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Asymmetric synthesis of planar chiral 2-mono- and 2,2′-disubstituted 1,1′-bisbenzoylferrocenes

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Abstract

An efficient and flexible asymmetric synthesis of planar chiral 2-mono- and 2,2′-disubstituted 1,1′-bisbenzoylferrocenes **4** and **6** is reported. Key step is a highly diastereoselective *ortho*-metalation of 1,1′-bisbenzoylferrocene **1** via the corresponding bis-SAMP-hydrazone **2** (de ≥ 96%), followed by trapping with various carbon, silicon, phosphorus and sulfur electrophiles. Cleavage of the monosubstituted hydrazones **3** led to monosubstituted ketones **4** (ee ≥ 98%). Further *ortho*-substitution of the hydrazones **3** afforded 2,2′-disubstituted hydrazones **5**, which could be cleaved to disubstituted ferrocenyl diketones **6** (ee ≥ 99%). The new methodology allows a broad and flexible fine-tuning of ferrocenyl ligands desired in asymmetric catalysis. Ozonolysis or reductive hydrazone cleavage using $TiCl_3$ or $SnCl_2$ were the methods of choice to remove the auxiliary.

Keywords: Asymmetric synthesis; *ortho*-Metalation; Hydrazones; 1,1′-Ferrocenyl diketones; Planar chirality

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1. Introduction

Planar chiral ferrocenes have received a surge of interest over the last years [1]. Although various methods for the asymmetric synthesis of planar chiral *ortho*-functionalised ferrocenes have been developed [2–11], the asymmetric synthesis of planar chiral ferrocenyl ketones turned out to be difficult. Predominantly, they have been prepared by resolution methods [12] or by oxidation of planar chiral alcohols [5,13], which in turn are accessible from the corresponding amines or aldehydes. In our group, we have recently developed a direct route to planar chiral *ortho*-functionalised ferrocenyl ketones, which turned out to be applicable in the asymmetric synthesis of selectively substituted 1,1′-ferrocenyl diketones, too [14–16].

2. Results and discussion

In this paper, we describe the enantioselective synthesis of mono- and di-*ortho*-substituted ferrocenyl diketones via our SAMP/RAMP-hydrazone method [17] (SAMP and RAMP = (*S*)- and (*R*)-1-amino-2-methoxymethylpyrrolidine). Key step is the stepwise diastereoselective *ortho*-metalation of 1,1′-ferrocenyl diketone bis-SAMP-hydrazone **2**. We started from 1,1′-bisbenzoylferrocene **1**, easily prepared by Friedel–Crafts-bisacylation of ferrocene in 87% yield [18]. For the conversion of **1** to the corresponding bis-SAMP-hydrazone **2**, a method previously described for the synthesis of *N*,*N*-dimethylhydrazones [19] and successfully applied in the synthesis of ferrocenyl mono-SAMP-hydrazones [16] was used. The usual methods for the synthesis of SAMP-hydrazones failed, because of the unfavourable steric and electronic effects. The conversion of **1** led almost exclusively to the *EE*-isomer of the bis-hydrazone **2**. The subsequent diastereoselective *ortho*-metalation selectively occurred at one ring with 2–2.5 equivalents of ^{n}BuLi in THF at −78 °C, followed by trapping with various types of electrophiles (Scheme 1). The use of ^{n}BuLi turned out to be most effective, because the application of ^{s}BuLi and ^{t}BuLi

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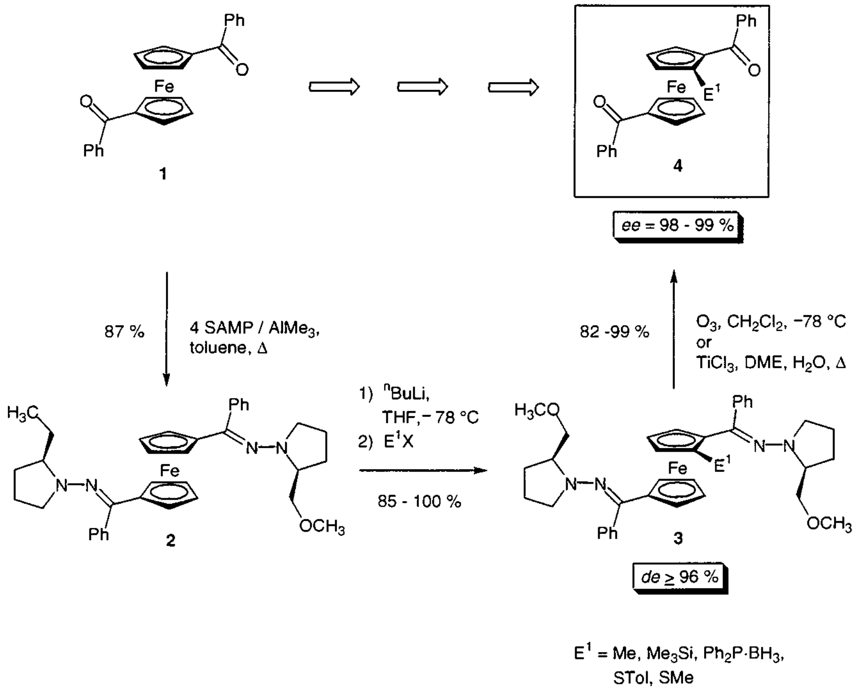


Scheme 1.

led to lower yields and the formation of disubstituted products.

Within our studies, we demonstrate the broad applicability of this method by using alkyl-, silyl-, phosphin- and sulfur electrophiles (Table 1). We obtained the desired products in very good yields (85–100%) and high diastereoselectivities (de $\geq$ 96%). It was observed that the phosphines prepared undergo a rapid oxidation and thus needed to be protected. The use of BH_3 turned out to be advantageous, as the borane adducts are very stable [16].

The absolute configuration of substituted mono-SAMP-hydrazones of ferrocene has been determined previously by NOE experiments and X-ray-structure analysis [16]. The configuration given for the present bishydrazones **3** are based on these assignments.

The monosubstituted bis-SAMP-hydrazones **3** prepared, could either undergo a second diastereoselective *ortho*-substitution under the same conditions to lead to 2,2′-substituted bis-SAMP-hydrazones **5** (Scheme 2) or could be cleaved to produce mono-substituted diketones **4** (Scheme 1).

In case of second substitutions we applied alkylation, silylation, phosphinylation, hydroxyalkylation and sulfenylation reactions in good yields (45–89%) and high diastereoselectivities (de $\geq$ 96%) (Table 2). In the second electrophilic substitution, the phosphinylation turned out to be more difficult probably due to steric and electronic effects, combined with the increasing tendency of oxidation. Nevertheless, the new method allows the successive highly diastereoselective introduction of two different electrophiles.

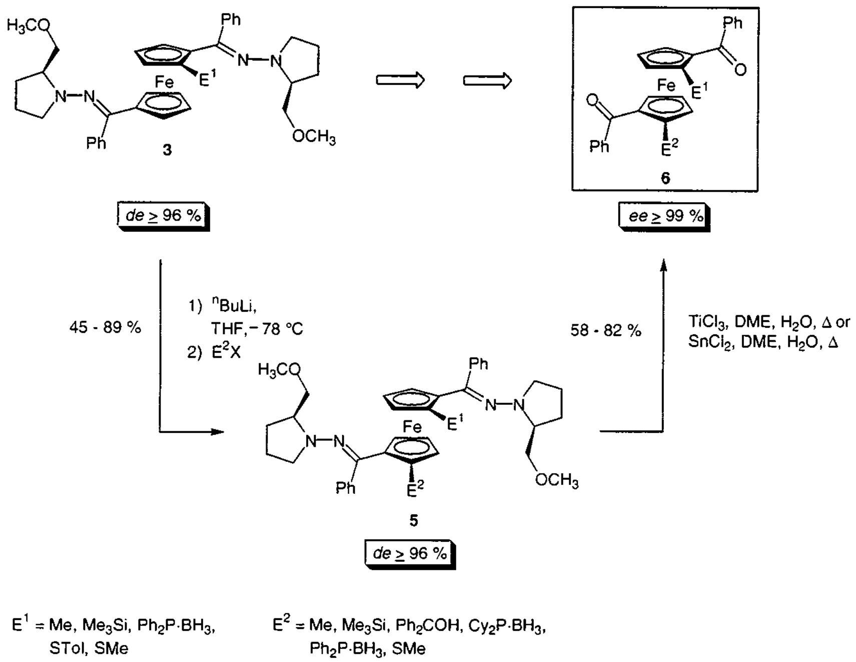
Using 2.4 equivalents ^{s}BuLi, it was possible to obtain the C_2-symmetrical disubstituted hydrazone **5a** in a one-pot-reaction in 54% yield and a diasteriomeric excess of 92%. The diastereoselectivities of the planar chiral hydrazones **3** and **5** were determined by ^{1}H- and ^{13}C-NMR spectroscopy.

To obtain the substituted diketones **4** and **6**, it was necessary to cleave the corresponding SAMP-hydrazones. For this purpose several methods turned out to be very effective. Ozonolysis in dichloromethane at -78 °C led to very good yields (92–99%). In some cases, the reductive cleavage with *Lewis* acids like $SnCl_2$ or $TiCl_3$ in refluxing DME [20] turned out to be an efficient alternative (Table 3).

Sn(II) and Ti(III) are oxidised to Sn(IV) and Ti(IV), respectively, forming a colourless precipitate. We sup-

Table 1
Diastereoselective synthesis of planar chiral monosubstituted bis-SAMP-hydrazones (**3**)

	E^1	Yield (%)	de (%)	Configuration
3a	Me	85	$\geq$96	(S, S, R_p)
3b	$SiMe_3$	90	$\geq$96	(S, S, S_p)
3c	$Ph_2P{\cdot}BH_3$	85	$\geq$96	(S, S, S_p)
3d	STol	86	$\geq$96	(S, S, S_p)
3e	SMe	100	$\geq$96	(S, S, S_p)



Scheme 2.

Table 2
Diastereoselective synthesis of planar chiral 1,1′-disubstituted bis-SAMP-hydrazones (**5**)

	E^1	E^2	Yield (%)	de (%)	Configuration
5a	Me	Me	54	92	(S, S, R_p, R_p)
5b	Me	$SiMe_3$	59	≥96	(S, S, S_p, R_p)
5c	Me	Ph_2COH	77	≥96	(S, S, S_p, R_p)
5d	$Ph_2P{\cdot}BH_3$	$Cy_2P{\cdot}BH_3$	45	≥96	(S, S, S_p, S_p)
5e	SMe	$Ph_2P{\cdot}BH_3$	46	≥96	(S, S, S_p, S_p)
5f	STol	SMe	89	≥96	(S, S, S_p, S_p)

Table 3
Synthesis of the planar chiral ketones **4** and **6**

	E^1	E^2	Yield (%)	Cleavage reagent	ee (%)	Configuration
4a	Me	–	92	O_3	98	(R_p)
4b	$SiMe_3$	–	99	O_3	99	(S_p)
4c	STol	–	82	$TiCl_3$	98	(S_p)
4d	SMe	–	84	$TiCl_3$	98	(S_p)
4e	$Ph_2P{\cdot}BH_3$	–	92	O_3	n.d.	(S_p)
6a	Me	Ph_2COH	58	$SnCl_2$	≥99	(R_p, R_p)
6b	SMe	STol	82	$TiCl_3$	≥99	(S_p, S_p)

pose that the reducing agent first cleaved the N–N bond leading to (*S*)-2-methoxymethylpyrrolidine (SMP) and the corresponding ferrocenyl-ketimine, which was easily hydrolysed to the ketone. A reductive cleavage of sulfur-substituted ferrocenes **3d** and **e** and **5f** with $TiCl_3$ was very successful and resulted in the mono- and bissulfenylated ketones **4c** and **d** and **6b**, in good yields (82–84%) and excellent enantiomeric exesses (*ee* = 98–≥ 99%).

