

Supporting Information for:

**Oxaziridine-Mediated Oxyamination of Indoles: An Approach to 3-Aminoindoles
and Enantioenriched 3-Aminopyrroloindolines**

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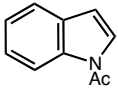
I. General Information.

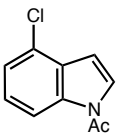
Commercially available tetrabutylammonium chloride was made anhydrous through azeotropic removal of water using benzene and was stored in an inert-atmosphere glovebox. CH₂Cl₂ and acetonitrile were distilled from CaH₂ immediately prior to use. Chloroform and acetone were distilled from K₂CO₃ before use. Acetyl chloride was fractionally distilled before use. Sodium methoxide was generated by adding sodium metal to methanol until all hydrogen evolution ceased. All other chemicals were purchased from Aldrich, EMD Chemicals or Chem-Impex and used without further purification. Silica gel chromatography was performed using SiliaFlash P60 silica gel (230-400 mesh). All reactions were conducted in flame-dried glassware.

Diastereomeric ratios were determined by ¹H NMR analysis of the unpurified reaction mixtures. ¹H and ¹³C NMR data were obtained using Varian Inova-500 (NSF CHE-9629688) and Varian Unity-500 (NSF CHE-8813550, NIH 1 S10 RR0 4981-10, NSF CHE-9629688) spectrometers. ¹H data were internally referenced to TMS (0.0 ppm) or DMSO (2.5 ppm); ¹³C spectra were referenced to CDCl₃ (77.23 ppm) or DMSO (39.50 ppm). NMR spectra were acquired at room temperature unless otherwise indicated. IR spectral data were obtained using a Bruker Vector 22 spectrometer. Melting points were obtained using a Mel-Temp II (Laboratory Devices, Inc., USA) and Digimelt MPA 160 (Stanford Research Systems, Inc.) melting point apparatuses. Mass spectrometry was performed with a Micromass LCT (electrospray ionization, time-of-flight analyzer). These facilities are supported by the NSF (CHE-9709005) and the University of Wisconsin. Enantiomer ratios were measured using a Berger SFC instrument using an Agilent UV detector (210 nm) and a Chiralcel OJ-H and AD columns (Daicel). Optical rotations were measured on an Autopol III polarimeter (Rudolph Research) at room temperature.

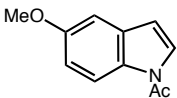
Trans-(2-Phenylsulfonyl)-3-phenyloxaziridine **3**,¹ 3,3-dimethyl benzenesulfonyl oxaziridine **9**,² and homotryptamine³ were synthesized as previously described.

II. Synthesis of starting materials.

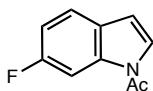
 ***N*-Acetyl indole.** Prepared using the method described by Illi.⁴ Indole (1.02g, 8.7 mmol) and Bu₄N⁺HSO₄⁻ (28 mg, 0.082 mmol) were dissolved in CH₂Cl₂ (23 mL). Powdered NaOH (860 mg, 21.5 mmol) was added, and then acetyl chloride (920 μL, 12.9 mmol) in CH₂Cl₂ (8 mL) was added dropwise to the vigorously stirring solution. After 1.5 h at room temperature, TLC showed complete consumption of the starting indole. Purification of the crude reaction mixture on SiO₂ using 8:1 to 4:1 hexane:EtOAc resulted in 1.35g (8.5 mmol, 97% yield) of acetylindole as a colorless liquid. The compound exhibited spectral data identical to those reported for *N*-acetylindole.⁴

 ***4*-Chloro-*N*-acetyl indole.** Prepared using the method described above using 4-chloroindole (356 mg, 2.37 mmol), Bu₄N⁺HSO₄⁻ (13 mg, 0.038 mmol), powdered NaOH (250 mg, 6.25 mmol), acetyl chloride (250 μL, 3.52 mmol), and CH₂Cl₂ (8 mL + 3 mL) with a reaction time of 45 min. Purification of the crude reaction mixture on SiO₂ using 2:1 to 1:1 dichloromethane:hexane resulted in 438 mg (2.26 mmol, 96% yield) of 4-chloro-*N*-acetylindole as a white solid.

IR (neat): 3139, 1685, 1426, 1339, 1182; ¹H NMR: (500 MHz, CDCl₃) 8.36 (t, J = 4.4 Hz, 1H), 7.46 (d, J = 3.8 Hz, 1H), 7.28 (d, J = 4.4 Hz, 2H), 6.78 (d, J = 3.8 Hz, 1H), 2.66 (s, 3H); ¹³C NMR: (125 MHz, CDCl₃) 168.8, 136.3, 129.3, 126.2, 126.0, 125.9, 123.6, 115.3, 107.3, 24.1; HRMS (EI⁺) calc'd for [C₁₀H₈ClNO]⁺ (M)⁺ requires *m/z* 193.0289, found *m/z* 193.0291. (mp = 33-35 °C).

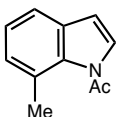
 ***5*-Methoxy-*N*-acetyl indole.** Prepared using the method described above using 5-methoxyindole (104 mg, 0.71 mmol), Bu₄N⁺HSO₄⁻ (6 mg, 0.018 mmol), powdered NaOH (83 mg, 2.08 mmol), acetyl chloride (73 μL, 1.03 mmol), and CH₂Cl₂ (2 mL + 670 μL) with a reaction time of 30 min. Purification of the crude reaction mixture on SiO₂ using 5:1 hexane:EtOAc resulted in 112 mg (0.59

mmol, 83% yield) of 5-methoxy-*N*-acetylindole as a white solid. The compound exhibited spectral data identical to those reported for 5-methoxy-*N*-acetylindole.⁵



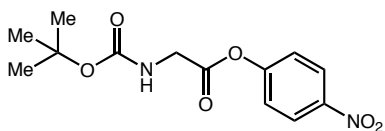
6-Fluoro-*N*-acetyl indole. Prepared using the method described above using 6-fluoroindole (358 mg, 2.65 mmol), Bu₄N⁺HSO₄⁻ (12 mg, 0.035 mmol), powdered NaOH (263 mg, 6.56 mmol), acetyl chloride (300 μL, 4.22 mmol), and CH₂Cl₂ (8 mL + 3 mL) with a reaction time of 30 min. Purification of the crude reaction mixture on SiO₂ using 5:1 hexane:EtOAc resulted in 437.6 mg (2.47 mmol, 93% yield) of 6-fluoro-*N*-acetylindole as a pinkish-white solid.

IR (neat): 3153, 3123, 2923, 1720, 1438, 1331, 1211; ¹H NMR: (500 MHz, CDCl₃) 8.17 (d, J = 9.6 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.34 (s, 1H), 7.00 (t, J = 9.6 Hz, 1H), 6.57 (s, 1H), 2.57 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) 168.8, 161.4 (¹J_{CF} = 242), 135.8 (³J_{CF} = 13), 126.7, 125.7 (⁴J_{CF} = 3), 121.5 (³J_{CF} = 10), 112.0 (²J_{CF} = 24), 108.9, 104.2 (²J_{CF} = 28), 23.8; HRMS (EI⁺) calc'd for [C₁₀H₈FNO]⁺ (M)⁺ requires *m/z* 177.0585, found *m/z* 177.0583. (mp = 35-37 °C)

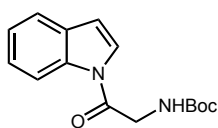


7-Methyl-*N*-acetyl indole. 7-Methylindole (145 mg, 1.11 mmol) and Bu₄N⁺HSO₄⁻ (8 mg, 0.024 mmol) were dissolved in CH₂Cl₂ (4 mL). Powdered NaOH (130 mg, 3.25 mmol) was added, and then acetyl chloride (130 μL, 1.83 mmol) in CH₂Cl₂ (1.5 mL) was added dropwise to the vigorously stirring solution. After 1 h, additional NaOH (130 mg, 3.25 mmol) and acetyl chloride (130 μL, 1.83 mmol) were added to the reaction vessel. Purification of the crude reaction mixture on SiO₂ using 2:1 dichloromethane:hexane resulted in 127.5 mg (0.736 mmol, 67% yield) of 7-methyl-*N*-acetylindole as a white solid.

IR (neat): 3152, 2978, 1706, 1361, 1312, 1211; ¹H NMR: (500 MHz, CDCl₃) 7.39 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 3.8 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 7.14 (d, J = 7.5 Hz, 1H), 6.61 (d, J = 3.8 Hz, 1H), 2.64 (s, 3H), 2.58 (s, 3H); ¹³C NMR: (125 MHz, CDCl₃) 167.9, 135.3, 132.2, 128.4, 126.9, 126.7, 124.3, 118.7, 109.2, 24.7, 22.9; HRMS (EI⁺) calc'd for [C₁₁H₁₁NO]⁺ (M)⁺ requires *m/z* 173.0836, found *m/z* 173.0833. (mp = 64-66 °C).

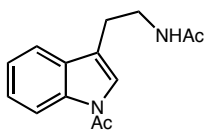


***N*-Boc glycine 4-nitrophenyl ester.** Prepared using a variation of the method described by Kovacs.⁶ *N*-Boc glycine (603 mg, 3.44 mmol), 4-Nitrophenol (470 mg, 3.38 mmol) and EDCI•HCl (970 mg, 5.06 mmol) were dissolved in 7.5 mL CH₂Cl₂, and the solution was stirred for 24 h. The reaction mixture was washed with water, and the aqueous phase was extracted with CH₂Cl₂. The combined organic phases were dried with Na₂SO₄, and the solvent was removed to yield 1.00 g crude product, which contained <10% nitrophenol. The crude was immediately used without further purification.



***N*-(Boc-glycyl) indole.** Prepared using a method described by Snider.⁷ Indole (268 mg, 2.29 mmol) was placed in a round-bottomed flask followed by crude *N*-Boc glycine 4-nitrophenyl ester (1.00 g, 3.37 mmol), KF (267 mg, 4.60 mmol), 18-crown-6 ether (610 mg, 2.31 mmol), *i*-Pr₂NEt (400 μL, 2.30 mmol), and acetonitrile (6 mL). The mixture was sonicated under argon for 30 min then stirred at room temperature. After 3 h, an additional 400 μL *i*-Pr₂NEt was added. After 20 h, the reaction was quenched with water, the aqueous phase was extracted twice with CH₂Cl₂, washed with sat. NaHCO₃ solution, dried over Na₂SO₄, and the volatiles were removed in vacuo. Purification of the crude reaction mixture on SiO₂ (gradient: 0 to 2% acetone in CH₂Cl₂) resulted in 259 mg (0.944 mmol, 41% yield) of the title compound as a white solid.

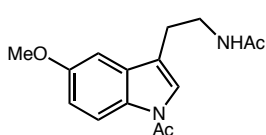
IR (neat): 3391, 2982, 1714, 1684, 1526, 1282, 1399, 1172; ¹H NMR: (500 MHz, CDCl₃) 8.39 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 7.9 Hz, 1H), 7.37 (m, 2H), 7.29 (t, J = 7.9 Hz, 1H), 6.67 (d, J = 3.3 Hz, 1H), 5.50 (br s, 1H), 4.56 (d, J = 4.4 Hz, 2H), 1.49 (s, 9H); ¹³C NMR: (125 MHz, CDCl₃) 167.5, 156.0, 135.7, 130.4, 125.7, 124.3, 123.4, 121.3, 116.6, 110.7, 80.5, 44.4, 28.5; HRMS (ESI⁺) calc'd for [C₁₅H₁₉N₂O₃]⁺ (M+H)⁺ requires *m/z* 275.1391, found *m/z* 275.1398. (mp = 156-158 °C)



***N,N'*-Diacetyl tryptamine.** Tryptamine (1.49 g, 9.30 mmol) and Bu₄N⁺HSO₄⁻ (80 mg, 0.24 mmol) were dissolved in CH₂Cl₂ (24 mL). Powdered NaOH (1.90 g, 47.5 mmol) was added, and then acetyl chloride (2.00 mL, 28.1 mmol) in CH₂Cl₂ (9 mL) was added dropwise to the vigorously

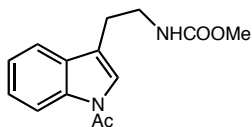
stirring solution. After 3 h, additional acetyl chloride (750 μ L, 10.5 mmol) was added to the reaction vessel followed by additional NaOH (500 mg, 12.5 mmol). After 24 h, the reaction was washed with a saturated solution of NH_4Cl , extracted with CH_2Cl_2 , dried with NaSO_4 and the volatiles were removed in vacuo. Purification of the crude reaction mixture on SiO_2 (gradient: 0 to 5% MeOH in EtOAc) gave 1.70 g (6.96 mmol, 75% yield) of *N,N'*-diacetyl tryptamine as a white solid.

