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Authors: Marcus Korb, Julia Mahrholdt, and Heinrich Lang

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FULL PAPER

(Planar-Chiral) Ferrocenylmethanols: From Anionic Homo Phospho-Fries Rearrangements to α-Ferrocenyl Carbenium Ions

Marcus Korb,[a] Julia Mahrholdt,[a] Heinrich Lang*[a]

Dedicated to Prof. Dr. Dieter Fenske on the occasion of his 75th birthday

Abstract: The reaction of $FcCH_2OH$ with chlorophosphates gave ferrocenyl phosphates $FcCH_2OP(O)(OR)_2$ (Fc = $Fe(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4)$), which readily separate into phosphate anions and ferrocenyl carbo-cations. The latter species undergoes consecutive reactions, *e. g*. electrophilic aromatic substitutions. When nitriles, instead of alcohols, are treated with FcLi or ^{t}BuLi and chlorophosphates, chiral-pool based ferrocenyl imino phosphoramidates $Fc\text{-}CR{=}N\text{-}P(O)(OR^*)_2$ are formed, which are promising candidates for anionic homo phospho-Fries rearrangements. Moreover, the sterically demanding chiral chlorophosphate with R* enabled oxidative couplings of the imines to form a diferrocenyl azine. Similarly, the reaction of Fc–Li with 9-anthrylnitrile produced a 10-ferrocenyl-substituted product, contrary to a reaction at the C≡N functionality. A planar-chiral *ortho*-$P(S)Ph_2$-functionalized ferrocenylmethanol also gave carbo-cations under acidic conditions. These species can be sulfurized in a unique way giving thio ethers, whereby the *in situ* formed 1,2-$P(S)Ph_2,CH_2^+$ ferrocene cation acts as the sulfur and electron source. However, lowering the substrate concentration prevents sulfur migration, resulting in electrophilic substitution reactions with aromatic solvents. Planar-chiral ferrocenylmethyl thio or anisyl derivatives were applied as ligands in Pd-catalyzed Suzuki-Miyaura *C,C* cross-coupling for the atropselective synthesis of hindered biaryls with up to 26 % *ee* at low catalyst loadings (1 mol-% Pd).

Introduction

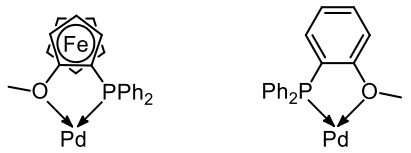
Ferrocenylphosphines and 1,2-disubtituted planar-chiral ferrocenes are, for example, essential in the field of catalysis.[1] Especially the synthesis of hindered biaryls by the Pd-catalyzed *C,C* cross-coupling reaction is still a challenging task, where ferrocenyl phosphines bearing *ortho*-donor atoms or groups, *e. g.* oxygen[2,3] , aryl[4] or vinyl,[5,6] have been shown to increase the catalytic activity. The vinyl fragment thereby acts as a hemi-labile group, which enables the planar-chirality of the ferrocenyl backbone to be transferred on a substrate, resulting in the formation of biaryls in an enantiomeric excess of up to 36 %.[5] It could be shown that the presence of an oxygen atom attached to the ferrocenyl backbone enhances the catalytic activity, as characteristic for a 2-alkyloxy substituted phosphine.[2,3] 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.[1,3] In contrast, a stereopure *ortho*-lithiation and functionalization with phosphorus electrophiles requires chiral, oxygen-functionalized *ortho*-directing groups. Since the ether motif is a rather weak *ortho*-directing group, predominantly 1,1'-functionalized products were obtained.[2,7,8] To investigate, if the planar-chiral ferrocenyl backbone can transfer its chirality to a *C,C* 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.[3] This intramolecular 1,3-O→C migration regioselectively gave access to a broad range of 1,2-P,O-substituted ferrocenes.[3] Using chiral pool alcohols allowed a diastereomeric proceeding with a *de* of the products exceeding 96 %.[9] The conversion of the formed phosphonate to the final phosphine also proceeded enantioselectively (99 % *ee*). Nevertheless, the use of this 1-PPh_2-2-OMe ferrocene as a ligand for *C,C* cross-coupling catalysis did not result in a detectable *ee* in the formed biaryls, due to the geometry of the ferrocenyl C_5H_3 ring and the low steric demand of the hemilabile methoxy group. Replacement of the methyl by an aryl group could therefore enhance the chirality transfer within the *C,C* cross-coupling protocol, due to steric reasons and attractive dispersion interactions.[4,10,11] Attempts to adopt this strategy on 1,2-P,O ferrocenes were successful by applying nucleophilic aromatic substitution reactions by using electron deficient arenes.[12,13] P,C bond-cleavage prevented the successful formation of the respective aryloxy ferrocenylphosphines.

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.[11,14] The usage of this type of sandwich compounds as ligands within Suzuki-Miyaura *C,C* cross-coupling reactions gave the respective biaryls with an *ee* of up to 37 %, most likely due to the planar as well as the C-central

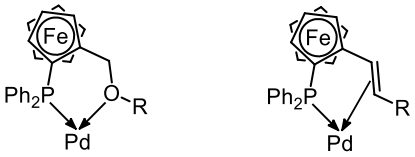
[a] Marcus Korb, Julia Marholdt, Prof. Dr. Heinrich Lang
Technische Universität Chemnitz, Faculty of Natural Sciences, Institute of Chemistry, Inorganic Chemistry, D-09107 Chemnitz, Germany
E-mail: heinrich-lang@chemie.tu-chemnitz.de

Supporting information for this article is given via a link at the end of the document. Text, Tables SI1–9, Figures SI1–19, and CIF files giving additional experimental and crystallographic data as well as spectroscopic details for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data are also available from the Cambridge Crystallographic Database as file numbers: CCDC 1525943 (**1g**), 1525944 (**8**), 1525945 (**11b**), 1525946 (**14**), 1525947 (**18b**), 1525948 (**18c** · EtOH), 1525949 (**19**), 1525950 (**20**), 1525951 (**22**), 1525952 (**32**), 1525953 (**33**), 1525954 (**34a**), 1525955 (**37**), 1525956 (**40a** · CH_2Cl_2).

chirality. The angle between the P- and O-donor atoms also seems to play a decisive role (Figure 1).



5-membered	(R_p)-**A**	**B**
P···O [Å]:	3.1656(13)	2.85
ee in biaryls:	0 %	non-chiral

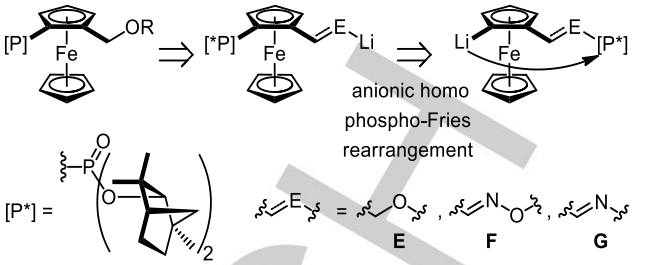


6-membered	(S_p)-**C**	(S_p)-**D**
P···O [Å]:	2.87/3.165, R = Me	3.18–3.28[a]
ee in biaryls:	12 %, R = CH_2-*p*-tol	up to 36 %
	37 %, R = (1*R*)-menthyl	R = H, Ar

Figure 1. Comparison between 5- (type **A**[9] and **B**[15] molecules) and 6-membered (type **C**[14] and **D**[16] molecules) 1,2-substituted phosphine Pd complexes and the resulting *ee* of formed biaryls within Suzuki-Miyaura *C*,*C* cross-coupling reactions. a) The vinyl group is η^2-coordinated to Pd, which in turn is rotated by 52 ° out of coplanarity.[16]

Whereas a 1,2-*P*,*O* substitution pattern at ferrocene gave a 5-membered Pd complex (type **A**[3] and **B**[15] molecules, Figure 1), the introduction of a methylene linking unit increases the size to a 6-membered cycle (**C** and **D**[5,6,16], Figure 1).[17] 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 1).[14] The study also showed that the increased *ee* is accompanied with a loss of activity.[14] The *ee* of 36 % for aromatic substituents can be explained by, *e.g.* attractive π-interactions.

Besides numerous protocols for the stereoselective introduction of *ortho*-substituents,[1] a procedure using cheap and easily available chiral-pool derivatives is pending. Thus, it seems convincible to apply the 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, Scheme 1). Oximes [18] (**F**) and imino-phosphoramidates [19,20,21] (**G**) could be used as linkers to the migrating phosphorus group. Furthermore, these structural motifs could be functionalized in a straightforward manner after a successful anionic phospho-Fries rearrangement, allowing the introduction of further substituents for optimizing the ligand system.



Scheme 1. Retrosynthesis for the preparation of 1,2-substituted ferrocenes by using the anionic homo phospho-Fries rearrangement.

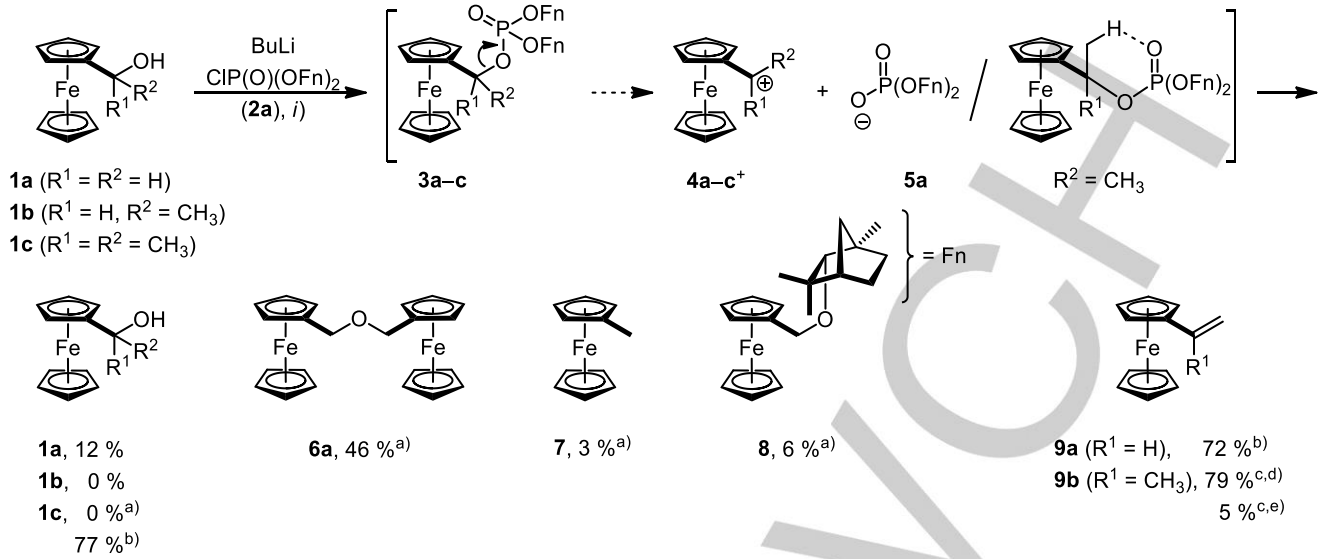
Results and Discussion

Anionic homo phospho-Fries rearrangement

As shown in Scheme 1, the simplest educts for anionic homo phospho-Fries rearrangements (*ahpFr*) are ferrocenyl methanols (Scheme 2). The usage of BuLi ensured complete deprotonation of alcohols **1a**–**c**.[9] Chiral-pool-derived chlorophosphate **2a**, bearing two (*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.[9] Thus, **2a** was used as the electrophile for phosphate formations reported herein. Upon treatment of **1a**–**c**–Li with **2a** the formation of phosphates **3a**–**c** was, however, not observed (Scheme 2). Instead, for **1a**-Li, the main product was identified as the respective ether **6a** (46 % yield), besides 12 % of the starting material **1a**, 3 % of methyl ferrocene (**7**) and 6 % of the fenchyl ether **8** (Scheme 2). The formation of **6a** indicates that **3a** has been formed *in situ*, which consecutively was attacked by further **1a**–Li to give **6a**. This nucleophilic attack is favored by the elimination of **5a** as a leaving group besides the formation of $\mathbf{4}^+$. [22] The generation of ferrocenylmethyl cations $\mathbf{4a}$–$\mathbf{c}^+$ is supported by an intramolecular Fe···C^+ interaction.[23,24] Thus, $\mathbf{4}^+$ might be a key intermediate.

The identity of **8** has *inter alia* been verified by applying single crystal X-ray diffraction analysis (Figure 2), revealing retention of the absolute configuration of the fenchyl group as (*1R*)/*endo*. The presence of one set of signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **8** confirmed the formation of solely one isomer (Experimental Section). Thus, an addition of a fenchylate at $\mathbf{3a}/\mathbf{4a}^+$ seems to be convincing, since the reaction of **1a**-Li at an OFn functionality would have resulted in the formation of the *exo*-derivative.

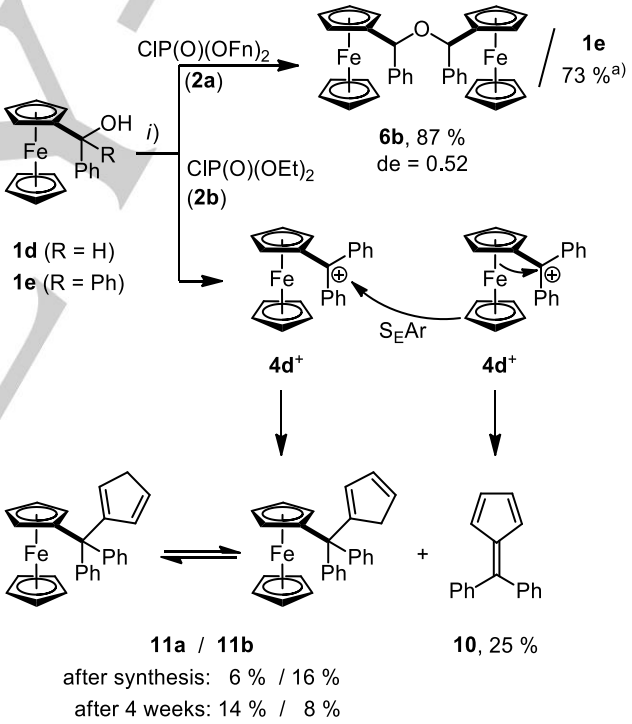
For methyl-substituted ferrocenyl methanols **1b**,**c**, formal dehydration occurred and ferrocenes **9a**,**b** were formed (Scheme 2). Thus, the elimination reaction of **3b**,**c** and the subsequent removal of H^+ was faster than a nucleophilic attack, probably due to the increased steric demand of the methyl groups. The *in situ* formed phosphates **3b**–**c** either underwent an intramolecular dehydrophosphorylation via a 6-membered transition state involving the P=O bond, or an intramolecular C–O bond cleavage.



