Supporting Information

Rhodium-Catalyzed Asymmetric Hydroarylation of Diphenylphosphinylallenes with Arylboronic Acids

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General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H , 125 MHz for ^{13}C , and 202 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR, chloroform- d (δ 77.16) for ^{13}C NMR, and external H_3PO_4 standard for ^{31}P NMR: the following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, sext: sextet, m: multiplet. Optical rotations were measured on a JASCO DIP-370 polarimeter.

Materials. THF was purified by passing through a neutral alumina column under nitrogen. 1,4-Dioxane was distilled over benzophenone ketyl under nitrogen. Rhodium complexes, $[\text{Rh}(\text{OH})(\text{cod})]_2$,¹ $[\text{Rh}(\text{OH})((R)\text{-binap})]_2$,² and $[\text{RhPh}(\text{PPh}_3)((R)\text{-binap})]_2$ ² were prepared according to the reported procedure. Diphenylphosphinylallenes were prepared by the modified procedure of reported one.³

Typical Procedure for Preparation of Diphenylphosphinylallene (1). To a mixture of 2-butyne-1-ol (4.2 g, 60 mmol), triethylamine (7.0 mL, 50 mmol), and CH_2Cl_2 (50 mL) in a 100 mL Schlenk flask was added dropwise chlorodiphenylphosphine (11.0 g, 50 mmol) at -78°C over 10 minutes under nitrogen. The mixture was allowed to warm to room temperature, and the stirring was continued for another 3 h. The mixture was poured into cold solution of HCl (concentrated, 2.5 mL) in water (20 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (20 mL $\times$ 3) and the combined organic layers were washed with brine and dried over MgSO_4 . After concentration, the residual white solid was subjected to column chromatography on silica gel with EtOAc–hexane (4/1) as an eluent to give **1** as a white solid (8.62 g, 33.9 mmol, 68%).

¹ Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, 23, 129.

² Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002**, 124, 5052.

³ (a) Boisselle, A. P.; Meinhardt, N. A. *J. Org. Chem.* **1962**, 27, 1828. (b) Rubin, M.; Markov, J.; Chuprakov, S.; Wink, D. J.; Gevorgyan, V. *J. Org. Chem.* **2003**, 68, 6251.

Compound **1**:³ white solid. ¹H NMR (CDCl₃) δ 1.94 (dt, $J_{\text{P-H}} = 11.8$, $J = 3.1$ Hz, 3H), 4.64 (dq, $J_{\text{P-H}} = 11.2$ Hz, $J = 3.0$ Hz, 2H), 7.40–7.55 (m, 6H), 7.70–7.80 (m, 4H); ¹³C NMR (CDCl₃) δ 14.3 (d, $J_{\text{P-C}} = 5.6$ Hz), 76.0 (d, $J_{\text{P-C}} = 12.9$ Hz), 92.5 (d, $J_{\text{P-C}} = 101.2$ Hz), 128.4 (d, $J_{\text{P-C}} = 12.4$ Hz), 131.6 (d, $J_{\text{P-C}} = 104.8$ Hz), 131.8 (d, $J_{\text{P-C}} = 9.3$ Hz), 132.0 (d, $J_{\text{P-C}} = 2.6$ Hz), 211.8 (d, $J_{\text{P-C}} = 7.3$ Hz); ³¹P NMR (CDCl₃) δ 30.3.

Compound **4**: white solid. ¹H NMR (CDCl₃) δ 1.10 (t, $J = 7.3$ Hz, 3H), 2.25 (dq, $J_{\text{P-H}} = 7.9$ Hz, $J = 7.3$, 3.6 Hz, 2H), 4.73 (dt, $J_{\text{P-H}} = 11.2$ Hz, $J = 3.6$ Hz, 2H), 7.42–7.54 (m, 6H), 7.70–7.77 (m, 4H); ¹³C NMR (CDCl₃) δ 12.7 (d, $J_{\text{P-C}} = 6.1$ Hz), 20.7 (d, $J_{\text{P-C}} = 6.3$ Hz), 78.0 (d, $J_{\text{P-C}} = 13.4$ Hz), 99.3 (d, $J_{\text{P-C}} = 100.7$ Hz), 128.3 (d, $J_{\text{P-C}} = 11.9$ Hz), 131.8 (d, $J_{\text{P-C}} = 9.8$ Hz), 131.9 (d, $J_{\text{P-C}} = 3.1$ Hz), 132.0 (d, $J_{\text{P-C}} = 105.0$ Hz), 211.0 (d, $J_{\text{P-C}} = 7.1$ Hz); ³¹P NMR (CDCl₃) δ 29.8. Anal. Calcd for C₁₇H₁₇OP: C, 76.10; H, 6.39. Found: C, 76.21; H, 6.35.

Compound **6**: colorless oil. ¹H NMR (CDCl₃) δ 0.85 (t, $J = 7.4$ Hz, 3H), 1.32 (sext, $J = 7.4$ Hz, 2H), 1.50 (quint, $J = 7.4$ Hz, 2H), 2.18–2.26 (m, 2H), 4.70 (dt, $J_{\text{P-H}} = 11.5$ Hz, $J = 3.4$ Hz, 2H), 7.42–7.48 (m, 4H), 7.49–7.54 (m, 2H), 7.70–7.76 (m, 4H); ¹³C NMR (CDCl₃) δ 13.9, 22.3, 27.0 (d, $J_{\text{P-C}} = 6.1$ Hz), 30.4 (d, $J_{\text{P-C}} = 5.6$ Hz), 77.5 (d, $J_{\text{P-C}} = 13.4$ Hz), 97.9 (d, $J_{\text{P-C}} = 100.2$ Hz), 128.4 (d, $J_{\text{P-C}} = 12.4$ Hz), 131.9 (d, $J_{\text{P-C}} = 9.4$ Hz), 131.9 (d, $J_{\text{P-C}} = 2.6$ Hz), 132.1 (d, $J_{\text{P-C}} = 104.8$ Hz), 211.2 (d, $J_{\text{P-C}} = 7.8$ Hz); ³¹P NMR (CDCl₃) δ 29.9. Anal. Calcd for C₁₉H₂₁OP: C, 77.01; H, 7.14. Found: C, 77.01; H, 7.25.

