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Supporting Information

Title

**Efficient Synthesis of Optically Active Atropisomeric Anilides
through Catalytic Asymmetric *N*-Arylation Reaction.**

Authored by

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The Contents of Supporting Information: Experimental procedures and characterization data for compounds **2a-2g**, **3a-3d**, **4a-4d**, **5b**; X-ray structural data and reaction scheme for the determination of absolute configuration of **2a**, **2c**, **2d**, **4b**; a list of chiral phosphine ligands examined.

Experimental Section

Melting points were uncorrected. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer. In ^1H and ^{13}C NMR spectra, chemical shifts were expressed in (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 catalytic asymmetric intermolecular *N*-arylation.

Under Ar atmosphere, to a suspension of *tert*-BuOK (78.5 mg, 0.7 mmol) in toluene (1.0 mL) was added anilide **1a** (103 mg, 0.5 mmol) and *p*-nitroiodobenzene (137 mg, 0.55 mmol). After being stirred for 5 min at rt, $\text{Pd}(\text{OAc})_2$ (4 mg, 0.017 mmol) and (R) -(-)-DTBM-SEGPHOS (29.5 mg, 0.025 mmol) in toluene (1.0 mL) were added to the mixture, and then the reaction mixture was stirred for 2 h at 80°C . 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 = 15) and subsequent MPLC (hexane/AcOEt = 9) gave **2a** (138 mg, 84%). The ee (93%ee) of **2a** was determined by HPLC analysis using a CHIRALPACK AS-H column [25 cm x 0.46 cm i.d.; 10% *i*-PrOH in hexane; flow rate, 0.2 mL/min; (-)-**2a** (minor); t_R = 35.6 min, (+)-**2a** (major); t_R = 37.7 min].

***N*-(2-*tert*-Butylphenyl)-*N*-(4-nitrophenyl)propanamide (2a).** **2a** (93%ee): pale yellow solid; mp 114-116 °C; $[\alpha]_D = +238.9$ ($c = 1.0$, CHCl_3); IR (KBr) 1688 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) : 8.10-8.16 (2H, m), 7.67 (1H, dd, $J = 1.5, 8.0$ Hz), 7.48-7.54 (2H, m), 7.46 (1H, dd, $J = 1.5, 8.0$ Hz), 7.38 (1H, dd, $J = 1.5, 8.0$ Hz), 7.11 (1H, dt, $J = 1.5, 8.0$ Hz), 2.24 (1H, qd, $J = 7.3, 17.0$ Hz), 2.13 (1H, qd, $J = 7.3, 17.0$ Hz), 1.21 (9H, s), 1.13 (3H, t, $J = 7.3$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) : 174.8, 148.4, 146.9, 143.2, 138.0, 132.6, 130.6, 129.7, 127.8, 123.9, 122.8, 36.2, 31.7, 31.2, 9.4; MS (m/z) 327 (MH^+); Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_3$: C, 69.92; H, 6.79; N, 8.58. Found: C, 69.80; H, 6.92; N, 8.19.

***N*-(2,5-Bis-*tert*-butylphenyl)-*N*-(4-nitrophenyl)propanamide (2b).** **2b** was prepared from **1b** (131 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of **2a** (80 °C, 3 h). Purification by column chromatography (hexane/AcOEt = 40) and subsequent MPLC (hexane/AcOEt = 17) gave **2b** (154 mg, 81%). The ee (95%ee) of **2b** was determined by HPLC analysis using a CHIRALPACK AS-H column [25 cm x 0.46 cm i.d.; 10 % *i*-PrOH in hexane; flow rate, 0.2 mL/min; (-)-**2b** (minor); $t_R = 20.1$ min, (+)-**2b** (major); $t_R = 21.2$ min]. **2b** (95%ee): pale yellow solid; mp 148-149 °C; $[\alpha]_D = +338.6$ ($c = 1.0$, CHCl_3); IR (KBr) 1685 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3) : 8.10-8.16 (2H, m), 7.57 (1H, d, $J = 8.5$ Hz); 7.44-7.52 (3H, m), 7.07 (1H, d, $J = 2.3$ Hz), 2.21 (1H, qd, $J = 7.3, 16.7$ Hz), 2.13 (1H, qd, $J = 7.3, 16.7$ Hz), 1.35 (9H, s), 1.18 (9H, s), 1.13 (3H, t, $J = 7.3$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) : 175.0, 151.2, 148.5, 143.5, 143.2, 137.5, 130.2, 129.5, 126.5, 123.9, 122.7, 35.7, 34.4, 31.6, 31.2, 31.1, 9.6; MS (m/z) 383 (MH^+); Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_3$: C, 72.22; H, 7.91; N, 7.32. Found: C, 72.23; H, 7.93; N, 7.01.

