

## Metal-free, one-pot synthesis of styrylquinolines *via* Friedländer annulation and sp<sup>3</sup> C-H activation using 1,3-dimethylurea and L-tartaric acid (3:1) as deep eutectic solvent

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### 1. Experimental Procedures:

**General:** The starting materials were purchased from Sigma-Aldrich, SRL, Spectrochem and SD-Fine and used as they are received. <sup>1</sup>H and <sup>13</sup>C-NMR spectra are recorded on Bruker 400 MHz spectrometer using CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as solvents and reported in δ ppm. The mass spectra were recorded on Shimadzu LCMS-2020 and Agilent QTOF machine. Melting points were recorded on Stuart melting point apparatus. UV-visible spectra were taken using Agilent-Cary 100 UV-Visible spectrometer. Emission spectra were recorded by Horiba FluoroLog spectrophotometer.

#### *General procedure for the one-pot synthesis of styrylquinoline derivatives:*

1.53g of Deep Eutectic Solvent (DES) was prepared by heating 1,3-dimethyl urea (0.975g, 11.11 mmol) + L-tartaric acid (0.555g, 3.7 mmol) at 80°C for 30 min. To this melt, 5-chloro-2-aminobenzophenone (0.231g, 1 mmol) and β-diketone/ketone/piperidone (1 mmol) was added and heating continued for another 30 minutes at 80°C to give the Friedländer annulation product (*in situ*). To the same pot aldehyde (1 mmol) was added and heating continued till the formation of

desired 2-styrylquinoline derivatives (monitoring by TLC). The reaction mixture was cooled to room temperature. Water was added to it and extracted by EtOAc (10X3 mL). The organic layers were separated and dried using sodium sulfate. Solvent was evaporated under vacuum. The crude product obtained was purified by silica gel column chromatography. Elution of the column using petroleum ether-ethyl acetate gave the pure product.

## 2. Confirmation of the reported molecules by reported melting points:

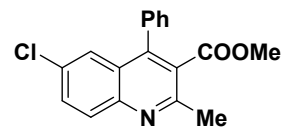
S. No.	Compound No.	M.P °C (Found)	M.P °C (Reported) <sup>5-6</sup>
1	<b>5a</b>	206-207	207-208
2	<b>5e</b>	200-201	199-200
3	<b>5f</b>	204-205	205-206
4	<b>5g</b>	142-143	143-145
5	<b>5j</b>	146-147	147-148
6	<b>5k</b>	171-172	170-171
7	<b>5n</b>	164-165	163-164
8	<b>5o</b>	161-162	160-161
9	<b>5q</b>	148-150	149-152

## References:

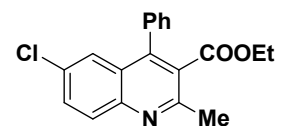
1. A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648–5652.
2. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.* 1988, **37**, 785–789
3. S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.* 2011, **32**, 1456–65.
4. S. F. Boys, F. Bernardi, *Mol. Phys.* 1970, 19, 553.
5. D. Kumar, A. Kumar, M. M. Qadri, Md. I. Ansari, A. Gautam, A. K. Chakraborti, *RSC Adv.*, 2015, **5**, 2920–2927.
6. P. Sarma, S. Saikia, R. Borah, *Synth. Commun.*, 2016, **46**, 1187–1196.

## 3. Characterizations of new compounds

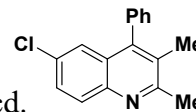
**Methyl-6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (3a):** (*E*)-Methyl 6-chloro-4-phenyl-2-styrylquinoline-3-carboxylate (**5a**): White solid, mp 206-207 °C, 88% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 2.0 Hz, 1H), 8.08 (d, *J* = 4.8 Hz, 1H), 7.67 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.53–7.49 (m, 4H), 7.41 – 7.33 (m, 5H), 7.25 (d, *J* = 16.0 Hz, 1H), 3.60 (s, 3H).



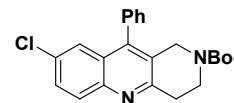
**Ethyl-6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (3b):** White solid, mp 175–176 °C, 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 6.0 Hz, 1H), 7.45–7.42 (m, 4H), 7.27–7.19 (m, 2H), 3.98 (s, 2H), 2.70 (s, 3H), 0.88 (s, 3H); IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3085, 2976, 1730, 1580, 1487, 1232, 842.



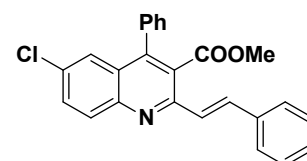
**6-Chloro-2,3-dimethyl-4-phenylquinoline (3c):** White solid, mp 210–211 °C, 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.53–7.48 (m, 4H), 7.26–7.20 (m, 3H), 2.74 (s, 3H), 2.17 (s, 3H); HRMS (ESI, *m/z*): Calcd. For C<sub>17</sub>H<sub>14</sub>ClN<sup>+</sup> 268.0888, found 268.0879.



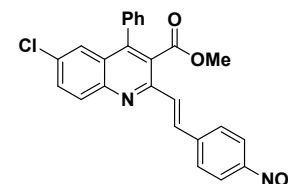
**Tert-butyl-8-chloro-10-phenyl-3,4-dihydrobenzo[b][1,6]naphthyridine-2(1H)-carboxylate (3f):** White solid, mp 178–179 °C, 90% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.9 Hz, 1H), 7.66–7.45 (m, 4H), 7.35 (s, 1H), 7.26–7.23 (m, 2H), 4.43 (s, 2H), 3.82 (t, *J* = 5.5 Hz, 2H), 3.25 (s, 2H), 1.44 (s, 9H); HRMS (ESI, *m/z*): Calcd. For C<sub>23</sub>H<sub>23</sub>ClN<sub>2</sub>O<sub>2</sub>H<sup>+</sup> 395.1531, found 395.1520.



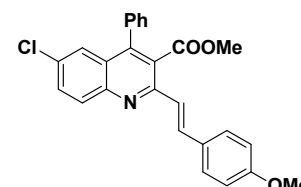
**(E)-Methyl 6-chloro-4-phenyl-2-styrylquinoline-3-carboxylate (5a):** White solid, mp 206–207 °C, 88% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 2.0 Hz, 1H), 8.08 (d, *J* = 4.8 Hz, 1H), 7.67 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 2H), 7.53–7.49 (m, 4H), 7.41–7.33 (m, 5H), 7.25 (d, *J* = 16.0 Hz, 1H), 3.60 (s, 3H).



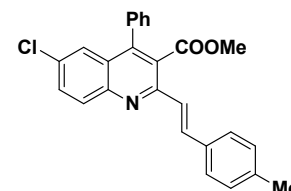
**Methyl-6-chloro-2-(3-nitrostyryl)-4-phenylquinoline-3-carboxylate (5b):** White solid, mp 210–211 °C, 95% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.25 (d, *J* = 8.8 Hz, 2H), 8.16–8.103 (m, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.72–7.69 (m, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.54–7.50 (m, 3H), 7.43 (d, *J* = 15.6 Hz, 1H), 7.37–7.35 (m, 2H), 3.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.4, 150.2, 147.6, 146.6, 146.5, 142.8, 134.9, 134.2, 133.3, 131.9, 131.3, 130.5, 129.1, 129.0, 128.9, 128.6, 128.5, 128.1, 127.6, 126.7, 125.4, 125.3, 124.1, 52.6; HRMS (ESI, *m/z*): Calcd. For C<sub>25</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>4</sub>H<sup>+</sup> 445.0950, found 445.0928; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3042, 2958, 1718, 1564, 1527, 1227, 835.



**Methyl-6-chloro-2-(4-methoxystyryl)-4-phenylquinoline-3-carboxylate (5c):** White solid, mp 169–170 °C, 85% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.08–8.03 (m, 2H), 7.65 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.52–7.50 (m, 4H), 7.36 (dd, *J* = 6.0, 1.6 Hz, 2H), 7.13 (d, *J* = 14.5 Hz, 1H), 6.92 (d, *J* = 6.8 Hz, 2H), 3.84 (s, 3H), 3.60 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 168.6, 160.4, 151.6, 146.6, 145.9, 136.6, 135.1, 132.3, 131.4, 131.1, 131.0, 129.2, 129.1, 128.8, 128.5, 127.4, 126.2, 125.2, 121.6, 114.2, 55.3, 52.4; HRMS (ESI, *m/z*): Calcd. For C<sub>26</sub>H<sub>20</sub>ClNO<sub>3</sub>H<sup>+</sup> 430.1132, found 430.1177; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3065, 2974, 1736, 1603, 1256, 1207, 1028, 829.

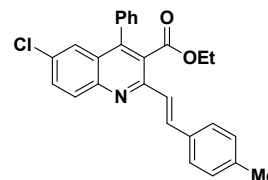


**Methyl-6-chloro-2-(4-methylstyryl)-4-phenylquinoline-3-carboxylate (5d):** White solid, mp 162–163 °C, 90% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02 (s, 1H), 8.00 (s, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.55–7.53 (m, 2H), 7.52–7.49 (m, 5H), 7.34–7.32 (m, 3H), 3.59 (s, 3H), 2.77 (s, 3H); <sup>13</sup>C NMR

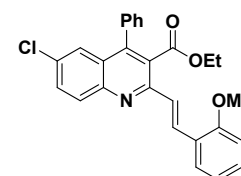


(125 MHz, CDCl<sub>3</sub>)  $\delta$  168.6, 154.9, 146.1, 145.6, 135.6, 134.9, 134.2, 132.4, 131.6, 131.2, 131.1, 130.5, 129.1, 128.9, 128.8, 128.5, 128.0, 125.9, 125.2, 124.4, 52.3, 23.7; HRMS (ESI, m/z): Calcd. For C<sub>26</sub>H<sub>20</sub>ClNO<sub>2</sub>H<sup>+</sup> 414.1255, found 414.0342; IR (KBr, thin film, cm<sup>-1</sup>):  $\nu_{\max}$  3080, 2986, 1729, 1633, 1215, 1177, 820.

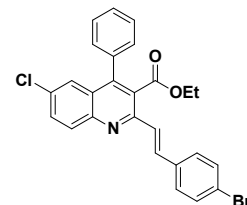
**Ethyl-6-chloro-2-(4-methylstyryl)-4-phenylquinoline-3-carboxylate (5h):** White solid, mp 162–163 °C, 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.09 (d,  $J$  = 3.2 Hz, 1H), 8.06 (d,  $J$  = 9.6 Hz, 1H), 7.66 (dd,  $J$  = 6.4, 2.4 Hz, 1H), 7.52–7.50 (m, 6H), 7.38–7.36 (m, 2H), 7.25 (d,  $J$  = 3.2 Hz, 1H), 7.19 (d,  $J$  = 7.6 Hz, 2H), 4.10 (q,  $J$  = 14.0, 6.8 Hz, 2H), 2.38 (s, 3H), 0.96 (t,  $J$  = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.0, 151.5, 146.5, 145.8, 139.1, 136.97, 135.1, 133.7, 132.4, 131.4, 131.1, 129.5, 129.4, 128.8, 128.6, 128.4, 127.6, 126.3, 125.2, 122.9, 61.6, 21.4, 13.7; HRMS (ESI, m/z): Calcd. For C<sub>27</sub>H<sub>22</sub>ClNO<sub>2</sub>H<sup>+</sup> 428.1412, found 428.1407; IR (KBr, thin film, cm<sup>-1</sup>):  $\nu_{\max}$  3050, 2952, 1724, 1621, 1214, 1156, 832.



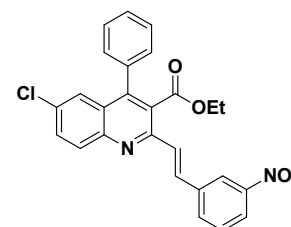
**Ethyl-6-chloro-2-(2-methoxystyryl)-4-phenylquinoline-3-carboxylate (5i):** Pale yellow solid, mp 164–165 °C, 86% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.08–8.07 (m, 2H), 7.65 (d,  $J$  = 8.8 Hz, 1H), 7.56 (d,  $J$  = 8.4 Hz, 2H), 7.50 (s, 4H), 7.38–7.36 (m, 2H), 7.18 (d,  $J$  = 15.6 Hz, 1H), 6.92 (d,  $J$  = 8.4 Hz, 2H), 4.10 (q,  $J$  = 13.8, 6.8 Hz, 2H), 3.84 (s, 3H), 0.96 (t,  $J$  = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  168.1, 160.3, 151.6, 146.5, 145.8, 136.5, 135.1, 132.2, 131.3, 131.0, 129.4, 129.3, 129.1, 128.7, 128.4, 127.6, 126.2, 125.2, 121.6, 114.2, 61.6, 55.3, 13.7; HRMS (ESI, thin film, m/z): Calcd. For C<sub>27</sub>H<sub>22</sub>ClNO<sub>3</sub>H<sup>+</sup> 444.1361, found 444.1371.



**Ethyl-2-(4-bromostyryl)-6-chloro-4-phenylquinoline-3-carboxylate (5l):** White solid, mp 189–190 °C, 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.45 (s, 1H), 8.19–8.10 (m, 3H), 7.92 (d,  $J$  = 7.6 Hz, 1H), 7.70 (d,  $J$  = 9.2 Hz, 1H), 7.59–7.57 (m, 5H), 7.44 (d,  $J$  = 15.6 Hz, 1H), 7.38 (d,  $J$  = 3.2 Hz, 2H), 4.12 (q,  $J$  = 13.8, 6.8 Hz, 2H), 0.95 (t,  $J$  = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>+DMSO-d<sub>6</sub>)  $\delta$  169.4, 156.3, 147.4, 141.2, 139.1, 135.8, 134.3, 133.8, 133.0, 132.8, 132.2, 131.7, 130.7, 130.0, 128.6, 127.1, 125.7, 124.3, 121.3, 117.4, 60.3, 15.1; HRMS (ESI, m/z): Calcd. For C<sub>26</sub>H<sub>19</sub>BrClNO<sub>2</sub>H<sub>2</sub><sup>+</sup> 493.0433, found 493.9371; IR (KBr, thin film, cm<sup>-1</sup>):  $\nu_{\max}$  3025, 2980, 1717, 1564, 1073, 835, 678.

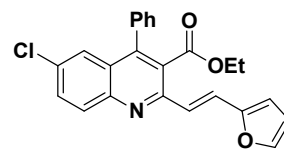


**Ethyl-6-chloro-2-(3-nitrostyryl)-4-phenylquinoline-3-carboxylate (5m):** White solid, mp 176–177 °C, 95% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.47 (s, 1H), 8.20–8.12 (m, 3H), 7.94 (d,  $J$  = 7.6 Hz, 1H), 7.72 (m, 1H), 7.60–7.54 (m, 5H), 7.48–7.39 (m, 3H), 7.28 (s, 1H), 4.14 (q,  $J$  = 6.8 Hz, 2H), 0.98 (t,  $J$  = 6.8 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  167.8, 150.3, 148.7, 146.4, 146.3, 138.2, 135.0, 134.2, 133.2, 133.1, 131.7, 131.2, 129.7, 129.3, 128.9, 128.5, 127.7,

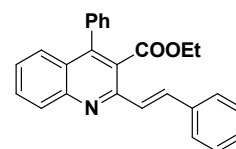


126.9, 126.7, 125.3, 123.2, 122.0, 61.9, 13.6; HRMS (ESI, m/z): Calcd. For  $C_{26}H_{19}ClN_2O_4H^+$  459.1106, found 459.0182; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  2990, 1737, 1604, 1540, 1350, 1256, 829.

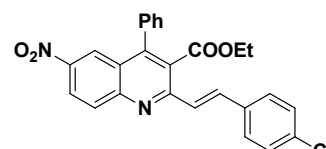
**Ethyl-6-chloro-2-(2-(furan-2-yl)vinyl)-4-phenylquinoline-3-carboxylate (5p):** White solid, mp 160–161 °C, 85% yield.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.04 (d,  $J = 9.0$  Hz, 1H), 7.90 (d,  $J = 15.5$  Hz, 1H), 7.65 (dd,  $J = 9.0, 2.0$  Hz, 1H), 7.53–7.49 (m, 4H), 7.46 (d,  $J = 1.5$  Hz, 1H), 7.38–7.37 (m, 1H), 7.36 (d,  $J = 2.0$  Hz, 1H), 7.20 (d,  $J = 15.3$  Hz, 1H), 6.58 (d,  $J = 3.0$  Hz, 1H), 6.47 (dd,  $J = 3.0, 1.5$  Hz, 1H), 4.12 (q,  $J = 18.0, 7.5$  Hz, 2H), 0.97 (t,  $J = 7.0$  Hz, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  168.6, 154.9, 146.1, 145.6, 135.6, 134.9, 133.0, 132.4, 131.6, 131.2, 131.1, 130.5, 129.0, 128.9, 128.8, 128.5, 128.0, 125.9, 125.28, 124.44, 52.31, 13.67; HRMS (ESI, m/z): Calcd. For  $C_{24}H_{18}ClNO_3H^+$  404.1048, found 404.1056. IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3012, 2982, 1732, 1610, 1542, 1217, 829.



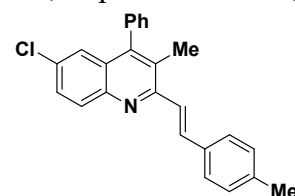
**(E)-Ethyl-4-phenyl-2-styrylquinoline-3-carboxylate (5q):** White solid, mp 186–187 °C, 85% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.09 (d,  $J = 8.4$  Hz, 1H), 8.02 (d,  $J = 15.6$  Hz, 1H), 7.66–7.62 (m, 1H), 7.55 (d,  $J = 7.6$  Hz, 2H), 7.48 (d,  $J = 8.4$  Hz, 1H), 7.41–7.39 (m, 3H), 7.35–7.23 (m, 7H), 4.02 (q,  $J = 7.2$  Hz, 2H), 0.88 (t,  $J = 7.2$  Hz, 3H); IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3075, 2976, 1740, 1615, 1520, 1460, 1055.



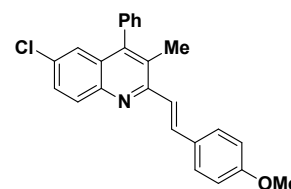
**(E)-Ethyl-2-(4-chlorostyryl)-6-nitro-4-phenylquinoline-3-carboxylate (5r):** yellow solid, mp 170–171 °C, 86% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.01–7.92 (m, 2H), 7.58 (d,  $J = 8.0$  Hz, 1H), 7.42 (s, 8H), 7.29–7.17 (m, 3H), 4.01 (d,  $J = 6.4$  Hz, 2H), 0.86 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  168.94, 152.02, 147.51, 147.11, 136.61, 136.42, 136.10, 133.75, 132.94, 132.54, 132.15, 130.36, 130.06, 129.85, 129.51, 128.64, 127.52, 126.27, 125.63, 123.89, 62.73, 14.66; HRMS (ESI, m/z): Calcd. For  $C_{26}H_{19}ClN_2O_4H^+$  459.1106, found 459.1107; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3083, 2986, 1736, 1620, 1545, 1452, 1063, 862.



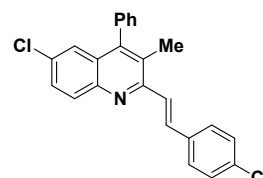
**6-Chloro-3-methyl-2-(4-methylstyryl)-4-phenylquinoline (6a):** White solid, mp 191–192 °C, 85% yield.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.04 (d,  $J = 9.0$  Hz, 1H), 8.00 (d,  $J = 15.5$  Hz, 1H), 7.57–7.52 (m, 5H), 7.50–7.47 (m, 2H), 7.26–7.24 (m, 3H), 2.38 (s, 3H), 2.31 (s, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  155.4, 146.2, 144.9, 138.7, 137.0, 136.3, 134.2, 131.4, 130.8, 129.5, 129.3, 129.1, 128.8, 128.0, 127.9, 127.8, 127.4, 124.9, 123.6, 21.4, 16.8; HRMS (ESI, m/z): Calcd. For  $C_{25}H_{20}ClNH^+$  370.1357, found 370.1372; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3014, 2985, 2919, 1631, 1572, 1163, 805.



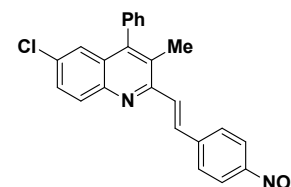
**6-Chloro-2-(4-methoxystyryl)-3-methyl-4-phenylquinoline (6b):** Yellow solid, mp 174–175 °C, 88% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03–7.96 (m, 2H), 7.62–7.49 (m, 6H), 7.43 (d, *J* = 15.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 3H), 6.93 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H), 2.31 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.1, 155.5, 146.2, 144.9, 137.1, 135.9, 131.3, 130.7, 129.7, 129.3, 129.3, 128.9, 128.7, 128.1, 127.8, 127.7, 127.7, 124.9, 122.3, 114.2, 55.3, 16.8; HRMS (ESI, *m/z*): Calcd. For C<sub>25</sub>H<sub>20</sub>ClNOH<sup>+</sup> 386.1306, found 386.1321; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 2924, 3010, 1627, 1603, 1443, 1171, 831.



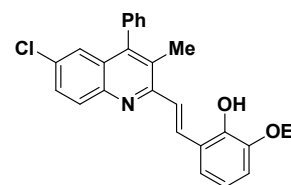
**6-Chloro-2-(4-chlorostyryl)-3-methyl-4-phenylquinoline (6c):** Pale yellow solid, mp 165–166 °C, 92% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 9.0 Hz, 1H), 7.97 (d, *J* = 15.5 Hz, 1H), 7.85 (s, 1H), 7.60–7.48 (m, 5H), 7.37–7.32 (m, 3H), 7.27 (s, 1H), 7.24 (d, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 2.32 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.0, 154.7, 146.3, 145.2, 144.8, 143.6, 136.8, 135.3, 134.8, 134.1, 130.8, 130.3, 129.2, 128.9, 128.7, 128.4, 127.8, 125.1, 124.8, 16.7; HRMS (ESI, *m/z*): Calcd. For C<sub>24</sub>H<sub>17</sub>Cl<sub>2</sub>NH<sup>+</sup> 390.0811, found 389.9901; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3064, 2910, 1571, 1420, 721, 702.



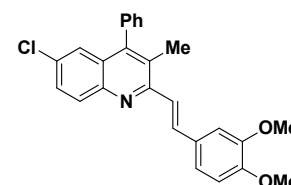
**6-Chloro-3-methyl-2-(4-nitrostyryl)-4-phenylquinoline (6d):** Yellow solid, mp 219–220 °C, 95% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 15.0 Hz, 1H), 8.05 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.51–7.45 (m, 6H), 7.27–7.23 (m, 3H), 2.32 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>+ DMSO-d<sub>6</sub>) δ 154.2, 148.6, 146.6, 144.9, 136.8, 133.1, 132.8, 132.1, 131.4, 131.2, 129.8, 129.6, 129.3, 128.9, 128.8, 128.2, 127.9, 124.8, 124.8, 16.8; HRMS (ESI, *m/z*): Calcd. For C<sub>24</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>2</sub>H<sup>+</sup> 401.1051, found 401.1065; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3010, 298, 1567, 1511, 1337, 1166, 824.



**5-(2-(6-Chloro-3-methyl-4-phenylquinolin-2-yl)-vinyl)-2-ethoxyphenol (6e):** White solid, mp 152–153 °C, 85% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 16.5 Hz, 1H), 7.54–7.49 (m, 5H), 7.40–7.36 (m, 2H), 7.25–7.21 (m, 3H), 7.14 (s, 1H), 4.19 (q, *J* = 14.0, 7.0 Hz, 2H), 2.31 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>+ DMSO-d<sub>6</sub>) δ 167.6, 149.8, 147.9, 144.1, 141.7, 140.4, 139.8, 139.7, 138.7, 137.7, 136.6, 136.2, 136.0, 135.8, 134.8, 134.0, 130.9, 129.4, 127.9, 127.1, 115.6, 61.0, 17.8, 13.5; HRMS (ESI, *m/z*): Calcd. For C<sub>26</sub>H<sub>22</sub>ClNO<sub>2</sub>H<sup>+</sup> 416.1412, found 416.1404.



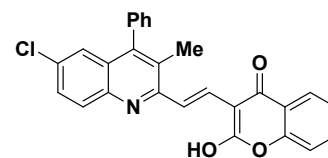
**6-Chloro-2-(3,4-dimethoxystyryl)-3-methyl-4-phenylquinoline (6f):** White solid, mp 175–176 °C, 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15–8.05 (m, 2H), 7.59–7.53 (m, 4H), 7.43 (d, *J* = 15.6 Hz, 1H), 7.30–7.28 (m, 4H), 7.23 (s, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 3.99 (s, 3H), 3.95 (s, 3H), 2.36 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.5, 155.4, 149.8, 149.1, 146.2, 144.9, 137.0,



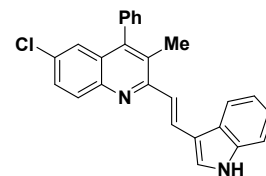
136.5, 136.3, 131.3, 130.7, 129.3, 128.8, 128.8, 128.1, 127.8, 127.7, 127.3, 124.9, 122.6, 121.0, 119.4, 111.2, 110.0, 56.0, 16.8; HRMS (ESI, m/z): Calcd. For  $C_{26}H_{22}ClNO_2H^+$  416.1412, found 416.1404; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3029, 2954, 1568, 1261, 1245, 1027, 828.

**3-(2-(6-Chloro-3-methyl-4-phenylquinolin-2-yl)-vinyl)-2-hydroxy-4H-chromen-4-one (6g):**

Dark red solid, 86% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.00 (d,  $J$  = 9.2 Hz, 1H), 7.93 (d,  $J$  = 15.6 Hz, 1H), 7.58–7.42 (m, 5H), 7.40–7.24 (m, 3H), 7.2–7.13 (m, 3H), 7.03 (d,  $J$  = 6.0 Hz, 1H), 2.26 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3+DMSO-d_6$ )  $\delta$  198.5, 172.0, 160.0, 152.7, 148.5, 141.4, 141.2, 133.6, 133.5, 132.5, 131.9, 131.7, 130.3, 129.7, 129.6, 129.4, 129.1, 129.0, 128.3, 127.7, 127.4, 124.7, 118.4, 85.6, 16.4; HRMS (ESI, m/z): Calcd. For  $C_{27}H_{18}ClNO_3H^+$  440.1048, found 440.1045; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3395, 3052, 2963, 1720, 1642, 1266, 1088, 748.

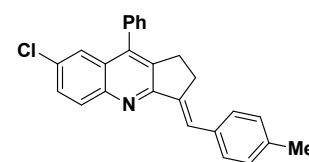


**2-(2-(1H-Indol-3-yl)vinyl)-6-chloro-3-methyl-4-phenylquinoline (6h):** White solid, mp 182–183 °C, 86% yield.  $^1H$  NMR (400 MHz,  $CDCl_3+DMSO-d_6$ )  $\delta$  7.95 (s, 1H), 7.89 (d,  $J$  = 10.4 Hz, 3H), 7.78 (d,  $J$  = 14.8 Hz, 1H), 7.71–7.64 (m, 5H), 7.42 (d,  $J$  = 6.4 Hz, 3H), 7.28 (d,  $J$  = 5.6 Hz, 2H), 2.29 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3+DMSO-d_6$ )  $\delta$  162.7, 145.3, 142.9, 140.8, 136.5, 136.3, 135.2, 133.9, 133.6, 132.0, 131.1, 130.2, 129.5, 129.1, 128.4, 127.4, 125.8, 124.6, 122.7, 120.7, 119.5, 113.5, 110.8, 17.7; HRMS (ESI, m/z): Calcd. For  $C_{26}H_{19}ClN_2H^+$  395.1310, found 395.1314; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3301, 3078, 2951, 1651, 1272, 1246, 1075, 742.



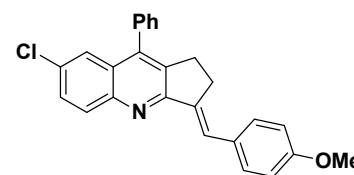
**7-Chloro-3-(4-methylbenzylidene)-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (7a):**

Yellow solid, mp 229–230 °C, 89% yield.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.06 (d,  $J$  = 9.0 Hz, 1H), 7.81 (s, 1H), 7.55–7.49 (m, 7H), 7.35 (d,  $J$  = 7.5 Hz, 2H), 7.24–7.20 (m, 2H), 3.15 (s, 2H), 3.0–2.98 (m, 2H), 2.38 (s, 3H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  162.2, 147.2, 142.7, 139.7, 137.6, 136.0, 135.9, 134.5, 131.4, 130.8, 129.5, 129.4, 129.3, 129.1, 128.8, 128.3, 127.8, 125.4, 124.4, 28.8, 27.7, 21.4; HRMS (ESI, m/z): Calcd. For  $C_{26}H_{20}ClNH^+$  382.1357, found 382.1353; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3030, 2917, 1600, 1585, 1163, 1075, 826.



**7-Chloro-3-(4-methoxybenzylidene)-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline (7b):**

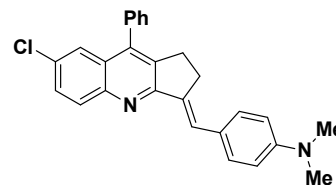
White solid, mp 168–169 °C, 85% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.06 (d,  $J$  = 8.8 Hz, 1H), 7.79 (s, 1H), 7.58–7.49 (m, 7H), 7.36 (d,  $J$  = 6.8 Hz, 2H), 6.96 (d,  $J$  = 8.4 Hz, 2H), 3.85 (s, 3H), 3.17–3.14 (m, 2H), 3.03–3.00 (m, 2H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  162.3, 159.1, 147.2, 142.6, 138.4, 136.0, 132.0, 131.2, 130.9, 130.7, 130.2, 129.4, 129.1, 128.8, 128.3, 127.8, 125.0, 124.3, 114.0, 55.3, 28.7, 27.7; HRMS (ESI, m/z):



Calcd. For C<sub>26</sub>H<sub>20</sub>ClNOH<sup>+</sup> 398.1306, found 398.1312; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 2974, 2835, 1632, 1604, 1252, 1128, 1028, 830.

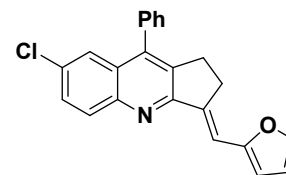
**4-((7-Chloro-9-phenyl-1H-cyclopenta[b]quinolin-3(2H)-ylidene)methyl)-N,N-dimethylaniline (7c):**

White solid, mp 218–219 °C, 85% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.54–7.50 (m, 3H), 7.49–7.46 (m, 3H), 7.27–7.23 (m, 3H), 6.75 (d, *J* = 9.0 Hz, 2H), 3.01 (s, 6H), 2.63 (t, *J* = 5.5 Hz, 2H), 1.79 (t, *J* = 6.0 Hz, 2H); <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>) δ 155.5, 149.5, 145.2, 144.8, 136.6, 132.3, 130.9, 130.6, 129.7, 129.3, 129.2, 128.7, 128.0, 127.4, 126.0, 124.5, 111.8, 40.3, 28.5, 28.5, 22.9; HRMS (ESI, m/z): Calcd. For C<sub>27</sub>H<sub>23</sub>ClN<sub>2</sub>H<sup>+</sup> 411.1623, found 411.162; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3385, 3101, 2932, 1613, 1566, 1265, 1163, 822.



**6-Chloro-2-(furan-2-ylmethylene)-8-phenyl-1,2-dihydrocyclobuta[b]quinoline (7d):** Brown

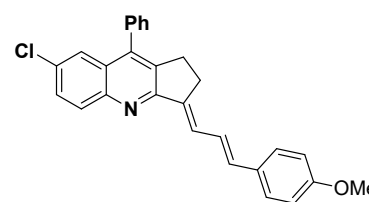
solid, mp 198–199 °C, 88% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.8 Hz, 1H), 7.63 (t, *J* = 2.4 Hz, 1H), 7.57–7.447 (m, 6H), 7.36 (d, *J* = 6.8 Hz, 2H), 6.53–6.49 (m, 2H), 3.17–3.16 (m, 2H), 3.02–2.99 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.5, 153.8, 143.0, 142.7, 138.8, 136.8, 135.9, 131.4, 130.7, 129.4, 129.0, 128.8, 128.3, 127.8, 124.3, 112.7, 112.6, 112.0, 111.7, 28.4, 27.4; HRMS (ESI, m/z): Calcd.



For C<sub>23</sub>H<sub>16</sub>ClNOH<sup>+</sup> 358.0993, found: 358.0990; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3059, 2942, 2884, 1683, 1537, 1268, 1073, 829.

**7-Chloro-3-((E)-3-(4-methoxyphenyl)allylidene)-9-phenyl-2,3-dihydro-1H-cyclopenta**

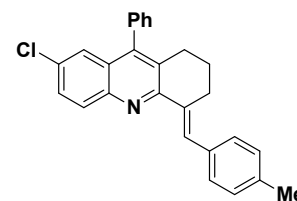
**[b]quinoline (7e):** Yellow solid, mp 170–171 °C, 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13–7.92 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.58–7.39 (m, 5H), 7.25 (d, *J* = 7.6 Hz, 4H), 6.94 (d, *J* = 8.0 Hz, 2H), 3.75 (s, 3H), 2.95 (d, *J* = 7.3 Hz, 2H), 2.19 (t, *J* = 7.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.22, 160.5, 145.6, 145.0,



141.2, 134.3, 133.2, 132.6, 131.7, 129.5, 129.3, 129.1, 128.9, 128.6, 128.2, 127.6, 124.8, 124.7, 123.0, 114.3, 97.4, 55.3, 27.5, 26.5; HRMS (ESI, m/z): Calcd. For C<sub>28</sub>H<sub>22</sub>ClNOH<sup>+</sup> 424.1463, found 424.1467; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3068, 2932, 1599, 1583, 1509, 1253, 1173, 818.

**7-Chloro-4-(4-methylbenzylidene)-9-phenyl-1, 2, 3, 4-tetrahydroacridine (7f):** White solid, mp

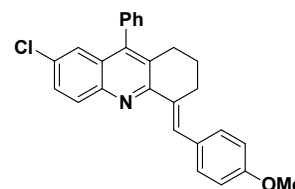
185–186 °C, 88% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.20 (s, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.55–7.47 (m, 5H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 2.5 Hz, 1H), 7.25–7.20 (m, 3H), 2.97 (t, *J* = 5.5 Hz, 2H), 2.65 (t, *J* = 6.0 Hz, 3H), 2.38 (s, 3H), 1.81–1.76 (m, 2H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 154.7, 145.3, 145.1, 137.0, 136.5, 135.4, 134.9, 131.4, 131.0, 130.0, 129.9, 129.8, 129.4, 129.2, 128.9, 128.8, 128.1, 127.6, 124.5, 28.6, 28.2, 22.9, 21.3; HRMS





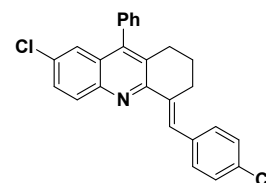
(ESI, m/z): Calcd. For  $C_{27}H_{22}ClNH^+$  396.1518, found 396.1514; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3102, 2958, 2863, 1602, 1540, 1169, 820.

**7-Chloro-4-(4-methoxybenzylidene)-9-phenyl-1,2,3,4-tetrahydroacridine (7g):** White solid, mp 174–175 °C, 85% yield.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.17 (s, 1H), 8.03 (d,  $J = 9.0$  Hz, 1H), 7.54–7.46 (m, 7H), 7.28–7.24 (m, 2H), 6.94 (d,  $J = 8.0$  Hz, 2H), 3.84 (s, 3H), 2.96 (t,  $J = 5.5$  Hz, 2H), 2.64 (t,  $J = 6.0$  Hz, 2H), 1.80 (p,  $J = 6.0, 5.5$  Hz, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  162.3, 159.1, 158.6, 147.2, 142.6, 138.4, 136.0, 135.9, 131.2, 130.9, 130.7, 130.2, 129.4, 129.1, 128.8, 128.3, 127.8, 125.0, 124.3, 114.0, 55.3, 28.7, 27.7; HRMS (ESI, m/z):

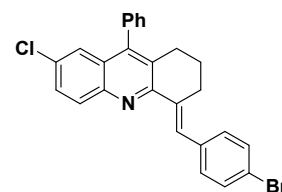


Calcd. For  $C_{27}H_{22}ClNOH^+$  412.1463, found 412.1467; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3069, 2948, 1602, 1536, 1167, 1031, 832.

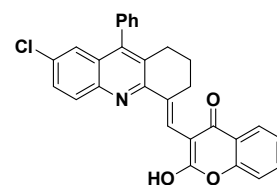
**7-Chloro-4-(4-chlorobenzylidene)-9-phenyl-1,2,3,4-tetrahydroacridine (7h):** White solid, mp 221–222 °C, 90% yield.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.17 (s, 1H), 8.03 (d,  $J = 9.0$  Hz, 1H), 7.55–7.52 (m, 3H), 7.51–7.47 (m, 2H), 7.36 (d,  $J = 8.0$  Hz, 2H), 7.30 (d,  $J = 2.0$  Hz, 1H), 7.25–7.23 (m, 2H), 2.93 (t,  $J = 7.0$  Hz, 2H), 2.66 (t,  $J = 6.5$  Hz, 2H), 1.82–1.77 (m, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  154.2, 145.5, 145.1, 136.7, 136.4, 136.2, 132.8, 131.6, 131.1, 129.8, 129.5, 129.2, 129.0, 128.8, 128.6, 128.4, 128.1, 127.7, 124.6, 28.5, 28.1, 22.9; HRMS (ESI, m/z): Calcd. For  $C_{26}H_{19}Cl_2NH^+$  416.0967, found 416.0968; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3080, 2940, 1565, 1474, 829, 820.



**4-(4-Bromobenzylidene)-7-chloro-9-phenyl-1,2,3,4-tetrahydroacridine (7i):** White solid, mp 237–238 °C, 92% yield.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.16 (s, 1H), 8.02 (d,  $J = 9.0$  Hz, 1H), 7.54–7.46 (m, 4H), 7.42–7.33 (m, 4H), 7.28 (d,  $J = 2.0$  Hz, 1H), 7.24–7.21 (m, 2H), 2.92–2.90 (m, 2H), 2.64 (t,  $J = 6.5$  Hz, 2H), 1.81–1.76 (m, 2H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  155.2, 149.0, 146.1, 139.3, 137.7, 137.2, 133.8, 132.6, 132.1, 131.3, 130.5, 130.2, 129.8, 129.6, 129.4, 129.1, 128.7, 128.0, 125.6, 29.5, 29.1, 23.9; HRMS (ESI, m/z): Calcd. For  $C_{26}H_{19}BrClNH_2^{+2}$  461.0535, found 461.9387; IR (KBr, thin film,  $cm^{-1}$ ):  $\nu_{max}$  3051, 2938, 1620, 1566, 1071, 830, 708.



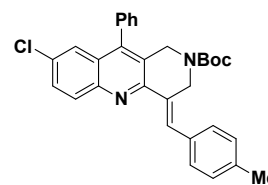
**3-((7-Chloro-9-phenyl-2,3-dihydroacridin-4(1H)-ylidene)methyl)-2-hydroxy-4H-chromen-4-one (7j):** Yellow solid, mp 205–206 °C, 85% yield.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.24 (s, 1H), 8.19 (d,  $J = 8.8$  Hz, 2H), 7.58 (d,  $J = 8.4$  Hz, 2H), 7.52–7.44 (m, 4H), 7.26 (d,  $J = 1.6$  Hz, 1H), 7.18 (d,  $J = 6.8$  Hz, 3H), 2.89 (t,  $J = 5.2$  Hz, 2H), 2.63 (t,  $J = 6.0$  Hz, 2H), 1.80–1.74 (m, 2H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  183.4, 172.6, 137.2, 136.3, 135.4, 134.2, 133.9, 133.7, 132.6, 132.3, 132.0, 131.8, 129.9, 129.3, 129.0, 128.9, 128.5, 128.5, 128.6, 127.1, 126.1,



125.8, 122.8, 120.4, 26.6, 22.7, 22.8; HRMS (ESI, m/z): Calcd. For C<sub>29</sub>H<sub>20</sub>ClNO<sub>3</sub> 465.1132, found 463.9975 (M-1); IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3420, 3050, 2931, 1651, 1291, 1271, 703.

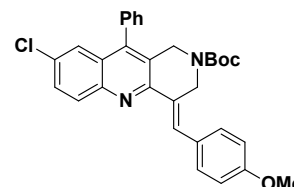
***Tert-butyl-8-chloro-4-(4-methylbenzylidene)-10-phenyl-3,4-dihydrobenzo[b][1,6] naphthyridin-2(1H)-carboxylate (8a)***: Pale yellow solid, mp 155–156 °C, 88% yield. <sup>1</sup>H

NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.31 – 7.28 (m, 3H), 7.22 – 7.14 (m, 4H), 4.70 (s, 2H), 4.39 (s, 2H), 2.31 (s, 3H), 1.21 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.6, 145.6, 145.0, 139.3, 137.8, 134.9, 133.6, 132.0, 131.9, 131.0, 130.1, 129.7, 129.1, 128.7, 128.7, 128.6, 128.3, 127.3, 126.0, 124.6, 80.2, 53.8, 44.5, 28.3, 21.3; HRMS (ESI, m/z): Calcd. For C<sub>31</sub>H<sub>29</sub>ClN<sub>2</sub>O<sub>2</sub>H<sup>+</sup> 497.1990, found 497.1991; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3345, 2976, 1689, 1623, 1259, 1148, 832.



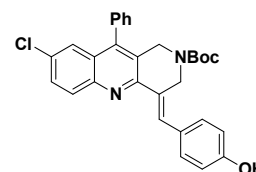
***Tert-butyl-8-chloro-4-(4-methoxybenzylidene)-10-phenyl-3,4-dihydrobenzo[b][1,6] naphthyridine-2(1H)-carboxylate (8b)***: White solid, mp 165–166 °C,

86% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (s, 1H), 7.55 – 7.36 (m, 6H), 7.29 (d, *J* = 2.0 Hz, 1H), 7.23 – 7.18 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.72 (s, 2H), 4.39 (s, 2H), 3.78 (s, 3H), 1.22 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>+ DMSO-d<sub>6</sub>) δ 163.3, 159.6, 152.9, 148.6, 146.8, 144.5, 139.1, 134.3, 132.5, 131.7, 130.1, 129.4, 128.3, 127.8, 126.7, 124.8, 122.7, 121.6, 117.8, 71.0, 57.7, 55.7, 50.3, 44.8, 28.1; HRMS (ESI, m/z): Calcd. For C<sub>31</sub>H<sub>29</sub>ClN<sub>2</sub>O<sub>3</sub>H<sup>+</sup> 513.1939, found 513.0981; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3411, 2921, 1604, 1254, 1165, 1032, 830.



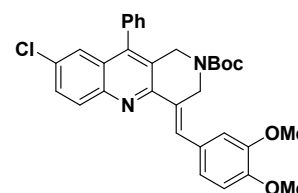
***Tert-butyl-8-chloro-4-(4-hydroxybenzylidene)-10-phenyl-3,4-dihydrobenzo[b][1,6]***

***naphthyridine-2(1H)-carboxylate (8c)***: Yellow solid, mp 172–173 °C, 86% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08–7.93 (m, 2H), 7.54–7.49 (m, 6H), 7.47 (s, 2H), 7.29–7.16 (m, 3H), 4.64 (s, 2H), 4.41 (s, 2H), 1.18 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.5, 150.3, 145.4, 144.6, 138.8, 136.3, 134.6, 132.1, 131.8, 131.0, 130.9, 130.1, 130.0, 129.0, 128.9, 128.7, 127.2, 125.9, 124.6, 115.6, 80.1, 64.1, 44.5, 28.3; HRMS (ESI, m/z): Calcd. For C<sub>30</sub>H<sub>27</sub>ClN<sub>2</sub>O<sub>3</sub>H<sup>+</sup> 499.1783, found 499.1799; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3778, 3348, 3024, 2975, 1633, 1570, 1170, 955, 829.



***Tert-butyl-8-chloro-4-(3,4-dimethoxybenzylidene)-10-phenyl-3,4-dihydrobenzo[b][1,6]***

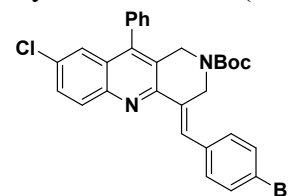
***naphthyridine-2(1H)-carboxylate (8d)***: Pale yellow solid, mp 140–141 °C, 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (s, 2H), 7.54 – 7.45 (m, 4H), 7.29 – 7.21 (m, 3H), 7.03 – 6.96 (m, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.73 (s, 2H), 4.40 (s, 2H), 3.86 (d, *J* = 4.4 Hz, 6H), 1.23 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.6, 148.9, 148.7, 145.6, 141.3, 134.6, 134.1, 133.2, 131.9, 131.0, 130.1, 130.1, 129.1, 128.7, 128.7, 128.3, 127.3, 126.0, 122.7, 118.4,



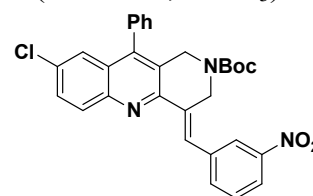
114.7, 111.0, 80.2, 55.9, 50.8, 45.0, 28.3; HRMS (ESI, m/z): Calcd. For C<sub>32</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>4</sub>H<sup>+</sup> 543.2045, found 543.2054; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3345, 3066, 2976, 1683, 1578, 1260, 1160, 1143, 1077, 827.

***Tert-butyl-4-(4-bromobenzylidene)-8-chloro-10-phenyl-3,4-dihydrobenzo[b][1,6]***

***naphthyridine-2(1H)-carboxylate (8e)***: White solid, mp 168–169 °C, 90% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (s, 1H), 7.99–7.88 (m 1H), 7.53–7.45 (m, 4H), 7.28–7.25 (m, 3H), 7.21–7.15 (m, 3H), 4.63 (s, 2H), 4.39–3.34 (m, 2H), 1.17 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.5, 151.2, 147.0, 141.6, 139.9, 136.6, 136.3, 134.2, 133.9, 133.6, 133.0, 132.2, 132.1, 131.1, 131.0, 130.7, 130.3, 129.3, 128.0, 126.6, 82.4, 60.6, 46.6, 30.3; HRMS (ESI, thin film, m/z): Calcd. For C<sub>30</sub>H<sub>26</sub>BrClN<sub>2</sub>O<sub>2</sub>H<sub>2</sub><sup>+</sup> 562.1012, found 562.9716; IR (KBr, cm<sup>-1</sup>): ν<sub>max</sub> 3410, 3030, 2974, 1689, 1242, 1149, 832, 703.

