

## Supporting Information

### Sodium sulphide promoted synthesis of fused quinoline at room temperature.

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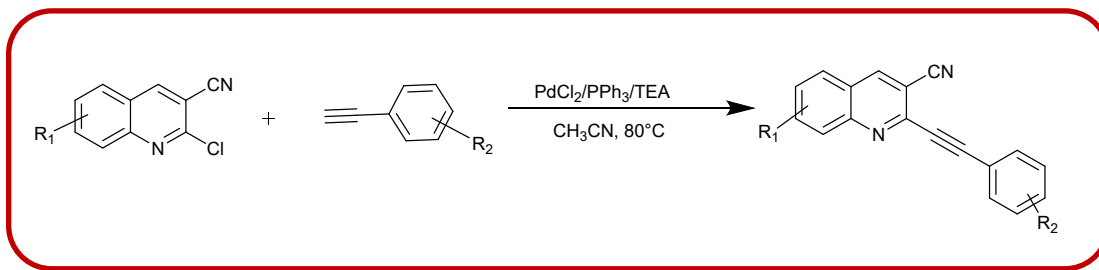
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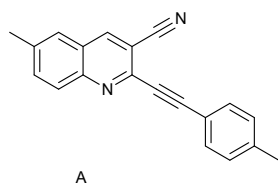
### Experimental Section:

**General Procedure-**  $^1\text{H}$ NMR spectra were recorded on JEOL Resonance ECX-500II (500 MHz); Chemical shifts (in ppm) and coupling constant (J in Hz) are calibrated either relative to internal solvent tetramethylsilane TMS ( $\delta\text{H} = 0.00\text{ppm}$ ) or  $\text{CDCl}_3$  ( $\delta\text{H} = 7.256\text{ppm}$ ). In the  $^1\text{H}$  NMR data, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, dd = double doublets, dt = double triplets, and brs = broad singlet.  $^{13}\text{C}$  NMR spectra were recorded on Jeol Resonance ECX-500II (125 MHz) in  $\text{CDCl}_3$ ; chemical shifts are calibrated relative to  $\text{CDCl}_3$  ( $\delta\text{C} = 77.0\text{ppm}$ ). IR spectra were recorded on Perkin Elmer FT-IR spectrometer -spectrum two. The reactions were monitored by Thin Layer Chromatography (TLC) using Merck silica gel plates (Merck® 60F254). The 2-(alkynyl)quinoline-3-carbonitriles were prepared according to literature procedure.<sup>[1-2]</sup>  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  was purchased from Sigma Aldrich. Solvents were purified prior to its use. Melting points of the compounds was measured by Buchi melting-point apparatus and are uncorrected.

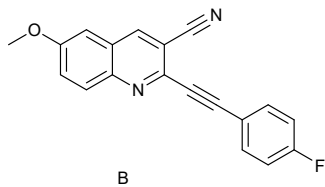
**General procedure for the synthesis of compound 2 and 3:** Solution of 2-chloroquinoline-3-carbonitrile (0.25 mmol), phenyl acetylene (0.26 mmol),  $\text{PdCl}_2$  (4 mol %),  $\text{CH}_3\text{CN}$  (4 ml) and TEA (0.5 mmol) was stirred under  $\text{N}_2$  at  $80^\circ\text{C}$  for 1.5-6 h (as monitored by TLC). The reaction mixture was concentrated in vacuo and residue obtained was purified by column chromatography hexane: ethyl acetate to afford. The Starting material of compound 2c and 3e is **A**, 2k and 3j is **B**, 3k is **C** and 3i is **D** respectively.



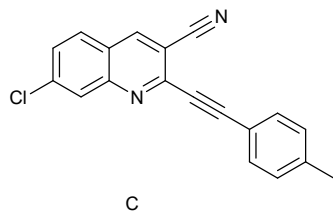
### Analytical data of the Products



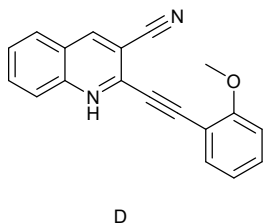
**8-methyl-2-(p-tolyethynyl)quinoline-3-carbonitrile (A):** Light Brown color solid, (88%), mp:  $165^\circ\text{C}$ . IR ( $4000\text{-}600\text{cm}^{-1}$ ):  $\nu_{\text{max}} = 2226, 2214\text{ cm}^{-1}$ .  $^1\text{H}$ NMR ( $\text{CDCl}_3$ , 500MHz): 8.47(s,1H), 7.68(dd, $J=14.9,6.8\text{Hz}$ ,3H), 7.55-7.51(m, 1H), 7.50-7.42(m,1H), 7.21(d, $J=8.0\text{Hz}$ ,2H), 2.83(s,3H), 2.40(s,3H).  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ 125MHz):  $\delta$ 147.90, 142.24, 140.49, 138.01, 133.35, 132.70, 132.43, 132.34, 131.68, 129.42, 128.45, 126.03, 125.08, 118.41, 116.90,109.57, 95.67, 86.54, 21.84, 18.07. HRMS (ESI) for  $\text{C}_{20}\text{H}_{14}\text{N}_2$  m/z  $[\text{M}+\text{H}]^+$  calculated:283.12,found:283.119.



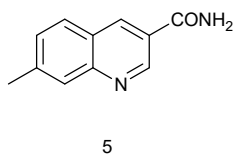
**2-((4-fluorophenyl)ethynyl)-6-methoxyquinoline-3-carbonitrile (B):** Black color solid, (88%), mp: 185°C. IR (4000-600cm<sup>-1</sup>):  $\nu_{\max}$  = 2220, 2210 cm<sup>-1</sup>. <sup>1</sup>HNMR (CDCl<sub>3</sub>, 500MHz):  $\delta$  8.39(s,1H), 8.04-8.02(d,  $J$ =9.1Hz,1H), 7.72–7.65(m,2H), 7.55–7.46(m,2H), 7.11–7.08(m,2H), 3.95(s,3H). <sup>13</sup>CNMR (CDCl<sub>3</sub>, 125MHz):  $\delta$  164.55, 162.54, 159.52, 145.01, 140.36, 134.74, 131.09, 126.41, 117.55, 116.71, 116.16, 115.98, 109.95, 105.14, 93.67, 86.12, 55.96. HRMS (ESI) for C<sub>19</sub>H<sub>12</sub>N<sub>2</sub>O m/z [M+H]<sup>+</sup>calculated: 303.0934, found: 303.0893.



**7-chloro-2-(p-tolyethynyl)quinoline-3-carbonitrile (C):** Brown color solid, (88 %), mp: 179°C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$ =2223, 2213 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz, )  $\delta$  8.49-8.48 (d,  $J$  = 8.6 Hz, 1H), 7.81 – 7.78 1H), 7.63 – 7.57 (m, 3H), 7.22-7.21 (d,  $J$  = 6.1 Hz, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, )  $\delta$  149.05, 144.31, 141.81, 141.00, 139.61, 132.82, 129.75, 129.50, 129.23, 128.62, 123.38, 117.90, 116.30, 109.98, 97.30, 85.85, 21.87. HRMS (ESI) for C<sub>19</sub>H<sub>11</sub>N<sub>2</sub>Cl m/z [M+H]<sup>+</sup> calculated: 303.0689, found: 303.0644.



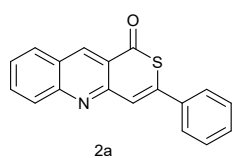
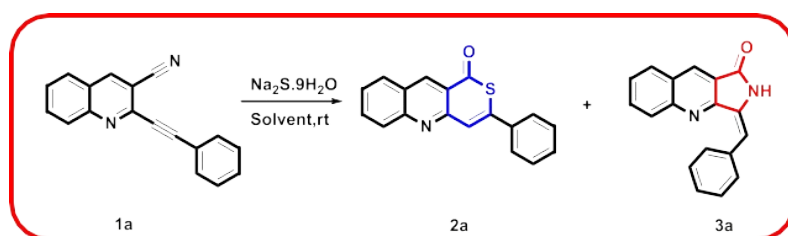
**2-((2-methoxyphenyl)ethynyl)quinoline-3-carbonitrile (D):** Black color solid, (88%), mp: 186°C. IR(4000-600cm<sup>-1</sup>):  $\nu_{\max}$ =2224, 2210cm<sup>-1</sup>. <sup>1</sup>HNMR (CDCl<sub>3</sub>,500MHz):  $\delta$  8.52 (s,1H), 8.14(d,  $J$ =84, Hz,1H), 7.94–7.81(m,2H), 7.70(d,  $J$ =55 Hz 2H), 7.68–7.56 (m,2H), 3.95(s,3H). <sup>13</sup>CNMR (CDCl<sub>3</sub>125MHz):  $\delta$  160.24, 147.84, 142.42, 141.15, 133.59, 132.30, 128.65,127.15, 124.00, 115.71, 113.43, 112.24, 108.72, 95.60, 84.79, 76.43, 76.17,75.92, 54.55. HRMS (ESI) for C<sub>19</sub>H<sub>12</sub>N<sub>2</sub>O m/z [M+H]<sup>+</sup>calculated: 285.1085, found: 285.1008.



**7-methylquinoline-3-carboxamide:** White color stiky solid, (88%), IR(4000-600cm<sup>-1</sup>):  $\nu_{\max}$ =1680, 1690cm<sup>-1</sup>. <sup>1</sup>HNMR (DMSO, 500MHz):  $\delta$  9.22 (d,  $J$ = 1.9 Hz, 1H), 8.74(d,  $J$ =1.8, Hz,1H), 7.92(d,  $J$ = 8.2Hz 1H), 7.82(s, 1H), 7.47 (d,  $J$ = 8.8 1H), 2.50(s,3H). <sup>13</sup>CNMR (DMSO, 125MHz):  $\delta$  166.67, 149.17, 141.42, 135.48, 129.50, 128.77, 127.69, 127.54, 126.16, 124.49, 21.53.

**Representative procedure for the synthesis of 3-phenyl-1*H*-thiopyrano[4,3-*b*]quinolin-1-one and (*E*)-3-benzylidene-2,3-dihydro-1*H*-pyrrolo[3,4-*b*]quinolin-1-one:**

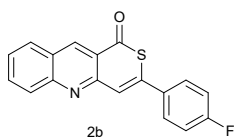
**Reaction conditions:** 2-(phenylethynyl)quinoline-3-carbonitrile (1a) (1 mmol), Na<sub>2</sub>S·9H<sub>2</sub>O (3 mmol) and DMSO (2 mL) at room temperature under air stirred for 15h and 30 h consequently h (as monitored by TLC). Chilled water was added to work up reaction. The reaction mixture was then extracted with EtOAc. Organic phase was washed with water, brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Solvent was then removed under reduced pressure and residue obtained was purified by column chromatography (hexane: ethyl acetate) to afford (2a-2m and 3a-3p).



**3-phenyl-1*H*-thiopyrano[4,3-*b*]quinolin-1-one(2a):** Brown color solid, (84 %), mp: 186 °C.

IR (4000-600 cm<sup>-1</sup>): ν<sub>max</sub> = 1688, 1615, 1580 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ<sub>H</sub> (ppm) 9.13 (s, 1H), 8.15 (d, 1H, *J* = 8.5 Hz), 8.09 (d, 1H, *J* = 8.0 Hz), 7.90 (t, 1H, *J* = 6.5 Hz), 7.82 (s, 1H), 7.71-7.77 (m, 2H), 7.63 (t, 1H, *J* = 7.0 Hz), 7.46-7.53 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):

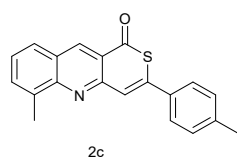
δ<sub>c</sub> (ppm) 187.8, 153.8, 151.1, 142.6, 136.7, 136.4, 133.4, 130.2, 130.0, 129.4, 129.2, 127.6, 127.1, 126.9, 122.3, 121.5. HR-MS (ESI) for C<sub>18</sub>H<sub>11</sub>NOS m/z [M+H]<sup>+</sup> calculated.: 290.0639, found: 290.0615.



**3-(4-fluorophenyl)-1*H*-thiopyrano[4,3-*b*]quinolin-1-one (2b):** Brown color solid, (88

%), mp: 248 °C. IR (4000-600 cm<sup>-1</sup>): ν<sub>max</sub> = 1651, 1617, 1604cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ<sub>H</sub> (ppm) 9.15 (s, 1H), 8.16 (d, 1H, *J* = 8.5 Hz), 8.05 (d, 1H, *J* = 8.0 Hz), 7.92 (t, 1H, *J* = 7.5 Hz), 7.78 (s, 1H), 7.65-7.73 (m, 2H), 7.64 (t, 1H, *J* = 7.5 Hz), 7.20 (t, 2H, *J* = 8.5

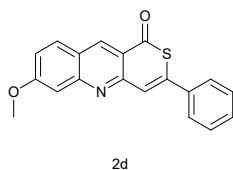
Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub> with few drops of DMSO-*d*<sub>6</sub>, 125 MHz): δ<sub>c</sub> (ppm) 187.1, 164.7, 162.6, 153.4, 150.8, 141.0, 136.2, 133.3, 132.6, 132.6, 129.7, 128.9, 128.6, 128.5, 127.4, 126.8, 121.9, 121.3, 116.3, 116.1. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 500 MHz): δ -110.09, HR-MS (ESI) for C<sub>18</sub>H<sub>10</sub>NFOS m/z [M+ H]<sup>+</sup> calculated: 308.0545, found: 308.0512.



**6-methyl-3-(*p*-tolyl)-1*H*-thiopyrano[4,3-*b*]quinolin-1-one (2c):** Yellow color solid,

(86%), mp: 211 °C. IR (4000-600 cm<sup>-1</sup>): ν<sub>max</sub> = 1650, 1610, 1508 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ<sub>H</sub> (ppm) 9.04 (s, 1H), 7.79-7.89 (m, 2H), 7.48 (t, 1H, *J* = 8.0 Hz), 7.70 (d, 1H, *J* = 7.0 Hz), 7.62 (d, 2H, *J* = 8.0 Hz), 7.29 (d, 2H, *J* = 8.0 Hz), 2.85 (s, 3H), 2.42 (s, 3H). <sup>13</sup>C

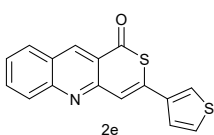
NMR (CDCl<sub>3</sub>, 125 MHz): δ<sub>c</sub> (ppm) 188.5, 153.0, 150.01, 141.8, 140.4, 137.5, 136.3, 134.0, 133.0, 130.0, 127.9, 127.3, 127.1, 126.7, 122.1, 121.6, 21.3, 18.8. HR-MS (ESI) for C<sub>20</sub>H<sub>15</sub>NOS m/z [M+H]<sup>+</sup> calculated: 318.0952, found: 318.0929.



**7-methoxy-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2d):** Brown color solid, (94 %), mp: 166 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1649, 1623, 1577 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 9.12 (s, 1H), 8.01 (s, 1H), 7.73 (d, 2H,  $J$  = 7.0 Hz), 7.63 (d, 1H,  $J$  = 8.0 Hz), 7.56 (t, 1H,  $J$  = 8.0 Hz), 7.45-7.52 (m, 3H), 7.23 (d, 1H,  $J$  = 7.5 Hz), 4.17 (s, 3H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 188.1, 154.1, 152.7, 143.1, 141.9, 136.5, 136.0,

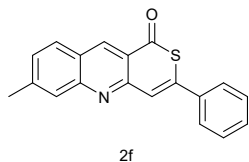
129.9, 129.1, 128.1, 127.6, 122.5, 121.8, 121.4, 110.5, 56.3. HR-MS (ESI) for C<sub>19</sub>H<sub>13</sub>NO<sub>2</sub>S m/z [M + H]<sup>+</sup> calculated: 320.0745, found: 320.0710.



**3-(thiophen-3-yl)-1H-thiopyrano[4,3-b]quinolin-1-one (2e):** Black color solid, (90%),

mp: 195 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1642, 1555, 1576 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 9.09 (s, 1H), 8.13 (d, 1H,  $J$  = 8.6 Hz), 8.01 (d, 1H,  $J$  = 8.0 Hz), 7.91-7.87 (m, 1H), 7.80 (s, 1H), 7.68-7.65 (m, 1H), 7.63-7.59 (m, 1H), 7.52-7.50 (m, 1H), 7.47 (dd,  $J$  = 48.29

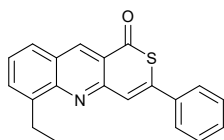
Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 187.0, 153.7, 151.1, 137.9, 136.9, 136.5, 133.5, 130.0, 129.1, 127.6, 127.5, 127.0, 125.1, 124.1, 122.6, 120.2. HR-MS (ESI) for C<sub>19</sub>H<sub>13</sub>NO<sub>2</sub>S m/z [M+H]<sup>+</sup> calculated: 296.0204, found: 296.0172.



**7-methyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2f):** Light green color solid,

(84%), mp: 182 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1624, 1586, 1492, cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 9.09 (s, 1H), 7.93 (d,  $J$  = 7.4 Hz, 2H), 7.81 (s, 1H), 7.73 (d,  $J$  = 6.8 Hz, 2H), 7.48 (dd,  $J$  = 16.0, 8.0 Hz, 4H), 2.63 (s, 3H). <sup>13</sup>C NMR

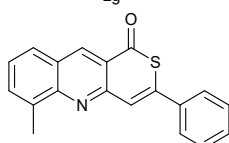
(CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 187.49, 154.10, 153.97, 151.39, 144.36, 142.53, 136.80, 136.03, 130.16, 129.62, 129.36, 128.01, 126.89, 125.37, 121.90, 121.69, 22.38. HR-MS (ESI) for C<sub>19</sub>H<sub>13</sub>NOS m/z [M+H]<sup>+</sup> calculated: 304.0796, found: 304.0752.



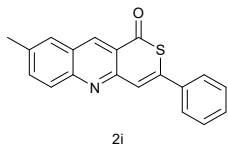
**6-ethyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2g):** Yellow color solid, (82%), mp:

188 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1646, 1608, 1561 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 9.08 (s, 1H), 7.84-7.90 (m, 2H), 7.70-7.77 (m, 3H), 7.44-7.58 (m, 4H), 3.37 (q, 2H,  $J$  = 7.5 Hz), 1.42 (t, 3H,  $J$  = 7.5 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 188.0, 152.6, 149.6,

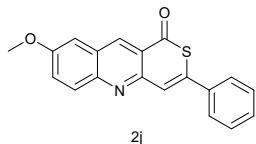
143.1, 141.4, 136.8, 136.2, 131.3, 129.9, 129.1, 127.7, 127.4, 127.1, 126.8, 122.3, 121.9, 24.5, 14.9. HR-MS (ESI) for C<sub>20</sub>H<sub>15</sub>NOS m/z [M+H]<sup>+</sup> calculated: 318.0953, found: 318.0933.



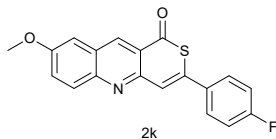
**6-methyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2h):** Light green color solid, (83 %), mp: 176 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1651, 1598, 1578 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 9.09 (s, 1H), 7.86-7.90 (m, 2H), 7.71-7.77 (m, 3H), 7.46-7.54 (m, 4H), 2.87 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 188.19, 152.90, 150.36, 141.77, 137.56, 136.89, 136.36, 133.08, 130.06, 129.31, 127.91, 127.39, 127.18, 126.95, 122.34, 122.14, 18.29. HR-MS (ESI) for C<sub>19</sub>H<sub>13</sub>NOS m/z [M+H]<sup>+</sup> calculated: 304.0796, found: 304.0764.



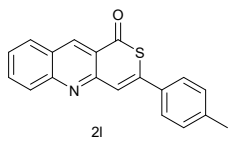
**8-methyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2i):** Light green color solid, (90 %), mp: 198°C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1650, 1622, 1575 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 9.03 (s, 1H), 8.05 (d, 1H,  $J$  = 8.5 Hz), 7.80 (m, 2H), 7.70-7.75 (m, 3H), 7.45-7.53 (m, 3H), 2.59 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 187.96, 153.01, 149.72, 141.85, 137.75, 136.68, 135.96, 135.32, 130.05, 129.29, 128.35, 127.12, 126.77, 122.30, 121.50, 21.81. HR-MS (ESI) for C<sub>19</sub>H<sub>13</sub>NOS m/z [M+H]<sup>+</sup> calculated: 304.0796, found: 304.0776.



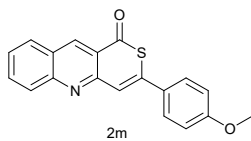
**8-methoxy-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2j):** Light green color solid, (92 %), mp: 220°C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1639, 1620, 1578 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 8.97 (s, 1H), 8.03 (d, 1H,  $J$  = 9.5 Hz), 7.78 (s, 1H), 7.67-7.73 (m, 2H), 7.54 (dd, 1H,  $J$  = 8.5 Hz,  $J$  = 2.5 Hz), 7.43-7.52 (m, 3H), 7.21 (d, 1H,  $J$  = 2.5 Hz), 4.00 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 188.0, 158.6, 151.8, 147.7, 141.0, 136.8, 134.2, 130.6, 130.0, 129.3, 128.3, 127.4, 126.8, 122.5, 121.5, 106.1, 55.9. HR-MS (ESI) for C<sub>19</sub>H<sub>13</sub>NO<sub>2</sub>S m/z [M+H]<sup>+</sup> calculated: 320.0745, found: 320.0723.



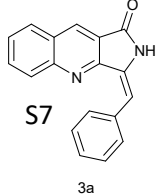
**3-(4-fluorophenyl)-8-methoxy-1H-thiopyrano[4,3-b]quinolin-1-one (2k):** Light green color solid, (91 %), mp: 263 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1650, 1625, 1573 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 9.04 (s, 1H), 8.09 (d,  $J$  = 9.2 Hz, 1H), 7.74 (dd,  $J$  = 15.6, 10.3 Hz, 2H), 7.60 (dd,  $J$  = 9.2, 2.2 Hz, 1H), 7.30-7.20 (m, 4H), 4.02 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz, )  $\delta$  187.73, 164.86, 162.87, 158.71, 151.75, 147.79, 139.97, 134.29, 133.05, 130.71, 128.80, 128.74, 128.43, 127.54, 122.45, 121.65, 116.57, 116.39, 105.91, 77.41, 55.95. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  -110.50. HR-MS (ESI) for C<sub>19</sub>H<sub>12</sub>FN<sub>2</sub>O<sub>2</sub>S m/z [M+H]<sup>+</sup> calculated: 338.0651, found: 338.0638.



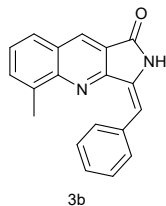
**3-(p-tolyl)-1H-thiopyrano[4,3-b]quinolin-1-one (2l):** Yellow color solid, (88%), mp: 175°C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1645, 1617, 1600 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 9.14 (s, 1H), 8.17 (d, 1H,  $J$  = 9.0 Hz), 8.04 (d, 1H,  $J$  = 8.0 Hz), 7.91 (t, 1H,  $J$  = 7.0 Hz), 7.82 (s, 1H), 7.60-7.65 (m, 3H), 7.31 (d, 2H,  $J$  = 7.5 Hz), 2.43 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub> in few drops of DMSO-d<sub>6</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 187.6, 153.7, 150.7, 140.6, 136.5, 133.6, 133.5, 129.9, 129.9, 128.8, 127.4, 126.9, 126.5, 122.1, 120.4, 21.2. HR-MS (ESI) for C<sub>19</sub>H<sub>13</sub>NOS m/z [M + H]<sup>+</sup> calculated: 304.0796, found: 304.0765



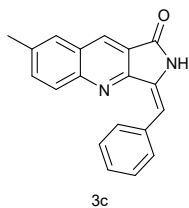
**3-(4-methoxyphenyl)-1H-thiopyrano[4,3-b]quinolin-1-one (2m):** Light green color solid, (86 %), mp: 242 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1633, 1615, 1588 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 9.07 (s, 1H), 8.09 (d, 1H,  $J$  = 9.0 Hz), 7.99 (d, 1H,  $J$  = 8.5 Hz), 7.62 (d, 2H,  $J$  = 8.5 Hz), 7.57 (t, 1H,  $J$  = 8.0 Hz), 7.71 (s, 1H), 7.85 (t, 1H,  $J$  = 8.0 Hz), 6.97 (d, 2H,  $J$  = 9.0 Hz), 3.83 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub> with few drops of DMSO-d<sub>6</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 187.4, 161.3, 154.0, 151.0, 142.3, 136.3, 133.4, 129.9, 128.9, 128.1, 127.3, 126.9, 122.1, 119.9, 114.7, 55.8. HR-MS (ESI) for C<sub>19</sub>H<sub>13</sub>NO<sub>2</sub>S m/z [M+H]<sup>+</sup> calculated: 320.0745, found: 320.0776.



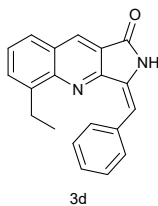
**(E)-3-benzylidene-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3a):** Brown color solid, (82 %), mp: 262°C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1708, 1626, 1504 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub> with few drops of DMSO-d<sub>6</sub>, 500 MHz):  $\delta_{\text{H}}$ (ppm)  $\delta$  9.43 (brs, NH), 8.69 (s, 1H), 8.25 (d,  $J$  = 8.5 Hz, 1H), 8.04 (d,  $J$  = 8.1 Hz, 1H), 7.88 (t,  $J$  = 7.5 Hz, 1H), 7.63 (dd,  $J$  = 19.7, 7.4 Hz, 3H), 7.46 (t,  $J$  = 7.3 Hz, 2H), 7.34 (d,  $J$  = 4.6 Hz, 1H), 7.22 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm)  $\delta$  166.51, 155.35, 150.84, 133.25, 132.23, 132.15, 130.04, 129.88, 129.48, 128.87, 128.27, 127.89, 127.35, 107.10. HR-MS (ESI) for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O m/z [M+H]<sup>+</sup> calculated: 273.1028, found: 273.1016.



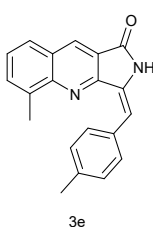
**(E)-3-benzylidene-5-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3b):** Light green color solid, (84%), mp: 270°C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1716, 1630, 1505 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 8.65 (s, 1H), 8.24 (s, 1H), 7.86 (d, 1H,  $J$  = 8.0 Hz), 7.72 (d, 1H,  $J$  = 6.5 Hz), 7.50-7.56 (m, 3H), 7.48 (t, 2H,  $J$  = 7.5 Hz), 7.35 (t, 1H,  $J$  = 7.0 Hz), 7.27 (m, 1H), 2.94 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 166.9, 154.2, 149.4, 137.5, 134.4, 132.5, 132.2, 131.6, 128.9, 128.8, 127.5, 127.4, 126.5, 120.1, 106.0, 18.5. HR-MS (ESI) for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O m/z [M+H]<sup>+</sup> calculated: 287.1184, found: 287.1171.



**(E)-3-benzylidene-7-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3c):** Light green color solid, (83%), mp: 268 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1704, 1688, 1494 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 8.87 (brs, NH), 8.57 (s, 1H), 8.14 (d, 1H,  $J$  = 8.5 Hz), 7.75 (s, 1H), 7.68 (d, 1H,  $J$  = 8.5 Hz), 7.54 (d, 2H,  $J$  = 7.5 Hz), 7.43 (t, 2H,  $J$  = 7.5 Hz), 7.30 (t, 1H,  $J$  = 7.5 Hz), 7.21 (s, 1H), 2.56 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 166.7, 154.6, 149.5, 137.5, 135.0, 134.6, 132.4, 132.3, 129.4, 128.8, 128.8, 128.2, 128.0, 120.8, 106.7, 21.7. HR-MS (ESI) for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O m/z [M+H]<sup>+</sup> calculated: 287.1184, found: 287.1148.

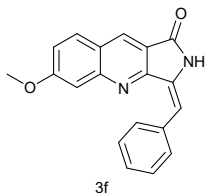


**(E)-3-benzylidene-5-ethyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3d):** yellow color solid, (88 %), mp: 238 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1718, 1629, 1505 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 8.65 (s, 1H), 8.24 (brs, NH), 7.86 (d, 1H,  $J$  = 8.0 Hz), 7.72 (d, 1H,  $J$  = 7.0 Hz), 7.51-7.60 (m, 3H), 7.48 (t, 2H,  $J$  = 7.5 Hz), 7.35 (t, 1H,  $J$  = 7.5 Hz), 7.23 (s, 1H), 3.44 (q, 2H,  $J$  = 7.0 Hz), 1.45 (t, 3H,  $J$  = 7.5 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub> with few drops of DMSO-d<sub>6</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 166.7, 154.2, 148.9, 143.4, 134.7, 132.5, 132.5, 132.4, 130.0, 128.8, 128.8, 127.6, 127.4, 126.6, 120.1, 105.9, 24.4, 14.8. HR-MS (ESI) for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O m/z [M+H]<sup>+</sup> calculated: 301.1341, found: 301.1321.

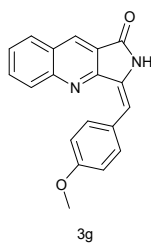


**(E)-5-methyl-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3e):** Brown color solid, (84 %), mp: 241 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 17011, 1635, 1507 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 8.63 (s, 1H), 8.40 (brs, NH), 7.84 (d, 1H,  $J$  = 8.5 Hz), 7.70 (d, 1H,  $J$  = 7.0 Hz), 7.50 (t, 1H,  $J$  = 7.5 Hz), 7.44 (d, 2H,  $J$  = 8.0 Hz), 7.28 (d, 2H,  $J$  = 8.0 Hz), 7.22 (s, 1H), 2.92 (s, 3H), 2.41 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 166.6, 154.2,

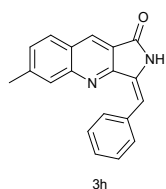
149.8, 138.1, 137.9, 133.0, 132.0, 131.9, 131.8, 130.0, 128.6, 127.8, 127.6, 126.8, 120.1, 106.6, 21.4, 18.2. HR-MS (ESI) for  $C_{20}H_{16}N_2O$   $m/z$   $[M+H]^+$  calculated: 301.1341, found: 301.1299.



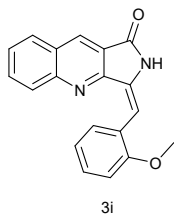
**(E)-3-benzylidene-6-methoxy-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3f):** Light brown color solid, (85 %), mp: 242 °C. IR (4000-600  $cm^{-1}$ ):  $\nu_{max}$  = 1707, 1688, 1502  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , with few drops of DMSO- $d_6$ , 500 MHz):  $\delta_H$  (ppm) 9.26 (brs, NH), 8.45 (s, 1H), 7.78 (d, 1H,  $J$  = 9.0 Hz), 7.49 (d, 2H,  $J$  = 5.0 Hz), 7.42 (s, 1H), 7.34 (t, 2H,  $J$  = 8.0 Hz), 7.21 (t, 1H,  $J$  = 7.5 Hz), 7.16 (dd, 1H,  $J$  = 9.5 Hz,  $J$  = 3.0 Hz), 7.04 (s, 1H), 3.91 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$ , in few drops of DMSO- $d_6$ , 125 MHz):  $\delta_C$  (ppm) 167.0, 1622.5, 156.0, 155.7, 152.6, 134.5, 132.1, 132.1, 128.9, 127.7, 122.9, 120.4, 118.7, 107.3, 106.3, 106.4, 55.6. HR-MS (ESI) for  $C_{19}H_{14}N_2O_2$   $m/z$   $[M+H]^+$  calculated: 303.1134, found: 303.1134.



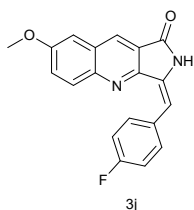
**(E)-3-(4-methoxybenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3g):** Light green color solid, (90%), mp: 222 °C. IR (4000-600  $cm^{-1}$ ):  $\nu_{max}$  = 1709, 1626, 1600  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta_H$  (ppm) 8.84 (brs, NH), 8.67 (s, 1H), 8.22 (d, 1H,  $J$  = 8.5 Hz), 8.00 (d, 1H,  $J$  = 8.0 Hz), 7.85 (t, 1H,  $J$  = 7.5 Hz), 7.61 (t, 1H,  $J$  = 7.5 Hz), 7.53 (d, 2H,  $J$  = 8.5 Hz), 7.18 (s, 1H), 6.99 (d, 2H,  $J$  = 8.5 Hz), 3.86 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz):  $\delta_C$  (ppm) 166.8, 159.6, 155.5, 150.8, 133.1, 132.0, 130.6, 130.5, 130.0, 129.8, 127.7, 127.3, 127.1, 120.7, 114.9, 107.3, 55.5. HR-MS (ESI) for  $C_{19}H_{14}N_2O_2$   $m/z$   $[M+H]^+$  calculated: 303.1133, found: 303.1096.



**(E)-3-benzylidene-6-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3h):** Yellow color solid, (86 %), mp: 272 °C. IR (4000-600  $cm^{-1}$ ):  $\nu_{max}$  = 1711, 1620, 1507  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta_H$  (ppm) 8.63 (s, 1H), 8.37 (brs, NH), 8.03 (s, 1H), 7.91 (d, 1H,  $J$  = 8.5 Hz), 7.54 (d, 2H,  $J$  = 7.5 Hz), 7.47 (t, 3H,  $J$  = 7.5 Hz), 7.34 (t, 1H,  $J$  = 7.0 Hz), 7.21 (s, 1H), 2.63 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz):  $\delta_C$  (ppm) 166.7, 155.5, 151.1, 143.0, 134.9, 132.8, 132.4, 129.7, 129.6, 129.5, 128.9, 128.9, 128.2, 126.0, 120.1, 106.8, 22.3. HR-MS (ESI) for  $C_{19}H_{14}N_2O$   $m/z$   $[M+H]^+$  calculated: 303.1134, found: 303.1147.



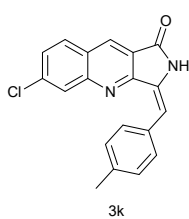
**(E)-3-(2-methoxybenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3i):** Brown color solid, (91 %), mp: 218 °C. IR (4000-600  $cm^{-1}$ ):  $\nu_{max}$  = 1712, 1625, 1490  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta_H$  (ppm) 8.95 (brs, NH), 8.92 (s, 1H), 8.25 (d, 1H,  $J$  = 9.0 Hz), 8.02 (d, 1H,  $J$  = 8.0 Hz), 7.86 (t, 1H,  $J$  = 7.0 Hz), 7.62 (t, 1H,  $J$  = 8.0 Hz), 7.49 (d, 1H,  $J$  = 7.5 Hz), 7.35 (t, 1H,  $J$  = 8.0 Hz), 7.23-7.26 (m, 1H), 7.07 (t, 1H,  $J$  = 7.5 Hz), 7.02 (d, 1H,  $J$  = 8.5 Hz), 4.00 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$  with few drops of DMSO- $d_6$ , 125 MHz):  $\delta_C$  (ppm) 165.8, 156.5, 155.6, 150.7, 133.0, 132.0, 131.9, 131.8, 130.0, 129.9, 129.8, 127.8, 127.1, 123.8, 121.7, 121.2, 112.1, 104.0, 56.2. HR-MS (ESI) for  $C_{19}H_{14}N_2O_2$   $m/z$   $[M+H]^+$  calculated: 303.1133, found: 303.1096.



**(E)-3-(4-fluorobenzylidene)-7-methoxy-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3j):**

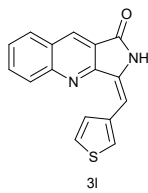


Brown color solid, (90 %), mp: 257 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1711, 1627, 1507 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$   $\delta$  8.52 (s, 1H), 7.57 (d,  $J$  = 9.3 Hz, 1H), 7.21 (dd,  $J$  = 8.1, 5.3 Hz, 2H), 7.09 (dd,  $J$  = 9.2, 2.2 Hz, 1H), 6.82 – 6.66 (m, 4H), 3.51 (s, 3H). (ppm). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) <sup>13</sup>C NMR (125 MHz, )  $\delta$  166.66, 158.08, 146.73, 131.96, 130.77, 130.45, 130.39, 128.79, 124.61, 120.96, 115.94, 115.77, 106.75, 104.49, 101.89, 55.30. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  -112.57, HR-MS (ESI) for C<sub>19</sub>H<sub>13</sub>FN<sub>2</sub>O<sub>2</sub> m/z [M + H]<sup>+</sup> calculated: 321.1039, found: 321.1034

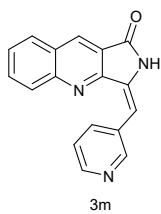


**(E)-6-chloro-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one**

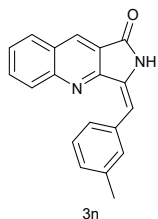
**(3k):** Light green color solid, (92%), mp: 265 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1715, 1623, 1603 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm).  $\delta$  8.69 (s, 1H), 8.30 (d,  $J$  = 17.3 Hz, 1H), 7.99 (d,  $J$  = 8.7 Hz, 1H), 7.62 (d,  $J$  = 8.3 Hz, 1H), 7.46 (d,  $J$  = 7.9 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.24 (s, 1H), 2.44 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 165.7, 155.8, 150.8, 138.3, 137.8, 132.6, 131.4, 130.8, 130.6, 129.8, 128.5, 127.9, 125.7, 120.5, 107.3, 20.9. HR-MS (ESI) for C<sub>19</sub>H<sub>13</sub>ClN<sub>2</sub>O m/z [M+H]<sup>+</sup> calculated: 321.0794, found: 321.0762.



**(E)-3-(thiophen-3-ylmethylene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3l):** Black color solid, (81 %), mp: 279 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1708, 1628, 1506 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 8.70 (s, 1H), 8.40 (brs, NH), 8.23 (d, 1H,  $J$  = 8.5 Hz), 8.02 (d, 1H,  $J$  = 8.0 Hz), 7.87 (t, 1H,  $J$  = 8.0 Hz), 7.64 (t, 1H,  $J$  = 7.5 Hz), 7.45-7.51 (m, 2H), 7.33 (d, 1H,  $J$  = 4.5 Hz), 7.20-7.24 (m 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 166.4, 161.0, 156.7, 155.4, 150.9, 135.8, 133.3, 132.1, 130.1, 129.9, 127.8, 127.6, 127.4, 127.3, 124.9, 101.7. HR-MS (ESI) for C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>OS m/z [M+H]<sup>+</sup> calculated: 279.0592, found: 279.0542.

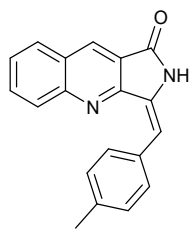


**(E)-3-(pyridine-3-ylmethylene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3m):** Brown color solid, (94 %), mp: 196 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1732, 1665, 1587 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm) 11.43 (brs, NH), 8.68 (s, 1H), 8.64 (d, 1H,  $J$  = 4.5 Hz), 8.25 (d, 1H,  $J$  = 9.0 Hz), 8.03 (d, 1H,  $J$  = 8.0 Hz), 7.87 (dt, 1H,  $J$  = 7.0 Hz,  $J$  = 1.5 Hz), 7.72 (dt, 1H,  $J$  = 7.5 Hz,  $J$  = 1.5 Hz), 7.65 (t, 1H,  $J$  = 7.0 Hz), 7.42 (d, 1H,  $J$  = 7.5 Hz), 7.14-7.19 (m, 1H), 6.99 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta_{\text{C}}$  (ppm) 166.2, 155.7, 155.7, 150.6, 149.3, 137.2, 137.0, 133.1, 132.0, 130.1, 129.9, 128.1, 127.5, 125.3, 121.7, 121.6, 102.8. HR-MS (ESI) for C<sub>18</sub>H<sub>12</sub>N<sub>2</sub>O m/z [M+H]<sup>+</sup> calculated: 274.0980, found: 274.1062.



**(E)-3-(3-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3n):** Brown color solid, (83%), mp: 256 °C. IR (4000-600 cm<sup>-1</sup>):  $\nu_{\max}$  = 1709, 1623, 1506 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta_{\text{H}}$  (ppm).  $\delta$  8.70 (s, 1H), 8.39– 8.32 (m, 1H), 8.26 (d,  $J$  = 8.5 Hz, 1H), 8.04 (d,  $J$  = 8.1 Hz, 1H), 7.88 (t,  $J$  = 7.6 Hz, 1H), 7.65 (t,  $J$  = 7.4 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.18 (dd,  $J$  = 22.0, 14.9 Hz, 2H), 2.43 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub> with few drops of DMSO d<sub>6</sub>, 125

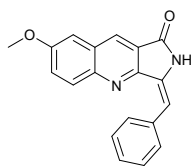
MHz):  $\delta_c$  (ppm)  $\delta$  166.70, 155.47, 150.43, 142.15, 140.77, 138.59, 134.36, 132.55, 131.73, 131.63, 129.69, 129.47, 129.44, 128.80, 128.64, 127.88, 127.75, 127.67, 127.54, 126.85, 126.23, 125.31, 124.36, 120.67, 106.87, 21.26. HR-MS (ESI) for  $C_{20}H_{15}NO$   $m/z$   $[M + H]^+$  calculated: 287.1184, found: 287.1154.



3o

**(E)-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3o):** Light green color solid, (88 %), mp: 268 °C. IR (4000-600  $cm^{-1}$ ):  $\nu_{max}$  = 1709, 1623, 1506  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , 500 MHz):  $\delta_H$  (ppm)  $\delta$  8.69 (s, 1H), 8.42 (s, 1H), 8.25 (d,  $J$  = 8.5 Hz, 1H), 8.03 (d,  $J$  = 8.5 Hz, 1H), 7.89 – 7.86 (m, 1H), 7.64 (t,  $J$  = 7.1 Hz, 1H), 7.44 (d,  $J$  = 7.8 Hz, 2H), 7.28 (d,  $J$  = 7.9 Hz, 2H), 7.22 (s, 1H), 2.41 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$  with few drops  $DMSO-d_6$ , 125 MHz):  $\delta_c$  (ppm)  $\delta$  166.66, 155.49, 150.47, 137.95, 132.67, 132.62, 131.68, 131.61, 131.22,

129.73, 129.47, 128.92, 127.54, 126.86, 120.65, 106.98, 21.25. HRMS (ESI) for  $C_{19}H_{14}N_2O$   $m/z$   $[M + H]^+$  calculated: 287.1184, found: 287.1171.



