Diastereoselective Synthesis of Ferrocenyl Sulfoximines with Planar and Central Chirality

Carsten Bolm,* Martin Kesselgruber, Kilian Muñiz, and Gerhard Raabe

Institut für Organische Chemie der RWTH Aachen, Prof.-Pirlet-Strasse 1, D-52074 Aachen, Germany

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The capability of the sulfonimidoyl moiety to serve as *ortho*-directing group for the diastereoselective lithiation of enantiopure ferrocenylsulfoximines is demonstrated. *(S)-N-p*-Tolylsulfonyl-*S*-ferrocenyl-*S*-*tert*-butylsulfoximine showed excellent diastereoselectivity concerning planar chirality of the products obtained after quenching of the lithium species with several electrophiles. Various electrophiles (MeI, Me_2S_2, Me_3SiCl, *p*-anisaldehyde, acetone, *n*-Bu_3SnCl, I_2) were introduced in yields from 36 to 78%. Only up to 10% of product substituted at both the cyclopentadienyl ring and the phenyl group of the tosyl moiety was isolated as byproduct. The relative configuration of the products was determined by chemical correlation and X-ray crystallographic analysis of *(S,R_p)-N-p*-tolylsulfonyl-*S*-*tert*-butyl-*S*-(2-iodoferrocenyl)sulfoximine. Taking into account the structure of the starting material, the *ortho*-directing effect can be ascribed to the oxygen atom of the sulfoximine.

Introduction

The synthesis of planar-chiral ferrocenes is of ongoing interest in organic synthesis because several of these compounds have revealed outstanding properties in asymmetric catalysis.[1−3] Many of them have been obtained by a stereoselective directed *ortho*-metalation (DoM),[4] and for that purpose various *ortho*-directing groups such as amines,[5] oxazolines,[6] and acetals[7] bearing stereogenic centers or even chiral anchor groups such as sulfoxides[8] proved suitable. The application of external chiral auxiliaries, e.g., (−)-sparteine,[9] (1*R*,2*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexanediamine,[10] or chiral lithium amide bases,[11] in combination with achiral *ortho*-directing groups has also been demonstrated, leading to planar-chiral ferrocenes with moderate to high enantiomeric excesses.

Sulfoximines have been in the focus of research for several years.[12] We ourselves employed bidentate derivatives as chiral ligands for metal complexes which proved useful in asymmetric transformations such as the diethylzinc addition to benzaldehyde,[13] the trimethylsilylcyanation of aldehydes,[14] and the enantioselective reduction of ketones and imine derivatives.[15]

* Corresponding author: Fax: Int. +49(241)8888391. E-mail: Carsten.Bolm@oc.rwth-aachen.de.

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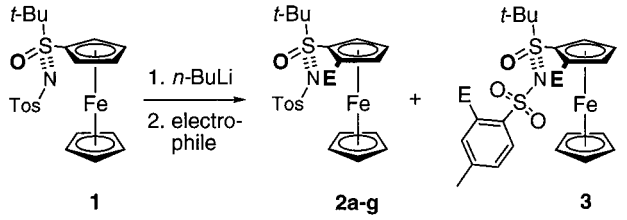
Scheme 1



Recently, we reported on the synthesis of the first nonracemic sulfoximines with a ferrocene backbone,[16] and we now describe the capability of the sulfonimidoyl moiety to serve as chiral *ortho*-directing group for the diastereoselective synthesis of planar-chiral enantiopure ferrocenyl sulfoximines.[17]

Results and Discussion

First preliminary lithiation experiments were carried out using (*S*)-*N*-*p*-tolylsulfonyl-*S*-ferrocenyl-*S*-tolylsulfoximine[16] as starting material and *N*,*N*-dimethylformamide as electrophile. To our delight, we found that the diastereoselectivity in the formation of the planar-chiral product as determined from the crude ^{1}H NMR spectra was very high. Unfortunately, with this substrate the metalation proceeded with unsatisfying chemoselectivity, giving complicated product mixtures, which we assumed to result from substitution at the cyclopentadienyl and the tolyl group, respectively. In addition, minor amounts of a ferrocene were detected by crude ^{1}H NMR which indicated incorporation of the electrophile onto both the cyclopentadienyl ring and the tolyl group. Separation of these compounds by column chromatography proved to be rather difficult, and further study of this sulfoximine was thus abandoned.

