Free Radical-Mediated Aryl Amination and its Use in a Convergent [3+2] Strategy for Enantioselective Indoline α -Amino Acid Synthesis

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General Experimental Details

Flame-dried (under vacuum) glassware was used for all non-aqueous reactions. All reagents and solvents were commercial grade and purified prior to use when necessary. Diethyl ether (Et₂O), tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), and benzene (C₆H₆) were dried by passage through a column of activated alumina as described by Grubbs.¹ Benzene was additionally passed through a column containing activated Q-5 reactant. Solvents other than benzene were degassed using the freeze-pump-thaw method when necessary. All additional solvents were dried by distillation from calcium hydride when necessary. Molecular sieves (spheres, 4Å) were calcined at 400 °C and stored at room temperature in an air-tight container. AIBN was recrystallized prior to use, and tri-*n*-butyl tin hydride ("Bu₃SnH) was used as received from Aldrich.² Magnesium sulfate was used to dry organic solutions unless otherwise noted.

Thin layer chromatography (TLC) was performed using glass-backed silica gel (250 μ) plates, and flash chromatography utilized 230–400 mesh silica gel from Scientific Adsorbents. Neutral Alumina was used as received from Scientific Adsorbents for chromatography of acid-sensitive intermediates or products. Products were visualized by UV light, iodine, and/or the use of ceric ammonium molybdate, potassium permanganate, ninhydrin, *p*-anisaldehyde, and potassium iodoplatinate solutions.

IR spectra were recorded on a Nicolet Avatar 360 spectrophotometer. Liquids and oils were analyzed as neat films on a salt plate (transmission), whereas solids were applied to a diamond plate (ATR). Nuclear magnetic resonance spectra (NMR) were acquired on either a Varian Inova-

¹ Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

²Two lots (purchased six months apart) from Alfa Aesar failed to effect the radical reactions.

400 or VXR-400 instrument. Chemical shifts are measured relative to tetramethylsilane, as judged by the residual partially deuterated solvent peak. Mass spectra were obtained using a Kratos MS-80 spectrometer using the ionization technique indicated. Combustion analyses were performed by Atlantic Microlab, Norcross, GA.

Ratios of diastereomers and isomeric products were measured directly from integration of ^1H NMR absorptions of protons common to the components. Precision was checked by varying the relaxation delay for measurements on the same compound. Where possible, ratios were corroborated using GC-mass spectrometry. Peak assignments were made from authentic samples in every case. Ratios reported generally represent a lower limit defined by multiple runs.

General Procedure for Ketimine Condensations

A rapidly stirred benzene solution of the amine (0.5 M), ketone (0.5 M), and 4Å MS (1:1 w/w) was stirred at 25 °C until complete conversion was achieved, as evidenced by ¹H NMR. The mixture was filtered through a pad of Celite and washed with Et₂O or benzene. The solvent was removed *in vacuo* to give the analytically pure ketimine which was used immediately.

The same procedure was used when the benzophenone ketimine was desired, except benzophenone imine³ was used in place of the ketone.⁴

General Procedure for Aryl Aminations

A benzene solution of the ketimine (0.01 M) was warmed to 85 °C in a round-bottomed flask equipped with a condenser. A benzene solution (1 mL) of ⁿBu₃SnH (1.1 equiv) and AIBN (0.4 equiv) was loaded into a gas-tight syringe and was attached to a syringe pump. The syringe needle was attached through a septum at the top of the condenser (w/N₂ line) such that the solution droplets would fall directly into the refluxing benzene. Following the addition, the reaction mixture was refluxed for an additional period (~1 h) and cooled to room temperature. At this point, an aliquot was removed, concentrated, and component ratios were measured by ¹H NMR and/or GC-MS. Typically, one of the following two work-up methods was employed:

Method 1: The solution was treated with NaBH₄ (1.1 equiv) and the slurry was stirred 4–5 hours. The mixture was concentrated *in vacuo*, diluted with Et₂O, and washed with water. The organic layer was separated, dried, and concentrated to furnish an oil. Flash chromatography of the crude mixture provided the analytically pure targeted compounds.

Method 2: The benzene was removed by vacuum, the residue was diluted with ether, and a satd aq. KF solution (~20 equiv) was added. The mixture was stirred for 2 h (a ppt usually forms at the interface) and the layers were separated. The organic layer was dried and concentrated, and the resulting oil was chromatographed.

³ Pickard, P. L.; Tolbert, T. L. in "Organic Syntheses"; Wiley: NY, 1973, Collective Vol. 5, pp. 520-2.

⁴ O'Donnell, M. J.; Polt, R. L. *J. Org. Chem.* **1982**, *47*, 2663.

***N*-(1-Methylbenzyl)indoline (2a).** Following the general procedure, *ortho*-bromophenethylamine (46 mg, 231 μ mol), acetophenone (27 μ L, 231 μ mol), and 4Å MS were stirred in benzene (1 mL) at room temperature for 12 h. Filtering of the mixture through Celite and removal of the solvent provided the ketimine as a >95:5 mixture of stereoisomers. IR (film) 3056, 1633 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (m, 2H), 7.57 (d, J = 6.9 Hz, 1H), 7.40 (t, J = 3.1 Hz, 3H), 7.34 (d, J = 6.0 Hz, 1H), 7.26 (t, J = 6.3 Hz, 1H), 7.10 (t, J = 6.0 Hz, 1H), 3.79 (dd, J = 7.8, 7.2 Hz, 2H), 3.22 (dd, J = 7.8, 7.2 Hz, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 166.0, 142.0, 140.0, 133.0, 131.7, 129.7, 128.5, 128.1, 127.6, 126.9, 124.1, 52.2, 37.8, 18.1; HRMS (ED): Exact mass calcd for $\text{C}_{16}\text{H}_{17}\text{BrN}$ $[\text{M}+\text{H}]^+$, 302.0544. Found 302.0516.

The phenethylamine ketimine was similarly prepared. IR (film) 3083, 1685 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (m, 2H), 7.40 (t, J = 3.0 Hz, 3H), 7.31 (m, 5H), 3.76 (dd, J = 7.6, 7.5 Hz, 2H), 3.10 (dd, J = 7.6, 7.5 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 165.9, 141.6, 140.9, 129.7, 129.3, 128.7, 128.5, 126.8, 126.3, 54.4, 37.8, 15.7; HRMS (ED): Exact mass calcd for $\text{C}_{16}\text{H}_{17}\text{N}$ $[\text{M}]^+$, 223.1361. Found 223.1360.

A three hour addition of a $t\text{Bu}_3\text{SnH}$ (68 μ L, 25 μ mol) and AIBN (15 mg, 93 μ mol) solution in benzene (0.7 mL) to a refluxing solution of the unpurified ketimine (69.6 mg, 231 μ mol) in benzene (23 mL) delivered, after flash chromatography (2% dichloromethane in hexanes), the indoline as a colorless oil (44.9 mg, 87%). R_f = 0.62 (30% CH_2Cl_2 /hexanes); IR (film) 3046, 1606 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.2 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 7.08 (d, J = 7.2 Hz, 1H), 7.00 (t, J = 7.8 Hz, 1H), 6.6 (t, J = 7.2 Hz, 1H), 6.36 (d, J = 7.8 Hz, 1H), 4.68 (q, J = 6.8 Hz, 1H), 3.42 (dd, J = 18.1, 9.1 Hz,

1H), 3.35 (dd, $J = 15.7, 7.4$ Hz, 1H), 2.96 (dd, $J = 8.5, 8.3$ Hz, 2H), 2.58 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 151.1 143.0 128.7, 127.4, 127.3 (2C), 127.1, 124.6, 117.2, 107.5, 54.8, 48.2, 28.5, 16.8; HRMS (EI): Exact mass calcd for $\text{C}_{16}\text{H}_{17}\text{N}$ $[\text{M}]^+$, 223.1361. Found 223.1366.

Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{N}$: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.09; H, 7.76; N, 6.38.

N-(1-Phenylbenzyl)indoline (2b). Following the general procedure, *ortho*-bromophenethylamine (471 mg, 2.35 mmol) and benzophenone imine (426 mg, 2.35 mmol) were stirred for 12 h in dichloromethane (4 mL). Removal of the solvent provided the ketimine. IR (film) 3056, 1660, 1623 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 6.8$ Hz, 2H), 7.49 (d, $J = 7.0$ Hz, 1H), 7.40 (m, $J = 3.8$ Hz, 3H), 7.35 (m, $J = 7.0$ Hz, 3H), 7.24 (t, $J = 5.8$ Hz, 1H), 7.19 (d, 6.8 Hz, 1H), 7.05 (t, $J = 5.8$ Hz, 1H), 6.98 (m, $J = 3.8$ Hz, 2H), 3.68 (dd, $J = 7.2, 7.2$ Hz, 2H), 3.14 (dd, $J = 7.4, 7.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 169.0, 140.0, 139.8, 136.9, 132.9, 131.6, 130.1, 128.65, 128.61, 128.4, 128.2, 127.9, 127.4, 125.0, 53.6, 37.9; HRMS (CI): Exact mass calcd for $\text{C}_{21}\text{H}_{19}\text{BrN}$ $[\text{M}+\text{H}]^+$, 364.0701. Found 364.0596.

The phenethylamine ketimine was similarly prepared. IR (film) 3080, 1623 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 6.8$ Hz, 2H), 7.40 (t, $J = 3.5$ Hz, 3H), 7.36 (t, $J = 7.0$ Hz, 3H), 7.25 (t, $J = 7.0$ Hz, 2H), 7.18 (d, $J = 7.0$ Hz, 1H), 7.16 (d, $J = 7.0$ Hz, 2H), 6.97 (d, $J = 3.5$ Hz, 2H), 3.66 (dd, $J = 7.4, 7.4$ Hz, 2H), 3.03 (dd, $J = 7.5, 7.5$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 168.7, 140.6, 140.1, 137.0, 130.1, 129.3, 128.6, 128.5, 128.4 (2C), 128.3, 127.9, 126.1, 55.8, 37.9; HRMS (EI): Exact mass calcd for $\text{C}_{21}\text{H}_{19}\text{N}$ $[\text{M}]^+$, 285.1517. Found 285.1517.

A three hour addition of a $t\text{Bu}_3\text{SnH}$ (70 μL , 254 μmol) and AIBN (5 mg, 9.2 μmol) solution in benzene (1.0 mL) to a refluxing solution of the unpurified ketimine in benzene (23 mL)

delivered, after flash chromatography (2% dichloromethane in hexanes), the desired indoline as a white solid (56.8 mg, 86%). mp 64–65 °C. R_f = 0.53 (10% EtOAc/hexanes); IR (film) 3025, 1605 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (m, 10H), 7.09 (d, J = 7.0 Hz, 1H), 6.92 (t, J = 7.5 Hz, 1H), 6.64 (t, J = 7.0 Hz, 1H), 6.20 (d, J = 7.5 Hz, 1H), 5.55 (s, 1H), 3.20 (dd, J = 8.3, 8.2 Hz, 2H), 2.96 (dd, J = 8.3, 8.2 Hz, 2H), ^{13}C NMR (100 MHz, CDCl_3) ppm 152.1, 141.5, 130.5, 128.7, 128.6, 127.4, 127.3, 124.5, 117.7, 108.3, 66.8, 51.6, 28.5; HRMS (EI): Exact mass calcd for $\text{C}_{21}\text{H}_{19}\text{N}$ $[\text{M}]^+$, 285.1517. Found 285.1520.

Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{N}$: C, 88.38; H, 6.71; N, 4.91. Found: C, 88.14; H, 6.75; N, 4.88.

***N*-[*(1-Methyl)-4-dimethylaminobenzyl*]-indoline (2c).** According to the general procedure, *ortho*-bromophenethylamine (100 mg, 500 μmol), (*para*-*N,N'*-dimethylamino) acetophenone (81.5 mg, 500 μmol), and 4Å MS were stirred in benzene (6 mL) at room temperature for 4 d to provide the ketimine as a >95:5 mixture of stereoisomers as an oil (151 mg, 88%). IR (film) 3050, 1602 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 9.0 Hz, 2H), 7.46 (dd, J = 8.1, 1.1 Hz, 1H), 7.25 (dd, J = 7.6, 1.6 Hz, 1H), 7.15 (dt, J = 7.4, 1.1 Hz, 1H), 6.98 (dt, J = 6.7, 1.6 Hz, 1H), 6.61 (d, J = 9.0 Hz, 2H), 3.65 (t, J = 7.4 Hz, 2H), 3.10 (t, J = 7.4 Hz, 2H), 2.91 (s, 6H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 165.4, 151.6, 143.1, 140.3, 132.9, 131.6, 129.5, 127.6, 128.0, 124.9, 111.7, 51.9, 40.6, 38.01, 15.09; HRMS (EI): Exact mass calcd for $\text{C}_{18}\text{H}_{21}\text{BrN}_2$ $[\text{M}]^+$, 344.0888. Found 344.0824.

In a similar manner, the ketimine of phenethylamine was prepared as a colorless solid, mp 59–62 °C; IR (film) 3059, 1659 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, J = 9.0 Hz, 2H), 7.22–7.18 (m, 4H), 7.13 (dd, J = 8.6, 4.5 Hz, 1H), 6.62 (d, J = 8.9 Hz,

2H), 3.64 (t, $J = 7.7$ Hz, 2H), 2.97 (t, $J = 7.8$ Hz, 2H), 2.92 (s, 6H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 165.2, 151.9, 141.2, 129.2, 128.5, 127.9, 126.1, 112.0, 54.1 (2C), 40.6, 38.0, 15.2; HRMS (EI): Exact mass calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2$ $[\text{M}]^+$, 266.1783. Found 266.1790.

A five hour addition of a $n\text{Bu}_3\text{SnH}$ (56 μL , 207 μmol) and AIBN (12 mg, 75 μmol) solution in benzene (1 mL) to a refluxing solution of the unpurified ketimine (65 mg, 188 μmol) in benzene (18 mL) delivered, after flash chromatography (SiO_2 , 50% dichloromethane in hexanes), the desired indoline as a crystalline solid (45 mg, 90%). mp 79-82 $^\circ\text{C}$; $R_f = 0.15$ (50% CH_2Cl_2 /hexanes); IR (film) 2960, 1653 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.28 (t, $J = 4.2$ Hz, 2H), 7.03 (dd, $J = 17.5, 7.2$ Hz, 2H), 6.73 (d, $J = 8.8$ Hz, 2H), 6.50 (t, $J = 7.3$ Hz, 1H), 6.44 (d, $J = 7.9$ Hz, 1H), 4.71 (q, $J = 6.8$ Hz, 1H), 3.37 (q, $J = 18.0, 9.2$ Hz, 1H), 3.27 (q, $J = 15.2, 8.4$ Hz, 1H), 2.95 (s, 6H), 2.93 (t, $J = 8.0$ Hz, 2H), 1.51 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 128.2 (2C), 127.4, 124.8, 116.8, 112.6 (2C), 107.3, 92.1, 86.3, 53.9, 47.9, 41.0, 28.4, 16.3; HRMS (EI): Exact mass calcd for $\text{C}_{18}\text{H}_{22}\text{N}_2$ $[\text{M}]^+$, 266.1783. Found 266.1774.

***N*-[(1-Methyl)-4-trifluoromethyl]-indoline (2d).** Following the general procedure, *ortho*-bromophenethylamine (429 mg, 2.14 mmol), *p*-trifluoromethyl acetophenone (404 mg, 2.14 mmol), and 4Å MS were stirred in benzene (5 mL) at room temperature for 4.5 h to provide the ketimine as a 93:7 mixture of stereoisomers. IR (film) 3064, 1636 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, $J = 8.2$ Hz, 2H), 7.46 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 7.8$ Hz, 1H), 7.38 (s, 1H), 7.33-7.21 (m, 1H), 7.10 (t, $J = 7.7$ Hz, 1H), 3.81 (t, $J = 7.3$ Hz, 2H), 3.23 (t, $J = 7.3$ Hz, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 164.9, 144.6, 139.8, 133.0, 131.7, 129.6, 128.7, 128.6, 127.6, 127.2, 125.6, 124.9, 52.3, 37.7, 15.7; HRMS (FAB): Exact mass calcd for $\text{C}_{17}\text{H}_{16}\text{BrF}_3\text{N}$ $[\text{M}+\text{H}]^+$, 370.0418. Found 370.0428.

In a similar manner, the ketimine of phenethylamine was prepared as a colorless oil; IR (film) 3063, 1623 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.3$ Hz, 2H), 7.65 (d, $J = 8.3$ Hz, 2H), 7.39 (s, 2H), 7.35-7.23 (m, 3H), 3.79 (t, $J = 7.4$ Hz, 2H), 3.11 (t, $J = 7.5$ Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 164.6, 131.6, 131.3, 129.2, 128.6, 127.2, 126.4, 125.5, 125.4, 123.0, 54.4, 37.6, 15.7; HRMS (FAB): Exact mass calcd for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{N}$ $[\text{M}+\text{H}]^+$, 292.1313. Found 292.1319.

A three hour addition of a $^n\text{Bu}_3\text{SnH}$ (91 μL , 337 μmol) and AIBN (20 mg, 123 μmol) solution in benzene (1 mL) to a refluxing solution of the unpurified ketimine (113 mg, 307 μmol) in benzene (31 mL) delivered, after flash chromatography (20% CH_2Cl_2 in hexanes), 65 mg (72%) of the desired indoline as a colorless oil; $R_f = 0.40$ (10% EtOAc/hexanes; IR (film) 3048, 1606 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 8.3$ Hz, 2H), 7.10 (d, $J = 6.9$ Hz, 1H), 7.01 (t, $J = 7.5$ Hz, 1H), 6.65 (t, $J = 7.1$ Hz, 1H), 6.31 (d, $J = 7.9$ Hz, 1H), 4.73 (q, $J = 6.8$ Hz, 1H), 3.43 (dd, $J = 17.9, 8.7$ Hz, 1H), 3.37 (dd, $J = 15.7, 7.4$ Hz, 1H), 2.99 (t, $J = 8.3$ Hz, 2H), 1.57 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 151.3, 147.5, 130.4, 129.6, 129.3, 127.5, 127.4, 125.7, 124.8, 117.7, 107.5, 54.9, 48.5, 28.5, 17.1; HRMS (EI): Exact mass calcd for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{N}$ $[\text{M}]^+$, 291.1235. Found 291.1234.

Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{N}$: C, 70.09; H, 5.54; N, 4.81. Found: C, 70.36; H, 5.54; N, 4.84.

1-[1-(2,4,5-Trifluorophenyl)ethyl]-2,3-dihydro-1H-indole (2e). Following the general procedure, ortho-bromophenethylamine (100 mg, 0.503 mmol), 2',4',5'-trifluoroacetophenone (87.0 mg, 503 μmol) were stirred in benzene (5.0 mL) at room temperature

for 5 h to provide the ketimine as a colorless oil (179 mg, 100%); IR (film) 3067, 1627 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (dd, $J = 8.1, 1.1$ Hz, 1H), 7.52-7.44 (m, 1H), 7.34-7.27 (m, 1H), 7.18 (td, $J = 7.9, 1.9$ Hz, 2H), 6.96-6.90 (m, 1H), 3.76 (t, $J = 7.4$ Hz, 2H), 3.22 (t, $J = 7.8$ Hz, 2H), 2.15 (d, $J = 3.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm

163.2, 139.6, 133.1, 131.6, 128.3, 127.7, 126.9, 124.9, 118.6, 117.8, 106.1, 51.8, 37.5, 18.9; HRMS (EI): Exact mass calcd for $\text{C}_{16}\text{H}_{14}\text{BrF}_3\text{N}$ $[\text{M}+\text{H}]^+$ 356.0262. Found 356.0293.

In a similar manner, phenethylamine (50.0 mg, 0.413 mmol), 2',4',5'-trifluoroacetophenone (54.0 μL , 0.413 mmol) were stirred in benzene (4.1 mL) at room temperature for 5 h to provide the ketimine as a colorless oil (110 mg, 90%): IR (film) 3065, 1627 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.42 (m, 1H), 7.36-7.22 (m, 4H), 7.11 (d, $J = 6.9$ Hz, 1H), 6.97-6.90 (m, 1H), 3.74 (t, $J = 7.4$, 2H), 3.10 (t, $J = 7.7$ Hz, 2H), 2.12 (d, $J = 3.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 162.9, 140.5, 140.1, 129.2, 129.2, 128.7, 128.6, 126.5, 118.1, 117.8, 106.1, 53.9, 37.4, 18.9; HRMS (EI): Exact mass calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}$ $[\text{M}]^+$, 277.1078. Found 277.1085.

Following the general procedure, a three-hour addition of $^n\text{Bu}_3\text{SnH}$ (59.0 μL , 0.219 mmol) and AIBN (11.0 mg, 68.0 μmol) solution in benzene (1 mL) to a refluxing solution of the unpurified ketimine (60.0 mg, 0.169 mmol) in benzene (17 mL) delivered, after flash chromatography (10% CH_2Cl_2 /hexanes), the desired indoline (31.0 mg, 65%) as a colorless solid. $R_f = 0.1$ (1% EtOAc/hexanes); IR (film) 3063, 1628 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.25 (m, 1H), 7.11 (d, $J = 7.2$ Hz, 1H), 7.03-6.93 (m, 2H), 6.67 (t, $J = 7.3$ Hz, 1H), 6.26 (d, $J = 7.8$ Hz, 2H), 4.84 (q, $J = 6.9$ Hz, 1H), 3.52 (td, $J = 7.8, 1.3$ Hz, 2H), 3.03 (t, $J = 7.9$ Hz, 2H), 1.55 (d, $J = 7.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 156.5, 154.2, 151.0, 148.3, 130.3, 127.6, 127.5, 124.7, 118.0, 116.2 (d, $J = 6.0$ Hz) 107.4, 105.9 (d, $J = 20.5$ Hz), 49.5, 49.1, 28.5, 18.2; HRMS (EI): Exact mass calcd or $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}$ $[\text{M}]^+$, 277.1078. Found 277.1088.

Anal. Calcd for $C_{16}H_{14}F_3N$: C, 69.30; H, 5.09; N, 5.05. Found: C, 69.39; H, 5.06; N, 5.03.

(2,6-Dimethoxyphenyl)ethyl-2,3-dihydro-1H-indole (2f). Following the general procedure, *ortho*-bromophenethylamine (200 mg, 0.999 mmol) and 2',6'-dimethoxyacetophenone (180 mg, 0.999 mmol) were stirred in benzene (10.0 mL) at room temperature for 10 h to provide the ketimine as a colorless oil (326 mg, 90%): IR (film) 2293, 1648, 1104 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 7.7$ Hz, 1H), 7.24–7.15 (m, 3H), 7.00 (td, $J = 6.3, 2.7$ Hz, 1H), 6.56 (d, $J = 8.3$ Hz, 2H), 3.77 (s, 6H), 3.32 (t, $J = 7.4$ Hz, 2H), 3.03 (dd, $J = 8.5, 5.8$ Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 164.9, 156.7, 155.9, 140.1, 132.5, 130.9, 129.5, 127.2, 124.6, 116.3, 103.9, 103.5, 55.8, 55.6, 53.3, 37.3, 32.3, 27.7; HRMS (EI): Exact mass calcd for $C_{18}H_{21}\text{BrNO}_2$ $[\text{M}+\text{H}]^+$, 362.0756. Found 362.0750.

In a similar manner, phenethylamine (50.0 mg, 0.413 mmol), 2',6'-dimethoxyacetophenone (74.4 mg, 0.413 mmol) were stirred in benzene (4.1 mL) at room temperature for 10 h to provide the ketimine as a colorless oil (108 mg, 87%): IR (film) 2922, 1643, 1115 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.25 (t, $J = 8.5$ Hz, 3H), 7.18–7.13 (m, 3H), 6.58 (d, $J = 8.3$ Hz, 2H), 3.78 (s, 6H), 3.33 (t, $J = 7.0$, 2H), 2.95 (t, $J = 7.9$ Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 164.7, 156.1, 141.1, 130.9, 129.9, 129.0, 128.4, 126.0, 116.6, 104.2, 103.9, 56.1, 55.8, 55.7, 37.5, 27.9; HRMS (EI): Exact mass calcd for $C_{18}H_{21}\text{NO}_2$ $[\text{M}]^+$, 283.1572. Found 283.1570.

Following the general procedure, a three hour addition of $t\text{Bu}_3\text{SnH}$ (232 μL , 0.866 mmol) and AIBN (43.0 mg, 0.266 mmol) in benzene (2 mL) to a refluxing solution of the unpurified ketimine (241 mg, 0.666 mmol) in benzene (66 mL) delivered, after flash chromatography (SiO_2 ,

30% dichloromethane in hexanes) the desired indoline (50.0 mg, 27%) as a colorless solid. R_f = 0.10 (30% CH_2Cl_2 /hexanes); IR (film) 2935, 1606 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.16 (t, J = 8.3 Hz, 1H), 7.00 (t, J = 6.8 Hz, 1H), 6.98 (d, J = 1.1 Hz, 1H), 6.56 (d, J = 8.3 Hz, 2H), 6.51-6.46 (m, 2H), 5.41 (q, J = 7.1 Hz, 1H), 3.84 (2, 6H), 3.68 (dd, J = 18.3, 9.0 Hz, 1H), 3.61 (dd, J = 18.7, 6.4 Hz, 1H), 2.98 (dd, J = 15.7, 6.7, 1H) 2.91 (dd, J = 15.7, 9 Hz 1H), 1.59 (d, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 159.0, 152.3, 129.5, 128.3, 127.5, 124.2, 119.5, 115.7, 105.9, 104.7, 56.0, 48.5, 46.2, 28.7, 16.4; HRMS (EI): Exact mass calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2$ $[\text{M}]^+$, 283.1572. Found 283.1581.

Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.56; H, 7.51; N, 4.91.

***N*-(1-Trifluoromethyl)benzyl indoline (2g).** Following the general procedure, *ortho*-bromophenethylamine (852 mg, 4.25 mmol), trifluoroacetophenone (590 μL , 4.21 mmol), and 4Å MS were stirred in toluene (10 mL) at room temperature for 12 h to provide the ketimine as a >95:5 mixture of stereoisomers. IR (film) 3062, 1669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, J = 7.9 Hz, 1H), 7.44 (t J = 7.4 Hz, 1H), 7.38 (t, J = 7.1 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 7.18 (d, J = 6.0 Hz, 1H), 7.10 (t, J = 6.0 Hz, 1H), 6.94 (d, J = 7.1 Hz, 2H), 3.69 (dd, J = 7.1, 7.1 Hz, 2H), 3.13 (dd, J = 7.1, 7.1 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 158.9, 138.4, 133.0, 131.7, 130.3, 130.1, 128.8, 128.4, 127.7, 127.5, 124.9, 52.8 36.8; HRMS (EI): Exact mass calcd for $\text{C}_{16}\text{H}_{13}\text{F}_3\text{N}$ $[\text{M}-\text{Br}]^+$, 276.1000. Found 276.1003.

The phenethylamine ketimine was similarly prepared. IR (film) 3063, 1669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.23 (m, J = 6.8 Hz, 3H), 7.10 (d, J = 6.7 Hz, 2H), 6.90 (d, J = 7.3 Hz, 2H), 3.65 (dd, J = 7.2, 7.2 Hz, 2H),

3.00 (dd, $J = 7.1, 7.1$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 158.9, 139.3, 130.4, 130.1, 129.3, 128.8, 128.6, 127.8, 126.6, 121.3, 118.5, 55.0, 36.7; HRMS (CI): Exact mass calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N} [\text{M}]^+$, 277.1078. Found 277.1081

A three hour addition of $^n\text{Bu}_3\text{SnH}$ (184 μL , 682 μmol) and AIBN (41 mg, 248 μmol) solution in benzene (2.5 mL) to a refluxing solution of the unpurified ketimine (220 mg, 620 μmol) in benzene (62 mL) delivered, after flash chromatography (5% CH_2Cl_2 in hexanes), 133 mg (77%) of the desired indoline as a colorless oil. $R_f = 0.35$ (5% EtOAc/hexanes); IR (film) 3031, 1607 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (m, 5H), 7.11 (t, $J = 7.9$ Hz, 1H), 7.09 (d, $J = 7.4$ Hz, 1H), 6.71 (t, $J = 7.4$ Hz, 1H), 6.62 (d, $J = 7.9$ Hz, 1H), 5.24 (q, $J = 8.7$ Hz, 1H), 3.62 (dd, $J = 14.2, 8.7$, Hz, 1H), 3.19 (dd, $J = 10.1, 8.9$, Hz, 1H), 3.01 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 150.5, 131.9, 129.3, 129.0 (2C), 127.6, 127.5, 125.1, 124.7, 118.5, 106.4, 62.0 (q, $J = 30.5$ Hz, 1C), 48.6, 28.5; HRMS (EI): Exact mass calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N} [\text{M}]^+$, 277.1078. Found 277.1071.

Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{F}_3\text{N}$: C, 69.30; H, 5.09; N, 5.05. Found: C, 69.33; H, 5.24; N, 5.04.

***N*-(1-Trifluoroethyl)-indoline (2h).** Following the general procedure, *ortho*-bromophenethylamine (200 mg, 999 μmol), trifluoroacetone (168 mg, 1.5 mmol), and 4Å MS were stirred in benzene (5 mL) at room temperature for 4 h to provide the ketimine as a >95:5 mixture of stereoisomers (264 mg, 90%). IR (film) 3059, 1686 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.3$ Hz, 1H), 7.29–7.22 (m, 2H), 7.13 (dt, $J = 6.8, 2.4$ Hz, 1H), 3.75 (t, $J = 7.3$ Hz, 2H), 3.17 (t, $J = 7.3$ Hz, 2H); 1.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 157.3 (q, $J = 33.6$ Hz), 138.6, 133.1, 131.8, 127.8, 124.7, 121.4, 118.6, 51.4, 36.6, 12.6; HRMS (EI): Exact mass calcd for $\text{C}_{11}\text{H}_{12}\text{BrF}_3\text{N} [\text{M}+\text{H}]^+$, 296.0086. Found 296.0088.

In a similar manner, the ketimine derived from phenethylamine was prepared. IR (film) 3088, 1686 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.34 (dd, $J = 7.0, 7.0$ Hz, 2H), 7.27 (t, $J = 6.6$ Hz, 1H), 7.26 (d, $J = 6.9$ Hz, 2H), 3.74 (t, $J = 7.3$ Hz, 2H), 3.06 (t, $J = 7.3$ Hz, 2H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 156.9 (q, $J = 32.8$ Hz), 139.6, 129.2, 128.8, 126.7, 120.1, 53.6, 36.4, 12.5; HRMS (EI): Exact mass calcd for $\text{C}_{11}\text{H}_{12}\text{F}_3\text{N}$ $[\text{M}]^+$, 215.0922. Found 215.0928.

In accord with the general procedure, a three hour addition of a $^n\text{Bu}_3\text{SnH}$ (133 μL , 495 μmol) and AIBN (30 mg, 180 μmol) solution in benzene (1 mL) to a refluxing solution of the unpurified ketimine (132 mg, 450 μmol) in benzene (44 mL) provided, after flash chromatography (100% hexanes), the desired indoline as a volatile colorless liquid (80 mg, 83%). $R_f = 0.15$ (hexanes); IR (film) 3050, 1490 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.07 (t, $J = 7.9$ Hz, 2H), 6.65 (t, $J = 7.3$ Hz, 1H), 6.44 (d, $J = 7.8$ Hz, 1H), 4.14 (m, 1H), 3.54 (t, $J = 8.5$ Hz, 2H), 3.03 (t, $J = 8.6$ Hz, 2H), 1.38 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 150.3, 129.3, 127.5, 125.0, 118.2, 114.0, 106.3, 52.8 (q, $J = 28.2$ Hz), 47.1, 28.5, 10.5; HRMS (EI): Exact mass calcd for $\text{C}_{11}\text{H}_{12}\text{F}_3\text{N}$ $[\text{M}]^+$, 215.0922. Found 215.0920.

***N*-(*iso*-Propyl)-indoline (2i).** Following the general procedure, *ortho*-bromophenethylamine (150 mg, 750 μmol), acetone (44 mg, 750 μmol) and 4Å MS were stirred in benzene (5 mL) at room temperature for 4 h to provide the ketimine. IR (film) 3055, 1653 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (d, $J = 8.3$ Hz, 1H), 7.24–7.18 (m, 2H), 7.04 (td, $J = 6.9, 2.3$ Hz, 1H), 3.46 (t, $J = 7.5$ Hz, 2H), 3.06 (t, $J = 7.7$ Hz, 2H), 1.99 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 168.3, 139.9, 133.0, 131.4, 128.1, 127.6, 124.9, 51.6, 37.7, 29.5, 18.6; HRMS (EI): Calcd for $\text{C}_{11}\text{H}_{15}\text{BrN}$ $[\text{M}+\text{H}]^+$, 240.0310. Found 240.0389.

The analogous phenethylamine ketimine was similarly prepared. IR (film) 3080, 1665 cm^{-1} ; ^1H

NMR (400 MHz, CDCl_3) δ 7.33 (t, $J = 8.1$ Hz, 2H), 7.28–7.24 (m, 3H), 3.52 (t, $J = 7.8$ Hz, 2H), 3.00 (t, $J = 7.8$ Hz, 2H), 2.05 (s, 3H), 1.74 (s, 3H), ^{13}C NMR (100 MHz, CDCl_3) ppm 169.9, 140.8, 129.1, 128.8, 126.3, 53.7, 37.7, 29.5, 18.6; HRMS (EI): Exact mass calcd for $\text{C}_{11}\text{H}_{15}\text{N}$ $[\text{M}]^+$, 161.1204. Found 161.1200.

A three-hour addition of $^n\text{Bu}_3\text{SnH}$ (154 μL , 573 μmol) and AIBN (34 mg, 208 μmol) solution in benzene (1 mL) to a refluxing solution of the unpurified ketimine (125 mg, 521 μmol) in benzene (50 mL) delivered, after flash chromatography (30% CH_2Cl_2 /Hexanes) 0.024 g (30%) of the desired indoline as a volatile colorless liquid. $R_f = 0.1$ (30% CH_2Cl_2 /hexanes); IR (film) 3047, 1607 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.04 (t, $J = 6.7$ Hz, 2H), 6.59 (t, $J = 7.4$ Hz, 1H), 6.42 (d, $J = 8.1$ Hz, 1H), 3.83 (sep, $J = 6.6$ Hz, 1H), 3.33 (t, $J = 8.5$ Hz, 2H), 2.93 (t, $J = 8.3$ Hz, 2H), 1.15 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) ppm 151.5, 130.5, 127.5, 124.6, 117.1, 107.3, 46.0, 45.7, 28.4, 18.4; HRMS (EI): Exact mass calcd for $\text{C}_{11}\text{H}_{15}\text{N}$ $[\text{M}]^+$, 161.1204. Found 161.1201.