3. Conclusions

In summary, we have developed a flexible synthesis of 2-mono- and 2,2′-disubstituted 1,1′-ferrocenyl diketones **4** and **6** in good yields and excellent enantioselectivities employing the SAMP/RAMP hydrazone method. The application of these novel compounds as ligands in asymmetric catalysis remains to be investigated.

4. Experimental

4.1. General remarks

All reactions with moisture- and air-sensitive compounds were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were dried and distilled prior to use. Column chromatography: Merck silica gel 60, 0.040–0.063 mm (230–400 mesh). Optical rotation values: Perkin–Elmer P 241 (254 nm), solvents Merck UVASOL quality. Melting points (uncorrected): Büchi 510. IR: Perkin–Elmer FT/IR 1750. Assinments of signals: w, weak; m, medium; s, strong; vs, very strong. NMR: Varian Gemini 300 (300 and 75 MHz for ^{1}H- and ^{13}C-, respectively), Varian Inova 400 (400, 100 and 162 MHz for ^{1}H-, ^{13}C- and ^{31}P-, respectively), Varian Unity 500 (500, 125, 202 and 160 MHz for ^{1}H-, ^{13}C-, ^{31}P- and ^{11}B-, respectively), C_6D_6 or $CDCl_3$ as solvent, TMS as internal standard. MS Finnigan MAT 212 (100 eV) and Finnigan SSQ 7000 (70 eV). Elemental analyses (C, H, N): Elementar Vario EL. High-resolution MS: Finnigan MAT, MAT 95. The diastereomeric excesses were determined by NMR-spectroscopy. The enantiomeric excesses were determined by HPLC employing chiral stationary phases.

4.2. 1,1′-Bisbenzoylferrocene (**1**)

To a suspension of $AlCl_3$ (15.20 g, 114.0 mmol) in 30 ml CH_2Cl_2 benzoylchloride (15.26 g, 108.6 mmol) was added. The resulting mixture was stirred until the dissolvation of the $AlCl_3$ was nearly over and then slowly added to a solution of ferrocene (10.0 g, 53.8 mmol) in 40 ml CH_2Cl_2. After 3 days stirring at room temperature (r.t.), the reaction mixture was poured onto crushed ice–aqueous saturated $NaHCO_3$. The aqueous phase was extracted four times with CH_2Cl_2. The collected organic phase was washed twice with saturated aqueous $NaHCO_3$ and three times with brine. After drying over $MgSO_4$ the solution was concentrated under reduced pressure. Finally, the crude product was purified by column chromatography on silica gel (pentane–Et_2O 2:1).

Yield: 18.48 g (87%, dark red crystals); m.p.: 105 °C. $R_f = 0.24$ (pentane–Et_2O 2:1). IR (KBr, cm^{-1}): ν 3109 (w), 3100 (w), 3084 (m), 3064 (w), 3036 (w), 1633 (vs), 1598 (m), 1577 (m), 1528 (w), 1449 (m), 1440 (m), 1400 (w), 1374 (m), 1318 (w), 1310 (w), 1289 (s), 1171 (m), 1053 (w), 1027 (m), 954 (w), 859 (m), 843 (w), 899 (w), 800 (w), 728 (w), 699 (m), 670 (w), 505 (w). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.58 (t, 4H, $J = 2.1$ Hz, Cp-H), 4.92 (t, 4H, $J = 2.1$ Hz, Cp-H), 7.43 (m, 4H, m-C_6H_5), 7.54 (m, 2H, p-C_6H_5), 7.79 (m, 4H, o-C_6H_5). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 72.99, 74.53, 79.36, 127.92, 128.13, 131.71, 138.89, 197.66. MS (100 eV, CI, H_2O); m/z (relative intensity, %): 395 ([$M^{+\bullet} + 1$], 6) 291 ([$M^{+\bullet} - COC_6H_5$], 12), 290 (68), 190 (11), 105 ([$C_6H_5CO^+$], 100), 78 (32), 77 (78), 51 (15). Anal. Found: C, 73.28; H, 4.68. Calc. for $C_{24}H_{18}FeO_2$ (394.24): C, 73.12; H, 4.60%.

4.3. 1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-(E)-[phenylmethylideneamino]}-ferrocene (**2**)

In a Schlenk flask with an attached reflux condenser, a solution of $AlMe_3$ (21 ml, 42.0 mmol, 2 M in toluene) in 80 ml toluene was placed and treated slowly with SAMP (5.48 g, 42.0 mmol). After the evolution of methane subsided, the mixture was refluxed for 7 h. A solution of ketone **1** (3.94 g, 10.0 mmol), dissolved in 40 ml toluene was added dropwise to the red–brown solution. The mixture was refluxed for additional 7 h, cooled to 0 °C and poured onto crushed ice–aqueous saturated $NaHCO_3$. The organic layer was separated and washed with saturated aqueous $NaHCO_3$ and brine. After drying over $MgSO_4$ and concentrating under reduced pressure, the crude product was purified by column chromatography on silica gel (pentane–Et_2O 4:1)

Yield: 4.69 g (76%, dark red crystals); m.p.: 72 °C. $R_f = 0.42$ (pentane–Et_2O 2:1). $[\alpha]_D^{25} = -813.6$ ($c = 0.76$, $CHCl_3$). IR ($CHCl_3$, cm^{-1}): ν 3081 (m), 3056 (m), 2971 (s), 2924 (s), 2874 (vs), 2826 (s), 2731 (w), 1565 (m), 1492 (m), 1460 (s), 1443 (s), 1382 (m), 1337 (m), 1321 (m), 1295 (m), 1280 (m), 1219 (s), 1195 (s), 1112 (vs), 1072 (s), 1053 (s), 1025 (s), 1002 (m), 970 (m), 904 (m), 877 (m), 825 (m), 774 (s), 757 (s), 721 (m), 700 (vs), 667 (m), 620 (w), 601 (w), 576 (m), 505 (s). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 1.49–1.93 (m, 8H, β-ring-CH_2), 2.27 (m, 2H, NCHH), 2.55 (m, 2H, NCHH), 3.42 (s, 6H, OCH_3), 3.50 (m, 2H, OCHH), 3.70 (dd, 2H, $J = 9.0$, 3.9 Hz, NCH), 4.21 (m, 4H, Cp-H), 4.38 (m, 4H, Cp-H), 7.27–7.38 (m, 6H, m-C_6H_5, p-C_6H_5), 7.43 (m, 4H, o-C_6H_5). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 23.05, 26.79, 54.55, 59.20, 66.30, 67.98, 68.17, 70.51, 70.55, 76.04, 86.93, 127.26, 127.66, 128.56, 138.02, 148.64. CIMS (100 eV, H_2O); m/z (relative intensity, %): 619 ([$M^{+\bullet} + 1$], 100), 618 ([$M^{+\bullet}$], 14), 617 ([$M^{+\bullet} - 1$], 11), 507 (19), 376 (18), 225 (11). Anal. Found: C, 69.89; H, 6.78; N, 8.90. Calc. for $C_{36}H_{42}FeN_4O_2$ (618.59): C, 69.90; H, 6.84; N, 9.06%.

4.4. General procedure for the preparation of the ortho-substituted hydrazones **3** and **5** (GP1)

A Schlenk flask was charged under argon with a solution of the hydrazone in dry THF (20–40 ml mmol^{-1}) and cooled to −78 °C. After the addition of ^{n}BuLi (1.6 M in hexane) the reaction mixture was stirred for 9 h at −78 °C before the electrophile was added dropwise. The reaction mixture was warmed up to r.t. overnight, cooled to 0 °C, quenched with saturated aqueous NH_4Cl and washed twice with brine. After drying over $MgSO_4$ and concentrating under reduced pressure, the crude product was purified by column chromatography on silica gel. Because deprotected phosphines are extremely sensitive to oxidation, in case of $EX = R_2PCl$, the reaction mixture was treated with borane dimethylsulfide complex (2.5 equivalents, 2 M in THF) for 2 h at 0 °C before quenching.

*4.5. [1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)phenylmethylideneamino]}]-[(R_p)-2-methyl]ferrocene (**3a**)*

According to GP1, a solution of the hydrazone **2** (590 mg, 0.95 mmol) in THF (15 ml) was first treated with ^{n}BuLi (1.4 ml, 2.3 mmol) and afterwards with MeI (156 μl, 2.5 mmol). The hydrazone **3a** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et_2O 6:1).

Yield: 522 mg (85%, dark red oil). $R_f = 0.51$ (pentane–Et_2O 2:1). de ≥ 96%. $[\alpha]_D^{25} = +447.0$ ($c = 0.44$, $CHCl_3$). IR ($CHCl_3$, cm^{-1}): ν 3080 (w), 3057 (w), 3006 (m), 2972 (m), 2925 (m), 2875 (m), 2827 (m), 2737 (w), 2676 (w), 1564 (w), 1459 (s), 1443 (s), 1378 (m), 1353 (w), 1337 (m), 1322 (w), 1294 (m), 1280 (m), 1218 (m), 1197 (m), 1100 (s), 1072 (m), 1055 (m), 1025 (m), 970 (m), 903 (w), 875 (w), 818 (m), 757 (vs), 723 (m), 700 (s), 667 (m), 508 (m). ^{1}H-NMR ($CDCl_6$, 400 MHz): δ 1.59 (m, 6H, β-ring-CH_2), 1.93 (m, 2H, N(CH_2)$_2$C*H*H), 2.06 (s, 3H, CH_3), 2.31 (m, 2H, NC*H*H), 2.59 (m, 2H, NCH*H*), 2.76 (m, 2H, NCH*H*), 3.38 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 3.68 (qd, 2H, $J = 9.1$, 3.9 Hz, OC*H*H), 3.85 (m, 1H, OCH*H*), 3.90 (m, 1H, NC*H*), 4.00 (t, 1H, $J = 2.5$ Hz, Cp-*H*), 4.14 (m, 2H, Cp-*H*), 4.23 (m, 1H, Cp-*H*), 4.36 (dt, 2H, $J = 9.6$, 1.1 Hz, Cp-*H*), 7.27–7.37 (m, 6H, *m*-C_6H_5, *p*-C_6H_5), 7.44 (m, 4H, *o*-C_6H_5). ^{13}C-NMR (C_6D_6, 100 MHz): δ 16.22, 22.96, 23.10, 26.77, 54.61, 54.68, 59.18, 66.39, 66.43, 67.59, 68.09, 69.60, 70.45, 70.80, 72.41, 74.54, 75.79, 76.02, 83.39, 84.17, 86.70, 127.21, 127.28, 127.62, 127.68, 128.63, 138.05, 138.63, 148.39, 150.53. EIMS (70 eV); *m*/*z*: (relative intensity, %) = 634 ([$M^{+\bullet} + 1$], 40), 633 ([$M^{+\bullet}$], 100), 390 (21), 351 (20), 337 (12), 306 (46), 292 (337 − [$CH_2OCH_3^+$], 21), 271 (17), 246 (26), 238 (12), 237 (29), 224 (21), 203 (17), 202 (46), 201 (10), 189 (15), 188 (29), 180 (11), 134 ([$CH_3C_5H_3Fe^+$], 12), 123 (13), 121 ([$CpFe^+$], 15). HRMS; *m*/*z*: 632.2813 ([M^+]; exact mass calc. for $C_{37}H_{44}{}^{56}FeN_4O_2$: 632.2814).

