Asymmetric Synthesis of Novel Ferrocenyl Ligands with Planar and Central Chirality and Their Application to Pd-Catalyzed Allylic Substitutions

Dieter Enders,*[a] René Peters,[a] René Lochtman,[a] Gerhard Raabe,[a] Jan Runsink,[a] and Jan W. Bats[b]

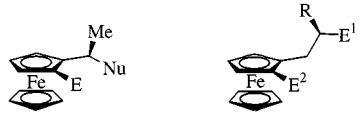
Dedicated to Professor Richard Neidlein on the occasion of his 70th birthday

Keywords: Asymmetric synthesis / Hydrazones / Ferrocenyl ligands / Asymmetric catalysis / Allylic substitution

An efficient and flexible asymmetric synthesis of planar chiral ferrocenyl ligands bearing a stereogenic centre at the β-position to the metallocene backbone is described. A variety of donor groups can be independently introduced as electrophiles, thus allowing electronic and steric fine-tuning of the ligands, which were investigated in Pd-catalyzed enantioselective allylic substitutions. By employing a *P,S* ligand, the alkylation of the standard test system (±)-1,3-diphenyl-2-propenyl acetate using dimethyl malonate/BSA as the nucleophile proceeded in a quantitative yield with an *ee* of 97%, which is the best value reported so far in this reaction for a P∪S ligand.

Introduction

The application of ferrocenyl ligands possessing planar chirality in asymmetric catalysis has recently received considerable interest.[1] In most cases, the employed ferrocene ligands are of type **A**, which is accessible from enantiomerically pure Ugi amine (Nu = NMe_2, E = H) by diastereoselective *ortho*-metallation, trapping of the resulting carbanion with a suitable electrophile and subsequent nucleophilic displacement of the dimethylamino functionality with retention of configuration via an intermediately formed carbocation.[1,2] In the meantime, several efficient stereoselective syntheses of the enantiomerically pure Ugi amine and related compounds have been developed.[3] Planar chiral ferrocenes **A**, which in addition possess a stereogenic centre in the α-position, have shown efficiency as ligands for catalytic asymmetric synthesis both in research and industrial processes.[4] We would therefore like to report a straightforward asymmetric synthesis of planar chiral ferrocenyl ligands of type **B** bearing a stereogenic centre in the β-position of the side chain. Parts of this work were recently published as preliminary communications.[5] The initial aim for synthesizing ligands of type **B** was to investigate the effect that changing the position of the chiral centre from the α- to the β-position would have on the levels of asymmetric induction for catalytic processes. The field of such planar chiral ferrocenes had been little studied before, because those compounds could not previously be synthesized stereoselectively. In 1981 Kumada et al. described the only synthesis of the homologous compound **B** (E^1 = NMe_2, E^2 = PPh_2) of di**p**henyl**p**hosphanyl**f**errocenylethyl**a**mine (PPFA), which required separation of racemates and diastereoisomers.[6]



A **B**

Results and Discussion

Our SAMP/RAMP-hydrazone method [SAMP and RAMP = (*S*)- and (*R*)-1-amino-2-methoxymethylpyrrolidin] seemed to be appropriate for the asymmetric synthesis of planar chiral ligands **B** bearing a stereogenic centre at the β-position of the ferrocene backbone, since not only would the highly diastereoselective alkylation α to the hydrazone functional group be possible,[7] but also the introduction of various heteroatom functionalities with similarly high asymmetric inductions. In the context of ligand synthesis, this would necessarily require the use of phosphorus,[8] sulfur,[9] and nitrogen electrophiles.[10] In addition, since we have recently demonstrated that benzoylferrocene-SAMP-hydrazones may be easily functionalized at the *ortho*-position with high diastereoselectivity,[11] it was decided to combine both synthetic strategies. As starting material, we used ferrocenyl ketones **1** with α-acidic protons, which may be accessed simply by Friedel−Crafts acylation.[12] Since the ketones were only weakly electrophilic, owing to the electron-donating character of the ferrocenyl system, quantitative conversion into mixtures of (*E*/*Z*)-

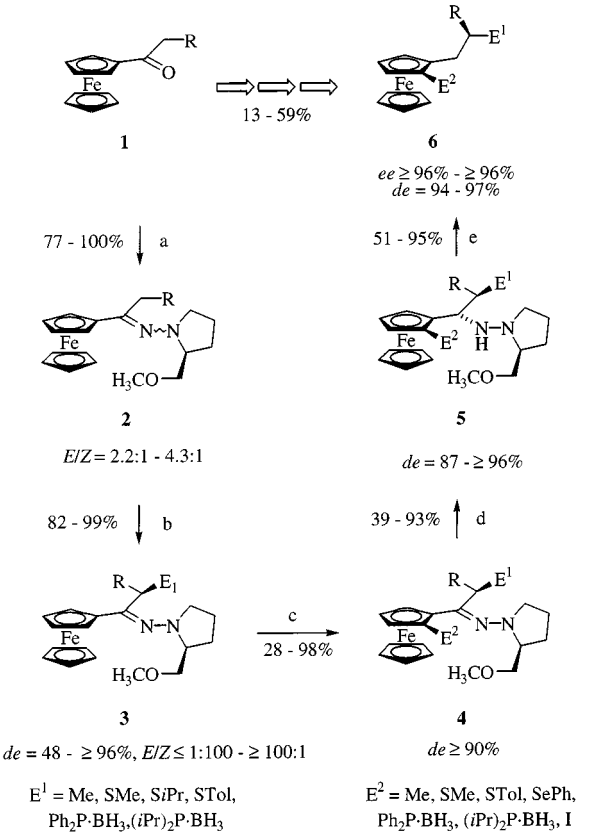
[a] Institut für Organische Chemie, Rheinisch-Westfälische Technische Hochschule,
Professor-Pirlet-Straße 1, 52074 Aachen, Germany
Fax: (internat.) + 49-241/8888-127
E-mail: enders@rwth-aachen.de
[b] Institut für Organische Chemie der Universität Frankfurt,
Marie-Curie-Straße 11, 60439 Frankfurt am Main, Germany

  1434−193X/00/1020−3399 $ 17.50+.50/0

SAMP-hydrazones **2** was achieved by using $AlMe_3$ activation (Table 1, Scheme 1).[11,13]

Table 1. Synthesis of ferrocenyl ketone-SAMP-hydrazones **2**

2	R	Yield [%]	(*E*)/(*Z*)
a	Me	95	2.8:1
b	Et	100	3.1:1
c	*i*Pr	84	2.2:1
d	Ph	77	4.3:1



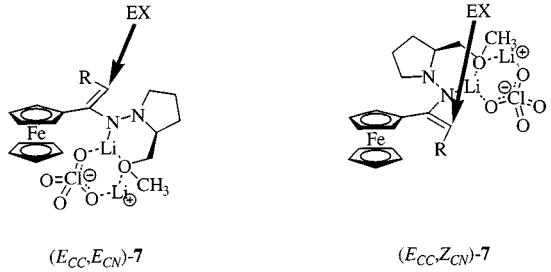
Scheme 1. Asymmetric synthesis of target ligands **6**: a) 2.0 equiv. SAMP/$AlMe_3$, toluene, *T*; b) 1) 1.2 equiv. LDA, 3.3 equiv. $LiClO_4$, Et_2O, roomp. temp., 2) E^1X, −100 °C; c) 1) *x* equiv. *t*BuLi, *y* equiv. $LiClO_4$, THF, −70 °C, 2) E^2X; d) catecholborane, CH_2Cl_2/Et_2O, −40 °C to room temp.; e) TFA/$NaBH_4$, CH_2Cl_2, 0 °C or 1) 2.5 equiv. HBF_4, 0 °C, CH_2Cl_2, 2) 5.0 equiv. $HBEt_3Li$

The regioselective metallation of the side chain was possible with lithium diisopropylamide (LDA). After trapping the azaenolate of **2** with electrophiles, we first obtained (*E*/*Z*)-hydrazone mixtures **3** (6.7:1 to 1:3.3), in which the new stereogenic centre in each of the (*E*) and (*Z*) isomers unexpectedly was found to bear the opposite configuration. It was therefore necessary to find conditions which would yield only one geometric hydrazone isomer. Accordingly, we examined the influence of base, solvent, co-solvent, additives, reaction time, reaction temperature, transition metal salts for transmetallation of the lithio azaenolates, and of SAMP-auxiliary derivatives on the (*E*/*Z*) ratio. Finally, we discovered that upon metallation in diethyl ether at room temperature, the addition of $LiClO_4$ resulted in the desired high (*E*/*Z*) ratios (Scheme 1). Without $LiClO_4$, azaenolates **7** formed yellow-orange precipitates. However, with $LiClO_4$, orange-brown homogeneous solutions were obtained. It is well-known that $LiClO_4$ leads to deaggregation of organolithium species, and this explains the differing solubilities and selectivities observed.[14] By trapping the metallated species at −100 °C with the required electrophile, the desired α-functionalized hydrazones **3** were available in good yields and with (*E*/*Z*) ratios up to ≥ 100:1 (Table 2). The (*E*) and (*Z*) isomers were diastereomerically pure, with the exception of **3b** where R is a phenyl group, presumably owing to epimerization caused by activation by the aromatic part. The residue R has a considerable influence on the (*E*/*Z*) selectivity. Whereas for R = Me, Et, Ph (*E*)-hydrazones are formed preferentially, the branched *i*Pr group yields (*Z*)-hydrazones.

Table 2. Regio- and diastereoselective functionalization of the side chain

3	R	E^1	(*E*)/(*Z*)	*de* [%]	Yield [%]
a	Et	Me	54:1	≥ 96	93
b	Ph	Me	≥ 100:1	48	95
c	Me	Ph_2PBH_3	20:1	≥ 96	91
d	Et	Ph_2PBH_3	44:1	≥ 96	97
e	Me	SMe	12:1	≥ 96	95
f	Et	SMe	28:1	≥ 96	93
g	Me	S*i*Pr	50:1	≥ 96	92
h	Et	S*i*Pr	9:1	≥ 96	97
i	Me	iPr_2PBH_3	9:1	≥ 96	96
j	*i*Pr	STol	≤ 1:100	≥ 96	88
k	*i*Pr	Me	≤ 1:50	≥ 96	95
l	*i*Pr	SMe	≤ 1:50	≥ 96	82
m	Et	STol	7:1	≥ 96	99

The different configurations of the new stereogenic centre α to the hydrazone moiety can be explained as shown in Scheme 2. Both azaenolates **7** will adopt the (E_{CC}) configuration as is usually the case for lithiated SAMP-hydrazones. The electrophilic attack occurs from the sterically less hindered *exo* side. The opposite configurations are the result of different conformations (rotation around the Cp−C bond). This assumption is based on the fact that *ortho*-lithiated (*E*)- and (*Z*)-ferrocenyl ketone SAMP-hydrazones bear different configurations with respect to planar chirality, showing that they also react in different conformations.[15]



Scheme 2

For our studies we chose alkyl, phosphorus, and sulfur electrophiles. The BH_3-protected phosphorus derivatives were found to undergo (*E*/*Z*) isomerization in diethyl ether or benzene at room temperature. In order to avoid this pro-

cess, the completed reaction had to be worked up rapidly and at low temperatures (0 °C). Purification by column chromatography was also avoided for this reason; filtration through silica gel and subsequent crystallization from hexane at −26 °C yielded the analytically pure compounds. The unprotected phosphanes were found to isomerize much faster than the BH_3-protected phosphanes. In addition, they were observed to undergo rapid oxidation. As a result, the use of the protecting group was preferred, since the protected compounds turned out to be highly robust. The sulfur derivatives did not show any tendency to undergo isomerization.

The regio- and diastereoselective metallation of the Cp ring *ortho* to the directing hydrazone moiety of **3** was achieved through optimization of the metallation conditions. Again the use of lithium perchlorate turned out to be advantageous. In the presence of anion-stabilizing RS[16] and R_2PBH_3 substituents,[17] the side chain is deprotonated in the position α to the hydrazone moiety in the absence of $LiClO_4$, thus destroying the new stereogenic centre and causing (*E*/*Z*) isomerization. However, in the presence of $LiClO_4$ in combination with *t*BuLi/THF at −70 °C, metallation of the side chain was completely avoided. In this step, the (*E*) isomers were further enriched, since the (*E*)-configured hydrazones **3** underwent *ortho*-metallation more readily than the (*Z*)-configured isomers. The low tendency of (*Z*)-hydrazones to undergo *ortho*-metallation also explains the low yield of *ortho*-functionalization of hydrazone (*Z*)-**3j** (Table 3). In order to achieve high yields with the R_2PBH_3-substituted hydrazones **3**, an excess of base was necessary (2.5 to 3 equiv.). However, this was not found to have any negative influence on the regio- or diastereoselectivity. A double metallation was not observed in any case. It is noteworthy that the planar chiral products **4** do not show any tendency to undergo (*E*/*Z*) isomerization at room temperature. The *ortho*-metallation of the thiolated hydrazones **3** proceeded using only 1 equiv. *t*BuLi. After the optimum reaction conditions had been found, we used various phosphorus, sulfur and selenium electrophiles for ligand synthesis (Table 3). The new method allows for the successive, highly diastereoselective introduction of two different electrophiles. Unfortunately we have not yet been able to introduce two diphenylphosphanyl groups in an acceptable yield. This is probably due to steric crowding.

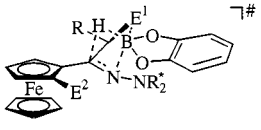
Subsequently, the planar chiral (*E*)-configured SAMP-hydrazones **4** could be transformed into the hydrazines **5** by reduction with catecholborane in diethyl ether/dichloromethane (1:1 to 2:1) (Table 4). With hydride reducing agents such as $LiAlH_4$, $HBEt_3Li$, $LiBH_4$, $NaBH_4$ etc., no reaction was observed under various reaction conditions owing to the electron-donating character of the ferrocene moiety, which significantly decreases the electrophilicity of the C=N double bond. Under acidic reaction conditions, solutions of ferrocenyl ketone SAMP-hydrazones show a dark red-brown or purple colour owing to the formation of a mesomerically stabilized cation. The same colour is observed with the addition of catecholborane, demonstrating that the Lewis-acidic boron atom is coordinated by the imino nitrogen atom, thus enhancing the electrophilicity of the C=N double bond and the nucleophilicity of the hydride (Scheme 3). (*Z*)-Hydrazones **4** did not undergo reduction. Compounds bearing a BH_3-protected phosphanyl group in the side chain had to be deprotected with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) to achieve acceptable yields. As the catecholborane reduction proceeds with high diastereoselectivity, the protocol described allows for the stereocontrolled generation of two contiguous stereogenic centres at the α- and β-positions in addition to the planar chirality.

Table 3. Regio- and diastereoselective functionalization of the *ortho*-Cp position

4	R	E^1	E^2	*x*	*y*	Yield [%]	*de* [%]
a	Et	Ph_2PBH_3	Me	4.0	6.0	55	96
b	Et	Ph_2PBH_3	SMe	3.0	6.0	65	≥ 90
c	Me	Ph_2PBH_3	SMe	2.5	6.0	94	≥ 90
d	Me	iPr_2PBH_3	STol	3.0	6.0	76	≥ 96
e	Et	SMe	Me	1.3	3.0	83	≥ 96
f	Me	SMe	Ph_2PBH_3	1.2	3.0	86	96
g	Et	SMe	Ph_2PBH_3	1.1	3.0	77	≥ 96
h	Et	SMe	iPr_2PBH_3	1.2	3.0	93	≥ 90
i	Me	S*i*Pr	Ph_2PBH_3	1.2	3.0	73	≥ 96
j	Et	SMe	SMe	2.0	4.0	98	≥ 90
k	Et	S*i*Pr	STol	1.1	3.0	89	≥ 90
l	Et	S*i*Pr	SePh	1.2	3.0	98	≥ 96
m	*i*Pr	STol	SMe	1.3	3.0	28	≥ 90
n	Me	Ph_2PBH_3	I	2.5	5.0	44	≥ 96

Table 4. Diastereoselective reduction of planar chiral hydrazones **4**

5	R	E^1	E^2	Yield [%]	*de* [%]
a	Et	SMe	Me	93	≥ 96%
b	Me	SMe	Ph_2PBH_3	39	≥ 96%
c	Et	SMe	Ph_2PBH_3	82	≥ 96%
d	Et	SMe	iPr_2PBH_3	55	≥ 96%
e	Me	S*i*Pr	Ph_2PBH_3	43	≥ 96%
f	Et	SMe	SMe	75	87
g	Et	S*i*Pr	STol	88	≥ 96%
h	Et	S*i*Pr	SePh	68	≥ 96%
i	Me	Ph_2PBH_3	SMe	58	≥ 96%
j	Et	Ph_2PBH_3	SMe	40	≥ 96%



Scheme 3

The X-ray structure analysis of **5e** (Figure 1) proves the absolute configuration shown in Scheme 1. The stereochemistry can be explained by the preferential *exo* attack of the reducing agent. Since uniform reaction pathways may be assumed, all compounds **5** were assigned as bearing the same absolute configuration. The configuration was confirmed by NOE measurements of hydrazine **5b** (^{11}B decoupling). The NMR studies also reveal the same conformation for molecules in solution and in crystalline form. In the

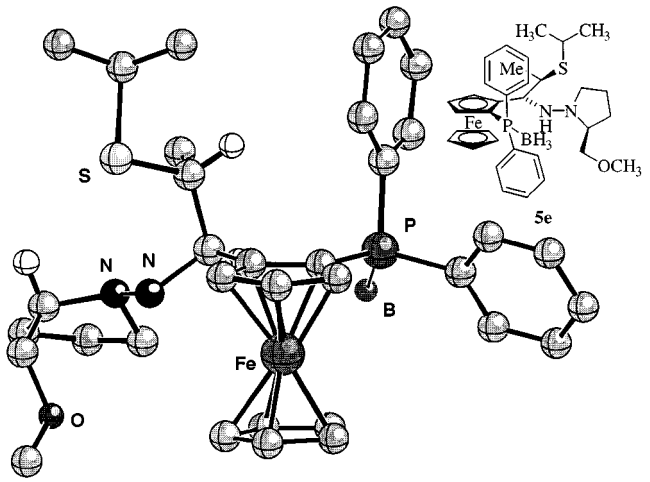


Figure 1. Crystal structure of hydrazine **5e**

side chain, H_α and H_β adopt a rigid *gauche* conformation ($^3J_{HH}$ = 1.6 Hz).

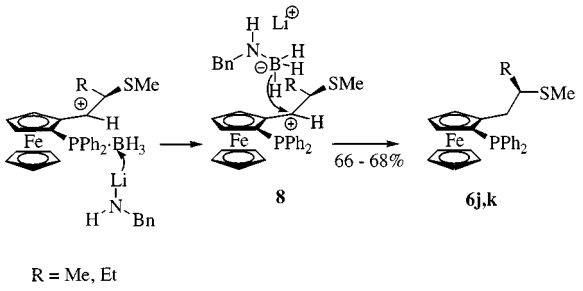
In order to remove the auxiliary, hydrazines **5** were protonated with either HBF_4 or trifluoroacetic acid. The method of choice for BH_3-protected P∪S ligands **6** was protonation with HBF_4 and trapping the resulting carbocation with *Superhydride*® ($HBEt_3Li$). The S∪S and the S∪Se ligands **6** were obtained by the combination TFA/$NaBH_4$.[18]

The cations of the latter systems turned out to be remarkably unstable. Therefore, the presence of the hydride reagent was necessary during the acidic reaction conditions. In contrast, the cations of the P∪S systems were found to be so stable that they could only be trapped using extremely nucleophilic reagents such as $HBEt_3Li$. The title compounds **6** were synthesized in virtually enantiomerically pure form

Table 5. Auxiliary cleavage

6	R	E^1	E^2	Yield [%]	*de* [%]	*ee* [%]	$[\alpha]_D^{25}$ ($CHCl_3$)
a	Me	Ph_2PBH_3	SMe	70	94	≥ 99[a]	+15.6
b	Et	Ph_2PBH_3	SMe	51	97	≥ 99[a]	−22.4
c	Me	SMe	Ph_2PBH_3	95	95	≥ 96[b]	−149.4
d	Et	SMe	Ph_2PBH_3	90	97	≥ 96[b]	−192.4
e	Et	SMe	iPr_2PBH_3	88	95	≥ 96[b]	+100.0
f	Me	S*i*Pr	Ph_2PBH_3	81	94	≥ 96[c]	−86.9
g	Et	SMe	SMe	95	94	≥ 99[b]	−181.3
h	Et	S*i*Pr	STol	84	97	≥ 99[a]	−5.9
i	Et	S*i*Pr	SePh	70	≥ 96	≥ 99[d]	−8.0

[a] Determined by HPLC on a chiral stationary phase (Chiracel OD-H). – [b] Determined by ^1H NMR using (−)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol as a chiral cosolvent. – [c] Determined by GC on a chiral stationary phase (Chirasil dex 25 m). – [d] Determined by HPLC on a chiral stationary phase (Chiracel OD-2).



Scheme 4

(*ee* ≥ 96% to ≥ 99%) and with high diastereoselectivity (*de* = 94−97%, Table 5).

Cleavage of the BH_3 protecting group was accomplished by the use of TMEDA. Phosphanyl groups bearing three aromatic substituents could be deprotected at room temperature, whereas deprotection of the alkyl-substituted phosphanes required higher temperatures (Table 6).

Protonation of hydrazines **5b**,**c** with $HBF_4 \cdot OEt_2$ followed by the addition of lithiated benzylamine furnished the deprotected phosphanes **6j−n** in a single step from hydrazines **5** (Scheme 4). Lithiated benzylamine removed the BH_3 protecting group yielding an anionic hydroborate reagent which traps carbocation **8**.

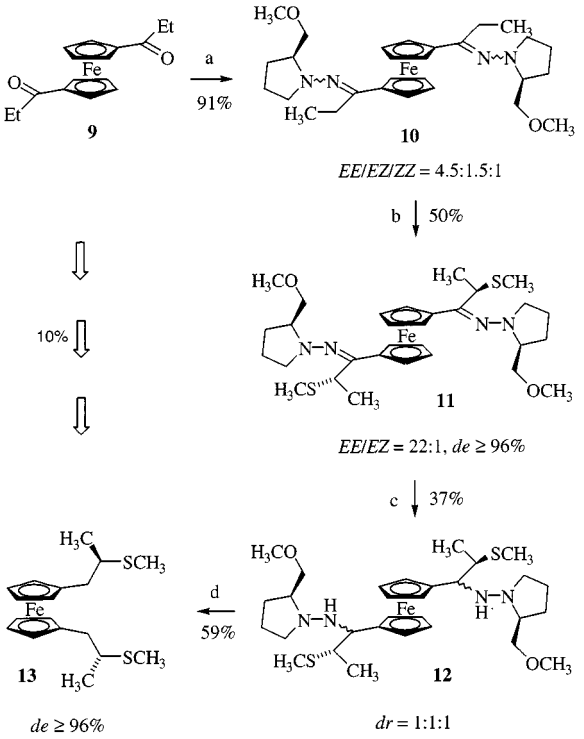
As could be shown for one example, the new methodology is also applicable in the generation of C_2-symmetric ligands possessing only central chirality (Scheme 5). Bis(hydrazone) **10**, easily accessible from diketone **9** in high yield, was transformed into a dianion with LDA. Trapping with $(MeS)_2$ yielded bis(thioether) **11**. Reduction with catecholborane in the absence of an *ortho* substituent furnished bis(hydrazine) **12**, without stereoselectivity, in moderate yield. Cleavage of the auxiliary provided S∪S ligand **13**.

In order to compare the efficiency in asymmetric catalysis of ligand type **B** with type **A**, we chose the Pd-catalyzed allylic substitution, since this reaction is one of the best understood catalytic asymmetric transformations.[19] During the catalytic course, a *meso*-type π-allyl species **14** is formed, if both residues R are identical (Scheme 6). The enantioselectivity of this reaction is determined by the regioselectivity of the nucleophilic attack. This goal is difficult to achieve when only taking the steric bulk of the ligand into account, since the new C−Nu bond is formed outside the coordination sphere of the metal centre. Therefore regioselective nucleophilic attack is often achieved by electronic means, employing bidentate hybrid ligands pos-

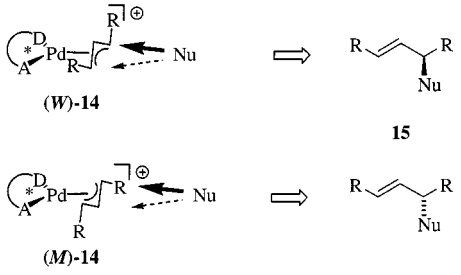
Table 6. BH_3 deprotection

6	R	E^1	E^2	TMEDA	Solvent	*T* [°C]	Yield [%]	*de* [%]	$[\alpha]_D^{25}$ ($CHCl_3$)
j	Et	SMe	PPh_2	5.0 eq	Et_2O	20	88	≥ 96	−263.1
k	Me	SMe	PPh_2	5.0 eq	Et_2O	20	51	≥ 96	−240.9
l	Et	SMe	$PiPr_2$	10.0 eq	toluene	90	95	97	−83.4
m	Me	S*i*Pr	PPh_2	5.0 eq	toluene/Et_2O	20	91	≥ 96	−186.0
n	Me	PPh_2	SMe	10.0 eq	toluene	90	59	≥ 96	+67.9

sessing two electronically different donor atoms. One is a σ-donor (like N or S) and one is a σ-donor−π-acceptor (e.g. P).



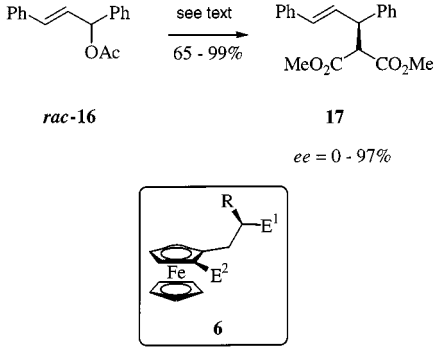
Scheme 5. Asymmetric synthesis of S∪S ligand **13**: a) 4.0 equiv. SAMP/$AlMe_3$, toluene, *T*; b) 1) 2.5 equiv. LDA, 9.0 equiv. $LiClO_4$, Et_2O, roomp. temp., 2) 3.0 equiv. $(MeS)_2$, −100 °C; c) 8.0 equiv. catecholborane, CH_2Cl_2/Et_2O, −50 °C to room temp.; d) TFA/$NaBH_4$, CH_2Cl_2, 0 °C



Scheme 6 D = σ-donor; A = σ-donor-π-acceptor

In general, (π-allyl)Pd^{II} complexes **14** adopt a square-planar coordination sphere around the central metal ion. Two bonds in a *trans* position compete for one metal d-orbital for a π-back bond. The stronger the π-acceptor ability of the ligand is, the more electronic density is removed from the metal d-orbital. That means the electronic density of the terminal allylic carbon atom is strongly reduced by a π-acceptor in a *trans* position, thus enhancing its electrophilicity. This strategy has previously been successfully applied by the use of P∪N−,[20] N∪S−[21] and P∪S−Pd chelates.[22] Another significant factor is the configuration of the allylic fragment. (*W*)- and (*M*)-**14** yield differently configured products **15** determining one of the ligands tasks: the preferential formation of one allylic isomer.

Ferrocenyl ligands of type **B** were investigated in the alkylation of the standard test system (±)-(*E*)-1,3-diphenyl-2-propenyl acetate (**16**) employing dimethyl malonate/BSA as nucleophile (Scheme 7, Table 7). All these ligands have at least one sulfur donor group (E^1 or E^2). The second donor atom may be P, Se, or another S. S∪S and S∪Se ligands **6h** and **6i** displayed low reactivity and selectivity. Even after 100 h in dichloromethane at room temperature the reaction was not complete. The low reactivity can be explained by the high electron density of the central metal ion owing to the weak π-acceptor abilities of the S and Se groups.[23] The low *ee* values of 20 and 44%, respectively, result from only minimum electronic differentiation. By employing P∪S ligands, we found a completely different situation. The (π-allyl)Pd complex is strongly activated by the P group as π-acceptor. In combination with the thioether



Scheme 7. Pd-catalyzed allylic alkylation; reaction conditions: *x* mol-% $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, *y* mol-% **6**, 1.0 mol-% KOAc, 3.0 equiv. dimethyl malonate/BSA, CH_2Cl_2, −20 °C or room temp.

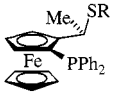
Table 7. Application of the novel ligands **6** in the Pd-catalyzed allylic alkylation (**16** → **17**)

6	E^1	E^2	R	*T* [°C]	*x* [mol-%]	*y* [mol-%]	*t* [h]	Yield [%]	*ee* [%][a]	Config.
h	S*i*Pr	STol	Et	20	2.5	5.5	100	84	20	(*R*)
i	S*i*Pr	SePh	Et	20	2.5	5.5	100	65	44	(*R*)
k	SMe	PPh_2	Et	20	2.5	5.5	0.16	99	90	(*R*)
k	SMe	PPh_2	Et	−20	1.0	2.2	24	99	97	(*R*)
j	SMe	PPh_2	Me	20	2.5	5.5	0.16	98	91	(*R*)
l	SMe	P*i*Pr_2	Et	20	2.5	5.5	1	99	70	(*R*)
m	S*i*Pr	PPh_2	Me	20	2.5	5.5	1	99	80	(*R*)
n	PPh_2	SMe	Me	20	2.5	5.5	1	99	0	−

[a] Determined by ^1H NMR with chiral shift reagent $Eu(tfc)_3$.

unit, we have a hybrid system that allows for electronic control of the nucleophilic attack on the allylic system. Using ligands **6j** and **6k**, the reaction proceeded quantitatively within 10 min at room temperature in CH_2Cl_2 (yield = 99 and 98%, respectively) affording product (*R*)-**17** with an enantiomeric excess of 90 and 91%, respectively. By changing the PPh_2 group of **6j** to the P*i*Pr_2 group (ligand **6l**), the *ee* was lowered from 90 to 70%, probably partly owing to the P*i*Pr_2 moiety being a weaker π-acceptor leading to a decrease in regioselectivity of the nucleophilic attack. The observed results indicate that the steric control also has to be fine-tuned. Since nucleophilic attack is preferred *cis* to the S donor group, this should be even more favourable with smaller thioether units. Changing the SMe group of **6k** to the S*i*Pr group (ligand **6m**) decreases the *ee* from 91 to 80%. The steric influence is demonstrated with P∪S ligand **6n**, which yields the racemic product, since the thioether group is connected to the bulky ferrocenyl core.

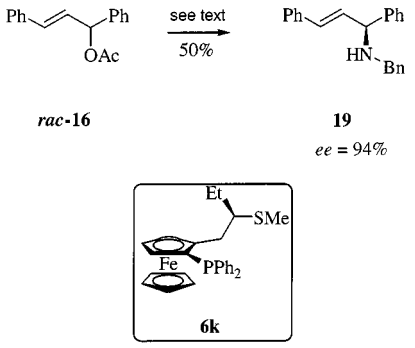
Owing to the high reactivity of the (allyl)Pd complexes with ligands **6j** and **6k**, it was possible to run the reaction at −20 °C in order to enhance the stereoselectivity. Subsequently, we concentrated on ligand **6j**, despite the fact that **6k** gave slightly better results, since the former can be obtained in higher yields and it is far less air-sensitive. The product could be isolated in quantitative yield and with an *ee* value of 97% by a simultaneous decrease in the amount of catalyst from $x = 2.5$ to $x = 1.0$ mol-% ($y = 2.2$ mol-% **6j**). The high selectivities are noteworthy, since ligands **18** bearing the stereogenic centre in the α-position yield the product with an *ee* of only 34% (R = ethyl) or 67% (R = cyclohexyl). By changing the alkyl group of the sulfur donor atom to a chiral sugar moiety Pregosin et al. were able to improve the *ee* to 88%.[22c] To the best of our knowledge, an enantiomeric excess of 97% is the best value for this reaction for a P∪S ligand reported to date. P∪S ligands have the advantage of higher reactivity and therefor much shorter reaction times than N∪S ligands.



18

A temperature effect similar to the alkylation noted before was found for the amination reaction using benzylamine as nucleophile (Scheme 8). Reducing the reaction temperature from +20 °C to −20 °C increased the *ee* of **19** from 84 to 94% [(*S*) configuration]. However, this higher selectivity was accompanied by a decrease in yield from 93 to 50%.

To be able to explain the high efficiency of our catalyst, we had to examine its configuration and structure. For $CDCl_3$ solutions of complex **20**, we observed four isomers in the ratio 86:9:3:2 with ^{31}P NMR chemical shifts of δ = 15.2, 14.9, 17.8, and 21.1, respectively. The configuration of the major isomer was unambiguously determined to be *exo-syn-syn* (*exo* refers to the relative orientation of the central allylic C−H vector pointing away from the ferrocenyl core;

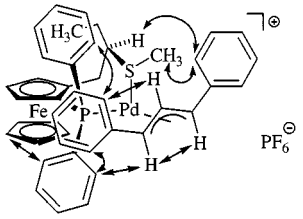


***rac*-16** **19** *ee* = 94%

6k

Scheme 8. Pd-catalyzed allylic alkylation; reaction conditions: 1.0 mol-% $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 2.2 mol-% **6j**, 1.0 mol-% KOAc, 2.5 equiv. $BnNH_2$, CH_2Cl_2, −20 °C

substituents on allylic ligands are named according to their configuration relative to the central C−H bond) by ^1H NMR NOE experiments (Figure 2). The terminal allylic proton *trans* to the thioether moiety shows a very intense interaction with the *ortho* protons of the *endo*-phenyl residue of the PPh_2 groups. The *ortho* protons of the phenyl ring on the allylic terminus *trans* to P interact significantly with the SCH_3 group and SCH. In combination with the intraallylic interactions, the *exo-syn-syn* configuration can unambiguously be assigned.



20

Figure 2. NOE connectivities for Pd complex **20**

The ^{13}C NMR chemical shifts for the allyl terminus *trans* to the phosphorus atom (δ = 102.5) and *trans* to sulfur atom (δ = 78.2) indicate that the carbon atom *trans* to the phosphorus atom should be much more electrophilic, thus allowing for regiocontrol of the nucleophilic attack (ground-state argument). Based on the plausible assumption that (*R*)-**17** and (*S*)-**19** result from preferential attack on this major *exo-syn-syn* isomer, then the nucleophilic attack proceeds as expected *trans* to the phosphorous atom.

More detailed information about the way in which our catalyst **20** works was obtained from the solid-state structure that also reveals the *exo-syn-syn* geometry with a distorted square-planar coordination around the palladium centre (Figure 3). The 1,3-diphenylallyl ligand is rotated in a clockwise manner along the Pd−allyl axis as seen from the allyl ligand towards the Pd atom so that the terminal allyl carbon atom *trans* to the phosphorus atom (C-7) is found to be 0.447 Å below the P−Pd−S coordination plane. In contrast, C(8) and C(9) are 0.450 Å and 0.136 Å, respectively, above this plane, indicating that the π-back bond to C(7) should be much less intense than to C(9) for orbital symmetry reasons. This means that C(7) should be much more electrophilic (ground-state argument). As ex-

pected, the Pd−C bond lengths are significantly different, with the carbon atom *trans* to the phosphorus atom having the longer distance [Pd−C(7) = 2.274(5) Å] than the one *trans* to the sulfur atom [Pd−C(9) = 2.176(4) Å] indicating again the higher *trans* influence of the phosphanyl moiety. The plane of the allyl fragment is tilted 22.8° from the perpendicular to the P−Pd−S coordination plane. Similar values have been observed for related compounds.

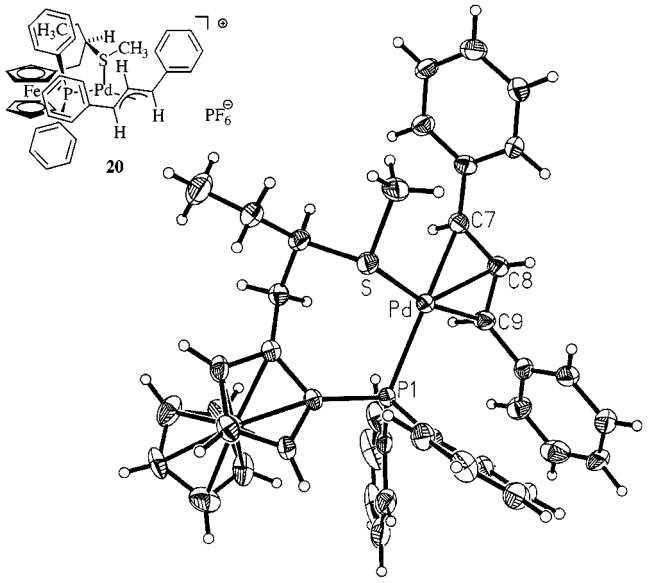


Figure 3. Crystal structure of Pd complex **20** (without anion and solvent) with 50% probability displacement ellipsoids; selected bond lengths are: Pd−S = 2.400(1), Pd−P1 = 2.326(1), Pd−C7 = 2.274(5), Pd−C8 = 2.188(4), Pd−C9 = 2.176(4), C7−C8 = 1.384(6) and C8−C9 = 1.404(6) Å

The preferred *exo-syn-syn* configuration is stabilized by two intramolecular C−H···π-arene interactions between one allylic phenyl group with the *exo*-phenyl ring of the PPh_2 group (H···π: 2.73 Å; C−H−π: 136°) and of the other allylic phenyl group with an SCH_3 proton (H···π: 2.77 Å; C−H−π: 131°). An additional intramolecular C−H···π interaction is found between a ferrocenyl C−H bond of the unsubstituted Cp ring and the *endo*-phenyl ring of the PPh_2 group with a C···π distance of 2.50 Å and a C−H−π angle of 150°.