1-(1-Ethylpropyl)-2,3-dihydro-1H-indole (2j). Following the general procedure, *ortho*-bromophenethylamine (200 mg, 1.00 mmol) and 3-pentanone (86.0 mg, 1.00 mmol) were stirred in benzene (5 mL) at room temperature for 48 h to provide the ketimine as a colorless oil (241 mg, 90%). IR (film) 3056, 1660 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.56 (dd, $J = 7.9, 0.9$ Hz, 1H), 7.32–7.24 (m, 2H), 7.10 (td, $J = 7.8, 1.9$ Hz, 1H), 3.61 (t, $J = 7.5$ Hz, 2H), 3.10 (t, $J = 7.9$ Hz, 2H), 2.30 (q, $J = 7.5$ Hz, 2H), 2.18 (q, $J = 7.7$ Hz, 2H), 1.12 (t, $J = 7.5$ Hz, 3H), 1.01 (t, $J = 7.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 176.2, 140.1, 132.9, 131.6, 128.0, 127.5, 124.8, 50.6, 38.0, 32.8, 24.0, 11.3, 11.1; HRMS (EI): Exact mass calcd for

$\text{C}_{13}\text{H}_{19}\text{BrN}$ $[\text{M}+\text{H}]^+$ 268.0703. Found 268.0690.

Following a similar procedure, the phenethylamine ketimine was prepared. IR

(film) 3084, 1647 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.19 (m, 5H), 3.58 (t, $J = 7.7$ Hz, 2H), 2.95 (t, $J = 7.9$ Hz, 2H), 2.28 (q, $J = 7.4$ Hz, 2H), 2.13 (q, $J = 7.7$, 2H), 1.11 (t, $J = 7.4$ Hz, 3H), 0.97 (t, $J = 7.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 176.0, 140.9, 129.2, 128.5, 126.2, 52.8, 38.0, 32.9, 24.0, 11.4, 11.1; HRMS (FAB) Exact mass calcd for $\text{C}_{13}\text{H}_{20}\text{N}$ $[\text{M}+\text{H}]^+$, 190.1596. Found 190.1592.

Following general procedure, a three hour addition of $^n\text{Bu}_3\text{SnH}$ (126 μL , 0.470 mmol) and AIBN (28 mg, 0.170 mmol) solution in benzene (1 mL) to a refluxing solution of the unpurified ketimine (114 mg, 0.425 mmol) in benzene (42 mL) delivered, after flash chromatography on silica gel (4% dichloromethane in hexanes) the desired indoline as a volatile colorless liquid (32.0 mg, 40%). $R_f = 0.10$ (4% CH_2Cl_2 /hexanes); IR (film) 3048, 1607 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.00 (t, $J = 7.3$ Hz, 2H), 6.51 (t, $J = 7.1$ Hz, 1H), 6.34 (d, $J = 8.1$ Hz, 1H), 3.34 (t, $J = 8.7$ Hz, 2H), 3.24 (p, $J = 7.1$ Hz, 1H), 2.96 (t, $J = 8.7$ Hz, 2H), 1.56–1.49 (m, 4H), 0.92 (t, $J = 7.4$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) ppm 152.6, 129.5, 127.5, 124.6, 115.8, 105.8, 58.2, 45.5, 28.4, 24.7, 11.9; HRMS (EI): Exact mass calcd for $\text{C}_{13}\text{H}_{19}\text{N}$ $[\text{M}]^+$, 189.1517. Found 189.1527.

2-(ortho-Bromophenyl)-propionamine. An ethereal solution of chilled AlCl_3 (1.0 M) was added via cannula to a chilled ethereal suspension of LiAlH_4 and stirred for 1 h. A solution of 2-(ortho-bromophenyl)propionitrile in ether (15 mL) was added dropwise and stirred overnight while warming to rt. The reaction was recooled in an ice bath, diluted with ether, and slowly quenched with NH_4OH . The organic layer was separated, dried, and concentrated to a yellow oil, which was distilled (68-69 °C, 200 mTorr) to furnish the amine as a clear, colorless oil. IR (film) 3370, 3058, 2962, 1589 cm^{-1} ; ^1H NMR (400MHz, CDCl_3) δ 7.56 (dd, $J = 7.9$, 1.2 Hz, 1H), 7.29 (t, $J = 8.3$ Hz, 1H), 7.22 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.06 (t, $J = 9.0$ Hz, 1H), 3.34 (dq, $J = 13.8$, 6.9 Hz, 1H), 2.90 (dd, $J = 14.5$, 7.3 Hz, 1H), 2.84 (dd, $J = 14.6$, 6.4 Hz, 1H), 1.23 (d, $J = 6.9$ Hz,

3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 144.1, 133.2, 127.98, 127.95, 127.5, 125.6, 48.7, 41.9, 18.6; HRMS (CI): Exact mass calcd for $\text{C}_9\text{H}_{12}\text{BrN}$ $[\text{M}-\text{H}]^+$, 212.0075. Found 212.0082.

***N*-(1-Phenethyl)-3-methylindoline (7a).** Following the general procedure, 2-(*ortho*-bromophenyl)-2-methyl-ethylamine (353 mg, 1.65 mmol), acetophenone (192 μL , 1.64 mmol), and 4Å MS were stirred in benzene (5 mL) at room temperature for 12 h to provide the ketimine as a >95:5 mixture of stereoisomers. IR (film) 3057, 1633 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.80 (m, 2H), 7.59 (d, J = 6.9 Hz, 1H), 7.39 (m, 4H), 7.31 (t, J = 6.9 Hz, 1H), 7.08 (t, J = 6.1 Hz, 1H), 3.76 (dd, J = 10.5, 6.3, Hz, 2H), 3.57 (dq, J = 13.8, 6.9 Hz, 1H), 2.19 (s, 3H), 1.45 (d, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 165.5, 144.9, 141.4, 133.0, 129.6, 128.4, 128.3, 127.8, 127.6, 126.8, 125.1, 58.1, 39.9, 18.8, 15.7; HRMS (EI): Exact mass calcd for $\text{C}_{17}\text{H}_{19}\text{BrN}$ $[\text{M}+\text{H}]^+$, 316.0701. Found 316.0588.

In a similar manner, the ketimine of 2-phenyl-1-propylamine was prepared. IR (film) 3083, 1634 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) 7.76 (m, 2H), 7.39 (t, J = 3.1 Hz, 3H), 7.30 (m, 4H), 7.24 (t, J = 3.9 Hz, 1H), 3.69 (dd, J = 13.9, 5.9 Hz, 1H), 3.59 (dd, J = 13.7, 7.9 Hz, 1H), 3.30 (dq, J = 13.8, 7.0 Hz, 1H), 2.13 (s, 3H), 1.44 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 165.4, 146.2, 141.6, 129.6, 128.5, 128.4, 127.6, 126.8, 126.3, 60.1, 41.5, 19.5, 15.7; HRMS (EI): Exact mass calcd for $\text{C}_{17}\text{H}_{19}\text{N}$ $[\text{M}]^+$, 237.1517. Found 237.1521.

A three hour addition of $t\text{Bu}_3\text{SnH}$ (84 μL , 314 μmol) and AIBN (18.7 mg, 114 μmol) benzene solution (1 mL) to a refluxing solution of the unpurified ketimine (90.3 mg, 286 μmol) in benzene (28 mL) afforded, after flash chromatography (SiO_2 , 1% ether in hexanes), the desired indoline as a yellow oil (58.4 mg, 86%) (58:42 mixture of diastereomers). R_f = 0.6 (10% EtOAc/hexanes); IR (film) 3024, 1605 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (d, J = 7.5 Hz,

4H), 7.35 (t, $J = 7.5$ Hz, 6H), 7.03 (d, $J = 8.0$ Hz, 2H), 7.01 (t, $J = 4.3$ Hz, 2H), 6.65 (t, $J = 7.4$ Hz, 2H), 6.36 (d, $J = 4.3$ Hz, 2H), 4.74 (q, $J = 6.9$ Hz, 1H), 4.68 (q, $J = 6.8$ Hz, 1H), 3.62 (dd, $J = 8.8, 8.8$ Hz, 1H), 3.45 (dd, $J = 8.6, 8.6$ Hz, 1H), 3.30 (dq, $J = 14.6, 7.3$ Hz, 2H), 2.95 (dd, $J = 8.8, 8.8$ Hz, 2H), 1.57 (d, $J = 7.0$ Hz, 3H), 1.52 (d, $J = 6.9$ Hz, 3H), 1.33 (d, $J = 6.7$ Hz, 3H), 1.27 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 151.5, 150.8, 146.4, 143.5, 142.8, 135.4, 135.3, 128.68, 128.62, 127.57, 127.53, 127.2, 127.1, 123.5, 123.1, 117.0, 107.5, 107.2, 56.5, 56.0, 54.9, 54.3, 35.0, 19.9, 18.3, 17.2, 16.5; HRMS (ED): Exact mass calcd for $\text{C}_{17}\text{H}_{19}\text{N} [\text{M}]^+$, 237.1517. Found 237.1509.

Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{N}$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.82; H, 8.02; N, 5.90.

1-(ortho-Bromophenyl)-acetone. 2-Bromophenylacetic acid (214 mg, 1 mmol) was dissolved in freshly distilled thionyl chloride (6 mL) and stirred for 2 h. Removal of SOCl_2 by vacuum provided the derived acid chloride quantitatively (232 mg). In a separate flask, a suspension of CuI (571 mg, 3 mmol) in chilled dry ether (8 mL) was treated with MeLi (4 mL, 1.5 M solution in hexanes), and the mixture was stirred for 5 m. The resulting clear orange-red solution was cooled to -78°C and the acid chloride (232 mg, 1 mmol) was added as a solution in ether (1 mL) and stirred for 30 m. Absolute methanol (0.5 mL) was then added and the mixture was allowed to warm to rt over a 2 h period. The contents were poured into an equal volume of satd aq ammonium chloride and stirred vigorously for 30 m. The aqueous layer was separated and washed with ether. The combined organic layers were washed with water, dried, and concentrated to a residue which was purified by flash column chromatography (SiO_2 , 5 % ethyl acetate in hexanes) to yield the desired ketone as a yellow oil (167 mg, 79 %). $R_f = 1.15$ (5% EtOAc/hexanes); IR (film) 3057, 1923, 1724, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (dd, $J =$

8.0, 1.0 Hz, 1H), 7.29 (dt, $J = 7.5, 1.0$ Hz, 1H), 7.22 (dd, $J = 7.5, 1.6$ Hz, 1H), 7.15 (dt, $J = 7.9, 1.8$ Hz, 1H), 3.87 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 205.1, 135.0, 133.1, 131.9, 129.1, 127.9, 125.3, 51.0, 30.1; HRMS (EI) Exact mass calcd for $\text{C}_9\text{H}_9\text{BrO}$ $[\text{M}]^+$, 211.9837. Found 211.9830.

1-(*ortho*-Bromophenyl)-2-amino-propane. To a solution of the ketone (60 mg, 0.283 mmol) in MeOH (1.1 mL) was added NaBH_3CN (18 mg, 0.283 mmol), NH_4OAc (218 mg, 2.83 mmol) and 4Å MS (53 mg). The resulting mixture was stirred for 18 h, and then conc. HCl (0.3 mL) was added dropwise to the solution until the pH of the mixture dropped to <3 and a white solid precipitated. The mixture was concentrated, water was added to the residue, and the resulting mixture was extracted with CH_2Cl_2 . 6M Aq NaOH was added to the aqueous phase until the pH was >12 . The solution was extracted with CH_2Cl_2 , and the organic layers were washed with water, dried, and concentrated to an oil that was purified by flash column chromatography (2.5 % methanol in dichloromethane) to obtain the desired amine as a colorless oil (43 mg, 72 %). $R_f = 1.2$ (2.5% MeOH/ CH_2Cl_2); IR (film) 3366, 3055, 1633, 1590, 1566 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (dd, $J = 7.9, 1.9$ Hz, 1H), 7.28-7.20 (m, 2H), 7.10-7.05 (m, 1H), 3.32-3.24 (m, 1H), 2.85 (dd, $J = 13.3, 5.7$ Hz, 1H), 2.66 (dd, $J = 13.3, 7.8$ Hz, 1H), 1.30-1.24 (bs, 2H), 1.14 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 139.3, 133.2, 131.7, 128.2, 127.6, 125.2, 47.3, 46.7, 23.6; HRMS (EI) Exact mass calcd for $\text{C}_9\text{H}_{12}\text{BrN}$ $[\text{M}]^+$, 214.0281. Found 214.0155.

The corresponding desbromo-ketone and amine were synthesized by similar procedures:

Benzyl methyl ketone: IR (film) 3062, 1712, 1616, 1602 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.37 (d, $J = 7.0$ Hz, 2H), 7.33-7.27 (m, 1H), 7.23 (d, $J = 7.0$ Hz, 2H), 3.72 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm

206.6, 134.6, 129.7, 129.0, 127.3, 51.2, 29.5; HRMS (EI) Exact mass calcd for $C_9H_{10}O$ $[M]^+$, 134.0732. Found 134.0729.

1-Phenylpropyl-2-amine: IR (film) 3370, 3065, 1635, 1605, 1566 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, $J = 7.6, 7.3$ Hz, 2H), 7.25-7.19 (m, 3H), 3.19 (bs, 1H), 2.73 (dd, $J = 13.1, 4.9$ Hz, 1H), 2.53 (dd, $J = 13.3, 8.0$ Hz, 1H), 1.44-1.28 (br s, 1H), 1.14 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 139.8, 129.5, 128.7, 126.5, 48.8, 46.8, 23.7; HRMS (EI) Exact mass calcd for $C_9H_{13}N$ $[M+H]^+$, 135.1128. Found 135.1122.

N-(1-Phenylbenzyl)-2-methylindoline (7b). Following the general procedure, 2-(*ortho*-bromophenyl)-1-methylethylamine (50 mg, 234 μ mol), benzophenone imine (42 mg, 233 μ mol) and 4Å MS were stirred in dichloromethane (2.5 mL) at room temperature for 3 days under argon atmosphere to provide the ketimine as a solid (85 mg, 96%). mp 59–61 °C; IR (film) 3057, 1726, 1661 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $J = 6.9$ Hz, 2H), 7.45 (d, $J = 7.4$ Hz, 1H), 7.37-7.30 (m, 6H), 7.20-7.14 (m, 2H), 7.03 (dt, $J = 6.9, 1.4$ Hz, 1H), 6.63 (d, $J = 6.7$ Hz, 2H), 3.81 (qd, $J = 7.8, 6.2$ Hz, 1H), 3.03 (d, $J = 4.5$ Hz, 1H), 3.01 (d, $J = 7.1$ Hz, 1H), 1.30 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 167.1, 140.2, 139.4, 137.3, 132.6, 130.3, 129.9, 128.6, 128.4, 128.2, 128.1, 127.8, 127.6, 127.1, 125.4, 57.4, 44.8, 22.4; HRMS (EI): Exact mass calcd for $C_{22}H_{20}BrN$ $[M]^+$, 377.0779. Found 377.0630.

In a similar manner, the ketimine of 1-methyl-2-phenylethylamine was prepared. IR (film) 3080, 1661 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, $J = 7.5$ Hz, 2H), 7.36-7.27 (m, 5H), 7.22-7.14 (m, 4H), 7.03 (d, $J = 7.4$ Hz, 2H), 6.66 (d, $J = 6.8$ Hz, 2H), 3.60 (qd, $J = 6.6, 6.0$ Hz, 1H), 2.92 (dd, $J = 13.0, 8.3$

Hz, 1H), 2.78 (dd, $J = 13.0, 5.1$ Hz, 1H), 1.25 (d, $J = 5.7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 140.2, 132.7, 130.3, 129.9, 128.6, 128.2, 127.7, 126.0, 59.9, 45.1, 22.4; HRMS (EI): Exact mass calcd for $\text{C}_{22}\text{H}_{21}\text{N} [\text{M}]^+$, 299.1674. Found 299.1667.

To a refluxing solution of the unpurified ketimine (20 mg, 53 μmol) in benzene (9 mL) was added $^n\text{Bu}_3\text{SnH}$ (15.6 μL , 58.2 μmol), followed by a four-hour addition of AIBN (10.4 mg, 63.5 μmol) dissolved in benzene (2 mL). After the first 2 h of the reaction, another lot of $^n\text{Bu}_3\text{SnH}$ (15.6 μL , 58.2 μmol) was added to the reaction mixture. After the complete addition of AIBN, the reaction mixture was refluxed for 1 h, followed by removal of solvent. Flash chromatography (SiO_2 , 5% CH_2Cl_2 in hexanes) yielded the desired indoline as a solid (13.1 mg, 78%). mp 58–61 $^\circ\text{C}$; $R_f = 0.15$, (5% CH_2Cl_2 /hexanes); IR (film) 3060, 1635 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.6$ Hz, 2H), 7.37–7.26 (m, 8H), 7.04 (d, $J = 7.1$ Hz, 1H), 6.82 (t, $J = 7.5$ Hz, 1H), 6.59 (t, $J = 7.3$ Hz, 1H), 5.97 (d, $J = 7.9$ Hz, 1H), 5.65 (s, 1H), 3.83 (qd, $J = 15.0, 6.2$ Hz, 1H), 3.25 (dd, $J = 15.6, 9.0$ Hz, 1H), 2.65 (dd, $J = 15.4, 6.9$ Hz, 1H), 1.16 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) ppm 138.9, 129.2, 129.0, 128.8, 127.6, 127.2, 124.7, 117.4, 109.4, 100.4, 65.5, 52.0, 37.6, 30.1, 21.0; HRMS (EI): Exact mass calcd for $\text{C}_{22}\text{H}_{21}\text{N} [\text{M}]^+$, 299.1674. Found 299.1682.

