonstrate that *P*,*O*-substituted ferrocenes, accessible through an *apFr*, are catalytically active for the synthesis of axial-chiral biaryls via Suzuki–Miyaura *C*,*C* couplings in the presence of palladium. Furthermore, the highly diastereomerically enriched phosphonate **31e** could be converted to (R_p)-**90**, revealing that the reaction conditions for the reduction of diethylferrocenyl phosphonate **16** can be adopted on the sterically more demanding fenchyl derivative **31e** (Figure 3.38).[239,240] When **90** was used under Pd-catalyzed Stelzer *P*,*C* cross-coupling reaction conditions,[15] the respective diphenylphosphino ferrocene (P_p)-**91** could be obtained in 65 % yield (80 % *ee*). Single recrystallization from hexane increased the *ee* to > 0.99, evidenced by chiral HPLC. However, using enantiopure (R_p)-**91** for the synthesis of **94b** and **94e** almost no *ee* (< 2 %) could be detected (Figure 3.41).

3.2 Oxygen-Functionalization of Hydroxyferrocenes

3.2.1 Reaction of Hydroxyferrocenes with Electrophiles

The results of the application of 2-methoxyferrocenyl phosphane in the Suzuki–Miyaura reaction for the synthesis of hindered biaryls[73,74] showed their good catalytic activity within this reaction.

The most important feature of molecule **91** is a better stabilization of the catalytically active species due to a hemilabile binding of the oxygen atom to the palladium atom.[74] Due to its potential planar chirality, the enantiopure ligand has been investigated for this catalytic transformation. However, the stereo information of the ferrocenyl backbone could not successfully be transferred to a substrate, due to the sterically *non*-demanding methoxy substituent (Figure 3.41). Thus, additional research on the functionalization of the oxygen moiety within this structural motif is required. It is important to note that for the final conversion of the phosphonates, obtained after *apFr*, into the 1,2-*P*,*O*-phosphanes, a reduction and Stelzer coupling process had to be carried out, which sets certain requirements on the tolerance of functional groups.

Aromatic ethers are promising structural motifs, since they are known to be stable under different reaction conditions without a C–O bond cleavage, a potentially increased steric demand, and a stabilizing effect on aromatic substrates.[243]

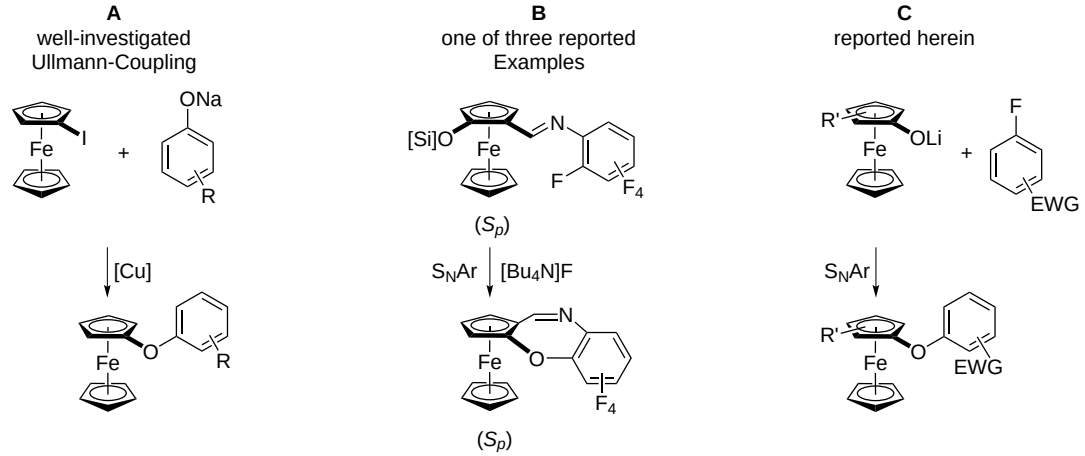


Figure 3.42 Synthetic methodologies resulting in the formation of ferrocenyl aryl ethers: (**A**) Recently reported copper-mediated Ullmann-Type coupling[157], and (**B**) S_NAr reactions showing one of the three examples known in ferrocene chemistry.[164,244] ([Si] = Si^{t}BuPh$_2$)

Possible routes were adopted from the synthesis of hydroxyl ferrocene in an Ullmann-type coupling starting from ferrocenyl halides.[147,157,167,194] This approach was extended to aromatic and aliphatic alcoholates to yield the respective ethers (**A**, Figure 3.42),[156,157,245] which, however, are not known to proceed for compounds bearing a phosphorus substituent in the *ortho* position. Furthermore, one example of a nucleophilic *C*,*C* aromatic substitution reaction (S_NAr) has been reported for an intramolecular cyclization of an enantiomerically pure (S_p)-perfluorinated phenyl imine (**B**, Figure 3.42), which has been observed accidentally.[164]

In addition, two examples of an S_NAr reaction with 4-chloroquinolines were reported.[244] Herein, the hydroxyferrocenes are obtained after *apFr*, which limits the hydroxy functionality to act as a nucleophilic substrate.

Substitution and Addition Reactions with Aliphatics

For the conversion of the ferrocene-hydroxyl group with electrophiles to ethers, we investigated the reaction of the deprotonated ferrocenol **5**–Li or its *ortho*-phosphonato-substituted derivative **16**–Li with well-known electrophiles, such as benzyl bromide (**a**), propargyl derivatives (**b**,**c**), the conversion to a THP (tetrahydropyran) (**d**), and chlorosilanes (**e**, **f**) (Figure 3.43). The results indicate a low nucleophilicity of ferrocenolates toward S_N2 reactions at carbon atoms containing bromide (**a**), tosylate (**b**, **c**) and phosphinates (**d**, **e**), due to a rapid oxidation of **5** by the required quinone for **d** and **e** (Figure 3.43).[246] In contrast, the nucleophilic addition reaction of 3,4-dihydro-2*H*-pyran (**f**, Figure 3.43) and ferrocenol derivatives is known to proceed with virtually quantitative yield[120,167] and can also successfully be applied to the *ortho*-phosphonato ferrocenol **16**–H, affording **95f** in 99 % yield, after an *apFr*. Interestingly, **95f** is not obtained as a racemic mixture but as a mixture of both diastereomers in the ratio 0.68 : 0.32.

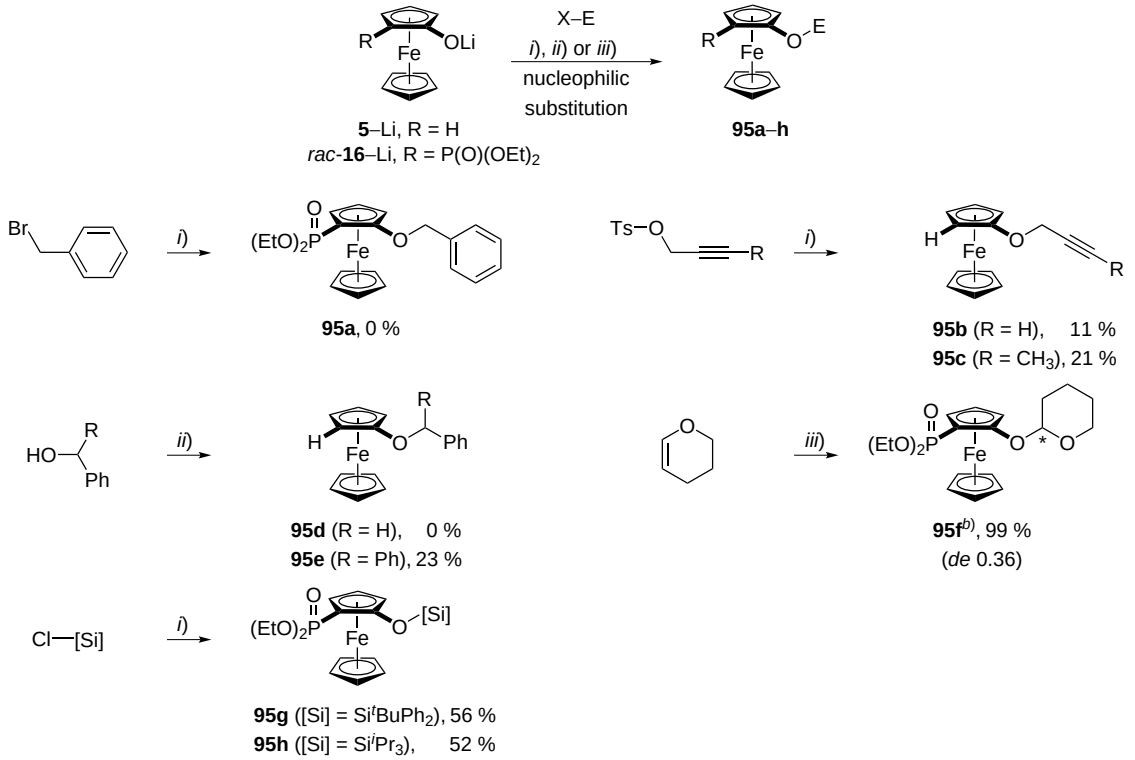


Figure 3.43 Nucleophilic substitution reactions (S_N2) of hydroxy ferrocenes with electrophiles.[b]

Yields are based on the ferrocenyl educts. Reaction conditions: *i*) Et_2O or THF, 18 h, 25 °C; *ii*) 1^{st} CH(OH)R'Ph, BuLi, $ClPPh_2$, THF, 2^{nd} ,6-dimethylcyclohexa-2,5-diene-1,4-dione, **5**, 18 h, 25 °C; *iii*) HCl (∼3 *M*, CH_2Cl_2, 18 h, 25 °C; a) The FcOLi compounds **5**–Li and *rac*-**16**–Li were generated either by lithiation of **5** using BuLi or by an *apFr* of **6**; b) A nucleophilic addition reactions occurred, instead of a substitution; Ts = SO_2-C_6H_4-*p*-CH_3). Yields are based on **5** or **6**.

The usage of chlorosilanes[164] allows the synthesis of the respective ferrocenyl silyl ethers *rac*-**95g** (56 %) and *rac*-**95h** (52 %). However, silyl and THP ethers are known to be unstable under long-term basic conditions at higher temperatures or in Pd-catalyzed reactions.[247] Phenols, as the benzene analogues of ferrocenols, can be converted into aromatic ethers, *e.g.*, by using iodonium[248] or diazonium compounds.[249] Attempts to adopt these reaction conditions for ferrocenol (**5**) to give the appropriate ferrocenyl phenyl ether **96d** by using diphenyliodonium triflate and phenyldiazonium tetrafluoroborate failed, probably due to the oxidation and decomposition of **5**.[250]

Nucleophilic Aromatic Substitution Reactions

A further possibility for the introduction of aryl substituents at oxygen-based nucleophiles is the usage of electron-deficient aryl halides in S_NAr reactions, which is well-known for phenyl derivatives,[251] whereas only three examples have been reported for ferrocenyl-based compounds, *i.e.* reaction **B** (Figure 3.42), and chloroquinones.[164,244] Thus, we reacted FcOLi (**5**–Li) with Sangers reagent[252], affording the respective ferrocenyl ether **96a** in 81 % yield (Figure 3.44). The reaction conditions were adopted from ref 251. The reaction of 4-nitrofluorobenzene with **5** resulted in the formation of **96b** in 74 % yield (Experimental Section). Less electron deficient derivatives such as **c**–**e** in Figure 3.44 did not undergo a S_NAr reaction, which is in accordance with the case for benzene-based compounds.[251] An activation of fluorobenzene to the respective tricarbonylchromium complex, known for alkoxy[253] and *N* nucleophiles,[254] did not enhance the reactivity. Nitrogen-containing aryl halides, *e.g.* pyridines, pyrimidines, and pyrazines, are also not suitable for the reaction of ferrocenol, in contrast to the phenyl-based derivatives.[255]

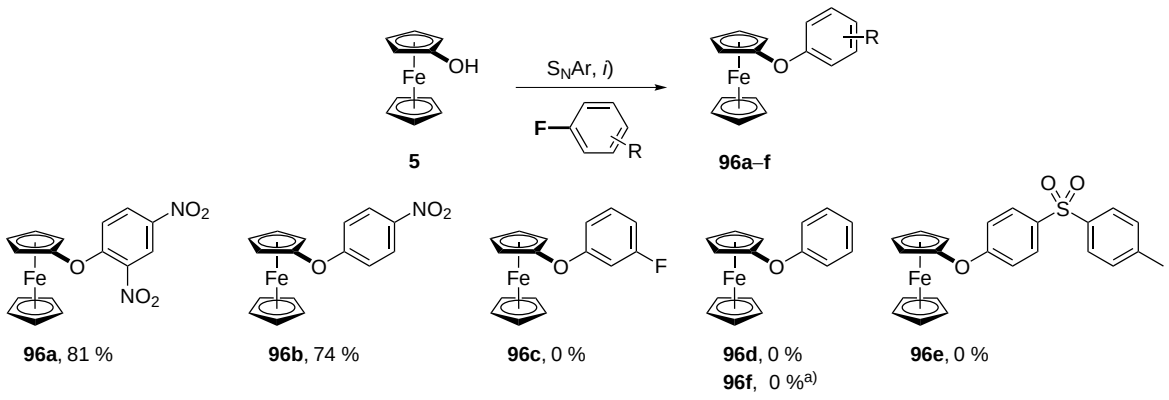


Figure 3.44 Synthesis of ferrocenyl aryl ethers **96a**–**f**.
Reaction conditions: *i*) BuLi, hexane, aryl fluoride, DMF, 70 °C, 18 h; a) the η^6-$Cr(CO)_3$ complex was used. Yields are based on **5**.

The dependence between reactivity and the presence of multiple electron-withdrawing substituents can be optically observed as a rapid color change in the conversion with 2,4-dinitrofluorobenzene to **96a**, whereas a decay of several minutes in the case of 4-nitrofluorobenzene indicates a decreased reactivity for the single nitro-substituted derivative. It should be noted that within the synthesis of **96**a the excess of Sanger's reagent could not

be removed, owing to an equal chromatographic behavior. Thus, it was necessary to further react the crude product of **96a** with dicyclohexylamine and K_2CO_3 in acetone at 40 °C to convert 2,4-dinitrofluorobenzene into 2,4-dinitro-*N*,*N*-dicyclohexylaniline, which could easily be separated by column chromatography. This workup step could be avoided by adding dicyclohexylamine directly to the reaction mixture.

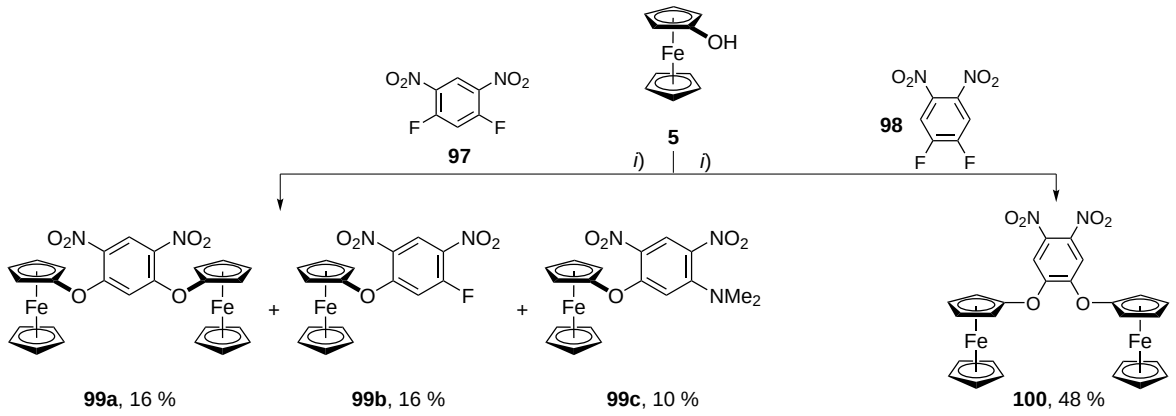


Figure 3.45 Synthesis of *ortho*-/*meta*-diferrocenyl dinitroaryl ethers **99a** and **100**.
Reaction conditions: *i*) 1^{st}, hexane, –30 °C, BuLi; 2^{nd}, DMF, **97**/**98**, 70 °C, 18 h. Yields are based on **5**.

The synthesis protocol for the ferrocenyl aryl ethers **96a**,**b** gave access to benzenes bearing two ferrocenyl ether groups by the treatment of **5** with the 1,3- (**97**) or 1,2-difluorobenzenes (**98**),[256] resulting in the formation of the first *meta*- (**99a**) and *ortho*-disubstituted (**100**) bis(ferrocenyloxy) benzenes (Figure 3.45). In the case of **97**, monofunctionalized **99b** and a product bearing an NMe_2 moiety (**99c**), which results from the nucleophilic attack of DMF (*N*,*N*-dimethylformamide) at a fluorine-bearing carbon atom,[257] were formed. In contrast to **97**,[258] compound **98** is not known to undergo a single substitution.[259] A SciFinder search for the conversion of **98** to a single substituted product found no reaction.

As shown in Section 3.1 ferrocenyl phosphates can undergo a 1,3-O→C *apFr*. The respective rearrangement products contain a hydroxy substituent that should be suitable for S_NAr reactions with aryl fluorides. This prompted us to extend the substrate scope to *ortho*-phosphonato and sulfonyl-substituted hydroxyl ferrocenes that can be obtained after the respective anionic phospho-(Section 3.1) and thia-Fries[167,194] rearrangements of **30a** and **101** (Figure 3.46). In a consecutive one-pot synthesis, ferrocenyl phosphate **30a** and triflate (**101**)[167,194] undergo the 1,3-O→C migration to give 1,2-*X*,*O* (X = P, S) substituted hydroxy ferrocenes respectively (Figure 3.46). Their reaction with nitro-aryl fluorides resulted in the formation of *ortho*-substituted ferrocenyl aryl ethers *rac*-**102a**,**b** and *rac*-**103a**, a rarely described structural motive in ferrocene chemistry. To date, the only reported examples for *ortho*-substituted ferrocenyl ethers are found in references 73, 164, 244 and[260]. In contrast to the phosphonato ferrocenes *rac*-**102a**,**b**, the respective sulfonyl derivatives possess a lower nucleophilicity of the hydroxyl oxygen, due to the highly electron withdrawing character of the SO_2CF_3 moiety (vide infra). Thus, no reaction with the less electrophilic 4-nitrofluorobenzene to ether *rac*-**103b** occurred. The *ortho*-substituted ferrocenyl phosphate **35a** and triflate

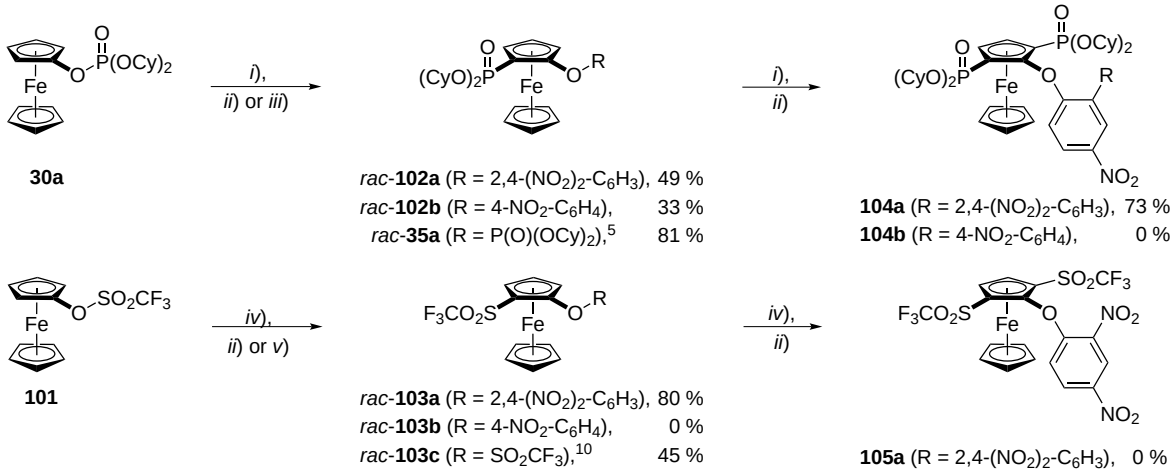


Figure 3.46 Synthesis of di- and trisubstitutied ferrocenyl nitroaryl ethers after anionic phospho- and thia-Fries rearrangements.
Reaction conditions: *i*) **30a**/**35a**, LDA, TMEDA, hexane, 25 °C; *ii*) 2,4-$(NO_2)_2$-C_6H_3F/4-NO_2-C_6H_4F, DMF, 70 °C, 18 h; *iii*) $ClP(O)(OCy)_2$; *iv*) LDA, –80 °C, 1 h; *v*) $O(SO_2CF_3)_2$, 25 °C. All yields are based on the respective ferrocenyl starting material.

103c can undergo a further anionic Fries rearrangement to result in the 1,3-disubstituted ferrocenes **104**–Li and **105**–Li (Section 3.1).[167,194] Subsequent reaction of **104**–Li with the most electrophilic 2,4-dinitrofluorobenzene afforded the di-*ortho*-substituted ferrocenyl aryl ether **104a** in 49 % yield. In comparison to **103**–Li, **105**–Li is less nucleophilic, due to one additional electron-withdrawing substituent, which obviously prevents the reaction with the less electrophilic mono-nitro aryl fluoride. This is comparable to SO_2CF_3-bearing **101**, which can only be converted using the dinitro derivative, whereas for doubly *ortho*-substituted **105**–Li, no reaction occurred. The reactivity can be estimated by the determination of the redox potential by cyclic voltammetry (CV) (Table 3.11, *vide infra*).

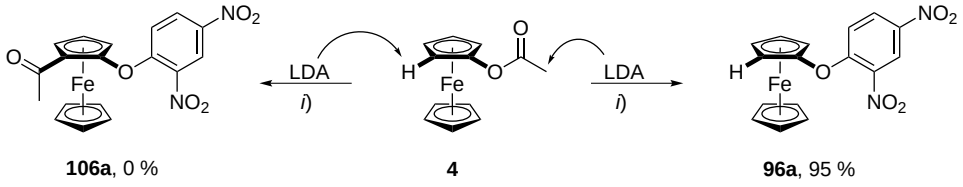


Figure 3.47 Attempted anionic carbo-Fries rearrangement of **4**.
Reaction conditions: *i*) LDA, –80 °C, THF, 2,4-dinitrobenzene, DMF, 40 °C. Yields are based on **4**.

A carbo-Fries rearrangement, which has been reported for phenyl-based derivatives, for example, alkyl amides, was also investigated by treating ferrocenyl acetate (**4**) with LDA at –80 °C. It should be noted that carbo-Fries rearrangements are solely described for carbamates.[178,223] However, instead of an *ortho* lithiation, a nucleophilic attack of LDA at the carbonyl carbon atom occurred, resulting in the formation of **5**–Li, and after subsequent reaction with the dinitro arylfluoride compound **96a** is formed exclusively instead of **106a** (Figure 3.47). Instead of a nucleophilic attack of LDA, this could also be explained by the deprotonation of the acetyl group and the release of ketene. The formed double bond, thus,

cleaved the FcO–C bond and the negative charge remains as the ferrocenolate ion.[261]
The Fries rearrangement to *ortho*-phosphonato ferrocenolates can additionally be performed with the chiral pool-based di(1*R*)-α-fenchyl ferrocenyl phosphate **30e**, affording ethers (R_p)-**107a** (0.81 *de*) and (R_p)-**107b** (0.74 *de*) (Figure 3.48), whereas the diastereomeric excess (*de*) was calculated on the basis of the integrated $^{31}P\{^1H\}$ NMR spectra.

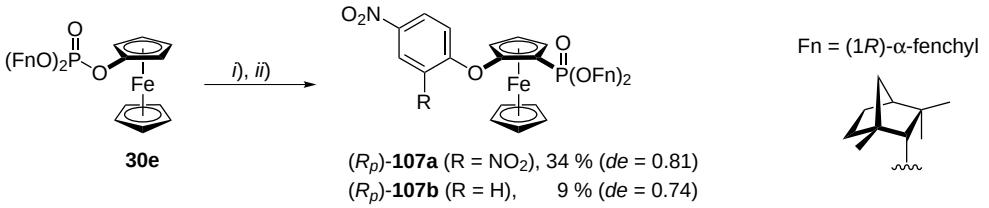


Figure 3.48 Synthesis of diastereoenriched planar-chiral 1,2-*P*,*O*-ferrocenyl aryl ethers. Reaction conditions: *i*) LiTMP, TMEDA, hexane, 25 °C; *ii*) 2,4-$(NO_2)_2$-C_6H_3F/4-NO_2-C_6H_4F, DMF, 70 °C. Yields are based on **30e**.

3.2.2 Characterization of Ferrocenyloxy Nitro Arenes

NMR Characterization

In the ^1H NMR spectra the resonances of the phenylic aromatic protons occur between 6.9 and 8.8 ppm. Compounds **99a**–**c** exhibit two resonances at 6.3–6.7 and 8.7–8.8 ppm for the protons located between the two nitro substituents. The electron-donating NMe_2 group in **99c** shifts the first signal to a higher field (6.26 ppm) in comparison to the OFc (**99a**, 6.68 ppm) or the rather electron-withdrawing F substituent in **99b**, which also splits both signals into doublets (6.87 and 8.83 ppm) due to a $J_{H,F}$ coupling of 11.9 (^3J) and 7.6 Hz (^4J). Characteristic resonance signals are also present at 2.57 ppm for the terminal C≡CH proton in **95b** and the methyl groups in **95c** (1.90 ppm) and **99c** (2.85 ppm). The $^{29}Si^1H$ NMR spectra of compounds *rac*-**95g**,**h** exhibit signals at 3.1 ppm for *rac*-**95g** and 17.8 ppm for *rac*-**95h**. The resonances in the $^{31}P\{^1H\}$ NMR spectra are found at 19.1 (*rac*-**102a**), 19.3 ppm (*rac*-**102b**), 20.5 ((R_p)-**107a**), and 21.2/22.2 ppm ((R_p)-**107b**). Solely the phosphorus atom in *rac*-**104a**, bearing two phosphonato substituents, is shifted to higher field (17.4 ppm). The electron-donating influences of the silyl (*rac*-**95g**, 24.9 ppm; *rac*-**95h**, 24.7 ppm) and phosphato moieties (*rac*-**102d**, 21.2 ppm) also shield the phosphorus atom. In the $^{13}C\{^1H\}$ NMR spectra, the decrease of the withdrawing character of the nitro substituents shifts the C–P or C–S carbon atom to higher field, as expected, from 63.4 (*rac*-**102a**) to 62.9 ppm (*rac*-**102b**), 69.4 (*rac*-**103a**) to 69.2 (*rac*-**103c**) ppm, and 61.9 ((R_p)-**107a**) to 60.6 ((R_p)-**107b**) ppm. The resonances of the P-C_{Fc} bond in phosphonates *rac*-**95g**,**h**, *rac*-**102a**,**b**, **104a**, and (R_p)-**107a**,**b** occur as doublets with a $^1J_{C,P}$ coupling constant of 214–219 Hz, similar to the ferrocenyl phosphonates reported in Section 3.1. Interestingly, the influence on the C–O binding carbon of the C_5H_4 and C_5H_3 rings is in contrast with the electron-withdrawing character of the aryl substituent, resulting in a downfield shift from 119.5 (**96a**) to 119.9 (**96b**) ppm, 119.3 (*rac*-**102a**) to 120.1 (*rac*-**102b**) ppm, and 120.8 ((R_p)-**107a**) to 121.6 ppm ((R_p)-**107b**). In the 1,3-bisphosphonato species **104a**, this

signal is observed at 118.6 ppm. Compound **104a** is formed as a mixture of two isomers regarding the rotation of the aromatic $C_6H_3(NO_2)_2$ moiety, due to two sets of signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra formed in a ratio of approximately 0.8 : 0.2. The two sets exhibit similar $J_{H,H}$ values in the ^{1}H NMR spectrum, whereas the sum of the integrals of both signals is required for a comparison with the integrals of the ferrocenyl and cyclohexyl protons and, thus, an impurity of further aromatic compounds can be excluded.

Solvatochromic Behavior

The presence of electron-donating ferrocenyl[262] and electronwithdrawing NO_2 substituents combined in one molecule prompted us to investigate the solvatochromic behavior of these species using UV/Vis spectroscopy (Table 3.10). Thus, we investigated the $\pi - \pi*$ absorption of compound **96a** in five different solvents from hexane (nonprotic, nonpolar) to ethanol (protic, polar) with concentrations of 3.10^{-5} mol L^{-1} (Table 3.10). The UV/Vis spectra of 96a contain one absorption between 250 and 350 nm, which can be ascribed to the $\pi - \pi*$ absorption band of the phenyl substituent. However, a shift of 13 nm indicates that a negligible positive solvatochromic behavior is present, probably due to the small $+M/+I$ effect of the oxygen ether atom.

Table 3.10 Solvatochromic behavior of **96a**.[a]

Entry	Solvent	λ_{max} / nm
1	hexane	281
2	toluene	284
3	*iso*propanol	285
4	DMF	289
5	ethanol	291
6	acetone	293

[a] The maximum refers to the $\pi - \pi*$ absorption.

Solid State Structures

The molecular structures of **96a**,**b**, **98**,[256] **99a-c**, **100**, and *rac*-**103a** in the solid state have been determined by single-crystal X-ray diffraction analysis at 110 K (Figures 3.49, 3.50, 3.51) and Figure SI7 in the Supporting Information of 263. Suitable single crystals of **98**, **99b**, and *rac*-**103a** were obtained by evaporation of hexane solutions at ambient temperature, those of **96a**,**b** and **99a**,**c** from boiling hexane, and those of **100** from boiling toluene solutions containing the respective compounds. The compounds crystallize in triclinic ($P\bar{1}$, **96a**, *rac*-**103a**) monoclinic ($P2_1/n$, **96b**, **99b**; $P2_1$, **99a**; $C2/c$, **100**) orthorhombic ($P2_12_12_1$, 7c) and tetragonal ($P4_32_12$, **98**) space groups with one (**96b**, **99a-c** and *rac*-**103a**) two (**96a**), or a half of a molecule (**98**) in the asymmetric unit.

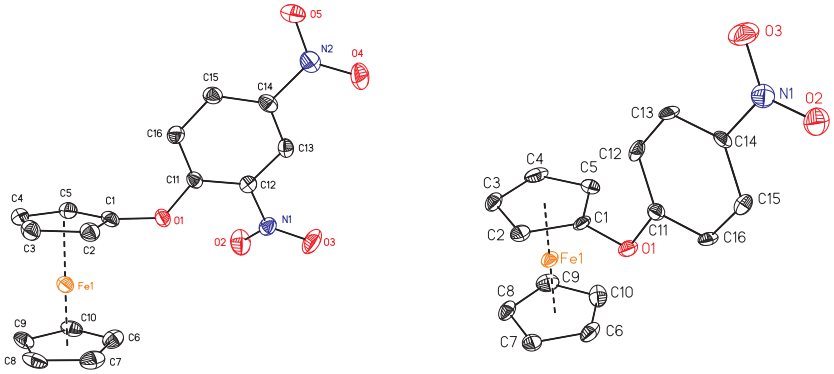


Figure 3.49 ORTEP (50 % probability level) of the molecular structures of **87a** (left) and **87b** (right) with the atom-numbering Scheme. All hydrogen atoms have been omitted for clarity.

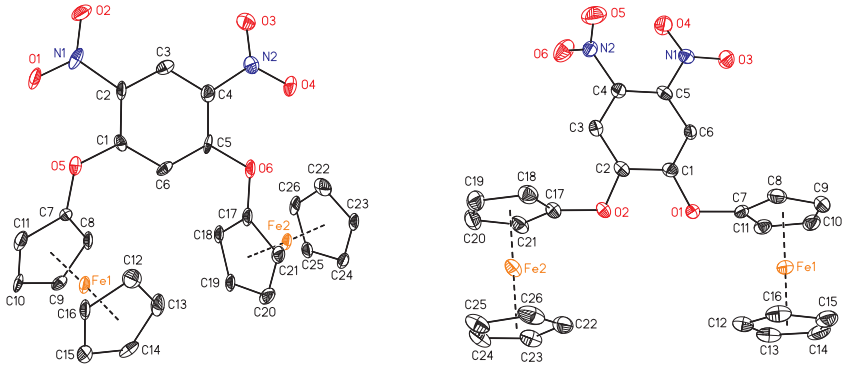


Figure 3.50 ORTEP (50 % probability level) of the molecular structures of **90a** (left) and **91** (right) with the atom-numbering Scheme. All hydrogen atoms and one molecule of CH_2Cl_2 in the asymmetric unit of **91** have been omitted for clarity. Intramolecular *T*-shaped π interaction between the centroids (Ct) of the C17–C21 and C12–C16 labeled cyclopentadienyls is shown: Ct$\cdots$Ct, 4.898(6) Å; intersection, 82.8(6) °.

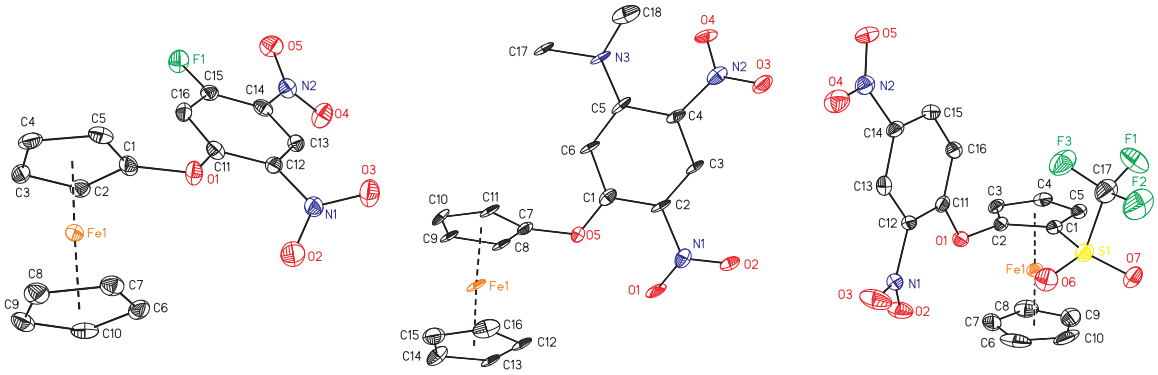


Figure 3.51 ORTEP (50 % probability level) of the molecular structures of **90b** (left), **90c** (middle) and 1,2-S,O-substituted *rac*-**94a** (right) with their atom-numbering Schemes. All hydrogen atoms and a second crystallographically independent molecule in the asymmetric unit of **90b** have been omitted for clarity.

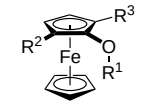
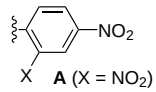
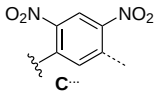
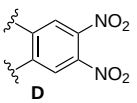
The ferrocenyl backbone adopts an eclipsed conformation for **96a**,**b**, **99a-c**, and **100** (0.1(2) to 5.97(18) °) and a staggered rotation for 1,2-*S*,*O*-substituted *rac*-**103a** (22.7(2) °). The phenyl ring mainly reveals a perpendicular orientation toward the cyclopentadienyls for **99a**,**b**, 100,

and *rac*-**103a** (82.00(11) to 88.74(10) °) or range between 42.7(4) and 69.90(10) °for **96a** and **99a-c**. In diferrocenyl-substituted compounds **99a** and **8** (Figure 3.50) the different substitution patterns (1,3 in **99a**; 1,2 in **100**) affects the orientation of the ferrocenyls with respect to each other. The increased distance of the 1,3-disubstitution allows for a more flexible rotation and, thus, a stabilization of the packing by an intramolecular *T*-shaped π interaction between a C_5H_5 and a C_5H_4 unit (Figure 3.50). In contrast, compound **100** reveals a nearly coplanar orientation of both ferrocenyls (deviation from coplanarity 5.16(18) °) with their backbones directed away from the phenylene core in perpendicular torsions (86.13(8), 85.65(8) °). The difference between the 1,2-/1,3-substitution pattern also affects the rotation of the nitro groups. Thus, they are approaching a coplanar orientation in **99a** (22.9(13) °), whereas the steric demand in 1,2-positioned **100** results in an almost orthogonal orientation (77.2(3) °). An electrostatic interaction between N2 and O4 is present, due to a separation far below the sum of the van der Waals radii ($\Sigma = 3.07$ Å) of 2.6032(1) Å. However, an interaction of O4 to the partially positively charged N1 atom of an adjacent molecule does not seem to be possible, due to a small N1–O4$\cdots$N1 angle of 94.49(14) °. Equal N1–O3/4 bond distances of 1.222(3) and 1.227(3) Å support this conclusion. The NO_2 substituents in **96a**,**b**, **99b**,**c**, and *rac*-**103a**, where steric reasons are excluded, adopt plane intersection angles toward the C6 phenyl plane between 0.04(4) °(**96b**) and 40.78(12) °(**99b**). Interestingly, the $NO_2\cdots C_6$ plane intersection of 37.0(5) °in **99c** is rather small, although an NMe_2 group in an *ortho* position with rather coplanar C6–N3–C18 torsions (24.9(11) and 22.5(18) °) is present. This results in a significant twisting of the C3 and C4 atoms above and C5 below the C6 ring (rms deviation 0.0381). The rms deviation for **96a**,**b** and **99a**,**b** does not exceed 0.0072 and is increased to 0.0143 for **103a**. The rms deviation in **99c** for C1,2,6 is 0.00, which corresponds to a shift of the N2 atom out of this plane be 0.52(7) Å and of N3 by –0.22(5) Å. The O-C_{Fc} and O-C_{Phenyl} bond lengths at the ether oxygen reveal a significantly enlarged O-C_{Fc} bond distance of 1.382(10)-1.416(14) Å in comparison to 1.325(15)-1.373(4) Å for O-C_{Phenyl}. The longer O-C_{Fc} bond (ca. 0.05 Å) might be due to the increased electron density at the ferrocenyl groups and thus a weakening of the O-C_{Fc} bond. In comparison to the four structures reported in the literature containing a ferrocenyl aryl ether motif, electron-rich *tert*-butylsubstituted phenyl ethers also exhibit enlarged O-C_{Fc} bonds (e.g., O-C_{Fc} 1.377(3) Å vs O-C_{Ar} 1.396(3) Å and O-C_{Fc} 1.370(2) Å vs O-C_{Ar} 1.401(2) Å), which excludes an electronic effect of the withdrawing aryl substituent. A CSD database search resulted in four examples of ferrocenyl aryl ethers, reported in references 73 and 164. O-alkyl, *e.g.* O-Me, ethers exhibit an opposite behavior owing to an sp^3-hybridized carbon atom. The angles of the ether oxygen atoms range from 116.14(18) to 122.2(7) °, whereas values above 120 °are caused by an intramolecular π interaction in **99a** or the distortion of the phenyl ring in **99c**. The present fluorine substituents also interact over short distances within the sum of the van der Waals radii, in *e.g.*, in F$\cdots$F (*rac*-**103a**) and F$\cdots$O (**99b**) interactions (Figure 3.51) .

Electrochemistry

The electrochemical behavior of **6**,[264] **30a**, **31a**, **35a**, **96a**,**b**, **99a-c**, **100**, **101**,[194] *rac*-**102a**,**b**, *rac*-**103a**, and *rac*-**104a**, were investigated by cyclic voltammetry and square wave voltammetry (Table 3.11). In the cyclic voltammograms of **6**, **30a**, **31a**, **35a**, and **101** one reversible redox event for the ferrocenyl unit was observed (Table 3.11). The ferrocenyl redox processes of **6**, **30a** and **31a** can be found between 20 and 50 mV, indicating similar electron densities at the ferrocenyl moieties in all three compounds. The second phosphonate group in **35a** and the triflate group in **101** led to decreased electron densities at the ferrocenyls, and therefore the values for $E_1{}^{\circ\prime}$ are shifted to higher potentials (335 mV (**101**), 170 mV (**35a**)). The cyclic voltammograms of **96a**,**b** show two (**96b**) or three (**96a**) redox processes in a potential range of –1800 mV to +190 mV. The cathodic events between –1800 and –1485 mV could be assigned to redox processes of the nitro substituents.[265] The second nitro group in **96a** leads to a somewhat increased potential for the ferrocenyl redox events (190 mV), in comparison to **96b** (105 mV).

Table 3.11 Cyclic voltammetry data of ferrocenyl nitroaryl ethers.[a]

Compd.	Ferrocenyl Derivative	R^1	R^2	R^3	$E_1{}^{\circ\prime}(NO_2)^b$ (ΔE_p)^c	$E_2{}^{\circ\prime}(NO_2)^b$ (ΔE_p)^c	$E_3{}^{\circ\prime}(Fc)^b$ (ΔE_p)^c	$E_4{}^{\circ\prime}(Fc)^b$ (ΔE_p)^c
6		[P]^1	H	H			45 (76)	
30a		[P]^2	H	H			20 (83)	
31a		[P]^2	Me	H			40 (74)	
35a		[P]^2	[P]^2	H			170 (63)	
96a		**A**	H	H	–1800 (86)	–1485 (70)	190 (64)	
96b		**B**	H	H	–1700 (92)		105 (70)	
99a	**A** (X = NO_2)	**C**–OFc	H	H	–1595 (89)		155 (79)	275 (85)
99b	**B** (X = H)	**C**–F	F	H	–1795 (89)	–1465 (85)	230 (85)	
99c		**C**–NMe_2	H	H	–1710 (96)		110 (80)	
100		**D**	H	H	–1560 (101)^d	–1330 (95)	130 (75)	340 (79)
101		[S]	H	H			335 (69)	
102a		A	[P]^2	H	–1830 (84)	–1490 (76)	345 (72)	
102b		B	[P]^2	H	–1750 (211)^d		275 (83)	
103a	**D**	A	[S]	H	–1755 (80)	–1425 (73)	725 (73)	
104a		A	[P]^2	[P]^2	–1535 (125)^d		520 (70)	

[a] All potentials are given in mV vs FcH/FcH^+, with an analyte concentration of 1.0 mmol L^{-1}. [P]^1 = $P(O)(OEt)_2$. [P]^2 = $P(O)(OCy)_2$. [S] = SO_2CF_3.
[b] $E^{\circ\prime}$ = formal potential.
[c] ΔE_p = difference between the anodic and cathodic peak potential.
[d] The redox processes are not reversible.

For *rac*-**102a**,**b**, *rac*-**103a**, and **103a** one reversible redox process for the ferrocenyl groups was observed during the electrochemical measurements (Figure 3.52). The redox events for Fc/Fc^+ in *rac*-**102a**,**b** are found at 345 mV (*rac*-**102a**) and 275 mV (*rac*-**102b**), respectively. An increasing number of phosphonate groups as well as a triflate group led to decreased electron densities at the ferrocenyl motifs, resulting in increased redox potentials (725 mV (*rac*-**103a**), 520 mV (**103a**)). In *rac*-**102a** and *rac*-**103a** two reversible redox events for the nitro groups between -1830 and -1425 mV are present. In contrast, during electrochemical measurements of *rac*-**102b** and **104a** in the same potential limits, irreversible redox events

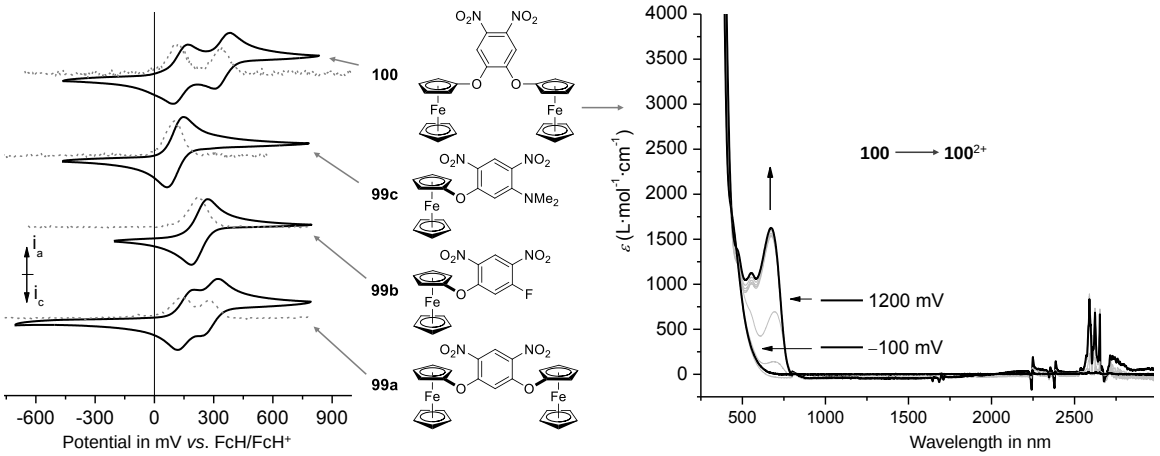


Figure 3.52 Left: Cyclic voltammograms (solid lines) and square wave voltammograms (dashed lines) of **99a**–**c** and **100**. Right: UV/Vis/NIR spectra of **100** (2.0 mmol L^{-1}) at rising potentials (–200 to 1200 mV vs Ag/AgCl). Compounds were measured as CH_2Cl_2 solutions at 25 °C with 0.1 mol L^{-1} $[N(Bu)_4][B(C_6F_5)_4]$supporting electrolyte.

occurred, indicating a decomposition of the compounds during the electrochemical studies. A comparison of the redox potentials of the ferrocenyl units of *rac*-**102a**,**b** with those of **96a**,**b** shows that the additional phosphonate group in *rac*-**102a**,**b** leads to a decreased electron density at the ferrocenyl and, therefore, to a shift of the redox events to higher potentials.
In the cyclic voltammograms of **99a-c** and **100** a reversible event for each ferrocenyl unit was observed (**99a**, 155 and 275 mV; **99b**, 230 mV; **99c**, 110 mV; **100**, 130 and 340 mV) (Figure 3.52). The potential of the first redox event in the series increases (**99c** < **99a** < **99b**), indicating an increased electron density at the ferrocenyl moiety in **99c**. The two ferrocenyl-related events in **100** (ΔE = 210 mV) exhibit a larger splitting in comparison to **99a** (ΔE = 120 mV). Furthermore, the CVs of **99a**–**c** and **100** show redox processes between –1795 and –1330 mV for the nitro groups. With the increased electron-withdrawing character of the substituent bonded to the C_6H_2 rings in **99a-c**, the potentials of the ferrocenyl redox processes are shifted toward higher potentials. The differences within the nucleophilicity can be confirmed by comparing the potential of the first ferrocene-related redox processes of the 2,4-dinitrophenyl ethers and **102a**/**104a** with their electronic properties solely determined by their *ortho* substituents. The potentials increase as *ortho* (190 mV, *o*-R = H) < **102a** (345 mV, *o*-R = $P(O)(OCy)_2$) < **104a** (520 mV, *o*-R = $(P(O)(OCy)_2)_2$) < **103a** (725 mV, *o*-R = SO_2CF_3), confirming the sulfonyl substituent to be even more electronically withdrawing than two phosphonato substituents. This leads to the conclusion that the respective lithium ferrocenolato compounds follow this trend within S_NAr reactions. The redox separation in **99a** and **100** could be caused by either electrostatic factors or an electronic interaction between the two redox sites. Therefore, UV/Vis/NIR measurements with **100** were carried out, for example. The UV/Vis/NIR studies of dichloromethane solutions containing **100** in different redox states are depicted in Figure 3.52. During the stepwise increase of the potentials (step heights: 100, 50, 25 mV) the compound was oxidized from the neutral **100**

to the mixed-valent $[\mathbf{100}]^+$ and finally to the fully oxidized species $[\mathbf{100}]^{2+}$. In the case of an electronic interaction between the Fc/Fc^+ termini an intervalence charge transfer (IVCT) band should develop in the NIR region during the oxidation to the mixed-valent species and disappear during the oxidation to the fully oxidized species. However, during the oxidation of **100** no such band developed and, thus, no significant electron transfer between the Fc/Fc^+ termini takes place, prohibited by the two oxygen atoms that prevent a conjugation. Therefore, the redox separations in **100** result solely from electrostatic interactions, implying that compound **99a** should exhibit a similar behavior. In contrast, for known compounds with ferrocenyl groups directly bonded to the benzene ring, IVCT absorptions of weak strength were found with the maximum for 1,4-diferrocenylbenzene.[266] To prove the reversibility after complete oxidation, compound **100** was reduced at –400 mV and the obtained UV/Vis/NIR spectrum was identical with the spectrum of the starting material.

3.2.3 Multi-Ferrocenyl Aryl Ethers derived by Nucleophilic Aromatic Substitution Reactions with Aryl Fluorides

Polyferrocenyl-containing aromatics are of interest not only because of their beauty but also because of their electrochemical properties. Thus, hexa-ferrocenyl (**A**, Figure 3.53)[267] hexa-ethynylferrocenyl (**B**, Figure 3.53)[268] as well as mixed ferrocenyl/ethynylferrocenyl benzene derivatives are examples discussed so far.[269] The latter could be fused to a multi-cyclic hexa-ferrocenyl containing benzene by reacting it with $[CoCp(CO)_2]$.[270] The approach was extended to polyferrocenyl-functionalized four-membered[271] and five-membered carbocycles,[272] heterocycles featuring main-group elements[273] (**F**, **G**; Figure 3.53) or transition-metal building blocks[274] and six-membered heterocyclic compounds[275] (**E**; Figure 3.53). A poly-*meso*-ferrocenyl porphyrin also counts as this class of compound.[276] The electrochemical behavior of such compounds is summarized in a recently published review, as most of these compounds show communication between the metallocenyl substituents in the mixed-valent state.[277] Based on the results obtained in Section 3.2.1, further substrates for the synthesis of poly-ferrocenyloxy-substituted compounds by S_NAr reactions, which are sparsely explored.

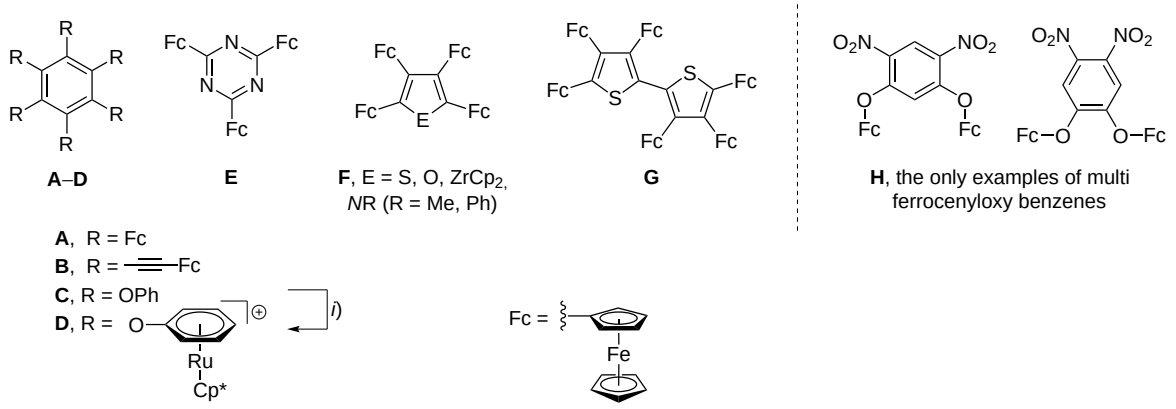


Figure 3.53 Selected examples of multi-ferrocenyl- and ferrocenylether-substituted arenes. Reaction conditions: *i*) 7 equiv of $[RuCp\cdot(CH_3CN)_3]OTf$ ($Cp\cdot = \eta^5$-$C_5(CH_3)_5$), CH_2Cl_2, 60 °C, 1 h, 40 %.

In contrast, S_NAr reactions involving phenol as the nucleophile and C_6F_6 as the electrophile have been applied to synthesize $C_6(OPh)_6$ (**C**; Figure 3.53) in 1982 by the group of MacNicol.[278] The substrate scope has also been extended to substituted phenols.[279] However, only a few examples involving *ortho*-substituted phenols have been synthesized to date,[280,281] which can probably be attributed to the high reaction temperature of 220 °C and the long reaction time of 48 h, indicating the difficulties associated with the conversion of electron-rich aryl fluorides into the respective ethers. Hexaphenoxybenzene (**C**; Figure 3.53) gave, upon its reaction with $[RuCp^*(CH_3CN)_3]OTf$ ($Cp^* = \eta^5$-C_5Me_5; $OTf = OSO_2CF_3$), the corresponding hexametallocenyl-substituted type **D** molecule (Figure 3.53), as the only reported organometallic aryl ether bearing three or more metallocenyl ether functionalities.[282] With our previous results by using the S_NAr approach (Section3.2.1), multi-ferrocenyloxy-substituted aryl benzenes are accessible by reacting ferrocenol with aryl fluorides, which is reported herein.

Reaction of Ferrocenol with Aryl Fluorides

The S_NAr reaction of ferrocenol (**5**) with dinitro aryl fluorides and 4-nitrofluorobenzene proceeded, as expected, to give the respective ferrocenyl ethers, whereas fluorobenzene and 1,3-difluorobenzene proved to be unsuitable. This low reactivity of C_6H_5F and $C_6H_4F_2$ has also been observed toward alkyloxy nucleophiles.[258] Due to the mechanism of the reaction,[283] a low electron density at the benzene ring enhances the reactivity and thus aryl fluorides with n = 3 − 6 (**108a-d**) fluoro substituents were investigated (Figures 3.54, 3.55, and 3.56). A well-prepared review giving a broad insight to the synthesis and reaction behavior of fluorinated aromatics can be found in references 284

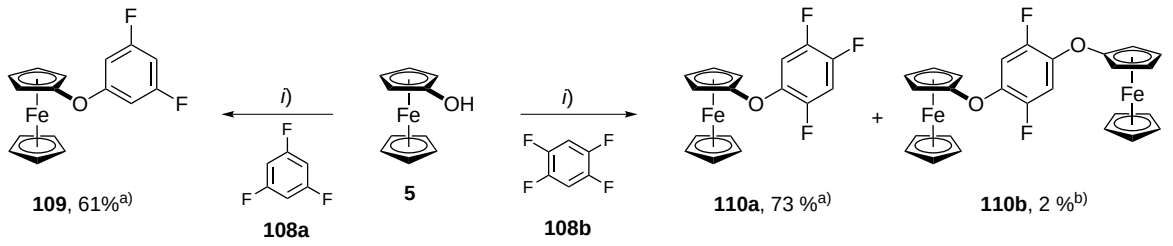


Figure 3.54 Reaction of ferrocenol (**5**) with *sym*-trifluoro (**108a**) and tetrafluoro benzene **108b**.
Reaction conditions: *i*) 1^{st} Et_2O, BuLi; 2^{nd} **108a/b**, DMF, 70 °C. a) 3 equiv of **108a/b** were used. Yields are based on **5**; b) 2 equiv of **5** were used. Yield based on **108b**.

According to our recently reported S_NAr protocol, **5** was lithiated in diethyl ether and the formed FcOLi species was further reacted with > 2.4 equiv of fluorobenzenes **108a-d** to give **109**, **110a**, **111a**, and **112a**,**b** (Figures 3.54, 3.55, and 3.56). The conversion of **5** within the S_NAr reaction increased with the number of fluorine atoms present, accordingly from 61 % (**109**) to 73 % (**110**), 92 % (**111**) and 98 % (**112**) based on the isolated yields of the respective products (see the Experimental Section). The use of highly activated C_6F_6 (**98d**) gave 1,4-substituted benzene **112b** in a yield of 12 % besides the formation of **112a** (86 %). To increase the number of organometallic ether substituents at benzenes **108a**,**b**, the amount

of **5** was increased to > 2 equiv relative to **108a**/**108b**. However, the yields of **109** and **110a** decreased to 12 % (**109**) and 35 % (**110a**), respectively. In addition, within this reaction a further substitution of a fluorine atom in **110a** by a FcO group was observed, resulting in the formation of **110b** in minor yield (2 %) (Figure 3.53, Experimental Section), whereas **108a** did not undergo a second substitution. A scifinder search revealed that multiple S_NAr reactions occur for aliphatic alconols[285], whereas solely single subsituted compounds were observed for aromatic derivatives[286] The constitution of **110b** as the 1,4-isomer could be verified by using single-crystal X-ray diffraction analysis (Figure 3.60). It is the first example of a double FcO-functionalized product derived from **108b** by applying the S_NAr reaction protocol. It should be noted that a similar molecule, bearing two 4-phenoxy substituents, was synthesized from 1,4-dibromo-2,5-difluoro benzene[287]

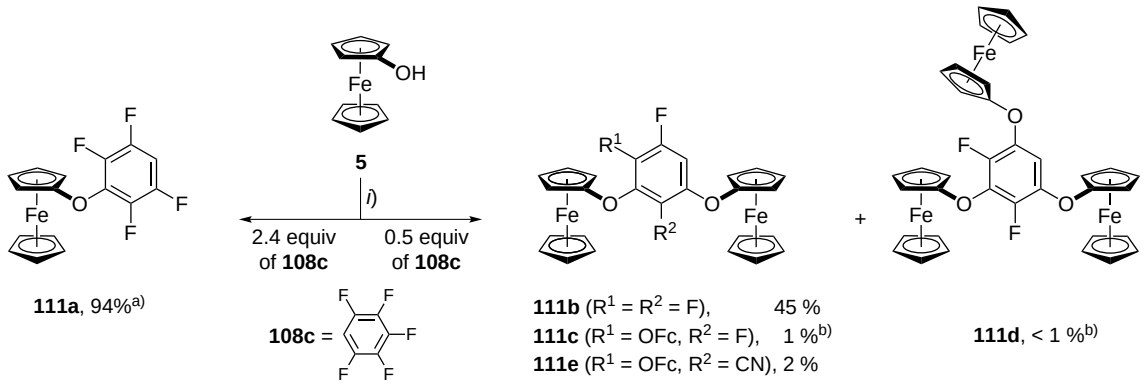


Figure 3.55 Reaction of ferrocenol (**5**) with pentafluorobenzene **108c** to afford arylferrocenyl ethers **111a**–**e**.
Yields are based on **108c**. Reaction conditions: *i*) 1^{st} Et_2O, BuLi; 2^{nd} **108c**, DMF, 70 °C; a) Yield based on **5**; b) Obtained as a non-separable mixture (2 % based on **108c**) in a ratio of **101c**/**111d** of 2 : 1.

S_NAr reaction of **5** with **108c** exclusively gave mono-ferrocenyl ether **111a** in 94 % yield (Figure 3.55, Experimental Section). The oxygen atom is positioned *para* to the hydrogen atom, which is known to be the most reactive position in **108c**, while no activating *para*-fluorine is present.[288–290] Changing the ratio of **108c**/**5** from 3 : 1 to 1 : 2 decreased the yield of **111a** from 94 to 47 % and resulted in the formation of **111b** in 45 % yield, where the second nucleophilic attack occurred *meta* to the OFc groups. Compounds **111c** and **111d** were isolated in a yield of 2 % as a 2 : 1 mixture of *asym*-**111c** and *sym*-**111d**. Compound **111c**, with its 1,4,5-substituted FcO moieties, is the first example of this type, but also molecules possessing a 1,3,5-substitution pattern, as observed in **111d**, have rarely been reported. A similar substitution pattern to that in **111d** has solely been described in reference 291,292. After appropriate workup, both isomers could be identified by ^1H and ^{19}F NMR spectroscopy (vide infra), but could not be separated, for example, by using chromatographic methods. As a further product, the formation of nitrile **111e** was observed within the reaction of FcOLi with **108c** in DMF as solvent. NMR spectroscopic investigations revealed the presence of one fluorine substituent *ortho* to the hydrogen atom (vide infra). Furthermore, a weak band at 2234 cm^{-1} could be assigned to the C≡N unit in the IR spectrum.[293–296] Based on the constitution of compounds **111a-c**, the structure of **111e** has

been formed as reported in Figure 3.55. The introduction of nitrile functionalities has been reported in copper-mediated reactions using DMF as the *in situ* cyanide source.[297] In the presence of ammonia as the nitrogen and DMF as the carbon source, the mechanism for the nitrile formation have been investigated for Grignard[298,299] and lithium[299] intermediates, or in Cu-[300,301] and Pd-[300] mediated reactions. Reacting an excess of C_6F_6 (**108d**) as the electrophile with **5** under S_NAr conditions gave **112a** in 86 % and **112b** in 12 % yield (Figure 3.56). The formation of a double substituted product is explained by the still highly activated C_6F_5 moiety in **112a**[288–290] and contrasts the reactions of **5** with **108b**,**c**, where multiple nucleophilic attacks also required an excess of the nucleophile. Compound **112b** has exclusively been formed as the 1,4-functionalized species. Examples for 1,2-disubstituted derivatives are rarely described and can be found in references 289 and 290. In general, the formation of *para*-substituted derivatives are favored and are, *e.g.*, reported in 288–290 and 302 Changing the ratio of **5**/**108d** from 1 : 2.4 to 3 : 1 maintains the level of conversion of the reaction at 99 %, whereby **112b** was formed as the main product in a yield of 79 %. Within this reaction, triple substituted *asym*-**112c** could also be isolated in a yield of 21 % after appropriate workup. Compound **112c** is thereby subsequently formed from **112b**.

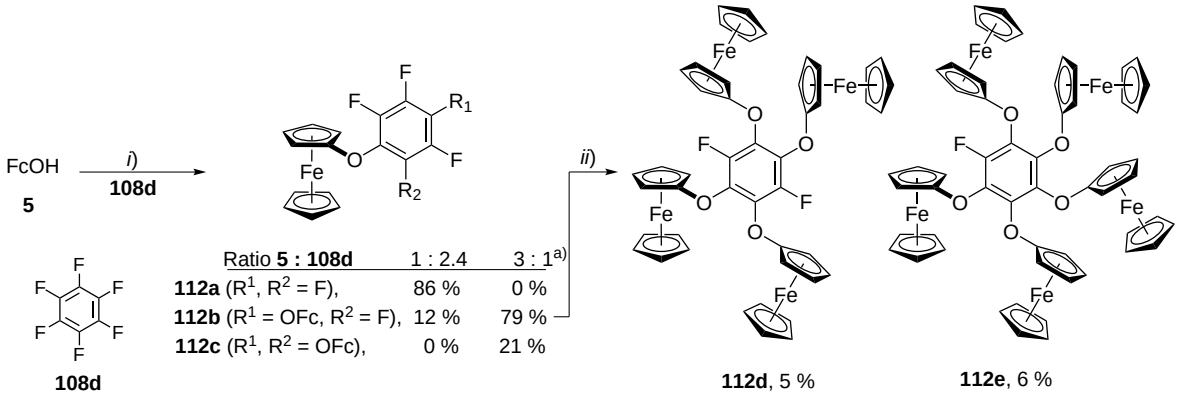


Figure 3.56 Reaction of ferrocenol (**5**) with hexafluorobenzene **108d** to afford arylferrocenyl ethers **112a**–**e**.
Yields are based on **5** (2.4 equiv of **108d**) or **108d** (0.33 equiv of **108d**). Reaction conditions: *i*) 1^{st} Et_2O, BuLi; 2^{nd} **108d**, DMF, 70 °C; *ii*) 9 equiv of **5**, **112b**, K_2CO_3 (19 equiv), 1,3-dimethyl-2-imidazolidinone, 18 °C, 18 h. Yields are based on **108d**, a) Reaction at 100 °C.

The four chemically equal fluorine atoms in **112b** resulted in the constitution of **112c** as shown in Figure 3.56. The identity and the substitution pattern of **112b** have, *inter alia*, been verified by using single-crystal X-ray diffraction analysis (Figure 3.60). It is the first reported example of a solid-state structure of a tetrafluoro-1,4-diether species derived from C_6F_6 (**108d**). For all examples derived by a CSD database search for 1,4-dioxygen-2,3,5,6-tetrafluoro benzenes that have been reported to date, see references 303 However, compounds bearing more than three FcO ether substituents were not obtained within this reaction protocol, probably because of the thermal instability of **5**[147,304] or the strong O···Li interaction.[258] Thus, **112b** and 9 equiv of **5** were reacted according to a protocol for the synthesis of $C_6(OPh)_6$ by using K_2CO_3 as the base instead of BuLi, and 1,3-dimethyl-2-imidazolidinone instead of DMF (Figure 3.56).[278,280] Molecules bearing four (**112d**) and five (**112e**) FcO

substituents could be isolated. Interestingly, FcH (**1**) was also formed as a side product in 3 % yield with respect to **5** and 23 % yield with respect to **112b**, which can be explained by the decomposition of **112b**, or higher functionalized products under these relatively harsh reaction conditions (180 °C). This assumption is supported by the absence of any starting material after the reaction. Several attempts to synthesize $C_6(OFc)_6$ failed, because of the low thermal stability of **5** compared with C_6H_5OH.[147,304] Compound **112e** is the second example of a molecule bearing five ether and one fluoro substituent.[305]

Aryl Fluorides after Anionic Phospho-Fries Rearrangements

Furthermore, the S_NAr etherification reaction protocol was applied to the *ortho*-phosphonato-functionalized hydroxy ferrocene **31e**−H by using nitro aryl fluorides, resulting in the respective nitrophenyl ethers (Section 3.2.1). Compound **31e**−H was obtained by applying an *apFr* on phosphate **30e**. Subsequent reaction of **31e**−H with **108d** resulted in the formation of ether **113** (52 % *de*, Figure 3.57). The poor overall yield of 20 % within this reaction sequence is most likely attributed to the reduced reactivity of **108d**, compared with nitro arenes and the steric hindrance of **31e**−H compared with **5**. The formation of multiple substituted aryl ethers, however, was not observed. The absolute configuration of the planar chirality of the main isomer is assigned to (R_p) based on the results obtained within Section 3.1.

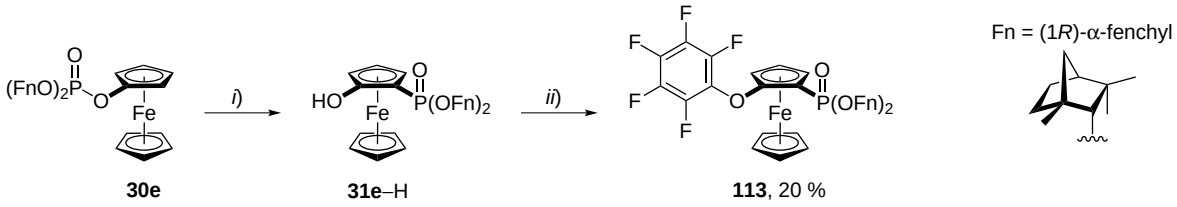


Figure 3.57 *ApFr* of fenchyl phosphate **30e** to phosphonate **31e**–H and subsequent S_NAr reaction with C_6F_6 to **113**.
Reaction conditions: *i*) LiTMP, TMEDA, hexane, **30e**, 18 h; *ii*) DMF, **108d**, 70 °C, 18 h, 20 % based on **30e**.

3.2.4 Characterization of Ferrocenyloxy Arylfluorides

NMR Spectroscopy

The identities of aryl ethers **109**, **110a**,**b**, **111a-e**, **112a-e**, and **113** were verified by ^{1}H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and ^{19}F NMR spectroscopy. The ^{19}F NMR resonance signals range between –162 ppm for the most electron-deficient (**112a**) and -131 ppm for the most electron-rich (**110a**) aryl units (see the Experimental Section). Solely, the ^{19}F resonance signal in **109** was observed at σ = –109 ppm, occurring as a multiplet of higher order, due to the overlapping $^3J_{F,H}$ and $^4J_{F,F}$ coupling constants in this AA'-spin system. In the ^{19}F NMR spectra of **109**, **110b**, **111d**,**e**, and **112b**,**d**,**e** one resonance signal was observed, due to the symmetrical structure. In non-hydrogen containing **112b**,**d**,**e**, the resonances occurred as singlets, whereas for **111e** a doublet with a typical $^3J_{F,H}$ coupling constant of 11.4 Hz was observed. The same coupling constant was found in the ^{1}H NMR spectrum of **111e** at

σ = 6.85 ppm. A typical distribution and coupling pattern[306] for the signals of the C_6F_5 substituents in **112a** and **113** in the $^{13}C\{^1H\}$ and ^{19}F NMR spectra is shown in Figure 3.58. Owing to *C*,*F* couplings, the resonances of the C_6F_5 ring exhibited a complex splitting pattern (Figure 3.58, Table 3.12). The *C*,*F* coupling constants in the $^{13}C\{^1H\}$ NMR spectra for **109**, **110a**,**b**, **111a**,**b** and **112a-c** decrease by ^1J (245–253 Hz) > ^3J (12–15 Hz) > ^2J (4–12 Hz) > ^4J (2–4 Hz) (Table 3.12). Parts of the spectra of **111b** and **112a** have been simulated from the fitted $^{13}C\{^1H\}$ NMR spectra (Table 3.12) to obtain the coupling constants. The fitting was verified by comparing the simulated spectra with the original spectra (Figure 3.58). The introduction of the *ortho*-phosphonato substituent in **113** resulted in a doubling of the signal sets in the $^{13}C\{^1H\}$ and the ^{19}F NMR spectra (Figure 3.58). The C_{Fc}−O signal appears as a doublet with $^2J_{C,P}$ = 9.3 Hz. In contrast, a ^5J, ^6J, and $^5J_{C,P}$ coupling for the *ortho*-, *meta*-, and *para*-carbon atoms in the C_6F_5 ring can be excluded. Thus, we assume steric hindrance around the C_{Fc}−O and C_{C6F5}−O bond, resulting in a magnetic inequality of the carbon atoms. The effect increases for the fluorine atoms because of their increased spatial proximity to the phosphonato moiety. Thus, the separation in the ^{19}F NMR spectra ranges from 13.7 Hz to 48.6 Hz for the *ortho*-substituted F atoms. A splitting based on ^6J, ^7J, and $^8J_{F,P}$ couplings can also be excluded. However, the exact *C*,*F* coupling constants could not be determined because of an overlap of both sets of signals (Figure 3.58). The presence of the *ortho* phosphonato group most significantly affects the shift of the *ipso* carbon atom of the C_6F_5 moiety, resulting in a highfield shift from 131.9 ppm in **112a** to 130.0 in **113** (see the Experimental Section and Figure 3.58).

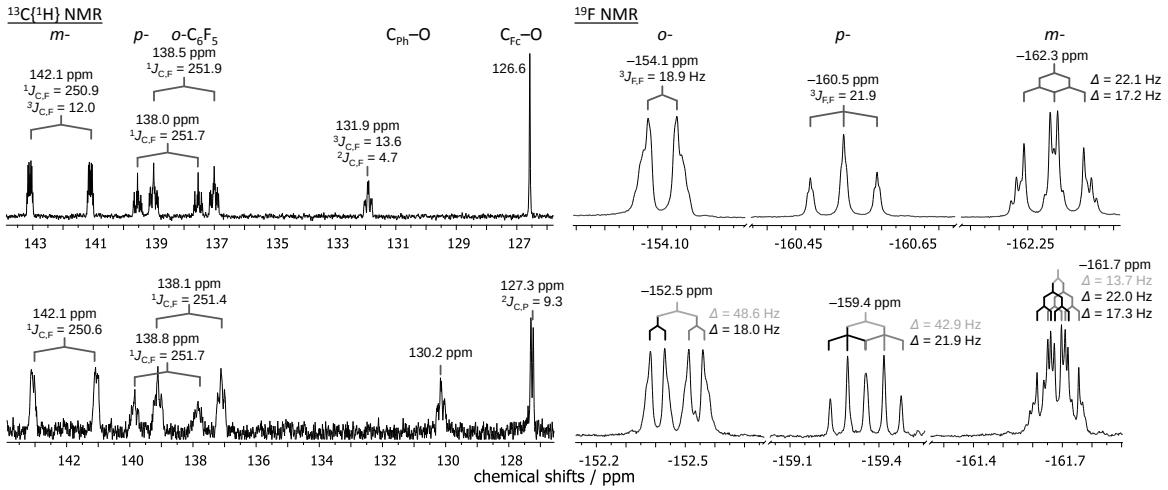


Figure 3.58 Comparison of the $^{13}C\{^1H\}$ (left) and ^{19}F NMR spectra (right) of **112a** (top) and **113** (bottom).
Coupling constants *J* are reported in Hz. The assignment of *o*-, *m*- and *p*- refers to the C1–O bond of the C_6F_5 ring. (Fn = (1*R*)-α-fenchyl)

Compound **111b** was obtained as the 1,3-substituted species, as indicated by the doublet in the $^{13}C\{^1H\}$ NMR spectrum for the C_{C6}−H signal at σ = 102.1 ppm with $^2J_{C,F}$ = 22.5 Hz to one *ortho*-positioned fluorine atom. Further examples for this type of substitution pattern are reported in references 307 and 308 In comparison, the C-H resonance for **111a** at σ = 101.5 ppm occurred as a triplet with $^3J_{C,F}$ = 23.0 Hz. The resonances of compounds **111c** and

111d were assigned within their mixture, predominantly by $J_{H,F}$, $J_{F,F}$, and $J_{C,F}$ couplings compared to other compounds reported herein. The presence of an *ortho* fluorine atom in **111c** compared with **111d**, resulted in a doublet for the C-H carbon atom in the $^{13}C\{^1H\}$ NMR spectrum at 101.9 ppm with $^3J_{C,F} = 24.6$ Hz, whereas **111d** occurred as a singlet (see the Experimental Section). The ^{19}F spectrum for **111c** showed resonances at $\sigma = -150.6$ ppm (dd, $^5J_{F,F} = 10.7$, $^4J_{F,H} = 7.6$ Hz), which could be assigned to the C2-bonded fluorine atom, and at $\sigma = 130.8$ ppm (dd, $^3J_{F,H} = 11.8$, $^5J_{F,F} = 10.3$ Hz) for the C5 bonded atom. The doublet for **111d** ($^4J_{F,H} = 7.5$ Hz) was observed at $\sigma = -150.5$ ppm. The values of the $^3J_{F,H}$ = and $^4J_{F,H}$ = coupling constants are also present in the ^1H NMR spectra. In **111e**, the resonance signal at 100.8 pm in the $^{13}C\{^1H\}$ NMR spectrum could be assigned to the C≡N carbon, which is consistent with a shift of 106 ppm for $C_6F_5C{\equiv}N$.[309]

Table 3.12 Summary of the C,F coupling constants of the $^{13}C\{^1H\}$ NMR signals of the phenyl substituents of **109**–**112**.[a]

Compd.	C_{Ph}–O /ppm[b]	Coupling constant / Hz $^2J_{C,F}$	$^3J_{C,F}$	$^4J_{C,F}$	Compd.	C–F /ppm[b]	Coupling constant /Hz $^1J_{C,F}$	$^2J_{C,F}$	$^3J_{C,F}$	$^4J_{C,F}$
109	161.5		13.4 (t)		**109**	163.4	246.8		15.4	
109	142.3	7.6	13.0	3.7	**110a**	144.9^{C4}	246.1	10.3	14.2	
						145.9^{C2}	245.4		13.4	3.6
						148.2^{C5}	247.1	9.0		3.1
110b	141.1	9.6	12.0		**110b**	148.7	246.0			4.6
111a	136.4	3.6(t)	13.2(t)		**111a**	141.5	249.9	4.6	14.7	2.4
						146.3	249.9	12.3[c]	12.3[c]	4.1
111b	135.8^{C3}	12.9/3.7	14.1		**111b**	140.2^{C2}	248.0		15.0	2.7
	142.8^{C1}	9.8[d]	10.8	3.6		143.3^{C5}	248.8	4.0		2.1
						146.3^{C4}	245.9	4.1	12.8	
112a	131.9	4.6(t)	16.7(t)	1.6	**112a**	138.0^{o-}	251.7	5.1	14.6/13.2	3.4
						138.5^{p-}	251.9	3.8(t)	13.6(t)	
						142.1^{m-}	251.0	4.2(t)	12.1	3.2
112b	132.6 multiplets non-resolvable				**112b**	142.0	252.5 multiplets non-resolvable			
112c	132.4^{C1}	2.2	15.2/13.2		**112c**	142.1^{C3}	249.7		12.6	4.2
	135.9^{C2}	4.0	12.8	2.7		142.7^{C5}	250.4	5.1	13.0	
	137.0^{C4}	2.7(t)	11.5			146.4^{C6}	250.1	4.1[c]		4.1[c]

[a] Except otherwise noted, the couplings are reported as doublets.
[b] The position within the phenyl ring follows the assignment in the experimental section.
[c] Occurred as a triplet.

Solid State Structures

The molecular structures of **110a**,**b**, **111a**, and **112a**,**b** in the solid state have been determined by single-crystal X-ray diffraction analysis (Figures 3.59 and 3.60). Suitable single crystals were obtained by evaporation of hexane solutions containing the respective compound at ambient temperature. The compounds crystallized in the monoclinic space groups $P2_1/c$ (**110b**), $P2_1/n$ (**111a**, **112a**,**b**) and the orthorhombic space group *Pnma* (**110a**) with one (**111a**, **112a**), a half (**110a**, **112b**), or one and a half (**110b**) crystallographically independent molecules in the asymmetric unit of these centrosymmetric space groups. Compounds **110a**,**b** and **112b** contain symmetry operations for generating equivalent atoms, which is

a C_2 axis in case of **110b** that is present in the middle of the phenyl plane and oriented perpendicular to it. For **112b**, an inversion center is present in the midpoint of the phenyl ring. In compound **110a**, the phenyl ring acts as a mirror plane that bisects the ferrocenyl groups through their C_β–C_β bonds.

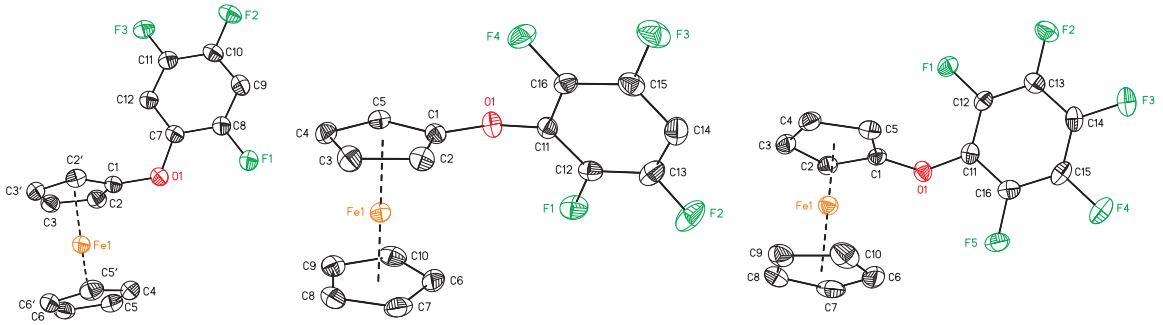


Figure 3.59 ORTEP (probability levels: 30 %, **110a**; 50 % **111a** and **112a**) of the molecular structures of **110a** (left), **111a** (middle) and **112a** (right) with the atom-numbering Scheme. All hydrogen atoms have been omitted for clarity. Symmetry operation for generating equivalent atoms ('): x, –y + 1/2, z.

The ferrocenyl backbones adopt ecliptic conformations for **110a**,**b** of 0.0(0)–7.3(2) °, whereas **111a** and **112a**,**b** are rather staggered with 18.3(2)–24.99(15) °. The phenyl rings mainly reveal a perpendicular orientation toward the cyclopentadienyls for **110a**,**b** of 90.000(3)–86.61(10) °and slightly deviate for **111a** and **112a**,**b** of 67.83(7)–69.92(7) °. Comparing their C_{Fc}–C_{Fc}–O–C_{Ar} torsion angles, they are either positioned above (**110a**,**b**: ca. 90 °) or in the cyclopentadienyl plane (**111a**, **112a**,**b**: ca. 12 °). Both ferrocenyl groups in **112b** and **110b** (Figure 3.60) are rotated anti toward each other. Shorter C_{Ar}–O bond lengths of 1.368(3)–1.375(3) Å and C_{Fc}–O of 1.390 Å are present in **111a** and **112a**,**b**, whereas no significant differences are observed for **110a**,**b**. This is in accordance with nitrosubstituted derivatives mentioned in Section 3.2.1, also possessing enlarged C_{Fc}–O bond lengths. Supramolecular features, for example T-shaped π interactions, or F$\cdots\pi$ interactions are discussed in the the Supporting Information of reference 263.

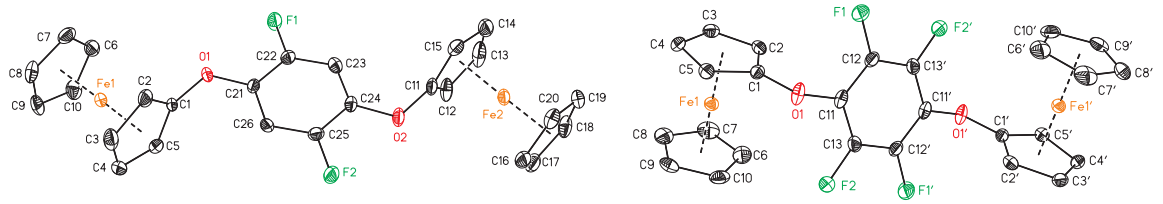


Figure 3.60 ORTEP (50 % probability level) of the molecular structures of **110b** (left) and **112b** (right) with the atom-numbering Scheme. All hydrogen atoms and a half-present molecule in the asymmetric unit of **110b** have been omitted for clarity. Symmetry operation for generating equivalent atoms (') : $-x+2, -y, -z+1$.

Electrochemistry

The electrochemical properties of **109**, **110a**,**b**, **111a-d**, and **112a-e** were investigated by cyclic and square wave voltammetry (Figure 3.61, Table 3.13). In the cyclic voltammograms of single FcO-substituted **109**, **110a**, **111a**, and **112a**, one reversible redox event for the ferrocenyl unit was observed between 44 and 77 mV, indicating similar electron densities at the ferrocenyl groups and solely a low impact of the substitution pattern at the aryl ether on the ferrocenyl groups. Compared with the nitro-substituted derivatives in Section 3.2.1, the first redox potential of **109**, **110a**,**b**, **111a**-e, and **112a-e** are cathodically shifted by approximately 50 mV, because of the lower mesomeric effect and thus, a lower electron-withdrawing character of the fluorine substituents, as compared to Section 3.2.1

Table 3.13 Cyclic voltammetry data of **109**–**112**.[a]

Compd.	$E_1^{\circ\prime c}$ (ΔE_p)	$E_2^{\circ\prime c}$ (ΔE_p)	$E_3^{\circ\prime c}$ (ΔE_p)	$E_4^{\circ\prime c}$ (ΔE_p)	$E_5^{\circ\prime c}$ (ΔE_p)	$\Delta E^{\circ\prime d}$
109	64 (62)					
110a	44 (78)					
110b	11 (67)	141 (71)				130
111a	77 (62)					
111b	20 (65)	145 (65)				125
111c,**d**	–40	80	200			120/120
111e[e]	13	103	298 (64)		90/195	
112a	68 (64)					
112b	66	114				48
112c	2	95	221			93/126
112d	–40	60	190	280		100/130/90
112e	–38	58 (70)	193 (50)	346 (80)	535 (55)	96/135/153/189

[a] All potentials are given in mV vs FcH/FcH^+ at 25 °C containing 0.1 mmol L^{-1} of $[N(Bu)_4][B(C_6F_5)_4]$as the supporting electrolyte.
[b] The number of each group, which is present in the molecule.
[c] $E^{\circ\prime}$ = formal potential in mV.
[d] ΔE_p = Difference between the anodic and cathodic peak potential.
[e] A C≡N substituent is present.

The exchange of fluorine atoms by FcO moieties accordingly shifts the values for the first redox potential $E_1^{\circ\prime}$ to more cathodic potentials (Table 3.13), with the exception of **111e**, **112b**, and **112e**. The electron-withdrawing nitrile functionality increases the potential from -40 mV for **111c** to 13 mV for **111d**. The four fluorine atoms in **112b** probably superimpose the effect of the electrondonating FcO unit,[279] maintaining the potential at 66 mV, similar to 68 mV for **112a**. The cyclic voltammograms of multi-ferrocenyl derivatives show two (**110b**, **111b** and **112b**), three (**111c**,**d** and **112c**), four (**112d**), or five (**112e**) reversible Fc/Fc^+ redox events, according to the number of ferrocenyl groups present in the molecule in a potential range of –40 mV to +535 mV (Figure 3.61). The redox splitting $\Delta E^{\circ\prime}$ of the redox events of **111c-e**, and **112b-d** occurred in close proximity to each other, resulting in an overlap of the potentials ($E^{\circ\prime}$) for each event in the CV. Thus, squarewave measurements were carried out to determine the potential of the respective events (Figure 3.61). The values

for the redox separations are comparable to, for example, β-ferrocenylethynyl-1H-pyrroles ($\Delta E^{\circ\prime}$ = 95–110 mV), for which no communication between the two redox centers could be observed, although conjugation was provided.[310]

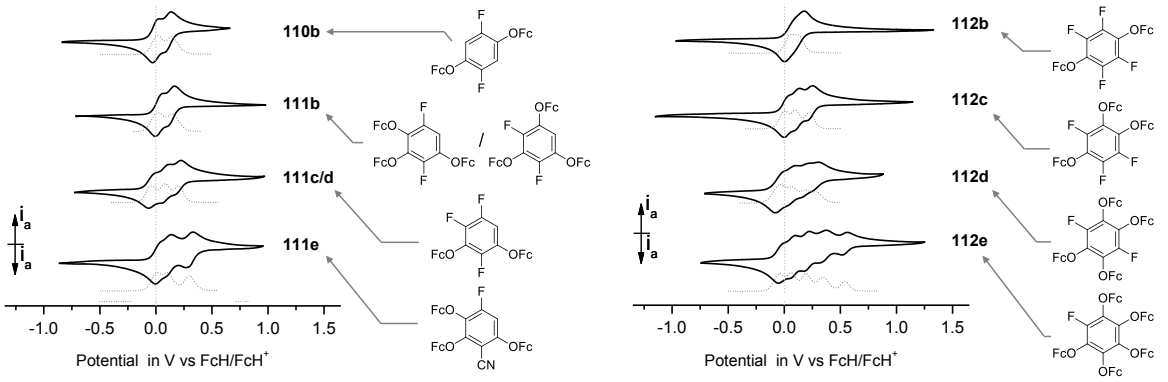


Figure 3.61 Cyclic voltammograms (solid lines) and square wave voltammograms (dotted lines) of **110b**, **111b**–**e**, and **112b**–**e** in CH_2Cl_2 solutions (1.0 mmol L^{-1}) at 25 °C containing 0.1 mmol L^{-1} of $[N(Bu)_4][B(C_6F_5)_4]$as the supporting electrolyte.

An interesting feature of **112e** is the increase of the redox splitting from **112e**/**112e**$^+$ ($\Delta E^{\circ\prime}$ = 96 mV) to **112e**$^{4+}$/112e^{5+} ($\Delta E^{\circ\prime}$ = 185 mV), owing to electrostatic interactions. This trend is also observed in **111e** (90 mV, 195 mV) and **112c** (93 mV, 126 mV). However, this differs for **112d** (100 mV, 130 mV, 90 mV), probably due to an electrostatic compensation of the positive charge at the ferrocenyl groups by the partially negatively charged *ortho*-fluorine atoms.[269] The smallest redox separation is observed in **112b** ($\Delta E^{\circ\prime}$ = 48 mV), revealing small electrostatic interactions through the para positioning of the OFc moieties. However, the redox events in *para*-substituted **110b** are separated by 130 mV, which might be attributed to the increased electron density and a better stabilization of the positive charge. This value is similar to **111b** ($\Delta E^{\circ\prime}$ = 125 mV), where a *meta* interaction is present, meeting the value reported in Section 3.2.1 1,5–$(OFc)_2$–2,4–$(NO_2)_2$–C_6H_2 ($E^{\circ\prime}$ = 120 mV). As has recently been confirmed, the redox separations are attributed to electrostatic interactions, the oxygen atoms prevent an electronic communication in the mixed-valent species. The impact of the substitution pattern in the mixture of **111c** and **111d** does not affect the redox potential of the ferrocenyl groups and resulted in three separated one-electron redox events (Figure 3.61).

Conclusion - Oxygen Functionalization

In addition to the methyl ethers mentioned in Section 3.2.1, hydroxyferrocenes could successfully be converted to aryl ethers by using the nucleophilic aromatic substitution reaction (S_NAr). As electrophiles, electron deficient aryl fluorides have been shown to be the most suitable reaction partners. Therefore electron-withdrawing fluoro and nitro-substituents had to be present in the aryl fluoride. In contrast, studies of ferrocenol and its *ortho*-phosphonato-substituted derivative have also been performed, indicating a low nucleophilicity of the oxygen atom in nucleophilic substitution reaction with, *e.g.*, benzyl bromide and propargyl tosylates. However, oxophilic chlorosilanes could be converted in high yield. In contrast, the S_NAr reac-

tion protocol also tolerated *ortho*-phosphonato and sulfonyl substituents, resulting in 1,2-X,O (X = S, P) ethers that can be obtained in a one-pot synthesis procedure including 1,3-O→C anionic phospho- and thia-Fries rearrangements. Also, the first 1,3-di-*ortho*-phosphonato functionalized ferrocenyl aryl ethers could be synthesized. Electrochemical studies of the redox potentials of the obtained compounds allowed conclusions on the reactivity by varying electronic properties and the electrophilicity of different aryl fluorides, which decreased from the dinitro (**96a**) to the mononitro (**96b**) and fianlly polyfluoro arylfluorides. The nucleophilicity and, thus, the reactivity toward S_NAr reactions of the functionalized oxyferrocenes was estimated by comparing the potential of the first ferrocene-related redox processes of dinitro benzenes, revealing the trend *ortho*-H (190 mV) < -P(O)(OCy)$_2$ (345 mV) < -(P(O)(OCy)$_2$)$_2$ (520 mV) < -SO_2CF_3 (725 mV). The usage of difluorodinitro multifluoro (F > 4) benzenes resulted in the first examples of double- and up to penta-FcO substituted benzenes. By changing the ratio of ferrocenol to multifluoro benzenes allowed the control of a singles or multi substitution. Electrochemical investigations revealed a splitting of the redox processes caused by electrostatic interactions, as confirmed by *in situ* UV/Vis/NIR measurements, due to the absence of an IVCT absorption in the mono-oxidized species.

3.2.5 Conversion of Phosphonates to Phosphines

The synthesis of phosphanes, suitable for *C*,*C* cross-coupling catalysis, required a further conversion of the phosphonates, derived after *apFr*, by applying a reduction and subsequent Stelzer coupling process. Assuming that the NO_2 groups are reduced by using Li[AlH_4], compound **96a** has been investigated under reducing reaction conditions (Figure 3.62). The obtained amine, which potentially gets oxidized, due to its high electron density, was subsequently acylated using acetic anhydride (Figure 3.62). The isolation of diamide **115** revealed the *in situ* formation of diamine **114**. Applying the *C*,*P* cross-coupling conditions for the conversion of PH_2-phosphanes to PPh_2-phosphines on amine-containing substrates, could additionally result in Buchwald Hartwig cross-couplings.[13,14,311] The mentioned difficulties within this coupling reaction (Section 3.1.5) would result in further complex product mixtures and thus, this substrates were not further investigated.

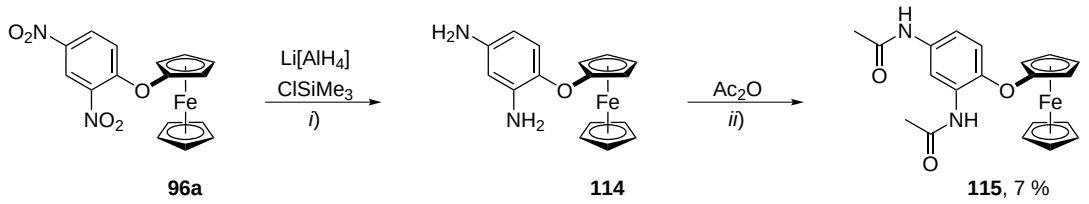
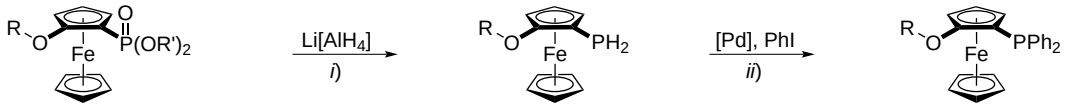


Figure 3.62 Reduction of dinitrophenyl ferrocenyl ether **96a** and subsequent acylation. Reaction conditions: *i*) Li[AlH_4], $ClSiMe_3$, THF, 45 °C, 12 h, H_2SO_4; *ii*) Et_2O, K_2CO_3, Ac_2O, 60 °C, 1 h. Yield based on **96a**.

In contrast, siloxanes **95g**,**h**, which could be obtained in high yields (Figure 3.43), and C_6F_5 ether **113** should be stable under reducing conditions and should give phosphanes **116a**–**c**. However, after the subsequent *C*,*P* Stelzer coupling, siloxanes **117a**,**b** were both obtained in a poor yield of 6 % (Figure 3.63). A compound derived from aryl ether **113** could not

be isolated. The formation of phosphine **117b** was *inter alia* verified by single-crystal X-ray diffraction analysis (Figure 3.64). However, a second trial did not result the desired product, revealing the difficulties within the Stelzer coupling process as mentioned in Section 3.1.5 (Figure 3.39).



rac-**95g** (R = Si^{t}BuPh$_2$, R' = Et) — **116a** (R = Si^{t}BuPh$_2$)[a)] — **117a** (R = Si^{t}BuPh$_2$), 6 %
rac-**95h** (R = Si^{i}Pr$_3$, R' = Et) — **116b** (R = Si^{i}Pr$_3$), 80 % — **117b** (R = Si^{i}Pr$_3$), 6 %
(R_p)-**113** (R = C_6F_5, R' = Fn) — **116c** (R = C_6F_5)[a)] — **117c** (R = C_6F_5), 0 %

Figure 3.63 Reduction of and subsequent Stelzer coupling of ferrocenyl silyl ethers **95g**,**h** and perfluorinated **113**.
Reaction conditions: *i*) Li[AlH$_4$], ClSiMe$_3$, THF, 45 °C, 12 h, H_2SO_4; *ii*) Et_2O, K_2CO_3, Ac_2O, 60 °C, 1 h. Fn = fenchyl. Yield based on **96a**.

Siloxyl phosphine **117b** crystallized in the centrosymmetric space group $P\bar{1}$ with one molecule in the asymmetric unit (Figure 3.64). Similar to phosphine *rac*-**91** (Figure 3.40) the lone pair of the phosphorus atom directs into the vacant space between both donor atoms. The increased steric demand of the silyl substituent, compared to a methyl group, rotates the O-bonded group out of the C_5H_3 planarity by 53.6(4) °.

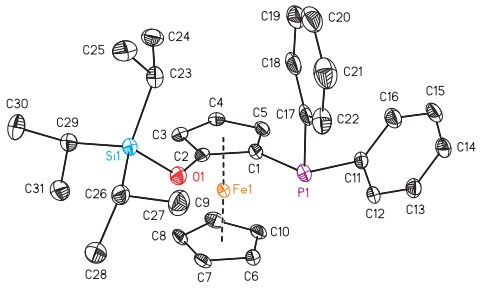


Figure 3.64 ORTEP (50 % probability level) of the molecular structure of **117b** with the atom-numbering Scheme. All hydrogen atoms have been omitted for clarity.

Concluding, a different approach for the synthesis of 1,2-*P*,*O*-ferrocenes is required, which allows for a better oxygen functionalization. The low transfer of the chiral information of 1,2-*P*,*O*-phosphanes on the biaryl substrate also required a change of the position of the P- and O- donor atoms in the molecule.

3.3 Anionic Homo Phospho-Fries Rearrangements

3.3.1 Conversion of Ferrocenylmethanol(-derivatives) to Phosphates

Retrosynthetic Considerations

Ferrocenylphosphines and 1,2-disubtituted planar-chiral ferrocenes are, for example, essential in the field of catalysis.[130] Especially the synthesis of hindered biaryls by the Pd-catalyzed *C*,*C* cross-coupling reaction is still a challenging task, where ferrococenyl phosphines bearing *ortho*-donor atoms or groups, e. g. oxygen[73,196], aryl[107] or vinyl[75,312] have been shown to increase the catalytic activity. The vinyl fragment thereby acts as a hemilabile group, which enables the planar-chirality of the ferrocenyl backbone to be transferred on a substrate, resulting in an enantiomeric excess of synthesized biaryls of up to 36 %.[75] It could also be shown that the presence of an oxygen atom attached to the ferrocenyl backbone, enhances the catalytic activity, as it could be shown by using a 2-alkyloxy substituted phosphine[73,196] However, a chiral 1,2-*P*,*O*-substitution pattern is difficult to achieve, due to a lack of oxygen electrophiles, when starting with chiral phosphines.[130,196] In contrast, the functionalization with phosphorus electrophiles required chiral, oxygen-functionalized *ortho*-directing groups to ensure an diastereoselective *ortho*-lithiation. Since the ether motif is a rather weak *ortho*-directing group, predominantly 1,1'-functionalized products were obtained.[73,74,76]

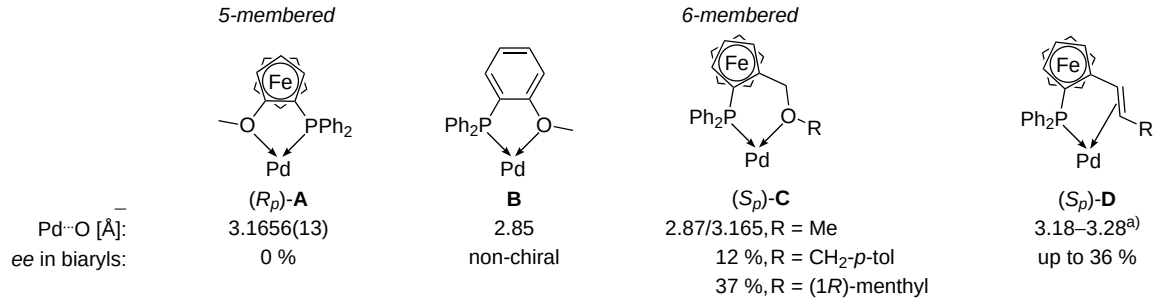


Figure 3.65 Comparison between 5- (**A**[168] and **B**[313]) and 6-membered (**C**[314] and **D**[313] 1,2-substituted phosphine Pd-complexes and the resulting *ee* of formed biaryls within Suzuki-Miyaura *C*,*C* cross-coupling reactions. a) The Pd atom is coordinated η^2 to the vinyl group, which in turn is rotated by 52 °out of planarity.

To investigate, if the planar-chiral ferrocenyl backbone can transfer its chirality to a coupling product, the presence of a further chiral group (P- or C-chiral) should be avoided. Thus, we recently applied the anionic phospho-Fries rearrangement on ferrocenes.[196] This intramolecular 1,3-O→ C migration regioselectively gave access to a broad range of 1,2-*P*,*O* substituted ferrocenes (Section 3.1). Using chiral pool alcohols also allowed a diastereomeric proceeding with a *de* of the product with up to 96 %.[168] The conversion of the formed phosphonate to the final phosphine also proceeded enantioselectively (99 % *ee*). Nevertheless, the usage of this ligand did not result in a detectable *ee* in the formed biaryls. The lack of the transfer of the chiral information from the planar-chiral ferrocenyl backbone in the catalytic reaction, has been attributed to the small, hemilabile methoxy group (Section 3.1). Replacement of the methyl by an aryl group could therefore enhance the chirality transfer within the *C*,*C*

cross-coupling reaction, due to steric reasons and attractive dispersion interactions.[107,111,243] Attempts to adopt this strategy on the 1,2-*P*,*O* ferrocenes were successful by applying nucleophilic aromatic substitution reactions by using electron deficient arenes,[263,315] whereby they cause side reactions within their conversion to a phosphine. In addition 1-PPh_2-2-CH_2OR ferrocenes, where an additional methylene group is present between the ferrocenyl backbone and the oxygen donor atom, were prepared.[111,314] The usage of this type of molecules as ligands within Suzuki-Miyaura *C*,*C* cross-coupling reactions gave the respective biaryls with an *ee* of up to 37 %, probably due to both, the planar and the C-central chirality. The angle between the P- and the O- donor atoms seems to play an important role (Figure 3.65).
Whereas a 1,2-*P*,*O* substitution pattern at ferrocene gave a 5-membered Pd-complex (type **A**[196] and **B**[316] molecules, Figure 3.65), the introduction of a methylene linking group increases the size to a 6-membered cycle (**C** and **D**[75,312,313], Figure 3.65). The P···O distance with 3.165 Å in the molecular solid state structure of complex **C** is slightly increased, due to a rotation of the CH_2O group out of the C_5H_3 plane by 38.5 °toward the ferrocenyl backbone. A mathematic transformation gave a minimum of 2.87 Å for the P···O distance.[317] While increasing the steric demand of R from ethyl to (1*R*)-menthyl in the type **C** species, also enhanced the *ee* from 0 to 37 % (Figure 3.65).[314] The study also showed, that the increased *ee* is accompanied with a loss of activity.[314] The *ee* of 36 % for aromatic substituents could also be explained by, *e.g.*, attractive π interactions.

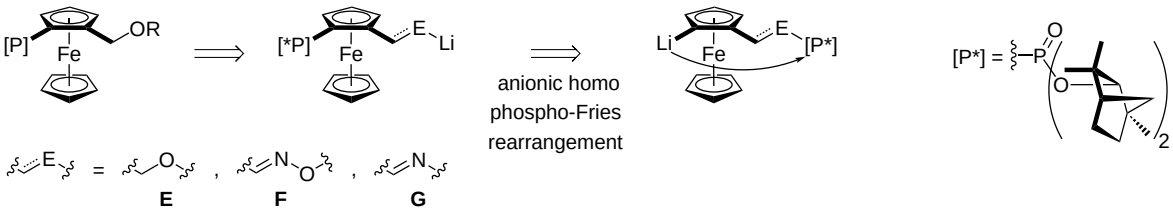


Figure 3.66 Retrosynthetic pathway for the synthesis of 1,2-substituted ferrocenes by using an anionic homo phospho-Fries rearrangement.

Besides numerous protocols for the stereoselective introduction of *ortho*-substituents,[130] a procedure using cheap and easily available chiral-pool derivatives is pending. Thus, it seems convincible to apply an anionic homo phospho-Fries rearrangement on ferrocenes. Based on our recent results on diastereoselective anionic phospho-Fries rearrangements, the use of a chiral pool derived phosphate seems promising (type **E** molecule, Figure 3.66). Furthermore, oximes[318] (**F**) and imino-phosphoramidates[319–321] (**G**) could be used as linkers to the migrating phosphorus group. Furthermore, these structural motifs could easily be functionalized after a successful rearrangement, enabling the introduction of further substituents.

Reactions of Ferrocenylmethanols with Chlorophosphates

As shown in Figure 3.65, the simplest educts for anionic homo phospho-Fries rearrangements (ahpFr) are ferrocenylmethanols (Figure 3.66). The usage of BuLi as base is beneficial to ensure the complete deprotonation of alcohols **118a**–**c** and their subsequent nucleophilic attack.[168] We could recently show that the chiral-pool-derived chlorophosphate **29e** bearing

(1R)-α-fenchyl (= Fn) groups, showed the best results for a diastereoselective proceeding of the lithiation and 1,3-O→C migration, as compared to other alcohols, *e.g.*, menthol, borneol and isopinocampheol, respectively. Thus, **29e** is used as the electrophile for the reactions reported herein.

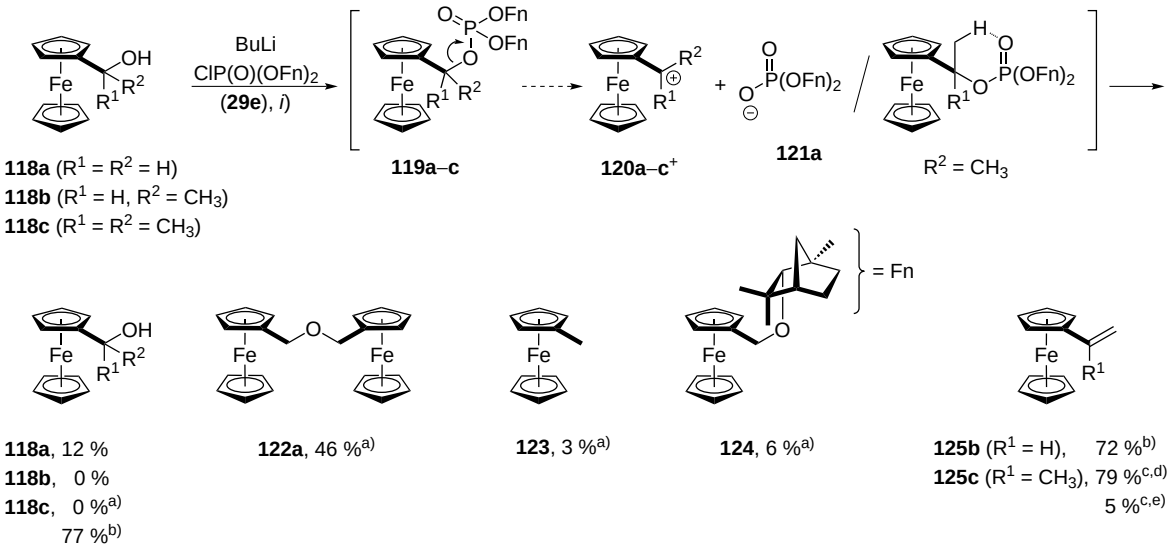


Figure 3.67 Reaction of ferrocenylmethanols **118a-c** with chlorophosphate **29e**.
Reaction conditions: *i*) THF, –50 °C, BuLi, **29e**, ambient temperature, 18 h. Yields are based on **118a**–**c**. a) **118a** as the starting material. b) **118b** as the starting material. c) **118c** as the starting material. d) 1 : 1 hexane/THF mixture, 60 °C, 18 h. e) Hexane, 60 °C, 1 h.

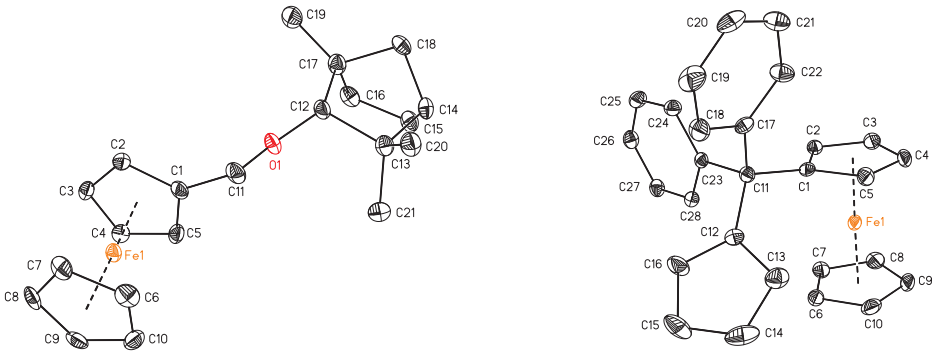


Figure 3.68 ORTEP (30 % probability levels) of the molecular structures of **124** (left) and **127b** (right) with the atom numbering schemes. All hydrogen atoms and a second crystallographically independent molecule of the asymmetric unit of **127b** have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°) for **124**: C11–O1 1.440(8), O1–C12 1.410(8); C1–C11–O1 106.7(6), C11–O1–C12 115.1(5), C5–C1–C11–O1 72.0(8); for **127b**: C12–C13 1.446(5), C13–C14 1.446(6), C14–C15 1.439(6), C15–C16 1.445(5), C16–C12 1.362(5), C2–C1–C11–C23 9.7(4), C5–C1–C11–C12 61.0(4).

Upon treatment of **118a**–**c**–Li with **29e** the formation of phosphates **119a**–**c** is expected (Figure 3.67). However, after appropriate workup they could not be isolated. In case of **118a**, the main product was identified as the respective ether **122a** (46 % yield), besides 12 % of the starting material **118a**, 3 % of methyl ferrocene (**123**) and 6 % of the fenchyl

ether **124**. The formation of **123a** indicates that **119a** has *in situ* been formed, which was consecutively attacked by **118a**–Li. The nucleophilic attack is favored by the cleavage of **121a** as a leaving group.[322] Reaction with water gives **118a** during the work up. It is known that ferrocenylmethyl cations can straightforward be formed, due to their stabilization in a benzyl-type position and by an intramolecular Fe$\cdots$C$^+$ interaction.[323,324] Thus, **120**$^+$ might be a key intermediate where nucleophilic attacks have occurred, which has *in situ* been formed in solution besides **121a**.

