

## EXPERIMENTAL

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on 600 MHz spectrometer. Chemical shifts are reported in  $\delta$  (ppm) from tetramethylsilane as an internal standard. Data are reported as follows: chemical shifts, relative integration value, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz). Infrared spectra were obtained using an FT spectrometer. Analytical thin layer chromatography was performed on Merck silica gel 60 F<sub>254</sub> TLC plates.

### General procedure for the synthesis of 9-spirofluorenes

To a solution of alkynyl alcohol **1** (0.1 mmol) and DTBP (0.05 mmol) in DCE (1 mL) was added diaryliodonium salt (0.11 mmol) and  $(\text{CuOTf})_2 \cdot \text{toluene}$  (0.005 mmol) at room temperature and stirred at 50 °C under argon. After completion of the reaction as monitored by TLC analysis, the reaction mixture was filtered through a short pad of silica gel with hexane/AcOEt (1:1) as eluent. The filtrate was concentrated in vacuo. Column chromatography on silica gel using hexane/ethyl acetate (20:1) as an eluent afforded the desired 9-spirofluorene **3**.

### 5-([1,1'-Biphenyl]-2-yl)-4-phenyl-2,3-dihydrofuran (**2a**)

Yellow oil;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  7.48–7.39 (m, 3H), 7.36–7.29 (m, 3H), 7.26–7.19 (m, 3H), 7.11–7.05 (m, 2H), 7.02 (d,  $J = 7.0$  Hz, 1H), 6.89 (d,  $J = 7.2$  Hz, 2H), 4.28 (t,  $J = 9.3$  Hz, 2H), 3.01 (t,  $J = 9.3$  Hz, 2H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ ):  $\delta$  151.9, 142.2, 141.1, 135.2, 131.2, 130.7, 130.4, 129.5, 128.4, 128.0, 127.8, 127.7, 126.9, 125.7, 125.2, 111.6, 69.0, 34.1; IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 1652, 1597, 1497, 1474, 1450, 1364, 1111, 1070, 1016, 916;

MS (EI):  $m/z = 298$  ( $M^+$ ); HRMS (EI):  $m/z$  calcd for  $C_{22}H_{18}O$ : 298.1358; found: 298.1362.

**5-(4'-Chloro-[1,1'-biphenyl]-2-yl)-4-phenyl-2,3-dihydrofuran (2b)**

Brown oil;  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.48–7.42 (m, 2H), 7.40–7.32 (m, 2H), 7.21–7.15 (m, 4H), 7.07 (t,  $J = 7.4$  Hz, 2H), 7.02 (t,  $J = 7.3$  Hz, 1H), 6.84 (d,  $J = 7.3$  Hz, 2H), 4.33 (t,  $J = 9.3$  Hz, 2H), 3.01 (t,  $J = 9.3$  Hz, 2H);  $^{13}C$ -NMR ( $CDCl_3$ ):  $\delta$  151.4, 140.9, 139.5, 135.0, 132.9, 131.2, 130.8, 130.2, 129.8, 129.6, 128.1, 128.0, 127.9, 125.8, 125.4, 111.9, 69.0, 34.1; IR ( $CHCl_3$ ,  $cm^{-1}$ ): 1645, 1599, 1495, 1476, 1447, 1366, 1092, 1018; MS (EI):  $m/z = 332$  ( $M^+$ ); HRMS (EI):  $m/z$  calcd for  $C_{22}H_{17}ClO$ : 332.0968; found: 332.0968.

