

# Supporting Information

## Thermal Induced Formal [3+2] Cyclization of *Ortho*-Aminoaryl-Tethered Alkylidenecyclopropanes: Facile Synthesis of Furoquinoline and Thienoquinoline Derivatives

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### Contents

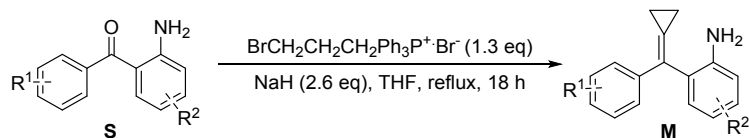
General remarks.....	S2
General procedure for the synthesis of ACPs <b>1i</b> , <b>1l</b> and <b>1m</b> .....	S3
Spectroscopic data for ACPs <b>1i</b> , <b>1l</b> and <b>1m</b> .....	S4
General procedure for the synthesis of products <b>2</b> .....	S7
Spectroscopic data for products <b>2</b> .....	S8
General procedure for the synthesis of products <b>3</b> .....	S26
Spectroscopic data for products <b>3</b> .....	S27
Transformations and scalable production of <b>2a</b> and <b>3a</b> .....	S45
Control experiments.....	S47
Spectroscopic data for products <b>5a</b> , <b>6a</b> and <b>8</b> .....	S49
The crystal data of <b>2c</b> , <b>3a</b> and <b>4c</b> .....	S52
Reference.....	S55

## General remarks

THF was distilled from sodium (Na) under argon (Ar) atmosphere. All other solvents were purchased from Adamas and used as received. Isatoic anhydride and other materials obtained from commercial suppliers were used without further purification. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. All NMR spectra were recorded on a AM-300 or AM-400 spectrophotometers in CDCl<sub>3</sub>, NMR chemical shifts are reported in ppm referenced to the solvent peaks of CDCl<sub>3</sub> (7.26 ppm for <sup>1</sup>H and 77.0 ppm for <sup>13</sup>C, respectively). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm<sup>-1</sup>. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Mass spectra were recorded by ESI, and HRMS were measured on a HP-5989 instrument.

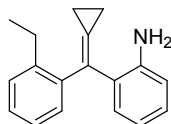
## General procedure for the synthesis of ACPs **1i**, **1l** and **1m**

Compounds **M** were partially prepared according to previously reported work<sup>[1]</sup> and 2-aminobenzophenones were prepared from isatoic anhydride according to related literature.<sup>[2]</sup>

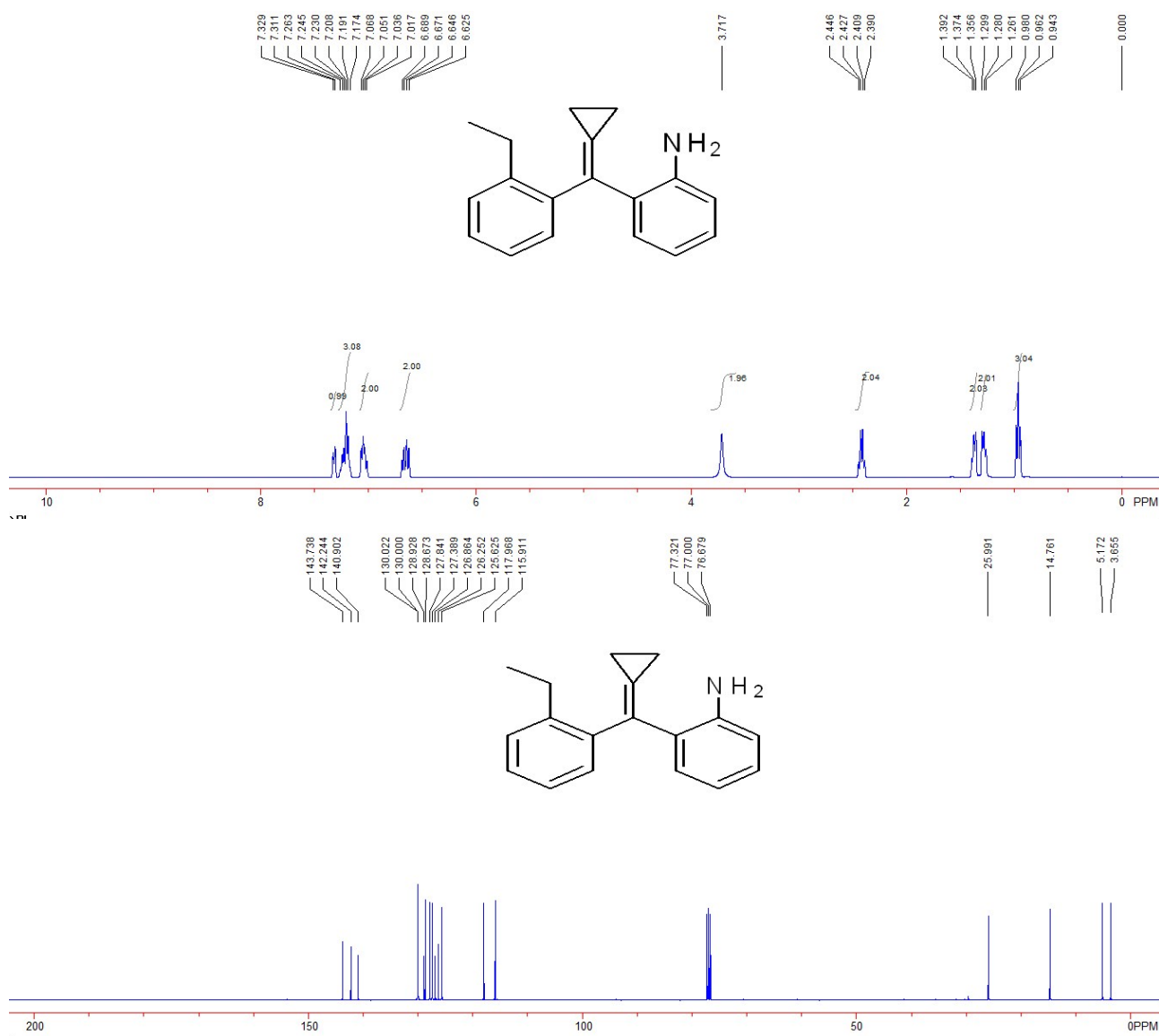


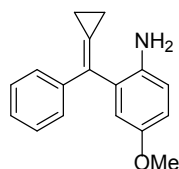
A solution of 3-bromopropyltriphenylphosphonium bromide (5.96 g, 13 mmol) and NaH (624 mg, 26 mmol) in THF (15 mL) was stirred at 70 °C under N<sub>2</sub> for 12 h. Afterwards compound **S** (10 mmol) in THF (10 mL) was added and the reaction solution was stirred at 70 °C for another 12 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 60 / 1 to 40 / 1) to afford the products **M** in moderate yields.

## Spectroscopic data for ACPs 1i, 1l and 1m

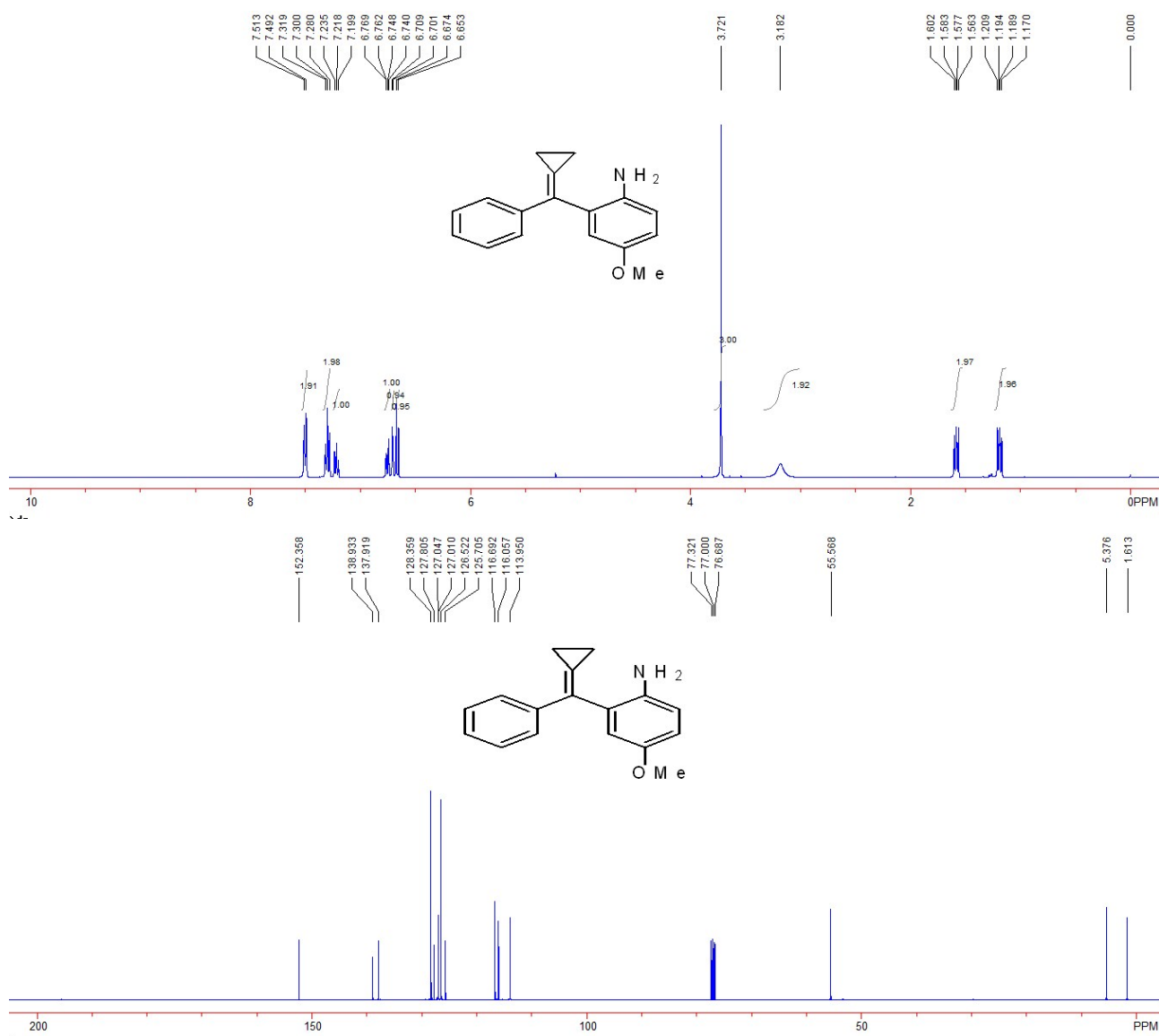


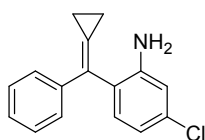
**Compound 1i:** 1.79 g, 72%, A colorless liquid; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3384, 2924, 1625, 1492, 1452, 1414, 1395, 1316, 1102, 1026, 755, 701 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  0.96 (t, 3H,  $J$  = 7.6 Hz), 1.28 (t, 2H,  $J$  = 7.6 Hz), 1.37 (t, 2H,  $J$  = 7.6 Hz), 2.42 (q, 2H,  $J$  = 7.6 Hz), 3.72 (s, 2H), 6.63-6.69 (m, 2H), 7.02-7.07 (m, 2H), 7.17-7.26 (m, 3H), 7.32 (d, 1H,  $J$  = 7.2 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.7, 5.2, 14.8, 26.0, 115.9, 118.0, 125.6, 126.3, 126.9, 127.4, 127.8, 128.7, 128.9, 130.00, 130.02, 140.9, 142.2, 143.7; MS (ESI)  $m/z$ : 250.2 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>20</sub>N<sup>+</sup> requires: 250.1590, Found: 250.1594.



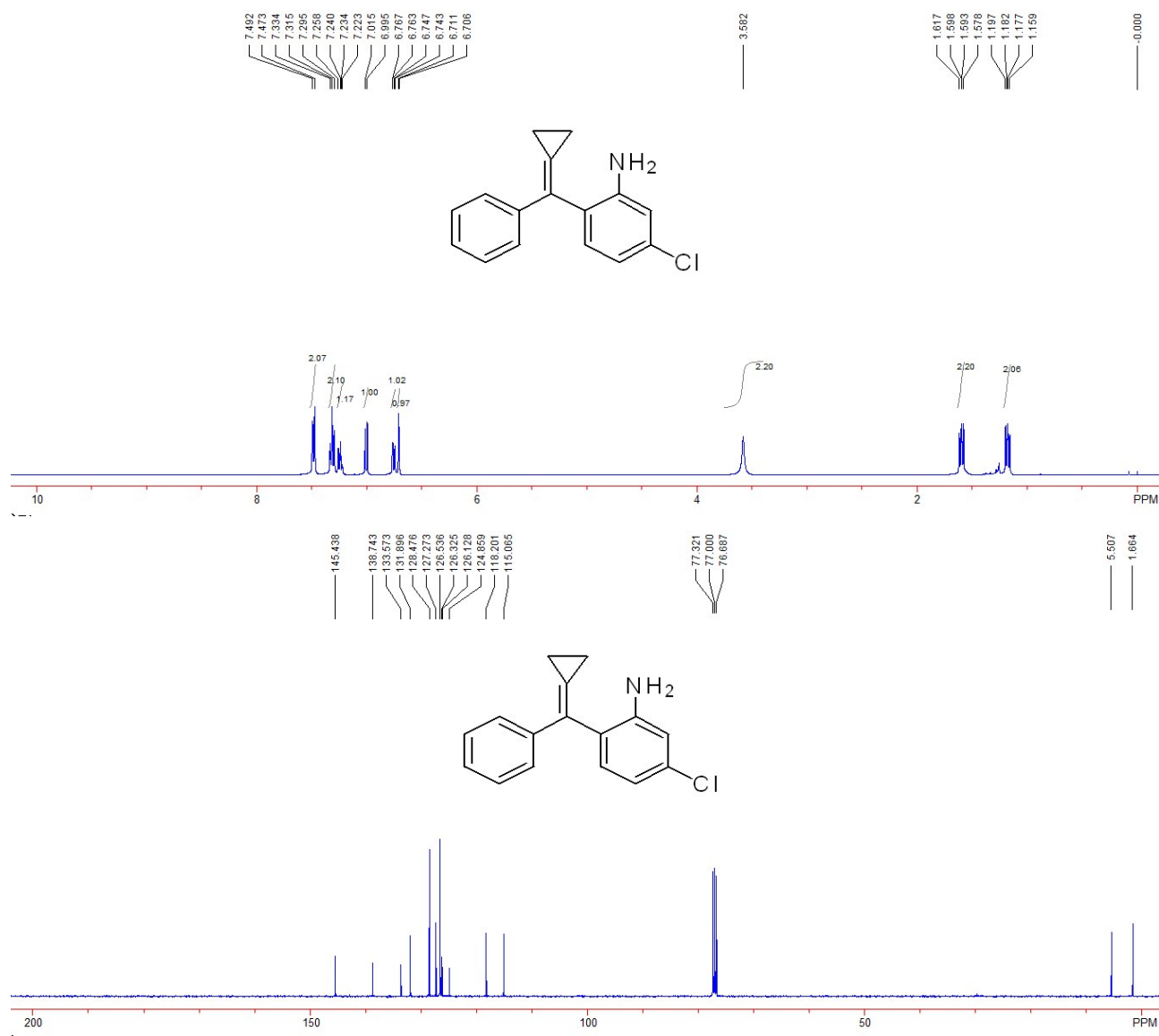


**Compound 11:** 1.36 g, 54%, A white solid, m.p. 94-96 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3434, 3346, 1494, 1447, 1424, 1277, 1226, 1161, 1033, 909, 814, 772, 609 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.17-1.21 (m, 2H), 1.56-1.60 (m, 2H), 3.18 (s, 2H), 3.72 (s, 3H), 6.66 (d, 1H,  $J = 8.4$  Hz), 6.71 (d, 1H,  $J = 3.2$  Hz), 6.76 (dd, 1H,  $J_1 = 8.4$  Hz,  $J_2 = 3.2$  Hz), 7.20-7.24 (m, 1H), 7.30 (t, 2H,  $J = 8.0$  Hz), 7.50 (d, 2H,  $J = 8.4$  Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.6, 5.4, 55.6, 114.0, 116.1, 116.7, 125.7, 126.5, 127.01, 127.05, 127.8, 128.4, 137.9, 138.9, 152.4; MS (ESI)  $m/z$ : 252.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>18</sub>NO<sup>+</sup> requires: 252.1383, Found: 252.1385.

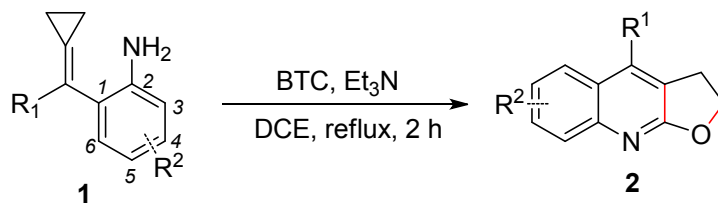




**Compound 1m:** 1.45 g, 57%, A white solid, m.p. 94-95 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3481, 3382, 2932, 1612, 1489, 1445, 1416, 1256, 1059, 916, 849, 763, 697 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.16-1.20 (m, 2H), 1.58-1.62 (m, 2H), 3.58 (s, 2H), 6.71 (d, 1H,  $J$  = 2.0 Hz), 6.76 (dd, 1H,  $J_1$  = 8.0 Hz,  $J_2$  = 1.6 Hz), 7.01 (d, 1H,  $J$  = 8.0 Hz), 7.22-7.26 (m, 1H), 7.32 (t, 2H,  $J$  = 7.6 Hz), 7.48 (d, 2H,  $J$  = 7.6 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.7, 5.5, 115.1, 118.2, 124.9, 126.1, 126.3, 126.5, 127.3, 128.5, 131.9, 133.6, 138.7, 145.4; MS (ESI)  $m/z$ : 256.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>16</sub>H<sub>15</sub>ClN<sup>+</sup> requires: 256.0888, Found: 256.0890.

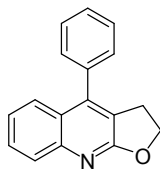


## General procedure for the synthesis of products 2

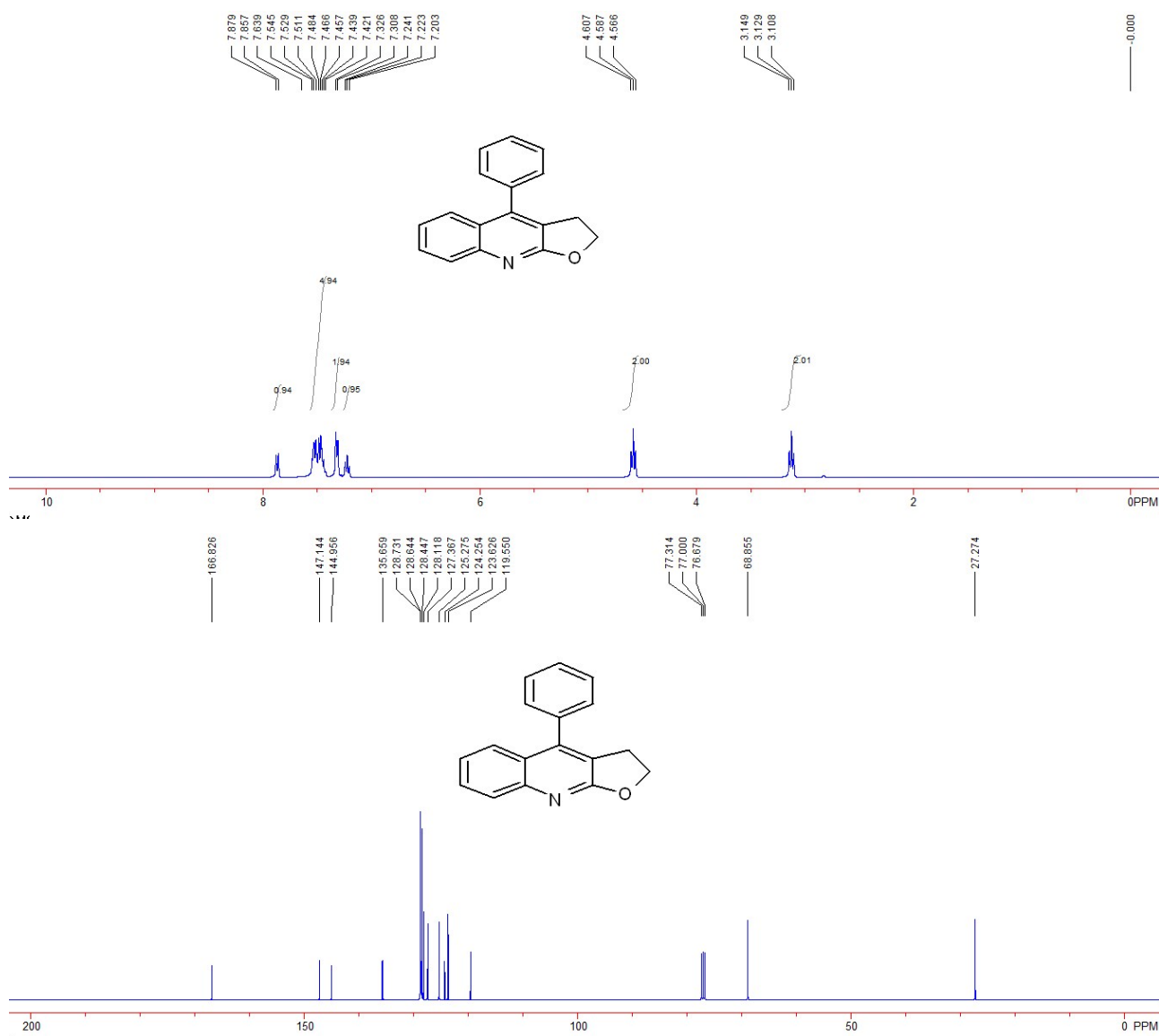


**1** (0.6 mmol) and triphosgene (0.2 mmol) were dissolved in DCE (6.0 mL), then  $\text{Et}_3\text{N}$  (0.25 mL) was added dropwise and the resulting reaction mixture was stirred at 85 °C. The reaction was stopped after 2 h and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the product **2** in excellent yield.

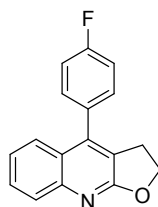
## Spectroscopic data for products 2



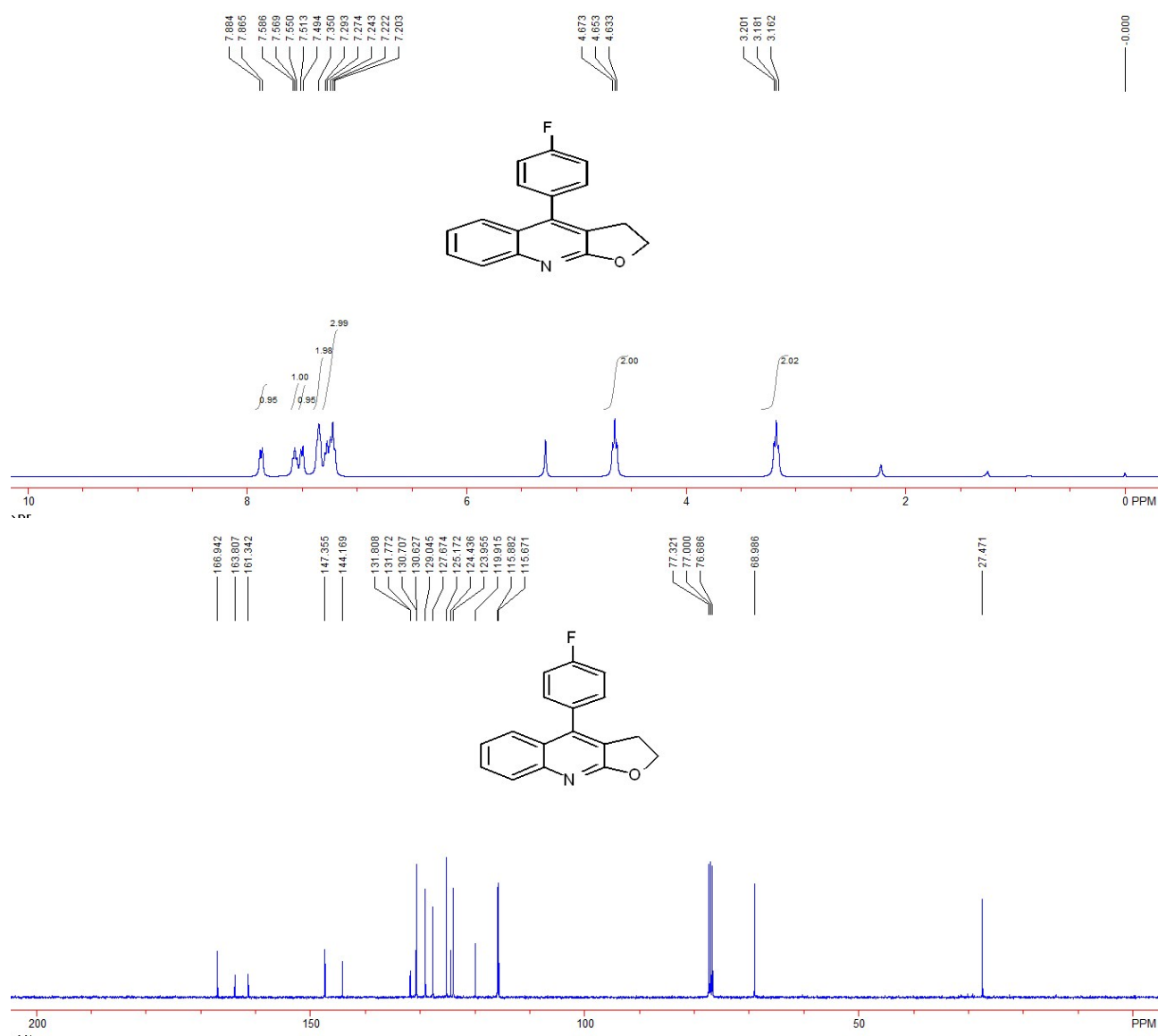
**Compound 2a:** 147 mg, 99%, A white solid, m.p. 178-180 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3050, 2917, 1625, 1588, 1418, 1396, 1332, 1315, 1032, 861, 758, 703 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.13 (t, 2H,  $J = 8.4$  Hz), 4.59 (t, 2H,  $J = 8.4$  Hz), 7.22 (t, 1H,  $J = 7.6$  Hz), 7.32 (d, 2H,  $J = 7.2$  Hz), 7.42-7.64 (m, 5H), 7.87 (d, 1H,  $J = 8.8$  Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  27.3, 68.9, 119.6, 123.6, 124.3, 125.3, 127.4, 128.1, 128.4, 128.6, 128.7, 135.7, 145.0, 147.1, 166.8; MS (ESI)  $m/z$ : 248.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>14</sub>NO<sup>+</sup> requires: 248.1070, Found: 248.1073.

