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# Efficient Asymmetric Synthesis of Planar-Chiral Bisferrocenes

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SAMP auxiliary-derived monosubstituted diferrocenyl ketones have been subjected to *ortho*-metalation/functionalization reactions to prepare chiral disubstituted bisferrocenes. The reactions proceeded in low to moderate yields (20–54 %) and excellent stereoselectivities (97 – ≥99 % *ee*, ≥96 % *de*), however low regio-selectivities were obtained in several cases. Monosubstituted bisferrocenes, containing only a planar-chiral element, were excellent substrates in the same *ortho*-metalation/functionalization reaction affording disubstituted bisferrocenes in moderate to excellent yields (39–99 %) and generally excellent levels of asymmetric induction (≥96 % *de*) with complete regiocontrol. The synthesis of related methylene-bridged mono- and di-substituted diferrocenyl ligands containing *N*-, *O*-, *P*- and/or *S*-donor atoms is also described.



## Introduction

The breadth of asymmetric metal-catalyzed reactions involving chiral ferrocene-based ligands is remarkable, ranging from hydrogenations of alkenes, imines and ketones to allylic alkylations and cycloaddition reactions.[1] 1,2-Disubstituted chiral ferrocenes **A** are most frequently occurring within the structurally-diverse range of ferrocenyl ligands that have been synthesized (e.g. 1-substituted, 1,1′-disubstituted, 1,2-disubstituted, 1,1′,2-trisubstituted, and 1,1′,2,2′-tetrasubstituted ferrocenes, bisferrocenes, polysubstituted ferrocenes, ferrocene-type heterocycles) (Figure 1). Interest in 1,2-disubstituted ferrocenyl ligands **A** is mainly due to: (i) their wide reaction scope and imparted catalytic efficiencies and (ii) their ease preparation. In most cases, ligands **A** are accessible from enantiomerically-pure Ugi amine (X = CH, Y = $NMe_2$) by diastereoselective *ortho*-metalation and trapping of the resulting carbanions with a suitable electrophile ($E^1X$).[2] Subsequent stereospecific unimolecular nucleophilic displacement of the dimethylamino functionality installs an alternate donor atom and occurs with retention of configuration. The sulfoxide method ($X = S^+$, $Y = O^-$) developed by Kagan and co-workers also involves an initial *ortho*-metalation/functionalization reaction yet allows subsequent sulfoxide substitution by an additional electrophile.[3]

Bisferrocenes **B** are interesting members of the ferrocenyl ligand family often displaying $C_2$-symmetry and providing tunable ligand bite angles through variation of the spacer unit (Z). A number of diferrocenyl ligands have been developed including, for example, TRAP ligands **1**,[4] diol **2**,[5] and dichalcogenides **3**[6] as well as the Pigiphos ligands,[7] bis(azaferrocenes),[8] bisPPFOMe,[9] oxazoline- and sulfoxide-disubstituted bisferrocenes[10] and others.[11]

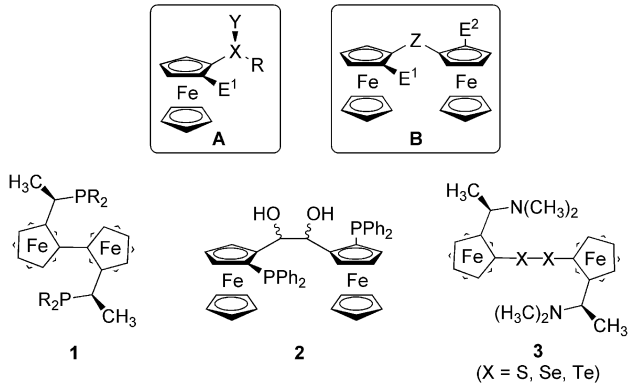


Figure 1. Generalized 1,2-disubstitued ferrocenyl ligands **A** and diferrocenyl ligands **B** with representative examples of ligand-type **B**.

Previous work in our laboratory has been focused on the asymmetric synthesis of chiral ferrocenyl ligands using the SAMP/RAMP-hydrazone methodology and exploring their use in catalytic asymmetric synthesis.[12] More recently this method was extended to bisferrocenes whereby valuable monosubstituted diferrocenyl ketones **6** could be efficiently synthesized.[12j]

We envisioned that this procedure could be further elaborated into a synthesis of disubstituted diferrocenyl ketones **7** (Figure 2). The SAMP-hydazone of diferrocenylmethanone (**4**)[13] would be *ortho*-metalated/funtionalized via route **A** as described previously.[12j] A second auxiliary-directed *ortho*-metalation/functionalization step of the first-formed monosubstituted hydrazone **5** would allow introduction of a second substituent. Auxiliary cleavage would

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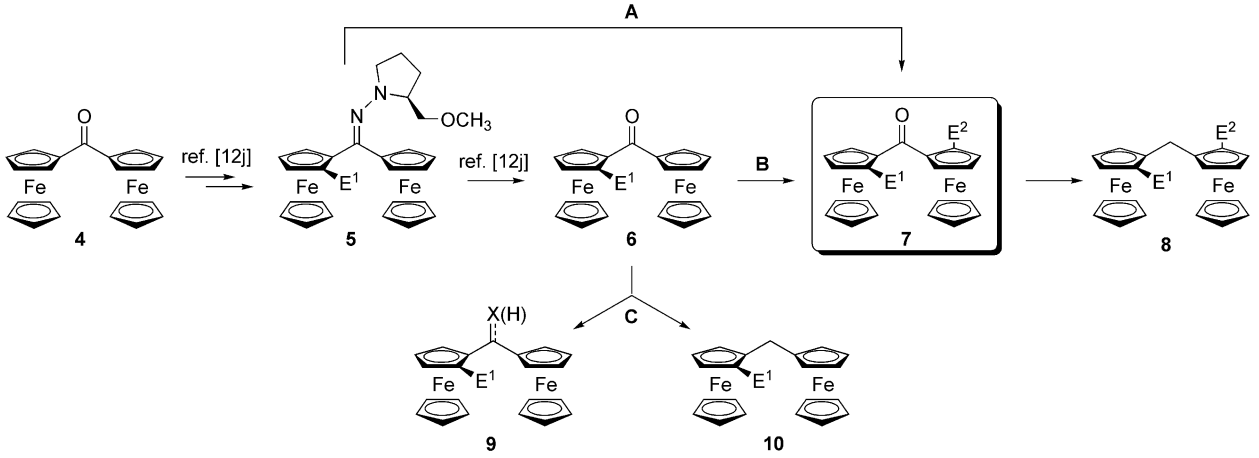
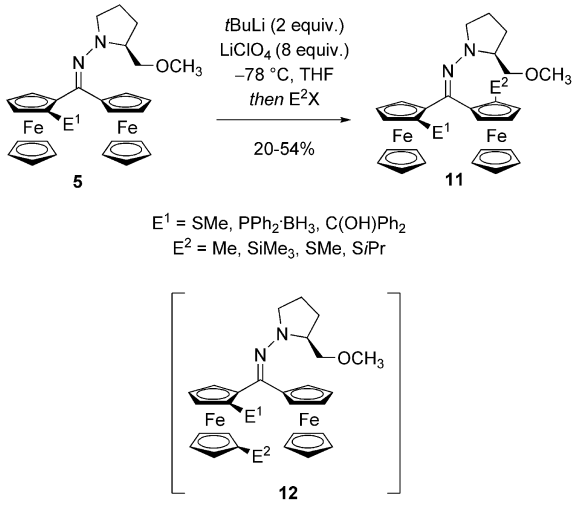



Figure 2. Proposed synthesis of disubstituted diferrocenyl ketones **7** and various ferrocenyl derivatives **8**, **9** and **10**.

then release disubstituted ketone **7**, which represents a chiral bidentate ligand if the two substituents ($E^1$,$E^2$) contain donor atoms. Initial auxiliary cleavage to form monosubstituted ketone **5** would initate route **B**. Next the planar chirality residing in monosubstituted ketone **6** could, in theory, control a substrate-directed *ortho*-metalation/functionalization step to form the same disubstituted ketones **7**. To the best of our knowledge, this would represent the first use of solely planar chirality within a diferrocenyl ligand to direct the formation of another planar chiral element within the structure. Deoxygentation of ketones **7** would then afford pseudo $C_2$-symmetric ligands ($E^1 \neq E^2$) for evaluation in asymmetric catalysis. As an addendum to our work on the asymmetric synthesis of monosubstituted diferrocenyl ketones **6**[12j] we also anticipated that valuable bidentate ligands **9** or monodentate structures **10** could be derived from ketones **6** through simple functional group interconversion (route **C**). Herein we report our investigations towards realizing these goals.




Scheme 1. Auxiliary-directed asymmetric synthesis of disubstituted products **11**.

## Results and Discussion

To test the viability of route A, monosubstituted SAMP-hydrazones **5** were subjected to a directed *ortho*-metalation/electrophile trapping using a variety of bases and solvents (Scheme 1). The reaction proved to depend significantly on the base and solvent employed as well as the resident *ortho*-substituent ($E^1$). For hydrazone **5a** ($E^1$ = STol), *ortho*-metalation using *n*BuLi and MeLi led to no reaction while the use of *t*BuLi (2.0 equiv., THF) and trapping with methyl iodide, as a test electrophile, afforded traces of the desired disubstituted product **11a** ($E^1$ = STol, $E^2$ = Me).

The Lochmann–Schlosser bases, formed in situ from KO*t*Bu and various alkylithiums all led to the formation of complex mixtures of products. Using *t*BuLi and switching to hydrazone **5b** ($E^1$ = SMe) resulted in a slight improvement and the product **11b** could be isolated, albeit in low yield (5%). Nevertheless, the diastereoselectivity of the process was found to be excellent (≥96% *de*) as determined by $^1$H and $^{13}$C NMR analysis. Encouraged by this initial result, we briefly investigated the role of solvent and additive. Ultimately the best conditions were found to involve the use of ether, *t*BuLi (2 equiv.) and $LiClO_4$ (8.0 equiv.) and the desired product could be isolated in moderate yield (54%) and excellent diastereoselectivity (≥96% *de*, Table 1, entry 1). Under the optimized conditions a series of electrophiles ($E^2X$) and hydrazones **5** with varying substituent ($E^1$) were screened. Trapping with disulfide electrophiles afforded products **11c** ($E^1$ = SMe, $E^2$ = S*i*Pr) and **11d** ($E^1$ = SMe, $E^2$ = SMe) in moderate yields and excellent diastereoselectivities (entries 2,3). In the latter case, a competitive reaction at the proximal ferrocene moiety occurred to form disubstitution product **12a** in 18% yield and ≥ 96% *de* (Scheme 1).

Trimethylsilylation of hydrazone **5b** ($E^1$ = SMe) proceeded to afford the desired product **11e** in moderate yield and ≥ 96% *de* but the process was not regioselective also giving adduct **12b** (20%, ≥ 96% *de*). The reaction tolerated phosphane-substitution as substrate **5c** ($E^1$ = $PPh_2$·$BH_3$) reacted to form the disubstituted product **11f** in 20% yield and ≥ 96% *de* (entry 5). Finally, monosubstituted SAMP-

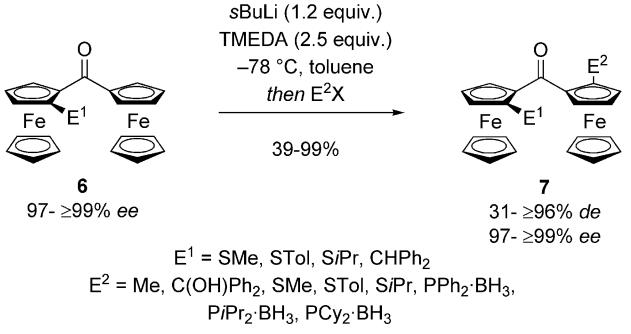
Table 1. Scope of auxiliary-directed *ortho*-metalation/functionalization.

| Entry | Product | $E^1$ | $E^2$ | % Yield | % *de*[a] |
|---|---|---|---|---|---|
| 1 | **11b** | SMe | Me | 54 | ≥96 |
| 2 | **11c** | SMe | S*i*Pr | 41 | ≥96 |
| 3 | **11d** (**12a**) | SMe | SMe | 37 (18)[b] | ≥96 |
| 4 | **11e** (**12b**) | SMe | $SiMe_3$ | 41 (20)[b] | ≥96 |
| 5 | **11f** | $PPh_2{\cdot}BH_3$ | SMe | 20 | ≥96 |
| 6 | – (**12c**) | $C(OH)Ph_2$ | SMe | 0 (25)[b] | ≥96 |

[a] Determined by $^1H$ and/or $^{13}C$ NMR analysis. [b] Refers to yield of regioisomeric product **12** formed in addition to disubstituted product **11**; ≥ 96% *de* in all cases.

hydrazone **5d** [$E^1$ = $C(OH)Ph_2$] also reacted under these condition but in this case the only observed regioisomer was disubstitution product **12c** formed in moderate yield (25%) and excellent diastereoselectivity (≥ 96 *de*, entry 6). Due to the low to moderate yields and lack of regioselectivity in certain cases, further work (e.g. auxiliary cleavage) based on route A was not conducted.

Route B was then investigated as a means to synthesize disubstituted bisferrocenes **7**. Initial attempts to lithiate monosubstituted diferrocenyl ketone **6** ($E^1$ = SMe) of high enantiomeric purity using *n*BuLi (2.0 equiv.) and trapping with methyl iodide, as a test electrophile, led to no reaction (Scheme 2). Metalation with *n*BuLi (2.0 equiv.) in the presense of TMEDA (2.0 equiv.) and subsequent reaction with methyl iodide, as a test electrophile, gave the desired product **7** in moderate yield (57%). Gratifyingly the diastereoselectivity of the process was excellent indicating that the relay of planar stereochemical information across the molecule was highly efficient (≥96% *de*). In addition the reaction proceeded with complete regiocontrol.




Scheme 2. Substrate-directed asymmetric synthesis of disubstituted diferrocenyl ketones **7**.

Additional additives (e.g. HMPA, 18-crown-6, DMAP, $LiClO_4$) in place of TMEDA gave lower yields. The effect of the base was also examined. *t*BuLi and PhLi did not produce the desired adduct **7** and with *s*BuLi the adduct **7** could be isolated in slightly higher yield (63%) and the same diastereoselectivity (≥ 96% *de*). The yield could be further improved to 84% by performing the reaction under dilute conditions (0.025 mM) with the slow addition of *s*BuLi. Therefore all further experiments were conducted under these conditions (Table 2, entry 1).

Table 2. Scope of substrate-directed *ortho*-metalation/functionalization.

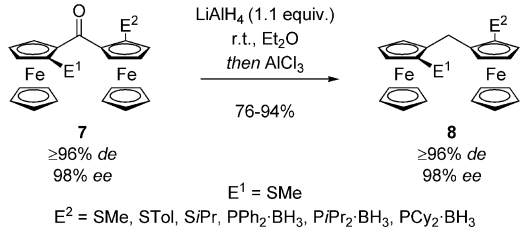
| Entry | Product | $E^1$ | $E^2$ | % Yield | % *de*[a] | Configuration[b] |
|---|---|---|---|---|---|---|
| 1 | **7a** | SMe | Me | 84 | ≥96 | ($S_p$,$R_p$) |
| 2 | **7b** | SMe | $C(OH)Ph_2$ | 82 | ≥96 | ($S_p$,$R_p$) |
| 3 | **7c** | SMe | SMe | 99 | ≥96 | ($S_p$,$S_p$) |
| 4 | **7d** | SMe | STol | 71 | ≥96 | ($S_p$,$S_p$) |
| 5 | **7e** | SMe | S*i*Pr | 58 | ≥96 | ($S_p$,$S_p$) |
| 6 | **7f** | SMe | $PPh_2{\cdot}BH_3$[c] | 52 | ≥96 | ($S_p$,$S_p$) |
| 7 | **7g** | SMe | $PiPr_2{\cdot}BH_3$[c] | 58 | ≥96 | ($S_p$,$S_p$) |
| 8 | **7h** | SMe | $PCy_2{\cdot}BH_3$[c] | 39 | ≥96 | ($S_p$,$S_p$) |
| 9 | **7i** | S*i*Pr | Me | 80 | 31 | ($S_p$,$R_p$) |
| 10 | **7j** | STol | Me | 64 | 51 | ($S_p$,$R_p$) |
| 11 | **7k** | STol | SMe | 41 | 48 | ($S_p$,$S_p$) |
| 12 | **7l** | $CHPh_2$ | SMe | 58 | ≥96 | ($S_p$,$R_p$) |

[a] Determined by $^1H$ and/or $^{13}C$ NMR analysis. [b] Determined by NOE analysis. [c] Corresponding chlorophosphane was used as the electrophile ($E^2X$) followed addition of $BH_3{\cdot}SMe_2$ to the crude reaction mixture.

A range or sulfur-, phosphorus- and carbon-based substituents ($E^1$) and electrophiles ($E^2X$) were tolerated in the reaction. The yield of the bisferrocene products **7** ranged from moderate to excellent (39–99%) and the diastereoselectivity of the process was generally excellent (≥96% *de*). The *ortho*-methylsulfanyl-containing substrate **6a** ($E^1$ = SMe) reacted with all electrophiles in excellent diastereoselectivity (≥96% *de*, entries 1–8). However in the case of *ortho*-isopropyl- and tolylsulfanyl compounds **6b** and **6c**, the diastereoselectivity decreased significantly (31–51% *de*, entries 9–11). Finally, the diphenylmethyl-substituted ketone **6d** reacted in 58% yield and at least 96% *de*.

NOE experiments established the configuration of the products **7** taking into account the known absolute $S_p$-configuration of the substrates, established previously by X-ray crystallographic analysis.[12j] Product **7c** ($E^1$ = $E^2$ = SMe) is $C_2$-symmetric and an accordingly-simple $^1H$ NMR spectrum was recorded for this compound.