*4.6. [1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)phenylmethylideneamino]}]-[(S_p)-2-(trimethylsilyl)]ferrocene (**3b**)*

According to GP1, a solution of the hydrazone **2** (1.24 g, 2.00 mmol) in THF (20 ml) was first treated with ^{n}BuLi (3.0 ml, 4.8 mmol) and afterwards with trimethylsilylchloride (570 μl, 5.0 mmol). The hydrazone **3b** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et_2O 4:1).

Yield: 1.25 g (90%, red oil). $R_f = 0.45$ (pentane–$Et_2O = 4$:1). de ≥ 96%. $[\alpha]_D^{25} = +246.4$ ($c = 0.43$, $CHCl_3$). IR (KBr, cm^{-1}): ν 3675 (m), 3438 (m), 3082 (m), 3057 (m), 3024 (m), 2949 (s), 2871 (s), 2825 (s), 2185 (w), 1725 (m), 1661 (m), 1627 (m), 1562 (m), 1446 (s), 1383 (m), 1342 (m), 1295 (m), 1242 (s), 1197 (s), 1110 (vs), 1020 (s), 970 (m), 901 (m), 832 (vs), 773 (s), 720 (m), 697 (s), 632 (m), 576 (w), 508 (m). ^{1}H-NMR (C_6D_6, 400 MHz): δ 0.51 (s, 9H, Si(CH_3)$_3$), 1.44 (m, 4H, NCH_2CH_2), 1.58 (m, 2H, N(CH_2)$_2$CH*H*, 1.89 (m, 2H, N(CH_2)$_2$CH*H*), 2.40 (q, 1H, $J = 7.6$ Hz, NCH*H*), 2.54 (q, 1H, $J = 8.2$ Hz, NCH*H*), 2.75 (m, 2H, NC*H*H), 3.21 (s, 3H, OCH_3), 3.23 (s, 3H, OCH_3), 3.27 (t, 1H, $J = 8.5$ Hz, OC*H*H), 3.43 (m, 1H, OC*H*H), 3.64 (dd, 1H, $J = 9.1$, 3.9 Hz, OCH*H*), 3.77 (m, 2H, OCH*H*, NC*H*), 3.90 (m, 1H, NC*H*), 4.05 (q, 1H, $J = 1.1$ Hz, Cp-*H*), 4.28 (m, 2H, Cp-*H*), 4.31 (m, 1H, Cp-*H*), 4.39 (m, 2H, Cp-*H*), 4.93 (m, 1H, Cp-*H*), 7.10–7.24 (m, 6H, *m*-C_6H_5, *p*-C_6H_5), 7.48 (d, 2H, $J = 7.2$ Hz, *o*-C_6H_5), 7.56 (d, 2H, $J = 7.2$ Hz, *o*-C_6H_5). ^{13}C-NMR (C_6D_6, 100 MHz): δ 1.78, 23.46, 23.71, 27.22, 27.62, 55.43, 56.04, 58.86, 65.64, 66.88, 67.80, 69.37, 69.62, 70.91, 71.80, 73.50, 74.11, 76.20, 76.36, 79.55, 86.76, 92.10, 127.43, 127.96, 128.85, 129.03, 138.58, 139.37, 147.82, 152.13. The remaining aromatic signals are covered by the solvent. EIMS (70 eV); *m*/*z*: (relative intensity, %) = 692 ([$M^{+\bullet} + 1$], 18), 691 ([$M^{+\bullet}$], 48), 690 ([$M^{+\bullet} - 1$], 100), 448 (13), 409 (26), 365 (10), 364 (47), 306 (10), 300 (34), 296 (15), 292 (11), 266 (34), 246 (11), 231 (54), 224 (10). Anal. Found: C, 68.04; H, 6.89; N, 7.85. Calc. for $C_{39}H_{50}FeN_4O_2Si$ (690.77): C, 67.81; H, 7.30; N, 8.11%.

*4.7. [1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)phenylmethylideneamino]}]-[(S_p)-2-(1-boranato-1,1-diphenylphosphino]ferrocene (**3c**)*

According to GP1, a solution of the hydrazone **2** (1.13 g, 1.82 mmol) in THF (30 ml) was first treated with ^{n}BuLi (2.5 ml, 4.0 mmol) and afterwards with chloro diphenylphosphine (738 μl, 4.0 mmol). Before quenching the reaction mixture was treated with borane dimethylsulfide complex (2.28 ml, 4.6 mmol, 2 M in THF) for 2 h at 0 °C. The hydrazone **3c** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et_2O 8:1).

Yield: 1.26 g (85%, orange–red oil). $R_f = 0.15$ (pentane–Et_2O 4:1). de ≥ 96%. $[\alpha]_D^{25} = +244.7$ ($c = 0.41$, $CHCl_3$). IR ($CHCl_3$, cm^{-1}): ν 3077 (w), 3056 (m), 2967 (m), 2924 (m), 2873 (s), 2826 (m), 2428 (m), 2390 (m), 2350 (m), 1562 (m), 1484 (m), 1458 (m), 1437 (m), 1383 (w), 1342 (m), 1322 (m), 1295 (m), 1283 (m), 1220 (m), 1197 (m), 1158 (m), 1106 (s), 1071 (s), 1023 (m), 1001 (w), 971 (m), 900 (m), 878 (w), 830 (m), 756 (vs), 723 (m), 698 (s), 667 (m), 636 (w), 525 (m), 499 (m), 481 (m), 457 (m). ^{1}H-NMR (C$_6$D$_6$, 300 MHz): δ 1.31 (m, 4H, NCH$_2$C*H*$_2$), 1.58 (m, 2H, N(CH$_2$)$_2$CH*H*), 1.89 (m, 2H, N(CH$_2$)$_2$CH*H*), 2.21 (m, 1H, NC*H*H), 2.60 (m, 3H, NC*H*H, OC*H*H), 2.82 (m, 1H, NCH*H*), 2.96 (m, 1H, NCH*H*), 3.04 (s, 3H, OC*H*$_3$), 3.21 (s, 3H, OC*H*$_3$), 3.40 (t, 1H, $J = 7.7$ Hz, OCH*H*), 3.65 (m, 2H, OC*H*H, NC*H*), 3.83 (m, 1H, NC*H*), 3.88 (br s, 1H, Cp-*H*), 4.29 (t, 1H, $J = 2.5$ Hz, Cp-*H*), 4.43 (br s, 1H, Cp-*H*), 4.48 (br s, 1H, Cp-*H*), 4.90 (br s, 1H, Cp-*H*), 4.97 (br s, 1H, Cp-*H*), 5.25 (br s, 1H, Cp-*H*), 6.95–7.27 (m, 14H, *p*-C$_6$*H*$_5$, *m*-C$_6$*H*$_5$, *o*-C$_6$H$_5$), 7.72–7.93 (m, 6H, *o*-C$_6$H$_5$). ^{13}C-NMR (C$_6$D$_6$, 75 MHz): δ 23.43, 24.36, 26.97, 27.02, 55.17, 57.28, 58.65, 59.00, 64.99, 66.85, 69.17, 71.04, 73.75, 73.87, 73.94, 74.50, 75.33, 76.15, 76.50, 88.58, 94.10, 94.23, 127.14, 128.17, 128.23, 128.98, 129.52, 129.87, 130.34, 132.68 (d), 134.67 (d), 138.54, 139.34, 141.89, 146.77. The remaining aromatic signals are covered by the solvent. ^{31}P-NMR (C$_6$D$_6$, 162 MHz): δ 18.74 (s). ^{11}B-NMR (C$_6$D$_6$, 160 MHz): δ −34.47 (s). EIMS (70 eV); *m*/*z*: (relative intensity, %) = 691 (11), 690 (41), 689 ([M$^{+\bullet}$ − C$_6$H$_{15}$NOB], 100), 406 (25), 337 (406 − [C$_4$H$_7$N$^+$], 37), 322 (28), 292 (406 − [C$_6$H$_{12}$NO$^+$], 27), 287 (18). HRMS; *m*/*z*: 688.2182 (C$_{48}$H$_{54}$-^{56}FeBN$_4$O$_2$P–C$_6$H$_{15}$NOB; exact mass calc. for C$_{42}$H$_{39}$ ^{56}FeN$_3$OP: 688.2180).

4.8. [1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)phenylmethylideneamino]}]-[(S$_p$)-2-(4-methylphenyl)sulfanyl]ferrocene (**3d**)

According to GP1, a solution of the hydrazone **2** (563 mg, 0.91 mmol) in THF (15 ml) was first treated with ^{n}BuLi (1.25 ml, 2.0 mmol) and afterwards with di-*p*-toluoyl disulfide (740 mg, 3.0 mmol). The hydrazone **3d** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et$_2$O 12:1).