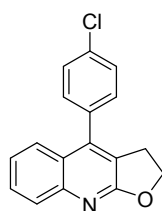
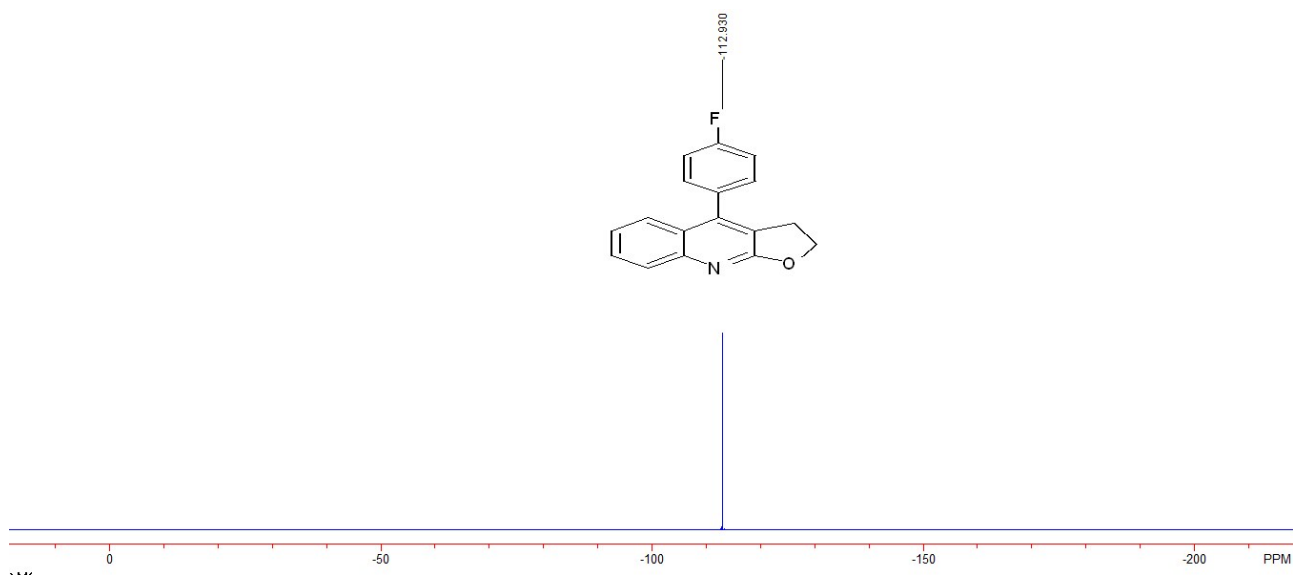




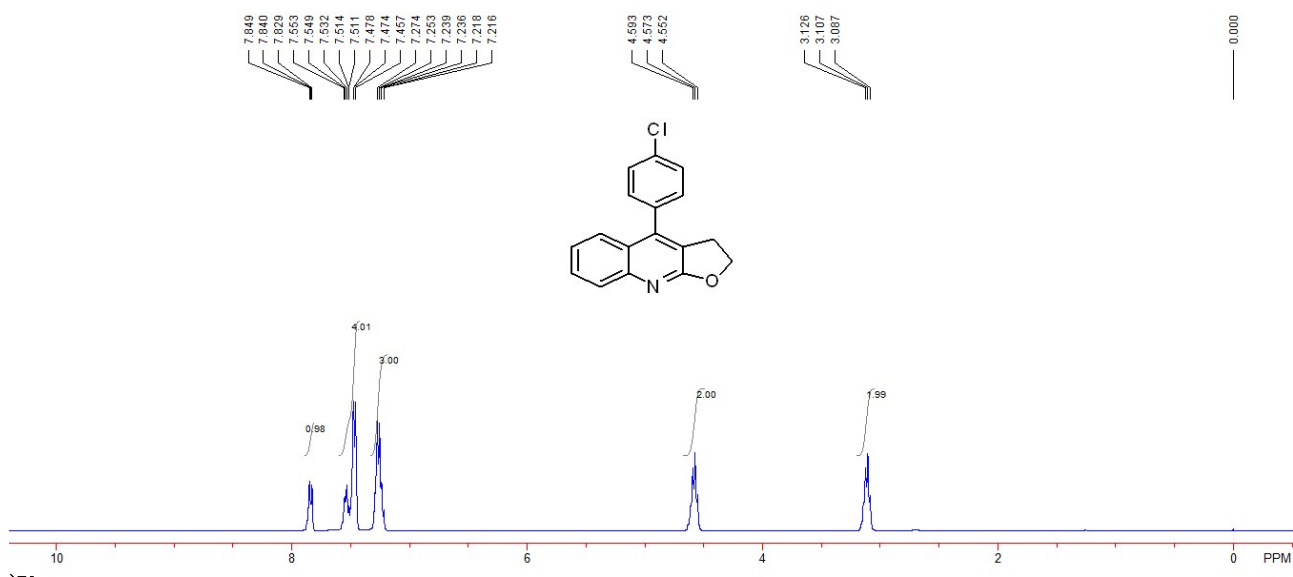


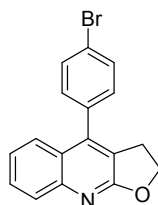
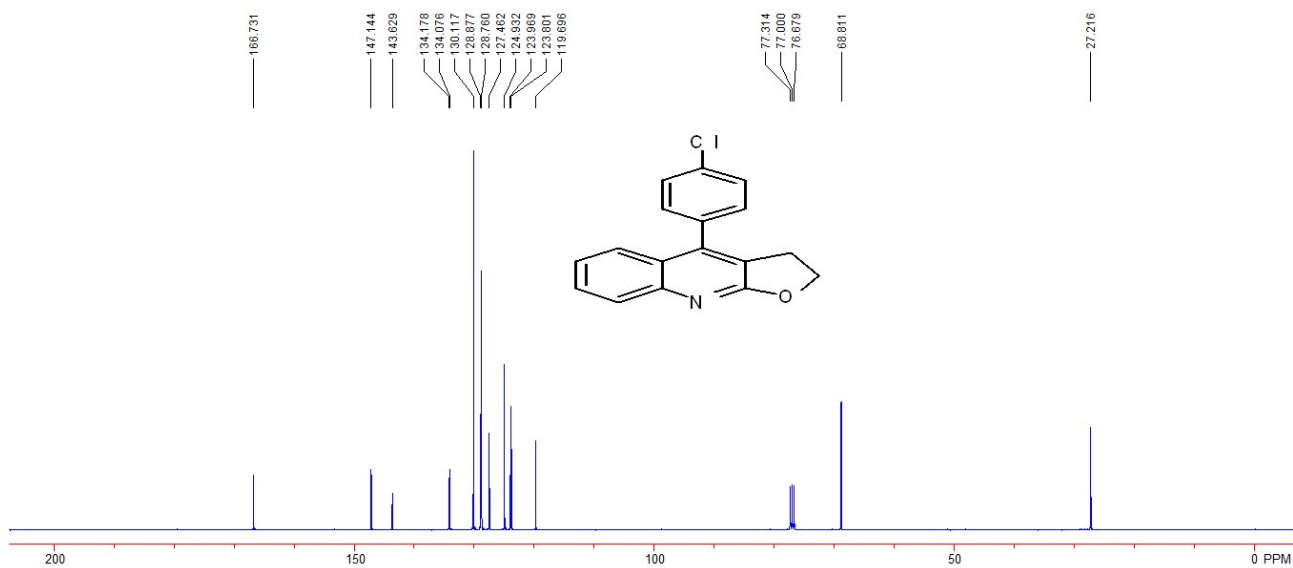
**Compound 2b:** 147 mg, 92%, A white solid, m.p. 170-172 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3060, 2920, 1624, 1600, 1504, 1396, 1370, 1316, 1218, 1160, 1007, 891, 842, 765 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.18 (t, 2H,  $J$  = 8.0 Hz), 4.65 (t, 2H,  $J$  = 8.0 Hz), 7.20-7.29 (m, 3H), 7.35 (brs, 2H), 7.50 (d, 1H,  $J$  = 7.6 Hz), 7.57 (t, 1H,  $J$  = 7.6 Hz), 7.87 (d, 1H,  $J$  = 7.6 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  27.5, 69.0, 115.8 (d,  $J_{C-F}$  = 21.1 Hz), 119.9, 124.0, 124.4, 125.2, 127.7, 129.0, 130.7 (d,  $J_{C-F}$  = 8.0 Hz), 131.8 (d,  $J_{C-F}$  = 3.6 Hz), 144.2, 147.4, 162.6 (d,  $J_{C-F}$  = 246.5 Hz), 166.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, CFCl<sub>3</sub>):  $\delta$  -112.9 (s); MS (ESI)  $m/z$ : 266.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>13</sub>FNO<sup>+</sup> requires: 266.0976, Found: 266.0978.



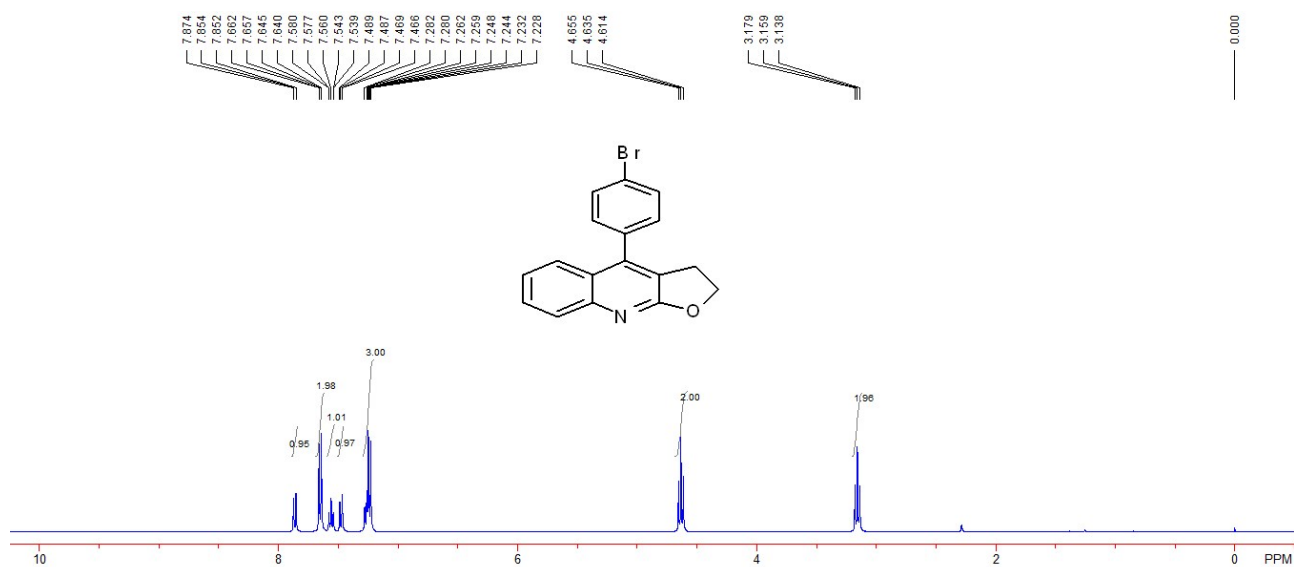


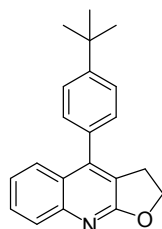
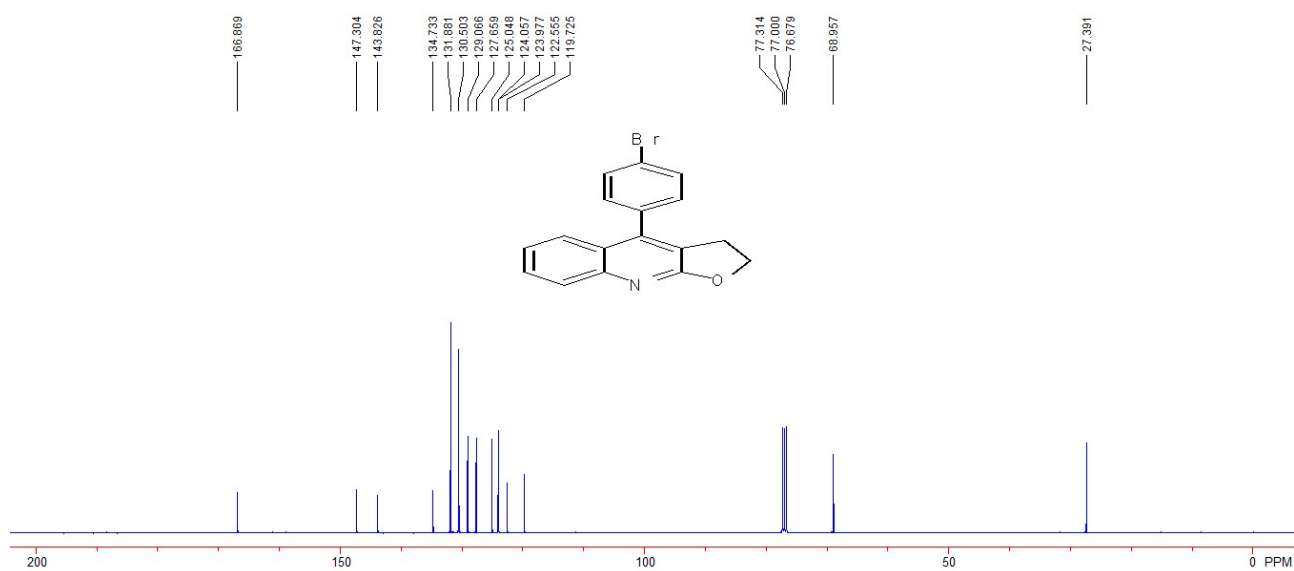
**Compound 2c:** 161 mg, 95%, A white solid, m.p. 187-189 °C; IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu$  3058, 2919, 1630, 1597, 1475, 1410, 1395, 1316, 1224, 1090, 828, 761  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  3.11 (t, 2H,  $J = 8.0$  Hz), 4.57 (t, 2H,  $J = 8.0$  Hz), 7.22-7.27 (m, 3H), 7.27-7.55 (m, 4H), 7.83-7.85 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$  27.2, 68.8, 119.7, 123.8, 124.0, 124.9, 127.5, 128.8, 128.9, 130.1, 134.1, 134.2, 143.6, 147.1, 166.7; MS (ESI)  $m/z$ : 282.1 ( $\text{M}+\text{H}^+$ , 100); HRMS (ESI) Calcd. for  $\text{C}_{17}\text{H}_{13}\text{ClNO}^+$  requires: 282.0680, Found: 282.0683.



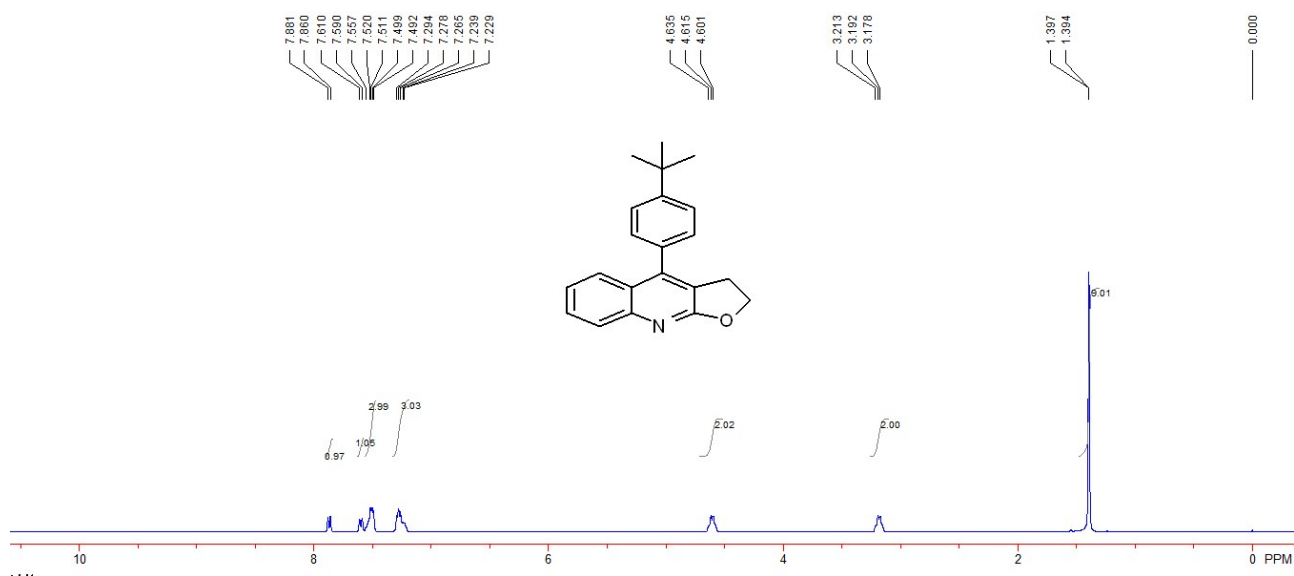


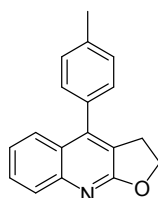
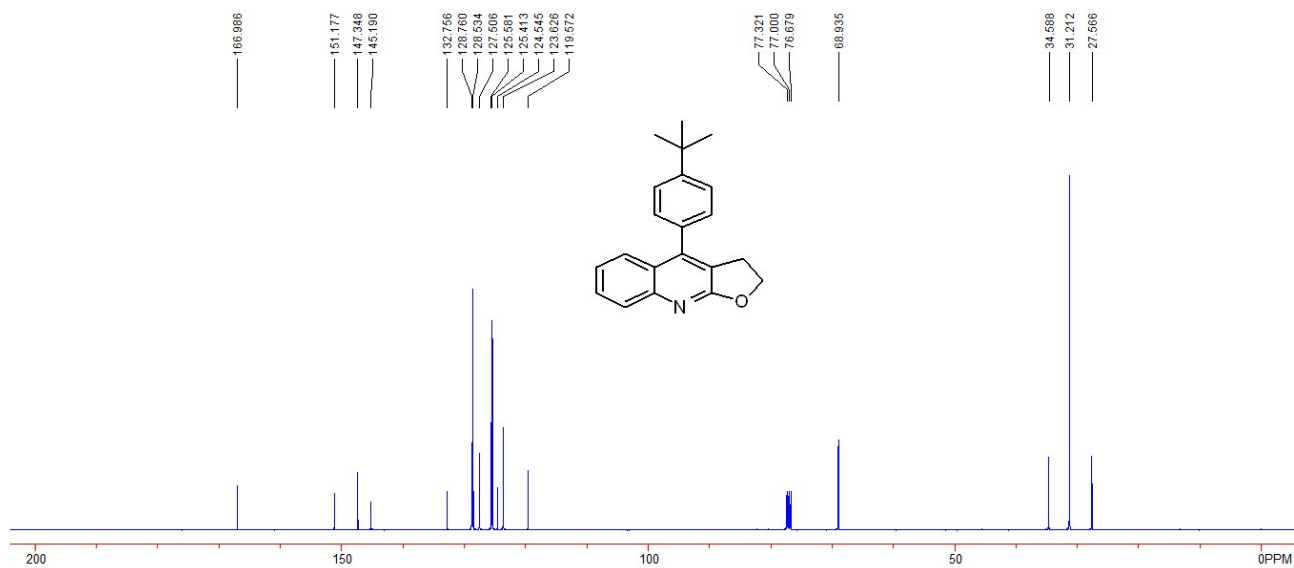
**Compound 2d:** 188 mg, 96%, A white solid, m.p. 212-214 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2975, 2920, 1626, 1594, 1476, 1412, 1394, 1257, 1225, 1101, 1004, 823, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 3.16 (t, 2H, *J* = 8.4 Hz), 4.64 (t, 2H, *J* = 8.4 Hz), 7.23-7.28 (m, 3H), 7.48 (dd, 1H, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 0.8 Hz), 7.56 (td, 1H, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 1.2 Hz), 7.65 (dd, 2H, *J*<sub>1</sub> = 6.8 Hz, *J*<sub>2</sub> = 2.0 Hz), 7.86 (dd, 1H, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 0.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 27.4, 69.0, 119.7, 122.6, 124.0, 124.1, 125.0, 127.7, 129.1, 130.5, 131.9, 134.7, 143.8, 147.3, 166.9; MS (ESI) *m/z*: 326.0 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>13</sub>BrNO<sup>+</sup> requires: 326.0175, Found: 326.0176.



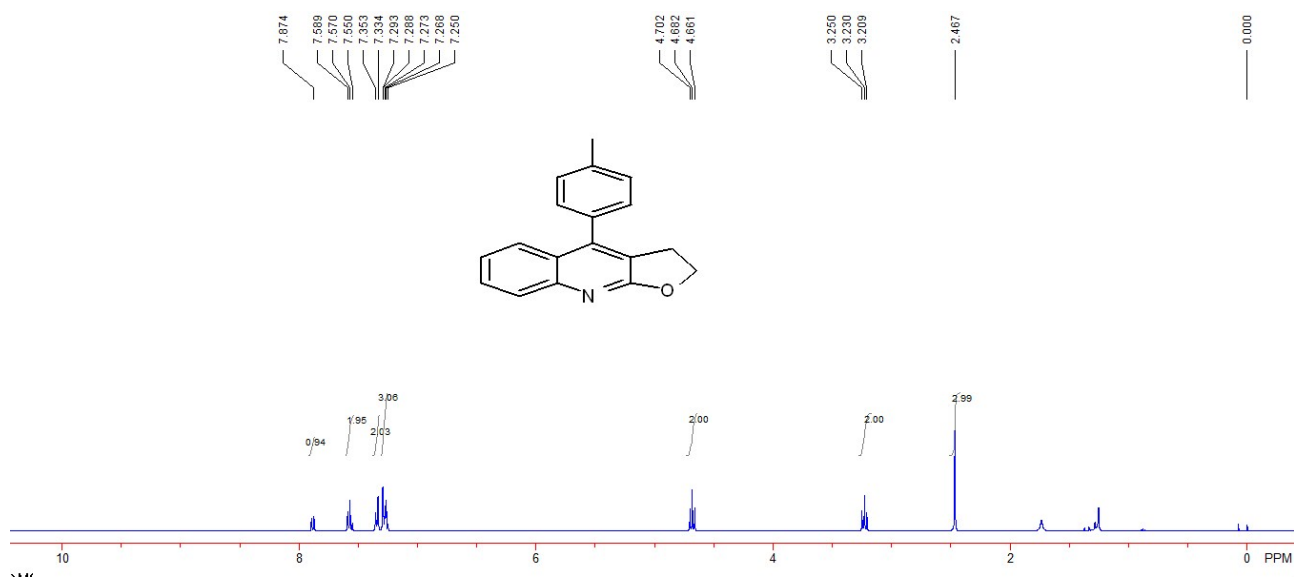


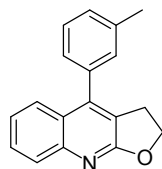
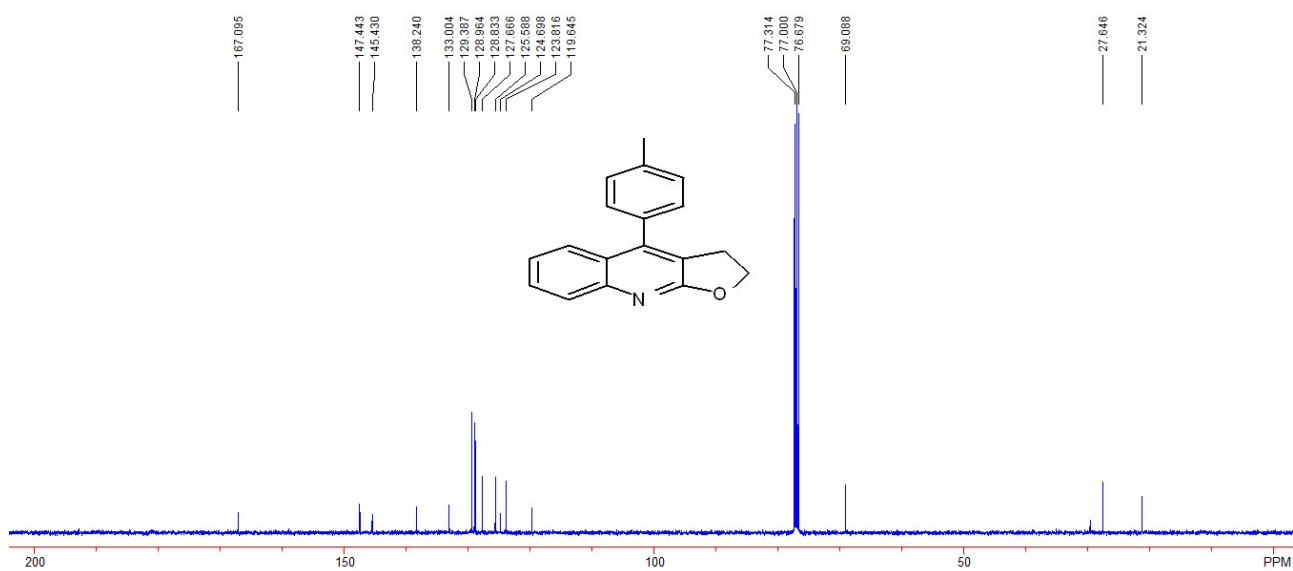
**Compound 2e:** 172 mg, 94%, A white solid, m.p. 222-224 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 3065, 2959, 1629, 1588, 1436, 1412, 1148, 1023, 850, 832, 763 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 1.39 (s, 9H), 3.19 (t, 2H, *J* = 8.0 Hz), 4.62 (t, 2H, *J* = 8.0 Hz), 7.23-7.29 (m, 3H), 7.49-7.56 (m, 3H), 7.60 (d, 1H, *J* = 8.0 Hz), 7.87 (d, 1H, *J* = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 27.6, 31.2, 34.6, 68.9, 119.6, 123.6, 124.5, 125.4, 125.6, 127.5, 128.5, 128.8, 132.8, 145.2, 147.3, 151.2, 167.0; MS (ESI) *m/z*: 304.2 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>21</sub>H<sub>22</sub>NO<sup>+</sup> requires: 304.1696, Found: 304.1698.



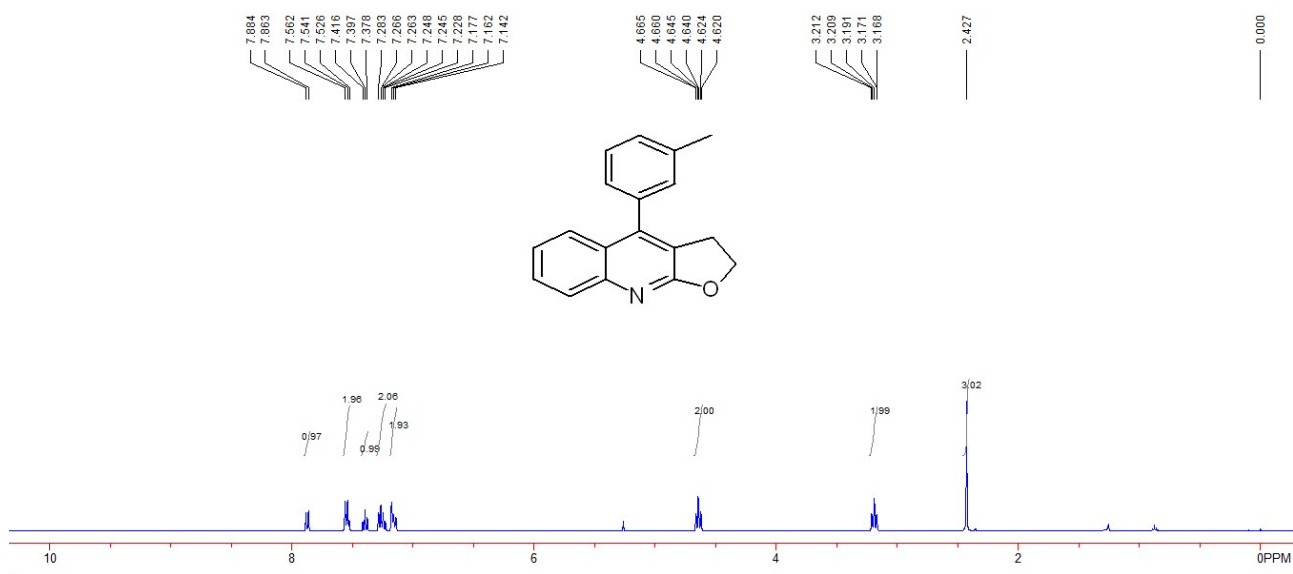


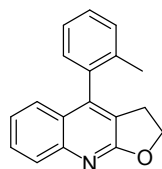
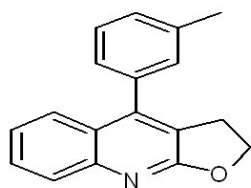
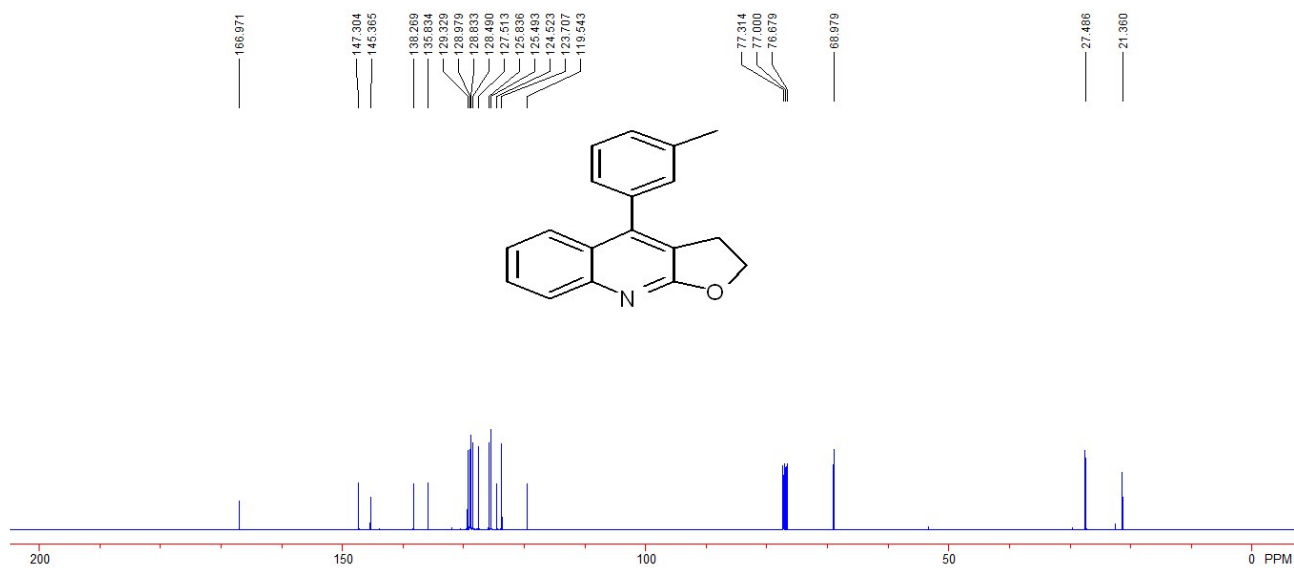
**Compound 2f:** 149 mg, 95%, A white solid, m.p. 190-192 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2919, 2851, 1592, 1506, 1394, 1256, 1222, 1188, 1022, 816, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 2.47 (s, 3H), 3.23 (t, 2H, *J* = 8.0 Hz), 4.68 (t, 2H, *J* = 8.0 Hz), 7.25-7.29 (m, 3H), 7.34 (d, 2H, *J* = 8.4 Hz), 7.57 (t, 2H, *J* = 8.0 Hz), 7.88 (d, 1H, *J* = 8.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 21.3, 27.6, 69.1, 119.6, 123.8, 124.7, 125.6, 127.7, 128.8, 129.0, 129.4, 133.0, 138.2, 145.4, 147.4, 167.1; MS (ESI) *m/z*: 262.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NO<sup>+</sup> requires: 262.1226, Found: 262.1229.



