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Enantioselective Synthesis of Diverse Sulfinamides and Sulfinylferrocenes from Phenylglycine-Derived Chiral Sulfinyl Transfer Agent

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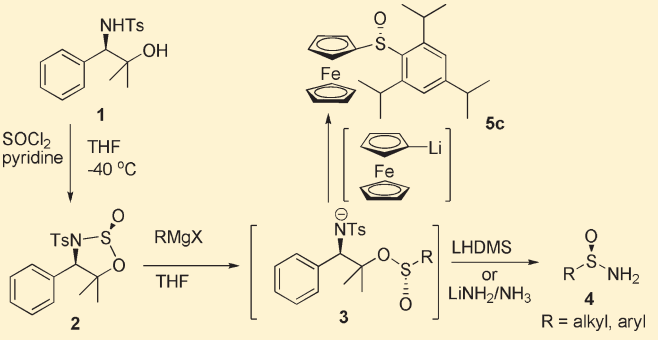
Supporting Information

ABSTRACT: A new chiral sulfinyl transfer auxiliary derived from readily available phenylglycine was developed. This auxiliary is utilized to synthesize a diverse array of alkyl- and arylsulfinamides and sulfinylferrocenes in high yields and excellent ee's. The desired products are produced in a one-pot sequence from the oxathiazolidine 2-oxide by two sequential nucleophilic additions that proceed in a stereospecific manner.

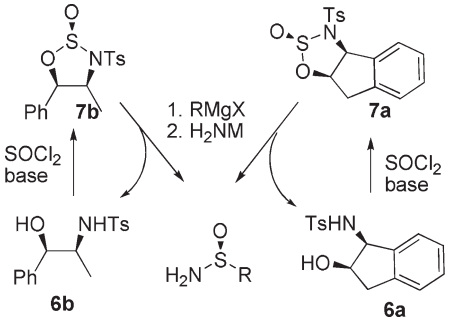


Chiral sulfinyl-containing reagents, such as sulfoxides and sulfinamides, have been recognized as useful tools in the asymmetric synthesis of complex organic molecules.[1] Although the power of chiral sulfinyl reagents in synthetic chemistry has long been recognized, methods for their synthesis have emerged slowly.[1c] A few methods have been developed in the past few decades, but a more general and economic method for their synthesis is necessary in order to meet today's need.[2]

Primarily, chiral sulfinyl transfer agents only have been used in the synthesis of chiral sulfoxides. Because of their limitation, few methods have been used in the synthesis of chiral sulfinamides.[2a−f] With the pioneering work by Davis et al.[3] for the synthesis of chiral *p*-toluenesulfinamide (*p*-TSA) from Anderson's reagent,[4] followed by Ellman et al.[5] for the synthesis of *tert*-butanesulfinamide (*t*-BSA), the power of their applications to the asymmetric synthesis of chiral amines was quickly realized. A wide range of natural products as well as many important pharmaceutical agents with chiral amine functionalities have been synthesized using this technology.[5]

Because of the limited availability of other sulfinamides, *t*-BSA and *p*-TSA have been commonly used in the asymmetric synthesis.[6,7] Many times, sulfinamides with diverse functionalities are needed in order to fine-tune for high stereoselectivity. To meet this need, we developed a unique double displacement method to prepare a variety of both alkane- and arenesulfinamides (Scheme 1).[8] This method is based on the use of a chiral and functionality differentiated oxathiazolidine *S*-oxide **7a** or **7b** derived from *cis*-(*R*,*S*)- or (*S*,*R*)-amino alcohols, such as *N*-tosylaminoindanol (**6a**) or *N*-tosylnorephedrine (**6b**). This technology was also employed successfully in the synthesis of a variety of important sulfoxides. However, the relatively expensive aminoindanol and regulated substance norephedrine hindered production of sufinamides on a large scale and in a more economic manner.

