Supporting Information

Syntheses of New Chiral Monodentate Phosphite Ligands and Their Use in Catalytic Asymmetric Hydrogenations

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General Method. ^1H , ^{31}P and ^{13}C NMR spectra were measured on a Varian Inova-400 NMR (400 MHz ^1H , 100 MHz ^{13}C and 162 MHz ^{31}P), a Varian Inova-500 NMR (500 MHz ^1H), or a Varian Gemini-2300 (300 MHz ^1H , 75 MHz ^{13}C and 121 MHz ^{31}P) spectrometer in a deuterated solvent using residual protons (CHCl_3 : 7.26 ppm ^1H , 77.0 ppm ^{13}C ; C_6H_6 : 7.15 ppm ^1H) as the internal standard or phosphoric acid as the external reference (0.0 ppm). Analytical gas chromatography was performed with a Hewlett-Packard 5890 Series II gas chromatograph (FID) with a Hewlett-Packard HP 3396A integrator using a Supelco Beta Dex-225 column. Melting points were measured on a Thomas Hoover Capillary melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter. TLC was performed on Merck DC-alufolien with Kieselgel 60F-254 and column chromatography was carried out on silica gel 60 (Merck; 230-400 mesh ASTM). High-resolution mass spectrometric analyses were carried out at the Mass Spectrometry Laboratory, University of Illinois Urbana-Champaign, Urbana, IL.

Materials. All solvent used as reaction media were distilled under nitrogen immediately before use: Ether and THF were distilled from Na/benzophenone ketyl, and CH_2Cl_2 was distilled from CaH_2 . Cationic rhodium complexes, $[\text{Rh}(\text{COD})_2]\text{BF}_4$ and $[\text{Rh}(\text{COD})_2]\text{SbF}_6$, were prepared following the literature method.¹ Solvents for extraction and chromatography were reagent grade and used as received. Chemicals and reagents were purchased from Aldrich or Fischer Scientific, and were used without further purification unless otherwise noted.

¹ Schenck, T.G.; Downes, J.M.; Milne, C.R.C.; Mackenzie, P.B.; Boucher, H.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1985**, 24, 2334.

(S)-5,5',6,6'-Tetramethyl-1,1'-biphenyl-2,2'-diol [(S)-2b]:

To a solution of (S)-2a (5.53 g, 15.6 mmol) in 80 mL C_6H_6 at $0\text{ }^\circ\text{C}$, AlCl_3 (3.33 g, 25.0 mmol) in 15 mL C_6H_6 and 30 mL CH_3NO_2 was added dropwise by cannula over 30 min. The mixture was stirred at $0\text{ }^\circ\text{C}$ for 20 min. The reaction was quenched by addition of water. The aqueous layer was extracted with Et_2O (3x15 mL), the combined organic layers were washed with brine and dried over Na_2SO_4 . The solution was concentrated under reduced pressure to give the crude product, which was recrystallized from hexane- CH_2Cl_2 to afford (S)-2b as a white solid (3.49 g, 92.4%). mp $198.5\text{--}200.0\text{ }^\circ\text{C}$; $[\alpha]_{\text{D}}^{22} -53.3$ (CH_2Cl_2 , c 0.90); $^1\text{H NMR}$ (300 MHz, CDCl_3) 1.90 (s, 6H), 2.26 (s, 6H), 4.52 (s, 2H), 6.82 (d, $J = 8.3\text{ Hz}$, 2H), 7.13 (d, $J = 8.3\text{ Hz}$, 2H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 16.5, 20.0, 112.8, 120.4, 129.4, 131.5, 137.1, 152.0; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$ 242.1307, found 242.1302 ($\delta = 1.8\text{ ppm}$).

