Synthesis and Application of Chiral Phospholane Ligands Bearing Sterically and Electrically Adjustable Moiety

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Supporting Information

General

All melting points were measured on a Yanaco MP-500D melting point apparatus. Optical rotations were measured on a JASCO DIP-4, and ^{1}H NMR and ^{31}P NMR spectra were obtained on a Bruker DRX500 (^{1}H: 500.13 MHz, ^{31}P: 202.46 MHz) spectrometer. Mass spectra were measured on a HITACHI M-80B mass spectrometer.

(*Z*)-*N*-Benzoyl-1-phenylpropenamine (3)

A solution of ethyl bromide (72.12 g, 662 mmol) in THF (450 mL) was added dropwise to a slurry of magnesium (15.32 g, 630 mmol) in THF (50 mL) at such a rate that the temperature remained between 30 and 35 °C while it was cooled in a cold-water bath. The resultant mixture was stirred at room temperature for 2 h and then cooled to 15–20 °C. To this mixture, benzonitrile (50.00 g, 485 mmol) was added dropwise, then the mixture was stirred at 45–50 °C for 15 h. The reaction mixture was cooled to 0 °C, and then a solution of 2-propanol (48.3 mL, 630 mmol) in THF (50 mL) was added. The mixture was stirred for 2 h at room temperature, and then the mixture was cooled to 0 °C. To the reaction mixture, triethylamine (87.9 mL, 630 mmol) was added, and then a solution of benzoyl chloride (88.6 g, 630 mmol) in THF (50 mL) was added dropwise at such a rate that the temperature remained between 0 and 10 °C while it was cooled in a cold-water bath. After the additions, the mixture was stirred for 3 h at room temperature, and then the mixture was poured into 1 N hydrochloric acid (500 mL). The two layers were separated and then the aqueous layer was extracted with ethyl acetate (500 mL). The combined organic layer was washed with water (300 mL) and brine (300 mL × 2), and then dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was recrystallized from ethyl acetate to give **3** as a white solid; yield: 64.1 g (56% yield); mp: 162–164 °C; ^{1}H NMR ($CDCl_3$): δ = 1.83 (3H, d, *J* = 7.0 Hz), 6.02 (1H, q, *J* = 7.0 Hz), 7.22–7.34 (4H, m), 7.40–7.44 (2H, m), 7.45–7.52 (2H, m), 7.52–7.58 (1H, m), 7.87–7.95 (2H, m); ^{13}C NMR ($CDCl_3$): δ = 14.17, 121.08, 125.55, 127.27, 127.81, 128.45, 128.73, 131.84, 134.08, 134.27, 138.09, 165.41; EI-MS: *m/z* 237 (M^+).

General procedure for hydrogenation

The solid UCAP–Rh complex catalyst was placed in a 100 mL stainless steel autoclave equipped with a Teflon-coated magnetic stirring bar, a pressure gauge and a gas inlet tube attached to a hydrogen source. Air present in the autoclave was replaced by nitrogen. Methanol and the substrate were added to the autoclave under a nitrogen stream. Air present in the gas inlet tube was removed by flushing with a stream of hydrogen. Hydrogen was initially introduced into the autoclave at a pressure of 0.2 MPa, before being reduced to 0.01 MPa by carefully releasing the stop valve. After this procedure was repeated three times, hydrogenation was carried out under the conditions listed in the Tables. The reaction mixture was measured by GLC or HPLC.

(*S*)-*N*-Benzoyl-1-phenylpropylamine (4); mp: 120–121 °C, $[\alpha]_D^{23}$ –29.1 (*c* 1.09, $CHCl_3$) (lit. mp: 119.0–119.5 °C, $[\alpha]_D^{25}$ –29.3 (*c* 1, $CHCl_3$), 100% ee (*S*), A. R. Katritzky, P. A. Harris, *Tetrahedron: Asymmetry* **1992**, *3*, 437–442) 99% ee by HPLC (Chiralcel OD-H, 15% 2-propanol in hexane, 0.5 mL/min, λ = 254 nm, , *S* isomer 15.2 min, *R* isomer 12.0 min).

(*S*)-*N*-Acetyl-1-phenylpropylamine; mp: 107–108 °C, $[\alpha]_D^{23}$ –129.3 (*c* 0.14, $CHCl_3$) (lit. mp: 105–107 °C, $[\alpha]_D^{25}$ +135 (*c* 0.12, $CHCl_3$), 95.4% ee (*R*), M. J. Burk, Y. M. Wang, J. R. Lee, *J. Am. Chem. Soc.* **1996**, *118*, 5142–5143) 94% ee by GLC (Cp Chirasil DEX CB, 130 °C, He 138 KPa, *S* isomer 18.6 min, *R* isomer 20.4 min).

Diethyl 2-(diphenylphosphino)phenylphosphonite

Under a nitrogen atmosphere, a 1.6 M solution of *n*-butyllithium in hexane (18.3 mL, 29.3 mmol) was added dropwise to a solution of (2-bromophenyl)diphenylphosphine (S. E. Tunney, J. K. Stille, *J. Org. Chem.* **1987**, *52*, 748–753) (10.00 g, 29.3 mmol) in THF (100 mL) at –78 °C for 30 min. The solution was stirred at –78 °C for 1 h, and then chlorodiethylphosphite (4.83 g, 29.3 mmol) was added dropwise over 30 min. The reaction mixture was allowed to warm to room temperature and then stirred for 1 h. After evaporation of THF, the residue was dissolved in diethyl ether (50 mL) and the insoluble material was filtered off. The filtrate was evaporated and the residue was purified by flash chromatography (hexane/ethyl acetate = 2/1) to give the title compound as a pale yellow oil; yield: 10.30 g (92% yield); ^{1}H NMR ($CDCl_3$): δ = 1.07 (6H, t, *J* = 7.1 Hz), 3.63–3.70 (2H, m), 3.79–3.86 (2H, m), 7.07–7.12 (1H, m), 7.25–7.40 (12H, m), 7.91–7.95 (1H, m); ^{31}P NMR ($CDCl_3$): δ = –17.1 (d, *J* = 156 Hz), 151.7 (d, *J* = 156 Hz); EI-MS: *m/z* 382 (M^+).

