Supporting Information

Unless otherwise specified, solvents were dried over activated alumina. Triethylamine (NEt_3) was distilled from CaH_2. Dimethylformamide (DMF) was dried over 3Å molecular sieves for 3 days and then distilled from P_2O_5. Analytical thin-layer chromatography (tlc) was run on K6F silica gel 60A and flash column chromatography was run with 230-400 mesh ASTM 60A silica gel. When specified, silica gel used for flash column chromatography was buffered by flushing with 1:1 CH_2Cl_2/NEt_3, blowing the silica gel dry under a stream of N_2, then flushing with ether, and again blowing the silica gel dry under a stream of N_2. All reactions were performed with either flame or oven dried glassware under an N_2 atmosphere.

4-Benzyloxy-3-oxazol-5-yl-1-triisopropylsilanyl-1H-indole (13). To a solution of indole **12**[3c] (237 mg, 0.816 mmol) in anhydrous THF (8.5 mL) was added NaH (40 mg of 60% dispersion in mineral oil, 0.98 mmol) at 0 °C. Once the H_2 evolution subsided, TIPSCl (0.21 mL, 189 mg, 0.98 mmol) was added and the cold bath was removed. Once at rt, the reaction was poured into a 50% saturated $NaHCO_3$ solution and extracted with ether. The ether was then dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (1:1 ether/hexanes) to afford 347 mg (95% yield) of **13** as a white powder; analytical tlc, 2:1 ether/hexanes, Rf= 0.47. Pure material was obtained by crystallization from ether/hexanes using the slow evaporation technique, mp 81 °C. Molecular ion calcd for $C_{27}H_{34}N_2O_2Si$: 446.2390; found m/e= 446.2405, error= 3 ppm; base peak= 446 amu; IR (neat, cm^{-1}) 2949; 2868; 1571; 500 MHz NMR ($CDCl_3$, ppm) δ 7.72 (1H, s) 7.49 (1H, s) 7.46-7.33 (5H, m) 7.25 (1H, s) 7.15-7.08 (2H, m) 6.67 (1H, d, J= 7.0 Hz) 5.22 (2H, s) 1.72 (3H, sept, J= 7.5 Hz) 1.17 (18H, d, J= 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 152.9, 148.8, 148.0, 143.2, 136.6, 129.2, 128.6, 128.2, 128.0, 123.1, 122.9, 117.8, 107.8, 107.0, 102.2, 70.3, 18.1, 12.8.

4-Benzyloxy-3-(2-methyloxazol-5-yl)-1-triisopropylsilanyl-1*H*-indole (16). The procedure of Monahan was used with modification.[17] (This reaction is sensitive to the quality of the $BH_3 \cdot THF$; fresh $BH_3 \cdot THF$ must be used.) To a solution of indole **13** (940 mg, 2.104 mmol) in anhydrous CH_2Cl_2 (19 mL) was added $BH_3 \cdot THF$ (2.53 mL of a 1 M solution in THF, 2.53 mmol, Aldrich) at rt and the solution was stirred for 30 min. The reaction was cooled to -78 °C and *n*-BuLi (1.71 mL of a 1.48 M solution in hexanes, 2.53 mmol) was added dropwise. The deep red solution was quenched with MeOTf (1.2 mL, 1.73 g, 10.52 mmol) and held at -25 °C for 4 h. A solution of 5% AcOH in EtOH (v/v, 40 mL) was then added to the clear, light orange solution and the reaction was stirred for 24 h at rt with frequent venting to prevent pressure buildup. The reaction was then poured into a saturated $NaHCO_3$ solution and extracted with ether twice. The ether was then dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (1:1 ether/hexanes) to afford 861 mg (89% yield) of **16** as a gummy oil; analytical tlc, 1.5% $MeOH/CH_2Cl_2$, Rf= 0.37. Molecular ion calcd for $C_{28}H_{36}N_2O_2Si$: 460.2546; found m/e= 460.2555, error= 2 ppm; base peak= 460 amu; IR (neat, cm^{-1}) 2949; 2868; 1571; 500 MHz NMR ($CDCl_3$, ppm) δ 7.44-7.32 (6H, m) 7.15-7.08 (2H, m) 7.07 (1H, s) 6.66 (1H, dd, J= 7.5, 1.0 Hz) 5.18 (2H, s) 2.36 (3H, s) 1.72 (3H, sept, J= 7.5 Hz) 1.16 (18H, d, J= 7.5 Hz). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 159.5, 153.2, 147.7, 143.5, 136.9, 129.0, 128.9, 128.4, 128.3, 123.5, 123.2, 118.2, 108.0, 107.6, 102.2, 70.6, 18.4, 14.2, 13.0.

***tert*-Butyl 4-benzyloxy-3-(2-methyloxazol-5-yl)-indole-1-carboxylate (17)**. To a solution of indole **16** (2.1 g, 4.56 mmol) in anhydrous THF (40 mL) was added TBAF (4.70 mL of a 1.0 M solution in THF, 4.70 mmol) at 0 °C. The reaction was stirred for 10 min, and was poured into a 50% saturated $NaHCO_3$ solution and extracted with ether. The ether was dried over $MgSO_4$, filtered, and concentrated; analytical tlc, 2.5% $MeOH/CH_2Cl_2$, Rf=0.30. This residue was dried under reduced pressure (0.1 torr) overnight and then dissolved in anhydrous THF (40 mL). To this solution was added NaH (365 mg of 60% dispersion in mineral oil, 9.12 mmol) at 0 °C. Once H_2 evolution subsided, solid $(Boc)_2O$ (2 g, 9.12 mmol) was added in one portion and the solution was stirred for 30 min. The reaction was then poured into a 50% saturated $NaHCO_3$ solution and extracted with ether. The ether was then dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (2:1 ether/hexanes) to afford 1.64 g (91% yield) of **17** as white crystals; analytical tlc, 2.5% $MeOH/CH_2Cl_2$, Rf= 0.65. Pure material was obtained by crystallization from ether/hexanes, mp 166-167 °C. Molecular ion calcd for $C_{24}H_{24}N_2O_4$: 404.1736; found m/e= 404.1730, error= 1 ppm; base peak= 348 amu; IR (neat, cm^{-1}) 1729, C=O; 1432; 1363; 500 MHz NMR ($CDCl_3$, ppm) δ 7.86 (1H, d, J= 8.0 Hz) 7.76 (1H, s) 7.44-7.34 (5H, m) 7.27 (1H, t, J= 8.0 Hz) 7.17 (1H, s) 6.80 (1H, d, J= 8.0 Hz) 5.20 (2H, s) 2.39 (3H, s) 1.68 (9H, s). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 160.4, 152.8, 149.8, 146.2, 144.1, 136.4, 129.0, 128.7, 128.3, 126.2, 125.7, 125.6, 122.7, 114.9, 108.9, 105.4, 84.5, 70.8, 28.4, 14.2.