3p

**(E)-3-benzylidene-7-methoxy-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3p):** Light brown color solid, (88 %), mp: 242 °C. IR (4000-600  $cm^{-1}$ ):  $\nu_{max}$  = 1710, 1634, 1508  $cm^{-1}$ .  $^1H$  NMR ( $CDCl_3$ , 500 MHz, ) :  $\delta_H$  (ppm)  $\delta$  8.41 (s, 1H), 8.05 (d,  $J$  = 9.2 Hz, 1H), 7.73 (s, 3H), 7.54–7.51 (m, 1H), 7.44 – 7.39 (m, 4H), 7.09 (s, 1H), 3.97 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 125 MHz, )  $\delta$  166.68, 158.44, 153.22, 147.05, 135.02, 132.33, 131.48, 131.11, 129.44, 129.14, 128.80, 128.09, 121.07,

106.92, 106.39, 55.89. HR-MS (ESI) for  $C_{19}H_{14}N_2O$   $m/z$   $[M+H]^+$  calculated: 303.1134, found: 303.1097.

### Crystal data of the product:

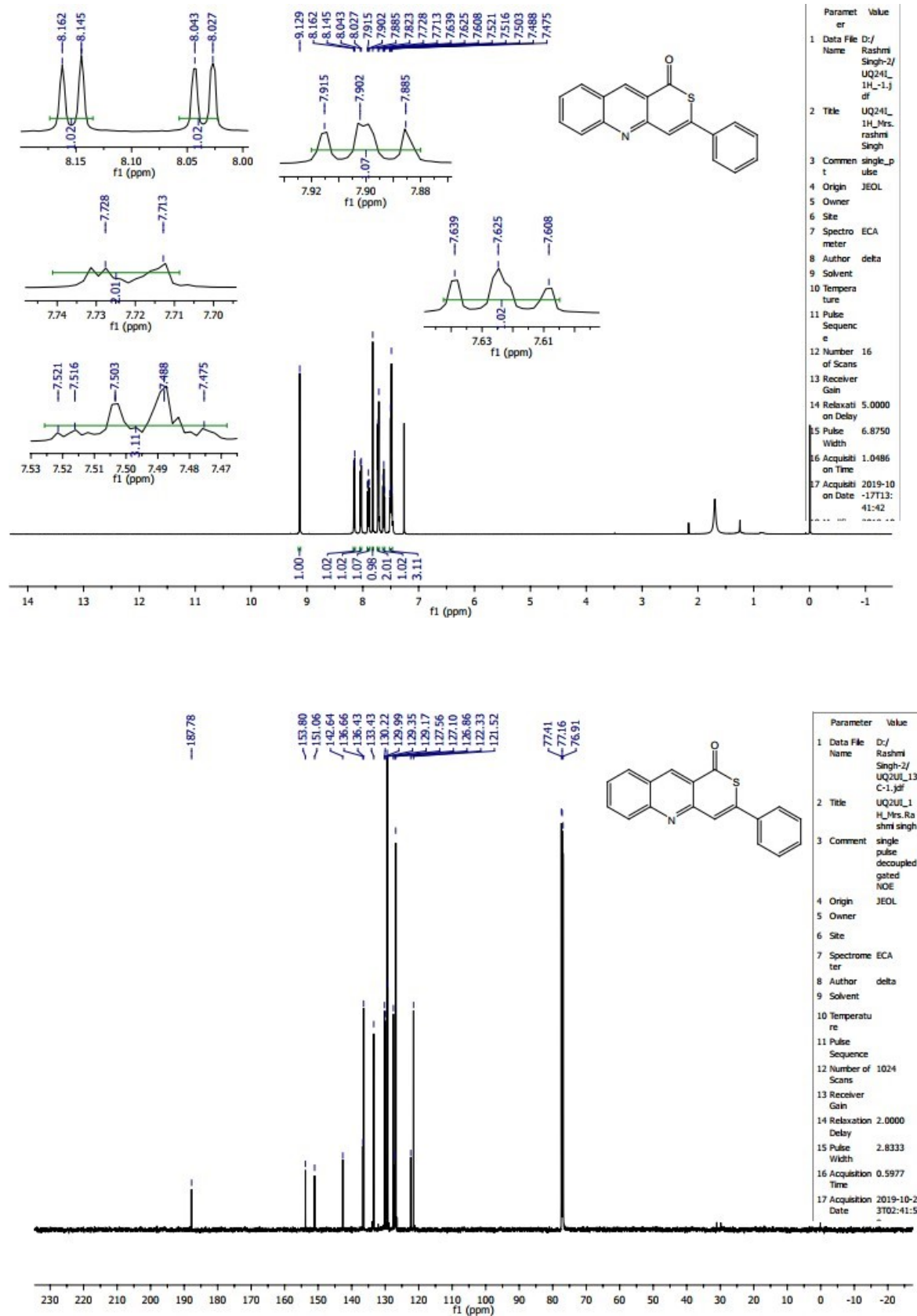
Crystal data were recorded on an Bruker single crystal X-ray diffractometer using graphite monochromatized Mo K $\alpha$  radiation (0.71073Å) at 298 K. The structures were solved by direct methods and refined by full matrix least square method using SHELXL-2014<sup>[3]</sup> and winGX version 2014<sup>[4]</sup>. All the non-hydrogen atoms were located from the difference Fourier map and refined anisotropically.

<b>Crystal Data &amp; Structure refinement of Compound 2j &amp; 3f</b>		
	Table 1 (2j)	Table 2 (3f)
Crystal Structure		
CCDC Number	2035021	2034674
Chemical formula	$C_{19}H_{11}NO_2S$	$C_{19}H_{14}N_2O_2$
$M_r$	317.35	302.32

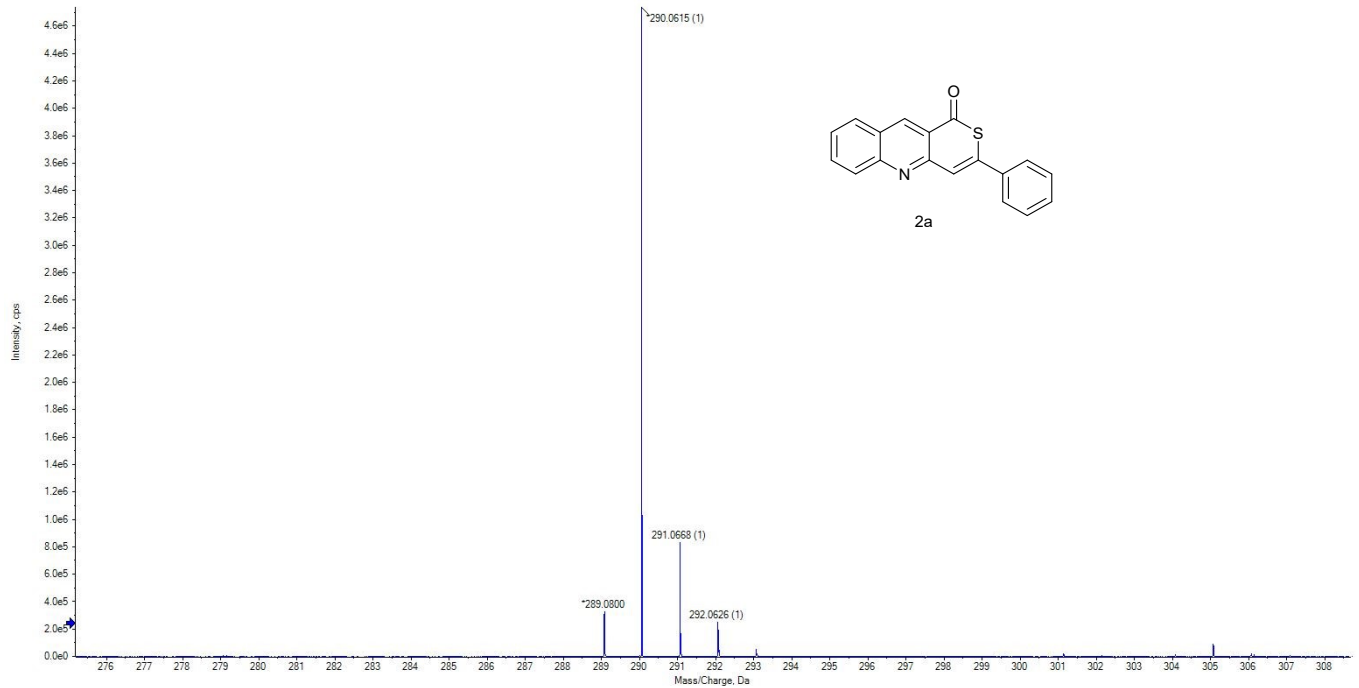
Crystal system, space group	Triclinic, <i>P</i>	Tetragonal, <i>I4<sub>1</sub>/a</i>
Temperature (K)	296	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.0134 (4), 7.0858 (5), 15.5319 (10)	
$\alpha$ , $\beta$ , $\gamma$ (°)	96.280 (4), 90.168 (4), 104.398 (4)	
<i>a</i> , <i>c</i> (Å)		29.725 (2), 7.0358 (8)
<i>V</i> (Å <sup>3</sup> )	742.77 (8)	6216.7 (11)
<i>Z</i>	2	16
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.23	0.09
Crystal size (mm)	0.45 × 0.40 × 0.38	0.56 × 0.52 × 0.49
Data collection		
Diffractometer	CCD area detector	CCD area detector
Absorption correction	Multi-scan	Multi-scan
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.945, 0.950	0.951, 0.956
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	16157, 4167, 2881	22591, 4777, 2463
<i>R</i> <sub>int</sub>	0.036	0.058
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.694	0.716
Refinement		
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.055, 0.184, 0.84	0.059, 0.187, 0.94
No. of reflections	4138	4755
No. of parameters	208	209
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho$ <sub>max</sub> , $\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	0.74, -0.22	0.17, -0.16

# 1. Copies of $^1\text{H}$ & $^{13}\text{C}$ NMR and HRMS spectra of the Products:

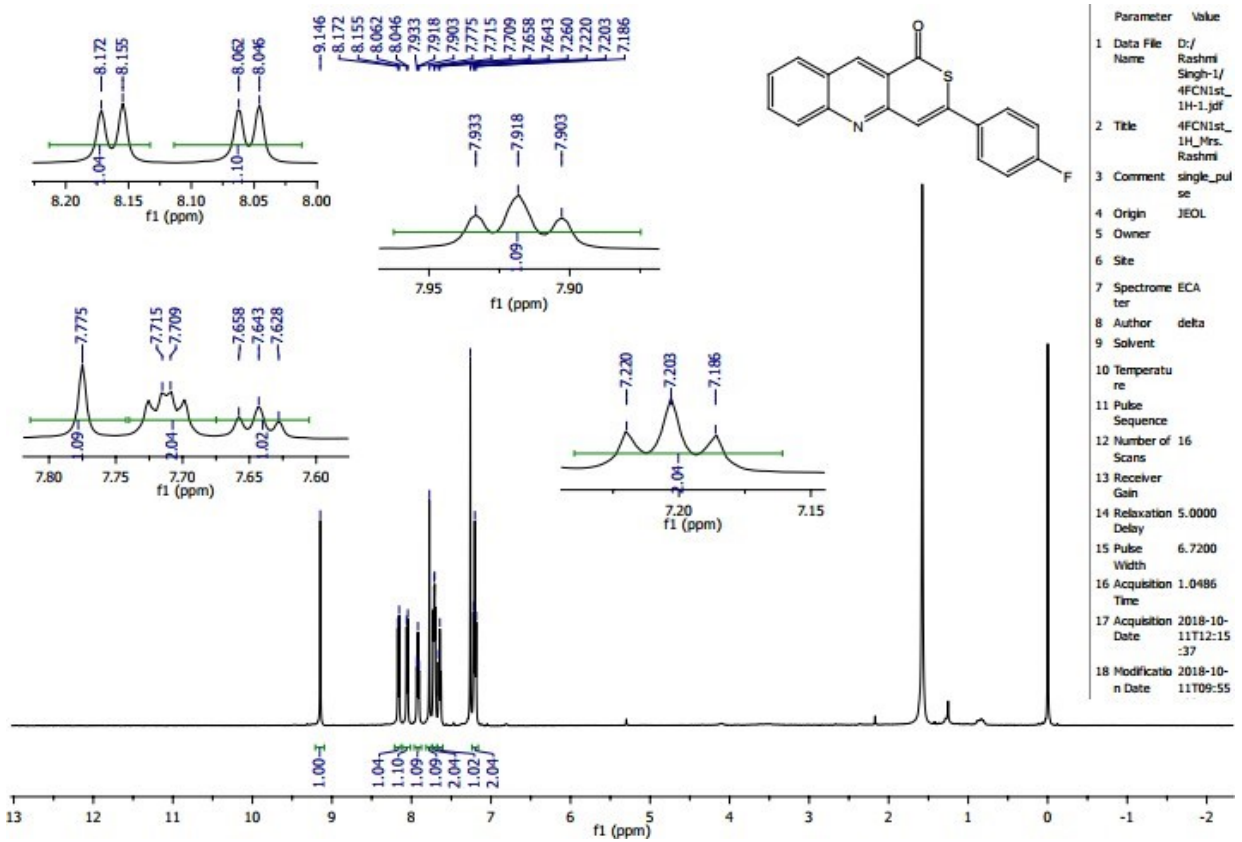
## 3-phenyl-1*H*-thiopyrano[4,3-*b*]quinolin-1-one (2a):

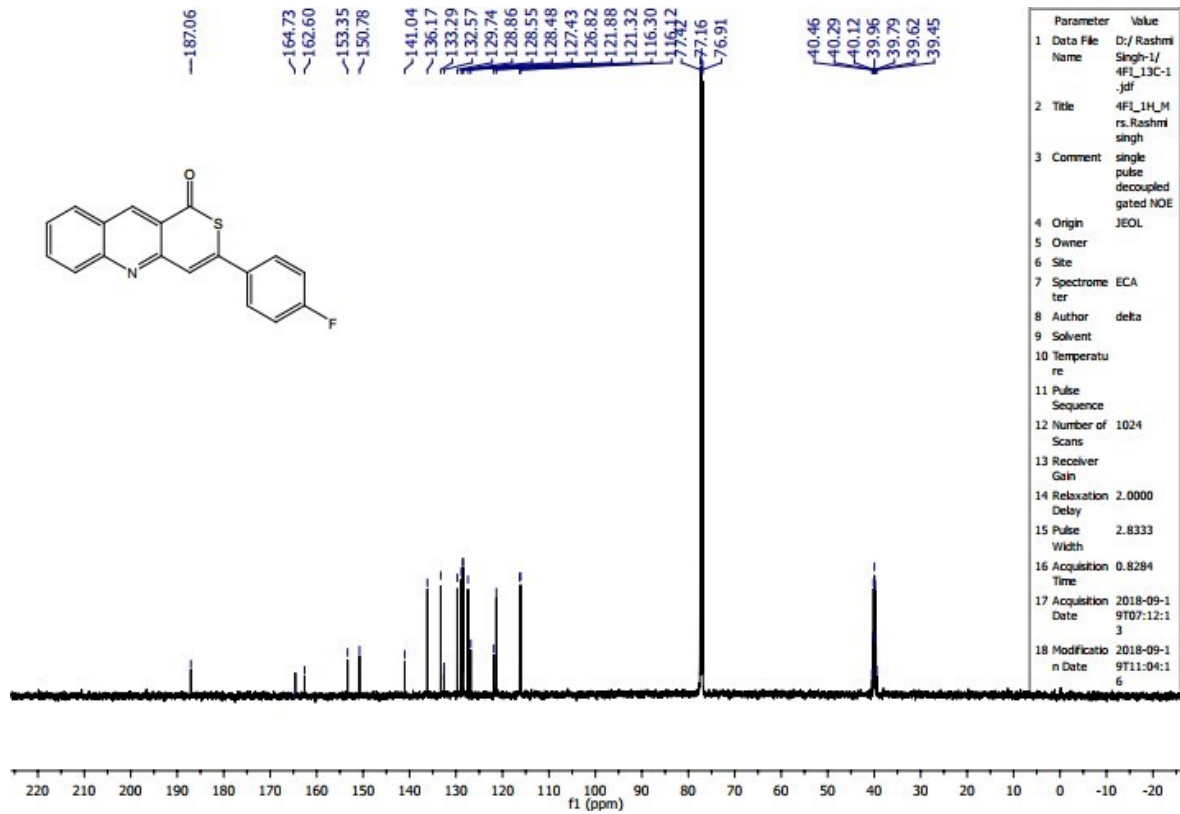


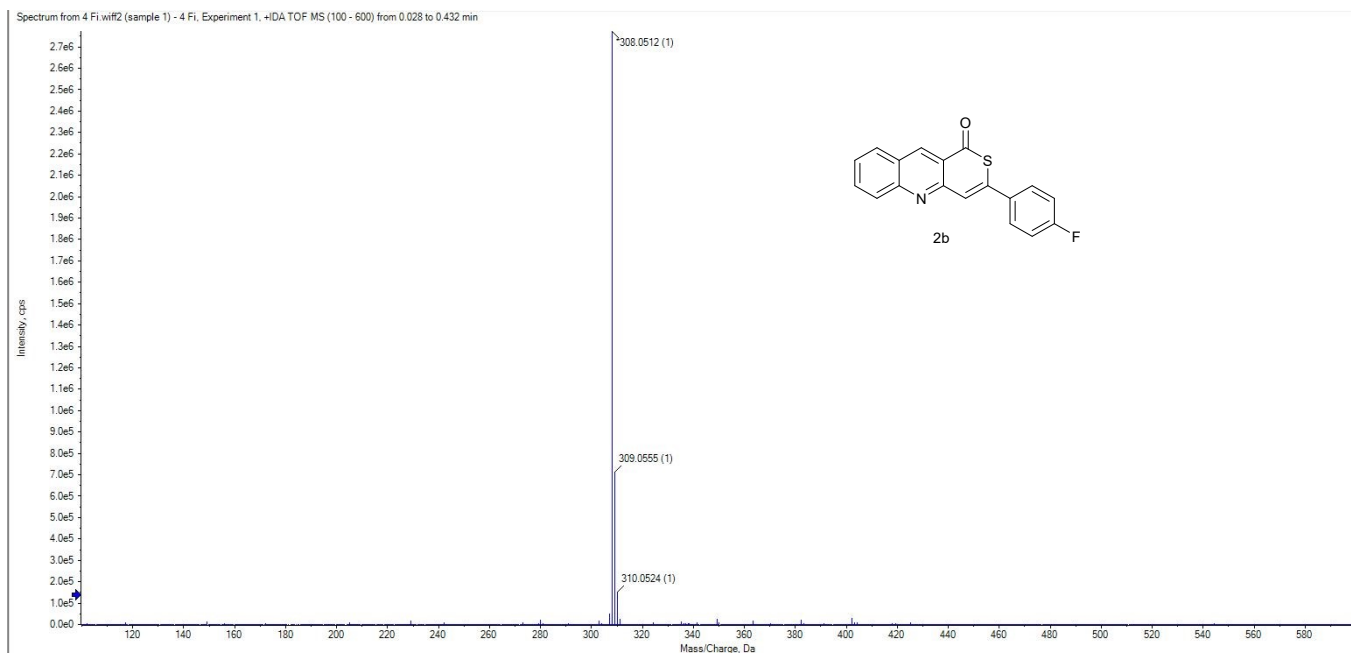
Spectrum from 4 Q 24.wi#2 (sample 1) - 4 Q 24, Experiment 1, +IDA TOF MS (100 - 600) from 0.040 to 0.411 min



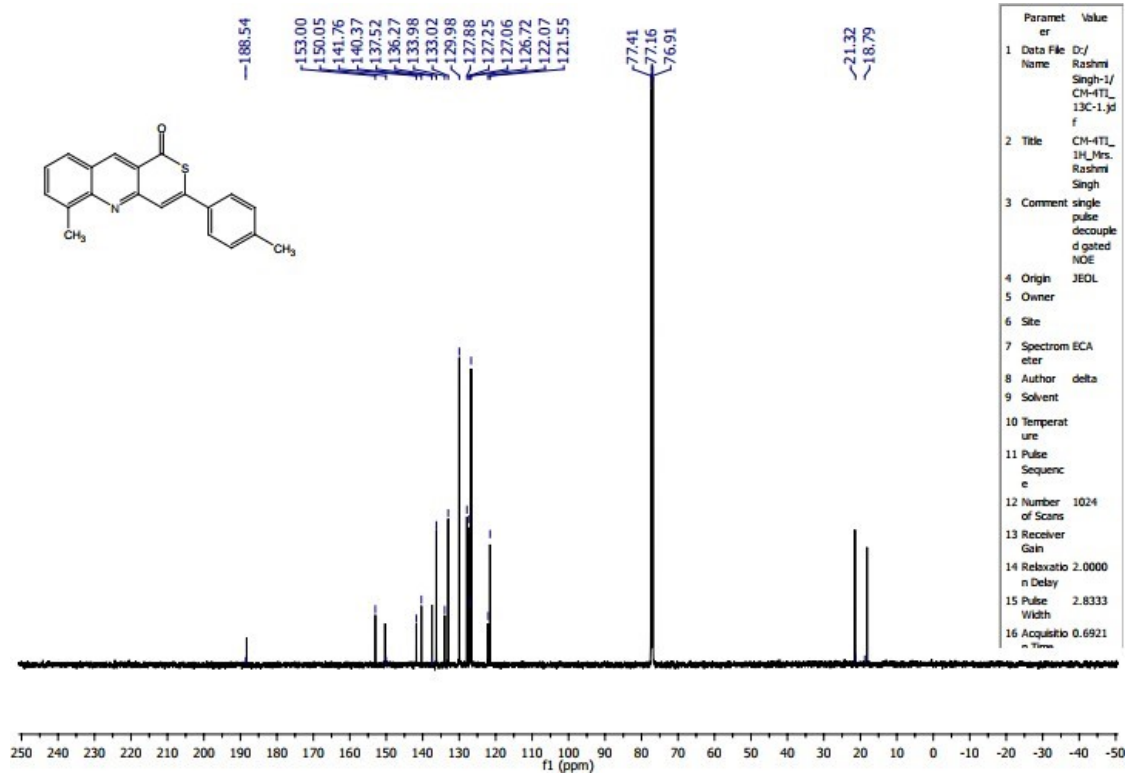
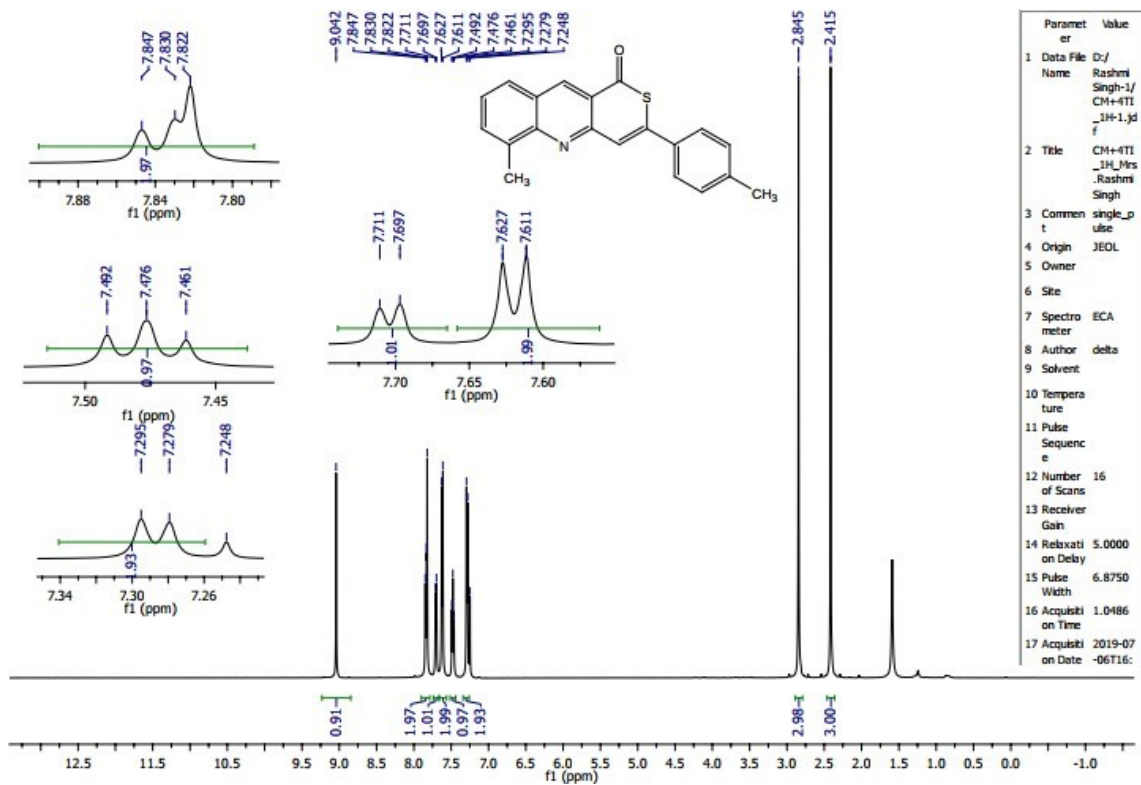
### 3-(4-fluorophenyl)-1H-thiopyrano[4,3-b]quinolin-1-one (2b):



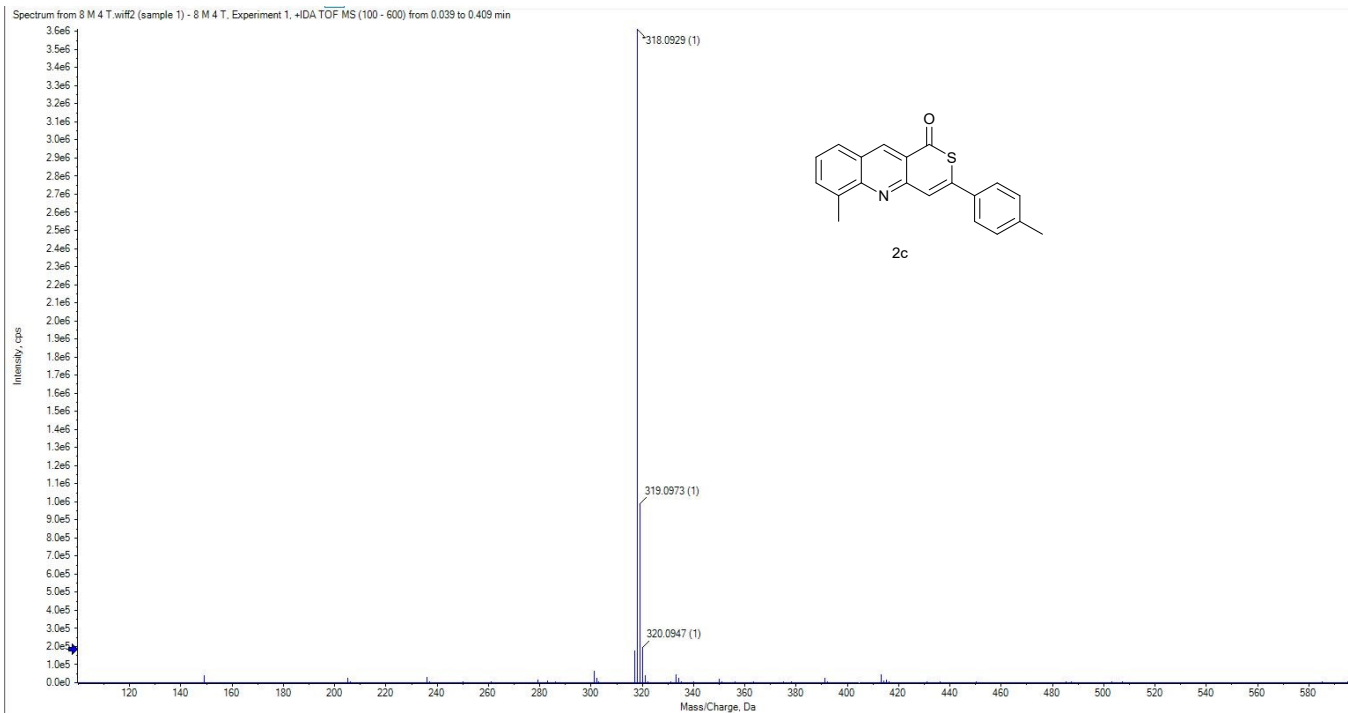




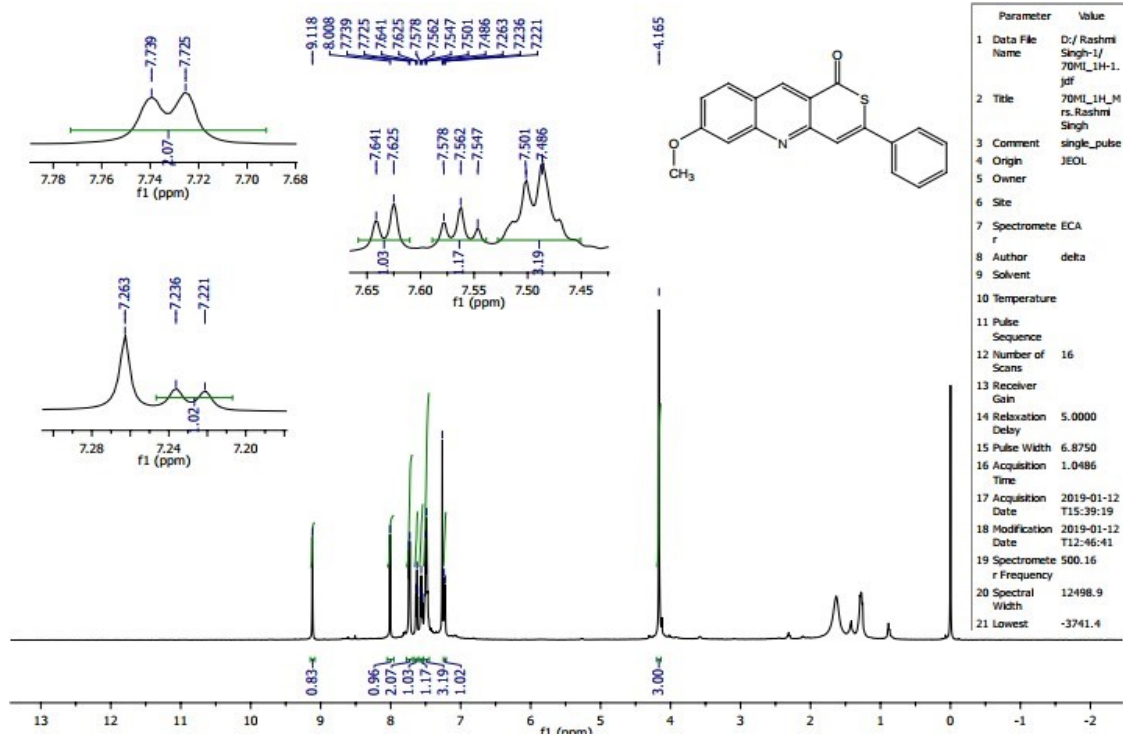
## 6-methyl-3-(p-tolyl)-1H-thiopyrano[4,3-b]quinolin-1-one(2c):

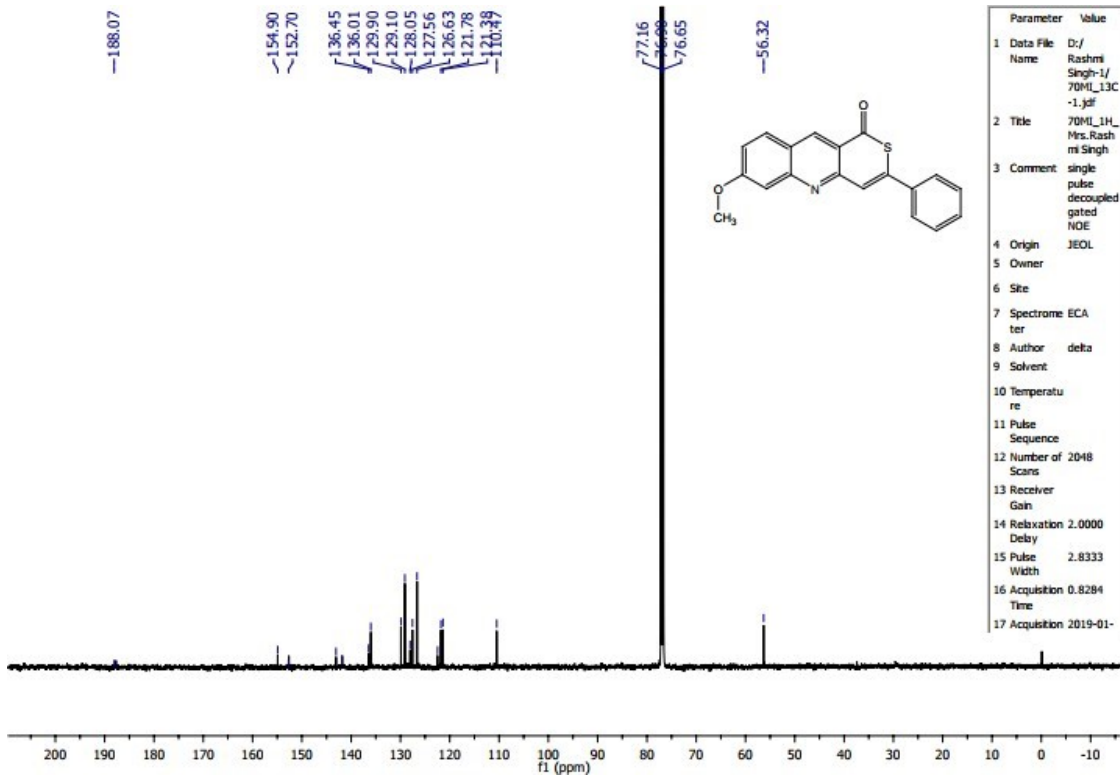




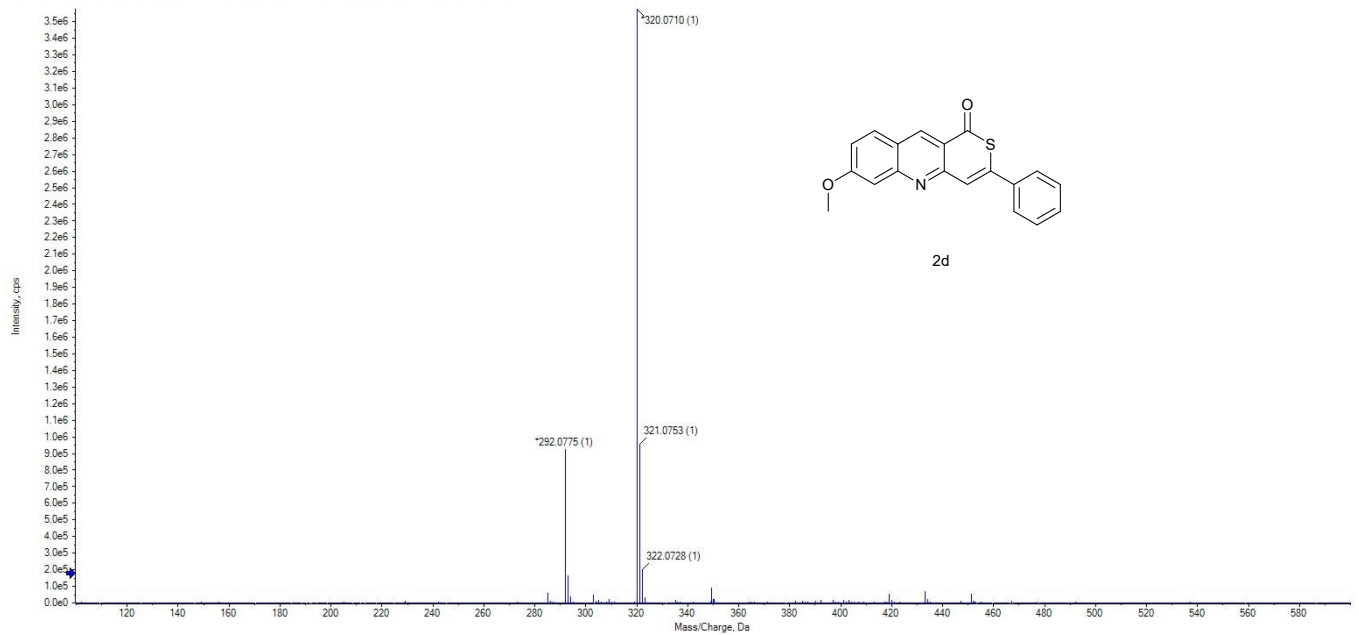


**7-methoxy-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one(2d):**

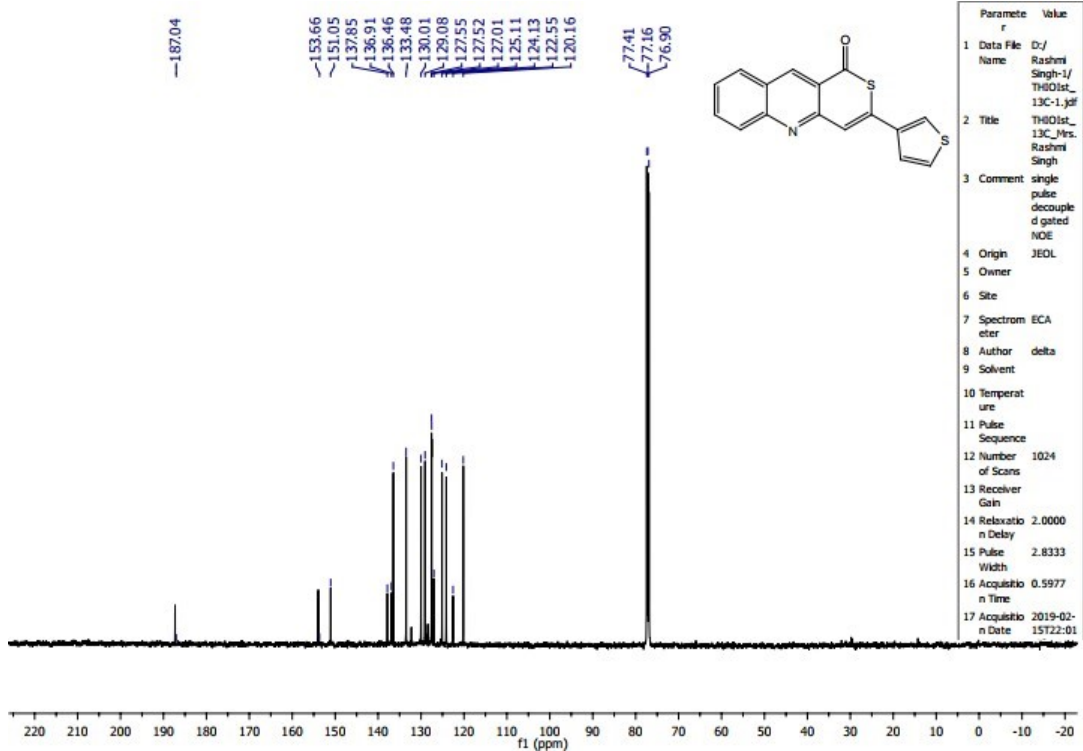
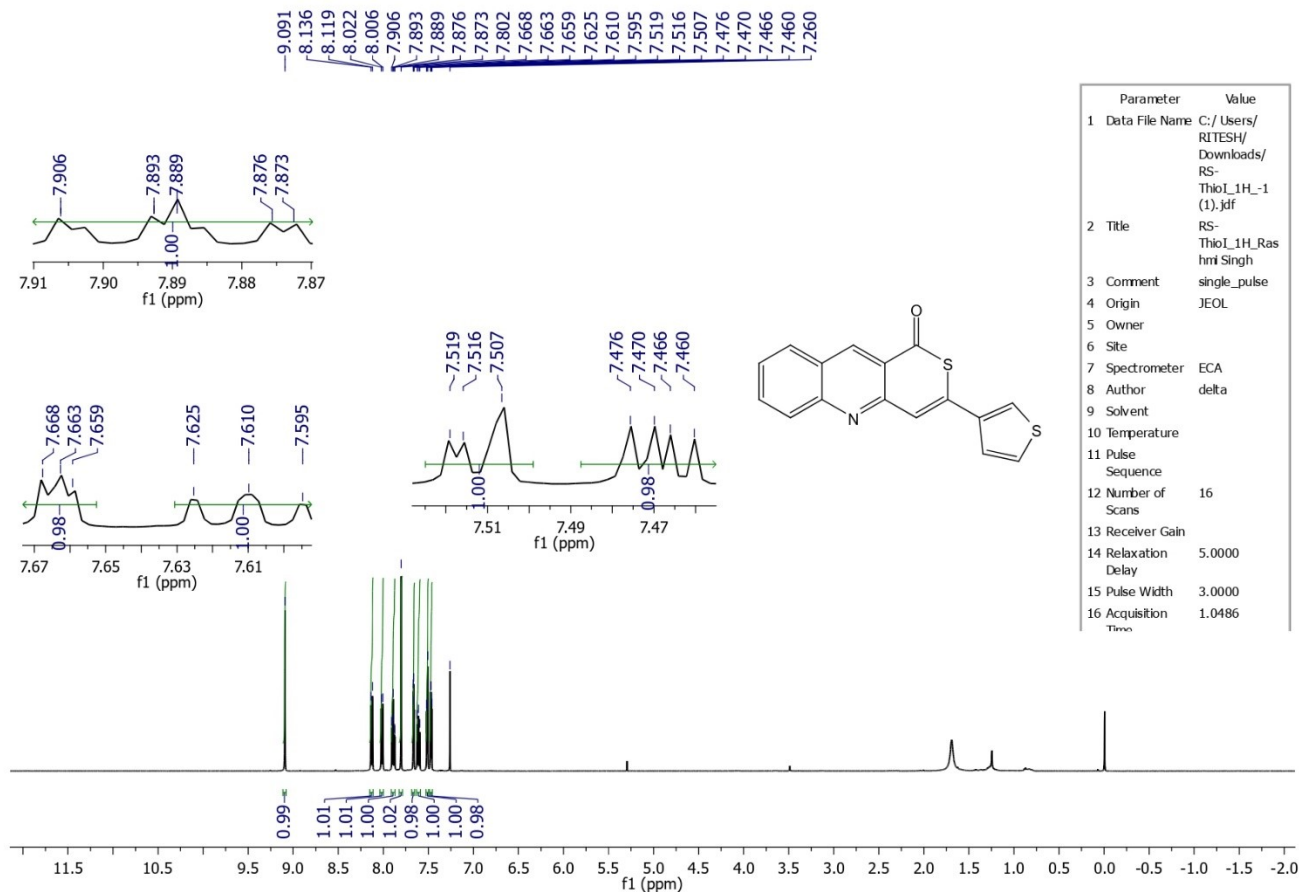