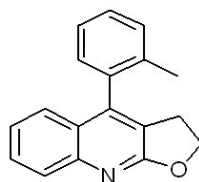
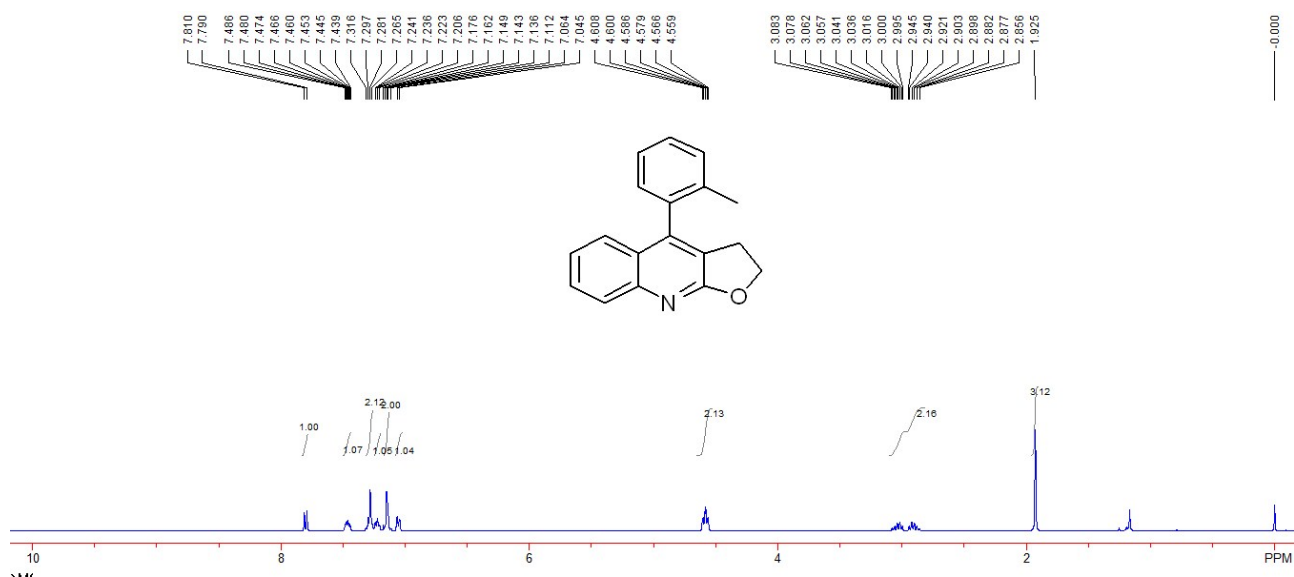


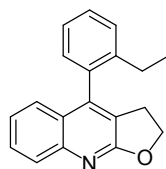
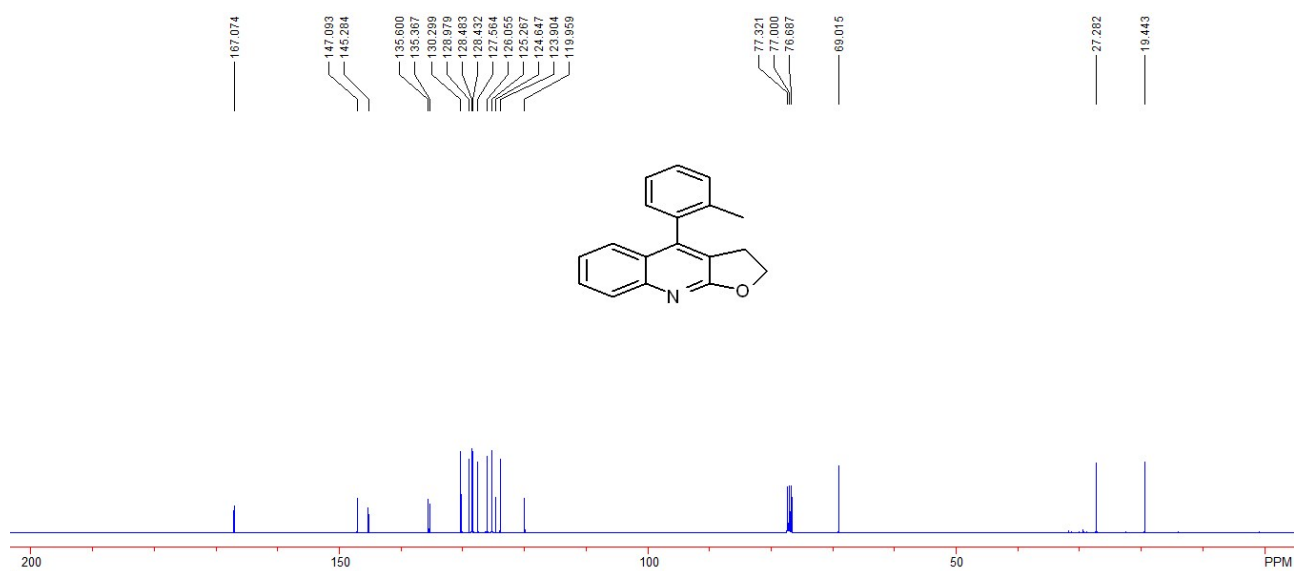
**Compound 2g:** 149 mg, 95%, A white solid, m.p. 164-166 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2968, 2914, 1622, 1591, 1477, 1410, 1395, 1316, 1170, 1010, 966, 790, 759, 702 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 2.43 (s, 3H), 3.17-3.21 (m, 2H), 4.62-4.67 (m, 2H), 7.14-7.17 (m, 2H), 7.23-7.28 (m, 2H), 7.40 (t, 1H, *J* = 7.6 Hz), 7.53-7.56 (m, 2H), 7.87 (d, 1H, *J* = 7.6 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 21.4, 27.5, 69.0, 119.5, 123.7, 124.5, 125.5, 125.8, 127.5, 128.5, 128.8, 129.0, 129.3, 135.8, 138.3, 145.4, 147.3, 167.0; MS (ESI) *m/z*: 262.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NO<sup>+</sup> requires: 262.1226, Found: 262.1229.



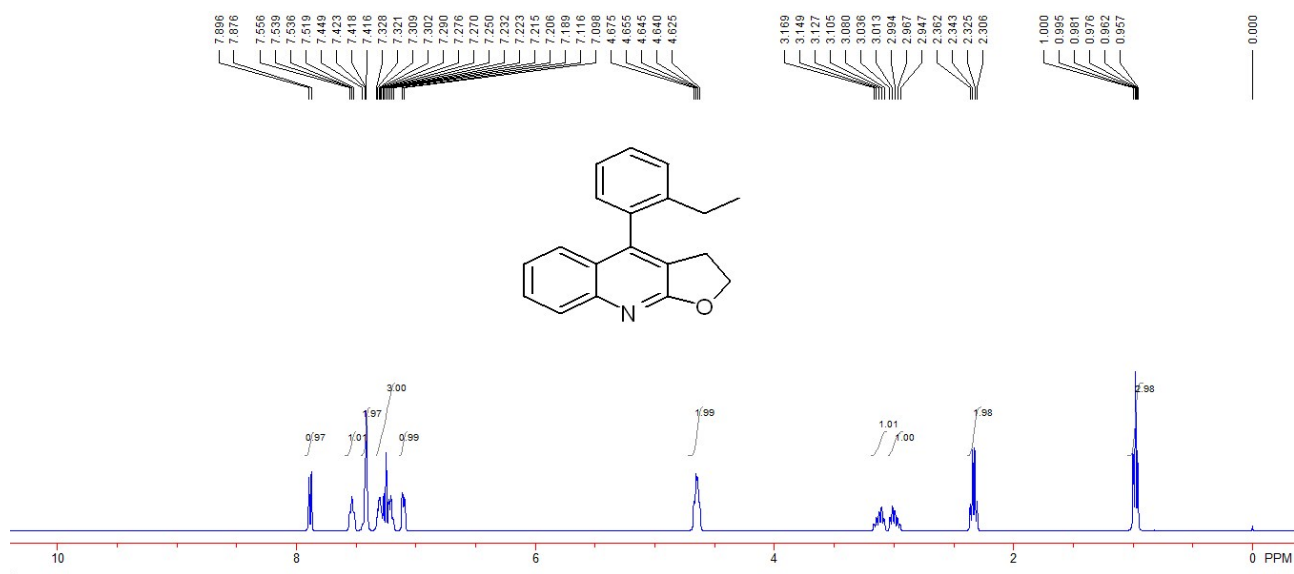


**Compound 2h:** 156 mg, 99%, A white solid, m.p. 144-146 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2917, 2851, 1621, 1590, 1407, 1393, 1315, 1255, 1099, 1003, 755, 702 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.93 (s, 3H), 2.86-2.95 (m, 1H), 3.00-3.08 (m, 1H), 4.56-4.61 (m, 2H), 7.05 (d, 1H,  $J$  = 7.6 Hz), 7.11-7.18 (m, 2H), 7.21-7.24 (m, 1H), 7.27-7.32 (m, 2H), 7.44-7.49 (m, 1H), 7.80 (d, 1H,  $J$  = 8.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  19.4, 27.3, 69.0, 120.0, 123.9, 124.6, 125.3, 126.1, 127.6, 128.4, 128.5, 129.0, 130.3, 135.4, 135.6, 145.3, 147.1, 167.1; MS (ESI)  $m/z$ : 262.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NO<sup>+</sup> requires: 262.1226, Found: 262.1229.

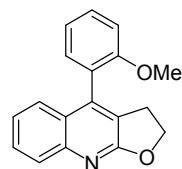
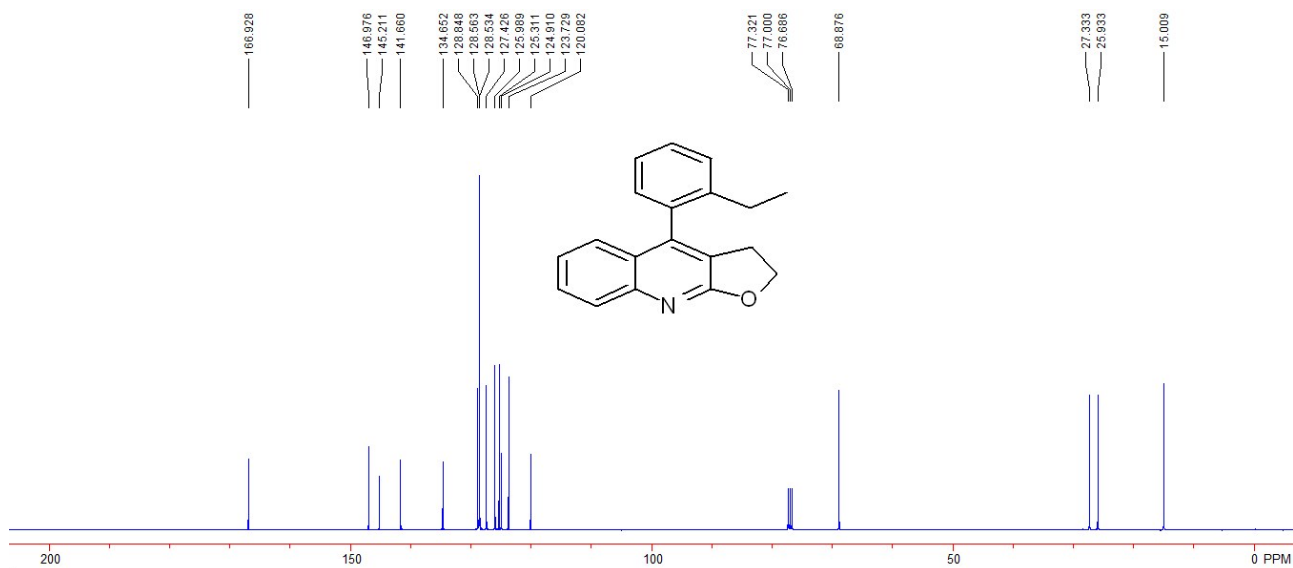




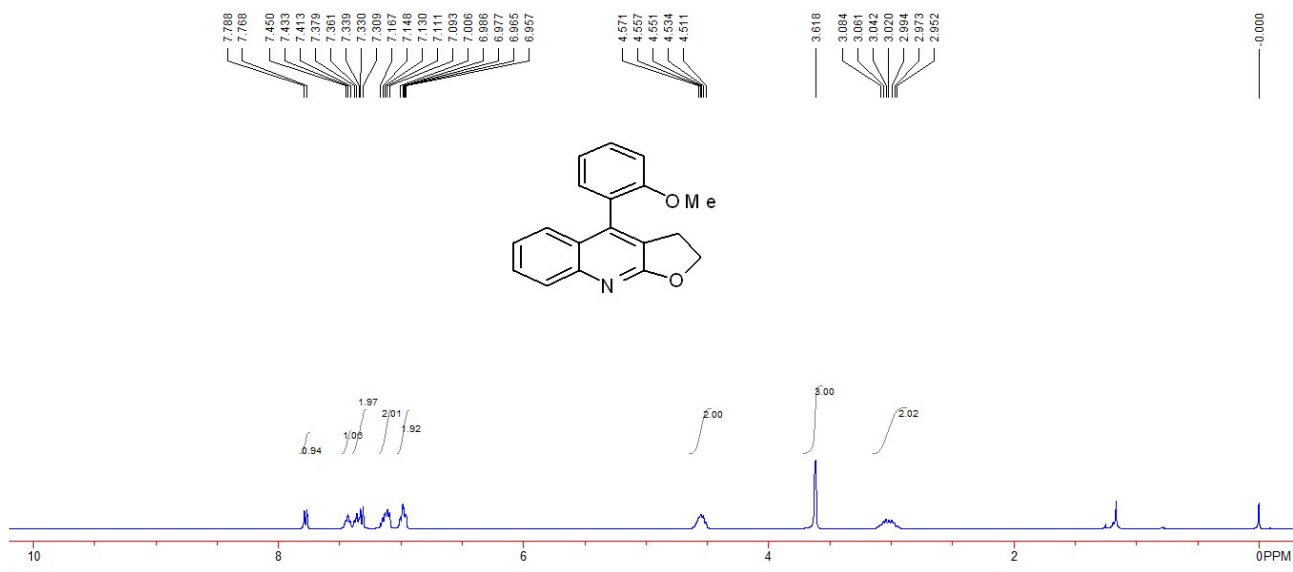
**Compound 2i:** 164 mg, 99%, A white solid, m.p. 156-158 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2966, 2874, 1624, 1588, 1415, 1395, 1316, 1226, 1145, 1001, 871, 760 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 0.96-1.00 (m, 3H), 2.33 (q, 2H, *J* = 7.6 Hz), 2.95-3.04 (m, 1H), 3.08-3.17 (m, 1H), 4.63-4.68 (m, 2H), 7.11 (d, 1H, *J* = 7.6 Hz), 7.19-7.33 (m, 3H), 7.42-7.45 (m, 2H), 7.52-7.56 (m, 1H), 7.89 (d, 1H, *J* = 8.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 15.0, 25.9, 27.3, 68.9, 120.1, 123.7, 124.9, 125.3, 126.0, 127.4, 128.5, 128.6, 128.8, 134.7, 141.7, 145.2, 147.0, 166.9; MS (ESI) *m/z*: 276.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>19</sub>H<sub>18</sub>NO<sup>+</sup> requires: 276.1383, Found: 276.1385.

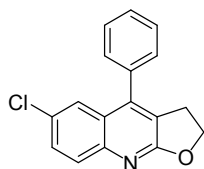
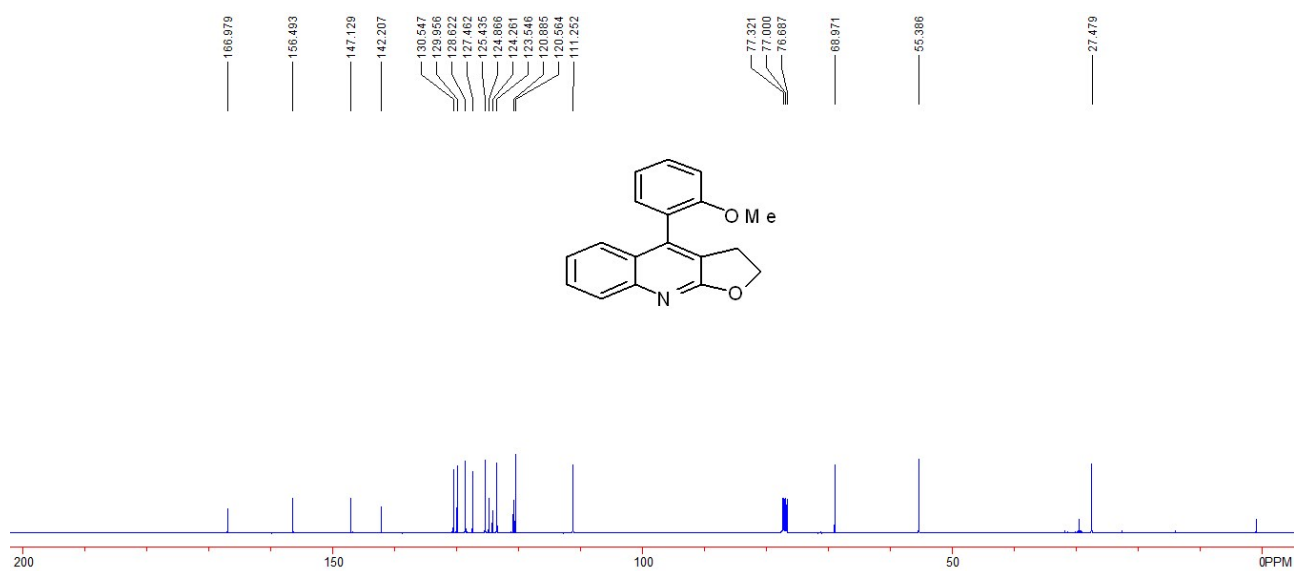




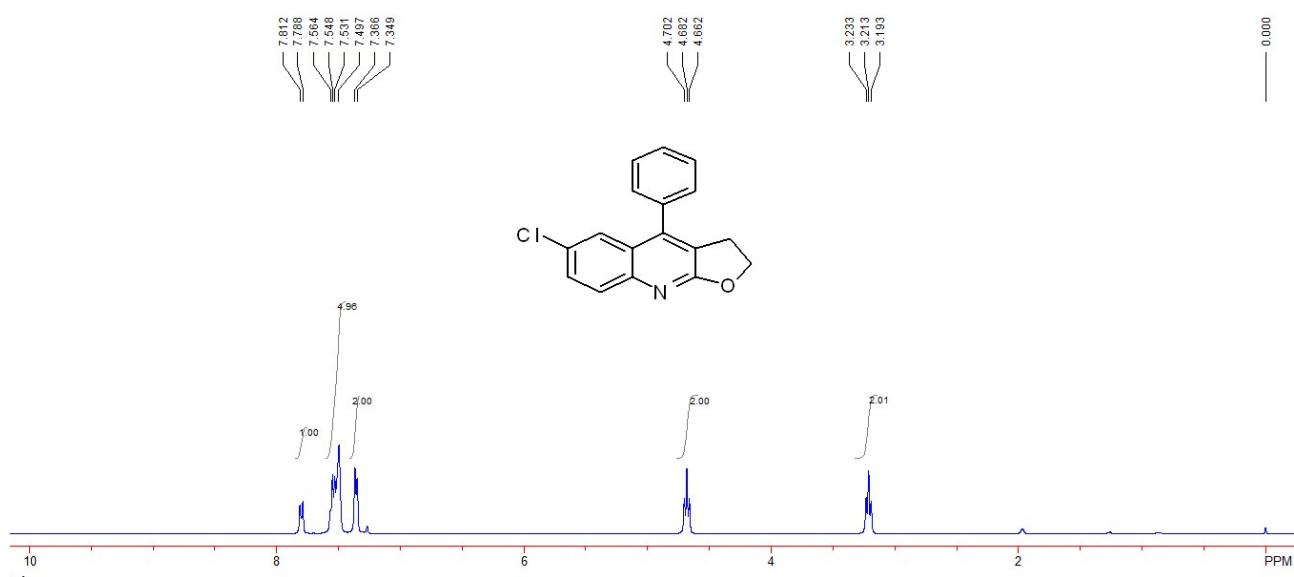


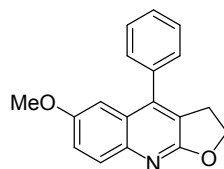
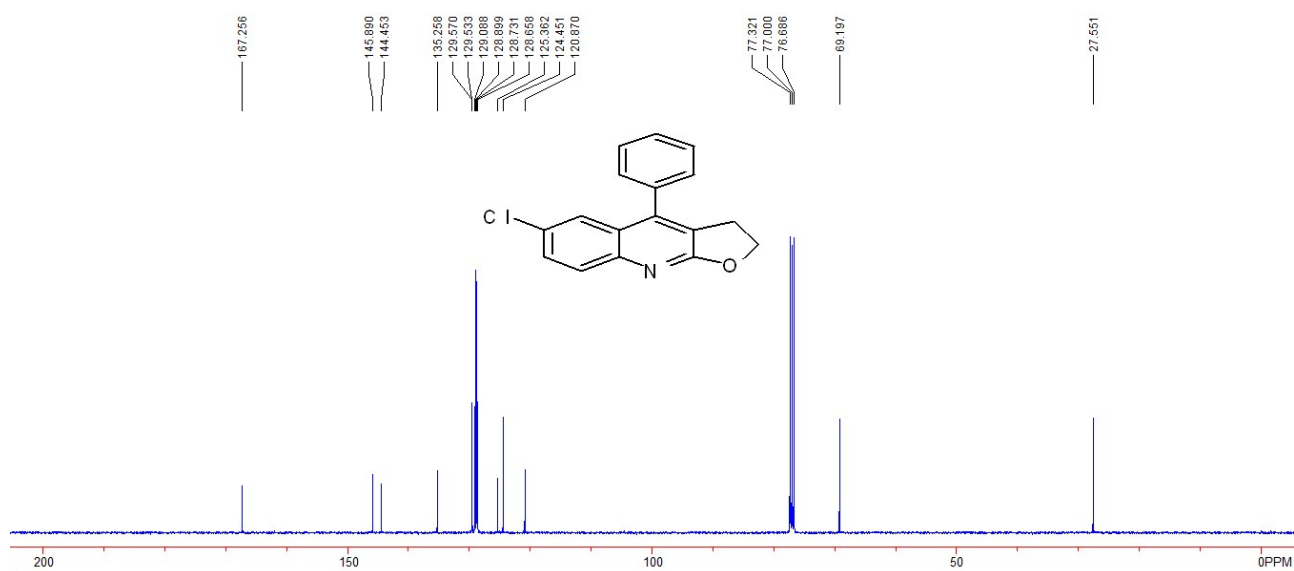
**Compound 2j:** 157 mg, 94%, A white solid, m.p. 169-171 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2964, 2851, 1626, 1598, 1492, 1413, 1395, 1226, 1025, 1002, 756, 701 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 2.95-3.08 (m, 2H), 3.62 (s, 3H), 4.51-4.57 (m, 2H), 6.96-7.01 (m, 2H), 7.09-7.17 (m, 2H), 7.31-7.38 (m, 2H), 7.43 (t, 1H, *J* = 8.0 Hz), 7.88 (d, 1H, *J* = 8.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 27.5, 55.4, 69.0, 111.3, 120.6, 120.9, 123.5, 124.3, 124.9, 125.4, 127.5, 128.6, 130.0, 130.5, 142.2, 147.1, 156.5, 167.0; MS (ESI) *m/z*: 278.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup> requires: 278.1176, Found: 278.1178.



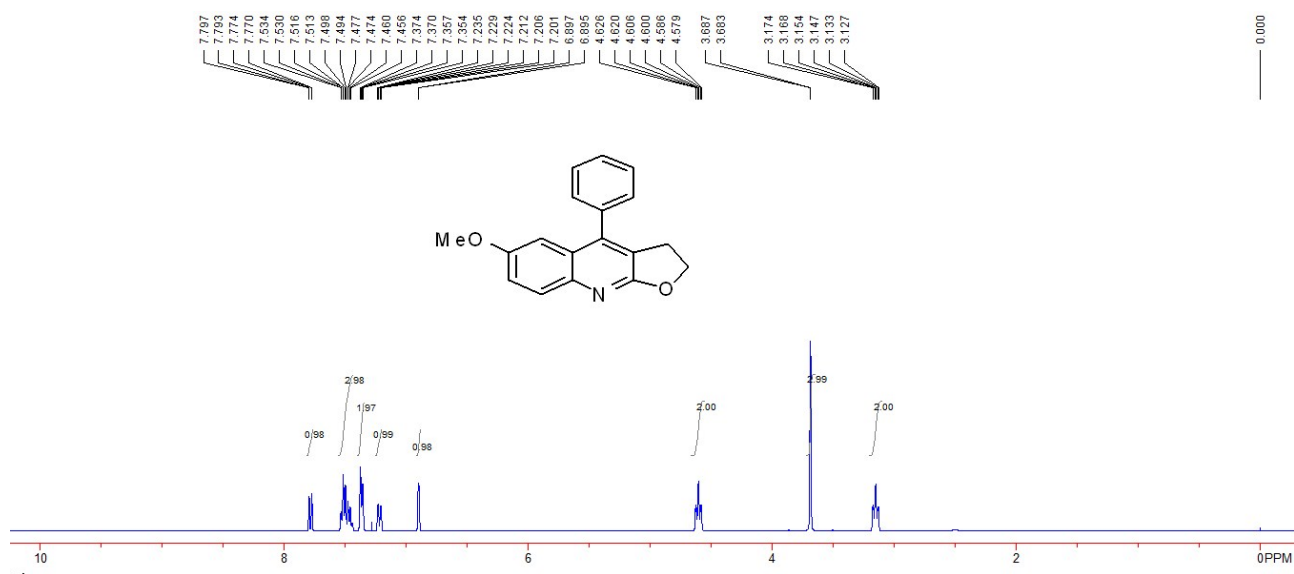


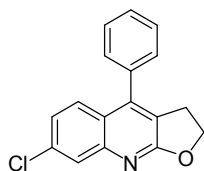
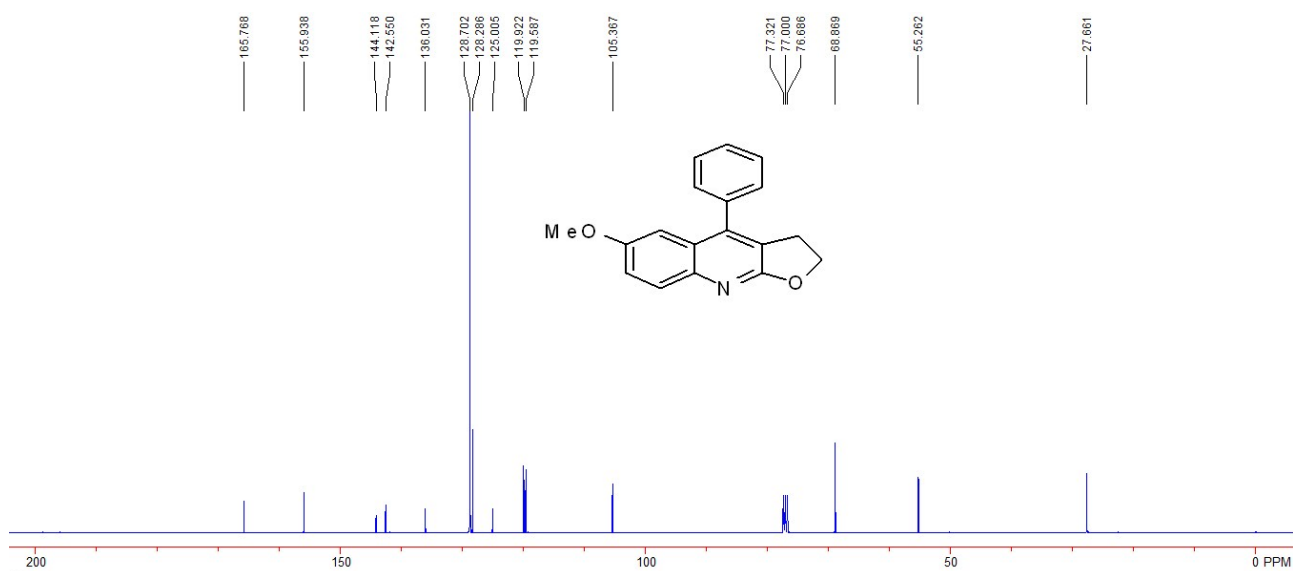
**Compound 2k:** 152 mg, 90%, A white solid, m.p. 177-179 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2977, 2921, 1628, 1513, 1416, 1390, 1321, 1222, 1081, 1007, 947, 824, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 3.21 (t, 2H, *J* = 8.0 Hz), 4.68 (t, 2H, *J* = 8.0 Hz), 7.36 (d, 2H, *J* = 8.0 Hz), 7.50-7.56 (m, 5H), 7.80 (d, 1H, *J* = 9.6 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 27.6, 69.2, 120.9, 124.5, 125.4, 128.66, 128.73, 128.9, 129.1, 129.5, 129.6, 135.3, 144.5, 145.9, 167.3; MS (ESI) *m/z*: 282.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>13</sub>ClNO<sup>+</sup> requires: 282.0680, Found: 282.0683.



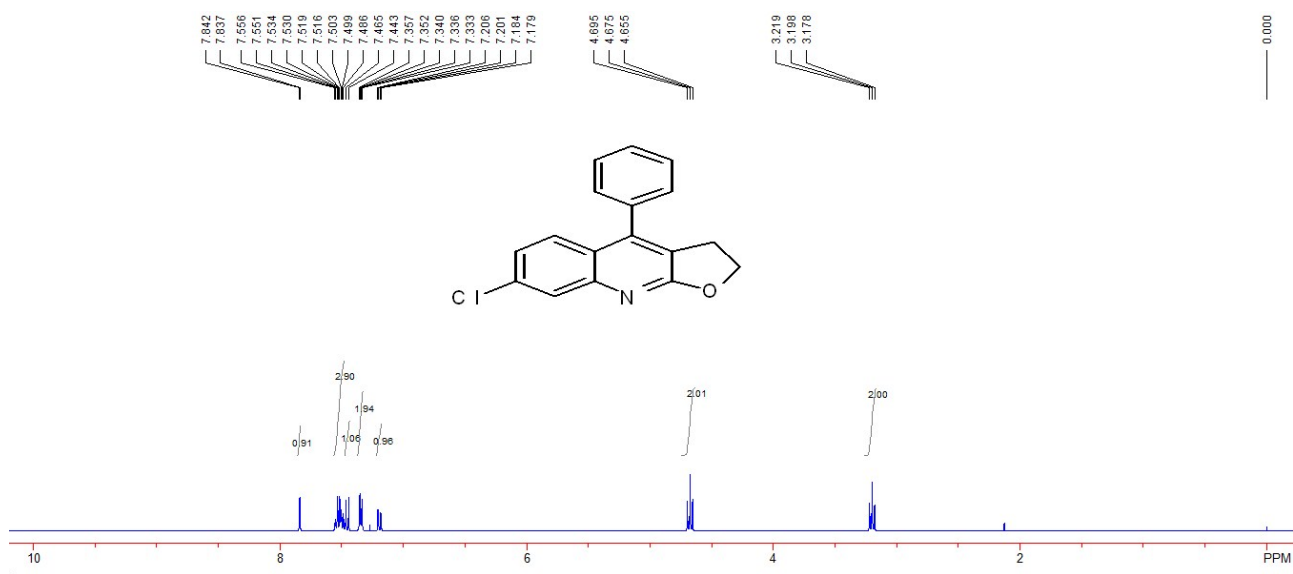


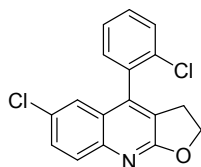
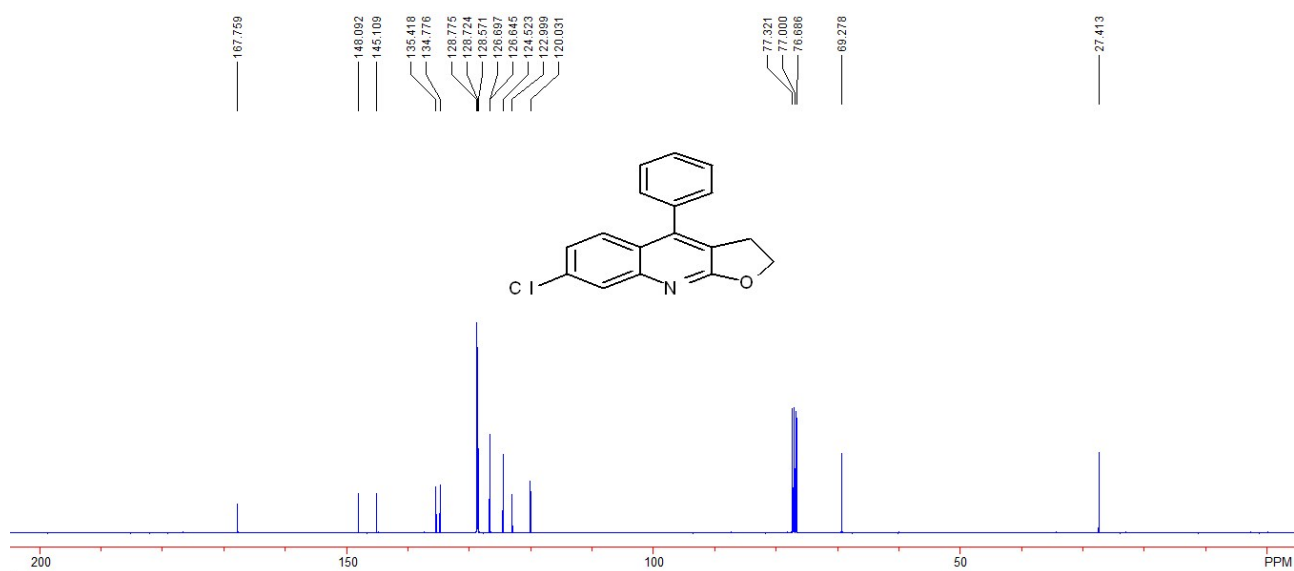
**Compound 2l:** 160 mg, 96%, A white solid, m.p. 144-146 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 3055, 2923, 1621, 1446, 1419, 1325, 1103, 1034, 1005, 827, 724, 706 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 3.15 (td, 2H, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.4 Hz), 3.69 (s, 3H), 4.60 (td, 2H, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.4 Hz), 6.90 (d, 1H, *J* = 0.8 Hz), 7.20-7.24 (m, 1H), 7.36 (dd, 2H, *J*<sub>1</sub> = 6.4 Hz, *J*<sub>2</sub> = 1.6 Hz), 7.46-7.53 (m, 3H), 7.78 (dd, 1H, *J*<sub>1</sub> = 6.4 Hz, *J*<sub>2</sub> = 1.6 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 27.7, 55.3, 68.9, 105.4, 119.6, 119.9, 125.0, 128.3, 128.7, 136.0, 142.6, 144.1, 155.9, 165.8; MS (ESI) *m/z*: 278.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup> requires: 278.1176, Found: 278.1178.



