Supporting information for:

**Chiral Monophosphites Derived from Carbohydrate:
Conformational Effect in Catalytic Asymmetric Hydrogenation**

Hanmin Huang, Zhuo Zheng^{*}, Huili Luo, Changmin Bai, Xinquan Hu, and Huilin Chen^{*}

Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian, 116023, P. R. China

zhengz@dicp.ac.cn

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General Procedures: All reactions and manipulations were performed in a nitrogen-filled glovebox or using standard Schlenk-type techniques. Melting points were determined using a Mettler FP5 melting apparatus in open capillaries and are uncorrected. Optical rotations were measured on a JASCO, P-1020 high sensitive polarimeter. ¹H NMR and ¹³C NMR spectra were obtained on BRUKER DRX 400 spectrometers with TMS as an internal standard, ³¹P NMR spectra were recorded with 85% H₃PO₄ as an external standard. High resolution mass spectra were recorded on Applied Biosystems Mariner System 5303. Enantiomeric excess (ee) were determined by GC analysis on an Agilent HP-4890 or 6890 GC instrument with FID as detector.

Materials: All solvents were dried and degassed by standard methods and stored under nitrogen. dimethyl itaconate was purchased from Acros. enamides, and chiral alcohols **7-10** derived from D-fructose and D-glucose were known compounds which were synthesized according to the literature procedure.¹ All other chemicals obtained commercially.

(A). Preparation and Physical data of ligands 3-6

Fig. 1. Structure of chiral alcohols and ligands 3-6

General procedure for synthesis of the ligands 3-6

Scheme 1. The synthesis route of monophosphite ligands

To a stirred solution of **7** (1.5 mmol) in THF (5 mL) was slowly added PCl₃ (132 μL, 1.5

mmol) as a solution in THF (4 mL) and the resulting mixture was stirred for 1 h at room temperature. The reaction mixture was then cooled to $-10\text{ }^{\circ}\text{C}$ and Et_3N (1.07 mL, 4.5 mmol) was slowly added. The reaction mixture was allowed to warm to room temperature, maintained under these conditions for 0.25 h, and then cooled to $0\text{ }^{\circ}\text{C}$, solid BINOL was added and the resulting mixture was allowed to warm to room temperature and stirred overnight prior to dilution with diethyl ether. The solid were removed by filtration through a pad of Celite, the solvent was removed in *vacuo* and the residue was purified by flash chromatography (EtOAc / hexane: 1 / 20~1 / 10)), furnished the title ligands as white foam in 75-90% yields.

The above procedure was followed using **7a** and R-BINOL. After workup, it gave **3a**. mp $121\text{--}122\text{ }^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{12} = -430.54$ (*c* 1.06, THF); ^1H NMR ($\text{DMSO-}d^6$): δ 1.27 (s, 3H), 1.34 (s, 3H), 1.43 (s, 3H), 1.53 (s, 3H), 3.99 (m, 3H), 4.09 (t, $J = 6.4\text{ Hz}$, 1H), 4.24 (d, $J = 9.2\text{ Hz}$, 1H), 4.30 (t, $J = 4.8\text{ Hz}$, 1H), 4.43 (t, $J = 8.4\text{ Hz}$, 1H), 7.21-7.24 (m, 2H), 7.34-7.36 (m, 2H), 7.47-7.57 (m, 4H), 8.05-8.10 (m, 3H), 8.17 (d, $J = 8.8\text{ Hz}$, 1H); ^{13}C NMR ($\text{DMSO-}d^6$): δ 26.15, 27.87, 59.96, 71.44, 73.35, 73.94, 74.11, 75.16, 103.74, 108.88, 111.62, 121.67, 122.00, 122.26, 123.56, 125.13, 125.37, 125.89, 126.01, 126.60, 126.78, 128.57, 128.71, 129.95, 130.75, 130.87, 131.20, 131.71, 132.02, 146.79, 147.36; ^{31}P NMR ($\text{DMSO-}d^6$): δ 159.37; HRMS (APCI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_8\text{P}$ ($\text{M}^+ + 1$): 575.1829, found: 575.1850.