Figure 4 shows the solid-state structure of Pd complex **21** possessing a chiral ferrocenyl ligand **18**.[22c] This complex was thus far the most successful catalyst bearing a P∪S ligand in the above-mentioned test reaction for allylic substitution. The structure is remarkable for the following reason: The 1,3-diphenylallylic system is rotated in an extreme fashion. The allylic carbon terminus *trans* to phosphorus atom is found to be 0.85 Å below the coordination plane P−Pd−S. This is the largest distortion known for a (π-allyl)Pd complex. The other two allylic carbon atoms now lie almost in the P−Pd−S coordination plane, thus preparing for a transition state forming a Pd^0 olefin structure. Consequently, to generate an (olefin)Pd^0 complex by nucleophilic attack, the reorientation of the ligand is negligible, thus favouring nucleophilic attack *trans* to the phosphorus atom (least-motion principle). Compared to complex **20** the thioether unit is in the sterically unfavourable *endo* position, whereas for **20** the SMe group is in the sterically favourable *exo* position. The bite angle for **21** is 96.5°. For **20** we found 91.2°, contradicting the theory that larger bite angles lead to higher inductions for allylic substitutions with comparable ligands, since the chirality information of the ligand should be closer to the allylic system.[19a]

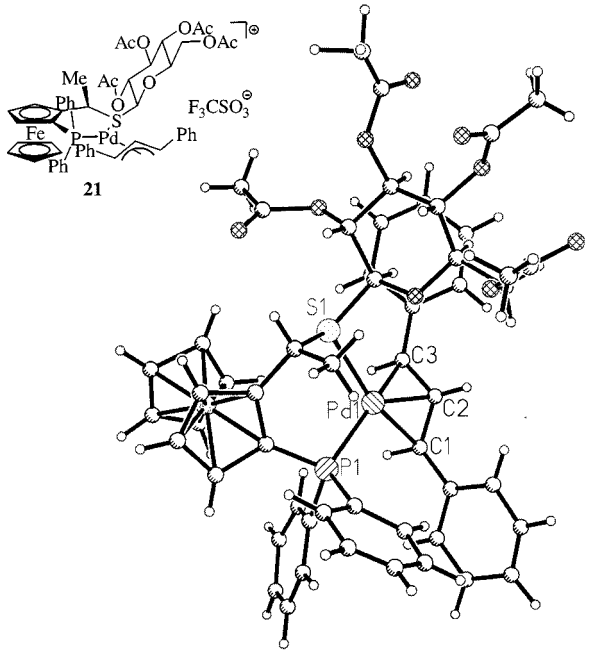


Figure 4. Crystal structure of the related Pd complex **21**

Figure 5 shows a schematic superposition of the structures of complexes **20** (smooth line) and **21** (dotted line). With the allylic carbon terminus *trans* to the sulfur atom being fixed, the ferrocenyl moieties are rotated nearly perpendicular to each other, thus resulting in a different ar-

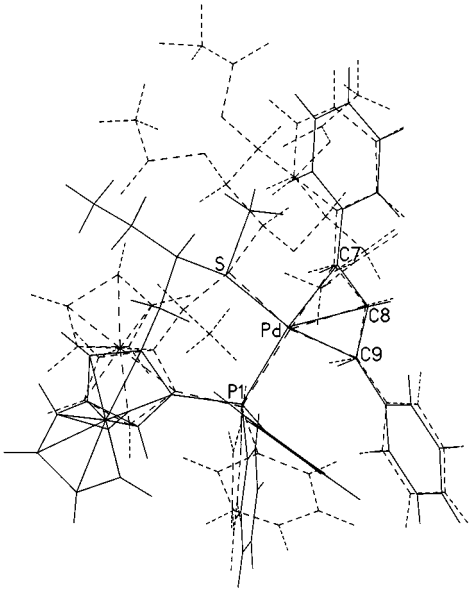


Figure 5. Schematic superposition of **20** (smooth line) and **21** (dotted line)

rangement of the Ph groups of the PPh_2 group and thus creating a totally different chiral environment. Now we should be able to explain the efficiency of our catalyst in the following way: a) The ligand allows for the regioselective control of the nucleophilic attack by electronic differentiation of the allylic carbon termini. b) The *exo-syn-syn* configuration is strongly favoured by intramolecular C−H···π interactions.

Conclusion

In summary, we have opened up an efficient and flexible approach to planar chiral ferrocenyl ligands bearing a stereogenic centre in the β-position of the side chain. We found that these ligands may be superior to α-functionalized ferrocenes in certain catalytic reactions, as demonstrated for the Pd-catalyzed allylic substitution.

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 determined by NMR spectroscopy. The enantiomeric excesses were determined by HPLC employing chiral stationary phases or by NMR spectroscopy using Pirkle alcohol as chiral co-solvent.

General Procedure for the Preparation of Ferrocenyl Ketones 1 (GP1): To a suspension of $AlCl_3$ (1.06 equiv.) in dichloromethane (0.5 mL/mmol) was added the acid chloride (1.01 equiv.). The mixture was stirred until the Al salt was dissolved nearly completely. The resulting solution was added to a solution of ferrocene (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 combined organic phases were washed with saturated aqueous $NaHCO_3$ and twice with brine. After drying with $MgSO_4$ and concentrating in vacuo, the crude product was dissolved in a minimum of dichloromethane and purified by filtration through silica gel.

1-Ferrocenyl-1-propanone (1a): According to GP1, a solution of ferrocene (30.00 g, 161.3 mmol) in CH_2Cl_2 (120 mL) was treated with a solution of $AlCl_3$ (22.80 g, 1.06 equiv.) and propionyl chloride (15.07 g, 1.01 equiv.) in CH_2Cl_2 (90 mL). After stirring for 15 h at room temperature, the reaction mixture was worked up and the product purified by filtration through silica gel (hexane/diethyl ether = 2:1). − Yield: 32.17 g (82%, dark red crystals). − R_f = 0.44 (hexane/diethyl ether = 2:1). − M.p.: 40 °C. − IR (Et_2O): $\tilde{\nu}$ = 3096 cm^{-1}, 2975, 2936, 2903, 2876, 1670, 1454, 1414, 1398, 1378, 1353, 1248, 1106, 1099, 1051, 1026, 1002, 962, 880, 823, 531, 495, 483, 460. − ^1H NMR (300 MHz, C_6D_6): δ = 1.17 (t, ^3J = 7.4 Hz, 3 H, CH_3), 2.43 (q, ^3J = 7.4 Hz, 2 H, CH_2), 3.90 (s, 5 H, C_5H_5), 4.09 (t, $^{3/4}J$ = 2.0 Hz, 2 H, *m*-C_5H_4R), 4.65 (t, $^{3/4}J$ = 2.0 Hz, 2 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 8.6 (CH_3), 32.7 (CH_2), 69.5, 71.9 (C_5H_4R), 69.8 (C_5H_5), 79.9 (*i*-C_5H_4R), 202.6 (C=O). − EI-MS; *m*/*z*: 242.0 (100) [M^+], 212.9 (59) [$M^+ - CH_2CH_3$], 184.9 (20) [Fc^+], 129.0 (80) [$C_{10}H_9^+$], 120.8 (41) [$CpFe^+$], 55.9 (34) [Fe^+]. − $C_{13}H_{14}FeO$ (242.1): C 64.49, H 5.83; found C 64.40, H 6.00.

1-Ferrocenyl-1-butanone (1b): According to GP1, a solution of ferrocene (10.00 g, 53.8 mmol) in CH_2Cl_2 (40 mL) was treated with a solution of $AlCl_3$ (7.60 g, 1.06 equiv.) and butyryl chloride (5.78 g, 1.01 equiv.) in CH_2Cl_2 (30 mL). After stirring for 48 h at room temperature, the reaction mixture was worked up and the product purified by filtration through silica gel (hexane/diethyl ether = 2:1). − Yield: 11.30 g (82%, dark red crystals). − R_f = 0.44 (petroleum ether ether/diethyl ether = 2:1). − M.p.: 36 °C. − IR (KBr): $\tilde{\nu}$ = 3120 cm^{-1}, 3085, 2954, 2930, 2893, 2870, 2254, 1786, 1668, 1456, 1408, 1378, 1348, 1301, 1237, 1122, 1104, 1061, 1027, 1000, 900, 883, 836, 817, 700, 745, 646, 595, 534, 500, 481, 464. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.74 (sext, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 2.68 (t, ^3J = 7.2 Hz, 2 H, $COCH_2$), 4.20 (s, 5 H, C_5H_5), 4.49 (t, $^{3/4}J$ = 2.0 Hz, 2 H, *m*-C_5H_4R), 4.78 (t, $^{3/4}J$ = 2.0 Hz, 2 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (CH_3), 18.0 (CH_2CH_3), 41.7 ($COCH_2$), 69.3, 72.1 (C_5H_4R), 69.7 (C_5H_5), 79.3 (*i*-C_5H_4R), 204.5 (C=O). − EI-MS; *m*/*z*: 256.1 (100) [M^+], 228.0 (11) [$M^+ - CO$], 213.0 (57) [$FcCO^+$], 185.0 (46) [Fc^+], 129.0 (30) [$Fc^+ - Fe$], 120.9 (21) [$CpFe^+$], 56.0 (21) [Fe^+]. − $C_{14}H_{16}FeO$ (256.1): calcd. C 65.65, H 6.30; found C 65.99, H 6.28.

1-Ferrocenyl-3-methyl-1-butanone (1c): According to GP1, a solution of ferrocene (10.00 g, 53.8 mmol) in CH_2Cl_2 (40 mL) was treated with a solution of $AlCl_3$ (7.60 g, 1.06 equiv.) and isovaleryl chloride (6.55 g, 1.01 equiv.) in CH_2Cl_2 (30 mL). After stirring for 15 h at room temperature, the reaction mixture was worked up and the product purified by filtration through silica gel (hexane/diethyl ether = 2:1). − Yield: 10.88 g (75%, red crystals). − R_f = 0.31 (hexane/ethyl acetate = 10:1). − M.p.: 60 °C. − IR (KBr): $\tilde{\nu}$ = 3114 cm^{-1}, 3088, 3081, 2961, 2953, 2937, 2904, 2882, 2864, 2706, 2463, 2406, 2253, 2055, 1702, 1661, 1468, 1451, 1412, 1396, 1375, 1360, 1341, 1294, 1238, 1171, 1135, 1109, 1092, 1065, 1030, 1000, 951, 919, 894, 859, 845, 823, 749, 648, 597, 534, 493, 481, 461. − ^1H NMR (300 MHz, C_6D_6): δ = 0.98 (dm, ^3J = 6.4 Hz, 6 H, CH_3), 2.42 [m, 3 H, $O=CCH_2$, $CH(CH_3)_2$], 3.93 (s, 5 H, C_5H_5), 4.08 (t, $^{3/4}J$ = 1.8 Hz, 2 H, *m*-C_5H_4R), 4.65 (t, $^{3/4}J$ = 2.0 Hz, 2 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 23.0 (CH_3), 25.0 [$CH(CH_3)_2$], 48.8 ($O=CCH_2$), 69.6, 71.9 (C_5H_4R), 69.8 (C_5H_5), 80.6 (*i*-C_5H_4R), 201.9 (C=O). − EI-MS; *m*/*z*: 270.1 (100) [M^+], 228.1 (36) [$M^+ - CH_2{=}CH\text{-}CH_3$], 213.1 (39) [$FcCO^+$], 186.1 (29) [$Cp_2Fe^+$], 185.0 (61) [$Fc^+$], 129.1 (51) [$C_{10}H_9^+$], 120.9 (50) [$CpFe^+$], 56.0 (13) [$Fe^+$]. − $C_{15}H_{18}FeO$ (270.2): calcd. C 66.69, H 6.72; found C 66.61, H 6.74.

1-Ferrocenyl-2-phenyl-1-ethanone (1d): According to GP1, a solution of ferrocene (7.50 g, 40.3 mmol) in CH_2Cl_2 (30 mL) was treated with a solution of $AlCl_3$ (5.64 g, 1.05 equiv.) and phenyl acetyl chloride (6.29 g, 1.01 equiv.) in CH_2Cl_2 (30 mL). After stirring for 15 h at room temperature, the reaction mixture was worked up and the product purified by filtration through silica gel (hexane/diethyl ether = 2:1). − Yield: 7.36 g (60%, red crystals). − R_f = 0.29 (hexane/diethyl ether = 4:1). − M.p.: 130 °C. − IR (KBr): $\tilde{\nu}$ = 3107 cm^{-1}, 3082, 3031, 2882, 1661, 1496, 1445, 1410, 1377, 1350, 1333, 1317, 1246, 1215, 1202, 1168, 1105, 1068, 1030, 1003, 989, 926, 888, 827, 777, 730, 702, 643, 575, 537, 498, 482, 455. − ^1H NMR (300 MHz, C_6D_6): δ = 3.72 (broad s, 2 H, CH_2), 3.81 (s,

5 H, C_5H_5), 4.05 (t, $^{3/4}J$ = 2.0 Hz, 2 H, *m*-C_5H_4R), 4.66 (t, $^{3/4}J$ = 2.0 Hz, 2 H, *o*-C_5H_4R), 7.06 (tt, ^3J = 7.4 Hz, ^4J = 1.4 Hz, 1 H, *p*-C_6H_5), 7.16 (m, 2 H, *m*-C_6H_5), 7.31 (dm, ^3J = 8.4 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 47.0 (CH_2), 69.97 (C_5H_5), 70.01, 72.2 (C_5H_4R), 79.7 (*i*-C_5H_4R), 126.9 (*p*-C_6H_5), 128.7, 129.8 (*o*/*m*-C_6H_5), 136.1 (*i*-C_6H_5), 200.0 (C=O). − EI-MS; *m*/*z*: 304.1 (100) [M^+], 213.1 (75) [$M^+ - C_7H_7$], 186.2 (10) [Cp_2Fe^+], 185.0 (73) [Fc^+], 129.2 (79) [$C_{10}H_9^+$], 120.9 (30) [$CpFe^+$], 91.1 (30) [$C_7H_7^+$], 65.1 (12) [$C_5H_5^+$], 56.0 (14) [Fe^+]. − $C_{18}H_{16}FeO$ (304.2): C 71.08, H 5.30; found C 71.21, H 5.32.

1,1′-Dipropionylferrocene 9: According to GP1, a solution of ferrocene (20.00 g, 107.5 mmol) in CH_2Cl_2 (100 mL) was treated with a solution of $AlCl_3$ (31.50 g, 2.20 equiv.) and propionyl chloride (21.88 g, 2.20 equiv.) in CH_2Cl_2 (150 mL). After stirring for 24 h at room temperature, the reaction mixture was worked up and the product purified by filtration through silica gel (hexane/diethyl ether = 2:1). − Yield: 28.63 g (89%, reddish-black crystals). − R_f = 0.20 (hexane/diethyl ether = 2:1). − M.p.: 52 °C. − IR (KBr): $\tilde{\nu}$ = 3096 cm^{-1}, 3079, 2968, 2933, 2909, 2874, 2377, 2224, 1758, 1673, 1457, 1412, 1375, 1338, 1242, 1100, 1048, 1023, 962, 883, 862, 828, 807, 703, 644, 591, 534, 506, 474. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, ^3J = 7.4 Hz, 6 H, CH_3), 2.74 (q, ^3J = 7.4 Hz, 4 H, CH_2), 4.53 (t, $^{3/4}J$ = 1.9 Hz, 4 H, *m*-C_5H_4R), 4.84 (t, $^{3/4}J$ = 1.9 Hz, 4 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 7.8 (CH_3), 32.7 (CH_2), 70.2, 72.9 (C_5H_4R), 79.9 (*i*-C_5H_4R), 203.8 (C=O). − EI-MS; *m*/*z*: 297.9 (100) [M^+], 268.8 (37) [$M^+ - CH_2CH_3$], 212.7 (25) [268.8 − Fe], 184.9 (11) [Fc^+], 120.6 (13) [$CpFe^+$]. − $C_{16}H_{18}FeO_2$ (298.2): calcd. C 64.45, H 6.09; found C 64.45, H 6.22.

General Procedure for the Preparation of Hydrazones 2 (GP2): A Schlenk flask with an attached reflux condenser and a silicon bubbler was charged under argon with $AlMe_3$ (2.0 equiv., 2 M in toluene, 1−2 mL/mmol). Then SAMP (2.0 equiv.) was added slowly. After the evolution of methane subsided, the mixture was heated at reflux for 7 h. Ferrocenyl ketone **1** (1.0 equiv.), dissolved in toluene (1−2 mL/mmol), was added dropwise to the red-brown solution. The mixture was heated at reflux until completion (TLC control), cooled down to 0 °C, poured onto crushed ice and washed with 5% aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, and concentrated in vacuo. The crude product was purified by filtration through silica gel.

SAMP-hydrazone 2a: According to GP2, a solution of ketone **1a** (4.00 g, 16.5 mmol) in toluene (40 mL) was added to a solution of SAMP/$AlMe_3$ (2.0 equiv.) in toluene (40 mL). After heating at reflux for 15 h, the reaction mixture was worked up. Purification by filtration through silica gel provided a mixture of (*E*)- and (*Z*)-**2a** (hexane/diethyl ether = 4:1; 2% NEt_3). − Yield: 5.57 g (95%, orange-brown powder). − (*E*)/(*Z*) = 2.8:1. − R_f = 0.23 (hexane/diethyl ether = 10:1; 2% NEt_3). − $[\alpha]_D^{25}$ = +266.3 ($CHCl_3$, *c* = 1.66). − M.p.: 55 °C. − IR (KBr): $\tilde{\nu}$ = 3088 cm^{-1}, 2966, 2932, 2869, 2824, 2804, 2726, 2371, 2232, 1674, 1637, 1601, 1458, 1411, 1381, 1339, 1301, 1277, 1245, 1199, 1187, 1121, 1106, 1042, 1001, 975, 915, 878, 819, 707, 610, 502. − ^{1}H NMR {(*E*) isomer [(*Z*) isomer], 300 MHz, C_6D_6}: δ = 1.17 (t, ^3J = 7.7 Hz, 3 H, CH_3), [1.35 (t, ^3J = 7.4 Hz, 3 H, CH_3)], 1.55−1.83 (m, 3 H, β-ring-CH_2), 2.04 (m, 1 H, β-ring-CH_2), 2.53 (m, 2 H, CH_2CH_3), 2.69 (m, 1 H, NCH_2), 3.09 (m, 1 H, NCH_2), 3.20 (s, 3 H, OCH_3), [3.24 (s, 3 H, OCH_3)], [3.28 (m, 1 H, NCH_2)], 3.35 (dd, ^2J = 8.5 Hz, ^3J = 7.4 Hz, 1 H, OCH_2), [3.43 (dd, ^2J = 8.8 Hz, ^3J = 7.1 Hz, 1 H, OCH_2)], 3.54 (qd, ^3J = 7.7 Hz, ^3J = 4.1 Hz, 1 H, NCH), 3.63 (dd, ^2J = 8.7 Hz, ^3J = 4.1 Hz, 1 H, OCH_2), [3.69 (dd, ^2J = 8.7 Hz, ^3J = 3.8 Hz, 1 H, OCH_2)], [4.01 (s, 5 H, C_5H_5)], 4.05 (s, 5 H, C_5H_5), 4.12 (m, 2 H, *m*-C_5H_4R), [4.42 (dt, ^3J = 2.8 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R)], 4.68 (dt, ^3J = 1.9 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 4.75 (dt, ^3J = 1.9 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), [5.27 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R)]. − ^{13}C NMR [(*E*) isomer, 75 MHz, C_6D_6]: δ = 13.0 (CH_3), 22.6 (NCH_2CH_2), 23.6 (CH_2CH_3), 27.6 ($NCHCH_2$), 55.8 (NCH_2), 58.9 (OCH_3), 66.9 (NCH), 67.6, 68.0, 69.8 (C_5H_4R), 69.5 (C_5H_5), 76.5 (OCH_2), 83.3 (*i*-C_5H_4R), 167.6 (C=N). − ^{13}C NMR [(*Z*) isomer, 75 MHz, C_6D_6]: δ = 13.4 (CH_3), 22.6 (NCH_2CH_2), 27.4 ($NCHCH_2$), 30.6 (CH_2CH_3), 53.9 (NCH_2), 58.9 (OCH_3), 67.2, 69.2, 69.5, 70.7, 71.9 (C_5H_4R, NCH), 69.8 (C_5H_5), 76.5 (OCH_2), 83.3 (*i*-C_5H_4R), 161.5 (C=N). − EI-MS; *m*/*z*: 354.2 (83) [M^+], 309.1 (47) [$M^+ - CH_2OCH_3$], 240.1 (100) [$M^+ - C_6H_{12}NO$], 211.0 (40) [$FcCN^+$], 186.2 (14) [Cp_2Fe^+], 185.0 (97) [Fc^+], 154.4 (16) [211.0 − Fe], 128.9 (35) [$C_{10}H_9^+$], 121.0 (62) [$CpFe^+$], 45.3 (17) [CH_3OCH_2]. − $C_{19}H_{26}FeN_2O$ (354.3): calcd. C 64.42, H 7.40, N 7.91; found C 64.30, H 7.52, N 7.42.

SAMP-hydrazone 2b: According to GP2, a solution of ketone **1b** (16.80 g, 65.7 mmol) in toluene (50 mL) was added to a solution of SAMP/$AlMe_3$ (2.0 equiv.) in toluene (50 mL). After heating at reflux for 15 h, the reaction mixture was worked up. Purification by filtration through silica gel provided a mixture of (*E*)- and (*Z*)-**2b** (hexane/diethyl ether = 4:1; 2% NEt_3). − Yield: 24.1 g (100%, orange-brown powder). − (*E*)/(*Z*) = 3.1:1. − R_f = 0.50 (petroleum ether ether/diethyl ether = 6:1; 2% NEt_3). − $[\alpha]_D^{25}$ = +508.8 [(*E*) isomer, $CHCl_3$, *c* = 0.91]; $[\alpha]_D^{25}$ = −375.0 [(*Z*) isomer, $CHCl_3$, *c* = 2.21). − M.p.: 66 °C. − IR (KBr): $\tilde{\nu}$ = 3083 cm^{-1}, 2962, 2932, 2913, 2866, 2821, 2798, 2736, 2252, 1604, 1465, 1455, 1410, 1378, 1343, 1303, 1291, 1276, 1242, 1201, 1183, 1123, 1107, 1058, 1045, 1026, 1002, 974, 914, 854, 817, 758, 699, 670, 618, 592, 500, 459. − ^{1}H NMR [(*E*) isomer, 300 MHz, C_6D_6]: δ = 0.96 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.60 (m, 1 H, CH_2CH_3), 1.64 (m, 1 H, NCH_2CH_2), 1.73 (m, 1 H, CH_2CH_3), 1.75 (m, 1 H, NCH_2CH_2), 1.78 (m, 1 H, $NCHCH_2$), 2.05 (m, 1 H, $NCHCH_2$), 2.56 (m, 1 H, NCH_2), 2.58 (m, 1 H, $N=CCH_2$), 2.65 (m, 1 H, $N=CCH_2$), 3.10 (m, 1 H, NCH_2), 3.20 (s, 3 H, OCH_3), 3.36 (dd, ^2J = 8.5 Hz, ^3J = 7.4 Hz, 1 H, OCH_2), 3.55 (m, 1 H, NCH), 3.64 (dd, ^2J = 8.5 Hz, ^3J = 3.8 Hz, 1 H, OCH_2), 4.05 (s, 5 H, C_5H_5), 4.12 (t, ^3J = 1.8 Hz, 2 H, *m*-C_5H_4R), 4.66 (m, 1 H, *o*-C_5H_4R), 4.80 (m, 1 H, *o*-C_5H_4R). − ^{1}H NMR [(*Z*) isomer, 300 MHz, C_6D_6]: δ = 1.06 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.56 (m, 1 H, NCH_2CH_2), 1.65 (m, 1 H, NCH_2CH_2), 1.76 (m, 1 H, $NCHCH_2$), 1.85 (sext, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 2.00 (m, 1 H, $NCHCH_2$), 2.33 (q, ^3J = 7.4 Hz, 1 H, NCH_2), 2.57 (m, 1 H, $N=CCH_2$), 2.64 (m, 1 H, $N=CCH_2$), 3.18 (m, 1 H, NCH_2), 3.24 (s, 3 H, OCH_3), 3.42 (m, 1 H, OCH_2), 3.53 (m, 1 H, NCH), 3.68 (dd, ^2J = 8.7 Hz, ^3J = 3.7 Hz, 1 H, OCH_2), 4.03 (s, 5 H, C_5H_5), 4.09 (m, 1 H, *m*-C_5H_4R), 4.15 (m, 1 H, *m*-C_5H_4R), 4.45 (m, 1 H, *o*-C_5H_4R), 5.29 (m, 1 H, *o*-C_5H_4R). − ^{13}C NMR [(*E*) isomer, 75 MHz, C_6D_6]: δ = 15.0 (CH_3), 21.9 (CH_2CH_3), 22.6 (NCH_2CH_2), 27.7 ($NCHCH_2$), 32.8 ($N=CCH_2$), 55.7 (NCH_2), 58.9 (OCH_3), 67.0, 67.7, 68.2, 69.77, 69.83 (C_5H_4R, NCH), 69.6 (C_5H_5), 76.6 (OCH_2), 83.8 (*i*-C_5H_4R), 166.4 (C=N). − ^{13}C NMR [(*Z*) isomer, 75 MHz, C_6D_6): δ = 14.4 (CH_3), 22.2 (NCH_2CH_2), 22.6 (CH_2CH_3), 27.3 ($NCHCH_2$), 39.4 ($N=CCH_2$), 53.9 (NCH_2), 58.9 (OCH_3), 67.1, 69.2, 69.8, 70.7, 71.9 (C_5H_4R, NCH), 69.7 (C_5H_5), 76.5 (OCH_2), 78.6 (*i*-C_5H_4R), 160.5 (C=N). − EI-MS; *m*/*z*: 368.0 (61) [M^+], 322.9 (36) [$M^+ - CH_2OCH_3$], 253.9 (100) [$M^+ - C_6H_{12}NO$], 210.9 (31) [$FcCN^+$], 184.8 (79) [Fc^+], 161.3 (12), 129.0 (37) [Fc^+ − Fe], 120.8 (44) [$CpFe^+$], 55.9 (13) [Fe^+]. − $C_{20}H_{28}FeN_2O$ (368.3): calcd. C 65.22, H 7.66, N 7.61; found C 65.21, H 7.39, N 7.50.

SAMP-hydrazone 2c: According to GP2, a solution of ketone **1c** (16.80 g, 65.7 mmol) in toluene (50 mL) was added to a solution of SAMP/$AlMe_3$ (2.0 equiv.) in toluene (50 mL). After heating at re-

flux for 15 h, the reaction mixture was worked up. Purification by filtration through silica gel provided a mixture of (*E*)- and (*Z*)-**2c** (hexane/diethyl ether = 4:1; 2% NEt_3). − Yield: 5.97 g (84%, red oil). − R_f = 0.39 (hexane/diethyl ether = 4:1). − (*E*)/(*Z*) = 2.2:1. − $[\alpha]_D^{25}$ = −33.5 ($CHCl_3$, *c* = 2.38). − IR ($CHCl_3$): $\tilde{\nu}$ = 3094 cm^{-1}, 2955, 2925, 2869, 2826, 2728, 1670, 1595, 1462, 1383, 1367, 1340, 1298, 1197, 1166, 1107, 1051, 1028, 1001, 971, 917, 894, 819, 756, 497. − ^1H NMR {(*E*) isomer [(*Z*) isomer], 300 MHz, C_6D_6}: δ = 0.97 (d, ^3J = 6.7 Hz, 3 H, CH_3), 0.98 (d, ^3J = 6.7 Hz, 3 H, CH_3), [1.05 (d, ^3J = 6.7 Hz, 3 H, CH_3)], [1.10 (d, ^3J = 6.7 Hz, 3 H, CH_3)], 1.54 − 1.81 (m, 3 H, β-ring-CH_2), 2.06 (m, 1 H, β-ring-CH_2), 2.28 (non, ^3J = 6.7 Hz, 1 H, C*H*(CH_3)$_2$), 2.41 (dd, ^2J = 12.8 Hz, ^3J = 7.1 Hz, 1 H, N=CC*H*$_2$), 2.68 (dd, ^2J = 12.8 Hz, ^3J = 7.7 Hz, 1 H, N=CC*H*$_2$), 3.18 (s, 3 H, OCH_3), 3.23 (m, 1 H, NCH_2), [3.24 (s, 3 H, OCH_3)], 3.32 (dd, ^2J = 8.7 Hz, ^3J = 7.7 Hz, 1 H, OCH_2), [3.44 (dd, ^2J = 8.7 Hz, ^3J = 7.4 Hz, 1 H, OCH_2)], 3.52 (m, 1 H, NCH), 3.62 (dd, ^2J = 8.7 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), [3.69 (dd, ^2J = 9.1 Hz, ^3J = 3.7 Hz, 1 H, OCH_2)], [4.03 (s, 5 H, C_5H_5)], 4.06 (s, 5 H, C_5H_5), 4.13 (m, 2 H, *m*-C_5H_4R), [4.46 (dt, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R),], 4.55 (dt, ^3J = 2.4 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R), 4.94 (dt, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R), [5.30 (dt, ^3J = 2.4, ^4J = 1.4, 1 H, *o*-C_5H_4R)]. − ^{13}C NMR [(*E*) isomer, 75 MHz, C_6D_6]: δ = 22.5 (NCH_2CH_2), 22.9, 23.3 (CH_3), 27.3 [*C*H(CH_3)$_2$], 27.7 (NCH*C*H$_2$), 39.5 (N=C*C*H$_2$), 55.2 (NCH_2), 58.8 (OCH_3), 67.0, 67.8, 68.4, 69.6, 69.9 (C_5H_4R, NCH), 69.6 (C_5H_5), 76.5 (OCH_2), 84.4 (*i*-C_5H_4R), 165.6 (C=N). − ^{13}C NMR [(*Z*) isomer, 75 MHz, C_6D_6]: δ = 22.6 (NCH_2CH_2), 22.8, 23.4 (CH_3), 27.7 (NCH*C*H$_2$), 27.8 [*C*H(CH_3)$_2$], 46.4 (N=C*C*H$_2$), 54.0 (NCH_2), 59.0 (OCH_3), 67.2, 69.3, 69.9, 70.8, 72.1 (C_5H_4R, NCH), 69.8 (C_5H_5), 76.6 (OCH_2), 79.0 (*i*-C_5H_4R), 159.8 (C=N). − EI-MS; *m*/*z*: 382.2 (48) [M^+], 337.1 (28) [$M^+ - H_2COCH_3$], 269.1 (21) [$M^+ - C_6H_{11}NO$], 268.1 (92) [$M^+ - C_6H_{12}NO$], 212.0 (14) [FcCNH$^+$], 211.0 (31) [FcCN$^+$], 202.0 (13) [268.1 − C_5H_6], 186.0 (24) [Cp_2Fe^+], 185.0 (100) [Fc$^+$], 168.7 (15), 149.0 (18), 129.1 (64) [$C_{10}H_9^+$], 128.1 (13), 121.0 (73) [CpFe$^+$], 91.1 (14), 71.2 (12), 70.2 (15), 57.2 (16) [$CH_2CH(CH_3)_2^+$], 56.1 (20) [Fe$^+$], 55.2 (14), 45.3 (20) [$H_3COCH_2^+$]. − $C_{21}H_{30}FeN_2O$ (382.3): calcd. C 65.97, H 7.91, N 7.33; found C 65.96, H 8.16, N 7.03.

SAMP-hydrazone 2d: According to GP2, a solution of ketone **1d** (3.00 g, 9.86 mmol) in toluene (50 mL) was added to a solution of SAMP/$AlMe_3$ (2.0 equiv.) in toluene (30 mL). After heating at reflux for 15 h, the reaction mixture was worked up. Purification by filtration through silica gel provided a mixture of (*E*)- and (*Z*)-**2d** (hexane/diethyl ether = 4:1; 2% NEt_3). − Yield: 3.15 g (77%, orange-brown powder). − R_f = 0.29 (hexane/diethyl ether = 4:1; 2% NEt_3). − (*E*)/(*Z*) = 4.3:1. − $[\alpha]_D^{25}$ = +415.7 ($CHCl_3$, *c* = 1.38). − M.p.: 92 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3085 cm^{-1}, 3060, 3025, 2970, 2922, 2872, 2826, 2730, 1766, 1664, 1595, 1582, 1494, 1453, 1382, 1342, 1298, 1196, 1186, 1106, 1076, 1054, 1031, 1002, 971, 913, 899, 876, 820, 754, 713, 666, 547, 489. − ^1H NMR {(*E*) isomer, [(*Z*) isomer], (300 MHz, C_6D_6): δ = 1.46−1.82 (m, 3 H, β-ring-CH_2), 1.99 (m, 1 H, β-ring-CH_2), [2.42 (m, 1 H, NCH_2)], 2.55 (q, $^{2/3}J$ = 8.8 Hz, 1 H, NCH_2), 2.96 (ddd, ^2J = 10.9 Hz, ^3J = 7.4 Hz, ^3J = 3.7 Hz, 1 H, NCH_2), 3.22 (s, 3 H, OCH_3), [3.25 (s, 3 H, OCH_3)], 3.36 (dd, ^2J = 8.4 Hz, ^3J = 6.7 Hz, 1 H, OCH_2), [3.48 (dd, ^2J = 8.7 Hz, ^3J = 7.1 Hz, 1 H, OCH_2)], 3.58 (m, 1 H, NCH), 3.63 (dd, ^2J = 8.7 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), [3.73 (dd, ^2J = 8.7 Hz, ^3J = 4.0 Hz, 1 H, OCH_2)], [3.96 (m, 2 H, *m*-C_5H_4R)], [3.97 (s, 5 H, C_5H_5)], 4.02 (s, 5 H, C_5H_5), 4.04 (m, 2 H, *m*-C_5H_4R), 4.09 (d, ^2J = 15.0 Hz, 1 H, N=CCH_2), 4.17 (d, ^2J = 14.8, 1 H, N=CCH_2), [4.50 (dt, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R),], 4.63 (dt, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R), 4.80 (dt, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), [5.27 (dt, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R)], 7.03 (tt, ^3J = 7.4 Hz, ^4J = 1.5 Hz, 1 H, *p*-C_6H_5), 7.14 (m, 2 H, *m*-C_6H_5), 7.27 (dm, ^3J = 7.4 Hz, 2 H, *o*-C_6H_5), [7.45 (broad d, ^3J = 7.4 Hz, 2 H, *o*-C_6H_5)]. − ^{13}C NMR [(*E*) isomer, 75 MHz, C_6D_6]: δ = 22.5 (NCH_2CH_2), 27.3 (NCH*C*H$_2$), 36.4 (N=C*C*H$_2$), 55.6 (NCH_2), 58.9 (OCH_3), 66.9, 68.3, 68.6, 69.8, 69.9 (NCH, C_5H_4R), 69.6 (C_5H_5), 76.3 (OCH_2), 83.8 (*i*-C_5H_4R), 126.2 (*p*-C_6H_5), 128.7, 128.8 (*o*/*m*-C_6H_5), 139.2 (*i*-C_6H_5), 164.2 (C=N). − ^{13}C NMR [(*Z*) isomer, 75 MHz, C_6D_6]: δ = 22.7 (NCH_2CH_2), 27.4 (NCH*C*H$_2$), 44.6 (N=C*C*H$_2$), 54.1 (NCH_2), 59.0 (OCH_3), 67.3 (NCH), 69.4, 69.7, 71.3, 72.0 (C_5H_4R), 69.9 (C_5H_5), 76.6 (OCH_2), 78.6 (*i*-C_5H_4R), 126.5 (*p*-C_6H_5), 128.7, 128.8 (*o*/*m*-C_6H_5). − EI-MS; *m*/*z*: 416.2 (66) [M^+], 371.1 (26) [$M^+ - CH_2OCH_3$], 302.0 (51) [$M^+ - C_6H_{12}NO$], 211.1 (100) [FcCN$^+$], 185.0 (26) [Fc$^+$], 129.2 (10) [$C_{10}H_9^+$], 121.0 (50) [CpFe$^+$], 91.1 (39) [$C_7H_7^+$]. − $C_{24}H_{28}FeN_2O$ (416.3): calcd. C 69.23, H 6.78, N 6.73; found C 68.89, H 7.05, N 6.73.

SAMP-bis(hydrazone) 10: According to GP2, a solution of diketone **9** (10.00 g, 33.5 mmol) in toluene (30 mL) was added to a solution of SAMP/$AlMe_3$ (4.0 equiv.) in toluene (100 mL). After heating at reflux for 15 h, the reaction mixture was worked up. Purification by filtration through silica gel provided a mixture of (*E*,*E*)-, (*E*,*Z*)-, and (*Z*,*Z*)-**10** (hexane/diethyl ether = 4:1). − Yield: 16.00 g (91%, red oil). − R_f = 0.23 (hexane/diethyl ether = 4:1). − (*EE*)/(*EZ*)/(*ZZ*) = 4.5:1.5:1. − IR ($CHCl_3$): $\tilde{\nu}$= 3093 cm^{-1}, 2971, 2935, 2874, 2826, 2732, 1676, 1642, 1600, 1550, 1451, 1379, 1345, 1316, 1295, 1278, 1247, 1198, 1109, 1046, 1027, 970, 914, 881, 829, 755, 665, 507. − ^1H NMR [(*E*,*E*) isomer, 400 MHz, C_6D_6]: δ = 1.18 (t, ^3J = 7.7 Hz, 6 H, CH_3), 1.60−2.12 (m, 12 H, β-ring-CH_2, *C*H_2CH$_3$), 2.59 (m, 1 H, NCH_2), 3.13 (m, 1 H, NCH_2), 3.21 (s, 6 H, OCH_3), 3.34 (dd, ^2J = 8.8 Hz, ^3J = 7.4 Hz, 2 H, OCH_2), 3.55 (qd, ^3J = 7.4 Hz, ^3J = 4.1 Hz, 2 H, NCH), 3.63 (dd, ^2J = 8.8 Hz, ^3J = 4.1 Hz, 2 H, OCH_2), 4.18 (td, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 2 H, C_5H_4R), 4.20 (td, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 2 H, C_5H_4R), 4.68 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 2 H, C_5H_4R), 4.70 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 2 H, C_5H_4R). − ^{13}C NMR [(*E*,*E*) isomer, 100 MHz, C_6D_6]: δ = 12.9 (CH_3), 22.7, 23.7 (*C*H_2), 27.7 (NCH*C*H$_2$), 55.9 (NCH_2), 58.9 (OCH_3), 67.0, 68.7, 69.1, 71.2, 71.4 (C_5H_4R, NCH), 76.6 (OCH_2), 84.3 (*i*-C_5H_4R), 166.7 (C=N). − EI-MS; *m*/*z*: 522.3 (100) [M^+], 408.2 (12) [$M^+ - C_6H_{12}NO$], 289.1 (96) [$M^+ - C_5H_4R$], 280.1 (49) [408.2 − $C_6H_{12}N_2O$], 244.1 (44) [289.1 − OCH_3], 234.1 (20) [$C_5H_4R^+$], 216.1 (40) [280.1 − C_5H_4], 205.9 (17), 188.9 (27), 181.6 (44), 147.0 (51). − $C_{28}H_{42}FeN_4O_2$ (522.5): calcd. C 64.36, H 8.10, N 10.72; found C 64.36, H 8.23, N 10.33.

General Procedure for the Preparation of Hydrazones 3 (GP3): A heated Schlenk flask was charged under argon with 1.2 equiv. diisopropylamine in dry diethyl ether (3 mL $mmol^{-1}$) at 0 °C. A solution of 1.2 equiv. *n*BuLi (1.5 M in hexane) was added dropwise. After 20 min, a $LiClO_4$ solution (4 M, 3 equiv.) in diethyl ether was injected. After stirring for a further 10 min, a solution of the hydrazone **2** in diethyl ether (2.5 mL $mmol^{-1}$) was added and the cooling bath was removed. The orange-brown solution was stirred for 6 h at room temperature, and then cooled to −100 °C.

Method A: Introduction of the Alkyl or Sulfur Substituent E[1]: The alkyl halide or the disulfide (1.4 equiv.) was added dropwise to the azaenolate solution. The cooling bath was filled with dry ice. After warming to room temperature overnight, the solution was cooled to 0 °C and quenched with saturated aqueous NH_4Cl, washed twice with brine and dried with $MgSO_4$. The crude product was filtered through silica gel and dried under high vacuum.

Method B: **Introduction of the Phosphorus Substituent E[1]:** Ph_2PCl (1.3 equiv.) was stirred for 30 min with BH_3DMS (1.3 equiv.) in

diethyl ether (1 mL mmol^{-1}) at 0 °C. The resulting solution was added dropwise to the azaenolate solution at −100 °C. The cooling bath was filled with dry ice and subsequently allowed to reach −20 °C overnight. The reaction mixture was quenched with saturated aqueous $NaHCO_3$, washed twice with brine (0 °C) and dried with $MgSO_4$ at 0 °C. The crude product was filtered through silica gel and then crystallized from hexane at −26 °C.