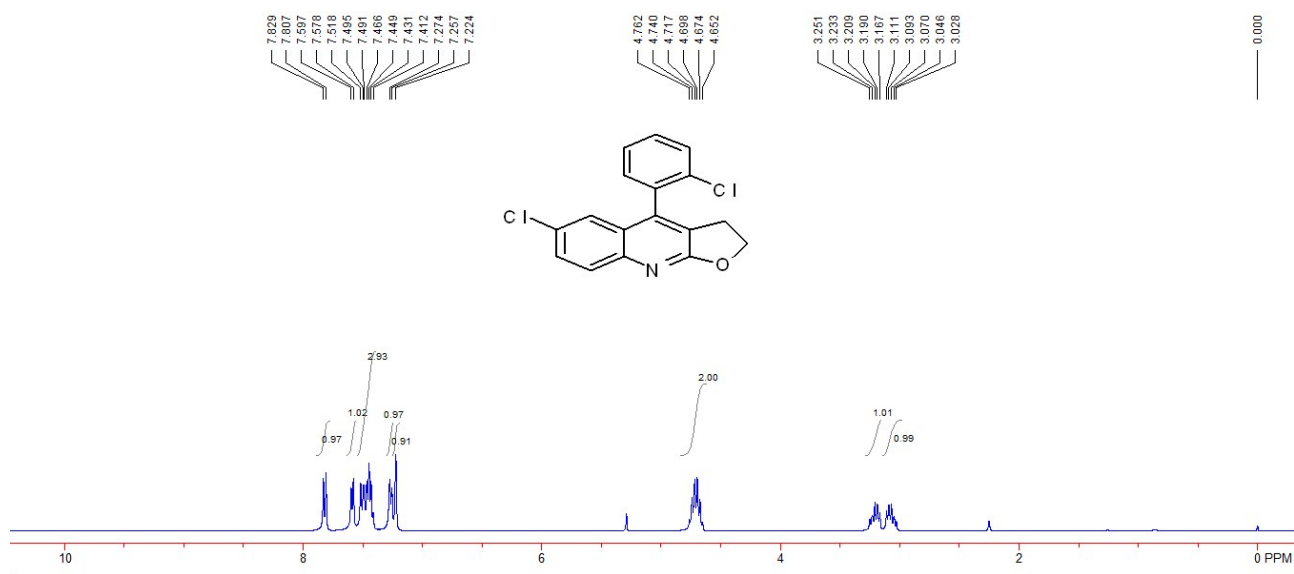


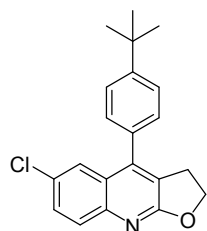
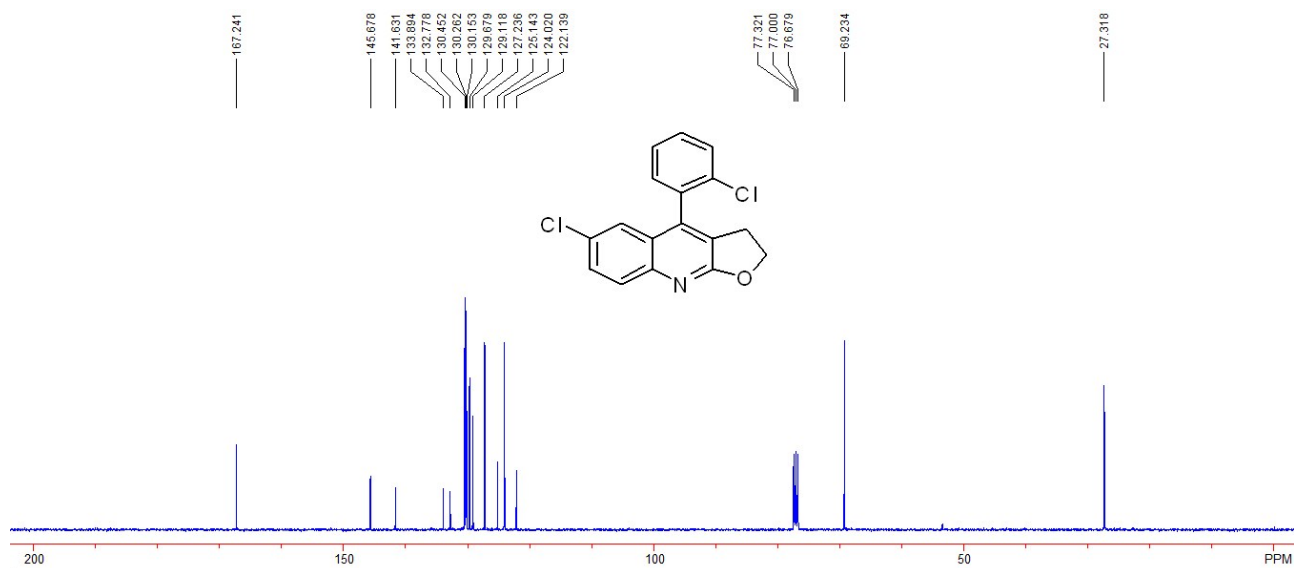
**Compound 2m** 166 mg, 98%, A white solid, m.p. 168-170 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3047, 2924, 1622, 1584, 1435, 1401, 1313, 1204, 1006, 884, 761, 702 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.20 (t, 2H,  $J$  = 8.0 Hz), 4.68 (t, 2H,  $J$  = 8.0 Hz), 7.18 (dd, 1H,  $J_1$  = 8.8 Hz,  $J_2$  = 2.0 Hz), 7.33-7.36 (m, 2H), 7.45 (d, 1H,  $J$  = 8.4 Hz), 7.49-7.56 (m, 3H), 7.84 (d, 1H,  $J$  = 2.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  27.4, 69.3, 120.0, 123.0, 124.5, 126.6, 126.7, 128.6, 128.7, 128.8, 134.8, 135.4, 145.1, 148.1, 167.8; MS (ESI)  $m/z$ : 282.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>13</sub>ClNO<sup>+</sup> requires: 282.0680, Found: 282.0682.



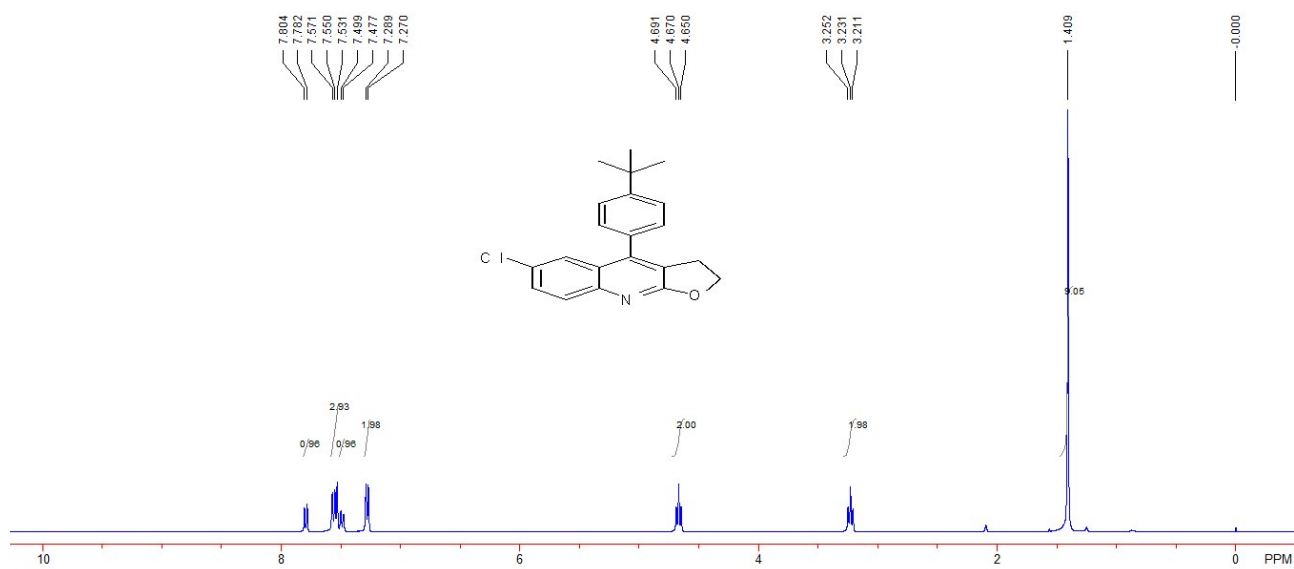


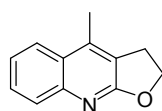
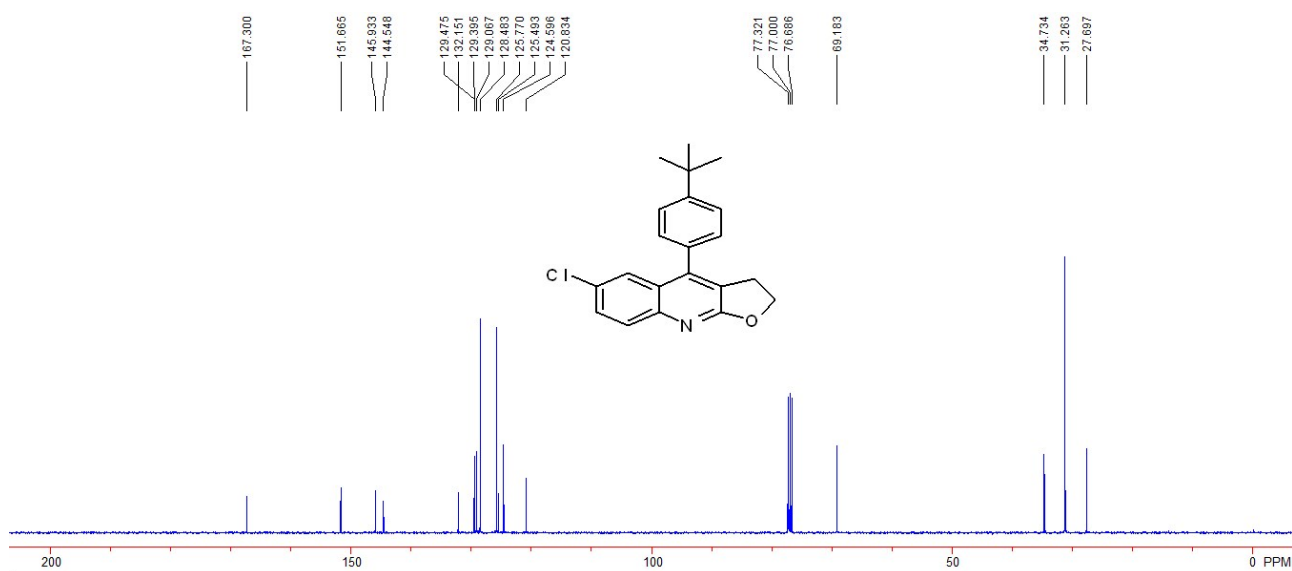
**Compound 2n:** 159 mg, 84%, A white solid, m.p. 195-197 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2972, 2908, 1630, 1511, 1473, 1417, 1220, 1111, 1006, 944, 825, 733 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.03-3.11 (m, 1H), 3.17-3.25 (m, 1H), 4.65-4.76 (m, 2H), 7.22 (s, 1H), 7.27 (d, 1H,  $J$  = 6.8 Hz), 7.41-7.52 (m, 3H), 7.59 (d, 1H,  $J$  = 7.6 Hz), 7.82 (d, 1H,  $J$  = 8.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  27.3, 69.2, 122.1, 124.0, 125.1, 127.2, 129.1, 129.7, 130.2, 130.3, 130.5, 132.8, 133.9, 141.6, 145.7, 167.2; MS (ESI)  $m/z$ : 316.0 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>12</sub>Cl<sub>2</sub>NO<sup>+</sup> requires: 316.0290, Found: 316.0293.



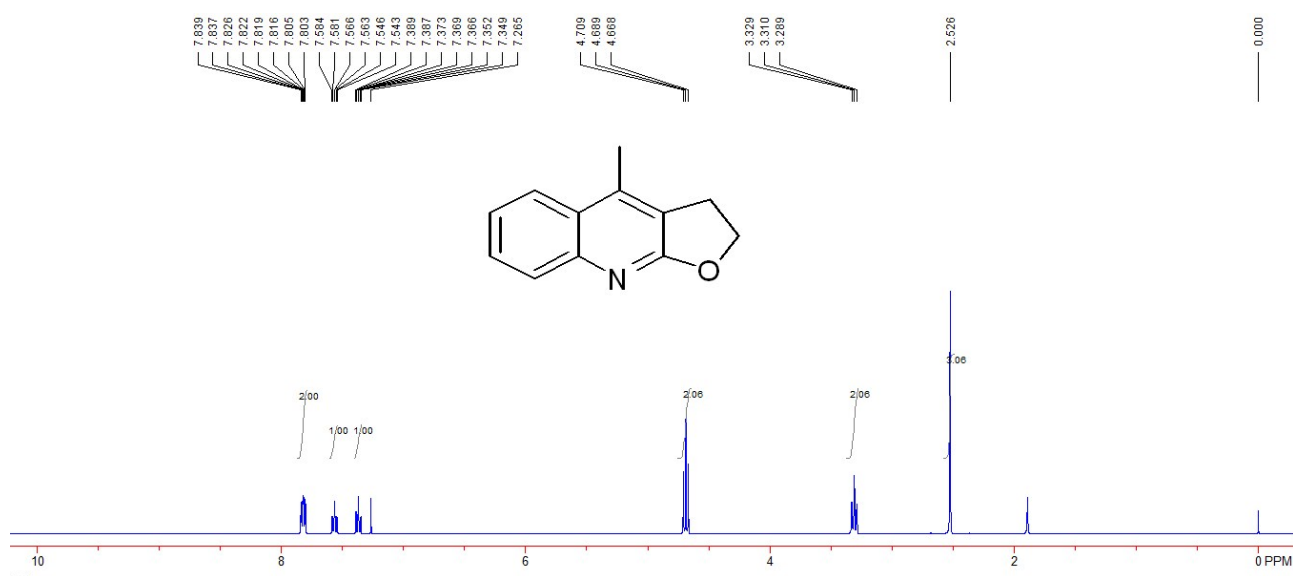


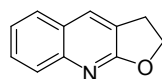
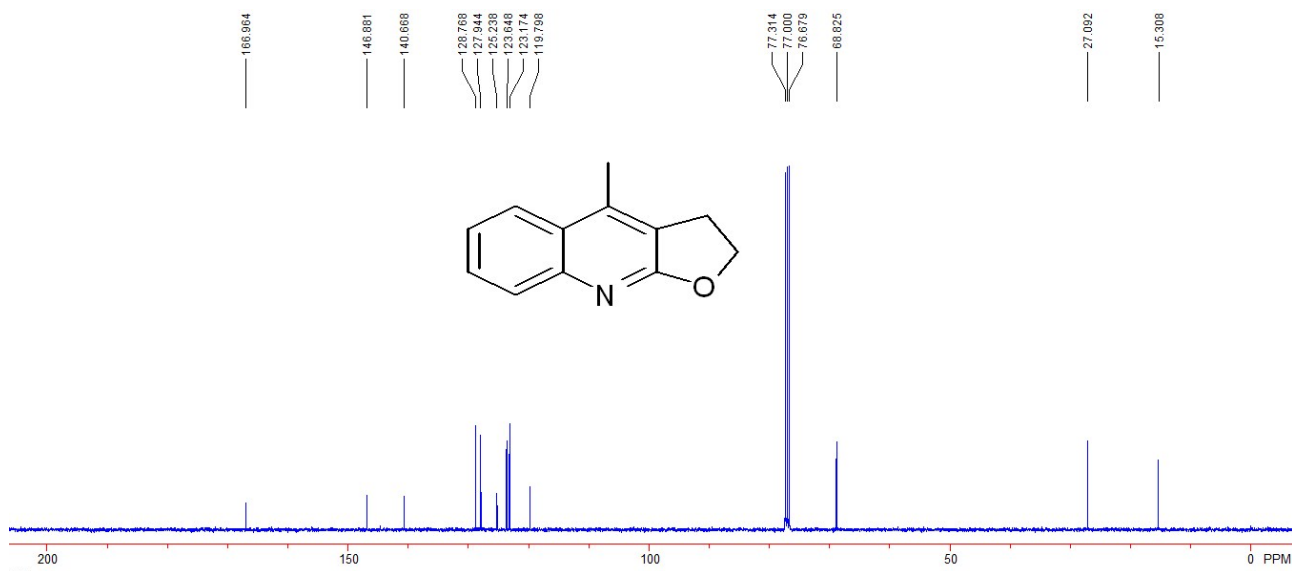
**Compound 2o:** 193 mg, 95%, A white solid, m.p. 182-184 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2959, 2865, 1623, 1586, 1416, 1391, 1322, 1255, 1105, 945, 825, 701 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.41 (s, 9H), 3.23 (t, 2H,  $J$  = 8.4 Hz), 4.67 (t, 2H,  $J$  = 8.4 Hz), 7.28 (d, 2H,  $J$  = 7.6 Hz), 7.49 (d, 1H,  $J$  = 8.8 Hz), 7.55 (t, 3H,  $J$  = 7.6 Hz), 7.79 (d, 1H,  $J$  = 8.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  27.7, 31.3, 34.7, 69.2, 120.8, 124.6, 125.5, 125.8, 128.5, 129.1, 129.4, 129.5, 132.2, 144.5, 145.9, 151.7, 167.3; MS (ESI)  $m/z$ : 338.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>21</sub>H<sub>21</sub>ClNO<sup>+</sup> requires: 338.1306, Found: 338.1308.



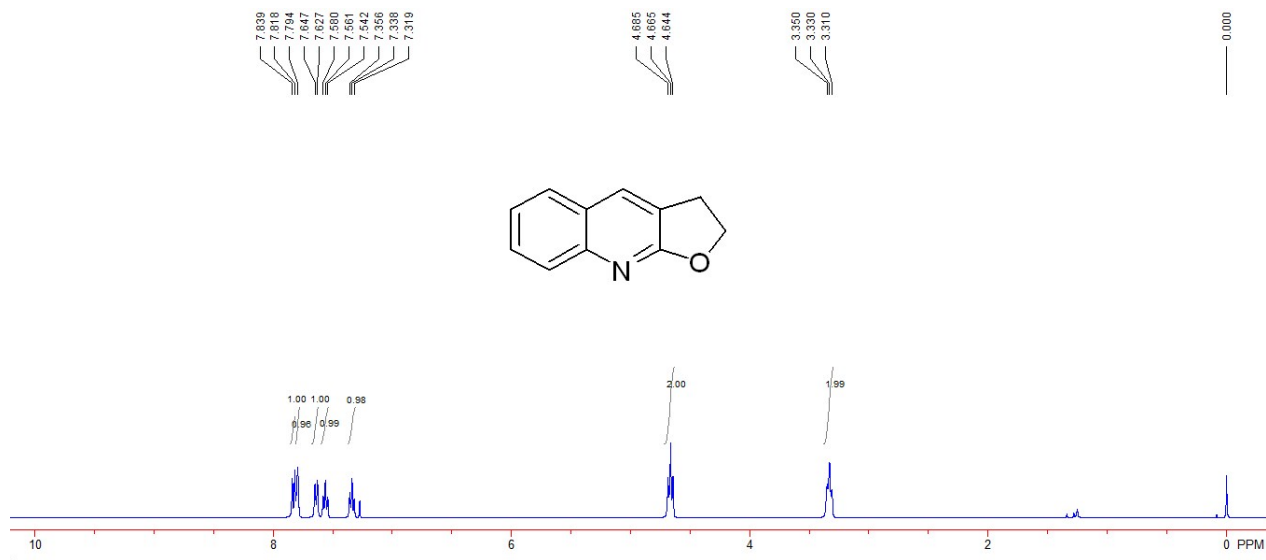


**Compound 2p:** 108 mg, 97%, A white solid, m.p. 155-157 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2968, 2908, 1633, 1588, 1476, 1397, 1317, 1229, 1018, 768, 705 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 2.53 (s, 3H), 3.31 (t, 2H, *J* = 8.0 Hz), 4.69 (t, 2H, *J* = 8.0 Hz), 7.35-7.39 (m, 1H), 7.56 (td, 1H, *J*<sub>1</sub> = 7.2 Hz, *J*<sub>2</sub> = 1.2 Hz), 7.80-7.84 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 15.3, 27.1, 68.8, 119.8, 123.2, 123.6, 125.2, 127.9, 128.8, 140.7, 146.9, 167.0; MS (ESI) *m/z*: 186.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>12</sub>H<sub>12</sub>NO<sup>+</sup> requires: 186.0913, Found: 186.0915.

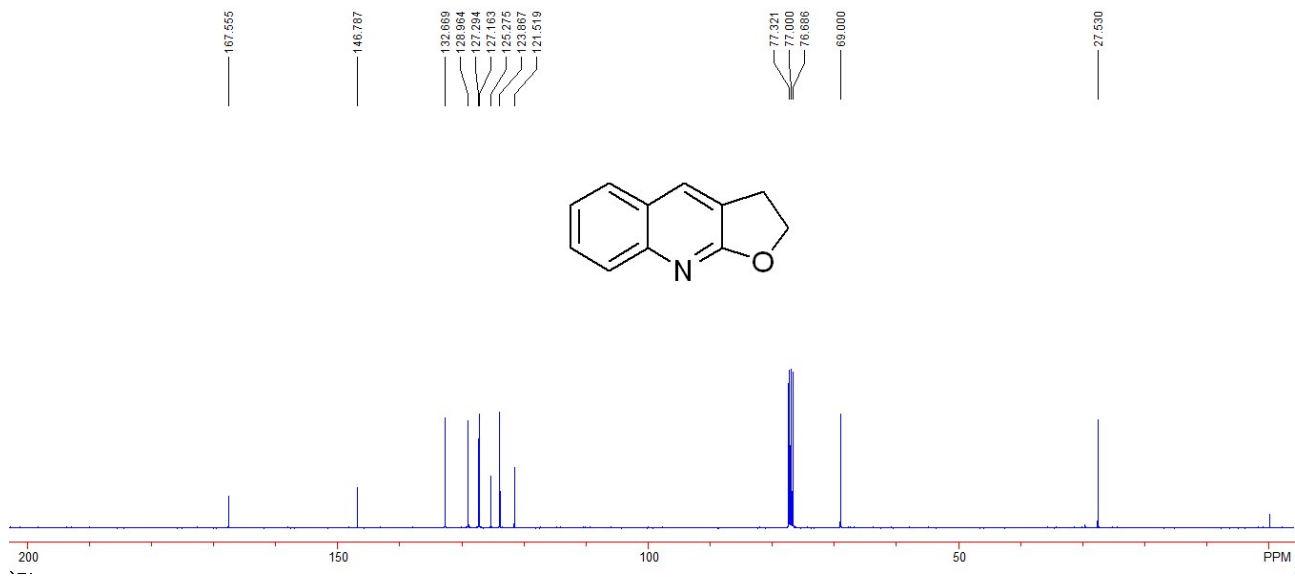




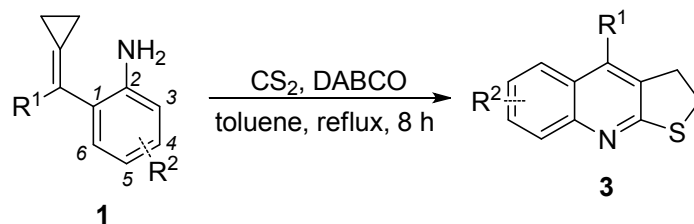
**Compound 2q:** 79 mg, 77%, A white solid, m.p. 150-152 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2972, 2914, 1636, 1586, 1475, 1420, 1311, 1247, 1003, 954, 751 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.33 (t, 2H, *J* = 8.0 Hz), 4.67 (t, 2H, *J* = 8.0 Hz), 7.34 (t, 1H, *J* = 7.6 Hz), 7.56 (t, 1H, *J* = 7.6 Hz), 7.64 (d, 1H, *J* = 8.0 Hz), 7.79 (s, 1H), 7.83 (d, 1H, *J* = 8.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  27.5, 69.0, 121.5, 123.9, 125.3, 127.2, 127.3, 129.0, 132.7, 146.8, 167.6; MS (ESI) *m/z*: 172.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>11</sub>H<sub>10</sub>NO<sup>+</sup> requires: 172.0757, Found: 172.0759.





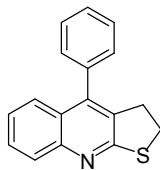


### General procedure for the synthesis of products 3

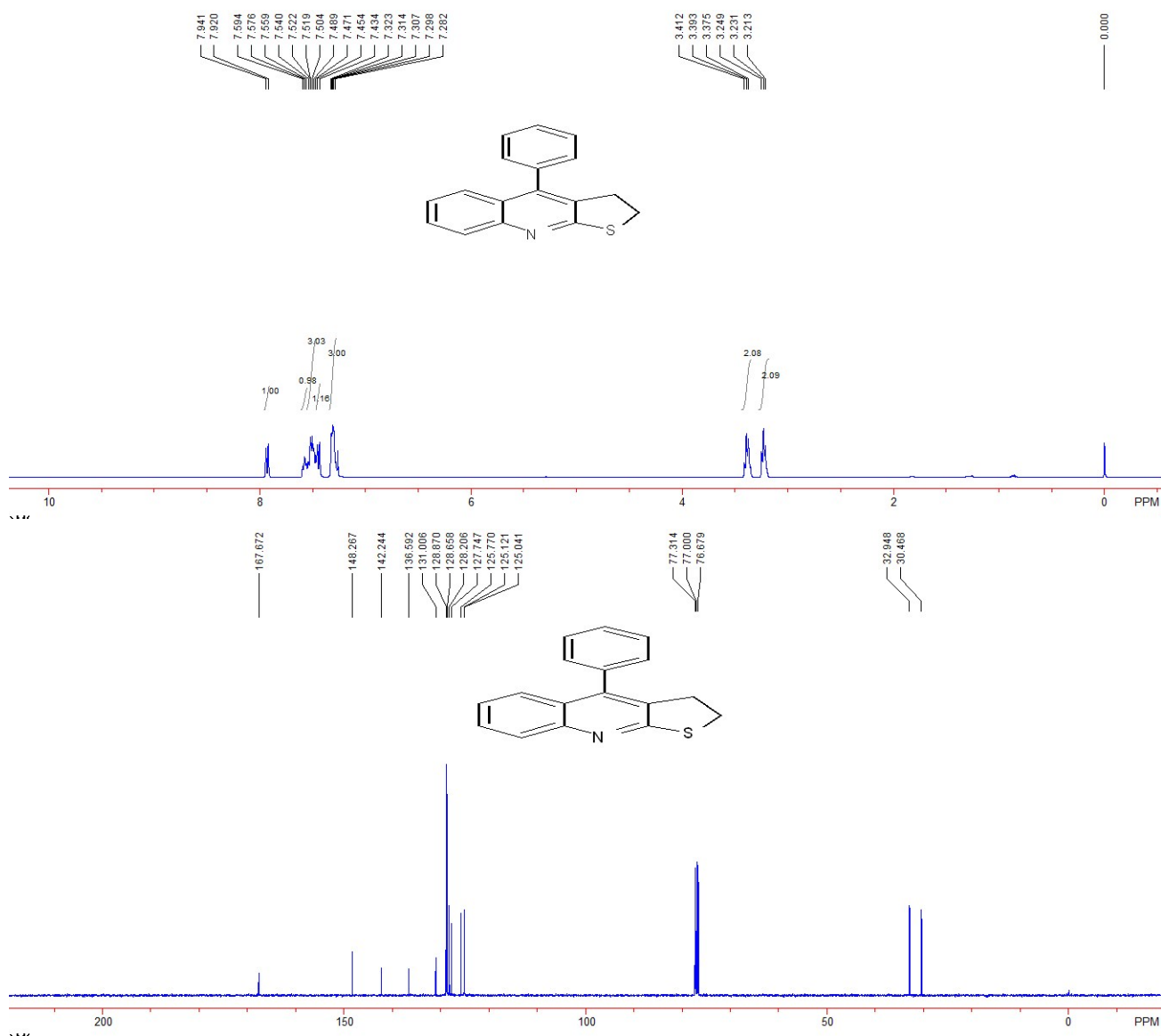


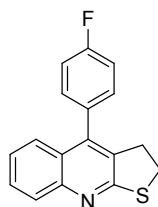
**1** (0.5 mmol) and DABCO (2.0 mmol) were dissolved in toluene (5.0 mL), then  $\text{CS}_2$  (0.12 mL) was added dropwise and the resulting reaction mixture was stirred at 80 °C. The reaction was stopped after 8 h and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product **3** in excellent yield.

