Enantioselective Synthesis of Planar Chiral *ortho*-Functionalized Ferrocenyl Ketones

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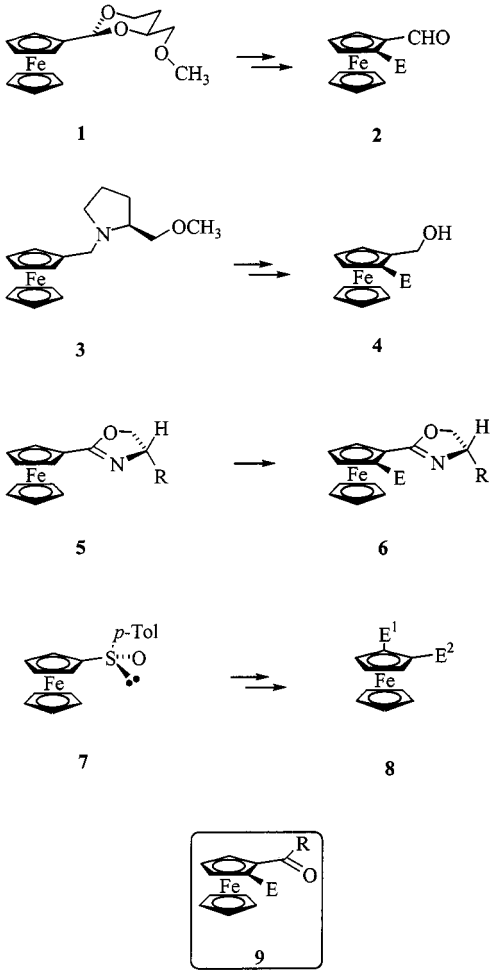
An efficient and flexible asymmetric synthesis of planar chiral *ortho*-functionalized ferrocenyl ketones in good overall yields (35–79%) and enantiomeric excesses (*ee* = 71–96%) is described. The key step of the procedure is the diastereoselective (*de* = 87–98%) orthometalation of ferrocenyl ketone SAMP hydrazones, followed by trapping with various electrophiles such as MeI, Me_3SiCl, Ph_2PCl, Ph_2CO, Me_2NCHO or I_2. Subsequent oxidative or reductive hydrazone cleavage leads to the title compounds.

Introduction

In recent years, planar chiral ferrocenes have been found to be extraordinarily efficient ligands for asymmetric catalysis in research and industry.[1] There has therefore been a renaissance of interest since the pioneering work of Ugi et al.[2] in developing modern methods for the asymmetric synthesis of planar chiral ferrocenyl ligands, thus enabling an extension to the variety of accessible derivatives. The modern auxiliary-based methodologies complement one another by the way they are able to access planar chiral ferrocenes at differing oxidation states (Scheme 1): chiral acetal **1** gives rise to planar chiral aldehydes **2**,[3] (*S*)-(2-methoxymethylpyrrolidin-1-yl)methylferrocene **(3)** yields planar chiral alcohols **4**[4] and oxazolines **5** are precursors for planar chiral carboxylic acid equivalent **6**.[5] Additionally, the chiral sulfoxides **7** provide a highly flexible approach to a wide range of planar chiral derivatives **8**, since the sulfoxide moiety may be substituted by different electrophiles.[6]

We report here the enantioselective synthesis of planar chiral ferrocenyl ketones **9** via diastereoselective orthometalation based on our SAMP/RAMP hydrazone method.[7] Parts of this work were recently published as a preliminary communication.[8]



Scheme 1. Modern auxiliary based methodologies to planar chiral ferrocenes at differing oxidation states

Results and Discussion

As has been known for nearly half a century, the ferrocenyl ketones **11** are easily accessible by Friedel–Crafts acylation of ferrocene **(10)**, demonstrating its strong aromatic character (Scheme 2).[9]

Since the electron-donating character of the ferrocenyl residue reduces the electrophilicity of the ketones **11**, they could not be transformed to the corresponding hydrazones using conventional methods such as stirring the ketone and hydrazine over molecular sieves or by azeotropic removal of the resulting water. In 1994, Bildstein et al. presented a method which allows the conversion of electron-rich ketones into their corresponding *N*,*N*-dimethylhydrazones by activating both the hydrazine and ketone with $AlMe_3$.[10] It

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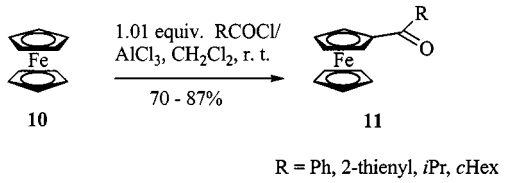
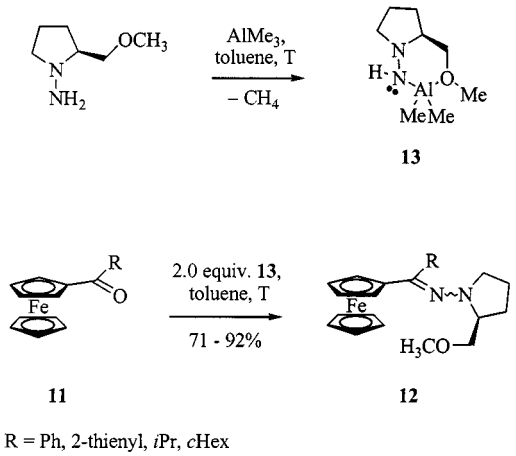


Scheme 2. Synthesis of ferrocenyl ketones **11** by Friedel–Crafts acylation

was found that this method is also applicable to the synthesis of SAMP hydrazones **12** (Scheme 3, Table 1).



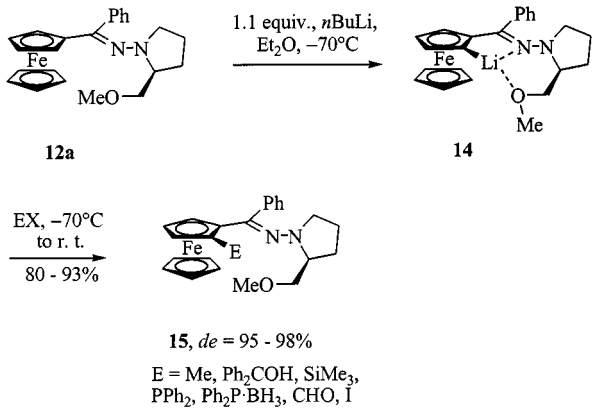
Scheme 3. Synthesis of ferrocenyl ketone SAMP hydrazones **12**

Table 1. Synthesis of ferrocenyl ketone SAMP hydrazones **12**

12	R	Yield [%]	*E*/*Z*
a	Ph	73	8.0:1
b	*i*Pr	75	1:2.9
c	*c*Hex	92	1:3.1
d	2-thienyl	71	4.9:1

SAMP [(*S*)-1-amino-2-methoxymethylpyrrolidine] and $AlMe_3$ were heated for several hours in refluxing toluene forming hydrazide complex **13** with evolution of methane. Two equivalents of **13** were required since the use of one equivalent resulted in the conversion of only 50%. This is a result of the formation of an *N*,*N*-ketal intermediate. When R is an aromatic residue (Ph, 2-thienyl), the (*E*)-hydrazones **12** are formed preferentially. Conversely, (*Z*)-**12** is formed if R is an α-branched alkyl moiety. With the exception of **12d**, the (*E*)- and (*Z*)-hydrazones are separated easily by flash chromatography.

(*E*)-Benzoylferrocene SAMP hydrazone **(12a)** is smoothly *ortho*-lithiated in diethyl ether at −70 °C using 1.1 equivalents of *n*BuLi (Scheme 4). The metalated species **14** can be trapped by a variety of electrophiles to give the resulting planar chiral hydrazones **15** in good yields (80–93%) and high diastereomeric excesses (*de* = 95–98%). The broad applicability of this method was demonstrated by an alkylation (EX = MeI), silylation (EX = Me_3SiCl), phosphinylation (EX = Ph_2PCl), hydroxyalkylation (EX = Ph_2CO), formylation (EX = Me_2NCHO) and iodination (EX = I_2) (Table 2).



Scheme 4. Diastereoselective *ortho*-functionalization of benzoylferrocene SAMP hydrazone **12a**

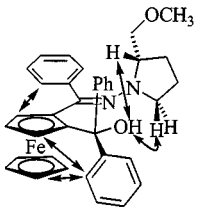
Table 2. Diastereoselective *ortho*-functionalization of ferrocenyl ketone SAMP hydrazones **12a**

15	E	Yield [%]	*de* [%]	Confg.
a	Me	85	97	(S,R_p)
b	$SiMe_3$	91	96	(S,S_p)
c	PPh_2	89	≥96	(S,S_p)
d	$Ph_2P{\cdot}BH_3$	80	≥96	(S,S_p)
e	Ph_2COH	86	98	(S,S_p)
f	CHO	93	≥96	(S,S_p)
g	I	82	95	(S,S_p)

Interestingly, the diastereoselectivity is strongly dependent on the chosen lithiation temperature. While metalation at room temperature led, after quenching with methyl iodide, to the (S,S_p)-configured product with a *de* of 47%, working at 0 °C decreased the *de* to 14%. Conversely, lithiation at −70 °C yielded the (S,R_p)-configured planar chiral hydrazone **15a** with a *de* of 97%. By employing other electrophiles (Me_3SiCl, Ph_2CO, Ph_2PCl), similar *de* values were obtained when performing the lithiation step at different temperatures as the diastereoselectivity is determined mainly by this lithiation step.

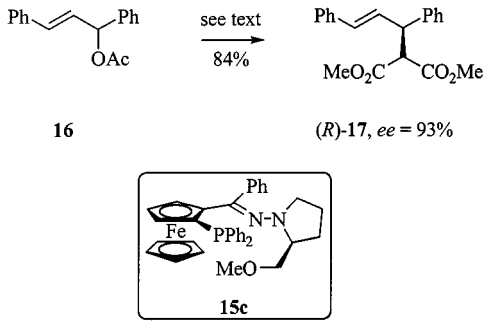
The planar chiral derivatives **15** were obtained in a microcrystalline, amorphous or oily state, thus preventing us from determining the absolute configuration by X-ray-analysis. However, it was possible to determine the absolute configuration by NOE experiments. Compound **15e** was found to be suitable for this purpose as the hydrogen bond between the hydroxyl proton and the imino nitrogen results in a rigid conformation. The intensive interactions between O*H* and NC*H* and between O*H* and NCH_2 *cis* to NC*H* can only be explained by the absolute configuration shown in Figure 1. To the best of our knowledge, this is the first determination of the absolute configuration of a planar chiral compound by means of NOE measurements. Since the configuration of *ortho*-functionalized benzoylferrocene SAMP hydrazones **15** is fixed predominantly by the lithiation step, the configurations of all the other derivatives given are based on a uniform reaction pathway.

The phosphanylhydrazone **15c** turned out to be an efficient *P*,*N*-ligand in the standard Pd-catalyzed allylic alkylation of (±)-1,3-diphenyl-2-propenyl acetate **(16)** with di-



15e

Figure 1. NOE connectivities for planar chiral *ortho*-hydroxyalkylated SAMP hydrazone **15e**

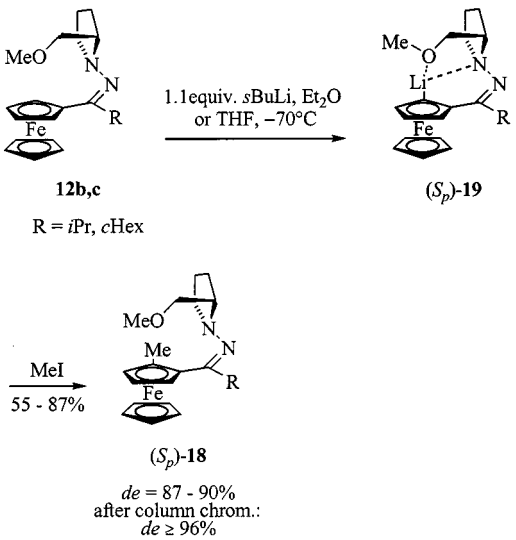


16 (*R*)-**17**, *ee* = 93%

Scheme 5. Pd-catalyzed allylic alkylation; reaction conditions: 1.0 mol-% $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 4.0 mol-% **15c**, 1.0 mol-% KOAc, 3.0 equiv. dimethylmalonate/BSA, CH_2Cl_2, room temp., 24 h

methylmalonate/*N*,*O*-bis(trimethylsilyl)acetamide (BSA, Scheme 5).[11] Employing 4.0 mol-% of ligand **15c** and 1.0 mol-% $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ yields (*R*)-**17** with an *ee* of 93% within 24 hours at room temperature in dichloromethane (yield 84%).

It was found that *n*BuLi was not basic enough to achieve the orthometalation of the (*Z*)-configured hydrazones **12b** and **12c**. However, by the use of 1.1 equiv. of *s*BuLi, the orthometalations proceed at −70 °C in diethyl ether or THF providing, after electrophilic trapping with methyl iodide, the planar chiral hydrazones **18** with *de* values of 87% (**18a**, R = *i*Pr) and 90% (**18b**, R = *c*Hex) (Scheme 6). After purification by flash chromatography the products



12b,c

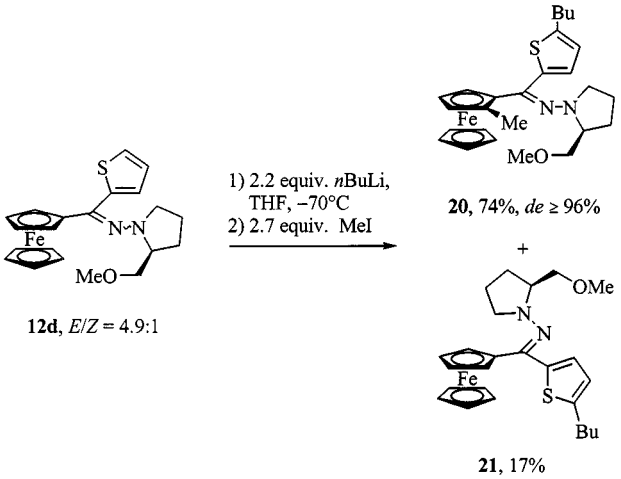
R = *i*Pr, *c*Hex

(S_p)-**19**

(S_p)-**18**

de = 87 - 90%
after column chrom.:
de ≥ 96%

Scheme 6. Diastereoselective *ortho*-alkylation of (*Z*)-ferrocenyl SAMP hydrazones



12d, *E*/*Z* = 4.9:1

20, 74%, *de* ≥ 96%

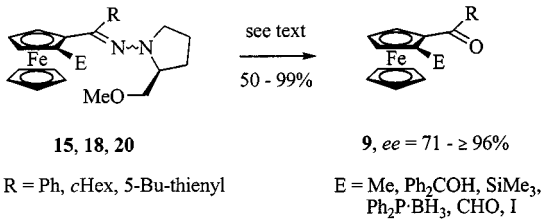
21, 17%

Scheme 7. Unexpected butyl addition to the thiophene ring in **12d**

were obtained diastereomerically pure [yield = 55% (**18a**) vs. 87% (**18b**)]. These results demonstrate that orthometalations proceeding via five-membered ring chelate systems, as in **14**, occur more smoothly and more selectively than those proceeding via six-membered ring chelate systems as in **19**. The determination of absolute configuration by NOE-experiments proved that (*Z*)-hydrazones are lithiated predominantly at the other *ortho*-position.