Methyl-(1-(*ortho*-bromophen)ethyl)-ketone. To a solution of diisopropyl amine (73 μL , 0.52 mmol) in THF (8 mL) at -40 $^\circ\text{C}$ was added $^n\text{BuLi}$ (1.96 M, 262 μL) and warmed to 0 $^\circ\text{C}$ over 30 m while stirring. The mixture was recooled to -78 $^\circ\text{C}$ and the ketone (100 mg, 0.47 mmol) was added as a solution in THF (1 mL) and stirred for 15 m prior to the addition of MeI (32 μL , 0.52 mmol) and warming to rt over 1.5 h. Water (0.5 mL) was then added and the solvent was removed by vacuum. The residue was diluted with ether, washed with 10% aq HCl, water, and brine. The organic layers were dried and concentrated to give the desired ketone as a yellow oil (105 mg, 98%) and in analytically pure form. $R_f = 1.12$ (5% EtOAc/hexanes); IR (film) 3414, 3064, 1923,

1716, 1589, 1567 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (dd, $J = 6.7, 1.3$ Hz, 1H), 7.30 (dt, $J = 7.5, 0.8$ Hz, 1H), 7.15 (dd, $J = 7.5, 1.3$ Hz, 1H), 7.13 (dd, $J = 6.7, 1.6$ Hz, 1H), 4.30 (q, $J = 6.8$ Hz, 1H), 2.10 (s, 3H), 1.38 (d, $J = 7$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 208.2, 140.4, 133.4, 128.9, 128.8, 128.3, 125.1, 52.5, 29.1, 16.7; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_{11}\text{BrO}$ $[\text{M}+\text{H}]^+$, 227.0080. Found 227.0082.

3-(*ortho*-Bromophenyl)-2-amino-butane. To a solution of the ketone (83.4 mg, 0.369 mmol) in MeOH (1.5 mL) was added NaBH_3CN (23 mg, 0.369 mmol), NH_4OAc (285 mg, 3.69 mmol) and 4Å MS (70 mg). The resulting mixture was stirred for 18 h. Conc. HCl (0.3 mL) was added dropwise to the solution until the *pH* of the mixture dropped below 3 and a white solid precipitated. Methanol was removed by vacuum, and water was added to the residue and washed with CH_2Cl_2 . 6M aq NaOH was added to raise the *pH* to >12. The solution was extracted with CH_2Cl_2 and washed with water, and the organic phase was separated, dried, and concentrated to a residue that was purified by flash chromatography (SiO_2 , 2.5% methanol in dichloromethane) to return the desired amine as a mixture of *anti* (24 mg, 29 %) and *syn* (5 mg, 6 %) diastereomers, both as oils. *Anti*: $R_f = 1.1$ (2.5% MeOH/ CH_2Cl_2); IR (film) 3373, 2873, 1590, 1566 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.33-7.27 (m, 2H), 7.08 (ddd, $J = 7.9, 6.9, 2.1$ Hz, 1H), 3.17 (q, $J = 7.4$ Hz, 1H), 3.12 (dq, $J = 6.3, 1.6$ Hz, 1H), 1.22 (dd, $J = 6.7, 1.6$ Hz, 3H), 1.17 (dd, $J = 6.2, 1.6$ Hz, 3H), 1.09 (bs, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 144.6, 133.3, 128.1, 127.9, 127.8, 125.9, 52.1, 46.8, 21.0, 17.8; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_{14}\text{BrN}$ $[\text{M}+\text{H}]^+$, 228.0390. Found 227.0310. *Syn*: IR (film) 3373, 2873, 1590, 1566 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.1$ Hz, 1H), 7.31-7.25 (m, 1H), 7.22 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.07 (ddd, $J = 8.6, 7.8, 1.6$ Hz, 1H), 3.25 (q, $J = 6.8$ Hz, 1H), 3.17

(dq, $J = 6.3, 6.3$ Hz, 1H), 2.02 (bs, 2H), 1.29 (d, $J = 7$ Hz, 3H), 1.07 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 144.6, 133.4, 128.5, 128.1, 127.7, 125.0, 52.1, 46.6, 20.6, 17.8; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_{14}\text{BrN}$ $[\text{M}+\text{H}]^+$, 228.0390. Found 227.0396.

Similarly, the corresponding desbromoketone and amine were synthesized following similar procedures:

(1-Phenylethyl) methyl ketone: IR (film) 3470, 3084, 1923, 1712, 1668, 1628 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.34 (m, 2H), 7.32-7.27 (m, 1H), 7.26-7.22 (m, 2H), 3.76 (dd, $J = 14.0, 7.0$ Hz, 1H), 2.06 (s, 3H), 1.41 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 209.1, 140.8, 138.0, 129.2, 128.1, 127.4, 54.1, 28.5, 17.7; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_{11}\text{BrO}$ $[\text{M}]^+$, 148.0888. Found 148.0895.

3-Phenyl-2-amino butane: IR (film) 3373, 2921, 1734, 1589, 1565 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (dd, $J = 7.8, 1.0$ Hz, 2H), 7.33-7.25 (m, 2H), 7.10 (dd, $J = 7.8, 1.2$ Hz, 1H), 3.15 (q, $J = 7.2$ Hz, 1H), 3.09 (dq, $J = 6.0, 1.5$ Hz, 1H), 1.22 (d, $J = 7.2$ Hz, 3H), 1.13 (d, $J = 7.2$ Hz, 3H), 1.09 (br s, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 130.5, 129.3, 128.1, 127.8, 127.6, 124.9, 52.1, 46.0, 22.0, 17.1; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_{15}\text{N}$ $[\text{M}+\text{H}]^+$, 149.1204. Found 149.1210.

***N*-(1-Phenylbenzyl)-2,3-*cis*-dimethylindoline (7c).** Following the general procedure, 2-(*ortho*-bromophenyl)-1,2-*trans*-dimethylethylamine (18 mg, 79.7 μmol), benzophenone imine (14.4 mg, 79.7 μmol) and 4Å MS were stirred in dichloromethane (1 mL) at room temperature for

7.5 days under argon atmosphere to provide the ketimine as an oil (210 mg, 95%); IR (film) 3059, 1624 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 7.1$ Hz, 2H), 7.62 (dt, $J = 7.4$, 1.2 Hz, 2H), 7.51 (t, $J = 7.7$ Hz, 3H), 7.39-7.32 (m, 4H), 7.16 (t, $J = 7.3$ Hz, 1H), 7.03 (t, $J = 7.7$ Hz, 1H), 6.80-6.79 (m, 1H), 3.61 (q, $J = 6.2$ Hz, 1H), 3.54 (q, $J = 6.7$ Hz, 1H), 1.33 (d, $J = 7.0$ Hz, 3H), 1.13 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 137.2, 132.9, 132.7, 130.3, 129.9, 129.0, 128.5, 128.3, 127.6, 127.3, 61.4, 29.9, 20.6, 16.7; HRMS (EI): Exact mass calcd for $\text{C}_{23}\text{H}_{23}\text{BrN}$ $[\text{M}+\text{H}]^+$, 392.1016. Found 392.1160.

In a similar manner, the ketimine of 1,2-*trans*-dimethyl-2-phenylethylamine was prepared. IR (film) 3081, 1661 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) 7.60 (d, $J = 7.2$ Hz, 2H), 7.49-7.11 (m, 13H), 3.48 (dq, $J = 6.4$, 6.3 Hz, 1H), 2.97 (dq, $J = 8.0$, 7.2 Hz, 1H), 1.26 (d, $J = 7.1$ Hz, 3H), 1.24 (d, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 166.2, 145.7, 140.6, 137.5, 130.6, 129.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 126.1, 63.6, 46.9, 20.2, 17.8; HRMS (EI): Exact mass calcd for $\text{C}_{23}\text{H}_{24}\text{N}$ $[\text{M}+\text{H}]^+$, 314.1910. Found 314.1913.

To a refluxing solution of the unpurified ketimine (5.1 mg, 13 μmol) in benzene (3 mL) was added $^n\text{Bu}_3\text{SnH}$ (4.6 μL , 16.9 μmol), followed by a 6 h addition of AIBN (6.4 mg, 39.0 μmol) dissolved in benzene (1 mL). After the first 3 h of reaction, another aliquot of $^n\text{Bu}_3\text{SnH}$ (4.6 μL , 16.9 μmol), was added to the reaction mixture. After the complete addition of AIBN, the reaction mixture was refluxed for a further 2 h, followed by evaporation of solvent under vacuum. Flash chromatography (SiO_2 , 5% dichloromethane in hexanes) yielded the desired product (3.4 mg, 84%) as a gum; $R_f = 0.12$ (5% CH_2Cl_2 /hexanes); IR (film) 3061, 1605 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 6.8$ Hz, 2H), 7.40 (d, $J = 7.2$ Hz, 2H), 7.34-7.23 (m, 6H), 7.03 (d, $J = 7.1$ Hz, 1H), 6.80 (t, $J = 7.5$ Hz, 1H), 6.63 (t, $J = 7.3$ Hz, 1H), 5.90 (d, $J = 7.8$ Hz, 1H), 5.51 (s, 1H), 3.78 (dq, $J = 7.5$, 6.4 Hz, 1H), 3.38 (dq, $J = 7.3$, 7.3 Hz, 1H), 1.22 (d, $J = 7.1$ Hz, 3H), 0.95 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 150.0, 142.4, 141.2, 135.5, 128.9, 128.7, 128.6, 127.9, 127.4, 127.2, 126.9, 123.1, 117.5, 109.9, 65.4, 62.4,

39.1, 13.6, 12.6; HRMS (FAB): Exact mass calcd for $C_{23}H_{23}N$ $[M]^+$, 313.1830. Found 313.1839.

Relative stereochemistry determined by NOE experiments (400 MHz NMR).

***N*-(1-Phenylbenzyl)-2,3-*trans*-dimethylindoline (7d).** Following the general procedure, 2-(*ortho*-bromophenyl)-1,2-*cis*-dimethylethylamine (127 mg, 562 μ mol), benzophenone imine (102 mg, 562 μ mol), and 4Å MS were stirred in dichloromethane (1.5 mL) at room temperature for 7.5 days under argon atmosphere to provide the ketimine as an oil (200 mg, 91%); IR (film) 3079, 1661 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 3H), 7.44-7.40 (m, 3H), 7.34-7.27 (m, 3H), 7.19 (q, J = 7 Hz, 1H), 7.18-7.16 (m, 1H), 7.00-6.95 (m, 3H), 3.67 (q, J = 6.3 Hz, 1H), 3.62 (q, J = 6.3 Hz, 1H), 1.44 (d, J = 6.6 Hz, 3H), 1.41 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 144.6, 140.6, 137.3, 132.7, 129.8, 129.6, 128.7, 128.4, 128.1, 127.5, 62.4, 53.6, 44.8, 19.7, 17.7; HRMS (EI): Exact mass calcd for $C_{23}H_{23}BrN$ $[M+H]^+$, 392.1016. Found 392.0913.

In a similar manner, the ketimine of 1,2-*cis*-dimethyl-2-phenylethylamine was prepared. IR (film) 3081, 1661 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) 7.60 (d, J = 7.2 Hz, 2H), 7.49-7.11 (series of m, 13H), 3.48 (dq, J = 6.4, 6.3 Hz, 1H), 2.97 (dq, J = 8.0, 7.2 Hz, 1H), 1.27 (d, J = 7.0 Hz, 3H), 1.02 (d, J = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 166.7, 145.8, 140.5, 137.7, 130.3, 130.0, 128.7, 128.4, 128.3, 128.1, 128.0, 127.8, 126.1, 63.4, 47.5, 21.2, 18.6; HRMS (EI): Exact mass calcd for $C_{23}H_{24}N$ $[M]^+$, 314.1910. Found 314.1913.

To a refluxing solution of the unpurified ketimine (12.6 mg, 32 μ mol) in benzene (5.5 mL) was added tBu_3SnH (9.5 μ L, 35 μ mol), followed by a 6 h addition of AIBN (13 mg, 80 μ mol) dissolved in benzene (1 mL). After the first 3 h of the reaction, another aliquot of tBu_3SnH (9.5

μL , 35.4 μmol) was added. After complete addition of AIBN, the reaction mixture was refluxed for further 1 h followed by evaporation of solvent under vacuum. Flash chromatography (SiO_2 , 5% dichloromethane in hexanes) yielded the desired indoline (7.9 mg, 79%) as a gum; IR (film) 2958, 1684 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 7.2$ Hz, 2H), 7.35-7.26 (m, 8H), 7.02 (d, $J = 7.2$ Hz, 1H), 6.83 (t, $J = 7.6$ Hz, 1H), 6.61 (t, $J = 7.3$ Hz, 1H), 5.99 (d, $J = 7.9$ Hz, 1H), 5.69 (s, 1H), 3.28 (dq, $J = 6.3, 6.3$ Hz, 1H), 2.87 (dq, $J = 6.9, 6.9$ Hz, 1H), 1.27 (d, $J = 6.4$ Hz, 3H), 1.19 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 150.4, 141.1, 140.5, 134.3, 128.9, 128.6, 127.4, 123.2, 117.2, 109.2, 66.5, 65.0, 43.8, 20.0, 18.8; HRMS (EI): Exact mass calcd for $\text{C}_{23}\text{H}_{23}\text{N}$ $[\text{M}]^+$, 313.1831. Found 313.1838.

Relative stereochemistry assigned by NOE experiments (400 MHz NMR).

***N*-(1-Methylbenzyl)-3,3-dimethylindoline (7e).** According to the general procedure, 2-(*ortho*-bromophenyl)-2,2-dimethyl ethylamine (733 mg, 3.21 mmol), acetophenone (370 μL , 3.18 mmol), and 4Å MS were stirred in toluene (25 mL) at room temperature for 12 h to provide the ketimine as a >95:5 mixture of stereoisomers, IR (film) 3058, 1635 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (m, 2H), 7.55 (d, $J = 9.1$ Hz, 1H), 7.50 (d, $J = 9.8$ Hz, 1H), 7.30 (t, $J = 1.8$ Hz, 3H), 7.23 (t, $J = 4.3$ Hz, 1H), 7.0 (t, $J = 9.4$ Hz, 1H), 3.98 (s, 2H), 2.20 (s, 3H), 1.64 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) ppm 164.3, 146.3, 141.5, 135.8, 130.0, 129.4, 128.2, 127.7, 127.3, 126.8, 122.8, 60.4, 41.8, 26.8, 26.5, 15.6; HRMS (CI): Exact mass calcd for $\text{C}_{18}\text{H}_{21}\text{BrN}$ $[\text{M}+\text{H}]^+$, 330.0857. Found 330.0818.

The ketimine of 2,2-dimethyl-2-phenyl ethylamine was similarly prepared. IR (film) 3085, 1636 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (m, 2H), 7.50 (d, $J = 8.1$ Hz, 2H), 7.38 (m, 3H), 7.33 (d, $J = 7.9$ Hz, 2H), 7.21 (t, $J = 7.4$ Hz, 1H), 3.57 (s, 2H), 2.13 (s, 3H), 1.51 (s, 6H);

^{13}C NMR (100 MHz, CDCl_3) ppm 164.5, 149.3, 141.5, 129.5, 128.5, 128.3, 128.2, 126.8, 126.4, 125.9, 64.3, 39.8, 27.1, 15.4; HRMS (EI): Exact mass calcd for $\text{C}_{18}\text{H}_{21}\text{N}$ $[\text{M}]^+$, 251.1674. Found 251.1670.

A three hour addition of $^n\text{Bu}_3\text{SnH}$ (72.0 μL , 267 μmol) and AIBN 16 mg, 97 μmol) benzene solution (1.0 mL) to a refluxing solution of the unpurified ketimine (80.2 mg, 243 μmol) in benzene (24 mL) furnished, after flash chromatography (SiO_2 , 1% ether in hexanes), of the desired indoline as a colorless oil (48.8 mg, 80%). R_f = 0.63 (10% EtOAc/hexanes); IR (film) 3024, 1604 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 7.4 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.26 (d, J = 7.3 Hz, 1H), 7.01 (t, J = 7.2 Hz, 1H), 7.01 (t, J = 7.2 Hz, 1H), 6.66 (t, J = 8.1 Hz, 1H), 6.35 (d, J = 8.1 Hz, 1H), 4.73 (q, J = 6.9 Hz, 1H), 3.18 (d, J = 8.3 Hz, 1H), 3.08 (d, J = 8.3 Hz, 1H), 1.54 (d, J = 6.9 Hz, 3H), 1.33 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 150.1, 143.4, 139.2, 128.6, 127.5, 127.2, 127.1, 121.8, 117.2, 107.3, 62.6, 54.3, 39.9, 28.3, 27.4, 17.0; HRMS (EI): Exact mass calcd for $\text{C}_{18}\text{H}_{21}\text{N}$ $[\text{M}]^+$, 251.1674. Found 251.1672.

Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{N}$: C, 86.01; H, 8.42; N, 5.57. Found: C, 85.74; H, 8.58; N, 5.57.

***N*-(1-Methylbenzyl)-5,6-dimethoxy indoline (9a).** Following the general procedure, (2-bromo-4,5-dimethoxyphenyl)ethan-1-amine (1.95 g, 7.5 mmol), acetophenone (0.87 mL, 7.5 mmol), and 4Å MS were stirred in toluene (10 mL) at room temperature for 12 h to provide the ketimine as a >95:5 mixture of stereoisomers. IR (film) 3055, 1633 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (m, 2H), 7.38 (m, 3H), 7.03 (s, 1H), 6.83 (s, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 3.77 (dd, J = 7.2, 7.2 Hz, 2H), 3.14 (dd, J = 7.4, 7.4 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 166.1, 158.0, 148.3, 148.2, 141.4, 131.9, 129.7, 128.5, 126.7, 115.6, 114.4, 56.3, 56.1,

52.2, 37.3, 15.6; HRMS (CI): Exact mass calcd for $C_{18}H_{21}BrNO_2$ $[M+H]^+$, 362.0756. Found 362.0747.

