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# Ferrocenyl bis-phosphine ligands bearing sulfinyl, sulfonyl or sulfenyl groups: applications in asymmetric hydrogenation and allylic alkylation reactions

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Received 10 August 2005; accepted 19 August 2005
Available online 10 November 2005

**Abstract**—A new series of chiral ferrocenyl bis-phosphine ligands have been synthesized. Elements of planar and central chirality have been incorporated into a ferrocene backbone through sulfinyl, sulfonyl and sulfenyl groups at the *ortho*-position to the phosphines. The effectiveness of these ligands has been demonstrated in Rh-catalyzed hydrogenations and Pd-catalyzed allylic alkylations.


## 1. Introduction

Bisphosphine ligands with a ferrocenyl backbone are an important class of ligands for homogenous catalysis. For example, 1,1′-bis(diphenylphosphino)ferrocene (dppf) **1a** is recognized as one of the most effective bis-phosphine ligands for organometallic transformations.[1] Pioneering work was carried out by Kumada et al. in the late 1970s on the use of dppf in Pd-catalyzed cross-coupling of Grignard reagents and organic bromides and allylic alcohols.[2,3] Dppf has also been tested for other nucleophilic substitutions[4] and olefin-hydrogenations.[5] Introducing elements of central and planar chirality in the dppf backbone is a well studied area.[6] Hayashi and Kumada's ligands (*R*)-*N*,*N*-dimethyl-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethylamine (PPFA) **1b** and (*R*)-*N*,*N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine (BPPFA) **1c** were some of the first ligands to be successfully employed in various asymmetric transformations.[7] Knochel's $C_2$-symmetric Ferriphos type ligand **1d** and Taniaphos **1e** also constitute significant contributions in this area (Fig. 1).[8,9] In summary, the planar chiral 1,2-disubstituted ferrocene unit has become one of the most useful backbones in designing new ligands. Herein, we report the synthesis and applications of ferrocenyl bis-phosphine ligands, which have *tert*-butyl-sulfinyl **2**, -sulfonyl **3** and -sulfenyl **4** groups at the *ortho*-position of each diphenylphosphino groups of dppf (Fig. 2).

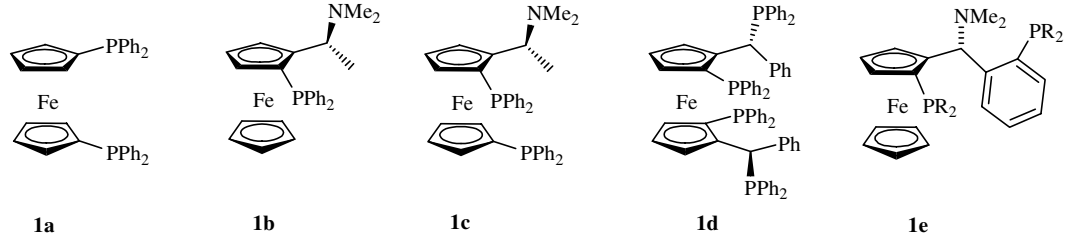


**Figure 1.** Ferrocenyl bis-phosphine ligands.

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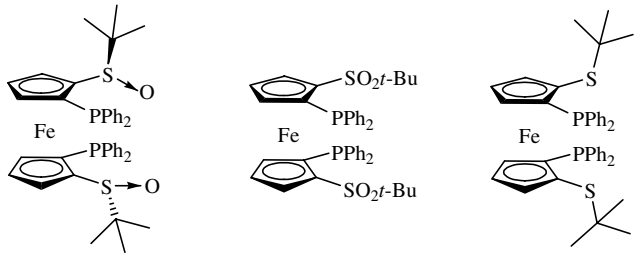
doi:10.1016/j.tetasy.2005.08.036




2 3 4

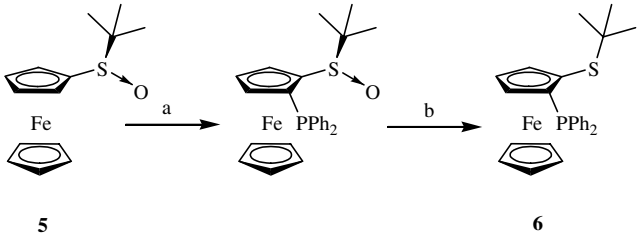
**Figure 2.** Bis-sulfinyl **2**, -sulfonyl **3a** and **3b** and -sulfenyl **4** ligands.