***N*-(2-*tert*-Butylphenyl)-*N*-(4-nitrophenyl)acetamide (2c).** **2c** was prepared from **1c** (96 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of **2a** (80 °C, 5 h). Purification by column chromatography (hexane/AcOEt = 8) and subsequent MPLC (hexane/AcOEt = 7) gave **2c** (117 mg, 75%). The ee (90%ee) of **2c** was determined by HPLC analysis using a CHIRALPACK AS-H column [25 cm x 0.46 cm i.d.; 10 % *i*-PrOH in hexane; flow rate, 0.5 mL/min; (-)-**2c** (minor); $t_R = 21.1$ min, (+)-**2c** (major); $t_R = 22.6$ min]. **2c** (90%ee): pale yellow solid; mp 163-165 °C; $[\alpha]_D = +254.1$ (90%ee, $c = 1.0$, CHCl_3); IR (KBr) 1685 cm^{-1} ; $^1\text{H-NMR}$

(CDCl₃) : 8.10-8.16 (2H, m), 7.66 (1H, dd, *J* = 1.5, 8.0 Hz), 7.48-7.52 (2H, m), 7.46 (1H, dd, *J* = 1.5, 8.0 Hz), 7.39 (1H, dt, *J* = 1.5, 8.0 Hz), 7.13 (1H, dd, *J* = 1.5, 8.0 Hz), 2.03 (3H, s), 1.23 (9H, s); ¹³C-NMR (CDCl₃) : 171.5, 148.2, 146.8, 143.3, 138.6, 132.6, 130.6, 129.7, 127.9, 123.9, 122.9, 36.2, 31.7, 26.2; MS (*m/z*) 313 (MH⁺); Anal. Calcd for C₁₈H₂₀N₂O₃: C, 69.21; H, 6.45; N, 8.97. Found: C, 69.34; H, 6.39; N, 8.75.

***N*-(2-*tert*-Butylphenyl)-*N*-(4-nitrophenyl)-3-phenylpropanamide (2d).** **2d** was prepared from **1d** (141 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of **2a** (80 °C, 6 h). Purification by column chromatography (hexane/AcOEt = 15) gave **2d** (168 mg, 84%). The ee (94%ee) of **2d** was determined by HPLC analysis using a CHIRALPACK AS-H column [25 cm x 0.46 cm i.d.; 10 % *i*-PrOH in hexane; flow rate, 0.2 mL/min; (-)-**2d** (minor); *t_R* = 40.1 min, (+)-**2d** (major); *t_R* = 41.2 min]. **2d** (94%ee): pale yellow solid; mp 145 °C; [*α*]_D = +198.7 (*c* = 1.0, CHCl₃); IR (KBr) 1684 cm⁻¹; ¹H-NMR (CDCl₃) : 8.10-8.16 (2H, m), 7.63 (1H, dd, *J* = 1.5, 8.2 Hz), 7.41-7.50 (3H, m), 7.15-7.33 (3H, m), 7.10 (2H, d, *J* = 6.8 Hz), 6.90 (1H, dd, *J* = 1.5, 8.2 Hz), 2.90-3.08 (2H, m), 2.53 (1H, ddd, *J* = 6.7, 8.5, 16.3 Hz), 2.42 (1H, ddd, *J* = 6.4, 8.8, 16.3 Hz), 1.16 (9H, s); ¹³C-NMR (CDCl₃) : 173.0, 148.2, 146.8, 143.2, 140.5, 137.6, 132.5, 130.5, 129.6, 128.4, 128.3, 127.8, 126.1, 123.8, 122.9, 39.7, 36.2, 31.7, 31.5; MS (*m/z*) 403 (MH⁺); Anal. Calcd for C₂₅H₂₆N₂O₃: C, 74.60; H, 6.51; N, 6.96. Found: C, 74.53; H, 6.49; N, 6.57.

