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Thiophosphine Derivatives

Reactivity of Planar-Chiral α-Ferrocenyl Carbocations towards Electron-Rich Aromatics

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Abstract: The reaction of the enantiopure, planar-chiral α-ferrocenyl carbocation (S_p)-2-(P(=S)Ph_2)FcCH_2^+ (Fc = Fe(η^5-C_5H_5)(η^5-C_5H_3)) towards electron-rich arenes C_6H_5E (E = NH_2, NMe_2, N*i*Pr_2, NPh_2, PPh_2, P(=S)Ph_2, OH, SH, SMe) regarding either a nucleophilic attack of the group E or an electrophilic aromatic substitution reaction of the arene at the CH_2^+ unit is reported. It was found that the amino, oxo or thio functionalities gave the respective ferrocenes in various product distributions, while the P-based species didn't. Appropriate thiophosphine derivatives could be reduced to their P^{III} species that were applied as supporting ligands in atropselective *C*,*C* cross-coupling reactions for the synthesis of sterically hindered biaryls, where sandwich compound (S_p)-1-(PPh_2)-2-(*o*-NMe_2-C_6H_4)CH_2-Fc gave an *ee* of 69 % (1 mol-% [Pd]), which is up to date the highest observed value for planar-chiral ferrocenes. The absolute configuration of the chiral ferrocenes was confirmed by single-crystal X-ray diffraction analysis. For seleno phosphane 1-(P(=Se)Ph_2)-2-(CH_2OH)-Fc a unique Se single-atom transfer occurred within its reaction with Sanger's reagent. The presence of two chemically different Se atoms in 1-(P(=Se)Ph_2)-2-(((2,4-$(NO_2)_2$-C_6H_3)Se)CH_2)-Fc was confirmed by ^{77}Se{^{1}H} NMR spectroscopy and single-crystal X-ray diffraction analysis, respectively.

Introduction

Recently, planar-chiral ferrocenes gained great importance as effective ligands within, for example, *C*,*C* cross-coupling catalysis.[1] Although a phosphine group is essential for the formation of stable, e.g. Pd complexes, additional substituents have been introduced to further increase the stability of the active site within the catalytic cycle.[2] It could be shown that ferrocenyl phosphines, bearing an additional *ortho*-substituent, significantly increase the catalytic activity of the respective Pd-catalysts, due to the additional hemilabile donor functionality.[2] A variety of groups has been investigated, including, e.g. arenes,[3] phosphonates,[4] C-stereogenic groups,[5] NHC ligands,[6] as well as vinyl,[7,8] aryloxy[9,10] and alkyloxy[11,2b,12] fragments. Some enantiopure examples were applied as ligands in order to investigate their ability to transfer planar-chirality within a catalytic reaction. The Suzuki–Miyaura reaction for the synthesis of hindered biaryls is a common test-reaction, whereby the *ee* of the formed coupling products expresses the transferability.[7] So far, a maximum *ee* of 54 % at catalyst loadings of low as 2 mol-% [Pd] could be reached.[3]

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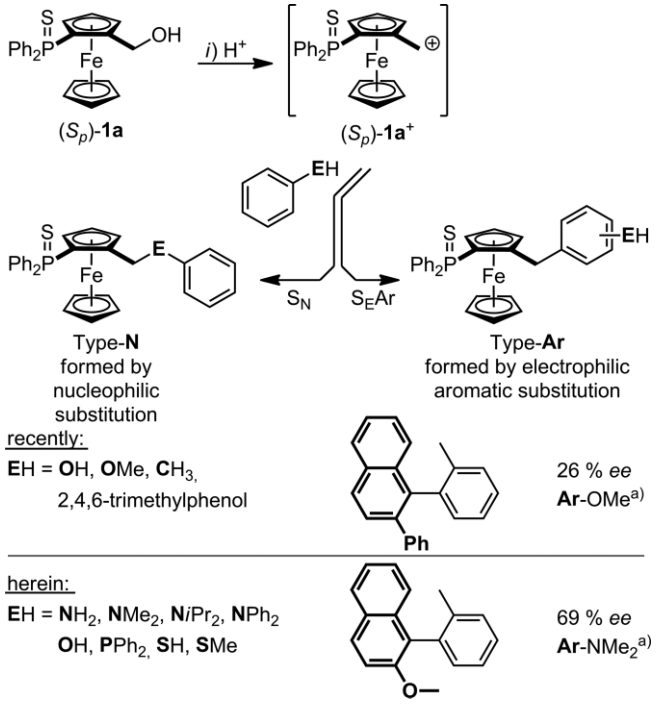
We recently extended the scope of suitable hemilabile ligands to methoxy-substituted ferrocenyl phosphines of type 2-OMe-1-PPh_2-Fc (Fc = Fe(η^5-C_5H_5)(η^5-C_5H_3)), applying the anionic phospho-Fries rearrangement for the synthesis of the diastereopure (R_p) species.[10,11] However, due to the low steric demand of the OMe group, a negligible *ee* was noticed within the catalytically formed biaryls. Extension from a FcOMe to a FcCH_2OR structure increased the *ee* significantly, attributed to a more flexible ligand backbone.[9,13] Within these studies, the formation of enantiopure α-ferrocenyl carbocations was observed as rarely described species for 1,2-substituted ferrocenes,[14] which allows for the introduction of various substitution patterns (Scheme 1).[13] Under acidic conditions, the feasible removal of the hydroxy group results in carbenium ions with a comparably high electrophilicity value *E* of –2.57 according to Mayr,[15] due to a stabilization by an intramolecular Fe•••CH_2^+ interaction.[16,17]

Although, this approach is well-studied for the functionalization of single- and 1,1′-substituted ferrocenyl methanols with various arenes and nucleophiles,[17b,18] 1,2-substituted derivatives had not been investigated. Therefore, we recently applied the 2-(CH_2OH)-1-(S=PPh_2)-substituted ferrocene as a substrate and studied its reaction with anisole, toluene and trimethylphenol.[13] The obtained ferrocenyl phosphines possessed planar-chirality as the sole stereo element.[13] Such ferrocenes were applied as supporting ligands for the synthesis of biaryls via Pd-catalyzed Suzuki–Miyaura reactions of bromo arenes with aryl boronic acids, which were obtained with up to 26 % *ee*.[13,19,20]

Variation of the donor properties of *E* in (S_p)-1-(PPh_2)-2-(*o*-*E*-C_6H_4)CH_2-Fc-type compounds from *E* = OMe to stronger func-



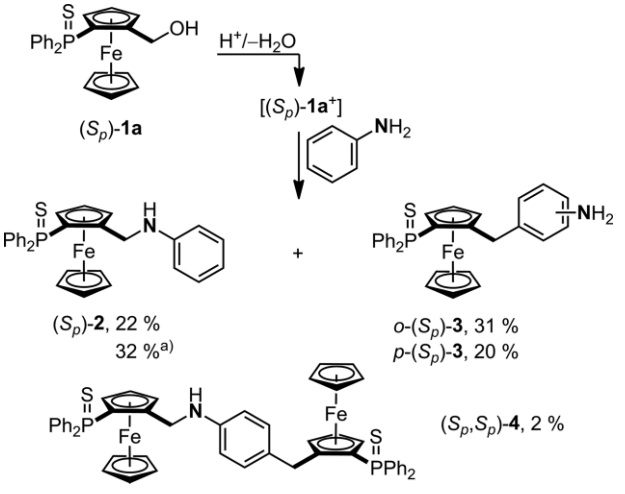
Scheme 1. Reaction strategy for the synthesis of *ortho*-substituted enantiopure ferrocenyl phosphines and their application as supporting ligands within Pd-catalyzed Suzuki–Miyaura C,C cross-coupling reactions for the synthesis of biaryls.[13] *i*) *p*TsOH·H_2O, 1,4-dioxane, 90 °C, 24 h; a) obtained from the respective bromo arenes (bold) and boronic acids.

tionalities should increase their bonding towards the Pd atom and therefore result in a higher *ee*. Herein, we extend the substrate scope of electron-rich arenes to *E* = amino, phosphino and thio units and investigate their tendency to result in either **N**- or **Ar**-type products within the reaction with enantiopure α-ferrocenyl carbocations (Scheme 1). Their efficiency towards a chirality transfer is evaluated within Suzuki–Miyaura *C,C* cross-coupling studies for the atropselective synthesis of sterically hindered biaryls.

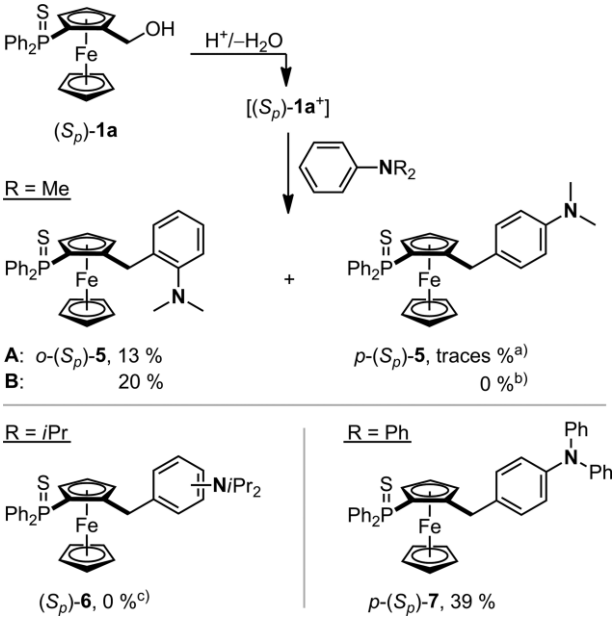
We recently reported about the transfer of a single sulfur atom from a P(=S)Ph_2 moiety towards the CH_2^+ group, resulting in a thiol functionality. This migration competed with the S_EAr of the substrate and therefore lowered the yield of the benzyl-type product.[13] In order to prevent this reaction pathway, the P···chalcogen bond strength was varied by using oxygen and selenium instead. Hence, the occurrence of similar intermolecular single-chalcogen-atom transfer is also reported herein.

Results and Discussion

The formation of the enantiopure α-ferrocenyl carbocation (S_p)-**1a**$^+$ is initiated by an acid-promoted release, respectively activation, of the OH functionality of (S_p)-**1a** by using a 3-fold excess of *p*TsOH·H_2O in dioxane at 90 °C, according to our recently optimized reaction protocol (Scheme 1).[13] Alcohol (S_p)-**1a** was synthesized according to a literature reported 7-step procedure starting from ferrocene.[9,21] Formation of (S_p)-**1a**$^+$ in the presence of amine functionalities required the addition of equimolar amounts of *p*TsOH·H_2O (Scheme 2, Scheme 3). In case of aniline, an overall conversion of 75 % was observed, whereby a mixture of S_N- and S_EAr-derived products was formed (Scheme 2). Although, protonation of the amino functionality occurred, a nucleophilic reaction of the N-atom towards the carbocation gave (S_p)-**2** in 22 %. The yield of (S_p)-**2** could slightly be increased by using 5 instead of 3 equiv of aniline and 6 equiv of *p*TsOH·H_2O, respectively. The presence of a NH functionality has *inter alia* been confirmed by single-crystal X-ray diffraction analysis (Figure 1) and by IR spectroscopy ($\tilde{\nu}_{NH}$ = 3388 cm^{-1}). Although the formation of an ammonium functionality lowers the electron density at the arene, S_EAr-type reactions occurred in overall 51 %, giving the *ortho*- and *para*-sub-



Scheme 2. Reaction of the α-ferrocenyl carbocation (S_p)-**1a**$^+$ with aniline. (Reaction conditions: 3 equiv of aniline, 6 equiv of *p*TsOH·H_2O, 1,4-dioxane, 90 °C; a) 5 equiv of $PhNH_2$ were used.)



Scheme 3. Reaction of the α-ferrocenyl carbocation (S_p)-**1a**$^+$ with *N*-substituted anilines. (Reaction conditions: 6 equiv of *p*TsOH·H_2O, 1,4-dioxane, 90 °C, **A**: 3 equiv of the respective aniline; **B**: 5 equiv of $PhNMe_2$ were used; a) 30 % of (S_p,S_p)-**12**; b) 34 % of (S_p,S_p)-**12**; c) 60 % of (S_p,S_p)-**12**.)

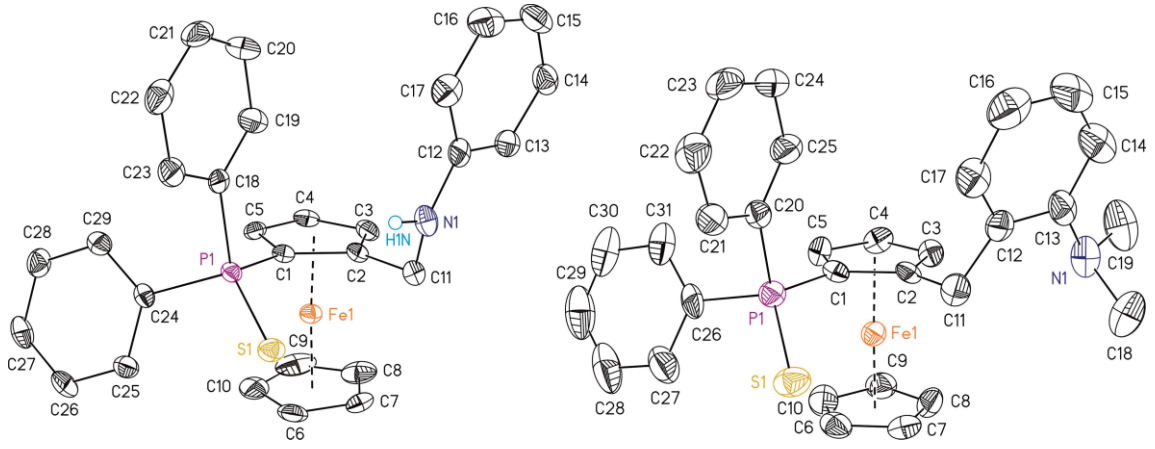


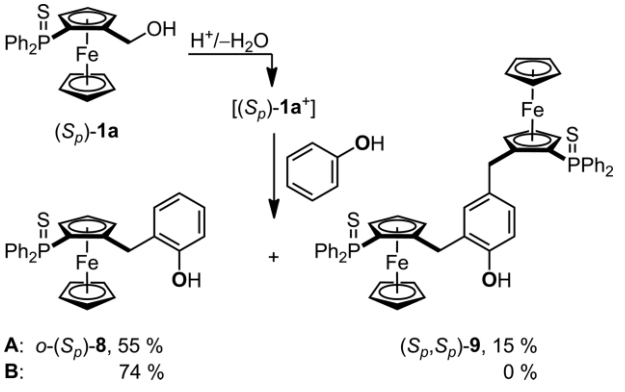
Figure 1. ORTEP drawing (50 % probability level) of the molecular structures of (S_p)-**2** (left) and *o*-(S_p)-**5** (right) with their atom-numbering schemes. All C-bonded hydrogen atoms have been omitted for clarity. (Selected bond properties are summarized in Table 1).

stituted products of (S_p)-**3** in a ratio of 3:2 (Scheme 2). The preferred formation of the *ortho*-derivative is probably due a pre-coordination of the N atom towards the positively charged CH_2^+ functionality, as observed for oxygen analogues,[13] and two (*o*-) instead of one (*p*-) available position. In addition to (S_p)-**2**,**3**, double substitution of aniline in *N*- and 4-position occurred, giving the diferrocenyl compound (S_p,S_p)-**4** (Scheme 2). The occurrence as the 1,4- instead of the 1,2-isomer was evidenced by NMR spectroscopy (vide infra) and might be due to steric effects.