SAMP-hydrazone 3a: According to GP3A, a solution of LDA (1.1 equiv.) and $LiClO_4$ (3.3 equiv.) in diethyl ether (2.5 mL) was treated with a solution of hydrazone **2b** (201 mg, 0.546 mmol) in diethyl ether (2 mL). After cooling to −100 °C, methyl iodide was added (51 µL, 1.5 equiv.). Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **3a**. − Yield: 195 mg (93%, yellow crystals). − R_f = 0.39 (hexane/diethyl ether = 4:1). − (*E*)/(*Z*) = 54:1. − *de* ≥ 96%. − $[\alpha]_D^{25}$ = +521.3 ($CHCl_3$, *c* = 1.03). − M.p.: 25 °C. − IR (KBr): ṽ = 3108 cm^{-1}, 3088, 2959, 2926, 2872, 2835, 2811, 2730, 2327, 2238, 2056, 1773, 1702, 1639, 1579, 1498, 1459, 1410, 1382, 1350, 1337, 1297, 1279, 1248, 1198, 1185, 1123, 1098, 1046, 1002, 968, 913, 882, 821, 790, 674, 645, 541, 518, 495, 481. − ^{1}H NMR [(*E*,2*R*) isomer, 500 MHz, C_6D_6]: δ = 0.87 (t, ^3J = 7.3 Hz, 3 H, CH_2CH_3), 1.23 (d, ^3J = 7.0 Hz, 3 H, $CHCH_3$), 1.55 (ddq, ^2J = 15.9 Hz, ^3J = 8.6 Hz, ^3J = 7.3 Hz, 1 H, CH_2CH_3), 1.60−1.80 (m, 4 H, CH_2CH_3, NCH_2CH_2, $NCHCH_2$), 2.06 (m, 1 H, $NCHCH_2$), 2.57 (dt, ^2J = 8.9 Hz, ^3J = 8.6 Hz, 1 H, NCH_2), 2.99 (ddd, ^2J = 9.1 Hz, ^3J = 7.6 Hz, ^3J = 3.7 Hz, 1 H, NCH_2), 3.22 (s, 3 H, OCH_3), 3.34 (dd, ^2J = 8.9 Hz, ^3J = 7.3 Hz, 1 H, OCH_2), 3.45 (qd, ^3J = 7.6 Hz, ^4J = 4.0 Hz, 1 H, NCH), 3.58 (dd, ^2J = 8.9 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 3.70 (dq, ^3J = 8.6 Hz, ^3J = 7.0 Hz, 1 H, N=CCH), 4.11 (s, 5 H, C_5H_5), 4.12 (m, 2 H, *m*-C_5H_4R), 4.73 (dt, ^3J = 1.8 Hz, ^4J = 1.5 Hz, 1 H, *o*-C_5H_4R), 4.81 (dt, ^3J = 1.8 Hz, ^4J = 1.5 Hz, 1 H, *o*-C_5H_4R). − ^{1}H NMR [(*Z*,2*S*) isomer, 300 MHz, C_6D_6]: δ = 0.86 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.27 (d, ^3J = 7.1 Hz, 3 H, $CHCH_3$), 1.35−1.83 (m, 5 H, CH_2CH_3, β-ring-CH_2), 2.06 (m, 1 H, β-ring-CH_2), 2.47 (q, $^{2/3}J$ = 8.8 Hz, 1 H, NCH_2), 3.03 (m, 1 H, NCH_2), 3.19 (s, 3 H, OCH_3), 3.32 (dd, ^2J = 8.7 Hz, ^3J = 7.1 Hz, 1 H, OCH_2), 3.57 (m, 1 H, NCH), 3.62 (dd, ^2J = 8.5 Hz, ^3J = 4.1 Hz, 1 H, OCH_2), 3.69 (m, 1 H, N=CCH), 4.08 (s, 5 H, C_5H_5), 4.10 (m, 2 H, *m*-C_5H_4R), 4.53 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 5.04 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R). − ^{13}C NMR [(*E*,2*R*) isomer, 75 MHz, C_6D_6]: δ = 13.2, 18.4 (CH_3), 22.3 (NCH_2CH_2), 27.5 ($NCHCH_2$), 27.7 (CH_2CH_3), 36.4 ($CHCH_3$), 56.0 (NCH_2), 58.9 (OCH_3), 66.8 (NCH), 68.6, 69.5 (*o*-C_5H_4R), 69.0, 69.2 (*m*-C_5H_4R), 69.8 (C_5H_5), 76.4 (OCH_2), 81.5 (*i*-C_5H_4R), 172.6 (C=N). − ^{13}C NMR [(*Z*,2*S*) isomer, 75 MHz, C_6D_6]: δ = 12.6, 18.9 (CH_3), 22.4 (NCH_2CH_2), 27.6 ($NCHCH_2$), 28.7 (CH_2CH_3), 36.5 ($CHCH_3$), 55.8 (NCH_2), 58.8 (OCH_3), 67.0 (NCH), 68.4, 69.0, 69.1 (C_5H_4R), 69.9 (C_5H_5), 76.7 (OCH_2), 81.4 (*i*-C_5H_4R), 170.5 (C=N). − EI-MS; *m*/*z*: 382.1 (70) [M^+], 337.1 (38) [$M^+ - CH_2OCH_3$], 317.1 (19) [$M^+ - C_5H_5$], 268.0 (100) [$M^+ - C_6H_{12}NO$], 210.9 (36) [$FcCN^+$], 184.9 (45) [Fc^+], 129.0 (29) [$C_{10}H_9^+$], 120.9 (38) [$CpFe^+$], 57.1 (10) [FeH^+], 45.3 (10) [$CH_3OCH_2^+$]. − $C_{21}H_{30}FeN_2O$ (382.3): calcd. C 65.97, H 7.91, N 7.33; found C 65.94, H 7.91, N 7.57.

SAMP-hydrazone 3b: According to GP3A, a solution of LDA (1.2 equiv.) and $LiClO_4$ (3.6 equiv.) in diethyl ether (2 mL) was treated with a solution of hydrazone **2d** (178 mg, 0.428 mmol) in diethyl ether (5 mL). After cooling to −100 °C, methyl iodide was added (40 µL, 1.5 equiv.). Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1; 2% NEt_3) provided hydrazone **3b**. − Yield: 175 mg (95%, red oil). − R_f = 0.33 (hexane/diethyl ether = 4:1; 2% NEt_3). − (*E*)/(*Z*) ≥ 100:1. − *de* = 48% (^{1}H NMR). − IR ($CHCl_3$): ṽ = 3083 cm^{-1}, 3057, 3023, 2972, 2921, 2871, 2825, 2731, 2227, 1744, 1700, 1655, 1600, 1571, 1494, 1458, 1409, 1378, 1338, 1295, 1259, 1185, 1106, 1046, 1022, 1000, 962, 910, 883, 825, 751, 698, 674, 640, 590, 561. − ^{1}H NMR (major isomer [minor isomer], 300 MHz, C_6D_6): δ = 1.53 (d, ^3J = 7.4 Hz, 3 H, CH_3), [1.59 (d, ^3J = 7.1 Hz, 3 H, CH_3)], 1.55−1.80 (m, 3 H, β-ring-CH_2), 2.01 (m, 1 H, β-ring-CH_2), 2.54 (q, $^{2/3}J$ = 8.5 Hz, 1 H, NCH_2), [2.75 (q, 1 H, $^{2/3}J$ = 8.5 Hz, NCH_2)], 3.01 (m, 1 H, NCH_2), [3.06 (m, 1 H, NCH_2)], [3.23 (s, 3 H, OCH_3)], 3.26 (s, 3 H, OCH_3), 3.32−3.74 (m, 3 H, NCH, OCH_2), 3.93 (m, 2 H, *m*-C_5H_4R), 3.95 (s, 5 H, C_5H_5), [4.52 (dt, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R)], 4.56 (dt, ^3J = 2.7 Hz, ^4J = 1.0 Hz, 1 H, *o*-C_5H_4R), 4.61 (dt, ^3J = 2.4 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R), [4.62 (dt, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R),], 5.32 (q, ^3J = 7.4 Hz, 1 H, $CHCH_3$), [5.47 (q, ^3J = 7.1 Hz, 1 H, $CHCH_3$),], 7.08 (t, ^3J = 7.2 Hz, 1 H, *p*-C_6H_5), 7.23 (m, 2 H, C_6H_5), [7.33 (dm, ^3J = 8.4 Hz, 2 H, *o*-C_6H_5)], 7.41 (dm, ^3J = 8.4 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (major isomer, 300 MHz, C_6D_6): δ = 16.3 (CH_3), 22.5 (NCH_2CH_2), 27.3 ($NCHCH_2$), 37.8 ($CHCH_3$), 55.8 (NCH_2), 58.8 (OCH_3), 66.9, 67.8, 68.9, 69.0, 70.6 (C_5H_4R, NCH), 70.0 (C_5H_5), 76.8 (OCH_2), 81.3 (*i*-C_5H_4R), 126.2 (*p*-C_6H_5), 127.6, 128.4 (*o*/*m*-C_6H_5), 142.8 (*i*-C_6H_5), 170.0 (C=N). − ^{13}C NMR (300 MHz, C_6D_6): δ = 17.5 (CH_3), 22.2 (NCH_2CH_2), 27.3 ($NCHCH_2$), 38.4 ($CHCH_3$), 56.0 (NCH_2), 58.9 (OCH_3), 66.6, 68.7, 69.6, 69.8, 70.3 (NCH, C_5H_4R), 70.0 (C_5H_5), 76.3 (OCH_2), 81.2 (*i*-C_5H_4R), 126.2 (*p*-C_6H_5), 127.5, 128.5 (*o*/*m*-C_6H_5), 143.1 (*i*-C_6H_5), 172.2 (C=N). − EI-MS; *m*/*z*: 430.3 (81) [M^+], 385.2 (33) [$M^+ - CH_2OCH_3$], 316.1 (55) [$M^+ - C_6H_{12}NO$], 252.2 (11), 230.1 (16), 215.0 (27), 212.1 (36), 211.1 (97) [$FcCN^+$], 192.6 (11), 184.9 (10) [Fc^+], 170.1 (10), 121.1 (39) [$CpFe^+$], 105.1 (100) [$PhCHCH_3^+$]. − $C_{25}H_{30}FeN_2O$ (430.4): calcd. C 69.77, H 7.03, N 6.51; found C 69.30, H 6.67, N 6.39.

SAMP-hydrazone 3c: According to GP3B, a solution of LDA (1.15 equiv.) and $LiClO_4$ (4.0 equiv.) in diethyl ether (2 mL) was treated with a solution of hydrazone **2a** (310 mg, 0.875 mmol) in diethyl ether (3 mL). After cooling to −100 °C, a solution of $Ph_2PCl{\cdot}BH_3$ (1.25 equiv.) in diethyl ether (1 mL) was added dropwise. Aqueous work up, purification by filtration through silica gel (hexane/diethyl ether = 4:1) and crystallization from hexane at −26 °C provided hydrazone **3c**. − Yield: 440 mg (91%, red crystals). − R_f = 0.30 (hexane/diethyl ether = 4:1). − (*E*)/(*Z*) = 20:1. − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −86.9 ($CHCl_3$, *c* = 1.05). − M.p.: 104 °C. − IR (neat): ṽ = 3095 cm^{-1}, 3082, 3056, 2973, 2934, 2875, 2829, 2734, 2388, 2285, 2107, 1659, 1589, 1565, 1462, 1438, 1415, 1385, 1352, 1338, 1300, 1281, 1250, 1185, 1160, 1124, 1106, 1055, 1030, 1001, 971, 911, 883, 821, 739, 699, 644, 609, 547, 500. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.53−1.73 (m, 3 H, β-ring-CH_2), 1.79 (dd, $^3J_{HP}$ = 17.0 Hz, ^3J = 7.7 Hz, 3 H, CH_3), 2.00 (m, 1 H, β-ring-CH_2), 2.37 (q, $^{2/3}J$ = 8.5 Hz, 1 H, NCH_2), 3.03 (m, 1 H, NCH_2), 3.12 (s, 3 H, OCH_3), 3.13 (dd, ^2J = 9.3 Hz, ^3J = 7.2 Hz, 1 H, OCH_2), 3.20 (dd, ^2J = 9.1 Hz, ^3J = 4.1 Hz, 1 H, OCH_2), 3.52 (qd, ^3J = 7.4 Hz, ^3J = 4.1 Hz, 1 H, NCH), 3.92 (s, 5 H, C_5H_5), 3.99 (td, ^3J = 2.2 Hz, ^4J = 1.1 Hz, 1 H, *m*-C_5H_4R), 4.06 (m, 1 H, *m*-C_5H_4R), 4.93 (m, 1 H, *o*-C_5H_4R), 5.13 (dd, ^3J = 2.8 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 5.16 (m, 1 H, PCH), 6.90 (m, 3 H), 7.10 (m, 3 H, *m*/*p*-C_6H_5), 7.76 (m, 2 H, *o*-C_6H_5), 8.31 (ddd, *J* = 9.6 Hz, *J* = 8.2 Hz, ^4J = 1.4 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 16.3 (d, $^2J_{CP}$ = 4.5 Hz, CH_3), 23.4 (NCH_2CH_2), 27.9 ($NCHCH_2$), 34.0 (d, $^1J_{CP}$ = 28.0 Hz, PCH), 57.0 (NCH_2), 59.4 (OCH_3), 68.0, 68.4, 70.0, 70.1, 71.2 (NCH, C_5H_4R), 70.5 (C_5H_5), 76.5 (OCH_2), 82.2 (*i*-C_5H_4R), 129.5 (d, $^3J_{CP}$ = 9.7 Hz, *m*-C_6H_5), 131.5 (d, $^4J_{CP}$ = 2.2 Hz), 131.8 (d, $^4J_{CP}$ = 2.2 Hz, *p*-C_6H_5), 134.3 (d, $^2J_{CP}$ = 9.2 Hz), 134.4 (d, $^2J_{CP}$ = 8.5 Hz, *o*-C_6H_5), 164.8 (C=N). − ^{31}P NMR (121 MHz, C_6D_6): δ = +24.8 (broad). − EI-MS; *m*/*z*: 538.2 (24) [$M^+ - BH_3$],

424.1 (24) [538.2 − $C_6H_{12}NO$], 354.2 (17), 353.1 (56) [538.2 − PPh_2], 239.9 (70), 213.1 (14), 212.2 (11), 210.9 (35) [$FcCN^+$], 186.1 (17) [Cp_2Fe^+], 184.9 (100) [PPh_2^+ or Fc^+], 183.0 (51), 147.1 (67), 128.9 (35) [$C_{10}H_9^+$], 120.9 (50) [$CpFe^+$], 109.1 (11) [$PhPH^+$], 108.1 (10) [PhP^+], 58.3 (13), 56.3 (16) [Fe^+], 45.3 (30) [$CH_2OCH_3^+$]. − HR-MS: $C_{31}H_{38}B^{56}FeN_2OP$ ($M^+ - BH_3$) calcd. 538.183649; found 538.183591. − $C_{31}H_{38}BFeN_2OP$ (552.3): calcd. C 60.00, H 7.05, N 7.00; found C 60.17, H 7.22; N 6.85.

SAMP-hydrazone 3d: According to GP3B, a solution of LDA (1.1 equiv.) and $LiClO_4$ (3.0 equiv.) in diethyl ether (10 mL) was treated with a solution of hydrazone **2b** (1.52 g, 4.13 mmol) in diethyl ether (16 mL). After cooling to −100 °C, a solution of $Ph_2PCl{\cdot}BH_3$ (1.2 equiv.) in diethyl ether (2 mL) was added dropwise. Aqueous work up, purification by filtration through silica gel (hexane/diethyl ether = 4:1) and crystallization from hexane at −26 °C provided hydrazone **3d**. − Yield: 2.27 g (97%, red crystals). − (*E*)/(*Z*) = 44:1. − R_f = 0.20 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −79.2 ($CHCl_3$, *c* = 0.53). − M.p.: 92 °C. − IR (KBr): $\tilde{\nu}$ = 3096 cm^{-1}, 3053, 2967, 2925, 2874, 2826, 2401, 2276, 1620, 1563, 1455, 1437, 1411, 1383, 1333, 1290, 1246, 1197, 1105, 1063, 1000, 972, 894, 815, 741, 700, 639, 607, 559, 499, 471. − ^{1}H NMR [(*E*) isomer, 300 MHz, C_6D_6]: δ = 0.99 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.53−1.90 (m, 6 H, β-ring-CH_2, BH_3), 1.95−2.33 (m, 3 H, β-ring-CH_2, C$H_2$$CH_3$), 2.43 (q, $^{2/3}J$ = 8.4 Hz, 1 H, NCH_2), 2.77 (m, 1 H, NCH_2), 3.13 (s, 3 H, OCH_3), 3.16−3.27 (m, 2 H, OCH_2), 3.46 (m, 1 H, NCH), 3.94 (s, 5 H, C_5H_5), 3.98 (td, ^3J = 2.4 Hz, ^4J = 1.0 Hz, 1 H, *m*-C_5H_4R), 4.08 (td, ^3J = 2.4 Hz, ^4J = 1.3 Hz, 1 H, *m*-C_5H_4R), 4.78 (dt, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R), 5.08 (ddd, $^1J_{CP}$ = 14.1 Hz, ^3J = 9.4 Hz, ^3J = 4.7 Hz, PCH), 5.14 (dt, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 6.88 (m, 3 H), 7.08−7.20 (m, 3 H, *m*/*p*-C_6H_5), 7.72 (m, 2 H), 8.50 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR [(*E*) isomer, 75 MHz, C_6D_6]: δ = 15.4 (d, $^3J_{CP}$ = 4.2 Hz, CH_3), 22.8 (NCH_2CH_2), 34.4 (d, $^2J_{CP}$ = 4.9 Hz, CH_2CH_3), 27.1 ($NCHCH_2$), 40.8 (d, $^1J_{CP}$ = 26.2 Hz, PCH), 56.7 (NCH_2), 58.8 (OCH_3), 67.5, 68.4, 68.9, 69.3, 70.6 (NCH, C_5H_4R), 70.0 (C_5H_5), 75.4 (OCH_2), 82.2 (*i*-C_5H_4R), 127.8 (d, $^3J_{CP}$ = 10.4 Hz), 128.8 (d, $^3J_{CP}$ = 9.7 Hz, *m*-C_6H_5), 129.4 (d, $^1J_{CP}$ = 52.5 Hz), 132.3 (d, $^1J_{CP}$ = 53.1 Hz, *i*-C_6H_5), 130.5 (d, $^4J_{CP}$ = 2.5 Hz), 131.1 (d, $^4J_{CP}$ = 2.4 Hz, *p*-C_6H_5), 133.8 (d, $^2J_{CP}$ = 6.7 Hz), 133.9 (d, $^2J_{CP}$ = 6.1 Hz, *o*-C_6H_5), 164.6 (C=N). − ^{31}P NMR (121 MHz, C_6D_6): δ = +23.2 (broad). − EI-MS; *m*/*z*: 552.3 (9) [$M^+ - BH_3$], 452.0 (42) [$M^+ - C_6H_{12}NO$], 438.1 (21) [452.0 − BH_3], 367.1 (64) [$M^+ - Ph_2P - BH_3$], 253.9 (73) [452.0 − Ph_2P − BH_3], 252.0 (53) [438.1 − Ph_2PH], 227.0 (32), 211.0 (32) [$FcCN^+$], 186.2 (27) [$CpFe^+$ or Ph_2PH^+], 185.0 (100) [Fc^+ or Ph_2P^+], 183.1 (44) [185.0 − H_2], 156.2 (55), 129.0 (28) [$C_{10}H_9^+$], 121.0 (36) [$CpFe^+$], 108.2 (13) [$C_6H_5P^+$]. − $C_{32}H_{40}BFeN_2OP$ (566.3): calcd. C 67.87, H 7.12, N 4.95; found C 67.70, H 7.05, N 4.64.

SAMP-hydrazone 3e: According to GP3A, a solution of LDA (1.2 equiv.) and $LiClO_4$ (3.0 equiv.) in diethyl ether (5 mL) was treated with a solution of hydrazone **2a** (669 mg, 1.82 mmol) in diethyl ether (5 mL). After cooling to −100 °C, dimethyl disulfide (0.29 mL, 1.7 equiv.) was added dropwise. Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **3e**. − Yield: 690 mg (95%, orange-red crystals). − R_f = 0.50 (hexane/diethyl ether = 4:1). − (*E*)/(*Z*) = 12:1. − *de* ≥ 96%. − $[\alpha]_D^{25}$ = +270.9 ($CHCl_3$, *c* = 0.62). − M.p.: 86 °C. − IR (KBr): $\tilde{\nu}$ = 3106 cm^{-1}, 2971, 2918, 2873, 2734, 2226, 2053, 1672, 1639, 1559, 1454, 1378, 1343, 1323, 1297, 1248, 1185, 1107, 1049, 1028, 999, 956, 884, 817, 762, 716, 688, 670, 630, 594, 534, 481. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.55 (d, ^3J = 7.4 Hz, 3 H, $CHCH_3$), 1.58−1.77 (m, 3 H, β-ring-CH_2), 1.92 (s, 3 H, SCH_3), 1.98 (m, 1 H, β-ring-CH_2), 2.42 (dt, ^2J = 8.5 Hz, ^3J = 8.2 Hz, 1 H, NCH_2), 2.91 (ddd, ^2J = 9.1 Hz, ^3J = 7.4 Hz, ^3J = 4.1 Hz, 1 H, NCH_2), 3.13 (s, 3 H, OCH_3), 3.25 (dd, ^2J = 8.8 Hz, ^3J = 6.9 Hz, 1 H, OCH_2), 3.51 (dd, ^2J = 8.8 Hz, ^3J = 4.1 Hz, 1 H, OCH_2), 3.58 (qd, ^3J = 7.4 Hz, ^3J = 4.1 Hz, 1 H, NCH), 4.09 (s, 5 H, C_5H_5), 4.14 (m, 2 H, *m*-C_5H_4R), 4.92 (q, ^3J = 7.7 Hz, 1 H, SC*H*), 4.97 (dt, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 5.27 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 15.3, 19.2 (CH_3), 22.5 (NCH_2CH_2), 27.3 ($NCHCH_2$), 39.2 (SCH), 56.2 (NCH_2), 58.7 (OCH_3), 67.1, 67.8, 69.1, 69.3, 70.8 (NCH, C_5H_4R), 69.9 (C_5H_5), 76.2 (OCH_2), 80.2 (*i*-C_5H_4R), 165.9 (C=N). − EI-MS; *m*/*z*: 400.1 (95) [M^+], 352.9 (11) [$M^+ - CH_3S$], 308.1 (12) [$M^+ - CH_3OCH_2SCH_3$], 307.0 (55), 286.0 (17) [$M^+ - C_6H_{12}NO$], 241.1 (12), 240.0 (30) [286.0 − CH_3OCH_3], 239.1 (12), 237.9 (16) [286.0 − H_3CSH], 230.1 (12), 213.0 (22), 212.1 (28), 210.9 (78) [$FcCN^+$], 187.1 (20), 186.0 (13) [Cp_2Fe^+], 184.9 (57) [Fc^+], 142.1 (46), 129.1 (19) [$C_{10}H_9^+$], 91.1 (33), 75.0 (100) [$H_3CSCHCH_3^+$], 55.9 (17) [Fe^+]. − $C_{20}H_{28}FeN_2OS$ (400.4): calcd. C 60.00, H 7.05, N 7.00; found C 60.17, H 7.22, N 6.85.

SAMP-hydrazone 3f: According to GP3A, a solution of LDA (1.2 equiv.) and $LiClO_4$ (3.0 equiv.) in diethyl ether (20 mL) was treated with a solution of hydrazone **2b** (3.74 g, 10.1 mmol) in diethyl ether (20 mL). After cooling to −100 °C, dimethyl disulfide (1.19 mL, 1.3 equiv.) was added dropwise. Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **3f**. − Yield: 3.91 g (93%, orange-red crystals). − R_f = 0.29 (hexane/diethyl ether = 4:1). − (*E*)/(*Z*) = 28:1. − *de* ≥ 96%. − $[\alpha]_D^{25}$ = +257.8 ($CHCl_3$, *c* = 0.79). − M.p.: 90 °C. − IR (KBr): $\tilde{\nu}$ = 3110 cm^{-1}, 2961, 2915, 2871, 2808, 2727, 2279, 2238, 2056, 1777, 1705, 1669, 1560, 1444, 1382, 1349, 1333, 1298, 1279, 1255, 1235, 1195, 1108, 1042, 1002, 962, 911, 883, 821, 757, 720, 686, 662, 594, 577, 519, 493, 455. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.06 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.57−2.05 (m, 6 H, C$H_2$$CH_3$, β-ring-$CH_2$), 2.00 (s, 3 H, SCH_3), 2.46 (dt, ^2J = 10.4 Hz, ^3J = 8.8 Hz, 1 H, NCH_2), 2.96 (ddd, ^2J = 9.1 Hz, ^3J = 8.4 Hz, ^3J = 4.4 Hz, 1 H, NCH_2), 3.15 (s, 3 H, OCH_3), 3.28 (dd, ^2J = 10.2 Hz, ^3J = 8.2 Hz, 1 H, OCH_2), 3.52 (dd, ^2J = 10.2 Hz, ^3J = 4.1 Hz, 1 H, OCH_2), 3.54 (m, 1 H, NCH), 4.15 (s, 5 H, C_5H_5), 4.16 (m, 1 H, *m*-C_5H_4R), 4.18 (td, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, *m*-C_5H_4R), 4.65 (dd, ^3J = 9.6 Hz, ^3J = 5.8 Hz, 1 H, SCH), 4.89 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 5.17 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.4, 15.5 (CH_3), 22.5 (NCH_2CH_2), 26.8, 27.3 (CH_2CH_3, $NCHCH_2$), 47.1 (SCH), 56.4 (NCH_2), 58.7 (OCH_3), 67.3, 68.1, 69.06, 69.11, 71.1 (NCH, C_5H_4R), 70.0 (C_5H_5), 76.1 (OCH_2), 80.9 (*i*-C_5H_4R), 166.2 (C=N). − EI-MS; *m*/*z*: 414.2 (100) [M^+], 367.1 (16) [$M^+ - CH_3S$], 321.1 (51), 299.9 (25) [$M^+ - C_6H_{12}NO$], 254.1 (23), 253.2 (25), 252.0 (52) [299.9 − CH_3SH], 227.0 (19), 212.2 (19), 211.0 (56) [$FcCN^+$], 201.0 (12), 186.1 (11) [Cp_2Fe^+], 184.9 (45) [Fc^+], 156.1 (27), 128.9 (18) [$C_{10}H_9^+$], 121.0 (42) [$CpFe^+$], 90.9 (14), 89.1 (56) [$H_3CSCHCH_2CH_3^+$]. − $C_{21}H_{30}FeN_2OS$ (414.4): calcd. C 60.87, H 7.30, N 6.76; found C 61.10, H 7.50, N 6.56.

SAMP-hydrazone 3g: According to GP3A, a solution of LDA (1.2 equiv.) and $LiClO_4$ (3.0 equiv.) in diethyl ether (20 mL) was treated with a solution of hydrazone **2a** (3.34 g, 9.44 mmol) in diethyl ether (15 mL). After cooling to −100 °C, diisopropyl disulfide (2.26 mL, 1.5 equiv.) was added dropwise. Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **3g**. − Yield: 3.74 g (92%, orange-brown crystals). − R_f = 0.48 (Hex/Et_2O = 4:1). − (*E*)/(*Z*) = 50:1. − *de* ≥ 96%. − $[\alpha]_D^{25}$ = +245.7 ($CHCl_3$, *c* = 0.60). − M.p.: 82 °C. − IR (KBr):

$\tilde{\nu}$ = 3113 cm^{-1}, 3096, 3082, 2966, 2926, 2888, 2870, 2827, 2809, 2731, 2371, 2248, 2057, 1786, 1737, 1719, 1701, 1686, 1655, 1565, 1459, 1410, 1379, 1365, 1352, 1337, 1297, 1282, 1253, 1196, 1154, 1121, 1104, 1045, 1028, 1001, 964, 910, 881, 836, 819, 770, 738, 692, 651, 630, 596, 548, 519, 482. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.15 [d, ^3J = 6.9 Hz, 3 H, CH(CH_3)$_2$], 1.33 [d, ^3J = 6.6 Hz, 3 H, CH(CH_3)$_2$], 1.55−1.73 (m, 3 H, β-ring-CH_2), 1.60 (d, ^3J = 7.7 Hz, 3 H, N=CCHCH_3), 2.01 (m, 1 H, β-ring-CH_2), 2.42 (dt, ^2J = 8.8 Hz, ^3J = 8.0 Hz, 1 H, NCH_2), 2.88 [sept, ^3J = 6.6 Hz, 1 H, CH(CH_3)$_2$], 3.01 (ddd, ^2J = 8.8 Hz, ^3J = 7.4 Hz, ^3J = 4.1 Hz, 1 H, NCH_2), 3.18 (s, 3 H, OCH_3), 3.32 (dd, ^2J = 8.5 Hz, ^3J = 7.2 Hz, 1 H, OCH_2), 3.60 (dd, ^2J = 8.5 Hz, ^3J = 4.4 Hz, 1 H, OCH_2), 3.63 (qd, ^3J = 7.7 Hz, ^3J = 4.4 Hz, 1 H, NCH), 4.09 (s, 5 H, C_5H_5), 4.14 (m, 2 H, *m*-C_5H_4R), 4.94 (q, ^3J = 7.4 Hz, 1 H, N=CCHCH$_3$), 4.98 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 5.24 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 20.4, 23.5, 24.8 (CH_3), 22.7 (NCH_2CH_2), 27.6 (NCHCH_2), 35.9, 36.8 (SCH), 56.5 (NCH_2), 58.9 (OCH_3), 67.3, 67.9, 69.2, 69.3, 71.0 (NCH, C_5H_4R), 70.1 (C_5H_5), 76.6 (OCH_2), 80.6 (*i*-C_5H_4R), 165.5 (C=N). − EI-MS; *m*/*z*: 429.0 (81) [MH^+], 428.1 (100) [M^+], 353.1 (12) [M^+ − SCH(CH_3)$_2$]. − $C_{22}H_{32}FeN_2OS$ (428.4): calcd. C 61.68, H 7.53, N 6.54; found C 61.74, H 7.66, N 6.38.

SAMP-hydrazone 3h: According to GP3A, a solution of LDA (1.1 equiv.) and $LiClO_4$ (3.0 equiv.) in diethyl ether (4 mL) was treated with a solution of hydrazone **2b** (530 mg, 1.44 mmol) in diethyl ether (3 mL). After cooling to −100 °C, diisopropyl disulfide (0.32 mL, 1.4 equiv.) was added dropwise. Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **3h**. − Yield: 616 mg (97%, orange-red crystals). − R_f = 0.59 (hexane/diethyl ether = 4:1). − (*E*)/(*Z*) = 9:1. − *de* ≥ 96%. − $[\alpha]_D^{25}$ = +327.8 ($CHCl_3$, *c* = 1.17). − M.p.: 81 °C. − IR (KBr): $\tilde{\nu}$ = 3102 cm^{-1}, 3084, 2961, 2926, 2869, 2824, 2731, 2248, 1673, 1640, 1566, 1455, 1411, 1381, 1331, 1299, 1250, 1199, 1182, 1156, 1106, 1052, 1024, 1000, 955, 922, 890, 822, 742, 684, 670, 649, 628, 553, 488. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.10 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.20 (d, ^3J = 6.8 Hz, 3 H, CHCH_3), 1.33 (d, ^3J = 6.6 Hz, 3 H, CHCH_3), 1.52−2.07 (m, 6 H, CH_2CH$_3$, β-ring-CH_2), 2.45 (td, $^{2/3}J$ = 8.8 Hz, ^3J = 7.7 Hz, 1 H, NCH_2), 2.96 [sept, ^3J = 6.6 Hz, 1 H, CH(CH_3)$_2$], 3.02 (m, 1 H, NCH_2), 3.18 (s, 3 H, OCH_3), 3.33 (dd, ^2J = 9.9 Hz, ^3J = 8.2 Hz, 1 H, OCH_2), 3.59 (dd, ^2J = 10.2 Hz, ^3J = 4.1 Hz, 1 H, OCH_2), 3.59 (m, 1 H, NCH), 4.14 (s, 5 H, C_5H_5), 4.15 (m, 2 H, *m*-C_5H_4R), 4.58 (dd, ^3J = 10.4 Hz, ^3J = 5.0 Hz, 1 H, N=CCHS), 4.89 (t, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 5.15 (dt, ^3J = 2.5 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.4, 23.6, 24.6 (CH_3), 22.6 (NCH_2CH_2), 27.3, 27.4 (CH_2CH_3, NCHCH_2), 35.8, 44.4 (SCH), 56.3 (NCH_2), 58.7 (OCH_3), 67.2, 68.1, 68.9, 69.0, 71.1 (NCH, C_5H_4R), 70.0 (C_5H_5), 76.4 (OCH_2), 81.1 (*i*-C_5H_4R), 166.8 (C=N). − EI-MS; *m*/*z*: 442.1 (100) [M^+], 367.1 (18) [M^+ − (H$_3$C)$_2$CHS], 327.9 (22) [M^+ − $C_6H_{12}NO$], 321.0 (40), 285.9 (27), 255.1 (17), 254.0 (35), 253.1 (48), 251.9 (62), 226.9 (19), 212.0 (18), 210.9 (45) [$FcCN^+$], 201.1 (16), 186.0 (12) [Cp_2Fe^+], 184.9 (45) [Fc^+], 156.1 (29), 128.9 (16) [$C_{10}H_9^+$], 120.9 (41) [$CpFe^+$], 117.0 (44) [(H$_3$C)$_2$CHS−CH−$CH_2CH_3^+$], 75.0 (23) [(H$_3$C)$_2$CHS$^+$]. − $C_{23}H_{34}FeN_2OS$ (442.4): calcd. C 62.44, H 7.75, N 6.33; found C 62.49, H 7.82, N 5.98.

SAMP-hydrazone 3i: According to GP3B, a solution of LDA (1.2 equiv.) and $LiClO_4$ (3.0 equiv.) in diethyl ether (4 mL) was treated with a solution of hydrazone **2a** (433 mg, 1.22 mmol) in diethyl ether (4 mL). After cooling to −100 °C, *i*Pr_2PCl (1.4 equiv.) was added dropwise. After warming to room temperature overnight, the solution was cooled to 0 °C and treated with 1.7 equiv. BH_3DMS for 3 h. Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 7:1) provided hydrazone **3i**. − Yield: 568 mg (96%, orange oil). − R_f = 0.48 (hexane/diethyl ether = 4:1). − (*E*)/(*Z*) = 9:1. − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −120.5 ($CHCl_3$, *c* = 0.52). − IR (neat): $\tilde{\nu}$ = 3096 cm^{-1}, 2964, 2934, 2874, 2827, 2733, 2379, 2277, 1673, 1563, 1462, 1415, 1384, 1353, 1338, 1249, 1199, 1185, 1107, 1055, 1002, 970, 932, 884, 821, 753, 684, 651, 597, 495. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.92 (dd, $^3J_{HP}$ = 13.2 Hz, ^3J = 6.8 Hz, 3 H), 1.05 (dd, $^3J_{HP}$ = 15.4 Hz, ^3J = 7.1 Hz, 3 H), 1.13 (dd, $^3J_{HP}$ = 12.6 Hz, ^3J = 6.9 Hz, 3 H), 1.20 [dd, $^3J_{HP}$ = 13.7 Hz, ^3J = 7.1 Hz, 3 H, PCH(CH_3)$_2$], 1.54−1.98 (m, 5 H, β-ring-CH_2, NCH_2), 1.73 (dd, $^2J_{HP}$ = 14.5 Hz, ^3J = 7.7 Hz, 3 H, N=CCHCH_3), 2.05 [dsept, $^2J_{HP}$ = 12.4 Hz, ^3J = 7.1 Hz, 1 H, CH(CH_3)$_2$], 2.39 [dsept, $^2J_{HP}$ = 16.7 Hz, ^3J = 7.1 Hz, 1 H, CH(CH_3)$_2$], 3.04 (ddd, ^2J = 9.3 Hz, ^3J = 6.9 Hz, ^3J = 4.1 Hz, 1 H, NCH_2), 3.08 (s, 3 H, OCH_3), 3.25 (dd, ^2J = 9.3 Hz, ^3J = 6.3 Hz, 1 H, OCH_2), 3.37 (dd, ^2J = 9.1 Hz, ^3J = 4.1 Hz, 1 H, OCH_2), 3.50 (m, 1 H, NCH), 3.98 (s, 5 H, C_5H_5), 4.10 (td, ^3J = 2.5 Hz, ^4J = 1.1 Hz, 1 H, *m*-C_5H_4R), 4.16 (td, ^3J = 2.5 Hz, ^4J = 1.7 Hz, 1 H, *m*-C_5H_4R), 4.23 (dq, $^2J_{HP}$ = 16.8 Hz, ^3J = 7.2 Hz, 1 H, N=CCH), 5.20 (m, 2 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 18.0 (d, $^2J_{CP}$ = 2.3 Hz), 18.9 [d, $^2J_{CP}$ = 1.1 Hz, CH(CH_3)$_2$], 18.3 (N=CCHCH_3), 21.7 (d, $^1J_{CP}$ = 29.8 Hz), 25.2 [d, $^1J_{CP}$ = 30.9 Hz, CH(CH_3)$_2$], 22.6 (NCH_2CH_2), 26.5 (NCHCH_2), 27.8 (d, $^1J_{CP}$ = 22.3 Hz, N=CCH), 56.1 (NCH_2), 58.7 (OCH_3), 67.0, 67.6, 69.66, 69.72, 71.4 (NCH, C_5H_4R), 69.9 (C_5H_5), 75.3 (OCH_2), 82.6 (*i*-C_5H_4R), 164.4 (C=N). − ^{31}P NMR (121 MHz, C_6D_6): δ = +43.8 (broad). − EI-MS; (75 MHz, C_6D_6): δ = 484.3 (2) [M^+], 427.1 (20) [M^+ − BH_3 − (H$_3$C)$_2$CH], 370.1 (100) [M^+ − $C_6H_{12}NO$], 241.1 (11), 210.9 (14) [$FcCN^+$], 184.9 (21) [Fc^+], 121.0 (25) [$CpFe^+$], 70.2 (12). − CI-MS (isobutane); *m*/*z*: 485.2 (43) [MH^+], 484.2 (45) [M^+], 483.2 (100) [M^+ − H], 482.2 (42) [M^+ − H_2], 370.1 (34) [M^+ − $C_6H_{12}NO$], 369.1 (19) [M^+ − $C_6H_{13}NO$], 119.1 (15), 116.0 (17), 114.1 (12). − $C_{25}H_{42}BFeN_2OP$ (485.3): calcd. C 62.01, H 8.74, N 5.78; found C 62.18, H 8.67, N 6.27.