Compound **8**: white solid. ¹H NMR (CDCl₃) δ 4.88 (d, $J_{\text{P-H}} = 10.8$ Hz, 2H), 7.18 (t, $J = 7.3$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 2H), 7.42 (td, $J = 7.6$, 2.7 Hz, 4H), 7.49 (td, $J = 6.7$, 1.2 Hz, 2H), 7.60 (d, $J = 7.3$ Hz, 2H), 7.70–7.80 (m, 4H); ¹³C NMR (CDCl₃) δ 78.5 (d, $J_{\text{P-C}} = 12.4$ Hz), 100.9 (d, $J_{\text{P-C}} = 100.2$ Hz), 127.7, 128.3 (d, $J_{\text{P-C}} = 5.1$ Hz), 128.4 (d, $J_{\text{P-C}} = 12.4$ Hz), 128.7, 131.9 (d, $J_{\text{P-C}} = 9.4$ Hz), 131.9 (d, $J_{\text{P-C}} = 3.1$ Hz), 131.4, 132.3 (d, $J_{\text{P-C}} = 107.0$ Hz), 213.6 (d, $J_{\text{P-C}} = 6.8$ Hz); ³¹P NMR (CDCl₃) δ 29.4. Anal. Calcd for C₂₁H₁₇OP: C, 79.73; H, 5.42. Found: C, 79.78; H, 5.60.

Compound **11**: white solid. ¹H NMR (CDCl₃) δ 1.26 (s, 9H), 4.57 (d, $J_{\text{P-H}} = 11.5$ Hz, 2H), 7.38–7.52 (m, 6H), 7.65–7.75 (m, 4H); ¹³C NMR (CDCl₃) δ 30.7 (d, $J_{\text{P-C}} = 3.6$ Hz), 35.8 (d, $J_{\text{P-C}} = 5.1$ Hz), 77.7 (d, $J_{\text{P-C}} = 13.4$ Hz), 106.7 (d, $J_{\text{P-C}} = 97.2$ Hz), 128.1 (d, $J_{\text{P-C}} = 11.8$ Hz), 131.5 (d, $J_{\text{P-C}} = 3.1$ Hz), 131.7 (d, $J_{\text{P-C}} = 9.3$ Hz), 134.3 (d, $J_{\text{P-C}} = 105.0$ Hz), 210.9 (d, $J_{\text{P-C}} = 8.8$ Hz); ³¹P NMR (CDCl₃) δ 29.9. Anal. Calcd for C₁₉H₂₁OP: C, 77.01; H, 7.14. Found: C, 76.94; H, 7.38.

Typical Procedure for Rhodium-Catalyzed Asymmetric Hydroarylation of Diphenylphosphinylallene **1 with *p*-Tolylboronic Acid.** To a mixture of [Rh(OH)((*R*)-binap)]₂ (2.3 mg, 0.005 mmol), **1** (50.9 mg, 0.20 mmol), and *p*-tolylboronic acid (54.4 mg, 0.40 mmol) in a screw cap test tube (7 mL) was added THF (0.40 mL) under Ar and the tube was capped tightly. Then, the mixture was stirred at 60 °C (bath temp.) for 1 h. The reaction mixture was cooled to room temperature and diluted with CH₂Cl₂. The mixture was washed with aqueous NaHCO₃ and brine. The organic layer was dried over MgSO₄, filtered, and concentrated under vacuum. The residue was subjected to column chromatography on silica gel with EtOAc-hexane (4/1) as an eluent to give **2a** as a white solid (59.6 mg, 0.17 mmol; 86% yield). All major products were isolated and identified by ¹H, ¹³C and ³¹P NMR, and C, H combustion analysis or HRMS (ESI). Compounds **2a** and **3a** were isolated as a mixture of isomers in Table 1. Isolation of **2f** was carried out using preparative HPLC after column chromatography to remove a small amount of impurities. When [Rh(OH)(cod)]₂ was used as a catalyst precursor, the mixture of [Rh(OH)(cod)]₂ and (*R*)-binap in THF was stirred for 15 min under nitrogen before the addition of substrates. The absolute configuration of (*S*)-**2e** was determined by X-ray crystallographic analysis. For others, they were assigned by consideration of the stereochemical pathway.