A series of pseudo $C_2$-symmetric chiral bidentate *S*,*S*- and *P*,*S*-ligands were prepared in one-step from disubstituted diferrocenyl ketones **7** (Scheme 3).[14–16] In one-pot, exposure of ketones to $LiAlH_4$ for 30 min prior to the addition of $AlCl_3$ effected deoxygenation in an efficient manner and methylene-bridged disubstituted bisferrocenes **8** were afforded in very good to excellent yields (76–94%). A range of sulfanyl-, boranato-protected phosphane-substituents were tolerated and the resultant chiral *S*,*S*- and *P*,*S*-ligands **8** were formed without any epimerization or racemization (≥96% *de*, 98% *ee*, Table 3). In the case of ketone **7b**




Scheme 3. Synthesis of pseudo-$C_2$-symmetric bidentate bisferrocenes **8** by deoxygentation of ketones **7**.

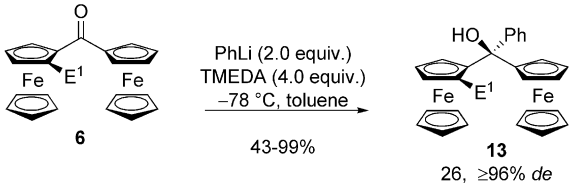
[$E^1$ = SMe, $E^2$ = C(OH)$Ph_2$], unproductive over-reduction occurred whereby the resident *tert*-alcohol group was also removed.

Table 3. Scope of the deoxygenation reaction.

| Entry | Product | $E^1$ | $E^2$ | % Yield[a] | Configuration |
|---|---|---|---|---|---|
| 1[b] | **8a** | SMe | SMe | 86 | ($S_p$,$S_p$) |
| 2 | **8b** | SMe | STol | 94 | ($S_p$,$S_p$) |
| 3 | **8c** | SMe | S*i*Pr | 76 | ($S_p$,$S_p$) |
| 4 | **8d** | SMe | $PPh_2$·$BH_3$ | 93 | ($S_p$,$S_p$) |
| 5 | **8e** | SMe | P*i*$Pr_2$·$BH_3$ | 83 | ($S_p$,$S_p$) |
| 6 | **8f** | SMe | $PCy_2$·$BH_3$ | 80 | ($S_p$,$S_p$) |

[a] ≥ 96% *de* as determined by $^1$H and/or $^{13}$C NMR analysis; 98% *ee* as determined by HPLC analysis on a chiral stationary phase. [b] $C_2$-symmetric.

The keto function of monosubstituted diferrocenyl ketone **6** could be transformed into valuable alcohol and amine groups in one- or two-synthetic steps, thus creating bidentate *S*,*O*-*S*,*N*-, *O*,*O*- and *N*,*O*-ligands in certain cases. In the first instance, treatment of ketone **6** ($E^1$ = Me) with an excess of PhLi (2.0 equiv.) in the presence of TMEDA (2.0 equiv.) cleanly effected a 1,2-addition reaction to afford the *tert*-alcohol **13a** ($E^1$ = Me) in nearly quantitative yield (99%) (Scheme 4, Table 4, entry 1). Unfortunately the diastereoselectivity of the process was low (26% *de*).




$E^1$ = Me, $CHPh_2$, C(OH)$Ph_2$, SMe, STol, S*i*Pr

Scheme 4. Substrate-directed asymmetric synthesis of *tert*-alcohols **13**.

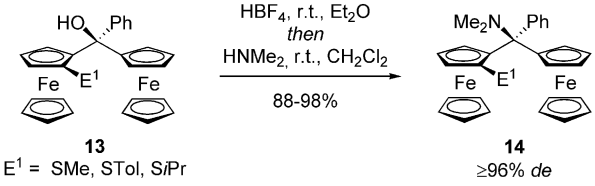
Table 4. Scope of *tert*-alcohols **13** synthesis.

| Entry | Product | $E^1$ | % Yield | % *de*[a] | Configuration |
|---|---|---|---|---|---|
| 1 | **13a** | Me | 99 | 26 | ($S$,$R_p$) |
| 2 | **13b** | $CHPh_2$ | 43 | ≥96 | ($S$,$R_p$) |
| 3 | **13c** | C(OH)$Ph_2$ | 73 | ≥96 | ($S$,$R_p$) |
| 4 | **13d** | SMe | 87 | ≥96 | ($S$,$S_p$) |
| 5 | **13e** | STol | 88 | ≥96 | ($S$,$S_p$) |
| 6 | **13f** | S*i*Pr | 72 | ≥96 | ($S$,$S_p$) |

[a] Determined by $^1$H and/or $^{13}$C NMR analysis.

Ketones **6** with substituents ($E^1$) that were sterically-more demanding or contained a heteroatom all gave excellent levels of asymmetric induction (≥96% *de*, entries 2–6). Moderate to high yields were maintained (43–88%) and this approach provided chiral nonracemic *S*,O- and *O*,*O*-ligands in four cases.

Next several of resultant *tert*-alcohols **13** were transformed into their corresponding monosubstituted diferrocenylamines **14** (Scheme 5). Following Allenmark's procedure, exposure of *tert*-alcohol **13d** ($E^1$ = SMe) to acid followed by the addition of dimethylamine resulted in a high yielding and diastereoselective synthesis of amine **14a**, with retention of configuration (95% yield, ≥ 96% *de*).[17] Two additional sulfur-substituted *tert*-alcohols **13e** ($E^1$ = STol) and **13f** (S*i*Pr) were also tolerated, reacting in high yield (98, 88%) and stereoselectivity (≥96% *de*).

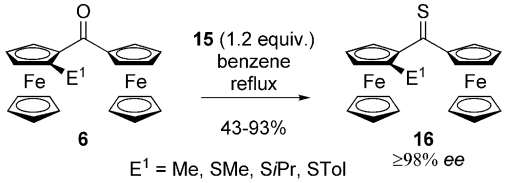



$E^1$ = SMe, STol, S*i*Pr

Scheme 5. Synthesis of chiral diferrocenyl *N*,*S*-ligands **14**.

Interestingly *tert*-alcohols **13** containing substituents ($E^1$) other than sulfanyl groups were found to decompose under these amination conditions. In addition, the use of phosphorus-based nucleophiles in place of dimethylamine (e.g. $Ph_2PH$, *i*$Pr_2PH$, $Ph_2PK$) resulted in no conversion and only unreacted starting material was isolated.

Monosubstituted diferrocenyl ketones **6** could be converted into a variety of thioketone-containing structures **16** in one synthetic step. Applying Bildstein's method using phosphorus pentasulfide provided only traces of the desired products.[18] However Sato and Asai's method using Lawesson's reagent (**15**) proved to be effective (Scheme 6).[19,20] The air and moisture-sensitive products **16** were obtained in moderate to high yield (43–93%, Table 5). No loss of stereochemical integrity could be observed during the process (≥98% *ee*) as determined by HPLC analysis on a chiral stationary phase.




$E^1$ = Me, SMe, S*i*Pr, STol

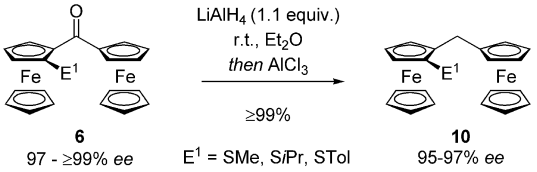
Scheme 6. Synthesis of thioketones **16** from ketones **6**.

Table 5. Scope of thioketone **16** formation.

| Entry | Product | $E^1$ | % Yield | Configuration |
|---|---|---|---|---|
| 1 | **16a** | Me | 59 | ($R_p$) |
| 2 | **16b** | SMe | 43 | ($S_p$) |
| 3 | **16c** | S*i*Pr | 93 | ($S_p$) |
| 4 | **16d** | STol | 52 | ($S_p$) |

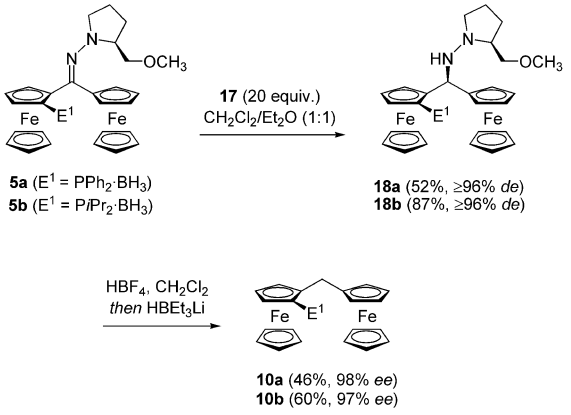
In analogy to the preparation of bidentate ligands **8**, deoxygenation of several monosubstituted diferrocenyl ketones **6** afforded monodentate *S*-ligands **10** (Scheme 7). Thus treatment of ketones **6** with $LiAlH_4$ then $AlCl_3$ in one-pot afforded the methylene-bridged monosubstituted bisferrocenes **10** in quantitative yields as essentially single enantiomers. In the case of ketone **6e** [$E^1$ = C(OH)$Ph_2$], unproductive over-reduction occurred and the *tert*-alcohol group was also removed.




Scheme 7. Synthesis of monodentate sulfanyl-substituted diferrocenes **10**.

In our previous work regarding the asymmetric synthesis of monodentate diferrocenyl ketones **6** via the SAMP/RAMP-hydrazone methodology, the chiral auxiliary was cleaved under oxidative or Lewis-acid promoted conditions. This allowed C-, S-, and Si-substituted ketones **6** to be prepared. However the attempted removal of the auxiliary in the case of *P*-substituted hydrazones led to significant decomposition. We have now developed a two-step procedure allowing for auxiliary removal and efficient *P*-substituted methylene-bridged bisferrocene **10** synthesis (Scheme 8). Hydrazone **5a** was reduced to hydrazine **18a** in moderate yield (52%) and excellent diastereoselectivity (≥96% *de*) using a large excess of catecholborane (**17**, 20 equiv.). Hydrazone **5b** was also tolerated well in the reduction reaction. Subsequent reductive C–N bond cleavage of hydrazines **18** under acidic conditions proceeded readily affording methylene-bridged bisferrocenes **10a** and **10b** in moderate yield (46, 60%). The process did not lead to any racemization and the products were isolated with high enantiomeric excesses (98, 97%).




Scheme 8. Synthesis of monodentate *P*-substituted bisferrocenes **10**.

## Conclusions

A chiral auxiliary- and substrate-directed *ortho*-metalation/functionalization reaction for the asymmetric synthesis of disubstituted bisferrocenes **7** have been examined. SAMP auxiliary-derived hydrazones **5** led to low to moderate yields (20–54%) and excellent stereoselectivities (97 to ≥99% *ee*, ≥96% *de*). However the process was not regioselective in several cases. Virtually enantiopure monosubstituted bisferrocenes **6**, containing only a planar chiral element, led to **7** in moderate to excellent yields (39–99%) and generally excellent levels of asymmetric induction (≥96% *de*), with complete regiocontrol. This conversion is one of the still rare cases of high asymmetric induction in the generation of a planar chiral unit caused by yet another planar chiral unit. The resultant disubstituted diferrocenyl ketones **7** were converted readily by deoxygenation into methylene-bridged diferrocenyl *S*,*S*- and *P*,*S*-ligands **8**. Monosubstituted bisferrocenes **6** were also elaborated into a series of *O*,*O*-, *N*,*O*-and *O*,*S*-ligands **13** and **14** by diastereoselective functionalization of the resident ketone function. Finally, several potential ligands containing only one donor atom were readily prepared. Current synthetic work is focused on the evaluation of several of these ligands in catalytic asymmetric synthesis.

## Experimental Section

**General:** All moisture-sensitive reactions were carried out using standard Schlenk techniques. All reagents employed were commercially available and used as supplied or purified by conventional methods. All solvents were dried and distilled prior to use. Preparative column chromatography was carried out using Merck silica gel 60, particle size 0.040–0.063 mm (230–240 mesh). Analytical TLC was performed with silca gel 60 $F_{254}$ plates purchased from Merck, Darmstadt. Optical rotation values were measured on a Perkin–Elmer P241 polarimeter in Merck UVASOL-quality solvents. Microanalyses were obtained with a Heraeus CHN-O-RAPID or a Vario EL element analyzer. Mass spectra (MS) were acquired on a Finnigan SSQ 7000 (CI 100 eV. EI 70 eV) spectrometer. High resolution MS were recorded on a Finnigan MAT 95 spectrometer. Infrared (IR) spectra were recorded on a Perkin–Elmer FT/IR 1760. The assignments of the signals are w (weak), m (medium), s (strong), vs. (very strong); Cp stands for cyclopentadienyl. $^1$H NMR (300, 400 and 500 MHz), $^{11}$B NMR (160 MHz), $^{13}$C NMR (75, 100 and 125 MHz) and $^{31}$P NMR (162 and 202 MHz) spectra were recorded on a Gemini 300, Varian Inova 400 or Varian Unity 500 spectrometer in $CDCl_3$ or $C_6D_6$ as solvents and using TMS as internal standard. Protons directly attached to boron are not listed in the $^1$H NMR spectroscopic data. Diastereomeric excess values (*de*) were determined by NMR spectroscopy. Enantiomeric excess values (*ee*) were determined by HPLC using a chiral stationary phase.

**General Procedure for the Synthesis of Disubstituted Diferrocenyl Ketones 7 (GP1):** To a solution of monosubstituted diferrocenyl ketone **6** (1.0 equiv.) in toluene (40 mL/mmol) was added TMEDA (2.5 equiv.) and the mixture was stirred for 15 min. It was then cooled to –78 °C, *s*BuLi (1.2 equiv.) was slowly added and stirring continued for an additional 9 h. The electrophile was added and the reaction mixture was slowly warmed up to room temperature overnight. The reaction was quenched with a saturated aqueous $NH_4Cl$ solution at 0 °C. The phases were separated and the organic layer was washed with brine and dried with $MgSO_4$. The residue was purified by column chromatography to provide the product **7** as either a red oil or solid. In the case where $E^2X = R_2PCl$, the reaction mixture was treated with $BH_3{\cdot}SMe_2$ complex (4.0 equiv., 2.0 M in THF) for 3 h at 0 °C before quenching with $NH_4Cl$ solution.

**($R_p$)-(2-Methylferrocenyl)-($S_p$)-[2-(methylsulfanyl)ferrocenyl]-methanone (7a):** According to GP1, a solution of ketone **6a**

(222 mg, 0.50 mmol) was stirred with TMEDA (145 mg, 1.25 mmol) in toluene (20 mL) at room temperature. Following addition of *s*BuLi (0.46 mL, 1,3 M in hexane) the solution was treated with MeI (0.13 mL, 2.0 mmol). Standard work-up and purification of the crude product by column chromatography (silica gel, pentane/diethyl ether, 8:1) provided the disubstituted ketone **7a** as a red oil. Yield 192 mg (84%). $R_f$ (pentane/$EtO_2$, 4:1) = 0.44. $[\alpha]_D^{25}$ = +708.9 ($c$ = 0.27, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3094 (m), 3006 (m), 2952 (w), 2920 (m), 1615 (vs), 1457 (m), 1430 (s), 1379 (m), 1343 (m), 1323 (m), 1265 (m), 1237 (m), 1198 (w), 1107 (m), 1038 (m), 1002 (m), 824 (s), 754 (vs), 684 (w), 666 (w), 587 (w), 567 (w), 483 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 2.15 (s, 3 H, SC$H_3$, C$H_3$), 2.50 (s, 3 H, SC$H_3$, C$H_3$), 3.93 (s, 5 H, $C_5H_5$), 4.00 (s, 5 H, $C_5H_5$), 4.09 (m, 2 H, Cp-*H*), 4.16 (m, 1 H, Cp-*H*), 4.26 (m, 1 H, Cp-*H*), 4.86 (m, 1 H, Cp-*H*), 4.93 (m, 1 H, Cp-*H*) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 14.8 (*C*$H_3$), 16.0 (*C*$H_3$), 67.3 (*Cp*), 67.8 (*Cp*), 67.9 (*Cp*), 71.1 (*Cp*), 71.2 (*Cp*), 72.6 (*Cp*), 69.8 (*Cp*), 70.6 (*Cp*), 77.9 (*Cp*-CO), 79.2 (*Cp*-CO), 86.6 (*Cp*-$SCH_3$), 90.6 (*Cp*-$SCH_3$), 198.7 (*C*O) ppm. MS (EI): *m*/*z* (%) = 459 (31) [$M^{\cdot+}$ + 1], 458 (100) [$M^{\cdot+}$], 456 (11), 443 (12). HRMS ($EI^+$): $C_{23}H_{22}Fe_2OS$: calcd. 458.00901; found 458.00903.

**($S_p$)-[2-(Methylsulfanyl)ferrocenyl]-($R_p$)-{2-[diphenyl(hydroxy)-methyl]ferrocenyl}methanone (7b):** According to GP1, a solution of ketone **6a** (444 mg, 1.00 mmol) was stirred with TMEDA (291 mg, 1.25 mmol) in toluene (40 mL) at room temperature. Following addition of *s*BuLi (0.92 mL, 1.3 M in hexane) the solution was treated with benzophenone (0.92 g, 5.0 mmol). Standard work-up and purification of the crude product by column chromatography (silica gel, pentane/diethyl ether, 8:1) provided the disubstituted ketone **7b** as a violet solid. Yield 514 mg, (82%); m.p. 214 °C. $R_f$ (pentane/diethyl ether, 4:1) = 0.37. $[\alpha]_D^{25}$ = +210.9 ($c$ = 0.11, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3676 (w), 3454 (m), 3195 (s), 3103 (m), 3020 (m), 2921 (m), 1595 (s), 1488 (m), 1434 (vs), 1387 (m), 1335 (s), 1252 (s), 1197 (w), 1173 (m), 1106 (m), 1092 (w), 1045 (m), 997 (m), 819 (s), 755 (s), 701 (vs), 656 (w), 627 (w), 598 (w), 487 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 2.04 (s, 3 H, SC$H_3$), 3.68 (s, 5 H, $C_5H_5$), 3.86 (m, 1 H, Cp-*H*), 3.98 (m, 3 H, Cp-*H*), 4.27 (s, 5 H, $C_5H_5$), 4.34 (m, 1 H, Cp-*H*), 4.55 (m, 1 H, Cp-*H*), 7.00–7.25 (m, 6 H, *Ph*), 7.59 (m, 2 H, *Ph*), 7.87 (m, 2 H, *Ph*), 8.79 (s, 1 H, $Ph_2CO$*H*) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 16.7 (S*C*$H_3$), 67.4 (*Cp*), 67.6 (*Cp*), 67.8 (*Cp*), 70.4 (*Cp*), 70.5 (*Cp*), 76.9 (*Cp*), 70.5 (*Cp*), 71.2 (*Cp*), 76.4 (*Cp*-CO), 76.6 (*Cp*-CO), 78.5 [*Cp*-C(OH)$Ph_2$], 94.0 (*Cp*-$SCH_3$), 105.6 [*C*(OH)$Ph_2$], 125.9 ($C_{Ar}$), 126.1 ($C_{Ar}$), 126.5 ($C_{Ar}$), 127.1 ($C_{Ar}$), 127.5 ($C_{Ar}$), 203.6 (*C*O) ppm. MS (EI): *m*/*z* (%) = 658 (11), 627 (35) [$M^{\cdot+}$ + 1], 626 (100) [$M^{\cdot+}$], 624 (12), 561 (46), 543 (28), 528 (13), 489 (17), 488 (55), 440 (32), 375 (11). $C_{35}H_{30}Fe_2O_2S$ (626.38): calcd. C 67.11, H 4.83; found C 66.93, H 5.33.