(S)-5,5',6,6'-Tetramethyl-1,1'-biphenyl-2,2'-diol [(S)-2c]:

To a solution of (S)-2b (3.47 g, 14.3 mmol) in 100 mL CHCl_3 , Br_2 (1.7 mL, 32.2 mmol) in 20 mL CHCl_3 was added dropwise over 20 min. The mixture was stirred at room temperature for 1 h. The reaction was quenched by addition of saturated Na_2SO_3 . The aqueous layer was extracted with Et_2O (3X20 mL), the combined organic layers were washed with water and brine, and dried over Na_2SO_4 . The solution was concentrated under reduced pressure to afford (S)-2c as an off-white solid (5.71 g, 99.7%). mp $171.0\text{--}172.5\text{ }^\circ\text{C}$; $[\alpha]_{\text{D}}^{22} +11.7$ (CH_2Cl_2 , c 0.77); $^1\text{H NMR}$ (300 MHz, CDCl_3) 1.86 (s, 6H), 2.25 (s, 6H), 5.11 (s, 2H), 7.34 (s, 2H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) 16.5, 20.0, 106.9, 123.7, 130.8, 133.0,

136.8, 148.0; HRMS(EI) calcd for $C_{16}H_{16}Br_2O_2$ $[M]^+$ 397.9517, found 397.9511 (δ = 1.4 ppm).

(S)-3,3'-Dibromo-5,5',6,6'-tetramethyl-2,2'-dimethoxy-1,1'-biphenyl [(S)-10]:

To a mixture of (S)-2c (5.60 g, 14.0 mmol), KOH (2.41 g, 42.0 mmol) and Bu₄NHSO₄ (515 mg, 1.4 mmol) in 100 mL CH₂Cl₂-H₂O (1:1), dimethyl sulfate (3.92 mL, 42.0 mmol) was added all at once. The biphasic mixture was stirred at room temperature overnight. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3x50 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and filtered. The solution was concentrated under reduced pressure and the resulting crude product was triturated with MeOH to afford (S)-10 as a white solid (5.68 g, 94.8%). mp 150.0-151.5 °C; $[\alpha]_D^{22}$ +38.3 (CH₂Cl₂, c 0.60); ¹H NMR (300 MHz, CDCl₃) 1.84 (s, 6H), 2.26 (s, 6H), 3.50 (s, 6H), 7.39 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) 16.9, 20.1, 60.5, 113.9, 133.2, 133.6, 134.2, 136.0, 152.7; HRMS (EI) calcd for $C_{18}H_{20}Br_2O_2$ $[M]^+$ 425.9830, found 425.9835 (δ = -1.2 ppm).

(S)-3,3'-Diphenyl-5,5',6,6'-tetramethyl-2,2'-dimethoxy-1,1'-biphenyl [(S)-11]:

A suspension of (S)-10 (1.18 g, 2.76 mmol) and Pd(PPh₃)₄ (191 mg, 0.17 mmol) in 25 mL DME was stirred at room temperature for 30 min to give a light green solution. To this solution a mixture of PhB(OH)₂ (741 mg, 6.08 mmol) and NaHCO₃ (1.39 g, 16.56 mmol) in 16 mL water was added. The mixture was heated to reflux with stirring and maintained at this temperature for 16 h. The reaction mixture was cooled to room temperature and diluted with ether. The organic layer was washed with brine, dried

over Na_2SO_4 and then concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (15:1 hexane-EtOAc) to afford (*S*)-**11** (0.96 g, 82.2%) as a white solid. mp 56.5-58.5 °C; $[\alpha]_{\text{D}}^{22} +143.6$ (CH_2Cl_2 , c 0.55); ^1H NMR (300 MHz, CDCl_3) 1.98 (s, 6H), 2.33 (s, 6H), 3.19 (s, 6H), 7.18 (s, 2H), 7.30-7.42 (m, 6H), 7.60-7.63(m, 4H); ^{13}C NMR (75 MHz, CDCl_3) 17.0, 20.4, 60.4, 126.9, 128.4, 129.3, 131.5, 131.6, 132.2, 132.6, 135.7, 139.5, 153.5; HRMS (EI) calcd for $\text{C}_{30}\text{H}_{30}\text{O}_2$ $[\text{M}]^+$ 422.2246, found 422.2253 ($\delta = -1.8$ ppm).

