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Unexpected 1,5-Dilithiation of Chiral *o*-TMS Blocked (Dimethylamino)phenylmethylferrocene: An Alternative Approach to Chiral Ferrocenyl 1,5-Diphosphanes

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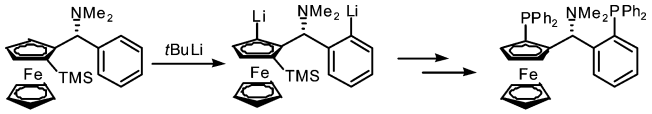
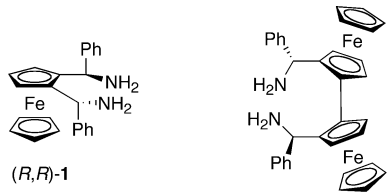


(*R*,*Sp*) (*R*,*Rp*) *dia*-Taniaphos

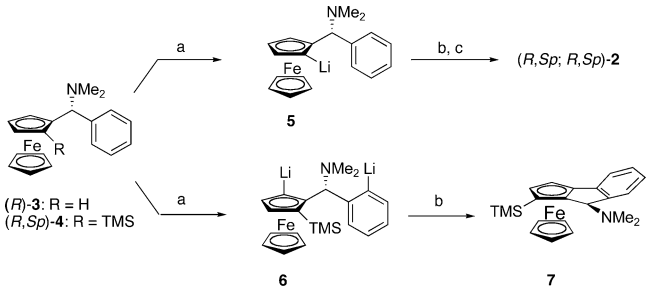
The 1,5-dilithiation of *o*-TMS blocked (dimethylamino)-phenylmethylferrocene **4** unexpectedly occurred even though one equimolar amount of *t*-BuLi was used and the 1,5-dilithiated ferrocene **6** was trapped by iodine followed by removal of the TMS group to give the 1,5-diiodoferrocene **11** in a reasonable yield. The 1,5-diiodoferrocene **11** was converted into the diastereomer of Taniaphos **12** by sequential dilithiation and trapping with Ph_2PCl. The rhodium and copper complex of **12** catalyzed well the asymmetric allylic alkylation with a Grignard reagent and hydrogenation with the α-acetamidocinnamic acid ester, respectively, with high enantioselectivities. The methoxy 1,5-diphosphane **14**, of which the enantiomer is known as a good ligand for the rhodium-catalyzed asymmetric hydrogenation, was obtained by the inversive substitution of the dimethylamino group of **11** by NaOMe and subsequent dilithiation and trapping with Ph_2PCl.

We previously reported the preparation of the chiral 1,2-ferrocenyl diamine **1** and asymmetric transfer hydrogenation to ketones by its ruthenium complex.[1] Although the enantiomeric excess of the products was moderate (up to 75% ee), the potential of the ferrocenyl diamine ligand was demonstrated. We have prepared the bisferrocenyl diamine **2** by the sequence of the homo-coupling of the *o*-lithio ferrocenyl amine **5** catalyzed by $Fe(acac)_3$,[2] the retentive substitution of the dimethylamino group by the azide group, and reduction to the primary amine (Scheme 1). The ruthenium complex of **2** and its monotosylate could undergo asymmetric transfer hydrogenation to acetophenone; however, the enantiomeric excess of the product was unsatisfactory (up to 55% ee). The low enantioselectivity may be due to stereochemical mismatching of the planar chirality and the central chirality of the amino carbon. We then tried to prepare the bisferrocenyl diamine having a reverse planar chirality to **2** by starting from the ortho-lithiation and the homo-coupling of the *o*-TMS blocked ferrocene **4**. Surprisingly, the expected bisferrocene was not obtained, and the cyclized ferrocene **7** was produced in 36% yield (Scheme 1). The product was assumed to be the result of the intramolecular coupling of the dilithio compound **6**.[3]

CHART 1. Chiral Ferrocenyl Diamine Ligands

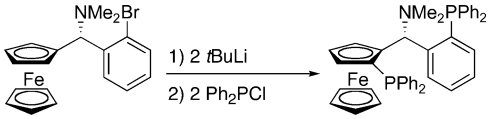


SCHEME 1. Mono- and Dilithiations of Chiral Amino Ferrocenes and Their Coupling Reaction by Fe(III)[a]



[a] Reagents: (a) *t*-BuLi (1.3 equiv), diethyl ether, 0 °C, 2 h. (b) $Fe(acac)_3$ (1.6 equiv), 0 °C to rt, 22 h. (c) Ac_2O; $TMSN_3/Cu(OTf)_2$ and then $LiAlH_4$.

