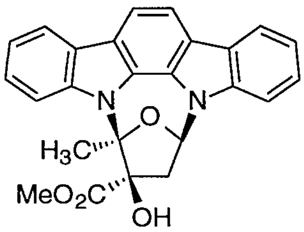
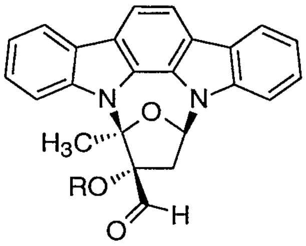


Ester (±)-21, Method A. To a suspension of indolo[2,3-a]carbazole (**18**) (1.0 g, 3.9 mmol, 1.0 equiv) in 1,2-dichloroethane (130 mL) was added furanose (±)-**19** (1.8 g, 8.2 mmol, 2.1 equiv) and CSA (100 mg, 0.43 mmol, 0.11 equiv). After heating at reflux for 48 h, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (100mL), and washed with 10% $NaHCO_3$ solution. The organic layer was dried over Na_2SO_4 and chromatographed on silica gel (3:1 hexanes:EtOAc eluent) to afford indolocarbazole (±)-**21** (1.37 g, 85% yield) as a yellow foam: mp 235-236 °C; IR (thin film/NaCl) 3501.3 (br m), 3047.5 (m), 3006.7 (m), 2950.6 (m), 1729.4 (s), 1640.2 (m), 1568.1 (m), 1441.1 (s), 1305.9 (s), 1230.3 (s), 1128.1 (s), 740.0 (s) cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) δ 8.18 (app.t, J = 6.6 Hz, 1H), 8.18 (app.t, J = 5.4 Hz, 1H), 8.00 (m, 2H), 7.89 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.44 (td, J = 0.9, 7.6 Hz, 1H), 7.38 (td, J = 1.0, 7.9 Hz, 1H), 7.26 (app.t, J = 6.9 Hz, 1H), 7.25 (app.t, J = 7.1 Hz, 1H), 7.10 (dd, J = 4.9, 7.3 Hz, 1H), 5.18 (s, 1H), 3.99 (s, 3H), 3.44 (dd, J = 7.5, 14.0 Hz, 1H), 2.21 (s, 3H), 2.19 (dd, J = 4.9, 14.0 Hz, 1H); ^{13}C NMR (125 MHz, acetone-d_6) δ 174.1, 140.8, 138.1, 127.7, 127.0, 125.6, 125.6, 125.5, 125.4, 121.6, 121.5, 121.2, 120.5, 120.4, 120.3, 115.0, 113.1, 112.8, 109.6, 99.9, 86.1, 86.0, 53.3, 43.2, 23.3; high resolution mass spectrum (EI) m/z 412.1419 [calcd for $C_{25}H_{20}N_2O_4$ (M^+) 412.1423].

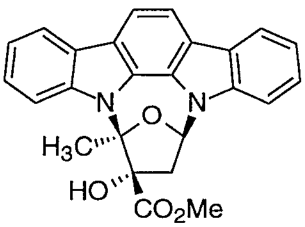
Ester (±)-21, Method B. To a solution of (±)-**28** (100 mg, 0.26 mmol) in 1:1 $MeOH/CH_2Cl_2$ (14 mL) was added copper (I) chloride (700 mg, 7.1 mmol, 27 equiv) and the mixture warmed to reflux for 6 h. Solvent was removed *in vacuo* and the resulting residue subjected to silica gel chromatography (2:1, hexane:EtOAc) to afford (±)-**21** (102 mg, 95% yield) as a colorless solid (mp 235-239 °C).



(±)-**23**, R = H
(±)-**24**, R = CH_2SCH_3

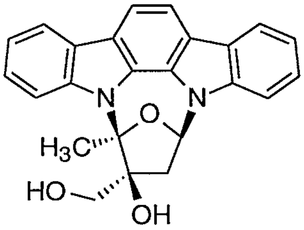
Thioether (±)-24 and Aldehyde (±)-23. To a stirred solution of diol (±)-**22** (100 mg, 0.26 mmol, 1.0 equiv) in 1:1 benzene:DMSO (1.8 mL) was added pyridinium trifluoroacetate (50 mg, 0.26 mmol, 1.0 equiv) followed by 1,3-dicyclohexylcarbodiimide (161 mg, 0.78 mmol, 3.0 equiv). The flask was quickly sealed with a septum, evacuated, and flushed with N_2 (3 x). The heterogeneous mixture was stirred for 7 h until reaction was complete as indicated by TLC. Benzene (4 mL) was added to the mixture and the 1,3-dicyclohexylurea (DCU) precipitate was filtered. The filtrate was washed with H_2O (3 x 10 mL), and the combined aqueous layers were back extracted with CH_2Cl_2 (3 x 15 mL). All organic layers were combined, dried over Na_2SO_4, and evaporated to an oily residue. A minimum amount of acetone (1 mL) was added to precipitate the remaining DCU. Filtration and evaporation gave a yellow oil. Flash chromatography (3:1 hexanes/EtOAc eluent) afforded two products. The first compound to elute was thioether **24** (15 mg, 13% yield) as a yellow foam: IR (thin film/NaCl) 3050.3 (w), 2922.7 (m), 2848.1 (w), 1725.3 (m), 1641.9 (m), 1570.4 (m), 1446.9 (s), 1302.6 (m), 1227.0 (m), 1009.4 (m), 745.1 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.16 (app.t, *J* = 8.5 Hz, 2H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.46-7.50 (comp m, 3H), 7.40 (app.t, *J* = 8.3 Hz, 1H), 7.29-7.33 (m, 2H), 7.04 (dd, *J* = 4.4, 7.2 Hz, 1H), 4.87 (d, *J* = 11.8 Hz, 1H), 4.70 (d, *J* = 11.9 Hz, 1H), 3.23 (dd, *J* = 7.3, 15.5 Hz, 1H), 2.80 (dd, *J* = 4.4, 15.6 Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.6, 137.7, 136.9, 126.5, 126.4, 125.3, 125.1, 124.7, 124.5, 121.4, 121.1, 120.8, 120.6, 120.4, 119.8, 113.1, 112.4, 112.2, 108.1, 102.3, 93.6, 86.3, 70.9, 35.4, 22.9, 14.6; high resolution mass spectrum (EI) *m/z* 442.1350 [calcd for $C_{26}H_{22}N_2O_3S$ (M^+) 442.1351].

The second compound to elute was aldehyde (±)-**23** (54 mg, 50% yield) as a white solid: mp 153-155 °C; IR (thin film/NaCl) 3426.4 (br m), 3049.7 (w), 2925.4 (m), 2853.1 (m), 1715.6 (m), 1640.0 (m), 1446.7 (s), 1302.8 (s), 1133.8 (s), 744.5 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.95 (s, 1H), 8.16 (app.t, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.24-7.49 (m, 6H), 7.08 (app.t, *J* = 5.8 Hz, 1H), 4.31 (br s, 1H), 2.71 (m, 2H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.3, 137.2, 136.9, 126.5, 126.4, 125.4, 125.2, 124.5, 124.2, 121.5, 120.9, 120.8, 120.6, 120.5, 119.9, 113.2, 112.2, 111.9, 108.1, 102.2, 88.0, 86.6, 42.6, 22.0; high resolution mass spectrum (EI) *m/z* 382.1313 [calcd for $C_{24}H_{18}N_2O_3$ (M^+) 382.1317].