**Bis($S_p$)-[2-(methylsulfanyl)ferrocenyl]methanone (7c):** According to GP1, a solution of ketone **6a** (222 mg, 0.50 mmol) was stirred with TMEDA (145 mg, 1.25 mmol) in toluene (20 mL) at room temperature. Following addition of *s*BuLi (0.46 mL, 1.3 M in hexane) the solution was treated with dimethyl disulfide (0.18 mL, 2.0 mmol). Standard work-up and purification of the crude product by column chromatography (silica gel, pentane/diethyl ether, 8:1) provided the disubstituted ketone **7c** as a red oil. Yield 234 mg (99%). $R_f$ (pentane/diethyl ether, 4:1) = 0.17. $[\alpha]_D^{25}$ = +398.5 ($c$ = 0.27, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3930 (m), 3675 (m), 3467 (s), 3089 (w), 2917 (m), 2859 (m), 1611 (vs), 1436 (vs), 1386 (m), 1329 (s), 1252 (m), 1107 (m), 1043 (w), 1002 (m), 972 (w), 823 (s), 768 (w), 610 (w), 581 (w), 480 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 2.14 (s, 6 H, SC$H_3$), 3.98 (s, 10 H, $C_5H_5$), 4.0 (s, 2 H, Cp-*H*), 4.25 (s, 2 H, Cp-*H*), 4.90 (s, 2 H, Cp-*H*) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 15.9 (S*C*$H_3$), 67.6 (*Cp*), 67.8 (*Cp*), 70.7 (*Cp*), 70.4 (*Cp*), 78.5 (*Cp*-CO), 91.3 (*Cp*-$SCH_3$), 197.7 (CO) ppm. MS (EI): *m*/*z* (%) = 490 (100) [$M^{\cdot+}$ + 1] 489 (23) (17) 475 (51) 258 (11) 290. $C_{23}H_{22}Fe_2OS_2$ (490.252): calcd. C 56.35, H 4.52; found C 56.74, H 4.99.

**($S_p$)-[2-(4-Methylphenylsulfanyl)ferrocenyl]-($S_p$)-[2-(methylsulfanyl)-ferrocenyl]methanone (7d):** According to GP1, a solution of ketone **6a** (444 mg, 1.00 mmol) was stirred with TMEDA (291 mg, 2.50 mmol) in toluene (40 mL) at room temperature. Following addition of *sBuLi* (0.92 mL, 1.3 M in hexane) the solution was treated with di(*p*-tolyl) disulfide (1.23 g, 5.00 mmol). Standard work-up and purification of the crude product by column chromatography (silica gel, pentane/diethyl ether, 14:1) provided the disubstituted ketone **7d** as a red solid. Yield 402 mg (71%); m.p. 156 °C. $R_f$ (pentane/diethyl ether, 4:1) = 0.26. $[\alpha]_D^{25}$ = +49.2 ($c$ = 0.25, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3093 (w), 3006 (m), 2918 (m), 1611 (s), 1491 (m), 1436 (vs), 1381 (m), 1328 (s), 1249 (m), 1217 (m), 1107 (m), 1042 (m), 1020 (w), 1003 (m), 968 (w), 819 (s), 753 (vs), 666 (w), 609 (w), 581 (w), 487 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 2.03 (s, 3 H, $C_6H_4CH_3$), 2.13 (s, 3 H, C$H_3$), 3.98 (s, 5 H, $C_5H_5$), 4.04 (m, 1 H, Cp-*H*), 4.08 (m, 1 H, Cp-*H*), 4.10 (s, 5 H, $C_5H_5$), 4.31 (m, 2 H, Cp-*H*), 4.76 (m, 2 H, Cp-*H*), 6.89 (d, $J$ = 8.1 Hz, 2 H, $C_6H_4$), 7.45 (d, $J$ = 8.1 Hz, 2 H, $C_6H_4$) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 16.9 (S*C*$H_3$), 19.9 ($C_{Ar}$-*C*$H_3$), 67.9 (*Cp*), 68.5 (*Cp*), 68.6 (*Cp*), 70.0 (*Cp*), 70.1 (*Cp*), 73.0 (*Cp*), 70.7 (*Cp*), 71.1 (*Cp*), 78.5 (*Cp*-CO), 79.8 (*Cp*-CO), 88.3 (*Cp*-$SC_{Ar}$), 92.0 (*Cp*-$SCH_3$), 129.0 ($C_{Ar}$), 130.6 ($C_{Ar}$), 133.8 ($C_{Ar}$-$CH_3$), 135.6 (S$C_{Ar}$), 196.8 (CO) ppm. MS (EI): *m*/*z* (%) = 568 (16) [$M^{\cdot+}$ +2], 567 (34) [$M^{\cdot+}$ + 1], 566 (100) [$M^{\cdot+}$], 564 (13), 428 (19). $C_{29}H_{26}Fe_2OS_2$ (566.349): calcd. C 61.50, H 4.63; found C 61.59, H 5.06.

**($S_p$)-[2-(Isopropylsulfanyl)ferrocenyl]-($S_p$)-[2-(methylsulfanyl)ferrocenyl]methanone (7e):** According to GP1, a solution of ketone **6a** (222 mg, 0.50 mmol) was stirred with TMEDA (145 mg, 1.25 mmol) in toluene (20 mL) at room temperature. Following addition of *s*BuLi (0.46 mL, 1.3 M in hexane) the solution was treated with diisopropyl sulfide (0.32 mL, 2.0 mmol). Standard work-up and purification of the crude product by column chromatography (silica gel, pentane/diethyl ether, 15:1) provided the disubstituted ketone **7e** as a red solid. Yield 150 mg (58%); m.p. 48 °C. $R_f$ (pentane/diethyl ether, 4:1) = 0.32. $[\alpha]_D^{25}$ = +364.9 ($c$ = 0.55, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3690 (w), 3676 (w), 3652 (w), 3435 (s), 3087 (w), 2956 (m), 2920 (m), 2858 (m), 1616 (s), 1433 (vs), 1381 (m), 1326 (s), 1244 (s), 1155 (m), 1106 (m), 1042 (m), 1001 (m), 968 (w), 820 (s), 767 (m), 609 (w), 518 (w), 478 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.28 [dd, $^3J$ = 6.7, $^4J$ = 2.2 Hz, 6 H, CH(C$H_3$)$_2$], 2.14 (s, 3 H, C$H_3$), 3.49 [sept, $^3J$ = 6.7 Hz, 1 H, C*H*(C$H_3$)$_2$], 4.02 (s, 5 H, $C_5H_5$), 4.05 (s, 5 H, $C_5H_5$), 4.06 (m, 2 H, Cp-*H*), 4.12 (m, 1 H, Cp-*H*), 4.26 (m, 1 H, Cp-*H*), 4.48 (m, 1 H, Cp-*H*), 4.90 (m, 1 H, Cp-*H*) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 16.0 (S*C*$H_3$), 22.2 (C-*C*$H_3$), 22.7 (C-*C*$H_3$), 37.7 [S*C*(C$H_3$)$_2$], 67.8 (*Cp*), 68.6 (*Cp*), 70.6 (*Cp*), 71.7 (*Cp*), 72.8 (*Cp*), 74.7 (*Cp*), 70.6 (*Cp*), 70.9 (*Cp*), 75.9 (*Cp*-CO), 77.1 (*Cp*-CO), 81.6 (*Cp*-S), 84.1 (*Cp*-S), 189.8 (CO) ppm. MS (EI): *m*/*z* (%) = 520 (10) [$M^{\cdot+}$ + 2], 519 (22) [$M^{\cdot+}$ + 1], 518 (100) [$M^{\cdot+}$], 516 (13), 528 (36), 507 (11). HRMS ($EI^+$): $C_{25}H_{26}Fe_2OS_2$: calcd. 518.01238; found 518.01254.

**($S_p$)-[2-(1-Boranato-1,1-diphenylphosphanyl)ferrocenyl]-($S_p$)-[2-(methylsulfanyl)ferrocenyl]methanone (7f):** According to GP1, a solution of ketone **6a** (333 mg, 0.75 mmol) was stirred with TMEDA (218 mg, 1.88 mmol) in toluene (30 mL) at room temperature. Following addition of *s*BuLi (0.69 mL, 1.3 M in hexane) the solution was treated with chlorodiphenylphosphane (0.39 mL, 1.95 mmol). Subsequently $BH_3$·SMe complex (2.00 mL,

4.00 mmol) was added at 0 °C and the mixture was stirred for an additional 3 h. A saturated $NH_4Cl$ solution was added and the organic phase was separated. Purification of the crude product by column chromatography (silica gel, pentane/diethyl ether, 8:1) provided the disubstituted ketone **7f** as a red oil. Yield 250 mg (52%). $R_f$ (pentane/diethyl ether, 4:1) = 0.13. $[\alpha]_D^{25}$ = +268.0 ($c$ = 0.35, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3871 (w), 3856 (w), 3838 (w), 3823 (w), 3804 (w), 3676 (m), 3653 (m), 3631 (m), 3613 (m), 3449 (vs), 3077 (w), 2923 (s), 2862 (s), 1622 (s), 1563 (m), 1545 (m), 1525 (w), 1510 (w), 1499 (w), 1479 (w), 1436 (s), 1384 (s), 1327 (m), 1243 (m), 1158 (m), 1107 (m), 1057 (m), 1001 (m), 917 (w), 900 (w), 826 (m), 740 (s), 695 (m), 628 (m), 596 (w), 578 (w), 540 (m), 500 (m), 476 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 2.01 (s, 3 H, SC$H_3$), 3.90 (s, 5 H, $C_5H_5$), 4.03 (m, 1 H, Cp-*H*), 4.14 (s, 5 H, $C_5H_5$), 4.20 (m, 1 H, Cp-*H*), 4.29 (m, 1 H, Cp-*H*), 4.60 (m, 1 H, Cp-*H*), 4.67 (m, 1 H, Cp-*H*), 5.01 (m, 1 H, Cp-*H*), 7.01–7.14 (m, 6 H, *Ph*), 7.82 (m, 2 H, *Ph*), 8.26 (m, 2 H, *Ph*) ppm. $^{11}B$ NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ = –34.07 ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 17.6 (S*C*$H_3$), 68.7 (*Cp*), 68.8 (*Cp*), 69.9 (*Cp*), 70.4 (*Cp*), 70.9 (*Cp*), 71.8 (*Cp*), 71.6 (*Cp*), 71.8 (*Cp*), 72.6 (*Cp*-CO), 72.6 (*Cp*-CO), 75.6 (*Cp*-$SCH_3$), 79.9 (d, $J_{CP}$ = 11.4 Hz, *Cp*-P), 128.0 ($C_{Ar}$), 129.9 ($C_{Ar}$), 130.5 ($C_{Ar}$), 133.7 ($C_{Ar}$), 132.9 (d, $J_{CP}$ = 10.4 Hz, $C_{Ar}$-P), 134.1 (d, $J_{CP}$ = 10.4 Hz, $C_{Ar}$-P), 194.5 (CO) ppm. MS (EI): *m*/*z* (%) = 630 (12) [$M^{\cdot+}$ + 2], 629 (30) [$M^{\cdot+}$ + 1], 628 (92) [$M^{\cdot+}$], 626 (12), 614 (13), 613 (31), 582 (22), 581 (65), 580 (13), 579 (22), 565 (17), 564 (47), 563 (100), 561 (13), 548 (14), 547 (14), 529 (17), 498 (21), 497 (26), 427 (34), 314 (11). HRMS ($EI^+$): $C_{34}H_{32}BFe_2OPS$: calcd. 628.07032; found 628.07058.

**($S_p$)-[2-(1-Boranato-1,1-diisopropylphosphanyl)ferrocenyl]-($S_p$)-[2-(methylsulfanyl)ferrocenyl]methanone (7g):** According to GP1, a solution of ketone **6a** (444 mg, 1.00 mmol) was stirred with TMEDA (291 mg, 2.50 mmol) in toluene (40 mL) at room temperature. Following addition of *s*BuLi (0.92 mL, 1.3 M in hexane) the solution was treated with chlorodiisopropylphosphane (0.56 mL, 3.50 mmol). Subsequently $BH_3$·SMe complex (2.00 mL, 4.00 mmol) was added at 0 °C and the mixture was stirred for an additional 3 h. A saturated $NH_4Cl$ solution was added and the organic phase was separated. Purification of the crude product by column chromatography (silica gel, pentane/diethyl ether, 8:1) provided the disubstituted ketone **7g** as a red solid. Yield 333 mg (58%); m.p. 195 °C. $R_f$ (pentane/diethyl ether, 4:1) = 0.34. $[\alpha]_D^{25}$ = +611.7 ($c$ = 0.35, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3449 (m), 2964 (m), 2915 (m), 2868 (m), 2367 (s), 2270 (m), 1620 (vs), 1437 (vs), 1385 (m), 1365 (w), 1332 (m), 1247 (s), 1219 (w), 1158 (m), 1114 (m), 1039 (s), 1003 (m), 878 (w), 824 (s), 771 (w), 685 (m), 665 (w), 562 (m), 495 (m), 477 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 0.98 {dd, $^3J_{HH}$ = 6.9, $^4J_{HP}$ = 13.3 Hz, 3 H, P[CH(C$H_3$)$_2$]$_2$}, 1.21 {dd, $^3J_{HH}$ = 6.9, $^4J_{HP}$ = 15.7 Hz, 3 H, P[CH(C$H_3$)$_2$]$_2$}, 1.40 {dd, $^3J_{HH}$ = 7.1, $^4J_{HP}$ = 15.4 Hz, 3 H, P[CH(C$H_3$)$_2$]$_2$}, 1.54 {dd, $^3J_{HH}$ = 7.1, $^4J_{HP}$ = 16.3 Hz, 3 H, P[CH(C$H_3$)$_2$]$_2$}, 2.04 (s, 3 H, SC$H_3$), 2.50 {sept, $^3J_{HH}$ = 6.9 Hz, 1 H, 1 H, P[C*H*(CH$_3$)$_2$]$_2$}, 3.29 {sept, $^3J_{HH}$ = 7.1 Hz, 1 H, P[C*H*(CH$_3$)$_2$]$_2$}, 3.98 (s, 5 H, $C_5H_5$), 4.08 (m, 1 H, Cp-*H*), 4.14 (s, 5 H, $C_5H_5$), 4.21 (m, 1 H, Cp-*H*), 4.30 (m, 1 H, Cp-*H*), 4.81 (m, 1 H, Cp-*H*), 5.12 (m, 1 H, Cp-*H*), 5.28 (m, 1 H, Cp-*H*) ppm. $^{11}B$ NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ = –41.46 ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$): $\delta$ = 15.7 (C-*C*H$_3$), 17.2 (C-*C*H$_3$), 17.4 (C-*C*H$_3$), 17.5 (C-*C*H$_3$), 18.8 (S*C*H$_3$), 22.3 [*C*(CH$_3$)$_2$], 23.5 [*C*-(CH$_3$)$_2$], 67.3 (*Cp*), 68.1 (*Cp*), 70.6 (*Cp*), 70.7 (*Cp*), 71.9 (*Cp*), 76.0 (*Cp*), 70.8 (*Cp*), 70.9 (*Cp*), 77.8 (*Cp*-CO), 81.7 (*Cp*-CO), 92.8 (*Cp*-$SCH_3$), 79.9 (d, $^1J_{CP}$ = 14.9 Hz, *Cp*-P*i*-Pr), 198.0 (*C*O) ppm. $^{31}P$ NMR (202 MHz, $C_6D_6$, 25 °C): $\delta$ = 40.09 ppm. MS (EI): *m*/*z* (%) = 576 (19) [$M^{\cdot+}$ + 2], 574 (57) [$M^{\cdot+}$], 573 (18), 561 (18), 560 (52), 545 (20), 518 (18), 517 (54), 497 (11), 496 (34), 495 (100), 494 (11), 493 (14), 480 (10), 429 (12), 427 (16), 359 (15). $C_{28}H_{36}BFe_2OPS$ (574.136): calcd. C 58.58, H 6.32; found C 58.71, H 6.56.