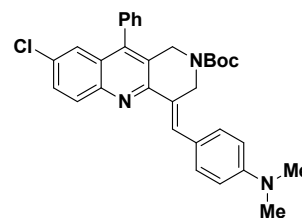


***Tert-butyl-8-chloro-4-(3-nitrobenzylidene)-10-phenyl-3,4-dihydrobenzo[b][1,6]-naphthyridine-2(1H)-carboxylate (8f)***: White solid, mp 185–186 °C, 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 8.8 Hz, 3H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.51–7.54 (m, 3H), 7.52–7.46 (m, 3H), 7.31 (s, 1H), 7.22–7.18 (m, 2H), 4.65 (s, 2H), 4.44 (s, 2H), 1.18 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153, 146.5, 145.3, 140.4, 134.9, 134.4, 132.4, 131.5, 131.0, 130.2, 129.7, 129.0, 128.7, 128.7, 128.6, 128.1, 127.4, 127.0, 126.2, 124.4, 123.5, 121.1, 80.3, 55.1, 44.3, 27.9; HRMS (ESI, m/z): Calcd. For C<sub>30</sub>H<sub>26</sub>ClN<sub>3</sub>O<sub>4</sub>H<sup>+</sup> 528.1685, found 528.1698; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3350, 3060, 2974, 2841, 1693, 1645, 1514, 1150, 834.



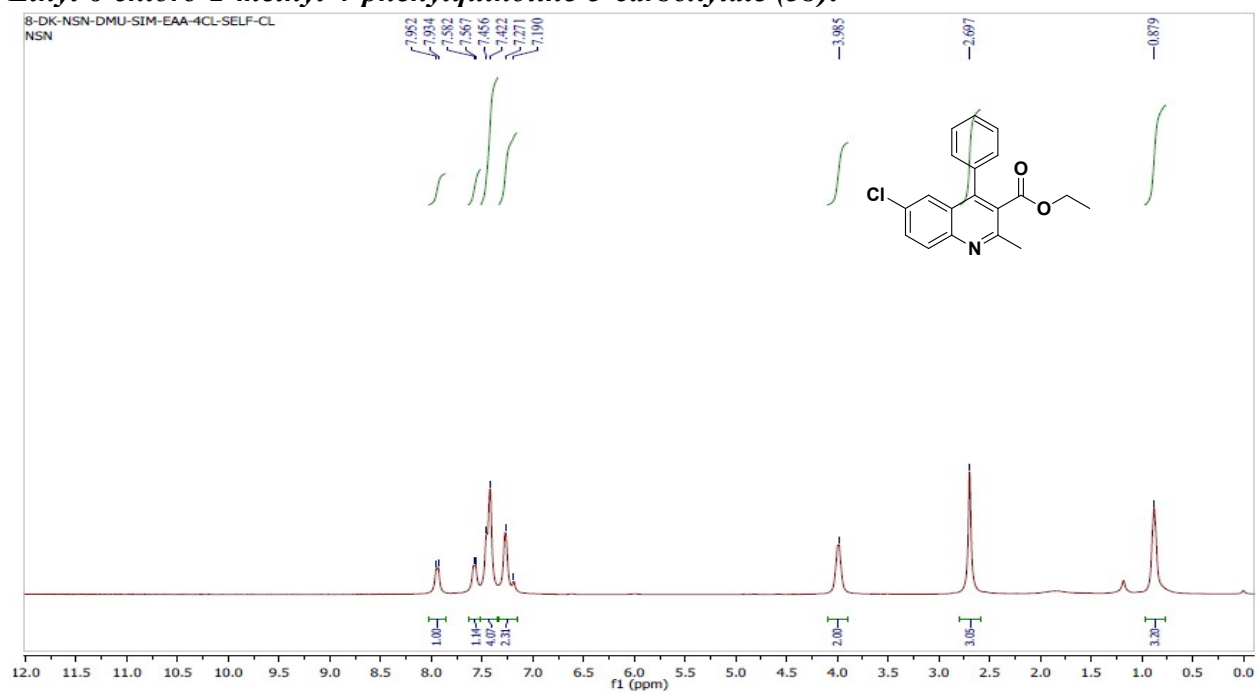
***Tert-butyl-8-chloro-4-(4-(dimethylamino)benzylidene)-10-phenyl-3,4-dihydrobenzo[b][1,6]***

***jnaphthyridine-2(1H)-carboxylate (8g)***: Yellow solid, mp 201–202 °C, 85% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.59–7.56 (m, 6H), 7.44 (d, *J* = 6.0 Hz, 1H), 7.37 (s, 1H), 7.32 (t, *J* = 6.8 Hz 1H), 6.77–6.71 (m, 2H), 4.85 (s, 2H), 4.46 (s, 2H), 3.04 (s, 6H), 1.34 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.5, 150.0, 145.7, 134.1, 131.9, 131.4, 130.8, 130.1, 130.0, 129.8, 129.1, 128.9, 128.7, 128.7, 128.5, 128.3, 126.0, 124.6, 111.9, 111.0, 80.1, 45.3, 44.3, 40.3, 28.2; HRMS (ESI, m/z): Calcd. For C<sub>32</sub>H<sub>32</sub>ClN<sub>3</sub>O<sub>2</sub>H<sup>+</sup> 526.2256, found 526.1048; IR (KBr, thin film, cm<sup>-1</sup>): ν<sub>max</sub> 3382, 2979, 2917, 1693, 1602, 1568, 1169, 818.

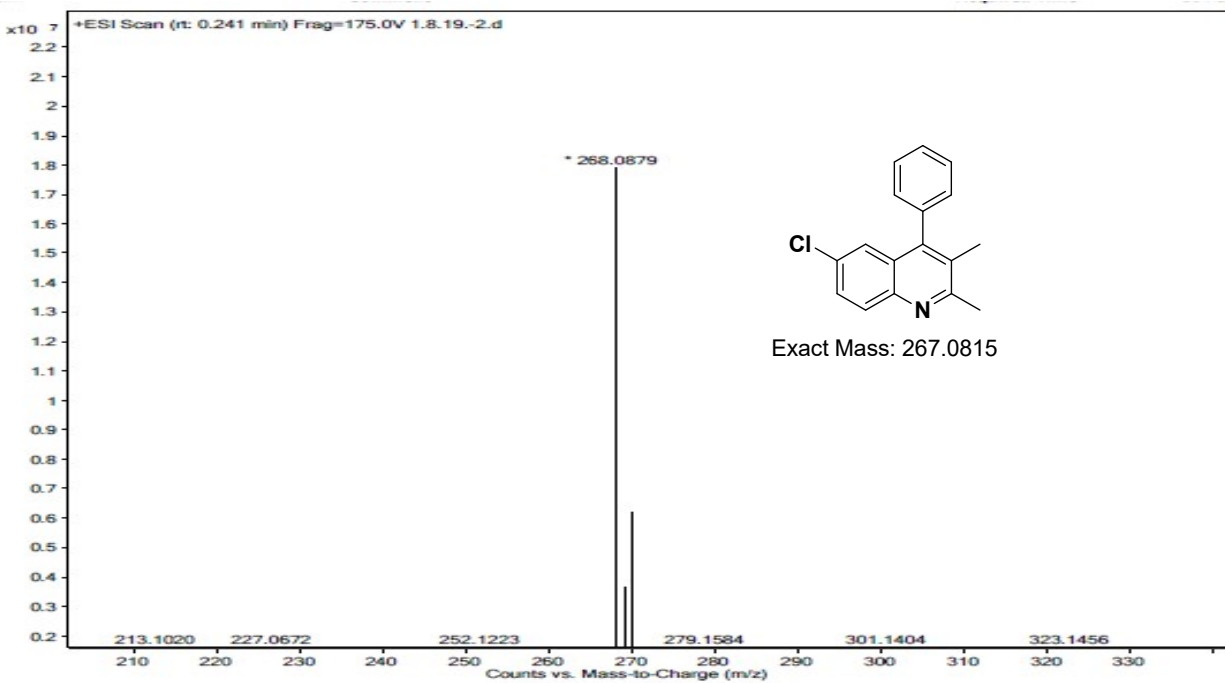
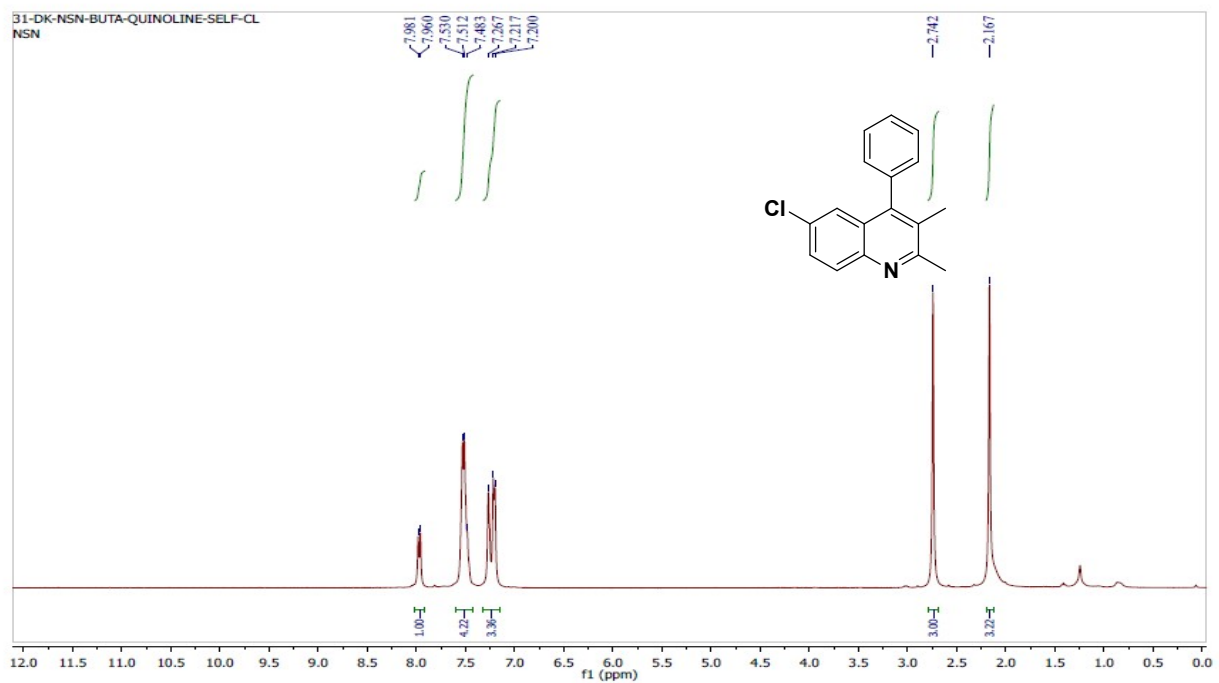


4.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and Mass spectra of the new compounds:

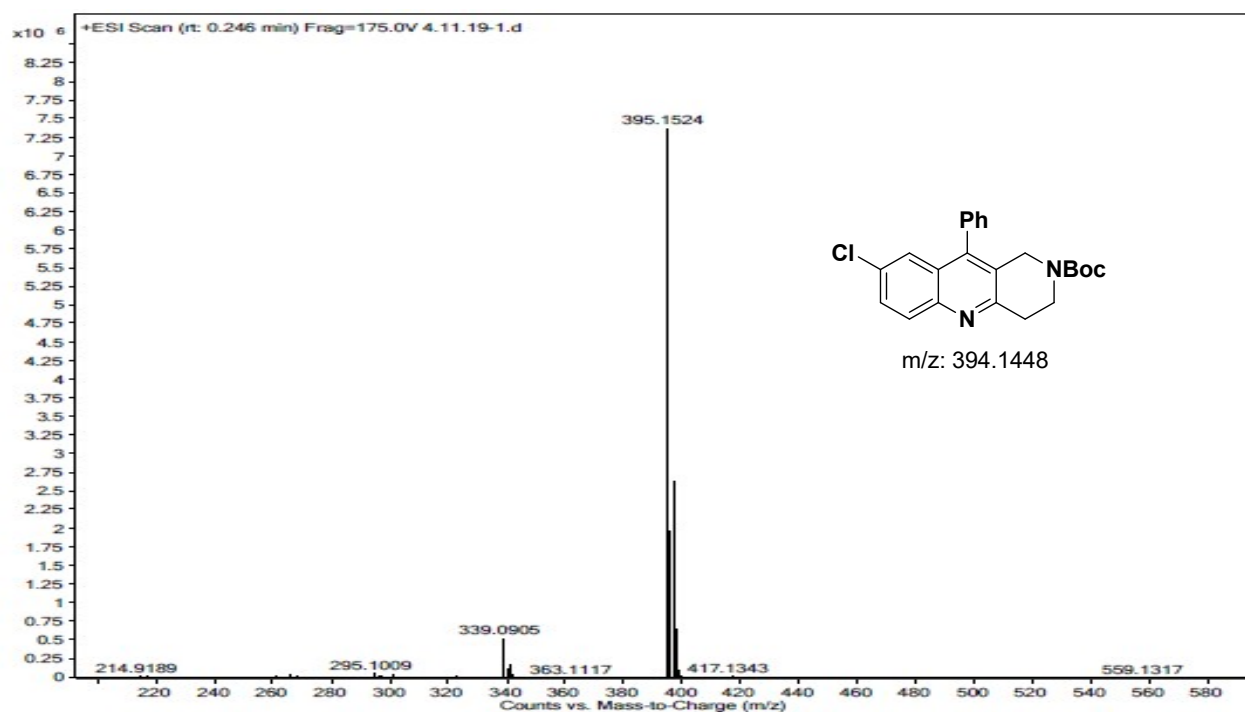
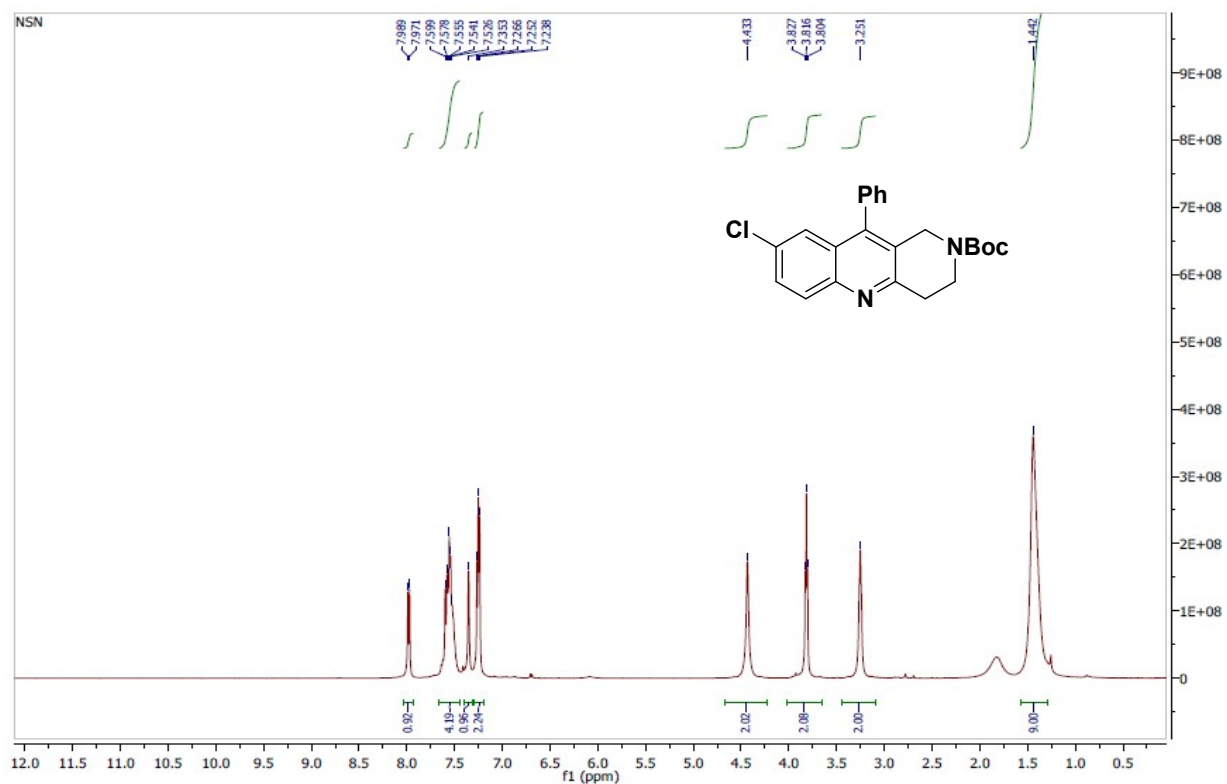
*Ethyl 6-chloro-2-methyl-4-phenylquinoline-3-carboxylate (3b):*



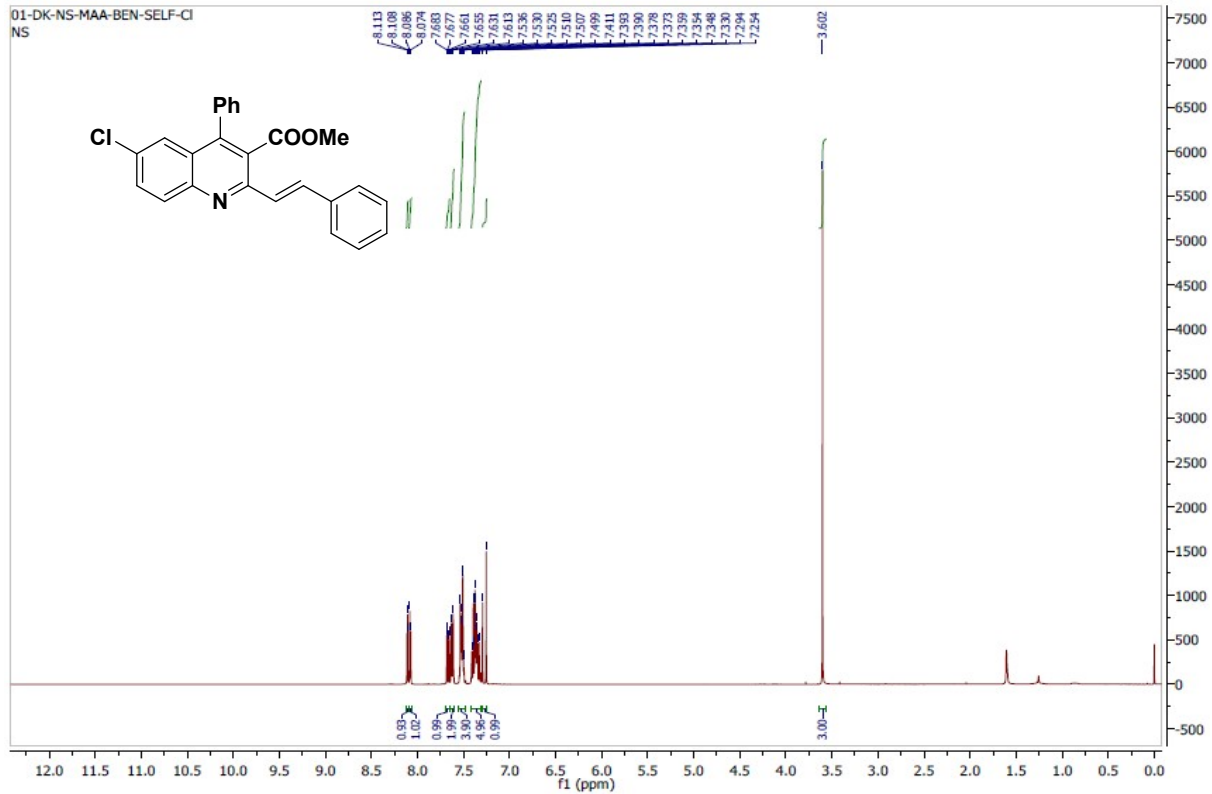
**6-Chloro-2,3-dimethyl-4-phenylquinoline (3c):**



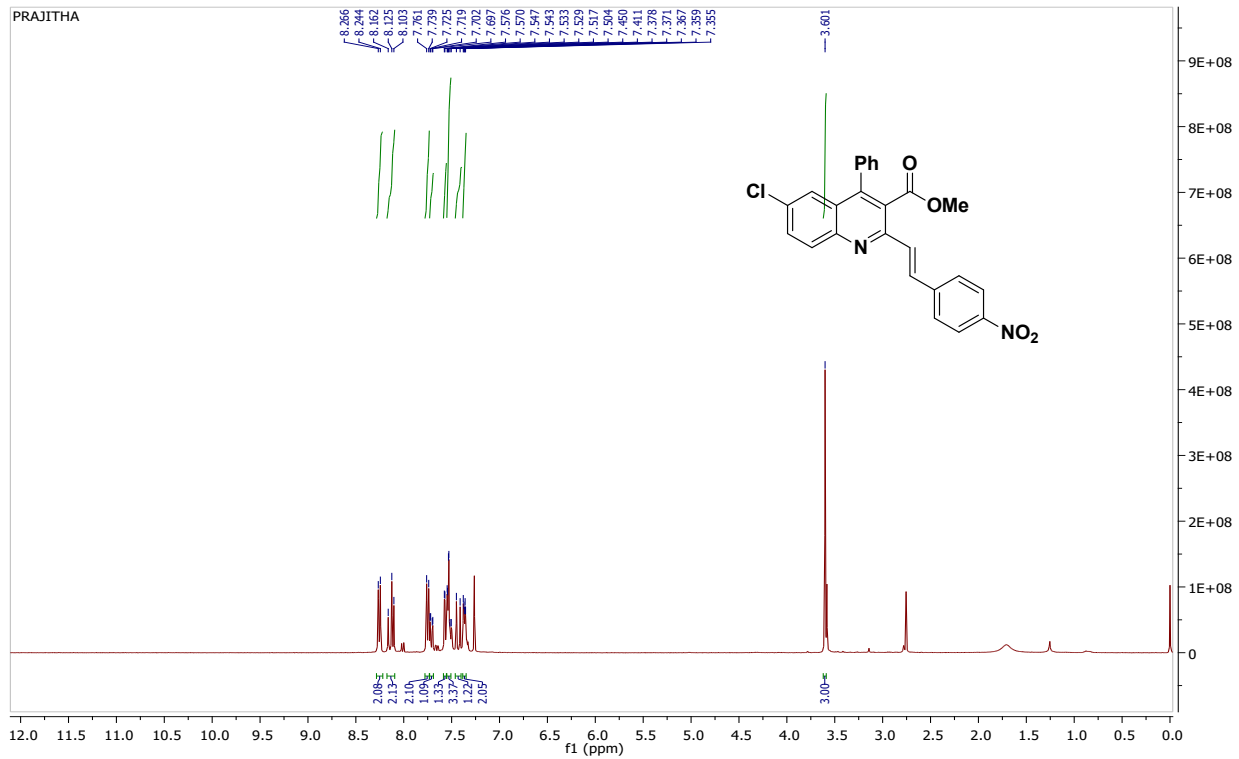
**Tert-butyl-8-chloro-10-phenyl-3,4-dihydrobenzo[b][1,6]naphthyridine-2(1H)-carboxylate (3f):**

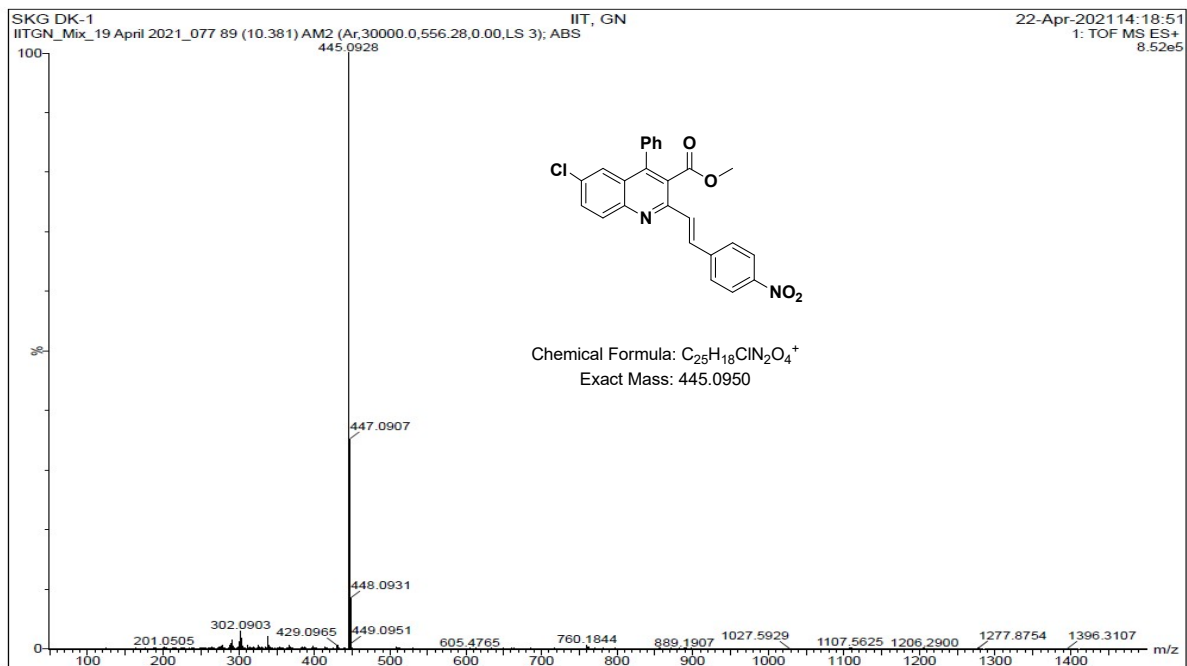
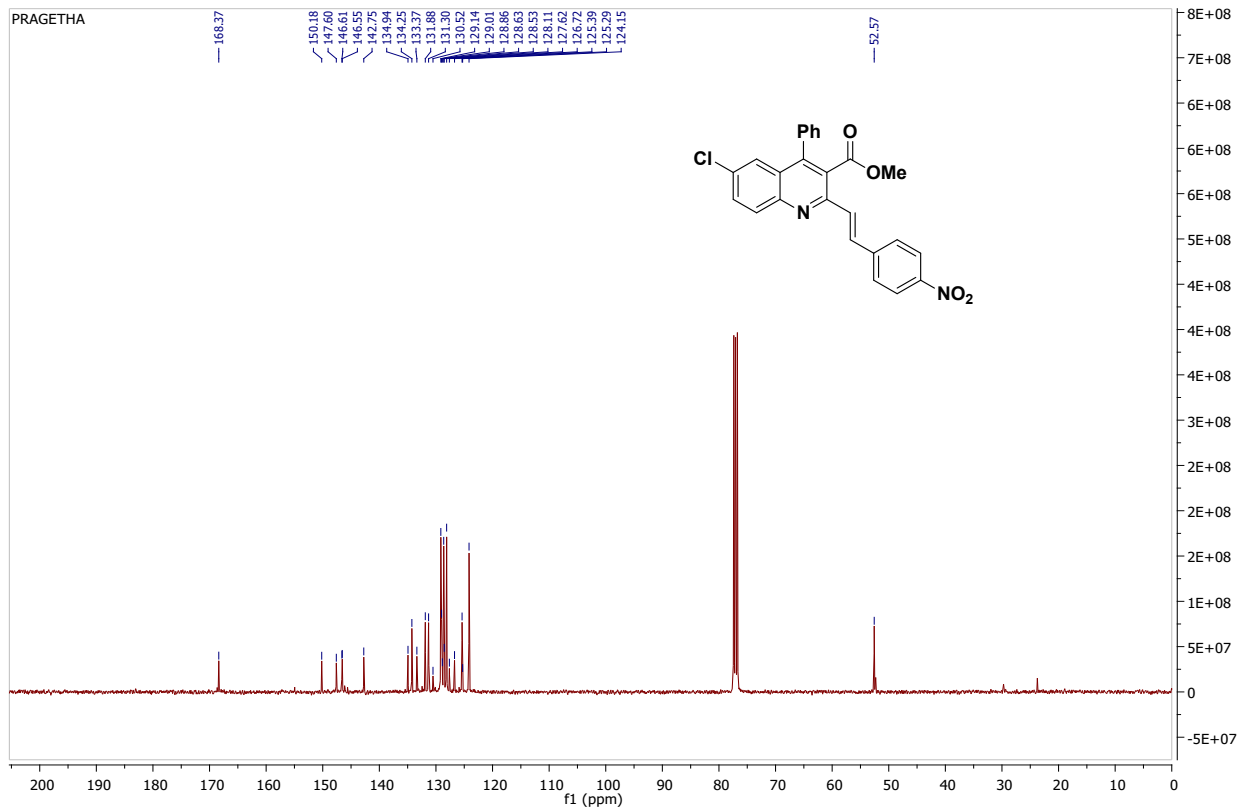


*(E)*-Methyl 6-chloro-4-phenyl-2-styrylquinoline-3-carboxylate (5a):



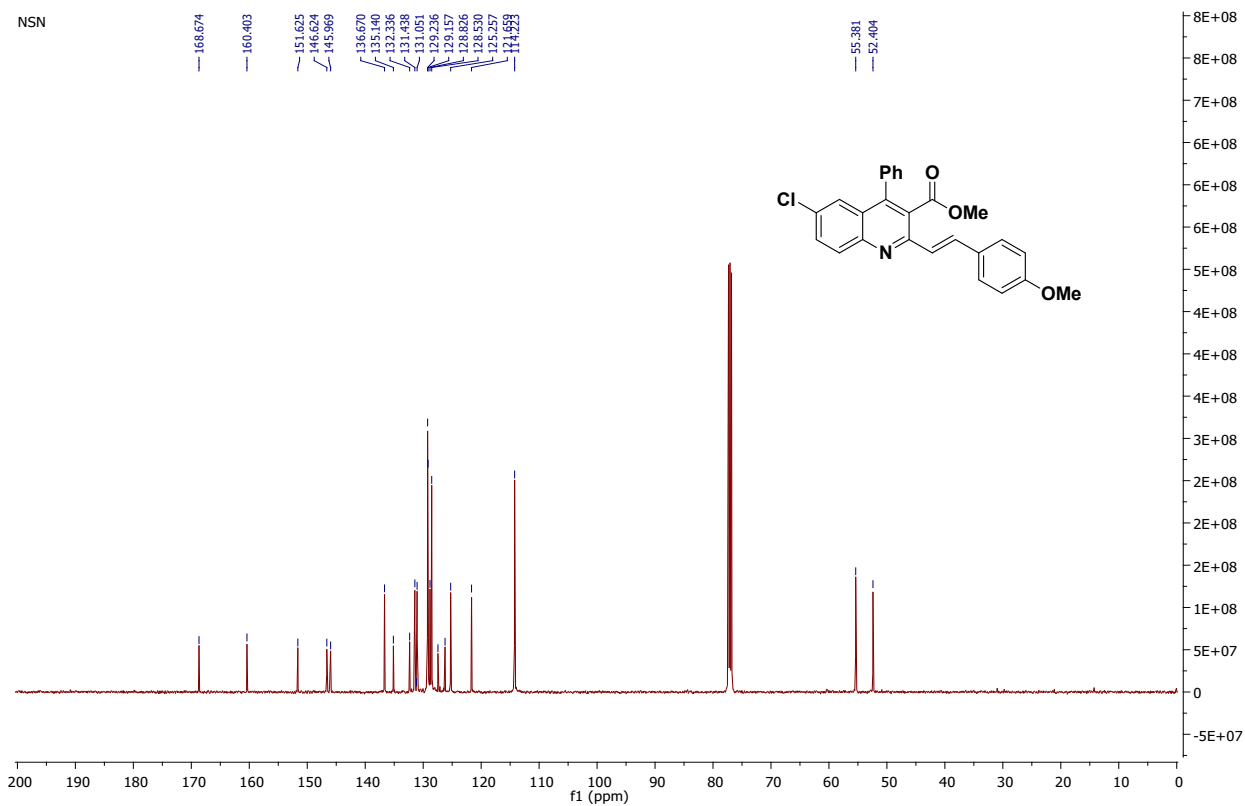
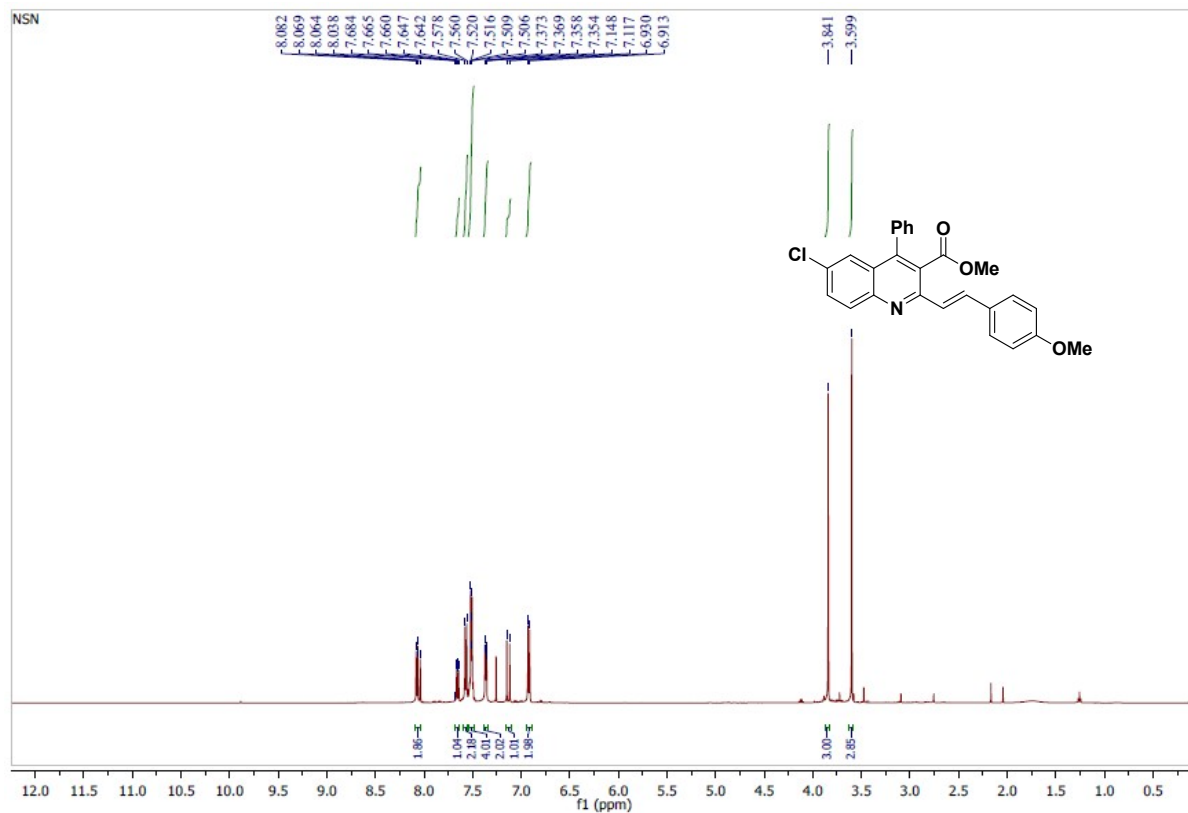
**Methyl- 6-chloro-2-(3-nitrostyryl)-4-phenylquinoline-3-carboxylate (5b):**

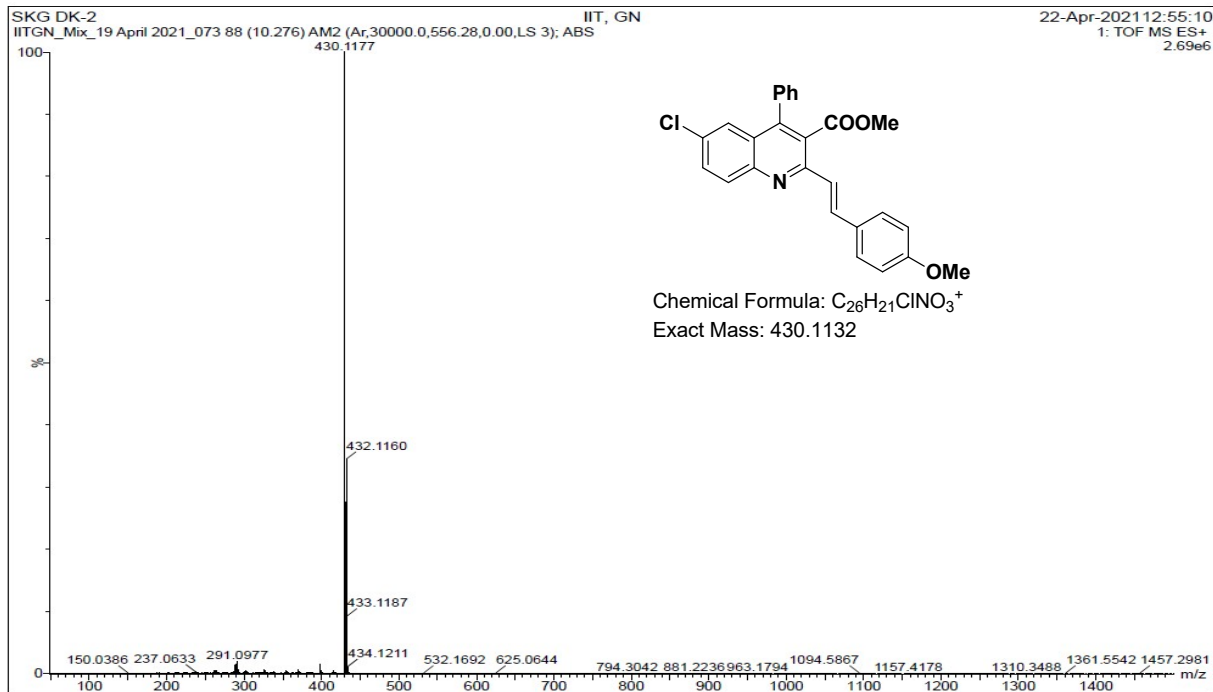




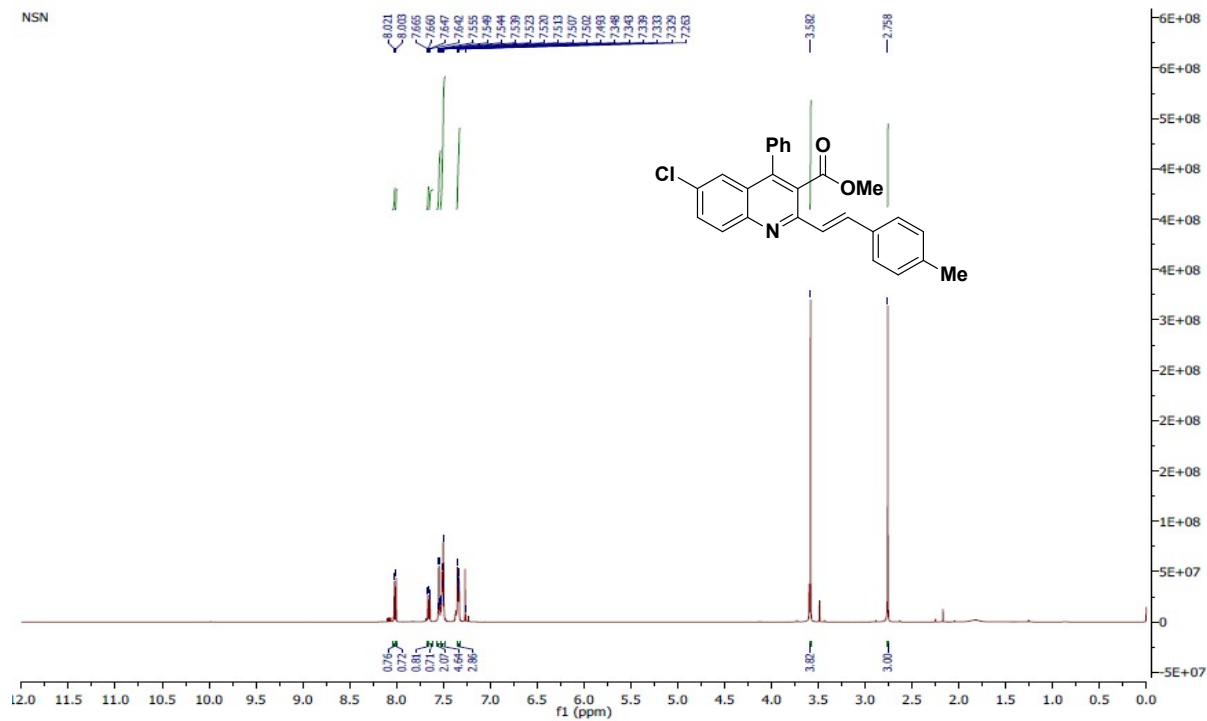
***Methyl-6-chloro-2-(4-methoxystyryl)-4-phenylquinoline-3-carboxylate (5c):***

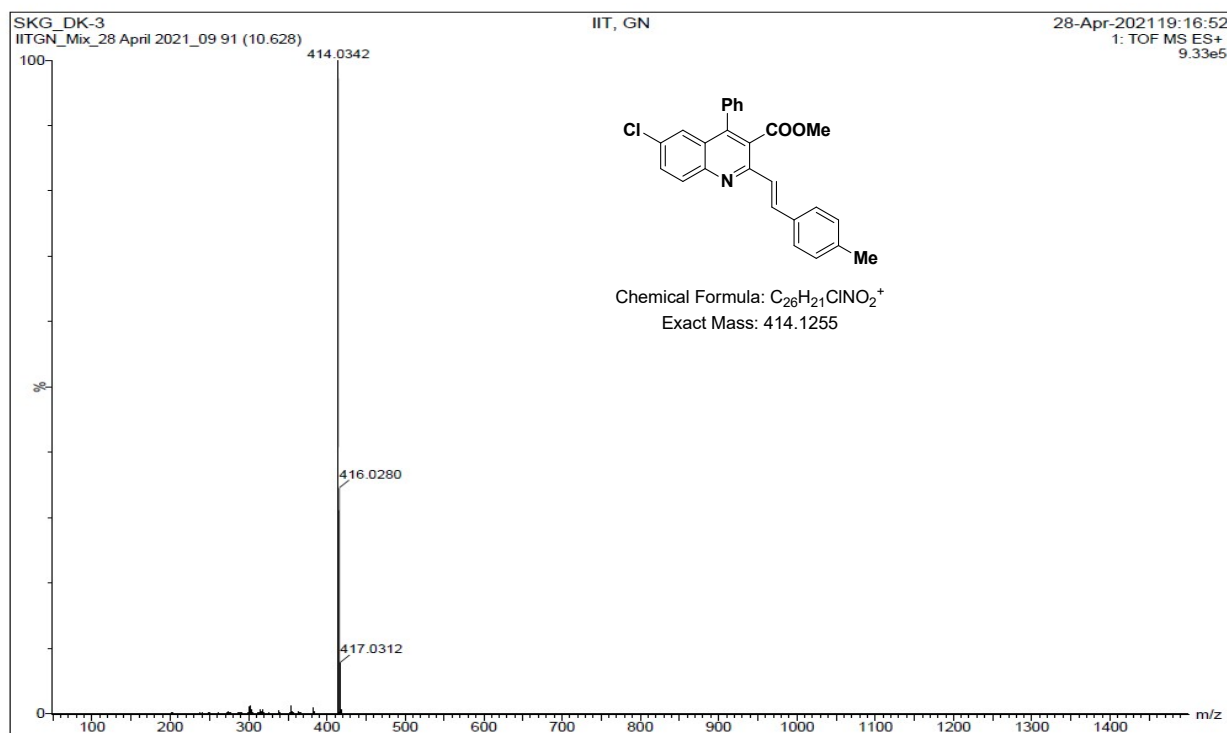
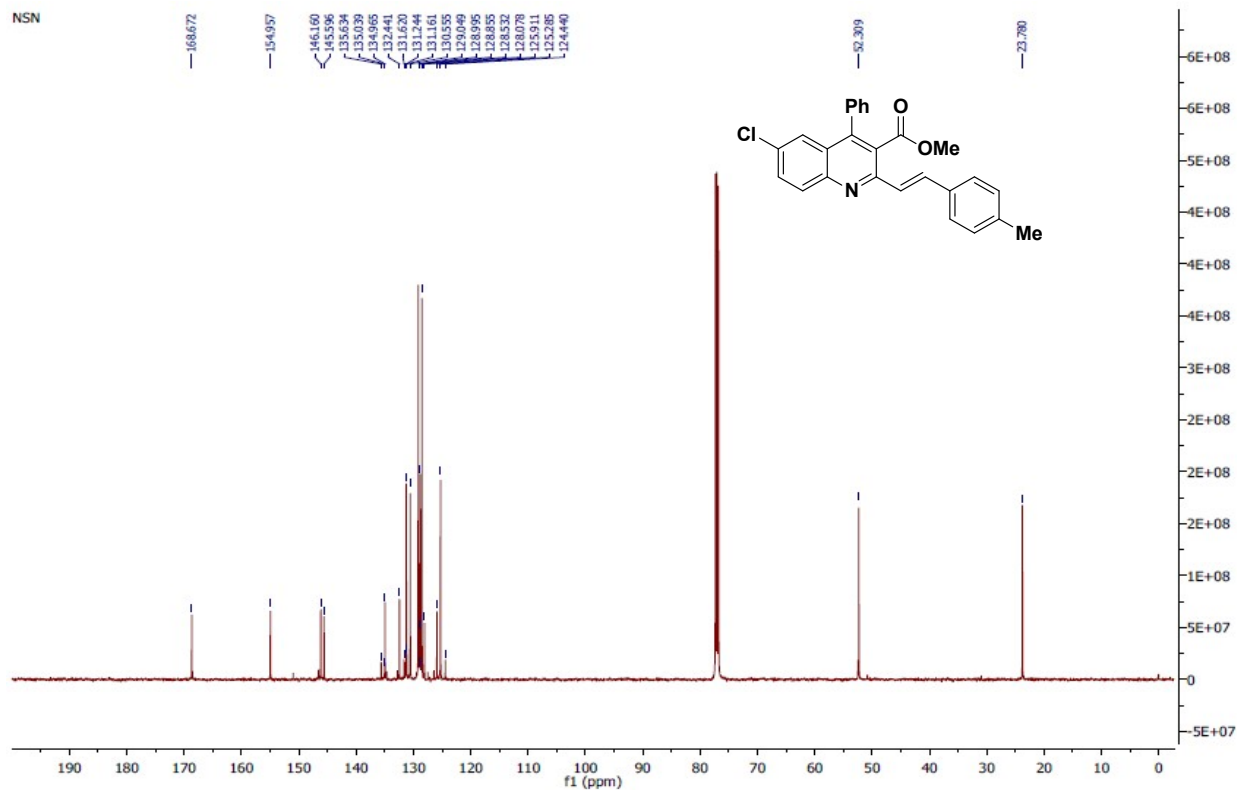