The identity of **124** has inter alia been verified by applying single-crystal X-ray diffraction analysis (Figure 3.68), revealing retention of the absolute configuration of the fenchyl group as (1*R*)/endo. Thus, an attack of a fenchylate at **119a**/**120a**$^+$ seems to be convincing, since the reaction of **118a**–Li at an OFn functionality would have resulted in the exo-derivative. For methyl substituted ferrocenylmethanols **118b**,**c**, the formation of the dehydration products **125a**,**b** was observed. Thus, the elimination reaction of **119b**,**c** and the subsequent removal of H$^+$ is faster than a nucleophilic attack, probably due to the increased steric demand. The *in situ* formed phosphates either underwent an intramolecular dehydrophosphorylation via a 6-membered transition state involving the P=O bond, or an intramolecular C–O bond cleavage (Figure 3.67).

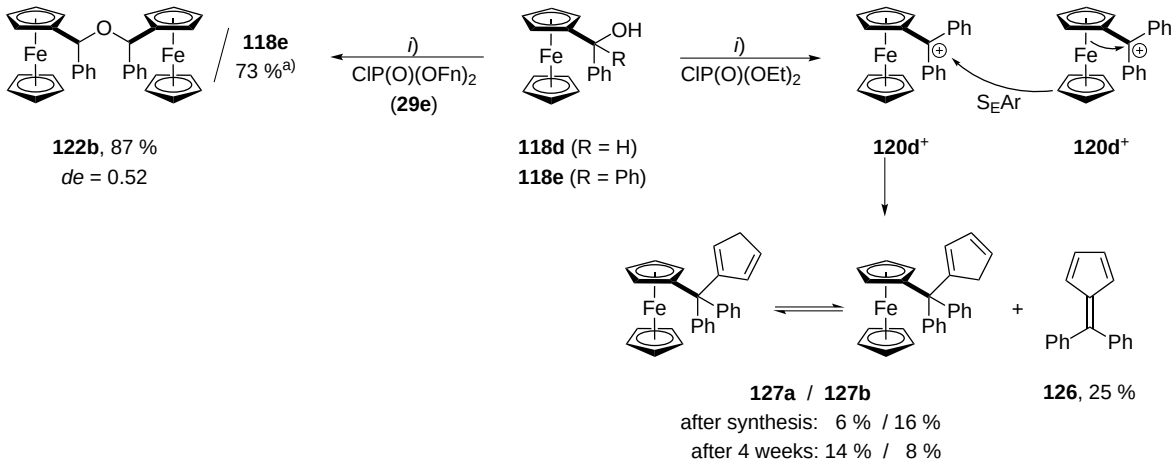


Figure 3.69 Reaction of ferrocenylphenylmethanols **118d**,**e** with chlorophosphates.
Reaction conditions: *i*) THF, BuLi, –50 °C, ClP(O)(OEt)$_2$/**29e**, ambient temperature, 18 h. Yields are based on **118d**,**e**. a) THF/hexane (1 : 1 mixture), 60 °C, 18 h.

To prevent the dehydration reaction by removing β-H atoms as observed for **118b** and **118c**, the alkyl chains were replaced by phenyls groups as characteristic for **118d**,**e** (Figure 3.69). Lithiation of **118b** with BuLi and subsequent treatment of **118b**–Li with **29e** gave the respective ether **122b** (dr = 1 : 0.315), whereas for **118e** solely the starting material could be recovered.

Compound **122b** was obtained in a high yield of 87 %, which solely was exceeded by a lewis acid catalyzed synthetic protocol using Yb(OTf)$_3$, giving **122b** in 95 % yield.[325] Since it is not clear if **118e**–Li did undergo the reaction with **29e** or has just been protonated during the workup procedure, we reduced the steric demand of the chlorophosphate from the steric demanding fenchyl to ethyl groups in ClP(O)(OEt)$_2$ (Figure 3.69).

The addition of $ClP(O)(OEt)_2$ to **118e**–Li immediately resulted in an exothermic reaction. Column chromatographic separation gave 6,6-diphenylfulvene (**126**) in 25 % yield and the cyclopentadiene-substituted ferrocenes **127a**,**b** (22 %). Similar to the mechanism depicted in Figure 3.67, the *in situ* formed ferrocenyl phosphate eliminates diethyl phosphate, leading to the cationic species $\mathbf{120d}^+$, stabilized by a benzyl- and the above mentioned interaction to the Fe atom.[322] This cation underwent an electrophilic aromatic substitution reaction with a hitherto nonsubstituted cyclopentadienyl, resulting in the release of a $Fe\cdots Cp^+$ fragment, which most probably decomposes to **126** and a Fe^{2+} ion. Compound **127** was obtained as a 3 : 8 cyclopentadiene isomeric mixture of **127a**/**127b** as indicated in Figure 3.69. After 4 weeks, the ratio had changed to 7 : 4, due to 1,5-sigmatropic rearrangements, confirming the 3-substituted derivative **127a** as the thermodynamically stable product. These rearrangements are typical for this kind of molecules.[326]

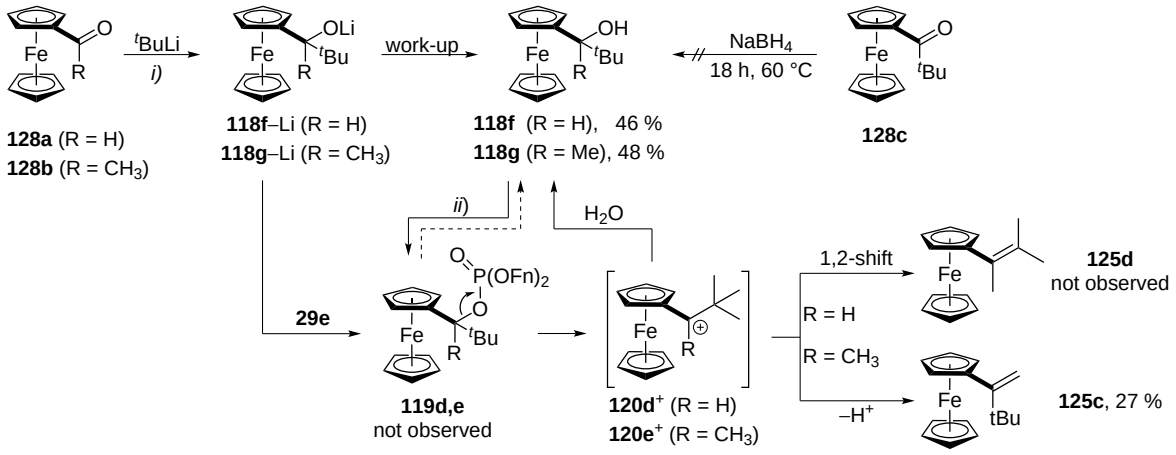


Figure 3.70 Reaction of ^{t}Bu substituted ferrocenylmethanols **118f**,**g** with chlorophosphate **29e**.
Reaction conditions: *i*) Et_2O, ^{t}BuLi. *ii*) Et_2O, ^{t}Buli, **29e**.

Replacement of the CH_2 by a CH(^{t}Bu) fragment (Figure 3.70) could prevent the ether formation, due to the increased steric demand, and the dehydration reaction, due to the absence of a β-hydrogen atom in **118f**. In principle, ferrocenylmethanols **118f**,**g** are accessible by reduction of pivaloylferrocene **128f**, or the reaction of acylferrocenes **128a**,**b** with ^{t}BuLi. Since treatment of **128f** with $NaBH_4$ at 60 °C solely gave the starting material, formyl- (**128a**, R = H) and acetylferrocene (**128b**, R = CH_3) were reacted with ^{t}BuLi and **29e** was subsequently added. In case of R = H, alcohol **118f** was obtained probably due to a nucleophilic attack of water to **120d** within the appropriate workup, which is supported by the absence of the Wagner-Meerwein rearrangement product **125d**. In contrast, for α-ferrocenylmethanol **118g** possessing a β-hydrogen atom, the elimination reaction involving a 6-membered cycle (Figure 3.67) or the formation of $\mathbf{120f}^+$ occurred, due to the stability of alkyl $\mathbf{4}^+$-type systems and the formation of **125c**.[327] The alkene formation could be prevented by introducing bicyclic systemssuch as 2-adamantyl and fenchyl (Figure 3.71). Compound **129** was available by reacting mono-lithiated ferrocene[328] with 2-adamantanone, resulting in the formation of alcohol **129** in good yields (73 %).

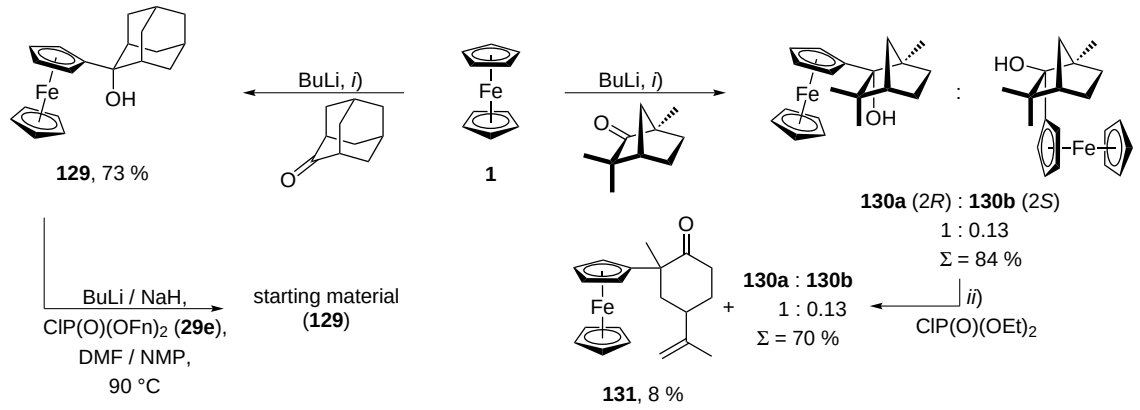


Figure 3.71 Synthesis of ferrocenyl alcohols **129** and **130a**, and their subsequent reaction with chlorophosphates $ClP(O)(OEt)_2$ and **29e** in the presence of a base.
Reaction conditions: *i*) ^{t}BuLi, THF, KO^{t}Bu, –80 °C, 2-adamantanone (**130**)/ (1*R*)-fenchone (**130**). Yields are based on **1**. *ii*) BuLi, Et_2O, –30 °C, $ClP(O)(OEt)_2$. Yields are based on **130**.

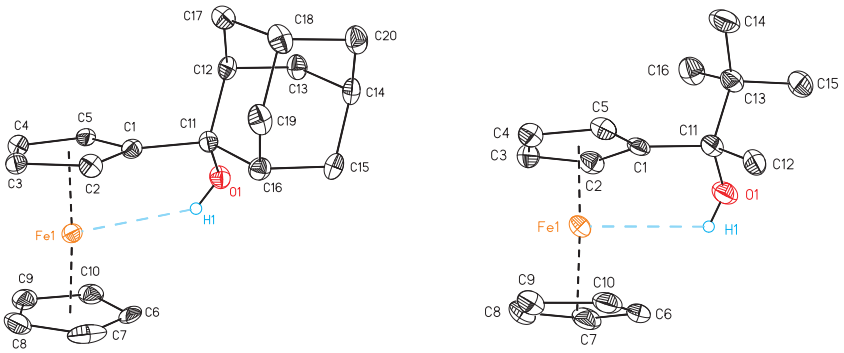
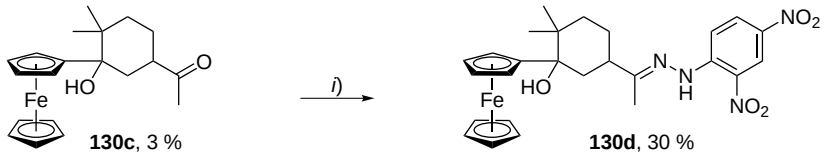


Figure 3.72 ORTEP (50 % probability levels) of the molecular structures of **129** (left) and **118g** (right) with the atom numbering schemes. C-bonded hydrogen atoms and a second crystallographically independent molecule of the asymmetric unit of **129** have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°) for **129**: C11–O1 1.451(5), C11–O1 1.440(3), O···Fe 3.370(3)/3.372(2), O–H···Fe 128.6/130.8, C–C1–C11– O1 48.0(4); for **118g**: O1···Fe1 3.575(2), O1–H1···Fe1 117.94, C2–C1–C11–C13, 85.0(4); C2–C1–C11–O1 31.7(4).

By reacting **1**–Li with the chiral-pool derived ketone (1*R*)-fenchone, alcohol **130** was formed.[329–331] Compared to an earlier synthetic methodology for **130**, where (1*R*)-fenchone was reacted in the presence of $CeCl_3$ with ferrocene, giving an epimeric ratio of 1 : 0.[329,330] Herein, the ratio was improved to 1 : 0.13 (Figure 3.71). Within the synthesis of **130**, the formation of a ferrocenyl-substituted non-bicyclic side product **130c** was produced (Figure 3.73). However, the formation of the latter species could not be unequivocally proven. Compound **130c** could be converted into the dinitrophenyl hydrazone derivative, verifying the presence of the keto functionality, which was further evidenced by the appearance of a resonance signal at 210.4 ppm in the $^{13}C\{^1H\}$ NMR spectrum. For the deprotonation reaction of **129**, BuLi and sodium hydride were used as bases to investigate the effect of the counter cation toward the nucleophilic attack at chlorophosphate **29e**. Treatment of **129**–Li/Na with

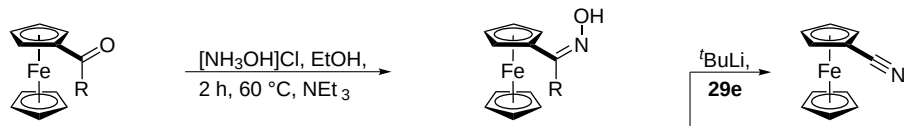
29e in DMF or *N*-methyl-2-pyrrolidone, respectively, at 90 °C, however, exclusively gave the starting material back. The same result was obtained when **130** was consecutively treated with BuLi followed by **29e** in hexane at 80 °C for 18 h, which was proven by $^{31}P\{^{1}H\}$ NMR spectroscopy. Replacing **29e** by the steric less demanding $ClP(O)(OEt)_2$, did not result in the formation of the corresponding phosphate, rather **131**, could be isolated as a single isomer (Figure 3.71). The molecular structure of **131** was based on NMR spectroscopic and mass-spectrometric studies (m/z = 336.1163 for $C_{20}H_{24}FeO$). The formation of **131** indicates a cationic isomerization reaction after release of diethyl phosphate, as characteristic for **127a**,**b** (Figure 3.69).



130c, 3 % **130d**, 30 %

Figure 3.73 Structural proposal of **130c** and its conversion into the dinitrophenylhydrazone. Reaction conditions: *i*) CH_2Cl_2, 2,4-dinitrophenylhydrazine, HCl_{aq}, 25 °C, 12 h. Yield based on **130c**.

The results derived by the reactions of ferrocenylmethanols **118a**–**g**, **129** and **130** with either the difenchyl chlorophosphate **29e** or $ClP(O)(OEt)_2$ indicate that they are rather unsuited starting materials for anionic homo phospho-Fries rearrangements, due to their rapid decomposition and elimination reaction of the *in situ* formed phosphates. Another structural motif, which could be converted to phosphates are oximes.[332] To prove, if this synthetic methodology is also applicable for ferrocene-based oximes, we prepared **132a**–**d** (Figure 3.74).



128a (R = H)
128b (R = Me)
128c (R = ^{t}Bu)
128d (R = Ph)

132a (R = H), 82 %
132b (R = Me), 50 %
132c (R = ^{t}Bu), 0 %
132d (R = Ph), 0 %

133, 72 %
+
118f, 3 %
128a, 8 %

Figure 3.74 Synthesis of ferrocenyl oximes **128a**,**b** and the reaction with chlorophosphate **29e**. Yield based on **128**.

Acylferrocenes **128a**–**d** were reacted with hydroxylammonium chloride in the presence of NEt_3 (Figure 3.74).[333] Nevertheless, only formylferrocene (**128a**) could be converted to oxime **132a** (82 % yield), while **128b**–**d** inhibited the formation of **132c**,**d**, which most likely can be explained by the increased electron density of **128b**–**d**. In case of **128b**, a 1 : 1 mixture of the starting materiel with the oxime **132b** was obtained after appropriate column chromatographic workup. Compound **132c** has yet not been reported in literature, most probably, due to its rapid hydrolysis to **128d**. We assume that compound **132d**[334] and partially **132b** were hydrolyzed during the column chromatographic workup. Deprotonation of **132a** was achieved using ^{t}BuLi as a steric demanding, non-nucleophilic base to avoid a

nucleophilic attack at the carbonyl carbon atom. Subsequent treatment of **132a**–Li with **29e** predominantly resulted in the formation of ferrocenylnitrile (**133**) in 72 %, along with **128a** (8 %) and **118f** (3 %), while phenyl oximes can be converted into their respective phosphates,[332] ferrocenyl based derivatives seem to undergo similar dehydration reactions as compared to the ferrocenylmethanols **118b**,**c**,**e** in the presence of **29e**.

Recently electron poor pyrrolyl, indolyl and carbazolyl-containing phosphoramidates were converted into stable ferrocenyl phosphoramidates.[335] Thus, the CR_2–O motif was replaced by a CR=N-bonded ferrocenyl unit. This imino phosphate motif (type **G** molecules, Figure 3.66) has sparsely been described, especially in ferrocene chemistry, where solely a C=N–$P(O)(Ph)_2$ unit has been reported, however, without its synthetic procedure.[336,337] The Fc–C=N–P structural motif is also present in 2*H*-azaphosphirenes, as found by a scifinder search.[338]

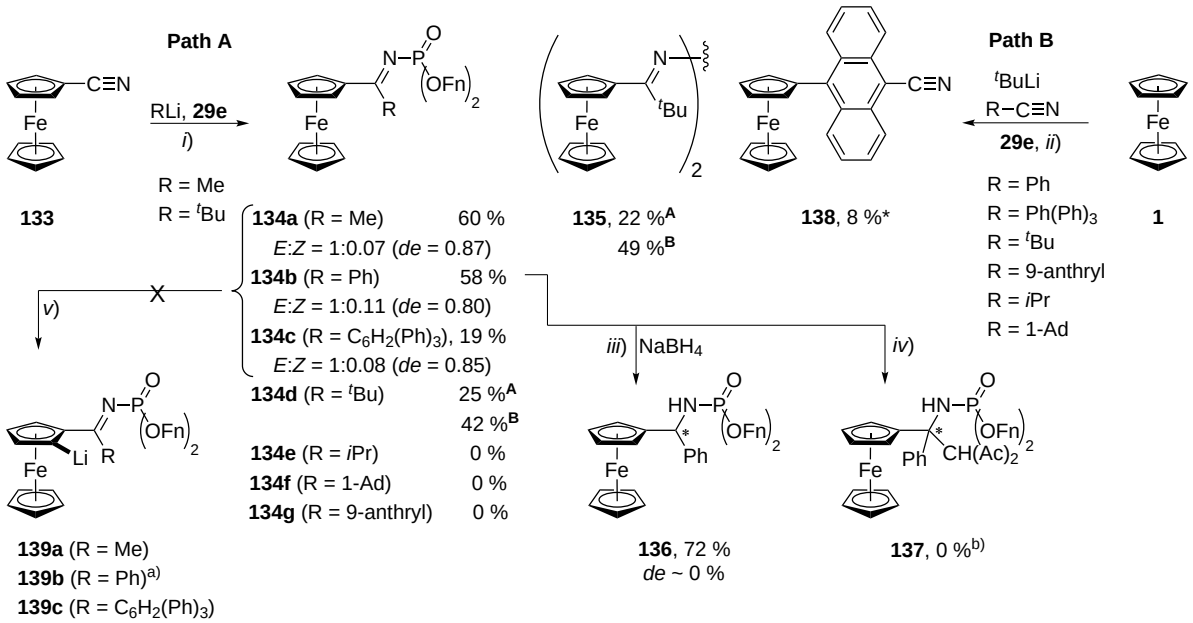


Figure 3.75 Synthesis of imino phosphates **134a**–**d**, azine **135** and anthrylferrocene **138**. Reaction conditions: *i*) THF, –80 °C, RLi, –30 °C, **29e**. Yields are based on **133**. *ii*) THF, KO^tBu, ^{t}BuLi, –80 °C, R–C≡N, –30 °C, **29e**. Yields are based on **29e**. *iii*) THF, $NaBH_4$, H_2O. Yield based on **134b**. *iv*) Acetylacetone, K_2CO_3, CH_2Cl_2, $MgSO_4$, 50 °C 18 h. *v*) LiTMP/LDA, hexane/THF, –40 °C/ 0 °C. *The product hardly separates from the starting material. a) 78 % of ketone **128d** were obtained; LiTMP, hexane, TMEDA, 25 °C, 48 h without Me_2SO_4.

The imino phosphato motif could, for example, be obtained by condensation reactions of carbonyl derivatives with NH_2-bearing phosphoramidates.[320] The synthesis of imino phosphoramidates by the condensation of an aminophosphate with a carbonyl compound in the presence of $TiCl_4$ was reported.[320,339,340] A protocol using oximes, tosylazide and chlorophosphates also allows to prepare imino phosphates.[341] In addition, reaction of organolithium compounds with nitriles could be applied in the synthesis of imino phosphates,[342] however, the alkyl-substituted imino phosphates rapidly isomerized into the respective enamine phosphoramidates.[340]

The latter approach was applied on ferrocenylnitrile (**133**), which was reacted with MeLi

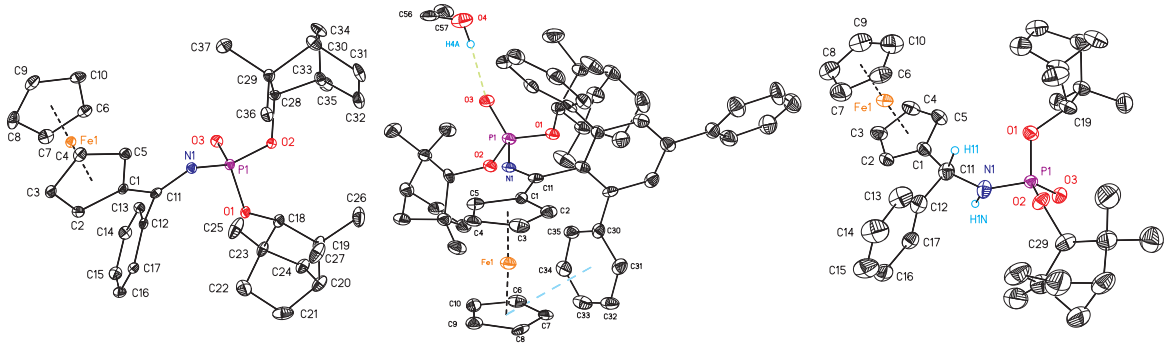


Figure 3.76 ORTEPs (30 % probability level) of the molecular structures of **134b** (left), **134c** (middle) and **136** (right) with the atom numbering schemes. Selected hydrogen atoms and three additional crystallographically independent molecules of the asymmetric unit of **136** have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°) for **134b**: C11=N1 1.286(4), N1–P1 1.645(3), C2–C1–C11–N1 175.5(3), C1–C11–N1–P1 178.3(2); for **134c**: C11=N1 1.288(11), N1–P1 1.635(8), C11– N1–P1 136.4(6), C1–C11–N1–P1 163.5(7), C2–C1–C11–N1 177.0(9); for **136**: C≡N 1.456(13)–1.468(15), N–P 1.589(9) –1.619(8). C2–C1–C11–N1 52.0(14)–65.8(14). Hydrogen bridge bond properties: C3···O4 2.781(9) Å, C3···H4A–O4 174 °. Intramolecular π interactions between involved centroids (Ct): Ct ···Ct 4.513(6), α 88.8(5) °.

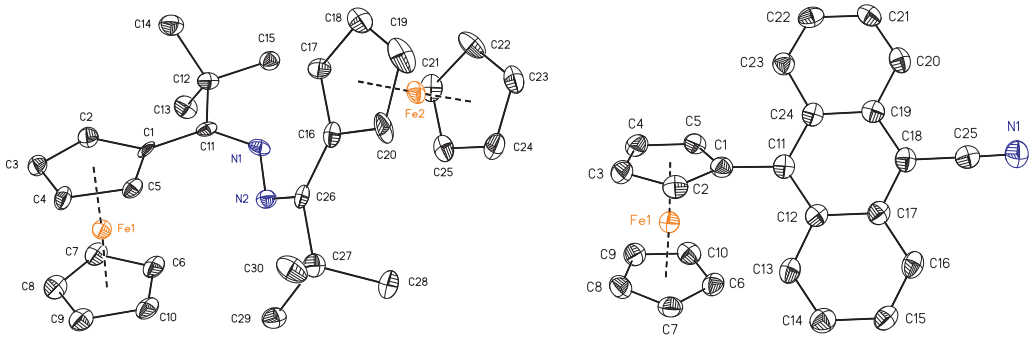


Figure 3.77 ORTEPs (50 % probability level) of the molecular structures of **135** (left) and **138** (right) with the atom numbering schemes. All hydrogen atoms and a second crystallographically independent molecule of the asymmetric unit of **135** have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°) for **135**: C=N 1.277(10)–1.293(10), N–N 1.389(9)/1.385(9), C1–C11–N1, C–N–N 120.2(7)–120.5(7), C–N–N–C 126.9(8)/127.6(8); for **138**: C25–N1, 1.142(4), C18–C25 1.441(5).

and ^{t}BuLi to imine anions. In addition, commercially available nitriles were treated with mono-lithio ferrocene **1**–Li (Figure 3.75). In both cases, the *in situ* formed imine anion was subsequently reacted with **29e** giving imino phosphates **134a**–**d** in up to 60 % yield (R = Me, Figure 3.75). The *E*-/*Z*-ratios for sterically non-demanding methyl (**134a**), phenyl (**134b**) and triphenylphenyl (**134c**) groups are similar and ranges between 1 : 0.07 and 1 : 0.11. Using the steric demanding ^{t}Bu derivative **134d** inverted the *E*-/*Z*- ratio to 0.26 : 1 (Figure 3.75). The assignment of the *E*-configuration at the C=N double bond for **134b**,**c** is derived from single-crystal X-ray diffraction analysis (Figures 3.76) and in similarity **134a**. Within

the reaction of ^{t}BuC≡N with **1**–Li or **133** with ^{t}BuLi the formation of oxidative coupled azine **135** is observed possessing a *Z*-/*Z*-configuration. Azines are in general available by reacting carbonyl compounds with hydrazine,[343] or oxidation of hydrazines with oxygen.[343] They are also accessible under oxidative conditions by reacting nitriles with RLi and subsequent treatment with $CuCl/O_2$,[343] or in the presence of perbenzoates.[344] In contrast, **135** is the first example, which has not been formed by a condensation reaction with hydrazines.[345] The use of isopropyl nitrile as a *CH* acidic compound, did not produce the respective phosphate, rather giving ferrocene. The 1-adamantyl derivative **134f** was not accessible, due to its steric demand. The reaction of 9-anthryl nitrile with **1**–Li and **29e** afforded, instead of the expected phosphate **134g**, compound **138** as a dark red solid. Similar to **135**, the formation of **138** can be explained by an oxidative coupling by **1**–Li with 9-anthryl nitrile. However, running the reaction of 9-anthryl nitrile with **1**–Li without chlorophosphate **29e** failed to give **138**, which is indicated by the absence of a color change from orange to dark red. We assume that a nucleophilic attack of **1**–Li occurred at the 10-positioin of the anthryl backbone, whereby the negative charge is stabilized by the nitrile substituent and the two attached aromatic rings. The removal of a hydride could be supported by chlorophosphate **29e**, since chlorophosphates can easily be reduced with metals (Na, K), potassium naphthalenide[346] or $NaBH_4$.[347] The 9,10-substitution pattern of **138** was, for example, verified by single-crystal X-ray diffraction analysis (Figure 3.77). The presence of a C≡N substituent was also evidenced by its $^{13}C\{^1H\}$ NMR signal at 118 ppm and the respective stretching in the IR spectra at 2208 cm^{-1}.[293] It should be noted that **138** was hardly separate from the initial anthracene nitrile. The applicability of alkylidene phosphoramidates **134a**–**f** as starting materials for anionic homo phospho-Fries rearrangements was proven by their treatment with lithium tetramethylpiperidide (LiTMP) or LDA in either hexane or THF. As described in sections 3.1.1 and 3.1.2 ethyl phosphates are preferably lithiated in THF at low temperature,[196,263] whereas steric demanding bicyclic, *e.g.* fenchyl groups require higher temperatures and a non-polar solvent.[168,315] However, the applied reaction conditions described, did not indicate a lithiation of the ferrocenyl backbone to form **139a**–**c**, whereas molecules derived from a nucleophilic attack of the base, *e.g.* 78 % of **128d** for **134b**, were detected (Figure 3.75). The reactivity of the C=N bond has exemplary been investigated by reacting **134b** with acetylacetone in the presence of K_2CO_3. In contrast to phenyl-based derivatives, where nucleophilic attacks at the carbonyl atoms proceed[336,348–351], solely the starting material was recovered in case of **134b**. Reduction of the C=N bond of **134b** by using $NaBH_4$ gave amine **136** (20 % yield) as a 1 : 0.86 : 0.23 mixture of three isomers as evidenced by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR measurements. Single-crystal X-ray diffraction analysis of **136** (Figure 3.76) revealed the crystallization of a racemic mixture of two epimers with respect to their configuration at the former carbonyl carbon atom. The redcution from **134b** to **135** could also be confirmed by IR spectroscopic measurements, where the $\upsilon_{C=N}$ vibration of the imino phosphoramidate **134b** at 1572 and 1611 cm^{-1} disappeared, while a new band at 3185 cm^{-1} (υ_{NH}) could be observed. The reaction of **134b** with MeLi indicated a nucleophilic attack at the carbonyl carbon, evidenced by the presence of phosphate **121a**. The absence of a phosphoryl moiety in azine **135** was verified by IR spectroscopy, since the C=N stretching frequency was shifted to

lower energy from 1572 and 1611 in **134b** to 1559 cm^{-1} in **135**. The C≡N triple bond in **138** absorbed at 2208 cm^{-1}. A remarkable feature of dark purple **138** is the bathochromic shift and the high absorption coefficient of 1850 L mol^{-1} cm^{-1} of the d→d at 536 nm compared to, for example, **135** (λ_{max} = 431 nm, ϵ = 883 L mol^{-1} cm^{-1}) (Table 3.14).

Table 3.14 UV/Vis-measurements of **129**, **134a-d**, **135**, **136** and **138**.[a])

Compd.	λ / nm (ϵ / L mol^{-1} cm^{-1})		Color of
	π-π^* band	Ferrocene band	the solid
129	329 (66)	447 (121)	Orange
134a	275 (7909)	464 (684)	Red
134b	362 (1652)	484 (1117)	Red
134c	372 (1281)	502 (1106)	Red
134d	281[c](8211)[d]	460[c](724)[d]	Red
135		463 (883)[b]	Red
136		431 (125)	Yellow
138	375 (5581)	536 (1850)	Dark
	408 (10230)		Purple
	424 (9248)		

[a] Measured in CH_2Cl_2 at 25 °C.
[b] Values derived from NIR measurements.
[c] Occurred as a shoulder.
[d] Molar mass based on the Elemental Analysis.

The absorption properties, and thus the colors of the products, strongly depend on the electronic properties of the substitutents. For compound **129**, bearing a electron-rich adamantyl group, the d→d transition was observed at 447 nm with ϵ = 121 L moL^{-1} cm^{-1}. While increasing the electron-withdrawing character of the attached substituents, *e.g.*, in imino phosphates **134a**–**f**, the maximum of the d→ d absorption shifts to lower energies, along with an increase of the absorption coefficient (Table 3.14). Replacement of a phosphoryl group in **134d** by a further –N=C group in azine **135** did not affect the energy of the $d \rightarrow d$ transition, although the electrochemical properties differ.

The presence of two ferrocenyl units within one molecule, separated by a π-conjugated bridge allows for the investigation of an electronic communication between both redox centers in the single-oxidized mixed valent species. Thus, the electrochemical behavior of ^{t}Bu-substituted, diferrocenyl compound **135** was investigated by cyclic voltammetry (CV) and square wave voltammetry (SWV), and compared with **134d** possessing a similar substitution pattern at the C=N carbon atom. Compound **135** showed two reversible one electron redox events, one was observed for **134d**, respectively. If the N=C group in **135** is replaced by the phosphoryl group in **134d**, the first redox event is shifted from 24 (for **135**) to –135 mV, ascribing the azine motif to be more electron-withdrawing as compared to the phosphoryl group. The redox events in 2,3-diazabutadiene **135** are separated by 201 mV, which is higher than for the literature known 1,4-diaza derivative (< 100 mV),[352] but lower than for 1,4-diferrocenylbutadiene (225 mV).[353] If the voltage within the CV measurement for **134d** is increased to more than 1300 mV, the redox event becomes irreversible, indicating the decomposition of this oxidized species. *In situ* UV/Vis/NIR spectroelectrochemical measurements were additionally carried

out for **135** to prove, if the redox separation of 201 mV is due to an electronic communication between both ferrocenyls, as observed for 1,4-diferrocenyl butadiene,[353] or caused by electrostatic interactions. However, an inter-valence charge transfer (IVCT) absorption, in the region between 1250 and 2750 nm[269,354] has not been observed, revealing that the redox separation is due to electrostatic interactions and no electronic communication between the Fc and Fc^+ fragments occurred in the mono-oxidized mixed-valent species. The absence of an electronic communication between the both ferrocenyls in **135** might be supported by the non-planar C=N–N=C moiety in the solid state structure (Figure 3.77) due a torsion angle of 53 °.

3.4 Functionalization of *ortho*-Diphenylphosphino Ferrocenylmethanols

Attempts to apply anionic homo phospho-Fries rearrangement at ferrocenylmethanols, oximes and imines showed that the additional methylene or CR_2 fragment causes side reactions and prevents a successful proceeding toward phosphates.

Acid Catalyzed and Base Mediated Reactions

The 1,2-P,CH_2OH substitution pattern, well-suitable for further functionalization, was synthesized by a literature known eight-step procedure was applied (Figure 3.78).[75,355]

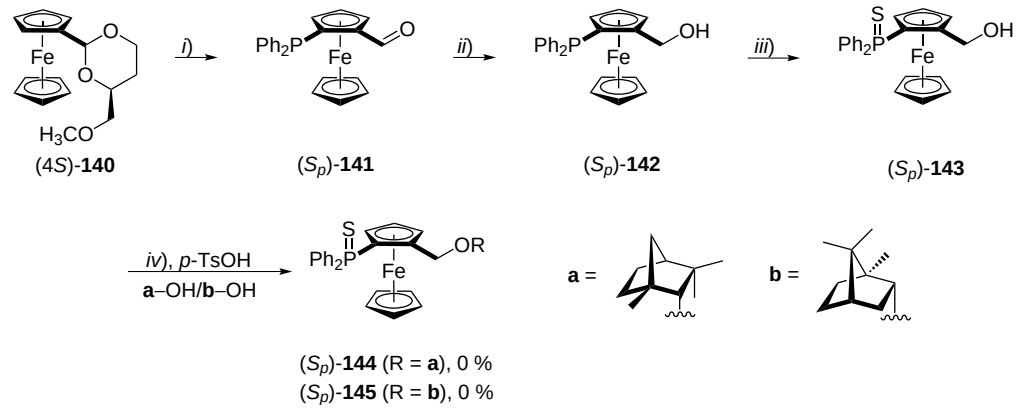


Figure 3.78 Synthesis of (S_p)-**143** and acid catalyzed reaction with chiral-pool alcohols. Reaction conditions: *i*) 1^{st}, ^{t}BuLi, Et_2O, –78 °C, $ClPPh_2$, –30 °C, 99 % *de*; 2^{nd}, *p*-TsOH, CH_2Cl_2/H_2O, reflux, 74 % based on (4*S*)-**140**. *ii*) $NaBH_4$, MeOH, 2 h, 25 °C, 92 % based on (S_p)-**141**. *iii*) S_8, 2 h, CH_2Cl_2, 25 °C, 95 % based on (S_p)-**142**. iv) *p*-TsOH, ROH, R = a/b.

Thus, formyferrocene[356] was first converted into the chiral acetal (4*S*)-**140**, followed by diastereoselective lithiation in *ortho* position with ^{t}BuLi and consecutive reaction with $ClPPh_2$ (Figure 3.78). After the cleavage of the acetal group in (4*S*)-**140**, the enantiopure phosphane (S_p)-**141** was obtained (Figure 3.78).[355] Aldehyde (S_p)-**141** was reduced to alcohol (S_p)-**143** by using $NaBH_4$, followed by the addition of sulfur to the reaction mixture, to protect the lone pair electron at the phosphorus atom as a sulfide. The reactions of compound (S_p)-**143** with ethanol, benzyl alcohol and menthol was recently reported, whereby the yields of the corresponding ethers reduced from 56 to 27 % in the same order.[314] Attempts to react (S_p)-**143** with the steric more demanding (1*R*)-α-fenchyl (Fn, Figure 3.78) and (1*S*)-borneyl alcohols (Bo) in the presence of *p*-TsOH afforded a mixture of non-separable ferrocenyl species instead of (S_p)-**144**/**145** (Figure 3.78).

Ferrocene (S_p)-**143** was also reacted with *p*-TsOH without adding a further electrophile to force the self-condensation to (S_p)-**148** (Figure 3.79). However, instead of the oxoether (S_p,S_p)-**148**, the thioether (S_p,S_p)-**149** was formed in 72 % yield. The replacement of the oxygen by a sulfur atom was evidenced by a shift of the adjacent CH_2 fragments in the $^{13}C\{^1H\}$ NMR spectra from 59.9 ppm (S_p)-**143**) to 31.3 ((S_p,S_p)-**149**) (Table 3.15).

The molecular structure of (S_p,S_p)-**149** in the solid state was additionally confirmed by single-

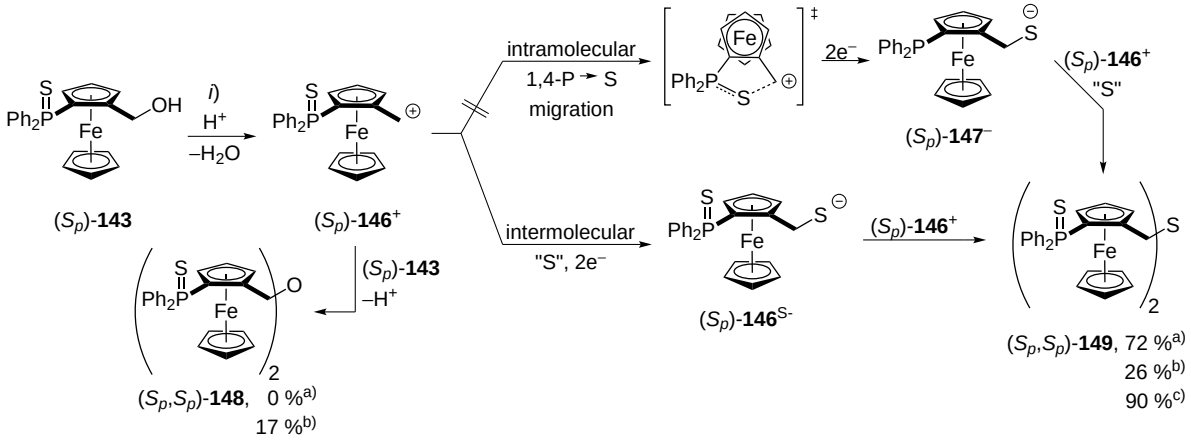


Figure 3.79 Acid induced formation of (S_p,S_p)-**149**.
Reaction conditions: *i*) *p*-TsOH·H_2O (3 equiv), toluene, 80 °C, 18 h. a) 48 mmol L^{-1}. b) 96 mmol L^{-1}. c) in 1,4-dioxane. Yields based on (S_p)-**143**, whereas for (S_p,S_p)-**149** the requirement of one molecule as the sulfur source has been taken into consideration.

crystal X-ray diffraction analysis (Figure 3.80). The presence of S_8 within the product after the sulfurization process of (S_p)-**142** can be excluded, due to its easy separation by column chromatography. The NMR data especially of the CH_2 moiety in (S_p)-**143** are in the range for CH_2–O fragments (Table 3.17),[314] Elemental analysis further evidenced the formation of (S_p)-**143** as shown in Figure 3.78. Addition of sulfur within the conversion of (S_p)-**143** to (S_p,S_p)-**149** remains the yield similar at 77 %, revealing that inorganic sulfur is rather not involved within the synthesis process, since a difference between 72 % (without S_8) and 77 % (with S_8) is a sufficient evidence might be questionable. Thus, (S_p)-**146**$^+$ is considered as the sulfur source.

Table 3.15 Optimization of the reaction conditions for the synthesis of (S_p,S_p)-**149** from (S_p)-**143**.

Entry	(S_p)-**143** / mg	Solvent / mL	c / mmol L^{-1}	S_8[a]	Product	Yield[b]
1	300	toluene (15)	48	–	(S_p,S_p)-**149**	72 %[c]
2[d]	1000	toluene (25)	96	–	(S_p,S_p)-**148**	17 %
					(S_p,S_p)-**149**	26 %[c]
3	500	toluene (25)	48	1 Equiv	(S_p,S_p)-**149**	77 %[c]
4	1000	toluene (85)	28	1 Equiv	(S_p)-**150**	71 %
5	500	1,4-dioxane (35)	34	1 Equiv	(S_p,S_p)-**149**	90 %
6	300	1,4-dioxane (25)	29	0 Equiv	(S_p,S_p)-**149**	80 %

[a] With respect to **143**.
[b] Isolated yield.
[c] The requirement of one molecule of **143** as the sulfur source has already been taken into consideration.
[d] The products were isolated as a non-separable mixture. Thus, the yields were obtained from the ratio of the integrals in the $^{31}P\{^1H\}$ NMR spectra.

For the calculation of the herein reported yields of (S_p,S_p)-**149**, three molecules of (S_p)-**143** were considered. Desulfurized (S_p)-**146**$^+$ most likely decomposed releasing two electrons, which are required for the formation of **149**. We assume that the other reaction components (dioxane or toluene, *p*-TsOH and H_2O) are unsuitable as electron donors under these reaction

conditions.

The removal of sulfur from (S_p)-**143** can be excluded, since the formed (S_p)-**142** can easily be re-oxidized. According to the above mentioned stability of ferrocenyl methyl carbenium ions, we assume the removal of the OH group in (S_p)-**143** under the acidic conditions and a migration of a P-bonded sulfur to the exo carbon atom, where the positive charge is present (Figure 3.79). This might have occurred *via* an inter- or intramolecular mechanism by passing a 5-membered transition state (Figure 3.79). In contrast to hydroxy, the formed thiol functionality is not removed acid catalyzed and reacts with (S_p)-**146**$^+$ forming thioether (S_p,S_p)-**149**. It should be noted, that for the conversion of ferrocenylmethanol (**118a**) to the respective thiol derivative, Lawesson's reagent is generally required as a sulfer source.[357]

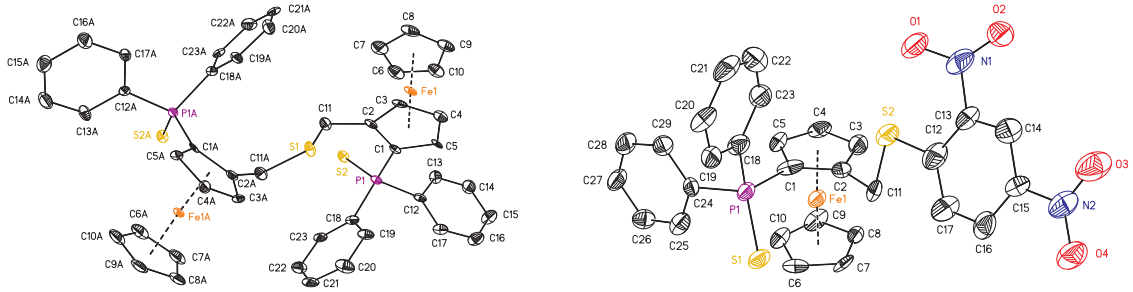


Figure 3.80 ORTEPs (50 % probability level) of the molecular structures of (S_p,S_p)-**149** (left) and (S_p)-**155** (right) with the atom numbering schemes. All hydrogen atoms and a second molecule in the asymmetric unit of (S_p)-**155** have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°) for (S_p,S_p)-**149**: P=S 1.952(5), C2–C11 1.494(17), C11–S1 1.814(13), C11–S1–C11A 103.0(9), C2–C11–S1 106.3(9), C2–C1–P1–S2 53.2(12), C1–C2–C11–S1 106.5(13); for (S_p)-**155**: P=S 1.954(5)/1.960(5), N–O 1.210(18)–1.235(19), C2–C11–S2 102.0(10)/103.6(10), C–S–C 103.7(8)/104.1(9). Symmetry operation for generating equivalent atoms (A): –y, –x, –z+1/2.

The reaction strongly depended on the concentration of (S_p)-**143** in the reaction mixture and lowers the yield of (S_p,S_p)-**149** to 26 % while changing from 48 mmol L^{-1} to 96 mmol L^{-1} (Table 3.15). Interestingly, the higher concentration preferably resulted in the formation of (S_p,S_p)-**148**, indicating that the reaction of (S_p)-**143** with (S_p)-**146**$^+$ is faster compared to the removal of an OH group and the migration of the sulfur atom. However, (S_p,S_p)-**148** could not be separated from its mixture with (S_p,S_p)-**149**, neither by crystallization nor column chromatography. Suggesting that a further decrease of the concentration of (S_p,S_p)-**149** would improve the yield, a 28 *mM* solution was used for the conversion. However, an electrophilic aromatic substitution of the solvent occurred (Figure 3.81), giving (S_p)-**150** in 71 % yield. The reaction of the carbocation (S_p)-**146**$^+$ with toluene was suppressed by changing the solvent to 1,4-dioxane, which increased the yield of (S_p,S_p)-**149** to 90 % (Figure 3.79, Table 3.15). Attempts to obtain (S_p,S_p)-**148** by a similar reaction, as observed for **122a** (Figure 3.67) or **122b** (Figure 3.69) by using ClP(O)(OEt)$_2$ gave, however, 50 % of the starting material back and an unidentifiable mix of compounds. The lowering of the concentration of (S_p)-**143** in the reaction mixture should not affect the sulfur migration, if

an intramolecular mechanism is considered and thus, the yield of (S_p,S_p)-**148** should not be decreased. However, the reaction of (S_p)-**146**$^+$ with the solvent (toluene), while reducing the concentration, instead of a sulfur migration, indicates an intermolecular proceeding.
The observed reaction of carbenium ion (S_p)-**146**$^+$ with the solvent toluene was further investigated, since this electrophilic aromatic substitution reaction are sparsely described so far.[324,358] Recently, ferrocenylmethanol (**118a**) was coupled with electron-rich aromatics, *e.g.*, 2-naphthol, pyrrole, giving 1-naphthylmethyl and 2-pyrrolylmethyl ferrocenes, by using $(NH_4)_2[Ce(NO_3)_6]$.[324] The use of highly activated salicylate anions predominantly occurred *ortho* to the OH group.[358] The Fc-CH_2-Ar pattern is also accessible by alkylation[322,359] or acylation of ferrocene,[360] followed by removal of the oxygen substituent.

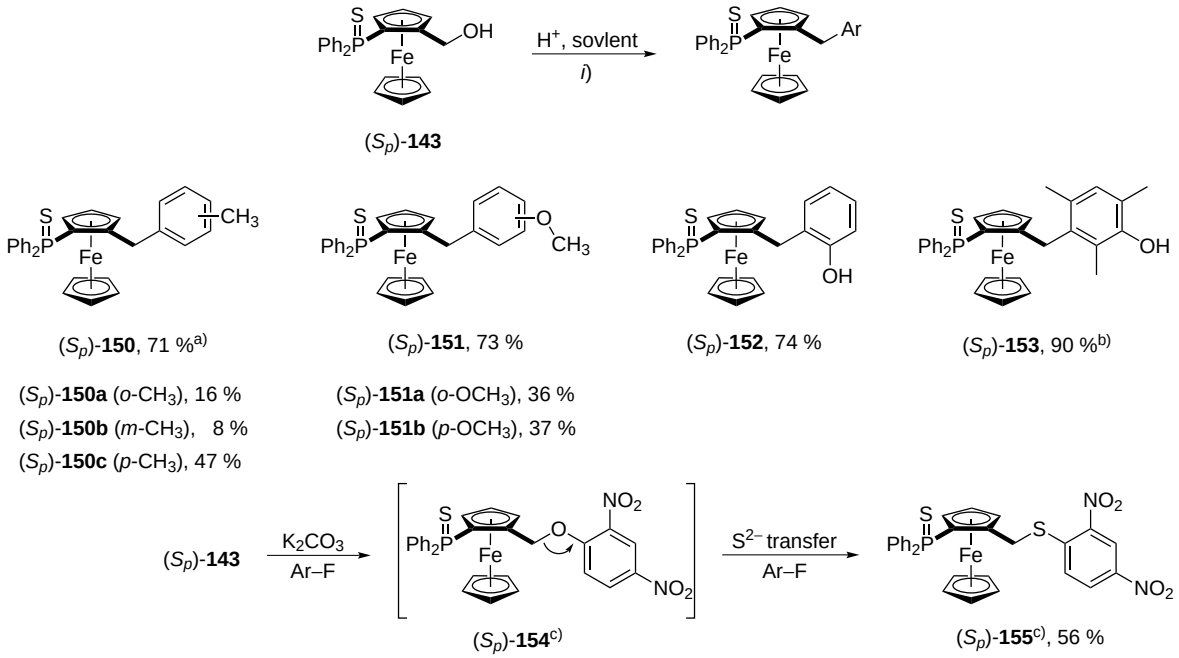


Figure 3.81 Electrophilic aromatic substitution of (S_p)-**143** with electron-rich arenes to **150**–**153** and nucleophilic aromatic substitution with an aryl fluoride to **155**.
Reaction conditions: *i*) *p*-TsOH, toluene (**150a**–**c**), anisole (**151a**,**b**), phenol (**152**), 80 °C; or CH_2Cl_2 and 2,4,6-trimethylphenole (**153**) at 50 °C. a) As a 2 : 1 : 6 mixture. b) CH_2Cl_2 50 °C; 72 h. c) K_2CO_3, 2,4-dinitrofluorobenzene, DMF. Yields based on (S_p)-143.

The scope of the electrophilic aromatic substitution reaction was extended by reacting planar-chiral ferrocenylmethanol (S_p)-**143** with further aromatics (Figure 3.81). Until toluene (S_p)-**150** was formed as a 2 : 1 : 6 mixture of the *o*-:*m*-:*p*-isomer. The three regioiseomers could not been separated from each other under a column chromatographic purification process. Thus, their ratio within the mixture was calculated from the integrals of the ^{1}H NMR spectra. Based on electronic and steric properties of the different isomers, the *para*-isomer has predominantly been formed, which is supported by NMR investigations and a solid state structure of (S_p)-**150a**. However, using anisole as the solvent afforded a 1 : 1 mixture of the *ortho*- and the *para*-isomers. A *meta*-isomer was not formed. The increased amount of *ortho*-substituted (S_p)-**151a** compared to the *para*-product (S_p)-**151b**, is due to an electrostatic attraction of the carbocation and the OMe substituents, superimposing the steric effect.

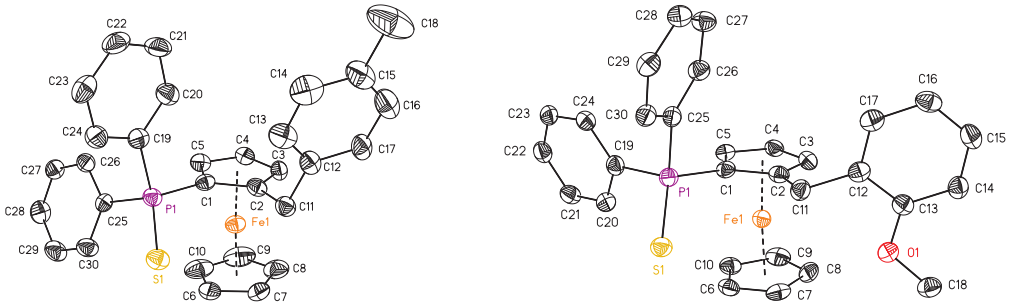


Figure 3.82 ORTEPs of the molecular structures of (S_p)-**150c** (left, 50 % probability level) and (S_p)-**151a** (right, 30 % probability level) with the atom numbering schemes. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°) for (S_p)-**150c**: P1=S1 1.9648(16), C11–C12 1.513(7), C2–C11–C12 112.7(4), C2–C1–P1–S1 35.2(5), C1–C2–C11–C12 77.3(6); for (S_p)-**151a**: P=S 1.955(2), C2–C11–C12 113.6(5), C2–C1–P1–S1 55.5(6), C1–C2–C11–C12 157.8(6).

The substitution patter in (S_p)-**151a** could *inter alia* been verified by single-crystal X-ray diffraction analysis (Figure 3.82). Using phenol within the electrophilic aromatic substitution reaction exclusively gave the *ortho*-substituted (S_p)-**152**. A nucleophilic attack of the oxygen functionality at the carbocation to an arylether was not observed under the acidic conditions, as it could be shown for a nucleophilic proceeding.[358] As shown in section 3.1.3, the nucleophilicity of hydroxy-aryl species, *e.g.* phenolates and naphtholates is rather low.[335,361] concluding that the electrophilic aromatic substitutuion is faster and irreversible. Attempts to force the nucleophilic attack of the oxygen atom by blocking the electronically preferred *ortho*- and *para*-positions in mesityl phenol, resulted in the formation of *meta*-substituted (S_p)-**153** (Figure 3.81). The *meta*-methoxy/hydroxy substitution pattern has rarely been described and usually has to be forced by reacting the respectively lihtio-arene with formyl ferrocene[362] cyanomethylferrocene[363] or by applying an S_EAr reaction of ferrocene with the respective aryl carbonyls.[364] It could also be shown in section 3.2.3 that ferrocenoles can undergo reactions with aryl fluorides, resulting in stable ferrocenyl aryl ethers even at ambient temperature by using, *e.g.*, 2,4-dinitrofluorobenzene (Sangers reagent).[263,315] Thus, (S_p)-**143** was activated using K_2CO_3 and reacted with Sangers reagent (Figure 3.81). Instead of giving the oxoether (S_p)-**154**, the thio derivative (S_p)-**155** was obtained. The presence of an ether sulfur was evidenced by single-crystal X-ray diffraction analysis (Figure 3.80). Most likely, a S_NAr-type reaction had occurred followed by removal of 2,4-dinitrophenolate, subsequent migration of a sulfur atom and attack of the formed thiol/thiolate in a further S_NAr reaction. Using IR spectroscopy verified the presence of the nitro groups in (S_p)-**155**, which were observed at 1520 and 1345 cm^{-1}. As expected,[365] the P=S stretching vibration was observed, *e.g.* for (S_p)-**153** and (S_p)-**155** at 643/645 cm^{-1}. In phenol (S_p)-**153**, the OH band occurred at 3403 cm^{-1}. The thioether group, as found in (S_p,S_p)-**149** and (S_p)-**155**, has up to now solely been achieved by a nucleophilic attack of thiols or thiophenols[366] at ferrocenylmethanols.

Desulfurization of Phosphinesulfides

The reduction of the P(V) species (S_p,S_p)-**149** and (S_p)-**151a**/**153** to the required P(III) phosphines was performed according to literature reported protocols by refluxing the phosphine sulfides with $P(NMe_2)_3$ in toluene (Figure 3.83).[314]

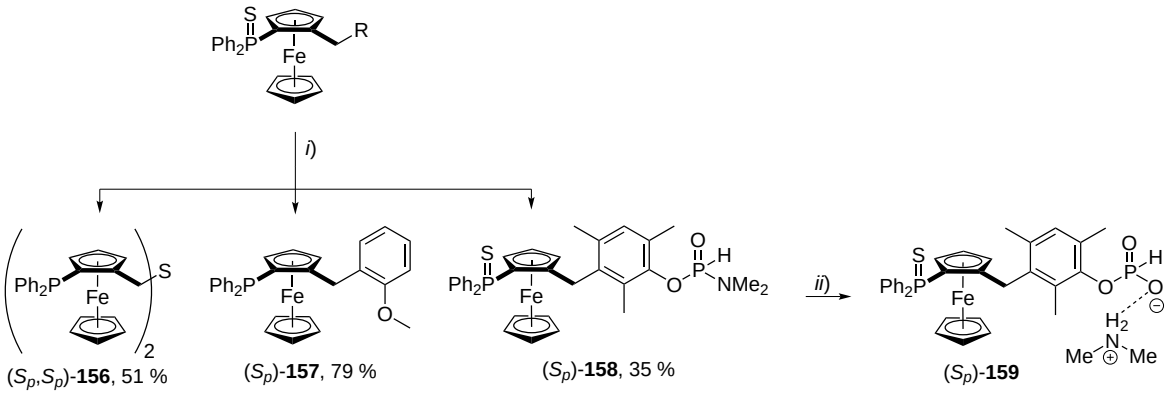


Figure 3.83 Desulfurization of (S_p,S_p)-**149**, (S_p)-**151a** and (S_p)-**153** using $P(NMe_2)_3$. Reaction conditions: *i*) $P(NMe_2)_3$, C_6H_5Cl for **156** and **157** or toluene for **158**, reflux, 18 h. Yields are based on the respective ferrocenyl educt. *ii*) Crystallization of a CH_2Cl_2 solution containing (S_p)-**158** gave a few single crystals of (S_p)-**159**, which were suitable for single-crystal X-Ray diffraction analysis.

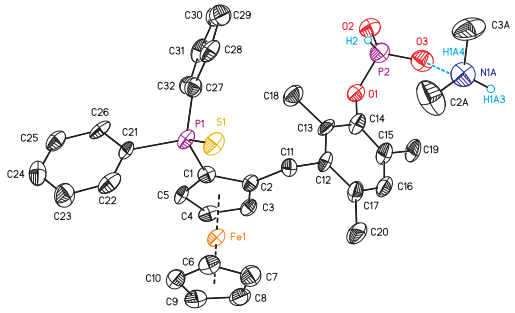


Figure 3.84 ORTEP (50 % probability level) of the molecular structure of (S_p)-**159** with the atom numbering scheme C-bonded hydrogen atoms and one molecule of CH_2Cl_2 have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°): P2–O1 1.627(10), P2–O2 1.482(11), P2–O3 1.486(11), P1=S1 1.948(5), C2–C11–C12 111.1(11), C2–C1–P1–S1 45.0(12), C13–C14–O1–P2 94.67(14). Hydrogen bridge bond properties (Å / °): O3···N1A 2.724(18), O2–N1A 2.708(18), O3···H1A4–N1A 155, O2–H1A3–N1A 160.

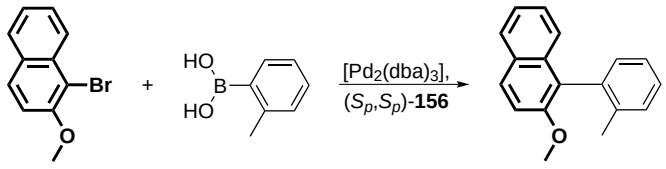
However, in case of (S_p,S_p)-**149** no product could be isolated under the standard conditions applied (refluxing toluene, 18 h). Optimization of the reaction conditions showed that with the higher boiling solvent chlorobenzene the reaction successfully proceeded at 130 °C. This allowed the isolation of (S_p,S_p)-**156** after appropriate workup in a yield of 51 % yield. We assume that the higher reaction temperatures required for the conversion, is due to a synergistic effect of both P=S groups, which is supported by the absence of a mono-desulfurized product. Attempts to desulfurize OH-functionalized (S_p)-**153** did not give the P(III) species (Figure 3.83). Instead, the hydroxy group bounds to $P(NMe_2)_3$ and partial hydrolysis to phosphite

(S_p)-**158** was observed after a flash column chromatographic purification process. The identity of (S_p)-**158** was *inter alia* verified as its ammonium phosphite (S_p)-**159** by single-crystal X-ray diffraction analysis. Hydrolysis occurred during the crystallization process (Figure 3.84). The occurrence of (S_p)-**158** and (S_p)-**159** as the P(O)H tautomer is evidenced by a $^1J_{H,P}$ coupling constant of 646.2 Hz for the PH fragment in the ^{1}H and ^{31}P NMR spectra.

C,C Cross-Coupling Reactions

Compounds (S_p,S_p)-**156** and (S_p)-**157** were investigated as stereopure, planar-chiral supporting ligands within Suzuki-Miyaura *C*,*C* cross-coupling reactions for the synthesis of hindered biaryls, using the standard reaction conditions used in Section 3.1.5 and in reference 74. The use of bidendate (S_p,S_p)-**156** required an optimization of the Pd/L ratio and concentration (Table 3.16), which has exemplarily been performed for the synthesis of **94e** by using Pd(dba)2 (dba = dibenzylideneacetone) as the Pd source. Starting with 1 mol-% of Pd and (S_p,S_p)-**156** as a ligand, biaryl **94e** was formed almost quantitatively in an *ee* of 17 %, which is higher than for the ethyl and benzyl derivatives.[314] While decreasing the Palladium loading to 0.5 mol-% and 0.1 mol-% respectively, reduced the *ee* to 12 % and 7 % associated with a lowering of the yield to 57 % (Entry 1–3, Table 3.16). However, a Pd/L ratio of 1 : 0.5 did not give **94e**.

Table 3.16 Optimization of the Pd/L ratio for the synthesis of **94e**.[a]



92 **93** **94e**

Entry	[Pd] / mol-%	(S_p,S_p)-**156** / mol-%	Yield / %	*ee* / %
1	1	1	97	17
2	0.5	0.5	97	12
3	0.1	0.1	57	7
4	1	0.5	0	–
5	1	1.5	98	20
6	1	2	0	–

[a] Reaction conditions: 1-bromo-2-methoxynaphthalene (1 mmol), 2-tolylboronic acid (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol), toluene (3 mL), 70 °C, 24 h.

Contrary, changing to a 1 : 1.5 Pd/L ratio slightly increased the *ee* to 20 %. A further increase of the phosphine loading prevented the formation of an active catalyst (Entry 6, Table 3.16). The substrate scope was extended using the conditions in entry 1 (Table 3.16) for (S_p,S_p)-**156** and compared with (S_p)-**157** as a *P*,*O*-substituted ferrocene (Figure 3.85).
Comparing the yield and *ee* of the 2-methoxy naphthyl derivatives **94e**–**g**,**i**,**j** reveals a dependency on the substitution pattern of the boronic acid. While a similar *ee* was observed for an OCH_3 (**94f**) and CH_3 (**94e**) group, an increase of the steric demand gave a racemic mixture for the phenyl derivative **94g**. In contrast, an *ortho*-phenyl substituted aryl halide gave the

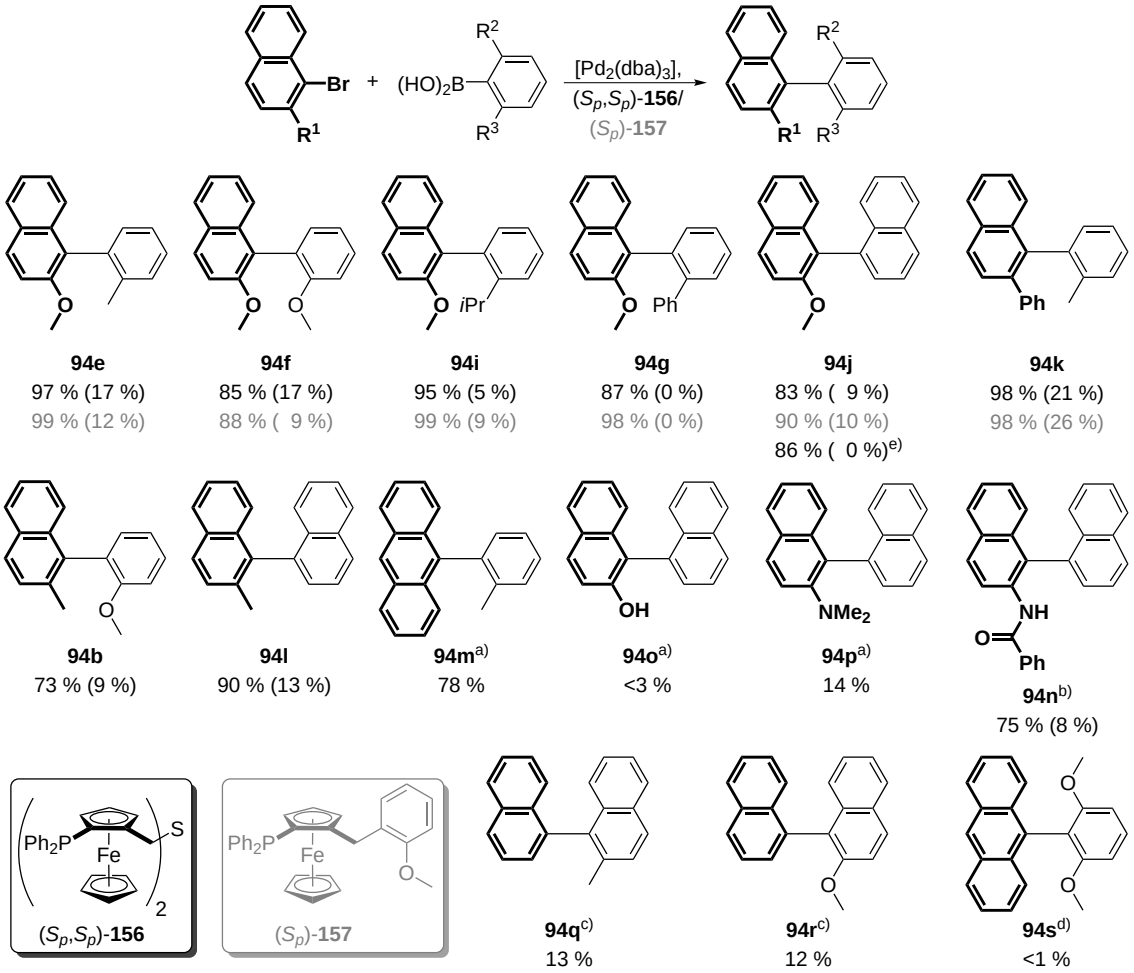


Figure 3.85 *C*,*C* Cross-coupling reaction for the synthesis of *ortho*-substituted biaryls **94b**–**o** by using *P*,*S* and *P*,*O* ferrocenes (S_p,S_p)-**156** and (S_p)-**157**.
Reaction conditions: aryl halide (1.0 mmol), boronic acid (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol), toluene (3 mL), 0.5 mol-% [$Pd_2(dba)_3$], 1.0 mol-%, (S_p,S_p)-**156**/ 2.0 mol-% (S_p)-**157**, 70 °C, 24 h. Reaction times were not minimized. Yields are based on isolated material as an average of two runs, except otherwise noted. a) 100 °C. b) The product has been obtained from the respective amine. It was converted into the amide by using PhC(O)Cl and NEt_3 at 65 °C for 6 h, due to its rapid decomposition. c) Yields are obtained from the NMR data of the crude product. d) 1,4-Dioxane, 100 °C, 48 h. e) using dppf as the ligand.

product **94k** with 26 % *ee*. The Suzuki-Miyaura reactions were also carried out by using (S_p)-**157**, giving similar or slightly higher yields, while a slightly decrease of the *ee* was observed for **94e**–**k** (Figure 3.85). Therefore, we assume a better stabilization during the catalytic cycle by the anisyl group. However, the flexibility of the OMe group and the distance to the planar-chiral backbone is not beneficial. The use of the non-chiral bis(diphenylphosphino)ferrocene (dppf) as the ligand gave **94j** with a similar yield as observed for (S_p,S_p)-**156** and (S_p)-**157**, respectively, and as expected, as a racemic mixture. Replacement of the OCH_3 by a CH_3 group in biaryls **94b**,**l** gave opposite results for yield and *ee* compared to **94f**,**j**. Larger condensed aromatics such as 9-bromoanthracene gave **94m** in a yield of 78 %. Substituents, which are able to form hydrogen-bridge bonds could interact with either the ligand or the active Pd catalyst.

Thus, OH, NMe_2 and NH_2 functionalities were investigated for the synthesis of **94n**–**p**. How-

ever, the presence of the hydroxy group gave **94n** with only 3 % yield besides 1,1'-binaphthyl and naphthalene. An interaction of the substrate molecules with the ligands is assumed, since type **94n** biaryls are known to be formed under similar reaction conditions [367] In similarity, **94o** was formed in 14 % yield, besides the starting halide and 1,1'-binaphthyl. Interestingly, the presence of a NH_2 group did not have a disadvantageous influence. Due to a reported rapid oxidation of the formed biaryls [368], the reaction mixture has directly been treated with benzoyl chloride, giving novel **94p** in 75 % yield and an *ee* of 8 %. However, (S_p,S_p)-**156** is unsuitable as a ligand in the Suzuki-Miyaura reaction, if double *ortho*-substituted boronic acids are used, as shown for **94q**–**s**. GC-MS analysis revealed the presence of the starting halide and hydro-deboronation product. Thus, the transmetallation process seems to be the decisive step within the catalytic cycle.

3.4.1 Characterization

NMR Spectroscopy

In similarity to the previous sections, the identity of all compounds was established by 1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Except for diferrocenylether **122a**, all compounds possessing a methylene group bonded to the ferrocenyl backbone also contain a further stereo center, caused by planar chirality (**142**, **143** and **149**–**155**) or by a chiral substituent (**124**). Thus, the CH_2 hydrogen atoms occurred diastereotopic with a $^2J_{H,H}$ coupling of 7 to 17 Hz (Table 3.17). The resonances of the CH_2 group in the $^{13}C\{^1H\}$ NMR suggests the type of the attached atoms. Thus, OH substituents in **142** and **143** gave a resonance signal at ∼ 59 ppm. Attachment of an alkyl group in **122a** and **124** resulted in a downfield shift to ∼ 68 ppm. The replacement of the oxygen by a sulfur or aromatic carbon atom shifts the value below 34 ppm. This also confirms that within the sulfurization reaction from **142** to **143** the OH group is not removed, which supports the postulated mechanism depicted in Figure 3.79. Compounds (S_p)-**142**, **156** and **157** bearing a PPh_2 group also showed a $^3J_{C,P}$ coupling of 9–12 Hz for the CH_2 units, in contrast to the $P(S)Ph_2$ derivatives. The exclusive formation of the (1*R*)-α-isomer for fenchyl derivative **124**, indicated by solely one set for the CH_2 signals, confirmed its formation within a nucleophilic attack at a $FcCH_2^+$ fragment.
The ratio of cyclopentadiene-substituted ferrocenyls **127a**,**b** could be obtained by integration of the C_5H_5 signals in the ^1H NMR spectra, whereas the assignment of the respective set of signals to **127a** and **127b** is based on $^{13}C\{^1H\}$ NMR spectroscopic studies. After synthesis, the product mixture of **127a**,**b** showed two sets of signals in the ^1H, whereas in the $^{13}C\{^1H\}$ NMR, solely the set of the C_5H_5 and C_5H_4 carbon atoms for the 2-substituted 1*H*-cyclopentadiene **127b** were observed (**127b**, C_5H_5, 69.2 ppm; C_5H_4, 67.3 and 71.2 ppm). After isomerization of the **127a**/**b** mixture for four weeks in solution, the amount of the thermodynamically stable 3-substituted product **127a** increased, and the **127a**/**127b** ratio changed from initially 3 : 8 to 7 : 4. However, the intensities of the mentioned ferrocenyl region in the $^{13}C\{^1H\}$ NMR decreased for **127b**, whereas a small increase of broad signals occurred for **127a** (**127a**, C_5H_5, 69.8; C_5H_4, 67.7 and 71.0 ppm), with a width of ∼20 Hz for each. This can be explained by a rapid 1,5-sigmatropic rearrangement of the 1H-hydrogen,

Table 3.17 NMR values of the CH_2 groups of Y-Fc-CH_2-E compounds **122a**, **124**, **142**, **143**, **149-153**, **155**.

Compd.	E	Y	CH_2-group-^{1}H ($^2J_{H,H}$ / Hz)	CH_2-group-$^{13}C\{^1H\}$
122a	OCH_2-	H	4.28(s)	67.9
124	OFn	H	4.20(11.4)/4.31(11.4)	69.4
142	OH	PPh_2	4.41(12.4, 5.9)[a]/4.54 (12.5, 5.6)[a]	59.9 (9.6)[c]
143	OH	$P(S)Ph_2$	4.31(12.9, 6.1)[a]/4.68 (12.9, 8.4)[a]	58.5
149	SCH_2-	$P(S)Ph_2$	3.72(13.5)/3.91(13.7)	31.3
150a	*o*-tol	$P(S)Ph_2$	3.89(16.3)/4.03(16.3)	32.0
150c	*p*-tol	$P(S)Ph_2$	3.87(15.1)/4.19(15.2)	33.7
151a	Ar-*o*-OMe	$P(S)Ph_2$	3.99(15.2)/4.12(15.2)	28.5
151c	Ar-*p*-OMe	$P(S)Ph_2$	3.83(15.1)/4.23(15.0)	33.2
152	Ar-*o*-OH	$P(S)Ph_2$	3.82(15.3)/4.13(15.3)	27.4
153	Ar-*m*-OH	$P(S)Ph_2$	3.30(17.2)/4.32(17.0)	29.1
155[d]	SAr	$P(S)Ph_2$	4.41(12.4)/4.96(12.4)	32.0
156	SCH_2-	PPh_2	3.60(12.1, 1.8)[b]/3.64(12.1)	32.1(11.7)[c]
157	Ar-*o*-OMe	PPh_2	3.86(15.1)/3.93(15.1, 2.0)[b]	28.6 (10.1)[c]

[a] $^3J_{H,H}$ in Hz.
[b] $^4J_{H,P}$ in Hz.
[c] $^3J_{C,P}$ in Hz.
[d] Overlaps with the signal of the C_5H_5 moiety.

which broadens the signal, as long as the shift again gives the 3-substituted derivative. The NMR spectroscopic data of **130c** (Figure 3.73) formed within the synthesis of **130a** (Figure 3.71) gave $^{13}C\{^1H\}$ NMR signals at 209.8 ppm (C=O), 147.8 ppm (C=CH_2), 108.7 ppm (C=$C$$H_2$), further three CH_2 groups (31.0, 36.8 and 42.6 ppm), one CH fragment (46.0 ppm) and solely one further quaternary carbon atom at 54.9 ppm. One of the signals for CH_3 groups (21.2, 28.3 ppm) occurred as a singlet in the ^{1}H NMR (1.45 ppm), whereas the other one is broadened, due to a $^4J_{H,H}$ coupling with the =CH_2 hydrogen atoms. However, the coupling constant is rather low and could not be resolved.

4 Experimental Part

4.1 Working Techniques and Analytic Methods

All reactions were carried out in Schlenk tubes under an atmosphere of nitrogen using standard Schlenk techniques. If working under moisture and oxygen free conditions was required, the Schlenk tubes were evacuated several times using oil pump vacuum, flushed with Argon (5.0 purity). During the evacuation process, the respective vessels were heated to 200 to 300 °C. The subsequent reactions were carried out with a permanent inert gas overpressure (0.1 bar). Liquid substances, solvents and solutions were added *via* a septum by using plastic single-use syringes with high-grade steel cannula. Solid compounds were, if possible, added under an inert gas flow. Otherwise, the Schlenk vessels were evacuated and subsequently flushed with argon, several times. If reactions carried out at low temperatures, the Schlenk vessels were put in insolated polyurethane vessels, filled with mixtures of crushed ice and sodium chloride (>–20 °C) or with isopropanol, which was cooled to the desired temperature using liquid nitrogen (< –20 °C). The temperature was controlled with an appropriate low-temperature thermometer. Solvents were dried under nitrogen (5.0 purity) followed by distillation: 1,4-dioxane, *N*-methyl-2-pyrrolidone and tetrahydrofuran over sodium. Diethyl ether, hexane, dichloromethane and toluene were dried by the solvent purification system MB SPS-800 (Fa. MBraun) and stored in Schlenk vessels of appropriate size, possibly over activated molecular sieve (4 Å of size), and used without further purification. DMF, TMEDA and *N*,*N*-diisopropylamine were refluxed over calcium hydride and distilled prior to use. $POCl_3$, acetonitrile and 2,4-dinitrofluorobenzene were distilled prior to use. All further solvents were used without further purification. If reactions components were potentially unstable towards oxygen, the solvents and reactions mixtures were degassed prior to the reaction. Therefore, the Schlenk vessels were placed in an ultrasonic bath, evacuated and subsequently flushed with argon. This procedure was repeated four times.
For column chromatography either silica with a particle size of 40–60 μm (230–400 mesh (ASTM); Fa. Macherey-Nagel GmbH & Co. KG) or alumina with a particle size of 90 μm (Standard; Fa. Macherey-Nagel GmbH & Co. KG) was used. The solid material was welled with the respective mobile phase and filled in a glass column containing a glass frit. The solvent mixtures were determined by thin layer chromatography. Filtrations were carried out using G 4 type glass frits covered with a 5 cm thick layer of celite (purified and calcined; Erg. B. 6 (Fa. Riedel de Häen).
The assignment and labeling of the H and C atoms; especially of bicyclic structures, follows the IUPAC recommendations.[218]

4.1.1 Nuclear Magnetic Resonance Spectroscopy - NMR

NMR spectra were recorded in deuterated solvents at 25 °C with a Bruker Avance III 500, or a Varian 400 spectrometer for the collection of ^{19}F spectra. Chemical shifts are reported

in δ units (parts per million) downfield from tetramethylsilane with the solvent as reference signal, external standards or with respect to the ^2H solvent lock signal.[369]

^{1}H (500.30 MHz):	Internal solvent reference
	($CDCl_3$: $\delta = 7.26$ ppm; rel. $SiMe_4$: $\delta = 0.00$ ppm)
	(C_6D_6: $\delta = 7.16$ ppm; rel. $SiMe_4$: $\delta = 0.00$ ppm)
	($(CD_3)_2SO$: $\delta = 2.50$ ppm; rel. $SiMe_4$: $\delta = 0.00$ ppm)
^{11}B (160.42 MHz):	^2H Solvent lock signal
^{13}C (125.80 MHz):	Internal solvent reference
	($CDCl_3$: $\delta = 77.00$ ppm; rel. $SiMe_4$: $\delta = 0.00$ ppm)
	(C_6D_6: $\delta = 128.06$ ppm; rel. $SiMe_4$: $\delta = 0.00$ ppm)
	($(CD_3)_2SO$: $\delta = 39.52$ ppm; rel. $SiMe_4$: $\delta = 0.00$ ppm)
^{19}F (376.31 MHz):	^2H Solvent lock signal
^{29}Si (99.33 MHz):	External reference
	rel. $SiMe_4$: $\delta = 0.00$ ppm)
^{31}P (202.53 MHz):	External reference
	($P(OMe)_3$: $\delta = 139.0$ ppm; rel. 85 %-ige H_3PO_4: $\delta = 0.0$ ppm)
^{119}Sn (186.57 MHz):	External Standard
	($SnMe_4$: $\delta = 0.0$ ppm)

Iterative spectra simulations were performed with spectra processing program MestReNova.

4.1.2 Mass Spectrometry

High-resolution ESI-TOF (Electro-Spray-Ionization-Time-of-Flight) mass spectra (HRMS) were recorded with a Bruker Daltonik micrOTOF-QII spectrometer.

4.1.3 Elemental Analysis

Elemental analyses were measured with the CHN-analysis device Thermo FlashEA 1112 instrument. All values are given in weight percent as the average of two measurements.

4.1.4 Melting Point

Melting or decomposition points were determined with a Gallenkamp MFB 595 010 M apparatus.

4.1.5 Single Crystal X-Ray Diffraction Analysis

The X-ray diffraction analysis were collected with graphite-monochromated Mo-K_α ($\lambda = 0.71073$ Å) or Cu-K_α ($\lambda = 1.54184$ Å) radiation with an Oxford Gemini S device containing a CCD-detector. The crystal preparation was performed in a perfluorinated polyalkylether (DuPont, Krytox GPL 107) to protect them from oxygen and moisture. Some measurements were carried out at at <120 K by using a low-temperature Oxford Cryojet instrument. The molecular structures were solved by direct methods using SHELXS-97[370] and refined by full-matrix least-squares procedures on F^2 using SHELXL-97.[371] All non-hydrogen atoms were

refined anisotropically, and a riding model was employed in the treatment of the hydrogen atom positions. The absolute structure parameter[372] for compounds, crystallizing in non-centrosymmetric space groups can be found in the attachment. The *cif* files were deposited at the *CSD* database and are available free of charge. The assigned numbers are provided in the appendix. The crystallographic *R*-values are defined as follows:

$$R_{int} = \frac{\sum_{hkl} |F_{obs}^2 - \overline{F_{obs}^2}|}{\sum_{hkl} F_{obs}^2} \quad (4.1) \qquad R_1 = \frac{\sum_{hkl} ||F_{obs}| - |F_{calc}||}{\sum_{hkl} |F_{obs}|} \quad (4.2)$$

$$wR_2 = \sqrt{\frac{\sum_{hkl} w(F_{obs}^2 - F_{calc}^2)^2}{\sum_{hkl} w(F_{obs}^2)^2}} \quad (4.3) \qquad S = \sqrt{\frac{\sum_{hkl} w(F_{obs}^2 - F_{calc}^2)^2}{N_{Ref} - N_{Par}}} \quad (4.4)$$

$$w = \frac{1}{\sigma^2(F_{obs}^2) + (a \cdot P)^2 + b \cdot P} \quad (4.5) \qquad P = \frac{F_{obs}^2 + 2 \cdot F_{calc}^2}{3} \quad (4.6)$$

Parameters a and b (Equation 4.5) are optimized automatically by the SHELX package.
The analysis and calculation of intermolecular interactions, e.g., π-interactions, and the removal of solvent molecules (SQUEEZE-procedure) was performed by using the PLATON.[373] Graphics of the molecular structures have been created by using the ORTEP program[372] the SHELXTL package.[374]

4.1.6 High-Performance Liquid Chromatography - HPLC

The HPLC measurements were performed with Knauer System containing a HPLC pump K-500 and an UV detector K-2000 operating at λ 245 nm. The enantiomeric excess was determined by using a Daicel CHIRACEL OD-H or OJ-H column (4.6 $\times$ 250 mm) using different solvent mixtures. Retention times t are reported in minutes.

4.1.7 Electrochemical Investigations

Electrochemical measurements using 0.1 mol L^{-1} $[N(Bu)_4][B(C_6F_5)_4]$ as the supporting electrolyte in anhydrous dichloromethane solutions were performed in a dried, argon-purged cell at 25 °C with a scan rate of 100 mV s^{-1}, and a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer. For the measurements a three-electrode cell containing a Pt auxiliary electrode, a glassy-carbon working electrode (surface area 0.031 cm^2), and an Ag/Ag^+ (0.01 mmol L^{-1} $[AgNO_3]$) reference electrode fixed on a Luggin capillary was used. The working electrode was pretreated by polishing on a Buehler microcloth first with 1 μm and then 1/4 μm diamond paste. The reference electrode was constructed from a silver wire inserted into a 0.01 mmol L^{-1} solution of $[AgNO_3]$ and 0.1 mol L^{-1} of an $[N(Bu)_4][B(C_6F_5)_4]$ acetonitrile solution in a Luggin capillary with a Vycor tip. This Luggin capillary was inserted in a second Luggin capillary containing a 0.1 mol L^{-1} $[N(Bu)_4][B(C_6F_5)_4]$ dichloromethane solution and a Vycor tip. Experiments un-

der the same conditions showed that all reduction and oxidation potentials were reproducible within ±5 mV. Experimental potentials were referenced against an Ag/Ag^+ reference electrode, but the presented results are referenced against ferrocene as an internal standard as required by IUPAC.[375] To achieve this, each experiment was repeated in the presence of 1 mmol L^{-1} of decamethylferrocene (Fc*). Data were processed on a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH^+ couple to 0.0 V. Under our conditions the Fc^*/Fc^{*+} couple was at –619 mV vs FcH/FcH^+, ΔE_p = 60 mV, while the FcH/FcH^+ couple itself was at 220 mV vs Ag/Ag^+, ΔE_p = 61 mV.[233]

4.1.8 Spectroelectrochemical Investigations

Potential-dependent spectroelectrochemical *in siut* UV-Vis/NIR measurements of 2.0 mmol L^{-1} solutions of the respective compound in dry dichloromethane containing 0.1 mol L^{-1} of $[N(Bu)_4][B(C_6F_5)_4]$ as the supporting electrolyte were performed in an OTTLE (OTTLE = Optically Transparent Thin-Layer Electrochemical)[376] cell with a Varian Cary 5000 spectrophotometer at 25 °C. The values obtained by deconvolution could be reproduced within ϵ_{max} 100 L mol^{-1} cm^{-1}; ν_{max} 50 cm^{-1}; $\Delta\nu_{1/2}$ 50 cm^{-1}. Within the measurements the potentials were increased progressively by 100, 50 or 25 mV. The spectra were recorded after ∼ 10 min after the change of the potential. The reversibility of the oxidation processes was examined by reducing the analyte at –500 mV and comparison of the obtained spectra with the initial one.

4.2 Starting Materials

The starting materials for the described syntheses were either purchased from commercial suppliers, present in the working group, synthesized according to literature procedures, or obtained as side products, however, with their spectroscopic data in agreement with those reported in literature:

Compound	Reference
Ferrocenol- (**5**) and 1,1'-ferrocenediol (**38**)	[147]
Dicyclohexyl chlorophosphate[a] **29a**	[377]
Bis((1*R*)-/(1*S*)-menthyl) chlorophosphate[a] **29b**,**c**	[378]
Bis((1*S*)-isopinocampheyl) chlorophosphate[a] **29f**	[378]
Cyclohexyl dichlorophosphate[a] **42a**	[377]
(1*R*)-Menthyl dichlorophosphate[a] **42b**	[379]
Chloro-*N*,*N*,*N*',*N*'-tetraethylphosphinediamine	[380]
Di(pyrrolidin-1-yl) chlorophosphinate	[381]
Dichloro-*N*,*N*-diethylphosphinediamine	[382]
2-Chloro-3-methyl-1,3,2-oxazaphospholidine	[383]
$[N(Bu)_4][B(C_6F_5)_4]$	[235]
Dichloro-1-naphthylphosphate[a] **46d**	[384]
Dichloro-2-naphthylphosphate[a] **46e**	[385]
P-Chloro-(*R*)-binolphosphate[a]	[386]
Dichloro(1*H*-indol-1-yl)phosphonate[a]	[228]
Triferrocenyl phosphate[a] (**47**)	[219]
Triphenylbenzaldehyde	[387]
Triphenylbenzonitrile	[388]
(S_p)-2-(Thiodiphenylphosphino)ferrocenylmethanol (S_p)-**143**	[389]
Ferrocenylmethanol **118a**	[355]
Benzoylferrocene	[390]
Ferrocenyldiphenylmethanol **118e**	[391]
Formylferrocene	[147]
Pivaloylferrocene **128c**	[293]
(1*R*, 2*R*, 4*S*)-2-Ferrocenylfenchole **130**	[329]
Ferrocenylaldehyde oxime **132a**	[333]

Compounds purchased from commercial suppliers were used without further purification. The spectra of all new compounds, described herein, can be found in the Supporting Information of the underlying publications. a) The respective compounds have been reported previously. However, they were synthesized under optimized conditions, giving higher yields, by replacing NEt_3 by BuLi.

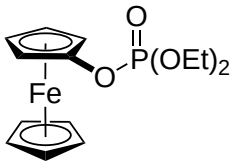
4.3 Synthetic Procedures

4.3.1 Synthesis of Ferrocenyl Phosphates

General Procedure for the Synthesis of Ferrocenyl Phosphates GP1

Ferrocenyl acetate (**4**, 1.00 g, 4.10 mmol) was dissolved in ethanol (30 mL), and 2 *M* oxygen-free aqueous KOH (2.5 mL, 5.00 mmol) was added with a syringe in a single portion. The reaction solution was heated to 70 °C and stirred for 15 min. After addition of 2 *M* oxygen-free aqueous HCl (2.5 mL, 5.00 mmol) in a single portion, all volatiles were removed under reduced pressure. The precipitate was dissolved in diethyl ether (30 mL) and filtered through a layer of Celite (5 cm column size) . Subsequent removal of the solvent under reduced pressure gave **5** as an orange solid in a yield of 805 mg (4.00 mmol, 97 % based on **4**). The synthesis of ferrocenediol (**38**) differs from that procedure by using the double amount of KOH and HCl solution. Afterwards, **5** was dissolved in 30 mL of the respective solvent and cooled to –30 °C. A base (BuLi or NEt_3) was added dropwise with a syringe followed by addition of the respective electrophile in a single portion. The reaction mixture was allowed to warm to ambient temperature where stirring was continued overnight. After removal of all volatiles the residue was collected in diethyl ether or CH_2Cl_2 (30 mL) and washed with water (100 mL). The organic layer was dried over $MgSO_4$ and all volatiles were removed under reduced pressure. Purification of the crude product was performed by column chromatography (column size below) using different solvent mixtures as eluents.

Diethyl Ferrocenyl Phosphate (6)

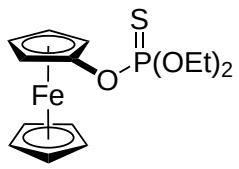


6

Ferrocenol (1.00 g, 4.1 mmol), NEt_3 (0.63 mL, 4.5 mmol) and diethyl chlorophosphate (0.65 mL, 4.5 mmol) were reacted in CH_2Cl_2 according to the general procedure GP1. Purification was performed by column chromatography (alumina, $3.5 \cdot 14.5$ cm column size) using CH_2Cl_2 as the eluent. After removal of all volatiles, compound **6** was obtained as an orange oil.

Yield: 1.032 g (3.05 mmol, 90 % based on **5**). Anal. calcd for $C_{14}H_{19}FeO_4P$ (338.12 g/mol): C, 49.73; H, 5.66. Found: C, 49.86; H, 5.79. IR data (NaCl, $\tilde{\nu}$/cm^{-1}): 3098 w, 2986 m, 2932 w, 2909 w, 2871 w, 1793 w, 1711 w, 1647 w, 1460 s, 1412 w, 1394 m, 1373 m, 1278 s, 1241 m, 1166 m, 1106 m, 1065 w, 1033 s, 959 s, 887 s, 820 s, 757 m, 640 m. ^{1}H NMR ($CDCl_3$, δ): 1.36 (td, $^3J_{H,H}$ = 7.0 Hz, $^2J_{H,P}$ = 0.9 Hz, 6 H, CH_3), 3.88 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.13–4.21 (m, 4 H, CH_2), 4.25 (s, 5 H, C_5H_5), 4.39 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 16.1 (d, $^3J_{C,P}$ = 6.9 Hz, CH_3), 59.6 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 62.7 (s, C_5H_4), 64.3 (d, $^2J_{C,P}$ = 6.2 Hz, 2 C, CH_2), 69.5 (s, C_5H_5), 117.7 (d, $^2J_{C,P}$ = 4.8 Hz, C_{C5H4}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –5.4. HRMS (ESI-TOF, m/z): calcd for $C_{14}H_{19}FeO_4P$ 338.0365, found 338.0367 $[M]^+$.

Diethyl Ferrocenyl Thiophosphate (7)

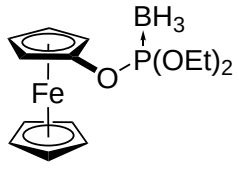


7

Ferrocenol (1.00 g, 4.1 mmol), NEt_3 (0.63 mL, 4.5 mmol) and diethyl chlorophosphate (0.71 mL, 4.5 mmol) were reacted in CH_2Cl_2 according to the general procedure GP1. Purification of the crude product was performed by column chromatography (silica, $3.5 \cdot 14.5$ cm column size) using toluene as the eluent, giving **7** as an orange oil.

Yield: 450 mg (1.27 mmol, 31 % based on **5**). IR data (NaCl, $\tilde{v}/cm^{-1}$): 3095 m, 2982 s, 2931 w, 2904 w, 2867 w, 1629 w, 1452 s, 1390 m, 1371 m, 1352 w, 1236 s, 1162 m, 1105 m, 1025 s, 945 s, 885 s, 818 s. ^{1}H NMR ($CDCl_3$, δ): 1.35 (td, $^3J_{H,H}$ = 7.0 Hz, $^4J_{H,P}$ = 0.4 Hz, 6 H, CH_3), 3.89 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, *m*-C_5H_4), 4.13–4.22 (m, 4 H, CH_2), 4.25 (s, 5 H, C_5H_5), 4.40 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, *o*-C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 15.9 (d, $^3J_{C,P}$ = 7.4 Hz, CH_3), 60.4 (d, $^3J_{C,P}$ = 3.5 Hz, *o*-C_5H_4), 62.8 (s, *m*-C_5H_4), 64.9 (d, $^2J_{C,P}$ = 5.7 Hz, CH_2), 69.5 (s, C_5H_5), 117.5 (d, $^2J_{C,P}$ = 4.7 Hz, C_{C5H4}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 63.8. HRMS (ESI-TOF, m/z): calcd for $C_{14}H_{19}FePSO_3$ 354.0136, found 354.0170 $[M]^+$.

Diethyl Ferrocenyl Phosphite· BH_3 (8)

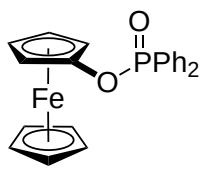


8

Ferrocenol (728 mg, 3.60 mmol), NEt_3 (0.55 mL, 3.96 mmol) and diethyl chlorophosphite (0.57 mL, 4.5 mmol) were reacted in CH_2Cl_2 according to the general procedure GP1. Afterwards, 1 *M* solution of BH_3 in tetrahydrofuran (4.00 mL, 3.95 mmol) was added and the mixture was stirred for 12 hours. Purification was realized by column chromatography (silica, $3 \cdot 16$ cm column size:) using a 1/1 (v/v) hexane/toluene mixture as the eluent. Compound **8** (R_f = 0.39) was obtained as an orange oil.

Yield: 910 mg (2.70 mmol, 76 % based on **5**). ^{1}H NMR (C_6D_6, δ): 1.06 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 3.92–4.03 (m, 4 H, CH_2), 3.72 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, m-C_5H_4), 4.22 (s, 5 H, C_5H_5), 4.46 (pt, $^{3,4}J_{H,H}$ = 2.0, 2 H, o-C_5H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 16.1 (d, $^3J_{C,P}$ = 5.5 Hz, CH_3), 60.8 (d, $^3J_{C,P}$ = 2.8 Hz, o-C_5H_4), 63.1 (s, m-C_5H_4), 63.4 (d, $^2J_{C,P}$ = 3.1 Hz, CH_2), 70.0 (s, 6C_5H_5), 117.7 (d, $^2J_{C,P}$ = 4.3 Hz, C_{C5H4}-O). $^{11}B\{^1H\}$ NMR (C_6D_6, δ): –42.7 (d, $^1J_{B,P}$ = 92 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 128.2 (q, $^1J_{P,B}$ = 92 Hz). HRMS (ESI-TOF, m/z): calcd for $C_{14}H_{22}BFeO_3P-BH_3$ 322.0416, found 322.0403 $[M–BH_3]^+$.

Ferrocenyl Diphenylphosphinate (9)



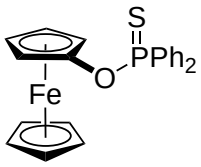
9

Ferrocenol (**5**, 830 mg, 4.1 mmol), NEt_3 (0.63 mL, 4.5 mmol) and chlorodiphenylphosphine (0.83 mL, 4.5 mmol) were reacted according to the general procedure GP1. Oxidation was realized by adding H_2O_2-solution (0.40 mL, ω = 35 %, 4.5 mmol) followed by stirring meanwhile the reaction mixture turned slightly darker. Purification was realized by column chromatography (silica, $4 \cdot 18$ cm column size) using 4/1 (v/v) CH_2Cl_2/ethyl

acetate mixture as the eluent, giving **9** as a yellow solid.

Yield: 1.41 g (3.5 mmol, 85 % based on **5**). ^{1}H NMR ($CDCl_3$, δ): 3.80 (s, 2 H, m-C_5H_4), 4.18 (s, 5 H, C_5H_5), 4.30 (s, 2 H, o-C_5H_4), 7.46 (td, $^{3}J_{H,H}$ = 7.4 Hz, $^{3}J_{H,P}$ = 3.6 Hz, 4 H, m-Ph), 7.54 (t, $^{3}J_{H,H}$ = 6.9 Hz, 2 H, p-Ph), 7.85 (dd, $^{2}J_{H,P}$ = 12.4 Hz, $^{3}J_{H,H}$ = 7.3 Hz, 4 H, o-Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 60.3 (d, $^{3}J_{C,P}$ = 3.7 Hz, o-C_5H_4), 62.7 (s, m-C_5H_4), 69.5 (s, C_5H_5), 117.5 (d, $^{2}J_{C,P}$ = 6.7 Hz, C_{C5H4}-O), 128.5 (d, $^{3}J_{C,P}$ = 13.1 Hz, m-Ph), 130.7 (s, Ph-P (HMBC); 132.8 (C_6D_6) (d, $^{1}J_{C,P}$ = 130.0 Hz, Ph-P)),[392] 131.8 (d, $^{2}J_{C,P}$ = 10.2 Hz, o-Ph), 132.3 (d, $^{4}J_{C,P}$ = 2.7 Hz, p-Ph). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 30.1. HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{19}FeO_2P$ 402.0467, found 402.0465 $[M]^+$.

Ferrocenyl Diphenylthiophosphinate (10)

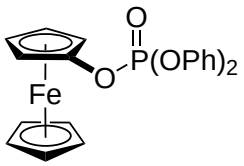


10

Ferrocenol (**5**, 828 mg, 4.1 mmol), NEt_3 (0.63 mL, 4.5 mmol) and chlorodiphenylphosphine (0.83 mL, 4.5 mmol) were reacted according to the general procedure GP1. Afterwards, sulfur (160 mg, 4.9 mmol) was added and stirred for additional ten min. Purification was realized by column chromatography (alumina, 3 · 10 cm column size) using first hexane to elute the excess of sulfur and then changing to CH_2Cl_2 which eluted the product as a yellow solid.

Yield: 1.65 g (3.9 mmol, 95 % based on **5**). Anal. calcd for $C_{22}H_{19}FeOPS$ (418.27 g/mol): C, 63.17; H, 4.58. Found: C, 63.03; H, 4.71. Mp.: 147–149 °C.^{1}H NMR ($CDCl_3$, δ): 3.82 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, m-C_5H_4), 4.20 (s, 5 H, C_5H_5), 4.24 (pt, $^{3,4}J_{H,H}$ = 1.8 Hz, 2 H, o-C_5H_4), 7.44–7.50 (m, 4 H, o-Ph), 7.50–7.56 (m, 2 H, p-Ph), 7.88–7.96 (m, 4 H, m-Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 61.1 (d, $^{3}J_{C,P}$ = 3.9 Hz, o-C_5H_4), 62.8 (s, m-C_5H_4), 69.5 (s, C_5H_5), 117.4 (d, $^{2}J_{C,P}$ = 5.6 Hz, C_{C5H4}-O), 128.4 (d, $J_{C,P}$ = 13.4 Hz, Ph), 131.4 (d, $J_{C,P}$ = 11.2 Hz, Ph), 132.0 (d, $^{4}J_{C,P}$ = 2.8 Hz, p-Ph), 134.2 (d, $^{1}J_{C,P}$ = 110.3 Hz, Ph-P). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 81.5.

Ferrocenyl Diphenyl Phosphate (11)



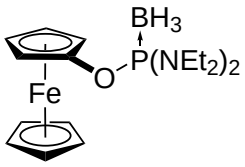
11

Ferrocenol (**5**, 1.080 g, 5.3 mmol), NEt_3 (0.81 mL, 5.8 mmol) and diphenyl chlorophosphate (1.2 mL, 5.9 mmol) were reacted according to the general procedure GP1. Purification was realized using column chromatography (alumina, 4 · 18 cm column size) using CH_2Cl_2 as the eluent, giving **11** as an orange oil.

Yield: 1.45 g (3.3 mmol, 62 % based on **5**). Anal. calcd for $C_{22}H_{19}FeO_4P$ (434.04 g/mol): C, 60.86; H, 4.41. Found: C, 60.86; H, 4.29. Mp.: 67 °C. ^{1}H NMR ($CDCl_3$, δ): 3.91 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, m-C_5H_4), 4.22 (s, 5 H, C_5H_5), 4.44 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, o-C_5H_4), 7.18–7.27 (m, 6 H, o, p-Ph), 7.36 (t, $^{3}J_{H,H}$ = 7.9 Hz, 4 H, m-Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.8 (d, $^{3}J_{C,P}$ = 3.8 Hz, o-C_5H_4), 62.9 (s, m-C_5H_4), 69.6 (s, C_5H_5), 117.9 (d, $^{2}J_{C,P}$ = 5.4 Hz, C_{C5H4}-O), 120.1 (d,$^{3}J_{C,P}$ = 5.3 Hz, $^{3}J_{C,P}$ = 2 Hz, o-Ph),

125.5 (s, p-Ph), 129.8 (s, m-Ph), 150.5 (d, $^2J_{C,P}$ = 7.4 Hz, Ph-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –16.9. HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{19}FeO_4P$ 434.0365, found 434.0362 $[M]^+$.

N,N,N',N'-Tetraethyl-1-(ferrocenyloxy)phosphinediamine·BH_3 (12)

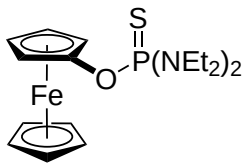


12

Ferrocenol (**5**, 1.037 g, 5.13 mmol), NEt_3 (0.75 mL, 5.41 mmol) and $ClP(NEt_2)_2$ (1.09 mL, 5.17 mmol) were reacted according to the general procedure GP1. After stirring for 12 h, a 1 *M* solution of BH_3 in tetrahydrofuran (5.2 mL, 5.2 mmol) was added in a single portion and stirring was continued for additional 2 h. Purification was realized by column chromatography (alumina, 3.5 · 13 cm column size) using a 8:2 hexane/diethyl ether mixture (v/v) as the eluent, giving **12** as an orange oil.

Yield: 1.02 g (2.61 mmol, 51 % based on **5**). Anal. calcd for $C_{18}H_{32}BFeN_2OP$ (390.09 g/mol): C, 55.42; H, 8.27; N, 7.18. Found: C, 55.55; H, 8.08; N, 6.92. IR data (NaCl, $\tilde{\nu}/cm^{-1}$): 3067, w, 3020 w, 2942 s, 2905 s, 2852 s, 2353 s (BH_3), 1446 s, 1399 w, 1366 s, 1285 m. ^1H NMR (C_6D_6, δ): 0.93 (t, $^3J_{H,H}$ = 7.1 Hz, 12 H, CH_3), 1.01–1.72 (br m, 3 H, BH_3), 2.86–3.03 (m, 8 H, CH_2), 3.67 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.19 (s, 5 H, C_5H_5), 4.42 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 14.3 (d, $^3J_{C,P}$ = 1.7 Hz, CH_3), 39.2 (d, $^2J_{C,P}$ = 6.3 Hz, CH_2), 61.4 (d, $J_{C,P}$ = 2.7 Hz, C_5H_4), 63.0 (C_5H_4), 69.7 (C_5H_4), 118.1 (d, $^2J_{C,P}$ = 1.4 Hz, C_{C5H4}-O). $^{11}B\{^1H\}$ NMR (C_6D_6, δ): –39.5 (d, $^1J_{B,P}$ = 95 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 130.7–132.1 (br m). HRMS (ESI-TOF, m/z): calcd for $C_{18}H_{32}BFeN_2OP$ 390.1693, found 390.1702 $[M]^+$.

N,N,N',N'-Tetraethyl-1-(ferrocenyloxy)phosphinediamine sulfide (13)

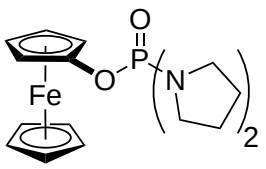


13

Ferrocenol (**5**, 1.102 g, 5.46 mmol), NEt_3 (0.77 mL, 5.55 mmol) and $ClP(NEt_2)_2$ (1.26 g, 5.98 mmol) were reacted according to the general procedure described above. After stirring for 12 h, sulfur (210 mg, 6.55 mmol) was added in a single portion and stirring was continued for additional 2 h. Purification was realized by column chromatography (alumina, 2.5 · 32 cm column size) using first hexane, to remove the excess of sulfur, followed by a 7:3 hexane/dichloromethane mixture (v/v) as the eluent, giving **13** as an orange oil.

Yield: 1.900 g (4.65 mmol, 85 % based on **5**). Anal. calcd for $C_{18}H_{29}FeN_2OPS$ (408.32 g/mol): C, 52.95; H, 7.16; N, 6.86. Found: C, 53.17; H, 7.55; N, 6.30. ^1H NMR (C_6D_6, δ): 0.99 (t, $^3J_{H,H}$ = 7.1 Hz, 12 H, CH_3), 3.00–3.09 (m, 8 H, CH_2), 3.70 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.22 (s, 5 H, C_5H_5), 4.50 (ptd, $^{3,4}J_{H,H}$ = 2.1 Hz, $J_{H,H}$ = 0.6 Hz, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 14.2 (d, $^4J_{C,P}$ = 3.2 Hz, CH_3), 40.6 (d, $^3J_{C,P}$ = 5.0 Hz, CH_2), 61.4 (d, $J_{C,P}$ = 3.6 Hz, C_5H_4), 62.9 (C_5H_4), 69.8 (C_5H_5), 117.6 (d, $^2J_{C,P}$ = 1.9 Hz, C_{C5H4}-O). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 90.9. HRMS (ESI-TOF, m/z): calcd for $C_{18}H_{29}FeN_2OPS$ 408.1082, found 408.1109 $[M]^+$.

Ferrocenyl Di(pyrrolidin-1-yl)phosphinate (14)

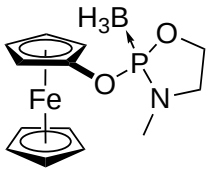


14

Ferrocenol (1, 370 mg, 1.83 mmol), BuLi (0.73 mL, 1.83 mmol) and di(pyrrolidin-1-yl) chlorophosphinate (408 mg, 1.83 mmol) were reacted at –80 °C according to the general procedure described above. Purification was realized by column chromatography (alumina, $4 \cdot 8$ cm column size) using a 1:1 dichloromethane/ethyl acetate mixture (v/v) as the eluent, giving **14** as an orange solid.

Yield: 512 mg (1.32 mmol, 72 % based on 1). Anal. calcd for $C_{18}H_{25}FeN_2O_2P$ (388.22 g/mol): C, 55.69; H, 6.49; N, 7.27. Found: C, 55.67; H, 6.54; N, 7.09. Mp.: 76–78 °C. ^{1}H NMR (C_6D_6, δ): 1.40–1.43 (m, 8 H, H3, H4-C_4N), 3.11–3.15 (m, 8 H, H2, H5-C_4N), 3.71 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.27 (s, 5 H, C_5H_5), 4.60 (ptd, $^{3,4}J_{H,H}$ = 1.9 Hz, $J_{H,P}$ = 0.6 Hz, 2 H, C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6, δ): 26.5 (d, $^3J_{C,P}$ = 8.9 Hz, C3, C4-C_4N), 46.8 (d, $^2J_{C,P}$ = 4.6 Hz, C2, C5-C_4N), 60.3 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 62.8 (C_5H_4), 69.9 (C_5H_5), 118.5 (d, $^2J_{C,P}$ = 4.3 Hz, C_{C5H4}-O). ^{31}P{^{1}H} NMR (C_6D_6, δ): 22.8. HRMS (ESI-TOF, m/z): calcd for $C_{18}H_{25}FeN_2O_2P$ + Na 411.0895, found 411.0895 $[M+Na]^+$.