### Spectroscopic data for products 3

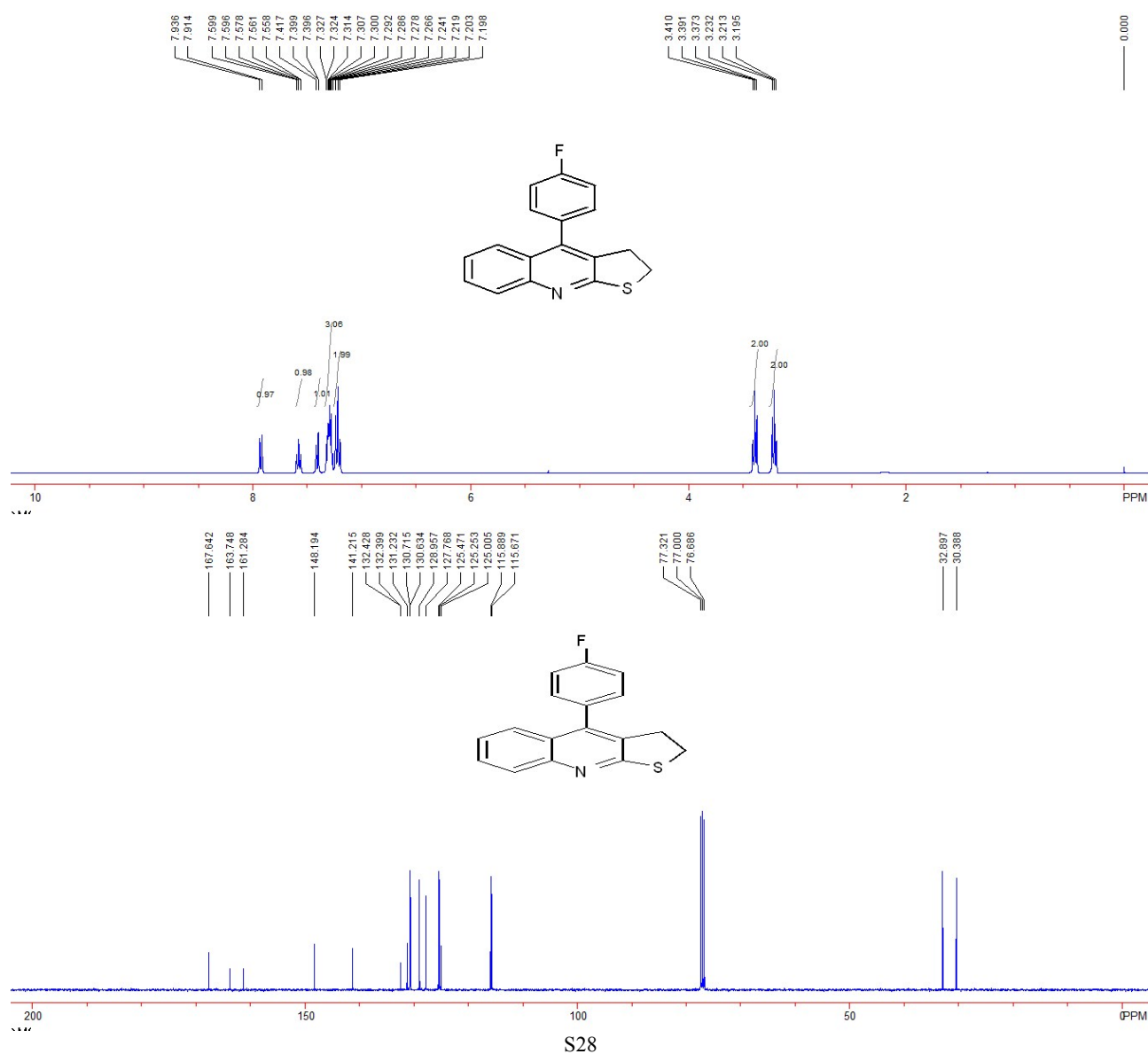


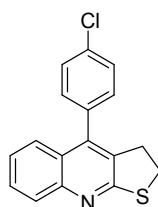
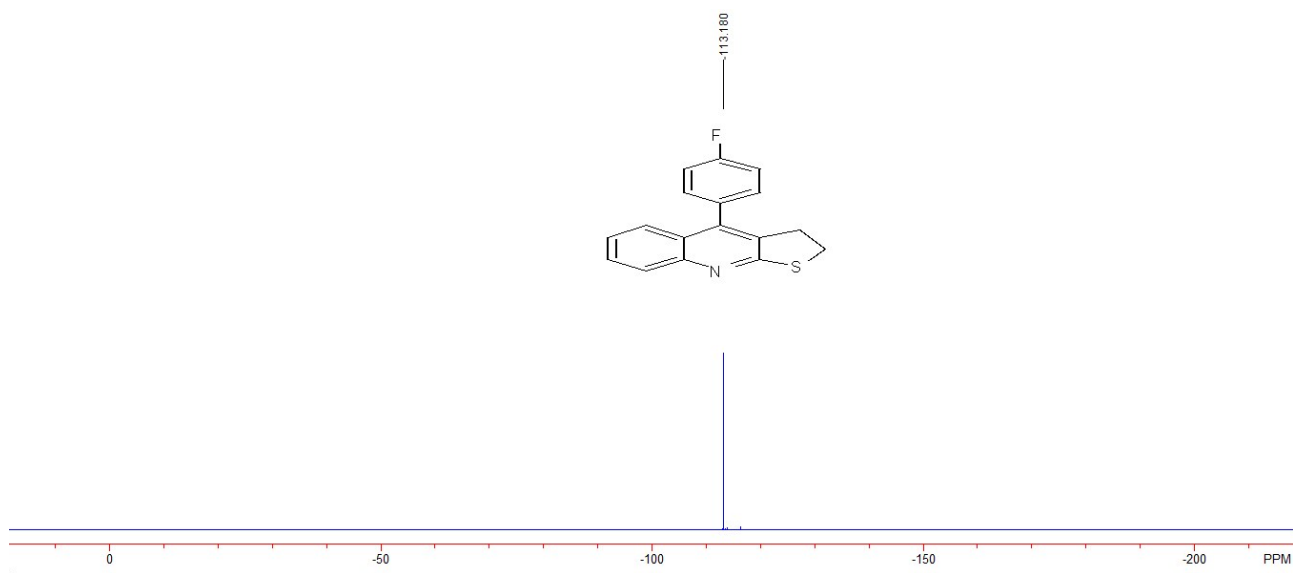
**Compound 3a:** 131 mg, 99%, A white solid, m.p. 152-154 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3043, 2919, 1584, 1556, 1488, 1391, 1299, 1072, 753, 705 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.23 (t, 2H,  $J = 7.2$  Hz), 3.39 (t, 2H,  $J = 7.2$  Hz), 7.28-7.32 (m, 3H), 7.43-7.59 (m, 5H), 7.93 (d, 1H,  $J = 8.4$  Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  30.5, 32.9, 125.0, 125.1, 125.8, 127.7, 128.2, 128.7, 128.9, 131.0, 136.6, 142.2, 148.3, 167.7; MS (ESI)  $m/z$ : 264.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>14</sub>NS<sup>+</sup> requires: 264.0841, Found: 264.0843.



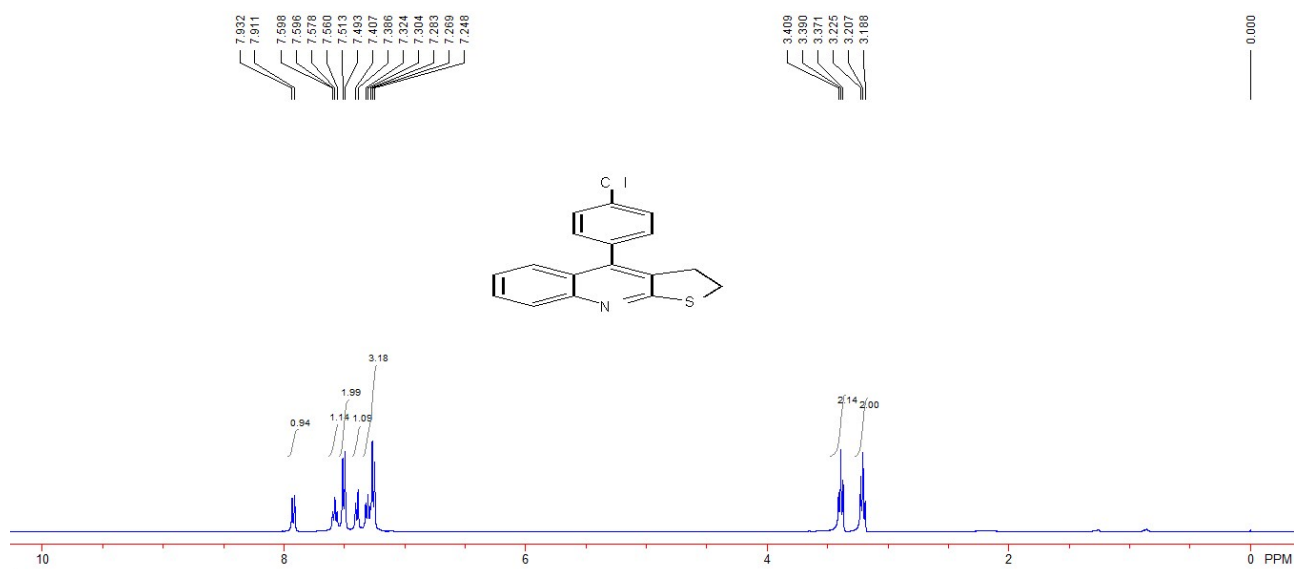


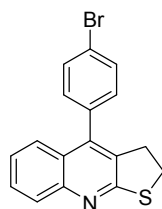
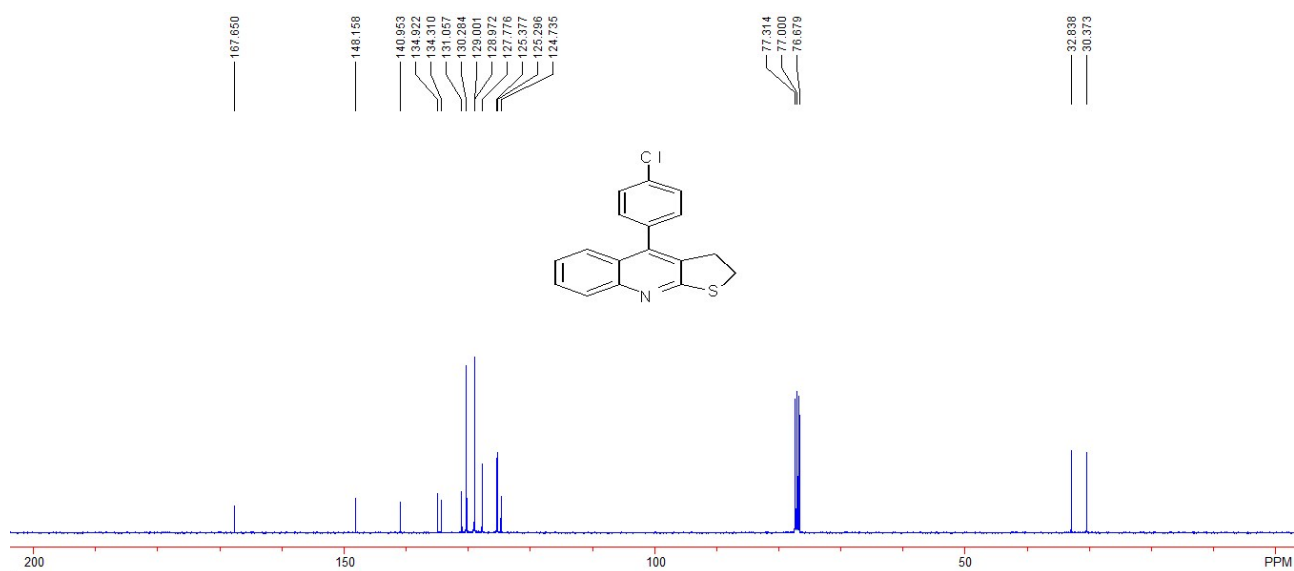
**Compound 3b:** 123 mg, 87%, A white solid, m.p. 185-187 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3052, 2952, 1595, 1508, 1219, 1157, 1093, 852, 818, 783, 765 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.21 (t, 2H,  $J$  = 7.2 Hz), 3.39 (t, 2H,  $J$  = 7.2 Hz), 7.20-7.27 (m, 2H), 7.28-7.33 (m, 3H), 7.41 (dd, 1H,  $J_1$  = 8.0 Hz,  $J_2$  = 1.2 Hz), 7.58 (td, 1H,  $J_1$  = 8.0 Hz,  $J_2$  = 1.2 Hz), 7.93 (d, 1H,  $J$  = 8.0 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  30.4, 32.9, 115.8 (d,  $J_{C-F}$  = 21.8 Hz), 125.0, 125.3, 125.5, 127.8, 129.0, 130.7 (d,  $J_{C-F}$  = 8.1 Hz), 131.2, 132.4 (d,  $J_{C-F}$  = 2.9 Hz), 141.2, 148.2, 162.5 (d,  $J_{C-F}$  = 246.4 Hz), 167.6; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, CFCl<sub>3</sub>):  $\delta$  -113.2 (s); MS (ESI)  $m/z$ : 282.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>13</sub>FNS<sup>+</sup> requires: 282.0747, Found: 282.0749.



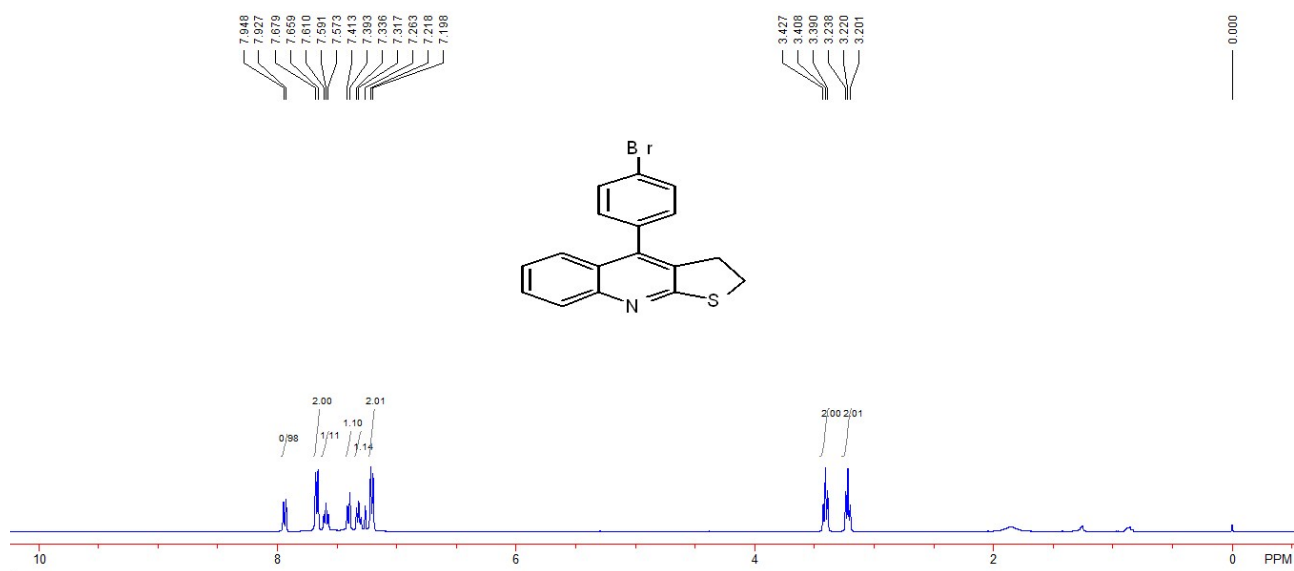


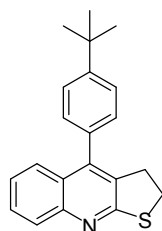
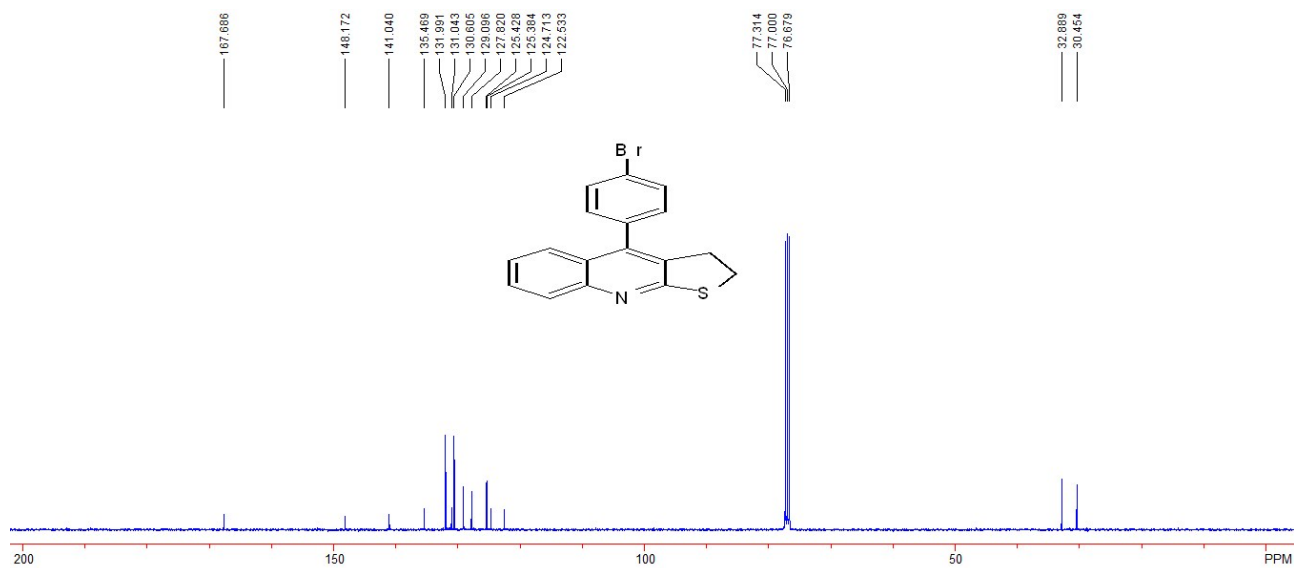
**Compound 3c:** 137 mg, 92%, A white solid, m.p. 180-182 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 3054, 2918, 1585, 1486, 1297, 1088, 1043, 1014, 805, 763 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 3.21 (t, 2H, *J* = 7.6 Hz), 3.39 (t, 2H, *J* = 7.6 Hz), 7.25-7.32 (m, 3H), 7.40 (d, 1H, *J* = 8.4 Hz), 7.50 (d, 2H, *J* = 8.0 Hz), 7.59 (td, 1H, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 0.8 Hz), 7.92 (d, 1H, *J* = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 30.4, 32.8, 124.7, 125.3, 125.4, 127.8, 128.97, 129.00, 130.3, 131.1, 134.3, 134.9, 141.0, 148.2, 167.7; MS (ESI) *m/z*: 298.0 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>13</sub>ClNS<sup>+</sup> requires: 298.0452, Found: 298.0454.



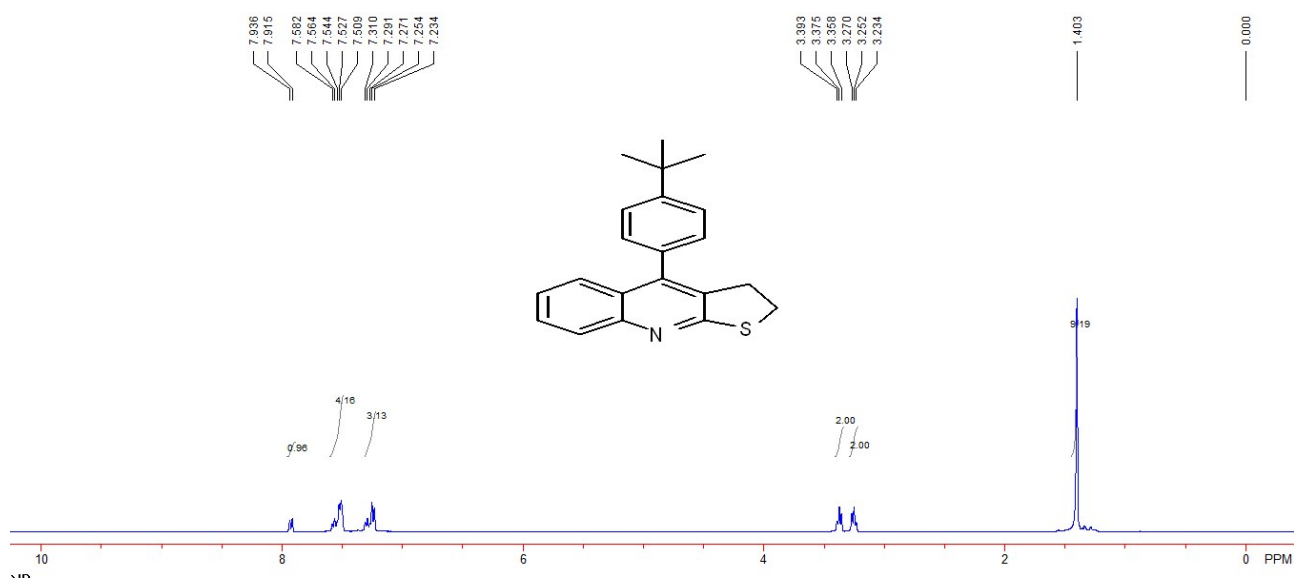


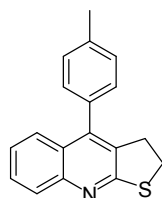
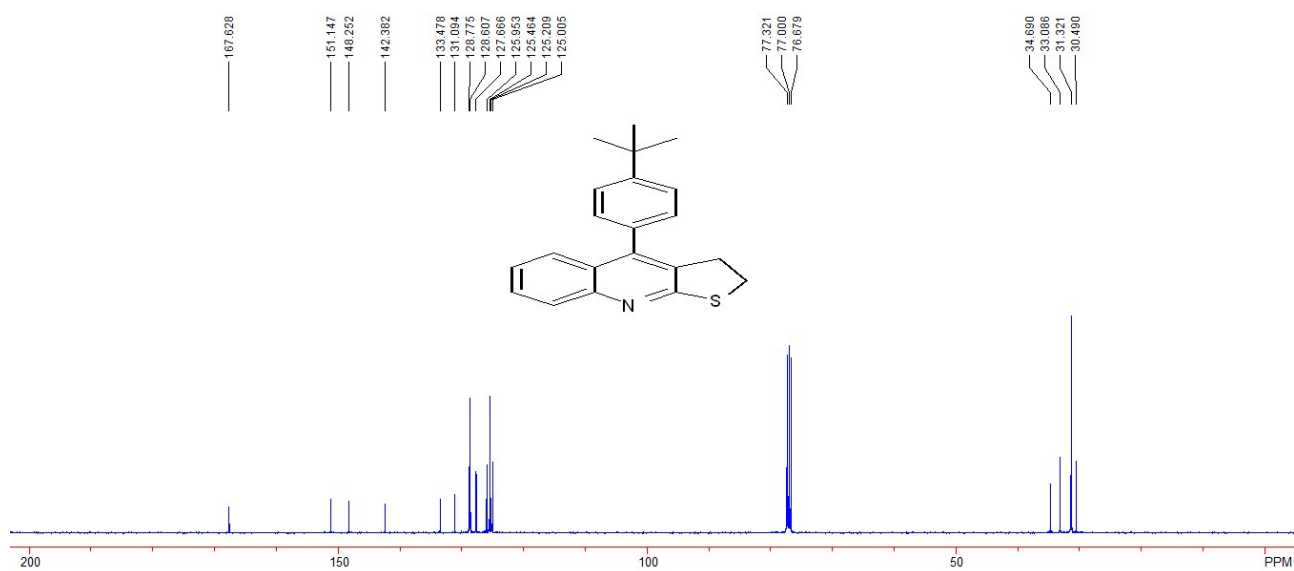
**Compound 3d:** 154 mg, 90%, A white solid, m.p. 220-222 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 3055, 2919, 1583, 1558, 1483, 1303, 1068, 1041, 801, 762 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 3.22 (t, 2H, *J* = 7.6 Hz), 3.41 (t, 2H, *J* = 7.6 Hz), 7.21 (d, 2H, *J* = 8.0 Hz), 7.32 (t, 1H, *J* = 7.6 Hz), 7.40 (d, 1H, *J* = 8.0 Hz), 7.59 (t, 1H, *J* = 7.6 Hz), 7.67 (d, 2H, *J* = 8.0 Hz), 7.94 (d, 1H, *J* = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 30.5, 32.9, 122.5, 124.7, 125.38, 125.43, 127.8, 129.1, 130.6, 131.0, 132.0, 135.5, 141.0, 148.2, 167.7; MS (ESI) *m/z*: 342.0 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>13</sub>BrNS<sup>+</sup> requires: 341.9947, Found: 341.9949.



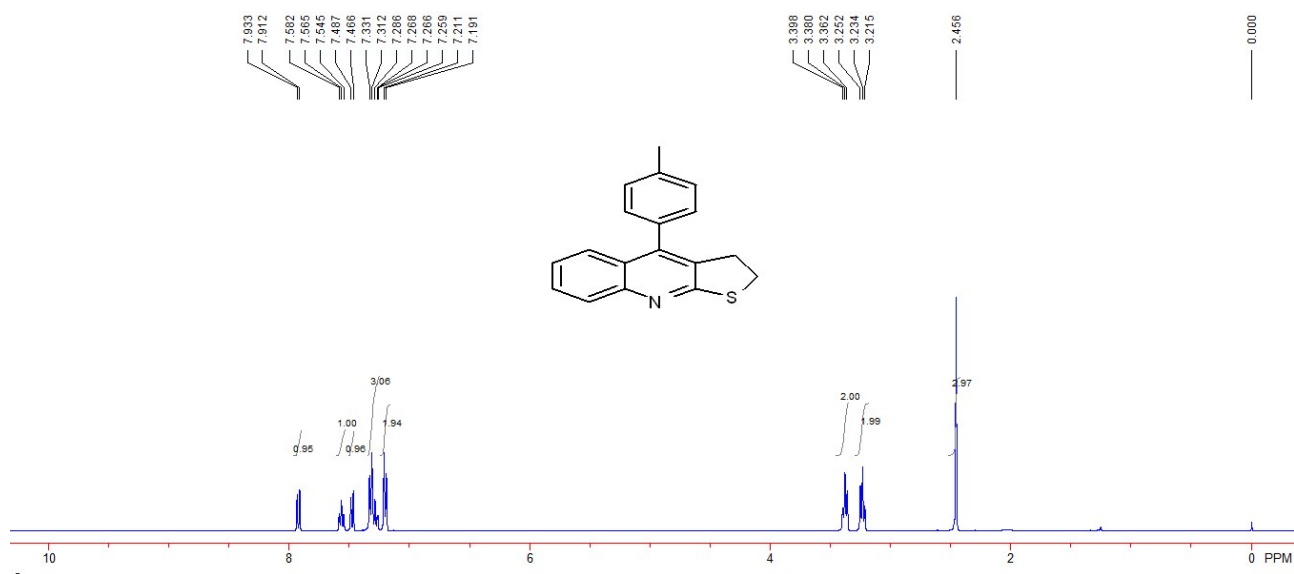


**Compound 3e:** 146 mg, 91%, A white solid, m.p. 229-231 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2923, 2853, 1585, 1493, 1301, 1184, 1025, 808, 769 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 1.40 (s, 9H), 3.25 (t, 2H, *J* = 7.2 Hz), 3.38 (t, 2H, *J* = 7.2 Hz), 7.23-7.31 (m, 3H), 7.51-7.58 (m, 4H), 7.93 (d, 1H, *J* = 7.6 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 30.5, 31.3, 33.1, 34.7, 125.0, 125.2, 125.5, 126.0, 127.7, 128.6, 128.8, 131.1, 133.5, 142.4, 148.3, 151.1, 167.6; MS (ESI) *m/z*: 320.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>21</sub>H<sub>22</sub>NS<sup>+</sup> requires: 320.1467, Found: 320.1469.