2-(Diphenylphosphino)phenylphosphine

Under a nitrogen atmosphere, trimethylsilyl chloride (8.52 g, 78.5 mmol) was added to a stirred solution of lithium aluminium hydride (2.98 g, 78.5 mmol) in THF (150 mL) at –30 °C. The resulting mixture was allowed to warm to room temperature and then stirred for 1.5 h. A solution of diethyl 2-(diphenylphosphino)phenylphosphonite (10.00 g, 26.2 mmol) in THF (30 mL) was added dropwise to the reducing mixture at –30 °C for 30 min. The resulting mixture was allowed to warm to room temperature and then stirred for 16 h. Water (15 mL) followed by 1 N aqueous sodium hydroxide (20 mL) was slowly added dropwise, and the two layers were separated. After the organic layer was concentrated, diethyl ether (100 mL) and water (20 mL) were added to the residue and then the two layers were separated. The organic layer was washed with water (20 mL × 2) and dried over sodium sulfate. After evaporation of diethyl ether, the residue was purified by chromatography through a short alumina column (diethyl ether) to give the title compound as a white powder; yield: 7.21 g (94% yield); mp: 82–83 °C; ^{1}H NMR ($CDCl_3$): δ = 3.89 (2H, dd, *J* = 11.8, 205.7 Hz), 6.75–6.85 (1H, m), 7.05–7.35 (12H, m), 7.45–7.55 (1H, m); ^{31}P NMR ($CDCl_3$): δ = –123.1 (d, *J* = 98 Hz), –10.1 (d, *J* = 98 Hz); EI-MS: *m/z* 294 (M^+).

1-((2*S*,5*S*)-2,5-Dimethylphospholano)-2-(diphenylphosphino)benzene (5a)

Under a nitrogen atmosphere, 1.6 M solution of *n*-butyllithium in hexane (6.7 mL, 10.71 mmol) was added dropwise to a solution of 2-(diphenylphosphino)phenylphosphine (3.00 g, 10.20 mmol) in THF (100 mL) at 0 °C. The solution was stirred at 0 °C for 1 h and then a solution of (2*R*,5*R*)-2,5-hexanediol cyclic sulfate (M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125–10138) (1.93 g, 10.71 mmol) in THF (30 mL) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and then stirred for 1 h. A 1.6 M solution of *n*-butyllithium in hexane (6.7 mL, 10.71 mmol) was again added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred at room temperature for 15 h. Methanol (3 mL) was added to quench any excess *n*-butyllithium remaining and the solvents were evaporated under reduced pressure. The residue was dissolved in diethyl ether (60 mL) and the insoluble material was filtered off. The filtrate was evaporated and the residue was purified by chromatography through a short alumina column (hexane/diethyl ether = 2/1) to give **5a** as a colorless oil; yield: 3.06 g (80% yield); $[\alpha]_D^{29}$ +192.3 (*c* 1.00, CH_2Cl_2); ^{1}H NMR ($CDCl_3$): δ = 0.84 (3H, dd, *J* = 7.1, 9.5 Hz), 1.11 (3H, dd, *J* = 7.1, 18.6 Hz), 1.31–1.39 (1H, m), 1.54–1.63 (1H, m), 2.01–2.08 (1H, m), 2.17–2.25 (1H, m), 2.32–2.41 (1H, m), 2.56–2.62 (1H, m), 6.91–6.95 (1H, m), 7.20–7.38 (12H, m), 7.52–7.55 (1H, m); ^{31}P NMR ($CDCl_3$): δ = –0.1 (d, *J* = 164 Hz), –11.5 (d, *J* = 164 Hz); EI-MS: *m/z* 376 (M^+).

1-((2*S*,5*S*)-2,5-Diethylphospholano)-2-(diphenylphosphino)benzene (5b)

The preparation of **5b** is analogous to the preparation of **5a** starting from (2-diphenylphosphino)phenylphosphine (0.50 g, 1.70 mmol) and (3*R*,6*R*)-3,6-octanediol cyclic sulfate (M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125–10138) (0.35 g, 1.70 mmol). Purification of the phosphine-phospholane was finally carried out by flash chromatography on silica (hexane/diethyl ether = 4/1) to give **5b** as a white solid; yield: 0.46 g (67% yield); mp: 65–66 °C; $[\alpha]_D^{29}$ +139.8 (*c* 1.04, CH_2Cl_2); ^{1}H NMR (CD_2Cl_2): δ = 0.60 (3H, t, *J* = 7.3 Hz), 0.78 (3H, t, *J* = 7.3 Hz), 0.87–0.98 (1H, m), 1.16–1.51 (5H, m), 1.91–2.06 (2H, m), 2.13–2.20 (1H, m), 2.27–2.35 (1H, m), 6.75–6.79 (1H, m), 7.11–7.19 (12H, m), 7.45–7.49 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = –7.2 (d, *J* = 167 Hz), –10.3 (d, *J* = 167 Hz); EI-MS: *m/z* 404 (M^+).

