

**Supporting Information for:**

**Fluorous-tagged indolylboron for the diversity-oriented synthesis of biologically-attractive bisindole derivatives**

## Experimental Section

**General Comments.** Toluene, benzene and dioxane were distilled from sodium benzophenone ketyl. DMF was distilled from CaH<sub>2</sub>. CH<sub>2</sub>Cl<sub>2</sub> was distilled from P<sub>2</sub>O<sub>5</sub>. MeOH was distilled from magnesium methoxide. Other dry solvents and reagents were purchased from commercial sources and used without further purification. Perfluorinated silica gel (FluoroFlash® Fluorous SPE Cartridges) was purchased from FLUOROUS Technologies Incorporated.

**Sulfonyl chloride 1b.** A mixture of PhI (3.95 ml, 35.3 mmol), C<sub>8</sub>F<sub>17</sub>I (9.5 ml, 35.5 mmol) and Cu powder (10.2 g, 160.5 mmol) in DMSO (50ml) was stirred for 22 h at 120 °C. The mixture was filtered by Celite® and washed with Et<sub>2</sub>O and H<sub>2</sub>O. The aqueous layer was extracted with Et<sub>2</sub>O (1×15 ml). The organic layer was washed with H<sub>2</sub>O and brine, and the organic layer was dried over MgSO<sub>4</sub>. The evaporation of the organic phase gave the crude product, and the crude product was purified by short-path silica gel column chromatography with hexane to afford 17.30 g (98%) of perfluorooctylbenzene.

ClSO<sub>3</sub>H (30 ml) was added to perfluorooctylbenzene (15.30 g, 30.8 mmol) at rt. The mixture was stirred for 2.5 h at 120 °C, and cooled to rt. The mixture was pipetted cautiously onto ice. The aqueous layer was extracted with AcOEt (3×10 ml). The organic layer was washed with saturated NaHCO<sub>3</sub> and brine, and the organic layer was dried over MgSO<sub>4</sub>. The evaporation of the organic phase gave the crude product, and the crude product was purified by silica gel column chromatography with hexane/AcOEt (85:15)-(60:40) to afford 15.8 g (87%) of **1b** as a solid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 8.29 (1H, d, *J* = 8.0 Hz), 8.27 (1H, s), 7.99 (1H, d, *J* = 8.0 Hz), 7.84 (1H, t, *J* = 8.0 Hz); IR (neat) 1380, 1241, 1198, 1146, 1171, 1086 cm<sup>-1</sup>; EIMS *m/z* (rel intensity) 558 (M<sup>+</sup>-Cl, 100%)

**Sulfonate 2b.** Et<sub>3</sub>N (1.1 ml, 7.8 mmol) was added to a stirred solution of **1b** (2.90 g, 4.88 mmol), 4-iodophenol (1.33 g, 6.03 mmol), DMAP (122.3 mg, 1.00 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (30ml) at 0 °C. The mixture was stirred for 12 h at rt, and the reaction was monitored by silica gel TLC. The mixture was quenched with H<sub>2</sub>O and evaporated. The mixture was purified by F-SPE (80% MeOH/H<sub>2</sub>O-AcOEt) using perfluorinated silica gel to afford 3.30 g (87%) of **2b** as a solid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 8.07 (1H, d, *J* = 8.0 Hz), 8.04 (1H, s), 7.91 (1H, d, *J* = 8.0 Hz), 7.74 (1H, t, *J* = 8.0 Hz), 7.62 (2H, d, *J* = 9.0 Hz), 6.73 (2H, d, *J* = 9.0 Hz); IR (neat) 1559, 1507, 1380, 1198, 1152 cm<sup>-1</sup>; EIMS *m/z* (rel intensity) 778 (M<sup>+</sup>, 100%), 219 (79); HRMS calcd. for C<sub>20</sub>H<sub>8</sub>O<sub>3</sub>F<sub>17</sub>SI 777.8967, found 777.8981.

**Sulfonyl chloride 1a.** Starting with PhI and C<sub>4</sub>F<sub>9</sub>I and following the procedure for the preparation of **1b** gave **1a** (2 steps 27%) as an oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.31 (1H, d, *J* = 8.0 Hz), 8.28 (1H, s), 8.01 (1H, d, *J* = 8.0 Hz), 7.87 (1H, t, *J* = 8.0 Hz); EIMS *m/z* (rel intensity) 394 (M<sup>+</sup>, 10%), 359 (100).

**Sulfonate 2a.** Starting with **1a** and following the procedure for the preparation of **2b** gave **2a** (85%) as an oil; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.06 (1H, d, *J* = 8.0 Hz), 8.02 (1H, d, *J* = 8.0 Hz), 7.91 (1H, d, *J* = 8.0 Hz), 7.74 (1H, t, *J* = 8.0 Hz), 7.62 (2H, d, *J* = 9.0 Hz), 6.72 (2H, d, *J* = 9.0 Hz); EIMS *m/z* (rel intensity) 578 (M<sup>+</sup>, 100%); HRMS calcd. for C<sub>16</sub>H<sub>8</sub>O<sub>3</sub>F<sub>9</sub>SI 577.9095, found 577.9091.