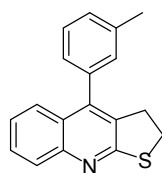
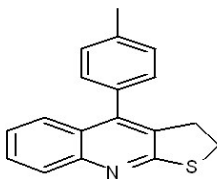
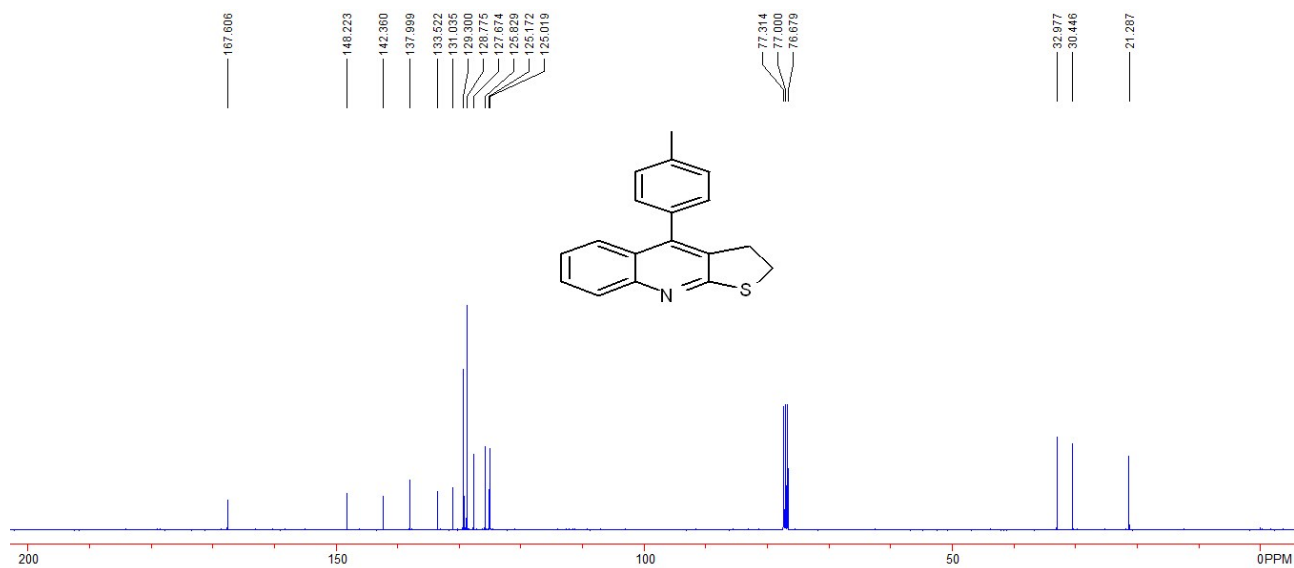




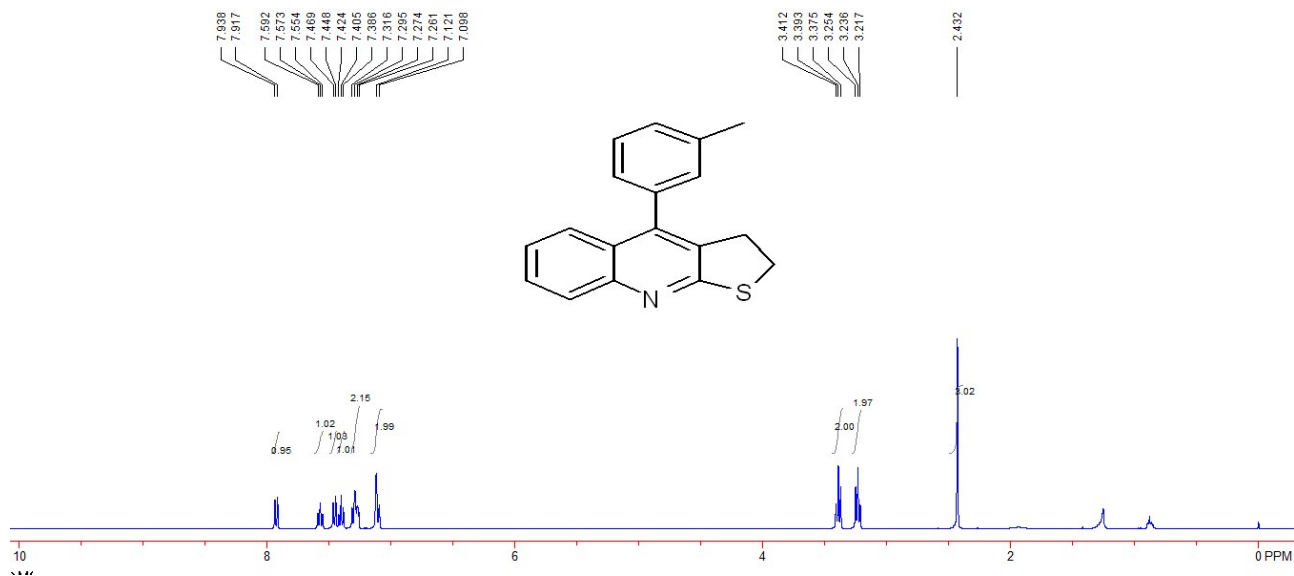
**Compound 3f:** 125 mg, 90%, A white solid, m.p. 173-175 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 3059, 2917, 1584, 1553, 1375, 1325, 1043, 806, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 2.46 (s, 3H), 3.23 (t, 2H, *J* = 7.2 Hz), 3.38 (t, 2H, *J* = 7.2 Hz), 7.20 (d, 2H, *J* = 8.0 Hz), 7.26-7.33 (m, 3H), 7.48 (d, 1H, *J* = 8.4 Hz), 7.57 (t, 1H, *J* = 8.0 Hz), 7.92 (d, 1H, *J* = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 21.3, 30.4, 33.0, 125.0, 125.2, 125.8, 127.7, 128.8, 129.3, 131.0, 133.5, 138.0, 142.4, 148.2, 167.6; MS (ESI) *m/z*: 278.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NS<sup>+</sup> requires: 278.0998, Found: 278.1001.

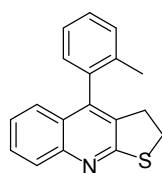
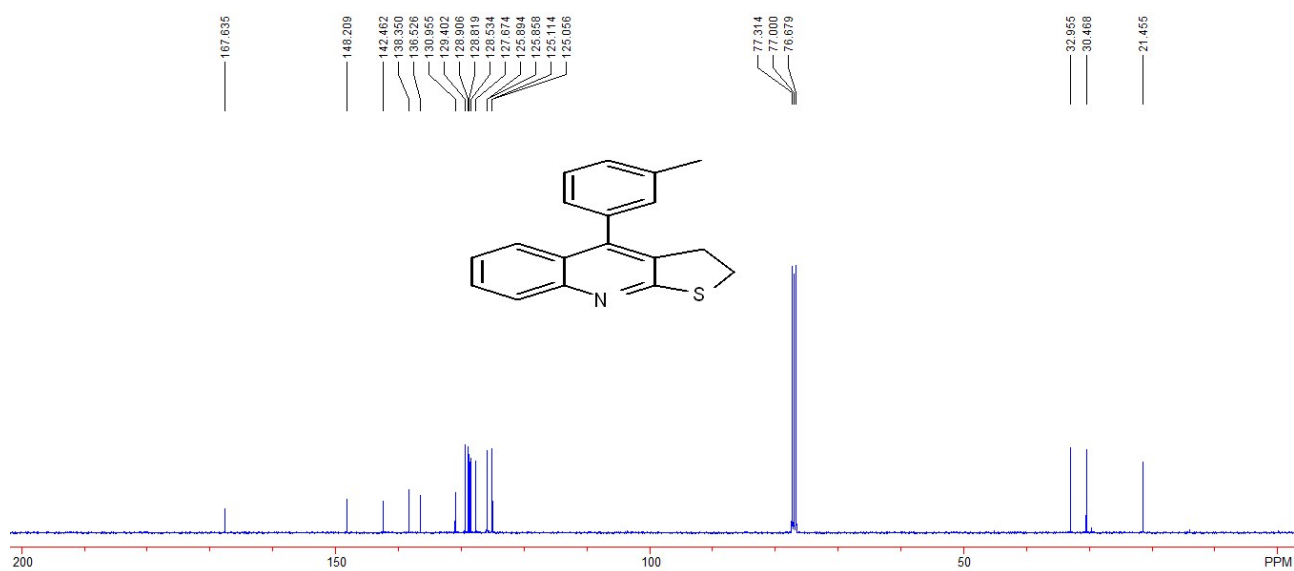




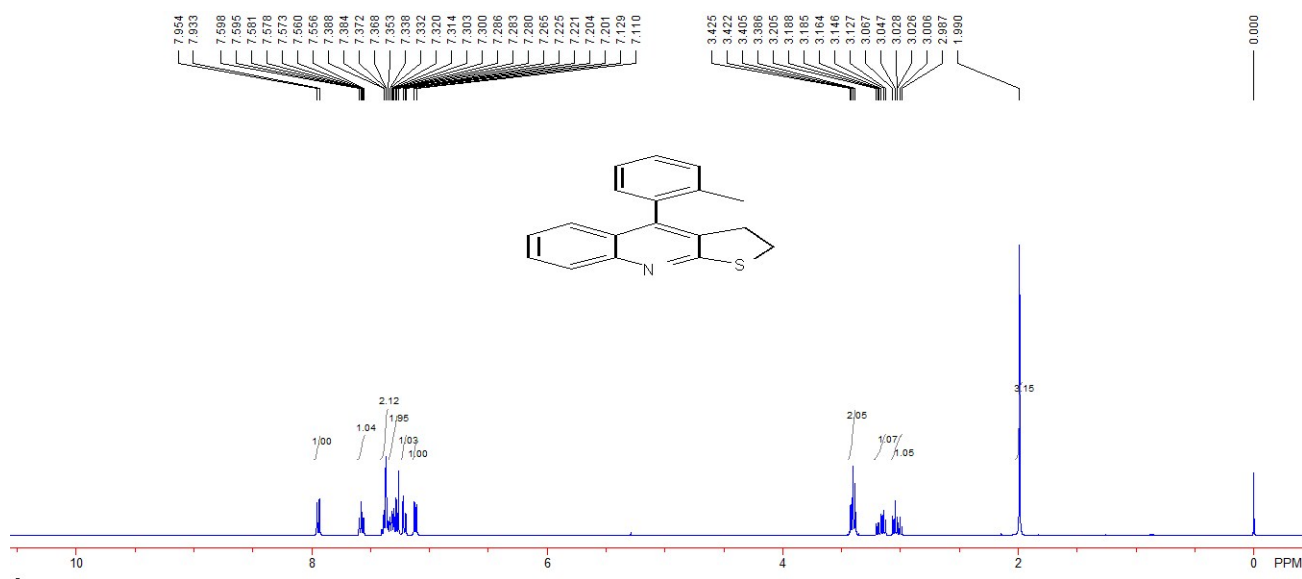


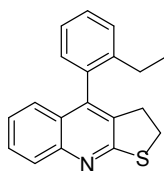
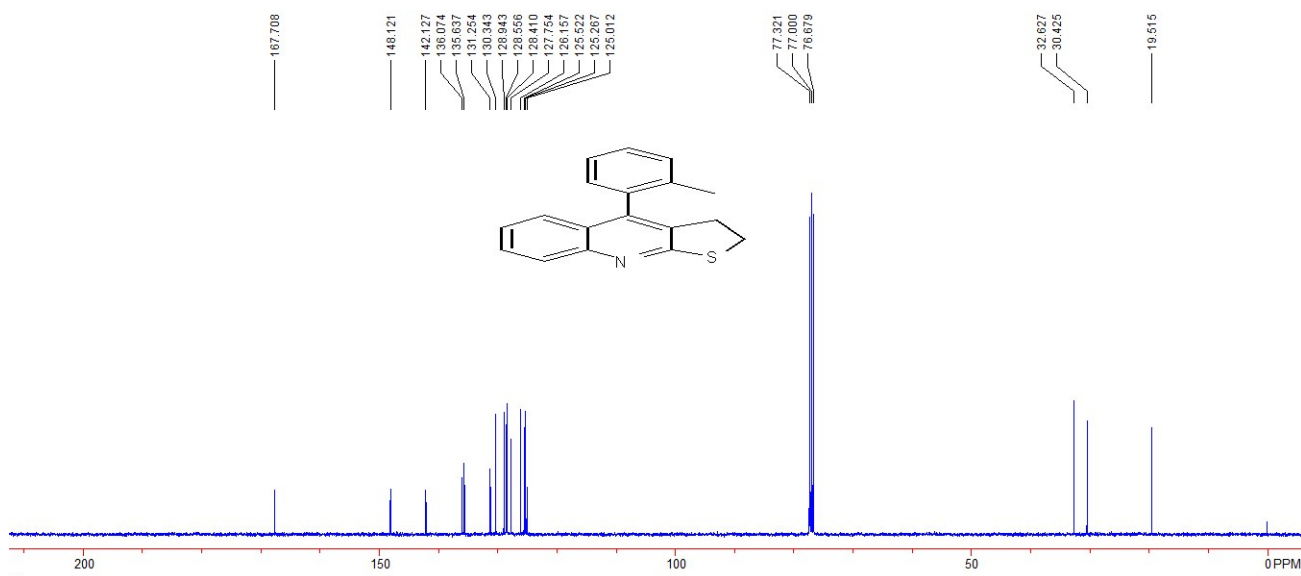
**Compound 3g:** 135 mg, 97%, A white solid, m.p. 180-182 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3052, 2925, 1588, 1552, 1376, 1320, 1156, 808, 758 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.43 (s, 3H), 3.24 (t, 2H,  $J = 7.6$  Hz), 3.39 (t, 2H,  $J = 7.6$  Hz), 7.10-7.12 (m, 2H), 7.26-7.32 (m, 2H), 7.41 (t, 1H,  $J = 7.6$  Hz), 7.46 (d, 1H,  $J = 8.4$  Hz), 7.57 (t, 1H,  $J = 7.6$  Hz), 7.93 (d, 1H,  $J = 8.4$  Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  21.5, 30.5, 33.0, 125.06, 125.11, 125.86, 125.89, 127.7, 128.5, 128.8, 128.9, 129.4, 131.0, 136.5, 138.4, 142.5, 148.2, 167.6; MS (ESI)  $m/z$ : 278.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NS<sup>+</sup> requires: 278.0998, Found: 278.1001.



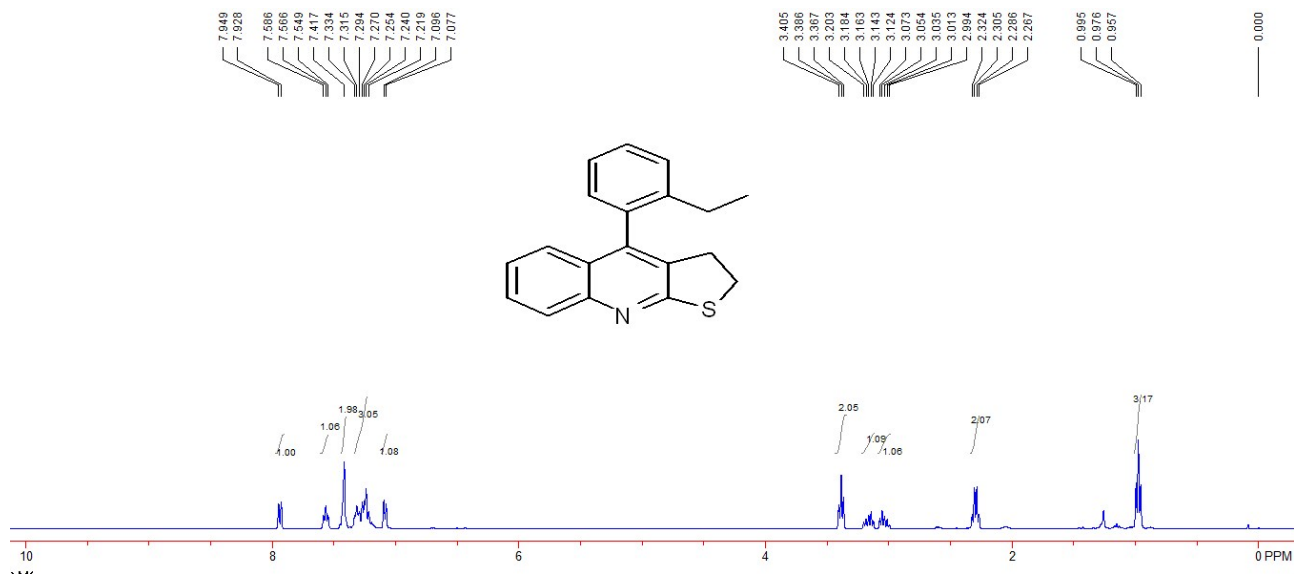


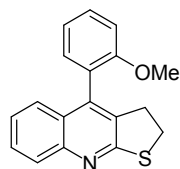
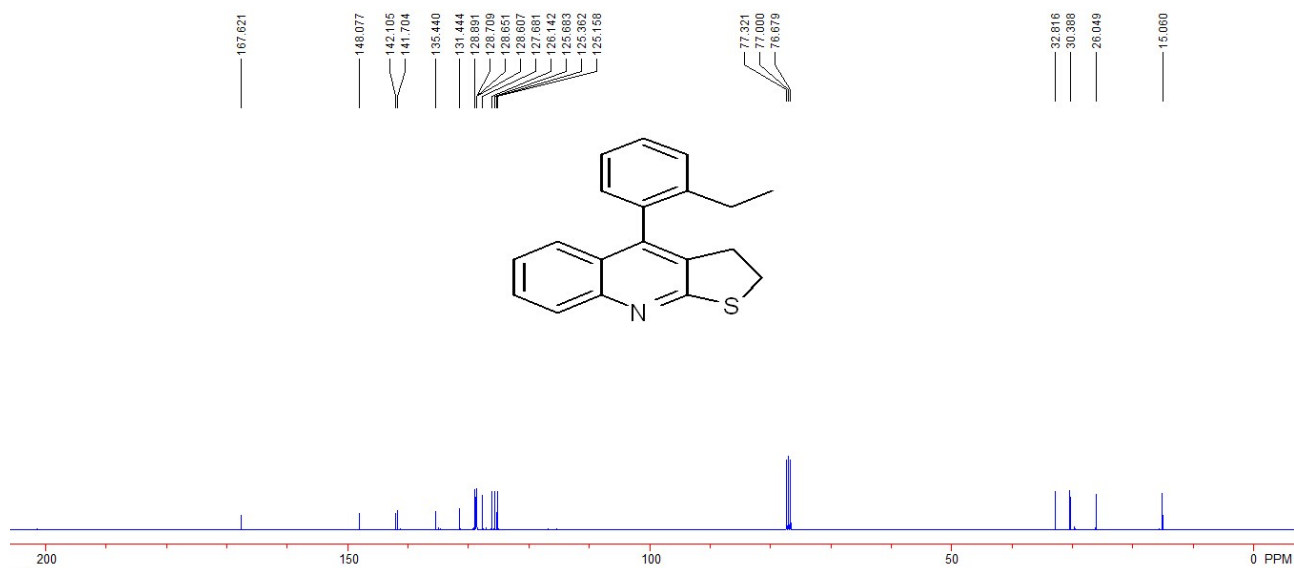
**Compound 3h:** 132 mg, 95%, A white solid, m.p. 167-169 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3065, 2925, 1575, 1548, 1366, 1318, 1040, 812, 765 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.99 (s, 3H), 2.99-3.07 (m, 1H), 3.13-3.21 (m, 1H), 3.39-3.43 (m, 2H), 7.12 (d, 1H,  $J$  = 7.6 Hz), 7.21 (dd, 1H,  $J_1$  = 8.0 Hz,  $J_2$  = 1.2 Hz), 7.27-7.34 (m, 2H), 7.35-7.39 (m, 2H), 7.56-7.60 (m, 1H), 7.94 (d, 1H,  $J$  = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  19.5, 30.4, 32.6, 125.0, 125.3, 125.5, 126.2, 127.8, 128.4, 128.6, 128.9, 130.3, 131.3, 135.6, 136.1, 142.1, 148.1, 167.7; MS (ESI)  $m/z$ : 278.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NS<sup>+</sup> requires: 278.0998, Found: 278.1001.



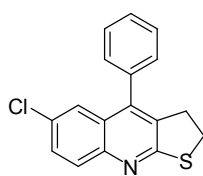
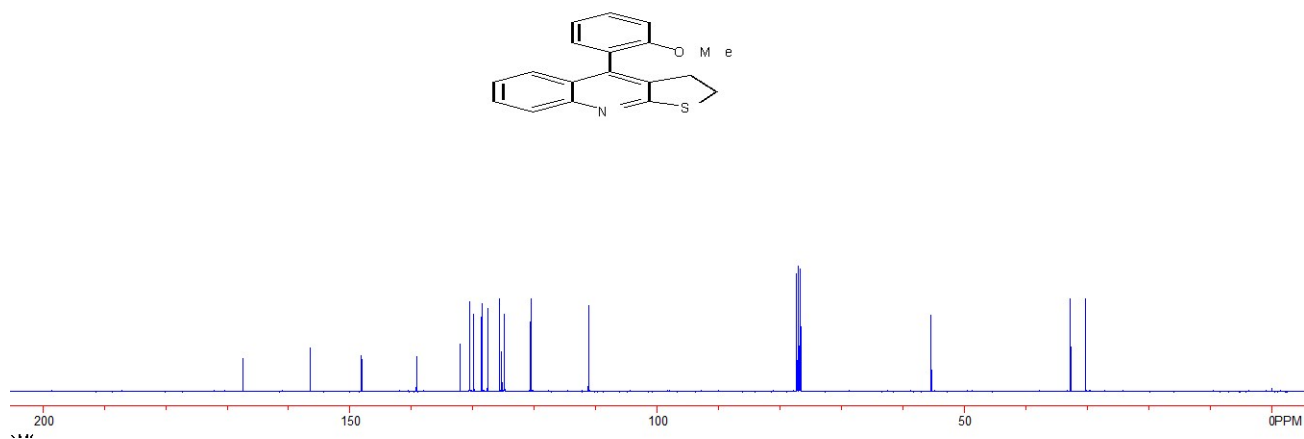
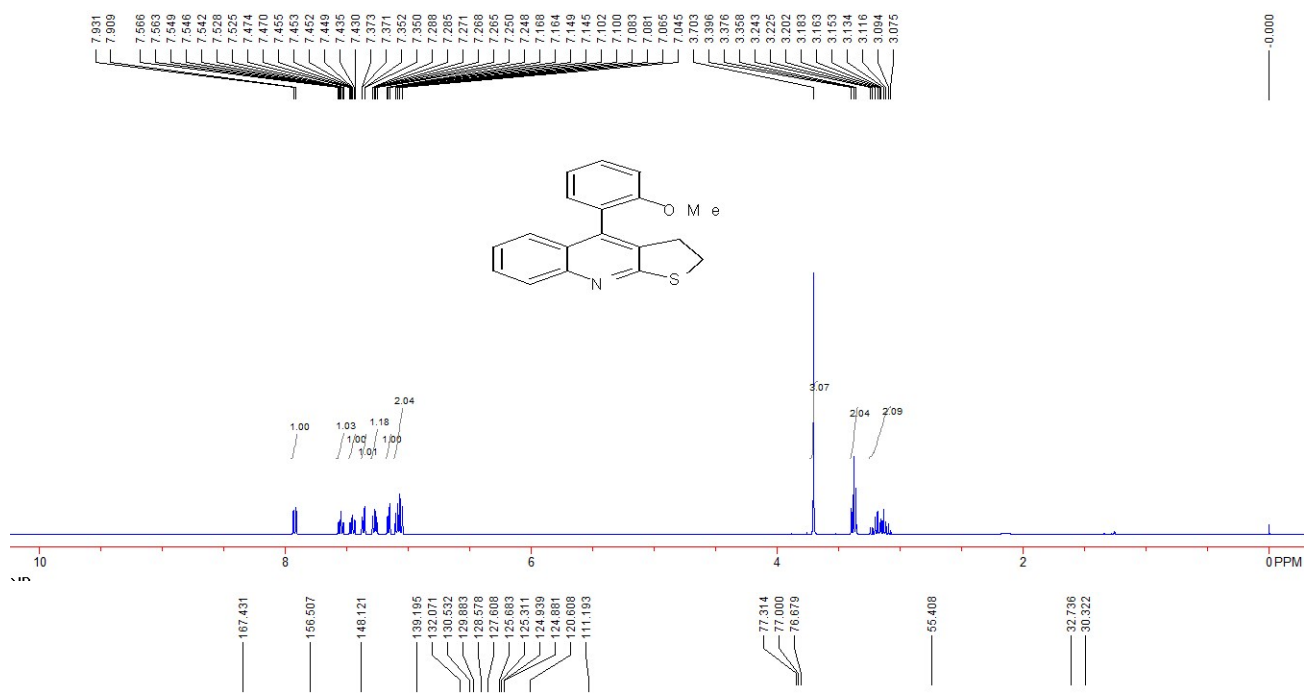


**Compound 3i:** 136 mg, 93%, A white solid, m.p. 156-158 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 2961, 2918, 1588, 1447, 1377, 1303, 1046, 793, 755 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 0.98 (t, 3H, *J* = 7.6 Hz), 2.30 (q, 2H, *J* = 7.6 Hz), 2.99-3.07 (m, 1H), 3.12-3.20 (m, 1H), 3.39 (t, 2H, *J* = 7.6 Hz), 7.09 (d, 1H, *J* = 8.4 Hz), 7.22-7.33 (m, 3H), 7.42 (brs, 2H), 7.57 (t, 1H, *J* = 8.0 Hz), 7.94 (d, 1H, *J* = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 15.1, 26.0, 30.4, 32.8, 125.2, 125.4, 125.7, 126.1, 127.7, 128.61, 128.65, 128.71, 128.9, 131.4, 135.4, 141.7, 142.1, 148.1, 167.6; MS (ESI) *m/z*: 292.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>19</sub>H<sub>18</sub>NS<sup>+</sup> requires: 292.1154, Found: 292.1157.

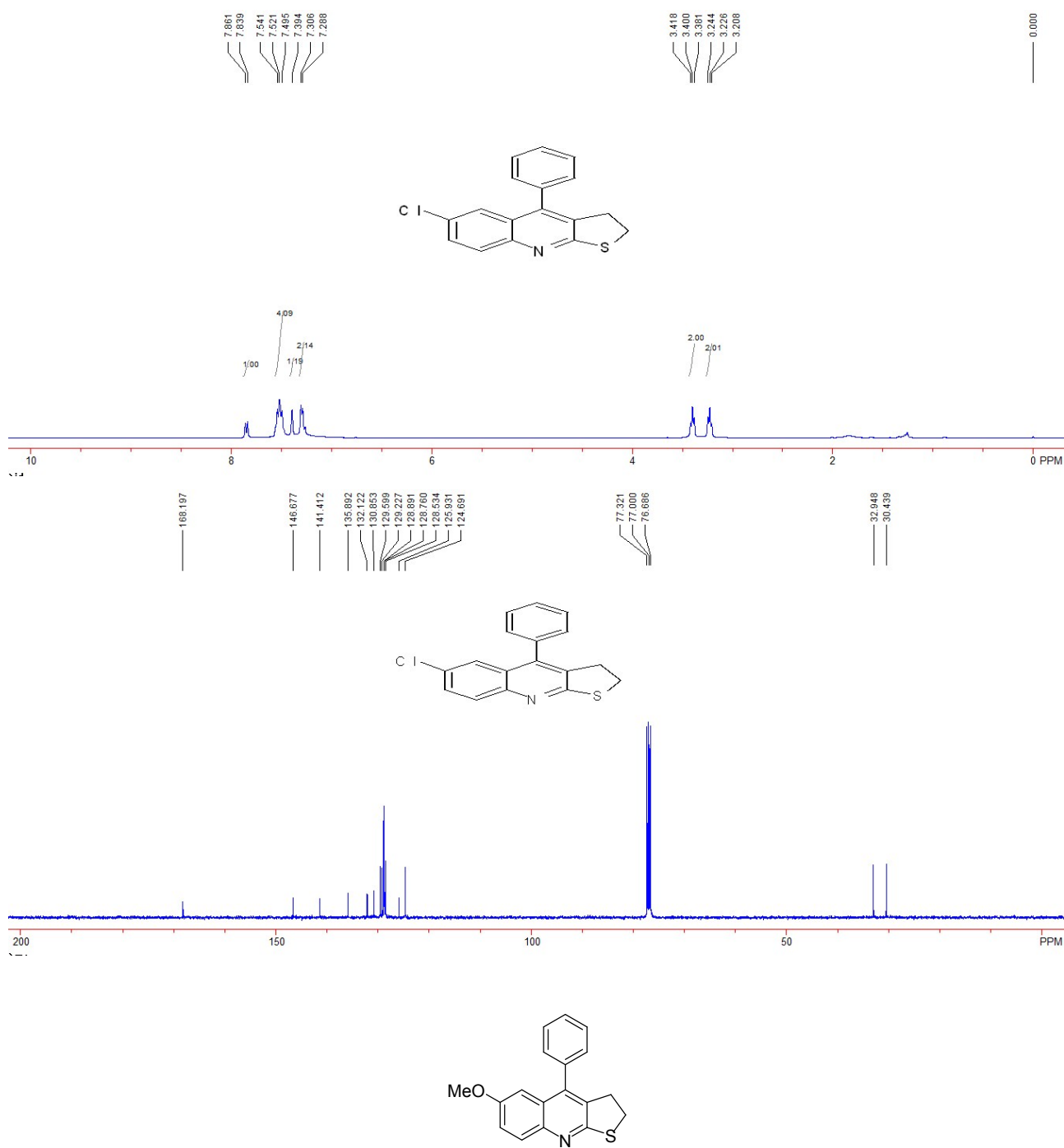




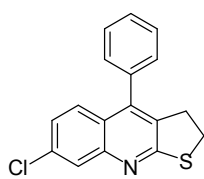
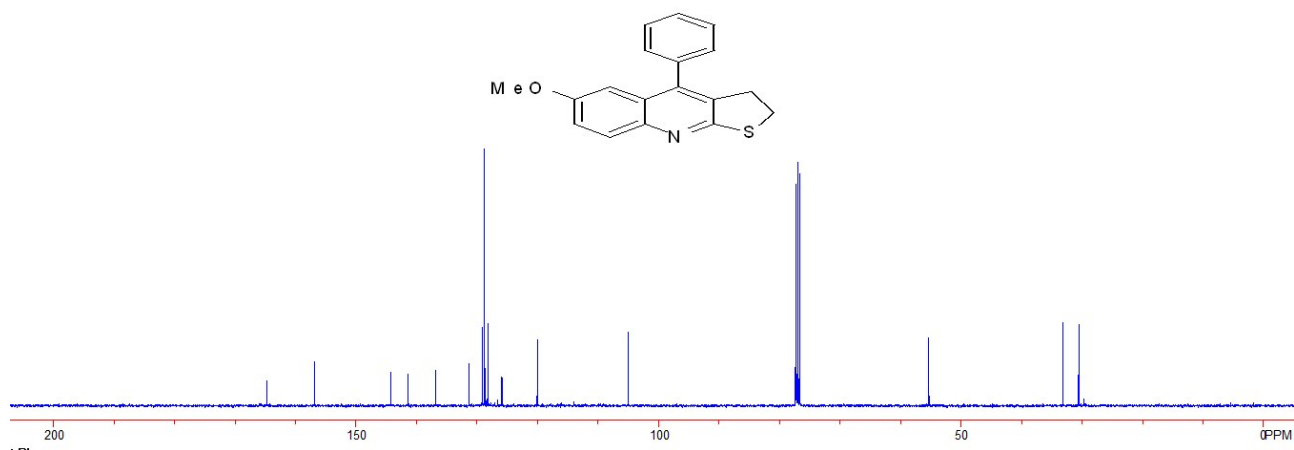
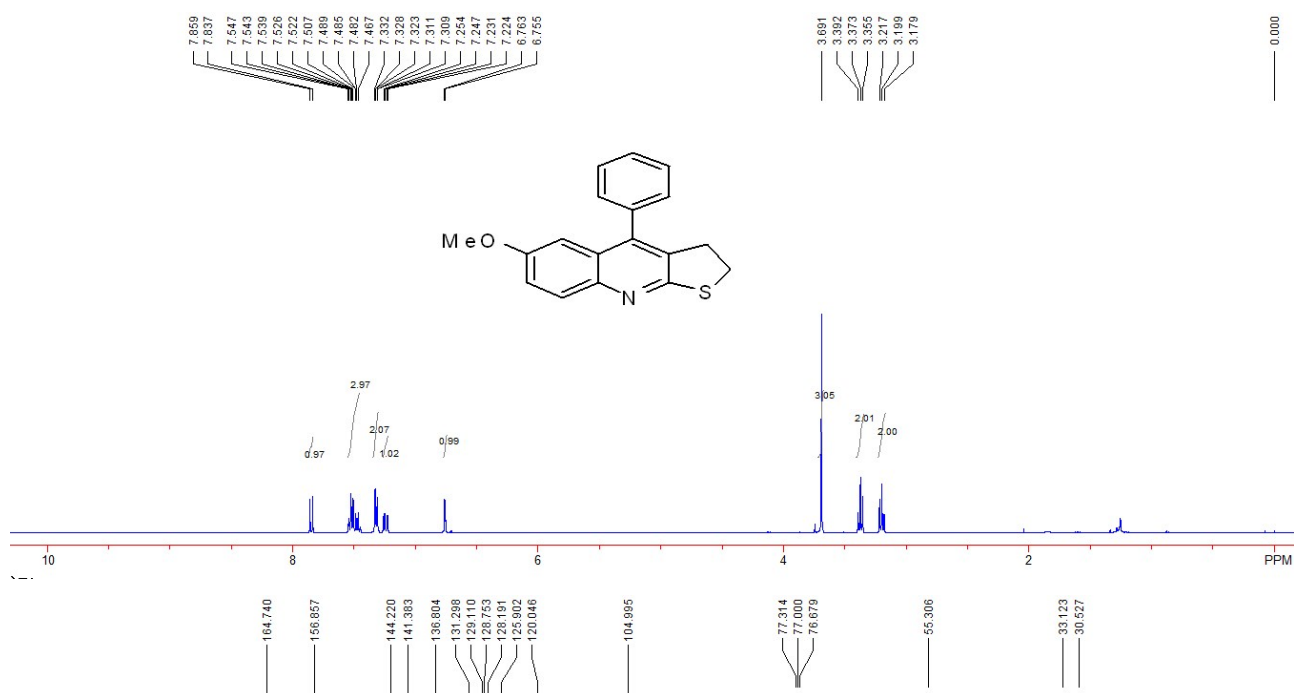
**Compound 3j:** 138 mg, 94%, A white solid, m.p. 155-157 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3012, 2920, 1604, 1589, 1486, 1324, 1229, 1024, 758 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.08-3.24 (m, 2H), 3.38 (t, 2H,  $J = 7.6$  Hz), 3.70 (s, 3H), 7.05-7.10 (m, 2H), 7.16 (dd, 1H,  $J_1 = 8.0$  Hz,  $J_2 = 1.6$  Hz), 7.25-7.29 (m, 1H), 7.36 (dd, 1H,  $J_1 = 8.4$  Hz,  $J_2 = 0.8$  Hz), 7.43-7.47 (m, 1H), 7.53-7.57 (m, 1H), 7.92 (d, 1H,  $J = 8.8$  Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  30.3, 32.7, 55.4, 111.2, 120.6, 124.88, 124.94, 125.3, 125.7, 127.6, 128.6, 129.9, 130.5, 132.1, 139.2, 148.1, 156.5, 167.4; MS (ESI)  $m/z$ : 294.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NOS<sup>+</sup> requires: 294.0947, Found: 294.0950.