The reaction of (S_p)-**1a** with *N*,*N*-dimethylaniline instead of $PhNH_2$ prevented the nucleophilic addition of the N atom at the CH_2^+ moiety, solely resulting in the S_EAr-derived compounds *o*- and *p*-(S_p)-**5** (Scheme 3). However, the higher basicity of the dimethyl derivative (pK_b = 8.93) compared to aniline itself (pK_b = 9.13) resulted in the formation of more stable ammonium ions.[22] The positively charged species acts as an electron deficient arene, which explains the low yield of 13 % for *o*-(S_p)-**5**. The respective *para*-isomer has just been observed in traces together with *o*-(S_p)-**5** and could not be separated by, e.g. chromatographic methods. Hence, applying the more electron-rich and sterically more demanding N*i*Pr_2 aniline prevented a reaction with the carbocation (S_p)-**1a**$^+$ and did not result in the formation of a type (S_p)-**6** species (Scheme 3). In this case, the absence of an appropriate and fast-reacting electrophile enabled the slower conversion to thioether (S_p,S_p)-**12** in up to 60 %, requiring three molecules of (S_p)-**1a** or (S_p)-**1a**$^+$. A proposed mechanism for the formation of this unusual species has recently been described and is additionally considered herein (see below).[13]

Applying NPh_3 allows for a distribution of the positive charge over three instead of one arene. Hence, *p*-(S_p)-**7** was formed within the reaction of NPh_3 with (S_p)-**1a**. The absence of the respective *ortho*-isomer of (S_p)-**7**, might be due to the steric influence of the NPh_2 moiety (Scheme 3).

First studies using phenols and anisole as arenes have recently been investigated.[13,23] The lower nucleophilicity[24] of oxygen as compared to nitrogen increased the ability to undergo S_EAr reactions and hence *o*-(S_p)-**8** was obtained in high yield (74 %, Scheme 4). However, the different reaction conditions of (S_p)-**1a** with phenol (CH_2Cl_2 at 50 °C)[13] prompted us to re-investigate it under the reaction conditions reported herein (1,4-dioxane at 90 °C), in order to compare the results (Scheme 4). Although the overall conversion remained similar (70 %), the formation of *ortho*- and *para*-substituted (S_p,S_p)-**9** (15 %) was observed. Most probably, *o*-(S_p)-**8** underwent an additional S_EAr reaction at 90 °C compared to 50 °C.

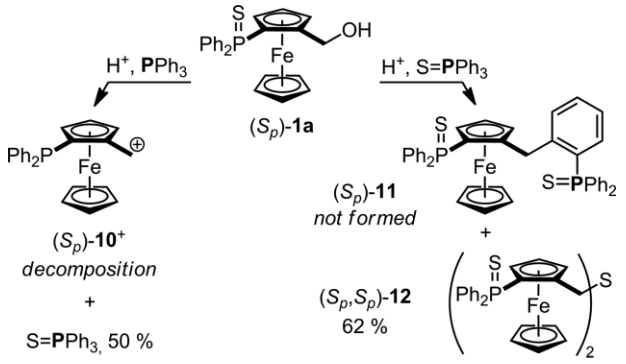


Scheme 4. Reaction of the α-ferrocenyl carbocation (S_p)-**1a**$^+$ with phenol. (Reaction conditions: **A**, 3 equiv of phenol, 3 equiv of *p*TsOH·H_2O, 1,4-dioxane, 90 °C; **B**: values derived from literature,[13] where CH_2Cl_2 and 50 °C were applied instead.)

In contrast to (S_p,S_p)-**4**, where a *N*,4-functionalization took place, the formation of compound (S_p,S_p)-**9**, possessing a 2,4-substitution pattern, is in accordance with the lower nucleophilicity of the oxygen compared to an amino moiety.[24] Most likely, a consecutively mechanism initially gave *o*-(S_p)-**8** followed by a subsequent S_EAr reaction in *para* position to afford (S_p,S_p)-**9**. The OH groups of both species were identified by IR spectroscopy showing the characteristic $\tilde{\nu}_{OH}$ = band at 3377 cm^{-1}.

With regard to the potential use of the *ortho* isomers of (S_p)-**3**,**5**,**8** as supporting ligands in Pd-catalyzed reactions, the introduction of an additional phosphine moiety would change the binding properties from hemilabile[7,12] to bidentate.[25] This would allow for a new access to such bis(phosphines), which are known to give a high *ee* within catalytic reactions.[26] Hence, the reaction of (S_p)-**1a** with PPh_3 was investigated in order to

obtain (S_p)-**11** (Scheme 5), or a product similar to the NPh_3 analogue (S_p)-**7** (Scheme 3).



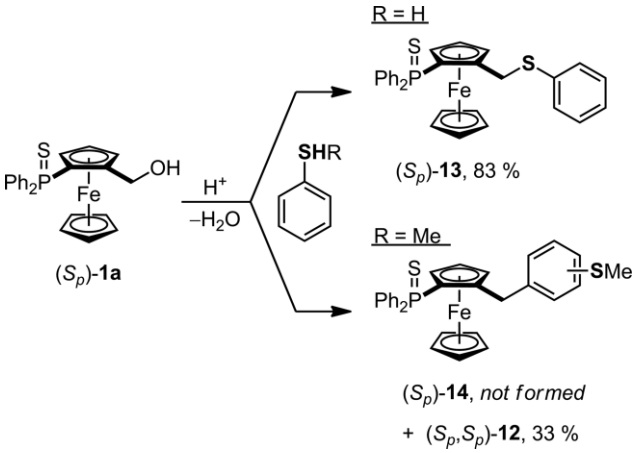
Scheme 5. Reaction of the α-ferrocenyl carbocation (S_p)-**1a**$^+$ with phosphines. (Reaction conditions: 3 equiv of the respective phosphine, 6 equiv of *p*TsOH•H_2O, 1,4-dioxane, 90 °C.)

However, ferrocenyl-based species were absent after the work-up, indicating that decomposition occurred during the reaction progress. The presence of $P(=S)Ph_3$ within the product mixture supports our recent mechanistic proposal regarding (S_p)-**1a**$^+$ acting as a sulfur source and the subsequent decomposition of the formed phosphine (S_p)-**10**$^+$. Therefore, the latter species could never be detected. We assume that the formation of (S_p)-**1a**$^+$ occurs rapidly under the reaction conditions applied, whereby the positive charge lowers the bond strength of the P=S bond. Hence, the higher σ donor ability of PPh_3 causes a sulfur transfer to form $P(=S)Ph_3$. Although, an excess of PPh_3 was used, no further reaction with the formed (S_p)-**10**$^+$ species occurred. The absence of (S_p,S_p)-**12** also indicates that (S_p)-**10**$^+$ is not suitable to form a similar desulfurized thioether.

The sulfur transfer was prevented by applying $P(=S)Ph_3$ as the starting material. However, the electron-withdrawing character of the P=S functionality reduced the ability of the phenyls to undergo S_EAr reactions, enabling the formation of (S_p,S_p)-**12**.

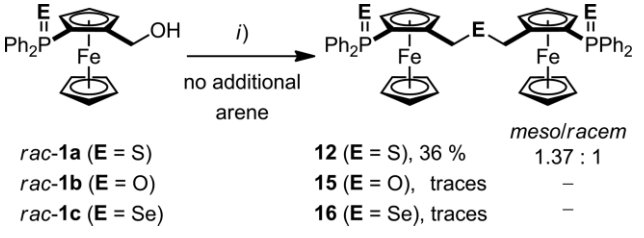
Interestingly, the comparably low yield of 62 % indicates that the addition of a phosphine sulfide does not contribute within the mechanism. This might be attributed to the higher electron density in PPh_3[27] compared to a cationic species, e.g. (S_p)-**1a**$^+$, and the therefore stronger P=S double bond in $P(S)Ph_3$ as, which is not able to act as a sulfur source.[8,13] Addition of elemental sulfur does also not significantly enhance the yield of (S_p,S_p)-**12**, as shown recently.[13]

In addition to N-,O- and P-containing arenes, also S-based functionalities may support the chirality transfer of a planar-chiral ferrocene within a catalytically active species towards the substrate. Therefore, the behavior of thiophenol and thioanisole within the reaction with (S_p)-**1a** was investigated (Scheme 6). The SH species exclusively underwent a nucleophilic addition to thioether (S_p)-**13** according to reference[14], whereas thioanisol did not react with (S_p)-**1a** to (S_p)-**14** and instead (S_p,S_p)-**12** was formed. This is contrary to the respective *O*-based substrates (Scheme 4),[13] but in accordance with reactions of non-*ortho*-functionalized ferrocenyl carbenium ions with thiols.[18] The identity of (S_p)-**13** has *inter alia* been confirmed by single-crystal X-ray diffraction analysis (Figure 3), in addition to NMR spectroscopic data. IR spectroscopy is rather unsuitable, since the CH_2–S stretching frequency at 500–700 could not specifically be addressed.[28]



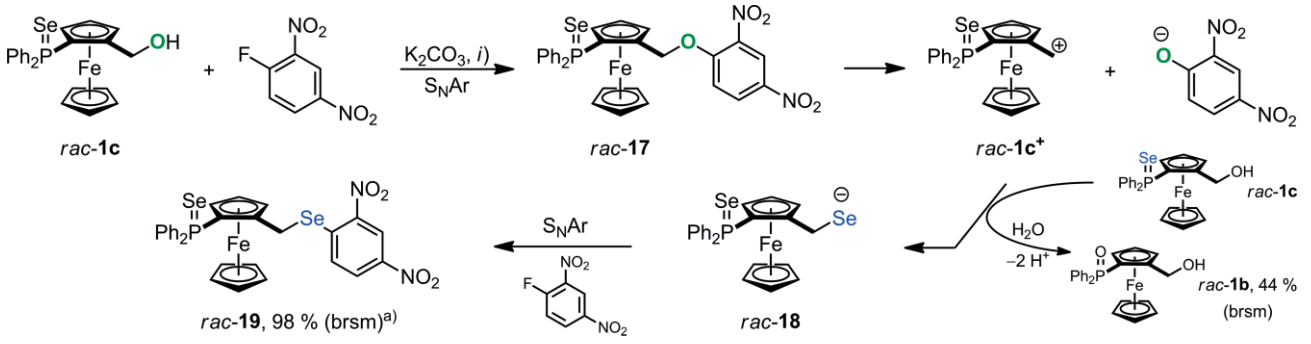
Scheme 6. Reaction of the α-ferrocenyl carbocation (S_p)-**1a**$^+$ with thiophenols. (Reaction conditions: 3 equiv of the respective thio arene, 6 equiv of *p*TsOH, 1,4-dioxane, 90 °C.)

In order to investigate if the formation of (S_p,S_p)-**12**[13] out of (S_p)-**1a** could be suppressed by using different P^V-chalcogenides, *rac*-**1b**[29] (E = O) and selenide *rac*-**1c** (E = Se) were synthesized (Experimental Section). In addition, the usage of the racemic mixtures of **1a**–**c** allows for the investigation of the diastereoselectivity of the reaction to either produce the *meso* (R_p,S_p) or a mixture of the *racem* isomers R_p,R_p and S_p,S_p, respectively (Scheme 7).



Scheme 7. Acid-catalyzed reaction of $E=P^V$ (E = O, S, Se) functionalized compounds *rac*-**1a**–**c** to ethers **12**, **15** and **16**, respectively. (*i*) 3 equiv of *p*TsOH•H_2O, 1,4-dioxane, 90 °C.)

Starting with *rac*-**1a**, thioether **12** was formed with a *meso*/*racem* ratio of 1.37:1 (*de* = 0.16), as confirmed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopic studies (Scheme 7), whereby for the yield of 36 %, three molecules of *rac*-**1a** were considered (ESI). The assignment of each diastereomer was achieved by comparison of the ^1H and $^{31}P\{^1H\}$ NMR spectroscopic data of the mixture of **12** with a stereopure sample of (S_p,S_p)-**12**[13] (see Schemes 5 and 6, and the ESI). In case of phosphine oxide **1b**, a column chromatographic work-up did neither give bis(ether) **15** in significant amount, nor any further product (Scheme 7), indicating that the α-ferrocenyl carbocation, formed upon treatment of *rac*-**1b** with acids, is less stable than its thio derivative **1a**$^+$. Similarly, seleno phosphine *rac*-**1c** resulted in the formation of a small amount of a soluble material, which still consists of a complex mixture of isomers and products that could not further be separated. Therefore, the migration of a chalcogene



Scheme 8. Reaction of seleno phosphine (S_p)-**1c** with Sanger's reagent to afford selane *rac*-**19**. (*i*) Degassed DMF, 40 °C, 18 h; a) brsm = based on recovered starting material; 43 % of *rac*-**1c** were recovered and two molecules of *rac*-**1c** were considered for the synthesis of *rac*-**19**.

from the respective phosphine towards a CH_2^+ functionality seems to be limited to sulfur for this type of reaction. It furthermore implies that **1b**,**c** are rather unsuitable for either S_N or S_EAr reactions with electron-rich aromatics, due to a rapid decomposition of the respective in situ formed carbo-cations.

To exclude, if the decomposition of **1b**,**c**$^+$ is due to the high reaction temperature (90 °C) and the acidic media, exemplarily, the reaction of **1c** with Sangers reagent was investigated (Scheme 8). It could recently be shown that a similar sulfur transfer to a thioether species occurred, while using (S_p)-**1a** as the starting material.[13] In similarity, a S_NAr reaction occurred to give *rac*-**17**, which in turn splits into α-ferrocenyl carbocation *rac*-**1c**$^+$ and a 2,4-dinitrophenolate anion, stabilized by a Fe•••C_α interaction[16,17] and a mesomeric push-pull system, respectively (Scheme 8). The latter species was identified as its protonated form by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

Consecutive intermolecular selenium transfer gave *rac*-**18**, which underwent an additional S_NAr reaction to give *rac*-**19** in a yield of 56 %, which already considers two molecules of *rac*-**1c** (Scheme 8). Taking into account that 43 % of *rac*-**1c** were recovered, the yield of *rac*-**19** was amended to 98 %. The proposed mechanism is supported by the isolation of *rac*-**1b**, derived from de-selenated *rac*-**1c**. Hence, *rac*-**1c** and *rac*-**19** were formed in almost stoichiometric amounts. The recovering of the starting material *rac*-**1c** indicates a rather low reaction rate to *rac*-**16**, wherefore it can be considered as a selenium source. Compound *rac*-**1c**$^+$ in contrast, cannot be considered, since the thio analogue **10**$^+$ has been shown to undergo rapid decomposition (Scheme 5). Possible pathways for the formation of *rac*-**1b** are proposed within Scheme S1. The proposed mechanism for the formation of *rac*-**19** also clarifies why the cationic species **1a**$^+$ cannot be generated by conversion of the alcohols **1a,c** into e.g. mesylates, due to their rapid fragmentation and subsequent chalcogene migration.

