Supporting information for:

Synthesis and Application of Chiral Spiro Phospholane Ligand in Pd-Catalyzed Asymmetric Allylation of Aldehydes with Allylic Alcohols

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General:

All reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glove box (VAC DRI-LAB HE 493) or using standard Schlenk techniques. Commercial reagents were used as received without further purification unless otherwise noticed. Anhydrous diethyl ether, tetrahydrofuran and toluene were distilled from sodium benzophenone ketyl under nitrogen. Anhydrous DMF were freshly distilled from calcium hydride. (*R*)-1,1'-Spirobiindane-7,7'-diol ((*R*)-**5**),¹ (*R*)-7,7'-bistriflate-1,1'-spirobiindane ((*R*)-**6**),² were prepared according to the previous papers. Melting points were measured on a RY-I apparatus and uncorrected. NMR spectra were recorded with a Bruker or Varian spectrometer at 300 MHz (^1H NMR), 75 MHz (^{13}C NMR) and 121.5 MHz (^{31}P NMR). Chemical shifts were reported in ppm down field from internal Me_4Si and external 85% H_3PO_4 , respectively. Optical rotations were determined using a Perkin Elmer Model 341

The dinitrile (*R*)-**7** (3.5 g, 13.0 mmol) was added to a mixture of H₂O (60 mL), HOAc (30 mL) and H₂SO₄ (90 mL) and stirred at 145 °C for 48 hours. The resulting mixture was diluted with water (600 mL), and extracted with ethyl acetate (300 mL) for three times. The organic layer was washed with saturated brine, dried over anhydrous MgSO₄ and concentrated in reduced pressure. The residue was chromatographed with ethyl acetate/petroleum ether 1:1 to afford (*R*)-**8** (4.0 g, 100%). Further purification by recrystallization with toluene gave a white solid, mp 230-231 °C. $[\alpha]_D^{20} +303$ (*c* 0.5, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 10.20 (bs, 2H, CO₂H), 7.63 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.39 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.12 (t, *J* = 7.5 Hz, 2H, Ar-H), 3.15-2.96 (m, 4H, CH₂), 2.53-2.21 (m, 4H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 172.1, 151.5, 145.5, 129.5, 128.8, 126.5, 125.2, 63.3, 38.2, 31.0; MS (EI) *m/z* 308 (*M*⁺, 6), 290 (100); Anal. calcd for C₁₉H₁₆O₄: C 74.01, H 5.23; Found: C 74.07, H 5.40.

Synthesis of (*R*)-7,7'-dihydroxymethyl-1,1'-spirobiindane ((*R*)-**9**)

To a suspension of LiAlH₄ (2.5 g, 64.9 mmol) in diethyl ether (60 mL), a solution of (*R*)-**8** (2.0 g, 6.49 mmol) in diethyl ether (120 mL) was added carefully with stirring at 0 °C within 0.5 hour. After further stirred for 0.5 hour under 0 °C, the system was heated to reflux for 22 hours. After cooling the reaction mixture to ambient temperature, water (100 mL) and 3 M

hydrochloric acid (60 mL) were added slowly. The layers were separated and the aqueous layer was extracted with diethyl ether (100 mL) for three times. The combined organic layer was washed with water (100 mL) and brine (100 mL), dried over anhydrous Na_2SO_4 , and concentrated in reduced pressure. The residue was chromatographed on silica gel with ethyl acetate/petroleum ether 1:2 to afford (*R*)-**9** (1.7 g, 94%) as a white solid, mp 107-108 °C. $[\alpha]_{\text{D}}^{21} +103$ (*c* 0.5, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 7.32-7.20 (m, 6H, Ar-H), 4.22 (dd, *J* = 22.8 and 12.3 Hz, 4H, CH_2), 3.05-3.00 (m, 4H, CH_2), 2.60 (s, 2H, OH), 2.36-2.29 (m, 2H, CH_2), 2.06-1.95 (m, 2H, CH_2); ^{13}C NMR (75 MHz, CDCl_3) δ 147.4, 143.6, 136.7, 128.7, 127.9, 124.4, 61.3, 60.3, 39.7, 31.0; MS (EI) *m/z* 262 ($\text{M}^+ - \text{H}_2\text{O}$, 80), 244 (100); Anal. calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$: C 81.40, H 7.19; Found: C 81.52, H 7.08.