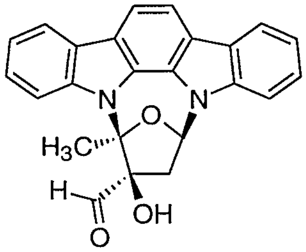


Ester (±)-25. A solution of aldehyde (±)-**23** (100 mg, 0.263 mmol, 1.0 equiv) in DMSO (10 mL) was treated sequentially with a saturated solution of NaH_2PO_4 that had been acidified to pH 2 with 1 N HCl (2.0 mL) and a solution of $NaClO_2$ (200 mg, 2.21 mmol, 8.4 equiv). The mixture was stirred for 10 min and then treated with CH_2N_2 in Et_2O until a yellow color persisted. The reaction mixture was diluted with H_2O (5 mL), extracted with Et_2O (3 x 10 mL), and the combined organic extracts dried over Na_2SO_4. Flash chromatography (1:1 EtOAc:hexanes eluent) provided ester (±)-**25** (92 mg, 85% yield) as a yellow foam: IR (thin film/NaCl) 3492.7 (br m), 3011.6 (m), 2951.6 (m), 2926.5 (m), 2851.6 (w), 1726.5 (s), 1640.2 (w), 1569.0 (w), 1440.8 (s), 1306.6 (s), 1230.9 (m), 1138.6 (s), 1093.4 (m), 743.4 (s) cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) δ 8.20 (app.t, *J* = 7.3 Hz, 2H), 8.01 (d, *J* = 8.2

Hz, 1H), 7.99 (d, $J = 8.3$ Hz, 1H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.59 (d, $J = 8.5$ Hz, 1H), 7.45 (app.t, $J = 7.5$ Hz, 1H), 7.39 (app.t, $J = 8.4$ Hz, 1H), 7.26 (app.t, $J = 7.4$ Hz, 2H), 7.23 (dd, $J = 4.5, 7.5$ Hz, 1H), 5.54 (s, 1H), 3.04 (dd, $J = 7.5, 14.9$ Hz, 1H), 2.96 (s, 3H), 2.81 (dd, $J = 4.7, 14.7$ Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 138.0, 137.0, 127.0, 126.2, 125.0, 124.9, 124.8, 124.5, 121.4, 120.8, 120.7, 120.3, 119.9, 119.7, 112.7, 112.1, 111.6, 108.2, 102.0, 85.9, 83.7, 53.4, 42.8, 21.9; high resolution mass spectrum (CI) *m/z* 413.1498 [calcd for $C_{25}H_{21}N_2O_4$ (M+H) 413.1501].

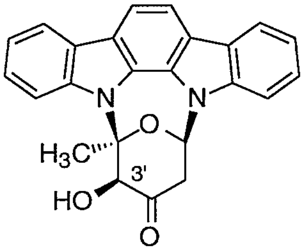


Diol (±)-26 To a stirred room temperature solution of ester (±)-**21** (1.0 g, 2.43 mmol, 1.0 equiv) in THF (24 mL) was added $LiBH_4$ (106 mg, 4.87 mmol, 2.0 equiv). After 20 min, the solvent was removed *in vacuo* to provide a white solid which was cooled to 0 °C and treated with 1.0 N HCl (50 mL). The suspension was stirred for 15 min and then extracted with CH_2Cl_2 (3 x 50 mL). The combined organic phases were dried over Na_2SO_4. Flash chromatography (1:1 hexanes:EtOAc eluent) afforded diol (±)-**26** (815 mg, 87% yield) as a white solid: mp >190 °C (dec.); IR (thin film/NaCl) 3416.8 (br s), 3052.9 (m), 3010.5 (m), 2955.4 (w), 1732.7 (w), 1640.9 (m), 1568.5 (m), 1492.6 (m), 1459.0 (s), 1441.4 (s), 1309.0 (s), 1233.1 (s), 1031.9 (s), 741.0 (s) cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) δ 8.18 (d, $J = 7.6$ Hz, 1H), 8.15 (d, $J = 7.8$ Hz, 1H), 7.96 (s, 2H), 7.89 (d, $J = 8.5$ Hz, 1H), 7.65 (d, $J = 8.1$ Hz, 1H), 7.42 (app.t, $J = 7.6$ Hz, 1H), 7.36 (app.t, $J = 8.2$ Hz, 1H), 7.25 (app.t, $J = 7.6$ Hz, 1H), 7.23 (app.t, $J = 7.4$ Hz, 1H), 6.91 (dd, $J = 5.2, 7.4$ Hz, 1H), 4.57 (s, 1H), 4.18 (app.t, $J = 5.9$ Hz, 1H), 4.06 (dd, $J = 5.4, 11.1$ Hz, 1H), 3.90 (dd, $J = 7.1, 11.1$ Hz, 1H), 3.30 (dd, $J = 7.6, 13.8$ Hz, 1H), 2.23 (dd, $J = 5.1, 13.8$ Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, acetone-d_6) δ 140.2, 137.4, 127.6, 126.3, 125.4, 125.0, 124.6, 124.6, 120.7, 120.6, 119.9, 119.5, 114.6, 112.2, 112.0, 108.8, 100.1, 84.2, 83.8, 65.5, 40.6, 21.5; high resolution mass spectrum (EI) *m/z* 384.1472 [calcd for $C_{24}H_{20}N_2O_3$ (M^+) 384.1474].

