



## Supporting Information

for

### **Mono or double Pd-catalyzed C–H bond functionalization for the annulative $\pi$ -extension of 1,8-dibromonaphthalene: a one pot access to fluoranthene derivatives**

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## Characterization data of synthesized compounds

### **7,8,9,10-Tetrafluorofluoranthene (1)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 1,2,3,4-tetrafluorobenzene (0.225 g, 1.5 mmol), **1** was isolated in 74% (0.203 g) yield as a yellow solid: mp 207-209 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 8.12 (dd, *J* = 7.0, 0.6 Hz, 1H), 7.96 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.72 (dd, *J* = 8.2, 7.0 Hz, 1H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -143.7, -157.1.

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 143.7 (d, *J* = 249.5 Hz), 132.4, 131.7, 129.8, 128.4, 127.8, 124.6, 21.8 (m).

HRMS calcd for [M]<sup>+</sup> C<sub>16</sub>H<sub>6</sub>F<sub>4</sub> 274.0400, found: 274.0399.

### **7,10-Difluorofluoranthene (2)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 1,4-difluorobenzene (0.171 g, 1.5 mmol), **2** was isolated in 68% (0.162 g) yield as a white solid: mp 139-141 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13 (d, *J* = 7.0 Hz, 2H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.70 (dd, *J* = 8.3, 7.0 Hz, 2H), 7.05 (t, *J* = 6.0 Hz, 2H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -124.1.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 155.1 (dd, *J* = 248.0, 3.8 Hz), 133.4, 131.5, 129.8, 128.2, 127.4, 127.3 (dd, *J* = 14.2, 11.3 Hz), 124.2 (t, *J* = 2.5 Hz), 115.7 (dd, *J* = 17.5, 14.0 Hz).

HRMS calcd for [M+H]<sup>+</sup> C<sub>16</sub>H<sub>9</sub>F<sub>2</sub> 239.0669, found: 239.0665.

### **7-Fluoro-10-methoxyfluoranthene (3)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 4-fluoroanisole (0.189 g, 1.5 mmol), **3** was isolated in 48% (0.120 g) yield as a yellow solid: mp 149-151 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.21 (d, *J* = 6.9 Hz, 1H), 8.12 (d, *J* = 7.0 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.70-7.64 (m, 2H), 7.06 (t, *J* = 8.9 Hz, 1H), 6.89 (dd, *J* = 8.9, 3.5 Hz, 1H), 4.08 (s, 3H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -128.4.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 153.9 (d, *J* = 237.6 Hz), 135.5 (d, *J* = 2.1 Hz), 133.9 (d, *J* = 2.2 Hz), 131.4, 129.6, 128.2, 127.9, 127.1, 126.5, 124.3, 123.8, 123.7, 115.1 (d, *J* = 22.3 Hz), 111.2 (d, *J* = 7.5 Hz), 56.0.

HRMS calcd for [M+H]<sup>+</sup> C<sub>17</sub>H<sub>12</sub>FO 251.0867, found: 251.0868.

### 7-Fluoro-10-methylfluoranthene (4)

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 4-fluorotoluene (0.165 g, 1.5 mmol), **4** was isolated in 45% (0.105 g) yield as a yellow solid: mp 79-81 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.13 (d, *J* = 6.9 Hz, 1H), 8.06 (d, *J* = 7.0 Hz, 1H), 7.93-7.88 (m, 2H), 7.72-7.67 (m, 2H), 7.15 (dd, *J* = 8.3, 4.9 Hz, 1H), 7.02 (t, *J* = 9.1 Hz, 1H), 2.77 (s, 3H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -122.7.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 157.7 (d, *J* = 237.3 Hz), 137.3 (d, *J* = 2.1 Hz), 133.9 (d, *J* = 2.0 Hz), 132.0, 131.0, 130.9, 130.1, 129.8, 128.2, 127.9, 126.8, 126.7, 123.6, 123.5 (d, *J* = 4.3 Hz), 114.4 (d, *J* = 20.1 Hz), 19.8.

HRMS calcd for [M+H]<sup>+</sup> C<sub>17</sub>H<sub>12</sub>F 235.0918, found: 235.0919.