(S)-3,3'-Diphenyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diol [(S)-2e]:

To a stirred solution of (*S*)-**11** (0.92 g, 2.17 mmol) dissolved in 20 mL CH₂Cl₂ at 0 °C was added BBr₃ (4.57 mL, 1.0 M solution in CH₂Cl₂) dropwise. The mixture was stirred at 0 °C for 1 h. The reaction was quenched by slow addition of water. The aqueous layer was extracted with ether and the combined organic layers were washed with brine and dried over Na₂SO₄. The solution was concentrated under reduced pressure to afford the crude product, which was purified by column chromatography on silica gel (5:1 hexane-EtOAc) to give (*S*)-**2e** (0.78 g, 91.2%) as a white solid. mp 153.0-154.0 °C; [α]_D²² +86.3 (CH₂Cl₂, c 0.53); ¹H NMR (300 MHz, CDCl₃) 1.99 (s, 6H), 2.32 (s, 6H), 4.88 (s, 2H), 7.23 (s, 2H), 7.30-7.35 (m, 2H), 7.41-7.45 (m, 4H), 7.58-7.61 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) 16.4, 19.8, 121.6, 125.6, 127.1, 128.4, 129.2, 126.3, 132.1, 136.4, 137.9, 148.4; HRMS (EI) calcd for C₂₈H₂₆O₂ [M]⁺ 394.1933, found 394.1928 (δ = 1.3 ppm).

(S)-5,5',6,6'-Tetramethyl-2,2'-dimethoxy-1,1'-biphenyl [(S)-12]:

To a stirred mixture of (S)-**2b** (0.49 g, 2.0 mmol), potassium hydroxide (0.33 g, 5.9 mmol) and tetrabutylammonium iodide (40 mg, 0.1 mmol) in CH_2Cl_2 -water (26 mL, 1:1) was added dimethylsulfate (0.57 mL, 6 mmol), and the biphasic mixture was stirred at room temperature overnight. The layers were separated and then the aqueous layer was extracted with CH_2Cl_2 (2x15 mL). The combined organic layers were washed with water (30 mL), ammonium hydroxide (30 mL) and brine (30 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel; hexanes/ethyl acetate; 10:1) to afford (S)-**12** as a white solid (0.46 g, 86%). mp 111.0-112.0 °C; ^1H NMR (400 MHz, CDCl_3) 1.83 (6H, s), 2.26 (6H, s), 3.66 (6H, s), 6.74 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100.0 MHz, CDCl_3) 16.4, 20.0, 55.9, 108.1, 126.8, 128.5, 128.9, 136.4, 155.2; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2$ $[\text{M}]^+$ 217.1620, found: 270.1616 (δ = 1.5 ppm).

(S)-3,3'-Dichloromethyl-5,5',6,6'-tetramethyl-2,2'-dimethoxy-1,1'-biphenyl [(S)-13]:

To a solution of 85% phosphoric acid (16 mL), concentrated hydrochloric acid (16 mL), glacial acetic acid (16 mL) and (S)-**12** (1.74 g, 6.44 mmol) was added paraformaldehyde (4.25 g). The mixture was heated to 90 °C and stirred for 42 h. The solution was allowed to cool to room temperature and then extracted with benzene (3x50 mL). The combined organic layers were washed with water (50 mL), saturated Na_2CO_3 (2x50 mL) and brine (50 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure to afford (S)-**13** as a white solid (mp 98.0-101.0 °C), which was pure enough for the

next step. ^1H NMR (400 MHz, CDCl_3) 1.95 (s, 6H), 2.30 (s, 6H), 3.38 (s, 6H), 4.58 (d, $J = 11.0$ Hz, 2H), 4.81 (d, $J = 11.2$ Hz, 2H), 7.27 (s, 1H), 7.37 (s, 1H); ^{13}C NMR (100.0 MHz, CDCl_3) 16.9, 20.2, 41.7, 60.9, 127.9, 128.2, 131.2, 131.4, 132.7, 137.4, 154.0; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{24}\text{Cl}_2\text{O}_2$ $[\text{M}]^+$ 366.1153, found: 366.1161 ($\delta = -2.0$ ppm).