IR (neat): 3291, 2946, 1696, 1635, 1551, 1474, 1390, 1221; ^1H NMR: (500 MHz, CDCl_3) 8.42 (s, 1H), 7.54 (d, $J = 7.5$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.29 (t, $J = 7.5$ Hz, 1H), 7.27 (s, 1H), 5.71 (br s, 1H), 3.62 (q, $J = 7.0$ Hz, 2H), 2.93 (t, $J = 7.0$ Hz, 2H), 2.58 (s, 3H), 1.96 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 170.5, 168.6, 135.9, 130.6, 125.4, 123.7, 122.7, 119.9, 118.9, 116.7, 39.1, 25.3, 23.9, 23.3; HRMS (ESI^+) calc'd for $[\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_2]^+$ ($\text{M}+\text{H}$) $^+$ requires m/z 245.1285, found m/z 245.1290. (mp: 163-164 $^\circ\text{C}$)



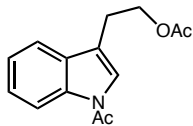
5-Methoxy *N,N'*-diacetyl tryptamine. Melatonin (482 mg, 2.08 mmol) and $\text{Bu}_4\text{N}^+\text{HSO}_4^-$ (30 mg, 0.1 mmol) were dissolved in CH_2Cl_2 (8 mL). Powdered NaOH (210 mg, 5.25 mmol) was added, and then acetyl chloride (220 μ L, 3.09 mmol) in CH_2Cl_2 (4 mL) was added dropwise to the vigorously stirring solution. After 1.5 h, additional powdered NaOH (210 mg, 5.25 mmol) and acetyl chloride (220 μ L, 3.09 mmol) was added to the solution. After an additional 1.5 h, the reaction mixture was washed with a saturated solution of NH_4Cl , extracted with CH_2Cl_2 , dried with Na_2SO_4 and the volatiles were removed in vacuo. Purification of the crude reaction mixture on SiO_2 (gradient: 0 to 5% MeOH in EtOAc) gave 511 mg (1.87 mmol, 90% yield) of 7-methoxy-*N*-acetylindole as a white solid.

IR (neat): 3300, 2921, 1701, 1654, 1477, 1392, 1035; ^1H NMR: (500.0 MHz, CDCl_3) 8.32 (s, 1H), 7.25 (s, 1H), 6.97 (m, 2H), 5.63 (br s, 1H), 3.87 (s, 3H), 3.61 (q, $J = 6.8$ Hz, 2H), 2.90 (t, $J = 6.8$ Hz, 2H), 2.58 (s, 3H), 1.97 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 170.4, 168.2, 156.7, 131.6, 130.8, 123.4, 119.6, 117.7, 113.7, 102.0, 55.9, 39.1, 25.5, 23.8, 23.5; HRMS (ESI^+) calc'd for $[\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_3]^+$ ($\text{M}+\text{H}$) $^+$ requires m/z 275.1391, found m/z 275.1387. (mp: 133-134 $^\circ\text{C}$)



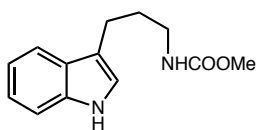
***N*-Acyl *N'*-methoxycarbamoyl tryptamine.** Tryptamine (763mg, 4.76 mmol) was dissolved in 10 mL CH₂Cl₂ and 10 mL aq. 10% Na₂CO₃ solution. Methyl chloroformate (500 μL, 6.47 mmol) was added, and the reaction was stirred vigorously for 15 min. The reaction was extracted with CH₂Cl₂, dried with Na₂SO₄, and the volatiles were removed in vacuo. The crude *N*-methoxycarbamoyl tryptamine and Bu₄N⁺HSO₄⁻ (17 mg, 0.05 mmol) were then dissolved in CH₂Cl₂ and treated with powdered NaOH (501 mg, 12.5 mmol). Acetyl chloride (530 μL, 7.45 mmol) in CH₂Cl₂ (10 mL) was added dropwise, and the reaction was stirred vigorously at room temperature. After 4 h, additional NaOH (501 mg, 12.5 mmol) and acetyl chloride (530 μL, 7.45 mmol) were added to the reaction, which was stirred overnight. The mixture was extracted with CH₂Cl₂, dried with Na₂SO₄ and the volatiles were removed in vacuo. Purification of the crude reaction mixture on SiO₂ (gradient: 2:1 to 1:1 hexane:1% acetone in EtOAc) gave 1.00 g (3.85 mmol, 81% yield over 2 steps) of *N*-methoxycarbamoyl *N'*-acyl tryptamine as a white solid.

IR (neat): 3346, 2920, 1702, 1536, 1453, 1389, 1250; ¹H NMR: (500 MHz, CDCl₃) 8.40 (s, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.34 (t, J = 7.7 Hz, 1H), 7.27 (t, J = 7.7 Hz, 1H), 7.22 (s, 1H), 5.08 (s, 1H), 3.66 (s, 3H), 3.51 (q, J = 6.8 Hz, 2H), 2.90 (t, J = 6.8 Hz, 2H), 2.53 (s, 3H); ¹³C NMR: (125 MHz, CDCl₃) 68.5, 157.2, 136.0, 130.5, 125.5, 123.7, 122.8, 119.6, 118.9, 116.8, 52.2, 40.5, 25.8, 24.0; HRMS (ESI⁺) calc'd for [C₁₄H₁₇N₂O₃]⁺ (M+H)⁺ requires *m/z* 261.1234, found *m/z* 261.1238. (mp: 124-126 °C)



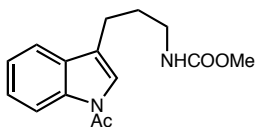
***N,O*-Diacyl tryptophol.** Tryptophol (815 mg, 5.05 mmol) and Bu₄N⁺HSO₄⁻ (40 mg, 0.12 mmol) were dissolved in CH₂Cl₂ (20 mL). Powdered NaOH (1.0 g, 25.0 mmol) was added, and then acetyl chloride (1.2 mL, 15 mmol) in CH₂Cl₂ (10 mL) was added dropwise to the vigorously stirring solution. After 2 h, additional NaOH (501 mg, 12.5 mmol) and acetyl chloride (530 μL, 7.45 mmol) were added to the reaction, which was stirring for an additional 15 min. The reaction was washed with a saturated solution of NH₄Cl, extracted with CH₂Cl₂, dried with Na₂SO₄ and the volatiles were removed in vacuo. Purification of the crude reaction mixture on SiO₂ using 3:1 hexane:EtOAc resulted in 1128 mg (4.60 mmol, 91% yield) of *N,O*-diacyl tryptophol as a white solid.

IR (neat): 2960, 1738, 1705, 1453, 1386, 1247; ¹H NMR: (500 MHz, CDCl₃) 8.43 (s, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H), 7.26 (s, 1H), 4.37 (t, J = 7.1 Hz, 2H), 3.04 (t, J = 7.1 Hz, 2H), 2.61 (s, 3H), 2.06 (s, 3H); ¹³C NMR: (125 MHz, CDCl₃) 171.2, 168.5, 136.0, 130.6, 125.6, 123.7, 122.8, 119.0, 118.8, 116.9, 63.6, 24.8, 24.2, 21.2; HRMS (ESI⁺) calc'd for [C₁₄H₁₅NO₃Na]⁺ (M+Na)⁺ requires *m/z* 268.0945, found *m/z* 268.0957. (mp: 41-43 °C)



***N*-Methoxycarbonyl homotryptamine.** Homotryptamine (289 mg, 1.66 mmol) was dissolved in 4 mL CH₂Cl₂ and 4 mL aq. 10% Na₂CO₃ solution. Methyl chloroformate (160 μL, 2.07 mmol) was added, and the reaction was stirred vigorously for 15 min. The reaction was extracted with CH₂Cl₂, dried with Na₂SO₄, and the volatiles were removed in vacuo. Purification of the crude reaction mixture on SiO₂ (gradient 3:1 to 1:1 hexane:EtOAc) gave 275 mg (1.18 mmol, 71% yield) of *N*-Moc homotryptamine as a white solid.

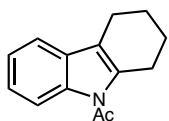
IR (neat): 3411, 3334, 2939, 1701, 1540, 1457, 1261; ¹H NMR: (500 MHz, CDCl₃) 7.98 (s, 1H), 7.59 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 7.7 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 7.12 (t, J = 7.7 Hz, 1H), 7.01 (s, 1H), 4.70 (s, 1H), 3.67 (s, 3H), 3.27 (q, J = 7.7 Hz, 2H), 2.80 (t, J = 7.7 Hz, 2H), 1.93 (p, J = 7.7 Hz, 2H); ¹³C NMR: (125 MHz, CDCl₃) 157.4, 136.6, 127.5, 122.2, 121.6, 119.4, 119.0, 115.8, 111.3, 52.2, 41.0, 30.4, 22.5; HRMS (ESI⁺) calc'd for [C₁₃H₁₆N₂O₂Na]⁺ (M+Na)⁺ requires *m/z* 255.1104, found *m/z* 255.1102. (mp: 74-75 °C)



***N*-Acyl *N'*-methoxycarbonyl homotryptamine.** *N*-Moc homotryptamine (552 mg, 2.38 mmol) and Bu₄N⁺HSO₄⁻ (21 mg, 0.06 mmol) were dissolved in CH₂Cl₂ (10 mL). Powdered NaOH (260 mg, 6.5 mmol) was added, and then acetyl chloride (300 μL, 4.22 mmol) in CH₂Cl₂ (3 mL) was added dropwise to the vigorously stirring solution. After 1 h, additional NaOH (100 mg, 2.5 mmol) and acetyl chloride (100 μL, 1.41 mmol) were added to the reaction, which was stirred for an additional 1 min. The reaction was washed with a saturated solution of NH₄Cl, extracted with CH₂Cl₂, dried with Na₂SO₄ and the volatiles were removed in vacuo. Purification of the crude reaction mixture on SiO₂ (gradient: 3:1

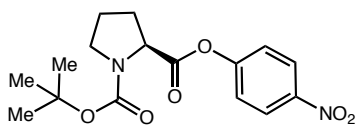
to 3:2 hexane:EtOAc) gave 542 mg (1.98 mmol, 83% yield) of *N*-acyl *N'*-Moc homotryptamine as a white solid.

IR (neat): 3346, 2928, 1700, 1533, 1453, 1388, 1249; ¹H NMR: (500 MHz, CDCl₃) 8.42 (s, 1H), 7.50 (d, J = 7.9 Hz, 1H), 7.35 (t, J = 7.9 Hz, 1H), 7.25 (s, 1H), 4.74 (s, 1H), 3.67 (s, 3H), 3.29 (q, J = 7.9 Hz, 2H), 2.74 (t, J = 7.9 Hz, 2H), 2.62 (s, 3H), 1.93 (p, J = 7.9 Hz, 2H); ¹³C NMR: (125 MHz, CDCl₃) 168.8, 157.4, 136.3, 130.6, 125.5, 123.6, 122.2, 122.2, 119.0, 117.0, 52.1, 40.9, 29.6, 24.2, 22.2; HRMS (ESI⁺) calc'd for [C₁₅H₁₉N₂O₃]⁺ (M+H)⁺ requires *m/z* 275.1391, found *m/z* 275.1396. (mp: 106-107 °C)



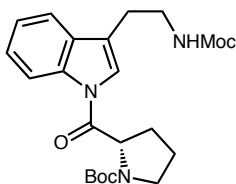
***N*-Acyl tetrahydrocarbazole.** Tetrahydrocarbazole (712 mg, 4.16 mmol) and Bu₄N⁺HSO₄⁻ (65 mg, 0.19 mmol) were dissolved in CH₂Cl₂ (15 mL). Powdered NaOH (400 mg, 10.0 mmol) was added, and then acetyl chloride (520 μL, 7.3 mmol) in CH₂Cl₂ (6 mL) was added dropwise to the vigorously stirring solution. After 1 h, additional NaOH (400 mg, 10.0 mmol) and acetyl chloride (530 μL, 7.45 mmol) were added to the reaction, which was stirred for an additional 1 hour. The reaction was washed with a saturated solution of NH₄Cl, extracted with CH₂Cl₂, dried with Na₂SO₄ and the volatiles were removed in vacuo. Purification of the crude reaction mixture on SiO₂ (gradient: 20:1 to 5:1 hexane:EtOAc) gave 773 mg (3.62 mmol, 87% yield) of *N*-acyl tetrahydrocarbazole as a white solid.

IR (neat): 2935, 2856, 1692, 1455, 1370, 1315; ¹H NMR: (500 MHz, CDCl₃) 8.06 (d, J = 7.3 Hz, 1H), 7.40 (d, J = 7.3 Hz, 1H), 7.26 (t, J = 7.3 Hz, 1H), 7.24 (t, J = 7.3 Hz, 1H), 2.99 (m, 2H), 2.68 (s, 3H), 2.66 (m, 2H), 1.90 (m, 2H), 1.84 (m, 2H); ¹³C NMR: (125 MHz, CDCl₃) 170.1, 136.1, 135.5, 130.5, 124.1, 123.2, 118.5, 118.0, 115.7, 27.4, 26.8, 24.0, 22.1, 21.3 HRMS (ESI⁺) calc'd for [C₁₄H₁₅NONa]⁺ (M+Na)⁺ requires *m/z* 236.1046, found *m/z* 236.1057. (mp: 76-77 °C)



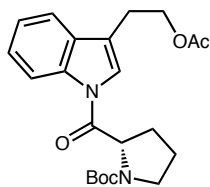
***N*-(L-Boc) proline 4-nitrophenyl ester.** Prepared using a variation of the method described by Kovacs.⁶ *N*-Boc L-proline (2.18 g, 10.1 mmol), 4-nitrophenol (1.45 g, 10.4 mmol) and EDCI•HCl (2.7 g, 14.1 mmol) were dissolved in 13 mL CH₂Cl₂ and the solution was stirred for 24 h. The reaction mixture was washed with water, and the

aqueous phase was extracted with CH₂Cl₂. The combined organic phases were dried with Na₂SO₄, concentrated in vacuo, and passed through a short silica plug using 2:1 hexanes:ethyl acetate as the eluent. The resulting 2.2 g yellow oil contained the desired product and <30% nitrophenol, and was used for the next step without further purification.



