Supporting information for:

Formation of Benzo[*b*]fluorenes and the Benzo[*a*]fluorene Core of the Fluostatins by Cyclization of Diaryldiynones

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Methods: NMR spectra were recorded at 23 °C. Elemental analyses were performed at the UAM (SIdI). Solvents were purified and dried using standard procedures. Chromatography purifications were carried out using flash grade silica gel with distilled solvents. All reactions except for the cyclizations under conditions B (Table 1), were carried out under an Ar atmosphere.

6a: *n*BuLi (0.39 mL 2.5 M in hexane) was slowly added to a solution of 2-ethynylanisole (**5a**) (129.4 mg, 0.98 mmol) in THF (4 mL) at 0 °C. After stirring for 30 min, a solution of **4** (200.0 mg, 0.98 mmol) in THF (4 mL) was added. The reaction mixture was stirred at room temperature for 5 h, diluted with EtOAc and washed with saturated aqueous NaCl solution. The organic layer was dried (Na_2SO_4), the solvent was evaporated, and the residue was chromatographed (30:1Hexane/EtOAc) to give **6a** as a yellow oil (235 mg, 71%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84 (dd, *J* = 8.1, 1.2Hz, 1H), 7.49 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.42 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.34 (td, *J* = 7.3, 1.2Hz, 1H), 7.29-7.22 (m, 2H), 6.88 (td, *J* = 8.5, 0.8 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 6.15 (s, 1H), 3.81 (s, 3H), 3.30 (br s, 1H, OH), 0.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 159.97 (C), 142.87 (C), 133.56 (CH), 132.44 (CH), 129.82 (CH), 128.93 (CH), 127.87 (CH), 126.81 (CH), 121.20 (CH), 120.20 (CH), 111.61 (C), 110.49 (C), 102.32 (C), 100.12 (C), 92.23 (C), 82.72 (C), 63.50 (CH), 55.55 (CH_3), -0.27 (CH_3).

6b: *n*BuLi (0.52 mL 2.5 M in hexane) was slowly added to a solution of phenylacetylene (**5b**) (133.8 mg, 1.31 mmol) in THF (10 mL) at 0 °C. After stirring for 30 min, a solution of **4** (264.8 mg, 1.31 mmol) in THF (10 mL) was added. The reaction mixture was stirred at room temperature for 16 h, diluted with EtOAc and washed with saturated aqueous NaCl solution. The organic layer was dried (Na_2SO_4), the solvent was evaporated, and the residue was chromatographed (7:1Hexane/EtOAc) to give **6b** as a yellow oil (203.5 mg, 51%): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.73 (d, *J* = 7.54 Hz, 1H), 7.53-7.43 (m, 3H), 7.40-7.28 (m, 5 H), 6.06 (s, 1H), 0.27 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 142.83 (C), 132.56 (CH), 131.61 (CH), 128.95 (CH), 128.28 (CH), 128.05 (CH), 127.88 (CH), 126.47 (CH), 122.41 (C), 120.94 (C), 102.27 (C), 100.47 (C), 88.17 (C), 86.14 (C), 63.46 (CH), 0.28 (CH_3).Anal. Calcd for $C_{20}H_{20}OSi$: C, 78.90; H, 6.62. Found: C, 78.52; H, 7.04.

6c: *n*BuLi (0.61 mL 2.5 M in hexane) was slowly added to a solution of 2-ethynyltoluene (**5c**) (178 mg, 1.53 mmol) in THF (5 mL) at 0 °C. After stirring for 30 min, a solution of **4** (309.6 mg, 1.53 mmol) in THF (5 mL) was added. The reaction mixture was stirred at room temperature for 16 h, diluted with EtOAc and washed with saturated aqueous NaCl solution. The organic layer was dried (Na_2SO_4), the solvent was evaporated, and the residue was chromatographed (7:1Hexane/EtOAc) to give **6c** as a yellow oil (373.5 mg, 77%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.83 (dd, *J* = 7.7, 1.2Hz, 1H), 7.59 (dd, *J* = 7.3, 1.2Hz, 1H), 7.52 (br d, *J* = 7.3Hz, 1H), 7.43 (td, *J* = 7.7, 1.6 Hz, 1H), 7.33 (td, *J* = 7.7, 1.6 Hz, 1H), 7.30-7.25 (m, 2H), 7.23-7.16 (m, 1H), 6.22 (s, 1H), 3.40 (br s, 1H, OH), 2.51 (s, 3H), 0.37 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 143.04 (C), 140.14 (C), 132.61 (CH), 131.94 (CH), 129.21 (CH), 128.96 (CH), 128.32 (CH), 127.84 (CH), 126.39 (CH), 125.31 (CH), 122.18 (C), 120.89 (C), 102.37 (C), 100.37 (C), 92.12 (C), 85.14 (C), 63.52 (CH), 20.55 (CH_3), -0.28 (CH_3). Anal. Calcd for $C_{21}H_{22}OSi$: C, 79.20; H, 6.96. Found: C, 78.78; H, 7.39.