Compound **2a**: white solid; [α]_D²⁰ -130 (*c* 1.01, CHCl₃, 97% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.3 mL/min, hexane/2-propanol = 9/1, 254 nm, *t*₁ = 24.9 min (*R*), *t*₂ = 28.6 min (*S*)); ¹H NMR (CDCl₃) δ 1.52 (dd, *J*_{P-H} = 16.1 Hz, *J* = 7.4 Hz, 3H), 2.29 (s, 3H), 3.56 (dq, *J*_{P-H} = 7.6 Hz, *J* = 7.4 Hz, 1H), 5.37 (d, *J*_{P-H} = 4.2 Hz, 1H), 5.61 (d, *J*_{P-H} = 4.0 Hz, 1H), 6.99 (s, 4H), 7.18–7.26 (m, 2H), 7.30–7.37 (m, 1H), 7.40–7.53 (m, 3H), 7.54–7.64 (m, 2H), 7.79–7.89 (m, 2H); ¹³C NMR δ 16.1 (d, *J*_{P-C} = 3.1 Hz), 21.1, 38.9 (d, *J*_{P-C} = 67.2 Hz), 117.3 (d, *J*_{P-C} = 7.6 Hz), 126.2, 128.1 (d, *J*_{P-C} = 11.4 Hz), 128.7 (d, *J*_{P-C} = 10.8 Hz), 129.0, 131.2 (d, *J*_{P-C} = 8.3 Hz), 131.3 (d, *J*_{P-C} = 8.8 Hz), 131.3 (d, *J*_{P-C} = 2.5 Hz), 131.6 (d, *J*_{P-C} = 2.6 Hz), 132.4 (d, *J*_{P-C} = 97.7 Hz), 132.9 (d, *J*_{P-C} = 93.5 Hz), 137.1, 140.2 (d, *J*_{P-C} = 5.8 Hz), 145.9 (d, *J*_{P-C} = 6.1 Hz); ³¹P NMR (CDCl₃) δ 33.6. Anal. Calcd for C₂₃H₂₃OP: C, 79.75; H, 6.69. Found: C, 79.46; H, 6.94.

Compound **3a**: white solid. The stereochemistry of (*E*)-**3a** was determined by different NOE analysis. ¹H NMR (CDCl₃) δ 1.51 (dq, *J*_{P-H} = 14.2 Hz, *J* = 1.6 Hz, 3H), 2.30 (dq, *J*_{P-H} = 2.8 Hz, *J* = 1.6 Hz, 3H), 2.35 (s, 3H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.43–7.57 (m, 6H), 7.70–7.80 (m, 4H); ¹³C NMR δ 21.0 (d, *J*_{P-C} = 14.4 Hz), 21.3, 25.0 (d, *J*_{P-C} = 8.3 Hz), 123.6 (d, *J*_{P-C} = 96.1 Hz), 127.1 (d, *J*_{P-C} = 1.0 Hz), 128.7 (d, *J*_{P-C} = 11.9 Hz), 129.2, 131.6 (d,

$J_{\text{P-C}} = 2.5$ Hz), 131.7 (d, $J = 9.9$ Hz), 134.1 (d, $J_{\text{P-C}} = 101.2$ Hz), 137.1, 141.1 (d, $J_{\text{P-C}} = 16.1$ Hz), 155.5 (d, $J_{\text{P-C}} = 8.3$ Hz); ^{31}P NMR (CDCl_3) δ 31.7. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{OP}$ ($\text{M}+\text{H}^+$) 347.1559, found 347.1542.

Compound **2b**: white solid; $[\alpha]_{\text{D}}^{20} -147$ (c 0.83, CHCl_3 , 98% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.8 mL/min, hexane/2-propanol = 9/1, 254 nm, $t_1 = 11.8$ min (*R*), $t_2 = 15.4$ min (*S*)); ^1H NMR (CDCl_3) δ 1.52 (dd, $J_{\text{P-H}} = 16.2$ Hz, $J = 7.3$ Hz, 3H), 3.55 (dq, $J_{\text{P-H}} = 7.9$ Hz, $J = 7.6$ Hz, 1H), 3.77 (s, 3H), 5.33 (d, $J_{\text{P-H}} = 4.3$ Hz, 1H), 5.55 (d, $J_{\text{P-H}} = 4.2$ Hz, 1H), 6.72 (d, $J = 8.8$ Hz, 2H), 7.04 (d, $J_{\text{P-H}} = 8.8$ Hz, 2H), 7.21–7.26 (m, 2H), 7.30–7.37 (m, 1H), 7.42–7.53 (m, 3H), 7.55–7.64 (m, 2H), 7.80–7.89 (m, 2H); ^{13}C NMR (CDCl_3) δ 16.0 (d, $J_{\text{P-C}} = 3.0$ Hz), 39.0 (d, $J_{\text{P-C}} = 67.2$ Hz), 55.4, 113.7, 116.7 (d, $J_{\text{P-C}} = 7.6$ Hz), 127.5 (d, $J_{\text{P-C}} = 1.0$ Hz), 128.1 (d, $J_{\text{P-C}} = 11.9$ Hz), 128.7 (d, $J_{\text{P-C}} = 10.8$ Hz), 131.2 (d, $J_{\text{P-C}} = 8.2$ Hz), 131.3 (d, $J_{\text{P-C}} = 8.8$ Hz), 131.3 (d, $J_{\text{P-C}} = 3.1$ Hz), 131.6 (d, $J_{\text{P-C}} = 3.0$ Hz), 132.5 (d, $J_{\text{P-C}} = 98.2$ Hz), 132.9 (d, $J_{\text{P-C}} = 93.5$ Hz), 135.7 (d, $J_{\text{P-C}} = 5.3$ Hz), 145.4 (d, $J_{\text{P-C}} = 6.3$ Hz), 159.1; ^{31}P NMR (CDCl_3) δ 33.4. HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{O}_2\text{P}$ ($\text{M}+\text{H}^+$) 363.1508, found 363.1490.