***N*-(*L*-Boc-proline) *N'*-Moc tryptamine.** Prepared using a variation of the method described by Snider.⁷ Moc-tryptamine (478 mg, 2.19 mmol) was placed in a round-bottomed flask followed by crude *N*-Boc L-proline 4-nitrophenyl ester (1.3 g), KF (507 mg, 8.73 mmol), 18-crown-6 ether (1.16 g, 4.38 mmol), *i*-Pr₂NEt (1.75 mL, 9.83 mmol) and MeCN (8.8 mL). The mixture was sonicated under argon for 60 min then stirred at 50 °C. After 42 h, the reaction was quenched with water, the aqueous phase was extracted twice with CH₂Cl₂, dried over Na₂SO₄, and the volatiles were removed in vacuo. Purification of the crude reaction mixture using 2:1 to 1:1 hexanes:EtOAc resulted in 897 mg (2.16 mmol, 99% yield) of *N*-(*L*-Boc-proline) *N'*-Moc tryptamine as a white solid. Chiral SFC analysis of the product showed that the stereochemical integrity of the L-proline was preserved (99% ee).

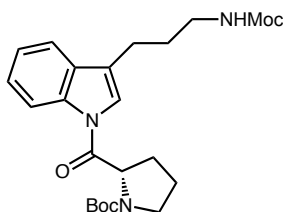
IR (neat): 3347, 2977, 1701, 1535, 1454, 1396; ¹H NMR: (500 MHz, DMSO, 120°C) 8.36 (d, *J* = 7.7 Hz, 1H), 7.75 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 6.71 (br s, 1H), 5.15 (dd, *J* = 8.4, 3.5 Hz, 1H), 3.58 (s, 3H), 3.52 (q, *J* = 7.0 Hz, 2H), 3.41 (q, *J* = 7.0 Hz, 2H), 2.90 (t, *J* = 7.0 Hz, 2H), 2.45 (m, 1H), 1.96 (m, 3H), 1.30 (s, 9H); ¹³C NMR: (125 MHz, DMSO, 120°C) 170.7, 156.1, 152.7, 135.3, 129.9, 124.1, 122.7, 121.7, 119.2, 118.2, 115.4, 78.4, 58.4, 50.4, 46.0, 39.7, 29.8, 27.3, 24.5, 22.9; HRMS (ESI⁺) calc'd for [C₂₂H₂₉N₃O₅Na]⁺ (M+Na)⁺ requires *m/z* 438.2000, found *m/z* 438.2012. (mp: 58-60 °C); [α]_D = -0.376° (c 1.0, CH₂Cl₂)



***N*-(*L*-Boc-proline) *O*-acyl tryptophol.** Prepared using the procedure above using *O*-acyl tryptophol⁸ (632 mg, 3.12 mmol), crude *N*-Boc L-proline 4-nitrophenyl ester (2 g), KF (725 mg, 12.5 mmol), 18-crown-6 ether (1.61 g, 6.09 mmol), *i*-Pr₂NEt (2.3 mL, 12.9 mmol) and

acetonitrile (11 mL). The mixture was sonicated under argon for 60 min then stirred at 50 °C. After 12 h, the reaction was quenched with water, the aqueous phase was extracted twice with CH₂Cl₂, dried over Na₂SO₄, and the volatiles were removed in vacuo. Purification of the crude reaction mixture (gradient: 4:1 to 2:1 hexanes:2% acetone in EtOAc) gave 1087 mg (2.71 mmol, 87% yield) of *N*-(*L*-Boc-proline) *O*-acyl tryptophol as a colorless liquid.

IR (neat): 2976, 2932, 2882, 1740, 1707, 1455, 1395, 1240; ¹H NMR: (500 MHz, DMSO, 120°C) 8.36 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.31 (t, J = 8.0 Hz, 1H), 5.16 (dd, J = 8.6, 3.6 Hz, 1H), 4.37 (t, J = 6.8 Hz, 2H), 3.52 (m, 2H), 3.05 (t, J = 6.8 Hz, 2H), 2.45 (m, 1H), 2.00 (s, 3H), 1.97 (m, 3H), 1.29 (s, 9H); ¹³C NMR: (125 MHz, DMSO, 120°C) 170.8, 169.4, 152.7, 135.2, 129.7, 124.2, 122.7, 122.2, 118.3, 117.9, 115.4, 78.4, 62.3, 58.4, 46.0, 29.8, 27.3, 23.5, 22.9, 19.8; HRMS (ESI⁺) calc'd for [C₂₂H₂₈N₂O₅Na]⁺ (M+Na)⁺ requires *m/z* 423.1891, found *m/z* 423.1909. [α]_D = -0.393° (c 1.0, CH₂Cl₂)



***N*-(*L*-Boc-proline) *N'*-Moc homotryptamine.** Prepared using the method described above using Moc-homotryptamine (826 mg, 3.56 mmol), crude *N*-Boc *L*-proline 4-nitrophenyl ester (2.2 g), KF (849 mg, 14.6 mmol), 18-crown-6 ether (1.89 g, 7.15 mmol),

i-Pr₂N₂Et (3.5 mL, 19.7 mmol) and acetonitrile (15 mL). The mixture was sonicated under argon for 60 min then stirred at 50 °C. After 12 h, 180 mg KF and 400 mg 18-crown-6 ether were added, the reaction was sonicated for 1 h and stirred at 50 °C. After 48 h, the reaction was quenched with water, the aqueous phase was extracted twice with CH₂Cl₂, dried over Na₂SO₄, and the volatiles were removed in vacuo. Purification of the crude reaction mixture using 2:1 to 1:3 hexanes:EtOAc resulted in 1446 mg (3.37 mmol, 95% yield) of *N*-(*L*-Boc-proline) *N'*-Moc homotryptamine as a white solid.

IR (neat): 3411, 3334, 2939; 1701, 1533, 1262; ¹H NMR: (500 MHz, DMSO, 120°C) 8.36 (d, J = 7.9 Hz, 1H), 7.73 (s, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.33 (t, J = 7.9 Hz, 1H), 7.29 (t, J = 7.9 Hz, 1H), 6.63 (br s, 1H), 5.15 (dd, J = 8.5, 3.5 Hz, 1H), 3.58 (s, 3H), 3.52 (m, 2H), 3.15 (q, J = 6.8 Hz, 2H), 2.74 (t, J = 7.4 Hz, 2H), 2.45 (m, 1H), 1.93 (m, 5H), 1.30 (s, 9H); ¹³C NMR: (125 MHz, DMSO, 120°C) 170.6, 156.1, 152.7, 135.3, 129.8,

124.0, 122.6, 121.4, 121.3, 118.3, 115.4, 78.3, 58.4, 50.4, 46.0, 39.7, 29.9, 28.5, 27.3, 22.9, 21.0; HRMS (ESI⁺) calc'd for [C₂₃H₃₂N₃O₅]⁺ (M+H)⁺ requires *m/z* 430.2337, found *m/z* 430.2347. (mp: 53-55 °C); [α]_D = -0.380° (c 1.0, CH₂Cl₂)

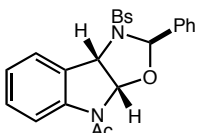
III. Racemic oxyaminations.

General procedure A for oxyamination. In a nitrogen-atmosphere glovebox, copper(II) chloride and tetrabutylammonium chloride were placed in a 1.5 dram vial with a stirbar. The vial was capped with a septum and transferred out of the glovebox. The vessel was charged with CH₂Cl₂ and the mixture was stirred under nitrogen for 30 min. The substrate and the oxaziridine were quickly added, and reaction was stirred under nitrogen. The reaction progress was monitored by ¹H NMR or TLC. Upon completion of the reaction, excess oxaziridine was quenched with dimethyl sulfide if TLC indicated it would interfere with the purification; then the reactions were loaded directly onto silica for purification by flash column chromatography. In some cases, addition of dichloromethane and heating of the crude reaction mixture was necessary to dissolve the product.

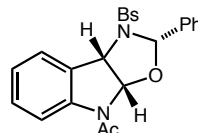
General procedure B for oxyamination. In a nitrogen-atmosphere glovebox, copper(II) chloride and tetrabutylammonium chloride were placed in a 1.5 dram vial with a stirbar. The vial was capped with a septum and transferred out of the glovebox. The vessel was charged with acetone and the mixture was stirred under nitrogen for 30 min. The substrate and the oxaziridine was quickly added, and reaction was stirred under nitrogen. The reaction progress was monitored by ¹H NMR or TLC. Upon completion of the reaction, the solvent was removed via vacuo and the residue was diluted with chloroform before loading directly onto silica for purification by flash column chromatography.

Compound 8 (Scheme 1). Prepared according to general procedure A using 42.3 mg (0.266 mmol) of *N*-acylindole, 0.8 mg (0.006 mmol) CuCl₂, 1.6 mg (0.006 mmol) TBACl, 134 mg (0.513 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 0.5 mL CH₂Cl₂. Reaction time was 1.5 h. The silica gel was loaded using dichloromethane and

the product was eluted with 1% acetone in dichloromethane. Isolated 94.6 mg (0.225 mmol, 85% yield) white solid. Yield 2: 42.0 mg (0.264 mmol) of substrate, 0.8 mg (0.006 mmol) CuCl₂, 1.6 mg (0.006 mmol) TBACl, 131 mg (0.501 mmol) oxaziridine and 0.5 mL CH₂Cl₂. Isolated 93.8 mg (0.224 mmol, 85% yield). The diastereoselectivity of the crude reaction mixture was 2:1.



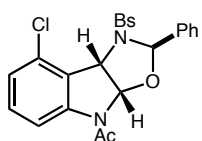
Major diastereomer: IR (neat): 2978, 1684, 1478, 1399, 1151; ¹H NMR (500 MHz, CDCl₃) 8.248 (d, J = 8.1 Hz, 1H), 7.939 (d, J = 7.6 Hz, 1H), 7.399 (t, J = 7.8 Hz, 2H), 7.266 (m, 2H), 7.213 (m, 4H), 7.123 (d, J = 7.3 Hz, 2H), 7.057 (t, J = 7.3 Hz, 2H), 6.267 (d, J = 6.3 Hz, 1H), 6.133 (d, J = 6.3 Hz, 1H), 5.610 (s, 1H), 2.382 (s, 3H); ¹³C NMR (125 MHz, CDCl₃); 169.9, 143.7, 140.6, 132.6, 131.3, 130.8, 130.0, 129.2, 128.7, 128.0, 127.8, 127.6, 125.9, 125.1, 116.4, 89.5, 89.5, 64.2, 24.1; HRMS (EI⁺) calc'd for [C₂₃H₂₁N₂O₄S]⁺ (M+H)⁺ requires *m/z* 421.1217, found *m/z* 421.1214. (mp = 200–203 °C). The regioselectivity and the relative stereochemistry were confirmed by X-ray crystallography.



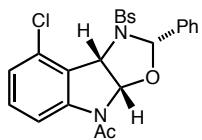
Minor Diastereomer: IR (neat): 2980, 1666, 1400, 1356, 1170; ¹H NMR (500 MHz, CDCl₃) 8.002 (d, J = 7.7 Hz, 2H), 7.730 (t, J = 7.7 Hz, 1H), 7.680 (d, J = 8.1 Hz, 1H), 7.637 (t, J = 7.7 Hz, 2H), 7.330 (d, J = 7.7 Hz, 1H), 7.094 (d, J = 7.3 Hz, 2H), 7.003 (m, 4H), 6.928 (t, J = 7.3 Hz, 1H), 6.638 (s, 1H), 5.636 (AB, J = 6.8 Hz, 2H), 2.311 (s, 3H); ¹³C NMR (125 MHz, CDCl₃); 169.3, 141.9, 137.7, 137.2, 134.1, 130.2, 129.9, 128.5, 128.1, 127.8, 126.2, 125.7, 125.6, 124.5, 116.4, 92.6, 91.3, 63.6, 24.0; HRMS (EI⁺) calc'd for [C₂₃H₂₁N₂O₄S]⁺ (M+H)⁺ requires *m/z* 421.1217, found *m/z* 421.1222. (mp = 195–197 °C). The regioselectivity and the relative stereochemistry were confirmed by X-ray crystallography.

Compound 10 (Figure 1). Prepared according to general procedure A using 43.4 mg (0.224 mmol) of *N*-acyl 4-chloroindole, 0.7 mg (0.005 mmol) CuCl₂, 1.4 mg (0.005 mmol) TBACl, 134 mg (0.513 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 0.5 mL CH₂Cl₂. Reaction time was 2 h. The silica gel was loaded using dichloromethane and the product was eluted with 2% acetone in dichloromethane. Isolated 87.1 mg (0.192 mmol, 86% yield) white solid. Yield 2: 47.8 mg (0.247 mmol) of substrate, 0.8 mg (0.006 mmol) CuCl₂, 1.8 mg (0.006 mmol) TBACl, 134 mg (0.513 mmol) oxaziridine and 0.5

mL CH₂Cl₂. Isolated 95.6 mg (0.210 mmol, 85% yield). The diastereoselectivity of the crude reaction mixture was 3:2.