Scheme 2. Reaction of ferrocenyl methanols **1a–c** with chlorophosphate **2a**. (*i*) THF, –50 °C, ^{n}BuLi, **2a**, ambient temperature, 18 h. Yields are based on 1a–c. a) **1a** as the starting material. b) **1b** as the starting material, c) **1c** as the starting material. d) Hexane/THF mixture (1:1 ratio, *v*/*v*), 60 °C, 18 h. e) Hexane, 60 °C, 1 h.)

To prevent *β*-H eliminations as observed for **1b** and **1c**, the alkyl chains were replaced by phenyl groups as characteristic for **1d**,**e** (Scheme 3). Lithiation of **1d** with BuLi and subsequent treatment of **1d**-Li with **2a** gave the respective ether **6b** (de = 0.52), whereas for **1e** the starting material could solely be recovered. Compound **6b** was obtained in a yield of 87 %.[25] Since it is not clear if **1e**-Li did react with **2a** or was protonated during the work-up procedure, the steric demand was reduced from fenchyl units in **2a** to ethyl groups in **2b** (Scheme 3). The addition of **2b** to **1e**-Li immediately resulted in an exothermic reaction. Column chromatic work-up gave 6,6-diphenylfulvene (**10**) in 25 % yield and the ferrocenylmethyl-substituted cyclopentadienes **11a,b** (22 %, Scheme 3). Similar to the mechanism depicted in Scheme 2, the *in situ* formed ferrocenyl phosphate eliminates diethyl phosphate, leading to the cationic species **4d**$^{+}$. This cation underwent an electrophilic aromatic substitution reaction with a hitherto *non*-substituted cyclopentadienyl group, resulting in the release of a Fe···Cp'$^{+}$ fragment, which most likely decomposes to **10** and a Fe^{2+} ion. Compound **11** was obtained as a 3:8 cyclopentadiene isomeric mixture of **11a**/**11b** (Scheme 3), whereas **11b** crystallized from this mixture (Figure 2). After 4 weeks in solution at ambient temperature, this ratio had changed to 7:4, due to a 1,5-sigmatropic rearrangement, confirming 3-substituted **11a** as the thermodynamically stable product, which is typical for this kind of molecules.[26] A rapid 1,5-sigmatropic shift in **11a** of the 1*H*-atom from the 3- to the 4-position, also gives **11a**. However, this equilibrium results in a broadening of the signals of the C_5H_5 and both C_5H_4 signals in the $^{13}C\{^{1}H\}$ NMR spectra (ESI).

The CH_2 moiety in **1a** was replaced by a CH(^{t}Bu) fragment in **1f** (Scheme 4) to prevent either the ether formation, by an increased steric demand, or the dehydration reaction, due to the absence of *β*-hydrogen atoms. Ferrocenyl methanols **1f**,**g** were accessible by the reduction of pivaloylferrocene **12f**, or the reaction of acylferrocenes **12a**,**b** with ^{t}BuLi. Since **12f** did not react with $NaBH_4$ at 60 °C, formyl- (**12a**, R = H) and acetylferrocene (**12b**, R = CH_3) were reacted with ^{t}BuLi and **2a** was subsequently added.



Scheme 3. Reaction of ferrocenylphenyl methanols **1d**,**e** with chlorophosphates **2a**,**b**. (*i*) THF, ^{n}BuLi, –50 °C, **2a**/**2b**, ambient temperature, 18 h. Yields are based on **1d**,**e**. a) THF/hexane mixture (1:1, *v*/*v*), 60 °C, 18 h.)

In case of R = H, alcohol **1f** was obtained within the appropriate work-up, which is supported by the absence of the Wagner-Meerwein rearrangement product **9d**. In contrast, for *α*-ferrocenyl methanol **1g** (R = CH_3), possessing a *β*-hydrogen atom, the elimination reaction involving a 6-membered cycle (Scheme 2) or the formation of **4f**$^{+}$ occurred, due to the stability of alkyl **4**$^{+}$-type systems and the formation of **9c**.[27]

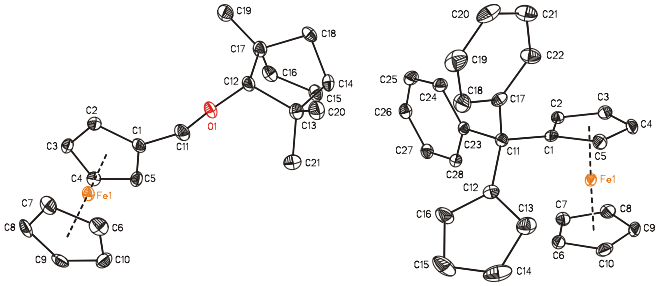
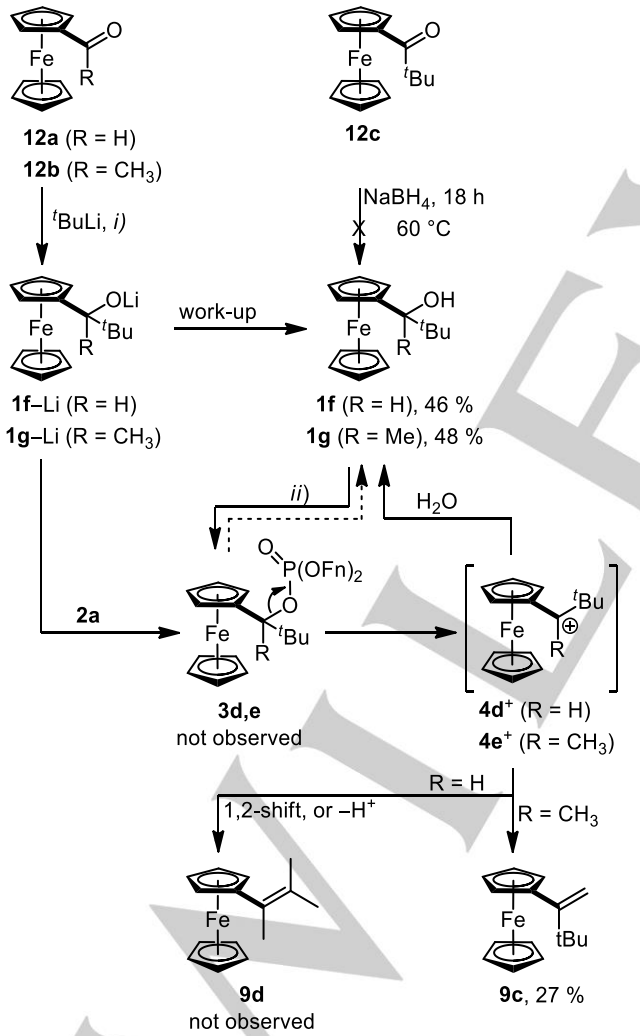


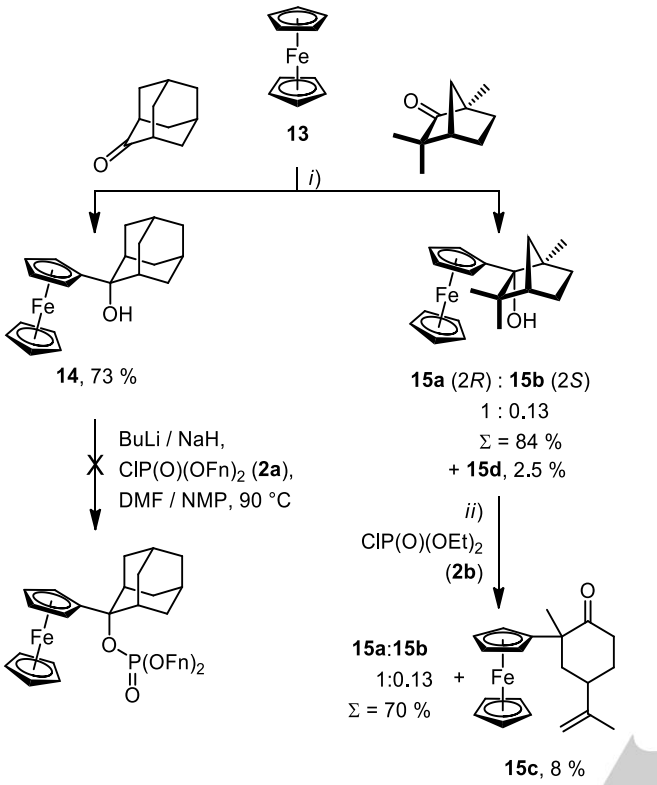
Figure 2. ORTEP (30 % probability level) of the molecular structures of **8** (left) and **11b** (right) with the atom numbering schemes. All hydrogen atoms and a second crystallographically independent molecule of the asymmetric unit of **11b** have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°) for **8**: 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 **11b**: 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).



Scheme 4. Reaction of ^{t}Bu-substituted ferrocenyl methanols **1f**,**g** with chlorophosphate **2a**. (*i*) Et_2O, ^{t}BuLi. *ii*) Et_2O, ^{t}Buli, **2a**.)

The alkene formation in **9c** was prevented by introducing bicyclic systems such as 2-adamantyl and fenchyl (Scheme 5). Compound **14** was available by reacting mono-lithiated ferrocene **13**–Li[28] with 2-adamantanone, resulting in the recovery of alcohol **14** in good yields (73 %). An interesting feature in the crystal structures of **14** (Figure 3) is the presence of a Fe···H–O interaction, due to the orientation of the hydroxy group towards the Fe atom, also found for **1g** (Figure 3). By reacting **13**–Li with the *chiral-pool* derived ketone (*1R*)-fenchone, alcohols **15a**,**b** were formed as diasteromers (Scheme 5). [29, 30] A reported synthetic methodology for **15** is the reaction of (*1R*)-fenchone with ferrocene in presence of $CeCl_3$, giving an epimeric ratio of 1:0.25.[29] With the herein reported synthetic protocol the epimeric ratio could be improved to 1:0.13 (Scheme 5). Within the synthesis of **15**, also the ferrocenyl-substituted *non*-bicyclic side product **15d** was formed (Figure SI2), which can be explained by a cationic isomerization reaction after release of a diethyl phosphate anion. Compound **15d** 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 (ESI).

For the deprotonation of **14**, BuLi and sodium hydride were used as bases to investigate the effect of the counter cation towards the nucleophilic attack at the chlorophosphate **2a**. Treatment of **14**-Li/Na with **2a** in DMF or *N*-methyl-2-pyrrolidone at 90 °C, however, exclusively gave the starting material back. The same result was obtained, when **15** was consecutively treated with BuLi followed by the addition of **2a** (hexane, 80 °C, 18 h). Replacing **2a** by the sterically less demanding diethyl derivative **2b**, did not result in the formation of the corresponding phosphate, rather **15c** could be isolated as a single isomer (Scheme 5). The molecular structure of **15c** is based on NMR spectroscopic (Figure SI3) and mass-spectrometric studies (m/z = 336.1163 for $C_{20}H_{24}FeO$). The formation of **15c** indicates a cationic isomerization reaction after release of diethyl phosphate, as characteristic for **11a**,**b** (Scheme 3).



Scheme 5. Synthesis of ferrocenyl alcohols **14** and **15a**,**b** and their subsequent reaction with chlorophosphates **2a**/**2b** in the presence of a base. (*i*) ^{t}BuLi, THF, KO^{t}Bu, –80 °C, 2-adamantanone (**14**)/ (1*R*)-fenchone (**15**). Yields are based on **13**. *ii*) BuLi, Et_2O, –30 °C, $ClP(O)(OEt)_2$ (**2b**). Yields are based on **15**.)

The results derived by the reaction of ferrocenyl methanols **1a**–**g**, **14** and **15a**,**b** with either the difenchyl (**2a**) or the diethyl chlorophosphate (**2b**) 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.

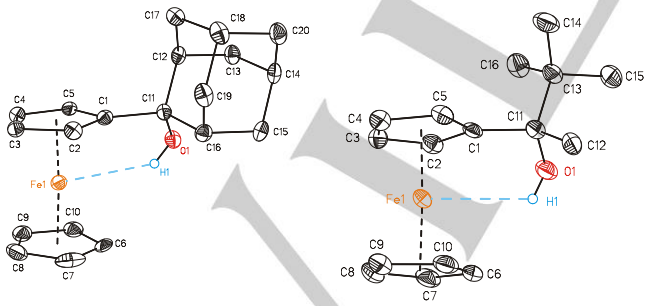
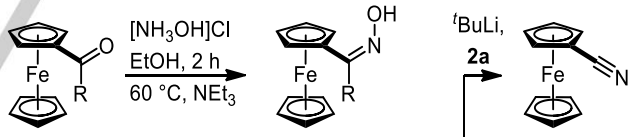


Figure 3. ORTEP (50 % probability level) of the molecular structures of **14** (left) and **1g** (right) with their atom numbering schemes. C-bonded hydrogen atoms and a second crystallographically independent molecule, present in the asymmetric unit of **14**, have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°) for **14**: 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 **1g**: O1···Fe1 3.575(2), O1–H1···Fe1 117.94, C2–C1–C11–C13, 85.0(4); C2–C1–C11–O1 31.7(4).

Another structural motif, suitable for a phosphate formation, are oximes. [31] To prove, if this synthetic methodology is also applicable for ferrocene-based oximes, **16a**,**b** were prepared (Scheme 6). Hence, acylferrocenes **12a**–**d** were reacted with hydroxylammonium chloride in the presence of NEt_3. [32] Nevertheless, only formylferrocene (**12a**) could be converted to oxime **16a** (82 % yield), while **12b**–**d** inhibited the formation of **16c**,**d**, which most likely is attributed to the increased electron density of **12b**–**d**. In case of **12b**, a 1:1 mixture of the starting material with the oxime **16b** was isolated after appropriate column chromatographic work-up. Compound **16c** has not yet been reported in literature, most probably, due to its rapid hydrolysis to give **12d**. We assume that **16d** [33] and partially **16b** were hydrolyzed during the column chromatographic workup. Deprotonation of **16a** was achieved using ^{t}BuLi as a sterically demanding, *non*-nucleophilic base to avoid a nucleophilic attack at the carbonyl carbon atom. Subsequent treatment of **16a**–Li with **2a** predominantly resulted in the formation of ferrocenylnitrile **17** in 72 % yield, along with **12a** (8 %) and **1f** (3 %). While phenyl oximes can successfully be converted into their respective phosphates,[31] ferrocenyl-based derivatives seem to undergo similar dehydration reactions as compared to the ferrocenyl methanols **1b**,**c**,**e** in the presence of **2a** (vide supra).