2-Ferrocenyloxy-3-methyl-1,3,2-oxaphospholidine·BH_3 (15)

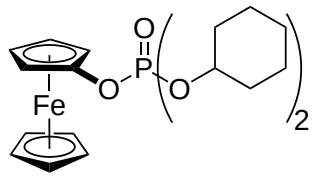


15

Ferrocenol (5, 508 mg, 2.51 mmol), NEt_3 (0.39 mL, 2.81 mmol) and 2-chloro-3-methyl-1,3,2-oxazaphospholidine (350 mg, 2.51 mmol) were reacted according to the general procedure described above. After stirring for 12 h, a 1 M solution of BH_3 in tetrahydrofuran (2.8 mL, 2.8 mmol) was added in a single portion and stirring was continued for additional 2 h. Purification was realized by column chromatography (alumina, $3.5 \cdot 13$ cm column size) using a 1:3 hexane/dichloromethane mixture (v/v) as the eluent, giving **15** as an orange oil. Crystals, suitable for single crystal X-ray diffraction analysis, were obtained by evaporation of a hexane solution at ambient temperature containing **15**.

Yield: 270 mg (0.847 mmol, 34 % based on **5**). Anal. calcd for $C_{13}H_{19}BFeNO_2P$ (318.92 g/mol): C, 48.96; H, 6.00; N, 4.39. Found: C, 49.28; H, 6.08; N, 4.35. Mp.: 153 °C. ^{1}H NMR ($CDCl_3$, δ): 0.31–0.86 (br m, 3 H, BH_3), 2.79 (d, $^3J_{H,H}$ = 10.1 Hz, 3 H, CH_3), 2.97 (ddd, $^3J_{H,P}$ = 13.1 Hz, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 4.8 Hz, 1 H, CH_2-N), 3.08 (dtd, $^3J_{H,P}$ = 11.9 Hz, $^3J_{H,H}$ = 8.0 Hz, $^3J_{H,H}$ = 5.9 Hz, 1 H, CH_2-N), 3.89 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.14–4.25 (m, 8 H, C_5H_5, C_5H_4, CH_2-O), 4.29–4.30 (m, 1 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 31.2 (d, $^2J_{C,P}$ = 9.9 Hz, CH_3), 49.2 (d, $^2J_{C,P}$ = 2.2 Hz, CH_2-N), 60.6 (d, $J_{C,P}$ = 1.4 Hz, C_5H_4), 61.2 (d, $J_{C,P}$ = 1.8 Hz, C_5H_4), 63.2 (d, $J_{C,P}$ = 19.1 Hz, C_5H_4), 67.9 (d, $^2J_{C,P}$ = 10.5 Hz, CH_2-O), 69.6 (C_5H_5), 116.5 (d, $^2J_{C,P}$ = 11.2 Hz, C_{C5H4}-O). ^{11}B{^{1}H} NMR ($CDCl_3$, δ): –42.6 (d, $^1J_{B,P}$ = 92 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 122.0 (br m). HRMS (ESI-TOF, m/z): calcd for $C_{13}H_{19}BFeNO_2P^+Na$ 342.0491, found 342.0499 $[M+Na]^+$; calcd for $C_{13}H_{19}BFeNO_2P-BH_3$ 305.0263305.0265 $[M-BH_3]^+$.

Dicyclohexyl Ferrocenyl Phosphate (30a)

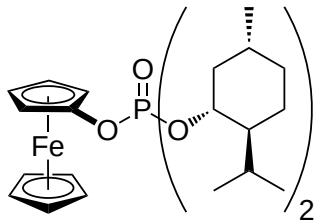


30a

Ferrocenol (**5**, 1.00 g, 4.95 mmol), BuLi (2.2 mL, 5.5 mmol) and dicyclohexyl chlorophosphate (**29a**, 1.54 g, 5.5 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, $4 \cdot 7$ cm column size) using a 97/3 (v/v) dichloromethane/ethyl acetate mixture, giving **30a** as an orange solid.

Yield: 1.49 g (3.46 mmol, 70 % based on **5**). ^{1}H NMR ($CDCl_3$, δ): 1.23–1.38 (m, 6 H, CH_2), 1.48–1.59 (m, 6 H, CH_2), 1.70–1.80 (m, 4 H, CH_2), 1.90–2.00 (m, 4 H, CH_2), 3.84–3.89 (m, 2 H, C_5H_4), 4.25 (s, 5 H, C_5H_5), 4.38–4.44 (m, 4 H, C_5H_4, H1). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 23.5 (CH_2), 25.1 (CH_2), 33.19 (CH_2), 33.23 (CH_2), 33.25 (CH_2), 33.29 (CH_2), 59.8 (d, $^3J_{C,P}$ = 3.8 Hz, C_5H_4), 62.6 (C_5H_4), 69.4 (C_5H_5), 77.8 (d, $^2J_{C,P}$ = 6.4 Hz, C1), 117.7 (d, $^2J_{C,P}$ = 5.0 Hz, C-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –6.8. HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{31}FeO_4P$ 446.1304, found 446.1302 $[M]^+$.

Ferrocenyl Di-(1*R*)-menthyl Phosphate (30b)

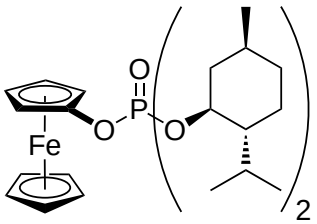


30b

Ferrocenol (**5**, 1.03 g, 5.09 mmol), BuLi (2.1 mL, 5.25 mmol) and di-(1*R*)-menthyl chlorophosphate (**29b**, 2.00 g, 5.09 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, $4 \cdot 10$ cm column size) using dichloromethane as the eluent (R_f = 0.37), giving **30b** as an orange solid.

Yield: 3.00 g (4.64 mmol, 91 % based on **5**). Anal. calcd for $C_{30}H_{47}FeO_4P$ (558.51 g/mol): C, 64.51; H, 8.48; found: C, 64.67; H, 8.69. Mp.: 79–80 °C. ^{1}H NMR ($CDCl_3$, δ): 0.77 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.82 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.83–0.87 (m, 2 H), 0.89 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.91 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.918 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3), 0.928 (d, $^3J_{H,H}$ = 6.5 Hz, 3 H, CH_3), 0.95–1.05 (m, 2 H), 1.11–1.18 (m, 2 H), 1.29–1.39 (m, 2 H), 1.40–1.50 (m, 2 H), 1.62–1.70 (m, 4 H), 2.11 (dsept, (s, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,H}$ = 2.5 Hz, 1 H, CH(CH_3)$_2$), 2.17 (dsept, (s, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,H}$ = 2.5 Hz, 1 H, CH(CH_3)$_2$), 2.21–2.30 (m, 2 H), 3.86 (s, 2 H, C_5H_4), 4.14–4.28 (m, 7 H, C_5H_5, H1), 4.39 (s, 1 H, C_5H_4), 4.44 (s, 1 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 15.8 (CH_3), 20.93 (CH_3), 20.94 (CH_3), 21.93 (CH_3), 21.99 (CH_3), 22.76 (CH_3), 22.85 (CH_3), 25.35 (CH), 25.42 (CH), 31.5 (d, $^4J_{C,P}$ = 2.78 Hz, C5), 34.0 (CH_2), 42.5 (CH_2), 42.7 (CH_2), 48.44 (C2) , 48.46 (C2), 48.50 (C2), 48.52 (C2), 60.0 (d, $^3J_{C,P}$ = 3.5 Hz, C_5H_4), 60.1 (d, $^3J_{C,P}$ = 3.2 Hz, C_5H_4), 62.62 (C_5H_4), 62.64 (C_5H_4), 69.5 (C_5H_5), 79.8 (d, $^2J_{C,P}$ = 6.9 Hz, C1), 118.625 (d, $^2J_{C,P}$ = 4.3 Hz, C-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –6.3. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{45}FeO_4P$ 568.2400, found 568.2453 $[M]^+$.

Ferrocenyl Di-(1*S*)-menthyl phosphate (30c)

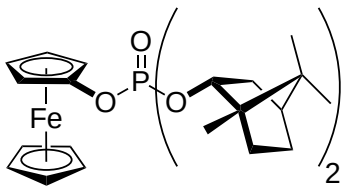


30c

Ferrocenol (**5**, 608 mg, 3.01 mmol), BuLi (1.3 mL, 3.25 mmol) and di-(1*S*)-menthyl chlorophosphate (**29c**, 1.18 g, 3.01 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, $4 \cdot 10$ cm column size) on silica using dichloromethane ($R_f = 0.37$), giving **30e** as an orange oil.

Yield: 1.40 g (2.51 mmol, 83 % based on **5**). ^{1}H NMR ($CDCl_3$, δ): 0.77 (d, $^3J_{H,H} = 7.0$ Hz, 3 H, CH_3), 0.82 (d, $^3J_{H,H} = 7.0$ Hz, 3 H, CH_3), 0.83–0.87 (m, 2 H), 0.89 (d, $^3J_{H,H} = 7.0$ Hz, 3 H, CH_3), 0.91 (d, $^3J_{H,H} = 7.0$ Hz, 3 H, CH_3), 0.918 (d, $^3J_{H,H} = 6.5$ Hz, 3 H, CH_3), 0.928 (d, $^3J_{H,H} = 6.5$ Hz, 3 H, CH_3), 0.95–1.05 (m, 2 H), 1.11–1.18 (m, 2 H), 1.23–1.39 (m, 2 H), 1.40–1.50 (m, 2 H), 1.62–1.70 (m, 4 H), 2.11 (dsept, $^3J_{H,H} = 7.0$ Hz, $^3J_{H,H} = 2.5$ Hz, 1 H, C*H*(CH_3)$_2$), 2.17 (dsept, $^3J_{H,H} = 7.0$ Hz, $^3J_{H,H} = 2.5$ Hz, 1 H, C*H*(CH_3)$_2$), 2.21–2.30 (m, 2 H), 3.85 (pt, $^{3,4}J_{H,H} = 2.0$ Hz, 2 H, C_5H_4), 4.16–4.25 (m, 7 H, C_5H_5, H1), 4.37 (dd, $J_{H,H} = 3.4$ Hz, $J_{H,H} = 1.5$ Hz, 1 H, C_5H_4), 4.44 (dd, $J_{H,H} = 3.4$ Hz, $J_{H,H} = 1.5$ Hz, 1 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 15.8 (CH(*C*H_3)$_2$), 20.93 (CH(*C*H_3)$_2$), 20.95 (CH(*C*H_3)$_2$), 21.93 (CH(*C*H_3)), 21.99 (CH(*C*H_3)), 22.76 (CH_2) , 22.85 (CH_2), 25.35 (CH(*C*H_3)$_2$) , 25.43 (CH(*C*H_3)$_2$), 31.5 (d, $^4J_{C,P} = 2.8$ Hz, C5), 34.0 (CH_2), 42.5 (CH_2), 42.7 (CH_2), 48.45 (C2) , 48.47 (C2), 48.51 (C2), 48.53 (C2), 60.0 (d, $^3J_{C,P} = 3.9$ Hz, C_5H_4), 60.1 (d, $^3J_{C,P} = 3.3$ Hz, C_5H_4), 62.52 (C_5H_4), 62.55 (C_5H_4), 69.4 (C_5H_5), 79.78 (d, $^{23}J_{C,P} = 6.8$ Hz, C1) , 79.79 (d, $^2J_{C,P} = 6.8$ Hz, C1), 117.8 (d, $^2J_{C,P} = 4.3$ Hz, C_{C5H4}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –6.3.

Di-(1*S*)-borneyl Ferrocenyl Phosphate (30d)



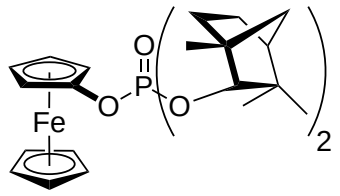
30d

Ferrocenol (**5**, 1.00 g, 4.95 mmol), BuLi (2.0 mL, 5.00 mmol) and di-(1*S*)-borneyl chlorophosphate (**29d**) (1.92 g, 4.95 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, $4 \cdot 15$ cm column size) using a 95/5 (*v*/*v*) toluene/diethyl ether mixture ($R_f = 0.33$), giving **30d** as an orange solid.

Yield: 1.26 g (2.27 mmol, 46 % based on **5**). Anal. calcd for $C_{30}H_{43}FeO_4P$ (554.48 g/mol): C, 64.98; H, 7.82; found: C, 64.88; H, 7.83. Mp.: 210–212 °C. ^{1}H NMR ($CDCl_3$, δ): 0.86–0.90 (m, 18 H, CH_3), 1.22–1.30 (m, 6 H), 1.66–1.69 (m, 2 H), 1.70–1.77 (m, 2 H), 1.91–1.97 (m, 2 H), 2.25–2.34 (m, 2 H), 3.86 (pt, $^{3,4}J_{H,H} = 1.9$ Hz, 2 H, C_5H_4), 4.24 (s, 5 H, C_5H_5), 4.39 (pt, $^3J_{H,H} = 1.9$ Hz, 2 H, C_5H_4), 4.58–4.62 (m, 2 H, H2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 13.28 (CH_3), 13.34 (CH_3), 18.8 (CH_3), 19.9 (CH_3), 26.4 (CH_2), 26.5 (CH_2), 27.9 (CH_2), 28.0 (CH_2), 36.8 (d, $^3J_{C,P} = 1.7$ Hz, C3), 37.1 (d, $^3J_{C,P} = 1.8$ Hz, C3), 44.8, 47.65 (C7), 47.66 (C7), 49.66 (d, $^3J_{C,P} = 1.3$ Hz, C1), 49.71 (d, $^3J_{C,P} = 1.3$ Hz, C1), 60.06 (d, $^3J_{C,P} = 0.6$ Hz, C_5H_4), 60.08 (d, $^3J_{C,P} = 1.0$ Hz, C_5H_4), 62.6 (C_5H_4), 69.4 (C_5H_5), 84.66 (d, $^2J_{C,P} = 2.2$ Hz, C2), 84.71 (d,

$^{2}J_{C,P}$ = 2.3 Hz, C2), 117.7 (d, $^{2}J_{C,P}$ = 4.6 Hz, C_{C5H4}-O). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): –4.8. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{43}FeO_4P$ 554.2243, found 554.2242 $[M]^+$.

Di-(1*R*)-α-fenchyl Ferrocenyl Phosphate (30e)

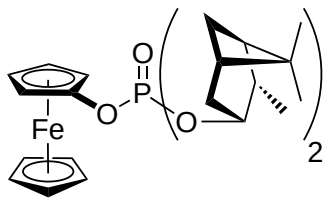


30e

Ferrocenol (**5**, 814 mg, 4.03 mmol), BuLi (1.65 mL, 4.13 mmol) and di-(1*R*)-α-fenchyl chlorophosphate (**29e**, 1.57 g, 4.04 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 · 7 cm column size) using dichloromethane as the eluent (R_f = 0.38), giving **30e** as an orange oil.

Yield: 1.85 g (3.33 mmol, 83 % based on **5**). Anal. calcd for $C_{30}H_{43}FeO_4P$ (554.48 g/mol): C, 64.98; H, 7.82; found: C, 64.67; H, 7.86. Mp.: 64–68 °C. ^{1}H NMR ($CDCl_3$, δ): 0.91 (s, 3 H, CH_3), 0.96 (s, 3 H, CH_3), 1.03–1.09 (m, 11 H), 1.14–1.20 (m, 5 H), 1.40–1.47 (m, 2 H), 1.49–1.53 (m, 2 H), 1.68–1.75 (m, 6 H), 3.85 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 3.97–4.01 (m, 2 H, C_5H_4), 4.24 (s, 5 H, C_5H_5), 4.41–4.45 (m, 2 H, H2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 19.36 (CH_3), 19.36 (CH_3), 20.8 (CH_3), 21.1 (CH_3), 25.67 (C5/C6), 25.74 (C5/C6), 25.95 (C5/C6), 25.98 (C5/C6), 29.9 (CH_3), 39.5 (d, $^{3}J_{C,P}$ = 2.5 Hz, C3), 39.7 (d, $^{3}J_{C,P}$ = 2.5 Hz, C3), 40.94 (CH_2), 40.97 (CH_2), 47.93 (C4), 47.95 (C4), 49.29 (C1), 49.33 (C1), 60.1–60.2 (m, C_5H_4), 62.6 (C_5H_4), 69.4 (C_5H_5), 91.0–91.2 (m, C2), 118.3 (HMBC, C_{C5H4}-O). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): –4.3. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{43}FeO_4P$ 554.2243, found 554.2265 $[M]^+$.

Ferrocenyl Di-(1*S*)-isopinocampheyl Phosphate (30f)



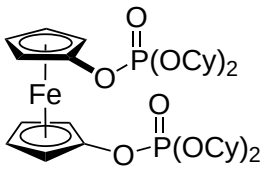
30f

Ferrocenol (**5**, 830 mg, 4.11 mmol), BuLi (1.65 mL, 4.13 mmol) and di-(1*S*)-isopinocampheyl chlorophosphate (**29f**) (1.60 g, 4.11 mmol) were reacted as described in the general procedure. Purification was realized by column chromatography (silica, 4 · 7 cm column size) using a 8/2 (v/v) hexane/diethyl ether mixture as the eluent (R_f = 0.32), giving **30f** as an orange oil.

Yield: 1.90 g (3.43 mmol, 83 % based on **5**). ^{1}H NMR ($CDCl_3$, δ): 0.92 (s, 3 H, H9/H10), 0.93 (s, 3 H, H9/H10), 1.107 (d, $^{3}J_{H,H}$ = 9.9 Hz, 1 H, H7), 1.112 (d, $^{3}J_{H,H}$ = 9.9 Hz, 1 H, H7), 1.16 (d, $^{3}J_{H,H}$ = 7.4 Hz, 3 H, H8), 1.19 (d, $^{3}J_{H,H}$ = 7.4 Hz, 3 H, H8), 1.22 (s, 6 H, H9/H10), 1.80–1.84 (m, 2 H, H1), 1.93–1.98 (m, 2 H, H5), 1.99–2.04 (m, 2 H, H4), 2.19–2.28 (m, 2 H, H2), 2.36–2.40 (m, 2 H, H7), 2.53–2.62 (m, 2 H, H4), 3.86 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.25 (s, 5 H, C_5H_5), 4.42 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.73–4.79 (m, 2 H, H3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 20.24 (C8), 20.26 (C8), 23.89 (C9/C10), 23.91 (C9/C10), 27.40 (C9/C10), 27.41 (C9/C10), 33.76 (C7), 33.79 (C7), 36.7 (d, $^{3}J_{C,P}$ = 3.0 Hz, C4), 36.8 (d, $^{3}J_{C,P}$ = 3.3 Hz, C4), 38.20 (C6), 38.22 (C6), 41.46 (C5), 45.19 (C2), 45.24 (C2), 45.27 (C2), 45.32 (C2), 47.7 (C1), 59.89 (C_5H_4), 59.91 (C_5H_4), 62.6 (C_5H_4), 69.5 (C_5H_5), 79.32 (C3), 79.34 (C3), 79.38 (C3), 79.40 (C3), 117.8–117.9 (m, C_{C5H4}-O). $^{31}P\{^{1}H\}$

NMR ($CDCl_3$, δ): –6.0. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{43}FeO_4P$ 554.2243, found 554.2246 $[M]^+$.

1,1'-Ferrocenediyl Tetracyclohexyl Bis(phosphate) (39a)

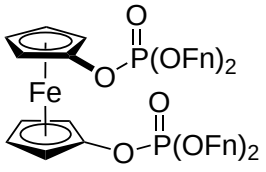


39a

Ferrocenediol (**38**, 515 mg, 2.36), BuLi (1.9 mL, 4.75 mmol) and dicyclohexyl chlorophosphate (**29a**, 1.40 g, 5.0 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, $4 \cdot 10$ cm column size) using a 80/20 (v/v) dichloromethane/ethyl acetate mixture as the eluent, giving **39a** as an orange oil.

Yield: 980 mg (1.39 mmol, 59 % based on **38**). ^{1}H NMR ($CDCl_3$, δ): 1.23–1.38 (m, 12 H, CH_2), 1.47–1.57 (m, 12 H, CH_2), 1.70–1.77 (m, 8 H, CH_2), 1.89–1.98 (m, 8 H, CH_2), 3.96 (pt, $^{3,4}J_{H,H} = 1.9$ Hz, 4 H, C_5H_4), 4.37–4.43 (m, 4 H, H1), 4.44 (pt, $^{3,4}J_{H,H} = 1.9$ Hz, 4 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.5 (CH_2), 25.1 (CH_2), 33.21 (CH_2), 33.25 (CH_2), 33.27 (CH_2), 33.30 (CH_2), 61.2 (d, $^3J_{C,P} = 3.7$ Hz, C_5H_4), 64.6 (C_5H_4), 77.9 (d, $^2J_{C,P} = 6.4$ Hz, C1), 118.1 (d, $^2J_{C,P} = 4.8$ Hz, C_{C5H4}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –6.9. HRMS (ESI-TOF, m/z): calcd for $C_{34}H_{52}FeO_8P_2$ + Na 729.2380, found 729.2333 $[M+Na]^+$.

1,1'-Ferrocenediyl Tetra-(1R)-α-fenchyl Bis(phosphate) (39b)



39b

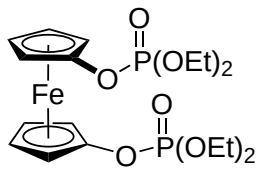
Ferrocenediol (**38**, 254 mg, 1.16 mmol), BuLi (0.95 mL, 2.38 mmol) and dicyclohexyl chlorophosphate (**29a**, 1.00 g, 2.58 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, $4 \cdot 10$ cm column size) using a 95/5 (v/v) dichloromethane/ethyl acetate mixture as the eluent, giving **39b** as an orange oil.

Yield: 400 mg (0.43 mmol, 37 % based on **38**). ^{1}H NMR ($CDCl_3$, δ): 0.90–1.19 (m, 44 H), 1.40–1.46 (m, 4 H, CH_2), 1.49–1.51 (m, 4 H, CH_2), 1.70–1.71 (m, 12 H, CH_2, CH), 3.95–4.00 (m, 8 H, C_5H_4, H2), 4.47–4.50 (m, 4 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.37 (CH_3), 19.39 (CH_3), 20.8 (CH_3), 21.0 (CH_3), 25.67 (C5/C6), 25.72 (C5/C6), 25.94 (C5/C6), 25.97 (C5/C6), 29.91 (CH_3), 29.93 (CH_3), 39.5–39.6 (m, C3), 40.93 (C7), 40.96 (C7), 47.92 (C4), 47.94 (C4), 49.28 (C1), 49.32 (C1), 61.3 (d, $^2J_{C,P} = 3.4$ Hz, C_5H_4), 61.4 (d, $^2J_{C,P} = 3.8$ Hz, C_5H_4), 64.59 (C_5H_4), 64.65 (C_5H_4), 91.1–91.2 (m, C2), 118.3 (d, $^2J_{C,P} = 4.4$ Hz, C_{C5H4}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –4.3. HRMS (ESI-TOF, m/z): calcd for $C_{50}H_{76}FeO_8P_2$ + H 923.4439, found 923.4426 $[M+H]^+$.

1,1'-Ferrocenediyl Tetraethyl Bis(phosphate) (39c)

1,1'-Diacetoxyferrocene (655 mg, 2.2 mmol), KOH (2.5 mL, 4.8 mmol), HCl (2.5 mL, 4.8 mmol), NEt_3 (0.60 mL, 4.8 mmol) and diethyl chlorophosphate (0.73 mL, 4.8 mmol) were reacted in dichloromethane according to the general procedure GP1. Purification was real-

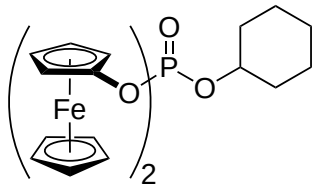
ized by column chromatography (silica, $3 \cdot 10$ cm column size) using a 3/1 (v/v) CH_2Cl_2/ethyl acetate mixture as the eluent, giving **39c** as an orange oil.



39c

Yield: 635 mg (1.30 mmol, 60 % based on diacetoxyferrocene). ^{1}H NMR ($CDCl_3$, δ): 1.36 (td, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,P}$ = 1.0 Hz , 12 H, CH_3), 3.99 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 4 H, C_5H_4), 4.14–4.21 (m, 8 H, CH_2), 4.46 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 4 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 16.1 (d, $^3J_{C,P}$ = 6.7 Hz, CH_3), 61.1 (d, $^3J_{C,P}$ = 3.8 Hz, C_5H_4), 64.4 (d, $^2J_{C,P}$ = 5.6 Hz, CH_2), 64.6 (s, C_5H_4), 118.0 (d, $^2J_{C,P}$ = 4.6 Hz, C_{C5H4}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –5.4. HRMS (ESI-TOF, m/z): calcd for $C_{18}H_{28}FeO_8P_2$ 490.0604, found 490.0633 $[M]^+$.

Cyclohexyl Diferrocenyl Phosphate (43a)

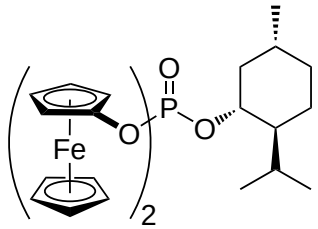


43a

Ferrocenol (**5**, 900 mg, 4.45 mmol), BuLi (1.8 mL, 4.5 mmol) and cyclohexyl dichlorophosphate (**42a**, 485 mg, 2.23 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, $4 \cdot 15$ cm column size) using a 95/5 (v/v) dichloromethane/ethyl acetate mixture as the eluent, giving **43a** as an orange solid.

Yield: 771 mg (1.41 mmol, 63 % based on **5**). Anal. calcd for $C_{26}H_{29}Fe_2O_4P$ (548.17 g/mol): C, 56.97; H, 5.33; found: C, 57.34; H, 5.43. Mp.: 90–93 °C. ^{1}H NMR ($CDCl_3$, δ): 1.31–1.40 (m, 2 H, CH_2), 1.49–1.63 (m, 4 H, CH_2), 1.71–1.81 (m, 2 H, CH_2), 1.92–2.01 (m, 2 H, CH_2), 3.87–3.92 (m, 4 H, C_5H_4), 4.26 (s, 10 H, C_5H_5), 4.37–4.43 (m, 4 H, C_5H_4), 4.46–4.53 (m, 1 H, H1). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 23.5 (CH_2), 25.0 (CH_2), 33.2 (d, $^3J_{C,P}$ = 2.9 Hz, C2/C6), 59.73–59.76 (m, C_5H_4), 62.73–62.74 (m, C_5H_4), 69.6 (C_5H_5), 79.0 (d, $^2J_{C,P}$ = 6.6 Hz, C1), 117.7 (d, $^2J_{C,P}$ = 5.3 Hz, C_{C5H4}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –10.9. HRMS (ESI-TOF, m/z): calcd for $C_{26}H_{29}Fe_2O_4P$ 548.0497, found 548.0490 $[M]^+$.

Diferrocenyl (1*R*)-Menthyl Phosphate (43b)



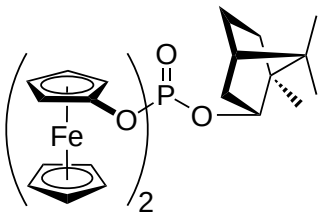
43b

Ferrocenol (**5**, 1.10 g, 5.44 mmol), BuLi (2.2 mL, 5.5 mmol), and (1*R*)-menthyl dichlorophosphate (**42b**,745 mg, 2.73 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, $4 \cdot 15$ cm column size) using a 5/95 (v/v) hexane/dichloromethane mixture as the eluent, giving **43b** as an orange solid.

Yield: 1.222 g (2.02 mmol, 74 % based on **5**). Anal. calcd for $C_{30}H_{37}Fe_2O_4P$ (604.28 g/mol): C, 59.63; H, 6.17; found: C, 59.88; H, 6.31. Mp.: 90–92 °C. ^{1}H NMR ($CDCl_3$, δ): 0.80 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 0.88–0.94 (m, 11 H), 0.98–1.06 (m, 1 H), 1.19, (q, $^3J_{H,H}$ = 11.9 Hz, 2 H), 1.35–1.50 (m, 2 H), 1.63–1.70 (m, 2 H), 2.07–2.15 (m, 1 H), 2.21–2.28 (m, 1 H), 3.86–3.92 (m, 4 H, C_5H_4), 4.20–4.35 (m, 11 H, C_5H_5, H1), 4.37–4.44 (m, 4 H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 15.7 (CH_3), 20.9 (CH_3), 21.9 (CH_3), 22.8 (d, $^3J_{C,P}$

= 27.0 Hz, CH_2), 25.4 (CH), 31.6 (CH), 33.9 (CH_2), 42.5 (CH_2), 48.4 (d, $^3J_{C,P}$ = 7.3 Hz, CH), 59.8–59.9 (m, C_5H_4), 62.71 (C_5H_4), 62.74 (C_5H_4), 69.53 (C_5H_5), 69.56 (C_5H_5), 81.0 (d, $^2J_{C,P}$ = 7.4 Hz, C1), 117.7 (d, $^2J_{C,P}$ = 5.9 Hz, C_{C5H4}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –10.7. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{37}Fe_2O_4P$ 604.1124, found 604.1167 $[M]^+$.

(1*S*)-Borneyl Diferrocenyl Phosphate (43c)

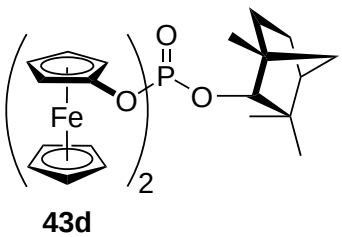


43c

The title compound was obtained as a by-product during the synthesis of **30d** by reacting ferrocenol (**5**, 1.00 g, 4.95 mmol), BuLi (2.0 mL, 5.00 mmol) and **29d** (1.92 mg, 4.95 mmol) according to the general procedure GP1. Purification was realized by column chromatography (silica, 4 · 15 cm column size) using a 95/5 (v/v) toluene/diethyl ether mixture (R_f = 0.43) as the eluent, giving **43c** as an orange solid.

Yield: 260 mg (0.43 mmol, 17 % based on **5**). Anal. calcd for $C_{30}H_{47}FeO_4P$ (602.26 g/mol): C, 59.83; H, 5.86; found: C, 60.44; H, 6.00. ^1H NMR ($CDCl_3$, δ): 0.86 (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3), 1.22–1.31 (m, 3 H, CH_2), 1.67 (t, $J_{H,H}$ = 4.5 Hz, H4), 1.70–1.78 (m, 1 H, CH_2), 1.89–1.95 (m, 1 H, H6), 2.26–2.33 (m, 1 H, H3), 3.89–3.90 (m, 4 H, C_5H_4), 4.261 (s, 5 H, C_5H_5), 4.264 (s, 5 H, C_5H_5), 4.40–4.43 (m, 4 H, C_5H_4), 4.64–4.68 (m, 1 H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 13.2 (CH_3), 18.8 (CH_3), 19.9 (CH_3), 26.4 (C5/C6), 27.9 (C5/C6), 36.7 (C3), 44.7 (C4), 47.8 (C7), 49.8 (d, $^3J_{C,P}$ = 6.2 Hz, C1), 59.79 (C_5H_4), 59.83 (C_5H_4), 59.86 (C_5H_4), 59.89 (C_5H_4), 62.76 (C_5H_4), 62.79 (C_5H_4), 69.6 (C_5H_5), 85.9 (d, $^2J_{C,P}$ = 6.8 Hz, C2), 117.64 (C_{C5H4}-O), 117.66 (C_{C5H4}-O), 117.68 (C_{C5H4}-O), 117.71 (C_{C5H4}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –9.8. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{35}Fe_2O_4P$ 602.0967, found 602.0963 $[M]^+$.

(1*R*)-α-Fenchyl Diferrocenyl Phosphate (43d)



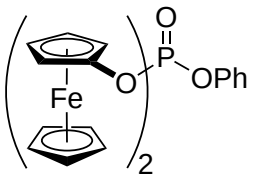
43d

Ferrocenol (**5**, 1.00 g, 4.95 mmol), BuLi (2.0 mL, 5.0 mmol), and **42d** (680 mg, 2.50 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, 4 · 15 cm column size) using a 95/5 (v/v) dichloromethane/ethyl acetate mixture as the eluent, giving **43d** as an orange solid.

Yield: 935 mg (1.55 mmol, 63 % based on **5**). Anal. calcd for $C_{30}H_{35}Fe_2O_4P$ (602.26 g/mol): C, 59.83; H, 5.86; found: C, 59.90; H, 6.00. Mp.: 129–132 °C. ^1H NMR ($CDCl_3$, δ): 0.90 (s, 3 H, CH_3), 1.04–10.8 (m, 4 H, CH_3, CH_2), 1.11 (s, 3 H, CH_3), 1.16–1.21 (m, 1 H, CH_2), 1.42–1.47 (m, 1 H, CH_2), 1.50–1.54 (m, 1 H, CH_2), 1.67–1.74 (m, 3 H, CH_2, CH), 3.87–3.90 (m, 4 H, C_5H_4), 4.04 (dd, $^3J_{H,P}$ = 8.5 Hz, $J_{H,H}$ = 1.8 Hz, 1 H, H2), 4.25 (s, 5 H, C_5H_5), 4.25 (s, 5 H, C_5H_5), 4.38–4.46 (m, 4 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.2 (CH_3), 20.8 (CH_3), 25.7 (C5/C6), 25.9 (C5/C6), 29.9 (CH_3), 39.6 (d, $^3J_{C,P}$ = 2.7 Hz, C3), 40.9 (C7), 47.9 (C4), 49.3 (d, $^3J_{C,P}$ = 5.1 Hz, C1), 59.91 (C_5H_4), 59.93 (C_5H_4), 59.94 (C_5H_4), 59.96 (C_5H_4),

59.98 (C_5H_4), 59.98 (C_5H_4), 62.71 (C_5H_4), 62.72 (C_5H_4), 62.75 (C_5H_4), 69.54 (C_5H_5), 59.54 (C_5H_5), 92.3 (d, $^2J_{C,P}$ = 7.4 Hz, C2), 117.77 (d, $^3J_{C,P}$ = 4.9 Hz, C_{C5H4}-O), 117.81 (d, $^2J_{C,P}$ = 4.7 Hz, C_{C5H4}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –9.8. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{35}Fe_2O_4P$ 602.0967, found 602.1005 $[M]^+$.

Diferrocenyl Phenyl Phosphate (48)

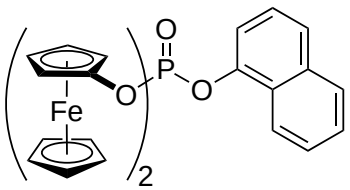


48

Ferrocenol (**5**, 850 mg, 4.21 mmol), Buli (1.7 mL, 4.25 mmol) and $Cl_2P(O)OPh$ (0.32 mL, 2.07 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, 2.5 · 12 cm column size) using an 4/1 hexane/dichloromethane mixture (v/v) as the eluent, giving 48 as an orange solid.

Yield: 706 mg (1.30 mmol, 63 % based on $Cl_2P(O)OPh$). Anal. calcd for $C_{26}H_{23}Fe_2O_4P$ (542.12 g/mol): C, 57.60; H, 4.28. Found: C, 57.70; H, 4.27. Mp.: 100–104 °C. ^1H NMR ($CDCl_3$, δ): 3.92 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, H3/4-C_5H_4), 4.25 (s, 10 H, C_5H_5), 4.44–4.46 (m, 4 H, H2/5-C_5H_4), 7.21–7.24 (m, 1 H, H4-C_6H_5), 7.26–7.28 (m, 2 H, H3/5-C_6H_5), 7.37–7.40 (m 2 H, H2/6-C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.68 (C2/5-C_5H_4), 59.70 (C2/5-C_5H_4), 59.72 (C2/5-C_5H_4), 59.73 (C2/5-C_5H_4), 62.9 (C3/4-C_5H_4), 69.6 (C_5H_5), 117.8 (d, $^2J_{C,P}$ = 5.4 Hz, C_{C5H4}-O), 120.0 (d, $^3J_{C,P}$ = 5.1 Hz, C2/6-C_6H_5), 125.5 (d, $^5J_{C,P}$ = 0.8 Hz, C4-C_6H_5), 129.8 (C3/5-C_6H_5), 150.4 (d, $^2J_{C,P}$ = 7.2 Hz, C_{C6H5}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –16.1. HRMS (ESI-TOF, m/z): calcd for $C_{26}H_{23}Fe_2O_4P$ 542.0028, found 542.0049 $[M]^+$.

Diferrocenyl 1-Naphthyl Phosphate (49)



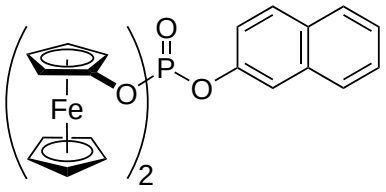
49

Ferrocenol (**5**, 600 mg, 2.97 mmol), BuLi (1.2 mL, 3.0 mmol) and 1-naphthyl dichlorophosphate (388 mg, 1.5 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, 2.5 · 15 cm column size) using a 9/1 dichloromethane/hexane mixture (v/v) as the eluent, giving **49** as an orange solid.

Yield: 195 mg (0.364 mmol, 25 % based on **5**). Anal. calcd for $C_{30}H_{25}Fe_2O_4P \cdot 1/6\ C_6H_{14}$ (592.18 · 1/6 86.18 g/mol): C, 61.39; H, 4.54. Found: C, 61.39; H, 4.63. Mp.: 130–134 °C. ^1H NMR ($CDCl_3$, δ): 3.91 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 4 H, H3,4-C_5H_4), 4.21 (s, 10 H, C_5H_5), 4.44–4.46 (m, 4 H, H2,5-C_5H_4), 7.45 (t, $^3J_{H,H}$ = 7.9 Hz, 1 H, H3-$C_{10}H_7$), 7.53–7.56 (m, 3 H, H2/6/7-$C_{10}H_7$), 7.72 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, H4-$C_{10}H_7$), 7.86–7.88 (m, 1 H, H5-$C_{10}H_7$), 8.11–8.13 (m, 1 H, H8-$C_{10}H_7$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.86 (d, $^3J_{C,P}$ = 3.9 Hz, C2/5-C_5H_4), 59.90 (d, $^3J_{C,P}$ = 3.7 Hz, C2/5-C_5H_4), 62.9 (C3/4-C_5H_4), 69.6 (C_5H_5), 115.1 (d, $^3J_{C,P}$ = 2.9 Hz, C2-$C_{10}H_7$), 117.9 (d, $^2J_{C,P}$ = 5.3 Hz, C_{C5H4}-O), 121.7 (C8-$C_{10}H_7$), 125.39 (C3-$C_{10}H_7$), 125.40 (C4$C_{10}H_7$), 126.3 (d, $^3J_{C,P}$ = 6.9 Hz, C8a-$C_{10}H_7$), 126.5 (C6/7-$C_{10}H_7$), 126.8 (C6/7-$C_{10}H_7$), 127.7 (C5-$C_{10}H_7$), 134.8 (C4a-$C_{10}H_7$), 146.4 (d, $^2J_{C,P}$ = 7.6 Hz, C1-$C_{10}H_7$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –15.6. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{25}Fe_2O_4P$

592.0185, found 592.0160 $[M]^+$.

Diferrocenyl 2-Naphthyl Phosphate (50)

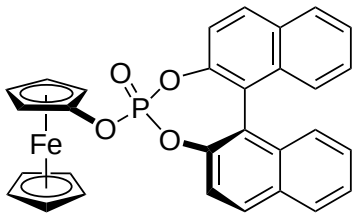


50

Ferrocenol (**5**, 836 mg, 4.138 mmol), BuLi (1.7 mL, 4.25 mmol), NEt_3 (0.6 mL, 4.3 mmol) and 2-naphthyl dichlorophosphate (515 mg, 1.973 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, $2.5 \cdot 35$ cm column size) using chloroform as the eluent, giving **50** as an orange oil.

Yield: 380 mg (0.64 mmol, 65 % based on the dichlorophosphate). Anal. calcd for $C_{30}H_{25}Fe_2O_8P_2 \cdot 1/3\ C_6H_{14}$ ($741.99 \cdot 1/3\ 86.18$ g/mol): C, 49.87; H, 3.75. Found: C, 49.65; H, 3.59. Mp.: >230 °C (decomp.). ^{1}H NMR ($CDCl_3$, δ): 3.93 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, H3,4-C_5H_4), 4.26 (s, 10 H, C_5H_5), 4.46–4.48 (m, 4 H, H2,5-C_5H_4), 7.39 (dd, $^3J_{H,H}$ = 8.9 Hz, $^4J_{H,H}$ = 2.4 Hz, 1 H, H3), 7.45–7.53 (m, 2 H, $C_{10}H_7$), 7.73–7.75 (m, 1 H, H1), 7.82–7.87 (m, 3 H, $C_{10}H_7$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.76 (d, $^3J_{C,P}$ = 4.1 Hz, C2/5-C_5H_4), 59.77 (d, $^3J_{C,P}$ = 4.0 Hz, C2/5-C_5H_4), 62.9 (s, C_5H_4), 69.7 (s, C_5H_5), 116.5 (d, $^3J_{C,P}$ = 5.0 Hz, C1), 117.9 (d, $^2J_{C,P}$ = 5.4 Hz, C_{C5H4}-O), 119.8 (d, $^3J_{C,P}$ = 5.0 Hz, C3), 125.7 ($C_{10}H_7$), 126.9 ($C_{10}H_7$), 127.6 ($C_{10}H_7$), 127.7 ($C_{10}H_7$), 130.0 (C4), 131.1 (C8a), 133.8 (C4a), 148.0 (d, $^2J_{C,P}$ = 7.4 Hz, C2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –16.0. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{25}Fe_2O_4P$ 592.0185, found 592.0160 $[M]^+$.

(*R*)-1,1'-Binaphthyl-2,2'-diyl Ferrocenyl Phosphate (70b)



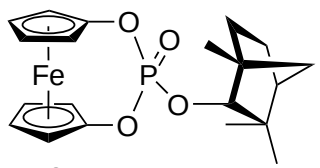
70b

Ferrocenol (**5**, 235 mg, 1.16 mmol), BuLi (0.47 mL, 1.18 mmol) and (*R*)-1,1'-binaphthyl-2,2'-diyl chlorophosphate (427 mg, 1.16 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, $2.5 \cdot 8$ cm column size) using a 99/1 dichloromethane/ethyl acetate mixture (v/v) as the eluent (R_f = 0.26), giving **70b** as an orange solid.

Yield: 305 mg (0.57 mmol, 49 % based on **5**). Anal. calcd for $C_{30}H_{21}FeO_4P \cdot 1/3\ C_6H_{14}$ ($532.31 \cdot 1/3\ 86.18$ g/mol): C, 68.51; H, 4.61. Found: C, 68.56; H, 4.48. Mp.: 247 °C. ^{1}H NMR ($CDCl_3$, δ): 3.89–3.91 (m, 1 H, H3/4-C_5H_4), 3.93–3.94 (m, 1 H, H3/4-C_5H_4), 4.31 (s, 5 H, C_5H_5), 4.34–4.40 (m, 1 H, H2/5-C_5H_4), 4.54–4.56 (m, 1 H, H2/5-C_5H_4), 7.30–7.41 (m, 4 H, $C_{10}H_8$), 7.14–7.52 (m, 3 H, $C_{10}H_8$), 7.65 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, $C_{10}H_8$), 7.96–7.98 (m, 2 H, $C_{10}H_8$), 8.03 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, $C_{10}H_8$), 8.07 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, $C_{10}H_8$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.8 (d, $J_{C,P}$ = 4.6 Hz, C_5H_4), 59.9 (d, $J_{C,P}$ = 3.5 Hz, C_5H_4), 62.9 (C_5H_4), 63.0 (C_5H_4), 69.8 (C_5H_5), 117.9 (d, $^2J_{C,P}$ = 5.0 Hz, C_{C5H4}-O), 120.2 (d, $J_{C,P}$ = 3.3 Hz, CH), 120.6 (d, $J_{C,P}$ = 2.9 Hz, CH), 121.2 (d, $^2J_{C,P}$ = 2.1 Hz, ^{q}C), 121.5 (d, $J_{C,P}$ = Hz, ^{q}C), 125.89 (CH), 125.92 (CH), 126.9 (CH), 127.0 (CH), 127.2 (CH), 128.45 (CH),

128.54 (CH), 131.1 (CH), 131.6 (CH), 131.7 (d, $J_{C,P}$ = 0.9 Hz, ^{q}C), 132.0 (d, $J_{C,P}$ = 1.1 Hz, ^{q}C), 132.26 (d, $J_{C,P}$ = 0.8 Hz, ^{q}C), 132.27 (d, $^{2}J_{C,P}$ = 1.0 Hz, ^{q}C), 146.1 (d, $^{2}J_{C,P}$ = 8.2 Hz, C2/2'), 147.4 (d, $^{2}J_{C,P}$ = 11.4 Hz, C2/2'). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –2.5. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{21}FeO_4P$ + Na 555.0419, found 555.0401 $[M+Na]^+$.

1,3-Dioxa-2-((1*R*)-α-fenchyl)(oxo)phospha-[3]ferrocenophane (72)



72

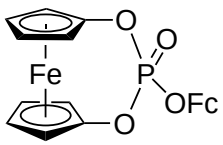
Ferrocenediol (**38**, 600 mg, 2.75 mmol), BuLi (2.20 mL, 5.50 mmol) and (1*R*)-α-fenchyl dichlorophosphate (749 mg, 2.752 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, 2.5 · 12 cm column size) using a 95/5 dichloromethane/ethyl acetate (v/v) mixture as the eluent, giving **72** as an orange solid.

Yield: 214 mg (0.51 mmol, 19 % based on **38**). Anal. calcd for $C_{20}H_{25}FeO_4P$ (416.23 g/mol): C, 57.71; H, 6.05. Found: C, 58.04; H, 6.35. Mp.: 130–133 °C. ^{1}H NMR ($CDCl_3$, δ): 1.01 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 1.13–1.17 (m, 1 H, H5/6), 1.20 (s, 3 H, CH_3), 1.22–1.24 (m, 1 H, H7), 1.46–1.52 (m, 1 H, H5/6), 1.56 (ddd, $^{3}J_{H,H}$ = 10.5 Hz, $J_{H,H}$ = 3.8 Hz, $J_{H,H}$ = 2.2 Hz, 1 H, H7), 1.74–1.85 (m, 3 H, H5/6, H4), 4.01 (ddd, $J_{H,P}$ = 3.9 Hz, $J_{H,H}$ = 2.6 Hz, $J_{H,H}$ = 1.3 Hz, 2 H, C_5H_4), 4.05–4.06 (m, 2 H, C_5H_4), 4.20 (dd, $^{3}J_{H,P}$ = 8.2 Hz, 1 H, H2), 4.38 (dtd, $J_{H,P}$ = 4.4 Hz, $J_{H,H}$ = 2.6 Hz, $J_{H,H}$ = 1.3 Hz, 2 H, C_5H_4), 4.63–4.64 (m, 2 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.1 (CH_3), 20.8 (CH_3), 25.83 (C5/6), 25.87 (C5/6), 29.8 (CH_3), 39.7 (d, $^{3}J_{C,P}$ = 2.6 Hz, C3), 40.9 (C7), 47.9 (C4), 49.3 (d, $^{3}J_{C,P}$ = 5.5 Hz, C1), 63.30 (C_5H_4), 63.32 (C_5H_4), 63.35 (C_5H_4), 63.36 (C_5H_4), 66.0 (C_5H_4), 66.92 (C_5H_4), 66.93 (C_5H_4), 93.9 (d, $^{2}J_{C,P}$ = 7.7 Hz, C2), 109.4 (d, $^{2}J_{C,P}$ = 10.3 Hz, C_{C5H4}-O), 109.5 (d, $^{2}J_{C,P}$ = 10.4 Hz, C_{C5H4}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 0.3. HRMS (ESI-TOF, m/z): calcd for $(C_{20}H_{25}FeO_4P)_2$ + Na 855.1574, found 855.1581 $[M_2+Na]^+$.

Synthesis of 70a and 75

Ferrocenediol (**38**, 150 mg, 0.688 mmol) was dissolved in 30 mL of diethyl ether and the solution was cooled to –30 °C. BuLi (0.55 mL, 1.375 mmol) was dropwise added and stirring was continued for 10 min at this temperature. Afterwards, the mixture was cooled to –70 °C and $POCl_3$ (0.125 mL, 1.376 mmol) was added in a single portion. Separately, ferrocenol (**5**, 603 mg, 2.98 mmol) was dissolved in 30 mL of diethyl ether, cooled to –30 °C and BuLi (1.2 mL, 3 mmol) was dropwise added. Both reaction mixtures were tempered at –30 °C and the mixture containing **5** was slowly added to the one containing **38** by using a transfer cannula. The cooling bath was removed and stirring was continued for 18 h, followed by the removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, 2 · 15 cm column size) resulting three fractions. Fraction 1 (dichloromethane, R_f = 0.52) contained $P(O)(OFc)_3$ (**47**, 330 mg, 0.415 mmol, 42 % based on **5**), fraction 2 compound **70a** (95/5 dichloromethane/ethyl acetate (v/v) mixture, R_f = 0.57) and fraction 3 contained **75** (95/5 dichloromethane/ethyl acetate (v/v) mixture, R_f = 0.41)

1,3-Dioxa-2-(ferrocenyloxy)(oxo)phospha-[3]ferrocenophane (70a)

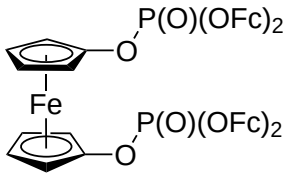


70a

The spectroscopic data of this compound are in agreement with those reported in reference[219]. Crystals, suitable for single crystal X-ray diffraction analysis, were obtained by crystallization from a boiling hexane solution containing **70a**.

Yield: 63 mg (0.136 mmol, 20 % based on **38**). ^{1}H NMR ($CDCl_3$, δ): 3.96 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 Hz, C_5H_4, FcO), 4.07 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 Hz, C_5H_4, ansa), 4.33 (s, 5 H, C_5H_5), 4.41–4.42 (m, 2 H, C_5H_4, ansa), 4.50 (pt, $^{3,4}J_{H,H}$ = 1.8 Hz, 2 Hz, C_5H_4, FcO), 4.58–4.59 (m, 2 H, C_5H_4, ansa). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.4 (d, $J_{C,P}$ = 4.4 Hz, C_5H_4, FcO), 62.8 (d, $J_{C,P}$ = 3.1 Hz, C_5H_4, ansa), 63.0 (s, C_5H_4, FcO), 63.7 (d, $J_{C,P}$ = 3.4 Hz, C_5H_4, ansa), 66.8 (s, C_5H_4, ansa), 69.8 (C_5H_5), 109.9 (d, $^{2}J_{C,P}$ = 12.5 Hz, C-O, ansa), 118.0 (d, $^{2}J_{C,P}$ = 6.1 Hz, C-O, FcO). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –5.6. HRMS (ESI-TOF, m/z): calcd for $C_{20}H_{17}Fe_2O_4P$ + H 464.9636, found 464.9608 $[M+H]^+$.

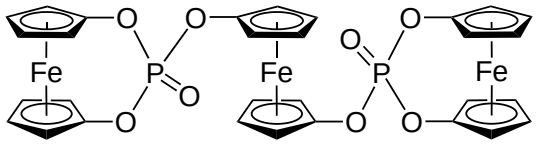
(1,1'-Ferrocenediyl)tetraferrocenyl bis(phosphate) (75)



75

Yield: 86 mg (0.077 mmol, 11 % based on **38**). Mp.: 167 °C. ^{1}H NMR ($CDCl_3$, δ): 3.93 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 8 H, FcO), 4.05 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, FcO_2), 4.28 (s, 20 H, C_5H_5), 4.44 (dd, $J_{H,P}$ = 4.4 Hz, $J_{H,H}$ = 2.1 Hz, 8 H, FcO), 4.52 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, FcO_2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.65 (C_5H_4, FcO), 59.66 (C_5H_4, FcO), 59.69, (C_5H_4, FcO), 59.70 (C_5H_4, FcO), 61.16 (C_5H_4, FcO_2), 61.20 (C_5H_4, FcO_2), 62.93 (C_5H_4, FcO), 62.94 (C_5H_4, FcO), 65.1 (C_5H_4, FcO_2), 69.7 (C_5H_5), 117.8 (d, $^{2}J_{C,P}$ = 5.5 Hz, C-O, FcO), 118.1 (d, $^{2}J_{C,P}$ = 5.4 Hz, C-O, FcO_2). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –15.3. HRMS (ESI-TOF, m/z): calcd for $C_{50}H_{44}Fe_5O_8P_2$ 1113.9260, found 1113.9205 $[M]^+$.

1,1'-Bis(1,3-dioxa-2-(oxo)phospha-[3]ferrocenophan-2-yloxy)ferrocene (76)



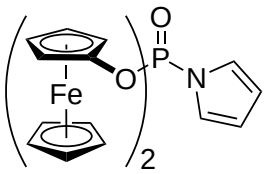
76

Ferrocenediol (**38**, 642 mg, 2.94 mmol) was split in three portions of 214 mg (0.982 mmol) and each of them was dissolved in 10 mL of diethyl ether. The solutions were cooled to –30 °C and BuLi (0.79 mL, 1.96 mmol) was dropwise added. The first portion was cooled to –70 °C, $POCl_3$ (0.18 mL, 1.96 mmol) was added quickly via syringe and the reaction mixture was slowly warmed to ambient temperature. After stirring for 10 min at this temperature, the reaction mixture was cooled again to –70 °C and the second portion of lithiated 1,1'-$Fc(OH)_2$ (**38**-Li_2) was added via a transfer cannula. The same procedure was repeated for the third fraction of **38**-Li_2. Afterwards, the mixture was allowed to warm to ambient temperature and stirred for 18 h. All volatiles were removed in vacuum. Purification was realized using column chromatography (silica, 2 · 12 cm column size) using a 95/5 dichloromethane/ethyl

acetate mixture (v/v) as the eluent, giving **76** as an orange solid. The spectroscopic date are in agreement with those reported in reference [219,220]. Crystals, suitable for single crystal X-ray diffraction analysis, were obtained by crystallization from a boiling hexane solution containing **76**.

Yield: 94 mg (0.127 mmol, 12 % based on **38**). Anal. calcd for $C_{30}H_{24}Fe_2O_8P_2 \cdot 1/3\ C_6H_{14}$ (741.99 · 1/3 86.18 g/mol): C, 49.87; H, 3.75. Found: C, 49.65; H, 3.59. Mp.: >230 °C (decomp.). ^{1}H NMR ($CDCl_3$, δ): 4.06–4.07 (m, 8 H, ansa), 4.17 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, open), 4.44–4.45 (m, 4 H, ansa), 4.56–4.57 (m, 4 H, ansa), 4.66 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 4 H, open). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 61.2 (d, $J_{C,P}$ = 4.5 Hz, open), 62.9 (d, $J_{C,P}$ = 3.0 Hz, ansa), 63.7 (d, $J_{C,P}$ = 3.6 Hz, ansa), 65.2 (open), 66.8 (ansa), 66.9 (ansa), 109.9 (d, $^2J_{C,P}$ = 12.8 Hz, C_{C5H4}-O, ansa), 118.3 (d, $^2J_{C,P}$ = 6.0 Hz, C_{C5H4}-O, open). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –5.6. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{24}Fe_3O_8P_2$ + Na 764.8889, found 764.8862 $[M+Na]^+$.

Diferrocenyl (1*H*-Pyrrol-1-yl)phosphonate (79)

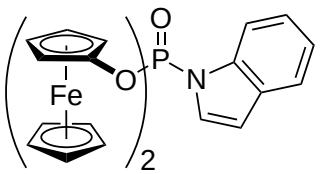


79

Ferrocenol (**5**, 836 mg, 4.14 mmol), BuLi (1.7 mL, 4.25 mmol) and (1*H*-pyrrol-1-yl) dichlorophosphonate (380 mg, 2.07 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, 2.5 · 12 cm column size) using a 98/2 dichloromethane/ethyl acetate mixture (v/v) as the eluent, giving **79** as an orange solid.

Yield: 468 mg (0.91 mmol, 44 % based on **5**). Anal. calcd for $C_{24}H_{22}Fe_2NO_3P$ (515.10 g/mol): C, 55.96; H, 4.30; N, 2.72. Found: C. 55.48; H, 4.48; N, 2.67. Mp.: 184 °C. ^{1}H NMR ($CDCl_3$, δ): 3.87–3.89 (m, 4 H, C_5H_4), 4.21 (s, 10 H, C_5H_5), 4.27–4.28 (m, 2 H, C_5H_4), 4.30–4.31 (m, 2 H, C_5H_4), 6.40 (ddd, $^4J_{H,P}$ = 4.7 Hz, $J_{H,H}$ = 2.2 Hz, $J_{H,H}$ = 2.2 Hz, 2 H, C3/4), 7.09 (ddd, $J_{H,H}$ = 2.2 Hz, $J_{H,H}$ = 2.2 Hz, $^3J_{H,P}$ = 2.2 Hz, 2 H, C2/5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.4 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 59.6 (d, $J_{C,P}$ = 4.6 Hz, C_5H_4), 62.96 (C_5H_4), 63.00 (C_5H_4), 69.7 (C_5H_5), 113.3 (d, $^3J_{C,P}$ = 11.5 Hz, C3/4), 117.3 (d, $^2J_{C,P}$ = 4.5 Hz, C_{C5H4}-O), 122.8 (d, $^2J_{C,P}$ = 6.5 Hz, C2/5). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –11.5. HRMS (ESI-TOF, m/z): calcd for $C_{24}H_{22}Fe_2NO_3P$ 515.0031, found 515.0014 $[M]^+$.

Diferrocenyl (1*H*-Indol-1-yl)phosphonate (80)



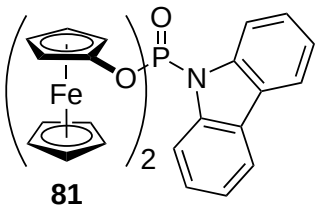
80

Ferrocenol (**5**, 836 mg, 4.14 mmol), BuLi (1.7 mL, 4.25 mmol) and (1*H*-indol-1-yl) dichlorophosphonate (484 mg, 2.07 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, 2.5 · 12 cm column size) using a 98/2 dichloromethane/ethyl acetate (v/v) mixture as the eluent, giving **80** as an orange solid. Crystals, suitable for single crystal X-ray diffraction analysis, were obtained by crystallization from a

boiling hexane solution containing **80**.

Yield: 945 mg (1.67 mmol, 81 % based on **5**). Anal. calcd for $C_{28}H_{24}Fe_2NO_3P$ (565.16 g/mol): C, 59.51; H, 4.28; N, 2.48. Found: C, 59.51; H, 4.30; N, 2.60. Mp.: ∼ 25 °C. ^{1}H NMR ($CDCl_3$, δ): 3.82 (ddd, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 2.7 Hz, $J_{H,H}$ = 1.5 Hz, 2 H, C_5H_4), 3.85 (ddd, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 2.7 Hz, $J_{H,H}$ = 1.5 Hz, 2 H, C_5H_4), 4.13 (s, 10 H, C_5H_5), 4.15–4.16 (m, 2 H, C_5H_4), 4.34–4.35 (m, 2 H, C_5H_4), 6.72 (ddd, $^4J_{H,P}$ = 3.6 Hz, $^3J_{H,H}$ = 2.7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1 H, H3), 7.29 (ddd, $^8J_{H,H}$ = 8.1 Hz, $^8J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.0 Hz, 1 H, H5/6), 7.39 (ddd, $^3J_{H,H}$ = 8.4 Hz, $^3J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.2 Hz, 1 H, H5/6), 7.46 (dd, $^3J_{H,H}$ = 3.5 Hz, $^3J_{H,P}$ = 2.1 Hz, 1 H, H2), 7.64–7.66 (m, 1 H, H4), 7.87 (d, $J_{H,H}$ = 8.3 Hz, 1 H, C7). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.3 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 59.6 (d, $J_{C,P}$ = 4.5 Hz, C_5H_4), 62.95 (C_5H_4), 62.98 (C_5H_4), 69.6 (C_5H_5), 108.3 (d, $^3J_{C,P}$ = 9.2 Hz, C3), 113.9 (C7), 117. 2 (d, $^2J_{C,P}$ = 4.0 Hz, C_{C5H4}-O), 121.3 (C4), 122.7 (C5/6), 123.9 (C5/6), 128.5 (d, $^2J_{C,P}$ = 7.4 Hz, C2), 131.1 (d, $^3J_{C,P}$ = 10.9 Hz, C3a), 136.9 (d, $^2J_{C,P}$ = 5.0 Hz, C7a). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –11.6. HRMS (ESI-TOF, m/z): calcd for $C_{28}H_{24}Fe_2NO_3P$ + Na 588.0086, found 588.0102 $[M+Na]^+$.

Diferrocenyl (9*H*-Carbazol-9-yl)phosphonate (81)



81

Ferrocenol (**5**, 835 mg, 4.13 mmol), BuLi (1.8 mL, 4.5 mmol) and (9*H*-carbazol-9-yl) dichlorophosphate (580 mg, 2.04 mmol) were reacted according to the general procedure GP1. Purification was realized by column chromatography (silica, 3.5 · 8 cm column size) using dichloromethane as the eluent, giving **81** as an orange solid. Crystals, suitable for single crystal X-ray diffraction analysis, were obtained by crystallization from a boiling hexane solution containing **81**.

Yield: 340 mg (0.553 mmol, 27 % based on **5**). Anal. calcd for $C_{32}H_{26}Fe_2NO_3P$ (615.22 g/mol): C, 62.47; H, 4.26; N, 2.28. Found: C, 62.69; H, 4.40; N, 2.29. Mp.: 160 °C. ^{1}H NMR ($CDCl_3$, δ): 3.76 (ddd, $J_{H,H}$ = 2.7 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 1.4 Hz, 2 H, C_5H_4), 3.81 (ddd, $J_{H,H}$ = 2.7 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 1.4 Hz, 2 H, C_5H_4), 4.07 (s, 10 H, C_5H_5), 4.12–4.14 (m, 2 H, C_5H_4), 4.35–4.36 (m, 2 H, C_5H_4), 7.40 (ddd, $^3J_{H,H}$ = 7.9 Hz, $^3J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 0.9 Hz, 2 H, $C_{12}H_8N$), 7.53 (ddd, $^3J_{H,H}$ = 8.5 Hz, $^3J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.3 Hz, 2 H, $C_{12}H_8N$), 8.04–8.06 (m, 2 H, $C_{12}H_8N$), 8.17 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, $C_{12}H_8N$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.3 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 59.5 (d, $J_{C,P}$ = 4.8 Hz, C_5H_4), 62.89 (C_5H_4), 62.94 (C_5H_4), 69.5 (C_5H_5), 114.9 (C1, C8), 117.2 (d, $^2J_{C,P}$ = 3.9 Hz, C_{C5H4}-O), 120.1, 122.8, 126.2 (d, $J_{C,P}$ = 9.2 Hz, C4a, C4b), 127.0, 140.15 (d, $J_{C,P}$ = 6.6 Hz, C8a, C9a). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –11.8. HRMS (ESI-TOF, m/z): calcd for $C_{32}H_{26}Fe_2NO_3P$ 615.0345, found 615.0332 $[M]^+$.

4.3.2 Compounds derived from Anionic Phospho-Fries Rearrangements

General Procedure for Anionic Phospho-Fries Rearrangements - Using LDA in THF GP2

In a Schlenk tube, tetrahydrofuran (3 mL) and diisopropylamine (0.05 mL, 0.36 mmol) were cooled to –30 °C. Afterwards, BuLi (0.15 mL, 0.38 mmol) was dropwise added. The mixture was stirred for 10 min at –30 °C and the desired reaction temperature was adjusted followed by the addition of the corresponding ferrocenyl phosphates. The obtained reaction mixture was stirred for the appropriate time followed by the addition of a methylation agent and stirring at 50 °C for 1 h to complete methylation. All volatiles were removed under reduced pressure. Purification was realized using column chromatography on silica using different solvent mixtures as eluents (see below).

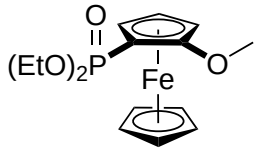
General Procedure for Anionic Phospho-Fries Rearrangements - Using LDA in Hexane GP3

In a Schlenk tube, hexane (3 mL) and diisopropylamine (0.05 mL, 0.36 mmol) were cooled to –30 °C. Afterwards, BuLi (0.15 mL, 0.38 mmol) was dropwise added followed by addition of a diamine (tetramethylethylenediamine: 0.05 mL, 0.33 mmol or (−)-Sparteine (0.08 mL, 0.35 mmol)). The mixture was stirred for 10 min at –30 °C and the corresponding ferrocenyl phosphates were added in a single portion. The obtained reaction mixture was allowed to warm to ambient temperature and stirring was continued overnight. The reaction was quenched by adding dimethyl sulfate (0.15 mL, 1.58 mmol) and stirred at 50 °C for 1 h to complete methylation. All volatiles were removed under reduced pressure. Purification was realized using column chromatography on silica using a 98/2 dichloromethane/ethyl acetate mixtures as eluent (see below).

General Procedure for Anionic Phospho-Fries Rearrangements - Using LiTMP GP4

In a Schlenk, tube LiTMP (56 mg, 0.38 mmol) was suspended in 3 mL of hexane and cooled to –30 °C. The addition of the diamine, the respective ferrocenyl phosphate as well as the reaction conditions and workup procedures were realized as described in procedure GP3.

Diethyl (2-Methoxyferrocenyl)phosphonate (*rac*-16)



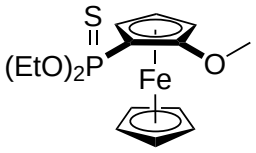
16

Diisopropylamine (1.25 mL, 8.9 mmol), BuLi (3.6 mL, 9.0 mmol) and phosphate **6** (1.5 g, 4.4 mmol) were reacted in 20 mL between –30 °C and –15 °C according to the general procedure GP2 followed by the addition of Me_2SO_4 (1.3 mL, 13.7 mmol). Purification was realized by column chromatography (alumina, $2 \cdot 8$ cm column size) using ethyl acetate as the eluent, giving *rac*-**16** as an orange oil.

Yield: 1.46 g (4.14 mmol, 94 % based on **6**). IR data (NaCl, $\tilde{\nu}/\mathrm{cm}^{-1}$): 3095 m, 2980 s, 2931

w, 2905 w, 2865 w, 1639 m, 1482 s, 1412 s, 1388 w, 1340 m, 1254 s, 1168 m, 1106 s, 1051 s, 1029 s, 964 s, 801 s, 753 m. ^{1}H NMR (C_6D_6, δ): 1.11 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.17 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 3.25 (s, 3 H, OCH_3), 3.71 (dd, $^{3}J_{H,H}$ = 2.7 Hz, 1 H, *m*-OCH_3), 3.76 (m, 1 H, *o*-OCH_3), 4.07 (m, 2 H, CH_2), 4.15 (m, 2 H, CH_2), 4.30 (s, 5 H, C_5H_5), 4.36 (m, 1 H, *o*-P(O)). ^{13}C{^{1}H} NMR (C_6D_6, δ): 16.6 (m, CH_3), 55.4 (d, $^{3}J_{C,P}$ = 11 Hz, *o*-OCH_3), 57.8 (s, OCH_3), 59.2 (d, $^{1}J_{C,P}$ = 213.7 Hz, C-P), 61.6 (m, CH_2), 63.8 (d, $^{3}J_{C,P}$ = 13.7 Hz, *m*-OCH_3), 67.7 (d, $^{2}J_{C,P}$ = 12.8 Hz, *o*-P(O)), 70.4 (s, C_5H_5), 129.0 (d, $^{2}J_{C,P}$ = 10.3 Hz, C-OCH_3). ^{13}C{^{1}H} NMR (C_6D_6, δ): 36.4. HRMS (ESI-TOF, m/z): calcd for $C_{15}H_{21}FeO_4P$ 352.0521, found 352.0602 $[M]^+$. HPLC (Chiralcel OD-H, flow rate 0.5 mL min^{-1}, 9/1 hexane/2-propanol): 19.6, 20.6.

Diethyl (2-Methoxyferrocenyl)thiaphosphonate (*rac*-17)

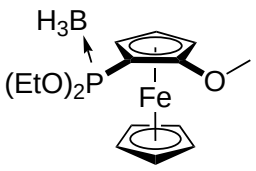


17

Instead of LDA, ^{s}BuLi (0.65 mL, 0.85 mmol) and diethyl ferrocenyl thiophosphate **7** (250 mg, 0.71 mmol) were reacted in 10 mL of tetrahydrofuran between –30 °C and –20 °C according to the general procedure GP2. Iodomethane (0.1 mL, 1.6 mmol) was added in a single portion as the methylation agent. Additional stirring for 18 h and removal of all volatiles afforded a residue which was purified by column chromatography (silica, 3.5 · 6.2 cm column size). First, unreacted **7** (46 %) was eluted with a 3/1 (v/v) toluene/hexane mixture. Afterwards, the eluent was changed to pure toluene and the product *rac*-**17** (R_f = 0.35) was obtained as an orange oil.

Yield: 130 mg (0.35 mmol, 49 % based on **7**). ^{1}H NMR ($CDCl_3$, δ): 1.30 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.39 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 3.70 (s, 3 H, OCH_3), 4.03 (q, $J_{H,H}$ = 2.8 Hz, 1 H, C_5H_3), 4.09–4.37 (m, 11 H, CH_2, C_5H_5, C_5H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 16.1 (d, $^{3}J_{C,P}$ = 7.9 Hz, CH_3), 16.2 (d, $^{3}J_{C,P}$ = 7.9 Hz, CH_3), 55.3 (d, $J_{C,P}$ = 10.1 Hz, C_5H_3), 58.2 (s, OCH_3), 62.1 (d, $^{3}J_{C,P}$ = 6.4 Hz, CH_2), 62.6 (d, $^{3}J_{C,P}$ = 5.7 Hz, CH_2), 63.4 (d, $J_{C,P}$ = 14.1 Hz, C_5H_3), 64.6 (d, $^{1}J_{C,P}$ = 174.6 Hz, γ-C_5H_3), 67.7 (d, $J_{C,P}$ = 15.7 Hz, C_5H_3), 70.2 (s, C_5H_5), 127.7 (d, $^{2}J_{C,P}$ = 9.0 Hz, C-OCH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 89.6. HRMS (ESI-TOF, m/z): calcd for $C_{15}H_{21}FeO_3PS$ 368.0293, found 368.0310 $[M]^+$.

Diethyl (2-Methoxyferrocenyl)phosphonite·BH_3 (*rac*-18)



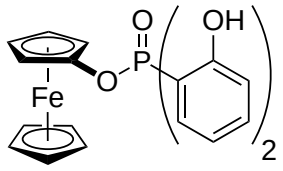
18

LDA was prepared by treating diisopropylamine (0.42 mL, 2.98 mmol) with BuLi (1.20 mL, 3.0 mmol) in tetrahydrofuran (10 mL) at –60 °C. After stirring for 10 min **8** (500 mg, 1.49 mmol) was added as a solution in tetrahydrofuran (2 mL) with a syringe in a single portion. The solution was stirred for 4 h between –30 °C and –20 °C, while the solution turned dark. The reaction was stopped by adding iodomethane (0.30 mL, 4.8 mmol) in a single portion. Purification was realized by column chromatography (silica, 2 · 16 cm column size) using a 2/1 (v/v) hexane/toluene mixture as the eluent, giving

first unreacted **8** (31 %) and second *rac*-**18** as an orange oil after removal of all volatiles.

Yield: 190 mg (0.55 mmol, 37 % based on **8**). ^{1}H NMR ($CDCl_3$, δ): 1.29 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.33 (t, $^{3}J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 3.69 (s, 3 H, OCH_3), 3.99–4.07 (m, 2 H, CH_2), 4.08–4.10 (m, 1 H, C_5H_3), 4.11–4.16 (m, 2 H, CH_2), 4.23–4.24 (m, 1 H, C_5H_3), 4.26–4.27 (m, 1 H, C_5H_3), 4.32 (s, 5 H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 16.5 (d, $^{3}J_{C,P}$ = 5.8 Hz, CH_3), 55.3 (d, $J_{C,P}$ = 6.5 Hz, C_5H_3), 58.2 (s, OCH_3), 60.1 (d, $^{1}J_{C,P}$ = 90.1 Hz, C-P), 62.6 (d, $^{2}J_{C,P}$ = 5.5 Hz, CH_2), 62.8 (d, $^{2}J_{C,P}$ = 4.9 Hz, CH_2), 64.2 (d, $J_{C,P}$ = 10.0 Hz, C_5H_3), 70.2 (s, C_5H_5), 128.7 (d, $^{2}J_{C,P}$ = 6.2 Hz, C-OCH_3). ^{11}B{^{1}H} NMR (C_6D_6, δ): -40.8 (d, $^{1}J_{B,P}$ = 89 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 135.4 (q, $^{1}J_{B,P}$ = 89 Hz). HRMS (ESI-TOF, m/z): calcd for $C_{15}H_{24}BFeO_3P$ + H 350.0903, found 350.0856 $[M+H]^+$.

Ferrocenyl Bis(2-hydroxyphenyl)phosphinate (19)

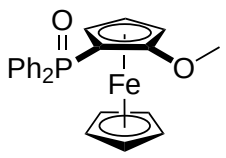


19

LDA was prepared by treating diisopropylamine (0.98 mL, 7.07 mmol) with BuLi (2.75 mL, 6.90 mmol) in tetrahydrofuran (10 mL) at –60 °C. After stirring for 10 min **11** (500 mg, 1.15 mmol) was added in a single portion. The solution was stirred for 5 h between –60 °C and –40 °C, while the solution turned dark. The reaction was stopped by adding iodomethane (0.43 mL, 1.6 mmol) in a single portion. The reaction mixture was allowed to warm to room temperature. Purification was realized by column chromatography (silica, 3 · 18 cm column size) using a 3/1 (v/v) CH_2Cl_2/ethyl acetate mixture as the eluent, giving **19** as an orange oil.

Yield: 40 mg (0.10 mmol, 8 % based on **11**). ^{1}H NMR ($CDCl_3$, δ): 3.85 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.22 (s, 5 H, C_5H_5), 4.29 (pt, $^{3,4}J_{H,H}$ = = 1.9 Hz, 2 H, C_5H_4), 6.92–6.98 (m, 4 H, Ph), 7.42–7.47 (m, 3 H, Ph), 7.48 (dd, $J_{H,H}$ = 7.8 Hz, $J_{H,H}$ = 1.6 Hz, 1 H, Ph), 9.86 (s, 2 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 60.0 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 63.1 (s, C_5H_4), 69.7 (C_5H_5), 111.1 (d, $^{1}J_{C,P}$ = 139.9 Hz, Ph-P), 117.1 (d, $^{2}J_{C,P}$ = 6.9 Hz, C_{C5H4}-O), 118.6 (d, $J_{C,P}$ = 9.4 Hz), 119.9 (d, $J_{C,P}$ = 12.8 Hz), 131.6 (d, $J_{C,P}$ = 8.0 Hz), 135.6 (d, $J_{C,P}$ = 1.8 Hz), 162.1 (d, $^{2}J_{C,P}$ = 5.9 Hz, C-OH). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 42.3. HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{19}FeO_4P$ 434.0365, found 434.0364 $[M]^+$.

(2-Methoxyferrocenyl)diphenylphosphine Oxide (*rac*-20)



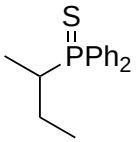
20

LDA was prepared by treating diisopropylamine (0.33 mL, 2.35 mmol) with BuLi (0.92 mL, 2.30 mmol) in tetrahydrofuran (10 mL) at –60 °C. After stirring for 10 min **9** (500 mg, 1.24 mmol) was added in a single portion. The solution was stirred for 4 h between –30 °C and –20 °C, while the reaction solution turned dark. The reaction was stopped by adding iodomethane (0.30 mL, 4.8 mmol) in a single portion. Purification was realized by column chromatography (silica, 3 · 14 cm column size) using a 2/1 (v/v) CH_2Cl_2/ethyl acetate mixture as the eluent, giving *rac*-**20** as an orange oil.

Yield: 45 mg (0.10 mmol, 8 % based on **9**). ^{1}H NMR ($CDCl_3$, δ): 3.58 (s, 3 H, OCH_3),

4.03–4.05 (m, 1 H, C_5H_3), 4.08 (dd, $J_{H,P}$ = 4.6 Hz, $J_{H,H}$ = 2.4 Hz, 1 H, C_5H_3), 4.20 (s, 5 H, C_5H_5), 4.28 (dd, 3.6 Hz, $J_{H,H}$ = 1.9 Hz, 1 H, C_5H_3), 7.40 (td, $J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 2.7 Hz, 2 H, Ph), 7.42–7.53 (m, 4 H, Ph), 7.63–7.68 (m, 2 H, Ph), 7.84–7.90 (m, 2 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.5 (d, $J_{C,P}$ = 8.0 Hz, C_5H_3), 58.1 (s, OCH_3), 62.4 (d, $^1J_{C,P}$ = 116.1 Hz, C_5H_3-P), 63.9 (d, $J_{C,P}$ = 10.8 Hz, C_5H_3), 68.3 (d, $J_{C,P}$ = 11.0 Hz, C_5H_3), 69.8 (s, C_5H_5), 127.9–128.1 (m, Ph), 128.4–128.6 (m, C-OCH_3), 131.3–131.4 (m, Ph), 131.9 (d, $J_{C,P}$ = 10.0 Hz, Ph), 133.6–135.0 (m, P-Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 28.3. HRMS (ESI-TOF, m/z): calcd for $C_{23}H_{21}FePO_2$ 416.0623, found 416.0658 $[M]^+$.

^{s}Butyldiphenylphosphine Sulfide (23)

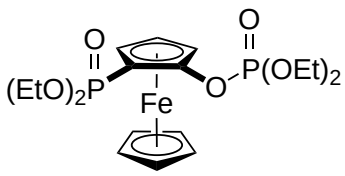


23

Ferrocenyl diphenylthiaphosphinate (**10**, 620 mg, 1.48 mmol) was dissolved in tetrahydrofuran (10 mL) and cooled to –60 °C. After dropwise addition of ^{s}BuLi (1.80 mL, 2.37 mmol) the reaction was stirred for 4 h at –40 °C and subsequently stopped by adding iodomethane (0.15 mL, 2.37 mmol) in a single portion. Purification was realized by column chromatography (silica, 3.5 · 11 cm column size). Ferrocenyl methyl ether (**22**, 86 %) was eluted using a 1/1 (v/v) hexane/toluene mixture followed by **23** using toluene.

Yield: 280 mg (1.01 mmol, 68 % based on **10**). Anal. calcd for $C_{16}H_{19}PS$ (274.36 g/mol): C, 70.04; H, 6.98. Found: C, 70.15; H, 6.93. Mp.: 93 °C. ^1H NMR ($CDCl_3$, δ): 0.97 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_2-CH_3), 1.15 (dq, $^2J_{H,P}$ = 19.4 Hz, $^3J_{H,H}$ = 6.8 Hz, 3 H, Ch-CH_3), 1.43–1.67 (m, 2 H, CH_2), 2.56–2.66 (m, 1 H, CH), 7.41–7.51 (m, 6 H, *m,p*-Ph), 7.89–7.97 (m, 4 H, *o*-Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 12.0 (s, CH-CH_3), 12.1 (d, $^3J_{C,P}$ = 15.2 Hz, CH_2-CH_3), 22.6 (s, CH_2), 34.8 (d, $^1J_{C,P}$ = 55.7 Hz, CH), 128.4–128.6 (m, *m*-Ph), 131.18–131.25 (m, *p*-Ph), 131.3–131.4 (m, *o*-Ph), 131.9 (d, $^1J_{C,P}$ = 76.4 Hz, Ph-P), 132.1 (d, $^1J_{C,P}$ = 76.3 Hz, Ph-P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 52.8. HRMS (ESI-TOF, m/z): calcd for $C_{16}H_{19}PS + H$ 275.1018, found 275.1005 $[M+H]^+$.

2-(Diethoxyphosphoryl)ferrocenyl Diethyl Phosphate (*rac*-32)



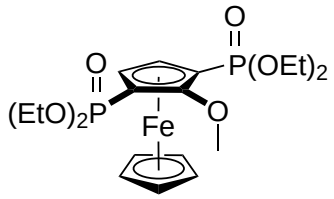
32

LDA was prepared by treating diisopropylamine (0.5 mL, 3.6 mmol) with BuLi (1.45 mL, 3.6 mmol) in tetrahydrofuran (20 mL) at –60 °C. After stirring for 10 min at this temperature phosphate **6** (600 mg, 1.8 mmol) was dropwise added. The solution was stirred for 4 h between –30 °C and –15 °C, while the color changed from orange to red. The reaction was stopped by adding diethyl chlorophosphate (0.75 mL, 5.2 mmol) in a single portion. The reaction mixture was allowed to warm to ambient temperature. Purification was realized by column chromatography (silica, 3 · 8 cm column size) using a 9/1 (v/v) ethyl acetate/methanol mixture as the eluent, giving **32** as an orange oil.

Yield: 290 mg (0.6 mmol, 33 % based on **6**). ^1H NMR ($CDCl_3$, δ): 1.33 (td, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,P}$ = 0.9 Hz, 3 H, CH_3), 1.34 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.38 (t, $^3J_{H,H}$ = 7.1 Hz,

3 H, CH_3), 1.43 (td, $^3J_{H,H}$ = 7.1 Hz, $^4J_{H,P}$ = 1.1 Hz, 3 H, CH_3), 4.09–4.33 (m, 10 H, CH_2, C_5H_3), 4.39 (s, 5 H, C_5H_5), 4.79 (ddd, $J_{H,P}$ = 2.3 Hz, $J_{H,H}$ = 2.3 Hz, $J_{H,H}$ = 1.5 Hz, 2 H C_5H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 15.8–16.0 (m, CH_3), 16.2–16.3 (m, CH_3), 58.1 (dd, $^1J_{C,P}$ = 208.7 Hz, $^3J_{C,P}$ = 7.1 Hz, C-P), 61.6 (d, $^2J_{C,P}$ = 5.7 Hz, CH_2), 61.8 (d, $^2J_{C,P}$ = 5.7 Hz, CH_2), 62.3 (d, $J_{C,P}$ = 10.2 Hz, C_5H_3), 64.4 (d, $^2J_{C,P}$ = 6.4 Hz, CH_2), 64.5 (d, $^2J_{C,P}$ = 6.4 Hz, CH_2), 65.0 (d, $J_{C,P}$ = 13.7 Hz, C_5H_3), 67.2 (d, $J_{C,P}$ = C_5H_3), 71.1 (s, C_5H_5), 118.3 (dd, $^2J_{C,P}$ = 9.1 Hz, $^2J_{C,P}$ = 4.5 Hz, C-O).$^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –6.1 (s, O–P(O)$(OEt)_2$), 22.2 (C–P(O)$(OEt)_2$). HRMS (ESI-TOF, m/z): calcd for $C_{18}H_{28}FeO_7P_2$ 497.0552, found 497.0635 $[M]^+$.

1,3-Bis(*O*,*O*'-diethylphosphonato)-2-methoxyferrocene (33)

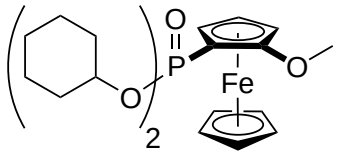


33

LDA was prepared by treating diisopropylamine (0.11 mL, 0.78 mmol) with BuLi (0.31 mL, 0.75 mmol) in tetrahydrofuran (10 mL) at –60 °C. After stirring for 10 minutes at this temperature **32** (183 mg, 0.39 mmol) was added in a single portion. The solution was stirred for 4 h between –30 °C and –20 °C, while the solution turned dark. The reaction was stopped by adding iodomethane (0.1 mL, 1.6 mmol) in a single portion. Purification was realized by column chromatography (silica, 2 · 15 cm column size) using a 9/1 (v/v) ethyl acetate/methanol mixture as the eluent, giving **33** as an orange oil.

Yield: 40 mg (0.08 mmol, 21 % based on **32**). ^1H NMR ($CDCl_3$, δ): 1.35 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.38 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 3.89 (s, 3 H, OCH_3), 4.13–4.26 (m, 8 H, CH_2), 4.43 (t, $^{H,P}J_2$ =.55 Hz, 2 H, C_5H_2), 4.49 (s, 5 H, C_5H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 16.4–16.5 (m, CH_3), 62.1 (t, $^2J_{C,P}$ = 5.5 Hz, CH_2), 63.1 (dd, $^1J_{C,P}$ = 211.9 Hz, $^3J_{C,P}$ = 10.7 Hz, C-P), 64.0 (s, OCH_3), 69.4 (t, $^2J_{C,P}$ = 13.6 Hz, C_5H_2), 128.7 (t, $^2J_{C,P}$ = 63.2 Hz, C-OCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 22.1. HRMS (ESI-TOF, m/z): calcd for $C_{19}H_{30}P_2O_7$ + Na 511.0709, found 511.0747 $[M+Na]^+$.

Dicyclohexyl (2-Methoxyferrocenyl)phosphonate (31a)



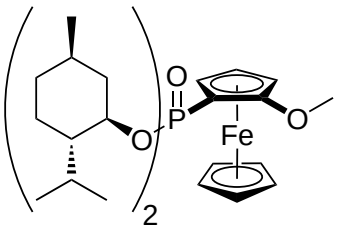
31a

Ferrocenyl dicyclohexyl phosphate (**30a**, 100 mg, 0.224 mmol) was reacted as described in the general procedure GP3. Compound **31a** was obtained as an orange oil.

Yield: 100 mg (0.217 mmol, 97 % based on **30a**). ^1H NMR ($CDCl_3$, δ): 1.26–1.38 (m, 6 H, CH_2), 1.17–1.62 (m, 6 H, CH_2), 1.72–1.80 (m, 4 H, CH_2), 1.87–1.98 (m, 4 H, CH_2), 3.68 (s, 3 H, OCH_3), 3.98–3.99 (m, 1 H, C_5H_3), 4.16–4.17 (m, 1 H, C_5H_3), 4.21–4.22 (m, 1 H, C_5H_3), 4.31 (s, 5 H, C_5H_5), 4.47–4.55 (m, 2 H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.57 (CH_2), 23.59 (CH_2), 25.35 (CH_2), 25.36 (CH_2), 33.6 (d, $^2J_{C,P}$ = 4.7 Hz, CH_2), 33.7 (d, $^2J_{C,P}$ = 3.2 Hz, CH_2), 33.8 (d, $^2J_{C,P}$ = 3.8 Hz, CH_2), 33.9 (d, $^2J_{C,P}$ = 3.2 Hz, CH_2), 55.0 (d, $J_{C,P}$ = 11.4 Hz, C_5H_3), 58.0 (OCH_3), 59.1 (d, $^1J_{C,P}$ = 216.6 Hz, C-P), 63.4 (d, $J_{C,P}$ = 14.0 Hz, C_5H_3), 67.1 (d, $J_{C,P}$

= 12.8 Hz, C_5H_3), 69.9 (C_5H_5), 74.76 (d, $^2J_{C,P}$ = 6.5 Hz, C1), 74.82 (d, $^2J_{C,P}$ = 7.2 Hz, C1), 128.4 (d, $^2J_{C,P}$ = 10.4 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 21.2 ($^1J_{P,C}$ = 216.8 Hz). HRMS (ESI-TOF, m/z): calcd for $C_{23}H_{33}FeO_4P$ + H 461.1539, found 461.1530 $[M+H]^+$.

Di-(1*R*)-menthyl (2-Methoxyferrocenyl)phosphonate (31b)

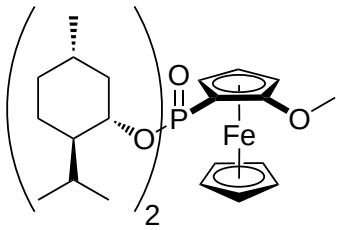


31b

Ferrocenyl di-(1*R*)-menthylphosphate (**30b**, 100 mg, 0.18 mmol) was reacted as described in procedure GP3. Compound **31b** was obtained as orange oil.

Yield: 101 mg (0.18 mmol, 99 % based on **30b**). Mixture of two diastereomers. ^1H NMR ($CDCl_3$, δ): 0.41–1.06 (m, 22 H), 1.12–1.50 (m, 6 H), 1.57–1.71 (m, 4 H), 2.02–2.48 (m, 4 H), 3.62–3.68 (m, 3 H, OCH_3), 3.92–4.32 (m, 10 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 15.4–15.8 (m, CH_3), 21.1–21.3 (m, CH_3), 22.01–22.04 (m, CH_3), 22.5–22.7 (m, CH_2), 24.6–25.4 (m, CH), 31.4–31.5 (m, CH), 34.1–34.2 (m, CH_2), 43.2–43.5 (m, CH_2), 48.7–49.1 (m, CH), 54.6–54.8 (m, C_5H_3), 57.4 (OCH_3), 57.5 (d, $^1J_{C,P}$ = 216.9 Hz, C-P), 57.9 (OCH_3), 58.5 (d, $^1J_{C,P}$ = 216.4 Hz, C-P), 63.4 (d, $J_{C,P}$ = 14.5 Hz, C_5H_3), 66.7 (d, $J_{C,P}$ = 11.8 Hz, C_5H_3), 68.1 (d, $J_{C,P}$ = 14.4 Hz, C_5H_3), 69.93 (C_5H_5), 69.96 (C_5H_5), 76.4 (d, $^2J_{C,P}$ = 6.3 Hz, C1), 76.6 (d, $^2J_{C,P}$ = 6.6 Hz, C1), 76.7 (d, $^2J_{C,P}$ = 6.8 Hz, C1), 76.9 (d, $^2J_{C,P}$ = 7.6 Hz, C1), 127.9 (d, $^2J_{C,P}$ = 9.0 Hz, C_{C5H3}-O), 129.0 (d, $^2J_{C,P}$ = 10.9 Hz, C_5H_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 20.6, 21.8. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{49}FeO_4P$ 572.2713, found 572.2733 $[M]^+$.

Di-(1*S*)-menthyl (2-Methoxyferrocenyl)phosphonate (31c)



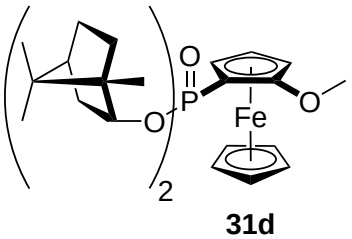
31c

Ferrocenyl di-(1*S*)-menthyl phosphate (**30c**, 100 mg, 0.18 mmol) was reacted as described in procedure GP3. Compound **31c** was obtained as an orange oil and a mixture of two diastereomers.

Yield: 101 mg (0.18 mmol, 99 % based on **30c**). ^1H NMR ($CDCl_3$, δ): 0.41–0.57 (m, 3 H, CH_3), 0.78–0.94 (m, 19 H, CH_2, CH_3), 0.98–1.49 (m, 6 H, CH_2, CH), 1.55–1.68 (m, 4 H, CH_2, CH), 2.00–2.49 (m, 4 H, CH_2, CH), 3.61–3.67 (3 H, OCH_3), 3.96–4.30 (m, 10 H, C_5H_5, C_5H_3, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 15.4–15.8 (CH_3), 20.9–21.3 (CH_3), 21.98 (CH_3), 22.02 (CH_3), 22.6–22.8 (CH_2), 24.6 (CH), 25.1 (CH), 25.4 (CH), 31.4–31.5 (CH), 34.1–34.2 (CH_2), 43.2–43.5 (m, C6), 48.7 (d, $^3J_{C,P}$ = 7.4 Hz, C2), 48.8 (d, $^3J_{C,P}$ = 7.4 Hz, C2), 48.9 (d, $^3J_{C,P}$ = 6.4 Hz, C2), 49.1 (d, $^3J_{C,P}$ = 7.4 Hz, C2), 54.7–54.9 (m, C_5H_3), 57.4 (OCH_3), 57.6 (d, $^1J_{C,P}$ = 216.7 Hz, C-P), 57.9 (OCH_3), 58.6 (d, $^1J_{C,P}$ = 216.6 Hz, C-P), 63.4 (d, $J_{C,P}$ = 13.6 Hz, C_5H_3), 66.7 (d, $J_{C,P}$ = 12.0 Hz, C_5H_3), 68.0 (d, $J_{C,P}$ = 14.2 Hz, C_5H_3), 69.92 (C_5H_5), 69.94 (C_5H_5), 76.4 (d, $^2J_{C,P}$ = 6.3 Hz, C1), 76.6 (d, $^2J_{C,P}$ = 6.6 Hz, C1), 76.7 (d, $^2J_{C,P}$ = 6.9 Hz, C1), 76.9 (d, $^2J_{C,P}$ = 7.6 Hz, C1), 127.9 (d, $^2J_{C,P}$ = 9.1 Hz, C_{C5H3}-O), 129.0 (d, $^2J_{C,P}$ = 10.9 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 20.6 ($^1J_{P,C}$ = 216.4 Hz), 21.8

($^1J_{P,C}$ = 216.9 Hz).

Di-(1*S*)-borneyl (2-Methoxyferrocenyl)phosphonate (31d)

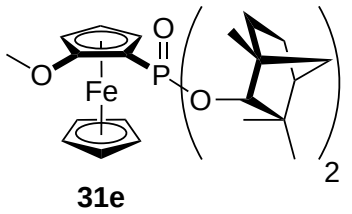


31d

Di-(1*S*)-borneyl ferrocenyl phosphate (**30d**, 100 mg, 0.18 mmol) was reacted as described in procedure GP3. Compound **31d** was obtained as an orange oil and a mixture of two diastereomers.

Yield: 102 mg (0.18 mmol, 99 % based on **30d**). ^{1}H NMR ($CDCl_3$, δ): 0.79–0.93 (m, 18 H, CH_3), 1.20–1.32 (m, 6 H, CH_2), 1.60–1.67 (m, 2 H, H4), 1.69–1.78 (m, 2 H, CH_2), 1.99–2.13 (m, 2 H, CH_2), 2.17–2.36 (m, 2 H, CH_2), 3.65–3.66 (m, 3 H, OCH_3), 3.98–4.00 (m, 1 H, C_5H_3), 4.15–4.17 (m, 1 H, C_5H_3), 4.20–4.24 (m, 1 H, C_5H_3), 4.32 (s, 5 H, C_5H_5), 4.59–4.73 (m, 2 H, H2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 13.2–13.4 (CH_3), 18.80–18.82 (m, CH_3), 19.90–19.93 (CH_3), 26.5–26.9 (C5/C6), 28.08–28.15 (C5/C6), 37.1–37.8 (m, C3), 44.86–44.93 (C4), 47.4–47.5 (C7), 49.6–49.7 (C1), 54.7–54.9 (m, C_5H_3), 57.7 (OCH_3), 57.9 (OCH_3), 58.3 (d, $^1J_{C,P}$ = 218.1 Hz, C-P), 58.7 (d, $^1J_{C,P}$ = 217.9 Hz, C-P), 63.41 (d, $J_{C,P}$ = 14.2 Hz, C_5H_3), 63.44 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 66.95 (d, $J_{C,P}$ = 12.8 Hz, C_5H_3), 67.03 (d, $J_{C,P}$ = 13.2 Hz, C_5H_3), 69.8 (C_5H_5), 69.9 (C_5H_5), 81.24 (d, $^2J_{C,P}$ = 6.9 Hz, C2), 81.27 (d, $^2J_{C,P}$ = 6.1 Hz, C2), 81.5 (d, $^2J_{C,P}$ = 7.1 Hz, C2), 81.7 (d, $^2J_{C,P}$ = 6.4 Hz, C2), 128.4 (d, $^2J_{C,P}$ = 9.9 Hz, C_{C5H3}-O), 128.6 (d, $^2J_{C,P}$ = 10.3 Hz, C_{C5H3}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 22.9, 23.2. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{45}FeO_4P$ 568.2400, found 568.2414 $[M]^+$.

(R_p)-Di-(1*R*)-α-fenchyl (2-Methoxyferrocenyl)phosphonate (31e)

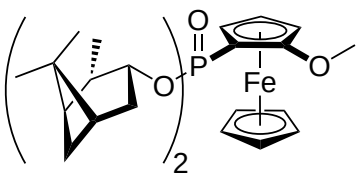


31e

Ferrocenyl di-(1*R*)-α-fenchyl phosphate (**30e**) (100 mg, 0.18 mmol) was reacted as described in procedure GP4. Compound **31e** was obtained as an orange solid. The spectroscopic data correspond to the single diastereomer, which is obtained after crystallization (0.80 *de*).

Yield: 90 mg (0.16 mmol, 88 % based on **30e**). Mp.: 186–188 °C. ^{1}H NMR ($CDCl_3$, δ): 0.87 (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3), 0.96–1.06 (m, 5 H), 1.10–1.18 (m, 8 H), 1.39–1.52 (m, 4 H), 1.64–1.87 (m, 6 H), 3.68 (s, 3 H, OCH_3), 3.99–4.06 (m, 3 H, H2, C_5H_3), 4.14–4.18 (m, 1 H, C_5H_3), 4.19–4.23 (m, 1 H, C_5H_3), 4.35 (s, 5 H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.2 (CH_3), 19.6 (CH_3), 21.1 (CH_3), 21.4 (CH_3), 25.8–26.2 (m, C5/C6), 29.7 (CH_3), 29.8 (CH_3), 39.1 (d, $^3J_{C,P}$ = 2.2 Hz, C7), 39.7 (d, $^3J_{C,P}$ = 2.2 Hz, C7), 41.07 (CH_2), 41.09 (CH_2), 48.0 (C4), 48.1 (C4), 49.25 (d, $^3J_{C,P}$ = 4.8 Hz, C1), 49.34 (d, $^3J_{C,P}$ = 4.4 Hz, C1), 54.8 (d, $J_{C,P}$ = 11.8 Hz, C_5H_3), 57.8 (OCH_3), 58.2 (d, $^1J_{C,P}$ = 216.6 Hz, C-P), 63.6 (d, $^1J_{C,P}$ = 13.6 Hz, C_5H_3), 67.2 (d, $^1J_{C,P}$ = 12.1 Hz, C_5H_3), 69.8 (C_5H_5), 87.8 (d, $^2J_{C,P}$ = 6.4 Hz, C2), 88.0 (d, $^2J_{C,P}$ = 6.7 Hz, C2), 128.8 (d, $^2J_{C,P}$ = 10.3 Hz, C_{C5H3}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 22.4. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{45}FeO_4P$ 568.2400, found 568.2433 $[M]^+$.

Di-(1*S*)-isopinocampheyl (2-Methoxyferrocenyl)phosphonate (31f)

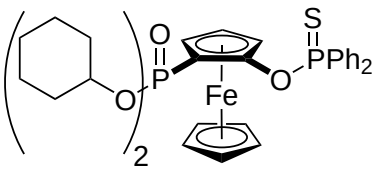


31f

Ferrocenyl di-(1*S*)-isopinocampheyl phosphate (**30f**, 100 mg, 0.18 mmol) was reacted as described in procedure GP3. Compound **31f** was obtained as an orange oil in a mixture of two diastereomers.

Yield: 85 mg (0.15 mmol, 80 % based on **30f**). ^{1}H NMR ($CDCl_3$, δ): 0.90–0.93 (m, 6 H), 1.05–1.21 (m, 14 H), 1.77–1.83 (m, 2 H), 1.89–2.08 (m, 4 H), 2.15–2.26 (m, 2 H), 2.33–2.39 (m, 2 H), 2.46–2.60 (m, 2 H), 3.67/3.68 (s, 3 H, OCH_3), 3.99–4.00 (m, 1 H, C_5H_3), 4.16–4.18 (m, 1 H, C_5H_3), 4.22–4.27 (m, 1 H, C_5H_3), 4.320/4.321 (s, 5 H, C_5H_5), 4.70–4.85 (m, 2 H, H1). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.95 (CH_3), 20.02 (CH_3), 23.78 (CH_3), 23.81 (CH_3), 23.83 (CH_3), 27.43 (CH_3), 27.47 (CH_3), 27.49 (CH_3), 27.50 (CH_3), 33.6 (CH_2), 33.7 (CH_2), 33.8 (CH_2), 37.1 (d, $^{3}J_{C,P}$ = 3.1 Hz, CH_2), 27.3 (d, $^{3}J_{C,P}$ = 2.87 Hz, CH_2), 37.4 (d, $^{3}J_{C,P}$ = 2.5 Hz, CH_2), 37.5 (d, $^{3}J_{C,P}$ = 2.2 Hz, CH_2), 38.15 (C6), 38.17 (C6), 38.20 (C6), 41.52 (C5), 41.53 (C5), 41.56 (C5), 41.60 (C5), 45.5–45.8 (m, C2), 47.7 (C1), 47.8 (C1), 55.03 (d, $J_{C,P}$ = 11.3 Hz, C_5H_3), 55.09 (d, $J_{C,P}$ = 11.3 Hz, C_5H_3), 57.96 (OCH_3), 57.99 (OCH_3), 58.5 (d, $^{1}J_{C,P}$ = 215.8 Hz, C-P), 58.7 (d, $^{1}J_{C,P}$ = 215.7 Hz, C-P), 63.4 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 63.4 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 67.2 (d, $J_{C,P}$ = 12.8 Hz, C_5H_3), 67.4 (d, $J_{C,P}$ = 12.9 Hz, C_5H_3), 70.0 (C_5H_5), 75.9 (d, $^{2}J_{C,P}$ = 6.8 Hz, C3), 76.0 (d, $^{2}J_{C,P}$ = 7.3 Hz, C3), 76.2 (d, $^{2}J_{C,P}$ = 6.8 Hz, C3), 76.3 (d, $^{2}J_{C,P}$ = 7.4 Hz, C3), 128.4 (d, $^{2}J_{C,P}$ = 10.1 Hz, C-O), 128.6 (d, $^{2}J_{C,P}$ = 10.2 Hz, C-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 21.24, 21.28. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{45}FeO_4P$ 568.24000, found 568.2453 $[M]^+$.

Dicyclohexyl (2-(Diphenylthiophosphinato)ferrocenyl)phosphonate (*rac*-34)



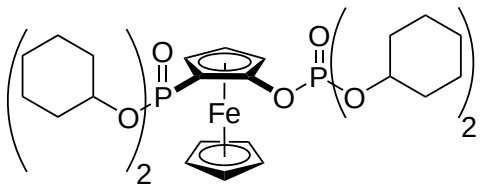
34

Dicyclohexyl ferrocenyl phosphate (**30a**, 100 mg, 0.22 mmol), diisopropylamine (0.07 mL, 0.50 mmol), BuLi (0.2 mL, 0.50 mmol), TMEDA (0.07 mL, 0.46 mmol), $ClPPh_2$ (0.17 mL, 0.93 mmol) and sulfur (60 mg, 1.9 mmol) were reacted according to the general procedure GP3. The obtained reaction mixture was filtered through a pad of celite using hexane to remove the excess of sulfur. Purification was realized by column chromatography (silica, 2 · 8 cm column size) using a 9/1 (v/v) dichloromethane/ethyl acetate mixture as the eluent, giving **34** as an orange oil.

Yield: 65 mg (0.098 mmol, 44 % based on **30a**). ^{1}H NMR ($CDCl_3$, δ): 1.19–1.31 (m, 6 H, CH_2), 1.41–1.54 (m, 6 H, CH_2), 1.63–1.78 (m, 4 H, CH_2), 1.82–1.88 (m, 1 H, CH_2), 1.88–2.02 (m, 3 H, CH_2), 3.96 (ddd, $J_{H,H}$ = $J_{H,H}$ = $J_{H,P}$ = 2.8 Hz, 1 H, C_5H_3), 4.19–4.23 (m, 6 H, C_5H_5, C_5H_3), 4.45–4.54 (m, 2 H, H1), 4.60–4.62 (m, 1 H, C_5H_3), 7.39–7.43 (m, 2 H, Ph), 7.45–7.49 (m, 1 H, Ph), 7.50–7.56 (m, 3 H, Ph), 7.96–8.00 (m, 2 H, Ph), 8.12–8.17 (m, 2 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 23.55 (CH_2), 23.64 (CH_2), 23.70 (CH_2), 23.72 (CH_2), 25.21 (CH_2), 25.24 (CH_2), 33.7 (d, $J_{C,P}$ = 4.5 Hz, CH_2), 33.9–34.0 (m, CH_2), 59.8 (dd, $^{1}J_{C,P}$ =

217.1 Hz, $^{3}J_{C,P}$ = 5.4 Hz, C_{C5H3}-P), 62.8 (dd, $J_{C,P}$ = 10.3 Hz, $J_{C,P}$ = 5.5 Hz, C_5H_3), 64.6 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 66.9 (d, $J_{C,P}$ = 12.8 Hz, C_5H_3), 71.3 (C_5H_5), 75.1 (d, $^{2}J_{C,P}$ = 6.3 Hz, C1), 75.2 (d, $^{2}J_{C,P}$ = 6.5 Hz, C1), 118.8 (dd, $^{2}J_{C,P}$ = 9.2 Hz, $^{2}J_{C,P}$ = 6.8 Hz, C_{C5H3}-O), 128.4 (d, $J_{C,P}$ = 5.5 Hz, Ph), 128.5 (d, $J_{C,P}$ = 5.5 Hz, Ph), 131.5 (d, $J_{C,P}$ = 11.8 Hz, Ph), 131.8 (d, $J_{C,P}$ = 11.9 Hz, Ph), 131.9 (d, $J_{C,P}$ = 3.0 Hz, Ph), 132.1 (d, $J_{C,P}$ = 3.0 Hz, Ph), 134.0 (d, $^{1}J_{C,P}$ = 111.1 Hz, C_{Ph}-P), 134.4 (d, $^{1}J_{C,P}$ = 111.4 Hz, C_{Ph}-P.) $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 20.4 (PO_3), 80.3 (P=S). HRMS (ESI-TOF, m/z): calcd for $C_{34}H_{40}FeO_4P_2S$ + H 663.1545, found 663.1477 $[M+H]^+$.

Dicyclohexyl (2-(*O*,*O*'-Dicyclohexylphosphonato)ferrocenyl) Phosphate (35a)

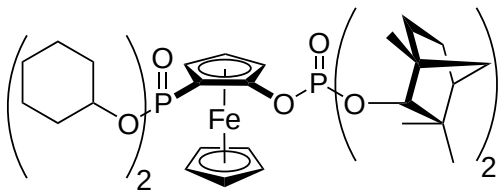


35a

Dicyclohexyl ferrocenyl phosphate (**30a**, 100 mg, 0.22 mmol), diisopropylamine (0.07 mL, 0.50 mmol), BuLi (0.2 mL, 0.50 mmol), TMEDA (0.07 mL, 0.46 mmol) and **29a** (375 mg, 1.7 mmol) were reacted according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 8 cm column size) using a 80/20 (v/v) dichloromethane/ethyl acetate mixture (R_f = 0.43) as the eluent, giving **35a** was obtained as and orange oil.

Yield: 150 mg (0.188 mmol, 81 % based on **30a**). ^{1}H NMR ($CDCl_3$, δ): 1.28–1.41 (m, 12 H, CH_2), 1.45–1.65 (m, 12 H, CH_2), 1.67–1.81 (m, 8 H, CH_2), 1.83–1.89 (m, 1 H, CH_2), 1.89–2.06 (m, 7 H, CH_2), 4.02–4.05 (m, 1 H, C_5H_3), 4.22–4.25 (m, 1 H, C_5H_3), 4.36 (s, 5 H, C_5H_5), 4.40–4.47 (m, 1 H, H1), 4.48–4.54 (m, 1 H, H1), 4.78–4.82 (m, 1 H, C_5H_3). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 23.45 (CH_2), 23.49 (CH_2), 23.60 (CH_2), 23.62 (CH_2), 23.7 (CH_2), 25.11 (CH_2), 25.14 (CH_2), 25.30 (CH_2), 25.34 (CH_2), 33.2 (d, $^{3}J_{C,P}$ = 4.7 Hz, CH_2), 33.27 (d, $^{3}J_{C,P}$ = 4.5 Hz, CH_2), 33.31 (d, $^{3}J_{C,P}$ = 4.2 Hz, CH_2), 33.5 (d, $^{3}J_{C,P}$ = 4.4 Hz, CH_2), 33.8 (d, $^{3}J_{C,P}$ = 3.7 Hz, CH_2), 33.9 (d, $^{3}J_{C,P}$ = 3.9 Hz, CH_2), 59.7 (dd, $^{1}J_{C,P}$ = 217.0 Hz, $^{3}J_{C,P}$ = 8.6 Hz, C-P), 62.0 (d, $J_{C,P}$ = 11.3, C_5H_3), 64.5 (d, $J_{C,P}$ = 13.8, C_5H_3), 67.4 (d, $J_{C,P}$ = 13.1, C_5H_3), 71.2 (C_5H_5), 74.9 (d, $^{2}J_{C,P}$ = 5.9 Hz, C1), 75.1 (d, $^{2}J_{C,P}$ = 6.6 Hz, C1), 77.91 (d, $^{2}J_{C,P}$ = 6.4 Hz, C), 77.94 (d, $^{2}J_{C,P}$ = 6.3 Hz, C1), 118.5 (dd, $^{2}J_{C,P}$ = 8.9 Hz, $^{2}J_{C,P}$ = 5.0 Hz, C_{C5H3}-O). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): –7.4 (PO_4), 19.8 (PO_3). HRMS (ESI-TOF, m/z): calcd for $C_{34}H_{52}FeO_7P_2$ + Na 713.2340, found 713.2373 $[M+Na]^+$.