***N*-(2-*tert*-Butylphenyl)-*N*-(4-nitrophenyl)cyclohexanecarboxamide (2e).** **2e** was prepared from **1e** (130 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of **2a** (80 °C, 6 h). Purification by column chromatography (hexane/AcOEt = 25) and subsequent MPLC (hexane/AcOEt = 9) gave **2e** (130 mg, 68%). The ee (89%ee) of **2e** was determined by HPLC analysis using a CHIRALPACK AS-H column [25 cm x 0.46 cm i.d.; 10 % *i*-PrOH in hexane; flow rate, 0.3 mL/min; (+)-**2e** (major); *t_R* = 20.1 min, (-)-**2e** (minor); *t_R* = 22.5 min]. **2e** (89%ee): pale yellow solid; mp 56-58 °C; [*α*]_D = +187.5 (*c* = 1.0, CHCl₃); IR (KBr) 1684 cm⁻¹; ¹H-NMR (CDCl₃) : 8.08-8.14 (2H, m), 7.68 (1H, dd, *J* = 1.5, 7.9 Hz), 7.40-7.50 (3H, m), 7.36 (1H, dt, *J* = 1.5, 7.9 Hz), 7.10 (1H, dd, *J* = 1.5, 7.9 Hz), 2.11 (1H, tt, *J* = 3.0, 11.4 Hz), 0.80-1.90 (10H, m), 1.24 (9H, s); ¹³C-

NMR (CDCl₃) : 177.2, 148.6, 146.9, 143.1, 137.7, 132.2, 130.5, 129.5, 127.4, 123.7, 123.3, 44.7, 36.4, 32.0, 30.4, 29.5, 25.7, 25.4; MS (*m/z*) 381 (MH⁺); HRMS. Calcd for C₂₃H₂₉N₂O₃ (MH⁺) 381.2178. Found: 381.2160.

(*E*)-*N*-(2-*tert*-Butylphenyl)-*N*-(4-nitrophenyl)-3-phenylpropenamide (2f). **2f** was prepared from **1f** (140 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of **2a** (80 °C, 3 h). Purification by column chromatography (hexane/AcOEt = 20) subsequent MPLC (hexane/AcOEt = 20) gave **2f** (81 mg, 40%). The ee (94%ee) of **2f** was determined by HPLC analysis using a CHIRALCEL OD-H column [25 cm x 0.46 cm i.d.; 5 % *i*-PrOH in hexane; flow rate, 0.5 mL/min; (-)-**2f** (minor); *t_R* = 25.2 min, (+)-**2f** (major); *t_R* = 26.9 min]. **2f** (94%ee): yellow solid; mp 146-147 °C; [*α*]_D = +323.0 (*c* = 1.0, CHCl₃); IR (KBr) 1671 cm⁻¹; ¹H-NMR (CDCl₃) : 8.14-8.20 (2H, m), 7.79 (1H, d, *J* = 15.5 Hz), 7.72 (1H, dd, *J* = 1.5, 7.6 Hz), 7.50-7.57 (3H, m), 7.39 (1H, dt, *J* = 1.5, 7.6 Hz), 7.28-7.33 (5H, m), 7.14 (1H, dd, *J* = 1.5, 7.6 Hz), 6.25 (1H, d, *J* = 15.5 Hz), 1.25 (9H, s); ¹³C-NMR (CDCl₃) : 166.6, 148.5, 147.5, 143.9, 143.3, 137.7, 134.5, 133.0, 130.4, 130.0, 129.7, 128.7, 127.9, 123.9, 123.2, 119.7, 36.3, 31.9; MS (*m/z*) 401 (MH⁺); HRMS. Calcd for C₂₅H₂₅N₂O₃ (MH⁺) 401.1865. Found: 401.1868.

(*E*)-*N*-(2-*tert*-Butylphenyl)-*N*-(4-nitrophenyl)butenamide (2g). **2g** was prepared from **1g** (109 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of **2a** (80 °C, 4 h). Purification by column chromatography (hexane/AcOEt = 20) and subsequent MPLC (hexane/AcOEt = 9) gave **2g** (67 mg, 40%). The ee (89%ee) of **2g** was determined by HPLC analysis using a CHIRALCEL OD-H column [25 cm x 0.46 cm i.d.; 5 % *i*-PrOH in hexane; flow rate, 0.3 mL/min; (-)-**2g** (minor); *t_R* = 26.9 min, (+)-**2g** (major); *t_R* = 28.6 min]. **2g** (89%ee): yellow solid; mp 99-100 °C; [*α*]_D = +355.0 (*c* = 1.0, CHCl₃); IR (KBr) 1673 cm⁻¹; ¹H-NMR (CDCl₃) : 8.10-8.16 (2H, m), 7.67 (1H, dd, *J* = 1.5, 7.6 Hz), 7.45-7.50 (3H, m), 7.37 (1H, dt, *J* = 1.5, 7.6 Hz), 7.08 (1H, qd, *J* = 7.0, 14.9 Hz), 7.07 (1H, dd, *J* = 1.5, 7.6 Hz), 5.67 (1H, dd, *J* = 1.5, 14.9 Hz), 1.79 (3H, dd, *J* = 1.5, 7.0 Hz), 1.21 (9H, s); ¹³C-NMR (CDCl₃) : 166.4, 148.5, 147.3, 144.1, 143.2, 137.7, 133.0, 130.3, 129.5, 127.7, 124.2, 123.8, 123.2, 36.2, 31.8, 18.4; MS (*m/z*) 339 (MH⁺); Anal. Calcd