SCHEME 2. Known Method for the Synthesis of Taniaphos



For **4**; the yield of the diiodide was naturally low

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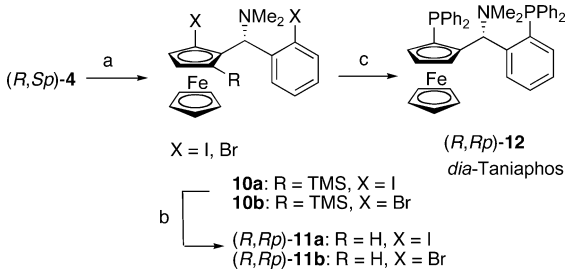
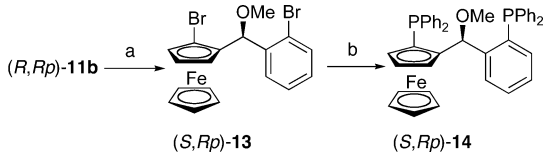
SCHEME 3. Synthesis of *dia*-Taniaphos[a]



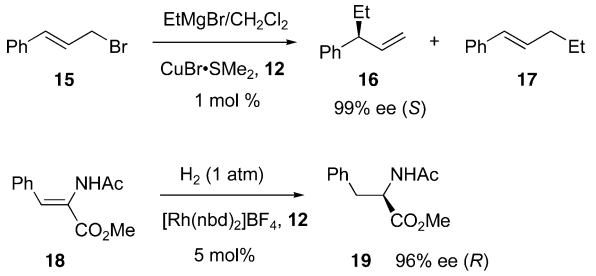
[a] Reagents: (a) *t*-BuLi (2.4 equiv) in diethyl ether, 0 °C, 2 h, then I_2 (2.5 equiv) or $BrCF_2CF_2Br$ (3 equiv). (b) *t*-BuOK (1.1 equiv) in DMSO, rt, 15 h. (c) *n*-BuLi (2.4 equiv) in diethyl ether, 0 °C, 2 h, and then Ph_2PCl (2.2 equiv).

SCHEME 4. Synthesis of Methoxy 1,5-Diphosphane[a]



[a] Reagents: (a) NaOMe (1.1 equiv), CH_3I (large excess) in methanol at rt for 10 h. (b) *t*-BuLi (4.4 equiv) in THF, 0 °C, 2 h, and then Ph_2PCl (2.2 equiv).

SCHEME 5. Representative *dia*-Taniaphos 12 Metal Complex-Catalyzed Asymmetric Reactions



(40%), and the formation of the mono-iodoferrocene was not observed in the ^{1}H NMR spectrum of the reaction mixture; 60% of unreacted **4** was recovered. When 2 molar equiv of *t*-BuLi was used for **4**, dilithiation adequately took place, and trapping with more than 2 molar equiv of iodine afforded the diiodide in 80% yield.[7] The treatment of **10a** with KOBu^t gave the TMS free **11a** in 84%. The 1,5-dilithiation of **11a** followed by trapping with 2 molar equiv of Ph_2PCl gave the diphosphane (i.e., *dia*-Taniaphos **12** bearing (*R*,*Rp*) stereochemistry) in 80% yield (Scheme 3). Thus, starting from the original amino ferrocene **3**, the *dia*-Taniaphos **12** was obtained in four steps in a 51% overall yield.