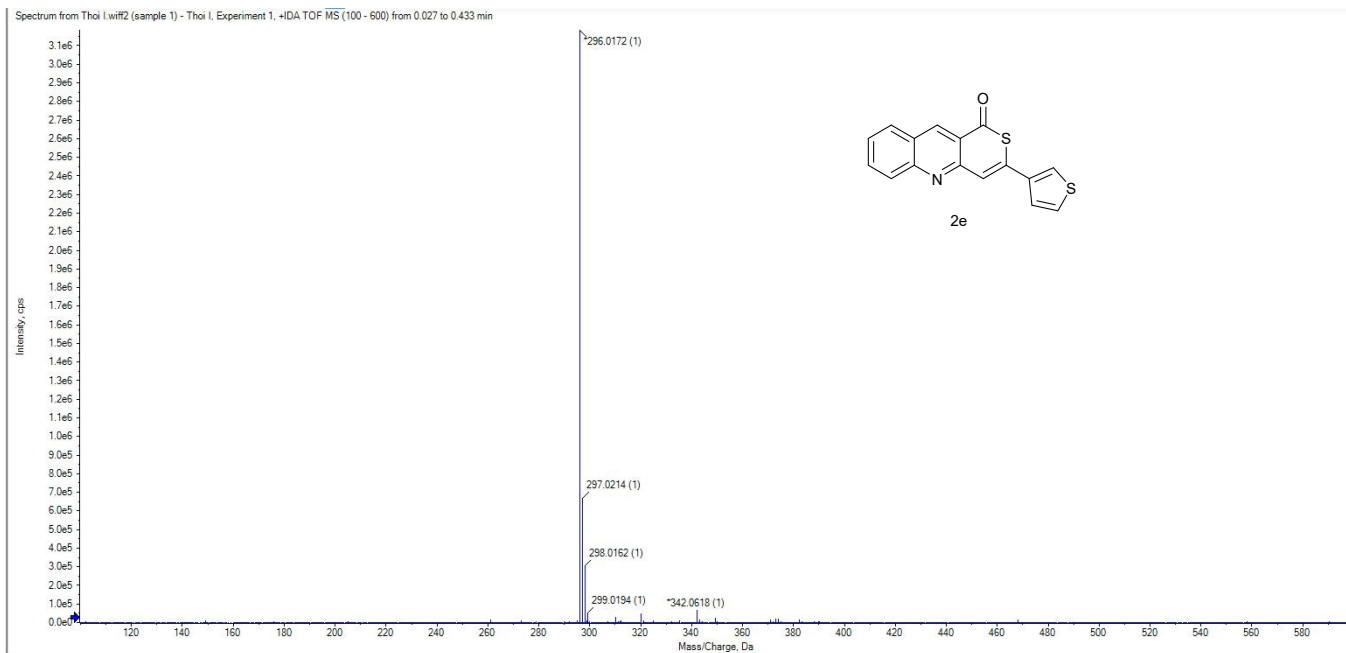


Spectrum from 70M 24 wif2 (sample 1) - 70M 24, Experiment 1, -IDA TOF MS (100 - 600) from 0.027 to 0.438 min

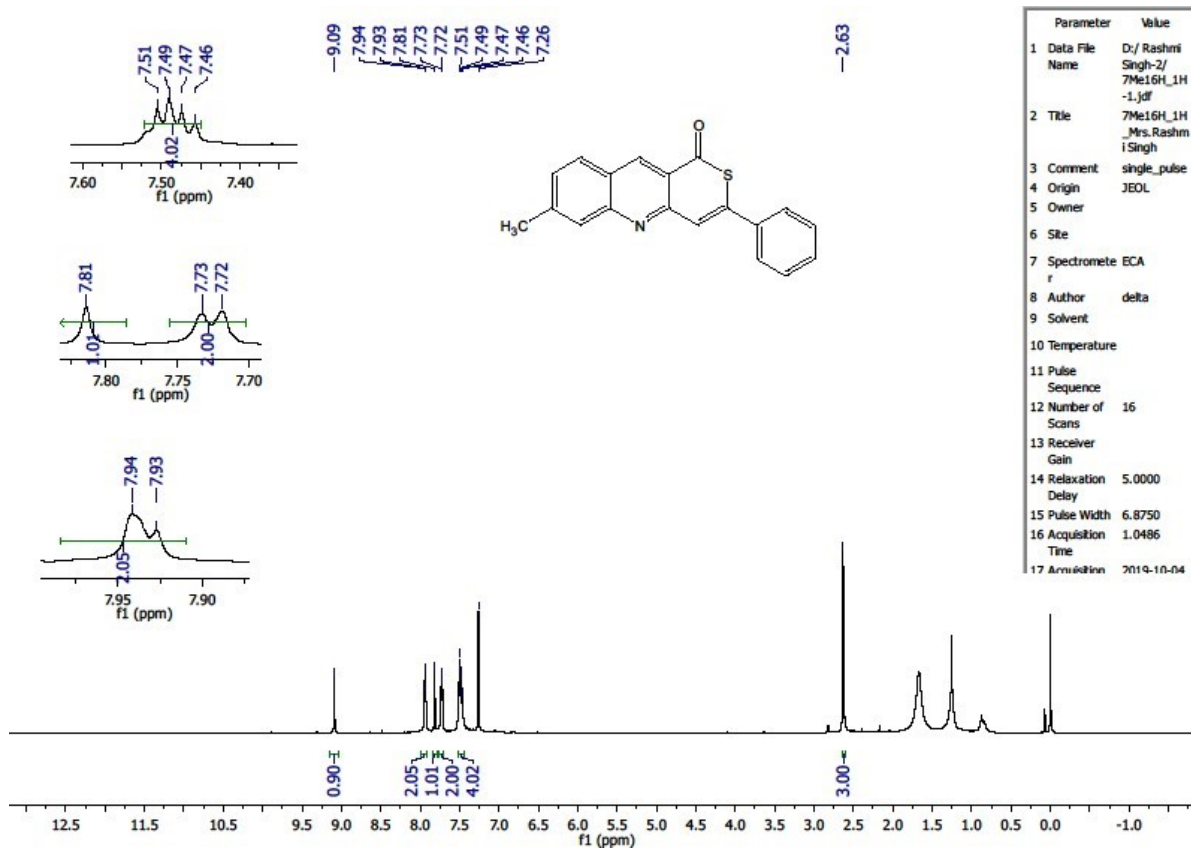


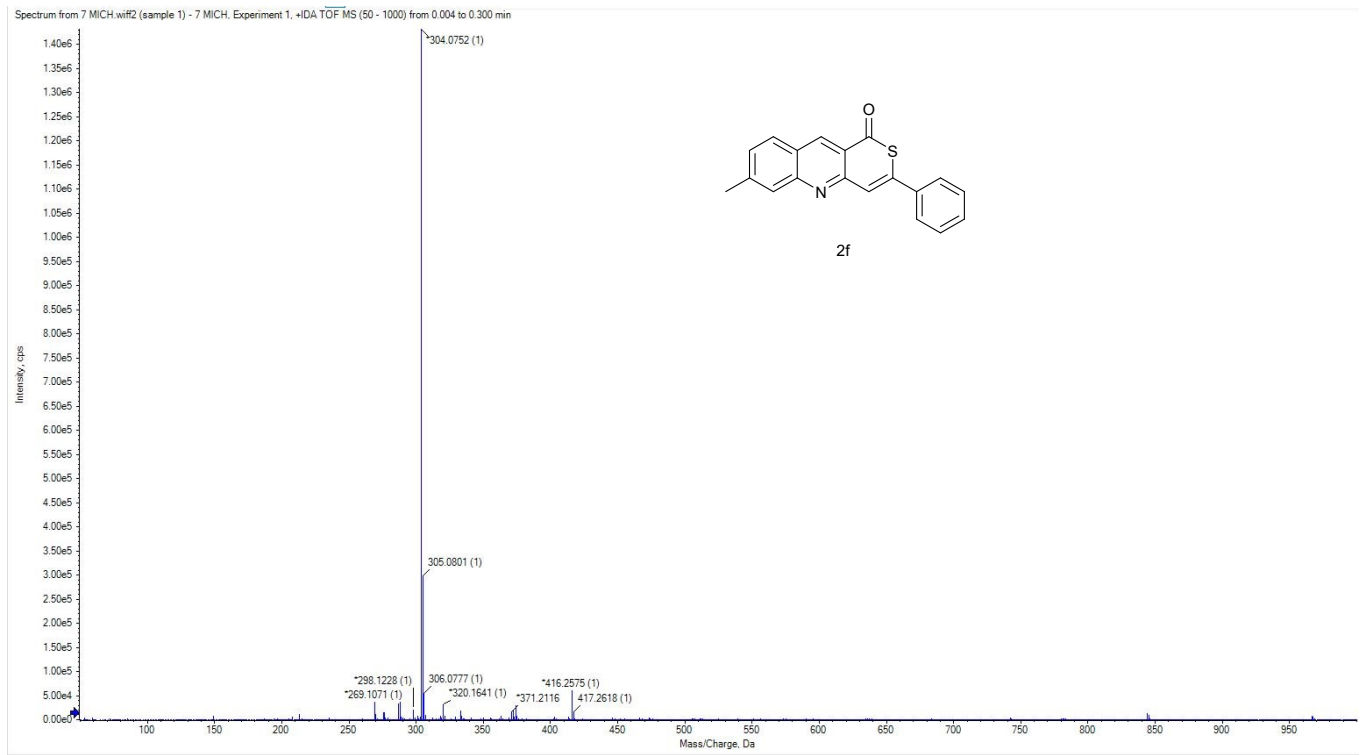
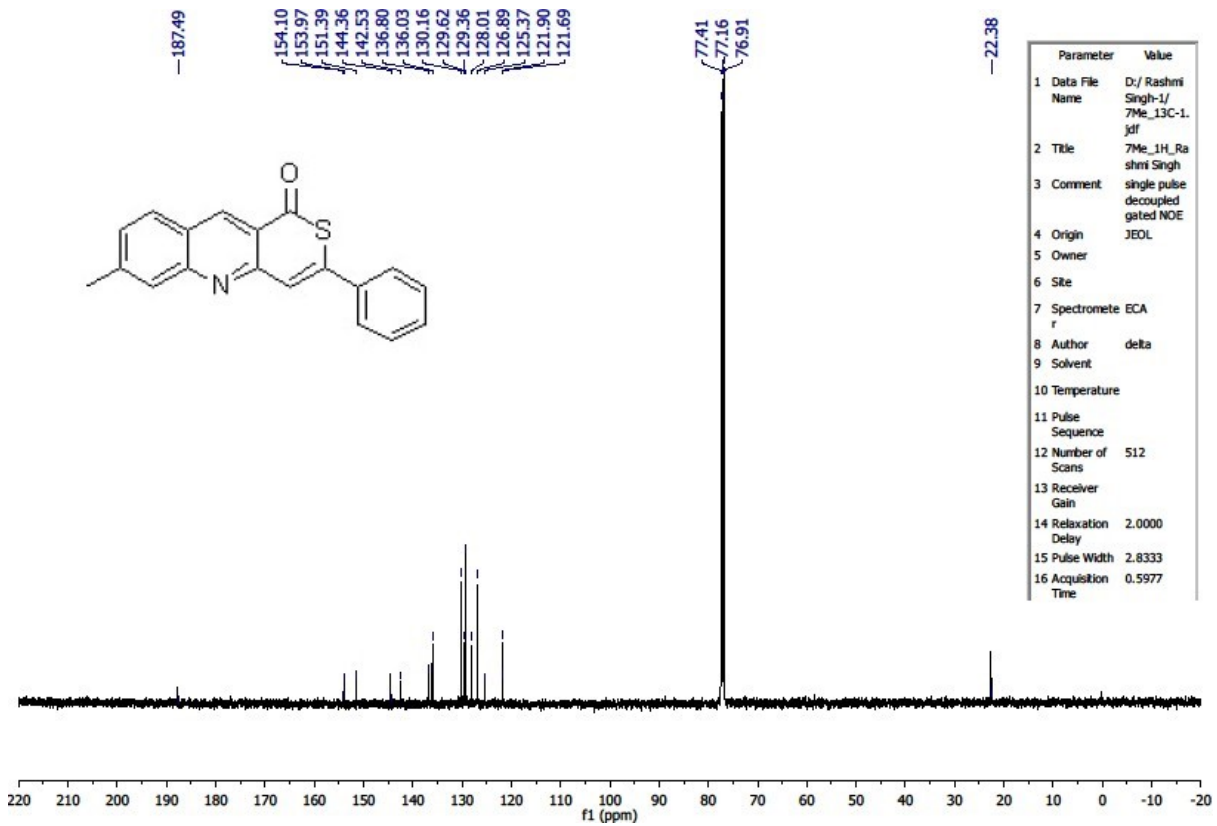
3-(thiophen-3-yl)-1H-thiopyrano[4,3-b]quinolin-1-one (2e):

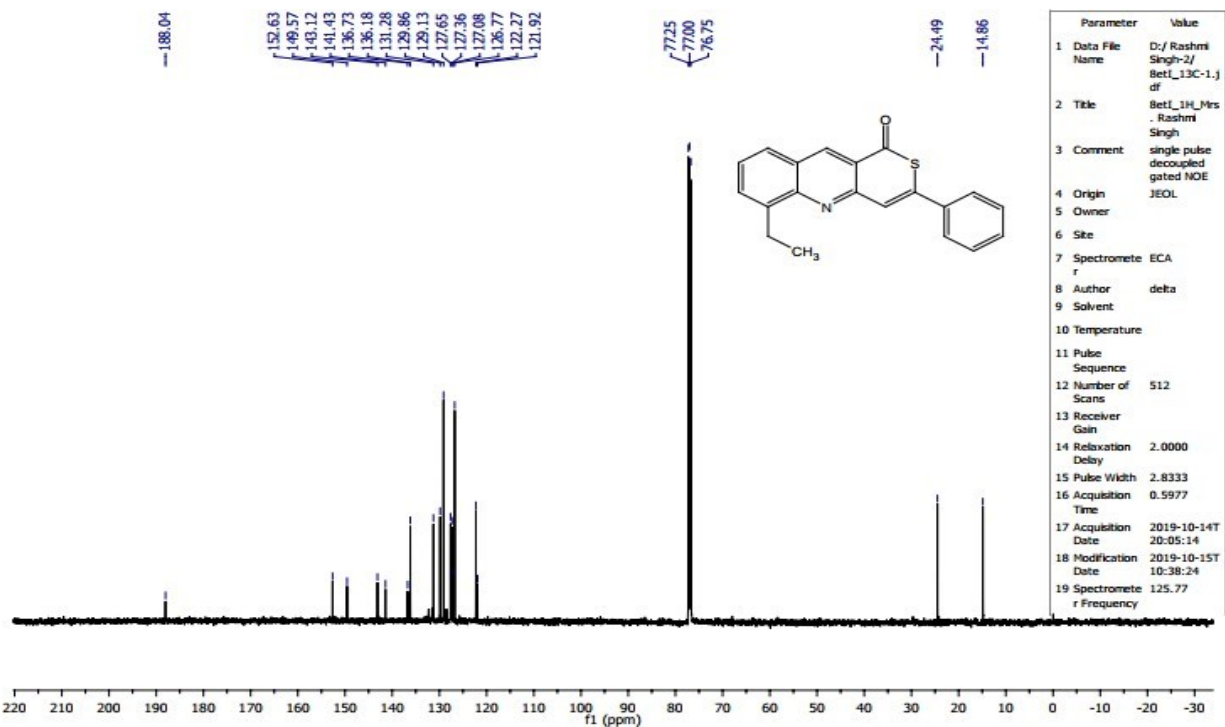
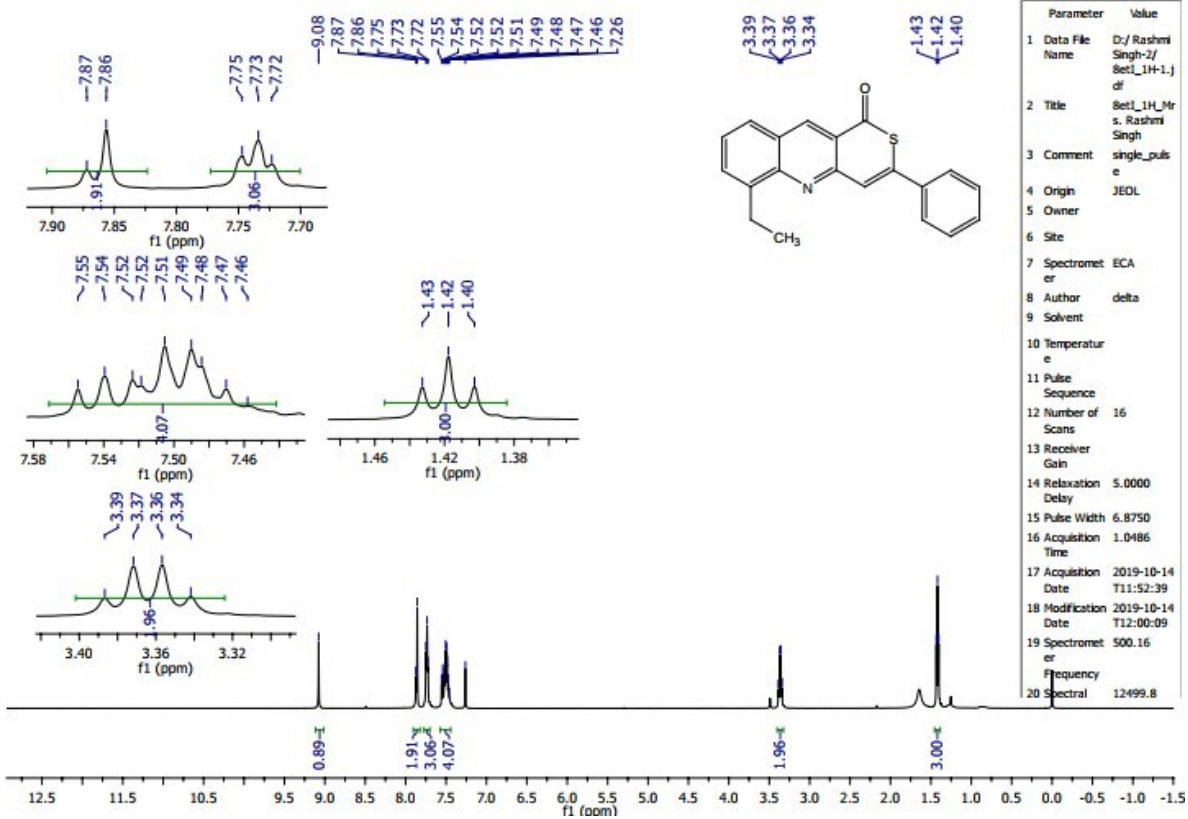


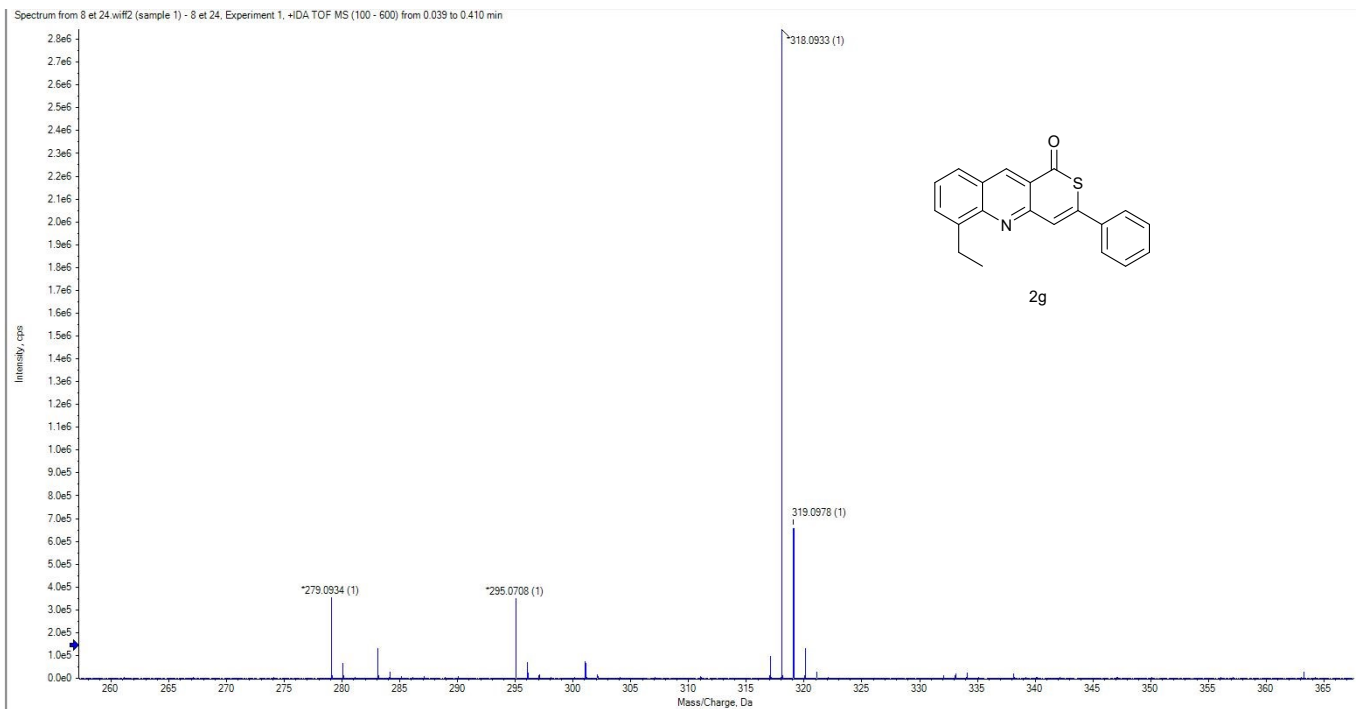


### 7-methyl-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2f):

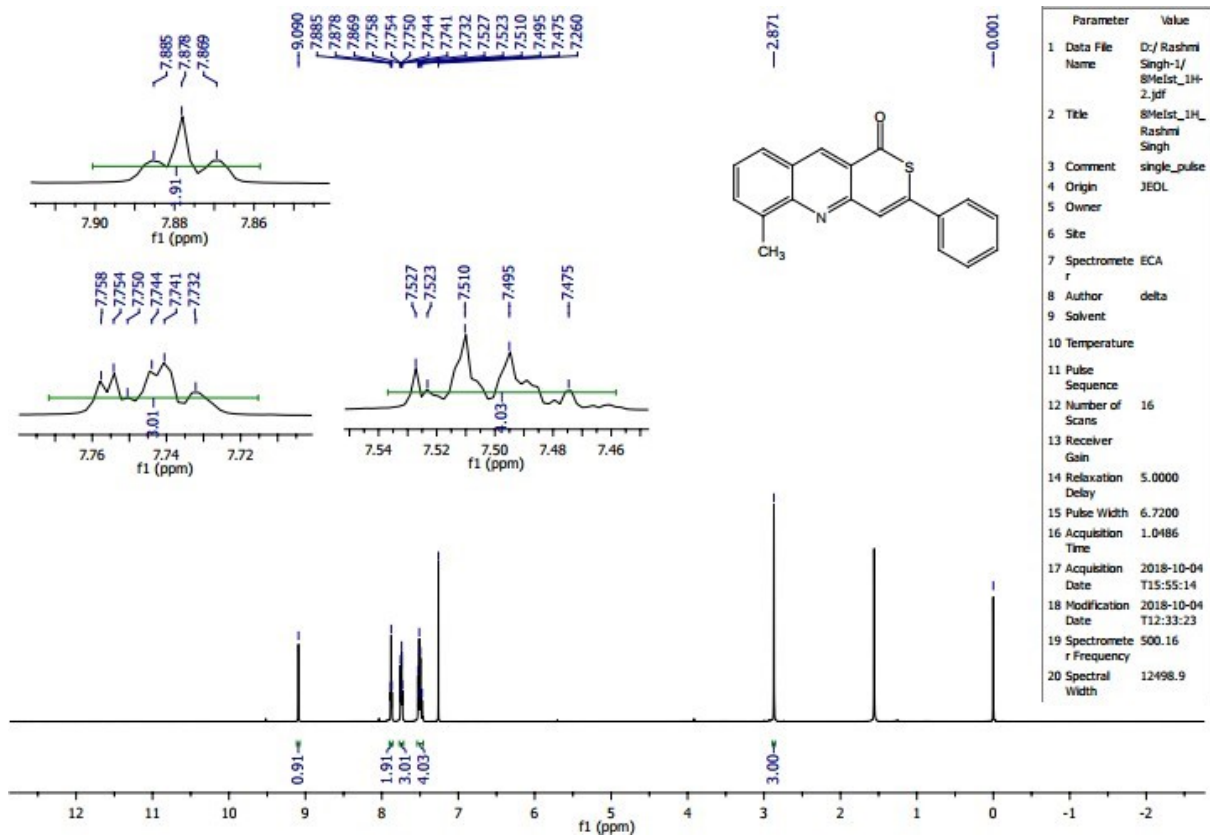


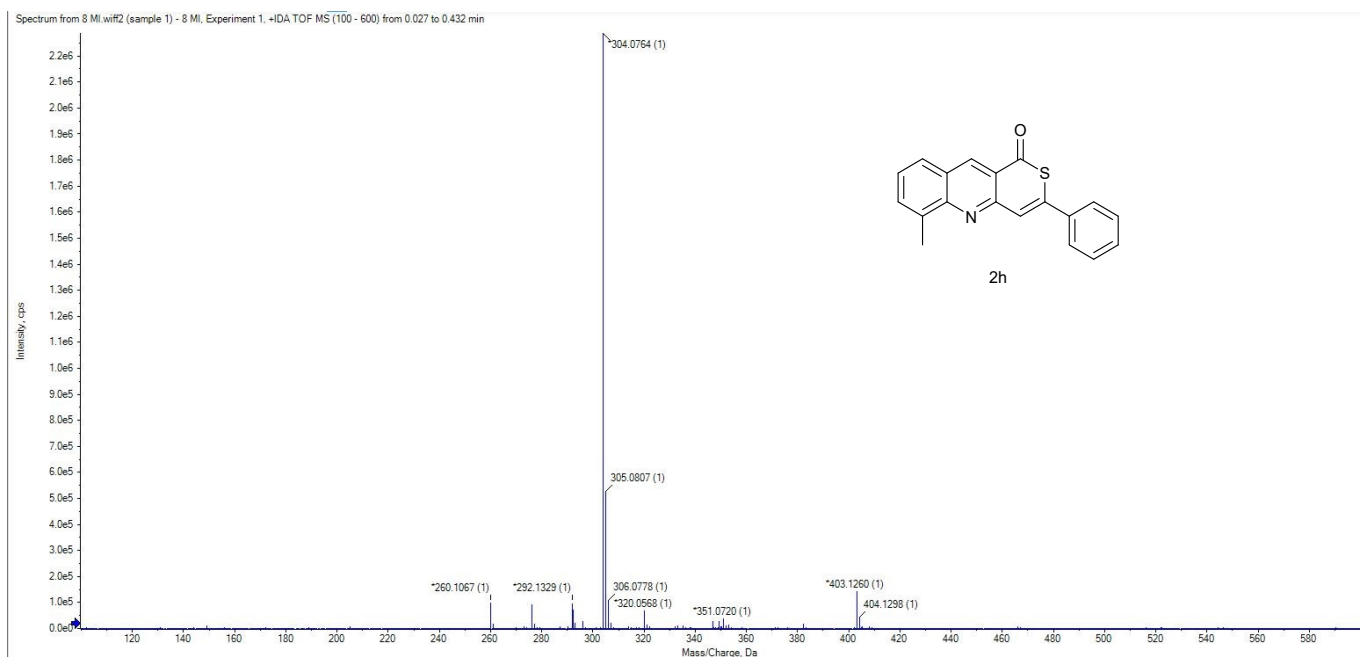
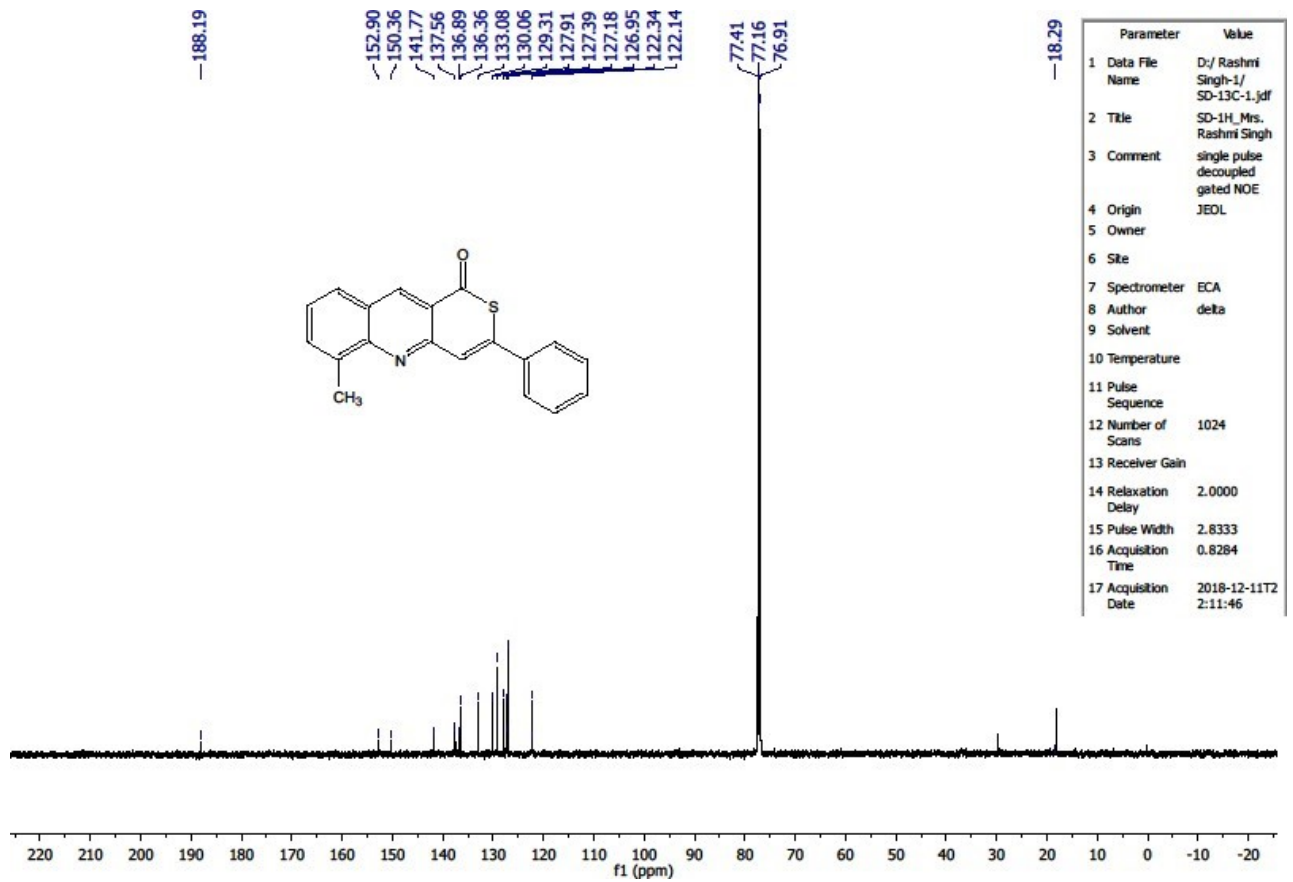


6-ethyl-3-phenyl-1*H*-thiopyrano[4,3-*b*]quinolin-1-one (2g):

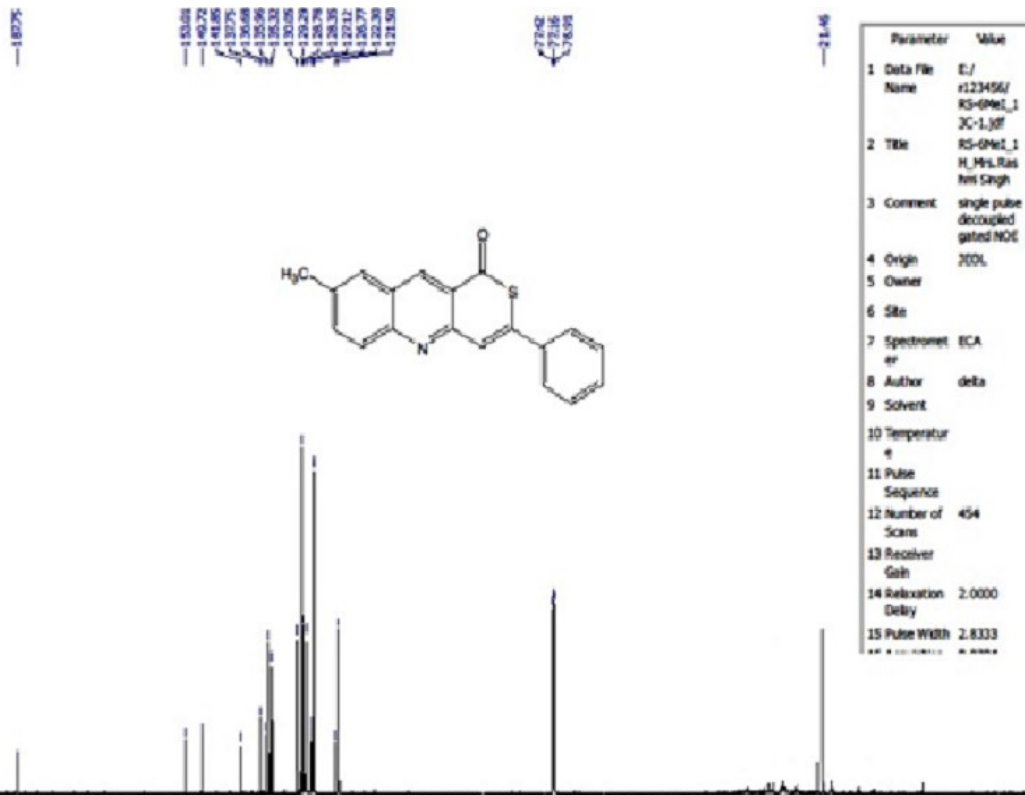
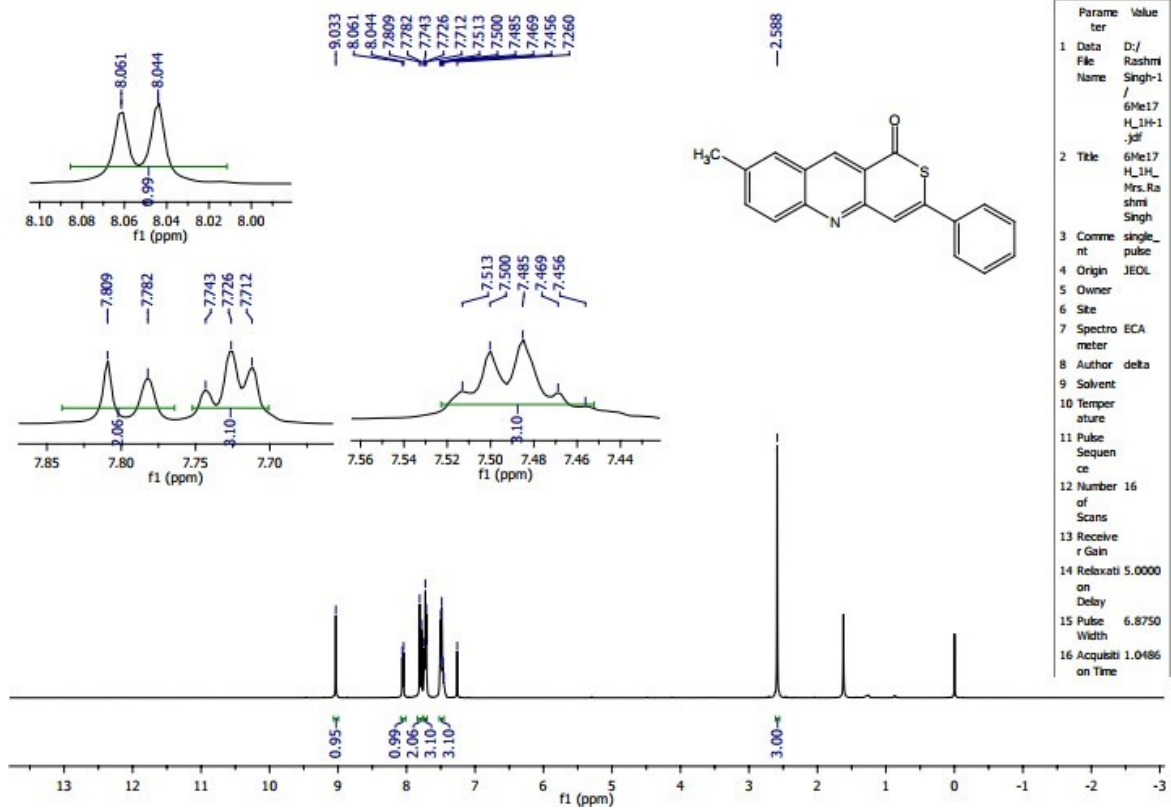


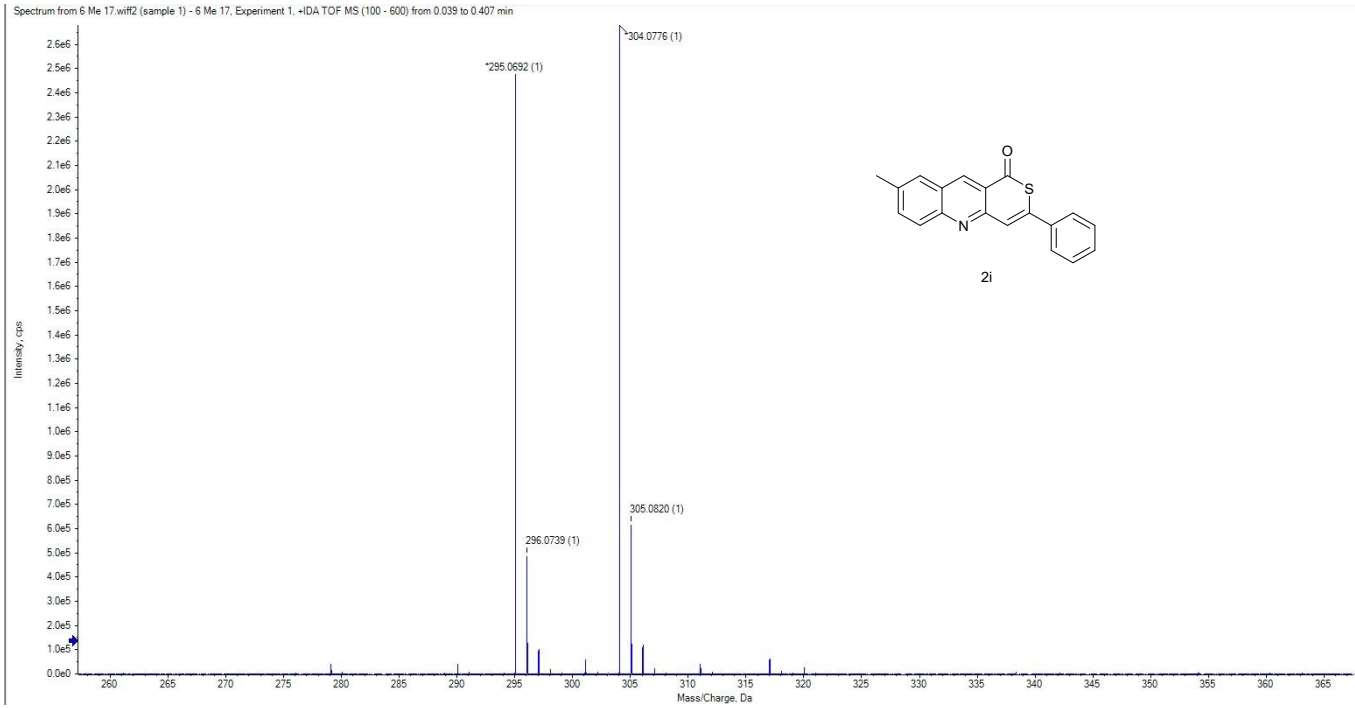
### 6-methyl-3-phenyl-1*H*-thiopyrano[4,3-*b*]quinolin-1-one (2h):