for $C_{20}H_{23}N_2O_3$: C, 70.99; H, 6.55; N, 8.28. Found: C, 71.04; H, 6.59; N, 8.03.

Starting materials 3a-3d: Starting materials **3a-3d** were prepared in accordance with following procedure.

***N*-(2-*tert*-Butylphenyl)-3-(2-iodophenyl)propanamide (3a).** Under Ar atmosphere, to 2-*tert*-butylaniline (656 mg, 4.4 mmol) in toluene (6.0 mL) was added 1M hexane solution of Me_3Al (6.0 mL, 6.0 mmol) at 0 °C. After being stirred for 20 min at 0 °C, ethyl 3-(2-iodophenyl)propanoate¹ (1.22 g, 4.0 mmol) was added to the mixture, and then the reaction mixture was stirred for 8 h at 80 °C. The mixture was poured into 2 % HCl. Insoluble materials were removed by filtration with a Celite pad, and the filtrate was 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 = 10) gave **3a** (1.08 g, 66 %). **3a**: white solide; mp 115-116 °C; IR (KBr) 3260, 1651 cm^{-1} ; 1H NMR ($CDCl_3$) : 7.83 (1H, d, J = 7.9 Hz), 7.56 (1H, d, J = 7.3 Hz), 7.13-7.38 (6H, m), 6.91 (1H, t, J = 7.6 Hz), 3.20 (2H, t, J = 8.0 Hz), 2.71 (2H, t, J = 8.0 Hz), 1.36 (9H, s); ^{13}C NMR ($CDCl_3$) : 169.4, 142.7, 142.2, 139.3, 134.7, 129.9, 128.5, 128.1, 127.6, 126.6, 126.3, 126.0, 100.1, 38.1, 36.7, 34.7, 30.9; MS (m/z) 408 (MH^+); Anal. Calcd for $C_{19}H_{22}INO$: C, 56.03; H, 5.44; N, 3.44. Found: C, 56.19; H, 5.53; N, 3.27.

***N*-(2,5-di-*tert*-Butylphenyl)-3-(2-iodophenyl)propanamide (3b).** **3b** was prepared from 2,5-bis-*tert*-butylaniline (1.03 g, 5.0 mmol) in accordance with the general procedure for the synthesis of **3a** (12 h at 80 °C). Purification by column chromatography (hexane/AcOEt = 10) gave **3b** (757 mg, 49 %). **3b**: white solid; mp 136-137 °C; IR (KBr) 3251, 1648 cm^{-1} ; 1H NMR ($CDCl_3$) : 7.83 (1H, d, J = 7.6 Hz), 7.58 (1H, d, J = 1.8 Hz), 7.28-7.36 (3H, m), 7.16 (1H, dd, J = 1.8, 8.2), 7.10 (1H, brs), 6.91 (1H, t, J = 7.6 Hz), 3.21 (2H, t, J = 7.9 Hz), 2.71 (2H, t, J = 7.9 Hz), 1.35 (9H, s), 1.32 (9H, s); ^{13}C NMR ($CDCl_3$) : 169.3, 149.3, 142.8, 139.3, 139.1, 134.4, 129.9, 128.4, 128.1, 126.0, 124.9, 122.8, 100.1, 38.2, 36.7, 34.4, 34.3, 31.4, 30.9; MS (m/z) 464 (MH^+); Anal. Calcd for $C_{23}H_{30}INO$: C, 59.61; H, 6.53; N, 3.02. Found: C, 59.65; H, 6.57; N, 2.83.