2-(Trifluoromethanesulfonyl)oxy-bromobenzene (6)

Trifluoromethanesulfonic anhydride (448.5 g, 1.59 mol) was added dropwise to a solution of 2-bromophenol (250.0 g, 1.45 mol) and pyridine (171.4 g, 2.168 mol) in dichloromethane (1.5 L) at 0 °C for 2 h. The mixture was allowed to warm to room temperature and then stirred for 2 h. The resulting mixture was poured into 2 N hydrochloric acid (500 mL) and stirred at room temperature for 30 min, and then the two layers were separated. The organic layer was washed with water (500 mL × 2) and brine (500 mL), and then dried over magnesium sulfate. After evaporation of dichloromethane, the residue was distilled under reduced pressure to give **6** as a colorless oil; yield: 425.3 g (97% yield); bp: 112–113 °C (15–16 mmHg); ^{1}H NMR ($CDCl_3$): δ = 7.20–7.40 (3H, m), 7.60–7.80 (1H, m)

Bis(3,5-di-*tert*-butyl-4-methoxyphenyl)(2-bromophenyl)phosphine oxide

Under a nitrogen atmosphere, a solution of **6** (15.00 g, 49.2 mmol), bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphine oxide (the phosphine oxide was similarly prepared according to the literature; see: H. R. Hays, *J. Org. Chem.* **1968**, *33*, 3690–3694) (28.71 g, 59.0 mmol), *N*,*N*-diisopropylethylamine (12.85 mL, 73.8 mmol), $Pd_2(dba)_3$•$CHCl_3$ (1.27 g, 2.5 mmol), and 1,3-bis(diphenylphosphino)propane (1.01 g, 2.5 mmol) in toluene (150 mL) was stirred at 110 °C for 15 h. The reaction mixture was cooled to room temperature and then poured into 1 N hydrochloric acid (150 mL). The mixture was stirred at room temperature for 30 min, and the two layers were separated. The aqueous layer was extracted with ethyl acetate (100 mL). The combined organic layer was washed with water (100 mL) and brine (100 mL), and then dried over magnesium sulfate. Finally, the solvent was removed under reduced pressure, and the residue was purified by flash

chromatography on silica gel (hexane/ethyl acetate = 2/1) to give the title compound as a white, waxy solid; yield: 30.83 g (98% yield); ^{1}H NMR ($CDCl_3$): δ = 1.35 (36H, s), 3.69 (6H, s), 7.35–7.45 (2H, m), 7.51 (4H, d, *J* = 13.2 Hz), 7.65 (1H, ddd, *J* = 1.2, 3.9, 7.7 Hz) 7.73 (1H, ddd, *J* = 1.9, 7.7, 12.5 Hz); ^{31}P NMR ($CDCl_3$): δ = 33.3 (s); EI-MS: *m/z* 642 (M^+).

Bis(3,5-di-*tert*-butyl-4-methoxyphenyl)(2-bromophenyl)phosphine (7)

The mixture of bis(3,5-di-*tert*-butyl-4-methoxyphenyl)(2-bromophenyl)phosphine oxide (28.81 g, 44.9 mmol), *N*,*N*-dimethylaniline (31.30 mL, 247.0 mmol), and trichlorosilane (22.66 mL, 224.5 mmol) was stirred in toluene (300 mL) at 110 °C for 15 h. The reaction mixture was cooled to 5 °C, and then 25 % aqueous sodium hydroxide (180 mL) was added carefully. The mixture was stirred at room temperature for 30 min. The aqueous layer was separated and extracted with toluene (100 mL). The combined organic layer was washed with 1 N hydrochloric acid (200 mL × 2), water (100 mL), and brine (100 mL). The solvent was removed under reduced pressure, and the residue was recrystallized from toluene–methanol to give **7** as a white solid; yield: 24.3 g (87 % yield); mp: 142–143 °C; ^{1}H NMR ($CDCl_3$): δ = 1.31 (36H, s), 3.68 (6H, s), 6.71–6.74 (1H, m), 7.07 (4H, d, *J* = 7.6 Hz), 7.15–7.23 (2H, m), 7.57–7.60 (1H, m); ^{31}P NMR ($CDCl_3$): δ = –3.1 (s); EI-MS: *m/z* 626 (M^+).

1-Bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino-2-((2*S*,5*S*)-2,5-dimethylphospholano)benzene (5d)

Under a nitrogen atmosphere, a 1.6 M solution of *n*-butyllithium in hexane (16.2 mL, 25.2 mmol) was added dropwise to a solution of **7** (15.00 g, 24.0 mmol) in THF (150 mL) at –78 °C for 30 min. The solution was stirred at –78 °C for 1 h and then diethyl chlorophosphonite (4.15 g, 25.2 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and then stirred for 15 h. After evaporation of the solvent, the residue was dissolved in diethyl ether (50 mL) and the insoluble material was filtered off. The filtrate was evaporated and the residue was purified by chromatography through a short alumina column (hexane/ethyl acetate = 4/1) to give a 77:23 mixture of **8** and bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phenylphosphine as a pale yellow, waxy solid. The ratio of a mixture was determined by ^{1}H NMR. The crude product **8** was used for the next reaction without further purification; yield: 14.03 g; ^{1}H NMR (CD_2Cl_2): δ (**8**) = 1.00 (6H, t, *J* = 7.0 Hz), 1.29 (36H, s), 3.51–3.57 (2H, m), 3.65 (6H, s), 3.78–3.82 (2H, m), 7.03 (4H, d, *J* = 7.7 Hz), 7.30–7.34 (2H, m) 7.39–7.40 (1H, m), 7.86–7.89 (1H, m), δ (bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phenylphosphine) = 1.32 (36H, s), 3.67 (6H, s), 7.13 (4H, d, *J* = 8.2 Hz), 7.24–7.29

(2H, m), 7.30–7.35 (3H, m); ^{31}P NMR (CD_2Cl_2): δ (**8**) = –17.5 (d, *J* = 149 Hz), 150.1 (d, *J* = 149 Hz), δ (bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phenylphosphine) = –4.3 (s).