With the assumption that a change of the substituent at the sulfur of the sulfoximido moiety would influence the approach of the base and the subsequent reaction of the resulting anion with the electrophile, we turned our attention toward reactions with (*S*)-*N*-*p*-tolylsulfonyl-*S*-ferrocenyl-*S*-*tert*-butylsulfoximine (**1**).[16] In fact, the chemoselectivity was now significantly enhanced, and products **2** and **3** were formed in an approximate 10:1 ratio (Scheme 1). Again, the diastereoselectivity was excellent, and no diastereomer was observed in the crude ^{1}H NMR spectra.

n-Butyllithium proved to be the base of choice, giving better chemoselectivity than LDA. The optimal reaction conditions for obtaining the highest ratio of monosubstituted to disubstituted products were the following: 30 min of lithiation with 1.1 equiv of *n*-butyllithium in dry THF at −78 °C, addition of the appropriate electrophile (neat), stirring at −78 °C for 1 h, and quenching with distilled water at this temperature. According to this protocol, several electrophiles reacted smoothly, giving the desired products in moderate to good yields (Table 1). On the basis of recovered starting material the yields were up to 20% higher because complete conversion could not be achieved.

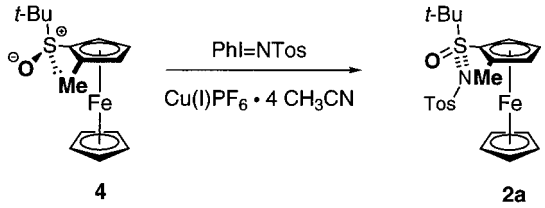
Quenching with *p*-anisaldehyde (Table 1, entry 3) gave a 1:1 mixture of diastereomers having opposite configuration at the newly introduced stereogenic center. Separation of these diastereomers proved difficult, but could be achieved by preparative HPLC. This technique was also employed in the purification of **2a**, **2b**, **2d**, and **2f** to remove unreacted starting material. In contrast to the electrophiles listed in Table 1, benzophenone and chlorophosphines ($ClPPh_2$ and $ClPCy_2$) reacted sluggishly with the generated anion, and only traces of the corresponding products were detected by NMR spectroscopy of the crude mixture.

Table 1. Yields of *ortho*-Functionalized Products 2a−g

entry no.	electrophile	product	yield [%][a,b]
1	MeI	**2a**	78 (90)
2	MeSSMe	**2b**	36 (43)
3	4-$MeOC_6H_4CHO$	**2c**	56 (68)[c]
4	Me_3SiCl	**2d**	43 (62)
5	MeC(O)Me	**2e**	53 (73)
6	*n*-Bu_3SnCl	**2f**	48 (64)
7	I_2	**2g**	68 (82)

[a] As single diastereomer. [b] Yields based on recovered starting material in parentheses. [c] Obtained as a 1:1 diastereomeric ratio concerning the newly formed stereogenic center.

Scheme 2



The relative configuration and thus the absolute configuration of the newly created element of planar chirality in the products was unambiguously determined by both chemical correlation and X-ray structure analysis.[18] Copper-catalyzed imination of sulfoxides with *N*-(*p*-tolylsulfonyl)iminophenyl-λ^3-iodane is known to occur with complete retention of configuration at sulfur.[16,19] Using Kagan's ferrocenylsulfoxide **4**[7,20] as starting material for this transformation gave the corresponding sulfoximine (Scheme 2), which had NMR spectra identical to those of compound **2a** prepared by the *ortho*-directed metalation route described above.