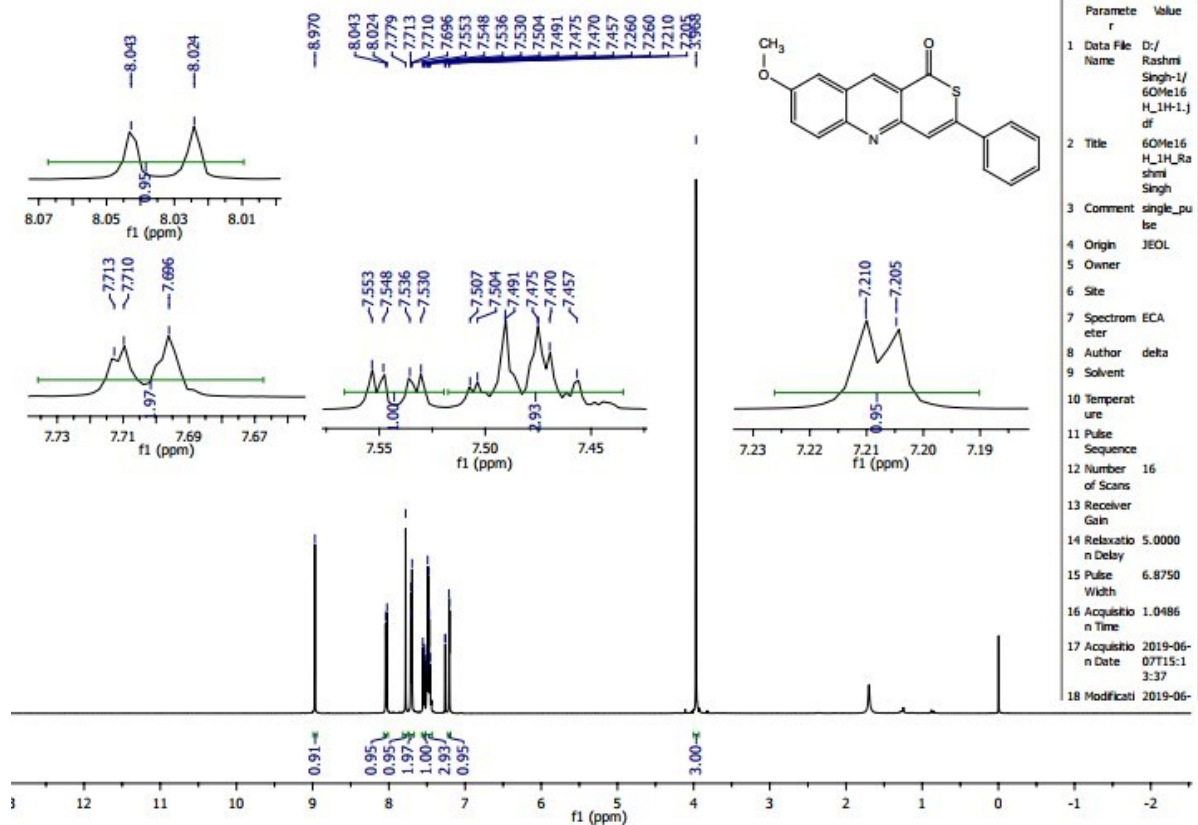


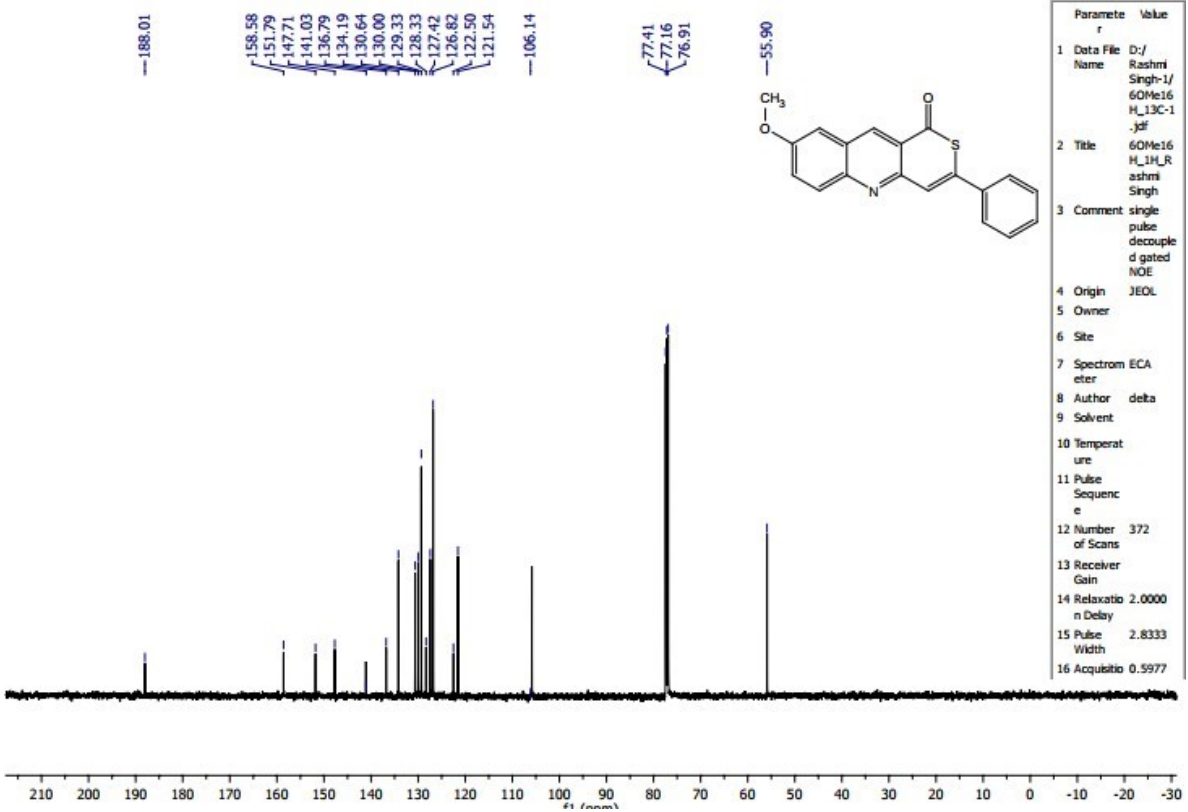


8-methyl-3-phenyl-1*H*-thiopyrano[4,3-*b*]quinolin-1-one (2i):

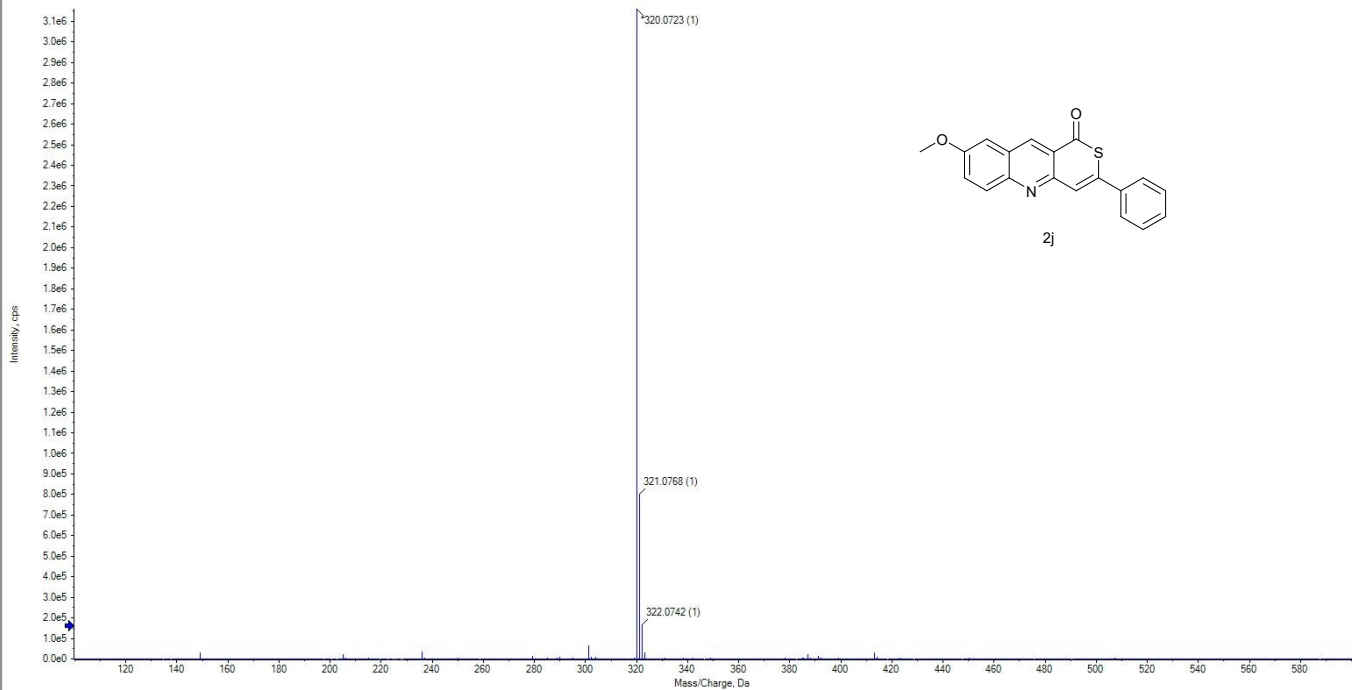


### 8-methoxy-3-phenyl-1H-thiopyrano[4,3-b]quinolin-1-one (2j):

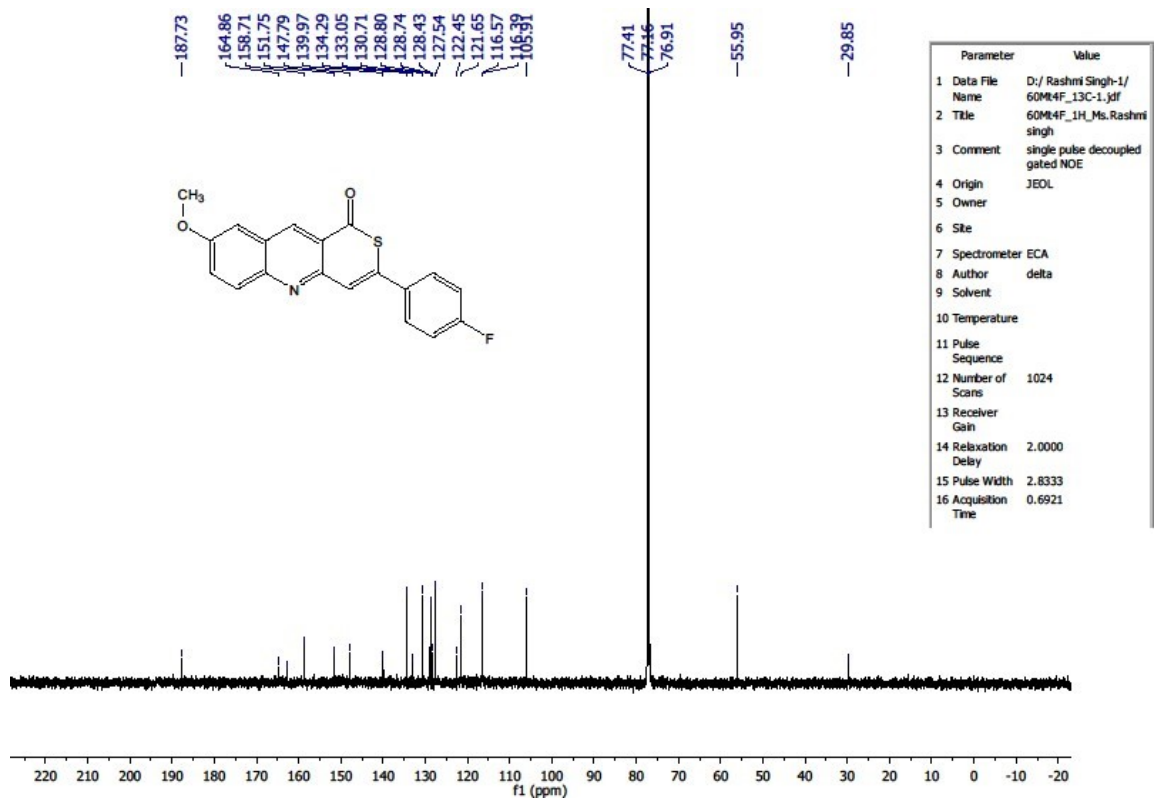
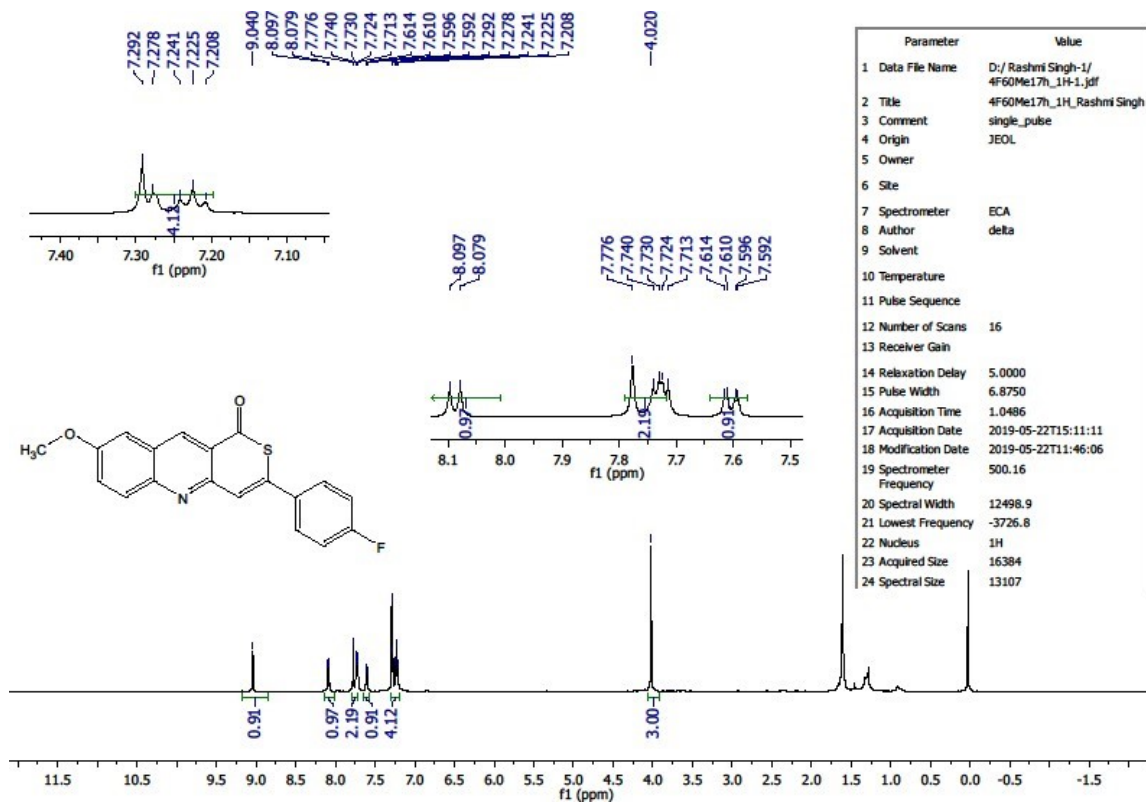




Spectrum from 60 M 16H.wi#2 (sample 1) - 60 M 16H, Experiment 1, +IDA TOF MS (100 - 600) from 0.039 to 0.407 min

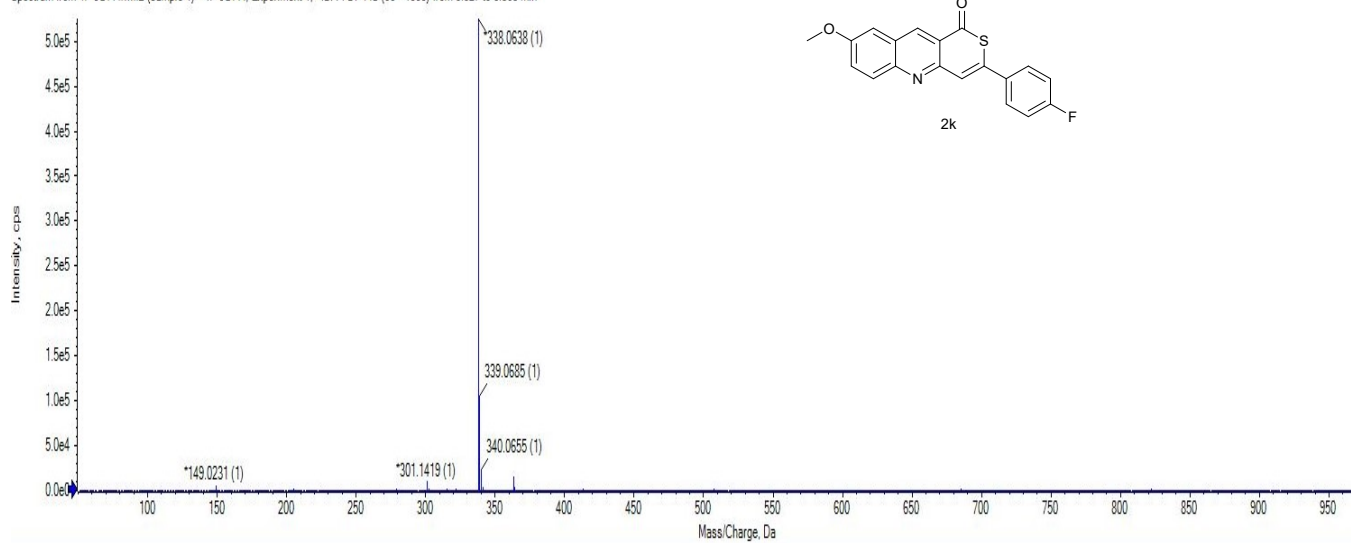


## 3-(4-fluorophenyl)-8-methoxy-1H-thiopyrano[4,3-b]quinolin-1-one (2k):

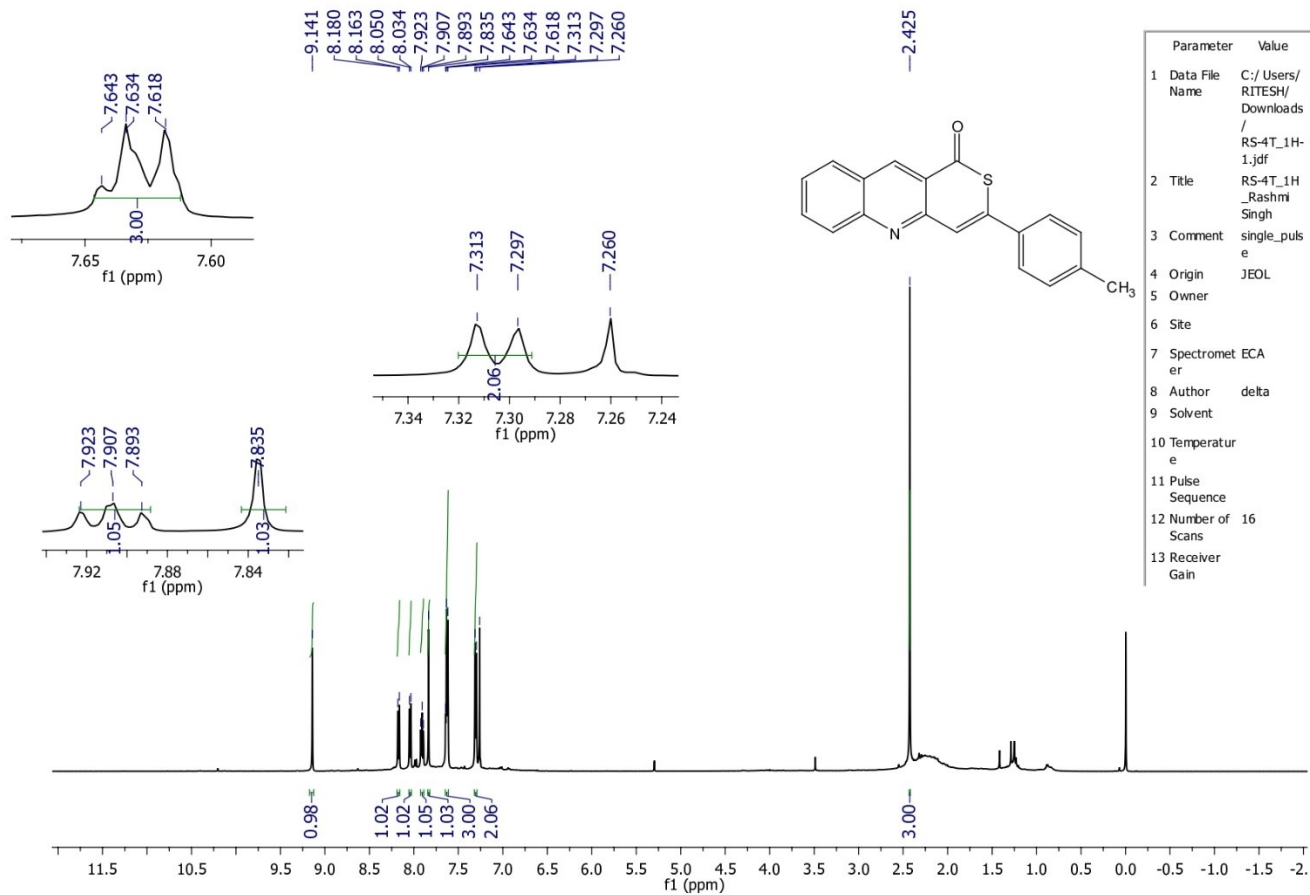


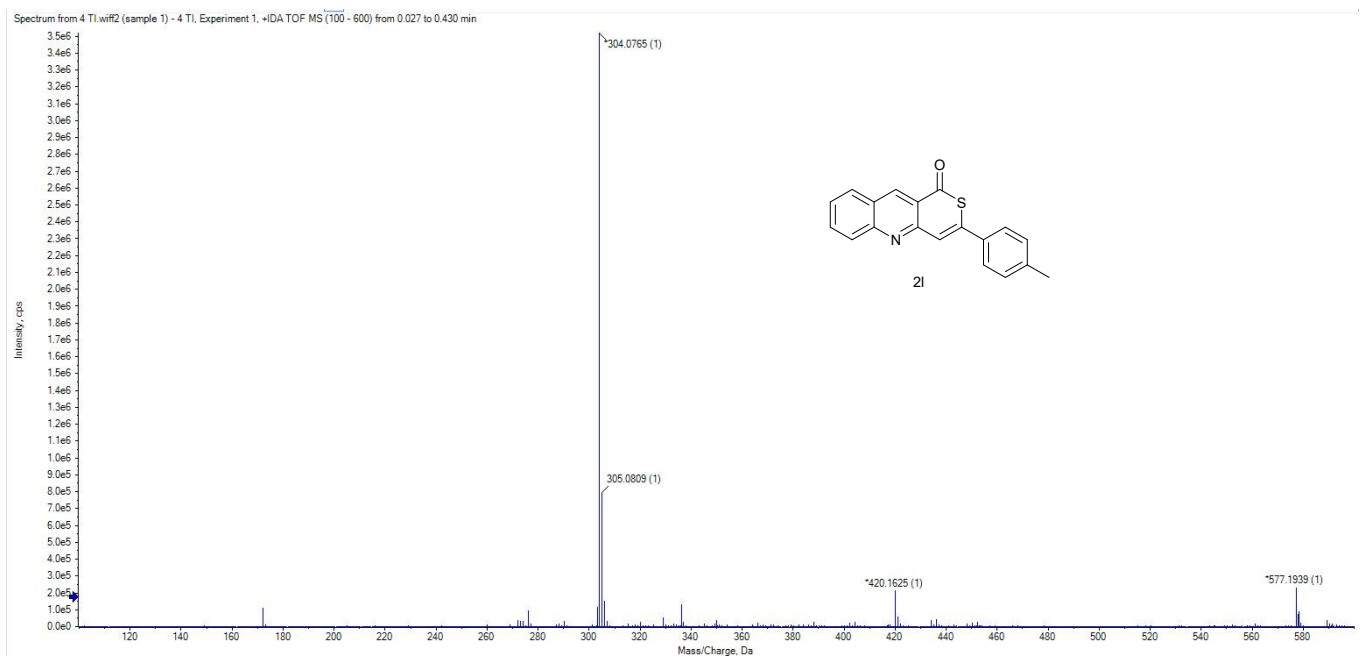
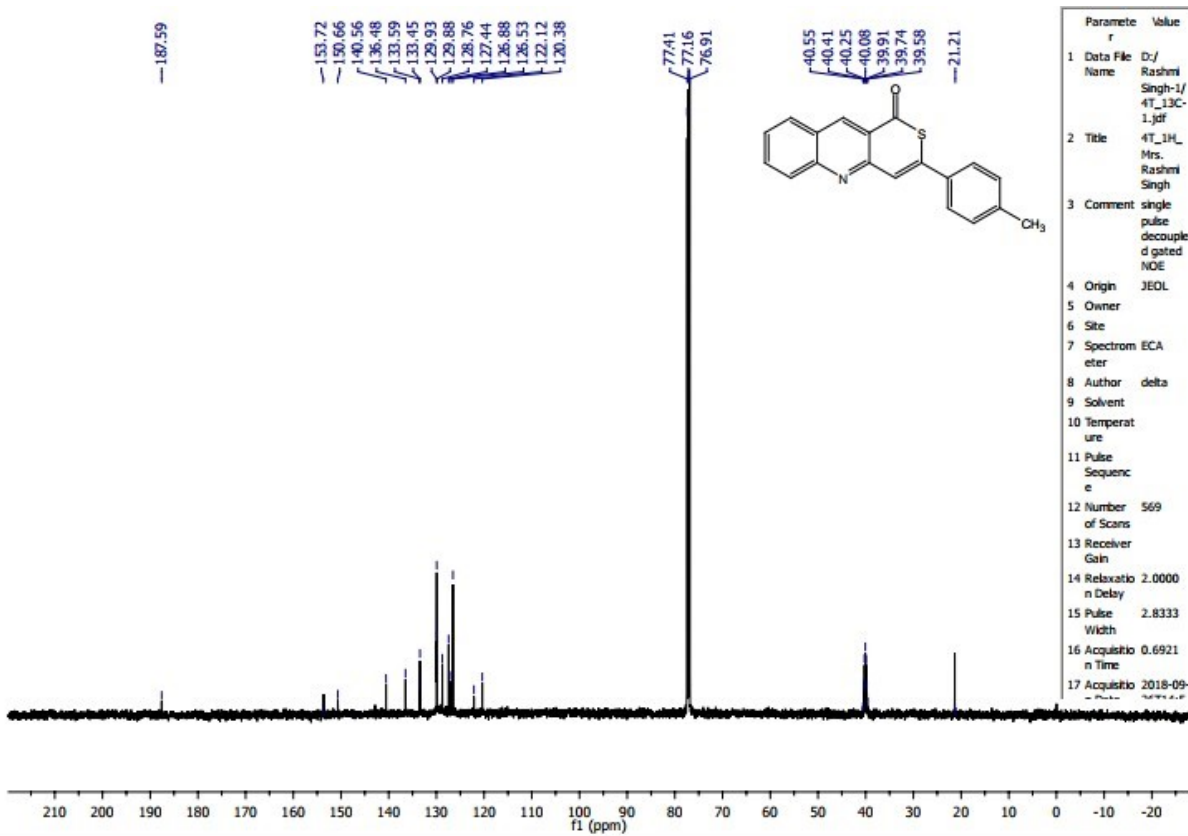


Spectrum from 4F 6OM I.wi#2 (sample 1) - 4F 6OM I, Experiment 1, +IDA TOF MS (50 - 1000) from 0.027 to 0.368 min

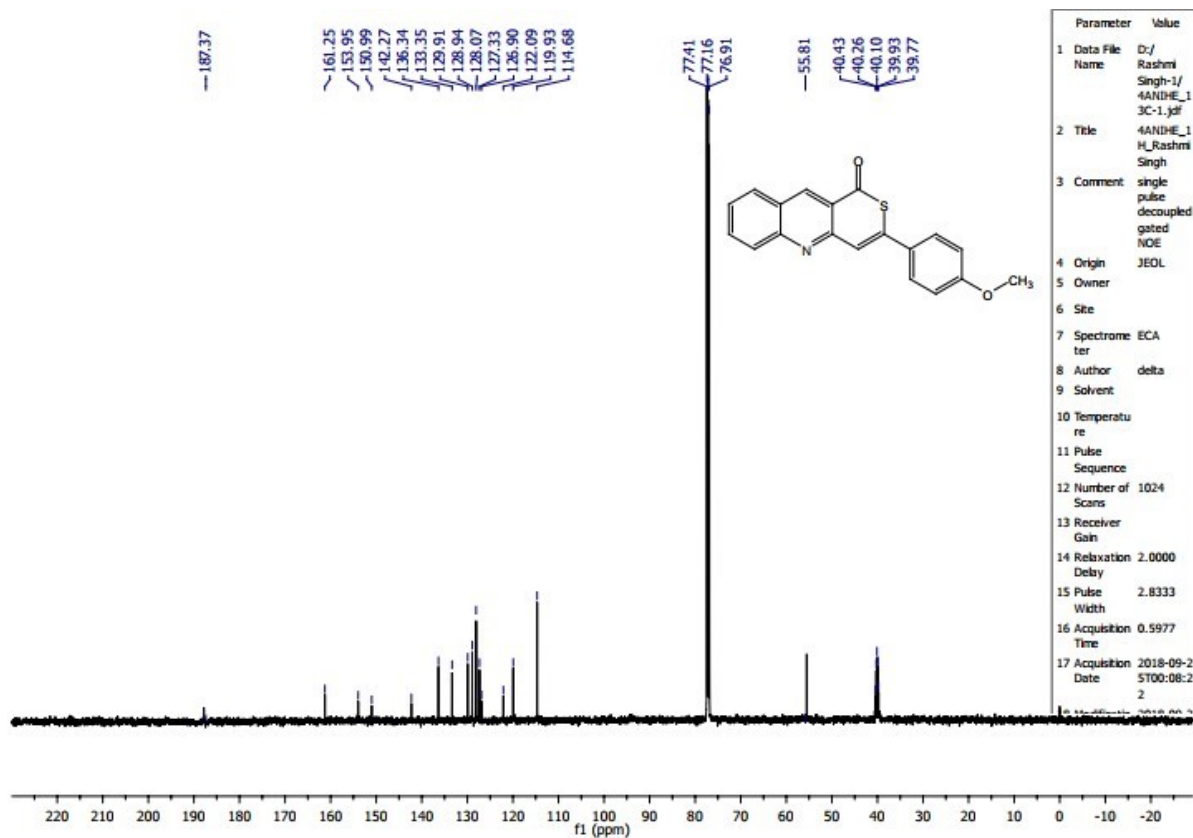
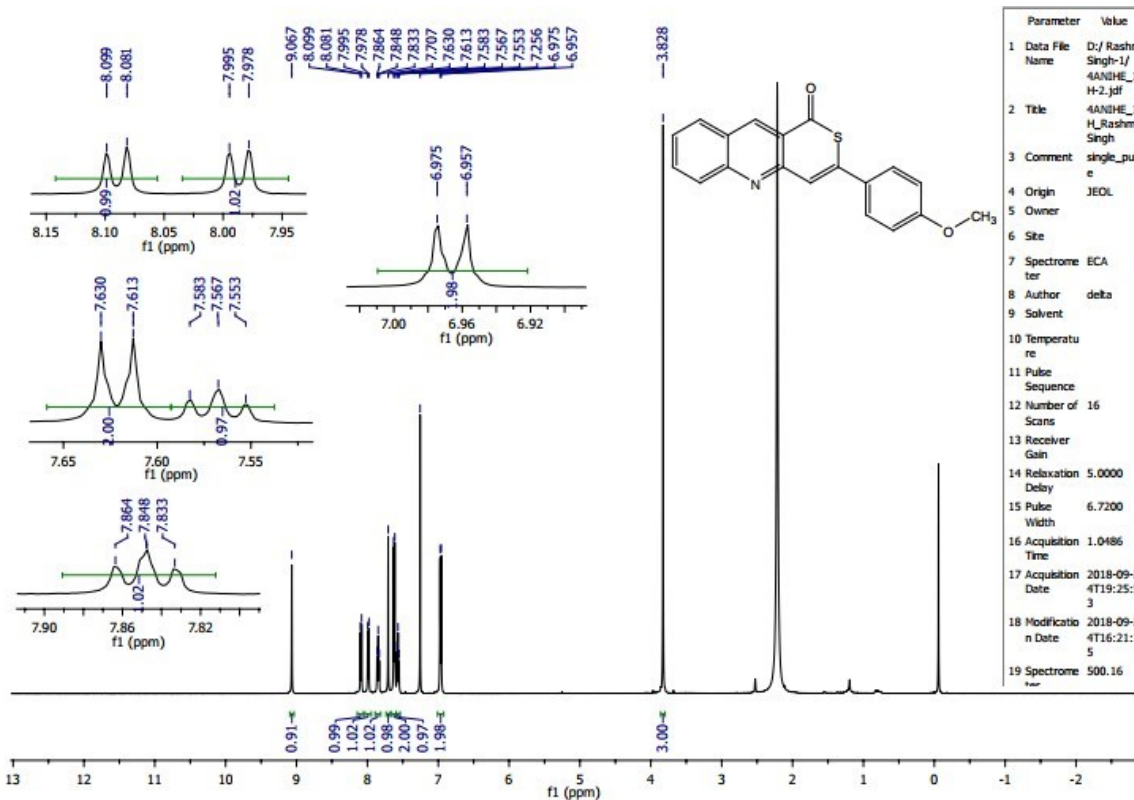


**3-(p-tolyl)-1H-thiopyrano[4,3-b]quinolin-1-one (2l):**

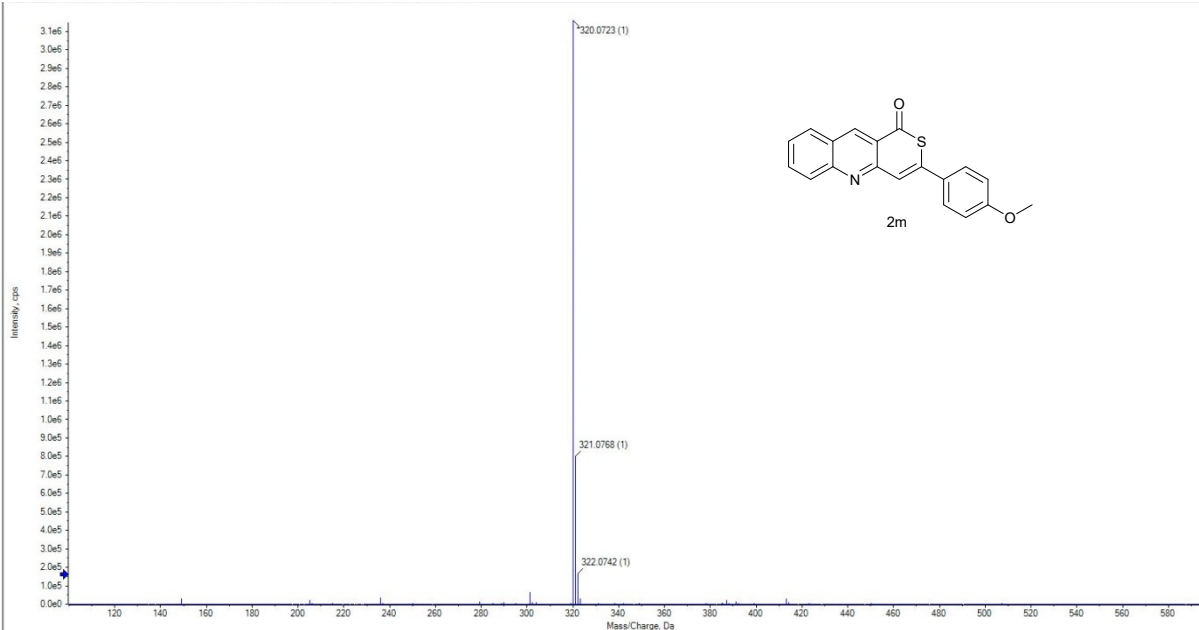




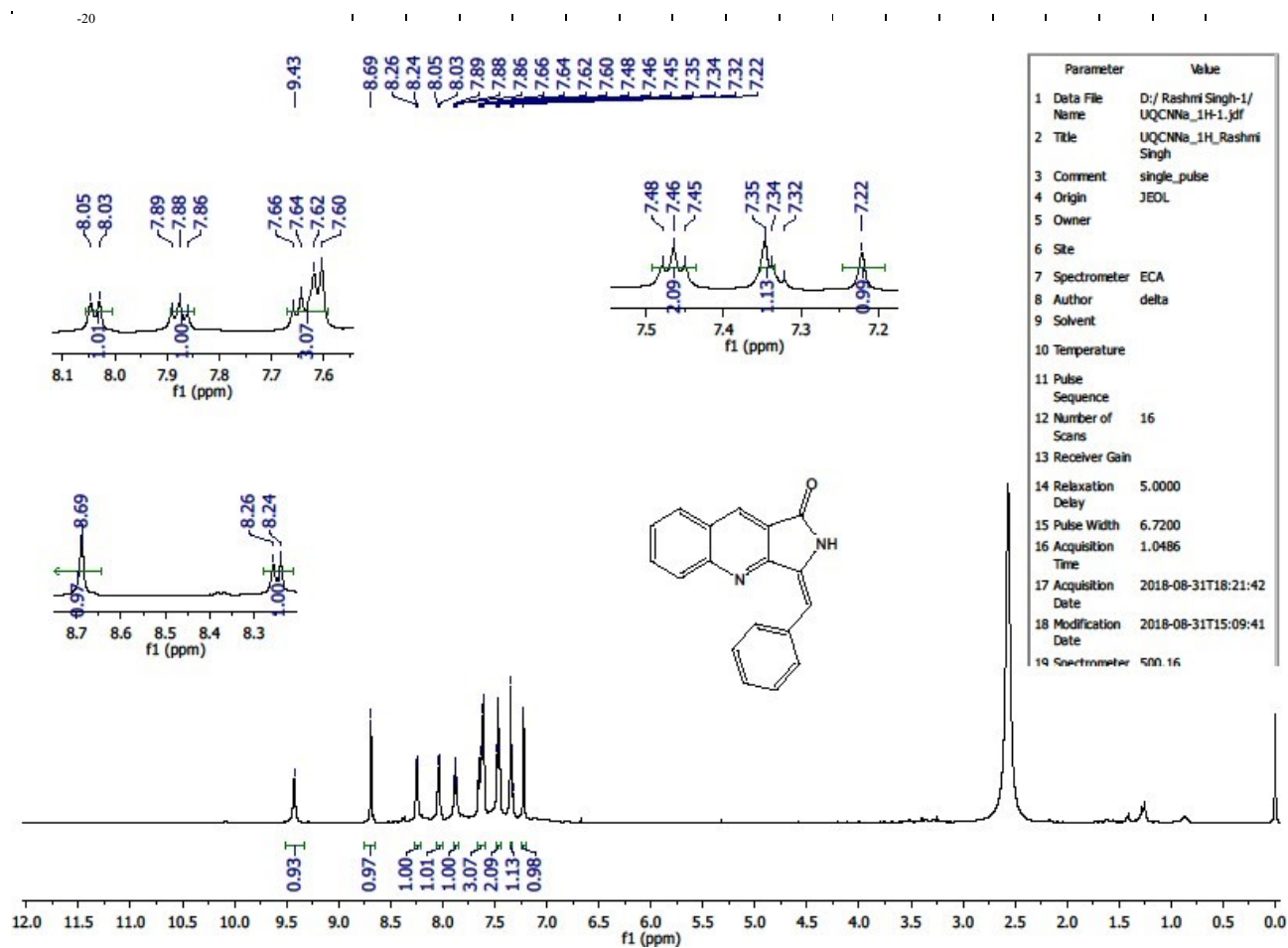
## 3-(4-methoxyphenyl)-1H-thiopyrano[4,3-b]quinolin-1-one (2m):