Under a nitrogen atmosphere, trimethylsilyl chloride (4.89 g, 45.0 mmol) was added to a suspension of lithium aluminium hydride (1.71 g, 45.0 mmol) in THF (75 mL) at –30 °C. The resulting mixture was allowed to warm to room temperature and then stirred for 1.5 h. A solution of the crude **8** (10.00 g) in THF (50 mL) was then added dropwise to the reducing mixture at –30 °C for 30 min. The resulting mixture was allowed to warm to room temperature and then stirred for 16 h. A solution of water (20 mL) in THF (20 mL) followed by 1 N aqueous sodium hydroxide (30 mL) was added slowly dropwise, and the two layers were separated. After the organic layer was concentrated, diethyl ether (50 mL) and water (20 mL) were added to the residue and then the two layers was separated. The organic layer was washed with water (20 mL × 2) and dried over sodium sulfate. The solvent was removed under reduced pressure to give a 70:30 mixture of **9** and bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phenylphosphine as a white, waxy solid. The ratio of a mixture was determined by ^{1}H NMR. The crude product **9** was used for the next reaction without further purification; yield: 8.2 g; ^{1}H NMR (CD_2Cl_2): δ (**9**) = 1.31 (36H, s), 3.67 (6H, s), 3.95 (2H, dd, *J* = 12.3, 205.3 Hz), 6.86–6.89 (1H, m), 7.07 (4H, d, *J* = 8.2 Hz), 7.21–7.22 (2H, m) 7.53–7.57 (1H, m); ^{31}P NMR (CD_2Cl_2): δ (**9**) = –124.3 (d, *J* = 92 Hz), –9.6 (d, *J* = 92 Hz).

Under a nitrogen atmosphere, a 1.6 M solution of *n*-butyllithium in hexane (5.67 mL, 9.1 mmol) was added dropwise to a solution of the crude **9** (5.00 g) in THF (100 mL) at 0 °C. The solution was stirred at 0 °C for 1 h and then a solution of (2*R*,5*R*)-2,5-hexanediol cyclic sulfate (M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125–10138) (1.64 g, 9.1 mmol) in THF (30 mL) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and then stirred for 1 h. A 1.6 M solution of *n*-butyllithium in hexane (5.67 mL, 9.1 mmol) was again added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred at room temperature for 15 h. Methanol (1 mL) was added to quench any excess *n*-butyllithium remaining and the solvents were evaporated under reduced pressure. The residue was dissolved in diethyl ether (60 mL) and the insoluble material was filtered off. The filtrate was evaporated and the residue was purified by flash chromatography on silica gel (hexane/dichloromethane = 3/1–1/1) to give **5d** as a white solid; yield: 2.41 g (total 36 % yield from **7**); mp: 65–66 °C; $[\alpha]_D^{29}$ +118.8 (*c* 1.00, CH_2Cl_2); ^{1}H NMR (CD_2Cl_2): δ = 0.73 (3H, dd, *J* = 7.2, 9.3 Hz), 1.05 (3H, *J* = 7.1, 13.7 Hz), 1.29 (18H, s), 1.30 (18H, s), 1.49–1.61 (2H, m), 2.00–2.06 (1H, m), 2.15–2.35 (2H, m), 2.48–2.58 (1H, m), 3.65 (3H, s), 3.65 (3H, s), 6.92–6.95 (1H, m), 7.05 (2H, d, *J* = 7.1 Hz), 7.09 (2H, d, *J* = 7.1 Hz), 7.21–7.24 (1H, m), 7.28–7.31 (1H, m), 7.50–7.52 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = 0.8 (d, *J* = 156 Hz), –10.4 (d, *J* = 156 Hz); EI-MS: *m/z* 660 (M^+).

1-Bis(3,5-dimethylphenyl)phosphino-2-((2*S*,5*S*)-2,5-dimethylphospholano)benzene (**5c**), 1-((2*S*,5*S*)-2,5-dimethylphospholano)-2-[di(1-naphthyl)phosphino]benzene (**5e**), and 1-bis(4-methoxyphenyl)phosphino-2-((2*S*,5*S*)-2,5-dimethylphospholano)benzene (**5f**) were prepared from **6** according to the procedure described for the preparation of **5d**.

1-Bis(3,5-dimethylphenyl)phosphino-2-((2*S*,5*S*)-2,5-dimethylphospholano)benzene (5c)

Purification of the phosphine-phospholane was carried out using a short alumina column (hexane/diethyl ether = 4/1) to give **5c** as a colorless oil; total yield: 67% from **6**; $[\alpha]_D^{29}$ +110.6 (*c* 1.20, CH_2Cl_2); ^{1}H NMR (CD_2Cl_2): δ = 0.77 (3H, dd, *J* = 7.1, 9.3 Hz), 1.04 (3H, dd, *J* = 7.1, 18.7 Hz), 1.18–1.30 (1H, m), 1.43–1.53 (1H, m), 1.92–1.98 (1H, m), 2.15 (6H, s), 2.16 (6H, s), 2.08–2.29 (2H, m), 2.48–2.54 (1H, m), 6.74 (1H, d, *J* = 7.7 Hz), 6.77–6.91 (5H, m), 7.12 (1H, t, *J* = 7.5 Hz), 7.20–7.50 (2H, m), 7.42–7.44 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = 0.8 (d, *J* = 156 Hz), –10.4 (d, *J* = 156 Hz); EI-MS: *m/z* 432 (M^+).

1-((2*S*,5*S*)-2,5-Dimethylphospholano)-2-[di(1-naphthyl)phosphino]benzene (5e)

Purification of the phosphine-phospholane was carried out by flash chromatography on silica (hexane:dichloromethane = 4/1–1/1) to give **5e** as a white solid; total yield: 9% from **6**; mp: 245–246 °C; $[\alpha]_D^{25}$ +226.0 (*c* 1.10, CH_2Cl_2); ^{1}H NMR (CD_2Cl_2): δ = 0.95–1.06 (6H, m), 1.25–1.35 (1H, m), 1.60–1.69 (1H, m), 2.00–2.08 (1H, m), 2.17–2.26 (1H, m), 2.27–2.40 (1H, m), 2.57–2.66 (1H, m), 6.75–6.78 (1H, m), 6.92–6.96 (2H, m), 7.08–7.11 (1H, m), 7.25 (1H, t, *J* = 7.6 Hz), 7.30–7.35 (2H, m), 7.38–7.52 (4H, m), 7.61–7.64 (1H, m), 7.84 (2H, t, *J* = 7.2 Hz), 7.89 (2H, dd, *J* = 4.4, 7.7 Hz), 8.39 (1H, dd, *J* = 4.7, 8.5 Hz), 8.50–8.52 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = 0.4 (d, *J* = 164 Hz), –28.0 (d, *J* = 164 Hz); EI-MS: *m/z* 475 (M^+).