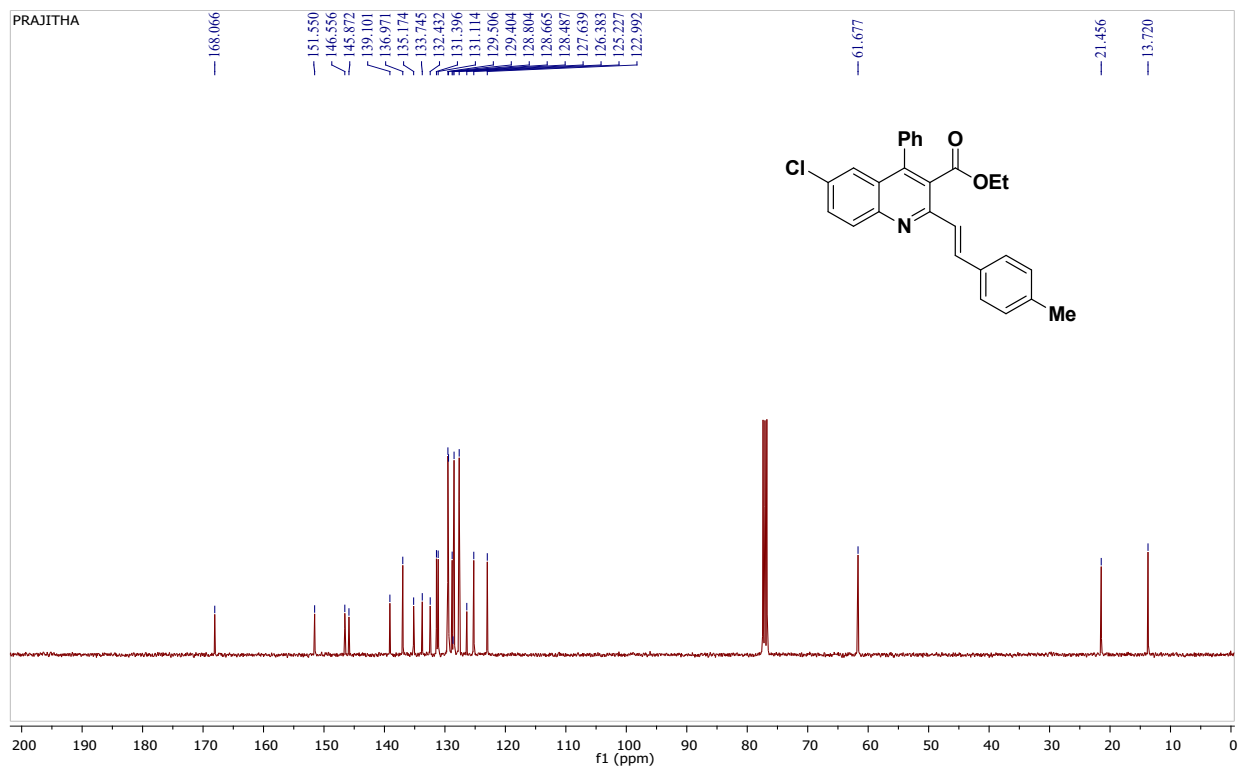
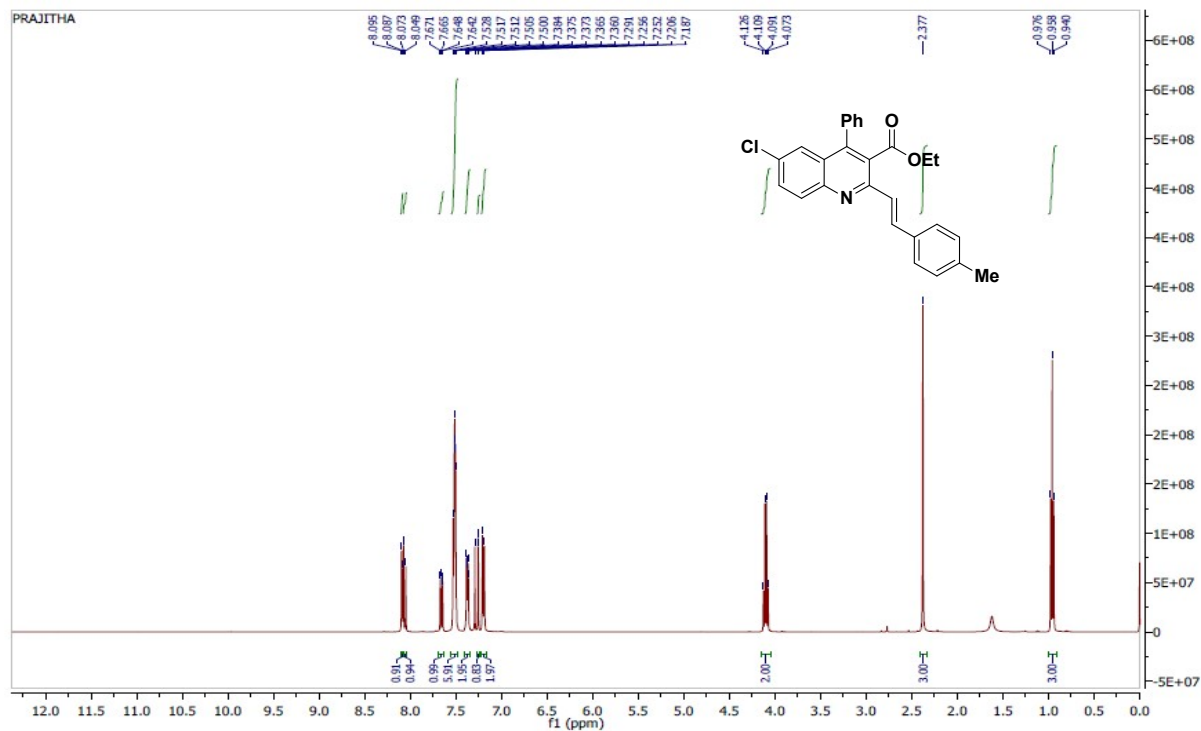


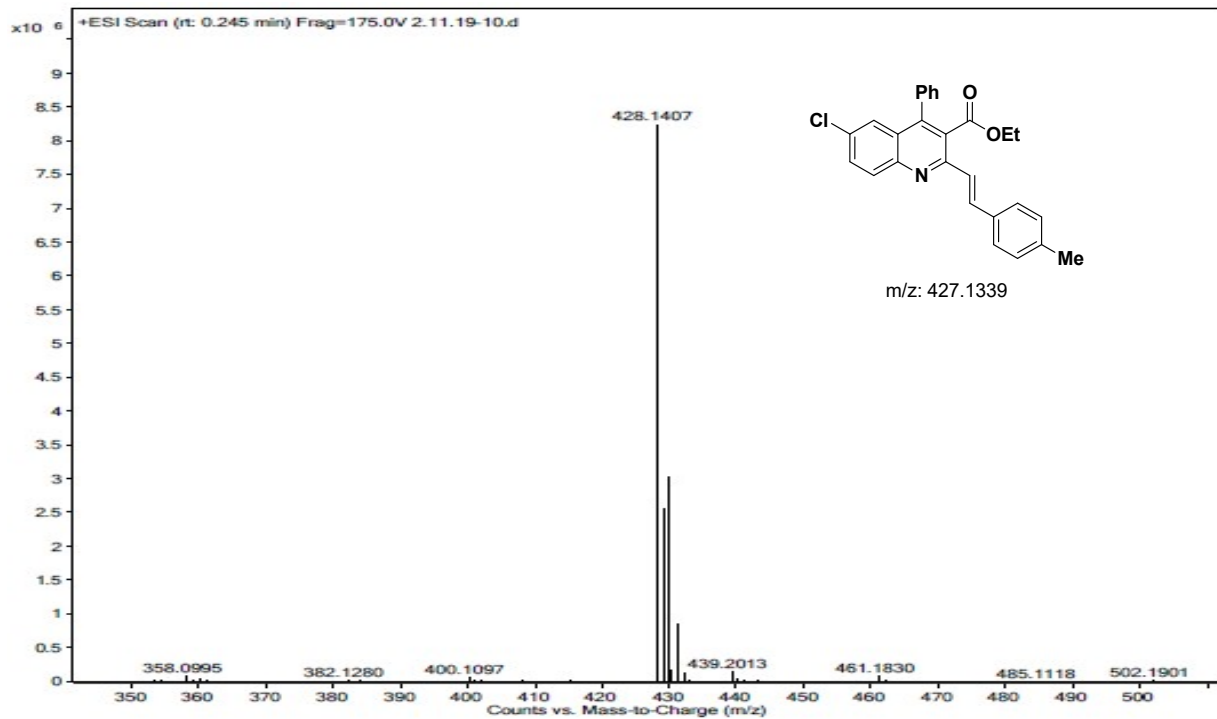
**Methyl -6-chloro-2-(4-methylstyryl)-4-phenylquinoline-3-carboxylate (5d):**



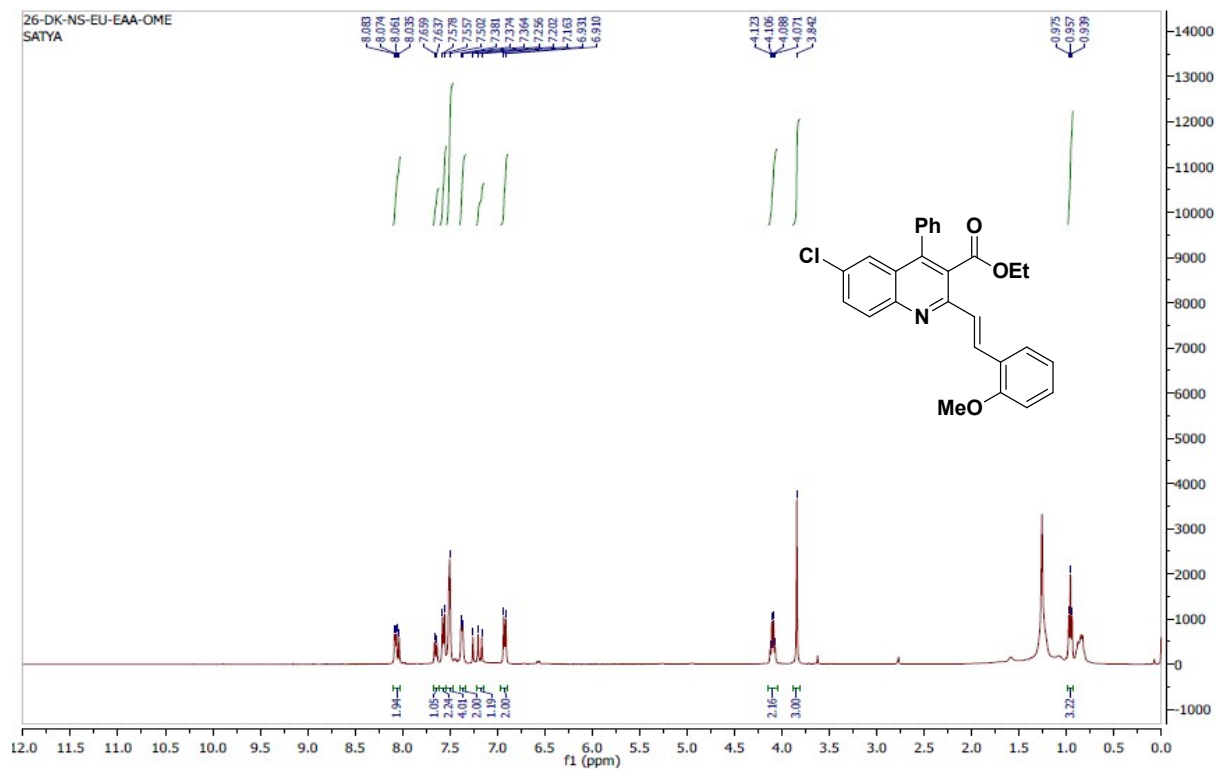


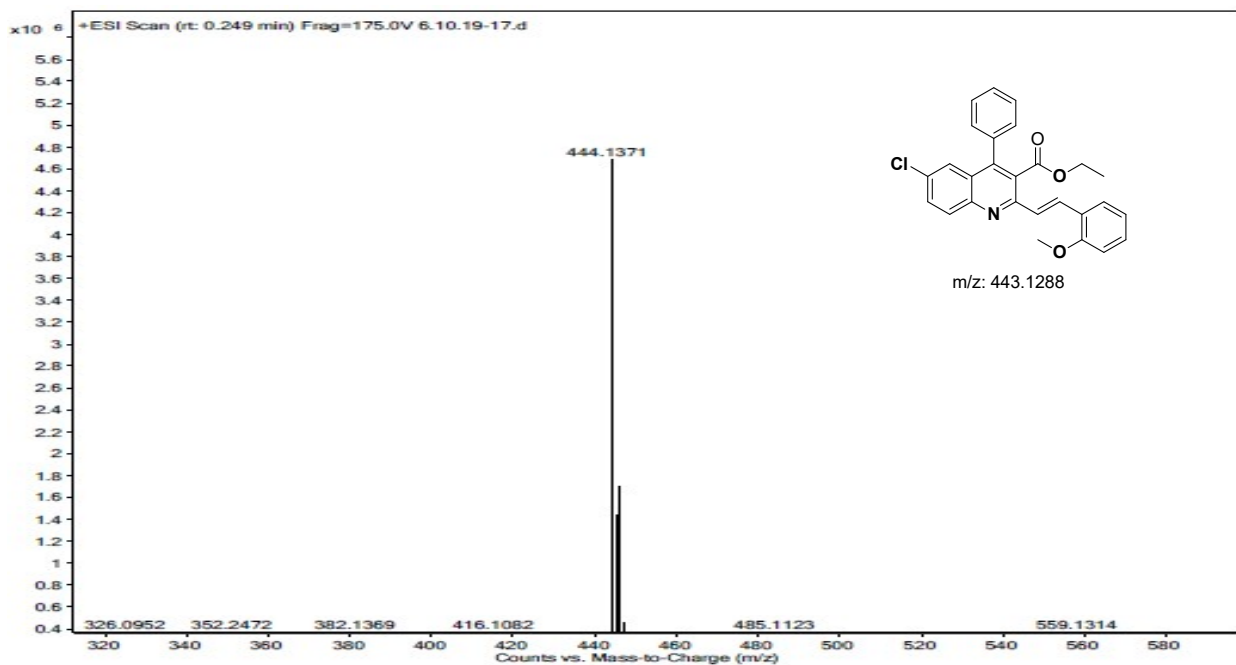
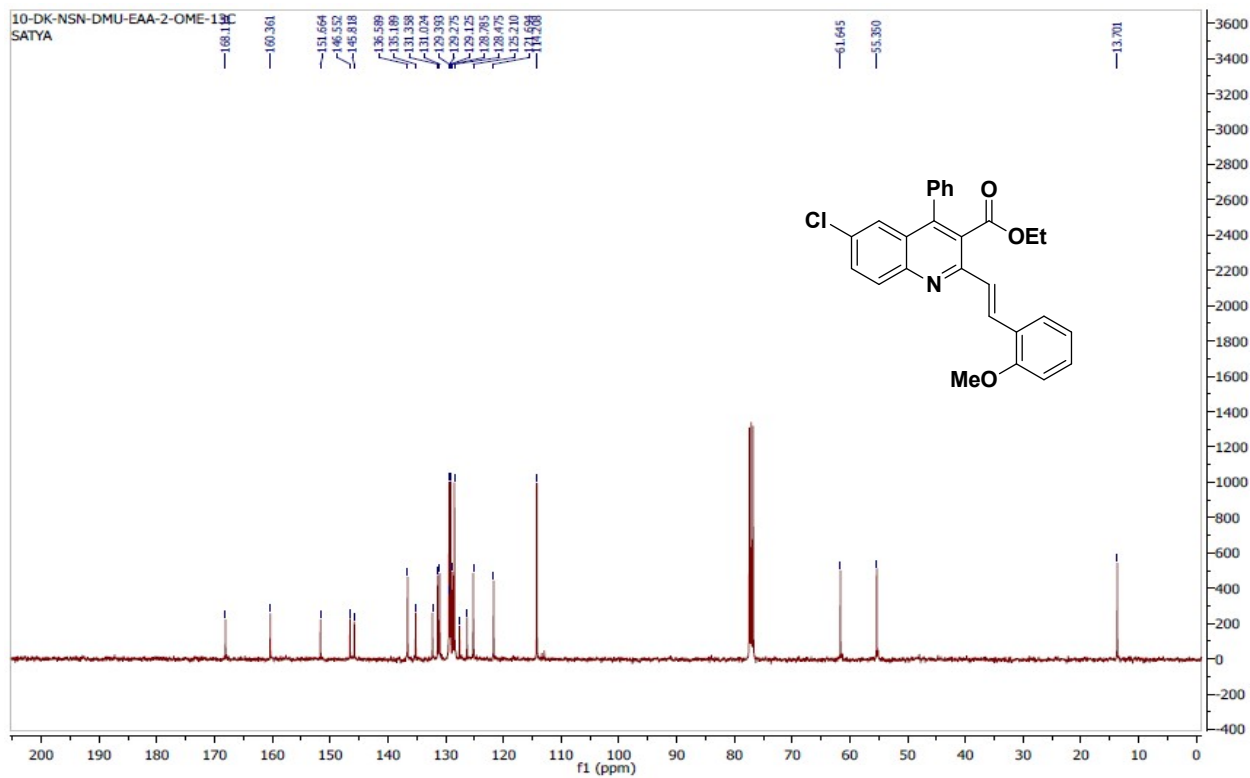
***Ethyl 6-chloro-2-(4-methylstyryl)-4-phenylquinoline-3-carboxylate (5h):***



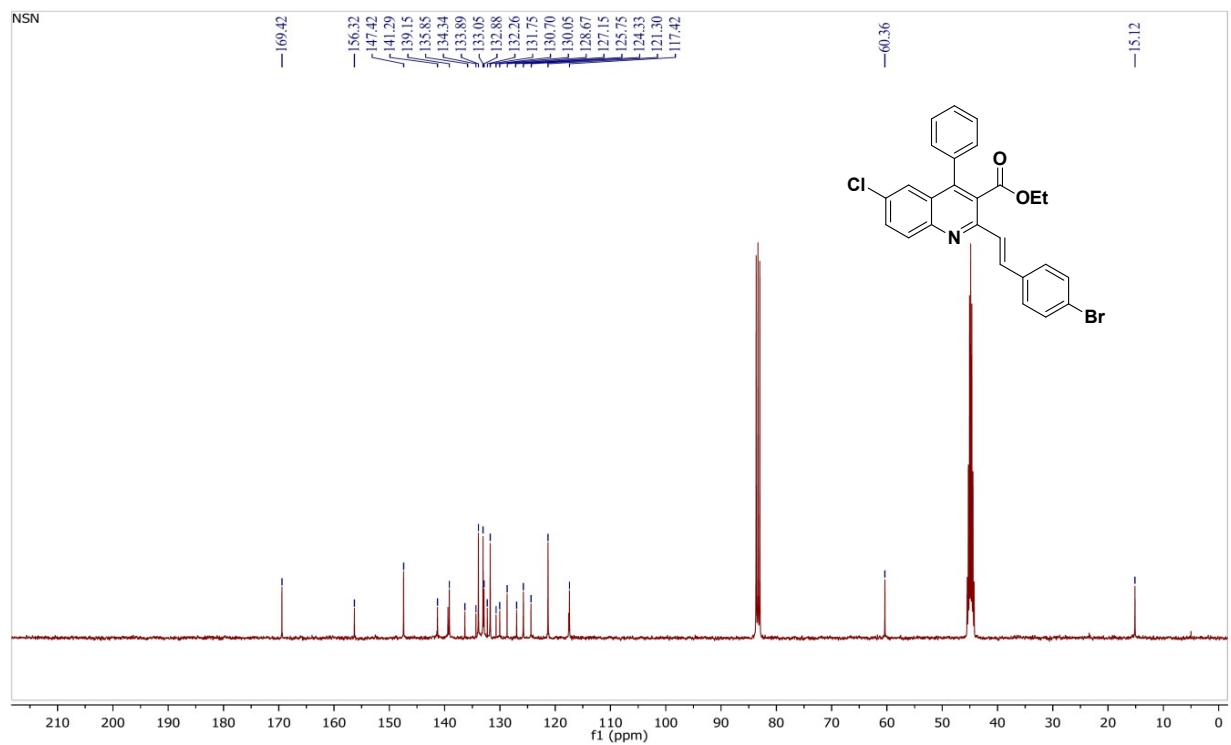
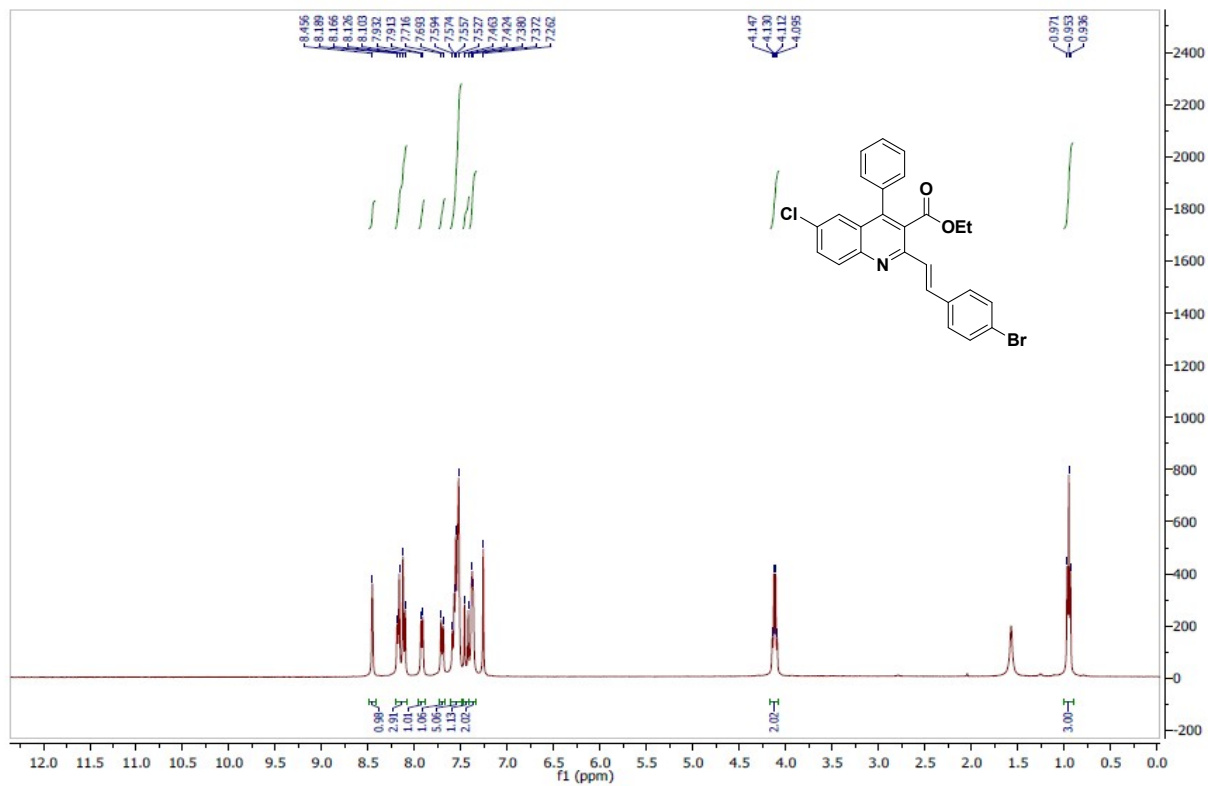


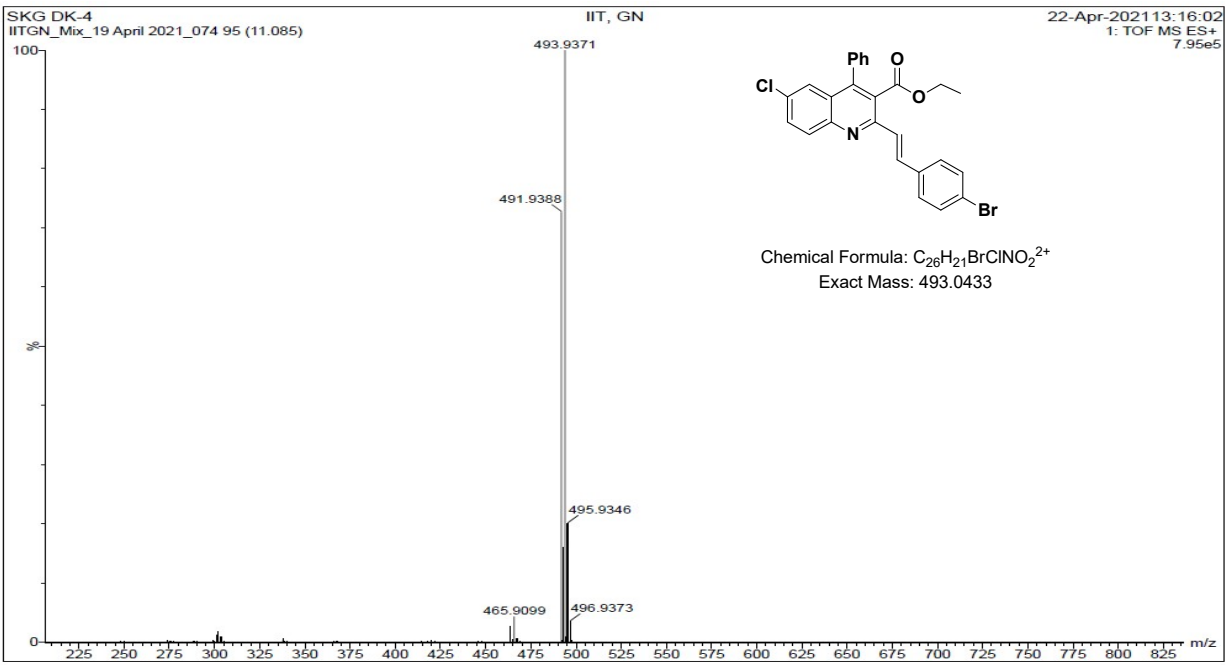
***Ethyl-6-chloro-2-(2-methoxystyryl)-4-phenylquinoline-3-carboxylate (5i):***





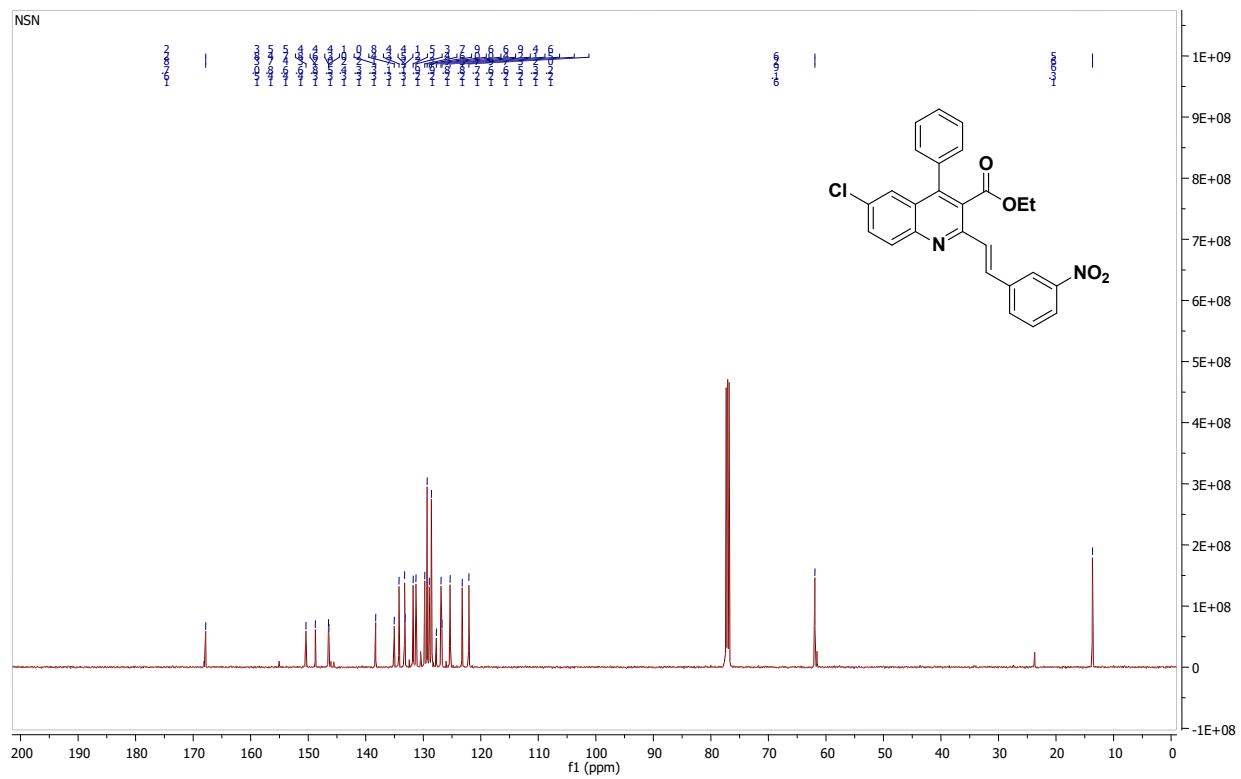
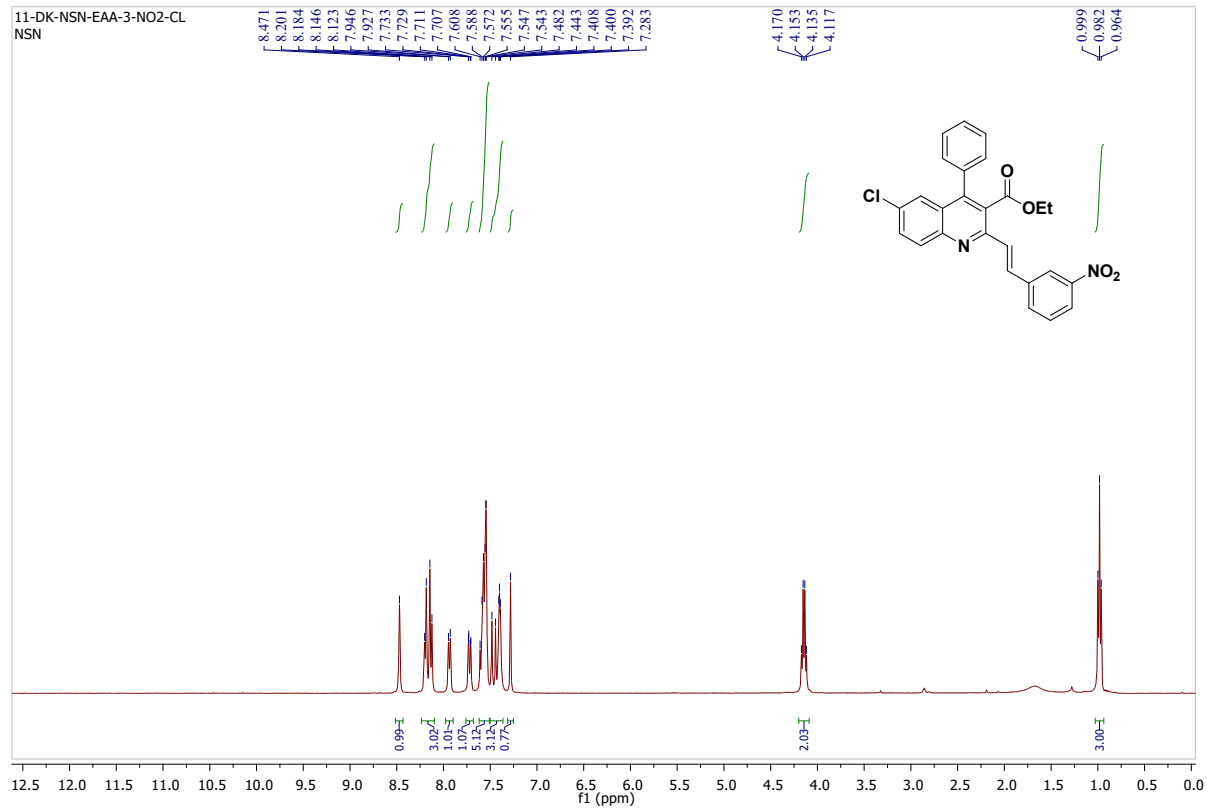
*Ethyl-2-(4-bromostyryl)-6-chloro-4-phenylquinoline-3-carboxylate (51):*

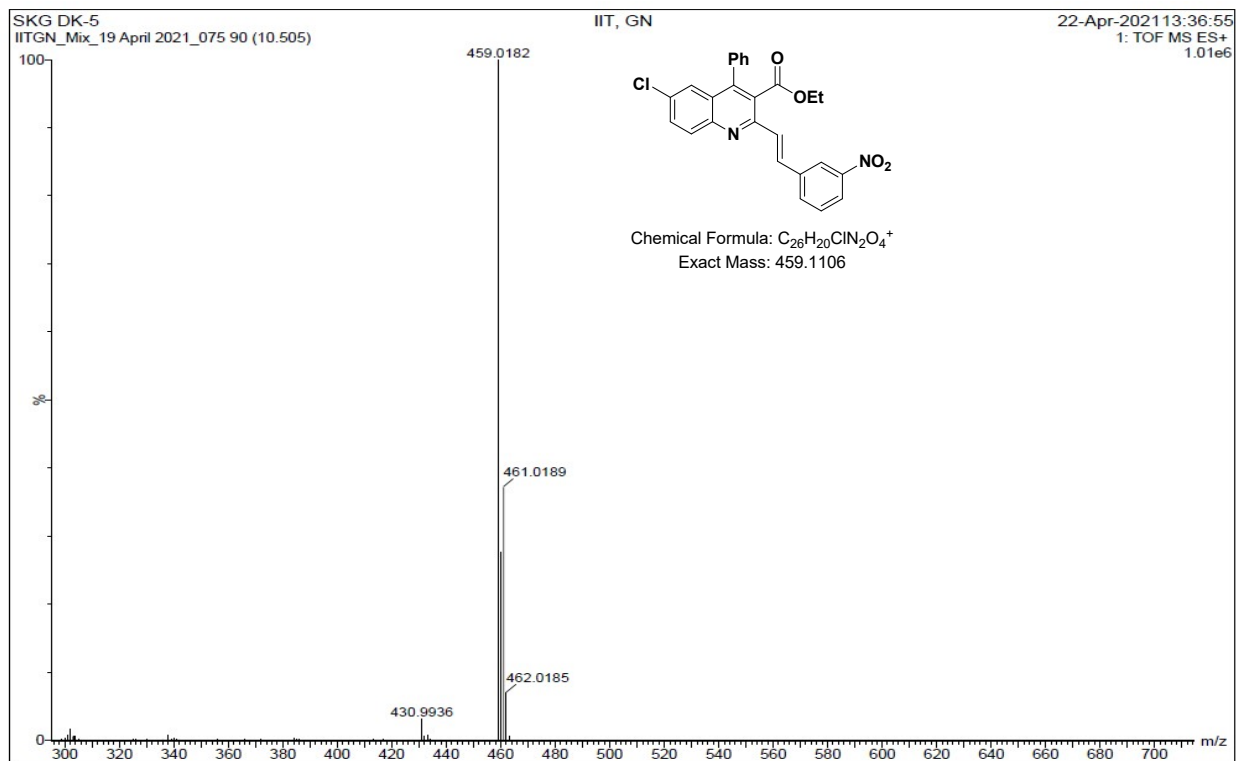




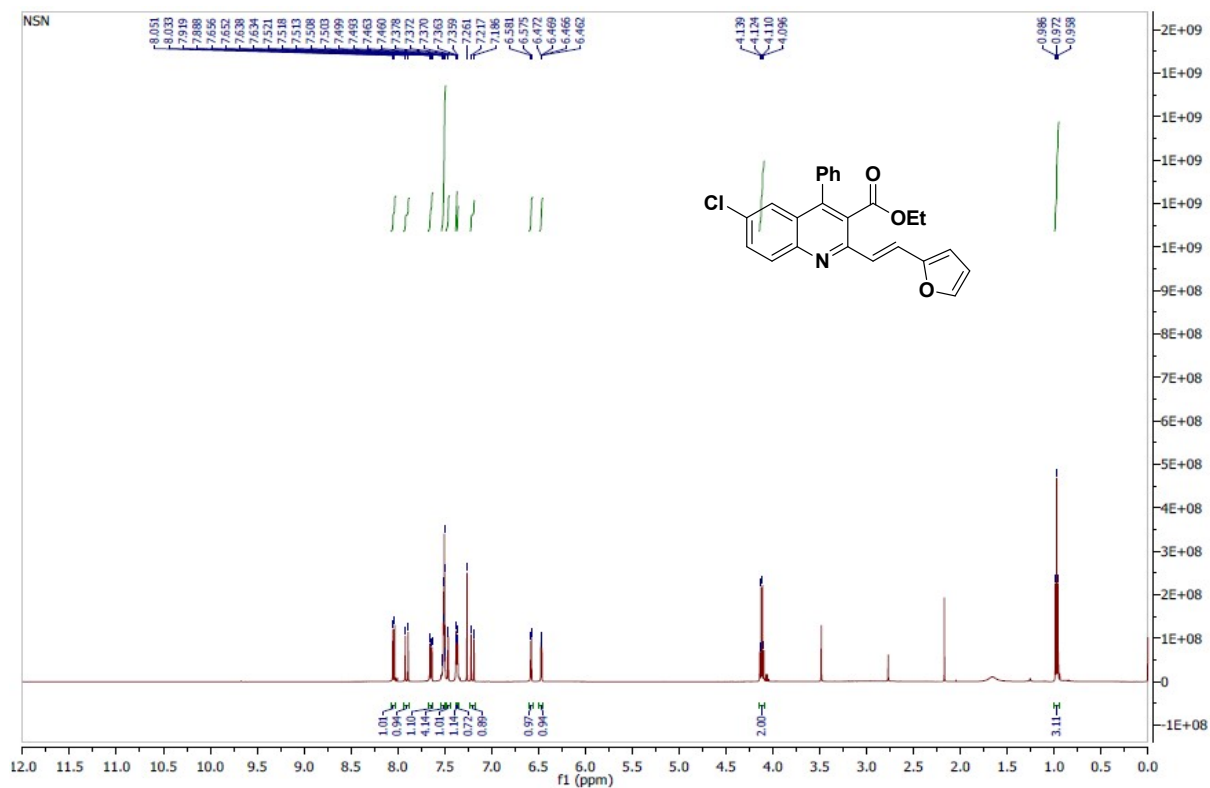
***Ethyl 6-chloro-2-(3-nitrostyryl)-4-phenylquinoline-3-carboxylate (5m):***

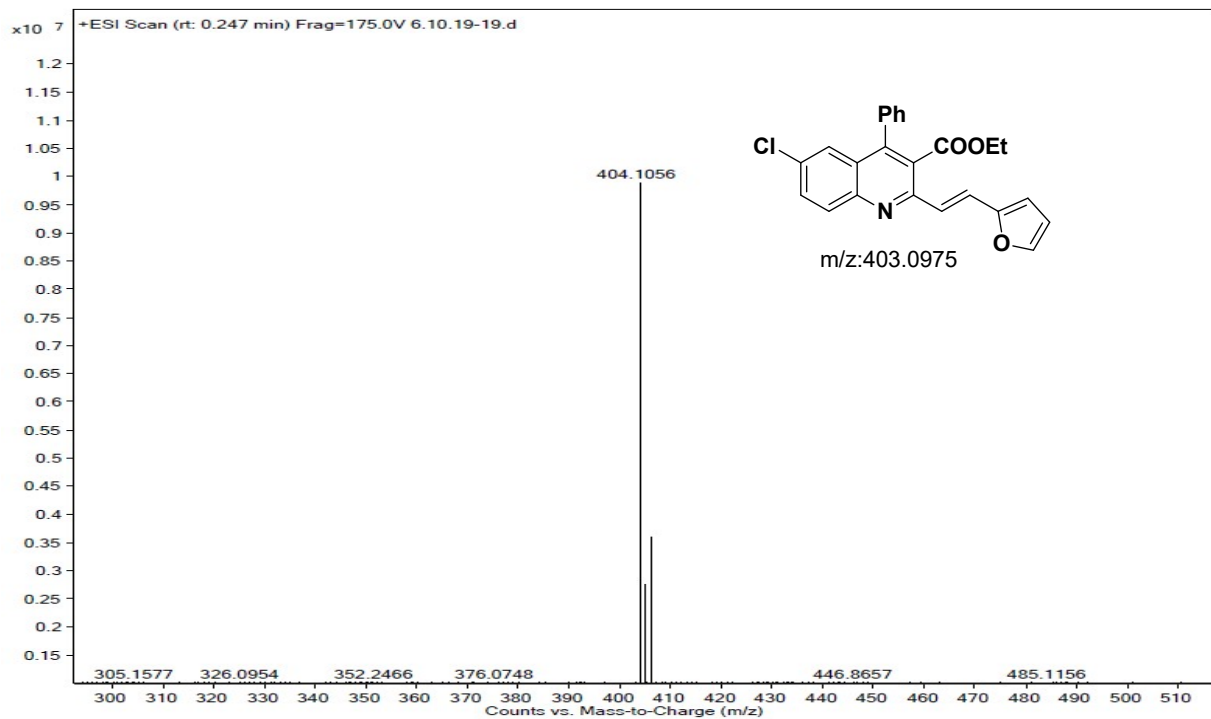
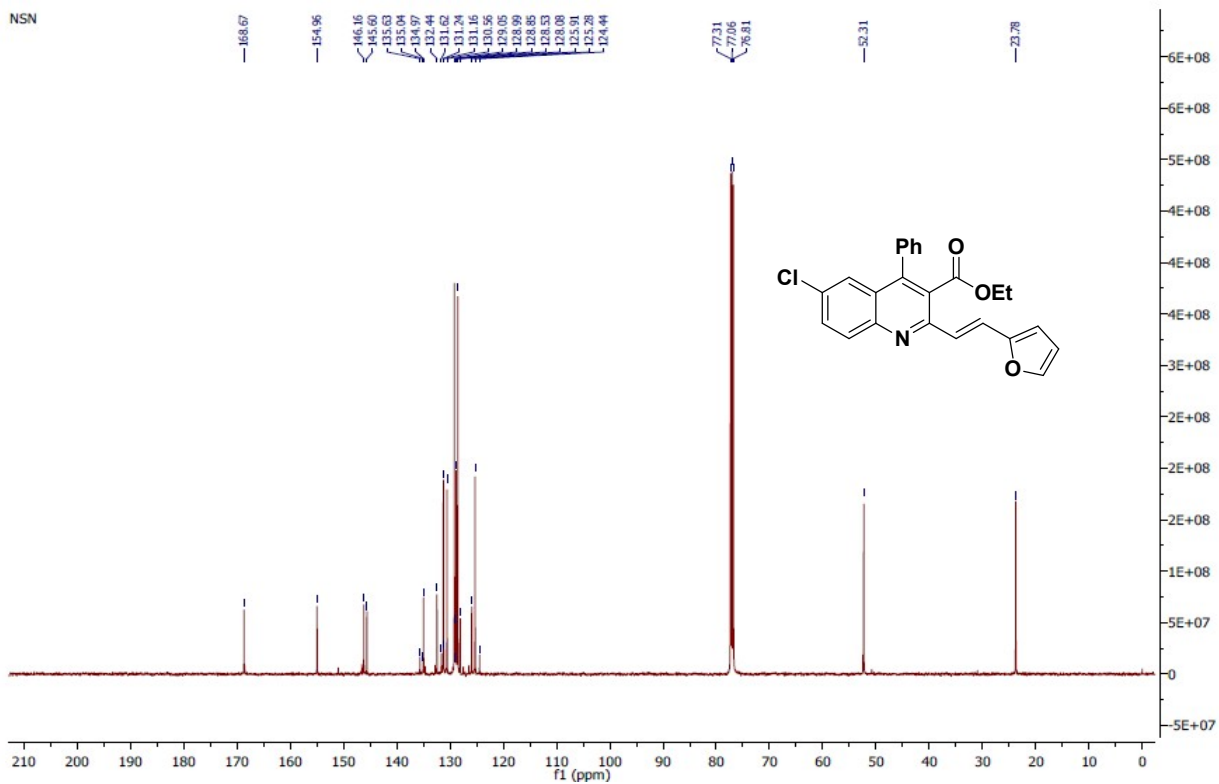




