

# An environmentally benign cascade reaction of chromone-3-carboxaldehydes with ethyl 2-(pyridine-2-yl)acetate derivatives for highly site-selective synthesis of quinolizines and quinolizinium salts in water<sup>†</sup>

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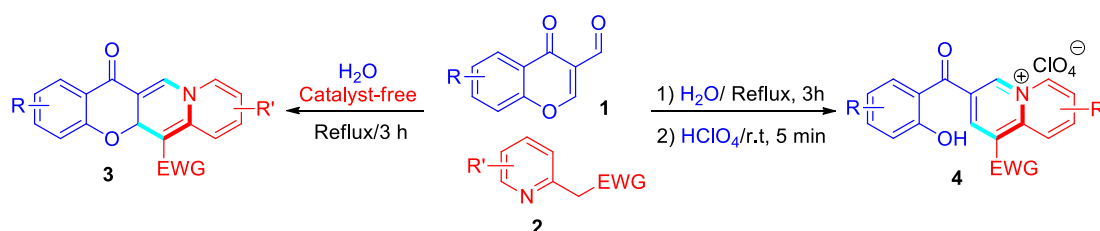
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## General Information

All compounds were fully characterised by spectroscopic data. The NMR spectra were recorded on a Bruker DRX600. Chemical shifts ( $\delta$ ) are expressed in ppm,  $J$  values are given in Hz, and deuterated DMSO- $d_6$  were used as solvent. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF<sub>254</sub>. The melting points were determined on a XT-4A melting point apparatus and are uncorrected. HRMs were performed on an Agilent LC/Msd TOF instrument. Materials used were purchased from Adamas-beta Corporation Limited.

The materials were purchased from Adamas-beta Corporation Limited. All chemicals and solvents were used as received without further purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh). The chromone-3-carboxaldehydes **1** and ethyl 2-(pyridine-2-yl)acetates **2** were commercially available reagents.

## General Procedure for the Preparation of 3 and 4



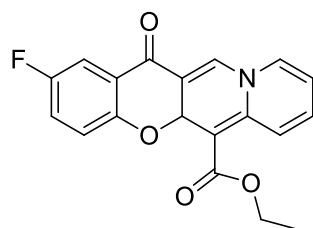
First, chromone-3-carboxaldehydes **1** (1.0 ml) was charged into a round-bottom flask. Then, water (5 ml) and ethyl 2-(pyridine-2-yl)acetate derivatives **2** (1.1 mmol) were added to the mixture. The mixture was stirred at reflux for approximately 3 hours and monitored by TLC until the intermediate was completely consumed. The reaction mixture was cooled to room temperature and then was filtered by a suction funnel and washing with a few drops of water or recrystallized by EtOH or acetone. Finally, the obtained red solid was dried using an infrared lamp. As a result, we obtained the target compounds **3** with good to excellent yields (85–96%).

First, chromone-3-carboxaldehydes **1** (1.0 ml) was charged into a round-bottom flask. Then, water (5 ml) and ethyl 2-(pyridine-2-yl)acetate derivatives **2** (1.1 mmol) were added to the mixture. The mixture was stirred at reflux for approximately 3

hours and monitored by TLC until the intermediate was completely consumed, and then was filtered by a suction funnel and washing with a few drops of water or recrystallized by EtOH or acetone. We can obtain the target compounds **3**. Then compounds **3** and H<sub>2</sub>O were charged in a round-bottom flask. Then, the mixture was added a few drops of perchloric acid and make the value of pH of the mixture is up to 1–2 at room temperature under the magneton agitation. Then, the mixture was filtered by suction funnel and washed by small of water. We obtained the target compounds **4** (yellow solid) with good to excellent yields. It should be noted that compounds **4** are in equilibrium with compounds **3** in the solution. The cascade reaction produces compounds **4** at strong acidic conditions (pH < 3) and obtains compounds **3** at neutral or basic conditions.

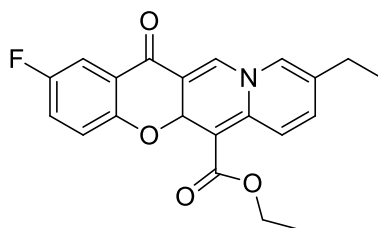
### Spectroscopic Data of 3–4

#### **Ethyl 2-fluoro-13-oxo-5a,13-dihydrochromeno[2,3-*b*]quinolizine-6-carboxylate (3a)**



Red solid; Mp: 266.3-267.1 °C; IR (KBr): 2928, 1671, 1648, 1597, 1528, 1492, 1478, 1385, 1366, 1196, 823, 801, 777, 765 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 1.28 (t, *J* = 7.0 Hz, 3H, CH<sub>3</sub>), 4.18 (d, *J* = 7.0 Hz, 2H, CH<sub>2</sub>), 7.17 (s, 2H, ArH), 7.47 (s, 1H, ArH), 7.51 (d, *J* = 7.5 Hz, 2H, ArH), 7.85 (t, *J* = 7.7 Hz, 1H, ArH), 7.94 (s, 1H, ArH), 8.38 (d, *J* = 5.5 Hz, 1H, ArH), 8.82 (d, *J* = 8.5 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>): δ = 15.0, 59.7, 89.1, 91.2, 106.3, 112.0, 112.2, 116.6, 120.7, 122.0, 123.3 (d, *J*<sub>2</sub> = 24.0 Hz), 125.1, 133.6, 139.4, 140.0, 148.0, 151.0, 165.2, 177.3. HRMS (TOF ES<sup>+</sup>): *m/z* calcd for C<sub>19</sub>H<sub>14</sub>FNO<sub>4</sub> [(M+H)<sup>+</sup>], 340.0980; found, 340.0979.

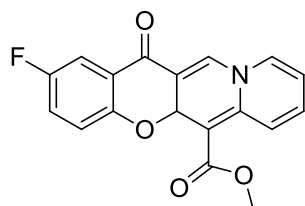
#### **Ethyl-9-ethyl-2-fluoro-13-oxo-5a,13-dihydrochromeno[2,3-*b*]quinolizine-6-carboxylate (3b)**



Red solid; Mp: 234.4-235.1 °C; IR (KBr): 2962, 2927, 1655, 1616, 1574, 1492, 1355, 1275, 1247, 1201, 1171, 1137, 837, 785, 758 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 1.22 (t, *J* =

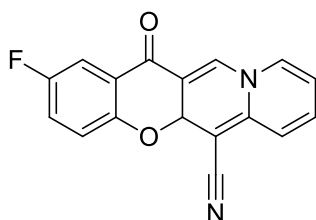
7.6 Hz, 3H, CH<sub>3</sub>), 1.27 (t, *J* = 7.1 Hz, 3H, CH<sub>3</sub>), 2.61-2.65 (m, 2H, CH<sub>2</sub>), 4.15-4.19 (m, 2H, CH<sub>2</sub>), 7.21 (s, 2H, ArH), 7.43 (s, 1H, ArH), 7.50 (s, 1H, ArH), 7.51 (s, 1H, ArH), 7.85 (d, *J* = 9.2 Hz, 1H, ArH), 7.93 (s, 1H, ArH), 8.25 (s, 1H, ArH), 8.81 (d, *J* = 9.0 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>): δ = 14.7, 14.9, 24.8, 59.6, 89.3, 90.9, 105.8, 112.0 (d, *J*<sub>2</sub> = 24.0 Hz), 120.9, 122.0, 123.1 (d, *J*<sub>2</sub> = 25.5 Hz), 125.3, 132.2, 133.6, 136.4, 141.2, 146.7, 151.0, 158.8, 165.2, 177.2. HRMS (TOF ES<sup>+</sup>): *m/z* calcd for C<sub>21</sub>H<sub>19</sub>FNO<sub>4</sub> [(M+H)<sup>+</sup>], 368.1293; found, 368.1289.

**Methyl 2-fluoro-13-oxo-5a,13-dihydrochromeno[2,3-*b*]quinolizine-6-carboxylate (3c)**



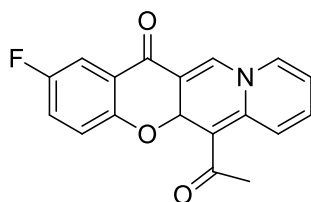
Red solid; Mp: 283.0-283.6 °C; IR (KBr): 2950, 1686, 1644, 1593, 1533, 1491, 1459, 1390, 1367, 1220, 1173, 878, 832, 777, 761 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 3.71 (s, 3H, CH<sub>3</sub>), 7.18 (d, *J* = 5.5 Hz, 2H, ArH), 7.48-7.52 (m, 3H, ArH), 7.87 (t, *J* = 7.9 Hz, 1H, ArH), 7.94 (s, 1H, ArH), 8.39 (d, *J* = 6.3 Hz, 1H, ArH), 8.82 (d, *J* = 8.9 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>): δ = 51.4, 89.1, 91.0, 106.5, 112.1 (d, *J*<sub>2</sub> = 22.5 Hz), 116.6, 120.8, 122.0, 123.3 (d, *J*<sub>2</sub> = 24.0 Hz), 125.2, 133.5, 139.5, 140.1, 148.0, 151.0, 158.0 (d, *J*<sub>1</sub> = 241.5 Hz), 165.6, 177.4. HRMS (TOF ES<sup>+</sup>): *m/z* calcd for C<sub>18</sub>H<sub>12</sub>FNO<sub>4</sub> [(M+H)<sup>+</sup>], 326.0823; found, 326.0821.

**2-Fluoro-13-oxo-5a,13-dihydrochromeno[2,3-*b*]quinolizine-6-carbonitrile (3d)**



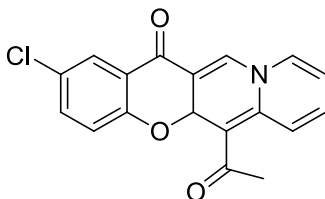
Red solid; Mp: 256.3-257.1 °C; IR (KBr): 2201, 1647, 1619, 1533, 1481, 1396, 1368, 1288, 1208, 1181, 875, 782, 766 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 7.14-7.19 (m, 2H, ArH), 7.40 (t, *J* = 5.9 Hz, 2H, ArH), 7.50-7.54 (m, 3H, ArH), 7.86 (t, *J* = 7.6 Hz, 1H, ArH), 8.38 (d, *J* = 6.7 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>): δ = 79.7, 89.0, 112.1 (d, *J*<sub>2</sub> = 22.5 Hz), 116.9, 119.4, 120.9 (d, *J*<sub>3</sub> = 7.5 Hz), 121.3, 123.5, 123.7, 125.0 (d, *J*<sub>3</sub> = 6.0 Hz), 132.7, 139.6, 140.7, 148.4, 150.9, 158.9, 176.7. HRMS (TOF ES<sup>+</sup>): *m/z* calcd for C<sub>17</sub>H<sub>9</sub>FN<sub>2</sub>O<sub>2</sub> [(M+H)<sup>+</sup>], 293.0721; found, 293.0720.

**6-Acetyl-2-fluorochromeno[2,3-*b*]quinolizin-13(5a*H*)-one (3e)**



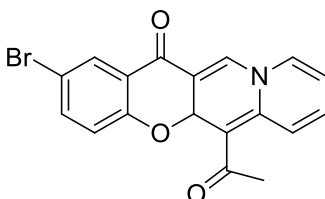
Red solid; Mp: 269.5-270.3 °C; IR (KBr): 2925, 1642, 1561, 1519, 1484, 1437, 1360, 1316, 1276, 1211, 1172, 1114, 780 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 2.37 (s, 3H, CH<sub>3</sub>), 7.19 (d, *J* = 4.7 Hz, 1H, ArH), 7.28 (t, *J* = 6.3 Hz, 1H, ArH), 7.45 (s, 1H, ArH), 7.52 (t, *J* = 7.3 Hz, 2H, ArH), 7.89 (s, 1H, ArH), 7.94 (t, *J* = 7.5 Hz, 1H, ArH), 8.49 (d, *J* = 6.2 Hz, 1H, ArH), 9.19 (d, *J* = 8.8 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>): δ = 28.6, 88.8, 101.2, 105.6, 112.1 (d, *J*<sub>2</sub> = 21.0 Hz), 117.9, 120.7, 123.0, 123.2 (d, *J*<sub>2</sub> = 24.0 Hz), 125.1, 134.9, 139.5, 141.1, 147.4, 151.0, 158.0 (d, *J*<sub>1</sub> = 244.5 Hz), 177.0, 192.4. HRMS (TOF ES<sup>+</sup>): *m/z* calcd for C<sub>18</sub>H<sub>12</sub>FNO<sub>3</sub> [(M+H)<sup>+</sup>], 310.0874; found, 310.0873.

#### 6-Acetyl-2-chlorochromeno[2,3-*b*]quinolizin-13(5*aH*)-one (3f)



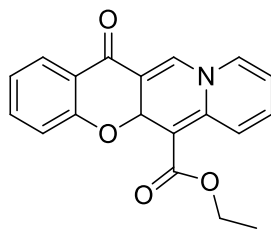
Red solid; Mp: 269.3-269.9 °C; IR (KBr): 2923, 1647, 1604, 1567, 1474, 1453, 1359, 1269, 1217, 1205, 1186, 1150, 1006, 817, 779, 733 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 2.38 (s, 3H, CH<sub>3</sub>), 7.18 (d, *J* = 8.6 Hz, 1H, ArH), 7.30 (s, 1H, ArH), 7.48 (s, 1H, ArH), 7.67 (t, *J* = 1.8 Hz, 1H, ArH), 7.76 (s, 1H, ArH), 7.90 (s, 1H, ArH), 7.95 (s, 1H, ArH), 8.49 (d, *J* = 6.2 Hz, 1H, ArH), 9.19 (d, *J* = 8.9 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>): δ = 28.6, 88.9, 101.3, 105.4, 118.0, 120.9, 123.0, 125.4, 126.0, 127.5, 135.0, 135.6, 139.5, 141.2, 147.4, 153.5, 176.8, 192.5. HRMS (TOF ES<sup>+</sup>): *m/z* calcd for C<sub>18</sub>H<sub>13</sub>ClNO<sub>3</sub> [(M+H)<sup>+</sup>], 326.0578; found, 326.0576.

#### 6-Acetyl-2-bromochromeno[2,3-*b*]quinolizin-13(5*aH*)-one (3g)



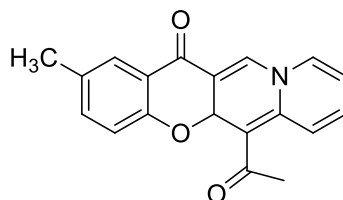
Red solid; Mp: 234.6-235.5 °C; IR (KBr): 2925, 1644, 1597, 1566, 1514, 1478, 1358, 1331, 1269, 1218, 1183, 814, 779, 713 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ = 2.37 (s, 3H, CH<sub>3</sub>), 7.11 (d, *J* = 8.6 Hz, 1H, ArH), 7.29 (t, *J* = 7.2 Hz, 1H, ArH), 7.48 (s, 1H, ArH), 7.77-7.78 (m, 1H, ArH), 7.89 (d, *J* = 6.4 Hz, 2H, ArH), 7.95 (t, *J* = 7.2 Hz, 1H, ArH), 8.49 (d, *J* = 6.1 Hz, 1H, ArH), 9.19 (d, *J* = 8.9 Hz, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>): δ = 28.6, 88.9, 101.3, 105.3, 115.1, 118.0, 121.2, 123.0, 125.8, 129.0, 135.0, 138.3, 139.5, 141.2, 147.4, 153.9, 176.6, 192.5. HRMS (TOF ES<sup>+</sup>): *m/z* calcd for C<sub>18</sub>H<sub>13</sub>BrNO<sub>3</sub> [(M+H)<sup>+</sup>], 370.0073; found, 370.0071.

#### Ethyl 13-oxo-5*a*,13-dihydrochromeno[2,3-*b*]quinolizine-6-carboxylate (3h)



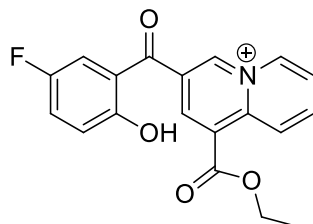
Red solid; Mp: 231.5-232.3 °C; IR (KBr): 2928, 1674, 1641, 1593, 1526, 1489, 1384, 1338, 1222, 1192, 1043, 773  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 1.21 (t,  $J$  = 7.0 Hz, 3H,  $\text{CH}_3$ ), 4.16-4.19 (m, 2H,  $\text{CH}_2$ ), 7.11-7.15 (m, 2H, ArH), 7.19 (t,  $J$  = 7.4 Hz, 1H, ArH), 7.48 (s, 1H, ArH), 7.63 (t,  $J$  = 7.4 Hz, 1H, ArH), 7.82-7.84 (m, 2H, ArH), 7.92 (s, 1H, ArH), 8.35 (d,  $J$  = 6.5 Hz, 1H, ArH), 8.83 (d,  $J$  = 9.1 Hz, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 14.9, 59.6, 89.0, 90.7, 107.3, 116.3, 118.6, 122.0, 123.2, 124.2, 127.1, 133.0, 136.2, 139.4, 139.7, 148.0, 154.8, 165.3, 178.5. HRMS (TOF ES<sup>+</sup>):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}\text{NO}_4$  [(M+H)<sup>+</sup>], 322.1074; found, 322.1071.

### 6-Acetyl-2-methylchromeno[2,3-*b*]quinolizin-13(5a*H*)-one (3i)



Red solid; Mp: 280.0-280.9 °C; IR (KBr): 2923, 1652, 1611, 1569, 1527, 1491, 1473, 1400, 1328, 1283, 1203, 1179, 1020, 813, 767, 703  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 2.33 (s, 3H,  $\text{CH}_3$ ), 2.37 (s, 3H,  $\text{CH}_3$ ), 7.03 (d,  $J$  = 7.2 Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.40 (s, 1H, ArH), 7.44 (d,  $J$  = 6.8 Hz, 1H, ArH), 7.64 (s, 1H, ArH), 7.86 (s, 1H, ArH), 7.91 (s, 1H, ArH), 8.44 (d,  $J$  = 4.2 Hz, 1H, ArH), 9.19 (d,  $J$  = 8.5 Hz, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  = 20.6, 28.6, 88.5, 100.7, 106.7, 117.6, 118.3, 122.9, 123.8, 126.7, 132.4, 134.1, 136.9, 139.4, 140.8, 147.4, 152.9, 178.3, 192.3. HRMS (TOF ES<sup>+</sup>):  $m/z$  calcd for  $\text{C}_{19}\text{H}_{16}\text{NO}_3$  [(M+H)<sup>+</sup>], 306.1125; found, 306.1122.

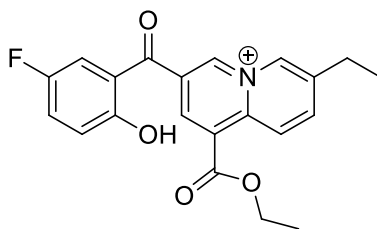
### 1-(Ethoxycarbonyl)-3-(5-fluoro-2-hydroxybenzoyl)quinolizin-5-ium (4a)



Yellow solid; Mp: 278.2-283.9 °C; IR (KBr): 3445, 2925, 1731, 1652, 1625, 1482, 1367, 1343, 1257, 1206, 1121, 1107, 1079, 792, 624  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 1.37 (t,  $J$  = 7.1 Hz, 3H,  $\text{CH}_3$ ), 4.46-4.50 (m, 2H,  $\text{CH}_2$ ), 7.04-7.07 (m, 1H, ArH), 7.38-7.44 (m, 2H, ArH), 8.23 (t,  $J$  = 6.8 Hz, 1H, ArH), 8.60 (t,  $J$  = 8.0 Hz, 1H, ArH), 8.89 (s, 1H, ArH), 9.24 (d,  $J$  = 8.9 Hz, 1H, ArH), 9.58 (d, 1H, ArH), 9.86 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 14.3, 63.6, 117.1, 117.2, 119.4 (d,  $J_3$  = 7.5 Hz), 122.8 (d,  $J_2$  = 22.5 Hz), 123.3 (d,  $J_3$  = 7.5 Hz), 125.3, 127.2, 131.5, 138.1, 140.1, 141.4, 142.3, 142.7, 154.4, 155.6 (d,  $J_1$  = 235.5 Hz), 163.2, 190.1. HRMS (ESI-TOF,  $[\text{M}-\text{ClO}_4]^+$ ): calcd for  $\text{C}_{19}\text{H}_{15}\text{FNO}_4^+$ , 340.0980; found, 340.0979.

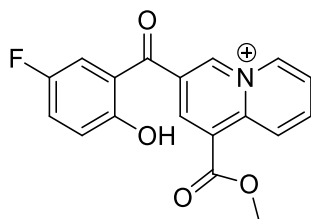


### 1-(Ethoxycarbonyl)-7-ethyl-3-(5-fluoro-2-hydroxybenzoyl)quinolizin-5-ium (4b)



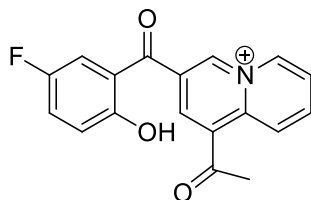
Yellow solid; Mp: 171.3-172.1 °C; IR (KBr): 3438, 2938, 1730, 1652, 1631, 1482, 1348, 1258, 1158, 1098, 1032, 855, 793, 678, 623  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 1.35 (t,  $J$  = 7.5 Hz, 3H,  $\text{CH}_3$ ), 1.42 (t,  $J$  = 7.1 Hz, 3H,  $\text{CH}_3$ ), 2.95-2.99 (m, 2H,  $\text{CH}_2$ ), 4.50-4.54 (m, 2H,  $\text{CH}_2$ ), 7.09-7.11 (m, 1H, ArH), 7.43-7.49 (m, 2H, ArH), 8.63 (d,  $J$  = 9.6 Hz, 1H, ArH), 8.88 (s, 1H, ArH), 9.19 (d,  $J$  = 9.2 Hz, 1H, ArH), 9.58 (s, 1H, ArH), 9.81 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 14.0, 14.4, 25.6, 63.5, 117.1 (d,  $J_2$  = 24.0 Hz), 119.4 (d,  $J_3$  = 7.5 Hz), 122.6 (d,  $J_2$  = 22.5 Hz), 123.6 (d,  $J_3$  = 7.5 Hz), 124.9, 127.1, 131.5, 137.2, 137.7, 140.8, 141.4, 142.4, 142.6, 154.3, 155.6 (d,  $J_1$  = 234.0 Hz), 163.3, 190.1. HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{21}\text{H}_{19}\text{FNO}_4^+$ , 368.1293; found, 368.1289.

### 3-(5-Fluoro-2-hydroxybenzoyl)-1-(methoxycarbonyl)quinolizin-5-ium (4c)



Yellow solid; Mp: 165.8-166.4 °C; IR (KBr): 3439, 2961, 2023, 1733, 1630, 1486, 1425, 1346, 1247, 1210, 1120, 1109, 801, 712, 624  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 4.05 (s, 3H,  $\text{CH}_3$ ), 7.08-7.11 (m, 1H, ArH), 7.44-7.46 (m, 1H, ArH), 7.48 (d,  $J$  = 3.0 Hz, 1H, ArH), 8.31 (t,  $J$  = 7.0 Hz, 1H, ArH), 8.67 (t,  $J$  = 8.2 Hz, 1H, ArH), 8.93 (s, 1H, ArH), 9.27 (d,  $J$  = 9.0 Hz, 1H, ArH), 9.66 (d,  $J$  = 6.7 Hz, 1H, ArH), 9.95 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 54.3, 117.2 (d,  $J_2$  = 24.0 Hz), 119.4, 122.8 (d,  $J_2$  = 22.5 Hz), 123.4, 125.4, 125.5, 126.9, 131.6, 138.2, 140.3, 141.5, 142.2, 142.8, 154.4, 155.7 (d,  $J_1$  = 234.0 Hz), 163.7, 190.1. HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{18}\text{H}_{13}\text{FNO}_4^+$ , 326.0823; found, 326.0820.

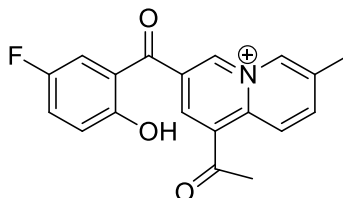
### 1-Acetyl-3-(5-fluoro-2-hydroxybenzoyl)quinolizin-5-ium (4d)



Yellow solid; Mp: > 300 °C; IR (KBr): 3439, 2927, 2021, 1694, 1630, 1581, 1486, 1363, 1347, 1279, 1218, 1121, 1108, 784, 683, 623  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 2.86 (s, 3H,  $\text{CH}_3$ ), 7.09-7.11 (m, 1H, ArH), 7.48 (t,  $J$  = 9.0 Hz, 2H, ArH), 8.29 (t,  $J$  = 6.8 Hz, 1H, ArH), 8.63 (t,  $J$  = 8.0 Hz, 1H, ArH), 8.97 (d,  $J$  = 8.9 Hz, 1H, ArH), 9.00 (s, 1H, ArH), 9.66 (d,  $J$  = 6.6 Hz, 1H, ArH), 9.87 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,

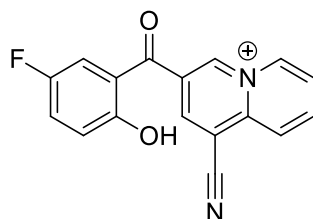
DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 30.6, 117.2 (d,  $J_2$  = 24.0 Hz), 119.5 (d,  $J_3$  = 7.5 Hz), 122.9 (d,  $J_2$  = 24.0 Hz), 123.4 (d,  $J_3$  = 7.5 Hz), 125.3, 125.7, 131.8, 134.1, 136.4, 140.0, 141.3, 141.4, 141.8, 154.6, 155.7 (d,  $J_1$  = 235.5 Hz), 190.3, 198.5. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>18</sub>H<sub>13</sub>FNO<sub>3</sub><sup>+</sup>, 310.0874; found, 310.0871.

#### 1-Acetyl-3-(5-fluoro-2-hydroxybenzoyl)-7-methylquinolizin-5-ium (4e)



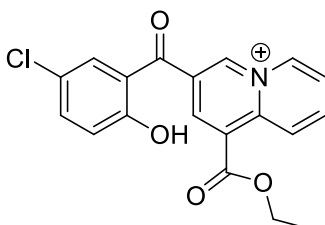
Yellow solid; Mp: > 300 °C; IR (KBr): 3439, 2933, 1701, 1650, 1624, 1487, 1365, 1346, 1284, 1211, 1108, 836, 789, 684, 624 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 2.61 (s, 3H, CH<sub>3</sub>), 2.86 (s, 3H, CH<sub>3</sub>), 7.09-7.11 (m, 1H, ArH), 7.45-7.50 (m, 2H, ArH), 8.52 (d,  $J$  = 9.2 Hz, 1H, ArH), 8.90 (d,  $J$  = 9.1 Hz, 1H, ArH), 8.95 (s, 1H, ArH), 9.52 (s, 1H, ArH), 9.69 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 18.4, 30.5, 117.1 (d,  $J_2$  = 22.5 Hz), 119.5 (d,  $J_3$  = 7.5 Hz), 122.7 (d,  $J_2$  = 24.0 Hz), 123.5 (d,  $J_3$  = 6.0 Hz), 125.0, 131.8, 134.0, 135.5, 136.1, 138.0, 139.7, 141.2, 143.3, 154.4, 155.7 (d,  $J_1$  = 234.0 Hz), 190.3, 198.5. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>19</sub>H<sub>15</sub>FNO<sub>3</sub><sup>+</sup>, 324.1030; found, 324.1031.

#### 1-Cyano-3-(5-fluoro-2-hydroxybenzoyl)quinolizin-5-ium (4f)



Yellow solid; Mp: 276.2-277.1 °C; IR (KBr): 3439, 2023, 1693, 1636, 1482, 1437, 1345, 1283, 1249, 1213, 1121, 1108, 1001, 784, 681, 624 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 7.05-7.08 (m, 1H, ArH), 7.38-7.39 (m, 1H, ArH), 7.43-7.45 (m, 1H, ArH), 8.34-8.35 (m, 1H, ArH), 8.72 (t,  $J$  = 2.8 Hz, 2H, ArH), 9.24 (d,  $J$  = 1.2 Hz, 1H, ArH), 9.66 (d,  $J$  = 6.8 Hz, 1H, ArH), 9.97 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 110.7, 113.8, 117.1 (d,  $J_2$  = 24.0 Hz), 119.6, 123.0 (d,  $J_2$  = 22.5 Hz), 123.2, 125.2, 126.3, 132.0, 140.4, 142.6, 142.8, 142.9, 143.0, 154.5, 154.9, 189.2. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>17</sub>H<sub>10</sub>FN<sub>2</sub>O<sub>2</sub><sup>+</sup>, 293.0721; found, 293.0720.

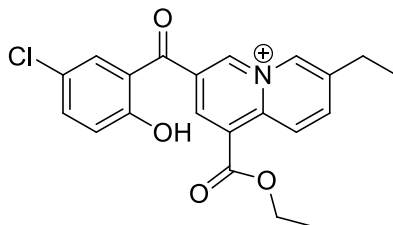
#### 3-(5-Chloro-2-hydroxybenzoyl)-1-(ethoxycarbonyl)quinolizin-5-ium (4g)



Yellow solid; Mp: 169.2-170.6 °C; IR (KBr): 3439, 2924, 2024, 1726, 1632, 1467, 1438, 1405, 1343, 1261, 1225, 1096, 785, 622 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 1.39 (t,  $J$  = 7.1 Hz, 3H, CH<sub>3</sub>), 4.47-4.51 (m, 2H, CH<sub>2</sub>), 7.07 (d,  $J$  = 9.1 Hz, 1H, ArH), 7.59 (t,  $J$  = 2.6 Hz, 2H, ArH), 8.27 (t,  $J$  = 6.9 Hz, 1H, ArH), 8.63 (t,  $J$  = 7.9 Hz, 1H, ArH), 8.90 (s,

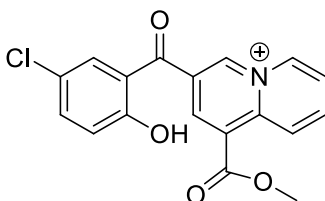
1H, ArH), 9.24 (d,  $J = 9.0$  Hz, 1H, ArH), 9.61 (d,  $J = 6.7$  Hz, 1H, ArH), 9.90 (s, 1H, ArH) ;  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta = 14.3, 63.6, 119.7, 123.8, 124.6, 125.3, 125.5, 127.2, 130.6, 131.4, 135.1, 138.0, 140.2, 141.4, 142.3, 142.9, 156.6, 163.2, 190.0$ . HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{19}\text{H}_{15}\text{ClNO}_4^+$ , 356.0684; found, 356.0686.

### 3-(5-Chloro-2-hydroxybenzoyl)-1-(ethoxycarbonyl)-7-ethylquinolizin-5-ium (4h)



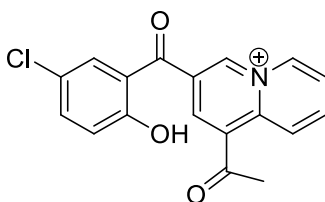
Yellow solid; Mp: 150.3-151.1 °C; IR (KBr): 3433, 2924, 1726, 1631, 1465, 1356, 1267, 1188, 1082, 776, 695, 623  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta = 1.35$  (t,  $J = 7.5$  Hz, 3H,  $\text{CH}_3$ ), 1.42 (t,  $J = 7.1$  Hz, 3H,  $\text{CH}_3$ ), 2.95-2.99 (m, 2H,  $\text{CH}_2$ ), 4.50-4.54 (m, 2H,  $\text{CH}_2$ ), 7.10 (d,  $J = 8.6$  Hz, 1H, ArH), 7.61 (d,  $J = 2.6$  Hz, 1H, ArH), 7.63 (d,  $J = 2.5$  Hz, 1H, ArH), 8.62 (d,  $J = 9.2$  Hz, 1H, ArH), 8.88 (s, 1H, ArH), 9.19 (d,  $J = 9.2$  Hz, 1H, ArH), 9.57 (s, 1H, ArH), 9.81 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta = 14.0, 14.3, 25.6, 63.5, 119.7, 123.7, 124.8, 124.9, 127.1, 130.5, 131.4, 135.0, 137.1, 137.6, 140.8, 141.4, 142.4, 142.6, 156.5, 163.3, 190.0$ . HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{21}\text{H}_{19}\text{ClNO}_4^+$ , 384.0997; found, 384.0996.

### 3-(5-Chloro-2-hydroxybenzoyl)-1-(methoxycarbonyl)quinolizin-5-ium (4i)



Yellow solid; Mp: > 300 °C; IR (KBr): 3439, 2926, 2025, 1735, 1654, 1637, 1470, 1426, 1341, 1280, 1266, 1102, 1002, 798, 780, 625  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta = 4.02$  (s, 3H,  $\text{CH}_3$ ), 7.08 (d,  $J = 9.4$  Hz, 1H, ArH), 7.59 (s, 1H, ArH), 7.60 (s, 1H, ArH), 8.28 (t,  $J = 6.8$  Hz, 1H, ArH), 8.64 (t,  $J = 7.9$  Hz, 1H, ArH), 8.90 (s, 1H, ArH), 9.25 (d,  $J = 8.9$  Hz, 1H, ArH), 9.63 (d,  $J = 6.6$  Hz, 1H, ArH), 9.92 (s, 1H, ArH) ;  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta = 54.3, 119.7, 123.8, 124.6, 125.4, 125.5, 126.9, 130.6, 131.5, 135.1, 138.1, 140.2, 141.5, 142.3, 142.8, 156.6, 163.7, 189.9$ . HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{18}\text{H}_{13}\text{ClNO}_4^+$ , 342.0528; found, 342.0529.

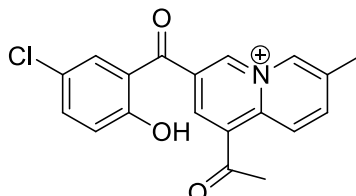
### 1-Acetyl-3-(5-chloro-2-hydroxybenzoyl)quinolizin-5-ium (4j)



Yellow solid; Mp: 138.8–139.4 °C; IR (KBr): 3433, 2923, 2022, 1694, 1632, 1510, 1472, 1359, 1343, 1284, 1208, 1176, 1097, 784, 697, 622  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,

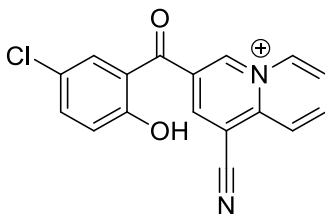
DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 2.82 (s, 3H, CH<sub>3</sub>), 7.08 (d, *J* = 8.5 Hz, 1H, ArH), 7.59 (d, *J* = 7.9 Hz, 1H, ArH), 7.60 (s, 1H, ArH), 8.24 (t, *J* = 6.9 Hz, 1H, ArH), 8.59 (t, *J* = 7.8 Hz, 1H, ArH), 8.94 (s, 1H, ArH), 8.95 (s, 1H, ArH), 9.59 (d, *J* = 6.7 Hz, 1H, ArH), 9.82 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 30.5, 119.9, 123.8, 124.6, 125.3, 125.7, 130.7, 131.7, 134.1, 135.2, 136.3, 139.9, 141.3, 141.4, 141.8, 156.8, 190.1, 198.5. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>18</sub>H<sub>13</sub>ClNO<sub>3</sub><sup>+</sup>, 326.0578; found, 326.0576.

#### 1-Acetyl-3-(5-chloro-2-hydroxybenzoyl)-7-methylquinolizin-5-ium (4k)



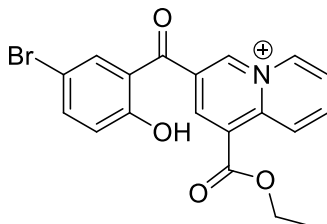
Yellow solid; Mp: 236.1-237.2 °C; IR (KBr): 3430, 2925, 1695, 1631, 1420, 1352, 1320, 1280, 1237, 1194, 1121, 1076, 824, 777, 621 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 2.60 (s, 3H, CH<sub>3</sub>), 2.85 (s, 3H, CH<sub>3</sub>), 7.10 (t, *J* = 4.7 Hz, 1H, ArH), 7.62 (d, *J* = 2.3 Hz, 2H, ArH), 8.51 (d, *J* = 9.0 Hz, 1H, ArH), 8.89 (d, *J* = 9.1 Hz, 1H, ArH), 8.93 (s, 1H, ArH), 9.51 (s, 1H, ArH), 9.68 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 18.4, 30.5, 119.8, 123.8, 124.8, 125.0, 130.6, 131.7, 134.0, 135.1, 135.4, 136.1, 138.0, 139.8, 141.3, 143.3, 156.7, 190.1, 198.5. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>19</sub>H<sub>15</sub>ClNO<sub>3</sub><sup>+</sup>, 340.0735; found, 340.0732.

#### 3-(5-Chloro-2-hydroxybenzoyl)-1-cyanoquinolizin-5-ium (4l)



Yellow solid; Mp: > 300 °C; IR (KBr): 3440, 2199, 1637, 1472, 1438, 1402, 1351, 1289, 1213, 1121, 1097, 848, 787, 702, 625 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 7.10 (d, *J* = 8.8 Hz, 1H, ArH), 7.60-7.63 (m, 1H, ArH), 7.64 (d, *J* = 2.6 Hz, 1H, ArH), 8.39-8.41 (m, 1H, ArH), 8.76 (t, *J* = 2.6 Hz, 2H, ArH), 9.30 (s, 1H, ArH), 9.70 (d, *J* = 6.7 Hz, 1H, ArH), 10.03 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$  = 110.6, 113.9, 119.9, 123.8, 124.4, 125.3, 126.3, 130.6, 132.0, 135.3, 140.5, 142.7, 142.8, 142.9, 143.0, 156.8, 189.1. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>17</sub>H<sub>10</sub>ClN<sub>2</sub>O<sub>2</sub><sup>+</sup>, 309.0425; found, 309.0421.

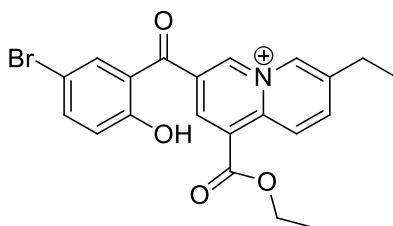
#### 3-(5-Bromo-2-hydroxybenzoyl)-1-(ethoxycarbonyl) quinolizin-5-ium (4m)



Yellow solid; Mp: 164.0–164.9 °C; IR (KBr): 3439, 2923, 1729, 1663, 1630, 1594, 1416, 1389, 1278, 1259, 1094, 982, 781, 662, 624 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta$

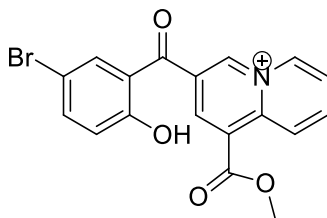
= 1.40 (t,  $J = 7.1$  Hz, 3H, CH<sub>3</sub>), 4.49-4.53 (m, 2H, CH<sub>2</sub>), 7.04 (d,  $J = 8.9$  Hz, 1H, ArH), 7.71 (s, 1H, ArH), 7.73(d,  $J = 2.4$  Hz, 1H, ArH), 8.29 (t,  $J = 7.0$  Hz, 1H, ArH), 8.65 (t,  $J = 8.2$  Hz, 1H, ArH), 8.91 (s, 1H, ArH), 9.25 (d,  $J = 9.0$  Hz, 1H, ArH), 9.64 (d,  $J = 6.7$  Hz, 1H, ArH), 9.92 (s, 1H, ArH) ; <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta = 14.3, 63.6, 111.1, 120.2, 125.2, 125.4, 125.5, 127.2, 131.5, 133.5, 137.9, 138.0, 140.2, 141.5, 142.3, 142.8, 157.0, 163.2, 189.9$ . HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>19</sub>H<sub>15</sub>BrNO<sub>4</sub><sup>+</sup>, 400.0179; found, 400.0177.

### 3-(5-Bromo-2-hydroxybenzoyl)-1-(ethoxycarbonyl)-7-ethylquinolizin-5-ium (4n)



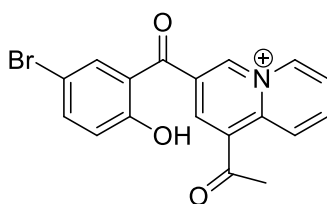
Yellow solid; Mp: 110.1–110.8 °C; IR (KBr): 3433, 2920, 1710, 1630, 1611, 1587, 1515, 1427, 1330, 1311, 1246, 1221, 1093, 989, 847, 772, 624 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta = 1.35$  (t,  $J = 7.5$  Hz, 3H, CH<sub>3</sub>), 1.41 (t,  $J = 7.1$  Hz, 3H, CH<sub>3</sub>), 2.96 (t,  $J = 7.5$  Hz, 2H, CH<sub>2</sub>), 4.51 (t,  $J = 7.1$  Hz, 2H, CH<sub>2</sub>), 7.05 (d,  $J = 8.8$  Hz, 1H, ArH), 7.71 (d,  $J = 2.2$  Hz, 1H, ArH), 7.72-7.74 (m, 1H, ArH), 8.61 (d,  $J = 9.2$  Hz, 1H, ArH), 8.87 (s, 1H, ArH), 9.19 (d,  $J = 9.2$  Hz, 1H, ArH), 9.56 (s, 1H, ArH), 9.80 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta = 13.9, 14.3, 25.6, 63.5, 111.1, 120.1, 124.9, 125.3, 127.0, 131.4, 133.3, 137.1, 137.6, 137.8, 140.8, 141.5, 142.4, 142.6, 156.8, 163.2, 189.9$ . HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>21</sub>H<sub>19</sub>BrNO<sub>4</sub><sup>+</sup>, 428.0492; found, 428.0490.

### 3-(5-Bromo-2-hydroxybenzoyl)-1-(methoxycarbonyl)quinolizin-5-ium (4o)



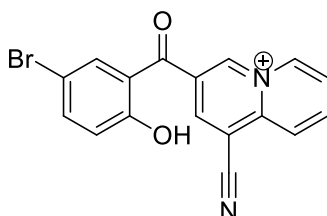
Yellow solid; Mp: 172.7–173.8 °C; IR (KBr): 3439, 2959, 1734, 1655, 1621, 1470, 1339, 1280, 1265, 1225, 1101, 1026, 798, 687, 624 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta = 4.05$  (s, 3H, CH<sub>3</sub>), 7.06 (t,  $J = 1.6$  Hz, 1H, ArH), 7.73 (s, 1H, ArH), 7.74 (d,  $J = 2.5$  Hz, 1H, ArH), 8.31-8.33 (m, 1H, ArH), 8.68 (t,  $J = 8.5$  Hz, 1H, ArH), 8.92 (d,  $J = 1.3$  Hz, 1H, ArH), 9.26 (d,  $J = 9.0$  Hz, 1H, ArH), 9.67 (d,  $J = 6.7$  Hz, 1H, ArH), 9.95 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>):  $\delta = 54.3, 111.2, 120.2, 125.3, 125.4, 125.5, 127.0, 131.5, 133.5, 137.9, 138.2, 140.3, 141.5, 142.3, 142.8, 157.0, 163.7, 189.8$ . HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>18</sub>H<sub>13</sub>BrNO<sub>4</sub><sup>+</sup>, 386.0022; found, 386.0020.

### 1-Acetyl-3-(5-bromo-2-hydroxybenzoyl)quinolizin-5-ium (4p)



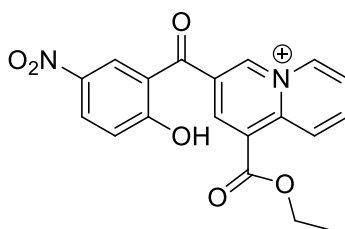
Yellow solid; Mp: >300 °C; IR (KBr): 3440, 2924, 1698, 1625, 1599, 1469, 1439, 1352, 1291, 1210, 1121, 1107, 1092, 790, 699, 636, 624 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 2.86 (s, 3H, CH<sub>3</sub>), 7.06 (d, *J* = 8.4 Hz, 1H, ArH), 7.75 (s, 1H, ArH), 7.76 (s, 1H, ArH), 8.30 (t, *J* = 6.8 Hz, 1H, ArH), 8.64 (t, *J* = 7.9 Hz, 1H, ArH), 8.97 (d, *J* = 8.9 Hz, 1H, ArH), 9.01 (s, 1H, ArH), 9.63 (d, *J* = 6.6 Hz, 1H, ArH), 9.88 (s, 1H, ArH), 10.97 (s, 1H, ArOH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 30.7, 111.2, 120.3, 125.3, 125.4, 125.7, 131.8, 133.5, 134.1, 136.3, 138.0, 140.0, 141.3, 141.4, 141.9, 157.2, 190.0, 198.6. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>18</sub>H<sub>13</sub>BrNO<sub>3</sub><sup>+</sup>, 370.0073; found, 370.0073.

### 3-(5-Bromo-2-hydroxybenzoyl)-1-cyanoquinolizin-5-ium (4q)



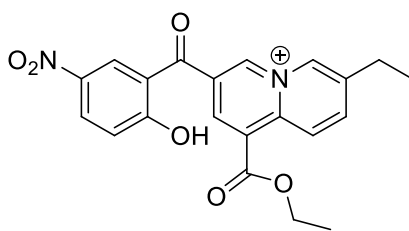
Yellow solid; Mp: >300 °C; IR (KBr): 3443, 2201, 1637, 1605, 1498, 1469, 1351, 1289, 1199, 1121, 1095, 809, 698, 625 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 6.95 (s, 1H, ArH), 7.61 (d, *J* = 6.5 Hz, 1H, ArH), 7.63 (d, *J* = 6.7 Hz, 1H, ArH), 8.28 (s, 1H, ArH), 8.65 (s, 2H, ArH), 9.18 (s, 1H, ArH), 9.59 (s, 1H, ArH), 9.91 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 110.6, 111.2, 113.9, 120.3, 125.0, 125.3, 126.3, 132.0, 133.4, 138.1, 140.4, 142.6, 142.8, 142.9, 143.1, 157.2, 189.0. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>17</sub>H<sub>10</sub>BrN<sub>2</sub>O<sub>2</sub><sup>+</sup>, 352.9920; found, 352.9917.

### 1-(Ethoxycarbonyl)-3-(2-hydroxy-5-nitrobenzoyl)quinolizin-5-ium (4r)



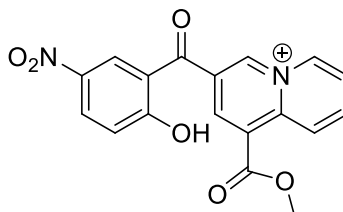
Yellow solid; Mp: 118.5–119.3 °C; IR (KBr): 3440, 2923, 1729, 1676, 1636, 1496, 1338, 1252, 1115, 1035, 984, 802, 736, 634 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 1.40 (t, *J* = 9.1 Hz, 3H, CH<sub>3</sub>), 4.49–4.52 (m, 2H, CH<sub>2</sub>), 7.24 (d, *J* = 8.8 Hz, 1H, ArH), 8.29 (t, *J* = 6.9 Hz, 1H, ArH), 8.42 (d, *J* = 2.6 Hz, 1H, ArH), 8.68 (s, 1H, ArH), 8.66 (t, *J* = 8.0 Hz, 1H, ArH), 8.94 (s, 1H, ArH), 9.25 (d, *J* = 8.9 Hz, 1H, ArH), 9.60 (d, *J* = 6.7 Hz, 1H, ArH), 9.94 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 14.3, 63.6, 118.5, 123.8, 125.4, 125.6, 127.3, 127.8, 130.2, 131.1, 137.6, 140.2, 140.3, 141.7, 142.4, 143.3, 163.0, 163.2, 189.2. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O<sub>6</sub><sup>+</sup>, 367.0925; found, 367.0922.

### 1-(Ethoxycarbonyl)-7-ethyl-3-(2-hydroxy-5-nitrobenzoyl)quinolizin-5-ium (4s)



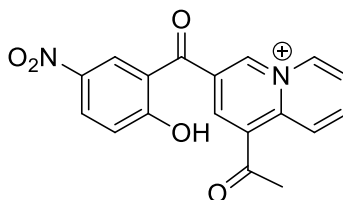
Yellow solid; Mp: 169.3–170.2 °C; IR (KBr): 3439, 2925, 1732, 1664, 1632, 1613, 1591, 1523, 1433, 1338, 1315, 1247, 1228, 1097, 1083, 989, 852, 777, 624  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 1.34 (t,  $J$  = 7.5 Hz, 3H,  $\text{CH}_3$ ), 1.42 (t,  $J$  = 7.1 Hz, 3H,  $\text{CH}_3$ ), 2.96(d,  $J$  = 7.5 Hz, 2H,  $\text{CH}_2$ ), 4.52(t,  $J$  = 7.1 Hz, 2H,  $\text{CH}_2$ ), 7.26 (d,  $J$  = 9.7 Hz, 1H, ArH), 8.44 (d,  $J$  = 2.5 Hz, 1H, ArH), 8.45 (s, 1H, ArH), 8.63 (d,  $J$  = 9.2 Hz, 1H, ArH), 8.91 (s, 1H, ArH), 9.19 (d,  $J$  = 9.2 Hz, 1H, ArH), 9.52 (s, 1H, ArH), 9.82(s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 14.0, 14.3, 25.6, 63.6, 118.5, 123.9, 125.0, 127.2, 127.7, 130.1, 131.1, 136.7, 137.7, 140.2, 140.9, 141.5, 142.8, 142.8, 162.9, 163.2, 189.3. HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{21}\text{H}_{19}\text{N}_2\text{O}_6^+$ , 395.1238; found, 395.1235.

### 3-(2-Hydroxy-5-nitrobenzoyl)-1-(methoxycarbonyl)quinolizin-5-ium (4t)



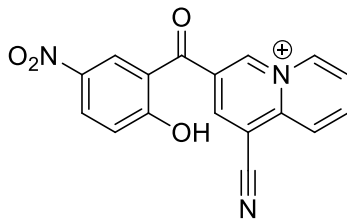
Yellow solid; Mp: 122.8–123.6 °C; IR (KBr): 3439, 2923, 1729, 1658, 1634, 1621, 1515, 1437, 1357, 1336, 1292, 1263, 1147, 1121, 1102, 1027, 998, 805, 685, 624  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 4.05 (s, 3H,  $\text{CH}_3$ ), 7.26 (d,  $J$  = 9.1 Hz, 1H, ArH), 8.33 (t,  $J$  = 6.9 Hz, 1H, ArH), 8.44-8.47 (m, 2H, ArH), 8.70 (t,  $J$  = 8.0 Hz, 1H, ArH), 8.96 (s, 1H, ArH), 9.26 (d,  $J$  = 8.9 Hz, 1H, ArH), 9.63 (d,  $J$  = 6.7 Hz, 1H, ArH), 9.98(s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 54.4, 118.5, 123.9, 125.5, 125.6, 127.1, 127.9, 130.2, 131.2, 137.8, 140.2, 140.4, 141.7, 142.4, 143.3, 163.0, 163.7, 189.2. HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_6^+$ , 353.0768; found, 353.0767.

### 1-Acetyl-3-(2-hydroxy-5-nitrobenzoyl)quinolizin-5-ium (4u)



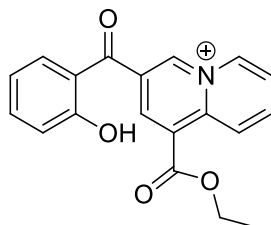
Yellow solid; Mp: 242.8-243.6 °C; IR (KBr): 3439, 2924, 1703, 1654, 1630, 1475, 1344, 1289, 1247, 1206, 1121, 1094, 906, 782, 747, 624  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 2.84 (s, 3H,  $\text{CH}_3$ ), 7.24 (d,  $J$  = 9.0 Hz, 1H, ArH), 8.27 (t,  $J$  = 6.9 Hz, 1H, ArH), 8.42 (d,  $J$  = 2.8 Hz, 1H, ArH), 8.43-8.45 (m, 1H, ArH), 8.62 (t,  $J$  = 8.0 Hz, 1H, ArH), 8.95 (d,  $J$  = 8.9 Hz, 1H, ArH), 9.0 (s, 1H, ArH), 9.57 (d,  $J$  = 6.7 Hz, 1H, ArH), 9.87(s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 30.6, 118.6, 123.9, 125.4, 125.8, 127.8, 130.2, 131.3, 134.3, 134.3, 135.9, 140.0, 140.2, 141.5, 142.3, 163.1, 189.4, 198.6. HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_5^+$ , 337.0819; found, 337.0818.

#### 1-Cyano-3-(2-hydroxy-5-nitrobenzoyl)quinolizin-5-ium (4v)



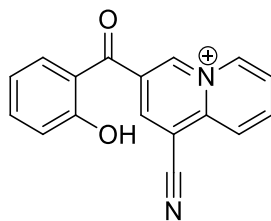
Yellow solid; Mp: >300 °C; IR (KBr): 3432, 2245, 1683, 1634, 1525, 1498, 1438, 1339, 1296, 1261, 1121, 1102, 898, 837, 627 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 7.25-7.26 (m, 1H, ArH), 8.40-8.43 (m, 2H, ArH), 8.45-8.46 (m, 1H, ArH), 8.76 (s, 1H, ArH), 8.78 (d, *J* = 3.4 Hz, 1H, ArH), 9.37 (d, *J* = 1.1 Hz, 1H, ArH), 9.69 (d, *J* = 6.7 Hz, 1H, ArH), 10.07(s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 110.6, 113.9, 118.7, 123.6, 125.3, 126.4, 127.9, 130.3, 131.6, 140.3, 140.5, 140.5, 142.6, 143.2, 143.2, 163.2, 188.6. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>17</sub>H<sub>10</sub>N<sub>3</sub>O<sub>4</sub><sup>+</sup>, 320.0666; found, 320.0660.