The standard metalation conditions for benzoylferrocene SAMP hydrazone **12a** (1.1 equiv. *n*BuLi, Et_2O, −70 °C) could not be applied to the orthometalation of the thiophene derivative **12d**, since the 3-position of the heterocycle is deprotonated preferentially, whereas in THF the 5-position is deprotonated. The addition of 2.2 equiv. of *n*BuLi in THF at −70 °C gave, instead of the expected formation of a dianion, an addition of the butyl residue to the 5-position of the heterocyclic system furnishing a mixture of **20** and **21** after electrophilic quenching with methyl iodide (Scheme 7). The oxidative rearomatization probably occurs during work up.

Cleavage of the auxiliary to regenerate the ketone functionality was generally accomplished by ozonolysis in dichloromethane at −78 °C (Scheme 8).



15, **18**, **20**

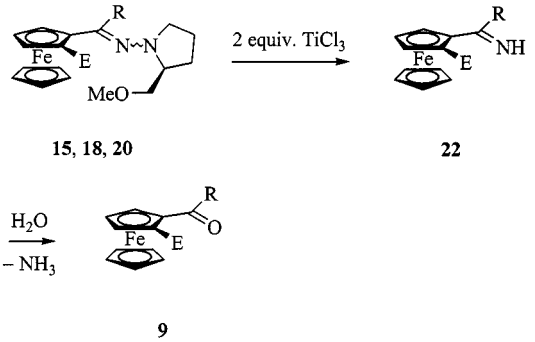
R = Ph, *c*Hex, 5-Bu-thienyl

9, *ee* = 71 - ≥ 96%

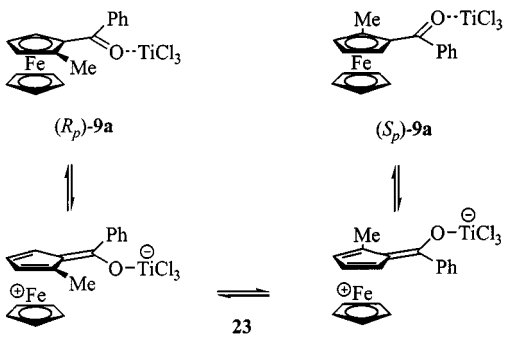
E = Me, Ph_2COH, $SiMe_3$, $Ph_2P{\cdot}BH_3$, CHO, I

Scheme 8. Regeneration of the ketone moiety; reaction conditions: O_3, CH_2Cl_2, −78 °C or $TiCl_3$, DME, H_2O, Δ*T* or $SnCl_2$, DME, H_2O, Δ*T* or $Cr(OAc)_2$, THF, H_2O, Δ*T* or VCl_2, THF, H_2O, Δ*T*

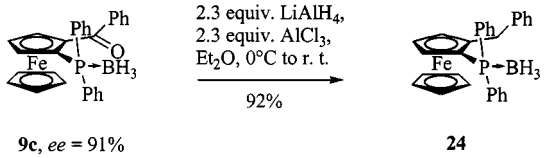
However, in several cases the planar chiral hydrazones **15**, **18** and **20** turned out to be rather sensitive towards oxidative reaction conditions. Furthermore, these compounds are not compatible with organic or mineral acids. Thus, we examined if the planar chiral hydrazones could be converted into the corresponding ketones **9** employing reducing Lewis acids. $TiCl_3$ is known for its ability to cleave the



Scheme 9. SAMP hydrazone cleavage employing the reductive Lewis acid $TiCl_3$



Scheme 10. Proposed racemization mechanism of planar chiral ferrocenyl ketones in the presence of Lewis acids like $TiCl_3$



Scheme 11. Reduction of ketone **9c** to planar chiral monophosphanyl ligand **24**

N−O bonds of oxime ethers[12] and the N−N bonds of 2,4-dinitrophenyl hydrazones[13] and tosylhydrazones.[14] In the case of ferrocenyl ketone SAMP hydrazones, we also assume that the N−N cleavage takes place yielding the ferrocenylketimine **22**, which rapidly hydrolyzes to form the corresponding ketone **9** (Scheme 9). During the cleavage, Ti^{III} is oxidized to Ti^{IV}, which hydrolyzes forming a TiO_2 precipitate. Alternatively, $SnCl_2$, VCl_2 and $Cr(OAc)_2$ were found to be efficient reductive cleavage reagents.[15]

All cleavage procedures mentioned here are accompanied by a low degree of racemization. However, the title *ortho*-functionalized ferrocenyl ketones **9** could be obtained, with one exception, in high enantiomeric purity (*ee* = 90−96%, Table 3).

Table 3. Cleavage of ferrocenyl ketone SAMP hydrazones **15**, **18** and **20** to their corresponding ketones **9**

9	E	R	Reagent	Yield [%]	*ee* [%]	Confg.
a	Me	Ph	$TiCl_3$	89	90[a]	(R_p)
a	Me	Ph	O_3	50	89[a]	(R_p)
b	$SiMe_3$	Ph	O_3	76	92[b]	(S_p)
c	$Ph_2P{\cdot}BH_3$	Ph	O_3	83	91[c]	(S_p)
d	Ph_2COH	Ph	$SnCl_2$	85	96[c]	(R_p)
d	Ph_2COH	Ph	O_3	70	85[c]	(R_p)
e	CHO	Ph	O_3	73	90[d]	(R_p)
f	I	Ph	$SnCl_2$	78	71[a]	(S_p)
g	Me	Cy	$TiCl_3$	99	≥96[c]	(S_p)
h	Me	5-butyl-2-thienyl	$Cr(OAc)_2$	67	[e]	(R_p)

[a] Determined by HPLC on a chiral stationary phase (Chiracel OD-2). − [b] Determined by HPLC on a chiral stationary phase [(*S*,*S*)-Whelk-O 1]. − [c] Determined by ^1H NMR spectroscopy using (−)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol as chiral cosolvent. − [d] Determined by ^1H NMR spectroscopy after quantitative reaction of the aldehyde with SAMP. − [e] Not determined yet.

As was demonstrated by Falk et al., the acid catalyzed racemization of ferrocenyl ketones such as **9a** proceeds intramolecularly.[16] The Lewis acid (here $TiCl_3$) coordinates to the ketone forming the enolate structure **23** (Scheme 10). The substituted cyclopentadienyl ring is decomplexed from the iron atom leaving the ligand in a solvent cage, where it turns upside down. Recoordination by the iron from the opposite face now furnishes the enantiomer of the initial ferrocene **9a**.

More curious is the racemization in the case of ozonolysis. The following observation may, however, be of interest: ozonolysis of a sample of **15e** with a *de* value of 2% gave rise to the planar chiral ketone **9d** with an *ee* value of 57% as one diastereomer reacted at a much slower rate. In order to convert **15e** into **9d**, prolonged reaction times had to be applied.

In order to reduce the ketone moiety to the corresponding methylene group, ketone **9c** was treated with $LiAlH_4$/$AlCl_3$ (2.3 equiv.) in diethyl ether (Scheme 11) to give the BH_3-protected planar chiral monophosphane ligand **24** in high yield (92%). This example demonstrates that the planar chiral ferrocenyl ketones **9** should be interesting compounds as precursors profiting from the versatile ketone chemistry.

Conclusion

In conclusion, we have developed a flexible enantioselective synthesis of planar chiral ferrocenyl ketones by diastereoselective orthometalation employing SAMP as a highly efficient chiral auxiliary. The broad applicability of this methodology was demonstrated by alkylation, silylation, phosphinylation, hydroxyalkylation, formylation and iodination.

Experimental Section

General Remarks: All solvents were dried and distilled prior to use. − Column chromatography: Merck silica gel 60, 0.040−0.063 mm (230−400 mesh) (flash). − Optical rotation values: Perkin−Elmer P 241, solvent UVASOL-quality. − Melting points (uncorrected): Büchi 510. − IR: Perkin−Elmer FT 1750. − NMR: Varian VXR 300 and Gemini 300 (300 and 75 MHz for ^1H and ^{13}C, respectively), Varian Inova 400 (400, 100 and 162 MHz for ^1H, ^{13}C and ^{31}P, respectively), Varian Unity 500 (500, 125 and 202 MHz for ^1H, ^{13}C and ^{31}P, respectively), C_6D_6 or $CDCl_3$ as solvent, TMS as internal standard. − MS: Finnigan MAT (70 eV). − Elemental analyses (C,H,N): elementar vario EL. − High Resolution MS: Finnigan MAT, MAT 95. − The diastereomeric excesses were deter-

mined by NMR-spectroscopy. The enantiomeric excesses were determined by HPLC employing chiral stationary phases or by NMR spectroscopy using the Pirkle alcohol as a chiral shift reagent.

General Procedure for the Preparation of Ferrocenyl Ketones 11 (GP1): To a suspension of $AlCl_3$ (1.06 equiv.) in dichloromethane (0.5 mL/mmol) was added 1.01 equiv. of an acid chloride. The mixture was stirred until the Al salt was almost completely dissolved. The resulting solution was added to a solution of ferrocene **10** (1.00 equiv.) in dichloromethane (0.75 mL/mmol). After stirring for the appropriate time (TLC control) at room temperature, the reaction mixture was poured onto crushed ice/aqueous saturated $NaHCO_3$. The aqueous phase was extracted three times with diethyl ether. The collected organic phase was washed with saturated aqueous $NaHCO_3$ and twice with saturated aqueous NaCl. After drying over $MgSO_4$ and concentrating in vacuo, the crude product was dissolved in a minimum of dichloromethane and purified by filtration through silica gel.

Cyclohexyl(ferrocenyl)methanone (11c): According to GP1, a solution of ferrocene **10** (10.00 g) in CH_2Cl_2 (40 mL) was treated with a solution of $AlCl_3$ (7.60 g, 1.06 equiv.) and cyclohexane carboxylic acid chloride (7.96 g, 1.01 equiv.) in CH_2Cl_2 (30 mL). After 48 h stirring at room temp. the reaction mixture was worked up and the product purified by filtration through silica gel (petroleum ether/diethyl ether = 2:1). − Yield: 11.10 g (70%, orange crystals). − R_f = 0.58 (petroleum ether/diethyl ether = 2:1). − M.p. 76 °C. − IR (KBr): $\tilde{\nu}$ = 3117 cm^{-1}, 3093, 2922, 2852, 2242, 1659, 1451, 1413, 1381, 1341, 1311, 1296, 1262, 1223, 1179, 1142, 1106, 1089, 1078, 1044, 1026, 1003, 978, 894, 838, 806, 767, 738, 547, 509, 485, 468. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.06−1.93 (m, 10 H, CH_2), 2.71 (tt, $^3J_{trans}$ = 11.5 Hz, $^3J_{cis}$ = 3.6 Hz, 1 H, COCH), 3.95 (s, 5 H, C_5H_5), 4.11 (t, $^{3/4}J$ = 1.9 Hz, 2 H, *m*-C_5H_4R), 4.69 (t, $^{3/4}J$ = 1.9 Hz, 2 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 26.26 (CH_2), 26.30 (CH_2), 30.1 (CH_2), 47.9 (*C*HCO), 69.75 (C_5H_5), 69.79, 72.0 (C_5H_4R), 79.3 (*i*-C_5H_4R), 205.7 (C=O). − EI-MS: *m*/*z* = 296.1 (100) [M^+], 213.0 (42) [$M^+ - C_6H_{11}$], 185.0 (29) [Fc^+], 129.1 (25) [$C_{10}H_9^+$], 120.9 (12) [$CpFe^+$], 55.9 (9) [Fe^+]. − $C_{17}H_{20}FeO$ (296.2): calcd. C 68.94, H 6.81; found C 68.82, H 6.88.

Ferrocenyl(2-thienyl)methanone (11d): According to GP1, a solution of ferrocene **10** (10.00 g) in CH_2Cl_2 (40 mL) was treated with a solution of $AlCl_3$ (7.60 g, 1.06 equiv.) and 2-thienyl carboxylic acid chloride (7.87 g, 1.01 equiv.) in CH_2Cl_2 (30 mL). After 48 h stirring at room temp. the reaction mixture was worked up and the product purified by filtration through silica gel (petroleum ether/diethyl ether = 2:1). − Yield: 13.65 g (87%, red crystals). − R_f = 0.41 (hexane/diethyl ether = 4:1). − M.p. 122 °C. − IR (KBr): $\tilde{\nu}$ = 3177 cm^{-1}, 3098, 3081, 2929, 2371, 2345, 2251, 1775, 1721, 1603, 1592, 1514, 1447, 1411, 1377, 1353, 1328, 1294, 1234, 1211, 1158, 1106, 1082, 1055, 1043, 1024, 1003, 924, 896, 875, 864, 857, 849, 830, 823, 799, 756, 745. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.22 (s, 5 H, C_5H_5), 4.59 (m, 2 H, *m*-C_5H_4R), 5.02 (m, 2 H, *o*-C_5H_4R), 7.15 (dd, ^3J = 4.7 Hz, ^3J = 4.0 Hz, 1 H, C_4H_3S), 7.61 (d, ^3J = 4.7, 1 H, C_4H_3S), 7.92 (d, ^3J = 3.4 Hz, 1 H, C_4H_3S). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 70.4 (C_5H_5), 71.0, 72.3 (C_5H_4R), 78.9 (*i*-C_5H_4R), 127.6, 131.5, 131.7 (C_4H_3S), 144.2 (*i*-C_4H_3S), 189.3 (C=O). − EI-MS: *m*/*z* = 295.9 (100) [M^+], 267.8 (12) [M^+ − CO], 147.0 (12) [$C_5H_4C_4H_3S^+$], 138.9 (21) [267.8 − $FeC_5H_4S^+$], 120.8 (18) [$CpFe^+$], 114.9 (12), 112.8 (12) [147.0 − H_2S], 110.9 (16) [$C_4H_3SCO^+$], 57.1 (12) [FeH^+], 56.1 (16) [Fe^+]. − $C_{15}H_{12}FeOS$ (296.2): calcd. C 60.83, H 4.08; found C 60.74, H 4.37.

General Procedure for the Preparation of Hydrazones 12 (GP2): A Schlenk flask fitted with a reflux condenser and a silicon oil bubbler was charged under argon with $AlMe_3$ (2.0 equiv., 2 M in toluene, 1−2 mL/mmol). SAMP **12** (2.0 equiv.) was then added slowly. After the evolution of methane subsided, the mixture was refluxed for 7 h. Ferrocenyl ketone **11** (1.0 equiv.) dissolved in toluene (1−2 mL/mmol) was added dropwise to the red-brown solution. The mixture was refluxed until completion (TLC control), cooled to 0 °C, poured onto crushed ice and washed with 5% aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by flash chromatography enabling separation of the (*E*)- and (*Z*)-isomers of **12** in most cases.