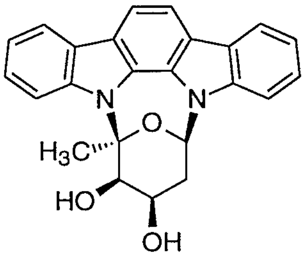


Aldehyde (±)-27. To a stirred solution of diol (±)-**26** (500 mg, 1.3 mmol, 1.0 equiv) in 1:1 benzene:DMSO (8.7 mL) was added pyridinium trifluoroacetate (250 mg, 1.3 mmol, 1.0 equiv) followed by 1,3-dicyclohexylcarbodiimide (810 mg, 3.9 mmol, 3.0 equiv). The flask was quickly sealed with a septum, evacuated, and flushed with N_2 (3 x). The heterogeneous mixture was stirred for 7 h until reaction was complete as indicated by TLC. Benzene (15 mL) was added to the mixture and the 1,3-dicyclohexylurea (DCU) precipitate was filtered. The filtrate was washed with H_2O (3 x 20 mL), and the combined aqueous layers were back extracted with CH_2Cl_2 (3 x 30 mL). All organic layers were combined, dried over Na_2SO_4, and evaporated to an oily residue. A minimum amount of acetone (2 mL) was added to precipitate the remaining DCU. Filtration and evaporation gave a yellow oil, which was purified by flash chromatography (3:1 hexanes:EtOAc eluent) to afford aldehyde (±)-**27** (373 mg, 73% yield, 63% yield 2 steps) as a yellow powder: mp >225 °C (dec.); IR (thin film/NaCl) 3486.7 (br m), 3054.6 (m), 3007.7 (m), 2945.3 (m), 2843.4 (w), 1723.9 (m), 1641.8 (m), 1568.6 (m), 1458.7 (m), 1441.1 (s), 1309.2 (s), 1232.5 (s), 1128.8 (m), 1004.2 (m), 741.7 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.99 (app.t, *J* = 7.3 Hz, 2H), 7.78 (s, 2H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.29 (app.t, *J* = 7.4 Hz, 1H), 7.24 (app.t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.17 (app.t, *J* = 7.9 Hz, 1H), 7.15 (app.t, *J* = 7.2 Hz, 1H), 6.59 (dd, *J* = 5.0, 7.4 Hz, 1H), 3.08 (s, 1H), 2.76 (dd, *J* = 7.6, 14.6 Hz, 1H), 1.99 (s, 3H), 1.83 (dd, *J* = 5.0, 14.7 Hz, 1H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 199.4, 139.3, 136.9, 126.3, 126.3, 125.1, 124.7, 124.1, 121.2, 121.1, 120.8, 120.3, 120.3, 119.9, 113.1, 112.9, 112.2, 108.0, 97.7, 87.7, 84.0, 39.7, 23.0; high resolution mass spectrum (EI) m/z 382.1319 [calcd for $C_{24}H_{18}N_2O_3$ (M^+) 382.1317].

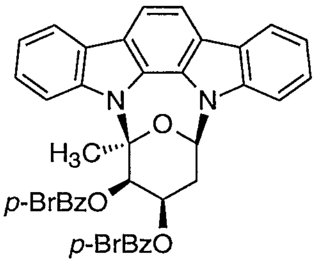


Hydroxy ketone (±)-28. A suspension of aldehyde (±)-**27** (75 mg, 0.196 mmol, 1.0 equiv) in Et_2O (5.0 mL) was treated with $BF_3 \bullet OEt_2$ (27 µL, 0.220 mmol, 1.1 equiv),and stirred vigorously for 6 h. After addition of CH_2Cl_2 (25 mL) to solubilize the suspension, the resulting solution was evaporated onto SiO_2 (100 mg) and chromatographed (2:1 hexanes:EtOAc eluent) to provide ketone (±)-**28** (45 mg, 60% yield) as a white powder: mp 235-239 °C (dec.); IR (thin film/NaCl) 3328.6 (br m), 3048.0 (w), 2923.7 (m), 2852.1 (w), 1731.4 (s), 1637.4 (m), 1441.5 (s), 1395.3 (m), 1312.0 (s), 1130.1 (m), 740.8 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 7.7 Hz, 1H), 8.10 (d, J = 7.7 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.43 (app.t, J = 7.7 Hz, 1H), 7.39 (app.t, J = 7.8 Hz, 1H), 7.32 (app.t, J = 7.4 Hz, 1H), 7.28 (app.t, J = 7.5 Hz, 1H), 7.25 (d, J = 8.1 Hz, 1H), 7.06 (d, J = 7.3 Hz, 1H), 4.89 (d, J = 6.0 Hz, 1H), 3.55 (dd, J = 7.5, 14.3 Hz, 1H), 3.49 (d, J = 6.5 Hz, 1H), 2.99 (d, J = 14.4 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.8, 140.2, 136.3, 126.4, 125.7, 125.4, 125.1, 124.8, 124.6, 121.4, 120.8, 120.4, 120.2, 119.8, 115.2, 112.7, 112.4, 112.1, 107.9, 100.3, 84.0, 81.6, 44.7, 29.5; high resolution mass spectrum (EI) m/z 382.1315 [calcd for $C_{24}H_{18}N_2O_3$ (M^+) 382.1317].



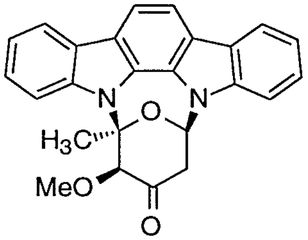
Diol (±)-29. To a stirred room temperature solution of ketone (±)-**28** (100 mg, 0.26 mmol, 1.0 equiv) in 1:1 MeOH: CH_2Cl_2 (10 mL) was added $NaBH_4$ (27 mg, 0.70

mmol, 2.7 equiv). After 5 min solvent was removed under reduced pressure to afford a white solid which was cooled to 0 °C and then treated with 1.0 N HCl (10 mL). After 5 min at 0 °C, the mixture was warmed to room temperature, stirred for 15 min at 25 °C, and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried with Na_2SO_4 and chromatographed (2:1 hexanes:EtOAc eluent) to afford diol (±)-**29** (95 mg, 95% yield) as a white solid: mp 235-238 °C (dec.); IR (thin film/NaCl) 3529.6 (br m), 3043.9 (m), 2930.2 (w), 1642.5 (m), 1564.1 (m), 1445.1 (s), 1314.4 (s), 1230.1 (m), 1129.9 (m), 1073.3 (m), 739.3 (s), 694.3 (m) cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) δ 8.16 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.40 (app.t, *J* = 7.6 Hz, 1H), 7.31 (ddd, *J* = 1.3, 7.0, 11.4 Hz, 1H), 7.24 (app.t, *J* = 7.3 Hz, 1H), 7.17 (app.t, *J* = 7.2 Hz, 1H), 6.71 (dd, *J* = 1.0, 5.8 Hz, 1H), 4.21 (m, 1H), 3.99 (dd, *J* = 3.3, 9.1 Hz, 1H), 3.59 (br s, 1H), 2.80 (d, *J* = 13.6 Hz, 1H), 2.74 (ddd, *J* = 3.0, 5.7, 14.9 Hz, 1H), 2.63 (ddd, *J* = 1.0, 3.3, 15.0 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 139.4, 136.1, 127.5, 126.6, 125.2, 124.2, 123.8, 123.7, 119.9, 119.1, 118.8, 118.5, 118.3, 115.1, 111.3, 110.5, 108.7, 92.2, 79.5, 73.3, 64.0, 34.4, 29.5; high resolution mass spectrum (EI) *m/z* 384.1469 [calcd for $C_{24}H_{20}N_2O_3$ (M^+) 384.1474].

