Supporting Information

Catalytic Asymmetric Synthesis of Optically Active Atropisomeric
Anilides through Enantioselective *N*-Allylation with Chiral Pd-tol-
BINAP Catalyst.

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Supporting Information Available. Experimental procedures for the preparation and characterization data of products **1c-1j**. This material is available free of charge via Internet at <http://pubs.acs.org>.

Experimental Section

Melting points were uncorrected. ^1H and ^{13}C NMR spectra were recorded on a 300-MHz or 400-MHz spectrometer. In ^1H and ^{13}C NMR spectra, chemical shifts were expressed in δ (ppm) downfield from CHCl_3 (7.26 ppm) and CDCl_3 (77.0 ppm), respectively. Mass spectra were recorded by electron impact or chemical ionization. Column chromatography was performed on silica gel (75-150 μm). Medium-pressure liquid chromatography (MPLC) was performed on a 30 X 4 cm i. d. prepacked column (silica gel, 50 μm) with a UV detector. High-performance liquid chromatography (HPLC) was performed on a 25 X 0.4 cm i. d. chiral column with a UV detector.

General procedure of asymmetric allylation using tol-BINAP-Pd complex. Under Ar atmosphere, to a solution of allylpalladium chloride dimer (4 mg, 0.011 mmol) and (*S*)-tol-BINAP (15 mg, 0.022 mmol) in THF (3 mL) was added diallyl carbonate (108 μL , 0.75 mmol), and then the reaction mixture was stirred for 10 min at rt. Subsequently, acryl amide **2a** (102 mg, 0.5 mmol) was added to the mixture. After being stirred for 15 h at rt, the mixture was poured into 2 % HCl solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over MgSO_4 , and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 20) gave **1a** (114 mg, 94 %).

(*S*)-*N*-Allyl-*N*-2-(*tert*-butyl)phenyl 2-butenamide [(+)-1c**].** (+)-**1c** was prepared from **2c** (109 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of (+)-**1a**. Purification by column chromatography (hexane/AcOEt = 12) gave (+)-**1c** (120 mg, 93 %). The ee (36 %ee) of **1c** was determined by HPLC analysis using CHIRALPACK AS column [25 cm x 0.46 cm i.d.; 1 % *i*-PrOH in hexane; flow rate, 0.5 mL/min; (-)-**1c** (minor); t_R = 16.9 min, (+)-**1c** (major); t_R = 18.9 min]. (+)-**2c**: colorless oil; $[\alpha]_D = +71.8$ (c = 1.0, CHCl_3 , 36 %ee); IR (neat) 1666, 1620 cm^{-1} ; ^1H NMR (CDCl_3) δ : 7.56 (1H, dd, J = 1.3, 8.2 Hz), 7.32 (1H, dt, J = 1.3, 8.0 Hz), 7.18 (1H, dt, J = 1.3, 8.0 Hz), 6.93 (1H, dd, J = 1.3, 7.6 Hz), 6.92 (1H, qd, J = 7.0, 15.0 Hz), 6.02 (1H, dddd, J = 5.1, 8.1, 10.0, 17.2 Hz), 5.56 (1H, dd, J = 1.5, 15.0 Hz), 5.15 (1H, d, J = 10.0 Hz), 5.08 (1H, d, J = 17.2 Hz), 4.98 (1H, dd,

$J = 5.1, 14.2$ Hz), 3.37 (1H, dd, $J = 8.1, 14.2$ Hz), 1.70 (3H, dd, $J = 1.5, 7.0$ Hz), 1.35 (9H, s); ^{13}C NMR (CDCl_3) δ : 165.6, 146.4, 140.8, 139.2, 132.5, 131.9, 129.3, 128.2, 126.4, 123.1, 118.1, 53.8, 35.7, 31.8, 17.5; MS (m/z) 257 (M^+); Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_2$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.33; H, 8.84; N, 5.45.