The above procedure was followed using **7a** and S-BINOL. After workup, it gave **3b**. mp $107\text{--}108\text{ }^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{12} = +196.98$ (*c* 1.20, THF); ^1H NMR ($\text{DMSO-}d^6$): δ 0.90 (s, 3H), 1.33 (s, 3H), 1.39 (s, 3H), 1.51 (s, 3H), 3.84 (d, $J = 9.2\text{ Hz}$, 1H), 3.95-3.99 (m, 3H), 4.27-4.37 (m, 3H), 7.21-7.23 (m, 2H), 7.33-7.35 (m, 2H), 7.51-7.54 (m, 3H), 7.61 (d, $J = 8.8\text{ Hz}$, 1H), 8.04-8.17 (m, 4H); ^{13}C NMR ($\text{DMSO-}d^6$): δ 25.19, 26.37, 26.60, 27.92, 59.61, 70.54, 73.16, 73.31, 73.43, 75.51, 103.54, 108.92, 111.69, 121.70, 122.04, 123.50, 125.08, 125.31, 125.87, 126.02, 126.49, 126.72, 128.54, 128.69, 129.99, 130.76, 131.17, 131.64, 132.07, 146.96, 147.36; ^{31}P NMR ($\text{DMSO-}d^6$): δ 158.48; HRMS (APCI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_8\text{P}$ ($\text{M}^+ + 1$): 575.1829, found: 575.1841 □

The above procedure was followed using **7b** and R-BINOL. After workup, it gave **3c**. mp $135\text{--}136\text{ }^{\circ}\text{C}$; $[\alpha]_{\text{D}}^{25} = -382.45$ (*c* 1.08, THF); ^1H NMR ($\text{DMSO-}d^6$): δ 1.24-1.75 (m, 20H), 3.97-4.04 (m, 3H), 4.10 (t, $J = 6.4\text{ Hz}$, 1H), 4.23 (d, $J = 9.2\text{ Hz}$, 1H), 4.30 (d, $J = 4.4\text{ Hz}$, 1H), 4.42 (t, $J = 8.4$

Hz, 1H), 7.21-7.24 (m, 2H), 7.33-7.38 (m, 2H), 7.46-7.53 (m, 4H), 8.05-8.09 (m, 3H), 8.18 (d, J = 8.8 Hz, 1H); ^{13}C NMR (DMSO- d_6): δ 23.32, 23.56, 23.68, 24.40, 24.54, 35.05, 35.16, 35.47, 37.32, 60.25, 71.06, 73.03, 74.25, 74.43, 74.80, 403.34, 109.45, 112.20, 121.49, 122.01, 122.32, 123.62, 125.14, 125.38, 125.89, 126.02, 126.62, 126.81, 128.59, 128.73, 129.76, 130.77, 130.95, 131.19, 131.73, 132.06, 146.83, 147.41; ^{31}P NMR (DMSO- d_6): δ 159.55; HRMS (APCI) calcd for $\text{C}_{38}\text{H}_{40}\text{O}_8\text{P}$ ($M^+ + 1$): 655.2455, found: 655.2508.

The above procedure was followed using **7b** and S-BINOL. After workup, it gave **3d**. mp 153-154 °C; $[\alpha]_D^{25} = +196.98$ (c 1.20, THF); ^1H NMR (DMSO- d_6): δ 1.07-1.69 (m, 20H), 3.83-4.00 (m, 4H), 4.30-4.32 (m, 2H), 4.38 (m, 1H), 7.21-7.22 (m, 2H), 7.32-7.36 (m, 2H), 7.47-7.62 (m, 4H), 8.05-8.17 (m, 4H); ^{13}C NMR (DMSO- d_6): δ 22.10, 22.54, 22.97, 23.38, 23.50, 24.28, 24.45, 34.29, 35.28, 36.05, 37.42, 59.78, 70.16, 73.14, 73.32, 73.47, 75.19, 103.19, 109.48, 112.17, 121.71, 121.96, 122.11, 123.52, 125.07, 125.32, 125.87, 126.01, 126.50, 126.73, 128.55, 128.70, 130.04, 130.77, 131.17, 131.67, 132.08, 146.99, 147.41; ^{31}P NMR (DMSO- d_6): δ 158.47; HRMS (APCI) calcd for $\text{C}_{38}\text{H}_{40}\text{O}_8\text{P}$ ($M^+ + 1$): 655.2455, found: 655.2481 □