#### 1-(Ethoxycarbonyl)-3-(2-hydroxybenzoyl) quinolizin-5-ium (4w)



Yellow solid; Mp: 170.3–171.1 °C; IR (KBr): 3439, 2925, 1730, 1647, 1635, 1620, 1487, 1342, 1258, 1222, 1156, 1104, 1078, 769, 665, 624 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 1.42 (t, *J* = 7.1 Hz, 3H, CH<sub>3</sub>), 4.51-4.54 (m, 2H, CH<sub>2</sub>), 7.05-7.10 (m, 2H, ArH), 7.60-7.66 (m, 2H, ArH), 8.31 (t, *J* = 7.0 Hz, 1H, ArH), 8.66-8.68 (m, 1H, ArH), 8.93 (s, 1H, ArH), 9.27 (d, *J* = 8.9 Hz, 1H, ArH), 9.66 (d, *J* = 6.5 Hz, 1H, ArH), 9.93 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 14.4, 63.5, 117.9, 120.3, 122.9, 125.3, 125.5, 127.1, 132.0, 132.0, 136.2, 138.3, 140.2, 141.3, 142.2, 142.5, 158.4, 163.3, 191.4. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>19</sub>H<sub>16</sub>NO<sub>4</sub><sup>+</sup>, 322.1074; found, 322.1071.

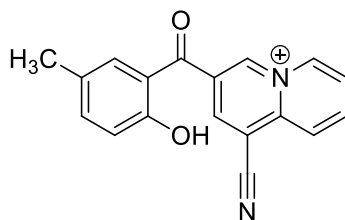
#### 1-Cyano-3-(2-hydroxybenzoyl)quinolizin-5-ium (4x)



Yellow solid; Mp: >300 °C; IR (KBr): 3439, 2197, 1637, 1611, 1485, 1436, 1351, 1319, 1287, 1242, 1174, 1121, 1096, 810, 705, 625 cm<sup>-1</sup>; <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 7.06 (d, *J* = 7.1 Hz, 1H, ArH), 7.09 (d, *J* = 8.3 Hz, 1H, ArH), 7.61 (d, *J* = 7.4 Hz, 1H, ArH), 7.64 (d, *J* = 8.0 Hz, 1H, ArH), 8.39 (s, 1H, ArH), 8.76 (s, 2H, ArH), 9.28 (s, 1H, ArH), 9.70 (d, *J* = 6.1 Hz, 1H, ArH), 10.01 (s, 1H, ArH); <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>): δ = 110.6, 113.9, 118.0, 120.3, 122.7, 125.2, 126.3, 132.1, 132.6, 136.4, 140.4, 142.5, 142.8, 142.8, 142.9, 158.5, 190.5. HRMS (ESI-TOF, [M-ClO<sub>4</sub>]<sup>+</sup>): calcd for C<sub>17</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, 275.0815; found, 275.0814.

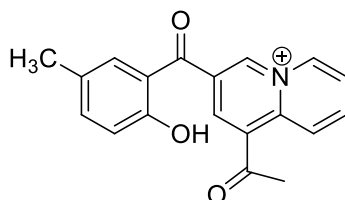


### 1-Cyano-3-(2-hydroxy-5-methylbenzoyl)quinolizin-5-ium (4y)



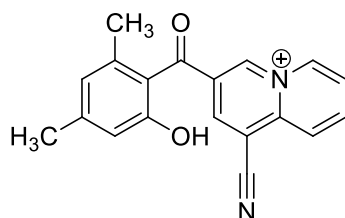
Yellow solid; Mp: >300 °C; IR (KBr): 3438, 2925, 2022, 1637, 1489, 1435, 1353, 1289, 1248, 1196, 1173, 1094, 919, 790, 678, 625  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 2.26 (s, 3H,  $\text{CH}_3$ ), 6.96 (d,  $J$  = 9.0 Hz, 1H, ArH), 7.41 (d,  $J$  = 7.0 Hz, 2H, ArH), 8.33-8.36 (m, 1H, ArH), 8.70 (s, 1H, ArH), 8.72 (d,  $J$  = 6.4 Hz, 1H, ArH), 9.22 (s, 1H, ArH), 9.66 (d,  $J$  = 6.7 Hz, 1H, ArH), 9.96 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 20.2, 110.6, 113.9, 117.9, 122.2, 125.2, 126.2, 129.2, 131.8, 132.6, 137.3, 140.3, 142.4, 142.6, 142.7, 142.9, 156.4, 190.6. HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_2^+$ , 289.0972; found, 289.0970.

### 1-Acetyl-3-(2-hydroxy-5-methylbenzoyl)quinolizin-5-ium (4z)



Yellow solid; Mp: 206.5–207.3 °C; IR (KBr): 3432, 2925, 1702, 1634, 1488, 1460, 1438, 1356, 1294, 1251, 1177, 1121, 1094, 785, 677, 624  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 2.34 (s, 3H,  $\text{CH}_3$ ), 2.89 (s, 3H,  $\text{CH}_3$ ), 7.04 (d,  $J$  = 8.4 Hz, 1H, ArH), 7.47-7.49 (m, 1H, ArH), 7.52 (s, 1H, ArH), 8.31 (t,  $J$  = 6.5 Hz, 1H, ArH), 8.64-8.66 (m, 1H, ArH), 9.02 (s, 1H, ArH), 9.04 (s, 1H, ArH), 9.65 (d,  $J$  = 6.7 Hz, 1H, ArH), 9.87 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 20.2, 30.5, 117.9, 122.3, 125.2, 125.6, 129.2, 131.9, 132.4, 134.0, 136.7, 137.2, 139.9, 141.1, 141.3, 141.3, 156.6, 191.7, 198.5. HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{19}\text{H}_{16}\text{NO}_3^+$ , 306.1125; found, 306.1122.

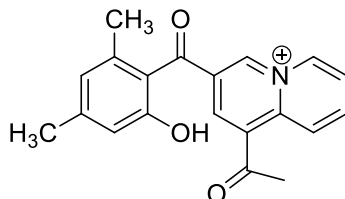
### 1-Cyano-3-(2-hydroxy-4,6-dimethylbenzoyl)quinolizin-5-ium (4a')



Yellow solid; Mp: 283.5–284.5 °C; IR (KBr): 3437, 2198, 1643, 1563, 1468, 1399, 1305, 1256, 1222, 1109, 837, 788, 624  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 2.19 (s, 3H,  $\text{CH}_3$ ), 2.31 (s, 3H,  $\text{CH}_3$ ), 6.68 (s, 1H, ArH), 6.73 (s, 1H, ArH), 8.34-8.37 (m, 1H, ArH), 8.74 (d,  $J$  = 4.1 Hz, 2H, ArH), 9.18 (d,  $J$  = 1.3 Hz, 1H, ArH), 9.77 (d,  $J$  = 6.8 Hz, 1H, ArH), 9.90 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 19.6, 21.6, 111.2, 113.8, 114.8, 121.3, 123.5, 125.2, 126.2, 132.2, 138.6, 140.6, 141.8, 142.9, 143.2, 143.2, 143.2, 156.4, 192.0. HRMS (ESI-TOF,  $[\text{M-ClO}_4]^+$ ): calcd for  $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_2^+$ , 303.1128; found,

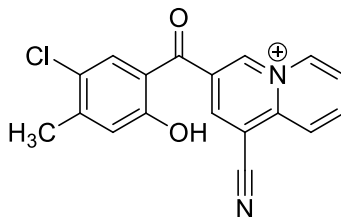
303.1120.

**1-Acetyl-3-(2-hydroxy-4,6-dimethylbenzoyl)quinolizin-5-ium (4b')**



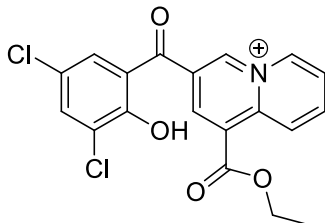
Yellow solid; Mp: 226.5–227.5 °C; IR (KBr): 3430, 1701, 1635, 1553, 1473, 1400, 1375, 1256, 1163, 1120, 1008, 804, 665, 625  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 2.21 (s, 3H,  $\text{CH}_3$ ), 2.31 (s, 3H,  $\text{CH}_3$ ), 2.86 (s, 3H,  $\text{CH}_3$ ), 6.68 (s, 1H, ArH), 6.73 (s, 1H, ArH), 8.23–8.25 (m, 1H, ArH), 8.59–8.62 (m, 1H, ArH), 8.94–8.97 (m, 2H, ArH), 9.69 (d,  $J$  = 6.8 Hz, 1H, ArH), 9.71 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 19.6, 21.6, 30.5, 114.8, 121.6, 123.4, 125.3, 125.7, 131.9, 134.6, 135.4, 138.4, 140.2, 141.4, 141.6, 142.0, 142.9, 156.3, 192.9, 198.5. HRMS (ESI-TOF,  $[\text{M}-\text{ClO}_4]^+$ ): calcd for  $\text{C}_{20}\text{H}_{18}\text{NO}_3^+$ , 320.1281; found, 320.1273.

**3-(5-Chloro-2-hydroxy-4-methylbenzoyl)-1-cyanoquinolizin-5-ium (4c')**



Yellow solid; Mp: >300 °C; IR (KBr): 3439, 2194, 1637, 1561, 1483, 1401, 1325, 1246, 1210, 1122, 1108, 824, 785, 625  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 2.37 (s, 3H,  $\text{CH}_3$ ), 7.04 (s, 1H, ArH), 7.60 (s, 1H, ArH), 8.36–8.39 (m, 1H, ArH), 8.72–8.75 (m, 2H, ArH), 9.26 (d,  $J$  = 1.1 Hz, 1H, ArH), 9.66 (d,  $J$  = 6.7 Hz, 1H, ArH), 9.99 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 20.6, 110.6, 113.9, 120.4, 122.1, 124.5, 125.2, 126.3, 131.3, 132.3, 140.3, 142.6, 142.7, 142.8, 143.0, 144.2, 157.0, 188.9. HRMS (ESI-TOF,  $[\text{M}-\text{ClO}_4]^+$ ): calcd for  $\text{C}_{18}\text{H}_{12}\text{ClN}_2\text{O}_2^+$ , 323.0582; found, 323.0573.

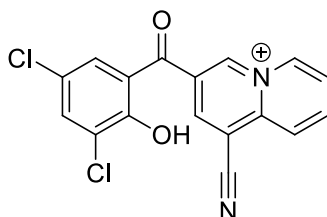
**3-(3,5-Dichloro-2-hydroxybenzoyl)-1-(ethoxycarbonyl)quinolizin-5-ium (4d')**



Yellow solid; Mp: >300 °C; IR (KBr): 3432, 3065, 1709, 1656, 1640, 1462, 1394, 1318, 1278, 1237, 1088, 1035, 919, 872, 797, 624  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 1.41 (t,  $J$  = 7.1 Hz, 3H,  $\text{CH}_3$ ), 4.49–4.53 (m, 2H,  $\text{CH}_2$ ), 7.61 (d, 1H,  $J$  = 2.6 Hz, ArH), 7.92 (d,  $J$  = 2.5 Hz, 1H, ArH), 8.28–8.31 (m, 1H, ArH), 8.65–8.68 (m, 1H, ArH), 8.93 (d,  $J$  = 1.5 Hz, 1H, ArH), 9.27 (d,  $J$  = 8.9 Hz, 1H, ArH), 9.58 (d,  $J$  = 6.7 Hz, 1H, ArH), 9.88 (s, 1H, ArH);  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ):  $\delta$  = 14.3, 63.6, 124.3, 125.5, 125.5, 126.4, 127.5, 129.8, 129.8, 130.9, 134.4, 137.6, 140.3, 141.7, 142.3, 143.2, 152.5, 163.1, 190.0.

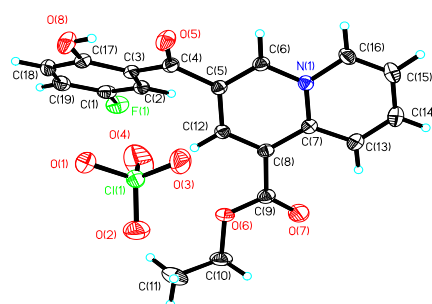
HRMS (ESI-TOF,  $[M-ClO_4]^+$ ): calcd for  $C_{19}H_{14}Cl_2NO_4^+$ , 390.0294; found, 390.0289.

**1-Cyano-3-(3,5-dichloro-2-hydroxybenzoyl)quinolizin-5-ium (4e')**



Yellow solid; Mp:  $>300$  °C; IR (KBr): 3440, 2197, 1637, 1600, 1560, 1483, 1401, 1325, 1217, 1189, 1103, 875, 848, 767, 700  $cm^{-1}$ ;  $^1H$  NMR (600 MHz,  $DMSO-d_6+HClO_4$ ):  $\delta$  = 7.53 (d,  $J$  = 2.5 Hz, 1H, ArH), 7.87 (d,  $J$  = 2.5 Hz, 1H, ArH), 8.34-8.36 (m, 1H, ArH), 8.73 (d,  $J$  = 4.2 Hz, 2H, ArH), 9.22 (d,  $J$  = 1.0 Hz, 1H, ArH), 9.62 (d,  $J$  = 6.6 Hz, 1H, ArH), 9.95 (s, 1H, ArH);  $^{13}C$  NMR (150 MHz,  $DMSO-d_6+HClO_4$ ):  $\delta$  = 111.0, 113.7, 124.5, 125.2, 126.2, 126.4, 129.7, 129.7, 131.3, 134.5, 134.5, 140.5, 142.1, 143.0, 143.1, 152.5, 189.2. HRMS (ESI-TOF,  $[M-ClO_4]^+$ ): calcd for  $C_{17}H_9Cl_2N_2O_2^+$ , 343.0036; found, 343.0031.

### X-ray Structure and Data<sup>2</sup> of 4a.



**Figure S1.** X-Ray crystal structure of **4a**

**Table S1.** Crystal data and structure refinement for **4a**

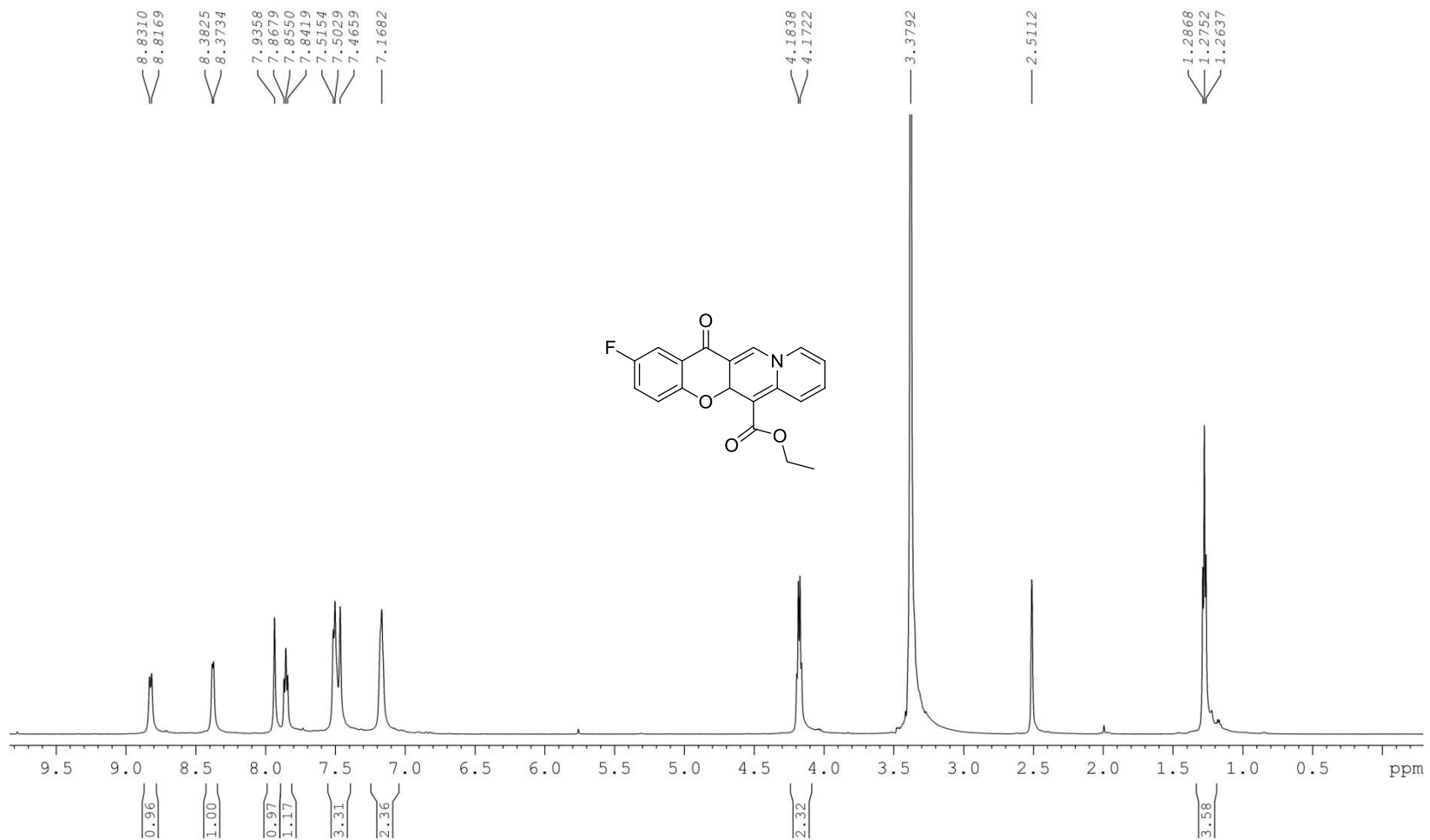
Identification code	1	
Empirical formula	C <sub>19</sub> H <sub>15</sub> Cl F N O <sub>8</sub>	
Formula weight	439.77	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 2 <sub>1</sub> /n 1	
Unit cell dimensions	a = 8.1097(12) Å b = 14.3670(19) Å c = 16.622(2) Å	α = 90°. β = 98.194(2)°. γ = 90°.
Volume	1916.9(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.524 Mg/m <sup>3</sup>	
Absorption coefficient	0.258 mm <sup>-1</sup>	
F(000)	904	
Theta range for data collection	2.660 to 27.867°.	
Index ranges	-10 ≤ h ≤ 10, -18 ≤ k ≤ 15, -21 ≤ l ≤ 20	
Reflections collected	11596	
Independent reflections	4491 [R(int) = 0.0209]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6873	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4491 / 0 / 273	
Goodness-of-fit on F <sup>2</sup>	1.034	
Final R indices [I > 2σ(I)]	R1 = 0.0431, wR2 = 0.1061	
R indices (all data)	R1 = 0.0628, wR2 = 0.1193	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.256 and -0.467 e.Å <sup>-3</sup>	

**Table S2.** Bond lengths [Å] and angles [deg] for **4a**

Cl(1)-O(1)	1.4236(16)	C(1)-C(2)-H(2)	120.5
Cl(1)-O(2)	1.4209(17)	C(1)-C(2)-C(3)	119.03(18)
Cl(1)-O(3)	1.4207(17)	C(3)-C(2)-H(2)	120.5
Cl(1)-O(4)	1.398(2)	C(2)-C(3)-C(4)	121.13(16)
F(1)-C(1)	1.362(2)	C(2)-C(3)-C(17)	118.73(17)
O(5)-C(4)	1.228(2)	C(17)-C(3)-C(4)	120.12(17)
O(6)-C(9)	1.319(2)	O(5)-C(4)-C(3)	122.24(17)
O(6)-C(10)	1.455(2)	O(5)-C(4)-C(5)	117.98(16)
O(7)-C(9)	1.197(2)	C(3)-C(4)-C(5)	119.78(16)
O(8)-H(8)	0.82	C(6)-C(5)-C(4)	118.47(16)
O(8)-C(17)	1.345(3)	C(6)-C(5)-C(12)	119.01(16)
N(1)-C(6)	1.379(2)	C(12)-C(5)-C(4)	122.43(15)
N(1)-C(7)	1.387(2)	N(1)-C(6)-H(6)	119.5
N(1)-C(16)	1.380(2)	C(5)-C(6)-N(1)	120.91(16)
C(1)-C(2)	1.361(3)	C(5)-C(6)-H(6)	119.5
C(1)-C(19)	1.378(3)	N(1)-C(7)-C(8)	116.75(15)
C(2)-H(2)	0.93	N(1)-C(7)-C(13)	117.23(16)
C(2)-C(3)	1.405(3)	C(13)-C(7)-C(8)	125.99(16)
C(3)-C(4)	1.464(3)	C(7)-C(8)-C(9)	121.14(15)
C(3)-C(17)	1.405(2)	C(12)-C(8)-C(7)	120.33(16)
C(4)-C(5)	1.501(2)	C(12)-C(8)-C(9)	118.53(16)
C(5)-C(6)	1.352(2)	O(6)-C(9)-C(8)	110.75(15)
C(5)-C(12)	1.407(2)	O(7)-C(9)-O(6)	123.78(18)
C(6)-H(6)	0.93	O(7)-C(9)-C(8)	125.47(18)
C(7)-C(8)	1.428(2)	O(6)-C(10)-H(10A)	110.3
C(7)-C(13)	1.402(3)	O(6)-C(10)-H(10B)	110.3
C(8)-C(9)	1.503(2)	O(6)-C(10)-C(11)	107.1(2)
C(8)-C(12)	1.365(2)	H(10A)-C(10)-H(10B)	108.5
C(10)-H(10A)	0.97	C(11)-C(10)-H(10A)	110.3
C(10)-H(10B)	0.97	C(11)-C(10)-H(10B)	110.3
C(10)-C(11)	1.488(3)	C(10)-C(11)-H(11A)	109.5
C(11)-H(11A)	0.96	C(10)-C(11)-H(11B)	109.5
C(11)-H(11B)	0.96	C(10)-C(11)-H(11C)	109.5
C(11)-H(11C)	0.96	H(11A)-C(11)-H(11B)	109.5

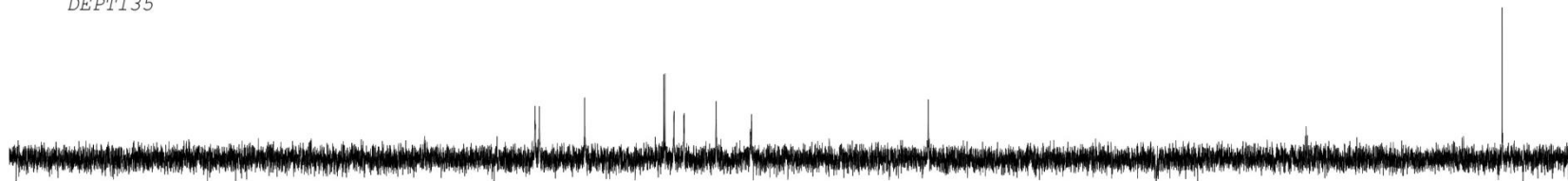
C(12)-H(12)	0.93	H(11A)-C(11)-H(11C)	109.5
C(13)-H(13)	0.93	H(11B)-C(11)-H(11C)	109.5
C(13)-C(14)	1.360(3)	C(5)-C(12)-H(12)	119.5
C(14)-H(14)	0.93	C(8)-C(12)-C(5)	120.93(16)
C(14)-C(15)	1.393(3)	C(8)-C(12)-H(12)	119.5
C(15)-H(15)	0.93	C(7)-C(13)-H(13)	119.3
C(15)-C(16)	1.342(3)	C(14)-C(13)-C(7)	121.35(19)
C(16)-H(16)	0.93	C(14)-C(13)-H(13)	119.3
C(17)-C(18)	1.392(3)	C(13)-C(14)-H(14)	120.1
C(18)-H(18)	0.93	C(13)-C(14)-C(15)	119.87(19)
C(18)-C(19)	1.370(3)	C(15)-C(14)-H(14)	120.1
C(19)-H(19)	0.93	C(14)-C(15)-H(15)	120.2
O(2)-Cl(1)-O(1)	109.03(10)	C(16)-C(15)-C(14)	119.69(19)
O(3)-Cl(1)-O(1)	109.07(12)	C(16)-C(15)-H(15)	120.2
O(3)-Cl(1)-O(2)	108.68(12)	N(1)-C(16)-H(16)	119.4
O(4)-Cl(1)-O(1)	109.14(15)	C(15)-C(16)-N(1)	121.10(19)
O(4)-Cl(1)-O(2)	110.89(16)	C(15)-C(16)-H(16)	119.4
O(4)-Cl(1)-O(3)	110.00(15)	O(8)-C(17)-C(3)	122.85(18)
C(9)-O(6)-C(10)	117.01(16)	O(8)-C(17)-C(18)	117.12(18)
C(17)-O(8)-H(8)	109.5	C(18)-C(17)-C(3)	120.02(19)
C(6)-N(1)-C(7)	122.04(15)	C(17)-C(18)-H(18)	119.7
C(6)-N(1)-C(16)	117.23(15)	C(19)-C(18)-C(17)	120.5(2)
C(16)-N(1)-C(7)	120.73(15)	C(19)-C(18)-H(18)	119.7
F(1)-C(1)-C(19)	118.62(18)	C(1)-C(19)-H(19)	120.6
C(2)-C(1)-F(1)	118.56(19)	C(18)-C(19)-C(1)	118.86(19)
C(2)-C(1)-C(19)	122.8(2)	C(18)-C(19)-H(19)	120.6

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**Figure S2.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) spectra of compound 3a

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-01  
Nov11-2019-chenli  
C13CPD DMSO

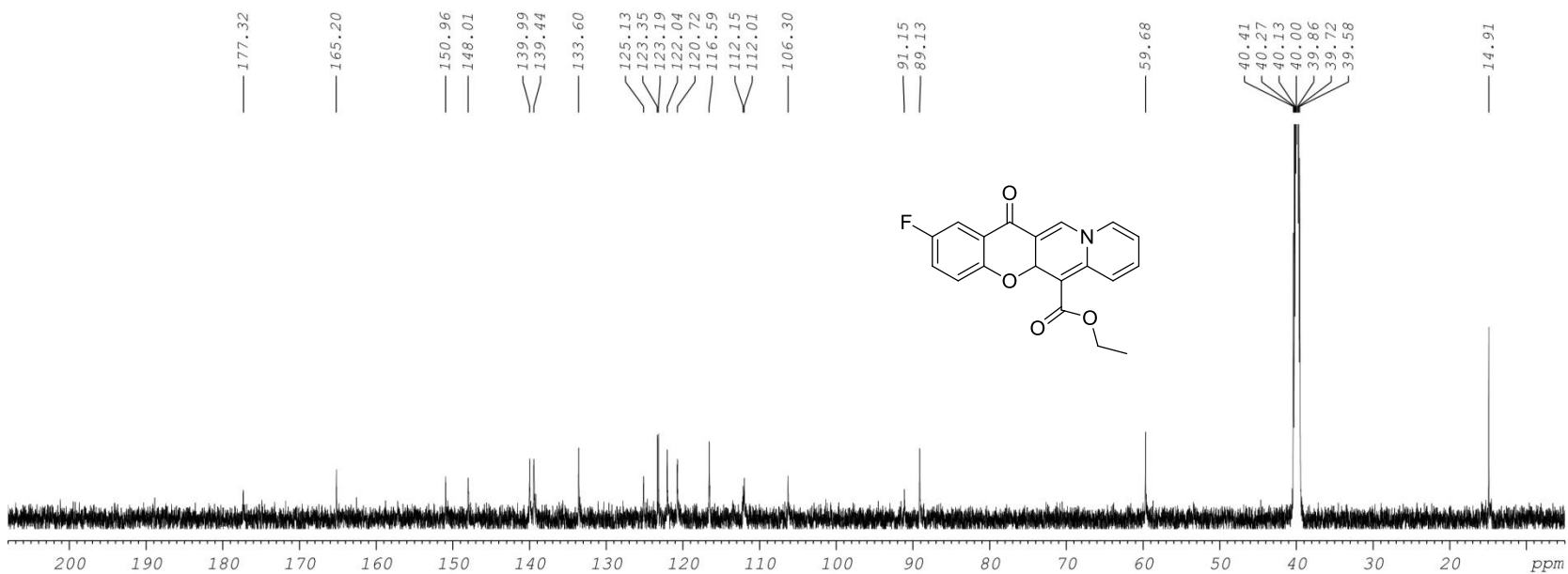
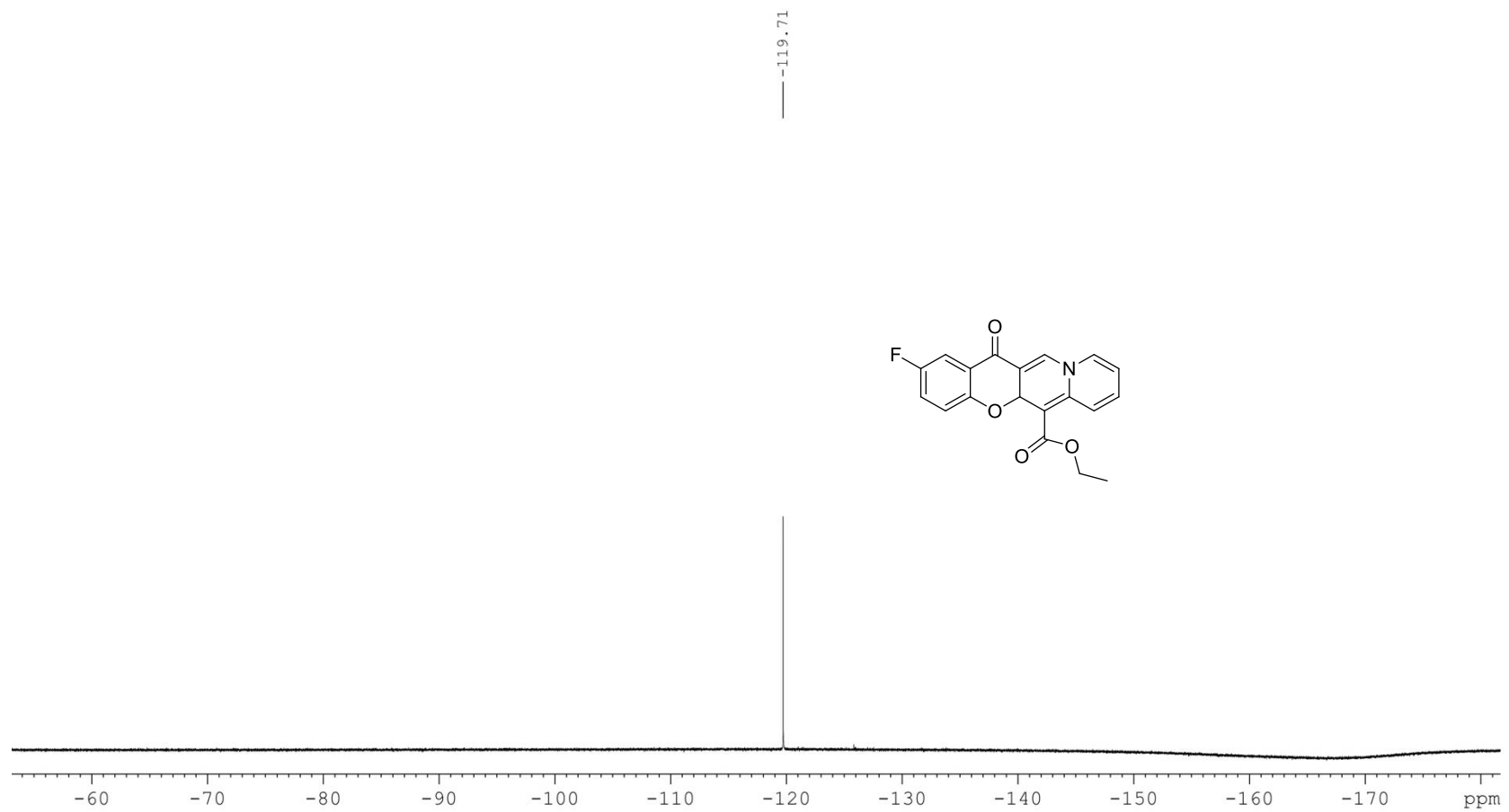
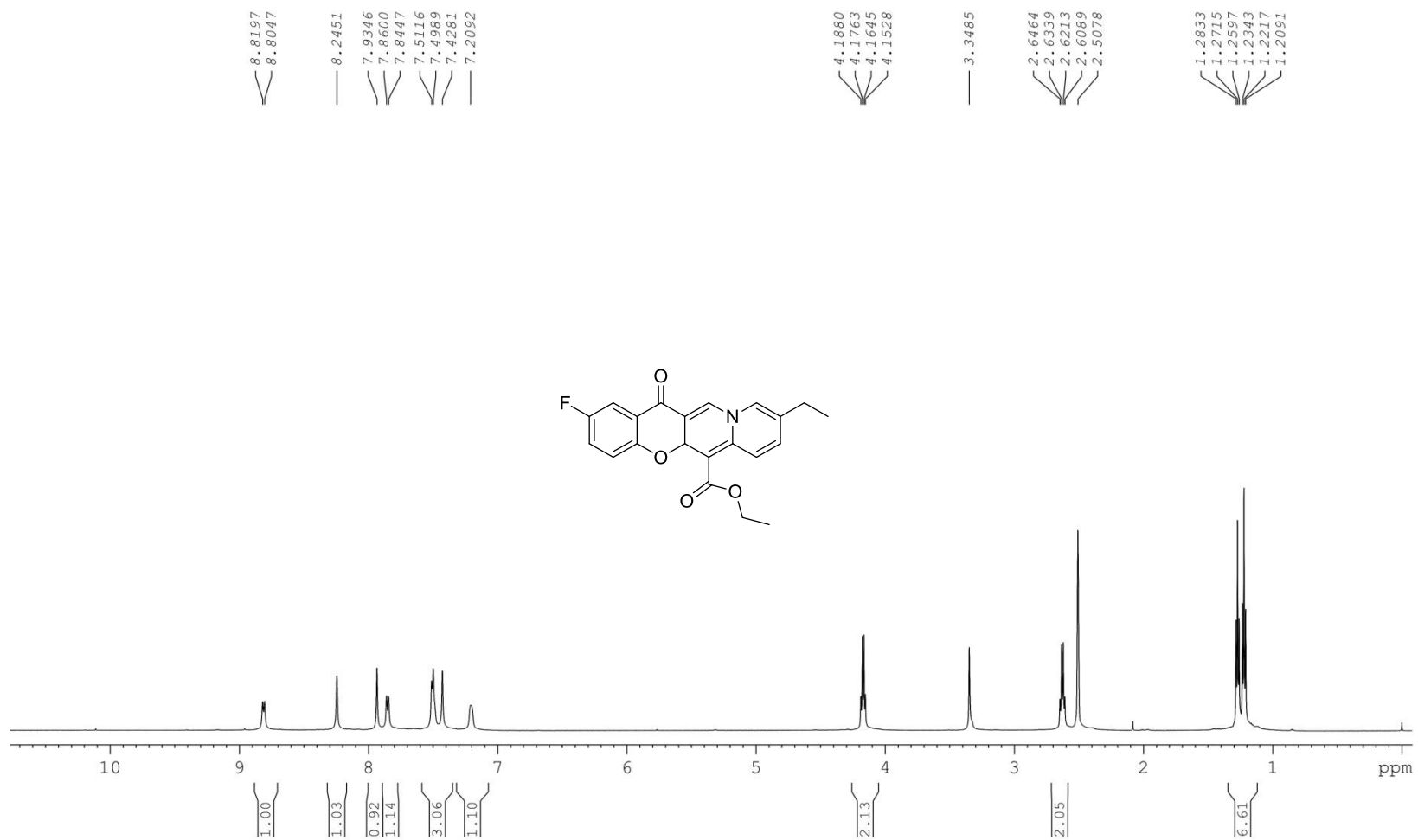


Figure S3.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectra of compound 3a





**Figure S4.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6$ ) spectra of compound **3a**



**Figure S5.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) spectra of compound **3b**

DEPT135

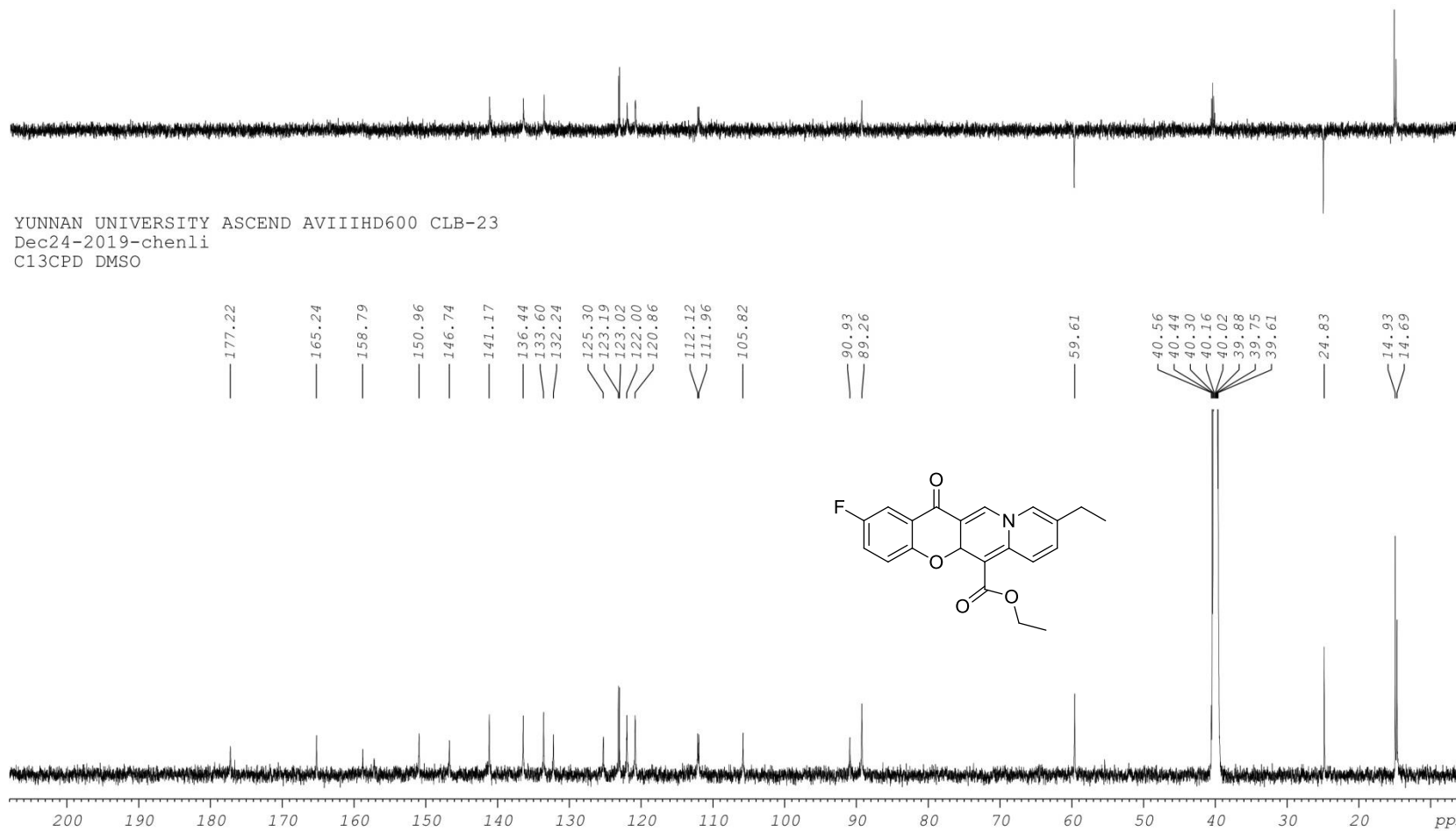
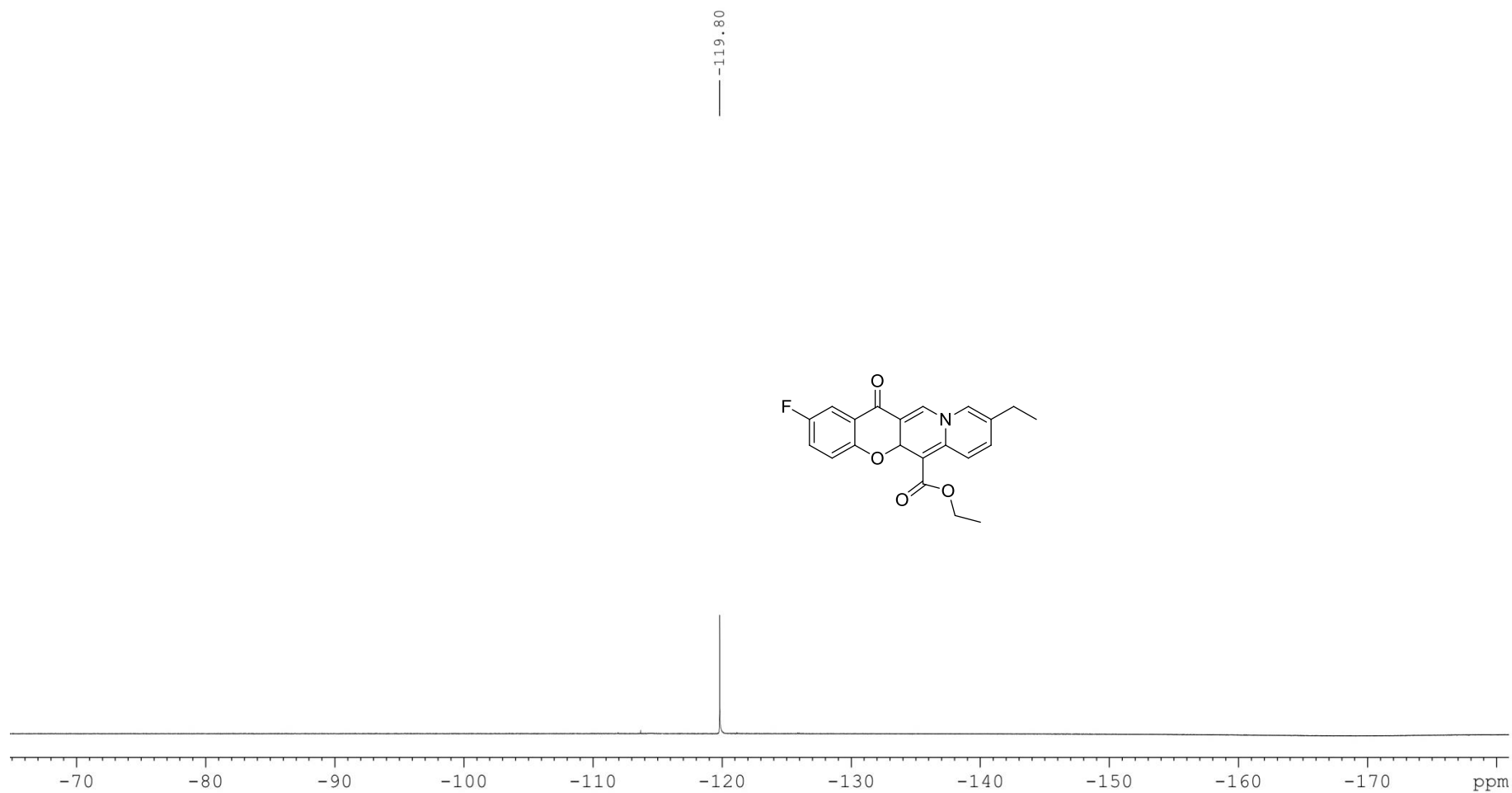
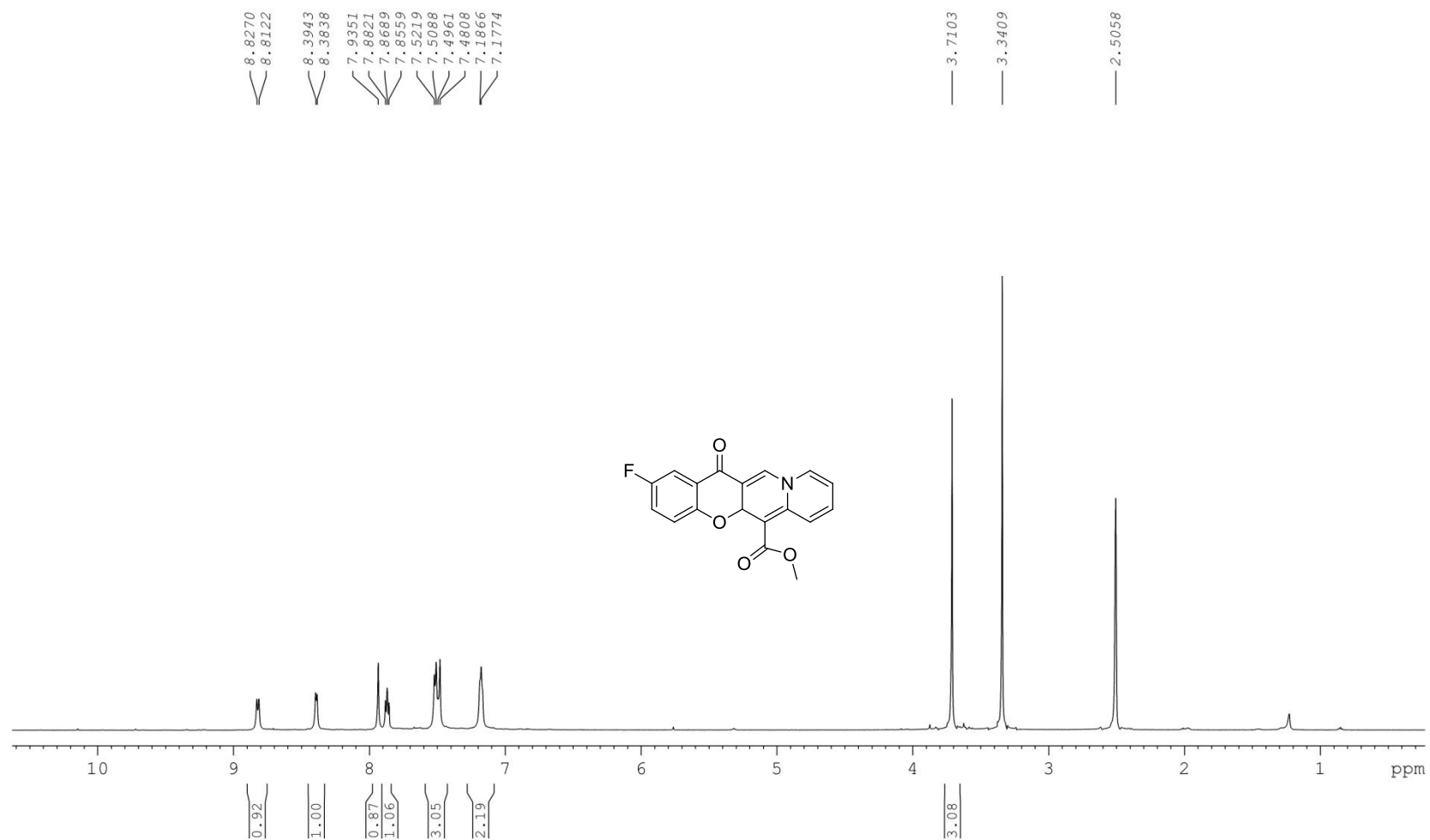


Figure S6.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectra of compound **3b**



**Figure S7.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6$ ) spectra of compound **3b**



**Figure S8.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) spectra of compound **3c**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-03  
Nov18-2019-chenli  
C13CPD DMSO

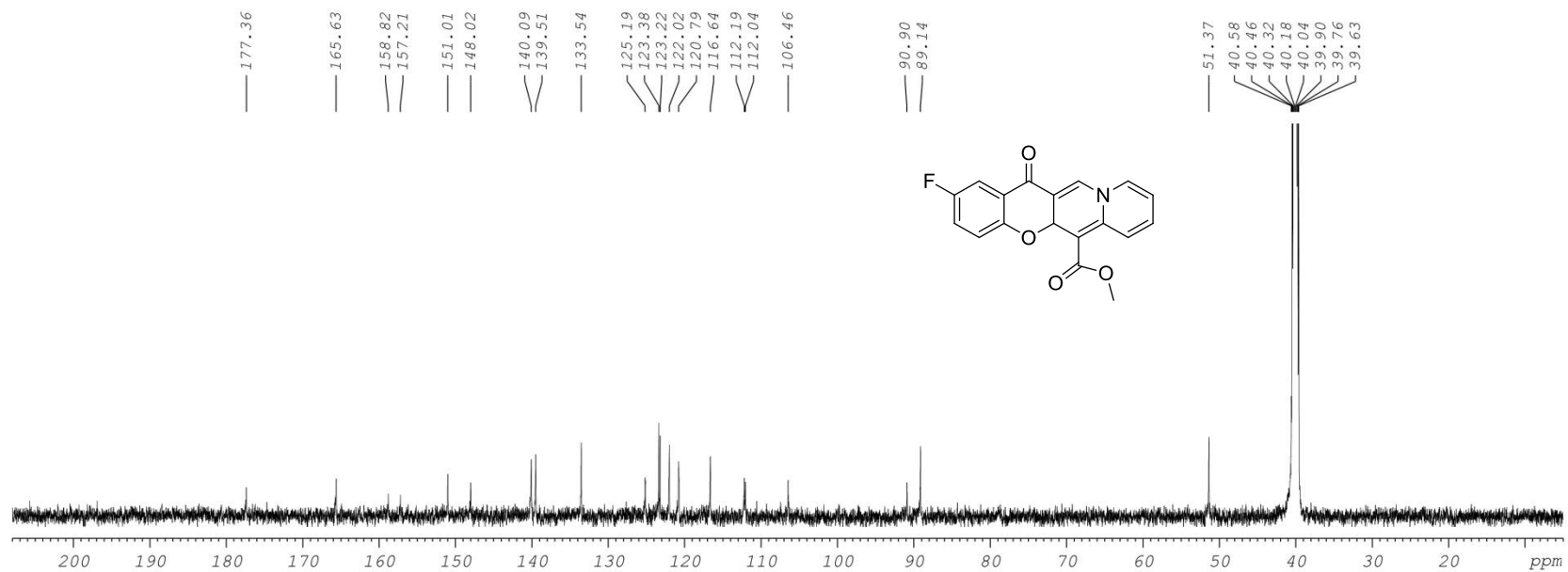
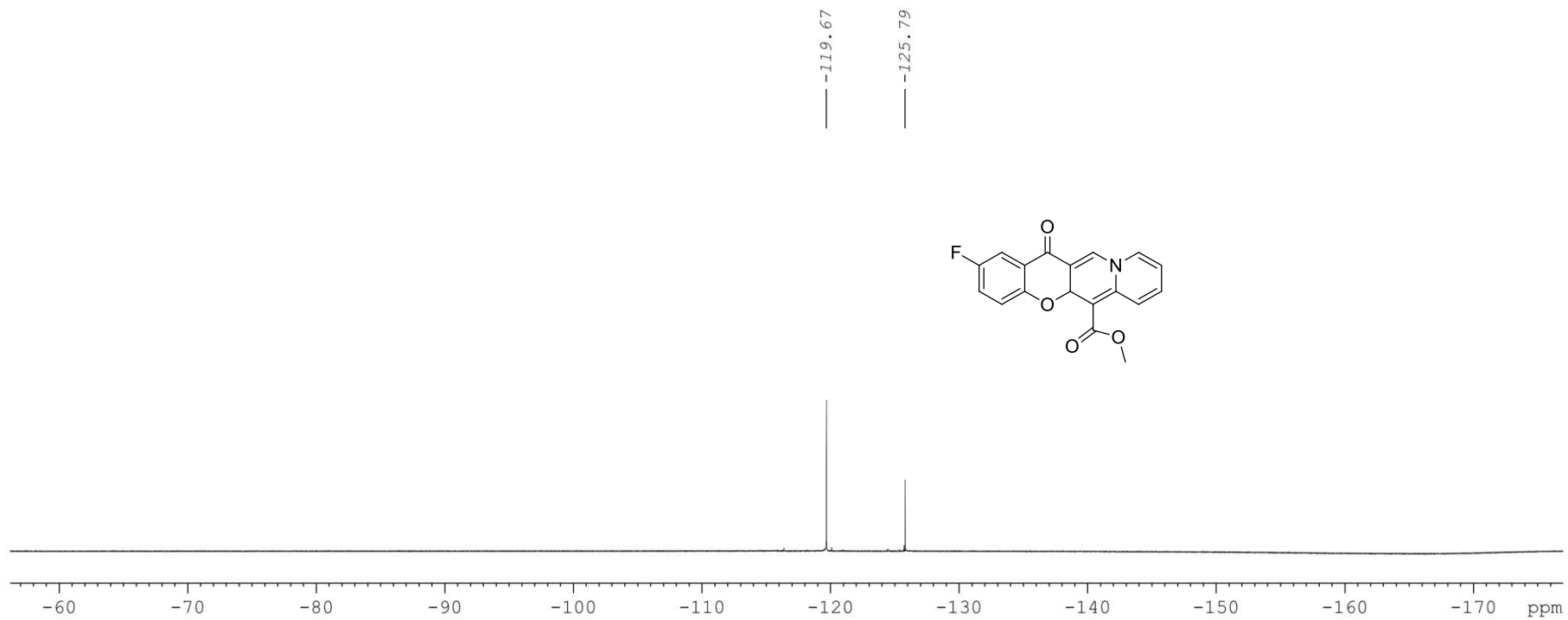
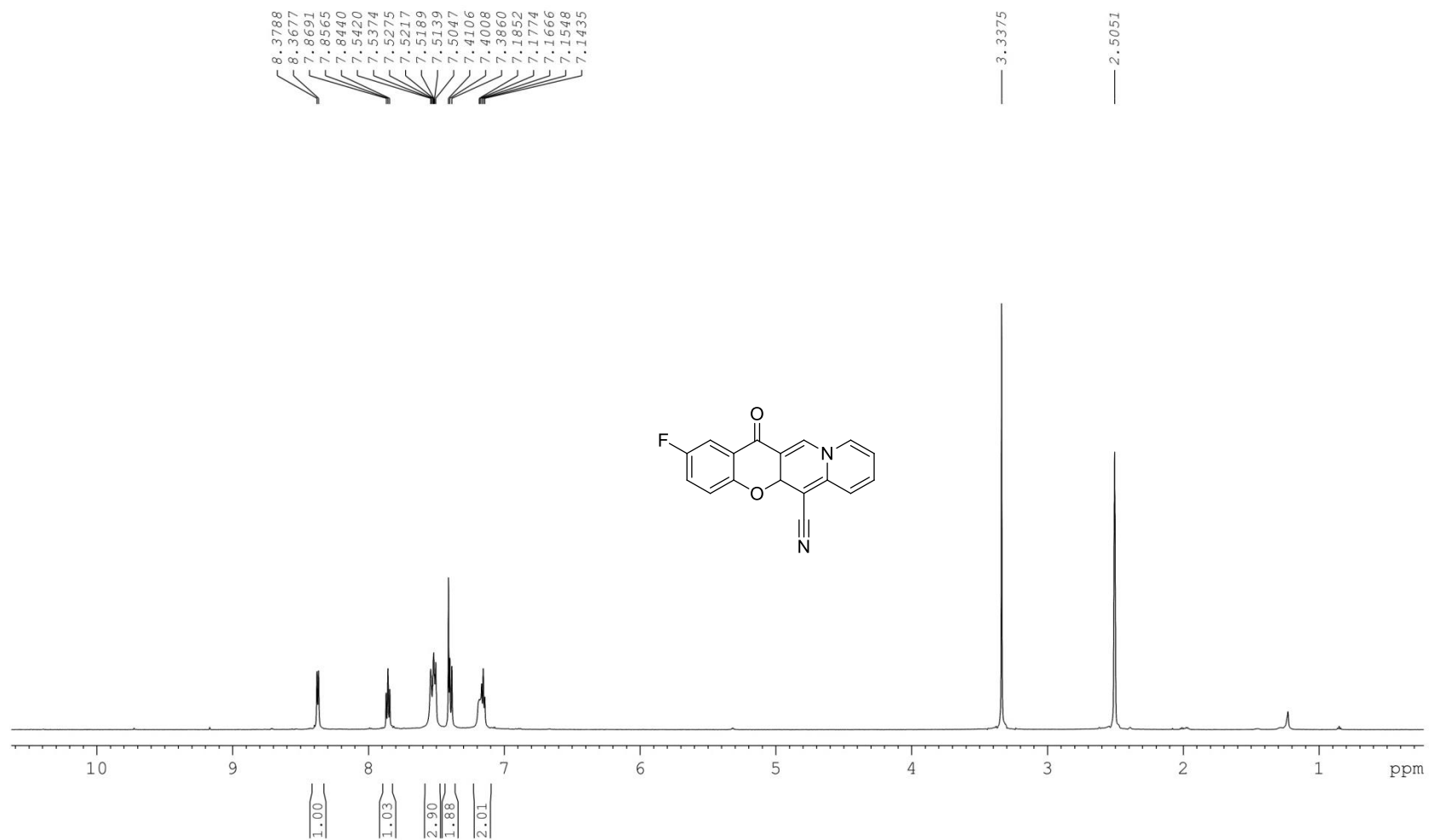