(2-(Dicyclohexylphosphonato) Ferrocenyl Di-(1*R*)-α-fenchyl Phosphate (35b)



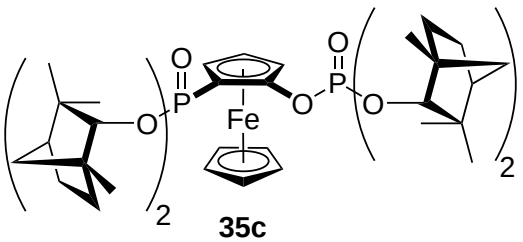
35b

Dicyclohexyl ferrocenyl phosphate (**30a**, 100 mg, 0.22 mmol), diisopropylamine (0.07 mL, 0.50 mmol), BuLi (0.2 mL, 0.50 mmol), TMEDA (0.07 mL, 0.46 mmol) and **29e** (370 mg, 0.95 mmol) were reacted according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 12 cm

column size) using a 80/20 (v/v) dichloromethane/ethyl acetate mixture ($R_f = 0.45$) as the eluent, giving **35b** as an orange oil in a mixture of two diastereomers (0.10 *de*).

Yield: 150 mg (0.188 mmol, 81 % based on **30a**). ^{1}H NMR ($CDCl_3$, δ): 0.84–1.58 (m, 40 H, C_6H_{11}, $C_{10}H_{17}$), 1.67–1.77 (m, 8 H, C_6H_{11}, $C_{10}H_{17}$), 1.92–2.03 (m, 4 H, C_6H_{11}), 3.98–4.13 (m, 3 H, C_5H_3, $C_{10}H_{17}$), 4.18–4.23 (m, 1 H, C_5H_3), 4.36 (s, 5 H, C_5H_5), 4.44–4.57 (m, 1 H, C_6H_{11}), 4.89–4.98 (m, 1 H, C_5H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.4–19.5 (m, CH_3), 20.7–21.1 (m, CH_3), 23.76–23.84 (m, $CyCH_2$), 25.7–26.0 (m, C5/C6), 29.8–30.0 (m, CH_3), 33.8–34.0 (m, $CyCH_2$), 39.5–39.7 (m, C3), 40.9–41.0 (m, C7), 47.9–48.0 (C4), 49.2–49.4 (m, C1), 59.7 (d, $^1J_{C,P} = 218.7$ Hz, $^3J_{C,P} = 8.4$ Hz, C-P), 62.5 (d, $J_{C,P} = 10.6$ Hz, C_5H_3), 62.7 (d, $J_{C,P} = 10.8$ Hz, C_5H_3), 64.30 (d, $J_{C,P} = 13.6$ Hz, C_5H_3), 64.36 (d, $J_{C,P} = 13.7$ Hz, C_5H_3), 67.5 (d, $J_{C,P} = 12.8$ Hz, C_5H_3), 67.6 (d, $J_{C,P} = 12.4$ Hz, C_5H_3), 71.21 (C_5H_5), 71.23 (C_5H_5), 74.9 (d, $^2J_{C,P} = 6.4$ Hz, CyC1), 75.05 (d, $^2J_{C,P} = 5.8$ Hz, CyC1), 75.18 (d, $^2J_{C,P} = 6.7$ Hz, CyC1), 91.3–91.5 (m, FnC1), 119.0–119.2 (m, C_{C5H3}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –4.4 (PO_4), -3.7 (PO_4), 19.88 (C-PO_3), 19.93 (C-PO_3). HRMS (ESI-TOF, m/z): calcd for $C_{42}H_{64}FeO_7P_2$ + H 799.3550, found 799.3496 $[M+H]^+$.

Di-(1*R*)-fenchyl (2-(Di-(1*R*)-α-fenchylphosphonato)ferrocenyl) Phosphate (35c)



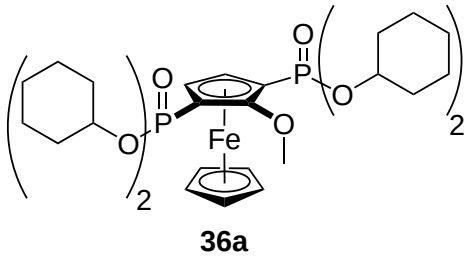
35c

Di-(1*R*)-α-fenchyl ferrocenyl phosphate (**30e**, 300 mg, 0,54 mmol), LiTMP (210 mg, 1,41 mmol), TMEDA (0,15 mL, 1,0 mmol) and **29e** (420 mg, 1,08 mmol) were reacted according to the general procedure GP4. Purification was realized by column chromatography (silica, $2 \cdot 12$ cm column size) using a 96/4 (v/v) dichloromethane/ethyl acetate mixture as the eluent, giving **35c** as an orange oil in a mixture of two diastereomers (0.95 *de*).

Yield: 422 mg (0.465 mmol, 86 % based on **30e**). ^{1}H NMR ($CDCl_3$, δ): 0.73 (s, 3 H, CH_3), 0.88–1.27 (m, 41 H, $C_{10}H_{17}$), 1.34–1.58 (m, 8 H, $C_{10}H_{17}$), 1.61–1.81 (m, 11 H, $C_{10}H_{17}$), 1.86–1.90 (m, 1 H, $C_{10}H_{17}$), 3.89 (dd, $^3J_{H,P} = 10.2$ Hz, $J_{H,H} = 1.5$ Hz, H2), 4.04–4.10 (m, 3 H, H2, C_5H_3), 4.14 (dd, $^3J_{H,P} = 8.7$ Hz, $J_{H,H} = 1.5$ Hz, H2), 4.23 (dd, $^3J_{H,P} = 9.5$ Hz, $J_{H,H} = 1.4$ Hz, H2), 4.41 (s, 5 H, C_5H_5), 4.97–4.98 (m, 1 H, C_5H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.2 (CH_3), 19.66 (CH_3), 19.67 (CH_3), 19.9 (CH_3), 20.9 (CH_3), 21.1 (CH_3), 21.5 (CH_3), 22.0 (CH_3), 25.77 (C5/C6), 25.81 (C5/C6), 25.89 (C5/C6), (C5/C6), 26.00 (C5/C6), 26.03 (C5/C6), 26.13 (C5/C6), 26.14 (C5/C6), 29.7 (CH_3), 29.86 (CH_3), 29.89 (CH_3), 30.1 (CH_3), 39.3 (d, $^3J_{C,P} = 1.4$ Hz, C3), 39.55 (d, $^3J_{C,P} = 2.5$ Hz, C3), 39.64 (d, $^3J_{C,P} = 2.6$ Hz, C3), 39.8 (d, $^3J_{C,P} = 1.2$ Hz, C3), 40.8 (C7), 41.0 (C7), 41.2 (C7), 47.96 (C4), 47.98 (C4), 48.05 (C4), 48.2 (C4), 49.1 (d, $^3J_{C,P} = 5.6$ Hz, C1), 49.4 (d, $^3J_{C,P} = 5.1$ Hz, C1), 49.5 (d, $^3J_{C,P} = 5.2$ Hz, C1), 59.1 (dd, $^1J_{C,P} = 217.1$ Hz, $^3J_{C,P} = 10.0$ Hz, C-P), 62.0 (d, $J_{C,P} = 10.8$, C_5H_3), 64.7 (d, $J_{C,P} = 12.8$, C_5H_3), 66.8 (d, $J_{C,P} = 10.3$, C_5H_3), 71.2 (C_5H_5), 87.6 (d, $^2J_{C,P} = 5.5$ Hz, C_2PO_3), 88.3 (d, $^2J_{C,P} = 7.8$ Hz, C_2PO_3), 91.1 (d, $^2J_{C,P} = 6.5$ Hz, C_2PO_4), 91.7 (d, $^2J_{C,P} =$

6.6 Hz, C_2PO_4), 120.69 (C_{C5H3}-O), 120.73 (C_{C5H3}-O), 120.78 (C_{C5H3}-O), 120.81 (C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –3.5 (d, $^4J_{P,P}$ = 0.9 Hz, PO_4), 19.6 (d, $^4J_{P,P}$ = 1.9 Hz, PO_3; dd $^1J_{P,C}$ = 216.9 Hz, 1.9 Hz). HRMS (ESI-TOF, m/z): calcd for $C_{50}H_{76}FeO_7P_2$ + H 907.4489, found 907.4409 $[M+H]^+$.

1,3-Bis(*O*,*O*'-dicyclohexylphosphonato)-2-methoxyferrocene (36a)

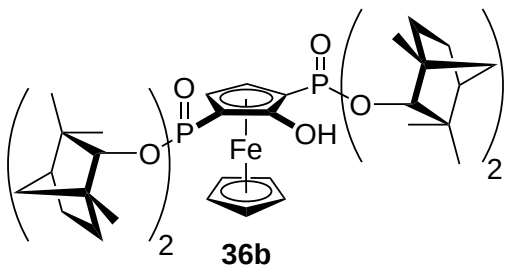


36a

Dicyclohexyl (2-(dicyclohexylphosphonato)ferrocenyl) phosphate (**35a**, 68 mg, 0.10 mmol), diisopropylamine (0.03 mL, 0.20 mmol), BuLi (0.08 mL, 0.20 mmol), TMEDA (0.03 mL, 0.20 mmol) and Me_2SO_4 (0.1 mL, 0.8 mmol) were reacted according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 10 cm column size) using a 95/5 (v/v) ethyl acetate/methanol mixture as the eluent, giving **36a** as an orange oil.

Yield: 28 mg (0.04 mmol, 41 % based on **35a**). ^1H NMR ($CDCl_3$, δ): 1.24–1.34 (m, 12 H, CH_2), 1.42–1.56 (m, 12 H, CH_2), 1.64–1.80 (m, 8 H, CH_2), 1.81–2.02 (m, 8 H, CH_2), 3.91 (m, 3 H, OCH_3), 4.35–4.22 (m, 2 H, C_5H_2), 4.43–4.57 (m, 9 H, C_5H_5, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.55 (CH_2), 23.57 (CH_2), 25.23 (CH_2), 33.50 (CH_2), 33.52 (CH_2), 33.53 (CH_2), 33.65 (CH_2), 33.77 (CH_2), 33.78 (CH_2), 33.79 (CH_2), 33.86 (CH_2), 63.7 (CH_3), 64.1 (dd, $^1J_{C,P}$ = 212.1 Hz, $^3J_{C,P}$ = 10.6 Hz, C-P), 69.3 (pt, $^{2,3}J_{C,P}$ = 13.6 Hz, C_5H_2), 72.1 (C_5H_5), 75.14 (C1), 75.19 (C1), 75.21 (C1), 75.27 (C1), 128.1 (t, $^2J_{C,P}$ = 10.9 Hz, C_{C5H2}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 19.8. HRMS (ESI-TOF, m/z): calcd for $C_{35}H_{54}FeO_7P_2$ + Na 727.2587, found 727.2589 $[M+Na]^+$.

1,3-Bis(*O*,*O*'-di-(1*R*)-α-fenchylphosphonato)-2-hydroxyferrocene (36b)



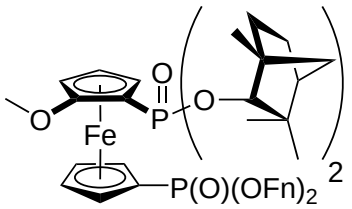
36b

Di-(1*R*)-α-fenchyl (2-(*O*,*O*-di-(1*R*)-α-fenchyl phosphonato)ferrocenyl) phosphate (**35c**, 100 mg, 0.11 mmol), diisopropylamine (0.05 mL, 0.36 mmol), BuLi (0.15 mL, 0.38 mmol), TMEDA (0.06 mL, 0.4 mmol) and Me_2SO_4 (0.2 mL, 2.1 mmol) were reacted according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 10 cm column size) using a 70/30 (v/v) dichloromethane/ethyl acetate mixture as the eluent, giving **36b** as an orange oil.

Yield: 99 mg (0.109 mmol, 99 % based on **35c**). ^1H NMR ($CDCl_3$, δ): 0.79 (s, 3 H, CH_3), 0.94–1.28 (m, 41 H), 1.30–1.35 (m, 1 H, CH_2), 1.39–1.56 (m, 6 H, CH_2), 1.59–1.61 (m, 1 H, CH_2), 1.65–1.89 (m, 11 H), 1.91–1.98 (m, 1 H, CH_2), 3.50 (dd, $^3J_{H,P}$ = 9.5 Hz, $J_{H,H}$ = 1.4 Hz, 1 H, H2), 3.87 (dd, $^3J_{H,P}$ = 9.7 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, H2), 4.12 (dd, J = 5.0 Hz, J = 2.6 Hz, 1 H, C_5H_2), 4.21 (dd, $^3J_{H,P}$ = 10.2 Hz, $J_{H,H}$ = 1.3 Hz, 1 H, H2), 4.30 (dd, $^3J_{H,P}$ = 9.0 Hz,

$J_{H,H}$ = 1.4 Hz, 1 H, H2), 4.42 (dd, J = 4.8 Hz, J = 2.7 Hz, 1 H, C_5H_2), 4.48 (s, 5 H, C_5H_5), 7.60 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.2 (CH_3), 19.4 (CH_3), 19.7 (CH_3), 19.8 (CH_3), 21.5 (CH_3), 21.6 (2 C, CH_3), 21.7 (CH_3), 25.81 (CH_2-CH_2), 25.87 (C5/C6), 25.95 (C5/C6), 25.97 (C5/C6), 26.02 (C5/C6), 29.4 (CH_3), 29.7 (CH_3), 29.9 (CH_3), 30.1 (CH_3), 39.24 (C3), 39.26 (C3), 39.4 (d, $^3J_{C,P}$ = 1.9 Hz, C3), 39.8 (d, $^3J_{C,P}$ = 1.9 Hz, C3), 40.4 (C7), 40.9 (C7), 41.0 (C7), 41.1 (C7), 47.83 (C4), 47.85 (C4), 48.09 (C4), 48.12 (C4), 49.1 (d, $^3J_{C,P}$ = 6.9 Hz, C1), 49.2 (d, $^3J_{C,P}$ = 4.9 Hz, C1), 49.4 (d, $^3J_{C,P}$ = 5.7 Hz, C1), 49.5 (d, $^3J_{C,P}$ = 4.7 Hz, C1), 53.8 (dd, $^1J_{C,P}$ = 211.0 Hz, $^3J_{C,P}$ = 11.1 Hz, C-P), 57.5 (dd, $^1J_{C,P}$ = 214.8 Hz, $^3J_{C,P}$ = 12.3 Hz, C-P), 65.0 (dd, $J_{C,P}$ = 13.2 Hz, $J_{C,P}$ = 12.6 Hz, C_5H_2), 68.9 (pt, $^{2+3}J_{C,P}$ = 13.7 Hz, C_5H_2), 72.0 (C_5H_5), 88.6 (d, $^2J_{C,P}$ = 6.5 Hz, C_{C5H2}-O), 88.8 (d, $^2J_{C,P}$ = 5.4 Hz, C_{C5H2}-O), 89.0 (d, $^2J_{C,P}$ = 7.3 Hz, C_{C5H2}-O), 90.9 (d, $^2J_{C,P}$ = 8.9 Hz, C_{C5H2}-O), 130.0 (dd, $^2J_{C,P}$ = 13.8 Hz, $^2J_{C,P}$ = 10.5 Hz, C-OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 21.3 (d, $^3J_{P,P}$ = 3.7 Hz), 25.8 (d, $^3J_{P,P}$ = 3.7 Hz).

1,1'-Bis(*O*,*O*'-di-(1*R*)-α-fenchylphosphonato)-2-methoxyferrocene (37)

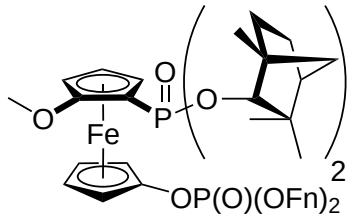


37

Phosphate **35c** (45 mg, 0.05 mmol), LiTMP (24 mg, 0.16 mmol), TMEDA (0,03 mL, 0.20 mmol) and Me_2SO_4 (0.1 mL, 1.05 mmol) were reacted according to the general procedure GP4. Purification was realized by column chromatography (silica, 2 · 12 cm column size) using a 85/15 (v/v) dichloromethane/ethyl acetate mixture as the eluent, giving **37** as an orange oil.

Yield: 12 mg (0.013 mmol, 26 % based on **35c**). ^1H NMR ($CDCl_3$, δ): 0.65 (s, 3 H, CH_3), 0.87–1.26 (m, 37 H, $C_{10}H_{17}$), 1.38–1.57 (m, 8 H, $C_{10}H_{17}$), 1.59–1.87 (m, 12 H, $C_{10}H_{17}$), 3.74–3.76 (m, 4 H, OCH_3, H2), 4.00–4.05 (m, 2 H, H2), 4.18 (dd, $J_{H,P}$ = 9.73 Hz, $J_{H,H}$ = 1.5 Hz, H2), 4.27–4.30 (m, 2 H, C_5H_3), 4.43–4.45 (m, 1 H, C_5H_4), 4.46–4.47 (m, 1 H, C_5H_3), 4.66–4.68 (m, 1 H, C_5H_4), 4.70–4.72 (m, 1 H, C_5H_4), 4.73–4.75 (m, 1 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.15 (CH_3), 19.23 (CH_3), 19.6 (CH_3), 19.7 (CH_3), 21.1 (CH_3), 21.45 (CH_3), 21.48 (CH_3), 21.7 (CH_3), 25.77 (C5/C6), 25.84 (C5/C6), 25.95 (C5/C6), 26.0 (C5/C6), 26.1 (C5/C6), 26.2 (C5/C6), 29.65 (CH_3), 29.67 (CH_3), 29.69 (CH_3), 29.74 (CH_3), 29.80 (CH_3), 39.10 (C3), 39.11 (C3), 39.15 (C3), 39.16 (C3), 39.70 (C3), 39.71 (C3), 39.72 (C3), 39.73 (C3), 40.8 (C7), 41.0 (C7), 41.1 (C7), 47.94 (C4), 47.98 (C4), 48.03 (C4), 48.08 (C4), 49.1 (d, $^3J_{C,P}$ = 5.4 Hz, C1), 49.2 (d, $^3J_{C,P}$ = 5.1 Hz, C1), 49.3 (d, $^3J_{C,P}$ = 4.7 Hz, C1), 49.4 (d, $^3J_{C,P}$ = 5.2 Hz, C1), 56.9 (d, $J_{C,P}$ = 11.4 Hz, C_5H_3), 58.0 (OCH_3), 58.7 (d, $^1J_{C,P}$ = 215.1 Hz, C_{C5H3}-P), 66.0 (d, $J_{C,P}$ = 13.2 Hz, C_5H_3), 68.0 (d, $J_{C,P}$ = 11.9 Hz, C_5H_3), 68.4 (d, $^1J_{C,P}$ = 216.8 Hz, C_{C5H4}-P), 71.8 (d, $J_{C,P}$ = 13.1 Hz, C_5H_4), 73.7 (d, $J_{C,P}$ = 13.4 Hz, C_5H_4), 74.6 (d, $J_{C,P}$ = 16.4 Hz, C_5H_4), 75.0 (d, $J_{C,P}$ = 14.0 Hz, C_5H_4), 88.0 (d, $^2J_{C,P}$ = 6.3 Hz, C2), 88.1 (d, $^2J_{C,P}$ = 6.5 Hz, C2), 88.3 (d, $^2J_{C,P}$ = 5.9 Hz, C2), 88.5 (d, $^2J_{C,P}$ = 7.8 Hz, C2), 129. 8 (d, $^2J_{C,P}$ = 10.4 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 21.3 (C_5H_3), 23.8 (C_5H_4).

1'-Di-(1*R*)-α-fenchlphosphato (2-Methoxyferrocenyl-*O*,*O*'-di-(1*R*)-α-fenchyl) phosphonate (40b)

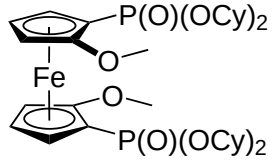


40b

1,1'-Ferrocenediyl tetra-(1*R*)-α-fenchyl bis(phosphate) (**39b**, 120 mg, 0.13 mmol), LiTMP (115 mg, 0.78 mmol), TMEDA (0.12 mL, 0.78 mmol) and Me_2SO_4 (0.22 mL, 2.3 mmol) were reacted according to the general procedure GP4. Purification was realized by column chromatography (silica, 2 · 12 cm column size) using a 90/10 (*v*/*v*) dichloromethane/ethyl acetate mixture as the eluent, giving **40b** as an orange oil in a mixture of both diastereomers (0.84 *de*).

Yield: 22 mg (0.024 mmol, 18 % based on **39b**). ^{1}H NMR ($CDCl_3$, δ): 0.85–1.28 (m, 44 H), 1.44–1.52 (m, 8 H, CH_2), 1.66–1.75 (m, 12 H, CH_2, CH), 3.74 (s, OCH_3), 3.95–4.04 (m, 4 H, H2), 4.13–4.14 (m, 2 H, C_5H_X), 4.21–4.23 (m, 2 H, C_5H_X), 4.28–4.29 (m, 1 H, C_5H_X), 4.49–4.50 (m, 1 H, C_5H_X), 4.58–4.59 (m, 1 H, C_5H_X). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.18 (CH_3), 19.37 (CH_3), 19.41 (CH_3), 19.61 (CH_3), 20.8 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 21.4, 25.6–26.2 (m, C5/C6), 29.7–29.8 (m, CH_3), 39.1 (d, $^3J_{C,P}$ = 2.2 Hz, C3), 39.5 (d, $^3J_{C,P}$ = 2.4 Hz, C3), 39.6 (d, $^3J_{C,P}$ = 2.4 Hz, C3), 39.7 (d, $^3J_{C,P}$ = 2.2 Hz, C3), 40.9–41.1 (m, C7), 47.9–48.1 (m, C4), 49.2–49.3 (m, C1), 57.5 (d, $J_{C,P}$ = 11.7 Hz, C_5H_3), 57.9 (OCH_3), 58.4 (d, $^1J_{C,P}$ = 218.4 Hz, C-P), 60.7 (d, $J_{C,P}$ = 3.5 Hz, C_5H_4), 62.0 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 64.8 (C_5H_4), 66.0 (d, $J_{C,P}$ = 13.8 Hz, C_5H_3), 66.3 (C_5H_4), 67.8 (d, $J_{C,P}$ = 12.0 Hz, C_5H_3) 87.8 (d, $^2J_{C,P}$ = 6.1 Hz, C2), 88.1 (d, $^2J_{C,P}$ = 8.7 Hz, C2), 91.3 (d, $^2J_{C,P}$ = 7.0 Hz, C2), 118.5 (d, $^2J_{C,P}$ = 4.4 Hz, C–OPO_4), 129.5 (d, $^2J_{C,P}$ = 10.1 Hz, C–OPO_3). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –4.5 (PO_4), 22.0 (PO_3, ma), 22.2 (PO_3, mi).

Tetracyclohexyl (2,2'-Dimethoxy-1,1'-ferrocenediyl)bis(phosphonate) (41a)



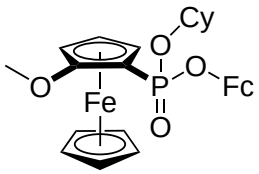
41a

Tetracyclohexyl 1,1'-ferrocenediyl bis(phosphate) (**39a**, 100 mg, 0.14 mmol), diisopropylamine (0.08 mL, 0.57 mmol), BuLi (0.23 mL, 0.58 mmol), TMEDA (0.09 mL, 0.60 mmol) and Me_2SO_4 (0.3 mL, 3.2 mmol) were reacted according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 10 cm column size) using a 95/5 (*v*/*v*) ethyl acetate/methanol mixture as the eluent, giving **41a** as an orange oil in a mixture of diastereomers (0.13 *de*).

Yield: 70 mg (0.095 mmol, 67 % based on **39a**). ^{1}H NMR ($CDCl_3$, δ): 1.18–1.39 (m, 12 H, CH_2), 1.43–1.60 (m, 12 H, CH_2), 1.63–1.80 (m, 8 H, CH_2), 1.87–1.98 (m, 8 H, CH_2), 3.71 (s, 3.6 H*, OCH_3), 3.83 (s, 2.4 H*, OCH_3), 4.12–4.17 (m, 1.6 H*, C_5H_3), 4.21–4.22 (m, 1 H, C_5H_3), 4.36–4.43 (m, 4 H, CyC1, C_5H_3), 4.45–4.57 (m, 3.4 H*, CyC1, C_5H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 23.5–23.7 (CH_2), 25.1–25.3 (CH_2), 33.5–33.9 (m, CH_2), 57.5 (d, $J_{C,P}$ = 11.1 Hz, C_5H_3), 58.0 (OCH_3), 58.2 (OCH_3), 58.4 (d, $^1J_{C,P}$ = 215.6 Hz, C-P), 58.5 (d, $^1J_{C,P}$ = 215.1 Hz, C-P), 59.4 (d, $J_{C,P}$ =11.1 Hz, C_5H_3), 64.8 (d, $J_{C,P}$ =13.8 Hz, C_5H_3), 67.8 (d, $J_{C,P}$ = 14.0 Hz, C_5H_3), 68.9 (d, $J_{C,P}$ = 13.1 Hz, C_5H_3), 74.68–74.73 (m, C1), 75.0 (d, $^2J_{C,P}$ = 6.2 Hz, C1),

75.22 (d, $^2J_{C,P}$ = 6.0 Hz, C1), 75.23 (d, $^2J_{C,P}$ = 6.9 Hz, C1), 129.0 (d, $^2J_{C,P}$ = 9.8 Hz, C_{C5H3}-O), 129.5 (d, $^2J_{C,P}$ =10.6 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 20.75 (ma), 20.81 (mi).

Cyclohexyl Ferrocenyl (2-Methoxyferrocenyl)phosphonate (44a)

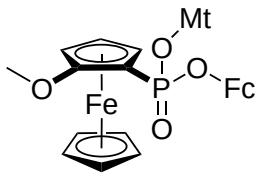


44a

Cyclohexyl diferrocenyl phosphate (**43a**, 100 mg, 0.18 mmol), diisopropylamine (0.1 mL, 0.72 mmol), BuLi (0.30 mL, 0.75 mmol), TMEDA (0.11 mL, 0.73 mmol) and Me_2SO_4 (0.3 mL, 3.2 mmol) were reacted according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 10 cm column size) using 85/15 a (*v*/*v*) dichloromethane/ethyl acetate mixture as the eluent, giving **44a** as an orange solid as a mixture of diastereomers (0.45 *de*).

Yield: 58 mg (0.10 mmol, 57 % based on **43a**). Mp.: 111–114 °C. Anal. calcd for $C_{27}H_{31}Fe_2O_4P$ (562.20 g/mol): C, 57.68; H, 5.56; found: C, 57.87; H, 5.66. ^1H NMR ($CDCl_3$, δ): 1.33–1.43 (m, 3 H, CH_2), 1.47–1.54 (m, 1 H, CH_2), 1.58–1.68 (m, 2 H, CH_2), 1.72–1.82 (m, 2 H, CH_2), 1.88–2.02 (m, 2 H, CH_2), 3.71/3.73 (s, 3 H, OCH_3), 3.81–3.85 (m, 2 H, $C_5H_{3/4}$), 4.04–4.07 (m, 1 H, $C_5H_{3/4}$), 4.16/4.19 (s, 5 H, C_5H_5), 4.21–4.24 (m, 1 H, $C_5H_{3/4}$), 4.29–4.31 (m, 1 H, $C_5H_{3/4}$), 4.32 (s, 5 H, C_5H_5), 4.38–4.40 (m, 1 H, $C_5H_{3/4}$), 4.42–4.47 (m, 1 H, $C_5H_{3/4}$), 4.55–4.66 (m, 1 H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.50 (CH_2), 23.54 (CH_2), 25.24 (CH_2), 25.29 (CH_2), 33.6–33.8 (m, CH_2), 55.26 (d, $J_{C,P}$ = 11.6 Hz, $C_5H_{3/4}$), 55.31 (d, $J_{C,P}$ = 11.6 Hz, $C_5H_{3/4}$), 57.0 (d, $^1J_{C,P}$ = 218.0 Hz, C-P), 58.2 (OCH_3), 60.0 (d, $J_{C,P}$ = 3.6 Hz, $C_5H_{3/4}$), 60.1 (d, $J_{C,P}$ = 3.9 Hz, $C_5H_{3/4}$), 60.26 (d, $J_{C,P}$ = 3.3 Hz, $C_5H_{3/4}$), 60.33 (d, $J_{C,P}$ = 3.6 Hz, $C_5H_{3/4}$), 62.4–62.5 (m, $C_5H_{3/4}$), 63.9 (d, $J_{C,P}$ = 13.7 Hz, $C_5H_{3/4}$), 64.0 (d, $J_{C,P}$ = 14.6 Hz, $C_5H_{3/4}$), 67.2 (d, $J_{C,P}$ = 12.8 Hz, $C_5H_{3/4}$), 67.4 (d, $J_{C,P}$ = 14.1 Hz, $C_5H_{3/4}$), 69.27 (C_5H_5), 69.33 (C_5H_5), 70.08 (C_5H_5), 70.13 (C_5H_5), 75.7 (d, $^2J_{C,P}$ = 6.2 Hz, C1), 76.1 (d, $^2J_{C,P}$ = 7.1 Hz, C1), 117.5 (d, $^2J_{C,P}$ = 4.8 Hz, C_{C5H4}-O), 128.6 (d, $^2J_{C,P}$ = 10.3 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 20.06 (mi), 20.09 (ma). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{27}H_{31}Fe_2O_4P$ 562.0654, found 562.0654 $[M]^+$.

Ferrocenyl (1*R*)-Menthyl (2-Methoxyferrocenyl)phosphonate (44b)



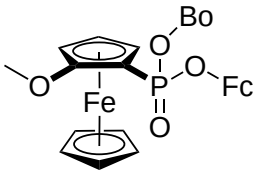
44b

Diferrocenyl (1*R*)-menthyl phosphate (**43b**, 200 mg, 0.33 mmol), diisopropylamine (0.09 mL, 0.65 mmol), BuLi (0.27 mL, 0.68 mmol), TMEDA (0.10 mL, 0.66 mmol) and Me_2SO_4 (0.2 mL, 2.1 mmol) were reacted according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 10 cm column size) using a 95/5 (*v*/*v*) dichloromethane/ethyl acetate mixture as the eluent, giving **44b** as an orange oil as as a mixture of isomers.

Yield: 155 mg (0.25 mmol, 74 % based on 43b). ^1H NMR ($CDCl_3$, δ): 0.74–0.96 (m, 10 H, CH_3, CH_2), 1.00–1.09 (m, 1 H, CH_2), 1.15–1.25 (m, 1 H, CH_2), 1.32–1.39 (m, 1 H, CH), 1.44–1.52 (m, 1 H, CH), 1.62–1.71 (m, 2 H, CH_2, CH), 2.11–2.49 (m, 2 H, CH_2), 3.67–3.72 (m,

3 H, OCH_3), 3.78–3.87 (m, 2 H, $C_5H_{3/4}$), 4.01–4.07 (m, 1 H, $C_5H_{3/4}$), 4.11–4.58 (m, 15 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 15.6–15.7 (m, CH_3), 21.1–21.2 (m, CH_3), 22.0–22.1 (m, CH_3), 22.6–22.8 (m, CH_2), 31.5–31.6 (m, CH_3), 34.07–34.13 (m, CH_2), 43.1–43.4 (m, CH_2), 48.6–49.0 (m, C1), 55.0–55.3 (m, C_5H_3), 56.17–56.21 (m, C-P), 56.8 (d, $^1J_{C,P}$ = 218.3 Hz, C-P), 57.90–57.94 (OCH_3), 58.1 (C-P), 59.8–60.5 (m, C_5H_4), 62.3–62.5 (m, C_5H_4), 63.7–64.0 (m, C_5H_3), 66.7–67.8 (m, C_5H_3), 69.2–69.3 (m, C_5H_5), 70.0–70.2 (m, C_5H_5), 77.6–78.3 (m, C1), 117.6–117.7 (m, C_{C5H4}-O), 128.3–128.9 (m, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 19.8, 20.1, 20.4, 21.0. HRMS (ESI-TOF, m/z): calcd for $C_{32}H_{41}Fe_2O_4P$ 632.1437, found 632.1400 $[M]^+$.

(1*S*)-Borneyl Ferrocenyl (2-Methoxyferrocenyl)phosphonate (44c)



44c

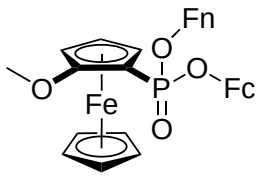
(1*S*)-Borneyl diferrocenyl phosphate (**43c**, 100 mg, 0.18 mmol), diisopropylamine (0.05 mL, 0.36 mmol), BuLi (0.15 mL, 0.38 mmol), TMEDA (0.05 mL, 0.33 mmol) and Me_2SO_4 (0.13 mL, 1.37 mmol) were reacted according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 10 cm column size) using a 80/20 (v/v) dichloromethane/ethyl acetate mixture as the eluent, giving **44c** as an orange oil in a mixture of isomers.

Yield: 55 mg (0.089 mmol, 49 % based on **43c**). ^1H NMR ($CDCl_3$, δ): 0.82 (s, 3 H, CH_3), 0.83 (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3), 1.19–1.33 (m, 3 H, CH_2), 1.60–1.64 (m, 1 H, H4), 1.66–1.74 (m, 1 H, CH_2), 1.91–2.10 (m, 1 H, CH_2), 2.12–2.35 (m, 1 H, H3), 3.63–3.66 (m, 3 H, OCH_3), 3.71–3.78 (m, 2 H, $C_5H_{3/4}$), 3.97–4.02 (m, 1 H, $C_5H_{3/4}$), 4.06–4.12 (m, 5 H, C_5H_5), 4.15–4.17 (m, 1 H, $C_5H_{3/4}$), 4.22–4.40 (m, 8 H, $C_5H_{3/4}$, C_5H_5), 4.64–4.75 (m, 1 H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 31 13.2 (CH_3), 13.3 (CH_3), 18.9 (CH_3), 20.0 (CH_3), 26.5 (C5/C6), 26.6 (C5/C6), 28.10 (C5/C6), 28.12 (C5/C6), 37.2 (d, $^3J_{C,P}$ = 1.3 Hz, C3), 37.6 (d, $^3J_{C,P}$ = 2.1 Hz, C3), 44.91 (C4), 44.95 (C4), 47.5 (C7), 47.6 (C7), 49.7 (d, $^3J_{C,P}$ = 6.5 Hz, C1), 49.8 (d, $^3J_{C,P}$ = 5.5 Hz, C1), 55.20 (d, $J_{C,P}$ = 11.7 Hz, C_5H_3), 55.25 (d, $J_{C,P}$ = 11.5 Hz, C_5H_3), 56.6 (d, $^1J_{C,P}$ = 218.4 Hz, C-P), 56.8 (d, $^1J_{C,P}$ = 218.8 Hz, C-P), 58.0 (OCH_3), 58.1 (OCH_3), 59.9 (d, $J_{C,P}$ = 3.5 Hz, C_5H_4), 60.0 (d, $J_{C,P}$ = 3.5 Hz, C_5H_4), 60.1 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 60.2 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 62.36 (C_5H_4), 62.39 (C_5H_4), 62.41 (C_5H_4), 63.99 (d, $J_{C,P}$ = 14.7 Hz, C_5H_3), 64.04 (d, $J_{C,P}$ = 14.6 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 14.2 Hz, C_5H_3), 67.5 (d, $J_{C,P}$ = 14.6 Hz, C_5H_3), 69.2 (C_5H_5), 69.3 (C_5H_5), 70.07 (C_5H_5), 70.09 (C_5H_5), 82.70 (d, $^2J_{C,P}$ = 7.5 Hz, C2), 82.73 (d, $^2J_{C,P}$ = 7.5 Hz, C2), 117.5 (m, C_{C5H4}-O), 128.5 (d, $^2J_{C,P}$ = 9.8 Hz, C_{C5H3}-OCH_3), 128.7 (d, $^2J_{C,P}$ = 10.0 Hz, C-OCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 20.54, 20.61, 21.06, 21.11. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{35}Fe_2O_4P$ 602.0967, found 602.0963 $[M]^+$.

(1*R*)-α-Fenchyl Ferrocenyl (2-Methoxyferrocenyl)phosphonate (44d)

(1*R*)-α-Fenchyl diferrocenyl phosphate (**43d**, 134 mg, 0.22 mmol), LiTMP (130 mg, 0.88 mmol), TMEDA (0.13 mL, 0.86 mmol) and Me_2SO_4 (0.3 mL, 3.2 mmol) were reacted according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 10 cm column size) using a 90/10 (v/v) dichloromethane/ethyl acetate mixture

as the eluent, giving **44d** as an orange oil in a mixture of isomers.

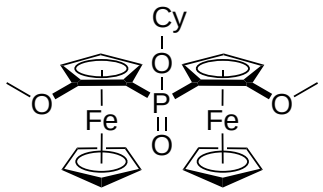


44d

Yield: 125 mg (0.20 mmol, 91 % based on **43d**). ^{1}H NMR ($CDCl_3$, δ): 0.93–1.22 (m, 11 H, CH_3, CH_2), 1.44–1.55 (m, 2 H, CH_2), 1.69–1.88 (m, 3 H, CH_2, CH), 3.38–3.72 (m, 3 H, OCH_3), 3.79–3.85 (m, 2 H, C_5H_4), 4.04–4.23 (m, 8 H, C_5H_5, C_5H_3, H2), 4.25–4.51 (m, 8 H, C_5H_5, $C_5H_{3/4}$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.18 (CH_3), 19.22 (CH_3), 19.27 (CH_3), 19.31 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 21.2 (CH_3), 21.3 (CH_3), 25.8–26.2 (C5/C6), 29.6–29.8 (CH_3), 39.40 (d, $^{3}J_{C,P}$ = 3.0 Hz, C3), 39.45–39.47 (m, C3), 39.6 (d, $^{3}J_{C,P}$ = 2.1 Hz, C3), 41.0–41.1 (C7), 47.85 (C4), 47.90 (C4), 47.99 (C4), 48.02 (C4), 49.16–49.25 (m, C1), 49.32 (d, $^{3}J_{C,P}$ = 4.7 Hz, C1), 55.0–55.3 (m, C_5H_3), 56.45 (d, $^{1}J_{C,P}$ = 219.7 Hz, C-P), 56.54 (d, $^{1}J_{C,P}$ = 219.1 Hz, C-P), 57.0 (d, $^{1}J_{C,P}$ = 219.6 Hz, C-P), 57.1 (d, $^{1}J_{C,P}$ = 218.3 Hz, C-P), 57.8–58.0 (OCH_3), 59.8 (d, $J_{C,P}$ = 3.4 Hz, C_5H_4), 59.8 (d, $J_{C,P}$ = 3.4 Hz, C_5H_4), 60.1–60.2 (m, C_5H_4), 60.3–60.4 (m, C_5H_4), 60.6 (d, $J_{C,P}$ = 3.1 Hz, C_5H_4), 62.3–62.4 (m, C_5H_4), 63.8–64.1 (m, C_5H_3), 66.8 (d, $J_{C,P}$ = 12.3 Hz, C_5H_3), 67.1 (d, $J_{C,P}$ = 13.2 Hz, C_5H_3), 67.2 (d, $J_{C,P}$ = 13.6 Hz, C_5H_3), 67.7 (d, $J_{C,P}$ = 14.2 Hz, C_5H_3), 69.17–62.22 (C_5H_5), 69.97–70.00 (C_5H_5), 88.5 (d, $^{2}J_{C,P}$ = 7.3 Hz, C2), 88.95 (d, $^{2}J_{C,P}$ = 7.4 Hz, C2), 89.02 (d, $^{2}J_{C,P}$ = 7.3 Hz, C2), 89.5 (d, $^{2}J_{C,P}$ = 7.9 Hz, C2), 117.7 (d, $^{2}J_{C,P}$ = 4.4 Hz, C_{C5H4}-O), 117.81 (d, $^{2}J_{C,P}$ = 4.6 Hz, C_{C5H4}-O), 117.84 (d, $^{2}J_{C,P}$ = 4.4 Hz, C_{C5H4}-O), 128.41 (d, $^{2}J_{C,P}$ = 9.9 Hz, C_{C5H3}-O), 128.44 (d, $^{2}J_{C,P}$ = 10.4 Hz, C_{C5H3}-O), 128.6 (d, $^{2}J_{C,P}$ = 10.4 Hz, C_{C5H3}-O), 129.0 (d, $^{2}J_{C,P}$ = 11.2 Hz, C_{C5H3}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 20.4, 20.7, 20.8, 21.5. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{37}Fe_2O_4P$ 616.1124, found 616.1063 $[M]^+$.

rac-/*meso*-Cyclohexyl Bis(2-methoxyferrocenyl)phosphinate (*rac*-/*meso*-45a)

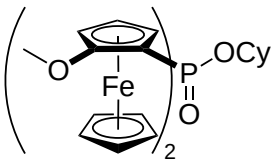
The title compounds were obtained as side products during the synthesis of **44a** by reacting cyclohexyl diferrocenyl phosphate (**43a**, 100 mg, 0.18 mmol), diisopropylamine (0.1 mL, 0.72 mmol), BuLi (0.30 mL, 0.75 mmol), TMEDA (0.11 mL, 0.73 mmol) and Me_2SO_4 (0.3 mL, 3.2 mmol) according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 10 cm column size) using a 97/3 (v/v) ethyl acetate/methanol mixture (*rac*-**45a**, R_f = 0.42; *meso*-**45a**, R_f = 0.38), both were obtained as orange oils.



meso-**45a**

meso-**45a**: Yield: 27 mg (0.072 mmol, 39 % based on **43a**). ^{1}H NMR ($CDCl_3$, δ): 1.32–1.46 (m, 3 H, CH_2), 1.49–1.62 (m, 2 H, CH_2), 1.69–1.89 (m, 4 H, CH_2), 2.05–212 (m, 1 H, CH_2), 3.67 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 3.96–3.97 (m, 2 H, C_5H_3), 4.01–4.09 (m, 2 H, C_5H_3), 4.14–4.17 (m, 2 H, C_5H_3), 4.33 (s, 5 H, C_5H_5), 4.34 (s, 5 H, C_5H_5), 4.72–4.78 (m, 1 H, H1). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 23.57 (CH_2), 23.61 (CH_2), 25.6 (CH_2), 33.8 (d, $^{3}J_{C,P}$ = 4.1 Hz, CH_2), 34.4 (d, $^{3}J_{C,P}$ = 3.2 Hz, CH_2), 55.0 (d, $J_{C,P}$ = 9.4 Hz, C_5H_3), 58.0 (OCH_3), 58.2 (OCH_3), 63.1 (d, $J_{C,P}$ = 11.6 Hz, C_5H_3), 63.3 (d, $^{2}J_{C,P}$ = 12.4 Hz, C_5H_3), 63.6 (d, $^{1}J_{C,P}$ = 161.2 Hz, C-P), 63.8 (d, $^{1}J_{C,P}$ = 155.3 Hz, C-P), 67.0 (d, $J_{C,P}$ = 15.1 Hz, C_5H_3), 67.1 (d, $J_{C,P}$ = 10.7 Hz,

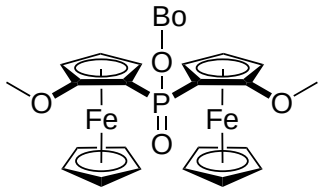
C_5H_3), 69.8 (C_5H_5), 69.8 (C_5H_5), 73.7 (d, $^2J_{C,P}$ = 5.4 Hz, C1), 128.3 (d, $^2J_{C,P}$ = 7.8 Hz, C_{C5H3}-O), 128.6 (d, $^2J_{C,P}$ = 10.6 Hz, C_{C5H3}-O.) $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 34.2.



rac-**45a**

rac-**45a**: Yield: 40 mg (0.105 mmol, 58 % based on **43a**). ^1H NMR ($CDCl_3$, δ): 1.29–1.33 (m, 3 H, CH_2), 1.44–1.47 (m, 1 H, CH_2), 1.53–1.60 (m, 1 H, CH_2), 1.71–1.78 (m, 2 H, CH_2), 1.81–1.89 (m, 2 H, CH_2), 3.72 (s, 6 H, OCH_3), 4.00–4.02 (m, 2 H, C_5H_3), 4.18–4.19 (m, 2 H, C_5H_3), 4.22–4.26 (m, 12 H, C_5H_5, C_5H_3), 4.46–4.53 (m, 1 H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.4 (CH_2), 25.5 (CH_2), 33.8 (d, $^3J_{C,P}$ = 3.6 Hz, C2/C6), 54.8 (d, $J_{C,P}$ = 9.0 Hz, C_5H_3), 58.2 (OCH_3), 63.1 (d, $^1J_{C,P}$ = 158.6 Hz, C-P), 63.6 (d, $J_{C,P}$ = 12.7 Hz, C_5H_3), 67.0 (d, $J_{C,P}$ = 14.6 Hz, C_5H_3), 69.9 (C_5H_5), 73.8 (d, $^2J_{C,P}$ = 6.9 Hz, C1), 128.9 (d, $^2J_{C,P}$ = 7.8 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 35.6. HRMS (ESI-TOF, m/z): calcd for $C_{28}H_{33}Fe_2O_4P$ + Na 599.0708, found 599.0716 $[M+Na]^+$.

(1*S*)-Borneyl Bis(2-methoxyferrocenyl)phosphinate (45c)



45c

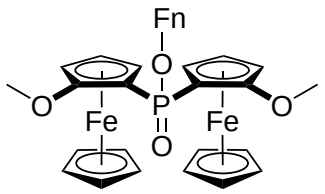
The title compounds was obtained as side product during the synthesis of **44c** by reacting (1*S*)-borneyl diferrocenyl phosphate (**43c**, 100 mg, 0.18 mmol), diisopropylamine (0.05 mL, 0.36 mmol), BuLi (0.15 mL, 0.38 mmol), TMEDA (0.05 mL, 0.33 mmol) and Me_2SO_4 (0.13 mL, 1.37 mmol) according to the general procedure GP3. Purification was realized by column chromatography (silica, 2 · 10 cm column size) using a 95/5 (*v*/*v*) ethyl acetate/methanol mixture as the eluent, giving **45c** as an orange oil in a mixture of diastereomers.

Yield: 42 mg (0.067 mmol, 37 % based on **43c**). ^1H NMR ($CDCl_3$, δ): 0.74 (CH_3), 0.80 (CH_3), 0.84 (CH_3), 1.17–1.30 (m, 3 H, CH_2), 1.59–1.60 (m, 1 H, H4), 1.68–1.76 (m, 1 H, CH_2), 2.07–2.14 (m, 1 H, CH_2), 2.16–2.24 (m, 1 H, CH_2), 3.71 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.98–4.00 (m, 1 H, C_5H_3), 4.00–4.02 (m, 1 H, C_5H_3), 4.13–4.14 (m, 1 H, C_5H_3), 4.18–4.19 (m, 3 H, C_5H_3), 4.27 (s, 5 H, C_5H_5), 4.31 (s, 5 H, C_5H_5), 4.66–4.71 (m, 1 H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 13.04 (CH_3), 18.7 (CH_3), 19.9 (CH_3), 26.4 (C5/C6), 28.2 (C5/C6), 37.5 (C3), 45.1 (C4), 47.3 (C7), 49.8 (d, $^3J_{C,P}$ = 6.2 Hz, C1), 54.6 (d, $J_{C,P}$ = 8.9 Hz, C_5H_3), 54.7 (d, $J_{C,P}$ = 8.9 Hz, C_5H_3), 58.0 (OCH_3), 58.1 (OCH_3), 62.2 (d, $^1J_{C,P}$ = 158.8 Hz, C-P), 62.7 (d, $^1J_{C,P}$ = 158.4 Hz, C-P), 63.5 (C_5H_3), 63.6 (C_5H_3), 67.0 (d, $J_{C,P}$ = 14.1 Hz, C_5H_3), 67.1 (d, $J_{C,P}$ = 14.5 Hz, C_5H_3), 69.8 (C_5H_5), 69.9 (C_5H_5), 80.4 (d, $^2J_{C,P}$ = 6.4 Hz, C2), 128.8 (d, $^2J_{C,P}$ = 7.6 Hz, C_{C5H3}-O), 129.3 (d, $^2J_{C,P}$ = 7.3 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 36.8. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{35}Fe_2O_4P$ 602.0967, found 602.0963 $[M]^+$.

(1*R*)-α-Fenchyl Bis(2-methoxyferrocenyl)phosphinate (45d)

(1*R*)-α-Fenchyl ferrocenyl (2-methoxyferrocenyl) phosphonate (**44d**, 168 mg, 0.27 mmol), diisopropylamine (0.08 mL, 0.55 mmol), BuLi (0.22 mL, 0.55 mmol), TMEDA (0.09 mL, 0.55 mmol) and Me_2SO_4 (0.3 mL, 3.16 mmol) were reacted according to the general procedure

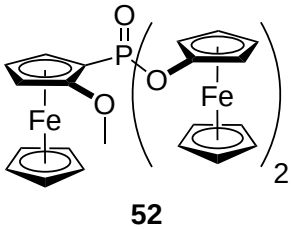
GP3. Purification was realized by column chromatography (silica, 2 · 10 cm column size) using a 98/2 (*v*/*v*) ethyl acetate/methanol mixture as the eluent, giving **45d** as an orange oil in a mixture of isomers.



45d

Yield: 171 mg (0.265 mmol, 97 % based on **44d**). ^{1}H NMR ($CDCl_3$, δ): 0.69–1.12 (m, 11 H, CH_3, CH_2), 1.39–1.46 (m, 2 H, CH_2), 1.61–1.67 (m, 1 H, H4), 1.71–1.78 (m, 1 H, CH_2), 1.85–1.97 (m, 1 H, CH_2), 3.55–4.07 (m, 9 H, OCH_3, H2, C_5H_3), 4.13–4.43 (m, 14 H, C_5H_5, C_5H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.1 (CH_3), 19.32 (CH_3), 19.35 (CH_3), 21.2 (CH_3), 21.5 (CH_3), 21.6 (CH_3), 25.8–26.9 (C5/C6), 29.3 (CH_3), 29.36 (CH_3), 29.40 (CH_3)29.7 (CH_3), 39.3 (d, $^{3}J_{C,P}$ = 1.7 Hz, C3), 39.4 (d, $^{3}J_{C,P}$ = 2.1 Hz, C3), 39.6 (d, $^{3}J_{C,P}$ = 3.3 Hz, C3), 41.1 (C7), 41.2 (C7), 41.3 (C7), 48.0 (C4), 48.1 (C4), 48.2 (C4), 49.25 (d, $^{3}J_{C,P}$ = 3.7 Hz, C3), 49.34 (d, $^{3}J_{C,P}$ = 4.8 Hz, C3), 54.3 (d, $J_{C,P}$ = 9.9 Hz, C_5H_3), 54.6 (d, $J_{C,P}$ = 9.3 Hz, C_5H_3), 54.7 (d, $J_{C,P}$ = 9.0 Hz, C_5H_3), 54.8 (d, $J_{C,P}$ = 8.9 Hz, C_5H_3), 57.40 (OCH_3), 57.44 (OCH_3), 57.78 (OCH_3), 57.85 (OCH_3), 58.0 (OCH_3), 58.2 (OCH_3), 61.7 (d, $^{1}J_{C,P}$ = 165.7 Hz, C-P), 62.1 (d, $^{1}J_{C,P}$ = 159.1 Hz, C-P), 62.4 (d, $^{1}J_{C,P}$ = 158.6 Hz, C-P), 62.6 (d, $^{1}J_{C,P}$ = 160.7 Hz, C-P), 63.0 (d, $J_{C,P}$ = 12.0 Hz, C_5H_3), 63.1 (d, $J_{C,P}$ = 11.6 Hz, C_5H_3), 63.5 (d, $J_{C,P}$ = 12.7 Hz, C_5H_3), 63.7 (d, $J_{C,P}$ = 12.9 Hz, C_5H_3), 67.1 (d, $J_{C,P}$ = 15.0 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 15.0 Hz, C_5H_3), 68.8 (d, $J_{C,P}$ = 9.7 Hz, C_5H_3), 68.8 (d, $J_{C,P}$ = 10.2 Hz, C_5H_3), 69.6 (C_5H_5), 69.7 (C_5H_5), 69.8 (C_5H_5), 87.5 (d, $^{2}J_{C,P}$ = 7.2 Hz, C2), 87.8 (d, $^{2}J_{C,P}$ = 7.2 Hz, C2), 88.0 (d, $^{2}J_{C,P}$ = 7.0 Hz, C2), 129.0 (d, $^{2}J_{C,P}$ = 7.5 Hz, C_{C5H3}-O), 129.1 (d, $^{2}J_{C,P}$ = 7.1 Hz, C_{C5H3}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 35.68, 35.74, 36.7, 38.0. HRMS (ESI-TOF, *m*/*z*): calcd for $C_{32}H_{39}Fe_2O_4P$ 630.1280, found 630.1222 $[M]^+$.

Diferrocenyl (2-Methoxyferrocenyl)phosphonate (52)



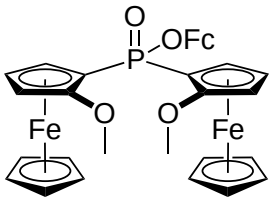
52

Triferrocenyl phosphate (**47**, 270 mg, 0.415 mmol), diisopropylamine (0.23 mL, 1.66 mmol), BuLi (0.66 mL, 1.66 mmol) and Me_2SO_4 (0.16 mL, 1.69 mmol) were reacted at –30 °C according to the general procedure GP2. Purification was realized by column chromatography (silica, 2.5 · 10 cm column size) using a 9/1 dichloromethane/ethyl acetate mixture (*v*/*v*) as the eluent, giving **52** as an orange solid.

Yield: 106 mg (0.16 mmol, 86 % based on **47**). Anal. calcd for $C_{31}H_{29}Fe_3O_4P \cdot 1/6\ C_6H_{14}$ (664.07 · 1/6 86.18 g/mol): C, 56.65; H, 4.65. Found: C, 56.65; H, 4.71. Mp.: 166–168 °C. ^{1}H NMR ($CDCl_3$, δ): 3.74 (s, 3 H, OCH_3), 3.85–3.90 (m, 4 H, C_5H_4), 4.09–4.11 (m, 1 H, C_5H_3/C_5H_4), 4.21 (s, 5 H, C_5H_5), 4.24 (s, 5 H, C_5H_5), 4.26–4.29 (m, 2 H, C_5H_4, C_5H_3), 4.31 (s, 5 H, C_5H_5), 4.41–4.43 (m, 1 H, C_5H_4), 4.47–4.49 (m, 2 H, C_5H_4), 4.49–4.51 (m, 1 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.3 (d, $^{1}J_{C,P}$ = 219.8 Hz, C-P), 55.5 (d, $J_{C,P}$ = 11.9 Hz, C_5H_3), 58.2 (OCH_3), 59.9 (d, $J_{C,P}$ = 3.7 Hz, C_5H_4), 60.1 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 60.25 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 60.29 (d, $J_{C,P}$ = 3.6 Hz, C_5H_4), 62.57–62.62 (m, C_5H_4), 64.4 (d, $J_{C,P}$ =

14.8 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 14.0 Hz, C_5H_3), 69.48 (C_5H_5), 69.53 (C_5H_5), 70.23 (C_5H_5), 117.4 (d, $^2J_{C,P}$ = 5.5 Hz, C_{C5H4}-O), 117.5 (d, $^2J_{C,P}$ = 6.0 Hz, C_{C5H4}-O), 128.9 (d, $^2J_{C,P}$ = 10.8 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 18.8. HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{29}Fe_3O_4P$ 663.9848, found 663.9809 $[M]^+$.

Ferrocenyl Bis(2-methoxyferrocenyl)phosphinate (53)

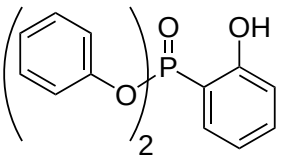


53

Diferrocenyl (2-methoxyferrocenyl)phosphonate (**52**, 135 mg, 0.203 mmol), diisopropylamine (0.13 mL, 0.87 mmol), BuLi (0.35 mL, 0.87 mmol) and Me_2SO_4 (0.1 mL, 1.05 mmol) were reacted 0 °C according to the general procedure GP2. Purification was realized by column chromatography (silica, 2.5 · 10 cm column size) using a 1/4 dichloromethane/ethyl acetate mixture (v/v) as the eluent, giving **53** as an orange solid. The title compound was obtained as a mixture of two diastereomers in a ratio of 1 : 0.128. Solely the data of the main diastereomer are reported, due to the low intensity of the minor one. Note for experiments with additional amounts of Phenol (6 equiv), diisopropylamine (6 equiv) and BuLi (12 equiv) were used. In this case, the product was obtained as a single diastereomer.

Yield: 121 mg (0.178 mmol, 86 % based on **52**). Anal. calcd for $C_{32}H_{31}Fe_3O_4P$ (678.09 g/mol): C, 56.68; H, 4.61. Found: C, 56.54; H, 4.62. Mp.: 193–197 °C. ^1H NMR ($CDCl_3$, δ): 3.69 (s, 6 H, OCH_3), 3.78 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.06–4.07 (m, 2 H, C_5H_3), 4.19–4.20 (m, 2 H, C_5H_3), 4.22 (s, 5 H, C_5H_5), 4.27 (s, 10 H, C_5H_5), 4.30 (pt, $^{3,4}J_{H,H}$ = 1.8 Hz, 2 H, C_5H_4), 4.39–4.40 (m, 2 H, C_5H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 54.8 (d, $J_{C,P}$ = 9.9 Hz, C_5H_3), 60.5 (d, $J_{C,P}$ = 3.4 Hz, C2/5C_5H_4), 62.1 (d, $^1J_{C,P}$ = 162.5 Hz, C-P), 62.4 (C3/4C_5H_4), 63.6 (d, $J_{C,P}$ = 12.2 Hz, C_5H_3), 68.0 (d, $J_{C,P}$ = 11.5 Hz, C_5H_3), 69.3 (C_5H_5), 69.9 (C_5H_5), 117.1 (d, $^2J_{C,P}$ = 5.8 Hz, C_{C5H4}-O), 128.5 (d, $^2J_{C,P}$ = 10.7 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 37.3. HRMS (ESI-TOF, m/z): calcd for $C_{32}H_{31}Fe_3O_4P$ 678.0004, found 677.9992 $[M]^+$.

Diphenyl (2-Hydroxyphenyl)phosphonate (56)



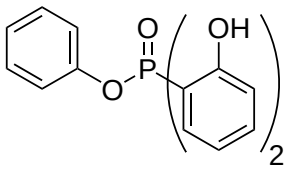
56

Triphenyl phosphate (**55**, 100 mg, 0.307 mmol), diisopropylamine (0.25 mL, 1.84 mmol), BuLi (0.74 mL, 1.84 mmol) and HCl (0.5 mL, 5 mmol) were reacted at –80 °C according to the general procedure GP2. Purification was realized by column chromatography (silica, 2.5 · 10 cm column size) using dichloromethane as the eluent, giving **56** as an colorless solid.

Yield: 75 mg (0.230 mmol, 75 % based on **55**). Anal. calcd for $C_{18}H_{15}O_4P$ (326.28 g/mol): C, 66.26; H, 4.63. Found: C, 66.27; H, 4.57. Mp.: 127–129 °C. ^1H NMR ($CDCl_3$, δ): 6.94–6.98 (m, 2 H, C5/6$_{C6H4}$), 7.16–7.20 (m, 6 H, C4/2/6$_{C6H5}$), 7.30–7.33 (m, 4 H, C3/5$_{C6H5}$), 7.45–7.48 (m, 1 H, C4$_{C6H4}$), 7.62 (ddd, $J_{H,P}$ = 14.8 Hz, $J_{H,H}$ = 7.9 Hz, $J_{H,H}$ = 1.5 Hz, 2 H, C3$_{C6H4}$), 9.86 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 107.4 (d, $^1J_{C,P}$ = 185.7 Hz, C1$_{C6H4}$-

P), 118.0 (d, $^{3}J_{C,P}$ = 12.7 Hz, C_6H_4), 119.8 (d, $^{2}J_{C,P}$ = 14.3 Hz, C_6H_4), 120.5 (d, $^{3}J_{C,P}$ = 4.6 Hz, C2/6$_{C6H5}$), 125.5 (d, $^{5}J_{C,P}$ = 1.1 Hz, C4$_{C6H5}$), 129.8 (C3/5$_{C6H5}$), 131.8 (d, $J_{C,P}$ = 6.0 Hz, C_6H_4), 136.0 (d, $^{4}J_{C,P}$ = 2.3 Hz, C4$_{C6H4}$), 149.8 (d, $^{2}J_{C,P}$ = 6.9 Hz, C1$_{C6H5}$-O), 162.2 (d, $^{2}J_{C,P}$ = 7.7 Hz, C2$_{C6H4}$-O). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 14.9. HRMS (ESI-TOF, m/z): calcd for $C_{18}H_{15}O_4P$ + H 327.0781, found 327.0767 $[M+H]^+$.

Phenyl Bis(2-hydroxyphenyl)phosphinate (57)

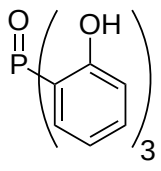


57

Triphenyl phosphate (**55**, 100 mg, 0.307 mmol), diisopropylamine (0.25 mL, 1.84 mmol), BuLi (0.74 mL, 1.84 mmol) and HCl (0.5 mL, 5 mmol) were reacted at –70 °C according to the general procedure GP2. Purification was realized by column chromatography (silica, 2.5 · 10 cm column size) using dichloromethane as the eluent, giving **57** as an colorless oil.

Yield: 45 mg (0.238 mmol, 45 % based on **55**). ^{1}H NMR ($CDCl_3$, δ): 6.93–6.97 (m, 4 H, C_6H_4), 7.12–7.15 (m, 1 H, C4$_{C6H5}$), 7.17–7.20 (m, 2 H, C_6H_5), 7.26–7.29 (m, 2 H, C3/5$_{C6H5}$), 7.41–7.45 (m, 2 H, C4$_{C6H4}$), 7.59 (ddd, $J_{H,P}$ = 13.5 Hz, $J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 1.7 Hz, 2 H, C_6H_4), 9.85 (s, 2 H, OH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 110.9 (d, $^{1}J_{C,P}$ = 140.3 Hz, C1$_{C6H4}$-P), 118.5 (d, $J_{C,P}$ = 9.7 Hz, C_6H_4), 119.9 (d, $J_{C,P}$ = 12.9 Hz, C_6H_4), 120.6 (d, $^{3}J_{C,P}$ = 5.0 Hz, C2/6$_{C6H5}$), 125.5 (d, $^{5}J_{C,P}$ = 0.9 Hz, C4$_{C6H5}$), 129.9 (d, $^{4}J_{C,P}$ = 0.5 Hz, C3/5$_{C6H5}$), 131.6 (d, $J_{C,P}$ = 7.8 Hz, C_6H_4), 135.6 (d, $^{4}J_{C,P}$ = 2.1 Hz, C4$_{C6H4}$), 150.0 (d, $^{2}J_{C,P}$ = 8.8 Hz, C1$_{C6H5}$-O), 162.2 (d, $^{2}J_{C,P}$ = 5.6 Hz, C2$_{C6H4}$-O). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 42.3. HRMS (ESI-TOF, m/z): calcd for $C_{18}H_{15}O_4P$ + H 327.0781, found 327.0767 $[M+H]^+$.

Tris(2-hydroxyphenyl)phosphine Oxide (58)



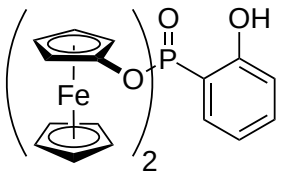
58

Applying the same reaction conditions as for the synthesis of **56** and **57** at 0 °C gave the title compound. The spectroscopic data correspond with those reported in reference 185.

Yield: 90 mg (276 mmol, 90 % based on **55**). ^{1}H NMR ($CDCl_3$, δ): 6.89–6.91 (m, 3 H), 6.99–7.05 (m, 6 H), 7.44–7.47 (m, 3 H), 9.20 (s, 3 H, OH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 111.9 (d, $^{1}J_{C,P}$ = 107.3 Hz, C1-P), 118.7 (d, $J_{C,P}$ = 7.3 Hz), 119.8 (d, $J_{C,P}$ = 12.9 Hz), 132.0 (d, $J_{C,P}$ = 10.5 Hz), 135.4 (d, $^{5}J_{C,P}$ = 1.6 Hz, C4), 162.2 (d, $^{2}J_{C,P}$ = 2.6 Hz, C2-O). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 51.1.

Diferrocenyl (2-Hydroxyphenyl)phosphonate (59a)

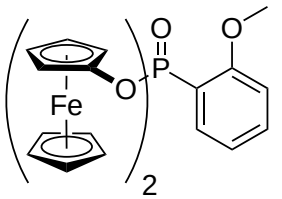
Diferrocenyl phenyl phosphate (**48**, 100 mg, 0.184 mmol), diisopropylamine (0.12 mL, 0.85 mmol), BuLi (0.30 mL, 0.75 mmol) and Me_2SO_4 (0.12 mL, 1.27 mmol) were reacted at –60 °C according to the general procedure GP2. Purification was realized by column chromatography (silica, 2.5 · 10 cm column size) using dichloromethane containing 0 - 50 % ethyl acetate (v/v) as the eluents giving **59a**,**b** and **60**.



59a

Orange Solid. Yield: 27 % based on **48**. Anal. calcd for $C_{26}H_{23}Fe_2O_4P$ (542.12 g/mol): C, 57.60; H, 4.28. Found: C, 57.29; H, 4.38. Mp.: 155–159 °C. ^{1}H NMR ($CDCl_3$, δ): 3.86–3.89 (m, 4 H, H3/4$_{C5H4}$), 4.19 (s, 10 H, C_5H_5), 4.30–4.31 (m, 2 H, H2/5$_{C5H4}$), 4.35–4.36 (m, 2 H, H2/5$_{C5H4}$), 6.94–7.01 (m, 2 H, C_6H_4), 7.44 (ddd, $^3J_{H,P}$ = 14.9 Hz, $J_{H,H}$ = 7.8 Hz, $J_{H,H}$ = 1.7 Hz, 1 H, C_6H_4), 7.47–7.51 (m, 1 H, C_6H_4), 9.98 (d, $^4J_{H,P}$ = 0.7 Hz, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.6 (d, $^3J_{C,P}$ = 3.8 Hz, C2,5$_{C5H4}$), 59.8 (d, $^3J_{C,P}$ = 4.4 Hz, C2,5$_{C5H4}$), 62.9 (C3,4$_{C5H4}$), 63.0 (C3,4$_{C5H4}$), 69.6 (C_5H_5), 107.7 (d, $^1J_{C,P}$ = 184.0 Hz, C1$_{C5H4}$-P), 117.1 (d, $^2J_{C,P}$ = 4.5 Hz, C$_{C5H4}$-O), 118.0 (d, $J_{C,P}$ = 12.7 Hz, C_6H_4), 119.7 (d, $J_{C,P}$ = 14.2 Hz, C_6H_4), 131.9 (d, $J_{C,P}$ = 6.0 Hz, C_6H_4), 136.0 (d, $^4J_{C,P}$ = 2.5 Hz, C4$_{C6H4}$), 162.2 (d, $^2J_{C,P}$ = 7.8 Hz, C2$_{C6H4}$-OH). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 15.8. HRMS (ESI-TOF, m/z): calcd for $C_{26}H_{23}Fe_2O_4P$ 542.0028, found 542.0035 $[M]^+$.

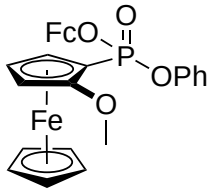
Diferrocenyl (2-Methoxyphenyl)phosphonate (59b)



59b

The orange oil was obtained under the same reactions conditions as **59a**. Yield: 13 % based on **48**. Anal. calcd for $C_{27}H_{25}Fe_2O_4P$ (556.15 g/mol): C, 57.60; H, 4.28. Found: C, 57.29; H, 4.38. ^{1}H NMR ($CDCl_3$, δ): 3.84 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, H3,4$_{C5H4}$), 3.92 (s, 3 H, OCH_3), 4.20 (s, 10 H, C_5H_5), 4.37–4.39 (m, 4 H, H2,5), 6.96 (dd, $J_{H,H}$ = 7.8 Hz, $J_{H,P}$ = 7.8 Hz, 1 H, C_6H_4), 7.05 (tdd, $J_{H,H}$ = 7.5 Hz, $J_{H,P}$ = 3.8 Hz, $J_{H,H}$ = 0.7 Hz, 1 H, C_6H_4), 7.55 (ddd, $J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 7.4 Hz, $J_{H,H}$ = 1.8 Hz, $J_{H,P}$ = 0.9 Hz, 1 H, C4$_{C6H4}$), 7.91 (ddd, $J_{H,P}$ = 15.5 Hz, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 1.7 Hz, 1 H, C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.8 (OCH_3), 59.9 (d, $^3J_{C,P}$ = 3.9 Hz, C2,5$_{C5H4}$), 60.0 (d, $^3J_{C,P}$ = 4.0 Hz, C2,5$_{C5H4}$), 62.61 (C3,4$_{C5H4}$), 62.65 (C3,4$_{C5H4}$), 69.5 (C_5H_5), 111.3 (d, $J_{C,P}$ = 9.8 Hz, C_6H_4), 115.1 (d, $^1J_{C,P}$ = 190.3 Hz, C1$_{C6H4}$-P), 117.3 (d, $^2J_{C,P}$ = 5.0 Hz, C$_{C5H4}$-O), 120.5 (d, $J_{C,P}$ = 15.3 Hz, C_6H_4), 135.1 (d, $^4J_{C,P}$ = 2.1 Hz, C4$_{C6H4}$), 135.6 (d, $J_{C,P}$ = 7.7 Hz, C_6H_4), 161.5 (d, $^2J_{C,P}$ = 2.7 Hz, C2$_{C6H4}$-OH). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 11.5. HRMS (ESI-TOF, m/z): calcd for $C_{27}H_{25}Fe_2O_4P$ 556.0185, found 556.0175 $[M]^+$.

Ferrocenyl Phenyl (2-Methoxyferrocenyl)phosphonate (60)

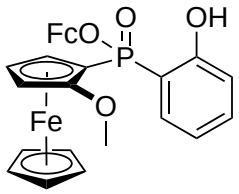


60

The orange oil was obtained under the same reactions conditions as **59a**. Yield: 29 % based on **48**. Anal. calcd for $C_{27}H_{25}Fe_2O_4P$ (556.15 g/mol): C, 58.31; H, 4.53. Found: C, 58.14; H, 4.74. ^{1}H NMR ($CDCl_3$, δ): 3.728 (s, 2.25 H, OCH_3), 3.734 (s, 0.75 H, OCH_3), 3.83–3.85 (m, 1.5 H, $C_5H_4/_3$), 3.86–3.87 (m, 0.5 H, $C_5H_4/_3$), 4.08–4.12 (m, 1 H, $C_5H_4/_3$), 4.15 (s, 3.75, OCH_3), 4.19–4.21 (m, 1.5 H, OCH_3, $C_5H_4/_3$), 4.24–4.28 (m, 6 H, C_5H_5, $C_5H_4/_3$), 4.30–4.31 (m, 0.25 H, $C_5H_4/_3$), 4.32–4.34 (m, 0.75 H, $C_5H_4/_3$), 4.37–4.38 (m, 0.75 H, $C_5H_4/_3$), 4.45–4.45 (m, 0.75 H, $C_5H_4/_3$), 4.50–4.51 (m, 0.25 H, $C_5H_4/_3$), 7.13–7.20 (m, 1 H, C4$_{C6H5}$), 7.27–7.38 (m, 4 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.4 (d,

$^{1}J_{C,P}$ = 221.4 Hz, C_{C5H3}-P), 55.55 (d, $J_{C,P}$ = 12.1 Hz, C_5H_3), 55.59 (d, $J_{C,P}$ = 12.1 Hz, C_5H_3), 58.2 (s, OCH_3), 59.9 (d, $J_{C,P}$ = 4.0 Hz, C_5H_4), 60.18–60.23 (m, C_5H_4), 60.4 (d, $J_{C,P}$ = 3.4 Hz, C_5H_4), 62.55–62.63 (m, C_5H_4), 64.40 (d, $J_{C,P}$ = 14.8 Hz, C_5H_3), 64.44 (d, $J_{C,P}$ = 14.9 Hz, C_5H_3), 67.19 (d, $J_{C,P}$ = 14.5 Hz, C_5H_3), 67.21 (d, $J_{C,P}$ = 14.5 Hz, C_5H_3), 69.40 (C_5H_5), 69.45 (C_5H_5), 69.47 (C_5H_5), 70.17 (C_5H_5), 117.5 (d, $^{2}J_{C,P}$ = 5.4 Hz, C_{C5H4}-O), 120.7 (d, $^{3}J_{C,P}$ = 4.7 Hz, C2/6$_{C6H5}$), 120.9 (d, $^{3}J_{C,P}$ = 4.8 Hz, C2/6$_{C6H5}$), 124.71 (d, $^{5}J_{C,P}$ = 0.7 Hz, C4$_{C6H5}$), 124.74 (d, $^{5}J_{C,P}$ = 0.7 Hz, C4$_{C6H5}$), 128.7 (d, $^{2}J_{C,P}$ = 10.6 Hz, C_{C5H3}-O), 129.4 (C3/5$_{C6H5}$), 129.5 (C3/5$_{C6H5}$), 150.9 (d, $^{2}J_{C,P}$ = 7.6 Hz, C1$_{C6H5}$-O). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 18.3 (100 %), 18.5 (27.9 %). HRMS (ESI-TOF, m/z): calcd for $C_{27}H_{25}Fe_2O_4P$ 556.0185, found 556.0181 $[M]^+$.

Ferrocenyl (2-Hydroxyphenyl)(2-methoxyferrocenyl)phosphinate (61a)



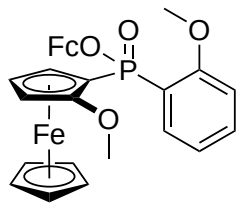
61a

Diferrocenyl phenyl phosphate (**48**, 100 mg, 0.184 mmol), diisopropylamine (0.18 mL, 1.29 mmol), BuLi (0.52 mL, 1.30 mmol) and Me_2SO_4 (0.24 mL, 2.54 mmol) were reacted at 0 °C according to the general procedure GP2. Purification was realized by column chromatography (silica, 2.5 · 10 cm column size) using dichloromethane containing 0 - 50 % ethyl acetate (v/v) as the eluents giving **61a**,**b**.

The orange oil was formed with a *de* of 0.04 (racemic mixture). Yield: 77 % based on **48**. ^{1}H NMR ($CDCl_3$, δ): 3.67 (s, 1.5 H, OCH_3), 3.78–3.80 (m, 1.5 H, $C_5H_4/_3$), 3.82–3.83 (m, 2 H, OCH_3, $C_5H_4/_3$), 4.10–4.12 (m, 0.5 H, $C_5H_4/_3$), 4.15–4.16 (m, 0.5 H, $C_5H_4/_3$), 4.17–4.23 (m, 9 H, C_5H_5, $C_5H_4/_3$), 4.26 (ptd, $J_{H,P}$ = 2.8, $^{3,4}J_{H,H}$ = 1.5 Hz, 0.5 H, $C_5H_4/_3$), 4.31–4.32 (m, 1 H, $C_5H_4/_3$), 4.41–4.42 (m, 3 H, C_5H_5, $C_5H_4/_3$), 4.47–4.48 (m, 0.5 H, $C_5H_4/_3$), 6.83 (tdd, $J_{H,H}$ = 7.5 Hz, $J_{H,P}$ = 2.9 Hz, $J_{H,H}$ = 1.0 Hz, 0.5 Hz, C_6H_4), 6.87–6.92 (m, 2 H, C_6H_4),6.96 (ddd, $J_{H,H}$ = 8.3 Hz, $J_{H,P}$ = 5.8 Hz, $J_{H,H}$ = 0.6 Hz, 0.5 H, C_6H_4), 7.35–7.42 (m, 1 H, C_6H_4), 7.44 (ddd, $J_{H,P}$ = 14.7 Hz, $J_{H,H}$ = 7.8 Hz, $J_{H,H}$ = 1.7 Hz, 0.5 H, C_6H_4), 7.52 (ddd, $J_{H,P}$ = 14.9 Hz, $J_{H,H}$ = 7.8 Hz, $J_{H,H}$ = 1.7 Hz, 0.5 H, C_6H_4), 10.95 (d, $J_{H,P}$ = 0.7 Hz, 0.5 H, OH), 10.99 (d, $J_{H,P}$ = 0.7 Hz, 0.5 H, OH). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 55.7 (d, $J_{C,P}$ = 10.2 Hz, C_5H_3), 55.9 (d, $J_{C,P}$ = 10.3 Hz, C_5H_3), 58.26 (s, OCH_3), 58.33 (s, OCH_3), 59.92 (d, $J_{C,P}$ = 4.2 Hz, C_5H_4), 59.94 (d, $^{1}J_{C,P}$ = 166.4 Hz, C_{C5H3}-P), 59.96 (d, $J_{C,P}$ = 4.2 Hz, C_5H_4), 60.01 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 60.3 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 62.7 (d, $J_{C,P}$ = 3.3 Hz, C_5H_4), 62.8 (d, $J_{C,P}$ = 6.8 Hz, C_5H_4), 64.4 (d, $J_{C,P}$ = 12.2 Hz, C_5H_3), 64.7 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 67.0 (d, $J_{C,P}$ = 15.9 Hz, C_5H_3), 67.4 (d, $J_{C,P}$ = 10.8 Hz, C_5H_3), 69.48 (C_5H_5), 69.51 (C_5H_5), 69.97 (C_5H_5), 70.18 (C_5H_5), 112.3 (d, $^{1}J_{C,P}$ = 134.0 Hz, C1$_{C6H4}$-P), 112.8 (d, $^{1}J_{C,P}$ = 139.1 Hz, C1$_{C6H4}$-P), 117.18 (d, $^{2}J_{C,P}$ = 6.6 Hz, C_{C5H4}-O), 117.23 (d, $^{2}J_{C,P}$ = 6.2 Hz, C_{C5H4}-O), 117.62 (C_6H_4), 117.69 (C_6H_4), 117.70 (C_6H_4), 118.9 (d, $J_{C,P}$ = 13.5 Hz, C_6H_4), 119.1 (d, $J_{C,P}$ = 13.5 Hz, C_6H_4), 128.2 (d, $^{2}J_{C,P}$ = 11.4 Hz, C_{C5H3}-O), 128.7 (d, $^{2}J_{C,P}$ = 8.5 Hz, C_{C5H3}-O), 131.3 (d, $J_{C,P}$ = 10.0 Hz, C_6H_4), 132.1 (d, $J_{C,P}$ = 9.5 Hz, C_6H_4), 134.6 (d, $^{4}J_{C,P}$ = 2.3 Hz, C4$_{C6H4}$), 134.7 (d, $^{4}J_{C,P}$ = 2.2 Hz, C4$_{C6H4}$), 162.15 (d, $^{2}J_{C,P}$ = 5.8 Hz, C2$_{C6H4}$-OH), 162.19 (d, $^{2}J_{C,P}$ = 5.4 Hz, C2$_{C6H4}$-OH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 43.4 (100 %), 43.5 (92.3 %). HRMS (ESI-TOF, m/z): calcd for $C_{27}H_{25}Fe_2O_4P$

556.0185, found 556.0120 $[M]^+$.

Ferrocenyl (2-Methoxyferrocenyl)(2-methoxyphenyl)phosphinate (61b)



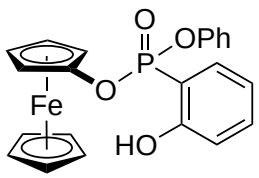
61b

The orange oil was formed within the synthesis of **61a** in 13% yield as a mixture of two diastereomers with a ratio of 0.55 (a = major) : 0.45 (b = mi) resulting a *de* of 0.11. Anal. calcd for $C_{28}H_{27}Fe_2O_4P \cdot 1/6\ C_6H_{14}$ (570.18 · 86.18 g/mol): C, 59.59; H, 5.05. Found: C, 59.78; H, 5.24. ^{1}H NMR ($CDCl_3$, δ): 3.60 (s, 1.65 H, OCH_3), 3.72 (s, 1.65 H, OCH_3), 3.74 (s, 1.35 H, OCH_3), 3.76–3.78 (m, 2 H, C_5H_3), 3.82 (s, 1.35 H, OCH_3), 4.01 (dpt, $J_{H,P}$ = 2.7 Hz, $^{3,4}J_{H,H}$ = 2.7 Hz, 0.45 H, C_5H_3), 4.05 (dpt, $J_{H,P}$ = 2.6 Hz, $^{3,4}J_{H,H}$ = 2.6 Hz, 0.55 H, C_5H_3), 4.11 (dpt, $J_{H,P}$ = 2.7 Hz, $^{3,4}J_{H,H}$ = 1.5 Hz, 0.45 H, $C_5H_4/_3$), 4.17–4.21 (m, 6.0 H, $C_5H_4/_3$, C_5H_5), 4.23–4.24 (m, 2.7 H, $C_5H_4/_3$, C_5H_5), 4.26–4.27 (m, 0.55 H, $C_5H_4/_3$), 4.37–4.39 (m, 1.1 H, $C_5H_4/_3$), 4.43–4.45 (m, 3.2 H, $C_5H_4/_3$, C_5H_5), 6.80 (dd, $J_{H,H}$ = 8.2 Hz, $J_{H,P}$ = 6.1 Hz, 0.55 Hz, C_6H_4), 6.89 (dd, $J_{H,H}$ = 8.1 Hz, $J_{H,P}$ = 6.2 Hz, 0.45 Hz, C_6H_4), 7.01 (dddd, $J_{H,H}$ = 7.5 Hz, $J_{H,H}$ = 7.5 Hz, $J_{H,P}$ = 2.8 Hz, $J_{H,H}$ = 1.0 Hz, 0.55 H, C_6H_4), 7.06 (dddd, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 7.3 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 0.9 Hz, 0.45 H, C_6H_4), 7.44 (dddd, $J_{H,H}$ = 8.4 Hz, $J_{H,H}$ = 7.4 Hz, $J_{H,H}$ = 1.8 Hz, $J_{H,P}$ = 0.8 Hz, 0.55 H, C_6H_4), 7.48 (dddd, $J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 1.8 Hz, $J_{H,P}$ = 0.9 Hz, 0.45 H, C_6H_4), 7.97 (ddd, $J_{H,P}$ = 14.1 Hz, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 1.8 Hz, 0.45 H, C_6H_4), 8.02 (ddd, $J_{H,P}$ = 14.1 Hz, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 1.8 Hz, 0.55 H, C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.0 (d, a, $J_{C,P}$ = 10.7 Hz, C_5H_3), 55.24 (s, a, OCH_3), 55.28 (d, b, $J_{C,P}$ = 9.8 Hz, C_5H_3), 55.4 (s, b, OCH_3), 58.26 (s, b, OCH_3), 58.29 (s, a, OCH_3), 60. 0 (d, a, $J_{C,P}$ = 3.9 Hz, C_5H_4), 60.4 (d, b, $J_{C,P}$ = 3.8 Hz, C_5H_4), 60.5 (d, a, $J_{C,P}$ = 3.6 Hz, C_5H_4), 60.6 (d, b, $J_{C,P}$ = 3.9 Hz, C_5H_4), 61.4 (d, a, $^1J_{C,P}$ = 164.5 Hz, C_{C5H3}-P), 62.30 (s, C_5H_4), 62.31 (s, C_5H_4), 62.38 (s, C_5H_4), 63.4 (d, a, $J_{C,P}$ = 12.2 Hz, C_5H_3), 63.8 (d, b, $J_{C,P}$ = 13.4 Hz, C_5H_3), 67.3 (d, b, $J_{C,P}$ = 16.4 Hz, C_5H_3), 67.7 (d, a, $J_{C,P}$ = 10.3 Hz, C_5H_3), 69.33 (s, a, C_5H_5), 69.35 (s, b, C_5H_5), 69.98 (s, b, C_5H_5), 70.00 (s, b, C_5H_5), 110.9 (d, a, $J_{C,P}$ = 7.6 Hz, C_6H_4), 111.1 (d, b, $J_{C,P}$ = 7.5 Hz, C_6H_4), 117.4 (d, a, $^2J_{C,P}$ = 4.4 Hz, C_{C5H4}-O), 117.9 (d, b, $^2J_{C,P}$ = 6.1 Hz, C_{C5H4}-O), 120.1 (d, a, $^1J_{C,P}$ = 135.1 Hz, $C1_{C6H4}$-P), 120.3 (d, b, $^1J_{C,P}$ = 138.3 Hz, C_{C6H4}-P), 120.5 (d, $J_{C,P}$ = 12.7 Hz, C_6H_4), 129.7 (d, a, $^2J_{C,P}$ = 12.8 Hz, C_{C5H3}-O), 134.00 ($C4_{C6H4}$), 134.02 ($C4_{C6H4}$), 134.05 ($C4_{C6H4}$), 135.1 (d, b, $J_{C,P}$ = 7.8 Hz, C_6H_4), 135.6 (d, a, $J_{C,P}$ = 7.5 Hz, C_6H_4), 160.7 (d, a, $^2J_{C,P}$ = 4.0 Hz, C_{C6H4}-O), 160.9 (d, b, $^2J_{C,P}$ = 3.5 Hz, C_{C6H4}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 29.9 (100 %), 33.7 (80.5 %). HRMS (ESI-TOF, m/z): calcd for $C_{28}H_{27}Fe_2O_4P$ 570.0341, found 556.0350 $[M]^+$.

Ferrocenyl Phenyl (2-Hydroxyphenyl)phosphonate (62)

Ferrocenyl diphenyl phosphate (**11**, 200 mg, 0.461 mmol), diisopropylamine (0.51 mL, 3.685 mmol), BuLi (1.47 mL, 3.675 mmol) and Me_2SO_4 (0.35 mL, 3.69 mmol) were at –70 °C reacted according to the general procedure GP2. Purification was realized by column chromatography (silica, 2.5 · 10 cm column size) using dichloromethane containing 0 - 40 % ethyl

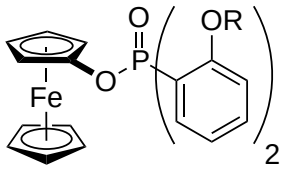
acetate (v/v) as the eluent, giving 62 as an orange oil.



62

Yield: 116 mg (0.267 mmol, 58 % based on **11**). Anal. calcd for $C_{22}H_{19}FeO_4P$ (434.20 g/mol): C, 60.86; H, 4.41. Found: C, 60.61; H, 4.75. ^{1}H NMR ($CDCl_3$, δ): 3.86–3.89 (m, 2 H, H3/4$_{C5H4}$), 4.18 (s, 5 H, C_5H_5), 4.33–4.35 (m, 1 H, H2/5$_{C5H4}$), 4.37–4.39 (m, 1 H, H2/5$_{C5H4}$), 6.94–6.99 (m, 2 H, C_6H_4), 7.16–7.19 (m, 3 H, C_6H_5), 7.30–7.34 (m, 2 H, C_6H_5), 7.46–7.49 (m, 1 H, C_6H_4), 7.53 (dddd, $J_{H,P}$ = 15.1 Hz, $J_{H,H}$ = 7.7 Hz, $J_{H,H}$ = 1.9 Hz, $J_{H,H}$ = 0.6 Hz, 1 H, C_6H_4), 9.92 (d, $^4J_{H,P}$ = 0.5 Hz, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.6 (d, $^3J_{C,P}$ = 3.8 Hz, C2/5$_{C5H4}$), 59.9 (d, $^3J_{C,P}$ = 4.2 Hz, C2/5$_{C5H4}$), 62.92 (s, C3/4$_{C5H4}$), 62.99 (s, C3/4$_{C5H4}$), 69.6 (C_5H_5), 107.5 (d, $^1J_{C,P}$ = 184.6 Hz, C$_{C6H4}$-P), 117.1 (d, $^2J_{C,P}$ = 4.5 Hz, C$_{C5H4}$-O), 118.0 (d, $J_{C,P}$ = 12.7 Hz, C_6H_4), 119.7 (d, $J_{C,P}$ = 14.3 Hz, C_6H_4), 120.4 (d, $J_{C,P}$ = 4.6 Hz, C_6H_5), 125.5 (d, $J_{C,P}$ = 1.0 Hz, C_6H_5), 129.8 (C_6H_5), 131.8 (d, $J_{C,P}$ = 6.1 Hz, C_6H_4), 136.0 (d, $J_{C,P}$ = 2.4 Hz, C_6H_4), 149.8 (d, $J_{C,P}$ = 6.9 Hz, C$_{C6H5}$-O), 162.2 (d, $J_{C,P}$ = 7.8 Hz, C$_{C6H4}$-OH). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 15.4. HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{19}FeO_4P$ 434.0365, found 434.0632 $[M]^+$.

Ferrocenyl (2-Hydroxyphenyl)(2-methoxyphenyl)phosphinate (63)

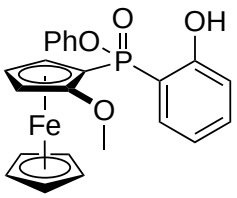


63 (R = H, CH_3)

Compound **63** was obtained by running the reaction for the synthesis of **62** at 0 °C. Compound **63** was obtained as an orange oil in a mixture with **64a**. Both compounds could not be separated applying several chromatographic methods. Yield: 11 % based on **11**. ^{1}H NMR ($CDCl_3$, δ): 3.76 (s, 3 H, OCH_3), 3.80–3.82 (m, 1 H, C_5H_4), 3.83–3.85 (m, 1 H, C_5H_4), 4.19 (s, 5 H, C_5H_5), 4.24–4.25 (m, 1.0 H, C_5H_4), 4.40–4.41 (m, 1 H, C_5H_4), 6.77–6.82 (m, 1 H, C_6H_4), 6.90–6.96 (m, 2 H, C_6H_4), 7.07–7.11 (m, 1 H, C_6H_4), 7.20–7.24 (m, 1 H, C_6H_4), 7.36–7.40 (m, 1 H, C_6H_4), 7.52–7.56 (m, 1 H, C_6H_4), 7.92 (ddd, $J_{H,P}$ = 13.3 Hz, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 1.7 Hz, 1 H, C_6H_4), 7.63 (ddd, $J_{H,P}$ = 14.8 Hz, $J_{H,H}$ = 7.9 Hz, $J_{H,H}$ = 1.7 Hz, 0.8 Hz, C_6H_4), 10.74 (d, $^4J_{H,P}$ = 0.4 Hz, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.8 (s, OCH_3), 60.0 (d, $^3J_{C,P}$ = 4.1 Hz, C_5H_4), 60.2 (d, $^3J_{C,P}$ = 4.1 Hz, C_5H_4), 62.80 (s, C_5H_4), 62.83 (s, C_5H_4), 69.6 (s, C_5H_5), 111.8 (d, $J_{C,P}$ = 8.3 Hz, C$_{C6H4}$OMe), 112.1 (d, $^1J_{C,P}$ = 135.6 Hz, C1$_{C6H4OH}$-P), 117.2 (d, $^2J_{C,P}$ = 6,4 Hz, C$_{C5H4}$-O), 118.9 (d, $J_{C,P}$ = 13.5 Hz, C_6H_4), 119.0 (d, $^1J_{C,P}$ = 146.9 Hz, C1$_{C6H4OMe}$-P), 120.6 (d, $J_{C,P}$ = 12.6 Hz, C_6H_4), 131.5 (d, $J_{C,P}$ = 9.7 Hz, C_6H_4), 133.2 (d, $J_{C,P}$ = 5.6 Hz, C_6H_4), 134.6 (d, $^4J_{C,P}$ = 2.4 Hz, C4$_{C6H4}$), 134.9 (d, $^4J_{C,P}$ = 1.8 Hz, C4$_{C6H4}$), 161.8 (d, $^2J_{C,P}$ = 5.0 Hz, C2$_{C6H4}$-OMe), 162.9 (d, $^2J_{C,P}$ = 5.7 Hz, C2$_{C6H4}$-OH). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 35.8. HRMS (ESI-TOF, m/z): calcd for $C_{23}H_{21}FeO_4P$ 448.0522, found 448.0518 $[M]^+$.

Phenyl (2-Hydroxyphenyl)(2-methoxyferrocenyl)phosphinate (64a)[1)]

1) Only the data of the first diastereomer are reported, which was obtained in a diastereomeric ratio of 0.798: 0.202 with **64a**-2). Compound **64a** was obtained by running the reaction for the synthesis of **62** at 0 °C. Orange solid.



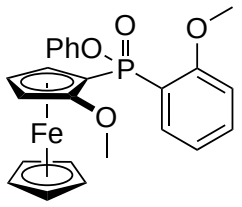
64a

Yield: 20 % based on **11**. Anal. calcd for $C_{23}H_{21}FeO_4P$ (448.23 g/mol): C, 61.63; H, 4.72. Found: C, 61.43; H, 4.63.* Mp.: 208–210 °C. ^{1}H NMR ($CDCl_3$, δ): 3.69 (s, 2.4 H, OCH_3), 3.83 (s, 0.6 H, OCH_3), 3.98–4.00 (m, 0.2 H, C_5H_3), 4.13–4.15 (m, 0.8 H, C_5H_3), 4.17 (s, 4.0 H, C_5H_5), 4.26–4.28 (m, 1.0 H, C_5H_3), 4.32–4.34 (m, 0.2 H, C_5H_3), 4.38 (s, 1.0 H, C_5H_5), 4.51–4.52 (m, 0.8 H, C_5H_3), 6.77–6.68 (m, 0.2 H, $C_6H_{5/4}$), 6.83–6.90 (m, 1.0 H, $C_6H_{5/4}$), 6.93 (ddd, $J_{H,H} = 8.4$ Hz, $J_{H,P} = 5.9$ Hz, $J_{H,H} = 0.6$ Hz, 0.8 H, C_6H_4), 7.06–7.10 (m, 1.0 H, C_6H_5), 7.14–7.16 (m, 1.6 H, $C_6H_{5/4}$), 7.20–7.25 (m, 2.4 H, $C_6H_{5/4}$), 7.30–7.33 (m, 0.2 H, C_6H_4), 7.36–7.39 (m, 0.8 H, C_6H_4), 7.49 (ddd, $J_{H,P} = 14.8$ Hz, $J_{H,H} = 7.8$ Hz, $J_{H,H} = 1.9$ Hz, 0.2 H, C_6H_4), 7.63 (ddd, $J_{H,P} = 14.8$ Hz, $J_{H,H} = 7.9$ Hz, $J_{H,H} = 1.7$ Hz, 0.8 Hz, C_6H_4), 10.90 (d, $^4J_{H,P} = 0.7$ Hz, 0.2 H, OH), 10.95 (d, $^4J_{H,P} = 0.7$ Hz, 0.8 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.9 (d, $J_{C,P} = 10.4$ Hz, C_5H_3), 58.3 (s, OCH_3), 61.3 (d, $^1J_{C,P} = 183.9$ Hz, C_{C5H3}-P), 64.4 (d, $J_{C,P} = 12.2$ Hz, C_5H_3), 67.5 (d, $J_{C,P} = 10.9$ Hz, C_5H_3), 69.97 (s, ma, C_5H_5), 70.17 (s, mi, C_5H_5), 112.6 (d, $^1J_{C,P} = 140.6$ Hz, $C1_{C6H4}$-P), 117.7 (d, $J_{C,P} = 9.8$ Hz, C_6H_4), 118.9 (d, $J_{C,P} = 13.7$ Hz, C_6H_4), 120.8 (d, $^3J_{C,P} = 4.9$ Hz, $C2,6_{C6H5}$), 124.8 (d, $^5J_{C,P} = 1.1$ Hz, $C4_{C6H5}$), 128.0 (d, $^2J_{C,P} = 11.2$ Hz, C_{C5H3}-O)**, 129.56 (s, $C3,5_{C6H5}$), 132.1 (d, $J_{C,P} = 9.5$ Hz, C_6H_4), 134.6 (d, $J_{C,P} = 2.2$ Hz, $C4_{C6H4}$), 150.7 (d, $^2J_{C,P} = 8.7$ Hz, $C1_{C6H5}$-O), 162.2 (d, $^2J_{C,P} = 6.1$ Hz, $C2_{C6H4}$-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 43.5 (100 %), 44.1 (25.3 %). HRMS (ESI-TOF, m/z): calcd for $C_{23}H_{21}FeO_4P$ 448.0522, found 448.0518 $[M]^+$. *The data are related to a single measurement, due to the low amount of substance. **This signal was taken from the ^{13}C{^{1}H} NMR spectra of the mixture of all three isomers.

Phenyl (2-Hydroxyphenyl)(2-methoxyferrocenyl)phosphinate (64a)[2)]

2) Only the data of the second diastereomer are reported. The diastereomeric ratio of 0.124: 0.876 is inverse compared to **64a**-1). Compound **64a**-2) was obtained as a mixture with **63**. Both compounds could not be separated by applying several chromatographic methods. Orange Oil. ^{1}H NMR ($CDCl_3$, δ): 3.83 (s, 3 H, OCH_3), 4.13–4.15 (m, 1 H, C_5H_3), 4.27–4.28 (m, 1 H, C_5H_3), 4.32–4.34 (m, 1 H, C_5H_3), 4.38 (s, 1 H, C_5H_5), 6.77–6.82 (m, 1 H, C_6H_4), 6.83–6.86 (m, 1 H, C_6H_4), 7.20–7.24 (m, 3 H, C_6H_5), 7.27–7.28 (m, 2 H, C_6H_5), 7.30–7.33 (m, 1 H, C_6H_4), 7.49 (ddd, $J_{H,P} = 14.5$ Hz, $J_{H,H} = 7.8$ Hz, $J_{H,H} = 1.6$ Hz, 1 H, C_6H_4), 10.91 (d, $^4J_{H,P} = 0.7$ Hz, 1 H, OH), 10.95 (d, $^4J_{H,P} = 0.7$ Hz, 0.1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.7 (d, $J_{C,P} = 10.2$ Hz, C_5H_3), 58.3 (s, OCH_3), 59.9 (d, $^1J_{C,P} = 166.7$ Hz, C_{C5H3}-P), 64.8 (d, $J_{C,P} = 14.0$ Hz, C_5H_3), 67.0 (d, $J_{C,P} = 16.0$ Hz, C_5H_3), 70.2 (s, C_5H_5), 112.0 (d, $^1J_{C,P} = 134.8$ Hz, $C1_{C6H4}$-P), 117.6 (d, $J_{C,P} = 9.5$ Hz, C_6H_4), 119.1 (d, $J_{C,P} = 13.5$ Hz, C_6H_4), 120.9 (d, $^3J_{C,P} = 5.1$ Hz, $C2,6_{C6H5}$), 124.8 (d, $^5J_{C,P} = 0.8$ Hz, $C4_{C6H5}$), 128.7 (d, $^2J_{C,P} = 8.6$ Hz, C_{C5H3}-O), 131.3 (d, $J_{C,P} = 9.7$ Hz, C_6H_4), 134.6 (m, C_6H_4), 151.0 (d, $^2J_{C,P} = 8.3$ Hz, $C1_{C6H5}$-O), 162.2 (d, $^2J_{C,P} = 5.4$ Hz, $C2_{C6H4}$-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 43.4 (100 %), 44.04 (14 %). HRMS (ESI-TOF, m/z): calcd for $C_{23}H_{21}FeO_4P$ 448.0522, found 448.0518 $[M]^+$.

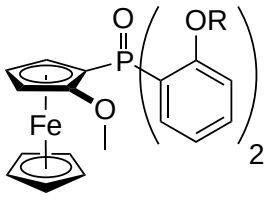
Phenyl (2-Methoxyferrocenyl)(2-methoxyphenyl)phosphinate (64b)



64b

Compound **64b** was obtained by running the reaction for the synthesis of **62** at 0 °C, and obtained as an orange oil with a ratio of both diastereomers of 1: 0.55. ^{1}H NMR ($CDCl_3$, δ): 3.60–3.76 (m, 6.5 H, OCH_3, C_5H_3), 4.03–4.46 (m, 7.5 H, C_5H_5, C_5H_3), 6.74–6.77 (m, 0.2 H, C_6H_4), 6.83–6.87 (m, 0.95 H, C_6H_4), 6.96–7.08 (m, 2 H), 7.21–7.25 (m, 2.4 H), 7.29–7.30 (m, 1 H), 7.38–7.42 (m, 0.25 H), 7.44–7.49 (m, 1 H), 7.93–8.03 (m, 1.2 H, C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.1 (d, $J_{C,P}$ = 10.9 Hz, C_5H_3), 55.2 (d, $J_{C,P}$ = 9.6 Hz, C_5H_3), 55.20 (s, C_6H_4-OCH_3), 55.3 (s, $C_6H_4OCH_3$), 55.6 (s, C_6H_4-OCH_3), 58.26 (C_5H_3-OCH_3), 58.32 (C_5H_3-OCH_3), 60.8 (d, $^{1}J_{C,P}$ = 163.7 Hz, C_{C5H3}-P), 63.5 (d, $J_{C,P}$ = 12.5 Hz, C_5H_3), 63.9 (d, $J_{C,P}$ = 13.7 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 16.2 Hz, C_5H_3), 67.7 (d, $J_{C,P}$ = 10.6 Hz, C_5H_3), 69.4 (C_5H_5), 69.96 (C_5H_5), 70.00 (C_5H_5), 110.8 (d, $J_{C,P}$ = 7.7 Hz, C_6H_4), 111.0 (d, $J_{C,P}$ = 7.7 Hz, C_6H_4), 111.3 (d, $J_{C,P}$ = 8.1 Hz, C_6H_4), 120.2 (d, $^{1}J_{C,P}$ = 138.8 Hz, $C1_{C6H4}$-P), 120.3–120.5 (m), 120.8 (d, $J_{C,P}$ = 5.0 Hz), 121.0 (d, $J_{C,P}$ = 5.0 Hz, C_6H_4), 123.89–123.97 (m), 129.06, 129.12 (d, $J_{C,P}$ = 7.9 Hz, C_{C5H3}-O), 129.2, 129.7 (d, $J_{C,P}$ = 13.0 Hz, C_{C5H3}-O), 133.8 (d, $J_{C,P}$ = 1.9 Hz), 134.1 (d, $J_{C,P}$ = 1.9 Hz), 134.1 (d, $J_{C,P}$ = 1.9 Hz), 134.7 (d, $J_{C,P}$ = 6.7 Hz, C_6H_4), 135.0 (d, $J_{C,P}$ = 7.9 Hz, C_6H_4), 135.6 (d, $J_{C,P}$ = 7.6 Hz, C_6H_4), 151.6 (d, $^{2}J_{C,P}$ = 8.0 Hz, $C2_{C6H5}$-O), 152.1 (d, $^{2}J_{C,P}$ = 8.4 Hz, $C2_{C6H5}$-O), 160.8 (d, $^{2}J_{C,P}$ = 3.3 Hz, $C2_{C6H4}$-O), 161.1 (d, $^{2}J_{C,P}$ = 4.3 Hz, $C2_{C6H4}$-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 30.3 (55.1 %), 33.7 (100 %). HRMS (ESI-TOF, m/z): calcd for $C_{24}H_{23}FeO_4P$ 462.0678, found 462.0644 $[M]^+$.

Bis(2-hydroxyphenyl)(2-methoxyferrocenyl)phosphine Oxide (65a)

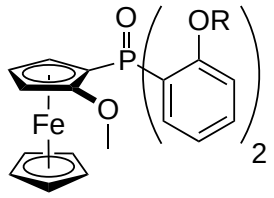


65a (R = H, H)

Compound **65a** was obtained by running the reaction for the synthesis of **62** at 0 °C. Orange Oil. Anal. calcd for $C_{23}H_{20}FeO_4P$ (447.22 g/mol): C, 57.60; H, 4.28. Found: C, 57.29; H, 4.38. ^{1}H NMR ($CDCl_3$, δ): 3.62 (s, 3 H, OCH_3), 3.95 (dt, $J_{H,P}$ = 2.8 Hz, $J_{H,H}$ = 2.0 Hz, C_5H_3), 4.15–4.17 (m, 1 H, C_5H_3), 4.35–4.37 (m, 6 H, C_5H_5, C_5H_3), 6.83 (tdd, $J_{H,H}$ = 7.5 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 0.9 Hz, 1 H, C_6H_4), 6.84 (tdd, $J_{H,H}$ = 7.5 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 0.9 Hz, 1 H, C_6H_4), 6.94 (ddd, $J_{H,H}$ = 8.4 Hz, $J_{H,P}$ = 5.1 Hz, $J_{H,H}$ = 1.0 Hz, 1 H, C_6H_4), 6.98 (ddd, $J_{H,H}$ = 8.4 Hz, $J_{H,P}$ = 4.9 Hz, $J_{H,H}$ = 1.1 Hz, 1 H, C_6H_4), 7.11 (ddd, $J_{H,P}$ = 13.6 Hz, $J_{H,H}$ = 7.8 Hz, $J_{H,H}$ = 1.6 Hz, 1 H, C_6H_4), 7.15 (ddd, $J_{H,P}$ = 14.4 Hz, $J_{H,H}$ = 7.8 Hz, $J_{H,H}$ = 1.6 Hz, 1 H, C_6H_4), 7.36–7.41 (m, 2 H, C_6H_4), 10.42 (s, 1 H, OH), 10.96 (s, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 56.5 (d, $J_{C,P}$ = 8.3 Hz, C_5H_3), 58.4 (s, OCH_3), 61.8 (d, $^{1}J_{C,P}$ = 120.0 Hz, C_{C5H3}-P), 64.7 (d, $J_{C,P}$ = 12.0 Hz, C_5H_3), 67.8 (d, $J_{C,P}$ = 13.0 Hz, C_5H_3), 70.0 (s, C_5H_5), 112.4 (d, $^{1}J_{C,P}$ = 107.7 Hz, $C1_{C6H4}$-P) , 113.4 (d, $^{1}J_{C,P}$ = 109.4 Hz, $C1_{C6H4}$-P), 118.2 (d, $J_{C,P}$ = 7.8 Hz, C_6H_4), 118.5 (d, $J_{C,P}$ = 7.6 Hz, C_6H_4), 119.0 (s, C_6H_4), 119.1 (s, C_6H_4), 128.8 (d, $^{2}J_{C,P}$ = 8.1 Hz, C_{C5H3}-O), 131.1 (d, $J_{C,P}$ = 10.3 Hz, C_6H_4), 131.8 (d, $J_{C,P}$ = 10.7 Hz, C_6H_4), 134.4 (d, $J_{C,P}$ = 12.1 Hz, C_6H_4), 162.2 (d, $^{2}J_{C,P}$ = 3.3 Hz, $C2_{C6H4}$-O), 162.9 (d, $^{2}J_{C,P}$ = 3.1 Hz, $C2_{C6H4}$-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 49.3. HRMS (ESI-TOF,

m/z): calcd for $C_{23}H_{21}FeO_4P$ 448.0522, found 448.0518 $[M]^+$.