Compound **2c**: viscous oil; $[\alpha]_{\text{D}}^{20} -149$ (c 1.19, CHCl_3 , 96% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.3 mL/min, hexane/2-propanol = 9/1, 254 nm, $t_1 = 26.6$ min (*R*), $t_2 = 37.4$ min (*S*)); ^1H NMR (CDCl_3) δ 1.54 (dd, $J_{\text{P-H}} = 16.0$ Hz, $J = 7.3$ Hz, 3H), 3.59 (dq, $J_{\text{P-H}} = 7.6$ Hz, $J = 7.3$ Hz, 1H), 5.40 (d, $J_{\text{P-H}} = 4.4$ Hz, 1H), 5.64 (d, $J_{\text{P-H}} = 4.1$ Hz, 1H), 7.06–7.10 (m, 2H), 7.15–7.24 (m, 5H), 7.31–7.35 (m, 1H), 7.44–7.52 (m, 3H), 7.55–7.61 (m, 2H), 7.82–7.88 (m, 2H); ^{13}C NMR (CDCl_3) δ 16.1 (d, $J_{\text{P-C}} = 3.1$ Hz), 38.9 (d, $J_{\text{P-C}} = 67.2$ Hz), 118.0 (d, $J_{\text{P-C}} = 8.2$ Hz), 126.3 (d, $J_{\text{P-C}} = 1.0$ Hz), 127.4, 128.1 (d, $J_{\text{P-C}} = 11.9$ Hz), 128.3, 128.8 (d, $J_{\text{P-C}} = 10.9$ Hz), 131.2 (d, $J_{\text{P-C}} = 8.8$ Hz), 131.3 (d, $J_{\text{P-C}} = 8.8$ Hz), 131.4 (d, $J_{\text{P-C}} = 3.1$ Hz), 131.7 (d, $J_{\text{P-C}} = 2.6$ Hz), 132.3 (d, $J_{\text{P-C}} = 98.1$ Hz), 133.1 (d, $J_{\text{P-C}} = 94.1$ Hz), 143.2 (d, $J_{\text{P-C}} = 5.1$ Hz), 146.0 (d, $J_{\text{P-C}} = 5.6$ Hz); ^{31}P NMR (CDCl_3) δ 33.4. Anal. Calcd for $\text{C}_{22}\text{H}_{21}\text{OP}$: C, 79.50; H, 6.37. Found: C, 79.20; H, 6.60.

Compound **2d**: white solid; $[\alpha]_{\text{D}}^{20} -105$ (c 0.50, CHCl_3 , 98% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.5 mL/min, hexane/2-propanol = 9/1, 254 nm, $t_1 = 20.6$ min (*R*), $t_2 = 28.5$ min (*S*)); ^1H NMR (CDCl_3) δ 1.61 (dd, $J_{\text{P-H}} = 16.0$ Hz, $J = 7.3$ Hz, 3H), 3.70 (dq, $J_{\text{P-H}} = 7.7$ Hz, $J = 7.3$ Hz, 1H), 5.52 (d, $J_{\text{P-H}} = 4.4$ Hz, 1H), 5.76 (d, $J_{\text{P-H}} = 4.2$ Hz, 1H), 7.10–7.17 (m, 2H), 7.21–7.27 (m, 2H), 7.40–7.51 (m, 6H), 7.56–7.63 (m, 2H), 7.65 (d, $J = 8.5$ Hz, 1H), 7.66–7.71 (m, 1H), 7.73–7.78 (m, 1H), 7.84–7.90

(m, 2H); ^{13}C NMR (CDCl_3) δ 16.1 (d, $J_{\text{P-C}} = 3.6$ Hz), 39.0 (d, $J_{\text{P-C}} = 67.2$ Hz), 118.5 (d, $J_{\text{P-C}} = 7.8$ Hz), 124.8, 125.0 (d, $J_{\text{P-C}} = 1.1$ Hz), 126.0, 126.2, 127.6, 128.0 (d, $J_{\text{P-C}} = 6.6$ Hz), 128.1 (d, $J_{\text{P-C}} = 6.6$ Hz), 128.7, 128.8, 131.2 (d, $J_{\text{P-C}} = 8.8$ Hz), 131.3 (d, $J_{\text{P-C}} = 9.3$ Hz), 131.4 (d, $J_{\text{P-C}} = 2.6$ Hz), 131.7 (d, $J_{\text{P-C}} = 2.5$ Hz), 132.3 (d, $J_{\text{P-C}} = 98.1$ Hz), 132.7, 132.7 (d, $J_{\text{P-C}} = 94.1$ Hz), 133.2, 140.5 (d, $J_{\text{P-C}} = 7.6$ Hz), 146.0 (d, $J_{\text{P-C}} = 5.6$ Hz); ^{31}P NMR (CDCl_3) δ 33.4. Anal. Calcd for $\text{C}_{26}\text{H}_{23}\text{OP}$: C, 81.66; H, 6.06. Found: C, 81.44; H, 6.18.