Recently electron-poor pyrrolyl-, indolyl- and carbazolyl-containing phosphoramidates were converted into stable ferrocenyl phosphoramidates. [34] Thus, the CR_2–*O* motif was replaced by a CR=*N*-bonded ferrocenyl unit. This imino phosphate motif (type **G** molecule, Scheme 1) has rarely been described, especially in ferrocene chemistry, where a sole C=N–$P(O)Ph_2$ unit has been reported, however, without its synthetic



12a (R = H)	**16a** (R = H), 82 %	**17**, 72 %
12b (R = Me)	**16b** (R = Me), 50 %	+
12c (R = ^{t}Bu)	**16c** (R = ^{t}Bu), 0 %	**1f**, 3 %
12d (R = Ph)	**16d** (R = Ph), 0 %	**12a**, 8 %

procedure.[35,36]

Scheme 6. Conversion of **12a**–**d** to ferrocenyl oximes **16a**,**b** and their reaction behavior towards chlorophosphate **2a**. Yields of **16a**,**b** are based on **12a**,**b**.

The imino phosphato motif could, *e.g.* be obtained by condensation reactions of carbonyl derivatives with NH_2-bearing phosphoramidates.[20,37,38] A protocol using oximes, tosylazide or chlorophosphates also allows the preparation of imino phosphates. [39] In addition, the reaction of organolithium compounds with nitriles could be applied in the synthesis of imino phosphates,[40] however, the alkyl-substituted imino phosphates rapidly isomerize into the respective enamine phosphoramidates.[38] The latter approach was applied on ferrocenylnitrile **17**, which was reacted with MeLi and ^{t}BuLi to afford imine anions. In addition, commercially available nitriles

owere treated with mono-lithio ferrocene **13**-Li (Scheme 7). In both cases, the *in situ* formed imine anions were subsequently reacted with **2a** giving imino phosphates **18**–**d** in up to 60 % yield (R = Me, Scheme 7). The *E*-/*Z*-ratios for sterically *non*-demanding methyl (**18a**), phenyl (**18b**) and triphenylphenyl (**18c**) groups are similar and ranges between 14.3:1 and 9.1:1 (Experimental Section). The sterically demanding ^{t}Bu derivative **18d** inverted the *E*-/*Z*- ratio to 1:3.85 (Scheme 7). The assignment of the *E*-configuration at the C=N double bond for **18b**,**c** is derived from single crystal X-ray diffraction analysis (Figures 4 and SI7) and is in accordance with **18a**. Within the reaction of ^{t}BuC≡N with **13**–Li or **17** with ^{t}BuLi the formation of oxidative coupled azine **19** is observed, possessing a *Z*-/*Z*-configuration as evidenced by single crystal X-ray diffraction analysis (Figure 5). Azines are in general available by reacting carbonyl compounds with hydrazine, [41,42] or oxidation of hydrazines with oxygen.[41,42] They are also accessible under oxidative conditions by reacting nitriles with RLi and subsequent treatment with $CuCl/O_2$,[42] or in the presence of perbenzoates.[43] In contrast, **19** is the first example, which has not been formed by a condensation reaction with hydrazines.[44]

The use of isopropyl nitrile, as a *CH* acidic compound, did not produce the respective phosphate, rather giving ferrocene (Scheme 7). The 1-adamantyl derivative **18f** was not accessible, due to its steric demand. The reaction of 9-anthryl nitrile with **13**–Li and **2a** afforded, instead of the expected phosphate **18g**, compound **22** as a dark red solid. Similar to **19**, the formation of **22** can be explained by an oxidative coupling of **13**–Li with 9-anthryl nitrile. However, running the reaction of 9-anthryl nitrile with **13**–Li without chlorophosphate **2a** failed to give **22**, which is indicated by the absence of a color change from orange to dark red. We assume that a nucleophilic attack of **13**–Li occurred at the 10-position 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 **2a**, since chlorophosphates can easily be reduced with metals (Na, K), potassium naphthalenide [45] or $NaBH_4$.[46] The 9,10-substitution pattern of **22** was *inter alia* verified by single crystal X-ray diffraction analysis (Figure 5). The presence of a C≡N substituent was also evidenced by its $^{13}C\{^1H\}$ NMR signal at 118 ppm and the respective stretching ferquency in the IR spectra at 2208 cm^{-1}.[47]

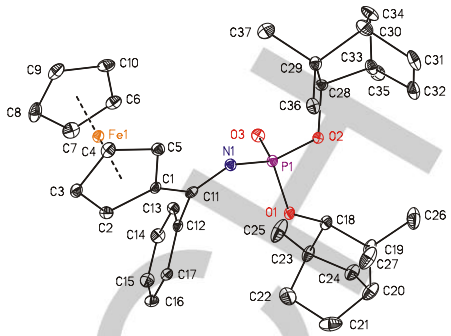
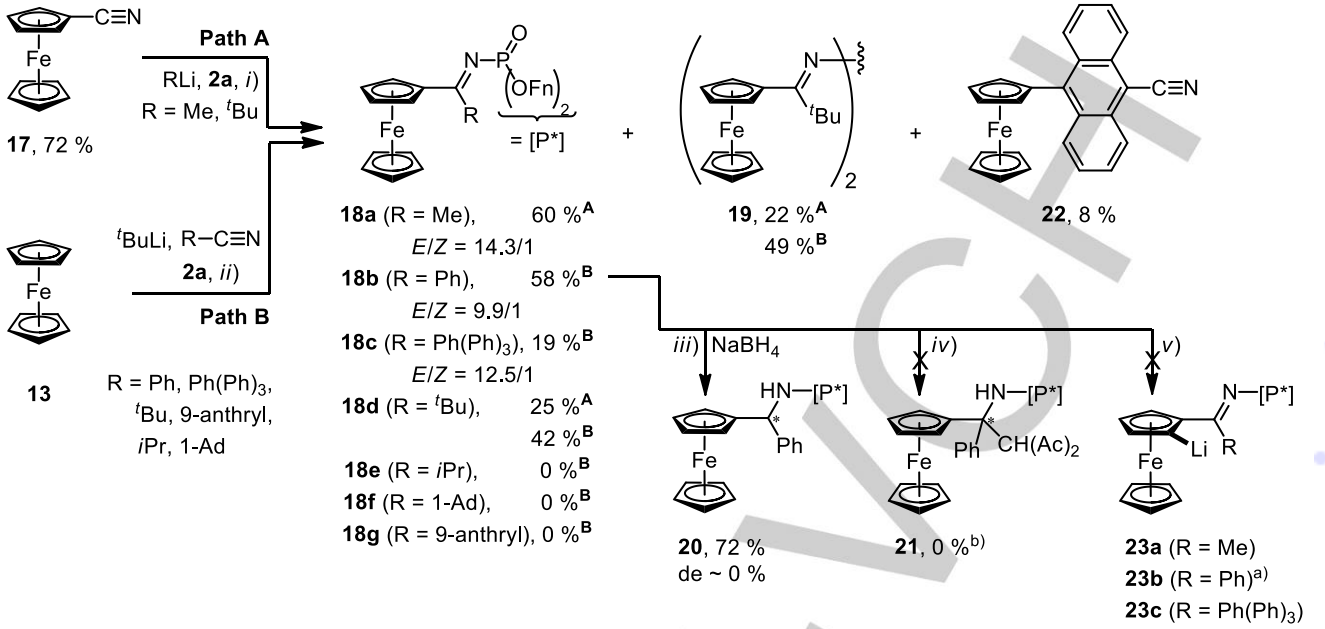


Figure 4. ORTEP (30 % probability level) of the molecular structure of **18b** with the atom numbering scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): C11=N1 1.286(4), N1–P1 1.645(3), P1–O1 1.569(2), P1–O2 1.583(3), P1–O3 1.457(2).

The applicability of alkylidene phosphoramidates **18a–d** as starting materials for anionic homo phospho-Fries rearrangements was proven by their treatment with lithium tetramethylpiperidide (Litmp) or lithium di*iso*propylamide in either hexane or THF (Experimental Section). In our recently published synthetic protocols for the completion of anionic phospho-Fries rearrangements, ethyl phosphates are preferably lithiated in THF at low temperature,[3,12] whereas steric demanding bicyclic, *e.g.* fenchyl groups, require higher temperatures and a *non*-polar solvent.[9,13] However, the applied reaction conditions described within our studies herein did not indicate a lithiation of the ferrocenyl backbone to form **23a**–**c**, whereas molecules derived from a nucleophilic attack of the base, e.g. 78 % of **12d** for **18b**, were detected (Scheme 7).

The reactivity of the C=N bond has exemplarily been investigated by reacting **18b** with acetylacetone in the presence of K_2CO_3. In contrast to phenyl-based derivatives, where nucleophilic attacks at the carbonyl atoms proceed[35a,48,49], solely the starting material was recovered in case of **18b**. Reduction of the C=N bond of **18b** by using $NaBH_4$ gave amine **20** (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 (Experimental Section). Single crystal X-ray diffraction analysis of **20** (Figure SI11) revealed the crystallization of a racemic mixture of two epimers with respect to their configuration at the former carbonyl carbon atom. The reduction from **18b** to **19** could also be confirmed by IR spectroscopic measurements, where the $\nu_{C=N}$ vibration of the imino phosphoramidate **18b** at 1572 and 1611 cm^{-1} disappeared, while a new band at 3185 cm^{-1} (ν_{NH}) could be observed.

The absence of a phosphoryl moiety in azine **19** was verified by IR spectroscopy, since the C=N stretching frequency in **18b** was shifted from 1572 and 1611 cm^{-1} to 1559 cm^{-1} in **19**. The C≡N unit in **22** absorbed at 2208 cm^{-1}. A remarkable feature of dark purple **22** is the bathochromic shift and the high absorption coefficient of 1850 L mol^{-1} cm^{-1} of the d→d transition at 536 nm as compared to, *e.g.* **19** (λ_{max} = 431 nm, ε = 883 L mol^{-1} cm^{-1}, Table SI7).



Scheme 7. Synthesis of imino phosphates **18a–d**, azine **19** and anthrylferrocene **22**. (*i*) THF, –80 °C, RLi (R = Me, ^{t}Bu), –30 °C, **2a**. Yields are based on **17**. *ii*) THF, KO^{t}Bu, ^{t}BuLi, –80 °C, R–C≡N (R = Ph, $C_6H_2(Ph)_3$, ^{t}Bu, 9-anthryl, *i*Pr, 1-adamantyl), –30 °C, **2a**. Yields are based on **2a**. *iii*) THF, $NaBH_4$, H_2O. Yield based on **18b**. *iv*) Acetylacetone, K_2CO_3, CH_2Cl_2, $MgSO_4$, 50 °C 18 h. *v*) Litmp or LDA, hexane or THF, –40 °C/ 0 °C. a) 78 % of ketone **12d** were obtained; Litmp, hexane, tmeda, 25 °C, 48 h without Me_2SO_4).

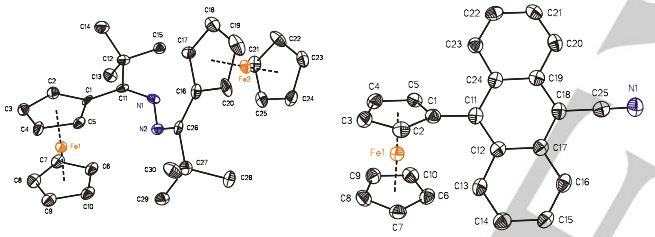


Figure 5. ORTEP (50 % probability level) of one of the crystallographically independent molecules of the asymmetric unit of **19** (top) and **22** (bottom). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (°) and torsion angles (°) for **19**: C=N 1.277(10)–1.293(10), 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 **22**: C25–N1, 1.142(4), C18–C25 1.441(5).

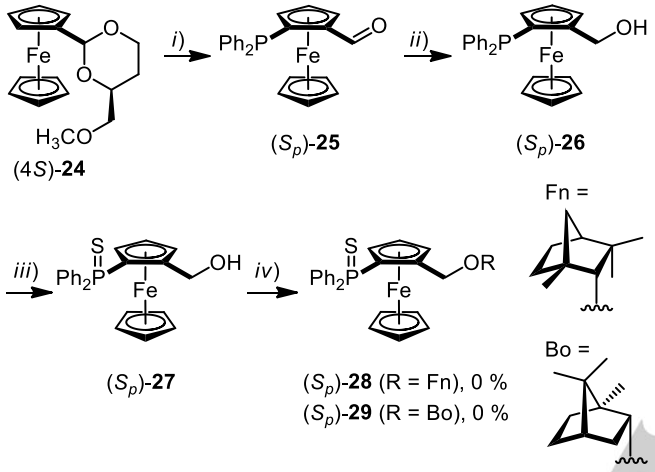
The presence of two ferrocenyl units within one molecule, separated by a π-conjugated bridge allows for the investigation of an electronic communication between the redox centers in the single-oxidized mixed-valent species. Thus, the electrochemical behavior of the diferrocenyl compound **19** was investigated by cyclic voltammetry (CV) and square-wave voltammetry (SWV) (Figure SI4), and compared with **18d** possessing a similar substitution pattern at the C=N carbon atom (Table SI8). Compound **19** showed two reversible one electron redox events at 24 and 225 mV, one was observed for **18d** (–135 mV). If the N=C group in **19** is replaced by the phosphoryl group in **18d**, the first redox event is shifted from 24 (for **19**) 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 **19** are separated by 201 mV, which is higher than for the literature known 1,4-diaza derivative (< 100 mV)[50], but lower than for 1,4-diferrocenylbutadiene (225 mV).[51] If the voltage within the CV measurement for **18d** is increased to > 1300 mV, the redox event becomes irreversible (Figure SI5), indicating the decomposition of this oxidized species.