(*S*)-3,3',5,5',6,6'-Hexamethyl-2,2'-dimethoxy-1,1'-biphenyl [(*S*)-14]:

To a stirred suspension of lithium aluminum hydride (0.64 g, 16.9 mmol) in THF (8 mL) was added (*S*)-**13** dropwise in THF (16 mL). The stirred mixture was refluxed for 3.5 h and then cooled to 0 °C. The reaction was carefully (one drop at a time) quenched with THF/water (6 mL, 3:1). The mixture was poured into a dilute solution of H_2SO_4 (8 mL; 1:1) and stirred for 30 min. The mixture was extracted with ether (3x20 mL) and the combined organic layers were washed with water (50 mL), dried over MgSO_4 , filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel; hexanes/ethyl acetate; 10:1) to afford (*S*)-**14** as a white solid (1.53 g, 80% yield for 2 steps). mp 74.0-75.0 °C; ^1H NMR (400 MHz, CDCl_3) 1.87 (s, 6H), 2.25 (s, 6H), 2.28 (s, 6H), 3.31 (s, 6H), 7.00 (s, 2H); ^{13}C NMR (100.0 MHz, CDCl_3) 16.1, 16.6, 20.1, 59.5, 127.4, 131.3, 131.5, 131.7, 133.4, 154.1; HRMS (EI) m/z calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2$ $[\text{M}]^+$ 298.1933, found: 298.1927 ($\delta = 2.0$ ppm).

(*S*)-3,3',5,5',6,6'-Hexamethyl-1,1'-biphenyl-2,2'-diol [(*S*)-2d]:

The biphenol (*S*)-**14** (1.45 g, 4.87 mmol) was dissolved in CH₂Cl₂ (2 mL) and cooled to 0 °C. To this solution was added BBr₃ (10 mL, 1.0 M in CH₂Cl₂) with stirring. The reaction temperature was maintained at 0 °C for 1 h and then the reaction was slowly quenched by addition of water (45 mL). The solution was extracted with CH₂Cl₂ (3x30 mL) and then the combined organic layers were washed with water (60 mL) and brine (60 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes:ethyl acetate = 10:1) to give (*S*)-**2d** as a white solid (1.14 g, 87%). mp 136.0-137.5 °C; ¹H NMR (400 MHz, CDCl₃) 1.85 (s, 6H), 2.23 (s, 12H), 4.53 (s, 2H), 7.00 (s, 2H); ¹³C NMR (100.0 MHz, CDCl₃) 15.8, 16.2, 19.7, 119.9, 121.3, 128.4, 132.6, 133.8, 149.8; HRMS (FAB) calcd for C₂₅H₃₅O₈ [M+H]⁺: 271.1698, found: 271.1699 (Δ = -0.3 ppm).

General procedure for the synthesis of monophosphite ligands: Synthesis of **8a** is described as a typical example.

To a solution of (1*S*,2*R*)-(+)-2-phenylcyclohexan-1-ol (154 mg, 0.88 mmol) in 5 mL of CH₂Cl₂ under nitrogen was added PCl₃ (0.15 mL, 1.76 mmol), and the mixture was allowed to stir at room temperature for 1 h. The solvent and excess PCl₃ were removed under reduced pressure. The resulting oil was redissolved in 2 mL of THF. To this solution was added a mixture of 2,2'-dihydroxyl-3,3'-di-*tert*-butyl-5,5',6,6'-tetramethylbiphenyl [(*S*)-**2a**] (312 mg, 0.88 mmol) and Et₃N (0.37 mL, 2.64 mmol) in 3 mL of THF. Upon addition, the formation of white precipitate was observed immediately. The mixture was stirred at room temperature overnight. The resulting precipitate was filtered off and the solution was concentrated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel (eluant: hexane/dichloromethane = 10/1) to afford (*S*)- 3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diyl-((1*S*,2*R*)-(+)-2-phenyl-1-cyclohexyl)phosphite (**8a**) as a white solid (368 mg, 75% yield): mp 62.0-64.0 °C; [α]_D²² +320.5 (c 0.68, CH₂Cl₂); ¹H NMR (400 MHz, C₆D₆) 0.81-1.74 (m, 8H), 1.47 (s, 9H), 1.49 (s, 9H), 1.63 (s, 3H), 1.65 (s, 3H), 1.99 (s, 3H), 2.04 (s, 3H), 2.25-2.30 (m, 1H), 2.59-2.65 (m, 1H), 6.91-7.15 (m, 7H); ³¹P NMR (162 MHz, C₆D₆) 139.9; HRMS (FAB) calcd. for C₃₆H₄₈O₃P [M+H]⁺ 559.3341, found 559.3341 (Δ = 0.0 ppm).