SAMP Hydrazone 12a: According to GP2, a solution of ketone **11a** (4.00 g) in toluene (70 mL) was added to a solution of hydrazide **13** (2.0 equiv.) in toluene (50 mL). After refluxing for 31 h, the reaction mixture was worked up. Flash chromatography (petroleum ether/diethyl ether = 4:1; 2% NEt_3) gave (*E*)-**12a**. − Yield: 4.06 g (73%, red-brown oil). − R_f = 0.58 (petroleum ether/diethyl ether = 2:1; 2% NEt_3). − $[\alpha]_D^{25}$ = +512.5 ($CHCl_3$, *c* = 1.20). − IR (neat): $\tilde{\nu}$ = 3093 cm^{-1}, 3057, 3024, 2970, 2925, 2873, 2825, 2731, 1600, 1566, 1491, 1459, 1443, 1381, 1336, 1321, 1295, 1218, 1195, 1106, 1071, 1054, 1024, 1002, 971, 904, 876, 818, 774, 721, 700, 600, 577, 501, 483. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.30−1.90 (m, 4 H, β-ring-CH_2), 2.36 (m, 1 H, NCH_2), 2.70 (m, 1 H, NCH_2), 3.28 (s, 3 H, OCH_3), 3.48 (dd, ^2J = 9.1 Hz, ^3J = 7.4 Hz, 1 H, OCH_2), 3.73 (m, 1 H, NCH), 3.84 (dd, ^2J = 8.7 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 4.08−4.14 (m, 2 H, C_5H_4R), 4.11 (s, 5 H, C_5H_5), 4.55 (m, 1 H, C_5H_4R), 4.68 (m, 1 H, C_5H_4R), 7.06−7.27 (m, 3 H, *m*-C_6H_5, *p*-C_6H_5), 7.50 (dm, ^3J = 8.1 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 23.3 (NCH_2CH_2), 27.3 ($NCHCH_2$), 55.1 (NCH_2), 59.0 (OCH_3), 66.9, 68.0, 68.4, 69.1, 69.4 (C_5H_4R, NCH), 69.7 (C_5H_5), 76.5 (OCH_2), 86.4 (*i*-C_5H_4R), 127.7 (*p*-C_6H_5), 128.2, 129.1 (*o*/*m*-C_6H_5), 139.1 (*i*-C_6H_5), 150.9 (C=N). − EI-MS: *m*/*z* = 402.0 (51) [M^+], 356.9 (37) [$M^+ - CH_2OCH_3$], 287.9 (100) [$M^+ - C_6H_{12}NO$], 274.9 (61), 210.9 (13), 184.9 (92) [Fc^+], 178.3 (23), 152.9 (10), 151.9 (12), 128.9 (71) [Fc^+ − Fe], 120.9 (45) [$CpFe^+$], 77 (12) [$C_6H_5^+$], 56 (14) [Fe^+]. − $C_{23}H_{26}FeN_2O$ (402.3): calcd. C 68.66, H 6.51, N 6.96; found C 69.04, H 6.51, N 6.81.

SAMP Hydrazone 12b: According to GP2, a solution of ketone **11b** (1.77 g) in toluene (50 mL) was added to a solution of hydrazide **13** (2.0 equiv.) in toluene (50 mL). After refluxing for 28 h, the reaction mixture was worked up. Flash chromatography (petroleum ether/diethyl ether = 4:1; 2% NEt_3) allowed a separation of (*Z*)-**12b** and (*E*)-**12b**. − Yield: 1.90 g (75%, red-brown oil). − *Z*/*E* = 2.9:1. − R_f = 0.48 [(*Z*)-isomer; petroleum ether/ethyl acetate = 15:1; 2% NEt_3]; R_f = 0.33 [(*E*)-isomer; petroleum ether/ethyl acetate = 15:1; 2% NEt_3]. − $[\alpha]_D^{25}$ = −620.1 [(*Z*)-isomer, $CHCl_3$, *c* = 1.43]. − IR ($CHCl_3$): $\tilde{\nu}$ = 3096 cm^{-1}, 2962, 2922, 2871, 2825, 1714, 1660, 1599, 1449, 1381, 1361, 1334, 1280, 1247, 1218, 1197, 1107, 1066, 1031, 1002, 970, 906, 875, 820, 757, 667, 634, 497, 482. − ^{1}H NMR [(*Z*)-isomer, 300 MHz, C_6D_6]: δ = 1.27 [d, ^3J = 6.6 Hz, 3 H, $CH(CH_3)_2$], 1.47 [d, ^3J = 6.6 Hz, 3 H, $CH(CH_3)_2$], 1.50−1.80 (m, 4 H, β-ring-CH_2), 1.98 (m, 1 H, NCH_2), 2.24 (q, $^{2,3}J$ = 8.6 Hz, 1 H, NCH_2), 2.95 [sept, ^3J = 6.6 Hz, 1 H, $CH(CH_3)_2$], 3.25 (s, 3 H, OCH_3), 3.43 (dd, ^2J = 8.8 Hz, ^3J = 7.1 Hz, 1 H, OCH_2), 3.51 (m, 1 H, NCH), 3.69 (dd, ^2J = 8.8 Hz, ^3J = 3.8 Hz, 1 H, OCH_2), 4.04 (s, 5 H, C_5H_5), 4.09 (m, 1 H, *m*-C_5H_4R), 4.14 (m, 1 H, *m*-C_5H_4R), 4.41 (m, 1 H, *o*-C_5H_4R), 5.31 (m, 1 H, *o*-C_5H_4R). − ^{1}H NMR [(*E*)-isomer, 300 MHz, C_6D_6): δ = 1.20 [d, ^3J = 7.1 Hz, 3 H, $CH(CH_3)_2$], 1.24 [d, ^3J = 7.4 Hz, 3 H, $CH(CH_3)_2$], 1.52−1.85 (m, 4 H, β-ring-CH_2), 2.04 (m, 1 H, NCH_2), 2.52 (q, $^{2,3}J$ = 8.5 Hz, 1 H, NCH_2), 2.84 [sept, ^3J = 6.9 Hz, 1 H, $CH(CH_3)_2$], 3.21 (s, 3 H, OCH_3), 3.33 (dd, ^2J = 8.8 Hz, ^3J = 7.1 Hz, 1 H, OCH_2), 3.49

(m, 1 H, NCH), 3.60 (dd, ^2J = 8.8 Hz, ^3J = 4.1 Hz, 1 H, OCH_2), 4.08 (s, 5 H, C_5H_5), 4.13 (m, 1 H, *m*-C_5H_4R), 4.66 (t, *J* = 1.7 Hz, 1 H, *m*-C_5H_4R), 4.71 (m, 1 H, *o*-C_5H_4R), 4.88 (m, 1 H, *o*-C_5H_4R). − ^{13}C NMR [(*Z*)-isomer, 75 MHz, C_6D_6]: δ = 21.0, 24.8 [$CH(CH_3)_2$], 22.5 (NCH_2CH_2), 27.3 ($NCHCH_2$), 34.9 [$CH(CH_3)_2$], 53.6 (NCH_2), 59.0 (OCH_3), 67.2, 69.3, 69.8, 70.6, 72.0 (C_5H_4R, NCH), 69.6 (C_5H_5), 76.5 (OCH_2), 78.9 (*i*-C_5H_4R), 164.7 (C=N). − ^{13}C NMR [(*E*)-isomer, 75 MHz, C_6D_6]: δ = 19.7, 21.1 [$CH(CH_3)_2$], 22.4 (NCH_2CH_2), 27.5 ($NCHCH_2$), 37.4 [$CH(CH_3)_2$], 55.9 (NCH_2), 58.9 (OCH_3), 66.9, 68.6, 69.19, 69.22, 72.0 (C_5H_4R, NCH), 69.9 (C_5H_5), 76.5 (OCH_2), 81.2 (*i*-C_5H_4R), 171.9 (C=N). − EI-MS: *m*/*z* = 368.0 (70) [M^+], 323.0 (49) [$M^+ - CH_2OCH_3$], 303.0 (16) [$M^+ - C_5H_5$], 257.9 (14), 253.9 (100) [$M^+ - C_6H_{12}NO$], 211.0 (26) [$FcCN^+$], 188.9 (11), 185.0 (52) [Fc^+], 161.5 (10), 129.0 (16) [$Fc^+ - Fe$], 56.0 (12) [Fe^+]. − $C_{20}H_{28}FeN_2O$ (368.3): calcd. C 65.22, H 7.66, N 7.61; found C 65.51, H 7.73, N 7.57.

SAMP Hydrazone 12c: According to GP2, a solution of ketone **11c** (2.04 g) in toluene (30 mL) was added to a solution of hydrazide **13** (2.0 equiv.) in toluene (30 mL). After refluxing for 10 h, the reaction mixture was worked up. Flash chromatography (petroleum ether/diethyl ether = 4:1; 2% NEt_3) allowed a separation of (*Z*)-**12c** and (*E*)-**12c**. − Yield: 2.60 g (92%, orange powder). − *Z*/*E* = 3.1:1. − R_f = 0.55 [(*Z*)-isomer; hexane/diethyl ether = 4:1; 2% NEt_3]; R_f = 0.49 [(*E*)-isomer; hexane/diethyl ether = 4:1; 2% NEt_3]. − $[\alpha]_D^{25}$ = −464.5 [(*Z*)-isomer, $CHCl_3$, *c* = 1.13]; $[\alpha]_D^{25}$ = +333.6 [(*E*)-isomer, $CHCl_3$, *c* = 0.97]. − M.p. 72 °C [(*Z*)-isomer]; M.p. 68 °C [(*E*)-isomer]. − IR (KBr): $\tilde{\nu}$ = 3138 cm^{-1}, 3098, 2970, 2956, 2922, 2878, 2852, 2812, 2722, 1655, 1591, 1476, 1451, 1412, 1382, 1345, 1331, 1305, 1276, 1254, 1226, 1199, 1182, 1156, 1127, 1107, 1094, 1061, 1045, 1035, 1023, 1002, 974, 915, 891, 817, 754, 724, 627, 522, 499, 482. − ^{1}H NMR [(*Z*)-isomer, 300 MHz, C_6D_6]: δ = 1.26−2.20 (m, 14 H, $(CH_2)_5$ and β-ring-CH_2), 2.26 (q, $^{2,3}J$ = 8.4 Hz, 1 H, NCH_2), 2.67 (tt, ^3J = 11.1 Hz, ^3J = 3.4 Hz, 1 H, N=CCH), 3.24 (m, 1 H, NCH_2), 3.26 (s, 3 H, OCH_3), 3.43 (dd, ^2J = 8.7 Hz, ^3J = 7.1 Hz, 1 H, OCH_2), 3.53 (qd, ^3J = 7.7 Hz, ^3J = 4.0 Hz, 1 H, NCH), 3.70 (dd, ^2J = 8.7 Hz, ^3J = 1.7 Hz, 1 H, OCH_2), 4.06 (s, 5 H, C_5H_5), 4.10 (td, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, *m*-C_5H_4R), 4.15 (td, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, *m*-C_5H_4R), 4.45 (dt, ^3J = 2.4 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R), 5.29 (dt, ^3J = 2.4 Hz, ^4J = 1.4 Hz, *o*-C_5H_4R). − ^{1}H NMR [(*E*)-isomer, 300 MHz, C_6D_6]: δ = 1.10−1.38 (m, 3 H), 1.60−1.95 [m, 11 H, $(CH_2)_5$ and β-ring-CH_2], 2.06 (m, 1 H, NCH_2), 2.55 (q, $^{2,3}J$ = 8.7 Hz, 1 H, NCH_2), 3.05 (tdd, ^3J = 9.1 Hz, ^3J = 7.7 Hz, ^3J = 3.7 Hz, 1 H, N=CCH), 3.23 (s, 3 H, OCH_3), 3.41 (dd, ^2J = 8.7 Hz, ^3J = 7.4 Hz, 1 H, OCH_2), 3.53 (qd, ^3J = 7.4 Hz, ^3J = 4.0 Hz, 1 H, NCH), 3.65 (dd, ^2J = 8.7 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 4.10 (s, 5 H, C_5H_5), 4.14 (m, 2 H, *m*-C_5H_4R), 4.80 (dt, ^3J = 2.7, ^4J = 1.3, 1 H, *o*-C_5H_4R), 4.96 (dt, ^3J = 2.4 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R). − ^{13}C NMR [(*Z*)-isomer, 300 MHz, C_6D_6]: δ = 22.5 (NCH_2CH_2), 26.8, 27.2, 27.3, 27.4, 30.7, 30.9 31.3, 35.7 (CH_2), 45.9 (N=C*C*H), 53.8 (NCH_2), 59.0 (OCH_3), 67.3, 69.2, 69.7, 70.5, 71.9 (C_5H_4R, NCH), 69.5 (C_5H_5), 76.5 (OCH_2), 79.1 (*i*-C_5H_4R), 164.0 (C=N). − ^{13}C NMR [(*E*)-isomer, 300 MHz, C_6D_6]: δ = 22.5 (NCH_2CH_2), 26.6, 27.0, 27.3, 27.6, 30.7, 30.9 (CH_2), 40.7 (N=C*C*H), 56.2 (NCH_2), 59.0 (OCH_3), 67.1, 69.0, 69.18, 69.22, 69.5 (C_5H_4R, NCH), 69.9 (C_5H_5), 76.5 (OCH_2), 82.1 (*i*-C_5H_4R), 170.6 (C=N). − EI-MS: *m*/*z* = 408.1 (43) [M^+], 363.0 (26) [$M^+ - CH_2OCH_3$], 242.0 (13) [$M^+ - C_5H_5$], 312.0 (11), 294.0 (100) [$M^+ - C_6H_{12}NO$], 212.0 (17) [294.0 − C_6H_{12}], 210.9 (27) [$FcCN^+$], 184.8 (33) [Fc^+], 128.8 (18), 120.9 (31) [$CpFe^+$], 55.1 (15). − $C_{23}H_{32}FeN_2O$ (408.4): C 67.65, H 7.90, N 6.86; found C 67.91, H 7.88, N 6.45.

SAMP Hydrazone 12d: According to GP2, a solution of ketone **11d** (2.04 g) in toluene (40 mL) was added to a solution of hydrazide **13** (2.0 equiv.) in toluene (30 mL). After heating to reflux for 9 h, the reaction mixture was worked up. Flash chromatography (petroleum ether/diethyl ether = 4:1; 2% NEt_3) provided a mixture of (*E*)-**12d** and (*Z*)-**12d**. − Yield: 1.96 g (71%, red-brown oil). − *E*/*Z* = 4.9:1. − R_f = 0.50 (hexane/diethyl ether = 4:1; 2% NEt_3). − $[\alpha]_D^{25}$ = +458.9 ($CHCl_3$, *c* = 1.31). − IR (neat): $\tilde{\nu}$ = 3094 cm^{-1}, 2970, 2924, 2873, 2727, 2732, 1640, 1553, 1459, 1425, 1383, 1352, 1336, 1282, 1228, 1195, 1159, 1107, 1055, 1024, 1002, 969, 903, 875, 820, 706, 576, 559, 499. − ^{1}H NMR [(*E*)-isomer, 300 MHz, C_6D_6]: δ = 1.36−1.98 (m, 4 H, β-ring-CH_2), 2.50 (ddd, ^2J = 9.7 Hz, ^3J = 8.4 Hz, ^3J = 6.7 Hz, 1 H, NCH_2), 3.02 (ddd, ^2J = 9.7 Hz, ^3J = 7.7 Hz, ^3J = 5.4 Hz, 1 H, NCH_2), 3.23 (s, 3 H, OCH_3), 3.46 (dd, ^2J = 9.7 Hz, ^3J = 8.4 Hz, 1 H, OCH_2), 3.75 (m, 2 H, OCH_2 and NCH), 4.13 (m, 2 H, *m*-C_5H_4R), 4.15 (s, 5 H, C_5H_5), 4.60 (dt, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 4.84 (dt, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 6.80 (dd, ^3J = 5.0 Hz, ^3J = 3.7 Hz, 1 H, C_4H_3S), 7.06 (dd, ^3J = 5.0 Hz, ^4J = 1.3 Hz, 1 H, C_4H_3S), 7.37 (dd, ^3J = 3.7 Hz, ^4J = 1.4 Hz, 1 H, C_4H_3S). − ^{13}C NMR [(*E*)-isomer, 75 MHz, C_6D_6): δ = 23.2 (NCH_2CH_2), 27.5 ($NCHCH_2$), 54.4 (NCH_2), 59.0 (OCH_3), 66.8, 67.8, 69.2, 69.4, 69.6 (C_5H_4R, NCH), 69.9 (C_5H_5), 76.4 (OCH_2), 86.1 (*i*-C_5H_4R), 125.3, 127.5, 129.6 (C_4H_3S), 138.8 (*i*-C_4H_3S), 147.3 (C=N). − EI-MS: *m*/*z* = 408.0 (92) [M^+], 363.0 (26) [$M^+ - CH_2OCH_3$] or [$M^+ - CH{=}S$], 293.9 (100) [$M^+ - C_6H_{12}NO$], 184.9 (68) [Fc^+], 181.4 (13), 128.8 (50), 120.8 (21) [$CpFe^+$], 55.8 (13) [Fe^+]. − $C_{21}H_{24}FeN_2OS$ (408.3): calcd. C 61.77, H 5.92, N 6.86; found C 61.87, H 6.06, N 7.17.