In situ UV-Vis/NIR spectroelectrochemical measurements were additionally carried out for **19** 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,[51] or caused by electrostatic interactions. However, an inter-valence charge transfer (IVCT) absorption in the region between 1250 and 2750 nm[52] has not been observed (Figure SI6), 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 **19** might be supported by the non-planar C=N–N=C moiety in the solid state structure (Figure 5), due to a torsion angle of ~53 °.

Planar-chiral Ferrocenyl Methanols

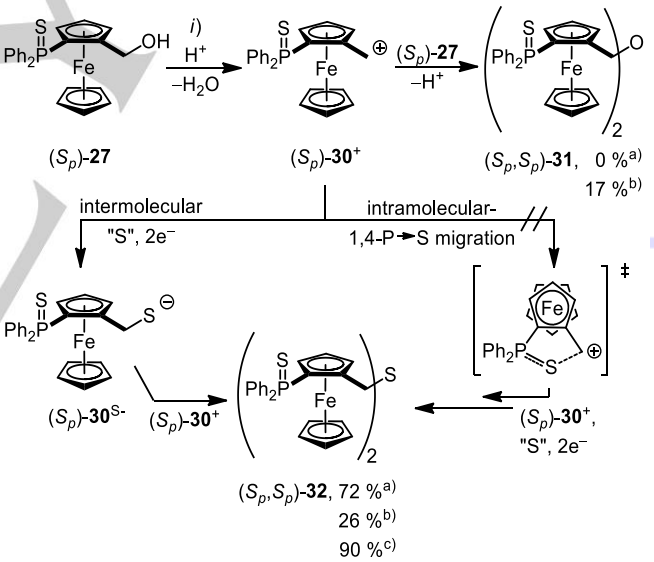
Attempts to apply the anionic homo phospho-Fries rearrangement at ferrocenyl methanols, oximes and imines showed that the additional methylene or CR_2 fragment, between the ferrocenyl and hydroxyl group, causes side reactions and prevents a successful formation of phosphates. The initial 1,2-P,CH_2OH substitution pattern, well-suitable for further functionalization, was synthesized by a known literature eight-step synthetic procedure (Scheme 8).[5,53] Thus, formylferrocene[54] was first converted into the chiral acetal (4S)-**24**, followed by diastereoselective lithiation in *ortho*-position with ^{t}BuLi and the consecutive reaction with $ClPPh_2$ (Scheme 8). After subsequent cleavage of the acetal

group the enantiopure phosphane (S_p)-**25** could be obtained.[53] Aldehyde (S_p)-**25** was reduced to alcohol (S_p)-**26** by using $NaBH_4$, followed by the addition of sulfur to the reaction mixture to protect the lone-pair of electrons at the phosphorus atom. The reaction of (S_p)-**27** with ethanol, benzyl alcohol or menthol was recently reported, whereby the yields of the corresponding ethers reduced from 56 to 27 % in the same order.[14] Attempts to react (S_p)-**27** with the sterically more demanding (1*R*)-*α*-fenchyl (Fn, Scheme 8) and (1*S*)-borneyl alcohols (Bo) in presence of *p*-TsOH afforded a mixture of *non*-separable ferrocenyl species rather than (S_p)-**28**/**29** (Scheme 8).



Scheme 8. Synthesis of (S_p)-**27** and its acid catalyzed reaction with chiral-pool alcohols. (*i*) 1st, ^{t}BuLi, Et_2O, –78 °C, $ClPPh_2$, –30 °C, 99 % *de*; 2nd, *p*-TsOH, CH_2Cl_2/H_2O, reflux, 74 % based on (4*S*)-**24**. *ii*) $NaBH_4$, MeOH, 2 h, 25 °C, 92 % based on (S_p)-**25**. *iii*) S_8, 2 h, CH_2Cl_2, 25 °C, 95 % based on (S_p)-**26**. *iv*) *p*-TsOH, ROH, R = Fn/Bo.)

Ferrocene (S_p)-**27** was also reacted with *p*-TsOH without adding a further electrophile to force the self-condensation to (S_p)-**31** (Scheme 9). However, instead of the oxoether (S_p,S_p)-**31**, the thioether (S_p,S_p)-**32** 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 spectrum from 59.9 ppm (**27**) to 31.3 ppm (**32**) (Table SI5). The molecular structure of **32** in the solid state was additionally confirmed by single crystal X-ray diffraction analysis (Figure 6). The NMR data especially of the CH_2 moiety in (S_p)-**27** are in the range for CH_2–O fragments (Table SI5).[14] Elemental analysis further evidenced the formation of (S_p)-**27**. Addition of sulfur within the conversion of (S_p)-**27** to (S_p,S_p)-**32** remains the yield at 77 %, revealing that inorganic sulfur is not involved within the formation of **32**. Thus, (S_p)-**30**$^+$ is considered as the sulfur source. For the calculation of the herein reported yields of (S_p,S_p)-**32**, three molecules of (S_p)-**27** must be considered. Desulfurized **30**$^+$ most likely decomposed releasing two electrons, which are required for the formation of **32**. 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)-**27** can be excluded, since the formed (S_p)-**26** 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)-**27** under acidic conditions and a migration of a P-bonded sulfur to the exo carbon atom, where the positive charge is present (Scheme 9). This might have occurred *via* an inter- or intramolecular mechanism by passing through a 5-membered transition state (Scheme 9). In contrast to hydroxy, the formed thiol functionality is not removed acid-catalyzed and reacts with (S_p)-**30**$^+$ forming thioether (S_p,S_p)-**32**. It should be noted that for the conversion of ferrocenyl methanol (**1a**) to the respective thiol derivative, Lawesson's reagent is generally required as a sulfur source.[55] The reaction strongly depends on the concentration of (S_p)-**27** in the reaction mixture and lowers the yield of (S_p,S_p)-**32** to 26 %, while changing from 48 mmol L^{-1} to 96 mmol L^{-1} (Table SI1). Interestingly, the higher concentration preferably resulted in the formation of (S_p,S_p)-**31**, indicating that the reaction of (S_p)-**27** with (S_p)-**30**$^+$ is faster as compared to the removal of an OH group and the migration of the sulfur atom. However, (S_p,S_p)-**31** could not be separated from its mixture with (S_p,S_p)-**32**, neither by crystallization nor column chromatography. Suggesting that a further decrease of the concentration of (S_p,S_p)-**32** would improve the yield, a 28 m*M* solution was used for the conversion. However, an electrophilic aromatic substitution of the solvent occurred (Scheme 10), giving (S_p)-**33** in 71 % yield. The reaction of the carbo-cation (S_p)-**30**$^+$ with toluene was suppressed by changing the solvent to 1,4-dioxane, which increased the yield of (S_p,S_p)-**32** to 90 % (Scheme 9, Table SI1).



Scheme 9. Acid-induced formation of (S_p,S_p)-**32**. Yields are based on (S_p)-**27**, whereas for (S_p,S_p)-**32** the requirement of one molecule of (S_p)-**27**, as the sulfur source has been taken into consideration. (*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.)

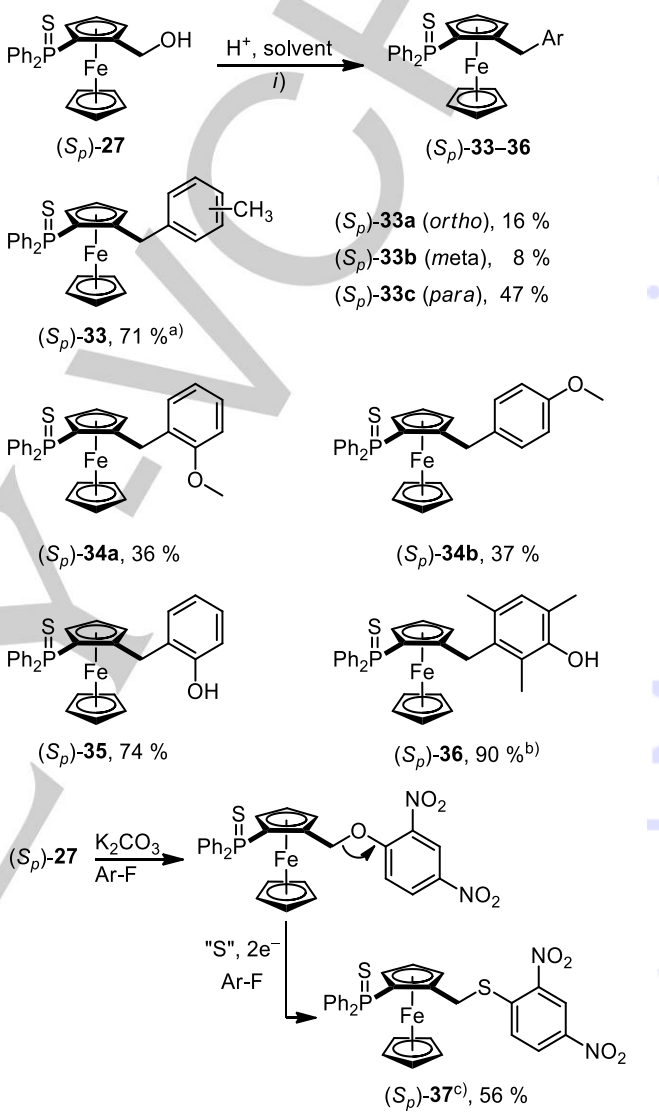
Attempts to obtain (S_p,S_p)-**31** by a similar reaction, as observed for **6a** (Scheme 2) or **6b** (Scheme 3), gave, however, 50 % of the starting material back and an unidentifiable mixture of compounds. The lowering of the concentration of (S_p)-**27** in the reaction mixture should not affect the sulfur migration, if an intramolecular mechanism is considered and thus, the yield of (S_p,S_p)-**32** should not be decreased. Instead, the reaction of **30**$^+$ with toluene was

observed, instead of a sulfur migration, indicating an intermolecular process.

The observed reaction of (S_p)-**30**$^+$ with the solvent toluene was further investigated, since this electrophilic aromatic substitution reactions are rarely described so far.[24,56] Recently, ferrocenyl methanol (**1a**) was coupled with electron-rich aromatics, *e.g.* 2-naphthol, pyrrole giving 1-naphthylmethyl and 2-pyrrolylmethyl ferrocenes by using $(NH_4)_2[Ce(NO_3)_6]$.[24] The use of highly activated salicylate anions predominantly occurred *ortho* to the OH group.[56] The Fc–CH_2-Ar pattern is also accessible by the alkylation[22,57] or acylation of ferrocene,[58,59] followed by removal of the oxygen substituent.

The scope of the electrophilic aromatic substitution reaction has been extended to planar-chiral derivatives by reacting (S_p)-**27** with further aromatics (Scheme 10). In toluene, compound (S_p)-**33** was formed as a 2:1:6 mixture of the *o*-:*m*-:*p*-isomer. The three regioisomers 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 (ESI) and the solid state structure of (S_p)-**33a** (Figure SI15). However, using anisole as the solvent afforded a 1:1 mixture of the *ortho*- and *para*-isomers, while the *meta*-isomer was not formed. The increased amount of *ortho*-substituted (S_p)-**34a**, compared to the *para*-product (S_p)-**34b**, is due to an electrostatic attraction of the carbo-cation and the OMe substituents, superimposing the steric effect. The *o*-OMe substitution pattern in (S_p)-**34a** could *inter alia* been verified by single crystal X-ray diffraction analysis (Figure SI17). Using phenol within the electrophilic aromatic substitution reaction exclusively gave *ortho*-substituted (S_p)-**35**. A nucleophilic attack of the oxygen functionality at the carbo-cation to an aryl ether has not been observed under the acidic conditions, as it could be shown for a nucleophilic process.[56] Recently, we could show that the nucleophilicity of hydroxy-aryl species, *e.g.* phenolates and naphtholates is rather low,[34,60] concluding that the electrophilic aromatic substitution is faster and irreversible. Attempts to force the nucleophilic attack of the oxygen atom by blocking the electronically preferred *ortho*- and *para*-positions as in mesityl phenol, resulted in the formation of *meta*-substituted (S_p)-**36** (Scheme 10). The *meta*-methoxy/hydroxy substitution pattern has rarely been described and usually has to be forced by reacting the appropriate lihtio-arene with formyl ferrocene [61], cyanomethylferrocene [62] or by applying an S_EAr reaction of ferrocene with the respective aryl carbonyls.[63] Ferrocenoles have also been shown to undergo reactions with aryl fluorides, resulting in stable ferrocenyl aryl ethers even at ambient temperature by using Sangers reagent (2,4-dinitrofluorobenzene).[12] Thus, (S_p)-**27** was activated with K_2CO_3 and reacted with Sangers reagent (Scheme 10). Instead of the oxo ether, the thio derivative (S_p)-**37** was formed, which was *inter alia* proven by single crystal X-ray diffraction analysis (Figure 6). Most likely, a S_NAr-type reaction had occurred followed by elimination of 2,4-dinitrophenolate, subsequent migration of sulfur from the substrate to the exo-carbo-cation and attack of the formed thiol/thiolate in a further S_NAr reaction.

IR spectroscopy verified the presence of the nitro groups in **37**, which were observed with their NO stretching frequency at 1520 and 1345 cm^{-1}. As expected,[64] the P=S stretching vibration was observed, *e.g.* for **35** and **37** at 643 and 645 cm^{-1}, respectively. In phenol **35**, the OH band was observed at 3403 cm^{-1}.



Scheme 10. Electrophilic aromatic substitution of (S_p)-**27** with electron-rich arenes giving (S_p)-**33**–**36** and its nucleophilic aromatic substitution with an aryl fluoride to produce (S_p)-**37**. Yields are based on (S_p)-**27**. (*i*) *p*-TsOH, toluene (**33a–c**), anisole (**34a**,**b**), phenol (**35**), 80 °C. a) As a 2:1:6 mixture. b) CH_2Cl_2, 50 °C, 72 h. c) K_2CO_3, 2,4-dinitrofluorobenzene, DMF. Yield calculated using two equiv of (S_p)-27.)