The ketimine of 2-(3,4-Dimethoxyphenyl)ethylamine, ketimine was similarly prepared. IR (film) 3056, 1684 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.39 (m, 5H), 6.83 (s, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.75 (dd, $J = 7.2, 7.2$, 2H), 3.04 (dd, $J = 7.5, 7.5$, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 165.8, 148.9, 147.5, 141.5, 133.6, 129.6, 128.5, 128.4, 126.7, 121.0, 112.7, 111.4, 56.1, 56.0, 54.4, 37.2, 15.6; HRMS (CI): Exact mass calcd for $C_{18}H_{21}NO_2$ $[M]^+$, 283.1572. Found 283. 1567.

A three-hour addition of nBu_3SnH (120 μL), 448 μmol) and AIBN (26.7 mg, 163 μmol) solution in benzene (1.1 mL) to a refluxing solution of the unpurified ketimine (148 mg, 408 μmol) in benzene (41 mL) afforded, after flash chromatography (SiO_2 , 15% ethyl acetate in hexanes), the desired indoline as a yellow oil (95.6 mg, 83%). $R_f = 0.27$ (20% EtOAc/hexanes); IR (film) 3059, 1614 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, $J = 7.6$ Hz, 2H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.27 (t, $J = 7.4$ Hz, 1H), 6.75 (s, 1H), 6.00 (s, 1H), 4.57 (q, $J = 6.8$ Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 3.34 (dd, $J = 16.2, 7.3$ Hz, 2H), 2.88 (dd, 7.9, 7.9 Hz, 2H), 1.53 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 149.0, 146.5, 143.6, 141.5, 128.6, 127.3, 127.1, 121.3, 111.2 (2C), 95.4, 57.6, 56.4, 49.6, 28.4, 17.5; HRMS (EI): Exact mass calcd for $C_{18}H_{21}NO_2$ $[M]^+$, 283.1572. Found 283.1578.

Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.21; H, 7.49; N, 5.08.

***N*-(1-Trifluoromethyl(benzyl))-5,6-dimethoxy indoline (9b).** Following the general procedure, (2-bromo-4,5-dimethoxy-phenyl)ethylamine (2.05 g, 7.88 mmol), trifluoroacetophenone (1.1 mL, 7.88 mmol), and 4Å MS were stirred in toluene (30 mL) at room

temperature for 12 h to give the ketimine as a >95:5 mixture of stereoisomers. IR (film) 3061, 1669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.43 (t, $J = 7.2$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 2H), 6.95 (s, 1H), 6.91 (d, $J = 7.1$ Hz, 2H), 6.70 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.67 (dd, $J = 8.2, 6.8$ Hz, 2H), 3.05 (dd, $J = 6.7, 6.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 159.5, 159.2, 148.5, 148.3, 130.4, 130.2, 130.1, 128.8, 128.5, 127.7, 121.1, 118.4, 115.5, 114.5, 114.2, 56.4, 56.1, 52.9, 36.4; HRMS (EI): Exact mass calcd for $\text{C}_{18}\text{H}_{17}\text{BrF}_3\text{NO}_2$ $[\text{M}]^+$, 415.0395. Found 415.0414.

2-(3,4-Dimethoxyphenyl)ethylamine ketimine was similarly prepared.

IR (film) 3061, 1669 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (t, $J = 7.2$ Hz, 1H), 7.36 (t, $J = 7.0$ Hz, 2H), 6.88 (d, $J = 7.0$ Hz, 2H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.63 (d, $J = 8.0$ Hz, 1H), 6.60 (s, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.64 (dd, $J = 6.7, 6.7$ Hz, 2H), 2.95 (dd, $J = 6.7, 6.7$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 158.8 (q, $J = 33.5$, 1C), 148.9, 147.8, 131.9, 130.4, 130.0, 128.7, 127.8, 121.1, 118.4, 112.5, 111.3, 56.1, 55.8, 55.1, 36.2; HRMS (EI): Exact mass calcd for $\text{C}_{18}\text{H}_{18}\text{F}_3\text{NO}_2$ $[\text{M}]^+$, 337.1290. Found 337.1274.

A three-hour addition of $^t\text{Bu}_3\text{SnH}$ (110 μL , 412 μmol) and AIBN (25 mg, 150 μmol) solution in benzene (1.0 mL) to a refluxing solution of the unpurified ketimine (156 mg, 375 μmol) in benzene (37 mL) provided, after flash chromatography (SiO_2 , 10% ethyl acetate in hexanes), the desired indoline as a white solid (113 mg, 89%). mp = 73-74 $^\circ\text{C}$; $R_f = 0.37$ (20% EtOAc/hexanes); IR (film) 2939, 1615 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.39 (m, 5H), 6.74 (s, 1H), 6.27 (s, 1H), 5.11 (q, $J = 8.6$ Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.57 (dd, $J = 15.1, 8.1$ Hz, 1H), 3.15 (dd, $J = 18.4, 9.3$ Hz, 1H), 2.89 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 149.3, 144.9, 142.4, 132.0, 128.9 (3C), 124.2, 120.2, 111.2, 94.2, 62.8 (q, $J = 29.7$ Hz, 1C), 57.4, 56.6, 49.6, 28.5; HRMS (EI): Exact mass calcd for $\text{C}_{18}\text{H}_{18}\text{F}_3\text{NO}_2$ $[\text{M}]^+$, 337.1290. Found 337.1280.

Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{F}_3\text{NO}_2$: C, 64.09; H, 5.38; N, 4.15. Found: C, 64.02; H, 5.31; N, 4.08.

N-(1-Phenylbenzyl)-5,6-dimethoxy indoline (9c). Following the general procedure, (2-bromo-4,5-dimethoxyphenyl)ethyl amine (343 mg, 1.32 mmol) and benzophenone imine (239 mg, 1.32 mmol) were stirred at room temperature in CH_2Cl_2 (3 mL) for 12 h to give the ketimine. IR (film) 3056, 1623 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 7.0$ Hz, 2H), 7.40 (dd, $J = 6.2, 3.4$ Hz, 3H), 7.36 (t, $J = 7.6$ Hz, 3H), 6.95 (s, 1H), 6.94 (d, $J = 2.3$ Hz, 2H), 6.73 (s, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.67 (dd, $J = 7.0, 7.0$ Hz, 2H), 3.07 (dd, $J = 7.2, 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 168.9, 148.2, 139.9, 136.8, 131.8, 128.5, 128.4, 128.3, 127.9, 115.5, 114.5, 114.2, 56.3, 56.1, 53.8, 37.4; HRMS (CI): Exact mass calcd for $\text{C}_{23}\text{H}_{23}\text{BrNO}_2$ $[\text{M}+\text{H}]^+$, 424.0912. Found 424.0910.

The analogous ketimine from 2-(3,4-dimethylphenyl)ethyl amine was similarly prepared. IR (film) 3056, 1623 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 6.8$ Hz, 2H), 7.39 (m, 3H), 7.35 (m, 3H), 6.93 (dd, $J = 7.1, 3.5$ Hz, 2H), 6.75 (d, $J = 8.1$ Hz, 1H), 6.67 (d, $J = 8.0$ Hz, 1H), 6.65 (s, 1H), 3.85 (s, 3H), 3.77 (s, 3H), 3.65 (dd, $J = 7.1, 7.1$ Hz, 2H), 2.96 (dd, $J = 7.1, 7.1$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 168.6, 148.9, 147.5, 140.1, 137.0, 133.3, 130.1, 128.6, 128.4, 128.3, 128.0, 121.2, 112.7, 111.4, 56.2, 55.9, 37.5; HRMS (CI): Exact mass calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_2$ $[\text{M}]^+$, 345.1729. Found 345.1734.

A three-hour addition of $n\text{Bu}_3\text{SnH}$ (75 μL , 278 μmol) and AIBN (17 mg, 101 μmol) solution in benzene (1.0 mL) to refluxing solution of the unpurified ketimine (107 mg, 252 μmol) in benzene (25 mL) provided, after flash chromatography (SiO_2 , 5% ethyl acetate in hexanes), the desired indoline as a white solid (46 mg, 64%). mp 105–106 $^\circ\text{C}$; $R_f = 0.20$ (10% EtOAc/hexanes); IR (film) 2931, 1597 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 4.7$ Hz, 4H), 7.35 (t, $J = 7.1$ Hz, 4H), 7.27 (t, $J = 4.7$ Hz, 2H), 6.75 (s, 1H), 5.79 (s, 1H), 5.33 (s, 1H), 3.80 (s, 3H), 3.51 (s, 3H), 3.16 (dd, $J = 8.3, 8.3$ Hz, 2H), 2.87 (dd, $J = 8.1, 8.1$ Hz, 2H); ^{13}C NMR (100

MHZ, CDCl₃) ppm 148.4, 146.9, 142.1, 141.8, 128.7, 128.5, 127.4, 121.7, 110.4, 96.5, 69.3, 57.3, 55.9, 53.6, 28.5; HRMS (CI): Exact mass calcd for C₂₃H₂₃NO₂ [M]⁺, 345.1729. Found 345.1713.

Anal. Calcd for C₂₃H₂₃NO₂: C, 79.97; H, 6.71; N, 4.05. Found: C, 79.87; H, 6.76; N, 4.08.

***N*-(1-(2-Methoxy)phenylbenzyl)-5,6-dimethoxy indoline (9d).** Following the general procedure, (2-bromo-4,5-dimethoxyphenyl)ethylamine (700 mg, 2.69 mmol), 2'-methoxy acetophenone (404 mg, 2.691 mmol), and 4 Å MS were stirred in benzene (20 mL) at room temperature for 12 h to provide the ketimine as a 1:1 mixture of stereoisomers. IR (film) 2999, 1651 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30, (m, 4H), 7.03, (s, 1H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.92 (s, 1H), 6.90 (t, *J* = 5.9 Hz, 1H), 6.83 (s, 1H), 6.75 (d, *J* = 5.9 Hz, 1H), 6.68 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.81 (m, 6H), 3.71 (t, *J* = 7.3 Hz, 2H), 3.33 (t, *J* = 6.9 Hz, 2H), 3.14 (t, *J* = 7.5 Hz, 2H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.26 (s, 3H), 2.07 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) ppm 169.0, 167.7, 157.0, 155.1, 148.3, 148.2, 148.0, 133.8, 133.1, 131.9, 130.6, 130.0, 129.5, 129.3, 128.5 (2C), 128.3, 127.3, 120.9, 120.7, 115.6, 115.5, 114.4, 114.3, 113.9, 111.7, 111.0, 110.9, 56.3, 56.2, 56.1, 55.7, 55.5, 53.6, 51.8, 37.2, 28.7, 19.4; HRMS (EI): Exact mass calcd for C₁₉H₂₂NO₃ [M-Br]⁺, 312.1600. Found 312.1586.

In a similar manner, the ketimine of 2-(3,4-dimethoxyphenyl)ethylamine, was prepared as a 1:1 mixture of stereoisomers. IR (film) 2997, 1648, cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30 (m, 3H), 7.26 (d, *J* = 1.7 Hz, 1H), 6.96 (d, *J* =

6.7 Hz, 1H), 6.93 (d, $J = 2.8$ Hz, 1H), 6.90 (t, $J = 3.4$ Hz, 2H), 6.88 (d, $J = 4.4$ Hz, 1H), 6.75 (s, 1H), 6.73 (s, 1H), 6.71 (d, $J = 1.7$ Hz, 1H), 6.64 (d, $J = 1.7$ Hz, 1H), 6.62 (t, $J = 2.8$ Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.84 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 3.68 (dd, $J = 7.4, 7.4$, 2H), 3.33 (dd, $J = 7.4, 7.4$, 2H), 3.04 (dd, $J = 7.7, 7.7$, 2H), 2.85 (dd, $J = 7.7, 7.7$, 2H), 2.25 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 168.6, 167.2, 157.0, 155.1, 148.9, 148.8, 147.5, 147.4, 133.6, 133.4, 133.2, 129.9, 129.5, 129.3, 128.4, 127.3, 120.99, 120.95, 120.90, 120.69, 112.6, 112.4, 111.4, 111.2, 111.0, 110.8, 56.1, 56.0, 55.9, 55.6, 55.57, 55.51, 54.1, 37.1, 37.0, 28.7, 19.4; HRMS (EI): Exact mass calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3$ $[\text{M}]^+$, 313.1678. Found 313.1689.

A three-hour addition of $n\text{Bu}_3\text{SnH}$ (115 μL , 427 μmol) and AIBN (25.5 mg, 155 μmol) solution in benzene (1.6 mL) to a refluxing solution of the unpurified ketimine (152 mg, 388 μmol) in benzene (39 mL) delivered, after flash chromatography (SiO_2 , 7% ethyl acetate in hexanes), the desired indoline as a yellow oil (63.6 mg (52 %)). $R_f = 0.12$ (10% EtOAc in hexanes); IR (film) 2934, 1614, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 6.0$ Hz, 1H), 7.24 (t, $J = 6.4$ Hz, 1H), 6.96 (d, $J = 8.3$ Hz, 1H), 6.90 (t, $J = 9.1$ Hz, 1H), 6.72 (s, 1H), 6.00 (s, 1H), 4.93 (q, $J = 7.0$ Hz, 1H), 3.86 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H), 3.47 (dd, $J = 7.2, 7.2$ Hz, 1H), 3.42 (dd, $J = 9.2$ Hz, 1H), 2.89 (dd, $J = 7.3, 7.3$ Hz, 2H), 1.48 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 156.7, 148.8, 146.8, 141.1, 132.1, 128.0, 127.7, 120.9, 120.8, 119.8, 110.8, 95.0, 57.5, 56.2, 55.7, 50.1, 28.5, 25.4, 18.1; HRMS (EI): Exact mass calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3$ $[\text{M}]^+$, 313.1678. Found 313.1683.

***N*-(1-(4-Methoxy)phenylbenzyl)-5,6-dimethoxy indoline (9e).** Following the general procedure, (2-bromo-4,5-dimethoxyphenyl)ethylamine (248 mg, 953 μmol), 4-methoxyacetophenone (143 mg, 953 μmol), and 4 Å MS were stirred in benzene (30 mL) at room

temperature for 12 h to provide the ketimine as a > 95:5 mixture of stereoisomers. IR (film) 2934, 1674 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, J = 8.9 Hz, 2H), 6.98 (s, 1H), 6.85 (d, J = 8.9 Hz, 2H), 6.78 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.74 (s, 3H), 3.70 (dd, J = 7.3, 7.3 Hz, 2H), 3.07 (dd, J = 7.3, 7.3 Hz, 2H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 165.3, 163.7, 160.9, 148.3, 134.1, 132.0, 130.8, 128.2, 115.5, 114.3, 113.6, 56.3, 56.1, 55.5, 52.1, 37.4, 15.3; HRMS (CI): Exact mass calcd for $\text{C}_{19}\text{H}_{23}\text{BrNO}_3$ $[\text{M}+\text{H}]^+$, 392.0861. Found: 392.0855.

In a similar manner, the ketimine of 2-(3,4-dimethoxyphenyl)ethylamine, was prepared and acquired as a white solid. mp = 83-86 $^{\circ}\text{C}$. IR (film); 2999, 1674 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.78 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.67 (dd, J = 7.6, 7.6 Hz, 2H), 2.97 (dd, J = 7.2, 7.2 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm; 160.9, 134.1, 133.6, 130.8, 128.5, 128.2, 120.9, 113.9, 113.6, 112.6, 111.3, 56.1, 56.0, 55.5, 54.3, 37.2, 15.4 HRMS (CI): Exact mass calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3$ $[\text{M}]^+$, 313.1678. Found: 313.1693.

A three-hour addition of $^n\text{Bu}_3\text{SnH}$ (48 μL , 180 μmol) and AIBN (11 mg, 65.7 μmol) solution in benzene (1.0 mL) to a refluxing solution of the unpurified ketimine (64.4 mg, 164 μmol) in benzene (16 mL) delivered, after flash chromatography (SiO_2 , 7% ethyl acetate in hexanes), the desired indoline as a yellow oil (24.1 mg, 47%). R_f = 0.20 (20% EtOAc/hexanes); IR (film) 2933, 1611, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.73 (s, 1H), 6.06 (s, 1H), 4.56 (q, J = 6.9 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.73 (s, 3H), 3.29 (dd, J = 8.6, 8.6 Hz, 2H), 2.86 (dd, J = 8.3, 8.3 Hz, 2H), 1.50 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 158.7, 148.9, 146.4, 141.4, 135.4, 128.4, 121.3, 113.9, 110.9, 95.1, 57.4, 56.3, 55.5, 55.4, 49.2, 28.4, 17.1; HRMS (CI): Exact mass calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3$ $[\text{M}]^+$, 313.1678. Found 313.1674.

Anal. Calcd for $C_{19}H_{23}NO_3$: C, 72.82; H, 7.40; N, 4.47. Found: C, 72.68; H, 7.63; N, 4.46.

N-(1-Phenylbenzyl)-6-azaindoline (9f). 2-Bromo-3-(2-aminoethyl) pyridine (163 mg, 811 μ mol) and benzophenone imine (147 mg, 811 μ mol) were stirred in CH_2Cl_2 at room temperature for 8 h to provide the ketimine. IR (film) 3056, 1622 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, $J = 4.7, 0.9$ Hz, 1H), 7.56 (t, $J = 7.8$ Hz, 3H), 7.43–7.40 (m, 3H), 7.37 (d, $J = 6.6$ Hz, 1H), 7.32 (t, $J = 7.9$ Hz, 2H), 7.16 (dd, $J = 7.4, 5.2$ Hz, 1H); 6.96 (t, $J = 3.4$ Hz, 2H), 3.69 (t, $J = 6.9$ Hz, 2H), 3.10 (t, $J = 6.9$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 169.2, 158.1, 147.7, 144.5, 139.5 (2C), 137.0, 136.5, 130.0, 128.5, 128.4, 128.3, 127.5, 122.6, 52.4, 36.8; HRMS (EI): Exact mass calcd for $C_{20}H_{17}BrN_2$ $[M]^+$, 364.0575. Found 364.0587.