Compound **2e**: white solid; $[\alpha]_{\text{D}}^{20} -142$ (c 0.47, CHCl_3 , 97% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.5 mL/min, hexane/2-propanol = 9/1, 254 nm, $t_1 = 14.3$ min (*R*), $t_2 = 15.7$ min (*S*)); ^1H NMR (CDCl_3) δ 1.52 (dd, $J_{\text{P-H}} = 16.0$ Hz, $J = 7.3$ Hz, 3H), 3.54 (dq, $J_{\text{P-H}} = 7.9$ Hz, $J = 7.3$ Hz, 1H), 5.37 (d, $J_{\text{P-H}} = 4.5$ Hz, 1H), 5.61 (d, $J_{\text{P-H}} = 4.2$ Hz, 1H), 7.01 (d, $J = 8.7$ Hz, 2H), 7.13 (d, $J = 8.7$ Hz, 2H), 7.20–7.27 (m, 2H), 7.32–7.38 (m, 1H), 7.44–7.61 (m, 5H), 7.82–7.88 (m, 2H); ^{13}C NMR (CDCl_3) δ 15.8 (d, $J_{\text{P-C}} = 3.6$ Hz), 39.1 (d, $J_{\text{P-C}} = 66.6$ Hz), 118.5 (d, $J_{\text{P-C}} = 7.6$ Hz), 127.8 (d, $J_{\text{P-C}} = 1.1$ Hz), 128.2 (d, $J_{\text{P-C}} = 11.9$ Hz), 128.4, 128.8 (d, $J_{\text{P-C}} = 11.3$ Hz), 131.2 (d, $J_{\text{P-C}} = 8.3$ Hz), 131.2 (d, $J_{\text{P-C}} = 9.3$ Hz), 131.4 (d, $J_{\text{P-C}} = 2.6$ Hz), 131.8 (d, $J_{\text{P-C}} = 3.1$ Hz), 132.2 (d, $J_{\text{P-C}} = 97.7$ Hz), 132.4 (d, $J_{\text{P-C}} = 94.1$ Hz), 133.2, 141.5 (d, $J_{\text{P-C}} = 4.6$ Hz), 145.0 (d, $J_{\text{P-C}} = 6.1$ Hz); ^{31}P NMR (CDCl_3) δ 32.9. Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{ClOP}$: C, 72.03; H, 5.50. Found: C, 71.88; H, 5.31.

Compound **2f**: white solid; $[\alpha]_{\text{D}}^{20} -151$ (c 1.05, CHCl_3 , 96% ee). The enantiomeric excess was measured by HPLC (Chiralpak AD-H column, 0.5 mL/min, hexane/2-propanol = 9/1, 254 nm, $t_1 = 25.2$ min (*S*), $t_2 = 30.2$ min (*R*)); ^1H NMR (CDCl_3) δ 1.51 (dd, $J_{\text{P-H}} = 15.9$ Hz, $J = 7.3$ Hz, 3H), 3.56 (dq, $J_{\text{P-H}} = 8.0$ Hz, $J = 7.3$ Hz, 1H), 5.41 (d, $J_{\text{P-H}} = 4.5$ Hz, 1H), 5.64 (d, $J_{\text{P-H}} = 4.4$ Hz, 1H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.15–7.21 (m, 2H), 7.27–7.33 (m, 1H), 7.37 (d, $J = 8.1$ Hz, 2H), 7.41–7.56 (m, 5H), 7.79–7.86 (m, 2H); ^{13}C NMR δ 15.7 (d, $J_{\text{P-C}} = 2.5$ Hz), 39.2 (d, $J_{\text{P-C}} = 66.6$ Hz), 119.7 (d, $J_{\text{P-C}} = 7.8$ Hz), 124.2 (q, $J_{\text{F-C}} = 271.9$ Hz), 125.2 (q, $J_{\text{F-C}} = 3.6$ Hz), 126.8 (q, $J_{\text{F-C}} = 1.0$ Hz), 128.2 (d, $J_{\text{P-C}} = 11.3$ Hz), 128.8 (d, $J_{\text{P-C}} = 11.4$ Hz), 129.3 (q, $J_{\text{F-C}} = 32.6$ Hz), 131.2 (d, $J_{\text{P-C}} = 8.3$ Hz), 131.2 (d, $J_{\text{P-C}} = 9.3$ Hz), 131.5 (d, $J_{\text{P-C}} = 2.6$ Hz), 131.8 (d, $J_{\text{P-C}} = 3.1$ Hz), 132.2 (d, $J_{\text{P-C}} = 97.6$ Hz), 132.3 (d, $J_{\text{P-C}} = 94.6$ Hz), 145.0 (d, $J_{\text{P-C}} = 6.1$ Hz), 146.5–146.9 (m); ^{31}P NMR (CDCl_3) δ 27.2. Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{F}_3\text{OP}$: C, 69.00; H, 5.04. Found: C, 68.75; H, 5.15.

Compound **5**: white solid; $[\alpha]_{\text{D}}^{20} -182$ (c 0.31, CHCl_3 , 97% ee). The enantiomeric excess was measured by HPLC (Chiralcel OJ-H column, 0.6 mL/min, hexane/2-propanol = 9/1, 254 nm, $t_1 = 13.5$ min (*R*), $t_2 = 18.1$ min (*S*)); ^1H NMR (CDCl_3) δ 1.03 (t, $J = 7.4$ Hz, 3H), 1.84–2.08 (m, 2H), 3.37