Up to date, several mechanism,[30] e.g. S_N reactions, radicalic couplings or rearrangements[31] have been reported for the synthesis of selanes, whereby S_NAr reactions are limited to a few examples.[32,33] The transfer of a single Se atom, as observed for the synthesis of *rac*-**19**, is unique and the first example for this type of selane formation at a sterically demanding *ortho*-substituted ferrocene. Usually $SeCN^-$,[34] $LiSeSiMe_3$,[35] H_2Se[36] or diselenides[37] are applied in Se transfer reactions. The identity of *rac*-**19** with its two Se atoms was confirmed by single-crystal X-ray diffraction analysis (Figure 4) and ^{77}Se{^{1}H} NMR spectroscopy. The latter studies revealed resonances at –261.3 ppm (d, $^1J_{Se,P}$ = 727.4 Hz) and 438.0 ppm (s). For comparison, compound *rac*-**1c** also showed a signal at –254.6 ppm (d, $^1J_{Se,P}$ = 709.0 Hz), which can therefore be ascribed to the P=Se functionality. The singlet at lower field was assigned to the CH_2–Se–arene functionality, whereby appropriate ^{77}Se NMR investigations of similar compounds are limited.[34b,37b]

The ^{31}P{^{1}H} chemical shifts of E=P ferrocenyl methanols **1a** (E = S), **1b** (E = O) and **1c** (E = Se) increase in the order Se (**1c**, 30.0 ppm) < O (**1b**, 33.6 ppm[29]) < S (**1a**, 41.7 ppm[13]). The ^{31}P^{77}Se couplings of 709.0 (*rac*-**1c**) and 727.4 Hz (*rac*-**19**) are similar to recently reported ferrocenyl phosphines,[8,13] revealing an increased donor strength for the latter species.

Further properties and analytical data are discussed in the ESI.

Solid State Structure

The molecular structures of (S_p)-**2**, *o*-(S_p)-**5**, *p*-(S_p)-**7**, *o*-(S_p)-**8**, (S_p)-**13**, *rac*-**1b**,**c** and *rac*-**19** in the solid state have been determined by single-crystal X-ray diffraction analysis. Suitable crystals were obtained by crystallization from saturated hexane solutions. The ORTEP diagrams are shown in Figure 1 ((S_p)-**2** and *o*-(S_p)-**5**), Figure 2 (*p*-(S_p)-**7** and *o*-(S_p)-**8**), Figure 3 ((S_p)-**13**) and Figure 4 (*rac*-**1c**, *rac*-**19**). Selected bond lengths (Å), bond angles (°) and torsion angles (°) are summarized in Table 1. The results of a measurement of a single crystal of *rac*-**1b** (Figure S7), obtained within the reaction of *rac*-**1c** to *rac*-**19** (Scheme 8), are in similarity with those reported in literature measured at 150 K.[29a] Herein, data from a measurement at 125 K are provided for comparison (Experimental Section, see the ESI).

Enantiopure phosphane sulfides (S_p)-**2**, *o*-**5**, *p*-**7**, *o*-**8** and **13** crystallize in *non*-centrosymmetric monoclinic (*o*-**5**, $P2_1$) and in the orthorhombic space group $P2_12_12_1$ (**2**, *p*-**7**, *o*-**8** and **13**) with one crystallographic independent molecule in the asymmetric unit. The absolute structure parameters[38] below 0.034(5) confirm the (S_p) configuration. Selenophosphanes *rac*-**1c** and *rac*-**19**, synthesized as a racemic mixture, crystallized in the centrosymmetric space groups $P\bar{1}$ (*rac*-**19**) and $P2_1/c$ (*rac*-**1c**).

All compounds exhibit similar tilt angles (Ct–Fe–Ct between 175.89(5) and 178.24(3) °; Ct = centroid) and a rather eclipsed

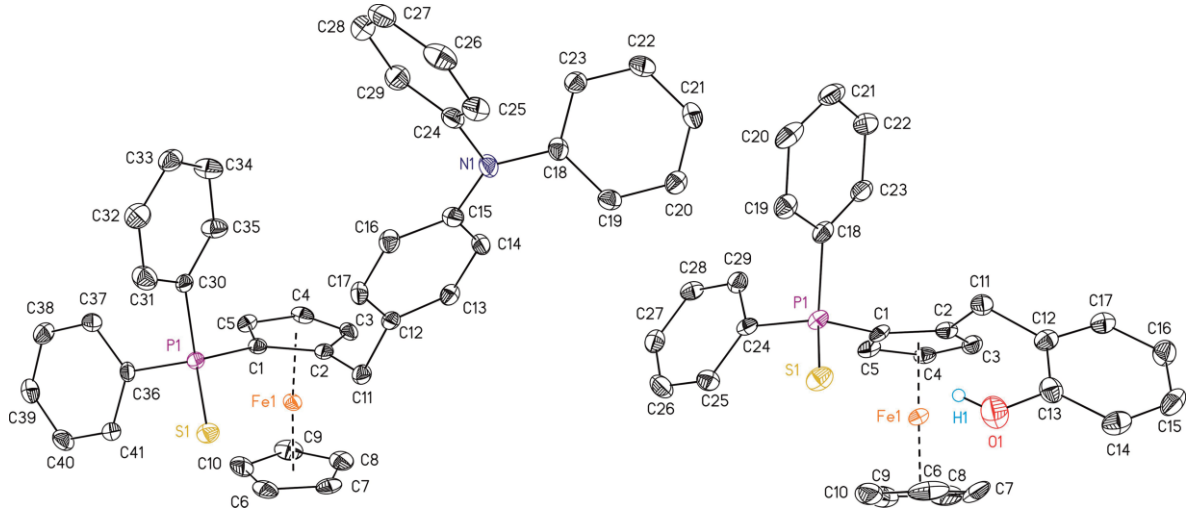


Figure 2. ORTEP drawing (50 % probability level) of the molecular structures of *p*-(S_p)-**7** (left) and *o*-(S_p)-**8** (right) with their atom-numbering schemes. All C-bonded hydrogen atoms have been omitted for clarity. (Selected bond properties are summarized in Table 1.)

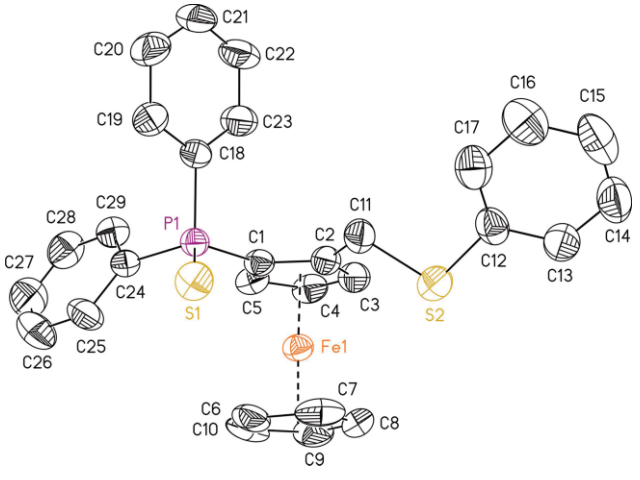


Figure 3. ORTEP drawing (50 % probability level) of the molecular structure of (S_p)-**13** with the atom-numbering scheme. All hydrogen atoms and the disordered C_5H_5 unit (occupancy ratio: 0.55/0.45) have been omitted for clarity. (Selected bond properties are summarized in Table 1.)

rotation of the cyclopentadienyls. The main difference is observed for the torsion angles of the P=E functionalities (E = S, Se), which are directed towards the *ortho* substituent and rotated below the C_5H_3 plane. The smallest value of 29.1(8) °, which is observed for *rac*-**1c**, may be caused by packing effects instead of a steric interaction of the Se with the Fe atom, since *rac*-**19** reveals an increased value of 40.4(4) °. The C2–C1–P1–S torsion angles increase to 35.5(3) and 35.8(3) ° for thio derivatives (S_p)-**2** and (S_p)-**7**. In both cases the *ortho* substituents are rotated above the C_5H_3 fragment by 71.9(4) and 100.0(4) °, respectively. An increased value is observed for *o*-**5** (42.9(7) °), due to an intermolecular *non*-classic S···H–C interaction with the C9 atom of an adjacent molecule (Figure S5). The rotation of the P=S moiety towards the Fe atom reaches a maximum for ferrocenes *o*-**8** (56.9(4) °) and **13** (48.7(3) °), due to a steric interaction with the *ortho*-CH_2 functionalities, exceptionally positioned below the C_5H_3 plane by 143.0(5) and 146.3(3) °. Consequently, the CH_2SPh moiety in **13**, showing the highest bending towards Fe1, results in an overlap of the van der Waals radii of 3.748 Å ($\Sigma_{S,Fe\text{-}max}$ = 3.94 Å),[39] indicating a weak intramolecular

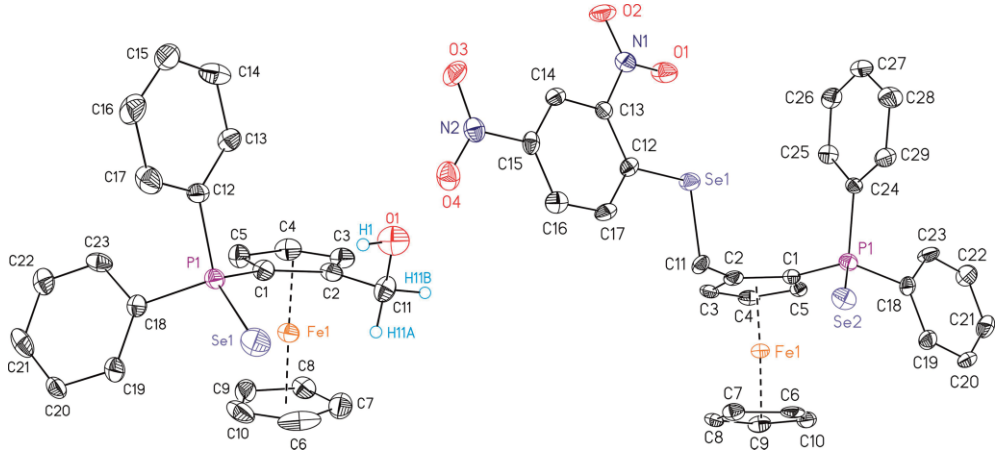


Figure 4. ORTEP drawing (50 % probability level) of the molecular structures of *rac*-**1c** (left) and *rac*-**19** (right) with the atom-numbering schemes Selected C-bonded hydrogen atoms have been omitted for clarity. (Selected bond properties are summarized in Table 1.)

Table 1. Selected bond properties (Å/°) of (S_p)-configured **2**, *o*-**5**, *p*-**7**, *o*-**8** and **13**, *rac*-**1c**, and *rac*-**19**.[a]

X, E	(S_p)-**2** NH, NH	*o*-(S_p)-**5** ^{i}C, NMe_2	*p*-(S_p)-**7** ^{i}C, NPh_2	*o*-(S_p)-**8** ^{i}C, OH	(S_p)-**13** S, S	*rac*-**1b**[b] OH, –	*rac*-**1c**[c] OH, –	*rac*-**19**[c] Se, Se
P=S	1.9640(11)	1.952(3)	1.9599(14)	1.9668(16)	1.9581(11)	1.4882(16)	2.116(2)	2.1223(13)
C2–C11	1.500(5)	1.491(10)	1.502(4)	1.493(6)	1.494(5)	1.498(3)	1.520(12)	1.493(6)
C11–X	1.458(5)	1.514(11)	1.512(4)	1.513(7)	1.811(4)	1.420(3)	1.410(11)	1.982(4)
E–^{i}C	1.387(5)	1.446(11)	1.427(4)	1.375(6)	1.768(4)	–	–	1.891(4)
C2–C1–P1–S	–35.5(3)	–42.9(7)	–35.8(3)	–56.9(4)	–48.7(3)	–39.1(2)	–29.1(8)	–40.4(4)
C1–C2–C11–X	–71.9(4)	–113.9(9)	–100.0(4)	143.0(5)	146.3(3)	161.7(2)	–68.2(11)	–85.9(5)

[a] Negative values represent counter-clockwise torsion angles. [b] P=O instead of P=S; values are in accordance with those reported in ref.[29a]. [c] P=Se instead of P=S.

stabilization. Contrary, the low rotation within (S_p)-**2** (35.5(3) °) shortens the S1···C11 distance to 3.476(3) Å, which is within the sum of the van der Waals radii ($\Sigma_{C,S\text{-}max}$ = 3.50 Å).[39] However, the different types of inter- and intramolecular weak interactions do not effect the P=S distance that remains within 1.952(3) and 1.9668(16) Å. For **1c** the P=Se distance is increased to 2.116(2) Å, which is within the range for ferrocenyl seleno phosphines.[12,13,40]

The OH functionality in *o*-**8** is stabilized by a weak interaction within the sulfur atom (S1···O1, 3.449(4) Å; $\Sigma_{O,S\text{-}max}$ = 3.50 Å). In contrast, compound **2** does not show any additional stabilization of the NH moiety.

The difference of the $^3J_{H,H}$ coupling constants of the CH_2 hydrogen atoms towards the OH group within phosphine sulfide **1a** and selenide **1c**, may be caused by a fixed orientation of the hydroxy moiety. Compounds **1a** and **1c** reveal almost similar conformational properties of the $P(E)Ph_2$ and CH_2OH substituents[29] and do not show any intra- or intermolecular hydrogen bridge bonds. In contrast, the different rotation of the CH_2OH moiety (Table 1) of phosphine oxide **1b** allows for dimeric structures based on P=O···H–O hydrogen bridge bonds in the crystal packing (Figure S7).[29] The therefore weakened O–H bond does not allow for a coupling with the CH_2 hydrogen atoms. Furthermore, a preferred *anti*-conformation of one of the CH_2 hydrogen atoms towards the O–H group in **1a** and **1c** can be assumed. Hence, the signal at 4.68 ppm ($^3J_{H,H}$ = 12.9 Hz) can be ascribed to H11B (Figure 4).

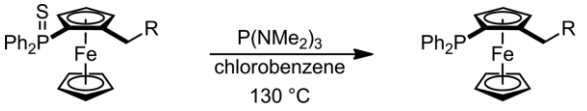
Recently, the crystal structure of racemic *o*-**8** has been reported.[23] Therein, the phenyl moiety is positioned above the C_5H_3 plane (–108.9°; herein 143.0(5) °) and the OH group is directed away from the P=S functionality, which results in the formation of hydrogen bridge bonds with the sulfur atoms of adjacent molecules, along the *a*-axis (Figure S8).

The triaryl moiety of *p*-**7** contains a sp^2 hybridized nitrogen atom based of the surrounding C–N–C angle sum of 359.0(3) °. The lowest value between the C_6H_5 groups (116.2(3) °) is due to their rather perpendicular intersection with the C_3N fragment of 50.11(13)/61.20(12) °. Contrary, the almost co-planar C_3N···C_6H_4 intersection (15.4(2) °) results in a steric repulsion and therefore increased C–N–C angles of 121.2(3)/121.6(3) °. This also causes a deformation of the C_6H_4 arene and hence an increased rms deviation of 0.0148, compared to 0.0039/0.0035 for C_6H_5. The nitrogen atom is positioned out of the surrounding C_3 plane by solely 0.084(4) Å.