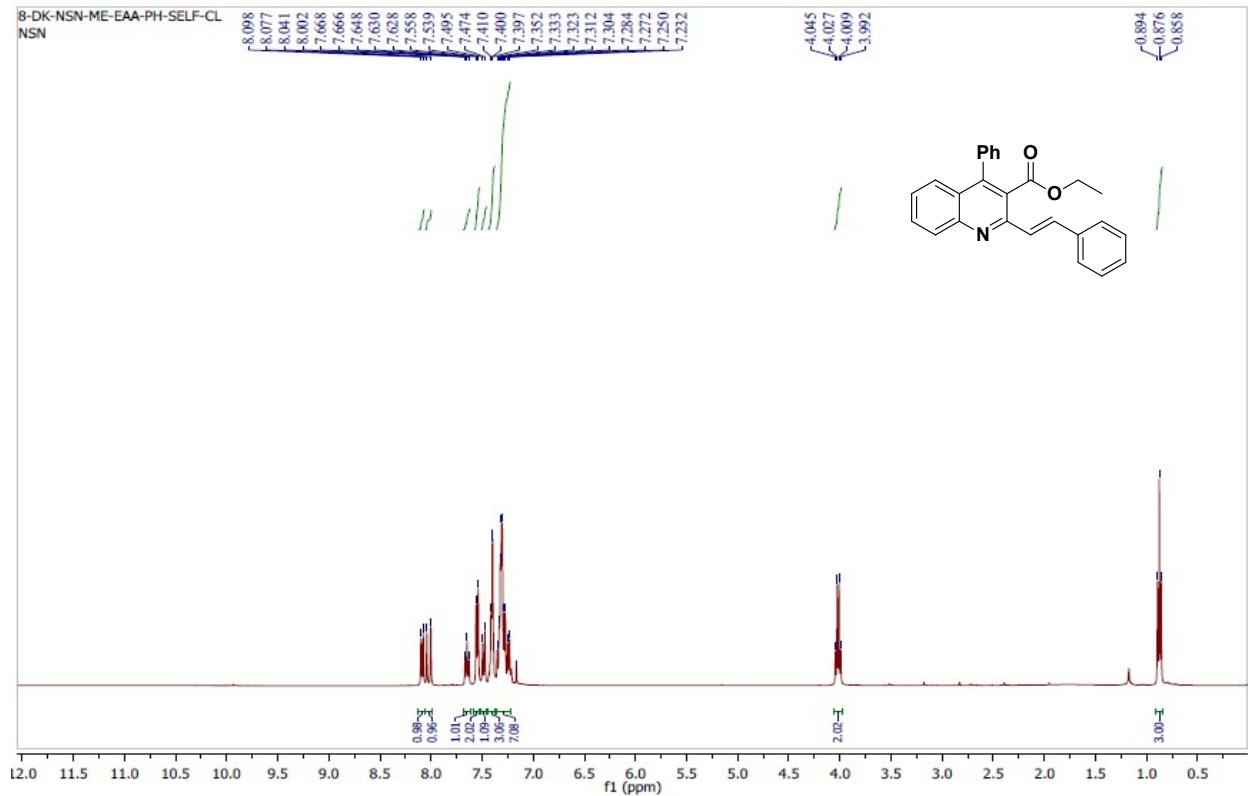


***Ethyl 6-chloro-2-(2-(furan-2-yl)vinyl)-4-phenylquinoline-3 carboxylate (5p):***

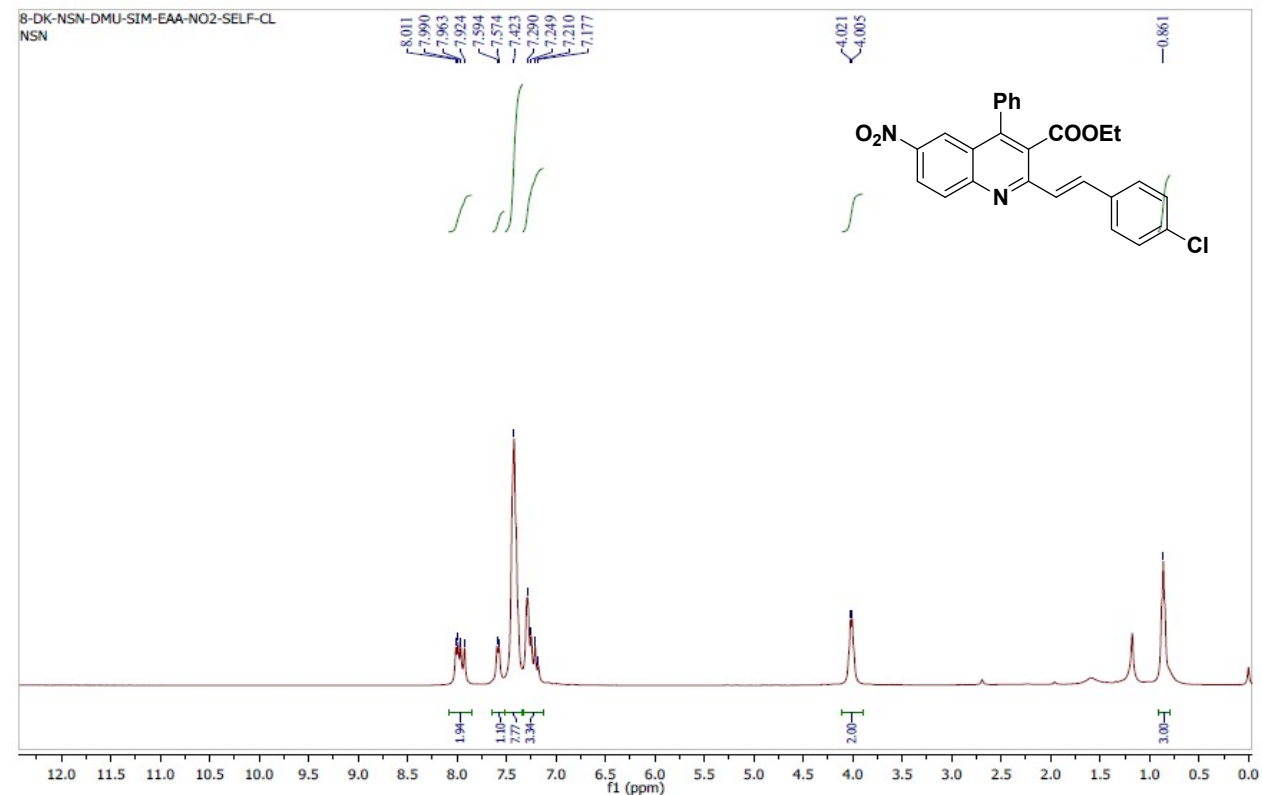


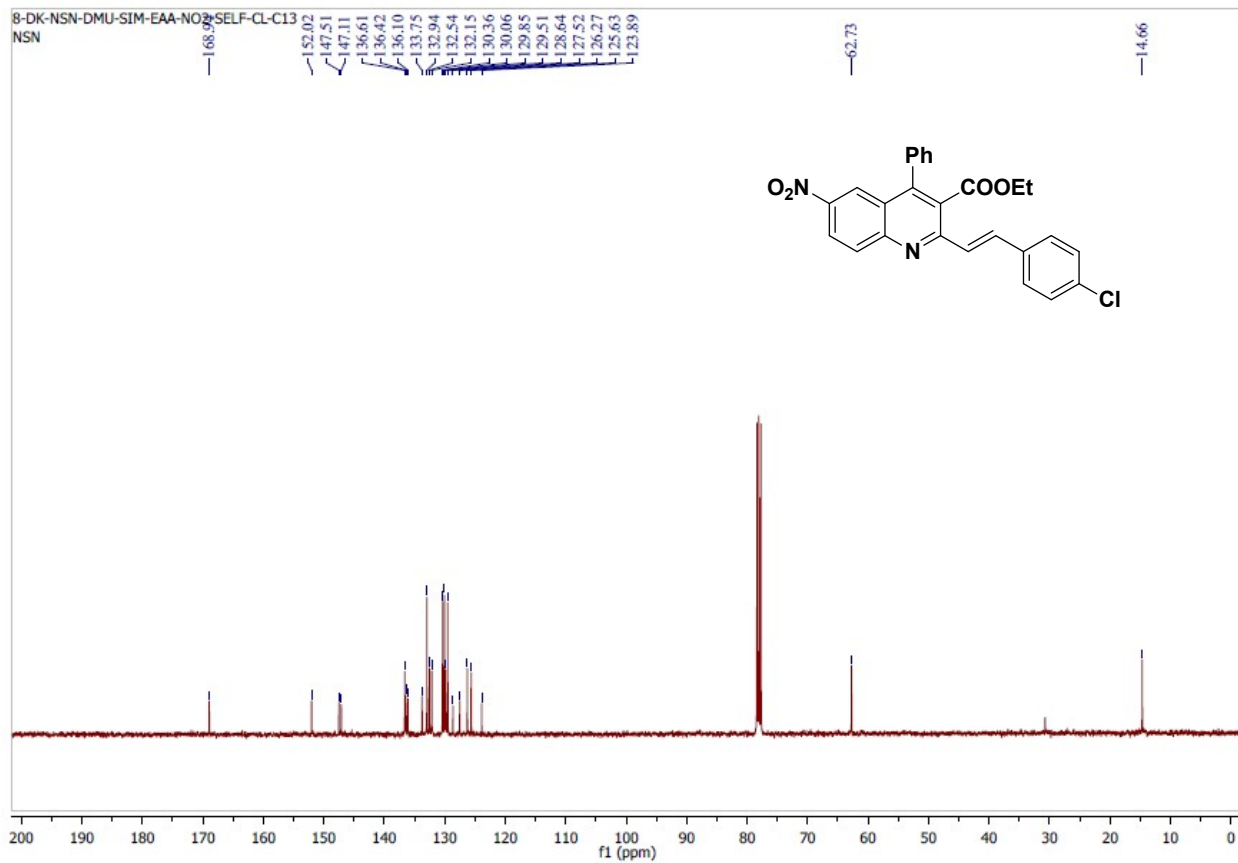


**(E)-Ethyl 4-phenyl-2-styrylquinoline-3-carboxylate (5q):**



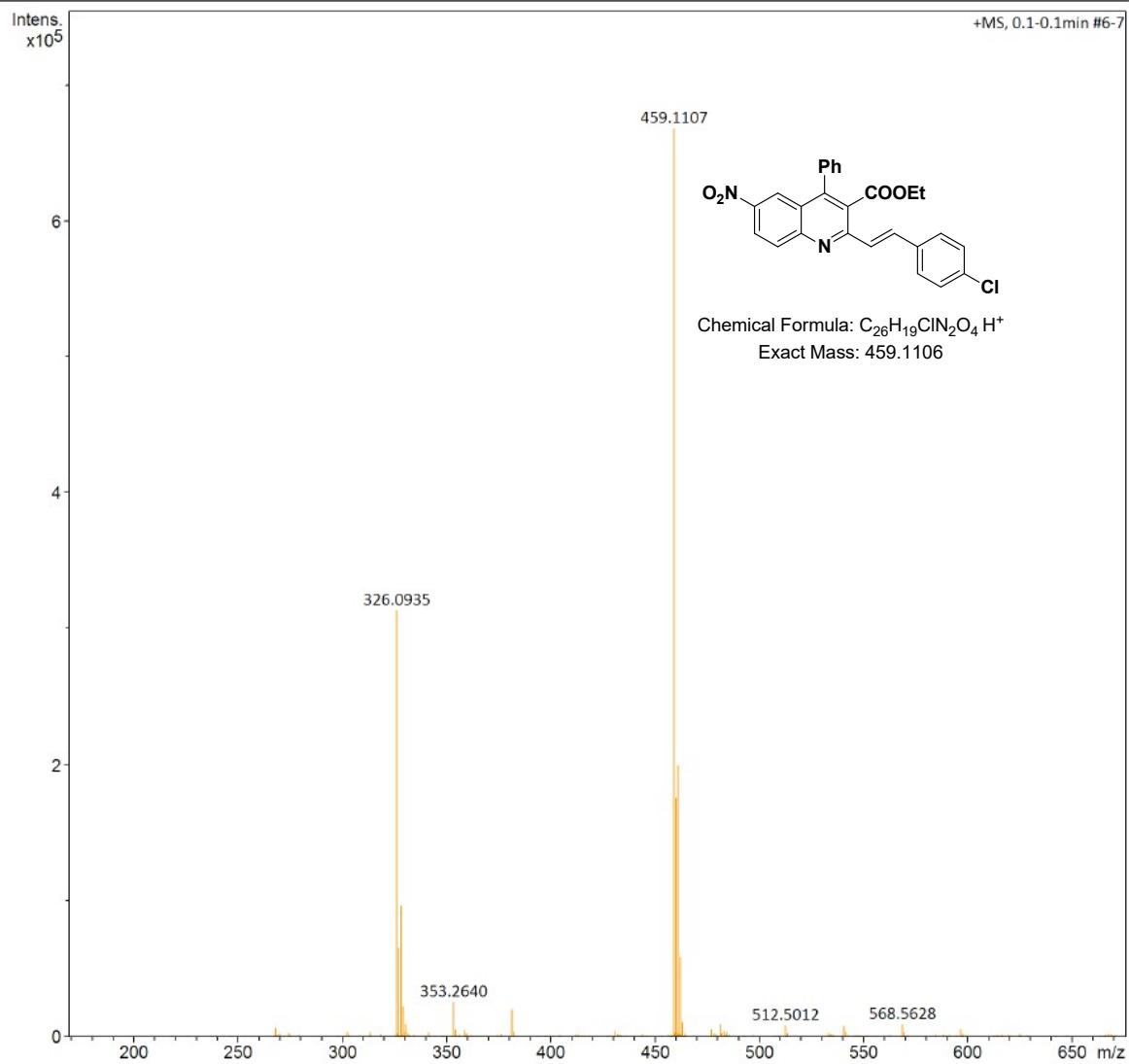
**(E)-Ethyl 2-(4-chlorostyryl)-6-nitro-4-phenylquinoline-3-carboxylate (5r):**





### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



5R.d

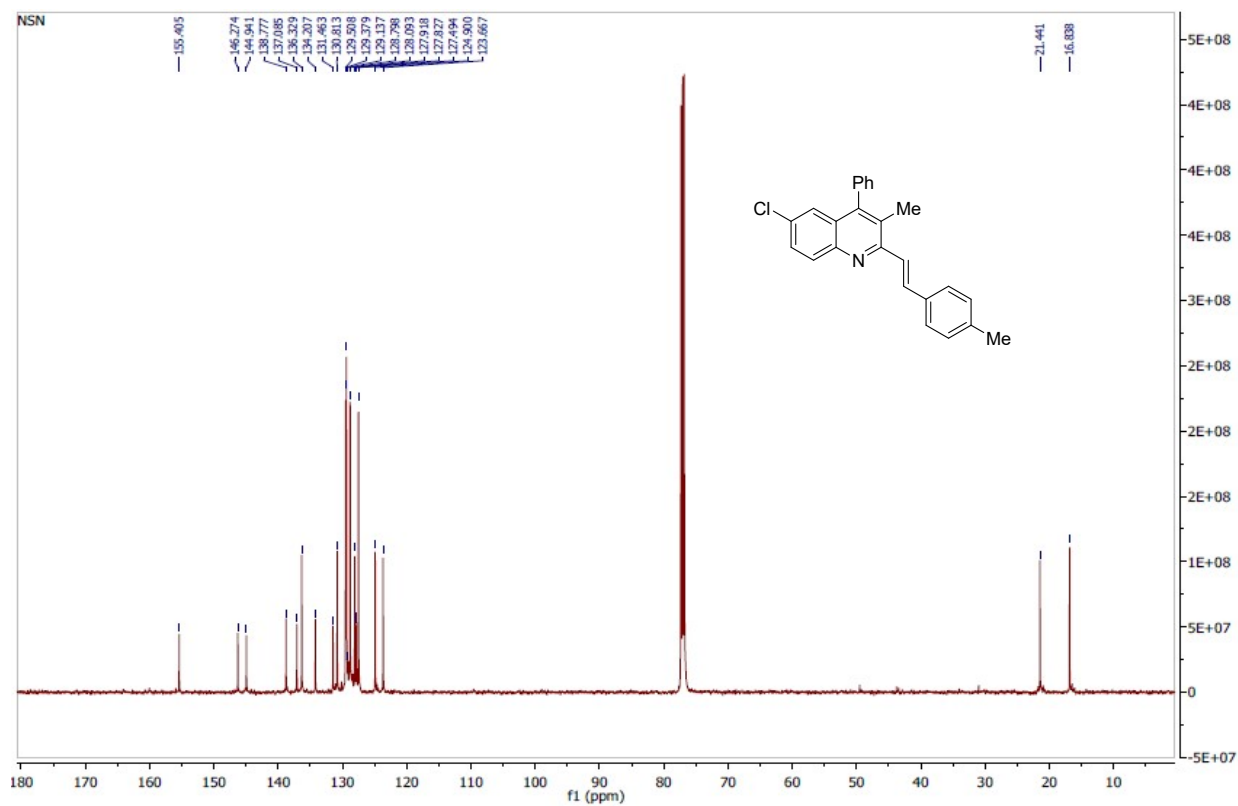
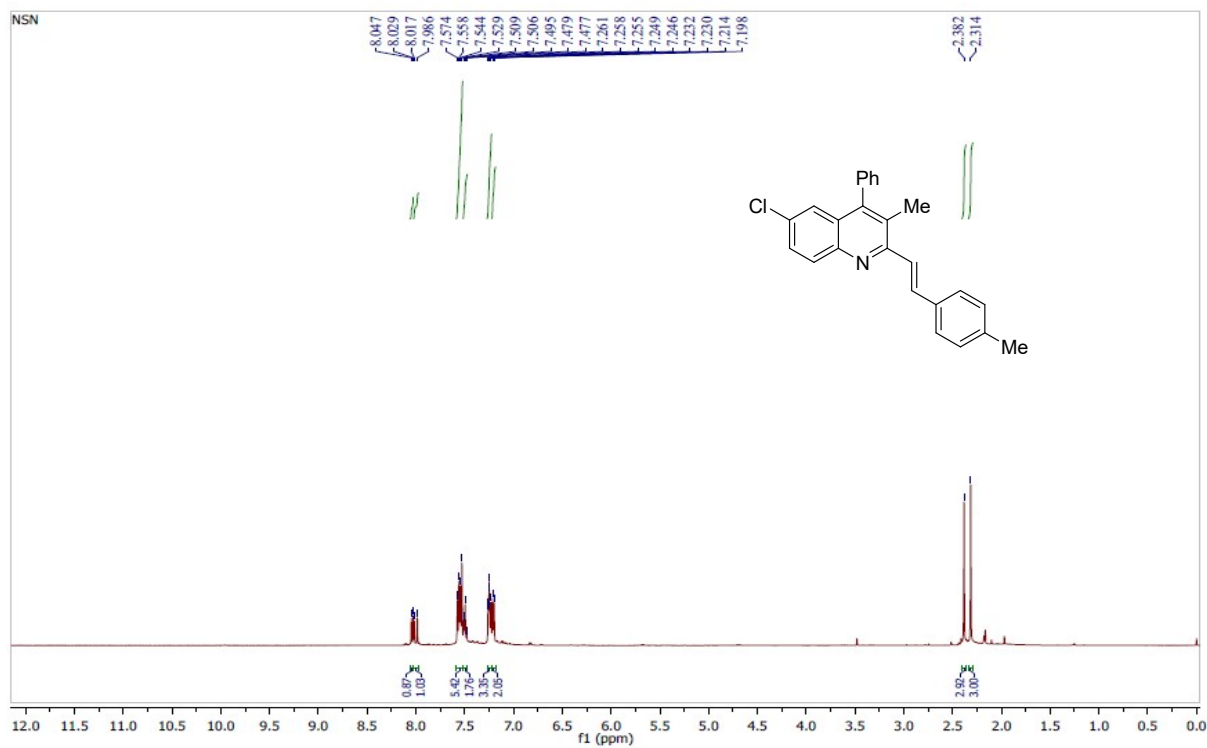
Bruker Compass DataAnalysis 4.2

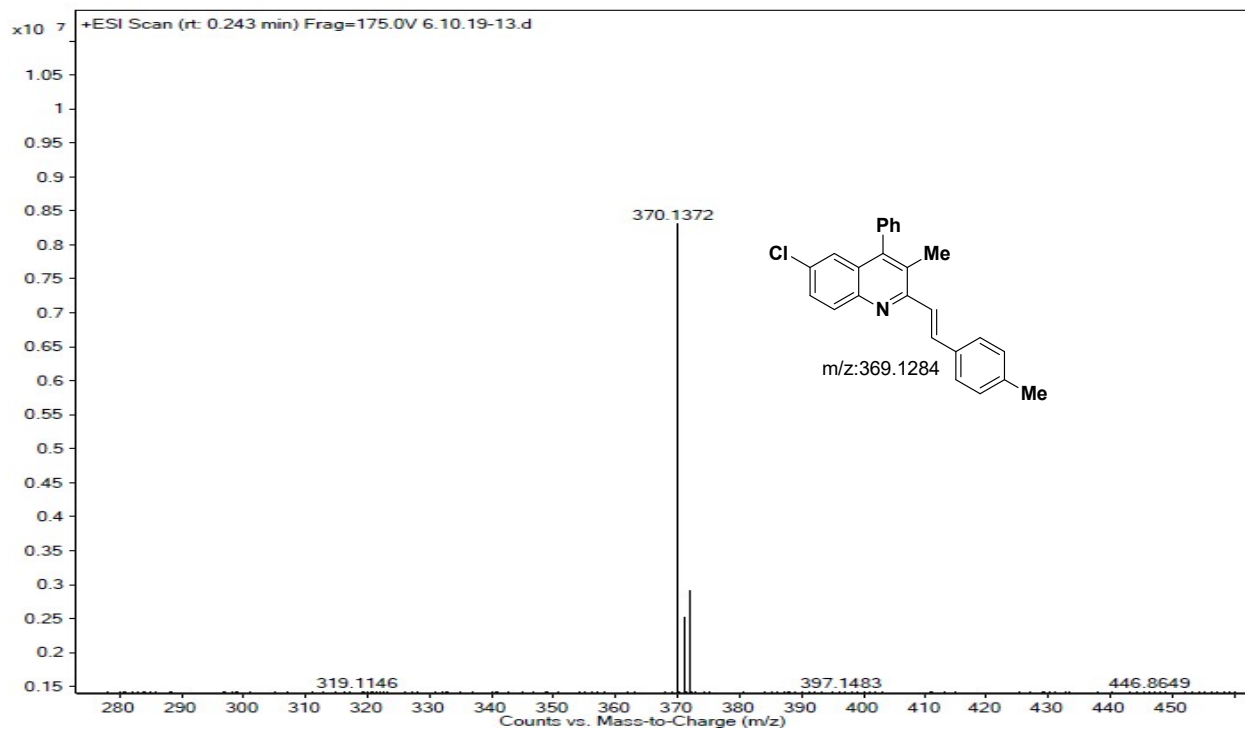
printed: 10/1/2021 3:40:55 PM

by: BDAL

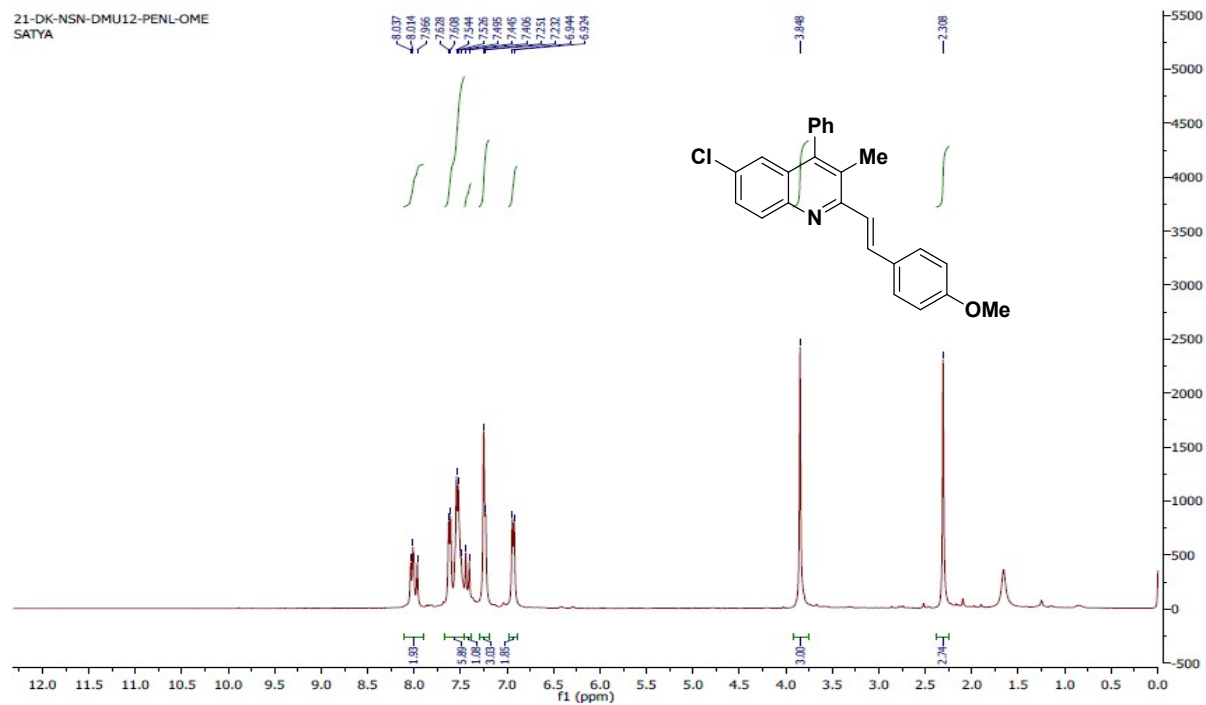
Page 1 of 1

**6-Chloro-3-methyl-2-(4-methylstyryl)-4-phenylquinoline (6a):**

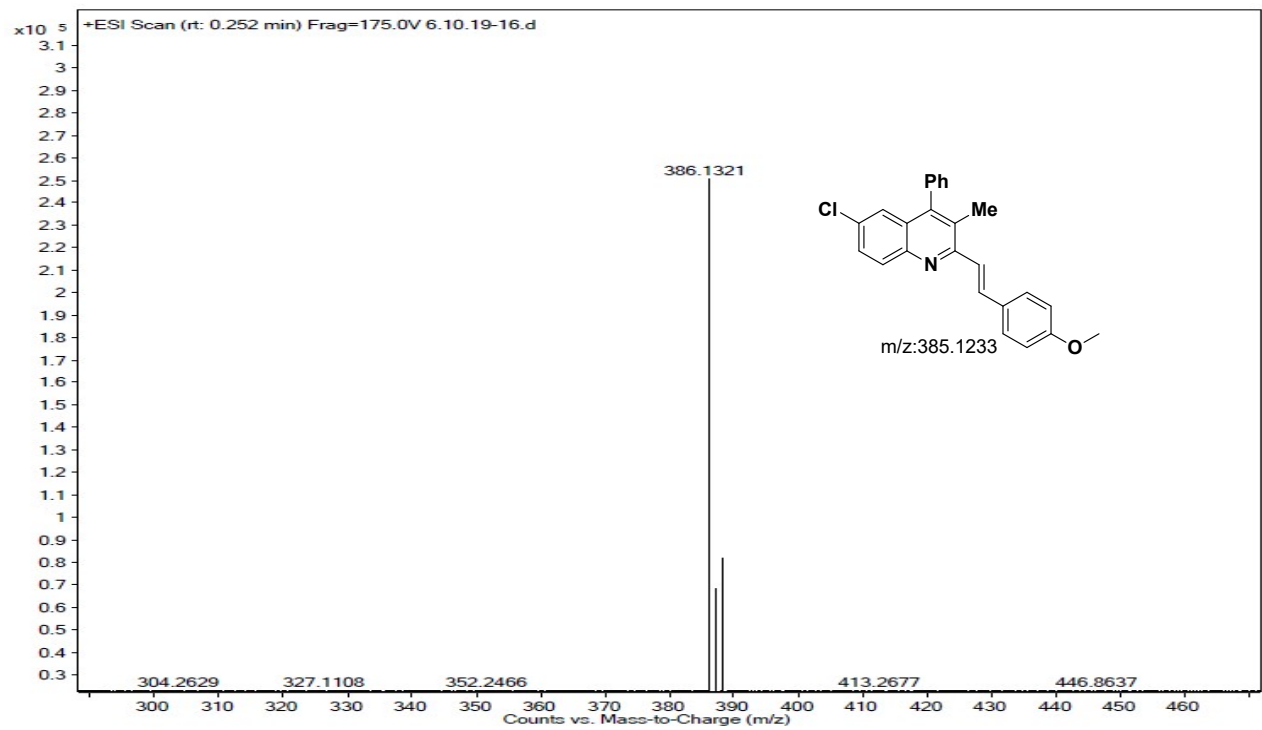
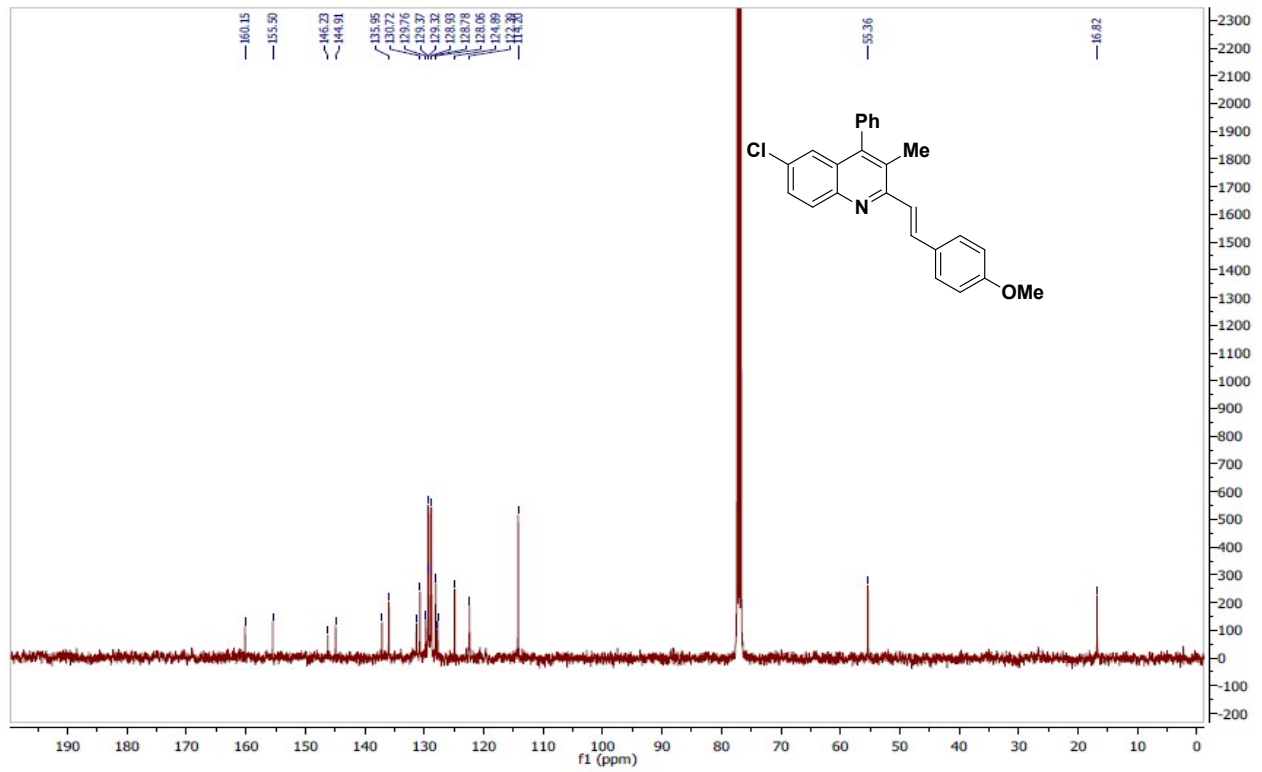




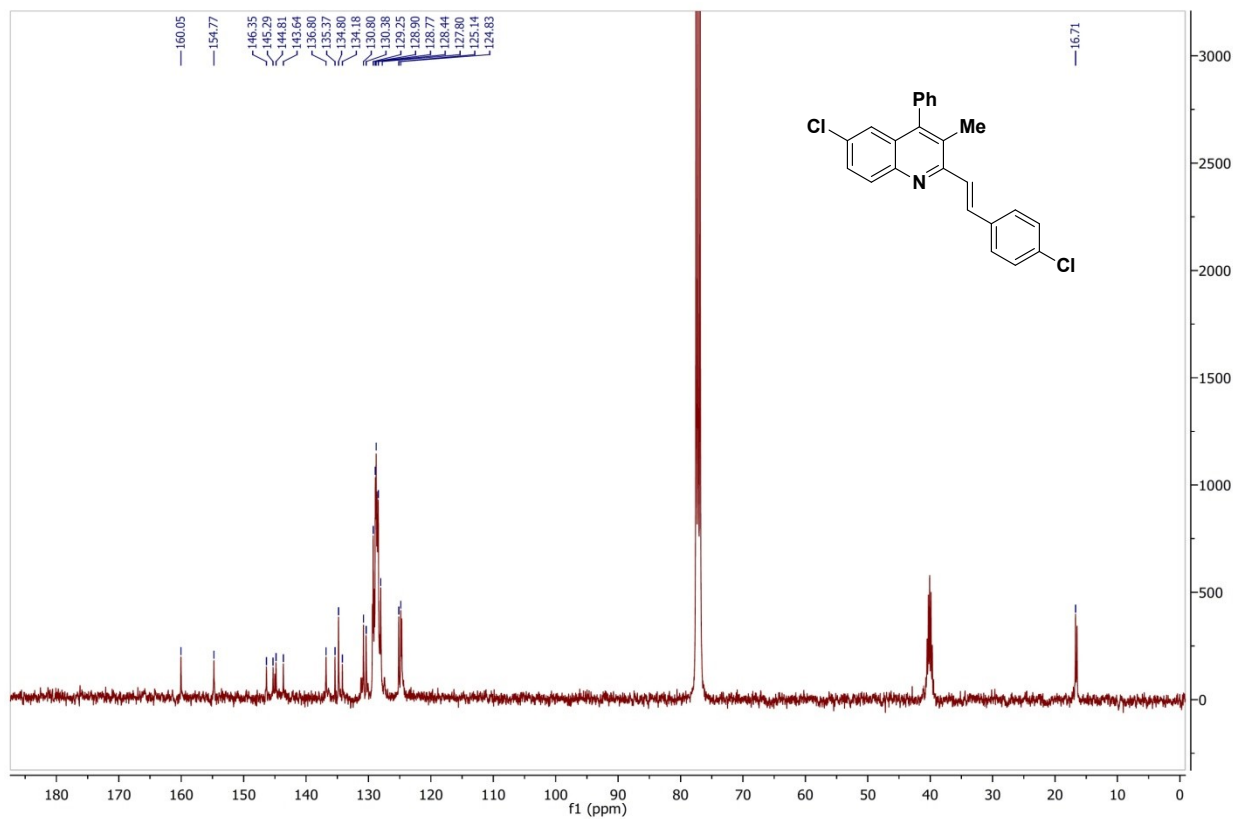
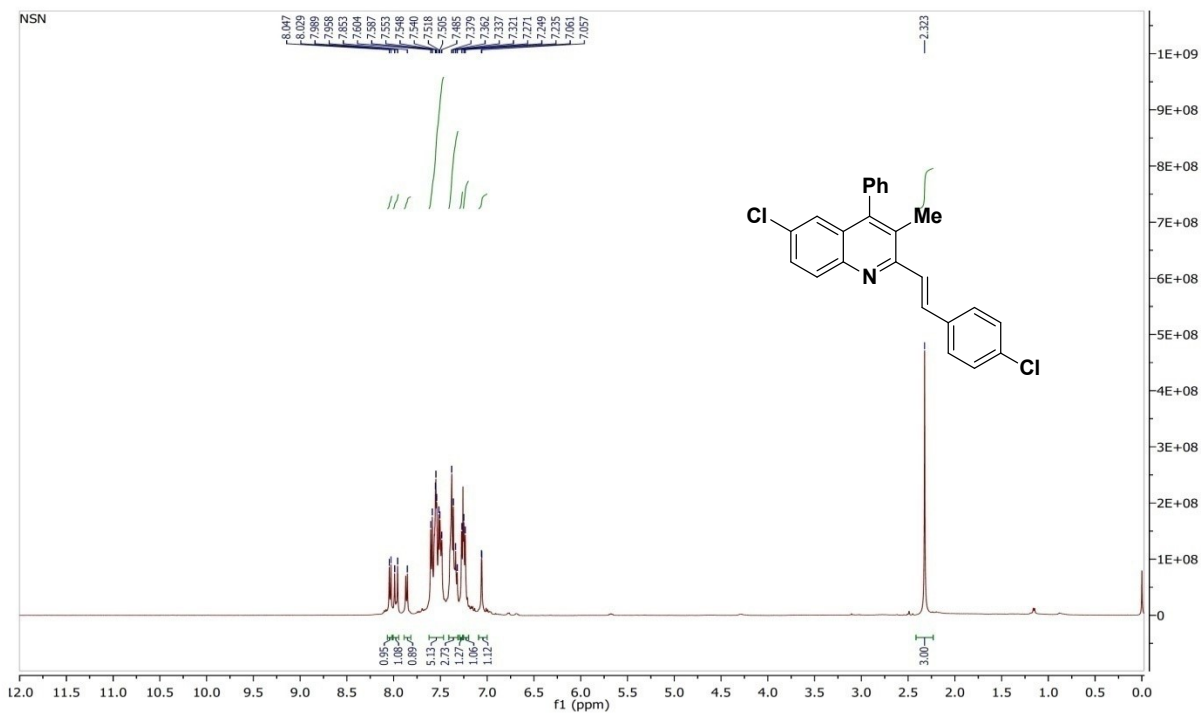
**6-Chloro-2-(4-methoxystyryl)-3-methyl-4-phenylquinoline (6b):**

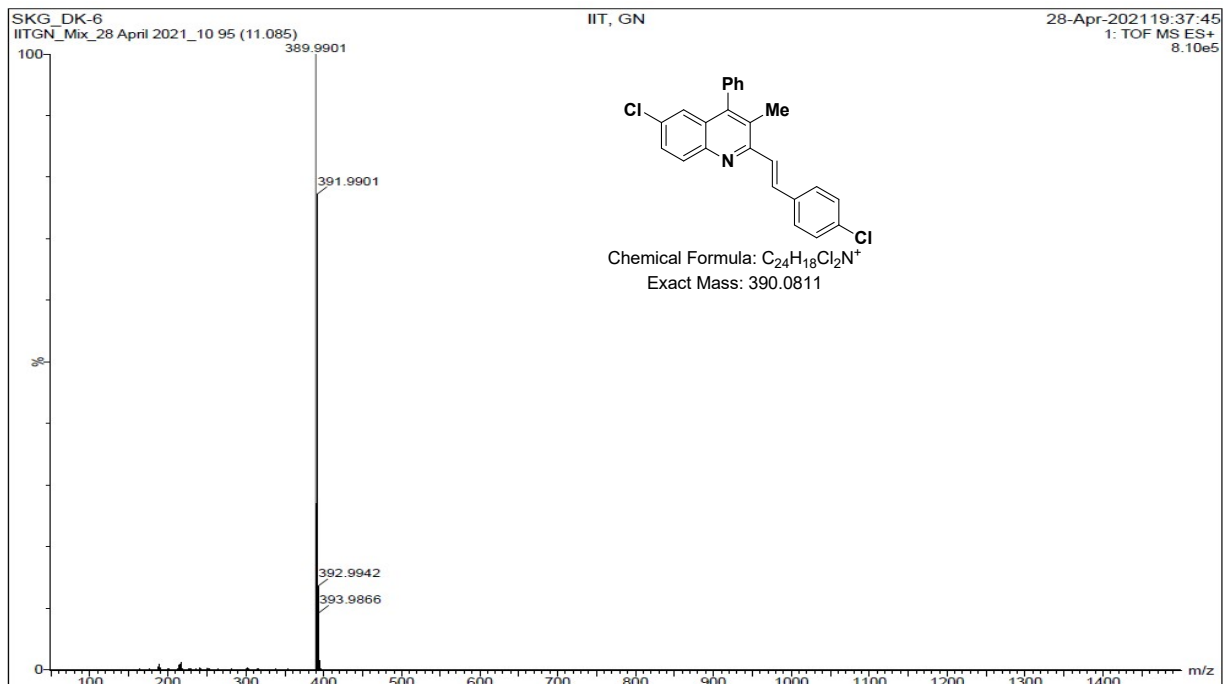




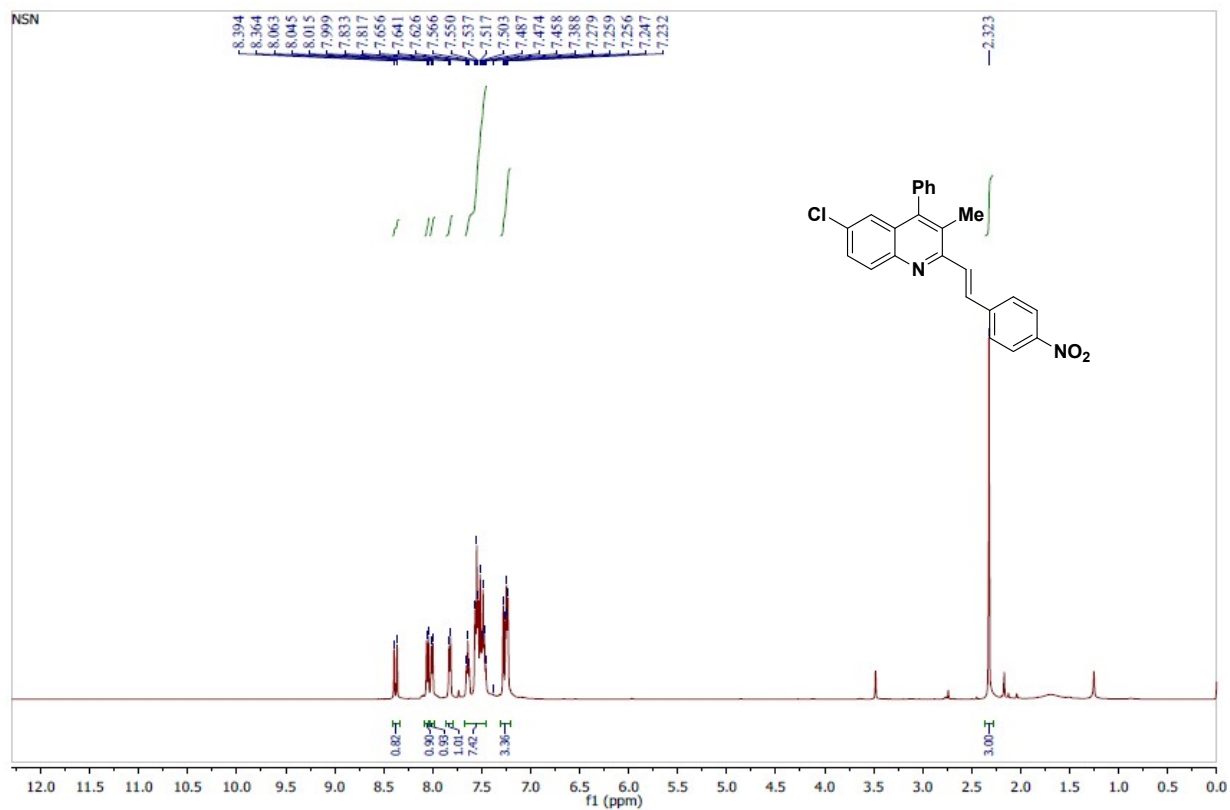


**6-Chloro-2-(4-chlorostyryl)-3-methyl-4-phenylquinoline (6c):**

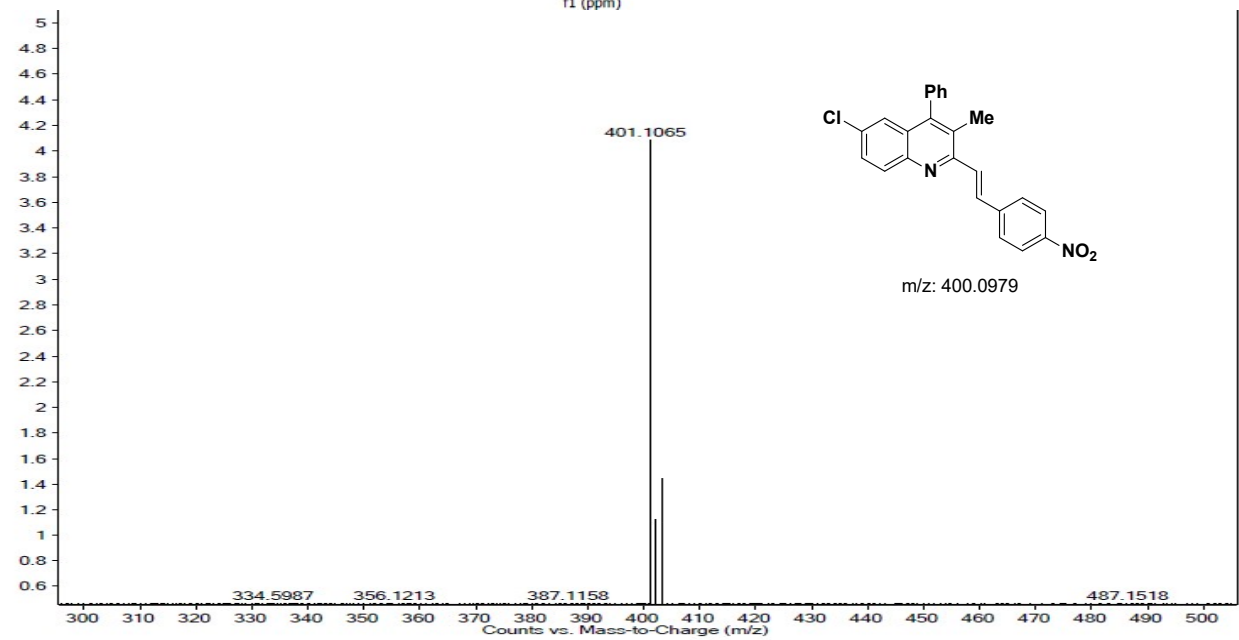
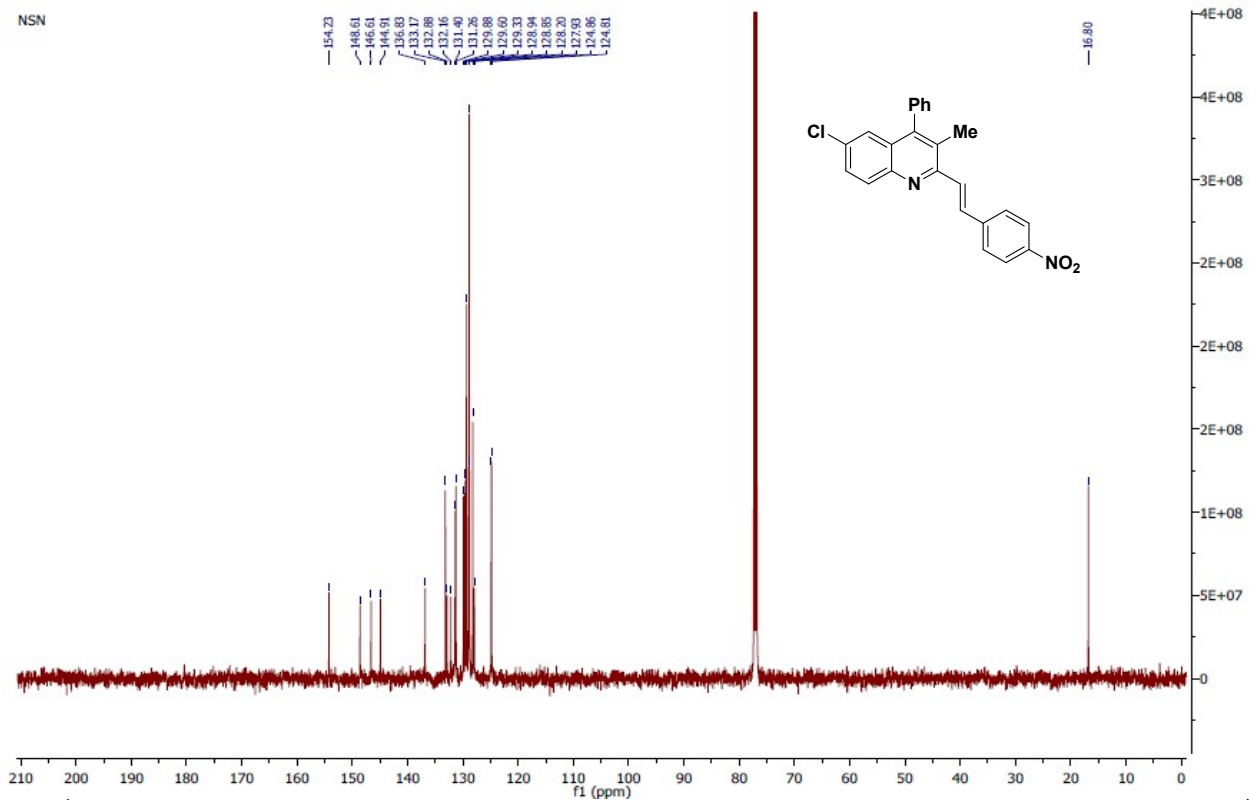