General Procedure for the *ortho*-Functionalization of Benzoylferrocene SAMP Hydrazone 12a (GP3): Hydrazone **12a** was dissolved in diethyl ether (10 mL/mmol) under argon and cooled down to −70 °C. A solution of *n*BuLi (1.1 equiv., 1.6 M in hexane) was added dropwise and the reaction mixture was stirred for 9 h at −70 °C. Then the electrophile (1.2 equiv.) was added. After warming to room temp. overnight, the solution was cooled to 0 °C and quenched with saturated aqueous NH_4Cl, washed with saturated aqueous NaCl and dried over $MgSO_4$. After concentrating in vacuo, the crude product was purified by flash chromatography.

Planar Chiral SAMP Hydrazone (*S*,*R*$_p$)-15a: According to GP3, a solution of (*E*)-**12a** (519 mg) in Et_2O (15 mL) was treated with a solution of *n*BuLi (1.1 equiv.) in hexane. After 9 h stirring at −70 °C, methyl iodide (122 μL) was added. The reaction mixture was allowed to warm to room temp. overnight. After work up, flash chromatography (petroleum ether/diethyl ether = 10:1; 2% NEt_3) provided the orthomethylated planar chiral hydrazone **17a**. − Yield: 457 mg (85%, red-brown oil). − R_f = 0.66 (petroleum ether/diethyl ether = 2:1; 2% NEt_3). − *de* = 97%. − $[\alpha]_D^{25}$ = +59.0 ($CHCl_3$, *c* = 1.20). − IR ($CHCl_3$): $\tilde{\nu}$ = 3387 cm^{-1}, 3092, 3057, 2972, 2946, 2922, 2874, 2827, 2731, 1642, 1598, 1578, 1460, 1444, 1428, 1377, 1348, 1322, 1277, 1227, 1198, 1106, 1072, 1036, 1028, 1002, 970, 941, 928, 903, 878, 850, 817, 773, 757, 724, 699, 667, 594, 508, 489. − ^{1}H NMR (major isomer, 500 MHz, C_6D_6): δ = 1.41 (m, 2 H, NCH_2CH_2), 1.58 (m, 1 H, $NCHCH_2$ *trans* to NCH), 1.88 (m, 1 H, $NCHCH_2$ *cis* to NCH), 2.29 (s, 3 H, CH_3), 2.44 (dt, ^2J = 9.8 Hz, ^3J = 7.4 Hz, 1 H, NCH_2 *cis* to NCH), 2.75 (dt, ^2J = 9.6 Hz, ^3J = 7.0 Hz, 1 H, NCH_2 *trans* to NCH), 3.25 (s, 3 H, OCH_3), 3.45 (dd, ^2J = 9.0 Hz, ^3J = 7.8 Hz, 1 H, OCH_2), 3.69 (m, 1 H, NCH), 3.82 (dd, ^2J = 9.0 Hz, ^3J = 3.9 Hz, 1 H, OCH_2), 3.93 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.02 (dd, ^3J = 2.6 Hz, ^4J = 1.5 Hz, 1 H, $C_5H_3R_2$), 4.09 (s, 5 H, C_5H_5), 4.11 (m, 1 H, $C_5H_3R_2$), 7.08 (tt, ^3J = 7.4 Hz, ^4J = 1.3 Hz, 1 H, *p*-C_6H_5), 7.17 (tm, ^3J = 7.6 Hz, 2 H, *m*-C_6H_5), 7.51 (ddm, ^3J = 8.3 Hz, ^4J = 1.4 Hz, 2 H, *o*-C_6H_5). − ^{1}H NMR (minor isomer, 500 MHz, C_6D_6): δ = 1.37 (m, 2 H, NCH_2CH_2), 1.55 (m, 1 H, $NCHCH_2$ *trans* to NCH), 1.83 (m, 1 H,

NCHCH_2 *cis* to NCH), 2.29 (m, 1 H, NCH_2 *cis* to NCH), 2.50 (s, 3 H, CH_3), 2.65 (m, 1 H, NCH_2 *trans* to NCH), 3.32 (s, 3 H, OCH_3), 3.55 (dd, ^2J = 9.1 Hz, ^3J = 7.4 Hz, 1 H, OCH_2), 3.64 (m, 1 H, NCH), 3.86 (dd, ^2J = 9.1 Hz, ^3J = 3.7 Hz, 1 H, OCH_2), 3.92 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 3.98 (dd, ^3J = 2.7 Hz, ^4J = 1.7 Hz, 1 H, $C_5H_3R_2$), 4.06 (s, 5 H, C_5H_5), 4.16 (dd, ^3J = 3.0 Hz, ^4J = 1.9 Hz, 1 H, $C_5H_3R_2$), 7.06 (tt, ^3J = 7.4 Hz, ^4J = 1.5 Hz, 1 H, *p*-C_6H_5), 7.16 (m, 2 H, *m*-C_6H_5), 7.39 (dd, ^3J = 8.4 Hz, ^4J = 1.4 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (major isomer, 125 MHz, C_6D_6): δ = 17.2 (CH_3), 23.2 (NCH_2CH_2), 27.4 (NCHCH_2), 55.1 (NCH_2), 59.1 (OCH_3), 66.5 ($C_5H_3R_2$), 67.1 (NCH), 70.5 (C_5H_5), 71.0 ($C_5H_3R_2$), 72.5 (C_5H_3R), 76.4 (OCH_2), 83.4, 84.5 (*i*-$C_5H_3R_2$), 127.7 (*p*-C_6H_5), 128.2, 129.2 (*o*/*m*-C_6H_5), 139.7 (*i*-C_6H_5), 152.9 (C=N). − ^{13}C NMR (minor isomer, 125 MHz, C_6D_6): δ = 16.6 (CH_3), 23.2 (NCH_2CH_2), 27.2 (NCHCH_2), 55.0 (NCH_2), 59.2 (OCH_3), 66.5 ($C_5H_3R_2$), 67.2 (NCH), 70.3 ($C_5H_3R_2$), 70.4 (C_5H_5), 72.5 ($C_5H_3R_2$), 76.6 (OCH_2), 84.00, 84.04 (*i*-$C_5H_3R_2$), 127.6 (*p*-C_6H_5), 128.1, 129.3 (*o*/*m*-C_6H_5), 139.8 (*i*-C_6H_5), 153.1 (C=N). − EI-MS: *m*/*z* = 416.0 (6) [M^+], 302.0 (12) [M^+ − $C_6H_{12}NO$], 198.9 (22) [$CH_3C_{10}H_8Fe^+$], 143.0 (49) [198.9 − Fe], 141.0 (18), 133.9 (11) [$CH_3C_5H_3Fe^+$], 128.0 (17), 125.0 (17), 123.0 (11), 120.9 (73) [$CpFe^+$], 119.0 (10), 113.1 (13), 111.1 (26), 109.0 (16), 105.0 (11), 99.0 (17), 97.0 (36), 96.0 (15), 95.0 (24), 85.0 (35), 83.0 (34), 81.0 (25), 79.0 (10), 77.0 (25) [$C_6H_5^+$], 71.1 (53), 69.0 (42), 67.0 (18), 57.1 (32), 55.9 (100) [Fe^+]. − $C_{24}H_{28}FeN_2O$ (416.3): calcd. C 69.24, H 6.78, N 6.73; found C 69.64, H 6.95, N 6.79.

Planar Chiral SAMP Hydrazone (*S*,*S*$_p$)-15b: According to GP3, a solution of (*E*)-**12a** (515 mg) in Et_2O (15 mL) was treated with a solution of *n*BuLi (1.1 equiv.) in hexane. After 9 h stirring at −70 °C, trimethylsilyl chloride (256 µL) was added. The reaction mixture was allowed to warm to room temp. overnight. After work up, flash chromatography (petroleum ether/diethyl ether = 4:1; 2% NEt_3) provided planar chiral *ortho*-silylated hydrazone **15b**. − Yield: 551 mg (91%, red-brown oil). − R_f = 0.83 (petroleum ether/diethyl ether = 2:1; 2% NEt_3). − *de* = 96%. − $[\alpha]_D^{25}$ = −26.3 ($CHCl_3$, *c* = 1.14). − IR ($CHCl_3$): ṽ = 3091 cm^{-1}, 3056, 2952, 2891, 2873, 2825, 1563, 1490, 1459, 1446, 1415, 1385, 1343, 1320, 1299, 1278, 1241, 1199, 1150, 1107, 1081, 1018, 1002, 969, 923, 901, 859, 835, 818, 775, 757, 722, 697, 668, 630, 578, 510, 454. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.54 (s, 9 H, $Si(CH_3)_3$), 1.38−1.64 (m, 3 H, β-ring-CH_2), 1.89 (m, 1 H, NCHCH_2), 2.56 (m, 1 H, NCH_2), 2.76 (m, 1 H, NCH_2), 3.20 (s, 3 H, OCH_3), 3.65 (dd, ^2J = 9.1 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 3.72 (dd, ^2J = 9.4 Hz, ^3J = 7.7 Hz, 1 H, OCH_2), 3.89 (dd, ^3J = 2.7 Hz, ^4J = 1.7 Hz, 1 H, $R_2C_5H_3$), 3.91 (m, 1 H, NCH), 4.12 (s, 5 H, C_5H_5), 4.16 (t, ^3J = 2.7 Hz, 1 H, $R_2C_5H_3$), 4.25 (dd, ^3J = 2.7 Hz, ^4J = 1.7 Hz, 1 H, $R_2C_5H_3$), 7.08−7.25 (m, 3 H, *m*/*p*-C_6H_5), 7.56 (dm, ^3J = 7.1 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 1.89 [$Si(CH_3)_3$], 23.8 (NCH_2CH_2), 27.8 (NCHCH_2), 56.2 (NCH_2), 59.0 (OCH_3), 65.9 (NCH), 71.1, 73.3, 76.6 ($R_2C_5H_3$), 69.1 (*i*-$R_2C_5H_3$), 69.7 (C_5H_5), 76.6 (OCH_2), 92.5 (*i*-$R_2C_5H_3$), 127.7, 129.3 (C_6H_5), 139.7 (*i*-C_6H_5), 152.6 (C=N). − EI-MS: *m*/*z* = 474.2 (100) [M^+], 364.1 (10), 360.1 (61) [M^+ − $C_6H_{12}NO$], 257.2 (31) [M^+ − PhC=N−SMP], 214.7 (11), 121 (9) [$CpFe^+$]. − HR-MS: $C_{26}H_{34}{}^{56}FeN_2OSi$: calcd. 474.17898; found 474.17861.

Planar Chiral SAMP Hydrazone (*S*,*S*$_p$)-15c: According to GP3, a solution of (*E*)-**12a** (855 mg) in Et_2O (20 mL) was treated with a solution of *n*BuLi (1.1 equiv.) in hexane. After 9 h stirring at −70 °C, chlorodiphenylphosphane (0.5 mL) was added. The reaction mixture was allowed to warm to room temp. overnight. After work up, flash chromatography (petroleum ether/diethyl ether = 7:1; 2% NEt_3) provided planar chiral *ortho*-phosphinylated hydrazone **15c**. − Yield: 1.11 g (89%, orange powder). − R_f = 0.69 (petroleum ether/diethyl ether = 2:1; 2% NEt_3). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −365.1 ($CHCl_3$, *c* = 0.56). − M.p. 55 °C. − IR (KBr): ṽ = 3050 cm^{-1}, 2966, 2923, 2870, 2850, 2823, 2245, 1950, 1886, 1809, 1654, 1573, 1475, 1447, 1433, 1383, 1341, 1323, 1302, 1279, 1254, 1198, 1159, 1107, 1070, 1001, 971, 893, 816, 773, 743, 722, 697, 630, 581, 527, 489, 456. − ^{1}H NMR (500 MHz, C_6D_6): δ = 1.35 (pent, ^3J = 7.0 Hz, 2 H, NCH_2CH_2), 1.59 (m, 1 H, NCHCH_2), 1.72 (m, 1 H, NCHCH_2), 2.60 (dt, ^2J = 10.1 Hz, ^3J = 7.3 Hz, 1 H, NCH_2), 2.64 (dd, ^2J = 9.2 Hz, ^3J = 7.3 Hz, 1 H, OCH_2), 2.74 (dd, ^2J = 9.2 Hz, ^3J = 3.7 Hz, 1 H, OCH_2), 2.81 (dt, ^2J = 9.8 Hz, ^3J = 6.7 Hz, 1 H, NCH_2), 3.03 (s, 3 H, OCH_3), 3.79 (m, 1 H, NCH), 3.80 (m, 1 H, $R_2C_5H_3$), 3.98 (td, *J* = 3.1 Hz, *J* = 0.6 Hz, 1 H, $R_2C_5H_3$), 4.14 (m, 1 H, $R_2C_5H_3$), 4.16 (s, 5 H, C_5H_5), 7.06 (tm, ^3J = 7.0 Hz, 1 H, C_6H_5), 7.12 (m, 6 H, C_6H_5), 7.21 (t, *J* = 7.1 Hz, 2 H, C_6H_5), 7.45 (tt, *J* = 7.0 Hz, *J* = 1.5 Hz, 2 H, C_6H_5), 7.68 (m, 2 H, C_6H_5), 7.74 (dm, *J* = 7.0 Hz, 2 H, C_6H_5). − ^{13}C NMR (125 MHz, C_6D_6): δ = 23.7 (NCH_2CH_2), 26.8 (NCHCH_2), 56.3 (NCH), 58.6 (OCH_3), 66.2 (NCH), 69.6, 71.9 ($R_2C_5H_3$), 73.9 (d, J_{CP} = 5.5 Hz, $R_2C_5H_3$), 71.0 (d, J_{CP} = 1.1 Hz, C_5H_5), 75.1 (OCH_2), 75.3 (d, $^2J_{CP}$ = 14.3 Hz, $R_2C_5H_3$), 91.4 (d, $^1J_{CP}$ = 12.1 Hz, $R_2C_5H_3$), 127.1, 128.15, 128.8 (*p*-C_6H_5), 128.13 (d, $^3J_{CP}$ = 6.6 Hz, P-*m*-C_6H_5), 128.3, 129.3 (N=C-*o*/*m*-C_6H_5), 132.6 (d, $^2J_{CP}$ = 18.1 Hz), 136.3 (d, $^2J_{CP}$ = 21.9 Hz, P-*o*-C_6H_5), 138.9 (N=C-*i*-C_6H_5), 141.7 (d, $^1J_{CP}$ = 18.1 Hz), 143.6 (d, $^1J_{CP}$ = 11.5 Hz, P-*i*-C_6H_5), 147.0 (C=N). − ^{31}P NMR (202 MHz, C_6D_6): δ = −17.76 (s). − EI-MS: *m*/*z* = 586.3 (0.1) [M^+], 472.0 (100) [M^+ − $C_6H_{12}NO$], 406.0 (2), 236.0 (3), 170.0 (1), 121.0 (2) [$CpFe^+$]. − $C_{35}H_{35}FeN_2OP$ (586.5): calcd. C 71.68, H 6.02, N 4.78; found C 71.36, H 6.50, N 4.67.

