

*Supporting information*

**A Formal [3+3] Cycloaddition of Allenyl Imide and Activated Ketones  
for the Synthesis of Tetrasubstituted 2-Pyrones**

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## General Information

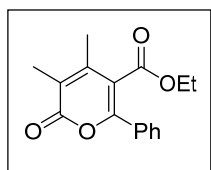
All reactions involving air-sensitive compounds were performed in oven-dried glassware by using standard Schlenk techniques. Anhydrous THF were distilled from sodium-benzophenone ketyl. Anhydrous CH<sub>2</sub>Cl<sub>2</sub>, DMF, EtOAc and CH<sub>3</sub>CN were distilled from CaH<sub>2</sub>. Allenyl imides were prepared according to the published procedure.<sup>[1]</sup>  $\beta$ -Ketoesters<sup>[2]</sup> and  $\beta$ -oxonitrile<sup>[3]</sup> were prepared according to the published procedure. All reactions were monitored by TLC, or by illumination with a UV lamp (254 nm). All flash chromatography was packed with silica-gel as the stationary phase. <sup>1</sup>H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from internal TMS with the solvent resonance as the internal standard (CDCl<sub>3</sub>,  $\delta$  = 7.26 ppm). <sup>13</sup>C NMR (126 MHz) spectra were recorded on a Bruker Avance 500 instrument, and chemical shifts were reported in ppm downfield from TMS with the solvent resonance as the internal standard (CDCl<sub>3</sub>,  $\delta$  = 77.2 ppm). <sup>19</sup>F NMR (471 MHz) spectra were recorded on a Bruker Avance 500 instrument. Infrared spectra were recorded on a NICOLET FT/IR-200 spectrometer. High resolution MS (ESI-orbitrap) were obtained on Thermo Fisher Q Exactive Mass Spectrometer. Melting points were recorded on a X-4 series microscope melting point apparatus at ambient pressure.

## General Procedure for the Synthesis of 2-Pyrones:

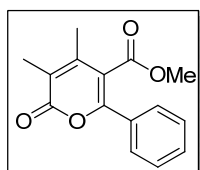
Cesium hydroxide monohydroxide (30 mol%) was added to mixture of allenyl imide (0.1 mmol) and  $\beta$ -ketoesters or  $\beta$ -oxonitrile (0.12 mmol) in dry DCM (0.5 mL). The reaction mixture was stirred at 30 °C for the time indicated in the main text. The reaction was monitored by TLC using petroleum ether/ethyl acetate (5:1). The mixture was directly subjected to PTLC (deactivated by Et<sub>3</sub>N) to afford desired products.

## Characterization Data of the Products:

### Ethyl 3,4-dimethyl-2-oxo-6-phenyl-2H-pyran-5-carboxylate (3a):



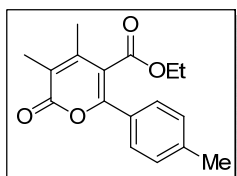
Colorless solid, 24.5 mg, 90% yield,  $R_f$  = 0.27 (PE:EA = 5:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (d,  $J$  = 7.0 Hz, 2H), 7.46–7.39 (m, 3H), 4.14 (q,  $J$  = 7.0 Hz, 2H), 2.18 (s, 3H), 2.14 (s, 3H), 1.06 (t,  $J$  = 7.0 Hz, 3H) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  166.8, 162.0, 156.9, 146.9, 132.1, 130.5, 128.4, 127.8, 120.5, 114.6, 61.8, 16.9, 13.5, 12.7 ppm; IR (KBr):  $\nu$  = 2996, 1714, 1637, 1556, 1334.0, 1255, 1102, 1015, 962 cm<sup>-1</sup>; mp = 85–87 °C; HRMS (ESI;  $m/z$ ): [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>17</sub>O<sub>4</sub><sup>+</sup>, 273.1049; Found: 273.1121.



### Methyl 3,4-dimethyl-2-oxo-6-phenyl-2H-pyran-5-carboxylate (3b):

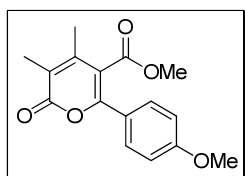
Colorless solid, 22.5 mg, 87% yield,  $R_f$  = 0.33 (PE:EA = 5:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.55 (d,  $J$  = 8.0 Hz, 2H), 7.46–7.40 (m, 3H), 3.66 (s, 3H), 2.17

(s, 3H), 2.14 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 162.0, 156.9, 146.9, 131.9, 130.6, 128.5, 127.6, 120.5, 114.2, 52.6, 17.0, 12.8 ppm; IR (KBr):  $\nu$  = 2959, 1713, 1636, 1555, 1336, 1256, 1131, 1045, 778  $\text{cm}^{-1}$ ; mp = 123–126  $^\circ\text{C}$ ; HRMS (ESI; m/z):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{15}\text{O}_4^+$ , 259.0892; Found: 259.0964.



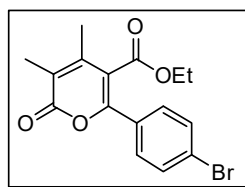
**Ethyl 3,4-dimethyl-2-oxo-6-(p-tolyl)-2H-pyran-5-carboxylate (3c) :**

Colorless solid, 24.4 mg, 85% yield,  $R_f$  = 0.44 (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J$  = 8.0 Hz, 2H), 7.22 (d,  $J$  = 8.0 Hz, 2H), 4.16 (q,  $J$  = 7.0 Hz, 2H), 2.38 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 1.10 (t,  $J$  = 7.0 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.0, 162.2, 157.0, 147.1, 141.0, 129.2, 129.1, 127.7, 120.1, 114.2, 61.9, 21.4, 17.0, 13.7, 12.8 ppm; IR (KBr):  $\nu$  = 2923, 1713, 1625, 1507, 1369, 1246 1102, 1042, 780  $\text{cm}^{-1}$ ; mp = 67–70  $^\circ\text{C}$ ; HRMS (ESI; m/z):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{19}\text{O}_4^+$ , 287.1205; Found: 287.1277.



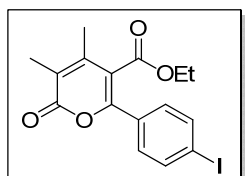
**Methyl 6-(4-methoxyphenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate (3d):**

Yellow solid, 23.7 mg, 82% yield,  $R_f$  = 0.20 (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J$  = 9.0 Hz, 2H), 6.94 (d,  $J$  = 9.0 Hz, 2H), 3.86 (s, 3H), 3.72 (s, 3H), 2.17 (s, 3H), 2.14 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 162.2, 161.5, 156.8, 147.1, 129.3, 124.3, 119.6, 114.0, 113.3, 55.4, 52.6, 17.0, 12.7 ppm; IR (KBr):  $\nu$  = 2925, 1709, 1619, 1506, 1355, 1255, 1176, 1042, 783  $\text{cm}^{-1}$ ; mp = 85–88  $^\circ\text{C}$ ; HRMS (ESI; m/z):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{17}\text{O}_5^+$ , 289.0998; Found: 289.1070.



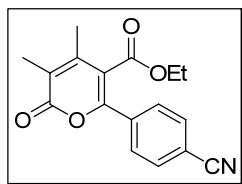
**Ethyl 6-(4-bromophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate (3e) :**

Colorless solid, 33.3 mg, 95% yield,  $R_f$  = 0.38 (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J$  = 8.5 Hz, 2H), 7.45 (d,  $J$  = 8.5 Hz, 2H), 4.17 (q,  $J$  = 7.0 Hz, 2H), 2.18 (s, 3H), 2.14 (s, 3H), 1.13 (t,  $J$  = 7.0 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 161.8, 155.5, 146.9, 131.8, 130.9, 129.3, 125.2, 121.0, 114.9, 62.1, 17.0, 13.7, 12.9; IR (KBr): 2990, 1712, 1626, 1586, 1373, 1244, 1105, 1006, 782  $\text{cm}^{-1}$ ; mp = 85–88  $^\circ\text{C}$ ; HRMS (ESI; m/z):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{16}\text{BrO}_4^+$ , 351.0154; Found: 351.0226.

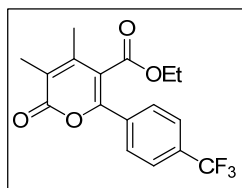


**Ethyl 6-(4-iodophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate (3f) :**

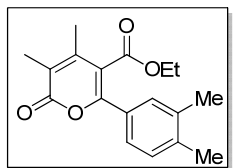
Colorless solid, 34.0 mg, 85% yield,  $R_f$  = 0.39 (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J$  = 8.5 Hz, 2H), 7.33 (d,  $J$  = 8.5 Hz, 2H), 4.16 (q,  $J$  = 7.0 Hz, 2H), 2.18 (s, 3H), 2.14 (s, 3H), 1.13 (t,  $J$  = 7.0 Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 161.8, 155.6, 146.9, 137.8, 131.4, 129.3, 121.0, 114.8, 97.3, 62.1, 17.0, 13.7, 12.9 ppm; IR (KBr):  $\nu$  = 2985, 17045, 1627, 1542, 1390, 1245, 1108, 1050, 782  $\text{cm}^{-1}$ ; mp = 99–101  $^\circ\text{C}$ ; HRMS (ESI; m/z):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{16}\text{IO}_4^+$ , 399.0015; Found: 399.0087.



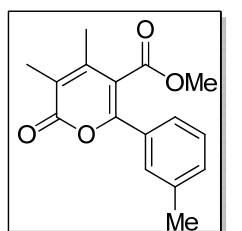
**Ethyl 6-(4-cyanophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate (3g):** Colorless solid, 26.0 mg, 87% yield,  $R_f = 0.20$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 8.5$  Hz, 2H), 7.78 (d,  $J = 8.5$  Hz, 2H), 4.17 (q,  $J = 7.0$  Hz, 2H), 2.18 (s, 3H), 2.15 (s, 3H), 1.11 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 161.3, 154.2, 146.6, 136.1, 132.3, 128.5, 122.2, 117.9, 115.9, 114.2, 62.3, 17.0, 13.7, 13.0 ppm; IR (KBr):  $\nu = 2977, 2227, 1760, 1630, 1501, 1369, 1246, 1143, 1048, 756$   $\text{cm}^{-1}$ ; mp = 150–153  $^\circ\text{C}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}-\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{14}\text{NO}_4^+$ , 296.1001; Found: 296.0928.



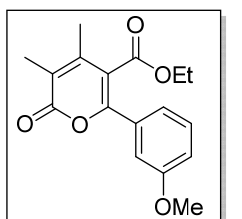
**Ethyl 3,4-dimethyl-2-oxo-6-(4-(trifluoromethyl)phenyl)-2H-pyran-5-carboxylate (3h):** Yellow solid, 20.5 mg, 60% yield,  $R_f = 0.46$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.69 (m, 4H), 4.17 (q,  $J = 7.0$  Hz, 2H), 2.20 (s, 3H), 2.16 (s, 3H), 1.09 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 161.6, 155.0, 146.7, 135.4, 132.4 (q,  $J = 32.9$  Hz), 128.3, 125.5 (q,  $J = 3.7$  Hz), 123.6 (q,  $J = 272.3$  Hz), 121.7, 115.5, 62.7, 17.0, 13.6, 12.9 ppm;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.0 (s, 3F) ppm; IR (KBr):  $\nu = 2988, 1721, 1616, 1511, 1327, 1246, 1116, 1069, 755$   $\text{cm}^{-1}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{16}\text{F}_3\text{O}_4^+$ , 341.0922; Found: 341.0995.



**Ethyl 6-(3,4-dimethylphenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate (3i):** Colorless solid, 25.5 mg, 85% yield,  $R_f = 0.41$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (s, 1H), 7.29 (d,  $J = 8.0$  Hz, 1H), 7.14 (d,  $J = 8.0$  Hz, 1H), 4.17 (q,  $J = 7.0$  Hz, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 1.12 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 162.3, 157.1, 147.1, 139.8, 136.9, 129.7, 129.4, 128.8, 125.2, 120.0, 114.1, 61.9, 19.8, 19.7, 17.0, 13.7, 12.8; IR (KBr):  $\nu = 2989, 1729, 1633, 1545, 1336, 1246, 1141, 1041, 780$   $\text{cm}^{-1}$ ; mp = 85–88  $^\circ\text{C}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{21}\text{O}_4^+$ , 301.1362; Found: 301.1434.

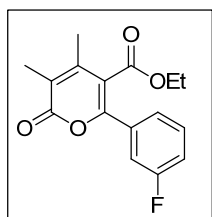


**Methyl 3,4-dimethyl-2-oxo-6-(m-tolyl)-2H-pyran-5-carboxylate (3j):** Yellow oil, 23.0 mg, 84% yield,  $R_f = 0.37$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 (s, 1H), 7.32 (m, 1H), 7.28–7.24 (m, 2H), 3.67 (s, 3H), 2.37 (s, 3H), 2.16 (s, 3H), 2.13 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5, 162.1, 157.1, 147.0, 138.5, 131.9, 131.5, 128.4, 128.3, 124.7, 120.4, 114.2, 52.6, 21.4, 17.0, 12.8 ppm; IR (KBr):  $\nu = 2950, 1717, 1631, 1552, 1354, 1252, 1137, 1042, 797$   $\text{cm}^{-1}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{17}\text{O}_4^+$ , 273.1049; Found: 273.1121.



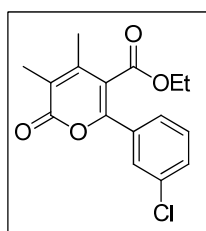
**Ethyl 6-(3-methoxyphenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate (3k):** Yellow oil, 28.8 mg, 95% yield,  $R_f = 0.26$  (PE:EA = 5:1).  $^1\text{H}$  NMR

(500 MHz, CDCl<sub>3</sub>)  $\delta$  7.30 (t,  $J = 7.9$  Hz, 1H), 7.13–7.11 (m, 2H), 6.98 (d,  $J = 8.4$  Hz, 1H), 4.15 (q,  $J = 7.0$  Hz, 2H), 3.81 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H), 1.09 (t,  $J = 7.0$  Hz, 3H) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  166.8, 162.0, 159.6, 156.6, 146.9, 133.2, 129.5, 120.6, 120.2, 116.8, 114.8, 112.9, 61.9, 55.4, 16.9, 13.6, 12.8 ppm; IR (KBr):  $\nu = 2927, 1717, 1632, 1553, 1371, 1245, 1104, 1039, 779$  cm<sup>-1</sup>; HRMS (ESI;  $m/z$ ): [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>19</sub>O<sub>5</sub><sup>+</sup>, 303.1154; Found: 303.1227.



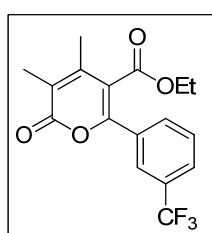
**Ethyl 6-(3-fluorophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate**

(3l): Colorless solid, 27.8 mg, 95% yield,  $R_f = 0.35$  (PE:EA = 5:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.41–7.35 (m, 2H), 7.32–7.29 (m, 1H), 7.17–7.13 (m, 1H), 4.18 (q,  $J = 7.0$  Hz, 2H), 2.18 (s, 3H), 2.14 (s, 3H), 1.11 (t,  $J = 7.0$  Hz, 3H) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  166.5, 162.6 (d,  $J = 221.5$  Hz), 161.5, 155.2 (d,  $J = 2.6$  Hz), 146.8, 133.9 (d,  $J = 8.1$  Hz), 130.2 (d,  $J = 8.2$  Hz), 123.6 (d,  $J = 3.1$  Hz), 121.3, 117.6 (d,  $J = 21.1$  Hz), 115.1, 115.0 (d,  $J = 23.6$  Hz), 62.1, 17.0, 13.6, 12.9 ppm; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -111.8 (s, 1F) ppm; IR (KBr):  $\nu = 2926, 1716, 1634, 1585, 1369, 1256, 1100, 1039, 794$  cm<sup>-1</sup>; mp = 67–70 °C; HRMS (ESI;  $m/z$ ): [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>16</sub>FO<sub>4</sub><sup>+</sup>, 291.0954; Found: 291.1027.



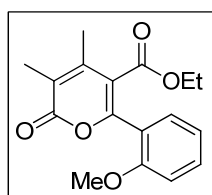
**Ethyl 6-(3-chlorophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate**

(3m): Yellow oil, 29.3 mg, 95% yield,  $R_f = 0.38$  (PE:EA = 5:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.58 (s, 1H), 7.45 (d,  $J = 8.0$  Hz, 1H), 7.41 (d,  $J = 8.0$  Hz, 1H), 7.36 (t,  $J = 8.0$  Hz, 1H), 4.18 (q,  $J = 7.0$  Hz, 2H), 2.18 (s, 3H), 2.14 (s, 3H), 1.12 (t,  $J = 7.0$  Hz, 3H) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  166.4, 161.6, 155.0, 146.8, 134.6, 133.6, 130.6, 129.8, 127.9, 125.9, 121.2, 115.1, 62.1, 16.9, 13.6, 12.8 ppm; IR (KBr):  $\nu = 2982, 1719, 1632, 1569, 1371, 1247, 1113, 1041, 757$  cm<sup>-1</sup>; HRMS (ESI;  $m/z$ ): [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>16</sub>ClO<sub>4</sub><sup>+</sup>, 307.0659; Found: 307.0731.



**Ethyl 3,4-dimethyl-2-oxo-6-(3-(trifluoromethyl)phenyl)-2H-pyran-5-carboxylate**

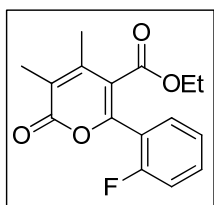
(3n): Yellow oil, 30.7 mg, 90% yield,  $R_f = 0.35$  (PE:EA = 5:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (s, 1H), 7.78 (d,  $J = 8.0$  Hz, 1H), 7.71 (d,  $J = 8.0$  Hz, 1H), 7.56 (t,  $J = 7.5$  Hz, 1H), 4.16 (q,  $J = 7.0$  Hz, 2H), 2.19 (s, 3H), 2.15 (s, 3H), 1.09 (t,  $J = 7.0$  Hz, 3H) ppm; <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  166.3, 161.6, 154.9, 146.8, 132.8, 131.1 (q,  $J = 32.9$  Hz), 131.1, 129.2, 127.1 (q,  $J = 3.7$  Hz), 124.7 (q,  $J = 7.8$  Hz), 123.6 (q,  $J = 272.5$  Hz), 121.6, 115.4, 62.2, 17.0, 13.6, 12.9 ppm; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -62.8 (s, 3F) ppm; IR (KBr):  $\nu = 2985, 1724, 1637, 1558, 1348, 1248, 1132, 1041, 782$  cm<sup>-1</sup>; HRMS (ESI;  $m/z$ ): [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>16</sub>F<sub>3</sub>O<sub>4</sub><sup>+</sup>, 341.0922; Found: 341.0995.



**Ethyl 6-(2-methoxyphenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate**

(3o): Yellow oil, 24.2 mg, 80% yield,  $R_f = 0.21$  (PE:EA = 5:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.42–7.37 (m, 2H), 7.03 (t,  $J = 8.0$  Hz, 1H), 6.93 (d,  $J$

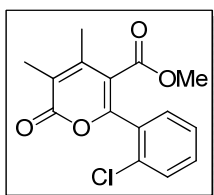
= 8.0 Hz, 1H), 4.03 (q,  $J = 7.0$  Hz, 2H), 3.81 (s, 3H), 2.26 (s, 3H), 2.16 (s, 3H), 0.95 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 162.4, 156.8, 156.6, 147.6, 131.7, 130.2, 122.0, 120.5, 120.4, 115.8, 110.6, 61.1, 55.4, 17.3, 13.4, 12.8 ppm; IR (KBr):  $\nu = 2931, 1715, 1629, 1548, 1372, 1255, 1137, 1045, 758$   $\text{cm}^{-1}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{19}\text{O}_5^+$ , 303.1154; Found: 303.1227.



**Ethyl 6-(2-fluorophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate**

(3p): Yellow oil, 25.3 mg, 87% yield,  $R_f = 0.32$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (t,  $J = 7.5$  Hz, 1H), 7.46 (q,  $J = 7.5$  Hz, 1H), 7.24 (t,  $J = 7.5$  Hz, 1H), 7.14 (t,  $J = 9.0$  Hz, 1H), 4.12 (q,  $J = 7.0$  Hz, 2H), 2.26 (s, 3H), 2.17 (s, 3H), 1.02 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.5, 161.8, 159.6 (d,  $J = 251.6$  Hz), 153.5, 147.3, 132.3 (d,  $J = 8.4$  Hz),

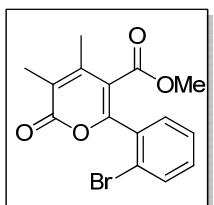
130.5 (d,  $J = 1.8$  Hz), 124.2 (d,  $J = 3.6$  Hz), 121.5, 120.9 (d,  $J = 14.3$  Hz), 116.4, 115.8 (d,  $J = 21.6$  Hz), 61.6, 17.4, 13.5, 12.9. ppm;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -112.8 (s, 1F) ppm; IR (KBr): 2995, 1734, 1644, 1563, 1366, 1256, 1115, 1044, 775  $\text{cm}^{-1}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_5^+$ , 291.0998, Found: 291.1027.



**Methyl 6-(2-chlorophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate**

(3q): Yellow solid, 23.5 mg, 80% yield,  $R_f = 0.26$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (d,  $J = 7.0$  Hz, 1H), 7.41–7.36 (m, 2H), 7.33 (t,  $J = 7.0$  Hz, 1H), 3.54 (s, 3H), 2.26 (s, 3H), 2.17 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.8, 161.6, 156.5, 147.0, 133.3, 131.7, 131.4, 130.4, 129.7,

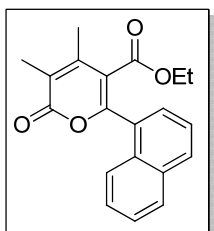
126.5, 121.7, 116.1, 52.3, 17.4, 12.9 ppm; IR (KBr):  $\nu = 3012, 1737, 1644, 1591, 1352, 1270, 1113, 1055, 771$   $\text{cm}^{-1}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{14}\text{ClO}_4^+$ , 293.0502; Found: 293.0575.



**Methyl 6-(2-bromophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate**

(3r): Colorless solid, 31.5 mg, 93% yield,  $R_f = 0.24$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 7.5$  Hz, 1H), 7.38–7.30 (m, 3H), 3.52 (s, 3H), 2.25 (s, 3H), 2.17 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 161.6, 157.6, 147.0, 133.7, 132.9, 131.4, 130.5, 127.1, 122.6, 121.7, 115.8,

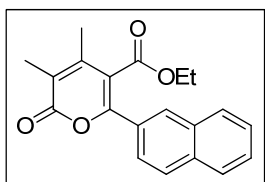
52.2, 17.4, 12.9 ppm; IR (KBr):  $\nu = 2923, 1732, 1643, 1560, 1335, 1267, 1132, 1045, 773$   $\text{cm}^{-1}$ ; mp = 118–121  $^\circ\text{C}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{14}\text{BrO}_4^+$ , 336.9997; Found: 336.0070.



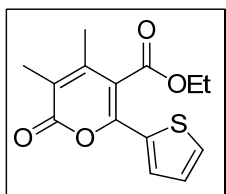
**Ethyl 3,4-dimethyl-6-(naphthalen-1-yl)-2-oxo-2H-pyran-5-carboxylate**

(3s): Colorless solid, 30.5 mg, 94% yield,  $R_f = 0.44$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J = 8.0$  Hz, 1H), 7.88–7.86 (m, 1H), 7.83–7.82 (m, 1H), 7.52–7.50 (m, 3H), 7.46 (t,  $J = 8.0$  Hz, 1H), 3.76 (q,  $J = 7.0$  Hz, 2H), 2.27 (s, 3H), 2.20 (s, 3H), 0.52 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.8, 161.1, 157.1, 146.2, 132.2, 130.0, 129.7,

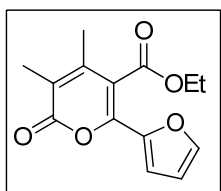
129.0, 127.2, 126.5, 126.1, 125.4, 124.0, 123.6, 120.0, 115.9, 60.2, 16.2, 12.0, 11.8 ppm; IR (KBr):  $\nu = 1707, 1629, 1557, 1371, 1244, 1127, 1046, 778 \text{ cm}^{-1}$ ; mp = 105–108 °C; HRMS (ESI; m/z):  $[M+H]^+$  Calcd for  $C_{20}H_{19}O_4^+$ , 323.1205; Found: 323.1277.



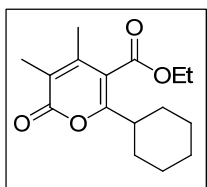
**Ethyl 3,4-dimethyl-6-(naphthalen-2-yl)-2-oxo-2H-pyran-5-carboxylate (3t):** Yellow solid, 27.5 mg, 85% yield,  $R_f = 0.38$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (s, 1H), 7.90–7.86 (m, 3H), 7.67 (d,  $J = 8.5$  Hz, 1H), 7.59–7.53 (m, 2H), 4.20 (q,  $J = 7.0$  Hz, 2H), 2.24 (s, 3H), 2.19 (s, 3H), 1.06 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.9, 162.1, 156.7, 147.0, 134.0, 132.6, 129.2, 128.7, 128.2, 128.2, 127.7, 127.6, 126.8, 124.3, 120.5, 114.9, 61.9, 16.9, 13.6, 12.8 ppm; IR (KBr):  $\nu = 2924, 1715, 1628, 1540, 1366, 1247, 1137, 1045, 767 \text{ cm}^{-1}$ ; mp = 117–120 °C; HRMS (ESI; m/z):  $[M+H]^+$  Calcd for  $C_{20}H_{19}O_4^+$ , 323.1205; Found: 323.1277.



**Ethyl 6-(thiophen-2-yl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate (3u):** Yellow solid, 25.7 mg, 92% yield,  $R_f = 0.38$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 5.0$  Hz, 1H), 7.47 (d,  $J = 5.0$  Hz, 1H), 7.08 (t,  $J = 5.0$  Hz, 1H), 4.36 (q,  $J = 7.0$  Hz, 2H), 2.13 (s, 3H), 2.12 (s, 3H), 1.31 (t,  $J = 7.0$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.6, 161.3, 149.9, 146.7, 133.3, 129.7, 129.0, 127.7, 120.3, 113.1, 62.3, 16.9, 13.8, 12.8 ppm; IR (KBr):  $\nu = 3106, 2987, 1718, 1624, 1541, 1373, 1262, 1144, 1033, 727 \text{ cm}^{-1}$ ; mp = 105–108 °C; HRMS (ESI; m/z):  $[M+H]^+$  Calcd for  $C_{14}H_{15}O_4S^+$ , 279.0613; Found: 279.0685.



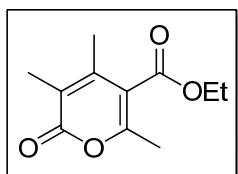
**Ethyl 6-(furan-2-yl)-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate (3v):** Yellow solid, 24.7 mg, 94% yield,  $R_f = 0.36$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 (s, 1H), 7.02 (d,  $J = 3.5$  Hz, 1H), 6.52 (d,  $J = 3.5$  Hz, 1H), 4.38 (q,  $J = 7.1$  Hz, 2H), 2.12 (s, 3H), 2.10 (s, 3H), 1.34 (t,  $J = 7.1$  Hz, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.1, 161.0, 146.8, 145.8, 145.5, 144.9, 120.3, 113.3, 112.3, 111.7, 62.0, 16.7, 14.1, 12.8 ppm; IR (KBr):  $\nu = 2963, 1719, 1638, 1530, 1367, 1262, 1113, 1014, 758 \text{ cm}^{-1}$ ; mp = 107–109 °C; HRMS (ESI; m/z):  $[M+H]^+$  Calcd for  $C_{14}H_{15}O_5^+$ , 263.0841; Found: 263.0914.



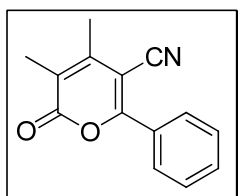
**Ethyl 6-cyclohexyl-3,4-dimethyl-2-oxo-2H-pyran-5-carboxylate (3w):** Yellow oil, 22.3 mg, 80% yield,  $R_f = 0.64$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.38 (q,  $J = 7.0$  Hz, 2H), 2.57 (t,  $J = 7.0$  Hz, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 1.84–1.77 (m, 4H), 1.69–1.66 (m, 3H), 1.39 (t,  $J = 7.0$  Hz, 3H), 1.28–1.24 (m, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 164.5, 162.5,



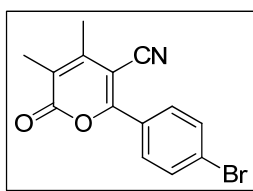
146.9, 119.2, 113.2, 61.6, 41.5, 29.9, 25.9, 25.4, 17.2, 14.1, 12.5 ppm; IR (KBr):  $\nu = 2933, 2857, 1720, 1630, 1564, 1372, 1263, 1142, 1039, 782 \text{ cm}^{-1}$ ; HRMS (ESI;  $m/z$ ):  $[M+H]^+$  Calcd for  $C_{16}H_{23}O_4^+$ , 279.1518; Found: 279.1590.



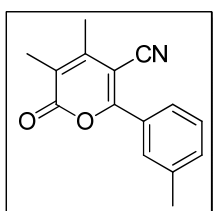
**Ethyl 3,4,6-trimethyl-2-oxo-2H-pyran-5-carboxylate (3x):** Yellow oil, 18.0 mg, 85% yield,  $R_f = 0.35$  (PE:EA = 5:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.35 (q,  $J = 7.5 \text{ Hz}$ , 2H), 2.32 (s, 3H), 2.14 (s, 3H), 2.07 (s, 3H), 1.36 (t,  $J = 7.0 \text{ Hz}$ , 3H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.2, 162.3, 159.0, 147.2, 119.3, 114.3, 61.6, 18.8, 17.4, 14.1, 12.5 ppm; IR (KBr):  $\nu = 2982, 1721, 1646, 1567, 1372, 1268, 1140, 1054, 760 \text{ cm}^{-1}$ ; HRMS (ESI;  $m/z$ ):  $[M+H]^+$  Calcd for  $C_{11}H_{15}O_4^+$ , 211.0892; Found: 211.0964.



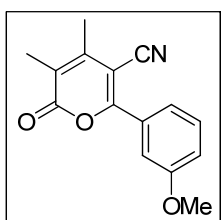
**3,4-dimethyl-2-oxo-6-phenyl-2H-pyran-5-carbonitrile (4a):** Yellow solid, 20.3 mg, 90% yield,  $R_f = 0.44$  (PE:EA = 5:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02–8.00 (m, 2H), 7.60 (t,  $J = 7.5 \text{ Hz}$ , 1H), 7.55 (t,  $J = 8.0 \text{ Hz}$ , 2H), 2.40 (s, 3H), 2.17 (s, 3H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.2, 160.2, 147.3, 132.4, 129.8, 128.9, 128.2, 120.5, 115.7, 93.8, 18.1, 13.0 ppm; IR (KBr):  $\nu = 2920, 2221, 1724, 1630, 1549, 1351, 1193, 1024, 704 \text{ cm}^{-1}$ ; mp = 142–144  $^\circ\text{C}$ ; HRMS (ESI;  $m/z$ ):  $[M-H]^+$  Calcd for  $C_{14}H_{10}NO_2^+$ , 224.0790; Found: 224.0717.



**6-(4-bromophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carbonitrile (4b):** Colorless solid, 24.4 mg, 80% yield,  $R_f = 0.41$  (PE:EA = 5:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.5 \text{ Hz}$ , 2H), 7.69 (d,  $J = 9.0 \text{ Hz}$ , 2H), 2.39 (s, 3H), 2.17 (s, 3H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 159.9, 147.2, 132.3, 129.6, 128.6, 127.4, 120.9, 115.5, 93.9, 18.2, 13.1 ppm; IR (KBr):  $\nu = 2922, 2229, 1733, 1629, 1586, 1342, 1190, 1008, 753 \text{ cm}^{-1}$ ; mp = 122–124  $^\circ\text{C}$ ; HRMS (ESI;  $m/z$ ):  $[M-H]^+$  Calcd for  $C_{14}H_9BrNO_2^+$ , 301.9895; Found: 301.9822.



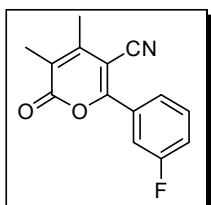
**3,4-dimethyl-2-oxo-6-(m-tolyl)-2H-pyran-5-carbonitrile (4c):** Colorless solid, 22.1 mg, 92% yield,  $R_f = 0.53$  (PE:EA = 5:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.83 (d,  $J = 8.5 \text{ Hz}$ , 1H), 7.79 (s, 1H), 7.43–7.38 (m, 2H), 2.44 (s, 3H), 2.39 (s, 3H), 2.17 (s, 3H) ppm;  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 160.3, 147.4, 138.9, 133.2, 129.8, 128.8, 128.7, 125.4, 120.3, 115.8, 93.6, 21.3, 18.2, 13.0 ppm; IR (KBr):  $\nu = 2924, 2229, 1737, 1627, 1552, 1346, 1194, 1031, 754 \text{ cm}^{-1}$ ; mp = 117–119  $^\circ\text{C}$ ; HRMS (ESI;  $m/z$ ):  $[M+H]^+$  Calcd for  $C_{15}H_{14}NO_2^+$ , 240.0946; Found: 240.1091.



**6-(3-methoxyphenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carbonitrile (4d):**

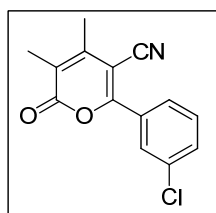
Colorless solid, 23.0 mg, 90% yield,  $R_f = 0.38$  (PE:EA = 5:1).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 7.8 \text{ Hz}$ , 1H), 7.48 (t,  $J = 2.0 \text{ Hz}$ , 1H), 7.42 (t,  $J$

= 8.1 Hz, 1H), 7.10 (dd,  $J = 8.3, 2.5$  Hz, 1H), 3.86 (s, 3H), 2.38 (s, 3H), 2.15 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  165.0, 160.2, 159.7, 147.3, 130.9, 130.0, 120.7, 120.6, 118.9, 115.7, 112.9, 93.9, 55.5, 18.2, 13.0 ppm; IR (KBr):  $\nu = 2921, 2224, 1732, 1626, 1551, 1349, 1114, 1030, 755$   $\text{cm}^{-1}$ ; mp = 137–139 °C; HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{14}\text{NO}_3^+$ , 256.0895; Found: 256.0968.



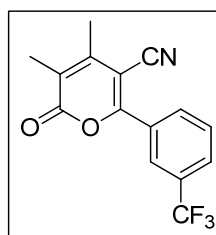
**6-(3-fluorophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carbonitrile (4e):**

Colorless solid, 23.2 mg, 95% yield,  $R_f = 0.44$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 7.9$  Hz, 1H), 7.68 (d,  $J = 9.5$  Hz, 1H), 7.50 (td,  $J = 8.1, 5.7$  Hz, 1H), 7.27 (td,  $J = 6.0, 2.5$  Hz, 1H), 2.38 (s, 3H), 2.16 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 163.5 (d,  $J = 2.7$  Hz), 160.4 (d,  $J = 218.6$  Hz), 147.1, 131.7 (d,  $J = 8.1$  Hz), 130.7 (d,  $J = 8.2$  Hz), 124.0 (d,  $J = 3.2$  Hz), 121.3, 119.5 (d,  $J = 21.1$  Hz), 115.3 (d,  $J = 24.3$  Hz), 115.4, 94.4, 18.2, 13.1;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -110.4 (s, 1F) ppm; IR (KBr):  $\nu = 2920, 2221, 1734, 1627, 1552, 1345, 1108, 1039, 753$   $\text{cm}^{-1}$ ; mp = 112–115 °C; HRMS (ESI;  $m/z$ ):  $[\text{M}-\text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{11}\text{FNO}_2^+$ , 242.0696; Found: 242.0622.



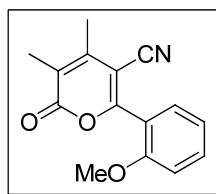
**6-(3-chlorophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carbonitrile (4f):**

Yellow solid, 22.8 mg, 88% yield,  $R_f = 0.45$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (t,  $J = 7.5$  Hz, 1H), 7.94 (td,  $J = 5.0, 2.0$  Hz, 1H), 7.57 (qd,  $J = 5.0, 2.0$  Hz, 1H), 7.50 (t,  $J = 8.5$  Hz, 1H), 2.40 (s, 3H), 2.18 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 159.8, 147.1, 135.2, 132.4, 131.4, 130.2, 128.2, 126.3, 121.2, 115.2, 94.4, 18.2, 13.1 ppm; IR (KBr):  $\nu = 2922, 2219, 1735, 1627, 1568, 1342, 1121, 1038, 753$   $\text{cm}^{-1}$ ; mp = 162–164 °C; HRMS (ESI;  $m/z$ ):  $[\text{M}-\text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_9\text{ClNO}_2^+$ , 258.0400, Found: 258.0327.