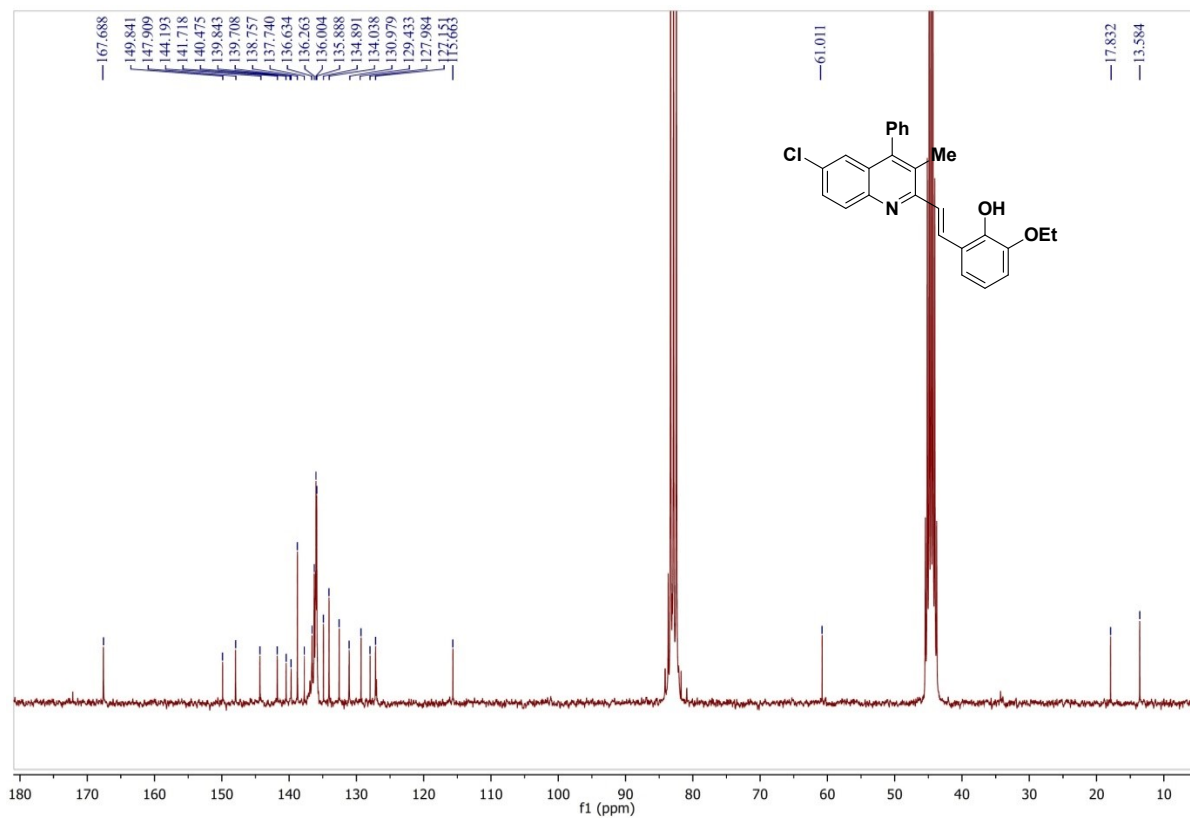
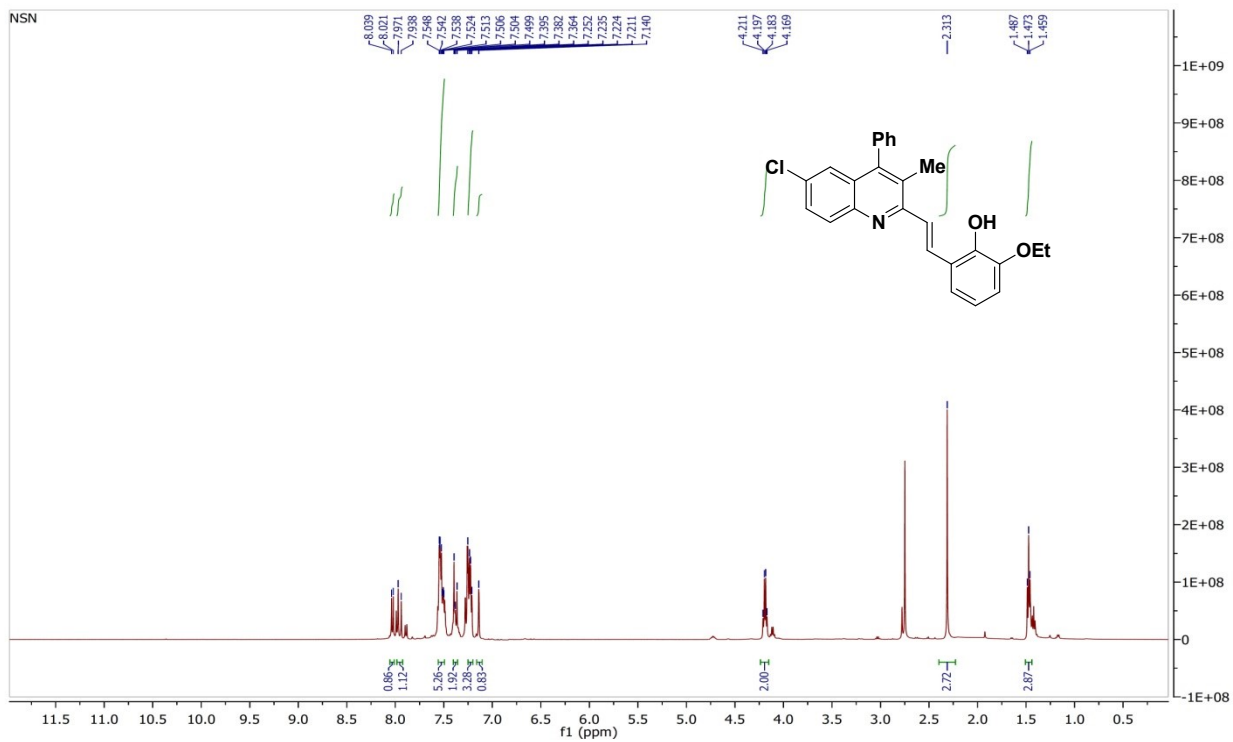
**6-Chloro-3-methyl-2-(4-nitrostyryl)-4-phenylquinoline (6d):**

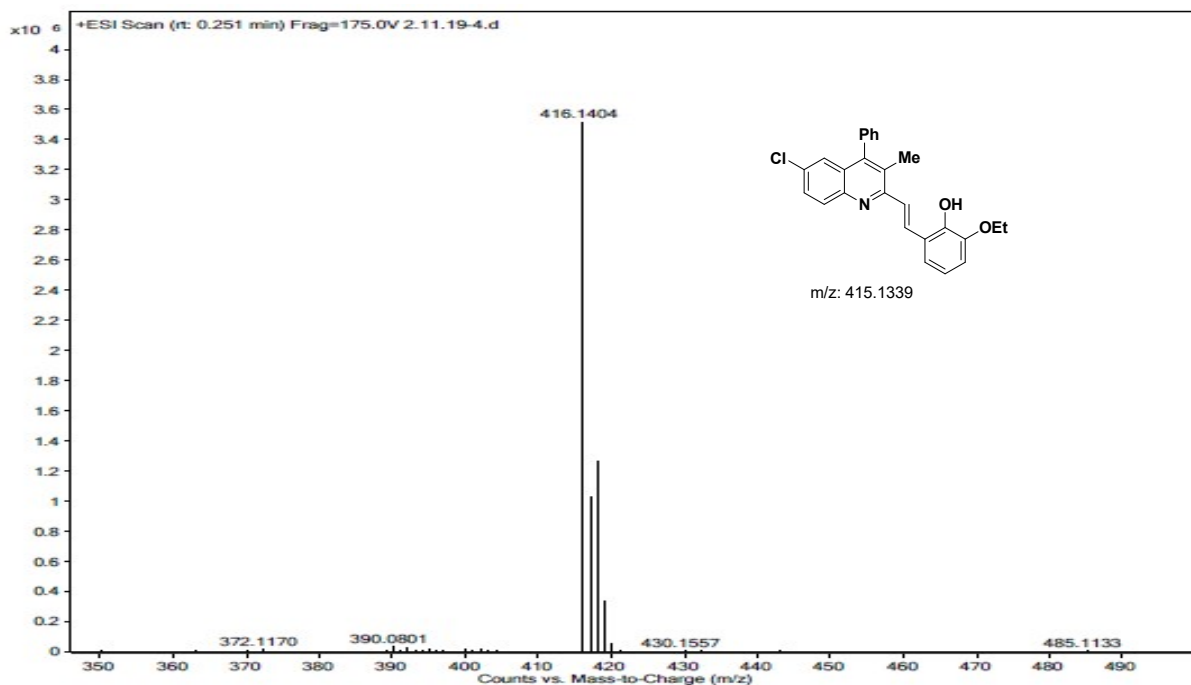


NSN

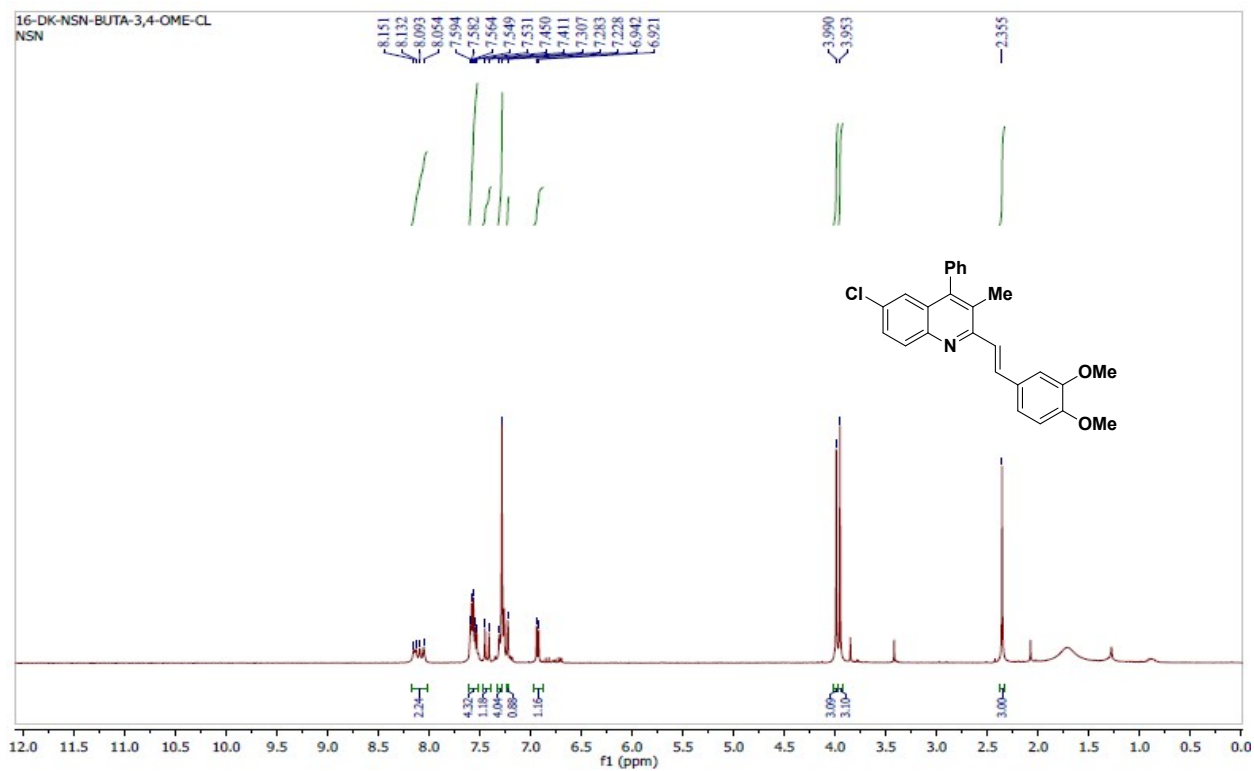


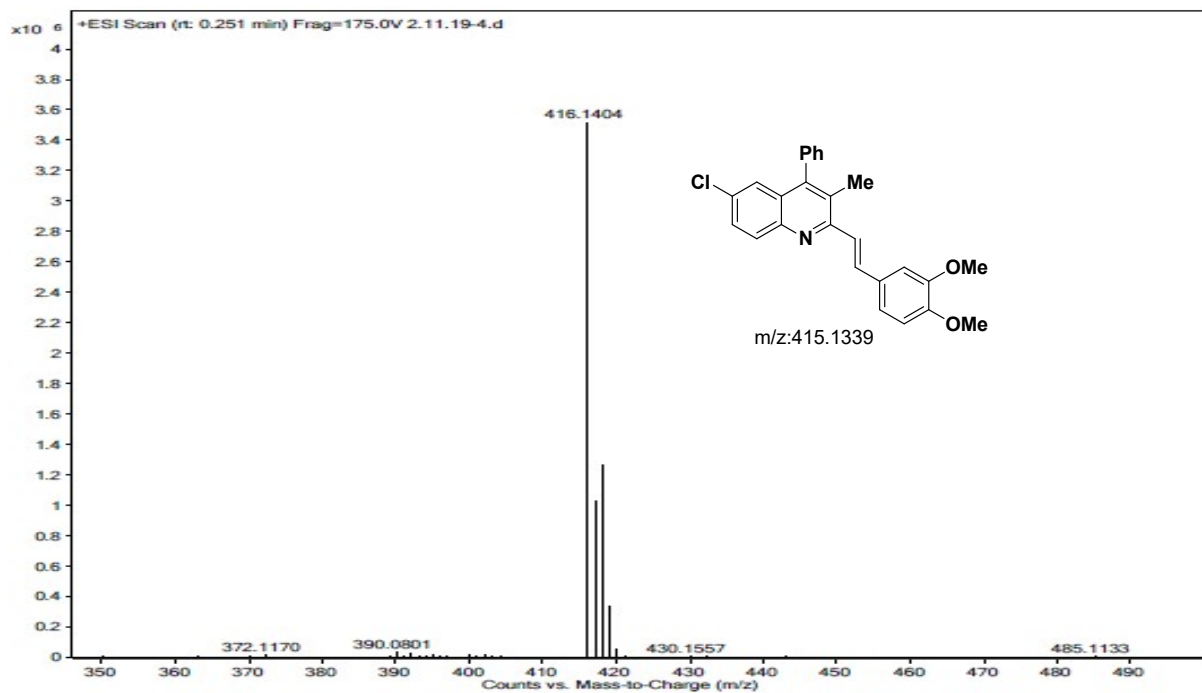
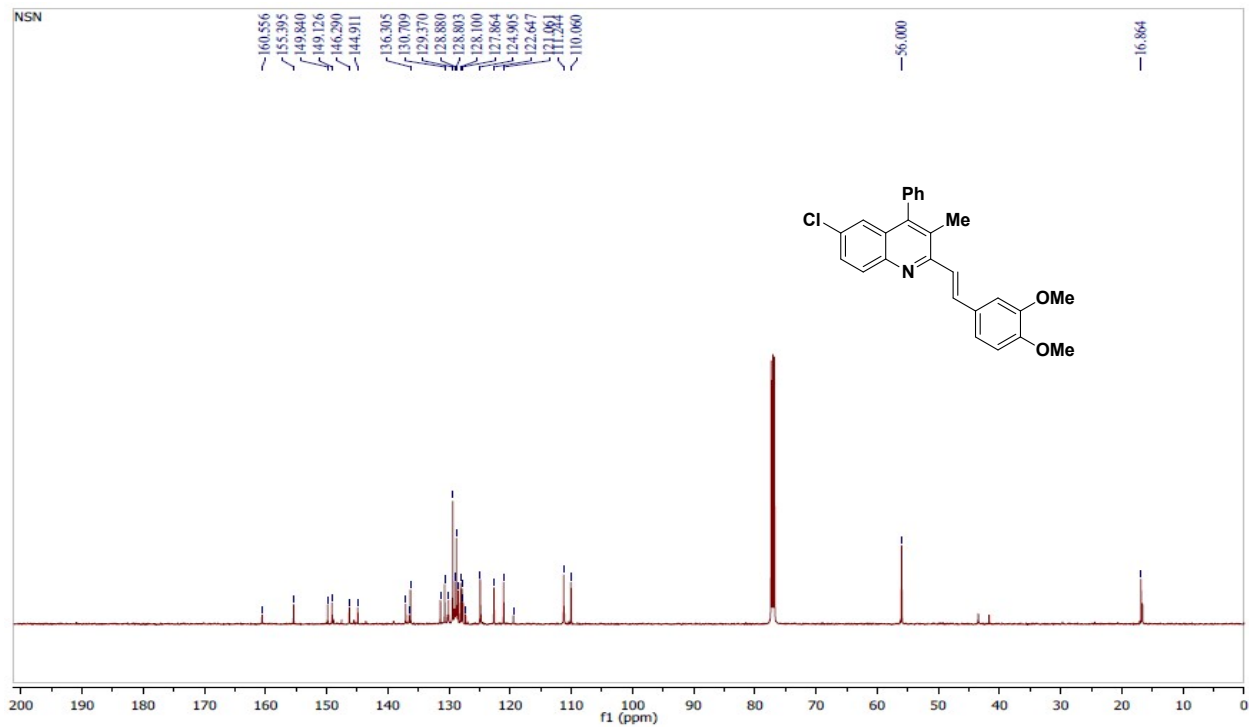
**(E)-2-(2-(6-Chloro-3-methyl-4-phenylquinolin-2-yl)vinyl)-6-ethoxyphenol (6e):**



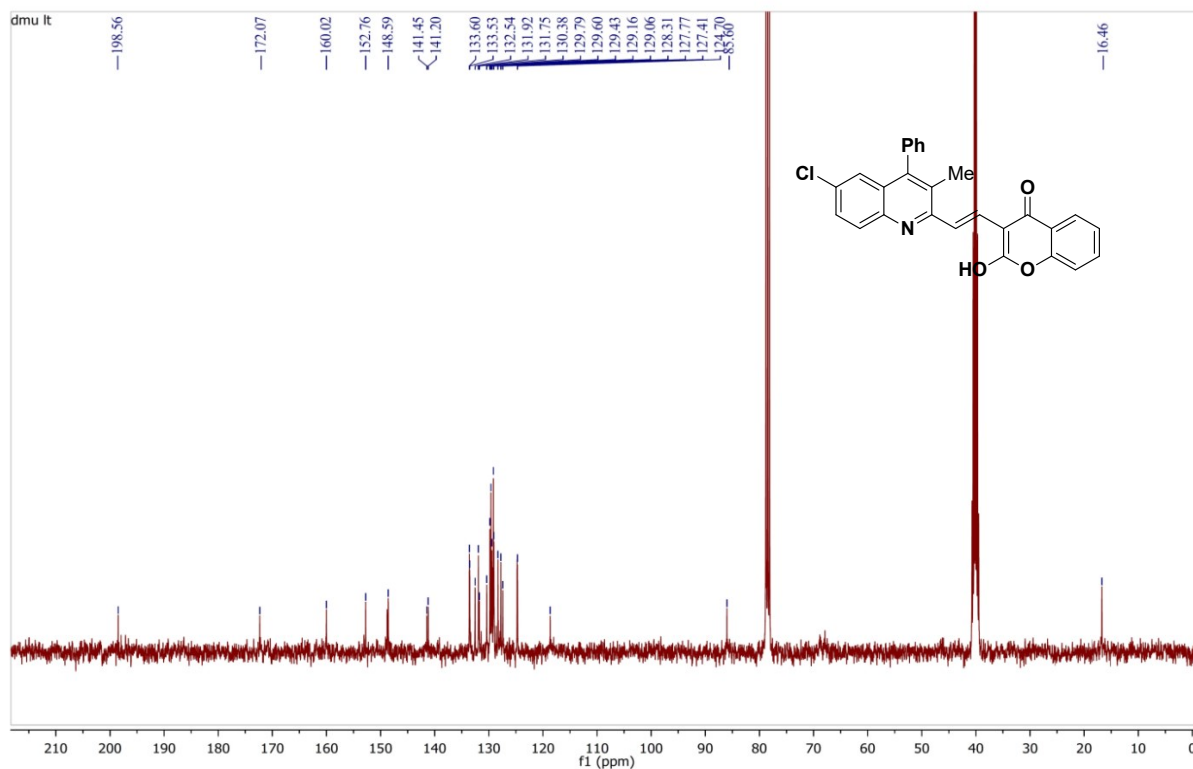
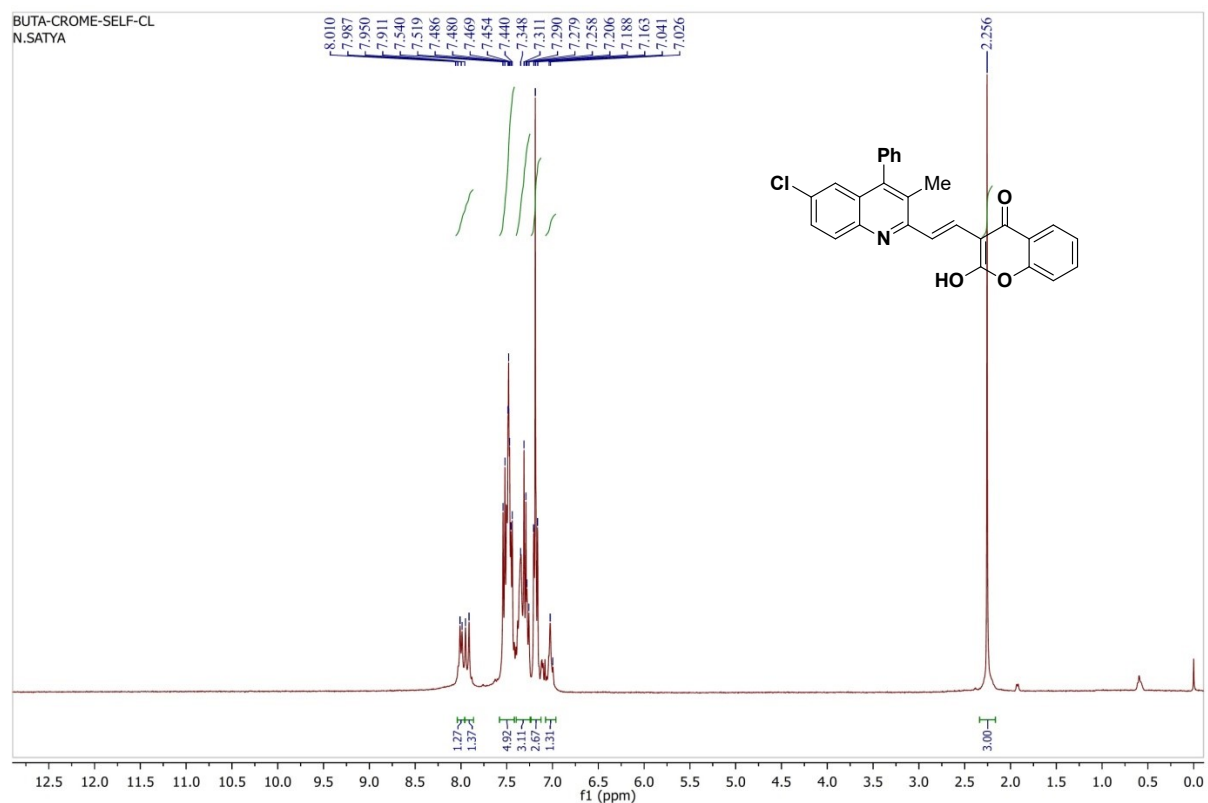


**6-Chloro-2-(3,4-dimethoxystyryl)-3-methyl-4-phenylquinoline (6f):**





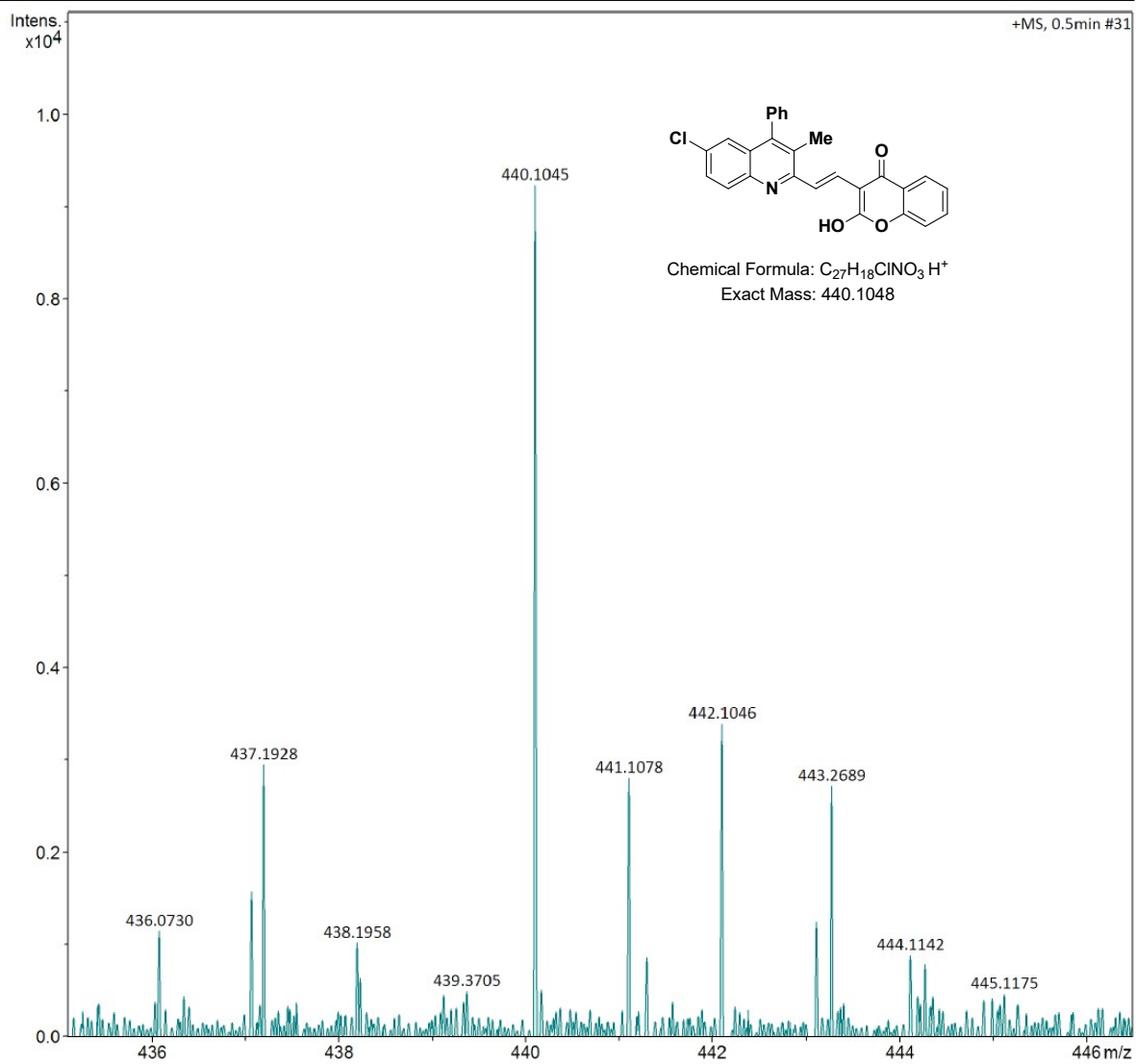
**3-(2-(6-Chloro-3-methyl-4-phenylquinolin-2-yl) vinyl)-2-hydroxy-4H-chromen-4-one (6g):**

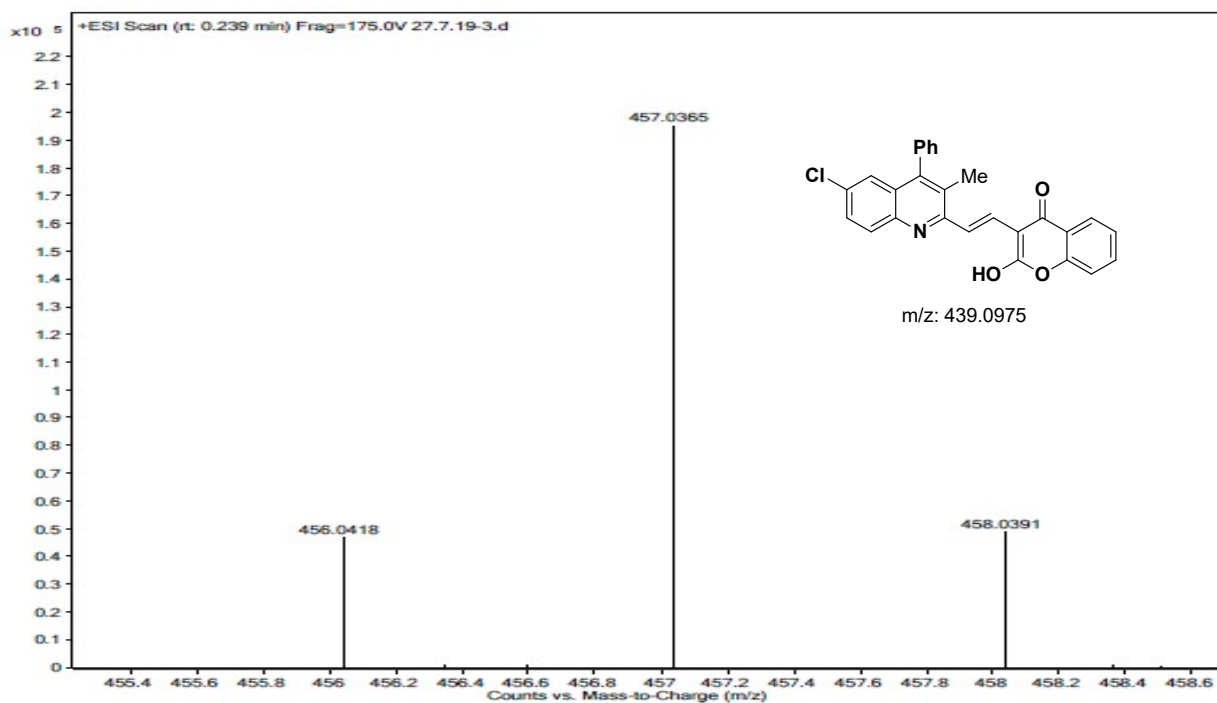




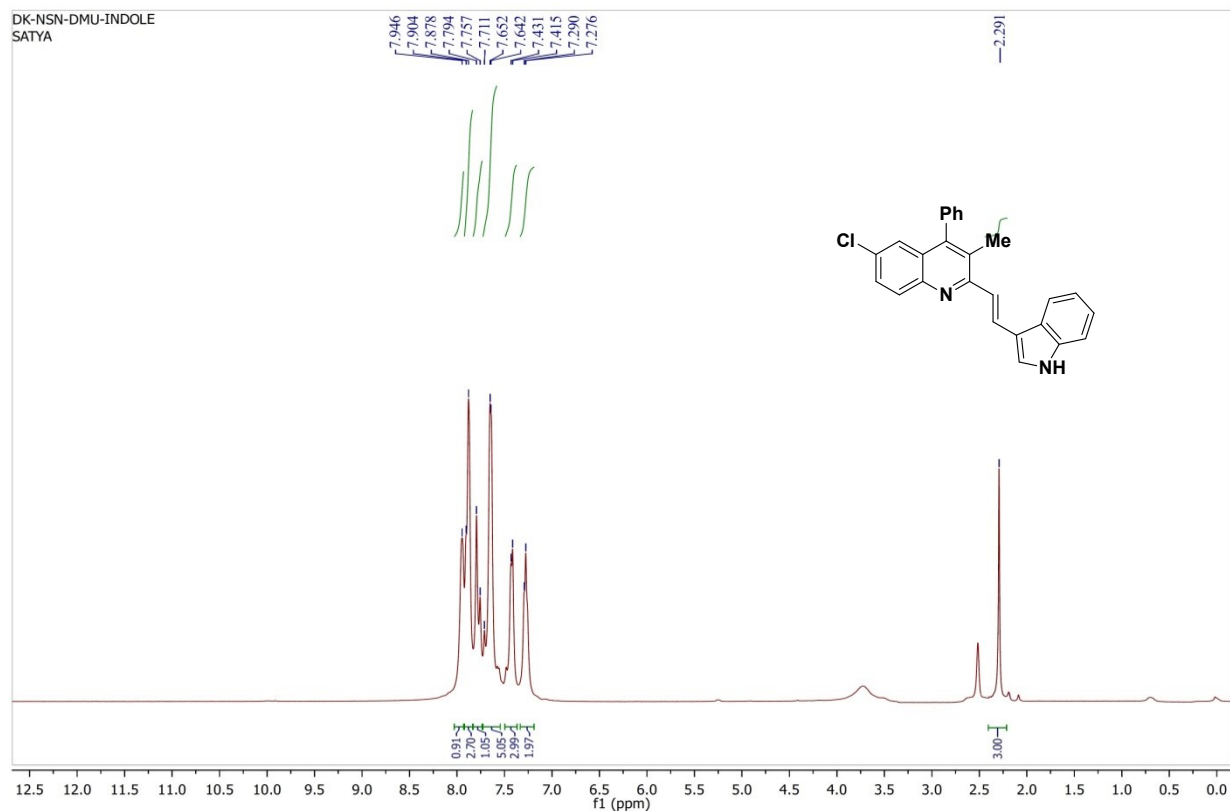
**Acquisition Parameter**

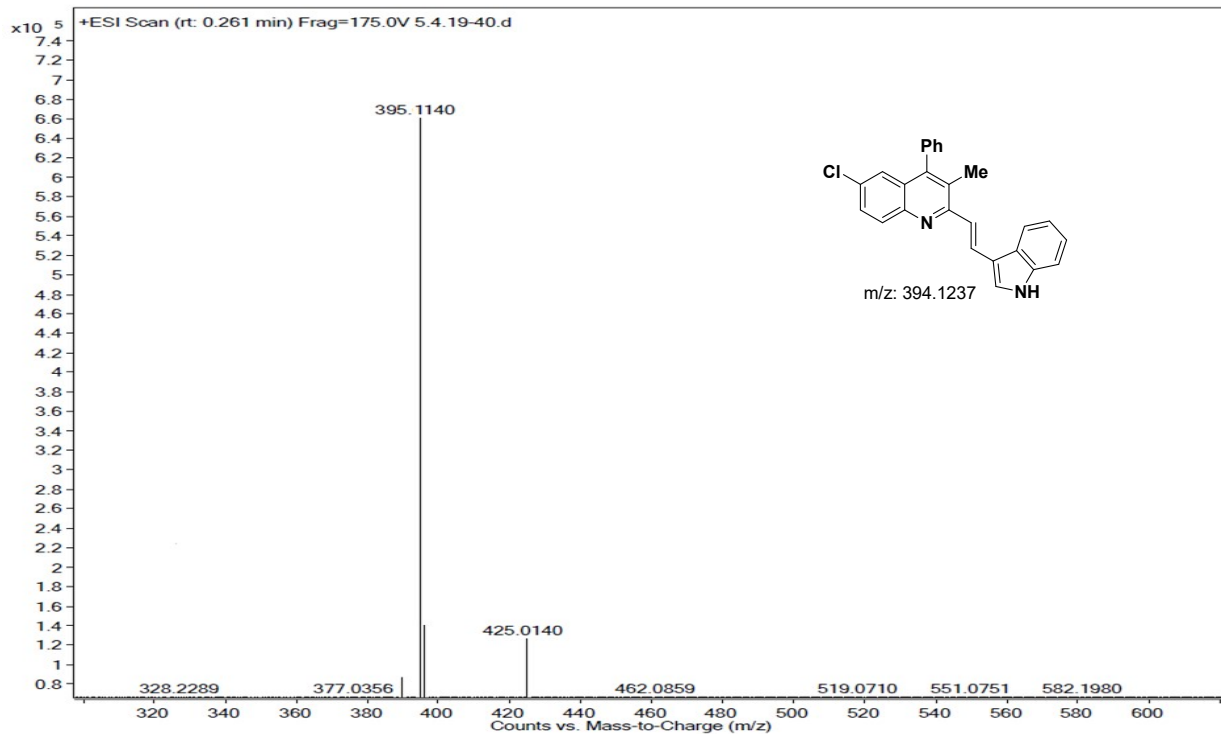
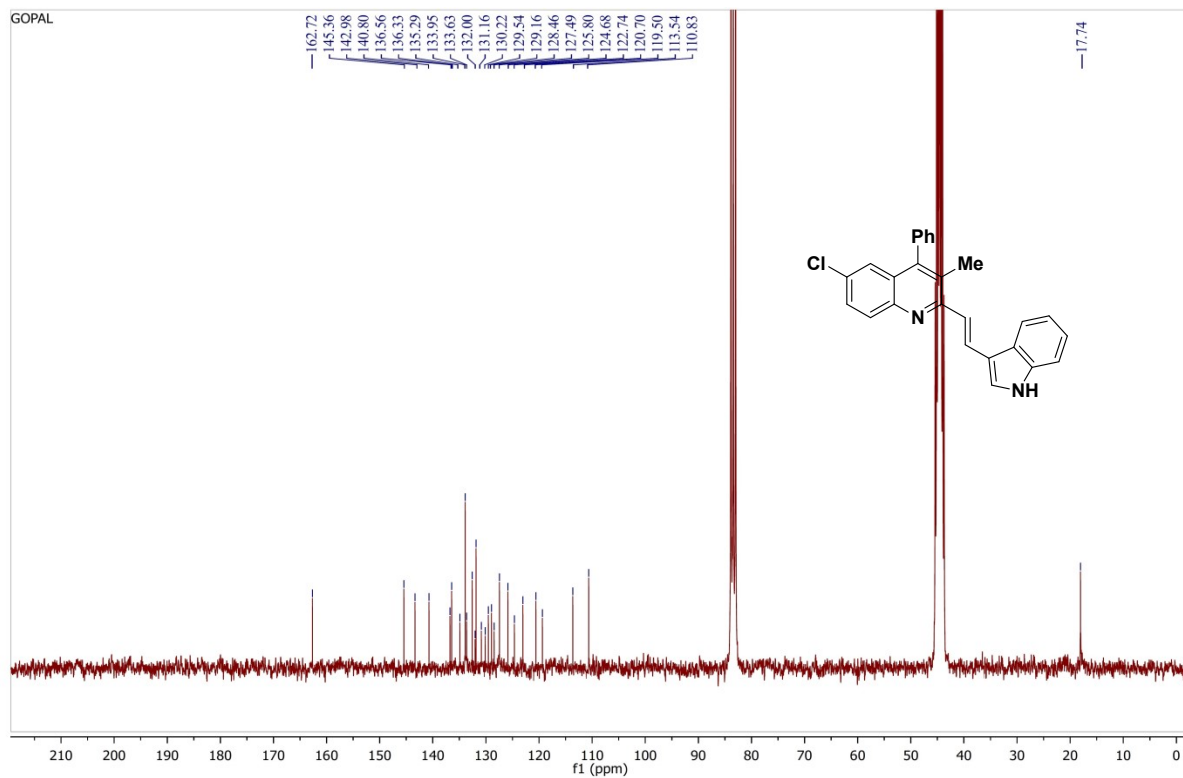
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Charging Voltage	0 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



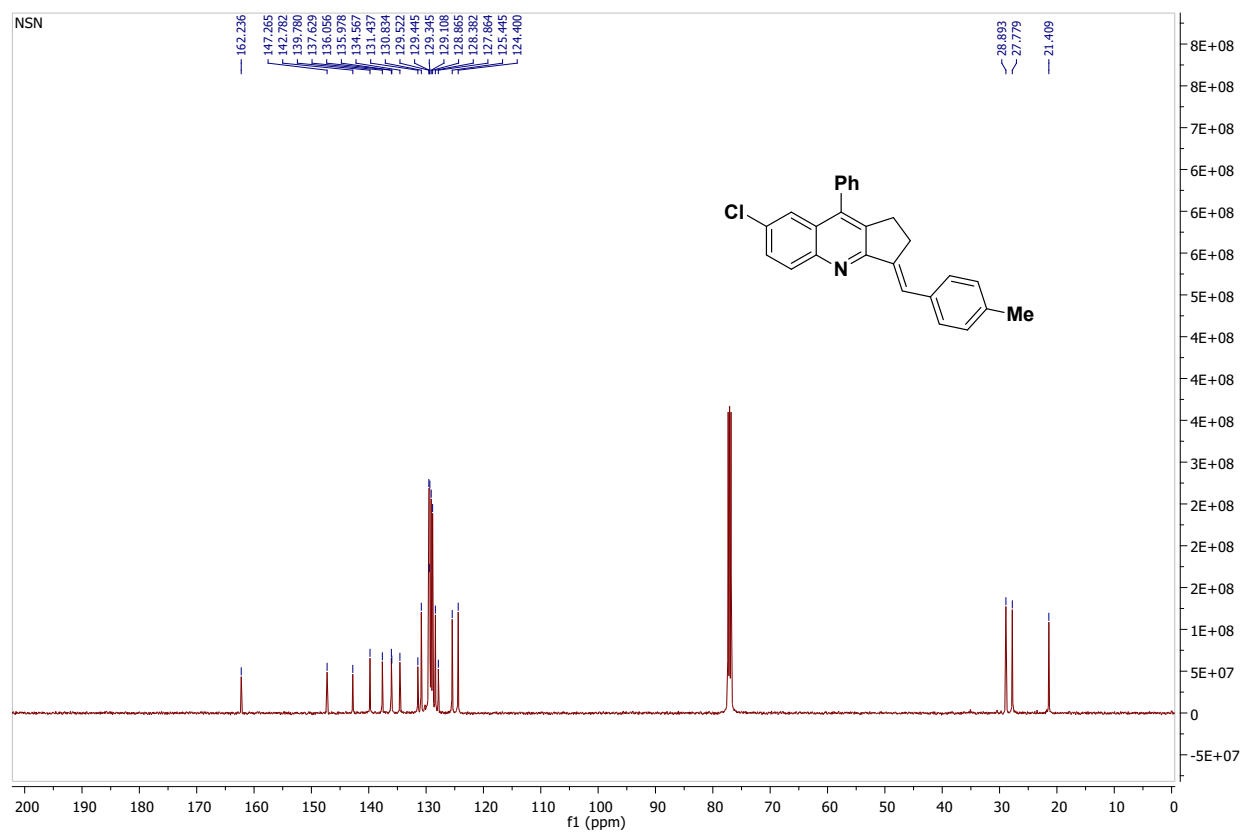
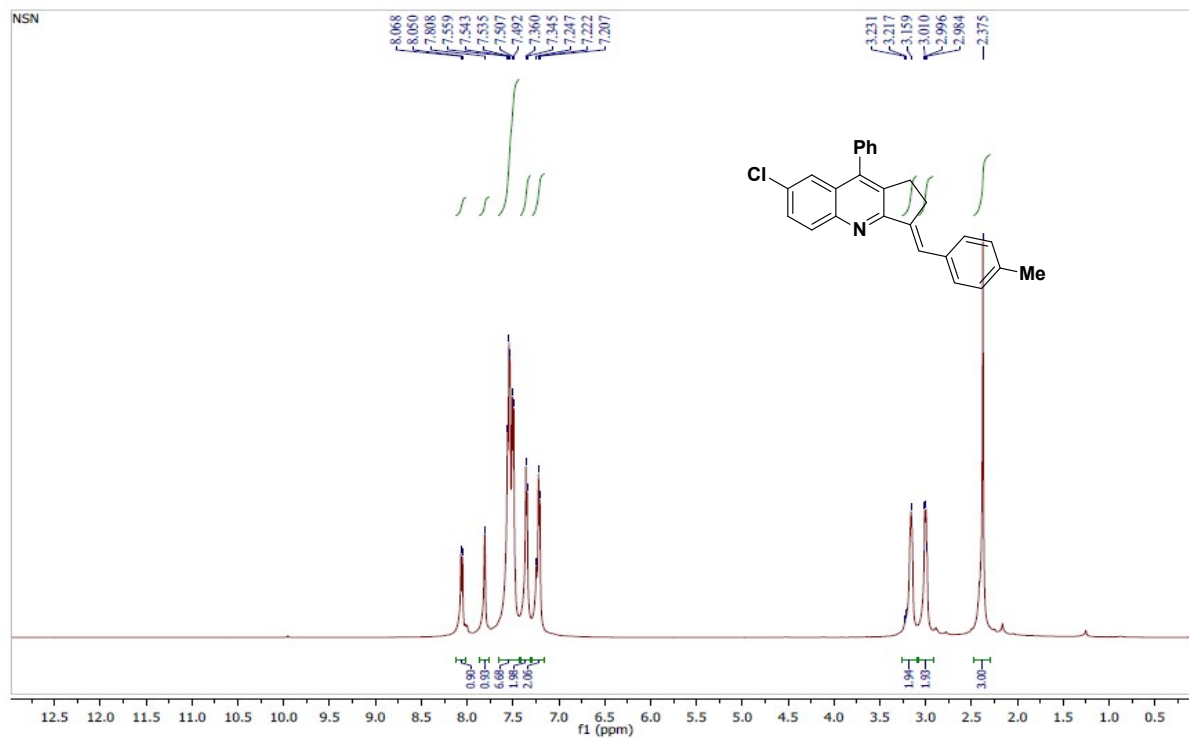


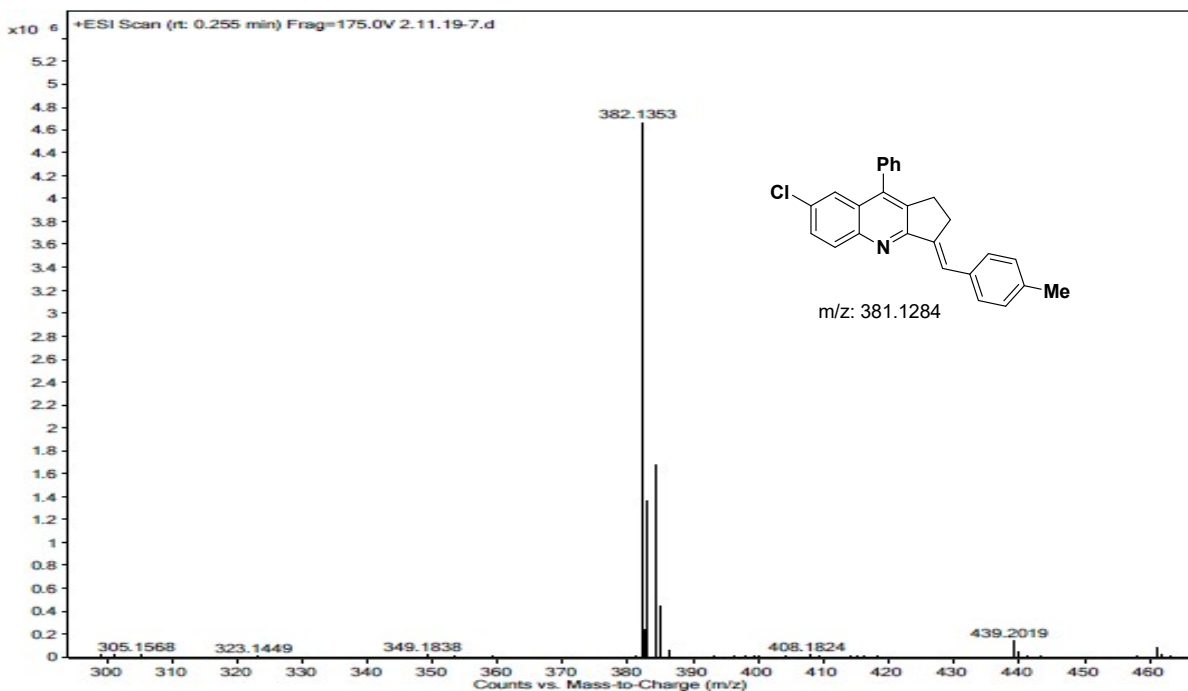
**2-(2-(1H-Indol-3-yl)vinyl)-6-chloro-3-methyl-4-phenylquinoline (6h):**