***tert*-Butyl 3-(2-methyloxazol-5-yl)-4-trifluoromethanesulfonyloxyindole (18)**. To a suspension of indole **17** (1.6 g, 3.97 mmol) in EtOH (45 mL) was added 10% Pd/C hydrogenation catalyst (170 mg). The suspension was stirred vigorously under a hydrogen atmosphere (balloon) for 24 h. The mixture was filtered through a pad of celite which was then washed with EtOH, ether, and EtOAc; analytical tlc, 2.5% MeOH/CH_2Cl_2, Rf= 0.18. The organics were concentrated and dried under reduced pressure (0.1 torr) overnight. The powdery residual solid was dissolved in anhydrous THF (40 mL). To this solution was added NaH (320 mg of 60% dispersion in mineral oil, 7.95 mmol) at 0 °C. The reaction was stirred for 15 min after which time the H_2 evolution had subsided. Solid *N*-phenyltrifluoromethanesulfonimide (2.4 g, 6.76 mmol, Aldrich) was then added in one portion. The reaction was then warmed to rt and was stirred for 1 h. The reaction was poured into a 50% saturated $NaHCO_3$ solution and extracted with ether. The ether was then dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (1:1 ether/hexanes) to afford 1.69 g (95% yield) of **18** as white crystals; analytical tlc, 2% MeOH/CH_2Cl_2, Rf= 0.45. Pure material was obtained by crystallization from hexanes, mp 94-96 °C; analysis calcd: C, 48.43; H, 3.84; N, 6.28; found: C, 48.45; H, 3.75; N, 6.15; M + H^+ calcd for $C_{18}H_{17}F_3N_2O_6S$: 447.0837; found m/e= 447.0839, error= 0 ppm; base peak= 172 amu; IR (neat, cm^{-1}) 1745, C=O; 1424; 1370; 500 MHz NMR ($CDCl_3$, ppm) δ 8.31 (1H, d, J= 8.0 Hz) 7.83 (1H, s) 7.41 (1H, t, J= 8.0) 7.27 (1H, d, J= 8.0) 7.16 (1H, s) 2.55 (3H, s) 1.70 (9H, s). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 162.1, 148.8, 143.5, 142.5, 126.9, 126.6, 125.7, 125.6, 120.5, 115.9, 115.7, 107.3, 85.6, 57.1, 28.3, 14.2.

2-Benzofuran-3-yl-6-bromophenol (20). To a solution of benzofuran **19**[3c] (1.0 g, 3.3 mmol) in freshly distilled DMF (13.8 mL) was added EtSH (625 mg, 0.75 mL, 10.0 mmol). NaH (400 mg of 60% dispersion in mineral oil, 10 mmol) was then added in one portion at rt and the reaction became yellow. The reaction was stirred for 15 min after which time the H_2 evolution had subsided. The temperature was raised to 165 °C and held at this temperature for 2.5 h. The orange and slightly turbid suspension was then cooled to rt and poured into a 1 M HCl solution and extracted with ether twice. The ether extract was then washed with water twice, dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (1:15 ether/hexanes) to afford 940 mg (98% yield) of **20** as off white crystals; analytical tlc, 1:10 ether/hexanes, Rf= 0.50. Pure material was obtained by crystallization from hexanes, mp 49-52 °C. Molecular ion calcd for $C_{14}H_9BrO_2$: 289.9765; found m/e= 289.9767, error= 1 ppm; base peak= 288 amu; IR (neat, cm^{-1}) 3491, O-H; 1444; 1111; 300 MHz NMR ($CDCl_3$, ppm) δ 7.97 (1H, s) 7.72 (1H, dd, J= 7.2, 1.8 Hz) 7.58-7.52 (2H, m) 7.46 (1H, dd, J= 8.1, 1.5 Hz) 7.36 (1H, dt, J= 7.5, 1.5 Hz) 7.27 (1H, dt, J= 7.5, 1.5 Hz) 6.89 (1H, t, J= 7.8 Hz) 5.83 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 155.2, 149.6, 144.1, 131.1, 129.3, 126.5, 124.6, 122.9, 121.6, 120.8, 120.0, 116.6, 111.7, 111.