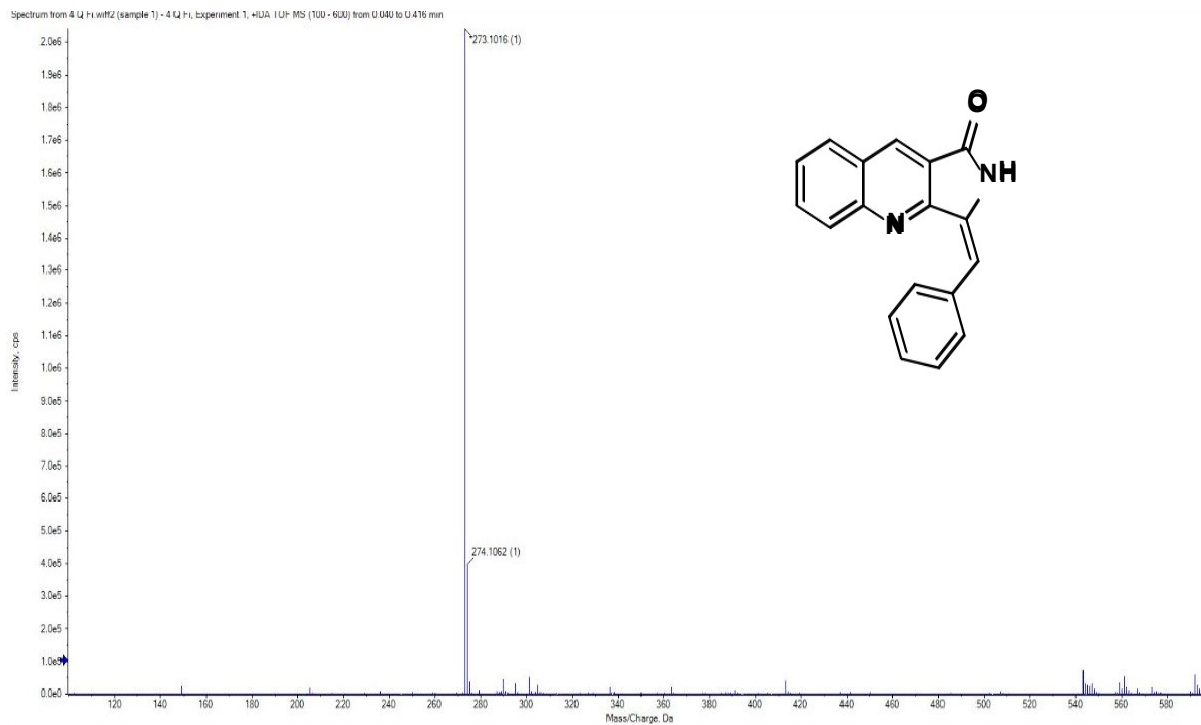
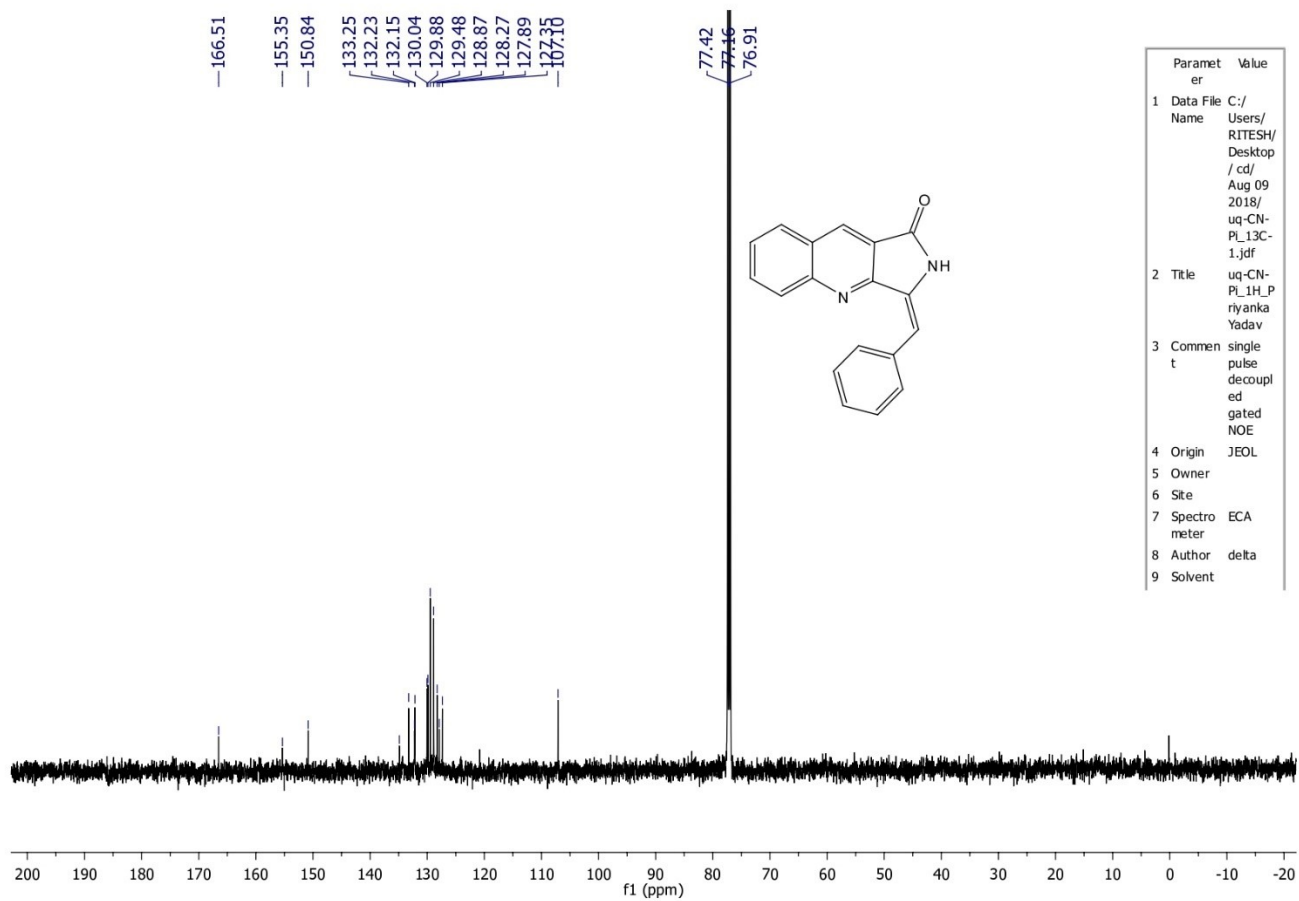


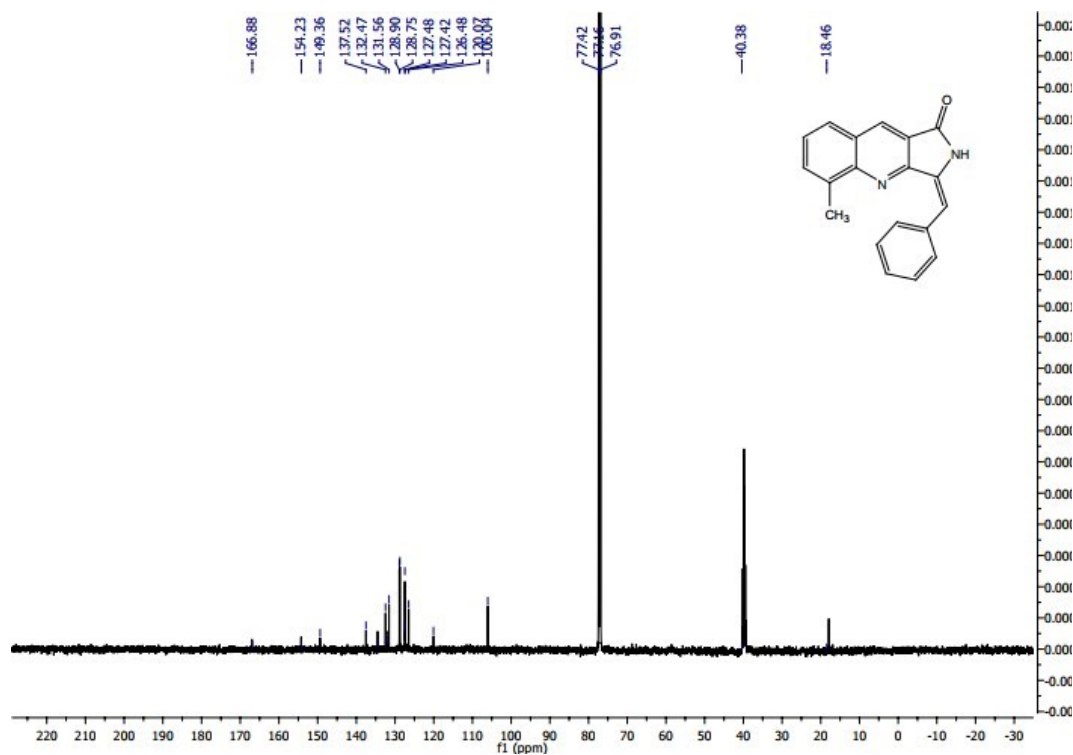
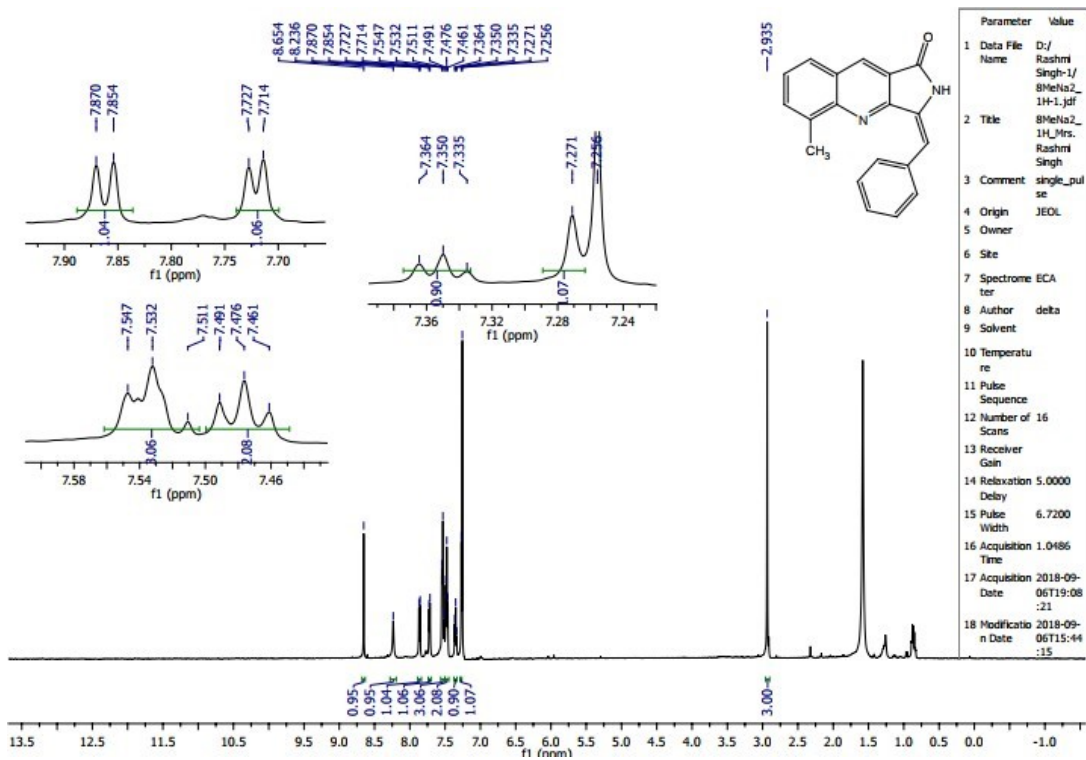


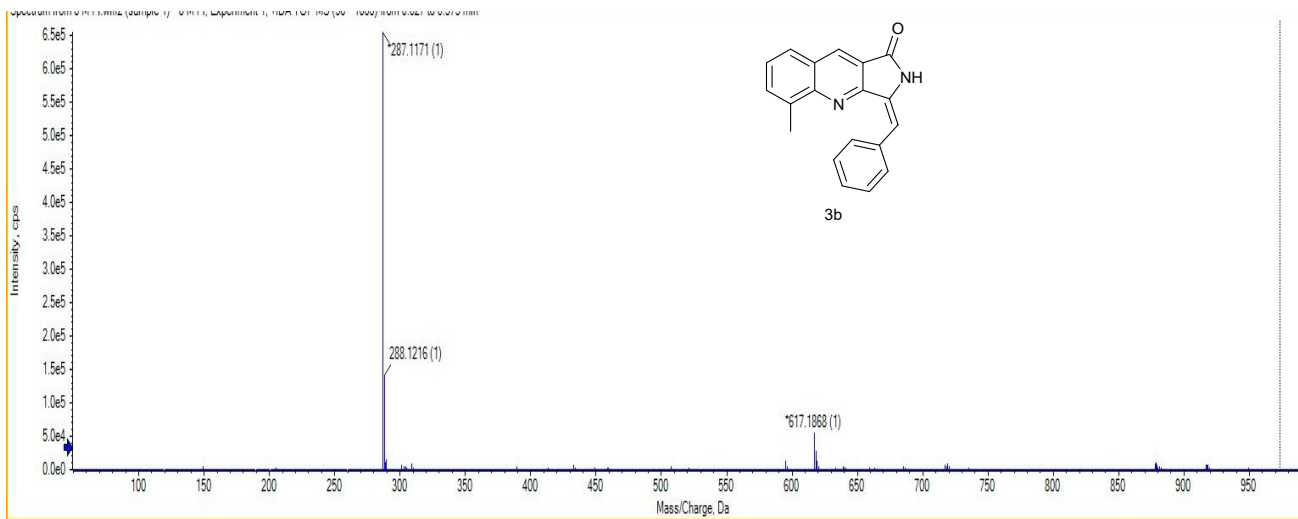


**(E)-3-benzylidene-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3a):**

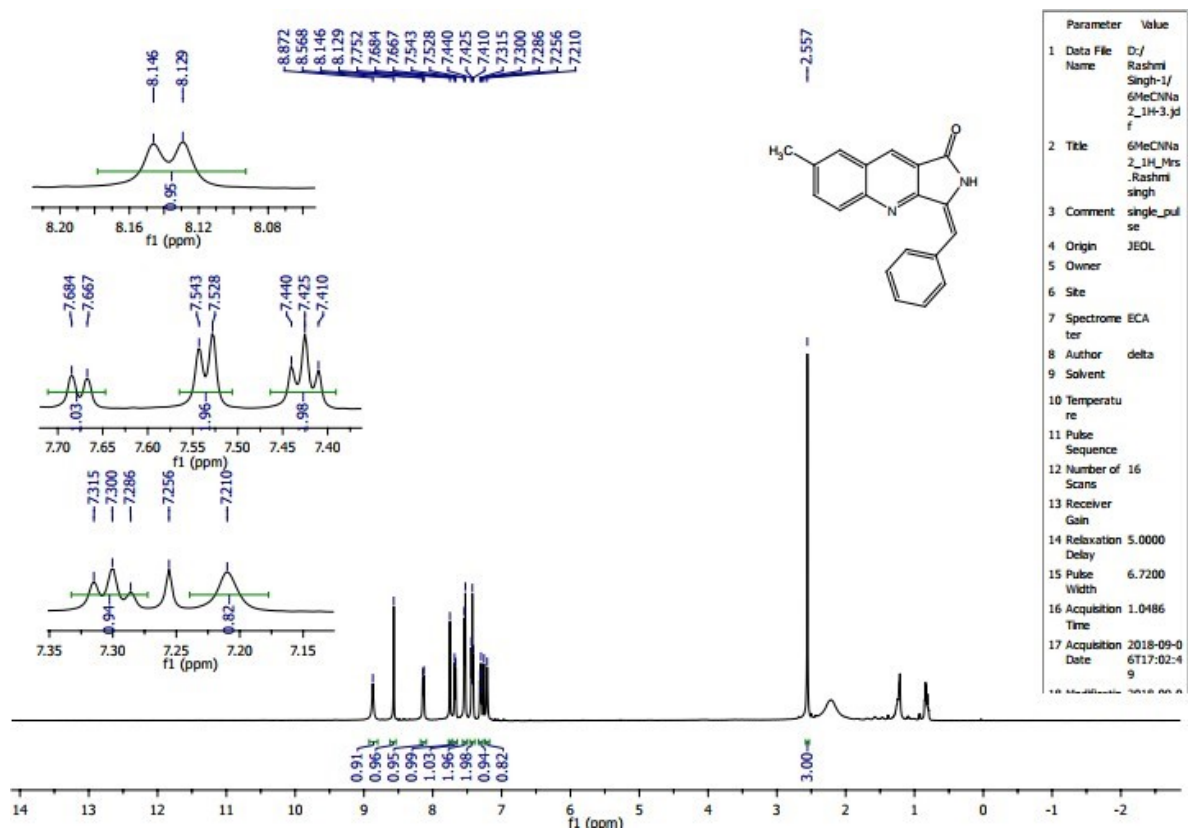


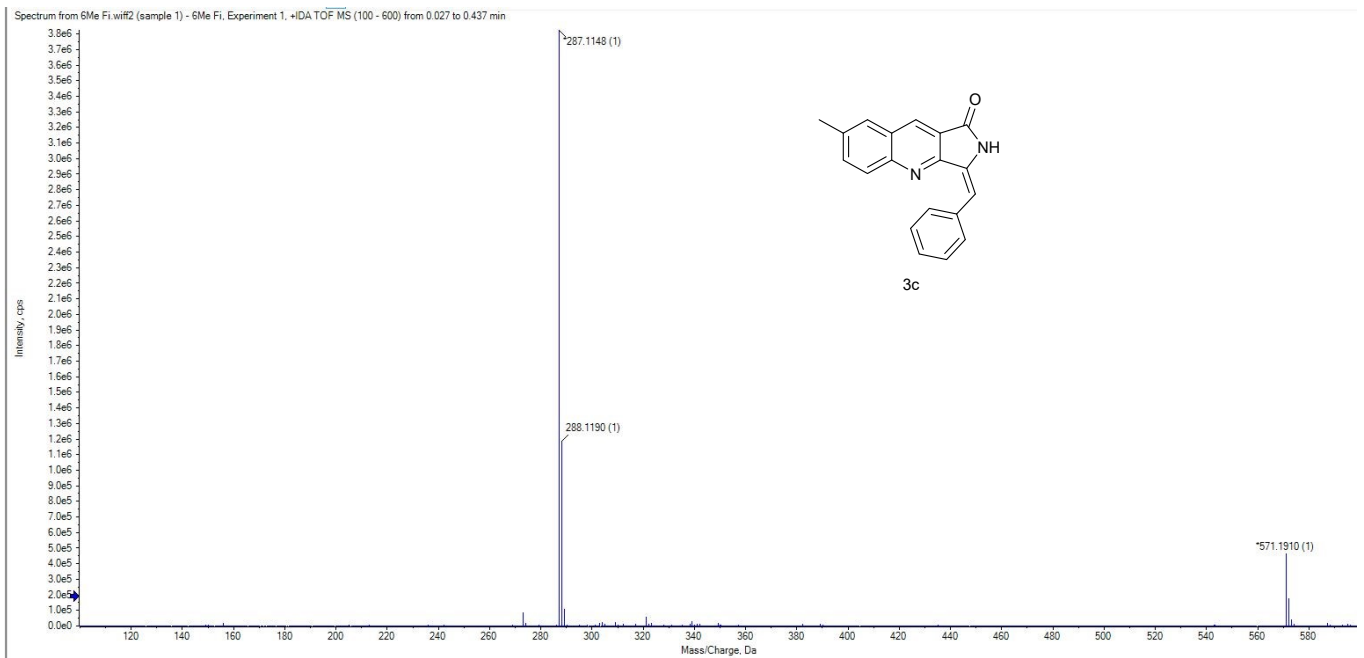
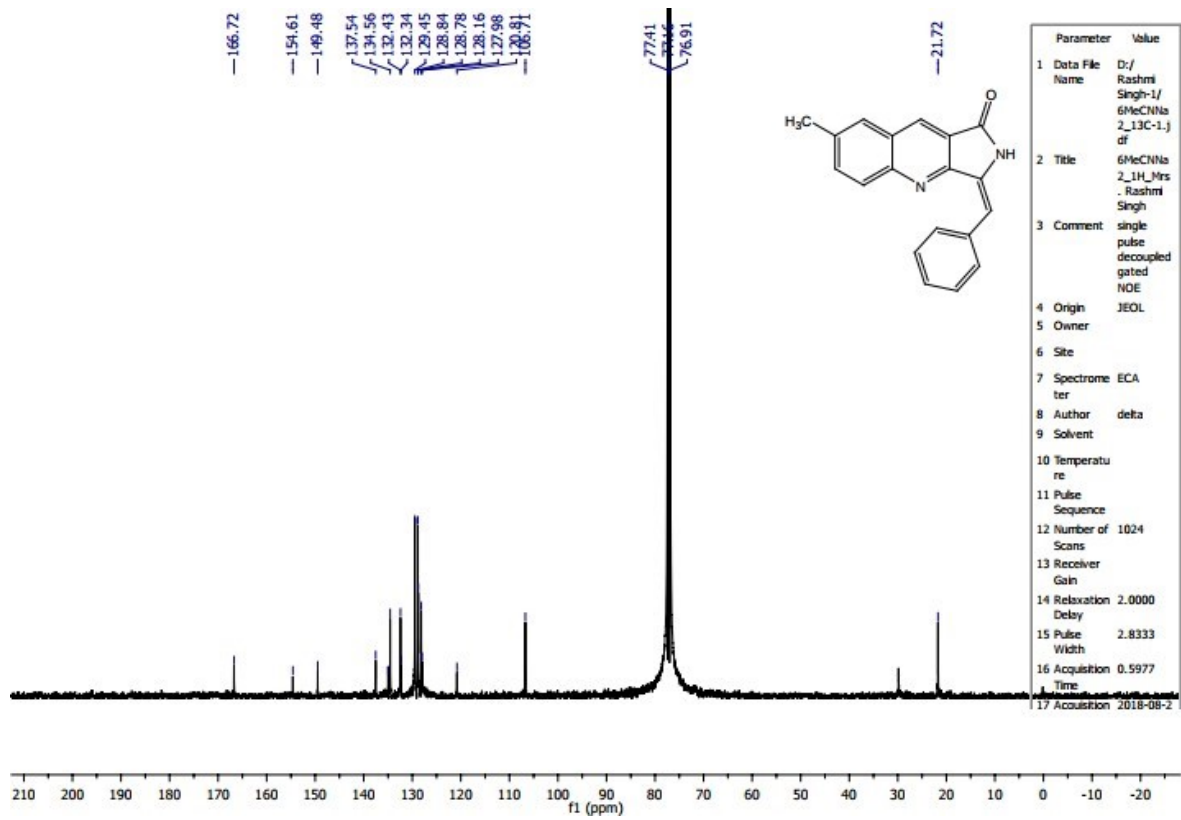


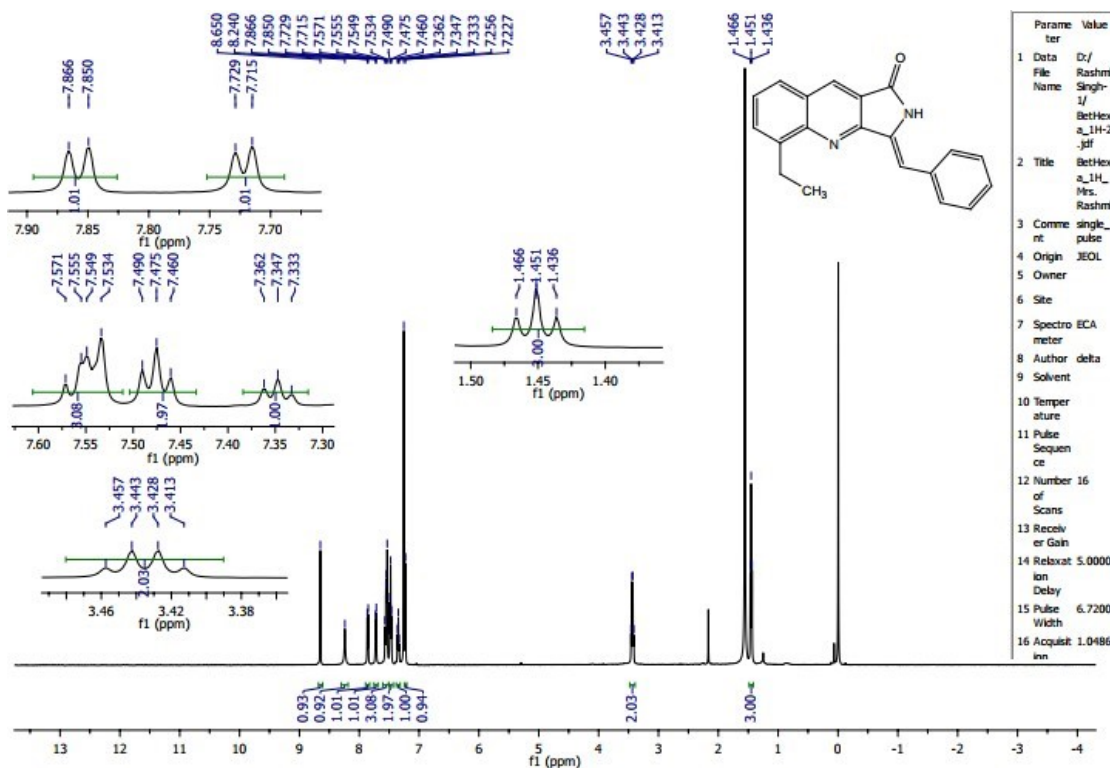
**(E)-3-benzylidene-5-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3b):**



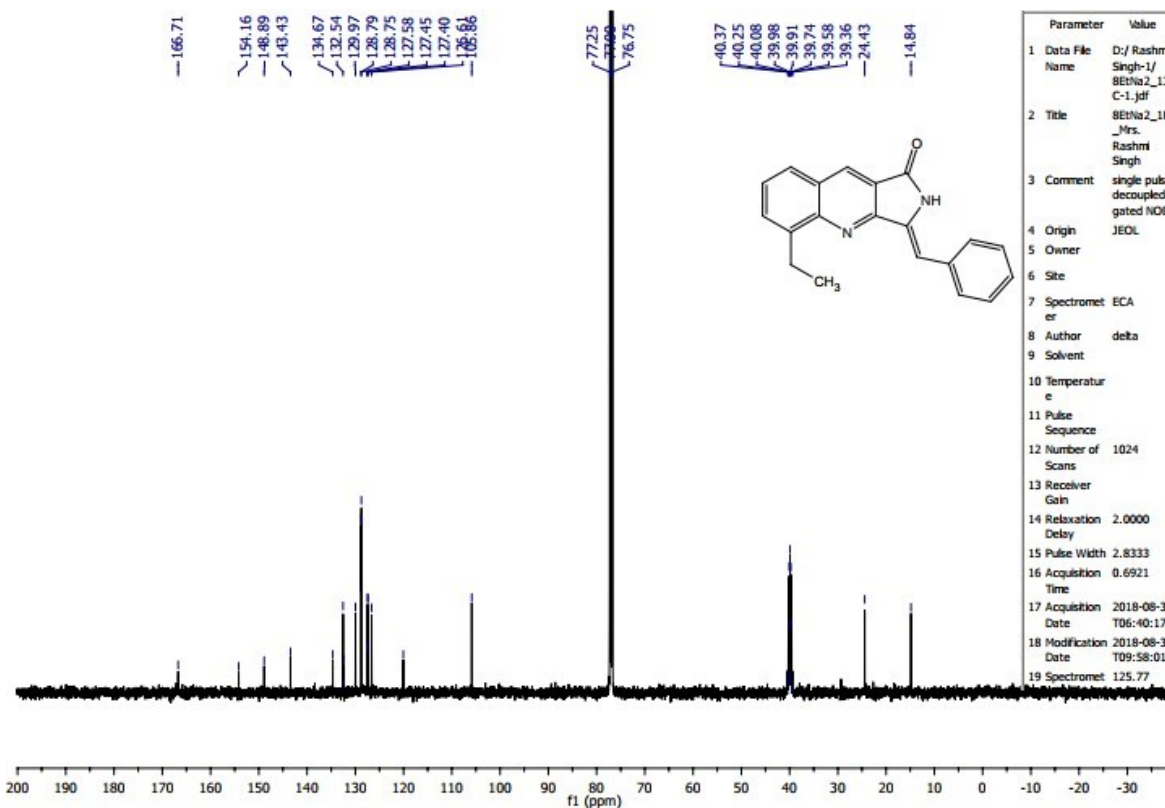
**(E)-3-benzylidene-7-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3c):**



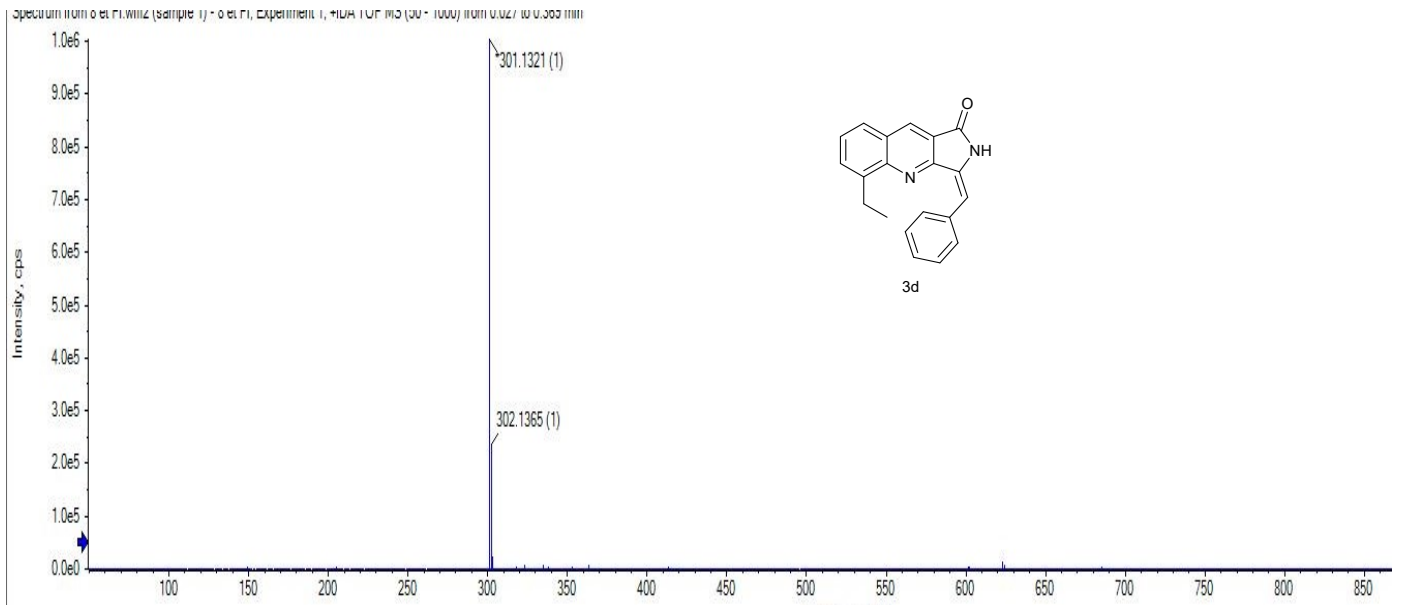


**(E)-3-benzylidene-5-ethyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3d):**

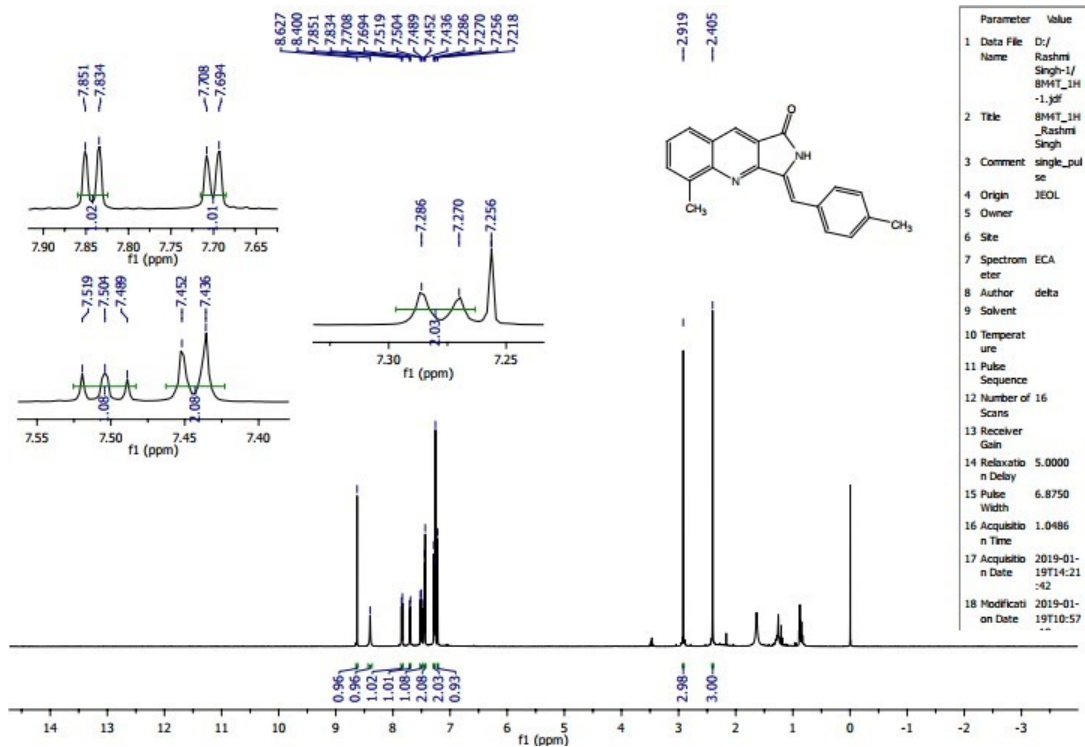
Parameter	Value
1 Data File	D:/ Rashmi Singh-1/ Bethex_a_1H-2 .jdf
2 Title	Bethex_a_1H_Mrs. Rashmi
3 Comment	single pulse
4 Origin	JEOL
5 Owner	
6 Site	
7 Spectrometer	ECA
8 Author	deta
9 Solvent	
10 Temperature	
11 Pulse Sequence	
12 Number of Scans	16
13 Receiver Gain	
14 Relaxation Delay	5.0000
15 Pulse Width	6.7200
16 Acquisition	1.0486

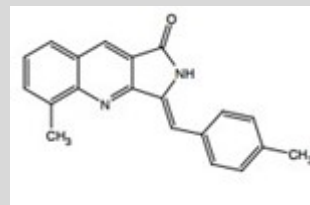
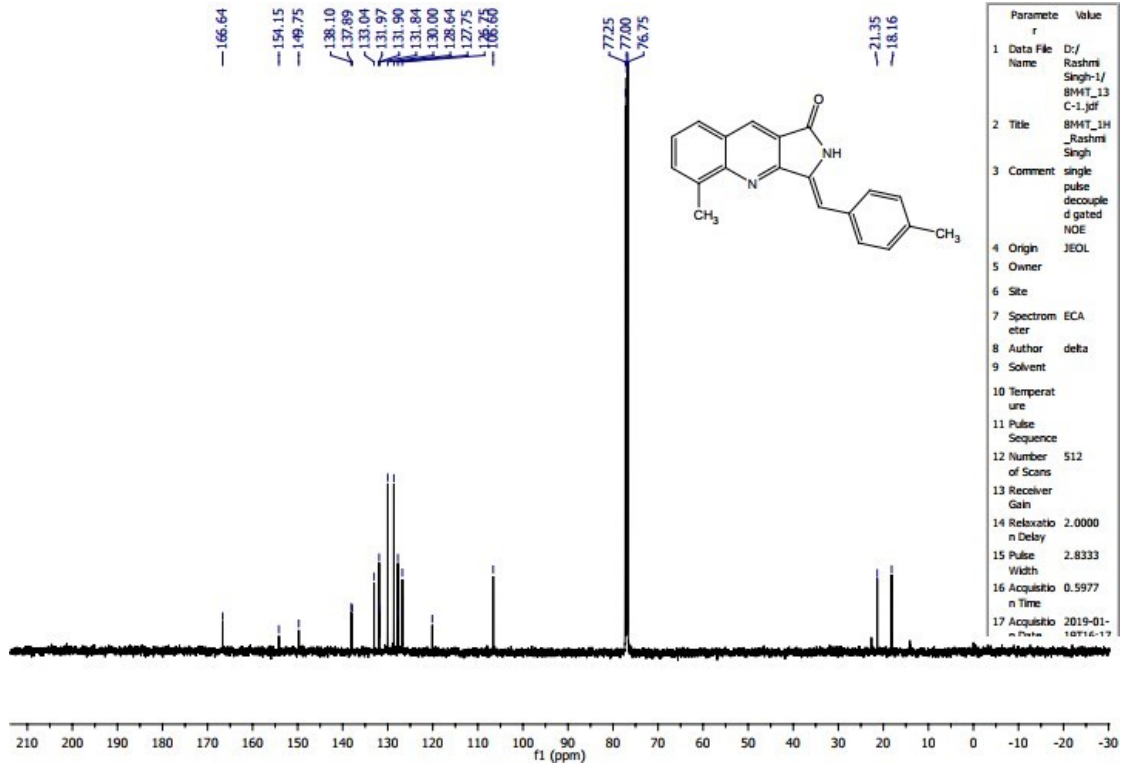


Parameter	Value
1 Data File	D:/ Rashmi Singh-1/ BEthx_2_13 C-1.jdf
2 Title	BEthx_2_1H_Mrs. Rashmi Singh
3 Comment	single pulse decoupled gated NOE
4 Origin	JEOL
5 Owner	
6 Site	
7 Spectrometer	ECA
8 Author	deta
9 Solvent	
10 Temperature	
11 Pulse Sequence	
12 Number of Scans	1024
13 Receiver Gain	
14 Relaxation Delay	2.0000
15 Pulse Width	2.8333
16 Acquisition Time	0.6921
17 Acquisition Date	2018-08-31 T06:40:17
18 Modification Date	2018-08-31 T09:58:01
19 Spectrometer	125.77

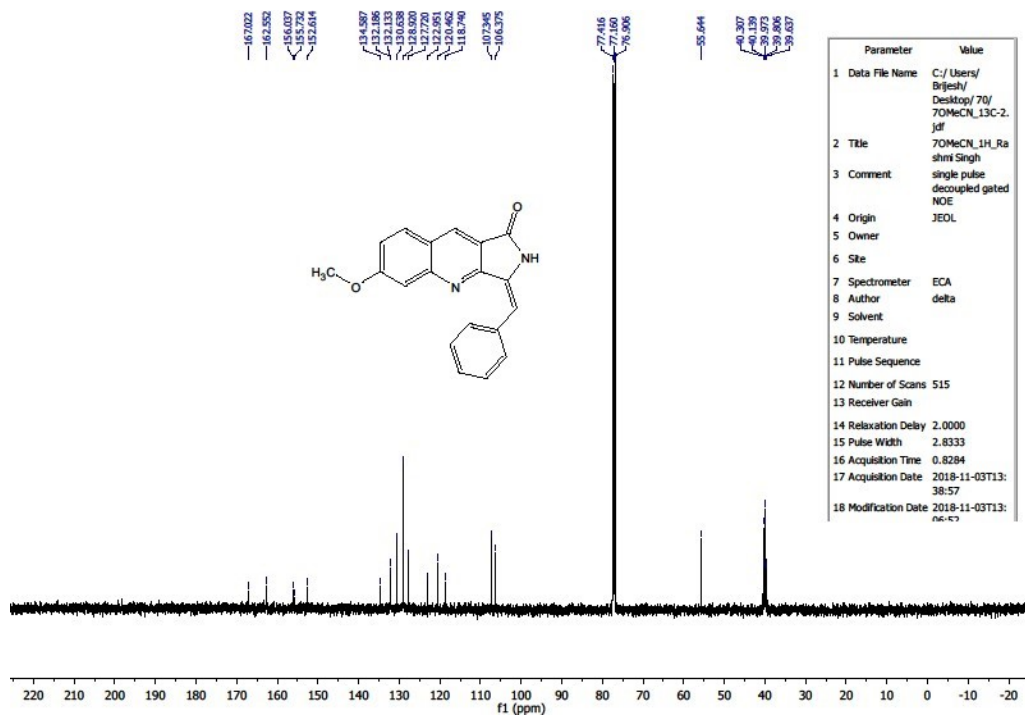
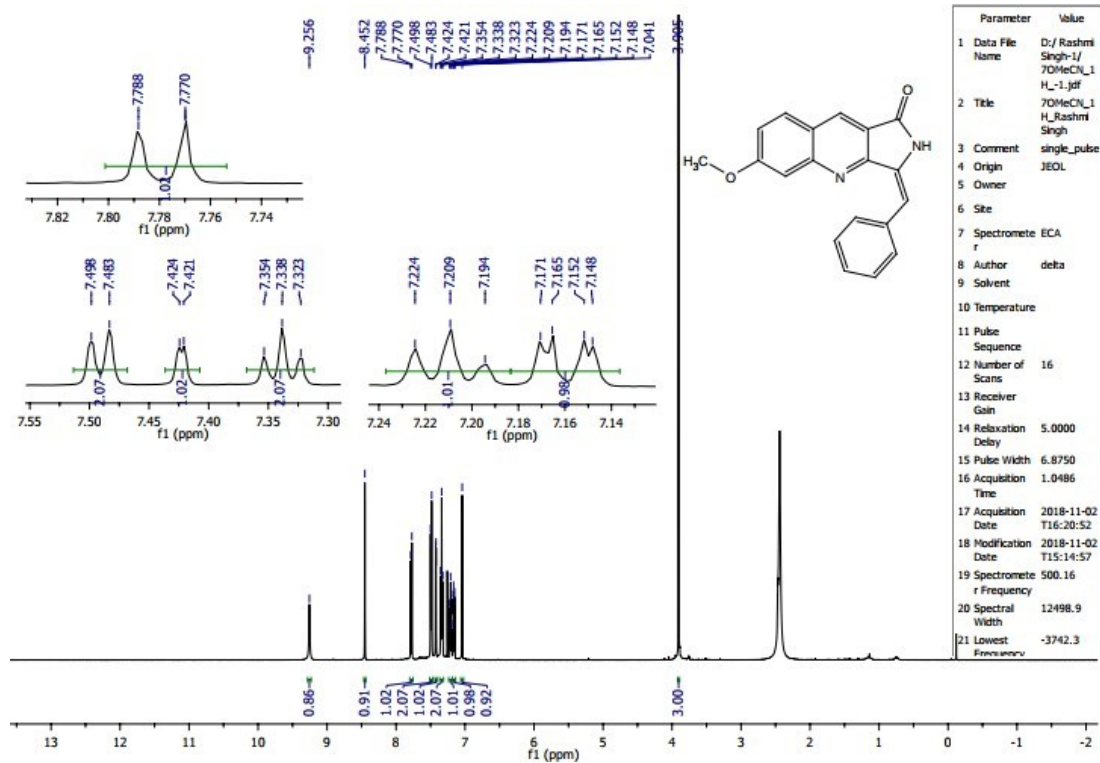