The above procedure was followed using **8a** and R-BINOL. After workup, it gave **4a**. mp 120-121 °C; $[\alpha]_D^{25} = -360.71$ (c 1.20, THF); ^1H NMR (DMSO- d_6): δ 1.27 (s, 3H), 1.33 (s, 3H), 1.40 (s, 3H), 1.46 (s, 3H), 3.57 (d, J = 13.2 Hz, 1H), 3.67 (d, J = 9.2 Hz, 1H), 3.82 (d, J = 13.2 Hz, 1H), 4.04 (d, J = 9.2 Hz, 1H), 4.40 (d, J = 7.6 Hz, 1H), 4.72 (d, J = 8.0 Hz, 1H), 4.91 (d, J = 10.4 Hz, 1H), 7.20-7.22 (m, 2H), 7.34-7.38 (m, 2H), 7.49-7.58 (m, 4H), 8.08-8.19 (m, 4H); ^{13}C NMR (DMSO- d_6): δ 24.60, 25.86, 26.06, 26.27, 62.59, 70.55, 71.09, 71.26, 73.40, 73.78, 104.70, 108.69, 109.02, 121.45, 121.98, 125.22, 125.47, 125.85, 126.01, 126.68, 126.85, 128.64, 128.72, 130.09, 130.86, 131.01, 131.26, 131.80, 132.03, 146.59, 147.08; ^{31}P NMR (DMSO- d_6): δ 157.75; HRMS (APCI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_8\text{P}$ ($M^+ + 1$): 575.1829, found: 575.1786 □

The above procedure was followed using **8a** and S-BINOL. After workup, it gave **4b**. mp 147-148 °C; $[\alpha]_D^{25} = +201.12$ (c 0.89, THF); ^1H NMR (DMSO- d_6): δ 1.23 (s, 3H), 1.32 (s, 3H), 1.48 (s, 3H), 1.58 (s, 3H), 3.58 (d, J = 13.2 Hz, 1H), 3.82-3.85 (m, 2H), 4.32-4.36 (m, 2H), 4.42-4.44 (m, 1H), 4.92 (m, 1H), 7.23-7.25 (m, 2H), 7.34-7.36 (m, 2H), 7.50-7.52 (m, 2H), 7.59 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 8.07-8.20 (m, 4H); ^{13}C NMR (DMSO- d_6): δ 24.49, 25.44,

25.98, 26.06, 62.65, 70.90, 72.82, 73.03, 73.51, 73.87, 105.07, 108.86, 109.07, 121.46, 122.04, 123.43, 125.24, 125.40, 125.88, 126.00, 126.65, 126.80, 128.57, 128.69, 130.27, 130.81, 130.92, 131.20, 131.75, 132.04, 146.69, 147.75; ^{31}P NMR (DMSO- d^6): δ 160.52; HRMS (APCI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_8\text{P}$ (M^++1): 575.1829, found: 575.1797□

The above procedure was followed using **8b** and R-BINOL. After workup, it gave **4c**. mp 134-135 °C; $[\alpha]_{\text{D}}^{25} = -325.42$ (c 1.05, THF); ^1H NMR (DMSO- d^6): δ 1.35-1.72 (m, 20H), 3.57 (d, $J = 13.2$ Hz, 1H), 3.67 (d, $J = 9.2$ Hz, 1H), 3.84 (d, $J = 12.8$ Hz, 1H), 4.00 (t, $J = 9.2$ Hz, 1H), 4.41 (d, $J = 7.6$ Hz, 1H), 4.72 (d, $J = 8.0$ Hz, 1H), 4.94 (d, $J = 10.4$ Hz, 1H), 7.20-7.24 (m, 2H), 7.34-7.37 (m, 2H), 7.48-7.57 (m, 4H), 8.08 (m, 3H), 8.17-8.20 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (DMSO- d^6): δ 23.24, 23.36, 23.50, 24.56, 33.77, 35.21, 35.33, 35.52, 62.69, 70.06, 71.10, 71.29, 73.13, 73.53, 104.18, 109.29, 109.67, 121.37, 121.99, 122.08, 123.52, 125.23, 125.48, 125.84, 126.01, 126.68, 126.86, 128.66, 128.72, 129.98, 130.87, 131.05, 131.26, 131.79, 132.04, 146.54, 147.10; ^{31}P NMR (DMSO- d^6): δ 153.43; HRMS (APCI) calcd for $\text{C}_{38}\text{H}_{40}\text{O}_8\text{P}$ (M^++1): 655.2455, found: 655.2434□