The NO_2 functionalities in compound *rac*-**19** are rotated away from the ferrocenyl backbone to prevent steric effects, resulting in electrostatic N···O interactions between two adjacent molecules. Together with parallel-displaced π···π contacts between the C_5H_5 groups a one-dimensional network along [210] is formed (Figure S6).

Catalysis

The P^{III} species necessary for Pd-catalyzed *C,C* cross-coupling reactions can be achieved by the reduction of the respective P^V compounds (S_p)-**2**,**5**,**8** and **13** by desulfurization/reduction with $P(NMe_2)_3$ according to our recent protocol. (Scheme 9).[13] The successful P^V/P^{III} reduction can be monitored by $^{31}P\{^1H\}$ NMR spectroscopy, where a shift from 41 ppm to –23 ppm occurs, similar to literature.[9,13]

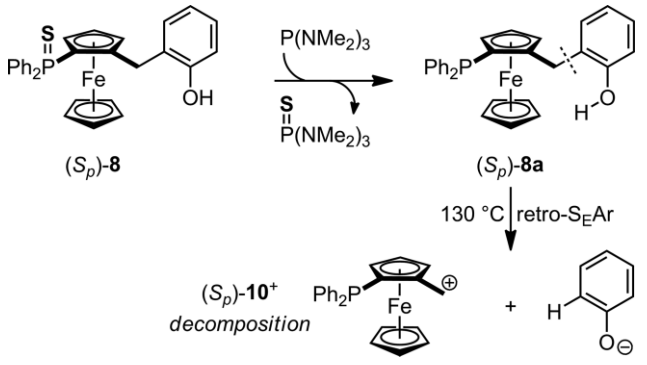


(S_p)-**2**	R = **N**HPh	(S_p)-**2a**, 76 %
(S_p)-**5**	R = 2-**N**Me_2-C_6H_4	(S_p)-**5a**, 68 %
(S_p)-**8**	R = 2-**O**H-C_6H_4	(S_p)-**8a**, 15 %
(S_p,S_p)-**12**	R = **S**CH_2Fc*	(S_p,S_p)-**12a**, 51 %[a]
(S_p)-**13**	R = **S**Ph	(S_p)-**13a**, 98 %

Scheme 9. Reduction of P^V thiophosphines (S_p)-**2**,-**5**,-**8**,-**12** and –**13** to give their respective P^{III} species. a) Literature value.[13]

The low yield of 15 % within the reduction of phenol-bearing (S_p)-**8** to (S_p)-**8a** is ascribed to a CH_2–arene bond cleavage and the formation of phenol within a retro-S_EAr-type[41] reaction (Scheme 10). This was observed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy of the first (S_p)-**8a**-containing fraction (Figure S4). It also confirms that the therein formed desulfurized α-carbon cation $\mathbf{10}^+$ rapidly decomposes, which lowers the yield of (S_p)-**8a** (Figure 5).

Enantiopure compounds (S_p)-**2a**, **5a**, **8a** and **13a** were investigated as ligands within Suzuki-Miyaura *C,C* cross-coupling reactions for the synthesis of in *ortho*-position hindered biaryls. The results are compared with those ones of structurally related compounds to (S_p)-**8a′** and (S_p,S_p)-**12a**, which resulted in 26 % *ee* as recently reported by our group.[13] To ensure a comparability of the results, the reaction conditions for the coupling reactions have been adopted.[13] The yields of the obtained biaryls at a catalyst loading of low as 1 mol-% [Pd] at 70 °C approaches up to 98 %. However, the presence of an OH-acidic group, as present in *o*-(S_p)-**8a**, decreased the yield of **22a** to 47 % (Figure 5).



Scheme 10. Attempted desulfurization of (S_p)-**8** to (S_p)-**8a** and a subsequent phenol formation.

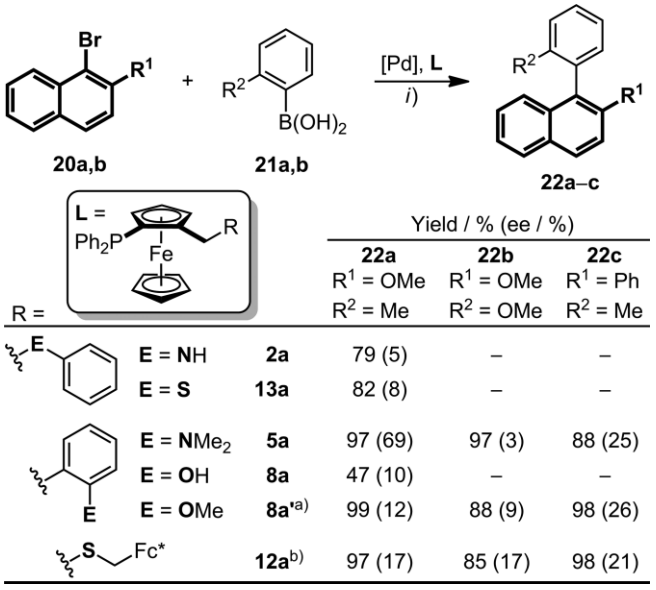


Figure 5. Atropselective Pd-catalyzed Suzuki-Miyaura *C,C* cross-coupling reactions for the synthesis of *ortho*-substituted biaryls **22a–c** using *o*-(S_p)-**5a**,**8a** and (S_p)-**2a**,**13a** as ligands **L**. Reaction conditions: *i*) aryl bromide (1 mmol), boronic acid (1.5 mmol), [$Pd_2(dba)_3$] (0.5 mol-%), **L** (2 mol-%), $K_3PO_4 \cdot H_2O$ (3 mmol), toluene (3 mL), 70 °C, 24 h. Reaction times have not been optimized; a) taken from reference 13; b) 1 mol-% of the ligand; Fc* = Fe(η^5-C_5H_5)(η^5-2-(PPh_2)-C_5H_3).

The enantiomeric excess (*ee*) of the resulting biaryls **22a–c** was determined with chiral HPLC (Figure S1). Most of the reactions resulted in an *ee* of 10–20 %. Comparison with recent results, indicate that this is based on the steric effect of the *ortho* CH_2R group instead of an effective hemilabile bonding of donor atoms. This is supported by the results of sterically most demanding biaryl **22c**, showing an in general higher *ee*. Ligand **13a** has been used within various catalytic reactions, with opposed stereoselectivities.[14,42] Its bidentate binding behavior is reported for several transition metals, including Pd.[43]

Herein, the highest *ee* was observed for *ortho* NMe_2-substituted *o*-(S_p)-**5a**, which gave **22a** in 69 % and hence the highest value for planar-chiral ferrocenes so far.

The absence of P and C stereocenters further verifies that exclusively using the planar-chirality of a ferrocenyl backbone can effectively be converted onto sterically demanding substrates. It should be noted that the *ee* within the biaryls strongly differs by the substrates applied, as shown on the example of sterically less demanding **22b**, where solely 3 % *ee* are characteristic. The high discrepancies of the *ee* for different substrates is in accordance with DFT calculations, where a complex interplay of all three catalytic steps was identified as enantio-determining, especially in case of the Suzuki-Miyaura reaction, and therefore highly susceptible to substrate shapes.[44] Comparison of the SPh functionalized species **13a** with the recently reported results of the OPh derivative reveals a similar *ee* of 8 % (Table 1) and 12 %, respectively, whereby different substrates were investigated.[9] The therein reported higher values of 37 % *ee*, observed for a CH_2–O–fenchyl ligand, are most likely due to the C-stereogenic of the fenchyl group, instead of the planar-chirality.[9]

Conclusions

The acid-catalyzed dehydration of ferrocene (S_p)-2-CH_2OH-1-($P(=S)Ph_2$)-Fc (Fc = Fe(η^5-C_5H_5)(η^5-C_5H_3)) to an α-ferrocenyl carbocation and its subsequent reaction with electron-rich arenes PhX (X = NH_2, NMe_2, N*i*Pr_2, NPh_2, PPh_2, $P(=S)Ph_2$, OH, SH, SMe) is reported. They either underwent electrophilic aromatic substitution reactions (S_EAr) in *ortho* and *para* position, or nucleophilically attacked the CH_2^+ group (S_N) with the hetero atom X, resulting in new planar-chiral benzyl-, or ether-type products, respectively. Phosphorus-based arenes (PPh_3, $P(=S)Ph_3$) did neither undergo S_N, nor S_EAr reactions with the carbocation. The more nucleophilic SH group exclusively underwent nucleophilic substitution to afford a CH_2SPh functionality, contrary to the respective phenol derivative, where *ortho*-functionalization took place. It could be shown that the $P(=S)Ph_2$ functionality could act as a sulfur source, which transfers a single S atom towards an in situ-formed 2-CH_2^+ unit, by starting with 2-CH_2OH-1-$P(=S)Ph_2$-Fc. This unique reaction pathway was extended to the isostructural selenium derivative 2-CH_2OH-1-$P(=Se)Ph_2$-Fc to investigate the influence of the P=E bond strength (E = S, Se). It was found that within these studies a single selenium atom transfer was observed, when 2-CH_2OH-1-($P(=Se)Ph_2$)-Fc was treated with Sangers reagent, which is a unique phenomenon for selenium compounds. $^{77}Se\{^1H\}$ NMR spectroscopy and single-crystal X-ray diffraction analysis confirmed the presence of two chemically different selenium atoms. The S_N- (CH_2XPh; X = NH, S) and S_EAr-derived (CH_2–(2-X-C_6H_4); X = NMe_2, OH) ferrocenes, bearing an *ortho*-$P(=S)Ph_2$ functionality, were reduced to their respective P^{III} species and applied in Suzuki-Miyaura *C,C* cross-coupling reactions for the synthesis of hindered biaryls. At catalyst loadings of 1 mol-% [Pd], biaryls with an *ee* of up to 69 % were formed, which is unique for planar-chiral ferrocenes. This confirms that the herein reported 2-NMe_2-C_6H_4-CH_2-substituted planar-chiral ferrocenyl backbone is in principle sufficient for an efficient chirality transfer within a catalytic cycle.

Experimental Section

General. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Reaction flasks were

heated at reduced pressure with a heat gun and flushed with argon. This procedure was repeated thrice. If necessary, solvents were deoxygenated by standard procedures. For column chromatography silica with a particle size of 40 – 60 μm (230 – 400 mesh (ASTM)) was used.

The assignment and labeling of the H and C atoms in the NMR spectra follows the IUPAC recommendations.[45]

Reagents. Tetrahydrofuran was purified by distillation from sodium/benzophenone ketyl. Dichloromethane, hexane and toluene were dried and purified with an MBraun SPS–800 purification system and stored over molecular sieve (4 Å). Aniline and *N*,*N*-dimethylaniline were distilled prior to use. Compounds (S_p)-**1a**,[9] (S_p)-**1b**,[29] (S_p)-2-CH_2OH-1-PPh_2-2-Fc (S_p)-**10**,[46] *rac*-**10**,[12] *N*,*N*-diisopropylaniline[47] and 1-bromo-2-phenylnaphthaline[48] were synthesized according to literature procedures reported elsewhere. All other chemicals were purchased from commercial suppliers and were used without further purification.

Instruments. *FT-IR* spectra were recorded as KBr pellets in the transition mode with a Nicolet IR 200 spectrometer (Thermo Comp). *NMR* spectra were recorded with a Bruker Avance III 500 spectrometer (500.3 MHz for ^{1}H, 125.8 MHz for ^{13}C, 202.5 MHz for ^{31}P and 95.4 MHz for ^{77}Se) are reported with chemical shifts in δ (ppm) units downfield from tetramethylsilane with the solvent as the reference signal ([D_1]chloroform$_1$: ^{1}H at 7.26 ppm and ^{13}C{^{1}H} at 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; ^{77}Se{^{1}H} relative to Ph_2Se_2, 463 ppm[49]) or by the ^{2}H solvent lock signal.[50] Two decimal places for ^{13}C{^{1}H} values are given to clarify the assignment of signals, which are in close proximity to each other. The *melting* or decomposition points were determined by using 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 mm) using hexane/isopropanol mixtures as the eluents. Retention times (*t*) are reported in minutes.

Single crystal X-ray diffraction analysis. Data were collected with an Oxford Gemini S diffractometer ((S_p)-**2**, *o*-(S_p)-**5**, *o*-(S_p)-**8,** *rac*-**1b** and *rac*-**19**) and a Venture D8 diffractometer (*p*-(S_p)-**7**, (S_p)-**13** and *rac*-**1c**) with Cu K $_\alpha$ radiation (λ = 1.54184 Å; (S_p)-**2**, *o*-(S_p)-**5**, *p*-(S_p)-**7**, *o*-(S_p)-**8**, (S_p)-**13** and *rac*-**1c**) and Mo K_α radiation (λ = 0.71073 Å, *rac*-**1b** and *rac*-**19**) at 100 K (*p*-(S_p)-**7**, *rac*-**1c**), 120–125 K ((S_p)-**2**, *o*-(S_p)-**5**, *o*-(S_p)-**8**, *rac*-**1b** and *rac*-**19**) and ambient conditions ((S_p)-**13**). Measurements with Cu K_α radiation at the D8 Venture device were performed with a fine-focus source. The molecular structures were solved by direct methods using SHELXS-13[51] and refined by full-matrix least-squares procedures on F^2 using SHELXL-13.[52,53] All non-hydrogen atoms were refined anisotropically and a riding model was employed in the treatment of the hydrogen atom positions, except otherwise noted. Graphics of the molecular structures have been created by using ORTEP.[54]

CCDC 1868002 (for (S_p)-**2**), 1868003 (for *o*-(S_p)-**5**), 1868004 (for *p*-(S_p)-**7**), 1868005 (for *o*-(S_p)-**8**), 1868006 (for (S_p)-**13**), 1868007 (for *rac*-**1b**), 1868008 (for *rac*-**1c**), and 1868009 (for *rac*-**19**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

General procedure for the reaction of (S_p)-1 with substituted benzenes (GP1)

Compound (S_p)-**1a** (1 equiv) was dissolved in 50 mL of 1,4-dioxane followed by the addition of *p*TsOH (3 or 6 equiv), the respective arene (3 or 5 equiv) and $MgSO_4$ (1.0 g). The reaction mixture was heated for 24 h at 90 °C followed by concentration in vacuo. The residue was collected in diethyl ether (50 mL) and washed with water. The aqueous phase was extracted thrice with diethyl ether (50 mL each). All organic phases were combined and dried with $MgSO_4$ followed by the removal of all volatiles in vacuo. Purification was realized by column chromatography on silica (column size see below) using various eluent mixtures followed by evaporation of all volatiles in vacuo.

Reaction of (S_p)-1a with aniline

Compound (S_p)-**1a** (600 mg, 1.40 mmol), *p*TsOH (1.58 g, 8.4 mmol) and aniline (0.38 mL, 4.2 mmol) were reacted according to *GP1*. Purification was realized by column chromatography (silica, 4 × 16 cm) using a 5:1 hexane/ethyl acetate mixture (v/v) as the eluent. As first fraction (S_p)-**2** could be eluted, followed by a mixture of *o*-(S_p)-**3** and (S_p)-**4** and finally *p*-(S_p)-**3**. A further column chromatographic work-up (silica, 2.5 × 20 cm, $CHCl_3$) separated the obtained mixture into (S_p)-**4**, as the first fraction and *o*-(S_p)-**3** as the second one.