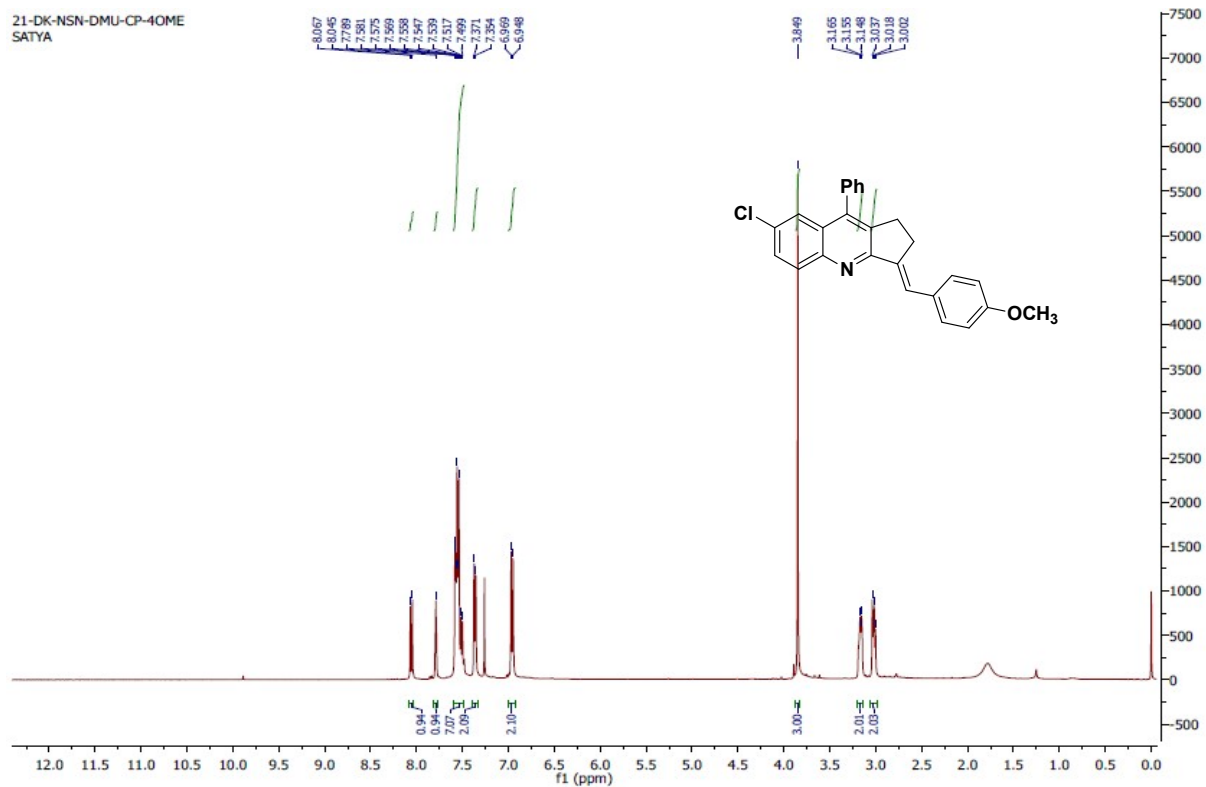


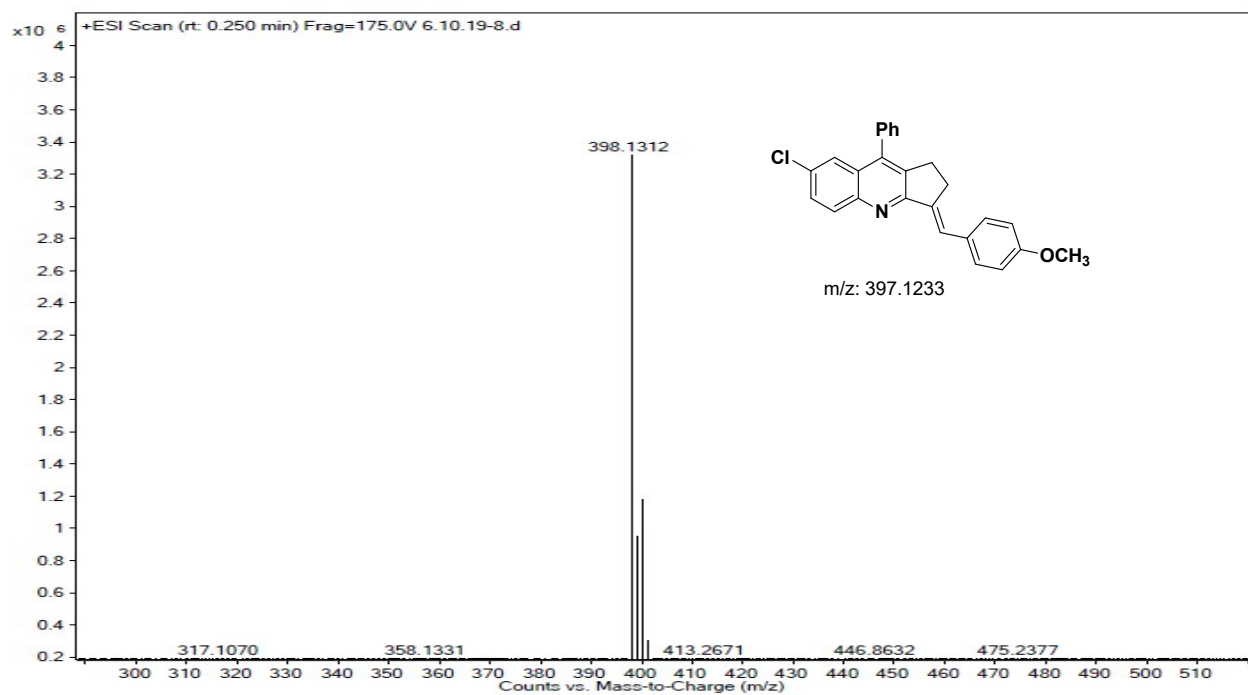
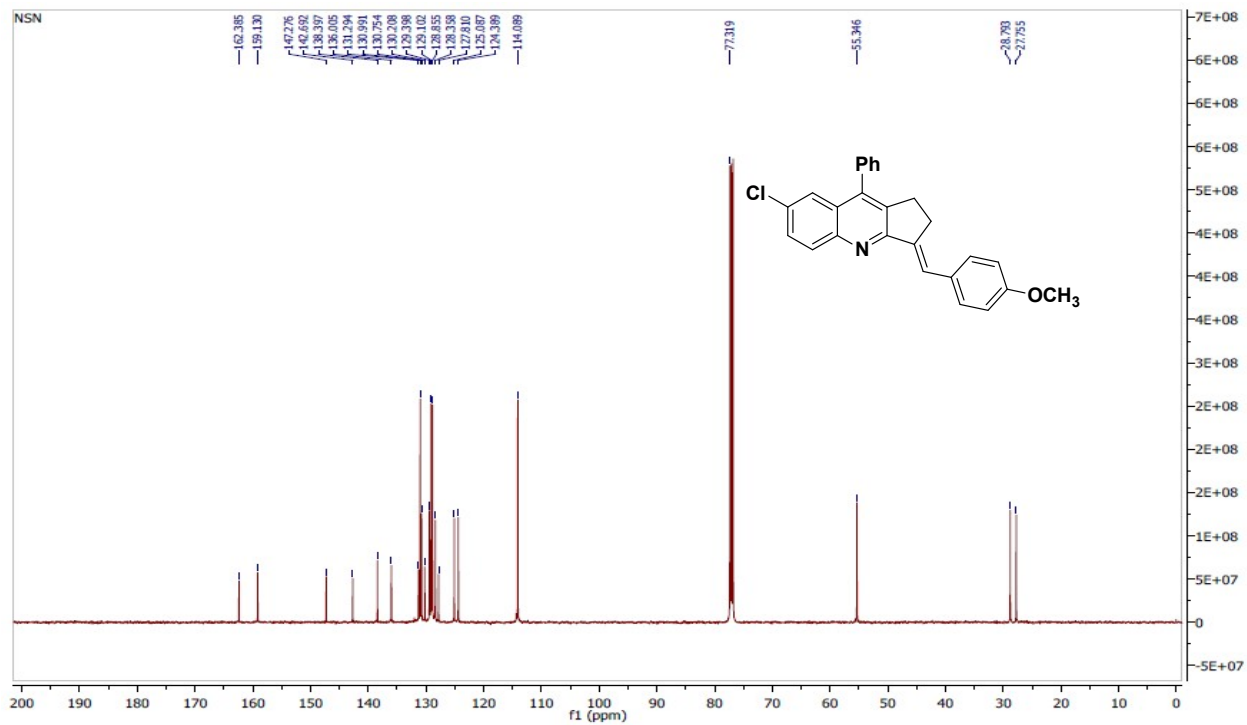
**7-Chloro-3-(4-methylbenzylidene)-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinolone(7a):**



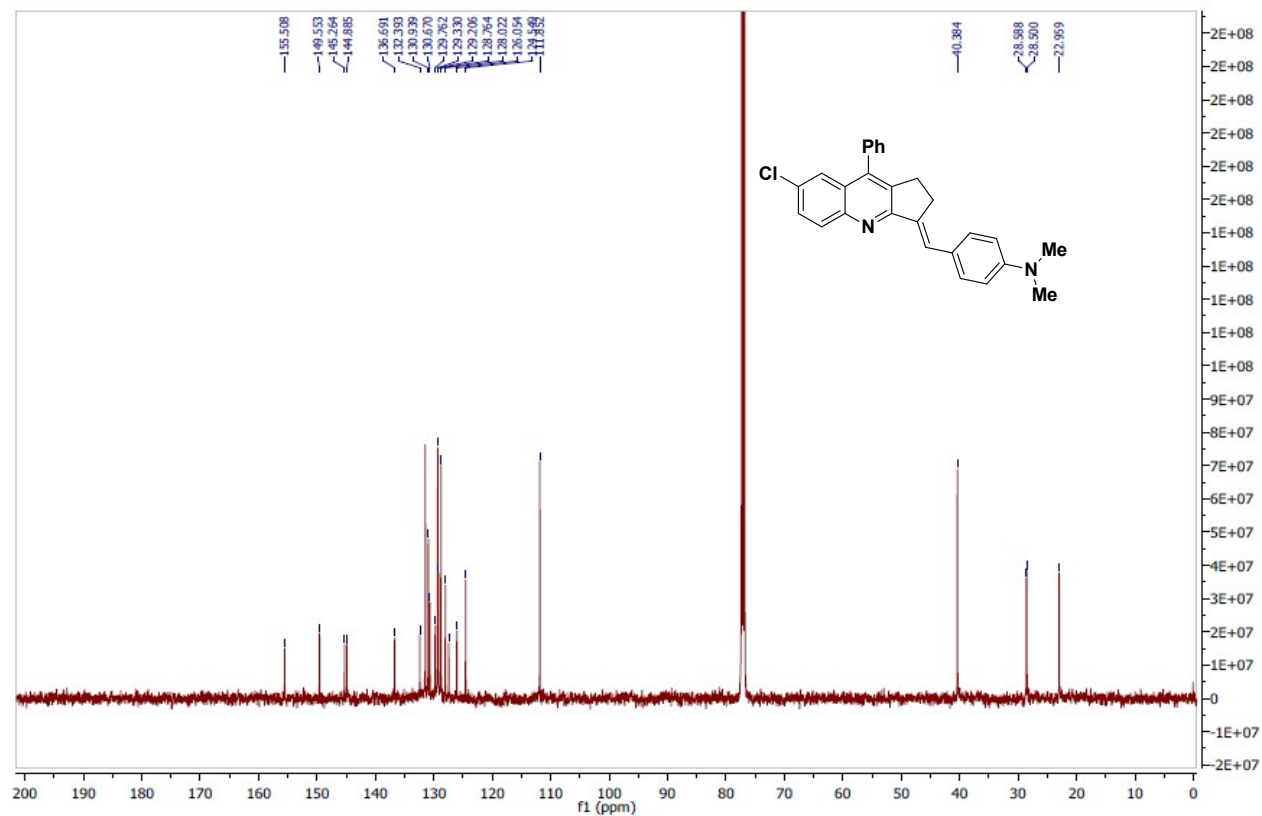
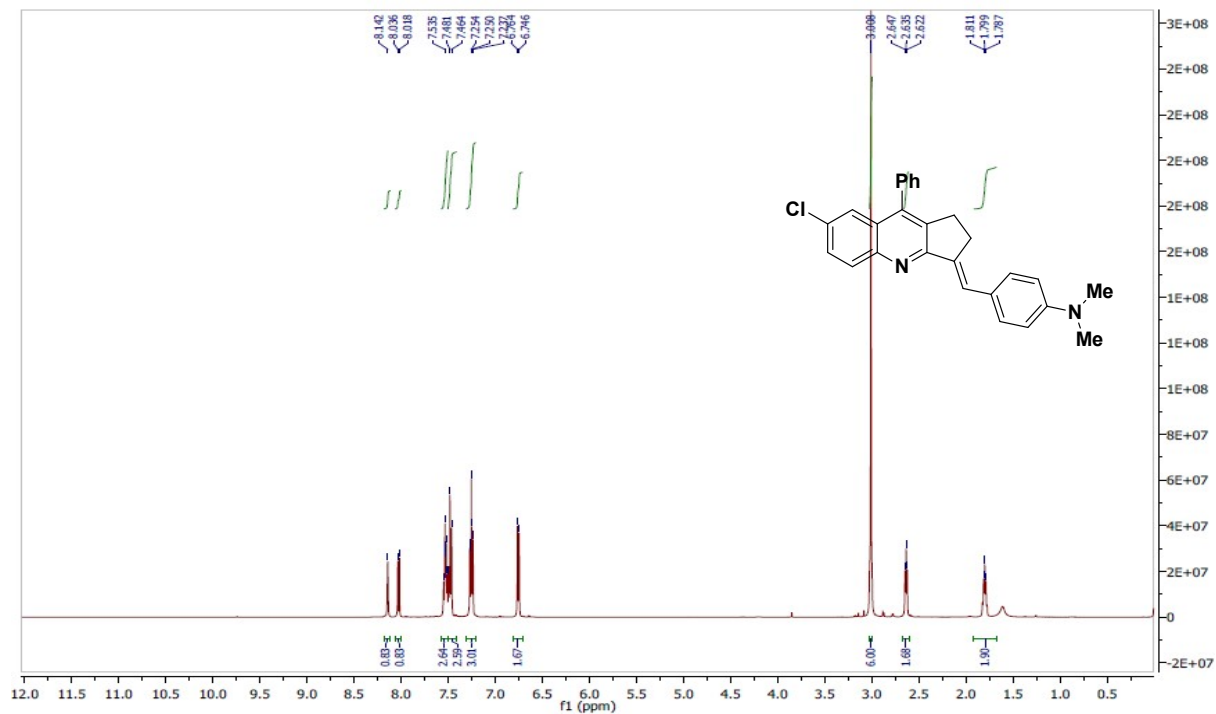


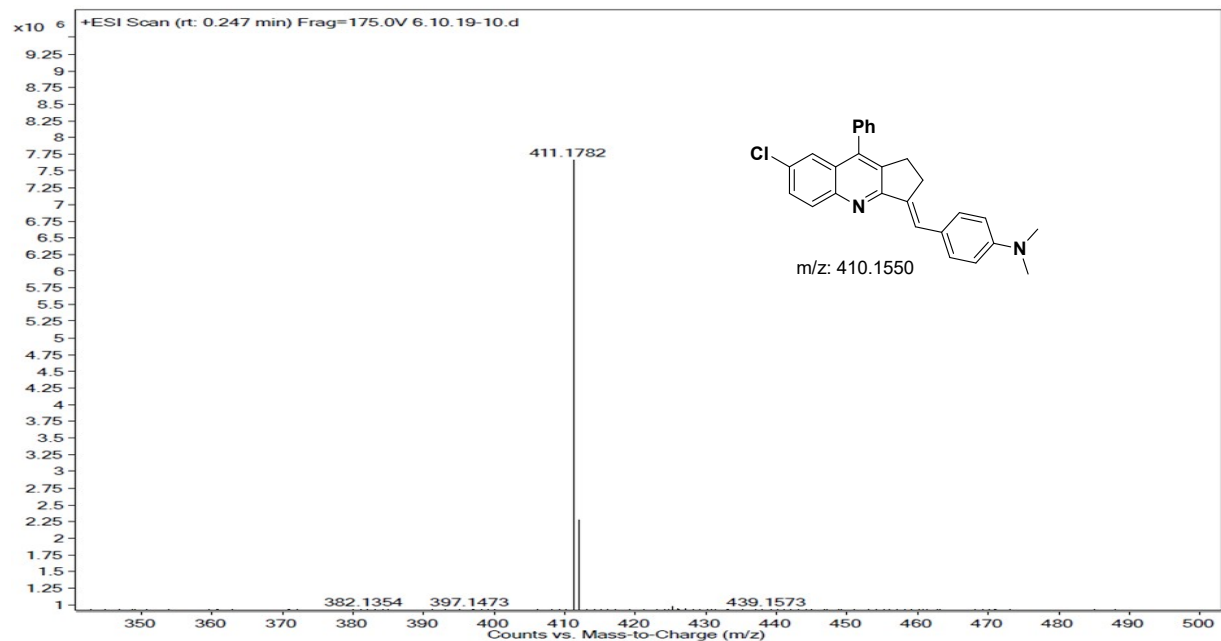
**7-Chloro-3-(4-methoxybenzylidene)-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinoline(7b):**



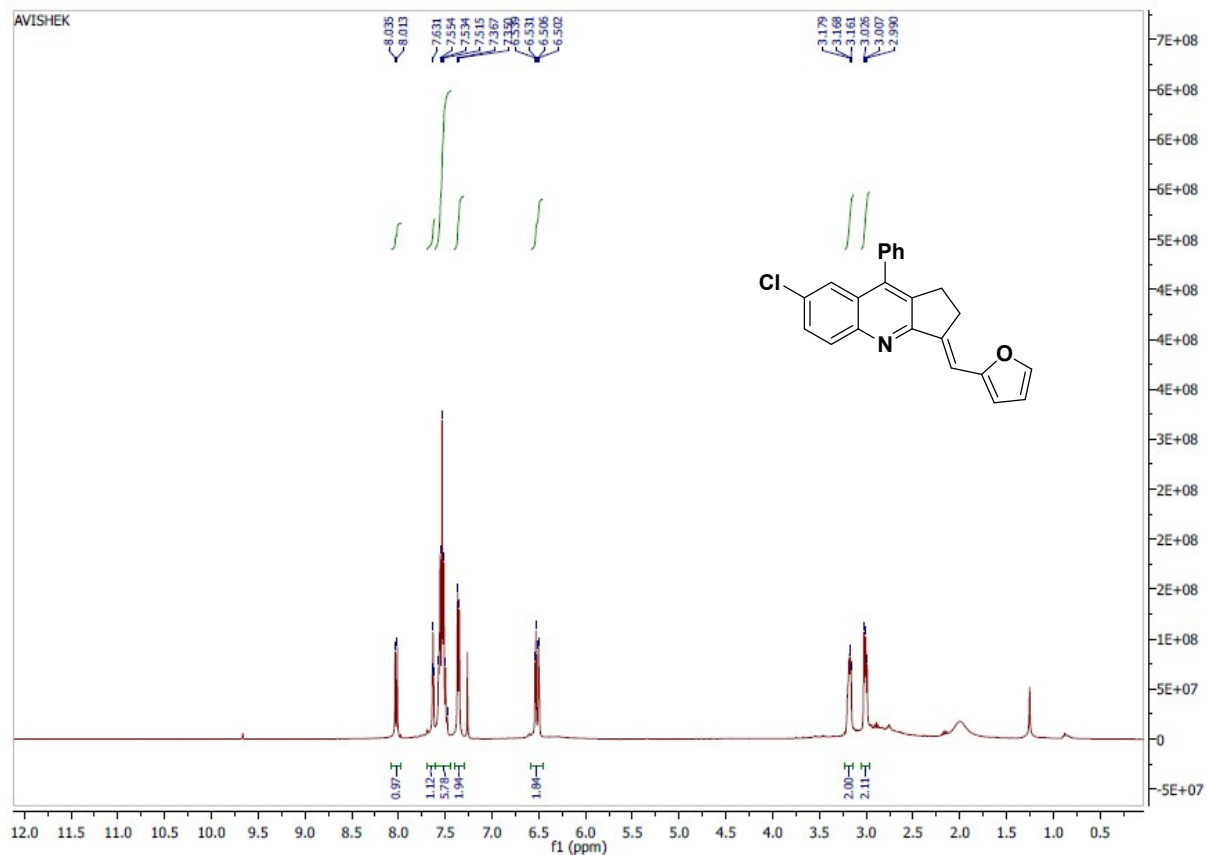


4-((7-Chloro-9-phenyl-1H-cyclopenta[b]quinolin-3(2H)-ylidene)methyl)-N,N-dimethylaniline (7c):



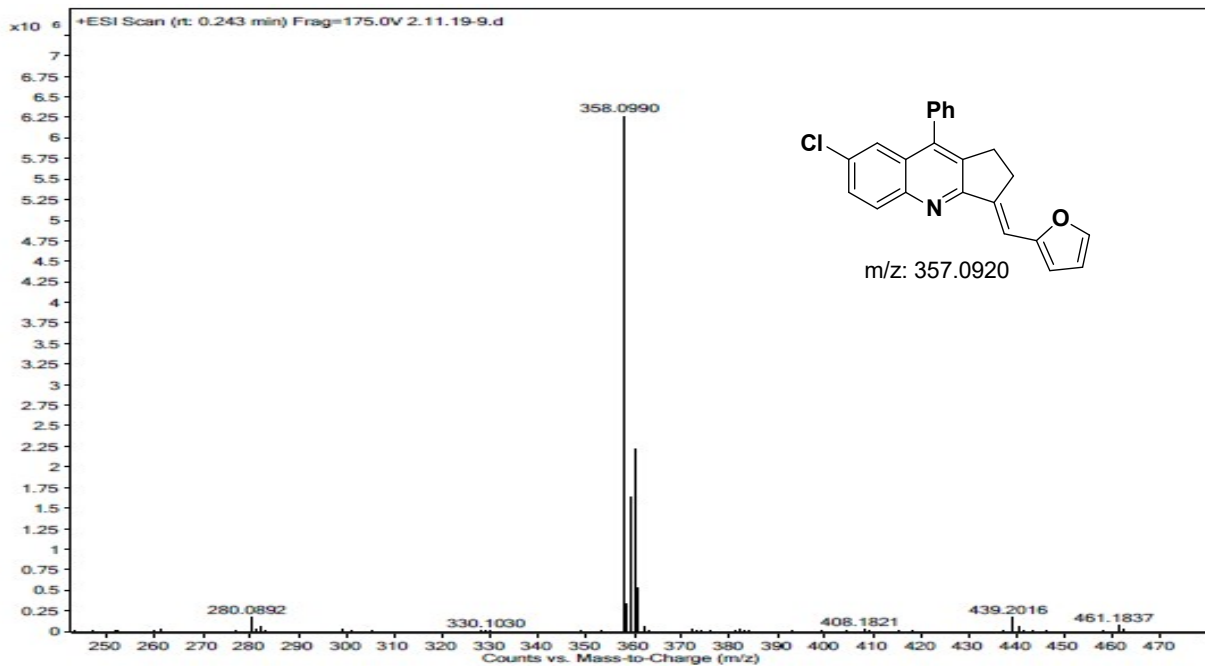
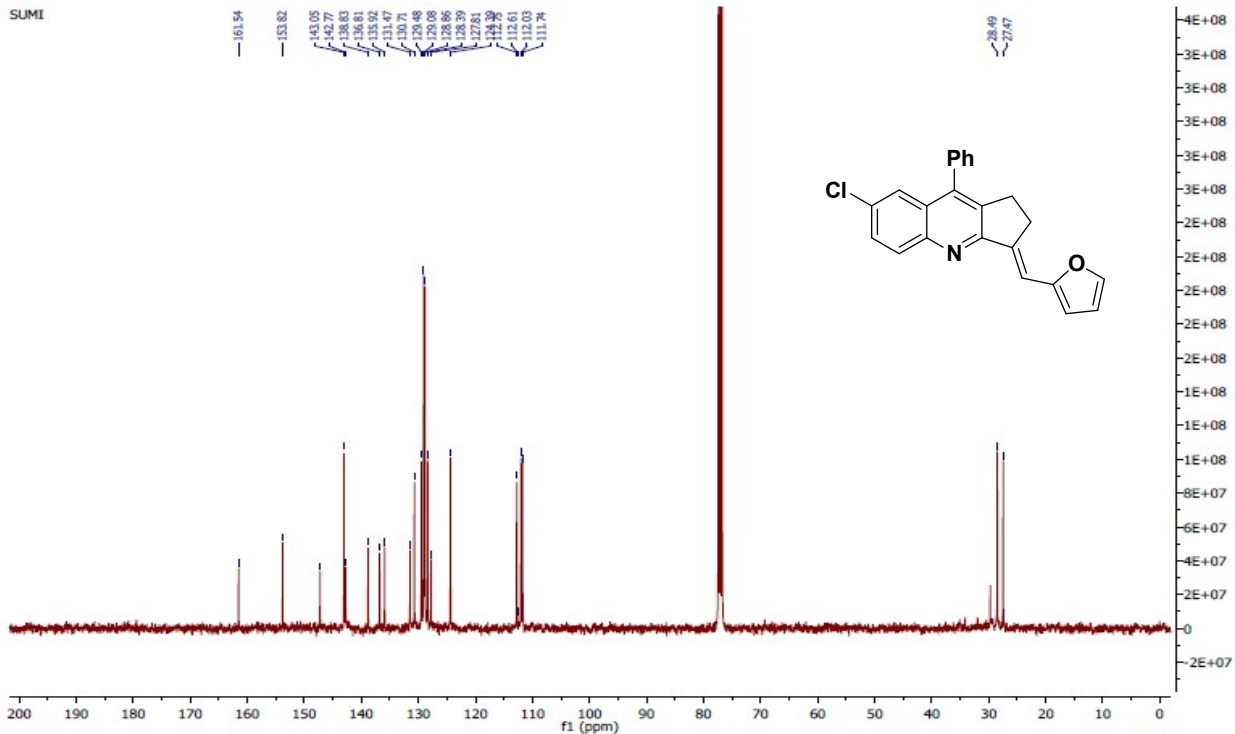


**6-Chloro-2-(furan-2-ylmethylene)-8-phenyl-1,2-dihydrocyclobuta[b]quinoline (7d):**

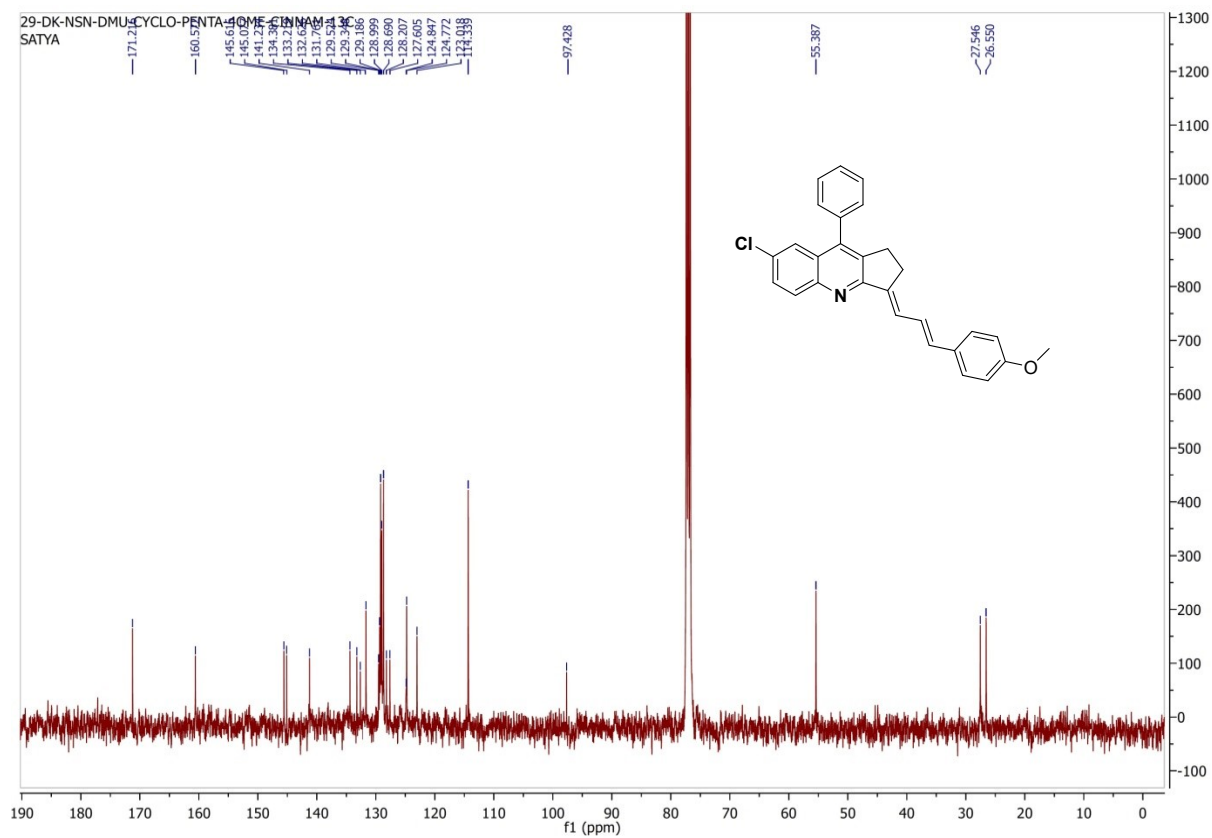
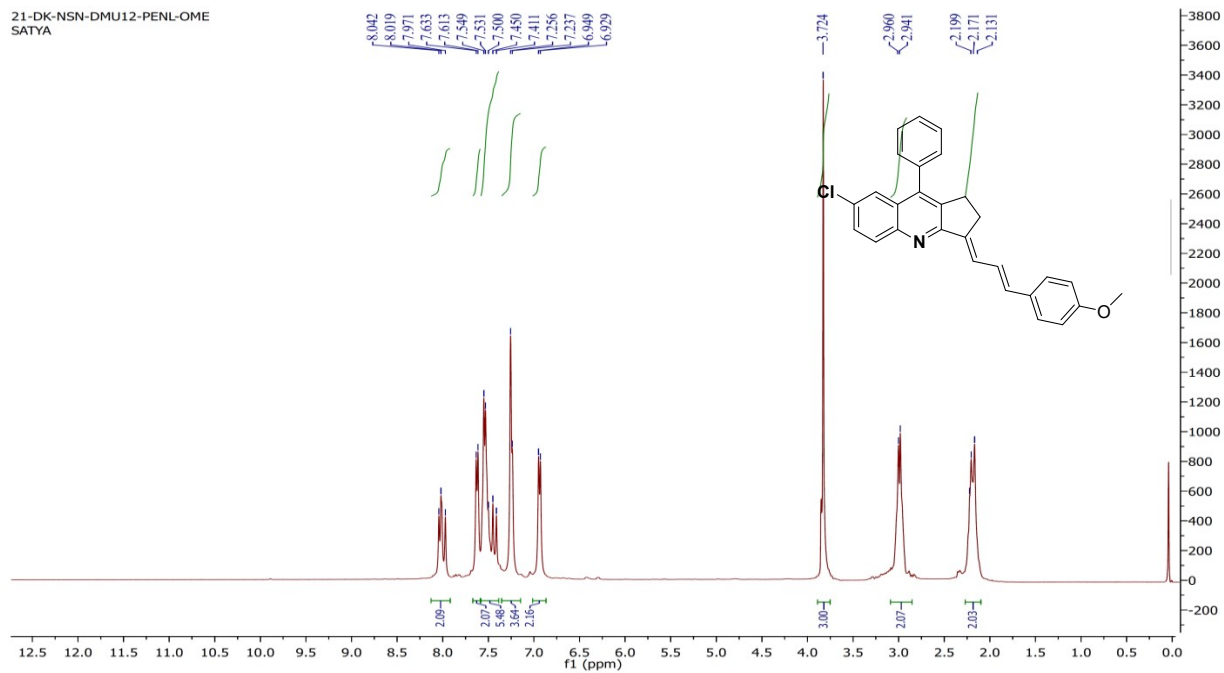


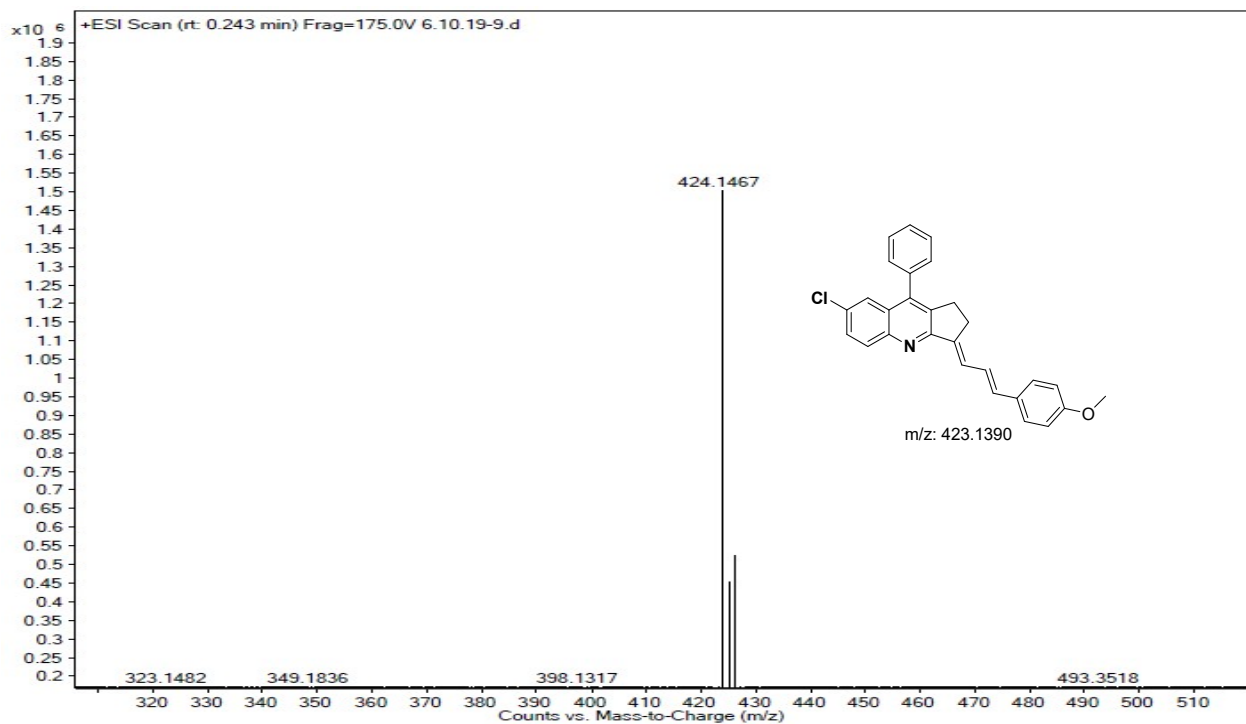


SUMI

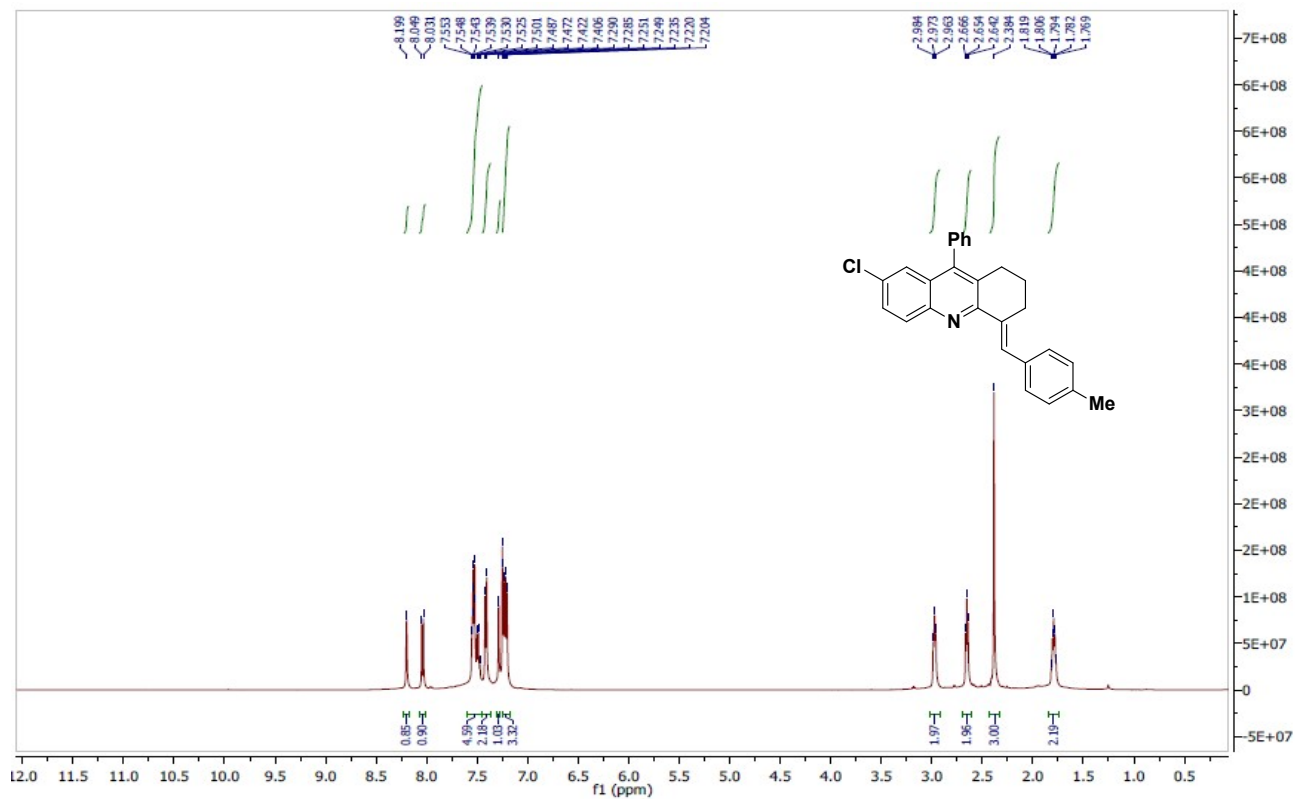


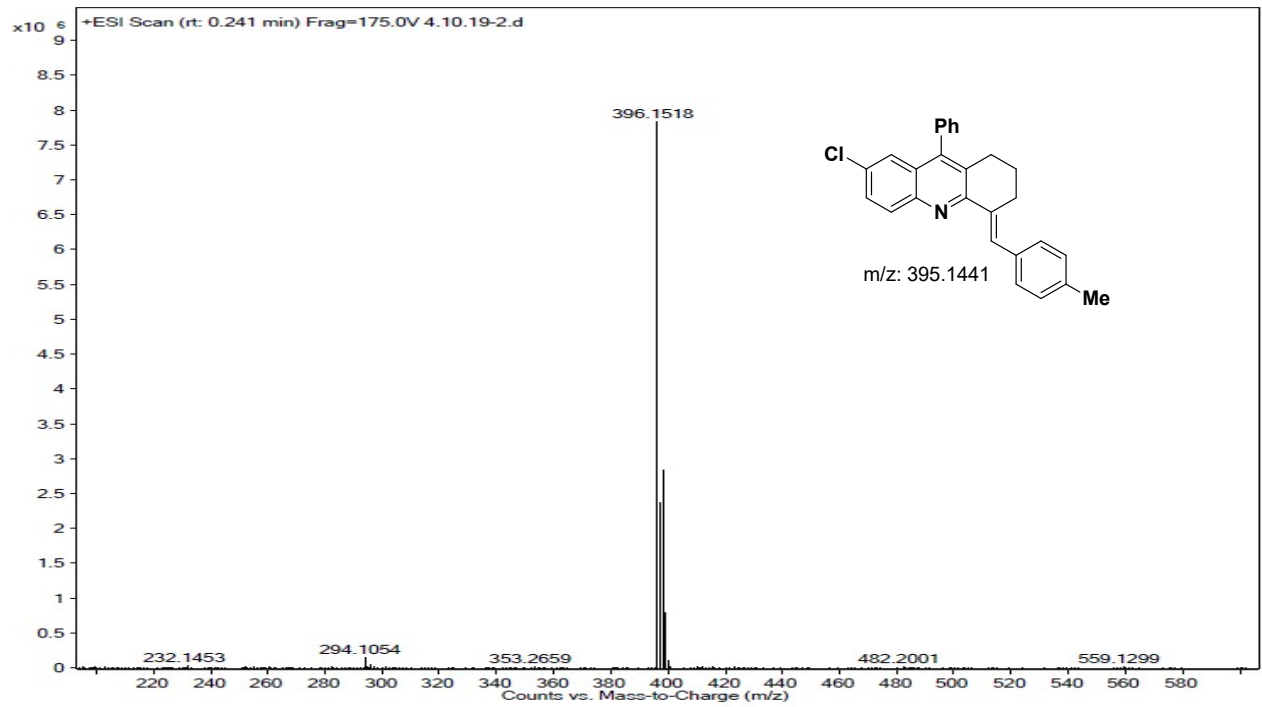
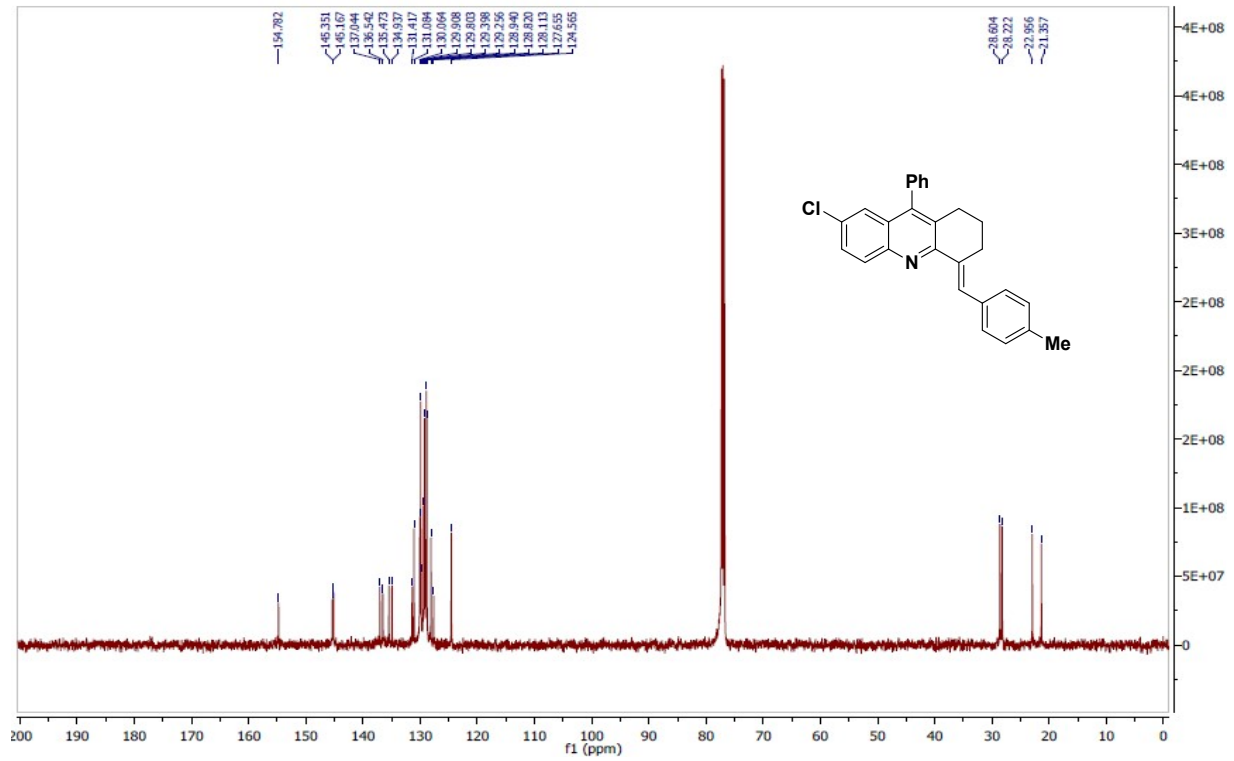
**7-Chloro-3-((E)-3-(4-methoxyphenyl)allylidene)-9-phenyl-2,3-dihydro-1H-cyclopenta[b]quinolone (7e):**



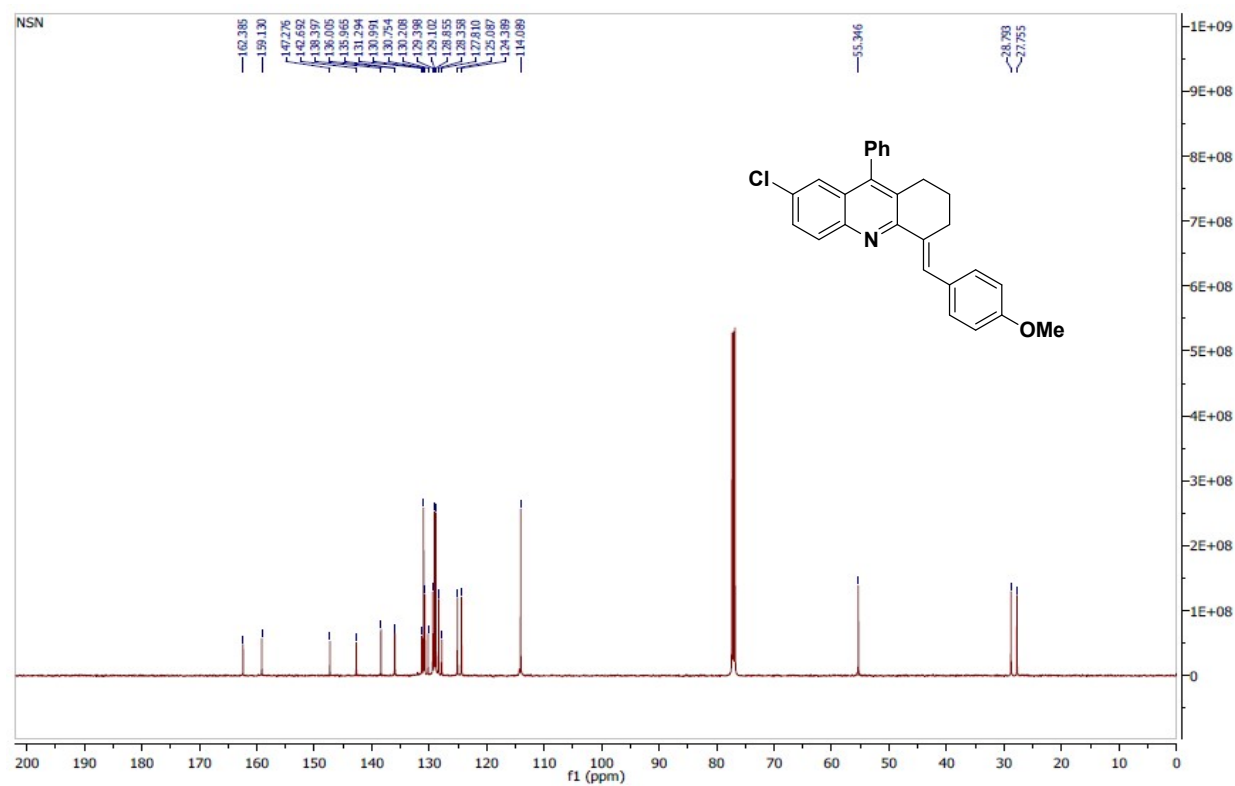
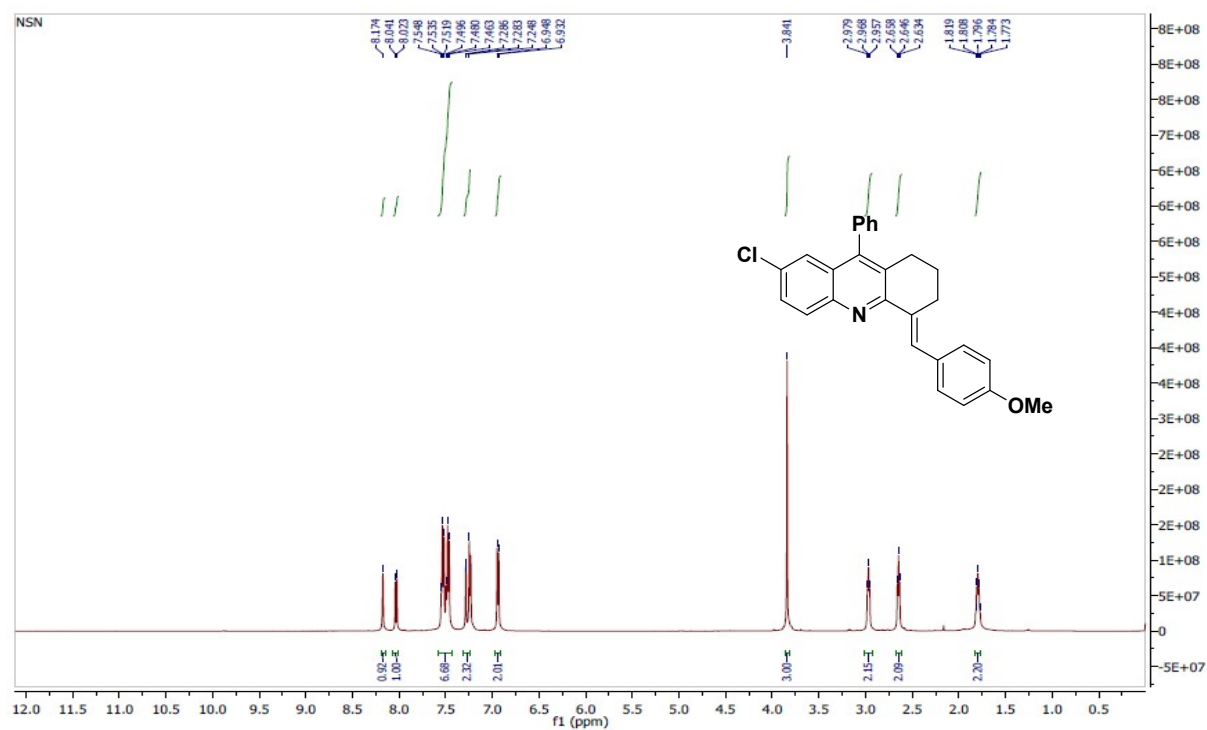


