Supporting Information

Facile Synthesis of Chiral Indolines through Asymmetric Hydrogenation of \textit{in situ} Generated Indoles

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1. General

Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. $^1$H NMR and $^{13}$C NMR spectra were recorded at room temperature in CDCl$_3$ on 400 MHz instrument with TMS (tetramethylsilane) as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh).

2. General Procedure for the Synthesis of Substrates

The compounds 2 can be prepared from compounds 1 and the corresponding Weinreb amides according to the known literature procedure with minor modification.[1] Compounds 1 could be conveniently prepared from di-tert-butyl dicarbonate and aryl amines.[2] Weinreb amides could be prepared from the corresponding acyl chloride and N,O-dimethylhydroxylamine hydrochloride.[3]

**General procedure**: Under nitrogen, compounds 1 (3 mmol) in THF (15 mL) was cooled to -40 °C. Then sec-butyllithium (s-BuLi, 6.90 mL of 1.0 M in hexane, 6.9 mmol) was added slowly. After stirring for one hour, a solution of Weinreb amide (3 mmol) in THF (5 mL) was added. The mixture was stirred at -40 °C over a period of thirty minutes and quenched with water (5 mL) carefully. Then the mixture was extracted with dichloromethane (10 mL×3), the combined organic layer was washed with brine, dried over sodium sulfate and concentrated in vacuo. The residue was purified by flash chromatography to give desired compounds 2.

**tert-Butyl (2-(2-oxo-3-phenylpropyl)phenyl)carbamate (2a)**: white solid, mp 98-99 °C, 91% yield, new compound, R$_f$ = 0.42 (hexanes/ethyl acetate 5/1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, $J = 8.1$ Hz, 1H), 7.37-7.27 (m, 4H), 7.26-7.21 (m, 1H), 7.18-7.13 (m, 2H), 7.05-6.99 (m, 2H), 3.81 (s, 2H), 3.72 (s, 2H), 1.50 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.5, 153.6, 137.4, 133.3, 130.6, 129.6, 128.9, 128.3, 127.4, 125.4, 124.3, 123.7, 80.3, 49.8, 45.7, 28.4. HRMS Calculated for C$_{20}$H$_{24}$NO$_3$ [M+H]$^+$ 326.1751, found: 326.1756.

**tert-Butyl (2-(2-oxo-3-(o-tolyl)propyl)phenyl)carbamate (2b)**: white solid, mp 104-105 °C, 72% yield, new compound, R$_f$ = 0.50 (hexanes/ethyl acetate 10/1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.76 (d, $J = 8.0$ Hz, 1H), 7.46 (brs, 1H), 7.28-7.22 (m, 2H), 7.22-7.14 (m, 3H), 7.12-7.08 (m, 1H), 7.04-6.94 (m, 2H), 3.82 (s, 2H), 3.71 (s, 2H), 2.09 (s, 3H), 1.50 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.7, 153.6, 137.4, 137.1, 132.2, 130.6, 130.6, 130.5, 128.3, 127.7, 126.4, 125.2, 124.3, 123.6, 80.3, 48.0, 45.8, 28.4, 19.4. HRMS Calculated for C$_{21}$H$_{25}$KNO$_3$ [M+K]$^+$ 378.1466, found: 378.1471.

**tert-Butyl (2-(2-oxo-3-(m-tolyl)propyl)phenyl)carbamate (2c)**: white solid, mp 109-110 °C, 48% yield, new compound, R$_f$ = 0.50 (hexanes/ethyl acetate 10/1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 (d, $J = 8.1$ Hz, 1H), 7.37 (brs, 1H), 7.28-7.20 (m, 2H), 7.10 (d, $J = 7.5$ Hz, 1H), 7.05-7.95 (m, 4H), 3.77 (s, 2H), 3.71 (s, 2H), 2.33 (s, 3H), 1.50 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.7, 153.6, 138.6, 137.4, 137.5, 137.1, 132.2, 130.6, 130.6, 128.3, 127.7, 126.4, 125.2, 124.3, 123.6, 80.3, 48.0, 45.8, 28.4, 19.4. HRMS Calculated for C$_{21}$H$_{25}$KNO$_3$ [M+K]$^+$ 378.1466, found: 378.1471.
tert-Butyl (2-(2-oxo-3-(p-tolyl)propyl)phenyl)carbamate (2d): white solid, mp 91-92 °C, 33% yield, new compound, Rf = 0.50 (hexanes/ethyl acetate 10/1). 1H NMR (400 MHz, CDCl3) δ 7.75 (d, J = 8.1 Hz, 1H), 7.38 (brs, 1H), 7.28-7.22 (m, 1H), 7.14 (d, J = 7.8 Hz, 2H), 7.08-6.98 (m, 4H), 3.76 (s, 2H), 3.70 (s, 2H), 2.33 (s, 3H), 1.49 (s, 9H); 13C NMR (100 MHz, CDCl3) δ 207.8, 153.6, 137.4, 130.6, 130.2, 129.6, 129.4, 128.2, 125.5, 124.3, 80.3, 49.4, 45.6, 28.4, 21.1. HRMS Calculated for C21H25KNO3 [M+H]+ 378.1466, found: 378.1468.