1-Di(4-methoxylphenyl)phosphino-2-((2*S*,5*S*)-2,5-dimethylphospholano)benzene (5f)

Purification of the phosphine-phospholane was carried out using a short alumina column (hexane/diethyl ether = 2/1) to give **5f** as a white solid; total yield: 38% from **6**; mp: 124–125 °C; $[\alpha]_D^{29}$ +171.5 (*c* 1.04, CH_2Cl_2); ^{1}H NMR (CD_2Cl_2): δ = 0.83 (3H, dd, *J* = 7.7, 7.7 Hz), 1.11 (3H, dd, *J* = 7.7, 18.7 Hz), 1.23–1.40 (1H, m), 1.50–1.61 (1H, m), 1.98–2.08 (1H, m), 2.14–2.26 (1H, m), 2.26–2.38 (1H, m), 2.52–2.63 (1H, m), 3.79 (6H, s), 6.89–6.98 (5H, m), 7.08–7.27 (5H, m), 7.27–7.36 (1H, m), 7.46–7.54 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = 0.7 (d, *J* = 156 Hz), –13.9 (d, *J* = 156 Hz); EI-MS: *m/z* 435 ($M–1^+$).

BH_3 Adduct of 1-((2*S*,5*S*)-2,5-Dimethylphospholano)-2-[di(4-trifluoromethylphenyl)-phosphino]benzene

A solution of 2-[di(4-trifluoromethylphenyl)phosphino]phenylphosphine (4.02 g, 9.33 mmol), which was prepared in the same manner as **9**, in THF (50 mL) was added to a stirred solution of sodium hydride (1.34 g, 56.0 mmol) in THF (80 mL) at 0 °C. HMPA (12.7 mL, 72.8 mmol) was added to the mixture. The resulting dark red suspension was stirred at 0 °C for 1 h and then a solution of (2*R*,5*R*)-2,5-hexanediol dimesylate (2.69 g, 9.80 mmol) in THF (90 mL) was added over 30 min. The resulting orange suspension was stirred at room temperature for 60 h. After cooling to 0 °C, it was hydrolyzed with brine (10 mL), and the two layers were separated. The aqueous layer was extracted with diethyl ether (40 mL). The combined organic layer was dried over sodium sulfate, and the solvents were removed under reduced pressure. The residue was dissolved in diethyl ether (30 mL) and the insoluble material was filtered off, and then the filtrate was evaporated. BH_3•SMe_2 (2.66 mL, 28.0 mmol) was added dropwise to a solution of the residue in dichloromethane (30 mL) at 0 °C. The resulting mixture was allowed to warm to room temperature and then stirred for 1 h. The reaction mixture was cooled to 0 °C, and then a mixture of diethyl ether (60 mL) and methanol (20 mL) was added carefully. The solvents were removed under reduced pressure, and then the residue was purified by flash chromatography on silica gel (hexane/diethyl ether = 9/1) to give the title compound as a white solid; yield: 2.11 g (43% yield); mp: 96–97 °C; ^{1}H NMR (CD_2Cl_2): δ = 0.70–1.40 (3H, m), 1.03 (3H, ddd, *J* = 1.2, 6.9, 18.4 Hz), 1.32 (3H, dd, *J* = 7.1, 17.5 Hz), 1.60–1.70 (1H, m), 1.76–1.86 (1H, m), 1.90–1.99 (1H, m), 2.01–2.16 (1H, m), 2.65–2.75 (1H, m), 3.84–3.96 (1H, m), 6.70–6.74 (1H, m), 7.01–7.07 (1H, m), 7.12–7.16 (1H, m), 7.18–7.23 (1H, m), 7.74–7.84 (6H, m), 7.96 (2H, m); ^{31}P NMR (CD_2Cl_2): δ = –5.7 (s), 38.4 (m); EI-MS: *m/z* 526 (M^+).

1-((2*S*,5*S*)-2,5-Dimethylphospholano)-2-[di(4-trifluoromethylphenyl)phosphino]benzene (5g)

The BH_3 adduct of 1-((2*S*,5*S*)-2,5-dimethylphospholano)-2-[di(4-trifluoromethylphenyl)-phosphino]benzene (2.11 g, 4.01 mmol) was treated with DABCO (0.54 g, 4.81 mmol) in toluene (20 mL) at 75 °C for 1.5 h. The reaction mixture was cooled to room temperature, and then the solvent was removed under reduced pressure. The residue was purified using a short alumina column (hexane/diethyl ether = 2/1) to give **5g** as a white solid; yield: 2.03 g (99% yield); mp: 79–80 °C; ^{1}H NMR (CD_2Cl_2): δ = 0.90–0.95 (3H, m), 1.18 (3H, dd, *J* = 7.0, 17.3 Hz), 1.26 (1H, br s), 1.65 (1H, br s), 1.89 (1H, br s), 2.13 (1H, br s), 2.46–2.56 (1H, m), 2.75–2.86 (1H, m), 6.76–6.81 (1H, m), 7.14–7.21 (2H, m), 7.28–7.32 (1H, m), 7.53–7.58 (2H, m), 7.60–7.64 (2H, m), 7.70–7.76

(2H, m), 7.76–7.84 (2H, m); ^{31}P NMR (CD_2Cl_2): δ = –10.5 (d, *J* = 166 Hz), 1.5 (d, *J* = 166 Hz); EI-MS m/z 513 ($M–1^+$).