**3,4-dimethyl-2-oxo-6-(3-(trifluoromethyl)phenyl)-2H-pyran-5-carbonitrile (4g):**

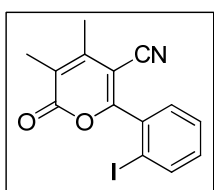
Colorless solid, 24.8 mg, 84% yield,  $R_f = 0.36$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24–8.22 (m, 2H), 7.85 (d,  $J = 8.0$  Hz, 1H), 7.71 (t,  $J = 8.0$  Hz, 1H), 2.42 (s, 3H), 2.19 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.4, 159.8, 147.0, 131.7 (q,  $J = 33.2$  Hz), 131.4, 130.7, 129.6, 128.9 (q,  $J = 3.6$  Hz), 125.3 (q,  $J = 3.8$  Hz), 123.4 (q,  $J = 272.8$  Hz), 121.6, 115.2, 94.8, 18.2, 13.1;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.9 (s, 3F) ppm; IR (KBr):  $\nu = 2921, 2850, 2225, 1740, 1629, 1527, 1360, 1314, 1177, 1130, 1078, 803, 755, 695$   $\text{cm}^{-1}$ ; mp = 100–102 °C; HRMS (ESI;  $m/z$ ):  $[\text{M}-\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_9\text{F}_3\text{NO}_2^+$ , 292.0664; Found: 292.0590.



**6-(2-methoxyphenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carbonitrile (4h):**

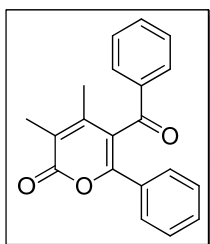
Colorless solid, 21.7 mg, 85% yield,  $R_f = 0.33$  (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.47 (m, 1H), 7.07 – 7.00 (m, 1H), 3.90 (s, 2H), 2.36

(s, 2H), 2.14 (s, 2H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.1, 160.9, 157.2, 146.9, 133.4, 130.5, 120.6, 120.3, 119.6, 115.0, 111.7, 97.7, 55.5, 18.1, 12.9 ppm; IR (KBr):  $\nu$  = 2982, 2922, 2225, 1740, 1627, 1598, 1551, 1489, 1453, 1345, 1282, 1257, 1124, 1012, 951, 895, 757, 678  $\text{cm}^{-1}$ ; mp = 115–118 °C HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{14}\text{NO}_3^+$ , 256.0895; Found: 256.0968.



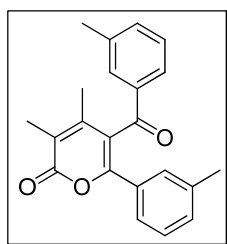
**6-(2-iodophenyl)-3,4-dimethyl-2-oxo-2H-pyran-5-carbonitrile (4i):**

Colorless solid, 28.2 mg, 80% yield,  $R_f$  = 0.31 (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J$  = 8.0 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.24 (td,  $J$  = 7.7, 1.8 Hz, 1H), 2.38 (s, 3H), 2.18 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 160.0, 146.3, 140.0, 135.6, 132.6, 130.4, 128.4, 121.7, 114.1, 97.8, 95.6, 18.1, 13.1 ppm; IR (KBr):  $\nu$  = 2921, 2850, 2373, 2313, 2229, 1732, 1691, 1581, 1560, 1509, 1456, 1434, 1342, 1258, 1194, 1114, 1025, 952, 897, 807, 751, 724, 684  $\text{cm}^{-1}$ ; mp = 113–115 °C; HRMS (ESI;  $m/z$ ):  $[\text{M}-\text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_9\text{INO}_2^+$  349.9756, Found: 349.9683.



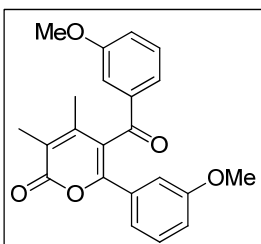
**5-benzoyl-3,4-dimethyl-6-phenyl-2H-pyran-2-one (4j):**

Colorless oil, 25.3 mg, 83% yield,  $R_f$  = 0.36 (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81–7.78 (m,  $J$  = 8.0 Hz, 2H), 7.52–7.48 (m, 3H), 7.38–7.33 (m,  $J$  = 8.0 Hz, 2H), 7.28–7.21 (m, 3H), 2.19 (s, 3H), 2.04 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.1, 162.4, 155.2, 147.8, 136.7, 134.1, 131.6, 130.4, 129.4, 128.8, 128.4, 128.3, 121.0, 118.7, 17.1, 12.8 ppm; IR (KBr):  $\nu$  = 3393, 2923, 2852, 1710, 1665, 1630, 1593, 1547, 1491, 1445, 1338, 1315, 1243, 1150, 1101, 1049, 911, 884, 756, 724, 688  $\text{cm}^{-1}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{20}\text{H}_{17}\text{O}_3^+$ , 305.1099; Found: 305.1172.



**3,4-dimethyl-5-(3-methylbenzoyl)-6-(m-tolyl)-2H-pyran-2-one (4k):**

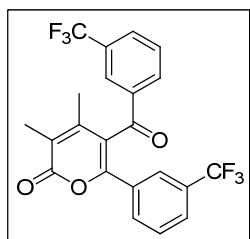
Colorless solid, 29.3 mg, 88% yield,  $R_f$  = 0.45 (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (s, 1H), 7.56 (d,  $J$  = 7.0 Hz, 1H), 7.35 (s, 1H), 7.31 (d,  $J$  = 8.0 Hz, 1H), 7.26 (q,  $J$  = 8.0 Hz, 2H), 7.10–7.05 (m, 2H), 2.32 (s, 3H), 2.42 (s, 3H), 2.19 (s, 3H), 2.03 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.3, 162.5, 155.3, 148.0, 138.6, 138.2, 136.8, 134.9, 131.5, 131.2, 129.6, 128.8, 128.6, 128.2, 126.8, 125.4, 120.8, 118.8, 21.2, 21.2, 17.1, 12.7 ppm; IR (KBr):  $\nu$  = 2918, 2850, 1710, 1663, 1582, 1556, 1480, 1333, 1263, 1144, 1105, 942, 813, 797, 759, 694  $\text{cm}^{-1}$ ; mp = 91–93 °C; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{21}\text{O}_3^+$ , 333.1412; Found: 333.1485.



**5-(3-methoxybenzoyl)-6-(3-methoxyphenyl)-3,4-dimethyl-2H-pyran-2-one (4l) :**

Colorless oil, 29.2 mg, 80% yield,  $R_f$  = 0.21 (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (s, 1H), 7.30 (d,  $J$  = 7.5 Hz, 1H), 7.24 (t,  $J$  = 8.0 Hz, 1H), 7.11 (t,  $J$  = 8.0 Hz, 1H), 7.06–7.00 (m, 3H), 6.82–6.77 (m,  $J$  = 6.0, 2.0 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 2.16 (s,

3H), 2.00 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  194.9, 162.3, 159.9, 159.4, 154.9, 147.7, 138.1, 132.8, 129.8, 129.6, 122.4, 121.0, 120.8, 120.8, 118.9, 117.0, 113.0, 112.9, 55.4, 55.2, 17.1, 12.7 ppm; IR (KBr):  $\nu$  = 3480, 2937, 2837, 1720, 1666, 1596, 1581, 1485, 1463, 1430, 1336, 1265, 1221, 1179, 1142, 1105, 1044, 948, 870, 797, 748, 690  $\text{cm}^{-1}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{21}\text{O}_5^+$ , 365.1311; Found: 365.1383.

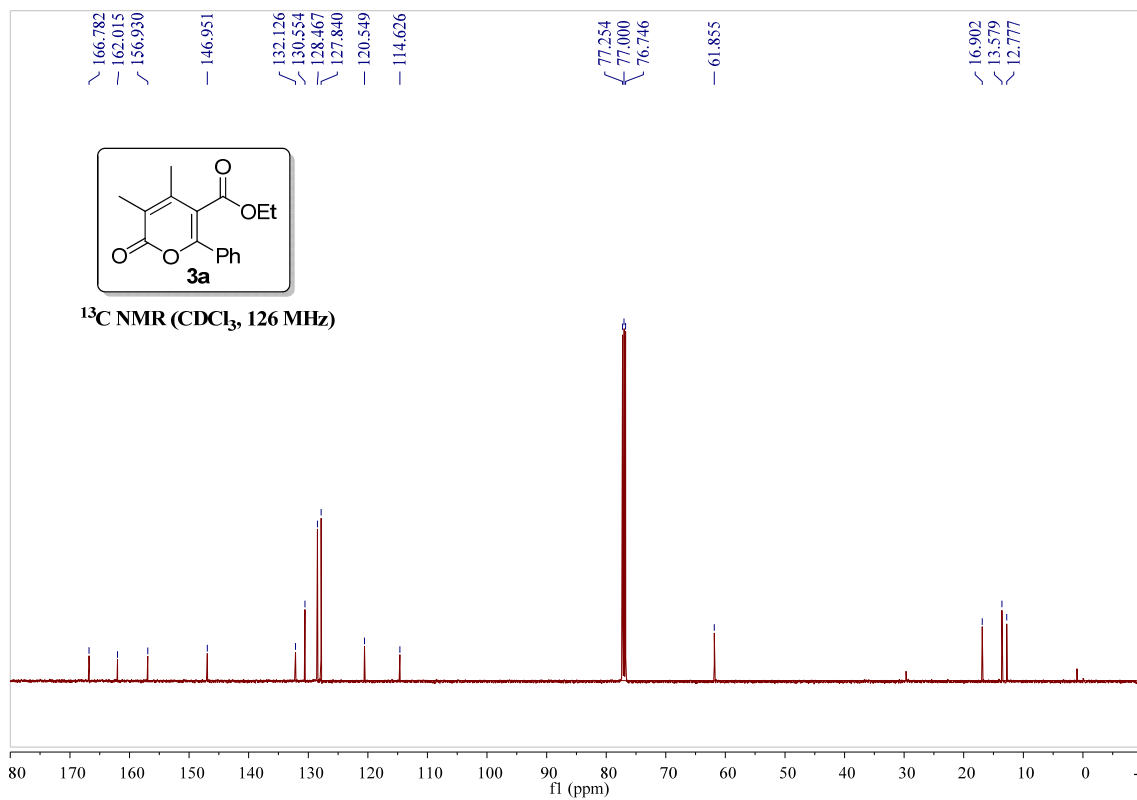
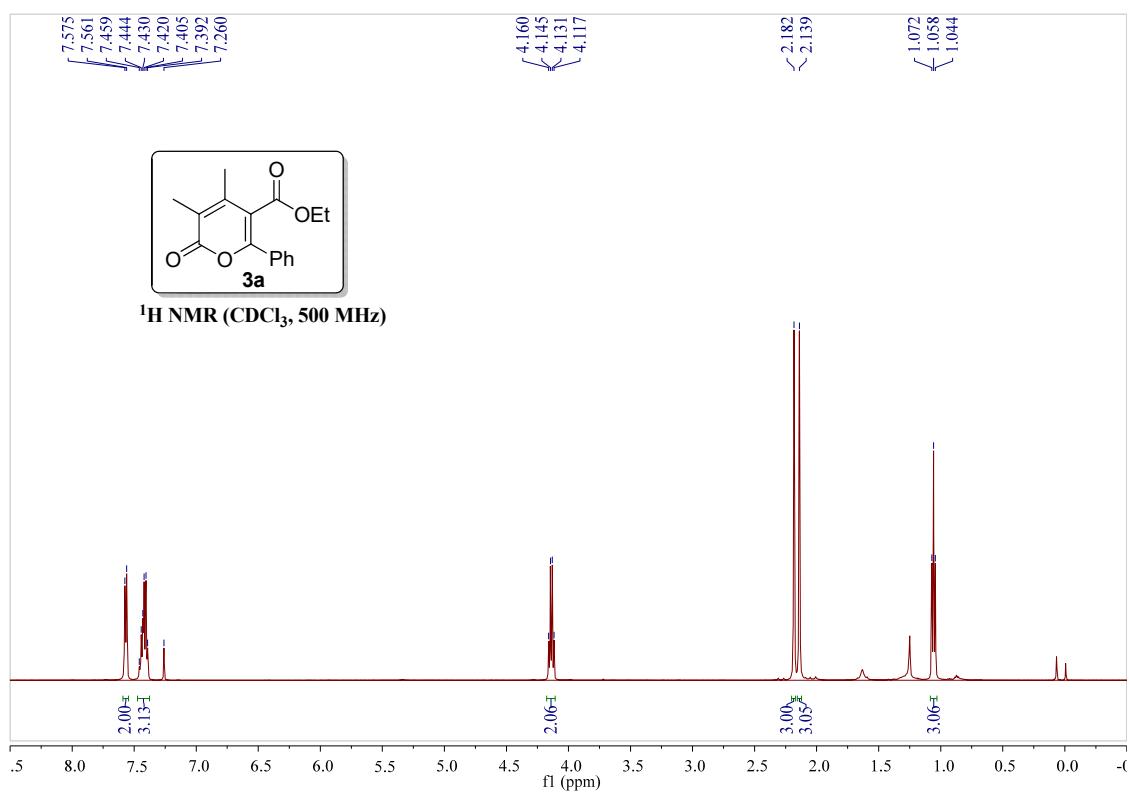


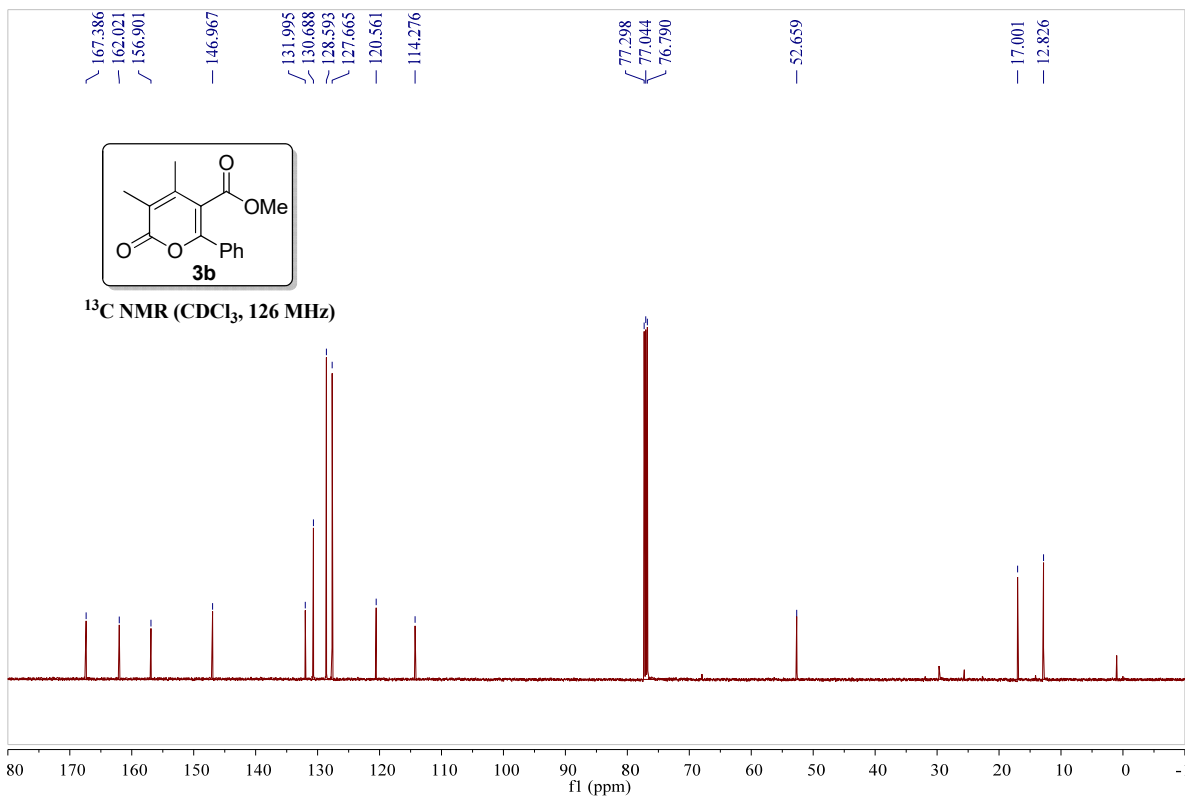
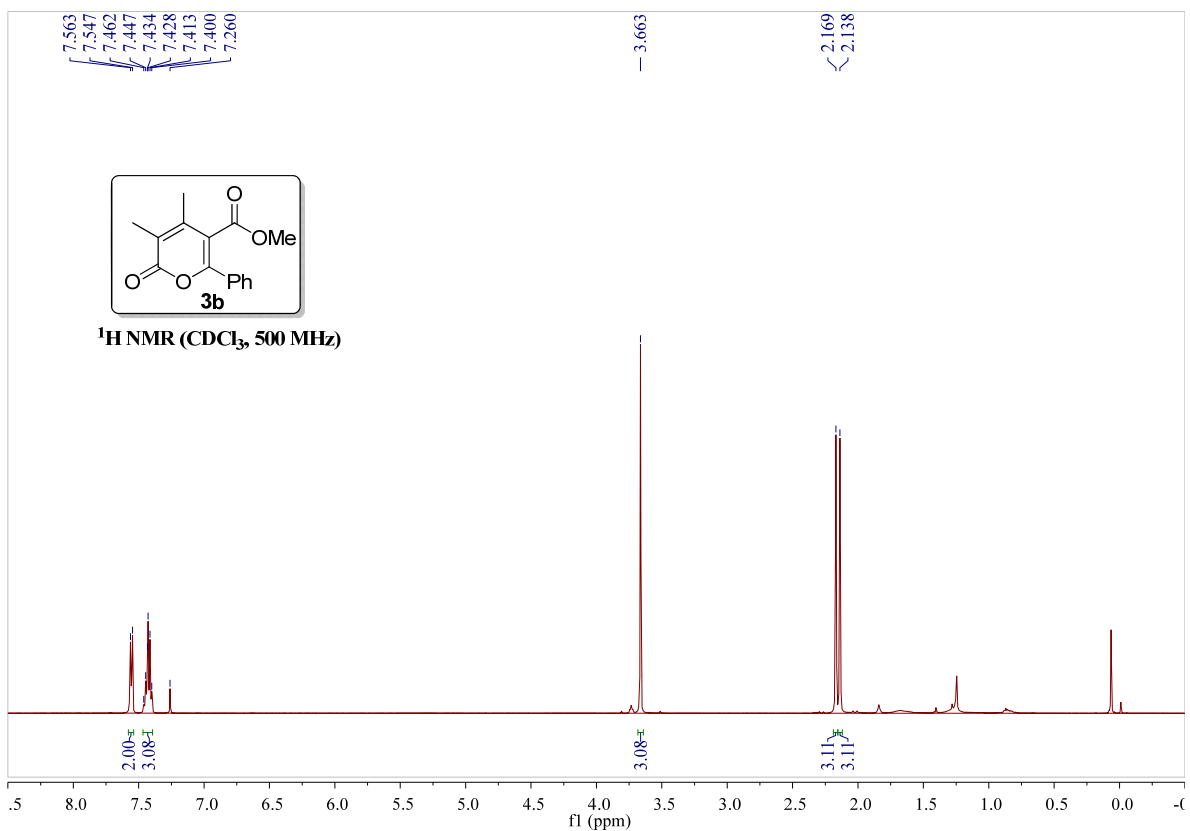
**3,4-dimethyl-5-(3-(trifluoromethyl)benzoyl)-6-(3-**

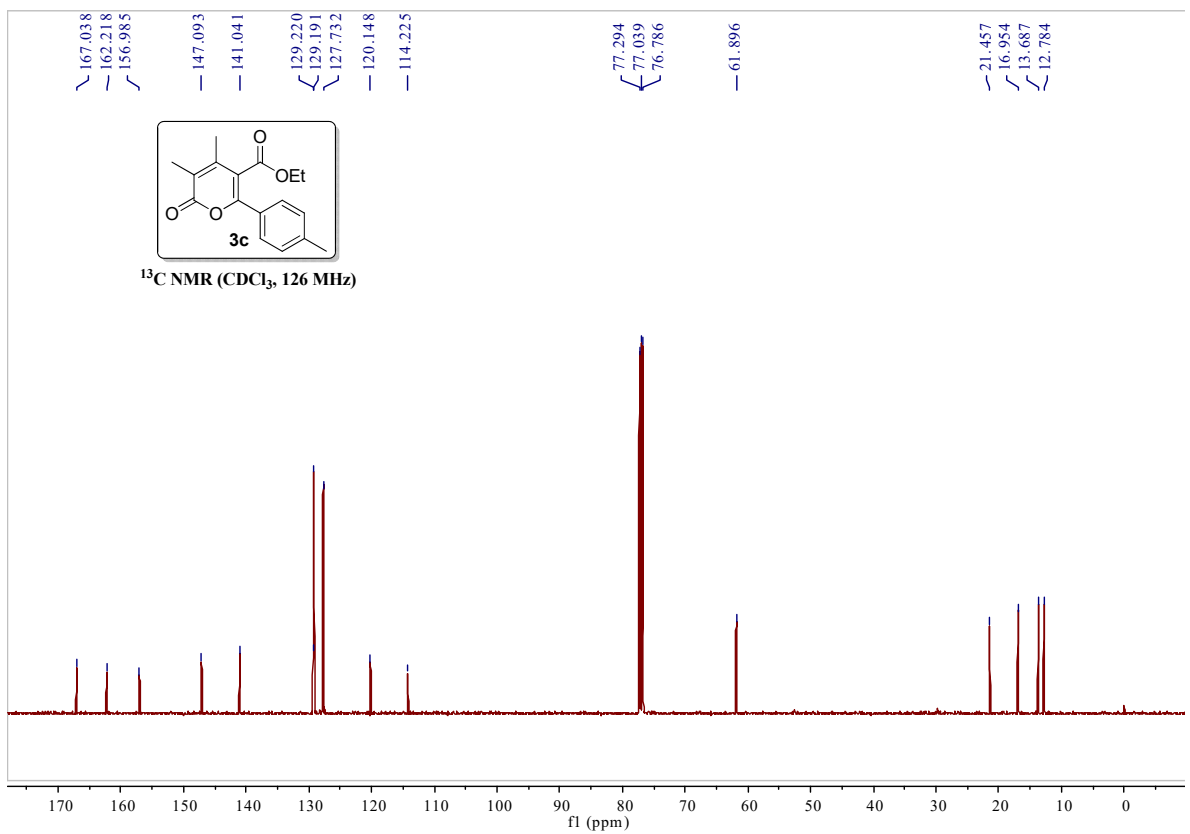
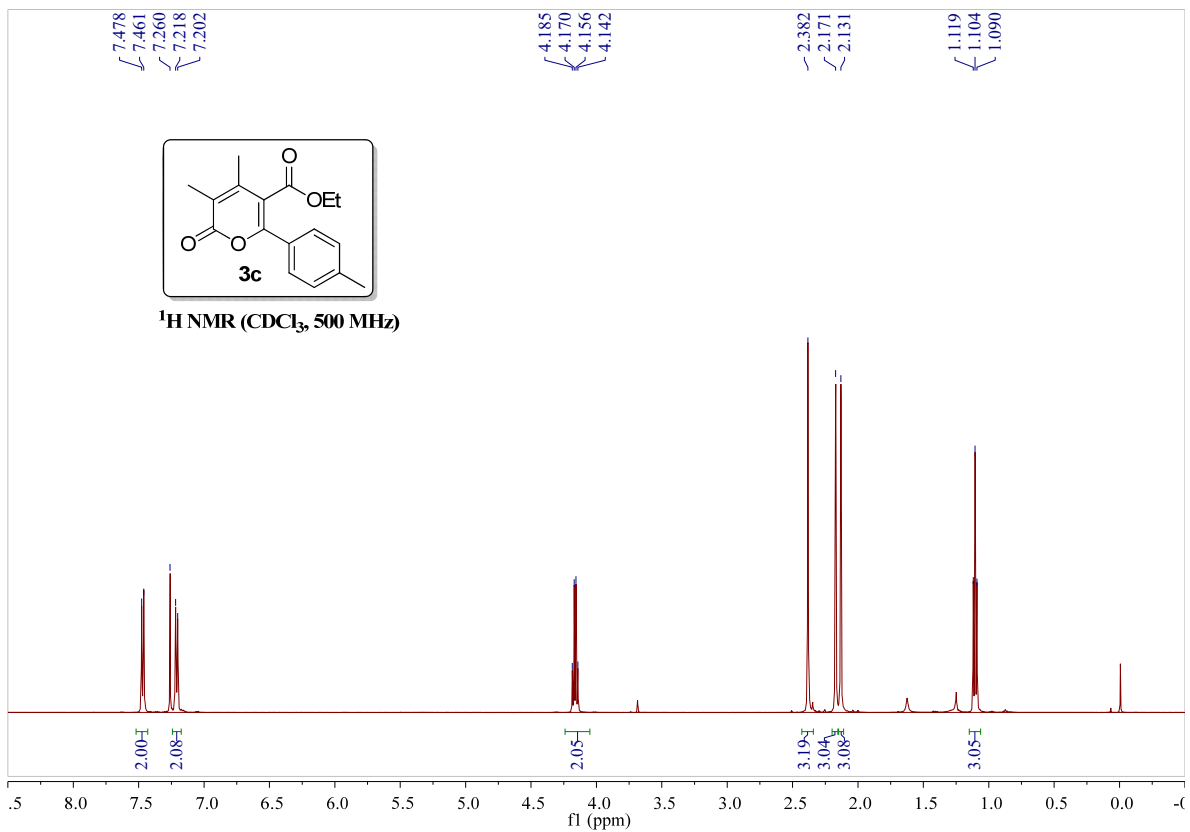
**(trifluoromethyl)phenyl)-2H-pyran-2-one (4m):** Yellow solid, 34.4 mg, 78% yield,  $R_f$  = 0.26 (PE:EA = 5:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (s, 1H), 7.91 (d,  $J$  = 8.0 Hz, 1H), 7.73–7.70 (m, 2H), 7.63 (d,  $J$  = 8.0 Hz, 1H), 7.52–7.46 (m, 2H), 7.39 (t,  $J$  = 8.0 Hz, 1H), 2.23 (s, 3H), 2.10 (s, 3H) ppm;  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  193.4, 161.6, 154.5, 147.3, 137.1, 132.3, 132.2, 131.9 (q,  $J$  = 33.2 Hz), 131.5, 131.2 (q,  $J$  = 33.0 Hz), 130.5

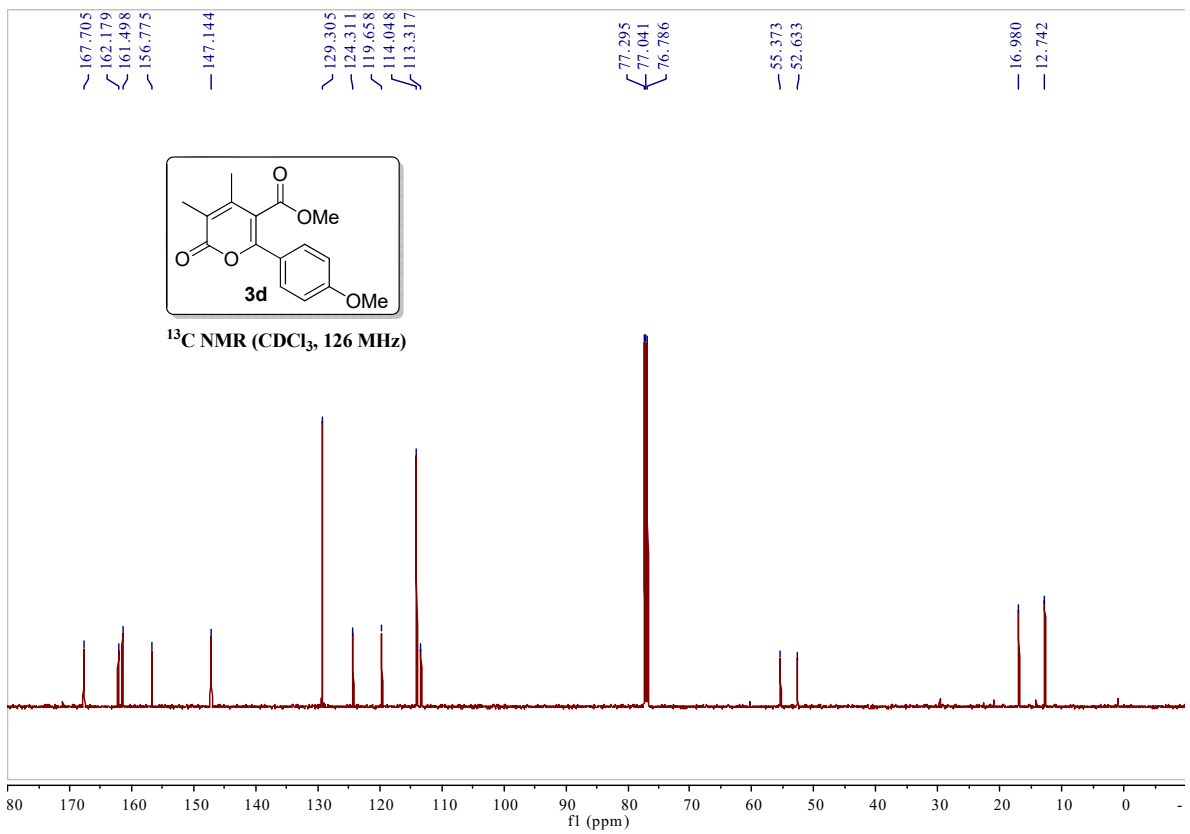
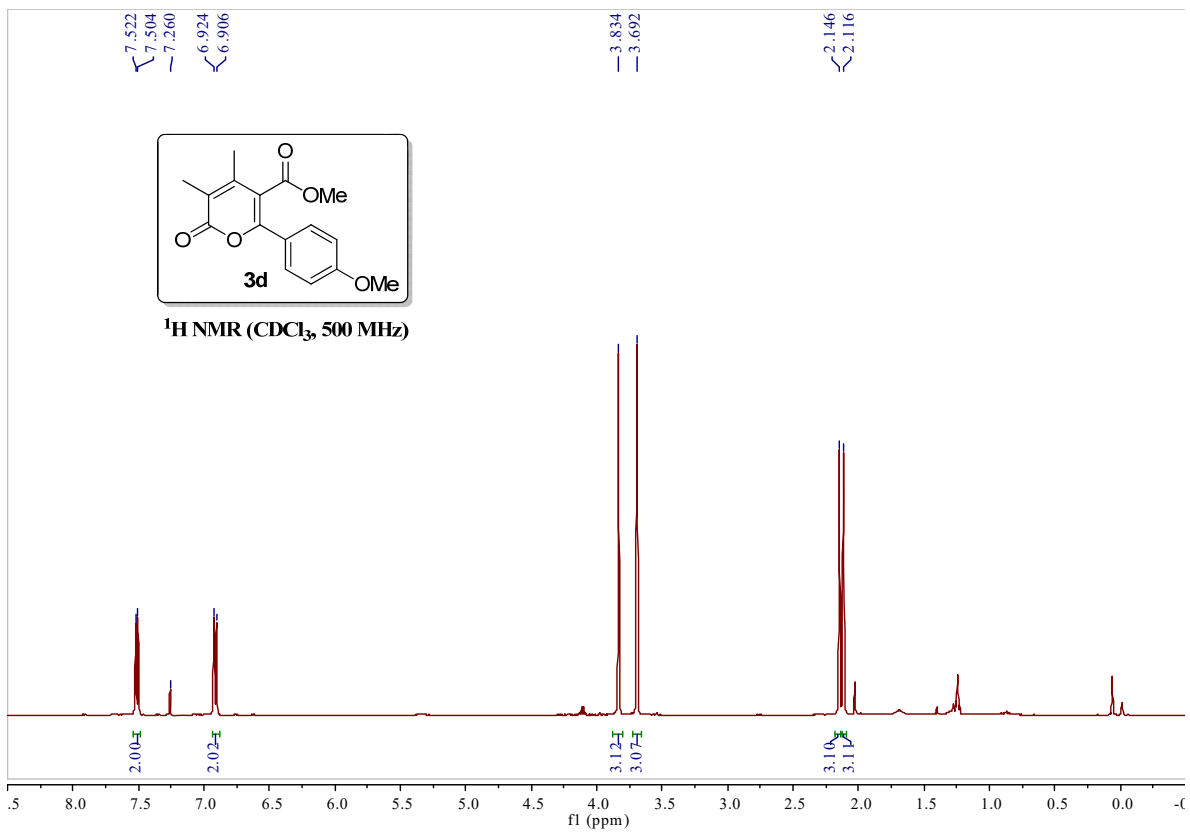
(q,  $J$  = 3.5 Hz), 129.6, 129.3, 127.3 (q,  $J$  = 3.6 Hz), 126.5, 126.0 (q,  $J$  = 3.7 Hz), 125.4 (q,  $J$  = 3.8 Hz), 123.2 (qd,  $J$  = 272.6, 2.9 Hz), 122.4, 118.8, 17.2, 13.0;  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -63.1 (s, 3F), -63.2 (s, 3F) ppm; IR (KBr):  $\nu$  = 3067, 2926, 2847, 1736, 1662, 1627, 1592, 1556, 1482, 1439, 1351, 1326, 1240, 1187, 1154, 1072, 923, 817, 770, 750, 700, 672  $\text{cm}^{-1}$ ; HRMS (ESI;  $m/z$ ):  $[\text{M}-\text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{13}\text{F}_6\text{O}_3^+$ , 439.0847, Found: 439.0763.