Planar Chiral SAMP Hydrazone (*S*,*S*$_p$)-15d: To a solution of hydrazone **15c** (200 mg) in THF (2 mL) was added a solution of BH_3·THF (1.2 equiv. 1 M in THF) at 0 °C. The reaction mixture was stirred for 3.5 h at this temp., it was then quenched with saturated aqueous NH_4Cl and washed with saturated aqueous NaCl. After drying over $MgSO_4$, borane protected phosphane **15d** was obtained by filtration though silica gel (CH_2Cl_2). − Yield: 180 mg (88%, orange crystals). − R_f = 0.69 (hexane/diethyl ether = 2:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −68.4 ($CHCl_3$, *c* = 0.79). − M.p. 84 °C. − IR (KBr): ṽ = 3077 cm^{-1}, 3053, 2964, 2961, 2869, 2823, 2387, 2346, 2265, 1959, 1891, 1810, 1705, 1639, 1549, 1482, 1436, 1384, 1341, 1324, 1282, 1250, 1217, 1196, 1159, 1106, 1060, 1021, 1003, 971, 923, 897, 822, 773, 741, 696, 635, 612, 574, 525, 498, 480. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.41 (m, 1 H, NCH_2CH_2), 1.55 (m, 1 H, NCH_2CH_2), 1.68 (m, 1 H, NCHCH_2), 1.90 (m, 1 H, NCHCH_2), 2.56 (m, 2 H, NCH_2), 2.80 (m, 1 H, OCH_2), 2.90 (m, 1 H, OCH_2), 3.03 (s, 3 H, OCH_3), 3.66 (td, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 3.83 (m, 1 H, NCH), 3.99 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.38 (s, 5 H, C_5H_5), 4.02 (m, 1 H, $C_5H_3R_2$), 7.02−7.22 (m, 9 H, C_6H_5), 7.65−7.77 (m, 4 H) and 7.88 (tm, 2 H, ^3J = 8.0 Hz, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 24.3 (NCH_2CH_2), 27.0 (NCHCH_2), 57.4 (NCH_2), 58.6 (OCH_3), 64.9 (NCH), 67.2 (d, J_{CP} = 75.9 Hz, *i*-$C_5H_3R_2$), 70.2 (d, J_{CP} = 6.9 Hz), 72.1 (d, J_{CP} = 7.8 Hz), 75.5 (d, J_{CP} = 4.0 Hz, $C_5H_3R_2$), 71.4 (C_5H_5), 75.3 (OCH_2), 93.6 (d, $^2J_{CP}$ = 9.2 Hz, *i*-$C_5H_3R_2$), 128.1 (N=C-*p*-C_6H_5), 128.3, 129.6 (N=C-*o*/*m*-C_6H_5), 129.6, 130.3 (d, $^4J_{CP}$ = 1.7 Hz, P-*p*-C_6H_5), 132.7 (d, $^2J_{CP}$ = 9.2 Hz), 134.7 (d, $^2J_{CP}$ = 8.0 Hz, P-*o*-C_6H_5), 134.0 (d, $^1J_{CP}$ = 52.7 Hz), 135.4 (d, $^1J_{CP}$ = 59.6 Hz, P-*i*-C_6H_5), 139.1 (N=C-*i*-C_6H_5), 142.1 (C=N). − EI-MS: *m*/*z* = 600.2 (1) [M^+], 486.1 (33) [M^+ − $C_6H_{12}NO$], 472.1 (100) [486.1 − BH_3], 406.0 (8) [472.1 − C_5H_6].− $C_{35}H_{38}BFeN_2OP$ (600.3): calcd. C 70.03, H 6.38, N 4.67; found C 69.93, H 6.68, N 4.26.

Planar Chiral SAMP Hydrazone (*S*,*S*$_p$)-15e: According to GP3, a solution of (*E*)-**12a** (877 mg) in Et_2O (20 mL) was treated with a solution of *n*BuLi (1.1 equiv.) in hexane. After 9 h stirring at −70 °C, 699 mg of benzophenone were added. The reaction mixture was allowed to warm to room temp. overnight. After work up, flash chromatography (petroleum ether/diethyl ether = 4:1; 2% NEt_3) provided planar chiral *ortho*-hydroxyalkylated hydrazone **15e**. − Yield: 1.10 g (86%, orange-red crystals). − R_f = 0.38 (petroleum ether/diethyl ether = 7:1; 2% NEt_3). − *de* = 98%. − $[\alpha]_D^{25}$ = −398.8 ($CHCl_3$, *c* = 0.74). − M.p. 55 °C. − IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1}, 3083, 3057, 3026, 2969, 2925, 2873, 2851, 2187, 1597, 1560, 1490, 1446, 1385, 1346, 1262, 1225, 1176, 1109, 1063, 1028, 1003, 952, 907, 817, 756, 701, 672, 516, 460. − ^{1}H NMR (500 MHz, C_6D_6): δ = 1.26 (m, 1 H, NCH_2CH_2 *trans* to NCH), 1.35 (m, 1 H, NCH_2CH_2 *cis* to NCH), 1.45 (m, 1 H, $NCHCH_2$ *trans* to NCH), 1.61 (m, 1 H, $NCHCH_2$ *trans* to NCH), 2.53 (dd, ^2J = 9.2 Hz, ^3J = 7.7 Hz, 1 H, OCH_2), 2.56 (m, 1 H, NCH_2), 2.59 (ddd, ^2J = 9.7 Hz, ^3J = 7.6 Hz, ^3J = 5.3 Hz, 1 H, NCH_2), 2.66 (dd, ^2J = 9.2 Hz, ^3J = 3.9 Hz, 1 H, OCH_2), 3.02 (s, 3 H, OCH_3), 3.16 (qd, ^3J = 7.6 Hz, ^3J = 3.8 Hz, 1 H, NCH), 3.82 (dd, ^3J = 2.7 Hz, ^4J = 1.6 Hz, 1 H, $C_5H_3R_2$), 3.86 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 3.90 (dd, ^3J = 2.7 Hz, ^4J = 1.7 Hz, 1 H, $C_5H_3R_2$), 4.31 (s, 5 H, C_5H_5), 7.01−7.17 (m, 9 H, *m*/*p*-C_6H_5), 7.22 (dm, ^3J = 9.4 Hz, 2 H, N=C-*o*-C_6H_5), 7.51 (broad d, ^3J = 7.3 Hz, 2 H, CpC-*o*-$C_6H_{5(up)}$), 7.85 (broad d, ^3J = 5.5 Hz, 2 H, CpC-*o*-$C_6H_{5(down)}$), 9.10 (s, 1 H, OH). − ^{13}C NMR (125 MHz, C_6D_6): δ = 22.8 (NCH_2CH_2), 26.9 ($NCHCH_2$), 56.2 (NCH_2), 58.5 (OCH_3), 66.6 (NCH), 67.5 ($C_5H_3R_2$), 71.1 (C_5H_5), 73.4 ($C_5H_3R_2$), 74.2 (OCH_2), 75.7 ($C_5H_3R_2$), 77.7, 79.1 (*i*-$C_5H_3R_2$), 100.0 (Cp*C*OH), 126.6, 126.7, 127.3, 127.6, 127.9, 128.2, 128.27, 128.34, 128.70 (*o*/*m*/*p*-C_6H_5), 139.0 (N=C-*i*-C_6H_5), 148.0, 151.0 (CpC-*i*-C_6H_5), 163.8 (C=N). − EI-MS: *m*/*z* = 584.3 (100) [M^+], 519.2 (74) [M^+ − C_5H_5], 470.1 (19) [M^+ − $C_6H_{12}NO$], 406.0 (71), 401.1 (26) [M^+ − Ph_2COH], 388.0 (13) [406.0 − H_2O], 332.1 (26) [388.0 − Fe], 285.0 (13) [519.2 − HOPhC=N-SMP], 284.0 (14), 229.1 (27) [285.0 − Fe], 228.1 (35) [284.0 − Fe]. − $C_{36}H_{36}FeN_2O_2$ (584.5): calcd. C 73.97, H 6.21, N 4.79; found C 73.79, H 6.67, N 4.60.

Planar Chiral SAMP Hydrazone (*S*,*S*$_p$)-15f: According to GP3, a solution of (*E*)-**12a** (174 mg) in Et_2O (20 mL) was treated with a solution of *n*BuLi (1.1 equiv.) in hexane. After 9 h stirring at −70 °C, 60 mg of DMF was added. The reaction mixture was allowed to warm to room temp. overnight. After work up, flash chromatography (petroleum ether/diethyl ether = 4:1; 2% NEt_3) provided planar chiral *ortho*-formylated hydrazone **15f**. − Yield: 173 mg (93%, orange powder). − R_f = 0.27 (petroleum ether/diethyl ether = 4:1; 2% NEt_3). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −40.7 ($CHCl_3$, *c* = 1.40). − M.p. 98 °C. − IR (KBr): $\tilde{\nu}$ = 3083 cm^{-1}, 2922, 2875, 2821, 2730, 2189, 1656, 1560, 1453, 1425, 1383, 1341, 1275, 1232, 1198, 1109, 1091, 1002, 905, 849, 821, 778, 715, 697, 499, 462. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.36 (m, 2 H, NCH_2CH_2), 1.55 (m, 1 H, $NCHCH_2$), 1.75 (m, 1 H, $NCHCH_2$), 2.45 (m, 1 H, NCH_2), 2.71 (m, 1 H, NCH_2), 3.16 (s, 3 H, OCH_3), 3.38 (m, 1 H, OCH_2), 3.57 (m, 1 H, OCH_2), 3.61 (m, 1 H, NCH), 4.01 (dd, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, $R_2C_5H_3$), 4.06 (s, 5 H, C_5H_5), 4.12 (td, ^3J = 2.7 Hz, *J* = 0.9 Hz, 1 H, $R_2C_5H_3$), 5.12 (m, 1 H, $R_2C_5H_3$), 7.08−7.21 (m, 3 H, *m*/*p*-C_6H_5), 7.46 (dm, ^3J = 6.6 Hz, 2 H, *o*-C_6H_5), 10.99 (s, 1 H, CHO). − ^{13}C NMR (75 MHz, C_6D_6): δ = 23.4 (NCH_2CH_2), 26.9 ($NCHCH_2$), 55.3 (NCH), 59.0 (OCH_3), 66.8, 69.3, 71.3, 74.0 ($R_2C_5H_3$, NCH), 71.0 (C_5H_5), 75.7 (OCH_2), 79.8, 90.9 (*i*-$R_2C_5H_3$), 128.1 (*p*-C_6H_5), 128.4, 129.2 (*o*/*m*-C_6H_5), 139.0 (*i*-C_6H_5), 146.5 (C=N), 194.0 (CHO). − EI-MS: *m*/*z* = 430.2 (25) [M^+], 316.1 (100) [M^+ − $C_6H_{12}NO$], 288.1 (22) [316.1 − CO], 185.1 (5) [Fc^+], 129.1 (11) [Fc^+ − Fe], 121.0 (11) [$CpFe^+$]. − $C_{24}H_{26}FeN_2O_2$ (430.3): calcd. C 66.99, H 6.09, N 6.51; found C 66.76, H 6.16, N 6.37.

Planar Chiral SAMP Hydrazone (*S*,*S*$_p$)-15g: According to GP3, a solution of (*E*)-**12a** (141 mg) in 5 mL Et_2O was treated with a solution of 1.1 equiv. *n*BuLi in hexane. After 9 h stirring at −70 °C, 134 mg of I_2 was added. The reaction mixture was allowed to warm to room temp. overnight. After work up, flash chromatography (petroleum ether/diethyl ether = 7:1; 2% NEt_3) provided planar chiral *ortho*-iodinated hydrazone **15g**. − Yield: 151 mg (82%, orange powder). − R_f = 0.68 (petroleum ether/diethyl ether = 2:1; 2% NEt_3). − *de* = 95% − $[\alpha]_D^{25}$ = −9.7 ($CHCl_3$, *c* = 1.13). − M.p. 70 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3094 cm^{-1}, 3082, 3056, 2923, 2872, 2827, 2732, 1640, 1598, 1578, 1490, 1459, 1447, 1414, 1376, 1353, 1338, 1321, 1281, 1259, 1217, 1198, 1154, 1107, 1071, 1026, 1003, 970, 920, 903, 880, 847, 819, 757, 722, 698, 680, 668, 504. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.33−1.52 (m, 2 H, NCH_2CH_2), 1.63 (dq, ^2J = 12.1 Hz, ^3J = 7.7 Hz, 1 H, $NCHCH_2$), 1.87 (m, 1 H, $NCHCH_2$), 2.47 (ddd, ^2J = 10.1 Hz, ^3J = 7.7 Hz, ^3J = 6.1 Hz, 1 H, NCH_2), 2.77 (ddd, ^2J = 10.1 Hz, ^3J = 7.7 Hz, ^3J = 6.4 Hz, 1 H, NCH_2), 3.29 (s, 3 H, OCH_3), 3.58 (dd, ^2J = 8.7 Hz, ^3J = 7.1 Hz, 1 H, OCH_2), 3.91 (t, ^3J = 2.5 Hz, 1 H, $R_2C_5H_3$), 3.95 (m, 1 H, NCH), 3.98 (dd, ^2J = 8.7 Hz, ^3J = 3.7 Hz, 1 H, OCH_2), 4.03 (dd, ^3J = 2.5 Hz, ^4J = 1.7 Hz, 1 H, $R_2C_5H_3$), 4.17 (s, 5 H, C_5H_5), 4.47 (dd, ^3J = 2.4 Hz, ^4J = 1.7 Hz, 1 H, $R_2C_5H_3$), 7.06 (tt, ^3J = 6.0 Hz, ^4J = 1.3 Hz, 1 H, *p*-C_6H_5), 7.14 (m, 1 H, *m*-C_6H_5), 7.43 (dm, ^3J = 6.7 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 23.5 (NCH_2CH_2), 27.3 ($NCHCH_2$), 55.2 (NCH_2), 59.1 (OCH_3), 66.6, 69.3, 70.2, 77.6 ($R_2C_5H_3$, NCH), 72.8 (*i*-$R_2C_5H_3$), 72.9 (C_5H_5), 76.1 (OCH_2), 87.1 (*i*-$R_2C_5H_3$), 127.8 (*p*-C_6H_5), 128.1, 129.6 (*o*/*m*-C_6H_5), 138.9 (*i*-C_6H_5), 145.8 (C=N). − EI-MS: *m*/*z* = 528.0 (71) [M^+], 413.9 (100) [M^+ − $C_6H_{12}NO$], 310.8 (21) [$C_5H_3IFeCp^+$], 286.0 (11) [413.9 − HI], 231.0 (16), 230.0 (17) [286.0 − Fe], 182.8 (15) [310.8 − HI], 128.0 (17) [HI^+], 127.0 (18) [I^+], 111.0 (13), 109.0 (10), 97.0 (19), 96.0 (10), 95.0 (17), 85.1 (16), 83.0 (17), 82.0 (12), 81.0 (14), 71.1 (28), 70.0 (13), 69.0 (23), 67.0 (12), 57.1 (45) [FeH^+], 56.1 (11) [Fe^+], 55.1 (27). − HR-MS: $C_{23}H_{25}{}^{56}FeIN_2O$: calcd. 528.036094; found 528.035966.

General Procedure for the *ortho*-Functionalization of (*Z*)-Ferrocenyl Ketone SAMP Hydrazones 12b and 12c (GP4): Hydrazone **12b−c** was dissolved in diethyl ether or THF (10 mL/mmol) under argon and cooled down to −70 °C. A solution of *s*BuLi (1.1 equiv., 1.2 M in cyclohexane) was added dropwise and the reaction mixture was stirred for 9 h at −70 °C. Then the electrophile (1.2 equiv.) was added. After warming to room temp. overnight, the solution was cooled to 0 °C and quenched with saturated aqueous NH_4Cl, washed with saturated aqueous NaCl and dried over $MgSO_4$. After concentrating in vacuo, the crude product was purified by flash chromatography.