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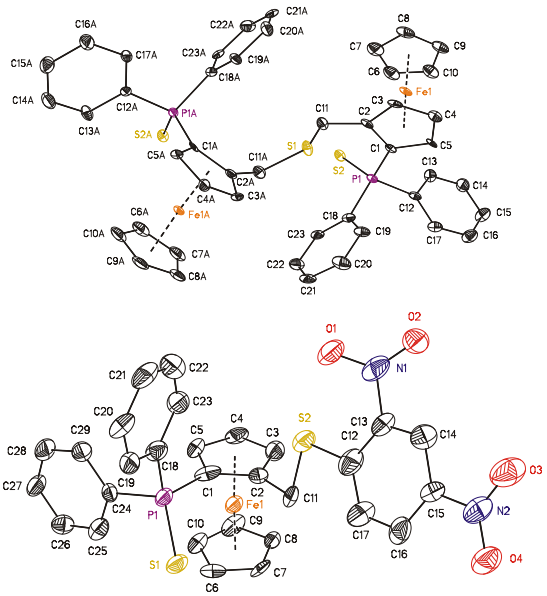
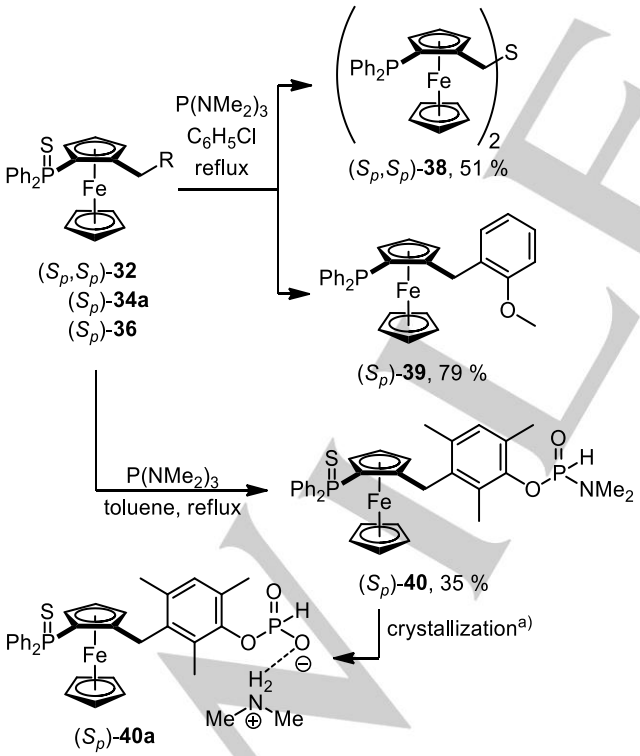


Figure 6. ORTEP (50 % probability level) of the molecular structures of (S_p,S_p)-**32** (top) and (S_p)-**37** (bottom) with their atom numbering scheme. Hydrogen atoms and a second molecule in the asymmetric unit of (S_p)-**37** have been omitted for clarity. Selected bond distances (Å) and angles (°) for (S_p,S_p)-**32**: P=S 1.952(5), C11–S 1.814(13), C11–S–C11A 103.0(9); for (S_p)-**37**: P=S 1.954(5)/1.960(5), C11–S2 1.858(17)/(1.833(16), S2–C12 1.757(17)/1.724(19), N–O 1.210(18)–1.235(19), C11–S2–C12 103.7(8)/104.1(9). Symmetry operation for generating equivalent atoms (A): –*y*, –*x*, –*z*+1/2.



Scheme 11. Desulfurization of (S_p,S_p)-**32**, (S_p)-**34a** and (S_p)-**36** using $P(NMe_2)_3$. a) Single crystals were obtained by crystallization of (S_p)-**40** from a dichloromethane solution.

The thio ether group in (S_p,S_p)-**32** and (S_p)-**37** has up to now solely been achieved by a nucleophilic attack of thiols or thiophenols[65] at ferrocenyl methanols. The reduction of the P^V species (S_p,S_p)-**32**, (S_p)-**34a**, and **37** to the appropriate P^{III} phosphines was performed according to literature reported protocols by refluxing the phosphine sulfides with $P(NMe_2)_3$ in toluene (Scheme 11).[14] However, in case of (S_p,S_p)-**32** no product could be isolated under the conditions applied (Supporting Information). Optimization of the reaction conditions (Table SI2) showed that with the higher boiling solvent chlorobenzene the reaction successfully proceeded at 130 °C. This allowed the isolation of (S_p)-**39** after appropriate work-up in a yield of 51 %.

Attempts to desulfurize (S_p)-**36** did not give the P^{III} species (Scheme 11). Instead, the hydroxy group reacts with $P(NMe_2)_3$ and partial hydrolysis of the phosporamidate to phosphite (S_p)-**40** took place after a flash column chromatographic purification process. The identity of (S_p)-**40** was *inter alia* verified in the form of its ammonium phosphite (S_p)-**40a** by single crystal X-ray diffraction analysis. Hydrolysis occurred during the crystallization process (Figure SI19). The occurrence of (S_p)-**40** and (S_p)-**40a** as the P(O)H tautomer is evidenced by a $^1J_{H,P}$ coupling constant of 646 Hz for the PH fragment in the ^{1}H and ^{31}P NMR spectra (Table SI4).

Suzuki-Miyaura Cross-Coupling Reactions

Compounds (S_p,S_p)-**38** and (S_p)-**39** were investigated as stereopure, planar-chiral supporting ligands within Suzuki-Miyaura *C*,*C* cross-coupling reactions for the synthesis of hindered biaryls, using the reaction conditions as reported in references 3 and 8. The use of bidendate (S_p,S_p)-**38** required an optimization of the Pd:L ratio and concentration (Table SI3), which has exemplarily been performed for the synthesis of **41a** by using $Pd(dba)_2$ (dba = dibenzylideneacetone) as the Pd source. Starting with 1 mol-% of Pd and (S_p,S_p)-**38** as a ligand, biaryl **41a** was formed almost quantitatively in an *ee* of 17 %, which is higher than for the ethyl and benzyl derivatives.[14] While decreasing the Palladium loading to 0.5 and 0.1 mol-%, respectively, reduced the *ee* to 12 % and 7 %, associated with a lowering of the yield to 57 % (Entries 1–3, Table SI3). However, a Pd:L ratio of 1:0.5 did not give **41a**. 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 SI3). The substrate scope was extended using the conditions in Entry 1 (Table SI3) for (S_p,S_p)-**38** and the results thereof are compared with (S_p)-**39** as a *P*,*O*-substituted ferrocene (Figure 7).

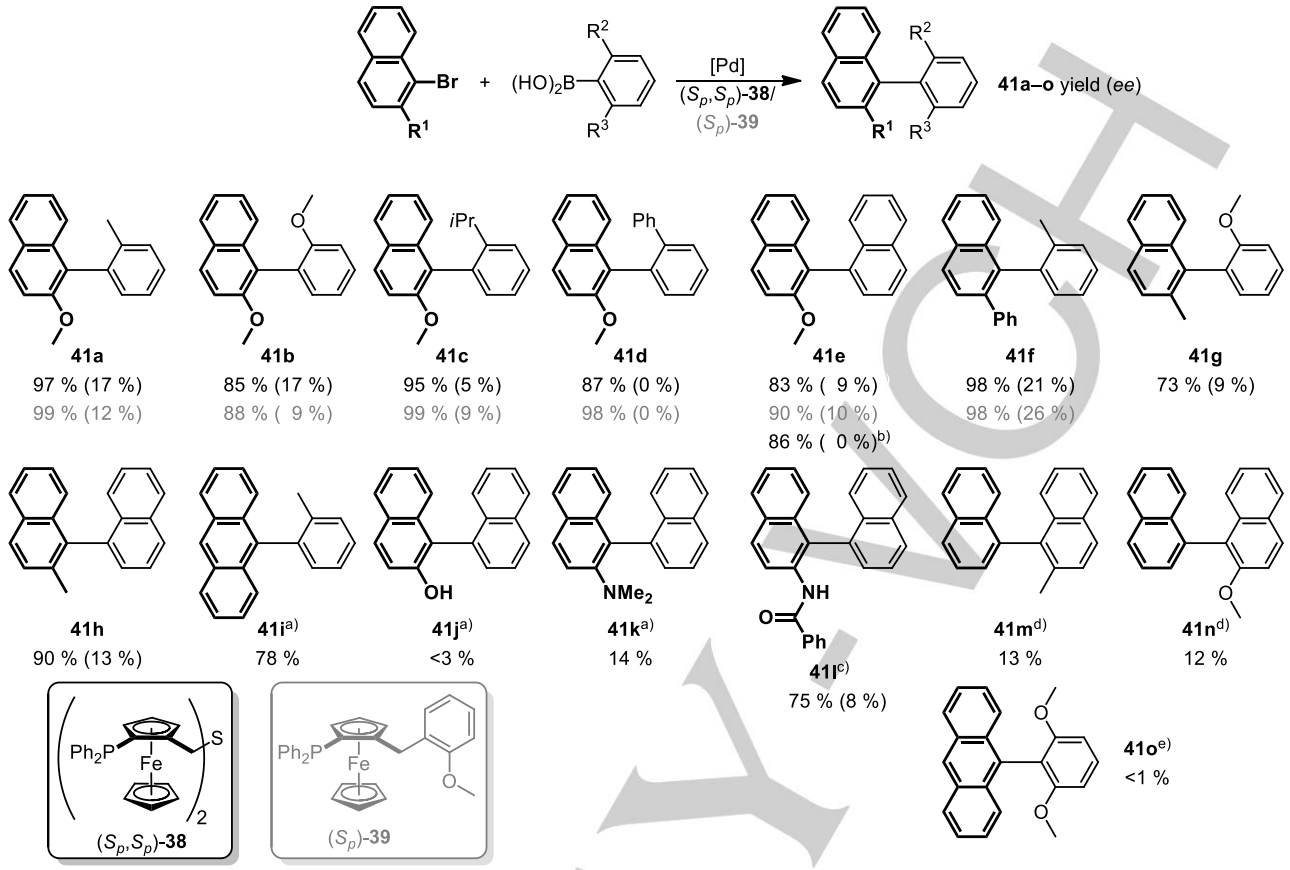


Figure 7. Suzuki-Miyaura *C*,*C* cross-coupling reactions for the synthesis of *ortho*-substituted biaryls **41a–o** using(S_p,S_p)-**38** and (S_p)-**39**. Reagents and conditions: aryl halide (1.0 mmol), boronic acid (1.5 mmol), $K_3PO_4 \cdot H_2O$ (3.0 mmol), toluene (3 mL), 0.5 mol-% [$Pd_2(dba)_3$], 1.0 mol-%, (S_p,S_p)-**38**/ 2.0 mol-% (S_p)-**39**, 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) Using dppf as the ligand. c) 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. d) Yields are obtained from the ^{1}H NMR data of the crude product. e) 1,4-Dioxane, 100 °C, 48 h.

Comparing the yield and *ee* of the 2-methoxy naphthyl derivatives **41a–e** (Figure 7) reveals a dependency on the substitution pattern of the boronic acid. While a similar *ee* was observed for an OMe (**41a**) and Me (**41b**) group, an increase of the steric demand gave a racemic mixture for the phenyl derivative **41d**. In contrast, an *ortho*-phenyl substituted aryl halide gave **41f** with 21 % *ee*. The Suzuki-Miyaura reactions were also carried out by using (S_p)-**39** as the ligand, giving similar or slightly higher yields of the respective biaryls, while a somewhat decrease of the *ee* was observed for **41a–f** (Figure 7). 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 ligand gave **41e** with a similar yield as observed for (S_p,S_p)-**38** and (S_p)-**39**, as a racemic mixture. Replacement of the OMe by a Me group in biaryls **41g**,**h** gave opposite results for yield and *ee*, when compared to **41b**,**h**. Larger condensed aromatics such as 9-bromoanthracene gave **41i** 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 **41j–l** (Figure 7). However, the presence of the hydroxy group gave **41j** in only 3 % yield, besides 1,1'-binaphthyl and naphthalene. An interaction of the substrate molecules with the ligands is assumed, since type **41j** biaryls are known to be formed under similar reaction conditions.[66] Similarly, **41k** was formed in 14 % yield, besides the starting halide and 1,1'-binaphthyl.

In contrast to OH, the presence of a NH_2 group did not have a disadvantageous influence. Due to a reported rapid oxidation of the formed biaryls[67], the reaction mixture has directly been treated with benzoyl chloride, giving **41l** in 75 % yield and an *ee* of 8 %. However, (S_p,S_p)-**38** is unsuitable as a ligand in the Suzuki-Miyaura reaction, if double *ortho*-substituted boronic acids are used, as shown for **41m–o** (Figure 7). GC-MS analysis revealed the presence of the starting halide and the respective hydro deboronation products. Thus, the transmetalation process seems to be the decisive step within the catalytic cycle.

Conclusion

The anionic homo phospho-Fries rearrangement was applied on ferrocenyl methanols for the synthesis of the respective planar-chiral 1,2-P,CH_2O-functionalized derivatives using phosphates as

key starting material. Within this reaction the addition of chlorophosphates resulted *in situ* in the formation of phosphates, which rapidly separate into phosphate and ferrocenyl carbenium ions. These cations underwent electrophilic reactions resulting in the formation of symmetric diferrocenylmethyl ethers. Replacement of the CH_2^+ unit by a CPh_2^+ fragment within the respective ferrocenyl methanols gave diphenyl fulvene. The formation of this species results from an electrophilic aromatic substitution reaction of the CPh_2^+ moiety with the hitherto *non*-substituted cyclopentadienyl ligand. A similar dehydration was observed for ferrocenyl oximes in the presence of phosphates giving a nitrile. Instead of alcohols, the treatment of nitriles with FcLi or ^{t}BuLi and subsequent addition of a chlorophosphate produced diverse chiral-pool-based ferrocenyl imino-phosphoramidates. Besides, the sterically demanding chlorophosphate enabled oxidative coupling of the imines to afford diferrocenyl azine. The reaction of 9-anthrylnitrile with FcLi gave a 10-ferrocenyl substituted product, in contrast to a nucleophilic attack at the C≡N functionality. Thus, ferrocenylmethyl phosphates are not suitable for anionic homo phospho-Fries rearrangements.

Applying *ortho*-P(S)Ph_2-substituted ferrocenylmethanol in an acid-catalyzed condensation reaction produced instead of the oxo- the respective thio-ether, whereby the 1,2-P(S)Ph_2,CH_2^+ ferrocene acted as the sulfur and the electron source. Lowering the substrate concentration, resulted in electrophilic substitution reactions in the presence of electron-rich aromatics.

Two stereopure ferrocenylmethyl phosphanes were used as supporting ligands in Pd-catalyzed Suzuki-Miyaura *C*,*C* cross-coupling reactions for the atropselective synthesis of hindered biaryls with up to 21 % *ee*. This verified that the P···O distance between the two donor atoms of the supporting ligand plays a decisive role for an efficient chirality transfer from the ferrocenyl backbone to the formed biaryl.