# $^1\text{H}$ , $^{13}\text{C}$ , and $^{19}\text{F}$ NMR spectra copies

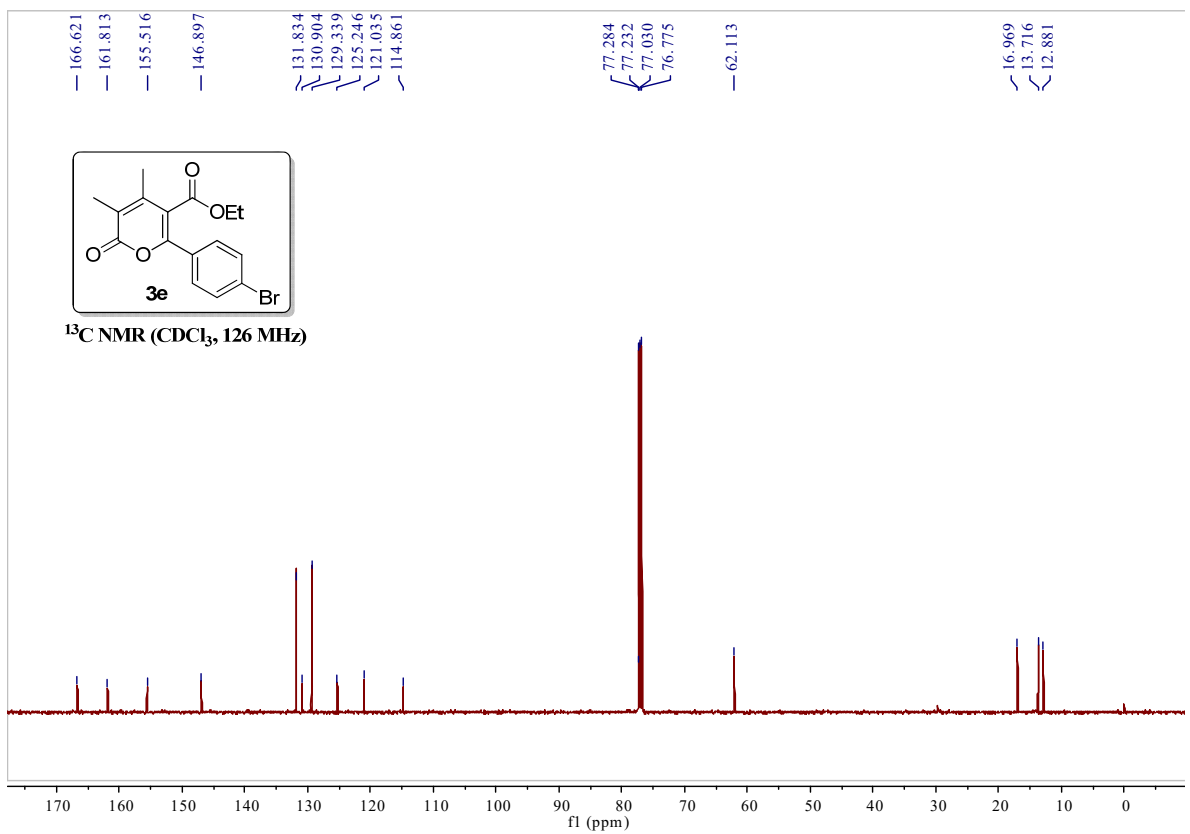
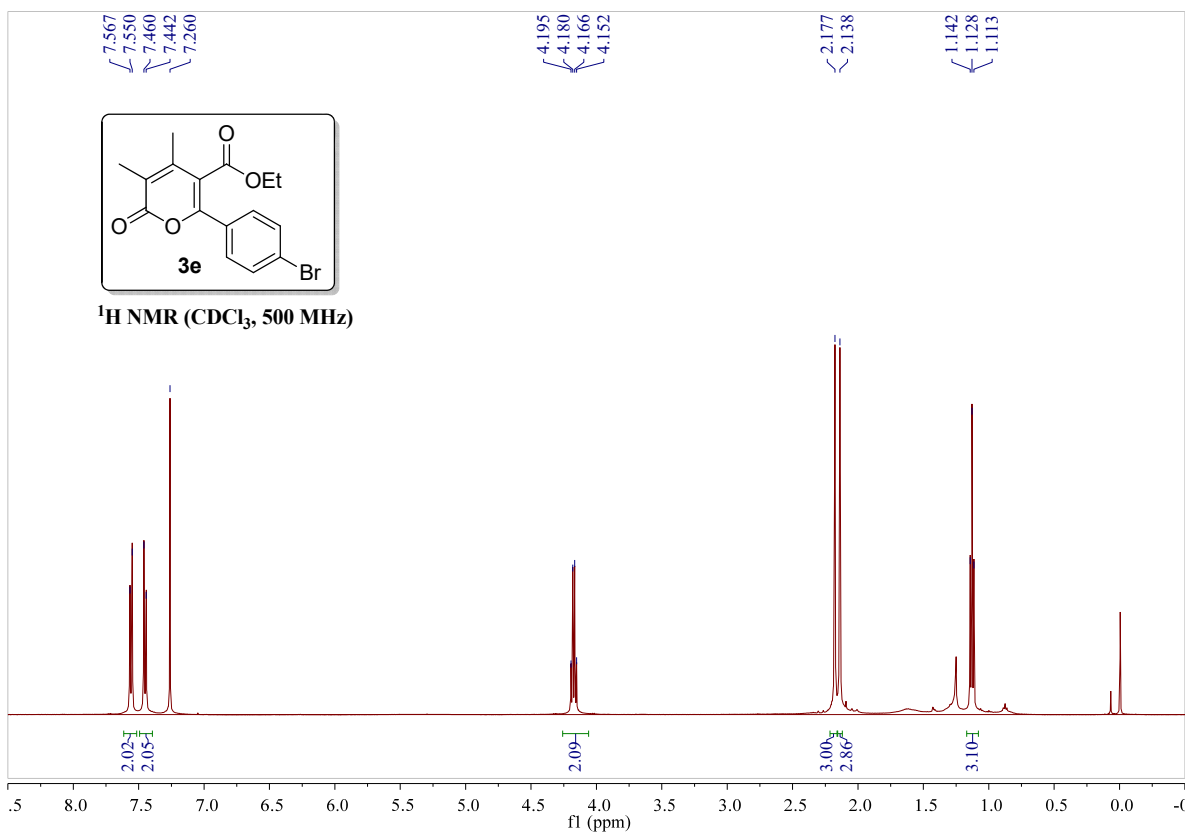


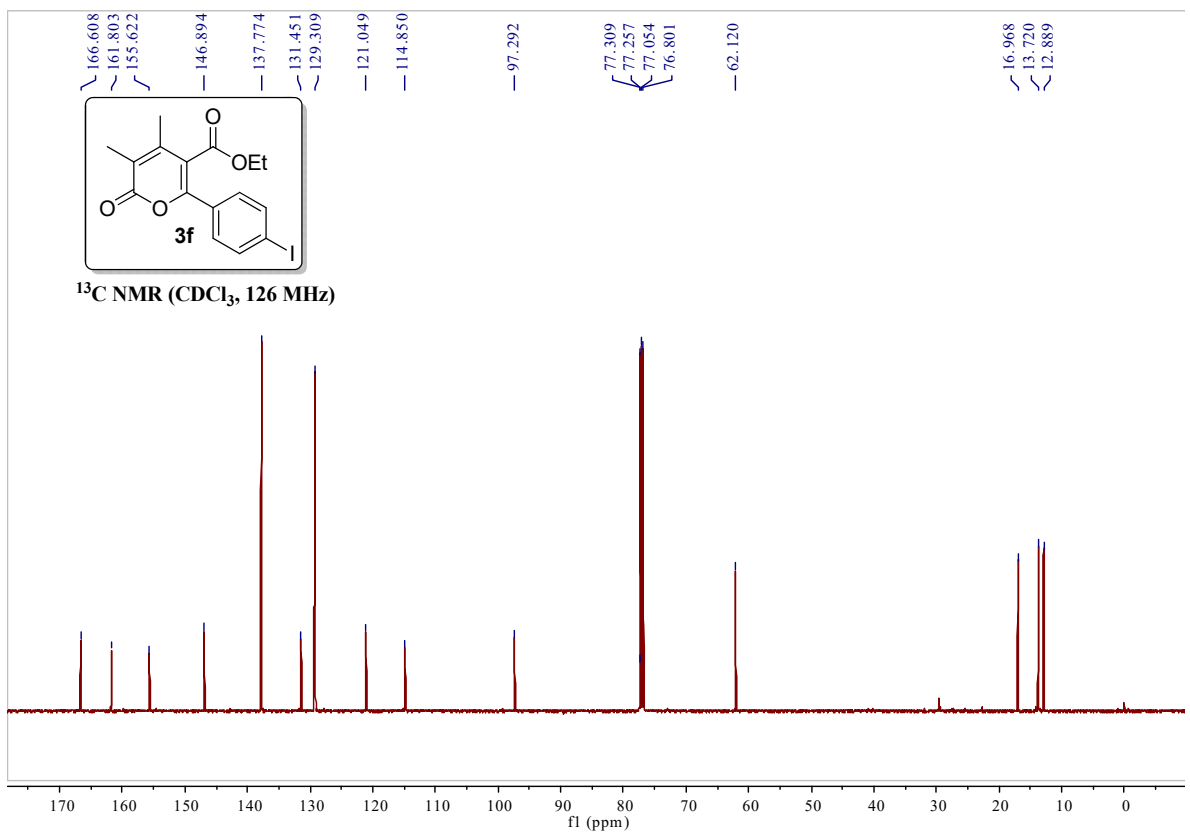
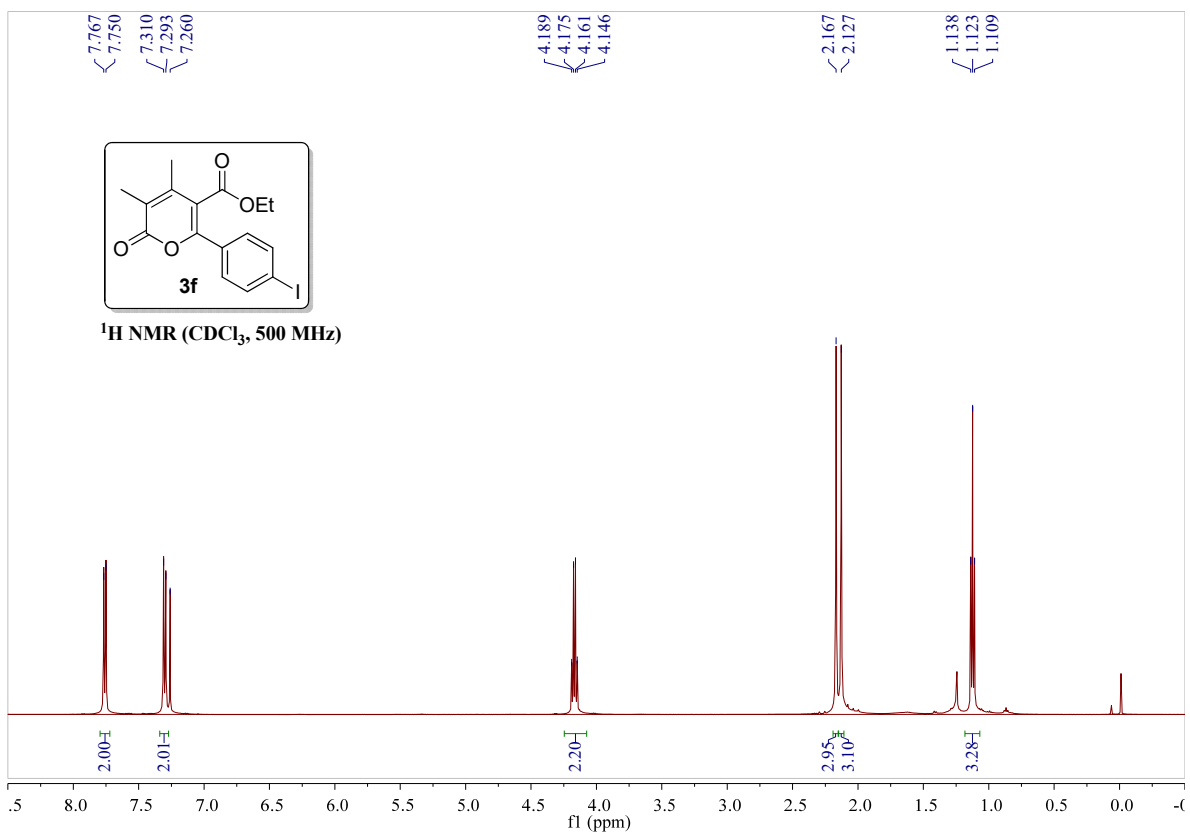


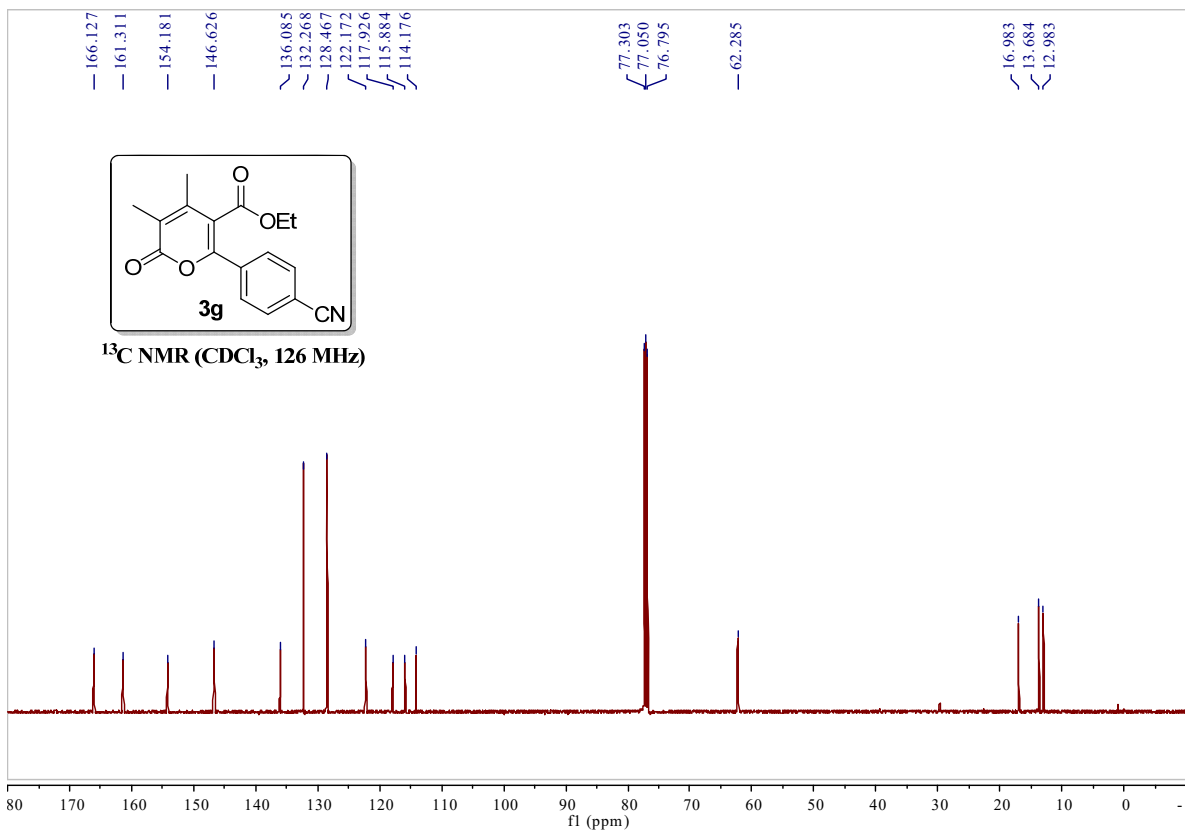
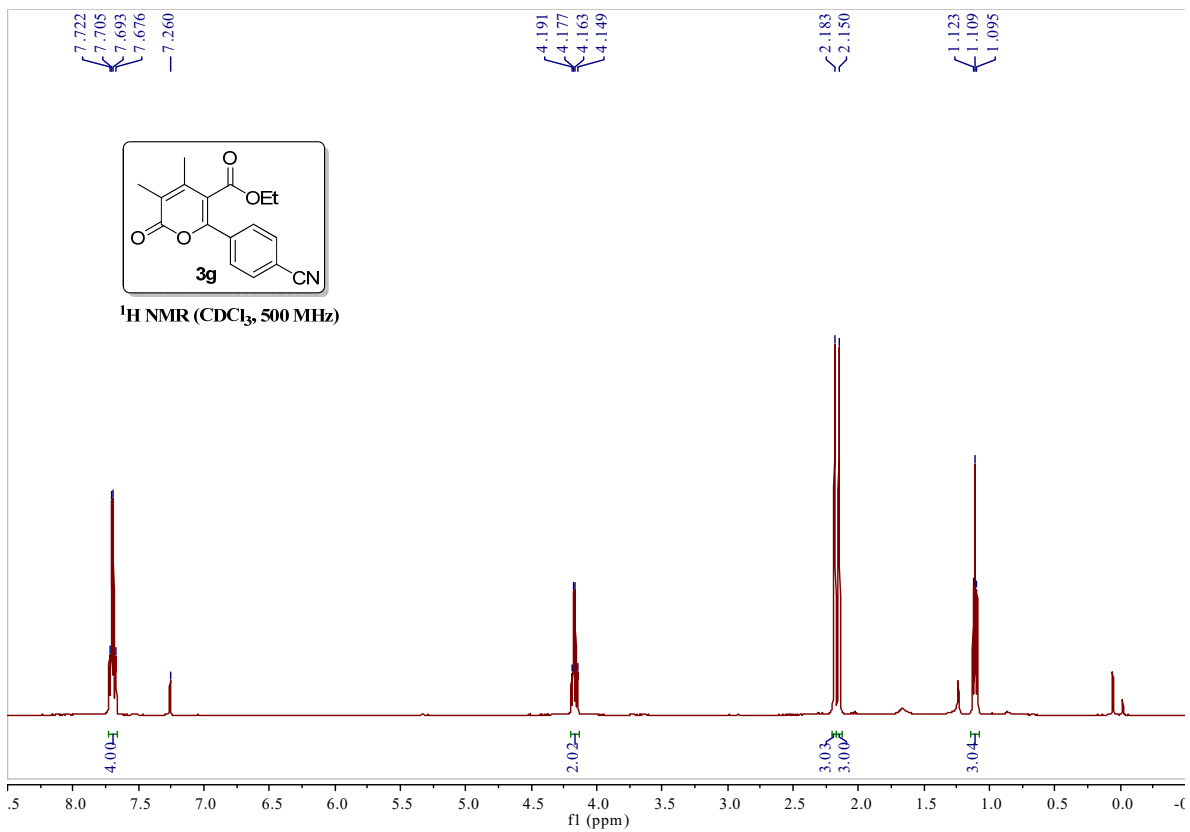


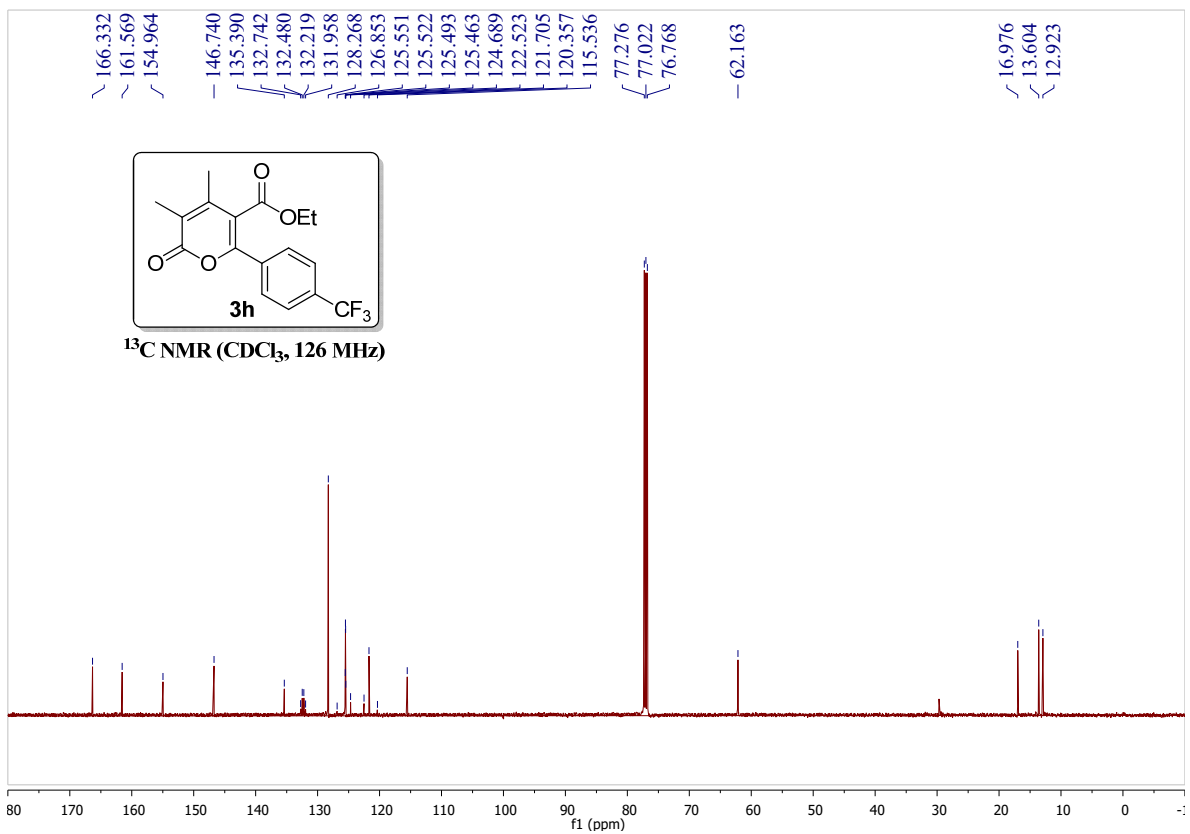
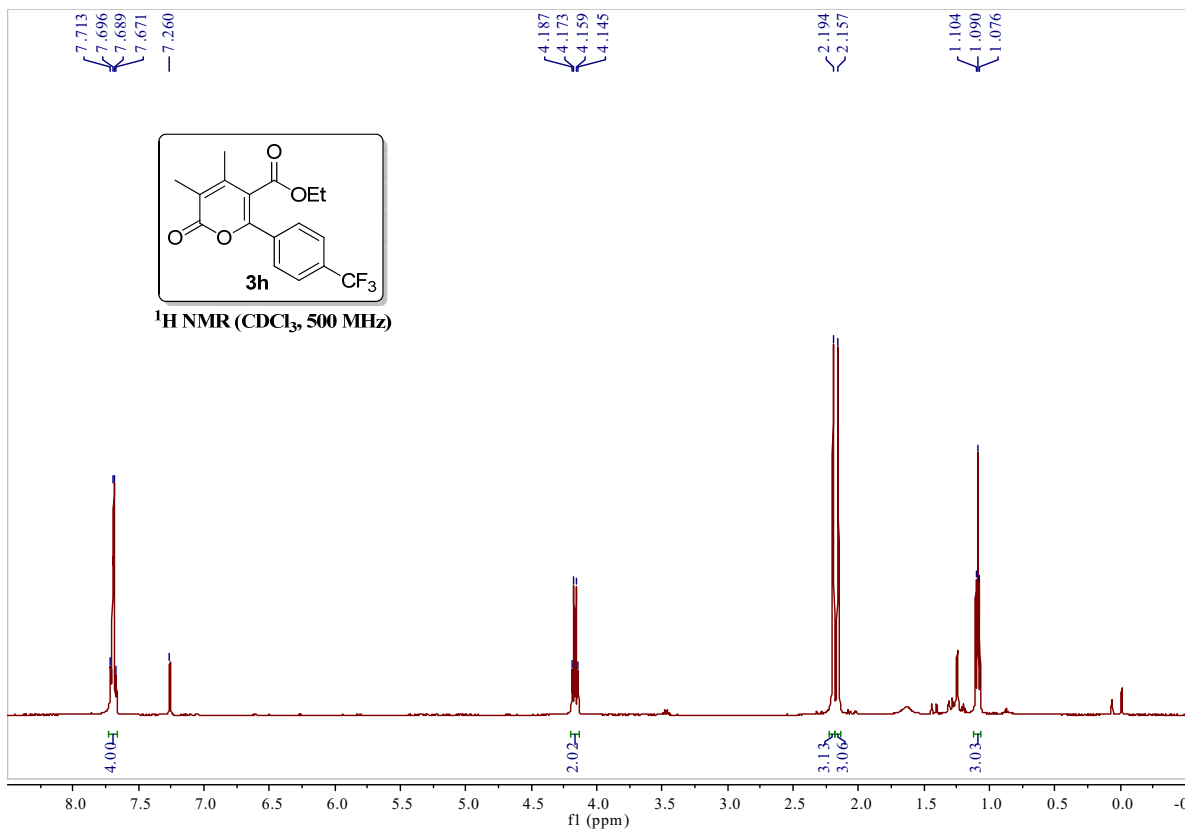


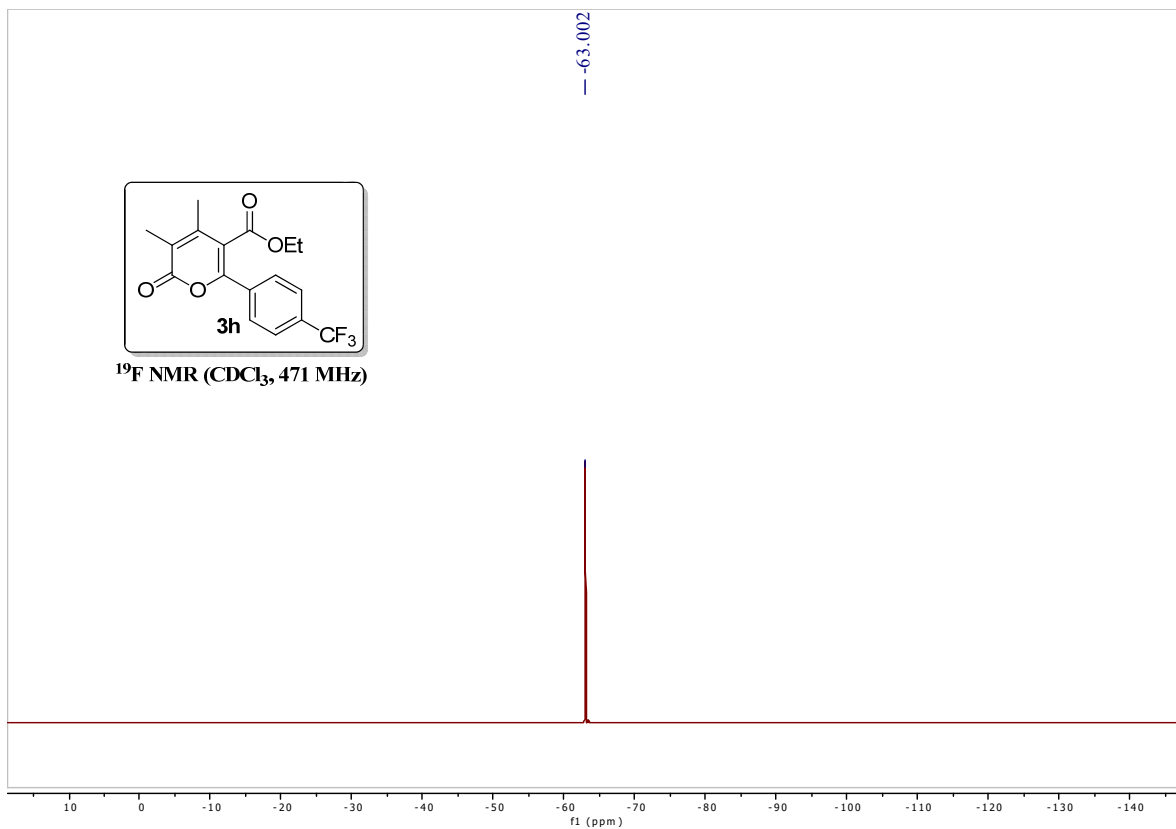










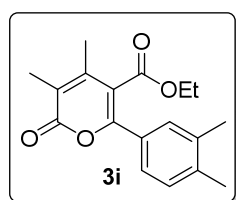


7.378  
7.301  
7.285  
7.260  
7.155  
7.140

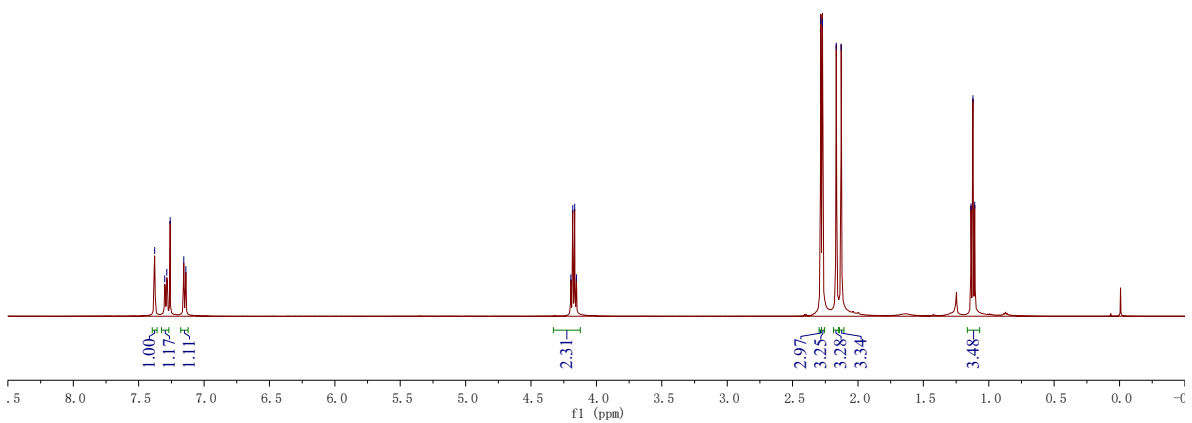
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4.181  
4.167  
4.153

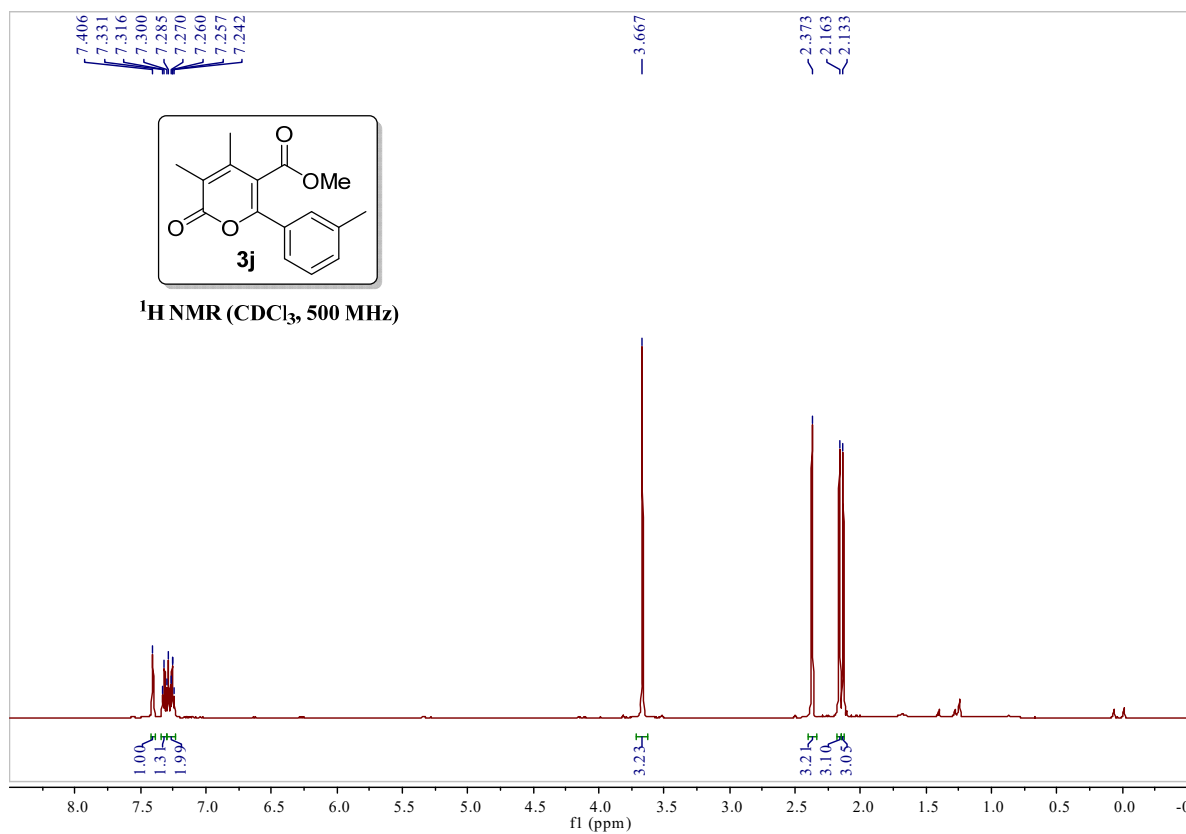
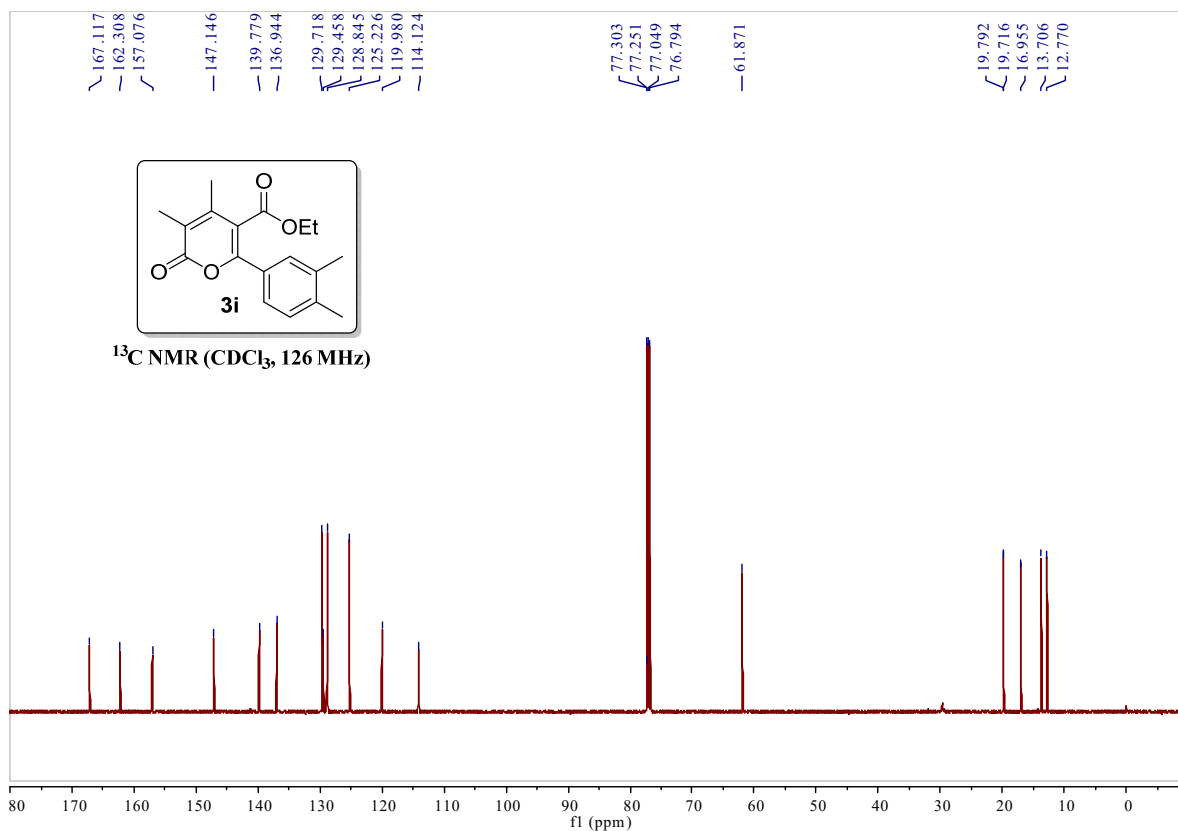
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2.271  
2.166  
2.128

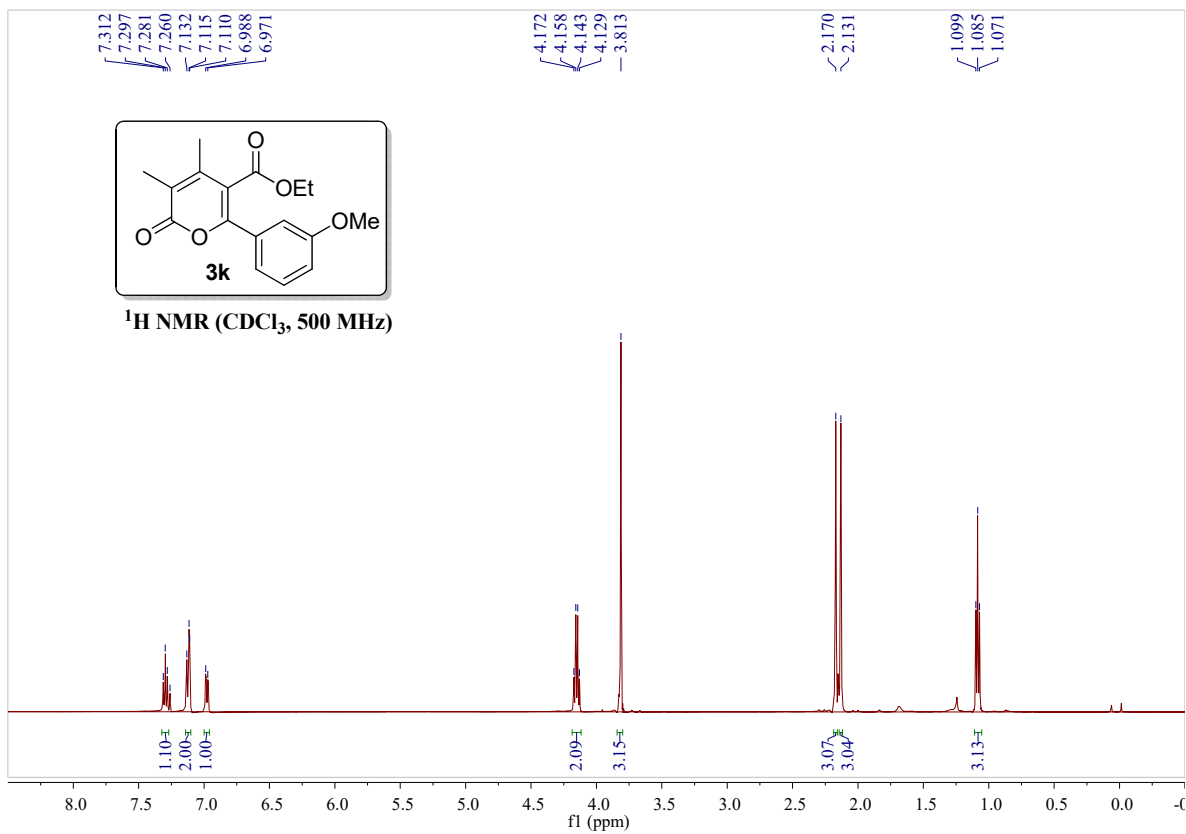
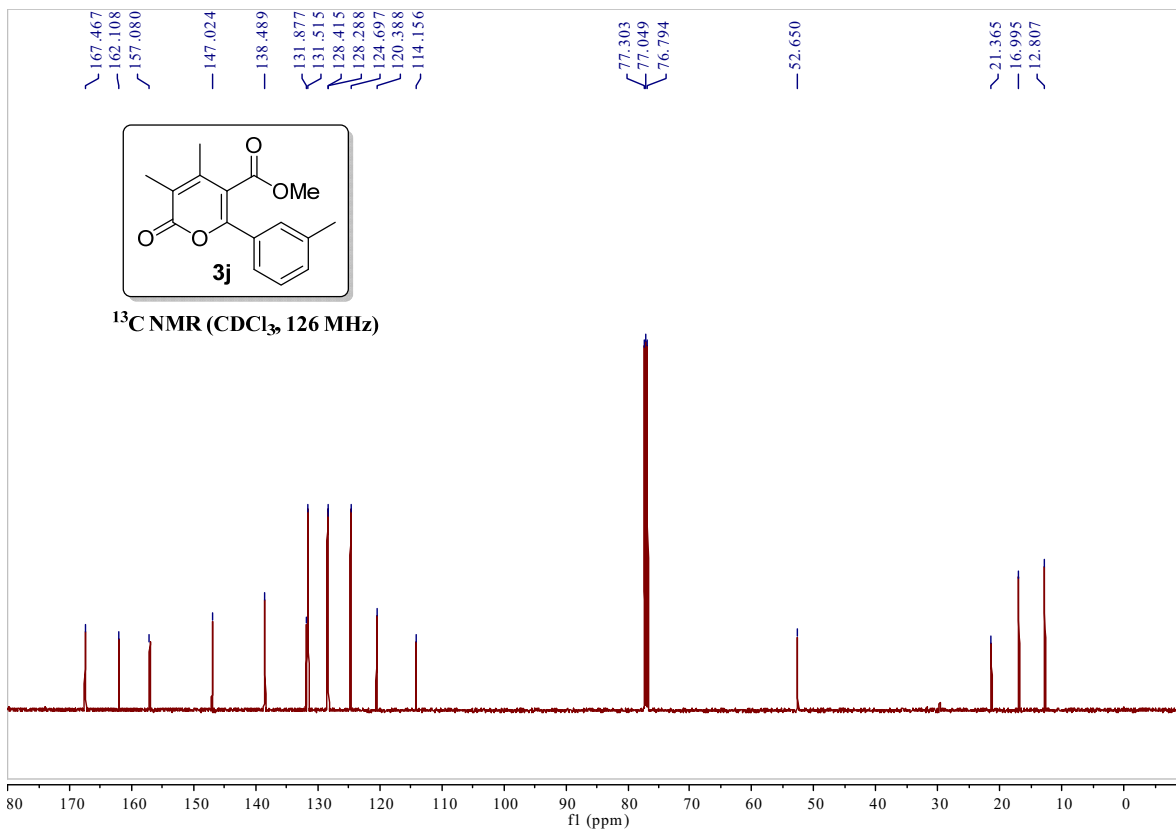
1.136  
1.121  
1.107