Figure S9.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectra of compound 3c



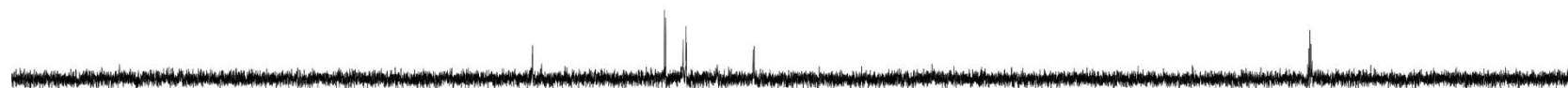
**Figure S10.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6$ ) spectra of compound **3c**



**Figure S11.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) spectra of compound **3d**



DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-04  
Nov18-2019-chenli  
C13CPD DMSO

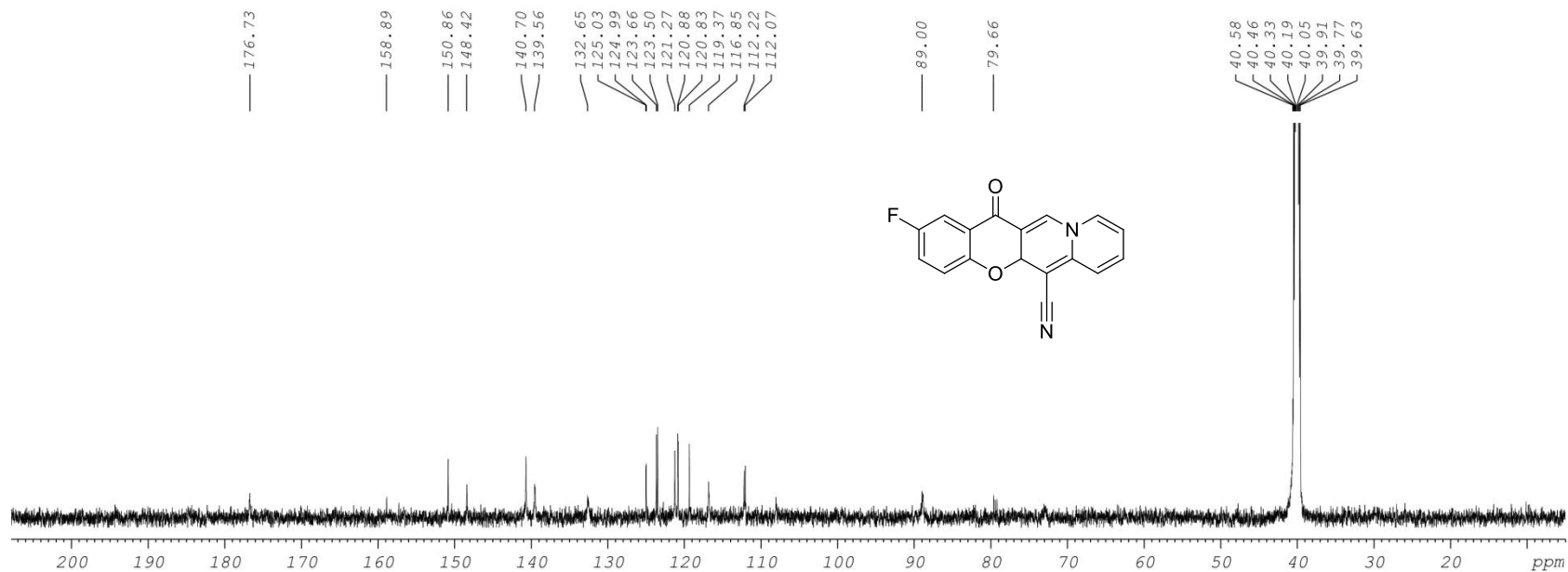
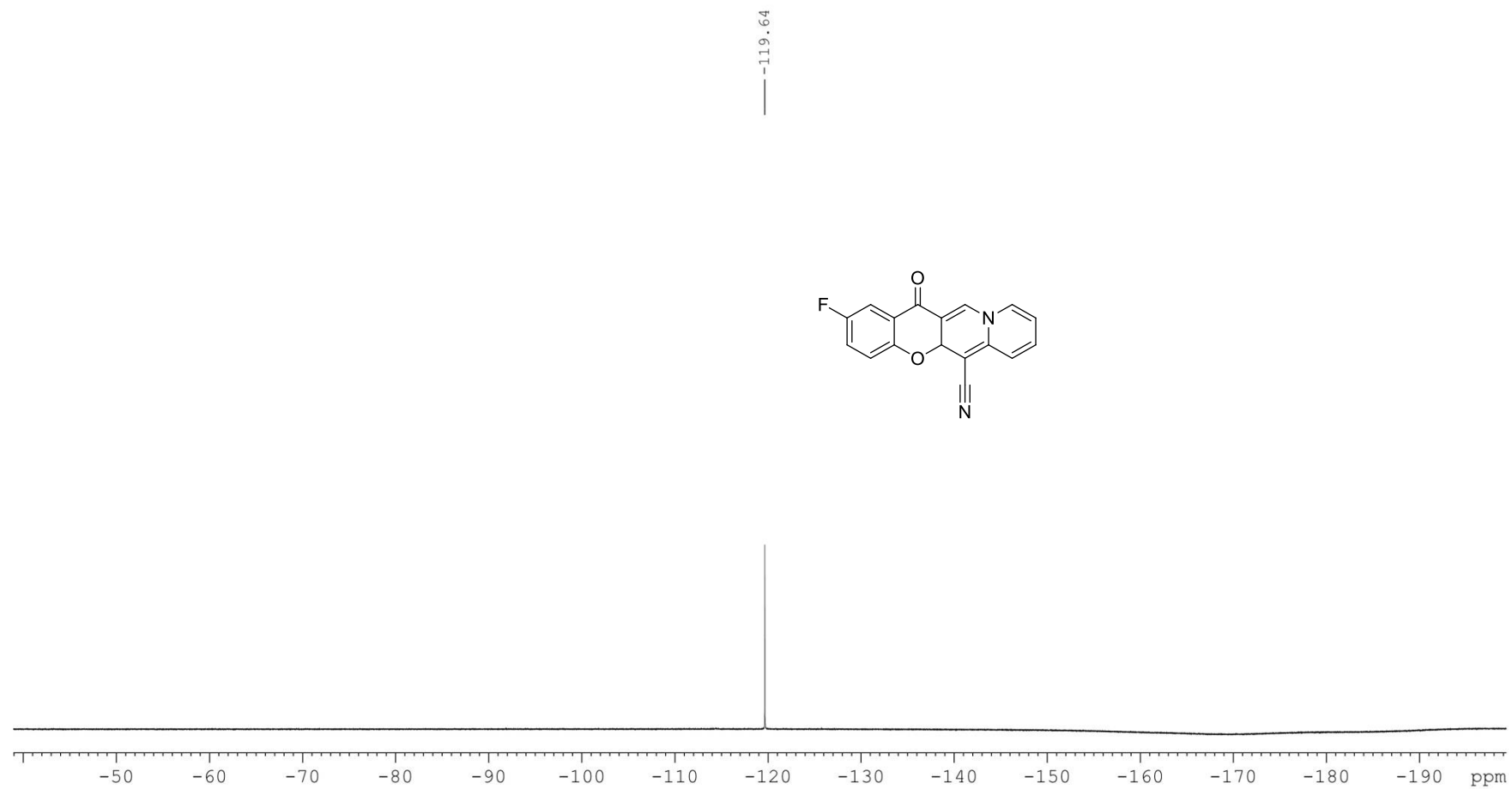
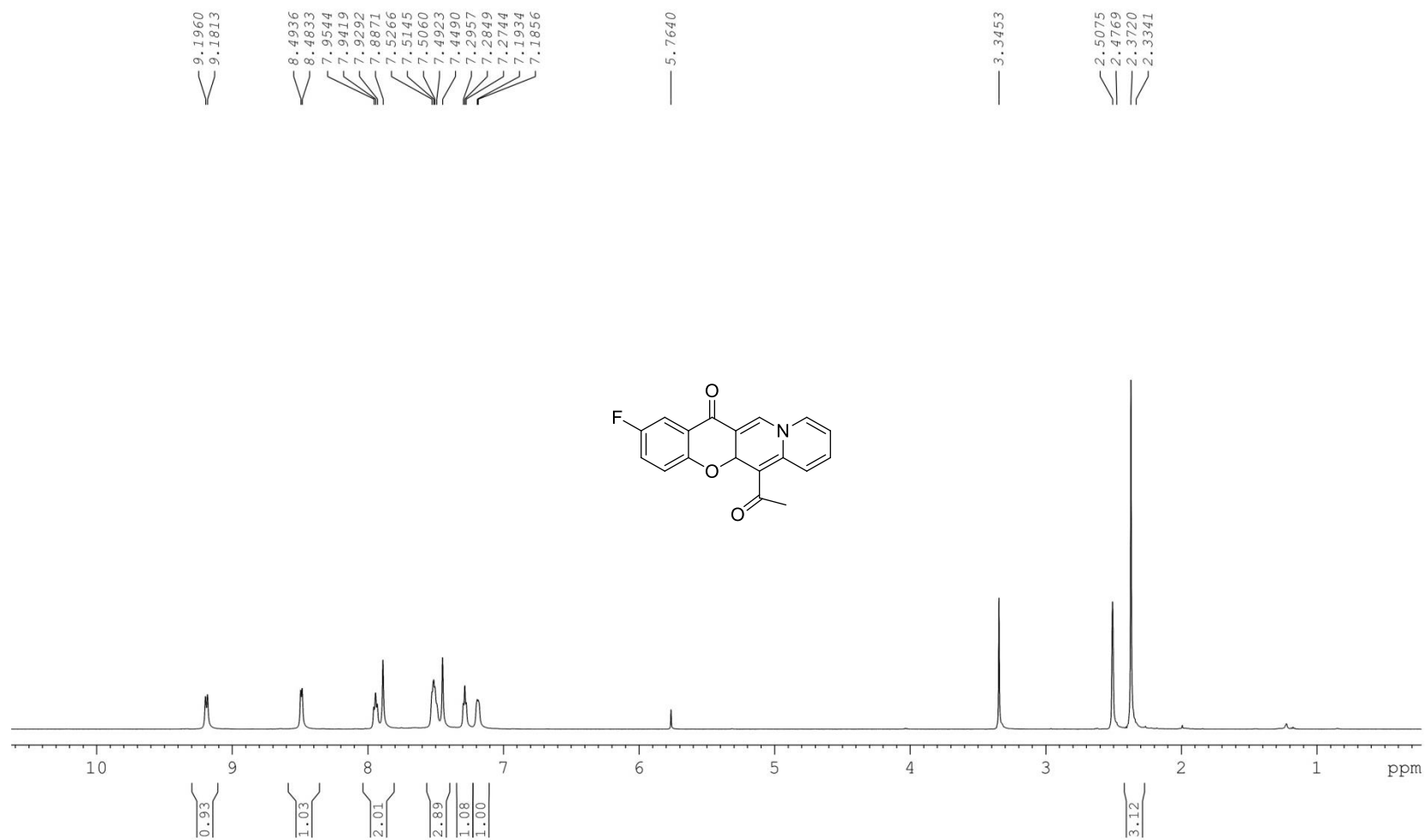


Figure S12.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectra of compound 3d



**Figure S13.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6$ ) spectra of compound **3d**



**Figure S14.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) spectra of compound **3e**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-07  
Nov15-2019-chenli  
C13CPD DMSO

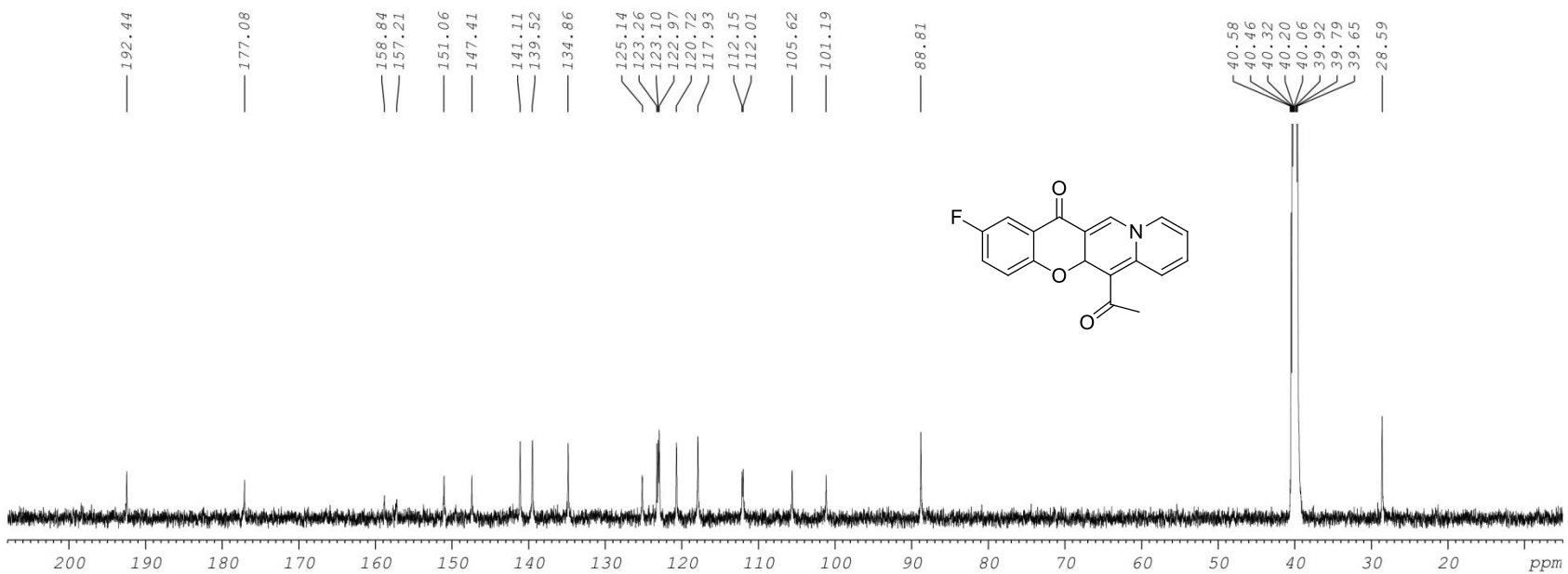
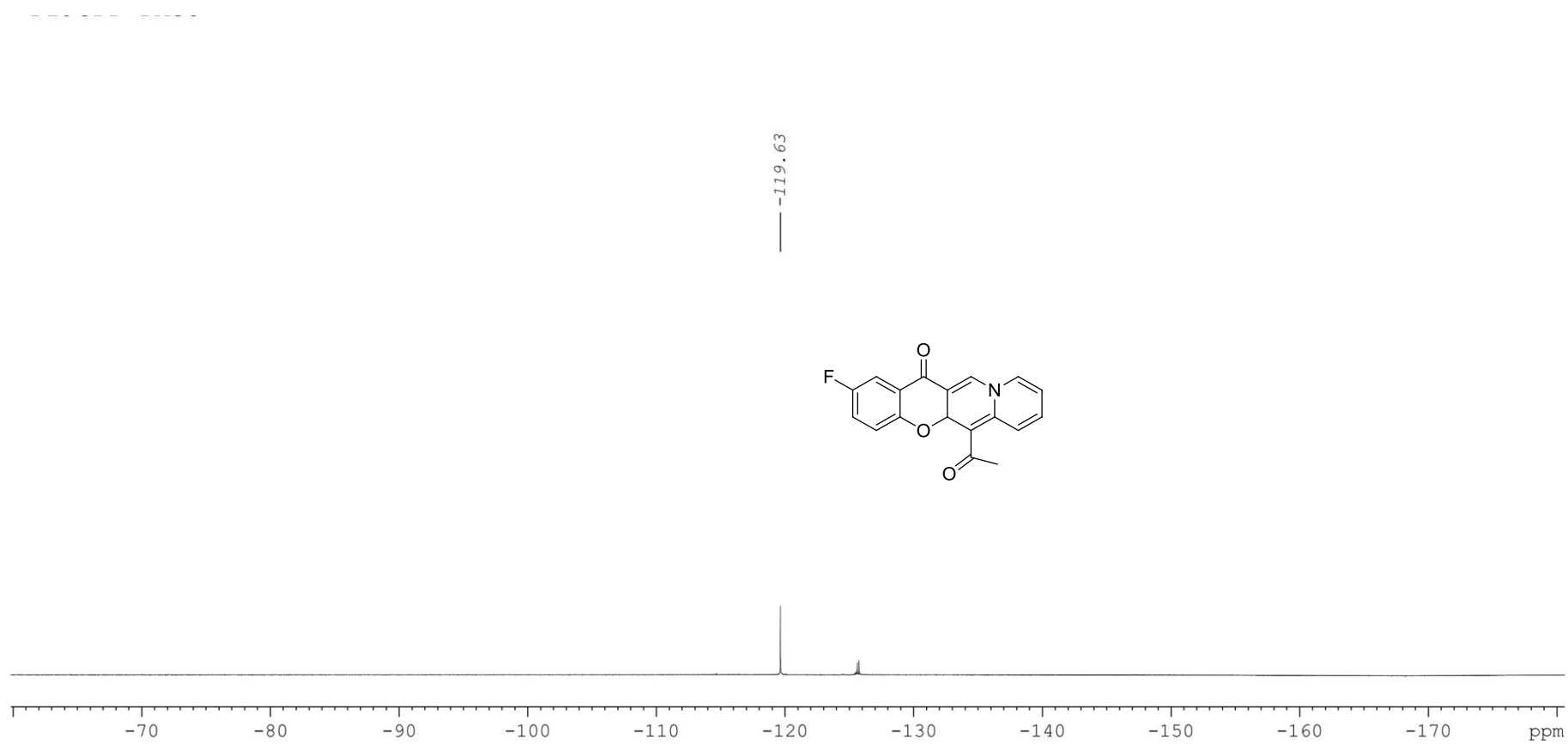
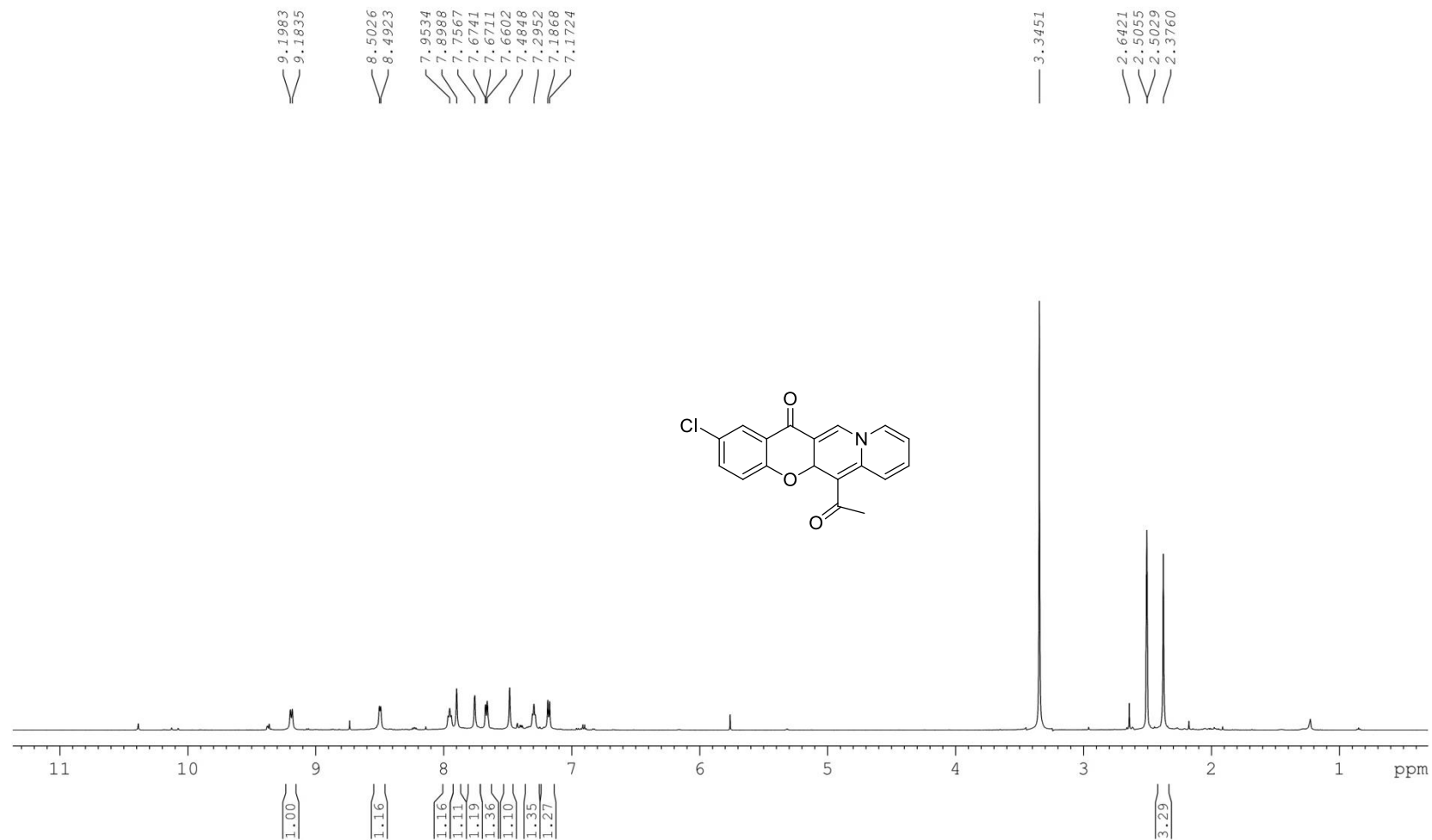


Figure S15.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectra of compound 3e



**Figure S16.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6$ ) spectra of compound **3e**



**Figure S17.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) spectra of compound **3f**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-08  
Nov27-2019-chenli  
C13CPD DMSO

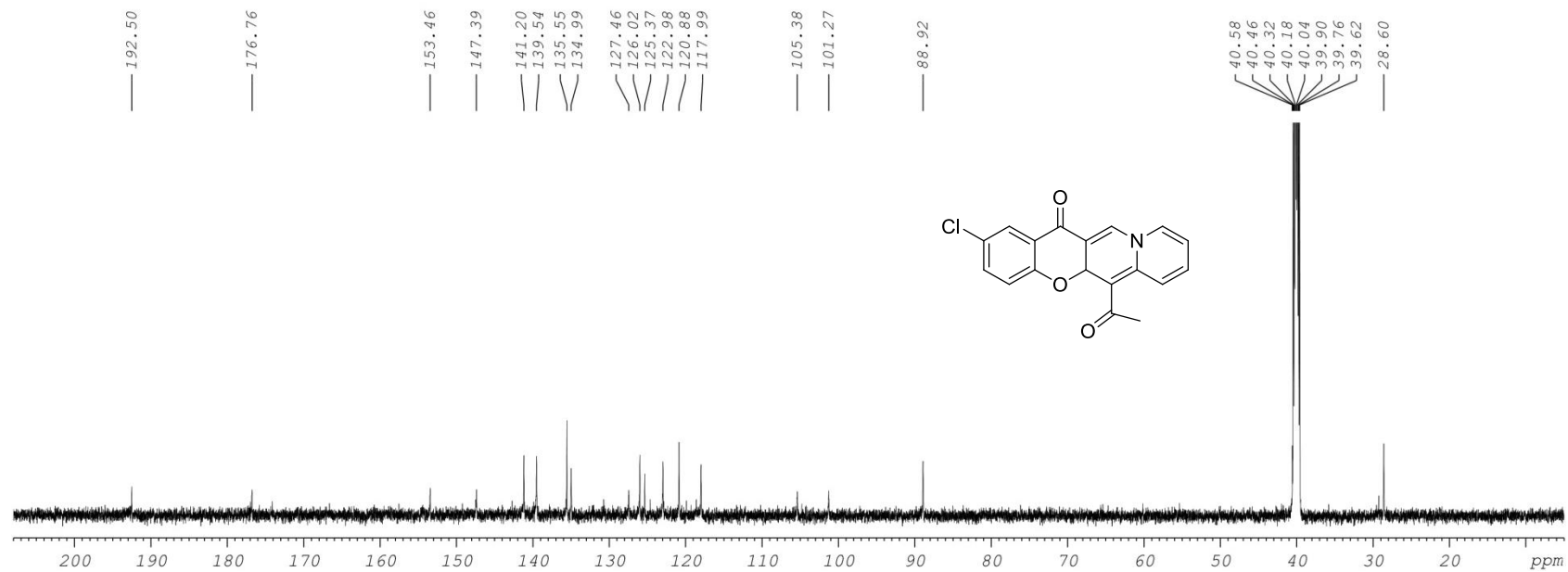
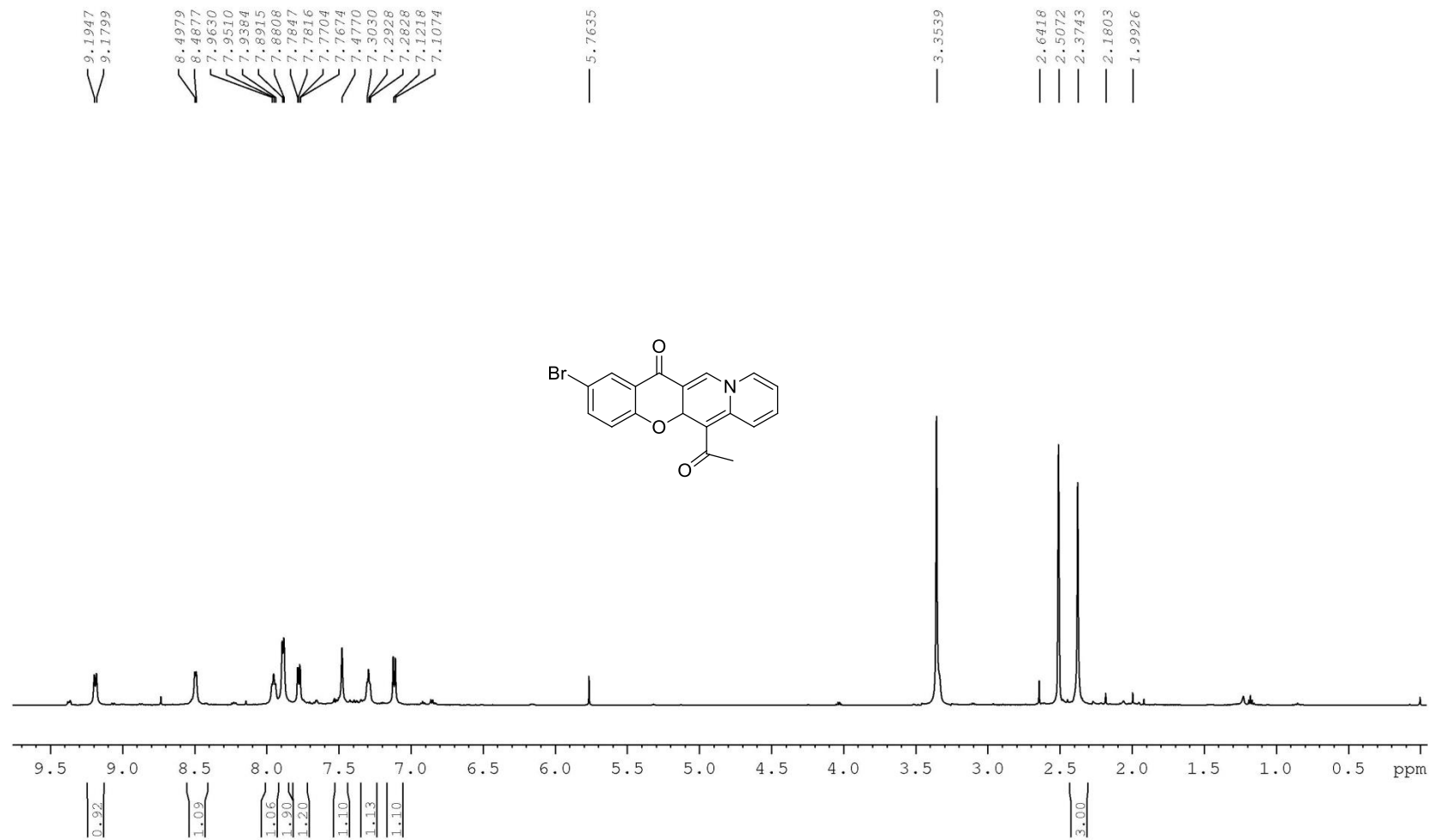


Figure S18.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectra of compound **3f**



**Figure S19.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) spectra of compound **3g**



DEPT135

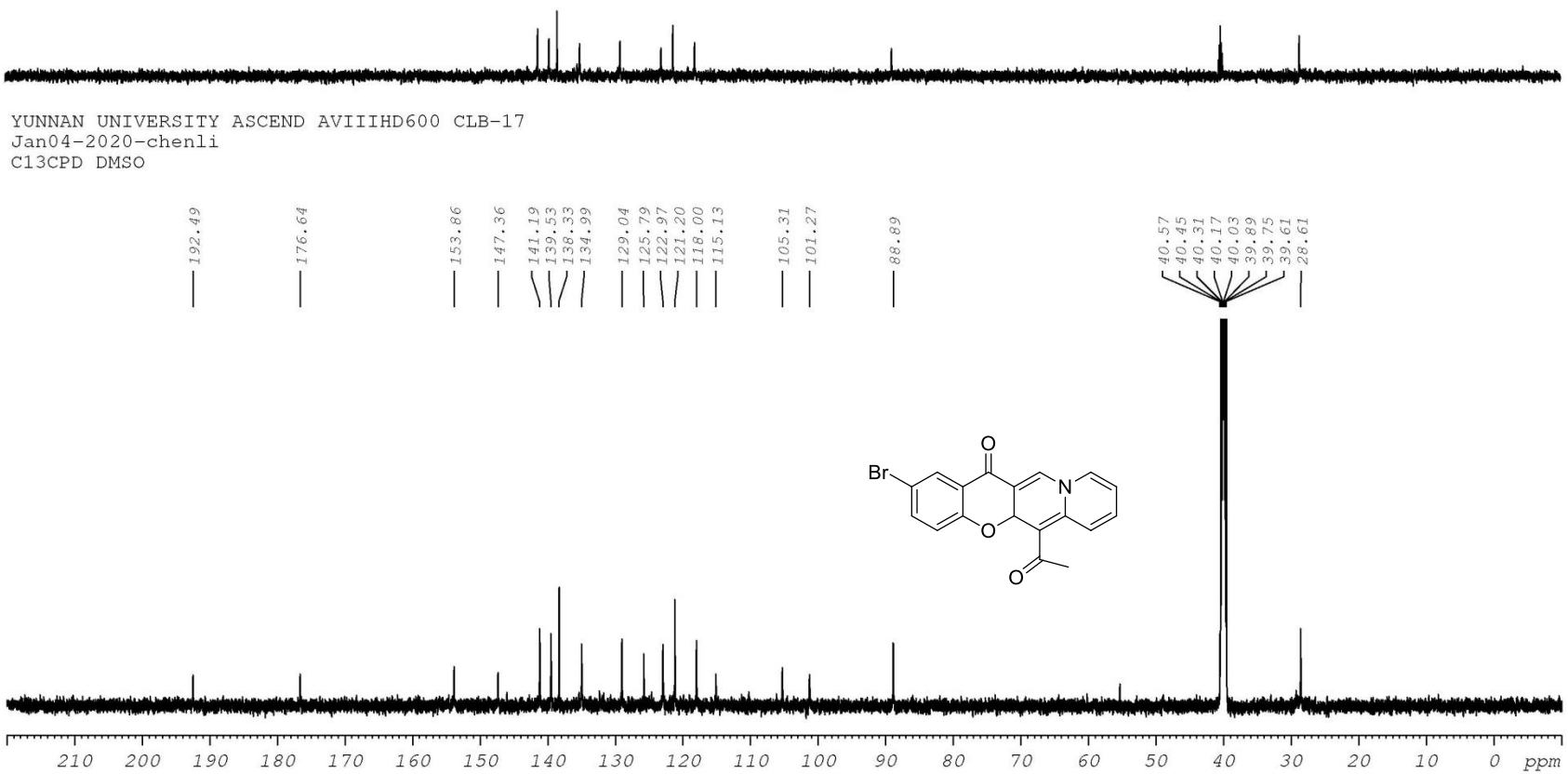
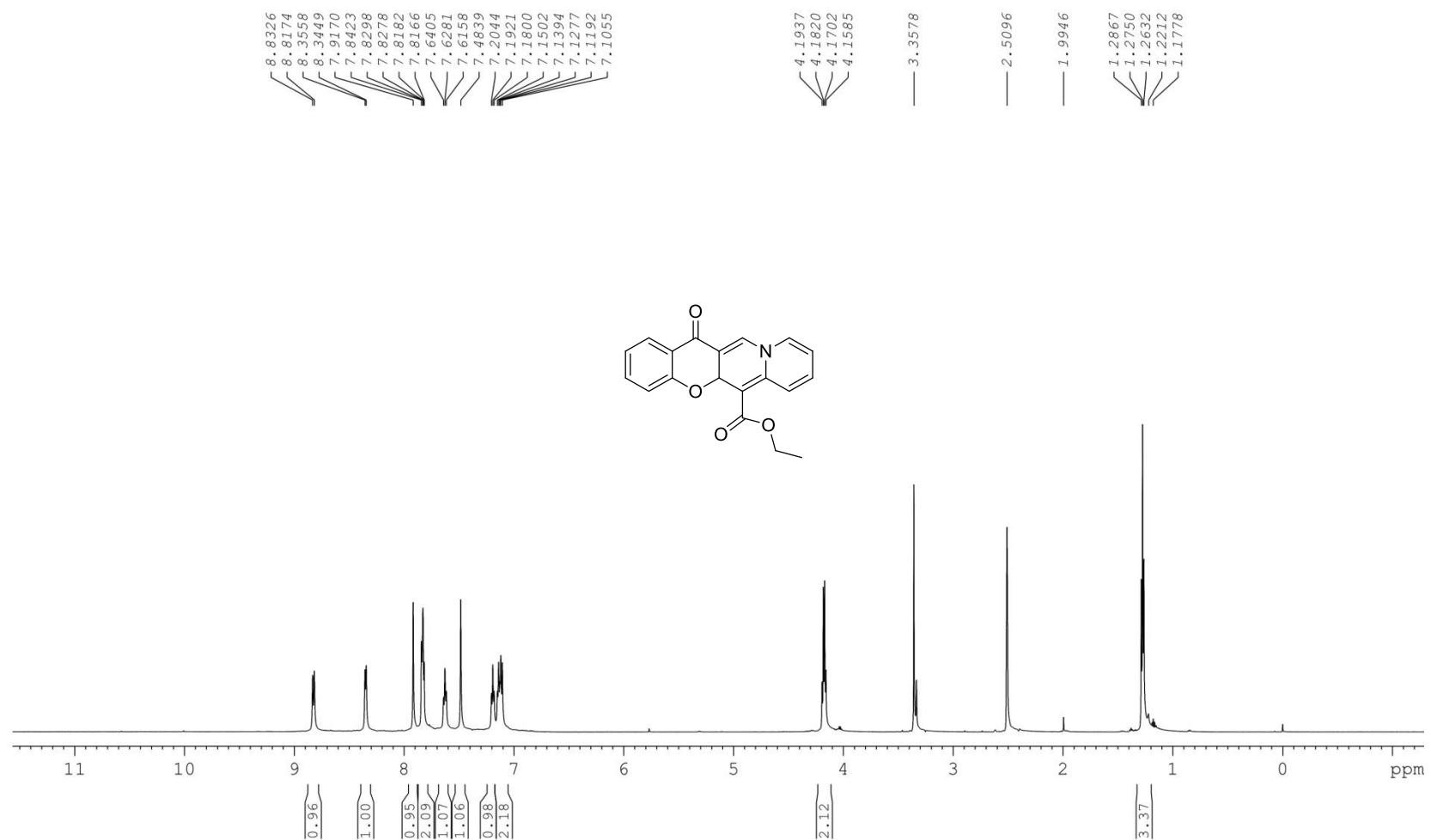


Figure S20.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectra of compound **3g**



**Figure S21.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6$ ) spectra of compound **3h**

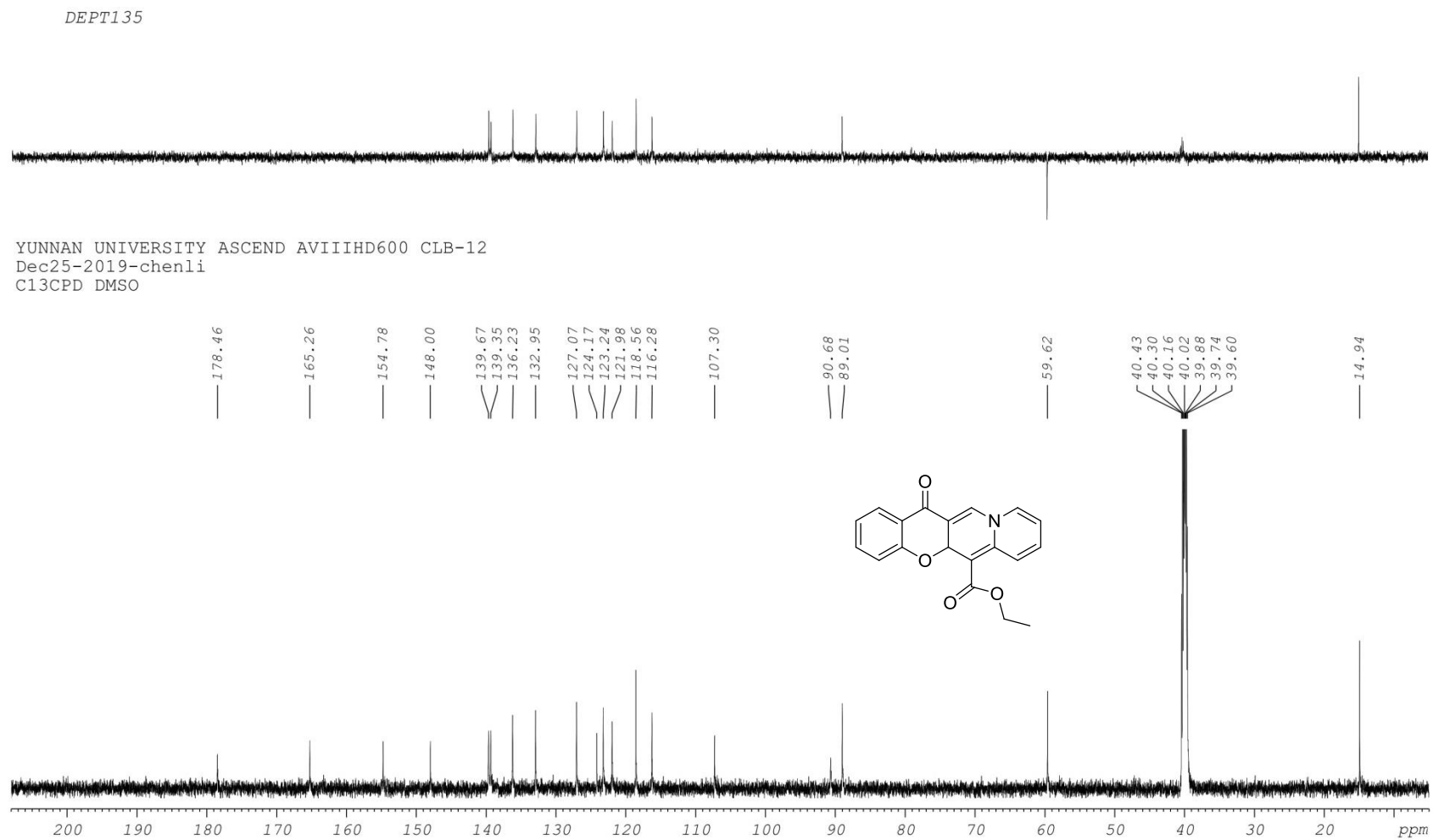
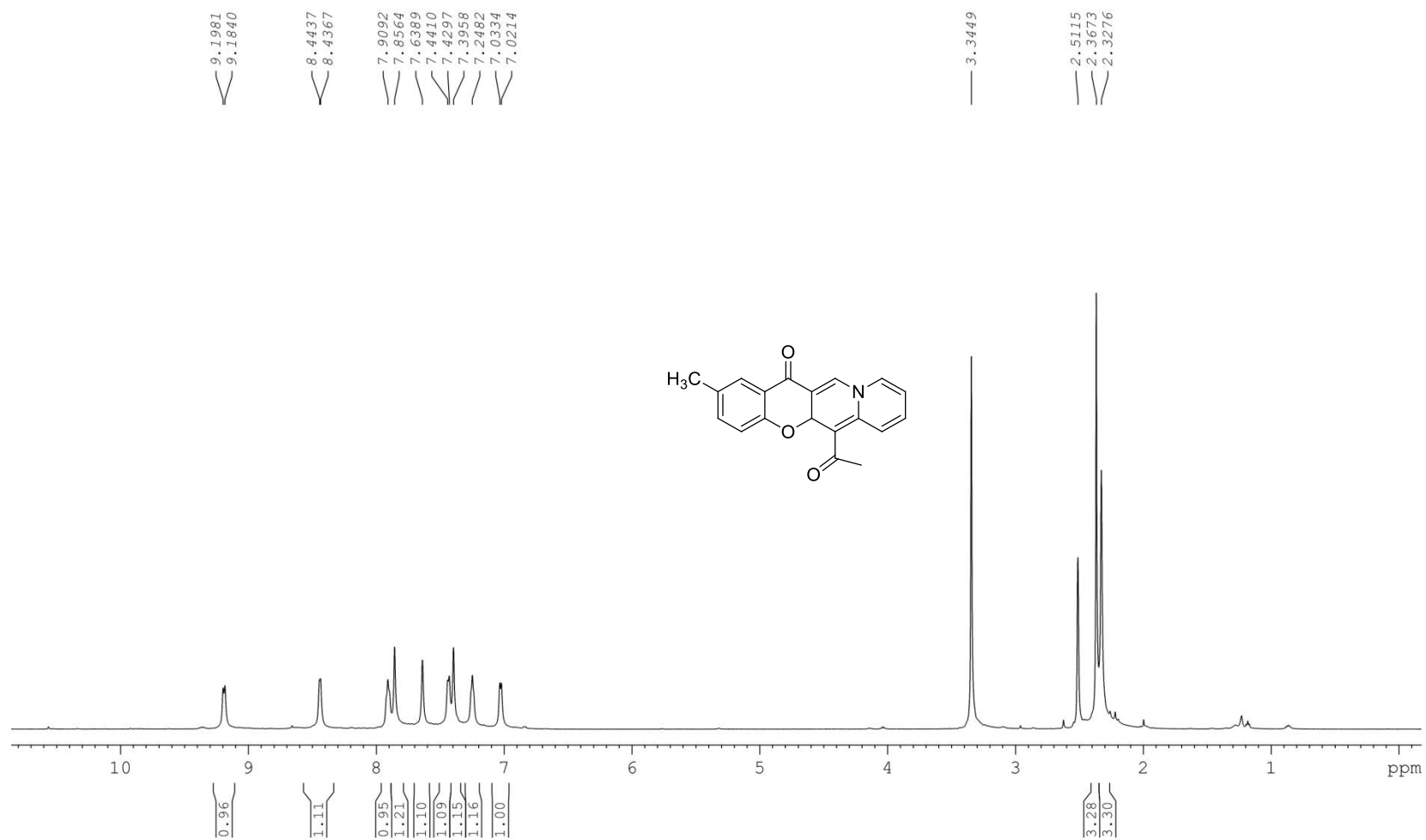


Figure S22.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectra of compound 3h



**Figure S23.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>) spectra of compound **3i**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-20  
Dec06-2019-chenli  
C13CPD DMSO

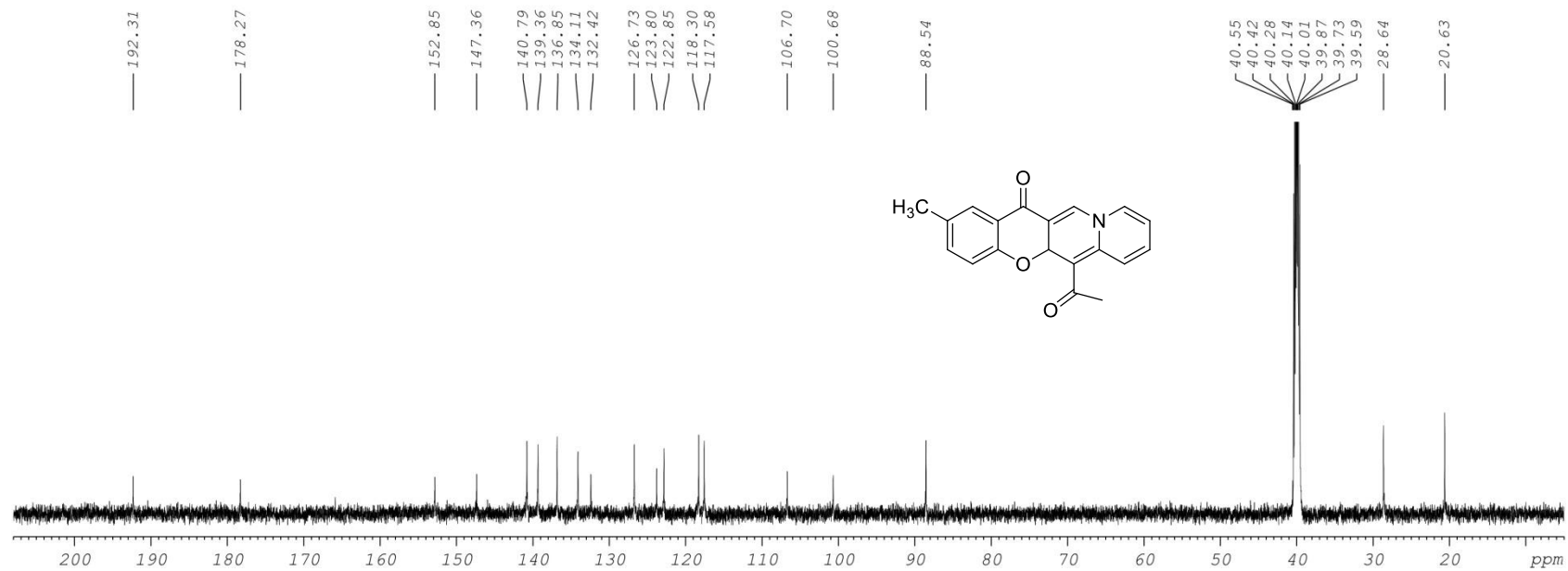
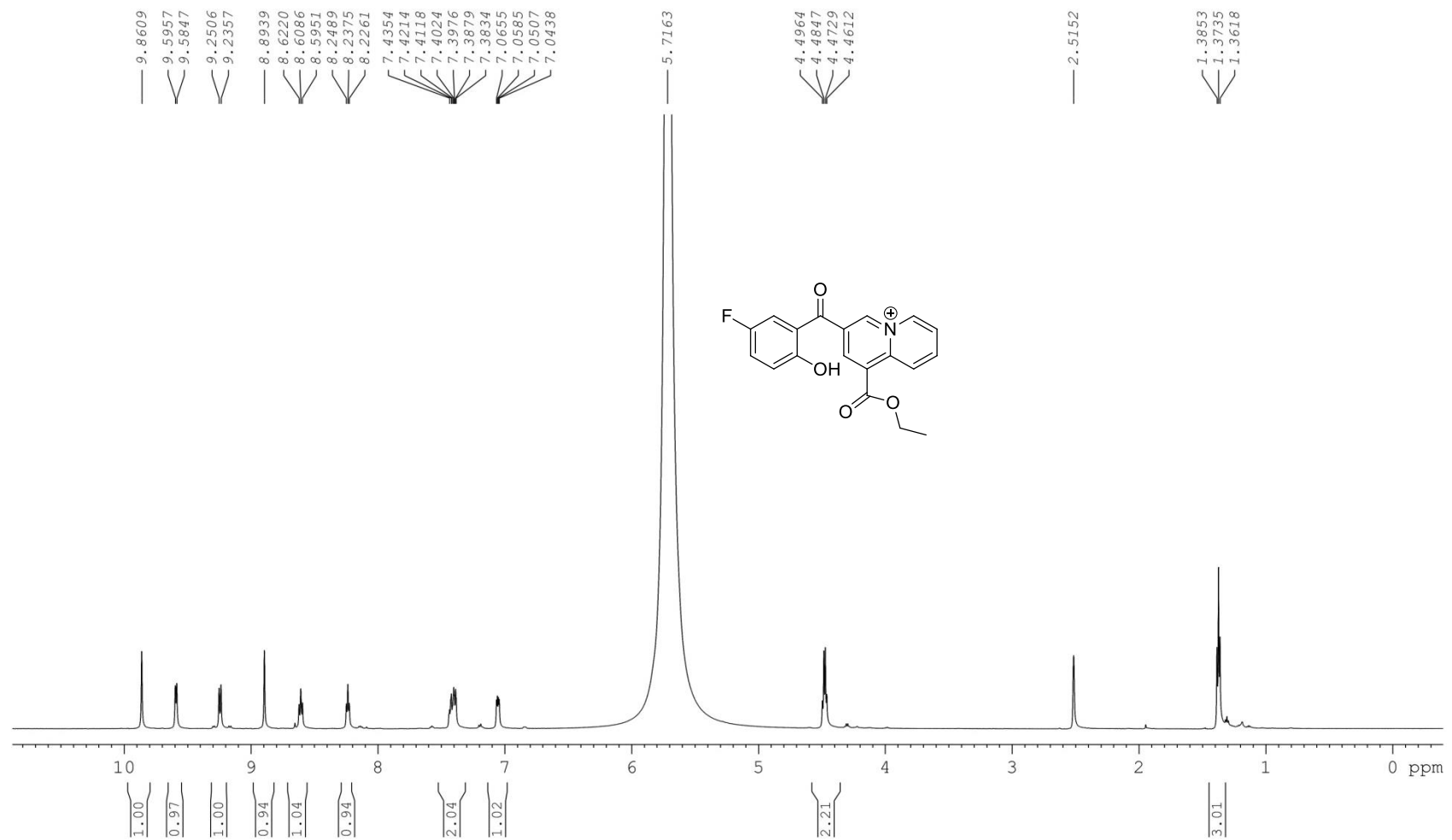


Figure S24.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6$ ) spectra of compound **3i**



**Figure S25.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4a**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-01  
Nov25-2019-chenli  
C13CPD DMSO