SAMP-hydrazone 3j: According to GP3A, a solution of LDA (1.2 equiv.) and $LiClO_4$ (3.0 equiv.) in diethyl ether (8 mL) was treated with a solution of hydrazone **2c** (2.01 g, 5.26 mmol) in diethyl ether (8 mL). After cooling to −100 °C, a solution of di-*p*-tolyl disulfide (1.94 g, 1.5 equiv.) in diethyl ether (6 mL) was added dropwise. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **3j**. − Yield: 2.33 g (88%, red oil). − R_f = 0.50 (hexane/diethyl ether = 4:1). − (*Z*)/(*E*) ≥ 100:1. − *de* ≥ 96%. − $[\alpha]_D^{25}$ = +677.9 ($CHCl_3$, *c* = 1.07). − IR (neat): $\tilde{\nu}$ = 3095 cm^{-1}, 3017, 2962, 2922, 2870, 2829, 2732, 1670, 1580, 1493, 1460, 1412, 1398, 1383, 1365, 1352, 1334, 1292, 1240, 1199, 1184, 1165, 1121, 1107, 1046, 1019, 1002, 970, 940, 916, 893, 812, 633, 496. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.82 [broad d, ^3J = 6.4 Hz, 3 H, CH(CH_3)$_2$], 1.19 [d, ^3J = 6.7 Hz, 3 H, CH(CH_3)$_2$], 1.55−2.85 (m, 3 H, β-ring-CH_2), 2.06 (s, 3 H, $C_6H_4CH_3$), 2.10 [m, 1 H, CH(CH_3)$_2$], 2.26 (m, 1 H, β-ring-CH_2), 2.55 (m, 1 H, NCH_2), 3.04 (m, 1 H, NCH_2), 3.16 (s, 3 H, OCH_3), 3.17 (m, 1 H, OCH_2), 3.51 (m, 1 H, NCH), 3.56 (dd, ^2J =8.7 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 4.13 (td, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, *m*-C_5H_4R), 4.15 (t, $^{3/4}J$ = 2.0 Hz, 1 H, *m*-C_5H_4R), 4.26 (s, 5 H, C_5H_5), 4.92 (broad s, 1 H, *o*-C_5H_4R), 5.01 (broad d, ^3J = 8.7 Hz, 1 H, SCH), 5.10 (broad s, 1 H, *o*-C_5H_4R), 6.95 (d, ^3J = 7.7 Hz, 2 H, C_6H_4), 7.69 (d, ^3J = 7.7 Hz, 2 H, C_6H_4). − ^{13}C NMR (75 MHz, C_6D_6): δ = 20.9, 21.6, 21.8 (CH_3), 22.5 (NCH_2CH_2), 27.8 (NCHCH_2), 33.4 [CH(CH$_3$)$_2$], 54.3 (SCH), 55.9 (NCH_2), 58.9 (OCH_3), 67.5, 68.9, 69.0, 69.3, 71.0 (NCH, C_5H_4R), 70.6 (C_5H_5), 76.1 (OCH_2), 129.9, 131.1 (C_6H_4), 168.5 (C=N). −

EI-MS; *m/z*: 505.1 (100) [MH^+], 504.1 (99) [M^+]. − $C_{28}H_{36}FeN_2OS$ (504.5): calcd. C 66.66, H 7.19, N 5.55; found C 66.59, H 7.36, N 5.53.

SAMP-hydrazone 3k: According to GP3A, a solution of LDA (1.2 equiv.) and $LiClO_4$ (3.0 equiv.) in diethyl ether (3 mL) was treated with a solution of hydrazone **2c** (170 mg, 0.445 mmol) in diethyl ether (3 mL). After cooling to −100 °C, methyl iodide (41 μL, 1.4 equiv.) was added dropwise. Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **3k**. − Yield: 168 mg (95%, red-brown oil). − R_f = 0.40 (hexane/diethyl ether = 4:1). − (*Z*)/(*E*) ≥ 50:1. − *de* ≥ 96%. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.81 [d, ^3J = 6.7 Hz, 3 H, CH(CH_3)$_2$], 0.93 [d, ^3J = 6.4 Hz, 3 H, CH(CH_3)$_2$], 1.30 (d, ^3J = 7.1 Hz, 3 H, N=CCHCH_3), 1.60−2.11 (m, 6 H, β-ring-CH_2, C*H*C*H*), 2.65 (dt, ^2J = 9.1 Hz, ^3J = 8.7 Hz, 1 H, NCH_2), 3.00 (dd, ^2J = 9.4 Hz, ^3J = 7.4 Hz, ^3J = 3.4 Hz, 1 H, NCH_2), 3.23 (s, 3 H, OCH_3), 3.38 (dd, ^2J = 9.1 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 3.52 (dd, ^2J = 9.1 Hz, ^3J = 7.4 Hz, 1 H, OCH_2), 3.56 (m, 1 H, NCH), 4.10 (td, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, *m*-C_5H_4R), 4.13 (td, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, *m*-C_5H_4R), 4.15 (s, 5 H, C_5H_5), 4.50 (dt, ^3J = 2.4 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R), 5.02 (dt, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 17.7, 21.2, 22.3 (CH_3), 22.2 (NCH_2CH_2), 27.5 ($NCHCH_2$), 31.0 [$CH(CH_3)_2$], 42.2 (N=*C*CH), 55.9 (NCH_2), 58.8 (OCH_3), 66.8, 68.6, 68.8, 69.1, 70.0 (NCH, C_5H_4R), 69.9 (C_5H_5), 76.4 (OCH_2), 82.1 (*i*-C_5H_4R), 174.2 (C=N). − EI-MS; *m/z*: 396.3 (55) [M^+], 351.3 (31) [M^+ − CH_2OCH_3], 331.3 (18) [M^+ − C_5H_5], 282.1 (100) [M^+ − $C_6H_{12}NO$], 211.0 (52) [$FcCN^+$], 186.1 (18) [Cp_2Fe^+], 185.0 (68) [Fc^+], 175.4 (20), 129.1 (41) [$C_{10}H_9^+$], 122.0 (12) [$C_5H_6Fe^+$], 121.0 (96) [$CpFe^+$], 83.1 (14), 77.2 (14), 71.2 (44) [$H_3CCHCH(CH_3)_2^+$], 70.2 (63) [$C_5H_{10}^+$], 69.2 (24) [$C_5H_9^+$], 68.2 (13) [$C_5H_8^+$], 67.2 (15) [$C_5H_7^+$], 66.2 (10) [$C_5H_6^+$], 59.2 (18), 58.2 (27), 57.2 (64) [FeH^+], 56.1 (78) [Fe^+], 55.2 (78), 54.1 (15), 53.1 (13), 51.1 (13), 45.3 (73) [$H_3COCH_2^+$]. − HR-MS: $C_{22}H_{32}{}^{56}FeN_2O$: calcd. 396.186340; found 396.186387.

SAMP-hydrazone 3l: According to GP3A, a solution of LDA (1.2 equiv.) and $LiClO_4$ (3.0 equiv.) in diethyl ether (6 mL) was treated with a solution of hydrazone **2c** (1.00 g, 2.62 mmol) in diethyl ether (4 mL). After cooling to −100 °C, dimethyl disulfide (0.40 mL, 1.7 equiv.) was added dropwise. Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **3l**. − Yield: 920 mg (82%, red oil). − R_f = 0.48 (hexane/diethyl ether = 4:1). − (*Z*)/(*E*) ≥ 50:1. − *de* ≥ 96%. − IR (KBr): $\tilde{\nu}$ = 3083 cm^{-1}, 2974, 2961, 2928, 2874, 2848, 2829, 2809, 2731, 2252, 1759, 1671, 1569, 1458, 1438, 1412, 1383, 1352, 1284, 1249, 1192, 1168, 1147, 1121, 1106, 1041, 999, 970, 940, 915, 890, 865, 842, 807, 729, 691, 629, 524, 484. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.79 (d, ^3J = 6.7 Hz, 3 H, CHCH_3), 1.21 (d, ^3J = 6.4 Hz, 3 H, CHCH_3), 1.52−1.78 (m, 3 H), 1.98−2.14 (m, 2 H, β-ring-CH_2, NCH_2), 2.21 (s, 3 H, SCH_3), 2.49 (q, $^{2/3}J$ = 8.4 Hz, 1 H, NCH_2), 3.06 [broad m, 1 H, C*H*(CH$_3$)$_2$], 3.18 (s, 3 H, OCH_3), 3.39 (dd, ^2J = 8.4 Hz, ^3J = 6.4 Hz, 1 H, OCH_2), 3.56 (m, 1 H, NCH), 3.62 (dd, ^2J = 8.4 Hz, ^3J = 4.4 Hz, 1 H, OCH_2), 4.12 (m, 2 H, *m*-C_5H_4R), 4.28 (s, 5 H, C_5H_5), 4.39 (m, 1 H, *o*-C_5H_4R), 4.98 (broad s, 1 H, SCH), 5.06 (dt, ^3J = 2.0 Hz, ^4J = 1.7 Hz, 1 H, *o*-C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 21.7, 21.8 (CH_3), 22.4 (NCH_2CH_2), 27.3 ($NCHCH_2$), 31.6 [$CH(CH_3)_2$], 52.6 (SCH), 56.2 (NCH_2), 58.7 (OCH_3), 67.7, 68.5, 68.6, 69.0, 71.7 (NCH, C_5H_4R), 70.2 (C_5H_5), 76.1 (OCH_2), 166.9 (C=N). − EI-MS; *m/z*: 428.2 (87) [M^+], 381.2 (31) [M^+ − SCH_3], 335.1 (30) [M^+ − $HSCH_3$ − Me_2O], 314.1 (19) [M^+ − $C_6H_{12}NO$], 268.1 (36) [314.1 − H_2C=S], 267.1 (36) [M^+ − H_2C=S − $C_6H_{13}NO$], 266.1 (100) [314.1 − $HSCH_3$], 251.1 (11), 215.2 (21), 212.2 (30) [$FcCNH^+$], 211.1 (64) [$FcCN^+$], 186.1 (17) [Cp_2Fe^+], 185.0 (58) [Fc^+], 170.2 (34), 167.7 (16), 129.1 (33) [$C_{10}H_9^+$], 128.1 (19) [$C_{10}H_8^+$], 121.0 (75) [$CpFe^+$], 103.1 (93) [$H_3CSCHCH(CH_3)_2^+$], 56.1 (16) [Fe^+], 55.2 (45), 45.3 (22) [$H_3COCH_2^+$]. − $C_{22}H_{32}FeN_2OS$ (428.4): calcd. C 61.68, H 7.53, N 6.54; found C 61.84, H 7.54, N 6.37.

SAMP-hydrazone 3m: According to GP3A, a solution of LDA (1.1 equiv.) and $LiClO_4$ (3.3 equiv.) in diethyl ether (5 mL) was treated with a solution of hydrazone **2c** (500 mg, 1.36 mmol) in diethyl ether (6 mL). After cooling to −100 °C, a solution of di-*p*-tolyl disulfide (435 mg, 1.3 equiv.) in diethyl ether (1 mL) was added dropwise. Aqueous work up and purification by flash chromatography through silica gel (hexane/ethyl acetate = 10:1; 2% NEt_3) provided hydrazone **3m**. − Yield: 659 mg (99%, orange crystals). − R_f = 0.38 (hexane/diethyl ether = 4:1; 2% NEt_3). − (*E*)/(*Z*) = 5:1. − *de* ≥ 96%. − M.p.: 85 °C. − IR (KBr): $\tilde{\nu}$ = 3093 cm^{-1}, 3083, 3034, 3019, 2966, 2925, 2871, 2847, 2822, 2810, 2732, 2242, 1764, 1719, 1687, 1655, 1637, 1599, 1569, 1495, 1477, 1458, 1409, 1382, 1350, 1336, 1298, 1275, 1253, 1213, 1198, 1182, 1127, 1105, 1096, 1096, 1074, 1050, 1022, 1000, 971, 935, 913, 886, 820, 804. − ^{1}H NMR (major isomer, 300 MHz, C_6D_6): δ = 0.84 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.58−1.76 (m, 3 H, β-ring-CH_2), 1.88−2.15 (m, 3 H, CH_2CH$_3$, β-ring-CH_2), 2.06 (s, 3 H, $C_6H_4CH_3$), 2.86 (q, ^3J = 7.3 Hz, 1 H, NCH_2), 3.14 (s, 3 H, OCH_3), 3.13−3.57 (m, 4 H, OCH_2, NCH, NCH_2), 4.20 (m, 2 H, *m*-C_5H_4R), 4.26 (s, 5 H, C_5H_5), 5.06 (dt, ^3J = 2.5 Hz, ^4J = 1.1 Hz, 1 H, *o*-C_5H_4R), 5.23 (m, 1 H, *o*-C_5H_4R), 5.32 (m, 1 H, SCH), 6.91 (d, ^3J = 8.0 Hz, 2 H, C_6H_4), 7.50 (d, ^3J = 8.0 Hz, 2 H, C_6H_4). − ^{1}H NMR (minor isomer, 300 MHz, C_6D_6): δ = 1.07 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.52−1.80 (m, 3 H, β-ring-CH_2), 1.88−2.15 (m, 3 H, CH_2CH$_3$, β-ring-CH_2), 2.01 (s, 3 H, $C_6H_4CH_3$), 2.52 (dt, ^2J = 9.1 Hz, ^3J = 8.1 Hz, 1 H, NCH_2), 3.19 (s, 3 H, OCH_3), 3.20 (m, 1 H, OCH_2), 3.46 (dd, ^2J = 9.1 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 3.56 (m, 1 H, NCH), 4.12 (s, 5 H, C_5H_5), 4.16 (m, 2 H, *m*-C_5H_4R), 4.99 (dt, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 5.14 (m, 1 H, SCH), 5.16 (dt, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, *o*-C_5H_4R), 6.91 (d, ^3J = 8.0 Hz, 2 H, C_6H_4), 7.52 (d, ^3J = 8.0 Hz, 2 H, C_6H_4). − ^{13}C NMR (major isomer, 75 MHz, C_6D_6): δ = 12.2, 20.9 (CH_3), 22.4 (NCH_2CH_2), 27.3 ($NCHCH_2$), 28.4 (CH_2CH_3), 47.9 (SCH), 55.9 (NCH_2), 58.7 (OCH_3), 66.7, 68.8, 69.2, 69.3, 69.5 (C_5H_4R, NCH), 70.5 (C_5H_5), 76.1 (OCH_2), 80.1 (*i*-C_5H_4R), 130.2, 132.1 (C_6H_4), 133.4, 137.0 (*i*-C_6H_4), 166.7 (C=N). − ^{13}C NMR (minor isomer, 75 MHz, C_6D_6): δ = 13.4, 21.0 (CH_3), 22.6 (NCH_2CH_2), 27.9, 28.0 (CH_2CH_3, $NCHCH_2$), 49.3 (SCH), 56.3 (NCH_2), 58.9 (OCH_3), 67.3, 68.6, 69.2, 69.4, 70.5 (C_5H_4R, NCH), 70.2 (C_5H_5), 76.5 (OCH_2), 80.8 (*i*-C_5H_4R), 129.9, 131.9 (C_6H_4), 132.2, 136.5 (*i*-C_6H_4), 166.8 (C=N). − EI-MS; *m/z*: 490.1 (52) [M^+], 367.0 (100) [M^+ − $H_3CC_6H_4S$], 321.0 (16), 254.0 (80) [367.0 − $C_6H_{11}NO$], 252.0 (73) [267.0 − $C_6H_{13}NO$], 227.9 (30), 210.9 (35) [$FcCN^+$], 184.9 (91) [Fc^+], 165.0 (13) [$H_3CC_6H_4SCHCHCH_3^+$], 156.0 (65), 129.0 (33) [$C_{10}H_9^+$], 122.9 (29) [$C_7H_7S^+$], 120.9 (51) [$CpFe^+$], 91.0 (25) [$C_7H_7^+$], 71.1 (20), 56.0 (13) [Fe^+], 45.2 (19) [$CH_3OCH_2^+$]. − $C_{27}H_{34}FeN_2OS$ (490.5): calcd. C 66.12, H 6.99, N 5.71; found C 65.90, H 6.70, N 5.59.

SAMP-bishydrazone 11: According to GP3A, a solution of LDA (1.2 equiv.) and $LiClO_4$ (3.0 equiv.) in diethyl ether (6 mL) was treated with a solution of hydrazone **10** (1.00 g, 2.62 mmol) in diethyl ether (4 mL). After cooling to −100 °C, dimethyl disulfide (0.40 mL, 1.7 equiv.) was added dropwise. Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **11**. − Yield: 231 mg (50%, orange-red oil). − (*EE*)/(*EZ*) = 22:1. − R_f = 0.15 (hexane/diethyl ether = 4:1). −

de ≥ 96%. − $[\alpha]_D^{25}$ = +421.5 ($CHCl_3$, *c* = 0.78). − IR ($CHCl_3$): $\tilde{\nu}$ = 3099 cm^{-1}, 2969, 2919, 2873, 2730, 1674, 1572, 1450, 1377, 1340, 1295, 1247, 1198, 1186, 1110, 1049, 1029, 963, 912, 881, 827, 756, 719, 666, 519, 493. − ^{1}H NMR (400 MHz, C_6D_6): δ = 1.61 (d, ^3J = 7.7 Hz, 6 H, CHCH_3), 1.63−2.08 (m, 8 H, β-ring-CH_2), 1.90 (s, 6 H, SCH_3), 2.52 (q, $^{2/3}J$ = 8.5 Hz, 2 H, NCH_2), 2.93 (ddd, ^2J = 11.6 Hz, ^3J = 4.6 Hz, ^3J = 2.5 Hz, 2 H, NCH_2), 3.12 (s, 6 H, OCH_3), 3.23 (dd, ^2J = 8.8 Hz, ^3J = 7.2 Hz, 2 H, OCH_2), 3.51 (dd, ^2J = 8.8 Hz, ^3J = 4.1 Hz, 2 H, OCH_2), 3.58 (qd, ^3J = 7.4 Hz, ^3J = 3.9 Hz, 2 H, NCH), 4.22 (m, 2 H, *m*-C_5H_4R), 4.29 (m, 2 H, *m*-C_5H_4R), 4.90 (q, ^3J = 7.4 Hz, 2 H, SC*H*CH_3), 4.98 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 2 H, *o*-C_5H_4R), 5.23 (dt, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 2 H, *o*-C_5H_4R). − ^{13}C NMR (100 MHz, C_6D_6): δ = 15.3 (SCH_3), 19.2 (CH_3), 22.5 (NCH_2CH_2), 27.5 (NCH*C*H_2), 39.3 (SCH), 56.1 (NCH_2), 58.7 (OCH_3), 67.2, 69.2, 71.2, 71.69, 71.71 (C_5H_4R, NCH), 76.3 (OCH_2), 80.0 (*i*-C_5H_4R), 164.9 (C=N). − EI-MS; *m*/*z*: 614.2 (100) [M^+], 568.3 (13) [$M^+ - H_2C{=}S$], 335.1 (56) [$M^+ - C_5H_4R$], 187.1 (37), 142.1 (21), 75.1 (19). − HR-MS: $C_{30}H_{46}{}^{56}FeN_4O_2S_2$: calcd. 614.241159; found 614.241145.

General Procedure for the Preparation of Hydrazones 4 (GP4): A heated Schlenk flask was charged under argon with a solution of hydrazone **3** in dry THF (10−20 mL $mmol^{-1}$), then with either 3.0 equiv. (E^1 = SR) or 6.0 equiv. (E^1 = Ph_2PBH_3) of a 4 M $LiClO_4$ solution in diethyl ether and cooled to −70 °C. In cases where the solution became difficult to stir, more THF was added. To this suspension, either 1.1 equiv. (E^1 = SR) or 2.5 to 3.0 equiv. (E^1 = Ph_2PBH_3) *t*BuLi (1.5M in hexane) was added dropwise and the reaction mixture was stirred for 7 h at −70 °C. Afterwards, the electrophile E^2X = RSSR or a solution of the electrophile E^2X = Ph_2ClPBH_3 in THF was added dropwise. After warming to room temperature overnight, the reaction mixture was cooled to 0 °C and quenched with saturated aqueous NH_4Cl (E^2 = SR) or with saturated aqueous $NaHCO_3$ (E^2 = Ph_2PBH_3), washed twice with brine, and dried with $MgSO_4$. The crude product was filtered through silica gel (hexane/ether = 4:1) and dried under high vacuum.

Planar Chiral SAMP-hydrazone 4a: According to GP4, a solution of hydrazone **3d** (141 mg, 0.249 mmol) and $LiClO_4$ (6.0 equiv.) in THF (4 mL) was first treated with *t*BuLi (4.0 equiv.) and afterwards with methyl iodide (69 μL, 4.5 equiv.). Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 7:1) provided hydrazone **4a**. − Yield: 80 mg (55%, orange crystals). − R_f = 0.33 (hexane/diethyl ether = 4:1). − *de* = 96%. − $[\alpha]_D^{25}$ = −86.9 ($CHCl_3$, *c* = 0.82). − M.p.: 147 °C. − IR (KBr): $\tilde{\nu}$ = 3090 cm^{-1}, 3051, 2924, 2855, 2802, 2738, 2395, 2344, 2268, 1909, 1806, 1737, 1721, 1685, 1657, 1626, 1568, 1525, 1456, 1437, 1383, 1342, 1320, 1284, 1244, 1205, 1173, 1142, 1105, 1062, 999, 988, 889, 816, 802, 738, 693, 660, 619. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.00 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.60−2.14 (m, 6 H, CH_2CH_3, β-ring-CH_2), 1.88 (s, 3 H, H_3CCp), 2.47 (dt, ^2J = 9.4 Hz, ^3J = 8.1 Hz, 1 H, NCH_2), 3.10 (ddd, ^2J = 9.7 Hz, ^3J = 7.1 Hz, ^3J = 4.4 Hz, 1 H, NCH_2), 3.19 (s, 3 H, OCH_3), 3.30−3.40 (m, 3 H, OCH_2, NCH), 3.92 (s, 5 H, C_5H_5), 3.93 (m, 1 H, $C_5H_3R_2$), 3.95 (m, 1 H, $C_5H_3R_2$), 4.87 (m, 1 H, $C_5H_3R_2$), 5.27 (ddd, $^2J_{HP}$ = 14.4 Hz, ^3J = 9.7 Hz, ^3J = 4.0 Hz, PCH), 6.89 (m, 3 H), 7.06 (m, 1 H), 7.12 (m, 2 H, *m*/*p*-C_6H_5), 7.67 (m, 2 H, *o*-C_6H_5), 8.39 (ddm, $^3J_{HP}$ = 9.4 Hz, ^3J = 7.7 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 15.4, 15.8 (CH_3), 22.9 (NCH_2CH_2), 24.7, 27.0 (CH_2CH_3, NCHCH_2), 40.2 (d, $^1J_{CP}$ = 28.7 Hz, PCH), 57.1 (NCH_2), 59.1 (OCH_3), 66.6, 67.9, 70.0, 71.9 (NCH, $C_5H_3R_2$), 71.0 (C_5H_5), 75.4 (OCH_2), 86.9 (*i*-$C_5H_3R_2$), 128.9 (d, $^3J_{CP}$ = 9.7 Hz, *m*-C_6H_5), 129.8 (d, $^1J_{CP}$ = 53.5 Hz), 132.6 (d, $^1J_{CP}$ = 51.9 Hz, *i*-C_6H_5), 130.6 (d, $^4J_{CP}$ = 2.4 Hz), 131.1 (d, $^4J_{CP}$ = 2.4 Hz, *p*-C_6H_5), 133.8 (d, $^2J_{CP}$ = 9.8 Hz), 134.0 (d, $^2J_{CP}$ = 9.1 Hz, *o*-C_6H_5), 167.1 (C=N). − ^{31}P NMR (121 MHz, C_6D_6): δ = +22.0 (minor isomer: +25.0) (broad). − EI-MS; *m*/*z*: 580.2 (1) [M^+], 566.2 (48) [$M^+ - BH_3$], 452.1 (30) [566.1 − $C_6H_{12}NO$], 381.1 (100) [566.2 − PPh_2], 267.9 (75) [452.1 − $Ph_2P{-}BH_2$], 266.0 (69) [452.1 − $HPPh_2$], 241.0 (36), 224.8 (55) [$H_3CC_{10}H_8CNFe^+$], 184.8 (50) [Fc^+], 183.0 (81), 156.1 (91), 143.0 (23), 121.0 (45) [$CpFe^+$]. − $C_{33}H_{42}BFeN_2OP$ (580.3): calcd. C 68.30, H 7.29, N 4.83; found C 68.29, H 7.66, N 4.81.

Planar Chiral SAMP-hydrazone 4b: According to GP4, a solution of hydrazone **3d** (1.54 g, 2.72 mmol) and $LiClO_4$ (6.0 equiv.) in THF (30 mL) was first treated with *t*BuLi (3.0 equiv.) and afterwards with dimethyl disulfide (0.86 mL, 3.5 equiv.). Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4b**. − Yield: 1.08 g (65%, red crystals). − R_f = 0.20 (hexane/diethyl ether = 4:1). − *de* ≥ 90%. − $[\alpha]_D^{25}$ = −310.1 ($CHCl_3$, *c* = 0.74). − M.p.: 141 °C. − IR (KBr): $\tilde{\nu}$ = 3090 cm^{-1}, 3051, 2962, 2914, 2885, 2869, 2826, 2806, 2738, 2395, 2348, 2268, 1975, 1910, 1832, 1803, 1740, 1676, 1619, 1569, 1483, 1475, 1437, 1382, 1320, 1275, 1234, 1185, 1139, 1105, 1062, 1000, 965, 946, 914, 886, 812, 767, 736, 693, 643. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.05 (t, ^3J = 7.4 Hz, 3 H, CH_3), 1.65−2.08 (m, 4 H, CH_2), 1.87 (s, 3 H, SCH_3), 2.22 (m, 1 H, CH_2), 2.56 (broad q, $^{2/3}J$ = 8.7 Hz, 1 H, NCH_2), 2.82 (m, 1 H, CH_2), 3.13 (m, 1 H, NCH_2), 3.21 (s, 3 H, OCH_3), 3.42 (dd, ^2J = 9.1 Hz, ^3J = 4.7 Hz, 1 H, OCH_2), 3.48 (dd, ^2J = 9.1 Hz, ^3J = 6.0 Hz, 1 H, OCH_2), 3.64 (m, 1 H, NCH), 3.94 (s, 5 H, C_5H_5), 3.95 (t, ^3J = 2.7 Hz, $C_5H_3R_2$), 4.03 (dd, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, $C_5H_3R_2$), 5.15 (dd, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, $C_5H_3R_2$), 5.20 (m, 1 H, PCH), 6.88 (m, 3 H), 7.06−7.20 (m, 3 H, *m*/*p*-C_6H_5), 7.70 (ddd, *J* = 9.4 Hz, *J* = 8.1 Hz, *J* = 1.7 Hz, 2 H, *o*-C_6H_5), 8.50 (ddd, *J* = 9.7 Hz, *J* = 8.7 Hz, *J* = 1.7 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 16.1, 17.7 (CH_3), 23.5 (NCH_2CH_2), 25.0 (CH_2CH_3), 27.4 (NCHCH_2), 41.0 (d, $^1J_{CP}$ = 26.9 Hz, PCH), 57.7 (NCH_2), 59.5 (OCH_3), 67.1, 68.0, 70.3, 70.6 (NCH, $C_5H_3R_2$), 72.3 (C_5H_5), 75.5 (OCH_2), 79.5, 92.1 (*i*-$C_5H_3R_2$), 128.3 (d, J_{CP} = 8.5 Hz), 129.4 (d, J_{CP} = 9.7 Hz, *m*-C_6H_5), 129.8 (d, $^1J_{CP}$ = 62.0 Hz), 133.2 (d, $^1J_{CP}$ = 53.2 Hz, *i*-C_6H_5), 130.8, 131.7 (*p*-C_6H_5), 134.2 (d, J_{CP} = 9.2 Hz), 134.4 (d, J_{CP} = 8.6 Hz, *o*-C_6H_5), 165.4 (C=N). − ^{31}P NMR (121 MHz, C_6D_6): δ = +22.1 (broad). − EI-MS; *m*/*z*: 598.1 (11) [$M^+ - BH_3$], 484.0 (24) [598.1 − $C_6H_{12}NO$], 430.1 (13), 413.0 (38) [598.1 − PPh_2], 300.0 (17), 297.9 (13), 284.9 (46), 282.9 (36), 256.9 (12), 254.0 (10), 241.8 (12), 217.0 (11), 207.0 (11), 186.0 (12) [Cp_2Fe^+], 185.0 (34) [PPh_2^+], 184.0 (10), 183.0 (37) [$Ph_2P^+ - H_2$], 156.1 (100). − $C_{33}H_{42}BFeN_2OPS$ (612.4): calcd. C 64.72, H 6.91, N 4.57; found C 64.66, H 7.17, N 4.53.

Planar Chiral SAMP-hydrazone 4c: According to GP4, a solution of hydrazone **3c** (1.69 g, 3.06 mmol) and $LiClO_4$ (6.0 equiv.) in THF (20 mL) was first treated with *t*BuLi (2.5 equiv.) and afterwards with dimethyl disulfide (0.77 mL, 2.8 equiv.). Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 7:1) provided hydrazone **4c**. − Yield: 1.72 g (94%, red crystals). − R_f = 0.33 (hexane/diethyl ether = 4:1). − *de* ≥ 90%. − $[\alpha]_D^{25}$ = −287.9 ($CHCl_3$, *c* = 1.25). − Mp: 146 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3081 cm^{-1}, 3056, 2973, 2920, 2873, 2829, 2736, 2387, 2278, 1574, 1438, 1385, 1354, 1335, 1315, 1278, 1242, 1218, 1187, 1106, 1058, 1030, 1001, 970, 905, 878, 818, 756, 699, 666, 649, 560, 517, 501, 470, 454. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.55−2.12 (m, 4 H, β-ring-CH_2), 1.82 (dd, $^3J_{HP}$ = 16.8 Hz, ^3J = 7.7 Hz, 3 H, CHCH_3), 1.86 (s, 3 H, SCH_3), 2.47 (td, $^{2/3}J$ = 9.1 Hz, ^3J = 7.4 Hz, 1 H, NCH_2), 3.08 (ddd, ^2J = 9.7 Hz, ^3J = 7.7 Hz, ^3J = 5.4 Hz, 1

H, NCH_2), 3.22 (s, 3 H, OCH_3), 3.41 (dd, ^2J = 9.1 Hz, ^3J = 7.1 Hz, 1 H, OCH_2), 3.54 (dd, ^2J = 9.1 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 3.72 (qd, ^3J = 7.7 Hz, ^3J = 3.7 Hz, 1 H, NCH), 3.92 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 3.93 (s, 5 H, C_5H_5), 4.02 (dd, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, $C_5H_3R_2$), 5.11 (dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 5.14 (dq, $^2J_{HP}$ = 16.5 Hz, ^3J = 7.7 Hz, 1 H, PCH), 6.88−7.13 (m, 6 H, 1 H, *m*/*p*-C_6H_5), 7.78 (ddd, *J* = 9.7 Hz, *J* = 8.4 Hz, *J* = 1.7 Hz, 2 H), 8.29 (ddd, *J* = 9.7 Hz, *J* = 8.5 Hz, *J* = 1.4 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 15.6 (d, $^2J_{CP}$ = 4.3 Hz, $CHCH_3$), 17.3 (SCH_3), 22.9 (NCH_2CH_2), 27.0 ($NCHCH_2$), 33.2 (d, $^1J_{CP}$ = 28.6 Hz, $CHCH_3$), 56.8 (NCH_2), 59.0 (OCH_3), 66.7, 67.4, 67.5, 69.9 (NCH, $C_5H_3R_2$), 71.7 (C_5H_5), 75.5 (OCH_2), 79.0, 91.0 (*i*-$C_5H_3R_2$), 128.9 (d, J_{CP} = 9.8 Hz, *m*-C_6H_5), 133.61 (d, J_{CP} = 9.1 Hz), 133.63 (d, J_{CP} = 8.6 Hz, *o*-C_6H_5), 129.8 (d, $^1J_{CP}$ = 48.2 Hz), 132.0 (d, $^1J_{CP}$ = 51.7 Hz, *i*-C_6H_5), 130.7 (d, $^4J_{CP}$ = 2.4 Hz), 131.1 (d, $^4J_{CP}$ = 2.5 Hz, *p*-C_6H_5), 163.7 (C=N). − ^{31}P NMR (121 MHz, C_6D_6): δ = +24.1 (broad). − EI-MS; *m*/*z*: 584.2 (5) [$M^+ - BH_3$], 399.0 (14) [384.2 − Ph_2P], 271.0 (21), 268.9 (11) [399.0 − $C_6H_{14}N_2O$], 185.1 (14) [Ph_2P^+], 183.0 (21) [$Ph_2P^+ - H_2$], 142.1 (100), 121.0 (13) [$CpFe^+$]. − $C_{32}H_{40}BFeN_2OPS$ (598.4): calcd. C 64.23, H 6.74, N 4.68; found C 64.01, H 6.62, N 4.57.

Planar Chiral SAMP-hydrazone 4d: According to GP4, a solution of hydrazone **3i** (140 mg, 0.289 mmol) and $LiClO_4$ (6.0 equiv.) in THF (6 mL) was first treated with *t*BuLi (2.5 equiv.) and afterwards with a solution of di-*p*-tolyl disulfide (249 mg, 3.5 equiv.) in THF (1 mL). Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 7:1) provided hydrazone **4d**. − Yield: 133 mg (76%, orange powder). − R_f = 0.61 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −294.2 ($CHCl_3$, *c* = 0.59). − M.p.: 133 °C. − IR ($CHCl_3$): ṽ = 3096 cm^{-1}, 1964, 2932, 2874, 2828, 2379, 1597, 1568, 1492, 1461, 1412, 1387, 1354, 1320, 1302, 1218, 1183, 1107, 1057, 1002, 970, 906, 886, 813, 757, 684, 667, 631, 507, 488. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.94 (dd, $^3J_{HP}$ = 12.6 Hz, ^3J = 6.9 Hz, 3 H), 1.07 (dd, $^3J_{HP}$ = 15.1 Hz, ^3J = 7.2 Hz, 3 H), 1.11 (dd, $^3J_{HP}$ = 12.9 Hz, ^3J = 7.1 Hz, 3 H), 1.16 (dd, $^3J_{HP}$ = 13.7 Hz, ^3J = 7.1 Hz, 3 H, $P[CH(CH_3)_2]_2$), 1.60−2.03 [m, 6 H, β-ring-CH_2, $PCH(CH_3)_2$], 2.06 (s, 3 H, $C_6H_4CH_3$), 1.76 (dd, $^2J_{HP}$ = 14.5 Hz, ^3J = 7.7 Hz, 3 H, N=CCHCH_3), 2.49 (td, ^2J = ^3J = 9.1 Hz, ^3J = 8.0 Hz, 1 H, NCH_2), 3.13 (s, 3 H, OCH_3), 3.15 (m, 1 H, NCH_2), 3.35 (dd, ^2J = 9.3 Hz, ^3J = 6.3 Hz, 1 H, OCH_2), 3.52 (dd, ^2J = 9.3 Hz, ^3J = 3.7 Hz, 1 H, OCH_2), 3.64 (m, 1 H, NCH), 3.99 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 4.03 (s, 5 H, C_5H_5), 4.13 (dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.23 (dq, $^2J_{HP}$ = 16.2 Hz, ^3J = 7.7 Hz, 1 H, N=CCH), 5.20 (dd, ^3J = 3.0 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 6.90 (br. d, ^3J = 7.7 Hz, 2 H, C_6H_4), 7.41 (dt, ^3J = 8.0 Hz, ^4J = 1.7 Hz, 2 H, C_6H_4). − ^{13}C NMR (75 MHz, C_6D_6): δ = 16.7, 17.6, 17.9, 18.5, 18.8, 21.0 (CH_3), 22.3 (d, $^1J_{CP}$ = 31.8 Hz), 24.7 (d, $^1J_{CP}$ = 30.3, PCH), 22.7 (NCH_2CH_2), 26.4 ($NCHCH_2$), 27.9 (d, $^1J_{CP}$ = 22.9, PCH) 56.6 (NCH_2), 58.7 (OCH_3), 67.5, 68.0, 71.1, 72.5 ($C_5H_3R_2$, NCH), 72.1 (C_5H_5), 74.6 (OCH_2), 80.1, 87.3 (*i*-$C_5H_3R_2$), 129.9, 131.7 (C_6H_4), 135.4, 136.4 (*i*-C_6H_4), 163.0 (C=N). − ^{31}P NMR (121 MHz, C_6D_6): δ = +43.0 (broad). − CI-MS (isobutane); *m*/*z*: 606.3 (56) [M^+], 605.2 (100) [$M^+ - H$], 593.2 (31) [$MH^+ - BH_3$], 592.2 (15) [$M^+ - BH_3$], 549.1 (13) [592.2 − $CH(CH_3)_2$], 492.1 (18) [$M^+ - C_6H_{12}NO$], 116.1 (11) [$(H_3C)_2C=PCH(CH_3)_2^+$]. − $C_{32}H_{48}BFeN_2OPS$ (606.4): calcd. C 62.01, H 8.74, N 5.78; found C 62.18, H 8.67, N 6.27.

Planar Chiral SAMP-hydrazone 4e: According to GP4, a solution of hydrazone **3f** (123 mg, 0.249 mmol) and $LiClO_4$ (3.0 equiv.) in THF (3.5 mL) was first treated with *t*BuLi (1.3 equiv.) and afterwards with methyl iodide (31 μL, 1.7 equiv.). Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4e**. − Yield: 104 mg (83%, yellow oil). − R_f = 0.50 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −90.2 ($CHCl_3$, *c* = 0.66). − IR (KBr): ṽ = 3086 cm^{-1}, 2962, 2923, 2872, 2825, 2724, 2247, 2066, 1704, 1659, 1561, 1454, 1426, 1377, 1345, 1277, 1254, 1231, 1159, 1129, 1104, 1047, 1001, 970, 905, 882, 822, 797, 718, 679, 650, 592, 490. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.17 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.55−2.05 (m, 6 H, CH_2CH_3, β-ring-CH_2), 1.84 (s, 3 H, SCH_3), 2.42 (s, 3 H, $CpCH_3$), 2.46 (m, 1 H, NCH_2), 3.02 (ddd, ^2J = 9.1 Hz, ^3J = 7.7 Hz, ^3J = 4.4 Hz, 1 H, NCH_2), 3.13 (s, 3 H, OCH_3), 3.27 (m, 1 H, OCH_2), 3.48 (m, 2 H, OCH_2, NCH), 3.99 (t, ^3J = 2.7 Hz, 1 H, C_5H_4R), 4.03 (s, 5 H, C_5H_5), 4.13 (dd, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, C_5H_4R), 4.50 (dd, ^3J = 2.8 Hz, ^4J = 1.4 Hz, 1 H, C_5H_4R), 4.65 (dd, ^3J = 10.2 Hz, ^3J = 5.0 Hz, 1 H, SCH). − ^{13}C NMR (75 MHz, C_6D_6): δ = 14.2, 15.7, 17.4 (SCH_3, CH_3), 23.0 (NCH_2CH_2), 27.4, 27.8 (CH_2CH_3, $NCHCH_2$), 48.6 (SCH), 57.4 (NCH_2), 59.3 (OCH_3), 67.1, 67.9, 70.2, 72.1 (C_5H_4R, NCH), 71.3 (C_5H_5), 76.5 (OCH_2), 80.6, 86.6 (*i*-C_5H_4R), 168.3 (C=N). − EI-MS; *m*/*z*: 428.1 (100) [M^+], 381.0 (11) [$M^+ - CH_3S$], 335.1 (15) [$M^+ - CH_3SH - CH_2OCH_3$], 314.1 (10) [$M^+ - C_6H_{12}NO$], 268.1 (16), 267.3 (12), 266.0 (37) [314.1 − CH_3SH], 243.9 (11), 241.0 (17), 226.0 (23), 224.9 (73) [$C_8H_{10}FeCH_3CN^+$], 158.8 (15), 156.1 (40), 143.0 (15), 133.8 (12), 121.0 (54) [$CpFe^+$], 90.9 (12), 89.1 (61), 45.3 (18) [$CH_3OCH_2^+$]. − HR-MS: $C_{22}H_{32}{}^{56}FeN_2OS$: calcd. 428.158472; found 428.158957.