Other monophosphite ligands were synthesized in a similar manner. The characterization data for these ligands are shown below.

(*S*)- **3,3'-Di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diyl-(phenyl)phosphite** (**4a**): white solid, 85% yield; mp 158.5-160.0 °C; [α]_D²² + 318.9 (c 0.63, CH₂Cl₂); ¹H NMR (400 MHz, C₆D₆) 1.45 (s, 9H), 1.55 (s, 9H), 1.68 (s, 6H), 2.00 (s, 6H), 6.71 -7.10 (m, 5H), 7.15 (s, 1H), 7.22

(s, 1H); ^{31}P NMR (162 MHz, C_6D_6) 133.9; HRMS (FAB) calcd. for $\text{C}_{30}\text{H}_{37}\text{O}_3\text{P}$ $[\text{M}]^+$ 476.2480, found 476.2479 (δ = 0.3 ppm).

(S)-5,5',6,6'-Tetramethyl-1,1'-biphenyl-2,2'-diyl-(phenyl)phosphite (4b): sticky white foam, 25% yield; ^1H NMR (400 MHz, C_6D_6) 1.74 (s, 3H), 1.76 (s, 3H), 1.92 (s, 6H), 6.76-7.02 (m, 9H); ^{31}P NMR (162 MHz, C_6D_6) 138.9.

(S)- 3,3'-Di-tert-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diyl-(2-naphthyl)phosphite (5a): white solid, 70% yield; mp 72.5-75.5 °C; $[\alpha]_{\text{D}}^{22} + 283.3$ (c 0.72, CH_2Cl_2); ^1H NMR (400 MHz, C_6D_6) 1.46 (s, 9H), 1.58 (s, 9H), 1.70 (s, 3H), 1.71 (s, 3H), 2.01 (s, 3H), 2.03 (s, 3H), 7.04-7.13 (m, 2H), 7.16 (s, 1H), 7.20 (dd, J = 9.2 Hz, 2.0 Hz, 1H), 7.25 (s, 1H), 7.33 (d, J = 9.2 Hz, 1H), 7.40 (s, 1H), 7.42 (s, 1H), 7.51 (s, 1H); ^{31}P NMR (162 MHz, C_6D_6) 132.9; HRMS (FAB) calcd. for $\text{C}_{34}\text{H}_{40}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$ 527.2715, found 527.2714 (δ = 0.2 ppm).

(S)-5,5',6,6'-Tetramethyl-1,1'-biphenyl-2,2'-diyl-(2-naphthyl)phosphite (5b): white foam, 66% yield; ^1H NMR (400 MHz, C_6D_6) 1.77 (s, 6H), 1.92 (s, 3H), 1.93 (s, 3H), 6.86 (d, J = 8.0 Hz, 2H), 7.0-7.7 (m, 7H), 7.37 (d, J = 8.8 Hz, 2H); ^{31}P NMR (162 MHz, C_6D_6) 136.5; HRMS (FAB) calcd. for $\text{C}_{26}\text{H}_{23}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$ 415.1463, found 415.1464 (δ = 0.1 ppm).

(S)- 3,3'-Di-tert-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diyl-((-)-menthyl)phosphite (6a): white solid, 63% yield; mp 57.0-59.0 °C; $[\alpha]_{\text{D}}^{22} + 230.5$ (c 0.73, CH_2Cl_2); ^1H NMR (400 MHz, C_6D_6) 0.50-1.84 (m, 8H), 0.61 (d, J = 6.4 Hz, 3H), 0.80 (d, J = 6.8 Hz, 3H), 0.86 (d, J = 7.2 Hz, 3H), 1.57 (s, 9H), 1.60 (s, 9H), 1.67 (s, 3H), 1.70 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 2.43-2.45 (m, 1H), 4.09-4.12 (m, 1H), 7.17 (s, 1H), 7.22 (s, 1H); ^{31}P NMR (162 MHz, C_6D_6) 137.9; HRMS (FAB) calcd. for $\text{C}_{34}\text{H}_{50}\text{O}_3\text{P}$ $[\text{M}-\text{H}]^+$ 537.3498, found 537.3499 (δ = -0.3 ppm).