Yield: 580 mg (86%, orange oil). $R_f = 0.20$ (pentane–Et$_2$O 4:1). de ≥ 96%. $[\alpha]_D^{25} = +395.2$ ($c = 0.38$, CHCl$_3$). IR (CHCl$_3$, cm^{-1}): ν 3055 (w), 2971 (m), 2923 (m), 2873 (m), 2827 (m), 1597 (w), 1565 (w), 1492 (m), 1459 (m), 1445 (m), 1385 (m), 1339 (m), 1323 (m), 1296 (m), 1279 (m), 1218 (m), 1197 (m), 1113 (s), 1090 (s), 1072 (m), 1054 (m), 1024 (m), 970 (w), 891 (w), 877 (w), 812 (m), 803 (m), 757 (vs), 723 (m), 701 (m), 667 (w), 506 (m), 486 (m). ^{1}H-NMR (C$_6$D$_6$, 400 MHz): δ 1.34 (m, 4H, NCH$_2$C*H*$_2$), 1.62 (m, 2H, N(CH$_2$)$_2$CH*H*), 1.87 (m, 2H, N(CH$_2$)$_2$CH*H*), 2.05 (s, 3H, C$_6$H$_4$-C*H*$_3$), 2.43 (m, 2H, NC*H*H), 2.76 (m, 2H, NCH*H*), 3.23 (s, 3H, OC*H*$_3$), 3.25 (s, 3H, OC*H*$_3$), 3.45 (m, 2H, OC*H*H), 3.73 (dd, 2H, $J = 9.2$, 3.7 Hz, OCH*H*), 3.90 (m, 2H, NC*H*), 4.00 (t, 1H, $J = 2.6$ Hz, Cp-*H*), 4.26 (m, 4H, Cp-*H*), 4.55 (m, 1H, Cp-*H*), 4.92 (m, 1H, Cp-*H*), 6.85 (d, 2H, $J = 8.0$ Hz, C$_6$H$_4$), 7.03–7.11 (m, 2H, *p*-C$_6$*H*$_5$), 7.22 (t, 4H, $J = 7.7$ Hz, *m*-C$_6$*H*$_5$), 7.35 (dt, 2H, $J = 8.2$, 1.9 Hz, C$_6$*H*$_4$), 7.70 (m, 4H, *o*-C$_6$H$_5$). ^{13}C-NMR (C$_6$D$_6$, 100 MHz): δ 20.94, 23.59, 27.14, 27.52, 55.61, 55.69, 58.88, 58.98, 66.64, 67.14, 68.44, 68.92, 71.38, 71.59, 71.64, 72.08, 74.68, 75.66, 76.58, 85.54, 88.31, 89.94, 127.48, 127.59, 127.72, 127.84, 127.97, 128.08, 129.53, 130.02, 135.25, 136.27, 138.60, 138.84, 144.87, 146.20. EIMS (70 eV); *m*/*z*: (relative intensity, %) 743 ([M$^{+\bullet}$ + 2], 13), 742 ([M$^{+\bullet}$ + 1], 46), 741 ([M$^{+\bullet}$], 100), 459 (12), 337 (12), 325 (13), 292 (14). Anal. Found: C, 69.31; H, 6.47; N, 7.36. Calc. for C$_{43}$H$_{48}$FeN$_4$O$_2$S (740.79): C, 69.72; H, 6.53; N, 7.56%.

4.9. [1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)phenylmethylideneamino]}]-[(S$_p$)-2-methylsulfanyl]ferrocene (**3e**)

According to GP1, a solution of the hydrazone **2** (563 mg, 0.91 mmol) in THF (15 ml) was first treated with ^{n}BuLi (1.25 ml, 2.0 mmol) and afterwards with methyl disulfide (270 µl, 3.0 mmol). The hydrazone **3e** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et$_2$O 9:1).

Yield: 605 mg (100%, red powder); m.p.: 49 °C. $R_f = 0.23$ (pentane–Et$_2$O 4:1). de ≥ 96%. $[\alpha]_D^{25} = -53.1$ ($c = 0.39$, CHCl$_3$). IR (CHCl$_3$, cm^{-1}): ν 3080 (w), 3057 (w), 2972 (m), 2920 (m), 2874 (m), 2828 (m), 1565 (w), 1491 (m), 1460 (m), 1443 (m), 1386 (m), 1334 (m), 1296 (m), 1279 (m), 1263 (m), 1218 (m), 1196 (m), 1135 (m), 1111 (s), 1094 (s), 1072 (m), 1054 (m), 1024 (m), 970 (m), 924 (w), 902 (w), 892 (m), 876 (m), 823 (m), 757 (vs), 723 (m), 701 (s), 667(m), 520 (m). ^{1}H-NMR (C$_6$D$_6$, 400 MHz): δ 1.37 (m, 4H, NCH$_2$C*H*$_2$), 1.62 (m, 2H, N(CH$_2$)$_2$CH*H*), 1.90 (m, 2H, N(CH$_2$)$_2$C*H*H), 2.14 (s, 3H, SC*H*$_3$), 2.35 (m, 1H, NC*H*H), 2.46 (m, 1H, NC*H*H), 2.79 (m, 2H, NCH*H*), 3.25 (s, 3H, OC*H*$_3$), 3.31 (s, 3H, OC*H*$_3$), 3.45 (t, 1H, $J = 8.8$ Hz, OC*H*H), 3.64 (t, 1H, $J = 8.2$ Hz, OC*H*H), 3.84 (m, 2H, OCH*H*), 3.98 (t, 1H, $J = 2.6$ Hz, Cp-*H*), 4.05 (m, 1H, Cp-*H*), 4.07 (m, 2H, NC*H*), 4.15 (dd, 1H, $J = 2.5$, 1.7 Hz, Cp-*H*), 4.19 (m, 1H, Cp-*H*), 4.25 (m, 1H, Cp-*H*), 4.32 (m, 1H, Cp-*H*), 4.89 (m, 1H, Cp-*H*), 7.06–7.11 (m, 2H, *p*-C$_6$*H*$_5$), 7.21 (t, 4H, $J = 7.7$ Hz, *m*-C$_6$*H*$_5$), 7.69 (m, 4H, *o*-C$_6$H$_5$). ^{13}C-NMR (C$_6$D$_6$, 100 MHz): δ 16.84, 23.46, 23.56, 27.30, 27.52, 55.52, 55.78, 58.97, 59.04, 66.62, 67.17, 67.29, 67.81, 69.69, 70.07, 70.13, 71.15, 72.81, 75.99, 76.53, 86.36, 88.64, 89.45, 127.59, 127.72, 127.84, 127.94, 129.41, 129.44, 138.56, 138.64, 146.32, 147.30. EIMS (70 eV); *m*/*z*: (relative intensity, %) 667 ([M$^{+\bullet}$ + 2], 13), 666 ([M$^{+\bullet}$ + 1], 43), 665 ([M$^{+\bullet}$], 88), 422 (18), 400 (22), 399 (100), 391 (11), 383 (13), 369 (13), 368

(26), 353 (422 − [$C_4H_7N^+$], 10), 352 (32), 338 (23), 337 (62), 336 (14), 292 (43), 288 (14), 287 (31), 286 (45), 281 (21), 280 (13), 253 (14), 246 (15), 245 (11), 237 (15), 236 (22), 235 (18), 234 (10), 224 (15), 222 (10), 218 (15), 216 (21), 211 (14), 198 (12), 189 (18), 170 (12), 168 (18), 167 (12), 152 (10), 123 (14), 114 ([$C_6H_{12}NO^+$], 13), 105 (15), 77 (16), 65 (10), 45 ([$CH_2OCH_3^+$], 41). Anal. Found: C, 66.45; H, 6.54; N, 8.16. Calc. for $C_{37}H_{44}FeN_4O_2S$ (664.69): C, 66.86; H, 6.67; N, 8.43%.

*4.10. [1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)phenylmethylideneamino]}]-[(R$_p$)-2,2′-bismethyl)]ferrocene (**5a**)*

A heated Schlenk flask was charged under argon with a solution of the hydrazone **3a** (155 mg, 0.25 mmol) in THF (10 ml) and cooled to − 78 °C. After the addition of ^{s}BuLi (0.46 ml, 0.6 mmol, 1.3 M in hexane) the reaction mixture was stirred for 9 h at − 78 °C before MeI (47 μl, 0.8 mmol) was added dropwise. The reaction mixture was warmed up to r.t. overnight, cooled to 0 °C, quenched with saturated aqueous NH_4Cl and washed twice with brine. After drying over $MgSO_4$ and concentrating under reduced pressure, the crude product was purified by column chromatography on silica gel (pentane–Et_2O 9:1).

Yield: 87 mg (54%, dark red oil). $R_f = 0.45$ (pentane–Et_2O 4:1). de = 92%. $[\alpha]_D^{25} = -105.0$ ($c = 0.20$, $CHCl_3$). IR (Kapillar, cm^{-1}): ν 3080 (m), 3057 (m), 3022 (m), 2971 (s), 2922 (s), 2875 (s), 2827 (s), 2732 (w), 2245 (w), 1641 (m), 1599 (m), 1577 (m), 1565 (m), 1490 (m), 1459 (vs), 1444 (vs), 1428 (s), 1376 (s), 1352 (s), 1100 (vs), 1038 (s), 1028 (s), 970 (s), 909 (s), 876 (m), 811 (m), 775 (s), 733 (vs), 700 (vs), 671 (m), 648 (m), 623 (w), 594 (m), 581 (m), 509 (s), 481 (m). ^{1}H-NMR (C_6D_6, 400 MHz): δ 1.48–1.68 (m, 6H, β-ring-CH_2), 1.92 (m, 2H, N(CH_2)$_2$CHH), 2.14 (s, 6H, CH_3), 2.36 (m, 2H, NCHH), 2.58 (m, 2H, NCHH), 3.38 (s, 6H, OCH_3), 3.48 (m, 2H, OCHH), 3.66 (dd, 1H, $J = 9.1$, 3.8 Hz, OCHH), 3.82 (t, 2H, $J = 1.9$ Hz, NCH), 4.04 (d, 4H, $J = 2.2$ Hz, Cp-H), 4.19 (m, 2H, Cp-H), 7.25–7.37 (m, 6H, m-C$_6H_5$, p-C$_6H_5$), 7.43 (m, 4H, o-C$_6H_5$). ^{13}C-NMR (C_6D_6, 100 MHz): δ 15.80, 22.97, 26.71, 54.67, 59.15, 66.47, 68.53, 70.68, 75.76, 83.21, 83.69, 127.17, 127.63, 128.57, 138.65, 150.63. EIMS (70 eV); m/z: (relative intensity, %) 647 ([$M^{+\bullet}$], 100), 364 (16), 352 (12), 351 (50), 315 (12), 307 (19), 306 (351 − [$CH_2OCH_3^+$], 96), 279 (10), 278 (65), 251 (19), 249 (23), 248 (19), 247 (13), 246 (46), 244 (48), 239 (145), 238 (61), 237 (351 − [$C_6H_{12}NO^+$], 17), 236 (14), 216 (22), 210 (15), 209 (90), 208 (14), 203 (33), 188 (61), 182 (14), 180 (32), 165 (13), 160 (12), 153 (11), 149 (23), 135 (28), 134 ([$CH_3C_5H_3Fe^+$], 30), 133 (11), 125 (13), 123 (14), 121 ([$CpFe^+$], 11), 111 (13), 104 (12), 97 (19), 95 (10), 85 (20), 84 (12), 83 (30), 82 (16), 81 (12), 79 (20), 77 (27), 73 (10), 71 (32), 70 (29), 69 (24), 67 (11), 60 (14), 57 (58), 56 ([Fe^+], 29), 55 (38), 46 (24), 45 ([$CH_2OCH_3^+$], 43). HRMS; m/z: 646.2971 ([M^+]; exact mass calc. for $C_{38}H_{46}\,^{56}FeN_4O_2$: 646.2970).