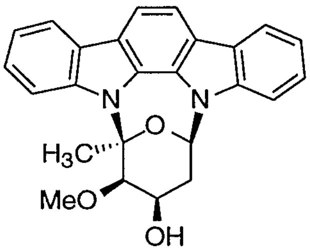


Bis *p*-bromobenzoate (±)-30. Diol (±)-**29** (30 mg, 0.078 mmol, 1.0 equiv), *p*-bromobenzoyl chloride (36 mg, 0.164 mmol, 2.1 equiv), Et_3N (23 μL, 0.164 mmol, 2.1 equiv), and 4-dimethylaminopyridine (2 mg, 0.016 mmol, 0.1 equiv) were heated to reflux in CH_2Cl_2 (1.0 mL) for 10 min. The reaction mixture was adsorbed onto SiO_2 and chromatographed (2:1 hexanes:EtOAc eluent) to afford (±)-**30** (45 mg, 77%

yield) as a white solid which when crystallized from $CHCl_3$/MeOH provided crystals suitable for X-ray analysis: mp 198-200 °C; IR (thin film/NaCl) 3044.9 (w), 2928.5 (w), 1725.4 (s), 1642.6 (w), 1589.4 (s), 1398.4 (m), 1258.6 (s), 1230.5 (m), 1091.8 (br s), 1009.9 (s), 844.4 (w), 739.5 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.5 Hz, 1H), 8.13 (d, J = 9.3 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H), 7.44 (app.t, J = 8.4 Hz, 1H), 7.42 (app.t, J = 7.5 Hz, 1H), 7.30 (s, 4H), 7.27 (m, 1H), 7.26 (app.t, J = 8.2 Hz, 1H), 7.21 (app.t, J = 7.4 Hz, 1H), 7.10 (ddd, J = 1.2, 7.2, 8.4 Hz, 1H), 7.00 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 5.5 Hz, 1H), 6.08 (d, J = 8.3 Hz, 2H), 5.85 (m, 1H), 5.84 (s, 1H), 2.94 (ddd, J = 3.6, 5.7, 15.4 Hz, 1H), 2.78 (dd, J = 2.8, 15.5 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 164.8, 138.6, 136.3, 131.8, 131.6, 131.1, 130.5, 129.0, 127.8, 127.1, 127.0, 126.8, 126.0, 125.0, 124.6, 124.5, 121.0, 120.7, 120.2, 120.0, 119.8, 119.8, 114.1, 112.5, 111.5, 107.7, 90.0, 79.6, 73.3, 63.7, 32.4, 30.2; high resolution mass spectrum (EI) m/z 748.0214 [calcd for $C_{38}H_{26}N_2O_5Br_2$ (M^+) 748.0208].



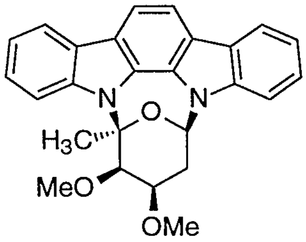
Methoxy ketone (±)-31. Montmorillonite clay K-10 (1.2 g) was mixed with trimethylorthoformate (1.78 mL, 16.3 mmol, 14.8 equiv) and immediately rinsed (3 mL $CHCl_3$) into a stirred solution of aldehyde (±)-**27** (414 mg, 1.1 mmol, 1.0 equiv) in $CHCl_3$ (11 mL). After approximately 0.5 h formation of the dimethyl acetal **33** was complete as indicated by TLC (3:1 hexanes:EtOAc). The reaction mixture was filtered and the filtrate evaporated *in vacuo*. The residue was dissolved in diethyl ether (110 mL) under N_2 and treated with $BF_3 \bullet OEt_2$ (2.85 mL, 23.1 mmol, 21.0 equiv). The resultant mixture was stirred for 4 days at 25 °C. After this time, Et_3N (6.1 mL) and CH_2Cl_2 (100 mL) were added and the product was adsorbed onto silica gel *in vacuo*. Flash chromatography (2:1 hexanes:EtOAc eluent) provided methoxy ketone (±)-**31** (214 mg, 50% yield) as a yellow foam: mp 275-280 °C (dec.); IR (thin film/NaCl) 3046.6 (br m), 3003.8 (br w), 2927.9 (m), 2835.6 (m), 1736.6 (s), 1640.5 (m), 1565.8 (m), 1492.7 (m), 1442.9 (s), 1311.5 (s), 1144.3 (m), 1126.1 (s), 740.2 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 8.21 (d, *J* = 7.7 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.46 (td, *J* = 1.0, 7.4 Hz, 1H), 7.37 (td, *J* = 1.1, 7.7 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.30 (app.t, *J* = 7.6 Hz, 1H), 7.23 (app.t, *J* = 7.4 Hz, 1H), 5.02 (s, 1H), 3.94 (dd, *J* = 7.2, 13.7 Hz, 1H), 3.39 (s, 3H), 2.62 (d, *J* = 13.9 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 199.8, 139.4, 135.7, 125.0, 124.8, 124.5, 124.1, 124.0, 120.0, 119.8, 119.4, 119.2, 114.9, 112.1, 111.3, 109.2, 99.0, 88.2, 84.4, 58.9, 45.4, 29.2; high resolution mass spectrum (EI) *m/z* 396.1474 [calcd for $C_{25}H_{20}N_2O_3$ (M^+) 396.1474].



Alcohol (±)-37. Method A. To a stirred solution of ketone (±)-**31** (12 mg, 0.03 mmol, 1.0 equiv) in 1:1 MeOH: CH_2Cl_2 (1.0 mL) was added $NaBH_4$ (3 mg, 0.08 mmol, 2.7 equiv) at room temperature. After 5 min the solvent was removed *in vacuo* to afford a white solid which was cooled to 0 °C and treated with 1.0 N HCl (1 mL). After 5 min at 0 °C, the mixture was warmed to room temperature, stirred for 15 min at 25 °C, and extracted with CH_2Cl_2 (3 x 1 mL). The combined organic layers were dried with Na_2SO_4 and chromatographed (2:1 hexanes:EtOAc eluent) to afford alcohol (±)-**37** (12 mg, 95% yield) as a white solid: mp 340-344 °C (dec.); IR (thin film/NaCl) 3528.3 (br m), 3048.1 (m), 3000.2 (m), 2928.4 (m), 1643.7 (m), 1564.8 (m), 1493.3 (m), 1445.1 (s), 1344.4 (m), 1311.6 (s), 1231.2 (s), 1109.5

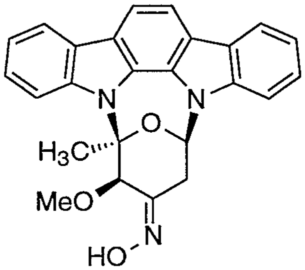
(br s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 7.7 Hz, 1H), 8.11 (d, J = 7.7 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.39 (td, J = 1.0, 8.1 Hz, 1H), 7.35 (ddd, J = 0.14, 7.1, 8.4 Hz, 1H), 7.25 (m, 3H), 6.54 (d, J = 5.6 Hz, 1H), 4.34 (m, 1H), 3.66 (d, J = 3.0 Hz, 1H), 3.53 (s, 3H), 2.71 (dd, J = 3.5, 14.9 Hz, 1H), 2.45 (m, 1H), 2.30 (s, 3H), 1.66 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 136.6, 128.3, 127.2, 126.5, 126.2, 124.8, 124.4, 123.9, 120.5, 120.3, 119.6, 119.3, 114.9, 112.1, 110.9, 107.6, 90.6, 83.1, 79.7, 60.5, 57.4, 33.7, 29.9; high resolution mass spectrum (EI) m/z 398.1633 [calcd for $C_{25}H_{22}N_2O_3$ (M^+) 398.1630].