Diethyl 2-[boranato(diisopropyl)phosphino]phenylphosphonate

Under a nitrogen atmosphere, a 1.6 M solution of *n*-butyllithium in hexane (33.7 mL, 53.9 mmol) was added to a solution of diisopropylamine (7.6 mL, 53.9 mmol) in THF (40 mL) at 0 °C. The resultant mixture was stirred at the same temperature for 1 h. It was then added dropwise to a solution of diethyl phenylphosphonate (11.00 g, 51.4 mmol) in THF (100 mL) at –78 °C for 30 min. The solution was stirred at –78 °C for 2 h and then chlorodiisopropylphosphine (7.84 g, 51.4 mmol) was added dropwise over 30 min. The reaction mixture was allowed to warm to room temperature and then stirred for 16 h. BH_3•SMe_2 (8.19 g, 107.8 mmol) was added dropwise to the reaction mixture at 0 °C over 30 min, and then the mixture was stirred at room temperature for 1 h. The resulting mixture was poured into a mixture of ethyl acetate (50 mL) and methanol (10 mL). The insoluble material was filtered off, and the filtrate was evaporated. The residue was purified by flash chromatography (hexane/ethyl acetate = 2/1–1/1) to give the title compound as a white solid; yield: 8.40 g (48% yield); mp: 86–87 °C; ^{1}H NMR ($CDCl_3$): δ = 0.30–1.00 (3H, m), 0.84 (6H, dd, *J* = 7.1, 15.9 Hz), 1.34 (6H, dd, *J* = 6.6, 15.9 Hz), 1.35 (6H, t, *J* = 6.6 Hz), 3.43–3.55 (2H, m), 4.07–4.19 (4H, m), 7.53–7.62 (2H, m), 7.91–7.97 (1H, m), 8.38–8.44 (1H, m); ^{31}P NMR ($CDCl_3$): δ = 18.2 (s), 50.6 (br d, *J* = 77 Hz); EI-MS m/z 343 ($M–1^+$).

2-[Boranato(diisopropyl)phosphino]phenylphosphine

Under a nitrogen atmosphere, trimethylsilyl chloride (7.58 g, 69.7 mmol) was added to a stirred solution of lithium aluminium hydride (2.45 g, 69.7 mmol) in THF (75 mL) at –30 °C. The resulting mixture was allowed to warm to room temperature and then stirred for 1.5 h. A solution of diethyl 2-[boranato(diisopropyl)phosphino]phenylphosphonate (8.00 g, 23.2 mmol) in THF (50 mL) was then added dropwise to the reducing mixture at –30 °C for 30 min. The resulting mixture was allowed to warm to room temperature and then stirred for 16 h. Water (10 mL) followed by 1 N aqueous sodium hydroxide (20 mL) was added slowly dropwise, and the two layers were separated. After the organic layer was concentrated, diethyl ether (100 mL) and water (20 mL) was added to the residue, and then the two layers were separated. The organic layer was washed with water (20 mL × 2) and dried over sodium sulfate. After the evaporation of diethyl ether, the residue was purified by chromatography through a short alumina column (hexane/diethyl ether = 3/1) to give the title compound as a white solid; yield: 5.38 g (96% yield); mp: 37–38 °C; ^{1}H NMR (CD_2Cl_2): δ = 0.20–1.00 (3H, m), 0.91 (6H, dd, *J* = 7.1, 15.4 Hz), 1.30 (6H, dd, *J* = 7.1, 15.4 Hz),

2.80–3.00 (1H, m), 4.20 (2H, d, J = 208.0 Hz), 7.33–7.39 (2H, m), 7.63–7.67 (1H, m), 8.00–8.05 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = –113.5 (s), 45.9 (m); EI-MS m/z 239 ($M–1^+$).

1-Boranato(diisopropyl)phosphino-2-((2*S*,5*S*)-2,5-dimethylphospholano)benzene

Under a nitrogen atmosphere, 1.6 M solution of *n*-butyllithium in hexane (5.5 mL, 8.8 mmol) was added dropwise to a solution of 2-[boranato(diisopropylphosphino)]phenylphosphine (2.00 g, 8.3 mmol) in THF (60 mL) at 0 °C. The solution was stirred at 0 °C for 1 h and then a solution of (2*R*,5*R*)-2,5-hexanediol cyclic sulfate (1.50 g, 8.3 mmol) in THF (20 mL) was added dropwise at 0 °C. The reaction mixture was allowed to warm to room temperature and then stirred for 1 h. A 1.6 M solution of *n*-butyllithium in hexane (5.5 mL, 8.8 mmol) was again added dropwise to the reaction mixture at 0 °C. The reaction mixture was stirred at room temperature for 15 h. Methanol (1.5 mL) was added to quench any excess *n*-butyllithium remaining and the solvents were evaporated under reduced pressure. The residue was dissolved in diethyl ether (30 mL) and the insoluble material was filtered off. The filtrate was evaporated and the residue was purified through a short alumina column (hexane/diethyl ether = 1/1) to give the title compound as a white solid; yield: 2.44 g (91 % yield); mp: 136–137 °C; $[\alpha]_D^{29}$ +36.5 (*c* 1.02, CH_2Cl_2); ^{1}H NMR (CD_2Cl_2): δ = 0.10–0.90 (3H, m), 0.71–0.82 (9H, m), 1.17–1.28 (9H, m), 1.28–1.37 (1H, m), 1.65–1.74 (1H, m), 2.03–2.10 (1H, m), 2.13–2.23 (1H, m), 2.34–2.45 (1H, m), 2.45–2.53 (1H, m), 3.19–3.28 (1H, m), 3.33–3.42 (1H, m), 7.30–7.34 (1H, m), 7.36–7.41 (1H, m), 7.59–7.63 (1H, m), 8.02–8.08 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = –2.9 (s), 45.5 (m); EI-MS m/z 321 ($M–1^+$).