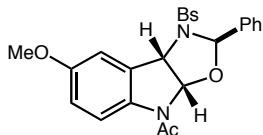


Major diastereomer: IR (ATR): 2957, 1672, 1599, 1456, 1388, 1168; ¹H NMR: (500 MHz, CDCl₃) 8.18 (d, J = 8.1 Hz, 1H), 7.38 (m, 3H), 7.33 (t, J = 8.1 Hz, 1H), 7.16 (m, 6H), 7.01 (t, J = 8.1 Hz, 2H), 6.60 (d, J = 6.4 Hz, 1H), 6.32 (d, J = 6.4 Hz, 1H), 5.46 (s, 1H), 2.47 (s, 3H); ¹³C NMR: (125 MHz, CDCl₃) 170.5, 145.8, 139.3, 132.8, 132.6, 132.2, 129.7, 129.4, 129.2, 128.6, 128.2, 127.6, 125.5, 123.0, 114.7, 90.6, 88.9, 62.8, 24.4; HRMS (ESI⁺) calc'd for [C₂₃H₂₀ClN₂O₄S]⁺ (M+H)⁺ requires *m/z* 455.0827, found *m/z* 455.0821. (mp = 232-235°C (dec))

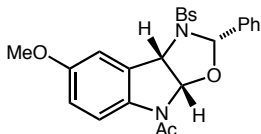


Minor Diastereomer: IR (ATR): 2929, 1673, 1592, 1454, 1361, 1170; ¹H NMR: (500 MHz, CDCl₃) 8.07 (d, J = 7.6 Hz, 2H), 7.73 (t, J = 7.3 Hz, 1H), 7.64 (t, J = 7.6 Hz, 2H), 7.55 (d, J = 7.9 Hz, 1H), 7.10 (m, J = 3.2 Hz, 2H), 6.96 (m, 3H), 6.86 (t, J = 8.1 Hz, 1H), 6.78 (d, J = 8.1 Hz, 1H), 6.74 (s, 1H), 5.93 (d, J = 6.2 Hz, 1H), 5.67 (d, J = 6.2 Hz, 1H), 2.37 (s, 3H); ¹³C NMR: (125 MHz, CDCl₃) 169.5, 143.6, 137.6, 136.9, 134.3, 131.6, 131.6, 129.8, 128.5, 128.5, 127.9, 125.0, 124.6, 123.3, 114.5, 92.6, 90.8, 63.6, 24.2; HRMS (ESI⁺) calc'd for [C₂₃H₂₀ClN₂O₄S]⁺ (M+H)⁺ requires *m/z* 455.0827, found *m/z* 455.0820. (mp = 241-243°C (dec))

Compound 11 (Figure 1). Prepared according to general procedure A using 46.1 mg (0.244 mmol) of *N*-acyl 5-methoxyindole, 0.6 mg (0.005 mmol) CuCl₂, 1.5 mg (0.005 mmol) TBACl, 131 mg (0.501 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 0.5 mL CH₂Cl₂. Reaction time was 1 h. The silica gel was loaded using dichloromethane and the product was eluted with 2% acetone in dichloromethane. The fractions containing the product were concentrated and purified again on silica gel using 2:1 hexane-ethyl acetate + 4% triethylamine. Isolated 91.6 mg (0.203 mmol, 83% yield) white solid. Yield 2: 47.0 mg (0.248 mmol) of substrate, 0.8 mg (0.006 mmol) CuCl₂, 1.6 mg (0.006 mmol) TBACl, 130 mg (0.498 mmol) oxaziridine and 0.5 mL CH₂Cl₂. Isolated 95.9 mg (0.213 mmol, 86% yield). The diastereoselectivity of the crude reaction mixture was 3:2.

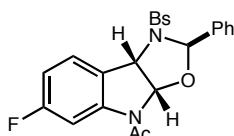


Major diastereomer: IR (neat): 2918, 1739, 1677, 1486, 1393, 1158; ^1H NMR: (500 MHz, CDCl_3) 8.16 (d, $J = 8.9$ Hz, 1H), 7.48 (d, $J = 2.6$ Hz, 1H), 7.40 (t, $J = 7.3$ Hz, 1H), 7.26 (d, $J = 7.3$ Hz, 2H), 7.20 (m, 3H), 7.11 (d, $J = 7.9$ Hz, 2H), 7.05 (t, $J = 7.9$ Hz, 2H), 6.93 (dd, $J = 8.9, 2.6$ Hz, 1H), 6.23 (d, $J = 6.3$ Hz, 1H), 6.07 (d, $J = 6.3$ Hz, 1H), 5.61 (s, 3H), 3.85 (s, 3H), 2.34 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 169.3, 157.2, 140.6, 137.3, 132.6, 131.2, 130.0, 129.2, 128.7, 127.9, 127.5, 127.2, 117.3, 116.5, 112.4, 89.7, 89.5, 64.3, 56.0, 23.8; HRMS (ESI^+) calc'd for $[\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_5\text{S}]^+$ ($\text{M}+\text{H}$) $^+$ requires m/z 451.1323, found m/z 451.1320. (mp: 195-197 °C (dec))

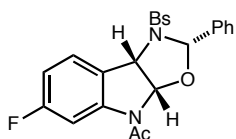


Minor Diastereomer: IR (neat): 2958, 2927, 1674, 1489, 1273, 1170; ^1H NMR: (500 MHz, CDCl_3) 8.00 (d, $J = 7.8$ Hz, 2H), 7.74 (t, $J = 7.4$ Hz, 1H), 7.65 (t, $J = 7.8$ Hz, 1H), 7.62 (d, $J = 8.8$ Hz, 1H), 7.12 (d, $J = 7.8$ Hz, 2H), 7.03 (m, 3H), 6.85 (d, $J = 2.6$ Hz, 1H), 6.64 (s, 1H), 6.58 (dd, $J = 8.8, 2.6$ Hz, 1H), 5.66 (d, $J = 6.3$ Hz, 1H), 5.61 (d, $J = 6.3$ Hz, 1H), 3.72 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 168.7, 156.9, 137.8, 137.2, 135.7, 134.2, 129.9, 128.6, 128.1, 127.9, 127.4, 125.7, 117.4, 116.4, 92.6, 91.7, 63.7, 56.0, 23.8; HRMS (ESI^+) calc'd for $[\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_5\text{S}]^+$ ($\text{M}+\text{H}$) $^+$ requires m/z 451.1323, found m/z 415.1307. (mp: 194-195 °C)

Compound 12 (Figure 1). Prepared according to general procedure A using 44.9 mg (0.253 mmol) of *N*-acyl 6-fluoroindole, 0.8 mg (0.006 mmol) CuCl_2 , 1.6 mg (0.006 mmol) TBACl, 134 mg (0.513 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 0.5 mL CH_2Cl_2 . Reaction time was 2 h. The silica gel was loaded using dichloromethane and the product was eluted with 1% acetone in dichloromethane. Isolated 91.2 mg (0.208 mmol, 82% yield) pinkish white solid. Yield 2: 44.8 mg (0.253 mmol) of substrate, 0.7 mg (0.005 mmol) CuCl_2 , 1.6 mg (0.006 mmol) TBACl, 132 mg (0.505 mmol) oxaziridine and 0.5 mL CH_2Cl_2 . Isolated 89.6 mg (0.204 mmol, 81% yield). The diastereoselectivity of the crude reaction mixture was 4:3.

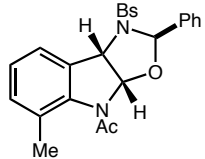


Major diastereomer: IR (ATR): 3071, 1691, 1601, 1399, 1335, 1157;
 ^1H NMR: (500 MHz, CDCl_3) 8.00 (d, $J = 10.3$ Hz, 1H), 7.91 (t, $J = 7.9$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.25 (dd, $J = 8.8, 1.8$ Hz, 2H), 7.20 (m, 3H), 7.11 (d, $J = 7.9$ Hz, 2H), 7.05 (t, $J = 7.5$ Hz, 2H), 6.91 (td, $J = 8.8, 2.5$ Hz, 1H), 6.29 (d, $J = 6.3$ Hz, 1H), 6.06 (d, $J = 6.3$ Hz, 1H), 5.62 (s, 1H), 2.36 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 169.9, 164.4 ($^1J_{\text{CF}} = 247$), 144.9 ($^3J_{\text{CF}} = 13$), 140.5, 132.7, 131.2, 130.1, 129.2, 128.9 ($^3J_{\text{CF}} = 12$), 128.7, 128.0, 127.5, 121.4, 111.9 ($^2J_{\text{CF}} = 23$), 104.4 ($^2J_{\text{CF}} = 29$), 90.2, 89.5, 63.7, 24.0; HRMS (ESI $^+$) calc'd for $[\text{C}_{23}\text{H}_{20}\text{FN}_2\text{O}_4\text{S}]^+$ (M+H) $^+$ requires m/z 439.1045, found m/z 439.1051. (mp = 212-213 $^\circ\text{C}$)

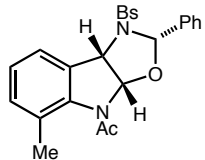


Minor diastereomer: IR (ATR): 2981, 1673, 1615, 1495, 1356, 1171; ^1H NMR: (500 MHz, CDCl_3) 8.00 (d, $J = 7.6$ Hz, 2H), 7.74 (t, $J = 7.6$ Hz, 1H), 7.64 (t, $J = 7.6$ Hz, 2H), 7.42 (d, $J = 10.0$ Hz, 1H), 7.28 (t, $J = 8.0$ Hz, 1H), 7.10 (d, $J = 7.6$ Hz, 2H), 7.04 (m, 3H), 6.66 (s, 1H), 6.63 (td, $J = 8.7, 2.4$ Hz, 1H), 5.69 (d, $J = 6.2$ Hz, 1H), 5.61 (d, $J = 6.2$ Hz, 1H), 2.32 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 169.3, 163.9 ($^1J_{\text{CF}} = 247$), 143.2 ($^3J_{\text{CF}} = 13$), 137.6, 137.0, 134.2, 129.9, 128.7, 128.0, 128.0, 126.5 ($^3J_{\text{CF}} = 11$), 125.6, 121.8, 111.5 ($^2J_{\text{CF}} = 24$), 104.4 ($^2J_{\text{CF}} = 29$), 92.7, 92.0, 63.2, 24.0; HRMS (ESI $^+$) calc'd for $[\text{C}_{23}\text{H}_{20}\text{FN}_2\text{O}_4\text{S}]^+$ (M+H) $^+$ requires m/z 439.1045, found m/z 439.1044. (mp = 223-225 $^\circ\text{C}$)

Compound 13 (Figure 1). Prepared according to general procedure A using 42.5 mg (0.245 mmol) of *N*-acyl 7-methylindole, 1.0 mg (0.007 mmol) CuCl_2 , 1.6 mg (0.006 mmol) TBACl, 131 mg (0.501 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 0.5 mL CH_2Cl_2 . Reaction time was 1.5 h. The silica gel was loaded using dichloromethane and 1% triethylamine and the product was eluted with 1% acetone in dichloromethane. Isolated 88.7 mg (0.204 mmol, 83% yield) slightly red white solid. Yield 2: 42.8 mg (0.247 mmol) of substrate, 0.8 mg (0.006 mmol) CuCl_2 , 1.6 mg (0.006 mmol) TBACl, 130 mg (0.498 mmol) oxaziridine and 0.5 mL CH_2Cl_2 . Isolated 82.7 mg (0.190 mmol, 77% yield). The diastereoselectivity of the crude reaction mixture was 4:3.

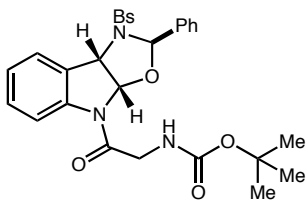


Major diastereomer: IR (neat): 2927, 1687, 1378, 1339, 1158; ^1H NMR: (500 MHz, CDCl_3) 7.83 (d, $J = 6.5$ Hz, 1H), 7.39 (t, $J = 7.3$ Hz, 1H), 7.25 (m, 4H), 7.19 (m, 3H), 7.09 (d, $J = 7.3$ Hz, 2H), 7.04 (t, $J = 7.8$ Hz, 2H), 6.26 (d, $J = 5.6$ Hz, 1H), 6.19 (d, $J = 5.6$ Hz, 1H), 5.49 (s, 1H), 2.40 (s, 3H), 2.29 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 169.2, 141.6, 140.8, 133.2, 132.5, 132.1, 129.9, 129.1, 129.0, 128.6, 128.3, 128.0, 127.5, 126.5, 124.6, 90.4, 89.9, 65.3, 24.0, 21.3; HRMS (ESI^+) calc'd for $[\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_4\text{S}]^+$ ($\text{M}+\text{H}$) $^+$ requires m/z 435.1374, found m/z 435.1361. (mp: 190-191 $^\circ\text{C}$)

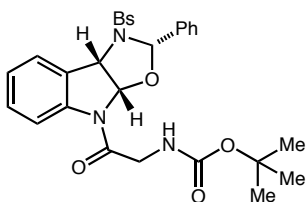


Minor diastereomer: IR (neat): 2959, 2926, 1688, 1355, 1169; ^1H NMR: (500 MHz, CDCl_3) 8.00 (d, $J = 8.1$ Hz, 2H), 7.73 (t, $J = 7.7$ Hz, 1H), 7.64 (d, $J = 7.7$ Hz, 2H), 7.13 (d, $J = 7.7$ Hz, 1H), 7.07 (d, $J = 8.1$ Hz, 2H), 6.99 (m, 3H), 6.87 (t, $J = 7.7$ Hz, 1H), 6.79 (d, $J = 7.7$ Hz, 1H), 6.54 (s, 1H), 5.72 (d, $J = 6.0$ Hz, 1H), 5.65 (d, $J = 6.0$ Hz, 1H), 2.29 (s, 3H), 1.87 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 169.2, 140.2, 137.9, 137.5, 134.1, 132.5, 129.9, 129.4, 128.4, 128.2, 128.1, 127.6, 126.0, 125.7, 123.0, 92.2, 92.1, 64.1, 23.8, 20.7; HRMS (ESI^+) calc'd for $[\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_4\text{S}]^+$ ($\text{M}+\text{H}$) $^+$ requires m/z 435.1374, found m/z 435.1360. (mp: 188-190 $^\circ\text{C}$)

Compound 14 (Figure 1). Prepared according to general procedure A using 68.7 mg (0.250 mmol) of *N*-(Boc-glycyl) indole, 0.7 mg (0.005 mmol) CuCl_2 , 1.5 mg (0.005 mmol) TBACl, 133 mg (0.509 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 0.5 mL CH_2Cl_2 . Reaction time was 6 h. The silica gel was loaded using 3:1 hexane: ethyl acetate + 2% triethylamine and the product was eluted using the same eluent. Isolated 99.8 mg (0.186 mmol, 75% yield) white solid. Yield 2: 68.7 mg (0.250 mmol) of substrate, 0.8 mg (0.006 mmol) CuCl_2 , 1.6 mg (0.006 mmol) TBACl, 134 mg (0.513 mmol) oxaziridine and 0.5 mL CH_2Cl_2 . Isolated 103.8 mg (0.194 mmol, 78% yield). The diastereoselectivity of the crude reaction mixture was 4:3.