Experimental

General: All reactions were carried out under an atmosphere of argon by using standard Schlenk techniques. For column chromatography, either silica with a particle size of 40–60 µm [230–400 mesh (ASTM)] or alumina with a particle size of 90 µm was used. The assignment and labeling of the H and C atoms in the NMR spectra follows the IUPAC recommendations.[68]

Reagents: Diethyl ether, tetrahydrofuran, toluene and hexane were purified by distillation from sodium/benzophenone ketyl; dichloromethane, *N*,*N*-diisopropyl amine, dmf, benzonitrile and TMEDA were purified by distillation from calcium hydride. Di(1*R*)-α-fenchyl (= Fn) ferrocenyl phosphate (**7**),[9] triphenylbenzaldehyde [69], triphenylbenzonitrile [70] and $[N^nBu_4][B(C_6F_5)_4]$, [71] ferrocenyl methanol (**1a**),[54] diphenylphosphino formylferrocene,[14] benzoylferrocene (**12d**) [72], ferrocenyldiphenylmethanol (**1e**)[73] and (S_p)-(2-thiodiphenylphosphino)hydroxymethylferrocene ((S_p)-**27**)[14] were synthesized according to published procedures. ^{n}BuLi (2.5 *M* in hexane), ^{t}BuLi (1.9 *M* in hexane), MeLi (1.6 *M* in Et_2O), PhLi (1.9 *M* in $^nBu_2O$) and all other compounds mentioned herein were purchased from commercial suppliers and were used without further purification.

Instruments: *FTIR* spectra were recorded between NaCl crystals or as KBr pellets in transition mode. *NMR* spectra were recorded with a Bruker Avance III 500 spectrometer (500.3 MHz for ^{1}H, 125.8 MHz for ^{13}C and 202.5 MHz for ^{31}P) and are reported with chemical shifts in δ (ppm) units downfield from tetramethylsilane with the solvent as the reference signal ($CDCl_3$: ^{1}H at δ = 7.26 ppm and ^{13}C{^{1}H} at δ = 77.00 ppm), by external standards (^{31}P{^{1}H} relative to 85 % H_3PO_4 0.0 ppm and $P(OMe)_3$ 139.0 ppm) or by the ^{2}H solvent lock signal. [74] For compounds consisting of mixtures of different diastereomers the main diastereomer was assigned to be the major (ma) and the remaining diastereomer to be the minor (mi) stereoisomer. The identity of all compounds was established by ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy. In addition, 2D experiments, such as COSY, HSQC and HMBC were carried out. Ferrocenyl related pseudo-triplets are abbreviated by pt. The *melting points* were determined with a Gallenkamp MFB 595 010 M melting point apparatus. *Elemental analyses* were performed with a Thermo FlashAE 1112 instrument. High-resolution *mass spectra* were recorded with a Bruker Daltonik - micrOTOF-QII spectrometer. *HPLC* measurements were performed with a Knauer system consisting of a HPLC Pump K-500 and an UV Detector K-2000 operating at 245 nm equipped with Chiralcel OD-H or OJ-H columns (4.6 · 250 mml column size). GC-MS analysis were performed with a GCMS-QP2010 SE system consisting of a coupled gas chromatograph mass spectrometer from Shimadzu using electron impact ionization.

Electrochemistry: Electrochemical measurements of **18d** and **19** (1.0 mmol L^{-1}) using $[N^nBu_4][B(C_6F_5)_4]$ (0.1 mol L^{-1}) as the supporting electrolyte in anhydrous dichloromethane were performed in a dried, argon-purged cell at 25 °C with a Radiometer Voltalab PGZ 100 electrochemical workstation interfaced with a personal computer.[75,76]

The spectroelectrochemical measurement of **19** (Figure SI4) was performed in an OTTLE cell (optically transparent thin-layer electrochemistry) placed in a Varian Cary 5000 UV/Vis–NIR absorption spectrometer using anhydrous dichloromethane solutions containing 2.0 mmol L^{-1} of **20** and 0.1 mol L^{-1} of $[N^nBu_4][B(C_6F_5)_4]$ as supporting electrolyte at 25 °C. [77,78]

Between the spectroscopic measurements the applied potentials have been increased step-wisely using step heights of 25, 50 or 100 mV. At the end of the measurements the analyte was reduced at –400 mV for 30 min and an additional spectrum was recorded to prove the reversibility of the oxidations. 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 with a Buehler microcloth first with a 1 micron and then with a 1/4 micron diamond paste. The reference electrode was constructed from a silver wire inserted into a solution of [$AgNO_3$] (0.01 mmol L^{-1}) and an $[N^nBu_4][B(C_6F_5)_4]$ (0.1 mol L^{-1}) acetonitrile solution in a Luggin capillary with a Vycor tip. This Luggin capillary was inserted in a second Luggin capillary containing a $[N^nBu_4][B(C_6F_5)_4]$ (0.1 mol L^{-1}) dichloromethane solution and a Vycor tip. Experiments under 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.[79] To achieve this, each experiment was repeated in the presence of decamethylferrocene (Fc*; 1 mmol L^{-1}). Data were processed with a Microsoft Excel worksheet to set the formal reduction potentials of the FcH/FcH^+ couple[79] to 0.0 V. Under our conditions, the Fc^*/Fc^{*+} couple was at –614 mV vs. FcH/FcH^+, ΔEp = 60 mV, whereas the FcH/FcH^+ couple itself was at 220 mV vs. Ag/Ag^+, ΔEp = 61 mV. [80]

Single-Crystal X-ray Diffraction Analysis: Data for **1g**, **8**, **11b**, **14**, **18b**,**d**, **19**, **20**, **22**, (S_p,S_p)-**32**, (S_p)-**33c**, (S_p)-**34a**, (S_p)-**37** and (S_p)-**40a** were collected at ≤ 120 K with graphite-monochromated Mo K_α (λ = 0.71073 Å) or Cu K_α radiation (λ = 1.54184 Å). The molecular structures were solved by direct methods using SHELXS-13[81] and refined by full-matrix least squares procedures on $F2$ using SHELXL-13.[82, 83] All non-hydrogen atoms were refined anisotropically. H atoms were introduced at calculated positions and treated as riding on their parent atoms and a riding model was employed in the treatment of the hydrogen atom positions, except otherwise noted. Graphics for the molecular structures were created by using ORTEP. [84]

(1*R*)-*α*-Fenchyloxymethylferrocene (**8**)

Ferrocenyl methanol (**1a**) (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 $ClP(O)(OFn)_2$ (**2a**) (3.65 g, 9.39 mmol) was added with a Pasteur pipette. The mixture was allowed to warm to ambient temperature and stirring was continued for 18 h at this temperature. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 4.5 x 22 cm column size) using hexane for the elution of methylferrocene **7**[85] (50 mg, 0.25 mmol, 3 % based on **1a**) and **8**, followed by a 1:1 hexane/dichloromethane mixture (*v*/*v*) giving bis(ferrocenyl-methyl)ether **6a**[86] (886 mg, 2.14 mmol, 46 % based on **1a**) and **1a** (242 mg, 1.12 mmol, 12 % based on **1a**). After evaporation of all volatiles in vacuum all compounds were obtained as orange solids. Crystals suitable for single-crystal X-ray diffraction analysis were obtained from boiling hexane solutions containing **8**.

Yield: 188 mg (0.534 mmol, 6 % based on **1a**). 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). $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 20.0 (C(*C*H$_3$)$_2$), 20.8 (C(*C*H$_3$)$_2$), 26.0 (C5/6), 26.2 (C5/6), 31.6 (C1(*C*H$_3$)), 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 $[M]^+$.

Cyclopentadien-1-yldiphenylferrocenylmethane (**11a**,**b**)

Ferrocenyldiphenylmethanol (**1e**, 1.00 g, 2.716 mmol) was dissolved in diethyl ether (50 mL) and cooled to –50 °C followed by dropwise addition of BuLi (1.1 mL, 2.75 mmol). After stirring for 10 min at this temperature and warming it afterwards to 0 °C, diethyl chlorophosphate (**2b**, 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 x 14 cm column size) using a 9:1 hexane/dichloromethane mixture (*v*/*v*) as the eluent. As the first fraction, compound **10** (155 mg, 0.637 mmol, 25 % based on **1e**) was eluted followed by **11**. They were obtained as orange oil (**10**) and solid (**11**) after removal of all volatiles in vacuum. Compound **11** was obtained as a mixture of the tautomeric forms **11a** and **11b**.

Yield: 251 mg (0.603 mmol, 22 % based on **1e**). 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, found 416.1187 $[M]^+$.

Cyclopenta-1,4-dien-1-yldiphenylferrocenylmethane (**11a**)

^{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), 6.43–6.50–6.51 (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 ($^qC_5H_5$–^qC).

Cyclopenta-1,3-dien-1-yldiphenylferrocenylmethane (**11b**)

^{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).

2-Ferrocenyl-2-adamantanol (**14**)

Ferrocene (**13**, 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. Afterward, ^{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 x 14 cm column size) using hexane for the removal of ferrocene followed by dichloromethane for the elution of **14**. After removal of all volatiles in vacuum, compound **14** was obtained as an orange solid.

Yield: 2.635 g (7.84 mmol, 73 % based on **13**). Anal. calcd for $C_{20}H_{24}FeO \cdot 1/6\ C_6H_{14}$ (366.25 · 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]$^+$.

2-Ferrocenyl-2-methyl-4-(prop-1-en-2-yl)cyclohexanone (**15c**)

Compound **15a** (300 mg, 0.887 mmol) was dissolved in 20 mL of diethyl ether and cooled to –80 °C. ^{n}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 $ClP(O)(OEt)_2$ (**2b**, 0.13 mL 0.90 mmol). After stirrting for 18 h at ambient temperature all volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 2.5 x 12 cm) using dichloromethane as the eluent. The title compound was obtained as an orange solid.

Yield: 24 mg (0.071 mmol, 8 % based on **15a**). ^{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{^{1}H} 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]$^+$. * See, Supporting Information.

(*E*)-Bis((1*R*)-α-fenchyl)(1-ferrocenylethylidene)phosphoramidate (**18a**)

Ferrocenylnitrile (**17**, 230 mg, 1.09 mmol) was dissolved in 20 mL of THF and this mixture was cooled to –80 °C. A 1.6 *M* solution of MeLi in diethyl ether (0.68 mL, 1.09 mmol) was dropwise added. The mixture was allowed to warm to –30 °C, stirred for 30 min at this temperature and afterward **2a** (423 mg, 1.09 mmol) was added with a Pasteur pipette. After warming the reaction mixture to ambient temperature, stirring was continued for 18 h. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 2 x 12 cm column size) using dichloromethane as the eluent for removing unreacted nitrile **17** (40 mg, 17 % based on **17**) followed by a 9:1 dichloromethane/ethyl acetate mixture (*v*/*v*) for eluting **18a**. After removal of all volatiles, compound **18a** 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 **17**). Anal. calcd for $C_{32}H_{46}FeNO_3P \cdot 0.5\ H_2O$ (579.53 · 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, C*H*$_3$–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, major), 4.20 (s, 5 H, C_5H_5, minor), 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{^{1}H} 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, C*H*$_3$–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, +C_5H_4), 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{^{1}H} NMR ($CDCl_3$, *δ*): 4.05 (minor), 4.18 (major). IR data (KBr, *v*/cm^{-1}): 3094 m, 2955 s, 2926 m, 2867 m, 1673 s, 1611 s (*v* 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 (**18b**)

Ferrocene (**13**, 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 stirring was continued until the solution turned dark-red. Afterward, chlorophosphate **2a** (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 x 12 cm column size) using a 1:1 hexane/dichloromethane mixture (*v*/*v*) to elute the excess of **13** (421 mg, 2.27 mmol), followed by a 9:1 dichloromethane/ethyl acetate mixture (*v*/*v*) as the eluent for **12d** (17 %) and a 4:1 dichloromethane/ethyl acetate mixture (*v*/*v*) for **18b**. After removal of all volatiles in vacuum, compound **18b** 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 **2a**). 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. ^{1}H 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, major), 4.23 (s, 0.5 H, C_5H_5, minor), 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, major), 7.66–7.68 (m, 0.22 H, C_6H_5, minor). ^{13}C{^{1}H} 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 ($C4_{C6H5}$), 139.9 (d, $^3J_{C,P}$ = 11.6 Hz, $C1_{C6H5}$), 183.8 (d, $^2J_{C,P}$ = 2.5 Hz, C=N). ^{31}P{^{1}H} NMR ($CDCl_3$, *δ*): 2.1 (1, major), 2.3 (0.11, minor). IR data (NaCl/$CHCl_3$, *ν*/cm^{-1}): 2958 s, 2870 m, 1611 s, 1591 w, 1572 w, 1452 m, 1377 w, 1293 m, 1056 s, 923 s. IR data (KBr, *ν*/cm^{-1}): 3093 w, 3047 w, 3029 w, 2945 s, 2920 s, 2868 s, 1608 s ($\nu_{N=C}$), 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-triphenylphenyl) methylene)phosphoramidate (**18c**)

According to the synthesis of **14**, ferrocene (**13**, 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 **13**–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 from orange to deep red followed by the addition of **2a** (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 x 16 cm column size) using a 1:1 hexane/dichloromethane mixture (*v*/*v*) to elute the excess of **13** followed by a 9:1 dichloromethane/ethyl acetate mixture (*v*/*v*) as the eluent for **18c**. After removal of volatiles in vacuum gave compound **18c** as a red solid and a mixture of the *E*- and *Z*-isomers 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 2,4,6-triphenylbenzonitrile). 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. ^{1}H 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{^{1}H} 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 (^{q}C), 138.3 (^{q}C), 139.7 (^{q}C), 139.8 (^{q}C), 140.2 (^{q}C), 140.78 (^{q}C), 140.83 (^{q}C), 140.9 (^{q}C), 181.3 (d, $^2J_{C,P}$ = 2.7 Hz, C=N). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 0.9 (minor), 1.7 (major). UV/Vis (in nm (*ε* in 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 $[M+H]^+$.