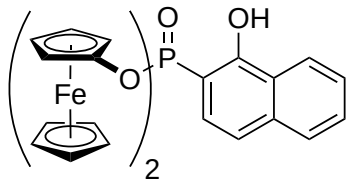
(2-Hydroxyphenyl)(2-methoxyferrocenyl)(2-methoxyphenyl)phosphine Oxide (65b)



65b (R = H, CH_3)

Compound **65b** was obtained by running the reaction for the synthesis of **62** at 0 °C. Orange Oil. Anal. calcd for $C_{24}H_{23}FeO_4P \cdot 1/6\ C_6H_{14}$ (462.26 · 86.18 g/mol): C, 63.00; H, 5.36. Found: C, 62.81; H, 5.45. ^{1}H NMR ($CDCl_3$, δ): 3.63 (s, 3 H, C_6H_4-OCH_3), 3.66 (s, 3 H, C_5H_3-OCH_3), 3.85 (dpt, $J_{H,P}$ = 2.83 Hz, $^{3,4}J_{H,H}$ = 1.7 Hz, 1 H, C_5H_3), 4.07 (ddd J = 2.6 Hz, 1 H, C_5H_3) , 4.33 (dpt, $J_{H,P}$ = 2.7 Hz, $^{3,4}J_{H,H}$ = 1.6 Hz, 1 H, C_5H_3), 4.37 (s, 5 H, C_5H_5), 6.73 (tdd, $J_{H,H}$ = 7.6 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 1.1 Hz, 1 H, C_6H_4-OH), 6.87 (dd, $J_{H,H}$ = 8.2 Hz, $J_{H,P}$ = 5.4 Hz, 1 H, C_6H_4-OCH_3), 6.95–7.04 (m, 3 H, C_6H_4), 7.36 (dddd, $J_{H,H}$ = 8.6 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.5 Hz, $J_{H,P}$ = 1.5 Hz, 1 H, C_6H_4-OH) , 7.45 (dddd, $J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.9 Hz, $J_{H,P}$ = 1.1 Hz, 1 H, C_6H_4-OCH_3) , 7.56 (ddd, $J_{H,P}$ = 14.6 Hz, $J_{H,H}$ = 7.6 Hz, $J_{H,H}$ = 1.7, 1 H, C_6H_4-OCH_3), 12.17 (s, 1 H, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.6 (d, $J_{C,P}$ = 7.8 Hz, C_5H_3), 55.9 (s, C_6H_4-OCH_3), 58.5 (s, C_5H_3-OCH_3), 63.2 (d, $^1J_{C,P}$ = 120.4 Hz, C_{C5H3}-P), 64.0 (d, $J_{C,P}$ = 11.7 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 13.1 Hz, C_5H_3), 70.0 (C_5H_5), 112.1 (d, $J_{C,P}$ = 6.7 Hz, C_6H_4-OCH_3), 113.2 (d, $^1J_{C,P}$ = 110.4 Hz, $C1_{C6H4OH}$-P), 117.9 (d, $J_{C,P}$ = 7.9 Hz, C_6H_4), 118.1 (d, $J_{C,P}$ = 13.1 Hz, C_6H_4-OH), 120.4 (d, $J_{C,P}$ = 12.6 Hz, C_6H_4), 122.0 (d, $^1J_{C,P}$ = 109.2 Hz, $C1_{C6H4OCH}$-P), 129.8 (d, $^2J_{C,P}$ = 6.6 Hz, C_{C5H3}-O), 130.5 (d, $J_{C,P}$ = 10.9 Hz, C_6H_4OH), 133.3 (d, $J_{C,P}$ = 2.2 Hz, C_6H_4), 133.9 (d, $J_{C,P}$ = 8.9 Hz, C_6H_4), 134.1 (d, $J_{C,P}$ = 2.0 Hz, C_6H_4), 161.5 (d, $^2J_{C,P}$ = 2.9 Hz, $C2_{C6H4}$-OCH_3), 163.9 (d, $^2J_{C,P}$ = 3.3 Hz, $C2_{C6H4}$-OH). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 38.2. HRMS (ESI-TOF, m/z): calcd for $C_{24}H_{23}FeO_4P$ + Na 485.0576, found 485.0559 $[M+Na]^+$.

Diferrocenyl (1-Hydroxynaphth-2-yl)phosphonate (66)



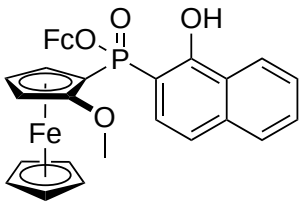
66

Phosphate **49** (70 mg, 0.131 mmol), diisopropylamine (0.11 mL, 0.783 mmol), BuLi (0.31 mL, 0.78 mmol) and dimethyl sulfate (0.1 mL, 1.05 mmol) were reacted at 0 °C for 2 h, according to the general procedure GP2. Purification was realized by column chromatography (silica, 2.5 · 12 cm column size) using a 95/5 dichloromethane/ethyl acetate mixture (v/v) as the eluent, resulting in the elution of two fractions. At first, the phosphonate **66** was eluted followed by the phosphinate **66**.

Orange solid. Yield: 13 mg (0.024 mmol, 19 % based on **49**). Anal. calcd for $C_{30}H_{25}Fe_2O_4P$ (592.18 g/mol): C, 60.85; H, 4.26. Found: C, 61.27; H, 4.56. Mp.: 163–168 °C. ^{1}H NMR ($CDCl_3$, δ): 3.83–3.84 (m, 2 H, C_5H_4), 3.85–3.86 (m, 2 H, C_5H_4), 4.19 (s, 10 H, C_5H_5), 4.30–4.31 (m, 2 H, C_5H_4), 4.38–4.39 (m, 2 H, C_5H_4), 7.32–7.40 (m, 2 H, H3/4), 7.54 (ddd, $J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 6.8 Hz, $J_{H,H}$ = 1.2 Hz, 1 H, C_6H_4), 7.62 (ddd, $J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 6.9 Hz, $J_{H,H}$ = 1.3 Hz, 1 H, C_6H_4), 7.77 (d, $J_{H,H}$ = 8.1 Hz, 1 H, C_6H_4), 8.40 (d, $J_{H,H}$ =

8.3 Hz, 1 H, C_6H_4), 10.99 (s, 1 H, OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.6 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 59.9 (d, $J_{C,P}$ = 4.2 Hz, C_5H_4), 62.9 (C_5H_4), 63.0 (C_5H_4), 69.6 (C_5H_5), 99.5 (d, $^1J_{C,P}$ = 185.2 Hz, C1), 117.1 (d, $^2J_{C,P}$ = 4.2 Hz, C_{C5H4}-O), 119.5 (d, $J_{C,P}$ =14.1 Hz, C4), 123.7 (C_6H_4), 124.8 (d, $^3J_{C,P}$ = 14.4 Hz, C8a), 125.4 (d, $J_{C,P}$ = 6.4 Hz, C3), 126.2 (C_6H_4), 127.6 (C_6H_4), 129.5 (C_6H_4), 137.2 (d, $^4J_{C,P}$ = 2.1 Hz, C4a), 161.5 (d, $^2J_{C,P}$ = 8.1 Hz, C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 17.7. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{25}Fe_2O_4P$ 592.0185, found 592.0202 $[M]^+$.

Ferrocenyl (1-Hydroxynaphth-2-yl)(2-methoxyferrocenyl)phosphinate (67)

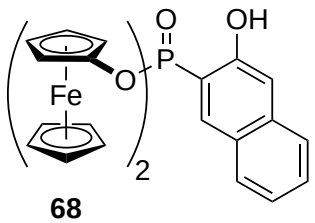


67

Orange solid. The compound was obtained in a ratio of both diastereomers of 1 : 0.78. Crystals, suitable for single crystal X-ray diffraction analysis, were obtained by slow evaporation of a hexane solution containing 24 at ambient temperature. Yield: 24 mg (0.040 mmol, 30 % based on **49**). Anal. calcd for $C_{31}H_{27}Fe_2O_4P$ (606.21 g/mol): C, 61.42; H, 4.49. Found: C, 61.58; H, 4.73. Mp.: 194–196 °C. ^1H NMR ($CDCl_3$, δ): 3.66 (s, 3 H, OCH_3, ma), 3.74–3.76 (m, 1.7 H, ma, mi), 3.76–3.79 (m, 1.7 H, ma, mi), 3.86 (s, 2.1 H, OCH_3, mi), 4.10 (dd, $J_{H,H}$ = 2.8 H, $J_{H,H}$ = 2.8 H, 0.7 H, C_5H_3, mi), 4.16 (dd, $J_{H,H}$ = 2.6 H, $J_{H,H}$ = 2.6 H, 1 H, C_5H_3, ma), 4.17–4.18 (m, 5.7 H, C_5H_5 ma, $C_5H_{3/4}$ mi), 4.19–4.21 (m, 9.5 H, C_5H_5 ma, C_5H_5 mi, $C_5H_{3/4}$ ma), 4.23 (ddd, $J_{H,H}$ = 2.7 Hz, $J_{H,P}$ = 2.2 Hz, $J_{H,H}$ = 1.5 Hz, 0.7 H, C_5H_3 mi), 4.26 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,P}$ = 2.8 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3 ma), 4.32 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 0.7 H, C_5H_3 mi), 4.36 (dddd, J = 2.7 Hz, J = 1.4 Hz, J = 1.4 Hz, J = 0.7 Hz, 1 H, ma), 4.42 (s, 3.5 H, C_5H_5, mi), 4.45 (dddd, J = 2.7 Hz, J = 1.4 Hz, J = 1.4 Hz, J = 0.6 Hz, 0.7 H, mi), 4.51 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,H}$ = 1.7 Hz, $J_{H,P}$ = 1.7 Hz, 1 H, ma), 7.26 (dd, $J_{H,H}$ = 8.5 Hz, $J_{H,P}$ = 3.0 Hz, 0.7 H, H3/4 mi), 7.30 (dd, $J_{H,H}$ = 8.6 Hz, $J_{H,P}$ = 2.9 Hz, 1 H, H3/4 ma), 7.39 (dd, $J_{H,P}$ = 12.8 Hz, $J_{H,H}$ = 8.6 Hz, 0.7 H, H3/4 mi), 7.44 (dd, $J_{H,P}$ = 13.1 Hz, $J_{H,H}$ = 8.6 Hz, 1 H, H3/4 ma), 7.48–7.52 (m, 1.7 H, ma, mi), 7.54–7.58 (m, 1.7 H, ma, mi), 7.71 (d, $J_{H,H}$ = 8.9 Hz, 0.7 H, mi), 7.73 (d, $J_{H,H}$ = 8.6 Hz, 1 H, ma), 7.38 (d, $J_{H,H}$ = 8.4 Hz, 0.7 H, mi), 8.42 (d, $J_{H,H}$ = 8.4 Hz, 1 H, ma), 11.96 (s, 0.7 H, OH, mi), 11.99 (s, 1 H, OH, ma). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.7* (d, $J_{C,P}$ = 10.1 Hz, C_5H_3), 55.8* (d, $J_{C,P}$ = 10.2 Hz, C_5H_3), 58.3 (OCH_3), 58.3 (OCH_3), 59.9 (d, $J_{C,P}$ = 4.3 Hz, C_5H_4), 60.0 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 60.1 (d, $J_{C,P}$ = 4.0 Hz, C_5H_4), 60.4 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 60.6 (C_{C5H3}-P, the second signal overlaps), 60.9 (C_{C5H3}-P, the second signal overlaps), 62.68 (C_5H_4), 62.76 (C_5H_4), 62.77 (C_5H_4), 62.9 (C_5H_4), 64.4 (d, $J_{C,P}$ = 12.2 Hz, C_5H_3), 64.6 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3), 67.0* (d, $J_{C,P}$ = 15.9 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 10.8 Hz, C_5H_3), 69.48 (C_5H_5), 69.49 (C_5H_5), 70.0 (C_5H_5), 70.2 (C_5H_5), 103.7 (C2, HMBC), 117.1 (d, $^2J_{C,P}$ = 6.8 Hz, C_{C5H4}-O), 128.3 (d, $^2J_{C,P}$ = 11.5 Hz, C_{C5H3}-O), 118.5* (d, $J_{C,P}$ = 13.5 Hz, $C_{10}H_6$), 118.7* (d, $J_{C,P}$ = 13.5 Hz, $C_{10}H_6$), 123.5* ($C_{10}H_6$), 123.68* ($C_{10}H_6$), 123.69* ($C_{10}H_6$), 125.5* ($C_{10}H_6$), 125.6* ($C_{10}H_6$), 125.62* ($C_{10}H_6$), 125.67* ($C_{10}H_6$), 126.2* ($C_{10}H_6$), 126.3* ($C_{10}H_6$), 127.3* ($C_{10}H_6$), 127.4* ($C_{10}H_6$), 128.1 (C_{C5H3}-O, HMBC), 128.5 (C_{C5H3}-O, HMBC), 136.5 (C4a/C8a, HMBC), 160.8 (C1, HMBC). (*Obtained from DEPT90 measurements). $^{31}P\{^1H\}$

NMR ($CDCl_3$, δ): 44.6 (ma), 44.7 (mi). HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{27}Fe_2O_4P$ + H 607.0373, found 607.0376 $[M+H]^+$.

Diferrocenyl (3-Hydroxynaphth-2-yl)phosphonate (68)

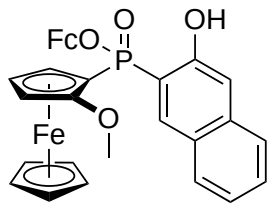


68

Phosphate **50** (82 mg, 0.17 mmol), diisopropylamine (0.14 mL, 1.01 mmol), BuLi (0.41 mL, 1.03 mmol) and Me_2SO_4 (0.3 mL, 3.15 mmol) were reacted at –80 °C (24) or 0 °C (25) for 2 h according to the general procedure GP2. Purification was realized by column chromatography (silica, 2.5 · 12 cm column size) using a 95/5 dichloromethane/ethyl acetate mixture (v/v) for **68** and **69a** or a 2/3 dichloromethane/ethyl acetate mixture (v/v) for **69b** as the eluents.

Orange oil. Yield: 32 mg (0.066 mmol, 39 % based on **50**). Anal. calcd for $C_{30}H_{25}Fe_2O_4P \cdot 1/4\ CHCl_3$ (592.18 · 119.38 g/mol): C, 58.41; H, 4.09. Found: C, 58.58; H, 4.43. ^{1}H NMR ($CDCl_3$, δ): 3.85–3.88 (m, 4 H, C_5H_4), 4.19 (s, 10 H, C_5H_5), 4.31–4.32 (m, 2 H, C_5H_4), 4.38–4.39 (m, 2 H, C_5H_4), 7.33–7.36 (m, 2 H, H4, H5/6/7/8), 7.51 (ddd, $J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 6.8 Hz, $J_{H,H}$ = 1.0 Hz, C_6H_4), 7.71 (d, $J_{H,H}$ = 8.3 Hz, C_6H_4), 7.80 (d, $J_{H,H}$ = 8.2 Hz, C_6H_4), 8.08 (d, $^3J_{H,P}$ = 17.0 Hz, H1), 9.70 (d, $^4J_{H,P}$ = 0.9 Hz, OH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.7 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 59.87 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 63.0 (C_5H_4), 63.1 (C_5H_4), 69.6 (C_5H_5), 112.1 (d, $^3J_{C,P}$ = 11.9 Hz, C4), 117.2 (d, $^2J_{C,P}$ = 4.6 Hz, C_{C5H4}-O), 122.4 (d, $^1J_{C,P}$ = 181.3 Hz, C2), 124.3 (C_6H_4), 126.7 (C_6H_4), 128.7 (C_6H_4), 129.2 (C_6H_4), 134.8 (d, $^2J_{C,P}$ = 5.5 Hz, C1), 138.0 (C4a/C8a), 139.6 (C4a/C8a), 156.6 (d, $^2J_{C,P}$ = 7.8 Hz, C3). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 14.6. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{25}Fe_2O_4P$ 592.0185, found 592.0156 $[M]^+$.

Ferrocenyl (3-Hydroxynaphth-2-yl)(2-methoxyferrocenyl)phosphinate (69a)

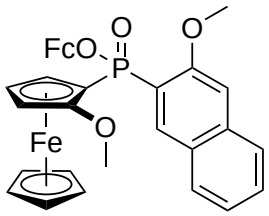


69a

Compound **69a** was obtained as an orange oil with a ratio of two diastereomers of 1:0.51. Yield: 45 mg (0.074 mmol, 44 % based on **50**). Anal. calcd for $C_{31}H_{27}Fe_2O_4P$ (606.21 g/mol): C, 61.42; H, 4.49. Found: C, 61.21; H, 4.94. Mp.: > 250 °C (decomp.). ^{1}H NMR ($CDCl_3$, δ): 3.667 (s, 1.5 H, OCH_3, mi), 3.68 (d, $J_{H,H}$ = 3.2 Hz, 1 H, C_5H_3, ma), 3.75–3.77 (m, 1.5 H, $C_5H_{3/4}$, mi, ma), 3.78–3.81 (m, 1.5 H, $C_5H_{3/4}$, mi, ma), 3.88 (s, 3 H, OCH_3, ma), 4.10–4.12 (m, 1 H, $C_5H_{3/4}$, ma), 4.17–4.20 (m, 11 H, C_5H_5 ma, C_5H_5 mi, $C_5H_{3/4}$ mi), 4.21–4.23 (m, 1 H, $C_5H_{3/4}$, ma), 4.26–4.28 (m, 0.5 H, $C_5H_{3/4}$, mi), 4.34–4.35 (m, 1.5 H, $C_5H_{3/4}$, ma, mi), 4.43 (s, 5 H, C_5H_5, ma), 4.44–4.46 (m, 1 H, $C_5H_{3/4}$, ma), 4.54–4.55 (m, 0.5 H, $C_5H_{3/4}$, mi), 7.26–7–32 (m, 3 H, H4, H5/6/7/8, ma, mi), 7.42–7.48 (m, 1.5 H, H5/6/7/8, ma, mi), 7.66 (d, $J_{H,H}$ = 8.2 Hz, 1 H, H5/6/7/8, ma), 7.69 (d, $J_{H,H}$ = 8.2 Hz, 0.5 H, H5/6/7/8, mi), 7.71 (d, $J_{H,H}$ = 8.2 Hz, 1 H, H5/6/7/8, ma), 7.75 (d, $J_{H,H}$ = 8.3 Hz, 0.5 H, H5/6/7/8, mi), 8.07 (d, $^3J_{H,P}$ = 16.5 Hz, 1 H, H1, ma), 8.16 (d, $^3J_{H,P}$ = 16.8 Hz, 0.5 H, H1, mi), 10.75 (d, $^4J_{H,P}$ = 0.9 Hz, 1 H, OH, ma), 10.83 (d, $^4J_{H,P}$ = 0.9 Hz, 0.5 H, OH, mi). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.89 (d, $J_{C,P}$ = 10.5 Hz, C_5H_3, mi), 55.92 (d, $J_{C,P}$ = 10.2 Hz, C_5H_3, ma), 58.3 (OCH_3, mi), 58.4

(OCH_3, ma), 59.97 (d, $^1J_{C,P}$ = 167.3 Hz, C_{C5H3}-P, ma), 59.98 (d, $J_{C,P}$ = 4.4 Hz, C_5H_4, mi), 60.03 (d, $J_{C,P}$ = 4.3 Hz, C_5H_4, ma), 60.05 (d, $J_{C,P}$ = 3.9 Hz, C_5H_4, mi), 60.3 (d, $J_{C,P}$ = 4.0 Hz, C_5H_4, ma), 62.77 (C_5H_4, mi), 62.80 (C_5H_4, mi), 62.86 (C_5H_4, ma), 62.91 (C_5H_4, ma), 64.5 (d, $J_{C,P}$ = 12.1 Hz, C_5H_3, mi), 64.8 (d, $J_{C,P}$ = 13.9 Hz, C_5H_3, ma), 67.1 (d, $J_{C,P}$ = 16.0 Hz, C_5H_3, ma), 67.4 (d, $J_{C,P}$ = 10.9 Hz, C_5H_3, ma), 69.62 (C_5H_5, ma), 69.54 (C_5H_5, mi), 70.0 (C_5H_5, mi), 70.2 (C_5H_5, ma), 111.42 (d, $^3J_{C,P}$ = 8.6 Hz, C4, mi), 111.48 (d, $^3J_{C,P}$ = 9.2 Hz, C4, ma), 115.6 (d, $^1J_{C,P}$ = 132.0 Hz, C2, ma), 117.32 (C_{C5H4}-O), 117.33 (C_{C5H4}-O), 117.37 (C_{C5H4}-O), 123.61 (C5/6/7/8, ma), 123.65 (C5/6/7/8, mi), 126.49 (C5/6/7/8, ma), 126.55 (C5/6/7/8, mi), 127.2 (d, $^2J_{C,P}$ = 14.6 Hz, C_{C5H3}-O, ma), 128.4 (C5/6/7/8, ma), 128.6 (C5/6/7/8, mi), 128.65 (C5/6/7/8, mi), 128.71 (C5/6/7/8, ma), 133.8 (d, $^2J_{C,P}$ = 9.9 Hz, C1, ma), 134.8 (d, $^2J_{C,P}$ = 9.3 Hz, C1, mi), 137.4 (C4a/C8a), 137.46 (C4a/C8a), 137.48 (C4a/C8a), 157.4 (d, $^2J_{C,P}$ = 6.1 Hz, C3, ma). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 42.6 (ma), 42.7 (mi). HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{27}Fe_2O_4P$ 606.0341, found 606.0316 $[M]^+$.

Ferrocenyl (2-Methoxyferrocenyl)(3-methoxy-2-naphthyl)phosphinate (69b)

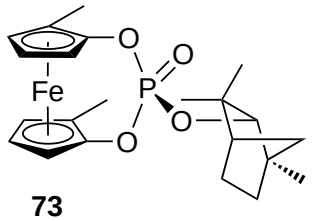


69b

Compound **96b** was obtained as an orange solid with a d.r. of 1 : 0.97. Crystals, suitable for single crystal X-ray diffraction analysis, were obtained by slow evaporation of a hexane solution containing **96b** at ambient temperature. Yield: 20 mg (0.032 mmol, 19 % based on **50**). Anal. calcd for $C_{32}H_{29}Fe_2O_4P \cdot 5/6\ C_6H_{14}$ (620.24 · 5/6 86.18 g/mol): C, 64.22; H, 5.92. Found: C, 64.00; H, 6.14. Mp.: 179 °C. ^1H NMR ($CDCl_3$, δ): 3.57 (s, mi, 3 H, OCH_3(Fc)), 3.72–3.76 (m, 4 H, C_5H_4), 3.77 (s, ma, 3 H, OCH_3(Fc)), 3.82 (s, ma, 3 H, $OCH_3(C_{10}H_6)$), 3.91 (s, mi, 3 H, $OCH_3(C_{10}H_6)$), 4.02 (dd, mi, $J_{H,P}$ = 5.4 Hz, $J_{H,H}$ = 2.7 Hz, 1 H, C_5H_3), 4.07 (dd, ma, $J_{H,P}$ = 5.2 Hz, $J_{H,H}$ = 2.6 Hz, 1 H, C_5H_3), 4.02 (td, mi, J = 2.7 Hz, J = 1.5 Hz, 1 H, C_5H_3), 4.17–4.19 (m, 1 H, C_5H_3), 4.20 (s, 5 H, C_5H_5), 4.21 (s, 5 H, C_5H_5), 4.22–4.26 (m, 7 H, C_5H_5, C_5H_4, C_5H_3), 4.34–4.36 (m, 1 H, C_5H_4), 4.44–4.45 (m, 2 H, C_5H_3, C_5H_4), 4.47–4.48 (m, 6 H, C_5H_5, C_5H_4), 7.02 (d, $^4J_{H,P}$ = 5.7 Hz, 1 H, H4), 7.12 (d, $^4J_{H,P}$ = 5.8 Hz, 1 H, H4), 7.33–7.40 (m, 2 H, $C_{10}H_7$), 7.47 (ddd, $^3J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 6.9 Hz, J = 1.3 Hz, 1 H, $C_{10}H_7$), 7.52 (ddd, $^3J_{H,H}$ = 8.2 Hz, $J_{H,H}$ = 6.9 Hz, J = 1.3 Hz, 1 H, $C_{10}H_7$), 7.67 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, $C_{10}H_7$), 7.73 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H, $C_{10}H_7$), 7.87 (d, $J_{H,H}$ = 8.2 Hz, 1 H, $C_{10}H_7$), 7.90 (d, $J_{H,H}$ = 8.2 Hz, 1 H, $C_{10}H_7$), 8.60 (d, $^2J_{H,H}$ = 15.7 Hz, 1 H, H1), 8.63 (d, $^2J_{H,P}$ = 15.5 Hz, 1 H, H1). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.0 (d, $J_{C,P}$ = 10.8, C_5H_3), 55.2 (s, $OCH_3(C_{10}H_6)$), 55.32 (d, $J_{C,P}$ = 10.8, C_5H_3), 55.34 (s, $OCH_3(C_{10}H_6)$), 58.2 (s, OCH_3(Fc)), 58.3 (s, OCH_3(Fc)), 60.0 (d, $^3J_{C,P}$ = 3.6 Hz, C2/5C_5H_4) , 60.2 (d, $^1J_{C,P}$ = 45.1 Hz, C-P), 60.4 (d, $^3J_{C,P}$ = 3.7 Hz, C2/5C_5H_4), 60.71 (d, $^1J_{C,P}$ = 164.4 Hz, C-P), 60.74 (d, $^3J_{C,P}$ = 3.9 Hz, C2/5$_{C5H4}$), 60.8 (d, $^3J_{C,P}$ = 4.3 Hz, C2/5$_{C5H4}$), 61.1 (d, $^1J_{C,P}$ = 166.2 Hz, C-P), 62.36 (s, C3/4$_{C5H4}$), 62.40 (s, C3/4$_{C5H4}$), 62.43 (s, C3/4$_{C5H4}$), 62.5 (s, C3/4$_{C5H4}$), 63.5 (d, $J_{C,P}$ = 12.6 Hz, C_5H_3), 63.9 (d, $J_{C,P}$ = 13.7 Hz, C_5H_3) , 67.3 (d, $J_{C,P}$ = 16.5 Hz, C_5H_3), 67.8 (d, $J_{C,P}$ = 10.4 Hz, C_5H_3), 69.35 (s, C_5H_5), 69.38 (s, C_5H_5), 70.0 (s, C_5H_5), 70.1 (s, C_5H_5), 105.6 (d, $^3J_{C,P}$ = 7.3 Hz, C4), 105.8 (d, $^3J_{C,P}$ = 7.4 Hz, C4), 117.3 (d,

$^2J_{C,P}$ = 5.7 Hz, C_{C5H4}-O), 117.8 (d, $^2J_{C,P}$ = 6.1 Hz, C_{C5H4}-O), 121.4 (d, $^1J_{C,P}$ = 133.2 Hz, C2), 122.0 (d, $^1J_{C,P}$ = 136.2 Hz, C2), 124.1 ($C_{10}H_7$), 124.2 ($C_{10}H_7$), 126.3 ($C_{10}H_7$), 126.4 ($C_{10}H_7$), 128.3 ($C_{10}H_7$), 128.5 ($C_{10}H_7$), 129.08 ($C_{10}H_7$), 129.14 ($C_{10}H_7$), 128.0 (d, $^3J_{C,P}$ = 8.2 Hz, C4a), 128.1 (d, $^3J_{C,P}$ = 8.1 Hz, C4a), 129.3 (d, $^2J_{C,P}$ = 7.6 Hz, C_{C5H3}-O), 129.9 (d, $^2J_{C,P}$ = 13.1 Hz, C_{C5H3}-O), 136.76 (C8a), 136.77 (C8a), 137.7 (d, $^2J_{C,P}$ = 7.3 Hz, C1), 138.2 (d, $^2J_{C,P}$ = 7.2 Hz, C1), 157.3 (d, $^2J_{C,P}$ = 4.3 Hz, C3-O), 157.5 (d, $^2J_{C,P}$ = 4.0 Hz, C3-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 29.4 (ma), 33.5 (mi). HRMS (ESI-TOF, m/z): calcd for $C_{32}H_{29}Fe_2O_4P$ 620.0502, found 620.0508 $[M]^+$.

1,3-Dioxa-2-((1*R*)-α-fenchyl)(oxo)phospha-[3](2,2'-dimethyl)-ferrocenophane ((1*R*)-73)

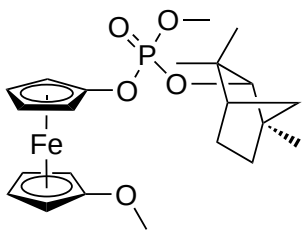


73

LiTMP (212 mg, 1.44 mmol) was dissolved in 10 mL of tetrahydrofuran and cooled to –50 °C. Compound **72** (150 mg, 0.36 mmol) was added in a single portion and stirring was continued for 4 h in a temperature range of -30 to –10 °C. Dimethyl sulfate (0.3 mL, 3.2 mmol) was added in a single portion and the reaction mixture was allowed to warm to ambient temperature. After 18 h, all volatiles were removed in vacuum. Purification was realized using column chromatography (silica, 2 · 25 cm column size) and dichloromethane as the eluent. Compound **73** was obtained as an orange solid as a mixture of three diastereomers in a ratio of 1 : 0.25 : 0.3. Single crystals, suitable for single crystal X-ray diffraction analysis, were obtained by slow evaporation of a hexane solution containing **73** at ambient temperature.

Yield: 84 mg (0.189 mmol, 53 % based on (1*R*)-**72**). Anal. calcd for $C_{22}H_{29}FeO_4P$ (444.28 g/mol): C, 59.48; H, 6.58. Found: C, 59.46; H, 6.86. Mp.: 84 °C. ^1H NMR ($CDCl_3$, δ): An assignment of the signals to hydrogen atoms is hardly possible, due to an overlap of all three diastereomers and their different ratio. For spectra see ESI. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 9.1 (d, $^4J_{C,P}$ = 5.9 Hz, $CH_3(C_5H_3)$), 11.5 (d, $^4J_{C,P}$ = 3.8 Hz, $CH_3(C_5H_3)$), 19.24 (CH_3), 19.26 (CH_3), 21.15 (CH_3), 21.17 (CH_3), 21.3 (CH_3), 25.96 (C5/6), 26.01 (C5/6), 26.32 (C5/6), 26.34 (C5/6), 26.6 (C5/6), 29.59 (CH_3), 29.66 (CH_3), 29.71 (CH_3), 39.78 (d, $^3J_{C,P}$ = 2.6 Hz, C3), 39.80 (d, $^3J_{C,P}$ = 2.4 Hz, C3), 39.85 (d, $^3J_{C,P}$ = 2.1 Hz, C3), 40.92 (C7), 40.97 (C7), 47.67 (C4), 47.74 (C4), 49.11 (d, $^3J_{C,P}$ = 5.9 Hz, C1), 49.15 (d, $^3J_{C,P}$ = 5.6 Hz, C1), 49.18 (d, $^3J_{C,P}$ = 5.6 Hz, C1), 60.14 (d, $J_{C,P}$ = 8.7 Hz), 61.2 (d, $J_{C,P}$ = 1.8 Hz), 61.3 (d, $J_{C,P}$ = 2.4 Hz), 64.08, 64.10, 64.14, 65.9, 66.55, 66.60, 67.4 (d, $J_{C,P}$ = 5.4 Hz), 68.1, 68.5 (d, $J_{C,P}$ = 4.2 Hz), 68.6 (d, $J_{C,P}$ = 4.1 Hz), 78.8 (d, $^3J_{C,P}$ = 5.4 Hz, C_{C5H3}-CH_3), 78.95 (d, $^3J_{C,P}$ = 5.9 Hz, C_{C5H3}-CH_3), 79.01 (d, $^3J_{C,P}$ = 5.6 Hz, C_{C5H3}-CH_3), 94.5 (d, $^2J_{C,P}$ = 8.0 Hz, C2), 94.6 (d, $^2J_{C,P}$ = 7.9 Hz, C2), 94.9 (d, $^2J_{C,P}$ = 8.1 Hz, C2), 109.40 (d, $^2J_{C,P}$ = 14.8 Hz, C_{C5H3}-O), 109.49 (d, $^2J_{C,P}$ = 13.9 Hz, C_{C5H3}-O), 109.58 (d, $^2J_{C,P}$ = 14.9 Hz, C_{C5H3}-O), 109.64 (d, $^2J_{C,P}$ = 14.1 Hz, C_{C5H3}-O), 110.8 (d, $^2J_{C,P}$ = 13.0 Hz, C_{C5H3}-O), 111.0 (d, $^2J_{C,P}$ = 13.1 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 0.77 (30 %), 0.87 (25 %), 0.96 (100 %). HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{29}FeO_4P$ 444.1148, found 444.1118 $[M]^+$.

(1*R*)-α-Fenchyl (1'-Methoxyferrocenyl) Methyl Phosphate (74)

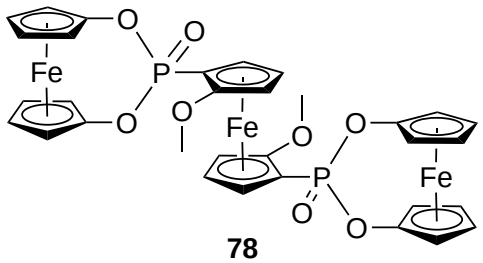


74

LiTMP (212 mg, 1.44 mmol) was dissolved in 10 mL of tetrahydrofuran and cooled to –50 °C. Compound (1*R*)-**72** (150 mg, 0.36 mmol) was added in a single portion and the reaction mixture was allowed to warm to ambient temperature. After stirring for 18 h, dimethyl sulfate (0.3 mL, 3.2 mmol) was added in a single portion and stirring was continued for additionally 6 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 2 · 18 cm column size) using a 95/5 dichloromethane/ethyl acetate mixture (*v*/*v*) for the elution of 1,1'-Fc(OMe)$_2$ (18 mg, 0.073 mmol, 20 % based on (1*R*)-**72**). Compound **74** was eluted using a 9/1 dichloromethane/ethyl acetate mixture (*v*/*v*) as the eluent (R_f = 0.37). The title compound was obtained as an orange oil as a mixture of two diastereomers in a 1 : 1 ratio.

Yield: 17 mg (0.037 mmol, 10 % based on (1*R*)-**72**). ^{1}H NMR ($CDCl_3$, δ): 0.89 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3), 1.05–1.07 (m, 8 H, CH_3, H5/6), 1.10 (s, 3 H, CH_3), 1.13 (s, 3 H, CH_3), 1.15–1.16 (m, 1 H, H7), 1.18–1.19 (m, 1 H, H7), 1.41–1.46 (m, 2 H, H5/6), 1.49–1.52 (m, 2 H, H7), 1.69–1.71 (m, 6 H, H5/6, H4), 3.366 (s, 3 H, C-O-CH_3), 3.370 (s, 3 H, C-O-CH_3), 3.808 (d, $^3J_{H,P}$ = 11.3 Hz, 3 H, P-O-CH_3), 3.815 (d, $^3J_{H,P}$ = 11.3 Hz, 3 H, P-O-CH_3), 3.91–3.93 (m, 8 H, C_5H_4), 3.99 (dd, $^3J_{H,P}$ = 8.4 Hz, $J_{H,H}$ = 1.9 Hz, 1 H, H2), 4.00 (dd, $^3J_{H,P}$ = 8.4 Hz, $J_{H,H}$ = 1.8 Hz, 1 H, H2), 4.14–4.15 (m, 4 H, C_5H_4), 4.41 (dd, $J_{H,P}$ = 3.5 Hz, $J_{H,P}$ = 1.8 Hz, 1 H, C_5H_4), 4.42–4.43 (m, 2 H, C_5H_4), 4.46 (dd, $J_{H,P}$ = 3.3 Hz, $J_{H,P}$ = 1.6 Hz, 1 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.2 (CH_3), 20.74 (CH_3), 20.75 (CH_3), 25.62 (C5/6), 25.65 (C5/6), 25.89 (C5/6), 25.90 (C5/6), 29.8 (CH_3), 39.53 (C3), 39.55 (C3), 40.92 (C7), 47.9 (C4), 49.21 (C1), 49.22 (C1), 49.25 (C1), 49.26 (C1), 54.58 (P-O-CH_3), 54.60 (P-O-CH_3), 54.63 (P-O-CH_3), 54.65 (P-O-CH_3), 56.31 (C_5H_4), 57.5 (C-O-CH_3), 60.29 (C_5H_4), 60.32 (C_5H_4), 60.35 (C_5H_4), 60.36 (C_5H_4), 60.37 (C_5H_4), 63.10 (C_5H_4), 63.12 (C_5H_4), 63.15 (C_5H_4), 63.15 (C_5H_4), 63.40 (C_5H_4), 63.41 (C_5H_4), 91.57 (C2), 91.60 (C2), 91.63 (C2), 91.66 (C2), 117.84 (C_{C5H4}-O-P), 117.85 (C_{C5H4}-O-P), 117.88 (C_{C5H4}-O-P), 117.89 (C_{C5H4}-O-P), 128.1 (C_{C5H4}-O-C). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –3.95, -3.91. HRMS (ESI-TOF, m/z): calcd for $C_{22}H_{29}FeO_5P$ 462.1259, found 462.1246 $[M]^+$.

meso-2,2'-Dimethoxy-1,1'-bis(1,3-dioxa-2-(oxo)phospha-[3]-ferrocenophan-2-yl)-ferrocene (78)



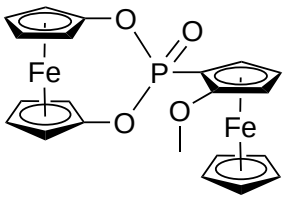
78

Phosphate **76** (36 mg, 0.067 mmol), diisopropylamine (0.04 mL, 0.27 mmol), BuLi (0.11 mL, 0.275 mmol) and dimethyl sulfate (0.05 mL, 0.527 mmol) were reacted at –30 °C for 2 h according to the general procedure GP2. Purification was realized by column chromatography (silica, 2 · 12 cm column size) using a 1/1

dichloromethane/ethyl acetate (v/v) mixture as the eluent. The title compound was obtained as an orange oil.

Yield: 32 mg (0.042 mmol, 62 % based on **76**). Anal. calcd for $C_{32}H_{28}Fe_3O_8P_2$ (770.04 g/mol): C, 49.91; H, 3.67. Found: C, 53.46; H, 6.34. (∗best match, too less compound) ^{1}H NMR ($CDCl_3$, δ): 3.82 (s, 6 H, OCH_3), 4.01–4.02 (m, 4 H, C_5H_4), 4.08–4.10 (m, 4 H, C_5H_4), 4.34–4.35 (m, 4 H, C_5H_4), 4.52 (dd, $J_{H,P} = 6.0$ Hz, $J_{H,H} = 2.9$ Hz, 2 H, C_5H_3), 4.66–4.68 (m, 4 H, C_5H_3), 4.71–4.72 (m, 2 H, C_5H_4), 4.73–4.74 (m, 2 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 52.9 (d, $^1J_{C,P} = 227.4$ Hz, C-P), 58.4 (d, $J_{C,P} = 12.1$ Hz, C_5H_3), 58.6 (s, OCH_3), 63.78 (C_5H_4), 63.82 (C_5H_4), 63.86 (C_5H_4), 63.88 (C_5H_4), 65.66 (C_5H_4), 65.69 (C_5H_4), 67.02 (C_5H_4), 67.04 (C_5H_4), 69.3 (d, $J_{C,P} = 15.0$ Hz, C_5H_3), 69.4 (d, $J_{C,P} = 14.0$ Hz, C_5H_3), 109.06 (d, $^2J_{C,P} = 11.8$ Hz, C_{C5H4}-O), 109.12 (d, $^2J_{C,P} = 12.1$ Hz, C_{C5H4}-O), 130.5 (d, $^2J_{C,P} = 10.5$ Hz, C_{C5H3}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 30.1. HRMS (ESI-TOF, m/z): calcd for $C_{32}H_{28}Fe_3O_8P_2$ + Na 792.9202, found 792.9191 $[M+Na]^+$.

1,3-Dioxa-2-(2-methoxyferrocenyl)(oxo)phospha-[3]ferrocenophane (71a)



71a

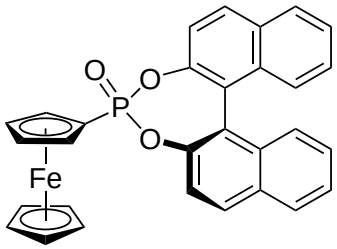
Phosphate **70a** (30 mg, 0.065 mmol), diisopropylamine (0.04 mL, 0.27 mmol), BuLi (0.11 mL, 0.27 mmol) and dimethyl sulfate (0.1 mL, 1.05 mmol) were reacted between –30 and –10 °C for 2 h according to the general procedure GP2. Purification was realized by column chromatography (silica, $2.5 \cdot 12$ cm column size) using a 95/5 dichloromethane/ethyl acetate mixture (v/v) as the eluent, giving **71a** as an orange solid.

Yield: 31 mg (0.0.065 mmol, 99 % based on 71a). Anal. calcd for $C_{21}H_{19}Fe_2O_8P_2$ (478.04 g/mol): C, 52.76; H, 4.01. Found: C, 52.02; H, 4.52. (∗best match). Mp.: >230 °C (decomp.). ^{1}H NMR ($CDCl_3$, δ): 3.76 (s, 3 H, OCH_3), 4.00–4.01 (m, 2 H, C_5H_4), 4.07–4.09 (m, 2 H, C_5H_4), 4.17 (dd, $J_{H,P} = 5.9$ Hz, $J_{H,H} = 2.8$ Hz, 1 H, C_5H_3), 4.32–4.35 (m, 3 H, C_5H_4, C_5H_3), 4.40 (s, 5 H, C_5H_5), 4.41–4.43 (m, 1 H, C_5H_3), 4.73–4.75 (m, 2 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 52.9 (d, $^1J_{C,P} = 228.6$ Hz, C-P), 56.0 (d, $J_{C,P} = 12.3$ Hz, C_5H_3), 58.5 (s, CH_3), 63.74 (d, $J_{C,P} = 5.7$ Hz, C_5H_4), 63.78 (d, $J_{C,P} = 5.6$ Hz, C_5H_4), 63.9 (d, $J_{C,P} = 6.2$ Hz, C_5H_4), 64.9 (d, $J_{C,P} = 15.3$ Hz, C_5H_3), 65.49 (C_5H_4), 65.52 (C_5H_4), 66.93 (C_5H_4), 67.2 (d, $J_{C,P} = 14.1$ Hz, C_5H_3), 70.5 (s, C_5H_5), 109.1 (d, $^2J_{C,P} = 11.8$ Hz, C_{C5H4}-O), 109.3 (d, $^2J_{C,P} = 11.8$ Hz, C_{C5H4}-O), 129.4 (d, $^2J_{C,P} = 10.8$ Hz, C_{C5H3}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 31.3. HRMS (ESI-TOF, m/z): calcd for $C_{50}H_{44}Fe_5O_8P_2$ + H 770.9382, found 770.9391 $[M+H]^+$.

(R,R_p)-1,1'-Binaphthyl-2,2'-diyl (2-Methoxyferrocenyl)phosphonate (71b)

Phosphate **70b** (100 mg, 0.188 mmol), diisopropylamine (0.16 mL, 1.15 mmol), BuLi (0.45 mL, 1.125 mmol) and dimethyl sulfate (0.3 mL, 3.16 mmol) were reacted in tetrahydrofuran at –70 °C for 2 h according to the general procedure described above. Purification was realized by column chromatography (silica, $2 \cdot 8$ cm column size) using a 9/1 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **71b** was obtained as an orange solid with

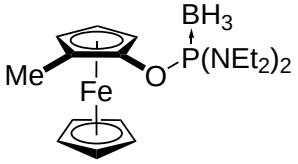
a d.r. of both diastereomers of 1 : 0.045 (0.91 *de*). Crystals, suitable for single crystal X-ray diffraction analysis, were obtained by crystallization from a boiling chloroform solution containing **71b**.



71b

Yield: 59 mg (0.108 mmol, 57 % based on **70b**). Anal. calcd for $C_{31}H_{23}FeO_4P \cdot 1/4\ CH_2Cl_2$ (546.33 · 1/4 84.93 g/mol): C, 66.13; H, 4.17. Found: C, 66.50; H, 4.37. Mp.: > 290 °C (decomp.). ^{1}H NMR ($CDCl_3$, δ): 2.63 (s, 3 H, OCH_3), 4.10 (ddd, $J_{H,P}$ = 3.2 Hz, $J_{H,H}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 4.15 (ddd, $J_{H,P}$ = 2.9 Hz, $J_{H,H}$ = 2.8 Hz, $J_{H,H}$ = 2.8 Hz, 1 H, C_5H_3), 4.37 (s, 5 H, C_5H_5), 4.54 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,P}$ = 2.2 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 7.15 (dd, $^3J_{H,H}$ = 8.8 Hz, $^3J_{H,P}$ = 0.9 Hz, 1 H, H3), 7.27–7.31 (m, 2 H, C_6H_4), 7.37–7.39 (m, 1 H, C_6H_4), 7.43–7.49 (m, 3 H, C_6H_4), 7.73 (dd, $^3J_{H,H}$ = 8.8 Hz, $^3J_{H,P}$ = 8.8 Hz, 1 H, H3'), 7.81 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, H4), 7.87–7.89 (m, 1 H, C_6H_4), 7.96–7.97 (m, 1 H, C_6H_4), 8.06 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, H4'). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 51.1 (d, $^1J_{C,P}$ = 214.3 Hz, C_{C5H3}-P), 55.9 (d, $J_{C,P}$ = 12.2 Hz, C_5H_3), 57.0 (s, OCH_3), 65.0 (d, $J_{C,P}$ = 15.3 Hz, C_5H_3), 67.7 (d, $J_{C,P}$ = 15.9 Hz, C_5H_3), 70.5 (s, C_5H_5), 121.2 (d, $^2J_{C,P}$ = 3.1 Hz, C3), 121.6 (d, $^2J_{C,P}$ = 2.3 Hz, C3'), 121.8 (d, $^3J_{C,P}$ = 2.4 Hz, C1/C1'), 122.3 (d, $^3J_{C,P}$ = 2.6 Hz, C1/C1'), 125.2, 125.4, 126.2, 126.5, 127.1, 127.2, 128.1, 128.4, 128.6 (d, $^2J_{C,P}$ = 9.8 Hz, C_{C5H3}-O), 130.0 (d, $^4J_{C,P}$ = 1.4 Hz, C4/C4'), 130.8 (d, $^4J_{C,P}$ = 0.9 Hz, C4/C4'), 131.5 (d, $^4J_{C,P}$ = 1.2 Hz, C4a/C4a'), 131.7 (d, $^4J_{C,P}$ = 1.2 Hz, C4a/C4a'), 132.60 (C8a/C8a'), 132.61 (C8a/C8a'), 146.7 (d, $^2J_{C,P}$ = 9.9 Hz, C2/C2'), 147.5 (d, $^2J_{C,P}$ = 10.0 Hz, C2/C2'). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 33.7 (4.5 %), 34.6 (95.5 %). HRMS (ESI-TOF, m/z): calcd for $C_{31}H_{23}FeO_4P$ 547.0757, found 547.0764 $[M]^+$.

N,*N*,*N*',*N*'-Tetraethyl-1-(2-methylferrocenyloxy)phosphinediamine·BH_3 (24)



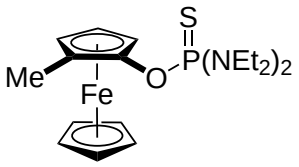
24

Compound **12** (519 mg, 1.33 mmol), ^{s}BuLi (1.23 mL, 1.60 mmol) and MeI (0.16 mL, 2.60 mmol) were reacted according to the general procedure GP2 between –20 and –10 °C for 3.5 h as described above. Purification was realized by column chromatography (alumina, 3.5 · 13 cm column size) using a 4/1 hexane/diethyl ether mixture (*v*/*v*) as the eluent. Compound **24** was obtained as a mixture in 436 mg consisting of the starting material **12** (91 mg, 0.24 mmol, 18 %) and **24**. Both compounds could not be separated from each other by column chromatography occurring in a ratio of 1 : 0.28.

Yield: 343 mg (0.85 mmol, 64 % based on **12**). ^{1}H NMR (C_6D_6, δ): 0.90 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 1.01 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 2.02 (s, 3 H, C_{C5H3}-CH_3), 2.87–3.00 (m, 8 H, CH_2), 3.62 (pt, $^{3,4}J_{H,H}$ = 2.6 Hz, 1 H, C_5H_4), 3.69–3.70 (m, 1 H, C_5H_4), 4.12 (s, 5 H, C_5H_5), 4.53 (dd, $J_{H,H}$ = 2.5 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6, δ): 12.4 (C_{C5H3}-CH_3), 14.2 (d, $^4J_{C,P}$ = 1.7 Hz, CH_3), 14.5 (d, $^4J_{C,P}$ = 1.7 Hz, CH_3), 39.3 (d, $^3J_{C,P}$ = 6.4 Hz, CH_2), 39.5 (d, $^3J_{C,P}$ = 6.4 Hz, CH_2), 60.7 (C_5H_3), 60.95 (d, $J_{C,P}$ = 3.0 Hz, C_5H_3),

64.5 (C_5H_3), 70.3 (C_5H_5), 74.6 (d, $^3J_{C,P}$ = 2.6 Hz, C_{C5H3}-CH_3), 117.4 (d, $^2J_{C,P}$ = 1.8 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 130.8–131.7 (br m). $^{11}B\{^1H\}$ NMR (C_6D_6, δ): -39.6 (d, $^1J_{B,P}$ = 91.3 Hz). HRMS (ESI-TOF, m/z): calcd for $C_{19}H_{34}BFeN_2OP$ + Na 427.1747, found 427.1724 $[M+Na]^+$.

N,N,N',N'-Tetraethyl-1-(2-methylferrocenyloxy)phosphinediamine Sulfide (25)

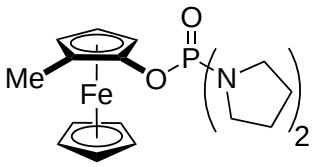


25

Compound **13** (250 mg, 0.61 mmol), ^{s}BuLi (0.75 mL, 0.98 mmol) and MeI (0.10 mL, 1.59 mmol) were reacted according to the general procedure GP2 between –20 and –10 °C for 3.5 h as described above. Purification was realized by column chromatography (alumina, 2.5 · 17 cm column size) using an 85/15 hexane/dichloromethane mixture (v/v) as the eluent. Compound **25** was obtained in a mixture of 135 mg along with the starting material **13**. Both compounds could not be separated from each other by column chromatography occurring in a ratio of 1 : 0.07.

Yield: 128 mg (0.302 mmol, 50 % based on 13). ^1H NMR (C_6D_6, δ): 0.97 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 1.06 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, CH_3), 2.04 (s, 3 H, C_{C5H3}-CH_3), 2.99–3.11 (m, 8 H, CH_2), 3.64 (pt, $^{3,4}J_{H,H}$ = 2.6 Hz, 1 H, C_5H_3), 3.71–3.72 (m, 1 H, C_5H_3), 4.14 (s, 5 H, C_5H_5), 4.61–4.62 (m, 1 H, C_5H_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 12.5 (C_{C5H3}-CH_3), 14.1 (d, $^4J_{C,P}$ = 3.3 Hz, CH_3), 14.4 (d, $^4J_{C,P}$ = 3.0 Hz, CH_3), 40.6 (d, $^3J_{C,P}$ = 5.0 Hz, CH_2), 40.9 (d, $^3J_{C,P}$ = 5.1 Hz, CH_2), 60.9 (C_5H_3), 61.0 (d, $J_{C,P}$ = 3.0 Hz, C_5H_3), 64.5 (C_5H_3), 70.3 (C_5H_5), 74.9 (d, $^3J_{C,P}$ = 4.0 Hz, C_{C5H3}-CH_3), 116.8 (d, $^2J_{C,P}$ = 1.3 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 90.9. HRMS (ESI-TOF, m/z): calcd for $C_{19}H_{31}FeN_2OPS$ 422.1239, found 422.1262 $[M]^+$.

(2-Methylferrocenyl) Di(pyrrolidin-1-yl)phosphinate (26)



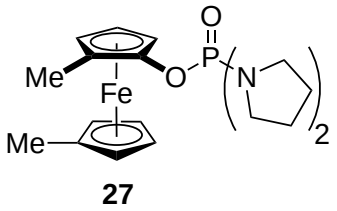
26

Compound **14** (206 mg, 0.53 mmol) was dissolved in hexane (**A**)/ diethyl ether (**B**), cooled to –30 °C and ^{s}BuLi (0.54 mL, 0.69 mmol) was dropwise added. The mixture was stirred for 18 h at ambient temperature (**A**) or 4 h between -40 and –30 °C (**B**). Afterwards, MeI (0.10 mL, 1.59 mmol) was added in a single portion and the reaction mixture was allowed to warm to ambient temperature, where stirring was continued for 18 h. Purification was realized by column chromatography (alumina, 2.5 · 17 cm column size) using a 9/1 dichloromethane/ethyl acetate mixture (v/v) as the eluent. The title compounds **26** and **27** were obtained as mixtures (**A**, 39 : 44 : 45 = 0.24 : 1 :< 0.05; **B**, 39 : 44 : 45 = 0.06 : 1 : 0.65) and could not be separated from each other by column chromatography.

Yield: **A**, 137 mg (0.34 mmol, 64 % based on **14**); **B**, 102 mg (0.25 mmol, 48 % based on **14**). ^1H NMR (C_6D_6, δ): 1.37–1.40 (m, 4 H, H3,H4-C_4N), 1.48–1.51 (m, 4 H, H3,H4-C_4N), 2.06 (s, 3 H, CH_3), 3.05–3.13 (m, 4 H, H2,H5-C_4N), 3.16–3.20 (m, 4 H, H2,H5-C_4N), 3.66–3.67 (m, 1 H, C_5H_3), 3.71–3.74 (m, 1 H, C_5H_3), 4.19 (s, 5 H, C_5H_5), 4.75–4.77 (m, 1 H, C_5H_3).

$^{13}C\{^1H\}$ NMR (C_6D_6, δ): 12.1 (CH_3), 26.5 (d, $^3J_{C,P}$ = 8.7 Hz, C3,C4-C_4N), 26.6 (d, $^3J_{C,P}$ = 9.0 Hz, C3,C4-C_4N), 46.8 (d, $^2J_{C,P}$ = 4.6 Hz, C2,C5-C_4N), 60.2 (d, $J_{C,P}$ = 1.9 Hz, C_5H_3), 60.7 (C_5H_3), 64.3 (C_5H_3), 70.5 (C_5H_5), 74.0 (d, $^3J_{C,P}$ = 5.3 Hz, C_{C5H3}-CH_3), 117.2 (d, $^2J_{C,P}$ = 4.0 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 22.9. HRMS (ESI-TOF, m/z): calcd for $C_{19}H_{27}FeN_2O_2P$ 402.1154, found 402.1158 $[M]^+$.

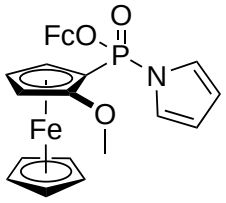
1',2-Dimethylferrocenyl Di(pyrrolidin-1-yl)phosphinate (27)



27

Yield: **A**, 7 mg (0.017 mmol, 3 % based on 39); **B**, 69 mg (0.165 mmol, 31 % based on **14**). ^1H NMR (C_6D_6, δ): 1.37–1.40 (m, 4 H, H3,H4-C_4N), 1.48–1.51 (m, 4 H, H3,H4-C_4N), 2.03 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3), 3.05–3.15 (m, 4 H, H2,H5-C_4N), 3.17–3.21 (m, 4 H, H2,H5-C_4N), 3.64 (pt, $^{3,4}J_{H,H}$ = 2.6 Hz, 1 H, C_5H_3), 3.66–3.70 (m, 1 H, $C_5H_{3/4}$), 4.00–4.02 (m, 1 H, C_5H_3), 4.08–4.11 (m, 3 H, C_5H_4), 4.71 (dd, J = 2.2 Hz, $J_{H,H}$ = 1.8 Hz, 1 H, C_5H_3). $^{13}C\{^1H\}$ NMR (C_6D_6, δ): 11.8 (CH_3), 13.9 (CH_3), 26.5 (d, $^3J_{C,P}$ = 8.7 Hz, C3,C4-C4N), 26.6 (d, $^3J_{C,P}$ = 9.0 Hz, C3,C4-C4N), 46.8 (d, $^2J_{C,P}$ = 5.1 Hz, C2,C5-C_4N), 60.9 (d, $J_{C,P}$ = 1.8 Hz, C_5H_3), 61.4 (C_5H_3), 64.8 (C_5H_3), 69.4 (C_5H_4), 69.6 (C_5H_4), 71.2 (C_5H_4), 71.9 (C_5H_4), 73.9 (d, $^3J_{C,P}$ = 5.0 Hz, C_{C5H3}-CH_3), 85.0 (C_{C5H4}-CH_3), 116.8 (d, $^2J_{C,P}$ = 3.8 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR (C_6D_6, δ): 23.0. HRMS (ESI-TOF, m/z): calcd for $C_{20}H_{29}FeN_2O_2P$ 416.1311, found 416.1336 $[M]^+$.

Ferrocenyl (2-Methoxyferrocenyl)1*H*-pyrrol-1-ylphosphinate (82)



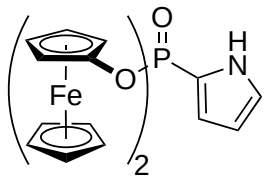
82

Phosphonate **79** (100 mg, 0.194 mmol), diisopropylamine (0.16 mL, 1.165 mmol), BuLi (0.46 mL, 1.15 mmol) and dimethyl sulfate (0.11 mL, 1.16 mmol) were reacted according to the general procedure GP2 at –70 °C for 4 h. Purification was realized by column chromatography (silica, 2.5 · 15 cm column size) using dichloromethane for the elution of FcOMe (13 mg, 0.060 mmol, 31 % based on **79**), a 98/2 dichloromethane/ethyl acetate mixture (v/v) for **79** (42 mg, 0.082 mmol, 42 %) and a 95/5 dichloromethane/ethyl acetate mixture (v/v) for the elution of **82** as the eluents. The title compound was obtained as a mixture of two diastereomers in a ratio of 1:0.89 as an orange solid, which rapidly decomposes in solution.

Yield: 25 mg (0.047 mmol, 24 % based on **79**). Anal. calcd for $C_{25}H_{24}Fe_2NO_3P$ (529.13 g/mol): C, 56.75; H, 4.57; N, 2.65. Found: C, 57.34; H, 5.40; N, 2.10 (∗best match). Mp.: 182–188 °C.^1H NMR ($CDCl_3$, δ): 3.70 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 3.80–3.83 (m, 3 H, C_5H_4), 3.85 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_4), 4.08 (dd, $J_{H,P}$ = 5.7 Hz, $J_{H,H}$ = 2.8 Hz, 1 H, C_5H_3), 4.11–4.15 (m, 4 H, C_5H_4, C_5H_3), 4.19 (s, 5 H, C_5H_5), 4.20 (s, 5 H, C_5H_5), 4.21–4.22 (m, 1 H, C_5H_4), 4.23 (s, 5 H, C_5H_5), 4.27 (ddd, $J_{H,P}$ = 3.2 Hz, $J_{H,H}$ = 2.8 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 4.28–4.30 (m, 1 H, C_5H_3), 4.33–4.34 (m, 1 H, C_5H_4), 4.38 (s, 5 H, C_5H_5), 4.43 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,P}$ = 2.0 Hz, $J_{H,H}$ = 1.4, 1 H, C_5H_3), 6.30–6.32 (m, 2 H, H3,4), 6.34–6.36 (m, 2 H, H3,4), 7.15–7.16 (m, 2 H, H2,5), 7.26–7.28

(m, 2 H, H2,5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.7 (d, $J_{C,P}$ = 11.6 Hz, C_5H_3), 55.9 (d, $J_{C,P}$ = 11.7 Hz, C_5H_3), 57.1 (d, $^1J_{C,P}$ = 207.7 Hz, C-P), 57.9 (d, $^1J_{C,P}$ = 206.3 Hz, C-P), 58.24 (OCH_3), 58.25 (OCH_3), 59.74 (d, $J_{C,P}$ = 3.8 Hz, C_5H_4), 59.77 (d, $J_{C,P}$ = 3.7 Hz, C_5H_4), 59.82 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4), 60.1 (d, $J_{C,P}$ = 3.7 Hz, C_5H_4), 62.76 (C_5H_4), 62.83 (C_5H_4), 62.85 (C_5H_4), 64.3 (d, $J_{C,P}$ = 14.2 Hz, C_5H_3), 64.6 (d, $J_{C,P}$ = 15.1 Hz, C_5H_3), 66.8 (d, $J_{C,P}$ = 15.8 Hz, C_5H_3), 67.8 (d, $J_{C,P}$ = 13.2 Hz, C_5H_3), 69.58 (C_5H_5), 69.60 (C_5H_5), 70.0 (C_5H_5), 70.3 (C_5H_5), 112.05 (d, $^3J_{C,P}$ = 9.7 Hz, C3,4), 112.13 (d, $^3J_{C,P}$ = 10.0 Hz, C3,4), 116.73 (d, $^2J_{C,P}$ = 7.3 Hz, C_{C5H4}-O), 116.76 (d, $^2J_{C,P}$ = 7.1 Hz, C_{C5H4}-O), 122.3 (d, $^2J_{C,P}$ = 6.2 Hz, C2,5), 122.5 (d, $^2J_{C,P}$ = 6.3 Hz, C2,5), 128.1 (d, $^2J_{C,P}$ = 11.1 Hz, C_{C5H3}-O), 128.7 (d, $^2J_{C,P}$ = 9.9 Hz, C_{C5H3}-O). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 17.8 (ma), 18.3 (mi). HRMS (ESI-TOF, m/z): calcd for $C_{25}H_{24}Fe_2NO_3P$ + H 530.0266, found 530.0269 $[M+H]^+$.

Diferrocenyl (1*H*-pyrrol-2-yl)phosphonate (85)



85

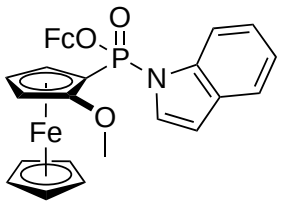
Phosphonate **79** (100 mg, 0.194 mmol), diisopropylamine (0.16 mL, 1.165 mmol), BuLi (0.46 mL, 1.15 mmol) and dimethyl sulfate (0.11 mL, 1.16 mmol) were reacted according to the general procedure GP2 at –40 °C for 4 h as described above. Purification was realized by column chromatography (silica, 2.5 · 15 cm column size) using a 98/2 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **85** was obtained as a yellow, weakly soluble solid. Thus, the sample was suspended in DMSO-d_6 and 10 % $CDCl_3$ was added to optimize the solubility.

Yield: 27 mg (0.052 mmol, 27 % based on **79**). Anal. calcd for $C_{24}H_{22}Fe_2NO_3P$ (515.10 g/mol): C, 55.96; H, 4.30; N, 2.72. Found: C. 55.71; H, 4.25; N, 2.82. Mp.: > 250 °C. ^1H NMR ($CDCl_3$, δ): 3.87 (br, m, 4 H, C_5H_4), 4.20 (br, m, 10 H, C_5H_5), 4.34 (br, m, 4 H, C_5H_4), 6.35 (br, m, 1 H, C_4H_4N), 6.84 (br, m, 1 H, C_4H_3N), 7.06 (br, m, 1 H, C_4H_3N), 9.08 (br, s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.9 (d, $J_{C,P}$ = 3.7 Hz, C_5H_4), 60.1 (d, $J_{C,P}$ = 4.0 Hz, C_5H_4), 62.8 (C_5H_4), 62.9 (C_5H_4), 69.6 (C_5H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 4.3. ^1H NMR (DMSO-d_6, δ): 3.87 (br, m, 4 H, C_5H_4), 4.14 (br, m, 10 H, C_5H_5), 4.31 (br, m, 4 H, C_5H_4), 6.24 (br, m, 1 H, C_4H_3N), 6.80 (br, m, 1 H, C_4H_3N), 7.13 (br, m, 1 H, C_4H_3N), 11.93 (br, s, 1 H, NH). $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 59.3∗ (d, $J_{C,P}$ = 3.9 Hz, C_5H_4), 59.4∗ (d, $J_{C,P}$ = 4.5 Hz, C_5H_4), 62.3 (C_5H_4), 62.4 (C_5H_4), 69.1 (C_5H_5), 109.2∗ (d, $J_{C,P}$ = 16.1 Hz, C_4H_3N), 114.7 (d, $^1J_{C,P}$ = 235.8 Hz, $C1_{C4H3N}$-P), 116.6 (d, $^2J_{C,P}$ = 4.8 Hz, C_{C5H4}-O), 120.2∗ (d, $J_{C,P}$ = 20.2 Hz, C_4H_3N), 125.3∗ (d, $J_{C,P}$ = 13.5 Hz, C_4H_3N). $^{31}P\{^1H\}$ NMR (DMSO-d_6, δ): 4.5. (∗Obtained from DEPT90 measurements). HRMS (ESI-TOF, m/z): calcd for $C_{24}H_{22}Fe_2NO_3P$ + Na 537.9929, found 537.9913 $[M+Na]^+$.

Ferrocenyl (1*H*-indol-1-yl)(2-methoxyferrocenyl)phosphinate (83)

Compound **80** (100 mg, 0.177 mmol), diisopropylamine (0.15 mL, 1.06 mmol), BuLi (0.43 mL, 1.08 mmol) and dimethyl sulfate (0.10 mL, 1.06 mmol) were reacted at –40 °C for 3 h according to the general procedure GP2 described above. Purification was realized by column chromatography (silica, 2.5 · 22 cm column size) using a 95/5 dichloromethane/ethyl acetate

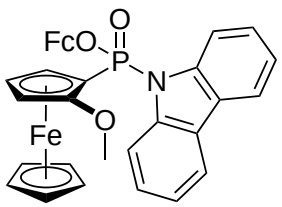
mixture (v/v) as the eluent. Compound **83** was obtained along with compound **86** in a ratio of 1/0.78 (53/50) as a mixture of two diastereomers. Crystals, suitable for single crystal X-ray diffraction analysis, were obtained by evaporation of a $CHCl_3$ solution containing the mixture of **86** or **83** at ambient temperature.



83

Yield: 25 mg (0.043 mmol, 24 % based on **80**). ^{1}H NMR ($CDCl_3$, δ): 3.56 (s, 3 H, OCH_3), 3.77–3.79 (m, 2 H, C_5H_4), 3.80–3.81 (m, 5 H, OCH_3, C_5H_4), 3.95–3.96 (m, 1 H, C_5H_3), 4.00–4.02 (m, 1 H, C_5H_3), 4.12–4.14 (m, 6 H, C_5H_5, C_5H_3), 4.17–4.19 (m, 7 H, C_5H_5, C_5H_4), 4.22–4.24 (m, 1 H, C_5H_3), 4.28–4.29 (m, 1 H, C_5H_3), 4.30–4.32 (m, 6 H, C_5H_5, C_5H_4), 4.35 (s, 5 H, C_5H_5), 4.40–4.42 (m, 1 H, C_5H_4), 4.48–4.49 (m, 1 H, C_5H_3), 6.64 (ddd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 0.8 Hz, 1 H, H3), 6.66 (ddd, $^3J_{H,H}$ = 3.4 Hz, $^4J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 0.8 Hz, 1 H, H3), 7.16–7.17 (m, 1 H, H4), 7.18–7.20 (m, 1 H, H4), 7.20–7.23 (m, 2 H, H5/6), 7.25–7.28 (m, 2 H, H5/6), 7.53 (dd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{H,P}$ = 2.8 Hz, 1 H, H2), 7.55 (dd, $^3J_{H,H}$ = 3.5 Hz, $^4J_{H,P}$ = 2.8 Hz, 1 H, H2), 7.92 (dd, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 1.2 Hz, 1 H, H7), 8.02 (dd, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 1.1 Hz, 1 H, H7). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.8 (d, $J_{C,P}$ = 11.4 Hz, C_5H_3), 56.0 (d, $J_{C,P}$ = 11.8 Hz, C_5H_3), 57.5 (d, $^1J_{C,P}$ = 207.5 Hz, C-P), 57.7 (d, $^1J_{C,P}$ = 206.4 Hz, C-P), 58.28 (OCH_3), 58.31 (OCH_3), 59.8–60.2 (m, C_5H_4), 62.79 (C_5H_4), 62.81 (C_5H_4), 62.83 (C_5H_4), 64.4 (d, $J_{C,P}$ = 13.6 Hz, C_5H_3), 64.5 (d, $J_{C,P}$ = 14.9 Hz, C_5H_3), 66.7 (d, $J_{C,P}$ = 16.0 Hz, C_5H_3), 67.3 (d, $J_{C,P}$ = 12.3 Hz, C_5H_3), 69.5 (C_5H_5), 69.54 (C_5H_5), 70.1 (C_5H_5), 70.3 (C_5H_5), 107.0 (d, $^3J_{C,P}$ = 7.4 Hz, C3), 107.4 (d, $^3J_{C,P}$ = 7.5 Hz, C3), 114.3 (C7), 114.5 (C7), 116.7 (d, $^2J_{C,P}$ = 7.0 Hz, C_{C5H4}-O), 116.9 (d, $^2J_{C,P}$ = 7.5 Hz, C_{C5H4}-O), 120.9, 121.8, 121.9, 122.2, 123.0, 123.2, 128.1 (d, $^2J_{C,P}$ = 6.6 Hz, C2), 128.6 (d, $^2J_{C,P}$ = 6.4 Hz, C2), 128.8 (d, $^2J_{C,P}$ = 9.7 Hz, C_{C5H3}-O), 128.9 (d, $^2J_{C,P}$ = 11.9 Hz, C_{C5H3}-O), 130.9 (d, $^3J_{C,P}$ = 8.3 Hz, C3a), 131.1 (d, $^3J_{C,P}$ = 8.6 Hz, C3a), 137.3 (d, $^2J_{C,P}$ = 5.0 Hz, C7a), 137.7 (d, $^2J_{C,P}$ = 4.6 Hz, C7a). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 16.8, 18.2. HRMS (ESI-TOF, m/z): calcd for $C_{29}H_{26}Fe_2NO_3P$ + H 580.0423, found 580.0430 $[M+H]^+$.

Ferrocenyl 9*H*-Carbazol-9-yl(2-methoxyferrocenyl)phosphinate (84)



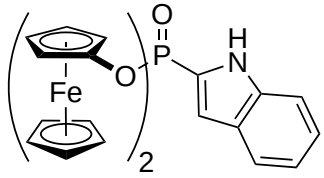
84

Compound **81** (100 mg, 0.163 mmol), diisopropylamine (0.14 mL, 0.98 mmol), BuLi (0.39 mL, 0.98 mmol) and dimethyl sulfate (0.09 mL, 0.98 mmol) were reacted at –60 °C for 3 h according to the general procedure GP2 described above. Purification was realized by column chromatography (silica, 2.5 · 16 cm column size) using a 95/5 dichloromethane/ethyl acetate mixture (v/v) as the eluent. The title compound was obtained as an orange solid and as a mixture of both diastereomers in a ratio of 1 : 0.28 (0.56 *de*). Crystals, suitable for single crystal X-ray diffraction analysis, were obtained by evaporation of a dichloromethane solution at ambient temperature containing **84**.

Yield: 58 mg (0.092 mmol, 56 % based on **81**). Anal. calcd for $C_{33}H_{28}Fe_2NO_3P$

(629.24 g/mol): C, 62.99; H, 4.49; N, 2.23. Found: C. 62.98; H, 4.56; N, 2.25. Mp.: 206 °C. ^{1}H NMR ($CDCl_3$, δ): 3.35 (s, 3 H, OCH_3, ma), 3.59 (ddd, $J_{H,H}$ = 2.7 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 1.5 Hz, 0.3 H, C_5H_3, mi), 3.73 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.4 Hz, 0.3 H, C_5H_4, mi), 3.76 (ddd, $J_{H,H}$ = 2.7 Hz, $J_{H,P}$ = 2.7 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_4, ma), 3.77–3–78 (m, 0.3 H, C_5H_4, mi), 3.79 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_4, ma), 3.83 (s, 0.9 H, OCH_3, mi), 3.89 (dpt, $J_{H,P}$ = 2.8 Hz, $^{3,4}J_{H,H}$ = 2.8 Hz, 0.3 H, C_5H_3, mi), 4.10–4.11 (m, 6 H, C_5H_5, C_5H_3, ma), 4.13 (s, 1.5 H, C_5H_5, mi), 4.15 (ddd, $J_{H,P}$ = 3.5 Hz, $J_{H,H}$ = 2.7 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3, ma), 4.19–4.20 (m, 0.3 H, C_5H_4, mi), 4.21–4.22 (m, 1 H, C_5H_4, ma), 4.27 (s, 1.5 H, C_5H_5, mi), 4.28 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,P}$ = 2.8 Hz, $J_{H,H}$ = 1.4 Hz, 0.3 H, C_5H_3, mi), 4.41–4.42 (m, 1 H, C_5H_4, ma), 4.44 (s, 5 H, C_5H_5, ma), 4.51–4.53 (m, 0.3 H, C_5H_4, mi), 4.54 (ddd, $J_{H,H}$ = 2.8 Hz, $J_{H,P}$ = 2.8 Hz, $J_{H,H}$ = 1.4 Hz, 1 H, C_5H_3, ma), 7.29 (ddd, $J_{H,H}$ = 7.9 Hz, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 1.0 Hz, 2 H, $C_{12}H_8$, ma), 7.34 (ddd, $J_{H,H}$ = 7.9 Hz, $J_{H,H}$ = 7.3 Hz, $J_{H,H}$ = 1.0 Hz, 0.6 H, $C_{12}H_8$, mi), 7.40 (ddd, $J_{H,H}$ = 8.5 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.3 Hz, 2 H, $C_{12}H_8$, ma), 7.45 (ddd, $J_{H,H}$ = 8.5 Hz, $J_{H,H}$ = 7.2 Hz, $J_{H,H}$ = 1.4 Hz, 0.6 H, $C_{12}H_8$, mi), 7.96–7.98 (m, 2 H, $C_{12}H_8$, ma), 8.02–8.04 (m, 0.6 H, $C_{12}H_8$, mi), 8.16–8.17 (m, 2 H, $C_{12}H_8$, ma), 8.28–8.30 (m, 0.6 H, $C_{12}H_8$, mi). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 55.8 (d, $J_{C,P}$ = 11.2 Hz, C_5H_3, mi), 56.0 (d, $J_{C,P}$ = 12.0 Hz, C_5H_3, ma), 58.3 (s, OCH_3, ma), 58.4 (s, OCH_3, mi), 58.5 (d, $^1J_{C,P}$ = 206.1 Hz, C-P, ma), 59.8 (d, $J_{C,P}$ = 4.1 Hz, C_5H_4, ma), 60.0 (d, $J_{C,P}$ = 4.0 Hz, C_5H_4, ma), 60.3 (d, $J_{C,P}$ = 3.7 Hz, C_5H_4, mi), 62.7 (C_5H_4, mi), 62.8 (C_5H_4, mi), 62.82 (C_5H_4, ma), 62.84 (C_5H_4, ma), 64.1 (d, $J_{C,P}$ = 15.1 Hz, C_5H_3, mi), 64.2 (d, $J_{C,P}$ = 13.8 Hz, C_5H_3, ma), 66.5 (d, $J_{C,P}$ = 15.6 Hz, C_5H_3, mi), 67.0 (d, $J_{C,P}$ = 11.6 Hz, C_5H_3, ma), 69.47 (C_5H_5, ma), 69.52 (C_5H_5, mi), 70.27 (C_5H_5, mi), 70.29 (C_5H_5, ma), 115.3 (CH, ma), 115.4 (CH, mi), 116.6 (d, $^2J_{C,P}$ = 7.5 Hz, C_{C5H4}-O, ma), 119.6 (CH, ma), 119.7 (CH, mi), 121.8 (CH, ma), 122.1 (CH, mi), 126.15 (d, $^2J_{C,P}$ = 7.2 Hz, C_{C5H3}-O, ma), 126.22 (CH, ma), 126.4 (CH, mi), 129.4 (d, $^3J_{C,P}$ = 12.6 Hz, 4a/4b, ma), 140.7 (d, $^2J_{C,P}$ = 5.6 Hz, 8a/9a, ma), 141.0 (d, $^2J_{C,P}$ = 5.5 Hz, 8a/ 9a, ma). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 17.0 (ma), 19.3 (mi). HRMS (ESI-TOF, m/z): calcd for $C_{33}H_{28}Fe_2NO_3P$ 629.0501, found 629.0510 $[M]^+$.

Diferrocenyl (1*H*-Indol-2-yl)phosphonate (86) (A)



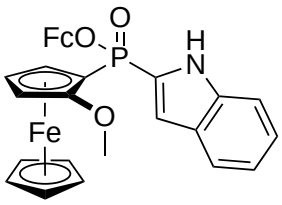
86

Compound **80** (100 mg, 0.177 mmol), diisopropylamine (0.15 mL, 1.06 mmol), BuLi (0.43 mL, 1.08 mmol) and dimethyl sulfate (0.10 mL, 1.06 mmol) were reacted at –40 °C for 3 h according to the general procedure described above. Purification was realized by column chromatography (silica, 2.5 · 22 cm column size) using a 95/5 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **86** was obtained in a mixture with compound **85** of ratio 1 : 0.78.

Yield: 31 mg (0.055 mmol, 31 % based on 47). ^{1}H NMR ($CDCl_3$, δ): 3.86–3.87 (m, 4 H, C_5H_4), 4.21 (s, 10 H, C_5H_5), 4.36–4.38 (m, 2 H, C_5H_4), 4.38–4.40 (m, 2 H, C_5H_4), 7.16–7.18 (m, 1 H, H3), 7.33 (ddt, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 7.0 Hz, $J_{H,H}$ = 1.0 Hz, 1 H, H5/H6), 7.46

(dd, $^3J_{H,H}$ = 8.4 Hz, $J_{H,H}$ = 1.1 Hz, 1 H, H7), 7.57–7.60 (m, 1 H, H5/H6), 7.70 (dd, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 1.1 Hz, 1 H, H4), 9.01 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 59.9–60.1 (m, C_5H_4), 62.9 (d, $J_{C,P}$ = 4.5 Hz, C_5H_4), 69.6 (C_5H_5), 112.1 (d, $^4J_{C,P}$ = 1.9 Hz, C7), 113.7 (d, $^2J_{C,P}$ = 17.5 Hz, C3), 117.2 (d, $^2J_{C,P}$ = 4.9 Hz, C_{C5H4}-O), 120.8 (C5/6), 122.1 (C4), 122.0 (d, $^1J_{C,P}$ = 227.4 Hz, C_{C2}-P), 125.1 (C5/6), 127.5 (d, $^3J_{C,P}$ = 16.5 Hz, C3a), 138.2 (d, $^3J_{C,P}$ = 13.0 Hz, C7a). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 4.0. HRMS (ESI-TOF, m/z): calcd for $C_{28}H_{24}Fe_2NO_3P$ + H 566.0266, found 565.0295 $[M+H]^+$.

Ferrocenyl (1*H*-Indol-2-yl)(2-methoxyferrocenyl)phosphinate (87)



87

Compound **80** (100 mg, 0.177 mmol), diisopropylamine (0.15 mL, 1.06 mmol), BuLi (0.43 mL, 1.08 mmol) and dimethyl sulfate (0.10 mL, 1.06 mmol) were reacted at 0 °C for 4 h according to the general procedure GP2 described above. Purification was realized by column chromatography (silica, 2.5 · 12 cm column size) using a 85/15 dichloromethane/ethyl acetate mixture (v/v) as the eluent. Compound **87** was obtained as a mixture of both diastereomers in a ratio of 1 : 0.098 (0.82 *de*).

Yield: 69 mg (0.119 mmol, 67 % based on 47). Anal. calcd for $C_{29}H_{26}Fe_2NO_3P$ (579.19 g/mol): C, 60.14; H, 4.52; N, 2.42. Found: C. 59.61; H, 4.30; N, 2.60. Mp.: ∼ 25 °C. ^1H NMR ($CDCl_3$, δ): 3.73–3.75 (m, 2 H, C_5H_4), 3.82 (s, 3 H, OCH_3), 3.89 (s, 0.3 H, OCH_3, mi), 3.98 (s, 5 H, C_5H_5), 4.14–4.16 (m, 6 H, C_5H_5, C_5H_3), 4.18–4.20 (m, 1 H, C_5H_4), 4.23 (s, 0.5 H, C_5H_5, mi), 4.24–4.26 (m, 1 H, C_5H_4), 4.32 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 4.43 (s, 0.5 H, C_5H_5, mi), 4.57 (ddd, $J_{H,H}$ = 2.6 Hz, $J_{H,P}$ = 2.6 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 7.17 (ddd, $^3J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 7.0 Hz, $J_{H,H}$ = 0.9 Hz, 1 H, H5/6), 7.32 (ddt, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 7.1 Hz, $J_{H,H}$ = 0.8 Hz, 1 H, H5/6), 7.36 (ddd, $^3J_{H,P}$ = 4.3 Hz, $J_{H,H}$ = 1.9 Hz, $J_{H,H}$ = 0.8 Hz, 1 H, H3), 7.50 (dd, $^3J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 0.7 Hz, 1 H, H7), 7.75 (dd, $^3J_{H,H}$ = 8.0 Hz, $J_{H,H}$ = 0.5 Hz, 1 H, H4), 9.59 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 56.4 (d, $J_{C,P}$ = 9.7 Hz, C_5H_3), 58.5 (OCH_3), 59.9 (d, $^1J_{C,P}$ = 167.6 Hz, C_{C5H3}-P), 60.03 (C_5H_4), 60.06 (C_5H_4), 60.08 (C_5H_4), 60.12 (C_5H_4), 62.56 (C_5H_4), 62.57 (C_5H_4), 64.4 (d, $J_{C,P}$ = 12.1 Hz, C_5H_3), 67.8 (d, $J_{C,P}$ = 11.1 Hz, C_5H_3), 69.5 (C_5H_5), 70.1 (C_5H_5), 111.7 (d, $^4J_{C,P}$ = 1.5 Hz, C7), 112.4 (d, $^2J_{C,P}$ = 16.1 Hz, C3), 117.3 (d, $^2J_{C,P}$ = 6.6 Hz, C_{C5H4}-O), 120.5 (C5/6), 122.3 (C4), 124.6 (C5/6), 127.0 (d, $^2J_{C,P}$ = 10.2 Hz, C_{C5H3}-O), 127.3 (d, $^3J_{C,P}$ = 10.2 Hz, C3a), 128.9 (d, $^1J_{C,P}$ = 172.2 Hz, C_{C2}-P), 137.9 (d, $^3J_{C,P}$ = 11.0 Hz, C7a). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 25.3 (mi), 25.9 (ma). HRMS (ESI-TOF, m/z): calcd for $C_{29}H_{26}Fe_2NO_3P$ 579.0344, found 579.0370 $[M]^+$.

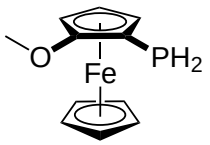
4.3.3 Synthesis of Phosphines and Phosphanes

General Procedure for the Reduction and the Stelzer Coupling - GP5

In a Schlenk tube, an excess of $Li[AlH_4]$ (0.6 g, 16 mmol) was suspended with ∼ 20 mL of THF, followed by the dropwise addition of $ClSiMe_3$ (1.65 mL, 12.9 mmol) at –30 °C. After the

suspension was stirred for 5 min, the respective phosphonate (~ 2 mmol) was added dropwise. The mixture was slowly heated to 45 °C until gas evaporation was no longer detectable. Afterwards, the oil bath was replaced by an ice bath. Acidification was realized by dropwise addition of oxygen-free H_2SO_4 (3 mL, $\omega = 30\,\%$) until the *pH* value declined below 7. Caution! During the addition an immense gas emission occurs. The mixture was extracted three times with oxygen-free diethyl ether ($3 \cdot 20$ mL) under an argon atmosphere. The organic layer was dried over degassed $MgSO_4$, and all volatiles were removed under reduced pressure. The PPh_2 derivative was obtained as an orange oil and subsequently used in further reactions. For the Stelzer coupling, the respective PPh_2 derivative (1 equiv), iodobenzene (2 equiv), K_3PO_4 (2 equiv), and [$PdCl_2$(dppf)] (4 mol-%) were dissolved in 6 mL of toluene. The reaction mixture was degassed carefully and stirred for 18 h at 110 °C. After the mixture was cooled to ambient temperature, water (30 mL) was added in a single portion and the mixture was extracted with diethyl ether ($3 \cdot 20$ mL). The organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (see below).

(2-Methoxyferrocenyl)diphenylphosphane (*rac*-90a)

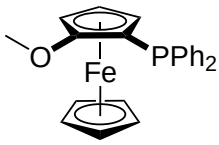


rac-**90a**

Compound *rac*-**16** (645 mg, 1.83 mmol), Li[AlH_4] (0.6 g, 16 mmol) and $ClSiMe_3$ (1.65 mL, 12.9 mmol) were reacted according to the general procedure GP5.

Yield: 450 mg (1.82 mmol, 99 % based on **16**). ^{1}H NMR ($CDCl_3$, δ): 3.62 (dd, $^1J_{H,P} = 202.6$ Hz, $^2J_{H,H} = 12.6$ Hz, 1 H, PH), 3.70 (s, 3 H, OCH_3), 3.81 (dd, $^1J_{H,P} = 207.8$ Hz, $^2J_{H,H} = 12.6$ Hz, 1 H, PH), 3.94 (ptd, $^{3,4}J_{H,H} = 2.6$ Hz, $J_{H,P} = 0.84$ Hz, 1 H, *o*-OCH_3), 4.01 (ddd, $J_{H,H} = 2.6$ Hz, $J_{H,P} = 1.4$ Hz, $J_{H,H} = 1.4$ Hz, 1 H, *o*-PH_2), 4.15 (dd, $J_{H,H} = 2.6$ Hz, $J_{H,H} = 1.4$ Hz, 1 H, *m*-OCH_3), 4.16 (s, 5 H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 54.0 (d, $^3J_{C,P} = 0.86$, *m*-OCH_3), 57.9 (s, OCH_3), 62.9 (d, $^3J_{C,P} = 5.0$ Hz, *o*-OCH_3), 69.5 (s, C_5H_5), 70.0 (d, $^2J_{C,P} = 19.9$ Hz, *o*-PH_2), 129.8 (C–OCH_3). (The C–PPh_2 carbon was neither detected in the ^{13}C nor in HMBC spectra. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –159.9 (dd, $^1J_{H,P} = 202.6$ Hz, $^1J_{H,P} = 207.8$ Hz.

(2-Methoxyferrocenyl)diphenylphosphine (*rac*-91)



91

(2-Methoxyferrocenyl)phosphine (**90a**; 480 mg, 1.94 mmol), iodobenzene (0.43 mL, 3.90 mmol), K_3PO_4 (825 mg, 3.90 mmol), and [$PdCl_2$(dppf)] (55 mg, 4 mol-%) were reacted according to the general procedure GP5. Purification was realized by column chromatography (silica, $2 \cdot 6$ cm column size) using a 7/3 (*v*/*v*) hexane/CH_2Cl_2 mixture, giving **91** ($R_f = 0.14$) as an orange solid.

Yield: 410 mg (1.01 mmol, 52 % based on **90a**). Anal. calcd for $C_{23}H_{21}FeOP$ (400.23 g/mol): C, 69.02; H, 5.29. Found: C, 68.48; H, 5.28. Mp.: 147 °C. ^{1}H NMR ($CDCl_3$, δ): 3.50 (ddd, $^3J_{H,H} = 2.5$ Hz, $^4J_{H,H} = 1.4$ Hz, $^3J_{H,P} = 1.3$ Hz, 1 H, *o*-PPh_2), 3.67 (s, 3 H, OCH_3), 3.98

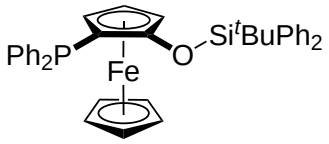
(dpt, $^4J_{H,P} = 0.5$ Hz, $^3J_{H,H} = 2.5$ Hz, 1 H, *m*-OCH_3), 4.11 (s, 5 H, C_5H_5), 4.26 (ddd, $^4J_{H,P} = 1.5$ Hz, $^4J_{H,H} = 1.4$ Hz, $^3J_{H,H} = 2.5$ Hz, 1 H, *o*-OCH_3), 7.24–7.29 (m, 5 H, o,m-Ph), 7.36–7.39 (m, 3 H, o,m-Ph), 7.53–7.58 (m, 2 H, *p*-Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 54.7 (d, $^3J_{C,P} = 2.6$ Hz, *o*-OCH_3), 58.0 (s, OCH_3), 63.1 (s, *m*-OCH_3), 65.0 (d, $^1J_{C,P} = 7.6$ Hz, C–PPh_2), 65.7 (d, $^2J_{C,P} = 2.0$ Hz, *o*-PPh_2), 69.3 (s, C_5H_5), 127.8 (s, *p*-Ph), 128.05 (d, $^3J_{C,P} = 6.0$ Hz, *m*-Ph), 128.10 (d, $^3J_{C,P} = 7.7$ Hz, *m*-Ph), 129.0 (s, *p*-Ph), 131.1 (d, $^2J_{C,P} = 18.0$ Hz, C–OCH_3), 132.3 (d, $J_{C,P} = 18.4$ Hz, *o*-Ph), 134.9 (d, $J_{C,P} = 21.1$ Hz, *o*-Ph), 137.3 (d, $^1J_{C,P} = 8.7$ Hz, C1-Ph), 139.6 (d, $^1J_{C,P} = 11.1$ Hz, C1-Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –23.97 (s). HRMS (ESI-TOF, m/z): calcd for $C_{23}H_{21}FeOP$ 400.0674, found 400.0754 $[M]^+$.

(2-Methoxyferrocenyl)diphenylphosphine (R_p)-91

Compound (R_p)-**31e** (570 mg, 1.00 mmol), $Li[AlH_4]$ (0.6 g, 16 mmol), $ClSiMe_3$ (1.65 mL, 12.9 mmol), iodobenzene (0.22 mL, 2.0 mmol), K_3PO_4 (425 mg, 2.0 mmol), and $[PdCl_2(dppf)]$ (30 mg, 4 mol-%) were reacted according to the general procedure GP5. The purification procedure is similar to *rac*-**91**. HPLC measurements were performed after single recrystallization from hexane. Crystals suitable for single crystal X-ray analysis of phosphine oxide (R_p)-**20** were obtained by dissolving (R_p)-**90** (2 mg) in 4 mL of a 95/5 hexane/^{t}BuOMe mixture. On exposure to atmospheric conditions for 14 days a few single crystals of (R_p)-**91** could be obtained from this solution.

Yield: 260 mg (0.65 mmol, 65 % based on **31e**). The spectroscopic data are in agreement with those for *rac*-**91**. HPLC (Chiralcel OD-H column, flow rate 0.8 mL min^{-1}, 95/5 hexane/^{t}BuOMe): *rac*-**91**, 26.410 (48.9 %), 42.110 (51.1 %); (R_p)-**91**, 25.485 (>99.9 %); *ee* = 0.99.

(2-(*tert*-Butyldiphenylsilyloxy)ferrocenyl)diphenylphosphine (*rac*-117a)



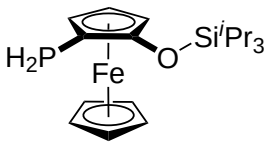
117a

Diethyl (2-(*tert*-butyldiphenylsilyloxy)ferrocenyl)phosphonate (*rac*-**95g**, 1.00 g, 1.74 mmol), $Li[AlH_4]$ (0.6 g, 16 mmol), $ClSiMe_3$ (1.65 mL, 12.9 mmol), iodobenzene (0.39 mL, 3.50 mmol), K_3PO_4 (745 mg, 3.50 mmol), and $[PdCl_2(dppf)]$ (52 mg, 4 mol-%) were reacted according to the general procedure GP5. Purification was realized by column chromatography (alumina, $2.5 \cdot 12$ cm column size) using a 9/1 (*v*/*v*) hexane/CH_2Cl_2 mixture, giving *rac*-**117a** ($R_f = 0.55$) as an orange oil.

Yield: 79 mg (0.126 mmol, 6 % based on **95g**). ^1H NMR ($CDCl_3$, δ): 0.92 (s, 9 H, CH_3), 3.33 (ddd, $^3J_{H,H} = 2.5$ Hz, $^4J_{H,H} = 1.4$ Hz, $J = 0.8$ Hz, 1 H, C_5H_3), 3.68 (ddd, $^3J_{H,H} = 2.7$ Hz, $J = 2.7$ Hz, $J = 0.5$ Hz, 1 H, C_5H_3), 3.71 (ddd, $^3J_{H,H} = 2.9$ Hz, $J = 2.9$ Hz, $J = 1.5$ Hz, 1 H, C_5H_3), 3.95 (s, 5 H, C_5H_5), 7.25–7.28 (m, 5 H, Ph), 7.35–7.39 (m, 6 H, Ph), 7.44–7.52 (m, 5 H, Ph), 7.55–7.59 (m, 2 H, Ph), 7.90–7.92 (m, 2 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.2 (^qC), 26.5 (CH_3), 61.3 (d, $J_{C,P} = 2.2$ Hz, C_5H_3), 62.7 (s, C_5H_3), 64.5 (d, $J_{C,P} = 3.1$ Hz, C_5H_3), 66.4 (d, $^1J_{C,P} = 5.6$ Hz, C_{Fc}-P), 69.9 (s, C_5H_5), 125.4 (d, $^2J_{C,P} = 19.1$ Hz, C_{Fc}-O),

127.43 (Ph_{Si}), 127.67 (Ph_{Si}), 127.99 (d, $J_{C,P} = 2.2$ Hz, Ph_P), 128.04 (d, $J_{C,P} = 1.5$ Hz, Ph_P), 128.08 (C4-Ph_P), 128.6 (C4-Ph_P), 129.8 (C4-Ph_{Si}), 130.0 (C4-Ph_{Si}), 132.1 (C1-Ph_{Si}), 133.2 (d, $J_{C,P} = 19.7$ Hz, Ph_P), 133.55 (C1-Ph_{Si}), 134.5 (d, $J_{C,P} = 20.4$ Hz, Ph_P), 135.9 (Ph_{Si}), 136.0 (Ph_{Si}), 137.7 (d, $^1J_{C,P} = 10.2$ Hz, C_{Ph}-P), 139.1 (d, $^1J_{C,P} = 12.2$ Hz, C_{Ph}-P). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, δ): –3.68. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –23.96 (s). HRMS (ESI-TOF, m/z): calcd for $C_{38}H_{37}FeOPSi$ 624.1696, found 624.1659 $[M]^+$.

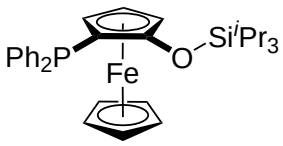
(2-(Triisopropylsilyloxy)ferrocenyl)diphenylphosphane (*rac*-116b) and phosphine (*rac*-117b)



116b

Diethyl (2-(triisopropylsilyloxy)ferrocenyl)phosphonate (*rac*-**95h**, 845 mg, 1.71 mmol), $Li[AlH_4]$ (0.6 g, 16 mmol) and $ClSiMe_3$ (1.65 mL, 12.9 mmol) were reacted according to the general procedure GP5. The phosphane was subsequently used in the Stelzer coupling reaction without further purification.

Yield: 537 mg (1.37 mmol, 80 % based on **95h**).^{1}H NMR ($CDCl_3$, δ): 1.07 (d, $^3J_{H,H} = 7.1$ Hz, 9 H, CH_3), 1.13 (d, $^3J_{H,H} = 6.8$ Hz, 9 H, CH_3), 1.16–1.23 (m, 3 H, CH(CH_3)$_2$), 3.61 (dd, $^1J_{H,P}$ = 199.9 Hz, $^2J_{H,H} = 12.6$ Hz, 1 H, PH), 3.84 (ddd, $^3J_{H,H} = 2.6$ Hz, $J_{H,P} = 2.6$ Hz, $J_{H,H}$ = 1.1 Hz, 1 H, C_5H_3), 3.86 (dd, $^1J_{H,P} = 207.7$ Hz, $^2J_{H,H} = 12.6$ Hz, 1 H, PH), 3.95 (ddd, $^3J_{H,H}$ = 2.8 Hz, $J_{H,P} = 2.8$ Hz, $J_{H,H} = 1.5$ Hz, 1 H, C_5H_3), 4.10 (s, 5 H, C_5H_5), 4.19 (dd, $^3J_{H,H}$ = 2.5 Hz, $J_{H,H} = 1.4$ Hz, 1 H, C_5H_3). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, δ): 16.83. ^{31}P NMR ($CDCl_3$, δ): –159.0 (dd, $^1J_{P,H} = 207.7$ Hz, $^1J_{P,H} = 199.9$ Hz).



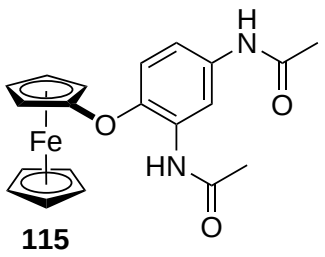
117b

Compound **116b** (537 mg, 1.37 mmol), iodobenzene (0.31 mL, 2.78 mmol), K_3PO_4 (583 mg, 2.75 mmol), and $[PdCl_2(dppf)]$ (40 mg, 4 mol-%) were reacted according to the general procedure GP5. Purification was realized by column chromatography (silica, $2.5 \cdot 12$ cm column size) using a 9/1 (v/v) hexane/CH_2Cl_2 mixture, giving *rac*-**117b** as an orange solid. Crystals suitable for single crystal X-Ray diffraction analysis were obtained by evaporation of an CH_2Cl_2 solution containing **117b** at ambient temperature.

Yield: 56 mg (0.103 mmol, 6 % based on **95h**). Mp.: 84–86 °C. ^{1}H NMR ($CDCl_3$, δ): 0.93–0.94 (m, 9 H, CH_3), 1.01–1.03 (m, 12 H, CH_3, CH(CH_3)$_2$), 3.38 (ddd, $^3J_{H,H} = 2.8$ Hz, $^4J_{H,H}$ = 1.4 Hz, $J = 0.8$ Hz, 1 H, C_5H_3), 3.87 (ddd, $^3J_{H,H} = 2.7$ Hz, $J = 2.7$ Hz, $J = 0.6$ Hz, 1 H, C_5H_3), 4.8 (s, 5 H, C_5H_5), 4.24 (ddd, $^3J_{H,H} = 2.6$ Hz, $J = 2.6$ Hz, $J = 1.6$ Hz, 1 H, C_5H_3), 7.23–7.24 (m, 3 H, Ph), 7.35–7.35 (m, 5 H, Ph), 7.53–7.57 (m, 2 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 12.3 (CH(CH_3)$_2$), 17.80 (CH_3), 17.89 (CH_3), 61.1 (d, $J_{C,P} = 2.3$ Hz, C_5H_3), 62.6 (s, C_5H_3), 65.0 (d, $J_{C,P} = 2.9$ Hz, C_5H_3), 66.2 (d, $^1J_{C,P} = 5.6$ Hz, C_{Fc}-P), 69.9 (s, C_5H_5), 125.8 (d, $^2J_{C,P} = 19.4$ Hz, C_{Fc}-O), 127.85 (C4-Ph_P), 127.9 (d, $J_{C,P} = 3.6$ Hz, Ph_P), 128.0 (d, $J_{C,P}$ = 4.8 Hz, Ph_P), 128.6 (C4-Ph_P), 133.2 (d, $J_{C,P} = 19.8$ Hz, Ph_P), 134.7 (d, $J_{C,P} = 20.6$ Hz, Ph_P), 137.8 (d, $^1J_{C,P} = 10.1$ Hz, C_{Ph}-P), 139.2 (d, $^1J_{C,P} = 11.9$ Hz, C_{Ph}-P). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, δ): 16.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –24.4 (s). HRMS (ESI-TOF, m/z): calcd for

$C_{31}H_{39}FeOPSi$ 542.1852, found 542.1821 $[M]^+$.

2,4-Diacetamidophenoxyferrocene (115)



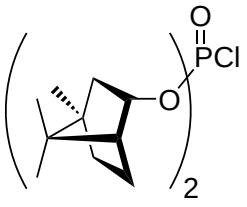
115

2,4-Dinitrophenoxyferrocene **96a** (200 mg, 0.543 mmol), $Li[AlH_4]$ (0.6 g, 16 mmol) and $ClSiMe_3$ (1.65 mL, 12.9 mmol) were reacted according to the general procedure GP5 for the conversion of phosphonates to phosphanes. After stirring of the reaction mixture for 12 h at 45 °C, the *pH* value was adjusted at ∼ 7 by using H_2SO_4 ($\omega = 30\,\%$) and K_2CO_3. The aqueous layer was extracted with diethyl ether under oxygen-free conditions until the organic layer remained colorless. The combined organic layers were dried over $MgSO_4$. To the mixture, acetic anhydride (0.5 mL, 4.9 mmol) was dropwise added. After stirring for 5 min, NEt_3 (0.5 mL, 3.6 mmol) was dropwise added. The mixture was heated to 60 °C and stirred for 60 min. After cooling to ambient temperature, the mixture was poured into water and extracted with diethyl ether ($3 \cdot 50$ mL) followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, $2.5 \cdot 14$ cm column size) using a 35/65 (v/v) dichloromethane/ethyl acetate mixture was the eluent, giving 115 as an yellow oil.

Yield: 15 mg (0.038 mmol, 7 % based on **96a**). ^{1}H NMR ($CDCl_3$, δ): 2.08 (s, 3 H, CH_3), 2.16 (s, 3 H, CH_3), 3.89 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.15 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.18 (s, 5 H, C_5H_5), 6.96 (d, $^3J_{H,H}$ = 8.9 Hz, 1 H, H6-Ph), 7.45 (s, 1 H, NH), 7.59 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 1.9 Hz, 1 H, H5-Ph), 7.63 (s, 1 H, NH), 8.07 (d, $^4J_{H,H}$ = 1.8 Hz, 1 H, H3-Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 24.4 (CH_3), 25.0 (CH_3), 59.0 (C_5H_4), 63.0 (C_5H_4), 69.3 (C_5H_5), 111.8 (C3-Ph), 115.8 (C5-Ph), 116.7 (C6-Ph), 122.9 (C_{Fc}-O), 128.9 (^{q}Ph), 133.4 (^{q}Ph), 143.0 (^{q}Ph), 168.30 (C=O), 168.38 (C=O).

4.3.4 Synthesis of Chloro and Dichlorophosphates

Bis((1*S*)-borneyl) Chlorophosphate (29d)



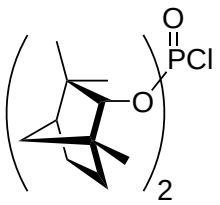
29d

(1*S*)-Borneol (**28d**; 5.82 g, 37.7 mmol), was dissolved in 10 mL of tetrahydrofuran; an equal volume of diethyl ether was added, and the mixture was cooled to –30 °C. The dropwise addition of BuLi (15.1 mL, 37.7 mmol) resulted in the formation of a colorless precipitate. The mixture was stirred for an additional 10 min at –30 °C. $POCl_3$ (1.8 mL, 18.9 mmol) was slowly added and the solution was warmed to ambient temperature and stirred overnight. All volatiles were removed under reduced pressure. The resulting residue was suspended in diethyl ether and filtered through a plug of Celite (minimum 5 cm thickness) with diethyl ether to remove the lithium salt. After removal of all volatiles chlorophosphate **29d** was obtained as a colorless oil and used without further purification.

Yield: 7.25 g (16.7 mmol, 99 % based on **28d**). ^{1}H NMR ($CDCl_3$, δ): 0.887 (s, 6 H, CH_3),

0.892 (s, 6 H, CH_3), 0.924 (s, 3 H, CH_3), 0.925 (s, 3 H, CH_3), 1.28–1.37 (m, 6 H), 1.70–1.80 (m, 4 H, CH_2, H4), 1.89–1.96 (m, 2 H, CH_2), 2.32–2.42 (m, 2 H, CH_2), 4.68–4.75 (m, 2 H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 13.1 (CH_3), 13.3 (CH_3), 18.75 (CH_3), 18.78 (CH_3), 19.9 (CH_3), 26.42 (CH_2), 26.47 (CH_2), 27.87 (CH_2), 27.90 (CH_2), 36.5 (d, $^3J_{C,P} = 1.3$ Hz, CH_2), 36.8 (d, $^3J_{C,P} = 1.5$ Hz, CH_2), 44.8, 47.68 (C1/C7), 47.72 (C1/C7), 49.78–49.88 (m, C1/C7), 86.86–86.98 (m, C2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 5.4. HRMS (ESI-TOF, m/z): calcd for $C_{20}H_{34}ClO_3P$ 411.1826, found 411.1850 $[M]^+$.

Bis((1*R*)-α-fenchyl) chlorophosphate (29e)

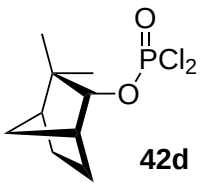


29e

(1*R*)-α-Fenchol (**28e**; 6.01 g, 39.0 mmol), was dissolved in 10 mL of tetrahydrofuran; an equal volume of diethyl ether was added, and the mixture was cooled to –30 °C. The dropwise addition of BuLi (15.6 mL, 39.0 mmol) resulted in the formation of a colorless precipitate. The mixture was stirred for an additional 10 min at –30 °C. $POCl_3$ (1.8 mL, 19.5 mmol) was slowly added and the solution was warmed to ambient temperature and stirred overnight. All volatiles were removed under reduced pressure. The resulting residue was suspended in diethyl ether and filtered through a plug of Celite (minimum 5 cm thickness) with diethyl ether to remove the lithium salt. After removal of all volatiles chlorophosphate **29e** was obtained as a colorless oil and used without further purification.

Yield: 7.51 g (19.3 mmol, 99 % based on **28e**). ^1H NMR ($CDCl_3$, δ): 0.973 (s, 3 H, CH_3), 0.977 (s, 3 H, CH_3), 1.05–1.11 (m, 8 H), 1.16 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.19–1.24 (m, 2 H), 1.41–1.51 (m, 2 H), 1.52–1.57 (m, 2 H), 1.68–1.75 (m, 6 H), 4.09 (dd, $^3J_{H,P} = 11.2$ Hz, $J_{H,H} = 1.8$, 1 H, H2), 4.14 (dd, $^3J_{H,P} = 11.5$ Hz, $J_{H,H} = 1.8$, 1 H, H2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.2 (CH_3), 19.4 (CH_3), 20.95 (CH_3), 20.98 (CH_3), 25.7–25.8 (m, C5/C6), 29.6 (CH_3), 29.9 (CH_3), 39.5–39.6 (m, C3), 40.8 (C7), 40.9 (C7), 47.9 (C4), 48.0 (C4), 49.3 (d, $^3J_{C,P} = 6.6$ Hz, C1), 49.5 (d, $^3J_{C,P} = 4.9$ Hz, C1), 93.0–93.1 (m, C2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 5.9. HRMS (ESI-TOF, m/z): calcd for $C_{20}H_{34}ClO_3P$ + Na 411.1826, found 411.1850 $[M + Na]^+$.

(1*R*)-α-Fenchyl Dichlorophosphate (42d)



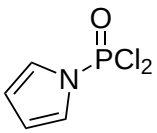
42d

(1*R*)-α-Fenchol (**28e**; 4.23 g, 27.4 mmol) was dissolved in 10 mL of diethyl ether and cooled to –30 °C. Dropwise addition of BuLi (12 mL, 30 mmol) resulted in the formation of a colorless precipitate. After it was stirred for additional 10 min at –30 °C, the suspension was added dropwise to a solution containing $POCl_3$ (8 mL, 85.5 mmol) in 30 mL of diethyl ether at –30 °C. Stirring was continued overnight followed by filtration through a pat of Celite (min 5 cm thickness) with diethyl ether to remove the lithium salt. After removal of all volatiles under reduced pressure, the title compound **42d** was obtained as a colorless

oil and used without further purification.

Yield: 7.36 g (27.1 mmol, > 95 %, based on **28e**). ^{1}H NMR ($CDCl_3$, δ): 0.99 (s, 3 H, CH_3), 1.12–1.18 (m, 7 H), 1.26–1.28 (m, 1 H), 1.48–1.54 (m, 1 H), 1.56–1.59 (m, 1 H), 1.69–1.76 (m, 2 H), 1.78–1.79 (m, 1 H), 4.33 (dd, $^{3}J_{H,P}$ = 13.1 Hz, $J_{H,H}$ = 1.8 Hz, 1 H, H2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.2 (CH_3), 21.0 (CH_3), 25.65 (C5/C6), 25.73 (C5/C6), 29.6 (CH_3), 39.8 (d, $^{3}J_{C,P}$ = 2.9 Hz, C3), 40.9 (C7), 47.9 (C4), 49.5 (d, $^{3}J_{C,P}$ = 5.9 Hz, C1), 97.0 (d, $^{2}J_{C,P}$ = 11.7 Hz, C2). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 8.4. HRMS (ESI-TOF, m/z): calcd for $C_{10}H_{17}Cl_2O_2P$ + Na 293.0235, found 293.0252 $[M+Na]^+$.