(S)-N-Allyl-N-2-(tert-butyl)phenyl 3-phenyl-propenamide [(+)-1d]. (+)-**1d** was prepared from **2d** (140 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of (+)-**1a**. Purification by column chromatography (hexane/AcOEt = 10) gave (+)-**1d** (153 mg, 96 %). The ee (37 %ee) of **1d** was determined by HPLC analysis using CHIRALCEL OD column [25 cm x 0.46 cm i.d.; 5 % *i*-PrOH in hexane; flow rate, 0.5 mL/min; (-)-**1d** (minor); $t_R = 10.9$ min, (+)-**1d** (major); $t_R = 13.8$ min]. (+)-**1d**: white solid; $[\alpha]_D = +75.1$ ($c = 1.0$, CHCl_3 , 37 %ee); mp 67.0-69.0 °C (37 %ee); IR (KBr) 1652, 1610 cm^{-1} ; ^1H NMR (CDCl_3) δ : 7.67 (1H, d, $J = 15.6$ Hz), 7.61 (1H, dd, $J = 1.4, 8.2$ Hz), 7.38 (1H, dt, $J = 1.4, 8.0$ Hz), 7.24-7.28 (5H, m), 7.21 (1H, dt, $J = 1.4, 8.0$ Hz), 7.01 (1H, dd, $J = 1.4, 7.7$ Hz), 6.17 (1H, d, $J = 15.6$ Hz), 6.08 (1H, dddd, $J = 5.1, 8.0, 10.1, 17.1$ Hz), 5.19 (1H, d, $J = 10.1$ Hz), 5.13 (1H, dd, $J = 1.1, 17.2$ Hz), 5.05 (1H, dd, $J = 5.1, 14.2$ Hz), 3.46 (1H, dd, $J = 8.0, 14.2$ Hz), 1.38 (9H, s); ^{13}C NMR (CDCl_3) δ : 165.9, 146.8, 141.6, 139.3, 134.9, 132.5, 132.1, 129.5, 129.3, 128.6, 128.5, 127.6, 126.7, 119.0, 118.6, 54.2, 35.9, 32.0; MS (m/z) 319 (M^+); Anal. Calcd for $\text{C}_{22}\text{H}_{25}\text{NO}$: C, 82.74; H, 7.89; N, 4.38. Found: C, 82.74; H, 7.92; N, 4.38.

(S)-N-Allyl-N-2-(tert-butyl)phenyl 2-oxo-2-phenylacetamide [(+)-1e]. (+)-**1e** was prepared from **2e** (141 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of (+)-**1a**. Purification by column chromatography (hexane/AcOEt = 12) gave (+)-**1e** (153 mg, 95 %). The ee (35 %ee) of **1e** was determined by HPLC analysis using CHIRALCEL OD column [25 cm x 0.46 cm i.d.; 5 % *i*-PrOH in hexane; flow rate, 1.0 mL/min; (-)-**1e** (minor); $t_R = 5.5$ min, (+)-**1e** (major); $t_R = 7.8$ min]. (+)-**1e**: white solid; $[\alpha]_D = +72.1$ ($c = 1.0$, CHCl_3 , 35 %ee); mp 114.5-115.0 °C (35 %ee); IR (KBr) 1680, 1638 cm^{-1} ; ^1H NMR (CDCl_3) δ : 7.84 (2H, dd, $J = 1.3, 7.8$ Hz), 7.55 (1H, d, $J = 8.5$ Hz), 7.52 (1H, dd, $J = 1.4, 8.1$ Hz), 7.43 (2H, t, $J = 7.8$ Hz), 7.24 (1H, dt, $J = 1.5, 8.0$ Hz), 6.83 (1H, dt, $J = 1.5, 7.6$ Hz), 6.71 (1H, dd, $J = 1.5, 7.8$ Hz), 6.08 (1H, dddd, $J = 5.7, 7.9, 10.2, 18.0$ Hz), 5.28 (1H, d, $J = 10.2$ Hz), 5.25 (1H, dd, $J = 1.2, 18.0$ Hz), 5.13 (1H, dd, $J = 5.7, 14.0$ Hz), 3.51 (1H, dd, $J = 7.9, 14.0$ Hz), 1.47 (9H, s); ^{13}C NMR (CDCl_3) δ : 189.8, 166.0, 147.6, 134.0, 133.9, 132.0, 131.3, 131.1, 130.9,