### 7-Chloro-10-fluorofluoranthene (5)

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 1-chloro-4-fluorobenzene (0.195 g, 1.5 mmol), **5** was isolated in 59% (0.150 g) yield as a yellow solid: mp 180-182 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.53 (d, *J* = 7.1 Hz, 1H), 8.16 (d, *J* = 7.0 Hz, 1H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.75 (t, *J* = 7.0 Hz, 1H), 7.72 (t, *J* = 7.0 Hz, 1H), 7.33 (dd, *J* = 8.7, 4.3 Hz, 1H), 7.08 (t, *J* = 8.8 Hz, 1H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -121.1.

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 157.6 (d, *J* = 249.8 Hz), 138.0 (d, *J* = 6.5 Hz), 135.1, 132.7, 131.7, 129.7, 129.5 (d, *J* = 17.7 Hz), 128.2, 128.1, 127.9, 127.5, 127.3 (d, *J* = 17.7 Hz), 125.2 (d, *J* = 2.7 Hz), 124.8, 124.1 (d, *J* = 4.5 Hz), 115.7 (d, *J* = 22.2 Hz).

HRMS calcd for [M+H]<sup>+</sup> C<sub>16</sub>H<sub>9</sub>ClF 255.0371, found: 255.0370.

### Cyclopropyl(10-fluorofluoranthene-7-yl)methanone (6)

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and cyclopropyl(4-fluorophenyl)methanone (0.246 g, 1.5 mmol), **6** was isolated in 52% (0.150 g) yield as a yellow solid: mp 125-127 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.50 (d, *J* = 7.2 Hz, 1H), 8.19 (d, *J* = 7.0 Hz, 1H), 7.96 (d, *J* = 7.1 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 8.4, 5.0 Hz, 1H), 7.73-7.65 (m, 2H), 7.20 (t, *J* = 8.8 Hz, 1H), 2.70-2.61 (m, 1H), 1.50-1.42 (m, 2H), 1.23-1.13 (m, 2H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -114.3.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  203.2, 160.5 (d,  $J = 254.7$  Hz), 139.8 (d,  $J = 7.3$  Hz), 135.0 (d,  $J = 2.2$  Hz), 133.0 (d,  $J = 3.0$  Hz), 132.5 (d,  $J = 1.9$  Hz), 132.2, 129.7, 129.6, 129.5, 128.4, 128.2, 127.9, 127.6, 126.7, 123.9 (d,  $J = 4.8$  Hz), 114.2 (d,  $J = 20.8$  Hz), 20.7, 12.6.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{20}\text{H}_{14}\text{FO}$  289.1023, found: 289.1026.

### **8-Chloro-7-fluorofluoranthene (7)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 1-chloro-2-fluorobenzene (0.195 g, 1.5 mmol), **7** was isolated in 68% (0.173 g) yield as a yellow solid: mp 107-109 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.14 (d,  $J = 6.9$  Hz, 1H), 7.98 (d,  $J = 7.0$  Hz, 1H), 7.93 (dd,  $J = 8.2$ , 2.0 Hz, 2H), 7.73-7.64 (m, 3H), 7.41 (t,  $J = 7.9$  Hz, 1H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -121.1.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.4 (d,  $J = 253.0$  Hz), 141.4 (d,  $J = 6.0$  Hz), 135.6 (d,  $J = 2.0$  Hz), 133.1 (d,  $J = 2.1$  Hz), 132.1, 129.9, 129.2, 128.4, 128.0, 127.5, 126.9 (d,  $J = 15.8$  Hz), 124.1 (d,  $J = 4.2$  Hz), 121.2, 120.0 (d,  $J = 16.9$  Hz), 117.8 (d,  $J = 3.6$  Hz).

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{16}\text{H}_9\text{ClF}$  255.0371, found: 255.0370.