Scheme 1. Synthesis of Sulfinamide via Amino Alcohol or Norephedrine



Recently, we have used **1** as a recyclable auxiliary in the asymmetric synthesis of sibutramine.[9] Reaction of an imine intermediate with **1** derived oxathiazolidine *S*-oxide (**2**) generates a chiral sulfinate imine that was reduced to provide the desired amine in high stereoselectivity. However, the application of **1** in the synthesis of chiral sulfinyl-containing compounds,

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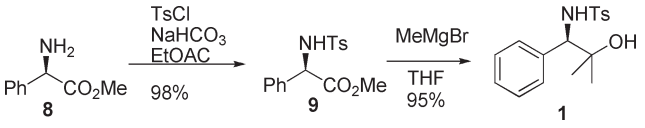
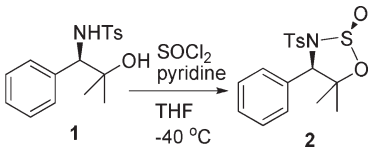
Scheme 2. Preparation of Auxiliary 1 from Phenylglycine



Scheme 3. Synthesis of 2 from 1



such as sulfinamides and sulfoxides, was never reported. Herein, we report the application of **1**, which contains one stereocenter, as a useful and inexpensive chiral sulfinyl transfer agent in the synthesis of sulfinamides and sulfoxides in high yields and excellent enantiopurity.

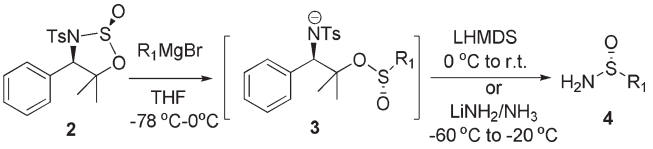
Both (*R*) - and (*S*)-phenylglycines are readily available and abundant. Its methyl ester (**8**) was easily converted to **9** via tosylation under Schotten−Baumann reaction conditions in excellent yield.[9] Reaction of **9** with 3 equiv of methylmagnesium bromide in THF yielded the desired amino alcohol **1** in 95% yield (Scheme 2). In contrary, reaction of methylmagnesium bromide with **8** resulted in very poor yield in the synthesis of the corresponding amino alcohol.

With **1** in hand, the synthesis of **2** in diastereomerically pure form on a large scale was investigated. Previously, we have demonstrated a methodology for the preparation of *N*-tosyl-1,2,3-oxathiazolidine 2-oxide **7a** or **7b** in high diastereoselectivity. The synthesis was achieved by a slow addition of an appropriate base to a mixture of either **6a** or **6b** and thionyl chloride in THF solution.[8b] Following a similar protocol, by slow addition of pyridine to a mixture of **1** with thionyl chloride in THF at −40 °C, (2*S*,4*R*)-5,5-dimethyl-4-phenyl-*N*-tosyl-1,2,3-oxathiazolidine 2-oxide (**2**)[10] was prepared in 96% yield and >90% de on 200 g scale. Compound **2** is crystalline, and its diastereomeric purity was enriched to 99% de by recrystallization from ethyl acetate/hexane in 90% yield (Scheme 3).

The synthesis of sulfinamides by using **2** was next investigated. Using different Grignard reagents and lithium bis(trimethylsilyl)-amide (LHMDS), as shown in Table 1, a series of enantiopure sulfinamides **4a**−**g** were synthesized in a one-pot fashion. Slow addition of a Grignard reagent to a solution of **2** in THF at −78 °C generated the sulfinate intermediate **3** in high yield by selectively opening the S−N bond.[8] After completion of the reaction, LHMDS was added directly to the reaction mixture, and the reaction mixture was warmed to ambient temperature to yield the desired sulfinamides in good yield and optical purity with recovery of auxiliary **1**. Sulfinamides with different functional groups, for example, of alkyl (**4a**,**b**), electron-withdrawing (**4c**), electron-donating (**4d**), phenyl (**3e**), and thiophene (**4g**), were prepared successfully.