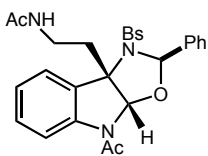


Major diastereomer: IR (neat): 3433, 2977, 2928, 1716, 1687, 1480, 1412, 1164; ^1H NMR: (500 MHz, CDCl_3) 8.23 (d, $J = 7.7$ Hz, 1H), 7.97 (d, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 8.1$ Hz, 2H), 7.26 (m, 3H), 7.21 (m, 3H), 7.10 (d, $J = 7.4$ Hz, 2H), 7.06 (t, $J = 7.7$ Hz, 2H), 6.31 (d, $J = 6.1$ Hz, 1H), 6.15 (d, $J = 6.1$ Hz, 1H), 5.60 (s, 1H), 5.39 (br s, 1H), 4.32 (dd, $J = 17.9, 5.7$ Hz, 1H), 4.19 (dd, $J = 17.9, 5.7$ Hz, 1H), 1.44 (s, 9H); ^{13}C NMR: (125 MHz, CDCl_3) 168.5, 156.1, 143.2, 140.5, 132.7, 130.9, 130.8, 130.1, 129.3, 128.7, 128.0, 127.6, 125.9, 125.6, 116.3, 89.7, 88.1, 80.2, 64.6, 44.1, 28.5; HRMS (ESI $^+$) calc'd for $[\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_6\text{S}]^+$ (M+H) $^+$ requires m/z 536.1850, found m/z 536.1867. (mp: 222-224 $^\circ\text{C}$ (dec))



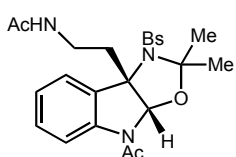
Minor diastereomer: IR (neat): 3424, 3063, 2979, 2933, 1712, 1686, 1481, 1366, 1169; ^1H NMR: (500 MHz, CDCl_3) 7.98 (d, $J = 7.8$ Hz, 2H), 7.75 (t, $J = 7.7$ Hz, 1H), 7.65 (t, $J = 7.8$ Hz, 3H), 7.10 (d, $J = 7.8$ Hz, 2H), 7.05 (t, $J = 8.0$ Hz, 2H), 6.99 (m, 4H), 6.64 (s, 1H), 5.68 (d, $J = 6.4$ Hz, 1H), 5.65 (d, $J = 6.4$ Hz, 1H), 5.38 (br s, 1H), 4.29 (dd, $J = 16.1, 5.4$ Hz, 1H), 4.12 (dd, $J = 16.1, 5.4$ Hz, 1H), 1.46 (s, 9H); ^{13}C NMR: (125 MHz, CDCl_3) 168.5, 156.1, 143.2, 140.5, 132.7, 130.9, 130.8, 130.1, 129.3, 128.7, 128.0, 127.6, 125.9, 125.6, 116.3, 89.7, 88.1, 80.2, 64.6, 44.1, 28.5. HRMS (ESI $^+$) calc'd for $[\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_6\text{S}]^+$ (M+H) $^+$ requires m/z 536.1850, found m/z 536.1854. (mp: 176-178 $^\circ\text{C}$ (dec))

Compound 15 (Figure 1). Prepared according to general procedure A using 62.4 mg (0.255 mmol) of *N,N'*-diacyl tryptamine, 0.8 mg (0.006 mmol) CuCl_2 , 1.6 mg (0.006 mmol) TBACl, 133 mg (0.509 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 0.5 mL CH_2Cl_2 . Reaction time was 2 h. The silica gel was loaded using ethyl acetate and the product was eluted using 3% MeOH in ethyl acetate. Isolated 71 mg (0.140 mmol, 55% yield) white solid. Yield 2: 60.4 mg (0.247 mmol) of substrate, 0.8 mg (0.006 mmol) CuCl_2 , 1.7 mg (0.006 mmol) TBACl, 132 mg (0.505 mmol) oxaziridine and 0.5 mL CH_2Cl_2 . Isolated 65 mg (0.129 mmol, 52% yield). The diastereoselectivity of the crude reaction mixture was 7:1.



Major diastereomer: IR (neat): 3314, 3067, 2933, 1654, 1480, 1395, 1162; ^1H NMR: (500 MHz, CDCl_3) 8.24 (s, 1H), 8.08 (d, $J = 7.7$ Hz, 1H), 7.38 (t, $J = 7.7$ Hz, 1H), 7.31 (t, $J = 7.7$ Hz, 1H), 7.18 (m, 6H), 7.10 (m, 4H), 6.27 (s, 1H), 5.74 (br s, 1H), 5.65 (s, 1H), 3.44 (dq, $J = 16.2, 6.2$ Hz, 1H), 3.24 (dq, $J = 16.2, 5.7$ Hz, 1H), 2.85 (m, 2H), 2.36 (s, 3H), 1.94 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 170.6, 170.1, 143.6, 140.4, 133.3, 132.4, 131.1, 130.3, 129.3, 128.5, 128.2, 128.0, 127.4, 127.3, 124.7, 116.3, 95.7, 91.1, 75.1, 37.0, 36.1, 24.2, 23.4; HRMS (ESI $^+$) calc'd for $[\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}_5\text{SNa}]^+$ (M+Na) $^+$ requires m/z 528.1564, found m/z 528.1541. (mp: 104-106 °C)

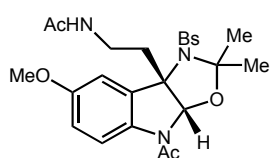
Compound 16 (Figure 1). Prepared according to general procedure B using 60.1 mg (0.246 mmol) of *N,N'*-diacyl tryptamine, 3.6 mg (0.027 mmol) CuCl_2 , 6.8 mg (0.024 mmol) TBACl, 119 mg (0.559 mmol) 3,3-dimethyl *N*-benzenesulfonyl oxaziridine and 0.5 mL acetone. Reaction time was 8 h. The silica gel was loaded using 20% acetone in dichloromethane and the product was eluted using 40% acetone in dichloromethane. Isolated 91.2 mg (0.199 mmol, 81% yield) white solid. Yield 2: 61.5 mg (0.252 mmol) of substrate, 3.7 mg (0.027 mmol) CuCl_2 , 6.9 mg (0.025 mmol) TBACl, 112 mg (0.525 mmol) oxaziridine and 0.5 mL acetone. Isolated 92.9 mg (0.203 mmol, 81% yield).



IR (neat): 3071, 2990, 2941, 1657, 1479, 1395, 1161; ^1H NMR: (500 MHz, CDCl_3) 8.23 (d, $J = 6.8$ Hz, 1H), 7.93 (d, $J = 7.6$ Hz, 1H), 7.50 (d, $J = 7.6$ Hz, 2H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.35 (m, 3H), 7.12 (t, $J = 6.8$ Hz, 1H), 6.17 (s, 1H), 5.79 (br s, 1H), 3.28 (ddd, $J = 17.4, 9.1, 5.3$ Hz, 1H), 3.15 (ddd, $J = 17.4, 9.1, 5.4$ Hz, 1H), 2.85 (ddd, $J = 13.6, 9.1, 5.3$ Hz, 1H), 2.73 (ddd, $J = 13.6, 9.1, 5.3$ Hz, 1H), 2.39 (s, 3H), 1.92 (s, 3H), 1.60 (s, 3H), 1.09 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 170.6, 170.1, 142.5, 142.3, 132.9, 130.9, 129.9, 129.1, 127.5, 126.8, 124.4, 116.9, 98.8, 95.6, 75.2, 37.5, 36.0, 29.2, 28.5, 24.2, 23.4. HRMS (ESI $^+$) calc'd for $[\text{C}_{23}\text{H}_{28}\text{N}_3\text{O}_5\text{S}]^+$ (M+H) $^+$ requires m/z 458.1745, found m/z 458.1758. (mp: 77-79 °C)

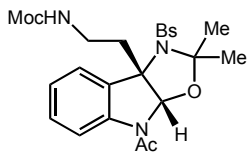
Compound 17 (Figure 1). Prepared according to general procedure B using 69.1 mg (0.252 mmol) of *N,N'*-diacyl 5-methoxytryptamine, 3.5 mg (0.026 mmol) CuCl_2 , 6.8 mg

(0.024 mmol) TBACl, 108 mg (0.506 mmol) 3,3-dimethyl *N*-benzenesulfonyl oxaziridine and 0.5 mL acetone. Reaction time was 3 h. The silica gel was loaded using 20% acetone in dichloromethane and the product was eluted using increasing proportions of acetone in dichloromethane. Isolated 111.0 mg (0.228 mmol, 90% yield) yellowish white solid. Yield 2: 68.5 mg (0.250 mmol) of substrate, 3.6 mg (0.026 mmol) CuCl₂, 7.0 mg (0.026 mmol) TBACl, 110 mg (0.516 mmol) oxaziridine and 0.5 mL acetone. Isolated 107.2 mg (0.220 mmol, 88% yield).



IR (neat): 3301, 2995, 2942, 1665, 1487, 1278, 1160; ¹H NMR: (500 MHz, CDCl₃) 8.15 (d, J = 8.8 Hz, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.50 (s, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.37 (t, J = 7.8 Hz, 2H), 6.89 (dd, J = 8.8, 2.7 Hz, 1H), 6.14 (s, 1H), 5.78 (br s, 1H), 3.76 (s, 3H), 3.26 (ddd, J = 18.3, 9.3, 5.5 Hz, 1H), 3.08 (ddd, J = 18.3, 9.3, 5.9 Hz, 1H), 2.89 (ddd, J = 13.6, 9.8, 5.9 Hz, 1H), 2.66 (ddd, J = 13.6, 9.8, 5.5 Hz, 1H), 2.37 (s, 3H), 1.92 (s, 3H), 1.58 (s, 3H), 1.15 (s, 3H); ¹³C NMR: (125 MHz, CDCl₃) 170.6, 169.5, 156.7, 142.7, 135.9, 132.8, 131.0, 129.1, 127.4, 117.8, 116.2, 112.1, 98.9, 95.8, 75.0, 55.9, 37.3, 36.0, 29.0, 28.6, 23.9, 23.3; HRMS (ESI⁺) calc'd for [C₂₄H₂₉N₃O₆SNa]⁺ (M+Na)⁺ requires *m/z* 510.1670, found *m/z* 510.1682. (mp: 72-74 °C)

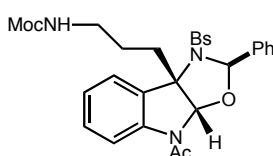
Compound 18 (Figure 1). Prepared according to general procedure B using 65.6 mg (0.252 mmol) of *N*-acyl, *N'*-Moc tryptamine, 3.4 mg (0.025 mmol) CuCl₂, 6.9 mg (0.025 mmol) TBACl, 110 mg (0.498 mmol) 3,3-dimethyl *N*-benzenesulfonyl oxaziridine and 0.5 mL acetone. Reaction time was 6 h. The silica gel was loaded using 1:1 hexane: ethyl acetate and the product was eluted using 2:3 hexane-ethyl acetate. Isolated 99.5 mg (0.210 mmol, 83% yield) white solid. Yield 2: 65.4 mg (0.251 mmol) of substrate, 3.5 mg (0.026 mmol) CuCl₂, 7.0 mg (0.026 mmol) TBACl, 110 mg (0.498 mmol) oxaziridine and 0.5 mL acetone. Isolated 96.2 mg (0.203 mmol, 81% yield) white solid.



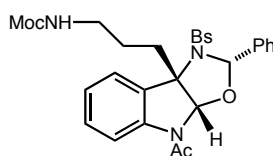
IR (neat): 3342, 2991, 2946, 1716, 1681, 1395, 1162, 1091; ¹H NMR: (500 MHz, CDCl₃) 8.22 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.51 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.34 (m, 3H), 7.12 (t, J = 7.5 Hz, 1H), 6.10 (s, 1H), 4.81 (br s, 1H), 3.64 (s, 3H), 3.14 (m, 2H), 2.87 (ddd, J = 13.5, 9.4, 5.5 Hz, 1H), 2.73 (m, 1H), 2.37 (s, 3H), 1.60

(s, 3H), 1.10 (s, 3H); ^{13}C NMR: (125 MHz, CDCl_3) 170.0, 157.3, 142.6, 142.3, 132.8, 130.9, 129.7, 129.1, 127.5, 126.9, 124.5, 116.8, 98.8, 95.7, 75.2, 52.4, 37.8, 37.5, 29.2, 28.5, 24.2; HRMS (ESI^+) calc'd for $[\text{C}_{23}\text{H}_{27}\text{N}_3\text{O}_6\text{SNa}]^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 496.1513, found m/z 496.1519. (mp: 86-88 °C)

Compound 19 (Figure 1). Prepared according to general procedure B using 69.4 mg (0.253 mmol) of *N*-acyl, *N'*-Moc homotryptamine, 3.5 mg (0.026 mmol) CuCl_2 , 7.1 mg (0.026 mmol) TBACl, 130 mg (0.498 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 0.5 mL acetone. Reaction time was 30 min. The silica gel was loaded using 1:1 hexane:ethyl acetate and the product was eluted using 1:4 hexane:ethyl acetate. Isolated 101.2 mg (0.189 mmol, 75% yield) white solid. Yield 2: 69.3 mg (0.253 mmol) of substrate, 3.4 mg (0.025 mmol) CuCl_2 , 7.1 mg (0.026 mmol) TBACl, 130 mg (0.498 mmol) oxaziridine and 0.5 mL acetone. Isolated 95.2 mg (0.177 mmol, 70% yield). The diastereoselectivity of the crude reaction mixture was 3:1.