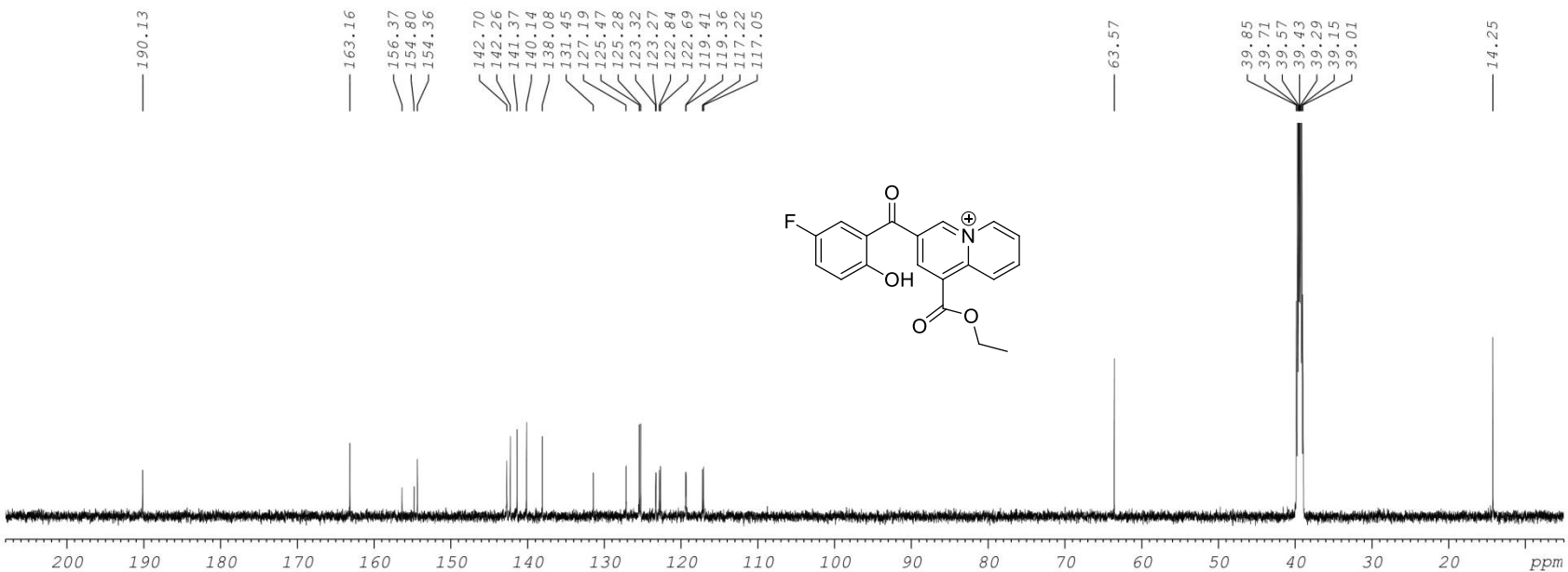
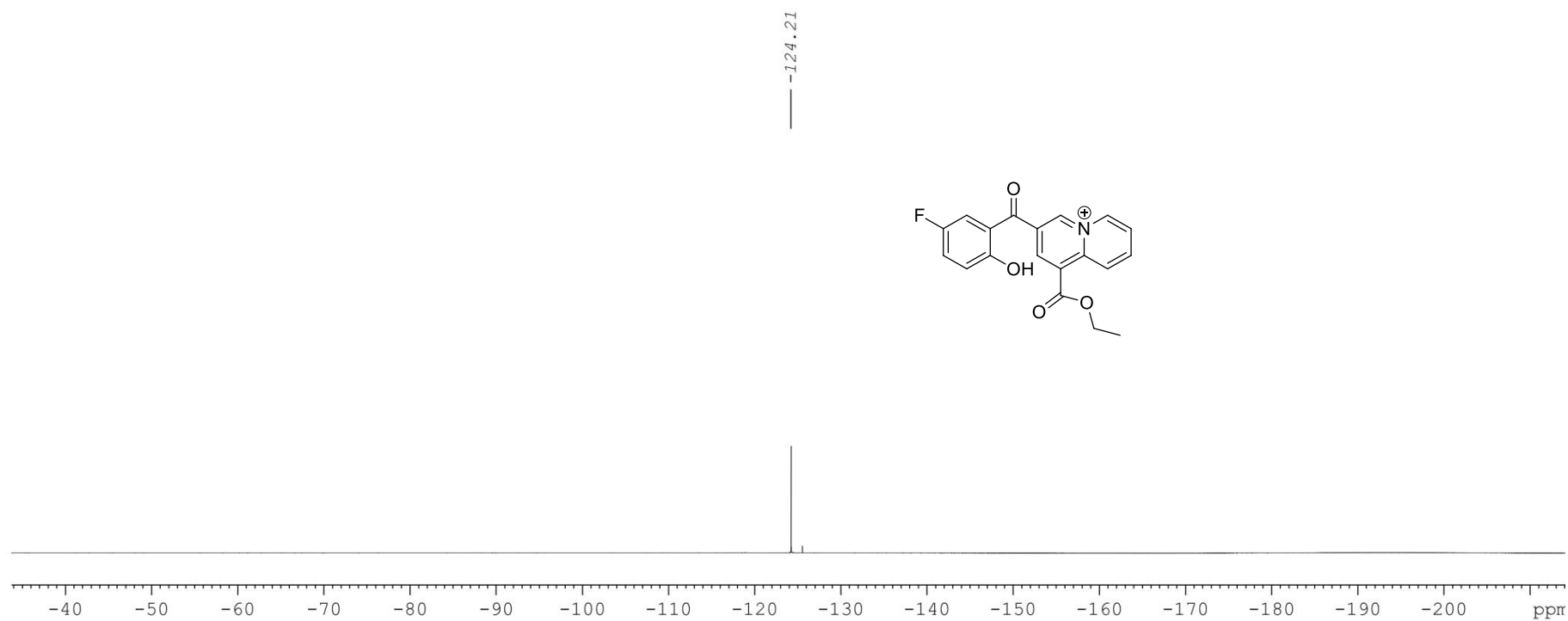
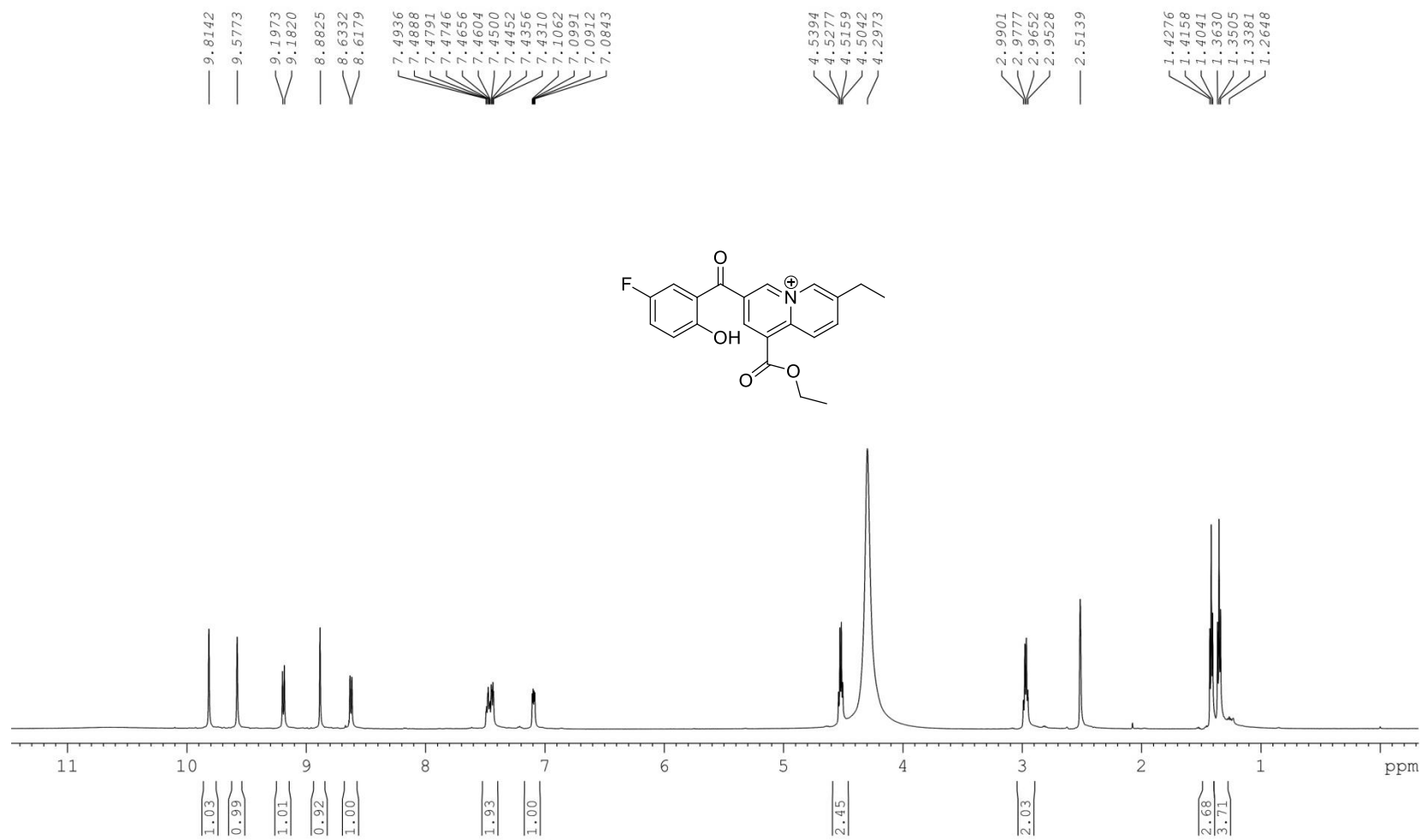


Figure S26.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4a



**Figure S27.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4a**





**Figure S28.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4b**

DEPT135

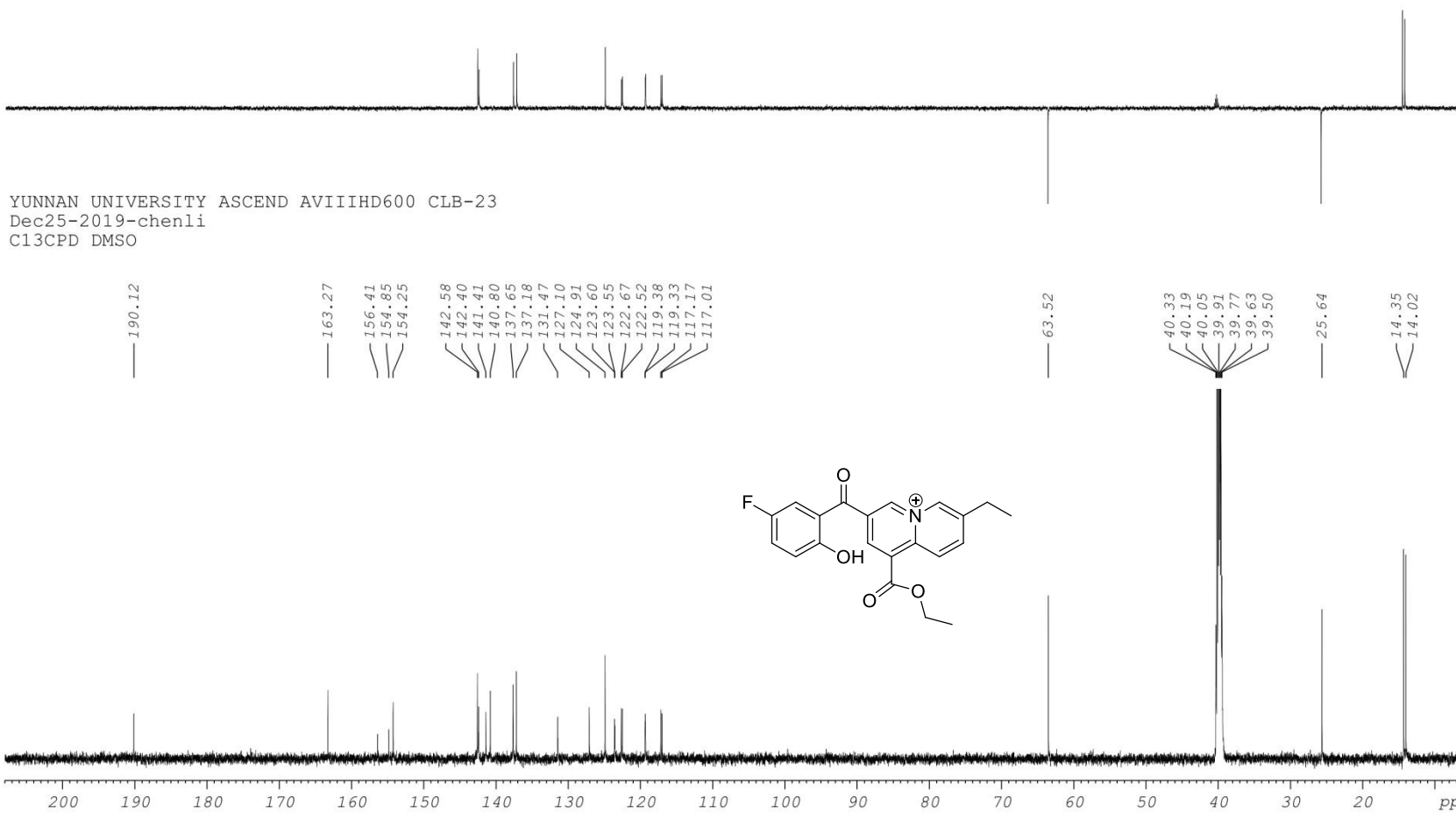
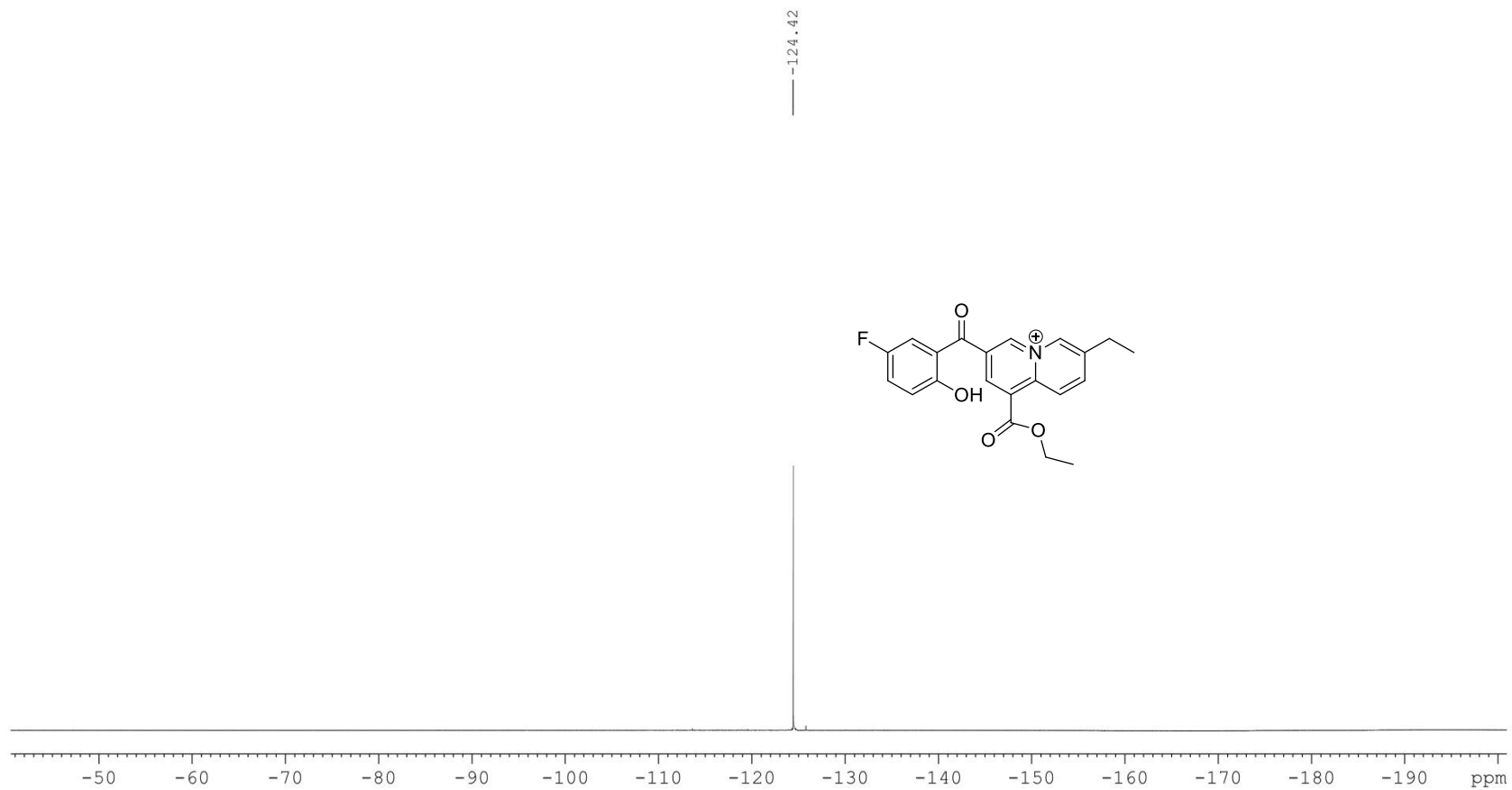
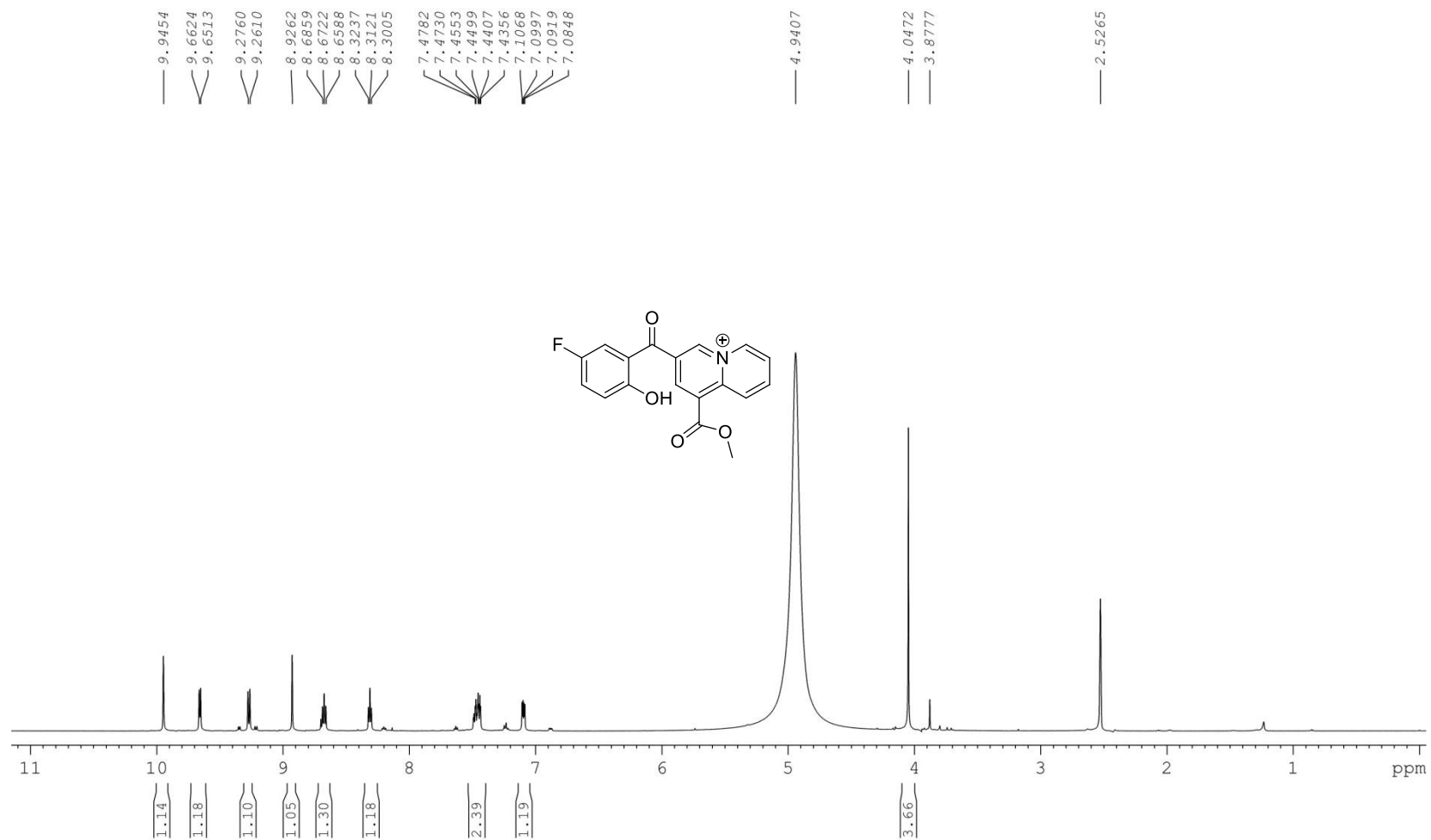


Figure S29.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound **4b**



**Figure S30.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4b**



**Figure S31.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4c**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIHD600 CLB-03  
Dec24-2019-chenli  
C13CPD DMSO

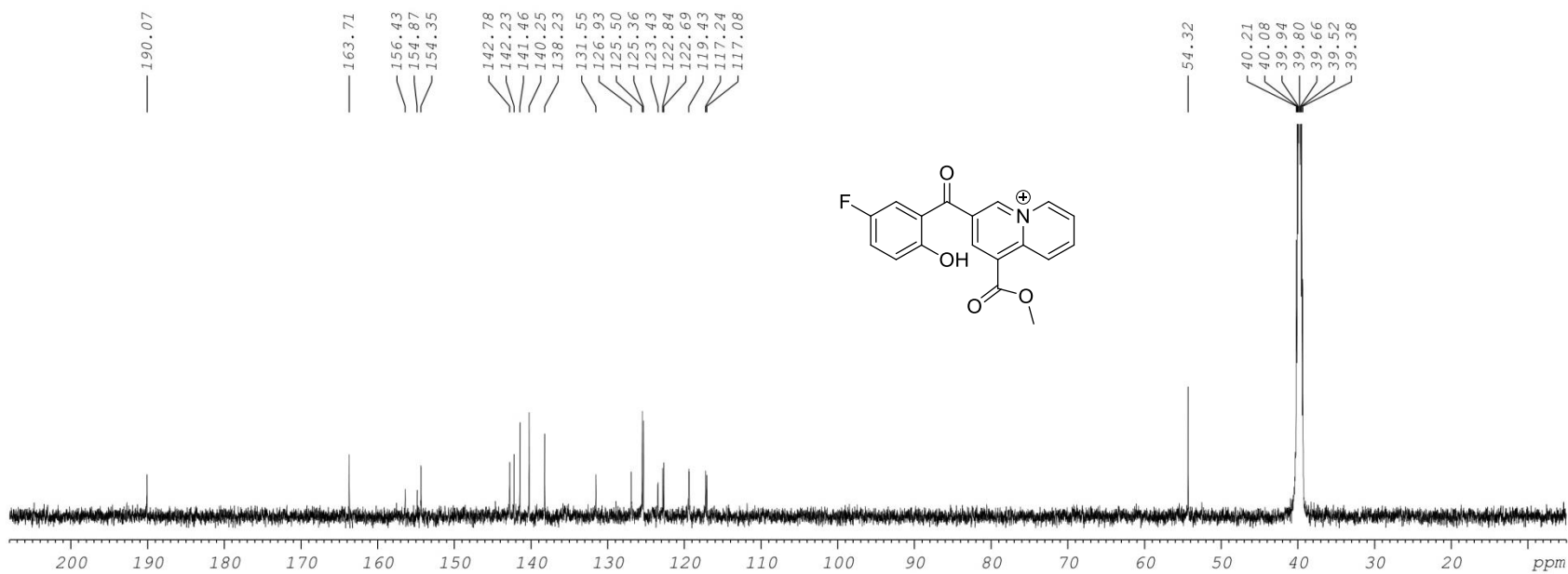
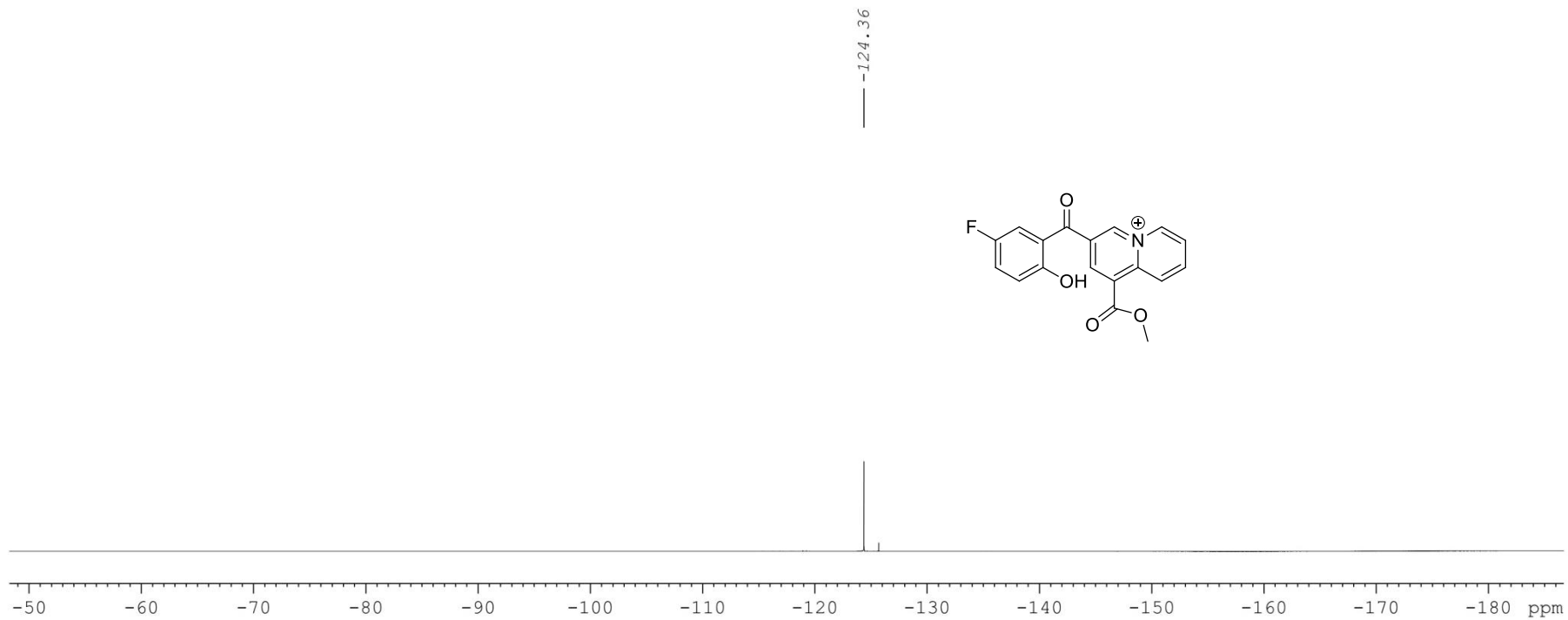
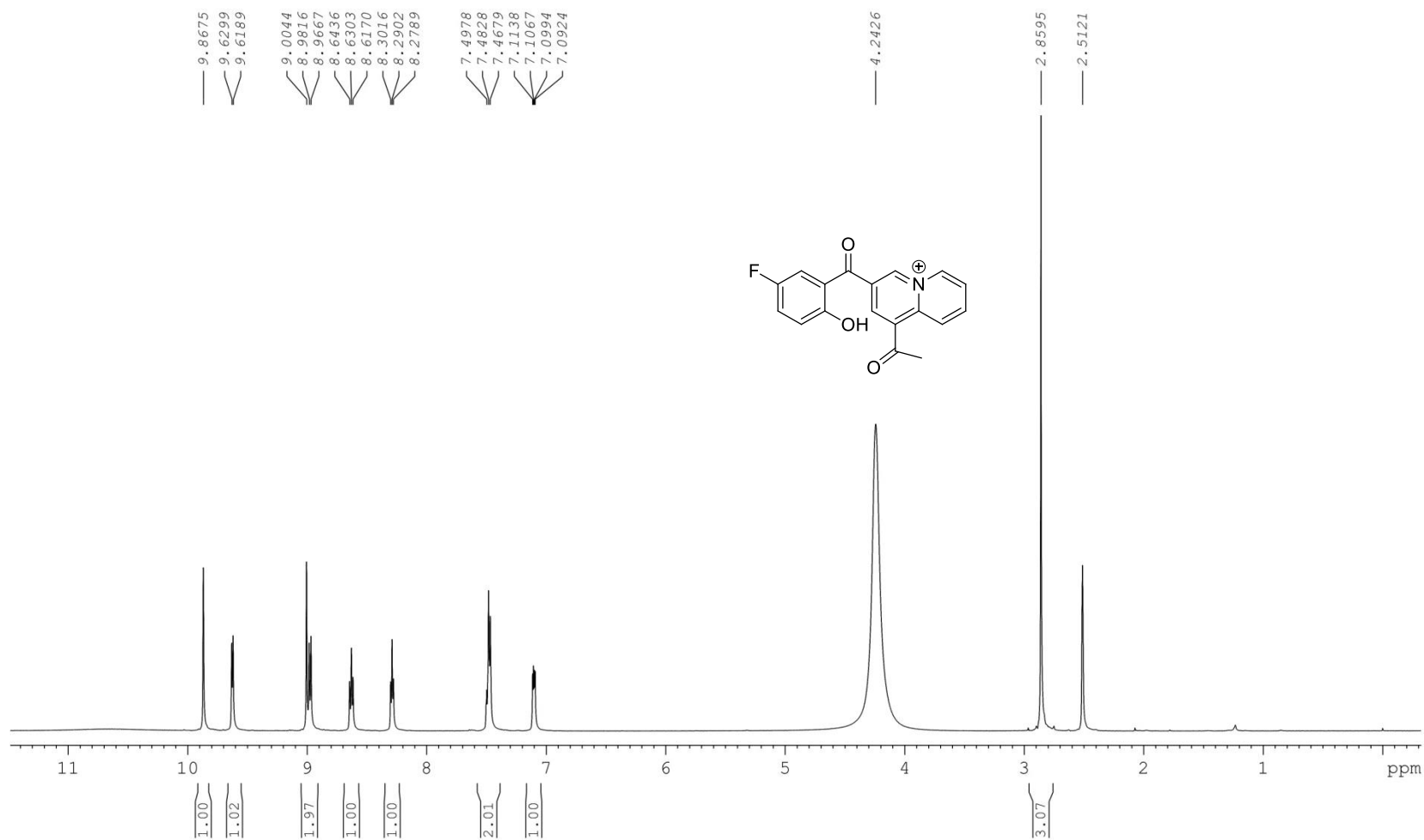


Figure S32.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4c



**Figure S33.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4c**



**Figure S34.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4d**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-07  
Dec27-2019-chenli  
C13CPD DMSO

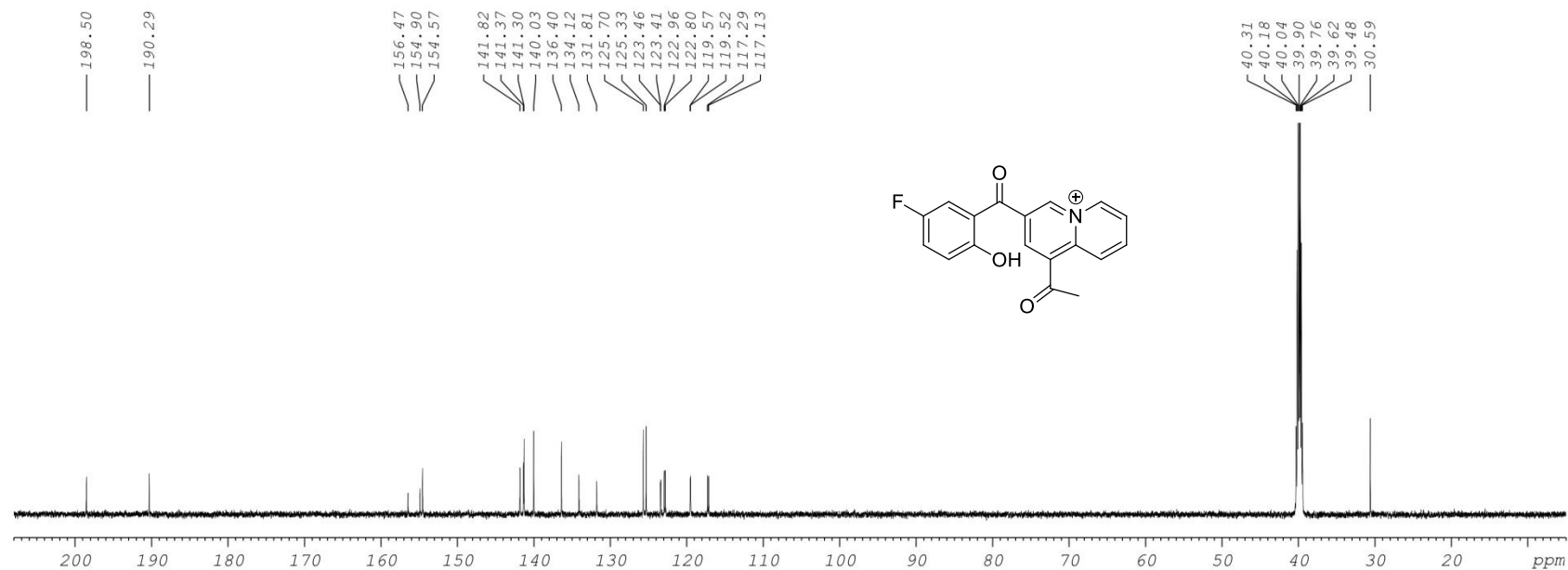
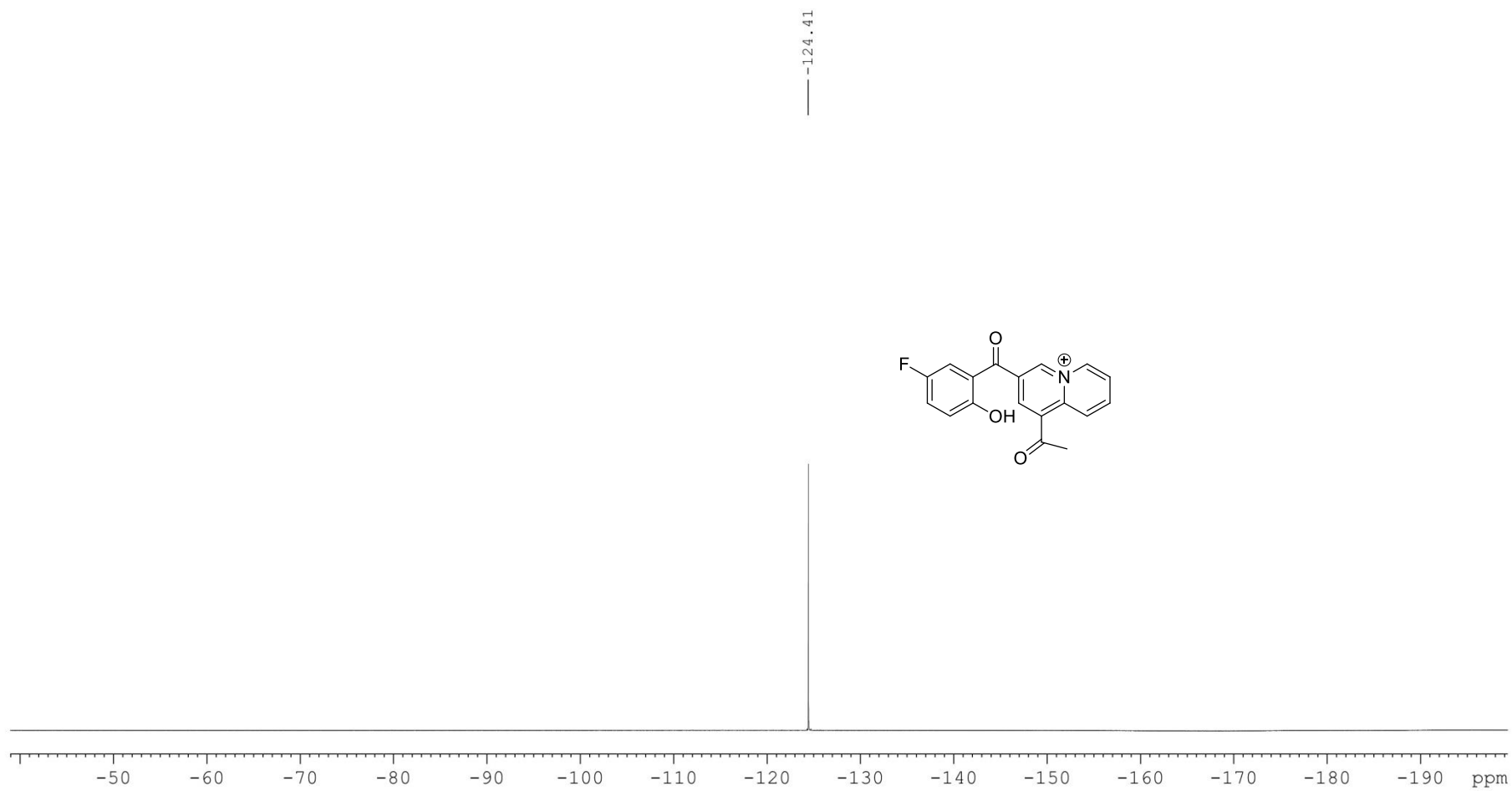
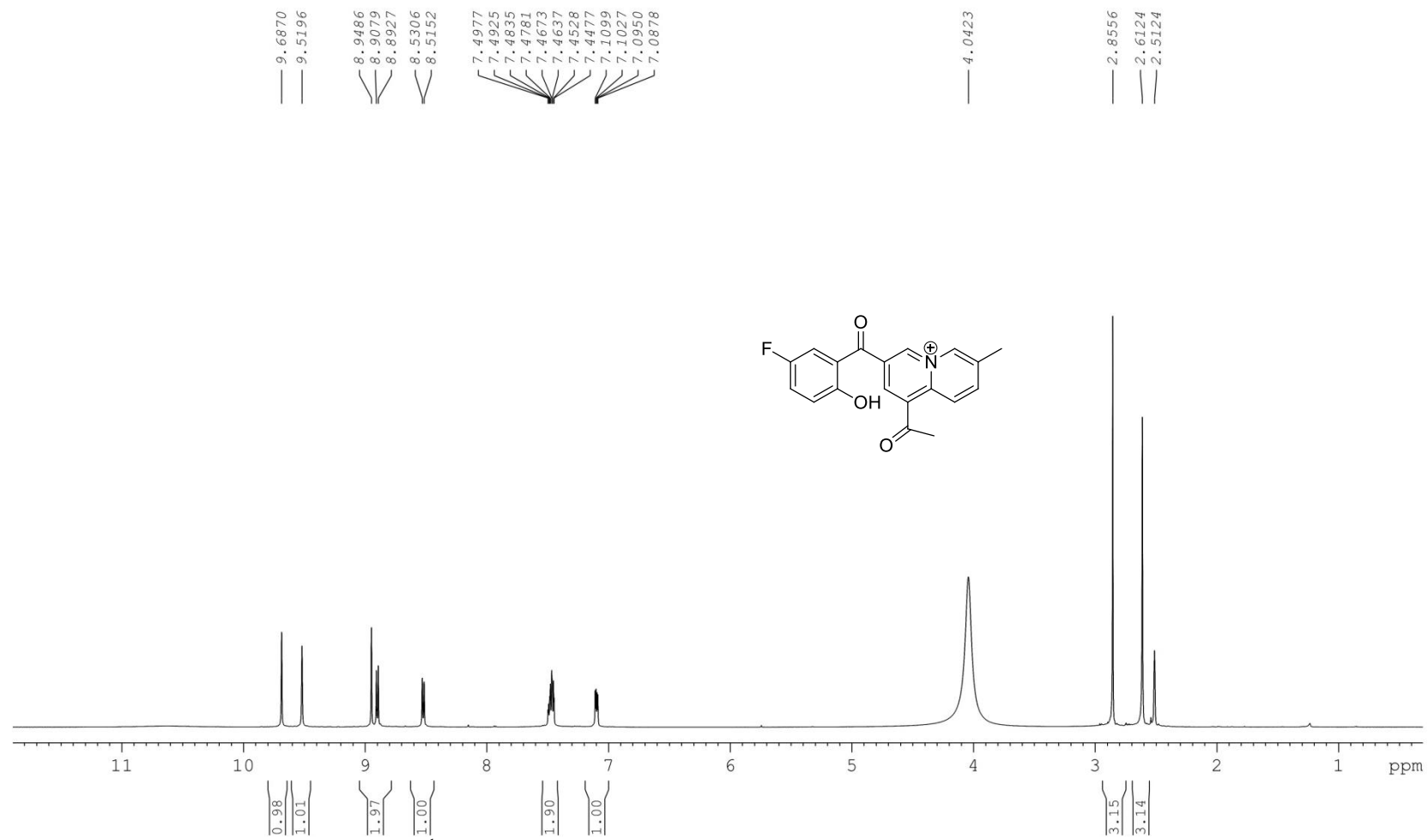


Figure S35.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4d





**Figure S36.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6$ + $\text{HClO}_4$ ) spectra of compound **4d**



**Figure S37.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4e**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-09  
Nov26-2019-chenli  
C13CPD DMSO

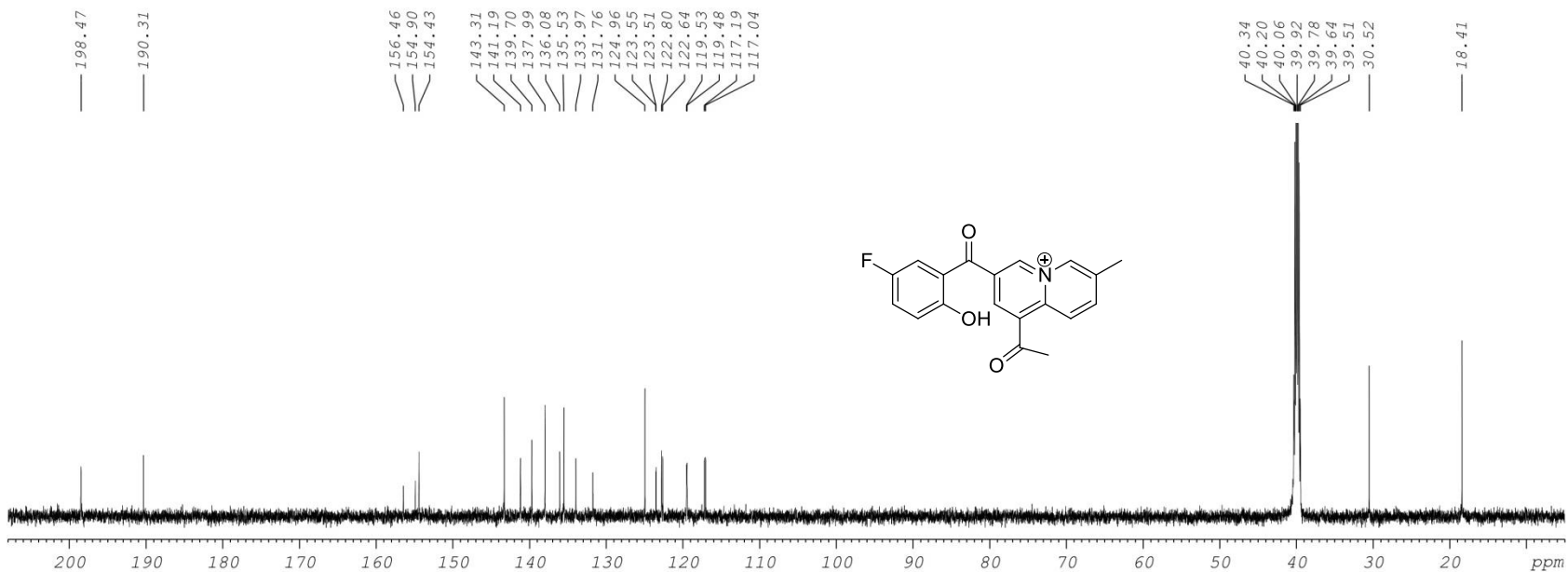
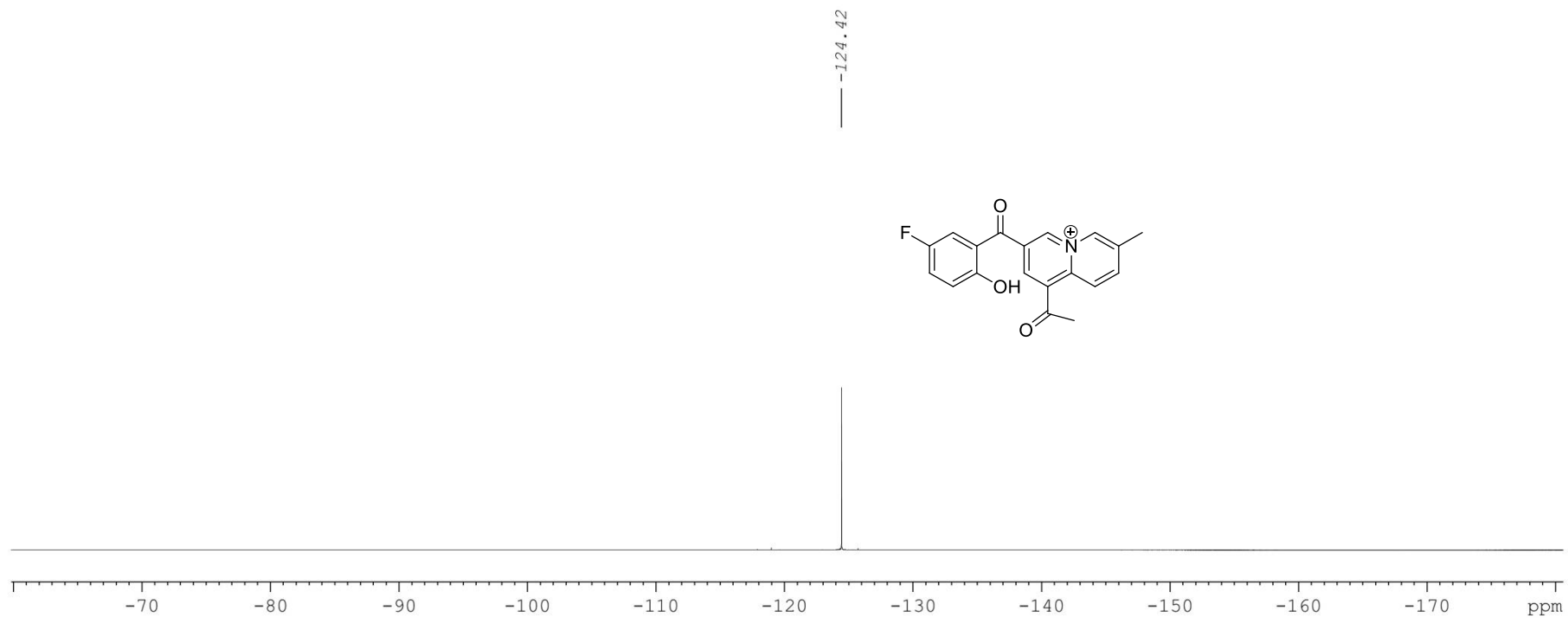
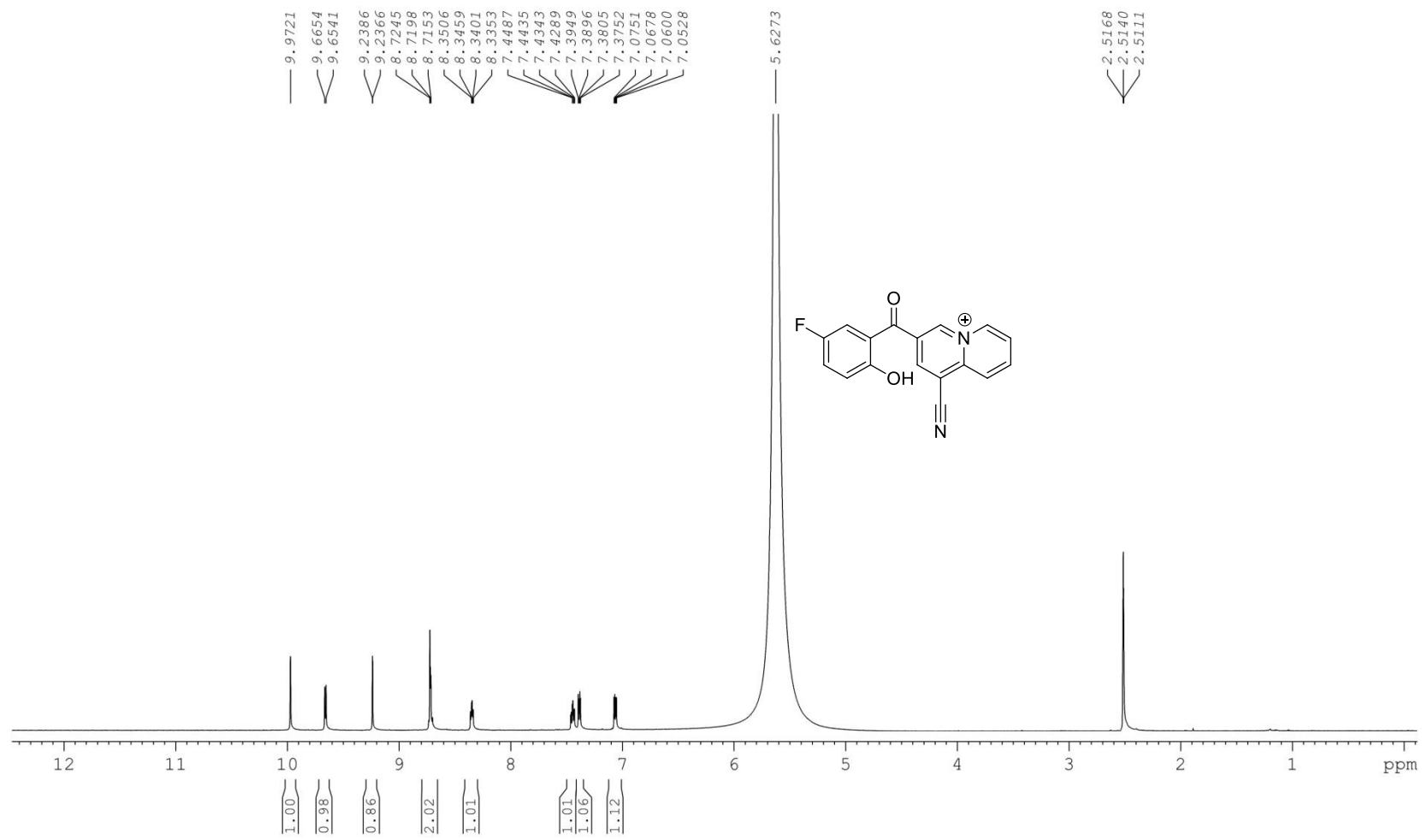


Figure S38.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound **4e**



**Figure S39.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6$ + $\text{HClO}_4$ ) spectra of compound **4e**



**Figure S40.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4f**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-04  
Jan07-2020-chenli  
C13CPD DMSO