ertert-Butyl (2-(2-oxopropyl)phenyl)carbamate (2e): white solid, mp 54-55 °C, 50% yield, new compound, Rf = 0.33 (hexanes/ethyl acetate 5/1). 1H NMR (400 MHz, CDCl3) δ 7.77 (d, J = 8.0 Hz, 1H), 7.34-7.22 (m, 2H), 7.15 (d, J = 7.6 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 3.71 (s, 2H), 2.25 (s, 3H), 1.52 (s, 9H); 13C NMR (100 MHz, CDCl3) δ 207.9, 153.6, 137.3, 130.6, 128.3, 125.4, 124.4, 123.6, 80.3, 47.7, 29.9, 28.4. HRMS Calculated for C14H20NO3 [M+H]+ 250.1438, found: 250.1442.

tert-Butyl (2-(2-oxobutyl)phenyl)carbamate (2f): pale yellow solid, mp 44-45 °C, 48% yield, new compound, Rf = 0.40 (hexanes/ethyl acetate 20/1). 1H NMR (400 MHz, CDCl3) δ 7.78 (d, J = 8.1 Hz, 1H), 7.58 (brs, 1H), 7.29-7.23 (m, 1H), 7.14 (d, J = 7.5, 1.2 Hz, 1H), 7.07-7.00 (m, 1H), 3.69 (s, 2H), 2.59 (q, J = 7.2 Hz, 2H), 1.52 (s, 9H), 1.04 (t, J = 7.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 210.8, 153.6, 137.4, 130.5, 128.2, 125.6, 124.2, 123.5, 80.2, 46.5, 36.0, 28.4, 7.5. HRMS Calculated for C15H21NNaO3 [M+Na]+ 286.1414, found: 286.1412.

tert-Butyl (2-(2-oxopentyl)phenyl)carbamate (2g): pale red solid, mp 67-68 °C, 35% yield, new compound, Rf = 0.50 (hexanes/ethyl acetate 20/1). 1H NMR (400 MHz, CDCl3) δ 7.78 (d, J = 8.1 Hz, 1H), 7.54 (brs, 1H), 7.28-7.23 (m, 1H), 7.17-7.12 (m, 1H), 7.04 (t, J = 7.4 Hz, 2H), 1.63-1.57 (m, 2H), 1.52 (s, 9H), 0.88 (t, J = 6.9 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 210.3, 153.6, 137.4, 130.5, 128.2, 125.5, 124.2, 123.5, 80.2, 46.9, 44.6, 28.4, 17.0, 13.5. HRMS Calculated for C16H23KNO3 [M+K]+ 316.1310, found: 316.1309.

tert-Butyl (2-(3-methyl-2-oxobutyl)phenyl)carbamate (2h): white solid, mp 73-74 °C, 58% yield, new compound, Rf = 0.55 (hexanes/ethyl acetate 5/1). 1H NMR (400 MHz, CDCl3) δ 7.76 (d, J = 8.0 Hz, 1H), 7.65 (brs, 1H), 7.28-7.22 (m, 1H), 7.13 (d, J = 6.5 Hz, 1H), 7.06-7.01 (m, 1H), 3.75 (s, 2H), 2.86-2.74 (m, 1H), 1.52 (s, 9H), 1.14 (d, J = 6.9 Hz, 6H); 13C NMR (100 MHz, CDCl3) δ 214.0, 153.6, 137.5, 130.5, 128.1, 126.0, 124.2, 123.7, 80.2, 44.6, 41.0, 28.4, 18.0. HRMS Calculated for C16H24NO3 [M+H]+ 278.1751, found: 278.1755.

tert-Butyl (2-(2-oxohexyl)phenyl)carbamate (2i): white solid, mp 51-52 °C, 50% yield, new compound, Rf = 0.60 (hexanes/ethyl acetate 5/1). 1H NMR (400 MHz, CDCl3) δ 7.79 (d, J = 8.0 Hz, 1H), 7.55 (brs, 1H), 7.30-7.21 (m, 1H), 7.16-7.11 (m, 1H), 7.07-7.01 (m, 1H), 3.68 (s, 2H), 2.56 (t, J = 7.3 Hz, 2H), 1.63-1.48 (m, 2H; s, 9H), 1.33-1.22 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 210.5, 153.6, 137.4, 130.5, 128.2, 125.5, 124.2, 123.5, 80.2, 44.6, 41.0, 28.4, 25.6, 22.2, 13.8. HRMS Calculated for C17H26NO3 [M+H]+ 292.1907, found: 292.1909.
**tert-Butyl (2-(2-oxoheptyl)phenyl)carbamate (2j):** white solid, mp 49-50 °C, 59% yield, new compound, Rf = 0.65 (hexanes/ethyl acetate 5/1). ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 8.1 Hz, 1H), 7.56 (brs, 1H), 7.30-7.21 (m, 1H), 7.16-7.11 (m, 1H), 7.08-7.02 (m, 1H), 3.68 (s, 2H), 2.55 (t, J = 7.4 Hz, 2H), 1.62-1.55 (m, 2H), 1.52 (s, 9H), 1.31-1.19 (m, 4H), 0.86 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 210.5, 153.6, 137.4, 130.5, 128.2, 125.4, 124.2, 123.4, 80.2, 46.9, 42.7, 31.2, 28.4, 23.2, 22.4, 13.9. HRMS Calculated for C₁₈H₂₈NO₃ [M+H]+ 306.2064, found: 306.2062.