The above procedure was followed using **8b** and S-BINOL. After workup, it gave **4d**. mp 143-144 °C; $[\alpha]_{\text{D}}^{25} = +151.82$ (c 1.23, THF); ^1H NMR (DMSO- d^6): δ 1.33-1.85 (m, 20H), 3.58 (d, $J = 13.2$ Hz, 1H), 3.79-3.85 (m, 2H), 4.29-4.41 (m, 3H), 4.91 (d, $J = 8.4$ Hz, 1H), 7.21-7.23 (m, 2H), 7.34-7.38 (m, 2H), 7.51 (m, 2H), 7.58 (d, $J = 8.8$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 8.06-8.10 (m, 2H), 8.14 (d, $J = 9.2$ Hz, 1H), 8.17 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (DMSO- d^6): δ 23.19, 23.34, 23.50, 24.56, 33.78, 34.56, 35.01, 35.48, 62.77, 70.58, 72.96, 73.18, 73.69, 104.72, 109.62, 109.72, 121.32, 121.49, 125.23, 125.42, 125.90, 126.01, 126.65, 126.78, 128.60, 128.67, 130.33, 130.80, 130.92, 131.21, 131.74, 132.02, 146.63; ^{31}P NMR (DMSO- d^6): δ 154.91; HRMS (APCI) calcd for $\text{C}_{38}\text{H}_{40}\text{O}_8\text{P}$ (M^++1): 655.2455, found: 655.2470□

The above procedure was followed using **9a** and R-BINOL. After workup, it gave **5a**. mp 113-114 °C; $[\alpha]_{\text{D}}^{25} = -303.13$ (c 1.14, THF); ^1H NMR (DMSO- d^6): δ 1.28 (s, 3H), 1.33 (s, 3H), 1.38 (s, 3H), 1.42 (s, 3H), 3.74-3.77 (m, 1H), 3.96-4.02 (m, 2H), 4.15-4.18 (m, 1H), 4.69 (d, $J = 9.6$ Hz, 1H), 4.81 (d, $J = 3.6$ Hz, 1H), 5.80 (d, $J = 3.2$ Hz, 1H), 7.21-7.23 (m, 2H), 7.34-7.37 (m, 2H), 7.49-7.53 (m, 2H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.66 (d, $J = 8.8$ Hz, 1H), 8.08-8.21 (m, 4H); ^{13}C NMR (DMSO- d^6): δ 25.33, 26.09, 26.54, 26.66, 66.41, 71.72, 77.69, 77.82, 80.12, 83.68, 104.53, 108.62,

111.59, 121.55, 121.85, 125.25, 125.51, 125.98, 126.05, 126.69, 126.86, 128.68, 128.74, 130.40, 130.77, 131.06, 131.28, 131.64, 131.99, 146.52, 147.66; ^{31}P NMR (DMSO- d^6): δ 147.75; HRMS (APCI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_8\text{P}$ (M^++1): 575.1829, found: 575.1802□

The above procedure was followed using **9a** and S-BINOL. After workup, it gave **5b**. mp 107-108 °C; $[\alpha]_D^{25} = +291.92$ (c 1.11, THF); ^1H NMR (DMSO- d^6): δ 1.20 (s, 3H), 1.38 (s, 3H), 1.39 (s, 3H), 1.42 (s, 3H), 3.80-3.83 (m, 1H), 3.96-4.00 (m, 1H), 4.08-4.10 (m, 1H), 4.22-4.25 (m, 1H), 4.59 (d, $J = 3.6$ Hz, 1H), 4.79-4.82 (m, 1H), 5.82 (d, $J = 3.6$ Hz, 1H), 7.20-7.22 (m, 2H), 7.35-7.36 (m, 2H), 7.49-7.52 (m, 2H), 7.57 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.8$ Hz, 1H), 8.08-8.21 (m, 4H); ^{13}C NMR (DMSO- d^6): δ 25.20, 25.86, 26.43, 26.55, 66.21, 71.88, 77.16, 77.31, 80.18, 83.74, 104.54, 108.57, 111.40, 121.56, 121.64, 121.95, 123.35, 125.30, 125.49, 125.95, 126.75, 126.87, 128.66, 128.74, 130.30, 130.82, 131.03, 131.28, 131.74, 132.00, 146.65, 147.25; ^{31}P NMR (DMSO- d^6): δ 152.58; HRMS (APCI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_8\text{P}$ (M^++1): 575.1829, found: 575.1795□