1-Benzyl-3-(2,5-di-*tert*-butylphenyl)-1-(2-iodophenyl)urea (3c). Under Ar atmosphere, to benzyl-(2-iodobenzyl)-amine² (636 mg, 1.97 mmol) in toluene (3.0 mL) was added 1M hexane

solution of Me₃Al (2.5 mL, 2.5 mmol) at 0 °C. After being stirred for 20 min at 0 °C, *N*-methoxycarbonyl-2,5-di-*tert*-butylaniline (432 mg, 1.64 mmol) was added to the mixture, and then the reaction mixture was stirred for 12 h at rt. The mixture was poured into 2 % HCl. Insoluble materials were removed by filtration with a Celite pad, and the filtrate was extracted with AcOEt. The AcOEt extracts were washed with brine, dried over MgSO₄, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 15) gave **3c** (587 mg, 65 %). **3c**: white solid; mp 155-156 °C; IR (KBr) 3277, 1633 cm⁻¹; ¹H NMR (CDCl₃) : 7.85 (1H, d, *J* = 7.9 Hz), 7.61 (1H, d, *J* = 2.3 Hz), 7.30-7.42 (7H, m), 7.22 (1H, d, *J* = 8.5 Hz), 7.08 (1H, dd, *J* = 2.3, 8.5 Hz), 7.01 (1H, m), 6.17 (1H, s), 4.71 (2H, s), 4.64 (2H, s), 1.32 (9H, s), 1.15 (9H, s); ¹³C NMR (CDCl₃) : 156.1, 149.2, 139.6, 138.5, 137.1, 135.8, 129.2, 128.7, 128.6, 127.7, 127.5, 127.3, 125.8, 124.4, 121.7, 98.1, 56.1, 51.1, 34.4, 33.9, 31.4, 30.6; MS (*m/z*) 555 (MH⁺); HRMS. Calcd for C₂₉H₃₆IN₂O (MH⁺): 555.1872, Found: 555.1855.

2-[Benzyl-(2-iodophenyl)amino]-*N*-(2,5-di-*tert*-butylphenyl)acetamide (3d). Under Ar atmosphere, to *N*-benzyl-2-iodoaniline³ (2.66 g, 8.6 mmol) and K₂CO₃ (2.49 g, 18.0 mmol) in acetone (20 mL) was added ethyl iodoacetate (1.5 mL, 13.0 mmol) at rt, , and then the reaction mixture was stirred for 36 h at 90 °C. The mixture was poured into 2 % HCl solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over MgSO₄, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 100) gave ethyl *N*-benzyl-*N*-(2-iodophenyl)aminoacetate (480 mg, 12 %). Under Ar atmosphere, to 2,5-di-*tert*-butylaniline (883 mg, 4.3 mmol) in toluene (5.0 mL) was added 1M hexane solution of Me₃Al (7.0 mL, 7.0 mmol) at 0 °C. After being stirred for 20 min at 0 °C, *N*-benzyl-*N*-(2-iodophenyl)aminoacetate (1.42 g, 3.6 mmol) was added to the mixture, and then the reaction mixture was stirred for 12 h at 80 °C. The mixture was poured into 2 % HCl. Insoluble materials were removed by filtration with a Celite pad, and the filtrate was extracted with AcOEt. The AcOEt extracts were washed with brine, dried over MgSO₄, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 100) gave **3d** (499 mg, 25 %). **3d**: white solid; mp 127-128 °C; IR (KBr) 3331, 1690 cm⁻¹; ¹H NMR (CDCl₃) : 8.52 (1H, brs), 7.92 (1H, dd,

$J = 1.5, 7.9$ Hz), 7.28-7.38 (7H, m), 7.19 (1H, dd, $J = 2.3, 8.5$ Hz), 7.07 (1H, dd, $J = 1.5, 7.9$ Hz), 6.93 (1H, dt, $J = 1.5, 7.9$ Hz), 6.83 (1H, d, $J = 2.3$ Hz) 4.27 (2H, s), 3.85 (2H, s), 1.33 (9H, s), 1.24 (9H, s); ^{13}C NMR (CDCl_3) : 168.7, 150.4, 149.3, 142.4, 140.1, 135.4, 134.1, 129.4, 129.2, 128.3, 127.8, 127.1, 127.0, 126.3, 124.3, 124.0, 99.1, 60.5, 56.9, 34.6, 34.3, 31.3, 31.2; MS (m/z) 555 (MH^+); HRMS. Calcd for $\text{C}_{29}\text{H}_{36}\text{IN}_2\text{O}$ (MH^+): 555.1872, Found: 555.1851.

General procedure of catalytic asymmetric intramolecular *N*-arylation.