### **7-Fluorofluoranthene-8-carbonitrile (8)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 2-fluorobenzonitrile (0.182 g, 1.5 mmol), **8** was isolated in 67% (0.164 g) yield as a yellow solid: mp 148-150 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.18 (d,  $J = 6.9$  Hz, 1H), 8.10 (d,  $J = 7.0$  Hz, 1H), 8.03 (d,  $J = 8.2$  Hz, 1H), 8.00 (d,  $J = 8.2$  Hz, 1H), 7.80 (d,  $J = 7.7$  Hz, 1H), 7.78-7.73 (m, 2H), 7.64 (dd,  $J = 7.7$ , 5.8 Hz, 1H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -113.2.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.0, 159.0 (d,  $J = 252.5$  Hz), 146.3, 134.7, 132.5, 132.1, 131.9 (d,  $J = 2.0$  Hz), 129.9, 129.2, 128.7, 128.2, 128.1, 124.8 (d,  $J = 3.7$  Hz), 122.8, 117.9 (d,  $J = 3.3$  Hz), 114.7, 99.7 (d,  $J = 15.1$  Hz).

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{17}\text{H}_9\text{FN}$  246.0714, found: 246.0714.

### **7,8,9-Trifluorofluoranthene (9)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 1,2,3-trifluorobenzene (0.132 g, 1.5 mmol), **9** was isolated in 71% (0.182 g) yield as a yellow solid: mp 145-147 °C.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.10 (d,  $J = 6.9$  Hz, 1H), 7.98-7.90 (m, 3H), 7.73-7.67 (m, 2H), 7.54 (ddd,  $J = 9.2, 6.0, 1.5$  Hz, 1H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -135.2, -139.6, -162.0.

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.1 (dm,  $J = 248.8$  Hz), 147.5 (dm,  $J = 258.7$  Hz), 139.6 (dm,  $J = 269.8$  Hz), 143.4, 135.1, 135.0, 132.6, 132.3, 129.9, 128.5, 128.1, 127.7, 127.3, 123.7 (d,  $J = 4.0$  Hz), 122.8 (dd,  $J = 10.0, 2.8$  Hz), 121.2, 105.9 (dd,  $J = 19.7, 3.2$  Hz).

HRMS calcd for  $[\text{M}]^+ \text{C}_{16}\text{H}_7\text{F}_3$  256.0494, found: 256.0495.

### **7,8-Difluoro-9-methylfluoranthene (10)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 1,2-difluoro-3-methylbenzene (0.192 g, 1.5 mmol), **10** was isolated in 45% (0.113 g) yield as a yellow solid: mp 111-113 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.07 (d,  $J = 6.9$  Hz, 1H), 7.93-7.84 (m, 3H), 7.68 (t,  $J = 87.8$  Hz, 1H), 7.65 (t,  $J = 87.8$  Hz, 1H), 7.50 (d,  $J = 3.4$  Hz, 1H), 2.46 (s, 3H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -143.9 (bs).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  136.0, 135.7 (m), 133.6 (d,  $J = 1.5$  Hz), 132.4, 129.9, 128.3, 128.0, 127.0, 126.7, 120.4, 118.8 (m), 15.0.

HRMS calcd for  $[\text{M}+\text{H}]^+ \text{C}_{17}\text{H}_{11}\text{F}_2$  253.0823, found: 253.0819.

### **8-Chloro-7-fluoro-10-methoxyfluoranthene (11)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 2-chloro-1-fluoro-4-methoxybenzene (0.240 g, 1.5 mmol), **11** was isolated in 58% (0.165 g) yield as a yellow solid: mp 148-150 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.17 (d,  $J = 7.0$  Hz, 1H), 8.12 (d,  $J = 7.0$  Hz, 1H), 7.92 (d,  $J = 8.2$  Hz, 1H), 7.87 (d,  $J = 8.2$  Hz, 1H), 7.68 (t,  $J = 7.0$  Hz, 1H), 7.66 (t,  $J = 7.0$  Hz, 1H), 6.94 (t,  $J = 5.3$  Hz, 1H), 4.06 (s, 3H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -131.0.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.2, 149.4 (d,  $J = 245.8$  Hz), 134.8 (m), 133.7 (d,  $J = 2.3$  Hz), 131.4, 129.6, 128.3, 128.0, 127.6, 126.7, 124.5, 124.3 (d,  $J = 4.3$  Hz), 119.9 (d,  $J = 18.5$  Hz), 111.9, 56.2.

HRMS calcd for  $[\text{M}+\text{H}]^+ \text{C}_{17}\text{H}_{11}\text{ClFO}$  285.0477, found: 285.0477.