Planar Chiral SAMP-hydrazone 4f: According to GP4, a solution of hydrazone **3e** (2.00 g, 5.00 mmol) and $LiClO_4$ (3.0 equiv.) in THF (30 mL) was first treated with *t*BuLi (1.2 equiv.) and afterwards with a solution of $Ph_2PCl{\cdot}BH_3$ (1.3 equiv.) in THF (3 mL). Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4f**. − Yield: 2.57 g (86%, orange crystals). − R_f = 0.23 (hexane/diethyl ether = 4:1). − *de* = 96%. − $[\alpha]_D^{25}$ = +10.8 ($CHCl_3$, *c* = 0.69). − M.p.: 131 °C. − IR ($CHCl_3$): ṽ = 3078 cm^{-1}, 3056, 3001, 2970, 2920, 2873, 2826, 2734, 2615, 2586, 2392, 2279, 2112, 1960, 1892, 1814, 1775, 1664, 1588, 1573, 1484, 1450, 1436, 1383, 1355, 1342, 1324, 1282, 1218, 1197, 1162, 1137, 1107, 1060, 1029, 1002, 971, 910, 825, 753, 696, 667, 633, 608, 550, 524. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.55−2.15 (m, 4 H, β-ring-CH_2), 1.66 (d, ^3J = 7.7 Hz, 3 H, $CHCH_3$), 1.79 (s, 3 H, SCH_3), 2.18 (dd, ^2J = 9.1 Hz, ^3J = 3.7 Hz, 1 H, OCH_2), 2.30 (dd, ^2J = 9.1 Hz, ^3J = 3.7 Hz, 1 H, OCH_2), 2.89 (s, 3 H, OCH_3), 3.00−3.20 (m, 2 H, NCH_2), 3.41 (td, ^3J = J_{HP} = 2.7 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.01 (td, ^3J = 2.7 Hz, $^4J_{HP}$ = 0.7 Hz, 1 H, $C_5H_3R_2$), 4.32 (s, 5 H, C_5H_5), 4.79 (q, ^3J = 7.7 Hz, 1 H, $CHCH_3$), 5.26 (dt, ^3J = 3.0 Hz, ^4J = $^4J_{HP}$ = 1.4 Hz, 1 H, $C_5H_3R_2$), 6.96−7.05 (m, 6 H, *m*/*p*-C_6H_5), 7.64 (tm, ^3J = 8.0 Hz, 2 H, *o*-C_6H_5), 7.77 (tm, ^3J = 7.5 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 15.0, 18.8 (CH_3, SCH_3), 24.4 (NCH_2CH_2), 28.0 ($NCHCH_2$), 39.7 (SCH), 58.4 (OCH_3), 59.2 (NCH_2), 64.8 (NCH), 70.9 (d, J_{CP} = 5.5 Hz), 74.1 (d, J_{CP} = 5.5 Hz), 76.0 (d, J_{CP} = 4.3 Hz, $C_5H_3R_2$), 71.6 (C_5H_5), 74.9 (OCH_2), 85.2 (d, $^1J_{CP}$ = 9.0 Hz, $C_5H_3R_2$), 129.7, 130.2 (*p*-C_6H_5), 132.5 (d, $^2J_{CP}$ = 8.0 Hz), 134.5 (d, $^2J_{CP}$ = 7.9 Hz, *o*-C_6H_5), 135.4 (d, $^1J_{CP}$ = 53.7 Hz, *i*-C_6H_5). − ^{31}P NMR (C_6D_6, 162 MHz): +19.0 (broad). − EI-MS; *m*/*z*: 537.1 (27) [$M^+ - BH_3 - SCH_3$], 424.0 (51) [$M^+ - BH_3 - H_2C=S - C_6H_{12}NO$], 240.0 (36), 186.0 (33) [Cp_2Fe^+], 185.0 (100) [PPh_2^+]. − $C_{32}H_{40}BFeN_2OPS$ (598.4): calcd. C 64.23, H 6.74, N 4.68; found C 64.24, H 6.60, N 4.66.

Planar Chiral SAMP-hydrazone 4g: According to GP4, a solution of hydrazone **3f** (2.31 g, 5.57 mmol) and $LiClO_4$ (3.0 equiv.) in THF (30 mL) was first treated with *t*BuLi (1.1 equiv.) and afterwards with a solution of $Ph_2PCl{\cdot}BH_3$ (1.3 equiv.) in THF (3 mL). Aque-

ous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4g**. − Yield: 2.62 g (77%, orange powder). − R_f = 0.47 (hexane/diethyl ether = 4:1). − *de* ≥ 90%. − $[\alpha]_D^{25}$ = −35.2 ($CHCl_3$, *c* = 0.52). − M.p.: 133 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3076 cm^{-1}, 3056, 2969, 2921, 2872, 2826, 2391, 2351, 2279, 1588, 1437, 1385, 1325, 1278, 1218, 1187, 1160, 1136, 1107, 1060, 1029, 1003, 970, 948, 906, 825, 755, 696, 667, 631, 524, 499. − ^{1}H NMR (300 MHz, C_6D_6): δ =1.25 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.57−2.12 (m, 7 H, CH_2CH_3, β-ring-CH_2, NCH_2), 1.80 (s, 3 H, SCH_3), 2.17 (dd, ^2J = 8.7 Hz, ^3J = 6.3 Hz, OCH_2), 2.88 (s, 3 H, OCH_3), 3.13 (dd, ^2J = 8.5 Hz, ^3J = 6.1 Hz, 1 H, OCH_2), 3.25 (m, 1 H, NCH_2), 3.44 (td, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 3.84 (m, 1 H, NCH), 4.06 (td, ^3J = 2.8 Hz, $^4J_{HP}$ = 0.6 Hz, 1 H, $C_5H_3R_2$), 4.34 (s, 5 H, C_5H_5), 4.56 (dd, ^3J = 10.4 Hz, ^3J = 4.1 Hz, 1 H, SCH), 5.17 (dt, ^3J = 2.4 Hz, ^4J = J_{HP} = 1.4 Hz, 1 H, $C_5H_3R_2$), 6.92−7.07 (m, 5 H), 7.43 (ddd, *J* = 9.6 Hz, *J* = 8.0 Hz, *J* = 1.7 Hz, 1 H, *m*/*p*-C_6H_5), 7.64 (tm, ^3J = 8.5 Hz, 2 H), 7.76 (tm, ^3J = 8.0, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 14.2, 14.7 (CH_3), 24.3 (NCH_2CH_2), 26.3, 27.8 (CH_2CH_3, $NCHCH_2$), 47.9 (SCH), 58.3 (OCH_3), 59.3 (NCH_2), 64.8 (NCH), 68.2 (d, $^1J_{CP}$ = 65.9, *i*-$C_5H_3R_2$), 70.7 (d, J_{CP} = 6.9 Hz), 74.3 (d, J_{CP} = 5.2 Hz), 74.7 ($C_5H_3R_2$), 71.5 (C_5H_5), 75.9 (OCH_2), 85.7 (d, $^2J_{CP}$ = 7.5 Hz, *i*-$C_5H_3R_2$), 129.1 (d, J_{CP} = 10.3 Hz), 132.4 (d, J_{CP} = 8.6 Hz, *m*-C_6H_5), 133.2 (d, J_{CP} = 9.2 Hz), 134.5 (d, J_{CP} = 8.0 Hz, *o*-C_6H_5), 129.6 (d, $^4J_{CP}$ = 2.3 Hz), 130.1 (d, $^4J_{CP}$ 1.7 Hz, *p*-C_6H_5), 135.3 (d, $^1J_{CP}$ = 49.9 Hz), 135.6 (d, $^1J_{CP}$ = 60.7 Hz, *i*-C_6H_5), 156.2 (d, $^3J_{CP}$ = 2.2 Hz, C=N). − ^{31}P NMR (121 MHz, C_6D_6): δ = +18.8 (broad). − EI-MS; *m*/*z*: 484.0 (9) [$M^+ - BH_3 - C_6H_{12}NO$], 438.0 (15) [484.0 − H_2C=S], 199.1 (11) [$Ph_2P-BH_3^+$], 185.0 (19) [PPh_2^+], 183.0 (16) [$PPh_2^+ - H_2$], 121.0 (11) [$CpFe^+$], 83.2 (13), 70.2 (13), 66.2 (100) [$C_5H_6^+$], 65.1 (75) [Cp^+], 63.2 (11), 48.2 (57), 47.1 (82) [H_3CS^+], 45.3 (37) [$H_3COCH_2^+$]. − $C_{33}H_{42}BFeN_2OPS$ (612.4): calcd. C 64.72, H 6.91, N 4.57; found C 65.09, H 7.09, N 4.24.

Planar Chiral SAMP-hydrazone 4h: According to GP4, a solution of hydrazone **3f** (210 mg, 0.507 mmol) and $LiClO_4$ (3.0 equiv.) in THF (6 mL) was first treated with *t*BuLi (1.2 equiv.) and afterwards with *i*Pr_2PCl (1.3 equiv.) in THF (3 mL). After warming to room temperature overnight, the solution was cooled down to 0 °C, treated with 1.7 equiv. BH_3DMS and stirred for 3 h. Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4h**. − Yield: 257 mg (93%, orange-red crystals). − R_f = 0.37 (hexane/diethyl ether = 4:1). − *de* ≥ 90%. − $[\alpha]_D^{25}$ = +52.6 ($CHCl_3$, *c* = 0.67). − M.p.: 90 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3098 cm^{-1}, 2965, 2927, 2872, 2731, 2377, 2278, 1711, 1660, 1565, 1461, 1384, 1322, 1284, 1252, 1219, 1200, 1109, 1060, 1005, 967, 946, 931, 886, 824, 757, 688, 667, 647, 578, 496, 462. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.07 (dd, $^3J_{HP}$ = 13.1 Hz, ^3J = 7.1 Hz, 3 H, $PCHCH_3$), 1.18 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.26 (dd, $^3J_{HP}$ = 14.8 Hz, ^3J = 7.1 Hz, 6 H, $PCHCH_3$), 1.55 (dd, $^3J_{HP}$ = 15.5 Hz, ^3J = 7.4 Hz, 3 H, $PCHCH_3$), 1.60−1.68 (m, 3 H), 1.93−2.12 (m, 3 H, CH_2CH_3, β-ring-CH_2), 1.86 (s, 3 H, SCH_3), 2.34 (dsept, $^2J_{HP}$ = 10.7 Hz, ^3J = 7.1 Hz, 1 H, PCH), 2.59 (dt, ^2J = 9.1 Hz, ^3J = 8.1 Hz, 1 H, NCH_2), 3.04 (s, 3 H, OCH_3), 3.10 (dd, ^2J = 9.1 Hz, ^3J = 6.7 Hz, 1 H, OCH_2), 3.10 (m, 1 H, NCH), 3.25 (dd, ^2J = 9.1 Hz, ^3J = 4.4 Hz, 1 H, OCH_2), 3.39 (dsept, $^2J_{HP}$ = 16.1 Hz, ^3J = 7.4 Hz, 1 H, PCH), 3.44 (td, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 3.72 (m, 1 H, NCH_2), 4.18 (s, 5 H, C_5H_5), 4.24 (td, ^3J = 2.7 Hz, $^4J_{HP}$ = 1.0 Hz, 1 H, $C_5H_3R_2$), 4.60 (m, 1 H, SCH), 4.98 (m, 1 H, $C_5H_3R_2$). − ^{13}C NMR (75 MHz, C_6D_6): δ = 14.1, 16.2 (CH_3), 18.0, 18.9 (d, $^2J_{CP}$ = 1.8 Hz), 19.1 (d, $^2J_{CP}$ = 1.9 Hz), 19.6 (d, $^2J_{CP}$ = 1.8 Hz, $PCHCH_3$), 23.3 (NCH_2CH_2), 24.3 (d, $^1J_{CP}$ = 27.4 Hz), 24.7 (d, $^1J_{CP}$ = 26.2 Hz, PCH), 27.7, 28.1 (CH_2CH_3, $NCHCH_2$), 48.7 (SCH), 57.8 (NCH_2), 58.8 (OCH_3), 66.1 (NCH), 71.1 (d, J_{CP} = 8.5 Hz), 75.5 (d, J_{CP} = 4.2 Hz), 78.4 (d, J_{CP} = 13.4 Hz, $C_5H_3R_2$), 71.8 (C_5H_5), 76.3 (OCH_2), 165.3 (C=N). − ^{31}P NMR (121 MHz, C_6D_6): δ = +36.6 (broad). − CI-MS (isobutane); *m*/*z*: 544.2 (40) [M^+], 543.1 (100) [$M^+ - H$], 31.1 (2) [$MH^+ - BH_3$], 497.2 (15) [$M^+ - SCH_3$], 496.3 (16) [$M^+ - HSCH_3$], 495.2 (2), 483.0 (28) [497.2 − BH_3], 430.0 (20) [$M^+ - C_6H_{12}NO$], 415.9 (15) [430.0 − BH_3], 75.2 (17). − $C_{27}H_{46}BFeN_2OPS$ (544.4): calcd. C 59.57, H 8.52, N 5.15; found C 59.94, H 8.63, N 4.74.

Planar Chiral SAMP-hydrazone 4i: According to GP4, a solution of hydrazone **3g** (1.05 g, 2.45 mmol) and $LiClO_4$ (3.0 equiv.) in THF (25 mL) was first treated with *t*BuLi (1.2 equiv.) and afterwards with a solution of Ph_2PClBH_3 (1.6 equiv.) in THF (6 mL). Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4i**. − Yield: 1.11 g (73%, orange powder). − R_f = 0.25 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −25.7 ($CHCl_3$, *c* = 0.51). − M.p.: 143 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3077 cm^{-1}, 3056, 3000, 2967, 2926, 2868, 2825, 2432, 2391, 2353, 2259, 1588, 1573, 1550, 1483, 1451, 1436, 1413, 1383, 1366, 1341, 1326, 1283, 1247, 1218, 1198, 1161, 1137, 1107, 1060, 1003, 973, 911, 825, 756, 696, 667, 638, 617, 593, 562. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.14 (d, ^3J = 7.1 Hz, 3 H, $SCHCH_3$), 1.25 (d, ^3J = 6.4 Hz, 3 H, $SCHCH_3$), 1.53−2.23 (m, 4 H, β-ring-CH_2), 1.71 (d, ^3J = 7.7 Hz, 3 H, N=$CCHCH_3$), 2.30 (dd, ^2J = 6.1 Hz, ^3J = 1.7 Hz, 2 H, OCH_2), 2.67 [sept, ^3J = 7.1 Hz, 1 H, $SCH(CH_3)_2$], 2.94 (s, 3 H, OCH_3), 3.06 (td, $^{2/3}J$ = 8.7 Hz, ^3J = 6.0 Hz, 1 H, NCH_2), 3.26 (dt, ^2J = 8.7 Hz, ^3J = 7.1 Hz, 1 H, NCH_2), 3.39 (td, ^3J = J_{HP} = 2.7 Hz, ^4J = 1.3 Hz, 1 H, $C_5H_3R_2$), 3.96 (m, 1 H, NCH), 4.00 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.33 (s, 5 H, C_5H_5), 4.79 (q, ^3J = 7.4 Hz, 1 H, N=CCH), 5.29 (dt, ^3J = 2.7 Hz, ^4J = $^4J_{HP}$ = 1.3 Hz, 1 H, $C_5H_3R_2$), 7.03 (m, 6 H, *m*/*p*-C_6H_5), 7.65 (m, 2 H, *o*-C_6H_5), 7.77 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 19.9, 23.9, 25.0 (CH_3), 24.4 (NCH_2CH_2), 28.0 ($NCHCH_2$), 36.0, 37.6 (SCH), 58.4 (OCH_3), 59.5 (NCH_2), 64.9 (NCH), 70.7 (d, J_{CP} = 6.7 Hz), 74.0 (d, J_{CP} = 4.9 Hz), 76.0 (d, J_{CP} = 4.3 Hz, $C_5H_3R_2$), 71.5 (C_5H_5), 75.3 (OCH_2), 129.5, 130.1 (*p*-C_6H_5), 132.5 (d, $^2J_{CP}$ = 8.6 Hz), 134.5 (d, $^2J_{CP}$ = 7.9 Hz, *o*-C_6H_5), 135.2 (d, $^1J_{CP}$ = 61.0 Hz), 135.3 (d, $^1J_{CP}$ = 49.4 Hz, *i*-C_6H_5), 157.0 (C=N). − ^{31}P NMR (C_6D_6, 162 MHz): +19.2 (broad). − CI-MS (isobutane): *m*/*z*: 627.2 (5) [MH^+], 626.2 (3) [M^+], 625.2 (5) [$M^+ - H$], 613.0 (50) [627.2 − BH_3], 537.2 (100) [610.0 − $HSCH(CH_3)_2$], 498.0 (26) [$M^+ - BH_3 - C_6H_{12}NO$], 424.0 (18) [498.0 − $S=C(CH_3)_2$], 128.0 (15) [$C_{10}H_8^+$], 126.0 (11), 116.1 (20), 114.0 (11) [$C_6H_{12}NO^+$], 77.2 (11) [$H_2SCH(CH_3)_2^+$]. − $C_{34}H_{44}BFeN_2OPS$ (626.4): calcd. C 65.19, H 7.08, N 4.47; found C 65.24, H 7.05, N 4.19.

Planar Chiral SAMP-hydrazone 4j: According to GP4, a solution of hydrazone **3f** (1.55 g, 3.75 mmol) and $LiClO_4$ (4.0 equiv.) in THF (30 mL) was first treated with *t*BuLi (2.0 equiv.) and afterwards with dimethyl disulfide (0.81 mL, 2.4 equiv.). Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4j**. − Yield: 1.70 g (98%, orange powder). − R_f = 0.50 (hexane/diethyl ether = 4:1). − *de* ≥ 90%. − $[\alpha]_D^{25}$ = −432.3 ($CHCl_3$, *c* = 0.55). − M.p.: 89 °C. − IR (KBr): $\tilde{\nu}$ = 3106 cm^{-1}, 3080, 2965, 2915, 2869, 2828, 2733, 2252, 1736, 1719, 1701, 1665, 1636, 1572, 1511, 1474, 1448, 1389, 1353, 1331, 1277, 1245, 1191, 1122, 1104, 1047, 1000, 969, 943, 913, 902, 815, 757, 717, 686, 668, 626, 594, 517, 500, 486, 460. − ^{1}H NMR (300 MHz, C_6D_6): δ =1.22 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.59−1.86 (m, 3 H), 1.94−2.12 (m, 3 H, CH_2CH_3, β-ring-CH_2), 1.87 (s, 3 H), 2.10 (s, 3 H, SCH_3), 2.58 (td, ^2J = 9.1 Hz, ^3J =

7.7 Hz, 1 H, NCH_2), 3.08 (ddd, ^2J = 9.1 Hz, ^3J = 7.4 Hz, ^3J = 4.4 Hz, 1 H, NCH_2), 3.18 (s, 3 H, OCH_3), 3.40 (dd, ^2J = 9.1 Hz, ^3J = 7.2 Hz, 1 H, OCH_2), 3.72 (dd, ^2J = 8.8 Hz, ^3J = 3.8 Hz, 1 H, OCH_2), 3.79 (qd, ^3J = 7.1 Hz, ^3J = 3.8 Hz, 1 H, NCH), 3.99 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 4.04 (s, 5 H, C_5H_5), 4.20 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.66 (dd, ^3J = 10.7 Hz, ^3J = 4.7 Hz, 1 H, SCH), 4.70 (dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.8, 15.1, 17.4 (CH_3), 22.6 (NCH_2CH_2), 26.6, 27.2 ($NCHCH_2$, CH_2CH_3), 47.6 (SCH), 56.9 (NCH_2), 58.7 (OCH_3), 66.6, 66.8, 67.1, 69.8 (NCH, $C_5H_3R_2$), 71.6 (C_5H_5), 75.6 (OCH_2), 79.0, 91.1 ($C_5H_3R_2$), 164.8 (C=N). − EI-MS; *m*/*z*: 460.0 (100) [M^+], 413.0 (11) [$M^+ - SCH_3$], 381.0 (22), 366.9 (11) [413.0 − H_2C=S], 345.9 (21) [$M^+ - C_6H_{12}NO$], 299.9 (11) [345.9 − H_2C=S], 298.9 (10) [345.9 − H_3CS], 297.9 (23) [345.9 − H_3CSH], 284.9 (22), 282.9 (28), 268.0 (19), 256.9 (23) [$H_3CS-C_{10}H_8Fe-CN^+$], 246.9 (15), 241.9 (14), 210.9 (11) [$FcCN^+$], 184.9 (15) [Fc^+], 170.0 (13), 156.0 (53), 120.9 (30) [$CpFe^+$], 89.0 (29). − $C_{22}H_{32}FeN_2OS_2$ (460.5): calcd. C 57.38, H 7.00, N 6.08; found C 57.33, H 6.90, N 6.01.

Planar Chiral SAMP-hydrazone 4k: According to GP4, a solution of hydrazone **3h** (697 mg, 1.58 mmol) and $LiClO_4$ (3.0 equiv.) in THF (8 mL) was first treated with *t*BuLi (1.1 equiv.) and afterwards with a solution of di-*p*-tolyl disulfide (600 mg, 1.7 equiv.) in THF (3 mL). Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4k**. − Yield: 792 mg (89%, orange crystals). − R_f = 0.69 (hexane/diethyl ether = 4:1). − *de* ≥ 90%. − $[\alpha]_D^{25}$ = −219.7 ($CHCl_3$, *c* = 0.84). − Mp: 105 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3017 cm^{-1}, 2960, 2923, 2868, 2827, 2732, 1631, 1596, 1491, 1451, 1382, 1331, 1304, 1274, 1244, 1199, 1182, 1108, 1050, 1017, 1002, 971, 944, 909, 806, 636, 486. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.05 (d, ^3J = 6.7 Hz, 3 H, $CHCH_3$), 1.24 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.29 (d, ^3J = 6.4 Hz, 3 H, $CHCH_3$), 1.52−2.07 (m, 6 H, β-ring-CH_2, CH_2CH_3), 2.03 (s, 3 H, $C_6H_4CH_3$), 2.58 (td, $^{2/3}J$ = 9.1 Hz, ^3J = 7.7 Hz, 1 H, NCH_2), 2.85 (sept, ^3J = 6.7 Hz, 1 H, $SCH(CH_3)_2$), 3.15 (m, 1 H, NCH_2), 3.20 (s, 3 H, OCH_3), 3.40 (dd, ^2J = 9.7 Hz, ^3J = 8.4 Hz, 1 H, OCH_2), 3.72 (m, 1 H, NCH), 3.73 (dd, ^2J = 10.1 Hz, ^3J = 3.7 Hz, 1 H, OCH_2), 3.97 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 4.12 (s, 5 H, C_5H_5), 4.24 (dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.58 (dd, ^3J = 10.1 Hz, ^3J = 4.7 Hz, 1 H, N=CCH), 4.61 (dd, ^3J = 2.7 Hz, ^4J = 1.3 Hz, 1 H, $C_5H_3R_2$), 6.88 (dm, ^3J = 8.4 Hz, 2 H, C_6H_4), 7.42 (dm, ^3J = 8.1 Hz, 2 H, C_6H_4). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.7, 20.9, 23.5, 24.6 (CH_3), 22.8 (NCH_2CH_2), 27.26, 27.31 ($NCHCH_2$, CH_2CH_3), 35.8, 45.6 (SCH), 57.0 (NCH_2), 58.8 (OCH_3), 67.4, 67.8, 69.7, 72.6 (NCH, $C_5H_3R_2$), 72.1 (C_5H_5), 75.7 (OCH_2), 81.1, 86.6 (*i*-$C_5H_3R_2$), 129.8, 130.8 (C_6H_4), 135.8, 136.4 (*i*-C_6H_4), 165.5 (C=N). − EI-MS; *m*/*z*: 564.1 (80) [M^+], 489.0 (18) [$M^+ - SCH(CH_3)_2$], 488.0 (28) [$M^+ - HSCH(CH_3)_2$], 443.0 (15) [488.0 − CH_2OCH_3], 376.0 (20) [$M^+ - C_5H_5 - SC_7H_7$], 375.1 (19), 374.0 (41) [488.0 − $C_6H_{12}NO$], 332.8 (34), 307.8 (19) [$Fc-S-C_7H_7^+$], 284.9 (23), 244.0 (15), 241.9 (15), 211.0 (15) [$FcCN^+$], 184.9 (26) [Fc^+], 156.0 (100) [$FcCNH^+ - Fe$], 151.0 (15), 120.9 (69) [$CpFe^+$], 117.0 (34), 91.0 (28) [$C_7H_7^+$], 76.1 (97), 75.1 (41) [$SCH(CH_3)_2$], 74.1 (61), 73.1 (15), 70.1 (25), 61.1 (60), 59.1 (82), 58.2 (20), 47.2 (19), 45.3 (77) [$CH_3OCH_2^+$]. − $C_{30}H_{40}FeN_2OS_2$ (564.6): calcd. C 63.82, H 7.14, N 4.96; found C 64.00, H 7.19, N 4.81.

Planar Chiral SAMP-hydrazone 4l: According to GP4, a solution of hydrazone **3h** (508 mg, 1.15 mmol) and $LiClO_4$ (3.0 equiv.) in THF (6 mL) was first treated with *t*BuLi (1.2 equiv.) and afterwards with a solution of phenyl selenenyl bromide (461 mg, 1.7 equiv.) in THF (1 mL). Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4l**. − Yield: 671 mg (98%, yellow-brown powder). − R_f = 0.70 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −440.0 ($CHCl_3$, *c* = 0.21). − M.p.: 145 °C. − IR (KBr): $\tilde{\nu}$ = 3101 cm^{-1}, 3065, 2958, 2923, 2866, 2242, 1876, 1656, 1572, 1473, 1448, 1409, 1377, 1330, 1275, 1246, 1198, 1179, 1155, 1125, 1107, 1065, 1049, 1021, 1000, 973, 932, 904, 828, 813, 743, 693, 665, 633, 591, 499, 479. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.07 (d, ^3J = 6.9 Hz, 3 H, $CHCH_3$), 1.27 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.29 (d, ^3J = 6.6 Hz, 3 H, $CHCH_3$), 1.60−1.85 (m, 3 H), 2.00−2.15 (m, 3 H, β-ring-CH_2, CH_2CH_3), 2.59 (td, $^{2/3}J$ = 9.1 Hz, ^3J = 8.0 Hz, 1 H, NCH_2), 2.82 [sept, ^3J = 6.6 Hz, 1 H, $SCH(CH_3)_2$], 3.15 (ddd, ^2J = 8.5 Hz, ^3J = 7.8 Hz, ^3J = 4.4 Hz, 1 H, NCH_2), 3.23 (s, 3 H, OCH_3), 3.48 (dd, ^2J = 9.1 Hz, ^3J = 7.2 Hz, 1 H, OCH_2), 3.82 (dd, ^2J = 9.1 Hz, ^3J = 3.9 Hz, 1 H, OCH_2), 3.88 (qd, ^3J = 8.5 Hz, ^3J = 3.8 Hz, 1 H, NCH), 3.93 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 3.97 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.02 (s, 5 H, C_5H_5), 4.62 (dd, ^3J = 11.4 Hz, ^3J = 3.5 Hz, 1 H, N=CCH), 4.76 (dd, ^3J = 2.5, ^4J = 1.4, 1 H, $C_5H_3R_2$), 7.07 (m, 2 H, C_6H_5), 7.50 (m, 1 H, *p*-C_6H_5), 7.78 (m, 2 H, C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.8, 23.5, 24.5 (CH_3), 20.9 (NCH_2CH_2), 27.3 (CH_2CH_3, $NCHCH_2$), 35.9, 45.0 (SCH), 57.1 (NCH_2), 58.8 (OCH_3), 67.0, 67.8, 69.7, 70.1 (NCH, $C_5H_3R_2$), 72.1 (C_5H_5), 75.7 (OCH_2), 78.1, 84.1 (*i*-$C_5H_3R_2$), 129.2, 136.7 (*o*/*m*-C_6H_5), 129.4 (*i*-C_6H_5), 131.6 (*p*-C_6H_5), 166.7 (C=N). − EI-MS; *m*/*z*: 598.0 (67) [M^+], 407.8 (27) [$M^+ - C_6H_{12}NO - SCH(CH_3)_2$], 366.8 (12) [$M^+$ − PhSe − S=$C(CH_3)_2$], 326.9 (25) [M^+ − PhSe − $C_6H_{12}NO$], 284.8 (36) [326.9 − $CH(CH_3)_2$], 252.9 (11) [326.9 − $SCH(CH_3)_2$], 245.0 (13), 210.9 (12) [$FcCN^+$], 184.9 (26) [Fc^+], 156.0 (100) [$C_6H_4Se^+$], 120.9 (21) [$CpFe^+$], 117.0 (31), 75.0 (19) [$SCH(CH_3)_2^+$]. − $C_{29}H_{38}FeN_2OSSe$ (597.5): calcd. C 58.30, H 6.41, N 4.69; found C 57.97, H 6.37, N 4.52.

Planar Chiral SAMP-hydrazone 4m: According to GP4, a solution of hydrazone **3j** (373 mg, 0.739 mmol) and $LiClO_4$ (3.0 equiv.) in THF (10 mL) was first treated with *t*BuLi (1.3 equiv.) and afterwards with dimethyl disulfide (1.5 equiv.) in THF (3 mL). Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4m**. − Yield: 792 mg (89%, orange crystals). − Yield: 114 mg (28%, red oil). − R_f = 0.61 (hexane/diethyl ether = 4:1). − *de* ≥ 90%. − $[\alpha]_D^{25}$ = −44.2 ($CHCl_3$, *c* = 0.78). − IR ($CHCl_3$): $\tilde{\nu}$ = 3096 cm^{-1}, 2970, 2920, 2870, 2829, 2733, 1598, 1582, 1492, 1461, 1447, 1384, 1365, 1353, 1334, 1314, 1277, 1240, 1217, 1200, 1184, 1164, 1107, 1050, 1019, 1002, 969, 924, 813, 757, 709, 667, 497, 454. − ^{1}H NMR (400 MHz, C_6D_6): δ = 1.32 (d, ^3J = 6.6 Hz, 3 H, $CHCH_3$), 1.75−2.60 (m, 7 H, β-ring-CH_2, NCH_2, $CH(CH_3)_2$), 2.03 (s, 3 H), 2.05 (d, ^3J = 6.0 Hz, 3 H, $CHCH_3$), 2.09 (s, 3 H, SCH_3, $ArCH_3$), 2.82 (br., 1 H, SCH), 3.18 (s, 3 H, OCH_3), 3.52 (qd, 1 H, ^3J = 7.2 Hz, ^3J = 4.1 Hz, NCH), 3.58 (dd, ^2J = 8.8 Hz, ^3J = 4.4 Hz, 1 H, OCH_2), 4.03 (t, ^3J = 2.6 Hz, 1 H, $C_5H_3R_2$), 4.13 (s, 5 H, C_5H_5), 4.28 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.40 (dd, ^3J = 2.6 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 6.89 (dm, ^3J = 7.7 Hz, 2 H, C_6H_4), 7.44 (dm, ^3J = 8.2 Hz, 2 H, C_6H_4). − ^{13}C NMR (100 MHz, C_6D_6): δ = 20.9, 22.1, 22.4, 32.8 (CH_3), 22.8 (NCH_2CH_2), 27.6 ($NCHCH_2$), 56.1, 58.8 (NCH, OCH_3), 57.2 (NCH_2), 67.1, 67.5, 68.5 ($C_5H_3R_2$), 70.5 (SCH), 71.7 (C_5H_5), 75.5 (OCH_2), 129.7, 129.9 (C_6H_4), 131.0, 131.7, 136.2 (C=N, *i*-C_6H_4). − EI-MS; *m*/*z*: 550.1 (43) [M^+], 472.0 (100) [$M^+ - SC_7H_7$], 426.1 (25) [$M^+ - HSC_7H_7$], 381.1 (28) [427.0 − S=CH_2], 314.0 (46) [427.0 − $C_6H_{12}NO$], 311.9 (33) [426.1 − $C_6H_{12}NO$], 298.9 (44) [314.0 − CH_3], 296.9 (32) [311.9 − CH_3], 268.0 (18) [314.0 − H_2C=S], 264.9 (28) [311.9 − H_3CS], 256.9 (15) [$H_3CSC_{10}H_8FeCN^+$], 241.9 (11), 230.9 (13), 213.5 (16), 210.9 (11) [$FcCN^+$], 185.9 (12) [Cp_2Fe^+], 184.9 (14)

[Fc^+], 179.0 (11) [$(H_3C)_2CHCHSC_7H_7^+$], 170.1 (81), 124.0 (16) [$HSC_7H_7^+$], 122.9 (15) [$SC_7H_7^+$], 120.9 (28) [$CpFe^+$], 91.0 (22) [$C_7H_7^+$]. − $C_{29}H_{38}FeN_2OS_2$ (550.6): calcd. C 63.26, H 6.96, N 5.09; found C 63.37, H 7.09, N 5.39.

Planar Chiral SAMP-hydrazone 4n: According to GP4, a solution of hydrazone **3c** (530 mg, 0.96 mmol) and $LiClO_4$ (5.0 equiv.) in THF (20 mL) was first treated with *t*BuLi (2.5 equiv.) and afterwards with a solution of 1,2-diiodoethane (730 mg, 2.7 equiv.) in THF (1 mL). Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **4n**. − Yield: 792 mg (89%, orange crystals). − Yield: 288 mg (44%, orange-brown crystals). − R_f = 0.40 (hexane/diethyl ether = 4:1). − (*E*)/(*Z*) = 11.7:1. − *de* ≥ 96%. − $[\alpha]_D^{25}$ = +12.8 ($CHCl_3$, *c* = 0.47). − M.p.: 68 °C. − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3055, 2969, 2926, 2871, 2827, 2380, 2346, 2265, 1737, 1655, 1638, 1577, 1482, 1437, 1376, 1308, 1275, 1241, 1187, 1106, 1062, 1001, 969, 890, 818, 739, 697, 655, 608, 558, 498. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.56−1.82 (m, 3 H), 2.06 (m, 1 H, β-ring-CH_2), 1.63 (dd, $^3J_{HP}$ = 16.2 Hz, ^3J = 7.7 Hz, 3 H, CHCH_3), 2.39 (td, $^{2/3}J$ = 9.1 Hz, ^3J = 7.7 Hz, 1 H, NCH_2), 3.09 (m, 1 H, NCH_2), 3.29 (s, 3 H, OCH_3), 3.51 (dd, ^2J = 9.9 Hz, ^3J = 8.3 Hz, 1 H, OCH_2), 3.73 (m, 2 H, OCH_2, NCH), 3.91 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 3.93 (s, 5 H, C_5H_5), 4.30 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.71 (dd, ^3J = 2.8 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 5.02 (dq, $^2J_{HP}$ = 15.7 Hz, ^3J = 7.7 Hz, 1 H, PCH), 7.05 (m, 6 H, *m*/*p*-C_6H_5), 7.81 (ddd, $^3J_{HP}$ = 9.6 Hz, ^3J = 8.2 Hz, ^4J = 1.7 Hz, 2 H, *o*-C_6H_5), 8.11 (ddd, $^3J_{HP}$ = 9.9 Hz, ^3J = 8.5 Hz, ^4J = 1.7 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 14.8 (d, $^2J_{CP}$ = 4.0 Hz, CH_3), 22.5 (NCH_2CH_2), 26.7 ($NCHCH_2$), 32.4 (d, $^1J_{CP}$ = 30.4 Hz, PCH), 56.4 (NCH_2), 58.6 (OCH_3), 67.1, 68.4, 69.1, 76.8 (NCH, $C_5H_3R_2$), 72.8 (*i*-C_6H_5), 75.4 (OCH_2), 80.8 (*i*-C_6H_5), 128.1 (d, $^3J_{CP}$ = 10.3 Hz), 128.3 (d, $^3J_{CP}$ = 9.8 Hz, *m*-C_6H_5), 130.5, 130.6 (*p*-C_6H_5), 132.6 (d, $^2J_{CP}$ = 8.6 Hz), 133.1 (d, $^2J_{CP}$ = 9.2 Hz, *o*-C_6H_5), 161.1 (C=N). − ^{31}P NMR (C_6D_6, 162 MHz): +24.8 (broad). − EI-MS; *m*/*z*: 424.2 (32) [M^+ − Ph_2P-BH_3 − Fe], 416.2 (27), 371.2 (38), 303.2 (16), 185.1 (100) [PPh_2^+], 183.1 (36) [185.1 − H_2], 66.2 (27) [$C_5H_6^+$]. − $C_{31}H_{37}BFeIN_2OP$ (678.2): calcd. C 54.90, H 5.50, N 4.13; found C 55.44, H 5.74, N 3.89.

General Procedure for the Preparation of Hydrazines 5 (GP5): The hydrazones **4** bearing a Ph_2PBH_3 group in the side chain, were deprotected first by stirring with TMEDA (5 equiv.) in dry diethyl ether for several hours. Since deprotected phosphanes **4** are extremely sensitive to oxidation, all synthetic manipulations were carried out with rigorous exclusion of oxygen. The solution was washed three times with saturated aqueous NH_4Cl, once with brine and dried with $MgSO_4$. The crude product was filtered under argon through silica gel and then dried under high vacuum for several hours. The hydrazones **4** were dissolved in CH_2Cl_2/diethyl ether (1:1 to 1:2) and cooled to −20 °C. To the solution, freshly distilled catecholborane (5−8 equiv.) was added dropwise with vigorous stirring, and the reaction mixture was warmed to room temperature. After completion of the reaction (TLC control with ninhydrin: hydrazones purple, hydrazines orange), the reaction was quenched at 0 °C with saturated aqueous NH_4Cl, washed twice with saturated aqueous K_2CO_3, once with brine, and dried with $MgSO_4$. The crude product was purified by flash chromatography (hexane/ether = 4:1 to 10:1). Hydrazines bearing an R_2P group in the side chain, are protected with BH_3DMS prior to workup (2 h, 0 °C).