Synthesis of **18d** and **19**

Two synthetic methodologies to prepare the title compounds exist:

A) Reaction of **17** with ^{t}BuLi and **2a**

Compound **17** (500 mg, 2.37 mmol) was dissolved in 30 mL of THF. At –80 °C ^{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. Afterward, **2a** (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 as given under B). First **19** (311 mg, 0.58 mmol, 49 % based on **17**) was eluted, followed by **18d** as a 1:2 mixture with **5a** (835 mg, 25 % of **18d** based on **17**).

B) Reaction of **13**–Li with tertbutylnitrile

According to the synthesis of **14**, ferrocene (**13**, 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 **2a** (2.44 g, 6.27 mmol) were reacted. All volatiles were removed in vacuum. Purification was realized by column chromatography (silica, 2 x 15 cm column size) using hexane to elute the excess of **13** followed by a 1:4 hexane/dichloromethane mixture (*v*/*v*) as the eluent for **19**. The solvent was changed to dichloromethane and finally a 9:1 dichloromethane/ethyl acetate mixture (*v*/*v*) was used for **12f** (430 mg, 1.59 mmol, 25 % based on ^{t}BuLi) and **18d** (538 mg, 25 % based on ^{t}BuLi). All volatiles were removed in vacuum.

*tert*Butylferrocenyl imino phosphate (**18d**)

Compound **18d** was obtained as a red oil with a ratio of the *E*-/*Z*-isomers of 0.259:1 (*de* = 0.59). 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 **18d** with the bis-(1*R*)-*α*-fenchyl phosphate (**5a**). The signals of **5a** have been avoided for clarity, but are present in the NMR spectra in the ESI.

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 · 2 370.46 · 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, $^{3}J_{H,P}$ = 8.9 Hz, $J_{H,H}$ = 1.7 Hz, 1 H, H2), 4.03 (dd, $^{3}J_{H,P}$ = 9.0 Hz, $J_{H,H}$ = 1.7 Hz, 1 H minor, H2), 4.09 (dd, $^{3}J_{H,P}$ = 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, $^{3}J_{C,P}$ = 21.0 Hz, *C*(CH_3)$_3$, mi), 44.69 (d, $^{3}J_{C,P}$ = 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, $^{3}J_{C,P}$ = 10.0 Hz, $^{i}C_5H_4$), 78.6 (d, $^{3}J_{C,P}$ = 10.4 Hz, $^{i}C_5H_4$), 89.4 (d, $^{2}J_{C,P}$ = 8.2 Hz, C2, mi), 89.4 (d, $^{2}J_{C,P}$ = 8.1 Hz, C2), 89.7 (d, $^{2}J_{C,P}$ = 8.6 Hz, C2), 191.5 (d, $^{2}J_{C,P}$ = 4.4 Hz, C=N), 191.8 (d, $^{2}J_{C,P}$ = 4.7 Hz, C=N, mi). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –1.8 (ma), –1.3 (mi). IR data (NaCl/$CHCl_3$, *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*)-*tert*Butylferrocenyl ketazine (**19**)

Compound **19** was obtained as a red solid in a mixture with the (*Z*,*E*)-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{^{1}H} 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/$CHCl_3$, *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]$^{+}$.

O,O'-Bis((1*R*)-*α*-fenchyl)(ferrocenyl(phenyl)methyl)phosphoramidate (**20**)

Compound **18b** (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 at 50 °C for 18 h, whereby the color changed from red to yellow. The reaction mixture was poured into ice-water (200 mL) and extracted with diethyl ether (3 x 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 x 10 cm column size) using dichloromethane as the eluent (R_f = 0.60). After removal of all volatiles compound **20** 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 **18b**). 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, $^{2}J_{H,P}$ = 9.2 Hz, $^{3}J_{H,H}$ = 9.2 Hz, NH), 3.18 (dd, $^{2}J_{H,P}$ = 9.7 Hz, $^{3}J_{H,H}$ = 8.1 Hz, NH), 3.27 (dd, $^{2}J_{H,P}$ = 9.4 Hz, $^{3}J_{H,H}$ = 9.4 Hz, NH), 3.63 (dd, $^{3}J_{H,P}$ = 9.2 Hz, $J_{H,H}$ = 1.7 Hz, H2), 3.66 (dd, $^{3}J_{H,P}$ = 9.6 Hz, $J_{H,H}$ = 1.7 Hz, H2), 3.87 (dd, $^{3}J_{H,P}$ = 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, $^{3}J_{H,H}$ = 8.8 Hz, $^{3}J_{H,P}$ = 8.3 Hz, CH), 5.25 (dd, $^{3}J_{H,H}$ = 9.8 Hz, $^{3}J_{H,P}$ = 8.2 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 Hz, C3), 39.24 (d, $^{3}J_{C,P}$ = 1.8 Hz, C3), 39.4 (d, $^{3}J_{C,P}$ = 1.3 Hz, C3), 39.6 (d, $^{3}J_{C,P}$ = 1.4 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 Hz, C1), 49.1 (d, $^{3}J_{C,P}$ = 3.2 Hz, C1), 49.12 (C1), 49.13 (C1), 49.2 (C1), 54.9 (d, $^{2}J_{C,P}$ = 0.7 Hz, CH–N), 55.0 (CH–N), 55.1 (d, $^{2}J_{C,P}$ = 0.8 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 Hz, C2), 88.4 (d, $^{2}J_{C,P}$ = 6.5 Hz, C2), 88.95 (d, $^{2}J_{C,P}$ = 6.4 Hz, C2), 88.98 (d, $^{2}J_{C,P}$ = 7.2 Hz, C2), 89.3 (d, $^{2}J_{C,P}$ = 7.0 Hz, C2), 93.5 (d, $^{3}J_{C,P}$ = 10.6 Hz, $^{i}C_5H_4$), 93.6 (d, $^{3}J_{C,P}$ = 10.9 Hz, $^{i}C_5H_4$), 93.8 (d, $^{3}J_{C,P}$ = 10.6 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, *v*/cm^{-1}): 3185 s (ν_{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 L mol^{-1} 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 (**22**)

According to the synthesis of **14**, ferrocene (**13**, 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 **2a** (2.435 g, 6.26 mmol) were reacted. Purification was realized by column chromatography (silica, 2.5 x 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 1st, and **22** as the 2nd fraction. It should be noted that both anthracenes, the

starting material and **22**, 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 **22** was obtained as a dark solid.

Yield: 207 mg (0.53 mmol, 8 % based on anthracene-9-carbonitrile). 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 Hz, 2 H, C_5H_4), 4.81 (pt, $^{3+4}J_{H,H}$ = 1.8 Hz, 2 H, C_5H_4), 7.56 (ddd, $^3J_{H,H}$ = 8.9 Hz, $^3J_{H,H}$ = 6.5 Hz, $^4J_{H,H}$ = 1.2 Hz, 2 H, H2/3), 7.67 (ddd, $^3J_{H,H}$ = 8.6 Hz, $^3J_{H,H}$ = 6.5 Hz, $^4J_{H,H}$ = 1.0 Hz, 2 H, H2/3), 8.45 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 1.1 Hz, 2 H, H4/5), 9.24 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 1.3 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 ($^iC_5H_4$), 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, *ν*/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)ferrocenylmethylen)sulfane ((*S*$_p$,*S*$_p$)-**32**)

Compound (*S*$_p$)-**27** (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 reaction 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 x 12 cm column size) using a 1:9 hexane/dichloromethane mixture (*v*/*v*) as the eluent. After removal of all volatiles in vacuum, (*S*$_p$,*S*$_p$)-**32** was obtained as an orange solid.

Yield: 0.619 mg (0.72 mmol, 90 % based on (*S*$_p$)-**27**). 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, $^1J_{P,C}$ = 95.1 Hz, C_{C5H3}–P), 74.2 (d, $J_{P,C}$ = 12.7 Hz, C_5H_3), 89.8 (d, $^2J_{P,C}$ = 11.9 Hz, C_{C5H3}–C), 127.9 (d, $^2J_{P,C}$ = 12.4 Hz, *o*-C_6H_5), 128.1 (d, $^2J_{P,C}$ = 12.5 Hz, *o*-C_6H_5), 131.0 (d, $^4J_{P,C}$ = 2.9 Hz, *p*-C_6H_5), 131.1 (d, $^4J_{P,C}$ = 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, $^1J_{P,C}$ = 86.0 Hz, C_{C6H5}–P), 134.6 (d, $^1J_{P,C}$ = 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*$_p$)-**33a**,**b**,**c**)

Compound (*S*$_p$)-**27**, *p*-TsOH (1.37 g, 7.2 mmol), sulfur (100 mg, 3.12 mmol) and $MgSO_4$ (1 g) (1.0 g, 2.4 mmol) were dissolved in 70 mL of toluene. The reaction 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 x 12 cm column size) using a 7:3 hexane/dichloromethane mixture (*v*/*v*) as the eluent. After evaporation in vacuum, (*S*$_p$)-**33** was obtained as an orange solid and as a 2:1:6 mixture of of the *ortho*- ((*S*$_p$)-**33a**) / *meta*- ((*S*$_p$)-**33b**) / *para*-isomers ((*S*$_p$)-**33c**). The three isomers showed an equal behavior during the column chromatographic work-up process and could thus, not be separated. 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*$_p$)-**27**). 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*$_p$)-2-(2Methylphenylmethyl)-1-(thiodiphenylphosphino)ferrocene ((*S*$_p$)-**33a**)

Yield: 192 mg (0.38 mmol, 16 % based on (*S*$_p$)-**27**). ^{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{^{1}H} NMR ($CDCl_3$, δ): 19.4 (CH_3), 32.0 (CH_2), 68.1 (d, $^2J_{P,C}$ = 10.4 Hz, C_5H_3), 70.8 (C_5H_5), 73.7 (d, $J_{P,C}$ = 9.8 Hz, C_5H_3), 74.2 (d, $J_{P,C}$ = 9.8 Hz, C_5H_3), 74.4 (d, $^1J_{P,C}$ = 57.6 Hz, C_{C5H3}–P), 92.1 (d, $J_{P,C}$ = 12.4 Hz, C_{C5H3}–C), 125.4 (C4-C_6H_5), 126.0 (C5-C_6H_5), 128.0 (d, $^4J_{P,C}$ = 3.9 Hz, *p*-C_6H_5), 128.2 (d, $^2J_{P,C}$ = 12.4 Hz, *o*-C_6H_5), 129.5 (C3-H_6H_5), 129.8 (C6-C_6H_4), 131.1 (d, $^4J_{P,C}$ = 3.0 Hz, *p*-C_6H_5), 131.8 (d, $^2J_{P,C}$ = 12.7 Hz, *o*-C_6H_5), 131.9 (d, $^3J_{P,C}$ = 10.6 Hz, *m*-C_6H_5), 133.4 (d, $^1J_{P,C}$ = 22.4 Hz, C_{C6H5}–P), 134.1 (d, $^1J_{P,C}$ = 22.5 Hz, C_{C5H6}–P), 136.3 (C_6H_4), 138.5 (C2-C_6H_4). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 41.8.

(*S*$_p$)-2-(4-Methylyphenylmethyl)-1-(thiodiphenylphosphino)ferrocene ((*S*$_p$)-**33c**)

Yield: 575 mg (1.14 mmol, 47 % based on (*S*$_p$)-**27**). ^{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, C_5H_6). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 20.9 (CH_3), 33.7 (CH_2), 68.5 (d, $J_{P,C}$ = 10.4 Hz, C_5H_3), 70.7 (C_5H_5), 73.7 (d, $^1J_{P,C}$ = 95.3 Hz, C_{C5H3}–P), 73.6 (d, $J_{P,C}$ = 9.8 Hz, C_5H_3), 74.3 (d, $J_{P,C}$ = 13.0 Hz, C_5H_3), 93.3 (d, $^2J_{P,C}$ = 12.6 Hz, C_{C5H3}–C), 127.8 (d, $^3J_{P,C}$ = 3.3 Hz, *m*-C_6H_5), 127.9 (d, $^3J_{P,C}$ = 3.0 Hz, *m*-C_6H_5), 128.4 (C2-C_6H_4), 128.8 (C3-C_6H_4), 130.5 (d, $^4J_{P,C}$ = 3.0 Hz, *p*-C_6H_5), 131.0 (d, $^4J_{P,C}$ = 2.9 Hz, *p*-C_6H_5), 131.9 (d, $^2J_{P,C}$ = 10.6 Hz, *o*-C_6H_5), 132.0 (d, $^2J_{P,C}$ = 10.7 Hz, *o*-C_6H_5), 133.6 (d,

$^{1}J_{P,C}$ = 52.2 Hz, C_{C6H5}–P), 134.3 (d, $^{1}J_{P,C}$ = 53.0 Hz, C_{C6H5}–P), 134.9 (C4-C_6H_4), 137.4 (C1-C_6H_4). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 42.0.

(S_p)-2-(2-Methoxyphenylmethyl)-1-(thiodiphenylphosphino) ferrocene ((S_p)-**34a**) *and* (S_p)-2-(4-methoxyphenylmethyl)-1-(thiodiphenylphosphino)ferrocene ((S_p)-**34c**)

Compound (S_p)-**27** (200 mg, 0.48 mmol), *p*-TsOH (270 mg, 1.4 mmol) and $MgSO_4$ (1 g) were dissolved in 20 mL of anisole. The reaction 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 x 18 cm column size) using a 3:9 hexane/dichloromethane mixture (*v*/*v*) for eluting (S_p)-**34a** followed by dichloromethane for (S_p)-**34c**. Both compounds were obtained as orange solids after removal of all volatiles in vacuum.