**tert-Butyl (2-methyl-6-(2-oxopropyl)phenyl)carbamate (2k):** white solid, mp 84-85 °C, 68% yield, new compound, Rf = 0.40 (hexanes/ethyl acetate 5/1). ¹H NMR (400 MHz, CDCl₃) δ 7.18-7.08 (m, 2H), 7.01 (d, J = 7.1 Hz, 1H), 6.34 (brs, 1H), 3.72 (s, 2H), 2.27 (s, 3H), 2.19 (s, 3H), 1.48 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 207.1, 153.8, 136.9, 134.7, 132.4, 130.0, 128.2, 127.1, 80.0, 47.7, 29.9, 28.3, 18.4. HRMS Calculated for C₁₅H₂₂NO₃ [M+H]+ 264.1594, found: 264.1594.

**tert-Butyl (2-methoxy-6-(2-oxopropyl)phenyl)carbamate (2l):** pale yellow oil, 69% yield, new compound, Rf = 0.40 (hexanes/ethyl acetate 5/1). ¹H NMR (400 MHz, CDCl₃) δ 7.16 (t, J = 8.0 Hz, 1H), 6.87-6.76 (m, 2H), 6.09 (brs, 1H), 3.83 (s, 3H), 3.76 (s, 2H), 2.17 (s, 3H), 1.48 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 206.4, 154.5, 154.4, 133.3, 127.2, 125.2, 122.8, 110.0, 80.2, 55.7, 47.3, 29.8, 28.3. HRMS Calculated for C₁₅H₂₁NNaO₄ [M+Na]+ 302.1363, found: 302.1359.

**tert-Butyl (4-methoxy-2-(2-oxopropyl)phenyl)carbamate (2m):** white solid, mp 82-83 °C, 70% yield, new compound, Rf = 0.35 (hexanes/ethyl acetate 5/1). ¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, J = 7.3 Hz, 1H), 6.92-6.78 (m, 1H; brs, 1H), 6.69 (d, J = 2.9 Hz, 1H), 3.77 (s, 3H), 3.68 (s, 2H), 2.23 (s, 3H), 1.50 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 207.3, 156.8, 154.1, 129.9, 128.8, 126.4, 116.2, 113.0, 80.1, 55.5, 47.6, 29.9, 28.4. HRMS Calculated for C₁₅H₂₁KNO₄ [M+K]+ 318.1102, found: 318.1106.

**tert-Butyl (2,4-dimethyl-6-(2-oxopropyl)phenyl)carbamate (2n):** white solid, mp 81-82 °C, 64% yield, new compound, Rf = 0.50 (hexanes/ethyl acetate 5/1). ¹H NMR (400 MHz, CDCl₃) δ 6.97 (s, 1H), 6.82 (s, 1H), 6.16 (brs, 1H), 3.69 (s, 2H), 2.27 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 1.48 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 207.2, 154.0, 136.7, 136.6, 132.3, 132.0, 130.6, 128.9, 79.7, 47.6, 29.7, 28.3, 20.9, 18.2. HRMS Calculated for C₁₆H₂₄NO₃ [M+H]+ 278.1751, found: 278.1752.

**tert-Butyl (2-(2-oxo-2-phenylethyl)phenyl)carbamate (2o):** white solid, 69% yield, known compound,[¹] Rf = 0.50 (hexanes/ethyl acetate 10/1). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, J = 5.2, 3.3 Hz, 2H), 7.79 (d, J = 7.9 Hz, 1H), 7.71-7.58 (m, 2H), 7.53 (dd, J = 10.5, 4.7 Hz, 2H), 7.31-7.26 (m, 1H), 7.23 (dd, J = 7.6, 1.3 Hz, 1H), 7.07 (dd, J = 7.5, 1.2 Hz, 1H), 4.31 (s, 2H), 1.54 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 199.1, 153.7, 137.6, 136.2, 133.8, 130.7, 128.8, 128.1, 124.4, 80.3, 42.0, 28.4.
3. Asymmetric Hydrogenation of in situ Generated Indoles

Ligand (R)-H8-BINAP (4.8 mg, 0.0076 mmol) and Pd(OCOCF3)2 (2.1 mg, 0.0063 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for one hour. The solvent was removed under vacuum to give the catalyst. This catalyst was taken into a glove box filled with nitrogen and dissolved in 2,2,2-trifluoroethanol (2 mL). To the mixture of compounds 2 (0.25 mmol) and ethanesulfonic acid (41 μL, 0.50 mmol) in toluene (2 mL), this catalyst solution was added, and then the mixture was transferred to an autoclave, which was charged hydrogen gas (300 psi). The autoclave was stirred at 40 °C for 24 h. After release of the hydrogen, the autoclave was opened and the reaction mixture was evaporated. Then, saturated sodium hydrogencarbonate (5 mL) was added. The mixture was extracted with dichloromethane (5 mL×3), the combined organic layer was dried over sodium sulfate and concentrated in vacuo. Purification was performed on silica gel using ethyl acetate/hexanes as the eluent to give the chiral products 3.

Racemates of 3 were prepared using (+)-BINAP/Pd(OCOCF3)2 as racemic catalyst.