Planar Chiral SAMP Hydrazone (*S*,*S*$_p$)-18a: According to GP4, a solution of (*Z*)-**12b** (181 mg) in Et_2O (5 mL) was treated with a solution of *s*BuLi (1.1 equiv.) in hexane. After 9 h stirring at −70 °C, methyl iodide (46 μL) was added. The reaction mixture was allowed to warm to room temp. overnight. After work up, flash chromatography (petroleum ether/diethyl ether = 10:1; 2% NEt_3) provided planar chiral orthomethylated hydrazone **18a**. − Yield: 103 mg (55%, yellow-brown crystals). − R_f = 0.76 (petroleum ether/diethyl ether = 2:1). − *de* = 87%; (after chromatography: *de* ≥ 96%). − $[\alpha]_D^{25}$ = −301.0 ($CHCl_3$, *c* = 1.09). − M.p. 62 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3095 cm^{-1}, 2963, 2922, 2870, 2826, 2731, 1667, 1592, 1456, 1416, 1377, 1356, 1321, 1278, 1256, 1195, 1132, 1107, 1051, 1001, 970, 955, 925, 904, 875, 819, 757, 682, 668, 484, 455. − ^{1}H NMR (major isomer, 300 MHz, C_6D_6): δ = 1.38 (m, 2 H,

NCH_2CH_2), 1.39 (d, ^3J = 7.7 Hz, 3 H, $CHCH_3$), 1.53 (m, 1 H, $NCHCH_2$ *trans* to NCH), 1.53 (d, ^3J = 6.7 Hz, 3 H, $CHCH_3$), 1.88 (m, 1 H, $NCHCH_2$ *cis* to NCH), 1.98 (s, 3 H, $RC_5H_3CH_3$), 2.06 (dt, ^3J = 7.4 Hz, $^{2,3}J$ = 9.1 Hz, 1 H, NCH_2 *cis* to NCH), 2.58 (ddd, ^2J = 9.7 Hz, ^3J = 7.4 Hz, ^3J = 5.7 Hz, 1 H, NCH_2 *trans* to NCH), 3.22 (sept, ^3J = 6.7 Hz, 1 H, $CH(CH_3)_2$), 3.22 (s, 3 H, OCH_3), 3.34 (t, $^{2,3}J$ = 8.2 Hz, 1 H, OCH_2), 3.63 (qd, ^3J = 7.4 Hz, ^3J = 4.7 Hz, 1 H, NCH), 3.77 (dd, ^2J = 8.8 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 3.91 (m, 1 H, $R_2C_5H_3$), 3.94 (m, 1 H, $R_2C_5H_3$), 3.97 (m, 1 H, $R_2C_5H_3$), 4.01 (s, 5 H, C_5H_5). − ^{1}H NMR (minor isomer, 300 MHz, C_6D_6): δ = 1.30−1.50 (m, 2 H, NCH_2CH_2), 1.42 (d, ^3J = 6.7 Hz, 3 H, $CHCH_3$), 1.53 (d, ^3J = 6.7 Hz, 3 H, $CHCH_3$), 1.62 (m, 1 H, $NCHCH_2$ *trans* to NCH), 1.88 (m, 1 H, $NCHCH_2$ *cis* to NCH), 1.88 (s, 3 H, $RC_5H_3CH_3$), 2.12 (dt, $^{2,3}J$ = 9.1 Hz, ^3J = 7.1 Hz, 1 H, NCH_2 *cis* to NCH), 2.73 (ddd, ^2J = 9.7 Hz, ^3J = 8.1 Hz, ^3J = 5.7 Hz, 1 H, NCH_2 *trans* to NCH), 3.14 (sept, ^3J = 6.7 Hz, 1 H, $CH(CH_3)_2$), 3.22 (s, 3 H, OCH_3), 3.36 (t, ^2J = 9.7 Hz, ^3J = 8.1 Hz, 1 H, OCH_2), 3.55 (qd, ^3J = 7.4 Hz, ^3J = 3.7 Hz, 1 H, NCH), 3.75 (dd, ^2J = 9.1 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 3.91 (t, ^3J = 2.4 Hz, 1 H, $R_2C_5H_3$), 3.97 (t, ^3J = 2.4 Hz, 1 H, $R_2C_5H_3$), 3.99 (s, 5 H, C_5H_5), 4.36 (dd, ^3J = 2.4 Hz, ^4J = 1.7 Hz, 1 H, OCH_2). − ^{13}C NMR (major isomer, 75 MHz, C_6D_6): δ = 16.0 ($RC_5H_3CH_3$), 21.3, 24.8 ($CHCH_3$), 23.2 (NCH_2CH_2), 27.5 ($NCHCH_2$), 38.4 ($CH(CH_3)_2$), 53.7 (NCH_2), 58.8 (OCH_3), 67.1, 67.2, 68.7, 68.9 ($R_2C_5H_3$, NCH), 70.1 (C_5H_5), 76.9 (OCH_2), 83.0, 89.0 (*i*-OCH_2), 156.6 (C=N). − ^{13}C NMR (minor isomer, 75 MHz, C_6D_6): δ = 14.5 ($RC_5H_3CH_3$), 22.9 (NCH_2CH_2), 23.2, 23.4 ($CHCH_3$), 27.5 ($NCHCH_2$), 37.8 ($CH(CH_3)_2$), 54.1 (NCH_2), 58.9 (OCH_3), 66.2, 66.9, 69.3, 69.6 ($R_2C_5H_3$, NCH), 69.9 (C_5H_5), 76.4 (OCH_2), 82.9, 87.4 (*i*-$R_2C_5H_3$), 157.7 (C=N). − EI-MS: *m*/*z* = 382.1 (100) [M^+], 337.1 (11) [$M^+ - CH_2OCH_3$], 317.0 (31) [$M^+ - C_5H_5$], 272.1 (22), 268.0 (59) [$M^+ - C_6H_{12}NO$], 225.0 (29), 199.0 (25) [$FcCH_3^+$], 120.9 (18) [$CpFe^+$]. − $C_{21}H_{30}FeN_2O$ (382.3): calcd. C 65.97, H 7.91, N 7.33; found C 65.67, H 7.85, N 7.19.

Planar Chiral SAMP Hydrazone (*S*,*S*$_p$)-18b: According to GP4, a solution of (*Z*)-**12c** (520 mg) in THF (15 mL) was treated with a solution of *s*BuLi (1.1 equiv.) in hexane. After 9 h stirring at −70 °C, methyl iodide (111 μL) was added. The reaction mixture was allowed to warm to room temp. overnight. After work up, flash chromatography (petroleum ether/diethyl ether = 7:1; 2% NEt_3) provided planar chiral orthomethylated hydrazone **18b**. − Yield: 467 mg (87%, orange powder). − R_f = 0.70 (hexane/diethyl ether = 4:1; 2% NEt_3). − *de* = 90% (after chromatography: *de* ≥ 96%). − $[\alpha]_D^{25}$ = −222.7 ($CHCl_3$, *c* = 0.77). − M.p. 89 °C. − IR (KBr): ṽ = 3096 cm^{-1}, 2936, 2916, 2852, 1654, 1584, 1445, 1419, 1373, 1340, 1298, 1279, 1264, 1226, 1193, 1137, 1107, 1093, 1044, 1001, 983, 970, 935, 904, 889, 817, 766, 690, 629, 590, 481. − ^{1}H NMR (major isomer, 300 MHz, C_6D_6): δ = 1.29−2.26 [m, 15 H, $(CH_2)_5$, β-ring-CH_2, NCH_2], 1.98 (s, 3 H, CH_3), 2.59 (ddd, ^2J = 9.7 Hz, ^3J = 7.4 Hz, ^3J = 6.0 Hz, 1 H, NCH_2), 2.90 (tt, ^3J = 11.4 Hz, ^3J = 3.4 Hz, 1 H, N=CCH), 3.22 (s, 3 H, OCH_3), 3.33 (t, $^{2,3}J$ = 8.2 Hz, 1 H, OCH_2), 3.62 (qd, ^3J = 7.4 Hz, ^3J = 4.0 Hz, 1 H, NCH), 3.77 (dd, ^2J = 7.7 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 3.90 (dd, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 3.95 (t, ^3J = 2.4 Hz, 1 H, $C_5H_3R_2$), 3.98 (m, 1 H, $C_5H_3R_2$), 4.05 (s, 5 H, C_5H_5). − ^{1}H NMR (minor isomer, 300 MHz, C_6D_6): δ = 1.30−1.96 (m, 15 H, $(CH_2)_5$, β-ring-CH_2, NCH_2), 1.91 (s, 3 H, CH_3), 2.77 (ddd, ^2J = 9.6 Hz, ^3J = 7.7 Hz, ^3J = 5.5 Hz, 1 H, NCH_2), 2.86 (tt, ^3J = 11.5 Hz, ^3J = 3.3 Hz, 1 H, N=CCH), 3.23 (s, 3 H, OCH_3), 3.39 (dd, ^2J = 8.8 Hz, ^3J = 8.0 Hz, 1 H, OCH_2), 3.58 (qd, ^3J = 7.4 Hz, ^3J = 3.6 Hz, 1 H, NCH), 3.79 (dd, ^2J = 8.8 Hz, ^3J = 3.9 Hz, 1 H, OCH_2), 3.91 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 3.97 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.04 (s, 5 H, C_5H_5), 4.40 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$). − ^{13}C NMR (major isomer, 75 MHz, C_6D_6): δ = 16.0 (CH_3), 23.2 (NCH_2CH_2), 26.7, 27.0, 27.3, 27.6, 31.5, 35.5 (CH_2), 49.0 (N=C*C*H), 53.8 (NCH_2), 58.8 (OCH_3), 67.0, 67.1, 68.7, 68.8 ($C_5H_3R_2$, NCH), 69.9 (C_5H_5), 76.9 (OCH_2), 83.0, 89.3 (*i*-$C_5H_3R_2$), 156.1 (C=N). − ^{13}C NMR (minor isomer, 75 MHz, C_6D_6): δ = 14.5 (CH_3), 23.0 (NCH_2CH_2), 26.7, 27.2, 27.3, 27.6, 33.6, 33.9 (CH_2), 48.6 (N=C*C*H), 54.3 (NCH_2), 59.0 (OCH_3), 66.2, 67.1, 69.4, 69.6 ($C_5H_3R_2$, NCH), 69.8 (C_5H_5), 76.5 (OCH_2), 83.0 (*i*-$C_5H_3R_2$), 156.2 (C=N). − EI-MS: *m*/*z* = 422.1 (81) [M^+], 377.0 (14) [$M^+ - CH_2OCH_3$], 357.0 (26) [$M^+ - C_5H_5$], 308.0 (100) [$M^+ - C_6H_{12}NO$], 224.9 (35) [$H_3CC_{10}H_8CN^+$], 198.9 (35) [Fc − CH_3^+], 187.9 (11), 143.0 (13) [198.9 − Fe], 120.9 (47) [$CpFe^+$], 83.1 (10) [$C_6H_{11}^+$], 70.1 (20), 56.1 (12) [Fe^+], 55.1 (38) [$C_4H_7^+$], 45.2 (19) [$CH_3OCH_2^+$]. − $C_{24}H_{34}FeN_2O$ (422.4): calcd. C 68.24, H 8.11, N 6.63; found C 67.89, H 8.36, N 6.40.

Planar Chiral SAMP Hydrazone (*S*,*R*$_p$)-20: To a solution of hydrazone **12d** (445 mg) in THF (10 mL) was added dropwise a solution of *n*BuLi (1.1 equiv., 1.5 M in hexane) at −70 °C. After 2 h stirring at this temp., another 1.1 equiv. of *n*BuLi was added and stirring was continued for 7 h. Then methyl iodide (183 μL) was added. The reaction mixture was allowed to warm to room temp. overnight and worked up according to GP3. Planar chiral hydrazone **20** was obtained after purification by flash chromatography (hexane/diethyl ether = 4:1). − Yield: 386 mg (74%, red oil). − R_f = 0.58 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = +227.3 ($CHCl_3$, *c* = 0.35). − IR (KBr): ṽ = 3093 cm^{-1}, 2957, 2928, 2872, 2828, 2732, 1686, 1655, 1618, 1570, 1528, 1456, 1378, 1346, 1291, 1225, 1199, 1123, 1107, 1054, 1002, 968, 925, 904, 876, 809, 757, 707, 668, 491, 454. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.80 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.22 (sext, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 1.54 (pent, ^3J = 7.7 Hz, 2 H, $C_4H_2SCH_2CH_2$), 1.50−1.84 (m, 3 H, β-ring-CH_2), 2.06 (m, 1 H, β-ring-CH_2), 2.18 (s, 3 H, $RC_5H_3CH_3$), 2.61 (t, ^3J = 7.7 Hz, 2 H, $C_4H_2SCH_2$), 2.64 (m, 1 H, NCH_2), 3.20 (s, 3 H, OCH_3), 3.27 (m, 1 H, NCH_2), 3.51 (dd, ^2J = 8.5 Hz, ^3J = 7.7 Hz, 1 H, OCH_2), 3.68 (m, 1 H, NCH), 3.74 (dd, ^2J = 8.5 Hz, ^3J = 4.1 Hz, 1 H, OCH_2), 4.00 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.10 (dd, ^3J = 1.9 Hz, ^4J = 1.7 Hz, 1 H, $C_5H_3R_2$), 4.22 (s, 5 H, C_5H_5), 4.33 (dd, ^3J = 2.5 Hz, ^4J = 1.7 Hz, 1H, $C_5H_3R_2$), 6.52 (d, ^3J = 3.8, 1H, C_4H_2S), 7.22 (d, ^3J = 3.9, 1 H, C_4H_2S). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.9 (CH_2CH_3), 15.6 ($RC_5H_3CH_3$), 22.5, 23.0 (CH_2CH_3, NCH_2CH_2), 27.9 ($NCHCH_2$), 29.9 ($C_4H_2SCH_2CH_2$), 34.0 ($C_4H_2SCH_2$), 54.7 (NCH_2), 59.0 (OCH_3), 66.3, 66.8, 70.7, 71.1 ($C_5H_3R_2$, NCH), 70.8 (C_5H_5), 76.5 (OCH_2), 84.2, 86.3 (*i*-$C_5H_3R_2$), 122.7, 132.0 (C_4H_2S), 134.1, 149.6 (*i*-C_4H_2S), 154.1 (C=N). − EI-MS: *m*/*z* = 478.1 (68) [M^+], 364.0 (100) [$M^+ - C_6H_{12}NO$], 224.9 (13) [$CH_3C_{10}H_8Fe^+$], 198.9 (50), 143.0 (35) [198.9 − Fe], 141.0 (12), 120.9 (38) [$CpFe^+$], 111.0 (12), 105.0 (10), 97.0 (14), 71.1 (10), 70.1 (14), 57.1 (13) [FeH^+], 56.0 (10) [Fe^+], 55.1 (13), 45.3 (23) [$CH{=}S^+$ or $CH_3OCH_2^+$]. − $C_{26}H_{34}FeN_2OS$ (478.5): calcd. C 65.27, H 7.16, N 5.85; found C 65.02, H 7.38, N 6.16.

General Procedure for Hydrazone Cleavage with Ozone (GP5): A solution of hydrazone **15** in dichloromethane (50 mL/mmol) was cooled to −78 °C. O_3 was then bubbled through the solution under TLC control (50 L/h). After warming to room temp. and concentrating in vacuo, the crude product was purified by flash chromatography.