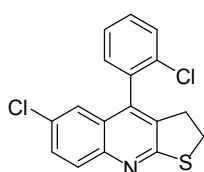
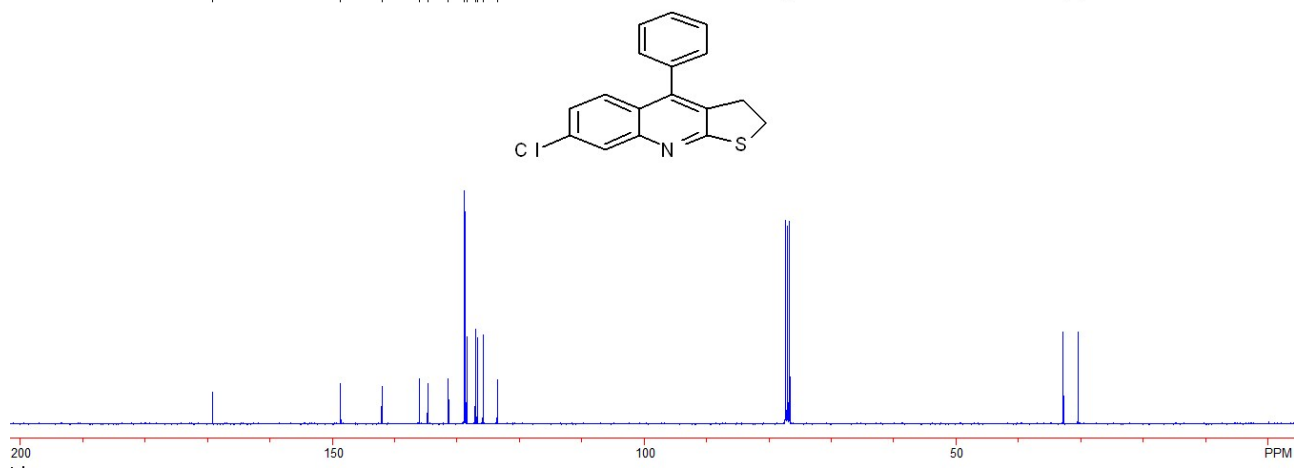
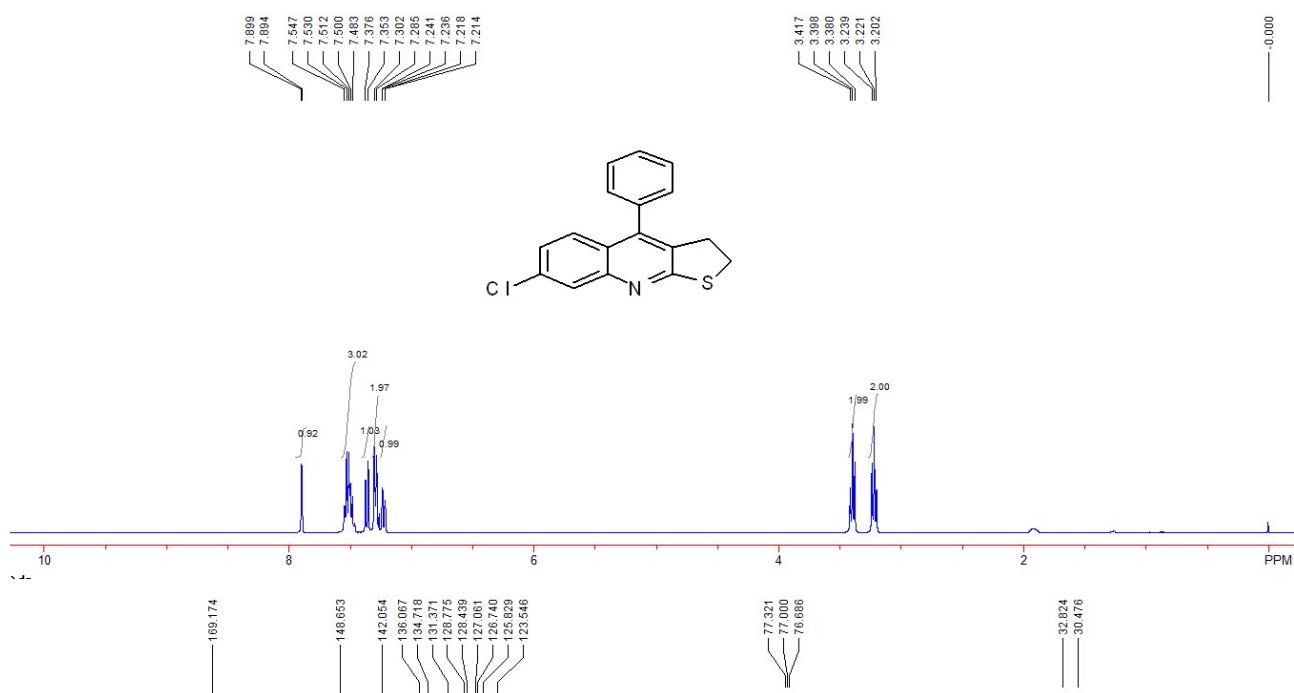
**Compound 3k:** 137 mg, 92%, A white solid, m.p. 145-147 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2918, 2850, 1589, 1486, 1381, 1261, 1047, 945, 816, 703 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.03 (t, 2H,  $J$  = 7.2 Hz), 3.40 (t, 2H,  $J$  = 7.2 Hz), 7.30 (d, 2H,  $J$  = 7.2 Hz), 7.39 (s, 1H), 7.50-7.54 (m, 4H), 7.85 (d, 1H,  $J$  = 8.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  30.4, 32.9, 124.7, 125.9, 128.5, 128.8, 128.9, 129.2, 129.6, 130.9, 132.1, 135.9, 141.4, 146.7, 168.2; MS (ESI)  $m/z$ : 298.0 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>13</sub>CIN<sup>+</sup> requires: 298.0452, Found: 298.0453.



**Compound 3l:** 132 mg, 90%, A white solid, m.p. 150-152 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>): ν 3033, 2909, 1610, 1576, 1495, 1315, 1225, 1019, 745 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS): δ 3.20 (t, 2H, *J* = 7.2 Hz), 3.37 (t, 2H, *J* = 7.2 Hz), 3.69 (s, 3H), 6.76 (d, 1H, *J* = 3.2 Hz), 7.22-7.25 (m, 1H), 7.31-7.33 (m, 2H), 7.47-7.55 (m, 3H), 7.85 (d, 1H, *J* = 8.8 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 30.5, 33.1, 55.3, 105.0, 120.0, 125.9, 128.2, 128.8, 129.1, 131.3, 136.8, 141.4, 144.2, 156.9, 164.7; MS (ESI) *m/z*: 294.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>16</sub>NOS<sup>+</sup> requires: 294.0947, Found: 294.0950.

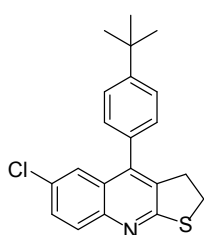
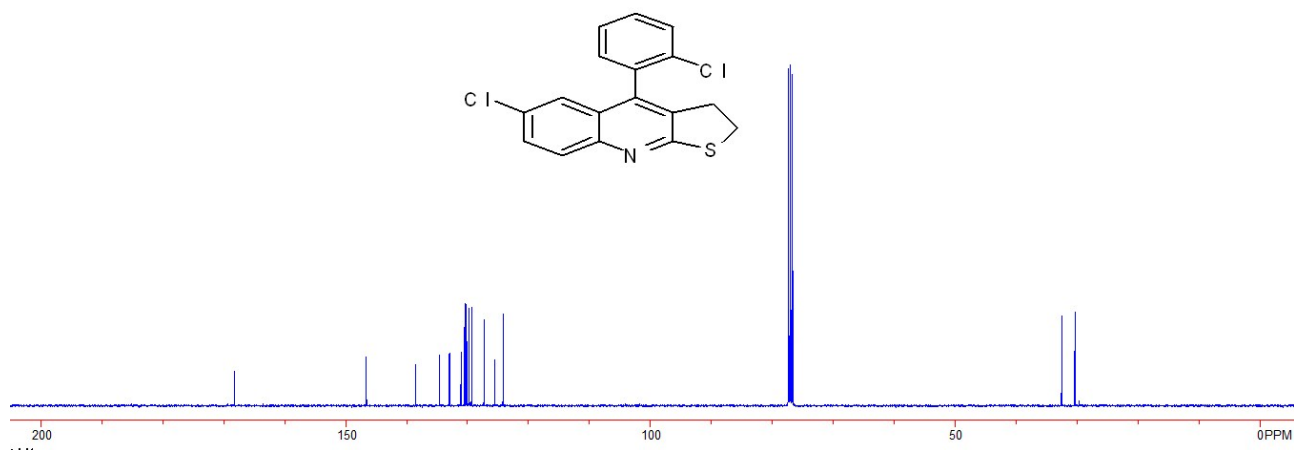
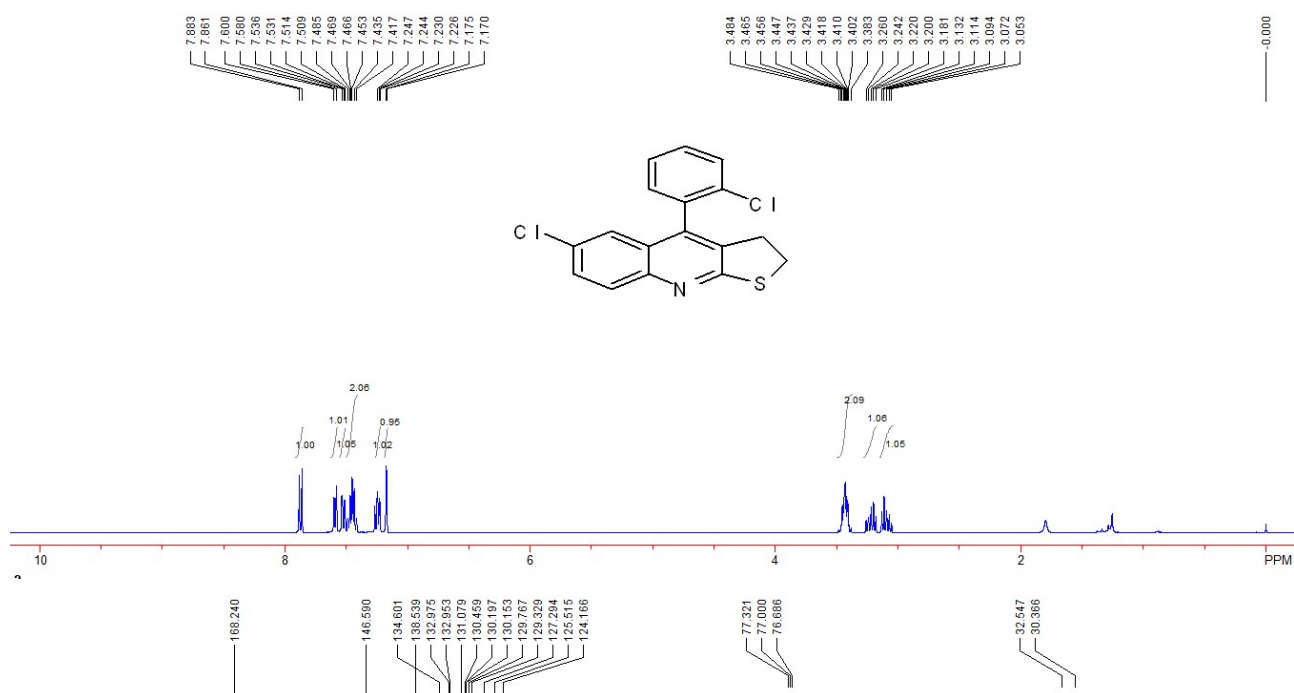


**Compound 3m:** 139 mg, 93%, A white solid, m.p. 175-177 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2925, 2845, 1586, 1551, 1387, 1298, 1073, 1045, 920, 816, 770, 702 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.22 (t, 2H,  $J = 7.6$  Hz), 3.40 (t, 2H,  $J = 7.6$  Hz), 7.23 (dd, 1H,  $J_1 = 8.0$  Hz,  $J_2 = 2.0$  Hz), 7.29 (d, 2H,  $J = 6.8$  Hz), 7.36 (d, 1H,  $J = 9.2$  Hz), 7.48-7.55 (m, 3H), 7.90 (d, 1H,  $J = 2.0$  Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  30.5, 32.8, 123.5, 125.8, 126.7, 127.1, 128.4, 128.8, 131.4, 134.7, 136.1, 142.1, 148.7, 169.2; MS (ESI)  $m/z$ : 298.0 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>13</sub>ClNS<sup>+</sup> requires: 298.0452, Found: 298.0454.

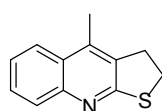
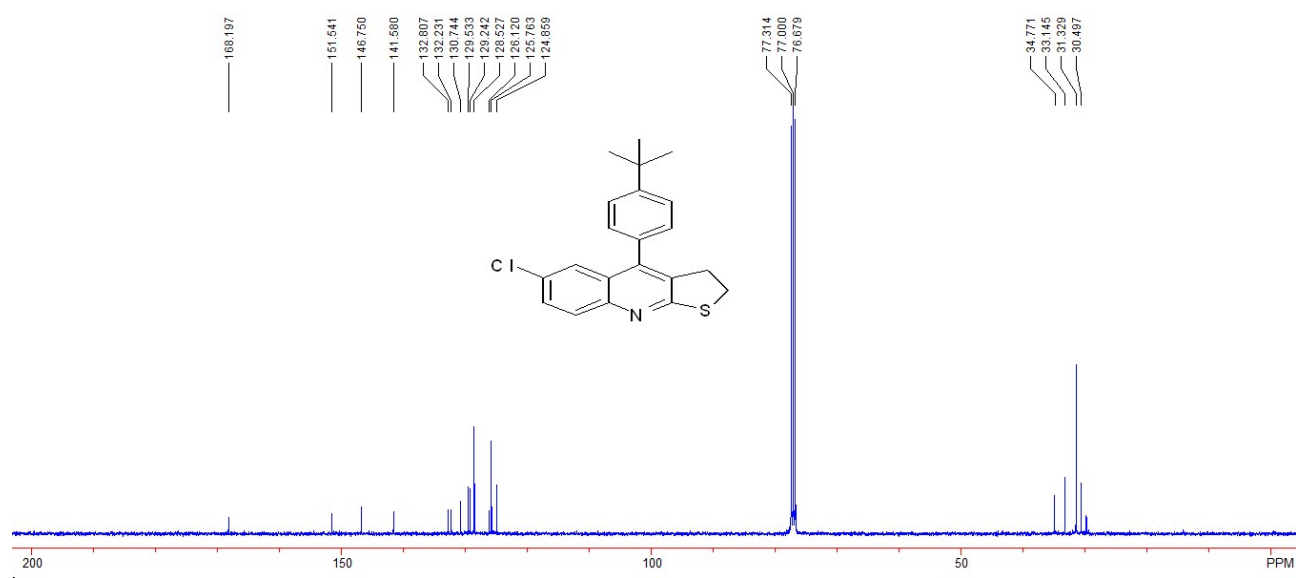


**Compound 3n:** 141 mg, 85%, A white solid, m.p. 193-195 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2921, 2851, 1601, 1470, 1384, 1317, 1062, 1037, 940, 822, 759 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.05-3.13 (m, 1H), 3.18-3.26 (m, 1H), 3.38-3.84 (m, 2H), 7.17 (s, 1H), 7.18-7.25 (m, 1H), 7.42-7.49 (m, 2H), 7.52 (dd, 1H,  $J_1 = 8.8$  Hz,  $J_2 = 2.0$  Hz), 7.59 (d, 1H,  $J = 8.0$  Hz), 7.87 (d, 1H,  $J = 8.8$  Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  30.4, 32.5, 124.2, 125.5, 127.3, 129.3, 129.8, 130.15, 130.20, 130.5, 131.1, 132.95, 132.98, 134.6, 138.5, 146.6, 168.2; MS (ESI)  $m/z$ : 332.0 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>12</sub>Cl<sub>2</sub>NS<sup>+</sup> requires: 332.0062, Found: 332.0063.

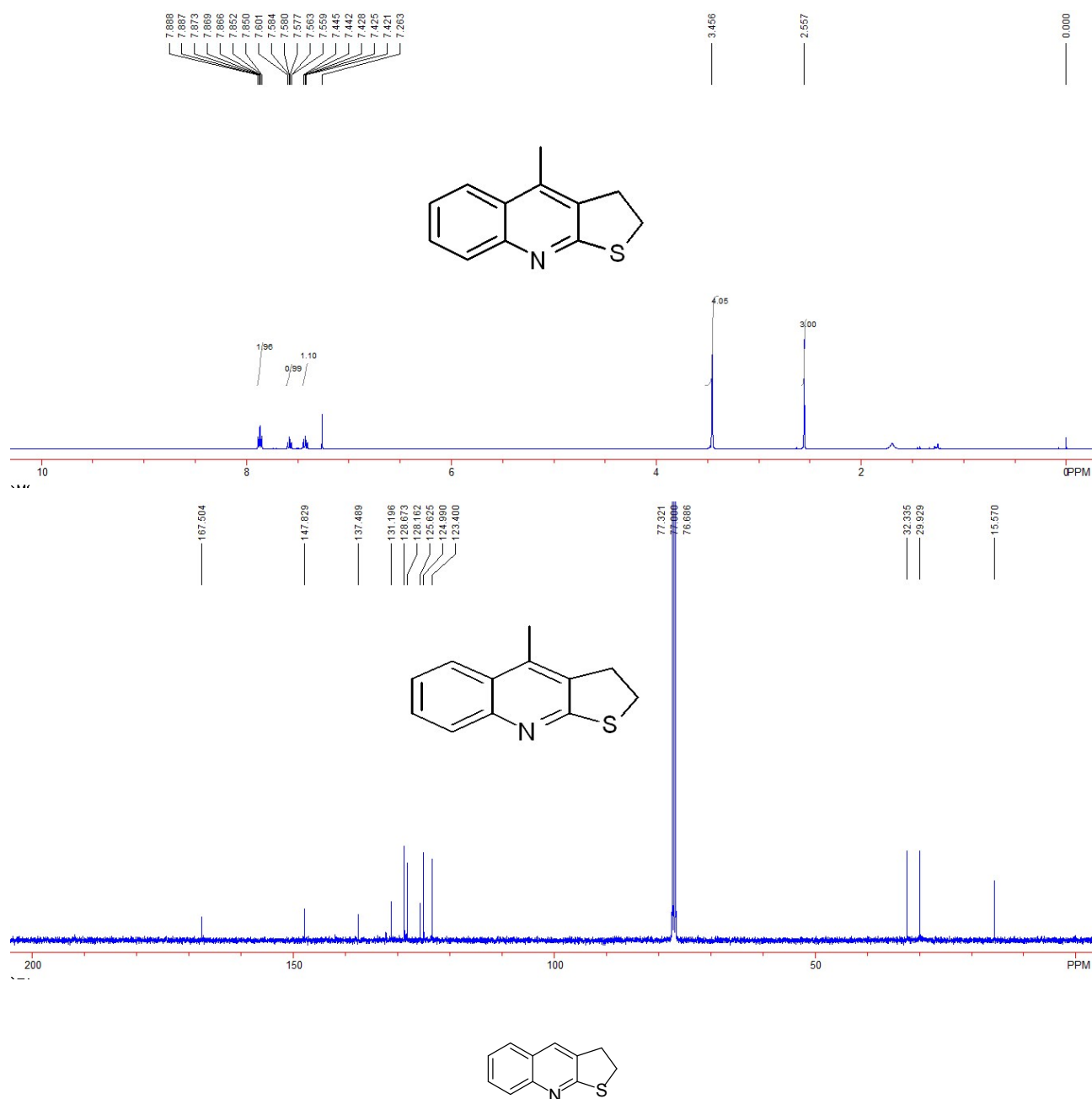




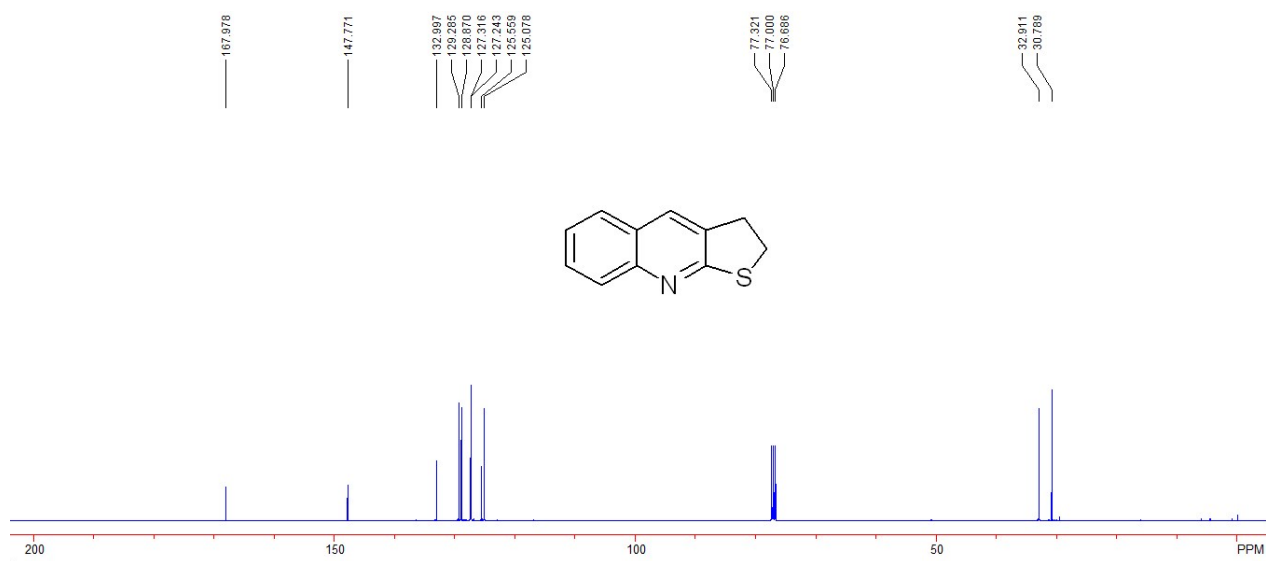
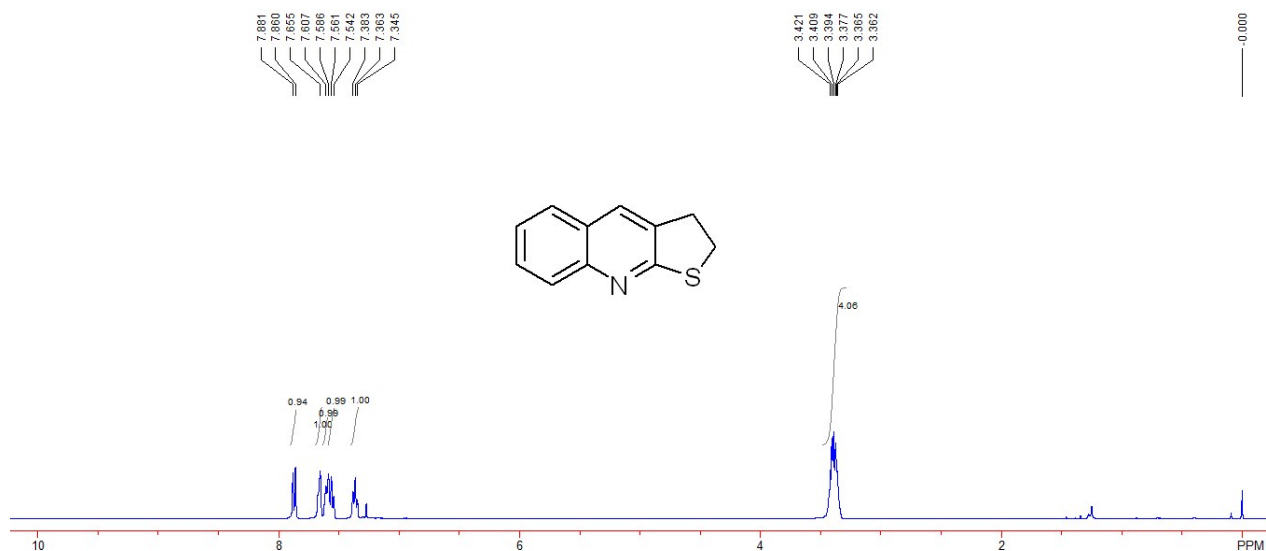
**Compound 3o:** 156 mg, 88%, A white solid, m.p. 210-212 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2925, 2855, 1622, 1585, 1476, 1400, 1313, 1267, 1108, 927, 761, 702 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.41 (s, 9H), 3.26 (t, 2H,  $J = 7.2$  Hz), 3.39 (t, 2H,  $J = 7.2$  Hz), 7.24 (t, 2H,  $J = 8.8$  Hz), 7.47-7.49 (m, 1H), 7.50-7.52 (m, 1H), 7.54 (d, 2H,  $J = 8.4$  Hz), 7.85 (d, 1H,  $J = 8.8$  Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  30.5, 31.3, 33.1, 34.8, 124.9, 125.8, 126.1, 128.5, 129.2, 129.5, 130.7, 132.2, 132.8, 141.6, 146.8, 151.5, 168.2; MS (ESI)  $m/z$ : 354.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>21</sub>H<sub>21</sub>CIN<sup>+</sup> requires: 354.1078, Found: 354.1080.



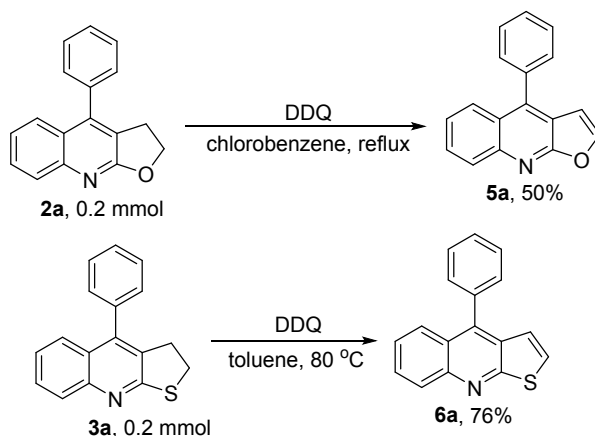
**Compound 3p:** 76 mg, 75%, A white solid, m.p. 174-176 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2975, 2888, 1625, 1578, 1465, 1397, 1320, 1222, 1035, 750, 702 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  2.56 (s, 3H), 3.46 (s, 4H), 7.42-7.45 (m, 1H), 7.56-7.60 (m, 1H), 7.85-7.89 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  15.6, 29.9, 32.3, 123.4, 125.0, 125.6, 128.2, 128.7, 131.2, 137.5, 147.8, 167.5; MS (ESI)  $m/z$ : 202.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>12</sub>H<sub>12</sub>NS<sup>+</sup> requires: 202.0685, Found: 202.0683.



**Compound 3q:** 91 mg, 98%, A white solid, m.p. 168-170 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3057, 2937, 1615, 1603, 1559, 1495, 1380, 1338, 1138, 1044, 903, 779, 751 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  3.36-3.42 (m, 4H), 7.36 (t, 1H, *J* = 7.6 Hz), 7.56 (t, 1H, *J* = 7.6 Hz), 7.60 (d, 1H, *J* = 8.4 Hz), 7.66 (s, 1H), 7.87 (d, 1H, *J* = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  30.8, 32.9, 125.1, 125.6, 127.2, 127.3, 128.9, 129.3, 133.0, 147.8, 168.0; MS (ESI) *m/z*: 188.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>11</sub>H<sub>10</sub>NS<sup>+</sup> requires: 188.0529, Found: 188.0530.