Under Ar atmosphere, to **3a** (204 mg, 0.5 mmol) in toluene (1.5 mL) was added Cs_2CO_3 (228 mg, 0.7 mmol). After being stirred for 5 min at rt, $\text{Pd}(\text{OAc})_2$ (4 mg, 0.017 mmol) and (*S*)-BINAP (15 mg, 0.025 mmol) in toluene (0.5 mL) were added to the mixture, and then the reaction mixture was stirred for 17 h at 80 °C. 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 = 10) gave **4a** (133 mg, 95%). The ee (70%ee) of **4a** was determined by HPLC analysis using a CHIRALPACK AS-H column [25 cm x 0.46 cm i.d.; 1% *i*-PrOH in hexane; flow rate, 1.0 mL/min; (+)-**4a** (major); $t_R = 11.9$ min, (-)-**4a** (minor); $t_R = 21.6$ min].

(S)-1-(2-*tert*-Butylphenyl)-3,4-dihydro-1H-quinoline-2-one (4a). **4a** (70%ee): white solid; $[\alpha]_D = +57.7$ ($c=1.0$, CHCl_3); mp 110-111 °C; IR (KBr) 1685 cm^{-1} ; ^1H NMR (CDCl_3) : 7.65 (1H, dd, $J = 1.7, 8.0$ Hz), 7.41 (1H, dt, $J = 1.7, 8.0$ Hz), 7.34 (1H, dt, $J = 1.7, 8.0$ Hz), 7.23 (1H, d, $J = 6.1$ Hz), 6.96-7.08 (3H, m), 6.23 (1H, dd, $J = 1.0, 8.2$ Hz), 3.12 (1H, ddd, $J = 6.5, 11.4, 15.7$ Hz), 3.02 (1H, td, $J = 6.0, 15.7$ Hz), 2.74 -2.93 (2H, m), 1.26 (9H, s); ^{13}C NMR (CDCl_3) : 170.7, 147.4, 142.0, 135.7, 131.9, 129.3, 128.5, 127.6, 127.5, 126.9, 124.9, 122.6, 117.0, 36.0, 32.5, 31.7, 25.5; MS (m/z) 280 (MH^+); Anal. Calcd for $\text{C}_{19}\text{H}_{21}\text{NO}$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.66; H, 7.36; N, 4.81.

1-(2,5-di-*tert*-Butylphenyl)-3,4-dihydro-1H-quinoline-2-one (4b). **4b** was prepared from **3b** (232 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of **4a** (80 °C, 22 h). Purification by column chromatography (hexane/AcOEt = 7) gave **4b** (159 mg, 95%). The ee (96 %ee) of **4b** was determined by HPLC analysis using a CHIRALPACK AD-H column [25 cm x 0.46 cm i.d.; 1 % *i*-PrOH in hexane; flow rate, 1.0 mL/min; (+)-**4b** (major); t_R = 11.3 min, (-)-**4b** (minor); t_R = 12.4 min]. **4b** (96%ee): white solid; $[\alpha]_D^{25} = +82.2$ (c=1.0, CHCl₃); mp 87.0-88.0 °C (96% ee); IR (KBr) 1683 cm⁻¹; ¹H NMR (CDCl₃) : 7.55 (1H, d, J = 8.5 Hz), 7.41 (1H, dd, J = 2.3, 8.5 Hz), 7.22(1H, d, J = 7.6 Hz), 7.05 (1H, dt, J = 1.5, 7.6 Hz), 6.98 (1H, dt, J = 1.2, 7.6 Hz), 6.93 (1H, d, J = 2.3 Hz), 6.21 (1H, dd, J = 1.2, 7.6 Hz), 3.13 (1H, ddd, J = 7.0, 11.0, 15.6 Hz), 3.02 (1H, td, J = 6.0, 15.6 Hz), 2.76-2.90 (2H, m), 1.31 (9H, s), 1.23 (9H, s); ¹³C NMR (CDCl₃) : 170.6, 150.4, 144.1, 142.2, 135.2, 128.9, 128.7, 127.6, 126.9, 125.6, 125.0, 122.5, 116.9, 35.5, 34.4, 32.6, 31.7, 31.4, 25.5; ; MS (m/z) 336 (MH⁺); Anal. Calcd for C₂₃H₂₉NO: C, 82.34; H, 8.71; N, 4.18. Found: C, 82.46; H, 8.51 ;N, 3.83.