The final confirmation for the stereochemical assignment was obtained by single-crystal X-ray structure analysis of compound **2g** (Figure 1).

Two points of the accomplished *ortho*-functionalizations on ferrocenyl sulfoximines deserve special mentioning. First, deprotonation can be accomplished by use of *n*-butyllithium, a reagent that in the deprotonation on related ferrocenyl sulfoxides can lead to a displacement of the sulfoxide moiety from the ferrocene or racemization of the stereogenic center.[21] Clearly, we have demonstrated that use of a sulfoximido group allows for circumventing such problems.

Second, the stereochemical outcome of the *ortho*-functionalization is interesting. So far, most chiral DoM

(18) Details on the X-ray analysis are given in the Experimental Section.

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(20) Sulfoxide **4** was synthesized from (*S*)-*S*-*tert*-butyl-*S*-ferrocenylsulfoxide as described in ref 8 with the exception that the lithiation was carried out at −78 °C instead of 0 °C.

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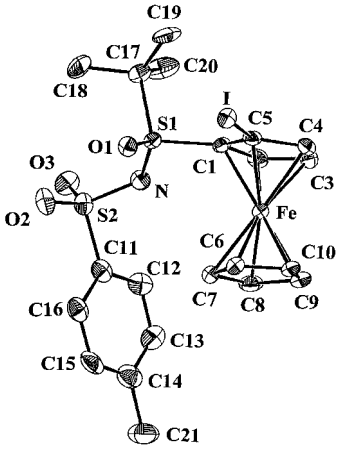


Figure 1. Molecular structure of **2g**. Selected bond distances [Å] and angles [deg]: S1−C1 1.753(5), S1−O1 1.440(3), S1−C17 1.842(5), S1−N 1.561(4), C5−I 2.093(5), O1−S1−C1 110.1 (2), O1−S1−C17 108.5(2), C1−S1−C17 105.0(2), O1−S1−N 120.1(2), C1−C5−I 128.9(3).

groups for *ortho*-deprotonation display only a single heteroatom that allows for a determined prechelation of the alkyllithium base and thus leads to a highly stereoselective deprotonation reaction. The only case where potentially two such heteroatoms could interfere in competition with each other is given for chiral oxazolines. In an elegant work, Sammakia has shown that the whole process relies on exclusive chelation via the nitrogen atom only.[22]

Taking into account the ground-state conformation of **1** as determined previously by X-ray crystallography[16] and the resulting relative configuration of the substitution products **2**, we conclude that in the present case the stereochemical outcome of the *ortho*-metalation of compounds bearing an *N*-tosylsulfonimidoyl moiety is a consequence of the directing effect of the sulfoximine oxygen rather than the sulfoximine nitrogen (Scheme 3).

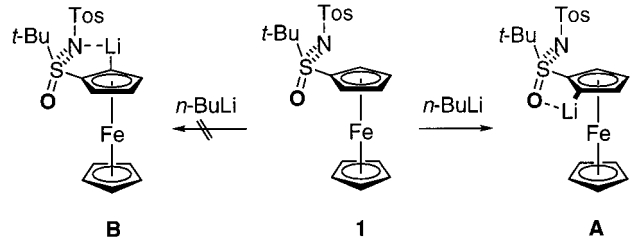
Apparently, the electronic properties and the size of the large *p*-tosyl group that is situated at nitrogen do not allow an accurate approach of the base. Therefore, the formation of a nitrogen-chelated intermediate **B** will meet with extreme difficulties. Thus, the observed stereochemical outcome of the reaction must solely be attributed to the existence of an intermediary lithio compound **A**.

Further studies are directed toward the application of the described new planar-chiral ferrocenes in asymmetric catalysis.