129.3, 129.0, 128.6, 125.9, 120.3, 53.9, 36.6, 32.3; MS (m/z) 321 (M⁺); Anal. Calcd for C₂₁H₂₃NO₂: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.33; H, 7.39; N, 4.17. In ¹H and ¹³C NMR spectra of **1e**, the minor signals on the basis of the existence of the amide C-N rotamer were also observed in a ratio of 4:1.

N-Allyl-N-2-(tert-butyl)phenyl propanamide [(+)-1f]. (+)-**1f** was prepared from **2f** (103 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of (+)-**1a**. Purification by column chromatography (hexane/AcOEt = 10) gave (+)-**1f** (110 mg, 90 %). The ee (32 %ee) of **1f** was determined by HPLC analysis using CHIRALCEL OD column [25 cm x 0.46 cm i.d.; 5 % *i*-PrOH in hexane; flow rate, 1.0 mL/min; (-)-**1f** (minor); *t_R* = 4.3 min, (+)-**1f** (major); *t_R* = 4.8 min]. (+)-**1f**: colorless oil; [α]_D = +44.2 (c = 1.0, CHCl₃, 32 %ee); IR (neat) 1659 cm⁻¹; ¹H NMR (CDCl₃) δ: 7.56 (1H, dd, *J* = 1.5, 8.2 Hz), 7.32 (1H, dt, *J* = 1.5, 7.9 Hz), 7.18 (1H, dt, *J* = 1.5, 7.9 Hz), 6.93 (1H, dd, *J* = 1.5, 7.9 Hz), 6.00 (1H, dddd, *J* = 5.3, 8.2, 10.3, 17.3 Hz), 5.15 (1H, d, *J* = 10.3 Hz), 5.07 (1H, dd, *J* = 1.2, 17.3 Hz), 4.95 (1H, dd, *J* = 5.3, 14.1 Hz), 3.32 (1H, dd, *J* = 8.2, 14.1 Hz), 1.97 (2H, q, *J* = 7.6 Hz), 1.37 (9H, s), 1.04 (3H, t, *J* = 7.6 Hz); ¹³C NMR (CDCl₃) δ: 173.8, 146.0, 139.8, 132.7, 131.6, 129.7, 128.3, 126.6, 118.4, 54.1, 36.3, 32.3, 28.8, 9.5; MS (m/z) 245 (M⁺); Anal. Calcd for C₁₆H₂₃NO: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.04; H, 9.49; N, 5.60.