The above procedure was followed using **9b** and R-BINOL. After workup, it gave **5c**. mp 121-122 °C; $[\alpha]_D^{25} = -267.67$ (c 1.13, THF); ^1H NMR (DMSO- d^6): δ 1.33-1.59 (m, 20H), 3.74 (m, 1H), 3.97-4.12 (m, 3H), 4.79 (m, 2H), 5.85 (d, $J = 3.6$ Hz, 1H), 7.22-7.24 (m, 2H), 7.35-7.37 (m, 2H), 7.50-7.54 (m, 3H), 7.65 (d, $J = 8.4$ Hz, 1H), 8.08-8.15 (m, 3H), 8.18 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (DMSO- d^6): δ 22.39, 23.22, 23.58, 24.30, 24.65, 32.39, 33.47, 34.46, 35.17, 35.43, 35.91, 36.03, 66.34, 71.43, 77.77, 77.94, 80.40, 83.29, 104.31, 105.33, 109.10, 112.13, 121.38, 121.73, 121.86, 123.53, 125.22, 125.49, 125.91, 126.04, 126.67, 126.85, 128.67, 130.36, 130.79, 131.03, 131.25, 131.70, 132.02, 146.58, 147.47; ^{31}P NMR (DMSO- d^6): δ 149.34; HRMS (APCI) calcd for $\text{C}_{38}\text{H}_{40}\text{O}_8\text{P}$ (M^++1): 655.2455, found: 655.2463□

The above procedure was followed using **9b** and S-BINOL. After workup, it gave **5d**. mp 118-119 °C; $[\alpha]_D^{25} = +262.74$ (c 1.08, THF); ^1H NMR (DMSO- d^6): δ 1.33-1.68 (m, 20H), 3.81-3.83 (m, 1H), 4.01-4.06 (m, 2H), 4.25-4.27 (m, 1H), 4.57 (m, 1H), 4.71 (d, $J = 9.6$ Hz, 1H), 5.87 (d, $J = 3.6$ Hz, 1H), 7.20-7.22 (m, 2H), 7.33-7.36 (m, 2H), 7.50-7.52 (m, 2H), 7.57 (d, $J = 8.8$ Hz, 1H), 7.65 (d, $J = 8.8$ Hz, 1H), 8.06-8.10 (m, 2H), 8.13 (d, $J = 8.8$ Hz, 1H), 8.18 (d, $J = 9.2$ Hz, 1H); ^{13}C NMR (DMSO- d^6): δ 23.19, 23.43, 23.51, 23.62, 24.31, 24.63, 34.34, 34.91, 35.74, 35.99, 66.18, 71.63, 77.49, 77.64, 80.33, 83.36, 104.28, 109.04, 111.81, 121.53, 121.92, 125.25, 125.44, 125.97,

126.70, 126.81, 128.60, 128.72, 130.38, 130.79, 131.00, 131.26, 131.77, 132.01, 146.69; ^{31}P NMR (DMSO- d^6): δ 149.05; HRMS (APCI) calcd for $\text{C}_{38}\text{H}_{40}\text{O}_8\text{P}$ (M^++1): 655.2455, found: 655.2507□

The above procedure was followed using **10a** and R-BINOL. After workup, it gave **6a**. mp 76-77 °C; $[\alpha]_{\text{D}}^{25} = -248.68$ (c 0.98, THF); ^1H NMR (DMSO- d^6): δ 1.28 (s, 3H), 1.30 (s, 3H), 1.33 (s, 3H), 1.44 (s, 3H), 3.74-3.78 (m, 1H), 3.98-4.08 (m, 2H), 4.20-4.23 (m, 1H), 4.53-4.60 (m, 2H), 5.73 (d, $J = 3.6$ Hz, 1H), 7.19-7.21 (m, 2H), 7.34-7.38 (m, 2H), 7.49-7.51 (m, 3H), 7.60 (d, $J = 8.8$ Hz, 1H), 8.07-8.19 (m, 4H); ^{13}C NMR (DMSO- d^6): δ 25.00, 26.15, 26.54, 26.63, 64.67, 73.88, 73.98, 74.71, 78.11, 78.44, 103.54, 108.89, 112.49, 121.62, 121.73, 121.88, 123.41, 125.21, 125.42, 125.90, 125.99, 126.67, 126.81, 128.61, 128.70, 130.12, 130.77, 130.95, 131.22, 131.77, 132.01, 146.70, 147.37; ^{31}P NMR (DMSO- d^6): δ 148.81; HRMS (APCI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_8\text{P}$ (M^++1): 575.1829, found: 575.1786□