Alcohol (±)-37. Method B. To a stirred suspension of NaH (6.1 mg of a 60% dispersion in mineral oil, 0.15 mmol, 1.1 equiv) in THF (1.0 mL) was added a solution of alcohol (±)-**29** (55 mg, 0.143 mmol, 1.0 equiv) in THF (5 mL). The resulting mixture was stirred for 10 min with the visible evolution of gas and for an additional 15 min thereafter. Addition of MeI (9.0 μL, 0.15 mmol, 1.1 equiv) produced a single product as evidenced by TLC (5:1 hexanes:acetone). After approximately 50 min the reaction was quenched by the sequential addition of 1.0 N HCl (1.0 mL) and H_2O (2.0 mL). Extraction of the solution with CH_2Cl_2 (3 x 10 mL), drying over Na_2SO_4, evaporation to a residue *in vacuo*, and chromatography (5:1 hexanes:acetone eluent) provided methyl ether (±)-**37** (42 mg, 70% yield) as a yellow foam.



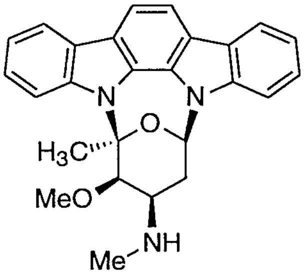
Bis Methyl ether (±)-35, Method A. A stirred room temperature solution of alcohol (±)-**37** (19 mg) in DMSO (3 mL) was treated with excess MeI (5-10 equiv) and KOH (5-10 equiv) for 5 min. After this time, the reaction was diluted with H_2O (5 mL) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over Na_2SO_4, and evaporated. Purification by flash chromatography (1:1 hexanes:EtOAc eluent) provided bis-methyl ether (±)-**35** (20 mg, 95% yield) as a yellow foam: mp 218-224 °C (dec.); IR (thin film/NaCl) 3048.0 (m), 3003.5 (m), 2930.1 (m), 2829.9 (m), 1642.3 (m), 1565.2 (m), 1492.8 (w), 1460.9 (s), 1444.8 (s), 1396.0 (s), 1314.4 (s), 1230.2 (s), 1118.9 (s), 1035.8 (m), 740.7 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.9 Hz, 1H), 8.09 (d, *J* = 7.0 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.41 (app.t, *J* = 7.3 Hz, 1H), 7.32 (ddd, *J* = 1.2, 7.2, 8.4 Hz, 1H), 7.28 (app.t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.20 (app.t, *J* = 7.4 Hz, 1H), 6.57 (d, *J* = 5.1 Hz, 1H), 3.99 (dt, *J* = 3.0, 6.4 Hz, 1H), 3.75 (d, *J* = 2.9 Hz, 1H), 3.52 (s, 3H), 2.85 (ddd, *J* = 0.9, 3.9, 15.0 Hz, 1H), 2.38 (s, 3H), 2.33 (ddd, *J* = 2.7, 5.5, 14.9 Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 136.3, 127.7, 126.6, 126.0, 124.9, 124.2, 124.0, 120.5, 119.6, 119.2, 119.0, 114.6, 111.4, 111.2, 107.3, 91.3, 84.3, 80.0, 68.6, 57.5, 55.7, 30.3, 29.9; high resolution mass spectrum (EI) *m/z* 412.1784 [calcd for $C_{26}H_{24}N_2O_3$ (M^+) 412.1787].

Bis Methyl Ether (±)-35, Method B. A procedure identical to that describe above for the alkylation of **37** was utilized for the conversion of diol (±)-**29** (20 mg) to (±)-**35** in 93% yield.



Oxime (±)-36. A suspension of ketone (±)-**31** (30 mg, 0.08 mmol, 1.0 equiv), hydroxylamine hydrochloride (17 mg, 0.24 mmol, 3.0 equiv), and NaOAc (20 mg, 0.24 mmol, 3.0 equiv) in 50% aqueous EtOH (2.0 mL) was heated gently to reflux for 30 min. After cooling to room temperature, the solvent was removed *in vacuo* and the derived residue was purified by flash chromatography (2:1 hexanes:EtOAc eluent) to provide oxime (±)-**36** (27 mg, 85% yield) as a yellow powder: mp >280

°C (dec.); IR (thin film/NaCl) 3249.5 (br m), 2918.3 (s), 2848.4 (s), 1728.1 (m), 1640.2 (m), 1443.1 (s), 1398.1 (m), 1312.0 (m), 1124.5 (s), 740.7 (s) cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6) δ 10.43 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 7.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 1H), 7.44 (app.t, *J* = 7.6 Hz, 1H), 7.34 (app.t, *J* = 7.7 Hz, 1H), 7.27 (app.t, *J* = 7.5 Hz, 1H), 7.20 (app.t, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 5.5 Hz, 1H), 4.70 (s, 1H), 3.61 (d, *J* = 14.1 Hz, 1H), 3.42 (s, 3H), 2.97 (dd, *J* = 5.7, 14.3 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 145.3, 139.3, 135.9, 126.0, 125.1, 124.9, 124.6, 124.2, 124.0, 120.0, 119.6, 119.4, 119.1, 119.1, 115.0, 111.8, 111.0, 109.1, 95.9, 83.7, 82.2, 58.3, 29.7, 28.4; high resolution mass spectrum (EI) *m/z* 411.1582 [calcd for $C_{25}H_{21}N_3O_3$ (M^+) 411.1583].

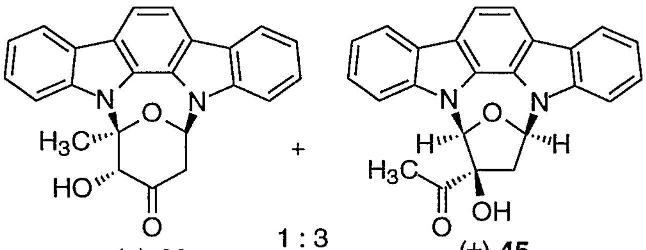


Amine (±)-38. A mixture of oxime (±)-**36** (20 mg, 0.049 mmol, 1.0 equiv) and PtO_2 (5 mg) in a 60% aqueous acetic acid (6.0 mL) was placed in a flasked capped with a H_2 filled balloon. The reaction was monitored by TLC (1:1 hexanes:EtOAc) and upon completion (2 h) was filtered through celite. The filtrate was evaporated *in vacuo* and the residue was dissolved in 1.0 N HCl (4.0 mL) and washed with EtOAc (1 x 4.0 mL). The aqueous layer was rendered basic with 3.0 N NaOH and then extracted with EtOAc (3 x 5.0mL). The combined organic layers were dried over Na_2SO_4 and evaporated to a residue which was used without further purification.

An analytical sample of the derived primary amine could be obtained by preparative TLC of the above residue (5% MeOH/CH_2Cl_2 eluent): mp >225 °C (dec.); IR (thin film/NaCl) 3373.6 (br w), 3048.2 (br w), 2926.7 (br m), 2851.2

(br w), 1641.4 (m), 1563.9 (m), 1492.2 (m), 1459.0 (s), 1444.2 (s), 1314.0 (s), 1231.1 (s), 1110.2 (s), 741.3 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.43 (app.t, J = 7.6 Hz, 1H), 7.38 (app.t, J = 7.6 Hz, 1H), 7.27 (m, 3H), 6.55 (dd, J = 1.0, 5.5 Hz, 1H), 3.71 (d, J = 3.7 Hz, 1H), 3.65 (br m, 1H), 3.41 (s, 3H), 2.64 (dt, J = 5.3, 14.6 Hz, 1H), 2.58 (ddd, J = 1.1, 3.4, 14.4 Hz, 1H), 2.3 (s, 3H), 1.24 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 136.8, 126.8, 126.1, 125.8, 124.9, 124.6, 124.2, 120.6, 120.5, 119.8, 119.7, 119.5, 119.4, 114.7, 112.2, 111.4, 108.0, 91.2, 84.0, 80.3, 57.6, 42.7, 34.5, 29.7; high resolution mass spectrum (EI) m/z 397.1789 [calcd for $C_{25}H_{23}N_3O_2$ (M^+) 397.1790].