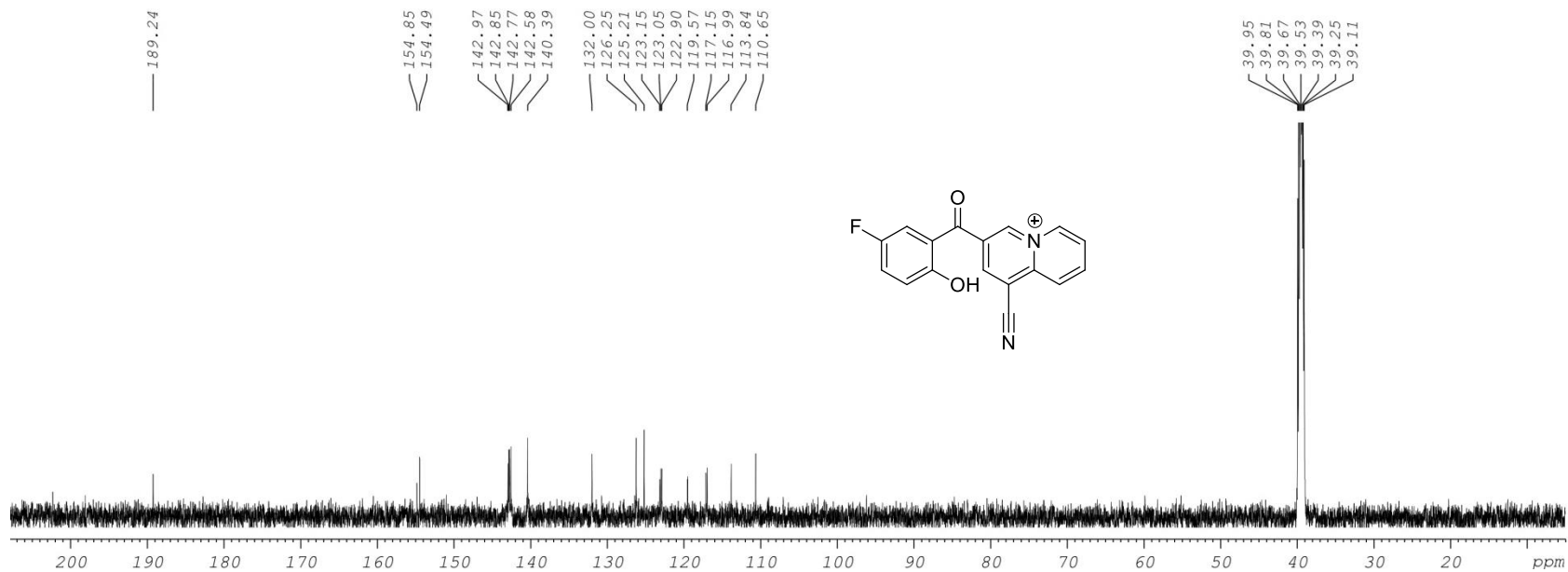
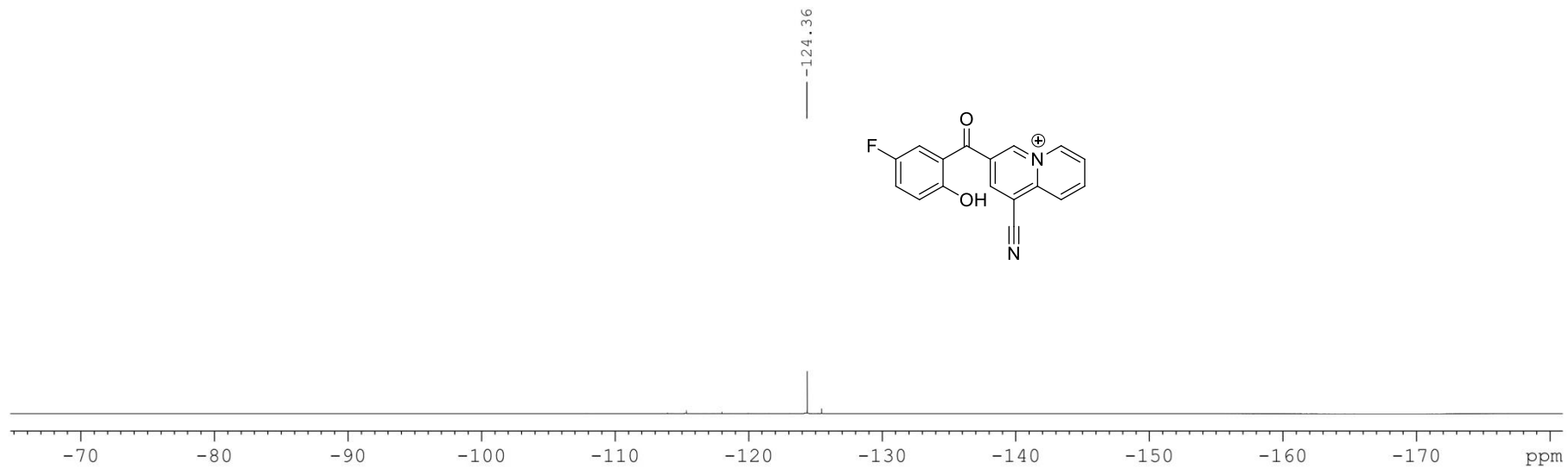
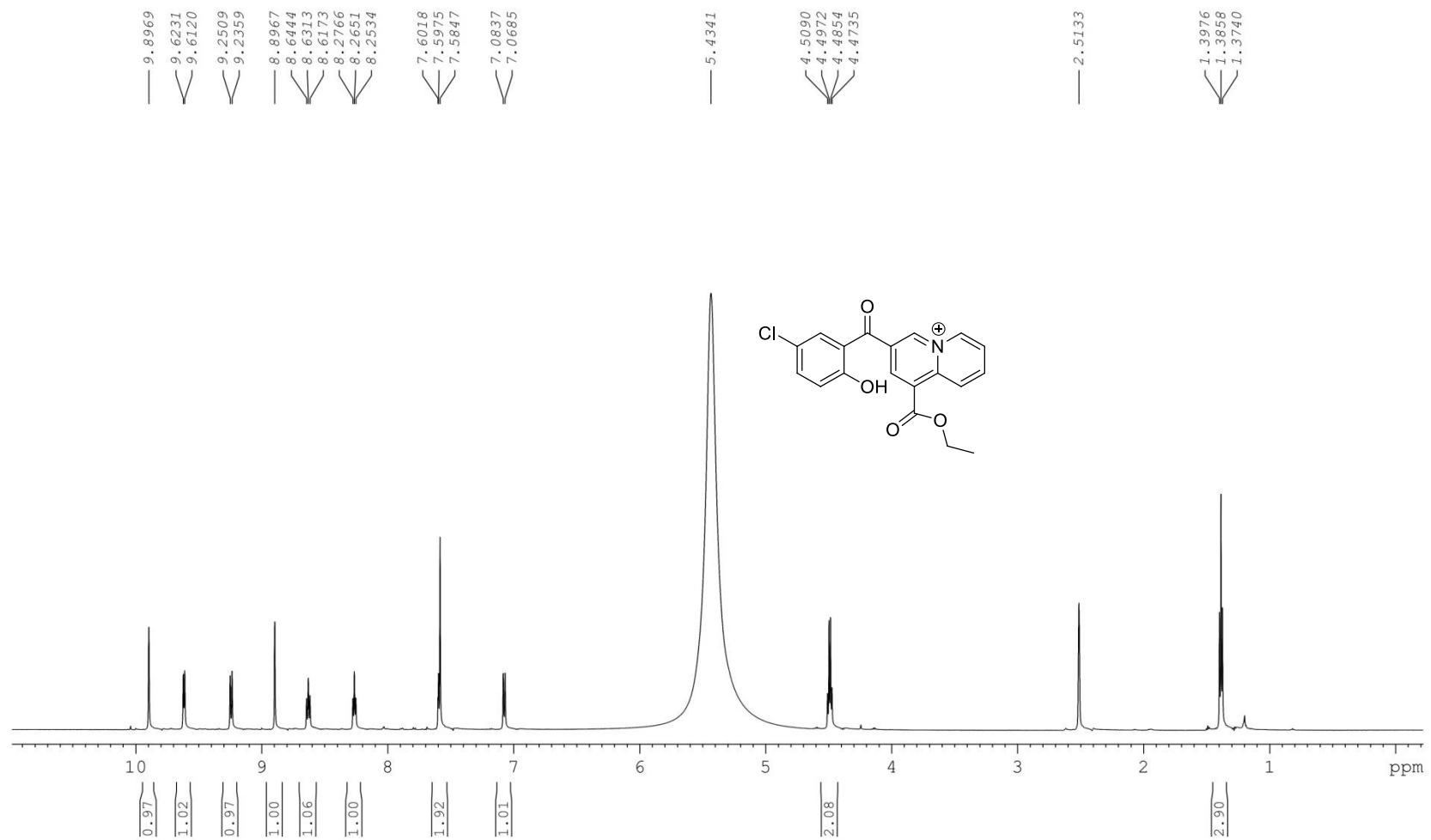


Figure S41.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound 4f



**Figure S42.**  $^{19}\text{F}$  NMR (564 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4f**



**Figure S43.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound 4g



DEPT135

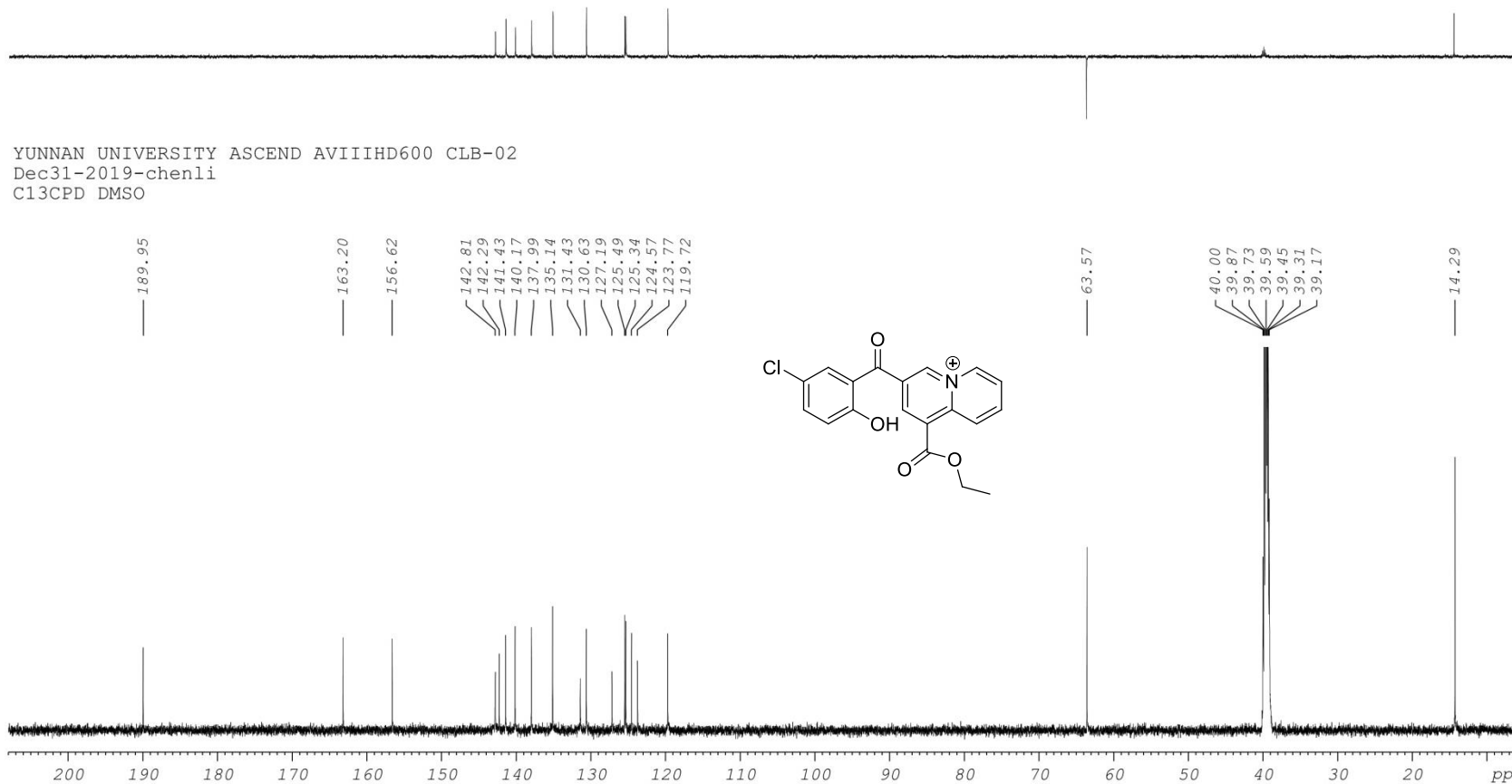
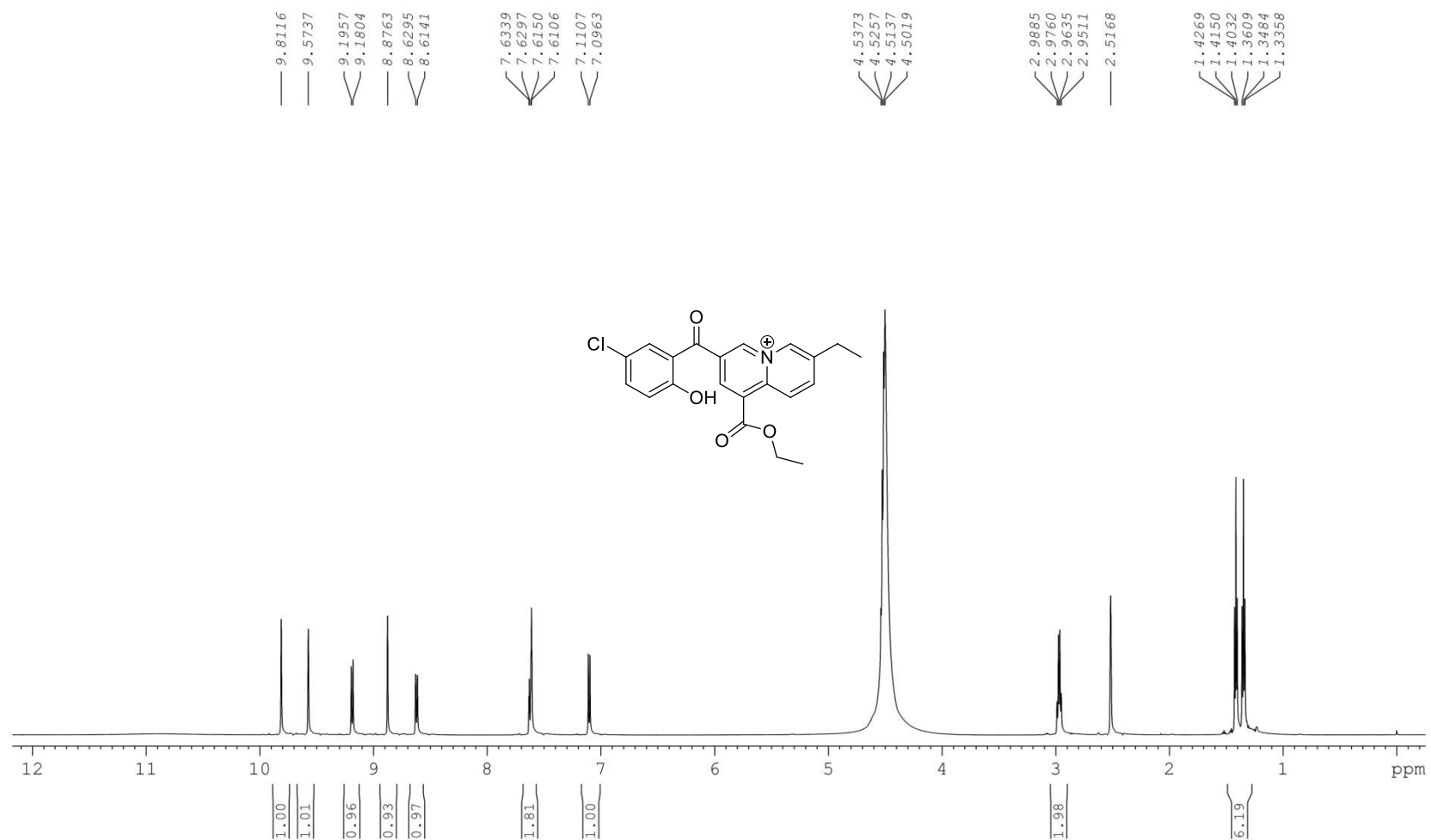


Figure S44.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound **4g**



**Figure S45.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4h**

DEPT135

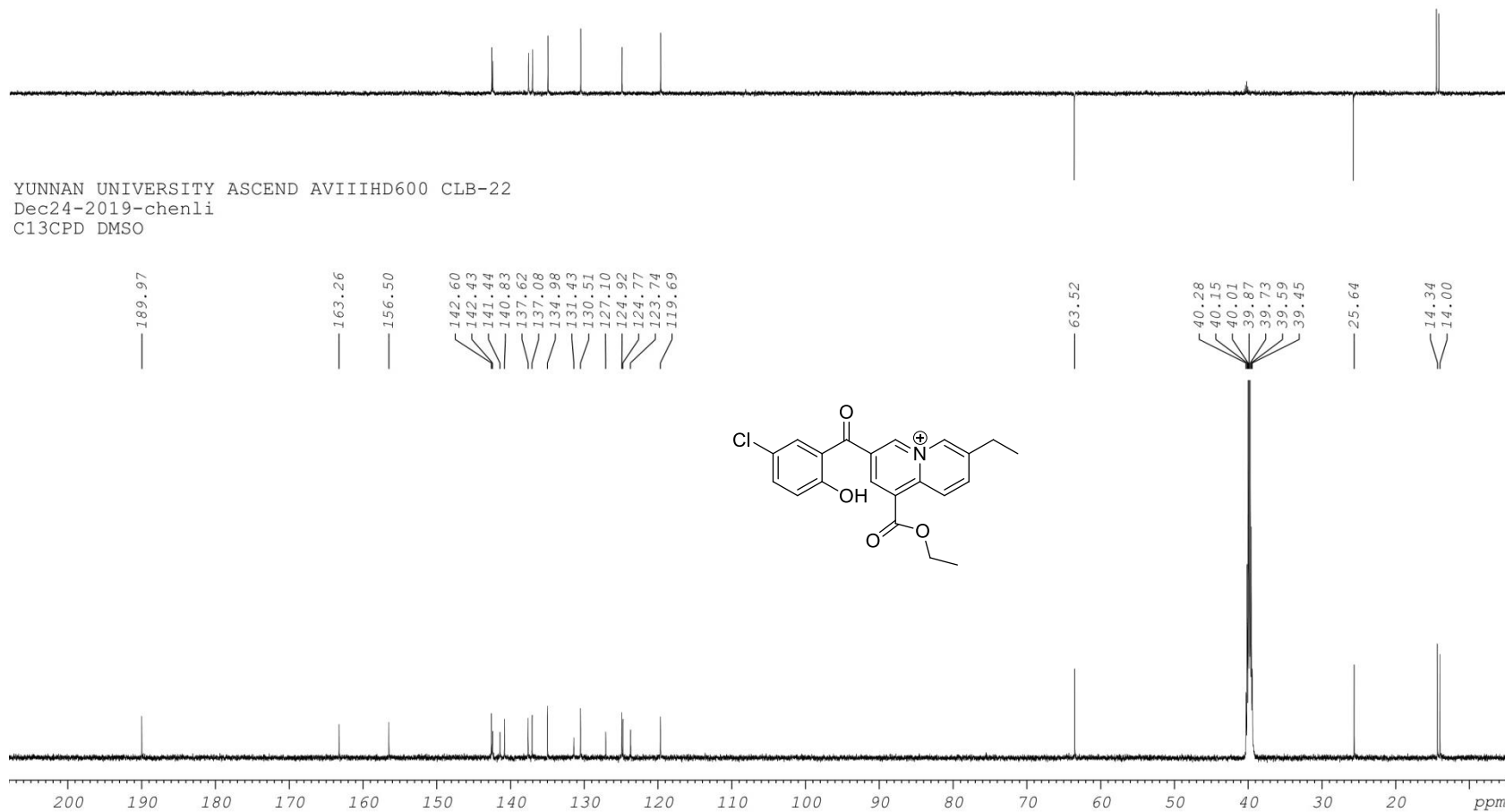
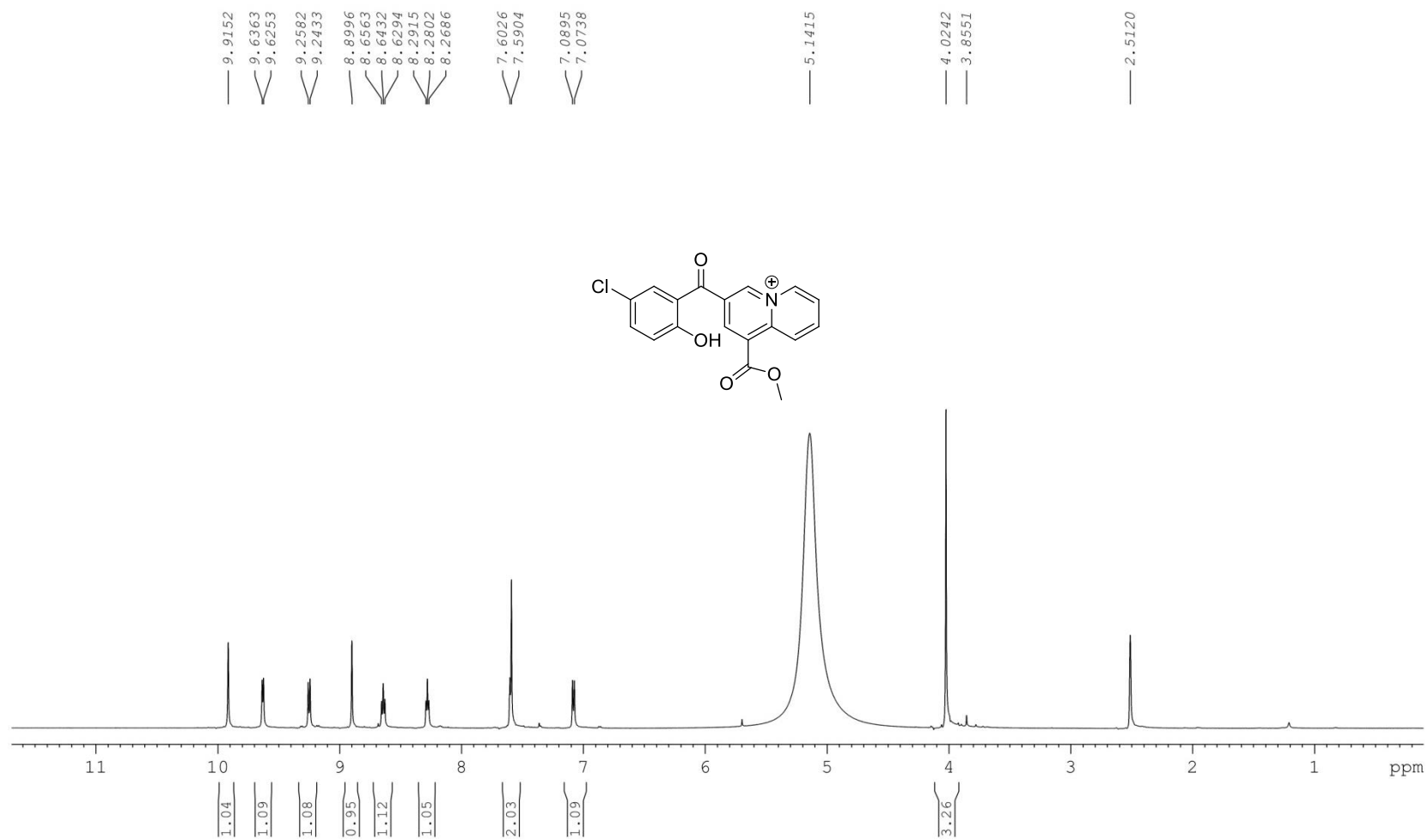


Figure S46.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound **4h**



**Figure S47.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4i**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-05  
Nov26-2019-chenli  
C13CPD DMSO

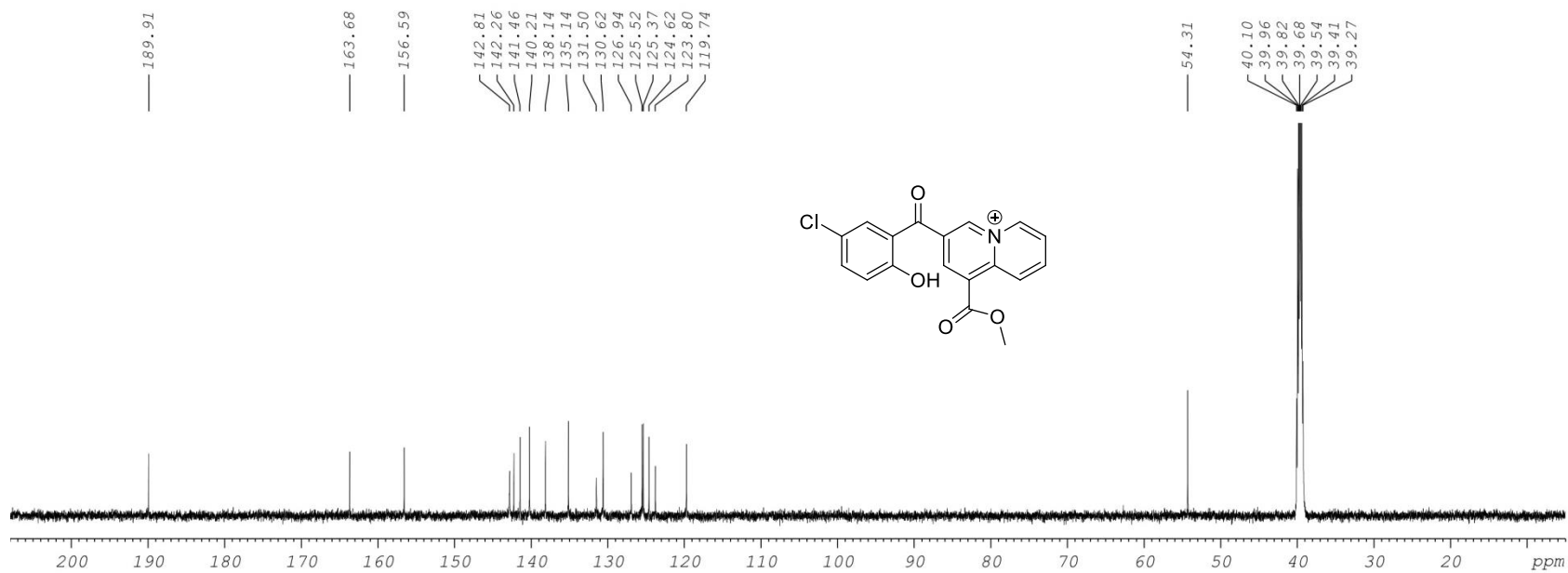
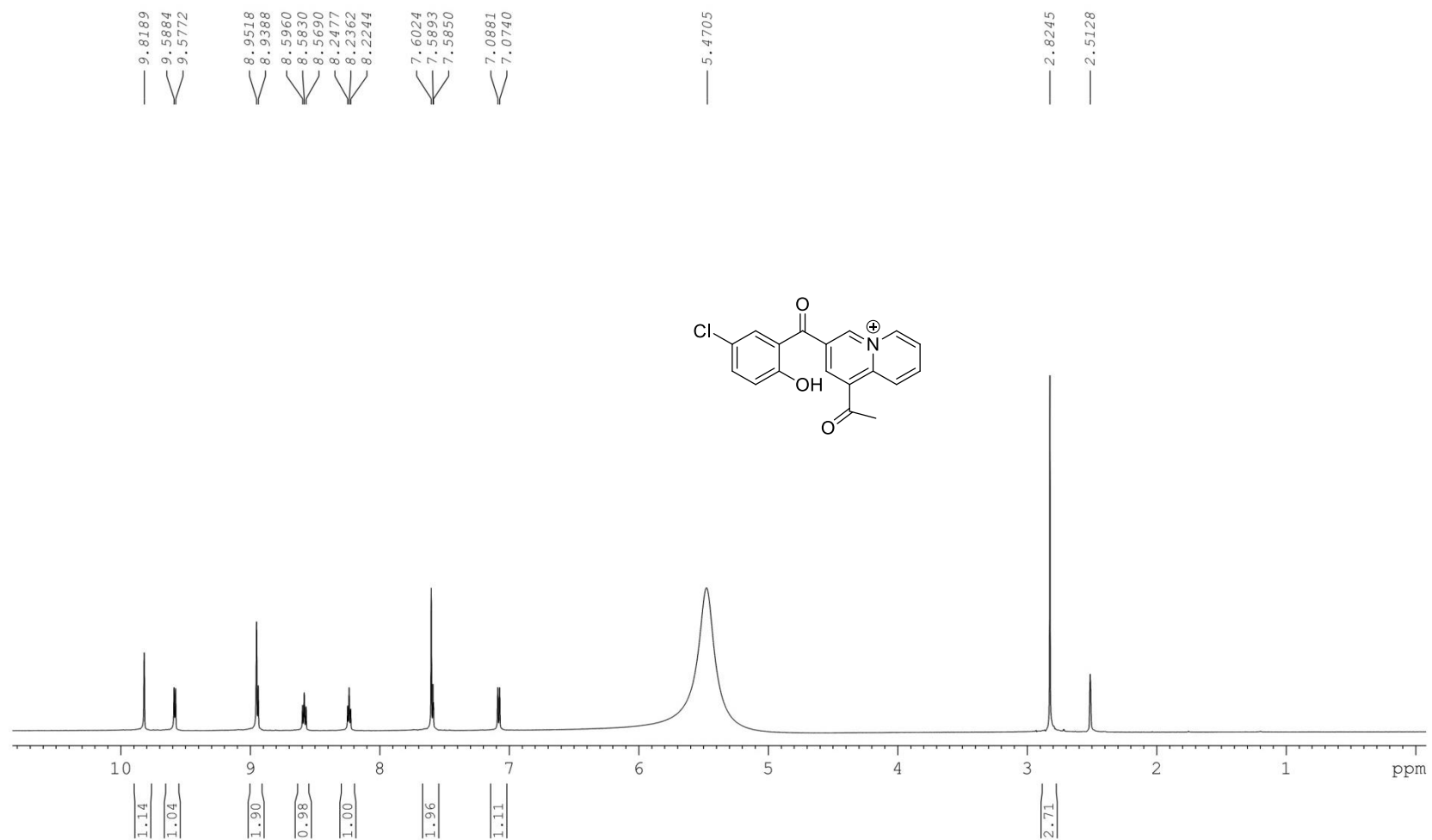
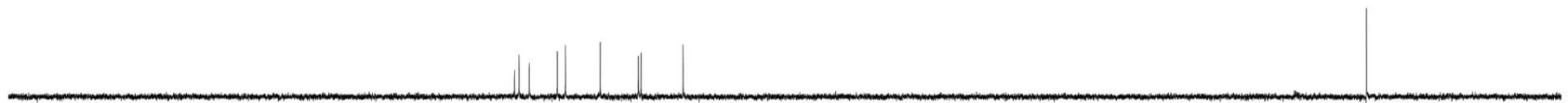


Figure S48.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4i



**Figure S49.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4j**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-08  
Dec27-2019-chenli  
C13CPD DMSO

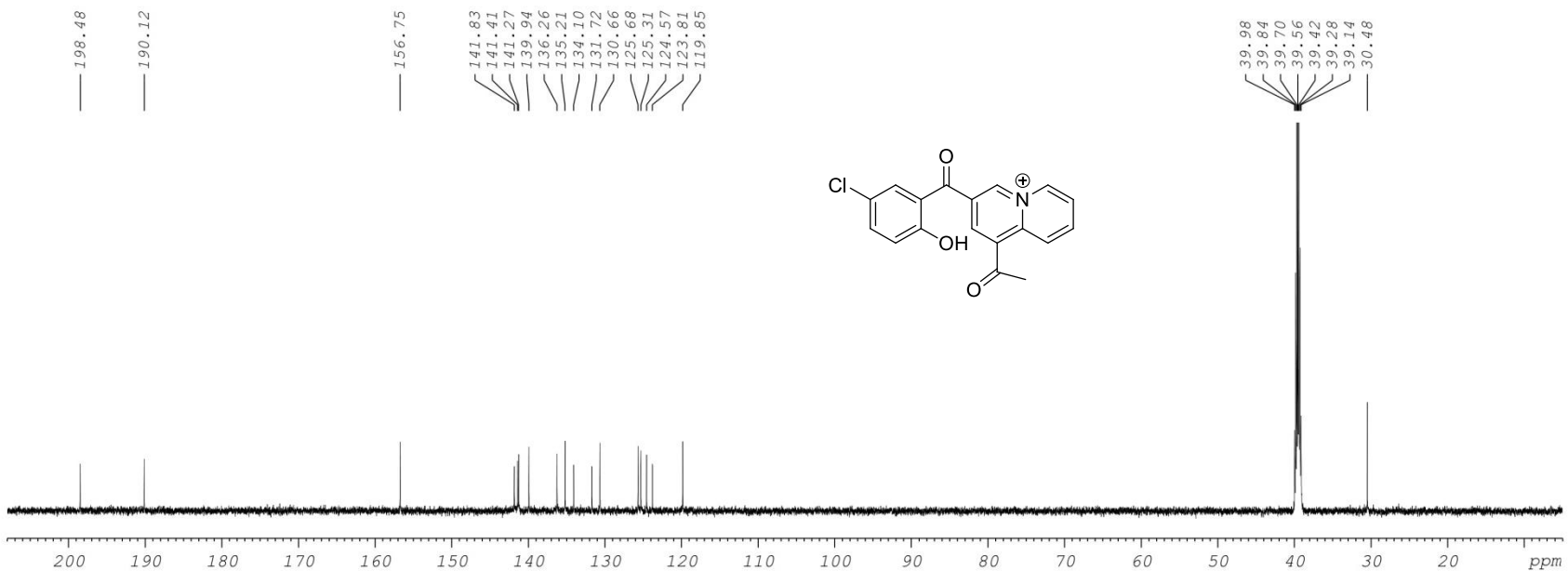
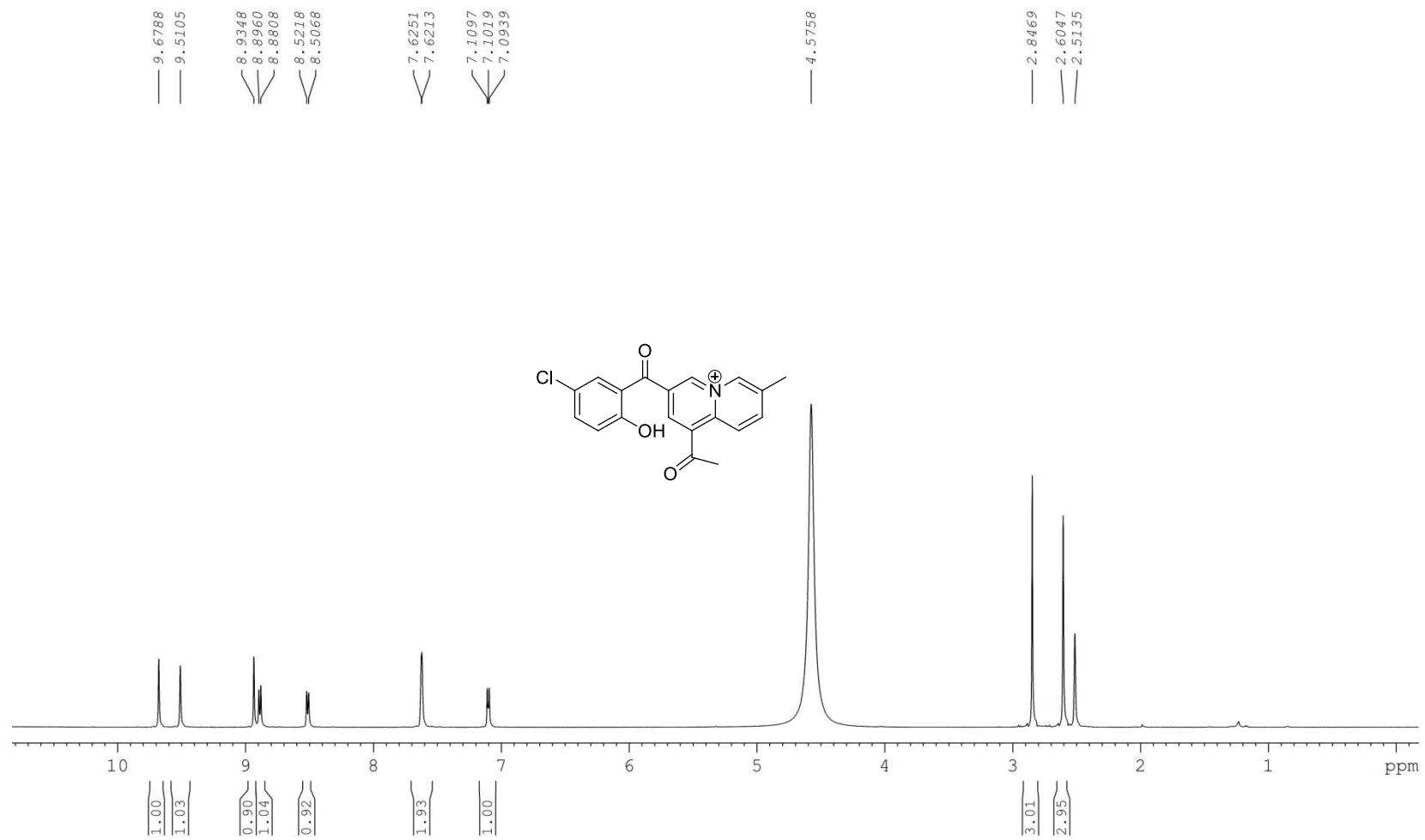


Figure S50.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound 4j



**Figure S51.**  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4k**



DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-10  
Dec09-2019-chenli  
C13CPD DMSO

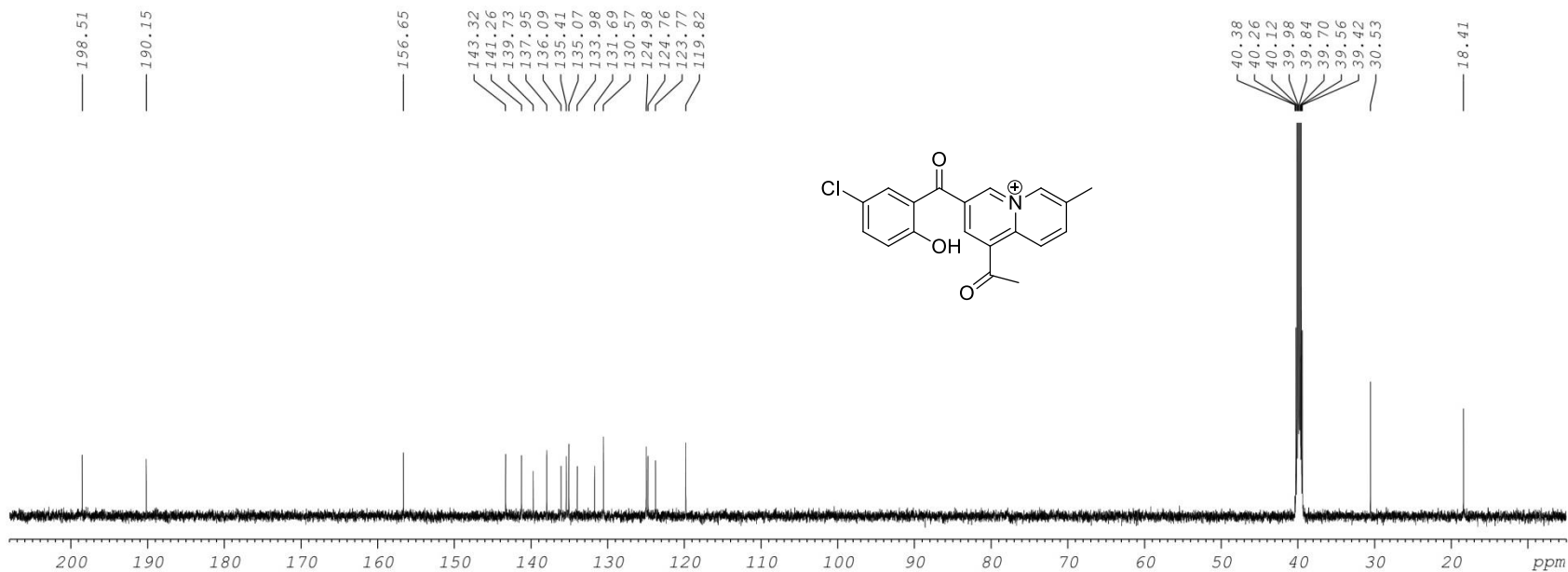
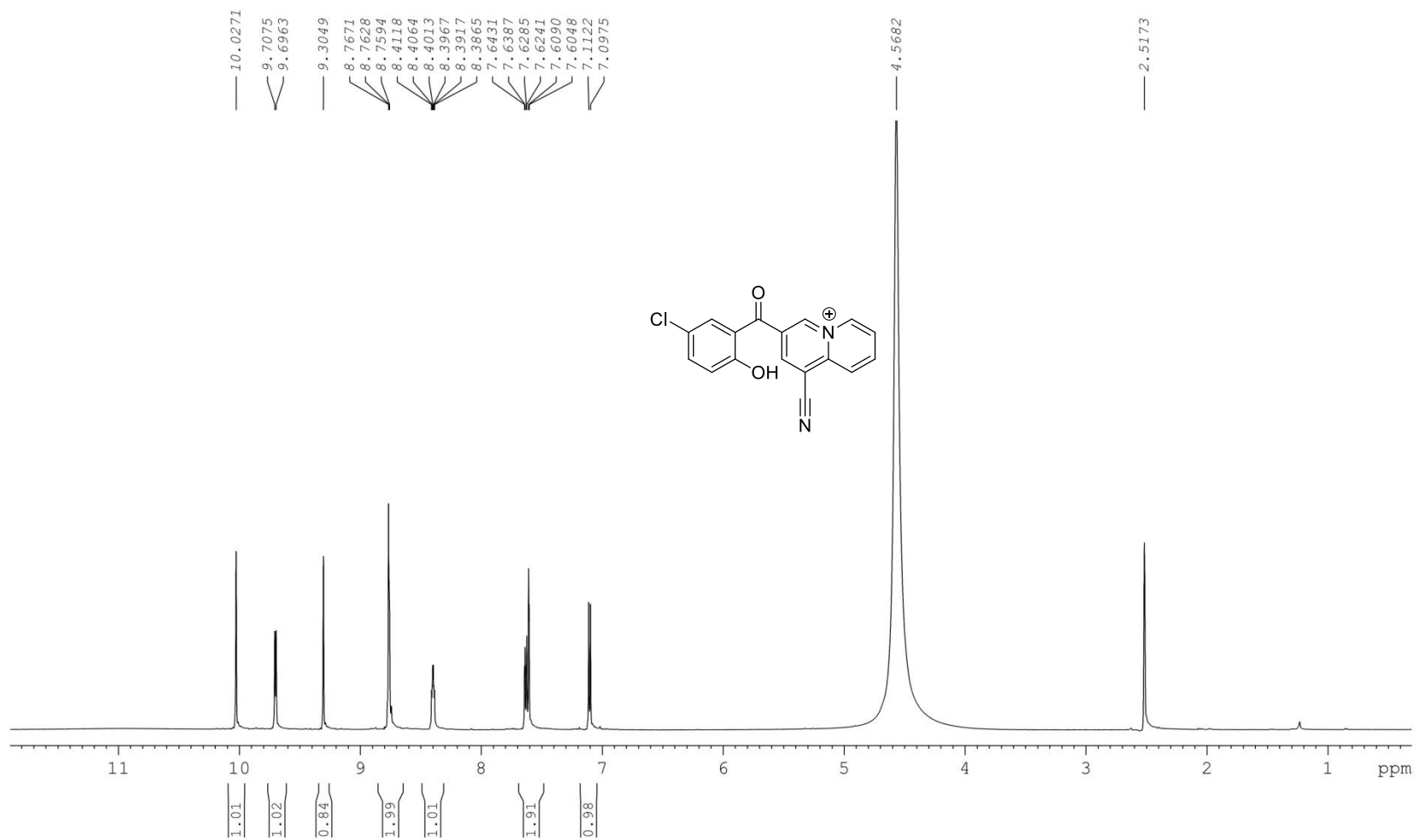


Figure S52.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound 4k



**Figure S53.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **41**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-06  
Nov26-2019-chenli  
C13CPD DMSO

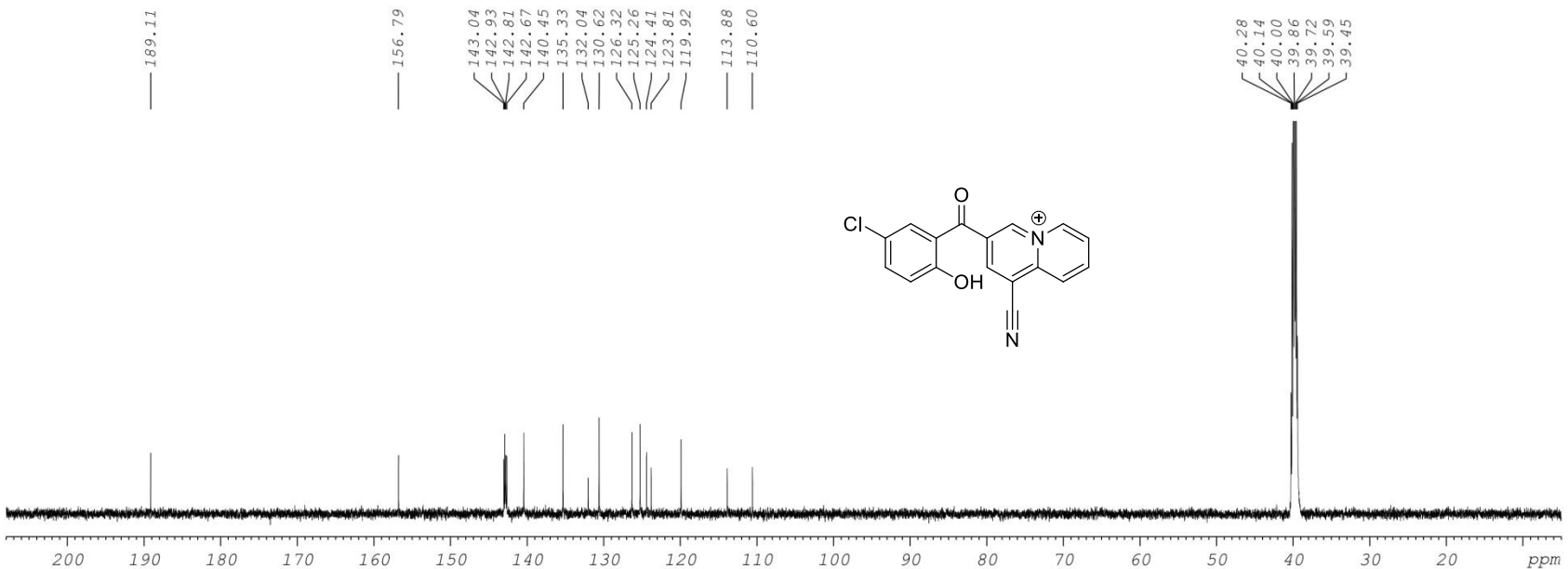


Figure S54.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4l

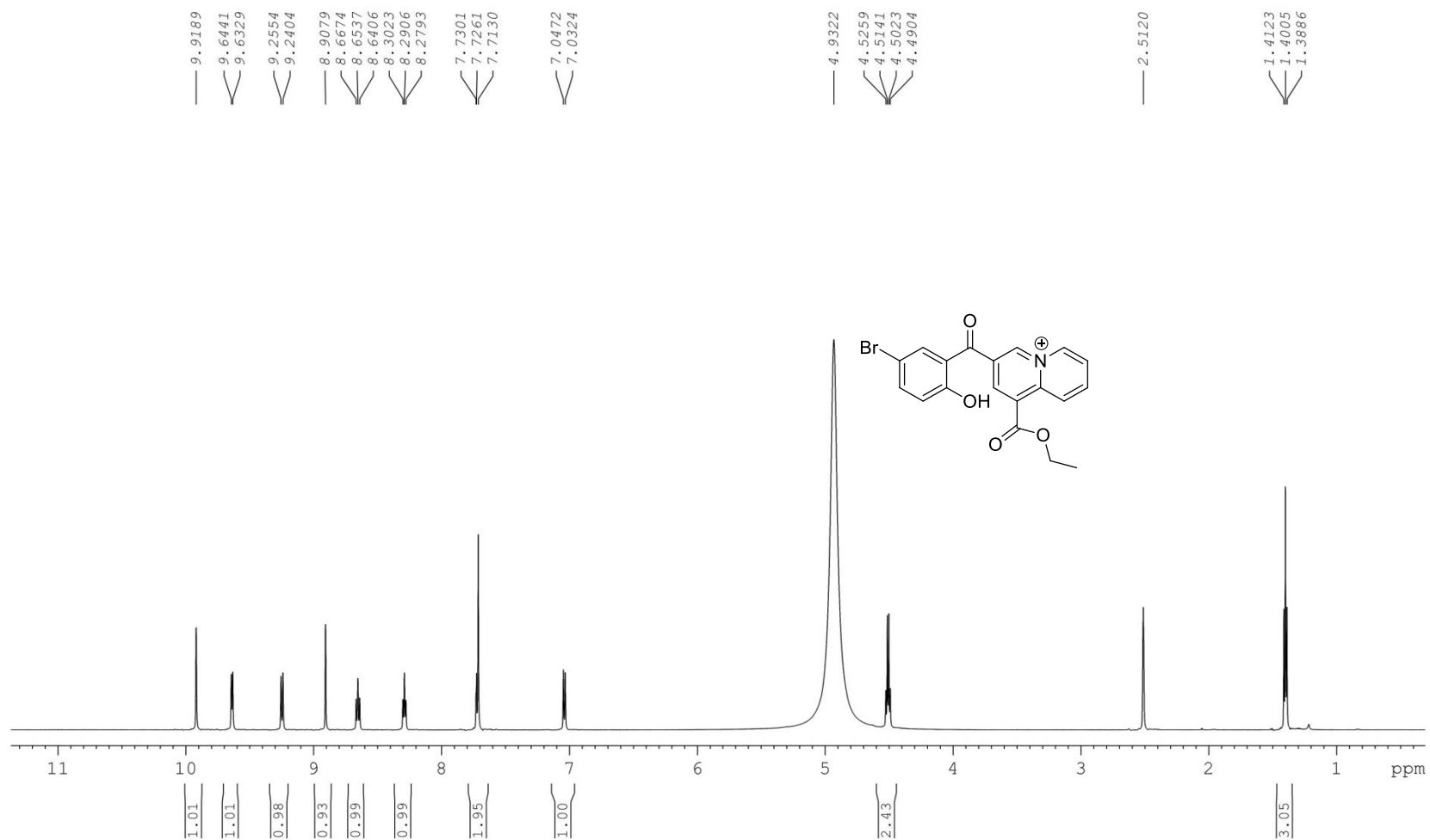


Figure S55.  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound 4m

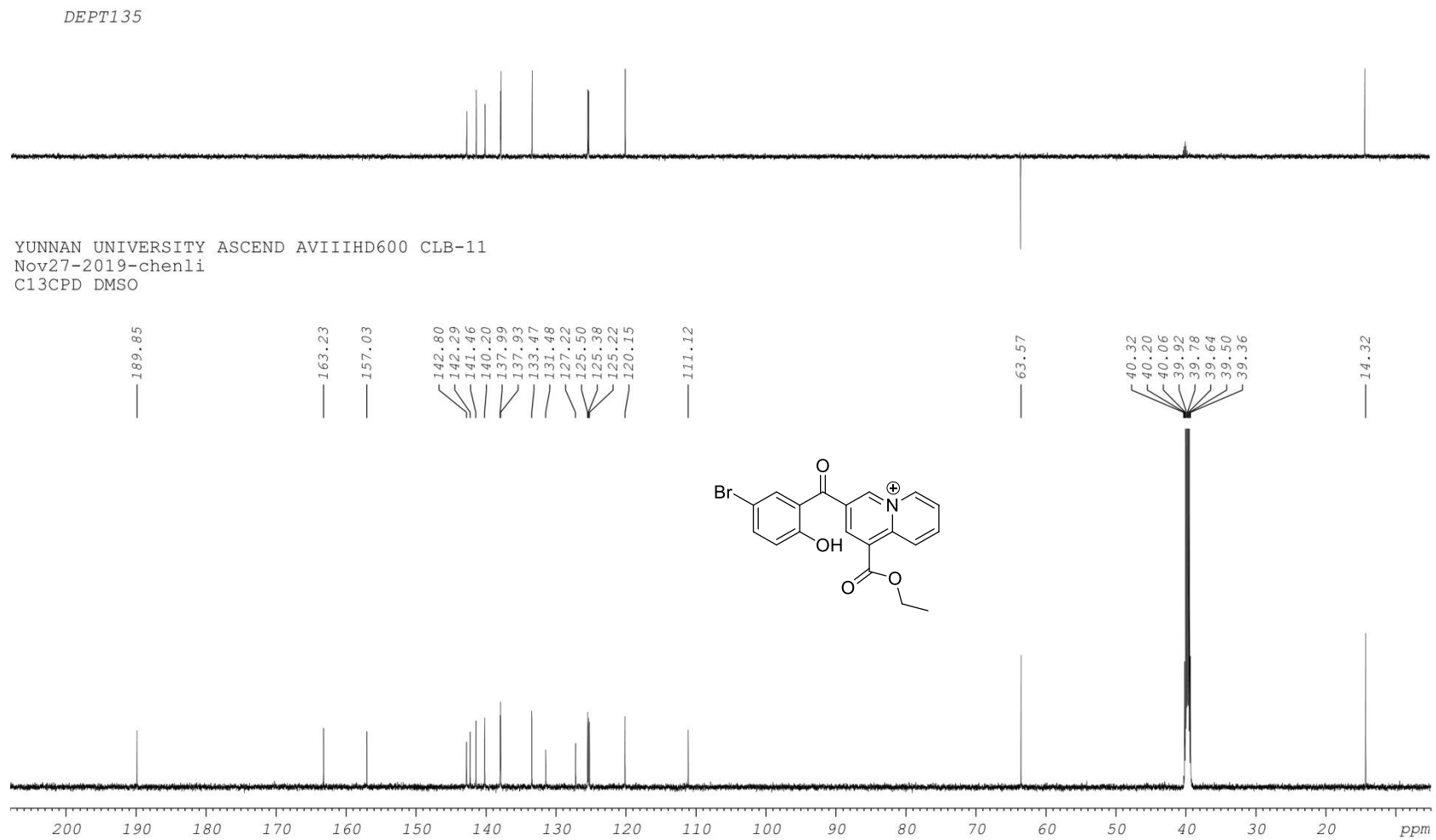
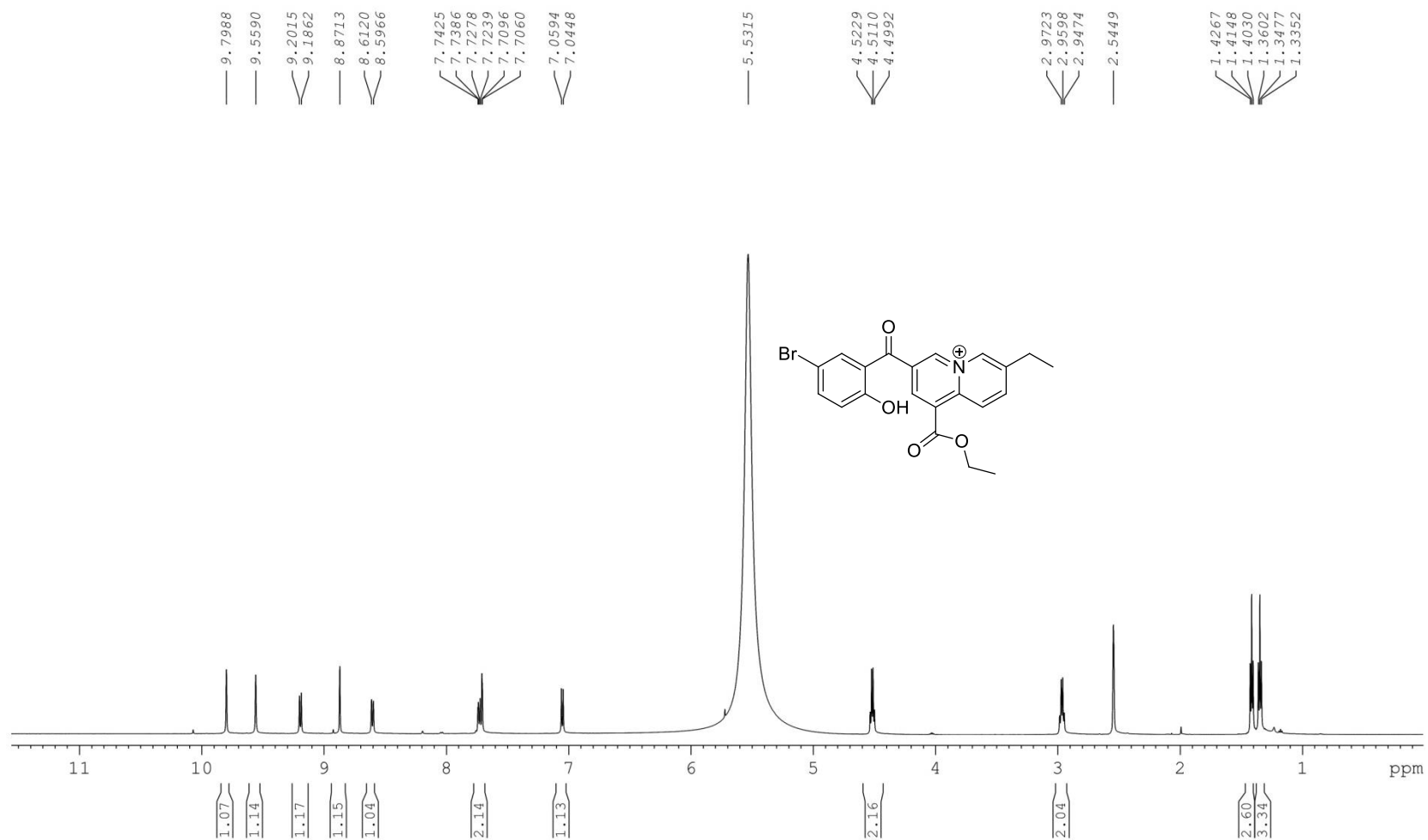
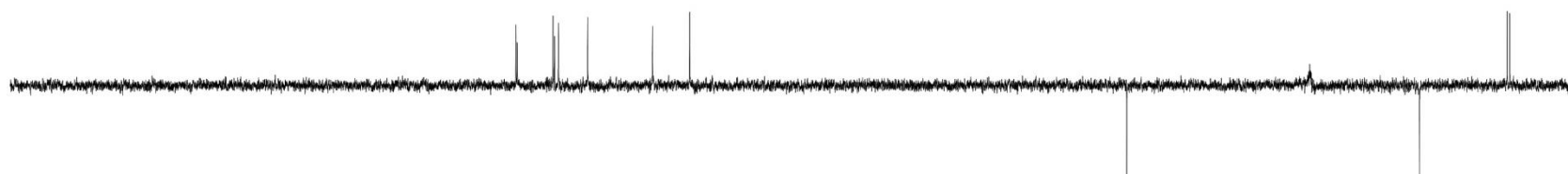