Synthesis of (*R*)-7,7'-dichloromethyl-1,1'-spirobiindane [(*R*)-**10**]

To a solution of (*R*)-**9** (1.45 g, 5.17 mmol) and pyridine (0.35 mL) in CHCl_3 (80 mL) was added fresh distilled SOCl_2 (3.8 mL, 51.7 mmol) in CHCl_3 (40 mL) at 0 °C. After the addition was over, the reaction mixture was stirred at 0°C for 30 min and then heated at reflux for 5 hours. After cooled to ambient temperature, the reaction was then quenched by slow addition of water (100 mL), and the organic layer was separated. The aqueous layer was extracted with CHCl_3 (100 mL) for three times. The combined organic layer was washed with saturated aqueous NaHCO_3 , brine, dried over anhydrous Na_2SO_4 and concentrated in reduced pressure. The residue was chromatographed on silica gel with ethyl acetate/petroleum ether 1:12 to afford (*R*)-**10** (1.41 g, 84%) as a white solid. Further purification by recrystallization from hexane afforded a colorless crystal, mp 168-169 °C. $[\alpha]_{\text{D}}^{21} +230$ (*c* 0.5, CH_2Cl_2); ^1H NMR (300 MHz, CDCl_3) δ 7.29-7.24 (m, 6H, Ar-H), 4.14 (d, *J* = 1.2 Hz, 4H, CH_2),

3.07-3.02 (m, 4H, CH₂), 2.38-2.21 (m, 4H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 147.2, 144.2, 133.8, 129.9, 128.4, 125.4, 61.6, 42.9, 39.0, 31.0; MS (EI) m/z 316 (M⁺, 14), 278 (100); Anal. calcd for C₁₉H₁₈Cl₂: C 71.93, H 5.92; Found: C 71.75, H 5.80.

Phospholane ligand (*R*)-4⁴

To a suspension of (*R*)-**10** (400 mg, 1.26 mmol) and NaH (95 mg, 3.96 mmol) in THF (22 ml) was added phenylphosphine (153 mg, 1.39 mmol) at $-78\text{ }^{\circ}\text{C}$ under nitrogen. The mixture was stirred at ambient temperature for 24 hours and then heated at refluxing for another 24 hours. After the reaction was completed (monitored by TLC), the solvent was removed in vacuum and the residue was passed through a silica gel plug with ethyl acetate/petroleum ether 1:10 under nitrogen atmosphere to afford the fairly pure product (*R*)-**4** (418 mg, 94%) as a solid, mp $148\text{--}150\text{ }^{\circ}\text{C}$. $[\alpha]_{\text{D}}^{21} +6$ (c 0.5, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.31-6.93 (m, 9H, Ar-H), 6.70 (t, $J = 7.5$ Hz, 1H, Ar-H), 5.71 (d, $J = 7.5$ Hz, 1H, Ar-H), 3.12-2.70 (m, 7H, CH₂), 2.58-2.51 (m, 1H, CH₂), 2.31-2.17 (m, 2H, CH₂), 1.99-1.73 (m, 2H, CH₂); ¹³C NMR (75 MHz, CDCl₃) δ 148.0, 146.8, 143.4, 142.7, 132.8, 132.6, 129.1, 128.7, 128.6, 128.4, 128.2, 128.0, 127.8, 126.4, 123.1, 122.6, 61.5, 38.7, 37.8, 30.9, 30.8, 30.6, 30.0, 29.6, 29.3, 25.7; ³¹P NMR (121 MHz, CDCl₃) δ -19.3 (s); HRMS (FAB) calcd for C₂₅H₂₃P: 355.1599; Found 355.1610.