**($S_p$)-[2-(1-Boranato-1,1-dicyclohexylphosphanyl)ferrocenyl]-($S_p$)-[2-(methylsulfanyl)ferrocenyl]methanone (7h):** According to GP1, a solution of ketone **6a** (333 mg, 0.75 mmol) was stirred with TMEDA (218 mg, 1.88 mmol) in toluene (30 mL) at room temperature. Following addition of *s*BuLi (0.69 mL, 1.3 M in hexane) the solution was treated with chlorodicyclohexylphosphane (0.44 mL, 1.95 mmol). Subsequently $BH_3$·SMe complex (2.00 mL, 4.00 mmol) was added at 0 °C and the mixture was stirred for an additional 3 h. A saturated $NH_4Cl$ solution was added and the organic phase was separated. Purification of the crude product by column chromatography (silica gel, pentane/diethyl ether, 12:1) provided the disubstituted ketone **7h** as a red solid. Yield 191 mg (39%); m.p. 92 °C. $R_f$ (pentane/diethyl ether, 4:1) = 0.35. $[\alpha]_D^{25}$ = +612.6 ($c$ = 0.23, $CHCl_3$). IR (capillary): $\tilde{\nu}$ = 3449 (m), 2964 (m), 2915 (m), 2868 (m), 2367 (s), 2270 (m), 1620 (vs), 1437 (vs), 1385 (m), 1365 (w), 1332 (m), 1247 (s), 1219 (w), 1158 (m), 1114 (m), 1039 (s), 1003 (m), 878 (w), 824 (s), 771 (w), 685 (m), 665 (w), 562 (m), 495 (m), 477 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 0.90–2.43 [m, 22 H, P(C$_6H_{11}$)$_2$], 2.05 (s, 3 H, SC$H_3$), 3.98 (s, 5 H, $C_5H_5$), 4.05 (m, 1 H, Cp-*H*), 4.18 (m, 1 H, Cp-*H*), 4.22 (s, 5 H, $C_5H_5$), 4.33 (m, 1 H, Cp-*H*), 4.86 (m, 1 H, Cp-*H*), 5.12 (m, 1 H, Cp-*H*), 5.33 (m, 1 H, Cp-*H*) ppm. $^{11}B$ NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ = –40.47 ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 15.7 (S*C*$H_3$), 25.4 (*Cy*), 25.6 (*Cy*), 26.3 (*Cy*), 26.5 (*Cy*), 26.6 (*Cy*), 27.0 (*Cy*), 27.1 (*Cy*), 27.3 (*Cy*), 27.8 (*Cy*), 28.7 (*Cy*), 32.4 (d, $J_{CP}$ = 15.4 Hz, P$C_{Cy}$), 32.8 (d, $J_{CP}$ = 14.9 Hz, P$C_{Cy}$), 67.4 (*Cp*), 68.2 (*Cp*), 70.5 (*Cp*), 71.7 (*Cp*), 71.8 (*Cp*), 75.8 (*Cp*), 70.7 (*Cp*), 71.0 (*Cp*), 77.7 (*Cp*-CO), 79.7 (d, $J_{CP}$ = 16.1 Hz, *Cp*-P$Cy_2$), 82.1 (*Cp*-CO), 92.8 (*Cp*-$SCH_3$), 197.8 (*C*O) ppm. $^{31}P$ NMR (202 MHz, $C_6D_6$, 25 °C): $\delta$ = 31.54 ppm. MS (EI): *m*/*z* (%) = 655 (11) [$M^{\cdot+}$ + 1], 654 (39) [$M^{\cdot+}$], 653 (10), 641 (26), 640 (59), 627 (17), 625 (44), 577 (40), 575 (100), 574 (14), 573 (13), 559 (13), 558 (14), 557 (34), 439 (21), 427 (14), 307 (11), 56 (12). $C_{34}H_{44}BFe_2OPS$ (654.266): calcd. C 62.42, H 6.78; found C 62.51, H 7.11.

**General Procedure for the Synthesis of Disubstituted Diferrocenylmethanes 8 (GP2):** To a solution of $LiAlH_4$ (1.1 equiv.) in diethyl ether (10 mL/mmol) was slowly added a solution of disubstituted ketone **7** (1.0 equiv.) in diethyl ether (10 mL/mmol). After 30 min $AlCl_3$ (1.1 equiv.) in diethyl ether (10 mL/mmol) was added to the reaction mixture and stirring was continued for an additional 45 min. The reaction was quenched by the addition of $H_2O$ (2 mL) and $H_2SO_4$ (2 mL, 6 M). The aqueous layer was extracted with diethyl ether (3 × 15 mL) and the combined organic extracts were washed with a saturated aqueous $NaHCO_3$ solution and brine and dried with $MgSO_4$. The crude product was purified by column chromatography affording either a yellow to orange oil or solid.

**Bis($S_p$)-[2-(methylsulfanyl)ferrocenyl]methane (8a):** According to GP2, to a solution of $LiAlH_4$ (4 mg, 0.09 mmol) in diethyl ether (5 mL) was added ketone **7c** (38 mg, 0.08 mmol) in diethyl ether (5 mL). The reaction mixture was then treated with $AlCl_3$ (12 mg, 0.09 mmol). The product **8a** was obtained by aqueous work-up and purification by column chromatography (silica gel, pentane/$Et_2O$, 4:1) as a yellow oil. Yield 32 mg (86%). $R_f$ (pentane/ether, 4:1) = 0.91. $[\alpha]_D^{25}$ = –198.7 ($c$ = 0.15, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3093 (m), 2982 (m), 2919 (s), 2855 (w), 1425 (m), 1219 (m), 1106 (m), 1030 (m), 1001 (m), 820 (s), 757 (vs), 667 (w), 489 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 2.01 (s, 6 H, SC$H_3$), 3.91 (d, $J$ = 14.5 Hz, 2 H, C$H_2$), 3.96 (s, 2 H, Cp-*H*), 4.10 (s, 10 H, $C_5H_5$), 4.19 (m, 2 H, Cp-*H*), 4.42 (m, 2 H, Cp-*H*) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 20.8 (S*C*$H_3$), 27.8 (*C*$H_2$), 67.3 (*Cp*), 70.2 (*Cp*),

72.0 (*Cp*), 70.4 (*Cp*), 83.0 (*Cp*-$CH_2$), 90.8 (*Cp*-$SCH_3$) ppm. MS (EI): *m/z* (%) = 478 (17) [$M^{\cdot+}$ +2], 477 (36) [$M^{\cdot+}$ +1], 476 (100) [$M^{\cdot+}$], 474 (16) [$M^{\cdot+}$ – 2], 429 (21), 348 (11), 139 (12). HRMS ($EI^+$): $C_{23}H_{24}Fe_2S_2$: calcd. 476.00182; found 476.00188.

**($S_p$)-[2-(4-Methylphenylsulfanyl)ferrocenyl]-($S_p$)-[2-(methylsulfanyl)-ferrocenyl]methane (8b):** According to GP2, to a solution of $LiAlH_4$ (10 mg, 0.28 mmol) in diethyl ether (5 mL) was added ketone **7d** (142 mg, 0.25 mmol) in diethyl ether (5 mL). The reaction mixture was then treated with $AlCl_3$ (35 mg, 0.28 mmol). The product **8b** was obtained by aqueous work-up and purification by column chromatography (silica gel, pentane/$Et_2O$, 9:1) as an orange-yellow oil. Yield 130 mg (94%). $R_f$ (pentane/diethyl ether, 4:1) = 0.84. $[\alpha]_D^{25}$ = –42.0 (*c* = 0.45, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3093 (m), 3012 (m), 2980 (m), 2918 (m), 2865 (w), 1492 (s), 1424 (m), 1218 (m), 1185 (w), 1106 (s), 1087 (m), 1030 (m), 1001 (s), 806 (vs), 756 (vs), 667 (w), 488 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.99 (s, 3 H, $C_6H_4CH_3$), 2.08 (s, 3 H, $SCH_3$), 3.68 (m, 2 H, $CH_2$), 3.98 (s, 5 H, $C_5H_5$), 4.05 (m, 4 H, Cp-*H*), 4.13 (s, 5 H, $C_5H_5$), 4.32 (m, 1 H, Cp-*H*), 4.52 (m, 1 H, Cp-*H*), 6.78 (d, *J* = 8.2 Hz, 2 H, $C_6H_4$), 7.04 (d, *J* = 8.2 Hz, 2 H, $C_6H_4$) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 20.6 ($CH_3$), 20.8 ($SCH_3$), 27.5 ($CH_2$), 67.1 (*Cp*), 68.7 (*Cp*), 69.0 (*Cp*), 70.7 (*Cp*), 71.0 (*Cp*), 71.1 (*Cp*), 70.3 (*Cp*), 70.7 (*Cp*), 72.3 (*Cp*-$CH_2$), 76.0 (*Cp*-$CH_2$), 90.0 (*Cp*-$SCH_3$), 92.6 (*Cp*-S*p*Tol), 126.2 ($C_{Ar}$), 129.6 ($C_{Ar}$), 134.2 ($SC_{Ar}$-$CH_3$), 138.0 ($SC_{Ar}$) ppm. MS (EI): *m/z* (%) = 554 (16) [$M^{\cdot+}$ +2], 553 (37) [$M^{\cdot+}$ +1], 552 (100) [$M^{\cdot+}$], 550 (12). $C_{29}H_{28}Fe_2S_2$ (552.366): calcd. C 63.06, H 5.12; found C 62.94, H 5.23.

**($S_p$)-[2-(Isopropylsulfanyl)ferrocenyl]-($S_p$)-[2-(methylsulfanyl)-ferrocenyl]methane (8c):** According to GP2, to a solution of $LiAlH_4$ (5.6 mg, 0.14 mmol) in diethyl ether (5 mL) was added ketone **7e** (178 mg, 0.25 mmol) in dry $Et_2O$ (5 mL). The reaction mixture was then treated with $AlCl_3$ (35 mg, 0.28 mmol). The product **8c** was obtained by aqueous work-up and purification by column chromatography (silica gel, pentane/$Et_2O$, 9:1) as an orange-yellow solid. Yield 52 mg (76%); m.p. 98 °C. $R_f$ (pentane/diethyl ether, 4:1) = 0.88. $[\alpha]_D^{25}$ = –67.8 (*c* = 0.32, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3092 (m), 2959 (s), 2918 (s), 2862 (m), 1441 (m), 1424 (m), 1364 (w), 1241 (m), 1154 (w), 1106 (m), 1051 (w), 1030 (m), 1000 (s), 818 (vs), 756 (vs), 490 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.13 [d, $^3J_{HH}$ = 6.8 Hz, 3 H, $SCH(CH_3)_2$], 1.18 [d, $^3J_{HH}$ = 6.8 Hz, 3 H, $SCH(CH_3)_2$], 2.01 (s, 3 H, $SCH_3$), 2.76 [sept, $^3J_{HH}$ = 6.8 Hz, 1 H, $SCH(CH_3)_2$], 3.93 (m, 2 H, $CH_2$), 4.01 (s, 1 H, Cp-*H*), 4.08 (s, 5 H, $C_5H_5$), 4.12 (s, 5 H, $C_5H_5$), 4.18 (m, 2 H, Cp-*H*), 4.30 (m, 1 H, Cp-*H*), 4.39 (m, 1 H, Cp-*H*), 4.47 (m, 1 H, Cp-*H*) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 20.7 ($SCH_3$), 23.1 [$CH(CH_3)_2$], 23.8 [$CH(CH_3)_2$], 27.8 ($CH_2$), 40.1 [$CH(CH_3)_2$], 67.1 (*Cp*), 67.7 (*Cp*), 70.3 (*Cp*), 70.9 (*Cp*), 71.8 (*Cp*), 75.2 (*Cp*), 70.4 (*Cp*), 70.6 (*Cp*), 78.7 (*Cp*-$SCH_3$), 83.4 (*Cp*-S*i*Pr), 90.7 (*Cp*-$CH_2$), 97.7 (*Cp*-$CH_2$) ppm. MS (EI): *m/z* (%) = 505 (31) [$M^{\cdot+}$ +1], 504 (100) [$M^{\cdot+}$], 502 (12) [$M^{\cdot+}$ – 2], 414 (16), 348 (14), 293 (13). HRMS ($EI^+$): $C_{25}H_{28}Fe_2S_2$: calcd. 504.03311; found 504.03311.

**($S_p$)-[2-(1-Boranato-1,1-diphenylphosphanyl)ferrocenyl]-($S_p$)-[2-(methylsulfanyl)ferrocenyl]methane (8d):** According to GP2, to a solution of $LiAlH_4$ (6.5 mg, 0.17 mmol) in diethyl ether (5 mL) was added the ketone **7f** (97 mg, 0.15 mmol) in diethyl ether (5 mL). The reaction mixture was then treated with $AlCl_3$ (22 mg, 0.17 mmol). The product **8d** was obtained by aqueous work-up and purification by column chromatography (silica gel, pentane/$Et_2O$, 12:1) as a yellow solid. Yield 88 mg (93%); m.p. 170 °C. $R_f$ (pentane/ether, 4:1) = 0.46. $[\alpha]_D^{25}$ = –157.0 (*c* = 0.23, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3616 (w), 3434 (vs), 3081 (w), 2925 (w), 2396 (m), 1637 (m), 1438 (w), 1384 (m), 1106 (m), 1061 (m), 821 (m), 739 (m), 696 (m), 640 (w), 508 (w), 484 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.95 (s, 3 H, $SCH_3$), 3.29 (m, 1 H, Cp-*H*), 3.57 (m, 1 H, Cp-*H*), 3.85 (m, 2 H, $CH_2$), 4.04 (m, 1 H, Cp-*H*), 4.14 (s, 5 H, $C_5H_5$), 4.22 (m, 1 H, Cp-*H*), 4.45 (s, 5 H, $C_5H_5$), 5.15 (m, 1 H, Cp-*H*), 6.30 (m, 1 H, Cp-*H*), 6.78–7.04 (m, 6 H, *Ph*), 7.30 (m, 2 H, *Ph*), 7.75 (m, 2 H, *Ph*) ppm. $^{11}B$ NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ = –35.67 ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 20.7 ($SCH_3$), 51.3 ($CH_2$), 66.9 (*Cp*), 67.1 (*Cp*), 67.9 (*Cp*), 68.7 (*Cp*), 71.4 (*Cp*), 71.7 (*Cp*), 77.7 (*Cp*-$SCH_3$), 85.8 (*Cp*-$PPh_2$), 86.9 (*Cp*-$CH_2$), 94.0 (*Cp*-$CH_2$), 130.3 ($C_{Ar}$), 133.0 ($C_{Ar}$), 133.2 ($C_{Ar}$), 134.0 ($C_{Ar}$), 134.1 ($C_{Ar}$), 136.2 ($C_{Ar}$-P), 141.9 ($C_{Ar}$-P) ppm. $^{31}P$ NMR (121 MHz, $C_6D_6$, 25 °C): $\delta$ = 16.43 ppm. MS (EI): *m/z* (%) = 630 (10) [$M^{\cdot+}$ +2], 614 (19) [$M^{\cdot+}$ – $BH_3$], 567 (10), 492 (20), 477 (11), 447 (14), 446 (46), 445 (100), 443 (15), 325 (11), 324 (37), 246 (11), 245 (12), 223 (21), 215 (19), 183 (12), 139 (20), 121 (10), 66 (26), 65 (18), 60 (16), 57 (15), 56 (13), 55 (17), 45 (18). HRMS ($EI^+$): $C_{34}H_{34}BFe_2PS$ – $BH_3$ = $C_{34}H_{31}Fe_2PS$: calcd. 614.05829; found 614.05872.

**($S_p$)-[2-(1-Boranato-1,1-diisopropylphosphanyl)ferrocenyl]-($S_p$)-[2-(methylsulfanyl)ferrocenyl]methane (8e):** According to GP2, to a solution of $LiAlH_4$ (11 mg, 0.28 mmol) in diethyl ether (5 mL) was added the ketone **7g** (144 mg, 0.25 mmol) in diethyl ether (5 mL). The reaction mixture was then treated with $AlCl_3$ (37 mg, 0.28 mmol). The product **8e** was obtained by aqueous work-up and purification by column chromatography (silica gel, pentane/$Et_2O$, 12:1) as an orange-yellow solid. Yield 116 mg (83%); m.p. 162 °C. $R_f$ (pentane/ether, 4:1) = 0.64. $[\alpha]_D^{25}$ = +6.5 (*c* = 0.20, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3890 (m), 3856 (m), 3841 (w), 3712 (w), 3691 (m), 3676 (m), 3652 (m), 3631 (m), 3444 (s), 3090 (m), 2967 (s), 2912 (s), 2873 (s), 2395 (s), 2311 (s), 2336 (s), 2254 (w), 1655 (w), 1638 (m), 1464 (m), 1425 (m), 1410 (w), 1385 (m), 1309 (w), 1247 (m), 1229 (m), 1164 (m), 1144 (w), 1106 (m), 1067 (s), 1033 (s), 998 (m), 971 (w), 891 (w), 839 (s), 810 (s), 749 (m), 618 (m), 679 (m), 630 (m), 575 (m), 512 (m), 486 (vs) $cm^{-1}$. $^1H$ NMR (500 MHz, $C_6D_6$, 25 °C): $\delta$ = 0.95 {dd, $^3J_{HH}$ = 7.3, $^3J_{HP}$ = 13.6 Hz, 3 H, $P[CH(CH_3)_2]_2$}, 1.13 {dd, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 14.2 Hz, 3 H, $P[CH(CH_3)_2]_2$}, 1.17 {dd, $^3J_{HH}$ = 7.3, $^3J_{HP}$ = 13.7 Hz, 3 H, $P[CH(CH_3)_2]_2$}, 1.32 {dd, $^3J_{HH}$ = 7.0, $^3J_{HP}$ = 14.0 Hz, 3 H, $P[CH(CH_3)_2]_2$}, 2.00 {m, 2 H, $P[CH(CH_3)_2]_2$}, 2.05 (s, 3 H, $SCH_3$), 3.89 (m, 2 H, Cp-*H*), 3.92 (s, 2 H, $CH_2$), 3.98 (m, 1 H, Cp-*H*), 4.07 (s, 5 H, $C_5H_5$), 4.15 (s, 1 H, Cp-*H*), 4.26 (s, 5 H, $C_5H_5$), 4.32 (s, 1 H, Cp-*H*), 4.49 (s, 1 H, Cp-*H*) ppm. $^{11}B$ NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ = –40.93 ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 15.5 [$CH(CH_3)_2$], 16.5 [$CH(CH_3)_2$], 16.6 [$CH(CH_3)_2$], 17.2 [$CH(CH_3)_2$], 18.8 ($SCH_3$), 21.3 [d, $J_{CP}$ = 35.0 Hz, $PCH(CH_3)_2$], 24.3 [d, $J_{CP}$ = 32.6 Hz, $PCH(CH_3)_2$], 27.3 ($CH_2$), 65.8 (*Cp*), 67.5 (*Cp*), 67.6 (*Cp*), 68.4 (*Cp*), 69.2 (*Cp*), 72.0 (*Cp*), 69.2 (*Cp*), 70.0 (*Cp*), 72.1 (*Cp*-$CH_2$), 83.4 (*Cp*-$CH_2$), 88.0 (*Cp*-$SCH_3$), 90.8 (d, $J_{CP}$ = 10.3 Hz, *Cp*-P*i*Pr) ppm. $^{31}P$ NMR (121 MHz, $C_6D_6$, 25 °C): $\delta$ = 32.22 ppm. MS (EI): *m/z* (%) = 562 (11) [$M^{\cdot+}$ +2], 562 (34) [$M^{\cdot+}$ + 1], 560 (100) [$M^{\cdot+}$], 559 (18) [$M^{\cdot+}$ – 1], 558 (18) [$M^{\cdot+}$ – 2], 547 (12), 546 (37) [$M^{\cdot+}$ – $BH_3$], 533 (10), 532 (31), 531 (98), 529 (13), 503 (20), 500 (34), 499 (100), 497 (14), 481 (11), 413 (20), 379 (23), 378 (70), 348 (12), 347 (14), 315 (15), 314 (15), 293 (14), 292 (28), 291 (14), 240 (15). $C_{28}H_{38}BFe_2PS$ (560.153): calcd. C 60.04, H 6.84; found C 59.75, H 6.65.