*4.11. [1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)-phenylmethylideneamino]}]-{(R$_p$)-2-methyl-(S$_p$)-2′-trimethylsilyl}ferrocene (**5b**)*

According to GP1, a solution of the hydrazone **3a** (100 mg, 0.16 mmol) in THF (10 ml) was first treated with ^{n}BuLi (0.15 ml, 0.2 mmol) and afterwards with trimethylsilyl chloride (47 μl, 0.4 mmol). The hydrazone **5b** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et_2O 9:1).

Yield: 66 mg (59%, dark red oil). $R_f = 0.55$ (pentane–Et_2O 4:1). de ≥ 96%. $[\alpha]_D^{25} = -611.6$ ($c = 0.47$, $CHCl_3$). IR ($CHCl_3$, cm^{-1}): ν 3082 (m), 3056 (m), 2951 (s), 2923 (s), 2874 (s), 2826 (m), 1565 (w), 1490 (m), 1458 (m), 1445 (s), 1382 (m), 1345 (m), 1321 (w), 1279 (m), 1241 (s), 1199 (s), 1150 (s), 1111 (s), 1075 (s), 1019 (m), 970 (m), 924 (m), 901 (m), 859 (m), 833 (vs), 772 (s), 757 (s), 723 (m), 698 (s), 629 (w), 594 (w), 578 (w), 512 (m). ^{1}H-NMR (C_6D_6, 400 MHz): δ 0.60 (s, 9H, Si(CH_3)$_3$), 1.33–1.62 (m, 8H, β-ring-CH_2), 1.89 (m, 2H, N(CH_2)$_2$CHH), 2.36 (s, 3H,CH_3), 2.53 (m, 1H, NCHH), 2.74 (dm, 2H, NCHH), 3.22 (s, 3H, OCH_3), 3.23 (s, 3H, OCH_3), 3.44 (m, 1H, OCHH), 3.63 (m, 1H, OCHH), 3.68 (dd, 1H, $J = 9.1$, 3.9 Hz, OCHH), 3.75 (dd, 1H, $J = 9.1$, 3.9 Hz, OCHH), 3.93 (m, 1H, NCH), 4.05 (t, 1H, $J = 2.5$ Hz, Cp-H), 4.14 (m, 1H, Cp-H), 4.21 (m, 2H, Cp-H), 4.29 (t, 1H, $J = 2.5$ Hz, Cp-H), 4.45 (t, 1H, $J = 1.9$ Hz, Cp-H), 7.08-7.16 (m, 6H, m-C$_6H_5$, p-C$_6H_5$), 7.40 (m, 2H, o-C$_6H_5$), 7.58 (m, 2H, o-C$_6H_5$). ^{13}C-NMR (C_6D_6, 100 MHz): δ 1.89, 16.99, 23.18, 23.76, 27.20, 27.76, 55.09, 56.12, 58.93, 65.73, 66.94, 68.87, 69.08, 72.57, 75.04, 76.74, 76.11, 76.54, 82.77, 84.76, 92.10, 127.04, 127.41, 128.67, 128.89, 129.15, 139.25, 139.50, 151.35, 152.69. The remaining aromatic signals are covered by the solvent. EIMS (70 eV); m/z: (relative intensity, %) 705 ([$M^{+\bullet} + 1$], 26), 704 ([$M^{+\bullet}$], 100), 364 (21), 307 (13), 306 (13), 238 (307 − [$C_4H_7N^+$], 26), 188 (12). HRMS; m/z: 704.3208 ([M^+]; exact mass calc. for $C_{40}H_{52}\,^{56}FeN_4O_2Si$: 704.3209).

*4.12. [1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)-phenylmethylideneamino]}]-{(R$_p$)-2-methyl-(S$_p$)-2′-[diphenyl(hydroxy)methyl]}-ferrocene (**5c**)*

According to GP1, a solution of the hydrazone **3a** (154 mg, 0.24 mmol) in THF (10 ml) was first treated with ^{n}BuLi (0.3 ml, 0.5 mmol) and afterwards with benzophenone (118 mg, 0.6 mmol). The hydrazone **5c** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et_2O 4:1).

Yield: 150 mg (77%, orange crystals); m.p.: 66 °C. $R_f = 0.11$ (pentane–$\mathrm{Et_2O}$ 4:1). de ≥ 96%. $[\alpha]_D^{25} = -717.8$ ($c = 0.56$, $\mathrm{CHCl_3}$). IR (KBr, $\mathrm{cm^{-1}}$): ν 3752 (w), 3676 (m), 3654 (m), 3432 (s), 3056 (s), 3025 (s), 2922 (s), 2871 (vs), 2188 (m), 1596 (m), 1489 (m), 1445 (s), 1384 (s), 1347 (s), 1281 (m), 1226 (s), 1179 (s), 1114 (vs), 1029 (s), 971 (s), 905 (s), 824 (m), 756 (s), 701 (vs), 516 (m). ^{1}H-NMR ($\mathrm{C_6D_6}$, 400 MHz): δ 1.20–1.40 (m, 8H, β-ring-$\mathrm{C}H_2$), 1.45–1.59 (m, 2H, $\mathrm{N(CH_2)_2C}H\mathrm{H}$), 1.65 (m, 1H, $\mathrm{N(CH_2)_2CH}H$), 1.81 (m, 1H, $\mathrm{N(CH_2)_2CH}H$), 1.89 (s, 3H, $\mathrm{C}H_3$), 2.35 (m, 1H, $\mathrm{NC}H\mathrm{H}$), 2.53 (m, 3H, $\mathrm{NC}H\mathrm{H}$), 2.70 (m, 2H, $\mathrm{NCH}H$), 3.04 (s, 3H, $\mathrm{OC}H_3$), 3.19 (s, 3H, $\mathrm{OC}H_3$), 3.26 (m, 1H, $\mathrm{OCH}H$), 3.44 (dd, 1H, $J = 9.1$, 7.4 Hz, $\mathrm{OC}H\mathrm{H}$), 3.61 (m, 1H, $\mathrm{OC}H\mathrm{H}$), 3.70 (dd, 1H, $J = 9.1$, 3.8 Hz, $\mathrm{OCH}H$), 3.75 (dd, 1H, $J = 9.1$, 3.9 Hz, $\mathrm{OCH}H$), 3.98 (m, 1H, $\mathrm{NC}H$), 4.14 (t, 1H, $J = 2.6$ Hz, Cp-H), 4.25 (t, 1H, $J = 2.5$ Hz, Cp-H), 4.28 (m, 1H, Cp-H), 4.43 (m, 1H, Cp-H), 5.18 (t, 1H, $J = 1.9$ Hz, Cp-H), 7.00–7.17 (m, 12H, m-$\mathrm{C_6}H_5$, p-$\mathrm{C_6}H_5$), 7.21–7.47 (m, 6H, o-$\mathrm{C_6}H_5$), 7.55 (br d, 2H, $J = 7.4$ Hz, o-$\mathrm{C_6}H_5$), 7.90 (br s, 2H, o-$\mathrm{C_6}H_5$), 9.14 (s, 1H, $\mathrm{O}H$). ^{13}C-NMR ($\mathrm{C_6D_6}$, 100 MHz): δ 15.95, 22.85, 23.31, 26.93, 27.24, 55.16, 56.10, 58.52, 58.94, 66.43, 66.80, 72.36, 72.84, 74.28, 75.40, 76.04, 76.14, 77.61, 79.55, 79.01, 83.64, 86.51, 126.33, 126.50, 127.22, 127.49, 128.30, 128.76, 129.07, 139.02, 139.28, 147.54, 151.31. The remaining aromatic signals are covered by the solvent. EIMS (70 eV); m/z: (relative intensity, %) 814 ([$\mathrm{M^{+\bullet}}$], 3), 446 (35), 407 (20), 406 (96), 405 (20), 402 (30), 401 (446 − [$\mathrm{CH_2OCH_3^+}$], 100), 333 (25), 332 (446 − [$\mathrm{C_6H_{12}NO^+}$], 96), 330 (11), 327 (11), 296 (13), 285 (12), 284 (23), 254 (24), 251 (17), 239 (11), 237 (14), 229 (42), 228 (77), 227 (29), 226 (15), 202 (14), 182 (19), 149 (19), 105 (27), 97 (13), 83 (18), 81 (12), 79 (30), 77 (32), 74 (11), 72 (14), 70 (21), 69 (20), 68 (10), 61 (12), 57 (12), 55 (34). HRMS; m/z: 814.3547 ([$\mathrm{M^+}$]; exact mass calc. for $\mathrm{C_{50}H_{54}\,{}^{56}FeN_4O_3}$: 814.3545).

4.13. [1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)-phenylmethylideneamino]}]-{(S_p)-2′-(1-boranato-1,1-dicyclohexylphosphino)-(S_p)-2-(1-boranato-1,1-diphenylphosphino)}ferrocene ***(5d)***

According to GP1, a solution of the hydrazone **3c** (162 mg, 0.20 mmol) in THF (15 ml) was first treated with ^{n}BuLi (0.2 ml, 0.3 mmol) and afterwards with chloro dicyclohexylphosphine (77 µl, 0.4 mmol). Before quenching the reaction mixture was treated with borane dimethylsulfide complex (0.2 ml, 0.4 mmol, 2 M in THF) for 2 h at 0 °C. The hydrazone **5d** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–$\mathrm{Et_2O}$ 8:1).