(S_p)-**34a**: Yield: 114 mg (0.17 mmol, 36 % based on (S_p)-**27**). 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, $^{2}J_{H,H}$ = 15.2 Hz, 1 H, CH_2), 4.12 (d, $^{2}J_{H,H}$ = 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, $^{3}J_{H,H}$ = 7.4 Hz, $^{4}J_{H,H}$ = 1.0 Hz, 1 H, H4-C_6H_4), 6.74 (dd, $^{3}J_{H,H}$ = 8.2 Hz, $^{4}J_{H,H}$ = 1.1 Hz, 1 H, H6-C_6H_4), 6.96 (dd, $^{3}J_{H,H}$ = 7.4 Hz, $^{4}J_{H,H}$ = 1.6 Hz, 1 H, H3-C_6H_4), 7.04 (td, $^{3}J_{H,H}$ = 8.0 Hz, $^{4}J_{H,H}$ = 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, $^{3}J_{P,C}$ = 10.6 Hz, C_5H_3), 70.7 (C_5H_5), 73.7 (d, $^{1}J_{P,C}$ = 95.6 Hz, C_{C5H3}–P), 73.9 (d, $J_{P,C}$ = 13.1 Hz, C_5H_3), 74.1 (d, $J_{P,C}$ = 9.8 Hz, C_5H_3), 92.7 (d, $^{2}J_{P,C}$ = 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, $^{2}J_{P,C}$ = 8.0 Hz, *o*-C_6H_5), 127.9 (d, $^{2}J_{P,C}$ = 8.0 Hz, *o*-C_6H_5), 129.0 (C2-C_6H_4), 130.8 (C3-C_6H_4), 130.8 (d, $^{4}J_{P,C}$ = 2.9 Hz, *p*-C_6H_5), 131.0 (d, $^{4}J_{P,C}$ = 2.9 Hz, *p*-C_6H_5), 132.0 (d, $^{3}J_{P,C}$ = 6.4 Hz, *m*-C_6H_5), 132.1 (d, $^{3}J_{P,C}$ = 6.6 Hz, *m*-C_6H_5), 133.8 (d, $^{1}J_{P,C}$ = 75.5 Hz, C_{C6H5}–P), 134.5 (d, $^{1}J_{P,C}$ = 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)-**34c**: Yield: 117 mg (0.18 mmol, 37 % based on (S_p)-**27**). 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, $^{2}J_{H,H}$ = 15.1 Hz, 1 H, CH_2), 4.23 (d, $^{2}J_{H,H}$ = 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, $^{3}J_{H,H}$ = 8.7 Hz, 2 H, H2-C_6H_4), 6.95 (d, $^{3}J_{H,H}$ = 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, $^{3}J_{P,C}$ = 10.5 Hz, C_5H_3), 70.7 (C_5H_5), 73.6 (d, $^{1}J_{P,C}$ = 95.4 Hz, C_{C5H3}–P), 73.6 (d, $^{3}J_{P,C}$ = 9.7 Hz, C_5H_3), 74.4 (d, $^{2}J_{P,C}$ = 12.8 Hz, C_5H_3), 93.5 (d, $^{2}J_{P,C}$ = 12.5 Hz, C_{C5H3}–C), 113.2 (C2-C_6H_4), 127.8 (d, $^{3}J_{P,C}$ = 4.5 Hz, *m*-C_6H_5), 127.9 (d, $^{3}J_{P,C}$ = 4.3 Hz, *m*-C_6H_5), 129.9 (C3-C_6H_4), 130.7 (d, $^{4}J_{P,C}$ = 2.9 Hz, *p*-C_6H_5), 131.1 (d, $^{4}J_{P,C}$ = 2.9 Hz, *p*-C_6H_5), 131.9 (d, $^{2}J_{P,C}$ = 10.7 Hz, *o*-C_6H_5), 132.0 (d, $^{2}J_{P,C}$ = 10.8 Hz, *o*-C_6H_5), 132.8 (C4-C_6H_4), 133.6 (d, $^{1}J_{P,C}$ = 60.9 Hz, C_{C6H5}–P), 134.3 (d, $^{1}J_{P,C}$ = 61.8 Hz, C_{C6H5}–P), 157.5 (C1-C_6H_4). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, *δ*): 42.0. HRMS (ESI-TOF, *m*/*z,* (rel. intensity)): see (S_p)-**34a**.

(S_p)-(Diphenylphosphino)-2-(2-hydroxyphenylmethyl)ferrocene ((S_p)-**35**)

Compound (S_p)-**27** (200 mg, 0.463 mmol) and phenol (436 mg, 4.63 mmol) were dissolved in 10 mL of dichloromethane followed by the addition of *p*-TsOH (264 mg, 1.53 mmol). The reaction 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 x 18 cm column size) using dichloromethane as the eluent. After removal of all volatiles, compound (S_p)-**35** was obtained as an orange solid.

Yield: 175 mg (0.344 mmol, 74 % based on (S_p)-**27**). Anal. calcd for $C_{29}H_{25}FeOPS \cdot 1/3\ C_6H_{14}$ (508.39 · 1/6 86.18 g/mol): C, 69.32; H, 5.57. Found: C, 69.30; H, 5.37. Mp: 223 °C. ^{1}H 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, $^{2}J_{H,H}$ = 15.3 Hz, 1 H, CH_2), 4.13 (d, $^{2}J_{H,H}$ = 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, $^{3}J_{H,H}$ = 8.1 Hz, $^{4}J_{H,H}$ = 1.1 Hz, 1 H, C_6H_4-H3), 6.71 (td, $^{3}J_{H,H}$ = 7.4 Hz, $^{4}J_{H,H}$ = 1.2 Hz, 1 H, C_6H_4-H5), 6.89 (s, 1 H, OH), 6.92 (td, $^{3}J_{H,H}$ = 7.9 Hz, $^{4}J_{H,H}$ = 1.7 Hz, 1 H, C_6H_4-H4), 7.02 (dd, $^{3}J_{H,H}$ = 7.6 Hz, $^{4}J_{H,H}$ = 1.6 Hz, 1 H, C_6H_4-H6), 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). $^{13}C\{^{1}H\}$ 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, $^{1}J_{C,P}$ = 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, $^{2}J_{C,P}$ = 12.7 Hz, C_{C5H3}–CH_2), 117.2 (C_6H_4-C3), 120.1 (C_6H_4-C5), 126.6 (C_6H_4–C1), 127.5 (C_6H_4-C4), 128.0 (d, $^{3}J_{C,P}$ = 12.7 Hz, C3/5-Ph), 128.1 (d, $^{3}J_{C,P}$ = 12.5 Hz, C3/5-Ph), 130.1 (C_6H_4-C6), 131.2 (d, $^{4}J_{C,P}$ = 3.0 Hz, C4-Ph), 131.5 (d, $^{4}J_{C,P}$ = 2.9 Hz, C4-Ph), 131.7 (d, $^{2}J_{C,P}$ = 10.8 Hz, C2/6-Ph), 132.1 (d, $^{2}J_{C,P}$ = 10.9 Hz, C2/6-Ph), 132.4 (d, $^{1}J_{C,P}$ = 86.8 Hz, C1-Ph), 133.5 (d, $^{1}J_{C,P}$ = 86.9 Hz, C1-Ph), 153.2 (C2–OH). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ): 42.6. IR data (KBr, *v*/cm^{-1}): 3403 m (*v* 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 (*v* 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-thiodiphenyl-phosphino)ferrocene (S_p)-**36**)

Compound (S_p)-**27** (150 mg, 0.347 mmol) and 2,4,6-trimethylphenol (473 mg, 3.47 mmol) were dissolved in 10 mL of dichloromethane followed by the addition of *p*-TsOH (178 mg, 1.04 mmol). The reaction 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 x 18 cm column size) using dichloromethane as the

eluent. After removal of all volatiles, compound (S_p)-**36** was obtained as an orange solid.

Yield: 173 mg (0.314 mmol, 90 % based on (S_p)-**27**). 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, 1H, 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 $[M]^+$; calcd for $C_{32}H_{31}FeOPS$+H 550.1178, found 550.1114 $[M+H]^+$.

(S_p)-2-((2,4-Dinitrophenyl)thiomethyl)-1-(thiodiphenylphosphino)ferrocene ((S_p)-**37**)

Compound (S_p)-**27** (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 darkened. The reaction mixture was heated to 40 °C and stirring was continued for 18 h at this temperature. After cooling the reaction mixture to ambient temperature, it was diluted with 50 mL of diethyl ether and washed with acidified (HCl) brine (50 mL). After extraction with diethyl ether (3 x 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 x 18 cm column size) using a 1:1 dichloromethane/ethyl acetate mixture (*v*/*v*) as the eluent. After removal of all volatiles, compound (S_p)-**37** was obtained as an orange solid.

Yield: 95 mg (0.155 mmol, 56 % based on (S_p)-**27**). 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, CH_2, 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, JH,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{^{1}H} NMR ($CDCl_3$, δ): 40.8. IR data (KBr, *v*/cm^{-1}): 3078 w, 3065 w, 2958 w, 2922 s, 2854 m, 1737 m, 1585 m, 1520 s (v_{as} NO_2), 1436 m, 1345 s (v_s NO_2), 1169 m, 1101 w, 1042 m, 835 m, 712 s, 692 m, 645 m (*v* 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)-**38**)

Compound (S_p,S_p)-**32** (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 reaction 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. This mixture was poured into water (200 mL) and extracted with dichloromethane (3 x 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 x 16 cm column size) using dichloromethane as the eluent. Compound (S_p,S_p)-**38** was recrystallized 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)-**32**). 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. ^{1}H 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{^{1}H} NMR ($CDCl_3$, *δ*): 32.0 (d, $^3J_{P,C}$ = 11.7 Hz, CH_2) 69.2 (C_5H_3), 69.7 (C_5H_5), 71.1 (d, $J_{P,C}$ = 3.9 Hz, C_5H_3), 71.3 (d, $J_{P,C}$ = 3.9 Hz, C_5H_3), 75.5 (d, $^1J_{P,C}$ = 7.8 Hz, C_{C5H3}–P), 90.9 (d, $^2J_{P,C}$ = 25.9 Hz, C_{C5H3}–C), 127.6 (*p*-C_6H_5), 127.9 (d, $^3J_{P,C}$ = 5.9 Hz *m*-C_6H_5), 128.0 (d, $^3J_{P,C}$ = 8.0 Hz, *m*-C_6H_5), 129.0 (*p*-C_6H_5), 132.2 (d, $^2J_{P,C}$ = 17.6 Hz, *o*-C_6H_5), 135.1 (d, $^2J_{P,C}$ = 21.4 Hz, *o*-C_6H_5), 137.7 (d, $^1J_{P,C}$ = 8.7 Hz, C_{C6H5}–P), 140.0 (d, $^1J_{P,C}$ = 9.4 Hz, C_{C6H5}–P). ^{31}P{^{1}H} 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)-**39**)

Compound (S_p)-**34a** (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 reaction 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 (200 mL) and extracted with dichloromethane (3 x 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 x 16 cm column size) using dichloromethane as the eluent. Compound (S_p)-**39** was recrystallized from boiling hexane and obtained as an orange solid after removal of all volatiles.

Yield: 145 mg (0.23 mmol, 79 % based on (S_p)-**34a**). 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, $J_{P,C}$ = 4.1 Hz, C_5H_3), 72.1 (d, $J_{P,C}$ = 4.0 Hz, C_5H_3), 75.3 (d, $^1J_{P,C}$ = 6.7 Hz, C_{C5H3}–P), 93.8 (d, $^2J_{P,C}$ = 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, $^3J_{P,C}$ = 6.0 Hz, *m*-C_6H_5), 128.0 (d, $^3J_{P,C}$ = 7.9 Hz, *m*-C_6H_5), 128.9 (*p*-C_6H_5), 129.4 (C2-C_6H_4), 130.3 (d, $^4J_{P,C}$ = 1.1 Hz, *p*-C_6H_5), 132.3 (d, $^2J_{P,C}$ = 18.0 Hz, *o*-C_6H_5), 135.2 (d, $^2J_{P,C}$ = 21.1 Hz, *o*-C_6H_5), 138.0 (d, $^1J_{P,C}$ = 8.5 Hz, C_{C6H5}–P), 139.8 (d, $^1J_{P,C}$ = 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)-**40** and (S_p)-**40a**

Compound (S_p)-**36** (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 reaction 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 x 16 cm column size) using dichloromethane as the eluent. After removal of all volatiles, compound (S_p)-**40** was obtained as a yellow solid as a 1:1 mixture of two diastereomers. Dissolving in boiling dichloromethane and slowly cooling the solution to ambient temperature gave single crystals of (S_p)-**40a**, 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)-**36**). ^{1}H NMR ($CDCl_3$, δ): 2.04 (s, 3 H, Mes-CH3-C2/6), 2.05 (s, 3 H, Mes-CH3-C2/6), 2.06 (s, 3 H, Mes-CH3-C2/6), 2.07 (s, 3 H, Mes-CH3-C2/6), 2.28 (s, 6 H, Mes-CH3-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{^{1}H} 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, 2JC,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{^{1}H} 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).

N-([1,1'-Binaphthalen]-2-yl)benzamide (**41l**)

The title compound was obtained from 2-amino-1-bromonaphtalene (222 mg) and 1-naphthylboronic acid (258 mg) by using the general procedure for Suzuki-Miyaura *C*,*C* cross-coupling reactions (Supporting Information). The conversion of the formed amine into amide **41l** was performed similar to a literature reported protocol.[87] Thus, the whole sample was transferred into a Schlenk tube by using dichloromethane (10 mL) 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 afterward allowed to cool to ambient temperature. The solution was poured into water (50 mL) and extracted with diethyl ether (3 x 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 x 23 cm column size) using a hexane/diethyl ehter mixture (*v*/*v*) as the eluent. The product is eluted as the 3rd fraction, after 1,1'-binaphthyl as the 1st, and a fluorescent fraction as the 2nd fraction. After removal of all volatiles **41l** 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. ^{1}H 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{^{1}H} 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}, hexane/*i*-PrOH (98:2)): 44.7, 58.1 min. IR data (KBr, *v*/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.

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Keywords: Ferrocene • Phosphate • Azine • Thioether • Suzuki-Miyaura Reaction • Imine

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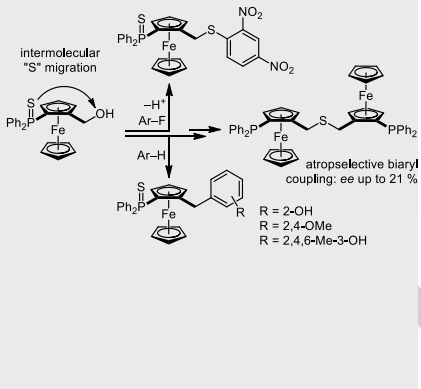
FULL PAPER

Acidic treatment of planar-chiral ferrocenylmethanols resulted in the formation of α-ferrocenyl carbo cations, which underwent electrophilic aromatic substitution reactions with electron-rich aromatics or could be sulfurized by the thiophosphinyl group by an intermolecular process, resulting in thio ethers.



Ferrocenylmethanols

*Marcus Korb, Julia Marholdt, Heinrich Lang**

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(Planar-Chiral) Ferrocenylmethanols: From Anionic Homo Phospho-Fries Rearrangements to α-Ferrocenyl Carbenium Ions