(+)-(R)-2-Benzylindoline (3a): 51 mg, 98% yield, colorless oil, known compound, Rf = 0.65 (hexanes/ethyl acetate 10/1), 95% ee, [α]D20 = +95.09 (c 1.02, CHCl3), [lit.[4]: [α]D20 = +80.2 (c 1.00, CHCl3) for 95% ee); 1H NMR (400 MHz, CDCl3) δ 7.36-7.29 (m, 2H), 7.28-7.20 (m, 3H), 7.07 (d, J = 7.3 Hz, 1H), 7.03-6.97 (m, 1H), 6.71-6.65 (m, 1H), 6.55 (d, J = 7.7 Hz, 1H), 4.12-4.02 (m, 1H), 3.81 (brs, 1H), 3.18-3.08 (m, 1H), 2.94-2.73 (m, 3H); 13C NMR (100 MHz, CDCl3) δ 150.6, 139.1, 129.2, 128.7, 128.4, 127.4, 126.5, 124.8, 118.6, 109.1, 61.0, 42.7, 36.0. HPLC (OD-H, elute: n-hexane/i-ProOH = 99/1, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), t1 = 14.8 min (maj), t2 = 16.6 min.

(+)-(R)-2-(2-Methylbenzyl)indoline (3b): 51 mg, 91% yield, colorless oil, known compound, Rf = 0.60 (hexanes/ethyl acetate 20/1), 94% ee, [α]D20 = +90.49 (c 1.00, CHCl3), [lit.[4]: [α]D20 = +74.8 (c 1.50, CHCl3) for 94% ee); 1H NMR (400 MHz, CDCl3) δ 7.19-7.12 (m, 4H), 7.08 (d, J = 7.2 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.71-6.67 (m, 1H), 6.54 (d, J = 7.7 Hz, 1H), 4.14-4.01 (m, 1H), 3.54 (brs, 1H), 3.13 (dd, J = 15.5, 8.4 Hz, 1H), 2.93-2.75 (m, 3H), 2.32 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 150.6, 137.3, 136.6, 130.6, 129.8, 128.4, 127.4, 126.6, 126.1, 124.9, 118.6, 109.2, 59.7, 39, 37, 36, 19.7. HPLC (OD-H, elute: n-hexane/i-ProOH = 99/1, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), t1 = 13.8 min (maj), t2 = 15.7 min.

(+)-(R)-2-(3-Methylbenzyl)indoline (3c): 50 mg, 90% yield, colorless oil, known compound, Rf = 0.55 (hexanes/ethyl acetate 20/1), 95% ee, [α]D20 = +86.69 (c 1.00, CHCl3), [lit.[4]: [α]D20 = +75.4 (c 1.60, CHCl3) for 94% ee); 1H NMR (400 MHz, CDCl3) δ 7.22-7.16 (m, 1H), 7.10-7.05 (m, 5H), 6.70-6.65 (m, 1H), 6.54 (d, J = 7.7 Hz, 1H), 4.10-3.99 (m, 1H), 3.57 (brs, 1H), 3.16-3.07 (m, 1H), 2.88-2.72 (m, 3H), 2.34 (s, 3H); 13C NMR (100 MHz, CDCl3) δ 150.6, 139.1, 138.3, 130.0, 128.6, 128.5, 127.4, 127.2, 126.2, 124.9, 118.6, 109.2, 61.0, 42.7, 36.0, 21.5. HPLC (OD-H,
elute: n-hexane/i-PrOH = 99/1, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), t1 = 11.6 min (maj), t2 = 12.9 min.

(+)-(R)-2-(4-Methylbenzyl)indoline (3d): 52 mg, 93% yield, colorless oil, known compound, Rf = 0.50 (hexanes/ethyl acetate 20/1), 95% ee, [α]_D^20 = +87.95 (c 0.98, CHCl₃), [lit.[4]: [α]_D^RT = +75.5 (c 1.50, CHCl₃) for 93% ee]; ¹H NMR (400 MHz, CDCl₃) δ 7.16-7.04 (m, 5H), 6.99 (t, J = 7.6 Hz, 1H), 6.70-6.65 (m, 1H), 6.54 (d, J = 7.7 Hz, 1H), 4.10-3.99 (m, 1H), 3.71 (brs, 1H), 3.16-3.06 (m, 1H), 2.89-2.73 (m, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 150.6, 136.0, 136.0, 129.4, 129.0, 128.5, 127.4, 124.9, 118.5, 109.1, 61.1, 42.3, 35.9, 21.1. HPLC (OD-H, elute: n-hexane/i-PrOH = 99/1, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), t1 = 11.6 min (maj), t2 = 12.9 min.

(+)-(R)-2-Methylindoline (3e): 32 mg, 96% yield, colorless oil, known compound, Rf = 0.75 (hexanes/ethyl acetate 10/1). 90% ee, [α]_D^20 = +3.98 (c 0.56, benzene), [lit.[4]: [α]_D^RT = +6.96 (c 0.63, benzene) for 91% ee]; ¹H NMR (400 MHz, CDCl₃) δ 7.06 (d, J = 7.1 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.71-6.65 (m, 1H), 6.59 (d, J = 7.7 Hz, 1H), 4.05-3.92 (m, 1H), 3.67 (brs, 1H), 3.18-3.07 (m, 1H), 2.67-2.59 (m, 1H), 1.27 (d, J = 6.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.0, 128.9, 127.3, 124.7, 118.6, 109.2, 55.2, 37.8, 22.3. HPLC (OD-H, elute: n-hexane/i-PrOH = 97/3, detector: 254 nm, 30 °C, flow rate: 0.8 mL/min), t1 = 11.0 min (maj), t2 = 12.5 min.