**Sulfonyl chloride 1c.** Starting with 1,3-diiodobenzene and C<sub>8</sub>F<sub>17</sub>I and following the procedure for the preparation of **1b** gave crude **1c** as a solid (chlorosulfonylation condition: MW irradiation, 300 W, 120 °C, 10 min). Further purification was not performed, because the title compound was decomposed by silica gel column chromatography.

**Sulfonate 2c.** Starting with **1c** and following the procedure for the preparation of **2b** gave **2c** (3 steps 44%) as a solid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.24 (2H, s), 8.08 (1H, s), 7.64 (2H, d, *J* = 9.0 Hz), 6.72 (2H, d, *J* = 9.0 Hz); EIMS *m/z* (rel intensity) 1195 (M<sup>+</sup>, 25%), 219 (100); HRMS calcd. for C<sub>28</sub>H<sub>7</sub>O<sub>3</sub>F<sub>34</sub>SI 1195.8618, found 1195.8610.

**Boronate 3.** A mixture of indole (2.34 g, 20.0 mmol) and KOH (4.30 g, 76.6 mmol) in DMF (30 ml) was stirred for 10 min. Then the DMF (20 ml) solution of iodine (5.26 g, 20.7 mmol) was added, and the mixture was stirred for 30 min. The mixture was poured into the solution (H<sub>2</sub>O 400 ml, 25% aqueous NH<sub>3</sub> 8 ml, Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> 400 mg), and the precipitation was filtrated with H<sub>2</sub>O. The precipitation was dissolved with CHCl<sub>3</sub>, and the organic layer was washed with brine and dried over MgSO<sub>4</sub>. The evaporation of the organic phase gave 3-iodoindole.

Et<sub>3</sub>N (3.2 ml, 22.8 mmol) was added to a stirred solution of 3-iodoindole, **1b** (8.91g, 15.0 mmol), DMAP (366.3 mg, 3.00 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (50 ml) at 0 °C. The mixture was stirred for 12 h at rt, and the reaction was monitored by silica gel TLC. The mixture was quenched with H<sub>2</sub>O and evaporated. The mixture was purified by F-SPE (80% MeOH/H<sub>2</sub>O-AcOEt) using perfluorinated silica gel to afford 10.54 g (88%) of 3-iodoindole protected by BsRf<sub>8</sub> as a solid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)

$\delta$  8.14 (1H, s), 8.04 (1H, d,  $J = 8.0$  Hz), 7.94 (1H, d,  $J = 8.0$  Hz), 7.77 (1H, d,  $J = 8.0$  Hz), 7.68 (1H, s), 7.62 (1H, t,  $J = 8.0$  Hz), 7.32-7.41 (3H, m), 1.26 (12H, s); IR (neat) 1383, 1198, 1144, 1117  $\text{cm}^{-1}$ ; EIMS  $m/z$  (rel intensity) 801 ( $M^+$ , 92%), 242 (100); HRMS calcd. for  $C_{22}H_9NO_2F_{17}SI$  801.9127, found 801.9136.

In a sealed tube,  $\text{Et}_3\text{N}$  (0.45 ml, 3.2 mmol) and pinacolborane (0.22 ml, 1.5 mmol) were added into a mixture of 3-iodoindole protected by  $\text{BsRf}_8$  (801.0 mg, 1.00 mmol),  $\text{PdCl}_2\text{dppf}$  complex with dichloromethane (1:1) (24.5 mg 0.03 mmol), and dioxane (5 ml), and the mixture was heated at 80 °C for 4 h. The evaporation of the mixture gave the crude product. The crude product was purified by F-SPE (80% MeOH/ $\text{H}_2\text{O}$ -AcOEt) using perfluorinated silica gel, and the product was recrystallized with hexane/ $\text{Et}_2\text{O}$  to afford 704.8 mg (88%) of **3** as a solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.18 (1H, s), 8.05 (1H, d,  $J = 8.0$  Hz), 7.97 (1H, s), 7.93 (2H, t,  $J = 8.0$  Hz), 7.74 (1H, d,  $J = 8.0$  Hz), 7.60 (1H, t,  $J = 8.0$  Hz), 7.26-7.33 (2H, m); IR (neat) 1391, 1198, 1146, 1129  $\text{cm}^{-1}$ ; EIMS  $m/z$  (rel intensity) 801 ( $M^+$ , 100%); HRMS calcd. for  $C_{28}H_{21}NO_4F_{17}SB$  801.1013, found 801.1035.

**Dibromobenzoquinone 4.**  $\text{AcCl}$  (1.2 ml, 16.8 mmol) was added to a mixture of 2,5-dihydroxybenzoquinone (7.00 g, 50 mmol) and MeOH (150 ml). the mixture was stirred for 24 h at 80 °C. The precipitation was filtration and washed with cold MeOH. The precipitation was dried *in vacuo* to afford 6.81 g (81%) of 2,5-dimethoxybenzoquinone.