**3'-Phenyl-4',5'-dihydro-3'*H*-spiro[fluorene-9,2'-furan] (3a)**

Pale yellow solid; mp 105–107 °C;  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.67–7.63 (m, 1H), 7.49–7.44 (m, 1H), 7.38–7.30 (m, 4H), 7.13 (td,  $J = 7.4, 1.2$  Hz, 1H), 7.09 (td,  $J = 7.4, 1.2$  Hz, 1H), 6.97–6.88 (m, 3H), 6.69 (d,  $J = 7.3$  Hz, 2H), 4.57 (ddd,  $J = 9.1, 8.7, 2.1$  Hz, 1H), 4.47 (ddd,  $J = 9.6, 8.7, 6.5$  Hz, 1H), 3.99 (dd,  $J = 12.4, 6.7$  Hz, 1H), 3.01 (dddd,  $J = 12.5, 12.4, 9.6, 9.1$  Hz, 1H), 2.63 (dddd,  $J = 12.5, 6.7, 6.5, 2.1$  Hz, 1H);  $^{13}C$ -NMR ( $CDCl_3$ ):  $\delta$  147.9, 146.2, 140.6, 139.9, 137.0, 129.0, 128.5, 127.9, 127.6, 127.5, 127.1, 126.6, 125.2, 123.6, 119.8, 119.7, 93.3, 68.3, 54.8, 31.2; IR ( $CHCl_3$ ,  $cm^{-1}$ ): 3458, 3065, 2886, 1605, 1497, 1450, 1045, 993, 932; MS (EI):  $m/z = 298$  ( $M^+$ ); HRMS (EI):  $m/z$  calcd for  $C_{22}H_{18}O$ : 298.1358; found: 298.1359. Crystal data for **3a** (CCDC 1916219):  $C_{22}H_{18}O$ ,  $M = 298.38$ , tetragonal, space group I 41/a,  $a = 23.9606(13)$  Å,  $b = 23.9606(13)$  Å,  $c = 11.4042(3)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 6547.3(5)$  Å<sup>3</sup>,  $Z = 16$ ,  $D_c = 1.211$  gcm<sup>-3</sup>,  $T = 296$  K, and  $R = 4.99\%$ .

**3'-(*p*-Tolyl)-4',5'-dihydro-3'*H*-spiro[fluorene-9,2'-furan] (3b)**

White solid; mp 117–120 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.67–7.62 (m, 1H), 7.50–7.45 (m, 1H), 7.39–7.33 (m, 4H), 7.16 (tdd, *J* = 7.4, 2.0, 1.2 Hz, 1H), 7.11 (tdd, *J* = 7.4, 2.1, 1.2 Hz, 1H), 6.72 (d, *J* = 7.1 Hz, 2H), 6.59 (d, *J* = 7.3 Hz, 2H), 4.56 (t, *J* = 8.7 Hz, 1H), 4.51–4.43 (m, 1H), 3.96 (dd, *J* = 12.2, 7.1 Hz, 1H), 3.05–2.94 (m, 1H), 2.67–2.59 (m, 1H), 2.10 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 147.9, 146.4, 140.7, 140.0, 136.0, 133.8, 129.0, 128.5, 128.3, 127.9, 127.4, 127.2, 125.3, 123.6, 119.8, 119.8, 93.2, 68.2, 54.4, 31.5, 21.0; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 1516, 1450, 1043; MS (EI): *m/z* = 312 (M<sup>+</sup>); HRMS (EI): *m/z* calcd for C<sub>23</sub>H<sub>20</sub>O: 312.1514; found: 312.1512.