The methoxy 1,5-diphosphane (*S*,*Rp*)-**14** could be prepared by displacement of the dimethylamino group of **11b** by NaOMe with inversion of the stereocenter of the methine carbon and the subsequent lithiation and trapping with Ph_2PCl in a good yield.[8] The enantiomer of **14** (i.e., (*R*,*Sp*)-**14**) has been prepared by way of chromatographic separation of an almost 1:1 diastereomeric mixture of its precursor.[9] It has been reported that the ligand was used for their rhodium complex-catalyzed asymmetric hydrogenation of alkenes with high enentioselectivities. Our new method conveniently provides a facile way for the preparation of the (*S*,*Rp*) isomer without separation of the diastereomers.[10]

dia-Taniaphos **12** was applied for the copper-catalyzed allylic alkylation of cinnamyl bromide **15** with a Grignard reagent[5b,11] and the rhodium-catalyzed asymmetric hydrogenation of the α-acetamidocinnamic acid ester **18**.[4,12] The reactions were carried out according to the literature methods. In each reaction, the product was obtained in high enantioselectivity (i.e., the allylic alkylation (99% ee, *S*) and hydrogenation (96% ee, *R*)). These results showed that **12** should be as efficient a ligand as the original Taniaphos **9** for asymmetric reactions.

Experimental Section

Preparation of (*Sp*)-1-Trimethylsilyl-2-[(*R*)-1-(dimethylamino)phenylmethyl]ferrocene 4. In a 300 mL three-neck round-bottomed flask containing a magnetic stirring bar were charged [1-(*R*)-dimethylaminophenylmethyl]ferrocene **3**[13] (>99% ee) (5.4 g, 17 mmol) and dry diethyl ether (60 mL) under a slight pressure of nitrogen. The flask was cooled in an ice bath, and a hexane solution of *t*-BuLi (1.6 M, 14 mL, 22 mmol) was then added using a syringe through the septum with magnetic stirring. After 2 h, trimethylsilyl chloride (2.8 g, 25.8 mmol) was injected into the mixture at the same temperature. When the addition was completed, the ice bath was removed, and the mixture was allowed to warm to room temperature and stirred for an additional 15 h. The reaction was quenched with water, and the solution was then extracted with three 30 mL portions of diethyl ether. The combined extracts were washed (brine), dried (K_2CO_3), and filtered, and the solvent was removed on a rotary evaporator to leave a brown residue. The crude product was purified by column chromatography on a silica gel (hexane/ethyl acetate/triethyl amine = 20:5:1) to give the pure **4** as a brown oil. Yield, 6.3 g, 16.1 mmol, 95%. $[\alpha]_D^{25} = -98.4$ (c = 0.19, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.49 (s, 9H), 2.14 (s, 6H), 3.77 (s, 5H), 4.12 (s, 1H), 4.16 (s, 1H), 4.42 (s, 1H), 4.56 (s, 1H), 7.37−7.64 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 0.99, 43.4, 68.6, 68.8, 70.1, 70.8, 71.5, 73.1, 96.2, 126.8, 127.8, 128.5, 143.3.

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(7) Treatment of (*R*)-**3** with 2 equiv of *t*-BuLi followed by trapping with an excess of $BrCF_2CF_2Br$ gave 93% of the corresponding (*R*,*Sp*)-mono bromide together with 7% of the 1,5-dibromide.

(8) We are surprised at the inversion of the stereochemistry because it has been reported that the displacement of a dimethylamino group in the chiral ferrocenyl amine by the methoxide ion proceeds with retention. The mechanism of the inversive dimethylaminophenylmethyl case may be different from that of the retentive dimethylaminoethyl case. (a) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389−5393. (b) Han, J. W.; Tokunaga, N.; Hayashi, T. *Helv. Chim. Acta*. **2002**, *85*, 3848−3854.

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(12) For a review of asymmetric hydrogenation, see: Ohkuma, T.; Kitamura, M.; Noyori, R. *Asymmetric Hydrogenation*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 1−110.

(13) (*R*)-**3** was prepared by the reported method starting from CBS reduction of benzoylferrocene.[4a] Fukuzawa, S.-i.; Fujimoto, K.; Komuro, Y.; Matsuzawa, H. *Org. Lett.* **2002**, *4*, 707−709.

Anal. calcd for $C_{22}H_{29}FeNSi$: C, 67.51; H, 7.47; N, 3.58. Found: C, 67.37; H, 7.64; N, 3.22.