3-Benyl-1-(2,5-di-*tert*-butylphenyl)-3,4-dihydro-1H-quinazoline-2-one (4c). **4c** was prepared from **3c** (277 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of **4a** (80 °C, 20 h). Purification by column chromatography (hexane/AcOEt = 10) gave **4c** (174 mg, 82%). The ee (94 %ee) of **4c** was determined by HPLC analysis using a CHIRALPACK AD-H column [25 cm x 0.46 cm i.d.; 3 % *i*-PrOH in hexane; flow rate, 1.0 mL/min; (-)-**4c** (minor); t_R = 13.4 min, (+)-**4c** (major); t_R = 14.9 min]. **4c** (94% ee): white solid; $[\alpha]_D^{25} = +58.3$ (c=1.0, CHCl₃); mp 110.0-111.0 °C; IR (KBr) 1656 cm⁻¹; ¹H NMR (CDCl₃) : 7.52 (1H, d, J = 8.5 Hz) 7.29-7.45 (6H, m), 7.09 (1H, d, J = 2.3 Hz), 7.03 (2H, t, J = 7.3 Hz), 6.91(1H, ddd, J = 1.2, 7.3, 8.2 Hz), 6.09 (1H, d, J = 8.2 Hz), 5.10 (1H, d, J = 14.5 Hz), 4.49 (1H, d, J = 14.5 Hz), 4.39 (1H, d, J = 14.5 Hz), 4.30 (1H, d, J = 14.5 Hz), 1.33 (9H, s), 1.25 (9H, s); ¹³C NMR (CDCl₃) : 154.5, 150.1, 144.6, 141.2, 136.9, 135.6, 129.7, 128.3, 128.3, 128.2, 127.5, 127.3, 125.2, 125.2, 121.4, 119.0, 115.2, 51.6, 47.7, 35.3, 34.3, 31.7, 31.4; MS (m/z) 427 (MH⁺); HRMS. Calcd for C₂₉H₃₅N₂O (MH⁺): 427.2749, Found: 427.2749.

4-Benzyl-1-(2,5-di-*tert*-butylphenyl)-3,4-dihydro-1H-quinoxaline-2-one (4d). **4d** was

prepared from **3d** (277 mg, 0.5 mmol) in accordance with the general procedure for the synthesis of **4a** (80 °C, 6 h). Purification by column chromatography (hexane/AcOEt = 10) gave **4d** (149 mg, 71%). The ee (95 %ee) of **4d** was determined by HPLC analysis using a CHIRALCEL OD-H column [25 cm x 0.46 cm i.d.; 3 % *i*-PrOH in hexane; flow rate, 0.5 mL/min; (+)-**4c** (major); t_R = 14.6 min, (-)-**4c** (minor); t_R = 17.1 min]. **4d** (95%ee): colorless oil; $[\alpha]_D = +22.6$ (c=0.8, CHCl₃); IR (neat) 1685 cm⁻¹; ¹H NMR (CDCl₃) : 7.56 (1H, d, J = 8.5 Hz), 7.43 (1H, dd, J = 2.3, 8.5 Hz), 7.26-7.37 (5H, m), 7.02 (1H, d, J = 2.3 Hz), 6.94 (1H, dt, J = 1.5, 8.0 Hz), 6.82 (1H, dd, J = 1.5, 8.0 Hz), 6.67 (1H, dt, J = 1.5, 8.0 Hz), 6.24 (1H, dd, J = 1.5, 8.0 Hz), 4.60 (1H, d, J = 14.9 Hz), 4.32 (1H, d, J = 14.9 Hz), 3.98 (1H, d, J = 15.2 Hz), 3.91 (1H, d, J = 15.2 Hz), 1.33 (9H, s), 1.26 (9H, s); ¹³C NMR (CDCl₃) : 166.8, 150.4, 144.2, 136.4, 136.3, 134.0, 131.9, 129.0, 128.7, 128.6, 127.5, 127.4, 125.9, 123.5, 118.9, 117.0, 112.4, 53.9, 53.8, 35.6, 34.4, 31.6, 31.4; Ms (m/z) 427 (MH⁺); HRMS. Calcd for C₂₉H₃₅N₂O (MH⁺): 427.2749, Found: 427.2771.