## 2. Results and discussion

### 2.1. Ligand synthesis

In 1993, Kagan et al. described the *ortho*-lithiation of the readily available (*R*)-*tert*-butyl sulfinyl ferrocene **5** as directed by the sulfinyl group occurring with complete selectivity at the C-2 (and not C-5).[10] The directing influences of the sulfinyl group have been explored by a few groups to prepare a variety of planar chiral ferrocenes.[11,12] Amongst these, the bidentate P,S-ferrocenyl ligand **6** has been successfully employed by Carretero et al. in asymmetric allylic alkylations and aza Diels–Alder reactions[13] (Scheme 1).

However, this idea has not been extended to bis-sulfinyl ferrocene. Our goal herein was to bring planar chirality elements at the *ortho*-positions of the two diphenylphosphino groups in dppf to make a new chiral ligand. We chose 1,1′-bis(*tert*-butylthio)ferrocene **7**, a known compound,[14] as the starting material. By preparing this compound from a pure dilithiumferrocene (TMEDA) salt,[15] we obtained disulfide **7** in up to 76% yield. Kagan's asymmetric oxidation of **7** led to 1,1′-bis-(*tert*-butylsulfinyl)ferrocene **8**. The overall yield after two recrystallizations was 40%. Crystallizations eliminated *meso*-**8** (as evidenced from $^1$H NMR) and gave the enantiomerically pure bis-sulfoxide. Based on Kagan's results, we assigned an ($R_S$,$R_S$)-configuration to **8**. *ortho*-Lithiation followed by the introduction of $PPh_2$ groups gave the primary desired ligand ($R_{Fc}$,$R_S$,$R_{Fc}$,$R_S$)-bis(*tert*-butylsulfinyl) phosphino ferrocene **2** (Scheme 2). The planar chirality configuration is assigned on the basis of the known *ortho*-lithiation of sulfoxide **5**.[10]




5 6

**Scheme 1.** Directing influence of sulfinyl group. Reagents and conditions: (a) *t*-BuLi, THF, −78 °C; $Ph_2PCl$; (b) $HSiCl_3$, $Et_3N$, toluene, 110 °C.

To test the activity of bis-phosphine ligand **2**, we set up Rh-catalyzed hydrogenation reactions of some common substrates (Fig. 3). Unfortunately, we found that the reaction did not occur with this ligand. A possible explanation for this is that the presence of two sulfur and two phosphorus donor atoms inhibits the catalytic activity. As a consequence, the idea of having only planar chirality, yet retaining the dppf **1a** motif appealed to us. Ligand **2** became our chiral synthon and we envisaged the conversion of the chiral sulfoxide of **2** to achiral sulfone **3** and sulfide **4**. Thus, the coordinating ability of S atoms would be altered.

To obtain sulfone **3**, we developed a synthesis method (Scheme 3, Route A). A dibromo sulfoxide intermediate **9a** was oxidized by *m*-CPBA to give dibromo sulfone **9b**. A lithium bromide exchange reaction followed by the