Figure S56.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4m**



**Figure S57.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4n**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-14  
Dec18-2019-chenli  
C13CPD DMSO

189.90

163.21

156.83

142.57

142.38

141.50

140.81

137.77

137.57

137.07

133.28

131.38

127.04

125.32

124.89

120.08

111.10

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39.60

39.46

39.32

39.18

25.61

14.29

13.94

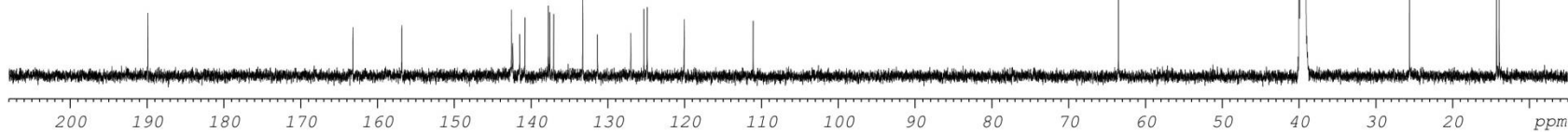
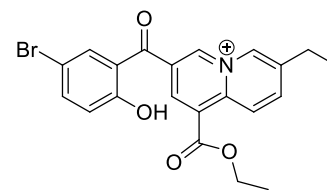
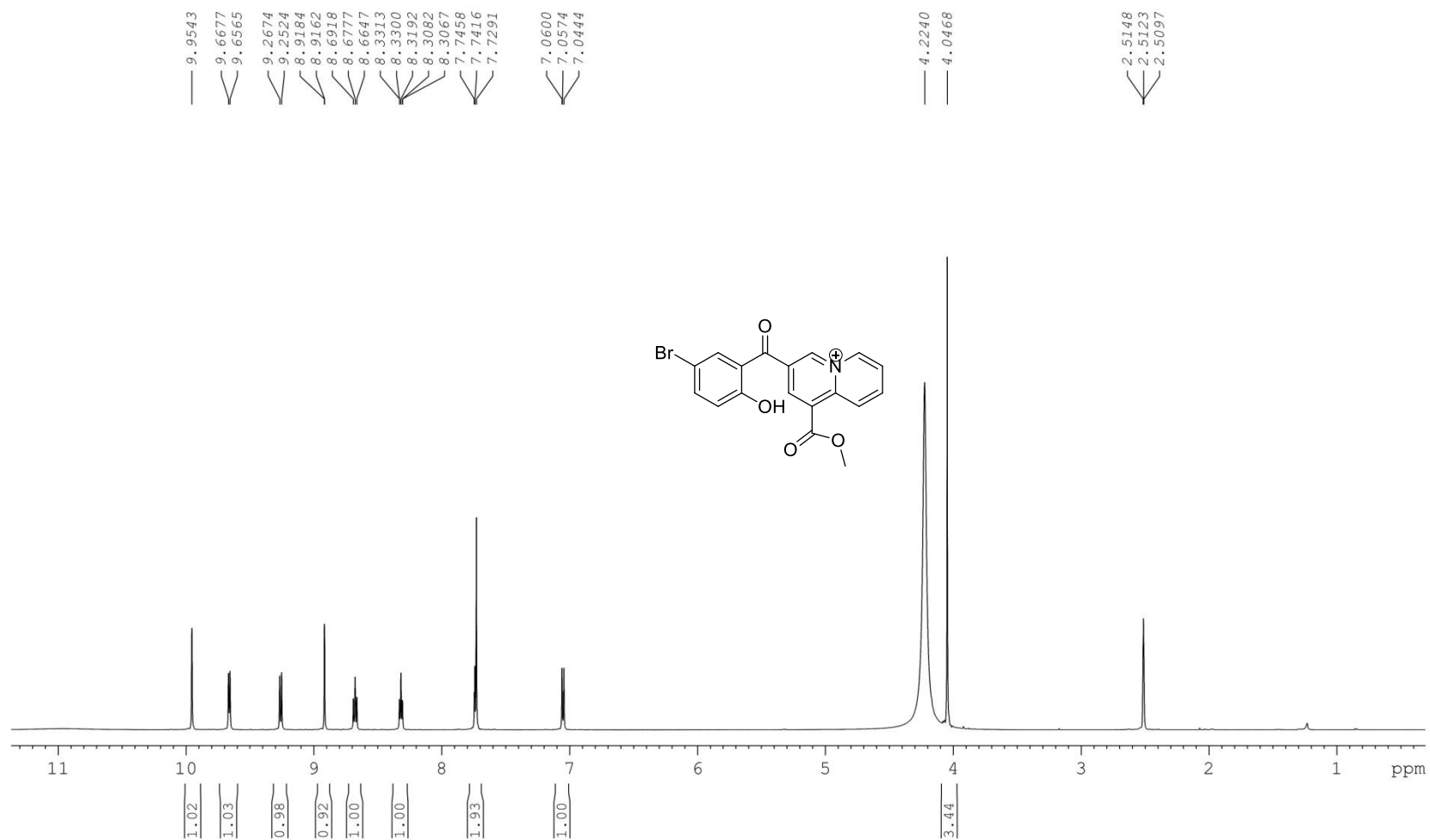


Figure S58.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4n**



**Figure S59.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **40**



DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-13  
Nov27-2019-chenli  
C13CPD DMSO

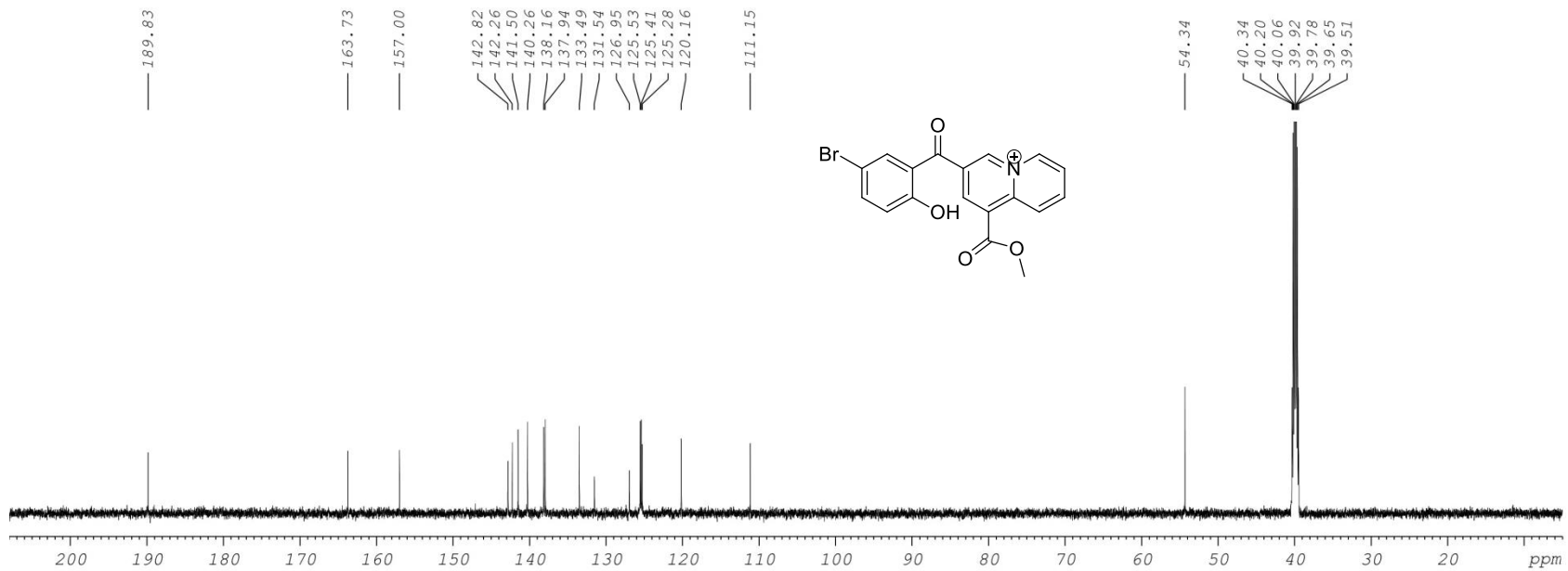
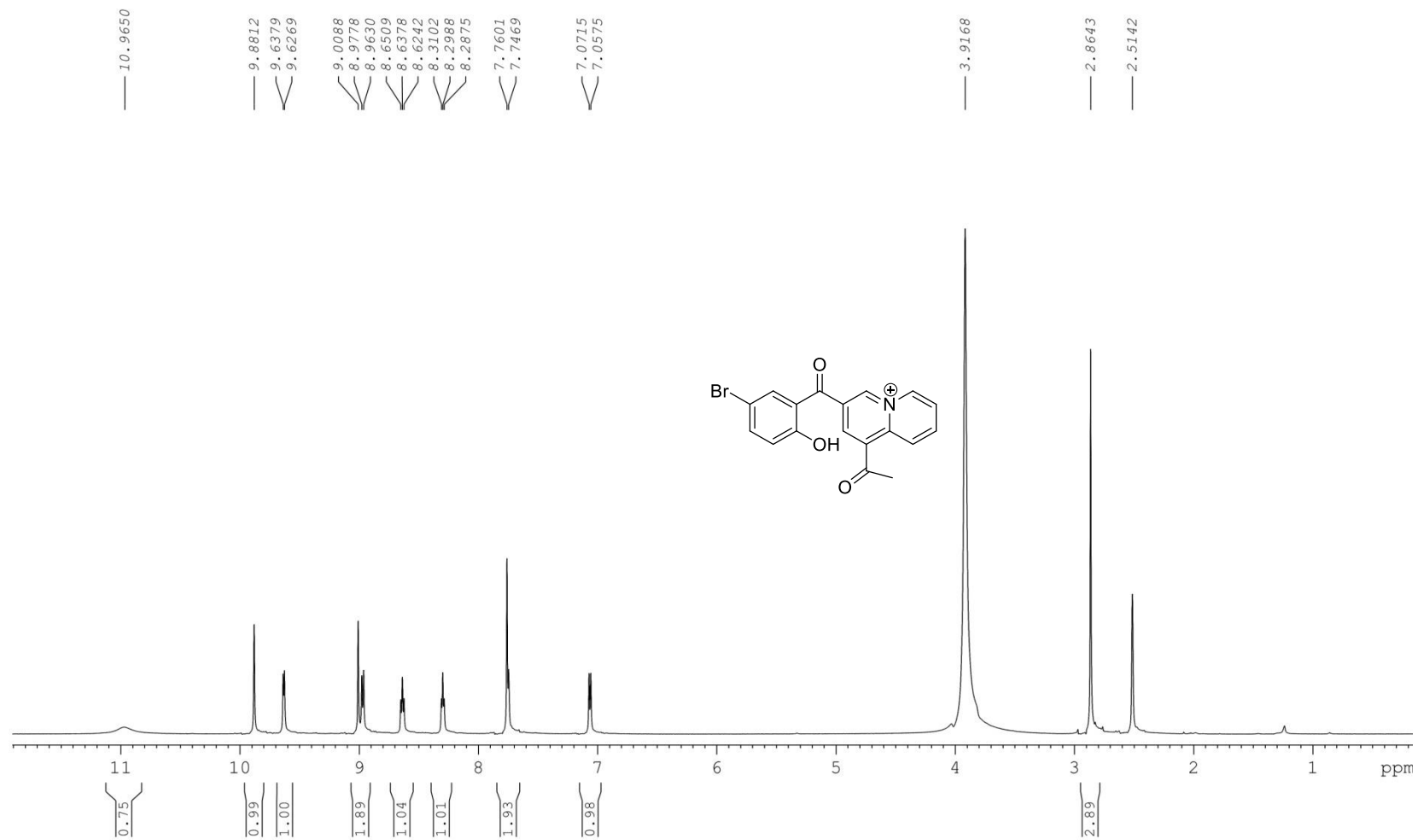


Figure S60.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound **4o**



**Figure S61.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4p**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-17  
Dec16-2019-chenli  
C13CPD DMSO

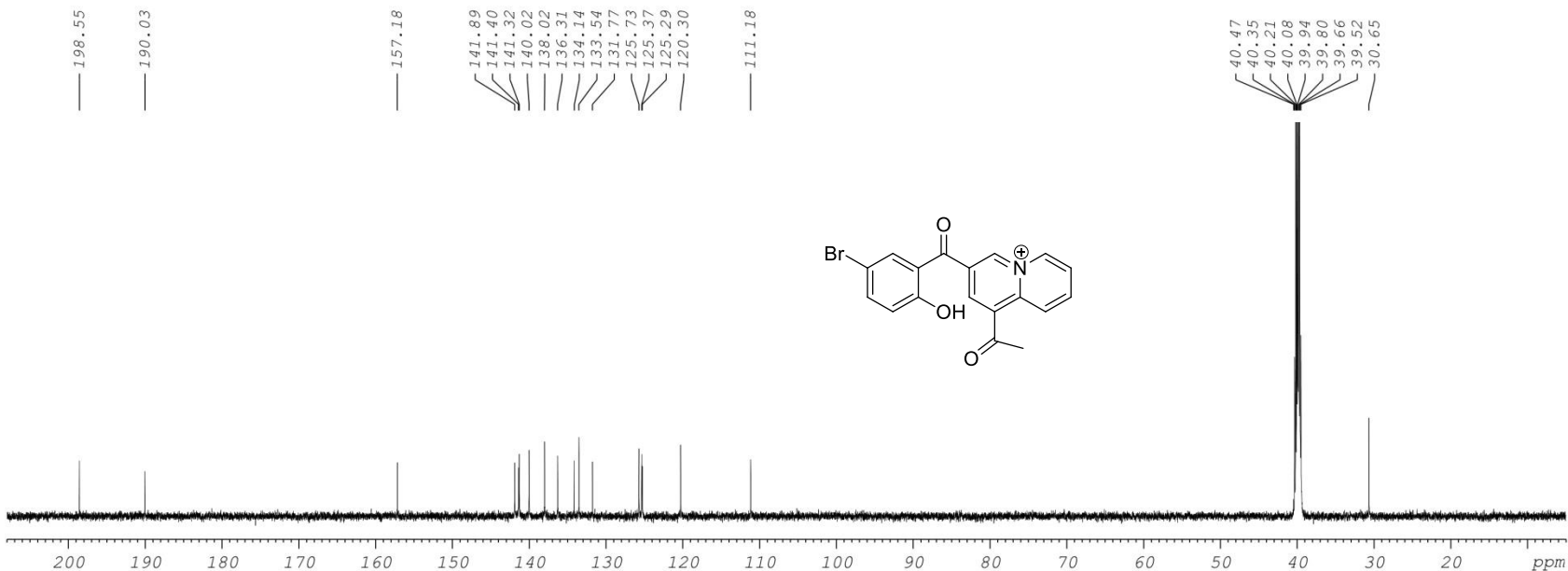
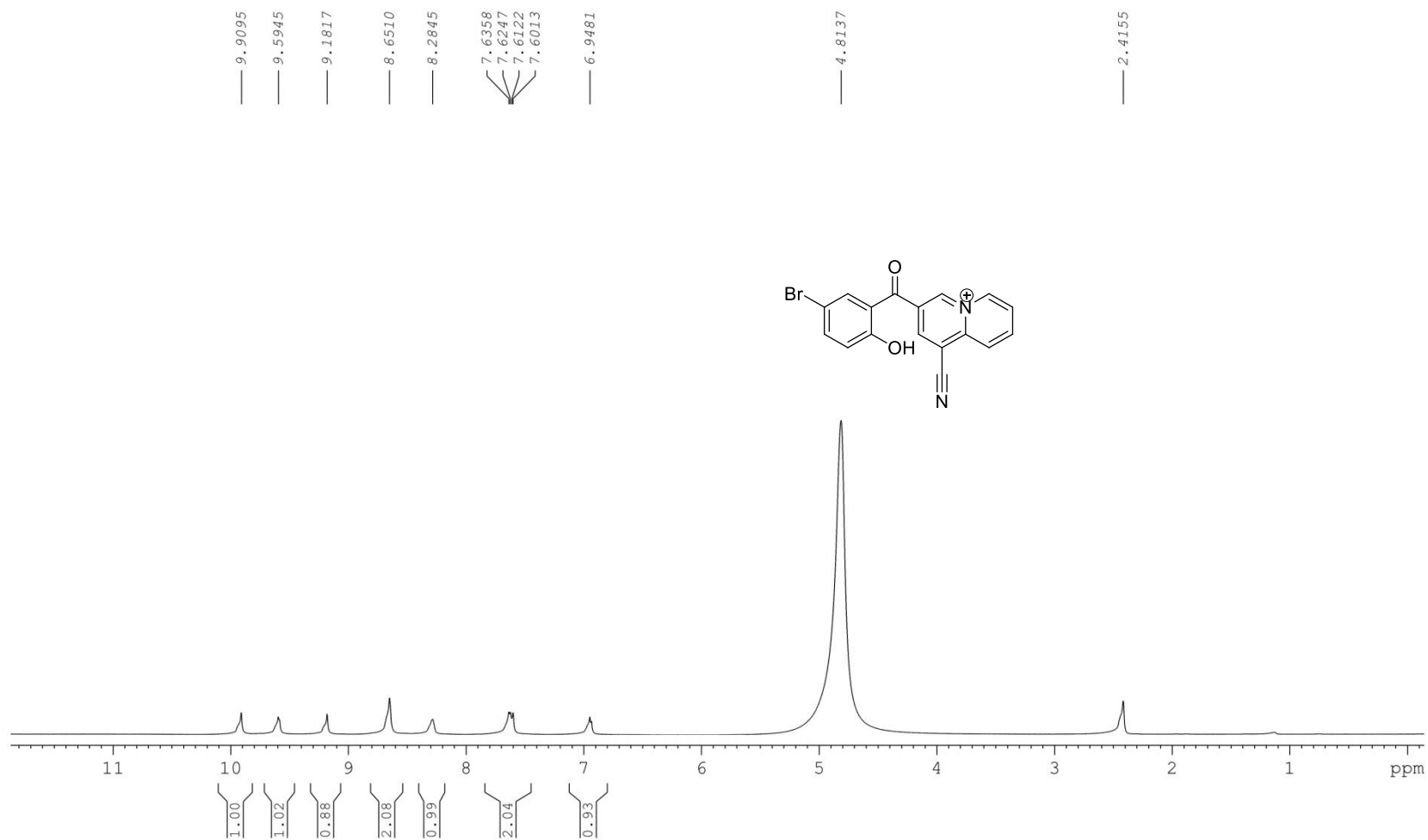


Figure S62.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4p



**Figure S63.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4q**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-15  
Nov28-2019-chenli  
C13CPD DMSO

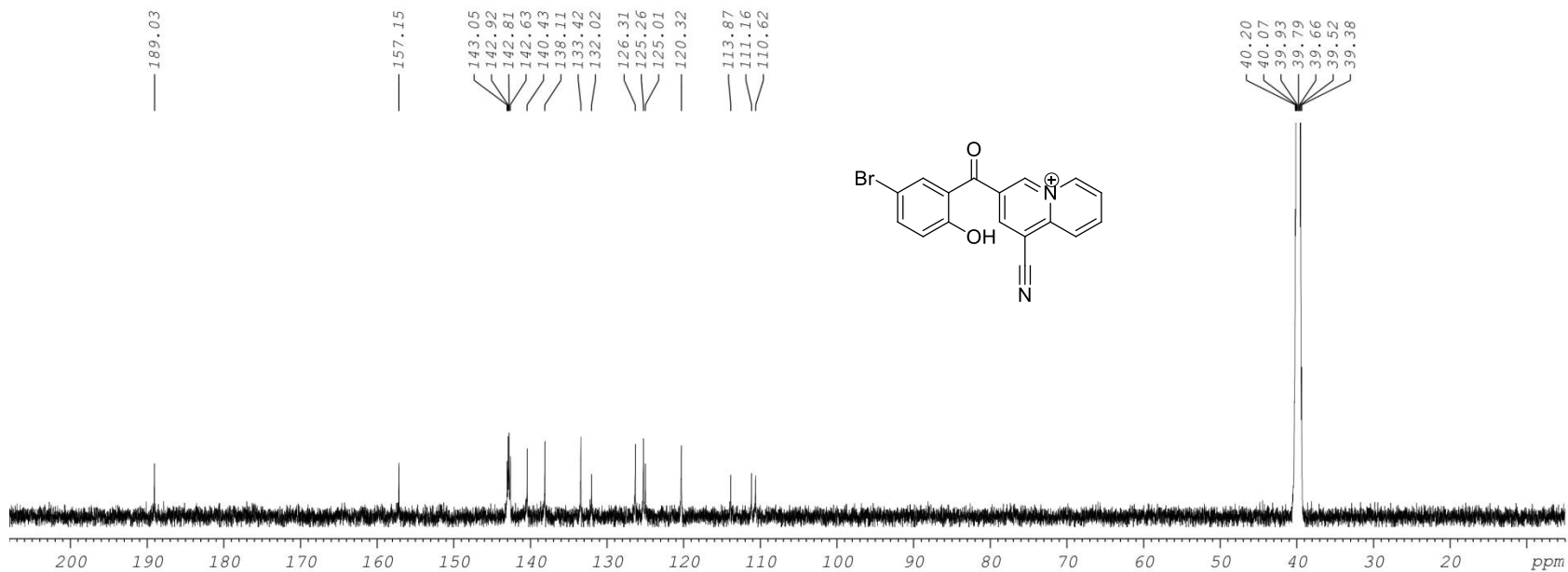
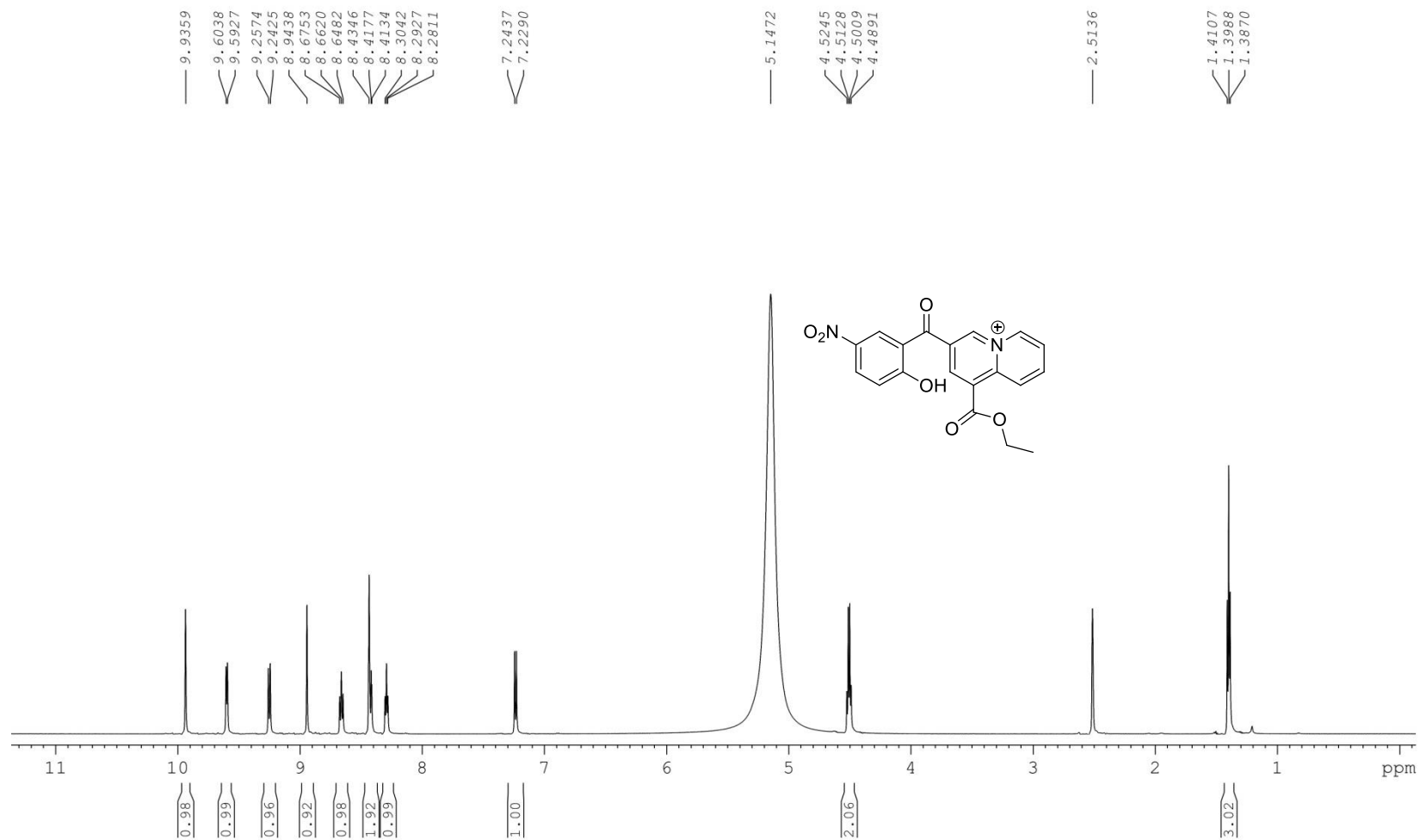
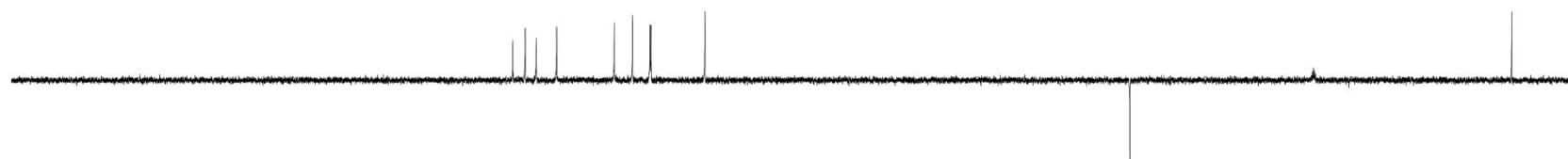


Figure S64.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4q



**Figure S65.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4r**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-24  
Dec16-2019-chenli  
C13CPD DMSO

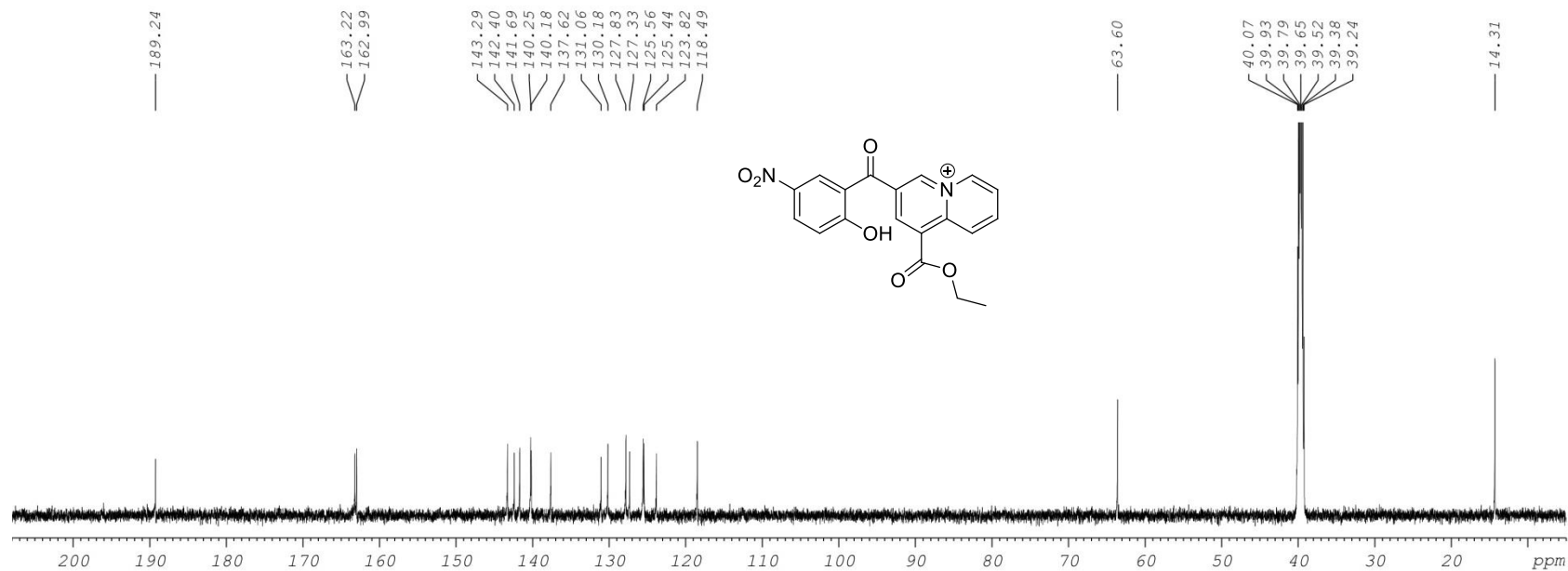
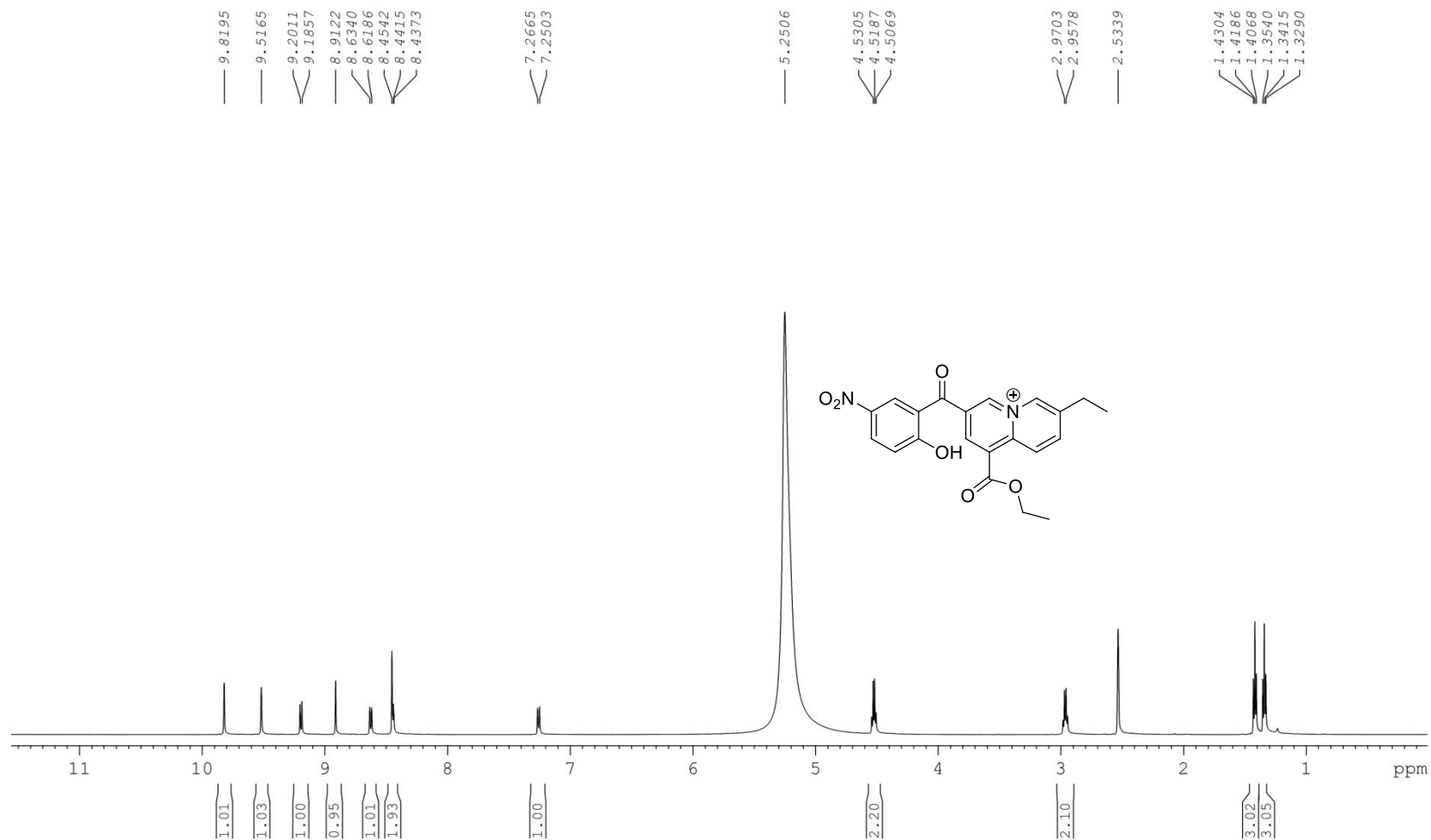


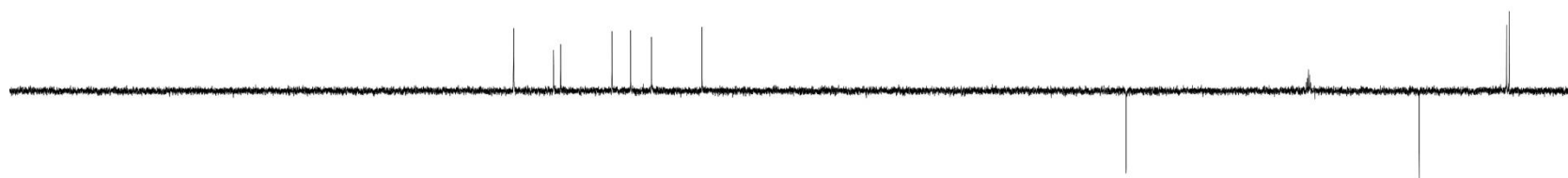
Figure S66.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4r



**Figure S67.**  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4s**



DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-18  
Dec18-2019-chenli  
C13CPD DMSO

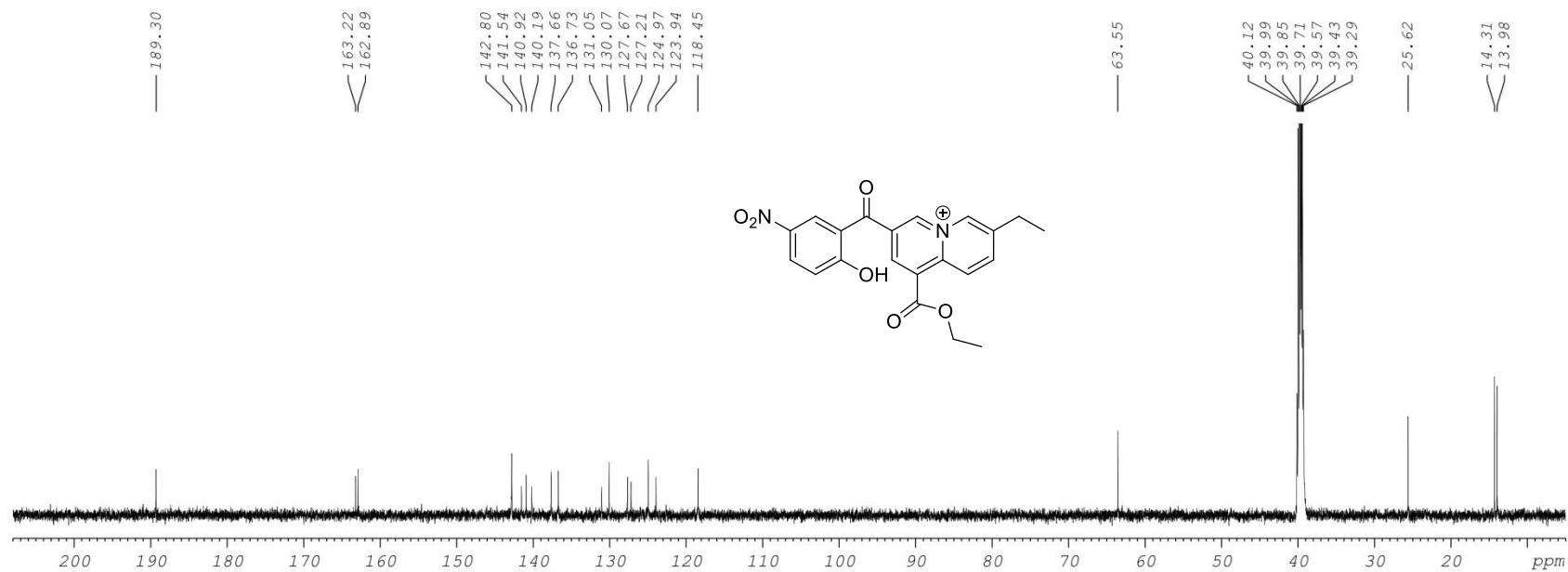
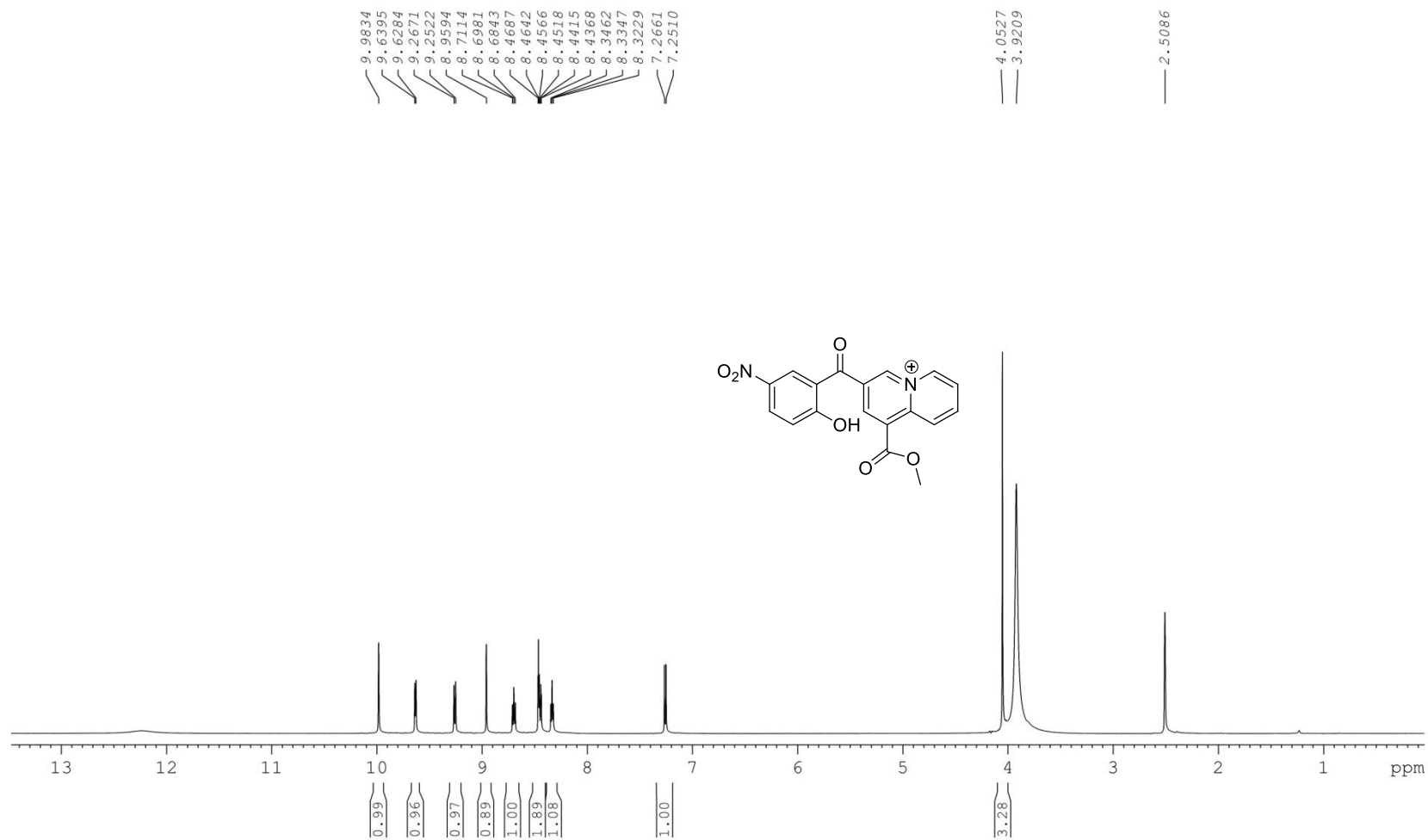


Figure S68.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound 4s



**Figure S69.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4t**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-21  
Dec18-2019-chenli  
C13CPD DMSO

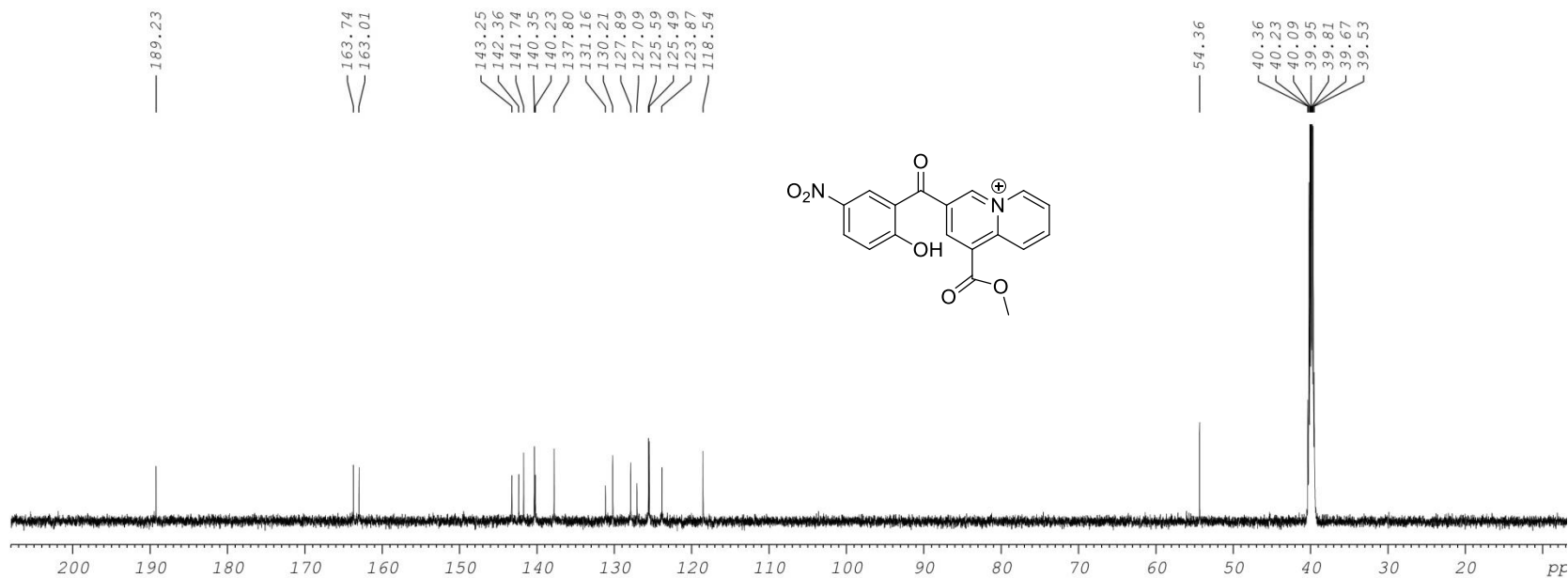
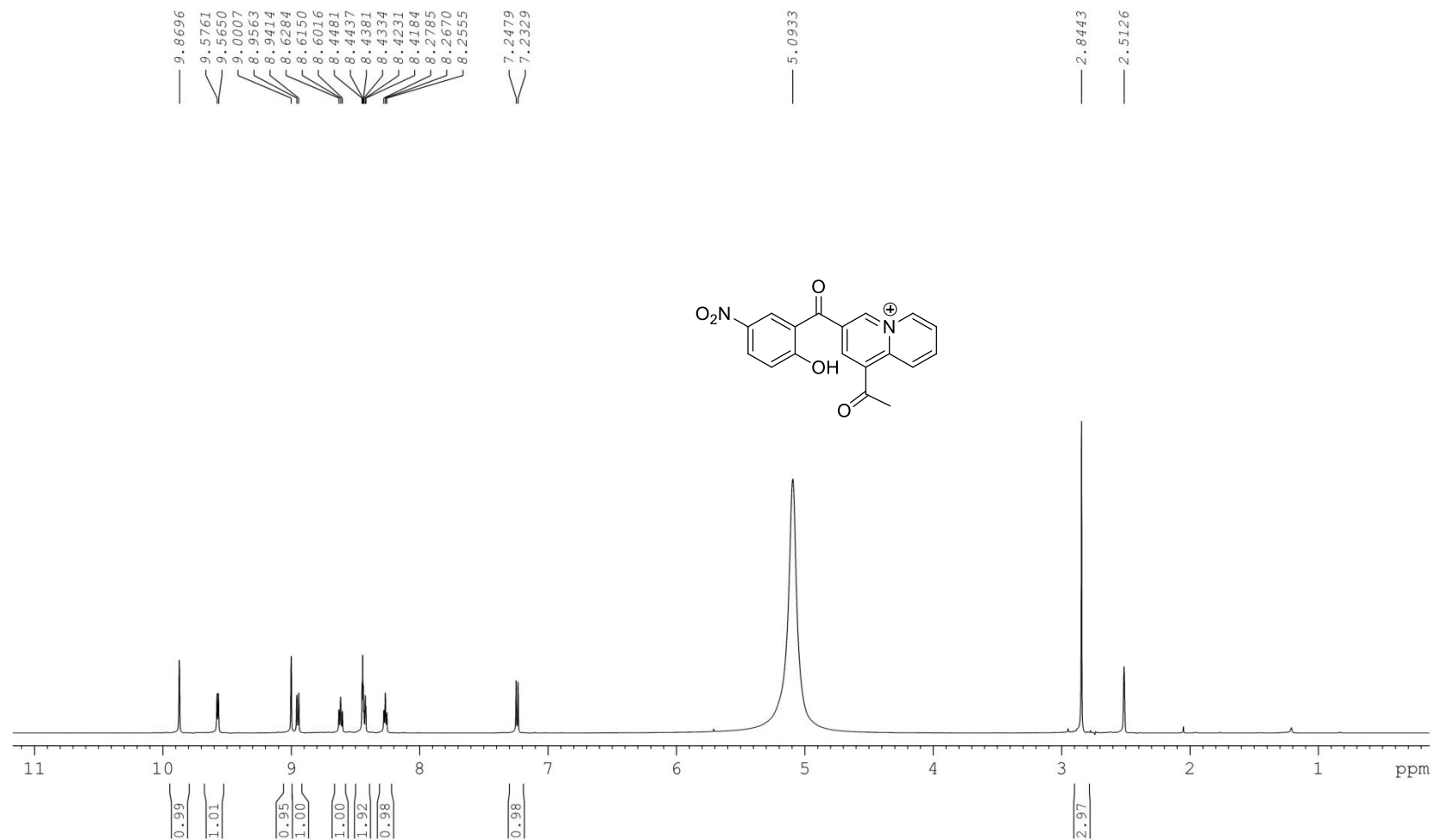


Figure S70.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4t



**Figure S71.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound 4u

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-25  
Dec16-2019-chenli  
C13CPD DMSO