1-Diisopropylphosphino-2-((2*S*,5*S*)-2,5-dimethylphospholano)benzene (5h)

1-Boranato(diisopropyl)phosphino-2-((2*S*,5*S*)-2,5-dimethylphospholano)benzene (0.20 g, 0.62 mmol) was treated with DABCO (0.084 g, 0.75 mmol) in toluene (3 mL) at 75 °C for 16 h. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified with a short alumina column (hexane/diethyl ether = 1/1) to give **5h** as a colorless oil; yield: 0.19 g (100 % yield); $[\alpha]_D^{29}$ +273.2 (*c* 1.15, CH_2Cl_2); ^{1}H NMR (CD_2Cl_2): δ = 0.79 (3H, dd, J = 7.1, 8.7 Hz), 0.91 (3H, dd, J = 7.0, 13.7 Hz), 0.95 (3H, dd, J = 7.2, 10.0 Hz), 1.10 (3H, dd, J = 7.2, 12.6 Hz), 1.33–1.41 (1H, m), 1.43–1.52 (1H, m), 1.98–2.05 (2H, m), 2.16–2.28 (2H, m), 2.32–2.44 (1H, m), 2.56–2.65 (1H, m), 7.26–7.30 (2H, m), 7.41–7.47 (2H, m); ^{31}P NMR (CD_2Cl_2): δ = –1.4 (d, J = 141 Hz), 2.2 (d, J = 141 Hz); EI-MS m/z 308 (M^+).

1-Dicyclohexylphosphino-2-((2*S*,5*S*)-2,5-dimethylphospholano)benzene (5i)

5i was prepared from diethyl phenylphosphonate according to the procedure described for the preparation of **5h**. Purification of the phosphine-phospholane was carried out using a short alumina column (hexane/diethyl ether = 3/1) to give **5i** as a white oil; total yield: 33% from **6**; $[\alpha]_D^{29}$ +201.5 (*c* 0.91, CH_2Cl_2); ^{1}H NMR (CD_2Cl_2): δ = 0.69 (3H, dd, *J* = 7.1, 8.6 Hz), 1.17 (3H, dd, *J* = 7.2, 18.2 Hz), 0.90–2.05 (24H, m), 2.06–2.17 (1H, m), 2.24–2.37 (1H, m), 2.46–2.56 (1H, m), 2.73–2.86 (1H, m), 7.16–7.22 (2H, m), 7.32–7.39 (2H, m); ^{31}P NMR (CD_2Cl_2): δ = –10.3 (d, *J* = 143 Hz), 2.4 (d, *J* = 143 Hz); EI-MS m/z 388 (M^+).

[Rh(cod)(5d)]OTf

Under a nitrogen atmosphere, a solution of **5d** (100.0 mg, 0.151 mmol) in dichloromethane (3 mL) was added dropwise to a stirred solution of $[Rh(cod)_2]OTf$ (67.5 mg, 0.144 mmol) in dichloromethane (2 mL) at room temperature. The mixture was stirred for 30 min, and the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane–diethyl ether to give the title complex as a orange-yellow solid; yield: 140.0 mg (95% yield); ^{1}H NMR (CD_2Cl_2): δ = 1.12 (3H, dd, *J* = 7.1, 15.3 Hz), 1.29–1.35 (3H, m), 1.33 (18H, s), 1.35 (18H, s), 1.52–1.64 (1H, m), 1.90–2.02 (1H, m), 2.08–2.18 (1H, m), 2.23–2.76 (11H, s), 3.71 (3H, s), 3.73 (3H, s), 4.68–4.75 (1H, m), 5.04–5.11 (1H, m), 5.42–5.54 (2H, m), 7.30 (2H, d, *J* = 12.1 Hz), 7.37 (2H, d, *J* = 12.1 Hz), 7.50–7.54 (1H, m), 7.56–7.61 (1H, m), 7.65–7.71 (1H, m), 7.73–7.77 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = 61.4 (dd, *J* = 27, 148 Hz), 74.8 (dd, *J* = 27, 148 Hz).

[Rh(cod)(5a)]OTf

This complex was prepared in a manner analogous to that described above with the exception that **5a** was used; yield: 91%; ^{1}H NMR (CD_2Cl_2): δ = 1.02 (3H, dd, *J* = 7.2, 15.3 Hz), 1.29 (3H, dd, *J* = 7.1, 18.4 Hz), 1.48–1.58 (1H, m), 1.82–1.93 (1H, m), 2.09–2.25 (2H, m), 2.26–2.49 (7H, m), 2.50–2.60 (2H, m), 2.61–2.72 (1H, m), 4.70–4.77 (1H, m), 4.92–5.00 (1H, m), 5.39–5.53 (2H, m), 7.38–7.57 (12H, m), 7.58–7.65 (1H, m), 7.65–7.70 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = 60.5 (dd, *J* = 27, 151 Hz), 75.3 (dd, *J* = 27, 147 Hz).

[Rh(cod)(5b)]OTf

This complex was prepared in a manner analogous to that described above with the exception that **5b** was used; yield: 91%; ^{1}H NMR (CD_2Cl_2): δ = 0.79 (3H, t, *J* = 7.3 Hz), 0.84 (3H, t, *J* = 7.3 Hz), 1.23–1.38 (1H, m), 1.40–1.54 (2H, m), 1.61–1.87 (3H, m), 2.13–2.25 (2H, m), 2.30–2.62 (10H, m), 4.75–4.82 (1H, m), 4.82–4.91 (1H, m), 5.29–5.36 (1H, m), 5.55–5.63 (1H, m), 7.26–

7.32 (2H, m), 7.38–7.57 (8H, m), 7.60–7.73 (4H, m); ^{31}P NMR (CD_2Cl_2): δ = 60.0 (dd, *J* = 26, 152 Hz), 74.5 (dd, *J* = 26, 147 Hz).