(S)- 5,5',6,6'-Tetramethyl-1,1'-biphenyl-2,2'-diyl-((-)-menthyl)phosphite (6b): white foam, 76% yield; ^1H NMR (400 MHz, C_6D_6) 0.3-1.5 (m, 8H), 0.67 (d, J = 6.0 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H), 0.89 (d, J = 7.0 Hz, 3H), 1.75 (s, 3H), 1.76 (s, 3H), 1.94 (s, 6H), 2.4-2.6 (m, 1H), 3.9-4.1 (m, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 7.12 (t, J = 8.4 Hz, 2H); ^{31}P NMR (162

MHz, C₆D₆) 147.1; HRMS (EI) m/z calcd. for C₂₆H₃₅O₃P [M]⁺ 426.2324, found 426.2322 (Δ = 0.2 ppm).

(S)- 3,3'-Di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diyl-((-)-8-phenylmenthyl) phosphite (6c): white solid, 81% yield; mp 137.0-139.0 °C; [α]_D²² +296.7 (c 0.60, CH₂Cl₂); ¹H NMR (300 MHz, C₆D₆) 0.57 (d, J = 6.6 Hz, 3H), 0.74-1.36 (m, 8H), 1.43 (s, 3H), 1.53 (s, 3H), 1.60 (s, 9H), 1.64 (s, 9H), 1.71 (s, 3H), 1.83 (s, 3H), 2.07 (s, 3H), 2.14 (s, 3H), 4.30-4.39 (s, 1H), 7.01-7.33 (m, 7H); ³¹P NMR (121 MHz, C₆D₆) 133.7; HRMS (FAB) calcd. for C₄₀H₅₆O₃P [M+H]⁺ 615.3967, found 615.3966 (Δ = 0.2 ppm).

(R)- 3,3'-Di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diyl-((-)-menthyl)phosphite (7a): white solid, 68% yield; mp 128.0-130.5 °C; [α]_D²² - 336.9 (c 0.87, CH₂Cl₂); ¹H NMR (400 MHz, C₆D₆) 0.56-1.94 (m, 8H), 0.63 (d, J = 5.2 Hz, 3H), 0.64 (d, J = 4.8 Hz, 3H), 0.73 (d, J = 6.4 Hz, 3H), 1.57 (s, 9H), 1.59 (s, 9H), 1.68 (s, 6H), 2.01 (s, 3H), 2.02 (s, 3H), 2.24-2.32 (m, 1H), 4.04-4.08 (m, 1H), 7.17 (s, 1H), 7.19 (s, 1H); ³¹P NMR (162 MHz, C₆D₆) 141.4; HRMS (FAB) calcd. for C₃₄H₅₂O₃P [M+H]⁺ 539.3654, found 539.3656 (Δ = -0.4 ppm).

(R)- 5,5',6,6'-Tetramethyl-1,1'-biphenyl-2,2'-diyl-((-)-menthyl)phosphite (7b): white solid, 75% yield, mp 53.0-55.0 °C; [α]_D²⁰ -124.6 (c 0.43, CH₂Cl₂); ¹H NMR (400 MHz, CD₂Cl₂): 0.7-1.8 (m, 8H), 0.82 (d, J = 7.2 Hz, 3H), 0.89 (d, J = 7.2 Hz, 3H), 0.98 (d, J = 6.4 Hz, 3H), 2.02 (s, 6H), 2.31 (s, 6H), 2.1-2.2 (m, 1H), 4.0-4.2 (m, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 7.17 (t, J = 7.6 Hz, 2H); ³¹P NMR (162 MHz, C₆D₆) 148.8; HRMS (EI) m/z calcd. for C₂₆H₃₅O₃P [M]⁺ 426.2324, found 426.2321 (Δ = 0.3 ppm).