3-[3-Bromo-2-(4-methoxybenzyloxy)-phenyl]-benzofuran (21). To a solution of benzofuran **20** (2.99 g, 10.34 mmol) in freshly distilled DMF (100 mL) was added NaH (1.0 g of 60% dispersion in mineral oil, 26 mmol) in one portion. The solution turned yellow upon addition of the NaH. The reaction was stirred for 15 min after which time the H_2 evolution had subsided. A large excess of *p*-methoxybenzyl bromide (13.5 g, 67.2 mmol) was then added via syringe. Upon addition, the solution lost the yellow color and became slightly turbid . The reaction was allowed to stir for 24 h at rt after which time the solution was nearly clear and slightly yellow. The solution was cooled to 0 °C and 3M NaOH (34 mL) was added (converting the excess *p*-methoxybenzyl bromide to *p*-methoxybenzyl alcohol). The mixture was allowed to warm to rt and then stirred for 1 h. The clear solution was poured into water and extracted with ether 3X. The ether was then washed with water 3X, dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography with buffered silica gel (1:30 ether/hexanes) to afford 4.1 g (97% yield) of **21** as off white crystals; analytical tlc, 1:10 ether/hexanes with 1% MeOH, Rf= 0.64. Pure material was obtained by crystallization from hexanes, mp 84-85 °C. Molecular ion calcd for $C_{22}H_{17}BrO_3$: 408.0361; found m/e= 408.0355, error= 1 ppm; base peak= 121 amu; IR (neat, cm^{-1}) 1513; 1231; 733; 500 MHz NMR ($CDCl_3$, ppm) δ 7.92 (1H, s) 7.72 (1H, ddd, J= 7.8, 1.5, 0.5 Hz) 7.60-7.52 (3H, m) 7.34 (1H, ddd, J= 8.5, 7.0, 1.0 Hz) 7.26 (1H, ddd, J= 8.0, 7.0, 1.0 Hz) 7.09 (1H, t, J= 8.0 Hz) 7.06-7.02 (2H, m) 6.74-6.70 (2H, m) 4.61 (2H, s) 3.72 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 159.5, 155.1, 153.1, 143.9, 132.5, 130.4, 129.3, 128.2, 127.9, 126.4, 125.6, 124.5, 122.9, 121.1, 118.9, 117.2, 113.5, 111.5, 74.4, 55.1.

3-[3-Bromo-2-(4-methoxybenzyloxy)-phenyl]-3*H*-benzofuran-2-one (22). The procedure of

Wang was used with slight modifications.[3b] To a solution of benzofuran **21** (845 mg, 2.064 mmol) in anhydrous CH_2Cl_2 (120 mL) was added CH_3CO_3H (12 mL of a 32% solution in AcOH and water, Aldrich). The reaction was stirred for 48 h, was poured into water and extracted with CH_2Cl_2. The CH_2Cl_2 was then washed with a 10% Na_2SO_3 solution, a saturated $NaHCO_3$ solution, dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (3:10 ether/hexanes) to afford 582 mg (66% yield) of **22** as a oil; analytical tlc, 3:10 ether/hexanes, Rf= 0.32. Molecular ion calcd for $C_{22}H_{17}BrO_4$: 424.0310; found m/e= 424.0318, error= 2 ppm; base peak= 121 amu; IR (neat, cm^{-1}) 1803, C=O; 1613; 1463; 500 MHz NMR ($CDCl_3$, ppm) δ 7.58 (1H, dd, J= 7.5, 2.5 Hz) 7.38 (2H, d, J= 8.5 Hz) 7.31 (1H, tt, J= 8.0, 1.5 Hz) 7.12-7.08 (2H, m) 7.03-6.94 (3H, m) 6.92-6.88 (2H, m) 5.22-5.15 (2H, m) 4.73 (1H, br s) 3.82 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 175.0, 159.6, 154.4, 153.9, 134.1, 131.9, 129.8, 129.2, 128.5, 127.8, 125.8, 124.8, 124.5, 117.9, 115.3, 113.8, 110.8, 94.7, 75.5, 55.3.

3-[3-Bromo-2-(4-methoxybenzyloxy)-phenyl]-3-methyl carboxylate-benzofuran-2-one (24). To a solution of benzofuranone **22** (2.0 g, 4.67 mmol) in anhydrous THF (40 mL) was added freshly distilled NEt_3 (3.4 mL, 2.37 g, 23.4 mmol) at 0 °C. During addition the solution turned yellow. Methyl chloroformate (1.5 mL, 1.77 g, 18.7 mmol) was then added slowly and the reaction became colorless and thick with a white precipitate. The reaction was warmed to rt, poured into a 0.1 M HCl solution and extracted with ether. The ether was dried over $MgSO_4$, filtered and concentrated. The residue was quickly purified by flash column chromatography on silica gel (3:10 ether/hexanes) to afford 2.19 g (97% yield) of **23** as a thick glassy oil; analytical tlc, 3:10 ether/hexanes, Rf= 0.29. This material was dried under reduced pressure (0.1 torr) overnight and then dissolved in anhydrous THF (40 mL). To this solution was added distilled methyl chloroformate (0.26 mL, 321 mg, 3.4 mmol). DMAP (553 mg, 4.53 mmol) was then added as a solution in anhydrous THF (2 mL). During the addition, a white precipitate began to form and the solution turned a deep inky purple. The reaction mixture was vigorously stirred for 24 h after which time the purple color had faded leaving a clear, colorless solution with the white precipitate. The reaction was then poured into a 0.1 M HCl solution and extracted with ether twice. The ether was dried over $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel (1:3 ether/hexanes) to afford 1.95 g (89% yield) of **24**

as a thick oil; analytical tlc, 1:3 ether/hexanes, Rf= 0.20. Molecular ion calcd for $C_{24}H_{19}BrO_6$: 482.0365; found m/e= 482.0349, error= 3 ppm; base peak= 121 amu; IR (neat, cm^{-1}) 1814, C=O; 1741, C=O; 1513; 500 MHz NMR ($CDCl_3$, ppm) δ 7.61 (1H, dd, J= 8.0, 1.5 Hz) 7.55-7.51 (2H, m) 7.41 (1H, ddd, J= 8.0, 7.5, 1.5 Hz) 7.34 (1H, ddd, J= 8.0, 1.5, 0.5 Hz) 7.21 (1H, ddd, J= 7.5, 7.5, 1.0 Hz) 7.15 (1H, d, J= 8.0 Hz) 6.94-6.90 (3H, m) 6.82 (1H, dd, J= 8.0, 1.5 Hz) 5.36 (1H, d, J= 10.0 Hz) 5.17 (1H, d, J= 10.0 Hz) 3.83 (3H, s) 3.43 (3H, s). ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 171.2, 167.3, 159.4, 154.7, 153.6, 135.2, 131.9, 130.6, 130.2, 129.0, 128.2, 126.4, 126.2, 125.0, 124.9, 118.0, 113.5, 111.0, 75.0, 61.1, 55.2, 53.4.