6d: *n*BuLi (0.5 mL 2.5 M in hexane) was slowly added to a solution of 3-ethynyltoluene (**5d**) (188 mg, 1.61 mmol) in THF (5 mL) at 0 °C. After stirring for 30 min, a solution of **4** (325.3 mg, 1.53 mmol) in THF (5 mL) was added. The reaction mixture was stirred at room temperature for 16 h, diluted with EtOAc and washed with saturated aqueous NaCl solution. The organic layer was dried (Na_2SO_4), the solvent was evaporated, and the residue was chromatographed (7:1Hexane/EtOAc) to give **6d** as a yellow oil (248.8 mg, 49%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.76 (br d, *J* = 7.3Hz, 1H), 7.53 (br d, *J* = 7.3Hz, 1H), 7.39 (br d, *J* = 7.3Hz, 1H), 7.31-7.27 (m, 3H), 7.21 (br t, *J* = 7.6 Hz, 1H), 7.14 (br d, *J* = 7.3Hz, 1H), 6.09 (s, 1H), 3.21 (s, 1H, OH), 2.32 (s, 3H), 0.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 142.90 (C), 137.74 (C), 132.64 (CH), 132.25 (CH), 129.24 (CH), 129.01 (CH), 128.70 (CH), 128.01 (CH), 127.95 (CH),126.11 (CH), 122.26 (C), 121.04 (C), 102.32 (C), 100.51 (C), 87.79 (C), 86.45 (C), 63.58 (CH), 21.03 (CH_3), -0.23 (CH_3). Anal. Calcd for $C_{21}H_{22}OSi$: C, 79.20; H, 6.96. Found: C, 78.63; H, 7.41.

6e: *n*BuLi (0.54 mL 2.5 M in hexane) was slowly added to a solution of 4-ethynyltoluene (**5e**) (157.1 mg, 1.35 mmol) in THF (10 mL) at 0 °C. After stirring for 30 min, a solution of **4** (273.3 mg, 1.31 mmol) in THF (10 mL) was added. The reaction mixture was stirred at room temperature for 16 h, diluted with EtOAc and washed with saturated aqueous NaCl solution. The organic layer was dried (Na_2SO_4), the solvent was evaporated, and the residue was chromatographed (7:1Hexane/EtOAc) to give **6e** as a yellow oil (230.4 mg, 54 %): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.74 (br d, *J* =7.5 Hz, 1H), 7.52 (br d, *J* =7.5 Hz, 1H), 7.43-7.25 (m, 5H), 7.12 (br d, *J* =7.5 Hz, 1H), 6.05 (d, *J* = 5.4 Hz, 1H), 2.91 (d, *J* = 5.4 Hz, 1H, OH), 2.35 (s, 3H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 142.88 (C), 138.26 (C), 132.45 (CH), 131.43 (CH), 128.89 (CH), 128.73 (CH), 127.77 (CH), 126.41 (CH), 120.89 (C), 119.31 (C), 102.33 (C), 100.35 (C), 87.44 (C), 86.25 (C), 63.41 (CH), 21.21 (CH_3), -0.28 (CH_3). Anal. Calcd for $C_{21}H_{22}OSi$: C, 79.20; H, 6.96. Found: C, 78.69; H, 7.13.

3a: $BaMnO_4$ (1.501 g, 5.86 mmol) was added to a solution of **6a** (980.2 mg, 2.93 mmol) in CH_2Cl_2 (20 mL) at room temperature. The reaction mixture was stirred for 3 days, filtered through Celite and evaporated. The residue was chromatographed (8:1Hexane/EtOAc) to give **3a** as a yellow solid (774 mg, 79%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.33-8.29 (m, 1H), 7.62-7.56 (m, 2H), 7.51-7.39 (m, 3H), 6.99-6.91 (m, 2H), 3.93 (s, CH_3), 0.22 (CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 177.21 (C), 161.76 (C), 138.89 (C), 134.98 (CH), 132.47 (CH), 132.05 (CH), 128.04 (CH), 122.57 (C), 120.59 (CH), 110.83 (CH), 109.55 (C), 992.00 (103.22 (C), 100.90 (C), 92.00 (C), 90.30 (C), 55.83 (CH_3), -0.25 (CH_3).