(+)-(R)-2-Ethylindoline (3f): 30 mg, 82% yield, colorless oil, known compound, Rf = 0.60 (hexanes/ethyl acetate 20/1). 94% ee, [α]_D^20 = +5.88 (c 0.34, CHCl₃), [lit.[5]: [α]_D^22 = -5.5 (c 0.2, CHCl₃) for 97% ee]; ¹H NMR (400 MHz, CDCl₃) δ 7.06 (d, J = 7.2 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.67 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 7.7 Hz, 1H), 3.81-3.72 (m, 1H), 3.45-3.05 (m, 1H; brs, 1H), 2.72-2.62 (m, 1H), 1.68-1.56 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.0, 128.9, 127.2, 124.7, 118.1, 109.1, 61.5, 35.8, 29.6, 10.7. HPLC (OD-H, elute: n-hexane/i-PrOH = 95/5, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), t1 = 8.0 min (maj), t2 = 9.0 min.

(+)-(S)-2-Propylindoline (3g): 34 mg, 84% yield, colorless oil, known compound, Rf = 0.60 (hexanes/ethyl acetate 20/1). 94% ee, [α]_D^20 = +11.50 (c 0.40, CHCl₃), [lit.[6]: [α]_D^25 = +9.3 (c 0.3, CHCl₃) for 96% e.e.]; ¹H NMR (400 MHz, CDCl₃) δ 7.06 (d, J = 7.2 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 6.67 (t, J = 7.2 Hz, 1H), 6.59 (d, J = 7.7 Hz, 1H), 3.91-3.50 (m, 1H; brs, 1H), 3.10-3.00 (m, 1H), 2.76-2.66 (m, 1H), 1.80-1.70 (m, 1H), 0.96 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.0, 128.9, 127.2, 124.7, 118.5, 109.1, 59.8, 39.1, 36.2, 19.8, 14.2. HPLC (OD-H, elute: n-hexane/i-PrOH = 95/5, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), t1 = 7.7 min (maj), t2 = 9.2 min.

(+)-(S)-2-Isopropylindoline (3h): 38 mg, 94% yield, colorless oil, known compound, [7] Rf = 0.80 (hexanes/ethyl acetate 10/1). 96% ee, [α]_D^20 = -12.86 (c 0.70, CHCl₃), [lit.[7]: [α]_D^25 = -9.3 (c 0.3, CHCl₃) for 94% e.e.]; ¹H NMR (400 MHz, CDCl₃) δ 7.04 (d, J = 7.2 Hz, 1H), 6.98 (t, J = 7.6 Hz, 1H), 6.65 (t, J = 7.4 Hz, 1H), 6.57 (d, J = 7.7 Hz, 1H), 3.95-3.50 (m, 1H; brs, 1H), 3.10-3.00 (m, 1H), 2.76-2.66 (m, 1H), 1.80-1.70 (m, 1H), 0.98 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 151.4, 129.2, 127.2, 124.5, 118.3, 108.8, 66.6, 34.2, 34.0, 19.6, 19.1. HPLC (OD-H, elute: n-hexane/i-PrOH = 99/1, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), t1 = 10.7 min (maj), t2 = 17.5 min.
(+)-(R)-2-Butylindoline (3i): 43 mg, 98% yield, colorless oil, known compound, Rf = 0.85 (hexanes/ethyl acetate 10/1). 94% ee, [α]20D = +16.28 (c 0.86, CHCl3), [lit.[4]: [α]RTD = +12.6 (c 1.1, CHCl3) for 93% ee]; 1H NMR (400 MHz, CDCl3) δ 7.05 (d, J = 7.2 Hz, 1H), 6.99 (t, J = 7.4 Hz, 1H), 6.67 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 7.7 Hz, 1H), 4.01-3.63 (m, 1H; brs, 1H), 3.16-3.06 (m, 1H), 2.70-2.62 (m, 1H), 1.66-1.54 (m, 2H), 1.41-1.30 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 151.0, 128.9, 127.2, 124.7, 118.4, 109.1, 60.1, 36.6, 36.2, 28.8, 22.8, 14.1. HPLC (OD-H, elute: n-hexane/i-ProH = 99/1, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), t1 = 9.5 min (maj), t2 = 13.1 min.

(+)-(R)-2-Pentylindoline (3j): 46 mg, 97% yield, colorless oil, known compound, Rf = 0.85 (hexanes/ethyl acetate 10/1). 93% ee, [α]20D = +15.87 (c 0.92, CHCl3), [lit.[4]: [α]RTD = +12.6 (c 1.1, CHCl3) for 92% ee]; 1H NMR (400 MHz, CDCl3) δ 7.08-6.96 (m, 2H), 6.69-6.56 (m, 2H), 4.10-3.3.54 (m, 1H; brs, 1H), 3.15-3.05 (m, 1H), 2.70-2.60 (m, 1H), 1.66-1.52 (m, 2H), 1.47-1.24 (m, 6H), 0.90 (t, J = 6.9 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 151.0, 128.9, 127.2, 124.6, 118.4, 109.1, 60.1, 38.8, 31.9, 26.3, 22.7, 14.0. HPLC (OD-H, elute: n-hexane/i-ProH = 99/1, detector: 254 nm, 30 oC, flow rate: 1.0 mL/min), t1 = 9.6 min (maj), t2 = 12.4 min.