A two-hour addition of tBu_3SnH (268 μ L, 997 μ mol) and AIBN (60 mg, 362 μ mol) solution in benzene (2 mL) to a refluxing solution of the unpurified ketimine (110 mg, 310 μ mol) in benzene (30 mL) delivered, after flash chromatography (SiO_2 , 5% ethyl acetate in hexanes), the desired indoline as an orange crystalline solid (50 mg, 60%). mp 101 $^\circ C$; $R_f = 0.1$ (5% EtOAc/hexanes); IR (film) 3058, 1611 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, $J = 5.2$ Hz, 1H), 7.34–7.26 (m, 10H), 7.17 (d, $J = 7.0$ Hz, 1H), 6.81 (s, 1H), 6.42 (t, $J = 6.5$ Hz, 1H), 3.34 (t, $J = 8.5$ Hz, 2H), 2.97 (t, $J = 8.5$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 162.8, 146.1, 140.2, 131.2, 129.1, 128.5, 127.4, 122.8, 112.4, 60.0, 45.6, 25.9; HRMS (EI): Exact mass calcd for $C_{20}H_{18}N_2$ $[M]^+$, 286.1470. Found 286.1468.

Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.84; H, 6.34; N, 9.71.

1-Methyl-*p*-Trifluoromethylbenzyl-7-aza-indoline (9g). Following the general procedure, (2-bromo-)ethylpyridyl amine (88.3 mg, 439 μ mol), 4-trifluoro acetophenone (82.6 mg, 439 μ mol), and 4 Å MS were stirred in benzene (20 mL) at room temperature for 12 h to provide the ketimine as a > 95:5 mixture of stereoisomers. IR (film) 2926, 1635 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.26 (dd, J = 4.6, 2.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.8 Hz, 3H), 7.22 (dd, J = 7.4, 4.7, Hz 1H), 3.82 (dd, J = 7.0, 7.0 Hz, 2H), 3.21 (dd, J = 7.0, 7.0 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 165.1, 148.2, 144.6, 144.2, 139.8, 139.2, 127.1, 125.9, 125.4, 122.9, 51.4, 36.8, 27.0, 15.8; HRMS (EI): Exact mass calcd for $\text{C}_{16}\text{H}_{15}\text{BrF}_3\text{N}_2$ $[\text{M}+\text{H}]^+$, 371.0371. Found 371.0368.

In a similar manner, the ketimine of 2-(3-pyridyl)ethylamine, was prepared. IR (film), 2927, 1691 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.57 (s, 1H), 8.49 (d, J = 3.3 Hz, 1H), 7.86 (d, J = 8.3, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.61 (t, J = 5.8 Hz, 1H), 7.23 (d, J = 5.8 Hz, 1H), 3.77 (dd, J = 6.9, 6.9, 2H), 3.12 (dd, J = 7.0, 7.0, 2H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 164.9, 150.6, 147.8, 144.2, 136.7, 136.0, 131.3, 127.0, 125.4, 123.4, 53.5,* 34.6, 15.8 HRMS (EI): Exact mass calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{N}_2$ $[\text{M}]^+$, 292.1187. Found. 292.1161.

A three-hour addition of *n*- Bu_3SnH (56.7 μL , 210 μmol) and AIBN (13 mg, 76.6 μmol) solution in benzene (1.0 mL) to a refluxing solution of the unpurified ketimine (70.9 mg, 191 μmol) in benzene (20 mL) delivered, after flash chromatography (7% EtOAc in hexanes), the desired indoline as a yellow oil (42.5 mg, 76 %). R_f = 0.14 (10% EtOAc/hexanes); IR (film) 3058, 1611 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 5.0 Hz, 1H), 7.59 (d, J = 8.2 Hz, 2H),

* The carbon bearing fluorine could not be observed.

7.51 (d, $J = 8.3$ Hz, 2H), 7.18 (d, $J = 7.0$ Hz, 1H), 6.45 (t, $J = 5.6$ Hz, 1H), 5.65 (q, $J = 6.1$ Hz, 1H), 3.51 (dd, $J = 8.9, 8.9$ Hz, 1H), 3.17 (dd, $J = 9.3, 9.3$ Hz, 1H), 2.95 (dd, $J = 9.0, 9.0$ Hz, 2H), 1.60 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 162.5, 146.0, 131.2, 128.5, 127.8, 125.4, 123.0, 112.4, 50.3, 43.7, * 25.7, 25.4, 15.9 HRMS (EI): Exact mass calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{N}_2$ $[\text{M}]^+$, 292.1187. Found 292.1182.

Anal. Calcd for $\text{C}_{16}\text{H}_{15}\text{F}_3\text{N}_2$: C, 65.74; H, 5.17; N, 9.58. Found: C, 65.69; H, 5.31; N, 9.54.

1-Methyl-4-(4-methoxyphenyl)-7-aza-indoline (9h). Following the general procedure, (2-bromo-)pyridylethylamine (244 mg, 1.21 mmol), 4-methoxy acetophenone (183 mg, 1.21 mmol), and 4 Å MS were stirred in benzene (20 mL) at room temperature for 12 h to provide the ketimine as a > 95:5 mixture of stereoisomers. IR (film) 3003, 1674 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.24 (dd, $J = 4.6, 1.9$, Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 2H), 7.66 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.20 (dd, $J = 7.5, 4.8$ Hz, 1H), 6.90 (d, $J = 8.9$ Hz, 2H), 3.89 (s, 3H), 3.77 (dd, $J = 7.1, 7.1$ Hz, 2H), 3.19 (dd, $J = 7.1, 7.1$ Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 163.7, 148.0, 130.8, 130.5, 128.2, 122.9, 113.9, 113.7, 55.7, 51.0, 37.0, 26.5; HRMS (EI): Exact mass calcd for $\text{C}_{16}\text{H}_{17}\text{BrN}_2\text{O}$ $[\text{M}]^+$, 332.0524. Found 332.0333.

In a similar manner, the ketimine of 2-(3,4-dimethoxyphenyl)ethylamine, was prepared. IR (film) 2934, 1600 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.56 (s, 1H), 8.45 (d, $J = 3.2$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 2H), 7.61 (d, $J = 4.1$ Hz, 1H), 7.21 (dd, $J = 4.9, 3.0$ Hz, 1H), 6.89 (d, $J = 8.9$ Hz, 2H), 3.84 (s, 3H), 3.72 (dd, $J = 7.1, 7.1$ Hz, 2H), 3.08 (dd, $J = 7.2, 7.2$ Hz, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 161.2, 150.6, 147.7, 142.3,

136.7, 133.2, 128.4, 125.7, 123.4, 113.7, 55.5, 53.1, 34.8, 15.5; HRMS (EI): Exact mass calcd for $C_{16}H_{18}N_2O$ $[M]^+$, 254.1419. Found 254.1417.

A three hour addition of an AIBN (31.5 mg, 192 μ mol) solution in benzene (5.0 mL) to a refluxing solution of nBu_3SnH (143 μ L, 531 μ mol) and the unpurified ketimine (107 mg, 320 μ mol) in benzene (64 mL) delivered, after flash chromatography (6% EtOAc in hexanes), the desired indoline as a yellow oil (50 mg, 55%). R_f = 0.050 (10% EtOAc/hexanes); IR (film) 2954, 1611 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 4.1 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 4.2 Hz, 1H), 6.87 (d, J = 8.9 Hz, 2H), 6.40 (dd, J = 6.9, 5.4 Hz, 1H), 5.56 (q, J = 6.9 Hz, 1H), 3.80 (s, 3H), 3.46 (dd, J = 17.1, 9.1 Hz, 1H), 3.13 (dd, J = 16.0, 9.9 Hz, 1H), 2.90 (dd, J = 17.1, 7.6 Hz, 2H), 1.55 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 162.7, 158.8, 145.9, 133.7, 130.9, 128.7, 123.3, 113.8, 111.9, 55.4, 50.0, 43.5, 25.7, 15.9; HRMS (CI): Exact mass calcd for $C_{16}H_{18}N_2O$ $[M]^+$, 254.1419. Found 254.1420.

3-(2,3-Dihydro-indol-1-yl)-butan-2-one (2l from 1l, 2m from 1m). *ortho*-Iodo phenethyl amine (180 mg, 729 μ mol), 2,3-butanedione (64 mL, 729 μ mol), and 4 Å MS were rapidly stirred in benzene for 12 h. The mixture was filtered through Celite, and concentrated to return the desired imine as a golden yellow oil (430 mg, 99%) and a 25:1 mixture of imine stereoisomers. Imino aryl iodide: IR (film) 3377, 3052, 2360, 1699, 1653 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.9 Hz, 1H), 7.29-7.26 (m, 2H), 6.94-6.92 (m, 1H), 3.73 (t, J = 7.2 Hz, 2H), 3.18 (t, J = 7.2 Hz, 2H), 2.40 (s, 3H), 1.87 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 200.8, 166.9, 142.7, 139.8, 130.7, 128.5, 100.9, 53.0, 41.5, 24.7, 12.0; HRMS (CI): Exact mass calcd for $C_{12}H_{15}INO$ $[M+H]^+$, 316.0200. Found 316.0204.

The imino aryl bromide was similarly formed as a yellow oil (860 mg, 86%). IR (film) 3028, 2980, 1699, 1660 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 7.9, 4.0 Hz, 1H),

7.32-7.23 (m, 2H), 7.26 (dd, $J = 9.1, 1.9$ Hz, 1H), 3.75 (t, $J = 7.1$ Hz, 2H), 3.19 (t, $J = 7.1$ Hz, 2H), 2.40 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 200.8, 167.0, 140.8, 136.2, 130.7, 128.5, 53.0, 41.6, 24.6, 11.9; HRMS (CI): Exact mass calcd for $\text{C}_{12}\text{H}_{14}\text{BrNO}$ $[\text{M}]^+$, 267.0259. Found 267.0318.

The phenethyl amine derivative was similarly prepared as a colorless oil.

IR (film) 3027, 2360, 1734, 1699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.38-7.24 (m, 5H), 3.74 (t, $J = 7.3$ Hz, 2H), 3.05 (t, $J = 7.3$ Hz, 2H), 2.40 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 200.8, 166.6, 140.3, 129.2, 128.6, 126.5, 54.8, 37.0, 24.6, 11.8; HRMS (EI): Exact mass calcd for $\text{C}_{12}\text{H}_{15}\text{NO}$ $[\text{M}]^+$, 189.1154. Found 189.1146.

The imino arylbromide (50 mg, 187 μmol) in benzene (19 mL, 10 mM) was treated with $n\text{Bu}_3\text{SnH}$ (55 μL , 205 μmol) and warmed to 85 $^\circ\text{C}$. A solution of AIBN (24.6 mg, 150 μmol) in benzene (1 mL) was added via syringe pump over 1 h, and the mixture was refluxed for an additional 1 h before cooling. The solution was concentrated, and the residue was purified by flash column chromatography (SiO_2 , 40% dichloromethane in hexanes) to provide the indoline as a white solid (14.4 mg, 41%). mp = 60-63 $^\circ\text{C}$; $R_f = 0.24$ (SiO_2 , 60% CH_2Cl_2 /hexanes); IR (film) 3408, 3049, 1720, 1664, 1606 cm^{-1} ; ^1H NMP (400 MHz, CDCl_3) δ 7.26 (dd, $J = 18.5, 8$ Hz, 2H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.53 (d, $J = 10.8$ Hz, 1H), 4.27 (q, $J = 6.9$ Hz, 1H), 3.66 (dd, $J = 17.7, 8.4$ Hz, 1H), 3.58 (q, $J = 8.2$ Hz, 1H), 3.22 (t, $J = 8.5$ Hz, 2H), 1.75 (s, 3H), 1.49 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 209.9, 130.1, 127.6, 125.0, 121.7, 118.1, 106.7, 61.0, 49.1, 28.7, 23.7, 11.1; HRMS (EI): Exact mass calcd for $\text{C}_{12}\text{H}_{15}\text{NO}$ $[\text{M}]^+$, 189.1154. Found 189.1151.

The imino aryl iodide (28.9 mg, 91.8 μmol) in benzene (9 mL, 10 mM) was treated with $n\text{Bu}_3\text{SnH}$ (37 μL , 138 μmol) and warmed to 85 $^\circ\text{C}$. A solution of AIBN (23 mg, 138 μmol) in benzene (1 mL) was added via syringe pump over 8 h, and the mixture was refluxed for an additional 2 h before cooling. The solution was concentrated, and the residue was purified by flash

column chromatography (SiO₂, 40% dichloromethane in hexanes) to provide the indoline as a white solid (14.2 mg, 82 %). mp = 60-63 °C.

Additionally, the tin adduct could also be identified as an oil (9 mg, 18%)

following flash column chromatography of the above reaction mixture (SiO₂, 50% dichloromethane in hexanes); R_f = 0.11 (SiO₂, 60 % CH₂Cl₂/hexanes);

IR (film) 2952, 1715, 1699, 1648 cm⁻¹; ¹H NMP (400 MHz, CDCl₃) δ 7.10

(d, *J* = 6.9 Hz, 1H), 6.95 (dd, *J* = 7.8, 7.5 Hz, 1H), 6.67 (dd, *J* = 7.2, 6.3 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 3.91 (ddd, *J* = 9.9, 9.5, 3.2 Hz, 1H), 3.73 (ddd, *J* = 11.3, 8.8, 1.8 Hz, 1H), 3.14-2.98 (m, 2H), 2.17 (s, 3H), 1.67 (s, 3H), 1.44-1.33 (m, 12H), 0.94 (t, *J* = 7.2 Hz, 9H); ¹³C NMR (100 MHz, CDCl₃) ppm 208.8, 136.8, 130.0, 127.1, 125.0, 118.4, 108, 8, 50.7, 29.9, 29.4, 28.3, 26.9, 24.7, 24.6, 16.6, 13.8; HRMS (CI): Exact mass calcd for C₂₄H₄₁NOSn¹¹⁸ [M]⁺, 477.2210. Found 477.2206; calcd for C₂₄H₄₁NOSn¹²⁰ [M]⁺, 479.2210. Found 479.2210; calcd for C₂₄H₄₁NOSn¹¹⁶ [M]⁺, 475.2210. Found 475.2209.

2-(2,3-Dihydro-indol-1-yl)-1,2-diphenylethanone (2n). *ortho*-Iodo phenethyl amine (135 mg, 547 μmol), benzil (115 mg, 547 μmol), and 4 Å MS were rapidly stirred in benzene for 4h. The mixture was filtered through Celite, concentrated, and placed under high vacuum for three days to return the desired imine as a yellow oil (240 mg, 95 %) and 25:1 mixture of imine stereoisomers. IR (film) 3059, 2360, 2342, 1672, 1628, 1596 cm⁻¹; ¹H NMP (400 MHz, CDCl₃) δ 7.79 (d, *J* = 7.1 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 3H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.46-7.37 (m, 5H), 7.25 (d, *J* = 4.2 Hz, 2H), 6.88 (td, *J* = 9.2, 4.6 Hz, 1H), 3.74 (t, *J* = 7.1 Hz, 2H), 3.18 (t, *J* = 7.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) ppm 199.1, 167.4, 142.6, 139.7, 135.4, 135.2, 134.8, 133.0, 131.6, 131.2, 130.7, 130.2, 129.5, 129.3, 128.9, 128.4, 128.3, 127.6, 53.8, 42.2; HRMS (EI): Exact mass calcd for C₂₂H₁₉INO [M+H]⁺, 440.0513. Found 440.0528.

The imine derived from phenethyl amine was similarly prepared as a yellow oil. IR (film) 3060, 2980, 1675, 1628 cm^{-1} ; ^1H NMP (400 MHz, CDCl_3) δ 8.00 (dd, $J = 7.1, 1.3$ Hz, 2H), 7.74 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.60 (dd, $J = 7.0, 1.5$ Hz, 1H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.54 (d, $J = 7.9$ Hz, 1H), 7.53 (d, $J = 7.6$ Hz, 1H), 7.46-7.38 (m, 3H), 7.26 (dd, $J = 9.1, 2.4$ Hz, 1H), 7.20 (dd, $J = 9.3, 1.3$ Hz, 1H), 7.17 (dd, $J = 7.2, 1.4$ Hz, 1H), 3.73 (t, $J = 7.4$ Hz, 2H), 3.06 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 199.3, 195.0, 140.2, 135.6, 135.4, 135.0, 133.4, 131.3, 130.4, 129.7, 129.6, 129.5, 129.4, 129.1, 128.8, 127.7, 126.6, 56.0, 37.9; HRMS (CI): Exact mass calcd for $\text{C}_{22}\text{H}_{19}\text{NO}$ $[\text{M}]^+$, 313.1467. Found 313.1470.