General Procedure for Hydrazone Cleavage with $TiCl_3$ (GP6): A 20% aqueous solution of $TiCl_3$ was added in one portion to a solution of hydrazone **15** or **18** in DME (40 mL/mmol) under argon. The reaction mixture was refluxed until the purple color became red. The mixture was diluted with diethyl ether and washed with

aqueous NH_3/NH_4Cl buffer, then with saturated aqueous NaCl. After drying over $MgSO_4$ and concentrating in vacuo, the crude product was purified by flash chromatography.

General Procedure for Hydrazone Cleavage with $SnCl_2$ (GP7): $SnCl_2{\cdot}2H_2O$ (1.1 equiv.) and H_2O (2.5 mL/mmol) were added separately to a solution of the hydrazone **15** in DME (40 mL/mmol) under argon. The reaction mixture was refluxed under TLC control. To drive the reaction to completion, it was necessary to add further portions of $SnCl_2{\cdot}2H_2O$ (1 to 6 equiv.), as the Sn^{II} species was deactivated after some time. The mixture was diluted with diethyl ether, washed with aqueous NH_3/NH_4Cl buffer (pH 10) and finally with saturated aqueous NaCl. After drying over $MgSO_4$ and concentrating in vacuo, the crude product was purified by flash chromatography.

(R_p)-(2-Methylferrocenyl)(phenyl)methanone (9a): a) According to GP6, a solution of hydrazone **15a** (201 mg) in DME (20 mL) was treated with a 20% aqueous solution of $TiCl_3$ (2.5 equiv.) and refluxed for 135 min. Work up and flash chromatography (CH_2Cl_2) provided planar chiral ketone **9a**. − b) According to GP5, ozone was bubbled through a solution of hydrazone **15a** (204 mg) in CH_2Cl_2 (25 mL) for 100 s. The product was obtained after purification by flash chromatography. − Yield: a) 131 mg (89%, dark red crystals); b) 75 mg (50%). − R_f = 0.68 (CH_2Cl_2). − a) *ee* = 90% (HPLC: Chiralcel OD2, *c*Hex/*i*PrOH = 95:5, 0.5 mL/min, ent-1: 8.6 min; ent-2: 9.7 min); b) *ee* = 89%. − $[\alpha]_D^{25}$ = +258.2 (*c* = 1.06, $CHCl_3$). − M.p. 107 °C. − IR (KBr): $\tilde{\nu}$ = 3066 cm^{-1}, 2986, 2959, 2925, 2854, 1626, 1594, 1574, 1453, 1412, 1380, 1344, 1275, 1223, 1182, 1107, 1076, 1050, 1036, 1003, 890, 828, 807, 729, 701, 669, 603, 539, 511, 489. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.37 (s, 3 H, CH_3), 4.13 (s, 5 H, C_5H_5), 4.33 (t, ^3J = 2.7 Hz, 1 H, $R_2C_5H_3$), 4.49 (m, 2 H, $R_2C_5H_3$), 7.43 (tm, ^3J = 7.4 Hz, 2 H, *m*-C_6H_5), 7.52 (tt, ^3J = 7.1 Hz, ^4J = 1.4 Hz, 1 H, *p*-C_6H_5), 7.85 (dm, ^3J = 6.7 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.6 (CH_3), 69.9, 73.0, 75.1 ($R_2C_5H_3$), 71.2 (C_5H_5), 76.7, 88.8 (*i*-$R_2C_5H_3$), 128.5, 128.6 (*o*/*m*-C_6H_5), 131.7 (*p*-C_6H_5), 140.9 (*i*-C_6H_5), 201.4 (C=O). − EI-MS: *m*/*z* = 304.2 (100) [M^+], 199.2 (34) [$M^+ - C_6H_5CO$], 153.2 (15), 152.1 (16), 149.1 (23), 121.1 (28) [$CpFe^+$], 105.1 (24) [$C_6H_5CO^+$], 83.1 (11), 81.1 (12), 77.1 (31) [$C_6H_5^+$], 73.1 (12), 71.2 (16), 70.2 (12), 69.2 (14), 57.1 (35) [FeH^+], 56.0 (27) [Fe^+], 55.1 (27), 51.1 (13), 45.9 (17). − $C_{18}H_{16}FeO$ (304.2): calcd. C 71.08, H 5.30; found C 71.03, H 5.38.

(S_p)-Phenyl[2-(1,1,1-trimethylsilyl)ferrocenyl]methanone (9b): According to GP5, ozone was bubbled through a solution of hydrazone **15b** (159 mg) in CH_2Cl_2 (25 mL) for 165 s. Product **9b** was obtained after purification by flash chromatography (CH_2Cl_2). − Yield: 92 mg (76%, dark red crystals). − R_f = 0.89 (petroleum ether/diethyl ether = 2:1). − *ee* = 92% [HPLC: (*S*,*S*)-Whelk-01, *c*Hex/*i*PrOH = 99:1, 0.5 mL/min, ent-1: 6.5 min; ent-2: 6.9 min]. − $[\alpha]_D^{25}$ = +269.2 ($CHCl_3$, *c* = 0.95). − M.p. 140 °C. − IR (KBr): $\tilde{\nu}$ = 3089 cm^{-1}, 3065, 2951, 2248, 1789, 1725, 1632, 1596, 1574, 1446, 1415, 1382, 1328, 1247, 1191, 1173, 1158, 1107, 1080, 1049, 1028, 1005, 886, 842, 825, 755, 729, 696, 640, 620, 574, 511, 493. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.36 [s, 9 H, $Si(CH_3)_3$], 4.22 (s, 5 H, C_5H_5), 4.57 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $R_2C_5H_3$), 4.64 (t, ^3J = 2.5 Hz, 1 H, $R_2C_5H_3$), 4.77 (dd, ^3J = 2.5 Hz, ^4J = 1.1 Hz, 1 H, $R_2C_5H_3$), 7.44 (tm, ^3J = 6.9 Hz, 2 H, *m*-C_6H_5), 7.52 (tt, ^3J = 7.3 Hz, ^4J = 1.4 Hz, 1 H, *p*-C_6H_5), 8.28 (dm, ^3J = 6.9 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.5 [$Si(CH_3)_3$], 70.1 (C_5H_5), 74.0, 76.7, 79.2 ($R_2C_5H_3$), 75.6, 83.0 (*i*-$R_2C_5H_3$), 128.1, 128.3 (*o*/*m*-C_6H_5), 131.3 (*p*-C_6H_5), 140.1 (*i*-C_6H_5), 199.9 (C=O). − EI-MS: *m*/*z* = 362.0 (44) [M^+], 347.0 (100) [$M^+ - CH_3$], 120.9 (9) [$CpFe^+$]. − HR-MS: $C_{20}H_{22}{}^{56}FeOSi$: calcd. 362.07893; found 362.07906.

(S_p)-[2-(1-Boranato-1,1-diphenylphosphanyl)ferrocenyl](phenyl)-methanone (9c): According to GP5, ozone was bubbled through a solution of hydrazone **15d** (207 mg) in CH_2Cl_2 (30 mL) for 85 s. The product was obtained after purification by flash chromatography (CH_2Cl_2). − Yield: 140 mg (83%, red crystals). − R_f = 0.74 (CH_2Cl_2). − *ee* = 91% (^{1}H NMR, Pirkle alcohol, $CDCl_3$). − $[\alpha]_D^{25}$ = −18.0 ($CHCl_3$, *c* = 0.94). − M.p. 174 °C. − IR (KBr): $\tilde{\nu}$ = 3098 cm^{-1}, 3072, 2922, 2850, 2455, 2379, 2348, 2261, 1885, 1814, 1777, 1739, 1721, 1705, 1687, 1632, 1597, 1575, 1547, 1527, 1498, 1481, 1435, 1415, 1384, 1354, 1320, 1251, 1165, 1151, 1139, 1105, 1060, 1028, 879, 850, 827, 801, 742, 720, 695, 644, 610, 566, 509, 483. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.36 (broad s, 1 H, $C_5H_3R_2$), 4.40 (s, 5 H, C_5H_5), 4.70 (broad s, 1 H, $C_5H_3R_2$), 4.93 (broad s, 1 H, $C_5H_3R_2$), 7.28−7.50 (m, 9 H, *m*/*p*-C_6H_5), 7.62 (m, 2 H), 7.75 (m, 2 H), 7.84 (d, ^3J = 7.1 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 72.6 (C_5H_5), 72.8 (*i*-$C_5H_3R_2$), 73.6 (d, J_{CP} = 7.4 Hz), 77.8 (d, J_{CP} = 6.8 Hz), 79.5 (d, J_{CP} = 8.0 Hz, $C_5H_3R_2$), 83.9 (d, $^1J_{CP}$ = 6.3 Hz, *i*-$C_5H_3R_2$), 128.7, 129.2 (O=C-*o*/*m*-C_6H_5), 128.85 (d, $^3J_{CP}$ = 9.8 Hz, P-*m*-C_6H_5), 128.87 (O=C-*p*-C_6H_5), 131.2 (d, $^4J_{CP}$ = 2.3 Hz), 131.3 (d, $^4J_{CP}$ = 2.3 Hz, P-*p*-C_6H_5), 131.5 (d, $^1J_{CP}$ = 60.7 Hz), 132.5 (d, $^1J_{CP}$ = 57.8 Hz, P-*i*-C_6H_5), 133.5 (d, $^2J_{CP}$ = 6.3 Hz), 134.3 (d, $^2J_{CP}$ = 6.9 Hz, P-*o*-C_6H_5), 139.4 (O=C-*i*-C_6H_5), 194.5 (C=O). − ^{31}P NMR (C_6D_6, 162 MHz): +21.50 (broad). − EI-MS: *m*/*z* = 488.0 (5) [M^+], 474.0 (100) [$M^+ - BH_3$], 408.0 (60) [474.0 − C_5H_6], 397.0 (11), 228.0 (13), 182.9 (10), 56.9 (10) [Fe^+]. − $C_{29}H_{26}BFeOP$ (488.2): calcd. C 71.35, H 5.37; found C 71.11, H 5.70.

(S_p)-[2-(1,1-Diphenylphosphanyl)ferrocenyl](phenyl)methanone: According to GP7, a solution of hydrazone **15c** (193 mg) in DME (15 mL) was treated with $SnCl_2{\cdot}2H_2O$ (82 mg) and H_2O (1.0 mL). The reaction mixture was refluxed for 4 h. Then further portions of $SnCl_2{\cdot}2H_2O$ (165 mg) and H_2O (1 mL) were added and refluxing was continued overnight. Work up and flash chromatography provided the planar chiral ketone (petroleum ether/diethyl ether = 4:1). − Yield: 55 mg (35%, red-brown crystals). − R_f = 0.82 (petroleum ether/diethyl ether = 2:1). − $[\alpha]_D^{25}$ = −116.0 ($CHCl_3$, *c* = 0.76). − M.p. 190 °C. − IR (KBr): $\tilde{\nu}$ = 3107 cm^{-1}, 3091, 3064, 3046, 3001, 2924, 2852, 2246, 1628, 1597, 1574, 1525, 1478, 1445, 1421, 1384, 1351, 1326, 1255, 1192, 1165, 1120, 1107, 1091, 1074, 1053, 1027, 1004, 938, 908, 877, 853, 826, 798, 752, 700. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.95 (m, 1 H, $R_2C_5H_3$), 4.21 (s, 5 H, C_5H_5), 4.55 (t, ^3J = 2.7 Hz, 1 H, $R_2C_5H_3$), 4.91 (m, 1 H, $R_2C_5H_3$), 7.20−7.56 (m, 13 H, C_6H_5), 7.90 (dm, ^3J = 7.1 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 71.5 (d, J_{CP} = 1.8 Hz, C_5H_5), 72.8, 75.9, 76.2 (d, J_{CP} = 4.9 Hz, $R_2C_5H_3$), 81.1 (d, $^1J_{CP}$ = 17.7 Hz, *i*-$R_2C_5H_3$), 128.0 (d, $^3J_{CP}$ = 8.0 Hz), 128.2 (d, $^3J_{CP}$ = 7.4 Hz, P-*m*-C_6H_5), 128.1, 128.9, 131.4 (*p*-C_6H_5), 132.2 (d, $^2J_{CP}$ = 19.5 Hz), 135.1 (d, $^2J_{CP}$ = 22.0 Hz, P-*o*-C_6H_5), 139.1 (d, $^1J_{CP}$ = 15.3 Hz), 139.7 (d, $^1J_{CP}$ = 12.2 Hz, P-*i*-C_6H_5), 139.5 (O=C-*i*-C_6H_5), 198.4 (C=O). − EI-MS: *m*/*z* = 474.0 (100) [M^+], 408.0 (100) [M^+ − CpH], 397.0 (22) [$M^+ - C_6H_5$], 361.0 (14), 360.0 (11), 353.0 (14) [M^+ − CpFe], 304.1 (12), 283.9 (11), 257.0 (13), 237.2 (14), 228.1 (43), 215.0 (14), 202.0 (12), 183.0 (13), 170.0 (15), 152.0 (12), 120.9 (38) [$CpFe^+$], 97.1 (11), 95.0 (10), 57.1 (14) [FeH^+], 56.0 (12) [Fe^+]. − HR-MS: $C_{29}H_{23}{}^{56}FeOP$: calcd. 474.08359; found 474.08342.

(R_p)-{2-[Hydroxy(diphenyl)methyl]ferrocenyl}(phenyl)methanone (9d): a) According to GP7, a solution of hydrazone **15e** (244 mg) in DME (20 mL) was treated with $SnCl_2{\cdot}2H_2O$ (104 mg) and H_2O (1.4 mL). The reaction mixture was refluxed for 10 h, adding a further portion of $SnCl_2{\cdot}2H_2O$ (6.0 equiv.) in the meantime. Work up

and flash chromatography (CH_2Cl_2) provided planar chiral ketone **9d**. − b) According to GP5, ozone was bubbled through a solution of hydrazone **15e** (235 mg) in CH_2Cl_2 (25 mL) for 80 s. Compound **9d** was obtained after purification by flash chromatography (CH_2Cl_2). − Yield: a) 168 mg (85%, dark red crystals). b) 133 mg (70%). − R_f = 0.61 (petroleum ether/diethyl ether = 2:1). − a) *ee* = 96% (^{1}H NMR, Pirkle alcohol, $CDCl_3$); b) *ee* = 85%. − $[\alpha]_D^{25}$ = +311.7 ($CHCl_3$, *c* = 0.97). − M.p. 198 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3450 cm^{-1}, 3227, 3104, 3086, 3055, 1609, 1575, 1533, 1488, 1446, 1427, 1405, 1385, 1339, 1252, 1222, 1196, 1177, 1150, 1121, 1066, 1038, 1024, 1009, 999, 932, 845, 836, 829, 762, 740, 700. − ^{1}H NMR (300 MHz, C_6D_6): δ = 3.94 (m, 1 H, $R_2C_5H_3$), 3.98 (m, 1 H, $R_2C_5H_3$), 4.15 (s, 5 H, C_5H_5), 4.28 (m, 1 H, $R_2C_5H_3$), 6.88−7.26 (m, 9 H, C_6H_5), 7.56 (t, ^3J = 7.7 Hz, 4 H, C_6H_5), 7.85 (d, ^3J = 7.1 Hz, 2 H, C_6H_5), 8.20 (s, 1 H, OH). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (m, 1 H, $R_2C_5H_3$), 4.34 (s, 5 H, C_5H_5), 4.45 (m, 1 H, $R_2C_5H_3$), 4.55 (m, 1 H, $R_2C_5H_3$), 7.05−7.66 (m, 15 H, C_6H_5), 7.72 (s, 1 H, OH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 70.3, 73.7, 78.9 ($R_2C_5H_3$), 72.0 (C_5H_5), 75.2, 77.7 (*i*-$R_2C_5H_3$), 106.9 (COH), 127.3, 127.5, 132.5 (*p*-C_6H_5), 127.89, 127.95, 128.01, 128.4, 128.7, 128.9 (*o*/*m*-C_6H_5), 140.4, 146.7, 149.5 (*i*-C_6H_5), 204.4 (C=O). − EI-MS: *m*/*z* = 472.0 (46) [M^+], 406.9 (100) [M^+ − Cp], 361.0 (31), 282.9 (12), 105.0 (17) [$PhCO^+$], 77.0 (16) [Ph^+], 60.0 (14), 59.1 (19), 57.1 (10) [FeH^+]. − $C_{30}H_{24}FeO_2$ (472.4): calcd. C 76.28, H 5.12; found C 76.30, H 5.53.