(+)-(R)-2,7-Dimethylindoline (3k): 35 mg, 94% yield, colorless oil, known compound, Rf = 0.65 (hexanes/ethyl acetate 10/1). 96% ee, [α]20D = +8.12 (c 0.48, CHCl3), 1H NMR (400 MHz, CDCl3) δ 6.96-6.82 (m, 2H), 6.63 (t, J = 7.4 Hz, 1H), 4.05-3.92 (m, 1H), 3.50 (brs, 1H), 3.20-3.10 (m, 1H), 2.70-2.60 (m, 1H), 2.12 (s, 3H), 1.30 (d, J = 6.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 149.6, 128.3, 128.2, 122.2, 118.7, 118.6, 55.2, 38.1, 22.5, 16.9. HPLC (OD-H, elute: n-hexane/i-ProH = 99/1, detector: 254 nm, 30 oC, flow rate: 1.0 mL/min), t1 = 11.1 min, t2 = 12.4 min (maj).

(+)-(R)-7-Methoxy-2-methylindoline (3l): 37 mg, 91% yield, colorless oil, new compound, Rf = 0.40 (hexanes/ethyl acetate 20/1). 80% ee, [α]20D = +8.09 (c 0.68, CHCl3), 1H NMR (400 MHz, CDCl3) δ 6.74 (d, J = 7.0 Hz, 1H), 6.71-6.61 (m, 2H), 4.07-3.96 (m, 1H), 3.81 (s, 3H), 3.59 (brs, 1H), 3.20-3.12 (m, 1H), 2.70-2.62 (m, 1H), 1.30 (d, J = 6.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 145.2, 139.9, 129.9, 119.1, 117.3, 119.1, 117.3, 119.1, 55.7, 55.3, 38.4, 22.3. HPLC (OD-H, elute: n-hexane/i-ProH = 99/1, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), t1 = 13.9 min, t2 = 16.6 min (maj). HRMS Calculated for C10H14NO [M+H]+ 164.1070, found: 164.1072.

(+)-(R)-5-Methoxy-2-methylindoline (3m): 33 mg, 81% yield, yellow oil, known compound, Rf = 0.40 (hexanes/ethyl acetate 20/1). 80% ee, [α]20D = +8.09 (c 0.68, CHCl3), 1H NMR (400 MHz, CDCl3) δ 6.71-6.61 (m, 2H), 4.07-3.96 (m, 1H), 3.81 (s, 3H), 3.59 (brs, 1H), 3.20-3.12 (m, 1H), 2.70-2.62 (m, 1H), 1.30 (d, J = 6.2 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 145.2, 139.9, 129.9, 119.1, 117.3, 119.1, 55.7, 55.3, 38.4, 22.3. HPLC (OD-H, elute: n-hexane/i-ProH = 99/1, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), t1 = 13.9 min, t2 = 16.6 min (maj). HRMS Calculated for C10H14NO [M+H]+ 164.1070, found: 164.1072.

(+)-(R)-2,5,7-Trimethylindoline (3n): 36 mg, 90% yield, colorless oil, new compound, Rf = 0.70 (hexanes/ethyl acetate 10/1). 94% ee, [α]20D = +10.48 (c 0.42, CHCl3), 1H NMR (400 MHz, CDCl3) δ 6.76 (s, 1H), 6.67 (s, 1H), 4.02-3.89 (m, 1H), 3.35 (brs, 1H), 3.15-3.05 (m, 1H),
2.65-2.55 (m, 1H), 2.22 (s, 3H), 2.09 (s, 3H), 1.29 (d, J = 6.2 Hz, 3H); \( ^{13} \text{C NMR} \) (100 MHz, CDCl \(_3\)) \( \delta \) 147.2, 128.8, 128.7, 128.2, 122.9, 118.6, 55.4, 38.2, 22.4, 20.8, 16.8.

HPLC (OD-H, elute: \( n \)-hexane/\( i \)-PrOH = 99/1, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), \( t_1 = 7.3 \) min, \( t_2 = 8.1 \) min (maj). HRMS Calculated for C\(_{11}\)H\(_{16}\)N [M+H]\(^+\) 162.1277, found: 162.1282.

(\(-\)-(\(S\))-2-Phenylindoline (3o): 27 mg, 55% yield, white solid, known compound, \( R_f = 0.70 \) (hexanes/ethyl acetate 10/1). 68% ee, [\( \alpha \])\(^20\) = -45.9 (c 0.54, CHCl \(_3\)), [lit.\(^[8]\)] [\( \alpha \])\(^25\) = -80.1 (c 1.0, CHCl \(_3\)) for > 99% ee of the (\(S\))-enantiomer; \( ^1 \text{H NMR} \) (400 MHz, CDCl \(_3\)) \( \delta \) 7.37-7.31 (m, 2H), 7.29-7.22 (m, 2H), 7.22-7.16 (m, 1H), 7.00 (dd, \( J = 12.6, 7.3 \) Hz, 2H), 6.68 (t, \( J = 7.3 \) Hz, 1H), 6.61 (d, \( J = 7.7 \) Hz, 1H), 4.88 (t, \( J = 9.0 \) Hz, 1H), 3.60 (br, 1H), 3.36 (dd, \( J = 15.6, 9.2 \) Hz, 1H), 2.92 (dd, \( J = 15.6, 8.8 \) Hz, 1H); \( ^{13} \text{C NMR} \) (100 MHz, CDCl \(_3\)) \( \delta \) 150.6, 144.5, 128.8, 128.5, 127.8, 127.7, 126.5, 124.8, 119.1, 109.5, 63.7, 39.7.

HPLC (OD-H, elute: \( n \)-hexane/\( i \)-PrOH = 90/10, detector: 254 nm, 30 °C, flow rate: 1.0 mL/min), \( t_1 = 12.7 \) min (maj), \( t_2 = 21.3 \) min.