Hydrazine 5a: According to GP5, a solution of hydrazone **4j** (100 mg, 0.233 mmol) in CH_2Cl_2 (20 mL) was treated with catecholborane (5.0 equiv.) at −40 °C. After warming to 10 °C, aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazine **5a**. − Yield: 93 mg (93%, yellow oil). − R_f = 0.61 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −164.8 ($CHCl_3$, *c* = 0.65). − IR ($CHCl_3$): $\tilde{\nu}$ = 3092 cm^{-1}, 2963, 2922, 2873, 2828, 1724, 1671, 1583, 1550, 1447, 1383, 1279, 1197, 1106, 1041, 1001, 960, 878, 816, 755, 715, 690, 665, 489. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.10 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.48−1.94 (m, 6 H, CH_2CH_3, β-ring-CH_2), 1.66 (s, 3 H, SCH_3), 1.99 (dt, ^2J = 9.4 Hz, ^3J = 8.1 Hz, 1 H, NCH_2), 2.34 (s, 3 H, $CpCH_3$), 2.76 (qd, ^3J = 8.1 Hz, ^3J = 3.4 Hz, 1 H, NCH_{ring}), 3.00 (broad s, 1 H, NH), 3.31 (s, 3 H, OCH_3), 3.35 (ddd, ^2J = 8.7 Hz, ^3J = 6.4 Hz, ^3J = 2.4 Hz, 1 H, NCH_2), 3.41 (td, ^3J = 8.1 Hz, ^3J = 2.4 Hz, 1 H, SCH), 3.58 (dd, ^2J = 8.7 Hz, ^3J = 6.7 Hz, 1 H, OCH_2), 3.87 (m, 1 H, $C_5H_3R_2$), 3.90 (m, 2 H, $C_5H_3R_2$), 3.92 (dd, ^2J = 9.1 Hz, ^3J = 3.7 Hz, 1 H, OCH_2), 4.02 (d, ^3J = 7.1 Hz, CpCHN), 4.03 (s, 5 H, C_5H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 12.9, 13.0, 16.1 (CH_3), 21.4 (NCH_2CH_2), 25.3, 26.7 (CH_2CH_3, $NCHCH_2$), 52.0 (SCH), 56.4 (NCH_2), 59.0 (OCH_3), 63.8 (FcCH), 66.39, 66.45, 69.2, 71.1 ($C_5H_3R_2$, NCH_{ring}), 69.5 (C_5H_5), 75.3 (OCH_2), 84.0, 87.3 (*i*-$C_5H_3R_2$). − EI-MS; *m*/*z*: 430.1 (4) [M^+], 428.1 (18) [M^+ − H_2], 341.1 (11) [M^+ − $H_3CSCHCH_2CH_3$], 340.1 (13) [M^+ − $H_3CSCH_2CH_2CH_3$], 301.1 (26) [M^+ − $C_6H_{13}N_2O$], 300.0 (35) [M^+ − $C_6H_{14}N_2O$], 268.1 (12), 265.9 (15) [M^+ − $C_6H_{12}NO$ − H_2 − H_3CSH], 255.1 (19) [300.0 − CH_2OCH_3], 254.0 (100) [300.0 − $H_2C=S$], 252.1 (15), 227.1 (12), 226.0 (41), 225.0 (25) [$C_{10}H_8FeCH_3CN^+$], 224.1 (12), 200.0 (15), 198.9 (40) [$C_{10}H_8FeCH_3^+$], 134.0 (10), 129.1 (12) [$C_{10}H_9^+$], 121.0 (41) [$CpFe^+$], 114.9 (12), 91.1 (13) [$H_3CSHCH_2CH_2CH_3^+$], 89.0 (20) [$H_3CSCHCH_2CH_3^+$], 56.1 (44) [Fe^+], 45.3 (12) [$CH_2OCH_3^+$]. − HR-MS: $C_{22}H_{32}{}^{56}FeN_2OS$: calcd. 428.158472; found 428.158450.

Hydrazine 5b: According to GP5, a solution of hydrazone **4f** (441 mg, 0.737 mmol) in diethyl ether/CH_2Cl_2 (2:1, 30 mL) was treated with catecholborane (8.0 equiv.) at −40 °C. After warming to room temperature, the reaction mixture was stirred for 72 h at room temperature. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazine **5b**. − Yield: 173 mg (39%, yellow crystals). − R_f = 0.21 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −174.4 ($CHCl_3$, *c* = 0.61). − M.p.: 74 °C. − IR (KBr): $\tilde{\nu}$ = 3078 cm^{-1}, 3055, 2959, 2917, 2871, 2824, 2389, 2346, 2260, 2202, 1737, 1719, 1703, 1654, 1637, 1564, 1545, 1481, 1459, 1436, 1384, 1312, 1265, 1237, 1186, 1160, 1105, 1061, 1002, 954, 917, 822, 741, 698, 631, 609, 505, 479. − ^{1}H NMR (500 MHz, C_6D_6): δ = 1.51 (m, 1 H, NCH_2CH_2), 1.52 (d, ^3J = 7.0 Hz, 3 H, CHCH_3), 1.57 (s, 3 H, SCH_3), 1.62 (m, 1 H, NCH_2CH_2), 1.71 (m, 1 H, $NCHCH_2$), 1.95 (dddd, ^2J = 15.6 Hz, ^3J = 12.5 Hz, ^3J = 9.8 Hz, ^3J = 5.9 Hz, 1 H, $NCHCH_2$), [^{11}B-decoupling: 2.26 (d, $^2J_{HP}$ = 14.6 Hz, 3 H, BH_3)], 2.56 (qd, ^3J = 5.1 Hz, ^3J = 1.9 Hz, 1 H, SCH), 2.59 (td, $^{2/3}J$ = 8.6 Hz, ^3J = 7.7 Hz, 1 H, NCH_2), 2.92 (qd, ^3J = 8.5 Hz, ^3J = 3.7 Hz, 1 H, NCH), 3.18 (broad, 1 H, NH), 3.37 (s, 3 H, OCH_3), 3.53 (ddd, ^2J = 8.6 Hz, ^3J = 7.4 Hz, ^3J = 3.7 Hz, 1 H, NCH_2), 3.66 (dd, ^2J = 8.9 Hz, ^3J = 7.0 Hz, 1 H, OCH_2), 3.86 (td, ^3J = $^3J_{HP}$ = 2.4 Hz, ^4J = 1.5 Hz, 1 H, PC-CH_{Cp}), 4.00 (dd, ^2J = 8.9 Hz, ^3J = 3.8 Hz, 1 H, OCH_2), 4.14 (t, ^3J = 2.5 Hz, 1 H, PC−CH−CH_{Cp}), 4.26 (s, 5 H, C_5H_5), 4.94 (d, ^3J = 1.7 Hz, 1 H, FcCH), 5.07 (dt, ^3J = 2.5 Hz, ^4J = $^4J_{HP}$ = 1.8 Hz, 1 H, PC-$(CH)_2-CH_{Cp}$), 6.93−7.05 (m, 6 H, *m*/*p*-C_6H_5), 7.76 (ddd, $^3J_{HP}$ = 10.5 Hz, ^3J = 7.7 Hz, ^4J = 1.5 Hz, 2 H, *o*-C_6H_{5ax}), 7.85 (ddd, $^3J_{HP}$ = 10.5 Hz, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 2 H, *o*-C_6H_{5eq}). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.8 (SCH_3), 19.4 ($CHCH_3$), 20.9 (NCH_2CH_2), 27.4 ($NCHCH_2$), 49.9 (SCH), 56.7 (NCH_2), 58.5 (FcCH, OCH_3), 66.0 (NCH), 69.4 (d, $^3J_{CP}$ = 5.7 Hz,

PC−CH−CH_{Cp}), 70.4 (C_5H_5), 72.3 (d, $^2J_{CP}$ = 2.8 Hz, PC−CH_{Cp}), 72.5 (d, $^3J_{CP}$ = 8.1 Hz, PC-$(CH)_2$−CH_{Cp}), 75.7 (OCH_2), 96.7 (d, $^1J_{CP}$ = 15.5 Hz, PC_{Cp}), 127.7 (d, $^3J_{CP}$ = 8.0 Hz, *m*-C_6H_5), 128.0 (d, $^3J_{CP}$ = 9.6 Hz, *m*-C_6H_5), 130.3 (d, $^4J_{CP}$ = 2.3 Hz, *p*-C_6H_5), 131.2 (d, $^1J_{CP}$ = 57.1 Hz, *i*-C_6H_5), 132.1 (d, $^1J_{CP}$ = 42.9 Hz, *i*-C_6H_5), 132.5 (d, $^2J_{CP}$ = 9.1 Hz, *o*-C_6H_{5ax}), 133.3 (d, $^2J_{CP}$ = 9.8 Hz, *o*-C_6H_{5eq}). − ^{31}P NMR (C_6D_6, 162 MHz): +15.5 (broad). − ^{11}B NMR (C_6D_6, 160 MHz): −36.1 (broad). − EI-MS; *m*/*z*: 586.1 (13) [$M^+ - BH_3$], 511.0 (98) [586.1 − $H_3CSCHCH_3$], 457.0 (69) [$M^+ - HNNC_6H_{12}O$], 395.9 (100) [511.0 − $C_6H_{13}NO$], 289.0 (44), 132.9 (60), 121.0 (31) [$CpFe^+$], 91.1 (61), 83.1 (37). − HR-MS: $C_{32}H_{39}{}^{56}FeN_2OPS$ ($M^+ - BH_3$): calcd. 586.187012; found 586.186785.

Hydrazine 5c: According to GP5, a solution of hydrazone **4g** (56 mg, 0.085 mmol) in diethyl ether/CH_2Cl_2 (2:1, 7.5 mL) was treated with catecholborane (8.0 equiv.) at −40 °C. After warming to room temperature, the reaction mixture was stirred for 72 h at room temperature. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazine **5c**. − Yield: 43 mg (82%, yellow oil). − R_f = 0.37 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −154.2 ($CHCl_3$, *c* = 0.67). − IR ($CHCl_3$): $\tilde{\nu}$ = 3078 cm^{-1}, 3058, 3006, 2963, 2923, 2872, 2830, 2396, 2353, 2264, 1483, 1462, 1437, 1384, 1337, 1313, 1289, 1217, 1200, 1187, 1163, 1106, 1062, 1029, 1002, 966, 921, 823, 737, 699, 667, 632, 613, 506, 479. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.88 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.49−2.00 (m, 6 H, β-ring-CH_2, CH_2CH_3), 1.55 (s, 1 H, NH), 1.71 (s, 3 H, SCH_3), 2.05 (dd, ^2J = 9.7 Hz, ^3J = 4.4 Hz, ^3J = 1.7 Hz, NCH_2), 2.78 (dt, ^2J = 8.4 Hz, ^3J = 7.7 Hz, 1 H, NCH_2), 2.98 (m, 1 H, NCH), 3.42 (m, 1 H, SCH), 3.42 (s, 3 H, OCH_3), 3.69 (dd, ^2J = 9.1 Hz, ^3J = 6.7 Hz, 1 H, OCH_2), 3.80 (q, $^{3/4}J$ = J_{HP} = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.01 (dd, ^2J = 9.1 Hz, ^3J = 3.7 Hz, 1 H, OCH_2), 4.12 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.29 (s, 5 H, C_5H_5), 4.94 (broad s, 1 H, FcCH), 5.06 (m, 1 H, $C_5H_3R_2$), 6.88−7.04 (m), 7.42 (ddd, *J* = 11.4 Hz, *J* = 8.1 Hz, *J* = 1.7 Hz, 6 H, *m*/*p*-C_6H_5), 7.76 (m, 2 H, *o*-C_6H_5), 7.86 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.4, 16.6 (CH_3), 21.7 (NCH_2CH_2), 28.0, 28.9 (CH_2CH_3, $NCHCH_2$), 57.5 (NCH_2), 58.8 (OCH_3), 59.1 (SCH), 66.7 (NCH), 69.8, 69.9, 72.8 ($C_5H_3R_2$), 71.0 (C_5H_5), 76.4 (OCH_2), 97.2 (*i*-$C_5H_3R_2$), 128.5 (d, $^3J_{CP}$ = 9.8 Hz, *m*-C_6H_5), 130.8, 131.0 (*p*-C_6H_5), 131.5 (d, $^1J_{CP}$ = 60.1 Hz), 132.0 (d, $^1J_{CP}$ = 60.1 Hz, *i*-C_6H_5), 133.5 (d, $^2J_{CP}$ = 9.2 Hz), 133.8 (d, $^2J_{CP}$ = 9.2 Hz, *o*-C_6H_5). − ^{31}P NMR (C_6D_6, 162 MHz): +11.9 (broad). − EI-MS; *m*/*z*: 615.2 (39) [MH^+], 614.2 (31) [M^+], 613.2 (33) [M^+ − H], 601.1 (25) [$MH^+ - BH_3$], 600.1 (11) [$M^+ - BH_3$], 583.1 (13), 418.1 (15), 417.0 (49), 416.1 (23) [$MH^+ - Ph_2P - BH_3$], 286.9 (17), 259.0 (29), 199.0 (11) [$Ph_2P\text{-}BH_2^+$], 187.0 (32), 128.1 (100) [$C_6H_{12}N_2O^+$], 91.1 (16). − $C_{33}H_{44}BFeN_2OPS$ (614.4): calcd. C 64.51, H 7.22, N 4.56; found C 64.03, H 7.46, N 4.07.

Hydrazine 5d: According to GP5, a solution of hydrazone **4h** (143 mg, 0.263 mmol) in diethyl ether/CH_2Cl_2 (2:1, 21 mL) was treated with catecholborane (8.0 equiv.) at −40 °C. After warming to room temperature, the reaction mixture was stirred for 15 h at room temperature. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 7:1) provided hydrazone **5d**. − Yield: 78 mg (55%, yellow crystals). − R_f = 0.64 (hexane/diethyl ether = 4:1). − *de* ≥ 90%. − $[\alpha]_D^{25}$ = +21.5 ($CHCl_3$, *c* = 0.14). − M.p.: 104 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3096 cm^{-1}, 2963, 2927, 2873, 2734, 2384, 2269, 1726, 1503, 1462, 1384, 1365, 1288, 1252, 1218, 1202, 1185, 1109, 1069, 1044, 1003, 964, 929, 885, 824, 756, 689, 667, 649, 507, 494, 481. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.03 (dd, $^3J_{HP}$ = 13.1 Hz, ^3J = 7.1 Hz, 3 H, PCHCH_3), 1.15 (dd, $^3J_{HP}$ = 14.4 Hz, ^3J = 7.1 Hz, 3 H, PCHCH_3), 1.20 (dd, $^3J_{HP}$ = 14.8 Hz, ^3J = 7.4 Hz, 3 H, PCHCH_3), 1.21 (t, ^3J = 6.7 Hz, 3 H, CH_2CH_3), 1.42 (dd, $^3J_{HP}$ = 15.1 Hz, ^3J = 7.1 Hz, 3 H, PCHCH_3), 1.55−1.96 (m, 5 H), 2.14−2.36 (m, 2 H, β-ring-CH_2, CH_2CH_3, PCH), 1.86 (s, 3 H, SCH_3), 2.51 (dsept, $^2J_{HP}$ = 12.8 Hz, ^3J = 7.4 Hz, 1 H, PCH), 2.68 (ddd, ^3J = 10.4 Hz, ^3J = 4.4 Hz, ^3J = 1.3 Hz, 1H, SCH), 3.08−3.18 (m, 3H), 3.65 (m, 1H, NH, NCH, NCH_2), 3.27 (s, 3 H, OCH_3), 3.61 (dd, ^2J = 9.1 Hz, ^3J = 3.7 Hz, 1H, OCH_2), 3.71 (dd, ^2J = 9.1 Hz, ^3J = 5.7 Hz, 1 H, OCH_2), 4.10 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 4.26 (m, 1 H, $C_5H_3R_2$), 4.30 (s, 5 H, C_5H_5), 4.39 (broad d, ^3J = 1.3 Hz, 1 H, FcCH), 4.93 (dt, ^3J = 2.4 Hz, ^4J = 1.3 Hz, 1 H, $C_5H_3R_2$). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.8 (CH_2CH_3), 17.0 (SCH_3), 17.1 (d, $^2J_{CP}$ = 2.4), 18.9 (broad), 19.1 (broad), 19.6 ($PCHCH_3$), 22.3 (NCH_2CH_2), 24.4 (d, $^1J_{CP}$ = 33.0 Hz), 25.4 (d, $^1J_{CP}$ = 33.6 Hz, PCH), 27.6 ($NCHCH_2$), 28.4 (CH_2CH_3), 56.8 (NCH_2), 58.3, 58.9, 59.0 (FcCH, SCH, OCH_3), 65.6 (NCH), 69.6 (d, J_{CP} = 6.7), 71.6 (d, J_{CP} = 6.7), 72.7 (d, J_{CP} = 9.2, $C_5H_3R_2$), 71.0 (C_5H_5), 75.8 (OCH_2), 94.4 (*i*-$C_5H_3R_2$). − ^{31}P NMR (162 MHz, C_6D_6): δ = +33.2 (broad). − EI-MS; *m*/*z*: 546.2 (19) [M^+], 457.1 (66) [$M^+ - H_3CSCHCH_2CH_3$], 443.1 (100) [457.1 − BH_3], 417.0 (92) [$M^+ - HNNC_6H_{12}O$], 403.0 (29) [417.0 − BH_3], 357.0 (27) [403.0 − S=CH_2], 342.0 (32) [457.1 − $HNC_6H_{12}O$], 330.0 (29), 327.9 (56) [342.0 − BH_3], 235.0 (27), 132.9 (36), 129.0 (50) [$HNC_6H_{12}O$]. − HR-MS: $C_{27}H_{48}{}^{56}FeN_2OPS$: calcd. 546.266742; found 546.266727.

Hydrazine 5e: According to GP5, a solution of hydrazone **4i** (100 mg, 0.160 mmol) in diethyl ether/CH_2Cl_2 (2:1, 15 mL) was treated with catecholborane (8.0 equiv.) at −40 °C. After warming to room temperature, the reaction mixture was stirred for 120 h at room temperature. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 7:1) provided hydrazine **5e**. − Yield: 43 mg (43%, yellow-orange crystals). − R_f = 0.27 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −153.2 ($CHCl_3$, *c* = 0.77). − Mp: 126 °C. − IR (KBr): $\tilde{\nu}$ = 3054 cm^{-1}, 2954, 2922, 2887, 2865, 2823, 2387, 2350, 2262, 1720, 1655, 1544, 1483, 1460, 1439, 1382, 1365, 1317, 1244, 1199, 1163, 1136, 1106, 827, 744, 699, 631, 611, 511, 479. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.89 [d, ^3J = 6.6 Hz, 3 H, $SCH(CH_3)_2$], 1.07 [d, ^3J = 6.6 Hz, 3 H, $SCH(CH_3)_2$], 1.56 [d, ^3J = 7.1 Hz, 3 H, $Fc(CH)_2CH_3$], 1.60−1.80 (m, 3 H, β-ring-CH_2), 1.96 (m, 2 H, β-ring-CH_2, NCH), 2.50 [sept, ^3J = 6.6 Hz, 1 H, $SCH(CH_3)_2$], 2.65 (qd, ^3J = 7.1 Hz, ^3J = 1.1 Hz, 1 H, SCHCHN), 2.84 (dt, ^2J = 8.5 Hz, ^3J = 8.0 Hz, 1 H, NCH_2), 3.04 (m, 1 H, NH), 3.41 (s, 3 H, OCH_3), 3.45 (m, 1 H, NCH_2), 3.72 (dd, ^2J = 8.8 Hz, ^3J = 6.9 Hz, 1 H, OCH_2), 3.86 (q, $^{3/4}J$ = J_{HP} = 1.8 Hz, 1 H, $C_5H_3R_2$), 4.03 (dd, ^2J = 8.8 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 4.12 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.23 (s, 5 H, C_5H_5), 4.89 (broad s, 1 H, FcCH), 5.02 (q, $^{3/4}J$ = J_{HP} = 1.8 Hz, 1 H, $C_5H_3R_2$), 7.04 (m, 6 H, *m*/*p*-C_6H_5), 7.78 (ddd, *J* = 9.9 Hz, *J* = 7.1 Hz, ^4J = 2.5 Hz, 2 H, *o*-C_6H_5), 7.87 (ddd, *J* = 9.9 Hz, *J* = 7.2 Hz, ^4J = 1.9 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 21.7 (NCH_2CH_2), 22.0, 24.0, 24.4 (CH_3), 28.0 ($NCHCH_2$), 34.1 [$SCH(CH_3)_2$], 47.4 (SCHCHN), 57.2 (NCH_2), 58.9 (OCH_3), 59.0 (d, J_{CP} = 6.8 Hz, FcCH), 66.6 (NCH), 66.9 (*i*-$C_5H_3R_2$), 70.0 (d, J_{CP} = 6.3 Hz), 70.9 (d, J_{CP} = 4.6 Hz), 72.7 ($C_5H_3R_2$), 70.8 (C_5H_5), 76.3 (OCH_2), 97.0 (d, $^1J_{CP}$ = 15.5 Hz, *i*-$C_5H_3R_2$), 128.3 (d, $^3J_{CP}$ = 9.2 Hz), 128.5 (d, $^3J_{CP}$ = 10.3 Hz, *m*-C_6H_5), 130.8 (*p*-C_6H_5), 131.9 (d, $^1J_{CP}$ = 60.1 Hz), 132.3 (d, $^1J_{CP}$ = 56.1 Hz, *i*-C_6H_5), 133.2 (d, $^2J_{CP}$ = 9.2 Hz), 133.7 (d, $^2J_{CP}$ = 9.2 Hz, *o*-C_6H_5). − ^{31}P NMR (C_6D_6, 162 MHz): +12.3 (broad). − CI-MS (isobutane); *m*/*z*: 629.3 (20) [MH^+], 628.3 (17) [M^+], 627.2 (16) [M^+ − H], 615.2 (100) [$MH^+ - BH_3$], 614.2 (10) [$M^+ - BH_3$], 539.1 (14) [615.2 − HS*i*Pr], 187.0 (13), 131.2 (12) [$C_6H_{15}N_2O$], 116.0 (29), 114.0 (34)

$[C_6H_{12}NO^+]$. − $C_{34}H_{46}BFeN_2OPS$ (628.5): calcd. C 64.98, H 7.38, N 4.46; found C 64.96, H 7.34, N 4.18.

Hydrazine 5f: According to GP5, a solution of hydrazone **4j** (105 mg, 0.228 mmol) in diethyl ether/CH_2Cl_2 (2:1, 15 mL) was treated with catecholborane (8.0 equiv.) at −40 °C. After warming to room temperature, the reaction mixture was stirred for 15 h at room temperature. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazine **5f**. − Yield: 79 mg (75%, orange crystals). − R_f = 0.30 (hexane/diethyl ether = 4:1). − *de* = 87%. − $[\alpha]_D^{25}$ = −211.4 ($CHCl_3$, *c* = 0.74). − M.p.: 105 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3093 cm^{-1}, 2963, 2918, 2871, 2826, 1725, 1660, 1642, 1610, 1450, 1384, 1351, 1310, 1283, 1233, 1200, 1186, 1107, 1034, 1002, 955, 921, 891, 817, 756, 681, 574, 498. − ^{1}H NMR (major isomer, 400 MHz, C_6D_6): δ = 1.26 (t, ^3J = 6.6 Hz, 3 H, CH_2CH_3), 1.47−1.66 (m, 4 H, β-ring-CH_2), 1.83 (m, 2 H, CH_2CH_3), 2.03 (s, 3 H), 2.26 (s, 3 H, SCH_3), 2.35 (td, ^3J = 6.6 Hz, ^3J = 3.0 Hz, 1 H, SCH), 2.86 (dt, ^2J =9.1 Hz, ^3J = 8.7 Hz, 1 H, NCH_2), 2.91 (m, 1 H, NCH), 3.14 (m, 1 H, NCH_2), 3.31 (s, 3 H, OCH_3), 3.52 (dd, ^2J = 9.1 Hz, ^3J = 5.0 Hz, 1 H, OCH_2), 3.56 (broad s, 1 H, NH), 3.56 (dd, ^2J = 9.1 Hz, ^3J = 5.2 Hz, 1 H, OCH_2), 3.96 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.20 (s, 5 H, C_5H_5), 4.29 (dd, ^3J = 2.5 Hz, ^4J = 1.7 Hz, 1 H, $C_5H_3R_2$), 4.32 (dd, ^3J = 2.8 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.48 (d, ^3J = 2.7 Hz, 1 H, FcCH). − ^{1}H NMR (minor isomer, 400 MHz, C_6D_6): δ = 1.28 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.35−2.15 (m, 5 H, β-ring-CH_2, CH_2CH_3), 2.29 (s, 3 H), 2.60 (s, 3 H, SCH_3), 2.35 (dt, ^2J =10.4 Hz, ^3J = 9.4 Hz, 1 H, NCH_2), 2.60 (m, 1 H, CH_2CH_3), 3.25 (m, 2 H), 4.14 (m, 2 H, NCH, NCH_2, OCH_2), 3.28 (s, 3 H, OCH_3), 3.52 (dt, ^3J = 11.8 Hz, ^3J = 2.7 Hz, 1 H, SCH), 3.99 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.05 (s, 5 H, C_5H_5), 4.30 (dd, ^3J = 2.8 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.31 (dd, ^3J = 2.2 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 5.34 (d, ^3J = 2.5 Hz, 1 H, FcCH), 6.31 (broad s, 1 H, NH). − ^{13}C NMR (major isomer, 100 MHz, C_6D_6): δ = 13.4, 15.0, 21.2 (CH_3), 21.7, 22.7 (CH_2CH_3, NCH_2CH_2), 27.8 ($NCHCH_2$), 51.4 (SCH), 58.3, 59.2 (FcCH, OCH_3), 58.6 (NCH_2), 67.4, 67.7, 68.1, 72.1 (NCH, $C_5H_3R_2$), 70.3 (C_5H_5), 76.5 (OCH_2), 84.6, 91.4 (*i*-$C_5H_3R_2$). − ^{13}C NMR (minor isomer, 100 MHz, C_6D_6): δ = 13.1, 15.6, 21.2 (CH_3), 21.1, 21.6 (CH_2CH_3, NCH_2CH_2), 24.2 ($NCHCH_2$), 51.2 (SCH), 58.8, 59.0 (FcCH, OCH_3), 65.8 (NCH_2), 67.3, 71.9, 72.5, 73.8 (NCH, $C_5H_3R_2$), 70.5 (C_5H_5), 72.3 (OCH_2), 83.2, 94.3 (*i*-$C_5H_3R_2$). − EI-MS; *m*/*z*: 462.0 (8) $[M^+]$, 373.0 (64) $[M^+ - H_3SCHCH_2CH_3]$, 333.0 (22) $[M^+ - C_6H_{13}N_2O]$, 285.9 (100) [333.0 − H_3CS], 242.9 (24), 129.0 (10) $[NH{-}NC_6H_{12}O^+]$. − HR-MS: $C_{22}H_{34}{}^{56}FeN_2OS_2$: calcd. 462.146196; found 462.146178.

Hydrazine 5g: According to GP5, a solution of hydrazone **4k** (42 mg, 0.074 mmol) in CH_2Cl_2 (3 mL) was treated with catecholborane (8.0 equiv.) at −60 °C. After warming to room temperature, aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **5g**. − Yield: 37 mg (88%, yellow oil). − R_f = 0.32 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −86.7 ($CHCl_3$, *c* = 3.0). − IR ($CHCl_3$): $\tilde{\nu}$ = 3096 cm^{-1}, 2961, 2925, 2870, 2826, 2732, 1724, 1678, 1596, 1563, 1492, 1452, 1412, 1399, 1381, 1366, 1306, 1287, 1243, 1217, 1199, 1185, 1154, 1118, 1108, 1088, 1037, 1018, 1002, 971, 923, 881, 805, 757, 667, 505, 488, 465. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.33 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.35 (d, ^3J = 6.7 Hz, 3 H, $CHCH_3$), 1.43 (d, ^3J = 6.7 Hz, 3 H, $CHCH_3$), 1.48 - 1.56 (m, 2 H), 1.72−1.86 (m, 3 H, β-ring-CH_2, CH_2CH_3), 1.99 (s, 3 H, $C_6H_4CH_3$), 2.13 (q, $^{2/3}J$ = 8.4 Hz, 1 H, NCH_2), 2.42 (dqd, ^2J = 14.8 Hz, ^3J = 7.4 Hz, ^3J = 3.4 Hz, 1 H, CH_2CH_3), 2.67 (qd, ^3J = 6.7 Hz, ^3J = 3.7 Hz, 1 H, NCH), 2.82 (broad s, 1 H, NH), 3.14 (s, 3 H, OCH_3), 3.18 [m, 2 H, NCH_2, $SCH(CH_3)_2$], 3.38 (ddd, ^3J = 11.1 Hz, ^3J = 3.0 Hz, ^3J = 2.0 Hz, 1 H, $SCHCH_2$), 3.80 (dd, ^2J = 8.7 Hz, ^3J = 4.0 Hz, 1 H, OCH_2), 4.02 (t, ^3J = 2.7 Hz, 1 H, $C_5H_3R_2$), 4.13 (s, 5 H, C_5H_5), 4.13 (dd, ^2J = 8.4 Hz, ^3J = 6.7 Hz, 1 H, OCH_2), 4.35 (dd, ^3J = 2.7 Hz, ^4J = 1.0 Hz, 1 H, $C_5H_3R_2$), 4.39 (dd, ^3J = 2.4 Hz, ^4J = 1.7 Hz, 1 H, $C_5H_3R_2$), 4.51 (d, ^3J = 2.0 Hz, 1 H, FcCH), 6.84 (dm, ^3J = 8.1 Hz, 2 H, C_6H_4), 7.23 (dm, ^3J = 8.1 Hz, 2 H, C_6H_4). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.3, 20.8 (CH_3), 21.3, 23.7 (CH_2CH_3, NCH_2CH_2), 24.1, 24.5 (CH_3), 27.5 ($NCHCH_2$), 36.2 ($SCH(CH_3)_2$), 54.1 (SCHCN), 56.5 (NCH_2), 58.8 (OCH_3), 60.6 (FcCH), 66.7, 68.8, 71.0, 74.7 (NCH, $C_5H_3R_2$), 70.5 (C_5H_5), 75.6 (OCH_2), 77.3, 95.5 (*i*-$C_5H_3R_2$), 127.1, 129.6 (C_6H_4) 134.9, 137.6 (*i*-C_6H_4). − EI-MS; *m*/*z*: 567.2 (38) $[MH^+]$, 566.2 (26) $[M^+]$, 437.0 (17) $[M^+ - C_6H_{13}N_2O]$, 436.0 (12) $[M^+ - C_6H_{14}N_2O]$, 419.0 (13), 363.0 (75), 362.0 (100) [437.0 − $SCH(CH_3)_2$], 133.0 (31), 125.0 (23), 119.0 (26), 117.0 (21), 114.0 (53), 77.1 (30) $[H_2SCH(CH_3)_2{}^+]$. − HR-MS: $C_{30}H_{42}{}^{56}FeN_2OS_2$: calcd. 566.208795; found 566.208816.

Hydrazine 5h: According to GP5, a solution of hydrazone **4l** (110 mg, 0.184 mmol) in diethyl ether/CH_2Cl_2 (2:1, 10.5 mL) was treated with catecholborane (8.0 equiv.) at −40 °C. After warming to room temperature, the reaction mixture was stirred for 48 h at room temperature. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazine **5h**. − Yield: 75 mg (68%, yellow oil). − R_f = 0.44 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −81.7 ($CHCl_3$, *c* = 0.18). − IR ($CHCl_3$): $\tilde{\nu}$ = 3095 cm^{-1}, 3070, 3055, 2960, 2926, 2870, 2824, 1725, 1676, 1579, 1477, 1461, 1439, 1414, 1380, 1366, 1287, 1242, 1218, 1198, 1155, 1124, 1108, 1069, 1035, 1023, 1001, 970, 922, 879, 829, 757, 736, 691, 667, 535, 491, 462. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.28−1.90 (m, 5 H, β-ring-CH_2, CH_2CH_3), 1.32 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.35 (d, ^3J = 6.6 Hz, 3 H, $CHCH_3$), 1.42 (d, ^3J = 6.6 Hz, 3 H, $CHCH_3$), 2.10 (dt, ^2J = 8.5 Hz, ^3J = 8.0 Hz, 1 H, NCH_2), 2.39 (dqd, ^2J = 15.6 Hz, ^3J = 7.4 Hz, ^3J = 3.3 Hz, 1 H, CH_2CH_3), 2.65 (qd, ^3J = 7.0 Hz, ^3J = 3.7 Hz, 1 H, NCH), 2.81 (broad s, 1 H, NH), 3.15 (s, 3 H, OCH_3), 3.20 [m, 3 H, OCH_2, NCH_2, $SCH(CH_3)_2$], 3.33 (ddd, ^3J = 11.0 Hz, ^3J = 3.3 Hz, ^3J = 2.2 Hz, 1 H, $SCHCH_2$), 3.82 (dd, ^2J = 8.8 Hz, ^3J = 3.8 Hz, 1 H, OCH_2), 4.03 (t, ^3J = 2.6 Hz, 1 H, $C_5H_3R_2$), 4.11 (s, 5 H, C_5H_5), 4.31 (dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.34 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.48 (d, ^3J = 2.2 Hz, 1 H, FcCH), 6.85−6.97 (m, 3 H, *m*/*p*-C_6H_5), 7.39 (dm, ^3J = 6.9 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 12.7 (CH_3), 20.7, 23.3 (CH_2CH_3, NCH_2CH_2), 23.6, 24.0 (CH_3), 26.9 ($NCHCH_2$), 35.6, 53.4 (SCH), 55.9 (NCH_2), 58.2 (OCH_3), 61.0 (FcCH), 66.1, 69.0, 70.2, 74.9 (NCH, $C_5H_3R_2$), 69.8 (C_5H_5), 74.6 (*i*-$C_5H_3R_2$), 75.1 (OCH_2), 94.9 (*i*-$C_5H_3R_2$), 125.5 (*p*-C_6H_5), 128.6, 129.2 (*o*/*m*-C_6H_5), 134.9 (*i*-C_6H_5). − EI-MS; *m*/*z*: 600.0 (12) $[M^+]$, 483.0 (73) $[M^+ - (H_3C)_2CHSCHCH_2CH_3]$, 470.9 (11) $[M^+ - C_6H_{13}N_2O]$, 395.9 (47), 326.0 (51), 314.0 (100), 280.9 (13), 210.9 (23), 129.0 (19), 120.9 (11) $[CpFe^+]$. − CI-MS (isobutane); *m*/*z*: 601.1 (100) $[MH^+]$, 70.9 (31) $[M^+ - C_6H_{13}N_2O]$, 468.9 (18). − HR-MS: $C_{29}H_{40}{}^{56}FeN_2OSSe$: calcd. 600.137595; found 600.137602.

Hydrazine 5i: According to GP5, a solution of hydrazone **4c** (60 mg, 0.103 mmol) in diethyl ether/CH_2Cl_2 (1:1, 14 mL) was treated with catecholborane (5.0 equiv.) at −20 °C after deprotection with TMEDA. After warming to room temperature, the reaction mixture was stirred for 15 h at room temperature, cooled to 0 °C and treated with BH_3DMS (7.0 equiv.). The solution was stirred for 3 h. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 7:1) provided hydrazone **5i**. − Yield: 36 mg (58%, orange oil). − R_f = 0.25 (hexane/

diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −112.7 ($CHCl_3$, *c* = 1.05). − IR ($CHCl_3$): $\tilde{\nu}$ = 3080 cm^{-1}, 3058, 3004, 2971, 2922, 2874, 2827, 2387, 2279, 1715, 1668, 1589, 1483, 1437, 1378, 1336, 1313, 1279, 1217, 1189, 1107, 1063, 1029, 1001, 969, 921, 896, 876, 822, 756, 698, 667, 611, 581, 498, 483. − ^{1}H NMR (400 MHz, C_6D_6): δ = 1.23−2.12 (m, 5 H, β-ring-CH_2, NCH_2), 1.60 (dd, $^3J_{HP}$ = 15.9 Hz, ^3J = 7.4 Hz, 3 H, $CHCH_3$), 2.03 (s, 3 H, SCH_3), 2.67 (ddd, ^2J = 9.1 Hz, ^3J = 7.1 Hz, ^3J = 4.4 Hz, 1 H, NCH_2), 2.84 (m, 1 H, NH), 3.02 (dd, ^2J = 8.5 Hz, ^3J = 7.7 Hz, 1 H, OCH_2), 3.10 (s, 3 H, OCH_3), 3.18 (m, 1 H, NCH), 3.41 (dd, ^2J = 9.1 Hz, ^3J = 3.3 Hz, 1 H, OCH_2), 3.79 (dqd, $^2J_{HP}$ = 15.1 Hz, ^3J = 7.4 Hz, ^3J = 1.7 Hz, 1 H, PCH), 3.89 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.07 (s, 5 H, C_5H_5), 4.16 (m, 1 H, $C_5H_3R_2$), 4.23 (dd, ^3J = 2.2 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.67 (dd, $^3J_{HP}$ = 9.6 Hz, ^3J = 1.7 Hz, 1 H, FcCH), 7.01−7.24 (m, 6 H, *m*/*p*-C_6H_5), 8.06 (m, 2 H, *o*-C_6H_5), 8.32 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (100 MHz, C_6D_6): δ = 10.0 (SCH_3), 20.6 (NCH_2CH_2), 21.9 ($PCHCH_3$), 26.9 ($NCHCH_2$), 38.4 (d, $^1J_{CP}$ = 30.3 Hz, PCH), 54.8 (FcCH), 57.3 (NCH_2), 58.7 (OCH_3), 65.7, 67.7, 70.9, 71.9 (NCH, $C_5H_3R_2$), 70.4 (C_5H_5), 75.1 (OCH_2), 83.0 (*i*-$C_5H_3R_2$), 128.8 (d, $^3J_{CP}$ = 9.2 Hz), 128.9 (d, $^3J_{CP}$ = 9.1 Hz, *m*-C_6H_5), 129.6 (d, $^1J_{CP}$ = 52.1 Hz), 130.4 (d, $^1J_{CP}$ = 58.4 Hz, *i*-C_6H_5), 131.0, 131.2 (d, $^4J_{CP}$ = 2.3 Hz, *p*-C_6H_5), 133.3 (d, $^2J_{CP}$ = 8.6 Hz), 134.0 (d, $^2J_{CP}$ = 8.1 Hz, *o*-C_6H_5). − ^{31}P NMR (162 MHz, C_6D_6): δ = +23.9 (broad). − EI-MS; *m*/*z*: 600.3 (11) [M^+], 471.2 (38) [$M^+ - C_6H_{13}N_2O$], 469.2 (51) [471.2 − H_2], 424.3 (21) [471.2 − SCH_3], 272.1 (100) [471.2 − Ph_2PBH_3], 185.2 (26) [PPh_2^+], 129.2 (18) [$C_{10}H_9^+$], 121.0 (13) [$CpFe^+$], 57.3 (15) [FeH^+]. − HR-MS: $C_{32}H_{42}B^{56}FeN_2OPS$: calcd. 600.219792; found 600.219805.