Yield: 92 mg (45%, orange oil). $R_f = 0.18$ (pentane–$\mathrm{Et_2O}$ 4:1). de ≥ 96%. $[\alpha]_D^{25} = -219.3$ ($c = 0.40$, $\mathrm{CHCl_3}$). IR (KBr, $\mathrm{cm^{-1}}$): ν 3691 (w), 3677 (w), 3652 (w), 3631 (w), 3618 (w), 3590 (w), 3569 (w), 3434 (m), 3055 (m), 3023 (w), 2925 (vs), 2852 (s), 2377 (s), 2345 (m), 2259 (m), 1656 (w), 1561 (m), 1485 (m), 1439 (m), 1382 (w), 1343 (m), 1323 (m), 1281 (m), 1219 (m), 1198 (m), 1109 (s), 1061 (s), 1019 (m), 971 (m), 921 (w), 900 (m), 832 (m), 741 (s), 697 (s), 634 (w), 613 (w), 520 (m), 496 (m), 458 (m). ^{1}H-NMR ($\mathrm{C_6D_6}$, 300 MHz): δ 0.80–1.01 (m, 8H, $\mathrm{C_6}H_{11}$), 1.35 (m, 4H, $\mathrm{NCH_2C}H_2$), 1.40–1.62 (m, 10H, $\mathrm{C_6}H_{11}$), 1.72 (m, 2H, $\mathrm{N(CH_2)_2CH}H$), 1.90 (m, 2H, $\mathrm{N(CH_2)_2CH}H$), 2.19 (m, 2H, $\mathrm{C_6}H_{11}$), 2.49 (m, 2H, $\mathrm{C_6}H_{11}$), 2.61 (m, 1H, $\mathrm{NC}H\mathrm{H}$), 2.71 (m, 2H, $\mathrm{NCH}H$), 2.89 (m, 2H, $\mathrm{NCH}H$), 3.04 (s, 3H, $\mathrm{OC}H_3$), 3.21 (s, 3H, $\mathrm{OC}H_3$), 3.41 (m, 2H, $\mathrm{OCH}H$), 3.79 (m, 2H, $\mathrm{NC}H$), 4.57 (br s, 1H, Cp-H), 4.66 (br s, 1H, Cp-H), 4.95 (br s, 2H, Cp-H), 5.11 (m, 1H, Cp-H), 6.01 (br s, 1H, Cp-H), 6.94–7.27 (m, 12H, p-$\mathrm{C_6}H_5$, m-$\mathrm{C_6}H_5$), 7.36 (d, 2H, $J = 7.7$ Hz, o-$\mathrm{C_6H_5}$), 7.52 (d, 2H, $J = 7.4$ Hz, o-$\mathrm{C_6H_5}$), 7.73 (m, 2H, o-$\mathrm{P(C_6}H_5\mathrm{)_2}$), 8.03 (m, 2H, o-$\mathrm{P(C_6}H_5\mathrm{)_2}$). ^{13}C-NMR ($\mathrm{C_6D_6}$, 75 MHz): δ 23.70, 24.25, 26.26, 26.33, 26.80, 27.09, 27.15, 27.23, 27.31, 27.43, 27.56, 27.65, 27.92, 28.51, 33.63, 34.05, 55.78, 56.73, 58.67, 59.03, 65.26, 66.66, 74.47, 74.90, 75.24, 77.02, 77.79, 77.87, 78.53, 80.92 (d), 94.77 (d), 95.06, 95.02, 127.41, 127.82, 128.25, 128.69, 128.81, 129.50, 129.65, 129.68, 130.02, 131.01, 131.03, 132.56 (d), 134.79 (d), 139.03, 139.25, 141.13, 144.26. ^{31}P-NMR ($\mathrm{C_6D_6}$, 162 MHz): δ 18.13 (s, $P\mathrm{(C_6H_5)_2}$), 30.67 (s, $P\mathrm{(C_6H_{11})_2}$). EIMS (70 eV); m/z: (relative intensity, %) 900 (23), 899 ([$\mathrm{M^+ - C_6H_{15}NOB}$], 39), 898 (12), 887 (17), 886 (56), 885 (899 − [$\mathrm{BH_3}$], 100), 689 (12), 688 ([$\mathrm{M^{+\bullet} - C_{18}H_{39}NOPB_2}$], 35), 406 (25), 337 (406 − [$\mathrm{C_4H_7N^+}$], 12), 126 (26), 82 (28). HRMS; m/z: 688.2184 ($\mathrm{C_{60}H_{78}FeB_2N_4O_2P_2}$–$\mathrm{C_{18}H_{39}NOPB_2}$; exact mass calc. for $\mathrm{C_{42}H_{39}\,{}^{56}FeN_3OP}$: 688.2180).

4.14. [1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)-phenylmethylideneamino]}]-{(S_p)-2′-(1-boranato-1,1-diphenylphosphino)-(S_p)-2-methylsulfanyl}ferrocene ***(5e)***

According to GP1, a solution of the hydrazone **3e** (258 mg, 0.39 mmol) in THF (10 ml) was first treated with ^{n}BuLi (0.4 ml, 0.6 mmol) and afterwards with chloro diphenylphosphine (148 µl, 0.8 mmol). Before quenching the reaction mixture was treated with borane dimethylsulfide complex (0.5 ml, 1 mmol, 2 M in THF) for 2 h at 0 °C. The hydrazone **5e** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–$\mathrm{Et_2O}$ 9:1).

Yield: 154 mg (46%, orange oil). $R_f = 0.12$ (pentane–$\mathrm{Et_2O}$ 4:1). de ≥ 96%. $[\alpha]_D^{25} = -260.0$ ($c = 0.40$, $\mathrm{CHCl_3}$). IR ($\mathrm{CHCl_3}$, $\mathrm{cm^{-1}}$): ν 058 (w), 3004 (m), 2958 (m), 2925 (m), 2854 (m), 2389 (w), 1438 (m), 1384 (m), 1346 (w), 1216 (m), 1105 (m), 1072 (m), 1021 (w), 757 (vs), 699 (m), 668 (m). ^{1}H-NMR ($\mathrm{C_6D_6}$, 400 MHz): δ 1.36 (m, 4H, $\mathrm{NCH_2C}H_2$), 1.50 (s, 3H, $\mathrm{SC}H_3$), 1.60 (m, 2H, $\mathrm{N(CH_2)_2CH}H$), 1.84 (m, 2H, $\mathrm{N(CH_2)_2CH}H$), 2.41 (m, 1H, NC*H*H), 2.59 (m, 1H, NC*H*H), 2.65 (m, 2H, NCH*H*), 2.94 (m, 1H, OC*H*H), 3.02 (s, 3H, OCH_3), 3.24 (s, 3H, OCH_3), 3.58 (dd, 1H, $J = 9.7$, 7.7 Hz, OC*H*H), 3.71 (m, 1H, OCH*H*), 3.85 (m, 1H, NC*H*), 3.94 (dd, 1H, $J = 9.7$, 3.6 Hz, OC*H*H), 4.11 (m, 1H, Cp-*H*), 4.32 (m, 1H, Cp-*H*), 4.35 (t, 1H, $J = 2.6$ Hz, Cp-*H*), 4.48 (m, 1H, Cp-*H*), 4.77 (m, 1H, Cp-*H*), 5.04 (t, 1H, $J = 2.6$ Hz, Cp-*H*), 6.95–7.13 (m, 12H, *p*-C_6H_5, *m*-C_6H_5), 7.29 (m, 2H, *o*-C_6H_5), 7.52 (m, 2H, *o*-C_6H_5), 7.74 (m, 2H, *o*-$P(C_6H_5)_2$), 8.05 (m, 2H, *o*-$P(C_6H_5)_2$). ^{13}C-NMR (75 MHz): δ 15.91, 23.43, 24.36, 26.86, 27.11, 55.28, 57.06, 58.66, 59.08, 65.10, 66.61, 69.47, 70.57, 74.51, 75.35, 75.58, 76.36, 77.92, 79.66, 85.52, 85.77, 90.51, 90.59, 127.41, 128.21, 129.34, 129.54, 130.02, 130.43, 132.43 (d), 135.24 (d), 138.40, 139.52, 140.77, 146.26. ^{31}P-NMR (C_6D_6, 162 MHz): δ 17.47 (s) ppm. EIMS (70 eV); *m*/*z*: (relative intensity, %) 737 (20), 735 (51), 734 ($[M^{+\bullet} - C_6H_{15}NOB]$, 100), 407 (17), 406 (59), 384 (10), 383 (38), 369 (11), 368 (48), 345 (19), 338 (11), 310 (10), 303 (19), 280 (12). Anal. Found: C, 68.24; H, 6.68; N, 6.26. Calc. for $C_{49}H_{56}FeBN_4PO_2S$ (862.70): C, 68.22; H, 6.54; N, 6.49%.

4.15. *[1,1′-Bis{N-[(2S)-2-(methoxymethyl)tetrahydro-1H-1-pyrrolyl]-N-[(E)-phenylmethylideneamino]}]-{(S$_p$)-2′-(4-methylphenyl)sulfanyl-(S$_p$)-2-methylsulfanyl}ferrocene (**5f**)*

According to GP1, a solution of the hydrazone **3d** (243 mg, 0.33 mmol) in THF (15 ml) was first treated with ^{n}BuLi (0.41 ml, 0.66 mmol) and afterwards with methyl disulfide (95 µl, 1.0 mmol). The hydrazone **5f** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et_2O 9:1).

Yield: 230 mg (89%, red oil). $R_f = 0.22$ (pentane–Et_2O 4:1). de ≥ 96%. $[\alpha]_D^{25} = -332.9$ ($c = 0.50$, $CHCl_3$). IR ($CHCl_3$, cm^{-1}): ν 3056 (w), 2972 (m), 2922 (m), 2873 (m), 2829 (m), 1565 (w), 1492 (m), 1447 (m), 1388 (m), 1343 (w), 1331 (w), 1299 (w), 1279 (w), 1262 (w), 1217 (w), 1199 (m), 1153 (m), 1114 (m), 1091 (m), 1073 (m), 1019 (m), 969 (w), 892 (w), 812 (m), 757 (vs), 726 (m), 702 (m), 667 (m), 508 (m), 485 (w). ^1H-NMR (C_6D_6, 300 MHz): δ 1.35 (m, 4H, NCH_2CH_2), 1.65 (m, 2H, $N(CH_2)_2$C*H*H), 1.87 (m, 1H, $N(CH_2)_2$CH*H*), 1.97 (m, 1H, $N(CH_2)_2$CH*H*), 2.06 (s, 3H, C_6H_4–CH_3), 2.16 (s, 3H, SCH_3), 2.38 (m, 2H, NC*H*H), 2.80 (m, 2H, NCH*H*), 3.23 (s, 3H, OCH_3), 3.33 (s, 3H, OCH_3), 3.44 (m, 1H, OC*H*H), 3.66 (m, 1H, OC*H*H), 3.78 (dd, 1H, $J = 9.1$, 3.6 Hz, OCH*H*), 4.02 (m, 2H, NC*H*), 4.05 (br s, 4H, Cp-*H*), 4.12 (m, 1H, Cp-*H*), 4.16 (m, 1H, Cp-*H*), 6.90 (d, 2H, $J = 7.7$ Hz, C_6H_4), 7.02–7.11 (m, 2H, *p*-C_6H_5), 7.22 (m, 4H, *m*-C_6H_5), 7.50 (br d, 2H, $J = 8.0$ Hz, C_6H_4), 7.77 (d, 2H, $J = 7.2$ Hz, *o*-C_6H_5), 7.84 (d, 2H, $J = 6.9$ Hz, *o*-C_6H_5). ^{13}C-NMR (C_6D_6, 75 MHz): δ 16.79, 21.03, 23.64, 23.76, 27.32, 27.52, 55.88, 56.18, 58.99, 59.18, 65.89, 66.75, 67.21, 67.47, 68.77, 72.57, 73.16, 73.53, 75.79, 76.17, 84.09, 88.16, 88.35, 90.34, 128.22, 129.77, 130.09, 131.89, 135.55, 136.11, 138.21, 138.46, 144.47, 144.62. The remaining aromatic signals are covered by the solvent. EIMS (70 eV); *m*/*z* (relative intensity, %): 788 ($[M^{+\bullet} + 1]$, 52), 787 ($[M^{+\bullet}]$, 100), 460 (21), 459 (63), 383 (26), 369 (12), 368 (44), 348 (19), 346 (19), 345 (15), 338 (17), 323 (10), 280 (18), 260 (14), 256 (10), 255 (10), 243 (11), 242 (30), 235 (13), 184 (10), 170 (19), 157 (10), 57 (21), 55 (14), 45 ($[CH_2OCH_3^+]$, 18). HRMS; *m*/*z*: 786.2726 ($[M^+]$; exact mass calc. for $C_{44}H_{50}{}^{56}FeO_2N_4O_2S_2$: 786.2726).