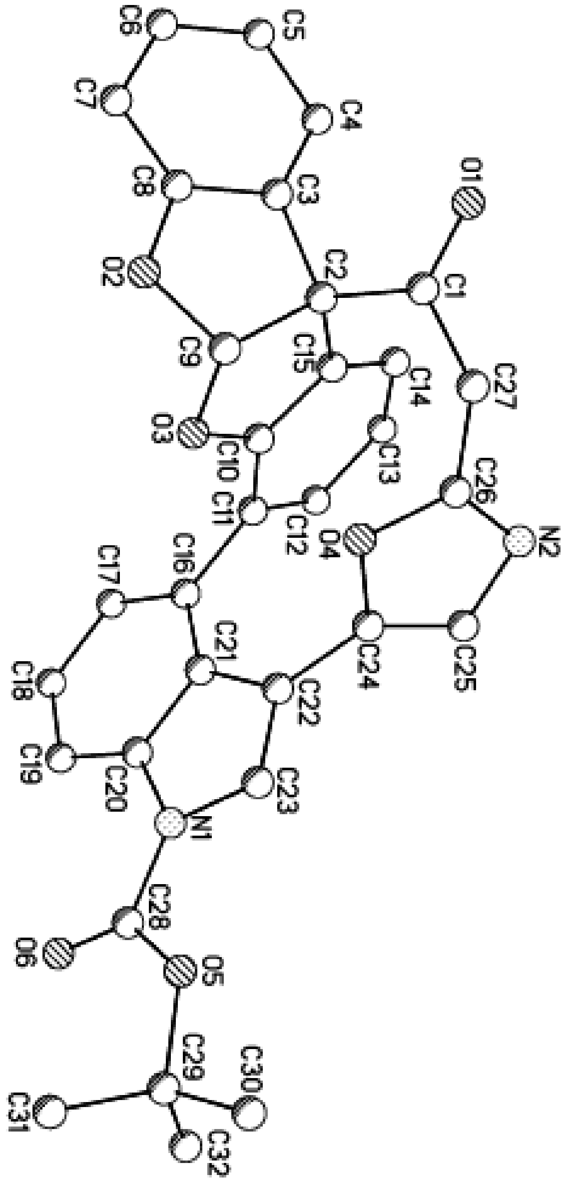
Methyl 4-bromo-benzo[*b*]benzo[4,5]furo[3,2-*d*]furan-10b-carboxylate (26). To a solution of vacuum dried (0.1 torr) benzofuranone **24** (1.90 g, 3.93 mmol) in anhydrous THF (40 mL) was added DIBAL (9.83 mL of a 1.0 M solution in toluene, 9.83 mmol) at -78 °C. The solution was stirred at -78 °C for 2 h. The reaction was then quenched with 1 M HCl (aq., 15 mL) at -78 °C. During the addition the solution foamed vigorously and then froze. The cold bath was then removed and the reaction mixture warmed to rt. A saturated Rochelle's salt solution (13 mL) was then added along with ether (8 mL). The reaction was stirred for 30 min at rt. The heterogeneous solution was poured into a 0.1 M HCl solution and extracted with ether. The ether was then washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was quickly purified by flash column chromatography on silica gel (2:5 ether/hexanes) to afford 1.65 g (87% yield) of **25** as a white solid; analytical tlc, 1:2 ether/hexanes, Rf= 0.28. This material was kept under reduced pressure (0.1 torr) overnight and then dissolved in anhydrous CH_2Cl_2 (35 mL). To this solution was added freshly distilled NEt_3 (0.73 mL, 510 mg, 5 mmol) at 0 °C. Distilled methanesulfonyl chloride (0.29 mL, 424 mg, 3.7 mmol) was added dropwise and the reaction was stirred for 30 min. Methanesulfonic acid (2.2 mL, 3.23 g, 33.6 mmol) was added in one portion and the cold bath was removed, warming the reaction to rt. After 1 min, the reaction was then recooled to slightly below 0 °C with a salt/ice water bath. Freshly distilled NEt_3 (7.4 mL, 5.14 g, 50.8 mmol) was added dropwise at a slow rate to avoid excessive warming. The cold bath was removed and the reaction warmed to rt. The solution was then poured into a 1 M HCl solution and extracted with ether several times. The ether was washed with a saturated $NaHCO_3$ solution, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography on silica gel (9:100 EtOAc/hexanes) to afford 1.05 g (89% yield) of **26** as a thick oil; analytical tlc, 1:1 ether/hexanes, Rf= 0.59. Molecular ion calcd for $C_{16}H_{11}BrO_4$: 345.9840; found m/e= 345.9824, error= 5 ppm; base peak= 314 amu; IR (neat, cm^{-1}) 1737, C=O; 1478; 1254; 400 MHz NMR ($CDCl_3$, ppm) δ 7.57 (1H, dd, J= 6.8, 1.6 Hz) 7.56 (1H, dd, J= 8.0, 1.2 Hz) 7.37 (1H, dd, J= 8.0, 1.2 Hz) 7.24-7.22 (2H, m) 6.99 (1H, td, J= 6.8, 1.2 Hz) 6.95 (1H, d, J= 8.0 Hz) 6.86 (1H, t, J= 8.0 Hz) 3.87 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.9, 157.8, 155.3, 133.2, 130.4, 127.6, 125.8, 124.2, 123.7, 123.3, 122.7, 114.2, 111.1, 103.4, 66.6, 53.7.