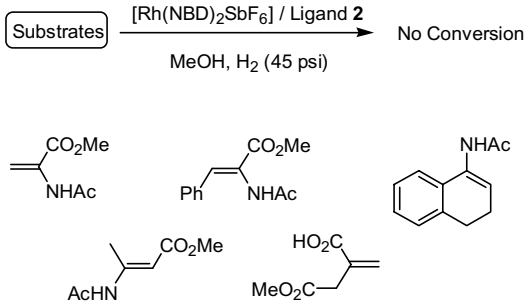
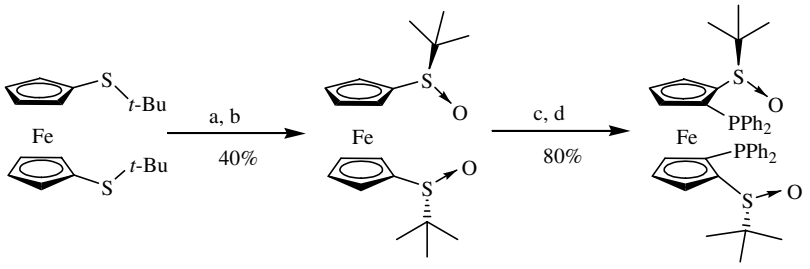
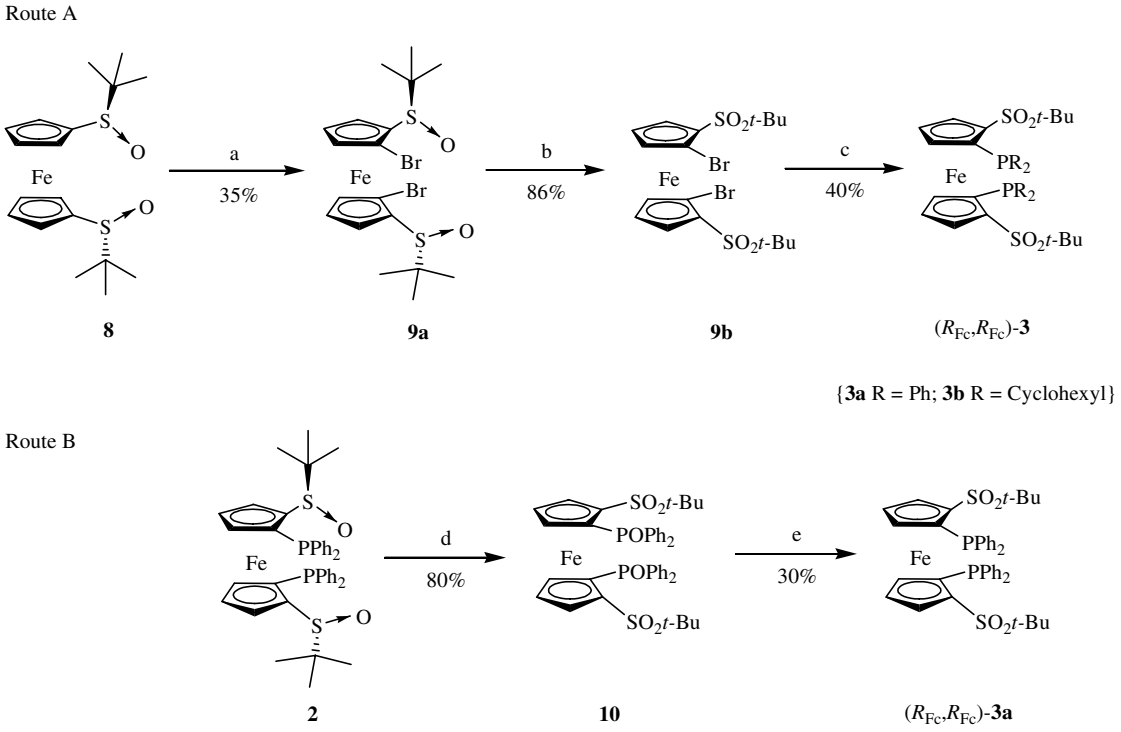



**Figure 3.** Common test substrates for Rh-catalyzed asymmetric hydrogenation.




7 ($R_S$,$R_S$)-**8** ($R_{Fc}$,$R_S$,$R_{Fc}$,$R_S$)-**2**

**Scheme 2.** Synthesis of ($R_{Fc}$,$R_S$,$R_{Fc}$,$R_S$)-bis(*tert*-butylsulfinyl)phosphino ferrocene **2**. Reagents and conditions: (a) Kagan's oxidation Ti(O*i*-Pr)$_4$/(+)DET/CHP/water, $CH_2Cl_2$, −23 °C; (b) recrystallization $CH_2Cl_2$/hexanes; (c) *n*-BuLi/hexane, THF, 0 °C; (d) $PPh_2Cl$, rt.




**Scheme 3.** Synthesis of ($R_{Fc}$,$R_{Fc}$)-bis(*tert*-butylsulfonyl)phosphino ferrocene **3**. Route A: (a) *n*-BuLi/hexane, THF, 0 °C, $C_2H_2Br_4$; (b) *m*-CPBA, acetone, 0°C–rt; (c) *n*-BuLi/hexane, THF, −78 °C, 1 h; $PR_2Cl$, rt. Route B: (d) *m*-CPBA, $CH_2Cl_2$, 0 °C; (e) $HSiCl_3$, $Et_3N$, toluene, 110 °C.

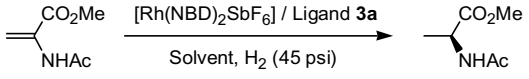
addition of a phosphine electrophile led to the desired ($R_{Fc}$,$R_{Fc}$)-bis(*tert*-butylsulfonyl)phosphino ferrocene **3**. Based on Route A, we prepared two ligands **3a** and **3b**. In order to improve the synthesis of **3**, we also devised an alternate route (Route B). Synthon **2** was completely oxidized at the sulfur and phosphorus centres and intermediate **10** was formed. Reduction of **10** with $HSiCl_3/Et_3N$ in refluxing toluene gave the desired sulfonyl phosphine **3**. The synthesis of bis-sulfenyl phosphine ligand **4** was carried out according to Carretero's procedure[11] who synthesized the first *P*,*S*-bidentate ligands possessing planar chirality. Following their methodology of $HSiCl_3/Et_3N$ reduction, we synthesized ligand **4** by reducing the sulfoxides of **2** to sulfides (Scheme 3).