### 8,10-Dichloro-7-fluorofluoranthene (12)

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 2,4-dichloro-1-fluorobenzene (0.248 g, 1.5 mmol), **12** was isolated in 63% (0.182 g) yield as a yellow solid: mp 169-171 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.47 (d,  $J = 7.1$  Hz, 1H), 8.16 (d,  $J = 7.0$  Hz, 1H), 7.98 (d,  $J = 8.2$  Hz, 2H), 7.73 (t,  $J = 8.2$  Hz, 2H), 7.41 (d,  $J = 5.9$  Hz, 1H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -123.6.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.2 (d,  $J = 252.3$  Hz), 136.5, 134.4, 132.2, 131.9, 129.7, 129.4, 127.3, 128.3 (m), 128.1 (d,  $J = 4.0$  Hz), 125.0, 124.6 (d,  $J = 6.6$  Hz), 120.4 (d,  $J = 18.5$  Hz).

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{16}\text{H}_8\text{Cl}_2\text{F}$  288.9982, found: 288.9980.

### 10-Chloro-7-fluoro-8-methylfluoranthene (13)

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 4-chloro-1-fluoro-2-methylbenzene (0.218 g, 1.5 mmol), **13** was isolated in 53% (0.143 g) yield as a yellow solid: mp 115-117 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.43 (d,  $J = 7.1$  Hz, 1H), 8.13 (d,  $J = 6.9$  Hz, 1H), 7.93 (d,  $J = 8.2$  Hz, 2H), 7.73-7.68 (m, 2H), 7.18 (d,  $J = 6.0$  Hz, 1H), 2.43 (s, 3H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -125.4.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.2 (d,  $J = 248.6$  Hz), 135.6, 135.2, 133.0, 131.9, 130.8 (d,  $J = 4.7$  Hz), 129.7, 128.1 (d,  $J = 2.3$  Hz), 127.3 (d,  $J = 2.4$  Hz), 125.9 (d,  $J = 18.3$  Hz), 124.5, 124.2, 123.9 (d,  $J = 4.8$  Hz), 14.5.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{17}\text{H}_{11}\text{ClF}$  269.0528, found: 269.0528.

### 8-Chloro-10-fluoro-7-methylfluoranthene (14)

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 2-chloro-4-fluoro-1-methylbenzene (0.216 g, 1.5 mmol), **14** was isolated in 62% (0.167 g) yield as a yellow solid: mp 144-146 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.05 (d,  $J = 6.9$  Hz, 1H), 8.02 (d,  $J = 6.9$  Hz, 1H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.87 (d,  $J = 8.0$  Hz, 1H), 7.66 (t,  $J = 7.5$  Hz, 2H), 7.15 (d,  $J = 9.1$  Hz, 1H), 2.75 (s, 3H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -120.8.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.4 (d,  $J = 250.5$  Hz), 140.2 (d,  $J = 6.7$  Hz), 136.6 (d,  $J = 2.6$  Hz), 133.9 (d,  $J = 9.1$  Hz), 132.9 (d,  $J = 2.2$  Hz), 132.0, 129.8, 128.2 (m), 127.9, 127.4, 126.9, 124.4 (d,  $J = 16.2$  Hz), 124.2, 115.4 (d,  $J = 31.1$  Hz), 16.1.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{17}\text{H}_{11}\text{ClF}$  269.0528, found: 269.0526.

### **7,9-Dichlorofluoranthene (15)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 1,3-dichlorobenzene (0.221 g, 1.5 mmol), **15** was isolated in 38% (0.103 g) yield as a yellow solid: mp 139-141 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.44 (d, *J* = 7.0 Hz, 1H), 7.99-7.93 (m, 3H), 7.82 (d, *J* = 1.8 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 1.7 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 142.4, 134.8, 134.7, 134.6, 133.3, 132.4, 130.3, 129.8, 128.3, 128.1, 128.0, 127.9, 127.5, 124.4, 121.1, 120.3.

HRMS calcd for [M+H]<sup>+</sup> C<sub>16</sub>H<sub>9</sub>Cl<sub>2</sub> 271.0076, found: 271.0075.

### **7,9-Dimethylacenaphtho[1,2-*c*]thiophene (16)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 2,5-dimethylthiophene (0.168 g, 1.5 mmol), **16** was isolated in 60% (0.142 g) yield as a yellow solid: mp 111-113 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 6.9 Hz, 2H), 7.56 (dd, *J* = 8.2, 6.9 Hz, 2H), 2.68 (s, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 140.5, 140.0, 133.9, 131.3, 128.2, 127.7, 124.4, 118.4, 13.8.