4-Bromo-benzo[b]benzo[4,5]furo[3,2-d]furan-10b-carboxylic acid (27). To a solution of methyl ester **26** (750 mg, 2.166 mmol) in MeOH (11.25 mL) and THF (7.5 mL) was added at rt NaOH (348 mg, 8.70 mmol) as a solution in water (3.75 mL). The reaction immediately turned yellow. The solution was stirred for 30 min and then was poured into a 1 M HCl solution and extracted with ether. The ether was then concentrated and residual solvents were removed under reduced pressure (0.1 torr). The residue was purified by flash column chromatography on silica gel (3% MeOH/0.5% AcOH/CH_2Cl_2) to afford 682 mg (94% yield) of **27** as a thick oil; analytical tlc, 3% MeOH/1% AcOH/CH_2Cl_2, Rf= 0.27. Molecular ion calcd for $C_{15}H_9BrO_4$: 331.9684; found m/e= 331.9693, error= 3 ppm; base peak= 84 amu; IR (neat, cm^{-1}) 2922, CO_2H; 1710, C=O; 1444; 500 MHz NMR ($CDCl_3$, ppm) δ 11.60 (1H, br s) 7.44-7.30 (2H, m) 7.10-7.00 (2H, m) 6.81-6.62 (3H, m) 6.43-6.39 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 175.4, 158.4, 156.1, 133.8, 131.0, 126.4, 124.5, 124.2, 123.6, 123.2, 114.9, 111.6, 104.2, 67.7, 23.4.

10b-Methoxycarbonyl-5a,10b-dihydro-benzo[b]benzo[4,5]furo[3,2-d]furan-4-boronic acid (30). To a solution of carboxylic acid **27** (600 mg, 1.8 mmol) in anhydrous THF (18 mL) was added NaH (144 mg of 60% dispersion in mineral oil, 86 mmol) at 0 °C in one portion. During addition the reaction mixture became yellow, and was stirred for 15 min after which time the H_2 evolution had subsided. The reaction was cooled to -78 °C and *n*-BuLi (2.3 mL of a 1.59 M solution in hexanes, 3.6 mmol) was added dropwise to prevent warming. The reaction was stirred for 10 min at -78 °C and was quenched with triisopropylborate (1.4 mL, 1.18 g, 6.3 mmol). The cold bath was then removed and the reaction warmed to rt. The reaction was stirred for 30 min at rt and was then poured into a 1 M HCl solution and extracted with ether. The ether was then concentrated and the residual water was removed under reduced pressure (0.1 torr). The residue was dissolved in MeOH (4 mL) and benzene (16 mL). To this solution was added trimethylsilyldiazomethane (2.0 mL, 4.0 mmol, 2.0 M solution in hexanes) slowly to prevent excessive foaming. Once the N_2 evolution had subsided, the yellow solution was quickly poured into a 1 M HCl solution and extracted with ether. The ether was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (1:2 acetone/hexanes) and then crystallized from ether/hexanes to afford 431 mg (77% yield) of **30** as white crystals sufficiently pure for use in the next step; analytical tlc, 1:2 acetone/hexanes, Rf= 0.37; mp 93-100 °C. IR (neat, cm^{-1}) 3540; 3428; 1741; 500 MHz NMR ($CDCl_3$, ppm) δ 7.78 (1H, d, J= 8.0 Hz) 7.58 (1H, dd, J= 7.5, 1.5 Hz) 7.48 (1H, d, J= 8.0 Hz) 7.04 (1H, s) 6.82 (1H, td, J= 7.5, 1.5 Hz) 6.74 (1H, t, J= 8.0 Hz) 6.72-6.65 (2H, m) 4.97 (2H, s) 3.10 (3H, s).

4-(10b-Methoxycarbonyl-5a,10b-dihydro-benzo[b]benzo[4,5]furo[3,2-d]furan-4-yl)-3-(2-methyloxazol-5-yl)-indole-1-carboxylic acid *tert*-butyl ester (9). Boronic acid **30** (62 mg, 0.1986 mmol), triflate **18** (132 mg, 0.298 mmol), Pd(dppf)Cl_2 (24 mg, 0.03 mmol, Aldrich), Cs_2CO_3 (194 mg, 0.5958 mmol), and a spinvane were all added to a 5 mL pear shaped flask with a reflux condenser fused to the top. The reaction vessel was evacuated under reduced pressure (0.1 torr) and then refilled with N_2; this was done ~10 times to ensure an N_2 atmosphere. The reaction vessel was then topped with a septum. Anhydrous, degassed (N_2 flushed) THF (2mL) was added via syringe. The septum was topped with vacuum grease and the reaction was heated at 65 °C for 18 h. The reaction mixture was then cooled to rt and transferred (via Pasteur pipet) to a 50% saturated $NaHCO_3$ solution. The cloudy suspension was then extracted with ether several times, the ether was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel (2:1 ether/hexanes) and then by preparative tlc (1:2 acetone/hexanes) to afford 64 mg (57% yield) of **9** as a glass; analytical tlc, 3:1 ether/hexanes, Rf= 0.20. Molecular ion calcd for $C_{33}H_{28}N_2O_7$: 565.1975; found m/e= 565.1999, error= 4 ppm; base peak= 154 amu; IR (neat, cm^{-1}) 1737, C=O; 1258; 1154; 400 MHz NMR ($CDCl_3$, 60 °C, ppm) δ 8.27 (1H, d, J= 8.4 Hz) 7.74 (1H, s) 7.56 (2H, d, J= 7.2 Hz) 7.41 (1H, t, J= 8.4 Hz) 7.23 (1H, s) 7.18 (1H, t, J= 7.2 Hz) 7.13-7.09 (1H, br s) 6.98-6.90 (3H, m) 6.82 (1H, d, J= 8.4 Hz) 6.29 (1H, s) 3.88 (3H, s) 2.2-1.2 (3H, br s; at 60 °C, these signals are near coalescence due to atropisomer interconversion and so broad that the signal maximum is easily overlooked; at 20 °C the methyl protons appear as two broad singlets, δ 2.09 and 1.41 ppm, corresponding to the slow rotation of the atropisomers) 1.69 (9H, s). 400 MHz NMR (toluene-d_8, 80 °C, ppm) δ 8.38 (1H, d, J= 8.4 Hz) 7.67 (1H, s) 7.52 (2H, t, J= 7.6 Hz) 7.21 (1H, t, J= 8.4 Hz) 7.08-6.95 (3H, m) 6.85 (1H, t, J= 7.6 Hz) 6.77-6.68 (2H, m) 6.61 (1H, d, J= 8 Hz) 6.30 (1H, s) 3.47 (3H, s) 1.76 (3H, br s) 1.42 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$, 60 °C, ppm) δ 170.5, 130.9, 130.0, 129.9, 126.1, 126.0, 125.5, 124.9, 124.1, 124.0, 123.1, 122.2, 121.8, 115.2, 114.2, 110.7, 94.6, 84.5, 53.3, 30.8, 28.3.