3b: $BaMnO_4$ (343.0 mg, 1.34 mmol) was added to a solution of **6b** (203.5 mg, 0.67 mmol) in CH_2Cl_2 (20 mL) at room temperature. The reaction mixture was stirred for 3H, filtered through Celite and evaporated. The residue was chromatographed (9:1Hexane/EtOAc) to give **3b** as a yellow oil (184.1 mg, 91%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10 (dd, *J* = 7.9, 1.9 Hz, 1H), 7.72-7.59 (m, 3H), 7.56-7.36 (m, 5H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 177.48 (C), 138.88 (CH), 134.99 (CH), 133.14 (CH), 132.27 (CH), 131.19 (CH), 130.77 (CH), 128.61 (CH), 128.24 (CH), 122.60 (C), 120.18 (C), 102.90 (C), 101.36 (C), 93.30 (C), 87.97 (C), -0.26 (CH_3). Anal. Calcd for $C_{20}H_{18}OSi$: C, 79.43; H, 6.00. Found: C, 79.15; H, 6.12.

3c: $BaMnO_4$ (395.1 mg, 1.54 mmol) was added to a solution of **6c** (245.3 mg, 0.77 mmol) in CH_2Cl_2 (15 mL) at room temperature. The reaction mixture was stirred for 17 h, filtered through Celite and evaporated. The residue was chromatographed (10:1hexane/EtOAc) to give **3c** as a yellow oil (227.5 mg, 93%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.59 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.58 (dd, *J* = 6.5, 1.0 Hz, 1H), 7.47 (td, *J* = 7.7, 1.6 Hz, 1H), 7.41 (td, *J* = 7.3, 1.2Hz, 1H), 7.31 (td, *J* = 7.7, 1.2Hz, 1H), 7.22 (br d, *J* = 8 Hz, 1H), 7.17 (br t, *J* = 8 Hz, 1H), 2.51 (s, 3H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 177.18 (C), 142.04 (C), 138.86 (C), 134.84 (CH), 133.50 (CH), 132.03 (CH), 130.97 (CH), 130.66 (CH), 129.63 (CH), 128.04 (CH), 125.70 (CH), 122.35 (C), 119.78 (C), 102.91 (C), 101.12 (C), 92.20 (C), 91.59 (C), 20.55 (CH_3), -0.42 (CH_3); EI-MS *m/z* 316 (M^+, 33), 301 (100).

3d: $BaMnO_4$ (356.0 mg, 1.38 mmol) was added to a solution of **6d** (221.1 mg, 0.69 mmol) in CH_2Cl_2 (15 mL) at room temperature. The reaction mixture was stirred for 17 h, filtered through Celite and evaporated. The residue was chromatographed (10:1Hexane/EtOAc) to give **3d** as a yellow solid (181.8 mg, 83%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.61 (dd, *J* = 6.9, 1.6 Hz, 1H), 7.50-7.40 (m, 4H), 7.30-7.25 (m, 2H), 2.34 (s, 3H), 0.22 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 177.37 (C), 138.86 (C), 138.27 (C), 134.87 (CH), 133.50 (CH), 132.11 (CH), 131.61 (CH), 131.05 (CH), 130.21 (CH), 128.41 (CH), 128.12 (CH), 122.49 (C), 119.89 (C), 102.85 (C), 101.21 (C), 93.59 (C), 87.68 (C), 21.03 (CH_3), -0.36 (CH_3); EI-MS *m/z* 316 (M^+, 33), 301 (100), 242 (19).