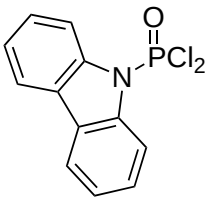
(1*H*-Pyrrol-1-yl) Dichlorophosphonate



In a Schlenk tube, 1*H*-pyrrole (1 mL, 14.46 mmol) and 30 mL of diethyl ether were cooled to –30 °C. To the solution BuLi (5.8 mL, 14.5 mmol) was dropwise added. In a second Schlenk tube, a solution of 50 mL diethyl ether and $POCl_3$ (5 mL, 54.8 mmol) were cooled to –80 °C. The mixture containing lithiated pyrrole was cooled to –80 °C and was very slowly added to the $POCl_3$ solution by using a transfer cannula. The workup procedure is similar to the general procedure, described above. The title compound was obtained as a colorless oil and used without further purification.

^{1}H NMR ($CDCl_3$, δ): 6.47 (dt, $^{4}J_{H,P}$ = 5.2 Hz, $J_{H,H}$ = 2.2 Hz, 2 H, H3,4), 7.18 (dt, $^{3}J_{H,P}$ = 3.4 Hz, $J_{H,H}$ = 2.2 Hz, 2 H, H2,5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 115.1 (d, $^{3}J_{C,P}$ = 13.2 Hz, C3,4), 122.4 (d, $^{2}J_{C,P}$ = 7.0 Hz, C2,5). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 5.5.

(9*H*-Carbazol-9-yl) Dichlorophosphonate



9*H*-Carbazole (2.393 g, 14.31 mmol), BuLi (5.8 mL, 14.5 mmol) and $POCl_3$ (4 mL, 43.83 mmol) were reacted according to the synthesis of **42d**. The title compound was obtained as a colorless oil and used without further purification.

^{1}H NMR ($CDCl_3$, δ): 7.45 (td, $^{3}J_{H,H}$ = 8.0 Hz, $^{H,P}J_0$ =.8 Hz, 2 H), 7.53 (dd, $^{3}J_{H,H}$ = 8.5 Hz, $^{H,H}J_7$ =.4 Hz, $^{3}J_{H,P}$ = 1.3 Hz, 2 H), 8.03–8.05 (m, 2 H), 8.16 (d, $^{3}J_{H,H}$ = 8.4 Hz, 2 H). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 0.5.

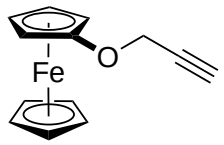
4.3.5 Synthesis of Ferrocenyl Aryl Ether

General Procedure for Nucleophilic Aromatic Substitutions - GP6

The deprotonated hydroxyferrocenes were either obtained by adding 1 equiv of BuLi to the respective compound in 10 to 30 mL of THF or diethyl ether at –30 °C (in case of **5**), or were present after an anionic phospho-/thia-Fries rearrangement. Subsequently, 3 mL of oxygen free *N*,*N*-dimethylformamide and 3 equiv of the aryl fluorides, or 0.5 equiv in case of **97** and **98**, were added. The solvent was reduced to about 3 mL in vacuum. After heating the mixture to 70 °C for 18 h, all volatiles were removed in vacuum. The residue was dissolved

in diethyl ether (50 mL), washed with brine (400 mL) and the latter one was extracted again with diethyl ether (3 · 50 mL). Purification was realized by column chromatography (silica, see below) using different solvent mixtures (see below).

(Prop-2-yn-1-yloxy)ferrocene (95b)

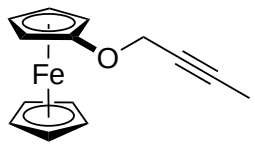


95b

Ferrocenol (**5**, 87 mg, 0.43 mmol) was diluted in 20 mL of diethyl ether and BuLi (0.18 mL, 0.45 mmol) was dropwise added at –30 °C. After stirring for 10 min at this temperature, propargyl tosylate (136 mg, 0.65 mmol) was added in a single portion. The reaction mixture was warmed to ambient temperature and stirring was continued overnight. Purification was realized by column chromatography (silica, 2 · 8 cm column size) using an 1:1 hexane/dichloromethane mixture (*v*/*v*) as the eluent, giving **95b** as an orange oil.

Yield: 11 mg (0.46 mmol, 11 % based on **5**). ^{1}H NMR ($CDCl_3$, δ): 2.57 (t, $^{4}J_{H,H}$ = 2.4 Hz, 1 H, CH), 3.85 (pt, 3,$^{4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.19 (pt, 3,$^{4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.22 (s, 5 H, C_5H_5), 4.48 (d, $^{4}J_{H,H}$ = 2.4 Hz, 2 H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 56.1 (C_5H_4), 58.4 (CH_2), 62.1 (C_5H_4), 68.7 (C_5H_5), 75.4 (C≡C), 79.1 (C≡C), 125.9 (C_{C5H4}-O). HRMS (ESI-TOF, m/z): decomposed before measurement.

(But-2-yn-1-yloxy)ferrocene (95c)

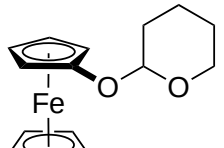


95c

According to the synthesis of compound **95b**, ferrocenol (**5**, 182 mg, 0.90 mmol), BuLi (0.36 mL, 0.90 mmol) and methylpropargyl tosylate (243 mg, 1.08 mmol) were reacted. Purification was realized by column chromatography on first silica (2 · 6 cm, dichloromethane) followed by alumina (4 · 6 cm column size) using dichloromethane as the eluent, giving **95c** as an orange oil.

Yield: 48 mg (0.46 mmol, 21 % based on **5**). ^{1}H NMR ($CDCl_3$, δ): 1.90 (dd, $^{5}J_{H,H}$ = 2.3 Hz, $^{5}J_{H,H}$ = 2.3 Hz, 3 H, CH_3), 3.84 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.16 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.21 (s, 5 H, C_5H_5), 4.44 (m, 2 H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 3.7 (CH_3), 55.9 (C_5H_4), 58.9 (CH_2), 62.0 (C_5H_4), 68.6 (C_5H_5), 74.4 (C≡C), 83.6 (C≡C), 125.8 (C_{C5H4}-O). HRMS (ESI-TOF, m/z): calcd for $C_{14}H_{14}FeO$ 254.0389, found 254.0404 $[M]^+$.

Diethyl (2-(Tetrahydro-2*H*-pyran-2-yloxy)ferrocenyl)phosphonate (95f)



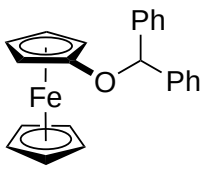
95f

Diethyl ferrocenyl phosphate (**6**, 1.08 g, 3.2 mmol), diisopropylamine (0.89 mL, 6.4 mmol) and BuLi (2.56 mL, 6.4 mmol) were reacted according to the general procedure GP2. Afterwards, oxygen free 10 *N* H_2SO_4 (1.3 mL, 12.8 mmol) and oxygen-free water (10 mL) were added in a single portion. The mixture was extracted using oxygen-free diethyl ether (3 · 50 mL) and the combined organic layers were filtered through oxygen-free $MgSO_4$, collected in a Schlenk tube and all volatiles were removed in vacuum. The

tetrahydropyranyl substituent was introduced related to reference [120] by diluting the precipitate with dichloromethane and HCl in tetrahydrofuran (0.3 mL, $\sim 3\ M$) and 3,4-dihydro-2*H*-pyran (0.87 mL, 9.6 mmol) were added. The reaction mixture was stirred overnight, poured into 100 mL of NaOH ($\omega = 5\,\%$) and extracted with diethyl ether ($3 \cdot 50$ mL). The combined organic layers were dried over Na_2CO_3 and all volatiles were removed in vacuum. The crude product was purified by column chromatography (alumina, $4 \cdot 10$ cm column size) using dichloromethane as the eluent, giving **95f** as an orange oil with a ratio of both diastereomers of 0.32 : 0.68.

Yield: 1.350 g (3.19 mmol, 99 % based on **6**). ^{1}H NMR ($CDCl_3$, δ): 1.24–1.41 (m, 6 H, CH_3), 1.54–1.69 (m, 3 H, CH_2), 1.74–1.92 (m, 3 H, CH_2), 3.58–3.61 (m, 0.68 H, CH_2), 3.69–3.71 (m, 0.32 H, CH_2), 3.76–3.81 (m, 0.68 H, CH_2), 4.05–4.39 (m, 12 H, CH_2, C_5H_5, C_5H_3), 4.48–4.51 (m, 0.32 H, C_5H_3), 4.93 (s, 0.32 H, CH) , 5.36 (s, 0.68 H, CH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 16.4–16.6 (m, CH_3), 18.4 (0.68 C, CH_2), 18.6 (0.32 C, CH_2), 25.2 (0.68 C, CH_2), 25.3 (0.32 C, CH_2), 30.2 (0.68 C, CH_2), 30.4 (0.32 C, CH_2), 58.3 (d, $^1J_{C,P} = 213.9$ Hz, C-P), 59.4 (d, $J_{C,P} = 11.2$ Hz, 0.68 C, C_5H_3), 60.3 (d, $J_{C,P} = 11.5$ Hz, 0.32 C, C_5H_3), 61.5–62.1 (m, CH_2), 64.5 (d, $J_{C,P} = 14.1$ Hz, 0.32 C, C_5H_3), 14.2 (d, $J_{C,P} = 14.2$ Hz, 0.68 C, C_5H_3), 66.8 (d, $J_{C,P} = 13.4$ Hz, 0.68 C, C_5H_3), 66.9 (d, $J_{C,P} = 13.7$ Hz, 0.32 C, C_5H_3), 70.1 (s, 3.4 C, C_5H_5), 70.6 (s, 1.6 C, C_5H_5), 99.6 (s, 0.68 C, CH), 99.9 (s, 0.32 C, CH), 124.9 (d, $^2J_{C,P} = 9.7$ Hz, C_{C5H3}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 23.7 (0.68 P), 24.1 (0.32 P). HRMS (ESI-TOF, m/z): calcd for $C_{19}H_{27}FeO_5P$ + Na 445.0838, found 455.0910 $[M+Na]^+$.

(Diphenylmethoxy)ferrocene (95e)



95e

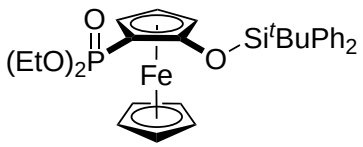
1,1-Diphenylmethanol (275 mg, 1.5 mmol) was dissolved in tetrahydrofuran, cooled to –30 °C and BuLi (0.6 mL, 1.5 mmol) was dropwise added. After 15 min of stirring at this temperature, $ClPPh_2$ (0.27 mL, 1.5 mmol) was dropwise added and stirring was continued for additional 30 min at ambient temperature. Afterwards, all volatiles were removed under reduced pressure and 2,6-dimethylquinone (136 mg, 1.0 mmol) and FcOH (**5**) (200 mg, 1.0 mmol) were added in a single portion. Oxygen-free dichloromethane (10 mL) was added and the reaction mixture was stirred for 18 h at ambient temperature. Purification was performed by column chromatography (silica, $4 \cdot 6$ cm column size) using hexane as the eluent, giving **95e** as an orange solid.

Yield: 83 mg (0.23 mmol, 23 % based on **5**). The spectroscopic data are in agreement with those reported in literature [156].

Diethyl (2-((*tert*-Butyldiphenylsilyl)oxy)ferrocenyl)phosphonate (*rac*-95g)

Diethyl ferrocenyl phosphate (**6**, 1.102 g, 3.26 mmol), diisopropylamine (0.92 mL, 6.52 mmol), BuLi (2.6 mL, 6.52 mmol) and TMEDA (0.95 mL, 6.52 mmol) were reacted according to the general procedure GP2. Afterwards, $ClSi^tBuPh_2$ (2.5 mL, 9.77 mmol) was added in a single portion at –30 °C. The cooling bath was removed and stirring was continued at ambient

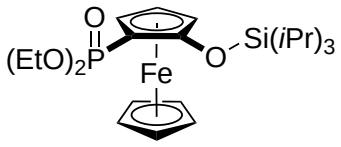
temperature for 18 h. Purification was per-formed by column chromatography (silica, $2 \cdot 15$ cm column size) using a 7/3 dichloromethane/ethyl acetate mixture (v/v) ($R_f = 0.31$) as the eluent, giving *rac*-**95g** as an orange oil.



95g

Yield: 1.06 g (1.84 mmol, 56 % based on **6**). ^{1}H NMR ($CDCl_3$, δ): 1.10 (s, 9 H, C(CH_3)3), 1.30 (t, $^3J_{H,H} = 7.1$ Hz, 3 H, CH_2-CH_3), 1.44 (t, $^3J_{H,H} = 7.0$ Hz, 3 H, CH_2-CH_3), 3.63 (ddd, $J_{H,H} = 2.8$, 2.8 Hz, $J_{H,P} = 1.5$ Hz, 1 H, C_5H_3), 3.76 (dd, $J_{H,H} = 2.8$, 2.8 Hz, 1 H, C_5H_3), 4.08–4.17 (m, 7 H, CH_2, C_5H_5), 4.19–4.21 (m, 1 H, C_5H_3), 4.26–4.36 (m, 2 H, CH_2), 7.32–7.35 (m, 2 H, 2,6-C_6H_5), 7.40–7.43 (m, 1 H, 4-C_6H_5), 7.46–7.54 (m, 3 H, 2,4,6-C_6H_5), 7.62–7.64 (m, 2 H, 3,5-C_6H_5), 7.91–7.93 (m, 2 H, 3,5-C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 16.4 (d, $^3J_{C,P} = 6.8$ Hz, CH_3), 16.6 (d, $^3J_{C,P} = 7.2$ Hz, CH_3), 19.4 (C(CH_3)3), 26.5 (C(CH_3)3), 57.1 (d, $^1J_{C,P} = 215.8$ Hz, C-P), 61.4–61.5 (m, CH_2), 62.1 (d, $J_{C,P} = 11.3$ Hz, C_5H_3), 63.8 (d, $J_{C,P} = 14.4$ Hz, C_5H_3), 66.3 (d, $J_{C,P} = 14.2$ Hz, C_5H_3), 70.5 (C_5H_5), 123.0 (d, $^2J_{C,P} = 9.0$ Hz, C_{C5H3}-O), 127.6 (2,6-C_6H_5), 127.8 (2,6-C_6H_5), 130.0 (4-C_6H_5), 130.2 (4-C_6H_5), 132.1 (1-C_6H_5), 133.4 (1-C_6H_5), 135.6 (3,5-C_6H_5), 135.8 (3,5-C_6H_5). ^{29}Si{^{1}H} NMR ($CDCl_3$, δ): -3.1. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 24.9. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{37}O_4FePSi$ 576.1543, found 576.1596 $[M]^+$.

Diethyl (2-((Triisopropylsilyl)oxy)ferrocenyl)phosphonate (*rac*-95h)

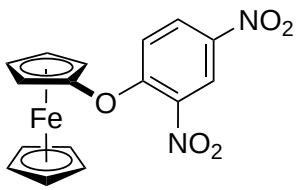


95h

In accordance to compound **95g**, **6** (1.122 g, 3.32 mmol), diisopropylamine (0.92 mL, 6.64 mmol), BuLi (2.65 mL, 6.63 mmol) and TMEDA (0.95 mL, 6.63 mmol) were reacted according to the general procedure GP2. Afterwards, ClSi*i*Pr_3 (1.4 mL, 6.63 mmol) was added in a single portion at –30 °C. The cooling bath was re-moved and stirring was continued at ambient temperature for 18 h. Purification was performed by column chromatography (silica, $2 \cdot 15$ cm column size) using a 7/3 dichloromethane/ethyl acetate mixture (v/v) as the eluent, giving *rac*-**95h** as an orange oil.

Yield: 845 g (1.71 mmol, 52 % based on **6**). ^{1}H NMR ($CDCl_3$, δ): 1.07 (d, $^3J_{H,H} = 7.1$ Hz, 9 H, CH(CH_3)2), 1.14 (d, $^3J_{H,H} = 7.1$ Hz, 9 H, CH(CH_3)2), 1.17–1.24 (m, 3 H, CH(CH_3)2), 1.29 (t, $^3J_{H,H} = 7.1$ Hz, 3 H, CH_2-CH_3), 1.39 (t, $^3J_{H,H} = 7.1$ Hz, 3 H, CH_2-CH_3), 3.95–3.96 (m, 1 H, C_5H_3), 4.02–4.14 (m, 2 H, CH_2), 4.17–4.31 (m, 9 H, C_5H_5, CH_2, C_5H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 12.5 (CH), 16.3 (CH_3), 16.4 (CH_3), 16.46 (CH_3), 16.51 (CH_3), 17.82 (CH(CH_3)2), 17.85 (CH(CH_3)2), 57.2 (d, $^1J_{C,P} = 215.5$ Hz, C-P), 61.29 (d, $^2J_{C,P} = 5.8$ Hz, CH_2), 61.34 (d, $^2J_{C,P} = 6.6$ Hz, CH_2), 61.9 (d, $J_{C,P} = 11.6$ Hz, C_5H_3), 63.5 (d, $J_{C,P} = 14.5$ Hz, C_5H_3), 66.7 (d, $J_{C,P} = 14.3$ Hz, C_5H_3), 70.53 (C_5H_5), 123.2 (d, $^2J_{C,P} = 9.3$ Hz, C_{C5H3}-O). ^{29}Si{^{1}H} NMR ($CDCl_3$, δ): 17.8. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 24.7. HRMS (ESI-TOF, m/z): calcd for $C_{23}H_{39}FeO_4PSi + H$ 495.1778, found 495.1717 $[M+H]^+$.

1-Ferrocenyloxy-2,4-dinitrobenzene (96a)

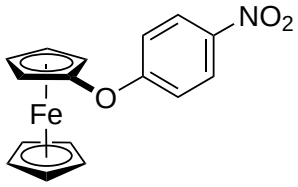


96a

To ferrocenol (**5**, 218 mg, 1 mmol) in toluene (10 mL), BuLi (0.43 mL) was added dropwise. Afterwards, the general procedure GP6 for S_NAr reactions was applied using 1-fluoro-2,4-dinitrobenzene (101 mg, 0.50 mmol). Dicyclohexylamine (97 mg, 0.54 mmol) was added in a single portion to the solution and stirring at 70 °C was continued for 3 h. Afterwards, the reaction mixture was cooled to ambient temperature, extracted with diethyl ether ($3 \cdot 50$ mL) and the solvent was removed under reduced pressure. Purification was performed by column chromatography (silica, $4 \cdot 8$ cm column size) using a 1/1 hexane/dichloromethane mixture (v/v) as the eluent, giving **96a** was obtained as an orange solid. Suitable single crystals were obtained by recrystallization from boiling hexane.

Yield: 323 mg (0.88 mmol, 81 % based on **5**). Mp.: 125–128 °C. ^{1}H NMR ($CDCl_3$, δ): 4.10 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.36 (s, 5 H, C_5H_5), 4.37 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 7.11 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, H6), 8.28 (dd, $^3J_{H,H}$ = 9.3 Hz, $^4J_{H,H}$ = 2.8 Hz, 1 H, H5), 8.79 (d, $^4J_{H,H}$ = 28 Hz, 1 H, H3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 61.1 (C_5H_4), 64.3 (C_5H_4), 70.1 (C_5H_5), 116.9 (C6-C_6H_3), 119.5 (C_{C5H4}-O), 121.7 (C3-C_6H_3), 128.7 (C5-C_6H_3), 138.6 (C2-C_6H_3), 140.9 (C4-C_6H_3), 157.7 (C1-C_6H_3). HRMS (ESI-TOF, m/z): calcd for $C_{16}H_{12}FeN_2O_5$ 368.0090, found 368.0090 $[M]^+$.

1-Ferrocenyloxy-4-nitrobenzene (96b)

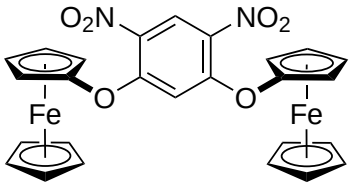


96b

To ferrocenol (**5**, 247 mg, 1.22 mmol) dissolved in toluene (10 mL), BuLi (0.50 mL, 1.25 mmol) was added dropwise at –30 °C. Afterwards, the general procedure GP6 for the S_NAr reaction was applied using 1-fluoro-4-nitrobenzene (86 mg, 0.61 mmol). Dicyclohexylamine (110 mg, 0.60 mmol) was added and stirring at 70 °C was continued for 3 h. Afterwards, the reaction mixture was cooled to ambient temperature and extracted with diethyl ether ($3 \cdot 50$ mL) and all volatiles were removed under reduced pressure. Purification was performed by column chromatography (silica, $4 \cdot 10$ cm column size) using an 1/1 hexane/dichloromethane mixture (v/v) as the eluent, giving **96b** as a dark orange solid. Suitable single crystals were obtained by recrystallization from boiling hexane.

Yield: 184 mg (0.57 mmol, 74 % based on **5**). Anal. calcd for $C_{16}H_{13}FeN_1O_3$ (323.12 g/mol): C, 59.47; H, 4.06; N, 4.33. Found: C, 59.96; H, 4.05; N, 4.29. Mp.: 102–104 °C. ^{1}H NMR ($CDCl_3$, δ): 4.05 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, H2,5-C_5H_4), 4.28 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, H3,4-C_5H_4), 4.32 (s, 5 H, C_5H_5), 6.96–7.00 (m, 2 H, H2,6-C_6H_4), 8.13–8.16 (m, 2 H, H3,5-C_6H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 61.0 (C3,4-C_5H_4), 63.8 (C2,5-C_5H_4), 69.7 (C_5H_5), 115.8 (C2,6-C_6H_4), 119.9 (C_{C5H4}-O), 125.6 (C3,5-C_6H_4), 142.3 (C4-C_6H_4), 164.8 (C1-C_6H_4). HRMS (ESI-TOF, m/z): calcd for $C_{16}H_{13}FeN_1O_3$ 323.0239, found 323.0257 $[M]^+$.

1,5-(Ferrocenyloxy)-2,4-dinitrobenzene (99a)

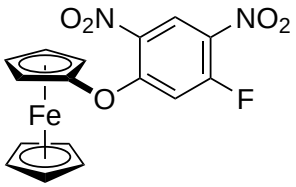


99a

To ferrocenol (**5**, 651 mg, 3.22 mmol) dissolved in toluene (10 mL), BuLi (1.30 mL, 3.3 mmol) was added dropwise. Afterwards, the general procedure for S_NAr reactions was applied using 1,5-difluoro-2,4-dinitrobenzene 328 mg, 1.61 mmol). Purification was performed by column chromatography (silica, $4 \cdot 10$ cm column size) using a 1/1 hexane/dichloromethane mixture (v/v) as the eluent, giving **99a** as a reddish-orange solid. Suitable single crystals were obtained by crystallization from boiling hexane.

Yield: 148 mg (0.26 mmol, 16 % based on **5**). Mp.: 167–170 °C. ^{1}H NMR ($CDCl_3$, δ): 3.96 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, C_5H_4), 4.19 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, C_5H_4), 4.29 (s, 10 H, C_5H_5), 6.68 (s, 1 H, H6), 8.75 (s, 1 H, H3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 60.5 (C_5H_4), 64.0 (C_5H_4), 70.0 (C_5H_5), 104.3 (C6-C_6H_2), 119.5 (C_{C5H4}-O), 125.1 (C3-C_6H_2), 132.0 (C2,C4-C_6H_2), 157.9 (C1,C5-C_6H_2). HRMS (ESI-TOF, m/z): calcd for $C_{26}H_{20}Fe_2N_2O_6$ 568.0015, found 568.0039 $[M]^+$.

1-Ferrocenyloxy-5-fluoro-2,4-dinitrobenzene (99b)



99b

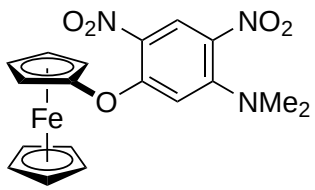
The title compound **99b** was obtained as a side product within the synthesis of **99a** by reacting ferrocenol (**5**, 651 mg, 3.22 mmol), BuLi (1.30 mL, 3.3 mmol) and 1,5-difluoro-2,4-dinitrobenzene (328 mg, 1.61 mmol). Purification was performed by column chromatography (silica, $4 \cdot 10$ cm column size) using a 1/1 hexane/dichloromethane mixture (v/v). All volatiles were removed in vacuum and compound **99b** was obtained as an orange solid. Suitable single crystals were obtained by crystallization from hexane.

Yield: 200 mg (0.52 mmol, 16 % based on **5**). Anal. calcd for $C_{16}H_{11}FFeN_2O_5 \cdot 0.3\,C_6H_{14}$ ($386.11 \cdot 0.3\ 86.18$ g/mol): C, 52.12; H, 3.81; N, 6.75. Found: C, 51.71; H, 3.41; N, 6.86. Mp.: 150–152 °C. ^{1}H NMR ($CDCl_3$, δ): . 4.13 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.37–4.38 (m, 7 H, C_5H_5, C_5H_4), 6.87 (d, $^3J_{H,F}$ = 11.9 Hz, 1 H, H6), 8.83 (d, $^4J_{H,F}$ = 7.6 Hz, 1 H, H3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 61.1 (C_5H_4), 64.6 (C_5H_4), 70.2 (C_5H_5), 106.2 (d, $^2J_{C,F}$ = 26.5 Hz, C6), 119.3 (C_{C5H4}-O), 125.1 (C3), 130.2 (d, $^2J_{C,F}$ = 7.9 Hz, C4), 134.4 (d, $^4J_{C,F}$ = 2.6 Hz, C2), 158.5 (d, $^1J_{C,F}$ = 273.9 Hz, C5), 159.1 (d, $^3J_{C,F}$ = 10.9 Hz, C1). HRMS (ESI-TOF, m/z): calcd for $C_{16}H_{11}FeN_2O_5F$ 385.9996, found 386.0024 $[M]^+$.

5-Ferrocenyloxy-*N*,*N*-dimethyl-2,4-dinitroaniline (99c)

The title compound was obtained as a side product within the synthesis of **99a** by reacting ferrocenol (**5**, 651 mg, 3.22 mmol), BuLi (1.30 mL, 3.3 mmol) and 1,5-difluoro-2,4-dinitrobenzene (328 mg, 1.61 mmol). Purification was performed by column chromatography (silica, $4 \cdot 10$ cm column size) using a 1/1 hexane/dichloromethane mixture (v/v), giving **99c** as an orange

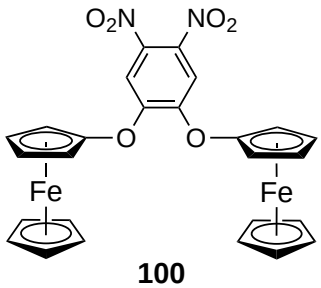
solid. Suitable single crystals were obtained by recrystallization from boiling hexane.



99c

Yield: 132 mg (0.32 mmol, 10 % based on **5**). Mp.: 170 °C. ^{1}H NMR ($CDCl_3$, δ): 2.85 (s, 6 H, CH_3), 4.06 (pt, $^{3,4}J_{H,H} = 2.0$ Hz, 2 H, C_5H_4), 4.35 (pt, $^{3,4}J_{H,H} = 2.0$ Hz, 2 H, C_5H_4), 4.36 (s, 5 H, C_5H_5), 6.26 (s, 1 H, H6), 8.69 (s, 1 H, H3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 42.3 (CH_3), 61.1 (C_5H_4), 64.0 (C_5H_4), 70.0 (C_5H_5), 102.3 (C6-C_6H_2), 119.2 (C_{C5H4}-O), 127.6 (C3-C_6H_2), 128.1 (C2/C4-C_6H_2), 130.6 (C2/C4-C_6H_2), 149.7 (C1-C_6H_2), 157.9 (C5-C_6H_2). HRMS (ESI-TOF, m/z): calcd for $C_{18}H_{17}FeN_3O_5$ 411.0512, found 411.0544 $[M]^+$.

1,2-Diferrocenyloxy-4,5-dinitrobenzene (100)

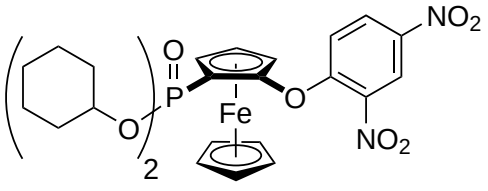


100

To ferrocenol (**5**, 864 mg, 4.25 mmol) dissolved in toluene (10 mL), BuLi (1.70 mL) was added dropwise. Afterwards, the general procedure GP6 for S_NAr reactions was applied using 1,2-difluoro-4,5-dinitrobenzene (437 mg, 2.14 mmol). Purification was performed by column chromatography (silica, $4 \cdot 10$ cm column size) using a 1/1 hexane/dichloromethane mixture (v/v) as the eluent, giving **100** as reddish-orange crystals. Crystals, suitable for single crystal X-ray diffraction analysis were obtained by recrystallization from boiling toluene.

Yield: 700 mg (1.02 mmol, 48 % based on **5**). Mp.: 182–184 °C. ^{1}H NMR ($CDCl_3$, δ): 4.10 (pt, $^{3,4}J_{H,H} = 2.0$ Hz, 4 H, C_5H_4), 4.35–4.36 (m, 14 H, C_5H_4), 7.49 (s, 2 H, C6H2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 60.4 (C_5H_4), 64.1 (C_5H_4), 69.8 (C_5H_5), 111.7 (C3,6-C_6H_2), 120.4 (C_{C5H4}-O), 137.1 (C4,5-C_6H_2), 151.7 (C1,2-C_6H_2). HRMS (ESI-TOF, m/z): calcd for $C_{26}H_{20}Fe_2N_2O_6$ 568.0015, found 568.0000 $[M]^+$.

Dicyclohexyl (2-(2,4-Dinitrophenoxy)ferrocenyl)phosphonate (*rac*-102a)



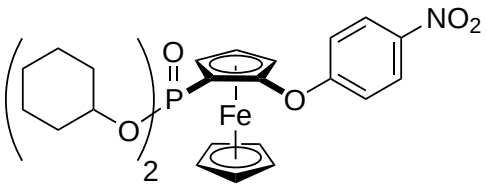
102a

Dicyclohexyl ferrocenyl phosphate (**30a**, 200 mg, 0.45 mmol), diisopropylamine (0.13 mL, 0.90 mmol), BuLi (0.36 mL, 0.9 mmol) and TMEDA (0.14 mL, 0.93 mmol) were reacted according to the general procedure B for anionic Fries rearrangements. Afterwards, 2,4-dinitrofluorobenzene (250 mg, 1.34 mmol) was applied within the general procedure GP6 for S_NAr reactions. Purification was performed by column chromatography (silica, $2 \cdot 15$ cm column size) using a 9/1 dichloromethane/ethyl acetate mixture (v/v) as the eluent, giving *rac*-**102a** as an orange oil.

Yield: 135 mg (0.22 mmol, 49 % based on **30a**). ^{1}H NMR ($CDCl_3$, δ): 1.22–1.39 (m, 10 H, CH_2), 1.48–1.53 (m, 3 H, CH_2), 1.58–1.68 (m, 3 H, CH_2), 1.72–1.81 (m, 2 H, CH_2), 1.83–1.89

(m, 1 H, CH_2), 1.91–2.00 (m, 1 H, CH_2), 4.27 (dd, $J_{H,H}$ = 2.7 Hz, $J_{H,H}$ = 2.7 Hz, 1 H, C_5H_3), 4.31–4.38 (m, 1 H, CH), 4.39–4.47 (m, 7 H, CH, C_5H_5, C_5H_3), 4.52 (m, 1 H, C_5H_3), 7.01 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, H6), 8.24 (dd, $^3J_{H,H}$ = 9.3 Hz, $^4J_{H,H}$ = 2.7 Hz, 1 H, H5), 8.79 (d, $^4J_{H,H}$ = 2.6 Hz, H3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.6–23.7 (m, CH_2), 25.1 (CH_2), 33.6–33.7 (m, CH_2), 33.8–33.9 (CH_2), 63.4 (d, $^1J_{C,P}$ = 219.2 Hz, C_{C5H3}-P), 64.5 (d, $J_{C,P}$ = 10.1 Hz, C_5H_3), 66.14 (d, $J_{C,P}$ = 13.6 Hz, C_5H_3), 68.8 (d, $J_{C,P}$ = 13.6 Hz, C_5H_3), 71.9 (C_5H_5), 75.5 (d, $^2J_{C,P}$ = 6.7 Hz, CH), 75.7 (d, $^2J_{C,P}$ = 6.3 Hz, CH), 117.4 (C6), 119.3 (d, $^2J_{C,P}$ = 9.2 Hz, C_{C5H3}-O), 121.6 (C3), 128.5 (C5), 138.3 (C2), 141.0 (C4), 157.6 (C1). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 19.1 ($^1J_{C,P}$ = 219.2 Hz). HRMS (ESI-TOF, m/z): calcd for $C_{28}H_{33}FeN_2PO_8$ + H 613.1397, found 613.1347 $[M+H]^+$.

Dicyclohexyl (2-(4-Nitrophenoxy)ferrocenyl)phosphonate (*rac*-102b)



102b

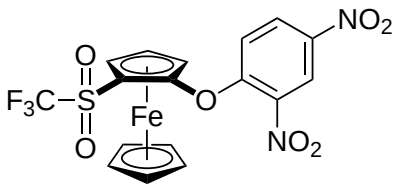
Dicyclohexyl ferrocenyl phosphate (**30a**, 200 mg, 0.45 mmol), diisopropylamine (0.13 mL, 0.90 mmol), BuLi (0.36 mL, 0.9 mmol) and TMEDA (0.14 mL, 0.93 mmol) were reacted according to the general procedure B for anionic Fries rearrangements. Afterwards, 4-nitrofluorobenzene (190 mg, 1.34 mmol) was applied in the general procedure GP6 for S_NAr reactions. Purification was performed by column chromatography (silica, 2 · 15 cm column size) using a 9/1 dichloromethane/ethyl acetate mixture (v/v) as the eluent, giving *rac*-**102b** as an orange oil.

Yield: 85 mg (0.15 mmol, 33 % based on **30a**). ^1H NMR ($CDCl_3$, δ): 1.23–1.33 (m, 6 H, CH_2), 1.38–1.52 (m, 6 H, CH_2), 1.64–1.72 (m, 4 H, CH_2), 1.79–1.88 (m, 4 H, CH_2), 4.23 (dd, $J_{H,H}$ = 2.7 Hz, $J_{H,H}$ = 2.7 Hz, 1 H, C_5H_3), 4.35–4.44 (m, 9 H, CH, C_5H_5, C_5H_3), 6.92–6.95 (m, 2 H, H2,6), 8.12–8.15 (m, 2 H, H3,5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 23.4–23.5 (m, CH_2), 25.17 (CH_2), 25.19 (CH_2), 33.6–33.8 (m, CH_2), 62.8 (d, $^1J_{C,P}$ = 218.3 Hz, C_{C5H3}-P), 64.5 (d, $J_{C,P}$ = 10.6 Hz, C_5H_3), 65.7 (d, $J_{C,P}$ = 13.7 Hz, C_5H_3), 68.6 (d, $J_{C,P}$ = 13.4 Hz, C_5H_3), 71.5 (C_5H_5), 75.1 (d, $^2J_{C,P}$ = 6.9 Hz, CH), 75.2 (d, $^2J_{C,P}$ = 6.1 Hz, CH), 115.9 (C2,6-C_6H_4), 120.1 (d, $^2J_{C,P}$ = 9.7 Hz, C_{C5H3}-O), 125.4 (C3,5-C_6H_4), 142.4 (C4-C_6H_4), 164.6 (C1-C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 19.3 ($^1J_{C,P}$ = 218.4 Hz). HRMS (ESI-TOF, m/z): calcd for $C_{28}H_{34}FeNO_6P$ + Na 590.1366, found 590.1331 $[M+Na]^+$.

2-(2,4-Dinitrophenoxy)-1-((Trifluoromethyl)sulfonyl)ferrocene (*rac*-103a)

Ferrocenyl triflate (**101**, 150 mg, 0.45 mmol), diisopropylamine (0.13 mL, 0.94 mmol) and BuLi (0.18 mL, 0.45 mmol) were reacted according to the general procedure GP2 for anionic Fries rearrangements at –80 °C. Afterwards, the reaction mixture was warmed to 0 °C and 2,4-dinitro-1-fluorobenzene (167 mg, 0.90 mmol) was applied within the general procedure GP6 for S_NAr reactions. Purification was performed by column chromatography (silica, 2 · 15 cm column size) using a 1/1 hexane/dichloromethane mixture (v/v) as the eluent, giv-

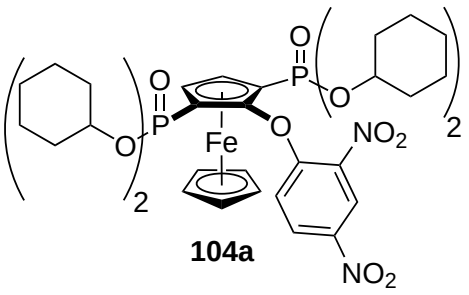
ing *rac*-**103a** as an orange solid. Crystals, suitable for single X-ray diffraction analysis were grown from a hexane solution containing *rac*-**103a** at ambient temperature.



103a

Yield: 180 mg (0.36 mmol, 80 % based on 10). Anal. calcd for $C_{17}H_{11}F_3FeN_2O_7S \cdot 1/6\ C_6H_{14}$ (500.18 · 0.17 86.18 g/mol): C, 42.02; H, 2.61; N, 5.44. Found: C, 41.78; H, 2.43; N, 5.54. Mp.: 172–174 °C. ^{1}H NMR ($CDCl_3$, δ): 4.62 (pt, $^{3,4}J_{H,H}$ = 2.9 Hz, 1 H, C_5H_3), 4.72 (s, 5 H, C_5H_5), 4.73 (dd, $J_{H,H}$ = 2.9 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 4.88 (dd, $J_{H,H}$ = 2.9 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_3), 7.00 (d, $^3J_{H,H}$ = 9.2 Hz, 1 H, H6), 8.33 (dd, $^3J_{H,H}$ = 9.2 Hz, $^4J_{H,H}$ = 2.7 Hz, 1 H, H5), 8.84 (d, $^4J_{H,H}$ = 2.7 Hz, 1 H, H3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 67.0 (C_5H_3), 68.0 (C_5H_3), 69.8 (C_5H_3), 69.4 (q, $^3J_{C,F}$ = 2.3 Hz, C2-C_5H_3), 73.7 (C_5H_5), 117.1 (C6), 119 (q, $^1J_{C,F}$ = 325.6 Hz, CF3), 119.6 (C_{C5H3}-O), 122.1 (C3), 128.6 (C5), 139.3 (C2), 142.1 (C4), 156.1 (C1). HRMS (ESI-TOF, m/z): calcd for $C_{17}H_{11}FeN_2O_7SF_3$ + Na 522.9481, found 522.9499 $[M+Na]^+$.

Tetracyclohexyl (2-(2,4-Dinitrophenoxy)ferrocenyl-1,3-diyl)bis(phosphonate) (*rac*-104a)



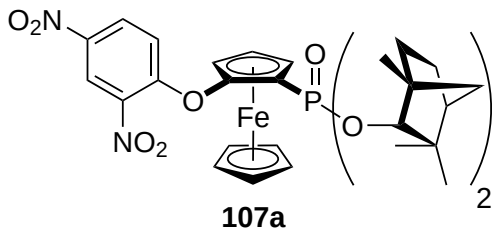
104a

Dicyclohexyl 2-(*O*,*O*'-dicyclohexyl phosphato)ferrocenylphosphonate (**35a**, 200 mg, 0.29 mmol), diisopropylamine (0.1 mL, 0.58 mmol), BuLi (0.24 mL, 0.6 mmol) and TMEDA (0.09 mL, 0.68 mmol) were reacted according to the general procedure GP3 for anionic Fries rearrangements. Afterwards, 2,4-dinitro-1-fluorobenzene (162 mg, 0.87 mmol) was applied within the general procedure GP6 for S_NAr reactions. Purification was performed by column chromatography (silica, 2 · 15 cm column size) using a 98/2 ethyl acetate/methanol mixture (v/v) as the eluent, giving *rac*-**104a** as an orange oil.

Yield: 177 mg (0.21 mmol, 73 % based on **35a**). ^{1}H NMR ($CDCl_3$, δ): 1.16–1.39 (m, 16 H, CH_2), 1.47–1.55 (m, 6 H, CH_2), 1.62–1.85 (m, 16 H, CH_2), 1.94–1.97 (m, 4 H, CH_2), 4.30–4.43 (m, 4 H, CH), 4.58–4.59 (m, 6 H, C_5H_5, C_5H_2), 4.67–4.76 (m, 1 H, C_5H_2), 6.93 (d, $^3J_{H,H}$ = 6.9 Hz, 0.8 H, H6), 7.02 (d, $^3J_{H,H}$ = 8.9 Hz, 0.2 H, H6), 8.22 (dd, $^3J_{H,H}$ = 9.3 Hz, $^4J_{H,H}$ = 2.7 Hz, 0.8 H, H5), 8.26 (dd, $^3J_{H,H}$ = 9.3 Hz, $^4J_{H,H}$ = 2.7 Hz, 0.2 H, H5), 8.81 (d, $^4J_{H,H}$ = 2.7 Hz, 0.8 H, H3), 8.84 (d, $^4J_{H,H}$ = 2.7 Hz, 0.2 H, H3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 23.4–23.8 (m, CH_2), 25.0–25.1 (m, CH_2), 33.5–33.9 (m, CH_2), 67.0 (dd, $^1J_{C,P}$ = 216.6 Hz, $^3J_{C,P}$ = 9.1 Hz, C-P), 70.3 (pt, 2,$^3J_{C,P}$ = 13.8 Hz, C_5H_2), 73.8 (s, C_5H_5), 76.0 (d, $^2J_{C,P}$ = 6.9 Hz, $C_{C6}H_{11}$-O), 76.2 (d, $^2J_{C,P}$ = 6.5 Hz, $C_{C6}H_{11}$-O), 117.8 (C6-C_6H_3), 118.6 (t, $^2J_{C,P}$ = 9.5 Hz, C_{C5H2}-O), 121.7 (C3-C_6H_3), 128.3 (C5-C_6H_3), 137.9 (C2-C_6H_3), 141.1 (C4-C_6H_3), 157.4 (C1-C_6H_3). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 17.4 ($^1J_{C,P}$ = 215.1 Hz). HRMS (ESI-TOF, m/z):

calcd for $C_{40}H_{54}FeN_2O_{11}P_2$ + H 857.2626, found 857.2593 $[M+H]^+$.

(R_p)-Bis((1R)-α-fenchyl) (2-(2,4-Dinitrophenoxy)ferrocenyl)phosphonate ((R_p)-107a)

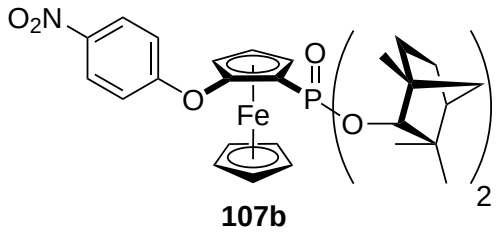


107a

Bis((1R)-α-fenchyl) ferrocenyl phosphate (**30e**, 521 mg, 0.94 mmol), LiTMP (227 mg, 1.88 mmol) and TMEDA (0.28 mL, 1.88 mmol) were reacted according to the general procedure GP3. Afterwards, 2,4-dinitro-1-fluorobenzene (524 mg, 2.82 mmol) was applied within the general procedure for S_NAr reactions. Purification was performed by column chromatography (silica, $2 \cdot 20$ cm column size) using a 98/2 dichloromethane/ethyl acetate mixture (v/v) as the eluent, giving (R_p)-**107a** as an orange oil as a mixture of two diastereomers (0.81 *de*). Except otherwise noted, the signals of the main diastereomer are reported.

Yield: 230 mg (0.32 mmol, 34 % based on **30e**). ^{1}H NMR ($CDCl_3$, δ): 067 (s, 3 H, CH_3), 0.76 (s, 3 H, CH_3), 0.90 (s, 3 H, CH_3), 0.99 (s, 3 H, CH_3), 1.08–1.21 (m, 10 H), 1.52–1.87 (m, 10 H), 3.96 (dd, $J_{H,H}$ = 1.68 Hz, $J_{H,H}$ = 10.1 Hz, 1 H, C_5H_3), 4.15 (dd, $J_{H,H}$ = 1.68 Hz, $J_{H,H}$ = 10.1 Hz, 1 H, C_5H_3), 4.29 (m, 1 H, C_5H_3), 4.47–4.50 (m, 2 H, H2), 4.53 (s, 5 H, C_5H_5), 7.34 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, H6), 8.31 (dd, $^3J_{H,H}$ = 9.3 Hz, $^4J_{H,H}$ = 2.7 Hz, 1 H, H5), 8.83 (d, $^3J_{H,H}$ = 2.7 Hz, 1 H, H3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.6 (CH_3), 19.8 (CH_3), 21.0 (CH_3), 21.6 (CH_3), 25.8 (C5/6), 25.9 (C5/6), 26.0 (C5/6), 26.1 (C5/6), 29.5 (CH_3), 30.1 (CH_3), 39.2 (d, $^3J_{C,P}$ = 2.3 Hz, C3), 39.6 (d, $^3J_{C,P}$ = 2.3 Hz, C3), 41.1 (C7), 41.2 (C7), 47.8 (C4), 47.9 (C4), 49.3 (d, $^3J_{C,P}$ = 4.8 Hz, C1), 49.5 (d, $^3J_{C,P}$ = 4.1 Hz, C1), 61.9 (d, $^1J_{C,P}$ = 217.9 Hz, C-P), 63.7 (d, $J_{C,P}$ = 10.2 Hz, C_5H_3), 66.1 (d, $J_{C,P}$ = 13.3 Hz, C_5H_3), 68.8 (d, $J_{C,P}$ = 12.7 Hz, C_5H_3), 71.9 (C_5H_5), 88.6 (d, $^2J_{C,P}$ = 7.0 Hz, C2), 89.5 (d, $^2J_{C,P}$ = 7.1 Hz, C2), 118.3 (C6-C_6H_3), 120.8 (d, $^2J_{C,P}$ = 7.0 Hz, C_{C5H4}-O), 122.0 (C3-C_6H_3), 128.4 (C5-C_6H_3), 139.3 (C2-C_6H_3), 141.4 (C4-C_6H_3), 157.0 (C1-C_6H_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 20.5. HRMS (ESI-TOF, m/z): calcd for $C_{36}H_{45}FeN_2O_8P$ + Na 743.2156, found 743.2149 $[M+Na]^+$.

(R_p)-Bis((1R)-α-fenchyl) (2-(4-nitrophenoxy)ferrocenyl)phosphonate ((R_p)-107b)



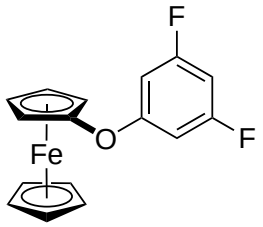
107b

Bis((1R)-α-fenchyl) ferrocenyl phosphate (**30e**, 1.00 g, 1.80 mmol), LiTMP (530 mg, 3.61 mmol) and TMEDA (0.54 mL, 3.61 mmol) were reacted according to the general procedure GP3. Afterwards, 4-nitrofluorobenzene (763 mg, 5.41 mmol) was applied within the general procedure GP6 for S_NAr reactions. Purification was performed by column chromatography (silica, $2 \cdot 14$ cm column size) using a 95/5 dichloromethane/ethyl acetate mixture (v/v) as the eluent, giving

(R_p)-**107b** as an orange oil as a mixture of two diastereomers (0.74 *de*).

Yield: 113 mg (0.17 mmol, 9 % based on **30e**). Except otherwise noted, merely the signals of the mainly formed diastereomer are reported. ^{1}H NMR ($CDCl_3$, δ): 0.73 (s, 3 H, CH_3), 0.82–1.84 (m, 31 H, $C_{10}H_{17}$), 3.63 (dd, $^{3}J_{H,P}$ = 9.8 Hz, $J_{H,H}$ = 1.6 Hz, 1 H, H2), 4.16 (dd, $^{3}J_{H,P}$ = 9.8 Hz, $J_{H,H}$ = 1.7 Hz, 1 H, H2), 4.25 (dd, $^{3,4}J_{H,H}$ = 2.5 Hz, 1 H, C_5H_3), 4.34–4.36 (m, 1 H, C_5H_3), 4.46 (s, mi, C_5H_5), 4.47 (s, 5 H, C_5H_5), 4.50–4.51 (m, 1 H, C_5H_3), 7.14–7.17 (m, 2 H, 2,6-C_6H_4), 8.16–8.20 (m, 2 H, 3,5-C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.3 (CH_3), 19.8 (CH_3), 21.3 (CH_3), 21.6 (CH_3), 25.8 (C5/C6), 26.0 (C5/C6), 26.1 (C5/C6), 29.1 (CH_3), 29.9 (CH_3), 39.3 (d, $^{3}J_{C,P}$ = 1.9 Hz, C3), 39.4 (d, $^{3}J_{C,P}$ = 1.3 Hz, C3), 40.8 (C7), 41.1 (C7), 47.9 (C4), 48.0 (C4), 49.1 (d, $^{3}J_{C,P}$ = 5.8 Hz, C1), 49.4 (d, $^{3}J_{C,P}$ = 4.8 Hz, C1), 60.6 (d, $^{1}J_{C,P}$ = 216.5 Hz, C-P), 63.7 (d, $J_{C,P}$ = 10.8 Hz, C_5H_3), 65.7 (d, $J_{C,P}$ = 13.2 Hz, C_5H_3), 68.0 (d, $J_{C,P}$ = 11.8 Hz, C_5H_3), 71.3 (C_5H_5, mi), 71.5 (C_5H_5, ma), 87.8 (d, $^{2}J_{C,P}$ = 6.1 Hz, C2), 89.1 (d, $^{2}J_{C,P}$ = 7.5 Hz, C2), 116.8 (2,6-C_6H_4), 121.6 (d, $^{2}J_{C,P}$ = 10.5 Hz, C_{C5H3}-O), 125.5 (3,5-C_6H_4), 142.6 (C4-C_6H_4), 163.9 (C1-C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 21.2 (100 %), 22.2 (6 %), 22.5 (9 %). HRMS (ESI-TOF, m/z): calcd for $C_{36}H_{46}FeNO_6P$ 675.2407, found 675.2395 $[M]^+$.

1-Ferrocenyloxy-3,5-difluorobenzene (109)

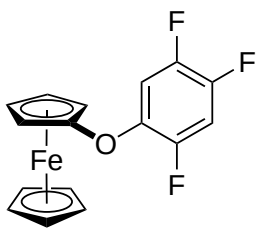


109

Ferrocenol (**5**, 150 mg, 0.74 mmol), BuLi (0.3 mL, 0.75 mmol) and 1,3,5-trifluorobenzene (**108a**, 0.23 mL, 2.25 mmol) were reacted according to the general procedure GP6. Purification was realized by column chromatography (silica, 4 · 20 cm column size) using a 3/1 hexane/dichloromethane mixture (v/v) as the eluent, giving **109** as an orange oil.

Yield: 141 mg (0.45 mmol, 61 % based on **5**). ^{1}H NMR ($CDCl_3$, δ): 4.01 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.26 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.30 (s, 5 H, C_5H_5), 6.42–6.48 (m, 3 H, C_6H_3). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 60.8 (C_5H_4), 63.5 (C_5H_4), 69.5 (C_5H_5), 97.5 (t, $^{2}J_{C,F}$ = 25.9 Hz, $C4_{C6H3}$), 99.8–100.0 (m, $C2/6_{C6H3}$), 120.3 (C_{C5H4}-O), 161.5 (t, $^{3}J_{C,F}$ = 13.4 Hz, $C1_{C6}$-O), 163.4 (dd, $^{1}J_{C,F}$ = 246.8 Hz, $^{3}J_{C,F}$ = 15.4 Hz, C3,5-F). ^{19}F NMR ($CDCl_3$, δ): –109.19 – –109.11 (m, 2 F). HRMS (ESI-TOF, m/z): calcd for $C_{16}H_{12}F_2FeO$ 314.0200, found 314.0199 $[M]^+$.

1-Ferrocenyloxy-2,4,5-trifluorobenzene (110a)



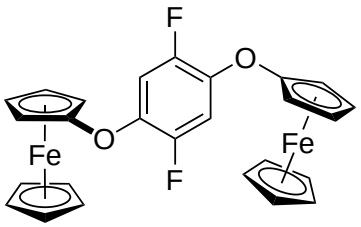
110a

Ferrocenol (**5**, 220 mg, 1.09 mmol), BuLi (0.44 mL, 1.1 mmol) and 1,2,4,5-tetrafluorobenzene (**108b**, 0.37 mL, 3.27 mmol) were reacted according to the general procedure GP6. Purification was realized by column chromatography (silica, 4 · 20 cm column size) using a 3/1 hexane/dichloromethane mixture (v/v) as the eluent, giving **110a** as an orange solid.

Yield: 264 mg (0.795 mmol, 73 % based on **5**). Anal. calcd for

$C_{16}H_{11}F_3FeO$ (332.11 g/mol): C, 57.87; H, 3.34. Found: C. 58.08; H, 3.46. Mp.: 94–96 °C. ^{1}H NMR ($CDCl_3$, δ): 3.97 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.23 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.28 (s, 5 H, C_5H_5), 6.91 (dt, $^3J_{H,F}$ = 11.1 Hz, $^4J_{H,F}$ = 7.7 Hz, 1 H, H6$_{C6H2}$) 7.00 (td, $^3J_{H,F}$ = 10.0 Hz, $^4J_{H,F}$ = 7.4 Hz, 1 H, H3$_{C6H2}$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.2 (C_5H_4), 63.1 (C_5H_4), 69.4 (C_5H_5), 105.9 (t, $^2J_{C,F}$ = 23.0 Hz, C3$_{C6}$), 107.7 (d, $^2J_{C,F}$ = 22.0 Hz, C6$_{C6}$), 122.6 (C_{C5H4}-O), 142.3 (ddd, $^3J_{C,F}$ = 13.0 Hz, $^2J_{C,F}$ = 7.6 Hz, $^4J_{C,F}$ = 3.7 Hz, C1$_{C6}$-O), 144.9 (ddd, $^1J_{C,F}$ = 246.1 Hz, $^2J_{C,F}$ = 14.2 Hz, $^3J_{C,F}$ = 10.3 Hz, C4$_{C6}$), 145.9 (ddd, $^1J_{C,F}$ = 245.4 Hz, $^3J_{C,F}$ = 13.4 Hz, $^4J_{C,F}$ = 3.6 Hz, C2$_{C6}$), 148.2 (ddd, $^1J_{C,F}$ = 247.1 Hz, $^2J_{C,F}$ = 9.0 Hz, $^4J_{C,F}$ = 3.1 Hz, C5$_{C6}$). ^{19}F NMR ($CDCl_3$, δ): –141.71 (ddd, $^3J_{F,F}$ = 22.1 Hz, $^3J_{F,H}$ = 9.9 Hz, $^4J_{F,H}$ = 7.9 Hz, 1 F, F4), –140.4 (dddd, $^3J_{F,F}$ = 22.1 Hz, $^5J_{F,F}$ = 13.4 Hz, $^3J_{F,H}$ = 11.1 Hz, $^3J_{F,H}$ = 7.4 Hz, 1 F, F5), –134.5 (ddd, $^5J_{F,F}$ = 13.4 Hz, $^3J_{F,H}$ = 10.1 Hz, $^4J_{F,H}$ = 7.7 Hz, 1 F, F2). HRMS (ESI-TOF, m/z): calcd for $C_{16}H_{11}F_3FeO$ 332.0106, found 332.0106 $[M]^+$.

1,4-Bis(ferrocenyloxy)-2,5-difluorobenzene (110b)

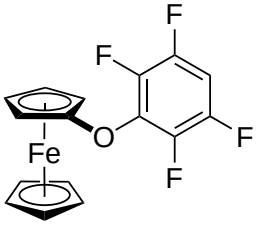


110b

Ferrocenol (**5**, 600 mg, 2.97 mmol), BuLi (1.2 mL, 3.0 mmol) and 1,2,4,5-tetrafluorobenzene (**108b**, 0.17 mL, 1.48 mmol) were reacted according to the general procedure GP6. Purification was realized by column chromatography (silica, 4 · 20 cm column size) using a 3/1 hexane/dichloromethane mixture (v/v) as the eluent. The title compound was isolated after the separation of 115 mg (0.329 mmol, 35 %) of **110a**. After evaporation of all volatiles the title compound (**110b**) was obtained as an orange solid.

Yield: 18 mg (0.035 mmol, 2 % based on **108b**). ^{1}H NMR ($CDCl_3$, δ): 3.95 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 4 H, C_5H_4), 4.23 (pt, $^{3,4}J_{H,H}$ = 4.0 Hz, 2 H, C_5H_4), 4.27 (s, 10 H, C_5H_5), 6.72 (t, $^{3,4}J_{H,F}$ = 9.5 Hz, 2 H, H3,6$_{C6H2}$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 59.1 (C_5H_4), 63.0 (C_5H_4), 69.4 (C_5H_5), 107.7 (dd, $^2J_{C,F}$ = 17.9 Hz, $^3J_{C,F}$ = 7.7 Hz, C3,6$_{C6}$), 123.2 (C_{C5H4}-O), 141.1 (dd, $^3J_{C,F}$ = 12.0 Hz, $^2J_{C,F}$ = 9.6 Hz, C1,4$_{C6}$-O), 148.7 (dd, $^1J_{C,F}$ = 246.0 Hz, $^4J_{C,F}$ = 4.1 Hz, C2,5$_{C6}$). ^{19}F NMR ($CDCl_3$, δ): –135.1 (t, $^{3,+4}J_{F,H}$ = 9.5 Hz). HRMS (ESI-TOF, m/z): calcd for $C_{26}H_{20}F_2Fe_2O_2$ 514.0125, found 514.0087 $[M]^+$.

3-Ferrocenyloxy-1,2,4,5-tetrafluorobenzene (111a)



111a

Ferrocenol (**5**, 190 mg, 0.94 mmol), BuLi (0.38 mL, 0.95 mmol) and 1,2,4,5-tetrafluorobenzene (**108c**, 0.44 mL, 3.96 mmol) were reacted according to the general procedure described above. Purification was realized by column chromatography (silica, 4 · 20 cm column size) using a 4/1 hexane/dichloromethane mixture (v/v) as the eluent, giving **111a** as an orange solid.

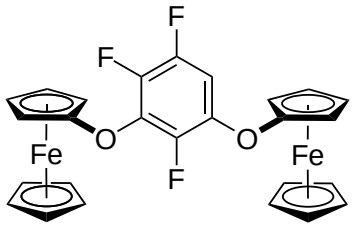
Yield: 308 mg (0.88 mmol, 94 % based on **5**). Anal. calcd for $C_{16}H_{10}F_4FeO$ (350.10 g/mol): C, 54.89; H, 2.88. Found: C, 55.02; H, 2.99. Mp.: 56 °C.

^{1}H NMR ($CDCl_3$, δ): 3.88 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.24 (s, 5 H, C_5H_5), 4.26 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 6.92 (tt, $^{3}J_{H,F}$ = 7.0 Hz, $^{4}J_{H,F}$ = 9.9 Hz, 1 H, C_6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 57.7 (C_5H_4), 62.4 (C_5H_4), 69.4 (C_5H_5), 101.5 (t, $J_{C,F}$ = 23.0 Hz, C6$_{C6}$-H), 126.4 (C_{C5H4}-O), 136.4 (tt, $^{3}J_{C,F}$ = 13.2 Hz, $^{2}J_{C,F}$ = 3.6 Hz, C3$_{C6}$-O), 141.5 (dddd, $^{1}J_{C,F}$ = 249.9 Hz, $^{3}J_{C,F}$ = 14.7 Hz, $^{2}J_{C,F}$ = 4.6 Hz, $^{4}J_{C,F}$ = 2.4 Hz, C-F) , 146.3 (dtd, $^{1}J_{C,F}$ = 248.2 Hz, $^{2,3}J_{C,F}$ = 12.3 Hz, $^{4}J_{C,F}$ = 4.1 Hz, C-F). ^{19}F NMR ($CDCl_3$, δ): –154.1 – –154.0 (m, 2 F, F1,5), –139.0 – –138.9 (m, 2 F, F2,4). HRMS (ESI-TOF, m/z): calcd for $C_{16}H_{10}F_4FeO$ 350.0012, found 350.0010 $[M]^+$.

Reaction of Ferrocenol (5) with C_6HF_5 (108c) to give 111b-e

Ferrocenol (**5**, 620 mg, 3.07 mmol), BuLi (1.23 mL, 3.07 mmol) and pentafluorobenzene (**108c**, 0.12 mL, 1.02 mmol) were reacted according to the general procedure GP6. Purification was realized by column chromatography (silica, 4 · 20 cm column size). Compounds **111a-e** were separated using hexane/dichloromethane eluent mixtures (v/v) starting from 4/1 (**111a**; 170 mg, 0.49 mmol; 47 % based on **108c**) to 7/3 (**111b**), 1/1 (**111c**/**111d**) and 1/4 (**111e**). After evaporation of all volatiles the compounds **111b-e** were obtained as orange solids.

1,3-Bis(ferrocenyloxy)-2,4,5-trifluorobenzene (111b)



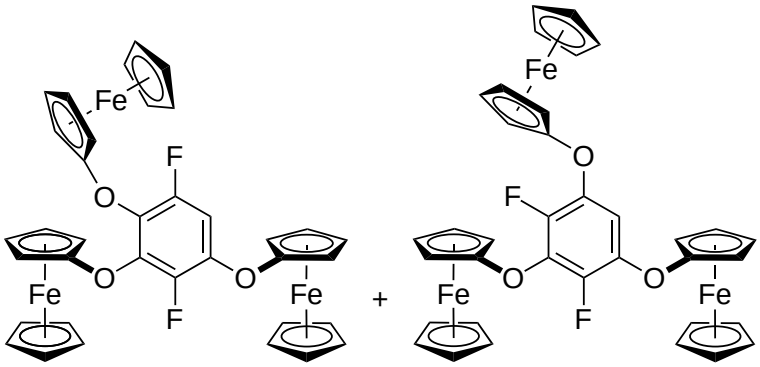
111b

Yield: 245 mg (0.46 mmol 0.05 mmol, 45 % based on **108c**). Anal. calcd for $C_{26}H_{19}F_3Fe_2O_2$ (532.12 g/mol): C, 58.69; H, 3.60. Found: C. 59.16; H, 3.77. Mp.: 101 °C. ^{1}H NMR ($CDCl_3$, δ): 3.87 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, $C_5H_4(1)$), 3.98 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, $C_5H_4(2)$), 4.24 (s, 5 H, C_5H_5), 4.25 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, $C_5H_4(2)$), 4.27 (pt, $^{3,4}J_{H,H}$ = 1.8 Hz, 2 H, $C_5H_4(1)$), 4.29 (s, 5 H, C_5H_5), 6.72 (dt, $^{3}J_{H,F}$ = 11.2 Hz, $^{4}J_{H,F}$ = 7.3 Hz, 1 H, C_6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 57.7 ($C_5H_4(1)$), 59.6 ($C_5H_4(2)$), 62.3 ($C_5H_4(1)$), 63.2 ($C_5H_4(2)$), 69.3 (C_5H_5), 69.5 (C_5H_5), 102.1 (d, $J_{C,F}$ = 22.5 Hz, C6$_{C6}$-H), 122.1 (C_{C5H4}-O), 126.4 (C_{C5H4}-O), 135.8 (ddd, $^{3}J_{C,F}$ = 14.1 Hz, $^{2}J_{C,F}$ = 12.9 Hz, $^{2}J_{C,F}$ = 3.7 Hz, C3$_{C6}$-O), 140.2 (ddd, $^{1}J_{C,F}$ = 248.0 Hz, $^{3}J_{C,F}$ = 15.0 Hz, $^{2}J_{C,F}$ = 2.7 Hz, C2-F), 142.8 (ddd, $^{3}J_{C,F}$ = 10.8 Hz, $^{2}J_{C,F}$ = 9.8 Hz, $^{4}J_{C,F}$ = 3.6 Hz, C_{C6}-O), 143.3 (ddd, $^{1}J_{C,F}$ = 248.8 Hz, $^{2}J_{C,F}$ = 4.0 Hz, $^{4}J_{C,F}$ = 2.1 Hz, C5-F), 146.32 (ddd, $^{1}J_{C,F}$ = 245.9 Hz, $^{3}J_{C,F}$ = 12.8 Hz, $^{2}J_{C,F}$ = 4.1 Hz, C4-F). ^{19}F NMR ($CDCl_3$, δ): –156.7 (dd, $^{3}J_{F,F}$ = 22.4 Hz, $^{4}J_{F,H}$ = 7.5 Hz, 1 F, F4), –150.2 (dd, $^{5}J_{F,F}$ = 10.2 Hz, $^{4}J_{F,H}$ = 7.6 Hz, 1 F, F2), –139.8 (ddd, $^{3}J_{F,F}$ = 22.0 Hz, $^{3}J_{F,H}$ = 10.8 Hz, $^{5}J_{F,F}$ = 10.8 Hz, 1 F, F5). HRMS (ESI-TOF, m/z): calcd for $C_{26}H_{19}F_3Fe_2O_2$ 532.0031, found 532.0048 $[M]^+$.

1,3,4-Tris(ferrocenyloxy)-2,5-difluorobenzene (111c) and 1,3,5-Tris(ferrocenyloxy)-2,4-difluorobenzene (111d)

Compounds **111c** and **111d** were obtained as one fraction in a ratio of 2/1 (**111c** : **111d**). Yield 14 mg (0.02 mmol, 2 % based on **108c**). However, the separation of **111c**,**d** from each other was not possible by using chromatographic methods, due to their similar physical

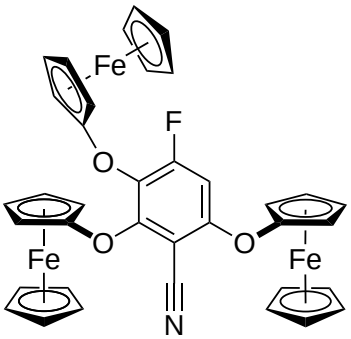
properties.



111c + **111d**

^{1}H NMR ($CDCl_3$, δ): 3.83 (pt, $^{3,4}J_{H,H}$ = 4.0 Hz, 4 H, C_5H_4), 3.84 (pt, $^{3,4}J_{H,H}$ = 4.0 Hz, 4 H, C_5H_4), 3.87 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4, d), 3.92 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, C_5H_4), 3.99 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, C_5H_4), 4.17 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, C_5H_4), 4.19 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, C_5H_4), 4.21 (s, 10 H, C_5H_5), 4.22–4.23 (m, 14 H, C_5H_4, C_5H_5), 4.25 (s, 5 H, C_5H_5, d), 4.28–4.29 (m, 6 H, C_5H_4, d, c), 4.30 (s, 10 H, C_5H_5), 6.69 (dd, $^{3}J_{H,F}$ = 11.2 Hz, $^{4}J_{H,F}$ = 7.3 Hz, 2 H, C-H, c), 6.81 (t, $^{4}J_{H,F}$ = 7.6 Hz, 1 H, C-H, d). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 57.6 (C_5H_4), 57.7 (C_5H_4), 58.0 (C_5H_4), 58.7 (C_5H_4), 59.8 (C_5H_4), 62.1 (C_5H_4), 62.16 (C_5H_4), 62.24 (C_5H_4), 62.9 (C_5H_4), 63.3 (C_5H_4), 57.6 (C_5H_4), 69.28 (C_5H_5), 69.32 (C_5H_5), 69.67 (C_5H_5), 69.39 (C_5H_5), 69.6 (C_5H_5), 101.9 (d, $^{3}J_{C,F}$ = 24.6 Hz, C_{C6}-H, c), 105.7 (s, C_{C6}-H, d), 122.1 (C_{C5H4}-O), 123.4 (C_{C5H4}-O), 126.3 (C_{C5H4}-O), 126.6 (C_{C5H4}-O). 133.7 (HMBC, c), 142.7 (HMBC, d, d, C-F), 143.4 (HMBC, d, c, C-F), 151.2 (HMBC, d, c, C-F). ^{19}F NMR ($CDCl_3$, δ): –150.6 (dd, $J_{F,F}$ = 10.7 Hz, $J_{F,H}$ = 7.6 Hz, 1 F, c), –150.5 (d, $^{4}J_{F,H}$ = 7.5 Hz, 1 F, d), –130.8 (dd, $^{3}J_{F,H}$ = 11.8 Hz, $J_{F,F}$ = 10.3 Hz, 1 F, c). HRMS (ESI-TOF, m/z): calcd for $C_{36}H_{28}F_2Fe_3O_3$ 714.0051, found 713.9989 $[M]^+$.

2,3,4-Tris(ferrocenyloxy)-5-fluorobenzonitrile (111e)

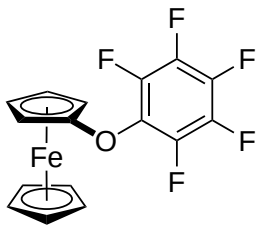


111e

Yield: 11 mg (0.015 mmol, 1.5 % based on **108c**). IR data (NaCl, $\tilde{\nu}$/cm^{-1}): 3094 m ($\tilde{\nu}$ C*Ar*-H), 2955 s, 2922 s, 2854 s, 2234 w ($\tilde{\nu}$ C≡N), 1734 vw, 1480 m, 1452 s, 1373 w, 1262 m, 1233 m. ^{1}H NMR ($CDCl_3$, δ): 3.89 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4(1)), 3.95 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4(2)), 3.97 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4(3)), 4.15 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4(3)), 4.19 (s, 5 H, C_5H_5), 4.27 (s, 5 H, C_5H_5), 4.30 (pt, $^{3,4}J_{H,H}$ = 1.6 Hz, 2 H, C_5H_4(1)), 4.33–4.35 (m, 7 H, C_5H_4(2), C_5H_5), 6.85 (d, $^{3}J_{H,F}$ = 11.4 Hz, 1 H, C_6H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 58.3 (C_5H_4(2)), 58.5 (C_5H_4(1)), 60.7 (C_5H_4(3)), 62.3 (C_5H_4(2)), 62.5 (C_5H_4(1)), 63.7 (C_5H_4(3)), 69.6 (C_5H_5), 69.69 (C_5H_5), 69.70 (C_5H_5), 100.8 (C≡N), 110.0 (d, $^{2}J_{C,F}$ = 23.9 Hz, C_{C6}-H), 120.4 (C_{C5H4}(3)-O), 126.7 (C_{C5H4}(1/2)-O), 126.8 (C_{C5H4}(1/2)-O), 141.0, 144.5, 149.0 (d, $J_{C,F}$ = 8.9 Hz), 151.0 (d, $^{1}J_{C,F}$ = 249.5 Hz, C-F). ^{19}F NMR ($CDCl_3$, δ): –126.5 (d, $^{3}J_{F,H}$ = 11.4 Hz, 1 F). HRMS

(ESI-TOF, m/z): calcd for $C_{37}H_{28}FFe_3NO_3$ 721.0101, found 721.0058 $[M]^+$.

1-Ferrocenyloxypentafluorobenzene (112a)



112a

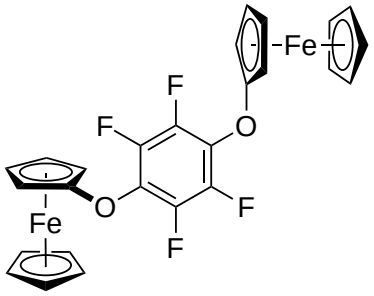
Ferrocenol (**5**, 225 mg, 1.11 mmol), BuLi (0.44 mL, 1.10 mmol) and hexafluorobenzene (**108d**, 0.30 mL, 2.60 mmol) were reacted according to the general procedure GP6. Purification was realized by column chromatography (silica, $4 \cdot 20$ cm column size) using a 5/1 hexane/dichloromethane mixture as the eluent. The title compound **112a** could be isolated followed by 71 mg (0.13 mmol, 12 % based on **5**) of **112b**. After evaporation of all volatiles compounds **112a** and **112b** were obtained as orange solids.

Yield: 353 mg (0.96 mmol, 86 % based on **5**). Anal. calcd for $C_{16}H_9F_5FeO$ (368.08 g/mol): C, 52.21; H, 2.46. Found: C. 52.59; H, 2.50. Mp.: 92–96 °C. ^{1}H NMR ($CDCl_3$, δ): 3.88 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.23–4.24 (m, 7 H, C_5H_5, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 57.7 (C_5H_4), 62.5 (C_5H_4), 69.4 (C_5H_5), 126.6 (C_{C5H4}-O), 131.9 (ttd, $^3J_{C,F}$ = 16.7 Hz, $^2J_{C,F}$ = 4.6 Hz, $^4J_{C,F}$ = 1.6 Hz, C_{C6}-O), 138.0 (ddddd, $^1J_{C,F}$ = 251.7 Hz, $^3J_{C,F}$ = 14.6 Hz, $^3J_{C,F}$ = 13.2 Hz, $^2J_{C,F}$ = 5.1 Hz, $^4J_{C,F}$ = 3.4 Hz, C2,6-C_6), 138.5 (dtt, $^1J_{C,F}$ = 251.9 Hz, $^3J_{C,F}$ = 13.6 Hz, $^2J_{C,F}$ = 3.8 Hz, C4$_{C6}$), 142.1 (ddq, $^1J_{C,F}$ = 251.0 Hz, $^2J_{C,F}$ = 12.2 Hz, $^3J_{C,F}$ = 4.0 Hz, C3,5$_{C6F5}$). ^{19}F NMR ($CDCl_3$, δ): –162.4 – –162.2 (m with the main coupling scheme to be a dd at –162.3; $^3J_{F,F}$ = 22.1 Hz, $J_{F,F}$ 21.6 Hz, 2 F, F3,5), –160.5 (t, $^3J_{F,F}$ = 21.9 Hz, 1 F, F4), –154.1 (d, $^3J_{F,F}$ = 18.7 Hz, 2 F, F2,6). HRMS (ESI-TOF, m/z): calcd for $C_{16}H_9F_5FeO$ 367.9917, found 367.9938 $[M]^+$.

Reaction of Ferrocenol (5) with C_6F_6 (108d) to give 112b,c

Ferrocenol (**5**, 828 mg, 4.097 mmol), BuLi (1.63 mL, 4.08 mmol) and hexafluorobenzene (**108d**, 0.16 mL, 1.37 mmol) were reacted according to the general procedure described above at 100 °C. Purification was realized by column chromatography (silica, $4 \cdot 20$ cm column size) using hexane/dichloromethane mixtures as the eluents starting from 5/1 (v/v) (**112b**) up to dichloromethane (**112c**). After evaporation of all volatiles the compounds were obtained as an orange solid (**112b**) or oil (**112c**).

1,4-Bis(ferrocenyloxy)-2,3,5,6-tetrafluorobenzene (112b)

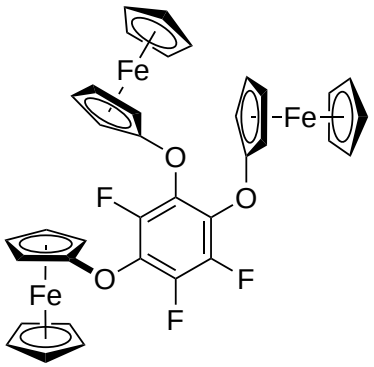


112b

Yield: 594 mg (1.08 mmol, 79 % based on **108d**). Anal. calcd for $C_{26}H_{18}F_4Fe_2O_2$ (550.10 g/mol): C, 56.77; H, 3.30. Found: C. 56.77; H, 3.41. Mp.: 165–169 °C. ^{1}H NMR ($CDCl_3$, δ): 3.89 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.24, (s, 5 H, C_5H_5), 4.27 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 57.8 (C_5H_4), 62.5 (C_5H_4), 69.4 (C_5H_5), 126.6 (C_{C5H4}-O), 132.4–132.7 (m, C_{C6}-O), 140.9–143.1 (m, C2,6$_{C6}$, C4$_{C6F4}$). ^{19}F NMR ($CDCl_3$, δ): –154.6

(s, 1 F). HRMS (ESI-TOF, m/z): calcd for $C_{26}H_{18}F_4Fe_2O_2$ 549.9937, found 549.9903 $[M]^+$.

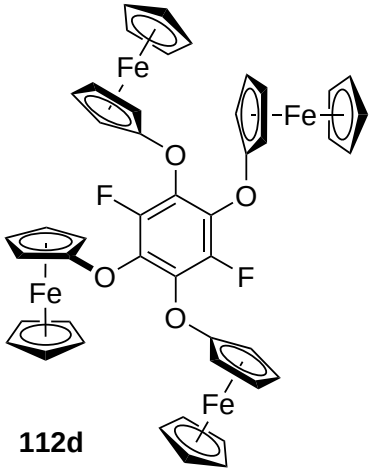
1,2,4-Tris(ferrocenyloxy)-3,5,6-trifluorobenzene (112c)



112c

Yield: 213 mg (0.29 mmol, 21 % based on **108d**). ^{1}H NMR ($CDCl_3$, δ): 3.86 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 3.87 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 3.89 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.21 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4), 4.236 (s, 10 H, C_5H_5), 4.240 (s, 5 H, C_5H_5), 4.28 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 2 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 57.69 (C_5H_4), 57.71 (C_5H_4), 58.00 (C_5H_4), 62.2 (C_5H_4), 62.3 (C_5H_4), 62.4 (C_5H_4), 69.30 (C_5H_5), 69.32 (C_5H_5), 69.35 (C_5H_5), 126.3 (C_{C5H4}-O), 126.4 (C_{C5H4}-O), 126.7 (C_{C5H4}-O), 132.4 (ddd, $^3J_{C,F}$ = 15.2 Hz, $^3J_{C,F}$ = 13.2 Hz, $^2J_{C,F}$ = 2.2 Hz, C1$_{C6}$-OFc4), 135.9 (ddd, $^3J_{C,F}$ = 12.8 Hz, $^2J_{C,F}$ = 4.0 Hz, $^4J_{C,F}$ = 2.7 Hz, C2$_{C6}$-OFc2), 137.0 (dt, $^3J_{C,F}$ = 11.5 Hz, $^2J_{C,F}$ = 2.7 Hz, C4$_{C6}$-OFc1), 142.1 (ddd, $^1J_{C,F}$ = 249.7 Hz, $^3J_{C,F}$ = 12.6 Hz, $^4J_{C,F}$ = 4.2 Hz, C3), 142.7 (ddd, $^1J_{C,F}$ = 250.4 Hz, $^3J_{C,F}$ = 13.0 Hz, $^2J_{C,F}$ = 5.1 Hz, C5), 146.4 (dt, $^1J_{C,F}$ = 250.1 Hz, $^{2,4}J_{C,F}$ = 4.1 Hz, C6). ^{19}F NMR ($CDCl_3$, δ): –154.5 (dd, $^3J_{F,F}$ = 22.4 Hz, $^5J_{F,F}$ = 7.2 Hz, 1 F, F6), –153.1 (d, $^3J_{F,F}$ = 22.4 Hz, 1 F, F5), –145.8 (d, $^5J_{F,F}$ = 7.2 Hz, 1 F, F3). HRMS (ESI-TOF, m/z): calcd for $C_{36}H_{27}F_3Fe_3O_3$ 731.9957, found 731.9949 $[M]^+$.

1,2,4,5-Tetrakis(ferrocenyloxy)-3,6-difluorobenzene (112d)

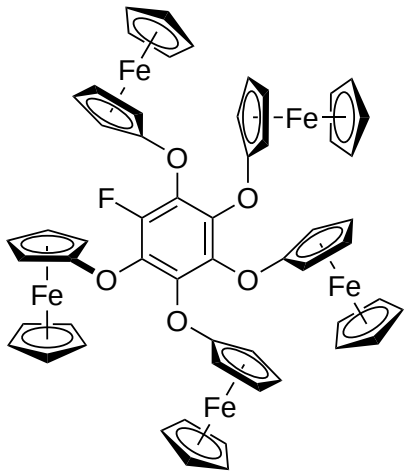


112d

Ferrocenol (**5**, 820 mg, 4.06 mmol), K_2CO_3 (1.20 g, 8.68 mmol) and 1,4-bis(ferrocenyloxy)-tetrafluorobenzene (**112b**, 250 mg, 0.45 mmol) were reacted in 1,3-dimethyl-2-imidazolidinone at 180 °C according to the general procedure described above. Purification was realized by column chromatography (silica, 4 · 20 cm column size) using hexane/dichloromethane mixtures as the eluents starting from 5/1 (v/v). As the first fraction, ferrocene (22 mg, 0.118 mmol, 3 % based on **5**) was eluted followed by **112d** using dichloromethane and **112e** (dichloromethane/ethyl acetate; ratio 4/1 (v/v)). After evaporation of all volatiles the compounds were obtained as orange solids.

1,2,4,5-Tetrakis(ferrocenyloxy)-3,6-difluorobenzene (**112d**). Yield: 21 mg (0.023 mmol, 5 % based on **112b**). ^{1}H NMR ($CDCl_3$, δ): 3.86 (pt, $^{3,4}J_{H,H}$ = 1.8 Hz, 8 H, C_5H_4), 4.22–4.23 (m, 28 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 57.9 (C_5H_4), 62.2 (C_5H_4), 69.4 (C_5H_5), 126.6 (C_{C5H4}-O), 129.8 (C_{C6}-O), the C-F multiplet could not be observed. ^{19}F NMR ($CDCl_3$, δ): –145.8. HRMS (ESI-TOF, m/z): calcd for $C_{46}H_{36}F_2Fe_4O_4$ 913.9978, found 914.0010 $[M]^+$.

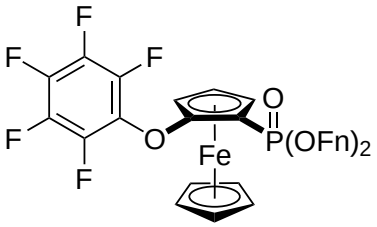
Pentakis(ferrocenyloxy)fluorobenzene (112e)



112e

Pentakis(ferrocenyloxy)fluorobenzene (**112e**). Yield: 27 mg (0.025 mmol, 6 % based on **112b**). ^{1}H NMR ($CDCl_3$, δ): 3.84 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 4 H, C_5H_4), 3.85 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 6 H, C_5H_4), 4.17 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 4 H, C_5H_4), 4.22–4.23 (m, 26 H, C_5H_4), 4.27 (s, 5 H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 57.5 (C_5H_4), 57.7 (C_5H_4), 57.9 (C_5H_4), 57.9 (C_5H_4), 60.00 (C_5H_4), 62.03 (C_5H_4), 62.17 (C_5H_4), 62.24 (C_5H_4), 69.32 (C_5H_5), 69.34 (C_5H_5), 69.35 (C_5H_5), 126.4 (C_{C5H4}-O), 126.52 (C_{C5H4}-O), 126.55 (C_{C5H4}-O), 126.6 (C_{C5H4}-O), 126.7 (C_{C5H4}-O), 136.8 (C_{C6}-O), 136.9 (C_{C6}-O), 141.62 (C_{C6}-O), 141.64 (C_{C6}-O), the C-F doublet could not be observed. ^{19}F NMR ($CDCl_3$, δ): –143.8. HRMS (ESI-TOF, m/z): calcd for $C_{56}H_{45}FFe_5O_5$ 1096.0001, found 1095.9975 $[M]^+$.

Bis((1*R*)-α-fenchyl) (2-(Pentafluorophenoxy)ferrocenyl)phosphonate (113)



113

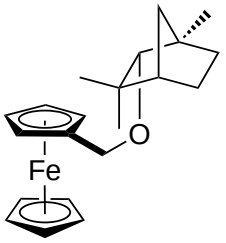
In a Schlenk tube, LiTMP (118 mg, 0.8 mmol) was suspended in 10 mL of hexane and TMEDA (0.12 mL, 0.8 mmol) was added. After stirring for 10 min, bis((1*R*)-α-fenchyl) ferrocenyl phosphate (**30e**, 220 mg, 0.39 mmol) was added in a single portion and the mixture was stirred overnight at ambient temperature. Afterwards, 2 mL of DMF and hexafluorobenzene (**108d**) (0.15 mL, 1.2 mmol) were added. The reaction mixture was heated to 70 °C and stirred for 18 h at this temperature. All volatiles were removed in vacuum and the residue was dissolved in diethyl ether (50 mL) and washed with brine (400 mL). The aqueous phase was extracted again with diethyl ether (3·50 mL). All volatiles of the combined organic extracts were removed in vacuum. Purification was realized by column chromatography (silica, 2.5 · 15 cm column size) using dichloromethane as the eluent. The title compound **113** was obtained as an dark orange oil with a *de* of 52 %, based on fitted integrals of the ^{31}P{^{1}H} NMR spectra.

Yield: 56 mg (0.078 mmol, 20 % based on **30e**). The intensities result of the approximated sum of both diastereomers in the ^{1}H NMR spectrum. In the ^{13}C{^{1}H} NMR spectrum solely the signals of the major diastereomer are reported, expect otherwise noted. ^{1}H NMR ($CDCl_3$, δ): 0.85–1.21 (m, 24.5 H, $C_{10}H_{17}$), 1.42–1.49 (m, 1.5 H, $C_{10}H_{17}$), 1.51–1.53 (m, 2 H, $C_{10}H_{17}$), 1.68–1.96 (m, 4 H, $C_{10}H_{17}$), 3.78–3.99 (m, 1.5 H, C_5H_3, $C_{10}H_{17}$), 4.02 (dd, $J_{H,H}$ = 2.6 Hz, 0.85 H, C_5H_3), 4.05–4.11 (m, 1.6 H, C_5H_3, $C_{10}H_{17}$), 4.29–4.33 (m, 1.05 H, C_5H_3, $C_{10}H_{17}$), 4.41 (m, 5 H, C_5H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.2 (CH_3), 19.6 (CH_3), 25.8 (C5/C6), 25.9 (C5/C6), 26.0 (C5/C6), 26.1 (C5/C6), 29.7 (CH_3), 29.8 (CH_3), 39.1 (d, $^{3}J_{C,P}$ = 2.3 Hz, C3),

39.6 (d, $^3J_{C,P}$ = 2.1 Hz, C3), 41.0 (C7), 41.1 (C7), 47.9 (C4), 48.1 (C4), 49.2 (d, $^3J_{C,P}$ = 4.5 Hz, C1), 49.3 (d, $^3J_{C,P}$ = 3.9 Hz, C1), 57.2 (d, $^1J_{C,P}$ = 217.6 Hz, C-P), 57.6 (d, $J_{C,P}$ = 9.9 Hz, C_5H_3), 63.7 (d, $J_{C,P}$ = 13.4 Hz, C_5H_3), 68.0 (d, $J_{C,P}$ = 12.2 Hz, C_5H_3), 71.0 (C_5H_5), 88.1 (d, $^2J_{C,P}$ = 6.7 Hz, C2), 88.9 (d, $^2J_{C,P}$ = 6.9 Hz, C2), 127.3 (d, $^2J_{C,P}$ = 9.3 Hz, C_5H_3-O), 130.0–130.3 (C1$_{C6F5}$-O), 137.0–139.3 (C2,6-$_{C6F5}$), 137.7–140.0 (C4-$_{C6F5}$), 141.0–143.2 (C3,5-$_{C6F5}$). ^{19}F NMR ($CDCl_3$, δ): –161.8 – –161.6 (m, -161.6, F3/5), –159.4 (dt, J = 42.9 Hz, $^3J_{F,F}$ = 21.9 Hz, F4), –152.6 – –152.4 (m with the main coupling scheme to be a dd at -152.5; J = 48.6 Hz, $^3J_{F,F}$ = 18.0 Hz, F2/6). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 20.9 (ma), 21.6 (mi). HRMS (ESI-TOF, m/z): calcd for $C_{36}H_{42}F_5FeO_4P$ + H 721.2164, found 721.2125 $[M+H]^+$.

4.3.6 Reactions at Ferrocenylmethanols

(1*R*)-α-Fenchyloxymethylferrocene (124)

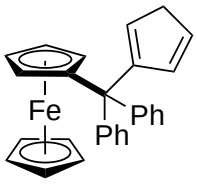


124

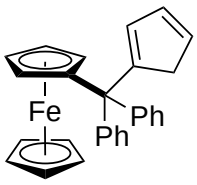
In a Schlenk tube, ferrocenylmethanol **118a** (2.017g, 9.335 mmol) was dissolved in THF (20 mL) and cooled to –50 °C followed by the dropwise addition of BuLi (4 mL, 10 mmol). Stirring was continued for 10 min and $ClP(O)(OFn)_2$ (**29e**, 3.65 g, 9.39 mmol) was added with a pasteur pipette. The mixture was allowed to warm to ambient temperature and stirred for 18 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 4.5 · 22 cm column size) using hexane for the elution of methylferrocene[212] (**123**, 50 mg, 0.25 mmol, 3 % based on **118a**) and **124**, followed by a 1:1 hexane/dichloromethane (v/v) mixture giving bis(ferrocenylmethyl)ether[393] (**122a**, 886 mg, 2.14 mmol, 46 % based on **118a**) and **118a** (242 mg, 1.12 mmol, 12 % based on **118a**). After evaporation of all volatiles in vacuum **124** was obtained as an orange solid. Crystals suitable for single-crystal X-ray diffraction analysis were obtained from boiling hexane solutions containing **124**.

Yield: 188 mg (0.534 mmol, 6 % based on **118a**). Anal. calcd for $C_{21}H_{28}FeO \cdot 1/8\ CH_2Cl_2$ (352.29 · 1/8 94.93 g/mol): C, 69.92; H, 7.85. Found: C, 69.59; H, 7.93. Mp.: 157 °C. ^{1}H NMR ($CDCl_3$, δ): 0.92 (s, 3 H, C(CH_3)$_2$), 0.96 (tdd, $^3J_{H,H}$ = 11.9 Hz, $J_{H,H}$ = 2.8 Hz, $J_{H,H}$ = 1.6 Hz, 1 H, H5/6), 1.01 (s, 3 H, C(CH_3)$_2$), 1.05–1.08 (m, 4 H, C1(CH_3), H7), 1.38 (tdd, $^3J_{H,H}$ = 12.4 Hz, $J_{H,H}$ = 5.8 Hz, $J_{H,H}$ = 4.1 Hz, 1 H, H5/6), 1.44 (ddd, $^3J_{H,H}$ = 10.0 Hz, $J_{H,H}$ = 4.0 Hz, $J_{H,H}$ = 2.2 Hz, 1 H, H7), 1.62–1.63 (m, 1 H, H4), 1.69 (ddt, $^3J_{H,H}$ = 12.0 Hz, $J_{H,H}$ = 9.1 Hz, $J_{H,H}$ = 2.8 Hz, 1 H, C5/6), 2.98 (d, $J_{H,H}$ = 1.8 Hz, 1 H, H2), 4.12 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, 1 H, C_5H_4), 4.14 (s, 5 H, C_5H_5), 4.20 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, CH_2), 4.22 (pt, $^{3,4}J_{H,H}$ = 1.8 Hz, 1 H, C_5H_4), 4.31 (d, $^2J_{H,H}$ = 11.4 Hz, 1 H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 20.0 (C(CH$_3$)$_2$), 20.8 (C(CH$_3$)$_2$), 26.0 (C5/6), 26.2 (C5/6), 31.6 (C1(CH$_3$)), 39.4 (C3), 41.4 (C7), 48.8 (C4), 49.2 (C1), 67.8 (C_5H_4), 67.9 (C_5H_4), 68.4 (C_5H_5), 68.6 (C_5H_4), 68.7 (C_5H_4), 69.8 (CH_2), 85.4 (C_{C5H4}C), 92.1 (C2). HRMS (ESI-TOF, m/z): calcd for $C_{21}H_{28}FeO$ 352.1484, found 352.1479 $[M]^+$.

Cyclopenta-1,4-dien-1-yldiphenylferrocenylmethane (127a) and Cyclopenta-1,4-dien-2-yldiphenylferrocenylmethane (127b)



127a



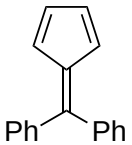
127b

In a Schlenk tube, ferrocenyldiphenylmethanol (**118e**, 1.00 g, 2.716 mmol) was dissolved in Et_2O (50 mL) and cooled to –50 °C followed by dropwise addition of BuLi (1.1 mL, 2.75 mmol). After stirring for 10 min and warming to 0 °C, diethyl chlorophosphate (0.40 mL, 2.77 mmol) was added in a single portion, resulting in an exothermic reaction. The mixture was allowed to warm to ambient temperature and stirring was continued for 18 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, $2 \cdot 14$ cm column size) using a 9:1 hexane/dichloromethane (v/v) mixture as the eluent. As the first fraction, 6,6'-diphenylfulvene (**126**, 155 mg, 0.637 mmol, 25 % based on **118e**) was eluted followed by **127**. They were obtained as an orange oil (**126**) and solid (**127**) after removal of all volatiles in vacuum. Compound **127** was obtained as a time dependent (vide supra) mixture of the tautomeric forms **127a** and **127b**.

Yield: 251 mg (0.603 mmol, 22 % based on **118e**). Anal. calcd for $C_{28}H_{24}Fe$ (416.34 g/mol): C, 80.78; H, 5.81. Found: C, 80.32; H, 5.86. Mp.: 143 °C. HRMS (ESI-TOF, m/z): calcd for $C_{28}H_{24}Fe$ 416.1227 416.1187, found [M]$^+$. **127a**: ^{1}H NMR ($CDCl_3$, δ): 3.05–3.06 (m, 2 H, CH_2), 3.98 (m, 7 H, C_5H_5, C_5H_4), 1.20 (m, 2 H, C_5H_4), 5.72–5.74 (m, 1 H, CH), 6.43–6.51 (m, 1 H, CH), 6.85–6.86 (m, 1 H, CH), 7.14–7.19 (m, 4 H, C_6H_5), 7.20–7.25 (m, 6 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 40.1 (CH_2), 55.1 (^qC), 67.6–67.7 (C_5H_4), 69.7–69.9 (C_5H_5), 70.9–71.1 (C_5H_4), 97.4–97.5 ($^qC_5H_4$, HMBC), 126.1 ($C4_{C6H5}$), 127.1 (C_6H_5), 129.7 (C_6H_5), 130.1 (CH), 131.7 (CH), 136.4 (CH), 147.6 ($C1_{C6H5}$), 152.9 ($^qC_{C5H5}$–^qC).

127b: ^{1}H NMR ($CDCl_3$, δ): 3.33 (m, 2 H, CH_2), 3.82 (pt, $^{3,4}J_{H,H} = 1.7$ Hz, 2 H, C_5H_4), 4.07 (s, 5 H, C_5H_5), 4.19–4.21 (m, 2 H, C_5H_4), 6.21 (dd, $J_{H,H} = 2.1$ Hz, $J_{H,H} = 1.2$ Hz, 1 H, CH), 6.43–6.51 (m, 2 H, CH), 7.04–7.06 (s, 4 H, C_6H_5), 7.20–7.25 (m, 6 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 43.9 (CH_2), 56.4 (^qC), 67.3 (C_5H_4), 69.2 (C_5H_5), 71.2 (C_5H_4), 97.3 ($^qC_5H_4$), 126.2 ($C4_{C6H5}$), 127.1 (C_6H_5), 129.6 (C_6H_5), 130.9 (CH), 131.3 (CH), 132.3 (CH), 147.7 ($C1_{C6H5}$), 155.0 ($^qC_{C5H5}$–^qC).

6,6-Diphenylfulvene (126)

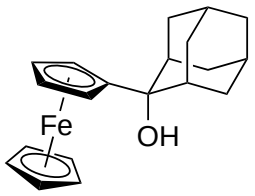


126

The title compound was obtained within the synthesis of **127a**,**b** by reacting ferrocenyldiphenylmethanol (**118e**, 1.00 g, 2.716 mmol), BuLi (1.1 mL, 2.75 mmol) and diethyl chlorophosphate (0.40 mL, 2.77 mmol). The spectroscopic data are in agreement with those reported in literature.[394]

Yellow Solid. Yield: 155 mg (0.637 mmol, 25 % based on **118e**). ^{1}H NMR ($CDCl_3$, δ): 6.32–6.34 (m, 2 H, CH), 6.62–6.64 (m, 2 H, CH), 7.33–7.36 (m, 4 H, C_6H_5), 7.37–7.42 (m, 6 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 124.4 (CH), 127.7 (C_6H_5), 128.7 ($C4_{C6H5}$), 132.1 (C_6H_5), 132.3 (CH), 141.3, 143.9, 152.0.

2-Ferrocenyl-2-adamantanol (129)

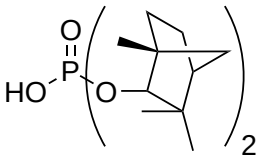


129

In a Schlenk tube, ferrocene (**1**, 2.00 g, 10.75 mmol) and KO^{t}Bu (163 mg, 1.45 mmol) were dissolved in 50 mL of THF and cooled to –80 °C. Afterwards, ^{t}BuLi (5.7 mL, 10.83 mmol) was dropwise added, the mixture was stirred for 30 min at this temperature followed by the addition of 2-adamantanone (1.776 g, 11.82 mmol). The mixture was allowed to warm to ambient temperature and stirred for additional 18 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, $4 \cdot 14$ cm column size) using hexane for the removal of ferrocene followed by dichloromethane for the elution of **129**. After removal of all volatiles in vacuum, compound **129** was obtained as an orange solid.

Yield: 2.635 g (7.84 mmol, 73 % based on **1**). Anal. calcd for $C_{20}H_{24}FeO \cdot 1/6\ C_6H_{14}$ ($366.25 \cdot 1/6$ 86.18 g/mol): C, 71.94; H, 7.57. Found: C, 71.98; H, 7.33. Mp.: 114 °C. ^{1}H NMR ($CDCl_3$, δ): 1.58–1.60 (m, 1 H, H5/H7), 1.60–1.62 (m, 1 H, H5/H7), 1.63–1.72 (m, 7 H), 1.81–1.83 (m, 1 H, H5/7), 1.91–1.93 (m, 2 H, H1/3), 2.47–2.50 (m, 1 H, CH_2), 2.50–2.53 (m, 1 H, CH_2), 2.82 (s, 1 H, OH), 4.20 (pt, $^{3,4}J_{H,H} = 1.7$ Hz, 2 H, C_5H_4), 4.24 (s, 5 H, C_5H_5), 4.38 (pt, $^{3,4}J_{H,H} = 1.6$ Hz, 2 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 27.2 (C5/7), 27.2 (C5/7), 33.7 (C4/6/9/10), 35.3 (C4/6/9/10), 38.0 (C8), 38.8 (C1/3), 67.2 (C_5H_4), 67.7 (C_5H_4), 68.2 (C_5H_5), 72.0 (C2), 102.3 ($^qC_5H_4$). UV/Vis (in nm (ϵ in L mol^{-1} cm^{-1}), CH_2Cl_2): 329 (66), 447 (121). HRMS (ESI-TOF, m/z): calcd for $C_{20}H_{24}FeO$ 336.11711, found 336.1170 $[M]^+$.

Bis((1*R*)-α-fenchyl) Phosphate (121a)

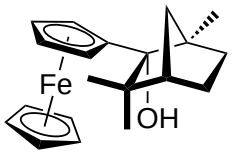


121a

The compound has ,*e.g.*, been obtained by the following reaction. Alcohol **129** (200 mg, 0.546 mmol) was dissolved in 20 mL of DMF. The solution was cooled to –30 °C followed by the dropwise addition of BuLi (0.22 mL, 0.546 mmol). After stirring for 10 min, the reaction mixture was allowed to warm to ambient temperature followed by the dropwise addition of chlorophosphate **29e** (215 mg, 0.55 mmol). The reaction mixture was heated to 90 °C for 4 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, $4 \cdot 23$ cm column size) using a 8:2 dichloromethane/ethyl acetate mixture (v/v) as the eluent. The compound was obtained as a colorless oil.

Yield: 116 mg (295 mmol, 54 % based on **129**). ^{1}H NMR ($CDCl_3$, δ): 0.92–1.21 (m, 22 H), 1.38–1.44 (m, 2 H), 1.48–1.52 (m, 2 H), 1.65–1.73 (m, 6 H), 4.04–4.06 (m, 1 H, H2), 4.14–4.16 (m, 1 H, H2). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.2 (CH_3), 19.4 (CH_3), 20.86 (CH_3), 20.94 (CH_3), 25.63 (CH_2), 25.66 (CH_2), 25.83 (CH_2), 25.87 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 39.5, 40.8 (CH_2), 40.9 (CH_2), 47.9 (CH), 48.0 (CH), 49.26, 49.29, 49.31, 91.1 (t, $J = 3.2$ Hz, C2), 91.5 (t, $J = 3.3$ Hz, C2). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –11.7. HRMS (ESI-TOF, m/z): calcd for $C_{20}H_{34}O_4P$ + Na 393.2165, found 393.2186 $[M+Na]^+$.

(1*R*,2*R*,4*S*)-2-Ferrocenylfenchole (130a)

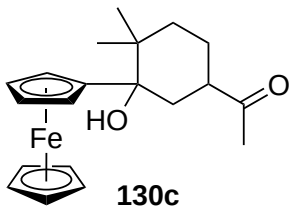


130a

In a Schlenk tube ferrocene (**1**, 2.00 g, 10.75 mmol) and KO^{t}Bu (163 mg, 1.45 mmol) were dissolved in 50 mL of THF and cooled to –80 °C. Afterwards, ^{t}BuLi (5.7 mL, 10.83 mmol) was dropwise added and the mixture was stirred for 30 min at this temperature followed by the addition of (1*R*)-fenchone (18 mL, 11.23 mmol). The mixture was allowed to warm to ambient temperature and stirred for additional 18 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 4 · 10 cm column size) using hexane to elute the excess of **1**, followed by a 30:1:0.1 hexane/diethyl ether/triethylamine (*v*/*v*/*v*) mixture as the eluent for **130a** and **130c**. After removal of all volatiles in vacuum, compound **130a** was obtained as an orange solid in a diastereomeric ratio of (2*R*):(2*S*) of 1:0.13. The spectroscopic data are in agreement with those reported in literature.[329]

Yield: 3.043 g (9.00 mmol, 84 % based on **1**). Anal. calcd for $C_{20}H_{26}FeO$ (338.28 g/mol): C, 71.01; H, 7.75. Found: C, 70.80; H, 8.10. Mp.: 92 °C. ^{1}H NMR ($CDCl_3$, δ): 0.46 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 1.05–1.08 (m, 1 H, CH_2), 1.09–1.12 (m, 1 H, CH_2), 1.32–1.40 (m, 1 H, CH_2), 1.42 (s, 3 H, CH_3), 1.62–1.63 (m, 1 H, CH), 1.79–1.84 (m, 1 H, CH_2), 2.29–2.35 (m, 1 H, CH_2), 4.05–4.06 (m, 1 H, C_5H_4), 4.10–4.12 (m, 1 H, C_5H_4), 4.13–4.15 (m, 1 H, C_5H_4), 4.17 (s, 5 H, C_5H_5), 4.21 (s, 0.65 H, C_5H_5 minor isomer), 4.26–4.28 (m, 1 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.4 (CH_3), 22.1 (CH_3), 25.3 (CH_2), 29.8 (CH_3), 31.9 (CH_2), 41.0 (CH_2), 44.7 (^{q}C), 49.8 (CH), 52.5 (^{q}C), 66.1 (C_5H_4), 66.6 (C_5H_4), 67.8 (C_5H_4), 68.6 (C_5H_5), 70.0 (C_5H_4), 80.5 (C2), 96.6 (^{q}C_5H_4). HRMS (ESI-TOF, *m*/*z*): calcd for $C_{20}H_{26}FeO$ 338.1328, found 338.1311 $[M]^+$.

1-(3-Ferrocenyl-3-hydroxy-4,4-dimethylcyclohexyl)ethanone (130c)



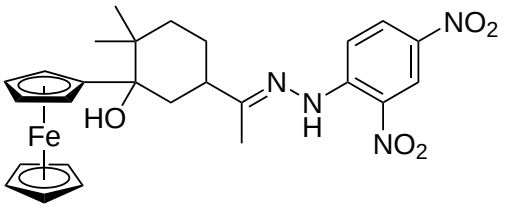
130c

The title compound was obtained within the synthesis of **130a**, by reacting ferrocene (**1**, 2.00 g, 10.75 mmol), KO^{t}Bu (163 mg, 1.45 mmol) and ^{t}BuLi (5.7 mL, 10.83 mmol). For Purification details see compound **130a**.

Orange Oil. Yield: 95 mg (0.268 mmol, 2.5 % based on **1**). ^{1}H NMR ($CDCl_3$, δ): 1.20 (s, 3 H, CH_3), 1.23 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.515 (ddt, $^2J_{H,H}$ = 12.3 Hz, $J_{H,H}$ = 9.4 Hz, $J_{H,H}$ = 8.6 Hz, 1 H, CH_2), 1.59–1.63 (m, 1 H, CH_2), 1.618 (s, 1 H, OH), 1.66 (dd, $^2J_{H,H}$ = 12.8 Hz, $^3J_{H,H}$ = 7.8 Hz, 1 H, CH–CH_2), 1.79 (dtdd, $^2J_{H,H}$ = 12.2 Hz, $^3J_{H,H}$ = 7.5 Hz, $J_{H,H}$ = 3.9 Hz, $J_{H,H}$ = 0.9 Hz, 1 H, CH_2), 2.15 (tt, $^3J_{H,H}$ = 10.2 Hz, $^3J_{H,H}$ = 7.8 Hz, CH), 2.25 (dd, $^2J_{H,H}$ = 12.8 Hz, $^3J_{H,H}$ = 10.4 Hz, CH–CH_2), 2.48 (ddd, $^3J_{H,H}$ = 12.5 Hz, $^3J_{H,H}$ = 8.6 Hz, $J_{H,H}$ = 4.1 Hz, CH_2), 4.19 (s, 5 H, C_5H_5), 4.47 (pt, $^{3,4}J_{H,H}$ = 8.6 Hz, 2 H, H3,4-C_5H_4), 4.80–4.81 (m, 1 H, H2,5-C_5H_4), 4.82–4.83 (m, 1 H, H2,5-C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 26.5 (CH_2), 27.3 (CH_3), 28.2 (CH_3), 28.6 (CH_3), 37.4 (CH_2), 38.3 (CH–CH_2), 49.5 (CH), 55.4 (^{q}C), 69.8 (C_5H_5), 70.8 (C_5H_4), 71.0 (C_5H_4), 71.27 (C_5H_4), 71.32 (C_5H_4), 71.6 (^{q}C), 76.7 (^{q}C_5H_4), 210.4 (C=O). IR data (KBr,

$\tilde{\nu}/cm^{-1}$): 3617 m (OH), 3490 m (br), 3101 m (CH_Ar), 2971 s, 2929 m, 2870 w, 1660 s (C=O), 1458 w, 1436 m, 1377 m, 1241 m. HRMS (ESI-TOF, m/z): calcd for $C_{20}H_{26}FeO_2$ 354.1282, found 354.1272 $[M]^+$.

5-(1-(2-(2,4-Dinitrophenyl)hydrazono)ethyl)-1-ferrocenyl-2,2-dimethylcyclohexanol (130d)

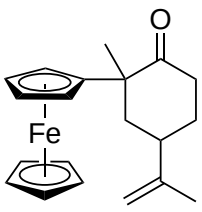


130d

Compound **130c** (95 mg, 0.281 mmol) and 2,4-dinitrophenylhydrazine (60 mg, 0.303 mmol) were dissolved in 5 mL of dichloromethane and one drop of aqueous HCl (w = 36 %) was added with a Pasteur pipette. The mixture was stirred for 12 h. Purification was realized by column chromatography (silica, 2.5 · 12 cm) using a 96:4 dichloromethane/ethyl acetate mixture (v/v) as the eluent. After removal of all volatiles compound **130d** was obtained as a yellow solid.