[Rh(cod)(5c)]OTf

This complex was prepared in a manner analogous to that described above with the exception that **5c** was used; yield: 82%; ^{1}H NMR (CD_2Cl_2): δ = 1.09 (3H, dd, *J* = 7.2, 15.3 Hz), 1.36 (3H, dd, *J* = 7.2, 18.4 Hz), 1.52–1.63 (1H, m), 1.88–1.99 (1H, m), 2.12–2.67 (1H, m), 2.30 (6H, s), 2.31 (6H, s), 2.67–2.77 (1H, m), 4.73–4.81 (1H, m), 4.95–5.02 (1H, m), 5.42–5.56 (2H, m), 7.07 (2H, d, *J* = 11.6 Hz), 7.08–7.21 (4H, m), 7.52–7.61 (2H, m), 7.62–7.68 (1H, m), 7.69–7.75 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = 60.7 (dd, *J* = 27, 148 Hz), 74.5 (dd, *J* = 27, 149 Hz).

[Rh(cod)(5e)]OTf

This complex was prepared in a manner analogous to that described above with the exception that **5e** was used; yield: 95%; ^{1}H NMR (CD_2Cl_2): δ = 1.01 (3H, dd, *J* = 7.1, 18.4 Hz), 1.24 (3H,dd, *J* = 7.1, 14.9 Hz), 1.46–1.56 (1H, m), 1.80–1.90 (1H, m), 1.96–2.55 (11H, m), 2.60–2.72 (11H, s), 4.96–5.02 (1H, m), 5.20–5.30 (2H, m), 5.30–5.38 (1H, m), 6.52–6.60 (1H, m), 7.01–7.16 (1H, m), 7.29–7.72 (10H, m), 7.74–7.81 (1H, m), 7.91–8.07 (1H, m), 9.40–9.46 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = 47.7 (dd, *J* = 23, 146 Hz), 75.9 (dd, *J* = 23, 146 Hz).

[Rh(cod)(5f)]OTf

This complex was prepared in a manner analogous to that described above with the exception that **5f** was used; yield: 100%; ^{1}H NMR (CD_2Cl_2): δ = 1.08 (3H, dd, *J* = 7.1, 15.3 Hz), 1.36 (3H, dd, *J* = 7.1, 18.5 Hz), 1.52–1.63 (1H, m), 1.88–1.98 (1H, m), 2.16–2.33 (2H, m), 2.34–2.66 (9H, m), 2.67–2.78 (1H, m), 3.84 (3H, s), 3.85 (3H, s), 4.74–4.81 (1H, m), 4.98–5.06 (1H, m), 5.45–5.56 (2H, m), 6.98–7.03 (4H, m), 7.38–7.44 (2H, m), 7.46–7.52 (2H, m), 7.52–7.60 (2H, m), 7.62–7.68 (1H, m), 7.69–7.74 (1H, m); ^{31}P NMR (CD_2Cl_2): δ = 58.7 (dd, *J* = 27, 152 Hz), 74.7 (dd, *J* = 27, 149 Hz).

[Rh(cod)(5g)]OTf

This complex was prepared in a manner analogous to that described above with the exception that **5g** was used; yield: 87%; ^{1}H NMR (CD_2Cl_2): δ = 1.00–1.18 (1H, m), 1.17 (3H, dd, *J* = 7.1, 12.5 Hz), 1.63 (3H, dd, *J* = 7.1, 17.4 Hz), 1.68–1.79 (1H, m), 2.07–2.58 (9H, m), 2.78–2.89 (1H, m), 2.90–3.00 (1H, s), 3.24–3.37 (1H, m), 4.15–4.24 (1H, m), 4.88–4.97 (1H, m) , 5.14–5.23

(1H, m), 5.29–5.36 (1H, m), 6.85–6.92 (1H, m), 7.25–7.30 (1H, m), 7.48–7.57 (1H, m), 7.65–8.04 (8H, m); ^{31}P NMR (CD_2Cl_2): δ = 57.1 (dd, *J* = 29, 146 Hz), 67.0 (dd, *J* = 27, 142 Hz).

[Rh(cod)(5h)]OTf

This complex was prepared in a manner analogue to that described above with the exception that **5h** was used; yield: 92%; ^{1}H NMR (CD_2Cl_2): δ = 0.92 (3H, dd, *J* = 7.0, 16.9 Hz), 1.00 (3H, dd, *J* = 6.8, 14.8 Hz), 1.16 (3H, dd, *J* = 7.0, 12.9 Hz), 1.17 (3H, dd, *J* = 7.1, 15.8 Hz), 1.44–1.56 (1H, m), 1.84–1.96 (1H, m), 2.21–2.72 (14H, m), 4.82–4.92 (1H, m), 5.21–5.29 (1H, m), 5.39–5.48 (1H, m), 5.88–5.98 (1H, m), 7.59–7.72 (4H, m); ^{31}P NMR (CD_2Cl_2): δ = 67.7 (dd, *J* = 24, 147 Hz), 75.2 (dd, *J* = 24, 147 Hz).

[Rh(cod)(5i)]OTf

This complex was prepared in a manner analogous to that described above with the exception that **5i** was used; yield: 91%; ^{1}H NMR (CD_2Cl_2): δ = 0.74–0.85 (1H, m), 1.06 (3H, dd, *J* = 6.9, 15.1 Hz), 1.39 (3H, dd, *J* = 7.1, 18.3 Hz), 1.01–1.44 (8H, m), 1.51–1.62 (1H, m), 1.66–2.07 (10H, m), 2.26–2.67 (16H, m), 4.88–4.96 (1H, m), 5.19–5.27 (1H, m), 5.47–5.56 (1H, m), 5.94–6.02 (1H, m), 7.63–7.79 (4H, m); ^{31}P NMR (CD_2Cl_2): δ = 61.1 (dd, *J* = 27, 150 Hz), 74.7 (dd, *J* = 27, 148 Hz).