NBS (7.20 g, 40.4 mmol) was slowly added to the mixture of 2,5-dimethoxybenzoquinone (3.36 g, 20.0 mmol) and DMF (100 ml). The mixture was stirred for 15 h at rt.  $\text{H}_2\text{O}$  was added to the reaction mixture, the aqueous layer was extracted with AcOEt (3 $\times$ 10 ml). The organic layer was washed with  $\text{H}_2\text{O}$  (two times) and brine (two times), and dried over  $\text{MgSO}_4$ . The evaporation of the organic phase gave the crude product, and the crude product was purified by silica gel column chromatography with hexane/ $\text{CHCl}_3$  (50:50)-(0:100) to afford 5.36 g (82%) of **4** as a solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  4.25 (6H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  174.51, 156.21, 114.80, 62.21; IR (neat) 1648, 1559, 1331, 1204, 1150  $\text{cm}^{-1}$ ; EIMS  $m/z$  (rel intensity) 324/326/328 ( $M^+$ , 33%,  $M^{+2}$ , 62%,  $M^{+4}$ , 35%), 297 (100); HRMS calcd. for  $C_8H_6O_4Br_2$  323.8633, found 323.8633.

**Monoindolylbenzoquinone 5.** In a sealed tube, A mixture of **3** (641.1 mg, 0.800 mmol), **4** (1.00 g, 3.08 mmol),  $\text{Ti}_2\text{CO}_3$  (1.121 g, 2.39 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (91.1 mg, 0.0788 mmol) in benzene (7 ml) was heated at 80 °C for 24 h. The mixture was filtered by Celite<sup>®</sup> and evaporated. The crude product was purified by F-SPE (80% MeOH/ $\text{H}_2\text{O}$ -AcOEt) using perfluorinated silica gel to afford 736.1 mg (quant.) of **5** as a solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.08 (1H, s), 8.04 (1H, d,  $J = 8.0$  Hz), 7.88 (1H, d,  $J = 8.0$  Hz), 7.69 (1H, s), 7.65 (1H, d,  $J = 8.0$  Hz), 7.52 (t,  $J = 8.0$  Hz), 7.23 (1H, t,  $J = 8.0$  Hz), 7.21 (1H, d,  $J = 8.0$  Hz), 7.14 (1H, t,  $J = 8.0$  Hz), 4.06 (3H, s), 3.75 (3H, s);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  179.86, 176.48, 156.90, 155.16, 138.85, 134.29, 132.13, 130.46, 130.22, 130.14, 129.73, 128.05, 125.43, 125.19, 123.94, 121.50, 118.39, 115.11, 113.35, 112.10, 61.81, 61.29, the other C of perfluoroalkyl chain were not assigned.; IR (neat) 1671, 1654, 1385, 1342, 1200, 1179, 1131  $\text{cm}^{-1}$ ; EIMS  $m/z$  (rel intensity) 921 ( $M^{+2}$ , 100%), 919 ( $M^+$ , 85%), HRMS calcd. for  $C_{30}H_{15}NO_6BrF_{17}S$  918.9532, found 918.9527.

**Boronate 6.** This was synthesized according to the reported procedure<sup>1)</sup>.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.96-8.00 (1H, m), 7.59 (1H, s), 7.40-7.43 (1H, m), 7.06-7.08 (2H, m), 1.65 (3H, sept,  $J = 7.6$  Hz), 1.28 (12H, s), 1.05 (18H, d,  $J = 7.6$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  141.73, 141.07, 135.03, 122.28, 121.41, 120.33, 113.63, 82.63 (2C), 25.01 (4C), 18.18 (6C), 12.79 (3C); IR (neat) 1534, 1449, 1387, 1136  $\text{cm}^{-1}$ ; EIMS  $m/z$  (rel intensity) 399 ( $M^+$ , 100%); HRMS calcd. for  $C_{23}H_{38}NO_2SiB$  399.2765, found 399.2757.