Experimental Section

General Comments. All manipulations except workup and purification steps were performed in oven-dried glassware under argon using common Schlenk techniques. All syntheses were repeated at least twice to ensure reproducibility. *n*-Butyllithium was obtained from Merck-Schuchardt as a 1.6 N solution in *n*-hexane. Tetrahydrofuran was distilled from sodium/benzophenone ketyl radical under argon. All other solvents were reagent grade and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 75 MHz, respectively, and chemical shifts are reported in ppm with internal referencing to chloroform (^{1}H 7.26 ppm, ^{13}C 77.0 ppm). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), and m (multiplet). Optical rotations were measured at 25 °C. Elemental analyses were carried out at the Institut für Organische Chemie der RWTH Aachen. IR spectra were recorded on a Perkin-Elmer 1760 S as KBr pellets. MS spectra were obtained on a Varian MAT 212 or a Finnigan SSQ7000 mass spectrometer. Melting points were measured on a Büchi B-540 melting point apparatus and are uncorrected. Preparative HPLC separations were conducted using a Gynkotek 305 pump, a Dynamax Macro 83-121-C HPLC column (10 μm particle size silica gel, 250 × 21 mm), and a Spectra-Physics Spetra Focus UV detector (254 nm).

Scheme 3



The descriptors for planar chirality are based on the rules introduced by Schlögl.[23]

General Procedure for the Lithiation of (*S*)-*N*-*p*-Tolylsulfonyl-*S*-*tert*-butyl-*S*-(ferrocenyl)sulfoximine (1). To a solution of **1** (150 mg, 0.33 mmol) in 4 mL of THF at −78 °C were added 0.22 mL (0.36 mmol) of *n*-butyllithium dropwise over a period of 5 min. The mixture was stirred at this temperature for 30 min, then 1.00 mmol of the electrophile was added neat. The mixture was stirred at −78 °C for 1 h, quenched with distilled water at this temperature, and extracted with diethyl ether (3 × 10 mL). The organic layers were collected, dried over $MgSO_4$, and evaporated to dryness. The product was then purified by column chromatography or preparative HPLC.

***(S,S$_p$)*-*N*-*p*-Tolylsulfonyl-*S*-*tert*-butyl-*S*-(2-methylferrocenyl)sulfoximine (2a).** Following the general procedure, the lithiated species was quenched with 142 mg (1.00 mmol) of iodomethane. The crude product was purified by preparative HPLC (eluent petroleum ether/diethyl ether, 1:1, 40 mL min^{-1}, t_R = 6.5 min), yielding 120 mg (78%) of **2a** as an orange solid and 20 mg of recovered **1**. Mp = 168 °C (dec); $[\alpha]_D^{25}$ = +77° (*c* = 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 9H), 2.18 (s, 3H), 2.40 (s, 3H), 4.35−4.42 (m, 7H), 4.61−4.65 (m, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.96 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 21.5, 23.5, 66.2, 69.2, 71.9, 73.0, 73.3, 84.4, 85.1, 126.3, 129.1, 142.0, 142.3; IR (KBr) 3467, 3108, 2987, 1598; MS (EI, 70 eV), *m*/*z* (rel intensity) = 473 (M$^+$, 18), 417 (34), 291 (100). Anal. Calcd for $C_{22}H_{27}FeNO_3S_2$: C, 55.81; H, 5.75; N, 2.96. Found: C, 56.07; H, 5.77; N, 3.02.