4. The Mechanistic Investigation

Under nitrogen, to a solution of compound 2a (32 mg, 0.1 mmol) in 2,2,2-trifluoroethanol/toluene (1 mL/1 mL) was added ethanesulfonic acid (16 \( \mu \)L, 0.2 mmol). After stirring for five minutes, the mixture was quenched with saturated sodium hydrogencarbonate (5 mL). Then the mixture was extracted with ethyl acetate (5 mL×3), the combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by flash chromatography to give tert-butyl 2-benzyl-1\( H \)-indole-1-carboxylate 4 (24 mg, 78% yield, colorless oil, known compound,\(^[1]\) \( R_f = 0.80 \) (hexanes/ethyl acetate 20/1). 1H NMR (400 MHz, CDCl \(_3\)) \( \delta \) 8.04 (d, \( J = 8.4 \) Hz, 1H), 7.35-7.30 (m, 1H), 7.26-7.19 (m, 2H), 7.19-7.07 (m, 5H), 6.05 (d, \( J = 0.5 \) Hz, 1H), 4.29 (s, 2H), 1.49 (s, 9H); \( ^{13} \text{C NMR} \) (100 MHz, CDCl \(_3\)) \( \delta \) 150.5, 140.5, 139.2, 136.9, 129.1, 129.0, 128.4, 126.3, 123.5, 122.7, 119.9, 115.6, 109.3, 83.9, 36.4, 28.1.

Under nitrogen, to a solution of compound 4 (46 mg, 0.15 mmol) in 2,2,2-trifluoroethanol/toluene (2 mL/2 mL) was added ethanesulfonic acid (24 \( \mu \)L, 0.30 mmol). After stirring for thirty minutes, the mixture was quenched with saturated sodium hydrogencarbonate (5 mL). Then the mixture was extracted with ethyl acetate (10 mL×3), the combined organic layer was washed with brine, dried over sodium sulfate, and concentrated in vacuo. The residue was purified by flash chromatography to give the 2-benzyl-1\( H \)-indole 5 (30 mg, 97% yield, pale yellow solid, known compound,\(^[6]\) \( R_f = 0.70 \) (hexanes/ethyl acetate 20/1). 1H NMR (400 MHz, CDCl \(_3\)) \( \delta \) 7.70 (brs, 1H), 7.53 (d, \( J = 7.6 \) Hz, 1H), 7.34-7.28 (m, 2H), 7.26-7.19 (m, 4H), 7.12-7.03 (m, 5H), 6.05 (d, \( J = 0.6 \) Hz, 1H), 4.09 (s, 2H); \( ^{13} \text{C NMR} \) (100 MHz, CDCl \(_3\)) \( \delta \) 138.6, 137.8, 136.3, 128.9, 128.8, 128.7, 126.8, 121.4, 120.0, 119.8, 110.5, 101.2, 34.8.
Ligand (R)-H8-BINAP (4.8 mg, 0.0076 mmol) and Pd(OCOCF3)2 (2.1 mg, 0.0063 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for one hour. The solvent was removed under vacuum to give the catalyst. This catalyst was taken into a glove box filled with nitrogen and dissolved in 2,2,2-trifluoroethanol (2.0 mL). To the mixture of compound 5 (51.8 mg, 0.25 mmol) and ethanesulfonic acid (41 µL, 0.50 mmol) in toluene (2 mL), this catalyst solution was added, and then the mixture was transferred to an autoclave, which was charged hydrogen gas (300 psi). The autoclave was stirred at 40 °C for 24 h. After release of the hydrogen, the autoclave was opened and the reaction mixture was evaporated. Purification was performed on silica gel using hexanes/ethyl acetate (20:1) as the eluent to give chiral products 3a (51 mg, 98% yield, 95% ee).

5. The Scale-up Experiment

Ligand (R)-H8-BINAP (47.9 mg, 0.076 mmol) and Pd(OCOCF3)2 (20.9 mg, 0.063 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for one hour. The solvent was removed under vacuum to give the catalyst. This catalyst was taken into a glove box filled with nitrogen and dissolved in 2,2,2-trifluoroethanol (10 mL). To the mixture of compound 2a (814 mg, 2.5 mmol) and ethanesulfonic acid (0.41 mL, 5 mmol) in toluene (10 mL), this catalyst solution was added, and then the mixture was transferred to an autoclave, which was charged hydrogen gas (300 psi). The autoclave was stirred at 40 °C for 24 h. After release of the hydrogen, the autoclave was opened and the reaction mixture was evaporated. Then, saturated sodium hydrogencarbonate (10 mL) was added. The mixture was extracted with dichloromethane (10 mL×3), and the combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Purification was performed on silica gel using ethyl acetate/hexanes (10:1) as the eluent to give chiral product 3a (477 mg, 91% yield, 94% ee).
6. References

7. Copy of NMR, HPLC for Compounds

1H NMR CY-26-49 In CDC13

2a 1H NMR (400 MHz, CDCl3)
$^{13}$C NMR CY-26-49 in CDCl$_3$

2a $^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR JW-9-8 in CDCl₃

2b 1H NMR (400 MHz, CDCl₃)
$^{13}$C NMR JW-9-8 in CDCl$_3$
1H JW-9-98 in CDCl3

2c 1H NMR (400 MHz, CDCl3)
$^1$H NMR JW-3-6 in CDCl$_3$

2d $^1$H NMR (400 MHz, CDCl$_3$)
1H NMR CY-26-30 in CDCl₃

NHBoc

2e ¹H NMR (400 MHz, CDCl₃)
$^{13}$C NMR CY-26-30 in CDCl$_3$
$^1$H NMR (400 MHz, CDCl$_3$)
13C NMR JW-9-12 in CDCl3