Hydrazine 5j: According to GP5, a solution of hydrazone **4b** (157 mg, 0.262 mmol) in diethyl ether/CH_2Cl_2 (1:1, 26 mL) was treated with catecholborane (5.0 equiv.) at −20 °C after deprotection with TMEDA. After warming to room temperature, the reaction mixture was stirred for 15 h at room temperature, cooled to 0 °C and treated with BH_3DMS (7.0 equiv.). The solution was stirred for 3 h. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 7:1) provided hydrazone **5j**. − Yield: 65 mg (40%, yellow oil). − R_f = 0.20 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −94.6 ($CHCl_3$, *c* = 1.23). − IR ($CHCl_3$): $\tilde{\nu}$ = 3080 cm^{-1}, 3058, 3005, 2968, 2923, 2875, 2827, 2388, 2271, 1723, 1665, 1589, 1483, 1461, 1437, 1384, 1337, 1313, 1259, 1217, 1188, 1107, 1065, 1029, 1001, 970, 918, 876, 822, 756, 699, 667, 611, 581, 540, 498, 482. − ^{1}H NMR (400 MHz, C_6D_6): δ = 0.89 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.25−1.53 (m, 3 H), 1.73 (m, 1 H, β-ring-CH_2), 2.00 (s, 3 H, SCH_3), 2.11 (dt, ^2J = 8.8 Hz, ^3J = 8.0 Hz, 1 H, NCH_2), 2.24 (m, 2 H, CH_2CH_3), 2.69 (ddd, ^2J = 9.1 Hz, ^3J = 7.4 Hz, ^3J = 4.4 Hz, 1 H, NCH_2), 2.81 (qd, ^3J = 7.3 Hz, ^3J = 3.6 Hz, 1 H, NCH), 3.06 (dd, ^2J = 8.8 Hz, ^3J = 7.4 Hz, 1 H, OCH_2), 3.15 (s, 3 H, OCH_3), 3.47 (dd, ^2J = 8.8 Hz, ^3J = 3.6 Hz, 1 H, OCH_2), 3.72 (dddd, $^2J_{HP}$ = 14.0 Hz, ^3J = 10.7 Hz, ^3J = 3.0 Hz, ^3J = 1.7 Hz, 1 H, PCH), 3.92 (t, ^3J = 2.6 Hz, 1 H, $C_5H_3R_2$), 4.20 (s, 5 H, C_5H_5), 4.20 (m, 1 H, $C_5H_3R_2$), 4.22 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.66 (dd, $^2J_{HP}$ = 11.5 Hz, ^3J = 1.1 Hz, 1 H, FcCH), 7.01−7.21 (m, 6 H, *m*/*p*-C_6H_5), 8.12 (m, 2 H, *o*-C_6H_5), 8.31 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 15.1 (d, $^3J_{CP}$ = 3.8 Hz, CH_2CH_3), 19.4 (d, $^2J_{CP}$ = 4.3 Hz, CH_2CH_3), 20.4 (SCH_3), 21.8 (NCH_2CH_2), 27.0 ($NCHCH_2$), 44.7 (d, $^1J_{CP}$ = 28.0 Hz, PCH), 55.9 (d, $^2J_{CP}$ = 2.8 Hz, FcCH), 57.2 (NCH_2), 58.8 (OCH_3), 65.5 (NCH), 67.8, 69.2 71.4 ($C_5H_3R_2$), 70.4 (C_5H_5), 75.0 (OCH_2), 84.1, 97.2 (d, J_{CP} = 12.6 Hz, *i*-$C_5H_3R_2$), 128.7 (d, $^3J_{CP}$ = 6.3 Hz), 128.9 (d, $^3J_{CP}$ = 6.3 Hz, *m*-C_6H_5), 130.2 (d, $^1J_{CP}$ = 52.1 Hz), 131.8 (d, $^1J_{CP}$ = 51.5 Hz, *i*-C_6H_5), 130.9 (d, $^4J_{CP}$ = 2.3 Hz), 131.0 (d, $^4J_{CP}$ = 2.3 Hz, *p*-C_6H_5), 133.5 (d, $^2J_{CP}$ = 8.6 Hz), 134.1 (d, $^2J_{CP}$ = 8.0 Hz, *o*-C_6H_5). − ^{31}P NMR (162 MHz, C_6D_6): δ = +23.2 (s). − EI-MS; *m*/*z*: 600.1 (3) [$M^+ - BH_3$], 471.0 (10) [600.1 − $C_6H_{13}N_2O$], 373.1 (26) [$M^+ - BH_3 - Ph_2PCHCH_2CH_3$], 286.0 (100) [471.0 − Ph_2P], 243.0 (14). − CI-MS (isobutane); *m*/*z*: 601.1 (100) [MH^+], 600.0 (84) [M^+]. − HR-MS: $C_{33}H_{41}{}^{56}FeN_2OPS$ ($M^+ - BH_3$): calcd. 600.202662; found 600.202770.

Bis(hydrazine) 12: According to GP5, a solution of hydrazone **11** (700 mg, 1.14 mmol) in CH_2Cl_2 (25 mL) was treated with catecholborane (8.0 equiv.) at −50 °C. After warming to room temperature, the reaction mixture was stirred for 24 h at room temperature. Aqueous workup and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided hydrazone **12**. − Yield: 263 mg (37%, red-orange oil). − R_f = 0.15 (hexane/diethyl ether = 4:1). − *dr* = 1:1:1. − IR (neat): $\tilde{\nu}$ = 3089 cm^{-1}, 2967, 2920, 2873, 2827, 2379, 2279, 1725, 1666, 1600, 1447, 1373, 1308, 1237, 1197, 1188, 1126, 1039, 1025, 946, 918, 879, 827, 710, 675, 604, 531, 501, 489. − ^{1}H NMR (300 MHz, C_6D_6, selected signals): δ = 1.73 (s, 3 H, SCH_3), 3.32 (s, 3 H, OCH_3), 4.63 (broad s, 1 H, FcCH). − EI-MS; *m*/*z*: 618.3 (21) [M^+], 413.1 (59) $M^+ - H_3CSCHCH_3 - C_6H_{14}N_2O$), 366.1 (33, 413.1 − SCH_3), 359.0 (62), 337.0 (71, 413.1 − $H_3CCH_2SCH_3$), 313.0 (55), 289.1 (40), 265.9 (49), 129.1 (100, $HNNC_6H_{12}O^+$). − HR-MS: $C_{30}H_{50}{}^{56}FeN_4O_2S_2$: calcd. 618.272458; found 618.271830.

General Procedure for the Preparation of P∪S Ligands 6 (GP6): $HBF_4{\cdot}OEt_2$ (2.5 equiv.) was added to a solution of hydrazine **5** in CH_2Cl_2 (25−60 mL $mmol^{-1}$) at 0 °C. After 30 s (E^1 = R_2PBH_3) or 1 h (E^1 = SR), a solution of $HBEt_3Li$ (1 M in THF, 5 equiv.) was added. The dark brown solution immediately underwent a colour change to yellow. After 10 min, the reaction was quenched with saturated aqueous NH_4Cl, washed with brine and dried with $MgSO_4$. The pure product was obtained by filtration through silica gel (hexane/ether = 4:1).

General Procedure for the Preparation of S∪S- and S∪Se Ligands 6 (GP7): To trifluoroacetic acid (S∪S ligands: 10 mL $mmol^{-1}$; S∪Se ligands: 10 equiv.) was added $NaBH_4$ (S∪S ligands: 0.5 g $mmol^{-1}$; S∪Se ligands: 5 equiv.) at 0 °C. Subsequently, the solution of hydrazine **5** in CH_2Cl_2 (20 mL $mmol^{-1}$) was injected and the mixture was allowed to reach room temperature slowly. After completion of the reaction, it was quenched with saturated aqueous NH_4Cl, washed twice with saturated aqueous K_2CO_3 and twice with brine, and dried with $MgSO_4$. The pure product was obtained by filtration through silica gel (hexane/ether = 10:1).

General Procedure for BH_3 Deprotection (GP8): A heated Schlenk flask was charged under argon with a solution of BH_3-protected phosphane **6a−f** in dry diethyl ether, THF or toluene (2 mL $mmol^{-1}$) depending on the solubility. Then TMEDA (2.5−5.0 equiv.) was added at room temperature. If the deprotection required higher temperatures (alkyl-substituted phosphanes), the reaction was run in toluene at 90 °C. After completion (TLC control) the solvent was removed in vacuo. The ligand was obtained after filtration through silica gel.

BH_3-Protected P∪S Ligand 6a: According to GP6, a solution of hydrazine **5i** (80 mg, 0.133 mmol) in CH_2Cl_2 (10 mL) was treated with HBF_4OEt_2 (2.5 equiv.) at 0 °C. After 30 s, a solution of $HBEt_3Li$ (5.0 equiv., 1 M in THF) was added. The reaction mixture was stirred for 10 min and worked up. Filtration through silica gel (hexane/diethyl ether = 4:1) provided BH_3-protected phosphane **6a**. − Yield: 44 mg (70%, yellow oil). − R_f = 0.38 (hexane/diethyl ether = 4:1). − *de* = 94%. − *ee* ≥ 99% (HPLC: Chiralcel OD-H, *c*Hex, 0.5 mL/min, ent-1: 66.87 min; ent-2: 44.27 min). − $[\alpha]_D^{25}$ = +15.6 ($CHCl_3$, *c* = 0.27). − IR ($CHCl_3$): $\tilde{\nu}$ = 3079 cm^{-1}, 3058,

3006, 2971, 2921, 2873, 2855, 2385, 2350, 2263, 1723, 1659, 1589, 1482, 1437, 1379, 1313, 1218, 1186, 1161, 1137, 1107, 1064, 822, 757, 696, 668, 588, 495, 453. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.20 (dd, $^3J_{HP}$ = 16.2 Hz, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.97 (s, 3 H, SCH_3), 2.66 (dqt, $^2J_{HP}$ = 14.2 Hz, ^3J = 7.1 Hz, ^3J = 1.9 Hz, 1 H, PCH), 3.05 (m, 2 H, $FcCH_2$), 3.81 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 3.84 (s, 5 H, C_5H_5), 3.92 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.10 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 7.02 (m, 6 H, *m*/*p*-C_6H_5), 7.79 (m, 2 H, *o*-C_6H_5), 7.88 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ =14.6 (d, $^2J_{CP}$ = 2.3 Hz, $CHCH_3$), 19.9 (SCH_3), 30.0 (d, $^2J_{CP}$ = 4.6 Hz, $FcCH_2$), 31.7 (d, $^1J_{CP}$ = 13.8 Hz, PCH), 67.2, 68.7, 70.9 ($C_5H_3R_2$), 70.4 (C_5H_5), 84.8, 88.8 (d, $^3J_{CP}$ = 13.8 Hz, *i*-$C_5H_3R_2$), 128.8 (d, $^3J_{CP}$ = 9.8 Hz), 128.9 (d, $^3J_{CP}$ = 9.2 Hz, *m*-C_6H_5), 129.6 (d, $^1J_{CP}$ = 52.1 Hz), 129.8 (d, $^1J_{CP}$ = 52.1 Hz, *i*-C_6H_5), 131.0 (d, $^4J_{CP}$ = 2.3 Hz), 131.1 (d, $^4J_{CP}$ = 2.8 Hz, *p*-C_6H_5), 133.02 (d, $^2J_{CP}$ = 8.6 Hz), 133.03 (d, $^2J_{CP}$ = 8.0 Hz, *o*-C_6H_5). − ^{31}P NMR (C_6D_6, 121 MHz): +24.4 (broad). − EI-MS; *m*/*z*: 472.2 (14) [M^+], 458.1 (49) [$M^+ - BH_3$], 443.1 (100) [458.1 − CH_3], 411.1 (15) [458.1 − SCH_3], 393.1 (13) [458.1 − C_5H_5], 226.1 (10) [$Ph_2P(BH_3)CH{=}CH_2^+$]. − HR-MS: $C_{26}H_{30}B^{56}FePS$: calcd. 472.124829; found 472.124732.

BH_3-Protected P∪S Ligand 6b: According to GP6, a solution of hydrazine **5j** (127 mg, 0.207 mmol) in CH_2Cl_2 (5 mL) was treated with HBF_4OEt_2 (2.5 equiv.) at 0 °C. After 30 s, a solution of $HBEt_3Li$ (5.0 equiv., 1 M in THF) was added. The reaction mixture was stirred for 10 min and worked up. Filtration through silica gel (hexane/diethyl ether = 10:1) provided BH_3-protected phosphane **6b**. − Yield: 44 mg (70%, yellow oil). − R_f = 0.38 (hexane/diethyl ether = 4:1). − Yield: 51 mg (51%, yellow oil). − R_f = 0.48 (hexane/diethyl ether = 4:1). − *de* = 97%. − *ee* ≥ 99% (HPLC: Chiralcel OD-H, *c*Hex, 0.5 mL/min, ent-1: 43.44 min; ent-2: 30.85 min). − $[\alpha]_D^{25}$ = −22.4 ($CHCl_3$, *c* = 0.92). − IR ($CHCl_3$): $\tilde{\nu}$ = 3080 cm^{-1}, 3059, 3007, 2961, 2923, 2874, 2852, 2386, 2268, 1723, 1667, 1483, 1461, 1437, 1381, 1314, 1217, 1185, 1160, 1139, 1106, 1063, 1030, 1001, 964, 822, 756, 696, 668, 590, 499. − ^{1}H NMR (400 MHz, C_6D_6): δ = 0.85 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.77 (m, 2 H, CH_2CH_3), 2.03 (s, 3 H, SCH_3), 2.61 (m, 1 H, PCH), 3.07 (ddd, ^2J = 14.8 Hz, ^3J = 9.3 Hz, ^3J = 6.1 Hz, 1 H, $FcCH_2$), 3.26 (dt, ^2J = 15.1 Hz, ^3J = 7.9 Hz, 1 H, $FcCH_2$), 3.64 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 3.84 (s, 5 H, C_5H_5), 3.92 (dd, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.01 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 6.98 (m, 6 H, *m*/*p*-C_6H_5), 7.86 (m, 4 H, *o*-C_6H_5). − ^{13}C NMR (100 MHz, C_6D_6): δ =13.9 (d, $^3J_{CP}$ = 8.6 Hz, CH_2CH_3), 19.6 (SCH_3), 24.0 (d, $^2J_{CP}$ = 2.8 Hz, CH_2CH_3), 29.1 (d, $^2J_{CP}$ = 4.6 Hz, $FcCH_2$), 38.1 (d, $^1J_{CP}$ = 33.2 Hz, PCH), 66.8, 69.5, 70.3 ($C_5H_3R_2$), 70.4 (C_5H_5), 84.6, 88.7 (*i*-$C_5H_3R_2$), 128.6 (d, $^3J_{CP}$ = 9.7 Hz, *m*-C_6H_5), 128.9 (d, $^3J_{CP}$ = 9.8 Hz, *m*-C_6H_5), 130.8 (d, $^4J_{CP}$ = 2.3 Hz, *p*-C_6H_5), 131.0 (d, $^4J_{CP}$ = 2.3 Hz, *p*-C_6H_5), 132.9 (d, $^2J_{CP}$ = 8.6 Hz, *o*-C_6H_5) 133.0 (d, $^2J_{CP}$ = 8.6 Hz, *o*-C_6H_5). − ^{31}P NMR (C_6D_6, 121 MHz): +23.0 (broad). − EI-MS; *m*/*z*: 486.4 (4) [M^+], 472.3 (41) [$M^+ - BH_3$], 457.2 (100) [472.3 − CH_3], 425.2 (38) [472.3 − SCH_3], 407.1 (13), 304.2 (45) [425.2 − CpFe], 286.1 (27) [$M^+ - Ph_2PBH_3$], 240.1 (37) [$Ph_2P(BH_3)CH{=}CHCH_3^+$], 185.1 (21) [Ph_2P^+], 183.1 (63) [185.1 − H_2], 121.0 (84) [$CpFe^+$], 109.1 (38), 91.2 (45), 57.3 (36), 56.2 (38) [Fe^+], 55.2 (35). − HR-MS: $C_{27}H_{29}{}^{56}FePS$ ($M^+ - BH_3$): calcd. 472.107695; found 472.107697.

BH_3-Protected P∪S Ligand 6c: According to GP6, a solution of hydrazine **5b** (36 mg, 0.060 mmol) in CH_2Cl_2 (3 mL) was treated with $HBF_4 \cdot OEt_2$ (2.5 equiv.) at 0 °C. After 45 min, a solution of $HBEt_3Li$ (5.0 equiv., 1 M in THF) was added. The reaction mixture was stirred for 10 min and worked up. Filtration through silica gel (hexane/diethyl ether = 10:1) provided BH_3-protected phosphane **6c**. − Yield: 44 mg (70%, yellow oil). − R_f = 0.38 (hexane/diethyl ether = 4:1). − Yield: 27 mg (95%, yellow crystals). − R_f = 0.53 (hexane/diethyl ether = 4:1). − *de* = 95%. − *ee* ≥ 96% (^{1}H NMR: 22.5 equiv. Pirkle alcohol in C_6D_6, C_5H_5: 4.020 v 4.024; SCH_3: 1.552 v 1.560; $CHCH_3$: 1.181 v 1.197 ppm). − $[\alpha]_D^{25}$ = −149.4 ($CHCl_3$, *c* = 0.33). − M.p.: 151 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3078 cm^{-1}, 3057, 3006, 2962, 2920, 2858, 2396, 2352, 2263, 1818, 1777, 1728, 1665, 1589, 1484, 1437, 1396, 1374, 1334, 1314, 1267, 1235, 1218, 1179, 1152, 1106, 1062, 1043, 1029, 1002, 956, 926, 893, 825, 743, 699, 667, 654, 636. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.24 (d, ^3J = 6.3 Hz, 3 H, $CHCH_3$), 1.60 (s, 3 H, SCH_3), 2.31 (dd, ^2J = 13.8 Hz, ^3J = 11.5 Hz, 1 H, $FcCH_2$), 2.43 (dqd, ^3J = 11.4 Hz, ^3J = 6.3 Hz, ^3J = 3.3 Hz, 1 H, SCH), 3.68 (dd, ^2J = 14.3 Hz, ^3J = 3.3 Hz, 1 H, $FcCH_2$), 3.71 (m, 1 H, $C_5H_3R_2$), 4.01 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.05 (s, 5 H, C_5H_5), 4.39 (dt, ^3J = 2.2 Hz, ^4J = J_{HP} = 1.8 Hz, 1 H, $C_5H_3R_2$), 6.94−7.03 (m, 6 H, *m*/*p*-C_6H_5), 7.66 (m, 2 H, *o*-C_6H_5), 7.78 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ =12.9, 22.0 (CH_3), 36.9 ($FcCH_2$), 43.9 (SCH), 70.2 (d, J_{CP} = 6.1 Hz), 73.3 (d, J_{CP} = 3.7 Hz), 76.1 (d, J_{CP} = 8.0 Hz, $C_5H_3R_2$), 70.8 (C_5H_5), 71.5, 91.7 (d, J_{CP} = 16.5 Hz, *i*-$C_5H_3R_2$), 128.5 (d, $^3J_{CP}$ = 9.7 Hz, *m*-C_6H_4), 130.7 (d, $^4J_{CP}$ = 2.5 Hz, *p*-C_6H_4), 130.9 (d, $^4J_{CP}$ = 2.4 Hz, *p*-C_6H_4), 131.9 (d, $^1J_{CP}$ = 59.9 Hz, *i*-C_6H_4), 132.95 (d, $^1J_{CP}$ = 56.2 Hz, *i*-C_6H_4), 132.95 (d, $^2J_{CP}$ = 9.2 Hz, *o*-C_6H_4), 133.8 (d, $^2J_{CP}$ = 9.1 Hz, *o*-C_6H_5). − ^{31}P NMR (C_6D_6, 162 MHz): +14.6 (broad). − EI-MS; *m*/*z*: 472.1 (2) [M^+], 458.0 (37) [$M^+ - BH_3$], 443.0 (100) [458.0 − CH_3], 376.9 (12), 225.9 (94) [$FcCH{=}CHCH_3^+$], 182.9 (35) [$PPh_2^+ - H_2$], 132.9 (10), 120.9 (12) [$CpFe^+$], 56.0 (11) [Fe^+] − CI-MS (isobutane); *m*/*z*: 472.0 (44) [M^+], 471.1 (100) [$M^+ - H$], 458.0 (6) [$M^+ - BH_3$]. − HR-MS: $C_{26}H_{27}{}^{56}FePS$ ($M^+ - BH_3$): calcd. 458.092049; found 458.092016.

BH_3-Protected P∪S Ligand 6d: According to GP6, a solution of hydrazine **5c** (112 mg, 0.182 mmol) in CH_2Cl_2 (4 mL) was treated with $HBF_4 \cdot OEt_2$ (2.5 equiv.) at 0 °C. After 45 min, a solution of $HBEt_3Li$ (5.0 equiv., 1 M in THF) was added. The reaction mixture was stirred for 10 min and worked up. Filtration through silica gel (hexane/diethyl ether = 10:1) provided BH_3-protected phosphane **6d**. − Yield: 44 mg (70%, yellow oil). − R_f = 0.38 (hexane/diethyl ether = 4:1). − Yield: 80 mg (90%, yellow crystals). − R_f = 0.52 (hexane/diethyl ether = 4:1). − *de* = 97%. − *ee* ≥ 96% (^{1}H NMR: 22 equiv. Pirkle alcohol in C_6D_6, C_5H_5: 4.058 v 4.065 ppm). − $[\alpha]_D^{25}$ = −192.4 ($CHCl_3$, *c* = 0.21). − M.p.: 142 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3077 cm^{-1}, 3057, 3006, 2962, 2924, 2872, 2855, 2392, 2351, 2262, 1667, 1484, 1460, 1437, 1383, 1336, 1313, 1295, 1261, 1218, 1179, 1149, 1197, 1062, 1043, 1029, 1001, 954, 924, 824, 757, 699, 667, 655, 624, 604, 539, 503, 480. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.95 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.55 (m, 2 H, CH_2CH_3), 1.58 (s, 3 H, SCH_3), 2.18 (m, 1 H, SCH), 2.38 (dd, ^2J = 14.3 Hz, ^3J = 11.3 Hz, 1 H, $FcCH_2$), 3.67 (dd, ^2J = 14.5 Hz, ^3J = 4.1 Hz, 1 H, $FcCH_2$), 3.70 (m, 1 H, $C_5H_3R_2$), 4.02 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.09 (s, 5 H, C_5H_5), 4.45 (dt, ^3J = 2.2 Hz, ^4J = J_{HP} = 1.7 Hz, $C_5H_3R_2$), 6.94−7.02 (m, 6 H, *m*/*p*-C_6H_5), 7.67 (m, 2 H, *o*-C_6H_5), 7.80 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 11.0, 12.4 (CH_3), 27.7 (CH_2CH_3), 34.5 ($FcCH_2$), 50.5 (SCH), 70.1 (d, J_{CP} = 6.3 Hz), 73.3, 76.0 (d, J_{CP} = 7.4 Hz, $C_5H_3R_2$), 70.8 (C_5H_5), 91.8 (*i*-$C_5H_3R_2$), 130.8, 130.9 (*p*-C_6H_5), 131.7 (d, $^1J_{CP}$ = 59.5 Hz), 133.8 (d, $^1J_{CP}$ = 69.8 Hz, *i*-C_6H_5), 133.1 (d, $^2J_{CP}$ = 9.1 Hz), 133.8 (d, $^2J_{CP}$ = 9.1 Hz, *o*-C_6H_5). − ^{31}P NMR (C_6D_6, 121 MHz): +14.0 (broad). − EI-MS; *m*/*z*: 472.1 (60) [$M^+ - BH_3$], 458.1 (37) [$M^+ - CH_2{=}CH_2$], 457.1 (100) [$M^+ - CH_2CH_3$], 240.0 (54) [$FcCH{=}CHCH_2CH_3^+$], 183.1 (38) [$PPh_2^+ - H_2$], 121.0 (68)

[CpFe$^+$], 56.1 (12) [Fe$^+$]. − HR-MS: $C_{27}H_{29}{}^{56}FePS$ ($M^+ - BH_3$): calcd. 472.107699; found 472.107688.

BH_3-Protected P∪S Ligand 6e: According to GP6, a solution of hydrazine **5d** (45 mg, 0.082 mmol) in CH_2Cl_2 (5 mL) was treated with $HBF_4 \cdot OEt_2$ (2.5 equiv.) at 0 °C. After 2 h, a solution of $HBEt_3Li$ (5.0 equiv., 1 M in THF) was added. The reaction mixture was stirred for 10 min and worked up. Filtration through silica gel (hexane/diethyl ether = 10:1) provided BH_3-protected phosphane **6e**. − Yield: 44 mg (70%, yellow oil). − R_f = 0.38 (hexane/diethyl ether = 4:1). − Yield: 30 mg (88%, yellow crystals). − R_f = 0.68 (hexane/diethyl ether = 4:1). − *de* = 95%. − *ee* ≥ 96% (^{1}H NMR: 15 equiv. Pirkle alcohol in C_6D_6, C_5H_5: 4.081 v 4.086 ppm). − $[\alpha]_D^{25}$ = +100.0 ($CHCl_3$, *c* = 0.08). − M.p.: 73 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 3096 cm^{-1}, 2923, 2854, 2727, 2384, 2350, 2263, 1739, 1659, 1643, 1579, 1462, 1379, 1293, 1261, 1154, 1108, 1068, 1044, 1033, 956, 932, 885, 822, 752, 722, 687, 652, 633, 586, 528, 483, 465. − ^{1}H NMR (400 MHz, C_6D_6): δ = 0.92 (dd, $^3J_{HP}$ = 13.8 Hz, ^3J = 7.1 Hz, 3 H, PCHCH_3), 1.10 (dd, $^3J_{HP}$ = 14.8 Hz, ^3J = 7.4 Hz, 3 H, PCHCH_3), 1.12 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.12 (dd, $^3J_{HP}$ = 14.3 Hz, ^3J = 7.4 Hz, 3 H, PCHCH_3), 1.21 (dd, $^3J_{HP}$ = 14.3 Hz, ^3J = 7.2 Hz, 3 H, PCHCH_3), 1.62 (dquint, ^2J = 14.0 Hz, ^3J = 7.2 Hz, 1 H, CH_2CH$_3$), 1.70 (tqd, ^2J = 14.3 Hz, ^3J = 7.1 Hz, ^3J = 4.7 Hz, 1 H, CH_2CH$_3$), 1.79 (s, 3 H, SCH_3), 1.93 (dsept, $^2J_{HP}$ = 11.0 Hz, ^3J = 7.1 Hz, 1 H, PCH), 1.99 (dsept, $^2J_{HP}$ = 11.0 Hz, ^3J = 7.2 Hz, 1 H, PCH), 2.64 (ddt, ^3J = 8.5 Hz, ^3J = 7.7 Hz, ^3J = 5.5 Hz, 1 H, SCH), 2.82 (dd, ^2J = 15.1 Hz, ^3J = 8.5 Hz, 1 H, $FcCH_2$), 3.20 (dd, ^2J = 15.4 Hz, ^3J = 5.2 Hz, 1 H, $FcCH_2$), 3.99 (dt, ^3J = 2.5 Hz, ^4J = 1.7 Hz, 1 H, $C_5H_3R_2$), 4.04 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.13 (s, 5 H, C_5H_5), 4.49 (dt, ^3J = 2.5 Hz, ^4J = J_{HP} = 1.4 Hz, 1 H, $C_5H_3R_2$). − ^{13}C NMR (75 MHz, C_6D_6): δ =11.7, 13.0 (SCH_3, CH_2CH_3), 17.0, 18.0, 18.6 (CHCH_3), 23.7 (d, $^1J_{CP}$ = 34.4 Hz), 25.3 (d, $^1J_{CP}$ = 33.2 Hz, PCH), 28.4 (CH_2CH$_3$), 30.2 ($FcCH_2$), 50.0 (SCH), 65.9 (*i*-$C_5H_3R_2$), 69.5, 71.9, 73.3 ($C_5H_3R_2$), 71.1 (C_5H_5), 90.3 (*i*-$C_5H_3R_2$). − ^{31}P NMR (C_6D_6, 121 MHz): +31.8 (broad). − EI-MS; *m*/*z*: 418.2 (12) [M^+], 404.3 (12) [$M^+ - BH_3$], 389.2 (100) [404.3 − CH_3] 357.2 (10) [404.3 − SCH_3], 271.1 (12) [389.2 − HP(*i*Pr)$_2$], 240.1 (36) [357.2 − P(*i*Pr)$_2$], 171.3 (13), 135.1 (11), 121.1 (25) [CpFe$^+$], 57.3 (40) [FeH$^+$], 56.3 (12) [Fe$^+$]. − HR-MS: $C_{21}H_{36}B^{56}FePS$: calcd. 418.171779; found 418.171788.

BH_3-Protected P∪S Ligand 6f: According to GP6, a solution of hydrazine **5e** (189 mg, 0.301 mmol) in CH_2Cl_2 (7 mL) was treated with $HBF_4 \cdot OEt_2$ (2.5 equiv.) at 0 °C. After 4 h, a solution of $HBEt_3Li$ (5.0 equiv., 1 M in THF) was added. The reaction mixture was stirred for 10 min and worked up. Filtration through silica gel (hexane/diethyl ether = 10:1) provided BH_3-protected phosphane **6f**. − Yield: 44 mg (70%, yellow oil). − R_f = 0.38 (hexane/diethyl ether = 4:1). − Yield: 122 mg (81%, yellow crystals). − R_f = 0.85 (hexane/diethyl ether = 4:1). − *de* = 94%. − *ee* ≥ 96% (^{1}H NMR: 17 equiv. Pirkle alcohol in C_6D_6, C_5H_5: 3.997 v 4.000 ppm). − $[\alpha]_D^{25}$ = −86.9 ($CHCl_3$, *c* = 0.63). − M.p.: 142 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3144 cm^{-1}, 3077, 3057, 3006, 2958, 2924, 2863, 2717, 2614, 2395, 2351, 2264, 1818, 1726, 1600, 1589, 1484, 1450, 1437, 1395, 1335, 1312, 1282, 1269, 1245, 1234, 1178, 1148, 1106, 1062, 1043, 1029, 1002, 926, 894, 824, 741, 699, 667, 644, 623, 602, 537, 502. − ^{1}H NMR (400 MHz, C_6D_6): δ = 0.89 [d, ^3J = 6.6 Hz, 3 H, CH(CH_3)$_2$], 1.08 [d, ^3J = 6.6 Hz, 3 H, CH(CH_3)$_2$], 1.32 (d, ^3J = 6.6 Hz, 3 H, H_2CCHCH_3), 2.42 (dd, ^2J = 14.0 Hz, ^3J = 11.0 Hz, 1 H, $FcCH_2$), 2.60 [sept, ^3J = 6.6 Hz, 1 H, SCH(CH_3)$_2$], 2.64 (dqd, ^3J = 11.0 Hz, ^3J = 6.3 Hz, ^3J = 3.3 Hz, 1 H, $FcCH_2CH$), 3.74 (q, $^{3/4}J$ = J_{HP} = 2.4 Hz, 1 H, $C_5H_3R_2$), 3.76 (dd, ^2J = 14.0 Hz, ^3J = 3.6 Hz, 1 H, $FcCH_2$), 4.01 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.01 (s, 5 H, C_5H_5), 4.52 (q, $^{3/4}J$ = J_{HP} = 2.0 Hz, 1 H, $C_5H_3R_2$), 7.00 (m, 6 H, *m*/*p*-C_6H_5), 7.67 (m, 2 H, *o*-C_6H_5), 7.79 (ddd, *J* = 10.7 Hz, *J* = 8.3 Hz, *J* = 2.7 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 23.3, 23.9, 24.0 (CH_3), 33.2, 41.4 (SCH), 37.5 ($FcCH_2$), 68.0 (d, $^2J_{CP}$ = 6.2 Hz, *i*-$C_5H_3R_2$), 70.4 (d, J_{CP} = 6.3 Hz), 70.6 (d, J_{CP} = 7.5 Hz), 76.2 ($C_5H_3R_2$), 70.8 (C_5H_5), 91.6 (d, $^1J_{CP}$ = 16.1 Hz, *i*-$C_5H_3R_2$), 128.5 (d, $^3J_{CP}$ = 8.0 Hz, *m*-C_6H_4), 130.7, 130.9 (*p*-C_6H_4), 132.0 (d, $^1J_{CP}$ = 60.1 Hz), 133.03 (d, $^1J_{CP}$ = 56.1 Hz, *i*-C_6H_4), 132.96 (d, $^2J_{CP}$ = 9.1 Hz), 133.8 (d, $^2J_{CP}$ = 9.1 Hz, *o*-C_6H_5). − ^{31}P NMR (C_6D_6, 162 MHz): +14.1 (broad). − EI-MS; *m*/*z*: 500.4 (2) [M^+], 486.3 (7) [$M^+ - BH_3$], 443.2 (68) [486.1 − $CH(CH_3)_2$], 279.3 (26), 226.1 (44) [FcCH=$CHCH_3^+$], 182.9 (23) [$PPh_2^+ - H_2$], 167.0 (58), 139.1 (16), 121.0 (23) [CpFe$^+$], 113.2 (23), 112.2 (15), 111.2 (17), 77.1 (46) [$C_6H_5^+$], 73.2 (42), 57.2 (100) [FeH$^+$], 55.1 (73), 45.3 (37). − HR-MS: $C_{28}H_{34}B^{56}FePS$: calcd. 500.156129; found 500.156166.

S∪S Ligand 6g: According to GP7, a mixture of TFA (1 mL) and $NaBH_4$ (13.3 equiv.) in CH_2Cl_2 (4 mL) was treated with a solution of hydrazine **5f** (65 mg, 0.140 mmol) in CH_2Cl_2 (2 mL). After warming to room temperature, the mixture was stirred for 8 h. Aqueous work up and purification by filtration through silica gel (hexane/diethyl ether = 4:1) provided S∪S ligand **6g**. − Yield: 44 mg (70%, yellow oil). − R_f = 0.38 (hexane/diethyl ether = 4:1). − Yield: 45 mg (95%, yellow crystals). − R_f = 0.80 (hexane/diethyl ether = 4:1). − *de* = 94%. − *ee* ≥ 99% (GC: Chirasil dex 25m, 140-1-190, ent-1: 56.8 min; ent-2: 57.2 min). − $[\alpha]_D^{25}$ = −181.3 ($CHCl_3$, *c* = 0.79). − Mp: 165 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3093 cm^{-1}, 2963, 2918, 2872, 2856, 1630, 1593, 1435, 1379, 1311, 1262, 1239, 1182, 1159, 1106, 1071, 1031, 1001, 957, 921, 875, 818, 757, 714, 667, 515, 498, 467, 452. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.08 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.58 (m, 2 H, CH_2CH$_3$), 1.76 (s, 3 H), 2.00 (s, 3 H, SCH_3), 2.48 (m, 1 H, SCH), 2.60 (dd, ^2J = 14.0 Hz, ^3J = 8.2 Hz, 1 H, $FcCH_2$), 3.13 (dd, ^2J = 14.0 Hz, ^3J = 5.7 Hz, 1 H, $FcCH_2$), 3.93 (t, ^3J = 2.6 Hz, 1 H, $C_5H_3R_2$), 3.99 (s, 5 H, C_5H_5), 4.18 (dd, ^3J = 2.5 Hz, ^4J = 1.7 Hz, 1 H, $C_5H_3R_2$), 4.24 (dd, ^3J = 2.5 Hz, ^4J = 1.7 Hz, 1 H, $C_5H_3R_2$). − ^{13}C NMR (75 MHz, C_6D_6): δ = 11.7, 13.4, 20.4 (CH_3), 27.7 (CH_2CH$_3$), 34.5 ($FcCH_2$), 51.2 (SCH), 67.5, 70.4, 71.7 ($C_5H_3R_2$), 70.3 (C_5H_5), 83.7, 88.6 (*i*-$C_5H_3R_2$). − EI-MS; *m*/*z*: 334.3 (70) [M^+], 245.1 (100) [M^+ − $H_3CSCHCH_2CH_3$], 121.0 (20) [CpFe$^+$]. − HR-MS: $C_{16}H_{22}{}^{56}FeS_2$: calcd. 334.051233; found 334.051258.

S∪S Ligand 6h: According to GP7, a mixture of TFA (2 mL) and $NaBH_4$ (13.2 equiv.) in CH_2Cl_2 (2 mL) was treated with a solution of hydrazine **5g** (77 mg, 0.136 mmol) in CH_2Cl_2 (2 mL). After warming to room temperature, the mixture was stirred for 15 h. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided S∪S ligand **6h**. − Yield: 44 mg (70%, yellow oil). − R_f = 0.38 (hexane/diethyl ether = 4:1). − Yield: 44 mg (70%, yellow oil). − R_f = 0.38 (hexane/diethyl ether = 4:1). − Yield: 50 mg (84%, yellow crystals). − R_f = 0.80 (hexane/diethyl ether = 4:1). − *de* = 97%. − *ee* ≥ 99% (HPLC: Chiralcel OD-H, *c*Hex, 0.5 mL/min, ent-1: 15.76 min; ent-2: 10.08 min). − $[\alpha]_D^{25}$ = −5.9 ($CHCl_3$, *c* = 0.46). − M.p.: 66 °C. − IR (KBr): $\tilde{\nu}$ = 3084 cm^{-1}, 3017, 2959, 2926, 2863, 2240, 1720, 1702, 1686, 1638, 1597, 1563, 1545, 1525, 1492, 1458, 1428, 1407, 1377, 1344, 1291, 1246, 1230, 1181, 1147, 1105, 1085, 1052, 1029, 1017, 1001, 939, 918, 882, 841, 805, 747. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.94 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.01 (d, ^3J = 6.7 Hz, 3 H, CHCH_3), 1.03 (d, ^3J = 6.7 Hz, 3 H, CHCH_3), 1.51 (quint, ^3J = 7.4 Hz, 2 H, CH_2CH$_3$), 1.99 (s, 3 H, $C_6H_4CH_3$), 2.33 (m, 1 H, $FcCH_2CH$), 2.45 (dd, ^2J = 14.1 Hz, ^3J = 10.4 Hz, 1 H, $FcCH_2$), 2.47 (sept, ^3J = 6.7 Hz, 1 H, SCH(CH_3)$_2$), 3.21 (dd, ^2J =

13.8 Hz, ^3J = 4.7 Hz, 1 H, $FcCH_2$), 4.01 (t, ^3J = 2.4 Hz, 1 H, $C_5H_3R_2$), 4.02 (s, 5 H, C_5H_5), 4.39 (dd, ^3J = 2.4 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.53 (dd, ^3J = 2.4 Hz, ^4J = 1.3 Hz, 1 H, $C_5H_3R_2$), 6.83 (d, ^3J = 8.1 Hz, 2 H, C_6H_4), 7.17 (dt, ^3J = 8.1 Hz, ^4J = 2.0 Hz, 2 H, C_6H_4). − ^{13}C NMR (75 MHz, C_6D_6): δ = 11.3, 20.8, 23.9, 24.2 (CH_3), 30.0 (CH_2CH_3), 34.9 [S*C*H(CH_3)$_2$], 35.6 ($FcCH_2$), 48.8 (S*C*HCH_2), 68.5, 72.4, 75.4 ($C_5H_3R_2$), 70.5 (C_5H_5), 90.6 (*i*-$C_5H_3R_2$), 127.1, 129.7 (C_6H_4), 138.9 (*i*-C_6H_4). − EI-MS; *m*/*z*: 438.3 (68) [M$^+$], 321.2 (100) [M$^+$ − $(H_3C)_2$CHSCHCH$_2$CH$_3$], 319.2 (17) [321.2 − H_2], 272.1 (16), 255.1 (34) [321.2 − C_5H_6], 199.2 (20) [255.1 − Fc], 165.1 (13), 153.1 (11), 121.1 (25) [CpFe$^+$], 115.1 (10), 91.2 (11) [$C_7H_7^+$], 75.2 (14) [$(H_3C)_2CHS^+$], 56.1 (15) [Fe$^+$]. − HR-MS: $C_{24}H_{30}{}^{56}FeS_2$: calcd. 438.113833; found 438.113712.