3e: $BaMnO_4$ (369.0 mg, 1.44 mmol) was added to a solution of **6e** (230.4 mg, 0.72 mmol) in CH_2Cl_2 (20 mL) at room temperature. The reaction mixture was stirred for 3H, filtered through Celite and evaporated. The residue was chromatographed (9:1Hexane/EtOAc) to give **3e** as a yellow oil (205.9 mg, 90%): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.09 (dd, *J* = 7.4, 1.3Hz, 1H), 7.61(dd, *J* = 7.7, 1.6 Hz, 1H), 7.54 (br d, *J* = 8.2Hz, 2H), 7.49 (td, *J* = 7.4, 1.6 Hz, 1H), 7.43 (td, *J* = 7.6, 1.5 Hz, 1H), 7.20 (br d, *J* = 8.0 Hz, 2H), 2.39 (3H), 0.21 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 177.61 (C), 141.48 (C), 139.07 (C), 134.94 (CH), 133.20 (CH), 132.11 (CH), 131.12 (CH), 129.39 (CH), 128.16 (CH), 122.55 (C), 117.10 (C), 102.90 (C), 101.25 (C), 94.02 (C), 87.89 (C), 21.74 (CH_3), -0.27 (CH_3). Anal. Calcd for $C_{21}H_{20}OSi$: C, 79.70; H, 6.37. Found: C, 79.38; H, 6.16.

Thermal cyclization of diaryldiynones in 1,2-dichlorobenzene. General procedure: A solution of **3a-e** in 1,2-dichlorobenzene (0.2 M for **3b**, 0.06-0-09 M for **3a** and **3c-3e**) was heated under refluxing conditions for the stated time (Table 1). The solvent was evaporated, and the residue was chromatographed (gravity column, 30:1 Hexane/EtOAc).

2-Methoxy-6-trimethylsilylbenzo[*a*]fluorene-11-one (7a). ^{1}H NMR (C_6D_6, 500 MHz) δ 8.84 (d, *J* = 2.5 Hz, H-1), 7.95 (s, H-5), 7.64 (d, *J* = 5.9 Hz, H-7 or H-10), 7.63 (d, *J* = 5.9 Hz, H-10 or H-7), 7.33 (d, *J* = 9.0 Hz, H-4), 7.09 (dd, *J* = 9.0, 2.6 Hz, H-3), 7.00 (td, *J* = 7.6, 1.2Hz, H-8 or H-9), 6.81 (t, *J* = 7.6 Hz, H-9 or H-8), 3.52 (s, 3H), 0.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz; DEPT) δ 196.24 (C), 161.21 (C), 151.40 (C), 144.95 (C), 142.70 (CH, C-5), 135.22 (C), 133.60 (CH), 132.08 (C), 130.10 (CH), 129.31 (CH), 129.20 (C), 128.63 (CH), 125.81 (C), 123.62 (CH), 119.96 (CH), 116.87 (C), 101.61 (CH, C-1), 55.54 (CH_3), 0.29 (CH_3). No long range correlation was observed between the downfield signals (δ 8.84 and 7.95) and the carbonyl signal. EI-MS *m/z* 332 (M^+, 98), 317 (100), 289 (47).

The ^{1}H NMR assignment was based on a COSY experiment (C_6D_6, 500 MHz). The ^{13}C NMR assignments were based on HMQC and HMBC experiments ($CDCl_3$, 75 MHz).

6-Trimethylsilylbenzo[*a*]fluorene-11-one (7b). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.06 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.16 (s, 1H), 7.77 (br d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.65-7.62 (m, 1H), 7.62-7.51 (m, 1H), 7.47-7.40 (m, 2H), 7.26 (td, *J* = 7.4, 0.9 Hz, 1H), 0.55 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.52, 151.30, 145.47, 143.50, 135.41, 134.11, 133.72, 132.62, 130.68, 130.27, 129.10, 128.85, 127.34, 126.98, 124.62, 124.05, 123.97, 0.66; EI-MS *m/z* 302 (M^+, 100), 287 (96), 259 (56).

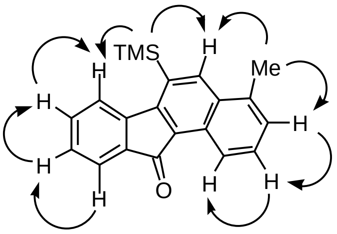
2-Methyl-6-trimethylsilylbenzo[*a*]fluorene-11-one (7c). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.87 (d, *J* = 0.6, 1H), 8.12 (s, 1H), 7.69-7.64 (m, 3H), 7.45 (td, *J* = 7.6, 1.1Hz, 1H), 7.28-7.25 (m, 2H), 2.56 (s, 3H), 0.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz; DEPT) δ 196.60 (C), 151.40 (C), 145.51 (C), 143.26 (CH), 140.70 (C), 135.49 (C), 134.02 (CH), 132.20 (C), 131.36 (C), 130.96 (C), 129.30 (CH), 128.99 (CH), 128.69 (CH), 126.75 (C), 123.93 (CH), 123.90 (CH), 123.49 (CH), 22.64 (CH_3), 0.71 (CH_3); EI-MS *m/z* 316 (M^+, 100), 302 (99), 243 (11).