(S_p)-2-(N-Phenylaminomethyl)-1-(thiodiphenylphosphino)-ferrocene (S_p)-2

Yield: 156 mg (0.308 mmol, 22 % based on (S_p)-**1a**). Orange solid. Anal. Calcd for $C_{29}H_{26}FeNPS{\cdot}2\ CH_2Cl_2$ (507.39•2 116.99 g/mol): C, 54.98; H, 4.46; N, 2.07; found C, 54,96; H, 4.76; N, 1.90. Mp: 35 °C. ^{1}H NMR ($CDCl_3$, δ): 3.71–3.72 (m, 1H, C_5H_3), 4.07 (s/br, 1H, NH), 4.16 (d, $^2J_{H,H}$ = 14.8 Hz, 1H, CH_2), 4.25–4.27 (m, 1H, C_5H_3), 4.32 (s, 5H, C_5H_5), 4.62–4.62 (m, 1H, C_5H_3), 4.77 (d, $^2J_{H,H}$ = 14.8 Hz, 1H, CH_2), 6.19 (d, $^3J_{H,H}$ = 7.7 Hz, 2H, 2,6-C_6H_5N), 6.56 (t, $^3J_{H,H}$ = 7.3 Hz, 1H, 4-C_6H_5N), 6.98 (dd, $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 7.5 Hz, 2H, 3,5-C_6H_5N), 7.25–7.29 (m, 2H, C_6H_5), 7.39–7.43 (m, 1H, C_6H_5), 7.45–7.54 (m, 5H, C_6H_5), 7.78–7.83 (m, 2H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 41.4 (1C, CH_2), 68.7 (d, $J_{C,P}$ = 10.3 Hz, 1C, C_5H_3), 70.6 (s, 5C, C_5H_5), 74.0 (d, $^1J_{C,P}$ = 95.0 Hz, 1C, C_{C5H3}–P), 74.56 (d, $J_{C,P}$ = 12.2 Hz, 1C, C_5H_3), 74.61 (d, $J_{C,P}$ = 9.6 Hz, 1C, C_5H_3), 90.8 (d, $^2J_{C,P}$ = 10.2 Hz, 1C, C_{C5H3}–C), 112.6 (2C, 2,6-C_6H_5N), 116.6 (1C, 4-C_6H_5N), 128.0 (d, $J_{C,P}$ = 12.4 Hz, 2C, C_6H_5), 128.3 (d, $J_{C,P}$ = 12.4 Hz, 2C, C_6H_5), 128.8 (2C, 3,5-C_6H_5N), 131.1 (d, $^4J_{C,P}$ = 2.9 Hz, 1C, 4-C_6H_5), 131.3 (d, $^4J_{C,P}$ = 3.0 Hz, 1C, 4-C_6H_5), 131.7 (d, $J_{C,P}$ = 10.7 Hz, 2C, C_6H_5), 132.0 (d, $J_{C,P}$ = 10.9 Hz, 2C, C_6H_5), 133.1 (d, $^1J_{C,P}$ = 86.1 Hz, 1C, $^qC_6H_5$), 134.6 (d, $^1J_{C,P}$ = 86.8 Hz, 1C, $^qC_6H_5$), 147.2 (1C, ^{q}C–NH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 41.7 ppm. IR data (KBr, $\tilde{\nu}$ =): 3388 (NH), 3072, 3059, 3039, 2964, 2929, 2851, 1598, 1503, 1479, 1436, 1309, 1207, 1165, 1043, 822, 756, 735 (P=S), 612, 552, 533 cm^{-1}.

Crystal Data for (S_p)-**2**: $C_{29}H_{26}FeNPS$, M = 507.39 g mol^{-1}, orthorhombic, $P2_12_12_1$, λ = 1.54184 Å, a = 8.8945(4) Å, b = 14.0045(8) Å, c = 19.5825(10) Å, V = 2439.3(2) Å^3, Z = 4, ρ_{calcd} = 1.382 Mg m^{-3}, μ = 6.502 mm^{-1}, T = 119.95(10) K, θ range 3.881–64.493°, 10108 reflections collected, 4055 independent reflections (R_{int} = 0.0277), R_1 = 0.0293, wR_2 = 0.0719 [$I > 2\sigma(I)$], absolute structure parameter[38] –0.009(2).

(S_p)-2-((2-Aminophenyl)methyl)-1-(thiodiphenylphosphino)-ferrocene o-(S_p)-3

Yield: 217 mg (0.427 mmol, 31 % based on (S_p)-**1a**). Orange solid. Anal. Calcd for $C_{29}H_{26}FeNPS{\cdot}4\ CH_2Cl_2$ (507.41•4 84.93 g/mol): C, 46.79; H, 4.05; N, 1.65; found C, 46.69; H, 4.45; N, 1.52 (*best match). Mp: 197–201 °C. ^{1}H NMR ($CDCl_3$, δ): 3.68 (dd, J = 3.8, 2.3 Hz, 1H,

C_5H_3), 3.81 (br, 2H, NH_2), 3.85 (d, $^2J_{H,H}$ = 15.9 Hz, 1H, CH_2), 3.93 (d, $^2J_{H,H}$ = 15.9 Hz, 1H, CH_2), 4.25 (dd, *J* = 4.1, 2.5 Hz, 1H, C_5H_3), 4.33 (s, 5H, C_5H_5), 4.45 (dd, *J* = 3.8, 1.9 Hz, 1H, C_5H_3), 6.43 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.1 Hz, 1H, C_6H_4), 6.57 (td, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.2 Hz, 1H, C_6H_4), 6.88 (td, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, C_6H_4), 6.97 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.4 Hz, 1H, C_6H_4), 7.22–7.26 (m, 2H, C_6H_5), 7.34–7.37 (m, 1H, C_6H_5), 7.45–7.53 (m, 5H, C_6H_5), 7.78–7.83 (m, 2H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 28.9 (1C, CH_2), 68.6 (d, $J_{C,P}$ = 10.5 Hz, 1C, C_5H_3), 70.8 (s, 5C, C_5H_5), 73.67 (d, $J_{C,P}$ = 9.8 Hz, 1C, C_5H_3), 73.73 (d, $^1J_{C,P}$ = 95.5 Hz, 1C, C_{C5H3}–P), 74.28 (d, $J_{C,P}$ = 13.0 Hz, 1C, C_5H_3), 92.0 (d, $^2J_{C,P}$ = 12.6 Hz, 1C, C_{C5H3}–C), 115.7 (1C, C_6H_4), 118.0 (1C, C_6H_4), 124.9 (1C, C_{C6H4}–C), 126.9 (1C, C_6H_4), 127.97 (d, $J_{C,P}$ = 12.5 Hz, 2C, C_6H_5), 128.01 (d, $J_{C,P}$ = 12.4 Hz, 2C, C_6H_5), 130.2 (1C, C_6H_4), 131.1 (d, $^4J_{C,P}$ = 2.9 Hz, 1C, 4-C_6H_5), 131.3 (d, $^4J_{C,P}$ = 2.9 Hz, 1C, 4-C_6H_5), 131.8 (d, $J_{C,P}$ = 10.6 Hz, 2C, C_6H_5), 132.0 (d, $J_{C,P}$ = 10.9 Hz, 2C, C_6H_5), 133.2 (d, $^1J_{C,P}$ = 86.2 Hz, 1C, $^qC_6H_5$), 133.8 (d, $^1J_{C,P}$ = 86.4 Hz, 1C, $^qC_6H_5$), 144.3 (1C, C–NH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 42.2 ppm.

(S_p)-2-((4-Aminophenyl)methyl)-1-(thiodiphenylphosphino)-ferrocene p-(S_p)-3

Compound *p*-(S_p)-**3** was obtained in a mixture with its *ortho*-derivative. NMR-Yield: 139 mg (0.247 mmol, 20 % based on (S_p)-**1a**). Orange solid.

^1H NMR ($CDCl_3$, δ): 3.47 (br, 2H, NH_2), 3.65 (dd, *J* = 3.7, 2.2 Hz, 1H, C_5H_3), 3.83 (d, $^2J_{H,H}$ = 15.2 Hz, 1H, CH_2), 4.06 (d, $^2J_{H,H}$ = 15.2 Hz, 1H, CH_2), 4.21 (dd, *J* = 4.0, 2.4 Hz, 1H, C_5H_3), 4.32 (s, 5H, C_5H_5), 4.36–4.37 (m, 1H, C_5H_3), 6.36 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, C_6H_4), 6.83 (d, $^3J_{H,H}$ = 8.2 Hz, 2H, C_6H_4), 7.22–7.25 (m, 2H, C_6H_5), 7.35–7.39 (m, 1H, C_6H_5), 7.42–7.51 (m, 5H, C_6H_5), 7.77–7.81 (m, 2H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 33.1 (1C, CH_2), 68.5 (d, $J_{C,P}$ = 10.6 Hz, 1C, C_5H_3), 70.7 (5C, C_5H_5), 73.5 (d, $J_{C,P}$ = 9.8 Hz, 1C, C_5H_3), 73.4 (d, $^1J_{C,P}$ = 95.5 Hz, 1C, C_{C5H3}–P), 74.3 (d, $J_{C,P}$ = 13.0 Hz, 1C, C_5H_3), 93.5 (d, $^2J_{C,P}$ = 12.5 Hz, 1C, C_{C5H3}–C), 114.7 (2C, C_6H_4), 127.91 (d, $J_{C,P}$ = 12.3 Hz, 2C, C_6H_5), 127.93 (d, $^1J_{C,P}$ = 12.5 Hz, 2C, C_6H_5), 129.8 (2C, C_6H_4), 130.6 (d, $^4J_{C,P}$ = 2.9 Hz, 1C, 4-C_6H_5), 130.7 (1C, C_{C6H4}–CH_2), 131.1 (d, $^4J_{C,P}$ = 2.9 Hz, 1C, 4-C_6H_5), 131.9 (d, $J_{C,P}$ = 10.6 Hz, 2C, C_6H_5), 132.0 (d, $J_{C,P}$ = 10.8 Hz, 2C, C_6H_5), 133.7 (d, $^1J_{C,P}$ = 85.9 Hz, 1C, $^qC_6H_5$), 134.2 (d, $^1J_{C,P}$ = 86.7 Hz, 1C, $^qC_6H_5$), 144.0 (1C, ^qC–NH_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 42.1 ppm.

(S_p,S_p)-N,4-Bis((2-(thiodiphenylphosphino)ferrocene-1-yl)methyl)aniline (S_p,S_p)-4

Yield: 20 mg (0.022 mmol, 2 % based on (S_p)-**1a**). Orange oil. ^1H NMR ($CDCl_3$, δ): 3.62 (dd, *J* = 3.7, 2.3 Hz, 1H, C_5H_3), 3.70 (dd, *J* = 3.7, 2.3 Hz, 1H, C_5H_3), 3.78 (d, $^2J_{H,H}$ = 15.2 Hz, 1H, CH_2), 3.86 (br, 1H, NH), 3.95 (d, $^2J_{H,H}$ = 15.2 Hz, 1H, CH_2), 4.10 (d, $^2J_{H,H}$ = 14.7 Hz, 1H, CH_2), 4.19 (dd, *J* = 4.1, 2.5 Hz, 1H, C_5H_3), 4.26 (dd, *J* = 4.0, 2.4 Hz, 1H, C_5H_3), 4.30 (s, 5H, C_5H_5), 4.31 (s, 5H, C_5H_5), 4.34 (dd, *J* = 3.7, 1.8 Hz, 1H, C_5H_3), 4.58 (dd, *J* = 3.8, 1.7 Hz, 1H, C_5H_3), 4.63 (d, $^2J_{H,H}$ = 14.7 Hz, 1H, CH_2), 5.91 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, C_6H_4), 6.67 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, C_6H_4), 7.16–7.20 (m, 2H, C_6H_5), 7.24–7.27 (m, 2H, C_6H_5), 7.28–7.32 (m, 1H, C_6H_5), 7.38–7.54 (m, 11H, C_6H_5), 7.76–7.82 (m, 2H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 33.1 (1C, CH_2), 41.6 (1C, CH_2), 68.4 (d, $J_{C,P}$ = 10.4 Hz, 1C, C_5H_3), 68.7 (d, $J_{C,P}$ = 10.3 Hz, 1C, C_5H_3), 70.6 (5C, C_5H_5), 70.7 (5C, C_5H_5), 73.29 (d, $^1J_{C,P}$ = 95.6 Hz, 1C, C_{C5H3}–P), 73.5 (d, $J_{C,P}$ = 9.9 Hz, 1C, C_5H_3), 73.9 (d, $^1J_{C,P}$ = 95.0 Hz, 1C, C_{C5H3}–P), 74.2 (d, $J_{C,P}$ = 12.9 Hz, 1C, C_5H_3), 74.50 (d, $J_{C,P}$ = 9.6 Hz, 1C, C_5H_3), 74.5 (d, $J_{C,P}$ = 12.6 Hz, 1C, C_5H_3), 91.0 (d, $^2J_{C,P}$ = 12.0 Hz, 1C, C_{C5H3}–C), 94.4 (d, $^2J_{C,P}$ = 12.5 Hz, 1C, C_{C5H3}–C), 112.4 (2C, C_6H_4), 127.9 (d, $J_{C,P}$ = 12.3 Hz, 2C, C_6H_5), 127.97 (d, $J_{C,P}$ = 12.4 Hz, 2C, C_6H_5), 128.04 (d, $J_{C,P}$ = 12.4 Hz, 2C, C_6H_5), 128.4 (d, $J_{C,P}$ = 12.5 Hz, 2C, C_6H_5), 128.9 (1C, C_{C6H4}–C), 129.4 (2C, C_6H_4), 130.9 (d, $^4J_{C,P}$ = 2.9 Hz, 1C, C_6H_5), 131.1 (d, $^4J_{C,P}$ = 3.0 Hz, 1C, C_6H_5), 131.2 (d, $^4J_{C,P}$ = 2.9 Hz, 1C, C_6H_5), 131.4 (d, $^4J_{C,P}$ = 2.8 Hz, 1C, C_6H_5), 131.7 (d, $J_{C,P}$ = 10.7 Hz, 2C, C_6H_5), 131.9 (d, $J_{C,P}$ = 10.6 Hz, 2C, C_6H_5), 132.0 (d, $J_{C,P}$ = 10.8 Hz, 4C, C_6H_5), 133.2 (d, $^1J_{C,P}$ = 85.9 Hz, 1C, $^qC_6H_5$), 133.7 (d, $^1J_{C,P}$ = 85.9 Hz, 1C, $^qC_6H_5$), 134.2 (d, $^1J_{C,P}$ = 86.7 Hz, 1C, $^qC_6H_5$), 134.6 (d, $^1J_{C,P}$ = 86.8 Hz, 1C, $^qC_6H_5$), 145.3 (1C, C_{C6H4}–NH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 41.7, 42.2 ppm.