Synthesis of chiral **4c** via subtilisin-catalyzed resolution of *N*-acylarylsulfinamide was reported but in very low yield.[11a] No synthesis of **4d** or **4e** in optically pure form has been reported.[11b] The application of **4f** in the synthesis of (*S*)-(−)-xylopinine was reported by Davis and co-workers,[11c]

Table 1. Synthesis of Sulfinamides with Different Functionalities



sulfinamide **4**	Yield[a]	ee[b]	abbrevation
4a[c]	93%	99%	pTSA
4b[c]	90%	99%	TMBSA
4c[c]	65%	99%	*p*ClBSA
4d[c]	73%	99%	oMBSA
4e[c]	92%	99%	oPBSA
4f[c]	87%	99%	oMNSA
4g[c]	94%	99%	2-MTPSA
4h[d]	80%	99%	*t*BSA
4i[d]	86%	99%	TIPPSA

[a] Isolated yield. [b] ee monitored by chiral HPLC. [c] One-pot protocol by using LHMDS as nucleophile. [d] Two-step protocol by using $LiNH_2/NH_3$ as nucleophile

and use of **4f** gave a better selectivity than both *p*TSA and *t*BSA in the synthesis of the key chiral amine intermediate.

For comparison purposes, the above method was applied to synthesize the more sterically hindered *tert*-butanesulfinamide (*t*-BSA) as well as triisopropylbenzenesulfinamide (TIPPSA) in excellent ee and in high yield. However, because of the increased steric bulk of both the *tert*-butyl and triisopropylphenyl groups, the above-discussed one-pot procedure cannot be used because there was no reaction was observed when LHMDS was used as nucleophile. Instead, $LiNH_2$ in ammonia was needed to make these sulfinamides.[5a,8a]

The scope of **2** in the synthesis of chiral sulfinyl compounds was extended to the synthesis of chiral sulfoxides and ferrocene−sulfinyl derivatives in particular. The ferrocene-bearing stereogenic sulfinyl group has recently emerged as highly serviceable agent in many asymmetric processes because it can act as an

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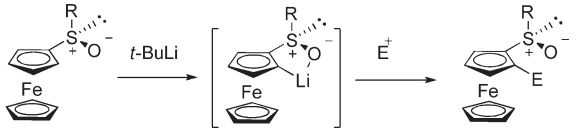
Scheme 4. Synthesis of Ferrocene Derivatives from Ferrocene−Sulfinyl Compound



ortho-directing group to afford ferrocene derivatives with planar and central chirality (scheme 4). On the other hand, they can be easily removed or substituted, providing a key method in the synthesis of enantiopure 1,2-disubstituted ferrocenyl ligands.[12] Few methods have addressed this issue except in the synthesis of *p*-tolylsulfinyl- and *tert*-butylsulfinylferrocenes in a tedious manner. In this case, the chiral sulfinyl transfer reagents have to be prepared individually, and therefore, it lacks generality and efficiency.[12a,i]

Use of **2** provides a general method for the synthesis of a variety of alkyl- or arylsulfinylferrocenes. The preparations of these ferrocenyl derivatives were accomplished in a one-pot process by double displacement. Addition of Grignard reagent afforded the sulfinate intermediate **3** and subsequent addition of ferrocenyllithium that was generated in THF by treatment of ferrocene with *t*-BuLi in the presence of *t*-BuOK as catalyst[12b] afforded the desired **5** in good yield and high enantiopurity. As shown in Figure 1, a few examples of structural diverse sulfoxides were prepared, which include alkyl and aryl groups. Attempts to prepare the ferrocenyl sulfinate intermediate by addition of ferrocenyllithium to **2** resulted in low yield. The major product is diferrocenyl sulfoxide, which is from the double addition due to the high reactivity of ferrocenyllithium as a nucleophile.

With sulfoxide **5** in hand, reactions with aldehydes in the synthesis of chiral alcohol **10** were investigated. Ferrocenyl chiral alcohols are also important intermediates used as transit in the synthesis of P- or N-containing ligands, and their synthesis in optically pure form was a tedious process.[12,13] On the other hand, the chiral alcohol generated from ferrocenyl sulfoxide would potentially provide a quick way in accessing *S*,*O*-ferrocenyl ligands. However, to the best of our knowledge, only the addition of lithiated *tert*-butylsulfinylferrocene to benzaldehyde was reported but the reaction yielded racemic alcohol.[12g]