3-Methyl-6-trimethylsilylbenzo[*a*]fluorene-11-one (7d). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.96 (d, *J* = 8.6 Hz, 1H), 8.10 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.2Hz, 1H), 7.57

(s, 1H), 7.46-7.43 (m, 2H), 7.27 (t, *J* = 7.4 Hz, 1H), 2.51 (s, 3H), 0.56 (s, 9H); ^{13}C NMR (CDCl$_3$, 125 MHz; DEPT) δ 196.67 (C), 150.41 (C), 145.67 (C), 142.77 (CH), 136.75 (C), 135.40 (C), 134.10 (CH), 134.03 (C), 132.63 (CH), 132.53 (C), 128.88 (CH), 127.76 (CH), 127.35 (C), 124.37 (CH), 123.99 (CH), 123.81 (CH), 113.02 (C), 22.12 (CH$_3$), 0.67 (CH$_3$); EI-MS *m/z* 316 (M$^+$, 100), 301 (82), 229(10).

4-Methyl-6-trimethylsilylbenzo[*a*]fluorene-11-one (7e). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.96 (d, *J* = 8.4 Hz, H-1), 8.39 (s, H-5), 7.67 (d, *J* = 7.6 Hz, H-7), 7.63 (dt, *J* = 7.1, 0.6 Hz, H-10), 7.48 (dd, *J* = 8.5, 6.9 Hz, H-2), 7.43 (td, *J* = 7.6, 1.3Hz, H-8), 7.29-7.24 (m, H-3 and H-9), 2.69 (s, 3H), 0.56 (s, 9H); ^{13}C NMR (CDCl$_3$, 75 MHz; DEPT) δ 196.08 (C), 150.32 (C), 144.85 (C), 138.91 (CH), 135.00 (C), 134.76 (C), 133.61 (CH), 132.33 (C), 131.61 (C), 130.54 (C), 129.65 (CH), 128.59 (CH), 127.34 (CH), 127.11 (C), 123.54 (CH), 123.43 (CH), 122.40 (CH), 19.41 (CH$_3$), 0.17 (CH$_3$); EI-MS *m/z* 316 (100, M$^+$), 301 (82), 273 (45).

The ^{1}H NMR assignment was based on a NOESY experiment (500 MHz, CDCl$_3$).



The figure shows the observed nOe enhancements.

9-Methoxy-5-trimethylsilylbenzo[*b*]fluorene-11-one (8a). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.70 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.52 (td, *J* = 7.5, 1.3Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.34 (t *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 4.00 (s, 3H), 0.60 (s, 9H); ^{13}C NMR (CDCl$_3$, 75 MHz; DEPT) δ 193.20 (C), 157.85 (C), 147.57 (C), 146.57 (C), 142.67 (C), 136.77 (C), 133.56 (CH), 132.21 (C), 128.73 (CH), 128.12 (CH), 126.45 (CH), 124.51 (C), 124.03 (CH), 122.29 (CH), 121.20 (C), 104.90 (CH), 55.66 (CH$_3$), 3.17 (CH$_3$), (one carbon signal was not observed); EI-MS *m/z* 322 (100, M$^+$), 317 (82), 273 (21).

5-Trimethylsilylbenzo[*b*]fluorene-11-one (8b). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.16 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 7.85 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.80-7.76 (m, 2H), 7.56-7.43 (m, 3H), 7.33 (td, *J* = 7.5, 0.8 Hz, 1H), 0.62 (s, 9H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 193.15, 146.90, 146.74, 141.57, 136.61, 135.05, 133.82, 133.00, 132.70, 131.12, 129.89, 128.78, 127.80, 126.57, 126.49, 126.25, 124.13, 3.16; EI-MS *m/z* 302 (M$^+$, 86), 287 (100), 259 (54).