Yield: 45 mg (0.084 mmol, 30 % based on **1**). ^{1}H NMR ($CDCl_3$, δ): 1.22 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 1.26 (s, 1 H, OH), 1.44 (s, 3 H, CH_3), 1.59–1.64 (m, 1 H, CH_2), 1.77–1.90 (m, 3 H, CH_2), 2.08 (dd, $^3J_{H,H}$ = 12.6 Hz, $^3J_{H,H}$ = 11.0 Hz, 1 H, CH_2), 2.20–2.29 (m, 2 H, CH_2, CH), 4.29 (s, 5 H, C_5H_5), 4.58 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.75–4.76 (m, 1 H, C_5H_4), 4.77–4.78 (m, 1 H, C_5H_4), 8.07 (d, $^3J_{H,H}$ = 9.7 Hz, 1 H, H6), 8.34 (ddd, $^3J_{H,H}$ = 9.6 Hz, 4JH,H = 2.6 Hz, $^5J_{H,H}$ = 0.5 Hz, 1 H, H5), 9.17 (d, 4JH,H = 2.6 Hz, 1 H, H3), 11.76 (s, 1 H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 25.7 (CH_2), 28.1 (CH_3), 28.2 (CH_3), 28.4 (CH_3), 38.6 (CH_2), 40.3 (CH–CH_2), 49.1 (CH), 52.2 (^{q}C), 69.4 (C_5H_4), 69.4 (C_5H_4), 70.0 (C_5H_5), 70.68 (C_5H_4), 70.70 (C_5H_4), 72.0 (^{q}C), 72.5 (^{q}C), 117.1 (C6), 123, 6 (C3), 129.5 (^{q}C), 130.0 (C5), 137.8 (^{q}C), 145.1 (^{q}C), 162.3 (C=N).

2-Ferrocenyl-2-methyl-4-(prop-1-en-2-yl)cyclohexanone (131)



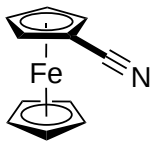
131

In a Schlenk tube, compound **130** (300 mg, 0.887 mmol) was dissolved in 20 mL of diethyl ether and cooled to –80 °C. Buli (0.35 mL, 0.875 mmol) was dropwise added and the mixture was slowly warmed to –30 °C followed by the dropwise addition of $ClP(O)(OEt)_2$ (0.13 mL 0.90 mmol). After stirring for 18 h at ambient temperature all volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 2.5 · 12 cm column size) using dichloromethane as the eluent, giving 131 as an orange solid.

Yield: 24 mg (0.071 mmol, 8 % based on **130**). ^{1}H NMR ($CDCl_3$, δ): 1.45 (s, 3 H, CH_3), 1.47–1.52 (m, 1 H, CH_2), 1.54–1.60 (m, 1 H, CH_2), 1.75* (s, 3 H, CH_3), 1.82 (ddd, $J_{H,H}$ = 12.9 Hz, $J_{H,H}$ = 6.8 Hz, $J_{H,H}$ = 1.0 Hz, 1 H, CH_2), 1.87–1.93 (m, 1 H, CH_2), 2.23 (dd, $J_{H,H}$ = 12.8 Hz, $J_{H,H}$ = 11.5 Hz, 1 H, CH_2), 2.626 (ddd, $^2J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 2.9 Hz, 1 H, CH_2), 2.64–2.68 (m, 1 H, CH), 4.18 (s, 5 H, C_5H_5), 4.47 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz,

4.70–4.72 (m, 1 H, $=CH_2$), 4.75–4.76 (m, 1 H, $=CH_2$), 4.78–4.79 (m, 1 H, C_5H_4), 4.80–4.81 (m, 1 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 21.2 (CH_3), 28.3 (CH_3), 31.0 (CH_2), 36.8 (CH_2), 42.6 (CH_2), 46.0 (CH), 54.9 (^qC), 69.8 (C_5H_5), 70.76 (C_5H_4), 70.83 (C_5H_4), 71.2 (C_5H_4), 71.3 (C_5H_4), 76.8 (^qC), 108.7 (CH_2), 147.8 (^qC), 209.8 (C=O). HRMS (ESI-TOF, m/z): calcd for $C_{20}H_{24}FeO$ 336.1171, found 336.1163 $[M]^+$.

Ferrocenylnitrile (133)

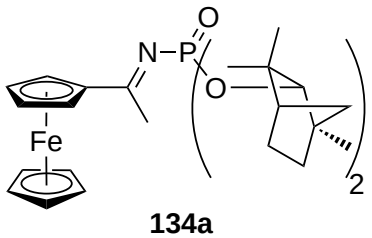


133

In a Schlenk tube, oxime **128a** (393 mg, 1.71 mmol) was dissolved in 50 mL of diethyl ether, cooled to –80 °C followed by the addition of ^{t}BuLi (0.9 mL, 1.71 mmol). After stirring for 30 min and warming to –30 °C, **29e** (667 mg, 1.715 mmol) was dropwise added with a Pasteur pipette. The mixture was allowed to warm to ambient temperature and stirred for 18 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, $2 \cdot 12$ cm column size) using a 1:3 hexane/dichloromethane (v/v) mixture as the eluent for removing **133**. By changing to a 95:5 dichloromethane/ethyl acetate (v/v) mixture **118f** (12 mg, 0.05 mmol, 3 %) and 12a (28 mg, 0.14 mmol, 8 % based on **132a**). The spectroscopic data are in agreement with those reported in literature.[293]

Yield: 260 mg (1.23 mmol, 72 % based on **132a**). ^{1}H NMR ($CDCl_3$, δ): 4.34 (s, 5 H, C_5H_5), 4.39 (pt, $^{3,4}J_{H,H}$ = 1.7 Hz, C_5H_4), 4.39 (pt, $^{3,4}J_{H,H}$ = 1.7 Hz, C_5H_4), 4.66 (pt, $^{3,4}J_{H,H}$ = 1.9 Hz, C_5H_4).

(*E*)-Bis((1*R*)-α-fenchyl) (1-Ferrocenylethylidene)phosphoramidate (134a)



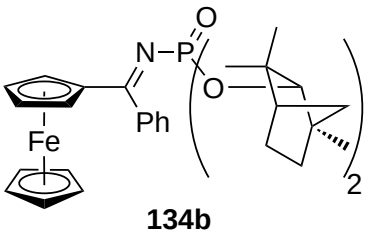
134a

In a Schlenk tube, ferrocenylnitrile (**133**, 230 mg, 1.09 mmol) was dissolved in 20 mL of THF and cooled to –80 °C. A 1.6 *M* solution of MeLi in Et_2O (0.68 mL, 1.09 mmol) was dropwise added. The mixture was allowed to warm to –30 °C, stirred for 30 min and **29e** (423 mg, 1.09 mmol) was added with a Pasteur pipette. After warming to ambient condition, stirring was continued for 18 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, $2 \cdot 12$ cm column size) using dichloromethane as the eluent for the removal of unreacted **133** (40 mg, 17 % based on **133**) followed by a 9:1 dichloromethane/ethyl acetate (v/v) mixture for **134a**. After removal of all volatiles, compound **134a** was obtained as a red oil in a 1 : 0.07 ratio of the (*E*)- to the (*Z*)-diastereomer.

Yield: 378 mg (0.65 mmol, 60 % based on **133**). Anal. calcd for $C_{32}H_{46}FeNO_3P \cdot 0.5\ H_2O$ ($579.53 \cdot 0.5$ 18.01 g/mol): C, 65.30; H, 8.05; N, 2.38. Found: C, 65.35; H, 7.91; N, 2.10. ^{1}H NMR ($CDCl_3$, δ): 0.97 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3), 1.03 (m, 2 H, H5/6, HSQC), 1.09 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 1.16 (m, 2 H, H7, HSQC), 1.17 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1-40–1.47 (m, 2 H, H5/6), 1.51–1.53 (m, 2 H, H7), 1.70–1.75 (m, 4 H, H5/6/7), 1.76–1.82 (m, 2 H, H5/6), 2.62 (d, $^4J_{H,P}$ = 2.3 Hz, 3 H, CH_3-C=N), 4.01 (dd, $^3J_{H,P}$ = 9.3 Hz, $J_{H,H}$ =

1.8 Hz, 1 H, H2), 4.04 (dd, $^3J_{H,P}$ = 9.6 Hz, $J_{H,H}$ = 1.7 Hz, 1 H, H2), 4.18 (s, 5 H, C_5H_5, ma), 4.20 (s, 5 H, C_5H_5, mi), 4.49–4.50 (m, 2 H, C_5H_4), 4.78 (dpt, $J_{H,H}$ = 2.5 Hz, $J_{H,H}$ = 1.4 Hz, 1 H, C_5H_4), 4.81 (dpt, $J_{H,H}$ = 2.6 Hz, $J_{H,H}$ = 1.4 Hz, 1 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.1 (CH_3), 19.8 (CH_3), 21.1 (CH_3), 21.2 (CH_3), 24.0 (d, $^3J_{C,P}$ = 10.8 Hz, CH_3-C=N), 25.9 (C5/6), 25.99 (C5/6), 26.02 (C5/6), 26.1 (C5/6), 29.9 (CH_3), 30.1 (CH_3), 39.46 (d, $^3J_{C,P}$ = 2.1 Hz, C3), 39.48 (d, $^3J_{C,P}$ = 1.9 Hz, C3), 41.0 (C7), 48.00 (C4), 48.06 (C4), 49.3 (d, $^3J_{C,P}$ = 4.7 Hz, C1), 49.4 (d, $^3J_{C,P}$ = 4.9 Hz, C1), 69.7 (d, $J_{C,P}$ = 1.0 Hz, C_5H_4), 69.8 (d, $J_{C,P}$ = 1.2 Hz, C_5H_4), 69.9 (C_5H_5), 72.16 (C_5H_4), 72.18 (C_5H_4), 82.9 (d, $^3J_{C,P}$ = 34.4 Hz, +C5H4), 89.18 (d, $^2J_{C,P}$ = 7.3 Hz, C2), 89.22 (d, $^2J_{C,P}$ = 7.7 Hz, C2), 186.2 (d, $^2J_{C,P}$ = 1.7 Hz, C=N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 4.05 (mi), 4.18 (ma). IR data (KBr, $\tilde{\nu}$/cm^{-1}): 3094 m, 2955 s, 2926 m, 2867 m, 1673 s, 1611 s (ν C=N), 1452 s, 1377 m, 1244 m, 1062 w, 1036 s, 1007 s, 929 m, 919 m, 819 m. UV/Vis (in nm (ϵ in L mol^{-1} cm^{-1}), CH_2Cl_2): 275 (7909), 464 (684). HRMS (ESI-TOF, m/z): calcd for $C_{32}H_{46}FeNO_3P$ + H 580.2638, found 580.2590 $[M+H]^+$.

(*E*)-Bis((1*R*)-α-fenchyl) (Ferrocenyl(phenyl)methylene)phosphoramidate (134b)



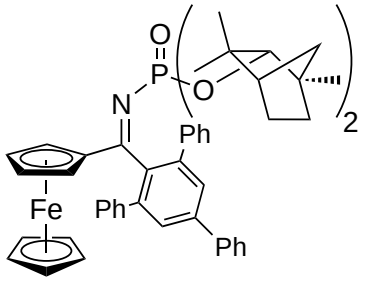
134b

In a Schlenk tube, ferrocene (**1**, 1,30 g; 7,00 mmol) and KO^{t}Bu (96 mg, 0.79 mmol) were dissolved in 50 mL of THF and cooled to –80 °C followed by the dropwise addition of ^{t}BuLi (3.35 mL, 6.35 mmol). The orange suspension was stirred for 30 min and benzonitrile (0.66 mL, 6.40 mmol) was dropwise added. The mixture was allowed to warm to ambient temperature and stirred until the solution turned dark-red. Afterwards, chlorophosphate **29e** (1.95 g, 5.01 mmol) was added with a Pasteur pipette and stirring was continued for 18 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 4 · 12 cm column size) using a 1:1 hexane/dichloromethane mixture (v/v) to elute the excess of **1** (421 mg, 2.27 mmol), followed by a 9:1 dichloromethane/ethyl acetate (v/v) mixture as the eluent for benzoylferrocene **128d**[390] (17 %) and a 4:1 dichloromethane/ethyl acetate (v/v) mixture for **134b**. After removal of all volatiles in vacuum, compound **134b** was obtained as a red solid in a 1 : 0.11 ratio of the (*E*)- to the (*Z*)-diastereomer.

Yield: 1.864 g (2.906 mmol, 58 % based on **29e**). Anal. calcd for $C_{37}H_{48}FeNO_3P \cdot 0.5\ H_2O$ (641.61 · 0.5 18.01 g/mol): C, 68.31; H, 7.59; N, 2.15. Found: C, 68.07; H, 7.58; N, 2.12. Mp.: 156 °C. ^1H NMR ($CDCl_3$, δ): 0.77–0.80 (m, 4 H, CH_3, $C_{10}H_{17}$), 0.85 (s, 3 H, CH_3), 0.88–0.99 (m, 1 H, $C_{10}H_{17}$), 1.06–1.13 (m, 14 H, CH_3, $C_{10}H_{17}$), 1.16–1.21 (m, 1 H, $C_{10}H_{17}$), 1.29–1.39 (m, 2 H, $C_{10}H_{17}$), 1.46–1.57 (m, 5 H, $C_{10}H_{17}$), 1.63–1.66 (m, 2 H, $C_{10}H_{17}$), 4.00 (dd, $^3J_{H,P}$ = 9.2 Hz, $J_{H,H}$ = 1.7 Hz, 1 H, H2), 4.10 (dd, $^3J_{H,P}$ = 9.5 Hz, $J_{H,H}$ = 1.7 Hz, 1 H, H2), 4.22 (s, 4.5 H, C_5H_5, ma), 4.23 (s, 0.5 H, C_5H_5, mi), 4.49–4.51 (m, 2 H, C_5H_4), 4.59–4.61 (m, 1 H, C_5H_4), 4.66–4.68 (m, 1 H, C_5H_4), 7.37–7.40 (m, 3 H, C_6H_5), 7.61–7.63 (m, 1.78 H, C_6H_5, ma), 7.66–7.68 (m, 0.22 H, C_6H_5, mi). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.5 (CH_3), 19.6 (CH_3), 20.8 (CH_3), 21.1 (CH_3), 25.6 (C5/6), 25.8 (C5/6), 25.9 (C5/6), 26.0 (C5/6), 29.9 (CH_3), 30.1 (CH_3), 39.2 (d, $^3J_{C,P}$ = 2.0 Hz, C3), 39.6 (d, $^3J_{C,P}$ = 2.4 Hz, C3), 40.99 (C7), 41.03 (C7), 47.95 (C4), 47.98 (C4), 49.1 (d, $^3J_{C,P}$ = 4.6 Hz, C1), 49.2 (d, $^3J_{C,P}$ = 4.9 Hz, C1),

70.1 (C_5H_5), 71.4 (C_5H_4), 71.6 (C_5H_4), 72.3 (C_5H_4), 72.4 (C_5H_4), 82.6 (d, $^3J_{C,P}$ = 2.0 Hz, C3), 82.6 (d, $^3J_{C,P}$ = 31.5 Hz, $^qC_5H_4$), 89.1 (d, $^2J_{C,P}$ = 8.3 Hz, C2), 89.2 (d, $^2J_{C,P}$ = 8.1 Hz, C1), 127.7 (C_6H_5), 127.6 (C_6H_5), 129.1 (C), 139.9 (d, $^3J_{C,P}$ = 11.6 Hz, C1$_{C6H5}$), 183.8 (d, $^2J_{C,P}$ = 2.5 Hz, C=N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 2.1 (1, ma), 2.3 (0.11, mi). IR data (KBr, $\tilde{\nu}$/cm^{-1}): 3093 w, 3047 w, 3029 w, 2945 s, 2920 s, 2868 s, 1608 s (ν N=C), 1596 w, 1577 m, 1447 m, 1438 w, 1376 m, 1358 w, 1336 w, 1293 m, 1274 w, 1243 s, 1055 s, 1008 s, 918 s. UV/Vis (in nm (ϵ in L mol^{-1} cm^{-1}), CH_2Cl_2): 362 (1652), 484 (1117). HRMS (ESI-TOF, m/z): calcd for $C_{37}H_{48}FeNO_3P$ + H 642.2795, found 642.2782 $[M+H]^+$.

(*E*)-Bis((1*R*)-α-fenchyl) (1-Ferrocenyl(2,4,6-triphenyl)methylene)phosphor amidate (134c)



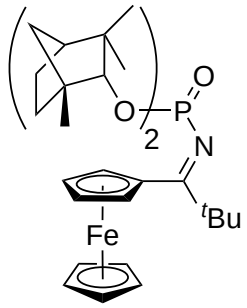
134c

According to the synthesis of **129**, ferrocene (**1**, 1.30 g, 6.99 mmol), KO^{t}Bu (96 mg, 0.79 mmol) and ^{t}BuLi (3.4 mL, 6.46 mmol) were reacted for the synthesis of **1**–Li. After stirring for 30 min at –80 °C 2,4,6-triphenylbenzonitrile (1.41 g, 4.25 mmol) was added in a single portion and the mixture was allowed to warm to ambient temperature. Stirring was continued until the color changed to deep red followed by the addition of **29e** (1.66 mg, 4.27 mmol) by using a Pasteur pipette. After stirring for 18 h at ambient temperature, all volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 4 · 16 cm column size) using a 1:1 hexane/dichloromethane mixture (v/v) to elute the excess of **1** followed by a 9:1 dichloromethane/ethyl acetate (v/v) mixture as the eluent, giving **134c** as a red solid and a mixture of two isomers in a ratio of 1:0.08. Crystals suitable for single crystal X-ray diffraction analysis were obtained by crystallization from ethanol.

Yield: 715 mg (0.822 mmol, 19 % based on the nitrile). Anal. calcd for $C_{55}H_{60}FeNO_3P$ (869.89 g/mol): C, 75.94; H, 6.95; N, 1.61. Found: C, 75.62; H, 7.22; N, 1.53. Mp.: 140–145 °C. ^1H NMR ($CDCl_3$, δ): 0.66 (s, 3 H, CH_3), 0.77–0.91 (m, 2 H, $C_{10}H_{17}$), 1.00–1.18 (m, 15 H, $C_{10}H_{17}$), 1.24 (s, 3 H, CH_3), 1.33–1.41 (m, 3 H, $C_{10}H_{17}$), 1.48–1.54 (m, 4 H, $C_{10}H_{17}$), 1.64–1.68 (m, 2 H, $C_{10}H_{17}$), 3.58 (s, 5 H, C_5H_5), 4.06–4.07 (m, 1 H, C_5H_4), 4.08–4.10 (m, 1 H, C_5H_4), 4.10–4.12 (m, 1 H, C_5H_4), 4.15–4.16 (m, 1 H, C_5H_4), 4.25–4.28 (m, 2 H, H2), 7.24–7.28 (m, 1 H), 7.31–7.38 (m, 6 H), 7.43–7.46 (m, 2 H), 7.48–7.49 (m, 1 H), 7.53–7.54 (m, 1 H), 7.63–7.65 (m, 4 H), 7.71–7.73 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.8 (CH_3), 19.9 (CH_3), 21.3 (CH_3), 21.9 (CH_3), 25.8 (CH_2), 25.96 (CH_2), 26.00 (CH_2), 29.9 (CH_3), 30.0 (CH_3), 39.4 (d, $^3J_{C,P}$ = 1.4 Hz, C3), 40.0 (d, $^3J_{C,P}$ = 0.7 Hz, C3), 41.1 (C7), 41.4 (C7), 47.8 (C4), 48.0 (C4), 49.3 (d, $^3J_{C,P}$ = 5.4 Hz, C1), 49.4 (d, $^3J_{C,P}$ = 5.1 Hz, C1), 69.4 (C_5H_5), 70.1 (C_5H_4), 70.3 (C_5H_4), 70.9 (C_5H_4), 71.6 (C_5H_4), 84.9 (d, $^3J_{C,P}$ = 29.5 Hz, $^iC_5H_4$), 89.8 (d, $^2J_{C,P}$ = 7.6 Hz, C2), 90.2 (d, $^2J_{C,P}$ = 8.3 Hz, C2), 127.1 (CH), 127.3 (CH), 127.4 (CH), 127.6 (CH), 127.8 (CH), 128.0 (CH), 128.6 (CH), 128.6 (CH), 128.8 (CH), 130.4 (CH), 130.4 (CH), 138.2 (^qC), 138.3 (^qC), 139.7 (^qC), 139.8 (^qC), 140.2 (^qC), 140.78 (^qC), 140.83 (^qC), 140.9 (^qC), 181.3 (d, $^2J_{C,P}$ = 2.7 Hz, C=N). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 0.9 (mi), 1.7 (ma). UV/Vis (in

nm (ϵ in $\mathrm{L\,mol^{-1}\,cm^{-1}}$), CH_2Cl_2): 372 (1281), 502 (1106). HRMS (ESI-TOF, m/z): calcd for $C_{55}H_{60}FeNO_3P + H$ 870.3734, found 870.3749 $[M+H]^+$.

tert-Butylferrocenylimino Bis((1*R*)-α-fenchyl) Phosphate (134d)



134d

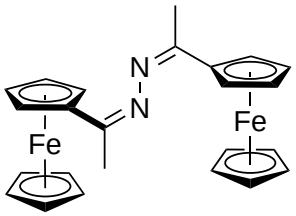
Path A: Reaction of **133** with ^{t}BuLi and **29e**: In a Schlenk tube, **133** (500 mg, 2.37 mmol) was dissolved in 30 mL of THF, cooled to –80 °C and ^{t}BuLi (1.25 mL, 2.38 mmol) was dropwise added. The mixture was allowed to warm to ambient temperature and stirred until the color changed to dark red. Afterwards, **29e** (921 mg, 2.37 mmol) was added with a Pasteur pipette and stirring was continued for 18 h. All volatiles were removed in vacuum. Purification was realized by column chromatography using the same conditions like in Path b, whereas the removal of ferrocene was not required. First **135** (311 mg, 0.58 mmol, 49 % based on **133**) was eluted, followed by **134d** as a 1:2 mixture with **121a** similar to path B (835 mg, 25 % of **134d** based on **133**).

Path B: Reaction of **1**–Li with *tert*-butylnitrile: According to the synthesis of **129**, ferrocene (**1**, 1.30 g, 6.99 mmol), KO^{t}Bu (96 mg, 0.79 mmol), ^{t}BuLi (3.4 mL, 6.46 mmol), *tert*-butylnitrile (0.70 g, 8.42 mmol) and **29e** (2.44 g, 6.29 mmol) were reacted. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, $2 \cdot 15$ cm column size) using hexane to elute the excess of **1** followed by a 1:4 hexane/dichloromethane (v/v) mixture as the eluent for **135**. The solvent was changed to dichloromethane and finally a 9:1 dichloromethane/ethyl acetate mixture was used for **128c** (430 mg, 1.59 mmol, 25 % based on ^{t}BuLi) and **134d**. After removal of all volatiles in vacuum compound **134d** was obtained as a red oil with a ratio of the *E*-/*Z*- isomers of 0.259:1 (59 % *de*). The two sets of signals in the ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR were assigned as major (ma) and minor (mi). The title compound occurred in a 1:2 mixture of the phosphate **134d** with the bis-(1*R*)-α-fenchyl phosphate **121a**-H. The signals of **121a**-H have been avoided for clarity.

Yield: 538 mg (1.62 mmol, 25 % based on ^{t}BuLi). Anal. calcd for $C_{35}H_{52}FeNO_3P \cdot 2\ C_{20}H_{35}O_4P \cdot CH_2Cl_2$ ($621.61 \cdot 2\ 370.46 \cdot 1\ 84.93$ g/mol): C, 63.06; H, 8.63; N, 0.97. Found: C, 62.88; H, 8.26; N, 1.02. ^{1}H NMR ($CDCl_3$, δ): 0.89 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3), 1.04 (s, 3 H, CH_3), 1.06 (s, 3 H, CH_3), 1.11 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 3.99 (dd, $^3J_{H,P}$ = 8.9 Hz, $J_{H,H}$ = 1.7 Hz, 1 H, H2), 4.03 (dd, $^3J_{H,P}$ = 9.0 Hz, $J_{H,H}$ = 1.7 Hz, 1 H mi, H2), 4.09 (dd, $^3J_{H,P}$ = 9.1 Hz, $J_{H,H}$ = 1.6 Hz, 1 H, H2), 4.22 (s, 5 H, C_5H_5), 4.46–4.48 (m, 2 H, C_5H_4), 5.23 (dpt, $J_{H,H}$ = 2.8 Hz, $J_{H,H}$ = 1.4 Hz, 1 H, C_5H_4), 5.25 (dpt, $J_{H,H}$ = 2.5 Hz, $J_{H,H}$ = 1.5 Hz, 1 H, C_5H_4). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.6 (CH_3), 19.89 (CH_3, mi), 19.92 (CH_3, mi), 25.92 (CH_2), 25.94 (CH_2), 26.0 (CH_2), 26.1 (CH_2), 29.8 (CH_3), 30.0 (CH_3), 30.9 ($C(CH_3)_3$), 31.5 ($C(CH_3)_3$, mi), 39.55 (C3), 39.57 (C3), 41.0 (C7), 41.1 (C7), 44.65 (d, $^3J_{C,P}$ = 21.0 Hz, $C(CH_3)_3$, mi), 44.69 (d, $^3J_{C,P}$ = 21.1 Hz, $C(CH_3)_3$), 47.9 (C4), 48.1 (C4), 49.33 (C1), 49.35 (C1), 49.39 (C1), 70.20 (C_5H_5, mi), 70.22 (C_5H_5), 70.85 (C_5H_4, mi), 70.87 (C_5H_4), 70.94 (C_5H_4), 72.4 (C_5H_4), 72.6 (C_5H_4, mi), 72.9 (C_5H_4), 78.2 (d, $^3J_{C,P}$ = 10.0 Hz,

$^{i}C_5H_4$), 78.6 (d, $^3J_{C,P}$ = 10.4 Hz, $^{i}C_5H_4$), 89.4 (d, $^2J_{C,P}$ = 8.2 Hz, C2, mi), 89.4 (d, $^2J_{C,P}$ = 8.1 Hz, C2), 89.7 (d, $^2J_{C,P}$ = 8.6 Hz, C2), 191.5 (d, $^2J_{C,P}$ = 4.4 Hz, C=N), 191.8 (d, $^2J_{C,P}$ = 4.7 Hz, C=N, mi). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –1.8 (ma), –1.3 (mi). IR data (NaCl/$CHCl_3$, $\tilde{v}$/cm^{-1}): 2961 s, 2874 s, 1715 m, 1585 m, 1468 m, 1286 m, 1027 s, 1017 s, 962 s. UV/Vis (in nm (ϵ in L mol^{-1} cm^{-1}), CH_2Cl_2): 281 (8211), 460 (724). HRMS (ESI-TOF, m/z): calcd for $C_{35}H_{52}FeNO_3P$ + H 622.3107, found 622.3078 $[M+H]^+$.

(1*Z*,2*Z*)-1,2-Bis(2,2-dimethyl-1-ferrocenylpropylidene)hydrazine (135)

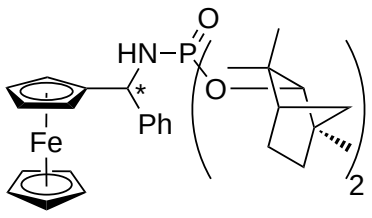


135

The compound was obtained within the synthesis of **134d** (see above) and obtained as a red solid in mixture with the other diastereomer in a ratio of 1 : 0.09.

Yield: 380 mg (0.71 mmol; 22 % based on ^{t}BuLi). Anal. calcd for $C_{30}H_{36}Fe_2N_2$ (536.32 g/mol): C, 67.19; H, 6.77; N, 5.22. Found: C, 66.99; H, 6.69; N, 5.08. Mp.: 148 °C. ^{1}H NMR ($CDCl_3$, δ): 1.54 (s, 9 H, CH_3), 4.14 (s, 5 H, C_5H_5), 4.30 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4), 4.79 (pt, $^{3,4}J_{H,H}$ = 2.0 Hz, 2 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 30.4 (CH_3), 39.7 (C(CH_3)3), 69.0 (C_5H_4), 69.4 (C_5H_5), 71.6 (C_5H_4), 75.9 ($^{q}C_5H_4$), 156.6 (C=N). IR data (NaCl/$CHCl_3$, $\tilde{v}$/cm^{-1}): 3098 w, 3007 m, 2990 s, 2952 m, 2932 w, 2903 w, 2867 w, 1770 w, 1692 w, 1650 w, 1559 s, 1474 s, 1455 m, 1390 s, 1367 s, 1104 s, 1069 s, 1004 m, 984 w, 884 m. UV/Vis (in nm (ϵ in L mol^{-1} cm^{-1}), CH_2Cl_2): 463 (883). HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{36}Fe_2N_2$ 536.1573, found 536.1585 $[M]^+$.

Bis((1*R*)-α-fenchyl) (Ferrocenyl(phenyl)methyl)phosphoramidate (136)



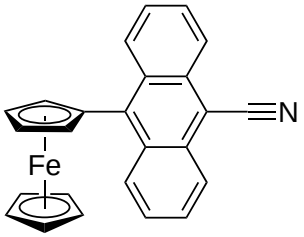
136

In a Schlenk tube, **134b** (125 mg, 0.196 mmol) was dissolved in 2 mL of THF. $NaBH_4$ (7.5 mg, 0.2 mmol) was carefully added and the mixture was stirred for at 50 °C for 18 h, whereby the color changed from red to yellow. The mixture was poured into an ice-water mixture and extracted three times with Et_2O (50 mL). The organic layers were combined, dried over $MgSO_4$ followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (alumina, 2 · 10 cm column size) using dichloromethane as the eluent (R_f = 0.60). After removal of all volatiles compound **136** was obtained as a yellow solid and as a ratio of three isomers of 1 : 0.86 : 0.23.

Yield: 90 mg (0.14 mmol, 72 % based on **134b**). Anal. calcd for $C_{37}H_{50}FeNO_3P$ (643.62 g/mol): C, 69.05; H, 7.83; N, 2.18. Found: C, 68.73; H, 8.00; N, 2.04. Mp.: 134–136 °C. ^{1}H NMR ($CDCl_3$, δ): 0.84–1.70 (m, 32 H), 3.12 (dd, $^2J_{H,P}$ = 9.2 Hz, $^3J_{H,H}$ = 9.2 Hz, NH), 3.18 (dd, $^2J_{H,P}$ = 9.7 Hz, $^3J_{H,H}$ = 8.1 Hz, NH), 3.27 (dd, $^2J_{H,P}$ = 9.4 Hz, $^3J_{H,H}$ = 9.4 Hz, NH), 3.63 (dd, $^3J_{H,P}$ = 9.2 Hz, $J_{H,H}$ = 1.7 Hz, H2), 3.66 (dd, $^3J_{H,P}$ = 9.6 Hz, $J_{H,H}$ = 1.7 Hz, H2), 3.87 (dd, $^3J_{H,P}$ = 9.5 Hz, $J_{H,H}$ = 1.6 Hz, H2), 3.89–3.96 (m, 2 H, H2, C_5H_4), 4.10–4.12 (m, 3 H, C_5H_4), 4.15/4.16 (s, 5 H, C_5H_5), 5.21 (dd, $^3J_{H,H}$ = 8.8 Hz, $^3J_{H,P}$ = 8.3 Hz,

CH), 5.25 (dd, $^{3}J_{H,H} = 9.8\,\text{Hz}$, $^{3}J_{H,P} = 8.2\,\text{Hz}$, CH), 7.22–7.27 (m, 1 H, C_6H_5), 7.30–7.40 (m, 4 H, C_6H_5). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 19.5 (CH_3), 19.60 (CH_3), 19.63 (CH_3), 20.7 (CH_3), 20.91 (CH_3), 20.92 (CH_3), 21.1 (CH_3), 21.2 (CH_3), 21.3 (CH_3), 25.6 (CH_2), 25.7 (CH_2), 25.8 (CH_2), 25.9 (CH_2), 25.97 (CH_2), 25.99 (CH_2), 26.01 (CH_2), 29.6 (CH_3), 29.7 (CH_3), 29.8 (CH_3), 29.8 (CH_3), 39.15 (d, $^{3}J_{C,P} = 2.0\,\text{Hz}$, C3), 39.24 (d, $^{3}J_{C,P} = 1.8\,\text{Hz}$, C3), 39.4 (d, $^{3}J_{C,P} = 1.3\,\text{Hz}$, C3), 39.6 (d, $^{3}J_{C,P} = 1.4\,\text{Hz}$, C3), 40.8 (C7), 40.89 (C7), 40.97 (C7), 41.00 (C7), 47.95 (C4), 47.97 (C4), 48.12 (C4), 48.15 (C4), 49.0 (d, $^{3}J_{C,P} = 4.1\,\text{Hz}$, C1), 49.1 (d, $^{3}J_{C,P} = 3.2\,\text{Hz}$, C1), 49.12 (C1), 49.13 (C1), 49.2 (C1), 54.9 (d, $^{2}J_{C,P} = 0.7\,\text{Hz}$, CH=N), 55.0 (CH=N), 55.1 (d, $^{2}J_{C,P} = 0.8\,\text{Hz}$, CH=N), 66.6 ($C_5H_4$), 66.7 ($C_5H_4$), 66.8 ($C_5H_4$), 67.5 ($C_5H_4$), 67.6 ($C_5H_4$), 67.68 ($C_5H_4$), 67.74 ($C_5H_4$), 67.86 ($C_5H_4$), 67.93 ($C_5H_4$), 68.1 ($C_5H_4$), 68-6 ($C_5H_5$), 68.7 ($C_5H_5$), 88.3 (d, $^{2}J_{C,P} = 6.2\,\text{Hz}$, C2), 88.4 (d, $^{2}J_{C,P} = 6.5\,\text{Hz}$, C2), 88.95 (d, $^{2}J_{C,P} = 6.4\,\text{Hz}$, C2), 88.98 (d, $^{2}J_{C,P} = 7.2\,\text{Hz}$, C2), 89.3 (d, $^{2}J_{C,P} = 7.0\,\text{Hz}$, C2), 93.5 (d, $^{3}J_{C,P} = 10.6\,\text{Hz}$, $^{i}C_5H_4$), 93.6 (d, $^{3}J_{C,P} = 10.9\,\text{Hz}$, $^{i}C_5H_4$), 93.8 (d, $^{3}J_{C,P} = 10.6\,\text{Hz}$, $^{i}C_5H_4$), 126.98 (C_6H_5), 127.02 (C_6H_5), 127.2 (C_6H_5), 127.3 (C_6H_5), 127.4 (C_6H_5), 127.91 (C_6H_5), 127.95 (C_6H_5), 128.03 (C_6H_5), 143.31 ($^{i}C_6H_5$), 143.33 ($^{i}C_6H_5$), 143.35 ($^{i}C_6H_5$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 6.9 (0.86), 7.3 (1.0), 7.4 (0.23). IR data (KBr, $\tilde{\nu}/\text{cm}^{-1}$): 3185 s ($\nu$ NH), 3101 w, 3062 w, 3026 w, 2951 s, 2926 m, 2870 m, 1734 w, 1708 vw, 1637 vw, 1601 w, 1455 s, 1374 m, 1361 w, 1328 w, 1309 w, 1234 s, 1225 s, 1108 m, 1053 s, 1030 s, 1004 s, 926 m, 816 m. UV/Vis (in nm (ϵ in $\text{L mol}^{-1}\,\text{cm}^{-1}$), CH_2Cl_2): 431 (125). HRMS (ESI-TOF, m/z): calcd for $C_{37}H_{50}FeNO_3P$ 643.2873, found 643.2882 $[M]^+$.

10-Ferrocenyl-9-carbonitrile (138)



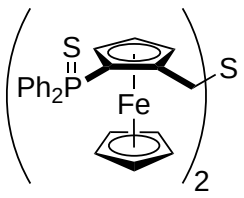
138

According to the synthesis of **129**, ferrocene (**1**, 1.30 g, 6.99 mmol), KO^{t}Bu (96 mg, 0.79 mmol) and ^{t}BuLi (3.4 mL, 6.46 mmol), anthracene-9-carbonitrile (1.29 g, 6.35 mmol) and **29e** (2.435 g, 6.26 mmol) were reacted. Purification was realized by column chromatography (silica, $2.5 \cdot 22$ cm column size) using hexane to remove the excess of ferrocene, followed by a 1:1 hexane/toluene mixture (v/v) giving the starting nitrile (82 mg) as the first, and **138** as the second fraction. It should be noted, that both anthracenes behave similar on the column. The success of the separation on the column could be observed by using UV-radiation showing the starting nitrile as a fluorescent band. After removal of all volatiles compound **138** was obtained as a black solid.

Yield: 207 mg (0.53 mmol, 8 % based on the nitrile). Anal. calcd for $C_{25}H_{17}FeN$ (387.25 g/mol): C, 77.54; H, 4.42; N, 3.62. Found: C, 77.16; H, 4.59; N, 3.84. Mp.: 218 °C. ^{1}H NMR ($CDCl_3$, δ): 4.22 (s, 5 H, C_5H_5), 4.66 (pt, $^{3,4}J_{H,H} = 1.8\,\text{Hz}$, 2 H, C_5H_4), 4.81 (pt, $^{3,4}J_{H,H} = 1.8\,\text{Hz}$, 2 H, C_5H_4), 7.56 (ddd, $^{3}J_{H,H} = 8.9\,\text{Hz}$, $^{3}J_{H,H} = 6.5\,\text{Hz}$, $^{4}J_{H,H} = 1.2\,\text{Hz}$, 2 H, H2/3), 7.67 (ddd, $^{3}J_{H,H} = 8.6\,\text{Hz}$, $^{3}J_{H,H} = 6.5\,\text{Hz}$, $^{4}J_{H,H} = 1.0\,\text{Hz}$, 2 H, H2/3), 8.45 (dd, $^{3}J_{H,H} = 8.7\,\text{Hz}$, $^{4}J_{H,H} = 1.1\,\text{Hz}$, 2 H, H4/5), 9.24 (dd, $^{3}J_{H,H} = 8.8\,\text{Hz}$, $^{4}J_{H,H} = 1.3\,\text{Hz}$, 2 H, H1/8). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ): 68.7 (C_5H_4), 70.2 (C_5H_5), 73.9 (C_5H_4), 82.9 ($^{i}C_5H_4$), 105.1 (C9), 118.0 (C≡N), 124.9 (CH), 125.6 (CH), 128.3 (CH), 128.6 (CH), 130.1 (^{q}C), 133.1

(^{q}C), 140.7 (^{q}C). UV/Vis (in nm (ϵ in L mol^{-1} cm^{-1}), CH_2Cl_2): 375 (5581), 408 (10230), 424 (9248), 536 (1850). HRMS (ESI-TOF, m/z): calcd for $C_{25}H_{17}FeN$ 387.0705, found 387.0689 $[M]^+$. IR data (KBr, $\tilde{\nu}$/cm^{-1}): 3094 w, 3081 w, 3046 w, 3020 w, 2955 w, 2919 w, 2851 w, 2208 s, 1621 w, 1556 s, 1442 s, 1273 m, 1104 m, 1036 m, 838 m, 767 vs, 653 m.

Bis((S_p)-(2-Thiodiphenylphosphino)ferrocenylmethyl)sulfane ((S_p,S_p)-149)



(S_p,S_p)-**149**

In a Schlenk tube, compound (S_p)-**143** (1.0 g, 2.4 mmol) was dissolved in 50 mL of dioxane followed by the addition of *p*-TsOH (1.37 g, 7.2 mmol), sulfur (100 mg, 3.12 mmol) and $MgSO_4$ (∼1 g). The mixture was heated to 90 °C and stirred for 24 h at this temperature followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, 2.5 · 12 cm column size) using a 1:9 hexane/dichloromethane (v/v) mixture as the eluent. After evaporation in vacuum, (S_p,S_p)-**149** was obtained as an orange solid.

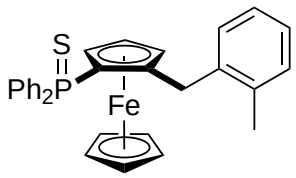
Yield: 0.619 mg (0.72 mmol, 90 % based on (S_p)-**143**). Anal. calcd for $C_{46}H_{40}Fe_2P_2S_3$ (862.63 g/mol): C, 64.04; H, 4.67. Found: C, 64.16; H, 4.94. Mp.: 115 °C. ^{1}H NMR ($CDCl_3$, δ): 3.72 (d, $^2J_{H,H}$ = 13.5 Hz, 2 H, CH_2), 3.72–3.73 (m, 2 H, C_5H_3), 3.91(d, $^2J_{H,H}$ = 13.7 Hz, 2 H, CH_2) 4.22–4.23 (m, 2 H, C_5H_3), 4.30 (s, 10 H, C_5H_5), 4.46–4.47 (m, 2 H, C_5H_3), 7.33–7.36 (m, 4 H, C_6H_5), 7.41–7.47 (m, 6 H, C_6H_5), 7.48–7.52 (m, 2 H, C_6H_5),7.58–7.62 (m, 4 H, C_6H_5), 7.76–7.80 (m, 4 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 31.2 (CH_2), 68.8 (d, $J_{P,C}$ = 10.4 Hz, C_5H_3), 70.8 (C_5H_5), 73.3 (d, $J_{P,C}$ = 9.3 Hz, C_5H_3) 73.6 (d, $^1J_{C,P}$ = 95.1 Hz, C_{C5H3}–P), 74.2 (d, $J_{C,P}$ = 12.7 Hz, C_5H_3), 89.8 (d, $^2J_{C,P}$ = 11.9 Hz, C_{C5H3}–C), 127.9 (d, $^2J_{C,P}$ = 12.4 Hz, *o*-C_6H_5), 128.1 (d, $^2J_{C,P}$ = 12.5 Hz, *o*-C_6H_5), 131.0 (d, $^4J_{C,P}$ = 2.9 Hz, *p*-C_6H_5), 131.1 (d, $^4J_{C,P}$ = 2.8 Hz, *p*-C_6H_5), 131.7 (d, $^3J_{C,P}$ = 11.1 Hz, *m*-C_6H_5), 131.8 (d, $^3J_{C,P}$ = 11.1 Hz, *m*-C_6H_5), 133.5 (d, $^1J_{C,P}$ = 86.0 Hz, C_{C6H5}–P), 134.6 (d, $^1J_{C,P}$ = 87 Hz, C_{C6H5}–P). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 41.7. HRMS (ESI-TOF, m/z): calcd for $C_{46}H_{40}Fe_2P_2S_3$ + Na 885.0360, found 885.0330 $[M+Na]^+$.

(S_p)-2-(2-/3-/4-Methylphenylmethyl)-1-(thiodiphenylphosphino)ferrocene ((S_p)-150a/b/c)

In a Schlenk tube, compound (S_p)-**143** (1.0 g, 2.4 mmol) was dissolved in 70 mL of toluene followed by the addition of *p*-TsOH (1.37 g, 7.2 mmol), sulfur (100 mg, 3.12 mmol) and $MgSO_4$ (∼1 g). The mixture was heated to 90 °C and stirred for 24 h at this temperature followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, 2.5 · 12 cm column size) using a 7:3 hexane/dichloromethane (v/v) mixture as the eluent. After evaporation in vacuum, (S_p)-**150** was obtained as an orange solid and as a 2 : 1 : 6 mixture of of the *ortho*- ((S_p)-**150a**)/ *meta*- ((S_p)-**150b**)/ *para*-Isomer ((S_p)-**150c**). The mixture could not further be purified. The yields of each isomer are based on the ratios of the integrals in the NMR spectra.

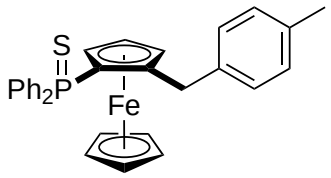
Yield: 862 mg (1.7 mmol, 71 % based on (S_p)-**143**). Anal. calcd for $C_{30}H_{27}FePS$

(506.42 g/mol): C, 71.15; H, 5.37. Found: C, 70.25; H, 6.13 (best match). Mp.: 135 °C. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{27}FePS$ 506.0915, found 506.0901 $[M]^+$.



(S_p)-**150a**

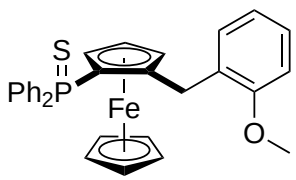
(S_p)-**150a**: Yield: 192 mg (0.38 mmol, 16 % based on (S_p)-**143**). ^{1}H NMR ($CDCl_3$, δ): 2.11 (s, 3 H, CH_3), 3.74–3.76 (m, 1 H, C_5H_3), 3.89 (d, $^2J_{H,H}$ = 16.3 Hz, 1 H, CH_2), 4.03 (d, $^2J_{H,H}$ = 16.3 Hz, 1 H, CH_2), 4.11–4.13 (m, 1 H, C_5H_3), 4.18–4.19 (m, 1 H, C_5H_3), 4.35 (s, 5 H, C_5H_5), 6.94–6.98 (m, 1 H, C_6H_4), 7.00–7.02 (m, 2 H, C_6H_4), 7.03–7.05 (m, 1 H, C_6H_4), 7.28–7.40 (m, 5 H, C_6H_5), 7.59–7.64 (m, 3 H, C_6H_5), 7.82–7.86 (m, 2 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.4 (CH_3), 32.0 (CH_2), 68.1 (d, $^2J_{C,P}$ = 10.4 Hz, C_5H_3), 70.8 (C_5H_5), 73.7 (d, $J_{C,P}$ = 9.8 Hz, C_5H_3), 74.2 (d, $J_{C,P}$ = 9.8 Hz, C_5H_3), 74.4 (d, $^1J_{C,P}$ = 57.6 Hz, C_{C5H3}–P), 92.1 (d, $J_{C,P}$ = 12.4 Hz, C_{C5H3}–C), 125.4 (C4-C_6H_5), 126.0 (C5-C_6H_5), 128.0 (d, $^4J_{C,P}$ = 3.9 Hz, p-C_6H_5), 128.2 (d, $^2J_{C,P}$ = 12.4 Hz, o-C_6H_5), 129.5 (C3-C_6H_5), 129.8 (C6-C_6H_4), 131.1 (d, $^4J_{C,P}$ = 3.0 Hz, p-C_6H_5), 131.8 (d, $^2J_{C,P}$ = 12.7 Hz, o-C_6H_5), 131.9 (d, $^3J_{C,P}$ = 10.6 Hz, m-C_6H_5), 133.4 (d, $^1J_{C,P}$ = 22.4 Hz, C_{C6H5}–P), 134.1 (d, $^1J_{C,P}$ = 22.5 Hz, C_{C6H4}–P), 136.3 (C_6H_4), 138.5 (C2-C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 41.8.



(S_p)-**150c**

(S_p)-**150c**: Yield: 575 mg (1.14 mmol, 47 % based on (S_p)-**143**). ^{1}H NMR ($CDCl_3$, δ): 2.20 (s, 3 H, CH_3), 3.65–3.66 (m, 1 H, C_5H_3), 3.88 (d, $^2J_{H,H}$ = 15.1 Hz, 1 H, CH_2), 4.19 (d, $^2J_{H,H}$ = 15.5 Hz, 1 H, CH_2), 4.21–4.22 (m, 1 H, C_5H_3), 4.33 (s, 5 H, C_5H_5), 4.39–4.40 (m, 1 H, C_5H_3), 6.80 (d, $^3J_{H,H}$ = 7.8 Hz, 2 H, H2-C_6H_4), 6.91 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H3-C_6H_4), 7.17–7.21 (m, 2 H, C_6H_5), 7.32–7.36 (m, 1 H, C_6H_5), 7.42–7.46 (m, 4 H, C_6H_5), 7.48–7.51 (m, 1 H, C_6H_5), 7.77–7.81 (m, 2 H, C6H5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 20.9 (CH_3), 33.7 (CH_2), 68.5 (d, $J_{C,P}$ = 10.4 Hz, C_5H_3), 70.7 (C_5H_5), 73.7 (d, $^1J_{C,P}$ = 95.3 Hz, C_{C5H3}–P), 73.6 (d, $J_{C,P}$ = 9.8 Hz, C_5H_3), 74.3 (d, $J_{C,P}$ = 13.0 Hz, C_5H_3), 93.3 (d, $^2J_{C,P}$ = 12.6 Hz, C_{C5H3}–C), 127.8 (d, $^3J_{C,P}$ = 3.3 Hz, m-C_6H_5), 127.9 (d, $^3J_{C,P}$ = 3.0 Hz, m-C_6H_5), 128.4 (C2-C_6H_4), 128.8 (C3-C_6H_4), 130.5 (d, $^4J_{C,P}$ = 3.0 Hz, p-C_6H_5), 131.0 (d, $^4J_{C,P}$ = 2.9 Hz, p-C_6H_5), 131.9 (d, $^2J_{C,P}$ = 10.6 Hz, o-C_6H_5), 132.0 (d, $^2J_{C,P}$ = 10.7 Hz, o-C_6H_5), 133.6 (d, $^1J_{C,P}$ = 52.2 Hz, C_{C6H5}–P), 134.3 (d, $^1J_{C,P}$ = 53.0 Hz, C_{C6H5}–P), 134.9 (C4-C_6H_4), 137.4 (C1-C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 42.0.

(S_p)-2-(2-Methoxyphenylmethyl)-1-(thiodiphenylphosphino)ferrocene ((S_p)-151a)



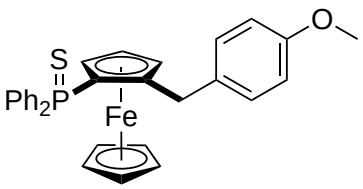
(S_p)-**151a**

In a Schlenk tube, compound (S_p)-**143** (200 mg, 0.48 mmol) was dissolved in 20 mL of anisole followed by the addition of p-TsOH (270 mg, 1.4 mmol) and $MgSO_4$ (∼1 g). The mixture was heated to 90 °C and stirred for 24 h at this temperature followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, 2.5 · 18 cm column size) using a 3:9

hexane/dichloromethane (v/v) mixture for eluting (S_p)-**151a** followed by dichloromethane for (S_p)-**151c**. Both compounds were obtained as orange solids after removal of all volatiles.

Yield: 114 mg (0.17 mmol, 36 % based on (S_p)-**143**). Anal. calcd for $C_{30}H_{27}FeOPS \cdot 1/6$ CH_2Cl_2 (522.42 · 1/6 84.93 g/mol): C, 67.53; H, 5.13. Found: C, 67.46; H, 5.44. Mp.: 107 °C. ^{1}H NMR ($CDCl_3$, δ): 3.67–3.68 (m, 1 H, C_5H_3), 3.76 (s, 3 H, OCH_3), 3.99 (d, $^2J_{H,H}$ = 15.2 Hz, 1 H, CH_2), 4.12 (d, $^2J_{H,H}$ = 15.2 Hz, 1 H, CH_2), 4.17–4.19 (m, 1 H, C_5H_3), 4.32 (s, 5 H, C_5H_5), 4.40–4.41 (m, 1 H, C_5H_3), 6.56 (td, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.0 Hz, 1 H, H4-C_6H_4), 6.74 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 1.1 Hz, 1 H, H6-C_6H_4), 6.96 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, H3-C_6H_4), 7.04 (td, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.7 Hz, 1 H, H5-C_6H_4), 7.26–7.29 (m, 2 H, C_6H_5), 7.36–7.40 (m, 1 H, C_6H_5), 7.43–7.52 (m, 3 H, C_6H_5), 7.55–7.59 (m, 2 H, C_6H_5), 7.80–7.85 (m, 2 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 28.5 (CH_2), 55.1 (OCH_3), 58.3 (d, $^3J_{C,P}$ = 10.6 Hz, C_5H_3), 70.7 (C_5H_5), 73.7 (d, $^1J_{C,P}$ = 95.6 Hz, C_{C5H3}–P), 73.9 (d, $J_{C,P}$ = 13.1 Hz, C_5H_3), 74.1 (d, $J_{C,P}$ = 9.8 Hz, C_5H_3), 92.7 (d, $^2J_{C,P}$ = 12.3 Hz, C_{C5H3}–C), 110.0 (C6-C_6H_4), 119.9 (C4-C_6H_4), 127.0 (C5-C_6H_4), 126.8 (d, $^2J_{C,P}$ = 8.0 Hz, *o*-C_6H_5), 127.9 (d, $^2J_{C,P}$ = 8.0 Hz, *o*-C_6H_5), 129.0 (C2-C_6H_4), 130.8 (C3-C_6H_4), 130.8 (d, $^4J_{C,P}$ = 2.9 Hz, *p*-C_6H_5), 131.0 (d, $^4J_{C,P}$ = 2.9 Hz, *p*-C_6H_5), 132.0 (d, $^3J_{C,P}$ = 6.4 Hz, *m*-C_6H_5), 132.1 (d, $^3J_{C,P}$ = 6.6 Hz, *m*-C_6H_5), 133.8 (d, $^1J_{C,P}$ = 75.5 Hz, C_{C6H5}–P), 134.5 (d, $^1J_{C,P}$ = 76.1 Hz, C_{C6H5}–P), 157.2 (C1-C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 42.2. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{27}FeOPS$ 522.0865, found 522.0845 $[M]^+$.

(S_p)-2-(4-Methoxyphenylmethyl)-1-(thiodiphenylphosphino)ferrocene ((S_p)-151b)



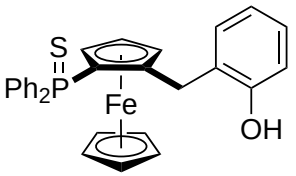
(S_p)-**151b**

The compound was obtained within the synthesis of (S_p)-**151a** by reacting (S_p)-**143** (200 mg, 0.48 mmol) and *p*-TsOH (270 mg, 1.4 mmol) in 20 mL of anisole. For purification detail see (S_p)-**151a**. Compound (S_p)-**151b** was obtained as an orange solid.

Yield: 117 mg (0.18 mmol, 37 % based on (S_p)-**143**). Anal. calcd for $C_{30}H_{27}FeOPS$ (522.42 g/mol): C, 68.97; H, 5.21. Found: C, 68.62; H, 5.21. Mp.: 196 °C. ^{1}H NMR ($CDCl_3$, δ): 3.64–3.65 (m, 1 H, C_5H_3), 3.69 (s, OCH_3), 3.83 (d, $^2J_{H,H}$ = 15.1 Hz, 1 H, CH_2), 4.23 (d, $^2J_{H,H}$ = 14.9 Hz, 1 H, CH_2), 4.21–4.23 (m, 1 H, C_5H_3), 4.33 (s, 5 H, C_5H_5), 4.40–4.41 (m, 1 H, C_5H_3), 6.52 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, H2-C_6H_4), 6.95 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, H3-C_6H_4), 7.17–7.21 (m, 2 H, C_6H_5), 7.31–7.35 (m, 1 H, C_6H_5), 7.40–7.46 (m, 4 H, C_6H_5), 7.47–7.51 (m, 1 H, C_6H_5), 7.76–7.82 (m, 2 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 33.2 (CH_2), 55.1 (OCH_3), 68.5 (d, $^3J_{C,P}$ = 10.5 Hz, C_5H_3), 70.7 (C_5H_5), 73.6 (d, $^1J_{C,P}$ = 95.4 Hz, C_{C5H3}–P), 73.6 (d, $^3J_{C,P}$ = 9.7 Hz, C_5H_3), 74.4 (d, $^2J_{C,P}$ = 12.8 Hz, C_5H_3), 93.5 (d, $^2J_{C,P}$ = 12.5 Hz, C_{C5H3}–C), 113.2 (C2-C_6H_4), 127.8 (d, $^3J_{C,P}$ = 4.5 Hz, *m*-C_6H_5), 127.9 (d, $^3J_{C,P}$ = 4.3 Hz, *m*-C_6H_5), 129.9 (C3-C_6H_4), 130.7 (d, $^4J_{C,P}$ = 2.9 Hz, *p*-C_6H_5), 131.1 (d, $^4J_{C,P}$ = 2.9 Hz, *p*-C_6H_5), 131.9 (d, $^2J_{C,P}$ = 10.7 Hz, *o*-C_6H_5), 132.0 (d, $^2J_{C,P}$ = 10.8 Hz, *o*-C_6H_5), 132.8 (C4-C_6H_4), 133.6 (d, $^1J_{C,P}$ = 60.9 Hz, C_{C6H5}–P), 134.3 (d, $^1J_{C,P}$ = 61.8 Hz,

C_{C6H5}–P), 157.5 (C1-C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 42.0. For HRMS see (S_p)-**151a**.

(S_p)-(Diphenylphosphino)-2-(2-hydroxyphenylmethyl)ferrocene ((S_p)-152)

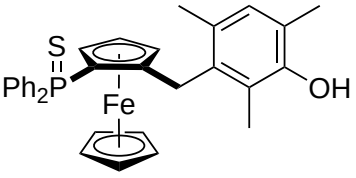


(S_p)-**152**

In a Schlenk tube, compound (S_p)-**143** (200 mg, 0.463 mmol) and phenol (436 mg, 4.63 mmol) was dissolved in 10 mL of dichloromethane followed by the addition of *p*-TsOH (264 mg, 1.53 mmol). The mixture was heated to 50 °C and stirred for 72 h at this temperature followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, $2.5 \cdot 18$ cm column size) using dichloromethane as the eluent, giving (S_p)-**152** as an orange solid.

Yield: 175 mg (0.344 mmol, 74 % based on (S_p)-**143**). Anal. calcd for $C_{29}H_{25}FeOPS \cdot 1/3$ C_6H_{14} ($508.39 \cdot 1/6$ 86.18 g/mol): C, 69.32; H, 5.57. Found: C, 69.30; H, 5.37. Mp.: 223 °C. ^1H NMR ($CDCl_3$, δ): 3.65 (dd, J = 2.4 Hz, J = 2.4 Hz, J = 1.5 Hz, 1 H, C_5H_3), 3.82 (d, $^2J_{H,H}$ = 15.3 Hz, 1 H, CH_2), 4.13 (d, $^2J_{H,H}$ = 15.3 Hz, 1 H, CH_2), 4.26 (s, 5 H, C_5H_5), 4.28–4.30 (m, 1 H, C_5H_3), 4.55 (ddd, J = 2.3 Hz, J = 2.3 Hz, J = 1.6 Hz, 1 H, C_5H_3), 6.59 (dd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 1.1 Hz, 1 H, H3-C_6H_4), 6.71 (td, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, H5-C_6H_4), 6.89 (s, 1 H, OH), 6.92 (td, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.7 Hz, 1 H, H4-C_6H_4), 7.02 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, H6-C_6H_4), 7.18–7.21 (m, 2 H, Ph), 7.30–7.34 (m, 1 H, Ph), 7.36–7.41 (m, 2 H, Ph), 7.45–7.49 (m, 2 H, Ph), 7.51–7.55 (m, 1 H, Ph), 7.76–7.80 (m, 2 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 27.4 (CH_2), 69.0 (d, $J_{C,P}$ = 10.5 Hz, C_5H_3), 70.8 (C_5H_5), 73.0 (d, $^1J_{C,P}$ = 95.8 Hz, C_{C5H3}–P), 73.6 (d, $J_{C,P}$ = 9.9 Hz, C_5H_3), 74.0 (d, $J_{C,P}$ = 12.9 Hz, C_5H_3), 92.7 (d, $^2J_{C,P}$ = 12.7 Hz, C_{C5H3}–CH_2), 117.2 (C3-C_6H_4), 120.1 (C5-C_6H_4), 126.6 (C1-C_6H_4), 127.5 (C4-C_6H_4), 128.0 (d, $^3J_{C,P}$ = 12.7 Hz, C3/5-Ph), 128.1 (d, $^3J_{C,P}$ = 12.5 Hz, C3/5-Ph), 130.1 (C6-C_6H_4), 131.2 (d, $^4J_{C,P}$ = 3.0 Hz, C4-Ph), 131.5 (d, $^4J_{C,P}$ = 2.9 Hz, C4-Ph), 131.7 (d, $^2J_{C,P}$ = 10.8 Hz, C2/6-Ph), 132.1 (d, $^2J_{C,P}$ = 10.9 Hz, C2/6-Ph), 132.4 (d, $^1J_{C,P}$ = 86.8 Hz, C1-Ph), 133.5 (d, $^1J_{C,P}$ = 86.9 Hz, C1-Ph), 153.2 (C2–OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 42.6. IR data (KBr, $\tilde{\nu}$/cm^{-1}): 3403 m (ν OH), 3069 w, 3049 w, 2955 m, 2919 s, 2848 m, 1710 w, 1580 m, 1484 s, 1432 s, 1260 w, 1208 m, 1166 m, 1101 s (ν C–O), 1043 w, 760 m, 715 s, 692 s, 643 m. HRMS (ESI-TOF, m/z): calcd for $C_{29}H_{25}FeOPS$ + H 509.0786, found 509.0743 $[M+H]^+$.

(S_p)-2-(3-Hydroxy-2,4,6-trimethylphenylmethyl)-1-thiodiphenylphosphino)-ferrocene (S_p)-153)



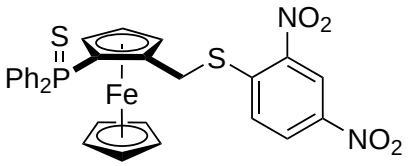
(S_p)-**153**

In a Schlenk tube, compound (S_p)-**143** (150 mg, 0.347 mmol) and trimethylphenol (473 mg, 3.47 mmol) was dissolved in 10 mL of dichloromethane followed by the addition of *p*-TsOH (178 mg, 1.04 mmol). The mixture was heated to 50 °C and stirred for 72 h at this temperature followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, $2.5 \cdot 18$ cm column size) using dichloromethane as the eluent.

After removal of all volatiles, compound (S_p)-**153** was obtained as an orange solid.

Yield: 173 mg (0.314 mmol, 90 % based on (S_p)-**143**). Anal. calcd for $C_{32}H_{31}FeOPS \cdot C_6H_{14}$ (550.47 · 86.18 g/mol): C, 69.93; H, 6.95. Found: C, 69.71; H, 6.92. ^{1}H NMR ($CDCl_3$, δ): 1.98 (s, 3 H, Mes-CH_3-C2), 2.02 (s, 3 H, Mes-CH_3-C6), 2.19 (s, 3 H, Mes-CH_3-C4), 3.30 (d, $^2J_{H,H}$ = 17.2 Hz, 1 H, CH_2), 3.81 (ddd, J = 2.5 Hz, J = 2.0 Hz, J = 1.5 Hz, 1 H, C_5H_3), 3.91 (dd, J = 3.6 Hz, J = 1.9 Hz, 1 H, C_5H_3), 4.11 (ddd, J = 2.5 Hz, J = 2.5 Hz, J = 1.6 Hz, 1 H, C_5H_3), 4.30 (s, 5 H, C_5H_5), 4.32 (d, $^2J_{H,H}$ = 17.0 Hz, 1 H, CH_2), 4.41 (s, 1 H, OH), 6.75 (s, 1 H, Mes-H), 7.40–7.44 (m, 2 H, Ph), 7.46–7.53 (m, 4 H, Ph), 7.80–7.84 (m, 2 H, Ph), 7.89–7.94 (m, 2 H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 12.5 (Mes-CH_3-C2), 15.8 (Mes-CH_3-C4), 19.8 (Mes-CH_3-C6), 29.1 (CH_2), 67.6 (d, $J_{C,P}$ = 10.3 Hz, C_5H_3), 70.9 (C_5H_5), 73.3 (d, $J_{C,P}$ = 10.0 Hz, C_5H_3), 73.4 (d, $J_{C,P}$ = 12.8 Hz, C_5H_3), 74.0 (d, $^1J_{C,P}$ = 96.0 Hz, C_{C5H3}–P), 93.0 (d, $^2J_{C,P}$ = 12.5 Hz, C_{C5H3}–CH_2), 120.3 (Mes-C4), 122.1 (Mes-C2), 128.1 (d, $^3J_{C,P}$ = 12.4 Hz, *m*-Ph), 128.26 (d, $^3J_{C,P}$ = 12.3 Hz, *m*-Ph), 128.33 (Mes-C6), 129.6 (Mes-C5), 131.2 (d, $^4J_{C,P}$ = 3.0 Hz, *p*-Ph), 131.3 (d, $^4J_{C,P}$ = 2.9 Hz, *p*-Ph), 132.0 (d, $^2J_{C,P}$ = 10.7 Hz, *o*-Ph), 132.3 (d, $^2J_{C,P}$ = 10.5 Hz, *o*-Ph), 133.5 (d, $^1J_{C,P}$ = 85.9 Hz, C_{Ph}–P), 133.8 (d, $^1J_{C,P}$ = 85.0 Hz, C_{Ph}–P), 135.9 (Mes-C1), 150.1 (Mes-OH). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 41.2. HRMS (ESI-TOF, m/z): calcd for $C_{32}H_{31}FeOPS$ 549.1194, found 549.1050 $[M]^+$.

(S_p)-2-((2,4-Dinitrophenyl)thiomethyl)-1-(thiodiphenylphosphino)ferrocene ((S_p)-155)



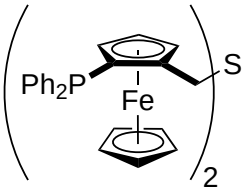
(S_p)-**155**

In a Schlenk tube, compound (S_p)-**143** (240 mg, 0.555 mmol), 1-fluoro-2,4-dinitrobenzene (310 mg, 1.67 mmol) and K_2CO_3 (384 mg, 2.78 mmol) were dissolved in 20 mL of DMF, whereby the color immediately turned dark. The mixture was heated to 40 °C and stirred for 18 h at this temperature. After cooling to ambient temperature, the reaction mixture was dissolved with 50 mL of Et_2O and washed with acidified (HCl) brine. After extraction with Et_2O (3 · 50 mL) all organic extracts were combined and dried over $MgSO_4$ followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, 2.5 · 18 cm column size) using a dichloromethane/ethyl acetate mixture (v/v) as the eluent, giving (S_p)-**155** as an orange solid.

Yield: 95 mg (0.155 mmol, 56 % based on (S_p)-**143**). Anal. calcd for $C_{29}H_{23}FeN_2O_4PS_2 \cdot 1/2$ C_6H_{14} (614.45 · 1/2 86.18 g/mol): C, 58.45; H, 4.60; N, 4.26. Found: C, 58.26; H, 4.27; N, 4.45. Mp.: 245 °C (explosive decomp.). ^{1}H NMR ($CDCl_3$, δ): 3.84–3.86 (m, 1 H, C_5H_3), 4.39–4.43 (m, 7 H, CH2, C_5H_5, C_5H_3), 4.66–4.68 (m, 1 H, C_5H_3), 4.96 (d, $^2J_{H,H}$ = 12.4 Hz, CH_2), 7.30–7.34 (m, 2 H, C_6H_5), 7.42–7.45 (m, 1 H, C_6H_5),7.47–7.51 (m, 2 H, C_6H_5), 7.53–7.59 (m, 4 H, C_6H_5, C_6H_3), 7.81–7.85 (m, 2 H, C_6H_5, C_6H_3), 8.21 (dd, $J_{H,H}$ = 9.0 Hz, $J_{H,H}$ = 2.5 Hz, C_6H_3), 8.94 (d, $J_{H,H}$ = 2.5 Hz, H3$_{C6H3}$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 32.0 (CH_2), 69.8 (d, $J_{C,P}$ = 10.1 Hz, C_5H_3), 71.3 (C_5H_5), 74.0 (d, $J_{C,P}$ = 8.9 Hz, C_5H_3), 74.8 (d, $^1J_{C,P}$

= 94.1 Hz, C_{C5H3}–P), 75.0 (d, $J_{C,P}$ = 11.8 Hz, C_5H_3), 85.2 (d, $^2J_{C,P}$ = 11.9 Hz, C_{C5H3}–CH_2), 121.4 (C3$_{C6H3}$), 126.7 (C5/6$_{C6H3}$), 127.6 (C5/6$_{C6H3}$), 128.18 (d, $^2J_{C,P}$ = 12.5 Hz, C3/5$_{C6H5}$), 128.22 (d, $^2J_{C,P}$ = 12.5 Hz, C3/5$_{C6H5}$), 131.55 (d, $^4J_{C,P}$ = 3.2 Hz, C4$_{C6H5}$), 131.57 (d, $^4J_{C,P}$ = 3.2 Hz, C4$_{C6H5}$), 131.9 (d, $^3J_{C,P}$ = 10.6 Hz, C2/6$_{C6H5}$), 132.0 (d, $^3J_{C,P}$ = 10.9 Hz, C2/6$_{C6H5}$), 132.7 (d, $^1J_{C,P}$ = 86.5 Hz, C1$_{C6H5}$), 134.1 (d, $^1J_{C,P}$ = 87.2 Hz, C1$_{C6H5}$), 143.6 (C2/4$_{C6H3}$), 144.1 (C2/4$_{C6H3}$), 146.9 (C1$_{C6H3}$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 40.8. IR data (KBr, $\tilde{\nu}$/cm^{-1}): 3078 w, 3065 w, 2958 w, 2922 s, 2854 m, 1737 m, 1585 m, 1520 s (ν_{as} NO_2), 1436 m, 1345 s (ν_s NO_2), 1169 m, 1101 w, 1042 m, 835 m, 712 s, 692 m, 645 m (ν P=S). HRMS (ESI-TOF, m/z): calcd for $C_{29}H_{23}FeN_2O_4PS_2$ 614.0181, found 614.0193 $[M]^+$.

Bis((S_p)-(2-diphenylphosphino)ferrocenylmethyl)sulfane ((S_p,S_p)-156)

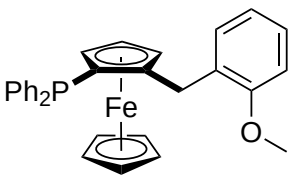


(S_p,S_p)-**156**

In a Schlenk tube, compound (S_p,S_p)-**149** (860 mg, 1.08 mmol) was dissolved in 50 mL of chlorobenzene followed by the dropwise addition of $P(NMe_2)_3$ (1.8 mL, 10 mmol). The mixture was heated to 130 °C and stirred for 18 h at this temperature and then allowed to cool to ambient temperature. Water (10 mL) was carefully added. The mixture was poured into water and extracted three times with dichloromethane (50 mL). The combined organic extracts were dried over $MgSO_4$ followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, 2.5 · 16 cm column size) using dichloromethane as the eluent. Compound (S_p,S_p)-**156** was crystallized from boiling hexane and obtained as an orange solid after removal of all volatiles.

Yield: 405 mg (0.51 mmol, 51 % based on (S_p,S_p)-**149**). Anal. calcd for $C_{46}H_{40}Fe_2P_2S$ (798.51 g/mol): C, 69.19; H, 5.05. Found: C, 69.62; H, 5.44. Mp.: 98 °C. ^1H NMR ($CDCl_3$, δ): 3.60 (dd, $^2J_{H,H}$ = 13.1 Hz, $^4J_{H,P}$ = 1.8 Hz, 2 H, CH_2), 3.64 (d, $^2J_{H,H}$ = 13.1 Hz, 2 H, CH_2), 3.73–3.74 (m, 2 H, C_5H_3), 3.91 (s, 10 H, C_5H_5), 4.21–4.22 (m, 2 H, C_5H_3), 4.31–4.32 (m, 2 H, C_5H_3), 7.16–7.19 (m, 4 H, C_6H_5), 7.22–7.25 (m, 6 H, C_6H_5), 7.36–7.38 (m, 6 H, C_6H_5), 7.53–7.57 (m, 4 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 32.0 (d, $^3J_{C,P}$ = 11.7 Hz, CH_2), 69.2 (C_5H_3), 69.7 (C_5H_5), 71.1 (d, $J_{C,P}$ = 3.9 Hz, C_5H_3), 71.3 (d, $J_{C,P}$ = 3.9 Hz, C_5H_3), 75.5 (d, $^1J_{C,P}$ = 7.8 Hz, C_{C5H3}–P), 90.9 (d, $^2J_{C,P}$ = 25.9 Hz, C_{C5H3}–C), 127.6 (p-C_6H_5), 127.9 (d, $^3J_{C,P}$ = 5.9 Hz, m-C_6H_5), 128.0 (d, $^3J_{C,P}$ = 8.0 Hz, m-C_6H_5), 129.0 (p-C_6H_5), 132.2 (d, $^2J_{C,P}$ = 17.6 Hz, o-C_6H_5), 135.1 (d, $^2J_{C,P}$ = 21.4 Hz, o-C_6H_5), 137.7 (d, $^1J_{C,P}$ = 8.7 Hz, C_{C6H5}–P), 140.0 (d, $^1J_{C,P}$ = 9.4 Hz, C_{C6H5}–P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): –23.7. HRMS (ESI-TOF, m/z): calcd for $C_{46}H_{40}FePS$ + H 799.1099, found 799.1120 $[M+H]^+$.

(S_p)-(Diphenylphosphino)-2-(2-methoxyphenylmethyl)ferrocene ((S_p)-157)



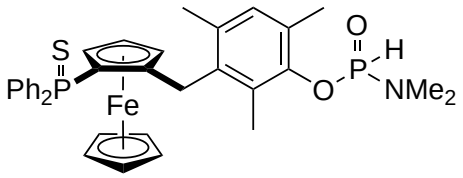
(S_p)-**157**

In a Schlenk tube, compound (S_p)-**151a** (192 mg, 0.29 mmol) was dissolved in 20 mL of chlorobenzene followed by the addition of $P(NMe_2)_3$ (0.6 mL, 2.88 mmol). The mixture was heated to 130 °C and stirred for 18 h at this temperature and then allowed to cool to ambient temperature. Water (5 mL) was carefully added. The mixture was poured into water and extracted three times with

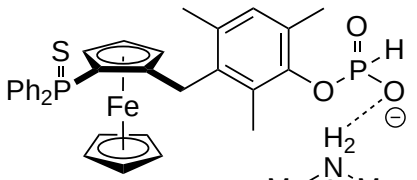
dichloromethane (40 mL). The combined organic extracts were dried over $MgSO_4$ followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, 2.5 · 16 cm column size) using dichloromethane as the eluent. Compound (S_p)-**157** was recrystallized from boiling pentane and obtained as an orange solid after removal of all volatiles.

Yield: 145 mg (0.23 mmol, 79 % based on (S_p)-**151a**). Anal. calcd for $C_{30}H_{27}FeOP \cdot 1.5\ C_5H_{12}$ (490.35 · 1.5 72.15 g/mol): C, 73.29; H, 7.38. Found: C, 73.71; H, 7.16. Mp.: 104 °C. ^{1}H NMR ($CDCl_3$, δ): 3.71 (s, 3 H, OCH_3), 3.72–3.73 (m, 1 H, C_5H_3), 3.86 (d, $^2J_{H,H}$ = 15.1 Hz, 1 H, CH_2), 3.93 (dd, $^2J_{H,H}$ = 15.1 Hz, $^4J_{H,P}$ = 2.1 Hz, 1 H, CH_2), 4.01 (s, 5 H, C_5H_5), 4.21–4.22 (m, 1 H, C_5H_3), 4.42–4.43 (m, 1 H, C_5H_3), 6.61 (td, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.0 Hz, 1 H, H4-C_6H_4), 6.67–6.70 (m, 1 H, H6-C_6H_4), 6.92 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.6 Hz, 1 H, H3-C_6H_4), 7.02–7.07 (m, 3 H, H5-C_6H_4, C_6H_5), 7.09–7.16 (m, 3 H, C_6H_5), 7.37–7.40 (m, 3 H, C_6H_5), 7.57–7.61 (m, 2 H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 28.6 (d, $^3J_{C,P}$ = 10.1 Hz, CH_2), 54.9 (OCH_3), 68.9 (C_5H_3), 69.7 (C_5H_5), 70.6 (d, $J_{C,P}$ = 4.1 Hz, C_5H_3), 72.1 (d, $J_{C,P}$ = 4.0 Hz, C_5H_3), 75.3 (d, $^1J_{C,P}$ = 6.7 Hz, C_{C5H3}–P), 93.8 (d, $^2J_{C,P}$ = 26.3 Hz, C_{C5H3}–C), 109.8 (C6-C_6H_4), 119.9 (C4-C_6H_4), 126.9 (C5-C_6H_4), 127.4 (C3-C_6H_4), 127.6 (d, $^3J_{C,P}$ = 6.0 Hz, *m*-C_6H_5), 128.0 (d, $^3J_{C,P}$ = 7.9 Hz, *m*-C_6H_5), 128.9 (p-C_6H_5), 129.4 (C2-C_6H_4), 130.3 (d, $^4J_{C,P}$ = 1.1 Hz, *p*-C_6H_5), 132.3 (d, $^2J_{C,P}$ = 18.0 Hz, *o*-C_6H_5), 135.2 (d, $^2J_{C,P}$ = 21.1 Hz, *o*-C_6H_5), 138.0 (d, $^1J_{C,P}$ = 8.5 Hz, C_{C6H5}–P), 139.8 (d, $^1J_{C,P}$ = 9.6 Hz, C_{C6H5}–P), 159.9 (C1-C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –22.5. HRMS (ESI-TOF, m/z): calcd for $C_{30}H_{27}FeOP$ 490.1144, found 490.1195 $[M]^+$.

3-(2-(Thiodiphenylphosphino)ferrocenylmethyl)-2,4,6-trimethylphenyl *N*,*N*-Dimethylphosphonamidate ((S_p)-158) and ((S_p)-159)



(S_p)-**158**



(S_p)-**159**

In a Schlenk tube, compound (S_p)-**153** (162 mg, 0.294 mmol) was dissolved in 20 mL of toluene followed by the addition of $P(NMe_2)_3$ (0.27 mL, 1.3 mmol). The mixture was refluxed for 18 h and then allowed to cool to ambient temperature. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 2.5 · 16 cm column size) using dichloromethane as the eluent. After removal of all volatiles compound (S_p)-**158** was obtained as a yellow solid as a 1:1 mixture of two diastereomers. Dissolving in boiling dichloromethane and slow cooling to ambient temperature gave single crystals of (S_p)-**159**, suitable for single crystal X-ray diffraction analysis. The compound decomposed rapidly in solution.

Yield: 66 mg (0.103 mmol, 35 % based on (S_p)-**153**). ^{1}H NMR ($CDCl_3$, δ): 2.04 (s, 3 H, Mes-CH_3-C2/6), 2.05 (s, 3 H, Mes-CH_3-C2/6), 2.06 (s, 3 H, Mes-CH_3-C2/6), 2.07 (s, 3 H,

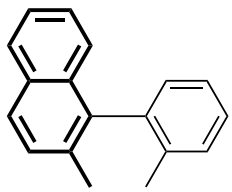
Mes-CH_3-C2/6), 2.28 (s, 6 H, Mes-CH_3-C4), 2.756 (d, $^3J_{H,P}$ = 11.0 Hz, 6 H, NMe_2), 2.760 (d, $^3J_{H,P}$ = 11.0 Hz, 6 H, NMe_2), 3.26 (d, $^2J_{H,H}$ = 17.1 Hz, 1 H, CH_2), 3.28 (d, $^2J_{H,H}$ = 17.2 Hz, 1 H, CH_2), 3.81–3.83 (m, 2 H, C_5H_3), 3.89–3.91 (m, 2 H, C_5H_3), 4.11–4.13 (m, 2 H, C_5H_3), 4.29 (s, 5 H, C_5H_5), 4.30 (s, 5 H, C_5H_5), 4.33 (d, $^2J_{H,H}$ = 17.3 Hz, 1 H, CH_2), 4.34 (d, $^2J_{H,H}$ = 17.2 Hz, 1 H, CH_2), 6.82 (s, 2 H, Mes-H5), 7.02 (d, $^1J_{H,P}$ = 646.1 Hz, 1 H, P-H), 7.04 (d, $^1J_{H,P}$ = 646.2 Hz, 1 H, P-H), 7.40–7.43 (m, 4 H, Ph), 7.47–7.54 (m, 8 H, Ph), 7.78–7.83 (m, 4 H, Ph), 7.89–7.93 (m, 4 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 14.26 (CH_3), 14.28 (CH_3), 17.3 (CH_3), 19.90 (CH_3), 19.92 (CH_3), 29.3 (CH_2), 34.34 (d, $^2J_{C,P}$ = 5.6 Hz, NMe_2), 34.35 (d, $^2J_{C,P}$ = 5.4 Hz, NMe_2), 67.71 (C_5H_3), 70.9 (C_5H_5), 71.0 (C_5H_5), 73.2 (d, $J_{C,P}$ = 9.8 Hz, C_5H_3), 73.5 (d, $J_{C,P}$ = 12.9 Hz, C_5H_3), 74.0 (d, $^1J_{C,P}$ = 95.0 Hz, C–P), 92.4 (d, $^2J_{C,P}$ = 12.2 Hz, C_{C5H3}–CH_2), 127.4 (^{q}C), 127.8 (^{q}C), 128.1 (d, $^3J_{C,P}$ = 12.5 Hz, *m*-Ph), 128.3 (d, $^3J_{C,P}$ = 12.3 Hz, *m*-Ph), 128.9 (^{q}C), 129.8 (^{q}C), 130.33 (CH), 130.34 (CH), 131.18 (CH), 131.20 (CH), 131.34 (CH), 131.37 (CH), 131.9 (CH), 132.0 (CH), 132.2 (CH), 132.3 (CH), 133.0 (^{q}C), 133.4 (^{q}C), 133.7 (^{q}C), 134.06 (^{q}C), 134.07 (^{q}C), 134.1 (^{q}C), 136.37 (^{q}C), 136.40 (^{q}C), 145.5 (d, $^2J_{C,P}$ = 9.5 Hz, C–O–P). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 12.25 ($^1J_{P,H}$ = 646 Hz, PHO_2N), 12.29 ($^1J_{P,H}$ = 646 Hz, PHO_2N), 41.13 (P=S), 41.15 (P=S).

4.3.7 Suzuki-Miyaura *C,C* Cross-Coupling Reactions

General Procedure for Suzuki-Miyaura Cross-Coupling Reactions - GP7

A glass vessel of 4 mL size was charged with $[Pd_2(dba)_3]$ (0.25 mol-%) and compound *rac*-/(R_p)-**91** (1 mol-%), or $[Pd_2(dba)_3]$ (0.5 mol-%) and compounds (S_p,S_p)-**156** (1 mol-%) or (S_p)-**157** (2 mol-%), boronic acid (1.5 mmol), powdered $K_3PO_4 \cdot H_2O$ (690 mg, 3.0 mmol), the appropriate aryl halide (1.0 mmol), and dry toluene (3 mL). The vessel was closed and the reaction mixture was stirred at 70 °C for 24 h, except as otherwise noted. After it was cooled to ambient temperature, the reaction mixture was diluted with water (25 mL) and extracted with diethyl ether (3 ·25 mL). The combined organic extracts were filtered through a pad of alumina and concentrated under reduced pressure. The obtained crude material was purified by flash chromatography on silica (4 · 12 cm column size) (hexane/diethyl ether mixtures). The obtained yields are based on the respective aryl halide and depend on the used ligand (L) and on the Pd/L concentration. They are shown in Figure 3.41 and 3.85.

2-Methyl-1-(*o*-tolyl)naphthalene (94a)



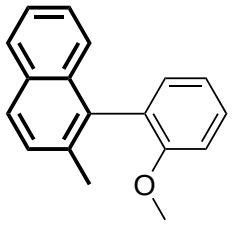
94a

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methylnaphthalene (221 mg) and *o*-tolylboronic acid (204 mg) were reacted. Purification was realized by column chromatography using hexane as the eluent. The spectroscopic data are in agreement with those reported in literature.[312]

^1H NMR ($CDCl_3$, δ): 1.94 (s, 3 H, CH_3), 2.18 (s, 3 H, CH_3), 7.14 (d, $J_{H,H}$ = 7.1 Hz, 1 H), 7.26 (d, $J_{H,H}$ = 8.4 Hz, 1 H), 7.31–7.34 (m, 2 H), 7.35–7.39 (m, 2 H), 7.41 (ddd, $J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 6.8 Hz, $J_{H,H}$ = 1.3 Hz, 1 H), 7.44 (d, $J_{H,H}$ = 8.4 Hz, 1 H), 7.80

(d, $J_{H,H}$ = 8.4 Hz, 1 H), 7.85 (d, $J_{H,H}$ = 8.6 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.5, 20.3, 124.7, 125.87, 125.7, 125.9, 127.1, 127.4, 127.8, 128.6, 129.97, 130.04, 132.0, 132.6, 133.1, 136.8, 137.5, 139.2.

1-(2-Methoxyphenyl)-2-methylnaphthalene (94b)

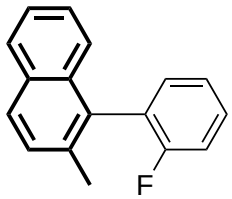


94b

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methylnaphthalene (221 mg) and 2-methoxyphenylboronic acid (228 mg) were reacted. Purification was realized by column chromatography using a 98/2 hexane/diethyl ether mixture (v/v) as the eluent. The spectroscopic data are in agreement with those reported in literature.[312]

^1H NMR ($CDCl_3$, δ): 2.22 (s, 3 H, CH_3), 3.68 (s, 3 H, OCH_3), 7.06–7.11 (m, 2 H), 7.14 (dd, $J_{H,H}$ = 7.4 Hz, $J_{H,H}$ = 1.8 Hz, 1 H), 7.29–7.32 (m, 1 H), 7.35–7.40 (m, 2 H), 7.42–7.45 (m, 2 H), 7.78 (d, $J_{H,H}$ = 8.4 Hz, 1 H), 7.83 (d, $J_{H,H}$ = 8.1 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 20.5 (CH_3), 55.6 (OCH_3), 111.2, 120.7, 124.6, 125.6, 125.9, 127.2, 127.8, 128.3, 128.5, 128.8, 131.8, 132.0, 132.9, 133.9, 134.6, 157.4.

1-(2-Fluorophenyl)-2-methylnaphthalene (94c)



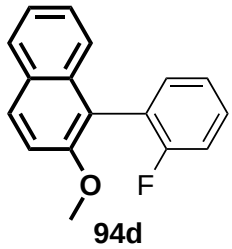
94c

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methylnaphthalene (221 mg), 2-fluorophenylboronic acid (210 mg) and $K_3PO_4 \cdot 3\,H_2O$ (800 mg, 3.0 mmol) were reacted. Purification was realized by column chromatography using a 99/1 hexane/diethyl ether mixture (v/v) as the eluent. The analytical data are in agreement with those reported in literature.[196]

^1H NMR ($CDCl_3$, δ): 2.27 (s, 3 H, CH_3), 7.21–7.30 (m, 3 H), 7.34–7.47 (m, 5 H), 7.82 (d, $J_{H,H}$ = 8.5 Hz, 1 H), 7.85 (d, $J_{H,H}$ = 8.1 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 20.5 (s, CH_3), 115.8 (d, $J_{C,F}$ = 22.3 Hz), 124.1 (d, $J_{C,F}$ = 3.6 Hz), 124.9, 125.5, 126.1, 126.8 (d, $^2J_{C,F}$ = 17.7 Hz, ^{i}C-Ph), 127.90, 127.96, 128.5, 129.4 (d, $J_{C,F}$ = 7.9 Hz), 131.6, 132.0, 132.4 (d, $J_{C,F}$ = 3.8 Hz), 132.7, 134.3, 160.2 (d, $^1J_{C,F}$ = 245.4 Hz, C–F). HRMS (ESI-TOF, m/z): calcd for $C_{17}H_{13}F$ + H 237.1074, found 237.1065 $[M+H]^+$.

1-(2-Fluorophenyl)-2-methoxynaphthalene (94d)

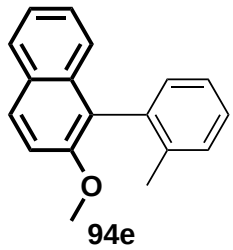
According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methoxynaphthalene (237 mg), 2-fluorophenylboronic acid (210 mg) and $K_3PO_4 \cdot 3\,H_2O$ (800 mg, 3.0 mmol) were reacted. Purification was realized by column chromatography using a 94/6 hexane/diethyl ether mixture (v/v) as the eluent. The analytical data are in agreement with those reported in literature.[67]



94d

^{1}H NMR ($CDCl_3$, δ): 3.88 (s, 3 H, OCH_3), 7.22 (ddd, $J_{H,H}$ = 9.3 Hz, $J_{H,H}$ = 8.3 Hz, $J_{H,H}$ = 1.0 Hz, 1 H), 7.28 (dd, $J_{H,H}$ = 7.4 Hz, $J_{H,H}$ = 1.2 Hz, 1 H), 7.32–7.40 (m, 4 H), 7.42–7.45 (m, 2 H), 7.82–7.85 (m, 1 H), 7.93 (d, $J_{H,H}$ = 9.0 Hz, 1 H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 56.8 (OCH_3), 113.6, 115.7 (d, $J_{C,F}$ = 22.5 Hz), 118.8, 123.6, 123.8 (d, $^2J_{C,F}$ = 17.3 Hz), 123.8 (d, $J_{C,F}$ = 3.6 Hz), 124.7, 126.6, 128.0, 129.0, 129.3 (d, $J_{C,F}$ = 8.0 Hz), 129.9, 133.1 (d, $J_{C,F}$ = 3.7 Hz), 133.4, 154.4, 160.6 (d, $^1J_{C,F}$ = 246.3 Hz, C–F). HRMS (ESI-TOF, m/z): calcd for $C_{17}H_{13}FO$ + H 253.1023, found 253.1036 $[M+H]^+$.

1-(*o*-Tolyl)-2-methoxynaphthalene (94e)

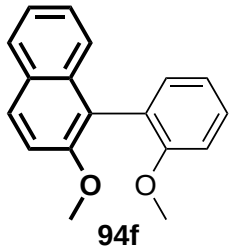


94e

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methoxynaphthalene (237 mg) and *o*-tolylboronic acid (204 mg) were reacted. Purification was realized by column chromatography using a 98/2 hexane/diethyl ether mixture (v/v) as the eluent. The spectroscopic data are in agreement with those reported in literature.[67]

^{1}H NMR ($CDCl_3$, δ): 2.00 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 7.19 – 7.20 (m, 1 H), 7.26–7.39 (m, 7 H), 7.83–7.85 (m, 1 H), 7.90 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.9 (CH_3), 56.8 (OCH_3), 113.8, 123.6, 124.7, 125.2, 125.8, 126.5, 127.6, 128.0, 129.1, 129.2, 130.0, 131.0, 133.6, 136.3, 137.8, 153.9. HPLC (Chiralcel OD-H, flow rate 0.5 mL/min, hexane): 40.8, 46.2 min.

1-(2-Methoxyphenyl)-2-methoxynaphthalene (94f)



94f

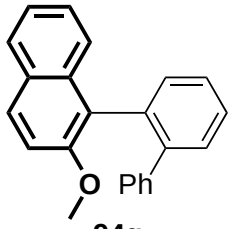
According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methoxynaphthalene (237 mg) and 2-methoxyphenylboronic acid (228 mg) were reacted. Purification was realized by column chromatography using a 95/5 hexane/diethyl ether mixture (v/v) as the eluent. The spectroscopic data are in agreement with those reported in literature.[312]

^{1}H NMR ($CDCl_3$, δ): 3.70 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 7.08–7.13 (m, 2 H), 7.24 (dd, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.7 Hz, 1 H), 7.31–7.35 (m, 2 H), 7.44 (ddd, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.8 Hz, 1 H), 7.82–7.84 (m, 1 H), 7.89 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 55.1 (OCH_3), 57.0 (OCH_3), 111.3, 114.2, 120.6, 122.1, 123.4, 125.3, 125.4, 126.1, 127.8, 128.8, 129.05, 129.08, 132.4, 133.7, 154.3, 157.8. HPLC (Chiralcel OD-H, flow rate 0.5 mL/min, hexane): 39.8, 45.5 min.

1-([1,1'-Biphenyl]2-yl)-2-methoxynaphthalene (94g)

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methoxynaphthalene (237 mg) and [1,1'-biphenyl]-2-ylboronic acid (297 mg) were

reacted.

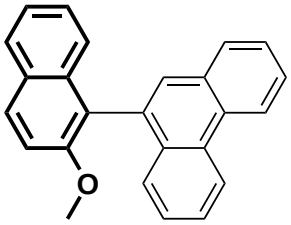


94g

Purification was realized by column chromatography using a 98/2 hexane/diethyl ether mixture (v/v) as the eluent. The spectroscopic data are in agreement with those reported in literature.[312]

^{1}H NMR ($CDCl_3$, δ): 3.52 (s, 3 H, OCH_3), 7.00–7.07 (m, 5 H), 7.12 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H), 7.29–7.36 (m, 3 H), 7.46–7.55 (m, 4 H), 7.76–7.78 (m, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 56.2 (OCH_3), 113.3, 123.4, 124.5, 125.4, 126.4, 126.5, 127.2, 127.4, 127.9, 128.0, 128.7, 129.0, 129.2, 130.0, 132.0, 134.0, 135.0, 141.9, 143.1, 153.7. HPLC (Chiralcel OD-H, flow rate 1.0 mL/min, hexane): 68.7, 94.9 min; 1.2 mL/min: 50.9, 70.0 min.

9-(2-Methoxy-1-naphthyl)phenanthrene (94h)

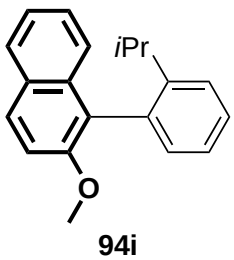


94h

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methoxynaphthalene (237 mg) and 9-phenanthrylboronic acid (333 mg) were reacted. Purification was realized by column chromatography using a 98/2 hexane/diethyl ether mixture (v/v) as the eluent. The analytical data are in agreement with those reported in literature.[196]

^{1}H NMR ($CDCl_3$, δ): 3.78 (s, 3 H, OCH_3), 7.22 (ddd, $J_{H,H}$ = 8.6 Hz, $J_{H,H}$ = 6.6 Hz, $J_{H,H}$ = 1.3 Hz, 1 H), 7.29–7.31 (m, 1 H), 7.34 (ddd, $J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 6.6, $J_{H,H}$ = 1.2, 1 H), 7.39–7.40 (m, 2 H), 7.48 (d, $J_{H,H}$ = 9.0, 1 H), 7.62–7.66 (m, 2 H), 7.71 (ddd, $J_{H,H}$ = 8.4 Hz, $J_{H,H}$ = 6.9 Hz, $J_{H,H}$ = 1.3 Hz, 1 H), 7.73 (s, 1 H), 7.89–7.91 (m, 2 H), 8.01 (d, $J_{H,H}$ = 9.0 Hz, 1 H), 8.81 (t, $J_{H,H}$ = 7.8 Hz, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 56.8 (OCH_3), 113.9, 122.6, 122.8, 123.2, 123.6, 125.5, 126.45, 126.52, 126.54, 126.6, 126.8, 127.8, 128.7, 129.1, 129.6, 130.3, 130.5, 131.9, 132.1, 133.2, 134.3, 154.8. HRMS (ESI-TOF, m/z): calcd for $C_{25}H_{18}O$ + Na 357.1250, found 357.1247 $[M+Na]^+$.

1-(2-*Iso*propylphenyl)-2-methoxynaphthalene (94i)



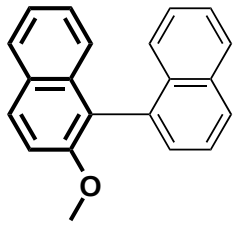
94i

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methoxynaphthalene (237 mg) and 2-*iso*propylboronic acid (246 mg) were reacted. Purification was realized by column chromatography using a 98/2 hexane/diethyl ether mixture (v/v) as the eluent. The spectroscopic data are in agreement with those reported in literature.[312]

^{1}H NMR ($CDCl_3$, δ): 0.98 (d, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$, 3 H), 1.13 (d, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$, 3 H), 2.57 (sept, $^3J_{H,H}$ = 6.9 Hz, $CH(CH_3)_2$, 1 H), 3.84 (s, 3 H, OCH_3), 7.12 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.0 Hz, 1 H), 7.24–7.35 (m, 4 H), 7.37 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H), 7.44 (td, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H), 7.48 (dd, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.1 Hz, 1 H), 7.82–7.83 (m, 1 H), 7.90 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 24.0 ($CH(CH_3)_2$), 24.1 ($CH(CH_3)_2$), 30.5 ($CH(CH_3)_2$), 56.5

(OCH_3), 113.5, 123.6, 124.7, 125.5, 125.5, 125.7, 126.4, 127.9, 128.1, 129.0, 129.1, 131.0, 134.3, 135.0, 148.5, 154.0. HPLC (Chiralcel OD-H, flow rate 0.5 mL/min, hexane): 33.9, 37.5 min.

2-Methoxy-1,1'-binaphthalene (94j)

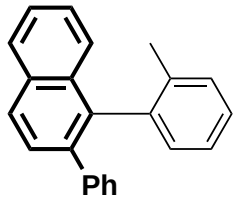


94j

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methoxynaphthalene (237 mg) and 1-naphthylboronic acid (258 mg) were reacted. Purification was realized by column chromatography using a 98/2 hexane/diethyl ether mixture (v/v) as the eluent. The spectroscopic data are in agreement with those reported in literature.[312]

^{1}H NMR ($CDCl_3$, δ): 3.76 (s, 3 H, OCH_3), 7.15–7.17 (m, 1 H), 7.21–7.29 (m, 2 H), 7.31–7.35 (m, 2 H), 7.43–7.48 (m, 3 H), 7.62 (dd, $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,H}$ = 7.0 Hz, 1 H), 7.87 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 7.94–7.96 (m, 2 H), 7.99 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 56.9 (OCH_3), 114.0, 123.4, 123.7, 125.7, 125.7, 125.8, 126.0, 126.3, 126.5, 127.9, 127.9, 128.4, 128.6, 129.2, 129.6, 133.1, 133.9, 134.4, 134.7, 154.8. HPLC (Chiralcel OD-H, flow rate 0.6 mL/min, hexane): 63.3, 74.3 min.

2-Phenyl-1-(*o*-tolyl)naphthalene (94k)

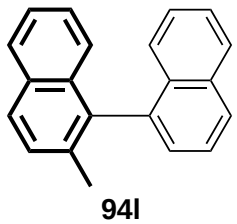


94k

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-phenylnaphthalene (283 mg) and *o*-tolylboronic acid (204 mg) were reacted. Purification was realized by column chromatography using hexane as the eluent. The spectroscopic data are in agreement with those reported in literature.[312]

^{1}H NMR ($CDCl_3$, δ): 1.96 (s, 3 H, CH_3), 7.19–7.36 (m, 9 H), 7.45–7.51 (m, 2 H), 7.55–7.58 (m, 1 H), 7.68 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H), 7.99–8.03 (m, 2 H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 19.9 (CH_3), 125.2, 125.7, 126.27, 126.32, 126.6, 127.3, 127.5, 127.6, 127.9, 128.2, 129.6, 129.7, 131.6, 132.5, 132.7, 136.9, 137.1, 138.2, 138.5, 141.9 ppm. HPLC (Chiralcel OD-H, flow rate 0.5 mL/min, hexane): 24.4, 25.3 min; (Chiralcel OJ-H, flow rate 0.5 mL/min, hexane): 43.1, 56.5 min.

2-Methyl-1,1'-binaphthalene (94l)



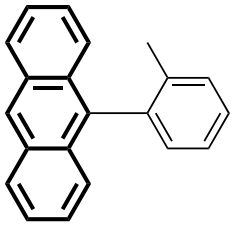
94l

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 1-bromo-2-methylnaphthalene (221 mg) and 1-naphthylboronic acid (258 mg) were reacted. Purification was realized by column chromatography using hexane as the eluent. The spectroscopic data are in agreement with those reported in literature.[395]

^{1}H NMR ($CDCl_3$, δ): 7.11 (2, 3 H, CH_3), 7.14–7.16 (m, 1 H), 7.20–7.22 (m, 1 H), 7.23–7.28 (m, 2 H), 7.37–7.41 (m, 2 H), 7.46–7.50 (m, 2 H), 7.59–7.63 (m, 1 H), 7.87–

7.89 (m, 2 H), 7.94–7.96 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 20.5 (CH_3), 124.8 (CH), 125.6 (CH), 125.85 (CH), 125.88 (CH), 126.0 (CH), 126.1 (CH), 126.3 (CH), 127.5 (CH), 127.6 (CH), 127.7 (CH), 127.8 (CH), 128.3 (CH), 128.6 (CH), 132.0, 132.6, 133.5, 133.8, 134.4, 136.1, 137.5. HPLC (Chiralcel OD-H, flow rate 0.5 mL/min, hexane): 43.1, 56.5 min.

9-(*o*-Tolyl)anthracene (94m)

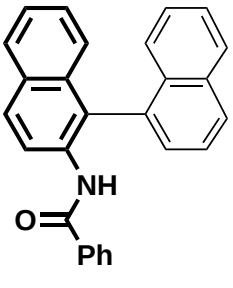


94m

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 9-bromoanthracene (257 mg) and *o*-tolylboronic acid (204 mg) were reacted. Purification was realized by column chromatography using a 95/5 hexane/diethyl ether mixture (v/v) as the eluent. The spectroscopic data are in agreement with those reported in literature.[312]

^1H NMR ($CDCl_3$, δ): 1.87 (s, 3 H, CH_3), 7.25–7.27 (m, 1 H), 7.34 (ddd, $^3J_{H,H}$ = 8.7 Hz, $^3J_{H,H}$ = 6.5 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 H), 7.37–7.40 (m, 1 H), 7.44–7.48 (m, 4 H), 7.50–7.52 (m, 2 H), 8.50 (s, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 19.9 (CH_3), 125.3, 125.6, 126.0, 126.5, 126.7, 128.0, 128.6, 130.1, 130.2, 131.4, 131.6, 136.6, 138.0, 138.3.

***N*-([1,1'-Binaphthalen]-2-yl)benzamide (94p)**



94p

According to the general procedure for Suzuki-Miyaura cross-coupling reactions GP7, 2-amino-1-bromonaphthalene (222 mg, 1 mmol) and 1-naphthylboronic acid (258 mg, 1.5 mmol) were reacted with 0.5 mol-% $[Pd_2(dba)_3]$ at 70 °C. The conversion of the amine into the amide was performed similar to a literature reported protocol.[396] The crude reaction mixture was cooled to ambient temperature and transferred into a Schlenk tube by using dichloromethane and diluted with 5 mL of THF. Benzoyl chloride (0.15 mL, 1.3 mmol) was added in a single portion followed by triethylamine (0.28 mL, 1.3 mmol). The reaction mixture was stirred at 65 °C for 6 h and afterwards allowed to cool to ambient temperature. The solution was poured into water and extracted three times with Et_2O (50 mL). The combined organic layers were dried over $MgSO_4$ followed by removal of all volatiles in vacuum. Purification was realized by column chromatography (silica, 4 · 23 cm column size) using a hexane/diethyl ether mixture (v/v) as the eluent. The product is eluted as the third fraction, after 1,1'-binaphthyl as the first, and a fluorescent fraction as the second fraction. After removal of all volatiles **94q** was obtained as a colorless oil.

Yield: 279 mg (0.747 mmol, 75 % based on 2-amino-1-bromonaphthalene). Anal. calcd for $C_{27}H_{19}NO \cdot 1.5\ H_2O$ (373.45 · 1.5 18.02 g/mol): C, 80.98; H, 5.54; N, 3.50. Found: C, 80.82; H, 5.06; N, 3.52. ^1H NMR ($CDCl_3$, δ): 7.14–7.16 (m, 2 H), 7.19–7.23 (m, 3 H), 7.28 (ddd, $^3J_{H,H}$ = 8.4 Hz, $^3J_{H,H}$ = 6.7 Hz, $J_{H,H}$ = 1.3 Hz, 1 H), 7.33–7.39 (m, 3 H), 7.43 (ddd, $^3J_{H,H}$ = 8.0 Hz, $^3J_{H,H}$ = 6.7 Hz, $J_{H,H}$ = 1.2 Hz, 1 H), 7.54 (ddd, $^3J_{H,H}$ = 8.1 Hz, $J_{H,H}$ = 4.0 Hz,

$J_{H,H}$ = 0.8 Hz, 1 H), 7.56 (dd, $^3J_{H,H}$ = 6.9 Hz, $J_{H,H}$ = 1.2 Hz, 1 H), 7.65 (s, br, 1 H, NH), 7.70 (dd, $^3J_{H,H}$ = 8.2 Hz, $^3J_{H,H}$ = 7.0 Hz, 1 H), 7.94 (d, $^3J_{H,H}$ = 8.2 Hz, 1 H), 8.02 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H), 8.06 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H), 8.07 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H), 8.84 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 120.1 (CH), 124.9 (CH), 125.0 (^{q}C), 125.6 (CH), 125.9 (CH), 126.0 (CH), 126.5 (CH), 126.6 (CH), 126.7 (CH), 127.2 (CH), 128.0 (CH), 128.6 (CH), 128.6 (CH), 129.0 (CH), 129.1 (CH), 129.2 (CH), 130.9 (^{q}C), 131.5 (CH), 132.3 (^{q}C), 133.0 (^{q}C), 133.2 (^{q}C), 134.1 (^{q}C), 134.2 (^{q}C), 134.7 (^{q}C), 165.0 (C=O). HRMS (ESI-TOF, m/z): calcd for $C_{27}H_{19}NO + H$ 374.1539, found 374.1541 $[M+H]^+$. HPLC (Chiralcel OD-H, flow rate 0.5 mL min$^-$1, *n*hexane:*i*PrOH (98:2)): 44.7, 58.1 min. IR data (KBr, $\tilde{\nu}$/cm^{-1}): 3412 m (NH), 3052 w, 2919 m, 2851 w, 1673 s, 1617 w, 1595 m, 1497 s, 1484 s, 1426 m, 1283 s, 780 m, 708 m.

5 Conclusion

The present Ph D thesis discusses the synthesis and characterization of planar-chiral 1,2-*P*,*O*-substituted ferrocenes and their application in (atropselective-) Suzuki-Miyaura *C*,*C*-cross coupling reactions of hindered biaryls. This hardly accessible substitution pattern of the ferrocenyl backbone shall be established by applying the anionic phospho-Fries rearrangement (*apFr*), as a new regioselective synthetic access to such 1,2-*P*,*O*-substituted ferrocenes.

The Ph D thesis is structured in four main parts:

3.1 Anionic Phospho-Fries Rearrangements

3.2 Oxygen-Functionalization of Hydroxyferrocenes

3.3 Anionic Homo Phospho-Fries Rearrangements

3.4 Functionalization of *ortho*-Diphenylphosphino Ferrocenylmethanols

Section 3.1.1 focused on the examination of the reactions conditions, the substrate scope and the limitations of the anionic phospho-Fries rearrangement at ferrocene. It could be shown for the first time that these type of 1,3-O→C migrations proceed at ferrocene. Electron deficient ferrocenyl phosphates turned out to be the preferred substrates and gave the rearranged ferrocenyl phosphonates in high yield. Based on the *ortho*-directing properties of phosphoryl-substituents, the *apFr* enabled an efficient and regioselective access to 1,2-*P*,*O*-ferrocenes. Examination of the substrate scope revealed that the electron density of the P-bonded group is decisive for the lithiation and rearrangement process (Figure 5.1). Thus, electron rich *N*-alkyl derivatives impeded the deprotonation and prevented a successful rearrangement, giving *ortho*-methylated compounds instead.

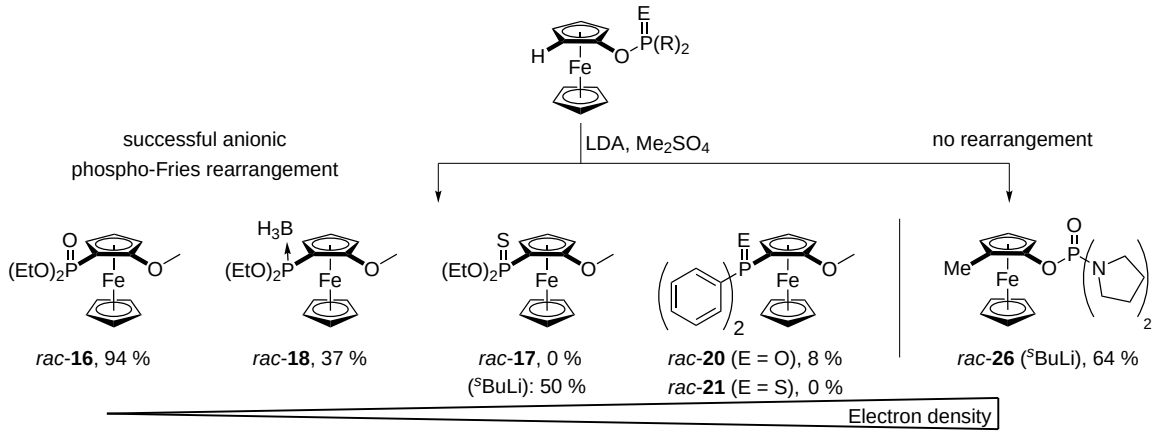


Figure 5.1 Substrate scope for successful anionic phospho-Fries rearrangements.