The above procedure was followed using **10a** and S-BINOL. After workup, it gave **6b**. mp 111-112 °C; $[\alpha]_{\text{D}}^{25} = +318.37$ (c 1.15, THF); ^1H NMR (DMSO- d^6): δ 1.33 (s, 3H), 1.37 (s, 3H), 1.38 (s, 3H), 1.46 (s, 3H), 3.73-3.76 (m, 1H), 3.96-4.01 (m, 2H), 4.17 (t, $J = 5.6$ Hz, 1H), 4.55-4.59 (m, 1H), 4.81 (t, $J = 4.2$ Hz, 1H), 5.75 (d, $J = 3.2$ Hz, 1H), 7.20-7.24 (m, 2H), 7.33-7.36 (m, 2H), 7.48-7.58 (m, 4H), 8.06-8.19 (m, 4H); ^{13}C NMR (DMSO- d^6): δ 25.17, 26.28, 26.54, 26.60, 65.11, 74.14, 74.30, 74.82, 77.41, 78.54, 103.44, 109.01, 112.29, 121.58, 121.84, 122.35, 123.56, 125.13, 125.43, 125.87, 126.05, 126.54, 126.80, 128.59, 128.71, 129.89, 130.93, 131.24, 131.67, 132.02, 146.71, 147.51; ^{31}P NMR (DMSO- d^6): δ 151.85; HRMS (APCI) calcd for $\text{C}_{32}\text{H}_{32}\text{O}_8\text{P}$ (M^++1): 575.1829, found: 575.1864□

The above procedure was followed using **10b** and R-BINOL. After workup, it gave **6c**. mp 110-111 °C; $[\alpha]_{\text{D}}^{25} = -192.45$ (c 1.00, THF); ^1H NMR (DMSO- d^6): δ 1.31-1.68 (m, 20H), 3.70-3.74 (m, 1H), 3.97-4.00 (m, 1H), 4.07-4.10 (m, 1H), 4.14-4.17 (m, 1H), 4.52-4.54 (m, 1H), 4.60 (t, $J = 4.0$ Hz, 1H), 5.75 (d, $J = 3.6$ Hz, 1H), 7.20-7.22 (m, 2H), 7.34-7.37 (m, 2H), 7.49-7.56 (m, 4H), 8.07-8.13 (m, 3H), 8.18 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (DMSO- d^6): δ 23.38, 24.32, 24.61, 34.20, 35.54, 35.83, 64.83, 74.71, 78.03, 78.25, 103.32, 109.42, 113.12, 121.52, 121.80, 122.00, 123.40, 125.15, 125.37, 125.89, 126.00, 126.61, 126.78, 128.61, 128.69, 130.07, 130.77, 130.92, 131.16, 131.77, 132.03, 146.90, 147.44; ^{31}P NMR (DMSO- d^6): δ 148.71; HRMS (APCI) calcd for

C₃₈H₄₀O₈P (M⁺+1): 655.2455, found: 655.2395□

The above procedure was followed using **10b** and S-BINOL. After workup, it gave **6d**. mp 131-132 °C; [α]_D²⁵ = +358.48 (*c* 1.00, THF); ¹H NMR (DMSO-d⁶): δ 1.37-1.65 (m, 20H), 3.70-3.74 (m, 1H), 3.92-3.95 (m, 1H), 3.98-4.02 (m, 1H), 4.15-4.18 (m, 1H), 4.60-4.66 (m, 1H), 4.82 (t, *J* = 4.0 Hz, 1H), 5.77 (d, *J* = 3.6 Hz, 1H), 7.20-7.25 (m, 2H), 7.33-7.39 (m, 2H), 7.48-7.57 (m, 4H), 8.07-8.09 (m, 3H), 8.18 (d, *J* = 8.8 Hz, 1H); ¹³C NMR (DMSO-d⁶): δ 23.46, 24.38, 24.71, 34.38, 35.63, 35.83, 65.25, 74.51, 74.70, 77.41, 78.18, 103.09, 109.55, 112.88, 121.33, 121.94, 122.46, 123.59, 125.15, 125.44, 125.83, 126.05, 126.57, 126.84, 128.60, 128.72, 129.75, 130.99, 131.21, 131.68, 132.05, 146.75, 147.48; ³¹P NMR (DMSO-d⁶): δ 153.48; HRMS (APCI) calcd for C₃₈H₄₀O₈P (M⁺+1): 655.2455, found: 655.2416□