HRMS calcd for [M+H]<sup>+</sup> C<sub>16</sub>H<sub>13</sub>S 237.0732, found: 237.0729.

### **7,8,9-Trimethyl-8H-acenaphtho[1,2-*c*]pyrrole (17)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 1,2,5-trimethylpyrrole (0.164 g, 1.5 mmol), **18** was isolated in 56% (0.130 g) yield as a yellow solid: mp 193-195 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.55-7.50 (m, 2H), 7.48-7.43 (m, 4H), 3.46 (s, 3H), 2.49 (s, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 137.6, 134.9, 131.0, 127.5, 123.9, 122.7, 122.1, 116.8, 27.0, 12.1.

HRMS calcd for [M+H]<sup>+</sup> C<sub>17</sub>H<sub>16</sub>N 234.1272, found: 234.1275.

### **1-(9-Methylacenaphtho[1,2-*c*]furan-7-yl)ethan-1-one (18)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and 1-(5-methylfuran-2-yl)ethan-1-one (0.186 g, 1.5 mmol), **17** was isolated in 53% (0.131 g) yield as a yellow solid: mp 147-149 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.36 (d, *J* = 7.0 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.71-7.67 (m, 2H), 7.61 (t, *J* = 7.1 Hz, 1H), 2.71 (s, 3H), 2.65 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 187.1, 146.9, 143.2, 139.2, 136.9, 131.0, 130.4, 129.9, 128.3, 127.6, 125.5, 124.8, 120.0, 26.5, 14.1.

HRMS calcd for [M+H]<sup>+</sup> C<sub>17</sub>H<sub>13</sub>O<sub>2</sub> 249.0910, found: 249.0910.

### 8-Ethoxyfluoranthene (19)

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and (4-ethoxyphenyl)boronic acid (0.249 g, 1.5 mmol), **19** was isolated in 69% (0.170 g) yield as a yellow solid: mp 110-112 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.92 (d, *J* = 6.8 Hz, 1H), 7.88-7.76 (m, 4H), 7.68-7.58 (m, 2H), 7.49 (d, *J* = 2.3 Hz, 1H), 6.93 (dd, *J* = 8.3, 2.3 Hz, 1H), 4.19 (q, *J* = 7.4 Hz, 2H), 1.53 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 159.3, 141.2, 137.1, 136.9, 132.9, 132.3, 130.0, 128.1, 127.8, 126.9, 125.4, 122.2, 119.9, 118.9, 113.4, 108.3, 63.8, 15.0.

HRMS calcd for [M+H]<sup>+</sup> C<sub>18</sub>H<sub>15</sub>O 247.1117, found: 247.1118.

### 8-Methylfluoranthene (20) [1]

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and *p*-tolylboronic acid (0.204 g, 1.5 mmol), **20** was isolated in 71% (0.153 g) yield as a yellow solid: mp 77-79 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.96-7.88 (m, 2H), 7.87-7.79 (m, 3H), 7.76 (s, 1H), 7.68-7.60 (m, 2H), 7.22 (d, *J* = 7.7 Hz, 1H), 2.52 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 139.8, 137.5, 137.1, 137.0, 136.9, 132.6, 130.0, 128.3, 127.9, 127.8, 126.5, 126.1, 122.3, 121.2, 119.8, 119.5, 21.8.

HRMS calcd for [M+H]<sup>+</sup> C<sub>17</sub>H<sub>13</sub> 217.1012, found: 217.1010.

### 8-Chlorofluoranthene (21) [2]

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and (4-chlorophenyl)boronic acid (0.234 g, 1.5 mmol), **21** was isolated in 63% (0.148 g) yield as a yellow solid: mp 108-110 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.01-7.82 (m, 6H), 7.72-7.64 (m, 2H), 7.38 (dd, *J* = 8.0, 1.9 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 141.0, 137.7, 135.9, 135.8, 133.3, 132.5, 130.0, 128.1, 128.0, 127.4, 127.3, 126.9, 122.3, 121.9, 120.6, 120.3.