(B) General Procedure for Asymmetric Allylation of Aldehydes

In a Schlenk tube, Pd(OAc)₂ (1.5 mg, 6.7 μmol), (*R*)-**4** (5 mg, 14.1 μmol) and THF (0.8 mL) were added under nitrogen. The reaction mixture was stirred at 25 °C for 30 min, then the fresh distilled benzaldehyde (18 mg, 1.7 mmol), cinnamyl alcohol (19 mg, 1.4 mmol) and Et₃B (0.7 mL, 1.0 M in hexane, 0.7 mmol) were added sequentially. After stirred at 25 °C for 12 hours, the consuming of cinnamyl alcohol was complete monitored by TLC. The reaction mixture was diluted with ethyl acetate (40 mL) and hydrolyzed with 3 M hydrochloric acid (10 mL). After separated with aqueous phase, the organic layer was washed with saturated aqueous NaHCO₃, and brine, dried over anhydrous Na₂SO₄ and concentrated in reduced pressure. The product was purified by a flash chromatography with ethyl acetate/petroleum ether 1:6 to afford *anti*-(1*R*,2*S*)-1,2-diphenylbut-3-en-1-ol **13a**⁵ as a colorless oil. The analytical data of products are listed as follow.

(C) Analytical Data of Allylation Products

***anti*-(1*R*,2*S*)-1,2-Diphenylbut-3-en-1-ol (13a):**⁵ colorless oil, 80% yield, 82% ee. [α]_D¹⁸ +6.5 (*c* 0.71, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.26-7.04 (m, 10H, Ar-H), 6.26 (ddd, *J* = 16.8, 10.2 and 8.7 Hz, 1H, CH), 5.29-5.21 (m, 2H, CH₂), 4.85 (dd, *J* = 7.8 and 2.4 Hz, 1H, CH), 3.55 (t, *J* = 8.4 Hz, 1H, CH), 2.30 (d, *J* = 2.7 Hz, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 142.1, 140.9, 138.1, 128.6, 128.2, 127.7, 126.9, 118.7, 77.5, 59.5; MS (EI) *m/z* 224 (M⁺, 2), 107 (100); HPLC (Chiralpak AD-H column, *n*-Hexane/2-PrOH = 98:2, 0.9 mL/min) *t*_R = 24.6 min (minor), *t*_R = 27.5 min (major).

***anti*-1-(4-Methoxyphenyl)-2-phenylbut-3-en-1-ol (13b):**⁶ colorless oil, 97% yield, 74% ee. [α]_D¹⁹ +6.8 (*c* 0.77, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.25-7.03 (m, 7H, Ar-H), 6.74-6.71 (m, 2H, Ar-H), 6.25 (ddd, *J* = 16.8, 10.2 and 9.0 Hz, 1H, CH), 5.28-5.21 (m, 2H,

CH₂), 4.80 (dd, $J = 8.1$ and 2.4 Hz, 1H, CH), 3.74 (s, 3H, CH₃), 3.52 (t, $J = 8.4$ Hz, 1H, CH), 2.29 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 159.0, 140.9, 138.4, 134.2, 129.0, 128.6, 128.1, 126.8, 118.5, 113.5, 77.0, 59.6, 55.4; MS (EI) m/z 254 (M^+ , 1), 137 (100); HPLC (Chiralpak AD-H column, *n*-Hexane/2-PrOH = 98:2, 0.9 mL/min) $t_R = 27.3$ min (major), $t_R = 31.4$ min (minor).