## 2.2. Applications in asymmetric catalysis

The planar chiral sulfones **3a** and **3b**, and sulfides **4** were tested for Rh-catalyzed asymmetric hydrogenation. The catalytic complex was prepared in situ by mixing $[Rh(NBD)_2]SbF_6$ and the ligand in solvent. Of the three ligands tested, **3a** offered the best results. Hydrogenation of commercially available α-(*N*-acetamido)acrylate **11** was initially chosen to demonstrate the ligand's effectiveness. The hydrogenated product **12** was obtained in up to 93% ee and over 99% conversion. Both conversion and ees were poor for ligands **3b** and **4**. We also screened a few solvents for the reaction with MeOH being found as the best choice (Table 1).

Encouraged by the hydrogenation results, we explored the application of sulfone phosphine ligand **3a** in C–C bond formation reactions such as Pd-catalyzed asymmetric allylic alkylations (AAA). 1,3-Diphenylpropenyl

**Table 1.** Optimization of the reaction solvent for the Rh-catalyzed hydrogenation with **3a**



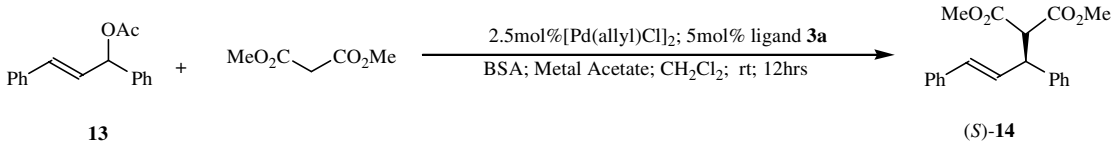

**11** **12**

| Entry[a] | Solvent | Conversion (%) | ee[b] (%) |
|---|---|---|---|
| 1 | Methanol | 99.7 | 93 |
| 2 | Dichloromethane | >99.9 | 88 |
| 3 | Ethanol | 95.9 | 91 |
| 4 | THF | >99.9 | 92 |
| 5 | Toluene | 76.4 | 73 |
| 6 | Isopropanol | 46.9 | 84 |
| 7 | Ethyl acetate | >99.9 | 88 |

[a] See Section 4 for details.
[b] Enantiomeric excess (ees) were determined by chiral GC (Chiralsil-VAL III FSOT). The (*S*)-configuration was assigned by the comparison of the specific rotation with the reported data.

acetate **13**, a typical substrate, was tested in conjunction with dimethyl malonate as the anion. Under standard conditions with $[Pd(\pi\text{-allyl})Cl]_2$ as the catalyst precursor and **3a** as the ligand, alkylation product **14** was obtained in high yields (up to 98%) and 86% ee (Scheme 4). The product was assigned an (*S*)-configuration based on its specific rotation.[16] In the literature, it is known that additive effects play a role in the Pd-catalyzed AAA reaction.[17] We tested alkali metal acetates from $Li^+$ through $Cs^+$ to see if there was any effect on the reactivity and enantioselectivity of this transformation.

The reaction yields remained similar (96–98% isolated yields) upon changing the additive. However, we




**13** (*S*)-**14**

**Scheme 4.** Pd-catalyzed allylic alkylations with ligand **3a**.

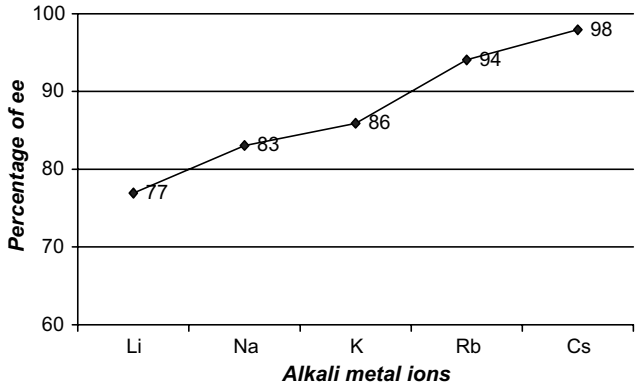



**Figure 4.** Effect of alkali metal acetates on the enantioselectivity of product **14**.

observed a dramatic increase in the enantioselectivity while changing the alkali metal ions $Li^+$ through $Cs^+$ (Fig. 4). By using CsOAc as the additive, up to 98% ee has been observed.