(R)- 3,3'-Di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diyl-((-)-8-phenylmenthyl) phosphite (7c): white solid, 63% yield; mp 75.0-77.0 °C; [α]_D²² -226.2 (c 0.43, CH₂Cl₂); ¹H NMR (300 MHz, C₆D₆) 0.67 (d, J = 6.3 Hz, 3H), 0.50-1.50 (m, 7H), 1.20 (s, 3H), 1.37 (s, 3H), 1.68 (s, 9H), 1.69 (m, 9H), 1.73 (s, 3H), 1.78 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 2.53-2.64 (m, 1H), 4.21-4.39 (m, 1H), 7.01-7.27 (m, 7H); ³¹P NMR (121 MHz, C₆D₆) 145.3; HRMS (FAB) calcd. for C₄₀H₅₆O₃P [M+H]⁺ 615.3967, found 615.3966 (Δ = 0.2 ppm).

(S)- 5,5',6,6'-Tetramethyl-1,1'-biphenyl-2,2'-diyl-(-((1R,2S)-(+)-2-phenyl-1-cyclohexyl) phosphite (8b): white solid, 61% yield; mp 149.0-151.0 °C; [α]_D²² +200.6 (*c* 0.58, CH₂Cl₂); ¹H NMR (400 MHz, C₆D₆) 0.81-1.63 (m, 7H), 1.69 (s, 3H), 1.72(s, 3H), 1.88 (s, 3H), 1.94 (s, 3H), 2.11-2.15 (m, 1H), 2.39-2.46 (m, 1H), 4.11-4.15 (m, 1H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.81 (d, *J* = 8.0 Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H), 6.96 (d, *J* = 8.0 Hz, 1 H), 7.11-7.24 (m, 5H); ³¹P NMR (162 MHz, C₆D₆) 146.9; HRMS (FAB) calcd. for C₂₈H₃₂O₃P [M+H]⁺ 447.2089, found 447.2088 (δ = 0.2 ppm).

(S)- 3,3'-Di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diyl-((1R, 2S)-(+)-2-phenyl-1-cyclohexyl)phosphite (9a): white solid, 60% yield; mp 67.0-69.0 °C; [α]_D²² +250.2 (*c* 0.88, CH₂Cl₂); ¹H NMR (300 MHz, CD₂Cl₂) 1.26 (s, 9H), 1.56 (s, 9H), 1.33-1.91 (m, 8H), 1.76 (s, 3H), 1.80 (s, 3H), 2.24 (s, 3H), 2.25 (s, 3H), 2.61-2.67 (m, 1H), 4.36-4.39 (m, 1H), 7.14-7.31 (m, 7H); ³¹P NMR (101 MHz, CD₂Cl₂) 137.9; HRMS (FAB) calcd. for C₃₆H₄₆O₃P [M-H]⁺ 557.3185, found 557.3185 (δ = -0.1 ppm).

(S)- 5,5',6,6'-Tetramethyl-1,1'-biphenyl-2,2'-diyl-(-((1S,2R)-(+)-2-phenyl-1-cyclohexyl) phosphite (9b): white solid, 64% yield; mp 67.5-70.0 °C; [α]_D²² +62.5 (*c* 0.40, CH₂Cl₂); ¹H NMR (300 MHz, C₆D₆) 0.89- 1.67 (m, 7H), 1.75 (s, 3H), 1.76(s, 3H), 1.96 (s, 3H), 2.01 (s, 3H), 2.14-2.19 (m, 1H), 2.48-2.55 (m, 1H), 4.31-4.36 (m, 1H), 6.26 (d, *J* = 8.1 Hz, 1H), 6.81 (dd, *J* = 15.9, 8.3 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 7.16-7.32 (m, 5H); ³¹P NMR (121 MHz, C₆D₆) 146.4; HRMS (FAB) calcd. for C₂₈H₃₂O₃P [M+H]⁺ 447.2089, found 447.2087 (δ = 0.5 ppm).

(S)- 3,3'-Diphenyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diyl-((1R,2S)-(+)-2-phenyl-1-cyclohexyl)phosphite (9c): white solid, 68% yield; mp 80.0-82.0 °C; [α]_D²² +207.5 (*c* 0.40, CH₂Cl₂); ¹H NMR (300 MHz, CD₂Cl₂) 0.88-1.56 (m, 8H), 1.85 (s, 3H), 1.87 (s, 3H), 2.02 (s, 6H), 2.21-2.35 (m, 1H), 3.70-3.81 (m, 1H), 6.74 (d, *J* = 6.6 Hz, 2H), 6.99-7.31 (m, 11H), 7.66 (t, *J* = 6.5 Hz, 4 H); ³¹P NMR (121 MHz, CD₂Cl₂) 141.9; HRMS (FAB) calcd. for C₄₀H₄₀O₃P [M+H]⁺ 599.2715, found 599.2717 (δ = -0.3 ppm).