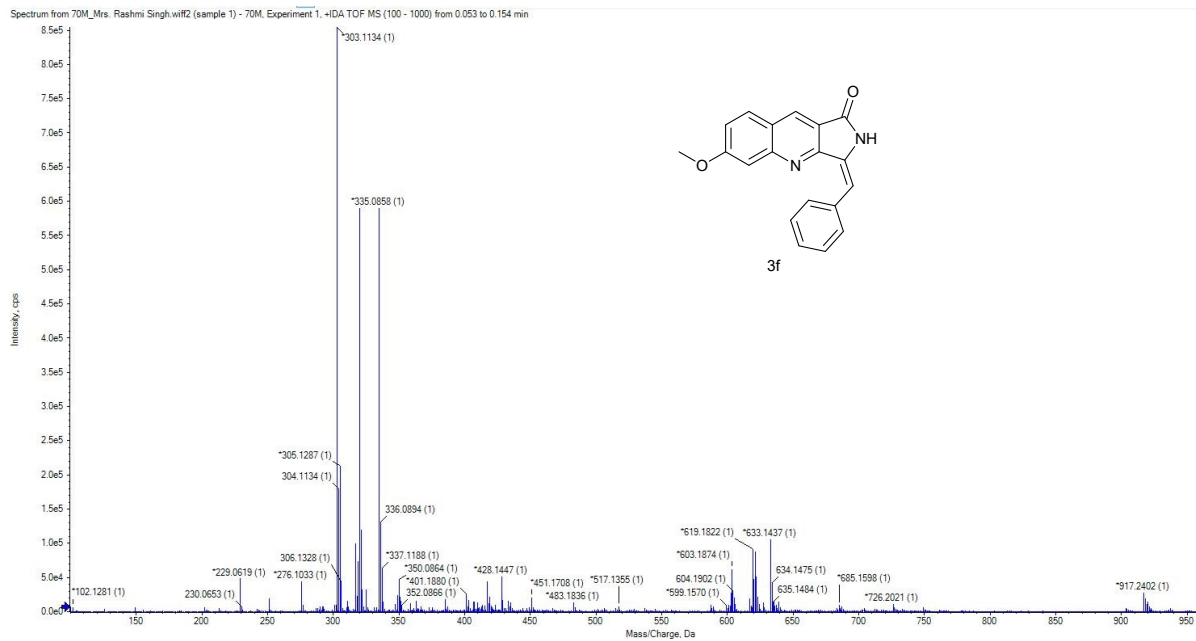
**(E)-5-methyl-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3e):**



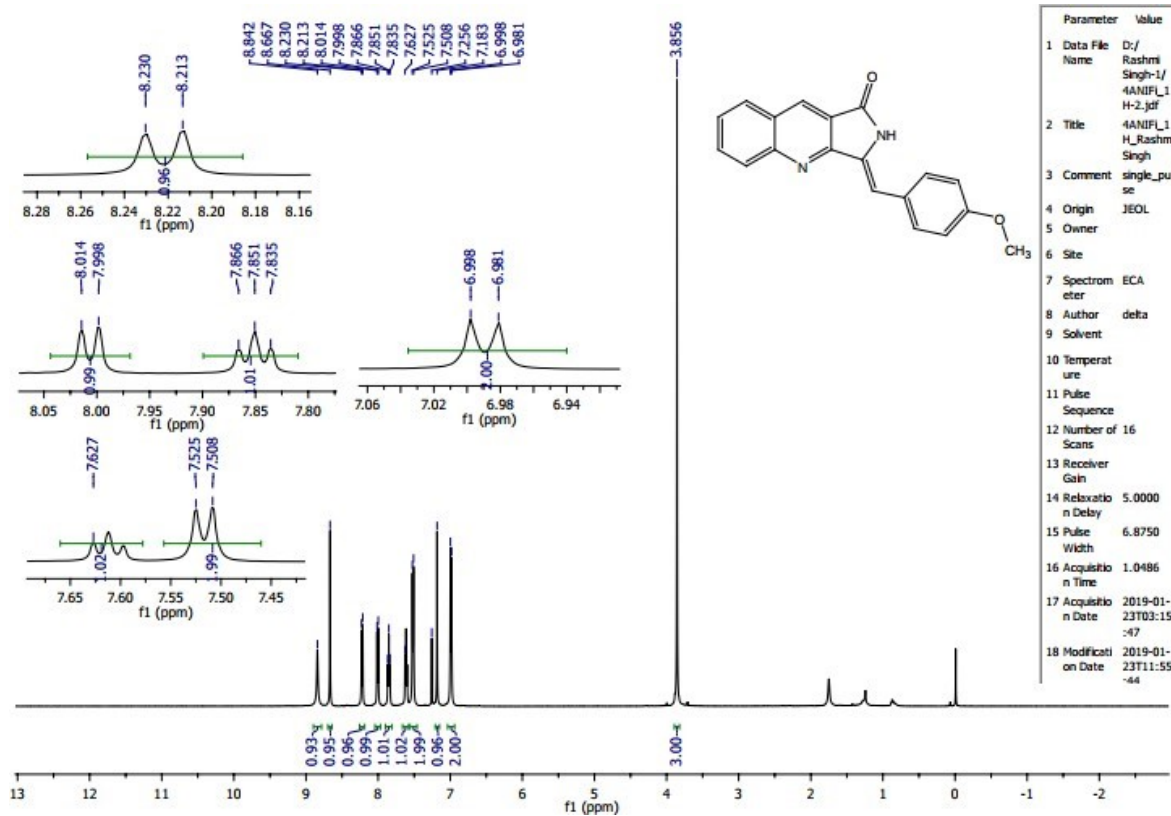


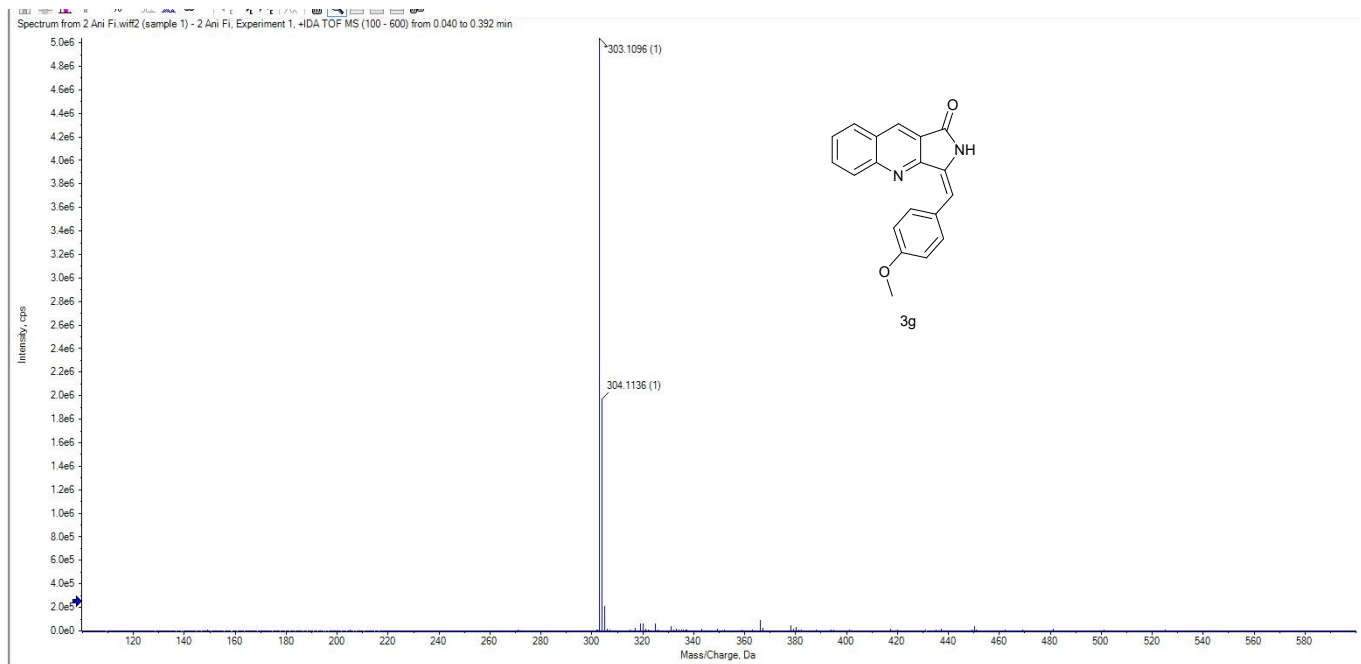
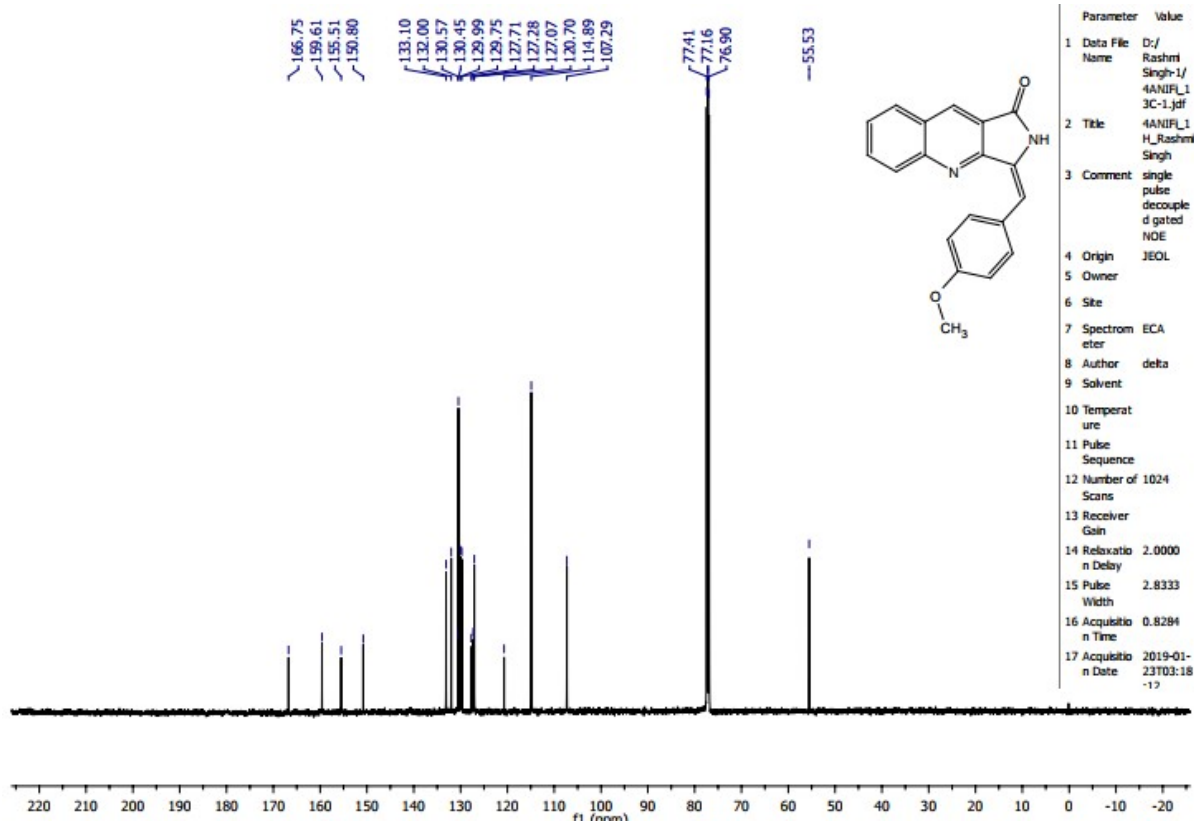


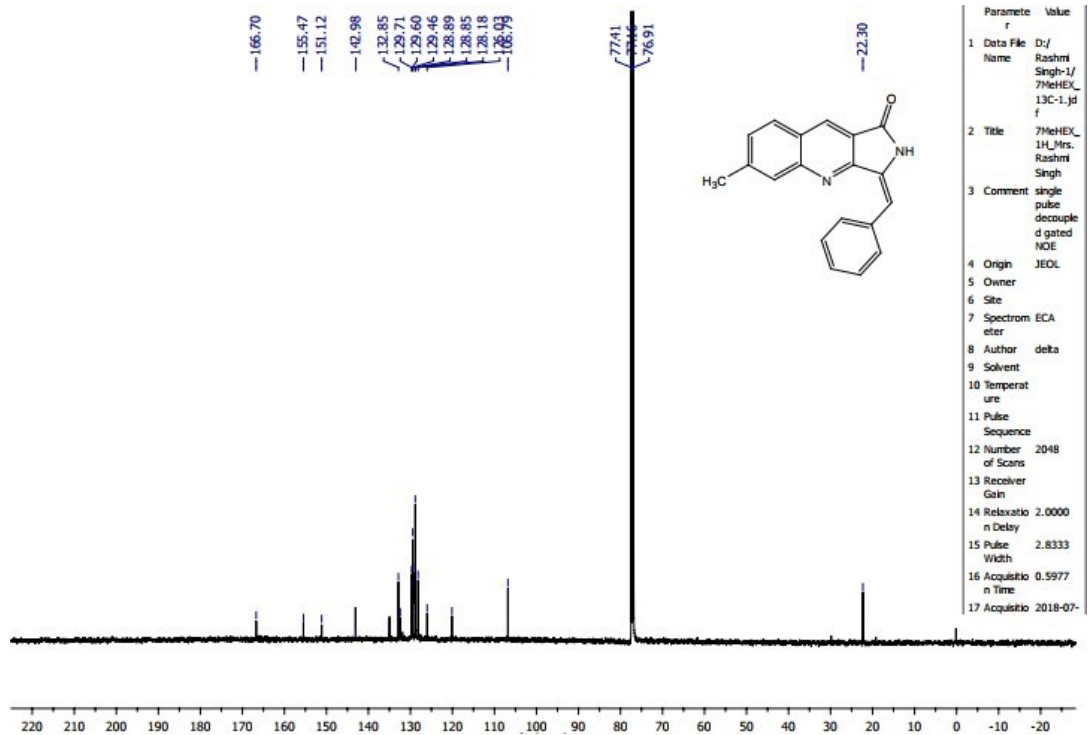
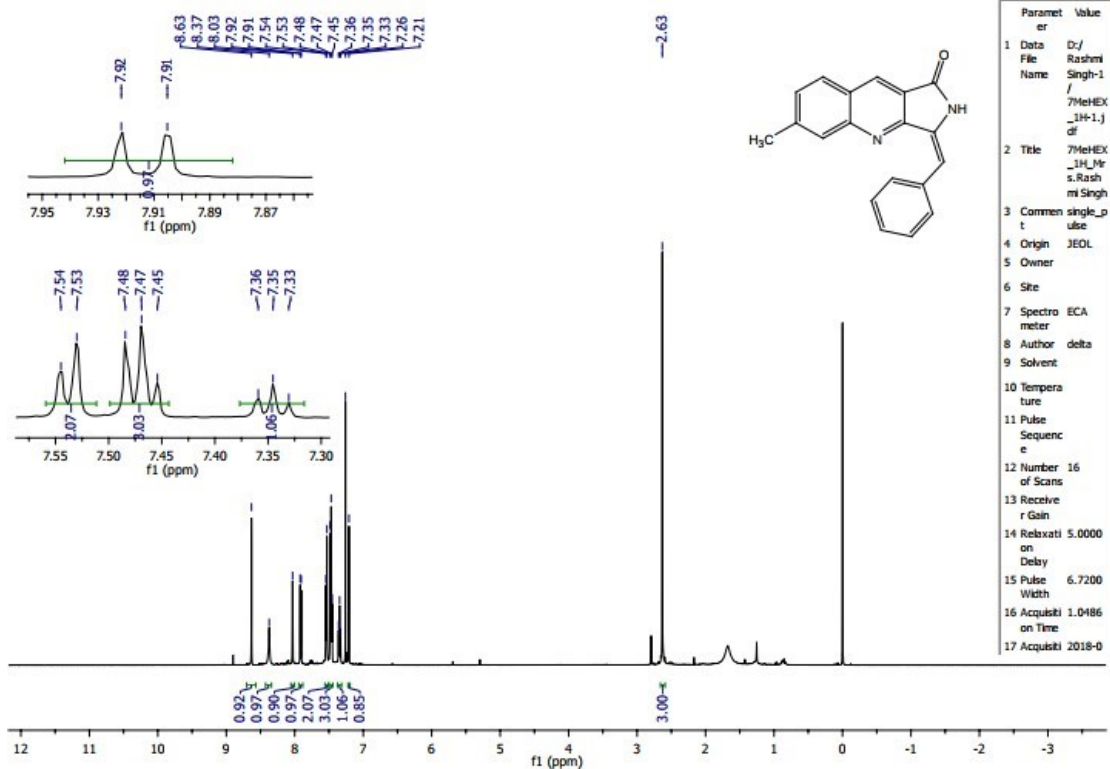
**(E)-3-benzylidene-7-methoxy-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3f):**

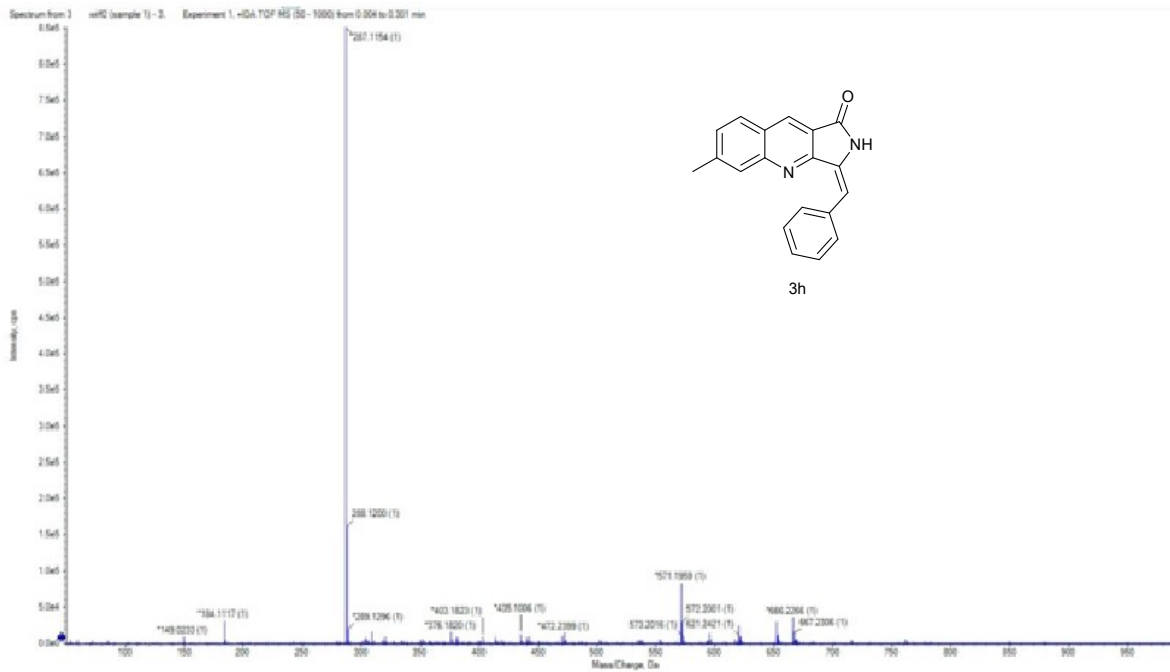


**(E)-3-(4-methoxybenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3g):**

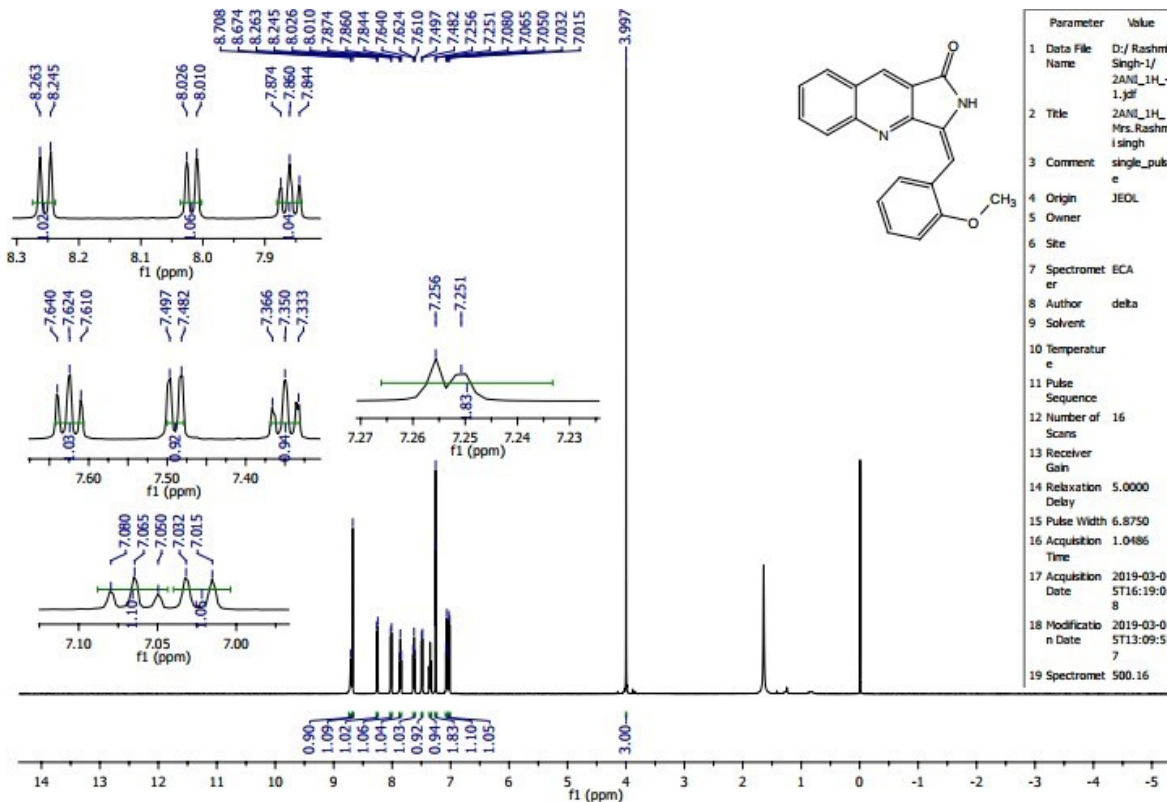


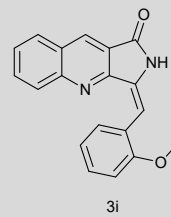
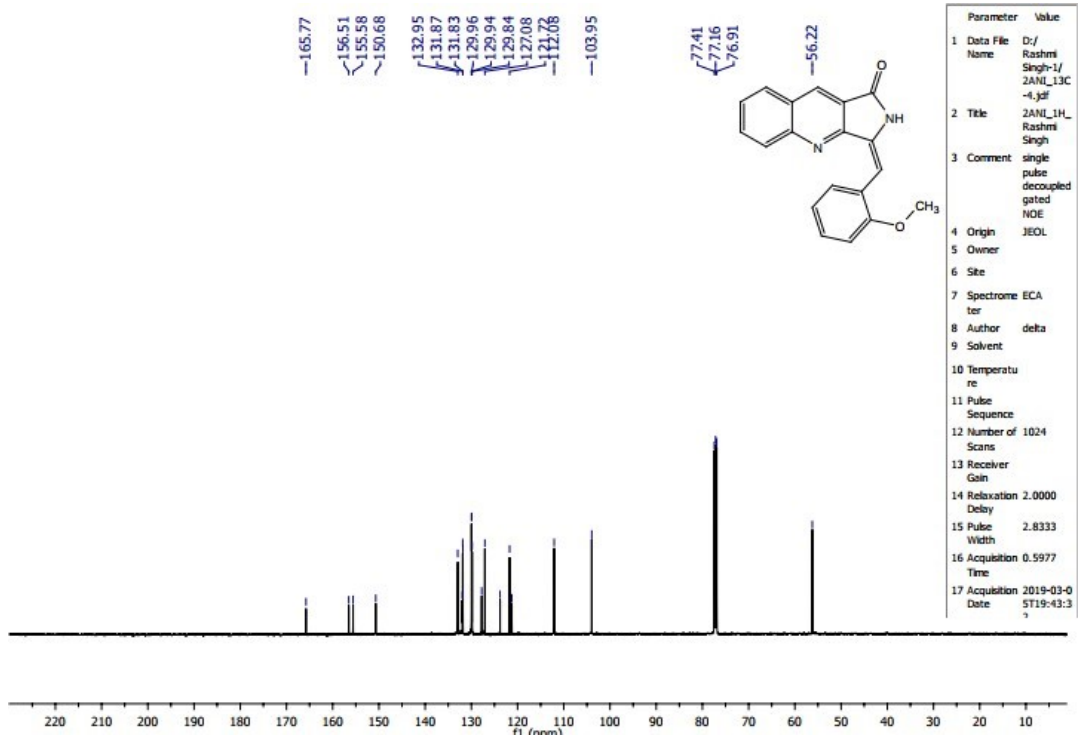


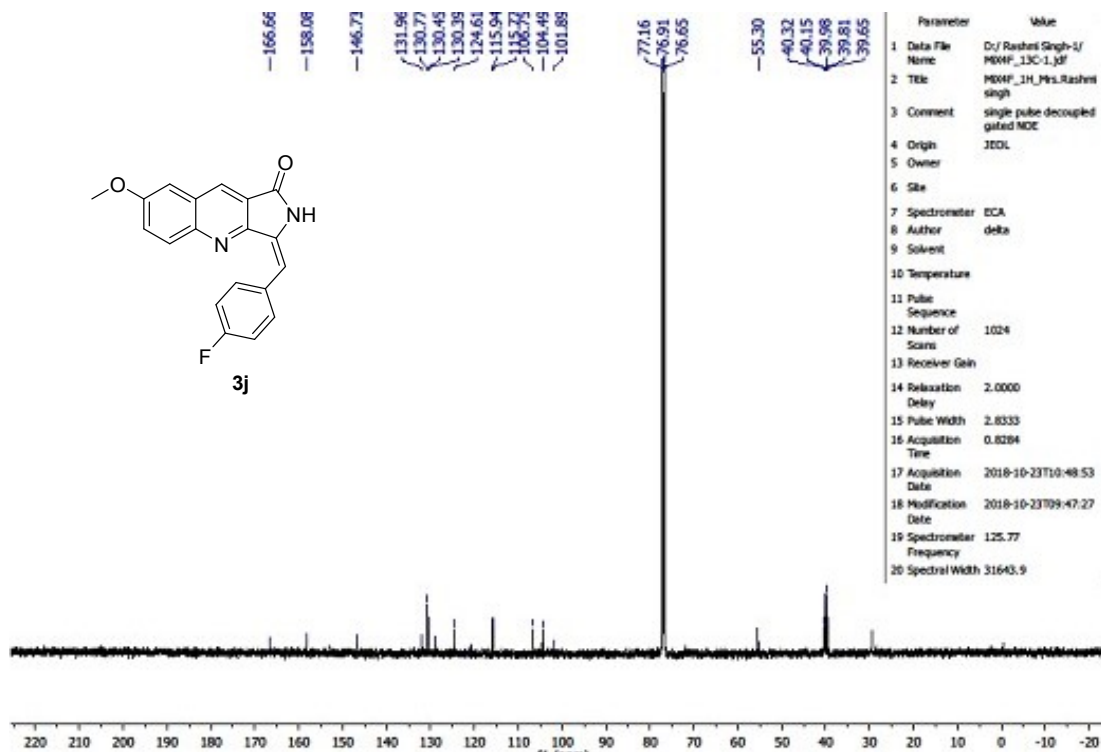
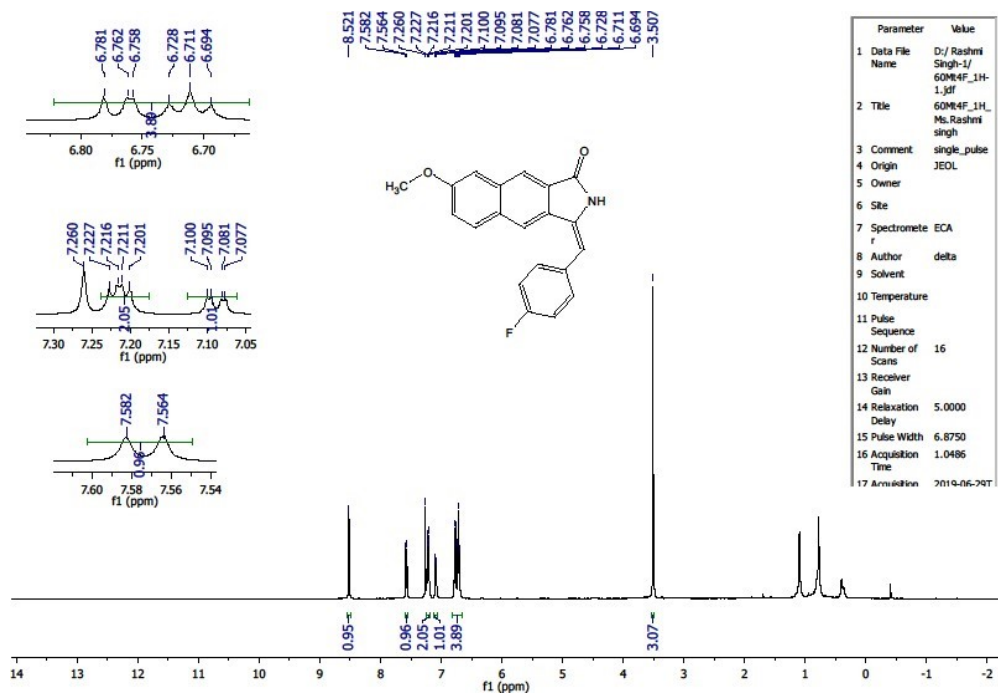
**(E)-3-benzylidene-6-methyl-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3h):**

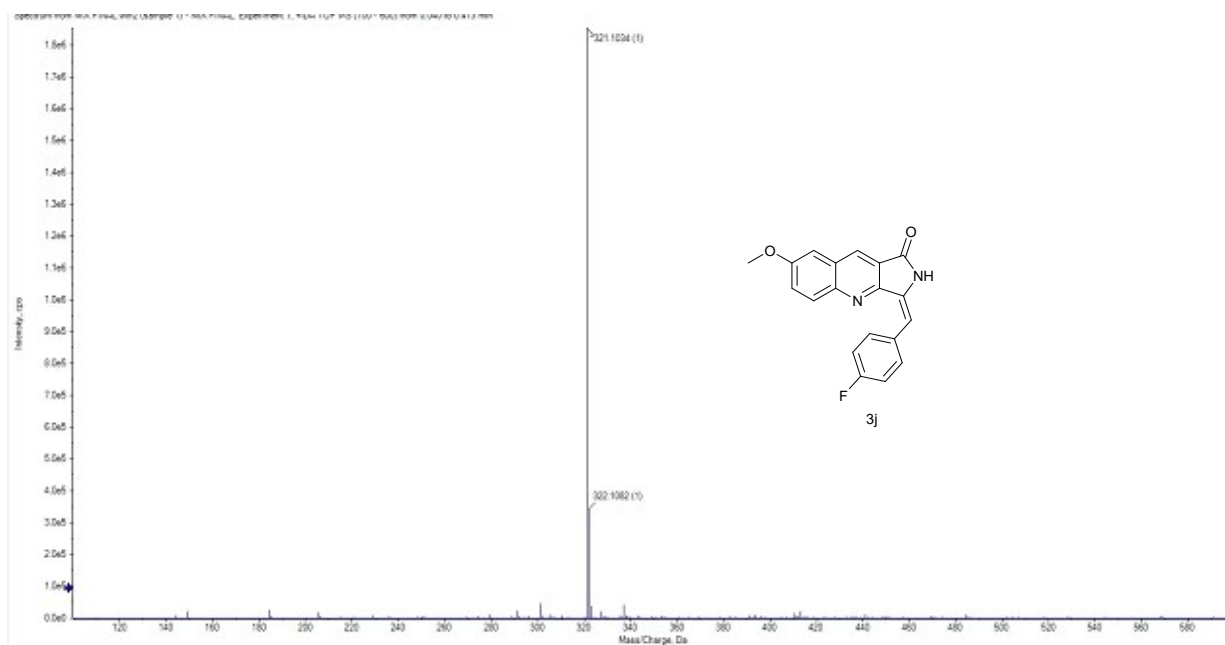
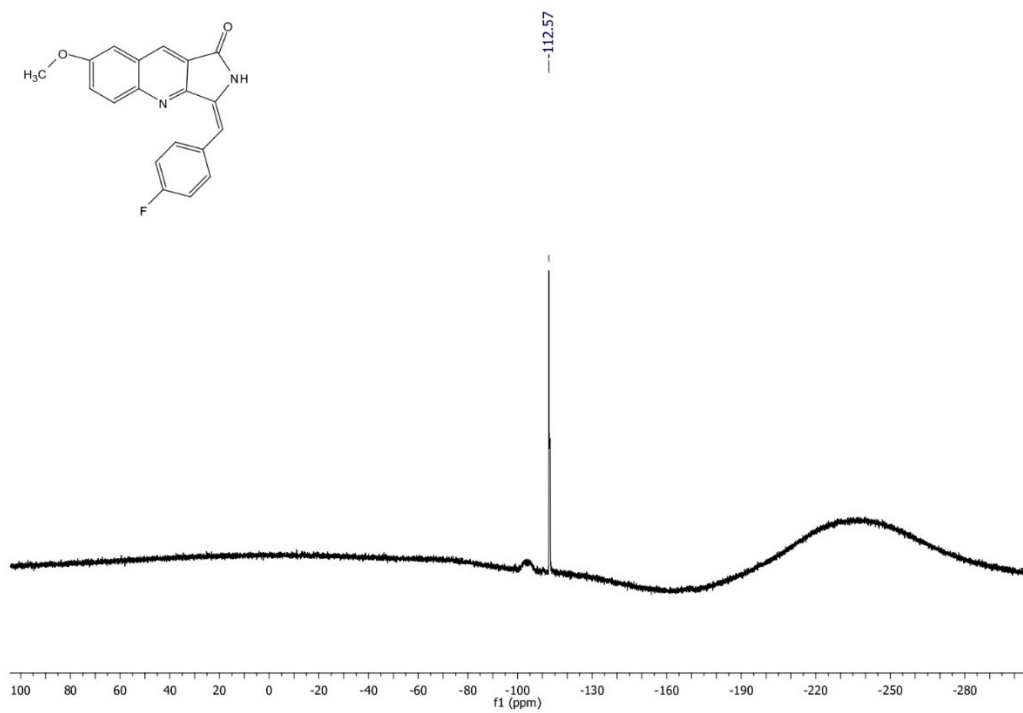


**(E)-3-(2-methoxybenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3i):**

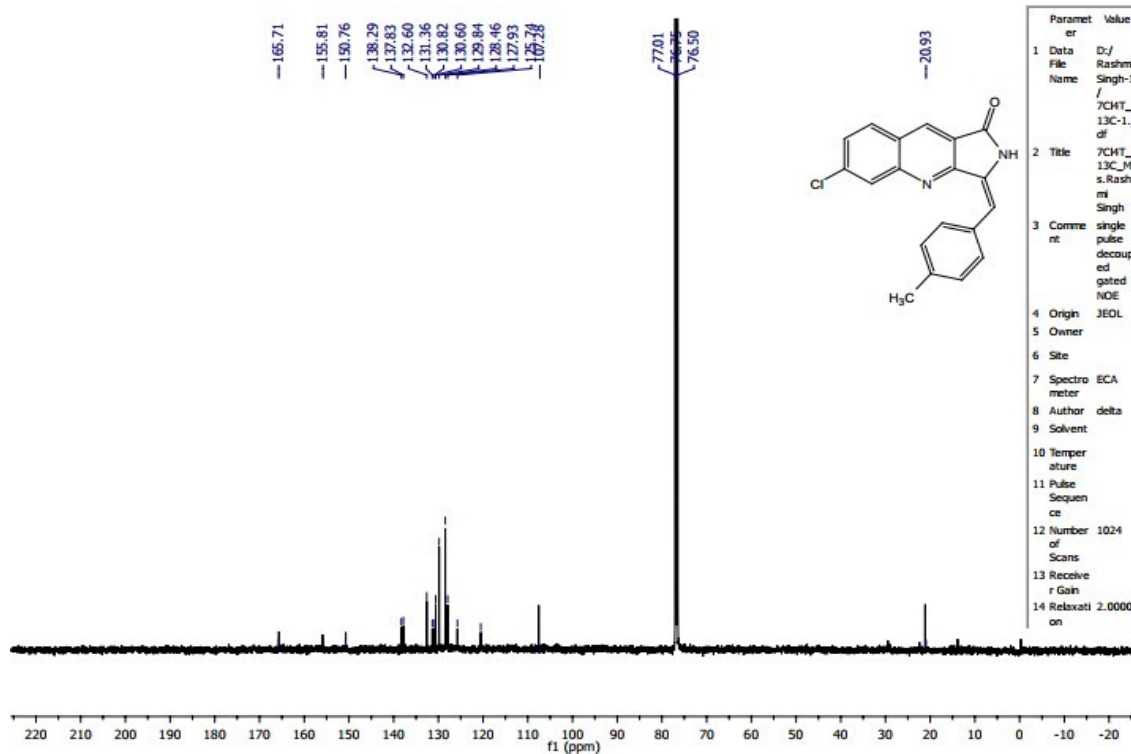
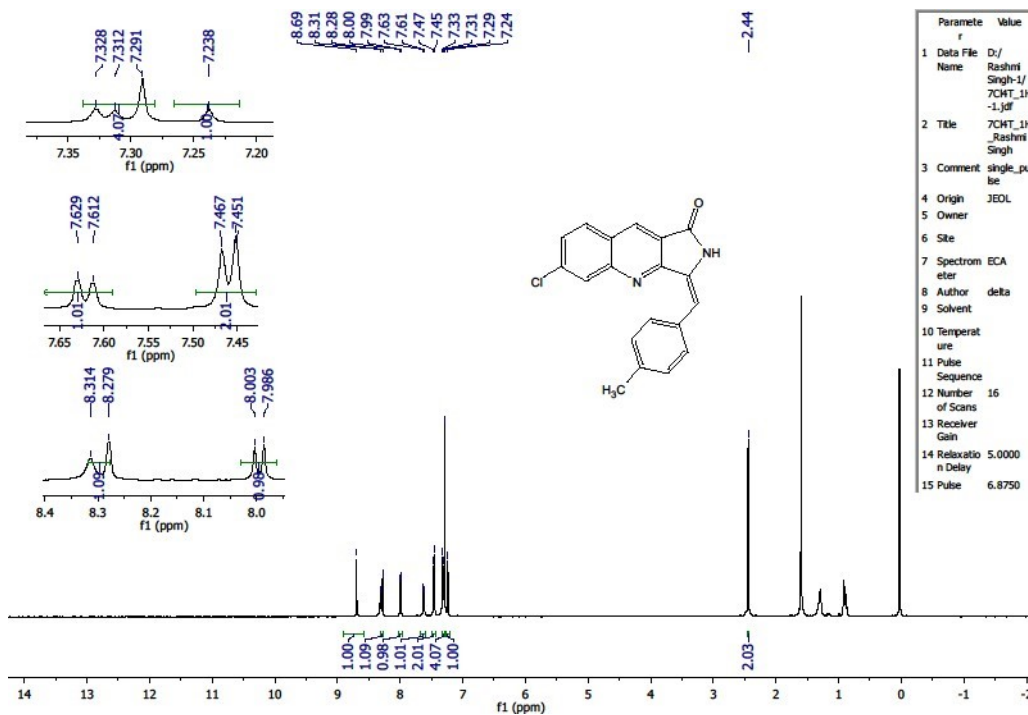