A solution of the imine (36.4 mg, 83.1 μmol) and $^n\text{Bu}_3\text{SnH}$ (33.6 μL , 124.7 μmol) in hot (85° C) benzene (7.5 mL) was treated with a solution of AIBN (20.5 mg, 125 μmol) in benzene (1 mL) over 8 h by syringe pump. The reaction mixture was refluxed for an additional 2 h, cooled, and concentrated to a viscous oil that was directly purified by flash column chromatography (SiO_2 , 40% dichloromethane in hexanes) to furnish the indoline as a colorless oil (17.1 mg, 65 %). $R_f = 0.15$ (40% CH_2Cl_2 /hexanes); IR (film) 3026, 2851, 2360, 2346, 1690, 1606 cm^{-1} ; ^1H NMP (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.5$ Hz, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.44-7.32 (m, 7H), 7.09 (d, $J = 7.1$ Hz, 1H), 6.99 (t, $J = 7.8$ Hz, 1H), 6.66 (t, $J = 7.2$ Hz, 1H), 6.37 (d, $J = 7.9$ Hz, 1H), 6.18 (s, 1H), 3.74 (dd, $J = 17.4, 8.3$ Hz, 1H), 3.17 (dt, $J = 9.6, 6.5$ Hz, 1H), 3.03 (dt, $J = 9.4, 6.3$ Hz, 1H), 2.94 (td, $J = 17.3, 8.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) ppm 198.0, 133.5, 129.8, 129.2, 129.0, 128.9, 128.6, 127.4, 124.9, 118.3, 109.6, 107.2, 106.7, 65.9, 50.6, 28.5; HRMS (EI): Exact mass calcd for $\text{C}_{22}\text{H}_{19}\text{NO}$ $[\text{M}]^+$, 313.1467. Found 313.1477.

2-(2,3-Dihydro-indol-1-yl)-propionic acid methyl ester (2o). Using the general procedure for imine formation, *ortho*-iodophenethyl amine (182.7 mg, 740 μmol), methyl pyruvate (67 mL, 740 μmol), and 4 Å MS in benzene (3 mL) were stirred for 6 h to provide the

condensation product as a colorless oil (241 mg, 99 %) and mixture of tautomers (imine:enamine = 4:3 (CDCl_3) and 5:4 (C_6D_6) at rt and 75 °C). IR (film) 3398 (br), 2949, 2360, 1722, 1654 cm^{-1} ; imine: ^1H NMR (400 MHz, CDCl_3) δ 7.82 (dd, $J = 7.9, 2.8$ Hz, 1H), 7.32-7.27 (m, 1H), 7.23 (dd, $J = 5.1, 2.0$ Hz, 1H), 6.92 (dd, $J = 7.6, 7.4$ Hz, 2H), 3.87 (s, 3H), 3.74 (dd, $J = 8.5, 7.1$ Hz, 2H), 3.16 (t, $J = 7.9$ Hz, 2H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 165.9, 161.1, 139.9, 133.2, 130.6, 128.5, 124.3, 101.0, 42.9, 41.5, 14.8; HRMS (CI): Exact mass calcd for $\text{C}_{12}\text{H}_{15}\text{INO}_2$ $[\text{M}+\text{H}]^+$, 332.0149. Found 332.0151.

The phenethyl ketimine was similarly prepared as a colorless oil (1 : 1 imine:enamine); IR (film) 3397 (br), 2950, 1724, 1696, 1654 cm^{-1} ; imine: ^1H NMR (400 MHz, CDCl_3) δ 7.19 (dd, $J = 6.9, 5.9$ Hz, 2H), 7.13-7.10 (m, 3H), 3.76 (s, 3H), 3.63 (dd, $J = 7.3, 2.2$ Hz, 2H), 2.78 (t, 6.9 Hz, 2H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 160.9, 139.8, 129.1, 128.9, 128.7, 126.6, 55.1, 45.2, 36.7, 21.5; HRMS (CI): Exact mass calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_2$ $[\text{M}]^+$, 205.1103. Found 205.1095.

In accord with the General Procedure, the imine (14.8 mg, 44.7 μmol) in benzene (18 mL, 5mM) was treated with $^n\text{Bu}_3\text{SnH}$ (26.5 μL , 98.4 μmol) and warmed to 85° C. A solution of AIBN (3.7 mg, 22.4 μmol) in benzene (1 mL) was added via syringe pump over 4h, and the mixture was refluxed for an additional 3h before cooling. The solution was concentrated, diluted with ether, and stirred with satd aq KF for 2h. The mixture was filtered through Celite, the layers were separated, and the organic layer was washed with water, dried, and concentrated. The residue was purified by flash column chromatography (neutral alumina, 30 % dichloromethane in hexanes) to provide the indoline as a colorless oil (6.9 mg, 75 %); $R_f = 0.25$ (Al_2O_3 , 30 % CH_2Cl_2 /hexanes); IR (film) 2952, 2361, 1734, 1607 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.09 (d, $J = 7.3$ Hz, 1H), 7.04 (dd, $J = 7.4, 7.0$ Hz, 1H), 6.67 (t, $J = 7.4$ Hz, 1H), 6.40 (d, $J = 7.9$ Hz, 1H), 4.31 (q, $J = 7.3$ Hz, 1H), 3.70 (s, 3H), 3.59 (t, $J = 9.7$ Hz, 1H), 3.57 (d, $J = 10.3$ Hz, 1H), 3.04-2.97 (m, 2H), 1.51 (d, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 130.1, 127.4, 124.8, 118.2, 106.8, 53.9, 52.0, 48.3, 28.5, 15.0; HRMS (CI): Exact mass calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_2$ $[\text{M}]^+$, 205.1103. Found 205.1093.

General Procedure for Asymmetric Phase Transfer Alkylations

A 0.34 M dichloromethane solution of benzophenone glycinyl imine *tert*-butyl ester (1 eq), catalyst (0.1 eq) and solid CsOH•H₂O (10 eq) was cooled to –78 °C followed by dropwise addition of benzylhalide (5 eq). The heterogeneous mixture was stirred for the time specified while maintaining the low temperature. The solution was diluted with Et₂O, washed with water, dried over MgSO₄, and concentrated prior to purification by chromatography (neutral alumina) which gave analytically pure ketimine.

General Procedure for Aryl Amination Using Chiral Schiff Base Substrates

A benzene solution of the ketimine (1 eq) and ⁿBu₃SnH (2.2 eq) was warmed to 85 °C followed by slow addition of AIBN (1.2 eq) using a syringe pump over 4–5 hrs. The solution was refluxed for an additional hour before concentration. The residue was treated with a 1:1 (by volume) solution of Et₂O and satd aq KF and the mixture stirred vigorously until a white solid precipitated. The organic layer was washed with water, filtered, and dried over MgSO₄, and concentrated prior to purification by silica gel chromatography to give the target indoline.

General Procedure for Preparation of Racemic Samples

A 0.34 M dichloromethane solution of benzophenone glycinyl imine *tert*-butyl ester (1 eq), benzyltriethyl ammonium chloride (0.2 eq), and benzylhalide (1.2 eq) was treated with 50% aq NaOH (20 eq). The mixture was stirred vigorously at room temperature for 4 h. The heterogeneous mixture was diluted with Et₂O, washed with water, dried, and concentrated prior to purification by column chromatography (neutral alumina) to yield pure racemic ketimines.

General Procedure for Imine Reduction

To a 0.02 M solution of ketimine (1 eq) in dry methanol, was added NaBH₄ (25 eq) at 0 °C. The mixture was warmed up to 25 °C, and stirred for 1–1.5 h. The solution was diluted with CH₂Cl₂, washed with water, dried, and concentrated prior to purification by silica gel chromatography to yield analytically pure amine for HPLC analysis.

Catalyst B. Catalyst **B** was prepared in an analogous manner to that reported for catalyst **A**⁵. yellow solid, recrystallized from CH₂Cl₂/Et₂O or purified by silica gel chromatography (2% methanol in dichloromethane); mp 140–142 °C; *R_f* = 0.1 (2% CH₃OH/CH₂Cl₂); IR (film) 3402, 1640, 1625 cm⁻¹; ¹H NMR (400 MHz, CD₃OD) δ 9.02 (d, *J* = 4.6 Hz, 1H), 8.94 (d, *J* = 9.0 Hz, 1H), 8.80 (s, 1H), 8.68 (m, 1H), 8.29 (d, *J* = 8.9 Hz, 1H), 8.20-8.16 (m, 3H), 7.93-7.90 (m, 3H), 7.83 -7.79 (m, 1H), 7.70-7.66 (m, 1H), 7.62-7.58 (m, 2H), 6.88 (bs, 1H), 6.45-6.36 (m, 1H), 6.05 (s, 2H), 5.98-5.89 (m, 1H), 5.71 (d, *J* = 17.3 Hz, 1H), 5.61 (d, *J* = 10.5 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 5.04 (d *J* = 17.2 Hz, 1H), 4.87 (s, 1H), 4.55-4.51 (m, 2H), 4.41-4.33 (m, 2H), 4.41-4.33 (m, 3H), 3.14 (t, *J* = 11.0 Hz, 1H), 2.82-1.75 (m, 1H), 2.54 (t, *J* = 11.8 Hz, 1H), 2.25 (d, *J* = 7.7 Hz, 1H), 1.82 (br s, 1H), 1.62 (m, 1H), 1.18 (m, 1H); ¹³C NMR (100 MHz, CD₃OD) ppm 151.9, 150.2, 143.3, 138.3, 135.6, 135.5, 134.6, 134.0, 133.8, 132.4, 132.2, 131.9, 131.2, 130.4, 130.2, 130.0, 128.0, 127.5, 127.3, 126.8, 125.9, 125.7, 122.3, 119.9, 119.8, 119.1, 118.8, 76.5, 72.1, 69.7, 59.9, 57.9, 57.5, 39.7, 28.3, 25.6, 24.3.; HRMS (EI): Exact mass calcd for C₃₇H₃₇NO₂ [M]⁺, 525.2906. Found 525.2880. [α]_D²² = +286° (*c* 1.6, CHCl₃)

ortho-Bromobenzylbromide (1.97 g, 7.87 mmol), the glycyl imine (465 mg, 1.574 mmol), and CsOH•H₂O (2.35 g, 15.74 mmol) stirred for 20 h in the presence of catalyst **A** (10 mol %) at < -65 °C. Work-up according to the general procedure provided the desired phenyl alanine derivative as a colorless oil (650 mg, 89%). *R_f* = 0.40 (10% EtOAc/hexanes); IR (film) 3058, 1732 cm⁻¹; ¹H

⁵ Corey, E. J.; Xu, F.; Noe, M. C. *J. Am. Chem. Soc.* **1997**, *119*, 12414

NMR (400 MHz, CDCl_3) δ 7.61 (dt, $J = 7.1, 0.9$ Hz, 2H), 7.44 (dd, $J = 9.0, 1.1$ Hz, 1H), 7.41–7.28 (m, 6H), 7.23 (dd, $J = 7.5, 1.6$ Hz, 1H), 7.15 (td, $J = 7.4, 1.3$ Hz, 1H), 7.05 (td, $J = 7.7, 1.8$ Hz, 1H), 6.61 (d, $J = 5.9$ Hz, 2H), 4.36 (dd, $J = 9.7, 4.0$ Hz, 1H), 3.49 (dd, $J = 13.3, 4.0$ Hz, 1H), 3.25 (dd, $J = 13.3, 9.7$ Hz, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) ppm 170.5, 139.5, 137.7, 136.2, 132.7, 132.5, 130.1 (2C), 128.8, 128.2, 128.1, 127.93, 127.86, 127.7, 126.9, 125.2, 81.1, 65.2, 39.6, 28.1; HRMS (EI): Exact mass calcd for $\text{C}_{26}\text{H}_{27}\text{BrNO}_2$ $[\text{M}+\text{H}]^+$, 464.1225. Found 464.1241.

Anal. Calcd for $\text{C}_{26}\text{H}_{27}\text{BrNO}_2$: C, 67.24; H, 5.64; N, 3.02. Found: C, 67.36; H, 5.71; N, 2.94.

HPLC (Chiralcel OD, 2% i PrOH/hexanes, 0.5 mL/min) t_r (*R*) = 10.5 m, t_r (*S*) = 11.0 m. (*S*)- 96% ee, $[\alpha]_{\text{D}}^{22} = -265^\circ$ (c 0.9, CHCl_3); (*R*)- 93% ee, $[\alpha]_{\text{D}}^{23} = +260^\circ$ (c 2.7, CHCl_3).

Use of cinchonine-derived catalyst **B** gave the enantiomer as a colorless oil (189 mg, 81%).

For chiral HPLC analysis, the imine was reduced according to the General Procedure (7 mg, 88%). Crystalline solid, mp 98–100 $^\circ\text{C}$; $R_f = 0.43$ (10% EtOAc/hexanes); IR (film) 3324, 1724 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 7.8$ Hz, 1H), 7.34 (dd, $J = 8.5, 1.3$ Hz, 2H), 7.29 (d, $J = 7.0$ Hz, 2H), 7.25 (d, $J = 4.2$ Hz, 2H), 7.17 (m, 7H), 4.81 (s, 1H), 3.46 (t, $J = 7.5$ Hz, 1H), 3.09 (dd, $J = 13.4, 6.6$ Hz, 1H), 3.03 (dd, $J = 13.6, 8.6$ Hz, 1H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) ppm, 174.1, 144.5, 142.6, 137.7, 132.6, 132.0, 128.5, 128.3, 128.1, 127.4, 127.2, 127.1, 127.0, 125.1, 81.2, 65.4, 59.6, 40.2, 28.1; HRMS (EI): Exact mass calcd for $\text{C}_{26}\text{H}_{29}\text{BrNO}_2$ $[\text{M}+\text{H}]^+$, 466.1382. Found 466.1358.

HPLC (Chiralcel AD, 2% i PrOH/hexanes, 1 mL/min) t_r (*S*) = 4.1 m, t_r (*R*) = 4.6 m. (*S*)- 95% ee, $[\alpha]_{\text{D}}^{24} = -30.6^\circ$ (c 2.2, CHCl_3). (*R*)- 93% ee, $[\alpha]_{\text{D}}^{23} = +29.4^\circ$ (c 0.9, CHCl_3).

(**10a**). According to the general procedure, use of the Schiff base (0.107 g, 0.23 mmol), Bu_3SnH (0.14 mL, 0.51 mmol), and AIBN (30 mg, 0.19 mmol) furnished, after silica gel chromatography (2% EtOAc in hexanes), a white solid (62 mg, 69%). mp 102–104 °C; R_f = 0.42 (10% EtOAc/hexanes); IR (film) 3061, 1736 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, J = 7.1 Hz, 2H), 7.37 (d, J = 7.1 Hz, 2H), 7.34–7.23 (m, 6H), 7.03 (d, J = 7.1 Hz, 1H), 6.87 (t, J = 7.7 Hz, 1H), 6.64 (t, J = 7.3 Hz, 1H), 6.01 (d, J = 7.9 Hz, 1H), 5.66 (s, 1H), 4.11 (dd J = 10.5, 5.4 Hz, 1H), 3.42 (dd, J = 15.9, 10.5 Hz, 1H), 3.0 (dd, J = 15.9, 5.4 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) ppm 172.6, 151.2, 141.2, 140.7, 129.2, 128.5, 128.4, 127.7, 127.3, 127.2, 123.8, 117.9, 80.8, 67.1, 65.0, 34.0, 27.9; HRMS (EI): Exact mass calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_2$ $[\text{M}]^+$, 385.2042. Found 385.2061.

HPLC (Chiralcel OD, 2% $^i\text{PrOH}$ /hexanes, 1 mL/min) t_r (*S*) = 4.1 m, t_r (*R*) = 4.7 m. (*S*)- 95% ee, $[\alpha]_{\text{D}}^{25}$ = -45.4° (c 1.0, CHCl_3). (*R*)- 93% ee, $[\alpha]_{\text{D}}^{23}$ = $+41.9^\circ$ (c 1.8, CHCl_3).

The enantiomeric indoline was similarly prepared using catalyst **B** (21.5 mg, 70%).

(*S*)-Indoline α -amino acid *tert*-butyl ester, formic acid salt. Indoline **10a** (55 mg, 142 μmol) was dissolved in dry MeOH (2 mL) and treated with 96% HCOOH (65 mg, 1.42 mmol) and 10% Pd/C (5.5 mg). The bomb was charged with hydrogen (100 psi): and the reaction was stirred for 48 h with frequent recharging of the hydrogen atmosphere. Filtration of the reaction mixture and evaporation of solvent gave a white solid (29 mg, 77%). mp 102–104 °C; R_f = 0.10 (15% EtOAc/hexanes); IR (film) 2978, 1736, 1672 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 9.00 (s, 1H), 7.25–7.20 (m, 3H), 7.10–7.05 (m, 1H), 4.94 (ddd, J = 11.1, 4.3, 0.8 Hz, 1H), 3.54 (dd, J = 16.8, 11.3 Hz, 1H), 3.15 (dd, J = 16.8, 4.3 Hz, 1H), 1.49 (s, 9H); ^{13}C NMR (100 MHz,

CDCl₃) ppm 169.7, 157.6, 128.3, 126.1, 124.6, 109.5, 82.6, 58.6, 45.0, 32.7, 28.2; HRMS (EI): Exact mass calcd for C₁₄H₁₇NO₃ [M-H₂O]⁺, 247.1208. Found 247.1215. (S)- 91% ee, [α]_D²⁵ = -103.7° (c 0.74, CHCl₃).

(S)-Indoline α-amino acid. The formic acid salt (32.5 mg, 123 μmol) was dissolved in 6*N* HCl (1 mL) and THF (several drops to solubilize) and refluxed for 3 h. The reaction mixture was cooled, neutralized with NaOH, and the solvent was removed by evaporation. The residue was extracted with 50% MeOH/CH₂Cl₂ and the extracts were concentrated to give a white solid (87%). [α]_D²¹ = -80.8° (c 0.40, 1*N* HCl). Literature: [α]_D²¹ = -114° (c 1, 1*N* HCl). The presence of (inseparable) NaCl in the synthetic material accounts for the slight depression of rotation.