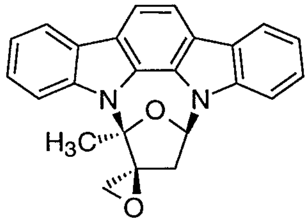
The derived residue was dissolved in THF (2.0 mL) and treated with an excess of formic acetic anhydride (3 equiv, prepared by treatment of 1.0 equiv acetic anhydride with 1.2 equiv formic acid followed by reflux for 2 h) in THF. TLC analysis showed rapid formation of a less polar substance. The solvent was evaporated with a stream of N_2 followed by high vacuum (ca. 1 torr) for 15 min. The derived residue was dissolved in THF (2.0 mL), cooled to 0 °C, and treated with BH_3•DMS (61 μL of a 2.0 N solution in toluene). The solution was heated to reflux for 2 h and then cooled to 0 °C. Methanolic HCl (4.0 mL) was added and the solution was refluxed for an additional hour. After cooling to room temperature, volatiles were removed *in vacuo* leaving a solid residue to which was added 1.0 N NaOH (1.5 mL). The mixture was extracted with EtOAc (3 x 3.5 mL) and the combined organic layers were dried over Na_2SO_4. Purification of the residue by flash chromatography (10% MeOH/CH_2Cl_2 eluent) provided methyl amine (±)-**38** (14 mg, 70% yield 2 steps) as a white powder: mp 238-242 °C (dec.); IR (thin film/NaCl) 3344.1 (w), 3043.9 (m), 3000.7 (m), 2929.4 (m), 2850.6 (m), 2796.2 (m), 1642.5 (m), 1562.9 (m), 1442.1 (s), 1396.0 (m), 1341.5 (m), 1311.0 (s), 1232.2 (s), 1111.4 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 1H), 8.16 (d, *J* = 7.3 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.44 (td, *J* = 1.0, 7.7 Hz, 1H), 7.39 (ddd, *J* = 1.3, 7.1, 8.4 Hz, 1H), 7.31 (app.t, *J* = 7.7 Hz, 1H), 7.27 (app.t, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 6.51 (dd, *J* = 1.3, 6.1 Hz, 1H), 3.83 (d, *J* = 3.5 Hz, 1H), 3.30 (s, 3H), 3.29 (dd, *J* = 4.1, 4.7 Hz, 1H), 2.63 (ddd, *J* = 1.5, 4.7, 14.5 Hz, 1H), 2.38 (ddd, *J* = 4.0, 6.1, 14.6 Hz, 1H), 2.34 (s, 3H), 1.69 (s, 3H), 0.84 (br s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2, 136.6, 128.2, 127.3, 126.0, 124.7, 124.2, 123.8, 120.3, 120.0, 119.5, 119.2, 119.0, 119.0, 114.2, 111.7, 110.8, 107.5, 91.3, 84.0, 80.5, 57.5, 50.8, 33.4, 30.6, 29.7; high resolution mass spectrum (EI) *m/z* 411.1944 [calcd for $C_{26}H_{25}N_3O_2$ (M^+) 411.1947].



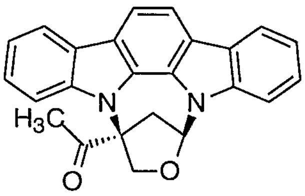
(±)-**44** (±)-**45**

Ketones (±)-44 and (±)-45. To a suspension of aldehyde (±)-**23** (56 mg, 0.147 mmol, 1.0 equiv) in Et_2O (15.0 mL) was added $BF_3{\bullet}OEt_2$ (20 μL, 0.161 mmol, 1.1 equiv). The mixture was stirred vigorously for 7 h and then treated with CH_2Cl_2 (25 mL) to solubilize the suspension. The resulting solution was adsorbed onto silica *in vacuo* and chromatographed (3:1 hexanes:EtOAc eluent) to provide two products. The first compound to elute, hydroxy ketone (±)-**44** (12 mg, 21% yield), was isolated as a yellow foam: IR (thin film/NaCl) 3461.9 (br m), 2924.5 (m), 1731.8 (s), 1570.7 (m), 1447.5 (m), 1389.4 (m), 1307.5 (s), 1227.4 (s), 1133.2 (s), 747.2 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 4.8 Hz, 1H), 8.17 (d, *J* = 4.7 Hz, 1H), 7.98 (s, 2H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.45-7.51 (comp m, 2H), 7.32-7.40 (comp m, 3H), 6.79 (dd, *J* = 4.8, 6.1 Hz, 1H), 5.13 (s, 1H), 3.65 (s, 1H), 3.41 (dd, *J* = 6.3, 15.9 Hz, 1H), 3.36 (dd, *J* = 4.7, 15.9 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.0, 138.4, 137.2, 126.2, 125.9, 125.8, 125.5, 125.4, 125.3, 121.8, 121.2, 120.9, 120.6, 120.5, 120.4, 113.2, 112.8, 111.7, 108.2, 99.6, 83.8, 78.9, 42.6, 23.7; high resolution mass spectrum (EI) *m/z* 382.1319 [calcd for $C_{24}H_{18}N_2O_3$ (M^+) 382.1317].

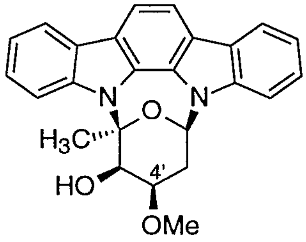
The second compound to elute, ketone (±)-**45** (36 mg, 64% yield), was isolated as a white solid: mp >230 °C (dec.); IR (thin film/NaCl) 3458.1 (br m), 3053.6 (w), 2924.4 (m), 2855.9 (m), 1706.1 (s), 1655.1 (m), 1568.7 (m), 1447.9 (s), 1404.9 (s), 1342.9 (s), 1036.7 (m), 747.1 (s) cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, 315 K) δ 8.19 (d, *J* = 7.9 Hz, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.45 (app.t, *J* = 7.6 Hz, 1H), 7.44 (app.t, *J* = 8.2 Hz, 1H), 7.36 (dd, *J* = 3.0, 7.5 Hz, 1H), 7.24-7.28 (m, 2H), 6.93 (s, 1H), 6.71 (s, 1H), 2.81 (dd, *J* = 7.5, 14.7 Hz, 1H), 2.47 (dd, *J* = 2.8, 14.8 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 206.0, 137.5, 137.0, 125.3, 124.9, 124.9, 124.3, 124.0, 123.9, 120.3, 120.3, 120.2, 119.7, 119.7, 119.5, 112.3, 112.2, 109.5, 109.4, 93.0, 87.8, 87.6, 42.8, 26.7; high resolution mass spectrum (EI) *m/z* 382.1312 [calcd for $C_{24}H_{18}N_2O_3$ (M^+) 382.1317].