**Bisindolylbenzoquinone 7.** In a sealed tube, A mixture of **5** (274.3 mg, 0.298 mmol), **6** (359.0 mg, 0.898 mmol),  $\text{Ti}_2\text{CO}_3$  (420.9 mg, 0.898 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (34.4 mg, 0.0298 mmol) in benzene (5 ml) was heated at 80 °C for 24 h. The mixture was filtered by Celite<sup>®</sup> and washed with AcOEt. The evaporation of the organic phase gave the crude product. The mixture of the above crude product, CsF (221.2 mg, 1.456 mmol), THF (5 ml), MeOH (5 ml) was stirred for 30 min at rt. The mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  and evaporated. The mixture was purified by F-SPE (80% MeOH/ $\text{H}_2\text{O}$  - AcOEt) using perfluorinated silica gel to afford 250.1 mg (2 steps 88%) of **7** as a solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.53 (1H, s), 8.22 (1H, s), 8.14 (1H, d,  $J = 8.0$  Hz), 8.04-8.06 (1H, m), 8.00 (1H, d,  $J = 8.0$  Hz), 7.87 (1H, s), 7.75 (1H, d,  $J = 8.0$  Hz), 7.62 (1H, d,  $J = 2.0$  Hz), 7.61 (1H, t,  $J = 8.0$  Hz), 7.53 (1H, d,  $J = 8.0$  Hz), 7.35-7.43 (3H, m), 7.27 (1H, t,  $J = 8.0$  Hz), 7.23 (1H, t,  $J = 8.0$  Hz), 3.83 (3H, s), 3.75 (3H, s); IR (neat) 1382, 1200, 1175, 1144, 1115  $\text{cm}^{-1}$ ; EIMS  $m/z$  (rel intensity) 956 ( $M^+$ , 100%), HRMS calcd. for  $C_{38}H_{21}N_2O_6F_{17}S$  956.0849, found 956.0864.

**Cleaved bisindolylbenzoquinone 8.** MeI (0.020 ml, 0.320 mmol) was added to the mixture of **7** (31.4 mg, 0.0328 mmol),  $\text{Cs}_2\text{CO}_3$  (48.7 mg, 0.150 mmol) and DMF (1 ml). The mixture was stirred for 1.5 h at rt. The mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  and evaporated. The mixture was purified by F-SPE (80% MeOH/ $\text{H}_2\text{O}$  - AcOEt) using perfluorinated silica

gel to afford alkylated product 30.5 mg (96%) as a solid;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.22 (1H, s), 8.16 (1H, d,  $J = 8.0$  Hz), 8.00 (1H, d,  $J = 8.0$  Hz), 7.86 (1H, s), 7.78 (1H, d,  $J = 8.0$  Hz), 7.66 (1H, t,  $J = 8.0$  Hz), 7.55 (1H, d,  $J = 8.0$  Hz), 7.50 (1H, s), 7.42 (1H, d,  $J = 8.0$  Hz), 7.27-7.39 (4H, m), 7.19 (1H, t,  $J = 8.0$  Hz), 3.90 (3H, s), 3.85 (3H, s), 3.78 (3H, s); EIMS  $m/z$  (rel intensity) 970 ( $\text{M}^+$ , 100%); HRMS calcd. for  $\text{C}_{39}\text{H}_{23}\text{N}_2\text{O}_6\text{F}_{17}\text{S}$  970.1005, found 970.1021.

The mixture of above product (8.4 mg, 0.00865 mmol), Mg (2.0 mg, 0.0823 mmol),  $\text{NH}_4\text{Cl}$  (4.7 mg, 0.0879 mmol), MeOH (1 ml), and THF (1 ml) was stirred for 2 h at rt. The mixture was quenched with saturated  $\text{NH}_4\text{Cl}$ , and the aqueous layer was extracted with AcOEt (3 $\times$ 5 ml). The organic layer was washed with brine, and dried over  $\text{MgSO}_4$ . The evaporation of the organic phase gave the crude product, and the crude product was purified by silica gel column chromatography with AcOEt/ $\text{CHCl}_3$  (10:90) to afford 3.4 mg (95%) of **8** as a solid;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.56 (1H, s), 7.60-7.61 (2H, m), 7.58 (1H, s), 7.51 (1H, s), 7.42 (1H, d,  $J = 8.0$  Hz), 7.37 (1H, d,  $J = 8.0$  Hz), 7.27 (1H, dt,  $J = 1.0, 8.0$  Hz), 7.24 (1H, dt,  $J = 1.0, 8.0$  Hz), 7.18 (2H, t,  $J = 8.0$  Hz), 3.89 (3H, s), 3.77 (6H, s); EIMS  $m/z$  (rel intensity) 412 ( $\text{M}^+$ , 100%); HRMS calcd. for  $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_4$  412.1423, found 412.1411.

**Bisindolylmaleimide 9.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.24 (1H, s), 8.02 (1H, d,  $J = 8.0$  Hz), 7.98 (1H, s), 7.93 (1H, d,  $J = 8.0$  Hz), 7.83 (1H, s), 7.79 (1H, d,  $J = 8.0$  Hz), 7.62 (1H, t,  $J = 8.0$  Hz), 7.27 (1H, d,  $J = 8.0$  Hz), 7.18 (1H, t,  $J = 8.0$  Hz), 7.03 (1H, t,  $J = 8.0$  Hz), 6.92 (1H, d,  $J = 8.0$  Hz), 6.84 (1H, t,  $J = 8.0$  Hz), 6.71 (1H, d,  $J = 8.0$  Hz), 6.46 (1H, t,  $J = 8.0$  Hz), 4.19 (2H, q,  $J = 7.0$  Hz), 3.18 (3H, s), 1.47 (3H, t,  $J = 7.0$  Hz); EIMS  $m/z$  (rel intensity) 927 ( $\text{M}^+$ , 52%), 369 (100); HRMS calcd. for  $\text{C}_{37}\text{H}_{22}\text{N}_3\text{O}_4\text{F}_{17}\text{S}$  927.1060, found 927.1076.