Macrocycle (8). To a -23 °C solution of macrocycle precursor **9** (40 mg, 0.070 mmol) in anhydrous THF (7 mL) was added LDA (0.3 mL of a 0.70 M solution in THF, 0.21 mmol) via syringe in one portion. The solution became yellow within 15 seconds and the color intensified slightly during the next min. After 5 min, the reaction was quenched with 0.1 M H_2SO_4 (aq, 2.2 mL), the cold bath was removed and the mixture was stirred vigorously for 10 min. The reaction mixture was then poured into a 0.1 M H_2SO_4 solution and extracted with ether several times. The ether was dried over $MgSO_4$, filtered, concentrated and the residue was purified by flash column chromatography on silica gel (3:20 acetone/hexanes) to afford 21.5 mg (57% yield) of **8** as a white powder; analytical tlc, 1:2 acetone/hexanes, Rf= 0.51; mp 198-200 °C. Molecular ion calcd for $C_{32}H_{24}N_2O_6$: 533.1713; found m/e= 533.1738, error= 5 ppm; base peak= 525 amu; IR (neat, cm^{-1}) 1740, C=O; 1715, C=O; 1364; 500 MHz NMR ($CDCl_3$, ppm) δ 8.28 (1H, d, J= 8.0 Hz) 7.78 (1H, s) 7.72 (1H, d, J= 8.5 Hz) 7.45 (1H, dd, J= 8.5, 7.5 Hz) 7.32 (1H, s) 7.22-7.18 (2H, m) 7.13 (1H, dd, J= 7.5, 1.5 Hz) 7.03 (1H, td, J= 7.5, 1.5 Hz) 6.94-6.84 (3H, m) 6.45 (1H, s) 4.15 (2H, ABq, J= 16.0 Hz) 1.70 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 196.9, 157.6, 155.8, 155.4, 144.4, 135.2, 131.2, 130.0, 129.9, 129.4, 129.0, 128.5, 126.3, 125.6, 125.4, 124.3, 123.2, 122.6, 122.4, 115.7, 113.2, 110.5, 107.6, 85.0, 77.4, 72.6, 54.4, 42.4, 28.4, 14.9.


C6
C5
C7
C4
O1
C8
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O2
C2
C1
C9
C15
C14
C27
O3
C10
C13
C26
C11
C12
O4
N2
C17
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C21
C24
C25
C18
C22
C19
C20
C23
N1
C28
O6
O5
C29
C30
C31
C32

Table 1. Crystal data and structure refinement for **8**.

Identification code	macro2
Empirical formula	C35 H31 N2 O6
Formula weight	575.62
Temperature	158(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions deg.	a = 8.0111(9) A alpha = 96.359(5)
	b = 9.4285(11) A beta =
96.457(5)deg.	c = 21.374(2) A gamma =
104.960(4)deg.	
Volume	1533.3(3) A^3
Z, Calculated density	2, 1.247 Mg/m^3
Absorption coefficient	0.086 mm^-1
F(000)	606
Crystal size	0.20 x 0.36 x 0.38 mm
Theta range for data collection	2.26 to 26.59 deg.
Limiting indices	-10<=h<=9, -11<=k<=11, -26<=l<=26
Reflections collected / unique	12728 / 6206 [R(int) = 0.0504]
Completeness to theta = 26.59	96.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6206 / 0 / 366
Goodness-of-fit on F^2	1.072
Final R indices [I>2sigma(I)]	R1 = 0.0748, wR2 = 0.2038
R indices (all data)	R1 = 0.1015, wR2 = 0.2175
Extinction coefficient	0.005(3)
Largest diff. peak and hole	0.333 and -0.382 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **8**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	6777(2)	4388(2)	5173(1)	34(1)
O(2)	5130(2)	6014(2)	3539(1)	31(1)
O(3)	4605(2)	3623(2)	2996(1)	29(1)
O(4)	3054(2)	1292(2)	3604(1)	27(1)
O(5)	-2593(3)	-2197(2)	1584(1)	44(1)
O(6)	-1637(3)	-1552(3)	673(1)	47(1)
N(1)	129(3)	-831(2)	1632(1)	31(1)
N(2)	4356(3)	-141(2)	4122(1)	31(1)
C(1)	5934(3)	3708(3)	4672(1)	27(1)
C(2)	6352(3)	4260(3)	4044(1)	27(1)
C(3)	7618(4)	5798(3)	4133(1)	29(1)
C(4)	9330(4)	6328(3)	4429(1)	34(1)
C(5)	10199(4)	7816(3)	4432(1)	39(1)
C(6)	9359(4)	8712(3)	4131(1)	39(1)
C(7)	7658(4)	8184(3)	3812(1)	36(1)
C(8)	6833(4)	6712(3)	3822(1)	29(1)
C(9)	4748(3)	4498(3)	3607(1)	27(1)
C(10)	5832(3)	2856(3)	3028(1)	26(1)
C(11)	5957(3)	1825(3)	2525(1)	27(1)
C(12)	7355(4)	1212(3)	2619(1)	31(1)
C(13)	8518(4)	1565(3)	3184(1)	33(1)
C(14)	8291(4)	2515(3)	3695(1)	31(1)
C(15)	6908(3)	3147(3)	3605(1)	26(1)
C(16)	4612(4)	1354(3)	1947(1)	29(1)
C(17)	4968(4)	1680(3)	1353(1)	38(1)
C(18)	3674(4)	1187(3)	815(1)	43(1)
C(19)	2026(4)	360(3)	849(1)	37(1)
C(20)	1664(4)	9(3)	1446(1)	31(1)
C(21)	2912(3)	504(3)	1996(1)	28(1)
C(22)	2107(3)	-92(3)	2522(1)	27(1)
C(23)	457(4)	-878(3)	2282(1)	30(1)
C(24)	2913(3)	13(3)	3181(1)	26(1)
C(25)	3663(4)	-844(3)	3503(1)	30(1)
C(26)	3972(3)	1102(3)	4149(1)	26(1)
C(27)	4434(4)	2337(3)	4693(1)	30(1)
C(28)	-1452(4)	-1569(3)	1229(1)	33(1)
C(29)	-4303(4)	-3228(4)	1299(2)	52(1)
C(30)	-5021(8)	-3724(8)	1864(2)	158(4)
C(31)	-5391(5)	-2431(4)	941(2)	64(1)
C(32)	-3989(6)	-4497(4)	869(3)	92(2)