***anti*-1-(2-Methoxyphenyl)-2-phenylbut-3-en-1-ol (13c):** colorless oil, 91% yield, 69% ee. $[\alpha]_D^{20} +5$ (c 0.12, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.17-7.07 (m, 7H, Ar-H), 6.79-6.68 (m, 2H, Ar-H), 6.22 (ddd, $J = 17.1$, 10.2 and 8.4 Hz, 1H, CH), 5.14-4.98 (m, 3H, CH and CH₂), 3.72-3.65 (m, 4H, CH and CH₃), 2.59 (d, $J = 6.0$ Hz, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 156.4, 141.7, 138.0, 130.2, 128.3, 128.1, 128.0, 126.3, 120.4, 117.6, 110.3, 73.9, 56.7, 55.2; MS (EI) m/z 254 (M^+ , 1), 137 (100); Anal. calcd for C₁₇H₁₈O₂: C 80.28, H 7.13; Found: C 80.35, H 6.97. HPLC (Chiralpak AD-H column, *n*-Hexane/2-PrOH = 95:5, 0.9 mL/min) $t_R = 22.0$ min (minor), $t_R = 26.5$ min (major).

***anti*-1-(4-Trifluoromethylphenyl)-2-phenylbut-3-en-1-ol (13d):** colorless oil, 71% yield, 58% ee. $[\alpha]_D^{20} +2.9$ (c 0.99, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.47-7.03 (m, 9H, Ar-H), 6.23 (ddd, $J = 17.1$, 10.2 and 9 Hz, 1H, CH), 5.32-5.22 (m, 2H, CH₂), 4.89 (dd, $J = 7.8$ and 2.4 Hz, 1H, CH), 3.50 (t, $J = 8.4$ Hz, 1H, CH), 2.40 (d, $J = 2.4$ Hz, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 145.7, 139.9, 137.2, 128.6, 128.2, 127.0, 124.9, 124.8, 119.2, 59.4; MS (EI) m/z 292 (M^+ , 6), 118 (100); Anal. calcd for C₁₇H₁₅F₃O: C 69.85, H 5.17; Found: C 69.72, H 5.12. HPLC (Chiralpak AD-H column, *n*-Hexane/2-PrOH = 98:2, 0.9 mL/min) $t_R = 14.9$ min (major), $t_R = 16.8$ min (minor).

***anti*-1-(1-Naphtyl)-2-phenylbut-3-en-1-ol (13e):** pale yellow oil, 99% yield, 79% ee. $[\alpha]_D^{15} +9$ (c 0.45, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 8.09-8.06 (m, 1H, Ar-H), 7.85-7.74 (m, 2H, Ar-H), 7.53-7.36 (m, 4H, Ar-H), 7.24-7.12 (m, 5H, Ar-H), 6.32 (ddd, $J = 16.5$, 10.2 and 8.4 Hz, 1H, CH), 5.67 (dd, $J = 5.1$ and 3.3 Hz, 1H, CH), 5.21 (dd, $J = 10.2$ and 1.2 Hz, 1H, CH₂), 4.99 (dd, $J = 17.1$ and 1.2 Hz, 1H, CH₂), 3.91 (dd, $J = 8.7$ and 5.4 Hz, 1H, CH), 2.32 (d, $J = 3.3$ Hz, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 141.7, 137.7, 136.7, 133.7,

130.5, 129.0, 128.5, 128.2, 128.1, 126.7, 125.9, 125.3, 125.1, 124.6, 123.2, 118.6, 74.2, 56.6; MS (EI) m/z 274 (M^+ , 6), 157 (100); Anal. calcd for $C_{17}H_{18}O_2$: C 87.56, H 6.61; Found: C 87.69, H 6.77. HPLC (Chiralpak AD-H column, *n*-Hexane/2-PrOH = 98:2, 0.9 mL/min) t_R = 39.9 min (minor), t_R = 57.2 min (major).