**Monoindolylbenzoquinone 10.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.21 (1H, s), 8.15 (1H, d,  $J = 8.0$  Hz), 8.00 (1H, d,  $J = 8.0$  Hz), 7.83 (1H, s), 7.77 (1H, d,  $J = 8.0$  Hz), 7.65 (1H, t,  $J = 8.0$  Hz), 7.41-7.46 (3H, m), 7.33-7.39 (4H, m), 7.23 (1H, t,  $J = 8.0$  Hz), 3.86 (3H, s), 3.81 (3H, s); EIMS  $m/z$  (rel intensity) 917 ( $\text{M}^+$ , 76%), 330 (100); HRMS calcd. for  $\text{C}_{36}\text{H}_{20}\text{NO}_6\text{F}_{17}\text{S}$  917.0740, found 917.0735.

**Bisindolylpyrazine 11.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.75 (1H, dd,  $J = 1.5, 8.0$  Hz), 8.62 (1H, s), 8.44 (1H, s), 8.24 (1H, s), 8.15 (1H, dd,  $J = 2.5, 9.0$  Hz), 8.07 (1H, d,  $J = 8.0$  Hz), 8.04 (1H, dd,  $J = 1.5, 8.0$  Hz), 7.81 (1H, s), 7.73 (1H, d,  $J = 8.0$  Hz), 7.58 (1H, t,  $J = 8.0$  Hz), 7.30-7.40 (3H, m), 7.06 (1H, dt,  $J = 2.5, 9.0$  Hz), 4.27 (3H, s), 4.24 (2H, q,  $J = 7.0$  Hz), 1.55 (3H, t,  $J = 7.0$  Hz); EIMS  $m/z$  (rel intensity) 944 ( $\text{M}^+$ , 74%), 385 (100); HRMS calcd. for  $\text{C}_{37}\text{H}_{22}\text{N}_4\text{O}_3\text{F}_{18}\text{S}$  944.1125, found 944.1144.

**Bisindolylpyrazine 12.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.74 (1H, d,  $J = 8.0$  Hz), 8.64 (1H, s), 8.44 (1H, s), 8.37 (1H, d,  $J = 8.0$  Hz), 8.24 (1H, s), 8.06 (1H, d,  $J = 8.0$  Hz), 8.03 (1H, dd,  $J = 1.5, 8.0$  Hz), 7.73 (1H, d,  $J = 8.0$  Hz), 7.71 (1H, s), 7.58 (1H, t,  $J = 8.0$  Hz), 7.29-7.39 (5H, m), 7.18-7.20 (2H, m), 6.94 (1H, dd,  $J = 2.0, 8.0$  Hz), 6.78 (1H, d,  $J = 2.0$  Hz), 5.35 (2H, s), 4.31 (3H, s), 3.83 (3H, s); EIMS  $m/z$  (rel intensity) 1018 ( $\text{M}^+$ , 80%), 459 (100); HRMS calcd. for  $\text{C}_{43}\text{H}_{27}\text{N}_4\text{O}_4\text{F}_{17}\text{S}$  1018.1482, found 1018.1456.

**Monoindolylpyridine 13.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.44 (1H, d,  $J = 8.0$  Hz), 8.14 (1H, s), 8.06-8.10 (3H, m), 7.89 (1H, d,  $J = 8.0$  Hz), 7.79 (1H, s), 7.68-7.74 (2H, m), 7.63 (1H, d,  $J = 8.0$  Hz), 7.45 (1H, d,  $J = 8.0$  Hz), 7.40 (1H, d,  $J = 8.0$  Hz), 7.25-7.31 (2H, m), 7.11 (2H, d,  $J = 9.0$  Hz), 4.24 (2H, q,  $J = 7.0$  Hz), 1.53 (3H, t,  $J = 7.0$  Hz); EIMS  $m/z$  (rel intensity) 844 ( $\text{M}^+$ , 100%); HRMS calcd. for  $\text{C}_{35}\text{H}_{21}\text{N}_2\text{O}_3\text{F}_{17}\text{S}$  872.1001, found 872.0994.