## 3. Conclusion

In conclusion, we have developed bis-sulfoxide **2**, sulfone **3** and sulfide **4** ferrocenyl bisphosphine ligands. Preliminary results demonstrating the asymmetric potentials of these ligands in hydrogenation and allylic alkylation reactions are encouraging. Further investigations on these ligands are underway and will be reported in due course.

## 4. Experimental

### 4.1. General procedure

All reactions were carried out under an inert atmosphere of nitrogen using standard Schlenk line techniques. Solvents were purified by standard procedures. All melting points were determined in open capillary tubes and are uncorrected. $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded in $CDCl_3$ using Bruker DPX-300, DPX-400 and AMX-360 spectrometers. Mass spectra were recorded on a KRATOS MS 9/50 for LR-ES and HR-ES or LS-APCI and HR-APCI. GC analysis was carried out on a Hewlett–Packard 6890 gas chromatograph with a flame ionization detector and chiral capillary column Chiralsil-VAL III FSOT (dimensions 25 m × 0.25 mm). HPLC analysis was performed on a Waters 600 chromatograph using a UV absorbance detector set at 254 nm for Chiralpak-AD® chiral HPLC column (Chiral Technologies, Inc.). Column chromatography was performed using EM silica gel 60 (200–400 mesh).

### 4.2. Ligand synthesis

**4.2.1. ($R_S$,$R_S$)-1,1′-Bis-(*tert*-butylsulfinyl)ferrocene 8.** Titanium tetra-isopropoxide (14.6 mL, 0.05 mol) was added to a solution of (*R*,*R*)-diethyl tartarate (17.5 mL, 0.10 mol) in dichloromethane (60.0 mL) at room temperature. The mixture was stirred for ca. 5 min and 0.9 mL of distilled water added. After 20 min, the solution was cooled to −23 °C while maintaining an inert atmosphere and bis(*tert*-butylthio)ferrocene **37** (9.0 g, 0.025 mol) then added. The stirring was continued for an additional 20 min. Cumene hydroperoxide (18.9 mL, 0.10 mol) was added dropwise and the whole system kept at −23 °C for ca. 3 days (unstirred). A solution of $FeSO_4{\cdot}7H_2O$ (140.0 g, 0.50 mol), citric acid (54.0 g, 0.25 mol) in water (1800 mL) was prepared for work-up. The organic layer was extracted with diethyl ether (3 × 250 mL). The combined organics were washed with 900 mL of 2 M aq NaOH solution. The biphasic mixture was stirred vigorously for 1 h to remove diethyl tartarate. After separation, the organic layer was dried over $MgSO_4$ and concentrated to give a yellow oily mixture. Flash silica gel chromatography with ethyl acetate/hexanes (1/1 to 2/1) as eluent gave bis-sulfoxide **8** (4.5 g, 50% yield). $^1H$ NMR revealed the presence of nearly 20% of *meso*-sulfoxide as impurity. Two recrystallizations with $CH_2Cl_2$/hexanes (1:4) afforded the desired pure chiral ($R_S$,$R_S$)-bis-sulfoxide **8** (3.8 g, 42% yield) as a yellow solid. $[\alpha]_D^{25} = -566.0$ (*c* 1, $CHCl_3$); $^1H$ NMR (360 MHz, $CDCl_3$) $\delta$ 4.83 (s, 2H), 4.76 (s, 2H), 4.69 (s, 2H), 4.63 (s, 2H), 1.16 (s, 18H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 88.88, 72.96, 72.84, 71.75, 67.12, 55.62, 23.14; APCI-MS (*m*/*z*): 417.0 [$M^+$+Na]; APCI-HRMS: calculated for $C_{18}H_{26}FeNaO_2S_2$ [$M^+$+Na]: 417.0616; found: 417.0621.