4.16. *General procedure for hydrazone cleavage with ozone (GP2)*

A solution of the hydrazone in CH_2Cl_2 (50 ml $mmol^{-1}$) was cooled to −78 °C. O_3 was bubbled through the solution (50 l h^{-1}) under TLC control. After warming up to r.t. and concentrating in vacuo, the crude product was purified by column chromatography on silica gel.

4.17. *General procedure for hydrazone cleavage with TiCl$_3$ (GP3)*

A 20% aqueous solution of $TiCl_3$ was added to a solution of the hydrazone in DME (40 ml $mmol^{-1}$) under argon. The reaction mixture was refluxed under TLC control. Afterwards the mixture was diluted with Et_2O and washed with aqueous buffer (pH 9) and brine. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. Finally the crude product was purified by column chromatography on silica gel.

4.18. *1,1′-Bisbenzoyl-(R$_p$)-2-methylferrocene (**4a**)*

According to GP2, a solution of the hydrazone **3a** (242 mg, 0.38 mmol) in CH_2Cl_2 (30 ml) was ozonolysed for 90 s. The ketone **4a** was obtained after purification by column chromatography on silica gel (pentane–Et_2O 4:1).

Yield: 144 mg (92%, dark red oil). $R_f = 0.19$ (pentane–Et_2O 4:1). ee = 98%. $[\alpha]_D^{25} = +165.1$ ($c = 0.42$, $CHCl_3$). IR ($CHCl_3$, cm^{-1}): ν 3083 (w), 3060 (w), 3014 (m), 2956 (w), 2923 (m), 2852 (w), 1642 (vs), 1598 (m), 1578 (m), 1450 (s), 1417 (s), 1375 (m), 1349 (m), 1314 (m), 1285 (s), 1226 (m), 1178 (m), 1075 (w), 1052 (m), 1027 (m), 887 (m), 854 (m), 799 (m), 757 (s), 730 (s), 699 (s), 668 (m), 494 (m). ^1H-NMR (C_6D_6, 300 MHz): δ 2.23 (s, 3H, CH_3), 3.98 (t, 1H, $J = 2.6$ Hz, Cp-*H*), 4.10 (m, 1H, Cp-*H*), 4.12 (m, 1H, Cp-*H*), 4.15 (m, 1H, Cp-*H*), 4.29 (m, 1H, Cp-*H*), 4.76 (m, 1H, Cp-*H*), 4.79 (m, 1H, Cp-*H*), 7.02–7.14 (m, 6H, *m*-C_6H_5, *p*-C_6H_5), 7.78 (m, 4H, *o*-C_6H_5). ^{13}C-NMR (C_6D_6, 75 MHz): δ 14.15, 71.21, 73.35, 73.72, 74.23, 75.23, 75.86, 76.33, 78.83, 80.21, 89.93, 128.27, 128.58, 128.80, 131.60, 131.64, 140.36, 142.46, 196.98, 198.64. The remaining aromatic signals are covered by the solvent. EIMS (70 eV); *m*/*z*: (relative intensity, %) 409 ($[M^{+\bullet}+1]$, 30), 408 ($[M^{+\bullet}]$, 100), 303 ($408-[C_6H_5CO^+]$, 26), 165 (10), 153 (13), 133 (13), 56 (Fe^+, 11). HRMS; *m*/*z*: 408.0811 ($[M^+]$; exact mass calc. for $C_{25}H_{20}{}^{56}FeO_2$: 408.0813).

4.19. 1,1′-Bisbenzoyl-(S_p)-2-trimethylsilyl-ferrocene (**4b**)

According to GP2, a solution of the hydrazone **3b** (173 mg, 0.25 mmol) in CH_2Cl_2 (30 ml) was ozonolysed for 90 s. The ketone **4b** was obtained after purification by column chromatography on silica gel (pentane–Et_2O 15:1).

Yield: 116 mg (99%, red oil). $R_f = 0.24$ (pentane–Et_2O 4:1). ee = 99%. $[\alpha]_D^{25} = -20.0$ ($c = 0.32$, $CHCl_3$). IR ($CHCl_3$, cm^{-1}): ν 3084 (w), 3060 (w), 3012 (w), 2952 (m), 2897 (m), 1643 (vs), 1599 (m), 1578 (m), 1491 (w), 1449 (s), 1424 (m), 1400 (m), 1376 (s), 1329 (s), 1316 (m), 1286 (s), 1247 (s), 1217 (m), 1194 (m), 1176 (m), 1157 (m), 1110 (w), 1082 (m), 1053 (m), 1027 (m), 1009 (m), 955 (w), 884 (m), 834 (vs), 800 (m), 755 (s), 729 (s), 698 (s), 672 (m), 638 (w), 510 (m). ^{1}H-NMR (C_6D_6, 300 MHz): δ 0.45 (s, 9H, $Si(CH_3)_3$), 4.26 (m, 2H, Cp-*H*), 4.35 (d, $J = 1.9$ Hz, 2H, Cp-*H*), 4.57 (t, 1H, $J = 1.8$ Hz, Cp-*H*), 4.78 (m, 1H, Cp-*H*), 4.93 (m, 1H, Cp-*H*), 7.04–7.62 (m, 6H, *m*-C_6H_5, *p*-C_6H_5), 7.72–7.85 (m, 4H, *o*-C_6H_5). ^{13}C-NMR (C_6D_6, 75 MHz): δ 0.61, 72.79, 73.62, 74.40, 74.64, 76.07, 78.08, 81.64, 77.88, 79.60, 84.62, 129.15, 129.24, 129.33, 131.66, 131.79, 139.81, 139.89, 196.67, 198.18. The remaining aromatic signals are covered by the solvent. EIMS (70 eV); *m*/*z*: (relative intensity, %) 467 ($[M^{+\bullet}+1]$, 17), 466 ($[M^{+\bullet}]$, 48), 452 (31), 451 (100), 225 (16), 197 (225 − CO, 13), 141 ($197-[Fe^+]$, 13), 133 (16), 105 (12). HRMS; *m*/*z*: 466.1051 ($[M^+]$; exact mass calc. for $C_{27}H_{26}{}^{56}FeO_2Si$: 466.1052).

4.20. 1,1′-Bisbenzoyl-(S_p)-2-((4-methylphenyl)-sulfanyl)ferrocene (**4c**)

According to GP3, a solution of the hydrazone **3d** (218 mg, 0.29 mmol) in DME (12 ml) was treated with a 20% aqueous solution of $TiCl_3$ (1.5 ml, 1.5 mmol) and refluxed for 1.5 h. The ketone **4c** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et_2O 4:1).

Yield: 125 mg (82%, orange oil). $R_f = 0.16$ (pentane–Et_2O 4:1). ee = 98%. $[\alpha]_D^{25} = +17.0$ ($c = 0.54$, $CHCl_3$). IR (Kapillar, cm^{-1}): ν 3084 (w), 3059 (m), 3025 (w), 2964 (w), 2922 (m), 2866 (w), 2279 (w), 1642 (vs), 1598 (m), 1578 (m), 1492 (m), 1449 (s), 1424 (s), 1375 (s), 1331 (s), 1286 (s), 1262 (s), 1176 (m), 1105 (w), 1075 (m), 1051 (m), 1027 (m), 1006 (m), 954 (w), 873 (m), 854 (m), 813 (m), 729 (s), 698 (s), 674 (m), 501 (s). ^{1}H-NMR (C_6D_6, 300 MHz): δ 1.99 (s, 3H, C_6H_4–CH_3), 4.01 (t, 1H, $J = 2.6$ Hz, Cp-*H*), 4.29 (m, 1H, Cp-*H*), 4.34 (m, 1H, Cp-*H*), 4.39 (m, 2H, Cp-*H*), 4.88 (m, 2H, Cp-*H*), 6.80 (d, 2H, $J = 8.0$ Hz, C_6H_4), 6.98–7.14 (m, 6H, *p*-C_6H_5, *m*-C_6H_5), 7.31 (br d, 2H, C_6H_4), 7.80 (m, 4H, *o*-C_6H_5). ^{13}C-NMR (C_6D_6, 75 MHz): δ 16.45, 72.02, 73.66, 74.53, 74.60, 75.88, 77.03, 77.09, 79.71, 80.79, 92.54, 128.70, 128.92, 130.11, 131.70, 131.89, 132.70, 132.98, 137.46, 139.51, 139.84, 196.31, 196.47. The remaining aromatic signals are covered by the solvent. EIMS (70 eV); *m*/*z*: (relative intensity, %) 517 ($[M^{+\bullet}+1]$, 29), 516 ($[M^{+\bullet}]$, 100), 105 ($[C_6H_5CO^+]$, 24). HRMS; *m*/*z*: 516.0847 ($[M^+]$; exact mass calc. for $C_{31}H_{24}{}^{56}FeO_2S$: 516.0846).

4.21. 1,1′-Bisbenzoyl-(S_p)-2-methylsulfanylferrocene (**4d**)

According to GP3, a solution of the hydrazone **3e** (260 mg, 0.39 mmol) in DME (16 ml) was treated with a 20% aqueous solution of $TiCl_3$ (2.0 ml, 2 mmol) and refluxed for 1.5 h. The ketone **4d** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et_2O 4:1).

Yield: 144 mg (84%, dark red oil). $R_f = 0.08$ (pentane–Et_2O 4:1). ee = 98%. $[\alpha]_D^{25} = +60.6$ ($c = 0.32$, $CHCl_3$). IR (Kapillar, cm^{-1}): ν 3085 (w), 3060 (w), 2919 (w), 1742 (w), 1641 (vs), 1598 (m), 1577 (m), 1448 (s), 1423 (s), 1394 (m), 1374 (m), 1334 (s), 1317 (m), 1286 (s), 1261 (s), 1195 (w), 1172 (m), 1075 (w), 1052 (m), 1027 (m), 1014 (m), 954 (w), 873 (m), 854 (m), 814 (m), 799 (m), 730 (s), 699 (s), 673 (m), 520 (m), 502 (s). ^{1}H-NMR (C_6D_6, 300 MHz): δ 1.95 (s, 3H, SCH_3), 4.03 (t, 1H, $J = 2.6$ Hz, Cp-*H*), 4.18 (m, 1H, Cp-*H*), 4.26 (br s, 2H, Cp-*H*), 4.37 (m, 1H, Cp-*H*), 4.78 (t, 1H, $J = 1.4$ Hz, Cp-*H*), 4.86 (t, 1H, $J = 1.4$ Hz, Cp-*H*), 7.02–7.14 (m, 6H, *m*-C_6H_5, *p*-C_6H_5), 7.80 (m, 4H, *o*-C_6H_5). ^{13}C-NMR (C_6D_6, 75 MHz): δ 16.45, 71.24, 71.46, 73.53, 73.66, 75.34, 76.04, 77.15, 77.97, 80.46, 95.85, 128.65, 128.69, 131.72, 131.75, 139.84, 139.96, 196.67, 197.24. The remaining aromatic signals are covered by the solvent. EIMS (70 eV); *m*/*z*: (relative intensity, %) 441 ($[M^{+\bullet}+1]$, 24), 440 ($[M^{+\bullet}]$, 83), 335 ($[M^{+\bullet}-C_6H_5CO^+]$, 12), 202 (14), 172 (16), 171 (12), 141 (10), 133 (10), 105 ($[C_6H_5CO^+]$, 100), 77 ($133-[Fe^+]$, 15). HRMS; *m*/*z*: 440.0535 ($[M^+]$; exact mass calc. for $C_{25}H_{20}{}^{56}FeO_2S$: 440.0533).