**Bisindolylpyridine 14.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.44 (1H, d,  $J = 8.0$  Hz), 8.26 (1H, d,  $J = 8.0$  Hz), 8.25 (1H, s), 8.10 (1H, s), 8.08 (1H, d,  $J = 8.0$  Hz), 8.04 (1H, d,  $J = 8.0$  Hz), 7.75 (1H, d,  $J = 8.0$  Hz), 7.72 (1H, d,  $J = 7.5$  Hz), 7.64 (1H, s), 7.60 (1H, t,  $J = 8.0$  Hz), 7.59 (1H, d,  $J = 8.0$  Hz), 7.45 (1H, d,  $J = 7.5$  Hz), 7.33-7.41 (2H, m), 6.89 (1H, dd,  $J = 2.0, 8.0$  Hz), 6.82 (1H, d,  $J = 2.0$  Hz), 3.92 (3H, s), 3.83 (3H, s); EIMS  $m/z$  (rel intensity) 911 ( $\text{M}^+$ , 100%), 352 (44); HRMS calcd. for  $\text{C}_{37}\text{H}_{22}\text{N}_3\text{O}_3\text{F}_{17}\text{S}$  911.1110, found 911.1099.

**Biindolylthiophene 15.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.20 (1H, s), 8.07 (1H, d,  $J = 8.0$  Hz), 8.04 (1H, d,  $J = 8.0$  Hz), 8.01 (1H, d,  $J = 8.0$  Hz), 7.95 (1H, d,  $J = 8.0$  Hz), 7.76 (1H, d,  $J = 8.0$  Hz), 7.76 (1H, s), 7.61 (1H, t,  $J = 8.0$  Hz), 7.33-7.42 (5H, m), 7.22-7.30 (3H, m), 5.99-6.09 (1H, m), 5.27 (1H, dd,  $J = 1.0, 9.0$  Hz), 5.19 (1H, dd,  $J = 1.0, 17.0$  Hz), 4.77 (2H, dt,  $J = 5.0, 1.0$  Hz); EIMS  $m/z$  (rel intensity) 912 ( $\text{M}^+$ , 37%), 353 (100); HRMS calcd. for  $\text{C}_{37}\text{H}_{21}\text{N}_2\text{O}_2\text{F}_{17}\text{S}_2$  912.0773, found 912.0770.

**Bisindolylthiophene 16.**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.20 (1H, s), 8.07 (1H, d,  $J = 8.0$  Hz), 8.03 (1H, d,  $J = 8.0$  Hz), 7.94 (1H, d,  $J = 8.0$  Hz), 7.76 (1H, d,  $J = 8.0$  Hz), 7.76 (1H, s), 7.60-7.65 (2H, m), 7.35-7.42 (3H, m), 7.33 (1H, d,  $J = 4.0$  Hz), 7.25-7.29 (1H, m), 7.22 (1H, d,  $J = 4.0$  Hz), 7.02 (1H, dt,  $J = 2.0, 9.0$  Hz), 5.97-6.07 (1H, m), 5.27 (1H, dd,  $J = 1.0,$

10.0 Hz), 5.17 (1H, dd,  $J = 1.0, 17.0$  Hz), 4.75 (2H, dt,  $J = 5.5, 1.0$  Hz); EIMS  $m/z$  (rel intensity) 930 ( $M^+$ , 44%), 371 (100); HRMS calcd. for  $C_{37}H_{20}N_2O_2F_{18}S_2$  930.0679, found 930.0668.

**Ester 17.** A mixture of Ethyl 4-iodobenzoate (3.30 ml, 19.6 mmol),  $C_8F_{17}I$  (5.40 ml, 20.2 mmol) and Cu powder (5.08 g, 80.0 mmol) in DMSO (15ml) was stirred for 24 h at 120 °C. The mixture was filtered by Celite® and washed with AcOEt and  $H_2O$ . The aqueous layer was extracted with AcOEt (2×15 ml). The organic layer was washed with  $H_2O$  (two times) and brine, and the organic layer was dried over  $MgSO_4$ . The evaporation of the organic phase gave the crude product, and the crude product was purified by short-path column chromatography over silica gel with hexane/ $CHCl_3$  (50:50) to afford 10.5 g (95%) of Ethyl 4-perfluorooctylbenzoate.  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  8.18 (2H, d,  $J = 8.0$  Hz), 7.67 (2H, d,  $J = 8.0$  Hz), 4.43 (2H, q,  $J = 7.0$  Hz), 1.42 (3H, t,  $J = 7.0$  Hz); EIMS  $m/z$  (rel intensity) 568 ( $M^+$ , 20%); HRMS calcd. for  $C_{17}H_9O_2F_{17}$  568.0331, found 568.0349.

**Bnzylbromide 18.** The THF (10 ml) solution of 17 (5.21 g, 9.20 mmol) was slowly added to a solution of  $LiAlH_4$  (570.1 mg, 15.0 mmol) and THF (30 ml) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C, and the reaction was monitored by silica gel TLC. The mixture was quenched with aqueous THF, and 1M HCl was added. The aqueous layer was extracted with AcOEt (3×10 ml). The organic layer was washed with saturated  $NaHCO_3$  and brine and dried over  $MgSO_4$ . The evaporation of the organic phase gave the crude product, and the crude product was purified by short-path column chromatography over silica gel with hexane/AcOEt (70:30)-(50:50) to afford 4.18 g (87%) of benzyl alcohol;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  7.56 (2H, d,  $J = 8.0$  Hz), 7.46 (2H, d,  $J = 8.0$  Hz), 4.72 (2H, s); EIMS  $m/z$  (rel intensity) 526 ( $M^+$ , 72%); HRMS calcd. for  $C_{15}H_7OF_{17}$  526.0225, found 526.0217.