S∪Se Ligand 6i: According to GP7, a mixture of TFA (86 μL) and $NaBH_4$ (10 equiv.) in CH_2Cl_2 (3 mL) was treated with a solution of hydrazine **5h** (134 mg, 0.224 mmol) in CH_2Cl_2 (2 mL). After warming to room temperature, a further portion of $NaBH_4$ (10 equiv.) was added and stirring was continued for 15 h. Afterwards, a further portion of TFA (172 μL) was added. The mixture was stirred for a further 6 h. Aqueous workup and purification by flash chromatography through silica gel (hexane/diethyl ether = 4:1) provided S∪Se ligand **6i**. − Yield: 74 mg (70%, yellow crystals). − R_f = 0.80 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − *ee* ≥ 99% (HPLC: Chiralcel OD-2, *c*Hex, 0.5 mL/min, ent-1: 14.36 min; ent-2: 10.55 min). − $[\alpha]_D^{25}$ = −8.0 ($CHCl_3$, *c* = 0.44). − M.p.: 59 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3094 cm^{-1}, 3071, 3058, 2958, 2925, 2858, 1728, 1641, 1579, 1477, 1460, 1439, 1380, 1366, 1342, 1290, 1261, 1244, 1219, 1178, 1155, 1125, 1106, 1070, 1051, 1023, 1001, 973, 921, 875, 821, 758, 735, 691, 668, 526, 506, 496, 465. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.94 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 0.98 (d, ^3J = 6.6 Hz, 3 H, CHCH_3), 1.00 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.51 (m, 2 H, CH_2CH$_3$), 2.21 (dtd, ^3J = 10.2 Hz, ^3J = 6.3 Hz, ^3J = 3.8 Hz, 1 H, $FcCH_2CH$), 2.43 [sept, ^3J = 6.6 Hz, 1 H, SC*H*(CH_3)$_2$], 2.43 (dd, ^2J = 14.0 Hz, ^3J = 10.2 Hz, 1 H, $FcCH_2$), 3.16 (dd, ^2J = 14.0 Hz, ^3J = 3.9 Hz, 1 H, $FcCH_2$), 3.99 (s, 5 H, C_5H_5), 4.02 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.38 (dd, ^3J = 2.2 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.50 (dd, ^3J = 2.7 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 6.86 (tt, ^3J = 7.2 Hz, ^4J = 1.4 Hz, 1 H, *p*-C_6H_5), 6.92 (tm, ^3J = 7.4 Hz, 2 H, *m*-C_6H_5), 7.33 (dd, ^3J = 8.0 Hz, ^4J = 1.1 Hz, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 11.3, 23.9, 24.2 (CH_3), 30.0 (CH_2CH_3), 35.0 [S*C*H(CH_3)$_2$], 36.6 ($FcCH_2$), 49.0 (SC*H*CH_2), 69.4, 72.3, 76.5 ($C_5H_3R_2$), 70.3 (C_5H_5), 91.0 (*i*-$C_5H_3R_2$), 126.0 (*p*-C_6H_5), 129.2, 129.6 (*o*/*m*-C_6H_5), 135.7 (*i*-C_6H_5). − EI-MS; *m*/*z*: 472.2 (100) [M$^+$], 355.1 (58) [M$^+$ − $(H_3C)_2$CHSCHCH$_2$CH$_3$], 289.1 (27) [355.1 − C_5H_6], 275.1 (13), 272.2 (22), 199.1 (10) [$FcCH_2^+$], 141.0 (12), 121.1 (13) [CpFe$^+$], 57.3 (10) [FeH$^+$]. − HR-MS: $C_{23}H_{28}{}^{56}FeSSe$ calcd. 472.042632; found 472.042739.

P∪S Ligand 6j: a) According to GP8, a solution of BH_3-protected phosphane **6d** (83 mg, 0.171 mmol) in diethyl ether (5 mL) was treated with TMEDA (5.0 equiv.) for 5 h at room temperature. Filtration through silica gel under argon (hexane/diethyl ether = 10:1) provided P∪S ligand **6j**. b) A heated Schlenk flask was charged under argon with a solution of hydrazine **5c** (65 mg, 0.106 mmol) in CH_2Cl_2 (4 mL) at 0 °C. After HBF_4OEt_2 (2.5 equiv.) was added, the solution was stirred for 45 min. *n*BuLi (5.0 equiv.) and benzylamine (0.1 mL) were added successively. After 1 h, the reaction mixture was worked up according to GP6 and the product **6j** was obtained by filtration through silica gel (hexane/diethyl ether = 10:1). − Yield: a) 71 mg (88%, yellow crystals); b) 36 mg (68%). − R_f = 0.71 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −263.1 ($CHCl_3$, *c* = 0.64). − M.p.: 107 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3050 cm^{-1}, 2962, 2925, 2855, 2183, 1900, 1719, 1686, 1656, 1638, 1584, 1545, 1498, 1474, 1459, 1433, 1380, 1348, 1325, 1290, 1262, 1228, 1205, 1179, 1147,1104, 1070, 1052, 1024, 1002, 955, 918, 835, 813, 743, 723, 699. − ^{1}H NMR (400 MHz, C_6D_6): δ = 0.90 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.45 (m, 2 H, CH_2CH$_3$), 1.66 (s, 3 H, SCH_3), 2.16 (dtd, ^3J = 10.4 Hz, ^3J = 6.3 Hz, ^3J = 4.1 Hz, 1 H, SCH), 2.55 (dd, ^2J = 14.3 Hz, ^3J = 10.4 Hz, 1 H, $FcCH_2$), 3.33 (ddd, ^2J = 14.3 Hz, ^3J = 3.9 Hz, $^4J_{HP}$ = 3.0 Hz, 1 H, $FcCH_2$), 3.82 (m, 1 H, $C_5H_3R_2$), 3.91 (s, 5 H, C_5H_5), 4.10 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.53 (td, ^3J = J_{HP} = 2.2 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 6.96−7.10 (m, 6 H, *m*/*p*-C_6H_5), 7.39 (tt, *J* = 6.6 Hz, ^4J = 1.7 Hz, 2 H, *o*-C_6H_5), 7.65 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 10.8, 12.7 (CH_3), 27.8 (CH_2CH_3), 34.4 (d, $^3J_{CP}$ = 10.3 Hz, $FcCH_2$), 50.6 (SCH), 69.0, 70.6, 73.3 (d, J_{CP} = 4.0 Hz, $C_5H_3R_2$), 69.5 (C_5H_5), 91.6 (*i*-$C_5H_3R_2$), 132.6 (d, $^2J_{CP}$ = 18.9 Hz), 134.8 (d, $^2J_{CP}$ = 21.2 Hz, *o*-C_6H_5). − ^{31}P NMR (C_6D_6, 162 MHz): −25.0 (s). − EI-MS; *m*/*z*: 472.1 (66) [M$^+$], 457.1 (100) [M$^+$ − CH_3], 424.2 (19) [M$^+$ − $HSCH_3$], 391.1 (11), 240.1 (62), 184.1 (35), 121.0 (15) [CpFe$^+$], 56.1 (11) [Fc$^+$]. − HR-MS: $C_{27}H_{29}{}^{56}FePS$: calcd. 472.107699; found 472.107765.

P∪S Ligand 6k: a) According to GP8, a solution of BH_3-protected phosphane **6c** (75 mg, 0.159 mmol) in diethyl ether (4 mL) was treated with TMEDA (5.0 equiv.) for 5 h at room temperature. Filtration through silica gel under argon (hexane/diethyl ether = 10:1) provided P∪S ligand **6k**. b) A heated Schlenk flask was charged under argon with a solution of hydrazine **5b** (79 mg, 0.132 mmol) in CH_2Cl_2 (4 mL) at 0 °C. After HBF_4OEt_2 (2.5 equiv.) was added, the solution was stirred for 45 min. *n*BuLi (5.0 equiv.) and benzylamine (0.3 mL) were added successively. After 1 h, the reaction mixture was worked up according to GP6 and the product **6k** was obtained by filtration through silica gel (hexane/diethyl ether = 10:1). − Yield: a) 37 mg (51%, yellow crystals); b) 40 mg (66%). − R_f = 0.73 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −240.9 ($CHCl_3$, *c* = 1.40). − Mp: 98 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3180 cm^{-1}, 3078, 3058, 2968, 2927, 2857, 1723, 1591, 1483, 1438, 1400, 1377, 1312, 1266, 1238, 1216, 1188, 1173, 1161, 1120, 1108, 1083, 1043, 1001, 948, 826, 756, 723, 702, 665, 573, 544, 508, 459. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.10 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.68 (s, 3 H, SCH_3), 2.43 (dqd, ^3J = 9.5 Hz, ^3J = 6.9 Hz, ^3J = 4.7 Hz, 1 H, SCH), 2.57 (dd, ^2J = 14.0 Hz, ^3J = 9.9 Hz, 1 H, $FcCH_2$), 3.24 (ddd, ^2J = 14.0 Hz, ^3J = 4.7 Hz, $^4J_{HP}$ = 2.8 Hz, 1 H, $FcCH_2$), 3.84 (m, 1 H, $C_5H_3R_2$), 3.88 (s, 5 H, C_5H_5), 4.09 (t, ^3J = 2.4 Hz, 1 H, $C_5H_3R_2$), 4.44 (td, ^3J = J_{HP} = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 6.95−7.11 (m, 6 H, *m*/*p*-C_6H_5), 7.39 (ddd, *J* = 8.3 Hz, *J* = 6.9 Hz, ^4J = 1.9 Hz, 2 H, *o*-C_6H_5), 7.66 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.4 (SCH_3), 22.1 (CHCH_3), 37.4 (d, $^3J_{CP}$ = 9.7 Hz, $FcCH_2$), 44.1 (SCH), 69.7, 71.3 (d, J_{CP} = 4.6 Hz), 73.6 (d, J_{CP} = 4.0 Hz, $C_5H_3R_2$), 70.1 (C_5H_5), 91.6 (*i*-$C_5H_3R_2$), 128.9, 129.2 (*p*-C_6H_5), 132.9 (d, $^2J_{CP}$ = 18.4 Hz), 135.5 (d, $^2J_{CP}$ = 21.2 Hz, *o*-C_6H_5). − ^{31}P NMR (C_6D_6, 162 MHz): −24.7 (s). − EI-MS; *m*/*z*: 474.2 (100) [MO$^+$], 427.1 (83) [474.2 − SCH_3], 399.2 (14) [474.2 − $H_3CCHSCH_3$], 361.1 (35) [427.1 − CpH], 333.1 (25) [399.2 − CpH], 226.2 (19) [427.1 − Ph_2PO], 57.1 (10) [FeH$^+$]. − HR-MS: $C_{26}H_{27}{}^{56}FePS$: calcd. 458.092049; found 458.092033.

P∪S Ligand 6l: According to GP8, a solution of BH_3-protected phosphane **6e** (87 mg, 0.210 mmol) in toluene (6 mL) was treated with TMEDA (10.0 equiv.) for 15 h at 90 °C. Filtration through silica gel under argon (hexane/diethyl ether = 10:1) provided P∪S ligand **6l**. − Yield: 80 mg (95%, orange oil). − R_f = 0.80 (hexane/diethyl ether = 4:1). − *de* = 97%. − $[\alpha]_D^{25}$ = −83.4 ($CHCl_3$, *c* = 1.69). − IR ($CHCl_3$): $\tilde{\nu}$ = 3095 cm^{-1}, 2954, 2920 (v), 2866, 1641, 1440, 1382, 1363, 1294, 1231, 1176, 1153, 1107, 1072, 1039, 1021,

1002, 956, 927, 880, 819, 753, 700, 661, 632, 599, 572, 493, 475. − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.88 (dd, $^3J_{HP}$ = 12.9 Hz, ^3J = 7.2 Hz, 3 H, PCHCH_3), 1.04 (dd, $^3J_{HP}$ = 13.5 Hz, ^3J = 6.9 Hz, 3 H, PCHCH_3), 1.12 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3), 1.26 (dd, $^3J_{HP}$ = 9.1 Hz, ^3J = 7.1 Hz, 3 H, PCHCH_3), 1.42 (dd, $^3J_{HP}$ = 16.5 Hz, ^3J = 7.7 Hz, 3 H, PCHCH_3), 1.55−1.85 (m, 3 H, CH_2CH$_3$, PCH), 1.79 (s, 3 H, SCH_3), 2.26 (septd, ^3J = 7.2 Hz, $^2J_{HP}$ = 3.8 Hz, 1 H, PCH), 2.67 (m, 1 H, $FcCH_2$), 2.71 (dd, ^2J = 22.5 Hz, ^3J = 9.1 Hz, 1 H, $FcCH_2$), 3.12 (dm, ^3J = 12.6 Hz, 1 H, SCH), 3.96 (dd, ^3J = 2.5 Hz, ^4J = 1.1 Hz, 1 H, $C_5H_3R_2$), 4.00 (s, 5 H, C_5H_5), 4.09 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.54 (m, 1 H, $C_5H_3R_2$). − ^{13}C NMR (75 MHz, C_6D_6): δ = 11.7, 13.0 (CH_2CH_3, SCH_3), 19.6 (d, $^2J_{CP}$ = 4.5 Hz), 21.2 (d, $^2J_{CP}$ = 13.7 Hz), 25.8 (d, $^2J_{CP}$ = 5.7 Hz), 25.9 (d, $^2J_{CP}$ = 5.7 Hz, PCHCH_3), 20.8 (d, $^1J_{CP}$ = 17.1 Hz), 23.3 (d, $^1J_{CP}$ = 24.1 Hz, PCH), 28.4 (CH_2CH_3), 35.1 (d, $^3J_{CP}$ = 10.9 Hz, $FcCH_2$), 50.6 (SCH), 68.9, 70.2 (d, J_{CP} = 4.3 Hz), 71.4 (d, J_{CP} = 4.0 Hz, $C_5H_3R_2$), 70.0 (C_5H_5), 79.9 (d, $^2J_{CP}$ = 24.0 Hz), 92.2 (d, $^1J_{CP}$ = 24.0 Hz, i-$C_5H_3R_2$). − ^{31}P NMR (C_6D_6, 162 MHz): −9.0 (s). − EI-MS; *m/z*: 404.2 (19) [M^+], 389.1 (100) [$M^+ - CH_3$], 357.2 (13) [$M^+ - SCH_3$], 271.1 (11) [389.1 − HP(iPr)$_2$], 240.0 (35) [357.2 − P(iPr)$_2$]. − HR-MS: $C_{21}H_{33}{}^{56}$FePS: calcd. 404.138999; found 404.138757.

P∪S Ligand 6m: According to GP8, a solution of BH_3-protected phosphane **6f** (122 mg, 0.244 mmol) in diethyl ether (6 mL)/toluene (4 mL) was treated with TMEDA (5.0 equiv.) for 8 h at room temperature. Filtration through silica gel under argon (hexane/diethyl ether = 10:1) provided P∪S ligand **6m**. − Yield: 108 mg (91%, yellow crystals). − R_f = 0.90 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = −186.0($CHCl_3$, *c* = 1.21). − Mp: 116 °C. − IR ($CHCl_3$): $\tilde{\nu}$ = 3068 cm^{-1}, 2960, 2922, 2864, 1661, 1586, 1435, 1380, 1327, 1309, 1266, 1237, 1179, 1155, 1104, 1071, 1030, 1002, 880, 818, 748, 699, 667, 641, 573, 500, 454. − ^{1}H NMR (400 MHz, C_6D_6): δ = 0.99 (d, ^3J = 6.6 Hz, 3 H), 1.10 (d, ^3J = 6.6 Hz, 3 H), 1.17 (d, ^3J = 6.6 Hz, 3 H, CH_3), 2.58−2.70 [m, 3 H, SCH(CH_3)$_2$, $FcCH_2CH$, $FcCH_2$], 3.29 (dt, ^2J = 12.9 Hz, ^3J = $^4J_{HP}$ = 3.0 Hz, 1 H, $FcCH_2$), 3.85 (m, 1 H, $C_5H_3R_2$), 3.86 (s, 5 H, C_5H_5), 4.08 (t, ^3J = 2.5 Hz, 1 H, $C_5H_3R_2$), 4.53 (td, ^3J = J_{HP} = 2.2 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 6.99−7.10 (m, 6 H, *m/p*-C_6H_5), 7.40 (tt, *J* = 7.1 Hz, *J* = 1.4 Hz, 2 H, *o*-C_6H_5), 7.67 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (100 MHz, C_6D_6): δ = 23.3, 23.8, 24.0 (CH_3), 38.1 (d, $^3J_{CP}$ = 10.8 Hz, $FcCH_2$), 41.4 (SCH), 69.7, 71.2 (d, J_{CP} = 4.1 Hz), 73.6 (d, J_{CP} = 4.0 Hz, $C_5H_3R_2$), 70.0 (C_5H_5), 76.2 (d, $^2J_{CP}$ = 7.4 Hz), 92.3 (d, $^1J_{CP}$ = 27.5 Hz, $C_5H_3R_2$), 128.4, 129.1 (*m*-C_6H_4), 133.0 (d, $^2J_{CP}$ = 18.3 Hz), 135.5 (d, $^2J_{CP}$ = 21.8 Hz, *o*-C_6H_5), 138.6 (d, $^1J_{CP}$ = 9.2 Hz), 141.3 (d, $^1J_{CP}$ = 10.3 Hz, *i*-C_6H_4). − ^{31}P NMR (C_6D_6, 162 MHz): −23.7 (s). − EI-MS; *m/z*: 502.2 (51) [MO^+], 486.3 (12) [M^+], 443.2 (100) [$M^+ - CH(CH_3)_2$], 427.1 (29) [443.2 − CH_4], 226.0 (46) [Fc−CH=CH−CH_3^+]. − HR-MS: $C_{28}H_{31}{}^{56}$FePS: calcd. 486.123349; found 486.123023.

P∪S Ligand 6n: According to GP8, a solution of BH_3-protected phosphane **6a** (70 mg, 0.148 mmol) in toluene (5 mL) was treated with TMEDA (10.0 equiv.) for 20 h at 90 °C. Filtration through silica gel under argon (hexane/diethyl ether = 10:1) provided P∪S ligand **6n**. − Yield: 40 mg (59%, yellow oil). − R_f = 0.52 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = +67.9 ($CHCl_3$, *c* = 1.03). − IR ($CHCl_3$): $\tilde{\nu}$ = 3071 cm^{-1}, 3053, 2964, 2919, 2866, 1585, 1480, 1434, 1375, 1312, 1218, 1183, 1159, 1118, 1106, 1096, 1071, 1028, 1000, 967, 889, 863, 821, 754, 722, 698, 666, 536, 509. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.11 (dd, $^3J_{HP}$ = 14.0 Hz, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.98 (s, 3 H, SCH_3), 2.53 (m, 1 H, PCH), 2.89 (t, ^2J = ^3J = 8.2 Hz, 2 H, $FcCH_2$), 3.90 (s, 5 H, C_5H_5), 3.91 (t, ^3J = 2.8 Hz, 1 H, $C_5H_3R_2$), 4.06 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 4.18 (dd, ^3J = 2.5 Hz, ^4J = 1.4 Hz, 1 H, $C_5H_3R_2$), 7.04−7.14 (m, 6 H, *m/p*-C_6H_5), 7.61 (m, 4 H, *o*-C_6H_5). − ^{13}C NMR (75 MHz, C_6D_6): δ = 16.9 (d, $^2J_{CP}$ = 14.3 Hz, CHCH_3), 20.2 (SCH_3), 32.6 (d, $^1J_{CP}$ = 22.3 Hz, PCH), 33.3 (d, $^2J_{CP}$ = 12.0 Hz, $FcCH_2$), 67.3, 68.9, 71.4 ($C_5H_3R_2$), 70.4 (C_5H_5), 84.3, 89.7 (d, J_{CP} = 14.9 Hz, $C_5H_3R_2$), 128.6−129.0 (*m/p*-C_6H_5), 133.8 (d, $^2J_{CP}$ = 18.9 Hz), 134.3 (d, $^2J_{CP}$ = 19.5 Hz, *o*-C_6H_5), 137.9 (d, $^1J_{CP}$ = 16.1 Hz), 138.4 (d, $^1J_{CP}$ = 15.5 Hz, *i*-C_6H_5). − ^{31}P NMR (C_6D_6, 162 MHz): −0.3 (s). − EI-MS; *m/z*: 458.1 (57) [M^+], 443.1 (100) [$M^+ - CH_3$], 411.1 (21) [$M^+ - SCH_3$], 393.1 (52) [$M^+ - C_5H_5$], 290.0 (34) [411.1 − CpFe], 225.9 (19) [$H_3CC(PPh_2)=CH_2^+$]. − HR-MS: $C_{26}H_{27}{}^{56}$FePS: calcd. 458.092049; found 458.091418.

S∪S Ligand 13: According to GP7, a mixture of TFA (1 mL) and $NaBH_4$ (13.2 equiv.) in CH_2Cl_2 (4 mL) was treated with a solution of hydrazine **12** (78 mg, 0.126 mmol) in CH_2Cl_2 (2 mL). After warming to room temperature, the mixture was stirred for 15 h. Aqueous work up and purification by flash chromatography through silica gel (hexane/diethyl ether = 10:1) provided S∪S ligand **13**. − Yield: 27 mg (59%, yellow oil). − R_f = 0.48 (hexane/diethyl ether = 4:1). − *de* ≥ 96%. − $[\alpha]_D^{25}$ = +78.8 ($CHCl_3$, *c* = 0.25). − IR ($CHCl_3$): $\tilde{\nu}$ = 3086 cm^{-1}, 2960, 2918, 2865, 1727, 1658, 1631, 1450, 1437, 1397, 1373, 1313, 1279, 1229, 1173, 1098, 1053, 1040, 1023, 955, 928, 880, 855, 825, 808, 757, 532, 509, 494. − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.15 (d, ^3J = 6.6 Hz, 6 H, CH_3), 1.81 (s, 6 H, SCH_3), 2.38 (dd, ^2J = 13.5 Hz, ^3J = 8.2 Hz, 2 H, $FcCH_2$), 2.52 (dqd, ^3J = 8.2 Hz, ^3J = 6.6 Hz, ^3J = 5.2 Hz, 2 H, SCH), 2.71 (dd, ^2J = 13.5 Hz, ^3J = 5.2 Hz, 2 H, $FcCH_2$), 3.90 (m, 8 H, C_5H_4R). − ^{13}C NMR (75 MHz, C_6D_6): δ = 13.8 (SCH_3), 20.5 (CH_3), 37.9 ($FcCH_2$), 43.5 (SCH), 68.6, 68.8, 70.0, 70.4 ($C_5H_3R_2$), 86.1 (*i*-$C_5H_3R_2$). − EI-MS; *m/z*: 362.1 (100) [M^+], 240.2 (24), 209.0 (49), 161.0 (35), 135.0 (8). − HR-MS: $C_{18}H_{26}{}^{56}FeS_2$: calcd. 362.082533; found 362.082403.

Pd−P∪S Complex 20: Bis[μ-Chloro(η^3-PhCHCHCHPh)palladium(II)] (38 mg, 0.056 mmol) was added to a solution of ligand **6j** (53 mg, 0.112 mmol) in acetone (10 mL). After stirring for 30 min at room temperature, $TlPF_6$ (39 mg, 0.112 mmol) was added. After 1 h, the mixture was decanted and TlCl filtered off (Celite). The solution was concentrated to $^1/_4$ under a stream of argon and *n*-pentane (30 mL) was added, causing deposition of a dark red oil. The pure compound was obtained in 97% yield after crystallization from CH_2Cl_2/Et_2O at −26 °C. − Yield: 100 mg (97%, red-brown crystals). − *dr* = 86:9:3:2. − $[\alpha]_D^{25}$ = +42.6 ($CHCl_3$, *c* = 0.66). − M.p.: 88 °C. − IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1}, 2964, 2928, 2873, 1543, 1491, 1462, 1436, 1386, 1316, 1250, 1186, 1157, 1100, 1001, 913, 839, 757, 730, 695, 648, 558, 514, 485, 468. − ^{1}H NMR (500 MHz, C_6D_6): δ = 1.05 (t, ^3J = 7.3 Hz, 3 H, CH_2CH_3), 1.11 (s, 3 H, SCH_3), 1.48−1.61 (m, 2 H, CH_2CH$_3$), 2.94 (tdd, ^3J = 7.3 Hz, ^3J = 4.7 Hz, ^3J = 2.6 Hz, 1 H, SCH), 3.26 (dd, ^2J = 15.7 Hz, ^3J = 2.6 Hz, 1 H, $FcCH_2$), 3.61 (s, 5 H, C_5H_5), 3.87 (dd, ^2J = 15.4 Hz, ^3J = 4.3 Hz, 1 H, $FcCH_2$), 4.03 (dt, ^3J = 2.6 Hz, ^4J = $^3J_{HP}$ = 1.3 Hz, 1 H, PCCH_{Cp}), 4.37 (t, ^3J = 2.5 Hz, 1 H, PCCHCH_{Cp}), 4.40 (td, ^3J = $^4J_{HP}$ = 2.4 Hz, ^4J = 1.2 Hz, PCCHCHCH_{Cp}), 5.17 (d, ^3J = 9.6 Hz, 1 H, C_6H_5CH *trans* to S), 6.27 (d, ^3J = 13.5 Hz, 1 H, C_6H_5CH *trans* to P), 6.32 (dd, ^3J = 13.5 Hz, ^3J = 9.5 Hz, 1 H, C_6H_5CHCH), 6.40 (ddd, $^3J_{HP}$ = 9.6 Hz, ^3J = 8.4 Hz, ^4J = 1.2 Hz, 2 H, P−*o*-C_6H_{5up}), 6.93 (dm, ^3J = 8.2 Hz, 2 H, CH *trans* to S−*o*-C_6H_5), 6.99 (t, ^3J = 7.5 Hz, 2 H, CH *trans* to S−*m*-C_6H_5), 7.10 (tm, ^3J = 8.2 Hz, 2 H, P−*m*-C_6H_{5up}), 7.18 (tq, ^3J = 7.3 Hz, ^4J = J_{HP} = 1.4 Hz, 1 H, CH *trans* to S−*p*-C_6H_5), 7.30 (tq, ^3J = 7.5 Hz, ^4J = $^5J_{HP}$ = 1.4 Hz, 1 H, P−*p*-C_6H_{5up}), 7.38 (m, 3 H, CH *trans* to P−*m*-C_6H_5, CH *trans* to P−*p*-C_6H_5), 7.54 (tdt, ^3J = 7.5 Hz, $^5J_{HP}$ = 2.1 Hz, ^4J = 1.1 Hz, 1 H, P−*p*-C_6H_{5down}), 7.59 (tdt,

^3J = 7.2 Hz, $^4J_{HP}$ = 2.3 Hz, ^4J = 1.6 Hz, 2 H, P−*m*-C_6H_{5down}), 7.69 (dm, ^3J = 6.7 Hz, 2 H, CH *trans* to P−*o*-C_6H_5), 7.85 (ddd, $^3J_{HP}$ = 12.4 Hz, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 2 H, P−*o*-C_6H_{5down}). − ^{13}C NMR (125 MHz, C_6D_6): δ = 12.1 (SCH_3), 12.2 (CH_3), 23.9 (CH_2CH_3), 32.6 ($FcCH_2$), 53.4 (SCH), 70.5 (PCCH*CH*$_{Cp}$), 70.9 (C_5H_5), 73.0 (PCCH$_{Cp}$), 78.2 (C_6H_5CH *trans* to S), 102.4 (d, $^2J_{CP}$ = 20.3 Hz, C_6H_5CH *trans* to P), 109.2 (C_6H_5CHCH), 127.7 (CH *trans* to S−*p*-C_6H_5), 128.1 (d, $^3J_{CP}$ = 9.3 Hz, P−*m*-C_6H_{5up}), 128.4 (CH *trans* to S−*o*-C_6H_5), 128.6 (CH *trans* to P-*o*-C_6H_5, CH *trans* to S−*m*-C_6H_5), 128.9 (d, $^3J_{CP}$ = 11.5 Hz, P−*m*-C_6H_{5down}), 129.7 (CH *trans* to P−*m*/*p*-C_6H_5), 129.9 (P−*p*-C_6H_{5up}), 131.0 (P−*i*-C_6H_{5up}), 131.2 (P−*p*-C_6H_{5down}), 131.9 (d, $^2J_{CP}$ = 10.4 Hz, P−*o*-C_6H_{5up}), 132.8 (P−*i*-C_6H_{5down}), 134.4 (d, $^2J_{CP}$ = 14.2 Hz, P−*o*-C_6H_{5up}), 136.2 (CH *trans* to S−*i*-C_6H_5), 137.0 (CH *trans* to P−*i*-C_6H_5). − ^{31}P NMR (C_6D_6, 162 MHz): −143.0 (sept, $^1J_{PF}$ = 714.9 Hz, PF_6^-), +15.2 (s, PPh_2). − EI-MS; *m*/*z*: 472.1 (43) [M^+ − Pd(PhCHCHCHPh)], 457.1 (80) [472.1 − CH_3], 425.3 (10) [472.1 − SCH_3], 240.2 (100) [425.2 − PPh_2], 193.2 (68) [PhCHCHCHPh$^+$], 183.1 (49) [PPh_2 − H_2], 165.2 (15), 152.2 (11), 121.0 (28) [$CpFe^+$], 115.2 (43), 107.2 (26). − $C_{42}H_{42}F_6FeP_2PdS \cdot CH_2Cl_2$ (1002): calcd. C 50.35, H 4.43; found C 50.61, H 4.41.

Malonate (*R*)-17: A mixture of (π-allyl)palladium(II) chloride dimer (3.7 mg, 0.01 mmol) and ligand **6j** (10.4 mg, 0.022 mmol) in CH_2Cl_2 (1.5 mL) was stirred at room temperature for 1 h. The solution was cooled to −20 °C and acetate **16** (1.0 mmol, 252 mg) in CH_2Cl_2 (0.5 mL) was added, followed sequentially by dimethyl malonate (3.0 equiv., 0.34 mL), *N*,*O*-bis(trimethylsilyl)acetamide (BSA, 3.0 equiv., 0.74 mL), and KOAc (1 mg). After 24 h at −20 °C, 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 with $MgSO_4$. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography (hexane/diethyl ether = 4:1). − Yield: 321 mg (99%, colourless oil). − *ee* = 97% [^{1}H NMR, Eu(tfc)$_3$, $CDCl_3$]. − $[\alpha]_D^{25}$ = +20.0 (EtOH, *c* = 1.05).

Amine (*S*)-19: A mixture of (π-allyl)palladium(II) chloride dimer (3.7 mg, 0.01 mmol) and ligand **6j** (10.4 mg, 0.022 mmol) in CH_2Cl_2 (1.5 mL) was stirred at room temperature for 1 h. The solution was cooled to −20 °C and acetate **16** (1.0 mmol, 252 mg) in CH_2Cl_2 (0.5 mL) was added, followed sequentially by benzylamine (2.5 equiv.) and KOAc (1.0 mg, 0.01 mmol). After 24 h at −20 °C, 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 with $MgSO_4$. After evaporation of the solvent in vacuo, the crude product was purified by column chromatography (hexane/diethyl ether = 4:1). − Yield: 150 mg (0.500 mmol, 50%, colourless oil). − *ee* = 94% (^{1}H NMR, Pirkle alcohol, $CDCl_3$). − $[\alpha]_D^{25}$ = +20.0 (EtOH, *c* = 1.05).

X-ray Crystallographic Study: X-ray structure analysis of **5e**. Suitable crystals were obtained by crystallization from hexane. The compound ($C_{34}H_{46}BFeN_2OPS$, $M_{calcd.}$ = 628.5) crystallizes in the monoclinic space group $P2_1$ (no.4), *a* = 9.410(1), *b* = 17.313(8), *c* = 11.183(3) Å, β = 109.99(1)°, *Z* = 2, $D_{calcd.}$ = 1.219 g cm^{-3}. Enraf−Nonius CAD4 diffractometer, Mo-K_α radiation (graphite monochromator, λ = 0.71069 Å). The structure solution was carried out using direct methods (SHELXS86[24]). Some of the hydrogen atoms could be localized, the rest were calculated. The hydrogen positions were not refined. 6291 observed reflections [$I > 2\sigma(I)$] in the final refinement (full-matrix least squares) of 369 parameters, *R* = 0.051, R_w = 0.039 ($w = \sigma^{-2}$), minimum/maximum residual electron density −0.64/+0.59eÅ^{-3}. Crystallographic data (excluding structure factors) for structure **5e** are stored as supplementary publication no. CCDC-116942 at the Cambridge Crystallographic Data Centre. Copies of these data can be ordered free of charge at the following address: CCDC, 12 Union Road, Cambridge CB21EZ [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

X-ray Structure Analysis of 20: $C_{42}H_{42}FePPdS^+PF_6^- \cdot CH_2Cl_2$; M_r = 1002; orthorhombic, $P2_12_12_1$; *a* = 10.239(1), *b* = 19.986(4), *c* = 20.559(3) Å; *V* = 4207(1) Å^3; *Z* = 4; D_x = 1.582 g cm^{-3}; μ(Mo-K_α) = 1.083 mm^{-1}; 147 K. Structure refinement with SHELXL-97; H atoms riding; final *R* = 0.061 for 9445 observed reflections. Crystallographic data (without structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135357. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (Leibniz-Preis), the Fonds der Chemischen Industrie, and the Forschungsverbund Katalyse Nordrhein-Westfalen. We thank Degussa-Hüls AG, BASF AG, the former Hoechst AG, Bayer AG, and Wacker Chemie for the donation of chemicals.

[1] [1a] C. J. Richards, A. J. Locke, *Tetrahedron: Asymmetry* **1998**, *9*, 2377−2407. − [1b] A. Togni, T. Hayashi, *Ferrocenes: Homogeneous Catalysis. Organic Synthesis. Materials Science*, VCH, Weinheim, **1995**.

[2] D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, I. Ugi, *J. Am. Chem. Soc.* **1970**, *92*, 5389−5393.

[3] [3a] J. Wright, L. Frambes, P. Reeves, *J. Organomet. Chem.* **1994**, *476*, 215−217. − [3b] Y. Matsumoto, A. Ohno, S. Lu, T. Hayashi, N. Oguni, *Tetrahedron: Asymmetry* **1993**, *4*, 1763−1766. − [3c] D. Enders, R. Lochtman, *Synlett* **1996**, 126−127. − [3d] D. Enders, R. Lochtman, *Eur. J. Org. Chem.* **1998**, 689−696.

[4] A. Togni, *Angew. Chem.* **1996**, *108*, 1581−1583; *Angew. Chem. Int. Ed.* **1996**, *35*, 1475−1477, and references cited therein.

[5] [5a] D. Enders, R. Peters, R. Lochtman, G. Raabe, *Angew. Chem.* **1999**, *111*, 2579−2581; *Angew. Chem. Int. Ed.* **1999**, *38*, 2421−2423. − [5b] D. Enders, R. Peters, J. Runsink, J. W. Bats, *Org. Lett.* **1999**, *1*, 1863−1866.

[6] [6a] T. Hayashi, M. Konishi, T. Hioki, M. Kumada, A. Ratajczak, H. Niedbaka, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3615−3616. − [6b] A. Ratajczak, H. Zmuda, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **1974**, *22*, 261−266. − [6c] A. Ratajczak, H. Zmuda, *Roczniki Chemii* **1975**, *49*, 215−219.

[7] D. Enders, in: *Asymmetric Synthesis*, vol. 3 (Ed.: J. D. Morrison), Academic Press, Orlando **1984**, p. 275−339.

[8] D. Enders, T. Berg, G. Raabe, J. Runsink, *Liebigs Ann./Recueil* **1997**, 345−363.

[9] D. Enders, T. Schäfer, W. Mies, *Tetrahedron* **1998**, *54*, 10239−10252.

[10] D. Enders, R. Joseph, C. Poiesz, *Tetrahedron* **1998**, *54*, 10069−10078.

[11] D. Enders, R. Peters, R. Lochtman, J. Runsink, *Synlett* **1997**, 1462−1464.

[12] R. B. Woodward, M. Rosenblum, M. C. Whiting, *J. Am. Chem. Soc.* **1952**, *74*, 3458−3459.

[13] B. Bildstein, P. Denifl, *Synthesis* **1994**, 158−160.

[14] D. Seebach, A. K. Beck, A. Studer, in: *Modern Synthetic Methods*, vol. 7 (Ed.: B. Ernst, C. Leumann), VCH, Weinheim, **1995**, p. 1−178.

[15] D. Enders, R. Peters, R. Lochtman, J. Runsink, *Eur. J. Org. Chem.*, in press.

[16] E. J. Corey, D. Seebach, *J. Org. Chem.* **1966**, *31*, 4097−4099.

[17] [17a] B. Carboni, L. Monnier, *Tetrahedron* **1999**, *55*, 1197−1248. − [17b] M. Ohff, J. Holz, M. Quirmbach, A. Börner, *Synthesis* **1998**, 1391−1415. − [17c] H. Schmidbaur, E. Weiß, B. Zimmer-

Gasser, *Angew. Chem.* **1978**, *90*, 126−127; *Angew. Chem. Int. Ed.* **1978**, *7*, 126−127.
[18] G. W. Gribble, *Chem. Soc. Rev.* **1998**, *27*, 395−404.
[19] [19a] B. M. Trost, D. L. van Vranken, *Chem. Rev.* **1996**, *96*, 395−422. − [19b] T. Hayashi, "Asymmetric Allylic Substitution and Grignard Cross-Coupling", in: *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), VCH, Weinheim, **1993**, pp. 325−365.
[20] Selected papers: [20a] S. Lee, C. W. Lim, C. E. Song, K. M. Kim ,C. H. Jun, *J. Org. Chem.* **1999**, *64*, 4445−4451. − [20b] K. H. Ahn, C.-W. Cho, J. Park, S. Lee, *Tetrahedron: Asymmetry* **1997**, *8*, 1179−1185. − [20c] A. Togni, U. Burckhardt, V. Gramlich, P. S. Pregosin, R. Salzmann, *J. Am. Chem. Soc.* **1996**, *118*, 1031−1037. − [20d] J. Sprinz, G. Helmchen, *Tetrahedron Lett.* **1993**, *34*, 1769−1772. − [20e] P. Von Matt, A. Pfaltz, *Angew. Chem.* **1993**, *105*, 614−615; *Angew. Chem. Int. Ed.* **1993**, *32*, 566−568. − [20f] G. J. Dawson, C. G. Frost, J. M. J. Williams, S. J. Coote, *Tetrahedron Lett.* **1993**, *34*, 3149−3152.
[21] Selected Papers: [21a] K. Boog-Wick, P. S. Pregosin, G. Trabesinger, *Organometallics* **1998**, *17*, 3254−3264. − [21b] B. Koning, A. Meetsma, R. M. Kellogg, *J. Org. Chem.* **1998**, *63*, 5533−5540. − [21c] J. C. Anderson, D. S. James, J. P. Mathias, *Tetrahedron: Asymmetry* **1998**, *9*, 753−756. − [21d] A. Chesney, M. R. Bryce, R. W. J. Chubb, A. S. Batsanov, J. A. K. Howard, *Tetrahedron: Asymmetry* **1997**, *8*, 2337−2346.
[22] Selected Papers: [22a] A. Albinati, J. Eckert, P. Pregosin, H. Rüegger, R. Salzmann, C. Stössel, *Organometallics* **1997**, *16*, 579−590. − [22b] P. Barbaro, A. Currao, J. Herrmann, R. Nesper, P. S. Pregosin, R. Salzmann, *Organometallics* **1996**, *15*, 1879−1888. − [22c] A. Albinati, P. S. Pregosin, K. Wick, *Organometallics* **1996**, *15*, 2419−2421. − [22d] J. Herrmann, P. S. Pregosin, R. Salzmann, *Organometallics* **1995**, *14*, 3311−3318.
[23] [23a] A. Müller, E. Diemann, in: *Comprehensive Coordination Chemistry*, vol. 2 (Ed.: G. Wilkinson), Thioethers. Pergamon Press, Oxford, **1987**, pp. 551−558. − [23b] A. T. Hutton, "Palladium(II): Sulfur Donor Complexes", in: *Comprehensive Coordination Chemistry*, vol. 5 (Ed.: G. Wilkinson), Pergamon Press, Oxford, **1987**, pp. 1131−1155.
[24] G. M. Sheldrick, in: *Crystallographic Computing 3* (Eds.: G. M. Sheldrick, C. Krueger, R. Goddard), Oxford University Press, Oxford, **1985**, p. 175−189.

Received March 28, 2000
[O00160]