(B) General procedure for asymmetric hydrogenation

In a nitrogen-filled glovebox, to a solution of [Rh(COD)₂]BF₄ (2.0 mg, 0.005 mmol) in anhydrous and degassed CH₂Cl₂ (1 mL) was added ligand (0.011 mmol). After stirring the mixture for 30 min, a substrate (0.5 mmol) dissolved in CH₂Cl₂ (1 mL) was added. The reaction mixture was transferred to a Parr stainless autoclave. The autoclave was purged three times with hydrogen and the pressure was set to 1.2 or 10 atm, the hydrogenation was performed at room temperature for 12 h. After carefully releasing the hydrogen, the reaction mixture was passed through a short silica-gel plug to remove the catalyst. The resulting solution was used directly for chiral GC to measure enantiomeric excesses.

(C) GC Conditions for Determination of enantiomeric excesses of hydrogenation products

The ee's were determined by GC analysis using a Supelco γ -DEX 225 column, 30m x 0.25mm. Oven temperature is 80 °C. t(S)=14.4, t(R)=15.3. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.²

The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 150 °C. t(S)=9.7, t(R)=10.3. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.³

The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 130 °C. t(S)=16.7, t(R)=18.3. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.³

The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 140 °C. t(S)=12.9, t(R)=13.6. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.³

The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 140 °C. t(S)=45.0, t(R)=46.9. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.³

The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 130 °C. t(S)=20.9, t(R)=22.0. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.³

The ee's were determined by GC analysis using a Chrompack chiral fused silica 25m x 0.25mm Chirasil-L-Val column. Oven temperature is 170 °C. t(S)=22.4, t(R)=24.0. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.³

The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 150 °C. t(S)=24.80, t(R)=25.50. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.³

The ee's were determined by GC analysis using a Supelco Chiral select 1000 column, 30m x 0.25mm. Oven temperature is 150 °C. t(S)=43.2, t(R)=45.1. Absolute configuration was determined by comparison of the sign of the optical rotation with reported value.³

References

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(D) NMR for monophosphite ligands 3-6

¹³C NMR (R-A-II in DMSO-d₆)

^{31}P NMR (R-A-II in DMSO-d_6)

¹³C NMR (S-A-II in DMSO-d₆)

^{31}P NMR (S-A-II in DMSO-d_6)

158.487

ppm

3b

^{31}P NMR (DMSO-d_6)

¹H NMR (R-A-I in DMSO-d₆)

¹³C NMR (R-A-I in DMSO-d₆)

³¹P NMR (R-A-I in DMSO-d₆)

159.556

ppm

3c

³¹P NMR (DMSO-d₆)

¹H NMR (S-A-I in DMSO-d₆)

¹³C NMR (S-A-I in DMSO-d₆)

^{31}P NMR (S-A-I in DMSO-d_6)

158.473

ppm

3d

^{31}P NMR (DMSO-d_6)

¹³C NMR (E-R-A-II in DMSO-d₆)

³¹P NMR (E-R-A-II in DMSO-d₆)

¹H NMR (E-S-A-II in DMSO-d₆)

4b

¹H NMR (DMSO-d₆)

¹³C NMR (E-S-A-II in DMSO-d₆)

³¹P NMR (E-S-A-II in DMSO-d₆)

160.520

ppm

4b

³¹P NMR (DMSO-d₆)

¹H NMR (E-R-A-I in DMSO-d₆)

¹³C NMR (E-R-A-I in DMSO-d₆)

³¹P NMR (E-R-A-I in DMSO-d₆)

153.437

ppm

¹³C NMR (E-S-A-I in DMSO-d₆)

^{31}P NMR (E-S-A-I in DMSO-d_6)

¹³C NMR (R-G-A-II in DMSO-d₆)

^{31}P NMR (R-G-A-II in DMSO-d_6)

147.753

ppm

¹³C NMR (S-G-A-II in DMSO-d₆)