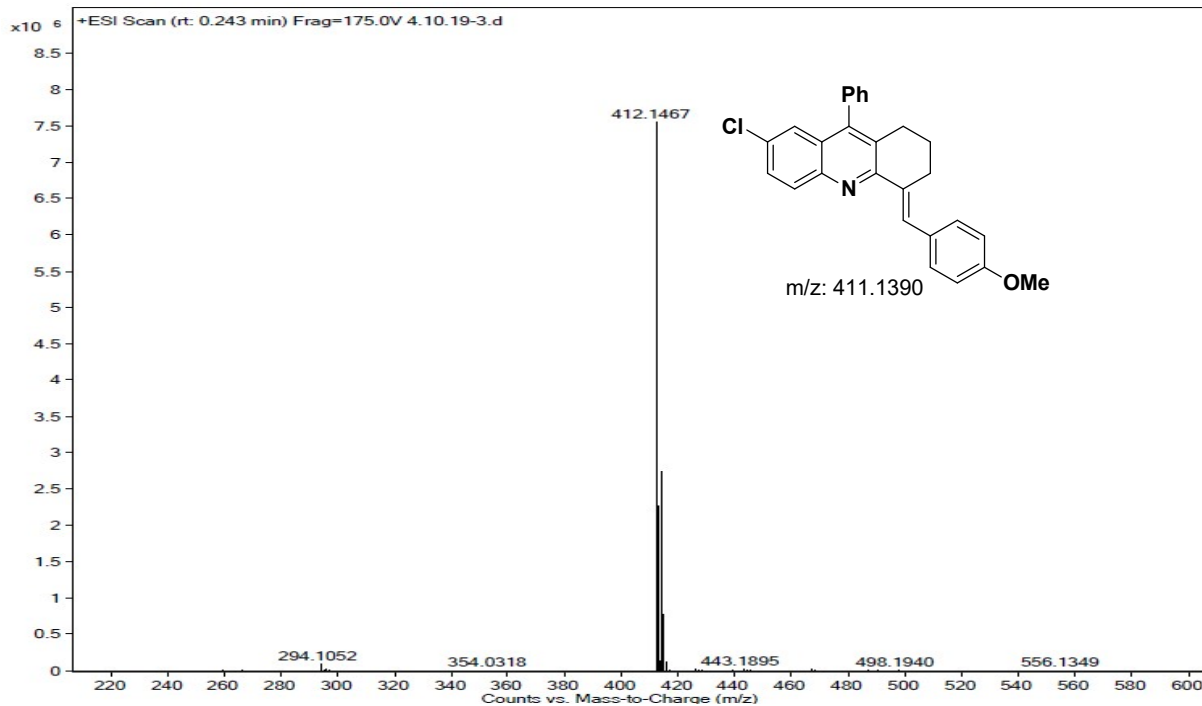
**7-Chloro-4-(4-methylbenzylidene)-9-phenyl-1,2,3,4-tetrahydroacridine (7f):**



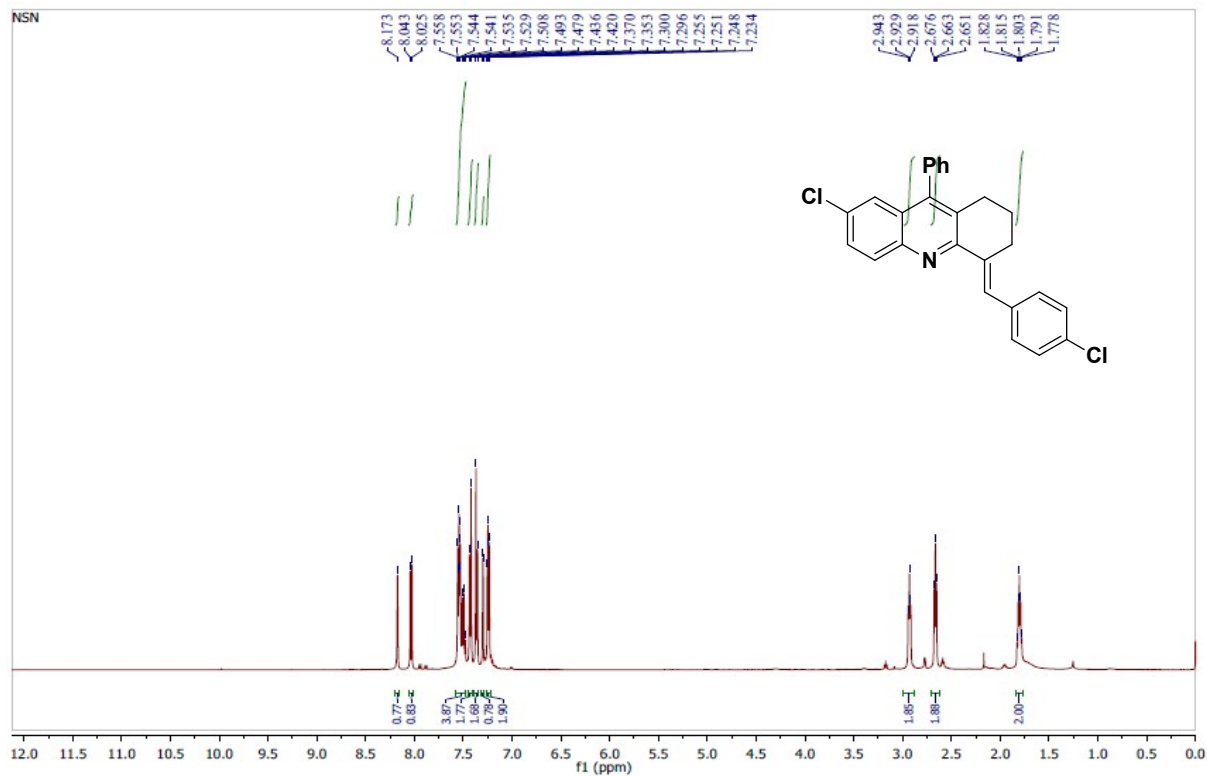


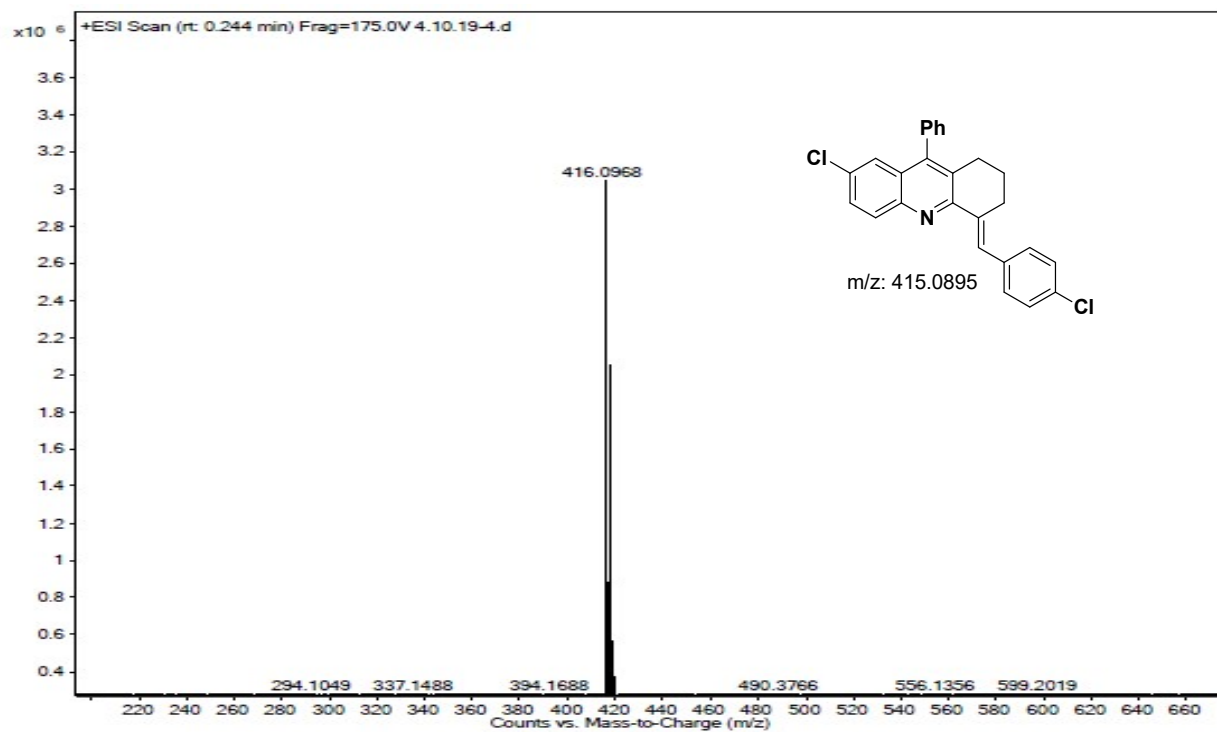
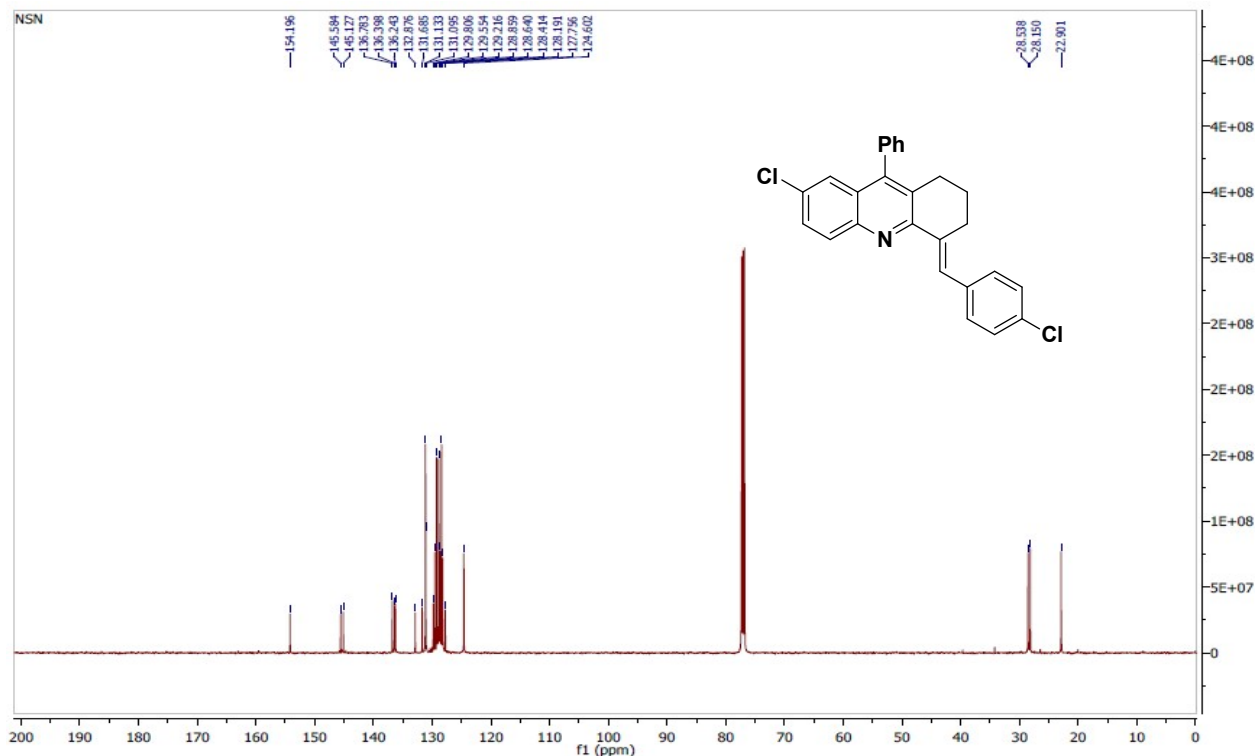
**7-Chloro-4-(4-methoxybenzylidene)-9-phenyl-1,2,3,4-tetrahydroacridine (7g):**



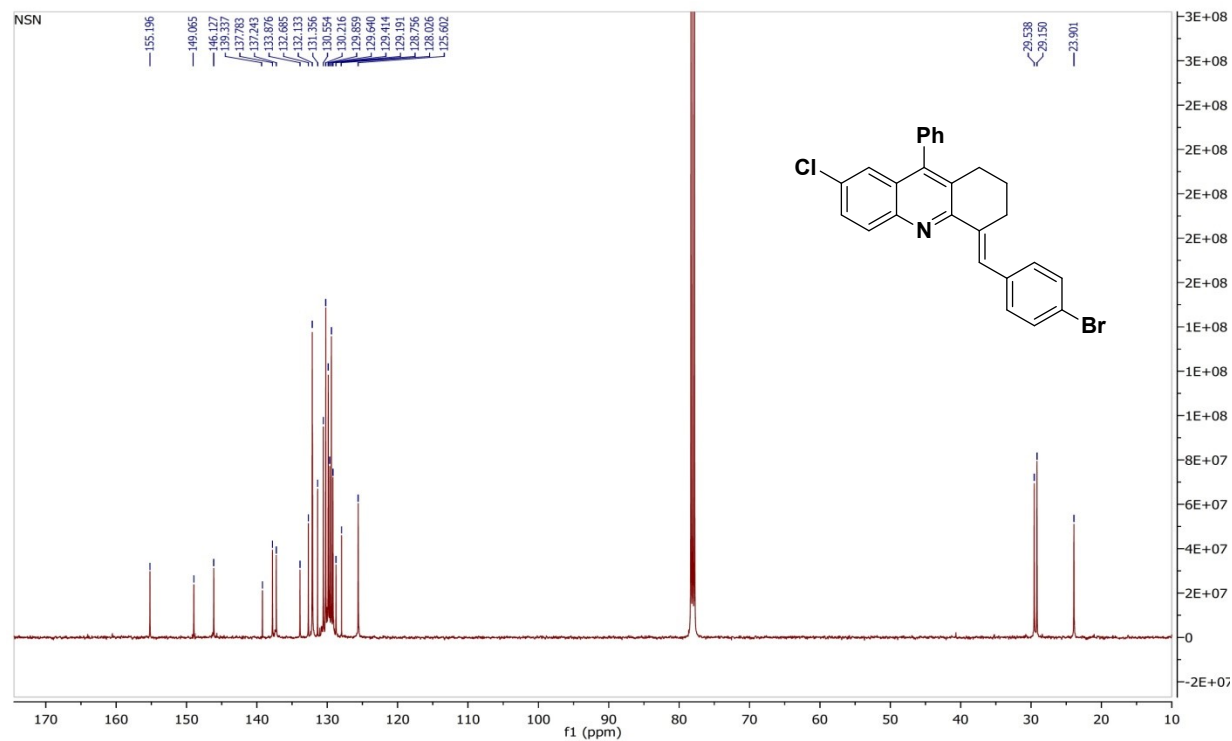
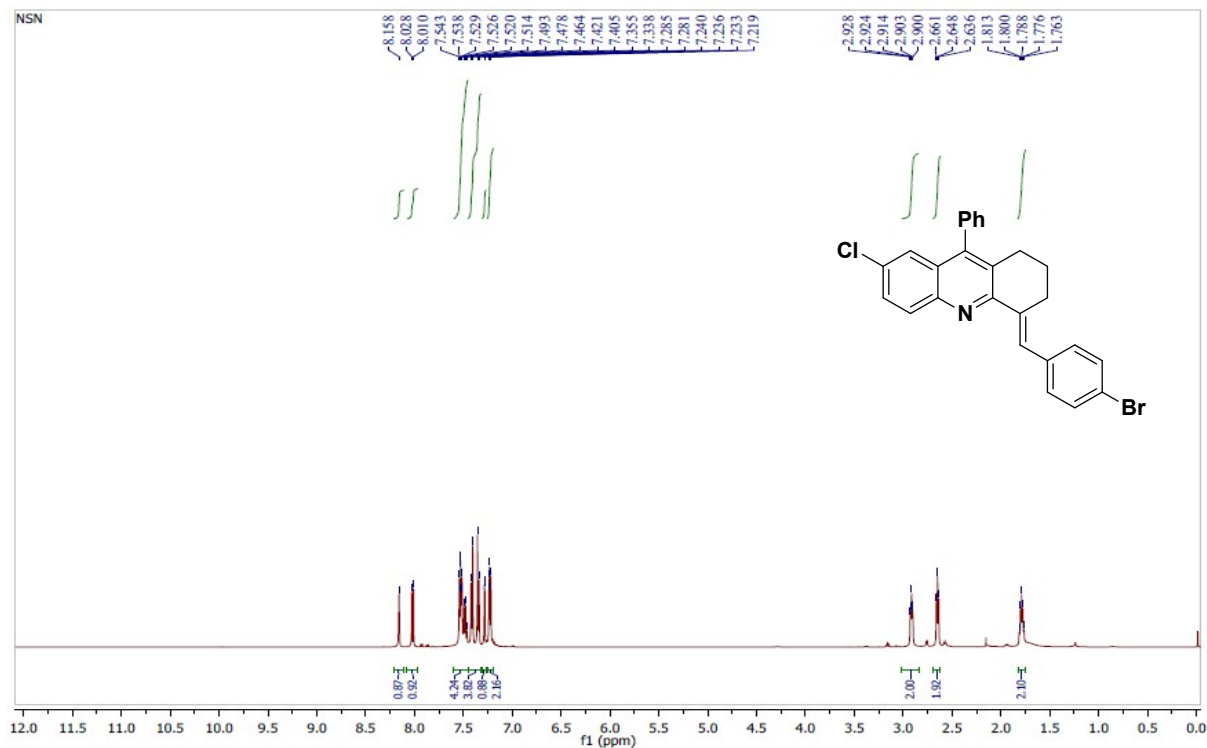


**7-Chloro-4-(4-chlorobenzylidene)-9-phenyl-1,2,3,4-tetrahydroacridine (7h):**

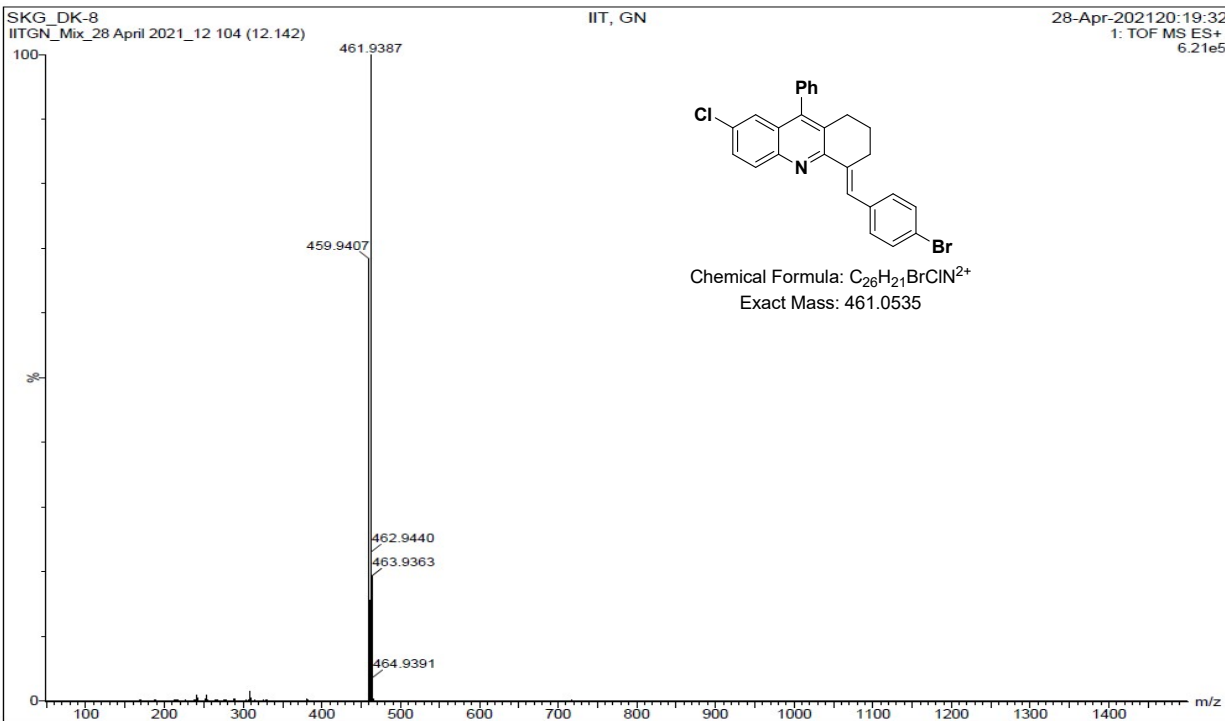




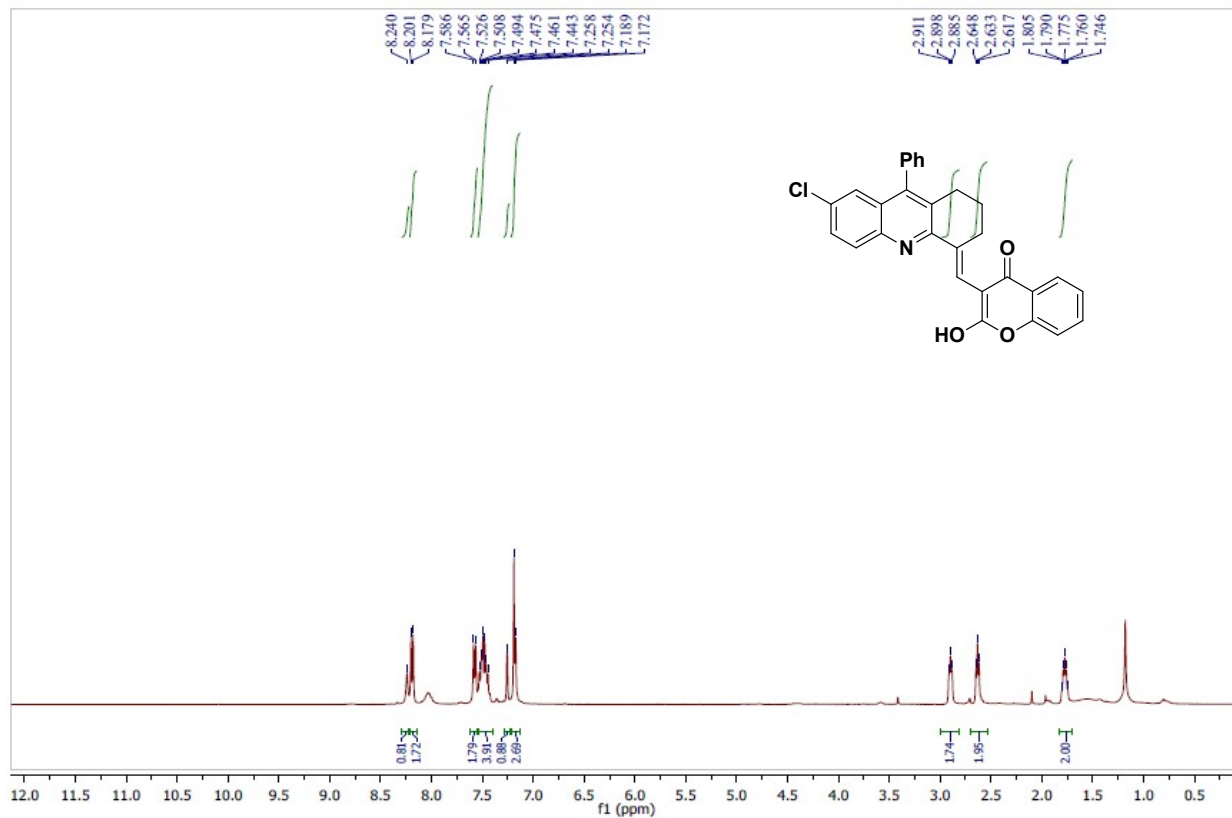
**4-(4-Bromobenzylidene)-7-chloro-9-phenyl-1,2,3,4-tetrahydroacridine (7i):**

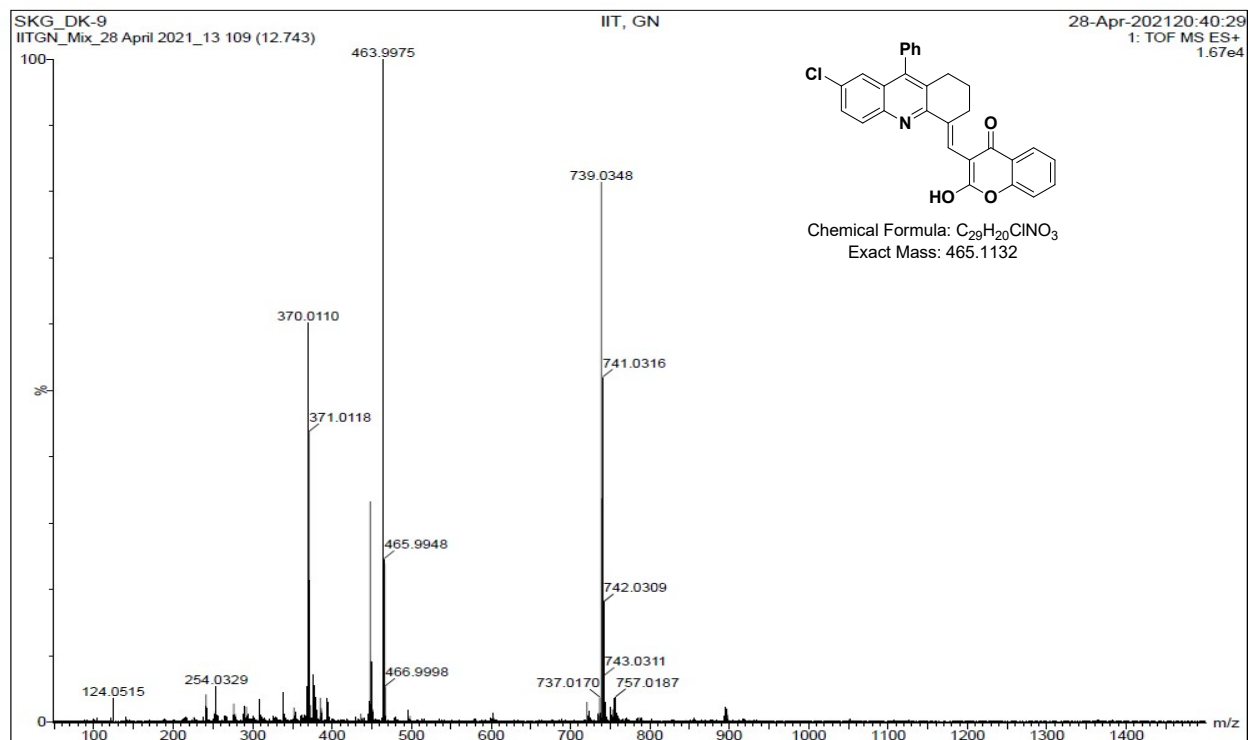
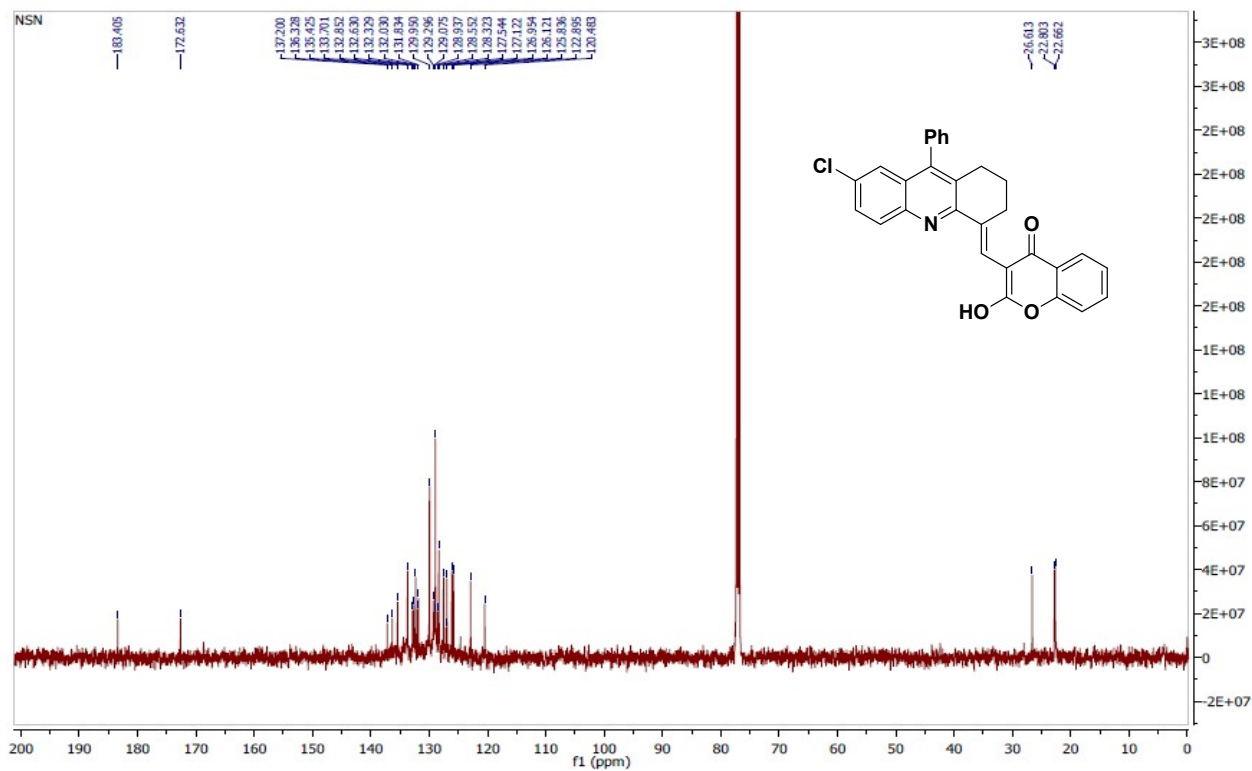


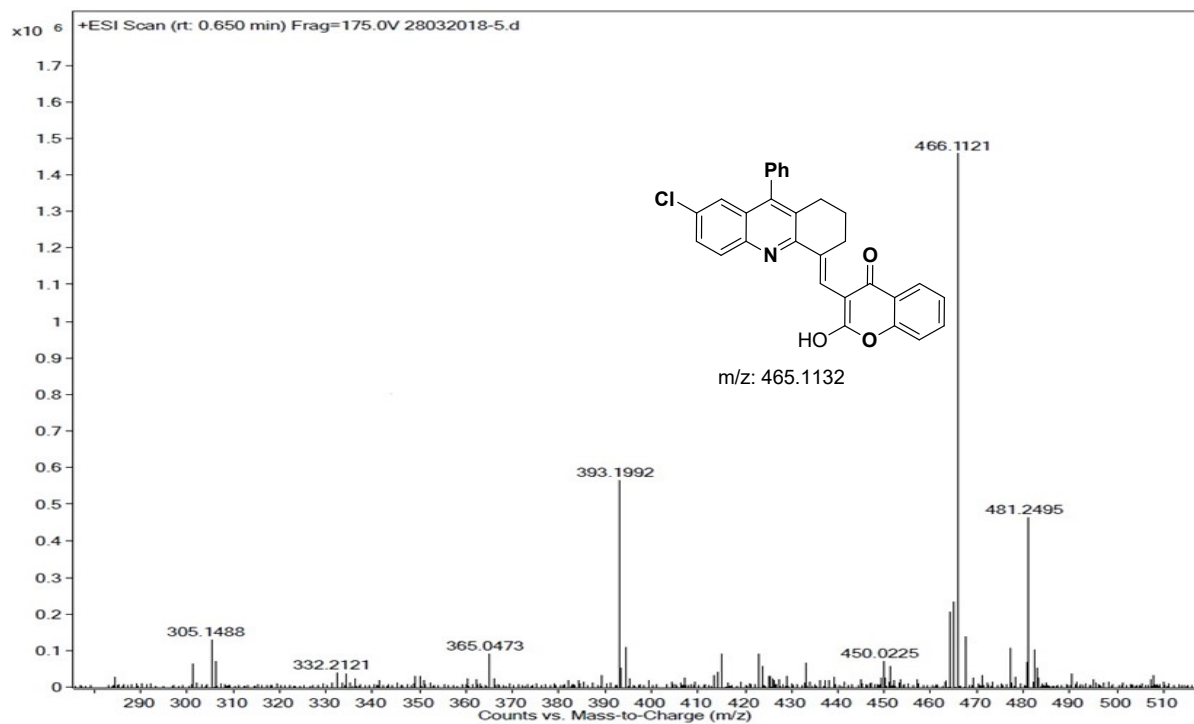




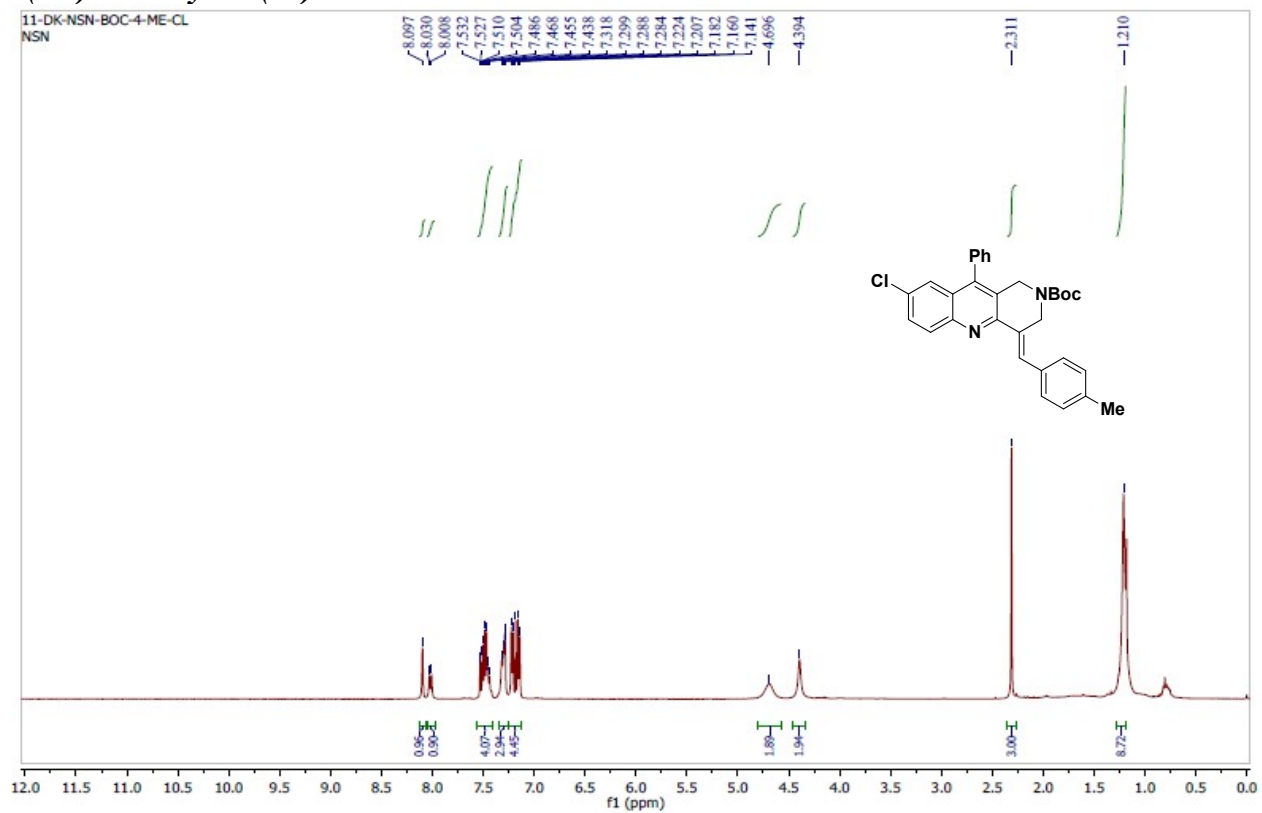
**3-((7-Chloro-9-phenyl-2,3-dihydroacridin-4(1H)-ylidene)methyl)-2-hydroxy-4H-chromen-4-one (7j):**

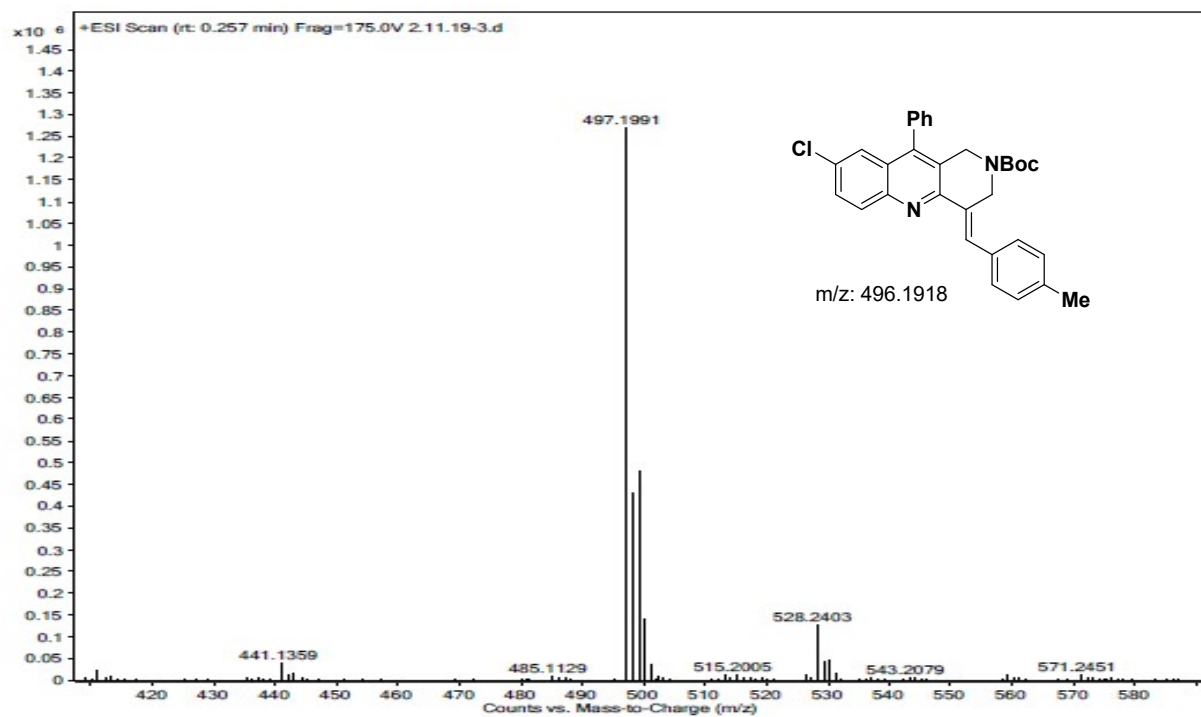
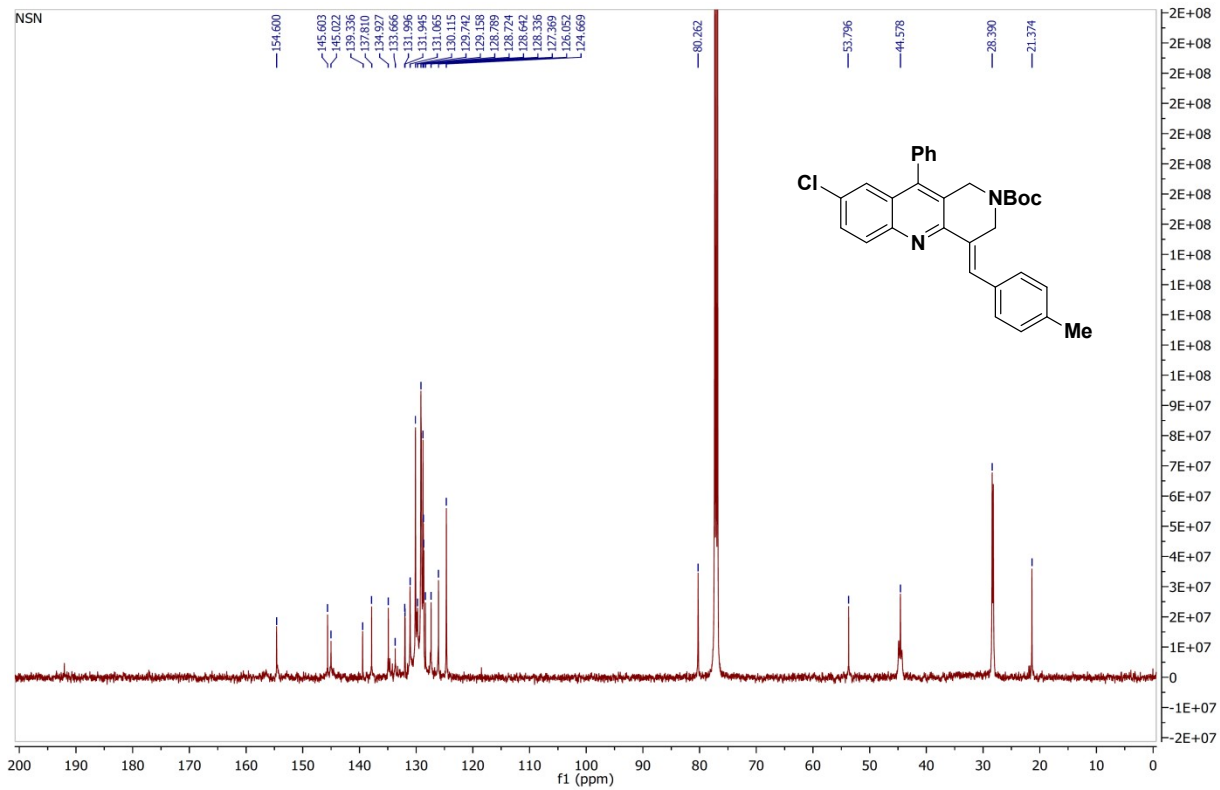