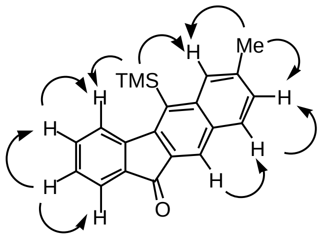
9-Methyl-5-trimethylsilylbenzo[*b*]fluorene-11-one (8c). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.43 (d, *J* = 0.8 Hz, 1H), 8.00 (d, *J* = 8.3Hz, 1H), 7.82 (d, *J* = 7.3Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.56 (td, *J* = 7.8, 1.3Hz, 1H), 7.42 (dd, *J* = 8.3, 7.0 Hz, 1H), 7.37 (td, *J* = 7.3, 0.8 Hz, 1H), 7.31 (d, *J* = 7.0 Hz, 1H), 2.75 (s, 3H), 0.63 (s, 9H); EI-MS *m/z* 316 (M$^+$, 89), 301 (100), 273 (38).

8-Methyl-5-trimethylsilylbenzo[*b*]fluorene-11-one (8d). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.09 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.63 (br s, 1H), 7.52 (td, *J* = 7.5, 1.1Hz, 1H), 7.35 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.32 (td, *J* = 7.4, 0.8 Hz, 1H), 2.72 (s, 3H), 0.61 (s, 9H); ^{13}C NMR (CDCl$_3$, 125 MHz; DEPT) δ 193.82 (C), 147.32 (C), 146.59 (C), 140.17 (C), 137.03 (C), 136.57 (CH), 134.89 (C), 134.25 (CH), 133.54 (C), 133.36 (C), 130.80 (CH), 130.39 (CH), 130.14 (CH), 129.01 (CH), 126.81 (CH), 126.60 (CH), 124.54 (CH), 21.60 (CH$_3$), 3.62 (CH$_3$); EI-MS *m/z* 316 (M$^+$, 98), 301 (100), 273 (52).

7-Methyl-5-trimethylsilylbenzo[*b*]fluorene-11-one (8e). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.15 (s, H-10), 7.93 (br d, *J* = 0.8 Hz, H-6), 7.81-7.78 (m, H-1, H-4, and H-9), 7.55 (td, *J* = 7.5, 1.3Hz, H-3), 7.36 (td, *J* = 7.5, 0.8 Hz, H-2), 7.30 (dd, *J* = 8.2, 1.5 Hz, H-8), 2.55 (s, 3H), 0.64

(s, 9H); ^{13}C NMR (CDCl$_3$, 75 MHz; DEPT) δ 193.15 (C), 147.08 (C), 146.69 (C), 141.78 (C), 137.91 (CH), 136.68 (C), 133.84 (C), 133.64 (CH), 132.33 (C), 130.88 (CH), 130.66 (C), 129.57 (CH), 128.65 (CH), 128.20 (CH), 126.39 (CH), 123.99 (CH), 22.08 (CH$_3$), 3.36 (s, CH$_3$), (one carbon signal was not observed); EI-MS *m/z* 316 (91, M$^+$), 301 (100), 273 (41).

Long range ^{1}H-^{13}C correlations were observed between the carbonyl carbon (δ 193.15) and H-10 (8.15, s) and H-1 (7.81-7.78 m). The ^{1}H NMR assignment was based on a NOESY experiment (500 MHz, CDCl$_3$).



The figure shows the nOe enhancements.

9-Methoxybenzo[*b*]fluorene-11-one (9a). ^{1}H NMR (CDCl$_3$, 300 MHz) δ 8.67 (s, 1H), 7.83 (s, 1H), 7.73-7.70 (m, 2H), 7.56 (td, *J* = 7.5, 1.1 Hz, 1H), 7.50-7.39 (m, 2H), 7.35 (td, *J* = 7.5, 1.0 Hz), 6.83 (dd, *J* = 7.6, 1.0 Hz, 1H), 4.01 (s, 3H); EI-MS *m/z* 260 (M$^+$, 100), 217 (75), 189 (28).

Benzo[*b*]fluorene-11-one (9b).[1] ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.17 (s, 1H), 7.89 (dt, *J* = 8.1, 0.6 Hz, 1H), 7.87 (s, 1H), 7.83 (dd, *J* = 8.1, 0.6 Hz, 1H), 7.75 (dt, *J* = 8.2, 0.7 Hz, 1H), 7.72 (dt, *J* = 7.5, 0.8 Hz, 1H), 7.56 (td, *J* = 7.4, 1.1Hz, 1H), 7.55 (td, *J* = 8.1, 1.3Hz, 1H), 7.47 (td, *J* = 8.1, 1.2Hz, 1H), 7.35 (dt, *J* = 7.4, 0.9 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz; DEPT) δ 193.53 (C), 145.28 (C), 138.84 (C), 137.36 (C), 136.62 (C), 135.43 (CH), 134.08 (C), 133.24 (C), 131.24 (CH), 129.61 (CH), 129.42 (CH), 129.19 (CH), 127.36 (CH), 126.13 (CH), 124.90 (CH), 121.41 (CH), 119.48 (CH); EI-MS *m/z* 230 (M$^+$, 100), 202 (22).