³¹P NMR (S-G-A-II in DMSO-d₆)

152.581

ppm

5b
³¹P NMR (DMSO-d₆)

¹H NMR (R-G-A-I in DMSO-d₆)

¹³C NMR (R-~~4~~-AI in DMSO-d₆)

^{31}P NMR (R-~~4~~-A1 in DMSO- d_6)

149.342

ppm

5c
 ^{31}P NMR (DMSO- d_6)

¹H NMR (S-G-A-I in DMSO-d₆)

5d

¹H NMR (DMSO-d₆)

¹³C NMR (S-G-A-I in DMSO-d₆)

^{31}P NMR (S-G-A-I in DMSO-d_6)

¹H NMR (REGA-II in DMSO-d₆)

¹³C NMR (REGA-II in DMSO-d₆)

³¹P NMR (RECA-II in DMSO-d₆)

148.815

ppm

6a
³¹P NMR (DMSO-d₆)

¹H NMR (SEGA-II in DMSO-d₆)

¹³C NMR (SEGA-II in DMSO-d₆)

31P NMR (SEGA-II in DMSO-d6)

Current Data Parameters
NAME nm-206
EXPNO 49
PROCNO 1

F2 - Acquisition Parameters

Date_ 500000
Time_ 9.49
INSTRUM DRX400
PROBHD BBI 5mm Z
PULPROG zgdc
TD 16384
SOLVENT DMSO
NS 400
DS 0
SWH 43103.449 Hz
FIDRES 2.630826 Hz
AQ 0.1901044 sec
RG 8192
DM 11.600 usec
DE 51.00 usec
TE 300.0 K
d11 0.0300000 sec
FL12 25.60 dB
CPDPRG2 waltz16
PCPD2 80.00 usec
SFO2 400.1320000 MHz
NUC2 1H
PL2 7.50 dB
D1 1.0000000 sec
P1 20.00 usec
DE 51.00 usec
SFO1 161.989872 MHz
NUC1 31P
PL1 0.00 dB

F2 - Processing parameters

SI 16384
SF 161.9755436 MHz
WDW EM
SSB 0
LB 6.00 Hz
GB 0
PC 2.00

1D NMR plot parameters

CX 20.00 cm
F1P 220.000 ppm
F1 35634.62 Hz
F2P -20.000 ppm
F2 -3239.51 Hz
PPMCM 12.00000 ppm/cm
HZCM 1943.70667 Hz/cm

ppm
151.859

6b
31P NMR (DMSO-d6)

¹H NMR (REGA-I in DMSO-d₆)

¹³C NMR (REGA-I in DMSO-d₆)

^{31}P NMR (REGA-I in DMSO-d_6)

148.714

ppm

6c
 ^{31}P NMR (DMSO-d_6)

¹H NMR (SEGA-I in DMSO-d₆)

¹³C NMR (SEGA-I in DMSO-d₆)

³¹P NMR (SEGA-I in DMSO-d₆)

Current Data Parameters
NAME hnm-206
* EXNO 46
PROCNO 1

F2 - Acquisition Parameters

Date_ 500000
Time_ 9.22
INSTRUM DRX400
PROBHD BBI 5mm Z
PULPROG zgpg30
TD 16384
SOLVENT DMSO
NS 200
DS 0
SWH 43103.449 Hz
FIDRES 2.630826 Hz
AQ 0.1901044 sec
RG 8192
DM 11.600 usec
DE 51.00 usec
TE 300.0 K
d11 0.0300000 sec
PL12 25.60 dB
CPDPRG2 waltz16
PCPD2 80.00 usec
SFO2 400.1320000 MHz
NUC2 ¹H
PL2 7.50 dB
D1 1.0000000 sec
P1 20.00 usec
DE 51.00 usec
SFO1 161.9899872 MHz
NUC1 ³¹P
PL1 0.00 dB

F2 - Processing parameters

SI 16384
SF 161.9755436 MHz
WDW EM
SSB 0
LB 6.00 Hz
GB 0
PC 2.00

1D NMR plot parameters

CX 20.00 cm
FIP 220.000 ppm
F1 35694.62 Hz
F2 -20.000 ppm
F2 -3239.51 Hz
PPMCM 12.00000 ppm/cm
HZCM 1943.70667 Hz/cm

ppm
153.484

6d
³¹P NMR (DMSO-d₆)