**3'-(4-Fluorophenyl)-4',5'-dihydro-3'*H*-spiro[fluorene-9,2'-furan] (3c)**

Yellow solid; mp 125–128 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.67–7.62 (m, 1H), 7.50–7.45 (m, 1H), 7.39–7.31 (m, 4H), 7.16 (td, *J* = 7.4, 1.1 Hz, 1H), 7.12 (td, *J* = 7.4, 1.1 Hz, 1H), 6.66–6.56 (m, 4H), 4.58 (ddd, *J* = 9.1, 8.7, 2.0 Hz, 1H), 4.48 (ddd, *J* = 9.7, 8.7, 6.5 Hz, 1H), 3.96 (dd, *J* = 12.5, 6.7 Hz, 1H), 2.96 (dddd, *J* = 12.5, 9.7, 9.1 Hz, 1H), 2.63 (dddd, *J* = 12.5, 6.7, 6.5, 2.0 Hz, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 161.56 (d, *J* = 244.3 Hz), 147.6, 146.1, 140.6, 139.9, 132.57 (d, *J* = 4.3 Hz), 129.1, 128.87 (d, *J* = 7.2 Hz), 128.6, 128.0, 127.2, 125.1, 123.6, 119.8, 114.41 (d, *J* = 21.6 Hz), 93.3, 68.3, 54.3, 31.4; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 2886, 1607, 1512, 1450, 1161, 1045; MS (EI): *m/z* = 316 (M<sup>+</sup>); HRMS (EI): *m/z* calcd for C<sub>22</sub>H<sub>17</sub>FO: 316.1263; found: 316.1268.

**2-Methyl-3'-phenyl-4',5'-dihydro-3'*H*-spiro[fluorene-9,2'-furan] (3d)**

Compound **3d** was obtained as a 54:46 mixture of diastereomers. Yellow solid; mp 65–70 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.66–7.57 (m, 0.46H), 7.47 (s, 0.54H), 7.44–7.40 (m,

0.46H), 7.36 (d,  $J = 7.6$  Hz, 0.54H), 7.33–7.28 (m, 2H), 7.23 (d,  $J = 7.6$  Hz, 0.46H), 7.15 (d,  $J = 7.6$  Hz, 0.54H), 7.13–7.09 (m, 1H), 7.06 (td,  $J = 7.5, 1.1$  Hz, 0.54H), 6.98 – 6.89 (m, 3.46H), 6.73–6.68 (m, 2H), 4.58 (tdd,  $J = 8.7, 6.7, 2.1$  Hz, 1H), 4.48 (ddd,  $J = 9.8, 8.5, 6.4$  Hz, 1H), 3.99 (dt,  $J = 12.2, 7.5$  Hz, 1H), 3.08–2.94 (m, 1H), 2.69–2.60 (m, 1H), 2.46 (s, 1.62H), 2.29 (s, 1.38H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  148.1, 147.9, 146.4, 146.1, 140.8, 140.1, 138.0, 137.9, 137.3, 137.2, 137.1, 136.9, 129.8, 129.2, 129.0, 128.4, 127.6, 127.5, 127.5, 126.7, 126.6, 126.1, 125.1, 124.3, 123.5, 119.6, 119.5, 119.4, 119.4, 93.2, 93.2, 68.3, 68.3, 54.7, 54.6, 31.3, 31.3, 21.9, 21.8; IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 2883, 1603, 1456, 1043; MS (EI):  $m/z = 312$  ( $\text{M}^+$ ); HRMS (EI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{20}\text{O}$ : 312.1514; found: 312.1515.

### **3-Methyl-3'-phenyl-4',5'-dihydro-3'*H*-spiro[fluorene-9,2'-furan] (3e)**

Compound **3e** was obtained as a 50:50 mixture of diastereomers. Yellow solid; mp 103–105 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.66–7.61 (m, 0.5H), 7.52 (d,  $J = 7.6$  Hz, 0.5H), 7.47–7.39 (m, 0.5H), 7.35–7.26 (m, 2.5H), 7.19 (d,  $J = 7.7$  Hz, 0.5H), 7.18–7.14 (m, 1H), 7.12 (td,  $J = 7.4, 1.2$  Hz, 0.5H), 7.07 (td,  $J = 7.4, 1.2$  Hz, 0.5H), 6.97–6.87 (m, 3.5H), 6.71 (d,  $J = 7.3$  Hz, 2H), 4.58–4.51 (m, 1H), 4.49–4.41 (m, 1H), 3.97 (ddd,  $J = 12.1, 6.9, 3.3$  Hz, 1H), 3.05–2.94 (m, 1H), 2.68–2.59 (m, 1H), 2.41 (s, 1.5H), 2.26 (s, 1.5H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  148.1, 146.6, 144.9, 143.3, 140.8, 140.7, 140.1, 140.1, 138.8, 138.2, 137.3, 137.2, 129.0, 128.8, 128.4, 128.0, 127.8, 127.6, 127.6, 127.6, 127.0, 126.5, 125.2, 125.0, 123.6, 123.3, 120.5, 120.5, 119.6, 119.5, 93.1, 93.0, 68.1, 68.0, 54.6, 54.4, 31.4, 31.3, 21.8, 21.6; IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 2884, 1616, 1603, 1491, 1452, 1043; MS (EI):  $m/z = 312$  ( $\text{M}^+$ ); HRMS (EI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{20}\text{O}$ : 312.1514; found: 312.1513.