The reactions of benzaldehyde with sulfoxides **5a** (*t*-Bu-FcSO), **5b** (Mes-FcSO), and **5c** (TIPP-FcSO) were primarily investigated in the synthesis of chiral alcohols (Figure 2). Sulfoxide was first lithiated with *t*-BuLi in THF at −78 °C, and then a THF solution of benzaldehyde was added dropwise. Upon completion, the reaction was quenched by addition of water. The conversion and dr were easily determined on the basis of the LC analysis. Reaction of **5a** with benzaldehyde resulted in the desired product **10a** in a high isolated yield of 92% but in poor stereoselectivity of 57:43 dr. When 2-mesitylsulfinylferrocene **5b** was used, the reaction was sluggish and the isolation of the desired product was not successful, which might be caused by the decomposition of the lithated product or other side reactions as observed in the case of *p*-tolylsulfinylferrocene.[12a] Use of nBuLi or LDA as lithiation reagent was found also not productive. However, when hindered **5c** was used, the reaction afforded the product **10c** in high yield of 94% with good dr of 82:18. Attempts to improve the selectivity by adding Lewis acids or Lewis bases, such as LiCl, $MgBr_2$, $AlMe_3$, $BF_3 \cdot OEt_2$, $ZnCl_2$, and TMEDA, to the reaction mixture were not successful. Those two diastereomers

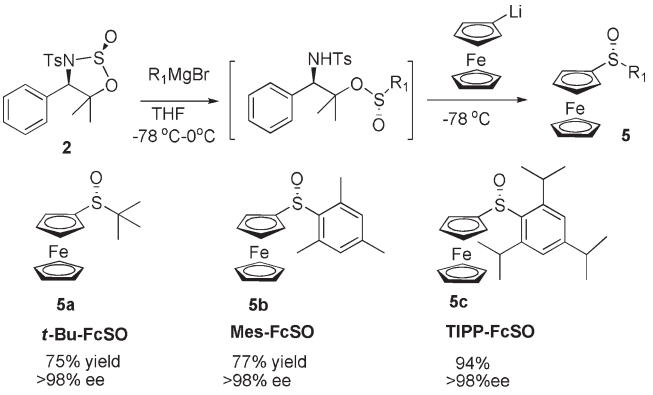


Figure 1. Synthesis of ferrocenyl sulfoxides.

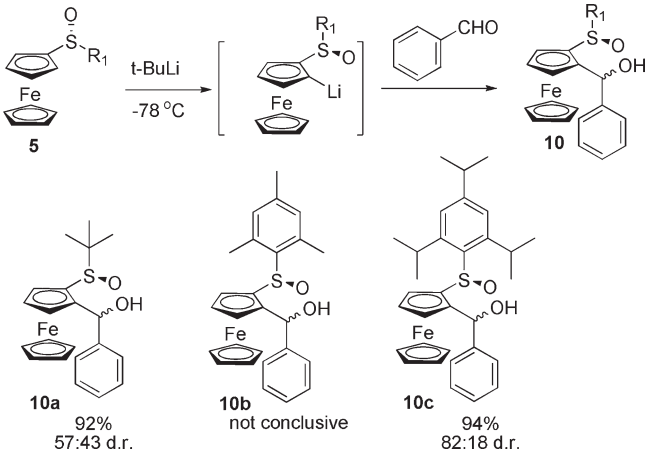


Figure 2. Synthesis of alcohol from ferrocenyl sulfoxides.

were separated by chromatography on silica gel to provide optically pure products.

In summary, a new and easily accessible chiral sulfinyl transfer agent **2** was developed. Its utilities have been extended to the synthesis of structurally diverse sulfinamides and ferrocenyl sulfoxides in excellent yields and enantiomeric purities. Ferrocenyl sulfixide **5c** that contains a triisopropylphenyl functionality shows superior stereoselectivity as compared to *tert*-butyl containing sulfoxide **5a** in the synthesis of chiral benzyl alcohol. The applications of **5c** in the synthesis of other ferrocenyl alcohols as well as the application of alcohols as ligands in asymmetric synthesis are under further investigation.