(S)- 3,3',5,5',6,6'-Hexamethyl-1,1'-biphenyl-2,2'-diyl-((1R,2S)-(+)-2-phenyl-1-cyclohexyl) phosphite (9d): white solid, 75% yield; mp 157-158 °C; [α]_D²² +57.2 (*c* 0.50, CH₂Cl₂);

^1H NMR (500 MHz, C_6D_6) 0.84-2.18 (m, 8H), 1.80 (s, 3H), 1.82 (s, 3H), 2.00 (s, 3H), 2.00 (s, 3H), 2.02 (s, 3H), 2.34 (s, 3H), 2.48-2.58 (m, 1H), 4.38-4.48 (m, 1H), 6.85 (s, 1H), 6.87 (s, 1H), 6.98-7.32 (m, 5H); ^{31}P NMR (121.5 MHz, C_6D_6) 143.0; HRMS (EI) calcd. for $\text{C}_{30}\text{H}_{35}\text{O}_3\text{P}$ $[\text{M}-\text{H}]^+$ 473.2246, found 473.2242 (δ = 0.4 ppm).

(S)- 3,3'-Dibromo-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diyl-((1R,2S)-(+)-2-phenyl-1-cyclohexyl)phosphite (9e): white solid, 76% yield; mp 76.0-79.0 °C; $[\alpha]_{\text{D}}^{22} +352.5$ (c 0.13, CH_2Cl_2); ^1H NMR (300 MHz, CD_2Cl_2) 0.86-1.37 (m, 7H), 1.51 (s, 3H), 1.54 (s, 3H), 1.71 (s, 3H), 1.75 (s, 3H), 2.23-2.38 (m, 1H), 2.66-2.75 (m, 1H), 4.48-4.59 (m, 1H), 7.05-7.29 (m, 7H); ^{31}P NMR (121 MHz, CD_2Cl_2) 145.8; HRMS (FAB) calcd. for $\text{C}_{28}\text{H}_{30}\text{O}_3\text{PBr}_2$ $[\text{M}+\text{H}]^+$ 603.0238, found 603.0244 (δ = -1.0 ppm).

General procedure for Rh(I)-catalyzed asymmetric hydrogenation of dimethyl itaconate:

The reaction of dimethyl itaconate using $[\text{Rh}(\text{COD})_2]\text{SbF}_6$ and ligand **8a**) is described as typical example.

In a 10 mL glass reaction vessel with a magnetic stirring bar under nitrogen, a mixture of $[\text{Rh}(\text{COD})_2]\text{SbF}_6$ (1.4 mg, 0.0025 mmol) and **8a** (3.0 mg, 0.0050 mmol) was dissolved in 5 mL 1,2-dichloroethane, and the solution was stirred at room temperature for 2 min. To this catalyst solution was added dimethyl itaconate (0.08 mL, 0.5 mmol). The reaction vessel was then placed in a 300 mL stainless steel autoclave, and the autoclave was pressurized and purged with hydrogen gas 5 times. The vessel was subsequently charged with hydrogen gas to 100 psi (6.8 atm). The autoclave was warmed to 50 °C and the reaction was carried out at this temperature for 20 h with stirring. The autoclave was allowed to cool to room temperature, and then the hydrogen gas was carefully released. The reaction mixture was filtered through a short pad of silica gel and the filtrate was subjected to gas chromatographic analysis using a Supelco Beta Dex-225 column for the determination of the conversion and enantiomeric purity of dimethyl methylsuccinate: The analysis showed that the conversion was 100% with 100% product selectivity and (*R*)-dimethyl methylsuccinate with 99.6% ee was formed.

Other reactions were performed practically in the same manner with variations in the reaction temperature, the Rh- catalyst precursor, and the solvent used.