### 3-Phenyl-4,5-dihydro-3*H*-spiro[furan-2,4'-indeno[1,2-*b*]thiophene] (3f)

Compound **3f** was obtained as a 62:38 mixture of diastereomers. Pale yellow oil; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.56 (d, *J* = 7.6 Hz, 0.62H), 7.32 (d, *J* = 4.9 Hz, 0.38H), 7.28–7.15 (m, 2.62H), 7.06 (d, *J* = 4.9 Hz, 1.38H), 7.04–6.97 (m, 3H), 6.95–6.89 (m, 0.38H), 6.84–6.75 (m, 2.62H), 4.56 (td, *J* = 8.7, 2.8 Hz, 0.38H), 4.47 (td, *J* = 8.9, 3.0 Hz, 0.62H), 4.45–4.37 (m, 1H), 3.92 (dd, *J* = 11.2, 7.2 Hz, 0.62H), 3.86 (dd, *J* = 10.4, 7.2 Hz, 0.38H), 2.96–2.79 (m, 1H), 2.73–2.63 (m, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 151.9, 150.0, 149.8, 148.6, 143.6, 143.3, 138.0, 137.7, 137.5, 136.9, 129.7, 129.1, 128.5, 128.3, 127.8, 127.7, 127.5, 126.8, 126.7, 126.2, 125.5, 125.1, 123.3, 122.9, 121.6, 119.1, 118.8, 115.4, 91.2, 91.1, 67.9, 67.6, 53.1, 52.8, 31.4, 31.4; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 2938, 1607, 1495, 1454, 1348, 1047; MS (EI): *m/z* = 304 (M<sup>+</sup>); HRMS (EI): *m/z* calcd for C<sub>20</sub>H<sub>16</sub>OS: 304.0922; found: 304.0927.

### 3-Phenyl-4,5-dihydro-3*H*-spiro[furan-2,8'-indeno[2,1-*b*]thiophene] (3g)

Compound **3g** was obtained as a 75:25 mixture of diastereomers. Pale yellow oil; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.59 (d, *J* = 7.3 Hz, 0.75H), 7.40 (dd, *J* = 4.9, 1.1 Hz, 0.25H), 7.32–7.22 (m, 2.75H), 7.18 (dd, *J* = 4.9, 1.1 Hz, 0.75H), 7.15 (d, *J* = 7.5 Hz, 0.25H), 7.11–6.99 (m, 3.25H), 6.94 (dd, *J* = 4.9, 1.1 Hz, 0.75H), 6.91–6.86 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 0.25H), 4.57 (td, *J* = 8.4, 4.0 Hz, 0.25H), 4.47–4.37 (m, 1.75H), 3.97 (dd, *J* = 11.0, 7.0 Hz, 0.75H), 3.77 (t, *J* = 8.0 Hz, 0.25H), 2.92–2.79 (m, 1H), 2.79–2.66 (m, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 150.4, 148.9, 148.7, 146.4, 146.2, 145.9, 138.7, 138.6, 138.6, 137.9, 137.2, 130.4, 130.2, 129.1, 128.5, 128.0, 127.9, 127.6, 126.9, 125.8, 125.3, 125.1, 123.5, 123.5, 119.5, 119.1, 118.9, 118.5, 92.2, 92.1, 67.4, 67.0, 54.5, 52.2, 31.6, 30.8;

IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 2886, 1607, 1489, 1454; MS (EI):  $m/z = 304$  (M<sup>+</sup>); HRMS (EI):  $m/z$  calcd for C<sub>20</sub>H<sub>16</sub>OS: 304.0922; found: 304.0924.