1-(2,5-di-*tert*-Butylphenyl)-3-methyl-3,4-dihydro-1H-quinoline-2-one (5b). Under Ar atmosphere, to 2,2,6,6-tetramethylpiperidine (0.12 mL, 0.7 mmol) in THF (2.0 mL) was added 1.57 M hexane solution of *n*-BuLi (0.38 mL, 0.6 mmol) at -78 °C. After being stirred for 30 min at -78 °C, lactam **4b** (168 mg, 0.5 mmol) was added to the mixture, and then the reaction mixture was stirred for 1 h at 0 °C. CH₃I was added at -78 °C, and the mixture was stirred for 5 min at -78 °C. The mixture was poured into NH₄Cl solution and extracted with AcOEt. The AcOEt extracts were washed with brine, dried over MgSO₄, and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt = 20) and subsequent MPLC (hexane/AcOEt = 5) gave (*R,S*)-**5b** (9 mg, 5%, less polar) and (*S,S*)-**5b** (117 mg, 67%, more polar). (*S,S*)-**5b** (96%ee): white solid; $[\alpha]_D = +52.9$ (c=1.0, CHCl₃); mp 188 °C; IR (KBr) 1681 cm⁻¹; ¹H NMR (CDCl₃) : 7.54 (1H, d, J = 8.5 Hz), 7.39 (1H, dd, J = 2.3, 8.5 Hz), 7.20 (1H, d, J = 7.9 Hz), 7.04 (1H, dt, J = 1.7, 7.3 Hz), 6.96 (1H, dt, J = 1.7, 7.3 Hz), 6.81 (1H, d, J = 2.3 Hz), 6.17 (1H, dd, J = 1.7, 7.3 Hz), 3.18 (1H, dd, J = 8.8, 18.7 Hz), 2.80-2.89 (2H, m), 1.32 (3H, d, J = 6.4 Hz), 1.29 (9H, s), 1.25 (9H, s); ¹³C NMR (CDCl₃) : 173.1, 150.4, 144.3, 142.0, 135.4, 129.1, 128.2, 128.0, 126.8, 125.4, 123.9, 122.3, 117.0, 36.3, 35.7, 34.3, 33.3, 31.8, 31.4, 15.8; MS (m/z) 350 (MH⁺); Anal. Calcd for C₂₄H₃₁NO: C, 82.47;

H, 8.94; N, 4.01. Found: C, 82.24; H, 8.83; N, 3.61. (*R,S*)-**5b**: colorless oil; $[\alpha]_D = -144.6$ (c=1.0, CHCl₃); IR (neat) 1686 cm⁻¹; ¹H NMR(CDCl₃) : 7.52 (1H, d, *J* = 8.5 Hz), 7.39 (1H, dd, *J* = 2.3, 8.5 Hz), 7.21 (1H, d, *J* = 7.3 Hz), 6.97-7.06 (2H, m), 6.93 (1H, d, *J* = 2.3 Hz), 6.18 (1H, dd, *J* = 1.5, 7.3 Hz), 3.00 (1H, dd, *J* = 6.4, 14.7 Hz), 2.90 (1H, t, *J* = 14.7 Hz), 2.78 (1H, quint and d, *J* = 6.4, 14.7 Hz), 1.40 (3H, d, *J* = 6.4 Hz), 1.32 (9H, s), 1.19 (9H, s); ¹³C NMR (CDCl₃) : 173.1, 150.3, 143.9, 142.3, 135.8, 129.0, 128.7, 127.4, 126.9, 125.3, 125.1, 122.3, 116.6, 36.2, 35.5, 34.4, 33.7, 31.7, 31.4, 16.1; (m/z) 350 (MH⁺); HRMS. Calcd for C₂₄H₃₂NO (MH⁺): 350.2484, Found: 350.2475

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(Survey of chiral phosphine ligands for catalytic asymmetric intermolecular *N*-arylation)

(*R,R*)-Troost-Ligand
(0%)

(*R,R*)-CHIRAPHOS
(0%)

(*S*)-PHANEPHOS
(0%)

(*R*)-(S)-BPPFOAc
(0%)

(*R,R*)-DIOP
(20%, 9%ee)

(*R,R*)-Me-DuPhos
(16%, 15%ee)

(*S,S*)-Et-FerroTANE
(12%, 33%ee)

(*R*)-MOP
(18%, 52%ee)

(*S*)-P,N-Ligand
(38%, 59%ee)

(*S*)-BINAP (Ar=C₆H₅) (78%, 77%ee)

(*S*)-xyl-BINAP (Ar=3,5-Me₂C₆H₃) (56%, 78%ee)

(*S*)-tol-BINAP (Ar=4-MeC₆H₄) (48%, 53%ee)

(*R*)-(-)-DTBM-SEGPHOS
(28%, 89%ee)

The absolute configurations of **2a**, **2c** and **2d** were determined on the basis of following conversion.

The absolute configuration of **4b** was determined on the basis of following conversion.