9-Methylbenzo[*b*]fluorene-11-one (9c). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.40 (s, 1H), 7.89 (s, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.1Hz, 1H), 7.58 (td, *J* = 7.4, 1.0 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.37 (td, *J* = 7.5, 0.8 Hz, 1H), 7.33 (d, *J* = 7.0 Hz, 1H), 2.74 (s, ·3H); ^{13}C NMR (CDCl$_3$, 125 MHz; DEPT) δ 193.82 (C), 145.27 (C), 138.51 (C), 138.12 (C), 137.67 (C), 136.68 (C), 135.39 (CH), 133.23 (C), 132.93 (CH), 129.54 (CH), 129.21 (CH), 128. 36 (CH), 127.61 (CH), 124.89 (CH), 122.53 (CH), 121.40 (CH), 120.11 (CH), 30.11 (CH$_3$); EI-MS *m/z* 244 (M$^+$, 100), 215 (43).

8-Methylbenzo[*b*]fluorene-11-one (9d). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.09 (s, 1H), 7.82 (s, 1H), 7.74 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.69 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.66 (br s, 1H), 7.55 (td, *J* = 7.5, 1.1Hz, 1H), 7.38 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.33 (td, *J* = 7.5, 0.9 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz; DEPT) δ 193.74 (C), 145.46 (C), 138.06 (C), 137.32 (CH), 136.55 (C), 135.48 (C), 135.39 (CH), 134.27 (C), 133.29 (C), 131.59 (CH), 130.46 (CH), 129.36 (CH), 128.97 (CH), 125.60 (CH), 124.85 (CH), 121.25 (CH), 119.30 (CH), 21.95 (CH$_3$); EI-MS *m/z* 244 (M$^+$, 100), 215 (41).

7-Methylbenzo[*b*]fluorene-11-one (9e). ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.13 (s, H-10), 7.79 (d, *J* = 8.1Hz, H-4), 7.78 (s, H-5), 7.75 (dt, *J* = 7.4, 0.8 Hz, H-9), 7.71 (dt, *J* = 7.5, 0.9 Hz, H-1), 7.61 (s, H-6), 7.55 (td, *J* = 7.5, 1.2Hz, H-2), 7.34 (td, *J* = 7.4, 1.0 Hz, H-3), 7.30 (dd, *J* = 8.3, 1.6 Hz, H-8), 2.52 (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz; DEPT) δ 193.15 (C), 144.85 (C), 139.33 (C), 138.55 (C), 137.18 (C),136.26 (C), 134.87 (CH), 132.08 (C), 131.74 (C), 130.57 (CH), 129.00 (CH), 128.12 (CH), 125.52 (CH), 124.35 (CH), 120.90 (CH), 118.47 (CH), 21.84 (CH$_3$); EI-MS *m/z* 244 (100, M$^+$), 215 (43).

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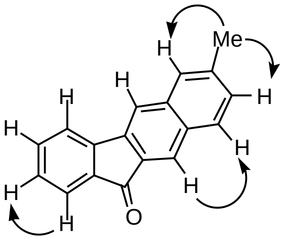
(1) Latif, A.; Soliman, G. *J. Chem. Soc.* **1944**, 56. Streiwieser, A.; Brown, S. M. *J. Org. Chem.* **1988**, *53*, 904. Rodríguez, D.; Navarro, A.; Castedo, L.; Domínguez, D.; Saá, C. *Org. Lett.* **2000**, *2*, 1497.

The ^{1}H NMR assignment was based on NOESY experiment (300 MHz, $CDCl_3$) and HMBC experiments ($CDCl_3$, 75 MHz). Long range ^{1}H-^{13}C correlations were observed between the carbonyl carbon (δ 193.15) and H-10 (8.13, s) and H-1 (7.71, dt).



The figure shows the nOe enhancements (only distinct cross-peaks).