**2',3-Diphenyl-4,5-dihydro-3*H*-spiro[furan-2,1'-indene] (3h)**

White solid; mp 143–145 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.87–7.82 (m, 2H), 7.46 (t,  $J = 7.7$  Hz, 2H), 7.40 (d,  $J = 7.5$  Hz, 1H), 7.37 (td,  $J = 7.6, 1.0$  Hz, 1H), 7.10–7.01 (m, 2H), 6.99–6.95 (m, 3H), 6.92 (d,  $J = 7.1$  Hz, 1H), 6.84–6.79 (m, 2H), 6.76 (s, 1H), 4.61 (t,  $J = 8.6$  Hz, 1H), 4.41 (ddd,  $J = 10.5, 8.5, 6.3$  Hz, 1H), 3.70 (dd,  $J = 13.2, 6.6$  Hz, 1H), 3.09–2.98 (m, 1H), 2.47 (dt,  $J = 12.9, 6.4$  Hz, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 148.5, 147.5, 141.3, 136.3, 135.5, 129.6, 128.9, 128.2, 128.1, 128.0, 127.4, 126.6, 125.4, 123.4, 121.3, 97.2, 68.1, 51.4, 30.9; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 2880, 2359, 1603, 1491, 1456, 1049, 1034; MS (EI):  $m/z = 324$  (M<sup>+</sup>); HRMS (EI):  $m/z$  calcd for C<sub>24</sub>H<sub>20</sub>O: 324.1514; found: 324.1512.

**2-(10-Phenylphenanthren-9-yl)ethan-1-ol (4a)**

Pale yellow solid; mp 164–166 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 8.81–8.76 (m, 1H), 8.72 (d,  $J = 8.3$  Hz, 1H), 8.25–8.20 (m, 1H), 7.70–7.65 (m, 2H), 7.59 (t,  $J = 7.6$  Hz, 1H), 7.51 (t,  $J = 7.5$  Hz, 2H), 7.46 (t,  $J = 7.3$  Hz, 1H), 7.41 (t,  $J = 7.6$  Hz, 1H), 7.32–7.28 (m, 3H), 3.82 (t,  $J = 7.7$  Hz, 2H), 3.21 (t,  $J = 7.7$  Hz, 2H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 140.3, 138.7, 132.3, 131.0, 130.5, 130.3, 129.9, 129.7, 128.7, 127.8, 127.5, 127.2, 126.6, 126.5, 126.2, 125.1, 123.3, 122.4, 63.0, 33.9; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3604, 1493, 1038; MS (EI):  $m/z = 298$  (M<sup>+</sup>); HRMS (EI):  $m/z$  calcd for C<sub>22</sub>H<sub>18</sub>O: 298.1358; found: 298.1359. Crystal data for **3a** (CCDC 1916221): C<sub>44</sub>H<sub>36</sub>O<sub>2</sub>,  $M = 596.77$ , monoclinic, space group P 1 21/n 11,  $a = 9.7466(3)$  Å,  $b = 12.9576(4)$  Å,  $c = 25.5428(9)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 100.623(7)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 3170.6(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.250$  gcm<sup>-3</sup>,  $T = 296$  K, and  $R = 6.64\%$ .