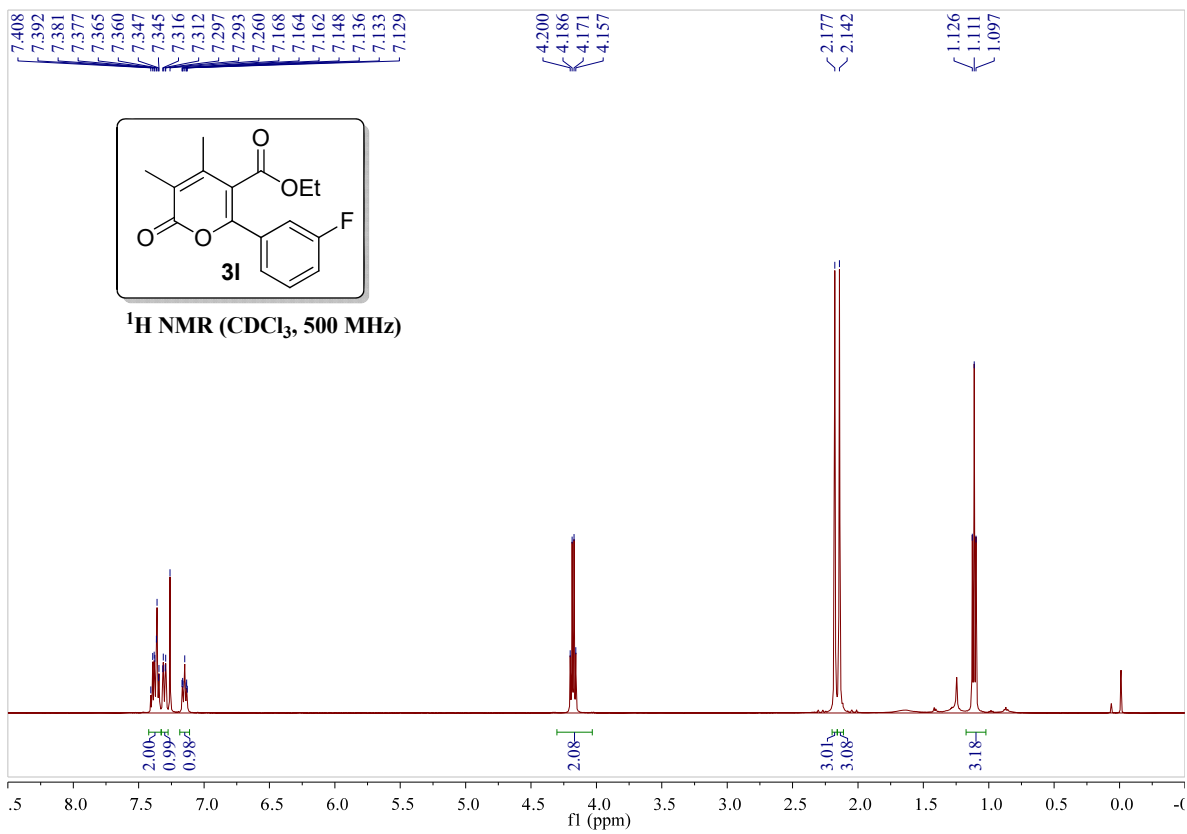
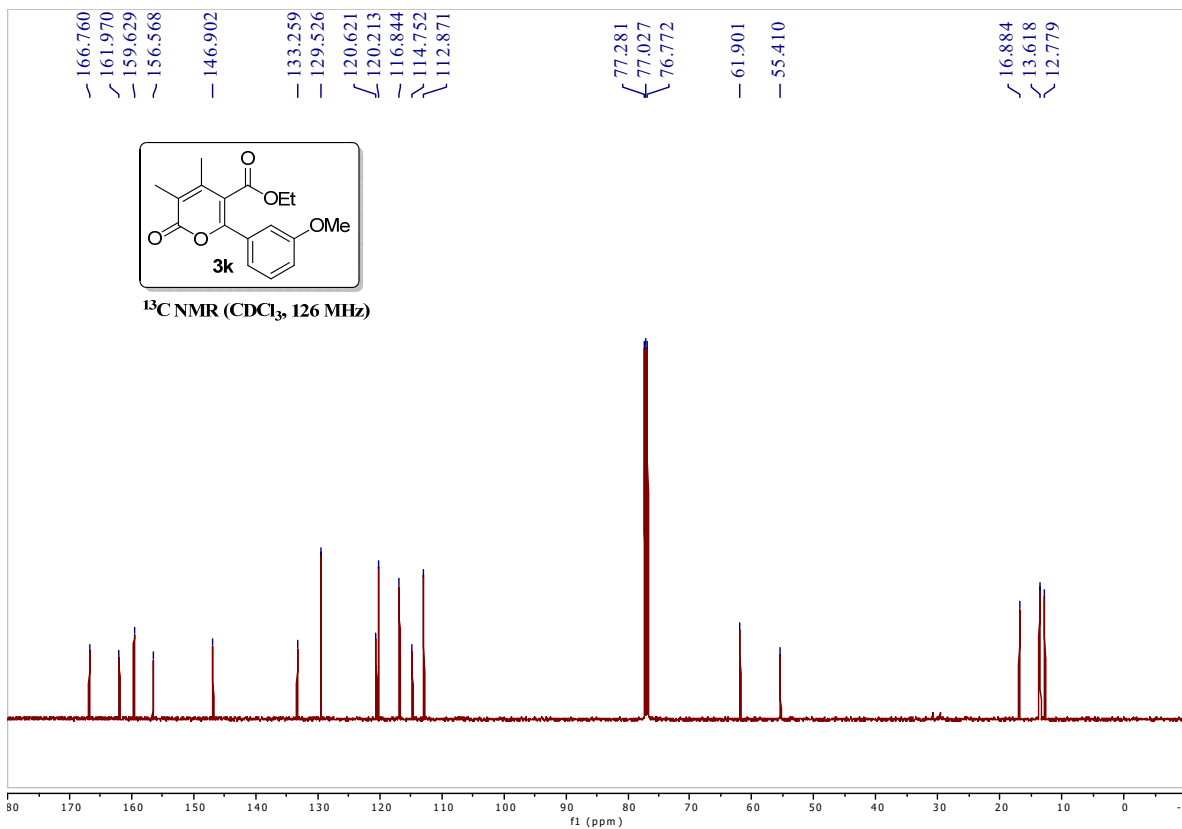


**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz)**

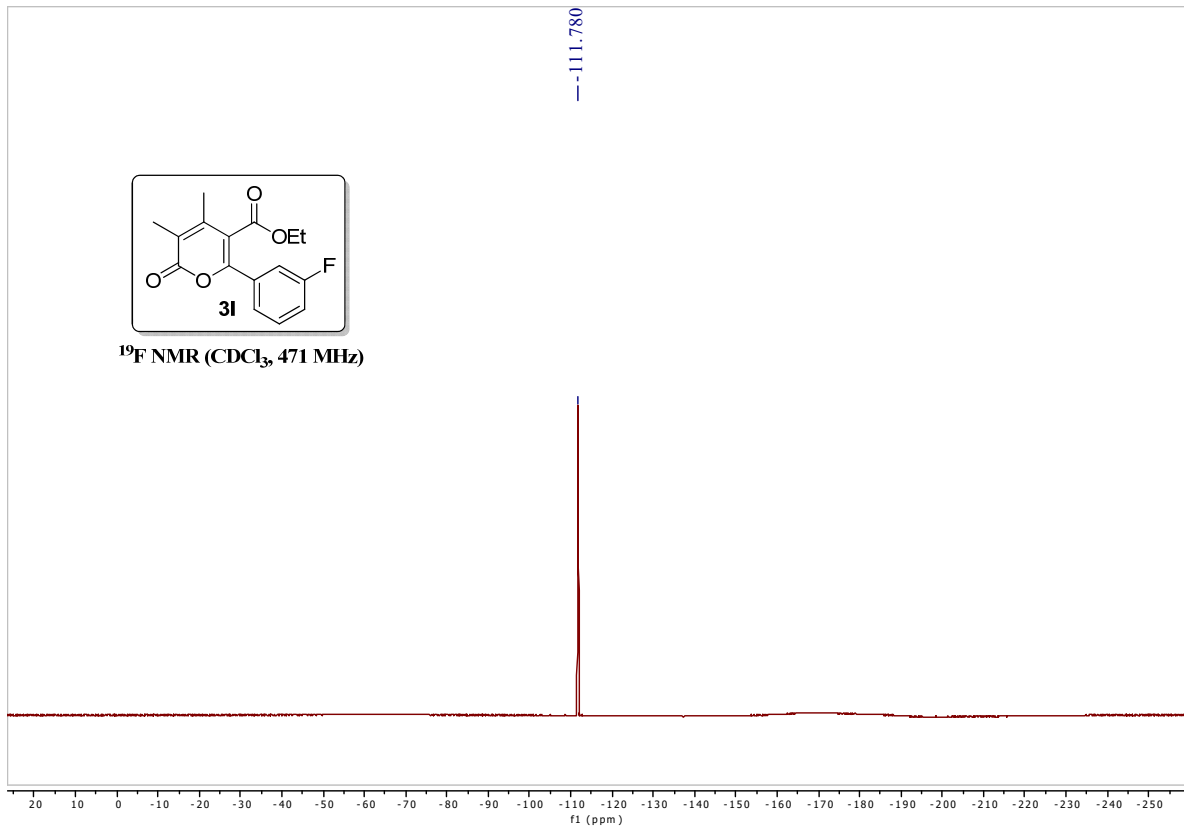
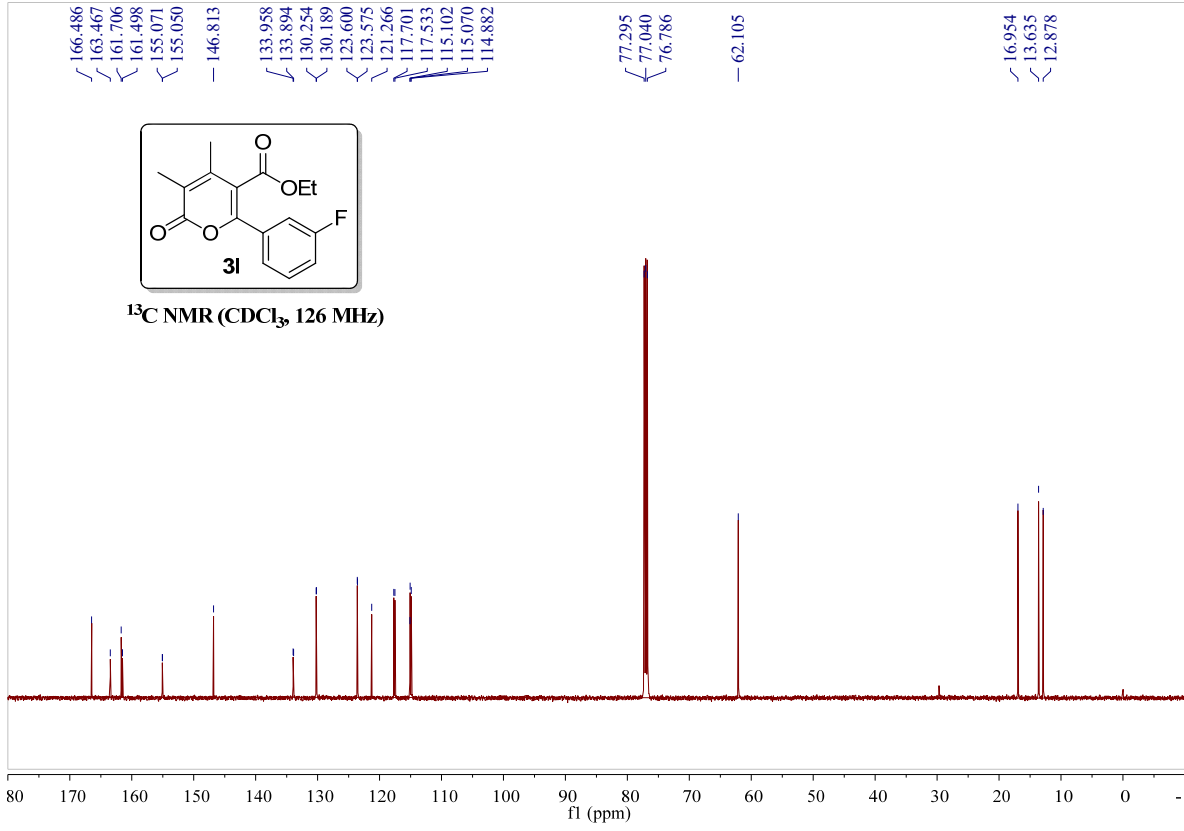


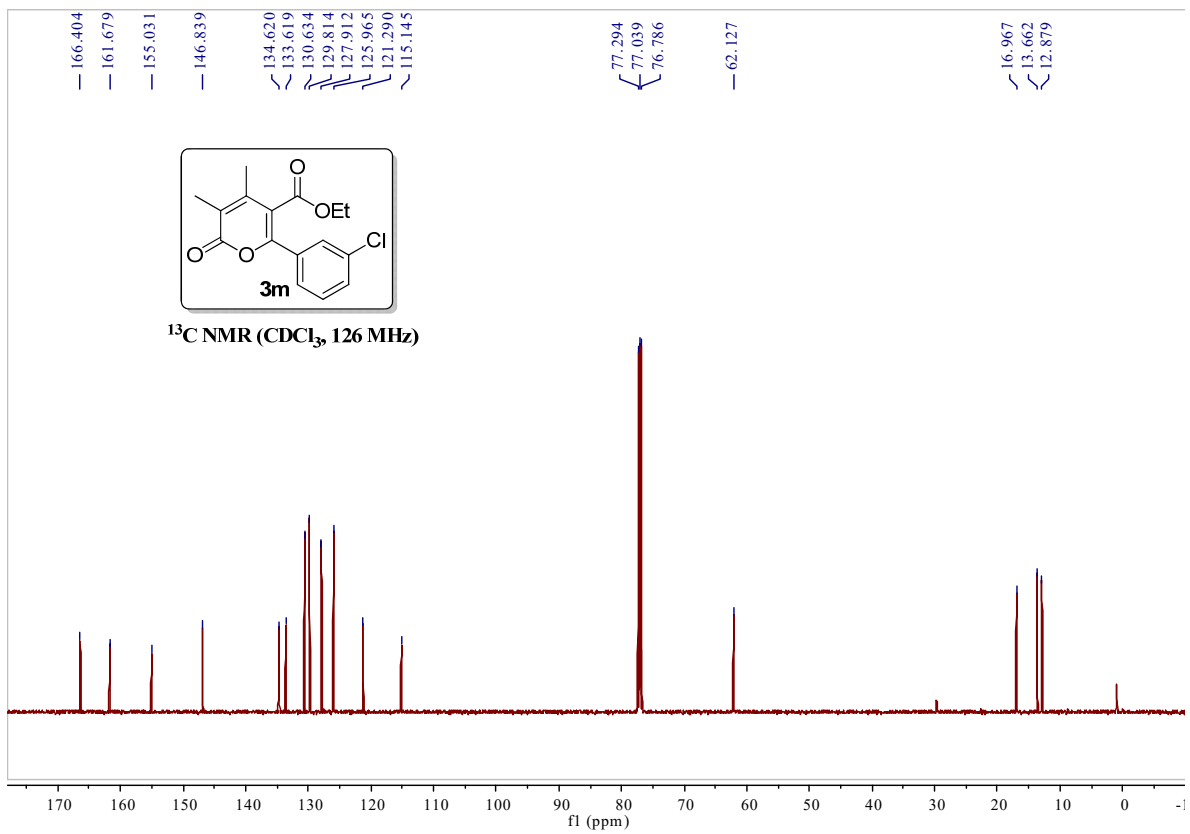
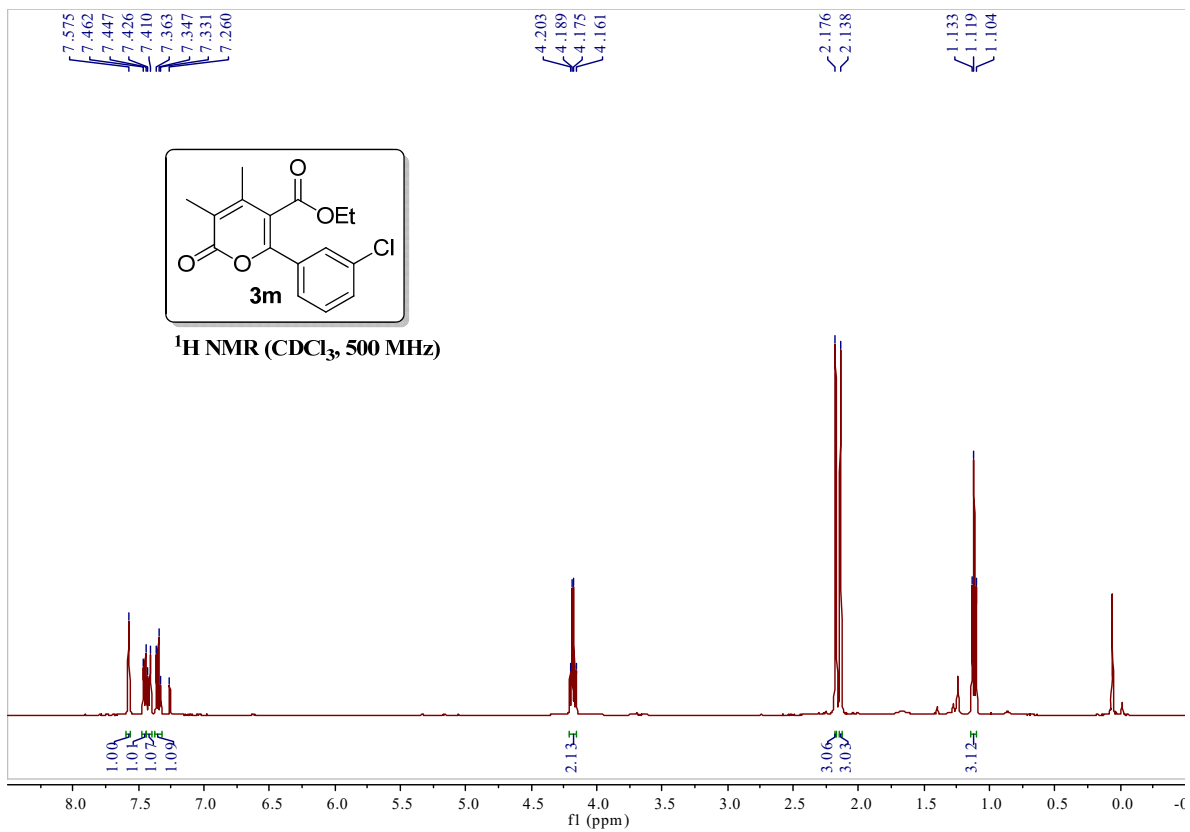


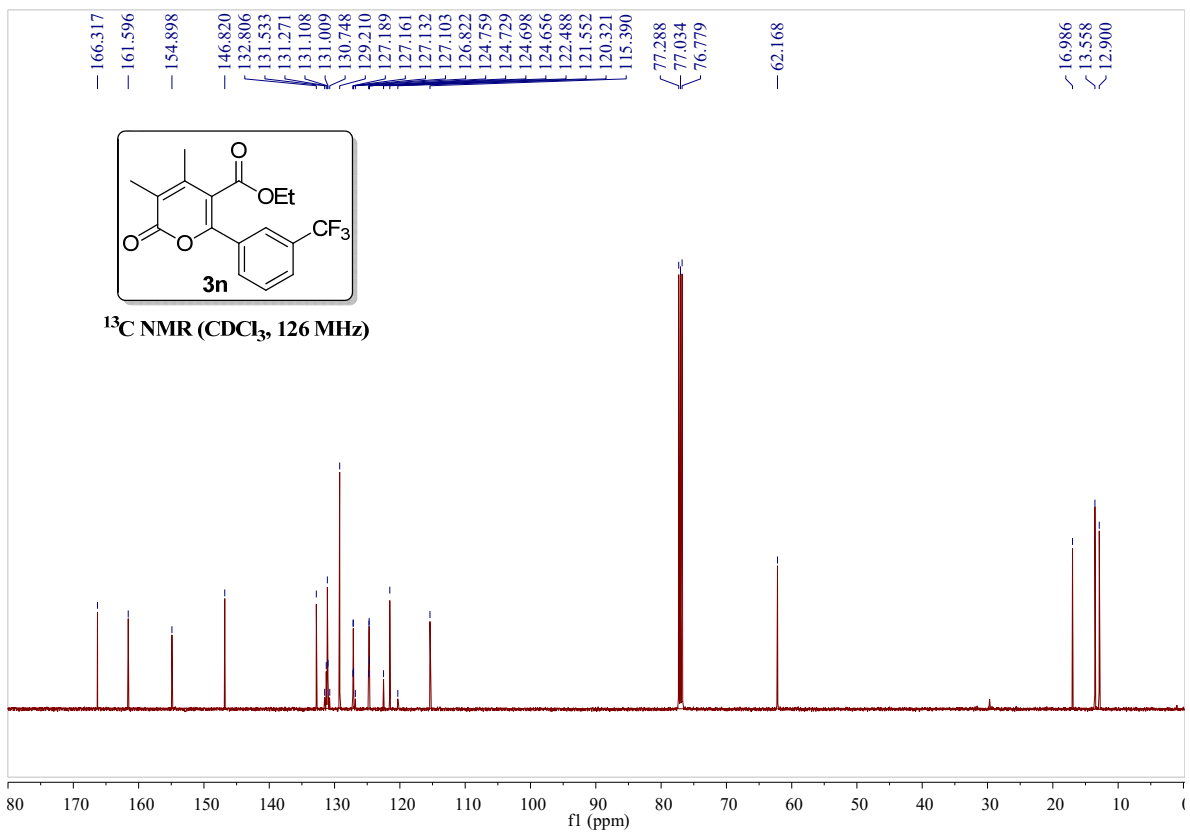
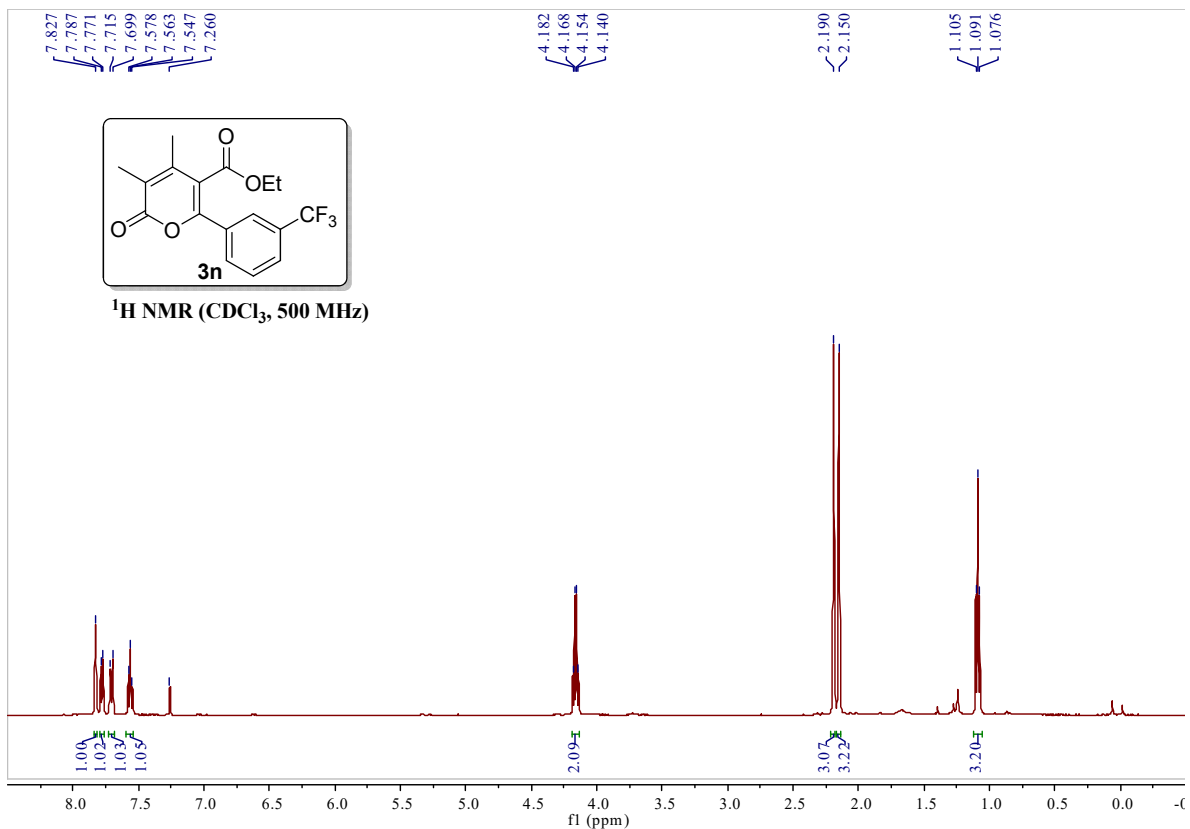


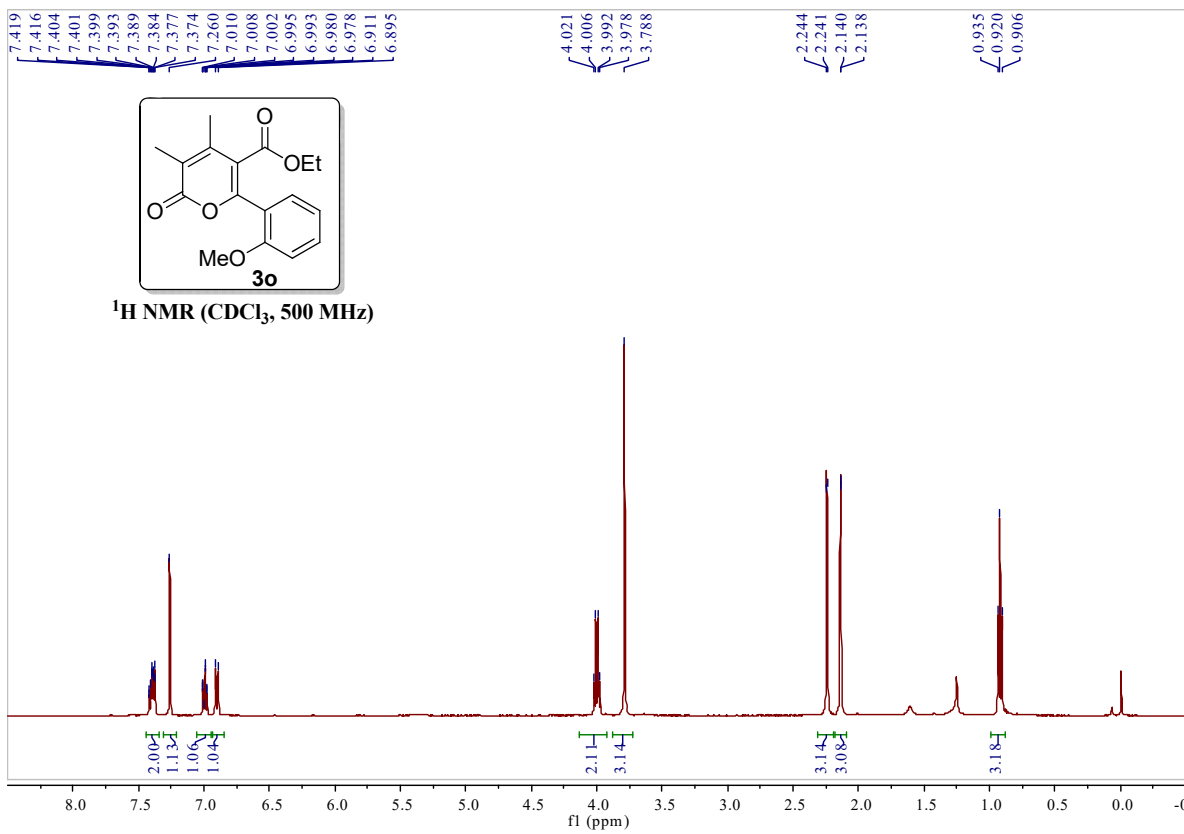
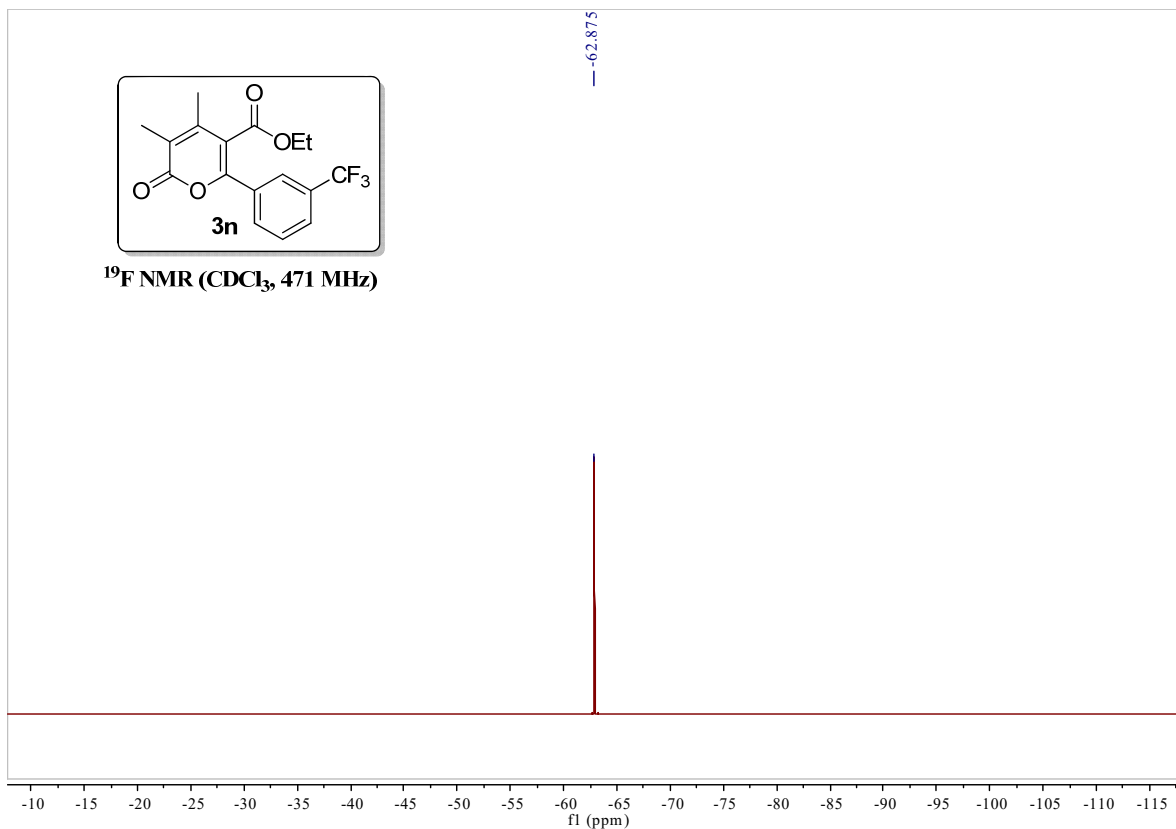


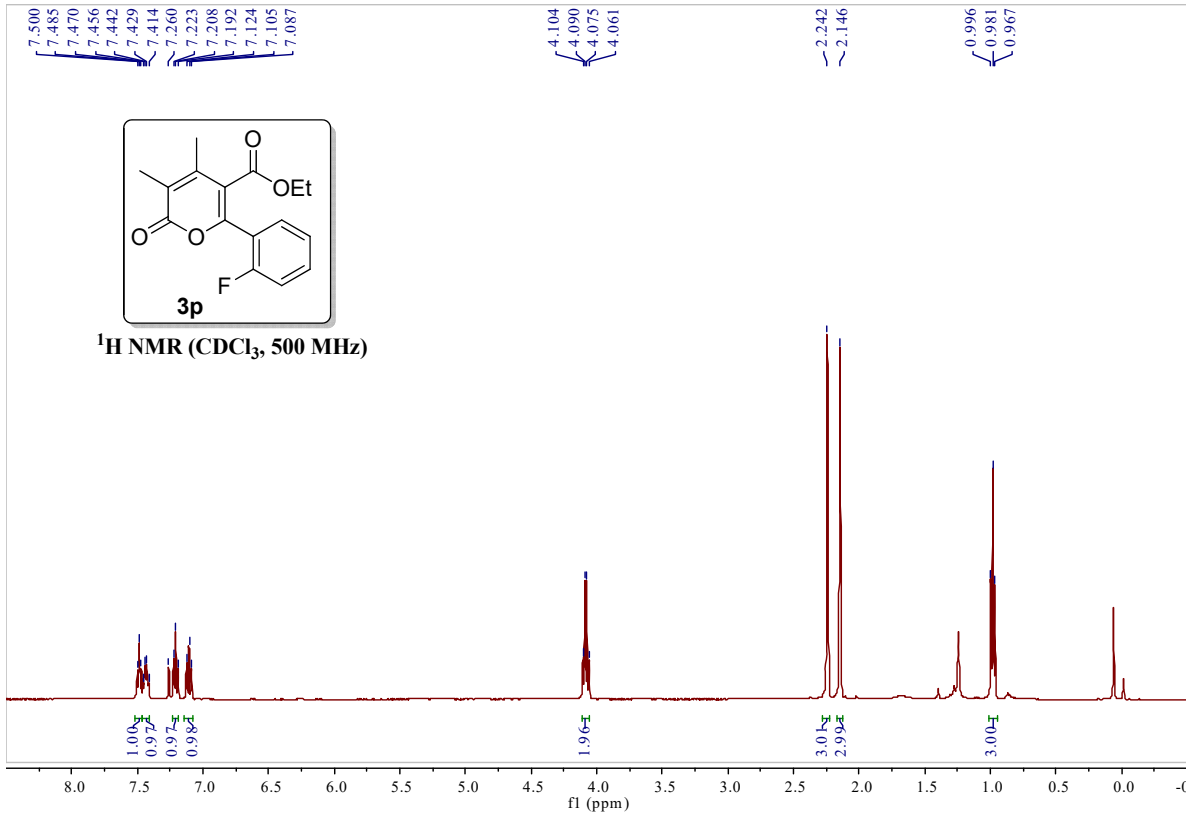
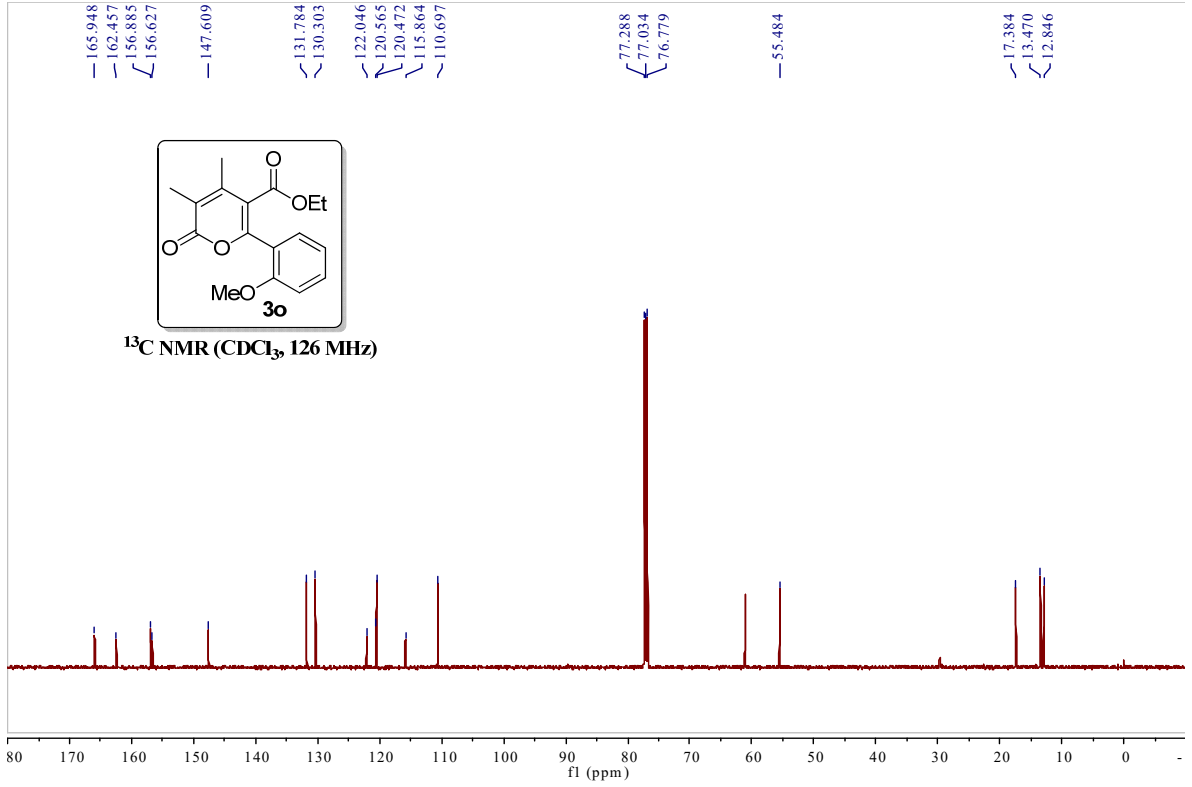