Epoxide (±)-46. To a solution of diol (±)-**26** (100 mg, 0.26 mmol, 1.0 equiv) and *p*-toluene sulfonyl chloride (52 mg, 0.27mmol, 1.05 equiv) in THF (2.6 mL) was added powdered KOH (36 mg, 0.65 mmol, 2.5 equiv) followed by *n*-Bu_4NBr (8 mg, 0.03 mmol, 0.1 equiv). The reaction mixture was stirred for 1 h, and solvent was removed *in vacuo*. Purification by flash chromatography (3:1→1:1 hexanes:EtOAc) provided epoxide **46** (86 mg, 90% yield) as a white foam: mp >260 °C (dec.); IR (thin film/NaCl) 3049.6 (w), 3010.0 (w), 2947.3 (br w), 1638.2 (m), 1567.7 (m), 1445.6 (s), 1347.0 (m), 1307.5 (s), 1225.4 (m), 1026.0 (m), 744.9 (s) cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.21 (app.t, *J* = 8.2 Hz, 2H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.45 (app.t, *J* = 7.6 Hz, 1H), 7.36 (app.t, *J* = 7.7 Hz, 1H), 7.28 (app.t, *J* = 8.2 Hz, 1H), 7.24 (app.t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 6.0 Hz, 1H), 3.28 (dd, *J* = 6.1, 14.9 Hz, 1H), 3.23 (d, *J* = 3.8 Hz, 1H), 2.98 (d, *J* = 4.2 Hz, 1H), 2.41 (s, 3H), 1.90 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 138.4, 136.5, 126.8, 125.2, 125.1, 124.9, 123.9, 120.4, 120.2, 120.1, 119.9, 119.6, 119.5, 112.6, 111.7, 111.6, 109.3, 96.7, 84.7, 66.5, 50.4, 37.4, 24.6; high resolution mass spectrum (EI) *m/z* 366.1363 [calcd for $C_{24}H_{18}N_2O_2$ (M$^+$) 366.1368].

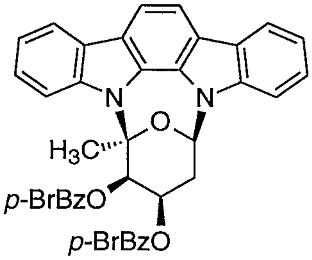


Ketone (±)-47. A solution of epoxide (±)-**46** (50 mg, 0.14 mmol, 1.0 equiv) in $CDCl_3$ (13.7 mL) was treated with $BF_3 \bullet OEt_2$ (18μL, 0.15 mmol, 1.05 equiv) and stirred at room temperature for 15 h. Following removal of solvent *in vacuo*, flash chromatography provided ketone **47** (47 mg, 92% yield) as a white foam: mp 180-183°; IR (thin film/NaCl) 3420.6 (br w), 3051.0 (w), 2924.3 (w), 1927.2 (w), 1717.8 (s), 1638.0 (m), 1568.9 (m), 1446.0 (s), 1347.6 (s), 1310.8 (s), 1219.7 (s), 1071.7 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.30-7.47 (comp m, 4H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 7.4 Hz, 1H), 4.89 (d, *J* = 9.7 Hz, 1H), 4.01 (dd, *J* = 0.9, 9.8 Hz, 1H), 3.17 (d, *J* = 13.6 Hz, 1H), 2.97 (dd, *J* = 7.5, 13.6 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 138.6, 138.6, 127.1, 125.6, 125.3, 125.3, 124.5, 121.8, 121.6, 120.7, 120.5, 120.4, 120.3, 113.0, 112.7, 109.5, 108.3, 83.1, 75.7, 71.9, 45.6, 27.6; high resolution mass spectrum (EI) *m/z* 366.1363 [calcd for $C_{24}H_{18}N_2O$ (M^+) 366.1368].



Ether (±)-50. A solution of diol (±)-**29** (38 mg, 0.10 mmol, 1.0 equiv) and $Bu_2Sn(OMe)_2$ (25 μL, 0.11 mmol, 1.1 equiv) in benzene (5.0 mL) was heated to reflux with azeotropic removal of H_2O (Dean-Stark apparatus) for 1 h. The solvent was removed *in vacuo*, followed by addition of CH_3CN (5.0 mL), MeI (6.8 μL, 0.11 mmol, 1.1 equiv), and Ag_2O (25 mg, 0.11, 1.1 equiv). The resulting mixture was heated at reflux over 4 h, diluted with H_2O (3 mL), and extracted with CH_2Cl_2 (3 x 2 mL). The combined organic extracts were dried over Na_2SO_4 and purified by flash chromatography (5:1 hexanes:acetone) to provide recovered diol (±)-**29** (8 mg) and ether (±)-**50** (6 mg, 15% yield) as a yellow foam: mp 213-217 °C (dec.); IR (thin film/NaCl) 3535.7 (br w), 3413.5 (w), 2963.2 (m), 2924.4 (s), 2853.7 (m), 1437.1 (m), 1314.6 (s), 735.0 (m) cm^{-1}; ^1H NMR (500 MHz, acetone-d_6) δ 8.18 (d, *J* = 7.0 Hz, 1H), 8.11 (d, *J* = 7.7 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.42 (app.t, *J* = 7.3 Hz, 1H), 7.30 (app.t, *J* = 8.4 Hz, 1H), 7.25 (app.t, *J* = 7.7 Hz, 1H), 7.17 (app.t, *J* = 7.7 Hz, 1H), 6.72 (d, *J* = 4.7 Hz, 1H), 4.27 (dd, *J* = 3.3, 10.0 Hz, 1H), 3.80 (m, 2H), 2.88 (ddd, *J* = 1.3, 3.6, 15.4 Hz, 1H), 2.58 (ddd, *J* = 2.8, 5.5, 15.4 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, acetone-d_6) δ 140.5, 137.0, 128.5, 126.6, 125.1, 125.1, 124.5, 120.7, 119.9, 119.8, 119.5, 115.7, 112.1, 111.4, 108.9, 93.3, 80.6, 74.7, 74.6, 74.1, 55.5, 30.1; high resolution mass spectrum (EI) *m/z* 398.1630 [calcd for $C_{25}H_{22}N_2O_3$ (M^+) 398.1630].