$2f^{13}C$ NMR (100 MHz, CDCl3)
$^{1}H$ NMR JW-3-13 in CDCl$_3$

NHBOc

$2g$ $^1H$ NMR (400 MHz, CDCl$_3$)
13C NMR JW-9-13 In CDCl3

2g 13C NMR (100 MHz, CDCl3)
1H NMR CY-26-85 in CDCl₃

2h "H NMR (400 MHz, CDCl₃)
13C NMR CY-26-85 in CDCl3

2h $^{13}$C NMR (100 MHz, CDCl3)
1H NMR CY-26-97 in CDCl3

2H NMR (400 MHz, CDCl3)
$^{13}$C NMR CY-26.97 in CDCl$_3$
1H NMR δ 2.691 in CDCl₃

2) ¹H NMR (400 MHz, CDCl₃)
$^1$H NMR $\delta 26.91$ in CDCl$_3$

$^13$C NMR (100 MHz, CDCl$_3$)
$\text{NHBOc}$

2k $^1$H NMR (400 MHz, CDCl$_3$)

1H NMR CY-27-17 in CDCl$_3$
$^{13}$C NMR of 22-17 in CDCl$_3$
$^1$H NMR JW-9-7 in CDCl$_3$

2$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

![Chemical Structure](image)

S33
$\text{NHBoc}$

$\text{OMe}$

$2\text{m} \ H\text{NMR (400 MHz, CDCl}_3\text{)}$
$^{13}$C NMR CY-27-19 in CDCl$_3$

$2^m$ $^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR CY-27-22 in CDCl$_3$
$^{13}$C NMR of CY-27-22 in CDC$_3$

2n $^{13}$C NMR (100 MHz, CDCl$_3$)
C13CPD CDCI3 [D8]NMR 400/201, NMR 13

2α-13C NMR (100 MHz, CDCl3)
1H NMR CY.28-101 in CDCl3

3a $^1$H NMR (400 MHz, CDCl3)
$^{13}$C NMR CY-26-101 in CDCl$_3$

$^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR JW-9-11A in CDCl₃

3b ¹H NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)

3b $^1$H NMR (400 MHz, CDCl$_3$)
$^{1}H$ NMR JW-9-11B in CDCl$_3$

$3c$ $^{1}H$ NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR: $3c\text{ }^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR JW-9-108 in CDCl$_3$

3d $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR JW-9-10B In CDCl$_3$
13C NMR CY-27-6 in CDCl3

$\textbf{3e}^{13\text{C}}$ NMR (100 MHz, CDCl3)
1H NMR JW-9-148 in CDCl3

3H NMR (400 MHz, CDCl3)
$^{13}$C NMR JW-9-14B In CDCl₃

$\text{3f}^{13}$C NMR (100 MHz, CDCl₃)
$^1$H NMR JW-3-15C in CDCl$_3$

3g $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR $J_{W-9-15C}$ in CDCl$_3$

$3g$ $^{13}$C NMR (100 MHz, CDCl$_3$)

![NMR spectrum graph]
$^{1}H$ NMR CY-27-13 in CDCl$_3$

$^{3}H$ $^{1}H$ NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR of 3h in CDCl$_3$
1H NMR CY-27-11 in CDCl₃

31H NMR (400 MHz, CDCl₃)
$^1$H NMR CY-27-11 in CDCl$_3$

$^{31}$C NMR (100 MHz, CDCl$_3$)
1H NMR CY-27-B in CDCl₃

3j \( ^1H \) NMR (400 MHz, CDCl₃)
$\text{13C NMR CY-27-8 in CDCl}_3$

$3j^{13}\text{C NMR (100 MHz, CDCl}_3)$

![NMR spectrum](image-url)
$^1$H NMR CY-27-28A in CDCl$_3$
$^{13}$C NMR CY-27-28A in CDCl$_3$

$^{3}$k$^{13}$C NMR (100 MHz, CDCl$_3$)
1H NMR JW-9-10A in CDCl₃

31³H NMR (400 MHz, CDCl₃)
$^{13}$C NMR JW-9-10A in CDCl$_3$

$^{31}$C NMR (100 MHz, CDCl$_3$)
1H NMR JW-3-14A in CDCl₃
$^{13}$C NMR JW-9-14A in CDCl₃

3m$^{13}$C NMR (100 MHz, CDCl₃)
$^{1}H$ NMR CY-27-288 in CDCl$_3$
$^{13}$C NMR of CY-27-288 in CDCl$_3$
PROTON CDC13 [D:\NMR400\02T4] nmr 2.

30 H NMR (400 MHz, CDCl3)
C13CPD CDC3 [D$_7$NMR400/02T4] nmr 21

30 $^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}$H NMR JW-9-24 in CDCl$_3$
13C NMR JW-9-24 In CDCl₃
1H NMR JW-9-17 in CDCl₃

5 ¹H NMR (400 MHz, CDCl₃)
$^{13}$C NMR JW-9-17 In CDCl$_3$
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- Location: Vial 1

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**Net Multipler x Dilution Factor with INTs**

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