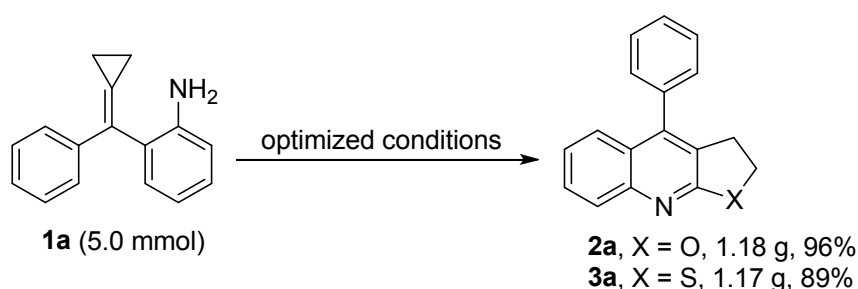
## Transformations and scalable production of **2a** and **3a**



**Scheme S1** Transformations of **2a**, **3a** into **5a**, **6a**

A solution of **2a** (49 mg, 0.2 mmol) and DDQ (68 mg, 0.3 mmol) in dry chlorobenzene was stirred under reflux under air atmosphere for 12 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product **5a** in 50% yield.

A solution of **3a** (52 mg, 0.2 mmol) and DDQ (68 mg, 0.3 mmol) in dry toluene was stirred at 80 °C under air atmosphere for 12 h. Upon completion, the reaction was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 20 / 1) to afford the product **6a** in 76% yield.



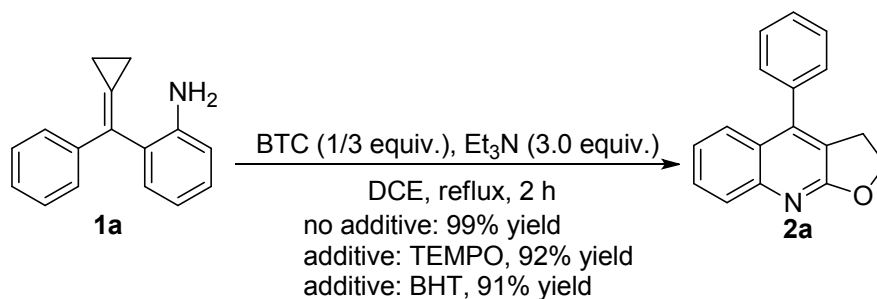
**Scheme S2** Scalable production of **2a** and **3a**

**1a** (1.11 g, 5.0 mmol) and triphosgene (496 mg, 1.67 mmol) were dissolved in DCE (50 mL), then Et<sub>3</sub>N (2.08 mL, 15.0 mmol) was added dropwise and the resulting reaction mixture was stirred at 85 °C. The reaction was stopped after 2 h and the solvent was removed under reduced pressure and the

residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the product **2a** in 96% yield.

**1a** (1.11 g, 5.0 mmol) and DABCO (2.24 g, 20 mmol) were dissolved in toluene (50 mL), then CS<sub>2</sub> (1.2 mL, 20 mmol) was added dropwise and the resulting reaction mixture was stirred at 80 °C. The reaction was stopped after 8 h and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product **3a** in 89% yield.

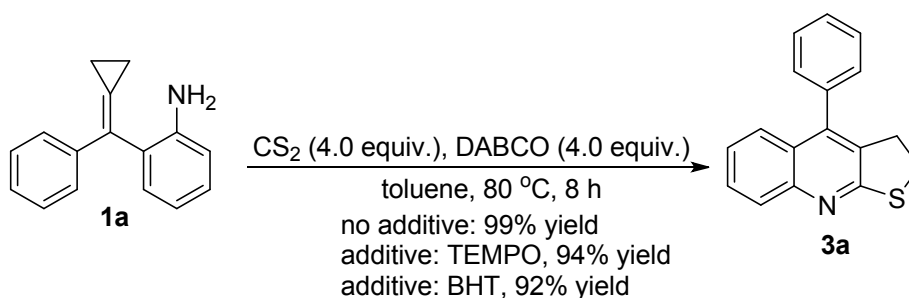
## Control experiments



**Scheme S3** Control experiments for the synthesis of **2a**

TEMPO experiment: **1a** (0.60 mmol) and TEMPO (1.2 mmol) triphosgene (0.20 mmol) were dissolved in DCE (6.0 mL), then Et<sub>3</sub>N (0.25 mL) was added dropwise and the resulting reaction mixture was stirred at 85 °C. The reaction was stopped after 2 h and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the product **2a** in 92% yield.

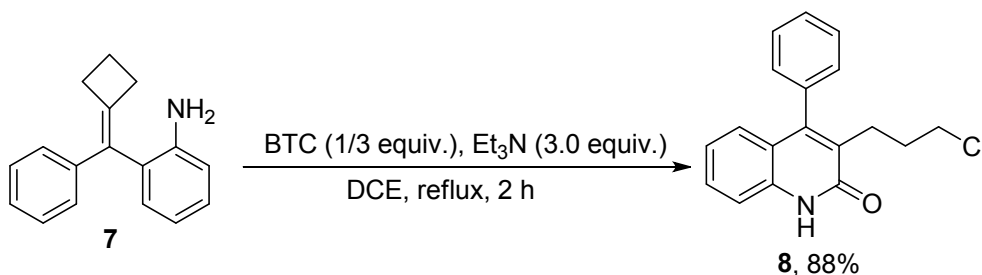
BHT experiment: **1a** (0.60 mmol) and BHT (1.2 mmol), triphosgene (0.20 mmol) were dissolved in DCE (6.0 mL), then Et<sub>3</sub>N (0.25 mL) was added dropwise and the resulting reaction mixture was stirred at 85 °C. The reaction was stopped after 2 h and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the product **2a** in 91% yield.



**Scheme S4** Control experiments for the synthesis of **3a**

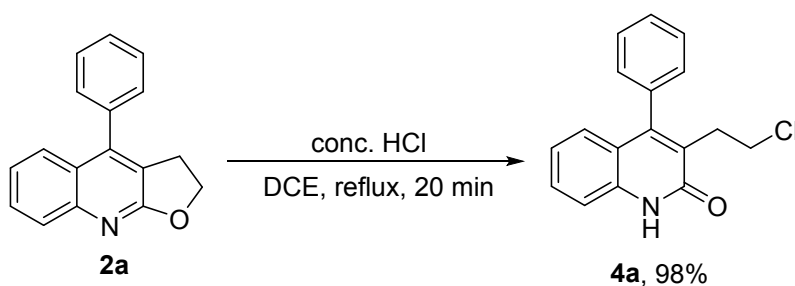
TEMPO experiment: **1a** (0.5 mmol) and TEMPO (1.0 mmol), DABCO (2.0 mmol) were dissolved in toluene (5.0 mL), then CS<sub>2</sub> (0.12 mL) was added dropwise and the resulting reaction mixture was stirred at 80 °C. The reaction was stopped after 8 h and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product **3a** in 94% yield.

BHT experiment: **1a** (0.5 mmol) and BHT (1.0 mmol), DABCO (2.0 mmol) were dissolved in toluene (5.0 mL), then CS<sub>2</sub> (0.12 mL) was added dropwise and the resulting reaction mixture was stirred at 80 °C. The reaction was stopped after 8 h and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product **3a** in 92% yield.



**Scheme S5** Reaction scope of aniline-tethered alkylidenecyclobutane

**7** (0.60 mmol) and triphosgene (0.20 mmol) were dissolved in DCE (6.0 mL), then Et<sub>3</sub>N (0.25 mL) was added dropwise and the resulting reaction mixture was stirred at 85 °C. The reaction was stopped after 2 h and the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the product **8** in 88% yield.

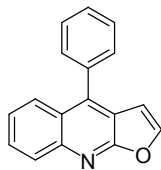


**Scheme S6** Transformation of **2a** into **4a**

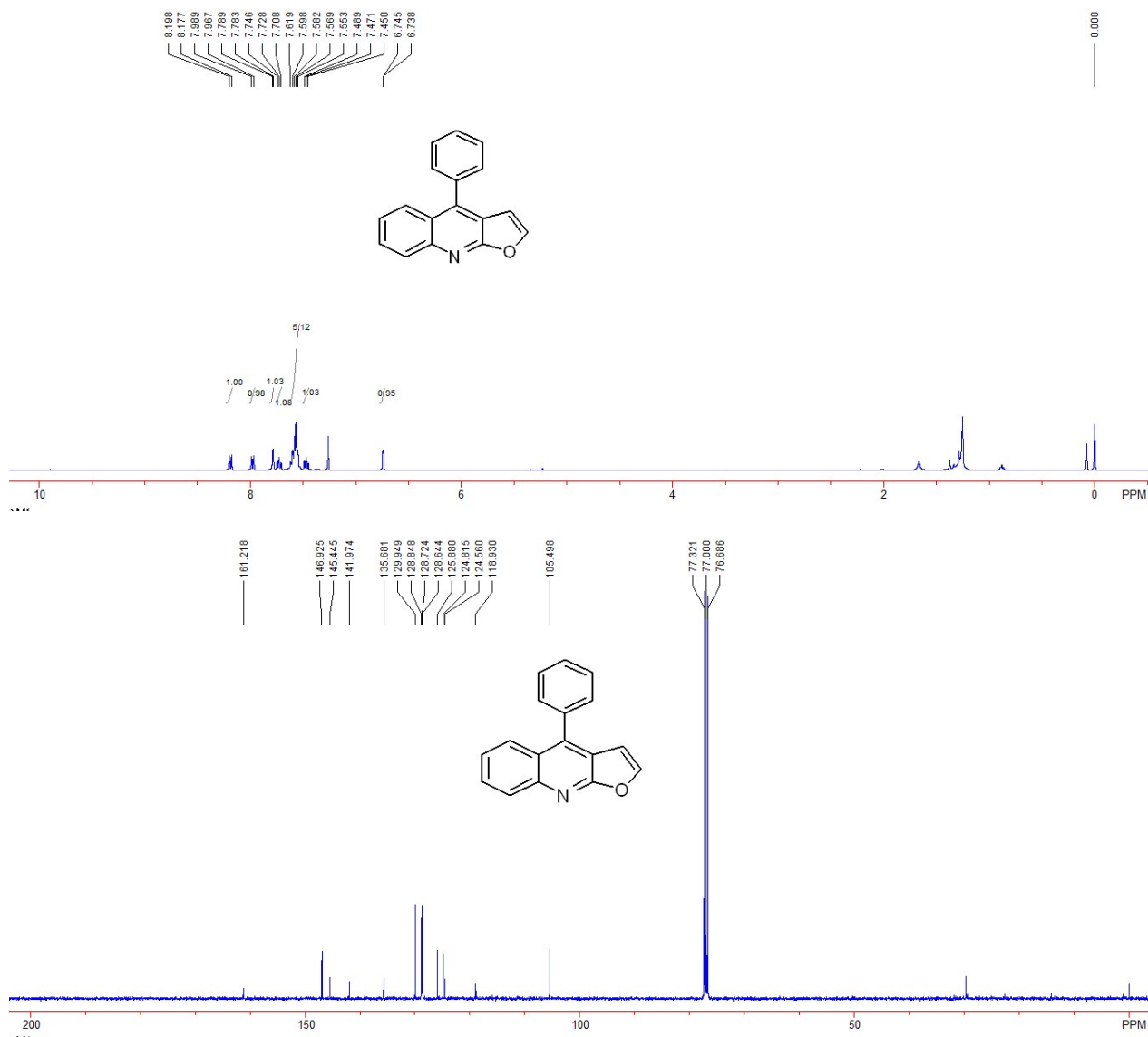
A solution of **2a** (0.20 mmol) and conc. HCl (2.0 mmol) was refluxed in DCE for 20 min. After cooling the reaction mixture to room temperature, it was made to be basic with addition of NaHCO<sub>3</sub>. The precipitated solid was filtered off and the mother liquid was extracted with ethyl acetate (5.0 mL) for 3 times. The combined organic layer was washed with saturated brine and dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated under reduced pressure. The residue and the above solid were combined and recrystallized from ethyl acetate to obtain **4a** in 98% yield.

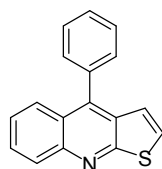


## Spectroscopic data for products 5a, 6a and 8

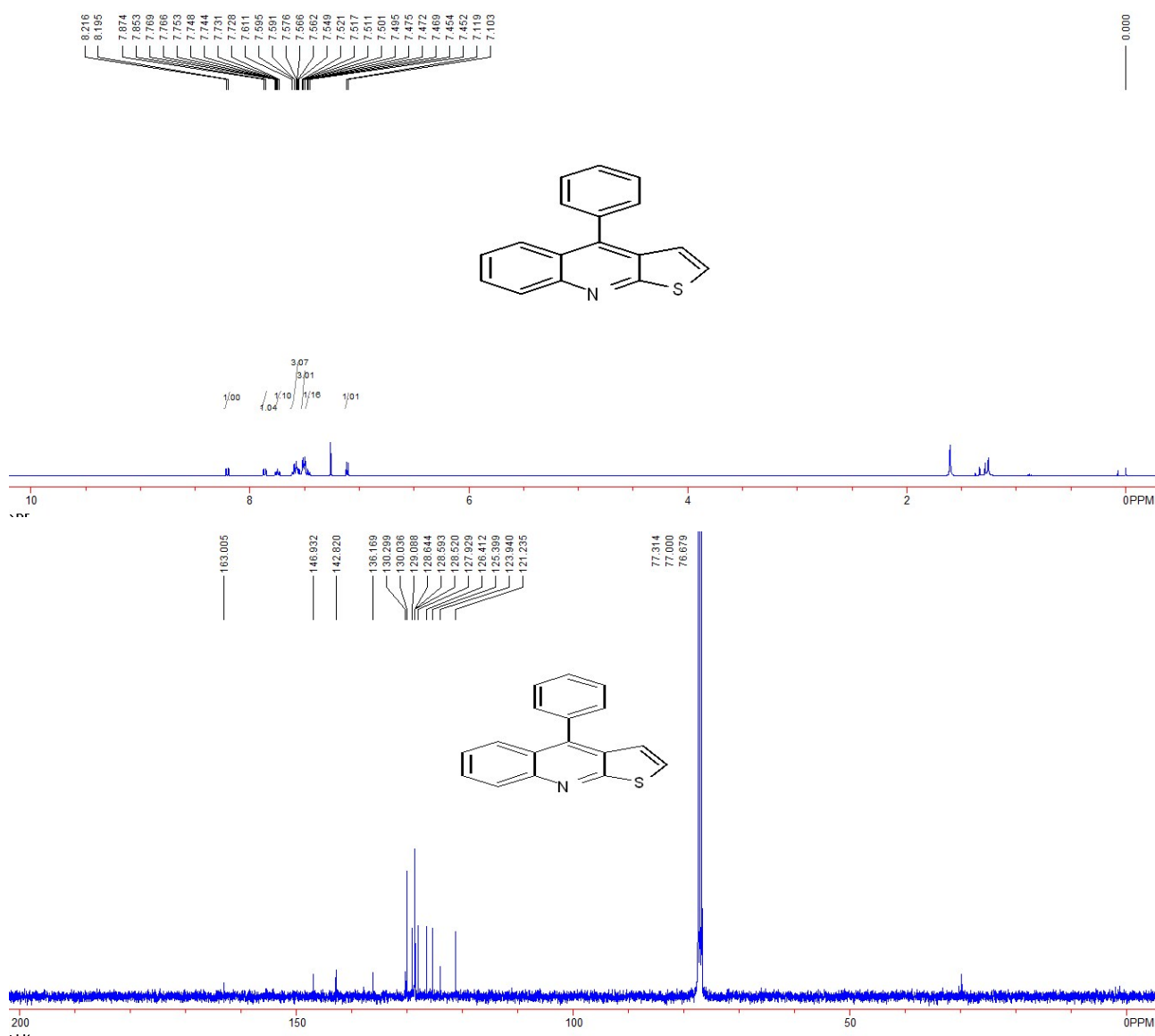


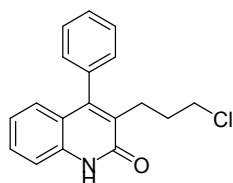
**Compound 5a:** 26 mg, 50%, A white solid, m.p. 157-159 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2924, 2851, 1590, 1540, 1382, 1361, 1308, 1149, 1136, 1028, 764, 742, 727, 702 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  6.47 (d, 1H,  $J$  = 2.8 Hz), 7.47 (t, 1H,  $J$  = 7.6 Hz), 7.55-7.62 (m, 5H), 7.73 (t, 1H,  $J$  = 7.6 Hz), 7.79 (d, 1H,  $J$  = 2.8 Hz), 7.98 (d, 1H,  $J$  = 8.4 Hz), 8.19 (d, 1H,  $J$  = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  105.5, 118.9, 124.6, 124.8, 125.9, 128.6, 128.7, 128.8, 129.9, 135.7, 142.0, 145.4, 146.9, 161.2; MS (ESI)  $m/z$ : 246.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>12</sub>NO<sup>+</sup> requires: 246.0914, Found: 246.0914.



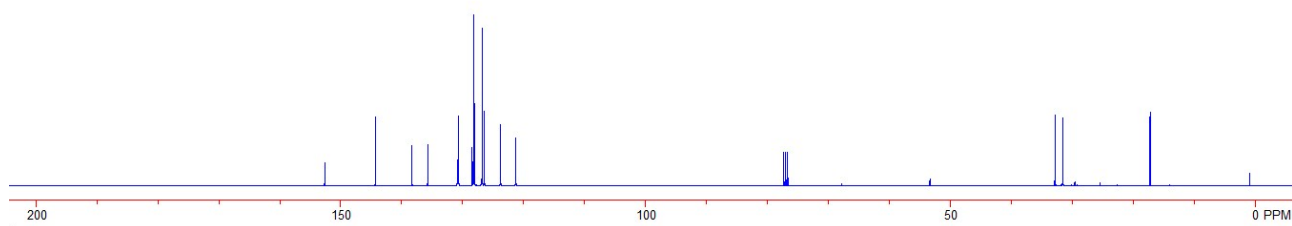
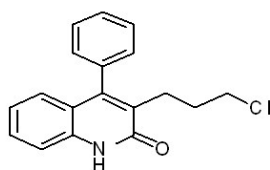
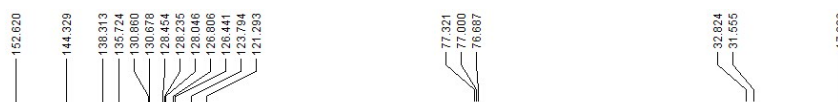
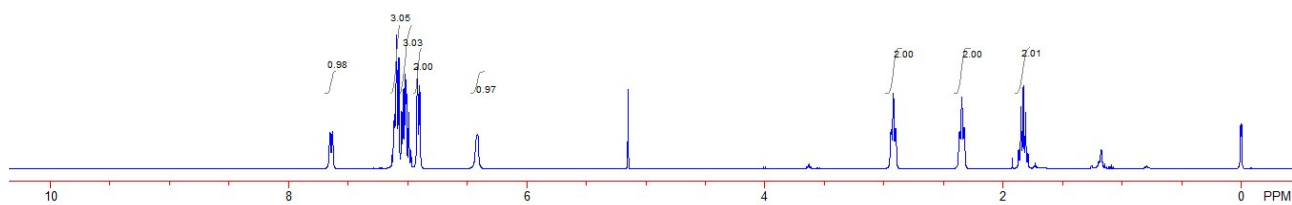
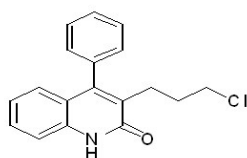


**Compound 6a:** 39 mg, 76%, A white solid, m.p. 165-167 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  2925, 2876, 1590, 1545, 1386, 1359, 1290, 1156, 1128, 1030, 756, 745, 725, 680 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  7.11 (d, 1H,  $J$  = 6.4 Hz), 7.46 (dd, 1H,  $J_1$  = 6.4 Hz,  $J_2$  = 1.2 Hz), 7.48-7.52 (m, 3H), 7.55-7.61 (m, 3H), 7.75 (td, 1H,  $J_1$  = 6.4 Hz,  $J_2$  = 1.2 Hz), 7.86 (d, 1H,  $J$  = 8.4 Hz), 8.21 (d, 1H,  $J$  = 8.4 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  121.2, 123.9, 125.4, 126.4, 127.9, 128.5, 128.59, 128.64, 129.1, 130.0, 130.3, 136.2, 142.8, 146.9, 163.0; MS (ESI)  $m/z$ : 262.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>12</sub>NS<sup>+</sup> requires: 262.0685, Found: 262.0686.

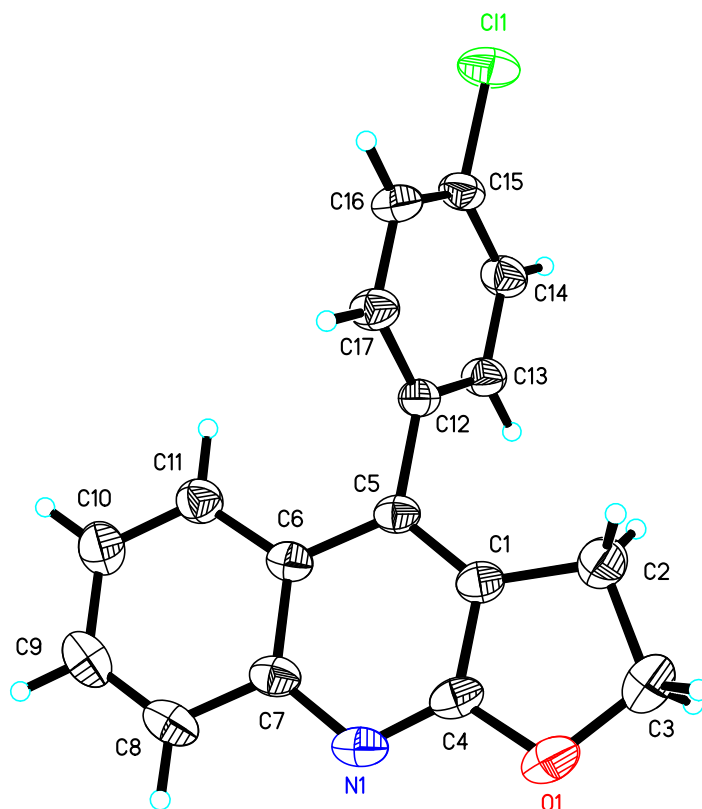




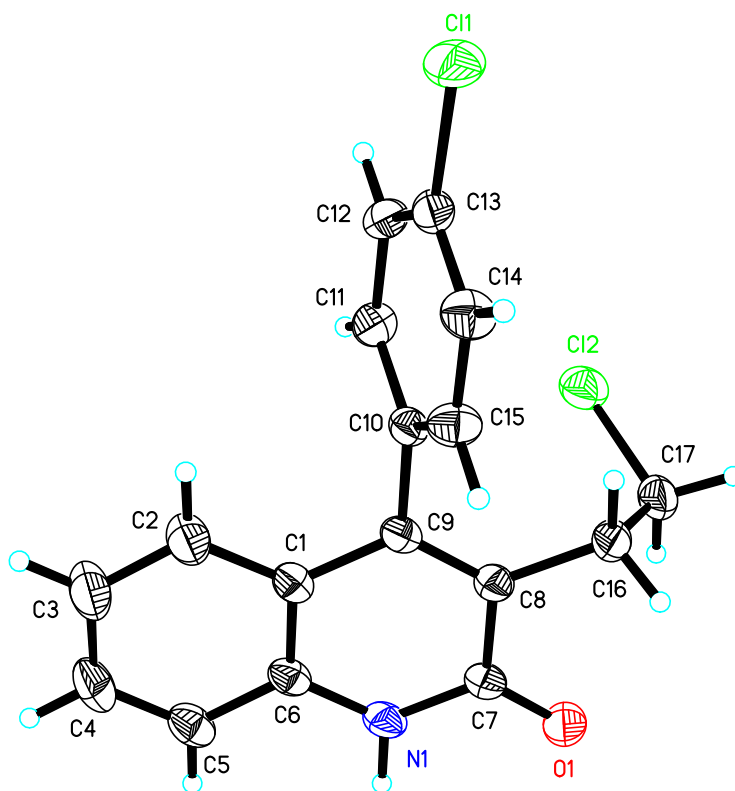
**Compound 8:** 157 mg, 88%, A white solid, m.p. 128-130 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$  3383, 2951, 1682, 1581, 1518, 1493, 1442, 1286, 1194, 754, 694 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  1.79-1.87 (m, 2H), 2.35 (t, 2H,  $J = 7.6$  Hz), 2.92 (t, 2H,  $J = 7.2$  Hz), 6.41 (s, 1H), 6.91 (d, 2H,  $J = 7.6$  Hz), 6.97-7.05 (m, 3H), 7.07-7.13 (m, 3H), 7.64 (d, 1H,  $J = 7.6$  Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  17.2, 31.6, 32.8, 121.3, 123.8, 126.4, 126.8, 128.0, 128.2, 128.5, 130.7, 130.9, 135.7, 138.3, 144.3, 152.6; MS (ESI)  $m/z$ : 298.1 (M+H<sup>+</sup>, 100); HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>17</sub>ClNO<sup>+</sup> requires: 298.0994, Found: 298.0995.



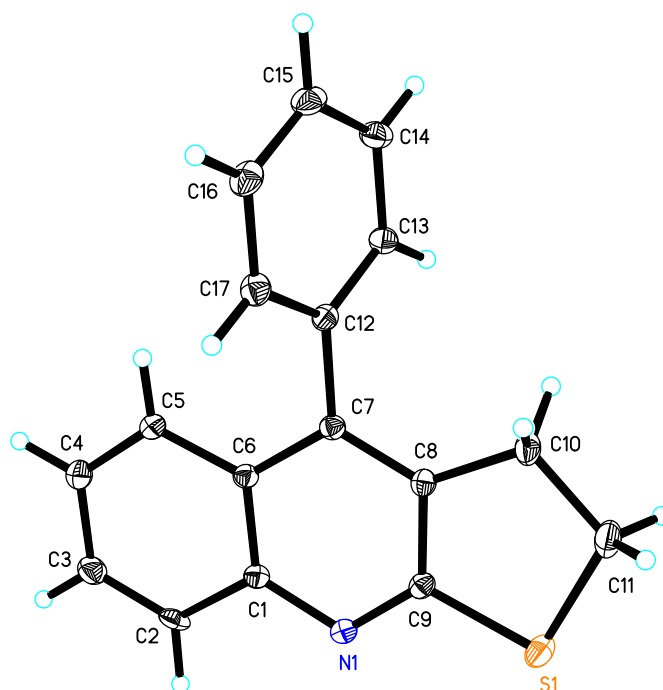
## The crystal data of 2c, 3a and 4c



The crystal data of **2c** have been deposited in CCDC with number 1430177. Empirical Formula:  $C_{17}H_{12}ClNO$ ; Formula Weight: 281.73; Crystal Color, Habit: colorless, Crystal Dimensions: 0.230 x 0.190 x 0.130 mm<sup>3</sup>; Crystal System: Triclinic; Lattice Parameters:  $a = 8.2770(12)\text{\AA}$ ,  $b = 8.8610(13)\text{\AA}$ ,  $c = 20.949(3)\text{\AA}$ ,  $\alpha = 78.278(3)^\circ$ ,  $\beta = 83.751(3)^\circ$ ,  $\gamma = 64.580(3)^\circ$ ,  $V = 1358.4(4)\text{\AA}^3$ ; Space group: P -1;  $Z = 4$ ;  $D_{calc} = 1.378\text{ g/cm}^3$ ;  $F_{000} = 584$ ; Final R indices [ $I > 2\sigma(I)$ ]  $R_1 = 0.0469$ ,  $wR_2 = 0.1163$ .



The crystal data of **4c** have been deposited in CCDC with number 1430157. Empirical Formula:  $C_{17}H_{13}Cl_2NO$ ; Formula Weight: 318.18; Crystal Color, Habit: colorless, Crystal Dimensions: 0.220 x 0.170 x 0.100 mm<sup>3</sup>; Crystal System: Triclinic; Lattice Parameters:  $a = 7.7899(17)\text{\AA}$ ,  $b = 9.516(2)\text{\AA}$ ,  $c = 11.134(2)\text{\AA}$ ,  $\alpha = 99.138(5)^\circ$ ,  $\beta = 97.433(5)^\circ$ ,  $\gamma = 109.903(5)^\circ$ ,  $V = 751.1(3)\text{\AA}^3$ ; Space group: P -1;  $Z = 2$ ;  $D_{calc} = 1.407\text{ g/cm}^3$ ;  $F_{000} = 328$ ; Final R indices [ $I > 2\sigma(I)$ ]  $R1 = 0.0586$ ,  $wR2 = 0.1510$ .



The crystal data of **3a** have been deposited in CCDC with number 1058933. Empirical Formula:  $C_{18}H_{14}Cl_3NS$ ; Formula Weight: 382.71; Crystal Color, Habit: colorless, Crystal Dimensions: 0.25 x 0.22 x 0.15 mm<sup>3</sup>; Crystal System: Triclinic; Lattice Parameters:  $a = 7.7687(6)\text{\AA}$ ,  $b = 9.4304(7)\text{\AA}$ ,  $c = 12.8027(10)\text{\AA}$ ,  $\alpha = 101.3420(10)^\circ$ ,  $\beta = 104.7500(10)^\circ$ ,  $\gamma = 102.5070(10)^\circ$ ,  $V = 853.44(11)\text{\AA}^3$ ; Space group: P -1;  $Z = 2$ ;  $D_{calc} = 1.489\text{ g/cm}^3$ ;  $F_{000} = 392$ ; Final R indices [ $I > 2\sigma(I)$ ]  $R1 = 0.0408$ ,  $wR2 = 0.1423$ .

## Reference

[1] (a) K. Utimoto, M. Tamura and K. Sisido, *Tetrahedron*, 1973, **29**, 1169-1171; (b) J. A. Stafford and J. E. McMurry, *Tetrahedron Lett.*, 1988, **29**, 2531–2534; (c) K. Chen, Z. Zhang, Y. Wei and M. Shi, *Chem. Commun.*, 2012, **48**, 7696–7698.

[2] (a) S. V. Frye, M. C. Johnson and N. L. Valvano, *J. Org. Chem.*, 1991, **56**, 3750-3752; (b) T. M. Acker, A. Khatri, K. M. Vance, C. Slabber, J. Bacsá, J. P. Snyder, S. F. Traynelis and D. C. Liotta, *J. Med. Chem.*, 2013, **56**, 6434-6456.