**4.2.2. ($R_{Fc}$,$R_S$,$R_{Fc}$,$R_S$)-Bis(*tert*-butylsulfinyl)phosphinoferrocene 2.** To an ice-cold solution of bis-sulfoxide **8** (0.98 mg, 2.5 mmol) in 40 mL of dry THF was added 2.5 mL of *n*-BuLi (2.2 equiv, 2.5 M in hexanes) over ca. 5 min. The lithiation was allowed to proceed at 0 °C for 1 h followed by the addition of $PPh_2Cl$ (1.3 mL, 7.0 mmol). The cooling bath was removed and the solution allowed to warm to room temperature and stirred for 1 h. As monitored by TLC (eluent ethyl acetate/hexanes 1/1), upon consumption of the starting material, work-up was done by adding 20 mL of saturated brine solution. The organic phase was extracted with 100 mL of $CH_2Cl_2$, washed with water, dried over $MgSO_4$ and concentrated to a red oil. Flash silica gel chromatography with ethyl acetate/hexanes (1/1 to

2/1) as eluent gave bis-sulfinyl diphosphine **2** (1.34 g, 71% yield) as an orange solid. $^1$H NMR (360 MHz, $CD_2Cl_2$) $\delta$ 7.27–7.09 (m, 20H), 5.02–4.98 (m, 4H), 3.37 (m, 2H), 0.96 (s, 18H); $^{13}$C NMR (90 MHz, $CD_2Cl_2$) $\delta$ 138.46, 135.57, 133.44, 129.99, 129.00, 128.93, 93.45, 93.23, 79.88, 79.56, 77.70, 56.97, 24.11; $^{31}$P NMR (145 MHz, $CD_2Cl_2$) −25.77; APCI-MS (*m*/*z*): 763.1 [$M^+$+H]; APCI-HRMS: calculated for $C_{42}H_{45}FeO_2P_2S_2$ [$M^+$+H]: 763.1720; found: 763.1714.

**4.2.3. Dibromosulfoxide 9a.** Under an inert atmosphere, bis-sulfoxide **8** (1.5 g, 3.8 mmol) was dissolved in 60 mL of dry THF and cooled to below 0 °C with ice-salt bath. A solution of *n*-BuLi (3.8 mL, 2.5 M in hexanes) was added over ca. 5 min and the lithiation allowed to be completed over 1 h. To the red solution was added 1,1,2,2-tetrabromoethane (2.0 mL, 17 mmol). After the addition, the reaction mixture was allowed to warm to room temperature and the work-up carried out after 3 h. A saturated brine solution (50 mL) was added and organic layer extracted with $CH_2Cl_2$, dried over $MgSO_4$ and concentrated to give a dark oily mixture. Purification was done by silica gel column chromatography with ethyl acetate/hexanes (1/1 to 2/1) as eluent. The desired product was obtained as a yellow solid (0.62 g, 30% yield). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.91–4.87 (m, 4H), 4.58 (m, 2H), 1.27 (s, 18H); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) $\delta$ 89.74, 73.06, 72.71, 71.97, 67.56, 55.60, 23.24; APCI-MS (*m*/*z*): 572.8 [$M^+$+Na]; APCI-HRMS: calculated for $C_{18}H_{24}Br_2FeNaO_2S_2$ [$M^+$+Na]: 572.8832; found: 572.8826.

**4.2.4. Dibromosulfone 9b.** Dibromosulfoxide **9a** (0.50 g, 0.9 mmol) was dissolved in 30 mL of acetone and cooled to 0 °C, under an inert atmosphere. A 10 mL acetone solution of *m*-chloroperbenzoic acid (400 mg, 2.3 mmol) was added to the reaction mixture in ca. 2 min. The reaction was allowed to warm to 25 °C and stirred for approx. 1 h. The solvent was removed under vacuum and diluted with 100 mL $CH_2Cl_2$. An aq NaOH solution (100 mL of 1 M) was used to wash the reaction and the organic phase was extracted with $CH_2Cl_2$ (3 × 50 mL), dried over $MgSO_4$ and concentrated. Purification involved passing the red oily mixture through a short silica gel plug with methanol/$CH_2Cl_2$ (1% v/v) as eluent. The desired product was obtained as a pure orange solid (423 mg, 80%). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.14 (m, 2H), 5.00 (s, 2H), 4.64 (s, 2H), 1.34 (s, 18H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 91.01, 86.90, 78.96, 75.45, 60.99, 42.80, 24.23; APCI-MS (*m*/*z*): 604.8 [$M^+$+Na]; APCI-HRMS: calculated for $C_{18}H_{24}Br_2FeNaO_4S_2$ [$M^+$+Na]: 604.8724; found: 604.8730.