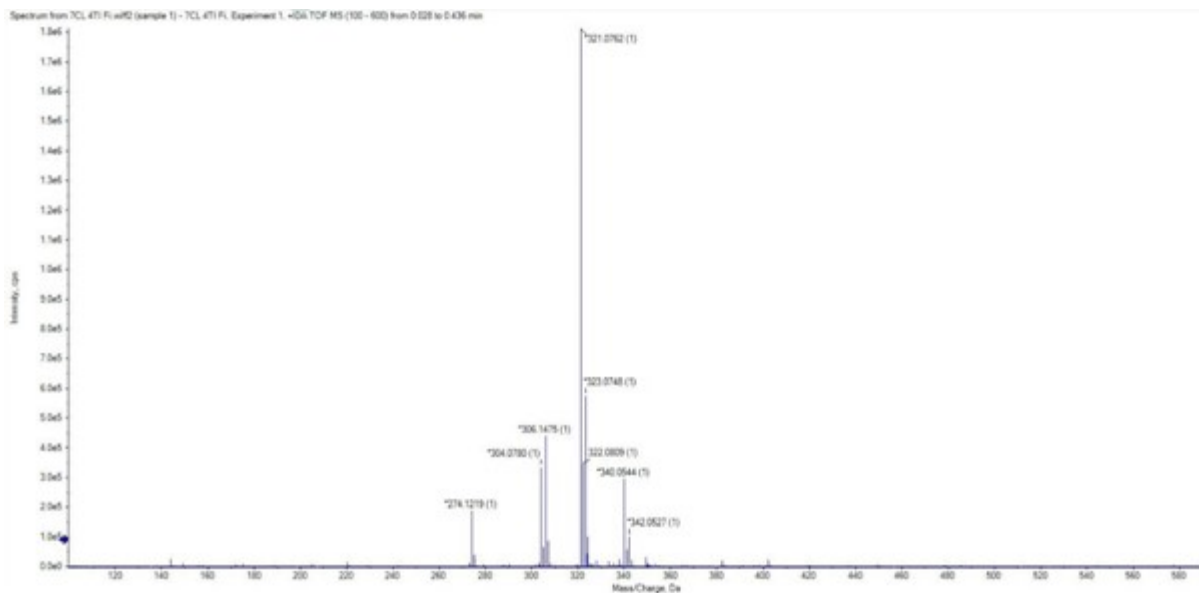


**(E)-3-(4-fluorobenzylidene)-7-methoxy-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3j):**

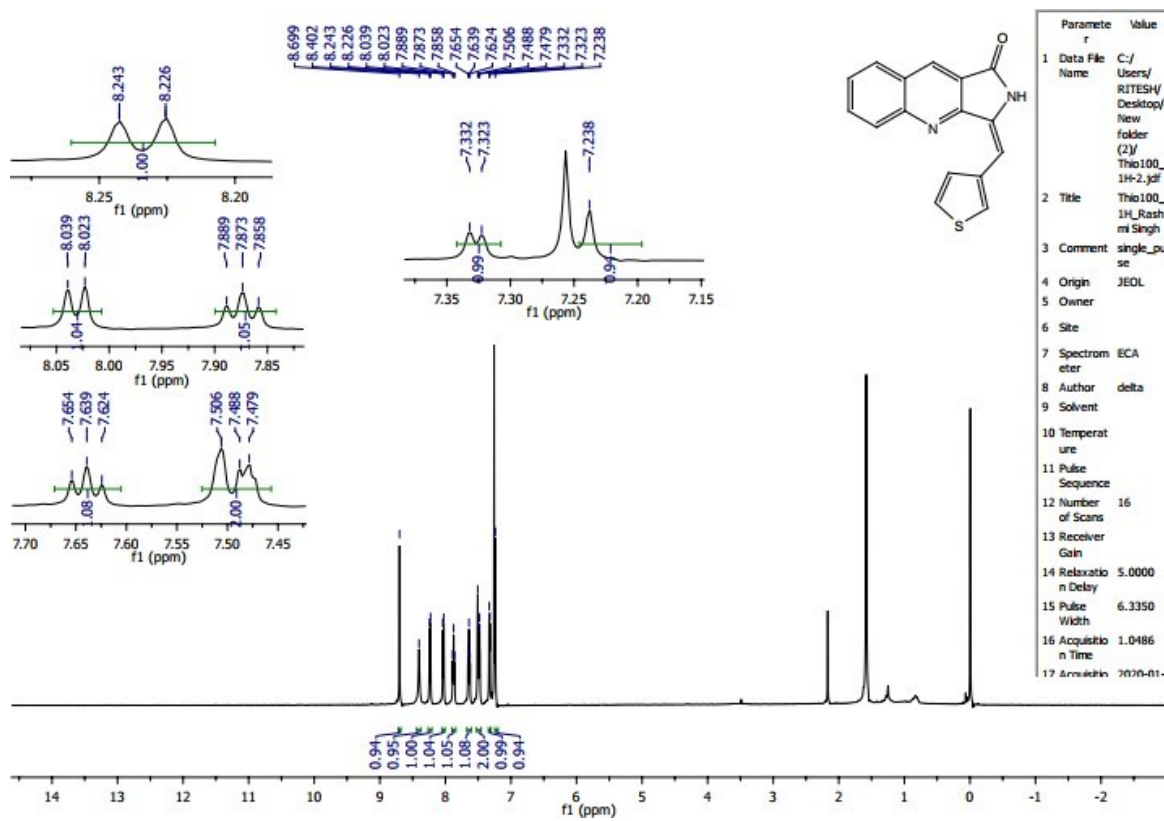


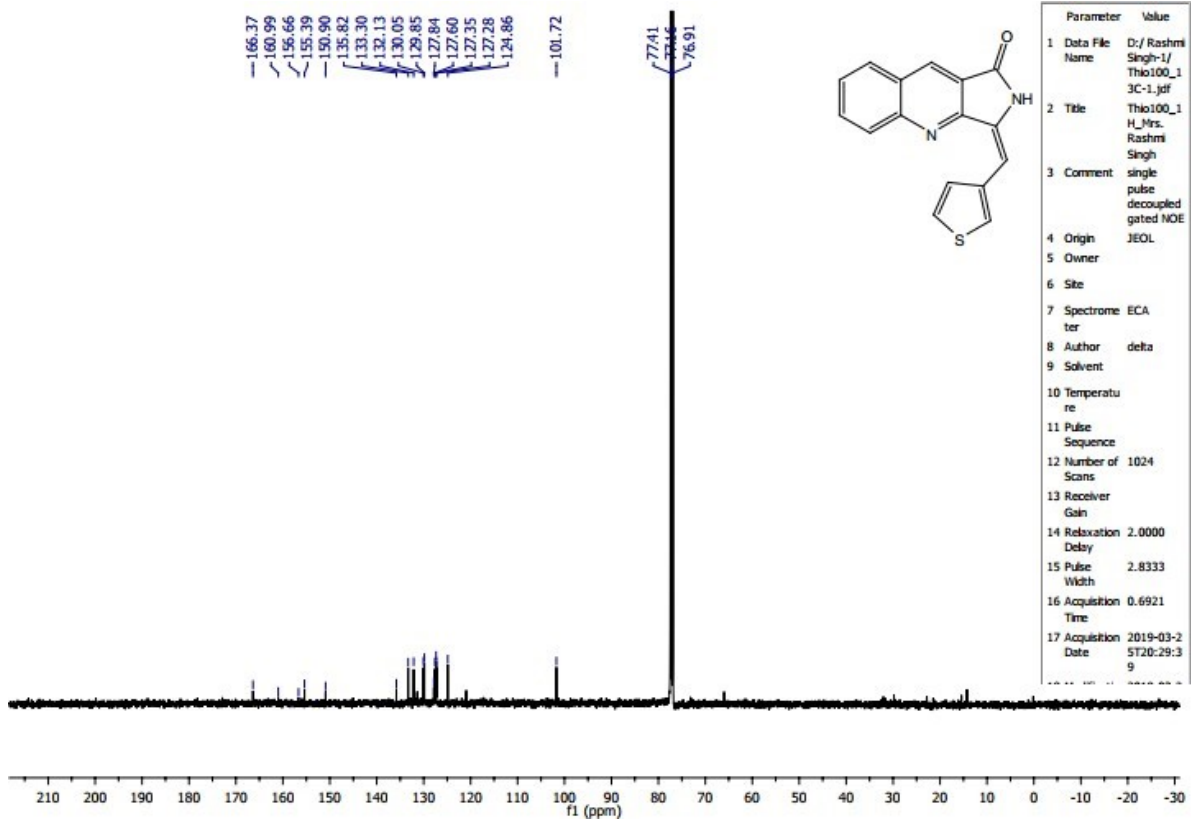


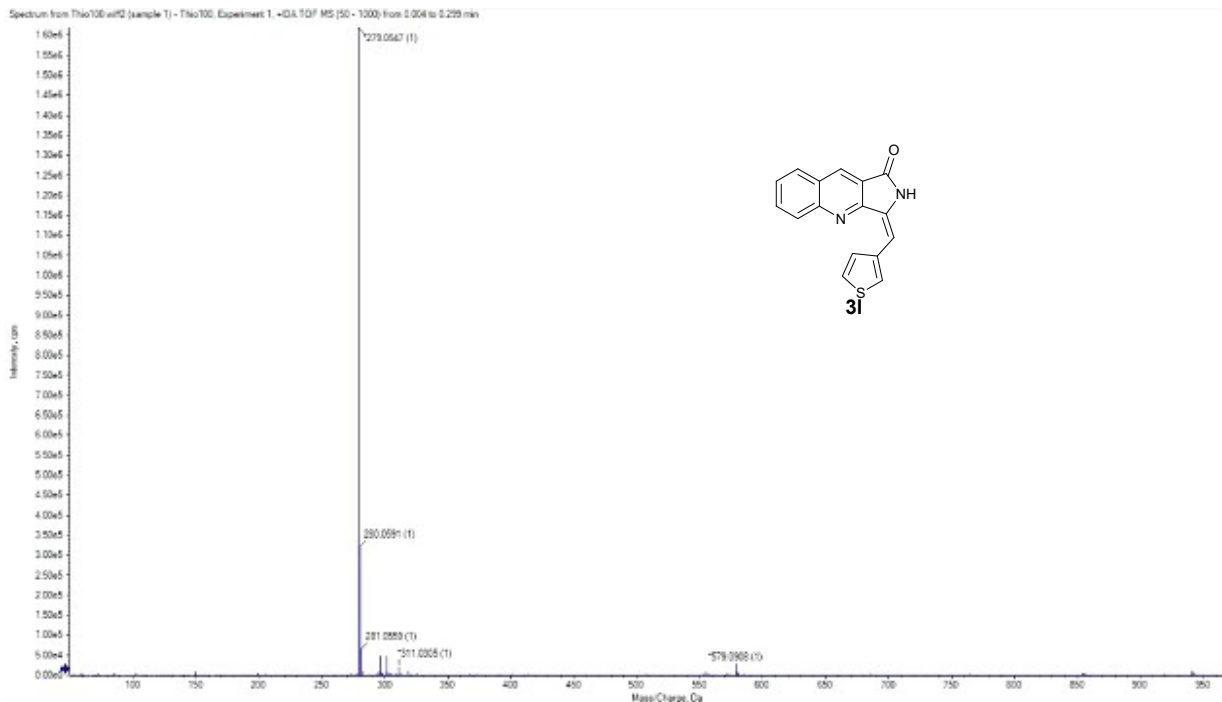
**(E)-6-chloro-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3k):**



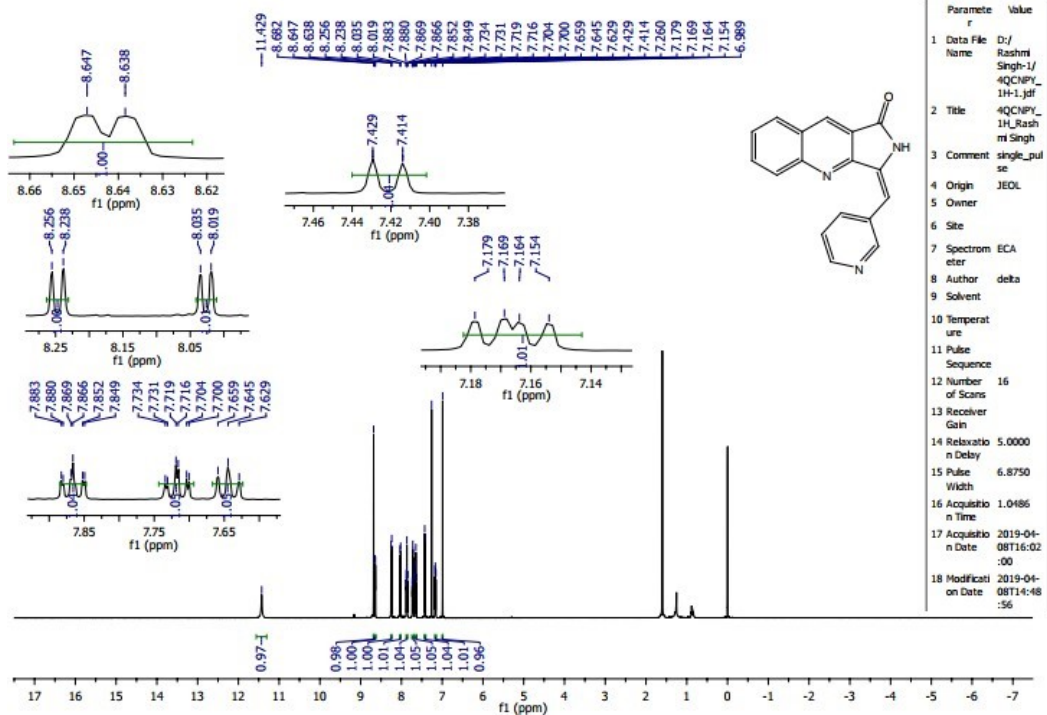
**(E)-3-(thiophen-3-ylmethylene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one (3l):**

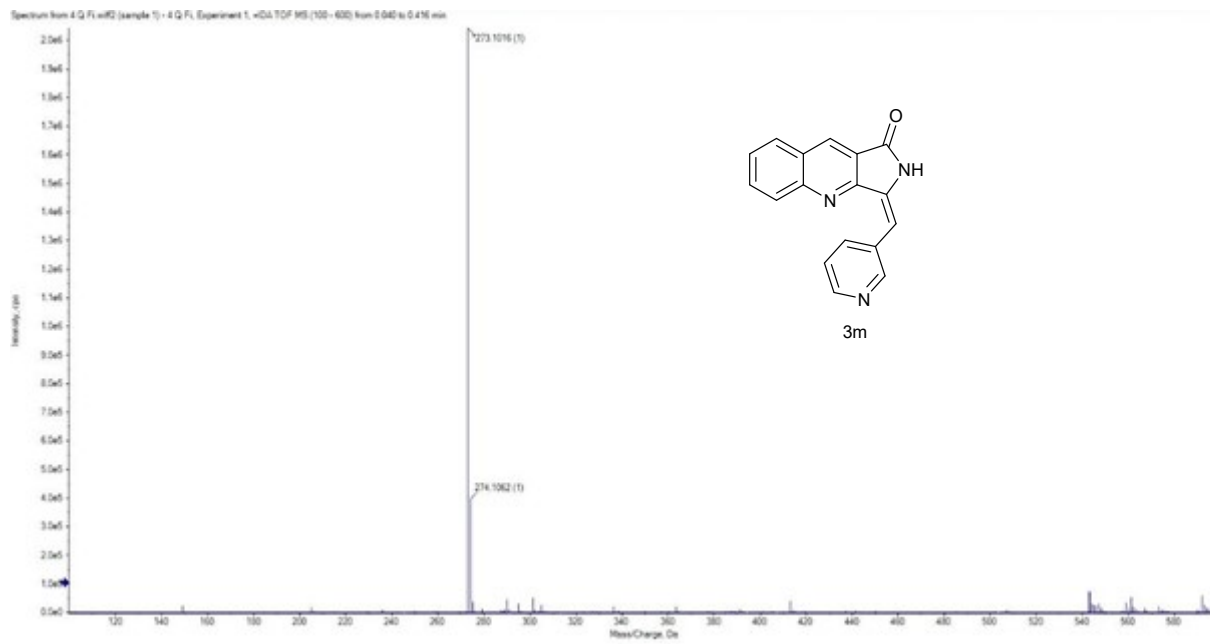
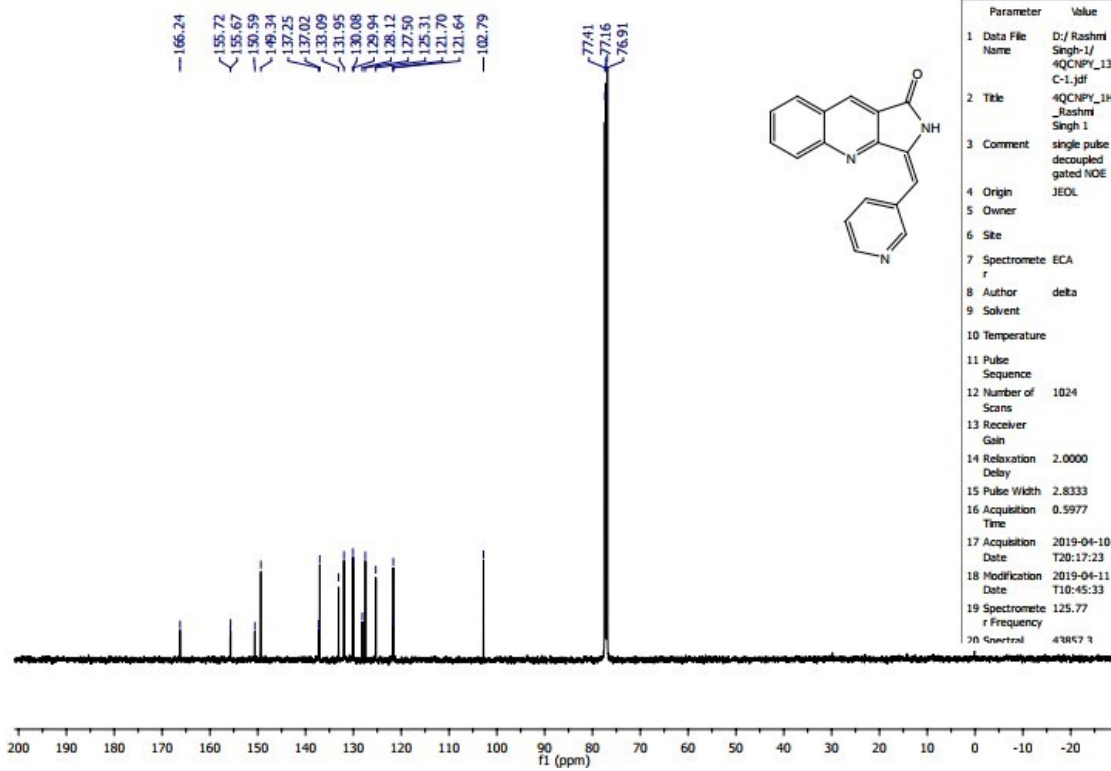


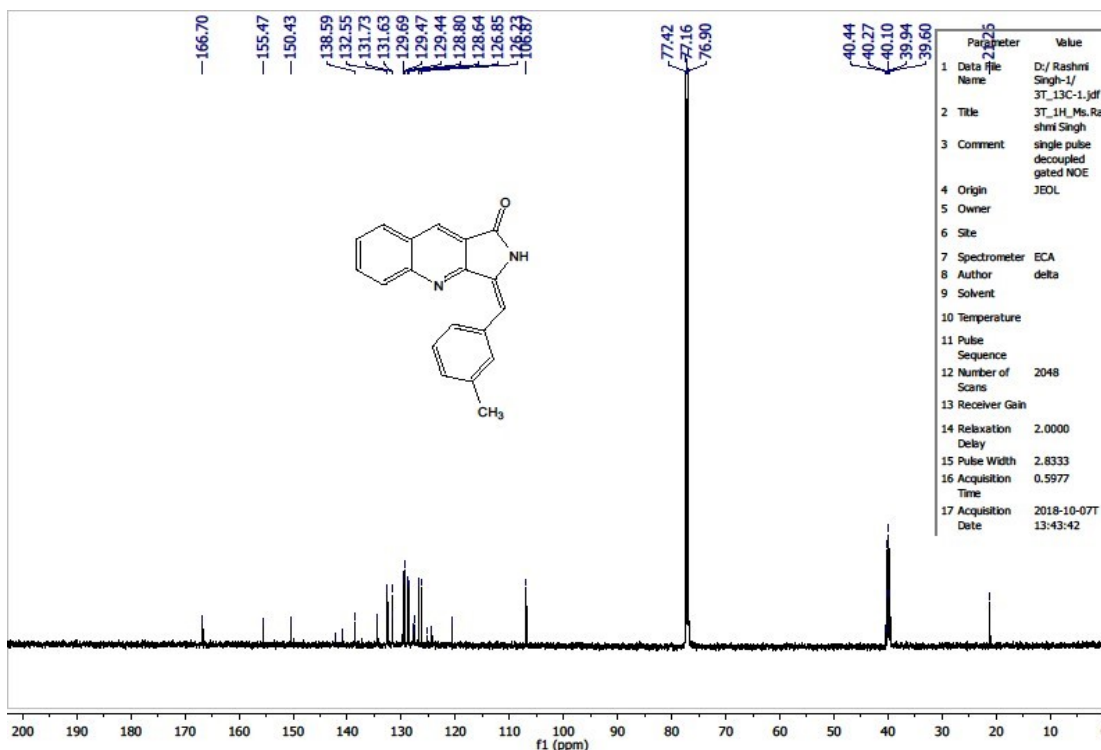
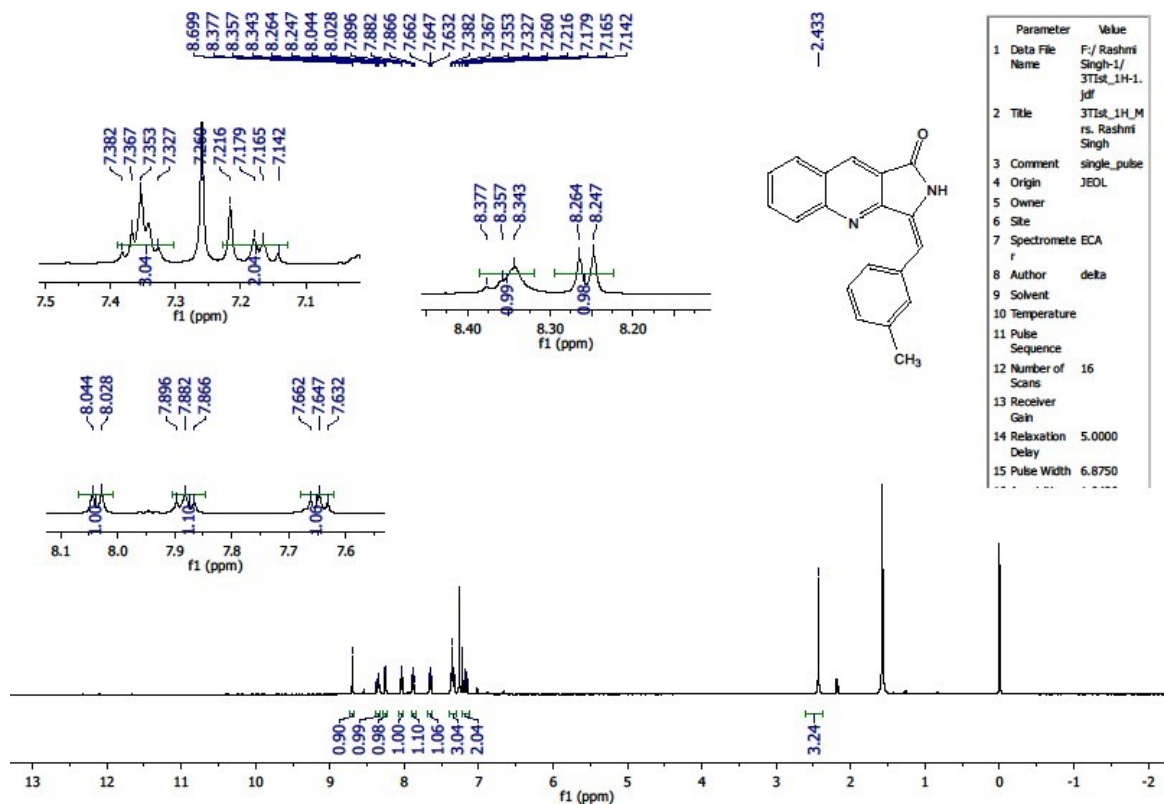


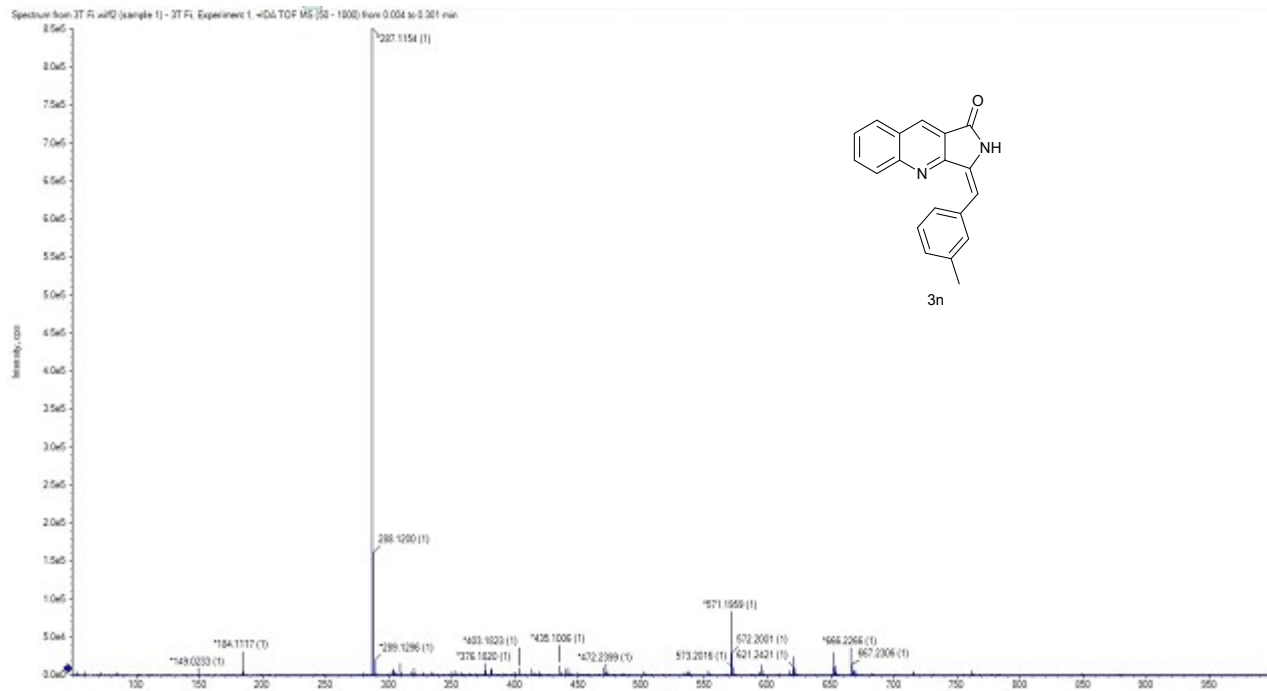


***(E)*-3-(pyridin-3-ylmethylene)-2,3-dihydro-1*H*-benzo[*f*]isoindol-1-one (3m):**

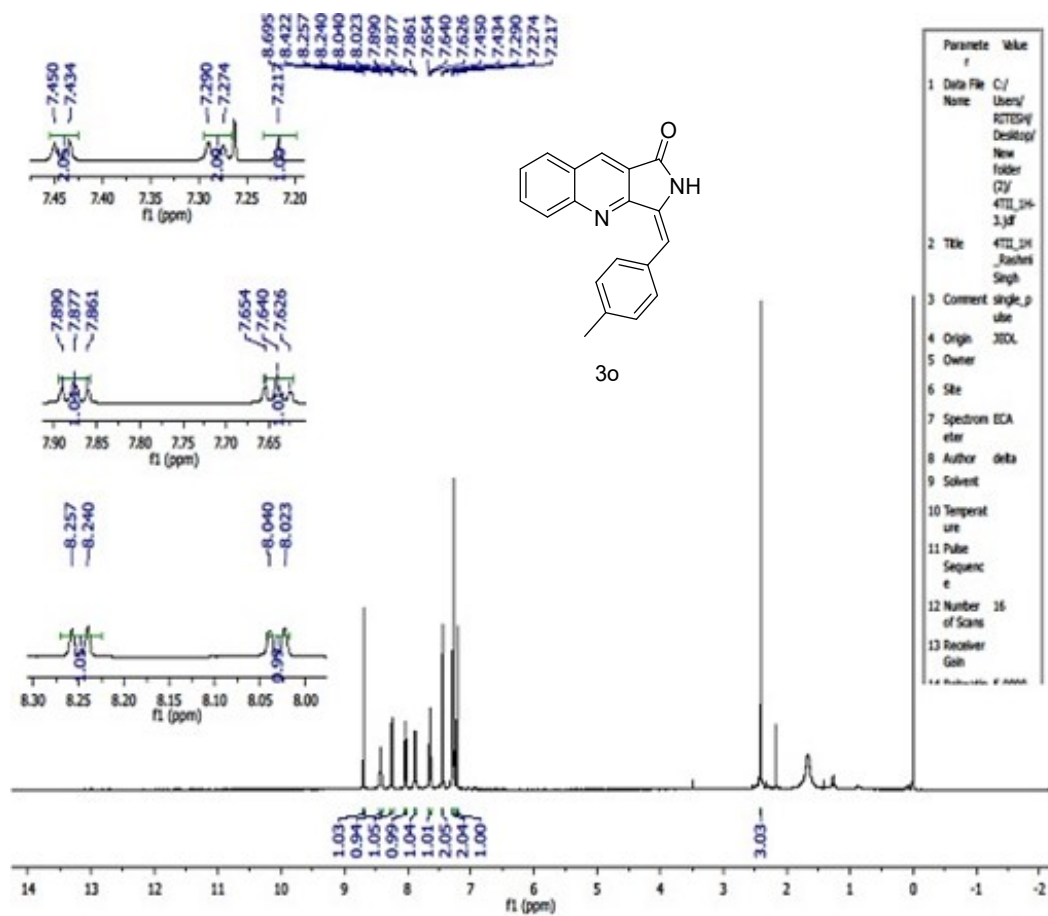


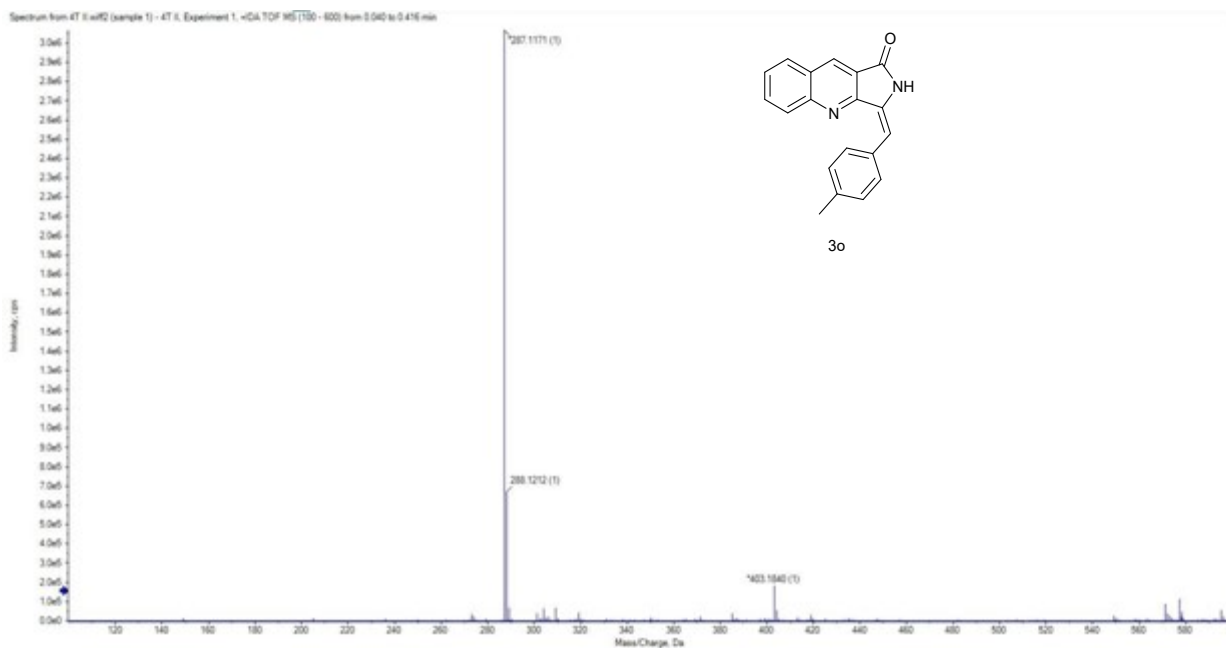
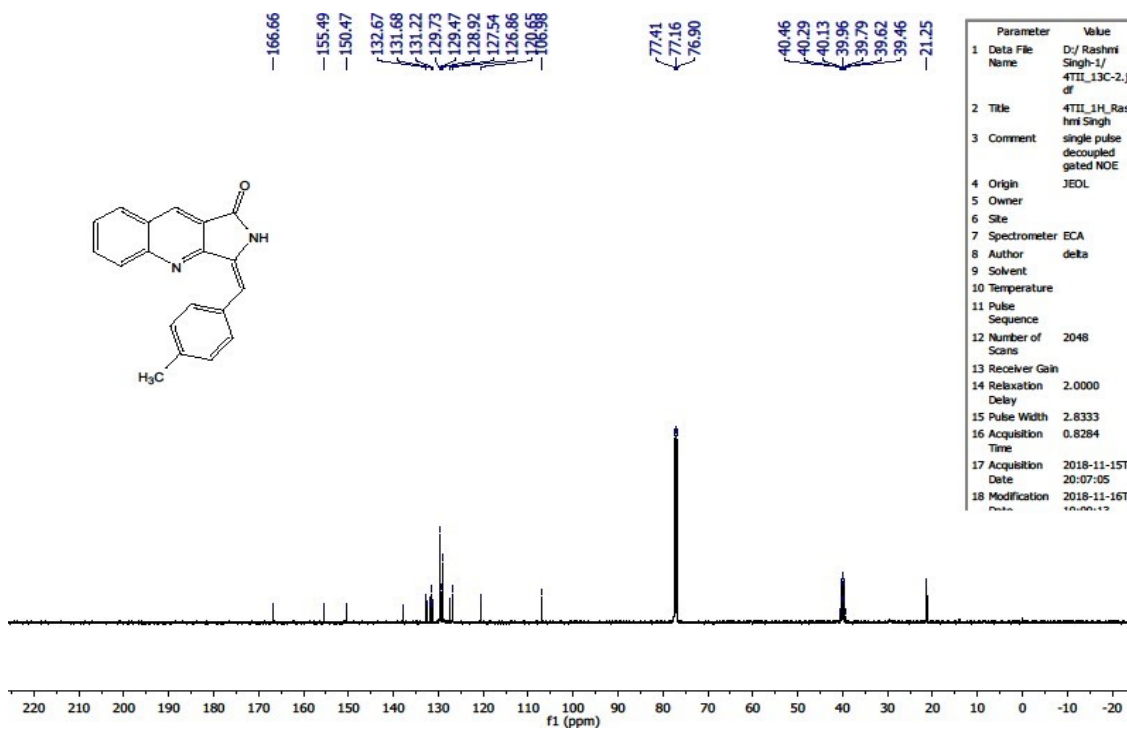


**(E)-3-(3-methylbenzylidene)-2,3-dihydro-1H-benzo[f]isoindol-1-one (3n):**

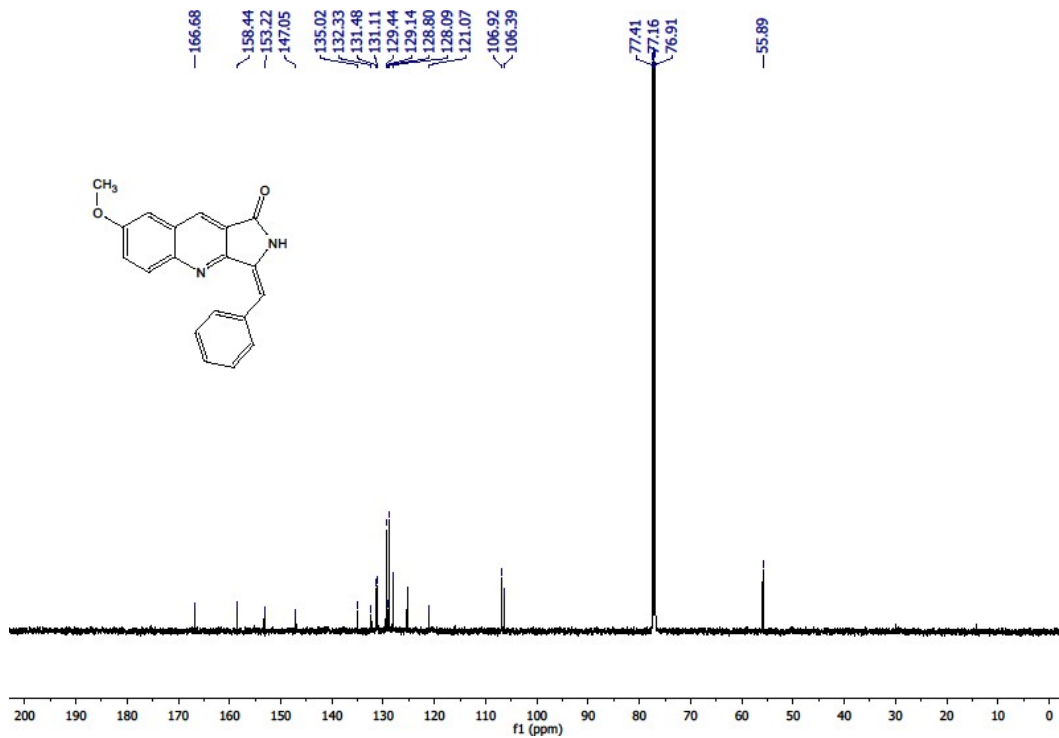
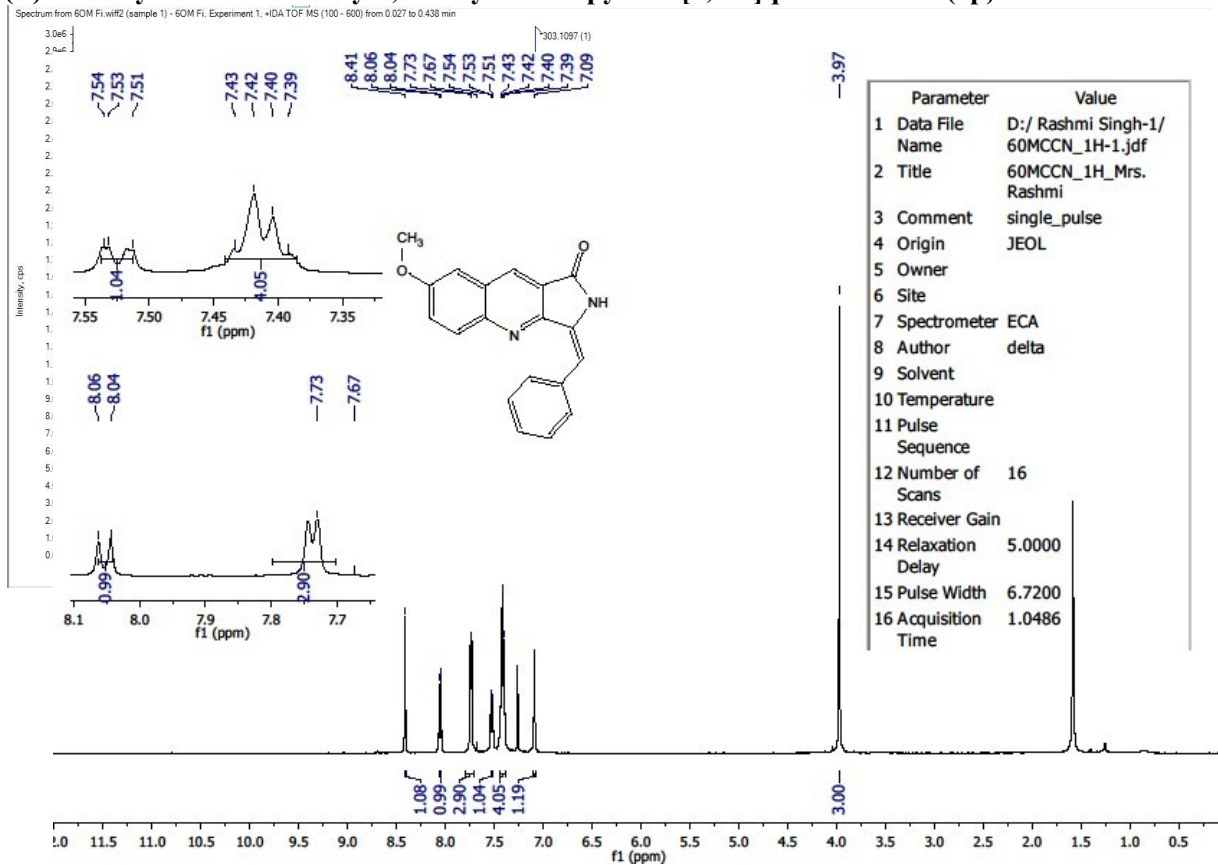


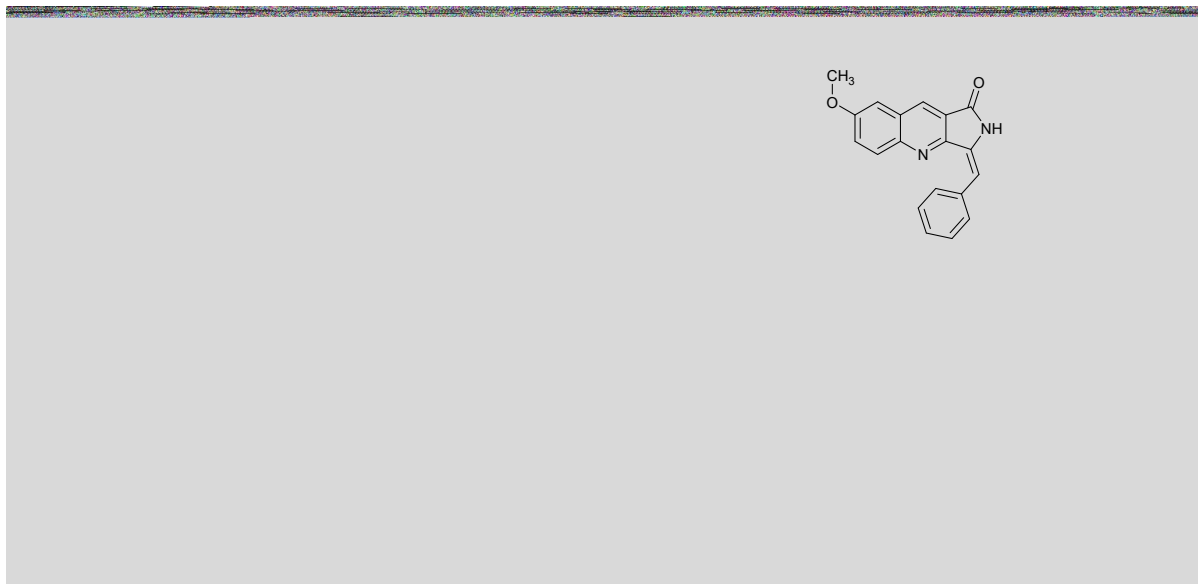
**(E)-3-(4-methylbenzylidene)-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one(3o):**