***(S,S$_p$)*-*N*-*p*-Tolylsulfonyl-*S*-*tert*-butyl-*S*-[2-(methylthio)-ferrocenyl]sulfoximine (2b).** Following the general procedure, the lithiated species was quenched with 94 mg (1.00 mmol) of dimethyl disulfide. The product was purified by preparative HPLC (eluent petroleum ether/diethyl ether, 1:1, 25 mL min^{-1}, t_R = 16.0 min), yielding 60 mg (36%) **2b** as an orange solid and 24 mg of recovered **1**. Mp = 145 °C (dec); $[\alpha]_D^{25}$ = +174° (*c* = 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 9H), 2.38 (s, 3H), 2.40 (s, 3H), 4.44−4.52 (m, 6H), 4.60−4.63 (m, 1H), 4.73−4.76 (m, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.4, 21.5, 23.7, 67.0, 69.8, 71.8, 72.9, 73.4, 84.6, 88.6, 126.4, 129.1, 142.0, 142.1; IR (KBr) 3435, 3114, 2984, 1597; MS (EI, 70 eV), *m*/*z* (rel intensity) = 505 (M$^+$, 34), 384 (27), 323 (22), 291 (100), 215 (56). Anal. Calcd for $C_{22}H_{27}FeNO_3S_2$: C, 52.27; H, 5.38; N, 2.77. Found: C, 51.96; H, 5.57; N, 2.57.

***(S,S$_p$,R/S)*-*N*-*p*-Tolylsulfonyl-*S*-*tert*-butyl-*S*-{2-[(4-methoxyphenyl)hydroxymethyl]ferrocenyl}sulfoximine (2c).** Following the general procedure, the lithiated species was quenched with 136 mg (1.00 mmol) of 4-methoxybenzaldehyde. The product was purified by preparative HPLC (eluent petro-

leum ether/diethyl ether, 5:8, 40 mL min^{-1}, t_R = 6.1 min, 10.2 min), yielding 56 mg (29%) and 53 mg (27%) of the two diastereomers of **6c** as orange solids and 27 mg of recovered **5**. Analytical data for the first eluting diastereomer: mp = 183 °C (dec); $[\alpha]_D^{25}$ = +43 (*c* = 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.24 (s, 9H), 2.41 (s, 3H), 3.82 (s, 3H), 3.96−4.02 (m, 2H), 4.34−4.42 (m, 1H), 4.57 (s, 5H), 4.66−4.70 (m, 1H), 5.61 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 7.29−7.39 (m, 4H), 7.97 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.3, 55.0, 66.9, 68.4, 68.9, 71.8, 72.9, 73.7, 83.9, 96.9, 113.3, 126.0, 127.9, 129.0, 133.0, 141.6, 142.1, 158.9; MS (EI, 70 eV), *m*/*z* (rel intensity) = 595 (M^+, 1), 521 (7), 304 (33), 171 (53), 155 (45), 91 (100); IR (KBr) 3527, 3485, 2961, 1609, 1513. Anal. Calcd for $C_{29}H_{33}FeNO_5S_2$: C, 58.48; H, 5.58; N, 2.35. Found: C, 58.32; H, 5.63; N, 2.27. Analytical data for the second eluting diastereomer: mp = 153 °C (dec); $[\alpha]_D^{25}$ = −97° (*c* = 0.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.18 (s, 9H), 2.40 (s, 3H), 3.21 (d, *J* = 6.1 Hz, 1H), 3.81−3.84 (s, 3H), 4.21 (s, 5H), 4.47−4.53 (m, 1H), 4.58−4.62 (m, 1H), 5.81 (d, *J* = 6.1 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.5, 55.0, 66.9, 69.8, 70.0, 71.7, 71.8, 71.9, 84.4, 93.8, 113.2, 126.0, 127.3, 128.9, 136.2, 141.7, 142.0, 158.7; MS (EI, 70 eV), *m*/*z* (rel intensity) = 595 (M^+, 1), 521 (97), 304 (100), 91 (85); IR (KBr) 3473, 2986, 1610, 1510. Anal. Calcd for $C_{29}H_{33}FeNO_5S_2$: C, 58.48; H, 5.58; N, 2.35. Found: C, 58.28; H, 5.39; N, 2.19.