EXPERIMENTAL SECTION

Large-Scale Synthesis of (2*S*,4*R*)-5,5-Dimethyl-4-phenyl-*N*-tosyl-1,2,3-oxathiazolidine 2-Oxide (2). To a stirred solution of **1** (200 g, 629 mmol) in THF (1 L) at −45 °C was slowly added thionyl chloride (69 mL, 944 mmol). Subsequently, pyridine (127 mL, 1.57 mol) diluted in THF (100 mL) was added slowly via an addition funnel. After addition, TLC analysis indicated no remaining starting material, and the reaction was quenched with aqueous $NaHCO_3$ (500 mL) and diluted with EtOAc (1 L). The reaction mixture was allowed to warm to ambient temperature, and the phases were separated. The organic layer was washed with brine, dried with Na_2SO_4, filtered, and concentrated under rotary evaporation to afford **2** (221 g, 96%) as a white solid with a dr = 95:5. Recrystallization of **2** from EtOAc and

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hexanes gave the desired product in >99:1 dr in 90% overall yield. Characterization data matches previously reported data.[9]

General Procedure for Grignard Addition to 2 in the Synthesis of 3i. To a stirred solution of **2** (1 g, 2.7 mmol) in THF (10 mL) at −78 °C was added freshly prepared triisopropyphenylmagnesium bromide solution (5.5 mL, 0.5 M in THF) dropwise. Upon completion of addition, TLC analysis showed no remaining starting material, and the reaction was quenched with aqueous $NaHCO_3$ (5 mL) and diluted with EtOAc (20 mL). The reaction mixture was allowed to warm to ambient temperature, and the phases were separated. The organic layer was washed with brine, dried with Na_2SO_4, filtered, and concentrated under rotary evaporation. The solid residue was purified with flash chromatography (0% → 50% EtOAc/hexanes) to afford **3i** in 91% yield (1.42 g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17−1.27 (m, 21H), 1.18 (s, 3H), 2.26 (s, 3H), 2.89 (sep, J = 6.8 Hz, 1H), 3.98 (sep, J = 6.8 Hz, 2H), 4.24 (d, J = 9.6 Hz, 1H), 6.15 (d, J = 9.6 Hz, 1H), 6.94 (d, J = 8.2 Hz, 2H), 6.98−7.03 (m, 4H), 7.07−7.09 (m, 3H), 7.37 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 23.6, 23.7, 24.2, 24.5, 24.5, 26.5, 26.7, 28.1, 34.4, 65.7, 86.3, 122.8, 126.8, 127.3, 127.6, 128.7, 128.9, 136.5, 137.6, 137.7, 142.5, 148.6; 152.9; HRMS calcd for $C_{32}H_{44}NO_4S_2$ (M + 1) 570.2718, found 570.2709.

(1R,R_S)-**3h** was obtained in 95% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.14 (s, 9H), 1.75 (s, 3H), 2.25 (s, 3H), 4.25 (d, J = 10.0 Hz, 1H), 6.52 (d, J = 10.0 Hz, 1H), 6.92 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 4.2 Hz, 4H), 7.08 (m, 1H), 7.36 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, CDC1$_3$) δ 21.3, 21.8, 25.4, 27.2, 57.3, 64.9, 85.5, 126. 7, 127.2, 127.5, 128.9, 129.1, 136.5, 138.0, 142.3; HRMS calcd for $C_{21}H_{30}NO_4S_2$ (M + 1) 424.1616, found 424.1611.

Typical Procedure for One-Pot Synthesis of (*R*)-2-Phenybenzenesulfinamide (4e). To a stirred solution of **2** (1 g, 2.7 mmol) in THF (10 mL) at −78 °C was added 0.5 M biphenyl-2-magnesium bromide (5.5 mL) in diethyl ether dropwise. Upon completion of addition, TLC analysis showed no remaining starting material, 1.0 M lithium bis(trimehtylsilyl)amide (4.1 mL) in THF was added, and the reaction mixture was allowed to slowly warm to ambient temperature. After completion of the reaction, water (5 mL) was added and the mixture diluted with EtOAc (20 mL). The phases were separated, and the organic phase was washed with brine (5 mL), dried with Na_2SO_4, filtered, and concentrated under rotary evaporation. The crude mixture was purified with flash chromatography (20% →100% EtOAc/hexanes) to afford **4e** (547 mg) in 92% yield and 99% ee and **1** (777 mg) in 89% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (s, 2H), 7.34 (m, 1H), 7.39−7.44 (m, 5H), 7.54−7.60 (m, 2H), 8.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 122.63, 127.81, 128.15, 128.24, 126.49, 130.69, 131.09, 138.34, 140.34, 145.24; HRMS calcd for $C_{12}H_{12}NOS$ (M + 1) 218.0640, found 218.0634. Chiral HPLC conditions: Chiralpak AS-H Column, 4.6 × 250 mm, 5 μm; 90:10 hexanes/ethanol, 1.0 mL/min; 254 nm; (*R*)-**4e**, t_R = 5.7 min; (*S*)-**4e** t_R = 29.0 min.