(ddd, $J_{\text{P-H}} = 11.9$ Hz, $J = 8.7, 3.2$ Hz, 1H), 3.37 (s, 3H), 5.39 (d, $J_{\text{P-H}} = 5.0$ Hz, 1H), 5.49 (d, $J_{\text{P-H}} = 4.7$ Hz, 1H), 6.70 (d, $J = 8.7$ Hz, 2H), 7.00 (d, $J = 8.7$, 2H), 7.13–7.23 (m, 2H), 7.27–7.34 (m, 1H), 7.41–7.59 (m, 5H), 7.82–7.91 (m, 2H); ^{13}C NMR δ 13.0 (d, $J_{\text{P-C}} = 13.9$ Hz), 23.4 (d, $J_{\text{P-C}} = 1.5$ Hz), 46.7 (d, $J_{\text{P-C}} = 66.6$ Hz), 55.4, 113.6, 116.8 (d, $J_{\text{P-C}} = 8.8$ Hz), 127.6, 128.0 (d, $J_{\text{P-C}} = 11.3$ Hz), 128.7 (d, $J_{\text{P-C}} = 10.8$ Hz), 131.2 (d, $J_{\text{P-C}} = 8.3$ Hz), 131.2 (d, $J_{\text{P-C}} = 3.6$ Hz), 131.3 (d, $J_{\text{P-C}} = 9.3$ Hz), 131.6 (d, $J_{\text{P-C}} = 2.6$ Hz), 132.5 (d, $J_{\text{P-C}} = 97.7$ Hz), 133.0 (d, $J_{\text{P-C}} = 92.9$ Hz), 136.4 (d, $J_{\text{P-C}} = 4.6$ Hz), 143.1 (d, $J_{\text{P-C}} = 6.6$ Hz), 158.9; ^{31}P NMR (CDCl_3) δ 32.3. Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{O}_2\text{P}$: C, 76.58; H, 6.69. Found: C, 76.10; H, 6.63. HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{26}\text{O}_2\text{P}$ ($\text{M}+\text{H}^+$) 377.1665, found 377.1649.

7

Compound **7**: viscous oil; $[\alpha]_{\text{D}}^{20} -162$ (c 0.86, CHCl_3 , 96% ee). The enantiomeric excess was measured by HPLC (Chiralpak AD–H column, 0.5 mL/min, hexane/2-propanol = 9/1, 254 nm, $t_1 = 52.7$ min (*R*), $t_2 = 57.6$ min (*S*)); ^1H NMR (CDCl_3) δ 0.77 (t, $J = 7.2$ Hz, 3H), 1.13–1.34 (m, 3H), 1.44–1.56 (m, 1H), 1.69–1.86 (m, 1H), 1.92–2.05 (m, 1H), 3.37–3.45 (m, 1H), 3.74 (s, 3H), 5.35 (d, $J_{\text{P-H}} = 5.1$ Hz, 1H), 5.46 (d, $J_{\text{P-H}} = 4.6$ Hz, 1H), 6.66 (d, $J = 8.7$ Hz, 2H), 6.96 (d, $J = 8.7$ Hz, 2H), 7.12–7.20 (m, 2H), 7.24–7.31 (m, 1H), 7.40–7.54 (m, 5H), 7.80–7.88 (m, 2H); ^{13}C NMR δ 13.9, 22.7, 29.8 (d, $J_{\text{P-C}} = 2.1$ Hz), 30.4 (d, $J_{\text{P-C}} = 12.9$ Hz), 45.0 (d, $J_{\text{P-C}} = 45.0$ Hz), 55.4, 113.6, 116.7 (d, $J_{\text{P-C}} = 8.3$ Hz), 127.6 (d, $J_{\text{P-C}} = 1.0$ Hz), 128.0 (d, $J_{\text{P-C}} = 11.9$ Hz), 128.8 (d, $J_{\text{P-C}} = 10.9$ Hz), 131.2 (d, $J_{\text{P-C}} = 2.5$ Hz), 131.2 (d, $J_{\text{P-C}} = 8.3$ Hz), 131.3 (d, $J_{\text{P-C}} = 8.8$ Hz), 131.7 (d, $J_{\text{P-C}} = 2.5$ Hz), 132.5 (d, $J_{\text{P-C}} = 97.7$ Hz), 132.9 (d, $J_{\text{P-C}} = 93.5$ Hz), 136.3 (d, $J_{\text{P-C}} = 4.1$ Hz), 143.4 (d, $J_{\text{P-C}} = 6.6$ Hz), 160.0; ^{31}P NMR (CDCl_3) δ 32.5. HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{30}\text{O}_2\text{P}$ ($\text{M}+\text{H}^+$) 405.1978, found 405.1968.

9

Compound **9**: white solid; $[\alpha]_{\text{D}}^{20} +132$ (c 1.06, CHCl_3 , 64% ee). The enantiomeric excess was measured by HPLC (Chiralpak AS column, 0.8 mL/min, hexane/2-propanol = 98/2, 254 nm, $t_1 = 36.0$ min (*R*), $t_2 = 40.9$ min (*S*)); ^1H NMR (CDCl_3) δ 3.75 (s, 3H), 4.55 (d, $J_{\text{P-H}} = 9.4$ Hz, 1H), 5.48 (s, 1H), 6.23 (d, $J_{\text{P-H}} = 2.3$ Hz, 1H), 6.74 (d, $J = 8.8$ Hz, 2H), 7.10 (d, $J = 8.8$ Hz, 2H), 7.14–7.44 (m, 12H), 7.44–7.51 (m, 1H), 7.76–7.84 (m, 2H); ^{13}C NMR δ 52.2 (d, $J_{\text{P-C}} = 65.1$ Hz), 55.4, 113.8, 118.4 (d, $J_{\text{P-C}} = 7.8$ Hz), 127.2 (d, $J_{\text{P-C}} = 2.6$ Hz), 127.4, 128.1 (d, $J_{\text{P-C}} = 11.4$ Hz), 128.4 (d, $J_{\text{P-C}} = 2.0$ Hz), 128.5 (d, $J_{\text{P-C}} = 11.9$ Hz), 130.2 (d, $J_{\text{P-C}} = 5.6$ Hz), 131.3 (d, $J_{\text{P-C}} = 8.8$ Hz), 131.4 (d, $J_{\text{P-C}} = 2.6$ Hz), 131.4 (d, $J_{\text{P-C}} = 8.8$ Hz), 131.6 (d, $J_{\text{P-C}} = 3.0$ Hz), 132.9 (d, $J_{\text{P-C}} = 97.7$ Hz), 133.0 (d, $J_{\text{P-C}} = 99.2$ Hz), 134.8 (d, $J_{\text{P-C}} = 6.3$ Hz), 135.7 (d, $J_{\text{P-C}} = 8.8$ Hz), 143.7 (d, $J_{\text{P-C}} = 3.6$ Hz), 159.2; ^{31}P NMR (CDCl_3) δ 32.6. Anal. Calcd for $\text{C}_{28}\text{H}_{25}\text{O}_2\text{P}$: C, 79.23; H, 5.94. Found: C, 79.24; H, 6.12.