***(S,S$_p$)*-*N*-*p*-Tolylsulfonyl-*S*-*tert*-butyl-*S*-[2-(trimethylsilyl)ferrocenyl]sulfoximine (2d).** Following the general procedure, the lithiated species was quenched with 109 mg (1.00 mmol) of chlorotrimethylsilane. The product was purified by column chromatography (eluent petroleum ether/diethyl ether, 2:1) yielding 75 mg (43%) of **2d** as an orange solid and 45 mg of recovered **1**. Mp = 172 °C (dec); $[\alpha]_D^{25}$ = −88° (*c* = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.36 (s, 9H), 1.21 (s, 9H), 2.39 (s, 3H), 4.36−4.42 (m, 6H), 4.65−4.67 (m, 1H), 4.84−4.87 (m, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 1.3, 21.2, 23.7, 66.1, 71.3, 73.3, 74.0, 74.5, 78.1, 91.6, 126.1, 128.8, 141.7, 141.9; MS (EI, 70 eV), *m*/*z* (rel intensity) = 531 (M^+, 16), 475 (50), 291 (82), 74 (56), 56 (100); IR (KBr) 3435, 3118, 2956, 1322. Anal. Calcd for $C_{24}H_{33}FeNO_3S_2Si$: C, 54.23; H, 6.26; N, 2.63. Found: C, 54.00; H, 6.31; N, 2.42.

***(S,S$_p$)*-*N*-*p*-Tolylsulfonyl-*S*-*tert*-butyl-*S*-[2-[(1-hydroxy-1-methyl)ethyl]ferrocenyl]sulfoximine (2e).** Following the general procedure, the lithiated species was quenched with 58 mg (1.00 mmol) of dry acetone. The product was purified by column chromatography (eluent petroleum ether/diethyl ether, 3:2), yielding 90 mg (53%) of **2e** as an orange solid and 40 mg of recovered **1**. Mp = 149 °C (dec); $[\alpha]_D^{25}$ = −198° (*c* = 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.38 (s, 9H), 1.48 (s, 3H), 1.62 (s, 3H), 2.39 (s, 3H), 4.43−4.49 (m, 7H), 4.60−4.65 (m, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.5, 23.3, 31.5, 32.9, 68.6, 69.2, 69.5, 71.4, 71.7, 72.4, 86.5, 101.6, 126.5, 129.3, 141.7, 142.5; MS (EI, 70 eV), *m*/*z* (rel intensity) = 517 (M^+, 1), 290 (31), 226 (72), 171 (48), 155 (46), 91 (100); IR (KBr) 3509, 3413, 3354, 2980, 1598. Anal. Calcd for $C_{24}H_{31}FeNO_4S_2$: C, 55.71; H, 6.04; N, 2.71. Found: C, 55.72; H, 5.94; N, 2.62.

***(S,R$_p$)*-*N*-*p*-Tolylsulfonyl-*S*-*tert*-butyl-*S*-[(tributylstannyl)ferrocenyl]sulfoximine (2f).** Following the general procedure, the lithiated species was quenched with 325 mg (1.00 mmol) of chlorotributylstannane. The product was purified by preparative HPLC (eluent petroleum ether/diethyl ether, 3:1, 40 mL min^{-1}, t_R = 14.5 min), yielding 108 mg (48%) of **2f** as an orange solid and 38 mg of recovered **1**. Mp = 110−112 °C; $[\alpha]_D^{25}$ = −8° (*c* = 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 9H), 1.04−1.13 (m, 6H), 1.24 (s, 9H), 1.30−1.44 (m, 6H), 1.46−1.62 (m, 6H), 2.39 (s, 3H), 4.21−4.32 (m, 6H), 4.64−4.67 (m, 1H), 4.82−4.87 (m, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 11.9, 13.7, 21.5, 24.1, 27.5, 29.1, 66.0, 70.9, 73.3, 74.4, 77.2, 78.0, 91.9, 126.5, 129.1, 142.0, 142.3; MS (EI, 70 eV), *m*/*z* (rel intensity) = 749 (M^+, 1), 474 (4), 291 (57), 269 (100), 155 (47); IR (KBr) 3448, 2956, 2923, 1600, 1543. Anal. Calcd for $C_{33}H_{51}FeNO_3S_2Sn$: C, 52.96; H, 6.87; N, 1.87. Found: C, 52.85; H, 6.87; N, 1.75.