Reaction of (S_p)-1 with N,N-dimethylaniline

Compound (S_p)-**1a** (600 mg, 1.40 mmol), *p*TsOH (1.58 g, 8.4 mmol) and aniline (0.48 mL, 4.2 mmol) were reacted according to *GP1*. Purification was realized by column chromatography (silica, 4 × 14 cm) using a 5:1 hexane/ethyl acetate mixture (v/v) as the eluent. At first *o*-(S_p)-**5** could be eluted, followed by (S_p,S_p)-**12** (126 mg, 0.438 mmol, 31 % based on (S_p)-**1a**) containing traces (< 5 %) of *p*-(S_p)-**5** in a *non*-separable mixture.

(S_p)-2-((2-(N,N-Dimethylamino)phenyl)methyl)-1-(thiodiphenylphosphino)-ferrocene o-(S_p)-5

Yield: 93 mg (0.18 mmol, 13 % based on (S_p)-**1a**). Orange solid. Anal. Calcd for $C_{31}H_{30}FeNPS$•1/6 C_6H_{14} (535.46•1/6 86.18 g/mol): C, 69.90; H, 5.93; N, 2.55; found C, 69.82; H, 6.22; N, 2.33. Mp: 167–170 °C. ^1H NMR ($CDCl_3$, δ): 2.56 (s, 6H, CH_3), 3.73 (dd, *J* = 3.7, 2.2 Hz, 1H, C_5H_3), 4.14 (s, 2H, CH_2), 4.18 (dd, *J* = 4.1, 2.4 Hz, 1H, C_5H_3), 4.24–4.25 (m, 1H, C_5H_3), 4.34 (s, 5H, C_5H_5), 6.76 (td, $^3J_{H,H}$ = 7.4 Hz, $^4J_{H,H}$ = 1.3 Hz, 1H, C_6H_4), 6.99 (dd, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.4 Hz, 1H, C_6H_4), 7.01 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.2 Hz, 1H, C_6H_4), 7.07 (td, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.5 Hz, 1H, C_6H_4), 7.30–7.34 (m, 2H, C_6H_5), 7.39–7.42 (m, 1H, C_6H_5), 7.44–7.52 (m, 3H, C_6H_5), 7.63–7.67 (m, 2H, C_6H_5), 7.82–7.87 (m, 2H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, δ): 29.7 (1C, CH_2), 45.0 (2C, CH_3), 68.2 (d, $J_{C,P}$ = 10.5 Hz, 1C, C_5H_3), 70.8 (5C, C_5H_5), 73.9 (d, $J_{C,P}$ = 13.1 Hz, 1C, C_5H_3), 73.8 (d, $^1J_{C,P}$ = 95.6 Hz, 1C, C_{C5H3}–P), 74.1 (d, $J_{C,P}$ = 9.9 Hz, 1C, C_5H_3), 93.4 (d, $^2J_{C,P}$ = 12.5 Hz, 1C, C_{C5H3}–C), 119.2 (1C, C_6H_4), 122.8 (1C, C_6H_4), 126.6 (1C, C_6H_4), 127.9 (d, $J_{C,P}$ = 12.4 Hz, 2C, C_6H_5), 128.0 (d, $J_{C,P}$ = 12.5 Hz, 2C, C_6H_5), 130.6 (1C, C_6H_4), 130.9 (d, $^4J_{C,P}$ = 2.9 Hz, 1C, 4-C_6H_5), 131.0 (d, $^4J_{C,P}$ = 3.0 Hz, 1C, 4-C_6H_5), 131.9 (d, $J_{C,P}$ = 10.2 Hz, 2C, C_6H_5), 132.0 (d, $J_{C,P}$ = 10.0 Hz, 2C, C_6H_5), 133.8 (d, $^1J_{C,P}$ = 85.9 Hz, 1C, 1-C_6H_5), 134.1 (d, $^1J_{C,P}$ = 86.2 Hz, 1C, 1-C_6H_5), 135.4 (1C, C_{C6H4}–C), 152.6 (1C, C–N) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 41.9 ppm. IR data (KBr, $\tilde{\nu}$ =): 3091, 3068, 2924, 2855, 1591, 1461, 1309, 1145, 1105, 1034, 945, 824, 765, 747, 692, 660, 545, 506 cm^{-1}. HRMS (ESI-TOF, *m/z*): calcd. for $C_{31}H_{30}FeNPS$ 536.1259, found 536.1302 $[M]^+$.

Crystal Data for o-(S_p)-**5**: $C_{31}H_{30}FeNPS$, *M* = 535.44 g mol^{-1}, monoclinic, $P2_1$, λ = 1.54184 Å, *a* = 9.9736(12) Å, *b* = 12.5762(14) Å, *c* = 11.1041(12) Å, β = 107.584(13) °, *V* = 1327.7(3) $Å^3$, *Z* = 2, ρ_{calcd} = 1.339 Mg m^{-3}, μ = 6.000 mm^{-1}, *T* = 120 K, θ range 4.177–64.490°, 4958 reflections collected, 3096 independent reflections (R_{int} = 0.0641), R_1 = 0.0548, wR_2 = 0.1211 [$I > 2\sigma(I)$], absolute structure parameter[38] 0.006(9).

Synthesis of 2-((4-(diphenylamino)phenyl)methyl)-1-(thiodiphenyl-phosphino)-ferrocene p-(S_p)-7

Compound (S_p)-**1a** (600 mg, 1.40 mmol), *p*TsOH (1.58 g, 8.4 mmol) and triphenylamine (1.72 g, 7.0 mmol) were reacted according to *GP1*. Purification was realized by column chromatography (silica, 4 × 14 cm) using a 5:1 hexane/ethyl acetate mixture (v/v) as the eluent, which gave o-(S_p)-**5** followed by (S_p,S_p)-**12** (126 mg, 0.438 mmol, 31 % based on (S_p)-**1a**) always containing traces (< 5 %) of *p*-(S_p)-**5** in a *non*-separable mixture. Removal of all volatiles in vacuo gave (S_p)-**6** as orange solid.

Yield: 357 mg (0.54 mmol, 39 % based on (S_p)-**1a**). Anal. Calcd for $C_{41}H_{34}FeNPS$ •[1]/2 EtOAc (659.60 •1/2 88.11 g/mol): C, 73.40; H, 5.44;

N, 1.99; found C, 73.50; H, 5.38; N, 2.17. Mp: 215 °C. ^{1}H NMR ($CDCl_3$, δ): 3.69 (dd, J = 2.2, 3.7 Hz, 1H, C_5H_3), 3.81 (d, $^2J_{H,H}$ = 15.1 Hz, 1H, CH_2), 4.26 (dd, J = 2.5, 4.1 Hz, 1H, C_5H_3), 4.33 (s, 5H, C_5H_5), 4.48 (d, $^2J_{H,H}$ = 15.1 Hz, 1H, CH_2), 4.41 (m, $J_{H,H}$ = 1.8, 3.7 Hz, 1H, C_5H_3), 6.74 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, H2-C_6H_4), 6.92 (d, $^3J_{H,H}$ = 8.5 Hz, 2H, H3-C_6H_4), 6.95–6.98 (m, 6H, C_6H_5), 7.19–7.25 (m, 6H, C_6H_5), 7.33–7.37 (m, 1H, C_6H_5), 7.44–7.52 (m, 5H, C_6H_5), 7.77–7.82 (m, 2H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 33.5 (CH_2), 68.9 (d, $^3J_{P,C}$ = 10.5 Hz, C_5H_3), 70.9 (C_5H_5), 73.7 (d, $^1J_{P,C}$ = 90.1 Hz, C_{C5H3}–P), 74.1 (d, $^3J_{P,C}$ = 9.8 Hz, C_5H_3), 74.5 (d, $^2J_{P,C}$ = 12.9 Hz, C_5H_3), 93.0 (d, $^2J_{P,C}$ = 12.6 Hz, C_{C5H3}–C), 122.4 (*p*-C_6H_5N, 2C), 123.8 (*o*-C_6H_5N, 4C), 124.3 (C2-C_6H_4, 2C), 128.0 (d, $^3J_{C,P}$ = 3.9 Hz, *m*-C_6H_5, 2C), 128.1 (d, $^3J_{C,P}$ = 3.7 Hz, *m*-C_6H_5, 2C), 129.2 (*m*-C_6H_5N, 4C), 129.7 (C3-C_6H_4, 2C), 131.1 (d, $^4J_{C,P}$ = 2.9 Hz, *p*-C_6H_5), 131.3 (d, $^4J_{C,P}$ = 2.9 Hz, *p*-C_6H_5), 132.1 (d, $^2J_{C,P}$ = 8.5 Hz, *o*-C_6H_5, 2C), 132.2 (d, $^2J_{C,P}$ = 8.7 Hz, *o*-C_6H_5, 2C), 133.8 (d, $^1J_{C,P}$ = 79.8 Hz, ^{q}C_6H_5), 134.4 (d, $^1J_{C,P}$ = 80.4 Hz, ^{q}C_6H_5), 135.7 (^{q}C_6H_4–C), 145.3 (^{q}C_6H_4–N), 148.0 (^{q}C_6H_5N, 2C) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 41.8 ppm. IR data (KBr, $\tilde{\nu}$ =): 3075, 3052, 3033, 2961, 2922, 2851, 1589, 1505, 1492, 1435, 1326, 1269, 1176, 1142, 1100, 1074, 813, 766, 693, 658, 642, 614, 546 cm^{-1}. HRMS (ESI-TOF, m/z): calcd. for $C_{41}H_{34}FeNPS$ 659.1494, found 659.1496 $[M]^+$.

Crystal Data for *p*-(S_p)-**7**: $C_{41}H_{34}FeNPS$, M = 659.57 g mol^{-1}, orthorhombic, $P2_12_12_1$, λ = 1.54184 Å, a = 9.664(5) Å, b = 10.122(5) Å, c = 32.681(5) Å, V = 3197(2) Å^3, Z = 4, ρ_{calcd} = 1.370 Mg m^{-3}, μ = 5.096 mm^{-1}, T = 100 K, θ range 2.704–65.438°, 10704 reflections collected, 4882 independent reflections (R_{int} = 0.0396), R_1 = 0.0321, wR_2 = 0.0720 [$I > 2\sigma(I)$], absolute structure parameter[38] 0.034(5).

Reaction of (S_p)-1a with phenol

Compound (S_p)-**1a** (600 mg, 1.40 mmol), *p*TsOH (792 mg, 4.2 mmol) and phenol (395 mg, 4.2 mmol) were reacted according to *GP1*. Purification was realized by column chromatography (silica, 4 × 20 cm) using a 1:5 hexane/dichloromethane mixture (v/v) as the eluent. The first fraction contained *o*-(S_p)-**8**[13] (391 mg, 0.768 mmol, 55 % based on (S_p)-**1a**), the second one (S_p,S_p)-**9**.

(S_p)-2-((2-Hydroxyphenyl)methyl)-1-(thiodiphenylphosphino)-ferrocene o-(S_p)-8

Yield: 391 mg (0.768 mmol, 55 % based on (S_p)-**1a**). Spectroscopic data are in agreement with those reported in reference 13.

Crystal Data for o-(S_p)-**8**: $C_{29}H_{25}FeOPS$, M = 508.37 g mol^{-1}, orthorhombic, $P2_12_12_1$, λ = 1.54184 Å, a = 10.0767(9) Å, b = 11.2024(10) Å, c = 20.4504(19) Å, V = 2308.5(4) Å^3, Z = 4, ρ_{calcd} = 1.463 Mg m^{-3}, μ = 6.892 mm^{-1}, T = 119.95(10) K, θ range 4.324–64.463°, 7582 reflections collected, 3611 independent reflections (R_{int} = 0.0386), R_1 = 0.0397, wR_2 = 0.0989 [$I > 2\sigma(I)$], absolute structure parameter[38] –0.018(5).

(S_p,S_p)-2,4-Bis((2-(thiodiphenylphosphino)ferrocene-1-yl)methyl)phenol (S_p,S_p)-9

Yield: 101 mg (0.212 mmol, 15 % based on (S_p)-**1a**). Orange solid. Anal. Calcd for $C_{54}H_{48}Fe_2OP_2S_2 \cdot 5/6\ C_6H_{14}$ (950.73 ·5/6 86.18 g/mol): C, 69.30; H, 5.88; found C, 69.04; H, 6.08. Mp: 138–141 °C. ^{1}H NMR ($CDCl_3$, δ): 3.36 (d, $^2J_{H,H}$ = 15.4 Hz, 1H, *o*-CH_2), 3.60–3.63 (m, 2H, C_5H_3), 3.65 (d, $^2J_{H,H}$ = 15.4 Hz, 1H, *o*-CH_2), 3.82 (d, $^2J_{H,H}$ = 15.1 Hz, 1H, *p*-CH_2), 4.06 (d, $^2J_{H,H}$ = 15.1 Hz, 1H, *p*-CH_2), 4.18 (s, 5H, C_5H_5), 4.20–4.21 (m, 1H, (*o*-)C_5H_3), 4.25–4.27 (m, 1H, (*p*-)C_5H_3), 4.32 (s, 5H, C_5H_5), 4.35–4.37 (m, 1H, (*o*-)C_5H_3), 4.40–4.42 (m, 1H, (*p*-)C_5H_3), 6.42 (d, $^3J_{H,H}$ = 8.2 Hz, 1H, H6-C_6H_3), 6.67 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.1 Hz, 1H, H5-C_6H_3), 6.73 (s, 1H, OH), 6.76 (d, $^4J_{H,H}$ = 2.1 Hz, 1H, H3-C_6H_3), 7.12 (td, $^3J_{H,H}$ = 7.8 Hz, J = 3.0 Hz, 2H, C_6H_5), 7.23–7.28 (m, 2H, C_6H_5), 7.35–7.55 (m, 12H, C_6H_5), 7.75–7.80 (m, 4H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 27.2 (*o*-CH_2), 33.4 (*p*-CH_2), 68.7 (d, $J_{C,P}$ = 10.5 Hz, C_5H_3), 69.2 (d, $J_{C,P}$ = 10.6 Hz, C_5H_3), 70.8 (5C, C_5H_5), 70.9 (5C, C_5H_5), 73.20 (d, $J_{C,P}$ = 9.8 Hz, C_5H_3), 73.27 (d, $^1J_{C,P}$ = 96.0 Hz, C_{C5H3}–P), 73.29 (d, $^1J_{C,P}$ = 95.7 Hz, C_{C5H3}–P), 73.6 (d, $J_{C,P}$ = 9.3 Hz, C_5H_3), 73.8 (d, $J_{C,P}$ = 13.1 Hz, C_5H_3), 74.5 (d, $J_{C,P}$ = 13.0 Hz, C_5H_3), 92.7 (d, $^2J_{C,P}$ = 12.8 Hz, C_{C5H3}–(*o*-)CH_2), 94.2 (d, $^2J_{C,P}$ = 12.6 Hz, C_{C5H3}–(*p*-)CH_2), 116.5 (C6-C_6H_3), 125.5 (C2-C_6H_3), 128.06 (d, $^3J_{C,P}$ = 12.4 Hz, C3/5-C_6H_5), 128.11 (d, $^3J_{C,P}$ = 12.3 Hz, C3/5-C_6H_5), 128.21 (d, $^3J_{C,P}$ = 12.3 Hz, C3/5-C_6H_5), 128.23 (C5-C_6H_3), 128.3 (d, $^3J_{C,P}$ = 12.1 Hz, C3/5-C_6H_5), 131.0 (d, $^4J_{C,P}$ = 2.8 Hz, C4-C_6H_5), 131.15 (C3-C_6H_3), 131.25 (d, $^4J_{C,P}$ = 2.8 Hz, C4-C_6H_5), 131.4 (d, $^4J_{C,P}$ = 2.8 Hz, C4-C_6H_5), 131.6 (d, $^4J_{C,P}$ = 2.8 Hz, C4-C_6H_5), 131.84 (d, $^4J_{C,P}$ = 10.6 Hz, 2C, C2/6-C_6H_5), 131.86 (d, $^4J_{C,P}$ = 10.7 Hz, 2C, C2/6-C_6H_5), 132.1 (d, $^4J_{C,P}$ = 9.9 Hz, 2C, C2/6-C_6H_5), 132.2 (d, $^4J_{C,P}$ = 10.4 Hz, 2C, C2/6-C_6H_5), 132.4 (d, $^1J_{C,P}$ = 86.9 Hz, ^{q}C_6H_5), 133.68 (d, $^1J_{C,P}$ = 86.5 Hz, ^{q}C_6H_5), 133.73 (d, $^1J_{C,P}$ = 85.8 Hz, ^{q}C_6H_5), 134.35 (d, $^1J_{C,P}$ = 86.6 Hz, ^{q}C_6H_5), 152.1 (C–OH) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 42.3, 42.7 ppm. IR data (KBr, $\tilde{\nu}$ =): 3378 (OH), 3075, 3053, 2951, 2924, 2853, 1500, 1480, 1436, 1101, 1040, 999, 821, 749, 712 ($\nu_{P=S}$), 692, 651, 541 cm^{-1}.