Functionalization of ferrocenyl phosphates with chiral pool derived alcohols (3.1.2) allowed for the investigation of a diastereoselective proceeding of the *apFr* by stereoselective *ortho*-directed metalation. The best results were obtained for the sterically most demanding (1*R*)-α-fenchyl substituent (= Fn), which gave 1,2-*P*,*O*-ferrocenes in a diastereomeric excess of up to 95 % (Figure 5.2). The steric demand of the bicyclic system, bearing three methyl groups close to the linking oxygen, even prevented the methylation of the hydroxy group in a 1,3-di-*ortho*-functionalized product, which was further stabilized by intramolecular hydrogen bridge bonds. The shielding of one *ortho*-position within the metalation with LiTMP gave a 1,1'-2-*P*,*P*,*O*-ferrocene with 95 % *de*.

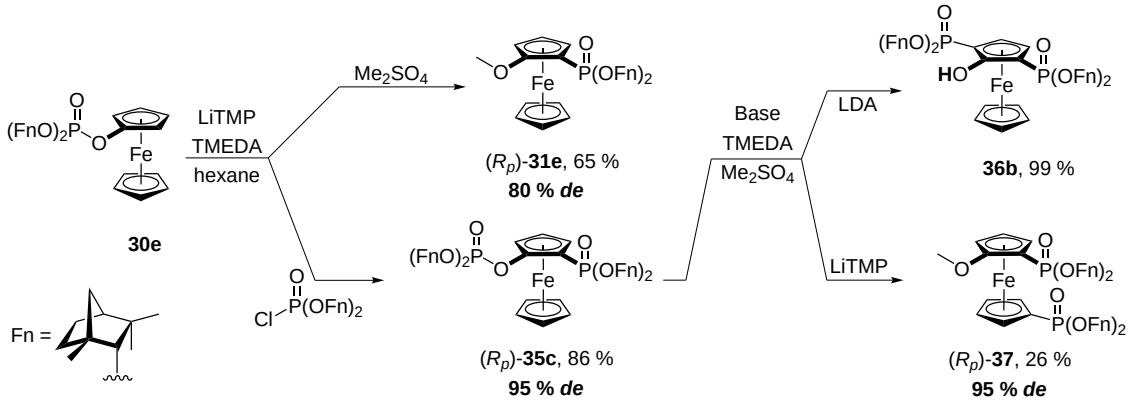


Figure 5.2 Diastereoselective anionic phospho-Fries rearrangements.

The investigation of triferrocenyl phosphate revealed that solely one ferrocenyl fragment undergoes an *apFr* per reaction step (Section 3.1.3). Nevertheless, the final phosphine oxide could not be synthesized (Section 3.1.3). This was in contrast to triphenyl phosphate, where the respective phosphine oxide is formed within one reaction step, and intermediate compounds had never been reported. Thus, basic investigations of triphenyl phosphate within *apFr* were performed, showing a temperature dependent formation of the phosphonate the phosphinate and finally the respective oxide. Mixed ferrocenyl phenyl phosphates also gave temperature-dependent mixtures, confirming both reaction behaviors, with a preferred lithiation at the phenyl-related rings. The introduction of electron-deficient *N*-heterocycles also gave the 1,2-*P*,*O*-ferrocenes, which is in contrast to the *N*-alkyl derivatives. Anchoring of the phosphates in a 1,3-dioxa[3]ferrocenophane structure allows *ortho*-lithiations, whereas subsequent *apFr* are prevented.

Ferrocene could be used as a probe for the investigation of the electronic properties of the different types of ferrocenyl phosphorus compounds (Section 3.1.3). Electrochemical investigations confirmed the relation between electron density and a successful nucleophilic attack at the phosphorus atom during the rearrangement process.

The suitability of these 1,2-*P*,*O*-ferrocenes as ligands for *C*,*C* cross-coupling catalysis was achieved by converting the obtained phosphonates into the respective PPh_2 derivatives, by

applying the *P*,*C* Stelzer-coupling at ferrocenyl phosphines (PH_2) for the first time. The hemilabile bonding of the oxygen atom or the 1,2-*P*,*O*-structural motif enhanced the catalytic activity of the Pd(0) species and gave the three-*ortho*-substituted biaryls in high yield and low catalyst loading. However, the usage of an enantiopure ligand did not result in an atropselective biaryl coupling, which was ascribed to the low steric demand of the methoxy substituent.

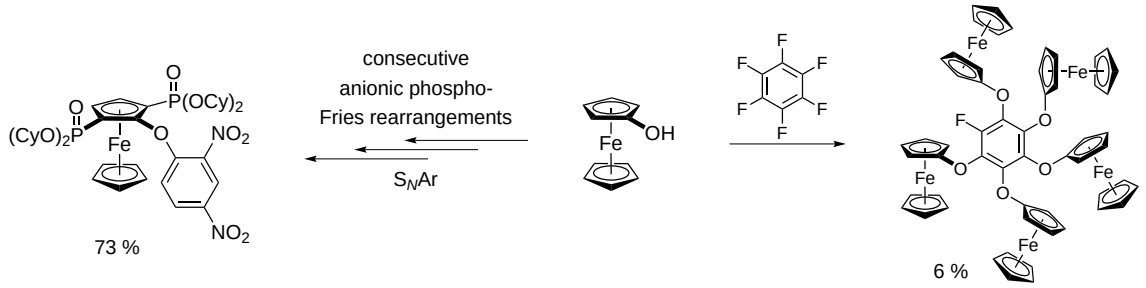


Figure 5.3 Diastereoselective anionic phospho-Fries rearrangements.

The hydroxy group was functionalized by reacting it with different electrophiles, whereas nucleophilic substitution reactions at aliphatic compounds proceeded poorly (3.2.1). Solely silyl ethers were obtained in moderate yield. A successful oxygen-functionalization could be achieved by applying nucleophilic aromatic substitutions (S_NAr) reactions at hydroxy ferrocene, which was hitherto sparsely investigated for this type of substrates (Figure 5.3). This approach gives access to a new regioselective synthetic pathway for (multi-)ferrocenyl aryl ether, despite Ullmann-type couplings (3.2.1). The S_NAr reaction tolerated *ortho*-substituents, which were introduced by anionic phospho- and thia-Fries rearrangements, whereas the electron-withdrawing character of these groups reduced the nucleophilicity of the hydroxy group and required strongly electron-deficient aryl fluorides for a successful conversion, which was supported by electrochemical investigations. Using multi-fluorinated aromatics gave multi-ferrocenyl aryl ethers with up to five ferrocenyls, as a unique example in chemistry (Figure 5.3).

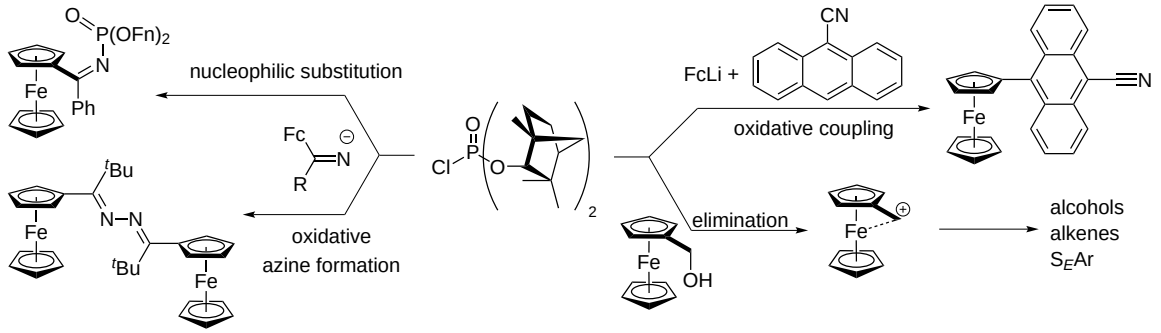


Figure 5.4 Application of a sterically hindered *chiral pool*-derived chloro phosphate as a phosphorylation and oxidative coupling agent.

Besides the classic anionic *ortho*-Fries also the C-elongated homo-Fries version was in-

vestigated (3.3.1). In contrast to ferrocenyl phosphates, which could easily be obtained, the conversion of ferrocenyl methanols into the respective phosphates was challenging. An isolation was not successful, due to their rapid elimination of phosphate anions and the consecutive reactions of the thus formed α-ferrocenylmethyl carbenium ions into alkenes, alcohols, or into arylated compounds by electrophilic aromatic substitution. Using imino-phosphoramidates as alcohol equivalents gave a variety of novel ferrocenyl derivatives. Interestingly, the sterically demanding chloro phosphate acted as a reducing agent, which has not been reported so far, giving oxidative coupled products, such as azines (Figure 5.4).

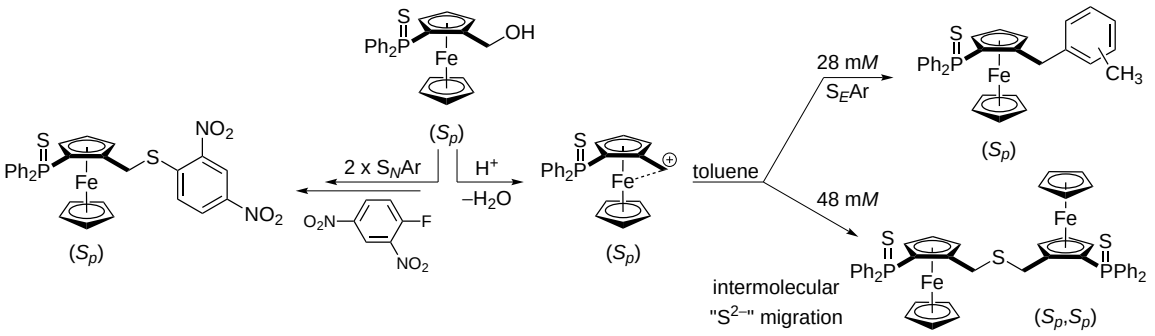


Figure 5.5 Carbocation formation of an enantiopure planar-chiral ferrocenyl methanol and subsequent intermolecular "S^{2-}" migration.

Anionic homo phospho-Fries rearrangements were circumvented and an enantiopure 1-PPh_2-2-CH_2OH compound was synthesized by a literature reported procedure. Its conversion into an aryl ether was investigated. It could be shown that the formation of ferrocenylmethyl carbenium ions takes place, which underwent electrophilic aromatic substitution (S_EAr) instead of an ether formation (Figure 5.5). Depending on the concentration of the reaction mixture a sulfur migration from the thiophosphinoyl group to the carbenium carbon takes place, giving the respective thioethers within an unique reaction mechanism. Nevertheless, the successfully isolated enantiopure arylated phosphines and a double-planar-chiral thio-ether derivative were investigated for atropselective biaryl couplings, which gave the products with up to 26 % *ee*.

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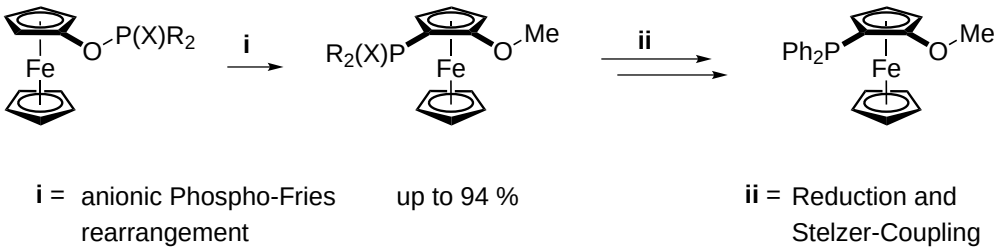
Appendix A

Anionic Phospho-Fries Rearrangement at Ferrocene: One-Pot Approach to P,O-Substituted Ferrocenes

Marcus Korb, Dieter Schaarschmidt and Heinrich Lang

published in *Organometallics* **2014**, *33*, 2099–2108.



Abstract

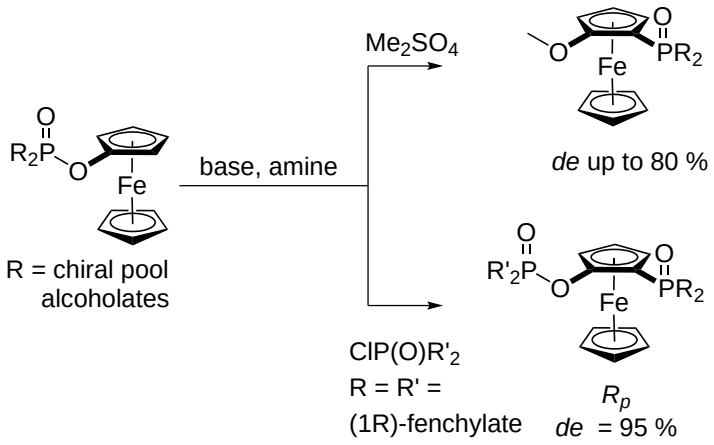
For the first time the anionic phospho-Fries rearrangement is successfully applied in ferrocene chemistry giving access to 1,2-*P*,*O*-substituted ferrocenes. The 1,3-(O→C) migration occurs at ferrocenyl phosphates, thiophosphates, phosphite-borane adducts and phosphinates by treatment with a base such as lithium diisopropylamide at low temperature, whereas the highest yields were obtained starting from diethylferrocenyl phosphate. Complete reduction of the phosphonate to a primary phosphine and subsequent Stelzer *P*,*C* cross-coupling allowed the synthesis of Fe(η^5-C_5H_3-2-OMe-PPh_2)(η^5-C_5H_5) (**1**). The qualification of **1** as supporting ligand in palladium-catalyzed Suzuki-Miyaura *C*,*C* couplings has been proven by the synthesis of sterically congested tri-ortho-substituted biaryls at mild reaction conditions in good to excellent yields.

Appendix B

Planar Chirality from the Chiral Pool: Diastereoselective Anionic Phospho-Fries Rearrangements at Ferrocene

Marcus Korb and Heinrich Lang

published in *Organometallics* **2014**, *33*, 6643–6659.



Abstract

Exclusively, the anionic phospho-Fries rearrangement has successfully been adopted on chiral ferrocenyl phosphates resulting in diastereomeric enriched 1,2-*P*,*O*-ferrocenes (up to 95 % *de*). A simple synthetic protocol for the preparation of all starting materials based on several chiral-pool alcohols, chiral (di-)chlorophosphates and the respective ferrocenyl phosphates is reported. Optimized reaction conditions for the anionic phospho-Fries rearrangement allow conversions at ambient temperature, the usage of variable lithium amid bases and diamines in hexane, ensure virtually quantitative yields and avoid side reactions. The (bi-)cyclic alkyl substituents result in air and moisture stable compounds and furthermore, allow the conversion of 1,1'-substituted derivatives to 1,1',2,2'-functionalized ferrocenes, which is reported for the first time. Simultaneous rearrangements at diferrocenylphosphates to phosphinates and even 2-hydroxy-1,3-bisphosphonato ferrocenes and their work-up under ambient conditions can be performed. Single crystal diffraction analysis allowed the determination of the absolute configuration of the planar chirality of two diastereomeric pure ferrocenes being the Rp

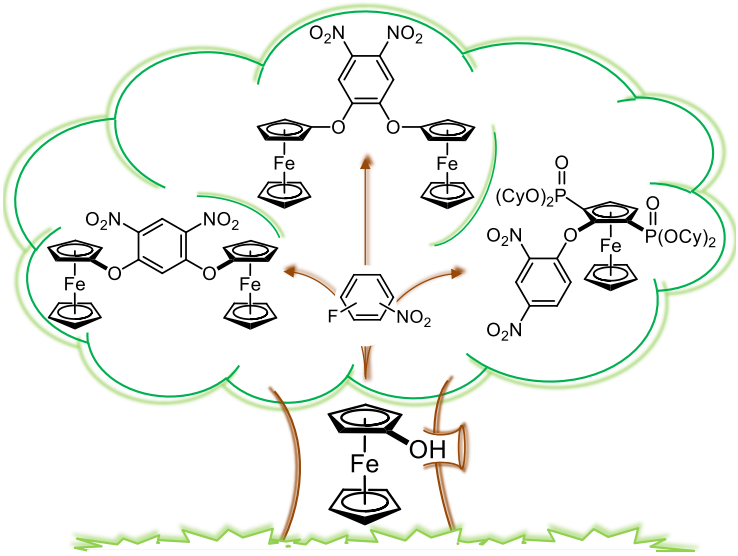
isomers. Furthermore, strong T-shaped π-π interaction patterns between aromatic C_5H_3 and C_5H_4 cycles for three compounds are observed.

Appendix C

Nucleophilic Aromatic Substitution Reactions for the Synthesis of Ferrocenyl Aryl Ethers

Marcus Korb, Pieter J. Swarts, Dominique Miesel, Alexander Hildebrandt, Jannie C. Swarts, and Heinrich Lang

published in *Organometallics* **2016**, *35*, 1287–1300.



Abstract

A range of ferrocenyl aryl ethers of type Fc–O–Ar [Fc = Fe(η^5-C_5H_5)(η^5-$C_5H_nX_{4-n}$); n = 2–4; X = H, P(O)(OEt)$_2$, SO_2CF_3; Ar = 2,4-$(NO_2)_2$-C_6H_3, 4-NO_2-C_6H_4] have successfully been prepared by using the nucleophilic aromatic substitution reaction (S_NAr) of Fc–OLi (**1a**–Li) and electron deficient aryl fluorides, enabling a new pathway to this rarely described family of organometallic compounds. Initial studies of **1a**–Li and *ortho*-phosphonato substituted hydroxyferrocenes (**1b**–Li) have also been performed, indicating a low nucleophilicity of the oxygen atom. The S_NAr reaction protocol tolerates *ortho*-substituents, *e.g.* phosphonato and sulfonyl groups resulting in 1,2-X,O (X = S, P) ferrocenyl ethers that can be obtained in an one-pot synthesis procedure including 1,3-O→C anionic phospho- and thia-Fries rearrangements. Within these studies, the first 1,3-diortho-functionalized ferrocenyl

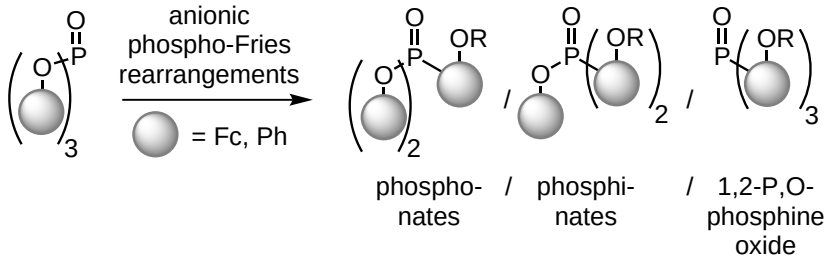
aryl ether could be synthesized. An electrochemical study of the redox potentials of the obtained compounds allows conclusions on the reactivity of the varying electronic properties and the electrophilicity of different aryl fluorides and the nucleophilicity of the functionalized hydroxyl ferrocenes, which is directly reflected by the potential of the first ferrocene related redox processes. Chiral-pool-based phosphonates rearrange to the aryl ethers with a diastereomeric excess of 74 and 81 % after the anionic Fries rearrangement. The usage of aryl-1,2/1,3-difluorides resulted in the synthesis of the first examples of bis(FcO) substituted benzenes. Their electrochemical investigations reveal a splitting of the two redox processes of the ferrocenyls that decreases from 155 mV (1,2-substitution) to 130 mV (1,3-substitution) based on electrostatic interactions.

Appendix D

A reactivity study of phenyl and ferrocenyl phosphates within the anionic phospho-Fries rearrangement

Marcus Korb and Heinrich Lang

published in *Inorg. Chem. Commun.* **2016**, *72*, 30–32.



Abstract

Temperature-dependent anionic phospho-Fries rearrangements of ferrocenyl/phenyl phosphates P(O)(OFc)n(OPh)$_{3-n}$ (Fc = Fe(η^5-C$_5$H$_5$)(η^5-C$_5$H$_4$); n = 0,1,2,3) were investigated. Whereas ferrocenyls solely undergo one rearrangement per reaction step, the number of phenyl-based 1,3-O→C shifts depends on the temperature. This results in different types of otherwise hardly accessible mixed ferrocenyl/phenyl organophosphorus compounds. Detailed investigations of the triple-rearrangement of triphenyl phosphate (n = 0) reveals a consecutive formation of its phosphonate and phosphinate prior to the known phosphane oxide.

Appendix E

Multi-Ferrocenyl Aryl Ethers - Applying Nucleophilic Aromatic Substitution Reactions to Aryl Fluorides

Marcus Korb and Heinrich Lang

published in *Eur. J. Inorg. Chem.* **2017**, *2017*, 276–287.

This article is part of "The Multifaceted Chemistry of Ferrocene" Cluster Issue.

Abstract

The reaction of ferrocenol [FcOH; Fc = Fe(η^5-C_5H_5)-(η^5-C_5H_4)] with aryl fluorides $ArH_{6-n}F_n$ (n = 3–6) within a nucleophilic aromatic substitution reaction (S_NAr) gave ferrocenyloxy-substituted fluorobenzenes of general type $C_6H_{0-3}F_{1-5}(OFc)_{1-5}$. For 1,3,5-$C_6H_3F_3$, 1,2,4,5-$C_6H_2F_4$, and $C_6H_{6-n}F_n$ (n = 5,6), one, two, and three F atoms, respectively, could be replaced by FcO units. The reaction of 1,4-$(OFc)_2$-C_6F_4 with additional amounts of FcOH afforded the tetra- and penta-substituted arenes 3,6-F_2-$C_6(OFc)_4$ and $C_6F(OFc)_5$. Electrochemical investigations of both compounds showed four or five Fc/Fc^+ related reversible redox processes that were attributed to electrostatic interactions. The addition of C_6F_6 as the electrophile after the anionic phospho-Fries rearrangement of a ferrocenyl phosphate (1,3-O→C migration) to the 1,2-substituted *ortho*-phosphonato ferrocenol, resulted in the formation of the respective ortho-functionalized ether. The constitution of all compounds was verified by using ^{19}F NMR spectroscopy. Steric hindrance of the *ortho*-substituent resulted in a doubling of the signal sets for the C_6F_5 moiety in the $^{13}C\{^1H\}$ and ^{19}F NMR spectra. The identity and substitution pattern of five compounds could also be determined by using single-crystal X-ray diffraction analysis, revealing the 1,4-constitution of double functionalized derivatives, intermolecular non-classical C–H···F interactions and π interactions.

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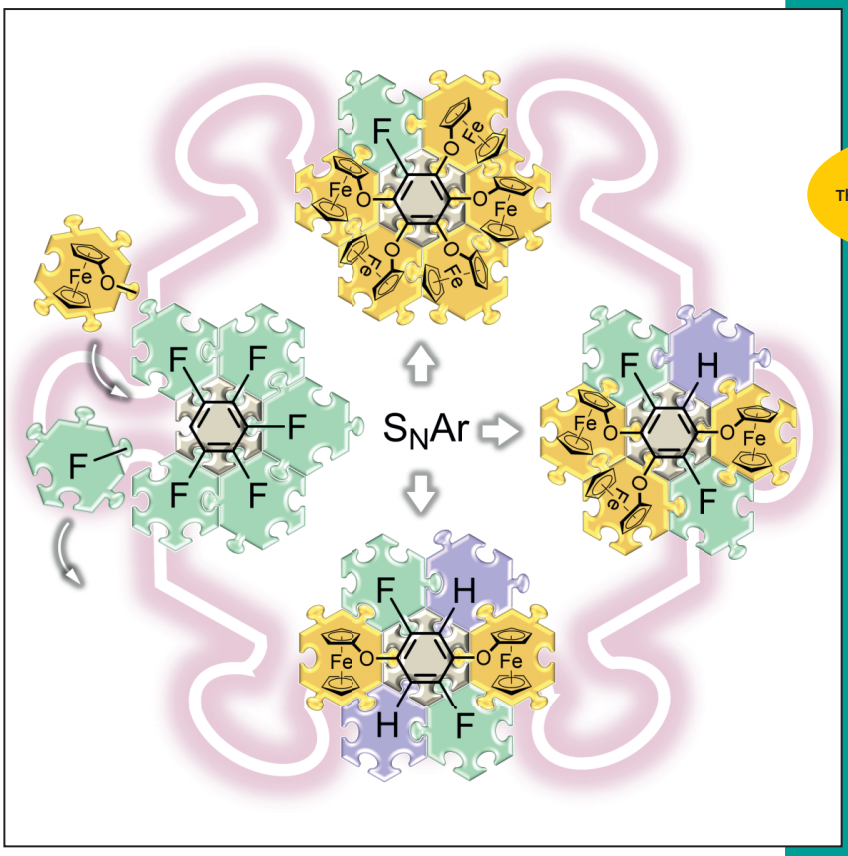
Cluster Issue:
The Multifaceted Chemistry of Ferrocene



Inside Cover

Marcus Korb and Heinrich Lang
Multi-Ferrocenyl Aryl Ethers – Applying Nucleophilic Aromatic Substitution Reactions to Aryl Fluorides

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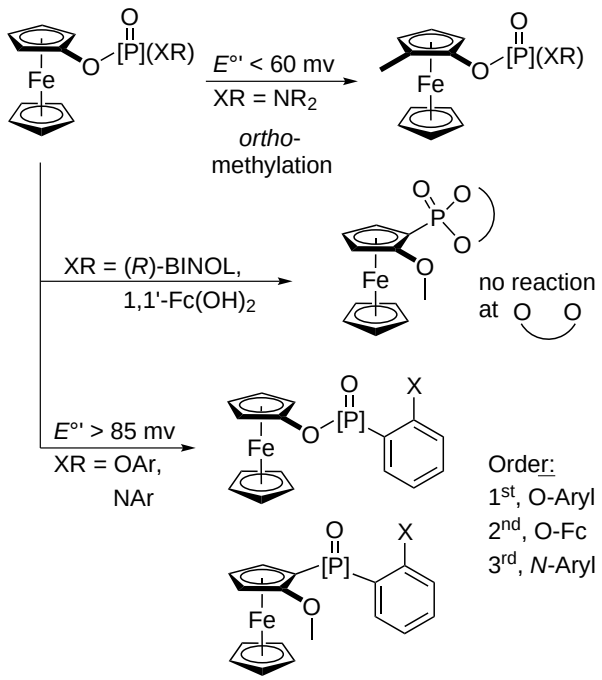
Appendix F

Reactivity of Ferrocenyl Phosphates Bearing (Hetero-)Aromatics and [3]Ferrocenophanes toward Anionic Phospho-Fries Rearrangements

Marcus Korb, Steve W. Lehrich and Heinrich Lang

published in *J. Org. Chem.* **2017**, *82*, 3102–3124.



Abstract

The temperature-dependent behavior within anionic phospho-Fries rearrangements (apFr) of $P(O)(OFc)_n(EAr)_{3-n}$ (Fc = Fe(η^5-C_5H_5)(η^5-C_5H_4); E = O; Ar = phenyl, naphthyls, (*R*)-BINOL, [3]ferrocenophanyl; E = N, 1*H*-pyrrolyl, 1*H*-indolyl, 9*H*-carbazolyl; n = 1–3) is reported. While Fc undergoes one, the Ph-based *apFr* depends on temperature. First, the aryls are lithiated and rearranged, followed by Fc and N-heterocycles. Addition of Me_2SO_4 thus gave methylated Fc, contrary to non-organometallic aromatics giving mixtures of HO

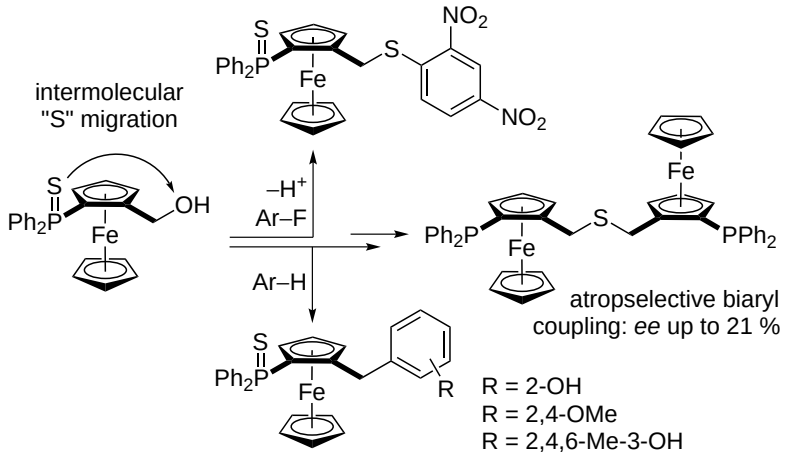
and MeO derivatives. The (*R*)-BINOL Fc phosphate gave Fc-rearranged phosphonate in 91% de. Exchanging O- with N-aliphatics prevented apFr, due to higher electron density at P. Also 1,2-N→C migrations were observed. X-ray analysis confirms 1D H bridge bonds for OH and NH derivatives. The differences in reactivity between N-aliphatic and N-aromatic phosphoramidates were verified by electrochemistry. The redox potentials revealed lower values for the electron-rich aliphatics, showing no apFr, preventing a nucleophilic attack at P after lithiation. Redox separations for multiple Fc molecules are based on electrostatic interactions.

Appendix G

P,C-Sulfur Migration from Thiophosphinylferrocenyl Carbenium Ions to Phosphinylthioethers

Marcus Korb, Julia Mahrholdt and Heinrich Lang

accepted by *Eur. J. Inorg. Chem.* 10.1002/ejic.201700645.



Abstract

The reaction of $FcCH_2OH$ with chlorophosphates gave ferrocenyl phosphates $FcCH_2OP(O)(OR)_2$ (Fc = $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)$), which are promising starting materials for anionic homo phospho-Fries rearrangements. However, the corresponding phosphates separate into phosphate anions and ferrocenyl carbo-cations of which the latter one undergoes consecutive reactions. Thus, electrophilic aromatic substitutions with the substrates occurred. As an alternative, treatment of nitriles in presence of FcLi or ^{t}BuLi and subsequent addition of chlorophosphates gave several novel chiral-pool based ferrocenyl imino phosphoramidates of type Fc–CR=N–P(O)$(OR^*)_2$ as auspicious educts for anionic homo phospho-Fries rearrange-ments. Unexpectedly, the sterically demanding chiral chlorophosphate with R* acted as a reducing agent, enabling oxidative coupling of the imines to a diferrocenyl azine. In similarity, the reaction of Fc–Li with 9-anthrylnitrile produced a 10-ferrocenyl-substituted product, contrary to a reaction at the C≡N functionality within this rarely described oxidative cou-pling. The ferrocenyl methanol 1,2-P(S)Ph_2,CH_2OH

motif was used for the synthesis of a novel planar-chiral ligand system. Under acidic conditions, however, dehydration occurs and the remaining ferrocenylmethyl carbo-cation was sulfurized in a unique way giving thio ethers as evidenced by single crystal X-ray diffraction analysis. The migration of sulfur to a carbo-cation was also observed under nucleophilic conditions, whereby the 1,2-P(S)Ph_2,CH_2OH ferrocene acts as unique sulfur and electron source. In contrast, the presence of electron-rich aromatics within this synthetic protocol resulted in several enantiopure planar-chiral *o*-, *p*- and *m*-substituted arylmethyl ferrocenes under S_EAr reactions conditions, depending on the carbo-cation concentration. For catalytic studies, a novel stereopure ferrocenylmethyl thio ether and a compound derived from the S_EAr reaction with anisol have been used as supporting ligands in Pd-catalyzed Suzuki-Miyaura *C*,*C* cross-coupling reactions for the atropselective synthesis of hindered biaryls with up to 26 % *ee* at low catalyst loadings (1 mol-% Pd). This verifies that the planar-chirality of the ferrocenyl backbone transfers the chiral information via a hemilabile bonding to the biaryl substrate.

Appendix H Crystallographic Data

Table 5.1 Crystal-, collection- and refinement details for **15**, **20** and **23**.

Compound	**15**	**20**	**23**
CCDC Number	1508136	1028721	978227
Empirical Formula	$C_{13}H_{19}BFeNO_2P$	$C_{23}H_{21}FeO_2P$	$C_{16}H_{19}PS$
Formula Weight / g·mol^{-1}	318.92	416.22	274.34
Temperature / K	107.35(10)	110.00(10)	110.00(10)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Orthorhombic	Orthorhombic	Triclinic
Space Group	Pbc	$P2_12_12_1$	$P\bar{1}$
a / Å	11.8453(10)	8.3581(4)	9.1715(7)
b / Å	11.2052(10)	8.5846(4)	11.9513(8)
c / Å	21.0840(15)	27.2615(14)	13.8640(10)
α / deg	–	–	86.089(6)
β/ deg	–	–	88.870(6)
γ/ deg	–	–	76.849(6)
Volume / Å^3	2798.5(4)	1956.04(16)	1476.34(18)
ρ_{ber} / g · cm^{-3}	1.514	1.413	1.234
$F(000)$	1328	864	584
Crystal Dimensions / mm	0.40 · 0.20 · 0.20	0.3 · 0.2 · 0.08	0.4 · 0.4 · 0.4
Z	8	4	4
Max. and min. Transmission	1.00000, 0.86648	1.00000, 0.97511	1.00000, 0.61599
μ / mm^{-1}	1.187	0.868	0.308
θ-Range / deg	3.162 to 25.997	2.99 to 25.50	3.00 to 25.00
Limiting indices	-14≤h≤13 –8≤k≤13 –26≤l≤22	–10≤h≤6 –10≤k≤10 –31≤l≤33	–10≤h≤10 –14≤k≤13 –16≤l≤11
Reflections Collected / Unique	7044 / 2722	5954 / 3481	9738 / 5158
Completeness to θ_{max} / %	99.2	99.8	99.2
Restraints / Parameters	0 / 185	93 / 246	5158 /
R_{int}	0.0481	0.0336	0.0700
R_1, wR_2 [I ≥ 2 σ(I)]	0.0559, 0.1429	0.0385, 0.0767	0.0907, 0.2353
R_1, wR_2 (all Data)	0.0699, 0.1488	0.0436, 0.0788	0.1004, 0.2484
Goodness-of-fit S	1.085	1.045	1.058
$\Delta\rho$ / e$^-$ Å^{-3}	1.190, –0.753	0.450, –0.298	1.776, –0.762
Absolute Structure Parameter	–	0.012(19)	–

Table 5.2 Crystal-, collection- and refinement details for **30a**, **30b** and **30e**.

Compound	**30a**	**30b**	**30e**
CCDC Number	1024126	1024118	1024119
Empirical Formula	$C_{22}H_{31}FeO_4P$	$C_{30}H_{47}FeO_4P$	$C_{60}H_{86}Fe_2O_8P_2$
Formula Weight / g·mol^{-1}	446.29	558.50	1108.92
Temperature / K	110.00(10)	110.00(10)	110.0(10)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Orthorhombic	Triclinic
Space Group	$P2_1/c$	$P2_12_12_1$	$P1$
a / Å	12.4882(12)	7.3970(2)	11.6913(4)
b / Å	18.1115(14)	18.0245(4)	11.8705(4)
c / Å	9.7751(9)	21.8203(6)	12.0874(4)
α / deg	–	–	62.396(3)
β/ deg	111.679(11)	–	77.005(3)
γ/ deg	–	–	69.734(3)
Volume / Å^3	2054.5(3)	2909.24(13)	1390.35(9)
ρ_{ber} / g · cm^{-3}	1.443	1.275	1.324
$F(000)$	944	1200	592
Crystal Dimensions / mm	0.4 · 0.4 · 0.25	0.35 · 0.25 · 0.20	0.2 · 0.2 · 0.1
Z	4	4	1
Max. and min. Transmission	1.00000, 0.23774	1.00000, 0.66822	1.00000, 0.84431
μ / mm^{-1}	0.838	0.606	0.633
θ-Range / deg	3.176 to 25.999	2.91 to 26.00	3.106 to 24.997
Limiting indices	–14≤h≤15 –20≤k≤22 –10≤l≤12	9≤h≤9 –22≤k≤14 –18≤l≤26	–12≤h≤13 –14≤k≤13 –14≤l≤14
Reflections Collected / Unique	9663 / 4006	18502 / 5616	10832 / 7207
Completeness to θ_{max} / %	99.3	99.7	99.7
Restraints / Parameters	0 / 253	0 / 331	4 / 672
R_{int}	0.0719	0.0590	0.0156
R_1, wR_2 [I ≥ 2 σ(I)]	0.0822, 0.2037	0.0382, 0.0879	0.0425, 0.1058
R_1, wR_2 (all Data)	0.0982, 0.2208	0.0439, 0.0912	0.0451, 0.1081
Goodness-of-fit S	1.007	1.035	1.043
$\Delta\rho$ / e$^-$ Å^{-3}	1.817, –1.076	0.496, –0.279	0.629, –0.527
Absolute Structure Parameter	–	–0.018(14)	0.012(8)

Table 5.3 Crystal-, collection- and refinement details for **31e**, **35c** and **43b**.

Compound	**31e**	**35c** · 0.25 $CHCl_2$	**43b**
CCDC Number	1024120	1024121	1024123
Empirical Formula	$C_{31}H_{45}FeO_4P$	$C_{50}H_{76}FeO_7P_2$ · 0.25 $CHCl_2$	$C_{30}H_{37}Fe_2O_4P$
Formula Weight / g·mol^{-1}	568.49	928.12	604.26
Temperature / K	110.00(10)	110.00(10)	110.2(6)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Orthorhombic	Monoclinic	Monoclinic
Space Group	$P2_12_12_1$	$C2$	$P2_1$
a / Å	7.7485(2)	43.1922(8)	14.1041(13)
b / Å	10.6896(3)	8.5461(2)	5.8359(5)
c / Å	34.4462(10)	26.5582(5)	16.704(2)
α / deg	–	–	–
β/ deg	–	90.458(2)	92.648(9)
γ/ deg	–	–	–
Volume / Å^3	2853.12(14)	9803.0(3)	1373.4(2)
ρ_{ber} / g · cm^{-3}	1.323	1.258	1.461
F(000)	1216	3988	632
Crystal Dimensions / mm	0.4 · 0.15 · 0.15	0.4 · 0.4 · 0.2	0.4 · 0.1 · 0.02
Z	4	8	2
Max. and min. Transmission	1.00000, 0.91937	1.00000, 0.91200	1.00000, 0.03517
μ / mm^{-1}	0.619	0.449	1.149
θ-Range / deg	2.88 to 26.00	2.875 to 25.500	2.892 to 24.997
Limiting indices	–9≤h≤9 –13≤k≤13 –41≤l≤42	–52≤h≤51 –8≤k≤10 –32≤l≤32	–16≤h≤14 –6≤k≤6 –18≤l≤19
Reflections Collected / Unique	25582 / 5602	41406 / 16504	5764 / 4257
Completeness to θ_{max} / %	99.4	99.0	99.5
Restraints / Parameters	0 / 341	56 / 1114	78 / 302
R_{int}	0.0363	0.0229	0.1381
R_1, wR_2 [I ≥ 2 σ(I)]	0.0269, 0.0580	0.0333, 0.0807	0.0908, 0.1454
R_1, wR_2 (all Data)	0.0308, 0.0595	0.0370, 0.0825	0.1476, 0.1790
Goodness-of-fit S	1.022	1.021	0.907
$\Delta\rho$ / e$^-$ Å^{-3}	0.217, –0.201	1.138, –0.546	1.291, –1.310
Absolute Structure Parameter	0.000(10)	0.005(4)	0.02(6)

Table 5.4 Crystal-, collection- and refinement details for **43e**, **44a** and **44c**.

Compound	**43e**	**44a**	**44c**
CCDC Number	1525260	1024125	1024122
Empirical Formula	$C_{24}H_{28}Fe_2NO_3P$	$C_{27}H_{31}Fe_2O_4P$	$C_{66}H_{84}Fe_4O_9P_2$
Formula Weight / g·mol^{-1}	521.14	562.19	1306.67
Temperature / K	110.00(10)	109.95(10)	109.95(10)
Wavelength / Å	0.71073	0.71073	1.54184
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$C2/c$	$P2_1/c$	$C2$
a / Å	51.506(2)	13.9652(7)	34.8430(15)
b / Å	7.4283(3)	8.1909(5)	8.2055(3)
c / Å	11.2434(5)	21.2807(12)	21.7894(11)
α / deg	–	–	–
β/ deg	90.380(4)	97.814(5)	106.881(5)
γ/ deg	–	–	–
Volume / Å^3	4301.7(3)	2411.6(2)	5961.2(5)
ρ_{ber} / g · cm^{-3}	1.609	1.548	1.456
$F(000)$	2160	1168	2744
Crystal Dimensions / mm	0.4 · 0.4 · 0.4	0.4 · 0.1 · 0.02	0.4 · 0.1 · 0.1
Z	8	4	4
Max. and min. Transmission	1.00000, 0.73288	1.00000, 0.73791	1.00000, 0.26850
μ / mm^{-1}	1.451	1.302	8.621
θ-Range / deg	3.164 to 26.000	2.945 to 24.998	3.846 to 63.590
Limiting indices	–63≤h≤63 –9≤k≤9 –13≤l≤13	–16≤h≤16 –9≤k≤9 –25≤l≤25	–40≤h≤39 –6≤k≤9 –25≤l≤22
Reflections Collected / Unique	27226 / 4196	11049 / 4244	13199 / 7006
Completeness to θ_{max} / %	99.3	99.6	98.9
Restraints / Parameters	0 / 282	0 / 308	220 / 753
R_{int}	0.0546	0.0399	0.0259
R_1, wR_2 [I ≥ 2 σ(I)]	0.0420, 0.1043	0.0404, 0.0913	0.0316, 0.0746
R_1, wR_2 (all Data)	0.0456, 0.1063	0.0570, 0.0985	0.0354, 0.0762
Goodness-of-fit S	1.096	1.031	0.985
$\Delta\rho$ / e$^-$ Å^{-3}	1.014, –0.548	0.804, –0.499	0.535, –0.418 e.
Absolute Structure Parameter	–	–	–0.003(5)

Table 5.5 Crystal-, collection- and refinement details for **44d**, **48** and **49**.

Compound	**44d**	**48**	**49**
CCDC Number	1024124	1474110	1508129
Empirical Formula	$C_{31}H_{37}Fe_2O_4P$	$C_{26}H_{23}Fe_2O_4P$	$C_{30}H_{25}Fe_2O_4P$
Formula Weight / g·mol^{-1}	616.27	542.11	592.17
Temperature / K	293(2)	110.5(3)	110.6(2)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1$	$P2_1/n$	$P2_1/c$
a / Å	14.7944(13)	9.7078(5)	15.6912(9)
b / Å	8.3537(7)	9.0603(4)	10.1639(4)
c / Å	22.2802(17)	24.536(3)	17.1179(9)
α / deg	–	–	–
β/ deg	96.930(7)	92.431(7)	117.157(7)
γ/ deg	–	–	–
Volume / Å^3	2733.4(4)	2156.1(3)	2429.1(3)
ρ_{ber} / g·cm^{-3}	1.498	1.670	1.619
$F(000)$	1288	1112	1216
Crystal Dimensions / mm	0.10 · 0.10 · 0.10	0.4 · 0.35 · 0.3	0.4 · 0.3 · 0.3
Z	4	4	4
Max. and min. Transmission	–	1.00000, 0.68673	1.00000, 0.84124
μ / mm^{-1}	1.156	1.453	1.298
θ-Range / deg	2.900 to 24.999	3.164 to 24.993	3.121 to 24.998
Limiting indices	–17≤h≤17 –9≤k≤9 –26≤l≤26	–8≤h≤11 –7≤k≤10 –28≤l≤29	–18≤h≤18 –11≤k≤12 –20≤l≤20
Reflections Collected / Unique	22814 / 9551	7984 / 3801	11444 / 4270
Completeness to θ_{max} / %	99.5	99.8	99.6
Restraints / Parameters	16 / 591	0 / 298	0 / 334
R_{int}	0.1117	0.0268	0.0222
R_1, wR_2 [I ≥ 2 σ(I)]	0.0679, 0.0825	0.0346, 0.0730	0.0675, 0.1637
R_1, wR_2 (all Data)	0.1636, 0.1003	0.0436, 0.0765	0.0762, 0.1719
Goodness-of-fit S	0.894	1.046	1.034
$\Delta\rho$ / e$^-$ Å^{-3}	0.514, –0.505	0.625, –0.488	0.950, –0.479
Absolute Structure Parameter	0.01(4)	–	–

Table 5.6 Crystal-, collection- and refinement details for **52**, **53** and **56**.

Compound	**52**	**53**	**56**
CCDC Number	1474107	1474108	1474109
Empirical Formula	$C_{31}H_{29}Fe_3O_4P$	$C_{32}H_{31}Fe_3O_4P$	$C_{18}H_{15}O_4P$
Formula Weight / g·mol^{-1}	664.06	678.09	326.27
Temperature / K	112.4(5)	111.8(2)	120.00(10)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Triclinic	Monoclinic	Orthorhombic
Space Group	$P\bar{1}$	$P2_1/c$	Pnm
a / Å	8.0069(5)	11.204(5)	13.5139(6)
b / Å	11.3428(11)	8.613(5)	16.1835(10)
c / Å	15.2484(14)	28.024(5)	7.1844(4)
α / deg	88.134(8)	–	–
β/ deg	76.822(7)	101.182(5)	–
γ/ deg	78.953(6)	–	–
Volume / Å^3	1323.3(2)	2653(2)	1571.24(15)
ρ_{ber} / g·cm^{-3}	1.667	1.698	1.379
$F(000)$	680	1392	680
Crystal Dimensions / mm	0.2 · 0.2 · 0.1	0.2 · 0.1 · 0.02	0.4 · 0.3 · 0.05
Z	2	4	4
Max. and min. Transmission	1.00000, 0.9513	1.00000, 0.73740	1.00000, 0.45363
μ / mm^{-1}	1.721	1.718	0.193
θ-Range / deg	3.258 to 24.998	3.180 to 25.000	3.929 to 25.994
Limiting indices	–9≤h≤9 –13≤k≤13 –18≤l≤18	–12≤h≤13 –10≤k≤10 –33≤l≤33	–16≤h≤14 –19≤k≤19 –8≤l≤7
Reflections Collected / Unique	7290 / 7290	16882 / 4664	4567 / 1589
Completeness to θ_{max} / %	99.6	99.7	99.3
Restraints / Parameters	0 / 354	823 / 455	0 / 118
R_{int}	–	0.0749	0.0473
R_1, wR_2 [I ≥ 2 σ(I)]	0.0409, 0.0772	0.0556, 0.1249	0.0465, 0.1099
R_1, wR_2 (all Data)	0.0653, 0.0812	0.0729, 0.1316	0.0646, 0.1206
Goodness-of-fit S	0.845	1.094	1.054
$\Delta\rho$ / e$^-$ Å^{-3}	0.646, –0.444	0.710, –0.559	0.287, –0.450
Absolute Structure Parameter	–	–	–

Table 5.7 Crystal-, collection- and refinement details for **59a**, **65b**, and **67**.

Compound	**59a**	**65b**	**67**
CCDC Number	1474111	1474112	1508130
Empirical Formula	$C_{26}H_{23}Fe_2O_4P$	$C_{24}H_{23}FeO_4P$	$C_{31}H_{27}Fe_2O_4P$
Formula Weight / g·mol^{-1}	542.11	462.24	606.19
Temperature / K	110.6(2)	120.00(10)	114(3)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic	Triclinic
Space Group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a / Å	13.4841(7)	9.1403(4)	7.3299(4)
b / Å	7.2373(4)	7.6690(5)	12.7651(8)
c / Å	23.0311(14)	28.9649(16)	15.0173(8)
α / deg	–	–	111.569(5)
β/ deg	106.700(6)	91.773(4)	97.970(4)
γ/ deg	–	–	94.641(4)
Volume / Å^3	2152.8(2)	2029.38(19)	1280.77(13)
ρ_{ber} / g·cm^{-3}	1.673	1.513	1.572
F(000)	1112	960	624
Crystal Dimensions / mm	0.3 · 0.1 · 0.02	0.2 · 0.2 · 0.02	0.1 · 0.1 · 0.02
Z	4	4	2
Max. and min. Transmission	1.00000, 0.57123	1.00000, 0.88379	1.00000, 0.89351
μ / mm^{-1}	1.455	0.852	1.233
θ-Range / deg	3.155 to 24.999	3.645 to 28.887	2.951 to 24.998
Limiting indices	–16≤h≤15 –8≤k≤8 –27≤l≤27	–12≤h≤11 –10≤k≤10 –38≤l≤35	–8≤h≤8 –15≤k≤15 –17≤l≤15
Reflections Collected / Unique	11446 / 3778	9840 / 4556	7844 / 7844
Completeness to θ_{max} / %	99.5	99.7	99.8
Restraints / Parameters	0 / 300	114 / 320	905 / 584
R_{int}	0.0693	0.0280	0.0749
R_1, wR_2 [I ≥ 2 σ(I)]	0.0516, 0.1036	0.0373, 0.0825	0.1138, 0.3270
R_1, wR_2 (all Data)	0.0827, 0.1137	0.0484, 0.0887	0.1718, 0.3500
Goodness-of-fit S	1.015	1.022	1.139
$\Delta\rho$ / e$^-$ Å^{-3}	1.338, –0.562	0.428, –0.328	0.38(4)
Absolute Structure Parameter	–	–	–

Table 5.8 Crystal-, collection- and refinement details for **69b**, **70a** and **71b**.

Compound	**69b**	**70a**	**71b** · $CHCl_3$
CCDC Number	1508131	1508132	1508133
Empirical Formula	$C_{32}H_{29}Fe_2O_4P$	$C_{20}H_{17}Fe_2O_4P$	$C_{31}H_{23}FeO_4P \cdot CHCl_3$
Formula Weight / g·mol^{-1}	620.22	464.01	665.68
Temperature / K	115(8)	120.00(10)	120.00(10)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Triclinic	Orthorhombic	Orthorhombic
Space Group	$P\bar{1}$	$Fdd2$	$P2_12_12_1$
a / Å	11.1871(6)	37.5107(16)	10.4155(3)
b / Å	11.4582(8)	29.4085(15)	11.6395(4)
c / Å	12.6451(9)	6.2109(4)	23.3299(12)
α / deg	67.616(7)	–	–
β/ deg	83.493(5)	–	–
γ/ deg	62.541(6)	–	–
Volume / Å^3	1326.08(17)	6851.5(6)	2828.31(19)
ρ_{ber} / g · cm^{-3}	1.553	1.799	1.563
$F(000)$	640	3776	1360
Crystal Dimensions / mm	0.10 · 0.05 · 0.05	0.25 · 0.18 · 0.15	0.3 · 0.3 · 0.2
Z	2	16	4
Max. and min. Transmission	1.00000, 0.79435	1.00000, 0.63392	1.00000, 0.81669
μ / mm^{-1}	1.192	1.812	0.912
θ-Range / deg	3.190 to 24.998	3.396 to 25.000	3.150 to 25.998
Limiting indices	–13≤h≤13 –11≤k≤13 –14≤l≤15	–32≤h≤44 –32≤k≤34 –7≤l≤5	–12≤h≤12 –9≤k≤14 –28≤l≤10
Reflections Collected / Unique	9547 / 4629	6036 / 2393	8885 / 5412
Completeness to θ_{max} / %	99.5	99.6	99.7
Restraints / Parameters	0 / 354	1 / 244	0 / 371
R_{int}	0.0400	0.0642	0.0348
R_1, wR_2 [I ≥ 2 σ(I)]	0.0461, 0.1101	0.0316, 0.0616	0.0433, 0.0920
R_1, wR_2 (all Data)	0.0648, 0.1169	0.0400, 0.0640	0.0528, 0.0965
Goodness-of-fit S	1.032	1.039	1.024
$\Delta\rho$ / e$^-$ Å^{-3}	1.024, –0.384	0.382, –0.326	0.481, –0.420
Absolute Structure Parameter	–	–0.01(2)	0.012(16)

Table 5.9 Crystal-, collection- and refinement details for **73**, **76** and **80**.

Compound	**73**	**76**	**80**
CCDC Number	1508134	1508135	1508137
Empirical Formula	$C_{22}H_{29}FeO_4P$	$C_{30}H_{24}Fe_3O_8P_2$	$C_{28}H_{24}Fe_2NO_3P$
Formula Weight / g·mol^{-1}	444.27	741.98	565.15
Temperature / K	120.00(10)	120.00(10)	115.00(10)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Triclinic	Monoclinic
Space Group	$P2_1$	$P\bar{1}$	$P2_1/c$
a / Å	11.8102(2)	6.2344(4)	14.7934(9)
b / Å	10.9946(2)	7.6337(6)	10.0854(5)
c / Å	16.4247(3)	13.7942(9)	16.8952(11)
α / deg	–	95.156(6)	–
β/ deg	108.344(2)	91.298(5)	112.527(7)
γ/ deg	–	97.059(6)	–
Volume / Å^3	2024.34(7)	648.50(8)	2328.4(3)
ρ_{ber} / g·cm^{-3}	1.458	1.900	1.612
$F(000)$	936	376	1160
Crystal Dimensions / mm	0.4 · 0.3 · 0.3	0.4 · 0.1 · 0.01	0.25 · 0.25 · 0.20
Z	4	1	4
Max. and min. Transmission	1.00000, 0.91165	1.00000, 0.92994	1.00000, 0.5350
μ / mm^{-1}	0.850	1.837	1.348
θ-Range / deg	3.454 to 25.999	2.957 to 24.996	3.602 to 24.998
Limiting indices	–14≤h≤13 –13≤k≤13 –20≤l≤19	–7≤h≤7 –9≤k≤8 –15≤l≤16	–17≤h≤17 –11≤k≤11 –12≤l≤20
Reflections Collected / Unique	17922 / 7731	4195 / 2277	10167 / 4067
Completeness to θ_{max} / %	99.5	99.9	99.3
Restraints / Parameters	1 / 505	0 / 196	0 / 316
R_{int}	0.0269	0.0241	0.0508
R_1, wR_2 [I ≥ 2 σ(I)]	0.0322, 0.0847	0.0339, 0.0873	0.0483, 0.0967
R_1, wR_2 (all Data)	0.0344, 0.0863	0.0380, 0.0896	0.0773, 0.1058
Goodness-of-fit S	1.032	1.070	1.026
$\Delta\rho$ / e$^-$ Å^{-3}	0.297, –0.299	0.827, –0.401	0.608, –0.452
Absolute Structure Parameter	0.002(8)	–	–

Table 5.10 Crystal-, collection- and refinement details for **81**, **84** and **85**.

Compound	**81**	**84** · 0.9 CH_2Cl_2	**85**
CCDC Number	1508138	1508139	1508140
Empirical Formula	$C_{32}H_{26}Fe_2NO_3$	$C_{33}H_{28}Fe_2NO_3P$ · 0.9 CH_2Cl_2	$C_{24}H_{22}Fe_2NO_3$
Formula Weight / g·mol^{-1}	615.21	705.67	515.09
Temperature / K	114(3)	112.8(6)	115.2(10)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Triclinic	Triclinic	Monoclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a / Å	10.113(5)	10.3336(7)	51.278(8)
b / Å	10.722(5)	12.6046(10)	7.6986(8)
c / Å	13.199(5)	13.4915(18)	10.4339(12)
α / deg	106.582(5)	117.494(10)	–
β/ deg	110.145(5)	95.558(8)	93.689(11)
γ/ deg	90.019(5)	96.286(6)	–
Volume / Å^3	1280.0(10)	1527.6(3)	4110.5(9)
ρ_{ber} / g · cm^{-3}	1.596	1.534	1.665
$F(000)$	632	724	2112
Crystal Dimensions / mm	0.23 · 0.15 · 0.01	0.40 · 0.35 · 0.30	0.10 · 0.01 · 0.01
Z	2	2	8
Max. and min. Transmission	1.00000, 0.78460	1.00000, 0.58117	1.00000, 0.4394
μ / mm^{-1}	1.233	1.196	1.517
θ-Range / deg	3.008 to 25.000	3.323 to 24.999	3.629 to 24.993
Limiting indices	–12≤h≤12 –12≤k≤12 –15≤l≤15	–12≤h≤12 –14≤k≤14 –16≤l≤15	–38≤h≤60 –9≤k≤8 –12≤l≤11
Reflections Collected / Unique	6100 / 6100	10217 / 5353	7967 / 3538
Completeness to θ_{max} / %	99.6	99.5	97.9
Restraints / Parameters	676 / 408	4 / 417	0 / 281
R_{int}	–	0.0369	0.0836
R_1, wR_2 [I ≥ 2 σ(I)]	0.0806, 0.2336	0.0777, 0.2109	0.0875, 0.1851
R_1, wR_2 (all Data)	0.1001, 0.2431	0.0954, 0.2253	0.1382, 0.2062
Goodness-of-fit S	1.029	1.053	1.059
$\Delta\rho$ / e$^-$ Å^{-3}	1.306, –1.013	1.778, –0.455	0.726, –0.496
Absolute Structure Parameter	–	–	–

Table 5.11 Crystal-, collection- and refinement details for **86**, **91** and **96a**.

Compound	**86** · $CHCl_3$	**91**	**96a**
CCDC Number	1508141	978226	1446860
Empirical Formula	$C_{28}H_{24}Fe_2NO_3P \cdot CHCl_3$	$C_{23}H_{21}FeOP$	$C_{16}H_{12}FeN_2O_5$
Formula Weight / g·mol^{-1}	684.52	400.22	368.13
Temperature / K	115.00(10)	107.1(2)	110(2)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic	Triclinic
Space Group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a / Å	14.5249(6)	8.1036(2)	7.6575(5)
b / Å	10.2459(5)	19.4551(4)	12.3403(8)
c / Å	19.6024(8)	12.1025(3)	16.1955(11)
α / deg	–	–	104.659(6)
β/ deg	107.309(4)	100.958(2)	92.163(5)
γ/ deg	–	–	98.373(5)
Volume / Å^3	2785.1(2)	1873.25(8)	1460.35(17)
ρ_{ber} / g · cm^{-3}	1.632	1.1419	1.674
F(000)	1392	832	752
Crystal Dimensions / mm	0.40 · 0.20 · 0.02	0.40 · 0.40 · 0.20	0.3 · 0.3 · 0.2
Z	4	4	4
Max. and min. Transmission	1.00000, 0.41575	0.8407, 0.7150	1.00000, 0.87739
μ / mm^{-1}	1.420	0.899	1.064
θ-Range / deg	2.991 to 24.998	2.99 to 25.99	2.961 to 25.000
Limiting indices	–17≤h≤17 –12≤k≤11 –23≤l≤21	–9≤h≤9 –23≤k≤23 –14≤l≤14	–9≤h≤8 –14≤k≤14 –19≤l≤19
Reflections Collected / Unique	17318 / 4883	8695 / 3655	9912 / 9912
Completeness to θ_{max} / %	99.5	99.6	99.4
Restraints / Parameters	674 / 413	0 / 236	0 / 434
R_{int}	0.0506	0.0240	–
R_1, wR_2 [I ≥ 2 σ(I)]	0.0418, 0.0861	0.0275, 0.0633	0.0397, 0.0830
R_1, wR_2 (all Data)	0.0612, 0.0924	0.0346, 0.0663	0.0507, 0.0880
Goodness-of-fit S	1.034	1.015	1.015
$\Delta\rho$ / e$^-$ Å^{-3}	0.407, –0.396	0.358, –0.233	0.586, –0.420
Absolute Structure Parameter	–	–	–

Table 5.12 Crystal-, collection- and refinement details for **96b**, **99a** and **99b**.

Compound	**96b**	**99a**	**99b**
CCDC Number	1446861	1446863	1446864
Empirical Formula	$C_{16}H_{13}FeNO_3$	$C_{26}H_{20}Fe_2N_2O_6$	$C_{16}H_{11}FFeN_2O_5$
Formula Weight / g·mol^{-1}	323.12	568.14	386.12
Temperature / K	110	110	110
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1$	$P2_1/n$
a / Å	11.065(3)	7.6777(6)	18.0108(4)
b / Å	10.792(2)	10.0784(6)	7.4492(2)
c / Å	11.8254(16)	14.2577(13)	22.7498(6)
α / deg	–	–	–
β/ deg	107.86(2)	105.261(9)	107.779(2)
γ/ deg	–	–	–
Volume / Å^3	1344.1(5)	1064.34(15)	2906.48(13)
ρ_{ber} / g · cm^{-3}	1.597	1.773	1.765
$F(000)$	664	580	1568
Crystal Dimensions / mm	0.1 · 0.1 · 0.01	0.2 · 0.1 · 0.02	0.3 · 0.3 · 0.1
Z	4	2	8
Max. and min. Transmission	1.00000, 0.89467	0.972, 0.844	1.00000, 0.88683
μ / mm^{-1}	1.131	1.414	1.083
θ-Range / deg	2.904 to 24.999	3.413 to 24.999	2.892 to 24.994
Limiting indices	–8≤h≤13 –12≤k≤10 –14≤l≤11	–8≤h≤9 –9≤k≤11 –15≤l≤16	–21≤h≤21 –8≤k≤8 –27≤l≤27
Reflections Collected / Unique	4798 / 2356	6350 / 3045	14857 / 5109
Completeness to θ_{max} / %	99.7	99.4	99.8
Restraints / Parameters	0 / 190	1 / 283	0 / 451
R_{int}	0.0536	0.0672	0.0314
R_1, wR_2 [I ≥ 2 σ(I)]	0.0483, 0.0790	0.0545, 0.1061	0.0354, 0.0773
R_1, wR_2 (all Data)	0.0779, 0.0878	0.0736, 0.1164	0.0496, 0.0822
Goodness-of-fit S	0.980	0.999	1.026
$\Delta\rho$ / e$^-$ Å^{-3}	0.466, –0.379	0.503, –0.783	0.503, –0.430
Absolute Structure Parameter	–	0.22(4)	–

Table 5.13 Crystal-, collection- and refinement details for **99c**, **100** and **103a**.

Compound	**99c**	**100** · $CHCl_3$	**103a**
CCDC Number	1446865	1446866	1446867
Empirical Formula	$C_{18}H_{17}FeN_3O_5$	$C_{26}H_{20}Fe_2N_2O_6 \cdot CHCl_3$	$C_{17}H_{11}F_3FeN_2O_7S$
Formula Weight / g·mol^{-1}	411.19	687.51	500.19
Temperature / K	110	110(2)	110(2)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Orthorhombic	Monoclinic	Triclinic
Space Group	$P2_12_12_1$	$C2/c$	$P\bar{1}$
a / Å	7.5258(7)	19.9437(9)	7.4788(5)
b / Å	10.2827(9)	9.7162(5)	8.7046(5)
c / Å	21.647(3)	28.3252(14)	14.8166(9)
α / deg	–	–	99.292(5)
β/ deg	–	94.255(4)	92.546(5)
γ/ deg	–	–	105.141(5)
Volume / Å^3	1675.1(3)	5473.6(5)	915.05(10)
ρ_{ber} / g·cm^{-3}	0.797	1.669	1.815
$F(000)$	848	2784	504
Crystal Dimensions / mm	0.4 · 0.2 · 0.01	0.4 · 0.3 · 0.2	0.3 · 0.2 · 0.1
Z	4	8	2
Max. and min. Transmission	0.991, 0.797	1.00000, 0.69295	1.00000, 0.76925
μ / mm^{-1}	0.938	1.399	1.015
θ-Range / deg	3.297 to 24.996	2.884 to 25.498	3.044 to 25.499
Limiting indices	–8≤h≤8 –4≤k≤12 –25≤l≤17	–24≤h≤22 –11≤k≤11 –34≤l≤34	–9≤h≤8 –9≤k≤10 –17≤l≤17
Reflections Collected / Unique	5577 / 2899	16021 / 5094	6303 / 3387
Completeness to θ_{max} / %	99.5	99.8	99.6
Restraints / Parameters	0 / 190	0 / 392	0 / 280
R_{int}	0-0669	0.0364	0.0270
R_1, wR_2 [I ≥ 2 σ(I)]	0.0877, 0.1995	0.0357, 0.0857	0.0357, 0.0811
R_1, wR_2 (all Data)	0.1113, 0.2130	0.0462, 0.0911	0.0449, 0.0863
Goodness-of-fit S	1.028	1.062	1.048
$\Delta\rho$ / e$^-$ Å^{-3}	1.611, –1.796	0.581, –0.452	0.359, –0.434
Absolute Structure Parameter	0.50(2)	–	–

Table 5.14 Crystal-, collection- and refinement details for **110a**, **110b** and **111a**.

Compound	**110a**	**110b**	**111a**
CCDC Number	1491684	1491685	1491686
Empirical Formula	$C_{16}H_{11}F_3FeO$	$C_{26}H_{20}F_2Fe_2O_2$	$C_{16}H_{10}F_4FeO$
Formula Weight / g·mol^{-1}	332.10	514.12	350.09
Temperature / K	119.95(10)	120.00(10)	119.95(10)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Orthorhombic	Monoclinic	Monoclinic
Space Group	Pnm	$P2_1/c$	$P2_1/n$
a / Å	19.3422(7)	15.3859(5)	9.9938(8)
b / Å	6.6879(3)	18.1868(5)	10.7044(9)
c / Å	10.2287(4)	11.8566(4)	12.2592(10)
α / deg	–	–	–
β/ deg	–	111.216(4)	96.973(7)
γ/ deg	–	–	–
Volume / Å^3	1323.17(9)	3092.85(19)	1301.76(19)
ρ_{ber} / g · cm^{-3}	1.667	1.656	1.786
$F(000)$	672	1572	704
Crystal Dimensions / mm	0.4 · 0.1 · 0.1	0.4 · 0.2 · 0.02	0.3 · 0.3 · 0.3
Z	4	6	4
Max. and min. Transmission	1.00000, 0.81777	1.00000, 0.6181	1.00000, 0.65555
μ / mm^{-1}	1.169	1.447	1.204
θ-Range / deg	3.640 to 25.980	3.649 to 28.937	3.132 to 24.992
Limiting indices	–22≤h≤23 –8≤k≤5 –12≤l≤8	–19≤h≤20 –24≤k≤22 –15≤l≤11	–11≤h≤11 –12≤k≤12 –13≤l≤14
Reflections Collected / Unique	4176 / 1409	16304 / 6978	5487 / 2280
Completeness to θ_{max} / %	99.4	99.6	99.7
Restraints / Parameters	0 / 115	0 / 433	0 / 199
R_{int}	0.0207	0.0358	0.0390
R_1, wR_2 [I ≥ 2 σ(I)]	0.0644, 0.1587	0.0426, 0.0909	0.0366, 0.0910
R_1, wR_2 (all Data)	0.0689, 0.1636	0.0662, 0.1012	0.0423, 0.0940
Goodness-of-fit S	1.095	1.018	1.041
$\Delta\rho$ / e$^-$ Å^{-3}	0.783, –0.464	0.716, –0.647	0.523, –0.694
Absolute Structure Parameter	–	–	–

Table 5.15 Crystal-, collection- and refinement details for **112a**, **112b** and **117b**.

Compound	**112a**	**112b**	**117b**
CCDC Number	1491687	1491688	1525592
Empirical Formula	$C_{16}H_9F_5FeO$	$C_{26}H_{18}F_4Fe_2O_2$	$C_{31}H_{39}FeOPSi$
Formula Weight / g·mol^{-1}	368.08	550.10	542.53
Temperature / K	120.00(10)	112.8(2)	108(2)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic	Triclinic
Space Group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a / Å	10.3964(4)	9.8166(3)	7.720(5)
b / Å	10.4918(4)	7.4008(3)	10.972(5)
c / Å	12.3964(4)	14.7097(6)	17.652(5)
α / deg	–	–	91.259(5)
β/ deg	99.464(3)	102.247(4)	99.143(5)
γ/ deg	–	–	107.072(5)
Volume / Å^3	1333.76(8)	1044.35(7)	1407.4(12)
ρ_{ber} / g·cm^{-3}	1.833	1.749	1.280
F(000)	736	556	576
Crystal Dimensions / mm	0.2 · 0.1 · 0.1	0.4 · 0.4 · 0.2	0.25 · 0.25 · 0.02
Z	4	2	2
Max. and min. Transmission	1.00000, 0.76693	1.00000, 0.96488	1.00000, 0.67875
μ / mm^{-1}	1.191	1.448	0.657
θ-Range / deg	3.403 to 24.999	4.193 to 25.998	2.94 to 25.50
Limiting indices	–8≤h≤12 –12≤k≤11 –13≤l≤14	–11≤h≤12 –9≤k≤9 –13≤l≤18	–9≤h≤9 –13≤k≤13 –21≤l≤17
Reflections Collected / Unique	4945 / 2343	4047 / 2038	8969 / 5185
Completeness to θ_{max} / %	99.5	99.5	98.7
Restraints / Parameters	0 / 208	0 / 154	0 / 322
R_{int}	0.0208	0.0224	0.0403
R_1, wR_2 [I ≥ 2 σ(I)]	0.0319, 0.0761	0.0284, 0.0625	0.0646, 0.1492
R_1, wR_2 (all Data)	0.0396, 0.0797	0.0344, 0.06551	0.0839, 0.1580
Goodness-of-fit S	1.089	1.072	1.073
$\Delta\rho$ / e$^-$ Å^{-3}	0.467, –0.437	0.294, –0.297	1.503, –0.511
Absolute Structure Parameter	–	–	–

Table 5.16 Crystal-, collection- and refinement details for **118q**, **124** and **127**.

Compound	**118g**	**124**	**127**
CCDC Number	1525943	1525944	1525945
Empirical Formula	$C_{16}H_{22}FeO$	$C_{21}H_{28}FeO$	$C_{28}H_{24}Fe$
Formula Weight / g·mol^{-1}	286.18	352.28	416.32
Temperature / K	112.3(3)	110(2)	110.3(5)
Wavelength / Å	0.71073	1.54184	0.71073
Crystal System	Monoclinic	Orthorhombic	Monoclinic
Space Group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
a / Å	10.7102(6)	7.7079(4)	23.946(5)
b / Å	7.5293(4)	8.5410(5)	8.927(5)
c / Å	17.0903(9)	26.6507(14)	20.292(5)
α / deg	–	–	–
β/ deg	94.419(6)	–	112.479(5)
γ/ deg	–	–	–
Volume / Å^3	1374.07(13)	1754.50(17)	4008(3)
ρ_{ber} / g · cm^{-3}	1.383	1.334	1.380
$F(000)$	608	752	1744
Crystal Dimensions / mm	0.2 · 0.1 · 0.1	0.4 · 0.02 · 0.02	0.2 · 0.2 · 0.15
Z	4	4	8
Max. and min. Transmission	1.00000, 0.38010	1.00000, 0.23357	1.00000, 0.81054
μ / mm^{-1}	1.083	6.887	0.764
θ-Range / deg	3.816 to 25.000	3.317 to 64.487	3.508 to 24.999
Limiting indices	–12≤h≤12 –8≤k≤8 –20≤l≤16	–9≤h≤7 –9≤k≤7 –31≤l≤30	–28≤h≤26 –10≤k≤10 –24≤l≤24
Reflections Collected / Unique	5493 / 2401)	5916 / 2715	19936 / 7037
Completeness to θ_{max} / %	99.4	98.3	99.6
Restraints / Parameters	0 / 164	0 / 208	0 / 523
R_{int}	0.0576	0.0607	0.0348
R_1, wR_2 [I ≥ 2 σ(I)]	0.0486, 0.1214	0.0560, 0.1301	0.0622, 0.1622
R_1, wR_2 (all Data)	0.0598, 0.1288	0.0703, 0.1393	0.0762, 0.1727
Goodness-of-fit S	1.014	0.984	1.039
$\Delta\rho$ / e$^-$ Å^{-3}	0.834, –0.453 e.	0.682, –0.384 e	2.907, –0.523
Absolute Structure Parameter	–	0.008(9)	–

Table 5.17 Crystal-, collection- and refinement details for **129**, **134b** and **134c**.

Compound	**129**	**134b**	**134c**
CCDC Number	1525946	1525947	1525948
Empirical Formula	$C_{20}H_{24}FeO$	$C_{37}H_{48}FeNO_3P$	$C_{55}H_{60}FeNO_3P \cdot C_2H_5OH$
Formula Weight / g·mol^{-1}	336.24	641.58	915.92
Temperature / K	110.00(10)	112.4(2)	114(10)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$I2$	$P2_1$	$P2_1$
a / Å	12.8033(3)	7.3930(2)	11.856(4)
b / Å	12.4511(4)	10.3937(3)	11.260(3)
c / Å	19.1644(6)	21.3467(6)	18.383(3)
α / deg	–	–	–
β/ deg	90.460(3)	92.463(3)	90.03(2)
γ/ deg	–	–	–
Volume / Å^3	3055.00(15)	1638.78(8)	2454.3(11)
ρ_{ber} / g $\cdot$ cm^{-3}	1.462	1.300	1.239
$F(000)$	1424	684	976
Crystal Dimensions / mm	0.2 · 0.2 · 0.18	0.25 · 0.2 · 0.1	0.12 · 0.10 · 0.01
Z	8	2	2
Max. and min. Transmission	1.00000, 0.74017	1.00000, 0.91533	1.00000, 0.61388
μ / mm^{-1}	0.987	0.546	0.387
θ-Range / deg	3.585 to 25.000	3.384 to 24.993	3.337 to 24.998
Limiting indices	–14≤h≤15 –14≤k≤9 –22≤l≤21	–8≤h≤8 –12≤k≤10 –25≤l≤25	–14≤h≤12 –13≤k≤13 –21≤l≤21
Reflections Collected / Unique	6105 / 3885	8098 / 4955	15314 / 7978
Completeness to θ_{max} / %	99.4	99.5	97.6
Restraints / Parameters	1 / 399	1 / 388	1 / 578
R_{int}	0.0364	0.0241	0.0976
R_1, wR_2 [I $\geq 2\,\sigma$(I)]	0.0305, 0.0651	0.0313, 0.0655	0.0775, 0.1344
R_1, wR_2 (all Data)	0.0356, 0.0673	0.0350, 0.0668	0.1488, 0.1609
Goodness-of-fit S	0.998	1.036	0.956
$\Delta\rho$ / e$^-$ Å^{-3}	0.357, –0.387	0.201, –0.228	0.797, –0.424
Absolute Structure Parameter	0.5	0.007(10)	–0.02(3)

Table 5.18 Crystal-, collection- and refinement details for (*E*/*E*)-**135**, **136** and **138**.

Compound	(*E*,*E*)-**135**	**136**	**138**
CCDC Number	1525949	1525950	1525951
Empirical Formula	$C_{30}H_{36}Fe_2N_2$	$C_{37}H_{50}FeNO_3P$	$C_{25}H_{17}FeN$
Formula Weight / g·mol^{-1}	536.31	643.60	387.24
Temperature / K	120.00(10)	120.05(10)	119.95(10)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Triclinic	Monoclinic
Space Group	$P2_1/n$	$P1$	$P2_1/c$
a / Å	10.6455(7)	12.1094(7)	10.0009(5)
b / Å	13.8398(8)	16.2782(9)	13.9488(8)
c / Å	34.351(2)	18.0207(10)	12.2166(7)
α / deg	–	104.163(5)	–
β/ deg	90.976(6)	93.995(5)	95.965(5)
γ/ deg	–	95.691(5)	–
Volume / Å^3	5060.3(5)	3411.0(3)	1694.99(16)
ρ_{ber} / g·cm^{-3}	1.408	1.253	1.517
$F(000)$	2256	1376	800
Crystal Dimensions / mm	0.3 · 0.3 · 0.2	0.2 · 0.2 · 0.05	0.40 · 0.10 · 0.0
Z	8	4	4
Max. and min. Transmission	1.00000, 0.66355	1.00000, 0.52199	1.00000, 0.565
μ / mm^{-1}	1.168	0.525	0.899
θ-Range / deg	2.944 to 24.999	2.960 to 24.999	3.353 to 24.998
Limiting indices	–12≤h≤12 –16≤k≤16 –40≤l≤39	–13≤h≤14 –19≤k≤19 –21≤l≤19	–11≤h≤10 –16≤k≤16 –14≤l≤14
Reflections Collected / Unique	26359 / 8786	26338 / 17228	7225 / 2979
Completeness to θ_{max} / %	98.5	99.6	99.6
Restraints / Parameters	126 / 671	2062 / 1565	0 / 244
R_{int}	0.0887	0.0501	0.0450
R_1, wR_2 [I ≥ 2 σ(I)]	0.1010, 0.2092	0.0812, 0.2244	0.0478, 0.0963
R_1, wR_2 (all Data)	0.1253, 0.2179	0.1019, 0.2425	0.0742, 0.1048
Goodness-of-fit S	1.079	1.028	1.014
$\Delta\rho$ / e$^-$ Å^{-3}	1.385, –1.119	0.899, –0.474	0.382, –0.283
Absolute Structure Parameter	–	0.02(2)	–

Table 5.19 Crystal-, collection- and refinement details for (S_p,S_p)-**149**, (S_p)-**150c** and (S_p)-**151a**.

Compound	(S_p,S_p)-**149**	(S_p)-**150c**	(S_p)-**151a**
CCDC Number	1525952	1525953	1525954
Empirical Formula	$C_{46}H_{40}Fe_2P_2S_3$	$C_{30}H_{27}FePS$	$C_{30}H_{27}FeOPS$
Formula Weight / g·mol^{-1}	862.60	506.39	522.39
Temperature / K	111.7(4)	114.90(14)	112.5(3)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal System	Tetragonal	Orthorhombic	Triclinic
Space Group	$P4_12_12$	$P2_12_12_1$	$P1$
a / Å	8.1715(3)	8.9846(4)	7.7256(5)
b / Å	–	14.1882(7)	8.4715(4)
c / Å	58.812(2)	19.1820(12)	10.1419(5)
α / deg	–	–	77.985(4)
β/ deg	–	–	71.170(5)
γ/ deg	–	–	83.905(5)
Volume / Å^3	3927.1(3)	2445.2(2)	613.93(6)
ρ_{ber} / g · cm^{-3}	1.459	1.376	1.413
F(000)	1784	1056	272
Crystal Dimensions / mm	0.2 · 0.2 · 0.1	0.35 · 0.35 · 0.25	0.30 · 0.25 · 0.15
Z	4	4	1
Max. and min. Transmission	1.00000, 0.52635	1.00000, 0.5814	1.00000, 0.81925
μ / mm^{-1}	1.013	0.784	0.786
θ-Range / deg	3.035 to 25.493	3.495 to 24.997	3.497 to 24.999
Limiting indices	–7≤h≤9 –9≤k≤9 –71≤l≤71	–10≤h≤10 –16≤k≤11 –22≤l≤22	–9≤h≤9 –10≤k≤10 –12≤l≤12
Reflections Collected / Unique	16166 / 3622	10406 / 4248	5387 / 3559
Completeness to θ_{max} / %	99.4	99.6	99.6
Restraints / Parameters	306 / 240	0 / 299	3 / 308
R_{int}	0.0963	0.0502	0.0236
R_1, wR_2 [I ≥ 2 σ(I)]	0.1051, 0.2174	0.0433, 0.0761	0.0463, 0.1111
R_1, wR_2 (all Data)	0.1118, 0.2202	0.0639, 0.0824	0.0483, 0.1129
Goodness-of-fit S	1.234	0.987	1.059
$\Delta\rho$ / e$^-$ Å^{-3}	0.734, –0.921	0.296, –0.239	0.542, –0.306
Absolute Structure Parameter	0.05(2)	–0.033(15)	0.007(12)

Table 5.20 Crystal-, collection- and refinement details for (S_p)-**155** and (S_p)-**159**.

Compound	(S_p)-**155**	(S_p)-**159** · CH_2Cl_2
CCDC Number	1525955	1525956
Empirical Formula	$C_{29}H_{23}FeN_2O_4PS_2$	$C_{34}H_{37}FeNO_3P_2S \cdot CH_2Cl_2$
Formula Weight / g·mol^{-1}	614.43	742.42
Temperature / K	119.9(3)	119.9(2)
Wavelength / Å	1.54184	1.54184
Crystal System	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$
a / Å	8.1644(8)	7.5912(15)
b / Å	25.333(5)	8.4182(9)
c / Å	25.871(3)	55.37(2)
α / deg	–	–
β/ deg	–	–
γ/ deg	–	–
Volume / Å^3	5350.8(12)	3538.3(17)
ρ_{ber} / g · cm^{-3}	1.525	1.394
$F(000)$	2528	1544
Crystal Dimensions / mm	0.1 · 0.1 · 0.01	0.2 · 0.1 · 0.02
Z	8	4
Max. and min. Transmission	1.00000, 0.39233	1.00000, 0.47774
μ / mm^{-1}	6.878	6.496
θ-Range / deg	3.837 to 64.487	4.792 to 64.497
	–9≤h≤6	–8≤h≤8
Limiting indices	–29≤k≤17	–5≤k≤9
	–30≤l≤27	–64≤l≤63
Reflections Collected / Unique	12308 / 8117	8453 / 5263
Completeness to θ_{max} / %	99.9	99.8
Restraints / Parameters	0 / 703	66 / 412
R_{int}	0.0884	0.0934
R_1, wR_2 [I ≥ 2 σ(I)]	0.0819, 0.1949	0.0889, 0.2042
R_1, wR_2 (all Data)	0.1425, 0.2440	0.1213, 0.2284
Goodness-of-fit S	0.952	1.028
$\Delta\rho$ / e$^-$ Å^{-3}	0.871, –0.671	0.930, –0.590
Absolute Structure Parameter	–0.009(12)	0.049(12)

Appendix I Curriculum Vitae

Persönliche Daten

Name:	Marcus Korb
Geburtsdatum:	06. Mai 1986
Geburtsort:	Annaberg-Buchholz
Familienstand:	ledig
Staatsangehörigkeit:	deutsch

Schulbildung

09/1992–06/1996	Grundschule, Cranzahl
08/1995–06/2004	St. Annen-Gymnasium, Annaberg-Buchholz
06/2004	Allgemeine Hochschulreife

Ausbildung

08/2004–09/2007	Ausbildung zum Chemielaborant, Nickelhütte Aue GmbH

Hochschulbildung

10/2007–09/2012	Diplomstudiengang Chemie, TU Chemnitz
12/2011–08/2012	Diplomarbeit: "*Ferrocenylfunktionalisierte (Makro-)Zyklen: Synthese, Charakterisierung und Redoxverhalten*", Professur für Anorganische Chemie, TU Chemnitz (Prof. Dr. Heinrich Lang)
09/2012	Diplomverteidigung (Note: 1.0); Gesamtnote: 1.0
10/2012–09/2017	Dissertation, Professur für Anorganische Chemie, TU Chemnitz (Prof. Dr. Heinrich Lang)

Stipendien und Auszeichnungen

03/2013–02/2015	Chemiefonds-Stipendium des Fonds der Chemischen Industrie
31.08–04.09/2014	Reisekostenstipendium der GDCH zum Besuch des 5^{th} EuCheMS Chemistry Congress in Istanbul
28.06–03.07/2014	65^{th} Nobelpreisträgertagung Lindau
08/2015	GDCh-NESACS-Studienreise des JCF nach Boston (USA)
10/2016	Summer School: Bio-Leaching and Metal Extraction Processes for Urban Mining: From Fundamental Principles to Practical Applications
02/2017	Teilstipendium zum Besuch des 15^{th} Ferrocene Colloquiums in Mainz

Appendix J List of Publications, Talks and Posters

Publications in Scientific Journals

(1) **A novel one-dimensional coordination polymer bearing tetrakis-carboxylato Co(II)$_2$ units interacting via P-donors based on 1-carboxylic-1'-(diphenylphosphino) ferrocene.**
A. A. M. Alya, T. Rüffer, B. Bräuer, M. Korb, L. Soracec, H. Lang, *Inorg. Chim. Acta* **2012**, *392*, 404–409.

(2) **Chlorido[1-diphenyl-phosphanyl-3-(phenylulfanyl)propane-κ^2*P*,*S*](η^5-pentamethylcyclopentadienyl)iridium(III) chloride monohydrate.**
G. Ludwig, M. Korb, T. Rüffer, H. Lang and D. Steinborn, *Acta Crystallogr., Sect. E* **2012**, *68*, m858.

(3) **A straightforward approach to oxide-free copper nanoparticles by thermal decomposition of a copper(I) precursor.**
D. Adner, M. Korb, S. Schulze, M. Hietschold, H. Lang, *Chem. Commun.* **2013**, *49*, 6855–6857.

(4) **Biological activity of neutral and cationic iridium(III) complexes with κ*P* and κ*P*,κ*S* coordinated Ph$_2$PCH$_2$S(O)(x)Ph (x = 0–2) ligands.**
G. Ludwig, S. Mijatović, I. Randelović, M. Bulatović, D. Miljković, D. Maksimović-Ivanić, M. Korb, H. Lang, D. Steinborn, G. N. Kaluderović, *Eur. J. Med. Chem.* **2013**, *69*, 216–222.

(5) **Cationic arene ruthenium(II) complexes with chelating *P*-functionalized alkyl phenyl sulfide and sulfoxide ligands as potent anticancer agents.**
G. Ludwig, G. N. Kaluderović, T. Rüffer, M. Bette, M. Korb, M. Block, R. Paschke, H. Lang, D. Steinborn, *Dalton Trans.* **2013**, *42*, 3771–3774.

(6) **Copper(II) and triphenylphosphine copper(I) ethylene glycol carboxylates: synthesis, characterisation and copper nanoparticle generation.**
D. Adner, S. Möckel, M. Korb, R. Buschbeck, T. Rüffer, S. Schulze, L. Mertens, M. Hietschold, M. Mehring, H. Lang, *Dalton Trans.* **2013**, *42*, 15599–15609.

(7) **Metal-Metal Interaction in Fischer Carbene Complexes: A Study of Ferrocenyl and Biferrocenyl Tungsten Alkylidene Complexes.**
B. Westhuizen, J. M. Speck, M. Korb, J. Friedrich, D. I. Bezuidenhout, H. Lang, *Inorg. Chem.* **2013**, *52*, 14253–14263.

(8) **Synthesis and (Spectro)electrochemical Behavior of 2,5-Diferrocenyl-1-pheny1-1*H*-phosphole.**
D. Miesel, A. Hildebrandt, M. Korb, P. J. Low, H. Lang, *Organometallics* **2013**, *32*, 2993–3002.

(9) **Tetrakis(ferrocenecarbonitrile) Copper(I) Complexes.**
F. Strehler, A. Hildebrandt, M. Korb, H. Lang, *Z. Anorg. Allg. Chem.* **2013**, *639*, 1214-1219.

(10) **(Spectro)electrochemical investigations on (ferrocenyl)thiophenes modified by tungsten Fischer carbenes**
B. Westhuizena, J. M. Speck, M. Korb, D. I. Bezuidenhout, H. Lang, *J. Organomet. Chem.* **2014**, *772–773*, 18–26.

(11) **1,3,5-Triferrocenyl-2,4,6-tris(ethynylferrocenyl)benzene - a new member of the family of multiferrocenyl-functionalized cyclic systems**
U. Pfaff, G. Filipczyk, A. Hildebrandt, M. Korb, H. Lang, *Dalton Trans.* **2014**, *43*, 16310–16321.

(13) **3,4-Ferrocenyl-Functionalized Pyrroles: Synthesis, Structure, and (Spectro)-Electrochemical Studies**
M. Korb, U. Pfaff, A. Hildebrandt, T. Rüffer, H. Lang, *Eur. J. Inorg. Chem.* **2014**, *2014*, 1051–1061.

(14) **Anionic Phospho-Fries Rearrangement at Ferrocene: One-Pot Approach to *P,O*-Substituted Ferrocenes**
M. Korb, D. Schaarschmidt, H. Lang, *Organometallics* **2014**, *33*, 2099–2108.

(15) **Anticancer Potential of (Pentamethylcyclopentadienyl)chloridoiridium(III) Complexes Bearing κP and $\kappa P,\kappa S$-Coordinated $Ph_2PCH_2CH_2CH_2S(O)_xPh$ (x = 0–2) Ligands**
G. Ludwig, I. Randelović, D. Maksimović-Ivanić, S. Mijatović, M. Z. Bulatović, D. Miljković, M. Korb, H. Lang, D. Steinborn, G. N. Kaluderović, *ChemMedChem* **2014**, *9*, 1586–1593.

(16) **Combining Cobalt-Assisted Alkyne Cyclotrimerization and Ring Formation through C–H Bond Activation: A "One-Pot"Approach to Complex Multimetallic Structures**
G. Filipczyk, A. Hildebrandt, U. Pfaff, M. Korb, T. Rüffer, H. Lang, *Eur. J. Inorg. Chem.* **2014**, *2014*, 4258–4262.

(17) **Crystal structure of 3-1'-[3,5-bis(trifluoromethyl)phenyl]ferrocenyl-4-bromothiophene**
E. A. Poppitz, M. Korb and H. Lang, *Acta Crystallogr., Sect. E* **2014**, *70*, 238–241.

(18) **Di(biferrocenyl)ethyne and -butadiyne: Synthesis, properties and electron transfer studies**
E. A. Poppitz, A. Hildebrandt, M. Korb, H. Lang, *J. Organomet. Chem.* **2014**, *752*, 133–140.

(19) **Ferrocenyl-Based *P,N* Catalysts for the Mono-α-Arylation of Acetone**
C. Gäbler, M. Korb, D. Schaarschmidt, A. Hildebrandt, H. Lang, *Adv. Synth. Catal.* **2014**, *356*, 2979–2983.

(20) **From Ferrocenecarbonitriles to Ferrocenylimines: Synthesis, Structure, and Reaction Chemistry**
F. Strehler, A. Hildebrandt, M. Korb, T. Rüffer, H. Lang, *Organometallics* **2014**, *33*, 4279–4289.

(21) **Planar Chirality from the Chiral Pool: Diastereoselective Anionic Phospho-Fries Rearrangements at Ferrocene**
M. Korb, H. Lang, *Organometallics* **2014**, *33*, 6643–6659.

(22) **Substituent Influence on Charge Transfer Interactions in α,α'-Diferrocenylthiophenes**
J. M. Speck, M. Korb, T. Rüffer, A. Hildebrandt, H. Lang, *Organometallics* **2014**, *33*, 4813–4823.

(23) **Synthesis of Unexpected Bifunctionalized Thiazoles by Nucleophilic Attack on Allenyl Isothiocyanate.**
B. J. Al-Hourani, F. Richter, K. Vrobel, K. Banert, M. Korb, T. Rüffer, B. Walfort, H. Lang, *Eur. J. Org. Chem.* **2014**, *2014*, 2899–2906.

(24) **Synthesis with Perfect Atom Economy: Generation of Furan Derivatives by 1,3-Dipolar Cycloaddition of Acetylenedicarboxylates at Cyclooctynes.**
K. Banert, S. Bochmann, A. Ihle, O. Plefka, F. Taubert, T. Walther, M. Korb, T. Rüffer, H. Lang, *Molecules* **2014**, *19*, 14022–14035.

(25) **Synthesis, Characterization, Electrochemistry, and Computational Studies of Ferrocenyl-Substituted Siloles.**
S. W. Lehrich, A. Hildebrandt, T. Rüffer, M. Korb, P. J. Low, H. Lang, *Organometallics* **2014**, *33*, 4836–4845.

(26) **Synthesis, Properties, and Electron Transfer Studies of Ferrocenyl Thiophenes.**
E. A. Poppitz, A. Hildebrandt, M. Korb, D. Schaarschmidt, H. Lang, *Z. Anorg. Allg. Chem.* **2014**, *640*, 2809–2816.

(27) **Thio- and selenosulfonato complexes of iron bearing aromatic and heterocyclic groups.**
M. El-khateeb, K. J. Asali, M. Al-Noaimi, E. Al-Rabaee, F. F. Awwadi, D. Taher, Marcus Korb, H. Lang, *Inorg. Chim. Acta* **2014**, *421*, 553–558.

(28) **Unusual Nitrile-Nitrile and Nitrile-Alkyne Coupling of Fc–C≡N and Fc–C≡C–C≡N.**
L. Becker, F. Strehler, M. Korb, P. Arndt, A. Spannenberg, W. Baumann, H. Lang, U. Rosenthal, *Chem. Eur. J.* **2014**, *20*, 3061–3068.

(29) **(Ferrocenylthienyl)phosphines for the Suzuki-Miyaura *C,C* coupling**
C. Gäbler, M. Korb, D. Schaarschmidt, J. M. Speck, A. Hildebrandt, H. Lang, *Inorg. Chem. Commun.* **2015**, *54*, 96–99.

(30) **1-Cyano-1'-ethynyl-ferrocene: Synthesis and reaction chemistry**
F. Strehler, M. Korb, E. A. Poppitz, H. Lang, *J. Organomet. Chem.* **2015**, *786*, 1–9.

(31) **4,5-Dihydro-1,2,3-oxadiazole: A Very Elusive Key Intermediate in Various Important Chemical Transformations**
K. Banert, N. Singh, B. Fiedler, J. Friedrich, M. Korb, H. Lang, *Chem. Eur. J.* **2015**, *43*, 15092–15099.

(32) **Atom Economic Ruthenium-Catalyzed Synthesis of Bulky beta-Oxo Esters**
J. Jeschke, M. Korb, To. Rüffer, C. Gäbler, H. Lang, *Adv. Synth. Catal.* **2015**, *357*, 4069–4081.

(33) **Crystal Structure and Magnetic Properties of a Hexanuclear Copper(II) Carboxylate**
D. Adner, M. Korb, C. Lochenie, B. Weber, H. Lang, *Z. Anorg. Allg. Chem.* **2015**, *641*, 1243–1246.

(34) **Crystal structure of paddle-wheel sandwich-type $[Cu_2(CH_3)_2CO\mu\text{-}Fe(\eta^5\text{-}C_5H_4C{\equiv}N)_{23}](BF_4)_2{\cdot}(CH_3)_2CO$**
F. Strehler, M. Korb, H. Lang, *Acta Crystallogr., Sect. E* **2015**, *71*, 244–247.

(35) **Crystal structure of ruthenocenecarbonitrile**
F. Strehler, M. Korb, H. Lang, *Acta Crystallogr., Sect. E* **2015**, *71*, 398–401.

(36) **Electronic modification of redox active ferrocenyl termini and their influence on the electrontransfer properties of 2,5-diferrocenyl-*N*-phenyl-1*H*-pyrroles**
S. W. Lehrich, A. Hildebrandt, M. Korb, H. Lang, *J. Organomet. Chem.* **2015**, *792*, 37–45.

(37) **Electronic Tuneable Dynamic and Electrochemical Behavior of *N*-(Diferrocenylmethylene)anilines**
S. Saloman, A. Hildebrandt, M. Korb, M. Schwind, H. Lang, *Z. Anorg. Allg. Chem.* **2015**, *641*, 2282–2290.

(38) **Ferrocenes Bridged by Ethylenediamino Thiophene: Varying Charge Transfer Properties in a Series of 3,4-Di-*N*-substituted 2,5-Diferrocenyl Thiophenes**
J. M. Speck, M. Korb, A. Schade, S. Spange, H. Lang, *Organometallics* **2015**, *34*, 3788–3798.

(39) **Five-Membered Heterocycles as Linking Units in Strongly Coupled Homobimetallic Group 8 Metal Half-Sandwich Complexes**
U. Pfaff, A. Hildebrandt, M. Korb, D. Schaarschmidt, M. Rosenkranz, A. Popov, H. Lang, *Organometallics* **2015**, *34*, 2826–2840.

(40) **Frontispiece: 4,5-Dihydro-1,2,3-oxadiazole: A Very Elusive Key Intermediate in Various Important Chemical Transformations.**
K. Banert, N. Singh, B. Fiedler, J. Friedrich, M. Korb, H. Lang, *Chem. Eur. J.* **2015**, *21*, Frontispiece.

(41) **Influence of P-Bonded Bulky Substituents on Electronic Interactions in Ferrocenyl-Substituted Phospholes**
D. Miesel, A. Hildebrandt, M. Korb, D. A. Wild, P. J. Low, H. Lang, *Chem. Eur. J.* **2015**, *21*, 11545–11559.

(42) **Intramolecular C–O Insertion of a Germanium(II) Salicyl Alcoholate: A Combined Experimental and Theoretical Study**
P. Kitschke, T. Rüffer, M. Korb, H. Lang, W. B. Schneider, A. A. Auer, M. Mehring, *Eur. J. Inorg. Chem.* **2015**, *2015*, 5467–5479.

(43) **Polyamide 6/silica hybrid materials by a coupled polymerization reaction.**
L. Kaßner, K. Nagel, R.-E. Grützner, M. Korb, T. Rüffer, H. Lang, S. Spange, *Polym. Chem.* **2015**, *6*, 6297–6304.

(44) **Ruthenium Carboxylate Complexes as Efficient Catalysts for the Addition of Carboxylic Acids to Propargylic Alcohols**
J. Jeschke, C. Gäbler, M. Korb, T. Rüffer, H. Lang, *Eur. J. Inorg. Chem.* **2015**, *2015*, 2939–2947.

(45) **Ruthenium Carboxylate Complexes as Efficient Catalysts for the Addition of Carboxylic Acids to Propargylic Alcohols**
J. Jeschke, C. Gäbler, M. Korb, T. Rüffer, H. Lang, *Eur. J. Inorg. Chem.* **2015**, *2015*, Cover Profile.

(46) **Surface-confined 2D polymerization of a brominated copper-tetraphenylporphyrin on Au(111)**
L. Smykalla, P. Shukrynau, M. Korb, H. Lang, M. Hietschold, *Nanoscale* **2015**, *7*, 4234–4241.

(47) **The influence of an ethynyl spacer on the electronic properties in 2,5-ferrocenyl-substituted heterocycles**
U. Pfaff, A. Hildebrandt, M. Korb, H. Lang, *Polyhedron* **2015**, *86*, 2–9.

(48) **Transition-Metal Carbonyl Complexes of 2,5-Diferrocenyl-1-phenyl-1*H*-phosphole**
D. Miesel, A. Hildebrandt, M. Korb, D. Schaarschmidt, H. Lang, *Organometallics* **2015**, *34*, 4293–4304.

(49) **Unprecedented Synthesis of 2*H*,6*H*-1,5-Dithiocines Reinvestigated: A Structural Corrigendum Revealing Isothiazole-3(2*H*)-thiones**
K. Banert, N. Singh, M. Korb, H. Lang, *Synthesis* **2015**, *47*, 533–537.

(50) **Bis(β-diketonato)- and allyl-(β-diketonato)-palladium(II) complexes: synthesis, characterization and MOCVD application**
K. Assim, M. Melzer, M. Korb, T. Rüffer, A. Jakob, J. Noll, C. Georgi, S. E. Schulz and H. Lang, *RSC Adv.* **2016**, *6*, 102557–102569.

(51) **Synthesis and isomerization behavior of cyano-vinyl ferrocenes**
F. Strehler, M. Korb, T. Rüffer, A. Hildebrandt, H. Lang, *J. Organomet. Chem.* **2016**, *820*, 89–97.

(52) **A Reactivity Study of Phenyl and Ferrocenyl Phosphates Within the Anionic Phospho-Fries Rearangement**
M. Korb, H. Lang, *Inorg. Chem. Commun.* **2016**, *72*, 30–32.

(53) **(Ferrocenylthienyl) phosphines: Synthesis, electrochemistry and their use in Suzuki-Miyaura *C,C* coupling**
C. Gäbler, J. M. Speck, M. Korb, D. Schaarschmidt, H. Lang, *J. Organomet. Chem.* **2016**, *813*, 26–35.

(54) **Chemical vapor deposition of ruthenium-based layers by a single-source approach**
J. Jeschke, S. Möckel, M. Korb, T. Rüffer, K. Assim, M. Melzer, G. Herwig, C. Georgi, S. E. Schulz, H. Lang, *J. Mater. Chem. C* **2016**, *4*, 2319-2328.

(55) **Crystal structure of (μ-1,4-dicarboxybutane-1,4-dicarboxylato) bis[bis(triphenylphosphane)silver(I)] dichloromethane trisolvate**
P. Frenzel, M. Korb, H. Lang, *Acta Crystallogr., Sect. E* **2016**, *72*, 215–219.

(56) **Crystal structure of 3-ferrocenyl-1-phenyl-1*H*-pyrrole, [Fe(η^5-C_5H_4 $^cC_4H_3$*N*Ph)(η^5-C_5H_5)]**
U. Pfaff, M. Korb, H. Lang, *Acta Crystallogr., Sect. E* **2016**, *72*, 92–95.

(57) **Crystal structure of bis[tetrakis(triphenylphosphane-κ*P*)silver(I)] (nitrilotriacetato-κ^4*N,O,O',O''*)(triphenylphosphane-κ*P*)argentate(I) with an unknown amount of methanol as solvate.**
J. Noll, M. Korb, H. Lang, *Acta Crystallogr., Sect. E* **2016**, *72*, 318–321.

(58) **Erratum: Crystal structure of 3-ferrocenyl-1-phenyl-1*H*-pyrrole, [Fe(η^5-C_5H_4 $^cC_4H_3$*N*Ph)(η^5-C_5H_5)]. Corrigendum.**
U. Pfaff, M. Korb, H. Lang, *Acta Crystallogr., Sect. E* **2016**, *72*, 878.

(59) **Electronic interactions in gold(I) complexes of 2,5-diferrocenyl-1-phenyl-1*H*-phosphole.**
D. Miesel, A. Hildebrandt, M. Korb, H. Lang, *J. Organomet. Chem.* **2016**, *803*, 104–110.

(60) **Electronically Strongly Coupled Divinylheterocyclic-Bridged Diruthenium Complexes**
U. Pfaff, A. Hildebrandt, M. Korb, S. Oßwald, M. Linseis, K. Schreiter, S. Spange, R. F. Winter, H. Lang, *Chem. Eur. J.* **2016**, *22*, 783–801.

(61) **Multi-functionalized ferrocenes: - Synthesis and characterization**
A. Hildebrandt, K. Al Khalyfeh, D. Schaarschmidt, M. Korb, *J. Organomet. Chem.* **2016**, *804*, 87–94.

(62) **Nucleophilic Aromatic Substitution Reactions for the Synthesis of Ferrocenyl Aryl Ethers**
M. Korb, P. J. Swarts, D. Miesel, A. Hildebrandt, J. C. Swarts, H. Lang, *Organometallics* **2016**, *35*, 1287–1300.

(63) **Coordination behavior of (ferrocenylethynyl)diphenylphosphane towards binuclear iron and cobalt carbonyls**
G. Filipczyk, A. Hildebrandt, T. Rüffer, M. Korb, H. Lang, *J. Organomet. Chem.* **2017**, *828*, 142–151.

(63) **Multiferrocenyl Cobalt-Based Sandwich Compounds.**
G. Filipczyk, S. W. Lehrich, A. Hildebrandt, T. Rüffer, D. Schaarschmidt, M. Korb, H. Lang, *Eur. J. Inorg. Chem.* **2017**, *2017*, 263–275.

(64) **Bismuth(III) Anthranilates: Synthesis and Characterization of a Coordination Polymer and a Polynuclear Oxido Cluster.**
L. Wrobel, T. Rüffer, M. Korb, H. Lang und M. Mehring, *Eur. J. Inorg. Chem.* **2017**, *2017*, 1032–1040.

(65) **Redox properties and electron transfer in a triarylamine-substituted HS-Co^{2+}/LS-Co^{3+} redox couple**
L. Schnaubelt, H. Petzold, J. M. Speck, E Dmitrieva, M. Rosenkranz, M. Korb, *Dalton Trans.* **2017**, *46*, 2690–2698.

(66) **Ferrocenyl Silyl Ethers: Synthesis, Characterization and Electrochemical Investigation.**
P. Frenzel, S. W. Lehrich, M. Korb, A. Hildebrandt und H. Lang, *J. Organomet. Chem.* **2017**, *doi.org/10.1016/j.jorganchem.2017.03.020*, in press.

(67) **Diferrocenyl-Cyclopropenone to Diferrocenyl-Cyclopropenylium Cations and Triferrocenyl-propenones: An Electrochemical Study.**
S. W. Lehrich, A. Hildebrandt, M. Korb und H. Lang, *J. Organomet. Chem.* **2017**, *doi.org/10.1016/j.jorganchem.2017.03.018*, in press.

(68) **Ferrocenyl thiocarboxylates: Synthesis, solid-state structure and electrochemical investigations**
D. Taher, F. F. Awwadi, J. M. Speck, M. Korb, C. Wagner, E. M. Hamed, M. Al-Noaimi, A. Y. Habashneh, M. El-khateeb, Sultan T. Abu-Orabi, K. Merzweiler, *J. Organomet. Chem.* **2017**, *doi.org/10.1016/j.jorganchem.2017.03.053*, in press.

(69) **Heterocyclic-based ferrocenyl carboselenolates: Synthesis, solid-state structure and electrochemical investigations**
D. Taher, F. F. Awwadi, J. M. Speck, M. Korb, D. Schaarschmidt, S. Weheabby, A. Y. Habashneh, M. Al-Noaimi, M. El-Khateeb, Sultan T. Abu-Orabi, H. Lang, *J. Organomet. Chem.* **2017**, *doi.org/10.1016/j.jorganchem.2017.02.024*, in press.

Talks

(1) **Ein neuer Zugang zu 1,2-*P*,*O* Ferrocenen – die anionische phospho-Fries Verschiebung.**
M. Korb, H. Lang, FCI Stipendiatentreffen, 17.12.2013, FSU Jena.

(2) **The Anionic Phospho-Fries Rearrangement: A Brilliant approach to 1,2-*P*,*O*-substituted Ferrocenes.**
M. Korb, H. Lang, 12^{th} Ferrocene Colloquium, 17–19.02.2014, Innsbruck.

(3) **Ein Streifzug durch die Anorganische Chemie - von Asymmetrischer Katalyse bis Zyklischer Voltammetrie**
M. Korb, H. Lang, Doktorandenseminar TU Chemnitz, 17.07.2014.

(4) **The Anionic Phospho-Fries Rearrangement: A new approach to 1,2-*P*,*O*-substituted Ferrocenes.**
M. Korb, H. Lang, 12. Mitteldeutsches Anorganiker-Nachwuchssymposium, 11.09.2014, Freiberg.

(5) **Ein Streifzug durch die Anorganische Chemie - von Asymmetrischer Katalyse bis Zyklischer Voltammetrie**
M. Korb, H. Lang, Doktorandenseminar TU Chemnitz, 18.06.2015.

(6) **The Anionic Phospho-Fries Rearrangement: A new approach to 1,2-*P*,*O*-substituted Ferrocenes.**
M. Korb, H. Lang, 6. JCF GDCh NESCAS-Studienreise, 250th ACS National Meeting & Exposition, 16.08.2015, Bosten.

(7) **Die Facetten der Metallorganischen Chemie**
M. Korb, H. Lang, Doktorandenseminar TU Chemnitz, 07.07.2016.

(8) **Ferrocenyl Aryl Ethers - Difficulties and Application in *C,C* Cross-Coupling Catalysis.**
M. Korb, H. Lang, 15^{th} Ferrocene Colloquium, 19–21.02.2017, Mainz.

Posters

(1) **Synthesis of a Porphyrin based on 3,4-Diferrocenyl-Pyrrole.**
M. Korb, H. Lang, 11^{th} Ferrocene Colloquium, 06.–08.02.2013, Hannover.

(2) **Chiral Alkenylferrocenes in Suzuki-Miyaura *C,C*-Couplings.**
D. Schaarschmidt, M. Korb, H. Lang, 7^{th} Heidelberg Forum of Molecular Catalysis, 28.06.2013, Heidelberg.

(3) **Ein neuer Zugang zu 1,2-*P,O* Ferrocenen - die anionische phospho-Fries Verschiebung.**
M. Korb, H. Lang, FCI Stipendiatentreffen, 17.12.2013, FSU Jena.

(4) **1,2-*P,O*-Ferrocenes in Suzuki-Miyaura *C,C*-couplings.**
M. Korb, H. Lang, 47. Jahrestreffen deutscher Katalytiker, 12.–14.03.2014, Weimar.

(5) **1,2-*P,O*-ferrocenes in Suzuki-Miyaura *C,C*-couplings.**
M. Korb, H. Lang, 5^{th} EuCheMS, 31.08.–04.09.2014, Istanbul.

(6) **The electronic properties of ferrocenyl aryl ethers - adjusted with anionic Fries rearrangements.**
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Selbstständigkeitserklärung

Hiermit erkläre ich an Eides statt, dass ich die vorliegende Dissertation mit dem Titel "*Anionic Phospho-Fries Rearrangements for the Synthesis of Planar-Chiral Ferrocenes and their Application in (atropselective) Suzuki-Miyaura Reactions*" selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel genutzt habe. Alle wissentlich verwendeten Textausschnitte, Zitate oder Inhalte anderer Verfasser wurden ausdrücklich als solche gekennzeichnet.

Chemnitz, den 11.09.2017

Marcus Korb