The following known compounds were isolated as pure samples and showed NMR spectra and the enantiomerically purity matching those of the reported compounds: *p*-TSA (**4a**),[2a] TMBSA (**4b**),[2a] *p*-ClBSA (**4c**),[11a] *o*-MNSA (**4f**),[14] *t*-BSA (**4h**),[2a] and TIPPSA (**4i**).[5b]

***(R)*-2-Methoxyphenylsulfinamide (4d).** The ^{1}H NMR and ^{13}C NMR data match that reported.[11b]

Chiral HPLC conditions: Chiralcel OD Column, 4.6 × 250 mm, 5 μm; 90:10 hexanes/ethanol, 1.0 mL/min; 254 nm; (*S*)-**4d**, t_R = 12.1 min; (*R*)-**4d**, t_R = 25.9 min.

(*R*)-3-Methylthiophene-2-sulfinamide (4g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 4.90 (br s, 2H), 6.85 (d, J = 5 Hz, 1H), 7.35 (d, J = 5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.19, 128.13, 131.44, 139.02, 142.65; HRMS calcd for $C_5H_8NOS_2$ (M + 1) 162.0047, found 162.0041. Chiral HPLC conditions: Chiralpak AS-H Column, 4.6 × 250 mm, 5 μm; 90:10 hexanes/ethanol, 1.0 mL/min; 254 nm; (*R*)-**4g**, t_R = 5.7 min; (*S*)-**4g**, t_R = 29.0 min.

Typical Procedure for the Synthesis of (*R*)-2,4,6-Triisopropylphenylsulfinylferrocene (5c). In a separate flask, triisopropylphenylmagnesium bromide (2.48 mL, 0.65 M in THF) was added to a solution of **2** (0.59 g, 1.6 mmol) in THF (5 mL) at −78 °C. The mixture was stirred for 1 h, warmed to rt, and stirred for 1 h to form sulfinate intermediate **3i**.

To a mixture of ferrocene (0.45 g, 2. 42 mmol) and *t*-BuOK (0.3 mL, 1 M in THF) in THF (7 mL) at −78 °C was added *t*-BuLi (3 mL, 1.6 M) dropwise under an inert atmosphere. The mixture was stirred for 15 min, warmed to rt, and stirred for 1 h.

Both flasks were cooled to −78 °C, and the lithiated ferrocene solution was transferred to the **3i** solution. The mixture was stirred at −78 °C for 15 min, warmed to rt, and stirred for 1 h to furnish the reaction. The reaction was quenched by addition of water and diluted with EtOAc and brine. The aqueous phase was removed and extracted once with EtOAc. The combined organic phases were dried over Na_2SO_4 and concentrated. The residue was purified on column to give 0.66 g of **5c** in 94% yield and 98% ee: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (bs, 6H), 1.22 (d, J = 6.9 Hz, 6H), 1.28 (d, J = 6.7 Hz, 6H), 2.85 (sep, J = 6.9 Hz, 1H), 3.89−3.96 (m, 3H), 4.21 (s, 1H), 4.33 (s, 5H), 4.35 (s, 1H), 4.99 (s, 1H), 7.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8, 24.0, 24.9, 28.5, 34.3, 66.4, 67.3, 68.8, 69.3, 69.9, 93.6, 122.9, 137.2, 152.5; HRMS calcd for $C_{25}H_{33}FeOS$ (M + 1) 437.1602, found 437.1596 (0.031 ppm). Chiral HPLC conditions: Chiralcel OD, 4.6 × 250 mm, 5 μm; 98:2, hexanes/IPA, 0.7 mL/min; 254 nm; (*R*)-**5c**, t_R = 9.0 min; (*S*)-**5c**, t_R = 6.8 min.