$PBr_3$  (0.50 ml, 5.26 mmol) was added to the mixture of benzyl alcohol (1.58 g, 3.00 mmol) and  $CH_2Cl_2$  (10 ml) at 0 °C. The reaction mixture was stirred for 2 h at rt, the mixture was quenched with saturated  $NaHCO_3$  at 0 °C. The aqueous layer was extracted with AcOEt (3×10 ml). The organic layer was washed with brine and dried over  $MgSO_4$ . The evaporation of the organic phase gave the crude product, and the crude product was purified by short-path column chromatography over silica gel with hexane/AcOEt (90:10) to afford 948.0 mg (54%) of benzylbromide **18** as a solid;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  7.57 (2H, d,  $J = 8.0$  Hz), 7.53 (2H, d,  $J = 8.0$  Hz), 4.51 (2H, s); EIMS  $m/z$  (rel intensity) 588 ( $M^+$ , 2%), 509 (100); HRMS calcd. for  $C_{15}H_6BrF_{17}$  587.9381, found 587.9348.

**Monoindolylpyrazine 19.** Starting with **3** and dihalo pyrazine<sup>2)</sup> and following the procedure for the preparation of **5** gave **21**.  $^1H$  NMR ( $CDCl_3$ , 500 MHz)  $\delta$  8.62 (1H, d,  $J = 8.0$  Hz), 8.45 (1H, s), 8.33 (1H, s), 8.22 (1H, s), 8.07 (1H, t,  $J = 8.0$  Hz), 8.02 (1H, d,  $J = 8.0$  Hz), 7.75 (1H, d,  $J = 8.0$  Hz), 7.59 (1H, t,  $J = 8.0$  Hz), 7.31-7.41 (2H, m), 4.19 (3H, s);  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz)  $\delta$  156.31, 138.95, 137.32, 136.71, 134.80, 132.63, 132.18, 130.56, 130.15, 130.06, 129.22, 128.42, 125.67 (2C), 124.52, 123.86, 117.18, 113.07, 54.93, the other C of perfluoroalkyl unit were not assigned.; IR (neat) 1526, 1382, 1200, 1152, 1142  $cm^{-1}$ ; EIMS  $m/z$  (rel intensity) 863 ( $M^{+2}$ , 100%), 861 ( $M^+$ , 93%), HRMS calcd. for  $C_{27}H_{13}N_3O_3BrF_{17}S$  860.9590, found 860.9570.

**Boronate 20.** This compound was synthesized by 3 steps. 1) Iodination of 2-ethoxycarbonylindole; 2) Protection using NaH (60%) and benzylbromide **18** in DMF; 3) Pd catalyzed borylation using HBPin;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  7.97 (1H, d,  $J = 8.0$  Hz), 7.45 (2H, d,  $J = 8.4$  Hz), 7.27-7.30 (2H, m), 7.21 (1H, t,  $J = 8.0$  Hz), 7.14 (2H, d,  $J = 8.4$  Hz), 5.81 (2H, s), 4.34 (2H, q,  $J = 7.0$  Hz), 1.44 (12H, s), 1.31 (3H, t,  $J = 7.0$  Hz); EIMS  $m/z$  (rel intensity) 823 ( $M^+$ , 100%); HRMS calcd. for  $C_{32}H_{27}NO_4F_{17}B$  823.1762, found 823.1759.

**Double tagged compound 21.** In a sealed tube, A mixture of **19** (42.6 mg, 0.0494 mmol), **20** (49.9 mg, 0.0606 mmol),  $Ti_2CO_3$  (46.8 mg, 0.100 mmol),  $Pd(PPh_3)_4$  (5.8 mg, 0.005 mmol) in benzene (2.5 ml) was heated at 80 °C for 24 h. The mixture was filtered by Celite® and washed with AcOEt. The evaporation of the organic phase gave the crude product. The crude product was purified by F-SPE (80% MeOH/ $H_2O$ -MeCN-THF) using perfluorinated silica gel. The MeCN eluent contained 72.1 mg (98%) of product **21** as a solid;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  8.79 (1H, d,  $J = 8.0$  Hz), 8.55 (2H, d,  $J = 3.0$  Hz), 8.26 (1H, s), 8.11 (1H, d,  $J = 8.0$  Hz), 8.06 (1H, d,  $J = 8.0$  Hz), 7.97 (1H, d,  $J = 8.0$  Hz), 7.76 (1H, d,  $J = 8.0$  Hz), 7.61 (1H, t,  $J = 8.0$  Hz), 7.52 (2H, d,  $J = 8.0$  Hz), 7.35-7.41 (4H, m), 7.25-7.28 (3H, m), 5.85 (2H, s), 4.23 (3H, s), 4.20 (2H, q,  $J = 7.0$  Hz), 1.04 (3H, t,  $J = 7.0$  Hz); EIMS  $m/z$  (rel intensity) 1478 ( $M^+$ , 100%); HRMS calcd. for  $C_{53}H_{28}N_4O_5F_{34}S$  1478.1238, found 1478.1244. The THF eluent contained the trace amount of unreacted **19** and excess **20**.