**4.2.5. ($R_{Fc}$,$R_{Fc}$)-Bis(*tert*-butylsulfonyl)diphenylphosphino ferrocene 3a.** Dibromosulfone **9b** (100 mg, 0.181 mmol) was dissolved in 5 mL of dry THF in a Schlenk tube under a $N_2$ atmosphere and cooled to −78 °C with dry ice/acetone bath. A solution of *n*-BuLi (0.26 mL 1.6 M in hexanes) was added slowly and allowed 30 min for the Li–Br exchange to take place. $PPh_2Cl$ (0.2 mL, 0.724 mmol) was added over ca. 5 min and the reaction mixture allowed to warm to room temperature after 1 h. Work-up was done with the addition of 30 mL saturated brine solution at 0 °C, extracted with $CH_2Cl_2$ (2 × 50 mL) and dried over $MgSO_4$. The solution was concentrated and purified by silica gel column chromatography with ethyl acetate/hexanes (10–25%) as eluent. Concentration of pure fractions gave the pure bis-phosphine ligand (55 mg, 41% yield). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.30–7.22 (m, 20H), 5.61 (s, 2H), 5.12 (s, 2H), 3.41 (s, 2H), 1.11 (s, 18H); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) $\delta$ 139.28, 137.63, 135.64, 133.27, 130.32, 128.88, 92.71, 82.95, 81.69, 79.95, 77.02, 60.61, 24.19; $^{31}$P NMR (145 MHz, $CD_2Cl_2$) −25.17; APCI-MS (*m*/*z*): 817.0 [$M^+$+Na]; APCI-HRMS: calculated for $C_{42}H_{44}FeNaO_4P_2S_2$ [$M^+$+Na]: 817.1398; found: 817.1403.

**4.2.6. ($R_{Fc}$,$R_{Fc}$)-Bis(*tert*-butylsulfonyl)dicyclohexylphosphino ferrocene 3b.** Ligand **3b** was obtained in about 33% yield as an orange solid following the procedure described for **3a** and using dicyclohexylphosphine chloride (0.1 mL, 0.72 mmol) as the electrophile. $^1$H NMR (360 MHz, $CD_2Cl_2$) $\delta$ 5.34–5.29 (s, 2H), 5.08–5.02 (s, 2H), 4.62–4.51 (s, 2H), 2.41 (m, 2H), 2.15 (m, 2H), 1.94–1.16 (m, 58H); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) $\delta$ 89.48, 88.36, 81.71, 78.72, 74.95, 60.73, 41.03, 34.76, 33.88, 32.55, 31.34, 27.16, 24.77; $^{31}$P NMR (145 MHz, $CD_2Cl_2$) −10.20; APCI-MS (*m*/*z*): 819.3 [$M^+$+H]; APCI-HRMS: calculated for $C_{42}H_{68}FeNaO_4P_2S_2$ [$M^+$+Na]: 841.3276; found: 841.3281.

**4.2.7. Bis(*tert*-butylsulfonyl) phosphonyl ferrocene 10.** Bis-sulfinyl diphosphine **2** (1.0 g, 1.31 mmol) was dissolved in 30 mL dry $CH_2Cl_2$ in a Schlenk flask under $N_2$ atmosphere and cooled to 0 °C. Excess of *m*-Chloroperbenzoic acid (3.65 g, 20 mmol) was dissolved in 40 mL of dry $CH_2Cl_2$ and added slowly over ca. 10 min to the above solution. The reaction mixture was allowed to stir for 1 h at this temperature. The progress of the reaction was monitored by TLC (eluent methanol/ethyl acetate 20%). Work-up involved addition of 50 mL of saturated aq $NaHCO_3$ solution and extraction with 2 × 50 mL of $CH_2Cl_2$. The organic phase was dried over $MgSO_4$ and concentrated to an orange oily mixture. Purification was done by silica gel column chromatography with methanol/ethyl acetate (5–10%) as eluent to obtain the pure phosphine oxide **10** (0.9 g, 80% yield). $^1$H NMR (300 MHz, $CD_2Cl_2$) $\delta$ 8.00–7.29 (m, 20H), 6.06–5.97 (m, 2H), 5.75 (m, 2H), 4.42–4.18 (m, 2H), 0.94 (s, 18H); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) $\delta$ 132.78, 132.42, 129.19, 129.03, 128.86, 128.07, 92.97, 88.36, 82.86, 81.71, 78.24, 61.90, 24.20; $^{31}$P NMR (145 MHz, $CD_2Cl_2$) 21.06; APCI-MS (*m*/*z*): 849.0 [$M^+$+Na]; APCI-HRMS: calculated for $C_{42}H_{44}FeNaO_6P_2S_2$ [$M^+$+Na]: 849.1296; found: 849.1302.