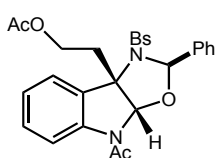
Major diastereomer: IR (neat): 3346, 2949, 1720, 1681, 1480, 1392, 1162, 1090; ^1H NMR: (500 MHz, CDCl_3) 8.20 (s, 1H), 8.04 (d, $J = 7.7$ Hz, 1H), 7.35 (t, $J = 7.7$ Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 1H), 7.22 (m, 3H), 7.13 (m, 7H), 5.95 (s, 1H), 5.76 (s, 1H), 4.83 (s, 1H), 3.66 (s, 3H), 3.24 (m, 2H), 2.63 (m, 1H), 2.52 (td, $J = 12.4, 4.4$ Hz, 1H), 2.33 (s, 3H), 1.68 (m, 1H), 1.44 (m, 1H); ^{13}C NMR: (125 MHz, CDCl_3) 169.8, 157.3, 143.5, 140.5, 133.9, 132.3, 130.8, 130.1, 129.1, 128.5, 128.3, 128.1, 127.3, 124.6, 116.1, 95.8, 91.3, 76.1, 52.3, 41.0, 34.8, 25.7, 24.2; HRMS (ESI^+) calc'd for $[\text{C}_{28}\text{H}_{29}\text{N}_3\text{O}_6\text{SNa}]^+$ ($\text{M}+\text{Na}$) $^+$ requires m/z 558.1670, found m/z 558.1670. (mp: 95-97 °C)



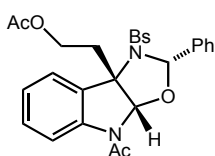
Minor diastereomer: IR (neat): 3347, 2927, 2854, 1718, 1684, 1480, 1394, 1163, 1098; ^1H NMR: (500 MHz, CDCl_3) 8.07 (s, 1H), 7.87 (d, $J = 7.6$ Hz, 1H), 7.31 (m, 2H), 7.14 (m, 5H), 7.03 (t, $J = 7.2$ Hz, 1H), 6.93 (m, 4H), 6.37 (s, 1H), 5.95 (s, 1H), 4.84 (s, 1H), 3.66 (s, 3H), 3.22 (q, $J = 6.4$ Hz, 2H), 2.53 (m, 2H), 2.28 (s, 3H), 1.67 (m, 1H), 1.48 (m, 1H); ^{13}C NMR: (125 MHz, CDCl_3) 169.9, 157.3, 141.7, 132.4, 130.6, 129.2, 129.1, 128.7, 128.5, 128.3, 128.0, 127.3, 126.9, 125.5, 124.5, 116.7, 97.4, 94.1, 76.0, 52.3, 40.9,

32.9, 25.5, 24.1; HRMS (ESI⁺) calc'd for [C₂₈H₂₉N₃O₆SNa]⁺ (M+Na)⁺ requires *m/z* 558.1670, found *m/z* 558.1688. (mp: 86-87 °C)

Compound 20 (Figure 1). Prepared according to general procedure B using 60.6 mg (0.247 mmol) of *N,N'*-diacyl tryptophol, 3.4 mg (0.025 mmol) CuCl₂, 7.0 mg (0.025 mmol) TBACl, 129 mg (0.494 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 0.5 mL acetone. Reaction time was 30 min. The silica gel was loaded using 4:1 hexane: ethyl acetate + 4% triethylamine and the product was eluted using the same eluent. The fractions containing the product were concentrated and purified again on silica gel using 2:1 hexane-ethyl acetate + 4% triethylamine. Isolated 97.4 mg (0.192 mmol, 78% yield) white solid. Yield 2: 61.6 mg (0.251 mmol) of substrate, 3.5 mg (0.026 mmol) CuCl₂, 7.2 mg (0.026 mmol) TBACl, 131 mg (0.501 mmol) oxaziridine and 0.5 mL acetone. Isolated 98.0 mg (0.193 mmol, 77% yield). The diastereoselectivity of the crude reaction mixture was 3:1.



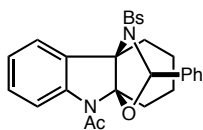
Major diastereomer: IR (neat): 3064, 2926, 1741, 1682, 1391, 1351, 1162; ¹H NMR: (500 MHz, CDCl₃) 8.23 (s, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.20 (m, 6H), 7.11 (m, 4H), 6.23 (s, 1H), 5.73 (s, 1H), 4.36 (dt, *J* = 11.3, 6.0 Hz, 1H), 4.04 (dt, *J* = 11.3, 5.8 Hz, 1H), 3.11 (dt, *J* = 14.8, 5.8 Hz, 1H), 2.87 (dt, *J* = 14.8, 6.0 Hz, 1H), 2.35 (s, 3H), 1.99 (s, 3H); ¹³C NMR: (125 MHz, CDCl₃) 166.7, 165.7, 139.7, 136.5, 129.6, 128.4, 127.1, 126.2, 125.2, 124.6, 124.3, 123.4, 120.7, 112.3, 92.1, 86.8, 71.1, 57.0, 32.0, 20.1, 17.0; HRMS (ESI⁺) calc'd for [C₂₇H₂₆N₂O₆SNa]⁺ (M+Na)⁺ requires *m/z* 529.1404, found *m/z* 529.1422. (mp: 150-152 °C)



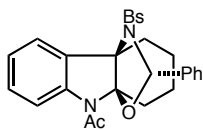
Minor diastereomer: IR (neat): 2959, 2925, 1742, 1682, 1480, 1393, 1164; ¹H NMR: (500 MHz, CDCl₃) 8.06 (s, 1H), 7.87 (d, *J* = 7.2 Hz, 1H), 7.33 (m, 2H), 7.17 (m, 5H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.93 (t, *J* = 7.2 Hz, 2H), 6.41 (s, 1H), 6.20 (s, 1H), 4.31 (m, 1H), 4.03 (m, 1H), 3.05 (dt, *J* = 14.3, 6.2 Hz, 1H), 2.78 (m, 1H), 2.30 (s, 3H), 1.98 (s, 3H); ¹³C NMR: (125 MHz, CDCl₃) 170.6, 169.7, 142.0, 141.7, 135.4, 132.5, 130.9, 129.2, 128.8, 128.0, 126.8, 125.8, 124.5, 116.9, 97.6, 93.7, 74.6, 60.7, 34.0, 24.1, 20.9;

HRMS (ESI⁺) calc'd for [C₂₇H₂₇N₂O₆S]⁺ (M+H)⁺ requires *m/z* 507.1585, found *m/z* 507.1580. (mp: 120-122 °C)

Compound 21 (Figure 1). Prepared according to general procedure B using 53.7 mg (0.252 mmol) of *N*-acyl tetrahydrocarbazole, 3.3 mg (0.025 mmol) CuCl₂, 6.7 mg (0.024 mmol) TBACl, 131 mg (0.501 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 0.5 mL acetone. Reaction time was 30 min. The silica gel was loaded using 5:1 hexane: ethyl acetate + 4% triethylamine and the product was eluted using 3:1 hexane-ethyl acetate + 4% triethylamine. Isolated 108 mg (0.228 mmol, 90% yield) white solid. Yield 2: 53.5 mg (0.251 mmol) of substrate, 3.3 mg (0.025 mmol) CuCl₂, 6.8 mg (0.024 mmol) TBACl, 130 mg (0.498 mmol) oxaziridine and 0.5 mL acetone. Isolated 107.2 mg (0.226 mmol, 90% yield). The diastereoselectivity of the crude reaction mixture was 2:1.



Major diastereomer: IR (neat): 2947, 2868, 1669, 1381, 1352, 1165; ¹H NMR: (500 MHz, CDCl₃) 7.77 (br s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.60 (m, 2H), 7.43 (m, 3H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 2H), 5.94 (s, 1H), 3.05 (dt, *J* = 14.7, 3.7 Hz, 1H), 2.57 (d, *J* = 14.3 Hz, 1H), 2.33 (td, *J* = 14.0, 4.0 Hz, 1H), 2.25 (s, 3H), 1.79 (dt, *J* = 14.3, 4.0 Hz, 1H), 1.54 (m, 3H), 1.13 (m, 1H); ¹³C NMR: (125 MHz, CDCl₃) 168.8, 143.1, 139.1, 137.3, 132.2, 130.9, 130.0, 128.6, 128.2, 127.6, 126.5, 125.4, 123.8, 117.4, 104.0, 92.5, 77.4, 72.2, 33.8, 32.4, 23.8, 20.7, 20.2; HRMS (ESI⁺) calc'd for [C₂₇H₂₆N₂O₄SNa]⁺ (M+Na)⁺ requires *m/z* 497.1506, found *m/z* 497.1506. (mp: 196-197 °C)

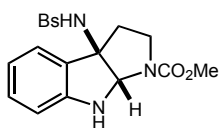


Minor diastereomer: IR (neat): 3068, 2938, 2867, 1664, 1381, 1351, 1163; ¹H NMR: (500 MHz, CDCl₃) 8.33 (d, *J* = 6.6 Hz, 1H), 7.87 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.48 (td, *J* = 8.1, 1.3 Hz, 1H), 7.27 (td, *J* = 7.5, 1.3 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (tt, *J* = 6.6, 1.6 Hz, 1H), 6.95 (m, 4H), 6.89 (t, *J* = 7.5 Hz, 2H), 6.49 (d, *J* = 7.5 Hz, 2H), 6.32 (s, 1H), 3.43 (d, *J* = 14.3 Hz, 1H), 2.61 (d, *J* = 11.8 Hz, 1H), 2.30 (td, *J* = 14.3, 4.2 Hz, 1H), 1.95 (s, 3H), 1.86 (d, *J* = 13.2 Hz, 1H), 1.57 (m, 3H), 1.21 (m, 1H); ¹³C NMR: (125 MHz, CDCl₃) 170.3, 142.2, 141.2, 134.6, 132.0, 131.0, 129.5, 128.8, 128.2, 128.2, 126.9, 126.6, 126.4, 123.7, 117.9, 104.7, 93.7, 74.5,

33.9, 30.2, 24.1, 21.5, 20.7; HRMS (ESI⁺) calc'd for [C₂₇H₂₇N₂O₄S]⁺ (M+H)⁺ requires *m/z* 475.1687, found *m/z* 475.1665. (mp: 193-195 °C)

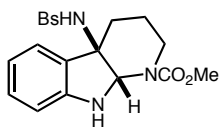
IV. Deprotection of racemic products.

General procedure for deprotections. The substrate was weighed in a 2 dram vial containing a stirbar, followed by dioxane and a 6 M solution of NaOH. The vial was flushed with argon and capped with a septum. The sealed vessel was placed in an oil bath heated to 80 °C, and the mixture was stirred rapidly. The reaction progress was monitored by TLC. Upon completion of the reaction, saturated ammonium chloride and dichloromethane were added to the reaction, and the aqueous phase was extracted with additional dichloromethane until TLC did not show any product in the organic extract. The combined organic phase was dried with sodium sulfate and most of the volatiles were removed prior loading onto silica for purification by flash column chromatography.



Pyrroloindoline 22 (Table 1, entry 1). Prepared according to general procedure using 70.9 mg (0.150 mmol) of aminal **18**, 1.5 mL of dioxane and 0.5 mL 6 N NaOH. Reaction time was 7 h. The silica gel was loaded using ethyl acetate and the product was eluted using the same solvent. Isolated 50.1 mg (0.134 mmol, 89% yield) white solid. Yield 2: 70.3 mg (0.148 mmol) of substrate, 1.5 mL of dioxane and 0.5 mL 6N NaOH. Isolated 44.9 mg (0.120 mmol, 81% yield).

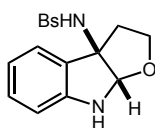
IR (neat): 3380, 3253, 2956, 2867, 1686, 1450, 1389, 1158; ¹H NMR: (500 MHz, DMSO, 100°C) 8.10 (s, 1H), 7.60 (d, J = 7.3 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.40 (t, J = 7.3 Hz, 2H), 6.93 (t, J = 7.3 Hz, 1H), 6.83 (d, J = 7.3 Hz, 1H), 6.49 (d, J = 7.3 Hz, 1H), 6.37 (t, J = 7.3 Hz, 1H), 6.17 (br s, 1H), 5.62 (s, 1H), 3.64 (s, 3H), 3.56 (td, J = 9.5, 3.4 Hz, 1H), 2.89 (td, J = 9.5, 6.5 Hz, 1H), 2.50 (m, 1H), 2.17 (m, 1H); ¹³C NMR: (125 MHz, DMSO, 100°C) 154.0, 149.4, 142.5, 131.2, 128.5, 128.0, 126.5, 125.6, 123.5, 116.9, 108.6, 79.5, 71.7, 51.4, 43.7, 37.0; HRMS (ESI⁺) calc'd for [C₁₈H₁₉N₃O₄SNa]⁺ (M+Na)⁺ requires *m/z* 396.0989, found *m/z* 396.0988. (mp: 134-136 °C).



Piperidineindoline 23 (Table 1, entry 2). Prepared according to general procedure using 78.2 mg (0.146 mmol) of amination **19**, 1.5 mL of dioxane and 0.5 mL 6 N NaOH. Reaction time was 7 h. The silica

gel was loaded using ethyl acetate and the product was eluted using the same solvent. Isolated 42.2 mg (0.109 mmol, 75% yield) white solid. Yield 2: 78.2 mg (0.146 mmol) of substrate, 1.5 mL of dioxane and 0.5 mL 6 N NaOH. Isolated 42.3 mg (0.109 mmol, 75% yield).