**($S_p$)-[2-(1-Boranato-1,1-dicyclohexylphosphanyl)ferrocenyl]-($S_p$)-[2-(methylsulfanyl)ferrocenyl]methane (8f):** According to GP2, to a solution of $LiAlH_4$ (6.3 mg, 0.17 mmol) in diethyl ether (5 mL) was added the ketone **7h** (98 mg, 0.15 mmol) in diethyl ether (5 mL). The reaction mixture was then treated with $AlCl_3$ (22 mg, 0.17 mmol). The product **8f** was obtained by aqueous workup and purification by column chromatography (silica gel, pentane/ $Et_2O$, 20:1) as a yellow solid. Yield 77 mg (80%); m.p. 162 °C. $R_f$ (pentane/ether, 4:1) = 0.91. $[\alpha]_D^{25}$ = +10.3 (*c* = 0.30, $CHCl_3$). IR (KBr):

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$\tilde{\nu}$ = 3905 (m), 3856 (w), 3713 (w), 3690 (m), 3676 (m), 3652 (m), 3631 (m), 3436 (s), 3092 (w), 2928 (vs), 2849 (s), 2370 (m), 2338 (m), 1654 (w), 1637 (w), 1446 (m), 1384 (m), 1167 (m), 1106 (m), 1061 (m), 1001 (m), 888 (w), 836 (w), 817 (s), 627 (w), 587 (w), 487 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 0.90–2.53 (m, 22 H, $C_6H_{11}$), 2.06 (s, 3 H, $SCH_3$), 3.92 (d, $J$ = 2.5 Hz, 2 H, $CH_2$), 4.03 (m, 2 H, Cp-*H*), 4.10 (s, 5 H, $C_5H_5$), 4.18 (m, 1 H, Cp-*H*), 4.27 (m, 1 H, Cp-*H*), 4.30 (s, 5 H, $C_5H_5$), 4.46 (m, 1 H, Cp-*H*), 4.59 (m, 1 H, Cp-*H*) ppm. $^{11}B$ NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ = –40.24 ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 20.3 ($SCH_3$), 26.3 ($C_{Cy}H_2$), 26.4 ($C_{Cy}H_2$), 27.1 ($C_{Cy}H_2$), 27.2 ($C_{Cy}H_2$), 27.2 ($C_{Cy}H_2$), 27.5 ($C_{Cy}H_2$), 27.7 ($C_{Cy}H_2$), 27.7 ($C_{Cy}H_2$), 28.2 ($C_{Cy}H_2$), 28.3 ($C_{Cy}H_2$), 28.9 ($CH_2$), 33.4 (d, $J_{CP}$ = 33.8 Hz, $PC_{Cy}H$), 35.6 (d, $J_{CP}$ = 32.1 Hz, $PC_{Cy}H$), 67.3 (*Cp*), 69.0 (*Cp*), 69.0 (*Cp*), 70.1 (*Cp*), 71.1 (*Cp*), 71.6 (*Cp*), 70.6 (*Cp*), 71.4 (*Cp*), 72.8 (*Cp*-$CH_2$), 84.5 (*Cp*-$CH_2$), 90.1 (d, $J_{CP}$ = 9.1 Hz, *Cp*-$PCy_2$) ppm. $^{31}P$ NMR (121 MHz, $C_6D_6$, 25 °C): $\delta$ = 25.81 ppm. MS (EI): *m*/*z* (%) = 642 (24) [$M^{\cdot+}$ +2], 641 (11) [$M^{\cdot+}$ +1], 640 (64) [$M^{\cdot+}$], 639 (21) [$M^{\cdot+}$ – 1], 626 (16) [$M^{\cdot+}$ – $BH_3$], 612 (31), 611 (76), 609 (10), 580 (39), 579 (100), 577 (11), 459 (11), 458 (18), 413 (13), 393 (12), 348 (13), 347 (13), 315 (12), 314 (12), 293 (21), 292 (16), 291 (11), 280 (18). $C_{35}H_{32}BFe_2PS$ (640.282): calcd. C 63.78, H 7.24; found C 63.50, H 7.23.

**General Procedure for the Synthesis of *tert*-Alcohols 13 (GP3):** To a solution of monosubstituted diferrocenylketone **6** in toluene (20 mL/mmol) was added TMEDA (4.0 equiv.) and the mixture was stirred for 15 min. The reaction mixture was cooled to –78 °C and a phenyllithium solution (2.0 equiv. 2 M in cyclohexane/ether, 7:13) was added dropwise over a period of 3 h. The reaction was quenched by the addition of saturated aqueous $NH_4Cl$ solution. The organic layer was washed with brine and dried with $MgSO_4$. The crude product **13** was purified by column chromatography to afford either a yellow or orange solid.

**Ferrocenyl-($R_p$)-(2-methylferrocenyl)-phenyl-(*S*)-methanol (13a):** According to GP3, TMEDA (56 mg, 0.48 mmol) was added to a solution of ketone **6e** (50 mg, 0.12 mmol) in toluene (10 mL). The reaction mixture was cooled down to – 78 °C, treated with phenyllithium (0.12 mL, 0.24 mmol) and stirred for 3 h. Aqueous work-up and purification by column chromatography (silica gel, pentane/$Et_2O$, 12:1) provided the alcohol **13a** as a yellow solid. Yield 58 mg (99%); m.p. 142 °C. $R_f$ (pentane/ether, 4:1) = 0.74. $[a]_D^{25}$ = –239.1 ($c$ = 0.55, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3526 (m), 3091 (m), 3008 (m), 2924 (m), 2856 (m), 1491 (m), 1446 (m), 1413 (m), 1379 (m), 1345 (m), 1328 (m), 1220 (m), 1168 (w), 1107 (s), 1051 (m), 1033 (m), 1005 (s), 878 (m), 818 (vs), 756 (vs), 703 (s), 668 (w), 520 (m), 845 (vs) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.69 (s, 3 H, $CH_3$), 3.39 (m, 1 H, O*H*), 3.73 (m, 2 H, Cp-*H*), 3.78 (m, 1 H, Cp-*H*), 3.83 (m, 1 H, Cp-*H*), 3.88 (m, 1 H, Cp-*H*), 3.91 (m, 1 H, Cp-*H*), 4.02 (s, 5 H, $C_5H_5$), 4.04 (s, 5 H, $C_5H_5$), 4.58 (m, 1 H, Cp-*H*), 7.06–7.23 (m, 3 H, *Ph*), 7.69 (m, 2 H, *Ph*) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$ 25 °C): $\delta$ = 14.4 ($CH_3$), 65.0 (*Cp*), 66.5 (*Cp*), 66.9 (*Cp*), 67.4 (*Cp*), 69.3 (*Cp*), 70.1 (*Cp*), 71.9 (*Cp*), 68.1 (*Cp*), 68.5 (*Cp*), 73.2 [*C*(OH)Ph], 82.0 (*Cp*-$CH_3$), 98.0 [*Cp*-C(OH)Ph], 98.5 [*Cp*-C(OH)Ph], 125.6 ($C_{Ar}$), 126.0 ($C_{Ar}$), 126.1 ($C_{Ar}$), 147.4 [$C_{Ar}$-C(OH)] ppm. MS (EI): *m*/*z* (%) = 491 (31) [$M^{\cdot+}$ + 1], 490 (100) [$M^{\cdot+}$], 488 (12), 352 (89), 350 (14). HRMS ($EI^+$): $C_{28}H_{26}Fe_2O$: calcd. 490.06824; found 490.06840.

**($R_p$)-[2-Benzhydrylferrocenyl]-ferrocenyl-phenyl-(*S*)-methanol (13b):** According to GP3, TMEDA (256 mg, 2.20 mmol) was added to a solution of ketone **6d** (320 mg, 0.55 mmol) in toluene (10 mL). The reaction mixture was cooled down to –78 °C, treated with phenyllithium (0.55 mL, 1.10 mmol) and stirred for 1 h. Following addition of TMSCl (119 mg, 1.10 mmol), stirring was continued for an additional 1 h. Finally PhLi (0.55 mL, 1.10 mmol) was added and the solution was warmed up to room temp. overnight. $NH_4F$ solution was added and stirring continued for an additional 2 h. The phases were separated and the organic layer was washed with brine. Purification by column chromatography (silica gel, pentane/ether, 9:1) provided the alcohol **13b** as an orange solid. Yield 152 mg (43%); m.p. 67 °C. $R_f$ (pentane/ether, 4:1) = 0.83. $[a]_D^{25}$ = –305.5 ($c$ = 0.31, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3514 (w), 3086 (w), 3060 (w), 3026 (m), 1493 (m), 1450 (w), 1219 (m), 1107 (m), 1078 (w), 1051 (m), 1031 (m), 1004 (m), 820 (m), 757 (vs), 700 (s), 524 (w), 485 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 3.65 (m, 1 H, O*H*), 3.73 (m, 1 H, Cp-*H*), 3.78 (s, 5 H, $C_5H_5$), 4.92 (m, 2 H, Cp-*H*), 4.05 (s, 5 H, $C_5H_5$), 4.10 (m, 1 H, Cp-*H*), 4.13 (m, 1 H, Cp-*H*), 4.56 (m, 1 H, Cp-*H*), 5.38 (m, 1 H, Cp-*H*), 6.59 (s, 1 H, $Ph_2CH$), 6.70–7.12 (m, 9 H, *Ph*), 7.43 (m, 6 H, *Ph*) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 47.5 ($CHPh_2$), 65.1 (*Cp*), 65.8 (*Cp*), 66.6 (*Cp*), 67.0 (*Cp*), 68.3 (*Cp*), 68.6 (*Cp*), 69.8 (*Cp*), 68.2 (*Cp*), 68.6 (*Cp*), 73.2 [*C*(OH)Ph], 89.1 (Cp-$CHPh_2$), 97.4 [*Cp*-C(OH)Ph], 100.9 [*Cp*-C(OH)Ph], 124.2 ($C_{Ar}$-H), 125.2 ($C_{Ar}$-H), 125.4 ($C_{Ar}$-H), 125.9 ($C_{Ar}$-H), 125.9 ($C_{Ar}$-H), 126.4 ($C_{Ar}$-H), 126.5 ($C_{Ar}$-H), 128.0 ($C_{Ar}$-H), 128.7 ($C_{Ar}$-H), 143.2 ($C_{Ar}$-CH), 143.6 ($C_{Ar}$-CH), 146.7 [$C_{Ar}$-C(OH)] ppm. MS (EI): *m*/*z* (%) = 644 ($M^{\cdot+}$+2, 11), 643 ($M^{\cdot+}$+1, 43), 642 ($M^{\cdot+}$, 10), 640 (11), 505 (16), 504 (42), 428 (15), 428 (45), 337 (31), 321 (15), 215 (11). $C_{40}H_{34}Fe_2O$ (642.402): calcd. C 74.79, H 5.33; found C 74.42, H 5.29.

**Ferrocenyl-($R_p$)-[2-(diphenylhydroxymethyl)ferrocenyl]-phenyl-(*S*)-methanol (13c):** According to GP3, TMEDA (232 mg, 2.00 mmol) was added to a solution of ketone **6f** (290 mg, 0.50 mmol) in toluene (10 mL). The reaction mixture was cooled down to –78 °C, treated with phenyllithium (0.50 mL, 1.00 mmol) and stirred for 1 h. Following addition of TMSCl (109 mg, 1.00 mmol), stirring was continued for an additional 1 h. Finally PhLi (0.50 mL, 1.00 mmol) was added and the solution was warmed up to room temp. overnight. $NH_4F$ solution was added and stirring continued for an additional 2 h. The phases were separated and the organic layer was washed with brine. Purification by column chromatography (silica gel, pentane/ether, 6:1) provided the alcohol **13c** as a yellow solid. Yield 240 mg (73%); m.p. 119 °C. $R_f$ (pentane/ether, 4:1) = 0.35. $[a]_D^{25}$ = –132.8 ($c$ = 0.29, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3907 (w), 3856 (w), 3691 (w), 3677 (w), 3652 (w), 3398 (s), 3086 (w), 3057 (m), 3024 (w), 2953 (m), 2924 (m), 2854 (m), 1656 (m), 1638 (m), 1600 (m), 1492 (m), 1447 (m), 1411 (m), 1385 (w), 1333 (w), 1234 (w), 1220 (w), 1168 (m), 1108 (m), 1057 (m), 1024 (m), 1003 (m), 888 (w), 818 (s), 753 (s), 737 (s), 700 (vs), 528 (m), 488 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 3.70 (m, 1 H, O*H*), 3.84 (m, 2 H, Cp-*H*), 3.93 (s, 5 H, $C_5H_5$), 4.00 (m, 1 H, Cp-*H*), 4.13 (m, 1 H, Cp-*H*), 4.21 (s, 5 H, $C_5H_5$), 4.28 (m, 1 H, Cp-*H*), 4.55 (m, 1 H, Cp-*H*), 4.71 (m, 1 H, Cp-*H*), 6.66–7.32 (m, 13 H, $C_6H_5$), 7.46 (m, 2 H, *Ph*), 9.35 (s, 1 H, $Ph_2CO$*H*) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 64.9 (*Cp*), 66.3 (*Cp*), 67.7 (*Cp*), 68.0 (*Cp*), 70.1 (*Cp*), 72.7 (*Cp*), 73.1 (*Cp*), 68.6 (*Cp*), 69.8 (*Cp*), 75.6 [*C*(OH)Ph], 77.6 [*Cp*-C(OH)$Ph_2$], 93.3 [*Cp*-C(OH)Ph], 94.8 [*Cp*-C(OH)Ph], 98.4 [*C*(OH)$Ph_2$], 125.5 ($C_{Ar}$), 125.8 ($C_{Ar}$-H), 126.1 ($C_{Ar}$-H), 126.2 ($C_{Ar}$-H), 126.6 ($C_{Ar}$-H), 126.8 ($C_{Ar}$-H), 126.9 ($C_{Ar}$-H), 126.9 ($C_{Ar}$-H), 127.5 ($C_{Ar}$-H), 144.0 ($C_{Ar}$-C), 146.2 ($C_{Ar}$-C), 146.6 ($C_{Ar}$-C) ppm. MS (EI): *m*/*z* (%) = 660 ($M^{\cdot+}$+2, 13), 659 ($M^{\cdot+}$+1, 49), 658 ($M^{\cdot+}$, 100), 656 (15), 641 (30), 640 (61), 520 (12), 502 (11), 438 (10), 437 (32), 426 (16), 383 (14), 382 (50), 337 (12), 329 (13), 305 (14), 304 (12), 303 (23), 302 (12), 291 (10), 290 (22), 289 (16), 215 (11). HRMS ($EI^+$): $C_{40}H_{34}Fe_2O_2$: calcd. 658.12575; found 658.12583.

**Ferrocenyl-($S_p$)-[2-(methylsulfanyl)ferrocenyl]-phenyl-(*S*)-methanol (13d):** According to GP3, TMEDA (349 mg, 3.00 mmol) was added

  

to a solution of ketone **6b** (333 mg, 0.75 mmol) in toluene (10 mL). The reaction mixture was cooled down to –78 °C, treated with phenyllithium (0.75 mL, 1.50 mmol) and stirred for 3 h. Aqueous work-up and purification by column chromatography (silica gel, pentane/$Et_2O$, 20:1) provided the alcohol **13d** as a yellow solid. Yield 340 mg (87%); m.p. 93 °C. $R_f$ (pentane/ether, 4:1) = 0.79. $[\alpha]_D^{25}$ = +75.6 ($c$ = 0.25, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3929 (w), 3443 (m), 3094 (m), 3058 (m), 3008 (m), 2921 (m), 2855 (w), 1770 (w), 1599 (w), 1490 (m), 1460 (m), 1446 (m), 1413 (m), 1391 (s), 1361 (m), 1335 (m), 1311 (m), 1223 (m), 1164 (m), 1107 (s), 1051 (s), 1037 (s), 1020 (s), 1003 (s), 971 (w), 882 (m), 819 (vs), 741 (s), 704 (s), 688 (m), 667 (m), 573 (m), 529 (s), 487 (s), 456 (w) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.21 (s, 3 H, $CH_3$), 3.69 (m, 1 H, O*H*), 3.80 (m, 2 H, Cp-*H*), 3.95 (m, 1 H, Cp-*H*), 4.11 (m, 1 H, Cp-*H*), 4.16 (m, 1 H, Cp-*H*), 4.19 (s, 5 H, $C_5H_5$), 4.27 (s, 5 H, $C_5H_5$), 4.80 (m, 1 H, Cp-*H*), 5.17 (m, 1 H, Cp-*H*), 7.03–7.15 (m, 3 H, *Ph*), 7.62 (m, 2 H, *Ph*) ppm. $^{13C}$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 18.7 ($SCH_3$), 66.2 (*Cp*), 66.3 (*Cp*), 66.4 (*Cp*), 66.9 (*Cp*), 68.1 (*Cp*), 71.5 (*Cp*), 74.7 (*Cp*), 68.3 (*Cp*), 69.7 (*Cp*), 71.3 [*C*(OH)Ph], 74.9 (*Cp*-$SCH_3$), 94.6 [*Cp*-C(OH)Ph], 103.7 [*Cp*-C(OH)Ph], 125.7 ($C_{Ar}$-H), 126.2 ($C_{Ar}$-H), 126.3 ($C_{Ar}$-H), 147.9 ($C_{Ar}$-C) ppm. MS (EI): $m/z$ (%) = 524 (10) [$M^{\cdot+}$ + 2], 523 (30) [$M^{\cdot+}$ + 1], 522 (95) [$M^{\cdot+}$], 520 (14), 385 (24), 384 (100), 369 (110), 338 (16), 337 (72), 336 (12), 261 (12), 216 (23), 215 (56). $C_{28}H_{26}Fe_2OS$ (522.272): calcd. C 64.39, H 5.02; found C 63.67, H 4.91.