Compound **10**: white solid. The stereochemistry of (*E*)-**10** was assigned by analogy with the structure of (*E*)-**3a**. ^1H NMR (CDCl_3) δ 2.51 (d, $J_{\text{P-H}} = 2.6$ Hz, 3H), 3.68 (s, 3H), 6.61 (d, $J = 8.7$ Hz, 2H), 6.68–6.75 (m, 2H), 6.77–6.85 (m, 3H), 6.95 (d, $J = 8.7$ Hz, 2H), 7.27–7.35 (m, 4H), 7.35–7.42 (m, 2H), 7.58–7.68 (m, 4H); ^{13}C NMR δ 24.6 (d, $J_{\text{P-C}} = 7.8$ Hz), 55.2, 113.2, 126.0 (d, $J_{\text{P-C}} = 2.0$ Hz), 127.6 (d, $J_{\text{P-C}} = 1.5$ Hz), 128.2 (d, $J_{\text{P-C}} = 12.4$ Hz), 129.4, 131.1 (d, $J_{\text{P-C}} = 4.8$ Hz), 131.2 (d, $J_{\text{P-C}} = 2.5$ Hz), 131.7 (d, $J_{\text{P-C}} = 9.3$ Hz), 132.4 (d, $J_{\text{P-C}} = 9.5$ Hz), 134.2 (d, $J_{\text{P-C}} = 10.2$ Hz), 135.7 (d, $J_{\text{P-C}} = 14.9$ Hz), 139.1 (d, $J_{\text{P-C}} = 10.9$ Hz), 156.5 (d, $J_{\text{P-C}} = 8.3$ Hz), 158.5; ^{31}P NMR (CDCl_3) δ 29.3. Anal. Calcd for $\text{C}_{28}\text{H}_{25}\text{O}_2\text{P}$: C, 79.23; H, 5.94. Found: C, 78.85; H, 6.13.

Compound **12**: white solid. The stereochemistry of (*E*)-**12** was determined by different NOE analysis. ^1H NMR (CDCl_3) δ 1.21 (s, 9H), 1.47 (d, $J_{\text{P-H}} = 2.5$ Hz, 3H), 3.77 (s, 3H), 6.83 (d, $J = 8.7$ Hz, 2H), 7.08 (d, $J = 8.7$ Hz, 2H), 7.40–7.49 (m, 6H), 7.71–7.82 (m, 4H); ^{13}C NMR δ 32.3 (d, $J_{\text{P-C}} = 10.9$ Hz), 33.1 (d, $J_{\text{P-C}} = 4.6$ Hz), 40.4 (d, $J_{\text{P-C}} = 9.3$ Hz), 55.3, 113.4, 128.5 (d, $J_{\text{P-C}} = 11.9$ Hz), 128.9, 131.0 (d, $J_{\text{P-C}} = 2.6$ Hz), 131.4 (d, $J_{\text{P-C}} = 9.9$ Hz), 136.2 (d, $J_{\text{P-C}} = 98.7$ Hz), 138.1 (d, $J_{\text{P-C}} = 87.3$ Hz), 138.7 (d, $J_{\text{P-C}} = 18.1$ Hz), 151.4 (d, $J_{\text{P-C}} = 11.4$ Hz), 158.9; ^{31}P NMR (CDCl_3) δ 36.6. Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{O}_2\text{P}$: C, 77.20; H, 7.23. Found: C, 77.20; H, 7.31.

A Sequence of Reactions Starting with $[\text{RhPh}(\text{PPh}_3)((R)\text{-binap})]$ (13**) in an NMR Sample Tube.** In an NMR sample tube, $[\text{RhPh}(\text{PPh}_3)((R)\text{-binap})]$ (**13**) (106.5 mg, 0.10 mmol) and **1** (25.4 mg, 0.10 mmol) were placed under argon and $\text{THF-}d_8$ (0.5 mL) was added at 25 °C. Then, the mixture was heated at 60 °C for 30 min. After cooling to room temperature, ^{31}P NMR was measured to show the complete conversion of **13** with the formation of complex **14**. ^{31}P NMR ($\text{THF-}d_8$) δ 46.9 (dd, $J_{\text{Rh-P}} = 198$ Hz, $J_{\text{P-P}} = 35$ Hz), 38.4 (ddd, $J_{\text{Rh-P}} = 197$ Hz, $J_{\text{P-P}} = 35$, 13 Hz), 34.9 (dd, $J_{\text{P-P}} = 13$ Hz, $J_{\text{Rh-P}} = 3$ Hz). ^1H NMR ($\text{THF-}d_8$) δ 1.35 (ddd, $J_{\text{P-H}} = 14.7$ Hz, $J = 4.4$, 1.5 Hz, 3H), 2.82 (s, 1H), 2.89 (d, $J = 5.8$ Hz, 1H). To the solution was added phenylboronic acid (24.4 mg, 0.2 mmol) and the mixture was heated at 60 °C for 30 min. The rhodium complex (**14**) was converted into $[\text{RhPh}(\text{PPh}_3)((R)\text{-binap})]$ with the formation of **2c**. For isolation of **14**, after the reaction of **1** and **13** in THF, hexane was slowly added to the reaction mixture and it was allowed to stand for several days. Red crystals were filtered and washed with THF/hexane (2/1) and dried under vacuum (75% yield).