Table 3. Bond lengths [A] and angles [deg] for **8**.

O(1)-C(1)	1.215(3)
O(2)-C(8)	1.387(3)
O(2)-C(9)	1.410(3)
O(3)-C(10)	1.363(3)
O(3)-C(9)	1.442(3)
O(4)-C(26)	1.360(3)
O(4)-C(24)	1.397(3)
O(5)-C(28)	1.319(3)
O(5)-C(29)	1.479(4)
O(6)-C(28)	1.183(3)
N(1)-C(23)	1.392(3)
N(1)-C(20)	1.405(3)
N(1)-C(28)	1.414(4)
N(2)-C(26)	1.283(3)
N(2)-C(25)	1.397(3)
C(1)-C(27)	1.529(4)
C(1)-C(2)	1.532(3)
C(2)-C(15)	1.515(3)
C(2)-C(3)	1.518(4)
C(2)-C(9)	1.581(4)
C(3)-C(8)	1.376(4)
C(3)-C(4)	1.383(4)
C(4)-C(5)	1.395(4)
C(5)-C(6)	1.378(4)
C(6)-C(7)	1.391(4)
C(7)-C(8)	1.378(4)
C(10)-C(15)	1.380(4)
C(10)-C(11)	1.398(3)
C(11)-C(12)	1.392(4)
C(11)-C(16)	1.488(4)
C(12)-C(13)	1.391(4)
C(13)-C(14)	1.393(4)
C(14)-C(15)	1.393(4)
C(16)-C(17)	1.382(4)
C(16)-C(21)	1.413(4)
C(17)-C(18)	1.407(4)
C(18)-C(19)	1.363(4)
C(19)-C(20)	1.396(4)
C(20)-C(21)	1.404(4)
C(21)-C(22)	1.453(3)
C(22)-C(23)	1.348(4)
C(22)-C(24)	1.464(4)
C(24)-C(25)	1.330(4)
C(26)-C(27)	1.492(3)
C(29)-C(30)	1.468(5)
C(29)-C(31)	1.492(5)
C(29)-C(32)	1.517(6)

C(8)-O(2)-C(9)	108.81(19)
C(10)-O(3)-C(9)	108.64(19)
C(26)-O(4)-C(24)	104.26(18)
C(28)-O(5)-C(29)	121.5(2)
C(23)-N(1)-C(20)	108.1(2)
C(23)-N(1)-C(28)	125.4(2)
C(20)-N(1)-C(28)	126.4(2)
C(26)-N(2)-C(25)	103.9(2)
O(1)-C(1)-C(27)	118.1(2)
O(1)-C(1)-C(2)	119.9(2)

C(27)-C(1)-C(2)	121.9(2)
C(15)-C(2)-C(3)	112.2(2)
C(15)-C(2)-C(1)	112.6(2)
C(3)-C(2)-C(1)	113.5(2)
C(15)-C(2)-C(9)	101.52(19)
C(3)-C(2)-C(9)	100.89(19)
C(1)-C(2)-C(9)	114.9(2)
C(8)-C(3)-C(4)	120.0(2)
C(8)-C(3)-C(2)	108.8(2)
C(4)-C(3)-C(2)	131.0(2)
C(3)-C(4)-C(5)	118.7(3)
C(6)-C(5)-C(4)	119.8(3)
C(5)-C(6)-C(7)	122.3(3)
C(8)-C(7)-C(6)	116.4(3)
C(3)-C(8)-C(7)	122.7(3)
C(3)-C(8)-O(2)	113.3(2)
C(7)-C(8)-O(2)	124.0(2)
O(2)-C(9)-O(3)	109.52(19)
O(2)-C(9)-C(2)	107.84(19)
O(3)-C(9)-C(2)	106.92(18)
O(3)-C(10)-C(15)	114.4(2)
O(3)-C(10)-C(11)	122.8(2)
C(15)-C(10)-C(11)	122.7(2)
C(12)-C(11)-C(10)	115.5(2)
C(12)-C(11)-C(16)	122.7(2)
C(10)-C(11)-C(16)	121.6(2)
C(13)-C(12)-C(11)	122.3(2)
C(12)-C(13)-C(14)	121.0(3)
C(13)-C(14)-C(15)	117.2(3)
C(10)-C(15)-C(14)	120.9(2)
C(10)-C(15)-C(2)	108.4(2)
C(14)-C(15)-C(2)	130.6(2)
C(17)-C(16)-C(21)	117.9(3)
C(17)-C(16)-C(11)	122.6(2)
C(21)-C(16)-C(11)	119.5(2)
C(16)-C(17)-C(18)	121.0(3)
C(19)-C(18)-C(17)	122.2(3)
C(18)-C(19)-C(20)	117.1(3)
C(19)-C(20)-C(21)	122.3(3)
C(19)-C(20)-N(1)	130.6(3)
C(21)-C(20)-N(1)	107.0(2)
C(20)-C(21)-C(16)	119.4(2)
C(20)-C(21)-C(22)	107.4(2)
C(16)-C(21)-C(22)	133.0(2)
C(23)-C(22)-C(21)	106.8(2)
C(23)-C(22)-C(24)	124.7(2)
C(21)-C(22)-C(24)	128.3(2)
C(22)-C(23)-N(1)	110.5(2)
C(25)-C(24)-O(4)	106.6(2)
C(25)-C(24)-C(22)	134.7(2)
O(4)-C(24)-C(22)	118.7(2)
C(24)-C(25)-N(2)	110.7(2)
N(2)-C(26)-O(4)	114.4(2)
N(2)-C(26)-C(27)	127.9(2)
O(4)-C(26)-C(27)	117.6(2)
C(26)-C(27)-C(1)	118.7(2)
O(6)-C(28)-O(5)	129.2(3)
O(6)-C(28)-N(1)	122.8(3)