**Ferrocenyl-($S_p$)-[2-(4-methylphenylsulfanyl)ferrocenyl]-phenyl-($S$)-methanol (13e):** According to GP3, TMEDA (349 mg, 3.00 mmol) was added to a solution of ketone **6a** (390 mg, 0.75 mmol) in toluene (10 mL). The reaction mixture was cooled down to –78 °C, treated with phenyllithium (0.75 mL, 1.50 mmol) and stirred for 3 h. Aqueous work-up and purification by column chromatography (silica gel, pentane/ether, 20:1) provided the alcohol **13e** as a yellow solid. Yield 395 mg (88%); m.p. 106 °C. $R_f$ (pentane/ether, 4:1) = 0.87. $[\alpha]_D^{25}$ = +53.1 ($c$ = 0.26, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3856 (w), 3843 (w), 3676 (m), 3439 (vs), 2926 (w), 1702 (w), 1686 (w), 1637 (m), 1596 (m), 1562 (w), 1491 (m), 1458 (w), 1443 (w), 1385 (s), 1359 (w), 1223 (w), 1211 (w), 1158 (w), 1107 (m), 1086 (w), 1044 (m), 1018 (m), 1003 (m), 989 (m), 816 (s), 803 (s), 741 (s), 702 (m), 539 (w), 524 (m), 485 (s) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.97 (s, 3 H, $C_6H_4CH_3$) 3.75 (m, 1 H, O*H*), 3.84 (m, 1 H, Cp-*H*), 3.90 (m, 1 H, Cp-*H*), 3.95 (m, 1 H, Cp-*H*), 4.11 (s, 5 H, $C_5H_5$), 4.13 (m, 1 H, Cp-*H*), 4.23 (m, 1 H, Cp-*H*), 4.28 (s, 5 H, $C_5H_5$), 4.81 (m, 1 H, Cp-*H*), 5.02 (m, 1 H, Cp-*H*), 6.54 (m, 4 H, $C_6H_4$), 6.88 (m, 3 H, *Ph*), 7.42 (m, 2 H, *Ph*) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 19.8 (Ph-$CH_3$), 66.5 (*Cp*), 66.7 (*Cp*), 67.1 (*Cp*), 68.1 (*Cp*), 69.4 (*Cp*), 71.7 (*Cp*), 75.8 (*Cp*), 68.3 (*Cp*), 70.1 (*Cp*), 71.0 [*C*(OH)Ph], 75.1 (*Cp*-S-*p*Tol), 94.7 [*Cp*-C(OH)Ph], 102.0 [*Cp*-C(OH)Ph], 125.1 ($C_{Ar}$-H), 125.8 ($C_{Ar}$-H), 126.1 ($C_{Ar}$-H), 128.2 ($C_{Ar}$-H), 133.4 ($C_{Ar}$-C), 133.7 ($C_{Ar}$-S), 146.4 [$C_{Ar}$-C(OH)] ppm. MS (EI): $m/z$ (%) = 599 (25) [$M^{\cdot+}$ +1], 597 (69) [$M^{\cdot+}$ – 1], 461 (24), 460 (82), 338 (21), 337 (100), 305 (20), 216 (11), 215 (43). $C_{34}H_{30}Fe_2OS$ (598.37): calcd. C 68.25, H 5.05; found C 67.92, H 5.19.

**Ferrocenyl-($S_p$)-[2-(isopropylsulfanyl)ferrocenyl]-phenyl-methanol (13f):** According to GP3, TMEDA (153 mg, 1.32 mmol) was added to a solution of ketone **6b** (162 mg, 0.33 mmol) in toluene (10 mL). The reaction mixture was cooled down to –78 °C, treated with phenyllithium (0.33 mL, 0.66 mmol) and stirred for 3 h. Aqueous work-up and purification by column chromatography (silica gel, pentane/ether, 20:1) provided the alcohol **13f** as a yellow solid. Yield 135 mg (72%); m.p. 86 °C. $R_f$ (pentane/ether, 4:1) = 0.91. $[\alpha]_D^{25}$ = –6.8 ($c$ = 0.28, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3675 (w), 3434 (s), 3094 (w), 2958 (m), 2922 (m), 2860 (w), 1702 (w), 1637 (w), 1460 (w), 1445 (m), 1386 (m), 1363 (m), 1243 (w), 1158 (w), 1106 (m), 1041 (m), 1021 (w), 1001 (m), 851 (w), 819 (s), 746 (m), 706 (m), 518 (w), 488 (s), 470 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 0.80 [dd, $J$ = 6.5/3.3 Hz, 6 H, $CH(CH_3)_2$], 1.26 [sept., $J$ = 6.5 Hz, 1 H, $CH(CH_3)_2$], 3.67 (m, 1 H, O*H*), 3.81 (m, 1 H, Cp-*H*), 3.85 (m, 1 H, Cp-*H*), 3.95 (m, 1 H, Cp-*H*), 4.16 (m, 2 H, Cp-*H*), 4.18 (s, 5 H, $C_5H_5$), 4.28 (s, 5 H, $C_5H_5$), 4.81 (m, 1 H, Cp-*H*), 5.38 (m, 1 H, Cp-*H*), 7.01–7.14 (m, 3 H, *Ph*), 7.57 (m, 2 H, *Ph*) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 21.03 (SCH-$CH_3$), 22.59 (SCH-$CH_3$), 37.06 [$SCH(CH_3)_2$], 66.32 (*Cp*), 66.44 (*Cp*), 66.86 (*Cp*), 68.12 (*Cp*), 71.77 (*Cp*), 73.36 (*Cp*), 76.11 (*Cp*), 68.31 (*Cp*), 69.88 (*Cp*), 71.68 [*C*(OH)Ph], 75.00 (*Cp*-S-*i*Pr), 94.60 [*Cp*-C(OH)Ph], 103.02 [*Cp*-C(OH)Ph], 125.63 ($C_{Ar}$-H), 126.13 ($C_{Ar}$-H), 126.24 ($C_{Ar}$-H), 148.35 [$C_{Ar}$-C(OH)] ppm. MS (EI): $m/z$ (%) = 551 (35) [$M^{\cdot+}$ + 1], 550 (100) [$M^{\cdot+}$], 548 (12), 412 (96), 370 (16), 369 (66), 337 (18), 275 (11), 216 (10), 215 (29), 57 (14), 45 (14). HRMS ($EI^+$): $C_{30}H_{30}Fe_2OS$: calcd. 550.07161; found 550.07154.

**General Procedure for the Synthesis of Chiral Diferrocenyl *N*,*S*-Ligands 14 (GP4):** To a solution of *tert*-alcohol **13** (1.0 equiv.) in diethyl ether (20 mL/mmol) was added 54% $HBF_4 \cdot Et_2O$ (0.75–1.00 mL/mmol). The dark precipitate was filtered, washed with diethyl ether and dissolved in $CH_2Cl_2$. Treatment of the solution with $Me_2NH$ gas resulted in the mixture turning orange. The reaction was quenched with 1.0 M NaOH and the organic layer was washed with brine and dried with $MgSO_4$ to afford the desired diferrocenylamine **14** as either an orange oil or solid.

**($S$)-{Ferrocenyl-($S_p$)-[2-(methylsulfanyl)ferrocenyl]-phenyl-methyl}-dimethylamine (14a):** According to GP4, alcohol **13d** (50 mg, 0.12 mmol) was treated with $HBF_4 \cdot Et_2O$ (0.2 mL, 1.45 mmol) in diethyl ether (6 mL). The precipitate was isolated and reacted with $Me_2NH$ gas. Aqueous-work up provided the product **14a** as an orange oil. Yield 157 mg (95%). $[\alpha]_D^{25}$ = –27.1 ($c$ = 0.07, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3856 (w), 3677 (m), 3653 (m), 3631 (m), 3450 (m), 3089 (m), 2965 (m), 2921 (m), 2859 (m), 2823 (m), 2780 (m), 1442 (m), 1385 (m), 1262 (m), 1222 (w), 1106 (s), 1042 (s), 1003 (s), 816 (vs), 747 (m), 705 (m), 675 (w), 542 (w), 491 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 2.40 (s, 3 H, $CH_3$), 3.64 [m, 6 H, $N(CH_3)_2$], 3.90 (m, 3 H, Cp-*H*), 4.12 (m, 2 H, Cp-*H*), 4.21 (s, 5 H, $C_5H_5$), 4.28 (m, 2 H, Cp-*H*), 4.41 (s, 5 H, $C_5H_5$), 7.15 (m, 1 H, *Ph*), 7.27 (m, 2 H, *Ph*), 7.47 (m, 2 H, *Ph*) ppm. $^{13}C$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ = 17.4 ($SCH_3$), 40.5 [$N(CH_3)_2$], 63.0 (*Cp*), 66.2 (*Cp*), 66.6 (*Cp*), 68.8 (*Cp*), 69.5 (*Cp*), 70.5 (*Cp*), 71.2 (*Cp*), 70.0 (*Cp*), 70.2 (*Cp*), 72.1 (*Cp*-$SCH_3$), 80.2 (*Cp*-CNPh), 87.5 (*Cp*-CNPh), 126.2 ($C_{Ar}$), 126.6 ($C_{Ar}$), 130.1 ($C_{Ar}$), 133.8 [$C_{Ar}$-C($NMe_2$)] ppm. MS (EI): $m/z$ (%) = 550 (12) [$M^{\cdot+}$ + 1], 549 (29) [$M^{\cdot+}$], 506 (13), 505 (30), 385 (24), 384 (95), 369 (15), 364 (11), 338 (25), 337 (97), 336 (18), 319 (24), 318 (100), 216 (31), 215 (83). HRMS ($EI^+$): $C_{30}H_{31}Fe_2NS$: calcd. 549.08760; found 549.08752.

**($S$)-{Ferrocenyl-($S_p$)-[2-(4-methylphenylsulfanyl)ferrocenyl]-phenyl-methyl}dimethylamine (14b):** According to GP4, alcohol **13e** (120 mg, 0.20 mmol) was treated with $HBF_4 \cdot Et_2O$ (0.2 mL, 1.45 mmol) in diethyl ether (5 mL). The precipitate was isolated and reacted with $Me_2NH$ gas. Aqueous-work up provided the product **14b** as an orange solid. Yield 123 mg (98%); m.p. 92 °C. $[\alpha]_D^{25}$ = –396.5 ($c$ = 0.31, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}$ = 3060 (m), 3012 (m), 2930 (w), 1706 (w), 1594 (m), 1491 (m), 1445 (m), 1218 (m), 1109 (m), 1079 (m), 1035 (m), 1004 (m), 821 (m), 756 (vs), 703 (s), 668 (m), 493 (m) $cm^{-1}$. $^1H$ NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 2.07 (s, 3 H, $C_6H_4CH_3$), 3.76 [m, 6 H, $N(CH_3)_2$], 3.95 (m, 3 H, Cp-*H*), 3.98 (s, 2 H, Cp-*H*), 4.12 (s, 5 H, $C_5H_5$), 4.17 (m, 2 H, Cp-*H*), 4.27 (s, 5 H, $C_5H_5$), 6.88 (m, 1 H, *Ph*), 6.94 (d, 2 H, $J$ = 7.9 Hz, $C_6H_4CH_3$), 7.28 (m, 2 H, *Ph*), 7.50 (m, 2 H, *Ph*), 7.64 (d, 2 H, $J$ = 7.9 Hz, $C_6H_4CH_3$) ppm. $^{13}C$ NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ =

  

20.1 ($C_{Ar}$-$CH_3$), 39.9 [N($CH_3$)$_2$], 63.1 (*Cp*), 65.3 (*Cp*), 65.7 (*Cp*), 66.0 (*Cp*), 67.5 (*Cp*), 70.1 (*Cp*), 71.1 (*Cp*), 69.4 (*Cp*), 70.3 (*Cp*), 73.7 (*Cp*-S-*p*Tol), 86.3 (*Cp*-NPh), 89.0 (*Cp*-NPh), 125.7 ($C_{Ar}$), 126.1 ($C_{Ar}$), 126.3 ($C_{Ar}$), 128.8 ($C_{Ar}$), 129.8 ($C_{Ar}$), 133.6 ($C_{Ar}$-CN), 134.9 ($C_{Ar}$-$CH_3$), 136.5 ($C_{Ar}$-S-Cp) ppm. MS (EI): *m*/*z* (%) = 551 (15), 550 (36), 461 (31), 460 (90), 338 (26), 337 (100), 336 (12), 305 (22), 244 (11), 216 (16), 215 (58), 149 (11), 57 (13), 45 (26). HRMS (EI$^+$): $C_{36}H_{35}Fe_2NS$ – $C_6H_3$ = $C_{30}H_{32}Fe_2NS$: calcd. 550.09542; found 550.09558.

**(*S*$_p$)-{Ferrocenyl-(*S*$_p$)-[2-(isopropylsulfanyl)ferrocenyl]-phenylmethyl}dimethylamine (14c):** According to GP4, alcohol **13f** (157 mg, 0.20 mmol) was treated with $HBF_4$·$Et_2O$ (0.2 mL, 1.45 mmol) in diethyl ether (5 mL). The precipitate was isolated and reacted with $Me_2NH$ gas. Aqueous work-up provided the product **14c** as an orange liquid. Yield 102 mg (88%). $[\alpha]_D^{25}$ = +1327.6 (*c* = 0.21, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3431 (s), 3078 (m), 2995 (w), 2963 (m), 2923 (m), 2857 (m), 2815 (m), 2776 (m), 1638 (m), 1598 (w), 1445 (m), 1380 (m), 1261 (m), 1239 (m), 1220 (m), 1154 (w), 1106 (s), 1043 (s), 1001 (s), 815 (vs), 747 (m), 705 (m), 677 (m), 546 (m), 534 (m), 491 (s) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.33 [m, 3 H, CH($CH_3$)$_2$], 1.82 [m, 3 H, CH($CH_3$)$_2$], 2.45 [m, 1 H, C*H*($CH_3$)$_2$], 3.78 [m, 6 H, N($CH_3$)$_2$], 3.98 (m, 2 H, Cp-*H*), 4.05 (m, 1 H, Cp-*H*), 4.08 (m, 1 H, Cp-*H*), 4.13 (s, 1 H, Cp-*H*), 4.17 (s, 1 H, Cp-*H*), 4.20 (s, 1 H, Cp-*H*), 4.29 (s, 5 H, $C_5H_5$), 4.30 (s, 5 H, $C_5H_5$), 7.21 (m, 1 H, *Ph*), 7.26 (m, 2 H, *Ph*), 7.44 (m, 2 H, *Ph*) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 23.1 [CH($CH_3$)$_2$], 23.4 [CH($CH_3$)$_2$], 39.9 [N($CH_3$)$_2$], 52.3 [CH($CH_3$)$_2$], 63.3 (*Cp*), 64.9 (*Cp*), 65.8 (*Cp*), 68.2 (*Cp*), 69.1 (*Cp*), 69.7 (*Cp*), 71.0 (*Cp*), 69.3 (*Cp*), 70.3 (*Cp*), 74.4 (*Cp*-S-*i*Pr), 82.3 (*Cp*-CNPh), 86.4 (*Cp*-CNPh), 125.6 ($C_{Ar}$), 125.8 ($C_{Ar}$), 129.9 ($C_{Ar}$), 134.9 ($C_{Ar}$-CN) ppm. MS (EI): *m*/*z* (%) = 413 (20), 412 (67), 370 (26), 369 (100), 337 (21), 318 (21), 216 (12), 215 (40), 45 (12). HRMS (EI$^+$): $C_{32}H_{35}Fe_2NS$: calcd. 577.14122; found 577.14133.

**General Procedure for the Synthesis of Diferrocenyl Thioketones 16 (GP5):** A solution of the ketone **6** (1.0 equiv.) and Lawesson's reagent (**15**, 1.2 equiv.) in benzene (100 mL/mmol) was heated at reflux for 3 h under argon in a Schlenk flask. The solvent was evaporated and the residue purified by column chromatography providing the thioketone **16** as either a dark oil or solid.