Preparation of (*Rp*)-3-Iodo-(*Sp*)-1-trimethylsilyl-2-[(*R*)-1-(dimethylamino)-*o*-iodophenylmethyl]ferrocene 10a. In a 300 mL three-neck round-bottomed flask containing a magnetic stirring bar were charged **4** (5.9 g, 15.1 mmol) and dry diethyl ether (60 mL) under a slight pressure of nitrogen. The flask was cooled in an ice bath, and a hexane solution of *t*-BuLi (1.6 M, 22.5 mL, 36 mmol) was then added using a syringe through the septum with magnetic stirring. After 2 h, a THF (40 mL) solution of iodine (9.6 g, 38 mmol) was injected into the mixture at the same temperature. When the addition was completed, the ice bath was removed, and the mixture was allowed to warm to room temperature and then stirred for an additional 15 h. The reaction was quenched with aqueous $Na_2S_2O_3$, and the solution was then extracted with three 30 mL portions of diethyl ether. The combined extracts were washed (brine), dried (K_2CO_3), and filtered, and the solvent was removed on a rotary evaporator to leave a brown residue. The crude product was purified by column chromatography on silica gel (hexane/diethyl ether/triethyl amine = 20:1:1) to give the pure **10a** as a reddish brown solid. Yield, 7.70 g, 12.1 mmol, 80%. Mp = 85 °C. $[\alpha]_D^{25} = +24.4$ ($c = 0.50$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.26 (s, 9H), 2.51 (s, 6H), 4.19 (s, 5H), 4.30 (s, 1H), 4.55 (s, 1H), 5.00 (s, 1H), 6.58 (d, 1H, $J = 7.5$ Hz), 6.83 (t, 1H, $J = 7.3$ Hz), 7.09 (t, 1H, $J = 7.5$ Hz), 7.81 (d, 1H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 1.6, 45.2, 69.8, 72.1, 72.6, 75.4, 77.7, 97.8, 105.8, 127.8, 128.5, 131.3, 139.0, 144.2. Anal. calcd for $C_{22}H_{27}FeI_2NSi$: C, 41.08; H, 4.23; N, 2.18. Found: C, 39.86; H, 4.25; N, 2.03.

(*Rp*)-3-Bromo-(*Sp*)-1-trimethylsilyl-2-[(*R*)-1-(dimethylamino)-*o*-bromophenylmethyl]ferrocene **10b** was similarly prepared by the previous procedure using $BrCF_2CF_2Br$ instead of I_2: Yellow solid, Mp = 118 °C. $[\alpha]_D^{25} = +65.0$ ($c = 0.20$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.30 (s, 9H), 2.38 (s, 6H), 4.17 (s, 5H), 4.19 (s, 1H), 4.55 (s, 1H), 5.21 (s, 1H), 7.00 (d, 1H, $J = 7.7$ Hz), 7.03 (t, 1H, $J = 7.9$. Hz), 7.12 (t, 1H, $J = 7.5$ Hz), 7.55 (dd, 1H, $J = 7.9$ Hz); ^{13}C NMR ($CDCl_3$) δ 1.6, 44.5, 67.3, 69.9, 71.6, 72.7, 73.3, 80.0, 94.5, 126.6, 126.8, 128.3, 131.9, 132.2, 140.6. Anal. calcd for $C_{22}H_{27}Br_2FeNSi$: C, 48.11; H, 4.96; N, 2.55; Found: C, 48.08; H, 4.83; N, 2.18.

Preparation of (*Rp*)-1-Iodo-2-[(*R*)-1-(dimethylamino)-*o*-iodophenylmethyl]ferrocene 11a. In a 300 mL round-bottomed flask containing a magnetic stirring bar were charged **10a** (3.5 g, 5.44 mmol) and dry DMSO (70 mL) under a slight pressure of nitrogen. The flask was cooled in an ice bath, *t*-BuOK (0.66 g, 5.9 mmol) was added, and the mixture was then stirred at 0 °C for 1 h followed by stirring at room temperature for an additional 15 h. The reaction was quenched with water, and the solution was extracted with three 30 mL portions of dichloromethane. The combined extracts were washed (brine), dried ($MgSO_4$), and filtered, and the solvent was removed on a rotary evaporator to leave a brown residue. The crude product was purified by column chromatography on silica gel (hexane/diethyl ether/triethyl amine = 20:1:1) to give pure **11a** as a yellow solid. Yield, 2.60 g, 4.55 mmol, 84%. Mp = 89 °C. $[\alpha]_D^{25} = +77.0$ ($c = 0.50$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.48 (s, 6H), 4.12 (s, 5H), 4.26 (s, 1H), 4.40 (s, 1H), 4.55(s, 1H), 4.90 (s, 1H), 6.89 (t, 1H, $J = 7.2$ Hz), 7.00 (d, 1H, $J = 7.6$ Hz), 7.20 (t, 1H, $J = 7.5$ Hz), 7.85 (d, 1H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 44.2, 67.6, 68.4, 72.0, 72.1, 75.0, 92.1, 104.7, 127.8, 128.5, 130.6, 139.1, 143.7. Anal. calcd for $C_{19}H_{19}FeI_2N$: C, 39.96; H, 3.35; N, 2.45. Found: C, 40.21; H, 3.13; N, 2.42.