**4.2.8. ($R_{Fc}$,$R_{Fc}$)-Bis-(*tert*-butyl-sulfenyl)diphenylphosphino ferrocene 4.** *Bis*-sulfinyl phosphine **2** (115 mg, 0.15 mmol) was dissolved in 4 mL of dry toluene in a Schlenk tube under an inert atmosphere. Trichlorosilane (0.4 mL, 30 equiv) and triethylamine (0.4 mL, 20 equiv) were added to the reaction mixture and heated to reflux (110 °C) for about 8 h. The progress of the reaction was monitored by TLC (hexane/ethyl acetate 1/1). The reaction mixture was diluted with 30 mL of $CH_2Cl_2$ and

10 mL of 3 M aq NaOH solution added to quench the excess silane. The organic phase was washed with brine ($2 \times 10$ mL) and dried over $MgSO_4$. Purification was done by column chromatography (ethyl acetate/hexane = 5–10%). The pure bis-sulfide phosphine ligand **4** was obtained (60 mg, 55% yield). $^1$H NMR (360 MHz, $CD_2Cl_2$) $\delta$ 7.31–7.25 (m, 10H), 7.21–7.12 (m, 10H), 4.60 (s, 2H), 4.47 (s, 2H), 3.20 (s, 2H), 0.97 (s, 18H); $^{13}$C NMR (90 MHz, $CD_2Cl_2$) $\delta$ 140.82, 138.78, 135.46, 133.37, 129.75, 128.68, 86.83, 86.51, 82.91, 82.82, 75.41, 46.79, 31.76; $^{31}$P NMR (145 MHz, $CD_2Cl_2$) −26.55; APCI-MS (*m*/*z*): 731.1 [$M^+$+H]; APCI-HRMS: calculated for $C_{42}H_{45}FeP_2S_2$ [$M^+$+H]: 731.1793; found: 731.1787.

### 4.3. General catalytic procedure

**4.3.1. Asymmetric hydrogenation.** A solution of [Rh(NBD)$_2$SbF$_6$] (2.3 mg, 0.0050 mmol) and ligand **3a** (4.4 mg, 0.0055 mmol) in solvent (5mL) was stirred in a glove box for 10 min to allow the formation of catalyst. The complex solution (1 mL) was then taken in each of the hydrogenation vials. The commercially available substrate α-(*N*-acetamido)acrylate **11** (14.3 mg, 0.1 mmol) was added and the mixture hydrogenated in an autoclave for 12 h. After carefully releasing the hydrogen, the reaction mixture was passed through a short silica-gel plug to remove the catalyst. Upon concentration, the desired product was subjected to chiral GC analysis to determine the enantiomeric excess.

**4.3.2. Asymmetric allylic alkylation.** A Schlenk flask under $N_2$ was charged with [Pd(π-allyl)Cl]$_2$ (4.5 mg, 2.5 mol %), ligand (5 mol %) and $CH_2Cl_2$ (2 mL). The catalyst solution was stirred for 30 min at 25 °C before adding (*E*)-1,3-diphenyl prop-2-enyl acetate **12** (126 mg, 0.5 mmol) as a solution in 1 mL of solvent. Dimethyl malonate (172 μL, 1.2 mmol) was then added followed by alkali metal acetate (2.0 mol %) and BSA (0.37 mL, 1.2 mmol). The reaction was complete in ca. 8 h as evidenced by TLC (eluent hexanes/ethyl acetate = 5/1; $KMnO_4$ viewing). The mixture was concentrated and directly subjected to silica gel chromatography with eluent hexanes/ethyl acetate (4/1) to give product **13** (reaction yields 65–98%). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.29–7.15 (m, 10H); 6.42 (d, 1H, $J = 15.8$ Hz); 6.30 (dd, 1H, $J = 15.7$ Hz and 8.4 Hz); 4.19 (dd, 1H, $J = 10.1$ Hz and 8.5 Hz); 3.93 (d, 1H, $J = 10.9$ Hz); 3.70 (s, 3H); 3.66 (s, 3H). The enantiomeric excess was determined by chiral HPLC. The Chiralpak-AD® column was used with the mobile phase as 90/10 hexane/*iso*-propanol, flow rate 1 mL/min and detector set at $\lambda = 254$ nm. $t_R = 15.3$, 20.5 min. $[\alpha]_D^{25b} = -17.2$ (*c* 1.6, ethanol) {literature[15] −17.6 (*c* 1.68, ethanol)}, indicating (*S*)-enantiomer for **13**.


## Acknowledgement

The authors wish to thank the National Institute of Health for financial support (GM-58832).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