### **1-([1,1'-Biphenyl]-2-yl)-4-methoxy-2-phenylbut-1-en-1-yl**

#### **trifluoromethanesulfonate (8)**

Compound 7 was obtained as a single isomer, but the double-bond geometry was not determined. Pale yellow solid; mp 63–65 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.45–7.37 (m, 3H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.23–7.18 (m, 5H), 7.10–7.00 (m, 3H), 6.80 (d, *J* = 8.2 Hz, 2H), 3.63 (td, *J* = 8.7, 8.0, 5.7 Hz, 1H), 3.60–3.54 (m, 1H), 3.37 (s, 3H), 2.82 (ddd, *J* = 14.3, 7.7, 6.3 Hz, 1H), 2.72 (dt, *J* = 15.2, 5.5 Hz, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 144.5, 142.4, 140.7, 137.1, 136.9, 136.5, 131.2, 130.7, 129.7, 129.2, 128.9, 128.0, 127.6, 127.5, 127.4, 127.1, 68.7, 59.0, 33.2; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 2928, 1414, 1142, 1123, 932; MS (EI): *m/z* = 462 (M<sup>+</sup>); HRMS (EI): *m/z* calcd for C<sub>24</sub>H<sub>21</sub>F<sub>3</sub>O<sub>4</sub>S: 462.1113; found: 462.1109.

#### **Methyl 3'-phenylspiro[fluorene-9,2'-pyrrolidine]-1'-carboxylate (10)**

NMR spectrum shows a double set of peaks (1:1) due to the *cis* and *trans* conformers around the tertiary carbamate. White solid; mp 48–50 °C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ 7.53–7.48 (m, 1H), 7.47 (d, *J* = 7.3 Hz, 0.5H), 7.43 (d, *J* = 7.3 Hz, 0.5H), 7.39–7.27 (m, 4H), 7.15–7.10 (m, 2H), 6.93–6.87 (m, 1H), 6.85–6.78 (m, 2H), 6.46 (d, *J* = 7.9 Hz, 1H), 6.42 (d, *J* = 7.9 Hz, 1H), 4.28 (d, *J* = 9.7 Hz, 0.5H), 4.19 (d, *J* = 9.7 Hz, 0.5H), 4.02–3.86 (m, 2H), 3.55 (s, 1.5H), 3.07 (s, 1.5H), 2.94–2.79 (m, 1H), 2.39–2.30 (m, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ 155.5, 153.3, 148.7, 147.9, 146.0, 145.4, 140.5, 140.2, 139.8, 135.5, 135.4, 128.2, 128.2, 128.0, 128.0, 127.8, 127.7, 127.6, 127.2, 126.8, 123.6, 123.5, 122.1, 122.1, 119.9, 119.8, 119.6, 119.5, 76.1, 75.8, 58.0, 57.0, 52.3, 52.1, 47.6, 47.1, 28.1, 27.5; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 2954, 2886, 1694, 1674, 1449, 1383, 1136, 1001; MS

(EI):  $m/z = 355$  ( $M^+$ ); HRMS (EI):  $m/z$  calcd for  $C_{24}H_{21}NO_2$ : 355.1572; found: 355.1573.

### **Methyl spiro[fluorene-9,2'-pyrrolidine]-1'-carboxylate (11)**

NMR spectrum shows a double set of peaks (1:1) due to the *cis* and *trans* conformers around the tertiary carbamate. White solid; mp 138–140 °C;  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.69–7.63 (m, 2H), 7.37–7.31 (m, 4H), 7.29–7.23 (m, 2H), 3.99 (t,  $J = 6.6$  Hz, 1H), 3.92 (t,  $J = 6.7$  Hz, 1H), 3.50 (s, 1.5H), 3.03 (s, 1.5H), 2.35–2.24 (m, 4H);  $^{13}C$ -NMR ( $CDCl_3$ ):  $\delta$  155.3, 153.2, 150.1, 149.3, 139.7, 139.3, 128.2, 128.0, 127.8, 127.7, 127.2, 127.2, 126.8, 122.2, 122.1, 120.1, 119.9, 72.3, 71.9, 52.2, 52.0, 49.3, 48.6, 42.1, 41.1, 24.1, 23.5; IR ( $CHCl_3$ ,  $cm^{-1}$ ): 2957, 2880, 1694, 1674, 1449, 1379, 1155, 1136, 1099, 968; MS (EI):  $m/z = 279$  ( $M^+$ ); HRMS (EI):  $m/z$  calcd for  $C_{18}H_{17}NO_2$ : 279.1259; found: 279.1255.