Data for X-ray Crystal Structure of $[(\eta^3\text{-(Ph}_2\text{P(O)C(Me)C(Ph)CH}_2\text{)Rh((R)\text{-binap}))}\cdot 2\text{THF (14}\cdot 2\text{THF)}$

Red crystals of complex **C** suitable for X-ray crystallographic analysis were obtained by recrystallization from THF- d_8 –hexane. The crystals contain THF- d_8 and the data was analyzed as **14**·**2THF**. The ORTEP drawing is shown in Figure S1.

Figure S1. ORTEP illustration of **14**·**2THF** with thermal ellipsoids drawn at 50% probability level (hydrogen atoms are omitted for clarity).

Table S1. Crystal Data of **14**·**2THF**

Empirical Formula	$\text{C}_{74}\text{H}_{52}\text{O}_3\text{P}_3\text{Rh}$
Formula Weight	1185.05
Crystal Color, Habit	red, prism
Crystal Dimensions	0.60 X 0.50 X 0.20 mm
Crystal System	monoclinic
Lattice Type	Primitive
Indexing Images	3 oscillations at 15.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	$a = 11.825(3) \text{ \AA}$ $b = 11.717(3) \text{ \AA}$ $c = 21.291(7) \text{ \AA}$ $\beta = 100.88(1)^\circ$ $V = 2896(1) \text{ \AA}^3$
Space Group	$P2_1$ (#4)
Z value	2
D_{calc}	1.358 g/cm ³
F_{000}	1220.00
$\mu(\text{MoK}\alpha)$	4.27 cm ⁻¹

Table S2. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoK α ($\lambda = 0.71075 \text{ \AA}$)
	graphite monochromated
Detector Aperture	280 mm x 256 mm
Data Images	74 exposures
ω oscillation Range ($\chi=45.0$, $\phi=30.0$)	130.0 - 190.0°
Exposure Rate	100.0 sec./°
ω oscillation Range ($c=45.0$, $f=210.0$)	0.0 - 162.0°
Exposure Rate	100.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{\max}$	55.0°
No. of Reflections Measured	Total: 27770
	Unique: 27763 ($R_{\text{int}} = 0.053$)
Corrections	Lorentz-polarization

Table S3. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	$\sum w (F_{\text{ol}} - F_{\text{cl}})^2$
Least Squares Weights	Chebyshev polynomial with 3 parameters
	181.1110, 235.6200, 82.3208,
$2q_{\max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 10.00\sigma(I)$)	13250
No. Variables	804
Reflection/Parameter Ratio	16.48
Residuals: R ($I > 10.00\sigma(I)$)	0.042
Residuals: R_w ($I > 10.00\sigma(I)$)	0.062
Goodness of Fit Indicator	1.043
Max Shift/Error in Final Cycle	0.003
Maximum peak in Final Diff. Map	1.44 e/ $\text{\AA}^3$
Minimum peak in Final Diff. Map	-2.40 e/ $\text{\AA}^3$

Data for X-ray Crystal Structure of (*S*)-**2e**

Colorless crystals of **2e** suitable for X-ray crystallographic analysis were obtained by recrystallization from EtOAc–hexane. The ORTEP drawing of **2e** is shown in Figure S2.

Figure S2. ORTEP illustration of **2e** with thermal ellipsoids drawn at 50% probability level.

Table S4. Crystal Data of **2e**

Empirical Formula	C ₂₂ H ₂₀ ClOP
Formula Weight	366.83
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.60 X 0.50 X 0.40 mm
Crystal System	triclinic
Lattice Type	Primitive
Indexing Images	3 oscillations at 30.0 seconds
Detector Position	127.40 mm
Pixel Size	0.100 mm
Lattice Parameters	a = 6.106(4) Å b = 13.973(6) Å c = 16.979(8) Å α = 81.21(2)° β = 87.89(2)° γ = 76.99(2)° V = 1394(1) Å ³
Space Group	P1 (#1)
Z value	3
D _{calc}	1.310 g/cm ³
F ₀₀₀	576.00
μ(MoKα)	2.98 cm ⁻¹

Table S5. Intensity Measurements

Diffractometer	Rigaku RAXIS-RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated

Detector Aperture	280 mm x 256 mm
Data Images	44 exposures
ω oscillation Range ($\chi=45.0$, $\phi=0.0$)	130.0 - 190.0°
Exposure Rate	50.0 sec./°
ω oscillation Range ($\chi=45.0$, $\phi=180.0$)	0.0 - 160.0°
Exposure Rate	50.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{\max}$	55.0°
No. of Reflections Measured	Total: 13623
Corrections	Lorentz-polarization

Table S6. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	$\sum w (F_o - F_c)^2$
Least Squares Weights	Chebyshev polynomial with 3 parameters
	281.2830, 384.9210, 113.3190,
$2\theta_{\max}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.10\sigma(I)$)	12069
No. Variables	737
Reflection/Parameter Ratio	16.38
Residuals: R ($I > 3.10\sigma(I)$)	0.047
Residuals: Rw ($I > 3.10\sigma(I)$)	0.071
Goodness of Fit Indicator	1.090
Flack Parameter	-0.03(5)
Max Shift/Error in Final Cycle	0.004
Maximum peak in Final Diff. Map	0.75 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.87 e ⁻ /Å ³