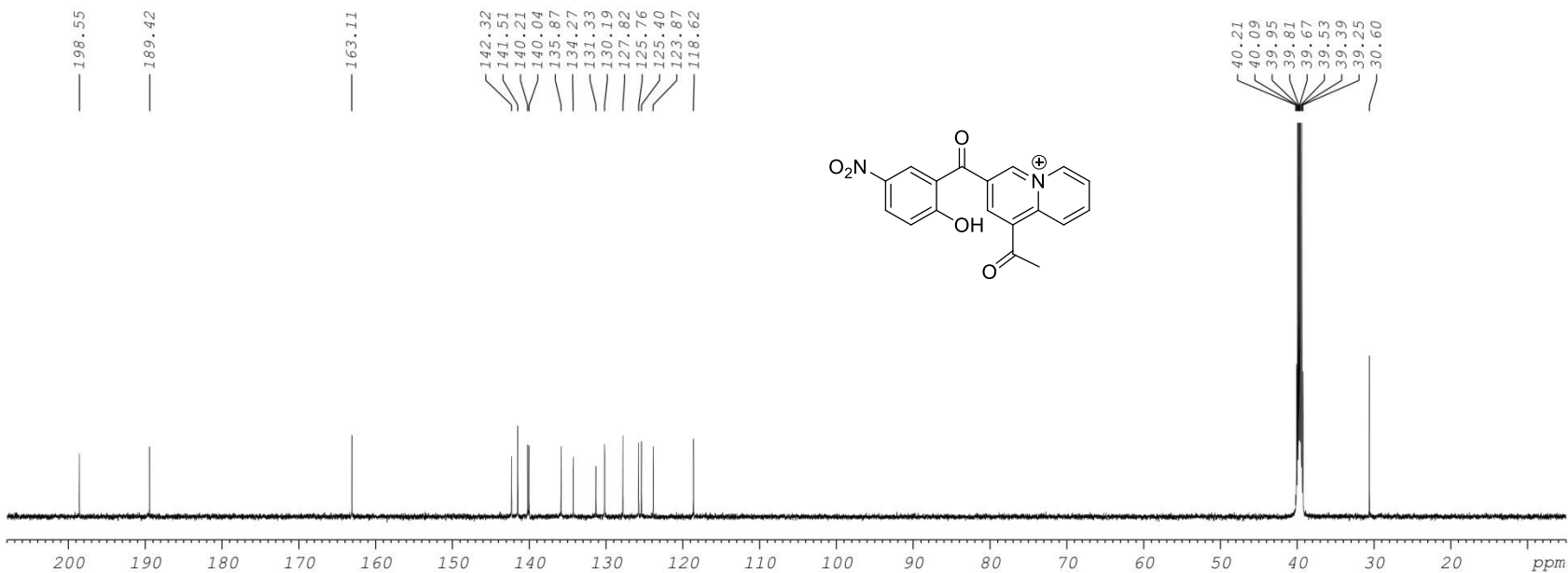
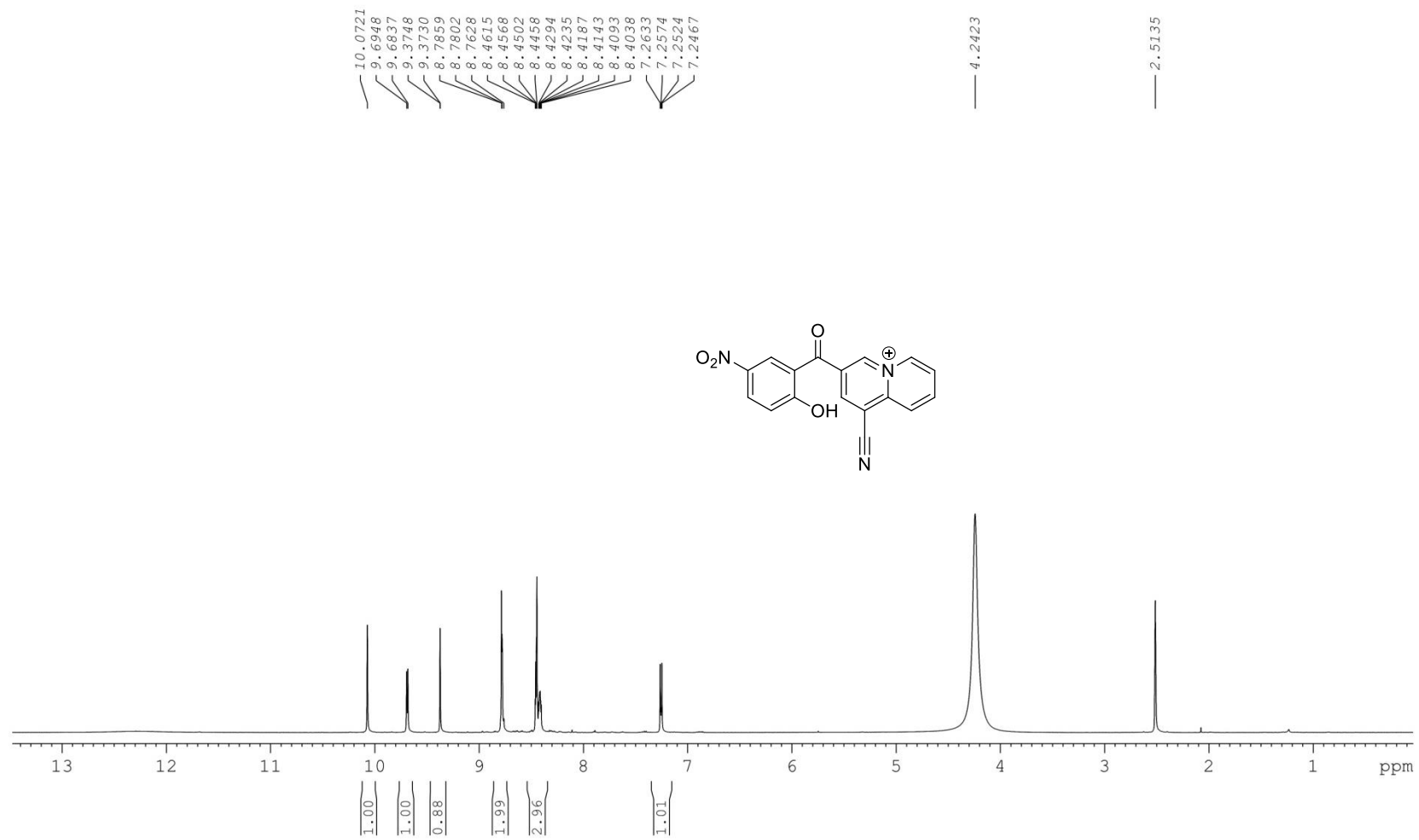


Figure S72.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4u**



**Figure S73.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4v**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-26  
Dec19-2019-chenli  
C13CPD DMSO

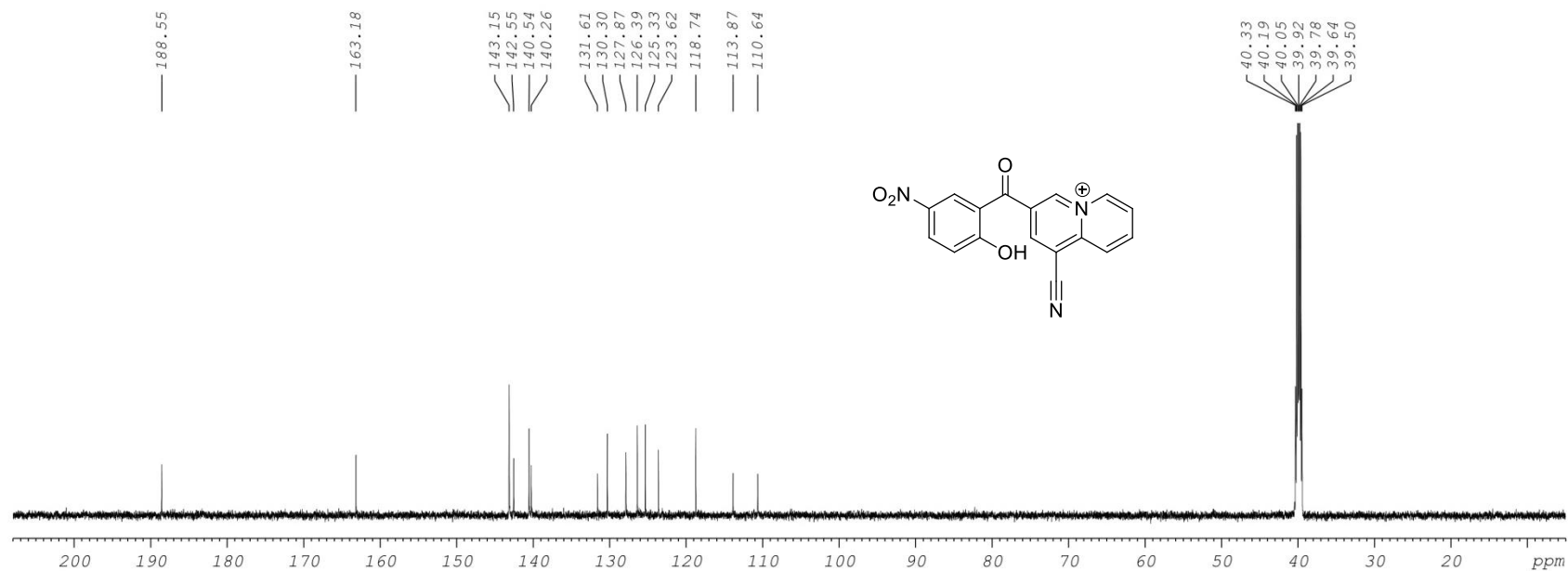
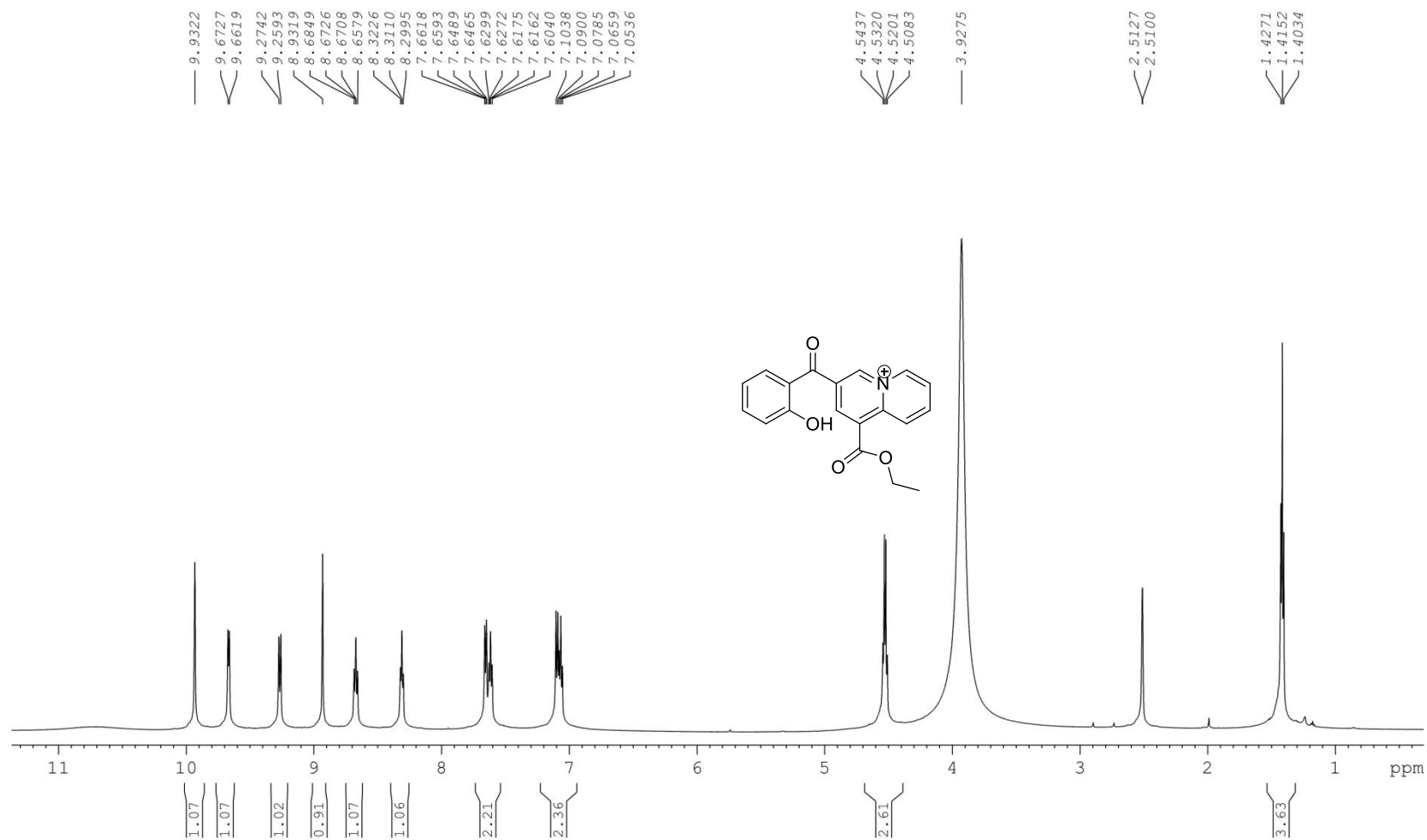


Figure S74.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4v



**Figure S75.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4w



DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-12  
Nov27-2019-chenli  
C13CPD DMSO

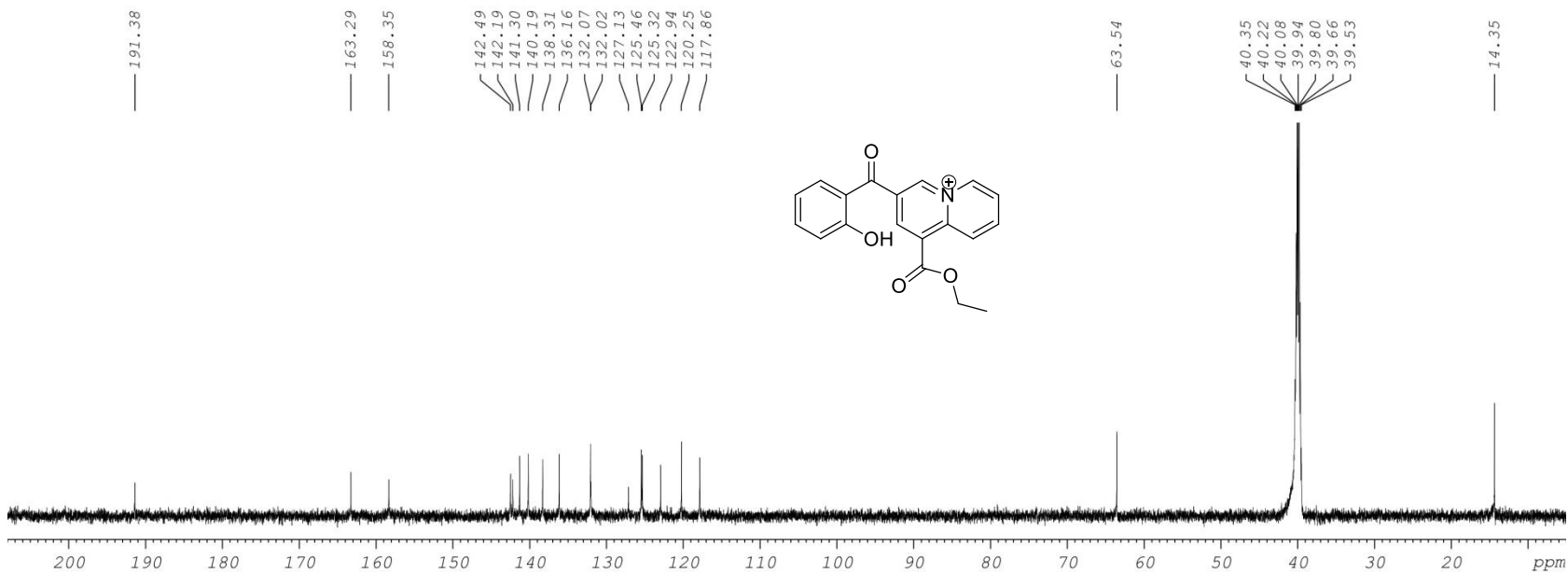
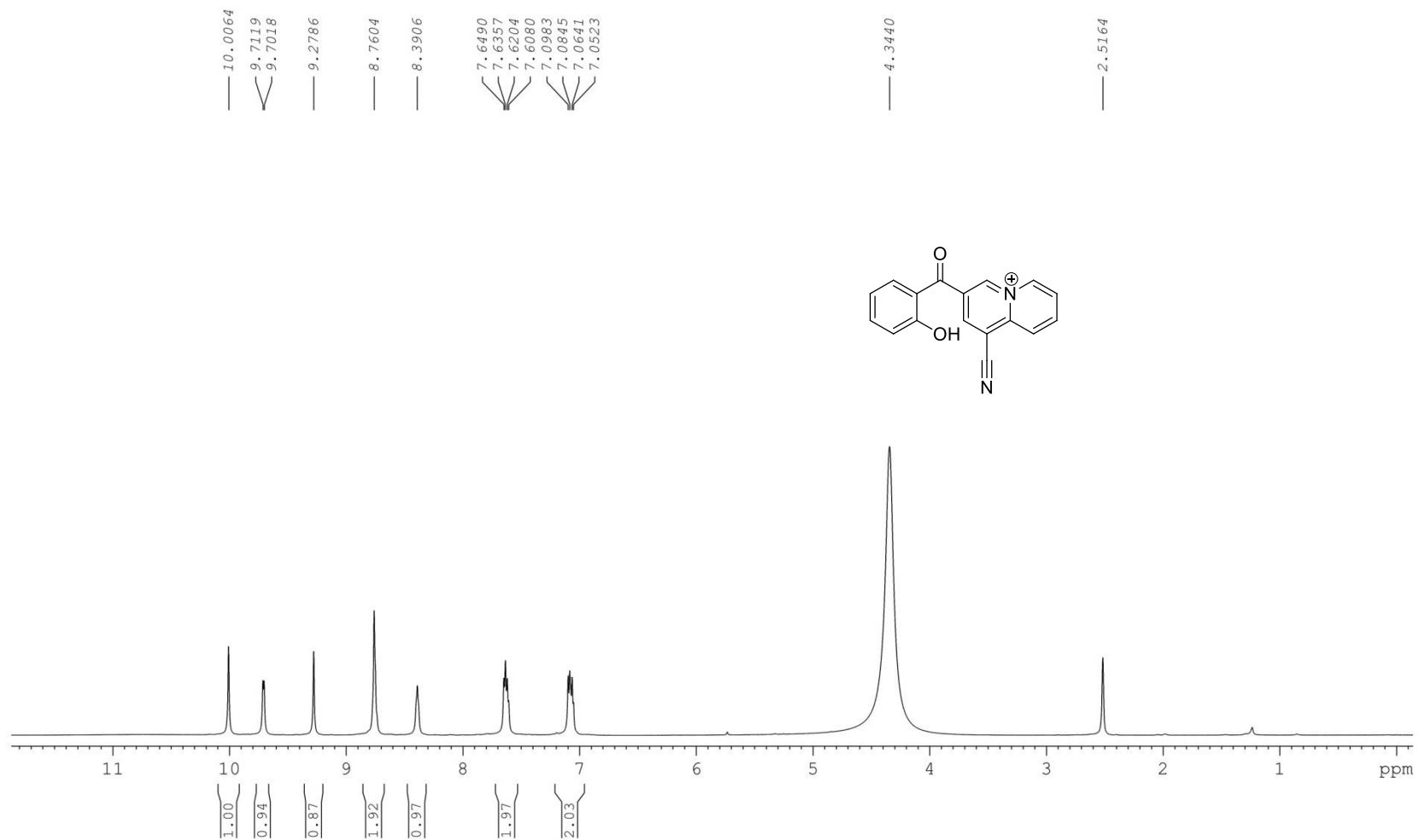


Figure S76.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4w



**Figure S77.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound 4x

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-16  
Nov28-2019-chenli  
C13CPD DMSO

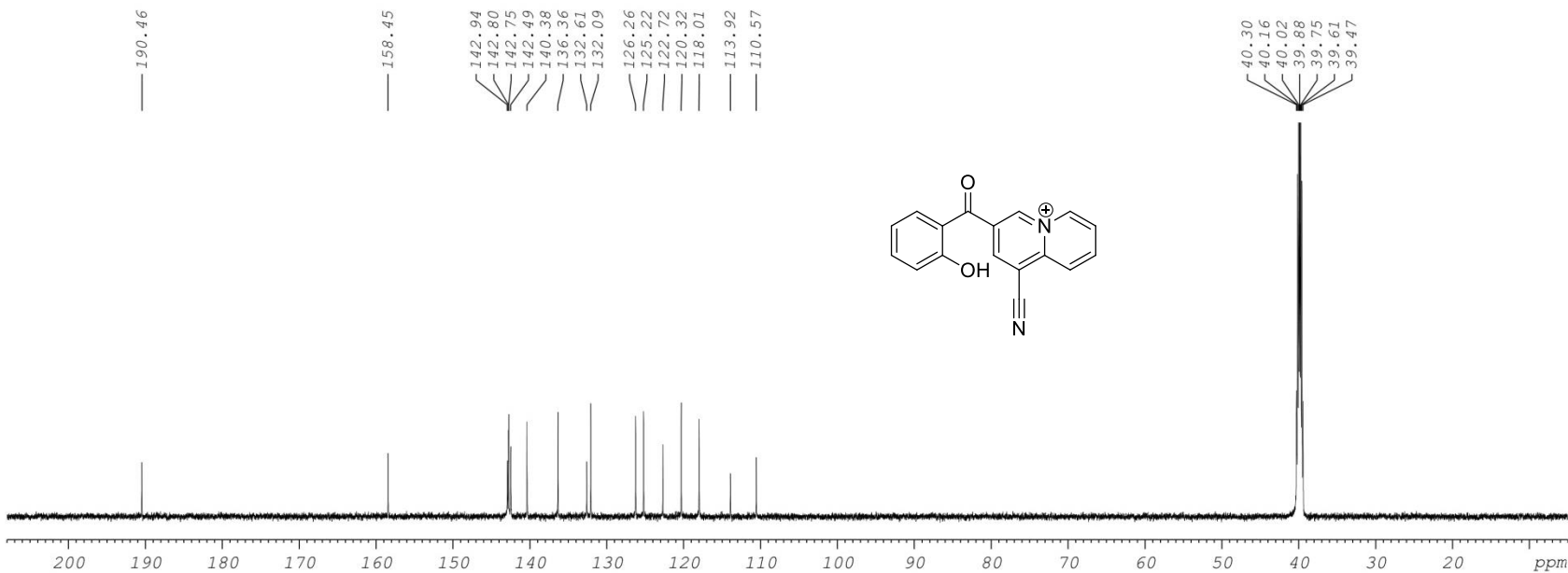
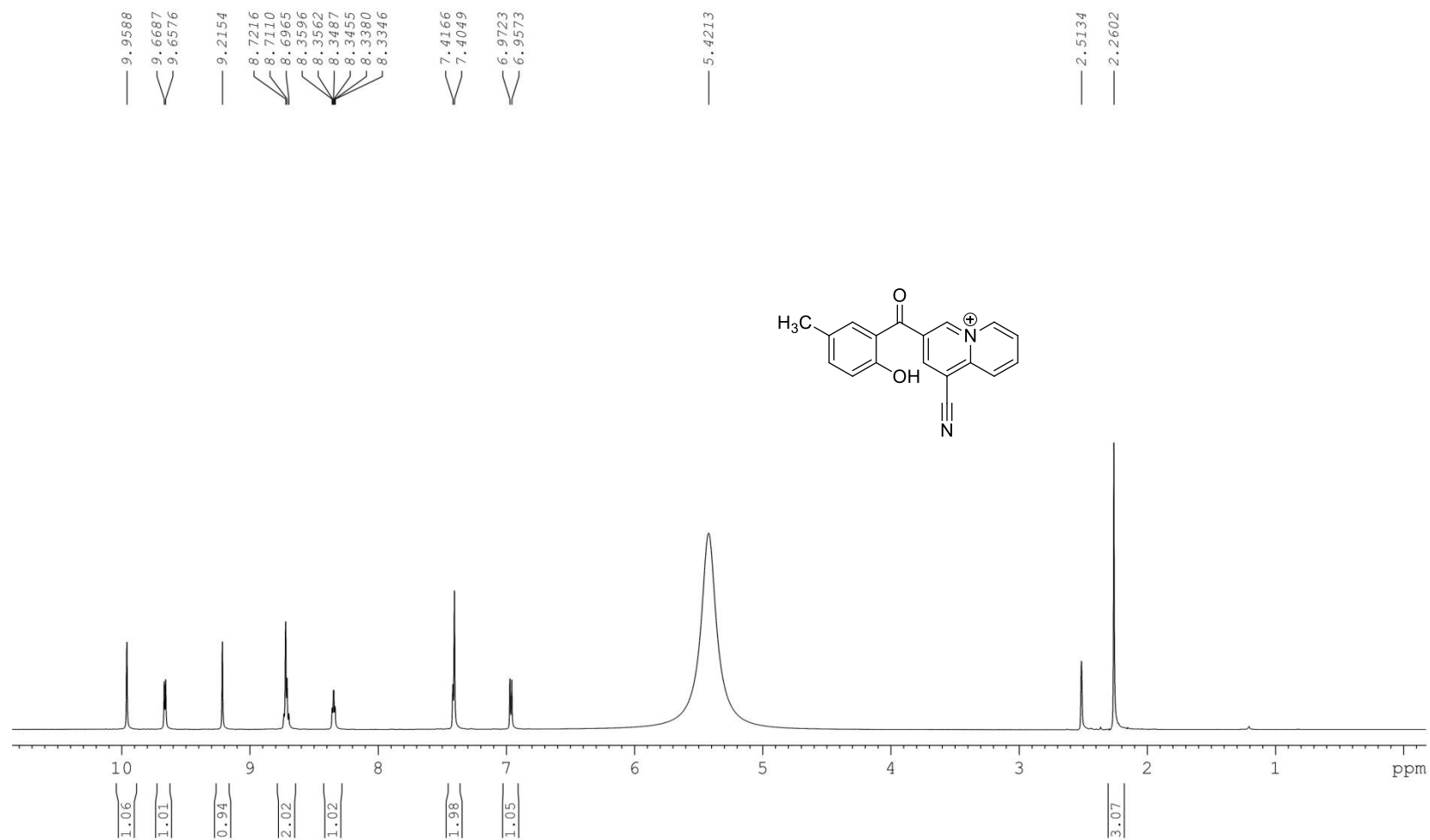


Figure S78.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound 4x



**Figure S79.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4y**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-19  
Dec06-2019-chenli  
C13CPD DMSO

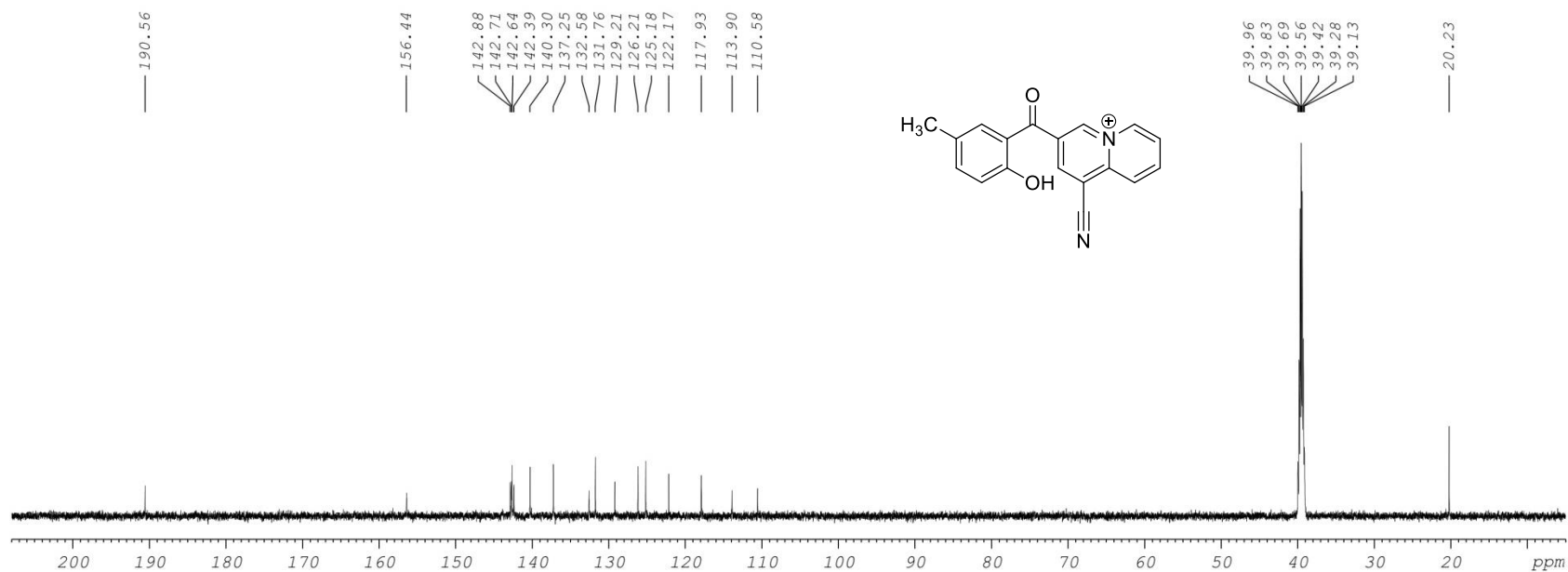
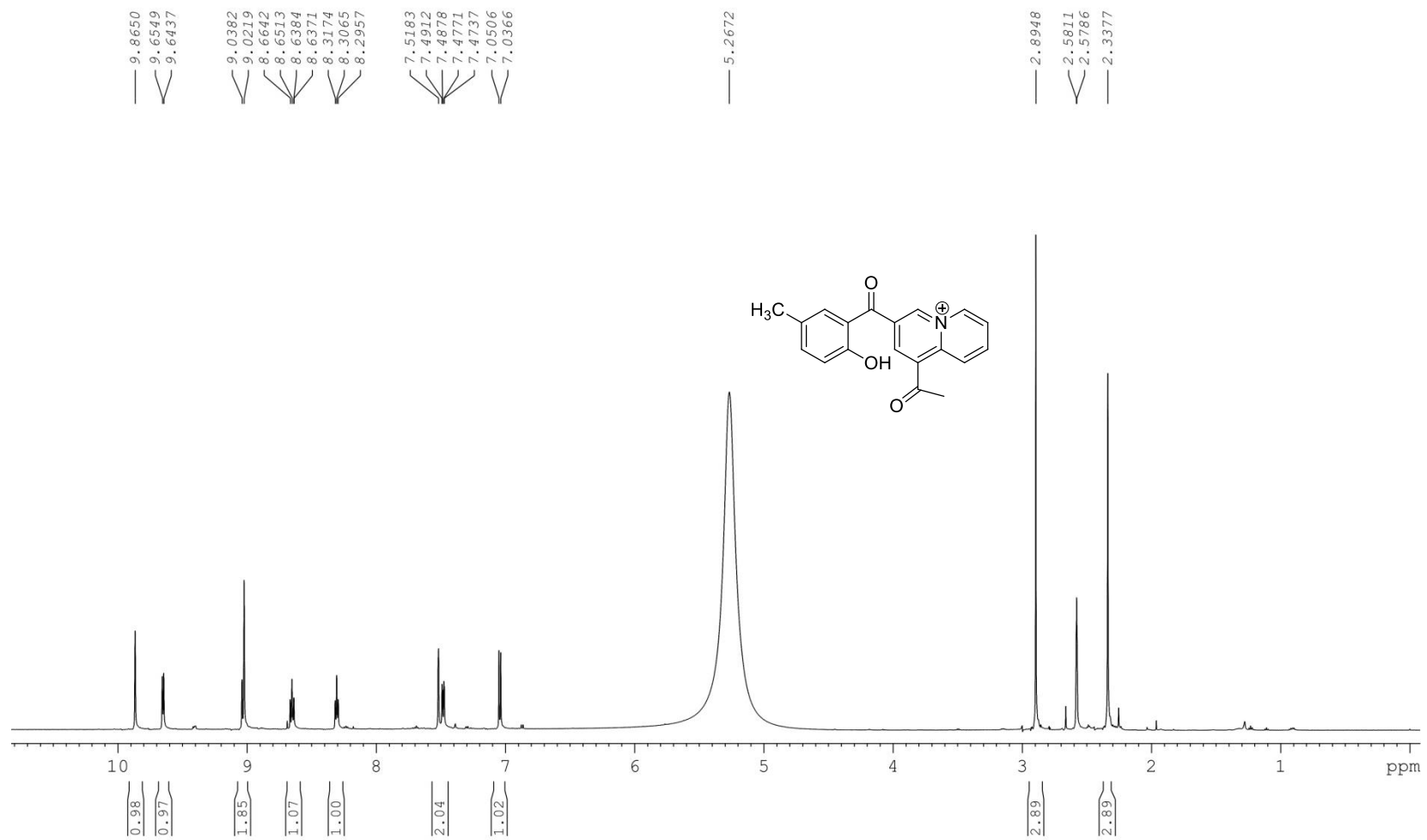


Figure S80.  $^{13}\text{C}$  NMR (150 MHz, DMSO- $d_6$ +HClO $_4$ ) spectra of compound **4y**



**Figure S81.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4z**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-20  
Dec30-2019-chenli  
C13CPD DMSO

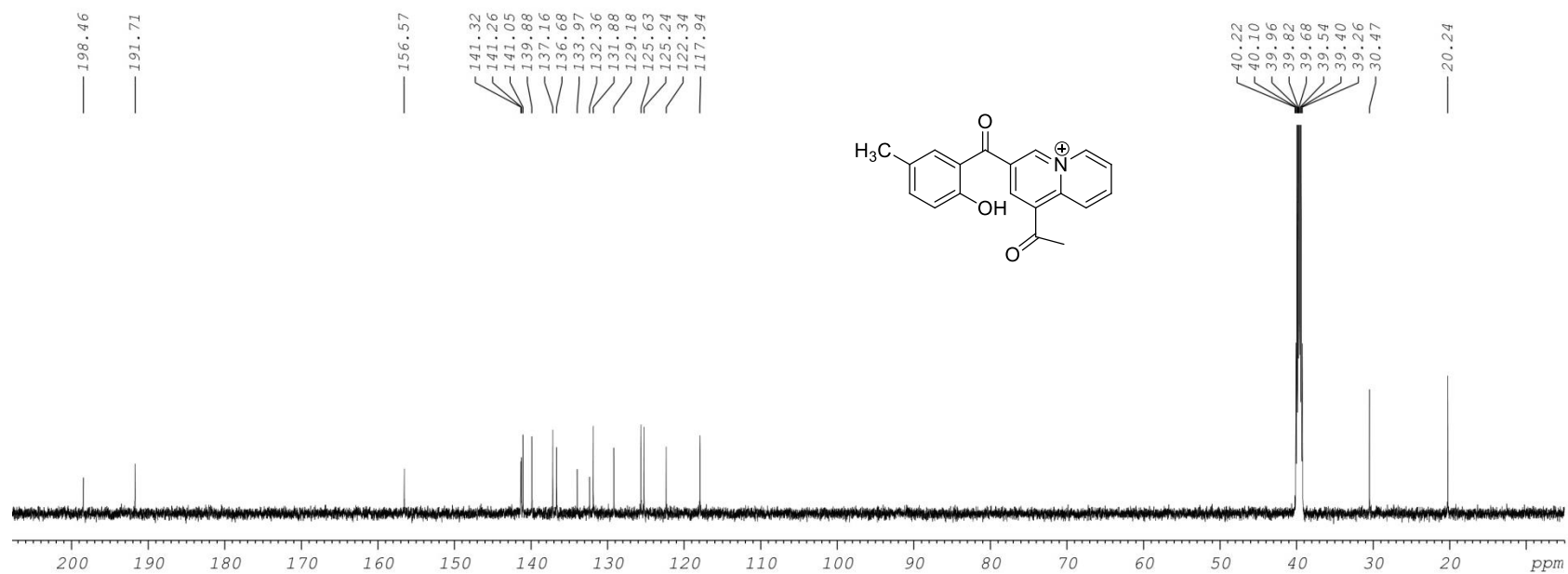
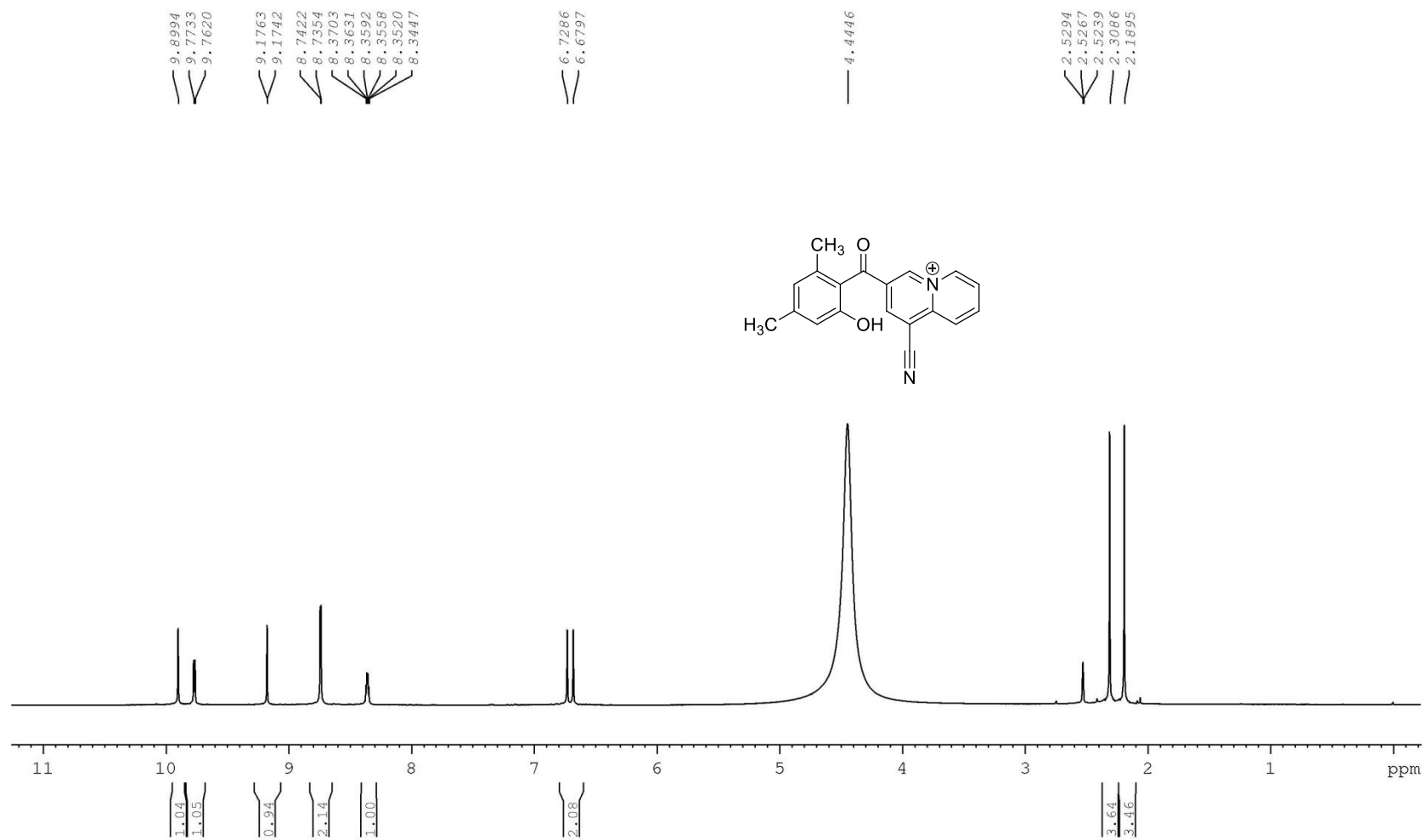


Figure S82.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4z



**Figure S83.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4a'**



DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-30  
Aug14-2020-chenli  
C13CPD DMSO

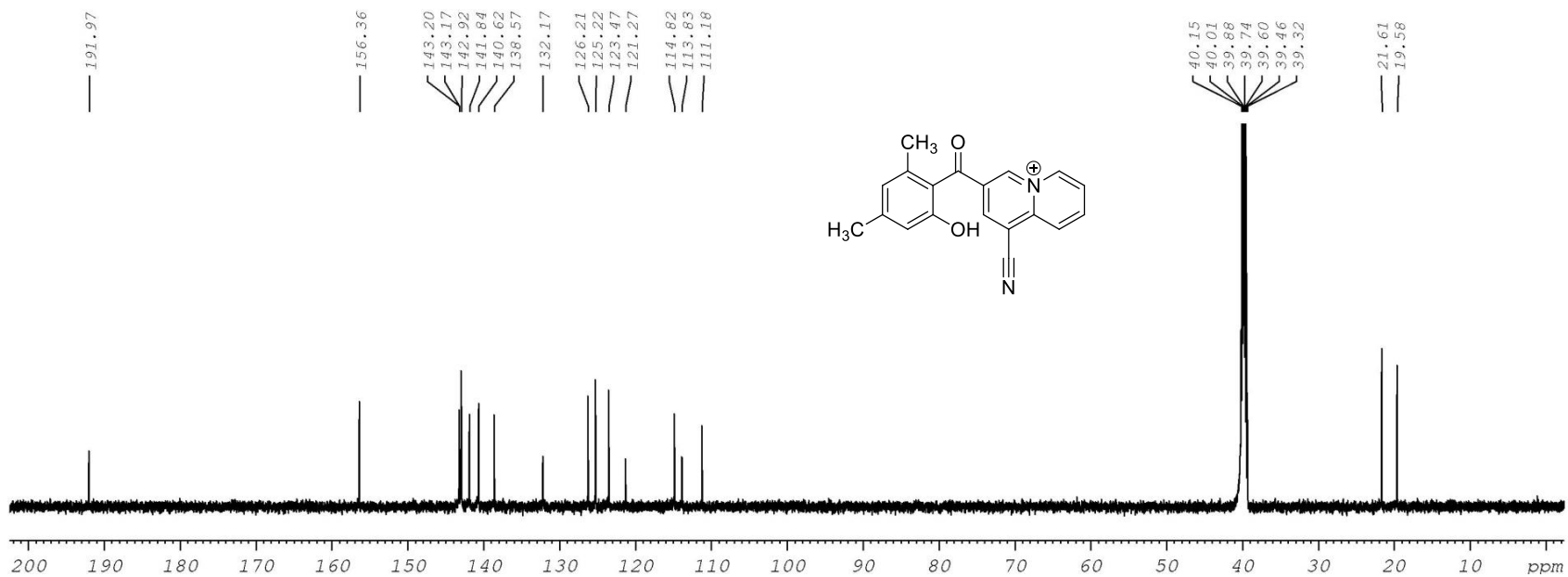
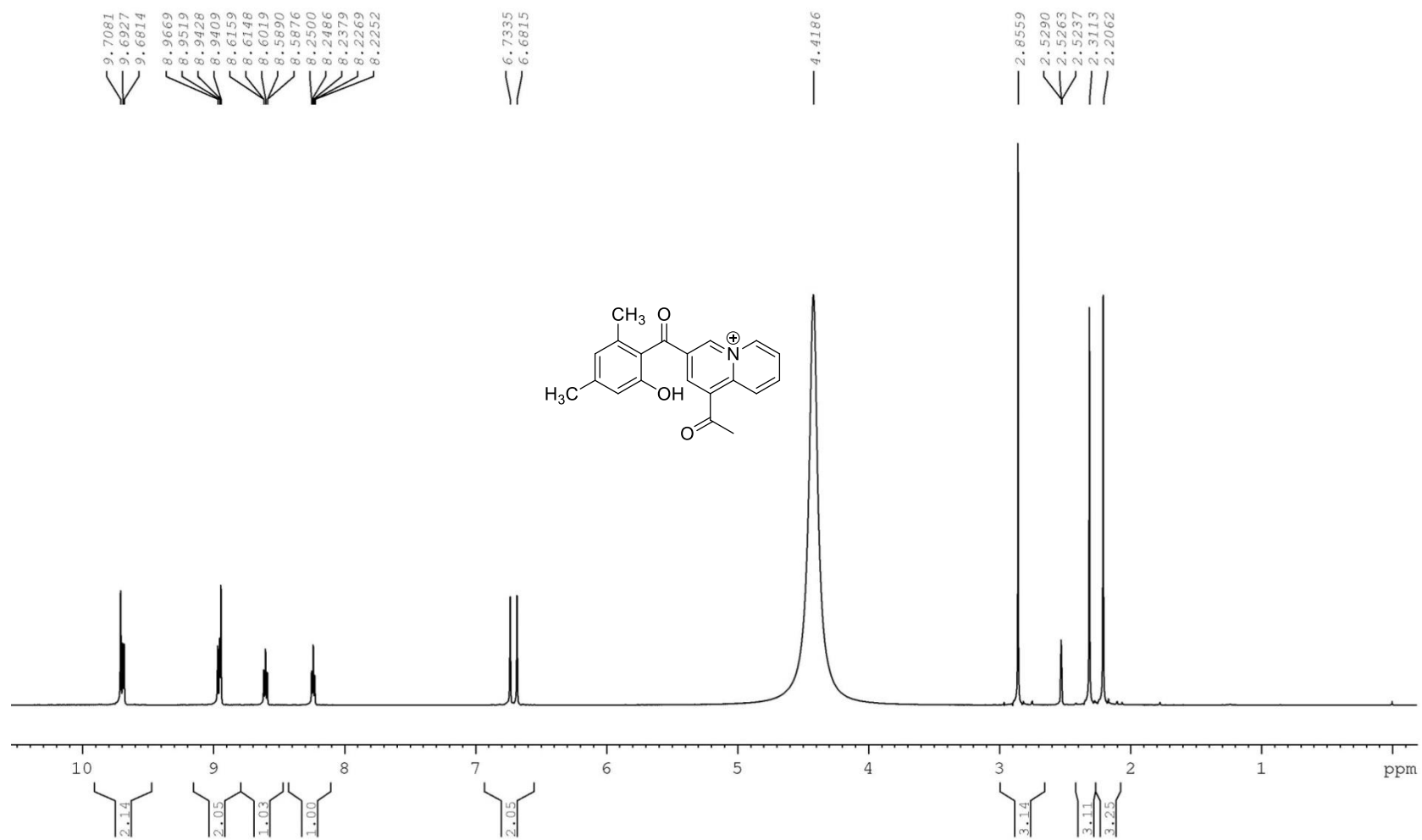


Figure S84.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4a'



**Figure S85.** <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4b'**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-31  
Aug14-2020-chenli  
C13CPD DMSO

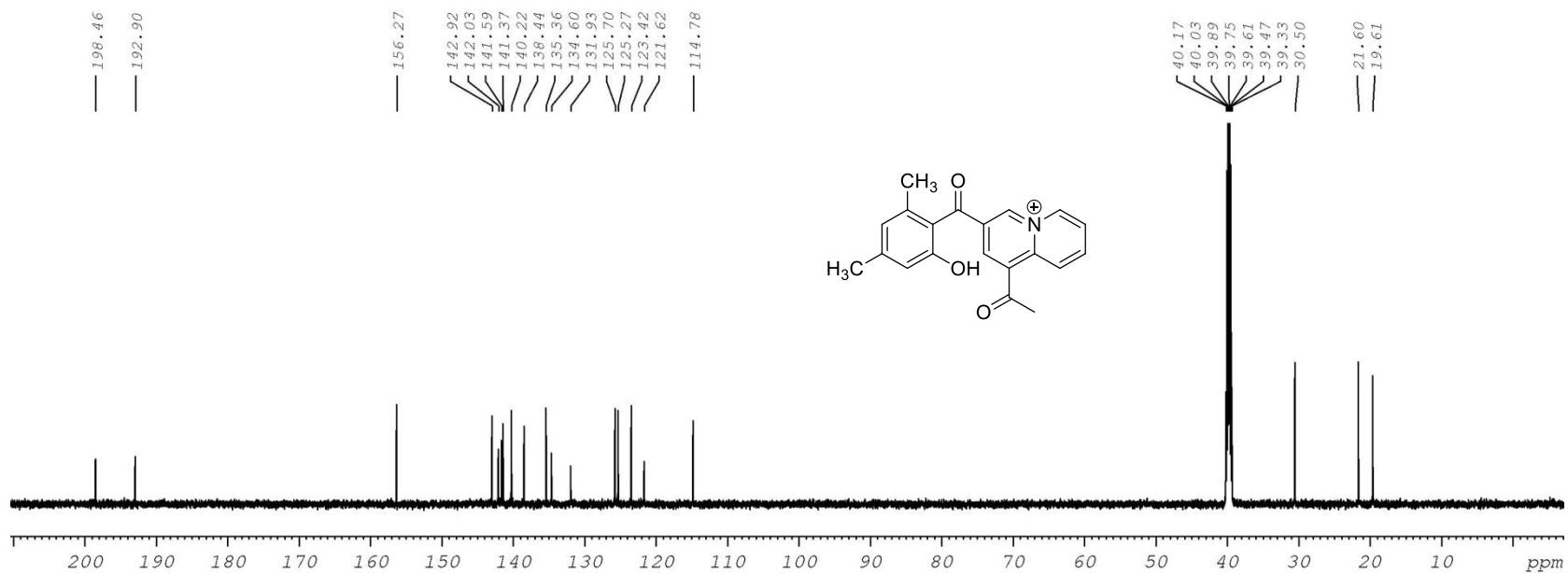
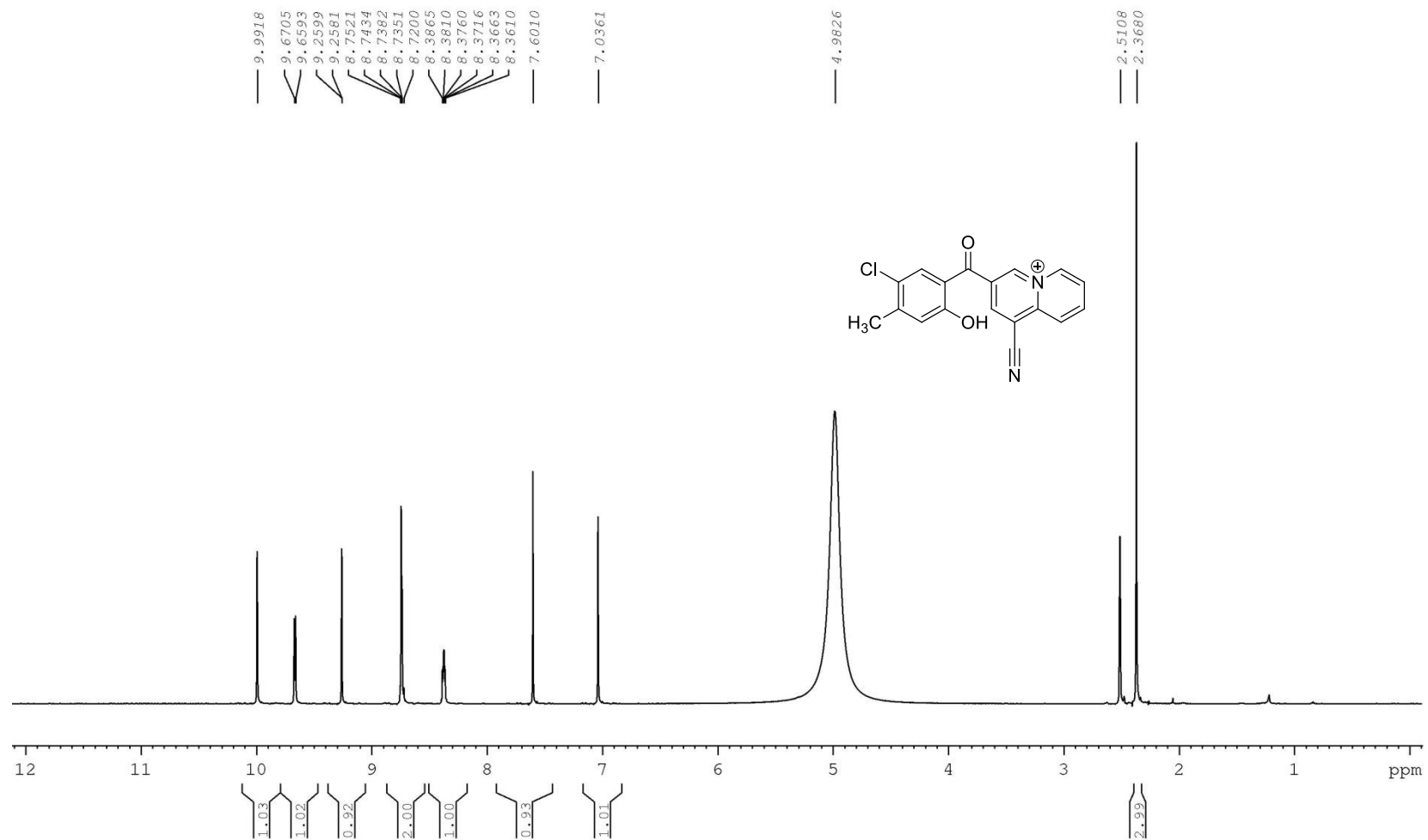


Figure S86. <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>+HClO<sub>4</sub>) spectra of compound **4b'**



**Figure S87.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4c'**

DEPT135



YUNNAN UNIVERSITY ASCEND AVIIIHD600 CLB-27  
May28-2020-chenli  
C13CPD DMSO

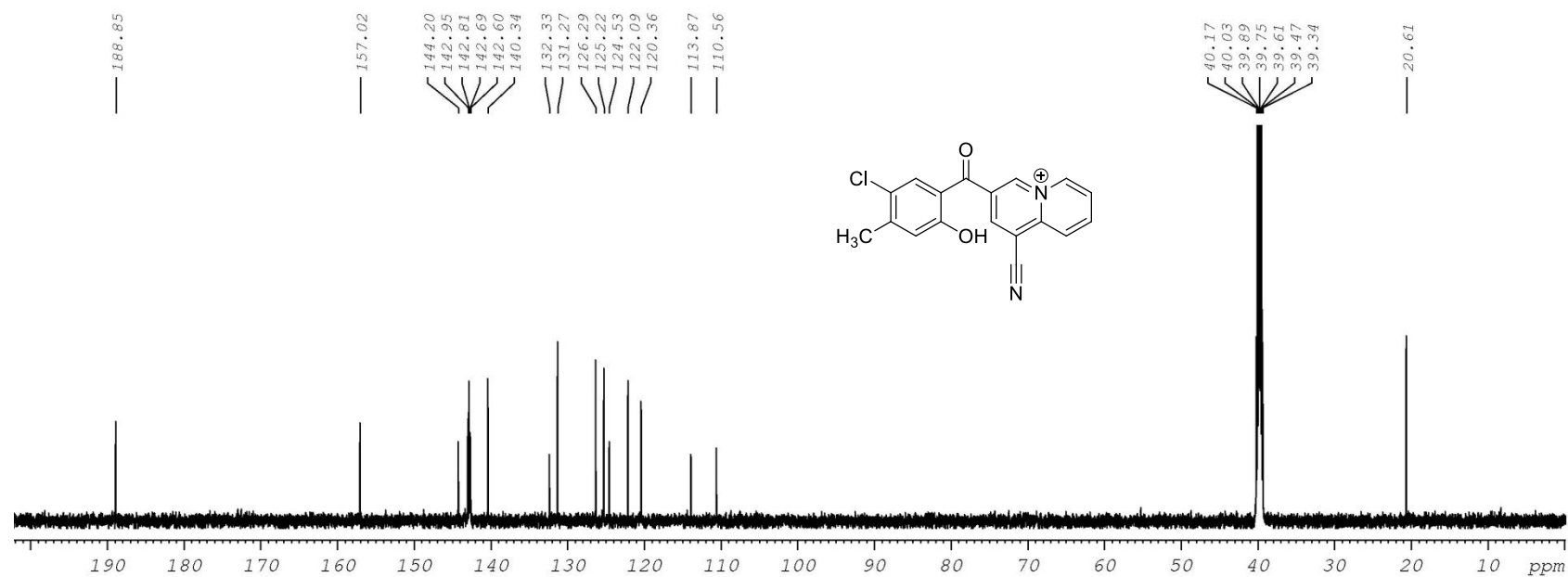
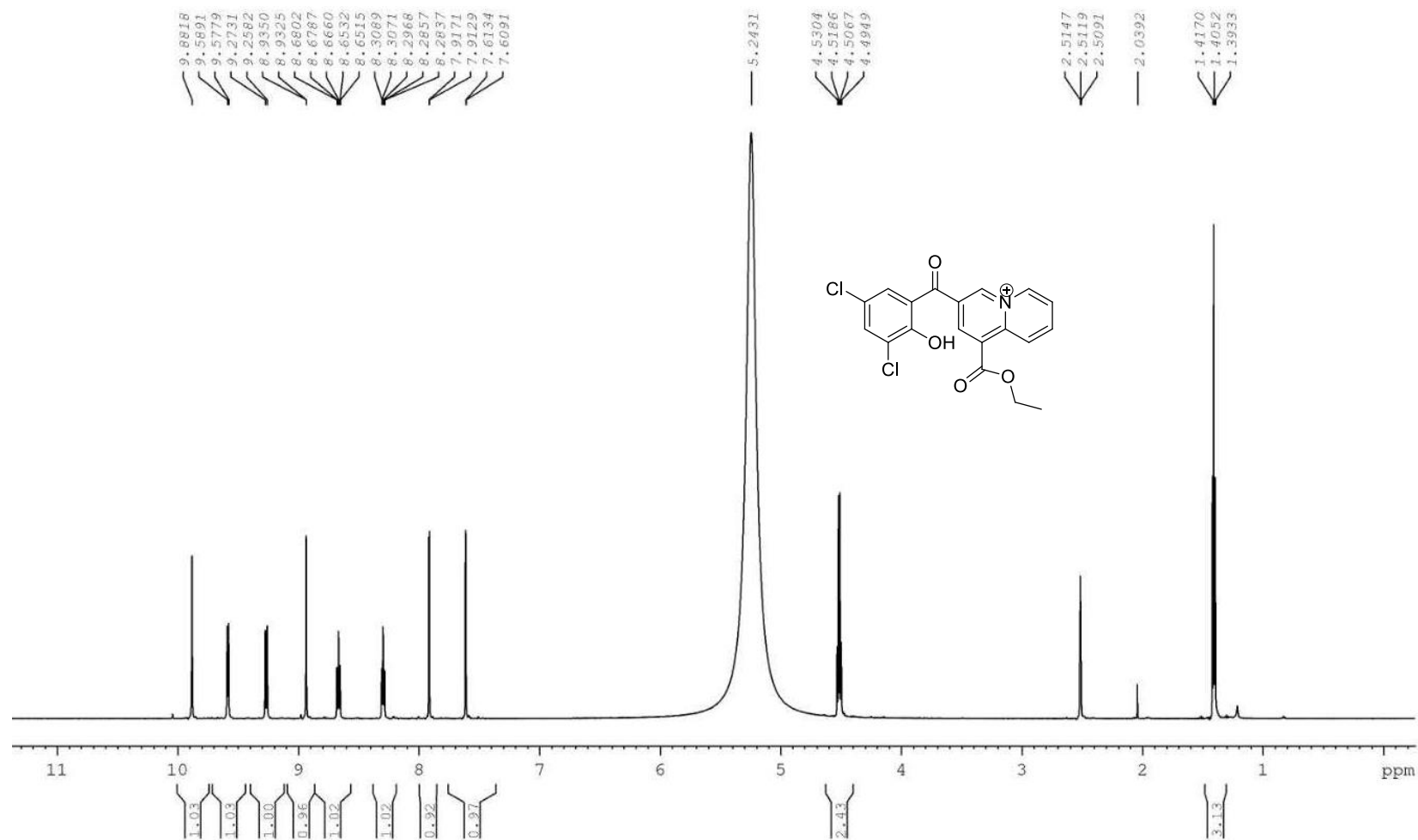