HRMS calcd for [M+H]<sup>+</sup> C<sub>16</sub>H<sub>10</sub>Cl 237.0466, found: 237.0466.

### Methyl fluoranthene-8-carboxylate (22) [3]

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and (4-(methoxycarbonyl)phenyl)boronic acid (0.270 g, 1.5 mmol), **22** was isolated in 76% (0.198 g) yield as a yellow solid: mp 89-91 °C.



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.55 (d, *J* = 1.3 Hz, 1H), 8.09 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.99 (d, *J* = 6.9 Hz, 1H), 7.97 (d, *J* = 6.8 Hz, 1H), 7.93-7.85 (m, 3H), 7.69-7.62 (m, 2H), 4.01 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 167.4, 143.5, 139.4, 136.0, 135.8, 132.9, 130.0, 129.2, 129.0, 128.2, 128.0, 127.8, 127.1, 122.6, 121.3, 121.1, 120.7, 52.2.

HRMS calcd for [M+H]<sup>+</sup> C<sub>18</sub>H<sub>13</sub>O<sub>2</sub> 261.0910, found: 261.0907.

### Fluoranthene-8-carbonitrile (**23**) [3]

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and (4-cyanophenyl)boronic acid (0.221 g, 1.5 mmol), **23** was isolated in 77% (0.175 g) yield as a yellow solid: mp 137-139 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.97 (s, 1H), 7.95-7.88 (m, 3H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.81 (dd, *J* = 7.8, 0.5 Hz, 1H), 7.70-7.61 (m, 2H), 7.56 (dd, *J* = 7.8, 1.4 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 142.9, 139.5, 134.9, 134.7, 132.5, 131.2, 129.9, 128.4, 128.2, 128.1, 127.8, 124.6, 121.8, 121.6, 121.2, 119.6, 110.3.

HRMS calcd for [M+H]<sup>+</sup> C<sub>17</sub>H<sub>10</sub>N 228.0808, found: 228.0807.

### 8-Nitrofluoranthene (**24**) [3]

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and (3-nitrophenyl)boronic acid (0.251 g, 1.5 mmol), **24** was isolated in 58% (0.143 g) yield as a yellow solid: mp 164-166 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.77 (d, *J* = 1.8 Hz, 1H), 8.33 (dd, *J* = 8.3, 2.1 Hz, 1H), 8.13 (d, *J* = 6.9 Hz, 1H), 8.11 (d, *J* = 6.9 Hz, 1H), 8.07-7.97 (m, 3H), 7.78 (d, *J* = 7.0 Hz, 1H), 7.75 (d, *J* = 7.0 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 144.9, 140.1, 135.7, 134.8, 134.6, 133.4, 130.1, 128.7, 128.4, 128.3, 128.1, 123.1, 122.4, 121.6, 121.3, 116.8.

HRMS calcd for [M+H]<sup>+</sup> C<sub>16</sub>H<sub>10</sub>NO<sub>2</sub> 248.0706, found: 248.0704.

### 8,9-Difluorofluoranthene (**25**)

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and (3,4-difluorophenyl)boronic acid (0.237 g, 1.5 mmol), **25** was isolated in 61% (0.145 g) yield as a yellow solid: mp 115-117 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.94-7.85 (m, 4H), 7.74-7.62 (m, 4H).

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -138.5.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.3 (dd,  $J = 249.0, 15.7$ , Hz), 135.6 (m), 135.4, 129.8, 128.1, 127.0, 120.4, 110.4 (dd,  $J = 13.2, 7.1$  Hz).

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{16}\text{H}_9\text{F}_2$  239.0667, found: 239.0667.

### **7,9-Difluorofluoranthene (26)**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and (3,5-difluorophenyl)boronic acid (0.237 g, 1.5 mmol), **26** was isolated in 73% (0.174 g) yield as a yellow solid: mp 83-85 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.06 (d,  $J = 6.9$  Hz, 1H), 7.97 (d,  $J = 7.0$  Hz, 1H), 7.94 (d,  $J = 8.2$  Hz, 1H), 7.88 (d,  $J = 8.3$  Hz, 1H), 7.71-7.65 (m, 2H), 7.45 (dd,  $J = 8.1, 2.0$  Hz, 1H), 6.87 (td,  $J = 9.5, 2.0$  Hz, 1H).