4.22. 1,1′-Bisbenzoyl-(S_p)-2-(1-boranato-1,1-diphenylphosphino]ferrocene (**4e**)

According to GP2, a solution of the hydrazone **3c** (100 mg, 0.12 mmol) in CH_2Cl_2 (12 ml) was ozonolysed for 60 s. The ketone **4e** was obtained after purification by column chromatography on silica gel (CH_2Cl_2).

Yield: 66 mg (92%, dark red oil). $R_f = 0.04$ (pentane–Et$_2$O 4:1). $[\alpha]_D^{25} = -113.5$ ($c = 0.16$, CHCl$_3$). IR (CHCl$_3$, cm^{-1}): ν 3060 (m), 3007 (m), 2928 (w), 2389 (m), 2351 (m), 2260 (w), 2112 (w), 1970 (w), 1907 (w), 1818 (w), 1646 (s), 1599 (m), 1579 (m), 1485 (m), 1450 (m), 1438 (m), 1426 (m), 1377 (m), 1330 (m), 1316 (m), 1286 (s), 1251 (m), 1217 (m), 1197 (m), 1168 (m), 1136 (w), 1105 (m), 1058 (m), 1028 (m), 1011 (m), 1001 (m), 955 (m), 877 (m), 853 (m), 799 (m), 755 (vs), 697 (s), 672 (m), 639 (m), 612 (w), 521 (w). ^{1}H-NMR (CDCl$_3$, 400 MHz): δ 4.41 (s, 1H, Cp-*H*), 4.62 (s, 1H, Cp-*H*), 4.86 (s, 1H, Cp-*H*), 4.92 (m, 3H, Cp-*H*), 5.02 (s, 1H, Cp-*H*), 6.98-7.43 (m, 14H, *p*-C$_6$*H*$_5$, *m*-C$_6$*H*$_5$, *o*-C$_6$H$_5$), 7.50–7.80 (m, 6H, *o*-C$_6$H$_5$). ^{13}C-NMR (CDCl$_3$, 100 MHz): δ 73.97, 74.67, 75.16, 75.23, 76.82, 78.34, 78.38, 79.93, 80.01, 84.82, 127.92, 128.04, 128.11, 128.14, 128.24, 128.31, 130.52, 130.71, 131.98, 132.10, 132.43, 132.52, 132.68, 132.78, 137.98, 138.40, 194.74, 197.10. ^{31}P-NMR (C$_6$D$_6$, 162 MHz): δ 19.49 (s) ppm. EIMS (70 eV); *m/z*: (relative intensity, %) 592 ([M$^{+\bullet}$], 3), 579 (36), 578 ([M$^{+\bullet}$ − BH$_3$], 100), 576 (18), 550 (11), 549 (5), 474 (15), 473 (578 − [C$_6$H$_5$CO$^+$], 45), 410 (7), 409 (10), 408 (22), 354 (7), 349 (8), 338 (14), 337 (17), 229 (7), 228 (6), 183 (7), 170 (9), 154 (7), 153 (12), 152 (8), 105 ([C$_6$H$_5$CO$^+$], 10), 77 (7). HRMS; *m/z*: 592.1426 ([M$^+$]; exact mass calc. for C$_{36}$H$_{30}$ ^{56}FeO$_2$BP: 592.1426).

4.23. 1,1′-Bisbenzoyl-(R_p)-2-methyl-(S_p)-2′-diphenyl(hydroxy)methylferrocene (**6a**)

A solution of the hydrazone **5c** (140 mg, 0.12 mmol) in DME (5 ml) was first treated with SnCl$_2$·2H$_2$O (0.09 g, 0.3 mmol) and afterwards with H$_2$O (0.43 ml). The reaction mixture was refluxed for 4 h. To drive the reaction to completion, it was necessary to add two further portions of SnCl$_2$·2H$_2$O as the Sn(II)-species was deactivated after some time. The mixture was diluted with Et$_2$O and washed with aqueous buffer (pH 9) and brine. The organic layer was dried over MgSO$_4$ and concentrated in vacuo. Finally the crude product was purified by preparative HPLC (pentane–Et$_2$O 4:1).

Yield: 42 mg (58%, dark red crystals); m.p.: 184 °C. $R_f = 0.59$ (pentane–Et$_2$O 4:1). ee ≥ 99%. $[\alpha]_D^{25} = -215.1$ ($c = 0.27$, CHCl$_3$). IR (CHCl$_3$, cm^{-1}): ν 3299 (w), 3060 (w), 3016 (m), 2955 (w), 2918 (m), 2850 (w), 1627 (m), 1598 (m), 1578 (m), 1490 (m), 1449 (s), 1421 (m), 1382 (m), 1339 (m), 1271 (m), 1264 (m), 1218 (m), 1179 (m), 1074 (w), 1044 (w), 1026 (m), 938 (w), 906 (w), 888 (w), 843 (w), 756 (vs), 700 (s), 668 (m), 518 (m). ^{1}H-NMR (C$_6$D$_6$, 400 MHz): δ 2.04 (s, 3H, C*H*$_3$), 4.02 (dd, 1H, $J = 2.8$, 1.7 Hz, Cp-*H*), 4.10 (t, 1H, $J = 2.6$ Hz, Cp-*H*), 4.40 (dd, 1H, $J = 2.8$, 1.7 Hz, Cp-*H*), 4.53 (m, 1H, Cp-*H*), 4.56 (dd, 1H, $J = 2.8$, 1.4 Hz, Cp-*H*), 4.82 (t, 1H, $J = 2.6$ Hz, Cp-*H*), 6.80–7.80 (m, 20H, C$_6$*H*$_5$). ^{13}C-NMR (C$_6$D$_6$, 100 MHz): δ 13.86, 73.65, 74.23, 75.03, 76.36, 76.96, 77.13, 77.26, 79.53, 90.45, 106.91, 126.83, 126.91, 127.41, 127.48, 127.52, 128.57, 131.55, 131.69, 139.60, 139.81, 146.15, 149.47, 197.97, 202.42. The remaining aromatic signals are covered by the solvent. EIMS (70 eV); *m/z*: (relative intensity, %) 590 ([M$^{+\bullet}$], 1), 407 (M$^{+\bullet}$] − Ph$_2$COH, 20), 369 (25), 368 (100), 350 (34), 334 (23), 309 (16), 254 (30), 251 (11), 237 (19), 229 (31), 228 (19), 226 (11), 202 (11), 186 (21), 182 (10), 180 (11), 105 ([C$_6$H$_5$CO$^+$], 28), 79 (12), 77 ([C$_6$H$_5^+$], 26), 57 (17), 55 (15). HRMS; *m/z*: 590.2996 ([M$^+$]; exact mass calc. for C$_{38}$H$_{30}$ ^{56}FeO$_3$: 590.1544).

4.24. 1,1′-Bisbenzoyl-(S_p)-2′-(4-methylphenyl)sulfanyl-(S_p)-2-methylsulfanylferrocene (**6b**)

According to GP3, a solution of the hydrazone **5f** (174 mg, 0.22 mmol) in DME (11 ml) was treated with a 20% aqueous solution of TiCl$_3$ (1.1 ml, 1.1 mmol) and refluxed for 1.5 h. The ketone **6b** was obtained by aqueous work up and purification by column chromatography on silica gel (pentane–Et$_2$O 4:1).

Yield: 101 mg (82%, orange oil). $R_f = 0.17$ (pentane–Et$_2$O 4:1). ee ≥ 99%. $[\alpha]_D^{25} = -1146.4$ ($c = 0.27$, CHCl$_3$). IR (CHCl$_3$, cm^{-1}): ν 3057 (w), 3016 (m), 2963 (w), 2921 (m), 2856 (w), 1637 (vs), 1597 (m), 1577 (m), 1491 (m), 1447 (s), 1423 (s), 1392 (m), 1378 (m), 1333 (s), 1262 (s), 1216 (w), 1195 (w), 1176 (m), 1105 (w), 1074 (m), 1051 (m), 1015 (m), 872 (s), 848 (m), 813 (m), 756 (s), 728 (s), 699 (m), 675 (m), 501 (m). ^{1}H-NMR (C$_6$D$_6$, 300 MHz): δ 1.99 (s, 3H, C$_6$H$_4$–C*H*$_3$), 2.20 (s, 3H, SC*H*$_3$), 4.08 (q, 1H, $J = 2.7$ Hz, Cp-*H*), 4.25 (q, 1H, $J = 2.7$ Hz, Cp-*H*), 4.38 (m, 1H, Cp-*H*), 4.43 (m, 2H, Cp-*H*), 4.50 (m, 1H, Cp-*H*), 6.86 (d, 2H, $J = 8.0$ Hz, C$_6$H$_4$), 6.96–7.12 (m, 6H, *p*-C$_6$*H*$_5$, *m*-C$_6$*H*$_5$), 7.51 (br d, 2H, C$_6$*H*$_4$), 7.69 (m, 4H, *o*-C$_6$H$_5$). ^{13}C-NMR (C$_6$D$_6$, 75 MHz): δ 16.48, 20.96, 73.33, 73.65, 74.11, 74.23, 74.32, 77.51, 79.18, 93.83, 97.49, 127.12, 128.55, 128.89, 130.12, 131.56, 131.91, 133.14, 133.56, 137.53, 139.47, 139.89, 196.59, 197.24. The remaining aromatic signals are covered by the solvent. EIMS (70 eV); *m/z*: (relative intensity, %) 564 ([M$^{+\bullet}$ + 1], 15), 563 ([M$^{+\bullet}$], 36), 562 ([M$^{+\bullet}$ − 1], 100), 392 (17), 292 (20), 229 (10), 216 (15), 172 (10), 171 (11), 105 ([C$_6$H$_5$CO$^+$], 90), 77 (22). HRMS; *m/z*: 562.0723 ([M$^+$]; exact mass calc. for C$_{32}$H$_{26}$ ^{56}FeO$_2$S$_2$: 562.0724).

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