***anti*-1-(2-Naphtyl)-2-phenylbut-3-en-1-ol (13f):** colorless oil, 95% yield, 73% ee. $[\alpha]_D^{15}$ -6 (c 0.54, CH_2Cl_2); 1H NMR (300 MHz, $CDCl_3$) δ 7.78-7.07 (m, 12H, Ar-H), 6.29 (ddd, J = 17.1, 10.2 and 9.0 Hz, 1H, CH), 5.29-5.21 (m, 2H, CH_2), 5.02 (dd, J = 7.8 and 2.4 Hz, 1H, CH), 3.66 (t, J = 8.1 Hz, 1H, CH), 2.41 (d, J = 2.7 Hz, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.6, 139.3, 137.8, 133.0, 132.9, 128.4, 128.3, 128.0, 127.1, 126.7, 125.9, 124.7, 118.6, 77.3, 59.1; MS (EI) m/z 274 (M^+ , 3), 157 (100); Anal. calcd for $C_{17}H_{18}O_2$: C 87.56, H 6.61; Found: C 87.35, H 6.58. HPLC (Chiralpak AD-H column, *n*-Hexane/2-PrOH = 95:5, 0.9 mL/min) t_R = 28.5 min (minor), t_R = 30.0 min (major).

***anti*-1-(2-Furyl)-2-phenylbut-3-en-1-ol (13g):** colorless oil, 73% yield, 78% ee. $[\alpha]_D^{15}$ $+47$ (c 0.19, CH_2Cl_2); 1H NMR (300 MHz, $CDCl_3$) δ 7.32-7.13 (m, 6H, Ar-H), 6.28-6.16 (m, 2H, Ar-H), 6.01 (d, J = 3.0 Hz, 1H, CH), 5.30-5.23 (m, 2H, CH_2), 4.89 (dd, J = 8.1 and 3.9 Hz, 1H, CH), 3.84 (t, J = 8.1 Hz, 1H, CH), 2.27 (d, J = 3.9 Hz, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 141.9, 140.3, 137.6, 128.4, 128.1, 126.8, 118.6, 110.1, 107.6, 70.9, 55.9; MS (EI) m/z 214 (M^+ , 2), 39 (100); Anal. calcd for $C_{14}H_{14}O_2$: C 78.48, H 6.59; Found: C 78.29, H 6.62. HPLC (Chiralpak AD-H column, *n*-Hexane/2-PrOH = 98:2, 0.9 mL/min) t_R = 20.2 min (major), t_R = 21.6 min (minor).

***anti*-1-Cyclohexyl-2-phenylbut-3-en-1-ol (13h):**⁷ colorless oil, 50% yield, 83% ee. $[\alpha]_D^{18}$ $+38$ (c 0.52, CH_2Cl_2); 1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.20 (m, 5H, Ar-H), 6.14 (ddd, J = 17.1, 8.1 and 6.9 Hz, 1H, CH), 5.22-5.16 (m, 2H, CH_2), 3.57-3.43 (m, 1H, CH), 1.81-1.01 (m, 12H, OH and CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 138.4, 128.7, 128.0, 126.5, 117.7, 78.1, 53.7, 39.6, 30.2, 26.5, 26.4, 26.0; MS (EI) m/z 117 (98), 95 (100); HPLC (Chiralpak AD-H column, *n*-Hexane/2-PrOH = 98:2, 0.9 mL/min) t_R = 11.4 min (major), t_R = 13.3 min (minor).

(R)-1-phenylbut-3-en-1-ol (16):⁸ colorless oil, 80% yield, 80% ee. $[\alpha]_D^{15} +22$ (*c* 0.14, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃) δ 7.35–7.24 (m, 5H, Ar-H), 5.89-5.75 (m, 1H, CH), 5.19-5.11 (m, 2H, CH₂), 4.74-4.69 (m, 1H, CH), 2.53-2.47 (m, 2H, CH₂), 2.16 (s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 144.1, 134.7, 128.7, 127.8, 126.1, 118.7, 73.5, 44.1; MS (EI) *m/z* 148 (M⁺, 8), 107 (100); HPLC (Chiralpak AD-H column, *n*-Hexane/2-PrOH = 98:2, 1.0 mL/min) *t*_R = 17.8 min (major), *t*_R = 18.7 min (minor).

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(D) Copies of ^1H and ^{13}C NMR Spectra