**Product 22.** TBAF (30.1 mg, 0.115 mmol) was added to the mixture of **21** (10.0 mg, 0.0067 mmol) and THF (1 ml), and the mixture was stirred for 1 h at rt. The reaction was monitored by TLC and quenched with saturated  $NH_4Cl$ . The mixture was evaporated, and purified by F-SPE (80% MeOH/ $H_2O$ -AcOEt) using perfluorinated silica gel. The 80% MeOH/ $H_2O$

eluent contained the hydrolyzed  $\text{BsRf}_8$ . The AcOEt eluent contained 6.1 mg (98%) of deprotected compound as a solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.85-8.87 (1H, m), 8.53 (1H, s), 8.50 (1H, s), 8.30 (1H, d,  $J = 3.0$  Hz), 7.99 (1H, d,  $J = 8.0$  Hz), 7.53 (2H, d,  $J = 8.4$  Hz), 7.45-7.47 (1H, m), 7.34-7.39 (2H, m), 7.26-7.31 (5H, m), 5.86 (2H, s), 4.21 (2H, q,  $J = 7.0$  Hz), 4.18 (3H, s), 1.05 (3H, t,  $J = 7.0$  Hz); EIMS  $m/z$  (rel intensity) 920 ( $\text{M}^+$ , 100%); HRMS calcd. for  $\text{C}_{39}\text{H}_{25}\text{N}_4\text{O}_3\text{F}_{17}$  920.1655, found 920.1642.

MeI (5  $\mu\text{l}$ , 0.08 mmol) was added to the mixture of the above deprotected product (6.1 mg,  $6.6 \times 10^{-3}$  mmol),  $\text{Cs}_2\text{CO}_3$  (16.0 mg, 0.049 mmol) and DMF (0.5 ml). The mixture was stirred for 1.5 h at rt. The mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  and the organic solvent was evaporated. The mixture was purified by F-SPE (80% MeOH/ $\text{H}_2\text{O}$ -AcOEt) using perfluorinated silica gel to afford 6.0 mg (97%) of **22** as a solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.86 (1H, d,  $J = 8.0$  Hz), 8.51 (1H, s), 8.14 (1H, s), 8.00 (1H, d,  $J = 8.0$  Hz), 7.52 (2H, d,  $J = 8.4$  Hz), 7.26-7.40 (8H, m), 5.86 (2H, s), 4.20 (2H, q,  $J = 7.0$  Hz), 4.19 (3H, s), 1.04 (3H, t,  $J = 7.0$  Hz); EIMS  $m/z$  (rel intensity) 934 ( $\text{M}^+$ , 100%); HRMS calcd. for  $\text{C}_{40}\text{H}_{27}\text{N}_4\text{O}_3\text{F}_{17}$  934.1812, found 934.1832.

**Product 23.**  $\text{PhCOCl}$  (5  $\mu\text{l}$ , 0.045 mmol) was added to the mixture of the above deprotected product (13.5 mg, 0.0147 mmol), DMAP (0.4 mg, 0.003 mmol),  $\text{Et}_3\text{N}$  (10  $\mu\text{l}$ , 0.070 mmol), and  $\text{CH}_2\text{Cl}_2$  (0.5 ml) at 0 °C. The mixture was stirred for 2 h at rt. The reaction was quenched with  $\text{H}_2\text{O}$ , and the organic solvent was evaporated. The mixture was purified by F-SPE (80% MeOH/ $\text{H}_2\text{O}$ -AcOEt) using perfluorinated silica gel to afford 13.8 mg (92%) of **23** as a solid;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  8.42-8.60 (1H, m), 8.57 (1H, s), 8.43-8.45 (1H, s), 8.39 (1H, s), 7.96 (1H, d,  $J = 8.0$  Hz), 7.86-7.88 (2H, m), 7.68 (1H, t,  $J = 8.0$  Hz), 7.58-7.61 (2H, m), 7.52-7.55 (3H, m), 7.45-7.47 (2H, m), 7.38-7.40 (2H, m), 7.26-7.29 (2H, m), 5.86 (2H, s), 4.21 (2H, q,  $J = 7.0$  Hz), 4.05 (3H, s), 1.05 (3H, s); EIMS  $m/z$  (rel intensity) 1024 ( $\text{M}^+$ , 100%); HRMS calcd. for  $\text{C}_{46}\text{H}_{29}\text{N}_4\text{O}_4\text{F}_{17}$  1024.1917, found 1024.1924.

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