N-Allyl-N-2-(tert-butyl)phenyl acetamide [(+)-1g]. (+)-**1g** was prepared from **2g** (96 mg, mmol) in accordance with the general procedure for the synthesis of (+)-**1a**. Purification by column chromatography (hexane/AcOEt = 10) gave (+)-**1g** (107 mg, 93 %). The ee (36 %ee) of **1g** was determined by HPLC analysis using CHIRALCEL OD column [25 cm x 0.46 cm i.d.; 5 % *i*-PrOH in hexane; flow rate, 0.5 mL/min; (-)-**1g** (minor); *t_R* = 10.8 min, (+)-**1g** (major); *t_R* = 11.9 min]. (+)-**1g**: colorless oil; [α]_D = +48.3 (c = 1.0, CHCl₃, 36 %ee); IR (neat) 1660 cm⁻¹; ¹H NMR (CDCl₃) δ: 7.56 (1H, dd, *J* = 1.5, 8.2 Hz), 7.32 (1H, dt, *J* = 1.5, 7.9 Hz), 7.18 (1H, dt, *J* = 1.5, 7.9 Hz), 6.94 (1H, dd, *J* = 1.5, 7.6 Hz), 6.00 (1H, dddd, *J* = 5.0, 8.2, 9.7, 17.0 Hz), 5.15 (1H, d, *J* = 9.7 Hz), 5.07 (1H, dd, *J* = 1.5, 17.0 Hz), 4.95 (1H, dd, *J* = 5.0, 14.1 Hz), 3.33 (1H, dd, *J* = 8.2, 14.2 Hz), 1.80 (3H, s), 1.39 (9H, s); ¹³C NMR (CDCl₃) δ: 170.9, 146.3, 140.4, 132.7, 131.9, 129.9, 128.5, 126.8, 118.6, 53.9, 36.1, 32.1, 23.4; MS (m/z) 231 (M⁺); HRMS calcd for C₁₁H₁₂NO (M⁺-*t*-Bu): 174.0919, found 174.0930.

***N*-Allyl-*N*-2,5-(bis-*tert*-butyl)phenyl propeamide [(+)-**1h**].** (+)-**1h** was prepared from **2h** (130 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of (+)-**1a**. Purification by column chromatography (hexane/AcOEt = 12) gave (+)-**1h** (138 mg, 92 %). The ee (35 %ee) of **1h** was determined by HPLC analysis using CHIRALCEL OD column [25 cm x 0.46 cm i.d.; 1 % *i*-PrOH in hexane; flow rate, 1.0 mL/min; (-)-**1h** (minor); t_R = 5.6 min, (+)-**1h** (major); t_R = 6.8 min]. (+)-**1h**: colorless oil; $[\alpha]_D^{25} = +54.7$ (c = 1.0, CHCl₃, 35 %ee); IR (neat) 1661, 1617 cm⁻¹; ¹H NMR (CDCl₃) δ : 7.47 (1H, d, J = 8.5 Hz), 7.34 (1H, dd, J = 2.4, 8.5 Hz), 6.90 (1H, d, J = 2.4 Hz), 6.37 (1H, dd, J = 2.1, 16.7 Hz), 6.07 (1H, dddd, J = 5.5, 8.2, 10.0, 17.3 Hz), 5.93 (1H, dd, J = 10.3, 16.7 Hz), 5.47 (1H, dd, J = 2.1, 10.3 Hz), 5.18 (1H, dd, J = 0.7, 10.0 Hz), 5.11 (1H, dd, J = 1.2, 17.3 Hz), 5.00 (1H, tdd, J = 1.2, 5.5, 13.8 Hz), 3.38 (1H, dd, J = 8.2, 13.8 Hz), 1.34 (9H, s), 1.26 (9H, s); ¹³C NMR (CDCl₃) δ : 165.4, 149.6, 143.2, 138.7, 132.5, 129.3, 128.9, 127.1, 125.1, 118.6, 54.4, 35.8, 34.3, 32.3, 31.2; MS (m/z) 300 (M^+ +1); Anal. Calcd for C₂₀H₂₉NO: C, 88.22; H, 9.76; N, 4.68. Found: C, 79.97; H, 9.54; N, 4.62. The lack of an aromatic carbon resonance in the ¹³C NMR of **1h** is due to overlap of signals.