5-Methoxy-2-bromo-benzyl bromide (474 mg, 1.69 mmol), the glycyl imine (100 mg, 339 μmol) and CsOH•H₂O (505 mg, 3.39 mmol) stirred for 2 hrs in the presence of catalyst A (10 mol %) while maintaining a temperature < -10 °C. Work-up according to the general procedure provided the desired phenyl alanine derivative as a colorless oil (136 mg, 81%). *R_f* = 0.28 (10% EtOAc/hexanes); IR (film) 3058, 1733 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.3 Hz, 2H), 7.40–7.28 (m, 8H), 6.76 (d, *J* = 2.7 Hz, 1H), 6.63 (dd, *J* = 8.7, 3.0 Hz, 2H), 4.38 (dd, *J* = 9.7, 3.9 Hz, 1H), 3.62 (s, 3H), 3.43 (dd, *J* = 13.3, 4.0 Hz, 1H), 3.22 (dd, *J* = 13.2, 9.9 Hz, 1H), 1.47 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) ppm 170.6, 158.4, 139.4, 138.4, 136.1, 132.9, 130.2, 128.7, 128.3, 128.1, 127.9, 127.7, 117.1, 115.5, 114.9, 81.2, 65.1, 55.2, 39.7, 28.0; HRMS (EI): Exact mass calcd for C₂₇H₂₉BrNO₃ [M+H]⁺, 494.1331. Found 494.1323.

HPLC (Chiralcel AD, 2% ⁱPrOH/hexanes, 1 mL/min) *t_r* (*R*) = 4.6 m, *t_r* (*S*) = 5.4 m. (S)- 94% ee [α]_D²⁵ = -211.7 (c 1.0, CHCl₃). (*R*)- 91% ee, [α]_D²³ = +201.1 (c 0.9, CHCl₃).

Similarly use of cinchonine based catalyst **B** gave the enantiomer as a colorless oil (120 mg, 74%).

(**10b**). According to the general procedure, use of the Schiff base (69.2 mg, 140 μmol), Bu_3SnH (188 μL , 700 μmol), and AIBN (37 mg, 224 μmol) furnished, after chromatography on neutral alumina (2% EtOAc in hexanes), a colorless oil (26 mg, 45%). $R_f = 0.1$ (3% EtOAc/hexanes); IR (film) 3060, 1733 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (dd, $J = 8.3, 1.4$ Hz, 2H), 7.39 (d, $J = 7.1$ Hz, 2H), 7.33–7.22 (m, 6H), 6.68 (d, $J = 2.4$ Hz, 1H), 6.42 (dd, $J = 8.6, 2.6$ Hz, 1H), 5.89 (d, $J = 8.6$ Hz, 1H), 5.59 (s, 1H), 4.07 (dd, $J = 10.2, 5.1$ Hz, 1H), 3.70 (s, 3H), 3.38 (dd, $J = 15.8, 10.2$ Hz, 1H), 2.96 (dd, $J = 15.9, 5.0$ Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) ppm 172.6, 152.7, 145.4, 141.6, 140.9, 129.3, 129.1, 128.4, 128.3, 128.2, 127.2, 127.0, 111.6, 111.3, 109.3, 79.8, 67.6, 65.3, 55.8, 34.1, 27.9; HRMS (EI): Exact mass calcd for $\text{C}_{27}\text{H}_{29}\text{NO}_3$ $[\text{M}]^+$, 415.2147. Found 415.2160.

HPLC (Chiralcel OD, 2% $^i\text{PrOH}$ /hexanes, 1 mL/min) t_r (*S*) = 5.4 m, t_r (*R*) = 6.0 m. (*S*)- 91% ee $[\alpha]_{\text{D}}^{23} = -41.2^\circ$ (c 1.3, CHCl_3). (*R*)- 87% ee, $[\alpha]_{\text{D}}^{23} = +37.5^\circ$ (c 0.7, CHCl_3).

The enantiomeric indoline was similarly prepared using cinchonine-derived catalyst **B** (24.3 mg, 55%).

2-Bromo-3-bromomethyl pyridine (213 mg, 850 μmol), glycinyll imine (50 mg, 170 μmol), and $\text{CsOH}\cdot\text{H}_2\text{O}$ (253 mg, 1.70 mmol) were stirred for 20 h in the presence of catalyst **A** (10 mol %) while maintaining a temperature $< -65^\circ\text{C}$. Work-up according to the general procedure provided the desired alanine derivative as a white solid (61 mg, 77%). mp $93\text{--}95^\circ\text{C}$; $R_f = 0.15$

(10% EtOAc/hexanes); IR (film) 3056, 1732 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.21 (dd, J = 4.7, 1.9 Hz, 1H), 7.60 (dd, J = 8.6, 1.5 Hz, 2H), 7.56 (dd, J = 7.5, 1.9 Hz, 1H), 7.41–7.28 (m, 6H), 7.12 (dd, J = 7.5, 4.7 Hz, 1H), 6.68 (d, J = 6.2 Hz, 2H), 4.40 (dd, J = 9.5, 4.3 Hz, 1H), 3.43 (dd, J = 13.7, 4.3 Hz, 1H), 3.22 (dd, J = 13.6, 9.4 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) ppm 171.1, 170.2, 148.0, 144.7, 140.7, 139.0, 135.9, 135.1, 130.3, 128.7, 128.5, 128.3, 127.9, 127.4, 122.4, 81.5, 64.4, 44.7, 28.0; HRMS (EI): Exact mass calcd for $\text{C}_{25}\text{H}_{26}\text{BrN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$, 465.1177. Found 465.1180.

Anal. Calcd for $\text{C}_{25}\text{H}_{25}\text{BrN}_2\text{O}_2$: C, 64.52; H, 5.41; N, 6.02. Found: C, 64.24; H, 5.48; N, 5.96.

HPLC (Chiralcel AD, 2% i PrOH/hexanes, 1 mL/min) t_r (*R*) = 7.4 m, t_r (*S*) = 8.9 m. (*S*)- >99% ee, $[\alpha]_{\text{D}}^{23} = -245.4^\circ$ (c 0.9, CHCl_3). (*R*)- 98% ee, $[\alpha]_{\text{D}}^{24} = +235.9^\circ$ (c 1.7, CHCl_3).

Similarly, use of cinchonine catalyst **B** gave the enantiomer as a white solid (60 mg, 76%).

(10c). According to the general procedure, use of the Schiff base (123 mg, 264 μmol), Bu_3SnH (157 μL , 582 μmol), and AIBN (34.7 mg, 211 μmol) furnished, after silica gel chromatography (10% EtOAc in hexanes), a white solid (72.5 mg, 71%). mp 104–106 $^\circ\text{C}$; R_f = 0.15 (10% EtOAc/hexanes); IR (film) 3060, 1740 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 5.4 Hz, 1H), 7.40 (d, J = 7.1 Hz, 2H), 7.30–7.17 (m, 9H), 6.49 (s, 1H), 6.46 (dd, J = 5.4, 1.6 Hz, 1H), 4.20 (dd, J = 10.7, 5.0 Hz, 1H), 3.42 (dd, J = 16.5, 10.7 Hz, 1H), 2.96 (dd, J = 16.5, 5.0 Hz, 1H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) ppm 171.8, 162.5, 146.4, 140.4, 140.1, 130.7, 129.8, 128.5, 128.3, 128.2, 127.2, 127.0, 120.4, 112.9, 81.1, 62.5, 61.0, 32.1, 27.7; HRMS (EI): Exact mass calcd for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_2$ $[\text{M}]^+$, 386.1994. Found 386.1992.

HPLC (Chiralcel AD, 10% i PrOH/hexanes, 1 mL/min) t_r (*S*) = 6.0 m, t_r (*R*) = 11.3 m. (*S*)- 91% ee, $[\alpha]_{\text{D}}^{24} = -61.8^\circ$ (c 0.9, CHCl_3). (*R*)- 89% ee, $[\alpha]_{\text{D}}^{23} = +58.6^\circ$ (c 0.6, CHCl_3).

The enantiomeric indoline was similarly prepared using catalyst **B** (37 mg, 60%).

5-Chloro-2-bromo benzyl bromide (1.16 g, 4.06 mmol), the glycyl imine (200 mg, 667 mmol) and CsOH•H₂O (1.01 g, 6.77 mmol) stirred for 22 hrs in the presence of catalyst **A** (10 mol %) while maintaining a temperature <−60 °C. Work-up according to the general procedure provided the desired phenyl alanine derivative as a white solid (250 mg, 74%); mp 98–100 °C; *R_f* = 0.43 (10% EtOAc/hexanes); IR (film) 3059, 1732 cm^{−1}; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.39–7.29 (m, 6H), 7.26 (s, 1H), 7.20 (d, *J* = 2.4 Hz, 1H), 7.01 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.73 (br d, *J* = 6.9 Hz, 2H), 4.31 (dd, *J* = 9.3, 4.6 Hz, 1H), 3.38 (dd, *J* = 13.4, 4.6 Hz, 1H), 3.24 (dd, *J* = 13.4, 9.3 Hz, 1H), 1.45 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) ppm 171.1, 170.3, 139.5, 136.1, 133.5, 132.8, 132.4, 130.3, 130.1, 128.8, 128.5, 128.3, 128.2, 128.0, 127.7, 122.9, 81.5, 65.0, 39.4, 28.0; HRMS (EI): Exact mass calcd for C₂₆H₂₅ClNO₂ [M−Br]⁺, 418.1574. Found 418.1586.

HPLC (Chiralcel OD, 2% ⁱPrOH/hexanes, 1 mL/min) *t_r* (*S*) = 4.1 m, *t_r* (*R*) = 4.6 m. (*S*)- 93% ee [α]_D²¹ = −194.3 (*c* 2.6, CHCl₃). (*R*)- 94% ee, [α]_D²¹ = +194.6 (*c* 0.74, CHCl₃).

Similarly, use of cinchonine-derived catalyst **B** gave the enantiomer as a white solid (240 mg, 71%).

(**10d**). According to the general procedure, use of the Schiff base (50 mg, 100 μ mol) $^n\text{Bu}_3\text{SnH}$ (81 μ L, 300 μ mol) and AIBN (26.3 mg, 160 μ mol) furnished, after silica gel chromatography (1% EtOAc in hexanes), a colorless oil (23 mg, 55%). R_f = 0.45 (10% EtOAc/hexanes); IR (film) 3062, 1733 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, J = 6.9 Hz, 2H), 7.38–7.25 (m, 8H), 6.98 (s, 1H), 6.81 (dd, J = 8.5, 1.9 Hz, 1H), 5.87 (d, J = 8.5 Hz, 1H), 5.64 (s, 1H), 4.12 (dd, J = 10.3, 4.7 Hz, 1H), 3.38 (dd, J = 16.0, 10.4 Hz, 1H), 2.96 (dd, J = 16.3, 4.7 Hz, 1H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) ppm 172.1, 149.7, 141.0, 140.2, 130.1, 129.7, 129.2, 128.6, 128.5, 128.0, 127.5, 127.3, 127.0, 124.1, 109.8, 81.2, 66.9, 65.2, 33.6, 27.8; HRMS (EI): Exact mass calcd for $\text{C}_{26}\text{H}_{26}\text{ClNO}_2$ $[\text{M}]^+$, 419.1652. Found 419.1657.

HPLC (Chiralcel AD, 2% $^i\text{PrOH}$ /hexanes, 1 mL/min) t_r (S) = 4.2 m, t_r (R) = 4.9 m. (S)- 93% ee $[\alpha]_{\text{D}}^{21} = -59.8$ (c 1.2, CHCl_3). (R)- 94% ee, $[\alpha]_{\text{D}}^{23} = +63.4$ (c 1.0, CHCl_3).

The enantiomeric indoline was similarly prepared using cinchonine-derived catalyst **B** (25.2 mg, 60%).

2-(2-Bromophenyl)-2-hydroxyethyl carbamic acid *tert*-butyl ester (13). Treatment of 0.215g (0.994 mmol) of 2-amino(2-bromo-phenyl)-ethanol⁶ with di-*tert*-butyl dicarbonate (0.217g, 0.994 mmol) and triethylamine (0.129 ml, 0.994 mmol) in CH₂Cl₂ (20 mL) provided after chromatography (SiO₂, 20% ethyl acetate in hexanes) the carbamate as a colorless oil (260 mg, 83%). *R*_f = 0.10 (20% EtOAc/hexanes); IR (film) 3427 (br), 1691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.10 (td, *J* = 7.8, 1.5 Hz, 1H), 5.21 (t, *J* = 5.4 Hz, 1H), 5.09 (d, *J* = 3.0 Hz, 1H), 4.50 (s, 1H), 3.48 (ddd, *J* = 14.2, 6.5, 3.0 Hz, 1H), 3.29-3.24 (m, 1H), 1.41 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) ppm 157.8, 141.0, 132.8, 129.2, 128.2, 127.8, 122.0, 80.0, 73.4, 46.8, 28.6; HRMS (EI): Exact mass calcd for C₁₃H₁₉BrNO₃ [M+H]⁺, 316.0548. Found 316.0544.

2-(2-Bromophenyl)-2-methoxyethyl carbamic acid *tert*-butyl ester. The carbamate (50.0 mg, 0.159 mmol) was treated with sodium hydride (7.00 mg, 0.152 mmol) at 0 °C in DMF (1 mL). Dimethyl sulfate (14.0 μL, 0.152 mmol) was added and the solution was warmed to room temperature. Stirring for 4 hours followed by aqueous work-up and flash chromatography (SiO₂, 5% ethyl acetate in hexanes) provided the ether as a colorless oil (35.0 mg, 70%). *R*_f = 0.10 (4% EtOAc/hexanes); IR (film) 3442, 3362, 3061, 1717 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.54 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.16 (td, *J* = 7.8, 1.6 Hz, 1H), 4.92 (s, 1H), 4.68 (br, d, *J* = 3.5 Hz, 1H), 3.53-3.44 (m, 1H), 3.27 (s, 3H),

⁶ Fleming, I.; Woolias, M.; *J. Chem. Soc., Perkin Trans. 1*, **1979**, 3, 829.

3.18 (ddd, $J = 12.8, 7.8, 5.0$ Hz, 1H), 1.41 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) ppm 177.2, 155.9, 138.4, 133.1, 129.6, 127.9, 123.6, 81.5, 79.5, 57.4, 45.4, 28.6; HRMS (EI): Exact mass calcd for $\text{C}_{14}\text{H}_{21}\text{BrNO}_3$ $[\text{M}+\text{H}]^+$, 330.0704. Found 330.0723.

2-(2-Bromophenyl)-2-methoxyethylamine. Treatment of the carbamate (14.6 mg, 0.044 mmol) with trifluoroacetic acid (10% v/v TFA: CH_2Cl_2) at room temperature for 2 h yielded the trifluoroacetate salt. This salt was dissolved in ether and washed with satd aq K_2CO_3 to give the amine in quantitative yield as a colorless oil. IR (film) 3384, 3311, 3062, 1726 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 7.4$ Hz, 1H), 7.41 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.33 (t, $J = 7.1$ Hz, 1H), 7.15 (td, $J = 7.7, 1.8$ Hz, 1H), 4.57 (dd, $J = 7.5, 3.4$ Hz, 1H), 3.30 (s, 1H), 2.94 (br, m, 1H), 2.79 (br, m, 1H), 1.53 (br, s, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 139.2, 133.1, 131.1, 129.3, 127.9, 123.4, 68.4. HRMS (EI): Exact mass calcd for $\text{C}_8\text{H}_8\text{BrO}$ $[\text{M}-\text{CH}_4\text{N}]^+$, 198.9759. Found 198.9758.

***N*-(1-Phenylbenzyl)-3-methoxyindoline (15).** 2-(*ortho*-Bromophenyl)-2-methoxyethylamine (43.4 mg, 189 μmol), benzophenone imine (32 μL , 189 μmol), and 4 Å MS were stirred in CH_2Cl_2 at room temperature for 7 h. Removal of the solvent provided the ketimine as a colorless oil. IR (film) 3058, 1626 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.3$ Hz, 2H), 7.52 (dd, $J = 8.1, 2.2$ Hz, 1H), 7.45–7.28 (m, 8H), 7.13 (dt, $J = 9.3, 1.6$ Hz, 1H), 7.07 (dd, $J = 7.5, 2.4$ Hz, 2H), 5.05 (dd, $J = 6.7, 4.5$ Hz, 1H), 3.71 (dd, $J = 14.0, 4.4$ Hz, 1H), 3.64 (dd, $J = 14.0, 6.9$ Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 169.8, 140.1 (2C),

137.0, 132.82, 130.2, 129.1, 128.8 (2C), 128.65, 128.6, 128.54, 128.2, 127.7, 123.8, 82.8, 59.2, 57.6; HRMS (EI): Exact mass calcd for $C_{22}H_{21}BrNO$ $[M+H]^+$, 394.0808. Found 394.0795.

A three hour addition of nBu_3SnH (38 μL , 143 μmol) and AIBN (8.5 mg, 52 μmol) in benzene (1 mL) to a refluxing solution of the unpurified ketimine (51.2 mg, 130 μmol) in benzene (13 mL) afforded, after flash chromatography on basic alumina (10% CH_2Cl_2 in hexanes), the desired indoline as a colorless oil (29 mg, 70%). R_f = 0.15 (10% CH_2Cl_2 /hexanes); IR (film) 3059, 1608 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.26 (m, 11H), 7.10 (dt, J = 8.1, 1.2 Hz, 1H), 6.71 (t, J = 7.25 Hz, 1H), 6.34 (d, J = 7.9 Hz, 1H), 5.70 (s, 1H), 4.79 (dd, J = 6.7, 2.6 Hz, 1H), 3.35 (s, 3H), 3.33 (dd, J = 11.3, 2.7 Hz, 1H), 3.27 (dd, J = 11.2, 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm 140.7, 130.1, 129.2, 128.8, 128.7, 128.4, 128.2, 127.7, 127.5, 126.1, 78.9, 65.7, 56.4, 55.4; HRMS (EI): Exact mass calcd for $C_{22}H_{21}NO$ $[M]^+$, 315.1623. Found 315.1623.