**Ferrocenyl-(*R*$_p$)-(2-methylferrocenyl)methanethione (16a):** According to GP5, a solution of ketone **6** (E$^1$ = Me, 288 mg, 0.70 mmol) and Lawesson's reagent (**15**, 340 mg, 0.84 mmol) in benzene (70 mL) was heated at reflux. Subsequently the solvent was evaporated and the thioketone **16a** was obtained following purification by column chromatography (silica gel, pentane/$Et_2O$, 2:1) as a violet oil. Yield 176 mg (59%). $R_f$ (pentane/ether, 4:1) = 0.71. IR ($CHCl_3$): $\tilde{\nu}$ = 3374 (m), 3092 (m), 2923 (m), 2856 (m), 1725 (m), 1431 (s), 1410 (s), 1377 (m), 1325 (m), 1274 (s), 1124 (m), 1107 (m), 1069 (m), 1003 (m), 820 (s), 771 (w), 753 (w), 553 (w), 482 (vs) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 2.33 (s, 3 H, C$H_3$), 3.96 (s, 5 H, $C_5H_5$), 4.00 (s, 5 H, $C_5H_5$), 4.11 (m, 1 H, Cp-*H*), 4.21 (m, 1 H, Cp-*H*), 4.29 (m, 2 H, Cp-*H*), 4.78 (m, 1 H, Cp-*H*), 5.18 (m, 2 H, Cp-*H*) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 16.0 ($CH_3$), 67.3 (*Cp*), 69.9 (*Cp*), 71.1 (*Cp*), 72.2 (*Cp*), 73.2 (*Cp*), 73.3 (*Cp*), 73.6 (*Cp*), 71.8 (*Cp*), 72.5 (*Cp*), 73.6 (*Cp*-$CH_3$), 82.4 (*Cp*-CS), 84.1 (*Cp*-CS), 231.8 (*C*S) ppm. MS (EI): *m*/*z* (%) = 428 (87) [M$^{\cdot+}$], 427 (18), 426 (11) [M$^{\cdot+}$ – 2], 413 (26), 412 (100) [M$^{\cdot+}$ – $CH_3$], 410 (13), 362 (20), 360 (18), 308 (15), 306 (14), 296 (12), 279 (11), 274 (16), 272 (13), 186 (22), 167 (15), 152 (15), 149 (32), 121 (15), 57 (11), 56 (10). HRMS (EI$^+$): $C_{22}H_{20}Fe_2S$: calcd. 427.99845; found 427.99837.

**Ferrocenyl-(*S*$_p$)-[2-(methylsulfanyl)ferrocenyl]methanethione (16b):** According to GP5, a solution of ketone **6** (E$^1$ = SMe, 222 mg, 0.50 mmol) and Lawesson's reagent (**15**, 243 mg, 0.60 mmol) in benzene (60 mL) was heated at reflux. Subsequently the solvent was evaporated and the thioketone **16b** was obtained following purification by column chromatography (silica gel, pentane/$Et_2O$, 7:1) as a violet solid. Yield 99 mg (43%); m.p. 57 °C. $R_f$ (pentane/ ether, 7:1) = 0.71. IR ($CHCl_3$): $\tilde{\nu}$ = 3356 (m), 3252 (m), 3094 (m), 2989 (m), 2917 (m), 2866 (w), 1433 (s), 1382 (m), 1351 (m), 1301 (m), 1252 (s), 1106 (m), 1056 (m), 1024 (m), 1003 (m), 480 (s) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 2.05 (s, 3 H, SC$H_3$), 4.01 (s, 5 H, $C_5H_5$), 4.04 (s, 5 H, $C_5H_5$), 4.11 (m, 1 H, Cp-*H*), 4.29 (m, 2 H, Cp-*H*), 4.44 (m, 1 H, Cp-*H*), 4.81 (m, 1 H, Cp-*H*), 5.09 (m, 1 H, Cp-*H*), 5.28 (m, 1 H, Cp-*H*) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 18.7 (S$CH_3$), 68.0 (*Cp*), 70.1 (*Cp*), 71.5 (*Cp*), 71.6 (*Cp*), 72.9 (*Cp*), 73.8 (*Cp*), 71.5 (*Cp*), 73.3 (*Cp*), 91.3 (*Cp*-CS), 93.0 (*Cp*-CS), 94.7 (*Cp*-$SCH_3$), 225.1 (*C*S) ppm. MS (EI): *m*/*z* (%) = 461 (28) [M$^{\cdot+}$ + 1], 460 (100) [M$^{\cdot+}$], 458 (13) [M$^{\cdot+}$ – 2], 446 (21), 445 (80), 444 (27), 379 (24), 346 (14), 272 (12), 259 (23), 203 (11), 186 (16), 171 (10), 139 (15). $C_{22}H_{20}Fe_2S_2$ (459.971): calcd. C 57.42, H 4.38; found C 57.01, H 4.81.

**Ferrocenyl-(*S*$_p$)-[2-(isopropylsulfanyl)ferrocenyl]methanethione (16c):** According to GP5, a solution of ketone **6** (E$^1$ = *i*Pr,156 mg, 0.33 mmol) and Lawesson's reagent (**15**, 160 mg, 0.40 mmol) in benzene (30 mL) was heated at reflux. Subsequently the solvent was evaporated and the thioketone **16c** was obtained following purification by column chromatography (silica gel, pentane/$Et_2O$, 2:1) as a violet oil. Yield 150 mg (93%). $R_f$ (pentane/ether, 9:1) = 0.36. IR (KBr): $\tilde{\nu}$ = 3094 (m), 2961 (m), 2923 (m), 2862 (m), 1435 (s), 1415 (m), 1379 (m), 1353 (w), 1295 (s), 1253 (s), 1219 (m), 1155 (m), 1107 (m), 1093 (m), 1068 (m), 1052 (m), 1021 (m), 1003 (m), 821 (s), 756 (vs), 704 (w), 666 (w), 479 (s) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.06 [m, 3 H, SCH(C$H_3$)$_2$], 1.14 [m, 3 H, SCH(C$H_3$)$_2$], 3.04 [m, 1 H, SC*H*($CH_3$)$_2$], 4.05 (s, 5 H, $C_5H_5$), 4.11 (s, 5 H, $C_5H_5$), 4.17 (m, 1 H, Cp-*H*), 4.28 (m, 2 H, Cp-*H*), 4.63 (m, 1 H, Cp-*H*), 4.77 (m, 1 H, Cp-*H*), 5.10 (m, 2 H, Cp-*H*) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 23.1 (SCH-$CH_3$), 23.4 (SCH-$CH_3$), 39.8 [S$CH$($CH_3$)$_2$], 68.0 (*Cp*), 68.2 (*Cp*), 69.5 (*Cp*), 72.9 (*Cp*), 73.4 (*Cp*), 74.3 (*Cp*), 76.0 (*Cp*), 71.5 (*Cp*), 73.6 (*Cp*), 89.6 (*Cp*-CS), 92.1 (*Cp*-CS), 94.3 (*C*-S*i*Pr), 234.3 (*C*S) ppm. MS (EI): *m*/*z* (%) = 488 (58) [M$^{\cdot+}$], 473 (25) [M$^{\cdot+}$ – $CH_3$], 472 (91), 470 (11), 447 (11), 446 (24), 445 (100), 443 (18), 430 (17), 428 (60), 379 (27), 364 (15), 346 (12), 334 (19), 332 (26), 331 (10), 259 (27), 203 (13), 202 (13), 186 (10), 171 (11), 149 (11), 139 (20), 97 (10), 73 (10), 71 (14), 69 (16), 57 (31), 55 (17), 45 (70). HRMS (EI$^+$): $C_{24}H_{24}Fe_2S_2$: calcd. 488.00182; found 488.00176.

**Ferrocenyl-(*S*$_p$)-[2-(4-methylphenylsulfanyl)ferrocenyl]methanethione (16d):** According to GP5, a solution of ketone **6** (E$^1$ = STol, 442 mg, 0.70 mmol) and Lawesson's reagent (**15**, 339 mg, 0.84 mmol) in benzene (70 mL) was heated at reflux. Subsequently the solvent was evaporated and the thioketone **16d** was obtained following purification by column chromatography (silica gel, pentane/$Et_2O$, 2:1) as a violet solid. Yield 195 mg (52%); m.p. 78 °C. $R_f$ (pentane/ether, 4:1) = 0.36. IR (KBr): $\tilde{\nu}$ = 3932 (w), 3431 (m), 3089 (w), 2918 (w), 1639 (w), 1489 (m), 1433 (s), 1411 (m), 1375 (m), 1295 (s), 1255 (s), 1182 (w), 1105 (m), 1068 (w), 1034 (m), 1016 (w), 1000 (m), 906 (w), 819 (vs), 766 (m), 702 (w), 643 (w), 484 (vs) cm$^{-1}$. $^1$HNMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.98 (s, 3 H, C$H_3$), 3.96 (s, 5 H, $C_5H_5$), 4.09 (s, 5 H, $C_5H_5$), 4.32 (m, 3 H, Cp-*H*), 4.59 (m, 1 H, Cp-*H*), 4.71 (m, 1 H, Cp-*H*), 4.93 (m, 1 H, Cp-*H*), 5.29 (m, 1 H, Cp-*H*), 6.85 (m, 2 H, $C_6H_4$), 7.23 (m, 2 H, $C_6H_4$) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 20.9 (*C*H$_3$-Ph), 68.2 (*Cp*), 68.4 (*Cp*), 70.2 (*Cp*), 72.8 (*Cp*), 73.9 (*Cp*), 74.8 (*Cp*), 76.8 (*Cp*), 71.7 (*Cp*), 73.8 (*Cp*), 90.4 (*Cp*-CS), 92.2 (*Cp*-CS), 94.8 (*Cp*-S-*p*Tol), 129.1 (*Ph*-H), 129.8 (*Ph*-H), 135.5 (*Ph*-$CH_3$), 136.8 (*Ph*-

  

SCp), 233.6 (*C*S) ppm. MS (EI): *m*/*z* (%) = 538 (16) [M$^{\cdot+}$ + 2], 537 (32) [M$^{\cdot+}$ + 1], 536 (100) [M$^{\cdot+}$], 534 (15) [M$^{\cdot+}$ – 2], 521 (13) [M$^{\cdot+}$ – $CH_3$], 520 (38), 471 (11), 470 (25), 413 (15), 380 (28), 348 (10), 346 (23), 291 (11), 186 (12). HRMS (EI$^+$): $C_{28}H_{24}Fe_2S_2$: calcd. 536.00182; found 536.00189.

**General Procedure for the Synthesis of Monosubstituted Diferrocenylmethanes 10 (GP6):** To a solution of $LiAlH_4$ (1.1 equiv.) in diethyl ether (10 mL/mmol) was added dropwise a solution of the monosubstituted ketone **6** (1.0 equiv.) in diethyl ether (10 mL/mmol). Following stirring for 30 min, a suspension of $AlCl_3$ (1.1 equiv.) in diethyl ether (10 mL/mmol) was added slowly. The reaction mixture was stirred for 45 min and then quenched by the addition of $H_2O$ (2 mL) and 6 M $H_2SO_4$ (2 mL). The aqueous layer was extracted with diethyl ether (3 × 15 mL) and the organic phase washed with a saturated aqueous $NaHCO_3$ solution and dried with $MgSO_4$. The solvent was evaporated under reduced pressure and the residue purified by column chromatography providing the diferrocenylmethane **10** as either a yellow oil or solid.

**Ferrocenyl-(*S*$_p$)-[2-(methylsulfanyl)ferrocenyl]methane (10a):** According to GP6, $LiAlH_4$ (21 mg, 0.55 mmol) in diethyl ether (5 mL) was added to a solution of ketone **6** (E$^1$ = SMe, 221 mg, 0.50 mmol) in diethyl ether (5 mL). Following the addition of $AlCl_3$ (73 mg, 0.55 mmol) in diethyl ether (5 mL) was the reaction mixture stirred for 45 min. The methane **10a** was obtained by quenching and purification by column chromatography (silica gel, pentane/ether, 9:1) as a yellow solid. Yield 213 mg (99%); m.p. 78 °C. $R_f$ (pentane/ether, 4:1) = 0.94. $[\alpha]_D^{25}$ = –42.7 (*c* = 0.3, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3919 (w), 3448 (m), 3092 (m), 2915 (m), 1637 (w), 1427 (m), 1410 (m), 1386 (w), 1312 (w), 1222 (w), 1171 (w), 1105 (m), 1033 (m), 1000 (s), 970 (m), 924 (w), 811 (vs), 524 (m), 491 (vs), 456 (w) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 2.00 (s, 3 H, SC$H_3$), 3.64 (m, 2 H, C$H_2$), 3.89 (m, 1 H, Cp-*H*), 3.93 (m, 2 H, Cp-*H*), 3.96 (m, 2 H, Cp-*H*), 4.04 (s, 5 H, $C_5H_5$), 4.05 (s, 5 H, $C_5H_5$), 4.15 (m, 1 H, Cp-*H*), 4.21 (m, 1 H, Cp-*H*) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 19.5 (S*C*H$_3$), 27.7 ($CH_2$), 66.2 (*Cp*), 66.5 (*Cp*), 66.7 (*Cp*), 68.4 (*Cp*), 71.1 (*Cp*), 68.0 (*Cp*), 69.3 (*Cp*), 81.2 (*Cp*-$SCH_3$), 87.5 (*Cp*-$CH_2$), 90.6 (*Cp*-$CH_2$) ppm. MS (EI): *m*/*z* (%) = 431 (30) [M$^{\cdot+}$ +1], 430 (100) [M$^{\cdot+}$], 428 (13) [M$^{\cdot+}$ – 2], 383 (33) [M$^{\cdot+}$ – $SCH_3$], 350 (12), 349 (20), 319 (11), 318 (12), 316 (12), 284 (11), 283 (25), 215 (16), 139 (11), 121 (10). $C_{22}H_{22}Fe_2S$ (430.176): calcd. C 61.43, H 5.16; found C 61.13, H 5.33.

**Ferrocenyl-(*S*$_p$)-[2-(isopropylsulfanyl)ferrocenyl]methane (10b):** According to GP6, $LiAlH_4$ (21 mg, 0.55 mmol) in diethyl ether (5 mL) was added to a solution of ketone **6** (E$^1$ = S*i*Pr, 236 mg, 0.50 mmol) in diethyl ether (5 mL). Following the addition of $AlCl_3$ (73 mg, 0.55 mmol) in diethyl ether (5 mL) was the reaction mixture stirred for 45 min. The methane **10b** was obtained by quenching and purification by column chromatography (silica gel, pentane/ether, 9:1) as a yellow oil. Yield 229 mg (100%); m.p. 92 °C. $R_f$ (pentane/ether, 4:1) = 0.93. $[\alpha]_D^{25}$ = +20.0 (*c* = 0.49, $CHCl_3$). IR (capillary): $\tilde{\nu}$ = 3092 (m), 2957 (m), 2922 (m), 2862 (m), 1640 (w), 1462 (m), 1444 (m), 1428 (m), 1411 (m), 1380 (w), 1364 (m), 1239 (m), 1155 (w), 1106 (s), 1050 (m), 1034 (m), 1001 (s), 925 (w), 818 (vs), 484 (vs) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.15 [m, 6 H, SCH(C$H_3$)$_2$], 2.82 [m, 1 H, SC*H*(CH$_3$)$_2$], 3.69 (m, 2 H, C$H_2$), 3.96 (m, 3 H, Cp-*H*), 4.02 (m, 1 H, Cp-*H*), 4.05 (s, 5 H, $C_5H_5$), 4.08 (m, 5 H, $C_5H_5$), 4.15 (s, 2 H, Cp-*H*), 4.32 (m, 1 H, Cp-*H*) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 22.3 (*C*H$_3$), 22.7 (*C*H$_3$), 27.7 (*C*H$_2$), 38.8 (*C*H), 64.9 (*Cp*), 66.5 (*Cp*), 66.6 (*Cp*), 68.1 (*Cp*), 68.7 (*Cp*), 68.8 (*Cp*), 74.2 (*Cp*), 68.0 (*Cp*), 69.4 (*Cp*), 76.9 (*Cp*-S*i*Pr), 87.3 (*Cp*-$CH_2$), 91.7 (*Cp*-$CH_2$) ppm. MS (EI): *m*/*z* (%) = 459 (30) [M$^{\cdot+}$ +1], 430 (100) [M$^{\cdot+}$], 456 (11) [M$^{\cdot+}$ – 2], 350 (26), 349 (13), 316 (11), 283 (18). HRMS (EI$^+$): $C_{24}H_{26}Fe_2S$: calcd. 458.04540; found 458.04538.

**Ferrocenyl-(*S*$_p$)-[2-(4-methylphenylsulfanyl)ferrocenyl]methane (10c):** According to GP6, $LiAlH_4$ (21 mg, 0.55 mmol) in diethyl ether (5 mL) was added to a solution of ketone **6** (E$^1$ = STol, 260 mg, 0.50 mmol) in diethyl ether (5 mL). Following the addition of $AlCl_3$ (73 mg, 0.55 mmol) in diethyl ether (5 mL) was the reaction mixture stirred for 45 min. The methane **10c** was obtained by quenching and purification by column chromatography (silica gel, pentane/ether, 9:1) as a yellow solid. Yield 253 mg (100%); m.p. 65 °C. $R_f$ (pentane/ether, 4:1) = 0.90. $[\alpha]_D^{25}$ = +100.7 (*c* = 0.27, $CHCl_3$). IR (capillary): $\tilde{\nu}$ = 3093 (m), 3012 (m), 2919 (w), 1492 (m), 1219 (m), 1106 (m), 1087 (w), 1023 (m), 1001 (m), 806 (s), 757 (vs), 485 (s) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.98 (s, 3 H, SC$H_3$), 3.63 (m, 2 H, C$H_2$), 3.85 (m, 3 H, Cp-*H*), 3.91 (m, 2 H, Cp-*H*), 3.96 (s, 5 H, $C_5H_5$), 4.07 (s, 5 H, $C_5H_5$), 4.12 (m, 1 H, Cp-*H*), 4.35 (m, 1 H, Cp-*H*), 6.82 (d, *J* = 8.0 Hz, 2 H, $C_6H_4$), 7.13 (d, *J* = 8.0 Hz, 2 H, $C_6H_4$) ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 19.8 (*C*H$_3$), 27.5 (*C*H$_2$), 66.5 (*Cp*), 66.7 (*Cp*), 67.5 (*Cp*), 68.1 (*Cp*), 68.4 (*Cp*), 69.2 (*Cp*), 74.0 (*Cp*), 67.9 (*Cp*), 69.5 (*Cp*), 74.7 (*Cp*-S-*p*Tol), 86.8 (*Cp*-$CH_2$), 92.5 (*Cp*-$CH_2$), 125.3 ($C_{Ar}$), 128.7 ($C_{Ar}$), 133.5 ($C_{Ar}$-$CH_3$), 136.7 ($C_{Ar}$-SCp) ppm. MS (EI): *m*/*z* (%) = 508 (11) [M$^{\cdot+}$ +2], 507 (36) [M$^{\cdot+}$ +1], 506 (100) [M$^{\cdot+}$], 504 (13) [M$^{\cdot+}$ – 2], 383 (15), 373 (10). HRMS (EI$^+$): $C_{28}H_{26}Fe_2S$: calcd. 506.04540; found 506.04550.