***N*-Allyl-*N*-2-(*tert*-butyl)phenyl 2-furamide [(+)-**1i**].** (+)-**1i** was prepared from **2i** (136 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of (+)-**1a**. Purification by column chromatography (hexane/AcOEt = 12) gave (+)-**1i** (136 mg, 96 %). The ee (34 %ee) of **1i** was determined by HPLC analysis using CHIRALCEL OD column [25 cm x 0.46 cm i.d.; 5 % *i*-PrOH in hexane; flow rate, 1.0 mL/min; (-)-**1i** (minor); t_R = 7.7 min, (+)-**1i** (major); t_R = 16.3 min]. (+)-**1i**: white solid; $[\alpha]_D^{25} = +35.7$ (c = 1.0, CHCl₃, 34 % ee); mp 71-72 °C (34 %ee); IR (KBr) 1637 cm⁻¹; ¹H NMR (CDCl₃) δ : 7.59 (1H, dd, J = 1.5, 7.9 Hz), 7.39 (1H, dt, J = 1.5, 7.6 Hz), 7.35 (1H, d, J = 1.8 Hz), 7.21 (1H, dt, J = 1.5, 7.6 Hz), 7.04 (1H, dd, J = 1.5, 7.6 Hz), 6.15 (1H, dd, J = 1.8, 3.5 Hz), 6.11 (1H, m), 5.38 (1H, d, J = 3.5 Hz), 5.08-5.22 (3H, m), 3.46 (1H, dd, J = 8.4, 14.3 Hz), 1.29 (9H, s); ¹³C NMR (CDCl₃) δ : 158.6, 147.0, 146.7, 144.2, 139.3, 132.2, 132.2, 129.9, 128.7, 126.6, 118.9, 116.3, 110.8, 55.3, 36.3, 32.3; MS (m/z) 283 (M^+); Anal. Calcd for C₁₈H₂₁NO₂: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.08; H, 7.70; N, 4.78.

***N*-Allyl-*N*-2-(*tert*-butyl)phenyl 2-benzamide [(+)-**1j**].** Under Ar atmosphere, to a suspension of NaH (20 mg, 0.5 mmol) in THF (2 mL) was added amide **1j** (127 mg, 0.5 mmol). After being stirred for 10 min at rt, allylpalladium chloride dimer (4 mg, 0.011 mmol), (*S*)-tol-BINAP (15 mg, 0.022

mmol) and allyl acetate (81 μ L, 0.75 mmol) in THF (1 mL) were added to the mixture, and then the reaction mixture was stirred for 1 h at rt. The mixture was poured into 2 % HCl solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over MgSO_4 , and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 12) gave **1j** (141 mg, 96 %). The ee (33 %ee) of **1j** was determined by HPLC analysis using CHIRALCEL OD column [25 cm x 0.46 cm i.d.; 5 % *i*-PrOH in hexane; flow rate, 0.5 mL/min; (-)-**1j** (minor); t_R = 14.9 min, (+)-**1j** (major); t_R = 16.5 min]. (+)-**1j**: colorless oil; $[\alpha]_D = +20.4$ (c = 1.0, CHCl_3 , 33 %ee); IR (KBr) 1637 cm^{-1} ; ^1H NMR (CDCl_3) δ : 7.11-7.60 (9H, m), 6.15 (0.8H, dddd, J = 5.0, 8.2, 10.0, 16.7 Hz), 5.82 (0.2H, m), 5.22 (0.8H, d, J = 10.0 Hz), 5.18 (0.8H, dd, J = 1.5, 16.7 Hz), 5.12 (0.8H, dd, J = 5.0, 14.1 Hz), 5.04 (0.2H, d, J = 10.0 Hz), 4.50 (0.2H, dd, J = 7.0, 15.3 Hz), 3.75 (0.2H, dd, J = 7.3, 15.3 Hz), 3.55 (0.8H, dd, J = 8.2, 14.1 Hz), 1.25 (9H, s); ^{13}C NMR (CDCl_3) δ : 168.7, 146.0, 140.0, 135.9, 132.8, 132.5, 130.6, 129.6, 129.3, 128.2, 127.4, 126.2, 118.7, 56.0, 36.2, 32.2; MS (m/z) 294 ($\text{M}^+ + 1$); Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{NO}$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.67; H, 8.01; N, 4.67.