(*R*)-*tert*-Butylsulfinylferrocene (5a). The ^{1}H- and ^{13}C NMR and the chiral HPLC data match that reported.[15]

(*R*)-2,4,6-Trimethylphenysulfinylferrocene (5b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.52 (s, 6H), 4.02 (s, 1H), 4.22 (s, 1H), 4.43 (s, 5H), 4.35 (s, 1H), 4.94 (s, 1H), 6.81 (s, 2H); ^{13}C NMR δ 19.4, 21.1, 66.1, 67.6, 69.0, 69.6, 69.9, 130.6, 138.4, 141.2; HRMS calcd for $C_{19}H_{21}FeOS$ (M + 1) 353.0662, found 353.0659 (0.52 ppm). Chiral HPLC conditions: Chiralcel OD, 4.6 × 250 mm, 5 μm; 98:2, hexanes/IPA, 0.7 mL/min; 220 nm; (*R*)-**5b**, t_R = 24.6 min; (*S*)-**5b**, t_R = 26.9 min.

Typical Procedure for the Synthesis of 10c. To a stirred solution of sulfinylferrocene **5c** (0.16 mmol) in dry THF (1 mL) at −78 °C under argon was added *tert*-butyllithium (1.3 equiv). After 30 min, the aldehyde (2 equiv) in 1 mL of THF was slowly added. The reaction mixture was stirred for an additional 30 min at −78 °C before it was quenched with H_2O, extracted with EtOAc, dried (Na_2SO_4), and concentrated. The reaction products were then analyzed by LC/MS and NMR and purified by chromatography to separate the diastereomers. **10c** major diasteromer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (d, J = 6.9 Hz, 6H), 1.24 (d, J = 6.9 Hz, 6H), 1.30 (d, J = 6.8 Hz, 6H), 2.88 (sep, J = 6.9 Hz, 1H), 3.67−3.71 (m, 2H), 3.87 (sep, J = 6.6 Hz, 2H), 3.99 (t, J = 2.5 Hz, 1H), 4.39 (s, 5H), 5.24 (d, J = 3.2 Hz, 1H), 5.89 (d, J = 3.1, 1H), 7.06 (s, 2H), 7.30−7.35 (m, 1H), 7.40 (t, J = 7.4 Hz, 2H), 7.60 (d, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 23.8, 24.8, 29.5, 34.4, 66.8, 67.4, 70.6, 71.6, 90.7, 95.1, 123.2, 127.2, 127.4, 128.0, 130.2, 133.5, 135.4, 142.0, 150.7, 153.5; HRMS calcd for $C_{32}H_{37}FeOS$ (M − OH) (major) 525.1915, found 525.1908 (0.293 ppm); calculated for $C_{32}H_{38}FeO_2S$ (M^+) 542.1942, found 524.1938 (0.381 ppm). LC−MS for the separation of diastereomers, major, t_R = 8.04 min, minor, t_R = 8.26 min.

10c minor diastereomer: ^{1}H NMR δ 1.12 (bs, 5H), 1.26 (d, J = 7.0 Hz, 13H), 2.90 (sep, J = 7.0 Hz, 1H), 3.61−3.62 (m, 1H), 3.76 (sep, 6.7 Hz, 2H), 3.97−3.98 (m, 1H), 4.05 (t, J = 2.6 Hz, 1H), 4.24 (s, 5H), 5.55 (d, J = 5.3 Hz, 1H), 6.05 (d, J = 5.2 Hz, 1H), 7.09 (s, 2H), 7.30−7.34 (m, 1H), 7.37−7.43 (m, 2H), 7.62 (d, J = 7.2 Hz, 2H); ^{13}C NMR δ 23.8, 24.8, 29.5, 34.4, 66.8, 67.4, 70.6, 71.6, 90.7, 95.1, 123.2, 127.2, 127.4, 128.0, 130.2, 133.5, 135.4, 142.0, 150.7, 153.5.

10a. The ^{1}H and ^{13}C NMR data match those reported.[12a] Retention time for the diastereomers: major t_R = 5.83 min, minor t_R = 6.09 min.

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■ ASSOCIATED CONTENT

Supporting Information. Additional procedures, spectral data and characterizations (^{1}H and ^{13}C NMR), and HRMS of all new products. This material is available free of charge via the Internet at http://pubs.acs.org.

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