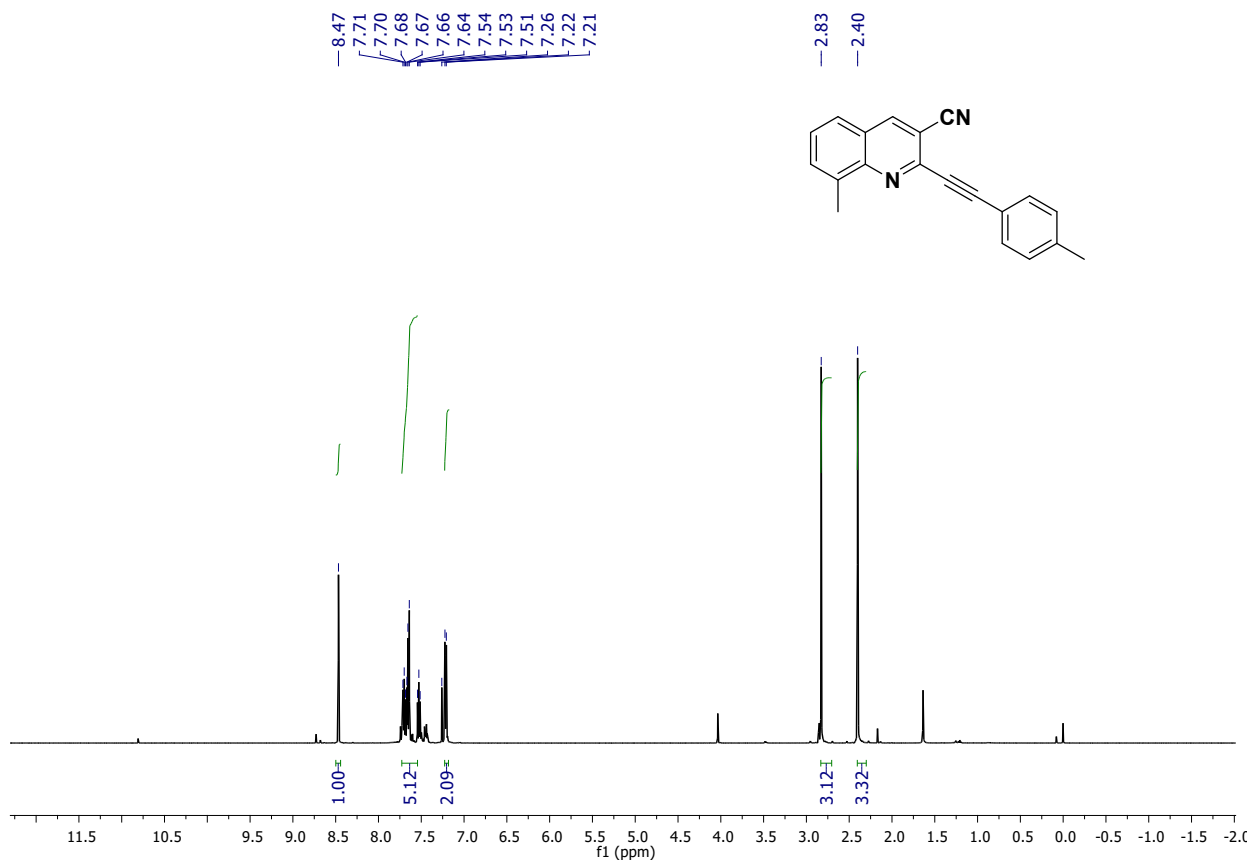


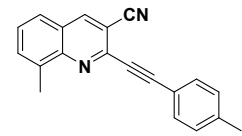
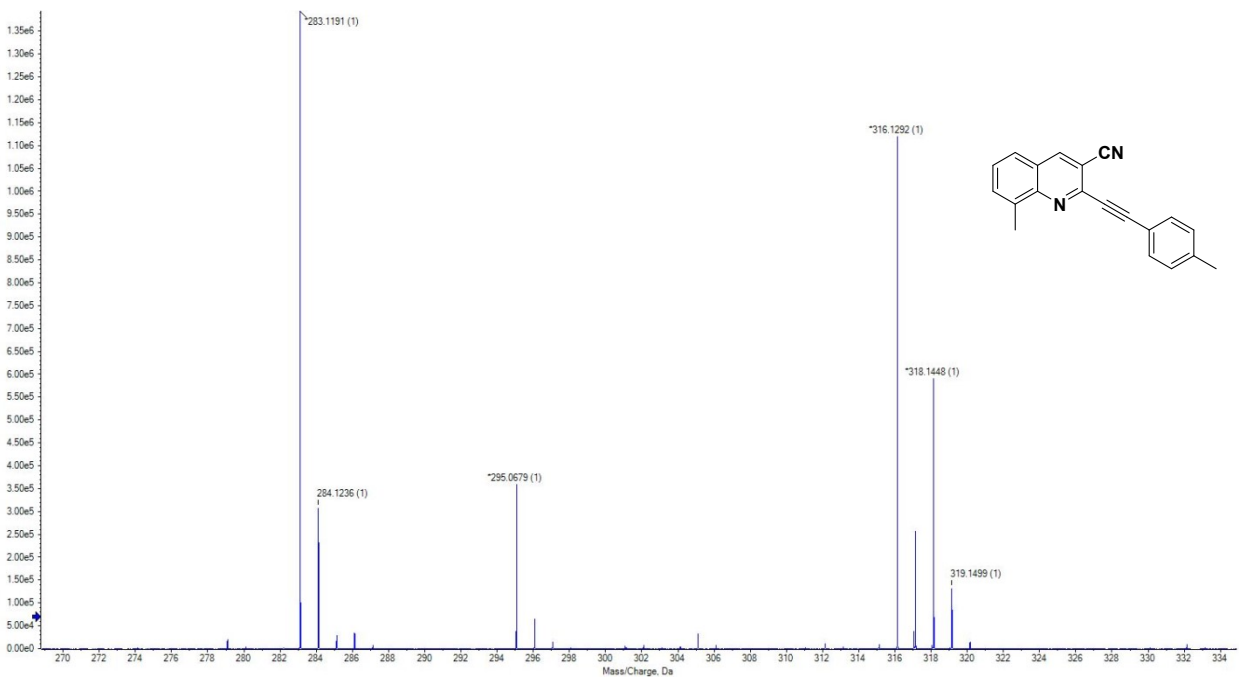
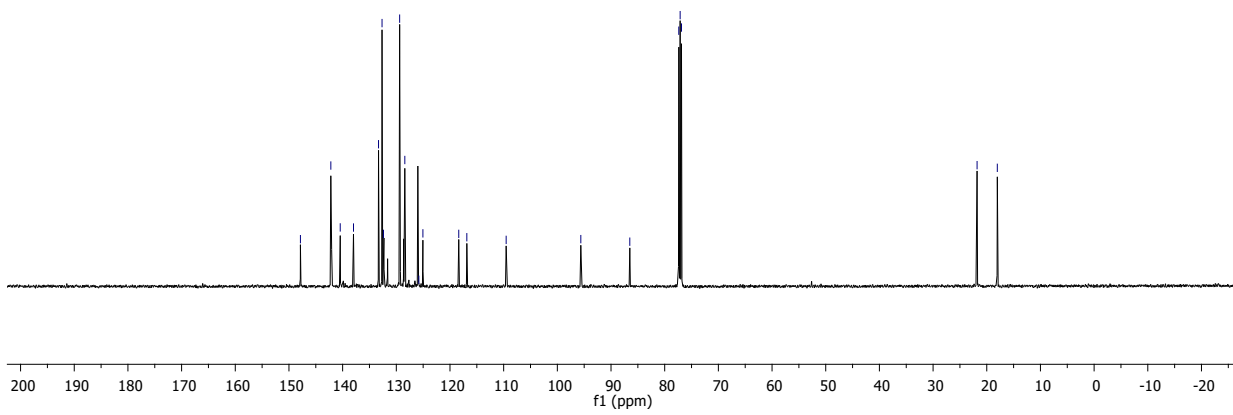
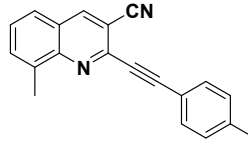


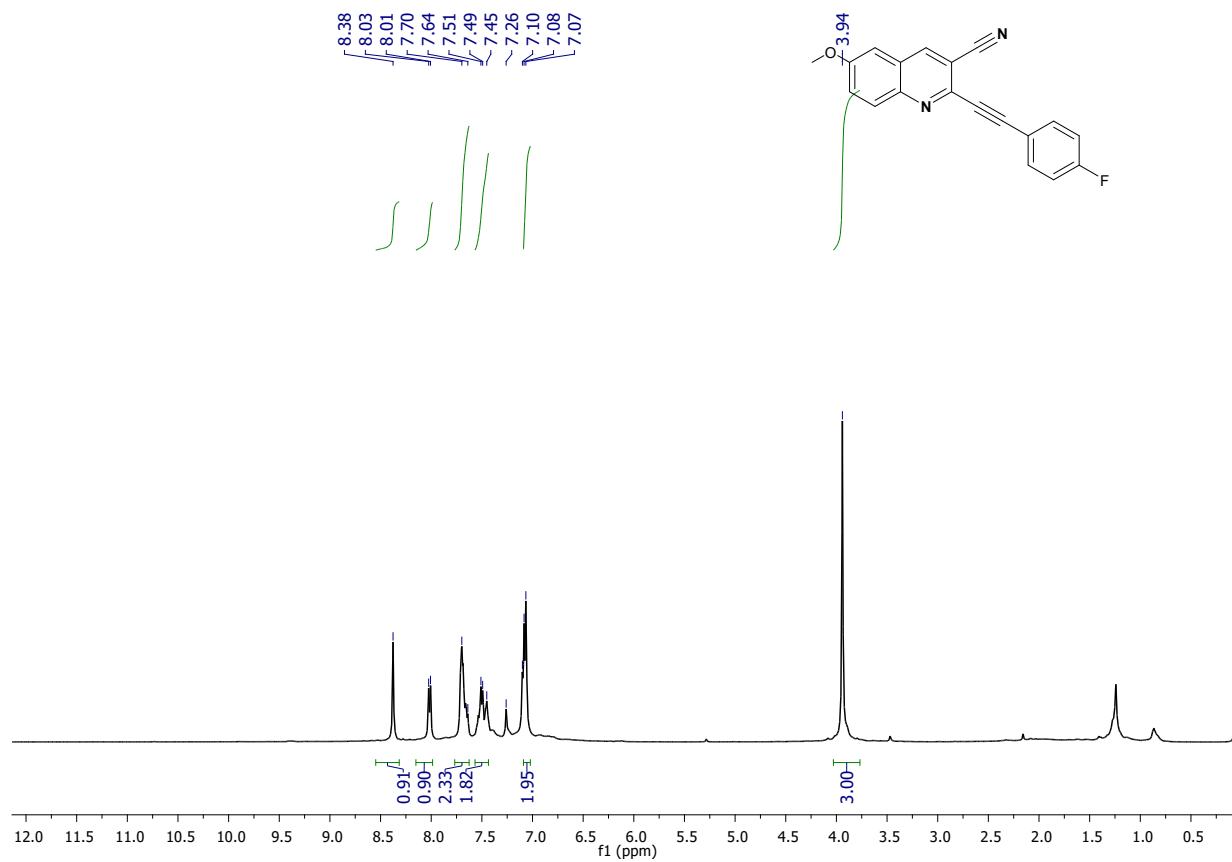
**(E)-3-benzylidene-7-methoxy-2,3-dihydro-1H-pyrrolo[3,4-b]quinolin-1-one(3p):**

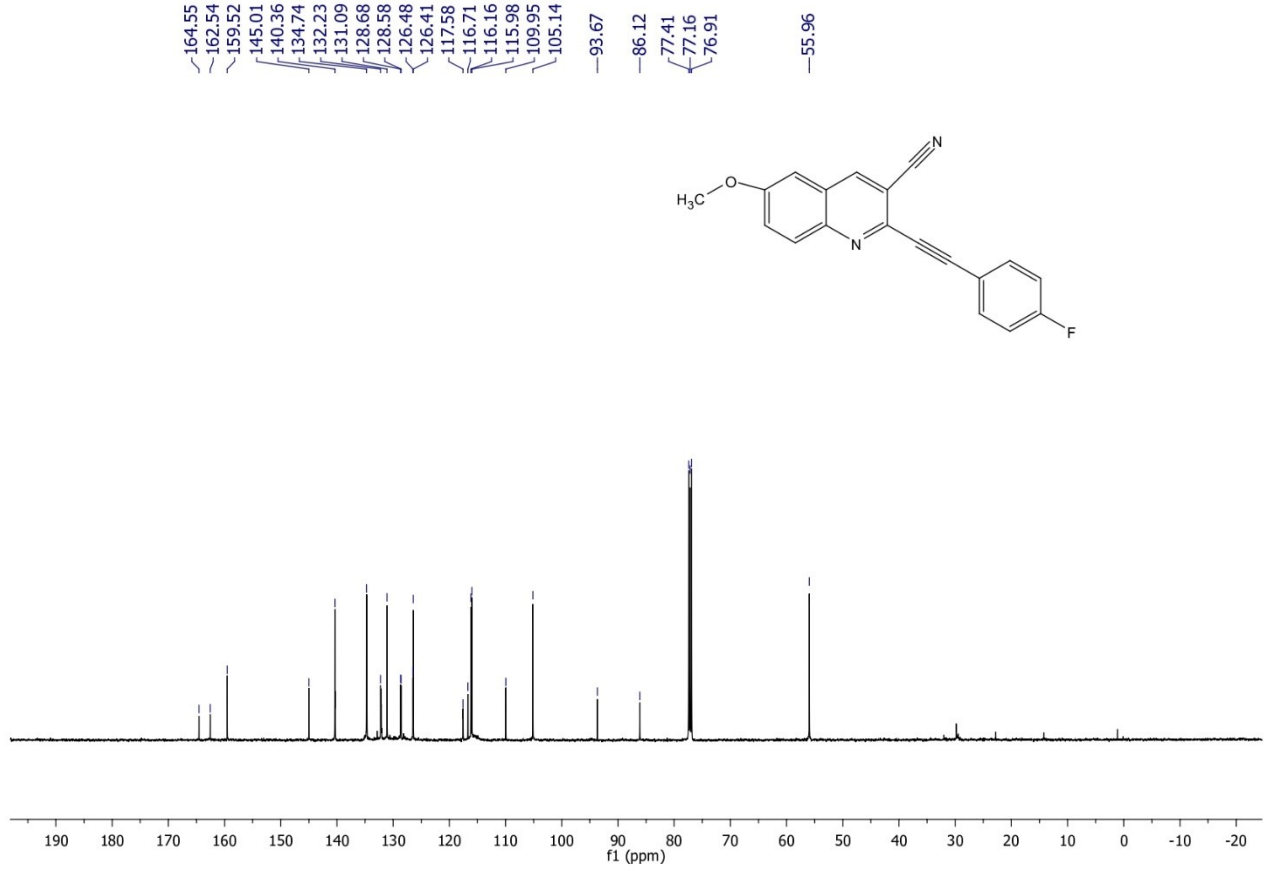


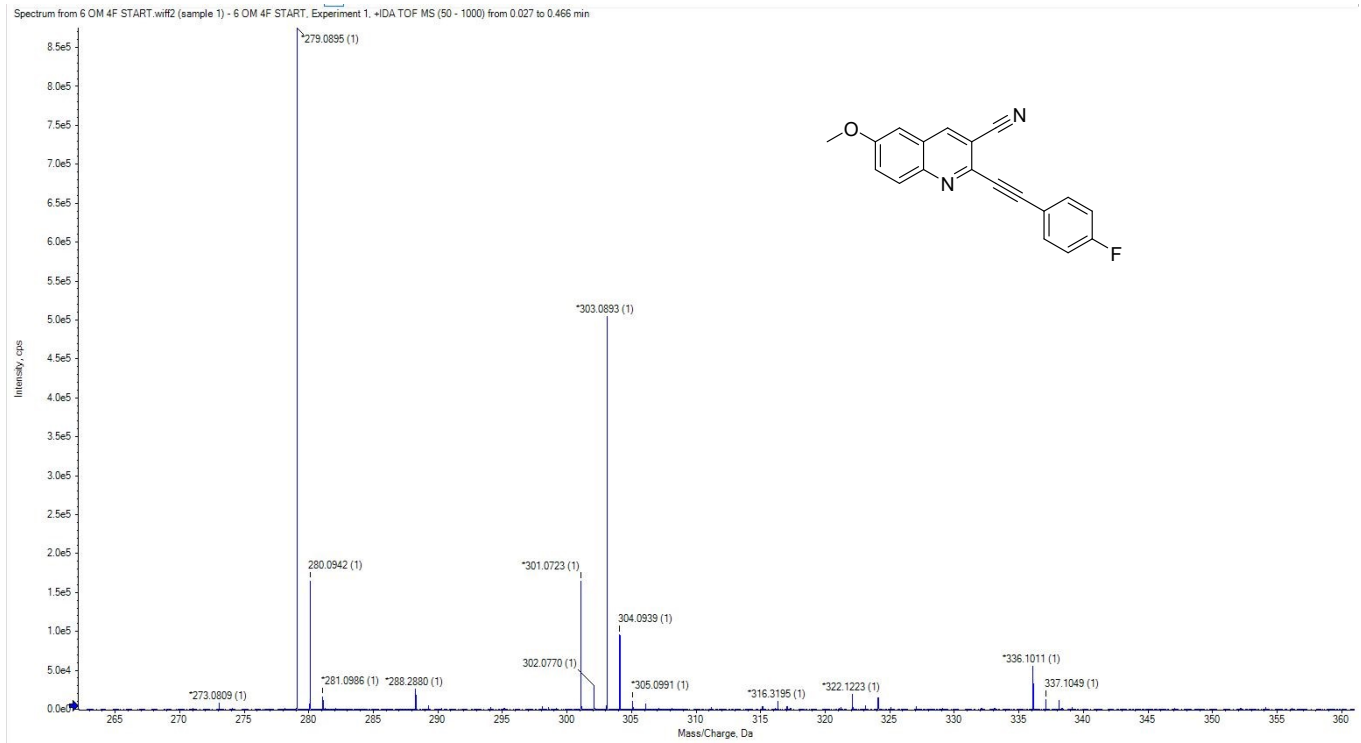
8-methyl-2-(p-tolyethynyl)quinoline-3-carbonitrile (A):



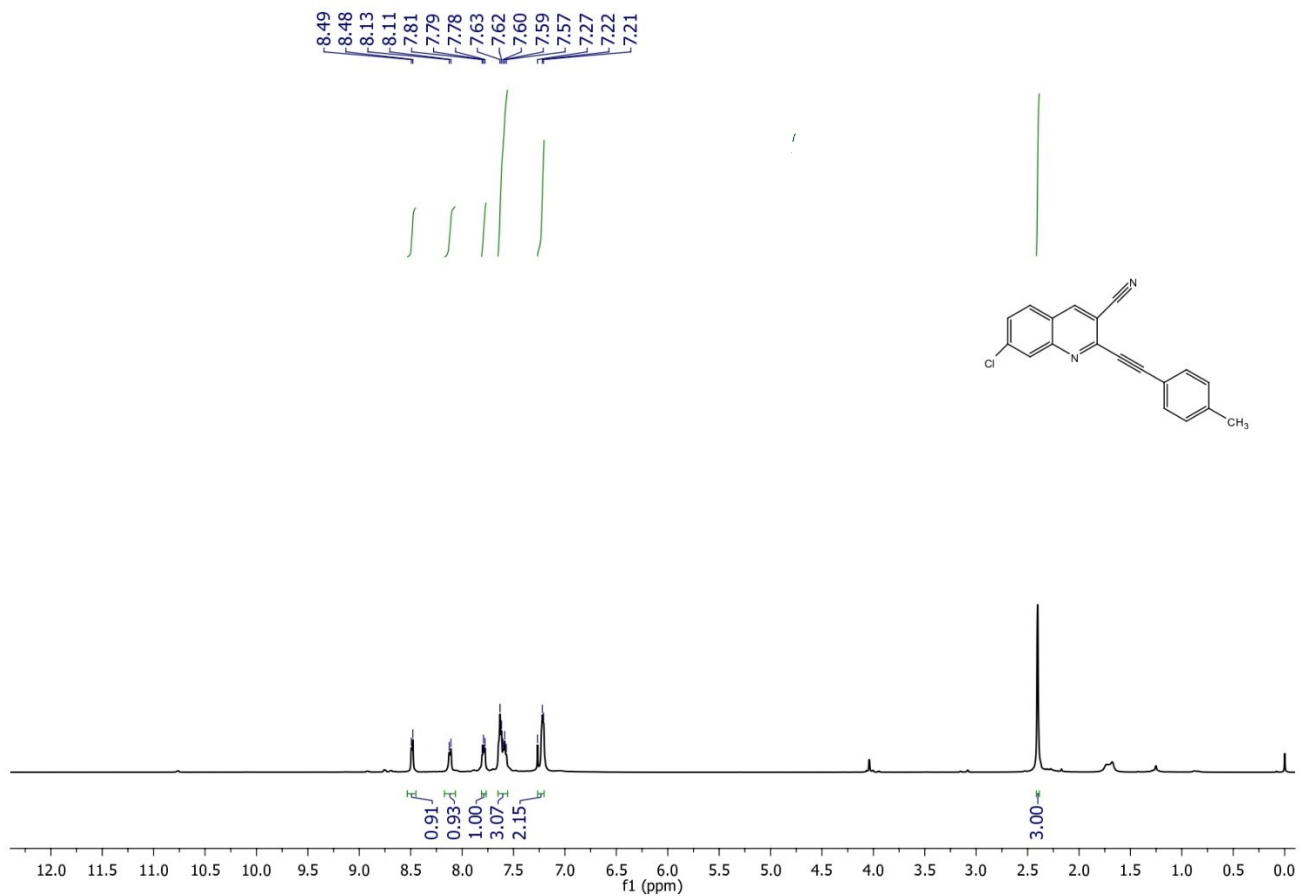


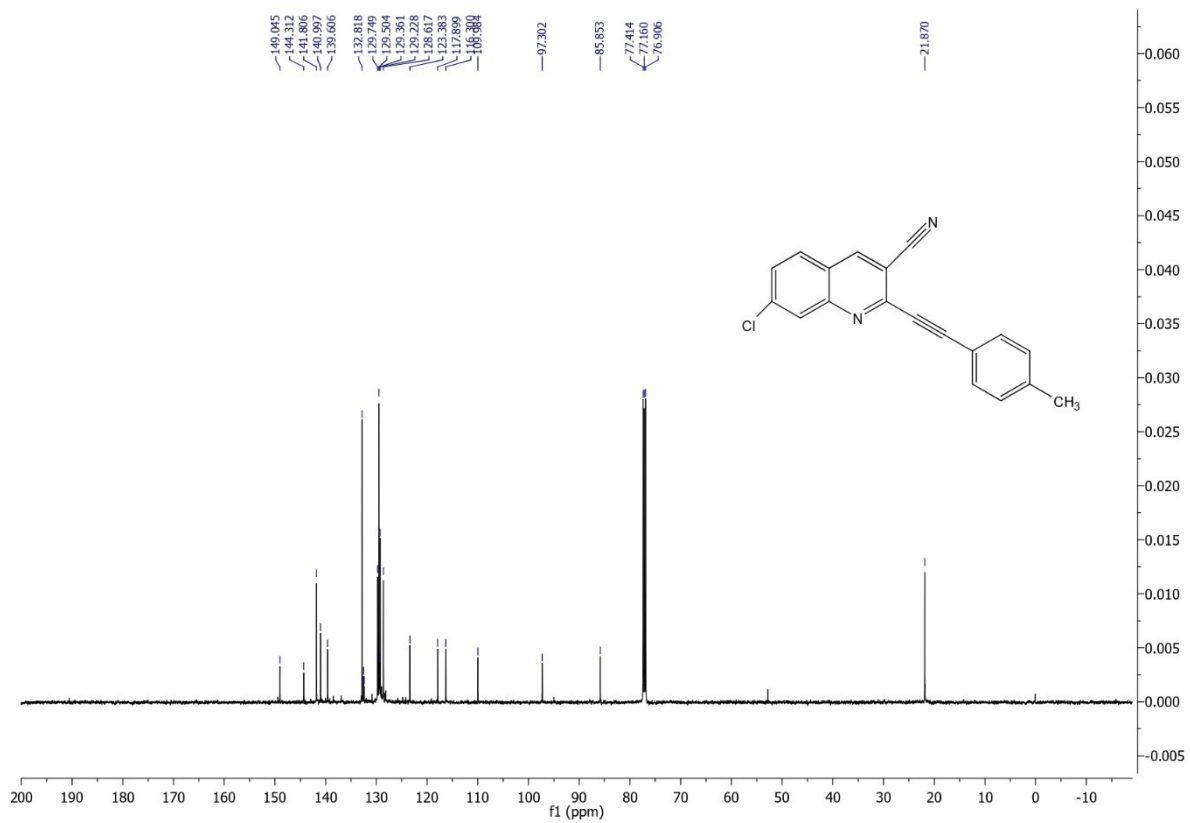
**2-((4-fluorophenyl)ethynyl)-6-methoxyquinoline-3-carbonitrile (B):**



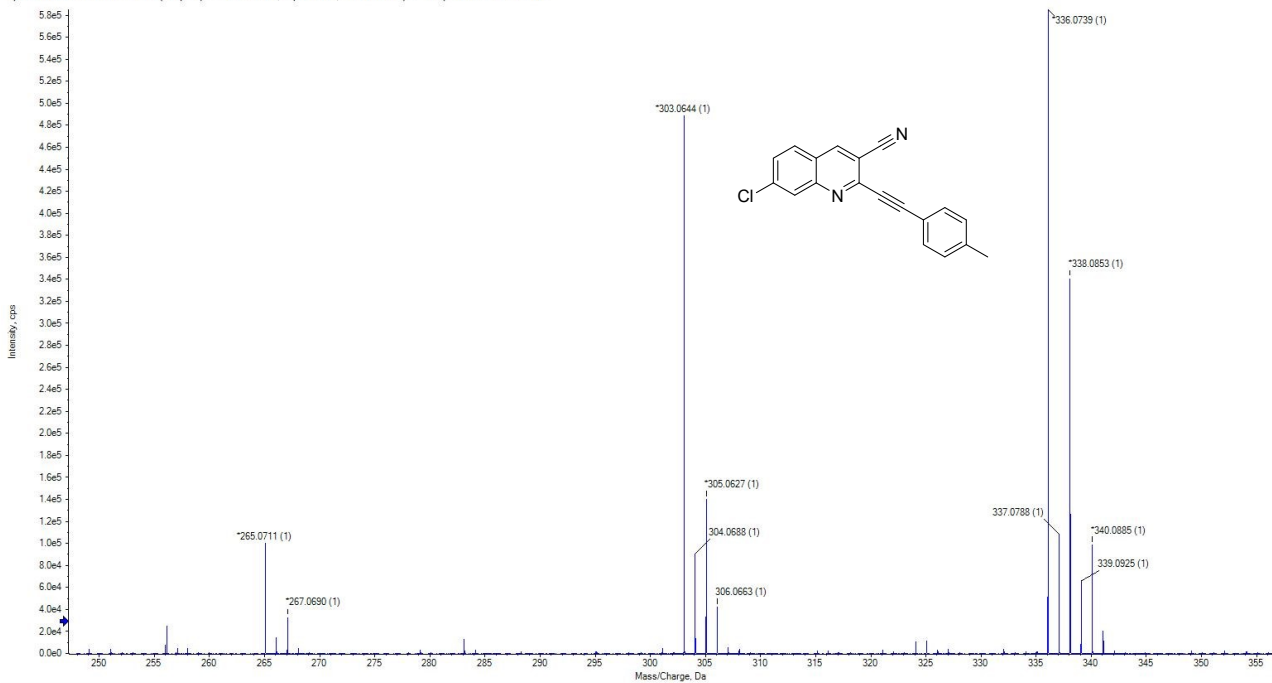


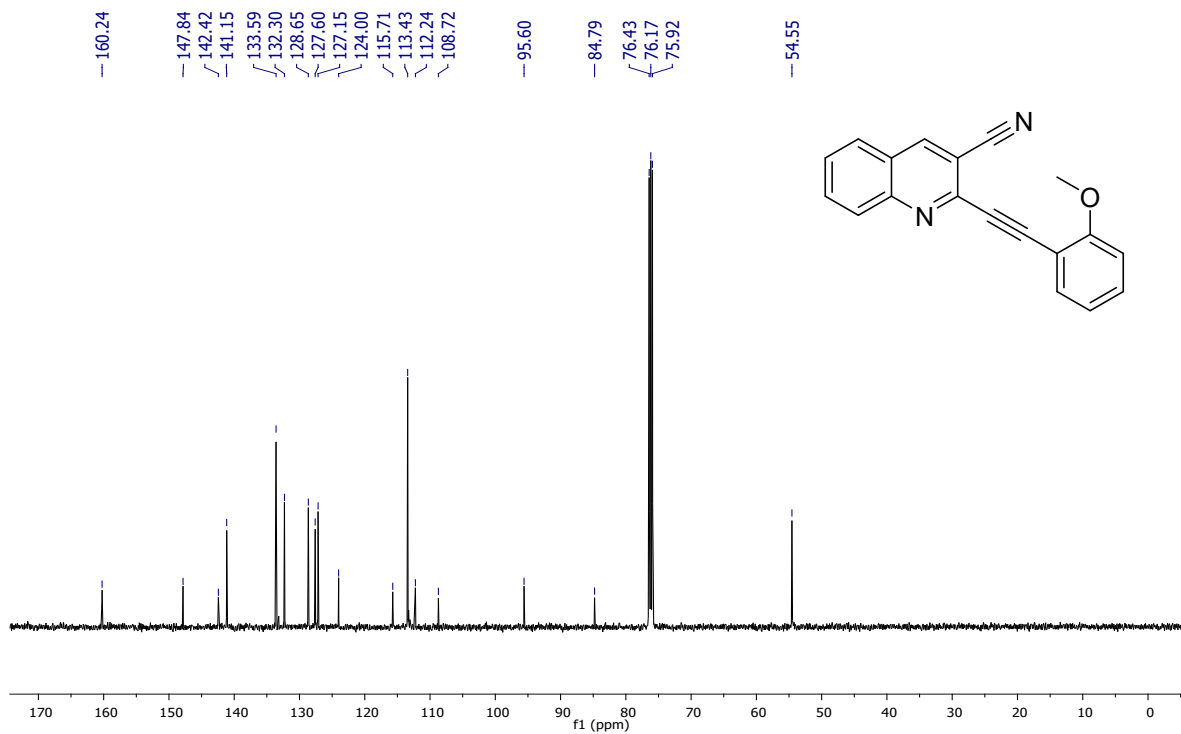
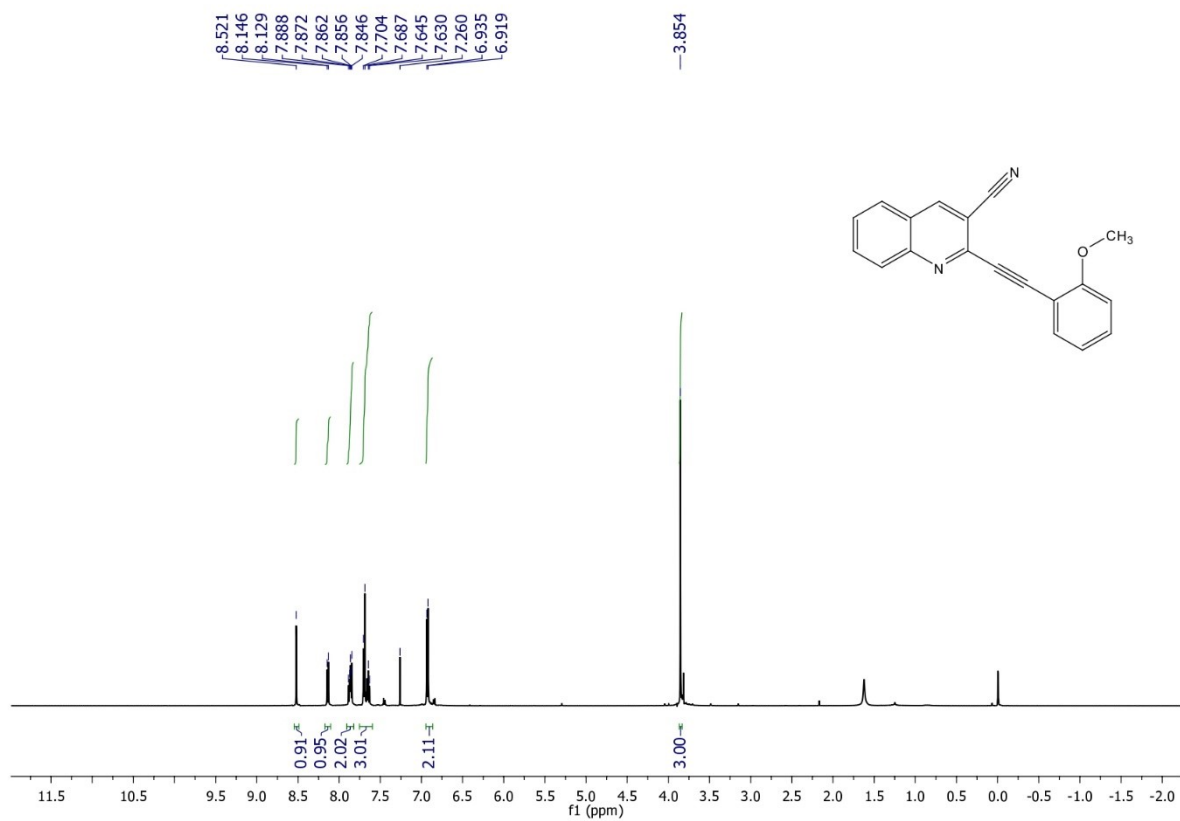
**7-chloro-2-(p-tolyethynyl)quinoline-3-carbonitrile (C):**



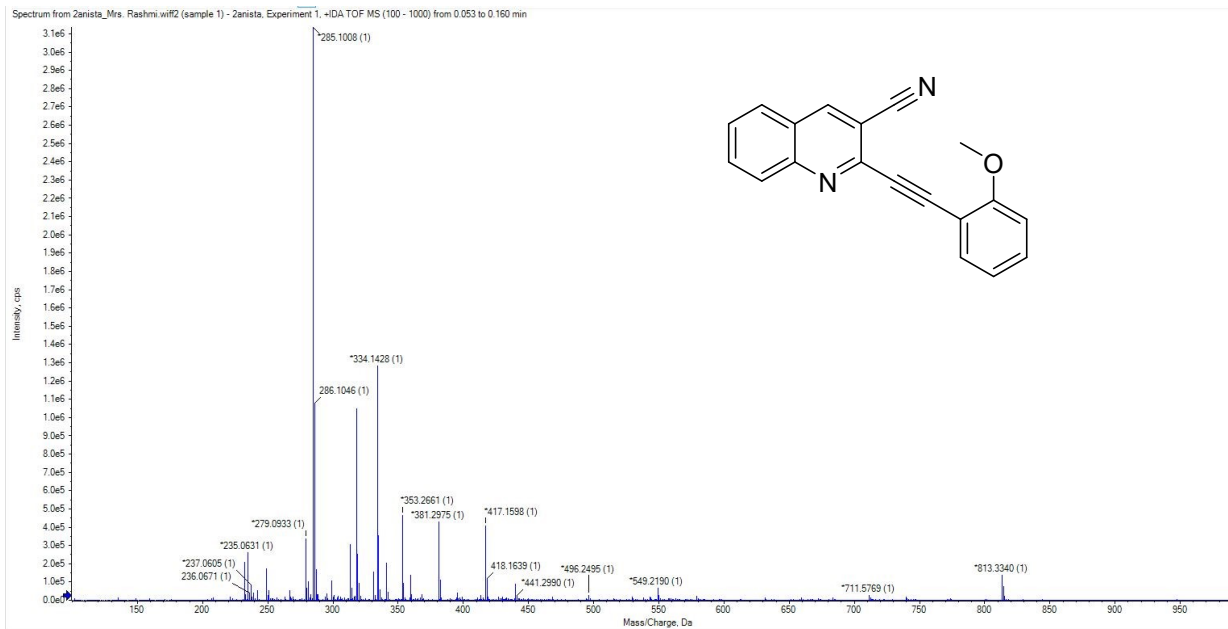


Spectrum from 7 CL 4T START wif2 (sample 1) - 7 CL 4T START, Experiment 1, +IDA TOF MS (50 - 1000) from 0.027 to 0.464 min

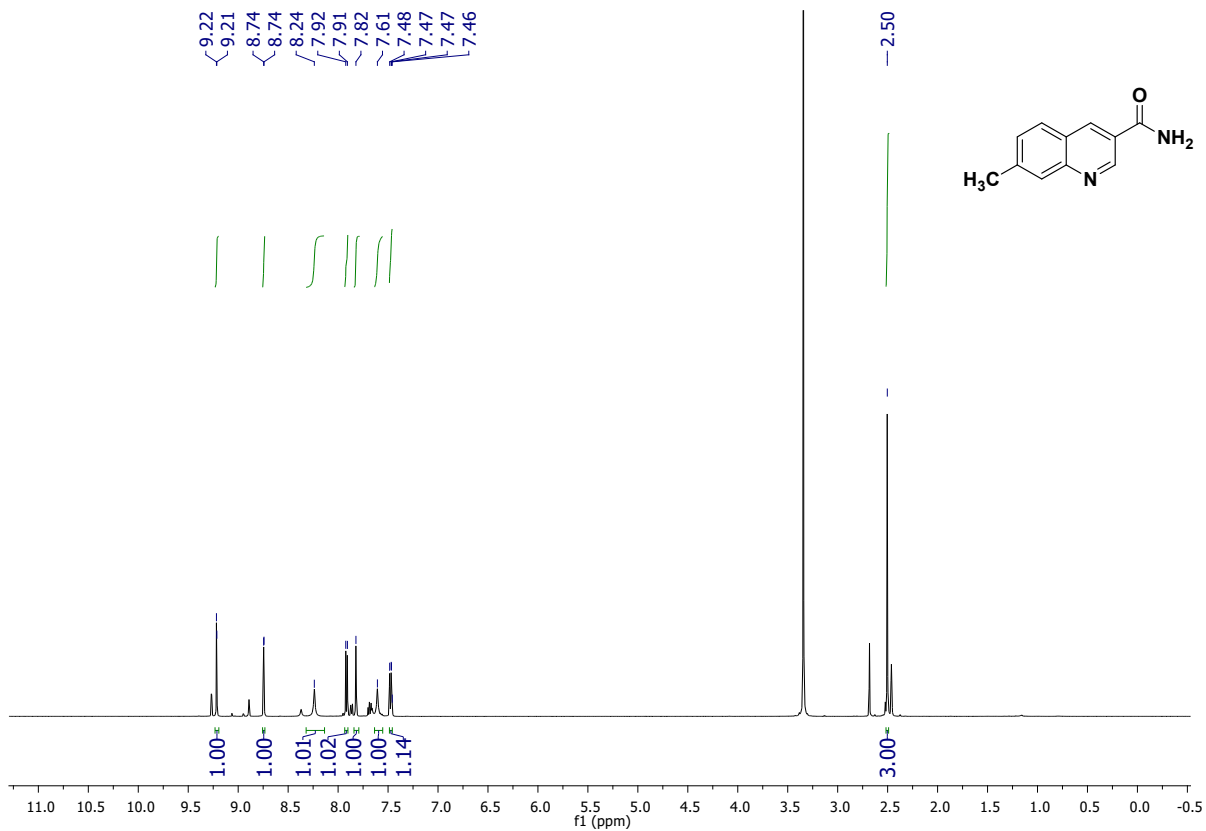


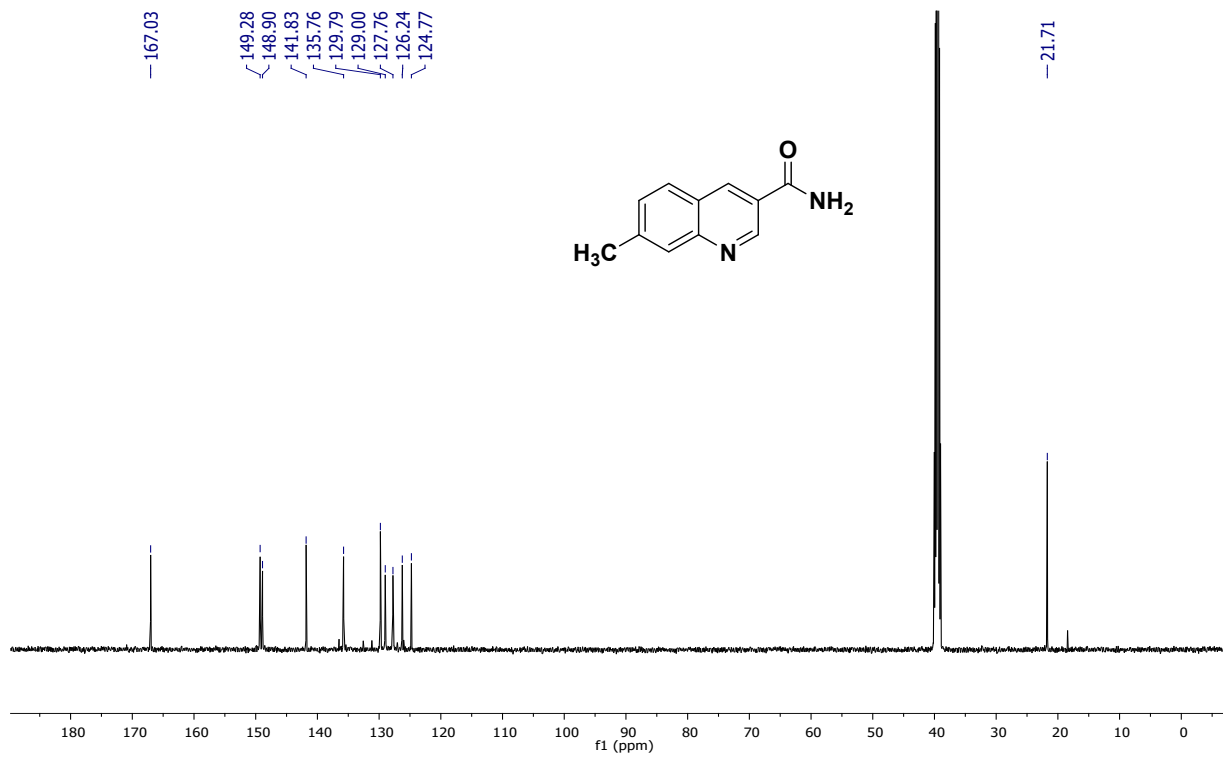
**2-((2-methoxyphenyl)ethynyl)quinoline-3-carbonitrile (D):**





### 7-methylquinoline-3-carboxamide(5)



**References:**

1. A. Chandra, B. Singh, S. Upadhyay, R. M. Singh, *Tetrahedron*, 2008, **64**, 11680-11685.
2. R. Kumar, R. M. Singh, *Orga. and biomol. chem.*, 2019,**17**, 5990.
3. Sheldrick, G. M., *ActaCryst.*; 2015. C71,3-8.
4. Farrugia, L. J.; *J. Appl. Cryst.*, 2012, **45**, 849-854.