(*Rp*)-1-Bromo-2-[(*R*)-1-(dimethylamino)-*o*-bromophenylmethyl]-ferrocene **11b**: Mp = 87 °C. $[\alpha]_D^{25} = +126$ ($c = 0.20$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 6H), 4.13 (s, 5H), 4.18 (s, 1H), 4.37 (t, 1H, $J = 2.0$ Hz), 5.02 (s, 1H), 7.05−7.21 (m, 3H), 7.57 (d, 1H, $J = 7.6$ Hz); ^{13}C NMR ($CDCl_3$) δ 44.5, 65.3, 67.1, 67.5, 70.3, 71.7, 77.2, 90.1, 126.1, 127.1, 128.3, 130.9, 132.3, 141.0. Anal. calcd for $C_{19}H_{19}Br_2FeN$: C, 47.84; H, 4.01; N, 2.94. Found: C, 47.92; H, 3.95; N, 2.85.

Preparation of (*Rp*)-1-Diphenylphosphanyl-2-[(*R*)-1-(dimethylamino)-*o*-diphenylphosphanylphenylmethyl]ferrocene 12; *dia*-Taniaphos. In a 50 mL Schlenk tube containing a magnetic stirring bar were charged **11a** (1.10 g, 1.93 mmol) and dry diethyl ether (60 mL) under a slight pressure of nitrogen. The flask was cooled in an ice bath, and a hexane solution of *n*-BuLi (1.6 M, 2.9 mL, 4.6 mmol) was then added using a syringe through the septum with magnetic stirring. After 2 h, Ph_2PCl (0.9 mL, 4.8 mmol) was injected into the mixture at the same temperature. When the addition was completed, the ice bath was removed, and the mixture was allowed to warm to room temperature and stirred for an additional 5 h. The reaction was quenched with water, and the solution was then extracted with three 30 mL portions of dichloromethane. The combined extracts were washed (brine), dried ($MgSO_4$), and filtered, and the solvent was removed on a rotary evaporator to leave a brown residue. The crude product was purified by column chromatography on silica gel (hexane/diethyl ether/triethyl amine = 20:2:1) to give pure **12** as a yellow solid. Yield, 1.06 g, 1.54 mmol, 80%. Mp = 68 °C. $[\alpha]_D^{25} = +260$ ($c = 0.50$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.10 (s, 6H), 3.90 (s, 5H), 3.96 (s, 1H), 4.37 (s, 1H), 4.61 (s, 1H), 6.08 (d, 1H, $J = 7.5$ Hz), 6.8−7.6 (m, 24H, aromatic signals); ^{13}C NMR ($CDCl_3$) δ 43.4, 68.8, 70.3, 71.4, 71.7, 73.4, 98.8, 126.6−139.6 (several aromatic signals), 147.4; ^{31}P NMR ($CDCl_3$) δ −18.6 ($J = 16.2$ Hz), −25.1 ($J = 16.2$ Hz). Anal. calcd for $C_{43}H_{39}FeNP_2$: C, 75.11; H, 5.72; N, 2.04. Found: C, 74.94; H, 5.77; N, 2.08. Crystals suitable for the X-ray analysis were obtained by recrystallization from $CHCl_3$-hexane. CCDC 624117.