IR (neat): 3334, 3266, 2955, 2926, 1685, 1448, 1323, 1159; ^1H NMR: (500 MHz, DMSO, 120°C) 7.72 (br s, 1H), 7.66 (d, $J = 7.5$ Hz, 2H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.43 (t, $J = 7.5$ Hz, 2H), 6.94 (t, $J = 7.7$ Hz, 1H), 6.72 (d, $J = 7.7$ Hz, 1H), 6.50 (d, $J = 7.7$ Hz, 1H), 6.40 (t, $J = 7.7$ Hz, 1H), 6.19 (s, 1H), 4.46 (br s, 1H), 3.63 (s, 3H), 3.61 (m, 1H), 2.94 (dt, $J = 12.8, 6.2$ Hz, 1H), 1.96 (ddd, $J = 13.7, 9.9, 4.0$ Hz, 1H), 1.72 (ddd, $J = 13.7, 7.5, 3.7$ Hz, 1H), 1.60 (m, 1H), 1.21 (m, 1H); ^{13}C NMR: (125 MHz, DMSO, 120°C) 155.6, 148.3, 143.2, 130.9, 128.9, 127.9, 127.8, 125.6, 122.7, 116.8, 108.4, 74.0, 64.4, 51.5, 37.5, 31.4, 17.1; HRMS (ESI $^+$) calc'd for $[\text{C}_{19}\text{H}_{21}\text{N}_3\text{O}_4\text{SNa}]^+$ (M+Na) $^+$ requires m/z 410.1145, found m/z 410.1154. (mp: 95-97 °C)

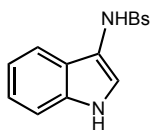


Furoindoline 24 (Table 1, entry 3). Prepared according to general procedure using 73.5 mg (0.145 mmol) of amination **20**, 1.5 mL of dioxane and 0.5 mL 6 N NaOH. Reaction time was 14 h. The silica gel was loaded

using 3:1 hexane: ethyl acetate and the product was eluted using 1:3 hexane: ethyl acetate. Isolated 43.8 mg (0.138 mmol, 95% yield) white solid. Yield 2: 74.7 mg (0.147 mmol) of substrate, 1.5 mL of dioxane and 0.5 mL 6N NaOH. Isolated 44.6 mg (0.141 mmol, 96% yield).

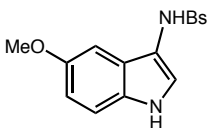
IR (neat): 3411, 3242, 2926, 2879, 1613, 1485, 1449, 1326, 1158; ^1H NMR: (500 MHz, DMSO) 8.55 (s, 1H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.44 (d, $J = 7.5$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 6.86 (t, $J = 7.5$ Hz, 1H), 6.70 (d, $J = 2.1$ Hz, 1H), 6.51 (d, $J = 7.5$ Hz, 1H), 6.39 (d, $J = 7.5$ Hz, 1H), 6.15 (t, $J = 7.5$ Hz, 1H), 5.71 (d, $J = 2.1$ Hz, 1H), 3.80 (t, $J = 7.7$ Hz, 1H), 3.22 (ddd, $J = 10.7, 6.5, 4.6$ Hz, 1H), 2.33 (td, $J = 11.5, 7.7$ Hz, 1H), 2.06 (dd, $J = 11.5, 4.3, 4.6$ Hz, 1H); ^{13}C NMR: (125 MHz, DMSO) 150.7, 142.6, 131.7, 128.7, 128.5,

126.5, 126.0, 124.3, 116.9, 107.6, 97.3, 72.6, 64.4, 41.4; HRMS (ESI⁺) calc'd for [C₁₆H₁₆N₂O₃SNa]⁺ (M+Na)⁺ requires *m/z* 339.0774, found *m/z* 339.0776. (mp: 188-190 °C)



3-(Benzenesulfonamino) indole 25 (Table 1, entry 4). Prepared according to general procedure using 65.1 mg (0.155 mmol) of aminal **8**, 1.5 mL of dioxane and 0.5 mL 6 N NaOH. Reaction time was 14 h. The silica gel was loaded using 5:1 hexane: ethyl acetate + 2% triethylamine and the product was eluted using 1:1 hexane-ethyl acetate + 2% triethylamine. Isolated 37.1 mg (0.136 mmol, 88% yield) white solid. Yield 2: 65.8 mg (0.157 mmol) of substrate, 1.5 mL of dioxane and 0.5 mL 6N NaOH. Isolated 38.1 mg (0.140 mmol, 89% yield).

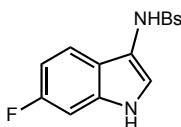
IR (ATR): 3412, 3240, 3123, 1296, 1152; ¹H NMR: (500 MHz, DMSO) 10.94 (s, 1H), 9.68 (s, 1H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.01 (m, 2H), 6.85 (t, *J* = 7.9 Hz, 1H); ¹³C NMR: (125 MHz, DMSO) 140.3, 134.3, 132.3, 128.9, 126.7, 123.4, 121.4, 120.5, 118.7, 117.8, 112.0, 111.6; HRMS (ESI⁺) calc'd for [C₁₄H₁₂N₂O₂SNa]⁺ (M+Na)⁺ requires *m/z* 295.0512, found *m/z* 295.0517. (mp: 195-197 °C (dec))



3-(Benzenesulfonamino) 5-methoxyindole 26 (Table 1, entry 5). Prepared according to general procedure using 66.2 mg (0.147 mmol) of aminal **11**, 1.5 mL of dioxane and 0.5 mL 6 N NaOH. Reaction time was 26 h. The silica gel was loaded using 3:1 hexane: ethyl acetate + 2% triethylamine and the product was eluted using 1:1 hexane-ethyl acetate + 2% triethylamine. Isolated 39.2 mg (0.130 mmol, 88% yield) white solid. Yield 2: 66.8 mg (0.148 mmol) of substrate, 1.5 mL of dioxane and 0.5 mL 6N NaOH. Isolated 39.0 mg (0.129 mmol, 87% yield).

IR (ATR): 3355, 3199, 2967, 1496, 1301, 1155, 1088 ¹H NMR: (500 MHz, DMSO) 10.81 (s, 1H), 9.56 (s, 1H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.15 (d, *J* = 9.1 Hz, 1H), 7.01 (d, *J* = 2.7 Hz, 1H), 6.63 (m, 2H), 3.57 (s, 3H); ¹³C NMR: (125 MHz, DMSO) 153.1, 140.5, 132.4, 129.4, 128.9, 126.8, 123.8, 121.7,

112.4, 111.8, 111.7, 99.0, 55.0; HRMS (ESI⁺) calc'd for [C₁₅H₁₅N₂O₃S]⁺ (M+H)⁺ requires *m/z* 303.0798, found *m/z* 303.0786. (mp: 153-154 °C (dec))

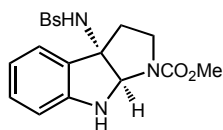


3-(Benzenesulfonamino) 6-fluoroindole 27 (Table 1, entry 6). Prepared according to general procedure using 65.4 mg (0.149 mmol) of amination **12**, 1.5 mL of dioxane and 0.5 mL 6N NaOH. Reaction time was 14 h. The silica gel was loaded using 3:1 hexane: ethyl acetate + 2% triethylamine and the product was eluted using 1:1 hexane-ethyl acetate + 2% triethylamine. Isolated 41.3 mg (0.142 mmol, 95% yield) white solid. Yield 2: 65.6 mg (0.150 mmol) of substrate, 1.5 mL of dioxane and 0.5 mL 6N NaOH. Isolated 39.8 mg (0.137 mmol, 91% yield).

IR (ATR): 3417, 3272, 2927, 1315, 1153, 1124, 1092; ¹H NMR: (500 MHz, DMSO) 10.98 (s, 1H), 9.71 (s, 1H), 7.67 (d, J = 7.7 Hz, 2H), 7.53 (t, J = 7.7 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.22 (dd, J = 9.2, 5.5 Hz, 1H), 7.02 (m, 2H), 6.71 (t, J = 9.2 Hz, 1H); ¹³C NMR: (125 MHz, DMSO) 158.9 (¹J_{CF} = 234), 140.0, 134.0 (³J_{CF} = 13), 132.4, 128.9, 126.7, 120.9, 120.1, 119.0 (³J_{CF} = 13), 112.3, 107.4 (²J_{CF} = 26), 97.5 (²J_{CF} = 26); HRMS (ESI⁺) calc'd for [C₁₄H₁₁FN₂O₂SNa]⁺ (M+Na)⁺ requires *m/z* 313.0418, found *m/z* 313.0404. (mp: 182-183 °C (dec))

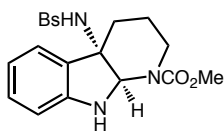
V. Asymmetric oxyaminations.

General procedure for the asymmetric oxyaminations. In a nitrogen-atmosphere glovebox, copper(II) chloride and tetrabutylammonium chloride were placed in a 1.5 dram vial with a stirbar. The vial was capped with a septum and transferred out of the glovebox. The vessel was charged with CHCl_3 and the mixture was stirred under nitrogen for 15 min. The substrate was added to a separate 1.5 dram vial equipped with stirbar, and the solution containing the catalyst was transferred via a syringe to this vial, which was then sealed with a Teflon cap. The mixture was cooled to the appropriate temperature, and after the oxaziridine was quickly added, the reaction was stirred at this temperature. Upon completion of the reaction as determined by TLC, the reaction mixture was loaded directly onto silica for purification by flash column chromatography using 2% MeOH in CH_2Cl_2 . The product diastereomers were collected, and placed into a clean, dry 2-dram vial for deprotection.

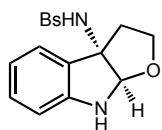


Enantioenriched pyrroloindoline 22 (Figure 3). Prepared according to general asymmetric procedure using 100 mg (0.241 mmol) of *N*-(*L*-Boc-proline) *N'*-Moc tryptamine, 3.4 mg (0.025 mmol) CuCl_2 , 7.3 mg (0.026 mmol) Bu_4NCl , 137 mg (0.524 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 1.25 mL chloroform. The reaction temperature was $-30\text{ }^\circ\text{C}$ and the reaction time was 24 h. After initial purification, the fractions containing the oxyamination product were concentrated and deprotected using 1.5 mL acetonitrile and 0.5 mL NaOMe under nitrogen for 2 h. Upon completion of the reaction, saturated ammonium chloride and dichloromethane was added to the reaction, and the aqueous phase was extracted with additional dichloromethane until TLC did not show any product in the organic extract. The combined organic phase was dried with sodium sulfate and most of the volatiles were removed prior loading onto silica for purification by flash column chromatography. The silica gel was loaded using 2:1 hexane-ethyl acetate and the product was eluted using increasing amount of ethyl acetate until it reached 1:2 ratio of hexane:ethyl acetate. Isolated 71 mg (0.189 mmol, 78% yield) of a white solid. The compound exhibited spectral data identical to those reported for the racemic

pyrroloindoline **22**. The enantioselectivity of the reaction was determined to be 91% ee by SFC analysis (Chiralcel OJ-H, 150 bar CO₂, 10% MeOH, 2 mL/min flow rate). $[\alpha]_D = 1.282^\circ$ (c 1.0, CH₂Cl₂)



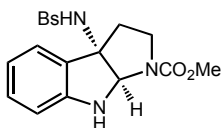
Enantioenriched piperidineindoline 23 (Figure 3). Prepared according to general asymmetric procedure using 103 mg (0.241 mmol) of *N*-(*L*-Boc-proline) *N'*-Moc homotryptamine, 3.4 mg (0.025 mmol) CuCl₂, 7.3 mg (0.026 mmol) Bu₄NCl, 133 mg (0.509 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 1.25 mL chloroform. The reaction temperature was -15 °C and the reaction time was 14 h. After initial purification, the fractions containing the oxyamination product were concentrated and deprotected using 1.5 mL acetonitrile and 0.5 mL NaOMe under nitrogen for two hours. Upon completion of the reaction, saturated ammonium chloride and dichloromethane were added to the reaction, and the aqueous phase was extracted with additional dichloromethane until TLC did not show any product in the organic extract. The combined organic phase was dried with sodium sulfate and most of the volatiles were removed prior loading onto silica for purification by flash column chromatography. The silica gel was loaded using 2:1 hexane:ethyl acetate and the product was eluted using increasing amount of ethyl acetate until it reached 1:2 ratio of hexane:ethyl acetate. Isolated 51 mg (0.132 mmol, 55% yield) white solid. The compound exhibited spectral data identical to those reported for the racemic piperidineindoline **23**. The enantioselectivity of the reaction was determined to be 88% ee by SFC analysis (Chiralcel OJ-H, 150 bar CO₂, 10% MeOH, 2 mL/min flow rate). $[\alpha]_D = 0.520^\circ$ (c 1.0, CH₂Cl₂)



Enantioenriched furanoindoline 24 (Figure 3). Prepared according to general asymmetric procedure using 104 mg (0.260 mmol) of *N*-(*L*-Boc-proline) *O*-Ac tryptophol, 3.4 mg (0.025 mmol) CuCl₂, 7.2 mg (0.026 mmol) Bu₄NCl, 134 mg (0.513 mmol) 3-phenyl *N*-benzenesulfonyl oxaziridine and 1.25 mL chloroform. The reaction temperature was 0 °C and the reaction time was 6 h. After initial purification, the fractions containing the oxyamination product were concentrated and deprotected using 2.5 mL dioxane and 0.85 mL 6 M NaOH under argon at 80 °C for