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -111.0, -114.9.

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  135.7, 133.2, 132.3, 129.9, 128.4, 128.0, 127.8, 126.5, 123.2 (dd,  $J = 3.9, 1.5$  Hz), 121.3, 105.3 (dd,  $J = 23.7, 3.4$  Hz), 103.0 (d,  $J = 24.4$  Hz), 102.7 (d,  $J = 24.4$  Hz).

HRMS calcd for  $[\text{M}]^+$   $\text{C}_{16}\text{H}_8\text{F}_2$  238.0587, found: 238.0589.

### **Acenaphtho[1,2-*c*]pyridine (27) [3]**

From 1,8-dibromonaphthalene (0.286 g, 1 mmol) and pyridin-4-ylboronic acid (0.185 g, 1.5 mmol), **27** was isolated in 53% (0.108 g) yield as a brown solid: mp 64-66 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.16 (d,  $J = 0.9$  Hz, 1H), 8.65 (d,  $J = 5.0$  Hz, 1H), 8.06-7.95 (m, 3H), 7.90 (d,  $J = 8.0$  Hz, 1H), 7.78 (dd,  $J = 5.0, 1.0$  Hz, 1H), 7.72-7.63 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  148.6, 146.1, 142.9, 134.6, 134.5, 134.1, 132.3, 130.1, 129.1, 128.3, 128.0, 127.4, 122.4, 121.3, 116.4.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{15}\text{H}_{10}\text{N}$  204.0808, found: 204.0807.

### **3-Methyl-9-phenylphenanthrene (28) [4]**

From 1,1-diphenylethylene (0.180 g, 1 mmol) and 3-bromo-4-iodotoluene (0.445 g, 1.5 mmol), **28** was isolated in 51% (0.137 g) yield as a white solid: mp 88-90 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.80 (d,  $J = 8.1$  Hz, 1H), 8.55 (s, 1H), 7.94 (d,  $J = 8.1$  Hz, 1H), 7.82 (d,  $J = 8.1$  Hz, 1H), 7.70-7.65 (m, 2H), 7.62-7.45 (m, 7H), 2.68 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.9, 137.8, 136.3, 131.2, 130.4, 130.1, 130.0, 129.5, 128.6, 128.5, 128.3, 127.4, 127.2, 126.9, 126.3, 126.2, 122.9, 122.3, 22.2.

HRMS calcd for  $[\text{M}+\text{H}]^+$   $\text{C}_{21}\text{H}_{17}$  269.1325, found: 269.1325.

### 2-Methyl-9-phenylphenanthrene (29) [4]

From 1,1-diphenylethylene (0.180 g, 1 mmol) and 4-bromo-3-iodotoluene (0.445 g, 1.5 mmol), **29** was isolated in 43% (0.115 g) yield as a white solid: mp 69-71 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.77 (d, *J* = 8.1 Hz, 1H), 8.65 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.72-7.65 (m, 3H), 7.60-7.45 (m, 7H), 2.61 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 140.9, 138.8, 136.6, 131.7, 130.8, 130.7, 130.1, 128.4, 128.3, 128.2, 127.9, 127.3, 126.9, 126.4, 126.1, 122.7, 122.5, 21.5.

HRMS calcd for [M+H]<sup>+</sup> C<sub>21</sub>H<sub>17</sub> 269.1325, found: 269.1322.

### 2,3-Dimethyl-9-phenylphenanthrene (30)

From 1,1-diphenylethylene (0.180 g, 1 mmol) and 1,2-dibromo-4,5-dimethylbenzene (0.400 g, 1.5 mmol), **30** was isolated in 66% (0.186 g) yield as a white solid: mp 126-128 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.78 (d, *J* = 8.1 Hz, 1H), 8.51 (s, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.70-7.46 (m, 9H), 2.60 (s, 3H), 2.52 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 141.1, 137.9, 136.2, 135.9, 130.9, 130.4, 130.1, 128.7, 128.3, 128.2, 127.2, 127.1, 126.8, 126.2, 125.9, 122.9, 122.7, 20.7, 20.0.

HRMS calcd for [M+H]<sup>+</sup> C<sub>22</sub>H<sub>19</sub> 283.1481, found: 283.1483.

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