Preparation of (*Rp*)-1-Bromo-2-[(*S*)-1-methoxy-*o*-bromophenylmethyl]ferrocene 13. In a 100 mL three-neck round-bottomed flask containing a magnetic stirring bar were charged **11b** (0.87 g, 1.82 mmol) and dry MeOH (10 mL) under a slight pressure of nitrogen. To the flask were successively added MeONa (0.110 g, 2.0 mmol) and a methanol solution of MeI (10.0 g, 70 mmol), and then the resulting mixture was stirred at room temperature for 15 h. The reaction was quenched with diluted HCl, and the solution was extracted with three 30 mL portions of dichloromethane. The combined extracts were washed (brine), dried ($MgSO_4$), and filtered, and the solvent was removed on a rotary evaporator to leave a brown residue. The crude product was purified by column chromatography on silica gel (hexane/diethyl ether = 20:1) to give pure **13** as a yellow oil. Yield, 0.53 g, 1.14 mmol, 63%. $[\alpha]_D^{25} = +80.0$ ($c = 0.21$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.23 (s, 3H), 3.98 (s, 5H), 4.10 (dd, 1H, $J = 1.4$, 2.7 Hz), 4.15 (t, 1H, $J = 2.6$ Hz), 4.50 (d, 1H, $J = 1.5$, 2.2 Hz), 5.77 (s, 1H), 7.25 (dt, 1H, $J = 1.7$, 7.7 Hz), 7.42 (t, 1H, $J = 7.4$ Hz), 7.67 (t, 1H, $J = 7.0$ Hz), 7.68 (t, 1H, $J = 7.7$ Hz); ^{13}C NMR ($CDCl_3$) δ 56.8, 65.2, 66.9, 70.4, 71.2, 78.7, 79.8, 86.0, 124.0, 127.5, 129.1, 129.4, 132.7, 140.2. Anal. calcd for $C_{18}H_{16}FeBr_2O$: C, 46.60; H, 3.48. Found: C, 46.75; H, 3.83.

Preparation of (*Rp*)-1-(Diphenylphosphanyl-2-[(*S*)-1-methoxy-*o*-diphenylphosphanylphenylmethyl]ferrocene 14. In a 50 mL Schlenk tube containing a magnetic stirring bar were charged **13** (0.45 g, 0.97 mmol) and dry THF (10 mL) under a slight pressure of nitrogen. The flask was cooled in a dry ice bath, and a hexane solution of *t*-BuLi (1.6 M, 2.7 mL, 4.3 mmol) was then added using a syringe through the septum with magnetic stirring. After 20 min, Ph_2PCl (0.39 mL, 2.1 mmol) was injected into the mixture at −78 °C and stirred for 2 h. When the addition was completed, the dry ice bath was removed, and the mixture was allowed to warm to room temperature and then stirred for an additional 15 h. The reaction was quenched with saturated $NaHCO_3$, and the solution was then extracted with three 30 mL portions of dichloromethane. The combined extracts were washed (brine), dried ($MgSO_4$), and filtered, and the solvent was removed on a rotary evaporator to leave a yellow residue. The crude product was purified by column chromatography on silica gel (hexane/diethyl ether = 20:1) to give pure **14** as a yellow solid. Yield, 0.52 g, 0.77 mmol, 80%. Mp = 66 °C. $[\alpha]_D^{25} = +247$ ($c = 0.10$, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 300

MHz) δ 2.32 (s, 3H), 3.78 (s, 1H), 3.81 (s, 5H), 4.25 (t, 1H, J = 2.6 Hz), 4.32 (s, 1H), 6.12 (dd, 1H, J = 5.1 Hz), 7.1−7.7 (m, 24H); ^{13}C NMR ($CDCl_3$) δ 55.8, 69.3, 69.6, 70.0, 71.5, 76.7, 94.7, 95.1, 125−145 (several aromatic signals); ^{31}P NMR ($CDCl_3$) δ −16.3 (J = 16.7 Hz), −21.8 (J = 16.7 Hz). Anal. calcd for $C_{42}H_{36}FeOP_2$: C, 74.79; H, 5.38. Found: C, 75.11; H, 5.55.

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Supporting Information Available: Experimental details for the preparation of compounds **2**, **7**, and related compounds including their ^{1}H and ^{13}C NMR spectra (PDF); the ^{1}H and ^{13}C NMR spectra of the ferrocene compounds **4** and **10**−**14** (PDF); and crystallographic data in CIF files for **7** and **12**. Experimental procedures for the metal complex-catalyzed asymmetric reactions using **12** as a ligand. This material is available free of charge via the Internet at http://pubs.acs.org.

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