Figure S88.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound 4c'



**Figure S89.**  $^1\text{H NMR}$  (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4d'**

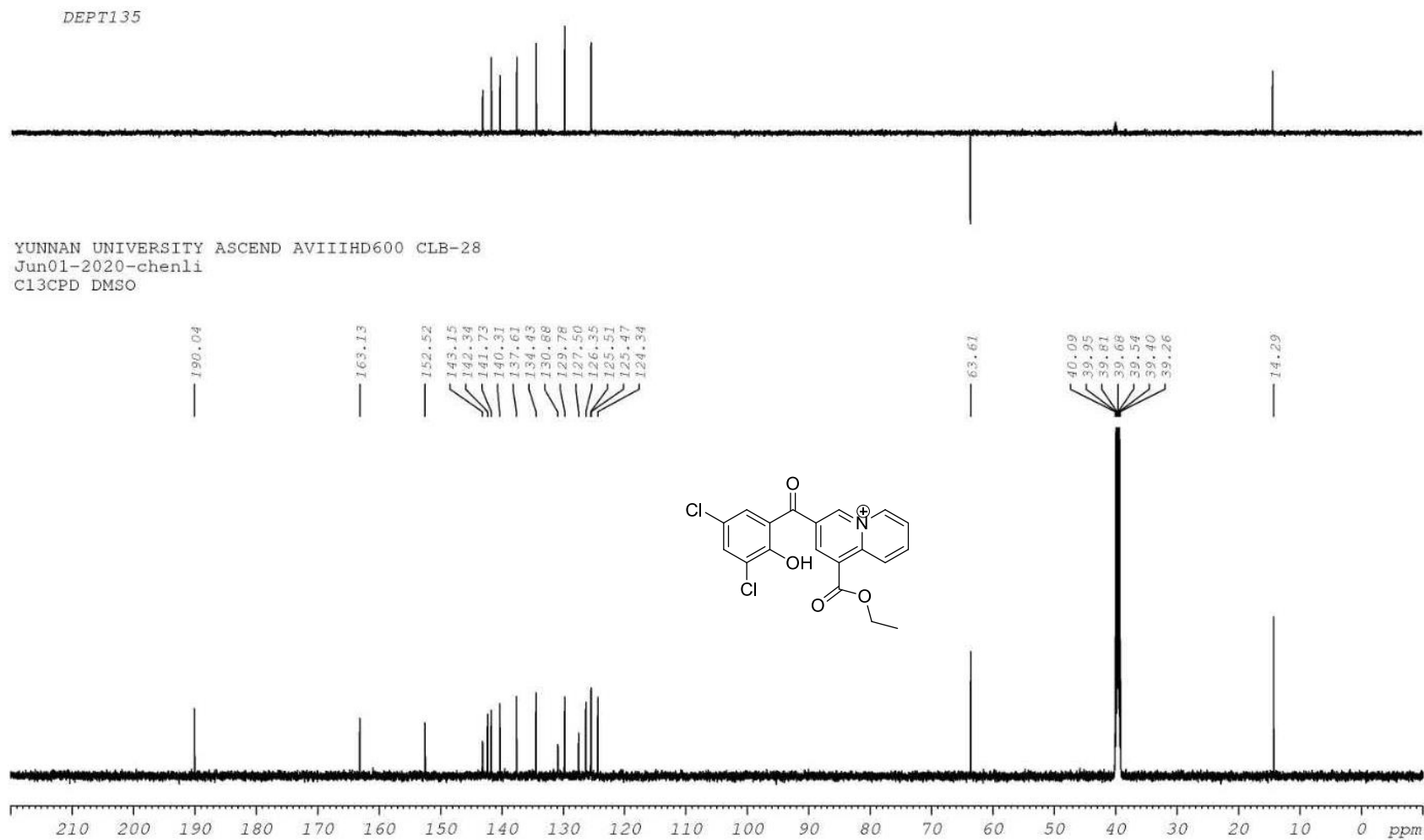
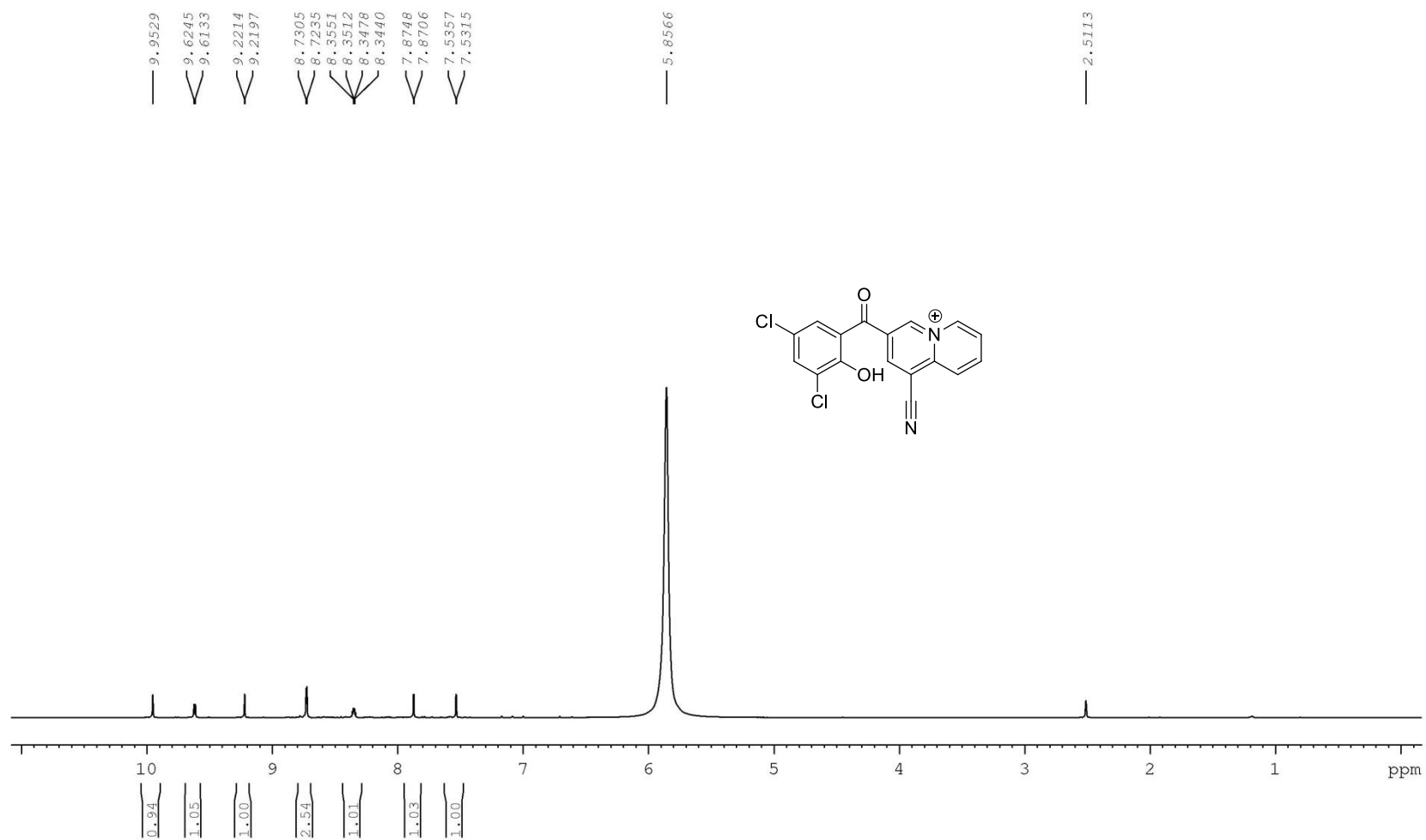


Figure S90.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound 4d'



**Figure S91.**  $^1\text{H}$  NMR (600 MHz,  $\text{DMSO-}d_6 + \text{HClO}_4$ ) spectra of compound **4e'**



DEPT135

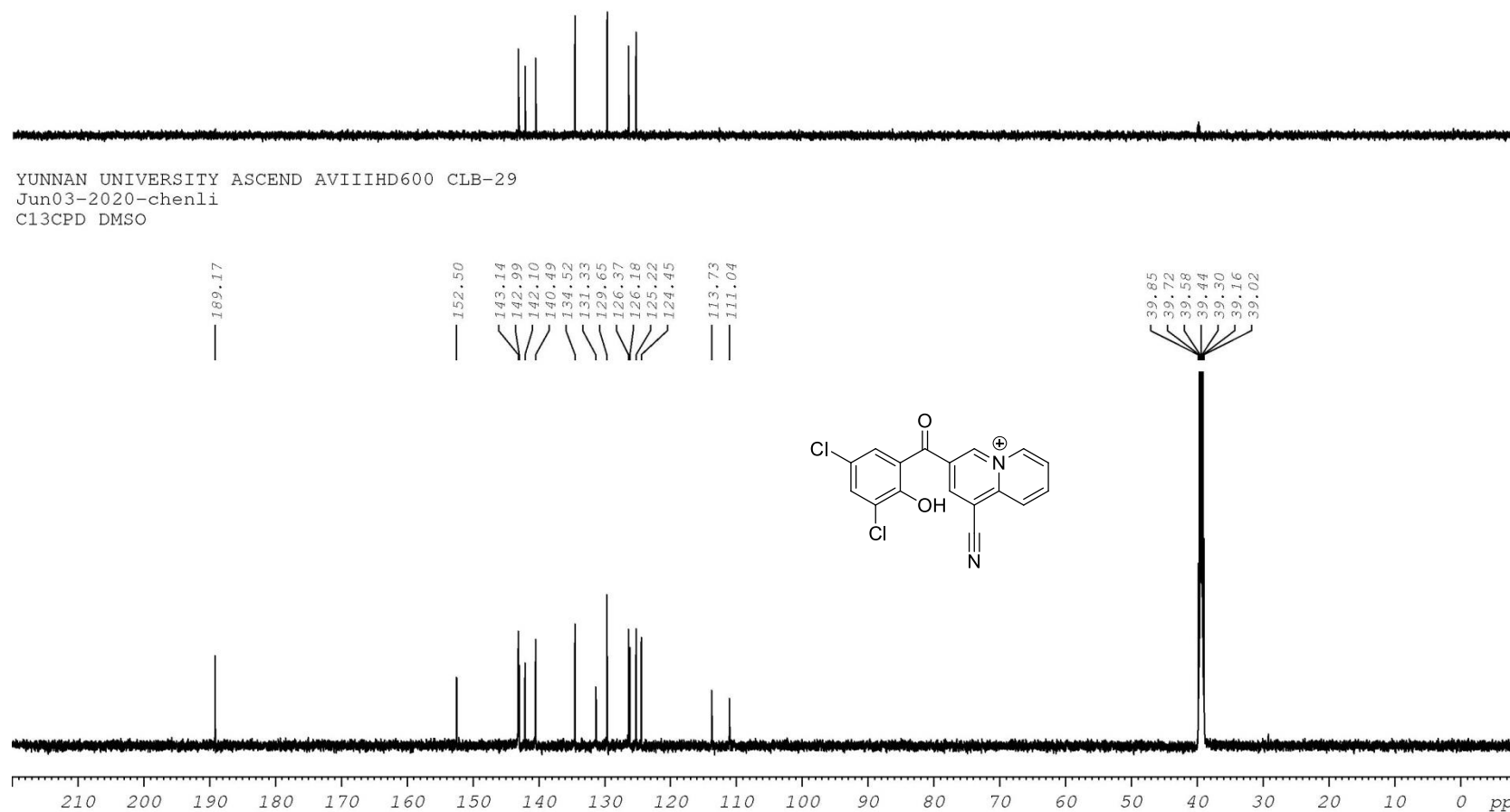


Figure S92.  $^{13}\text{C}$  NMR (150 MHz,  $\text{DMSO-}d_6+\text{HClO}_4$ ) spectra of compound **4e'**

RT: 0.00 - 3.50

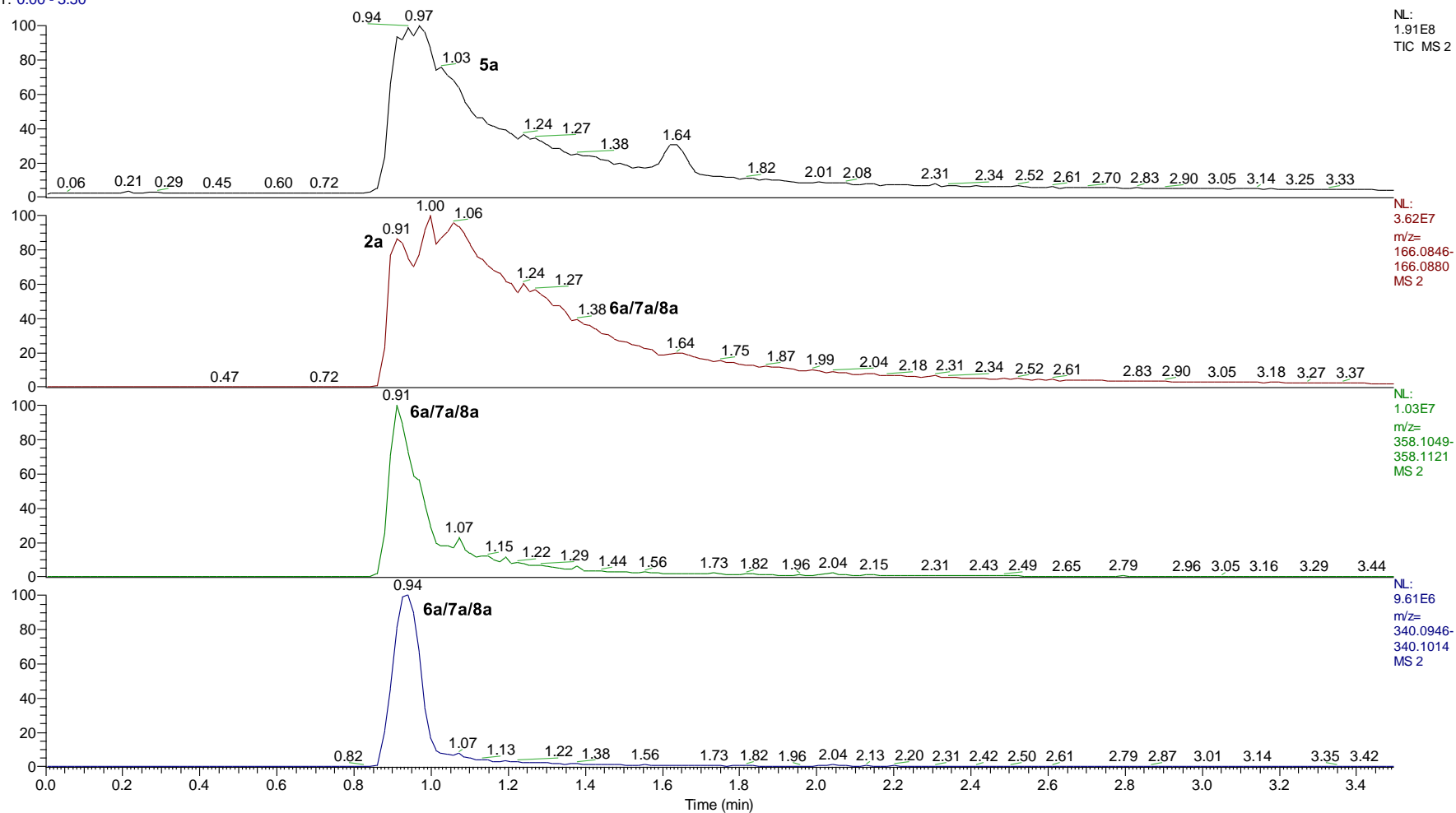


Figure S93. HPLC of the reaction mixture

2 #49 RT: 0.92 AV: 1 NL: 3.04E7  
T: FTMS + c ESI Full ms [100.00-400.00]

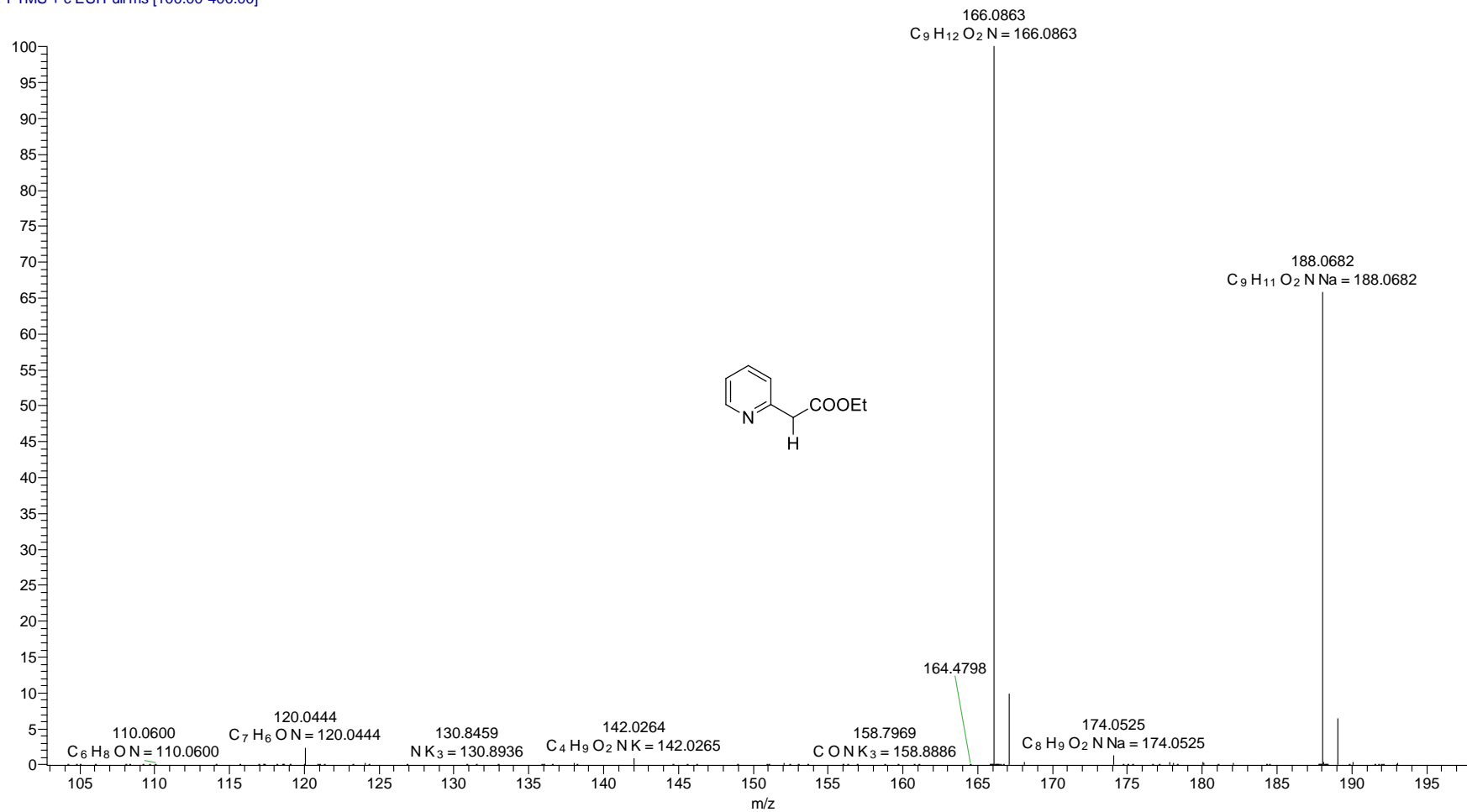


Figure S94. HRMS of substrate 2a

2 #57 RT: 1.04 AV: 1 NL: 3.30E7  
T: FTMS + c ESI Full ms [100.00-400.00]

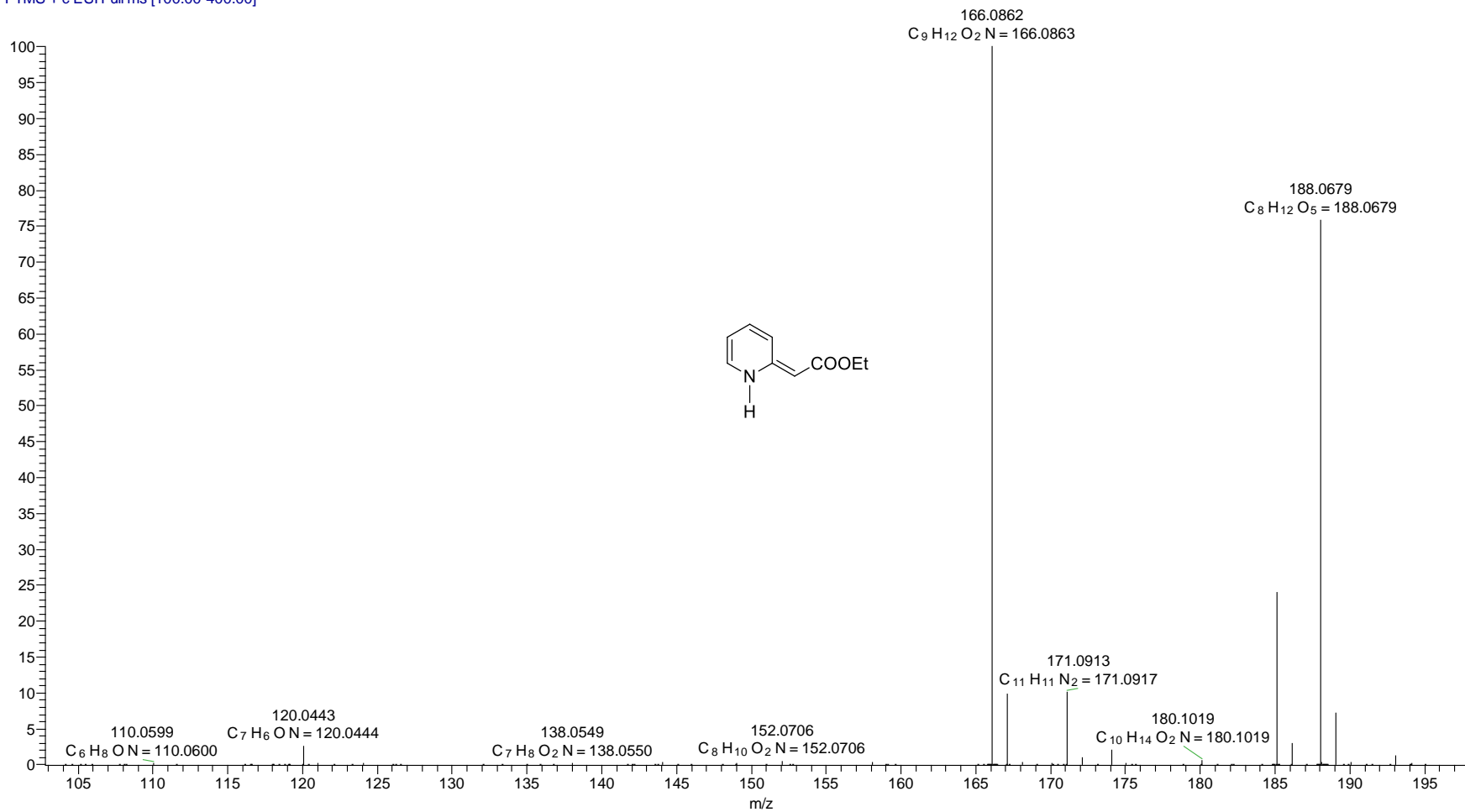


Figure S95. HRMS of intermediate 5a

2 #48 RT: 0.91 AV: 1 NL: 1.03E7  
T: FTMS + c ESI Full ms [100.00-400.00]

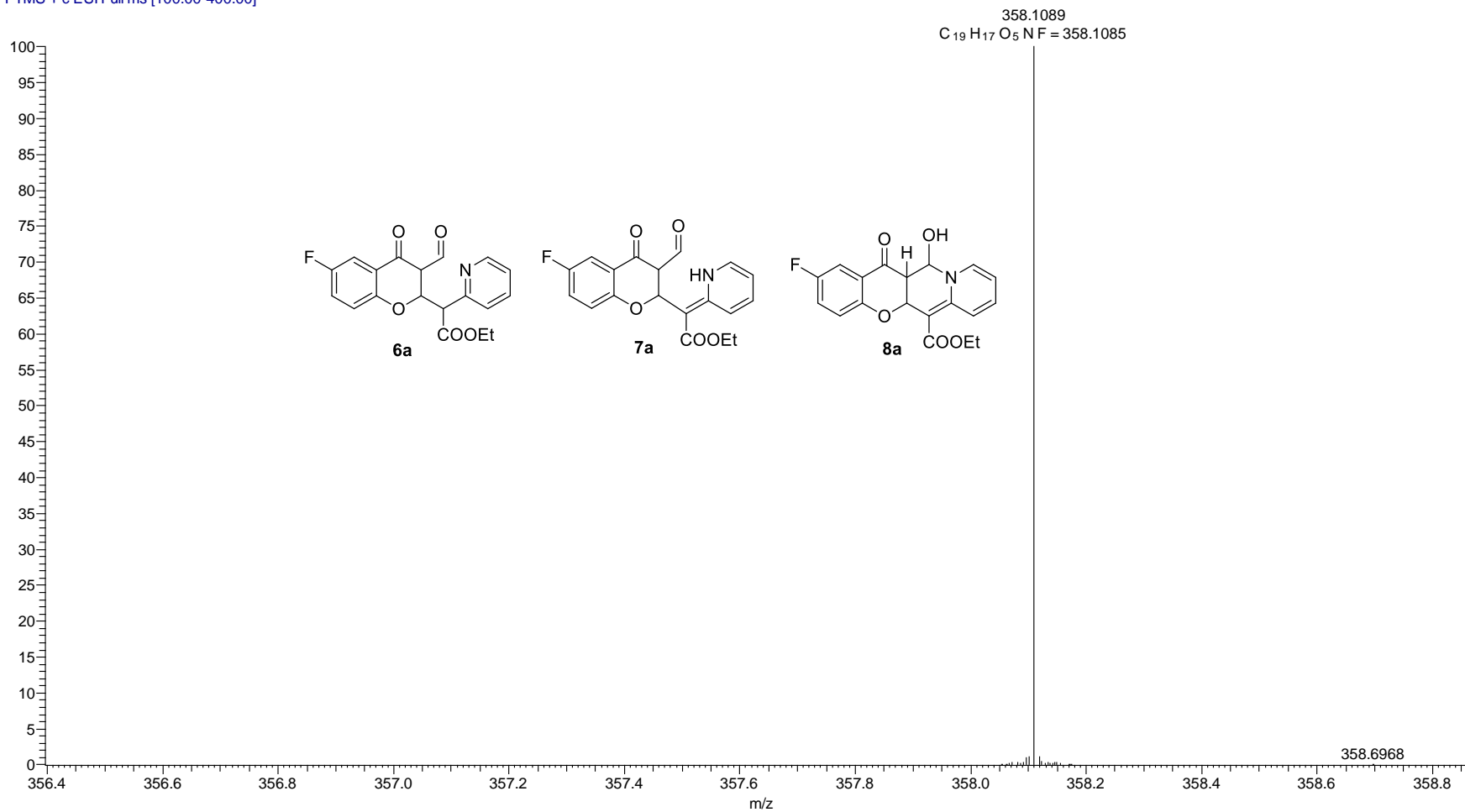


Figure S96. HRMS of intermediate **6a/7a/8a**

2 #52 RT: 0.97 AV: 1 NL: 5.85E6  
T: FTMS + c ESI Full ms [100.00-400.00]

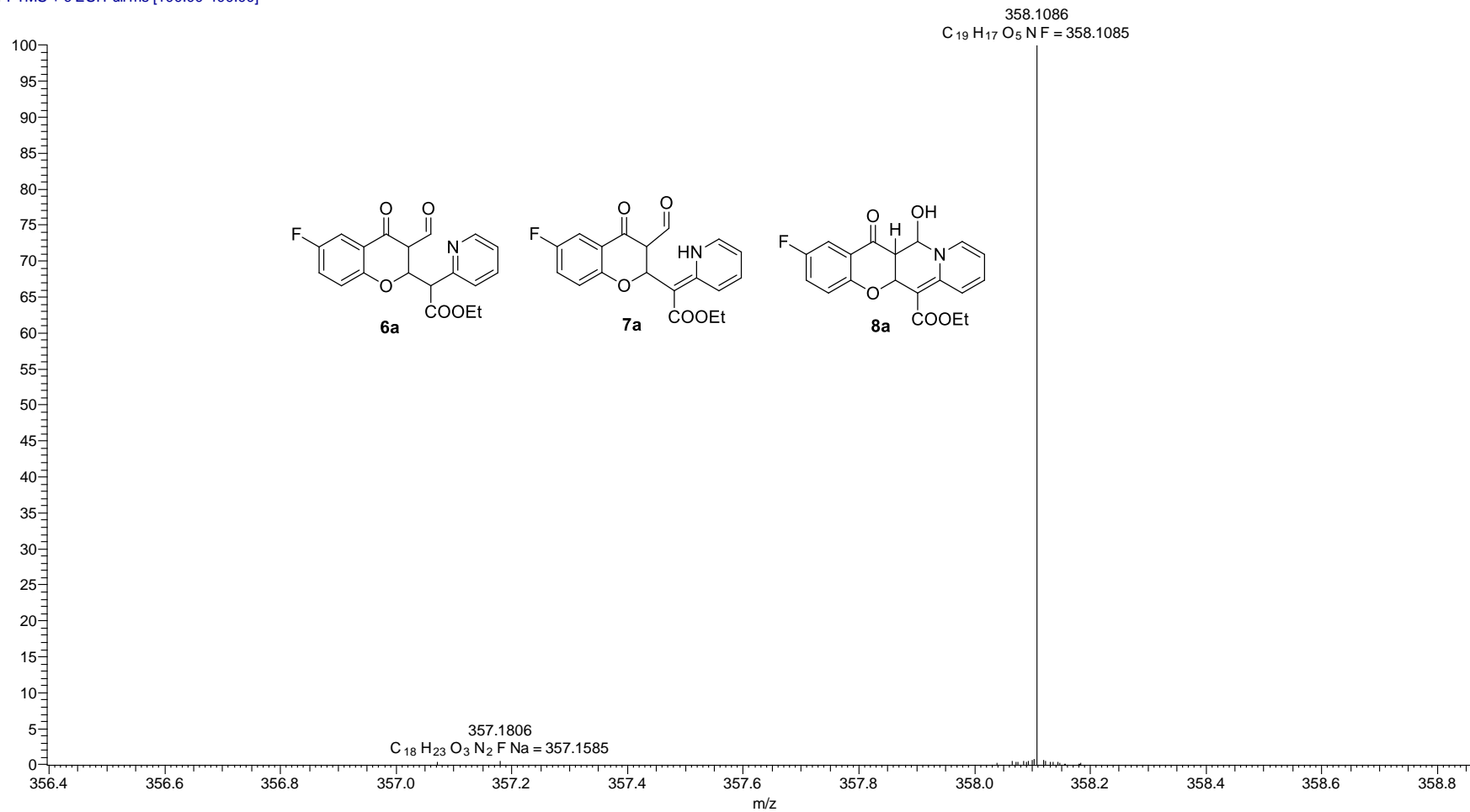


Figure S97. HRMS of intermediate **6a/7a/8a**

2 #79 RT: 1.38 AV: 1 NL: 6.17E5  
T: FTMS + c ESI Full ms [100.00-400.00]

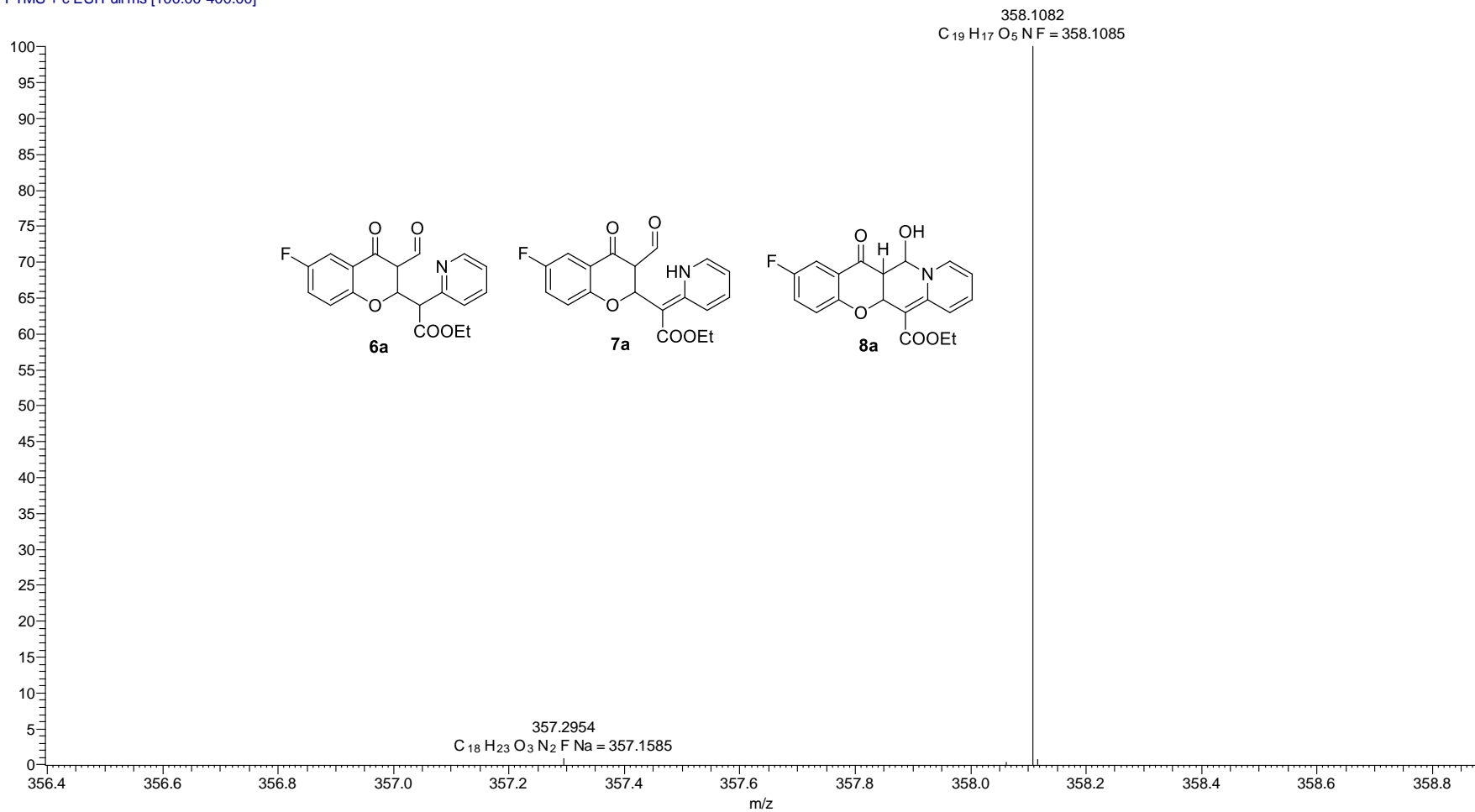


Figure S98. HRMS of intermediate 6a/7a/8a

2 #49 RT: 0.92 AV: 1 NL: 9.52E6  
T: FTMS + c ESI Full ms [100.00-400.00]

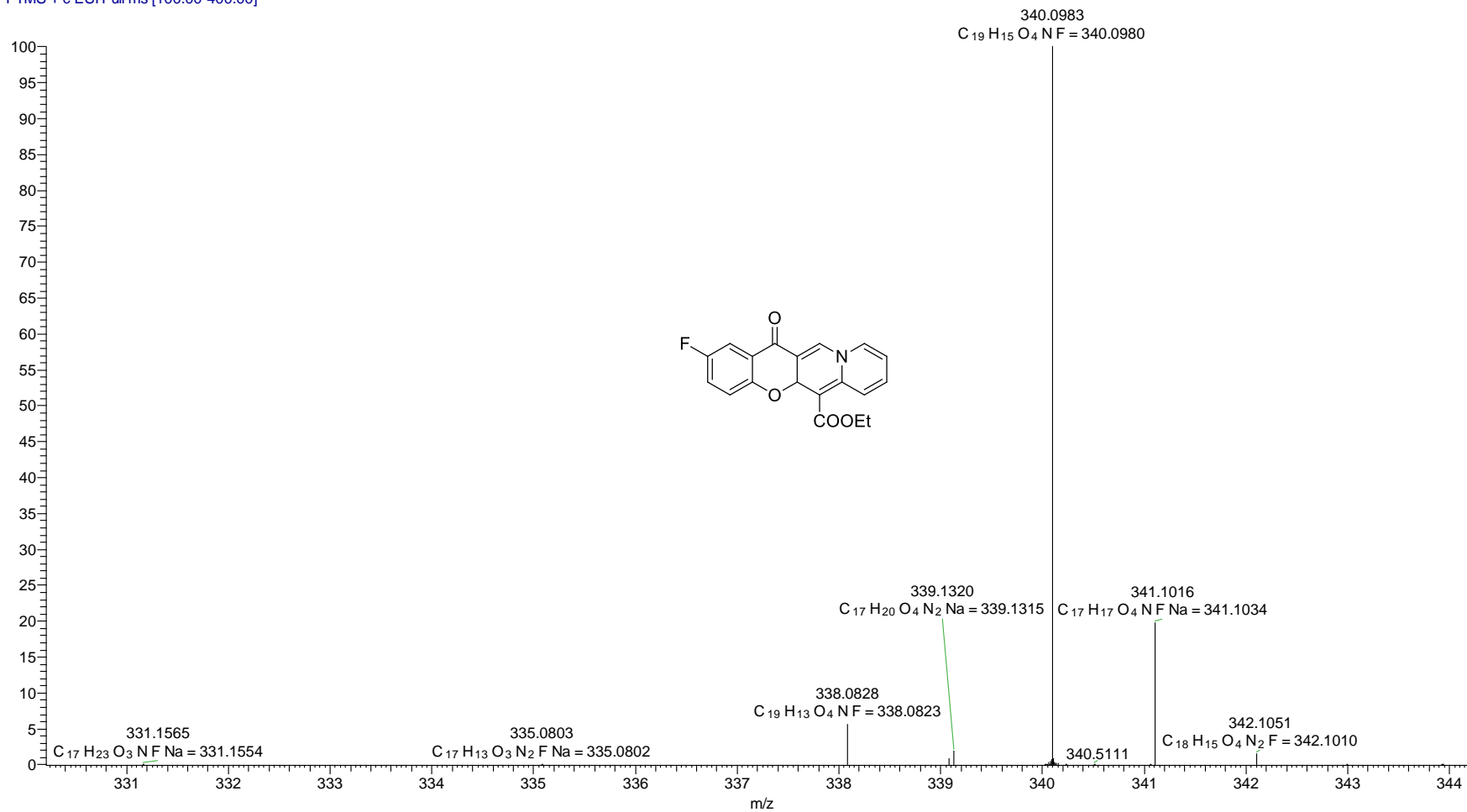


Figure S99. HRMS of compound 3a



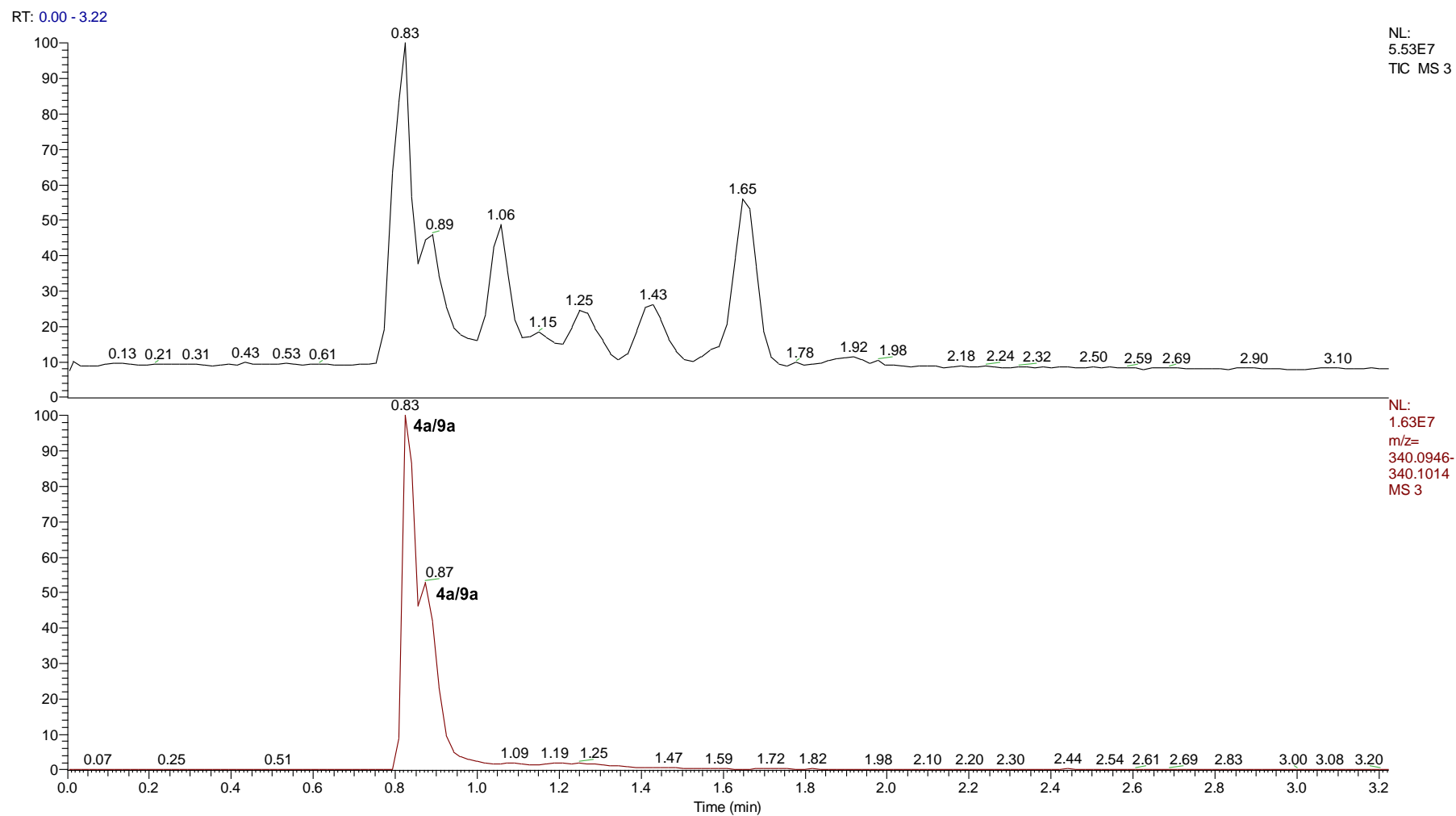


Figure S100. HPLC of the reaction mixture

3 #43 RT: 0.83 AV: 1 NL: 1.63E7  
T: FTMS + c ESI Full ms [100.00-400.00]

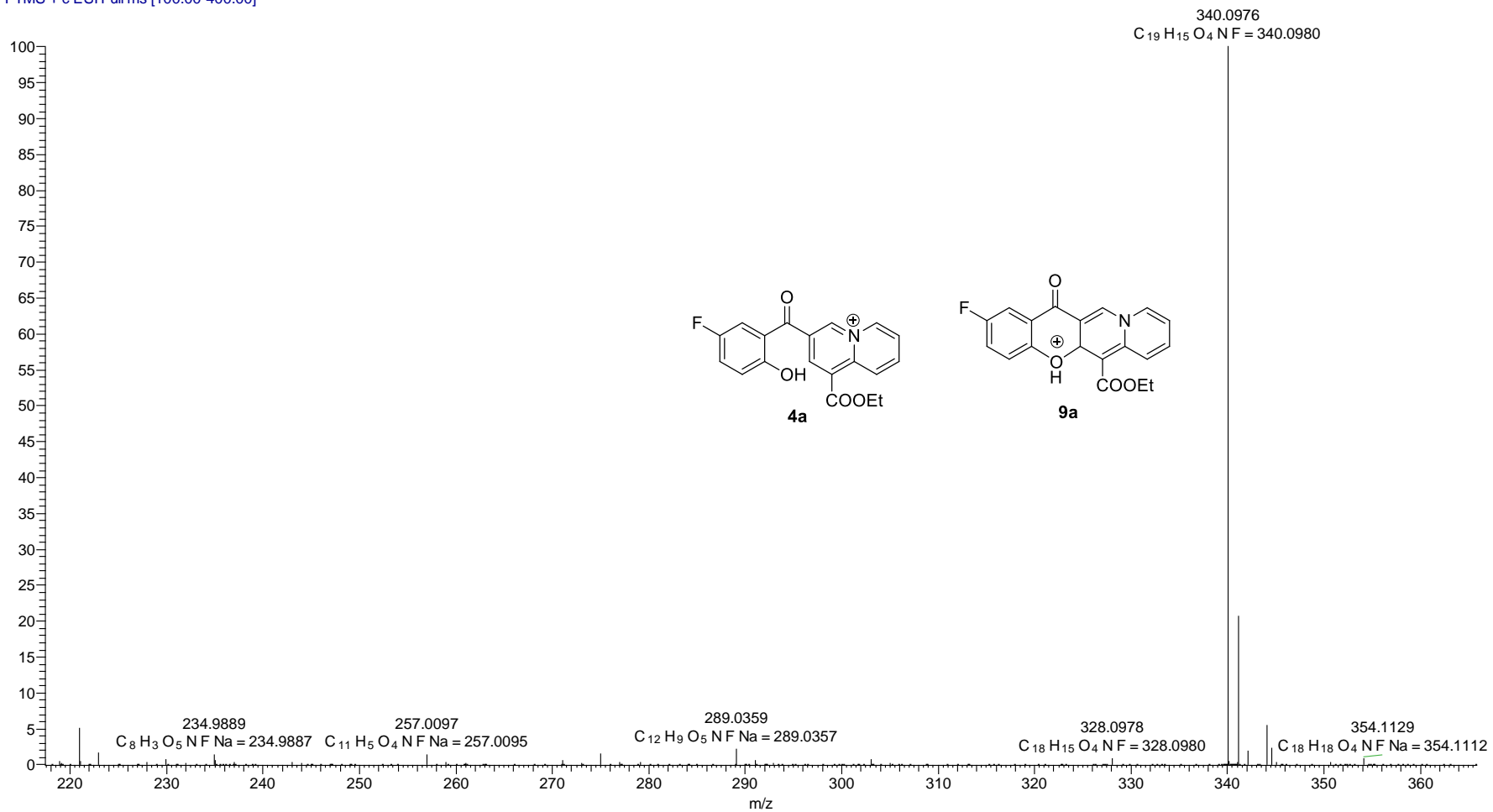


Figure S101. HRMS of compound 4a/9a

3 #46 RT: 0.87 AV: 1 NL: 8.62E6  
T: FTMS + c ESI Full ms [100.00-400.00]

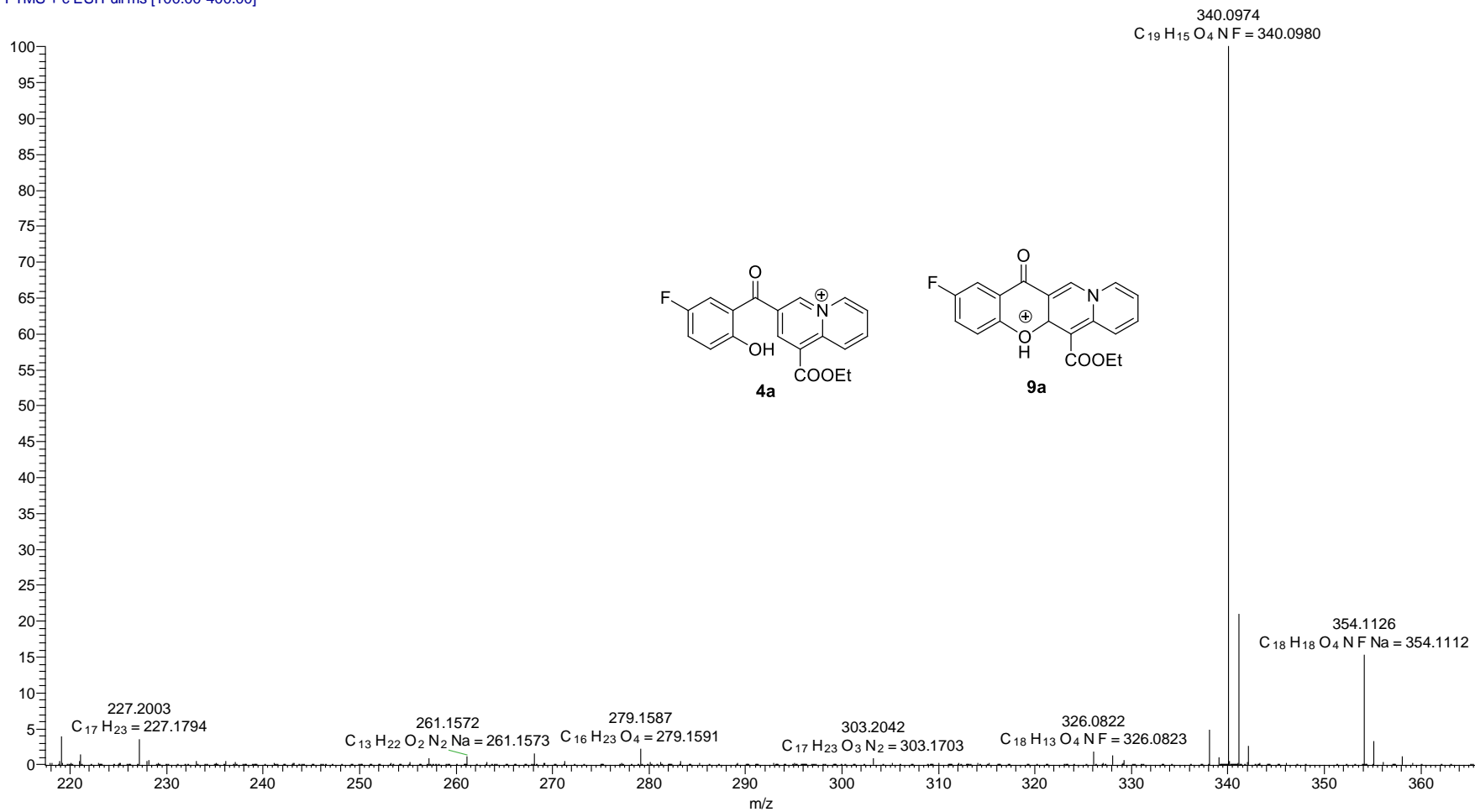


Figure S102. HRMS of compound 4a/9a