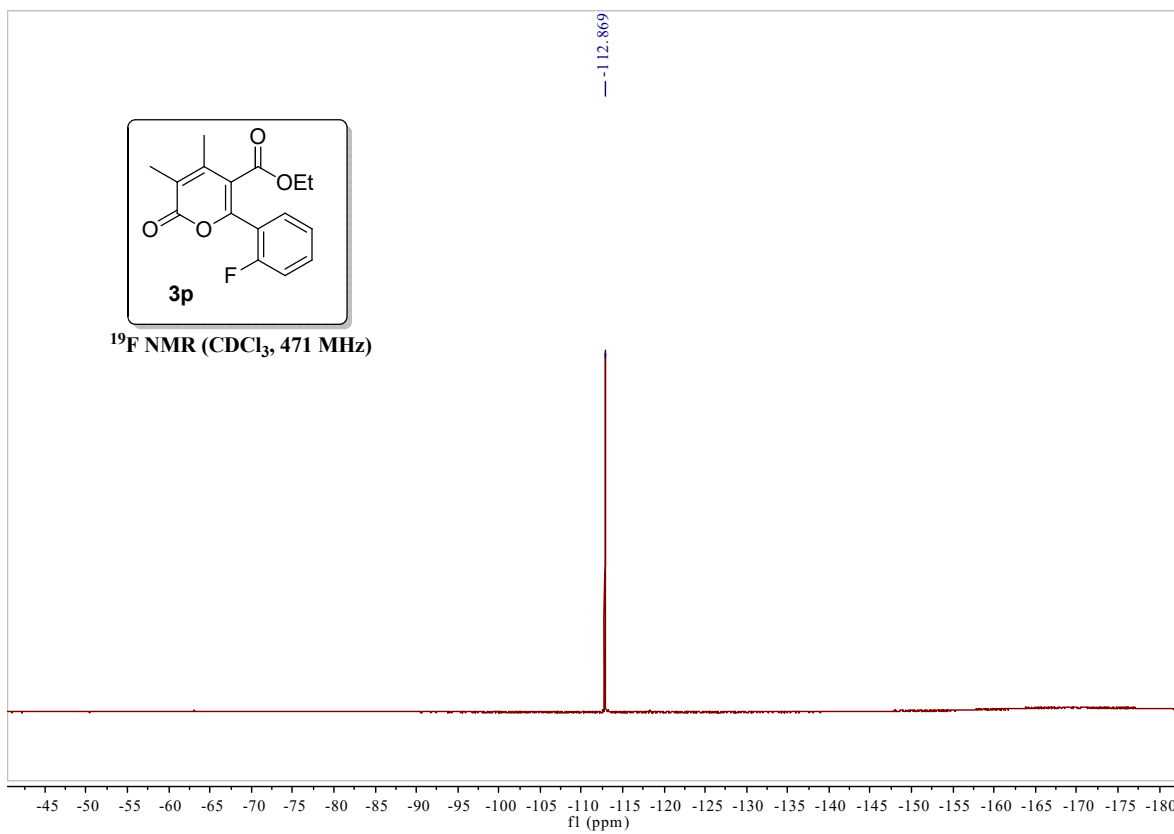
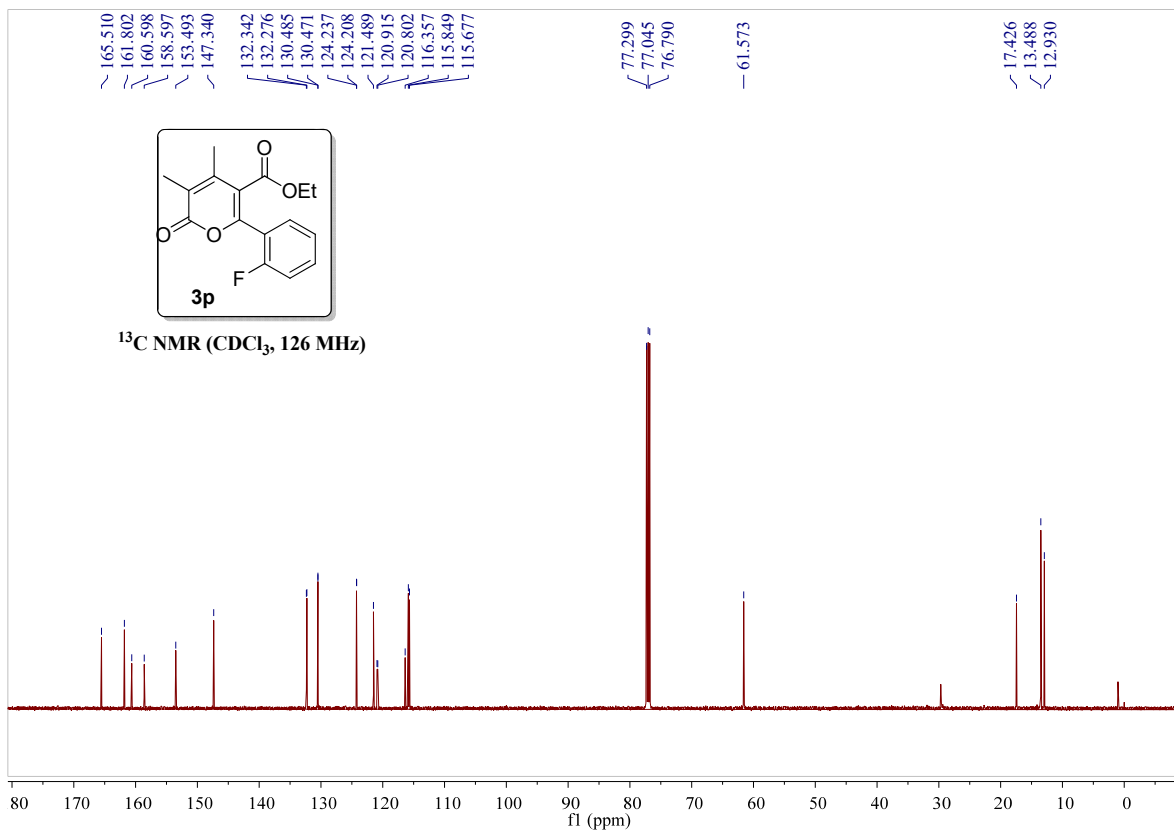


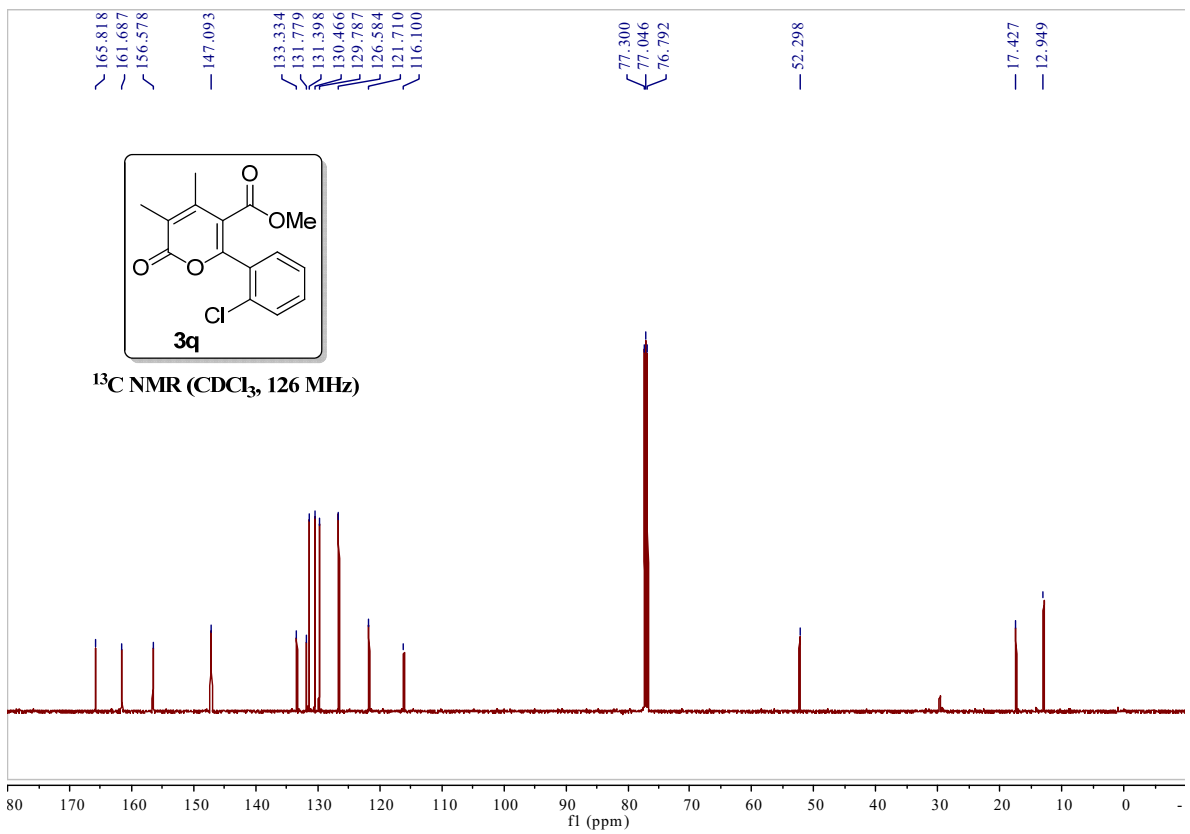
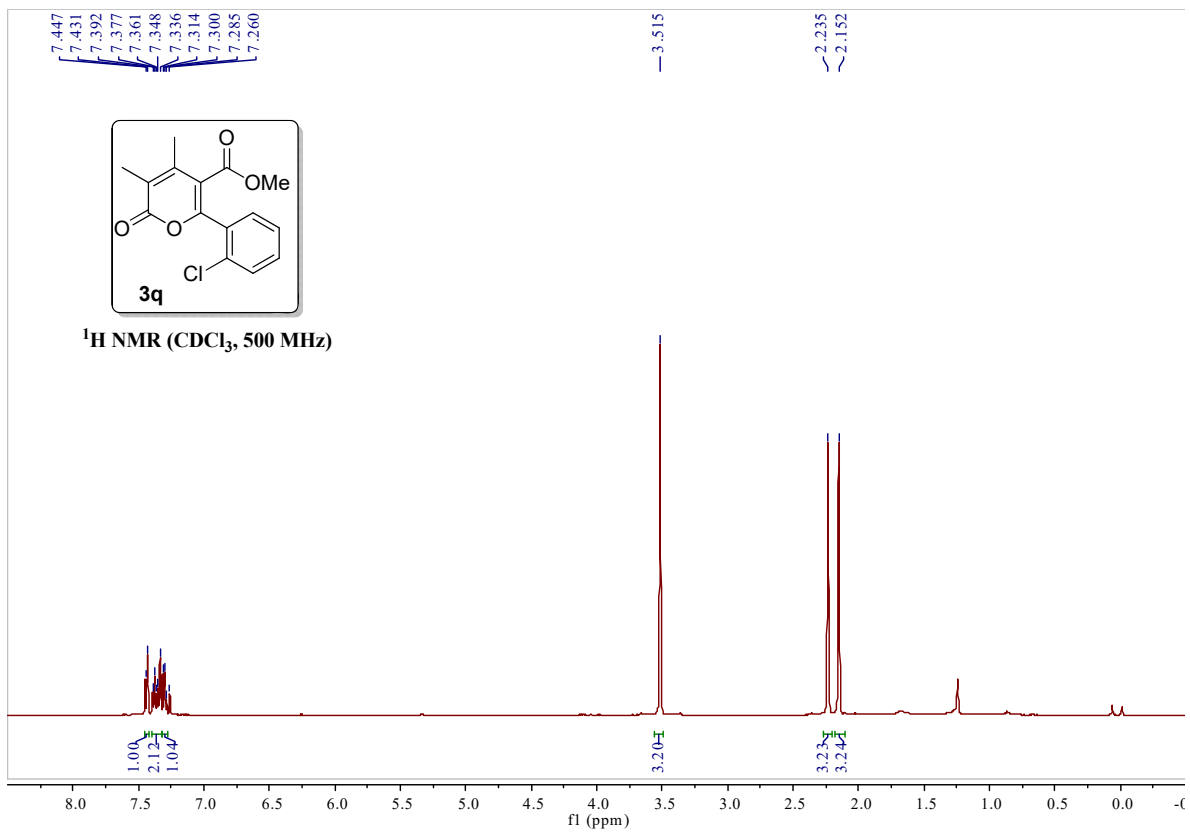


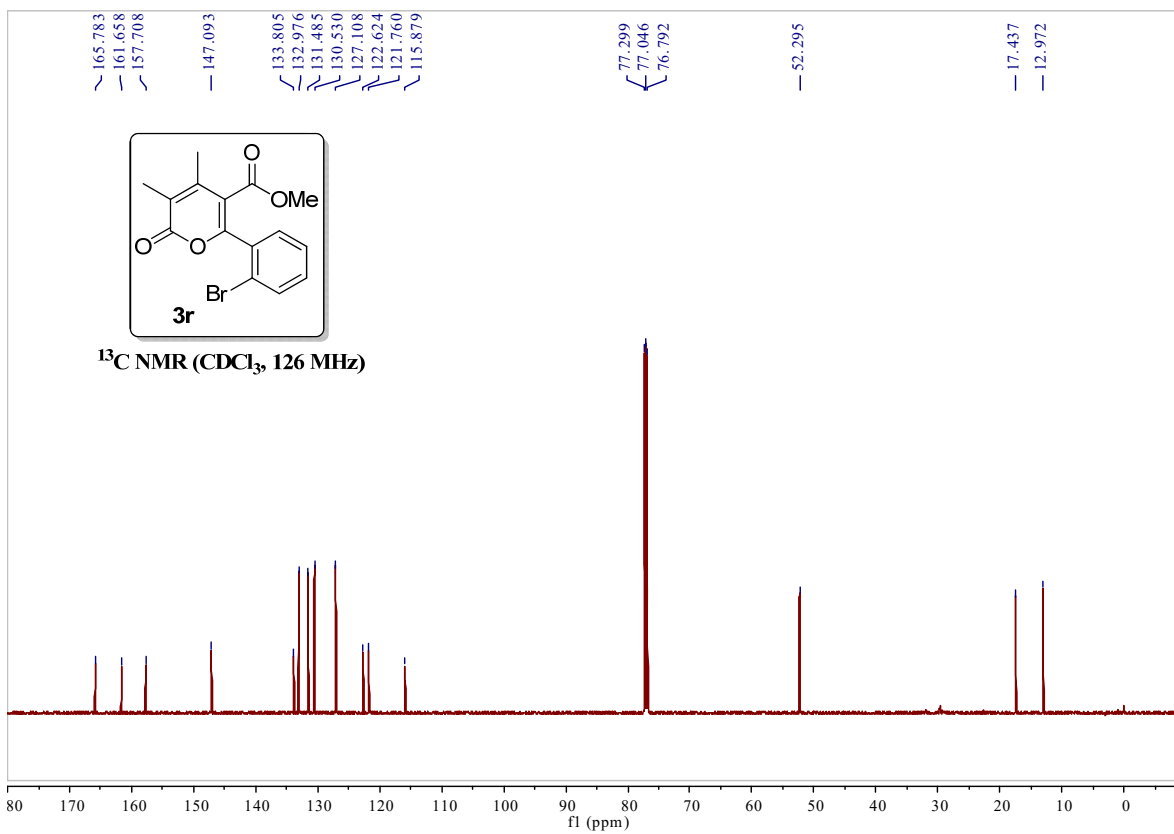
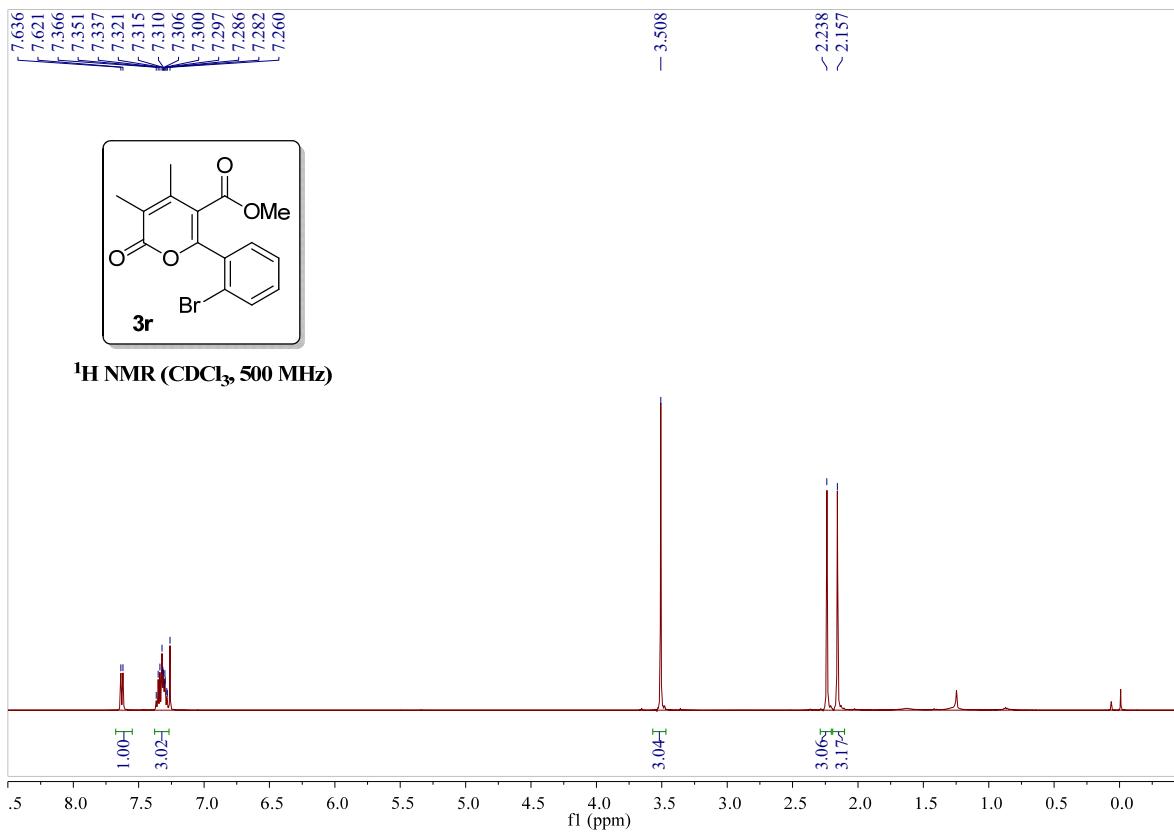




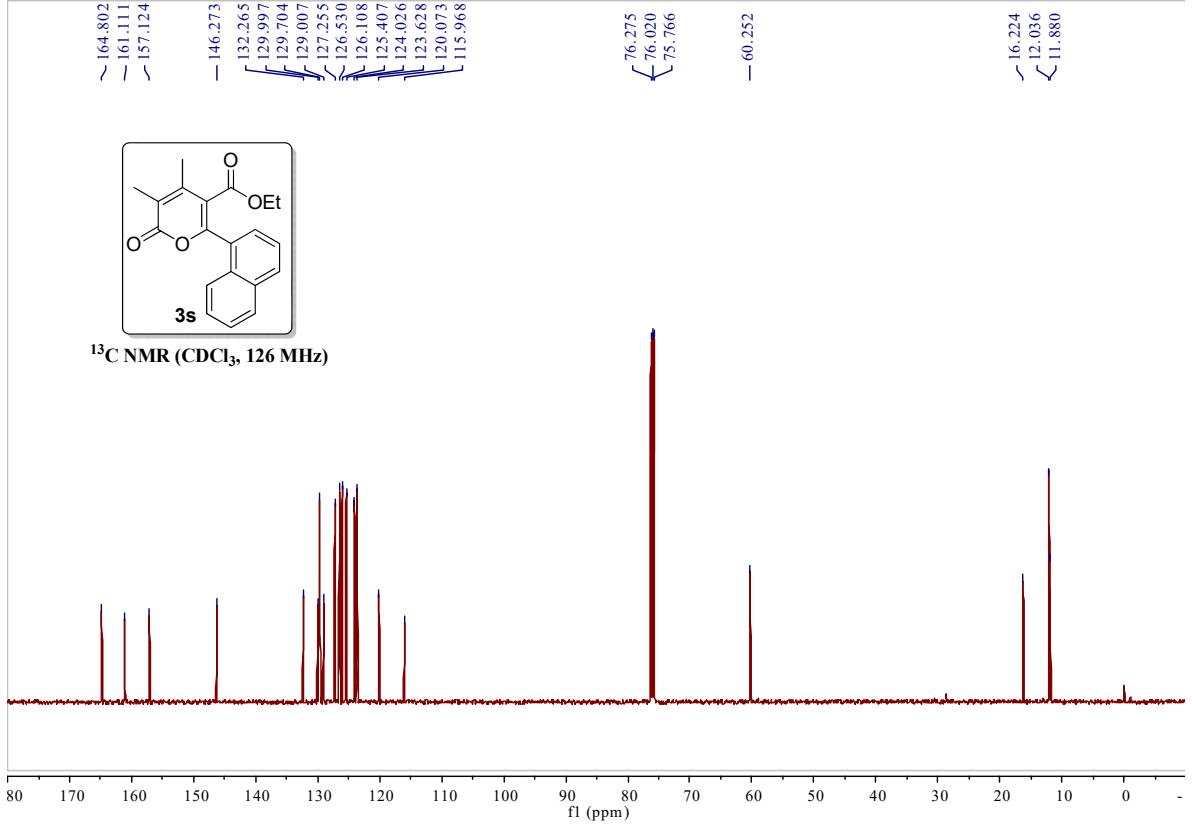
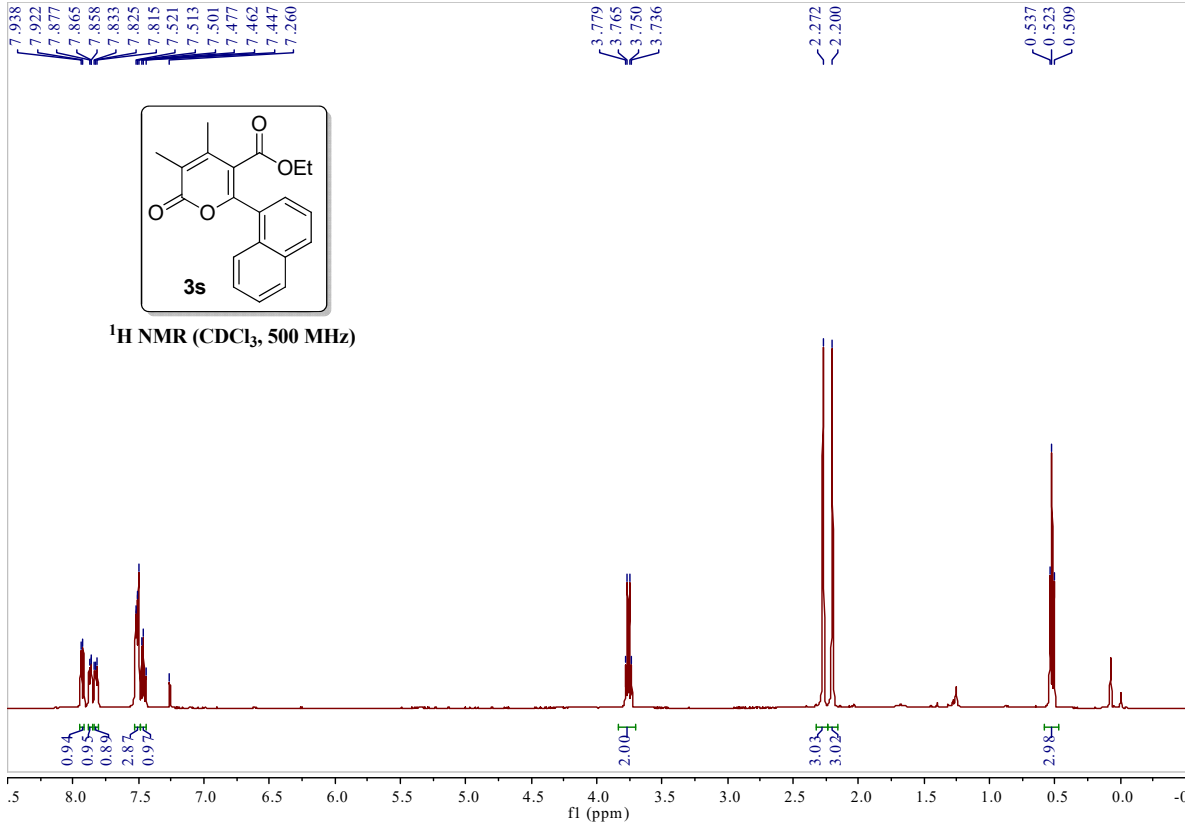


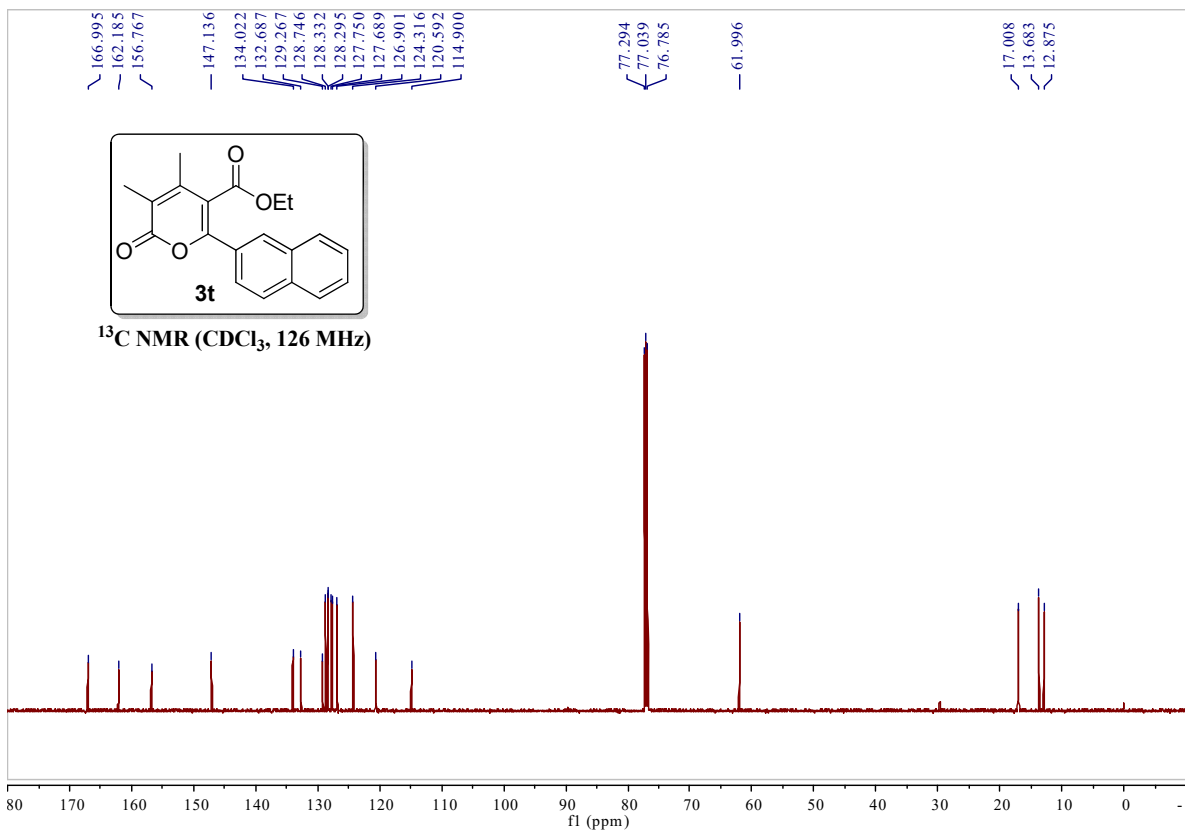
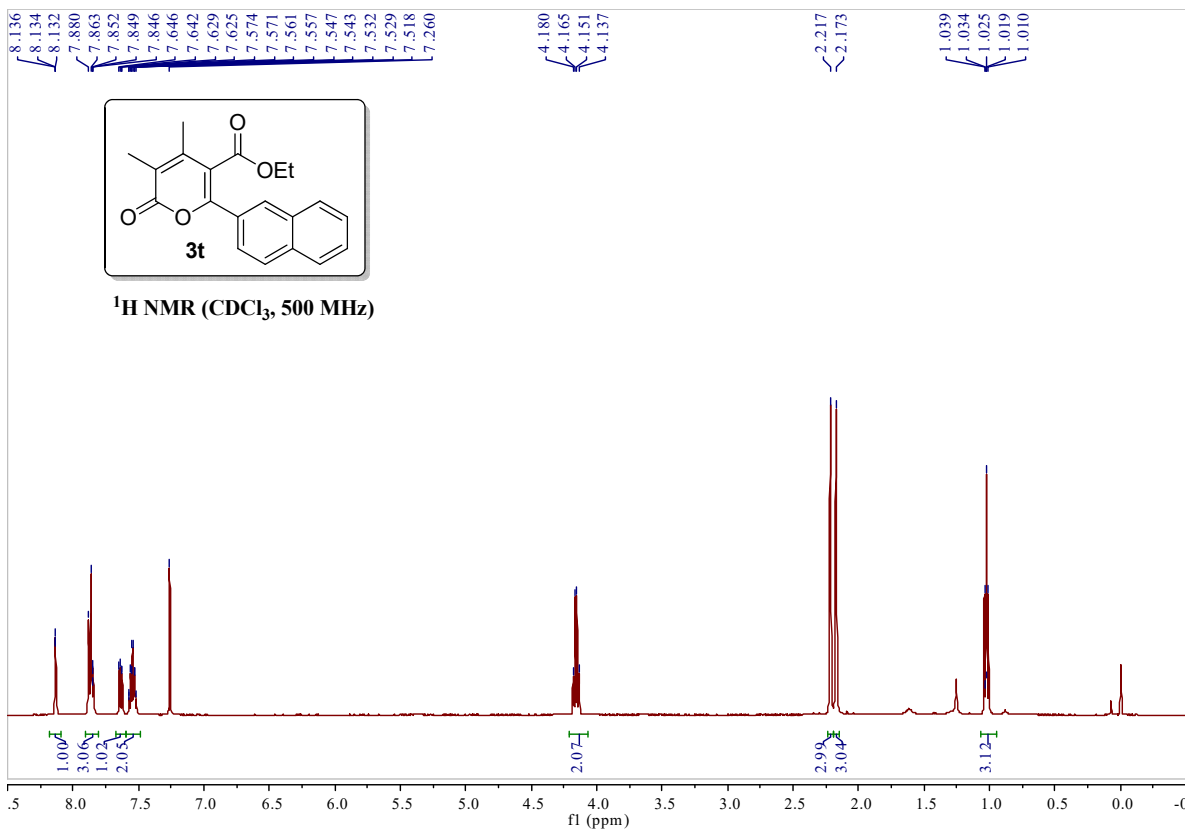


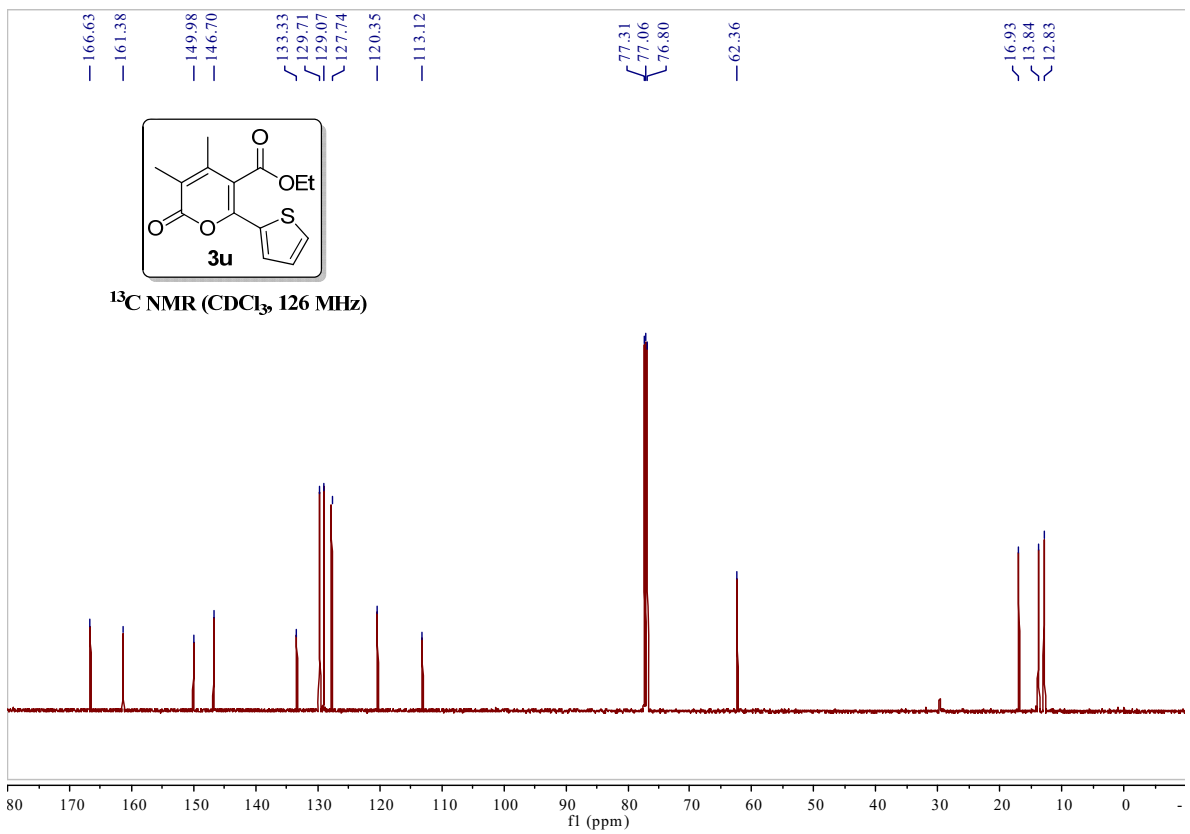
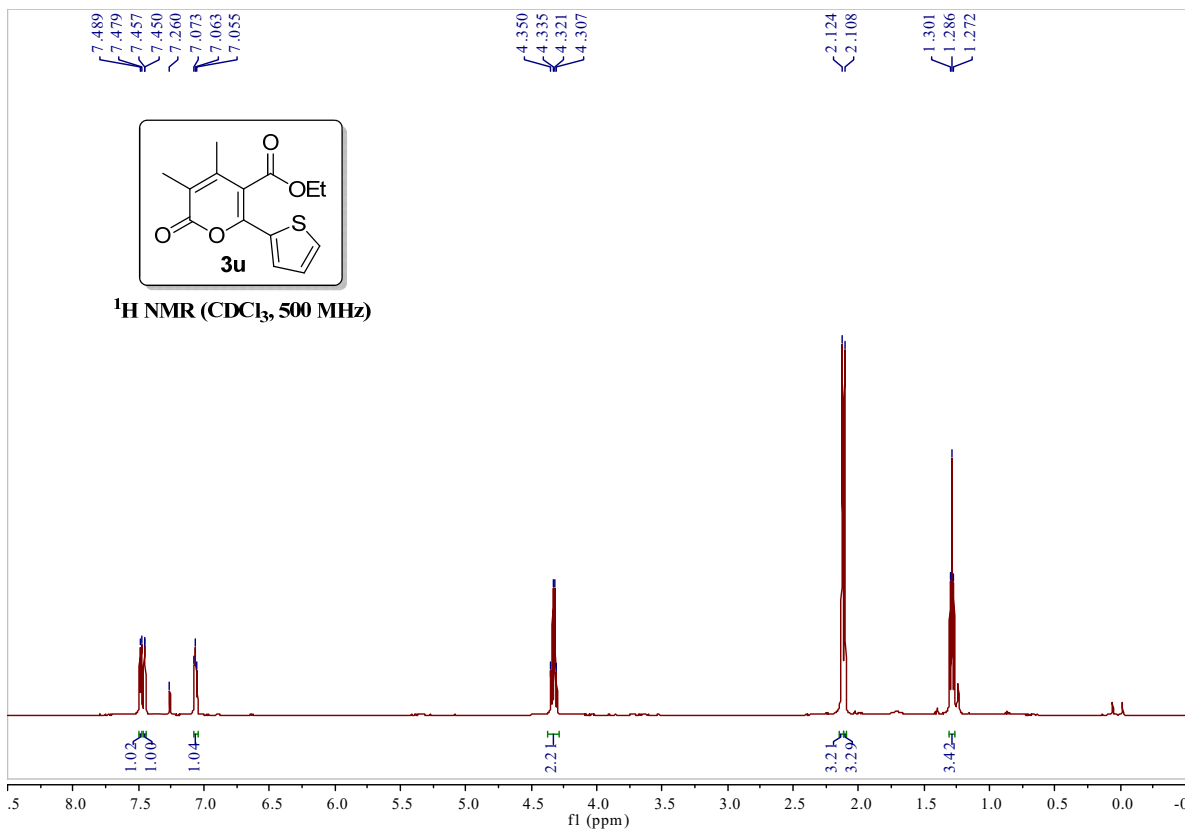