X-RAY CHRYSTALLOGRAPHY REPORT FOR INDOLOCARBAZOLE (±)-**30**



EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{38.5}H_{26}N_2O_{6.5}$Br2
Formula Weight	780.45
Crystal Color/Habit	colorless needle
Crystal Dimensions (mm)	0.08 X 0.11 X 0.30
Crystal System	monoclinic
No. Reflections Used for Unit Cell Determination (2θ range)	25(10.2-18.0°)
Lattice Parameters:	
a	30.141 (5)Å
b	15.689 (2)Å
c	14.803 (3)Å
β	91.45 (2)°
V	6998 (3)Å^3
Space Group	C2/c (#15)
Z value	8
Dcalc	1.481 g/cm^3
F000	3144
μ(MoKα)	23.41 cm-1

B. Intensity Measurements

Diffractometer	Enraf-Nonius CAD-4
Radiation	MoKα (λ = 0.71069 Å)
Temperature	23°C
Attenuator	Zr foil (factor = 20.4)
Take-off Angle	2.8°
Detector Aperture	2.0-2.5 mm hor/2.0 mm vert.
Crystal to Detector Distance	21 cm
Scan Type	ω-2θ
Scan Rate	1.0 - 16.5°/min (in omega)

Scan Width	(0.95 + 0.83 tanθ)°
2θmax	52.6°
No. of Reflections Measured	
Total:	7660
Unique:	7369 (Rint = .041)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.72 - 1.51) Decay (-27.00% decline)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\lvert Fo\rvert - \lvert Fc\rvert)^2$
Least-squares Weights	$4Fo^2/\sigma^2(Fo^2)$
p-factor	0.03
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I>3.00\sigma(I)$)	2877
No. Variables	436
Reflection/Parameter Ratio	6.60
Residuals:	R; Rw 0.077; 0.080
Goodness of Fit Indicator	4.61
Max Shift/Error in Final Cycle	0.00
Maximum Peak in Final Diff. Map	1.21 e-/Å^3
Minimum Peak in Final Diff. Map	-1.23 e-/Å^3

Positional parameters and B(eq) for indolocarbazole (±)-**30**

atom	x	y	z	B(eq)
Br1	0.40970(6)	0.3656(1)	0.2089(1)	5.95(8)
Br2	0.51935(5)	0.7625(2)	0.6198(1)	8.0(1)
O1	0.2819(2)	0.7003(4)	0.3297(4)	2.5(3)
O2	0.3088(3)	0.6663(5)	0.4695(5)	3.9(4)

O2'	0.2427(2)	0.8807(4)	0.2135(4)	2.3(3)
O3	0.3263(2)	0.8463(5)	0.3919(4)	2.7(3)
O4	0.3024(3)	0.8720(5)	0.5334(5)	3.0(3)
N11	0.3181(3)	0.8396(5)	0.2080(5)	2.5(4)
N12	0.2267(3)	0.7433(5)	0.1596(5)	2.4(4)
C1	0.1527(4)	0.6739(8)	0.1322(7)	3.5(6)
C1'	0.2939(4)	0.9828(7)	0.2587(8)	3.2(5)
C2	0.1312(4)	0.6120(8)	0.0805(8)	3.8(6)
C2'	0.2843(4)	0.8870(6)	0.2577(7)	2.5(5)
C3	0.1547(5)	0.5632(7)	0.0199(8)	4.1(7)
C3'	0.2811(3)	0.8535(7)	0.3578(6)	2.3(5)
C4	0.1995(4)	0.5732(7)	0.0079(7)	3.1(6)
C4A	0.2223(4)	0.6356(6)	0.0592(6)	2.4(5)
C4B	0.2670(4)	0.6646(7)	0.0641(6)	2.5(5)
C4'	0.2568(3)	0.7695(7)	0.3681(6)	2.6(5)
C5	0.3064(4)	0.6382(7)	0.0213(7)	3.2(5)
C5'	0.2122(4)	0.7770(7)	0.3203(7)	3.0(5)
C6	0.3452(4)	0.6778(8)	0.0426(7)	3.1(5)
C6A	0.3465(4)	0.7457(7)	0.1060(7)	2.6(5)
C6B	0.3820(4)	0.7979(7)	0.1409(7)	3.0(5)
C6'	0.2148(3)	0.8098(7)	0.2236(7)	2.5(5)
C7	0.4266(4)	0.802(1)	0.1208(9)	4.6(7)
C8	0.4526(4)	0.860(1)	0.165(1)	5.5(8)
C9	0.4352(4)	0.915(1)	0.2277(9)	4.3(7)
C10	0.3910(4)	0.9142(8)	0.2495(8)	3.6(6)
C10A	0.3637(4)	0.8560(8)	0.2036(7)	3.0(5)

C11	0.3067(4)	0.6529(7)	0.3893(8)	2.8(5)
C11A	0.3075(3)	0.7724(7)	0.1485(6)	2.5(5)
C11B	0.2683(3)	0.7311(6)	0.1268(6)	2.0(4)
C12	0.3316(3)	0.5845(7)	0.3432(7)	2.5(5)
C12A	0.1980(4)	0.6851(6)	0.1196(7)	2.5(5)
C13	0.3614(4)	0.5361(8)	0.3948(8)	3.3(6)
C14	0.3847(4)	0.4703(8)	0.354(1)	4.2(7)
C15	0.3773(4)	0.4559(7)	0.2634(9)	3.5(6)
C16	0.3494(4)	0.5036(8)	0.2121(8)	3.6(6)
C17	0.3258(4)	0.5687(7)	0.2510(7)	3.1(5)
C18	0.3313(4)	0.8527(7)	0.4834(7)	2.7(5)
C19	0.3779(4)	0.8341(7)	0.5133(7)	2.8(5)
C20	0.3913(4)	0.8571(8)	0.6000(7)	3.7(6)
C21	0.4342(5)	0.8375(9)	0.6300(9)	4.4(7)
C22	0.4620(4)	0.797(1)	0.575(1)	4.9(7)
C23	0.4499(5)	0.772(1)	0.490(1)	5.2(7)
C24	0.4071(4)	0.7938(9)	0.4581(8)	4.3(6)
O5	0.0452(5)	0.135(1)	0.230(1)	10.1(4)
O6	-0.018(1)	0.063(2)	0.096(2)	13(1)
C25	-0.014(3)	0.086(5)	0.201(5)	20(3)
H1	0.1371	0.7074	0.1746	4.2
H2	0.1003	0.6030	0.0866	4.5
H3	0.1392	0.5212	-0.0147	4.9
H4	0.2147	0.5387	-0.0340	3.8
H5	0.3055	0.5933	-0.0218	3.8
H6	0.3717	0.6600	0.0149	3.7

H7	0.4387	0.7651	0.0770	5.5
H8	0.4834	0.8628	0.1525	6.6
H9	0.4543	0.9553	0.2569	5.1
H10	0.3797	0.9515	0.2939	4.3
H11	0.2954	1.0031	0.1984	3.9
H12	0.2709	1.0117	0.2888	3.9
H13	0.3214	0.9931	0.2895	3.9
H14	0.2664	0.8955	0.3923	2.8
H15	0.2526	0.7586	0.4304	3.1
H16	0.1988	0.7222	0.3188	3.6
H17	0.1944	0.8151	0.3535	3.6
H18	0.1857	0.8281	0.2066	3.0
H19	0.3659	0.5478	0.4574	3.9
H20	0.4051	0.4362	0.3882	5.1
H21	0.3460	0.4925	0.1492	4.4
H22	0.3058	0.6023	0.2155	3.7
H23	0.3715	0.8858	0.6385	4.5
H24	0.4438	0.8529	0.6894	5.3
H25	0.4696	0.7402	0.4537	6.2
H26	0.3984	0.7808	0.3975	5.1