(R_p)-[(2-Formyl)ferrocenyl](phenyl)methanone (9e): According to GP5, ozone was bubbled through a solution of hydrazone **15f** (160 mg) in CH_2Cl_2 (25 mL) for 100 s. Compound **9e** was obtained after purification by flash chromatography (CH_2Cl_2) . − Yield: 86 mg (73%, black-red crystals). − R_f = 0.34 (CH_2Cl_2). − *ee* = 90% (^{1}H NMR after quantitative conversion with SAMP). − $[\alpha]_D^{25}$ = −409.3 ($CHCl_3$, *c* = 0.53). − M.p. 80 °C (decomposition). − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 3062, 3028, 2960, 2929, 2871, 2768, 2649, 2519, 2279, 2267, 1777, 1673, 1639, 1598, 1576, 1489, 1440, 1421, 1384, 1333, 1269, 1230, 1179, 1160, 1108, 1076, 1051, 1027, 1004, 898, 855, 832, 800, 763, 728, 699, 667, 629, 619, 504, 490, 463. − ^{1}H NMR (300 MHz, C_6D_6): δ = 3.85 (s, 5 H, C_5H_5), 4.11 (t, ^3J = 2.7 Hz, 1 H, $R_2C_5H_3$), 4.43 (dd, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, $R_2C_5H_3$), 5.16 (dd, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, $R_2C_5H_3$), 7.06−7.19 (m, 3 H, *m*-C_6H_5, *p*-C_6H_5), 7.78 (dm, ^3J = 6.7 Hz, 2 H, *o*-C_6H_5), 11.03 (s, 1 H, CHO). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 72.7 (C_5H_5), 73.1, 75.1, 78.2 ($R_2C_5H_3$), 81.1, 82.1 (*i*-$R_2C_5H_3$), 129.0, 129.1 (*o*/*m*-C_6H_5), 132.9 (*p*-C_6H_5), 140.0 (*i*-C_6H_5), 196.0 (CHO), 200.0 (FcCOPh). − EI-MS: *m*/*z* = 318.0 (100) [M^+], 290.0 (74) [M^+ − CO], 252.9 (16) [M^+ − C_5H_5], 196.9 (24) [M^+ − C_5H_5Fe], 184.9 (12) [Fc^+], 152.0 (26), 141.0 (37), 139.0 (15), 132.9 (15), 120.9 (20) [$CpFe^+$], 115.0 (15), 105.0 (10) [$C_6H_5CO^+$], 77.1 (16) [$C_6H_5^+$], 55.9 (18) [Fe^+]. − $C_{18}H_{14}FeO_2$ (318.2): calcd. C 67.95, H 4.44; found C 67.70, H 4.88.

(S_p)-(2-Iodoferrocenyl)(phenyl)methanone (9f): According to GP7, a solution of hydrazone **15g** (140 mg) in DME (15 mL) was treated with $SnCl_2{\cdot}2H_2O$ (78 mg) and H_2O (1.2 mL). The reaction mixture was refluxed for 9 h, adding a further portion of $SnCl_2{\cdot}2H_2O$ (2.0 equiv.) in the meantime. Work up and flash chromatography (CH_2Cl_2) provided planar chiral ketone **9f**. − Yield: 86 mg (78%, red crystals). − R_f = 0.80 (CH_2Cl_2). − *ee* = 71% (HPLC, Chiralcel OD2, *c*Hex/*i*PrOH = 95:5, 0.5 mL/min, ent-1: 9.5 min, ent-2: 11.9 min). − $[\alpha]_D^{25}$ = +187.7 ($CHCl_3$, *c* = 0.47). − M.p. 83 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3097 cm^{-1}, 3060, 3013, 2925, 1721, 1645, 1598, 1577, 1447, 1421, 1372, 1353, 1319, 1254, 1217, 1191, 1177, 1157, 1108, 1066, 1048, 1027, 1003, 986, 860, 848, 829, 797, 756, 726, 698, 672, 506, 485. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.23 (s, 5 H, C_5H_5), 4.52 (t, ^3J = 2.7 Hz, 1 H, $R_2C_5H_3$), 4.59 (dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, $R_2C_5H_3$), 4.85 (dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, $R_2C_5H_3$), 7.45 (tm, ^3J = 7.7 Hz, 2 H, *m*-C_6H_5), 7.55 (tt, ^3J = 7.4 Hz, ^4J = 1.3 Hz, 1 H, *p*-C_6H_5), 7.85 (dm, ^3J = 7.1 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 71.5, 72.3, 80.1 ($R_2C_5H_3$), 72.7 (*i*-$R_2C_5H_3$), 73.2 (C_5H_5), 128.2, 128.7 (*o*/*m*-C_6H_5), 132.0 (*p*-C_6H_5), 139.2 (*i*-C_6H_5), 197.8 (C=O). − EI-MS: *m*/*z* = 415.9 (100) [M^+], 287.9 (63) [M^+ − HI], 259.9 (69) [287.9 − CO], 204.0 (24) [259.9 − Fe], 203.0 (30), 202.0 (27), 182.8 (11) [287.9 − C_6H_5CO], 139.0 (21), 104.9 (11) [$C_6H_5CO^+$], 77.0 (14) [$C_6H_5^+$]. − HR-MS: $C_{17}H_{13}{}^{56}FeIO$: calcd. 415.936046; found 415.936171.

(S_p)-Cyclohexyl(2-methylferrocenyl)methanone (9g): According to GP6, a solution of hydrazone **18b** (98 mg) in DME (10 mL) was treated with a 20% aqueous solution of $TiCl_3$ (2.5 equiv.) and refluxed for 60 min. Work up and filtration through silica gel (CH_2Cl_2) provided planar chiral ketone **9g**. − Yield: 71 mg (99%, red crystals). − R_f = 0.68 (CH_2Cl_2). − *ee* ≥ 96% (^{1}H NMR, Pirkle alcohol, $CDCl_3$). − $[\alpha]_D^{25}$ = −343.5 ($CHCl_3$, *c* = 0.52). − IR (KBr): $\tilde{\nu}$ = 3095 cm^{-1}, 2924, 2853, 2669, 2236, 1660, 1450, 1421, 1378, 1360, 1346, 1308, 1293, 1261, 1233, 1202, 1175, 1158, 1104, 1067, 1038, 1002, 975, 944, 921, 981, 849, 812, 770, 736, 670, 596, 512, 491, 468. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.08−2.00 [m, 10 H, $(CH_2)_5$], 2.76 (m, 1 H, O=CCH), 2.41 (s, 3 H, CH_3), 3.92 (s, 5 H, C_5H_5), 3.98 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 4.10 (dd, ^3J = 2.0 Hz, ^4J = 1.8 Hz, 1 H, $C_5H_3R_2$), 4.32 (dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$). − ^{13}C NMR (75 MHz, C_6D_6): δ = 15.5 (CH_3), 26.1, 26.3, 26.5, 29.1, 31.3 (CH_2), 48.4 (O=C*C*H), 69.2, 70.4, 74.6 ($C_5H_3R_2$), 70.3 (C_5H_5), 87.4, 89.4 (*i*-$C_5H_3R_2$), 207.7 (C=O). − EI-MS: *m*/*z* = 310.0 (100) [M^+], 226.9 (37) [M^+ − C_6H_{11}], 198.9 (43) [226.9 − CO], 143.0 (16) [198.9 − Fe], 121.0 (20) [$CpFe^+$], 56.0 (Fe^+) [11], 55.1 (15). − $C_{18}H_{22}FeO$ (310.2): calcd. C 69.69, H 7.15; found C 69.51, H 7.36.

(R_p)-(5-Butyl-2-thienyl)(2-methylferrocenyl)methanone (9h): Hydrazone **20** (87 mg) dissolved in THF/H_2O (4:0.5 mL) was treated with $Cr(OAc)_2$ (1.0 g). The reaction mixture was refluxed for 4 h and cooled down to room temp. After filtration from undissolved Cr salts, the filtrate was diluted with diethyl ether, washed twice with saturated aqueous NaCl and dried over $MgSO_4$. Compound **9h** was obtained by filtration through silica gel (hexane/diethyl ether = 4:1). − Yield: 46 mg (67%, red oil). − R_f = 0.54 (hexane/diethyl ether = 4:1). − $[\alpha]_D^{25}$ = +384.0 ($CHCl_3$, *c* = 1.75). − IR ($CHCl_3$): $\tilde{\nu}$ = 3093 cm^{-1}, 2956, 2928, 2860, 1665, 1612, 1530, 1456, 1420, 1378, 1345, 1281, 1228, 1159, 1106, 1042, 1002, 874, 816, 756, 666, 611, 502, 489. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.78 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.16 (sext, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 1.45 (pent, ^3J = 7.6 Hz, 2 H, $CH_2CH_2CH_3$), 2.41 (s, 3 H, $CpCH_3$), 2.49 (t, ^3J = 7.7 Hz, 2 H, $C_4H_2SCH_2$), 3.95 (s, 5 H, C_5H_5), 4.02 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 4.13 (dd, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.66 (dd, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, $C_5H_3R_2$), 6.54 (d, ^3J = 3.7 Hz, 1 H, C_4H_2S), 7.70 (d, ^3J = 3.7, 1 H, C_4H_2S). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.8, 15.1 (CH_3), 22.4 (CH_2CH_3), 30.3 ($CH_2CH_2CH_3$), 33.7 ($C_4H_2SCH_2$), 68.9, 71.7, 73.7 ($C_5H_3R_2$), 71.1 (C_5H_5), 78.8, 87.9 (*i*-$C_5H_3R_2$), 125.1, 132.3 (C_4H_2S), 143.9, 153.5 (*i*-C_4H_2S), 189.7 (C=O). − EI-MS: *m*/*z* = 366.1 (100) [M^+], 199.0 (23) [$C_{10}H_8FeCH_3^+$], 121.0 (12) [$CpFe^+$]. − $C_{20}H_{22}FeOS$ (366.3): calcd. C 65.58, H 6.05; found C 65.94, H 6.54.

(S_p)-(2-Benzylferrocenyl)(boranato)(diphenyl)phosphane (24): A mixture of $LiAlH_4$ (2.3 equiv.) and $AlCl_3$ (2.3 equiv.) in Et_2O (1 mL) was treated with a solution of ketone **9c** (74 mg) in Et_2O (1 mL) at 0 °C. The mixture was stirred for 15 h at room temp. After cooling to 0 °C, the suspension was treated with saturated aqueous NH_4Cl and washed twice with saturated aqueous NaCl.

After drying over $MgSO_4$, **24** was purified by filtration through silica gel (hexane/diethyl ether = 2:1). − Yield: 66 mg (92%, yellow crystals). − R_f = 0.50 (hexane/diethyl ether = 4:1). − $[\alpha]_D^{25}$ = −1.9 ($CHCl_3$, c = 0.42). − M.p. 143 °C. − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 3085, 3074, 3057, 3026, 3004, 2949, 2924, 2908, 2851, 2408, 2389, 2342, 2255, 1958, 1889, 1815, 1775, 1708, 1686, 1655, 1602, 1586, 1573, 1544, 1493, 1481, 1454, 1435, 1410, 1385, 1341, 1325, 1308, 1289, 1276, 1239, 1177, 1158, 1130, 1105, 1062, 1039, 1030, 1000, 921, 841, 823, 740, 712, 651, 622, 600, 568, 530, 500. − ^{1}H NMR (300 MHz, C_6D_6): δ = ca. 2.40 (broad, $^1J_{BH}$ = 120 Hz, 3 H, BH_3), 3.70 (dd, ^3J = 3.7 Hz, ^4J = 2.4 Hz, 1 H, $C_5H_3R_2$), 3.85 (d, ^2J = 15.5 Hz, 1 H, CH_2), 3.96 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 4.14 (dd, ^3J = 3.7 Hz, ^4J = 1.4 Hz, 1 H, *o*-$C_5H_3R_2$), 4.16 (s, 5 H, C_5H_5), 4.20 (d, ^2J = 15.5 Hz, 1 H, CH_2), 6.83−7.11 (m, 11 H, C_6H_5), 7.49 (ddd, $^3J_{HP}$ = 10.0 Hz, ^3J = 8.4 Hz, ^4J = 1.7 Hz, 2 H, P-*o*-C_6H_5), 7.78 (ddd, $^3J_{HP}$ = 9.4 Hz, ^3J = 7.7 Hz, ^4J = 1.7 Hz, 2 H, P-*o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 34.8 (CH_2), 69.2 (d, $^1J_{CP}$ = 62.2 Hz, *i*-$C_5H_3R_2$), 70.0 (d, J_{CP} = 6.1 Hz), 73.4 (d, J_{CP} = 4.9 Hz), 73.8 (d, J_{CP} = 7.3 Hz, $C_5H_3R_2$), 70.9 (C_5H_5), 93.6 (d, $^2J_{CP}$ = 24.6 Hz, *i*-$C_5H_3R_2$), 126.1 (CH_2-*p*-C_6H_5), 128.4, 129.3 (CH_2-*o*/*m*-C_6H_5), 130.6 (d, $^4J_{CP}$ = 2.4 Hz), 130.9 (d, $^4J_{CP}$ = 2.5 Hz, P-*p*-C_6H_5), 131.65 (d, $^1J_{CP}$ = 59.8 Hz), 131.67 (d, $^1J_{CP}$ = 56.2 Hz, P-*i*-C_6H_5), 133.1 (d, $^2J_{CP}$ = 9.1 Hz), 133.8 (d, $^2J_{CP}$ = 9.7 Hz, P-*o*-C_6H_5), 140.9 (CH_2-*i*-C_6H_5). − EI-MS: *m*/*z* = 474.0 (1) [M^+], 459.9 (100) [$M^+ - BH_3$], 274.9 (42) [459.9 − PPh_2], 183.0 (20), 121.0 (12) [$CpFe^+$]. − $C_{29}H_{28}BFeP$ (474.2): calcd. C 73.46, H 5.95; found C 73.69, H 6.24.

Malonate (*R*)-17:[17] A mixture of (π-allyl)palladium chloride dimer (3.7 mg, 0.01 mmol) and ligand **15c** (23.5 mg, 0.04 mmol) in CH_2Cl_2 (1.5 mL) was stirred at room temp. for 1 h. A solution of 1,3-diphenyl-2-propenyl acetate **(16)** (1.0 mmol, 252 mg) in CH_2Cl_2 (0.5 mL) was added, followed by dimethylmalonate (3.0 mmol, 0.34 mL), *N*,*O*-bis(trimethylsilyl)acetamide (BSA, 3.0 mmol, 0.74 mL) and KOAc (0.01 mmol, 1.0 mg), sequentially. After 24 h, the reaction mixture was diluted with Et_2O (20 mL), quenched with saturated aqueous NH_4Cl (20 mL) and washed with saturated brine (20 mL). The organic layer was dried over $MgSO_4$. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography (hexane/diethyl ether = 4:1). − Yield: 272 mg (84%, colorless oil). − *ee* = 93% [^{1}H NMR, Eu(tfc)$_3$, $CDCl_3$]. − $[\alpha]_D^{25}$ = +18.9 (EtOH, c = 1.05).

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