**General Procedure for the Synthesis of *P*-Substituted SAMP Hydrazines 18 (GP7):** The phosphane-substituted hydrazone **5** was dissolved in $CH_2Cl_2$/ether (1:1, 10 mL/mmol) and cooled to –20 °C. Catecholborane (20 equiv.) was added and the mixture was warmed to room temperature upon completion of the reaction. The solution was re-cooled to 0 °C and quenched with a saturated aqueous $NH_4Cl$ solution. The phases were separated and the organic layer was washed twice with a saturated aqueous $K_2CO_3$ solution and brine. Following drying over $MgSO_4$ the crude product was purified by column chromatography to afford either an orange oil or solid.

***N*-1-(*S*)-[(*S*$_p$)-[2-(1-Boranato-1,1-diphenylphosphanyl)ferrocenylmethyl]-[(2*S*)-(2-methoxymethyl-1-pyrrolidin]amine (18a):** According to GP7, hydrazone **5a** (710 mg, 1.00 mmol) was treated with catecholborane (2.40 g, 20 mmol) for 24 h in $CH_2Cl_2$/ether (1:1, 40 mL). Following aqueous work-up and purification by column chromatography (silica gel, pentane/ether, 9:1) the product **18a** was obtained as an orange solid. Yield 369 mg (52%); m.p. 92 °C. $R_f$ (pentane/ether, 4:1) = 0.55. $[\alpha]_D^{25}$ = –408.7 (*c* = 0.23, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3857 (w), 3433 (vs), 3080 (w), 3054 (w), 2965 (m), 2921 (m), 2968 (s), 2821 (m), 2435 (m), 2389 (m), 2347 (m), 1637 (m), 1533 (w), 1483 (w), 1436 (m), 1384 (m), 1319 (w), 1257 (m), 1221 (m), 1198 (w), 1158 (m), 1106 (vs), 1061 (s), 1002 (m), 924 (w), 822 (s), 741 (s), 695 (s), 628 (w), 612 (m), 592 (w), 534 (w), 492 (vs) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 1.60 [m, 1 H, N(CH$_2$)C$H_2$], 1.74 [m, 1 H, N(CH$_2$)C$H_2$], 2.09 [m, 2 H, N(CH$_2$)$_2$C$H_2$], 2.50 (m, 2 H, NC$H_2$), 2.64 (m, 1 H, NC*H*CH$_2$), 2.93 (m, 1 H, NC*H*), 3.11 (s, 3 H, OC$H_3$), 3.48 (m, 1 H, N*H*), 3.58 (m, 2 H, OC$H_2$), 3.98 (m, 1 H, Cp-*H*), 4.07 (s, 5 H, $C_5H_5$), 4.12 (m, 2 H, Cp-*H*), 4.22 (m, 1 H, Cp-*H*), 4.43 (s, 5 H, $C_5H_5$), 4.91 (m, 1 H, Cp-*H*), 5.44 (m, 1 H, Cp-*H*), 5.82 (m, 1 H, Cp-*H*), 7.07 (m, 6 H, *Ph*), 7.80 (m, 4 H, *Ph*) ppm. $^{11}$B NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ = –33.45 ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 24.4 (*C*H$_2$-CH$_2$N), 27.8 (*C*H$_2$-CHN), 57.2 (*C*H$_2$-N), 58.8 (O*C*H$_3$), 68.3 (*Cp*), 68.8 (*Cp*), 69.5 (*Cp*), 71.9 (*Cp*), 72.5 (*Cp*), 72.9 (*Cp*), 72.8 (*Cp*), 64.7 (*C*HN), 70.3 (*Cp*), 71.6 (*Cp*), 75.4 (*C*H$_2$-OCH$_3$), 76.3 (*Cp*-CHN), 79.7 (*Cp*-CHN), 90.1 (*Cp*-$PPh_2$), 128.2 ($C_{Ar}$), 129.4

  

($C_{Ar}$), 130.2 ($C_{Ar}$), 131.7 (d, $J_{CP}$ = 8.6 Hz, $C_{Ar}$H-$C_{Ar}$P), 134.7 (d, $J_{CP}$ = 8.0 Hz, $C_{Ar}$H-$C_{Ar}$P), 135.2 (d, $J_{CP}$ = 20.1 Hz, $C_{Ar}$-P), 136.0 (d, $J_{CP}$ = 35.1 Hz, $C_{Ar}$-P), 146.4 (*C*HN) ppm. $^{31}$P NMR (121 MHz, $C_6D_6$, 25 °C): $\delta$ = 20.25 ppm. MS (EI): *m*/*z* (%) = 581 (40) [$M^{\cdot+}$ + 1], 580 (100) [$M^{\cdot+}$], 578 (12), 290 (11). $C_{39}H_{44}BFe_2N_2OP$ (710.389): calcd. C 65.94, H 6.24, N 3.94; found C 65.89, H 6.12, N 3.89.

***N*-1-(*S*)-[(*S*$_p$)-2-(1-Boranato-1,1-diisopropylphosphanyl)ferrocenylmethyl]-[(2*S*)-2-methoxymethyl-1-pyrrolidin]amine (18b):** According to GP7, hydrazone **5b** (640 mg, 1.00 mmol) was treated with catecholborane (2.40 g, 20 mmol) for 30 h in $CH_2Cl_2$/ether (1:1, 40 mL). Following aqueous work-up and purification by column chromatography (silica gel, pentane/ether, 9:1) the product **18b** was obtained as a red solid. Yield 559 mg (87%); m.p. 162 °C. $R_f$ (pentane/ether, 4:1) = 0.50. $[a]_D^{25}$ = –861.1 (*c* = 0.45, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3926 (w), 3452 (m), 3095 (m), 2975 (s), 2945 (s), 2876 (s), 2841 (s), 2813 (m), 2382 (vs), 2264 (m), 1641 (w), 1576 (m), 1451 (s), 1413 (m), 1384 (m), 1330 (m), 1250 (m), 1200 (m), 1185 (m), 1151 (m), 1124 (s), 1105 (s), 1058 (s), 1040 (s), 1004 (m), 975 (m), 932 (m), 883 (m), 827 (vs), 750 (w), 681 (m), 480 (s) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 0.97 {dd, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 13.5 Hz, 3 H, P[CH(C*H*$_3$)$_2$]$_2$}, 1.13 {m, 6 H, P[CH(C*H*$_3$)$_2$]$_2$}, 1.35 (m, 1 H, NC*H*CH$_2$), 1.62 {dd, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 16.2 Hz, 3 H, P[CH-(C*H*$_3$)$_2$]$_2$}, 1.68–1.82 [m, 4 H, (NCH$_2$)C*H*$_2$, (NCH$_2$)$_2$C*H*$_2$], 2.04 {m, 2 H, P[C*H*(CH$_3$)$_2$]$_2$, NCH*H*}, 2.59 (m, 1 H, NCH*H*), 3.00 {sept., $^3J_{HH}$ = 7.1 Hz, 1 H, P[C*H*(CH$_3$)$_2$]$_2$}, 3.21 (s, 3 H, OC*H*$_3$), 3.30 (m, 1 H, NC*H*), 3.48 (m, 1 H, OC*H*$_2$), 3.60 (m, 1 H, OC*H*$_2$), 3.75 (m, 1 H, N*H*), 3.94 (m, 1 H, Cp-*H*), 3.96 (s, 5 H, $C_5H_5$), 4.12 (m, 2 H, Cp-*H*), 4.25 (m, 1 H, Cp-*H*), 4.45 (s, 5 H, $C_5H_5$), 4.79 (m, 1 H, Cp-*H*), 4.95 (m, 1 H, Cp-*H*), 5.23 (m, 1 H, Cp-*H*) ppm. $^{11}$B NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ = –41.29 ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 17.9 [CH(*C*H$_3$)$_2$], 18.2 [CH(*C*H$_3$)$_2$], 18.4 [CH(*C*H$_3$)$_2$], 20.1 [CH(*C*H$_3$)$_2$], 22.7 [d, $^1J_{CP}$ = 34.1 Hz, P*C*H-(CH$_3$)$_2$], 23.4 (*C*H$_2$-CH$_2$N), 23.7 [d, $^1J_{CP}$ = 32.6 Hz, P*C*H(CH$_3$)$_2$], 27.9 (*C*H$_2$-CHN), 54.7 (*C*H$_2$-N), 59.1 (O*C*H$_3$), 67.0 (*C*HN), 68.3 (*Cp*), 69.8 (*Cp*), 70.8 (*Cp*), 72.4 (*Cp*), 74.4 (*Cp*), 74.4 (*Cp*), 76.2 (*Cp*), 76.4 (*Cp*), 70.0 (*Cp*), 72.0 (*Cp*), 76.5 (d, $^1J_{CP}$ = 15.0 Hz, *Cp*-P*i*Pr$_2$), 76.6 (*C*H$_2$-OCH$_3$), 79.7 (*Cp*-CHN), 91.5 (*Cp*-CHN), 157.6 (*C*NHCp$_2$) ppm. $^{31}$P NMR (121 MHz, $C_6D_6$, 25 °C): $\delta$ = 38.32 ppm. MS (EI): *m*/*z* (%) = 527 (27) [$M^{\cdot+}$ +1], 526 (100) [$M^{\cdot+}$], 525 (27) [$M^{\cdot+}$ – 1], 524 (14), 512 (37) [$M^{\cdot+}$ – $BH_3$], 511 (41), 510 (14), 425 (19). $C_{33}H_{48}BFe_2N_2OP$ (642.230): calcd. C 61.72, H 7.53, N 4.36; found C 61.86, H 7.16, N 4.00.

**General Procedure for the Synthesis of *P*-Substituted Diferrocenylmethanes 10 (GP8):** A solution of the phosphane-substituted hydrazine **18** (1.0 equiv.) in $CH_2Cl_2$ (50 mL/mmol) was cooled to 0 °C and $HBF_4$ (3.0 equiv.) was added dropwise. Following stirring for 60 min, $HBEt_3Li$ (5.0 equiv.) was added. The reaction mixture was stirred for an additional 15 min and then quenched by the addition of a saturated aqueous $NH_4Cl$ solution (2 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL), the combined organic extracts were washed with brine and dried with $MgSO_4$. The crude product **10** was purified by column chromatography to yield either an orange-yellow oil or solid.

**[(*S*$_p$)-2-(1-Boranato-1,1-diphenylphosphanyl)ferrocenyl]-ferrocenylmethane (10a):** According to GP8, $HBF_4$ (0.15 mL, 1.10 mmol) was added to hydrazine **18a** (213 mg, 0.30 mmol) in $CH_2Cl_2$ (15 mL). Following stirring for 60 min the solution was slowly treated with $HBEt_3Li$ (4.5 mL, 4.50 mmol). Quenching the reaction mixture and purification by column chromatography (silica gel, pentane/ether, 30:1) yielded the product **10a** as an orange oil. Yield 80 mg (46%). $R_f$ (pentane/ether, 4:1) = 0.77. $[a]_D^{25}$ = –102.2 (*c* = 0.45, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3446 (vs), 3088 (m), 3057 (w), 2925 (w), 2390 (s), 2348 (m), 1637 (m), 1482 (w), 1436 (w), 1384 (w), 1172 (w), 1106 (s), 1062 (m), 1000 (m), 821 (s), 741 (s), 698 (s), 640 (m), 608 (w), 482 (s) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 3.41 (s, 2 H, C*H*$_2$), 3.73 (m, 1 H, Cp-*H*), 3.78 (m, 1 H, Cp-*H*), 3.86 (m, 1 H, Cp-*H*), 3.91 (m, 1 H, Cp-*H*), 3.96 (m, 1 H, Cp-*H*), 3.98 (s, 5 H, $C_5H_5$), 4.07 (m, 1 H, Cp-*H*), 4.17 (s, 5 H, $C_5H_5$), 4.22 (m, 1 H, Cp-*H*), 6.94–7.04 (m, 6 H, *Ph*), 7.57 (m, 2 H, *Ph*), 7.78 (m, 2 H, *Ph*) ppm. $^{11}$B NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ = –35.46 ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 29.4 (CH$_2$), 67.5 (*Cp*), 67.6 (*Cp*), 69.7 (*Cp*), 69.5 (*Cp*), 69.8 (*Cp*), 69.9 (*Cp*), 70.6 (*Cp*), 69.1 (*Cp*), 70.9 (*Cp*), 72.9 (*Cp*-CH$_2$), 73.0 (*Cp*-CH$_2$), 87.5 (*Cp*-PPh$_2$), 127.7 ($C_{Ar}$), 128.0 ($C_{Ar}$), 128.4 ($C_{Ar}$), 128.5 ($C_{Ar}$), 128.7 ($C_{Ar}$), 130.9 ($C_{Ar}$), 133.1 ($C_{Ar}$), 133.2 ($C_{Ar}$), 133.7 ($C_{Ar}$), 133.9 ($C_{Ar}$), 182.1 ($C_{Ar}$-P), 185.3 ($C_{Ar}$-P) ppm. $^{31}$P NMR (121 MHz, $C_6D_6$, 25 °C): $\delta$ = 16.66 ppm. MS (EI): *m*/*z* (%) = 582 (22) [$M^{\cdot+}$ – 2], 581 (14) [$M^{\cdot+}$], 580 (24) [$M^{\cdot+}$], 569 (40), 568 (100) [$M^{\cdot+}$ – $BH_3$], 566 (13), 503 (16), 501 (13), 251 (11). $C_{33}H_{32}BFe_2P$ (582.095): calcd. C 68.09, H 5.54; found C 68.35, H 5.84.

**[(*S*$_p$)-2-(1-Boranato-1,1-diisopropylphosphanyl)ferrocenyl]-ferrocenyl-methane (10b):** According to GP8, $HBF_4$ (0.15 mL, 1.10 mmol) was added to hydrazine **18b** (192 mg, 0.30 mmol) in $CH_2Cl_2$ (15 mL). Following stirring for 60 min the solution was slowly treated with $HBEt_3Li$ (1.5 mL, 1.5 mmol). Quenching the reaction mixture and purification by column chromatography (silica gel, pentane/ether, 40:1) yielded the product **10b** as an orange-yellow solid. Yield 92 mg (60%); m.p. 86 °C. $R_f$ (pentane/ether, 4:1) = 0.79. $[a]_D^{25}$ = +90.9 (*c* = 0.34, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3924 (w), 3438 (s), 3081 (w), 2982 (m), 2926 (s), 2871 (m), 2400 (s), 2367 (s), 2338 (s), 2271 (s), 1640 (w), 1466 (s), 1424 (m), 1409 (m), 1384 (m), 1367 (w), 1275 (m), 1250 (m), 1227 (m), 1157 (m), 1133 (m), 1104 (m), 1088 (w), 1068 (m), 1044 (s), 1029 (m), 1000 (m), 931 (w), 888 (m), 825 (vs), 761 (m), 695 (m), 635 (m), 599 (m), 583 (m), 529 (w), 495 (s), 479 (s) cm$^{-1}$. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ = 0.95 {dd, $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 14.0 Hz, 3 H, P[CH(C*H*$_3$)$_2$]$_2$}, 1.09 {dd, $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 14.0 Hz, 3 H, P[CH(C*H*$_3$)$_2$]$_2$}, 1.10 {dd, $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 14.3 Hz, 3 H, P[CH(C*H*$_3$)$_2$]$_2$}, 1.27 {dd, $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 14.0 Hz, 3 H, P[CH(C*H*$_3$)$_2$]$_2$}, 1.96 {m, 2 H, P[C*H*-(CH$_3$)$_2$]$_2$}, 3.74 (m, 2 H, C*H*$_2$), 3.98 (m, 4 H, Cp-*H*), 4.09 (s, 5 H, $C_5H_5$), 4.12 (m, 2 H, Cp-*H*), 4.17 (s, 5 H, $C_5H_5$), 4.21 (m, 1 H, Cp-*H*) ppm. $^{11}$B NMR (160 MHz, $C_6D_6$, 25 °C): $\delta$ = –40.98 ppm. $^{13}$C NMR (75 MHz, $C_6D_6$, 25 °C): $\delta$ = 17.1 (*C*H$_3$), 17.7 (*C*H$_3$), 17.8 (*C*H$_3$), 18.6 (*C*H$_3$), 22.7 [d, $^1J_{CP}$ = 34.4 Hz, P*C*H(CH$_3$)$_2$], 25.2 [d, $^1J_{CP}$ = 33.3 Hz, P*C*H(CH$_3$)$_2$], 30.1 (CH$_2$), 67.6 (*Cp*), 67.8 (*Cp*), 68.9 (*Cp*), 69.0 (*Cp*), 69.5 (*Cp*), 69.8 (*Cp*), 71.5 (*Cp*), 69.2 (*Cp*), 71.1 (*Cp*), 87.1 (*Cp*-CH$_2$), 93.0 (*Cp*-CH$_2$), 115.0 (*Cp*-P*i*Pr) ppm. $^{31}$P NMR (121 MHz, $C_6D_6$, 25 °C): $\delta$ = 33.25 ppm. MS (EI): *m*/*z* (%) = 515 (23) [$M^{\cdot+}$ +1], 514 (68) [$M^{\cdot+}$], 513 (18) [$M^{\cdot+}$ – 1], 512 (13) [$M^{\cdot+}$ – 2], 501 (35), 500 (100) [–$BH_3$], 499 (17), 498 (15), 458 (24), 457 (51), 434 (26), 349 (16), 348 (28), 347 (21), 346 (14), 217 (12). HRMS (EI$^+$): $C_{27}H_{36}BFe_2P$: calcd. 514.13464; found 514.13457.

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