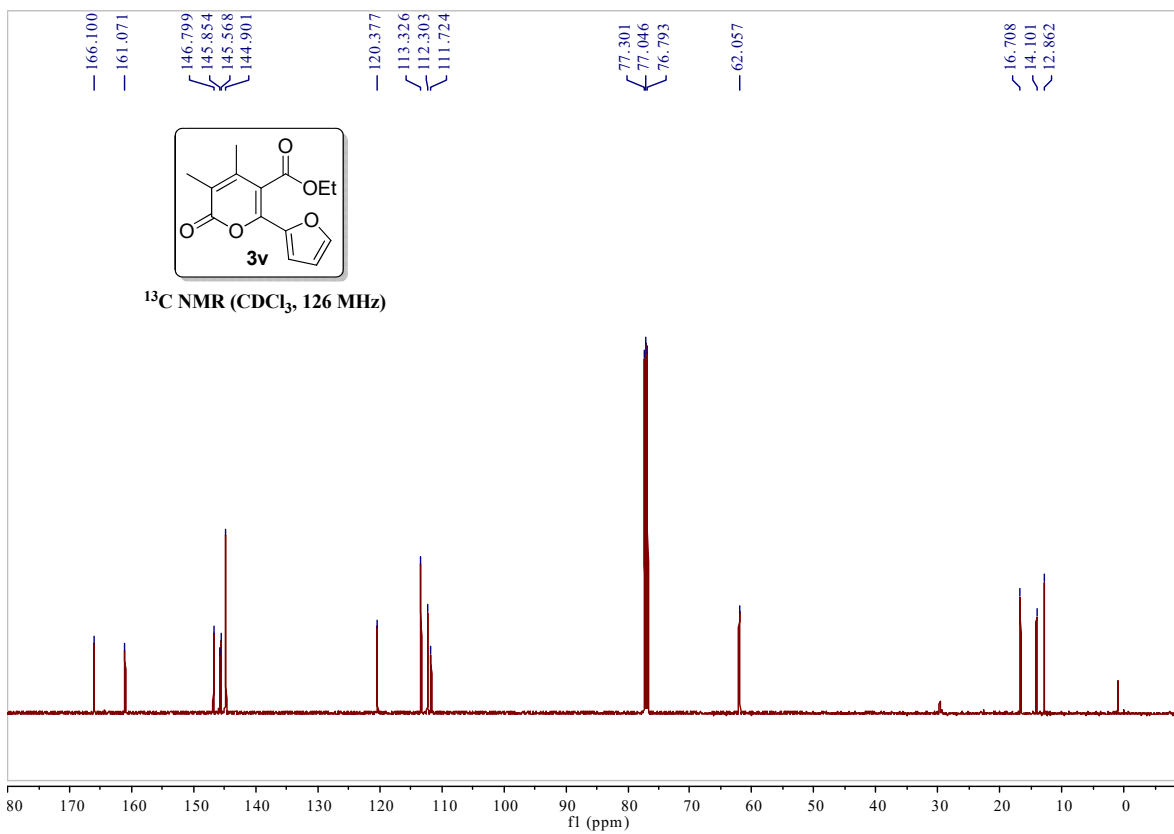
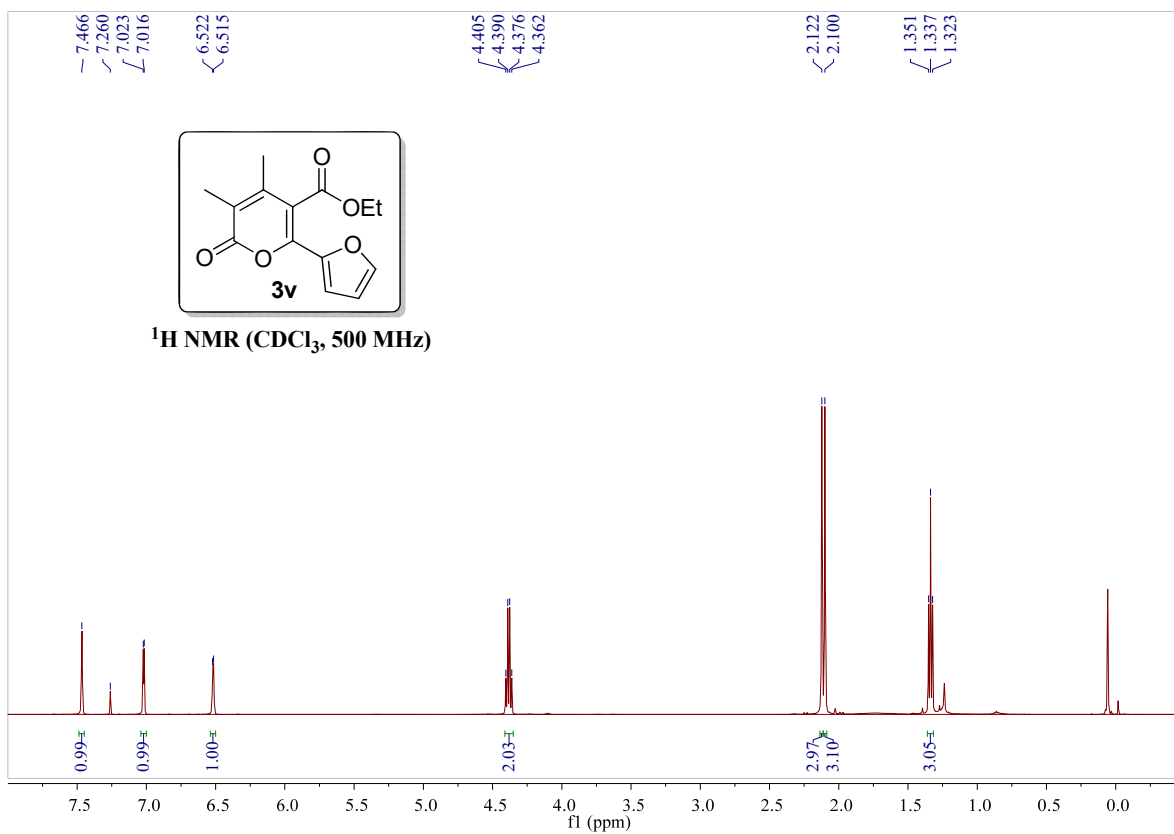


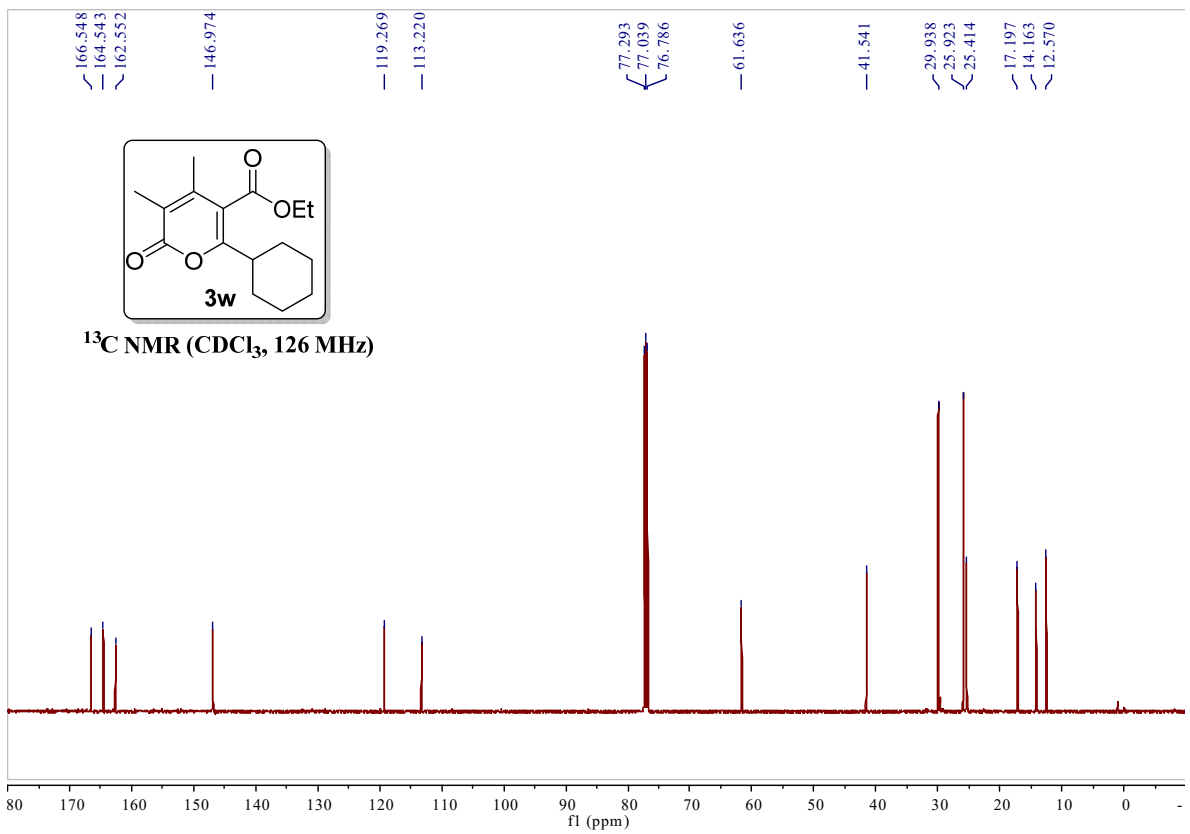
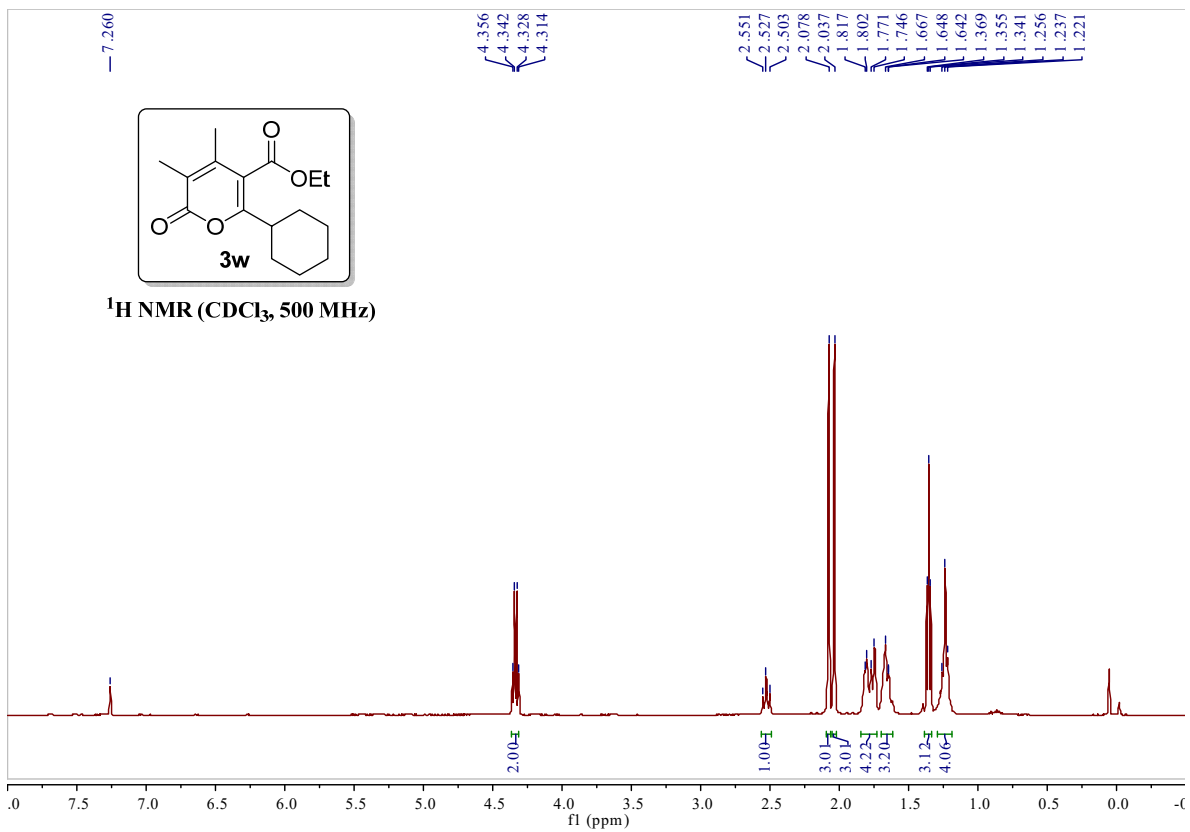


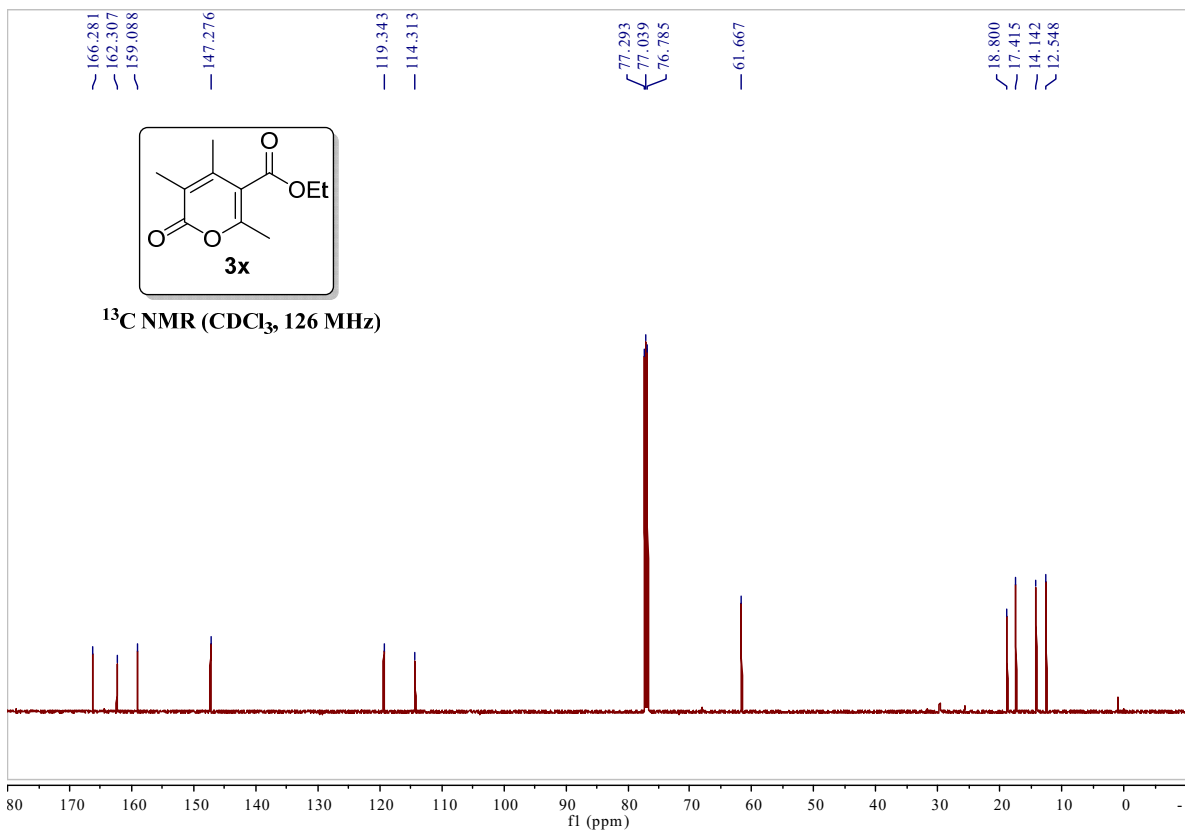
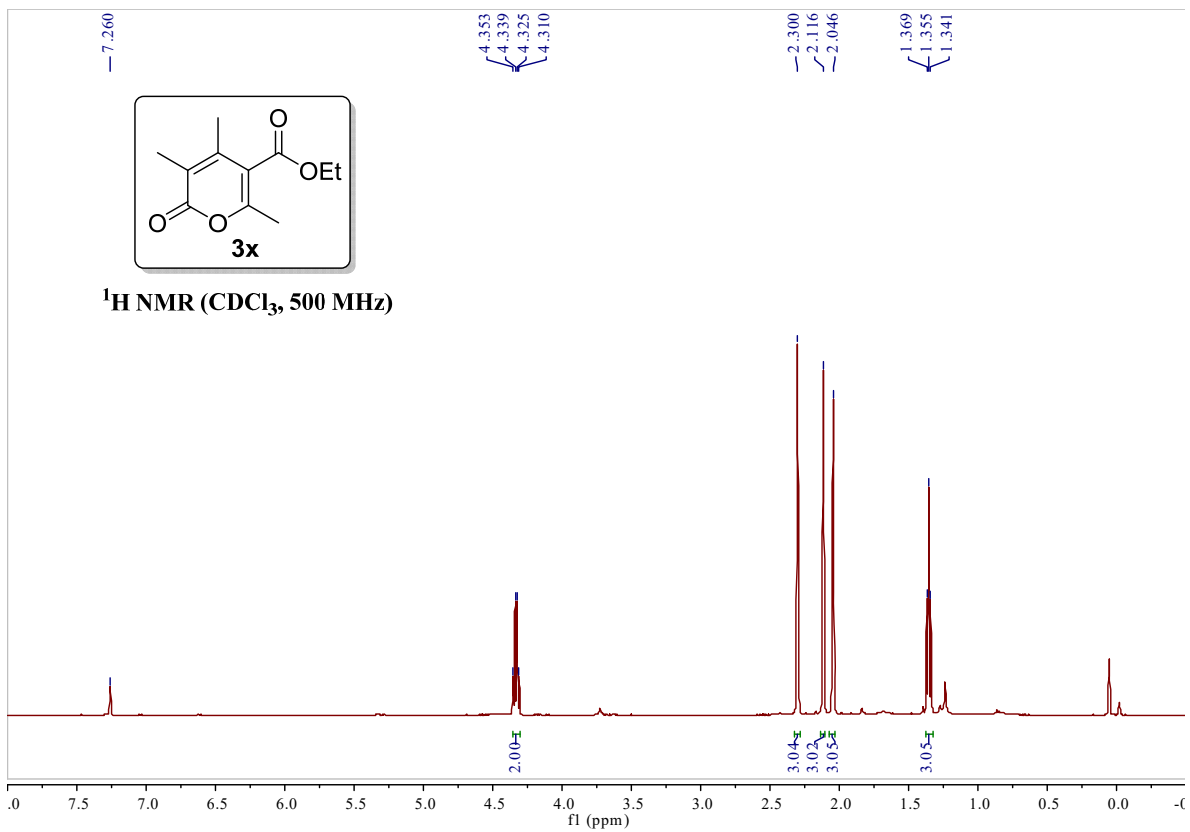


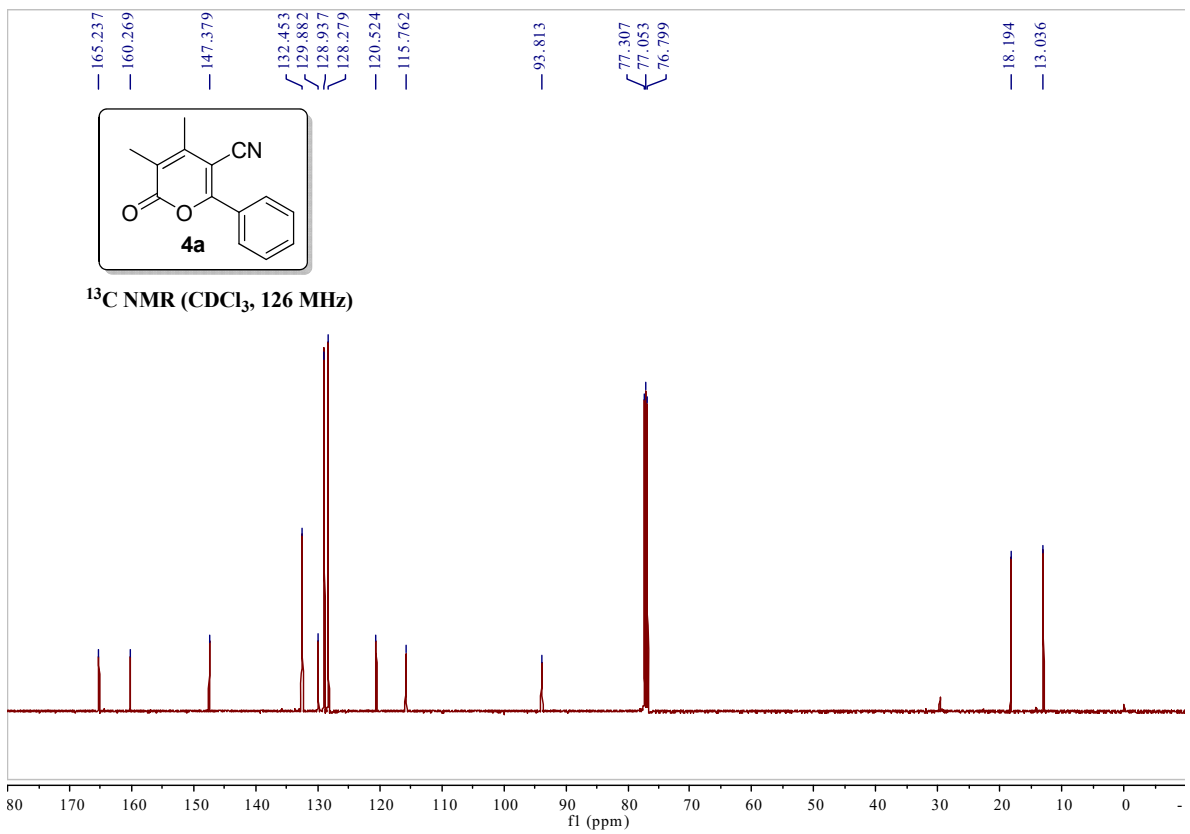
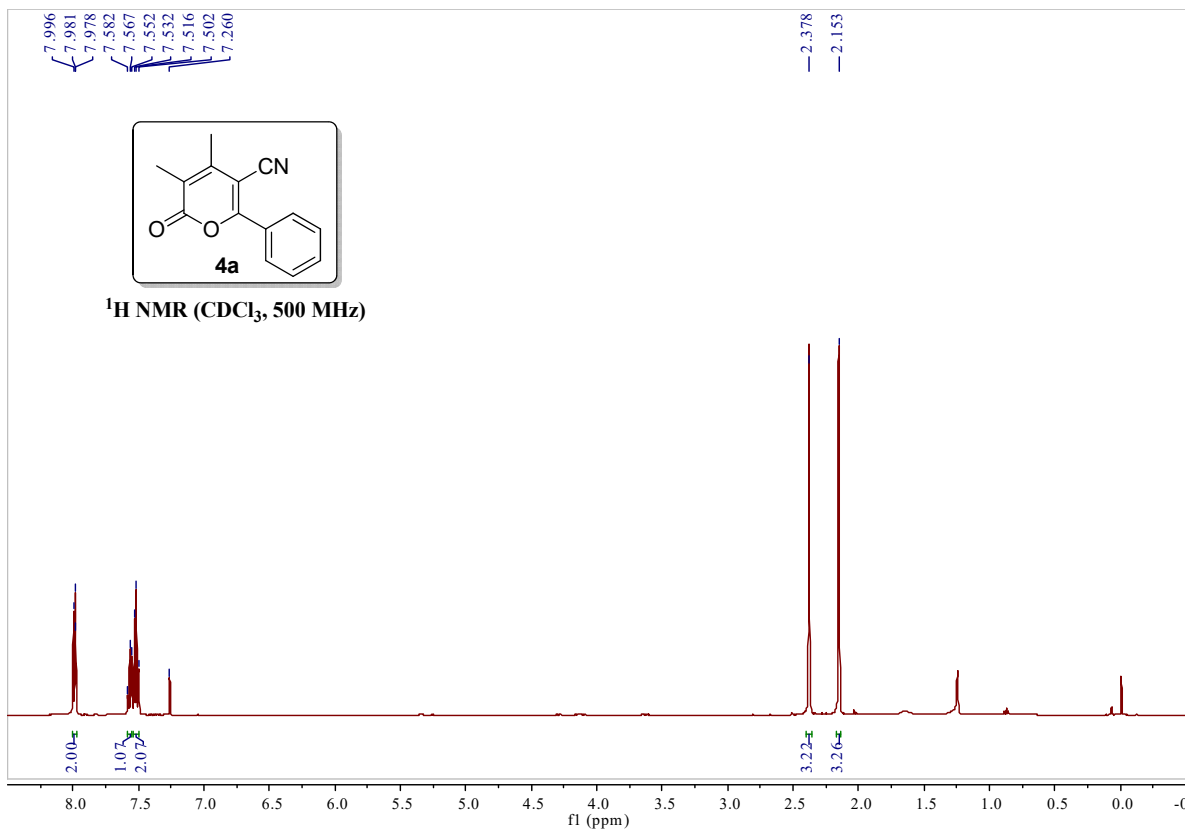


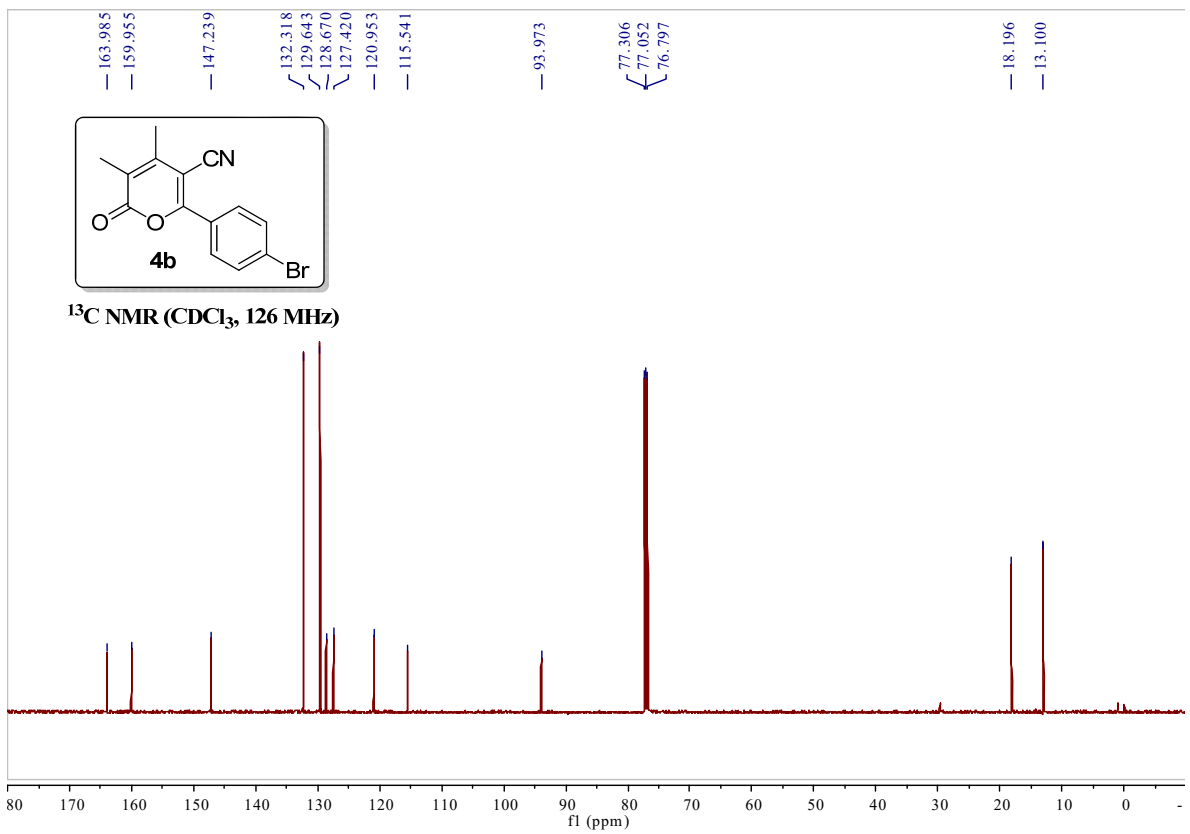
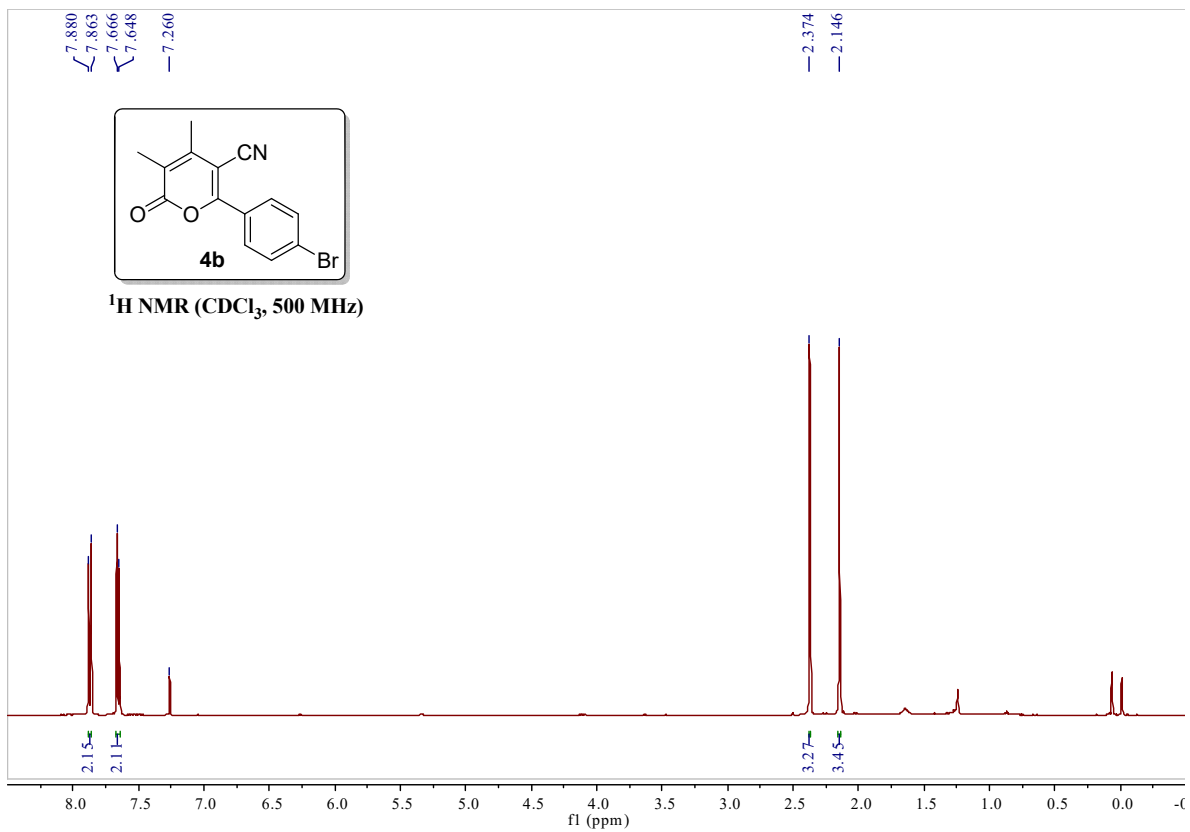




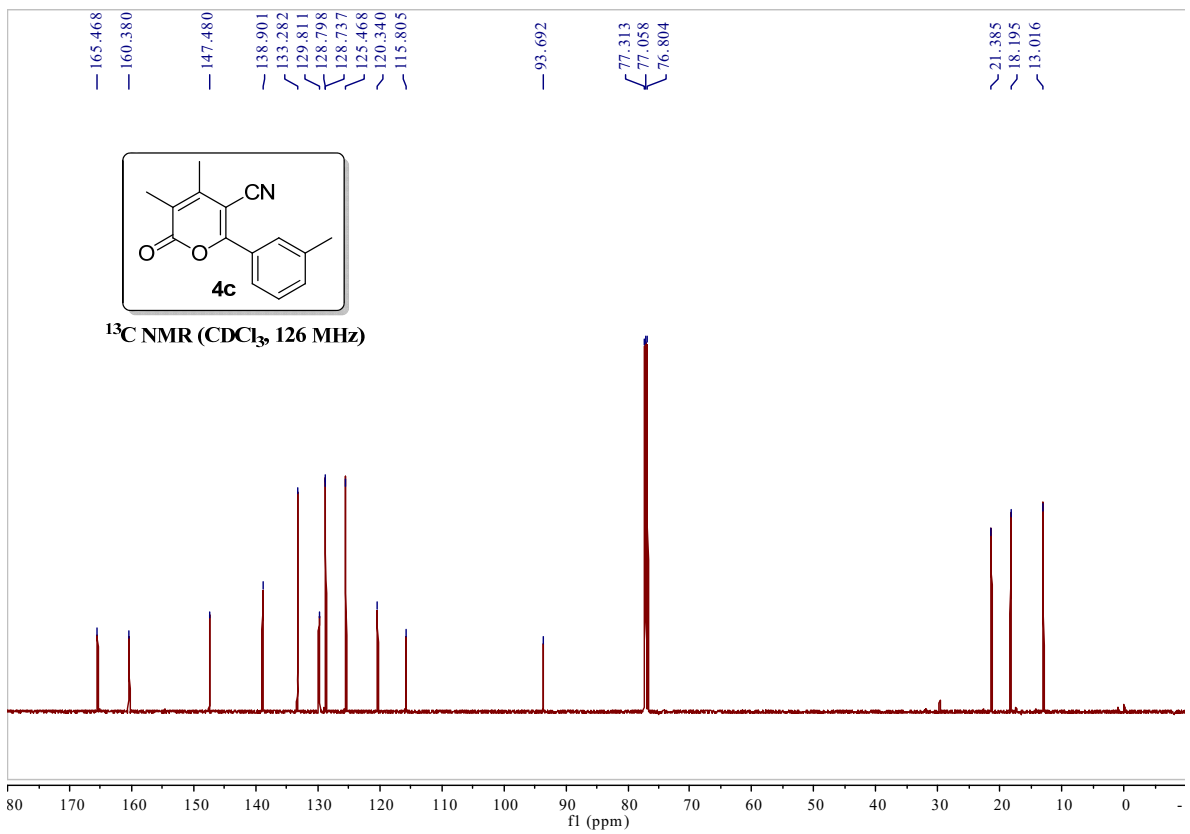
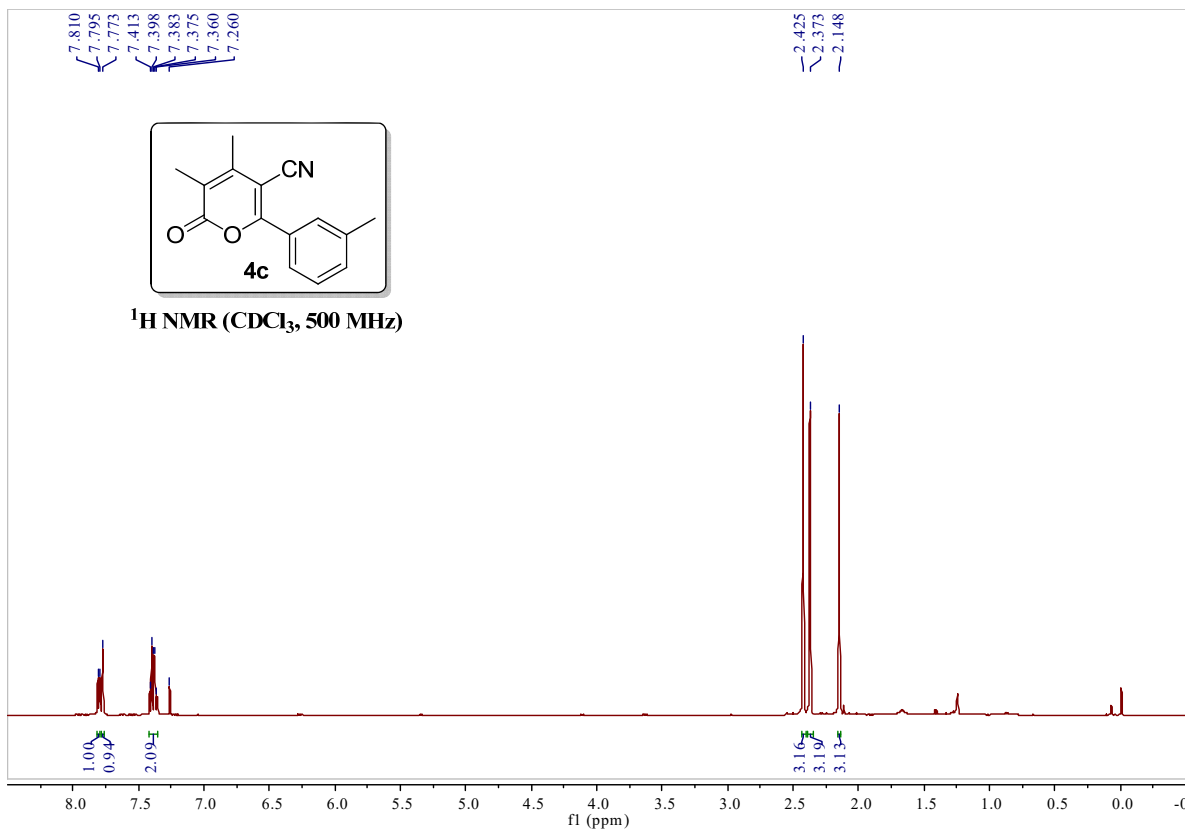