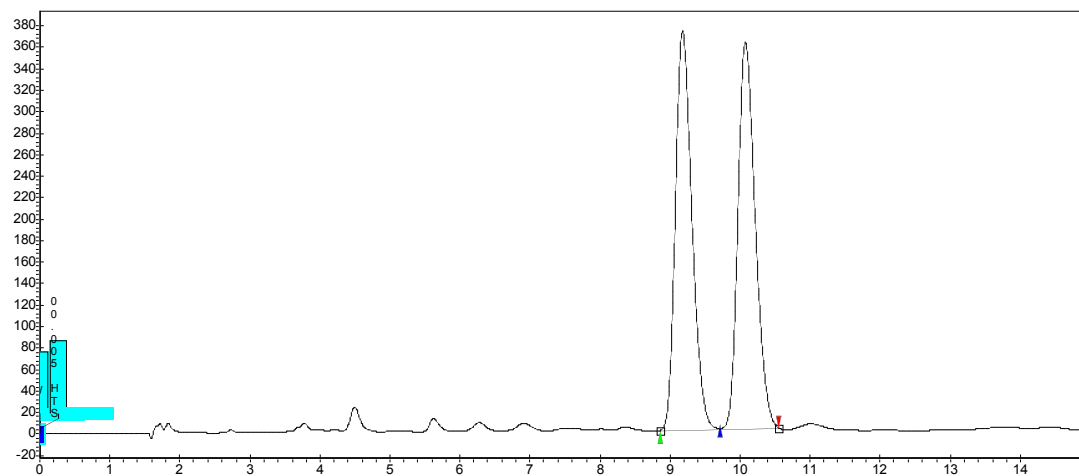
14 h. Upon completion of the reaction, saturated ammonium chloride and dichloromethane were added to the reaction, and the aqueous phase was extracted with additional dichloromethane until TLC did not show any product in the organic extract. The combined organic phase was dried with sodium sulfate and most of the volatiles were removed prior loading onto silica for purification by flash column chromatography. The silica gel was loaded using ammonia in dichloromethane and the product was eluted using the same eluent. Isolated 66 mg (0.208 mmol, 80% yield) white solid. The compound exhibited spectral data identical to those reported for the racemic furanoindoline **24**. The enantioselectivity of the reaction was determined to be 86% ee by SFC analysis (Chiralcel AD, 150 bar CO₂, 18% MeOH, 3 mL/min flow rate). $[\alpha]_D = 0.741^\circ$ (c 1.0, CHCl₃) The absolute stereochemistry was determined via X-ray crystallography.

VI. SFC data.



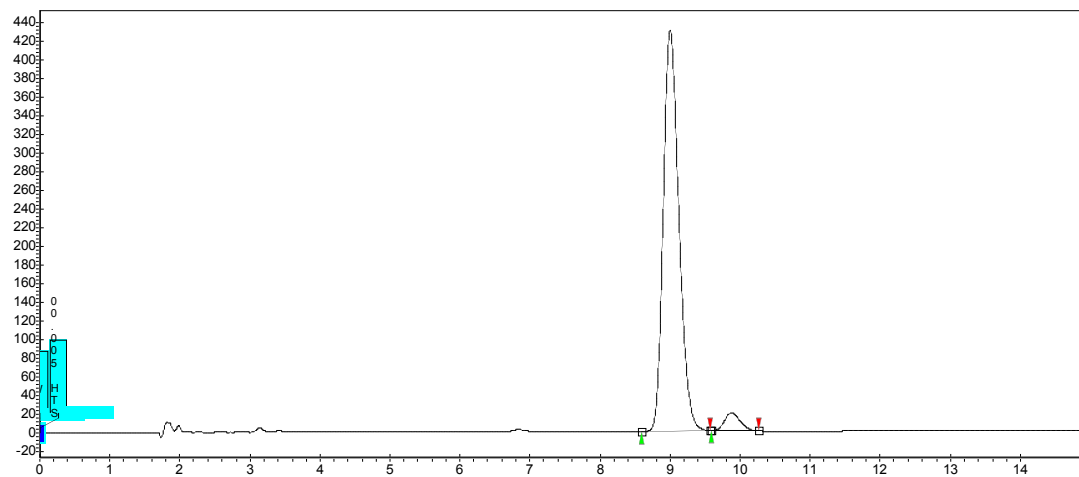
Chiralcel OJ-H 150 bar CO₂, 10% MeOH, 2 mL/min flow rate

Racemic:

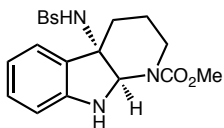


| entry | peak time (min) | peak area | % area |
|-------|-----------------|-----------|--------|
| 1 | 9.18 | 101.3 | 49.6% |
| 2 | 10.08 | 103.1 | 50.4% |

Enantioenriched:

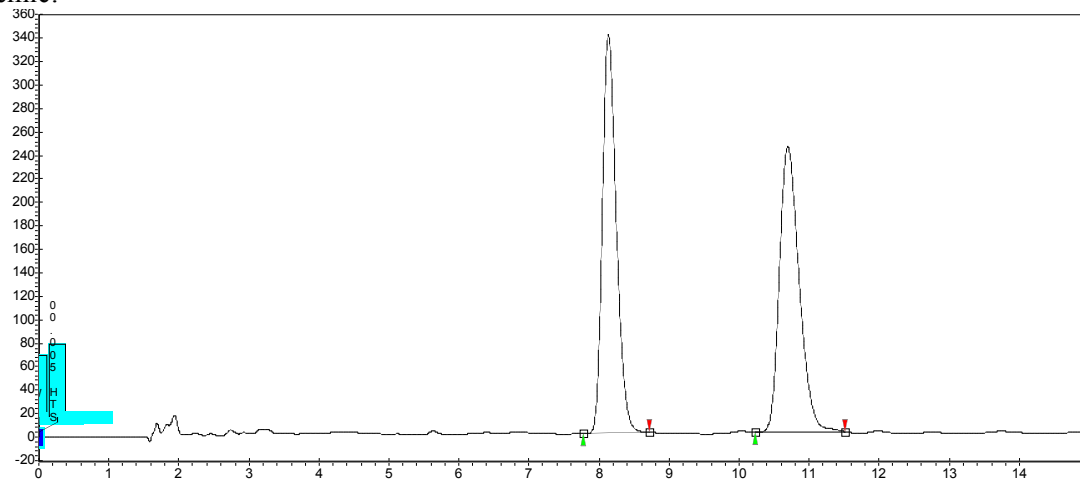


| entry | peak time (min) | peak area | % area |
|-------|-----------------|-----------|--------|
| 1 | 9.00 | 110.9 | 95.6% |
| 2 | 9.88 | 5.1 | 4.4% |



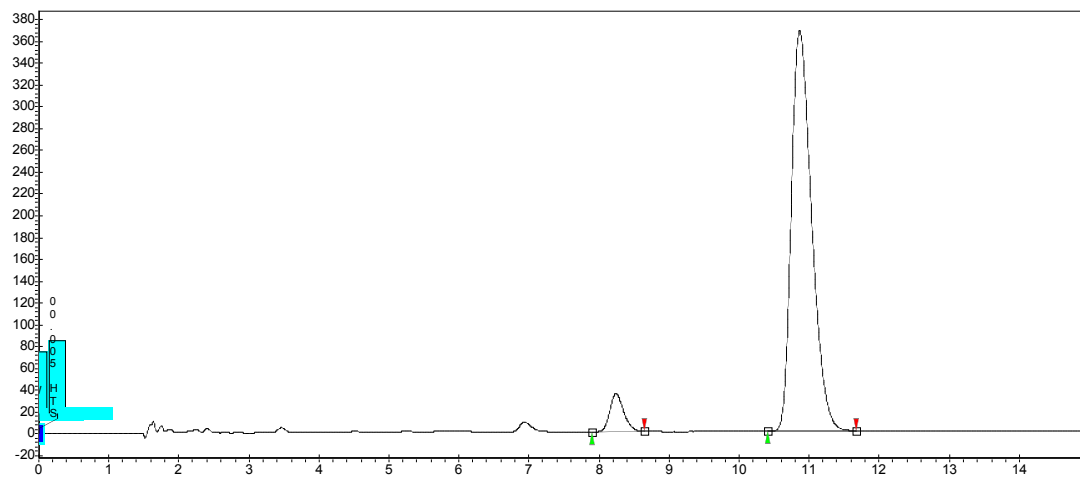
Chiralcel OJ-H 150 bar CO₂, 10% MeOH, 2 mL/min flow rate

Racemic:

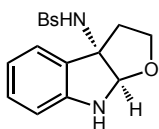


| entry | peak time (min) | peak area | % area |
|-------|-----------------|-----------|--------|
| 1 | 8.13 | 78.0 | 49.5% |
| 2 | 10.69 | 79.6 | 50.5% |

Enantioenriched:

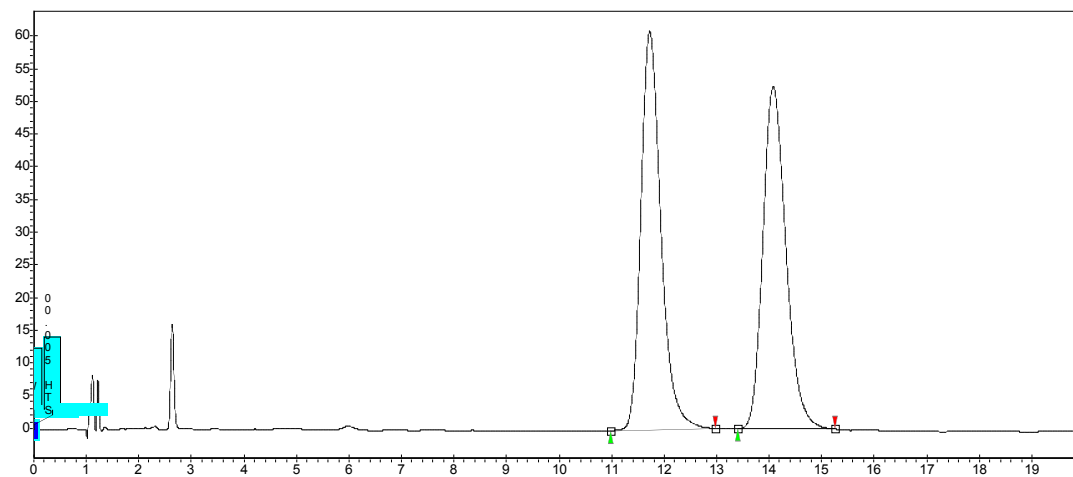


| entry | peak time (min) | peak area | % area |
|-------|-----------------|-----------|--------|
| 1 | 8.24 | 7.9 | 6.0% |
| 2 | 10.86 | 123.3 | 94.0% |



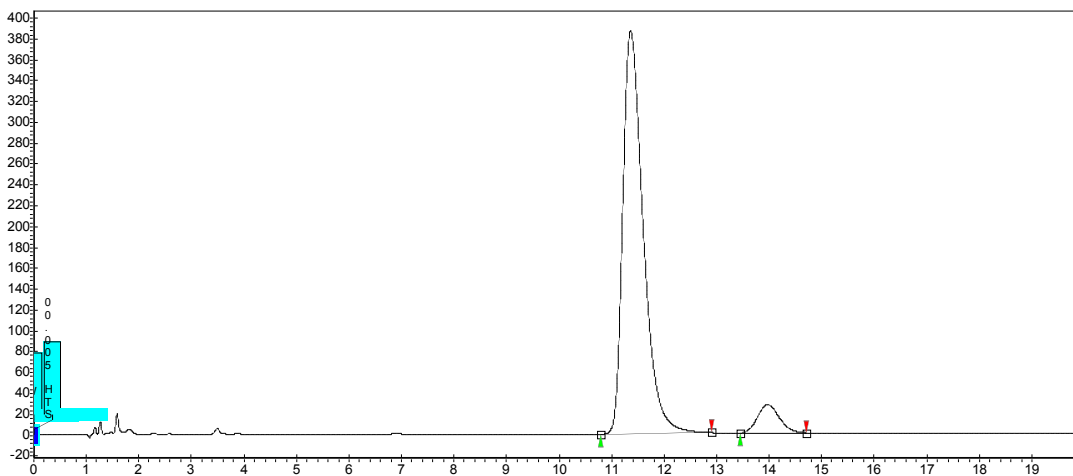
Chiralcel AD 150 bar CO₂, 18% MeOH, 3 mL/min flow rate

Racemic:



| entry | peak time (min) | peak area | % area |
|-------|-----------------|-----------|--------|
| 1 | 11.72 | 27.0 | 50.3% |
| 2 | 14.08 | 26.7 | 49.7% |

Enantioenriched:



| entry | peak time (min) | peak area | % area |
|-------|-----------------|-----------|--------|
| 1 | 11.36 | 173.7 | 93.0% |
| 2 | 13.97 | 13.0 | 7.0% |

VII. References.

- ¹ L. C. Vishwakarma; O. D. Stringer; F. A. Davis; checked by J. Pribish; E. Vedejs *Org. Syn.* **1993**, *8*, 546; *Org. Syn.* **1988**, *66*, 203. b) F. A. Davis; S. Chattopadhyay; J. C. Towson; S. Lal; T. Reddy *J. Org. Chem.* **1988**, *53*, 2087.
- ² W. B. Jennings; S. P. Watson; D. R. Boyd *J. Chem. Soc., Chem. Commun.* **1988**, 931–932.
- ³ M. E. Kuehne, S. D. Cowen, F. Xu, L. S. Borman, *J. Org. Chem.*, **2001**, *66*, 5303–5316.
- ⁴ V. O. Illi *Synthesis*, **1979**, *5*, 387–388.
- ⁵ T. Kametani; T. Ohsawa; M. Ihara *J. Chem. Soc. Perkin I.* **1981**, 290–294.
- ⁶ J. Kovacs; R. L. Rodin *J. Org. Chem.* **1968**, *33*, 2418–2420.
- ⁷ B. B. Snider; H. Zeng *J. Org. Chem.* **2003**, *68*, 545–563.
- ⁸ B. L. Pagenkopf; B. Bajtos *Org. Lett.* **2009**, *11*, 2780–2783.