(S_p)-2-(Phenylthiomethyl)-1-(thiodiphenylphosphino)-ferrocene (S_p)-13

Compound (S_p)-**1a** (600 mg, 1.40 mmol), *p*TsOH (792 mg, 4.2 mmol) and thiophenol (0.43 mL, 4.2 mmol) were reacted according to *GP1*. Purification was realized by column chromatography (silica, 4 × 16 cm) using a 6:1 hexane/ethyl acetate mixture (v/v) as the eluent. Removal of all volatiles in vacuo gave (S_p)-**6** as an orange solid. The analytical data are in agreement with those reported in literature.[14]

Yield: 605 mg (1.15 mmol, 83 % based on (S_p)-**1a**). Anal. Calcd for $C_{29}H_{25}FePS_2$ (524.46 g/mol): C, 66.41; H, 4.80; found C, 66.01; H, 4.79. Mp: 150–153 °C. ^{1}H NMR ($CDCl_3$, δ): 3.78 (dd, J = 3.8, 2.3 Hz, 1H, C_5H_3), 4.26 (dd, J = 4.1, 2.5 Hz, 1H, C_5H_3), 4.32 (s, 5H, C_5H_5), 4.32 (d, $^2J_{H,H}$ = 13.6 Hz, 1H, CH_2), 4.39 (d, $^2J_{H,H}$ = 13.7 Hz, 1H, CH_2), 4.48–4.49 (m, 1H, C_5H_3), 7.12–7.16 (m, 1H, Ph), 7.20–7.24 (m, 4H, Ph), 7.37–7.41 (m, 2H, Ph), 7.45–7.50 (m, 3H, Ph), 7.50–7.54 (m, 1H, Ph), 7.64–7.68 (m, 2H, (P)Ph), 7.80–7.84 (m, 2H, (P)Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 32.9 (1C, CH_2), 69.1 (d, $J_{C,P}$ = 10.4 Hz, 1C, C_5H_3), 71.0 (s, 5C, C_5H_5), 73.7 (d, $J_{C,P}$ = 9.1 Hz, 1C, C_5H_3), 74.1 (d, $^1J_{C,P}$ = 95.2 Hz, 1C, C_{C5H3}–P), 74.6 (d, $J_{C,P}$ = 12.4 Hz, 1C, C_5H_3), 89.0 (d, $^2J_{C,P}$ = 11.9 Hz, 1C, C_{C5H3}–C), 126.0 (1C, 4-(S)Ph), 128.1 (d, $J_{C,P}$ = 12.4 Hz, 2C, (P)Ph), 128.3 (d, $J_{C,P}$ = 12.5 Hz, 2C, (P)Ph), 128.7 (2C, (S)Ph), 129.7 (2C, (S)Ph), 131.31–131.35 (m, 2C, 4-(P)Ph), 132.12 (d, $J_{C,P}$ = 10.7 Hz, 2C, (P)Ph), 132.13 (d, $J_{C,P}$ = 10.8 Hz, 2C, (P)Ph), 133.5 (d, $^1J_{C,P}$ = 86.2 Hz, 1C, ^{q}(P)Ph), 134.5 (d, $^1J_{C,P}$ = 87.2 Hz, 1C, ^{q}(P)Ph), 136.9 (1C, ^{q}(S)Ph) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 41.5 ppm. IR data (KBr, $\tilde{\nu}$ =): 3072, 3042, 2922, 2854, 1479, 1434, 1237, 1099, 1044, 1026, 998, 822, 743, 715 (P=S), 694, 648, 546, 515 cm^{-1}. HRMS (ESI-TOF, m/z): calcd. for $C_{29}H_{25}FePS_2$ 524.0480, found 524.0491 $[M]^+$.

Crystal Data for (S_p)-**13**: $C_{29}H_{25}FePS_2$, M = 524.43 g mol^{-1}, orthorhombic, $P2_12_12_1$, λ = 1.54184 Å, a = 9.5219(11) Å, b = 14.9476(17) Å, c = 17.7190(19) Å, V = 2521.9(5) Å^3, Z = 4, ρ_{calcd} = 1.381 Mg m^{-3}, μ = 7.049 mm^{-1}, T = 300 K, θ range 3.869–65.465°, 43520 reflections collected, 4203 independent reflections (R_{int} = 0.0437), R_1 = 0.0275, wR_2 = 0.0687 [$I > 2\sigma(I)$], absolute structure parameter[38] 0.033(5).

rac-2-(Hydroxymethyl)-1-(selanyldiphenylphosphino)-ferrocene rac-1c

rac-1-(Diphenylphosphino)-2-(hydroxymethyl)ferrocene *rac*-**10** (400 mg, 1 mmol) and selenium (240 mg, 3 mmol) were suspended in 50 mL of degassed dichloromethane and stirred for 18 h at 25 °C.

The excess of Se was removed by filtration thru silica by using dichloromethane as the eluent. After removal of all volatiles, (S_p)-**1c** was obtained as an orange solid.

Yield: 478 mg (1 mmol, 99 % based on *rac*-**10**). Anal. Calcd for $C_{23}H_{21}FeOPSe$ (479.18 g/mol): C, 57.65; H, 4.42; found C, 58.06; H, 4.34. Mp: 187–190 °C. ^{1}H NMR ($CDCl_3$, δ): 3.23 (dd, $^2J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 6.5 Hz, 1H, CH_2), 3.74–3.76 (m, 1H, C_5H_3), 4.30–4.33 (m, 2H, C_5H_3, OH), 4.33 (s, 5H, C_5H_5), 4.60–4.61 (m, 1H, C_5H_3), 4.80 (dd, $^3J_{H,H}$ = 12.9 Hz, $^2J_{H,H}$ = 8.3 Hz, 1H, CH_2), 7.35–7.39 (m, 2H, C_6H_5), 7.42–7.46 (m, 1H, C_6H_5), 7.47–7.51 (m, 2H, C_6H_5), 7.52–7.58 (m, 3H, C_6H_5), 7.82–7.86 (m, 2H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 58.4 (CH_2), 69.0 (d, $J_{C,P}$ = 9.8 Hz, C_5H_3), 70.7 (5C, C_5H_5), 73.1 (d, $^1J_{C,P}$ = 86.2 Hz, C_{C5H3}–P), 74.8 (d, $J_{C,P}$ = 11.0 Hz, C_5H_3), 75.2 (d, $J_{C,P}$ = 9.8 Hz, C_5H_3), 93.5 (d, $^2J_{C,P}$ = 13.1 Hz, C_{C5H3}–C), 128.3 (d, $^2J_{C,P}$ = 12.5 Hz, *o*-C_6H_5), 128.6 (d, $^2J_{C,P}$ = 12.6 Hz, *o*-C_6H_5), 131.56 (d, $^4J_{C,P}$ = 3.0 Hz, *p*-C_6H_5), 131.65 (d, $^1J_{C,P}$ = 77.8 Hz, ^{q}C_6H_5), 131.8 (d, $^4J_{C,P}$ = 3.1 Hz, *p*-C_6H_5), 132.1 (d, $^3J_{C,P}$ = 10.9 Hz, *m*-C_6H_5), 132.8 (d, $^3J_{C,P}$ = 11.1 Hz, *m*-C_6H_5), 134.2 (d, $^1J_{C,P}$ = 79.0 Hz, ^{q}C_6H_5) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 30.0 ($^1J_{31P,77Se}$ = 709.0 Hz) ppm. ^{77}Se {^{1}H} NMR ($CDCl_3$, δ): –254.6 (d, $^1J_{C,P}$ = 709.0 Hz) ppm. IR data (KBr, $\tilde{\nu}$ =): 3448 (OH), 3078, 3046, 2942, 2922, 2861, 1478, 1435, 1356, 1308, 1242, 1182, 1099, 993, 932, 830, 755, 694, 629, 569, 542cm^{-1}.

Crystal Data for *rac*-**1c**: $C_{23}H_{21}FeOPSe$, M = 479.18 g mol^{-1}, monoclinic, $P2_1/c$, λ = 1.54184 Å, a = 8.674(5) Å, b = 17.656(5) Å, c = 13.345(5) Å, β = 104.990(5) °, V = 1974.2(15) Å^3, Z = 4, ρ_{calcd} = 1.612 Mg m^{-3}, μ = 9.070 mm^{-1}, T = 100 K, θ range 4.246–65.997°, 13895 reflections collected, 3411 independent reflections (R_{int} = 0.1082), R_1 = 0.0849, wR_2 = 0.1899 [$I > 2\sigma(I)$].

rac-2-((2,4-Dinitrophenyl)selenylmethyl)-1-(selanyldiphenylphos-phino)-ferrocene rac-19

Compound *rac*-**1c** (160 mg, 0.334 mmol), 1-fluoro-2,4-dinitrobenzene (207 mg, 1.115 mmol) and K_2CO_3 (260 mg, 1.86 mmol) were dissolved in 20 mL of DMF, whereby the color immediately darkened from orange to black. 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 × 50 mL) all organic extracts were combined and dried with $MgSO_4$ followed by removal of all volatiles in vacuo. Purification was realized by column chromatography (silica, 2.5 × 18 cm column size) using a 9:1 hexane/dichloromethane mixture (*v*/*v*) as the eluent for a first fraction, containing *rac*-**19**, 1-fluoro-2,4-dinitrobenzene and 2,4-dinitrophenol. The eluent was changed to a 4:1 dichloromethane/ethyl acetate mixture for *rac*-**1c** (70 mg, 0.144 mmol, 43 % based on *rac*-**1c**) and a 9:1 ethyl acetate/methanol mixture for eluting *rac*-**1b** (35 mg, 0.083 mmol, 44 % based on reacted *rac*-**1c**, ESI). After removal of all volatiles of the first fraction a solid material was obtained, which was treated with boiling hexane (3 × 50 mL) to remove the further excess of both 2,4-dinitroarenes. After removal of the boiling hexane layer, compound *rac*-**19** was obtained as a purple solid.

Yield: 67 mg (0.093 mmol, 56 % based on used *rac*-**1c** and 98 % based on reacted *rac*-**1c**). Anal. Calcd for $C_{29}H_{23}FeN_2O_4PSe_2$ (708.23 g/mol): C, 49.18; H, 3.27; N, 3.96; found C, 48.96; H, 3.20; N, 4.00. Mp: 245 °C (rapid decomp.). ^{1}H NMR ($CDCl_3$, δ): 3.80–3.82 (m, 1H, C_5H_3), 4.37 (d, $^2J_{H,H}$ = 11.3 Hz, 1H, CH_2), 4.37–4.39 (m, 1H, C_5H_3), 4.42 (s, 5H, C_5H_5), 4.64–4.65 (m, 1H, C_5H_3), 5.19 (d, $^2J_{H,H}$ = 11.3 Hz, 1H, CH_2), 7.27–7.31 (m, 2H, C_6H_5), 7.38–7.42 (m, 1H, C_6H_5), 7.46–7.58 (m, 5H, C_6H_5), 7.79 (d, $^3J_{H,H}$ 8.9 Hz, 1H, C_6H_3), 7.79–7.84 (m, 2H, C_6H_5), 8.22 (dd, $^3J_{H,H}$ = 8.9, $^4J_{H,H}$ = 2.5 Hz, 1H, C_6H_3), 8.22 (d, $^4J_{H,H}$ = 2.5 Hz, 1H, C_6H_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 26.2 (1C, CH_2), 69.7 (d, $J_{C,P}$ = 9.5 Hz, 1C, C_5H_3), 71.6 (5C, C_5H_5), 73.3 (d, $^1J_{C,P}$ = 85.3 Hz, 1C, C_{C5H3}–P), 74.6 (d, $J_{C,P}$ = 8.8 Hz, 1C, C_5H_3), 75.2 (d, $J_{C,P}$ = 10.6 Hz, 1C, C_5H_3), 86.6 (d, $^2J_{C,P}$ = 12.7 Hz, 1C, C_{C5H3}–C), 121.5 (1C, C_6H_3), 126.8 (1C1, C_6H_3), 128.33 (d, $^4J_{C,P}$ = 12.5 Hz, 1C, *o*-C_6H_5), 128.35 (d, $^4J_{C,P}$ = 12.5 Hz, 1C, *o*-C_6H_5), 130.9 (1C, C_6H_3), 131.7 (d, $^1J_{C,P}$ = 77.7 Hz, 1C, 1-C_6H_5), 131.74–131.78 (m, 4C, *p*-C_6H_5), 132.6 (d, $^2J_{C,P}$ = 10.7 Hz, 2C, C_6H_5), 132.7 (d, $^2J_{C,P}$ = 11.0 Hz, 2C, C_6H_5), 133.0 (d, $^1J_{C,P}$ = 78.5 Hz, 1C, 1-C_6H_5), 144.7 (1C, C_6H_3–NO_2), 144.8 (1C, C_6H_3–NO_2), 145.4 (1C, C_{C6H3}–Se) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): 29.8 ($J_{31P,77Se}$ = 727.4 Hz) ppm. ^{77}Se{^{1}H} NMR ($CDCl_3$, δ): –261.3 (d, $^1J_{Se,P}$ = 727.4 Hz, P=Se), 438.0 (Se–CH_2) ppm. IR data (KBr, $\tilde{\nu}$ =): 3104, 3072, 2932, 2851, 1590 (NO_2), 1508, 1437, 1342 (NO_2), 1298, 1098, 1040, 916, 822, 695, 560, 538 cm^{-1}.