### **3-Phenyl-4,5-dihydro-3*H*-spiro[furan-2,9'-xanthene] (13)**

Orange solid; mp 93–95 °C;  $^1H$ -NMR ( $CDCl_3$ ):  $\delta$  7.74 (dd,  $J = 7.6, 1.7$  Hz, 1H), 7.52–7.47 (m, 1H), 7.31–7.20 (m, 2H), 7.19–7.11 (m, 2H), 7.07 (t,  $J = 7.2$  Hz, 1H), 7.00–6.91 (m, 3H), 6.74–6.69 (m, 1H), 6.38 (d,  $J = 8.1$  Hz, 2H), 4.72 (t,  $J = 8.4$  Hz, 1H), 4.51 (ddd,  $J = 11.1, 8.4, 5.8$  Hz, 1H), 3.37 (dd,  $J = 13.1, 6.2$  Hz, 1H), 2.72 (dtd,  $J = 13.1, 12.6, 8.4$  Hz, 1H), 2.28 (ddd,  $J = 12.6, 6.2, 5.8$  Hz, 1H);  $^{13}C$ -NMR ( $CDCl_3$ ):  $\delta$  151.0, 136.0, 128.5, 128.4, 128.1, 127.9, 127.5, 127.1, 126.6, 125.4, 125.0, 123.8, 122.8, 115.9, 115.7, 82.2, 70.0, 62.0, 30.8; IR ( $CHCl_3$ ,  $cm^{-1}$ ): 2876, 1601, 1574, 1476, 1450, 1321, 1271, 1047; MS (EI):  $m/z = 314$  ( $M^+$ ); HRMS (EI):  $m/z$  calcd for  $C_{22}H_{18}O_2$ : 314.1307; found: 314.1305.

### **3'-Fluoro-3'-phenyl-4',5'-dihydro-3'*H*-spiro[fluorene-9,2'-furan] (14)**



White solid; mp 139–140 °C;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  7.86 (dd,  $J = 7.0, 4.0$  Hz, 1H), 7.45 (d,  $J = 7.3$  Hz, 1H), 7.42–7.32 (m, 3H), 7.32–7.27 (m, 1H), 7.16–7.09 (m, 2H), 7.02 (t,  $J = 7.4$  Hz, 1H), 6.93 (t,  $J = 7.7$  Hz, 2H), 6.78 (d,  $J = 8.1$  Hz, 2H), 4.72 (ddd,  $J = 10.2, 8.5, 6.5$  Hz, 1H), 4.65 (ddd,  $J = 9.7, 8.5, 1.8$  Hz, 1H), 3.45 (dddd,  $J = 42.5, 13.8, 10.2, 9.7$  Hz, 1H), 2.80 (dddd,  $J = 17.5, 13.8, 6.5, 1.8$  Hz, 1H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  145.45 (d,  $J = 5.7$  Hz), 142.4, 141.3, 140.3, 135.28 (d,  $J = 23.1$  Hz), 129.6, 129.0, 128.2, 128.05 (d,  $J = 8.5$  Hz), 127.6, 127.4, 127.2, 125.50 (d,  $J = 6.7$  Hz), 124.2, 119.9, 119.4, 105.73 (d,  $J = 186.4$  Hz), 96.14 (d,  $J = 21.9$  Hz), 67.0, 35.91 (d,  $J = 21.9$  Hz); IR ( $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 2897, 2359, 1609, 1449, 1313, 1107, 1053; MS (EI):  $m/z = 316$  ( $\text{M}^+$ ); HRMS (EI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{17}\text{FO}$ : 316.1263; found: 316.1269.