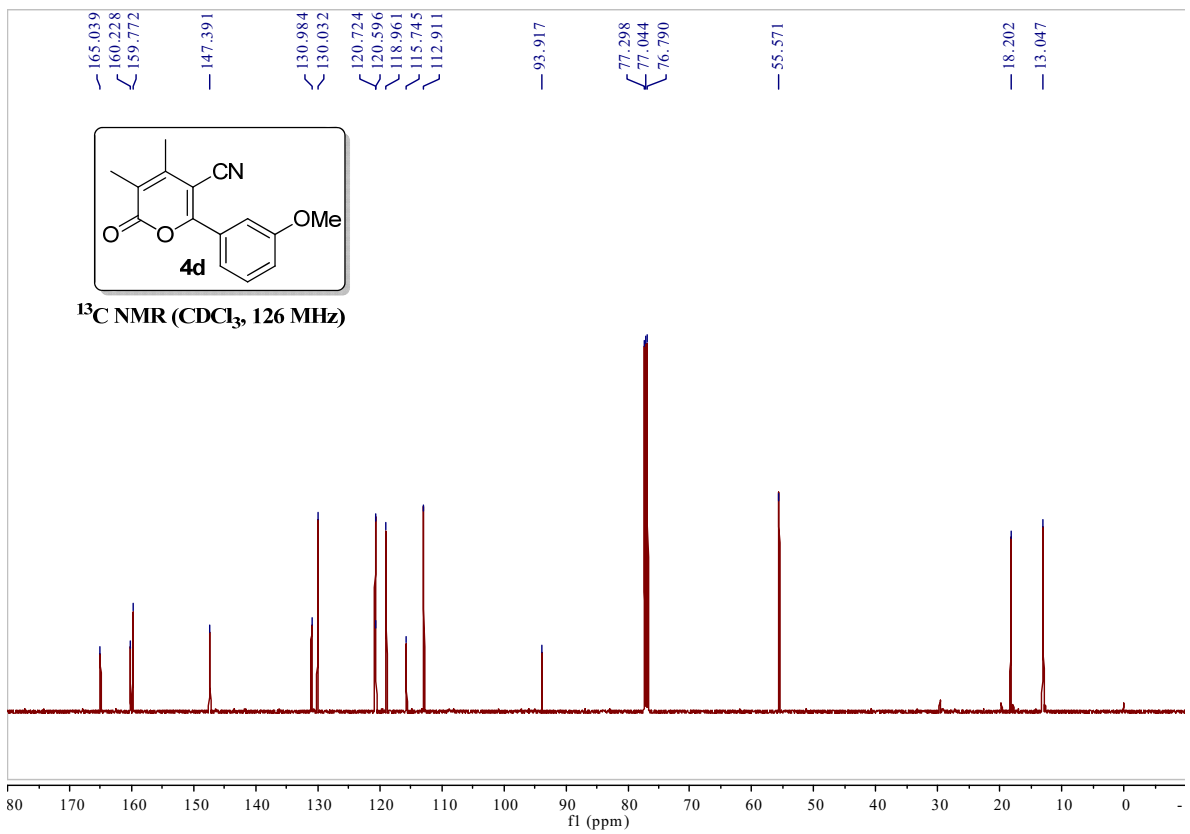
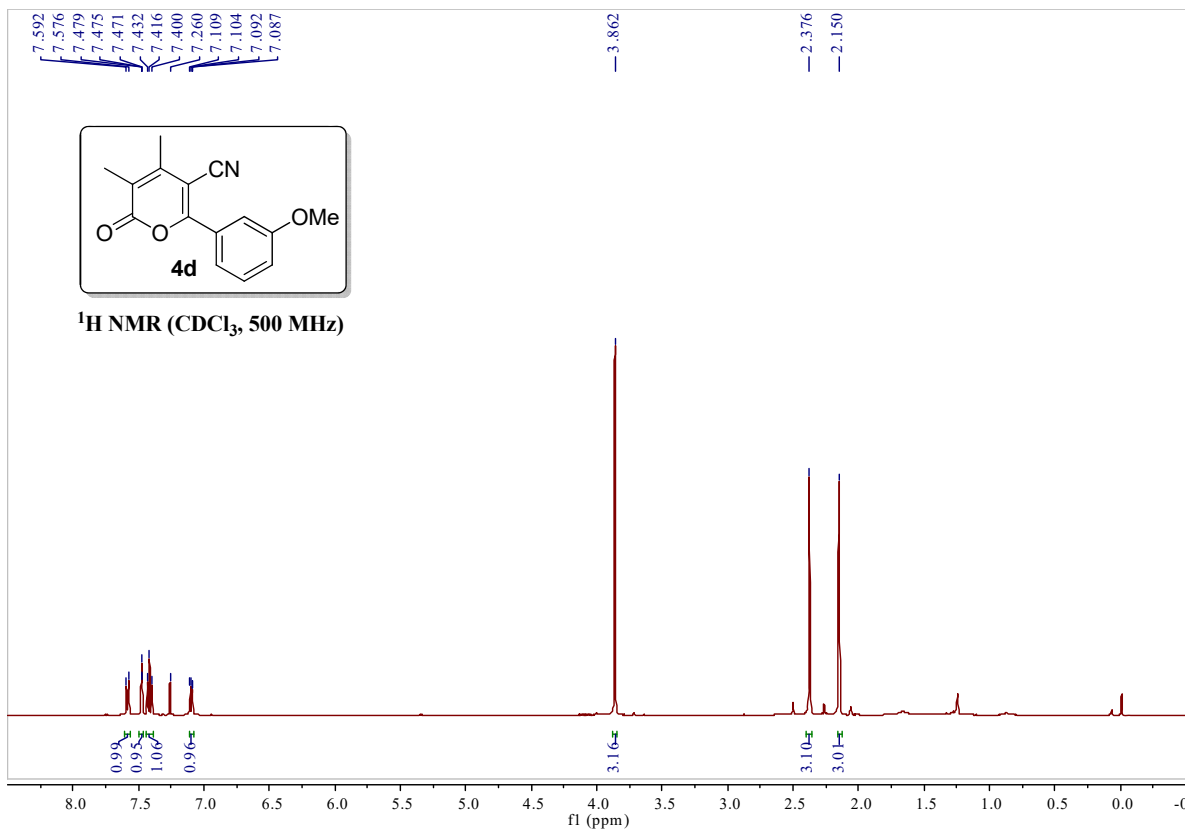


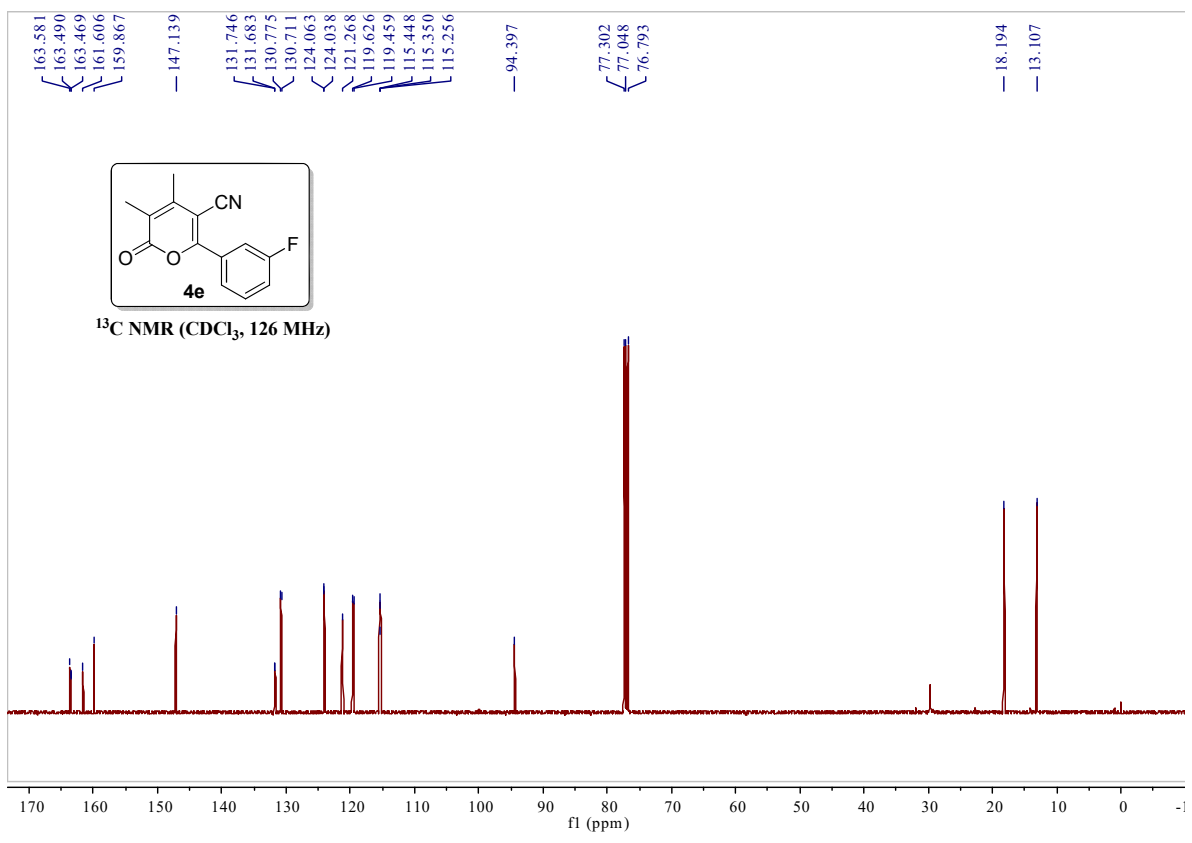
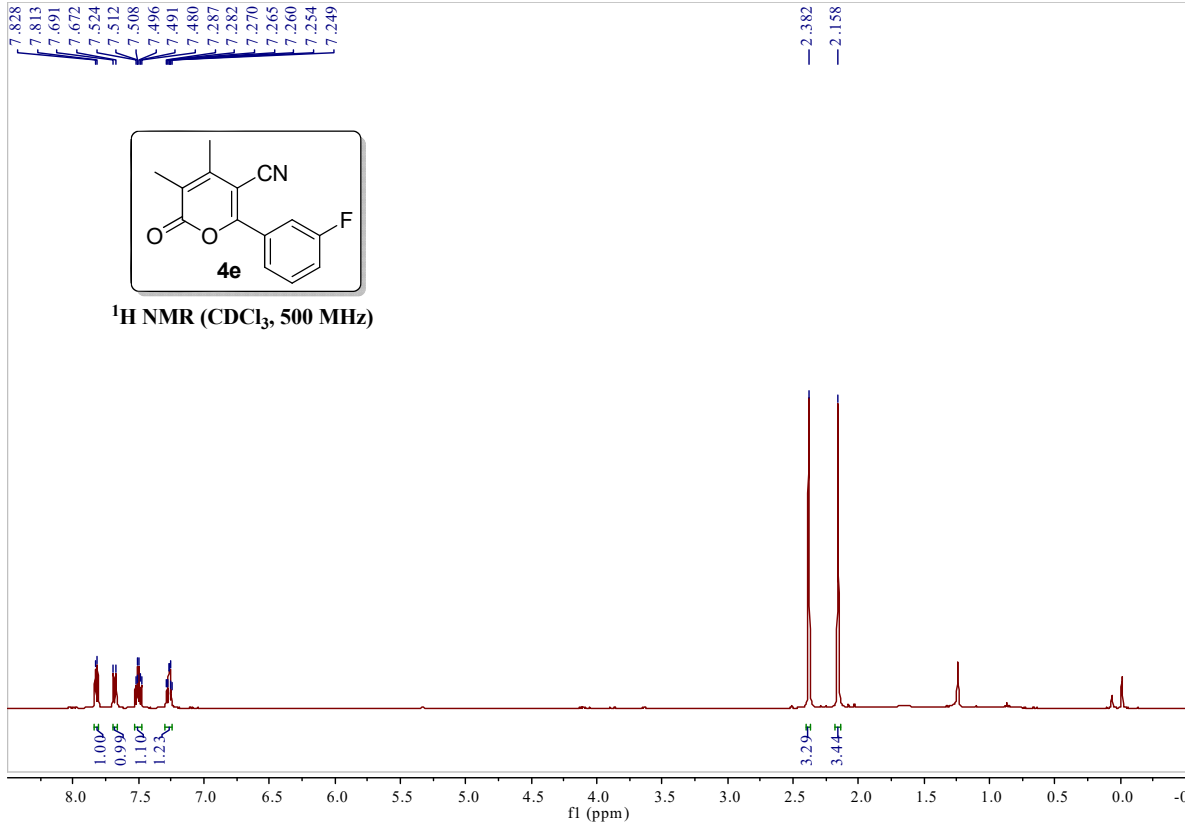


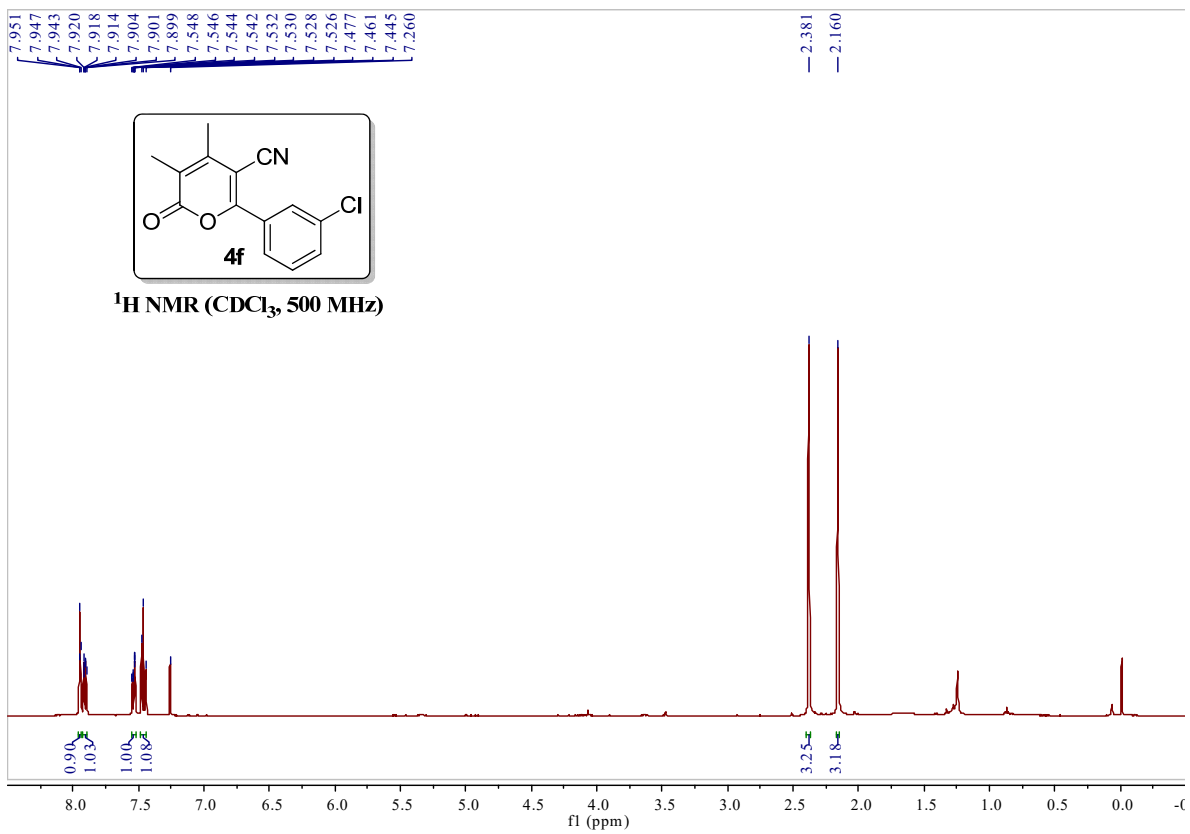
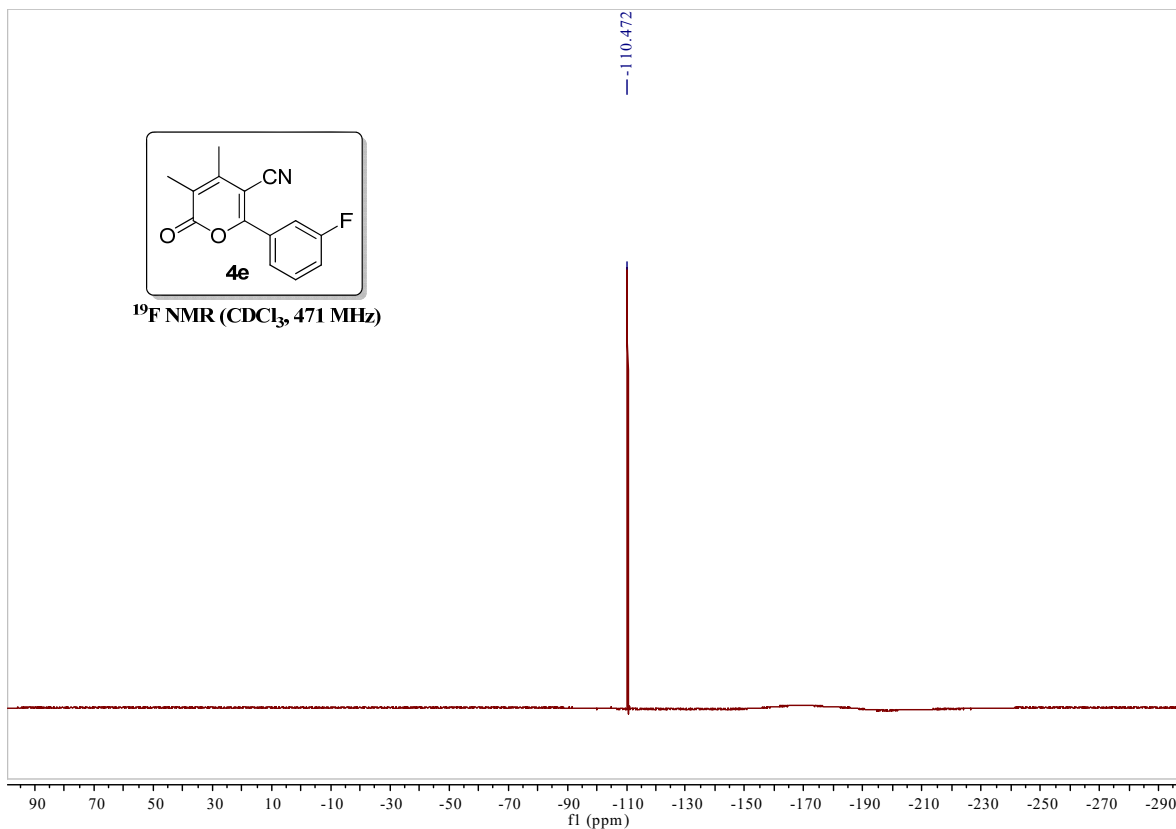


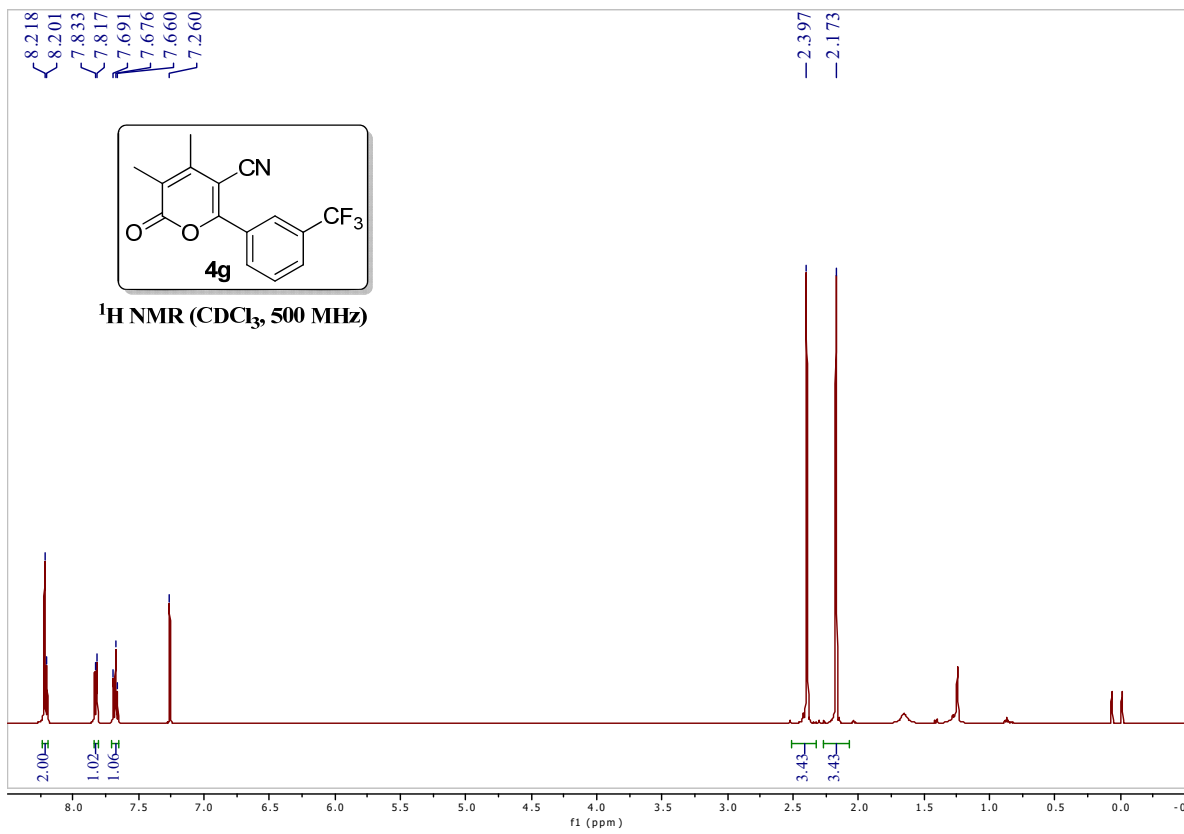
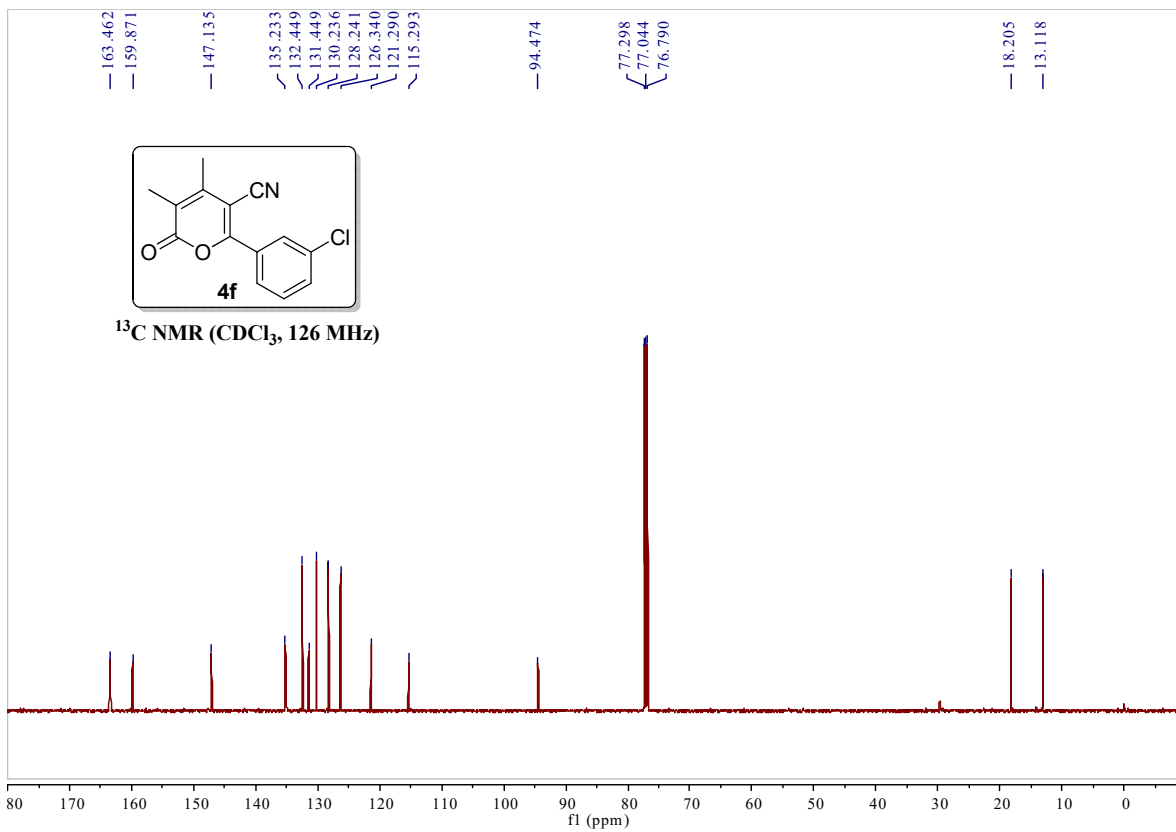


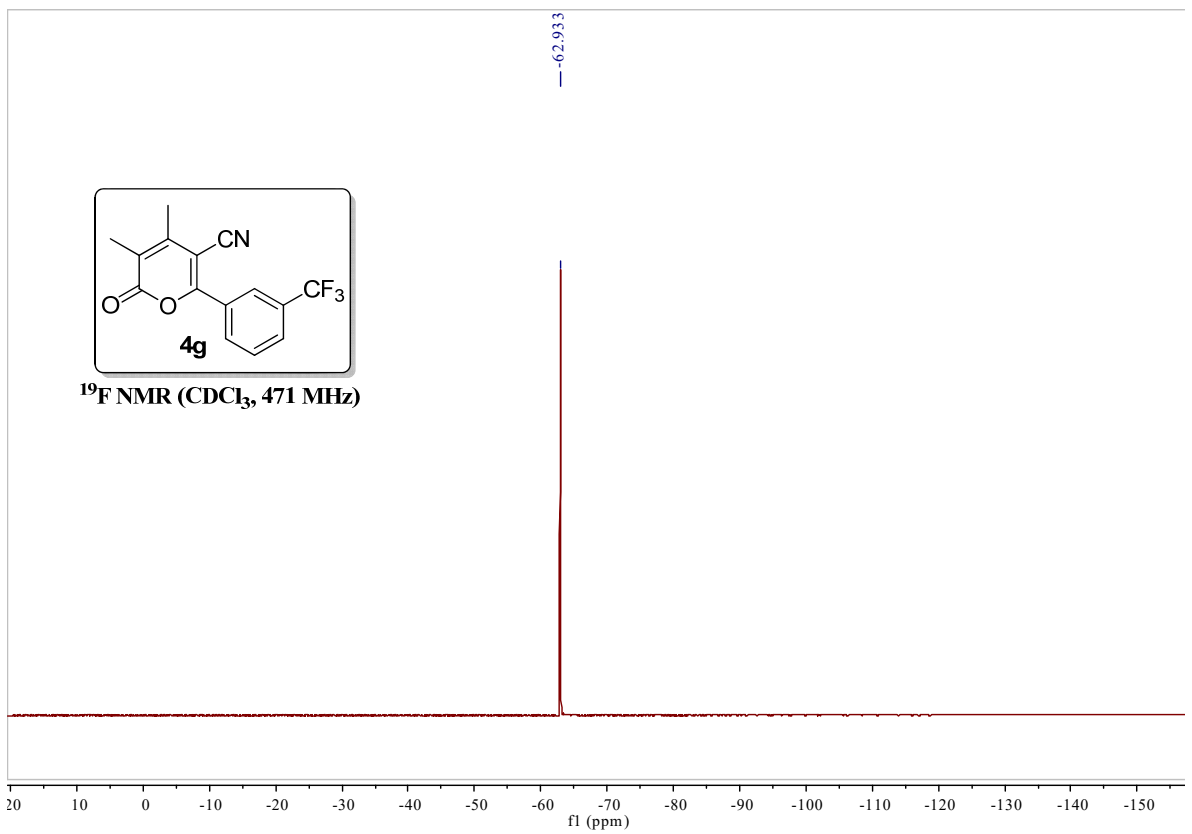
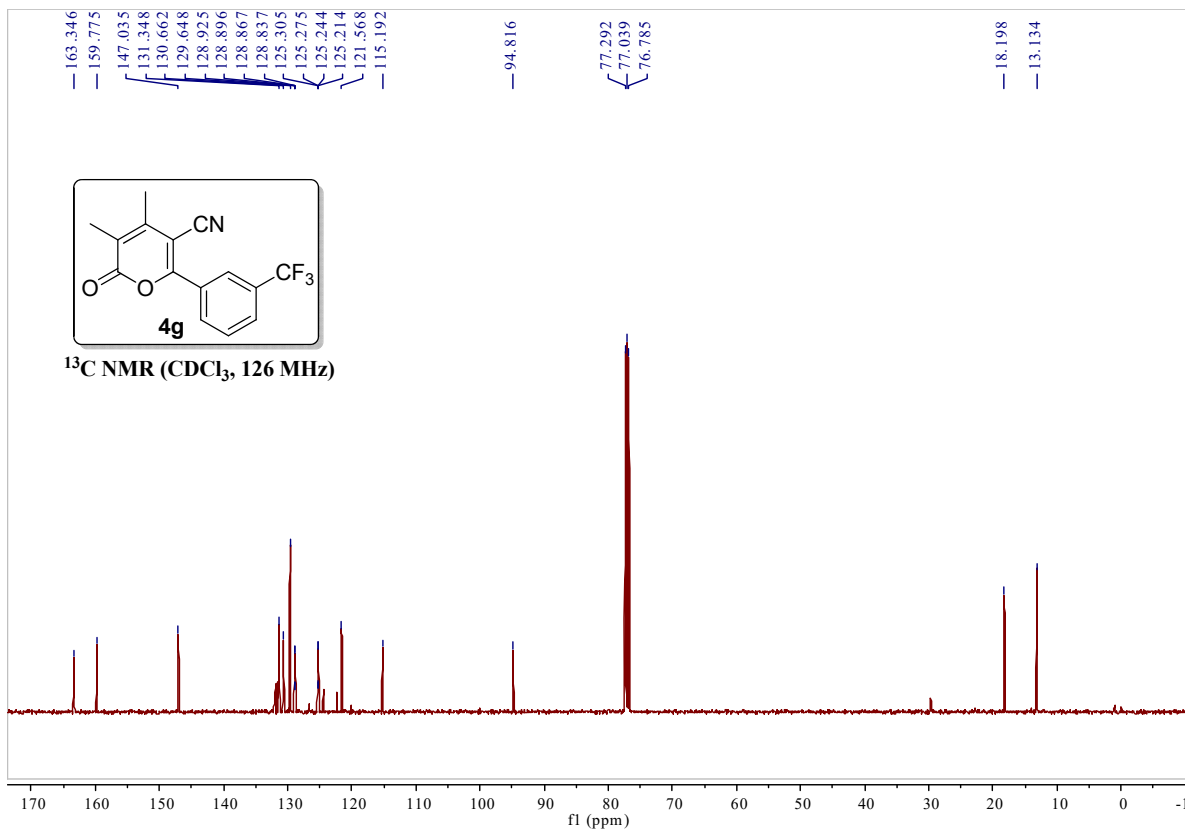


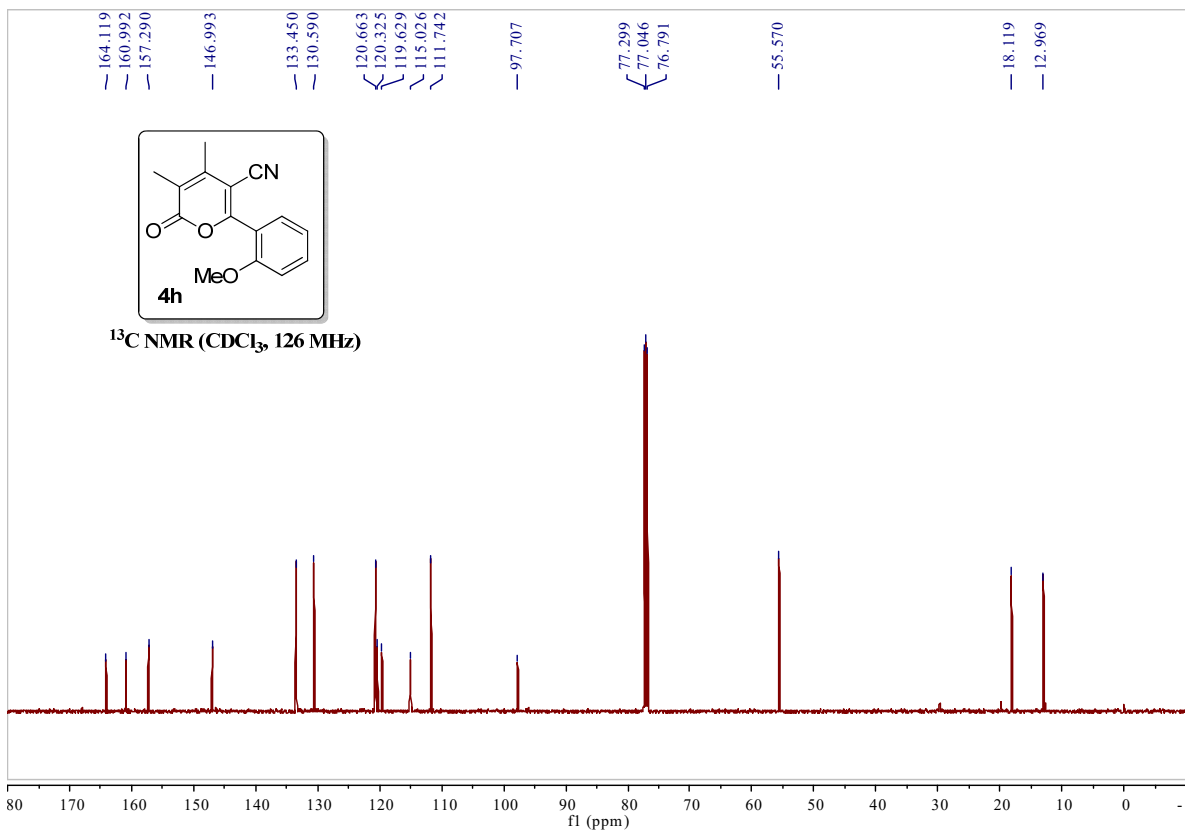
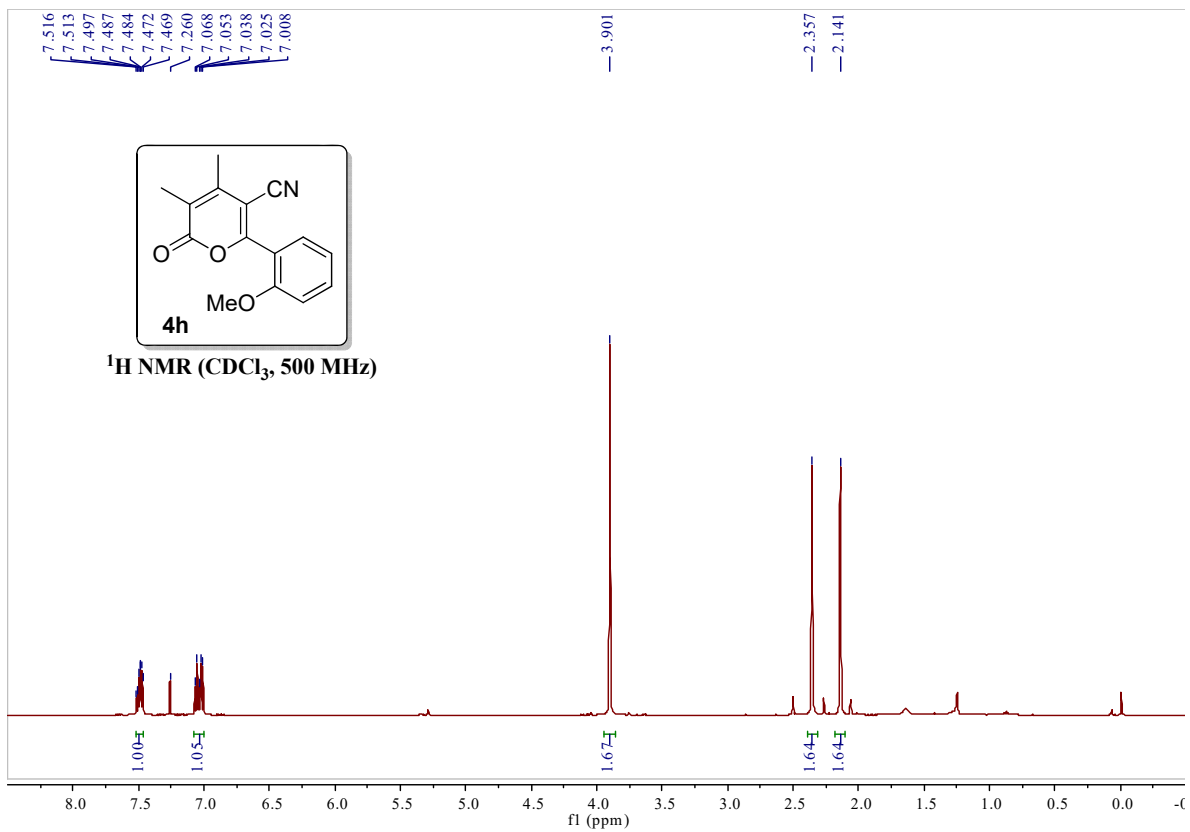