Crystal Data for *rac*-**19**: $C_{29}H_{23}FeN_2O_4PSe_2$, M = 708.23 g mol^{-1}, triclinic, $P\bar{1}$, λ = 0.71073 Å, a = 9.1387(9) Å, b = 10.7598(11) Å, c = 13.8989(15) Å, α = 80.958(9), β = 83.840(8), γ = 77.922(9) °, V = 1315.9(2) Å^3, Z = 2, ρ_{calcd} = 1.787 Mg m^{-3}, μ = 3.441 mm^{-1}, T = 125(1) K, θ range 2.860–24.997°, 17128 reflections collected, 4623 independent reflections (R_{int} = 0.0813), R_1 = 0.0439, wR_2 = 0.0675 [$I > 2\sigma(I)$].

General procedure for the reduction of phosphine sulfides into phosphines (GP2)

The respective thiodiphenylphospines (S_p)-**2,5,8** and **12** were dissolved in 50 mL of chlorobenzene followed by the dropwise addition of $P(NMe_2)_3$ (10 equiv). The reaction mixture was heated for 18 h to 130 °C and was then cooled to ambient temperature. Water (10 mL) was carefully added. This mixture was poured into water (200 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic extracts were dried with $MgSO_4$ followed by removal of all volatiles in vacuo. Purification was realized by column chromatography on silica (column size see below) using various eluent mixtures followed by evaporation of all volatiles in vacuo for each fraction.

(S_p)-2-(N-Phenylaminomethyl)-1-(diphenylphosphino)-ferrocene (S_p)-2a

Compound (S_p)-**2** (155 mg, 0.30 mmol) and $P(NMe_2)_3$ (0.92 mL, 3.0 mmol) were reacted according to *GP2*. Purification was realized by column chromatography (silica, 4 × 12 cm) using a 1:2 hexane/dichloromethane (v/v) mixture as the eluent. Removal of all volatiles in vacuo gave (S_p)-**2a** as an orange solid.

Yield: 110 mg (0.23 mmol, 76 % based on (S_p)-**2**). Anal. Calcd for $C_{29}H_{26}FeNP$ (475.35 g/mol): C, 73.28; H, 5.51; N, 2.95; found C, 73.30; H, 6.40; N, 2.51 (best match). Mp: 140 °C. ^{1}H NMR ($CDCl_3$, δ): 3.47 (s, 1H, NH), 3.72–3.74 (m, 1H, C_5H_3), 4.10–4.12 (s, 6H, C_5H_5, CH_2), 4.17 (dd, $^2J_{H,H}$ = 13.3, J = 1.7 Hz, 1H, CH_2), 4.26–4.27 (m, 1H, C_5H_3), 4.51–4.52 (m, 1H, C_5H_3), 6.35–6.37 (m, 2H, H2-C_6H_5N), 6.64–6.67 (m, 1H, H4-C_6H_5N), 7.08–7.12 (m, 2H, H3-C_6H_5N), 7.19–7.22 (m, 2H, C_6H_5), 7.27–7.30 (m, 3H, C_6H_5), 7.38–7.40 (m, 3H, C_6H_5), 7.51–7.55 (m, 2H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 42.6 (d, $^3J_{C,P}$ = 10.0 Hz, CH_2), 69.3 (C_5H_3), 69.8 (5C, C_5H_5), 71.5 (d, $J_{P,C}$ = 3.8 Hz, C_5H_3), 72.0 (d, $J_{P,C}$ = 3.6 Hz, C_5H_3), 76.6 (d, $^1J_{P,C}$ = 7.2 Hz, C_{C5H3}–P), 90.9 (d, $^2J_{P,C}$ = 23.6 Hz, C_{C5H3}–C), 113.1 (2C, C2-C_6H_5N), 117.4 (C4-C_6H_5N), 128.3 (d, $^3J_{P,C}$ = 7.6 Hz, 2C, C3/5-C_6H_5), 128.5 (d, $^3J_{P,C}$ = 6.3 Hz, 2C, C3/5-C_6H_5), 128.6 (C4-C_6H_5), 129.1 (2C, C3-C_6H_5N), 129.3 (C4-C_6H_5), 132.8 (d, $^2J_{P,C}$ = 18.8 Hz, C2/4-C_6H_5), 134.8 (d, $^2J_{P,C}$ = 20.62 Hz, C2/4-C_6H_5), 137.0 (d, $^1J_{P,C}$ = 9.0 Hz,^{q}C_6H_5), 139.6 (d, $^1J_{P,C}$ = 10.3 Hz, ^{q}C_6H_5), 147.9 (C1-C_6H_5N) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –23.7 ppm. IR data (KBr, $\tilde{\nu}$ =): 3390 (NH), 3068, 3046, 3020, 2955, 2925, 2854, 1602, 1505, 1431, 1310, 1106, 997, 818, 748, 703, 690 cm^{-1}. HRMS (ESI-TOF, *m*/*z*): calcd. for $C_{29}H_{26}FeNP$ 474.1069, found 474.1082 [M]$^+$.

(S_p)-2-((2-(N,N-Dimethylamino)phenyl)methyl)-1-(diphenylphosphino)-ferrocene o-(S_p)-5a

Compound *o*-(S_p)-**5** (171 mg, 0.32 mmol) and $P(NMe_2)_3$ (0.98 mL, 3.2 mmol) were reacted according to *GP2*. Purification was realized by column chromatography (silica, 2.5 × 16 cm) using dichloromethane as the eluent. Removal of all volatiles in vacuo gave *o*-(S_p)-**5a** as a yellow solid.

Yield: 110 mg (0.22 mmol, 68 % based on *o*-(S_p)-**5**). Anal. Calcd for $C_{31}H_{30}FeNP{\cdot}C_5H_{10}$ (503.40•70.13 g/mol): C, 75.13; H, 7.36; N, 2.43; found C, 74.87; H, 7.79; N, 2.16. Mp: 79 °C. ^{1}H NMR ($CDCl_3$, δ): 2.60 (s, 6H, CH_3), 3.72–3.73 (m, 1H, C_5H_3), 3.90 (d, $^2J_{H,H}$ = 15.6 Hz, 1H, CH_2), 4.07 (s, 5H, C_5H_5), 3.09 (d, $^2J_{H,H}$ = 15.6 Hz, $^4J_{H,P}$ = 2.1 Hz, 1H, CH_2), 4.23 (dd, *J* = 2.4, 2.4 Hz, 1H, C_5H_3), 4.37 (dd, *J* = 3.5, 2.0 Hz, 1H, C_5H_3), 6.76 (td, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.2 Hz, 1H, C_6H_4), 6.91 (dd, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.0 Hz, 1H, C_6H_4), 6.98–7.01 (m, 2H, C_6H_4), 7.03–7.15 (m, 5H, C_6H_5), 7.38–7.39 (m, 3H, C_6H_5), 7.56–7.60 (m, 2H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 29.4 (d, $^3J_{C,P}$ = 10.3 Hz, 1C, CH_2), 44.9 (2C, CH_3), 68.7 (1C, C_5H_3), 69.8 (5C, C_5H_5), 70.8 (d, $J_{C,P}$ = 4.0 Hz, 1C, C_5H_3), 72.4 (d, $J_{C,P}$ = 4.0 Hz, 1C, C_5H_3), 75.5 (d, $^1J_{C,P}$ = 6.4 Hz, 1C, C_{C5H3}–P), 94.1 (d, $^1J_{C,P}$ = 26.0 Hz, 1C, C_{C5H3}–C), 118.8 (1C, C_6H_4), 122.7 (1C, C_6H_4), 126.4 (1C, C_6H_4), 127.4 (1C, C_6H_5), 127.7 (d, $J_{C,P}$ = 6.2 Hz, 2C, C_6H_5), 128.0 (d, $J_{C,P}$ = 7.7 Hz, 2C, C_6H_5), 128.9 (1C, C_6H_5), 130.0 (1C, C_6H_4), 132.4 (d, $J_{C,P}$ = 18.4 Hz, 2C, C_6H_5), 135.0 (d, $J_{C,P}$ = 20.9 Hz, 2C, C_6H_5), 135.6 (1C, C_{C6H4}–C), 137.9 (d, $J_{C,P}$ = 8.8 Hz, 1C, 1-C_6H_5), 139.3 (d, $J_{C,P}$ = 9.8 Hz, 1C, 1-C_6H_5), 152.2 (1C, C–N) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –22.8 ppm. IR data (KBr, $\tilde{\nu}$ =): 3068, 3053, 2955, 2925, 2854, 2818, 2780, 1452, 1307, 1262, 1182, 1095, 1049, 1001, 947, 816, 742, 697, 570 cm^{-1}. HRMS: $C_{31}H_{30}FeNP$+H calcd: 504.1544, found 504.1537 $[M + H]^+$.

(S_p)-2-((2-Hydroxyphenyl)methyl)-1-(diphenylphosphino)-ferrocene o-(S_p)-8a

Compound *o*-(S_p)-**8** (155 mg, 0.33 mmol) and $P(NMe_2)_3$ (0.98 mL, 3.2 mmol) were reacted according to *GP2*. Purification was realized by column chromatography (silica, 2.5 × 16 cm) using a 1:9 hexane/dichloromethane mixture (v/v) as the eluent. Removal of all volatiles in vacuo gave *o*-(S_p)-**8a** as a yellow solid in a *non*-separable 2:1 mixture together with phenol. (The resonances of phenol are omitted from the data given below but can be found in the SI). Crystallization of the mixture from hexane further purified *o*-(S_p)-**8a**.

Yield: 25 mg (0.05 mmol, 15 % based on *o*-(S_p)-**8**). Anal. Calcd for $C_{29}H_{25}FeOP$ (476.33 g/mol): C, 73.12; H, 5.29; found C, 71.57; H, 6.96 (best match). Mp: 300 °C. ^{1}H NMR ($CDCl_3$, δ): 3.75–3.77 (m, 2H, CH_2), 3.79–3.80 (m, 1H, C_5H_3), 3.88 (s, 5H, C_5H_5) 4.26–4.27 (m, 1H, C_5H_3), 4.43–4.44 (m, 1H, C_5H_3), 5.64 (d, *J* = 2.8 Hz, 1H, OH), 6.69–6.72 (m, 2H, C_6H_4), 6.97–7.05 (m, 4H, C_6H_4, C_6H_5), 7.11–7.18 (m, 3H, C_6H_5), 7.39–7.42 (m, 3H, C_6H_5), 7.60–7.63 (m, 2H, C_6H_5). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 29.8 (d, $^3J_{C,P}$ = 1.8 Hz, CH_2), 69.3 (C_5H_3), 69.9 (5C, C_5H_5), 70.7 (d, $J_{C,P}$ = 4.1 Hz, C_5H_3), 71.7 (d, $^2J_{C,P}$ = 4.5 Hz, C_5H_3), 74.8 (d, $^1J_{C,P}$ = 2.8 Hz, C_{C5H3}–P), 94.2 (d, $^2J_{C,P}$ = 27.9 Hz, C_{C5H3}–C), 116.3 (H3/6-C_6H_4), 120.6 (H3/6-C_6H_4), 127.8 (H4/5-C_6H_4), 127.84 (H4/5-C_6H_4), 127.85 (C_{C6H4}–C), 128.1 (d, $^3J_{C,P}$ = 6.2 Hz, *m*-C_6H_5), 128.3 (d, $^3J_{C,P}$ = 8.3 Hz, *m*-C_6H_5), 129.6 (*p*-C_6H_5), 130.7 (*p*-C_6H_4), 132.1 (d, $^4J_{C,P}$ = 17.3 Hz, *p*-C_6H_5), 135.3 (d, $^4J_{C,P}$ = 20.8 Hz, *p*-C_6H_5), 136.9 (d, $^1J_{C,P}$ = 4.3 Hz, ^{q}C_6H_5), 139.1 (d, $^1J_{C,P}$ = 5.8 Hz, ^{q}C_6H_5), 153.5 (C_{C6H4}-O). ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –22.9.

(S_p)-2-(Phenylthiomethyl)-1-(diphenylphosphino)-ferrocene (S_p)-13a

Compound (S_p)-**13** (200 mg, 0.381 mmol) and $P(NMe_2)_3$ (0.92 mL, 3.0 mmol) were reacted according to *GP2*. Purification was realized by column chromatography (silica, 4 × 12 cm) using a 1:2 hexane/dichloromethane (v/v) mixture as the eluent. Removal of all volatiles in vacuo gave (S_p)-**13a** as an orange solid.

Yield: 187 mg (0.37 mmol, 98 % based on (S_p)-**13**). Anal. Calcd for $C_{29}H_{25}FePS$ (492.39 g/mol): C, 70.74; H, 5.12; found C, 70.92; H, 5.17. Mp: 78–81 °C. ^{1}H NMR ($CDCl_3$, δ): 3.78–3.79 (m, 1H, C_5H_3), 4.02 (s, 5H, C_5H_5), 4.06 (dd, $^2J_{H,H}$ = 13.1 Hz, $^4J_{H,P}$ = 2.2 Hz, 1H, CH_2), 4.14 (d, $^2J_{H,H}$ = 13.1 Hz, 1H, CH_2), 4.26 (t, *J* = 2.4 Hz, 1H, C_5H_3), 4.42 (dd, *J* = 3.7, 1.9 Hz, 1H, C_5H_3), 7.13–7.16 (m, 1H, C_6H_5), 7.17–7.26 (m, 9H, C_6H_5), 7.38–7.40 (m, 3H, C_6H_5), 7.55–7.58 (m, 2H, C_6H_5) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 33.7 (d, $^3J_{C,P}$ = 12.3 Hz, 1C, CH_2), 69.5 (1C, C_5H_3), 69.8 (5C, C_5H_5), 71.3 (d, $J_{C,P}$ = 3.7 Hz, 1C, C_5H_3), 71.5 (d, $J_{C,P}$ = 3.6 Hz, 1C, C_5H_3), 75.9 (d, $^1J_{C,P}$ = 7.8 Hz, 1C, C_{C5H3}–P), 89.8 (d, $^2J_{C,P}$ = 25.5 Hz, 1C, C_{C5H3}–C), 126.0 (1C, 4-Ph), 127.7 (1C, 4-Ph), 127.9 (d, $J_{C,P}$ = 5.9 Hz, 2C, (P)Ph), 128.1 (d, $J_{C,P}$ = 8.0 Hz, 2C, (P)Ph), 128.7 (2C, (S)C_6H_5), 129.1 (1C, 4-Ph), 129.6 (2C, (S)Ph), 132.3 (d, $J_{C,P}$ = 17.7 Hz, 2C, (P)Ph), 135.0 (d, $J_{C,P}$ = 21.2 Hz, (P)Ph), 137.4 (1C, ^{q}Ph-S), 137.4 (d, $^1J_{C,P}$ = 8.2 Hz, 1C, ^{q}Ph-P), 139.7 (d, $^1J_{C,P}$ = 8.9 Hz, 1C, ^{q}Ph-P) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, δ): –24.0 ppm. IR data (KBr, $\tilde{\nu}$ =): 3068, 3048, 2925, 2854, 1478, 1434, 1236, 1106, 1024, 1002, 826, 750, 741, 702, 688, 627 cm^{-1}. HRMS (ESI-TOF, *m*/*z*): calcd. for $C_{29}H_{25}FePS$ 492.0759, found 492.0787 $[M]^+$.

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Keywords: Ferrocene · Planar chirality · C,C Cross-coupling · Phosphine · Chiral biaryls · Selenium atom transfer

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