***(S,R$_p$)*-*N*-*p*-Tolylsulfonyl-*S*-*tert*-butyl-*S*-(2-iodoferrocenyl)sulfoximine (2g).** Following the general procedure, the lithiated species was quenched with 254 mg (1.00 mmol) of iodine. The crude product was purified by preparative HPLC (eluent petroleum ether/diethyl ether, 1:1, 40 mL min^{-1}, t_R = 6.8 min), yielding 131 mg (68%) of **2g** as an orange solid and 26 mg of recovered **1**. Mp = 165 °C (dec); $[\alpha]_D^{25}$ = +26° (*c* = 0.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.27 (s, 9H), 2.41 (s, 3H), 4.51 (s, 5H), 4.52−4.55 (m, 1H), 4.76−4.80 (m, 2H), 7.28 (d, *J* = 7.7 Hz, 2H), 7.97 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.2, 23.8, 35.6, 67.0, 72.4, 73.1, 74.4, 80.1, 86.2, 126.1, 128.9, 141.7, 141.9; MS (EI, 70 eV), *m*/*z* (rel intensity) = 585 (M^+, 10), 529 (21), 291 (100); IR (KBr) 3435, 3111, 2979, 1597. Anal. Calcd for $C_{21}H_{24}FeINO_3S_2$: C, 43.09; H, 4.13; N, 2.39. Found: C, 43.11; H, 4.44; N, 2.17.

Imination of (*S*,*S$_p$*)-*S*-*tert*-Butyl-*S*-(2-methylferrocenyl)sulfoxide (4). A solution of 200 mg (0.66 mmol) of **4** and 50 mg (0.13 mmol) of $Cu(I)PF_6 \cdot 4CH_3CN$ in 10 mL of anhydrous acetonitrile was treated portionwise with 294 mg (0.79 mmol) of *N*-(*p*-tolylsulfonyl)iminophenyl-λ^3-iodane under an argon atmosphere at room temperature. The mixture was stirred for 48 h at this temperature, filtered, and evaporated. The product was purified by column chromatography (eluent petroleum ether/diethyl ether, 1:1), yielding 150 mg (48%) of **2a** as an orange solid and 90 mg of recovered **4**. ^1H NMR and ^{13}C NMR data were identical with those of compound **2a** prepared by directed *ortho*-metalation.

X-ray Crystallography. Crystal data for **2g**: X-ray data were collected on a Bruker SMART CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). $C_{21}H_{24}FeINO_3S_2$, *M* = 585.3, orthorhombic, space group $P2_12_12_1$, *a* = 9.3188(4) Å, *b* = 12.5815(6) Å, *c* = 19.3691(9) Å, *V* = 2270.92 $Å^3$, *Z* = 4, D_c = 1.712 g cm^{-3}, μ = 25.27 cm^{-1}, absorption correction with SADABS (max./min.: 1.00/0.74), $2\theta_{max}$ = 66.4°; 24 972 measured, 4796 unique, and 3738 observed ($|I| > 2\sigma(I)$) reflections. All observed reflections were included in the final full-matrix least-squares refinement (on *F*) of 263 parameters, terminating at *R* = 0.039, *wR* = 0.040 ($w = (\sigma^2(F) + 0.0004F^2)^{-1}$), a goodness of fit of 1.2439, and a residual electron density of −1.65/+1.58 e/$Å^3$.

The structure was solved by means of direct methods (GENSIN, GENTAN) as implemented in the XTAL3.4 package of crystallographic routines.[24] Further details can be obtained from the Cambridge Crystallographic Data Center under the following CCDC number: CCDC 138944.

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Supporting Information Available: Full spectral characterization (^1H and ^{13}C NMR spectra) for all new ferrocenes and crystallographic data regarding the X-ray structure of **2g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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