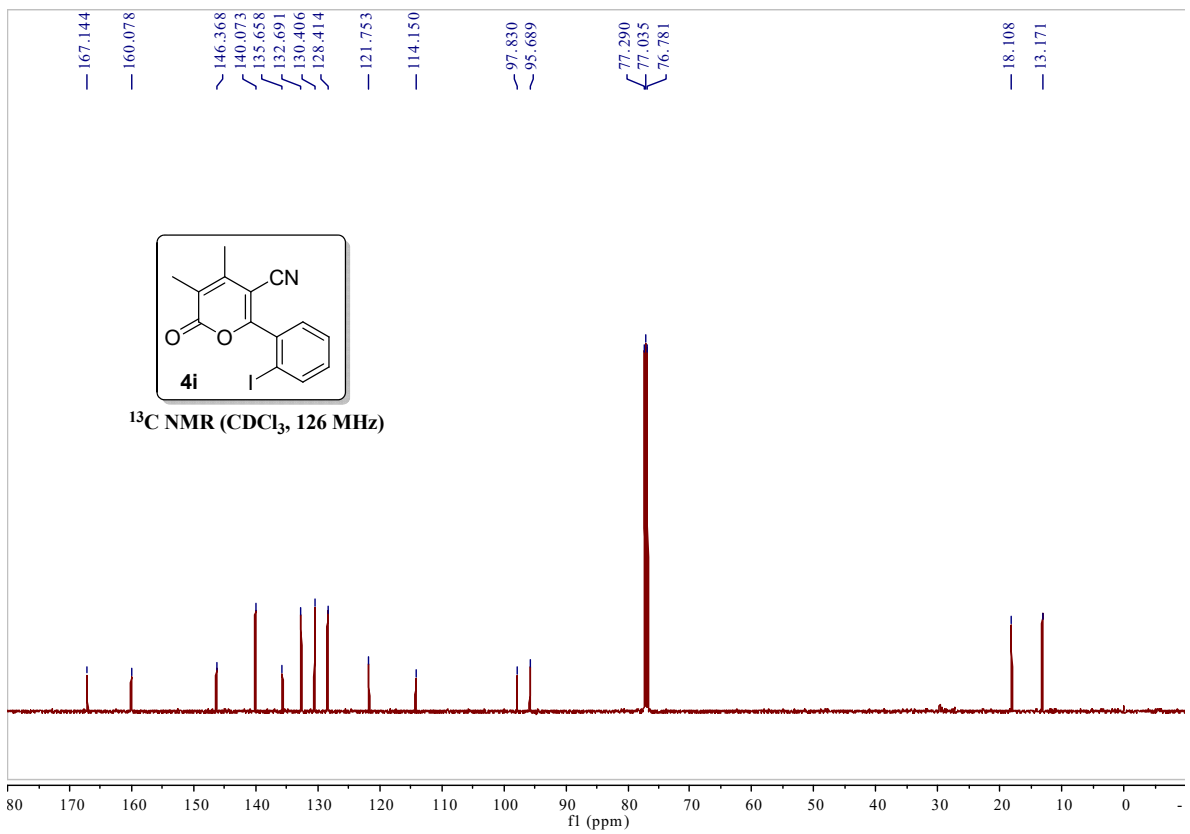
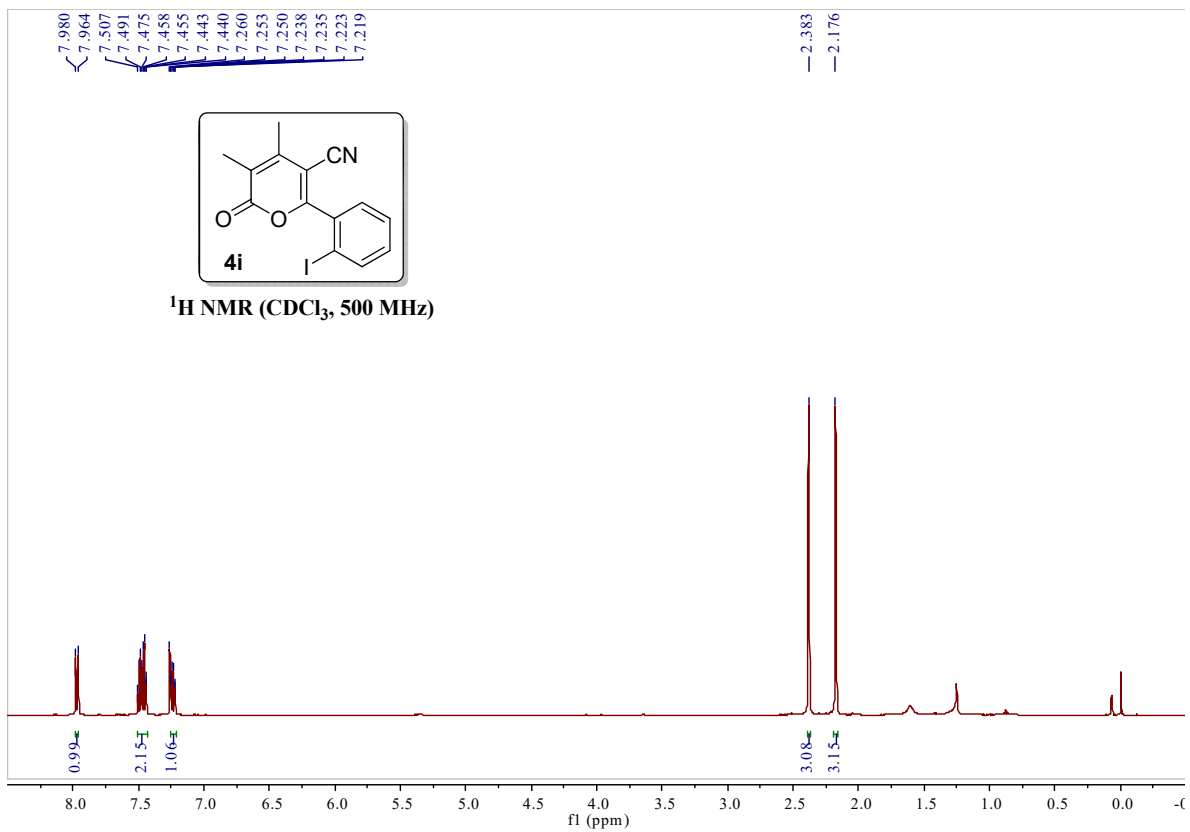




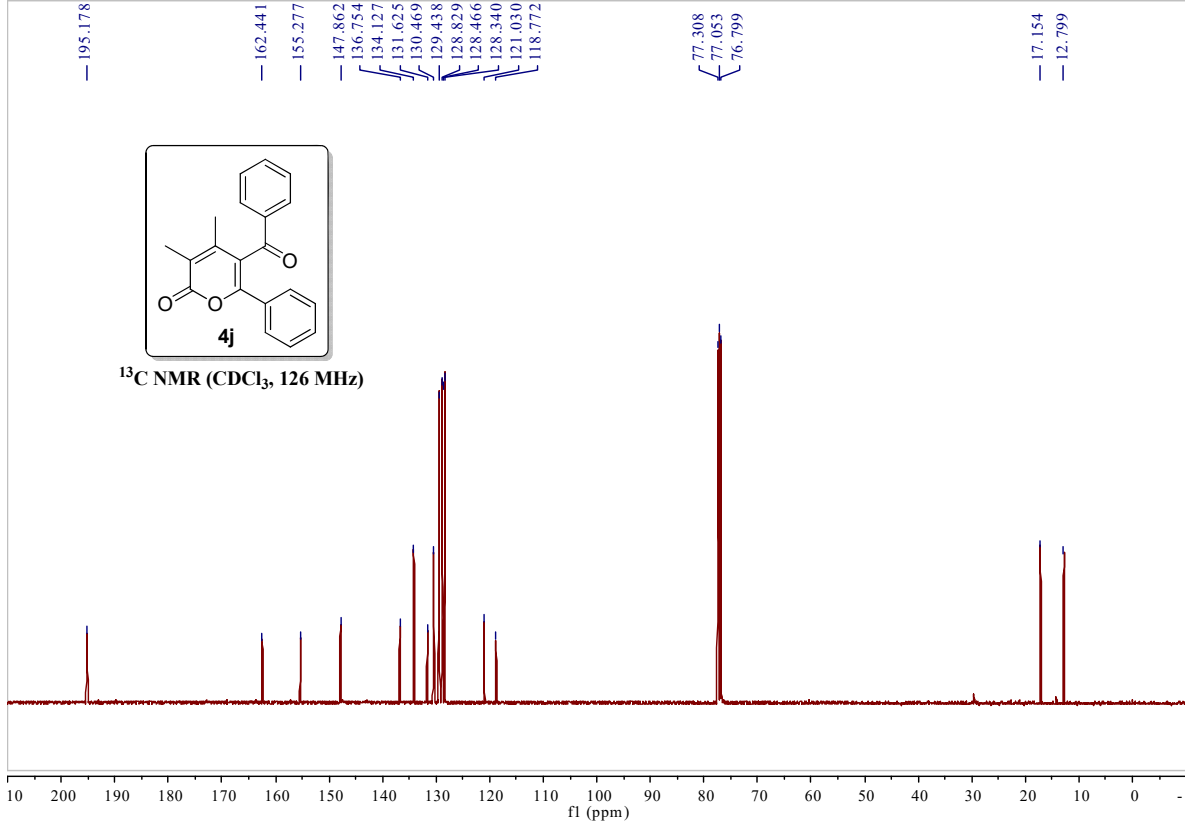
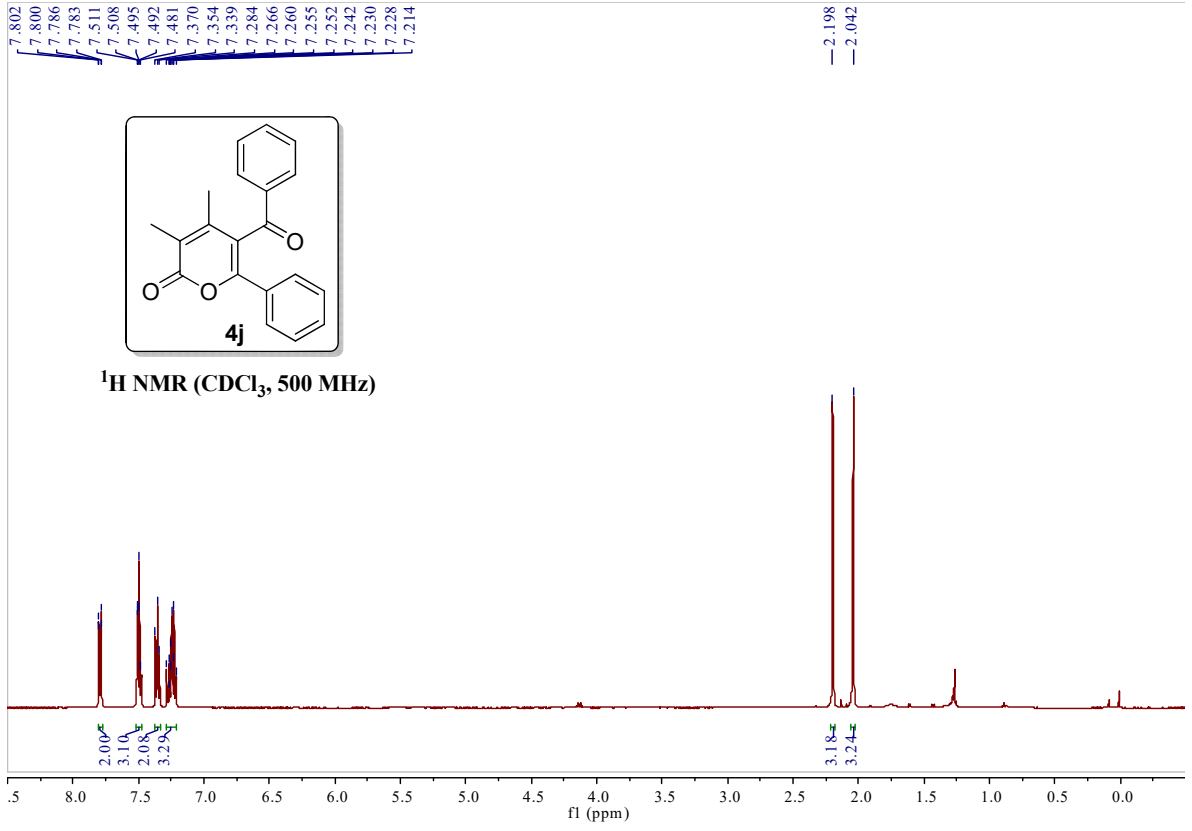


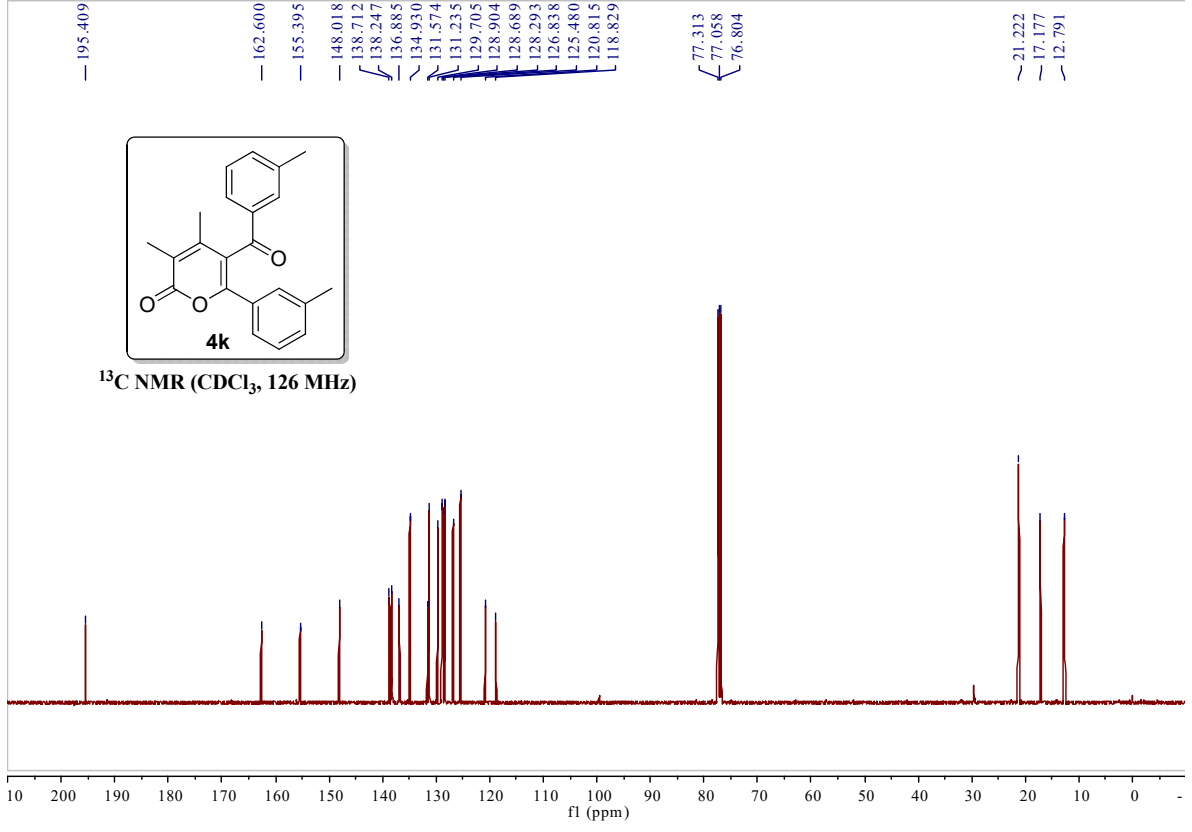
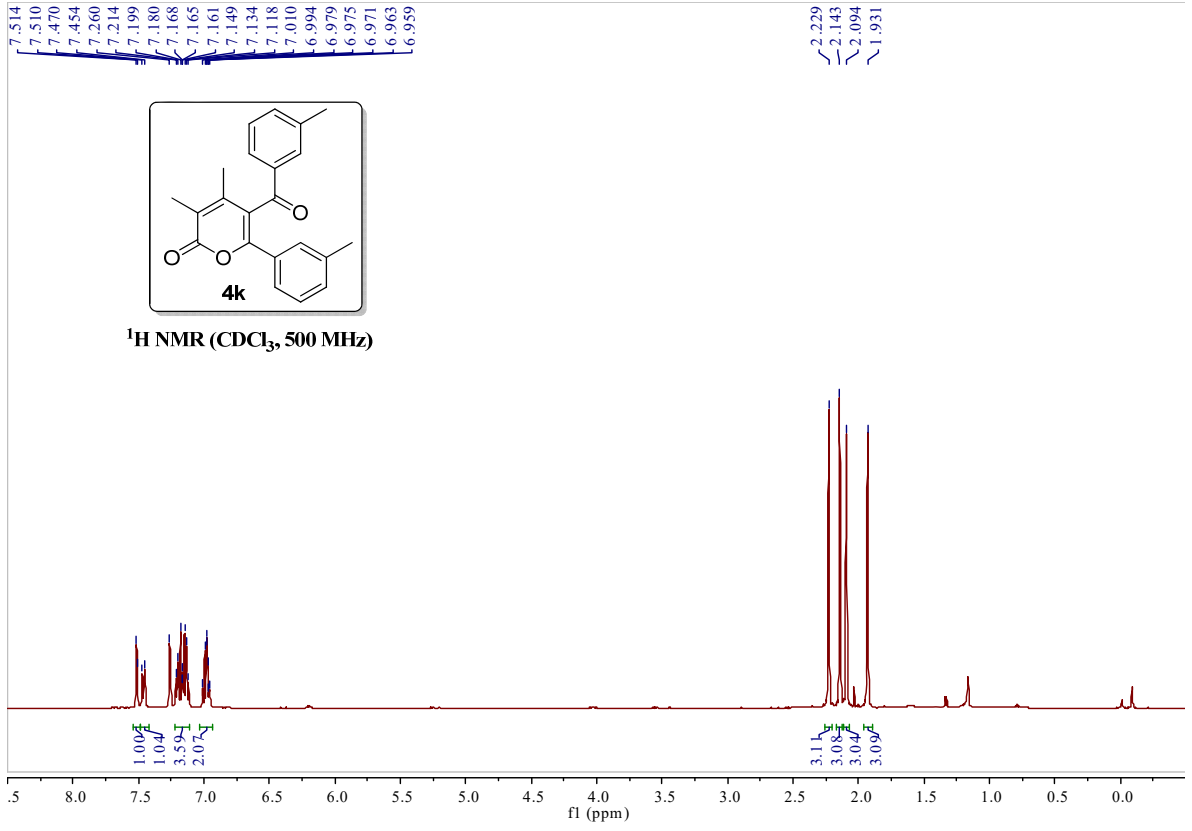


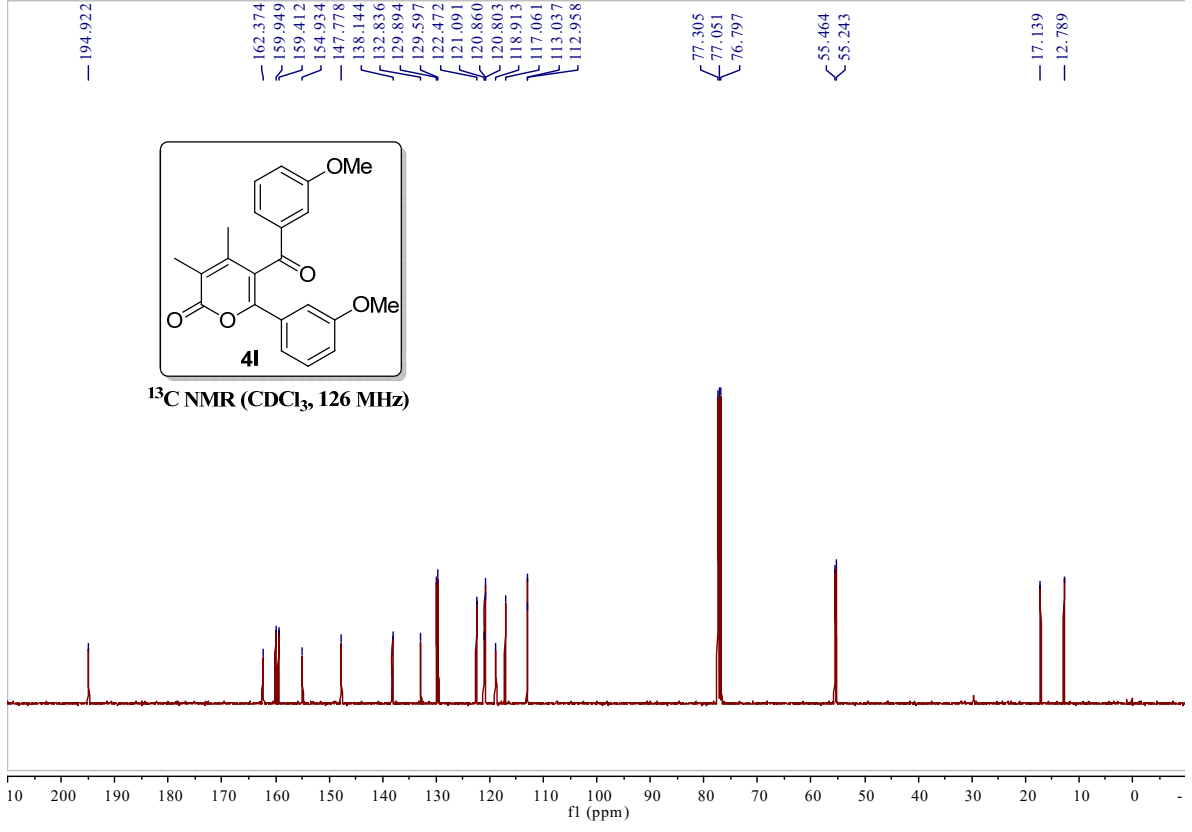
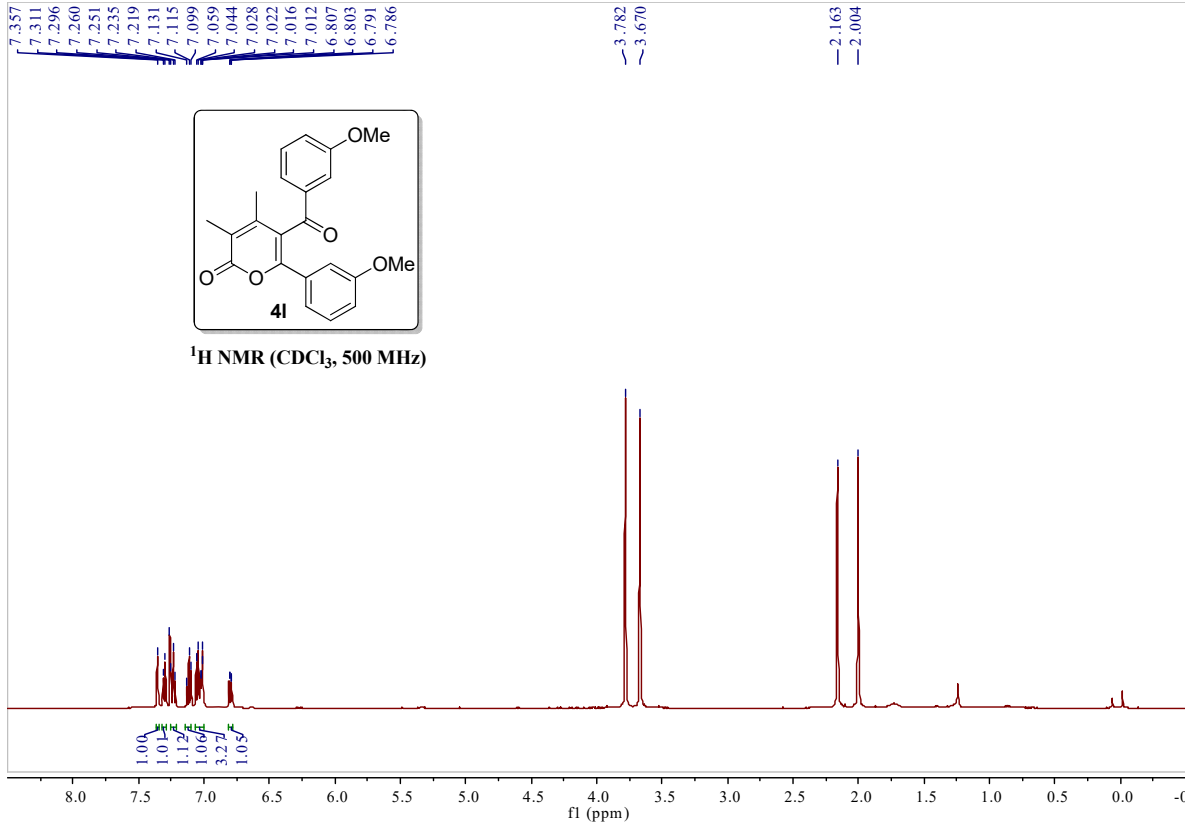


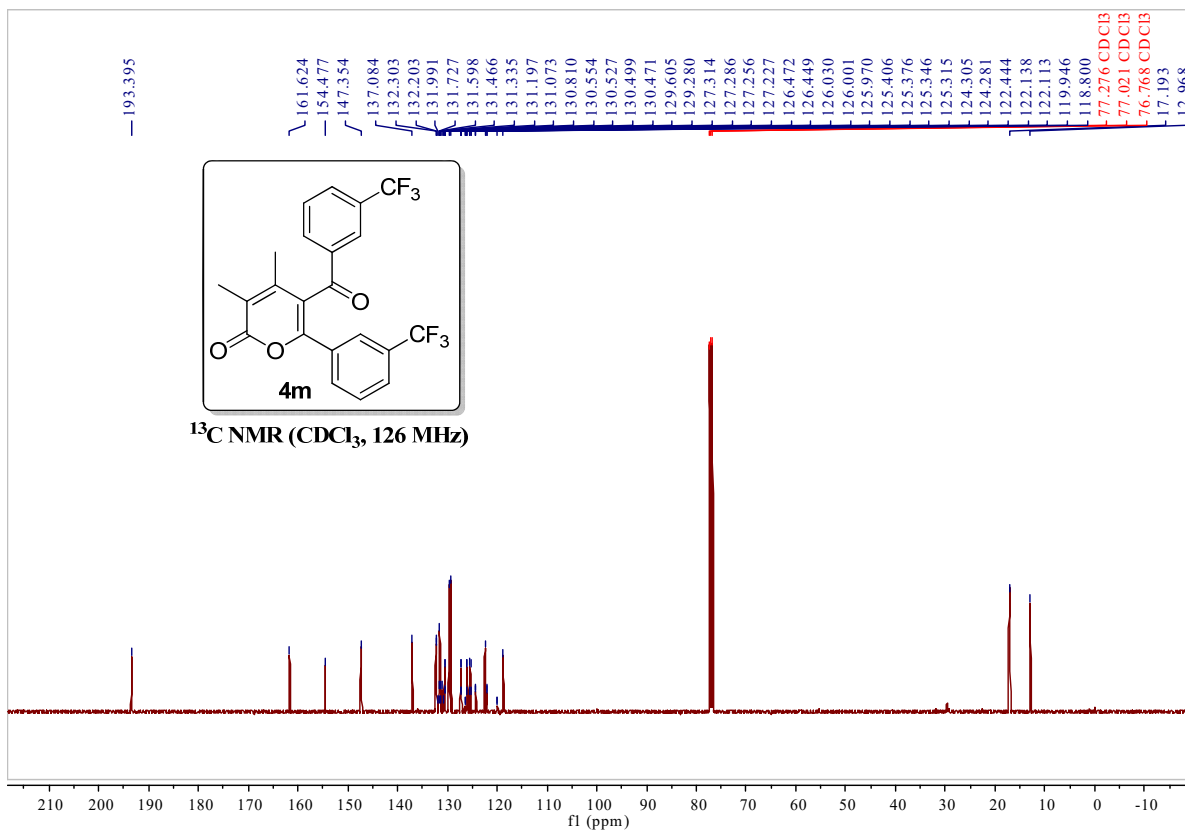
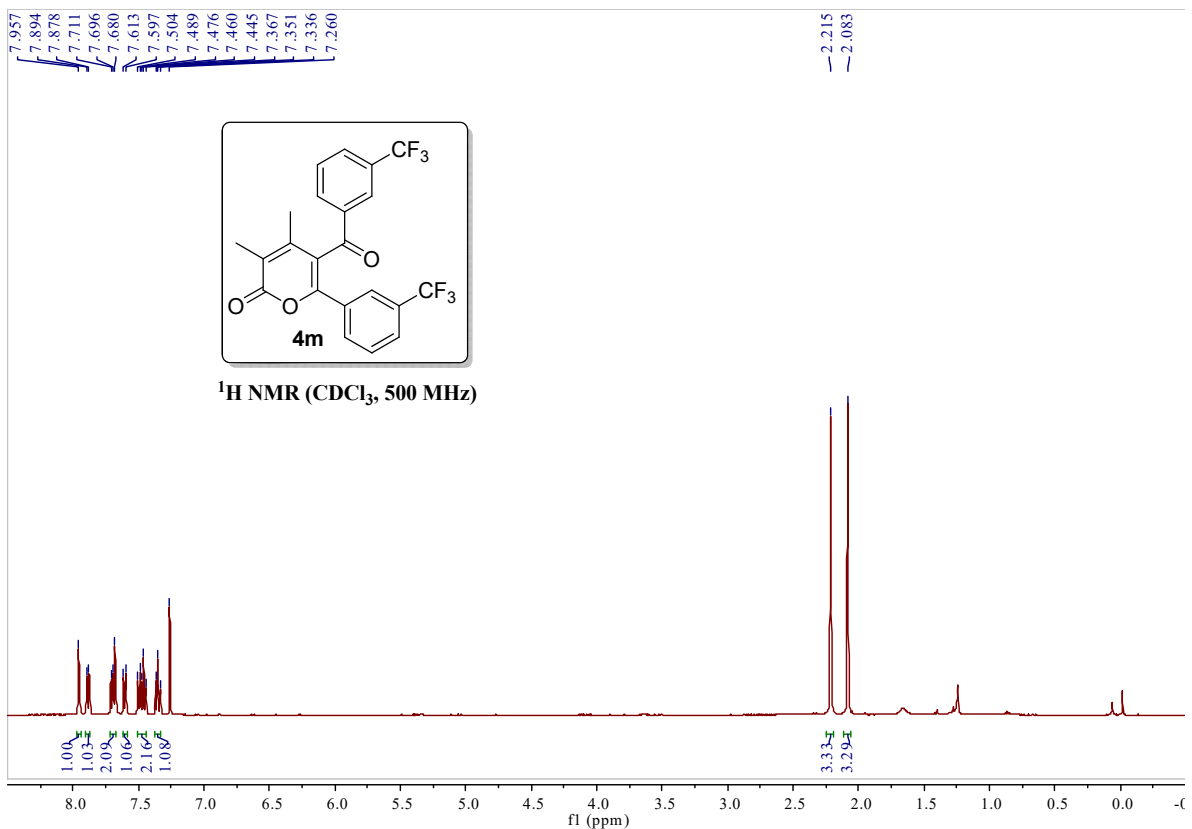


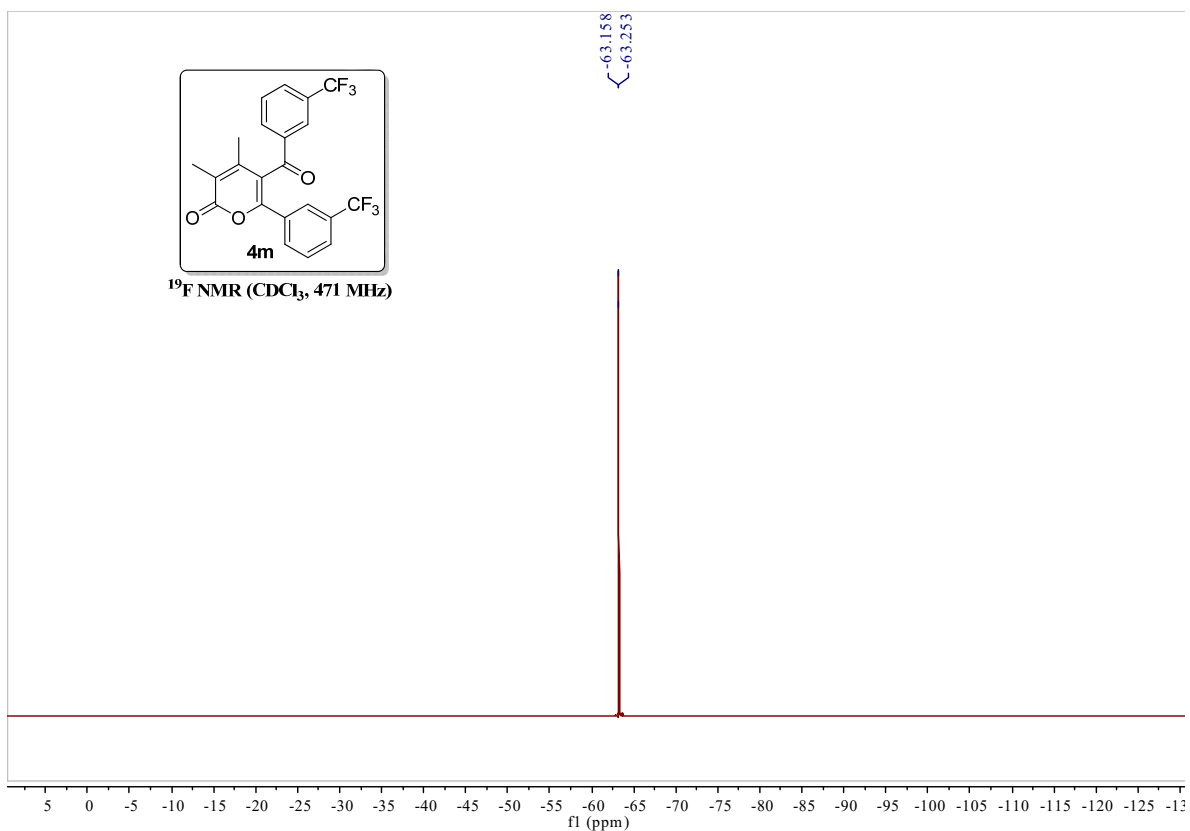












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