O(5)-C(28)-N(1)	108.1(2)
C(30)-C(29)-O(5)	101.7(3)
C(30)-C(29)-C(31)	112.6(4)
O(5)-C(29)-C(31)	110.4(3)
C(30)-C(29)-C(32)	111.7(5)
O(5)-C(29)-C(32)	108.6(3)
C(31)-C(29)-C(32)	111.4(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **8.**
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(1)	37(1)	41(1)	21(1)	0(1)	0(1)	8(1)
O(2)	32(1)	30(1)	32(1)	5(1)	2(1)	13(1)
O(3)	33(1)	34(1)	22(1)	-2(1)	-1(1)	15(1)
O(4)	33(1)	29(1)	20(1)	1(1)	2(1)	11(1)
O(5)	38(1)	55(1)	27(1)	1(1)	-2(1)	-6(1)
O(6)	38(1)	71(2)	25(1)	4(1)	-5(1)	6(1)
N(1)	31(1)	38(1)	24(1)	-1(1)	1(1)	11(1)
N(2)	38(1)	30(1)	25(1)	3(1)	1(1)	10(1)
C(1)	30(1)	30(1)	22(1)	0(1)	1(1)	15(1)
C(2)	31(1)	29(1)	20(1)	0(1)	2(1)	10(1)
C(3)	38(2)	30(1)	21(1)	2(1)	5(1)	10(1)
C(4)	36(2)	38(2)	28(1)	6(1)	0(1)	12(1)
C(5)	36(2)	40(2)	37(2)	4(1)	4(1)	4(1)
C(6)	42(2)	32(1)	41(2)	5(1)	8(1)	6(1)
C(7)	39(2)	34(1)	35(2)	7(1)	6(1)	12(1)
C(8)	31(2)	34(1)	23(1)	1(1)	4(1)	10(1)
C(9)	31(2)	29(1)	22(1)	1(1)	2(1)	12(1)
C(10)	29(1)	27(1)	26(1)	6(1)	7(1)	10(1)
C(11)	30(2)	30(1)	20(1)	2(1)	4(1)	5(1)
C(12)	34(2)	33(1)	27(1)	3(1)	7(1)	12(1)
C(13)	38(2)	34(1)	33(2)	4(1)	10(1)	17(1)
C(14)	31(2)	35(1)	27(1)	6(1)	3(1)	10(1)
C(15)	30(1)	28(1)	22(1)	3(1)	5(1)	9(1)
C(16)	35(2)	31(1)	23(1)	0(1)	4(1)	13(1)
C(17)	40(2)	45(2)	29(2)	5(1)	6(1)	13(1)
C(18)	47(2)	54(2)	24(2)	6(1)	6(1)	8(2)
C(19)	40(2)	47(2)	23(1)	4(1)	-2(1)	12(1)
C(20)	36(2)	35(1)	24(1)	3(1)	2(1)	15(1)
C(21)	34(2)	29(1)	24(1)	0(1)	2(1)	15(1)
C(22)	30(2)	30(1)	22(1)	-1(1)	2(1)	11(1)
C(23)	33(2)	37(1)	21(1)	1(1)	0(1)	11(1)
C(24)	29(1)	26(1)	23(1)	-3(1)	5(1)	8(1)
C(25)	33(2)	31(1)	24(1)	-1(1)	0(1)	10(1)
C(26)	27(1)	31(1)	20(1)	4(1)	3(1)	9(1)
C(27)	37(2)	30(1)	22(1)	2(1)	4(1)	9(1)
C(28)	34(2)	38(2)	25(2)	-2(1)	-2(1)	12(1)
C(29)	46(2)	57(2)	35(2)	6(2)	-8(2)	-12(2)

C(30)	106(4)	226(7)	52(3)	37(4)	-14(3)	-108(5)
C(31)	37(2)	69(2)	76(3)	-8(2)	2(2)	6(2)
C(32)	89(3)	39(2)	125(4)	-6(2)	-40(3)	5(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **8**.

	x	y	z	U(eq)
H(4)	9902	5692	4626	62(2)
H(5)	11367	8210	4641	62(2)
H(6)	9962	9727	4142	62(2)
H(7)	7096	8804	3598	62(2)
H(9)	3650	4184	3797	62(2)
H(12)	7521	530	2286	62(2)
H(13)	9482	1152	3222	62(2)
H(14)	9050	2723	4089	62(2)
H(17)	6104	2245	1308	62(2)
H(18)	3957	1440	414	62(2)
H(19)	1162	35	482	62(2)
H(23)	-367	-1393	2523	62(2)
H(25)	3720	-1804	3334	62(2)
H(27A)	4719	1921	5084	62(2)
H(27B)	3376	2673	4739	62(2)
H(30A)	-5225	-2882	2126	62(2)
H(30B)	-4189	-4124	2112	62(2)
H(30C)	-6126	-4497	1733	62(2)
H(31A)	-6593	-3064	830	62(2)
H(31B)	-4912	-2193	551	62(2)
H(31C)	-5382	-1511	1206	62(2)
H(32A)	-5051	-5328	782	62(2)
H(32B)	-3028	-4818	1080	62(2)
H(32C)	-3685	-4164	468	62(2)