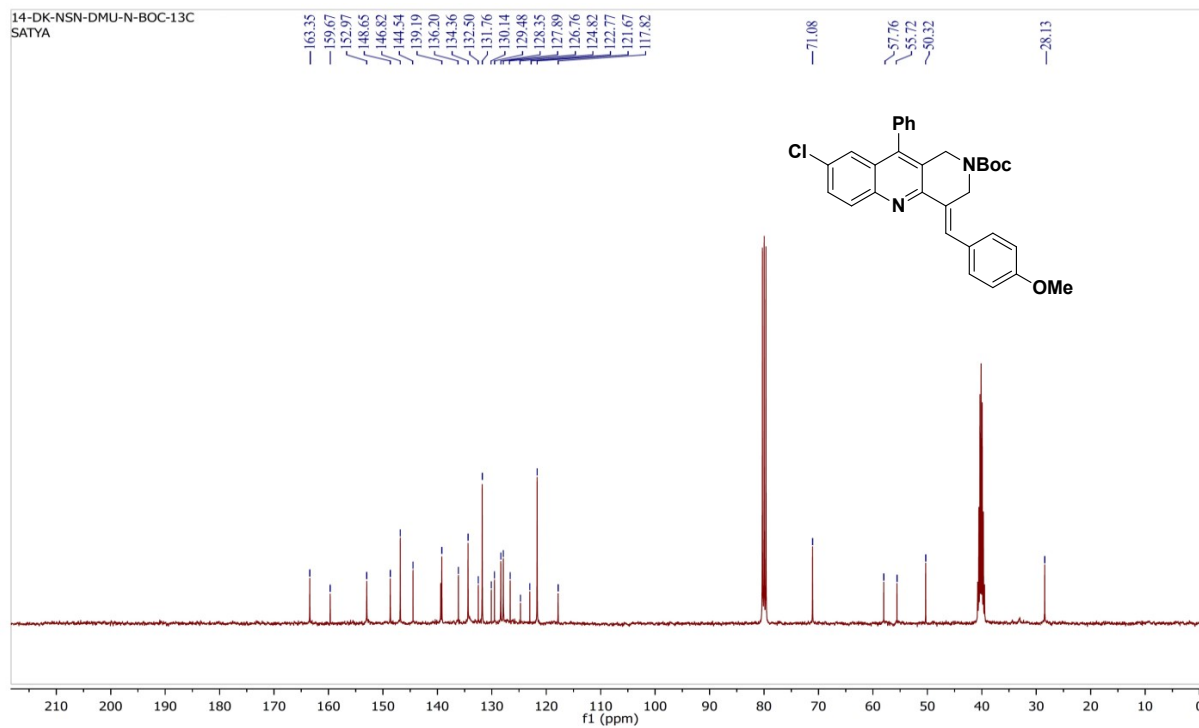
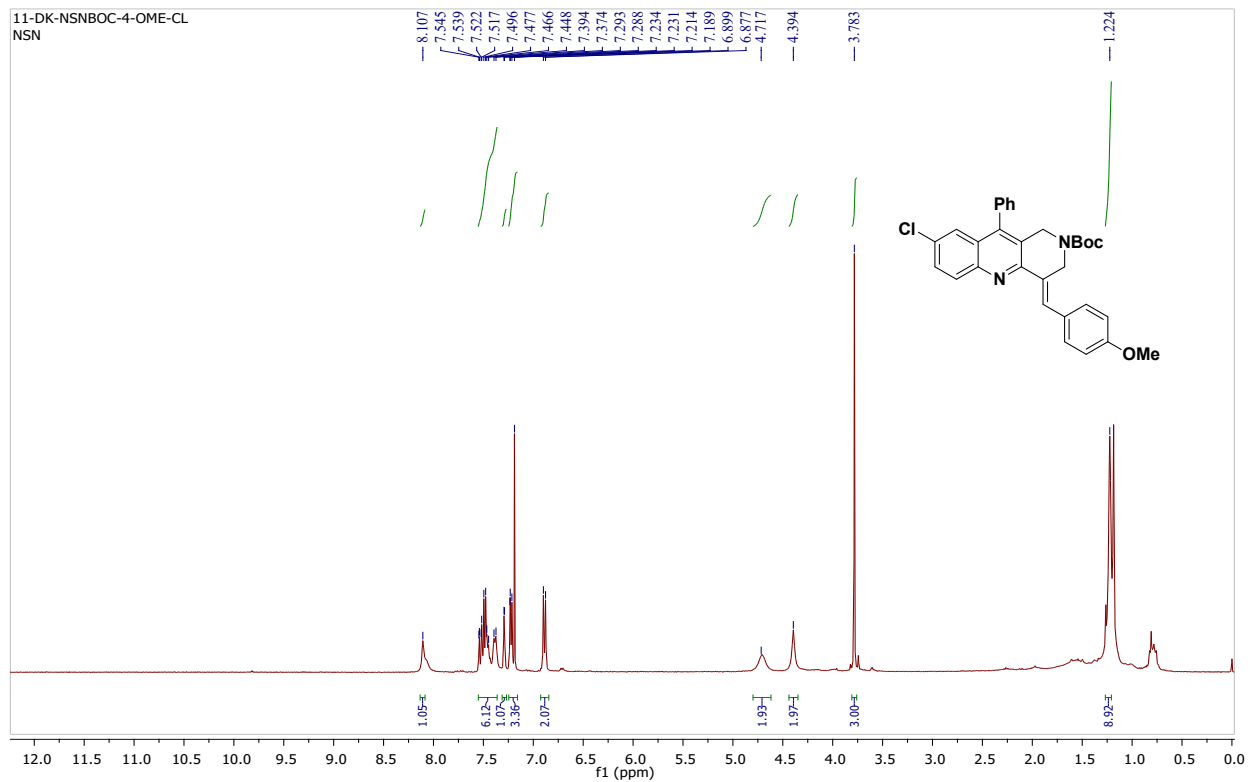


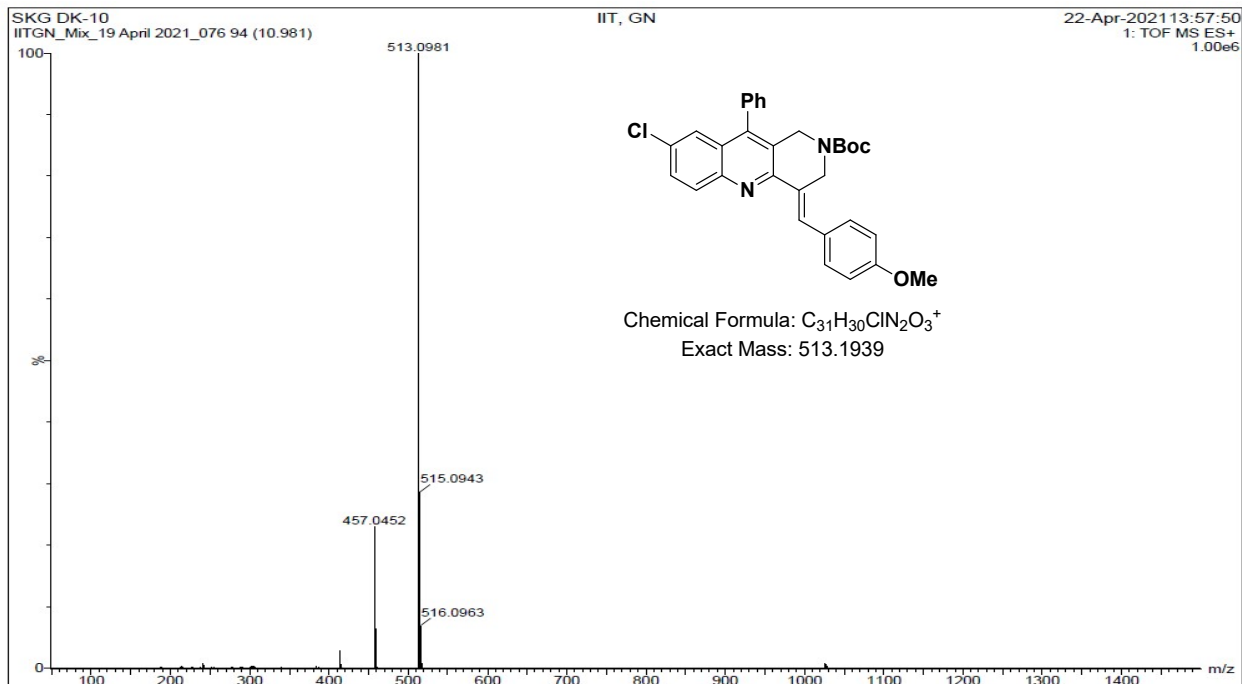
***Tert-butyl-8-chloro-4-(4-methylbenzylidene)-10-phenyl-3,4-ihydrobenzo[b][1,6]naphthyridine-2(1H)-carboxylate (8a):***



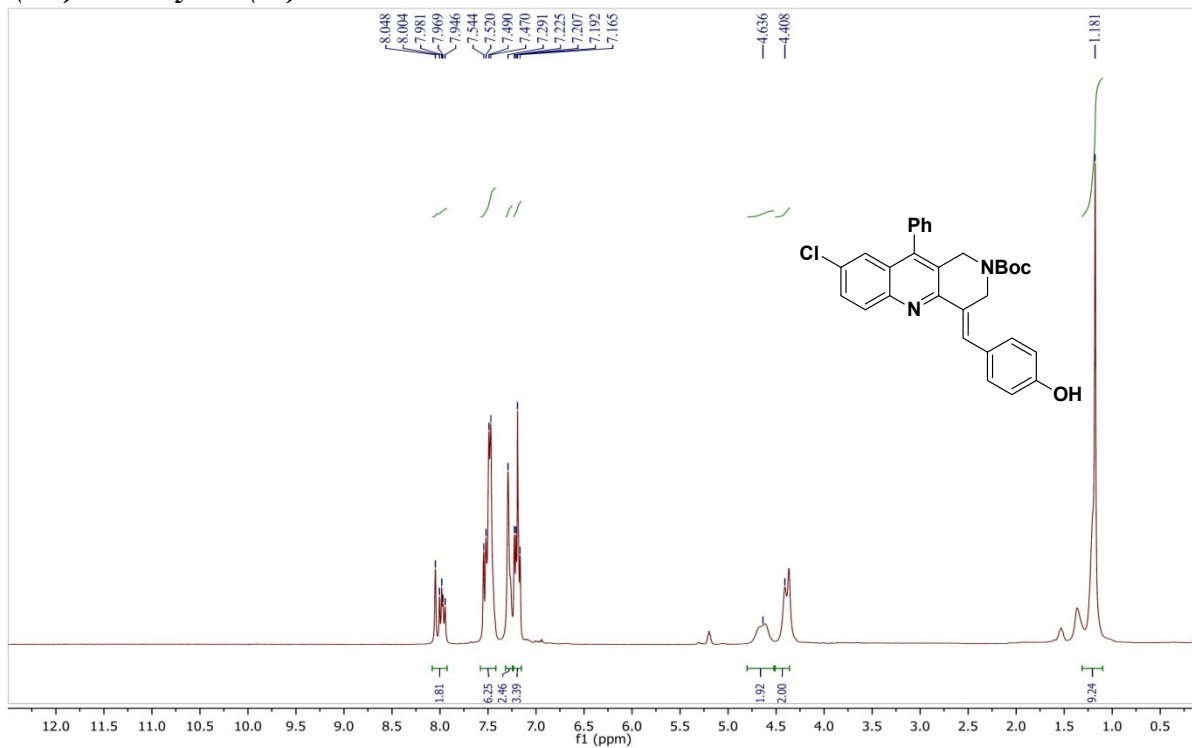


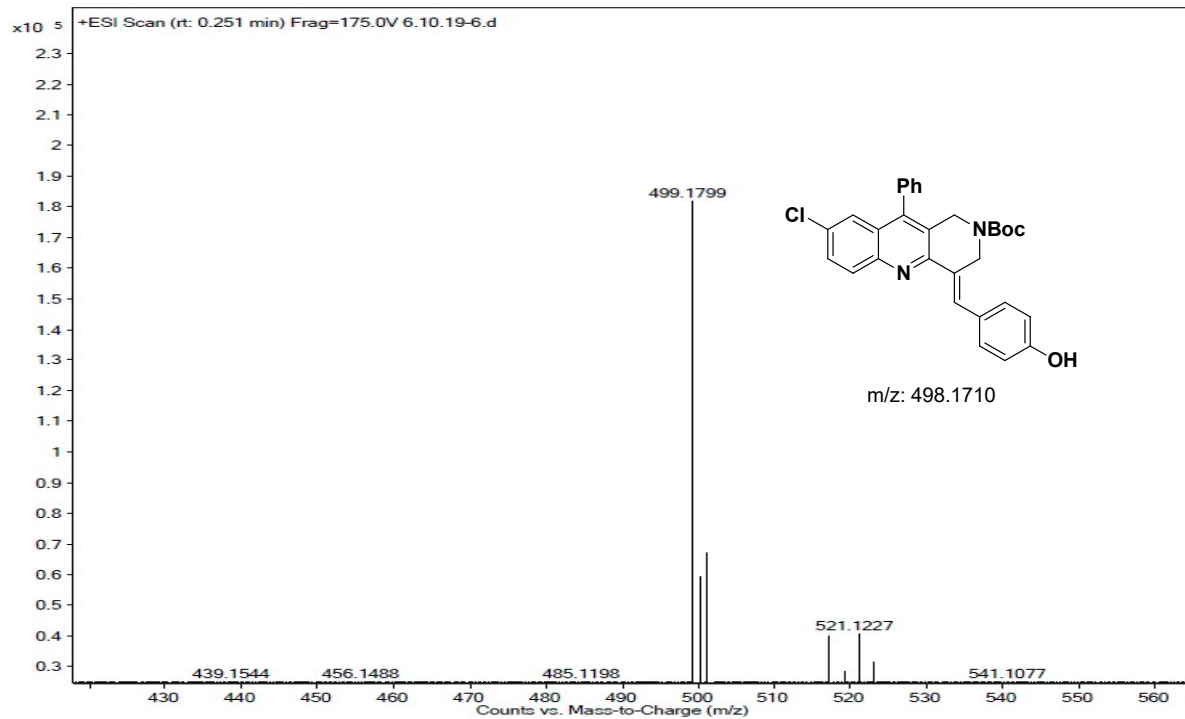
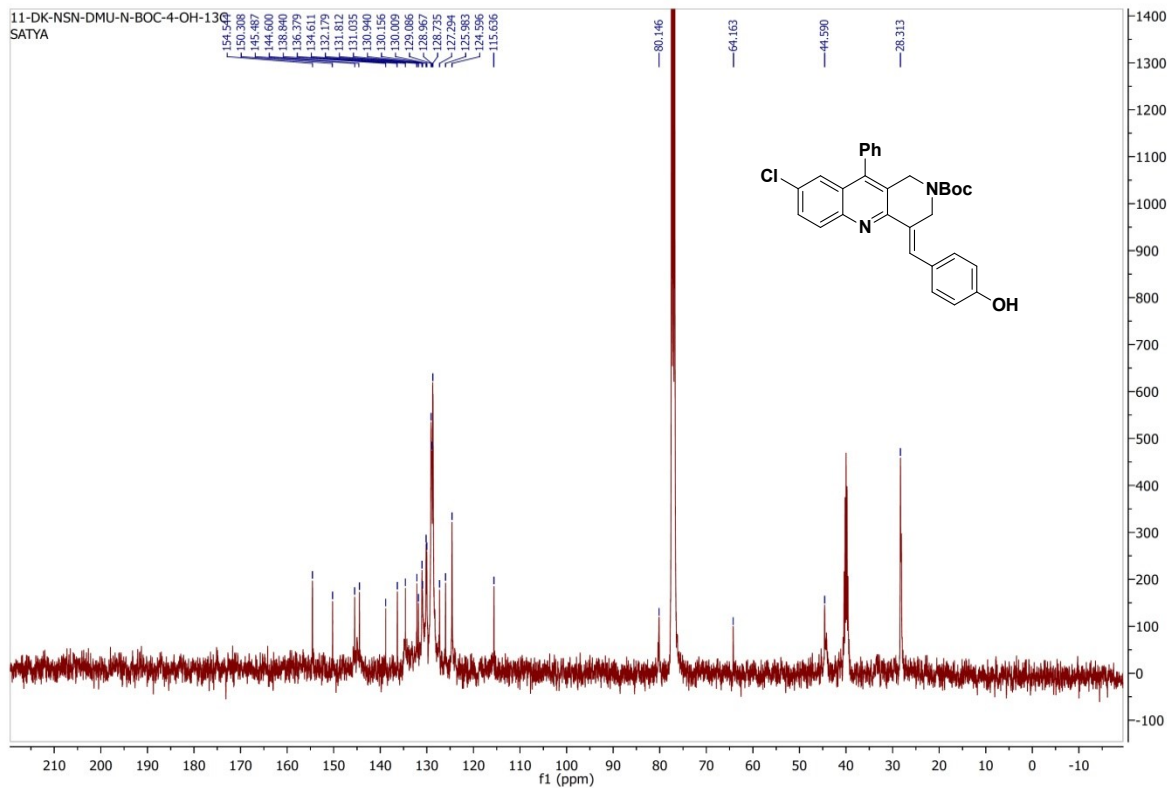
***Tert-butyl-8-chloro-4-(4-methoxybenzylidene)-10-phenyl-3,4-dihydrobenzo[b]-[1,6]-naphthyridine-2(1H)-carboxylate (8b):***



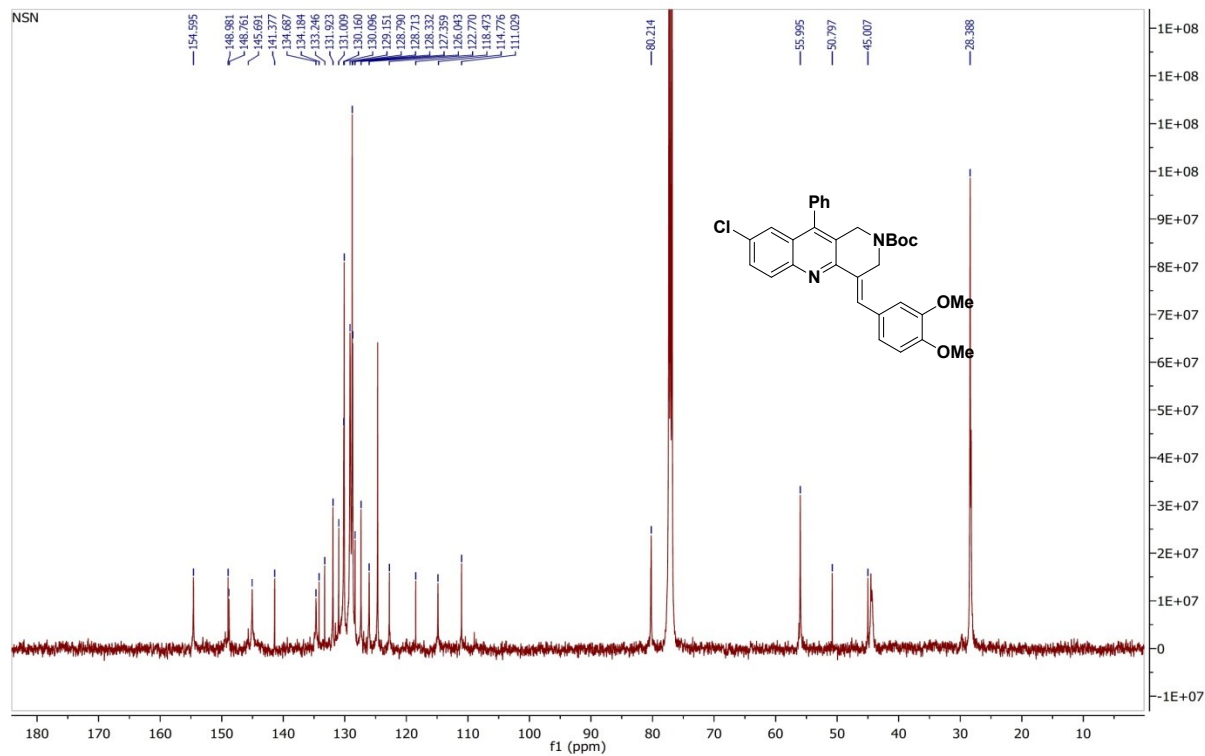
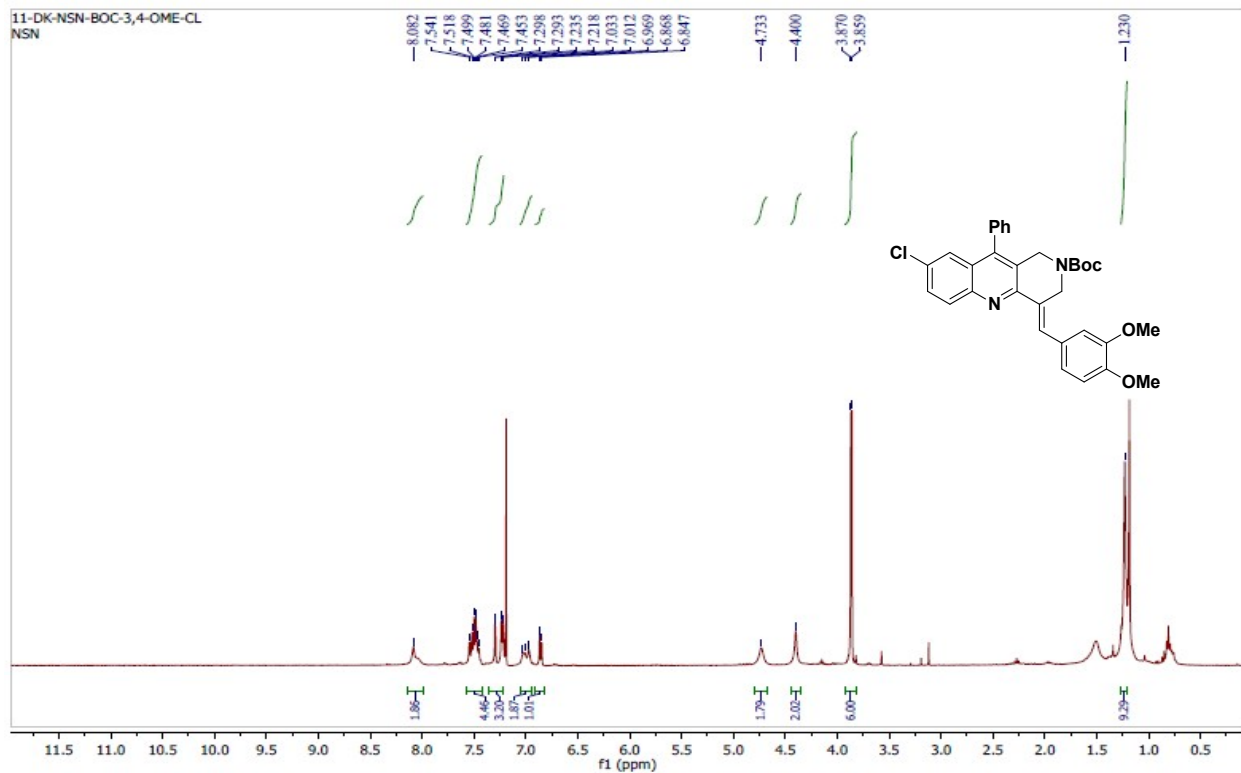


***Tert-butyl-8-chloro-4-(4-hydroxybenzyl)-10-phenyl-3,4-dihydrobenzo-[b][1,6]naphthyridine-2(1H)-carboxylate (8c):***

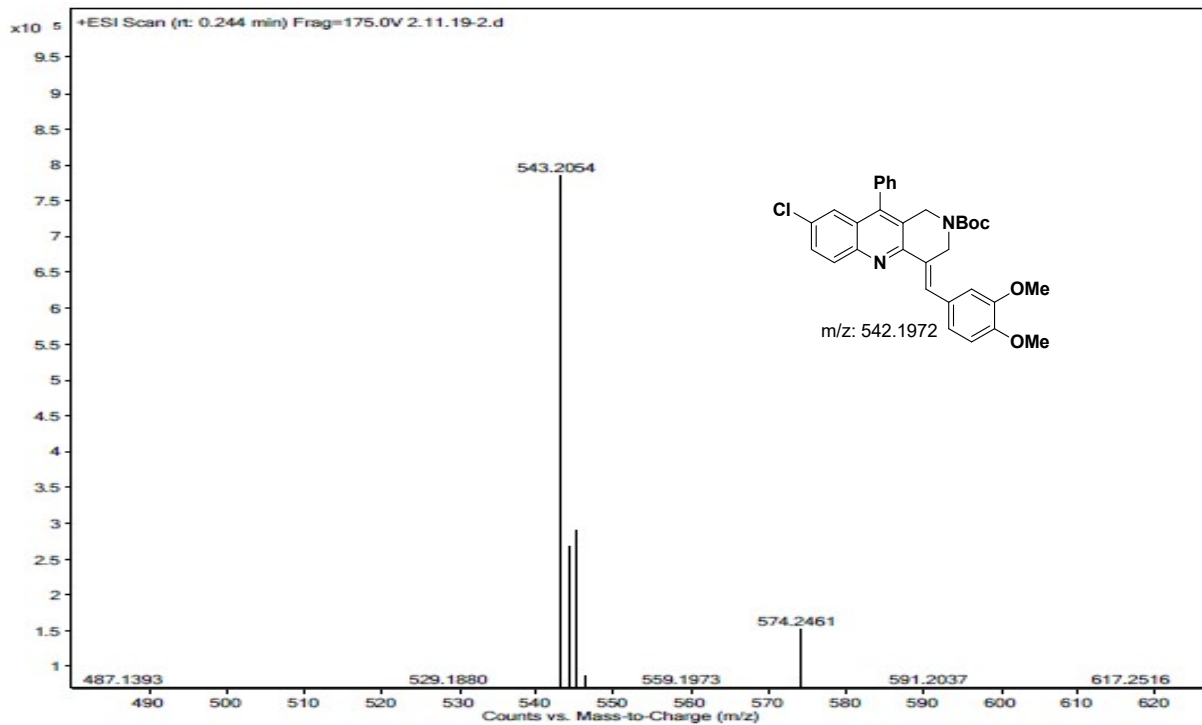




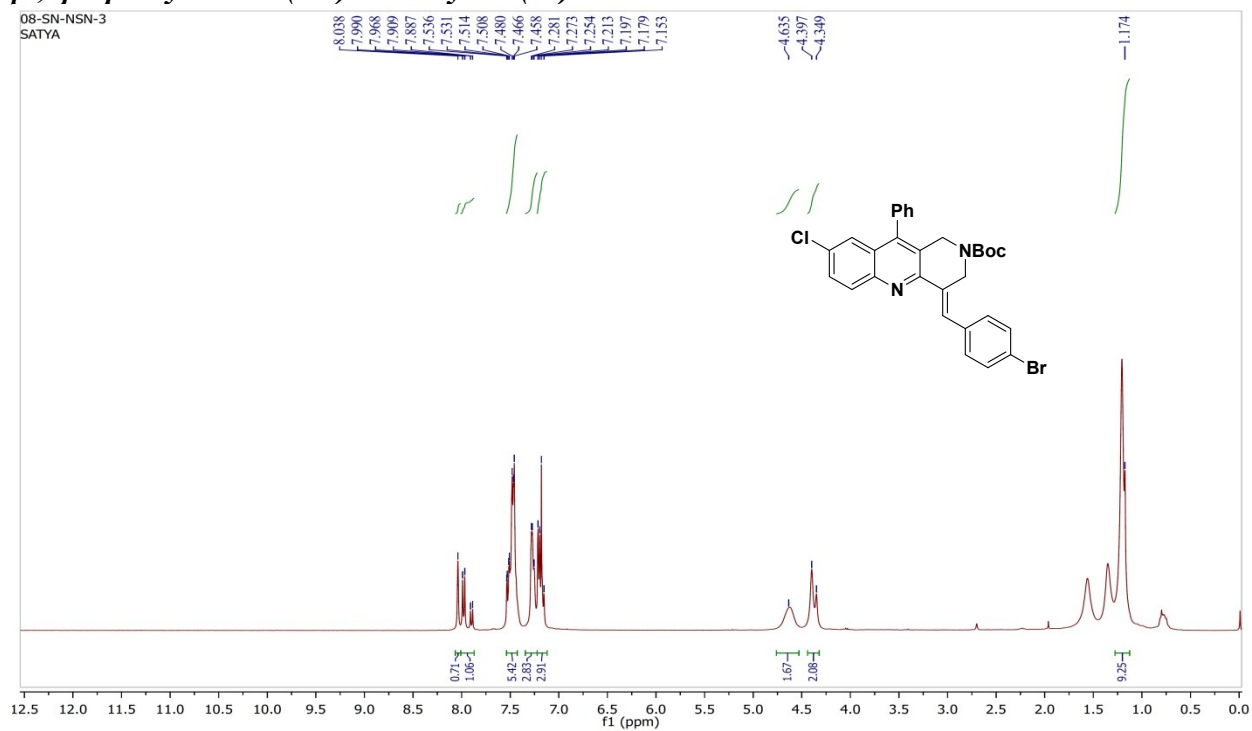
***Tert-butyl-8-chloro-4-(3,4-dimethoxybenzylidene)-10-phenyl-3,4-dihydrobenzo[b][1,6]naphthyridine-2(1H)-carboxylate (8d):***

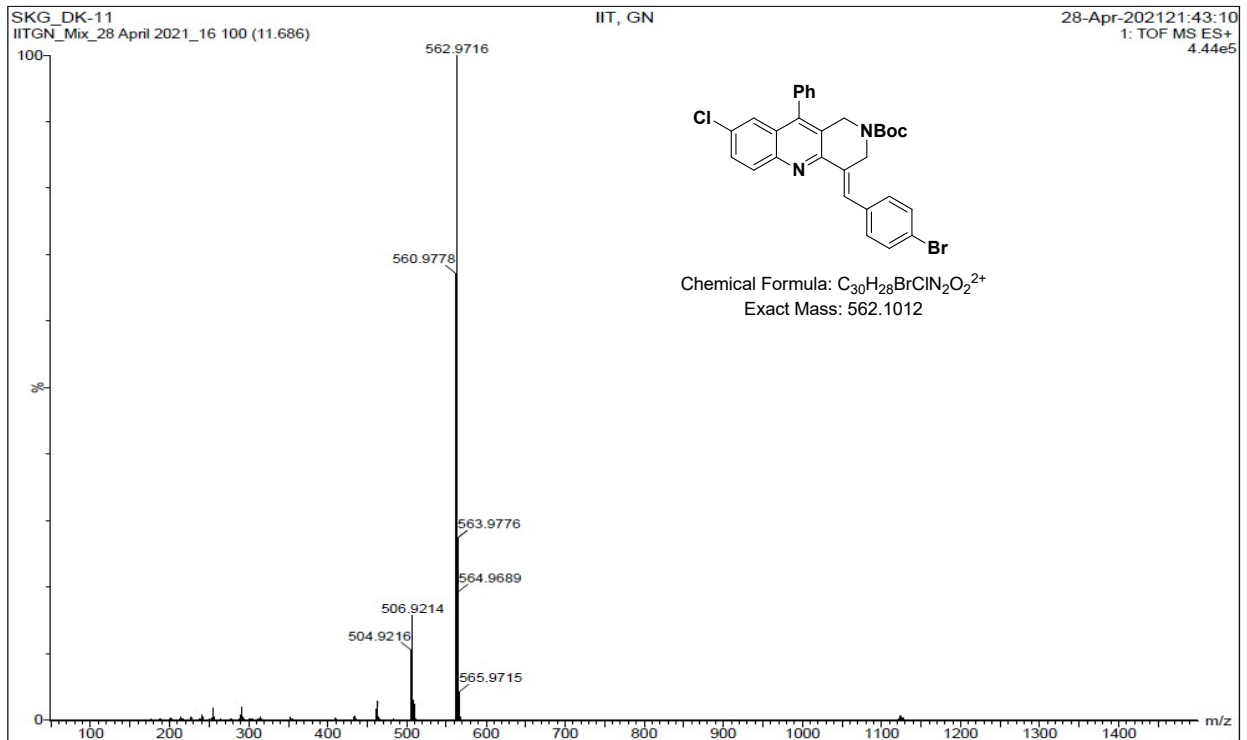
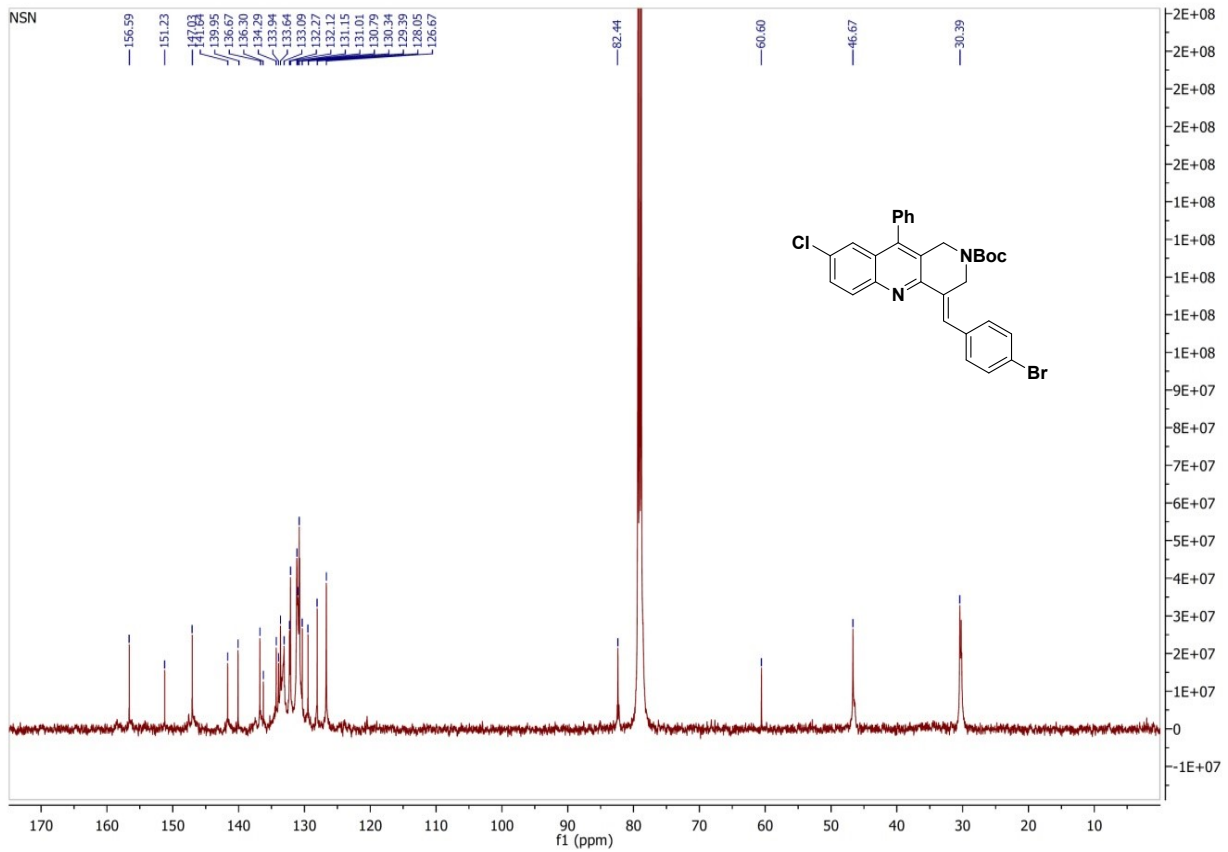


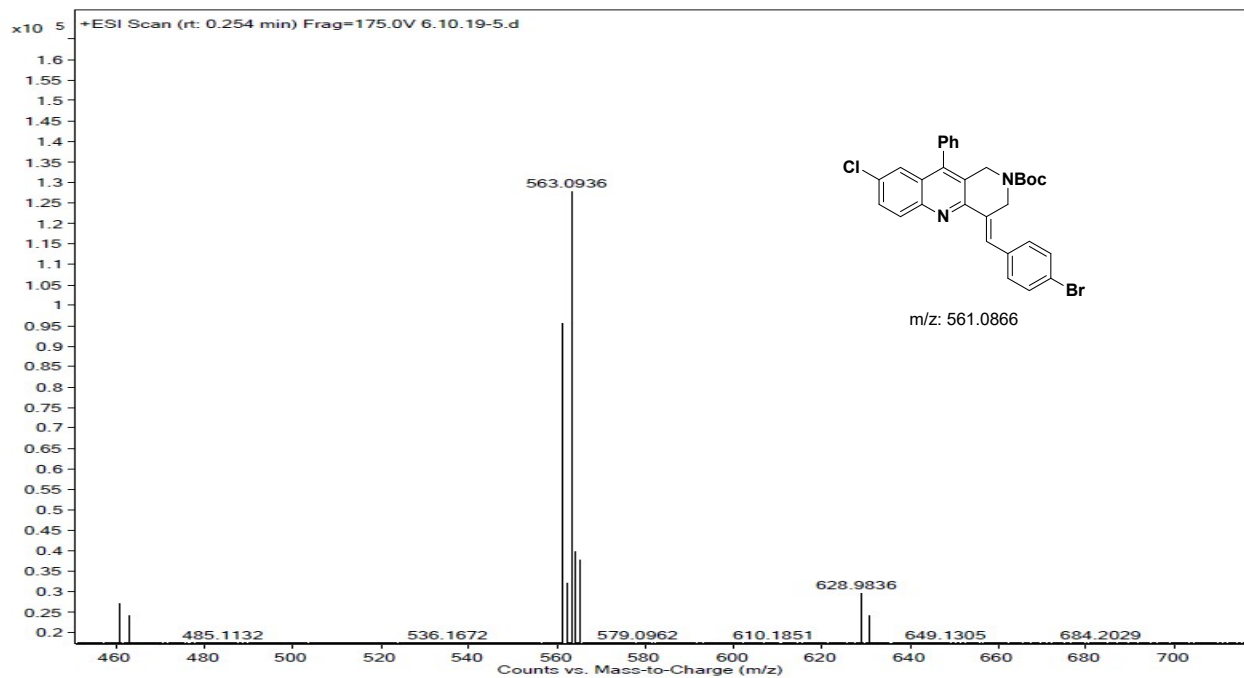




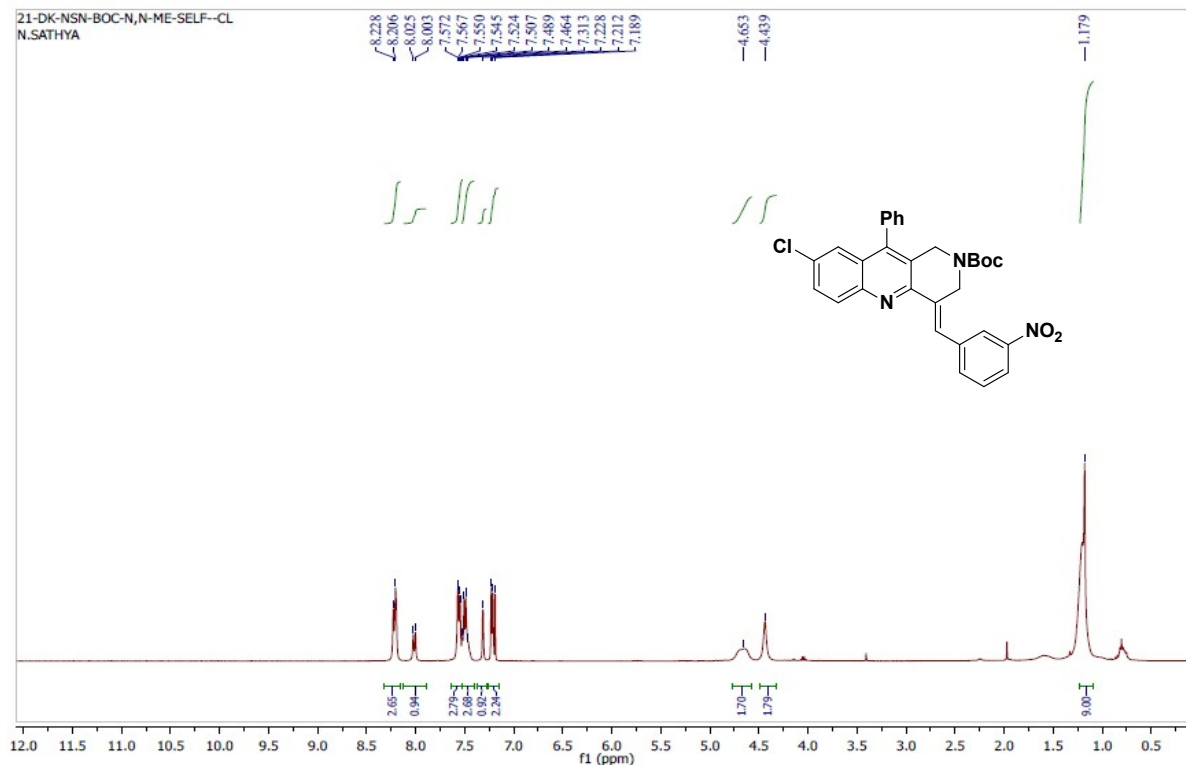
***Tert-butyl-4-(4-bromobenzylidene)-8-chloro-10-phenyl-3,4-dihydrobenzo[b][1,6]naphthyridine-2(1H)-carboxylate (8e):***

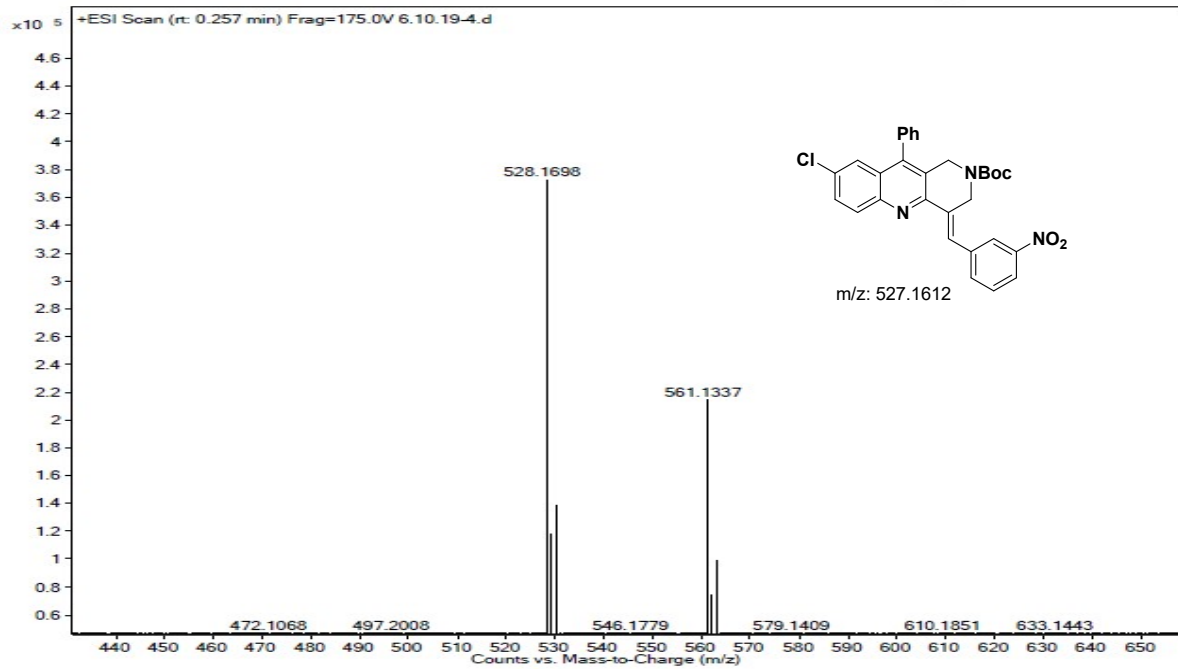
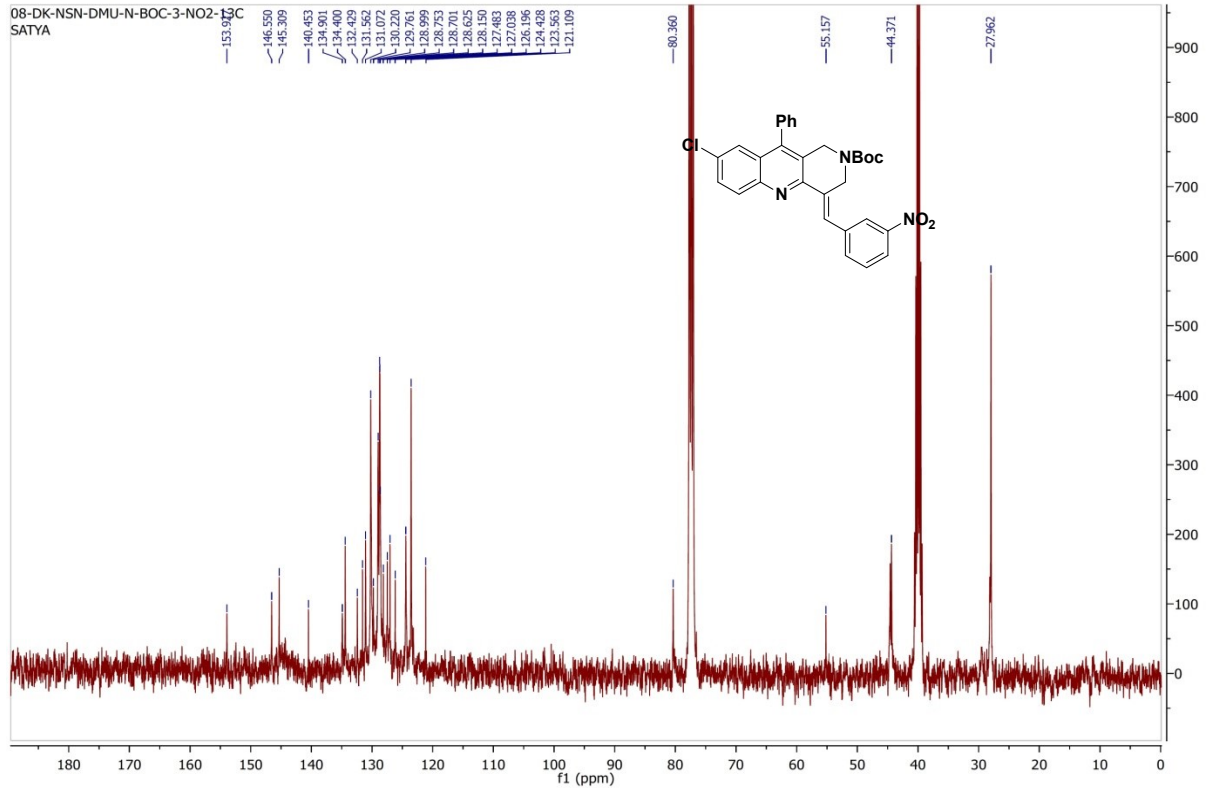




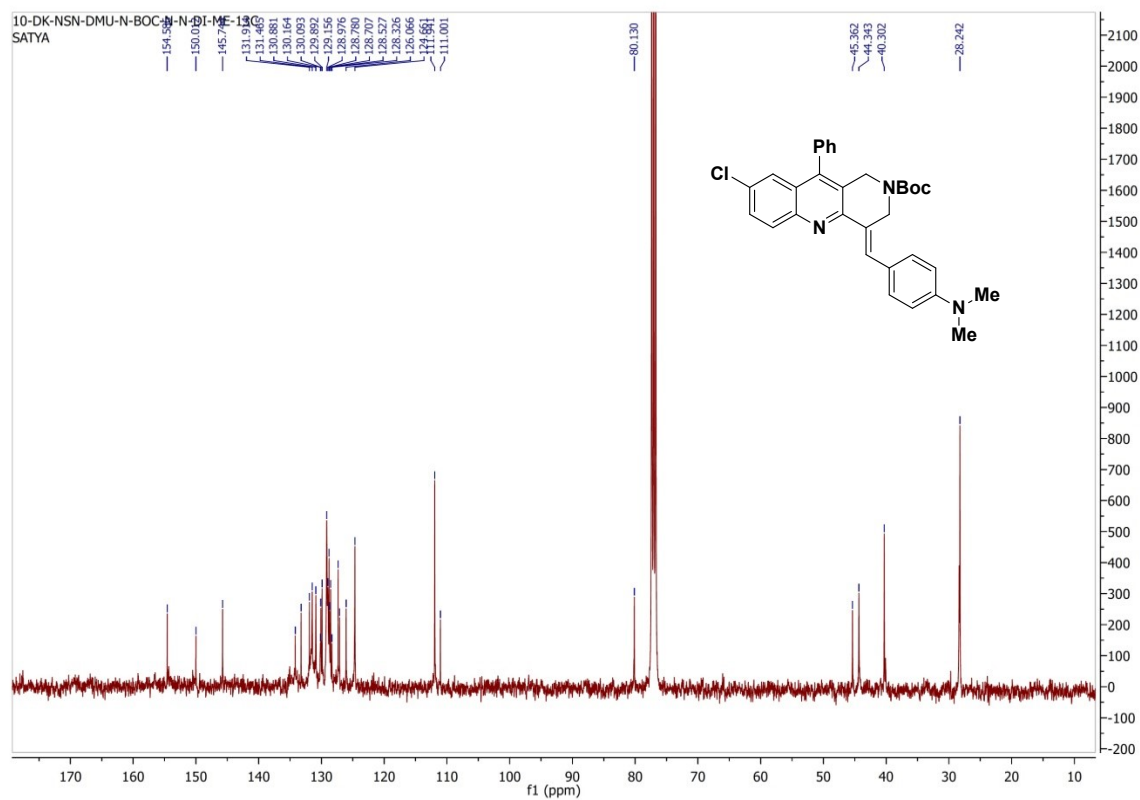
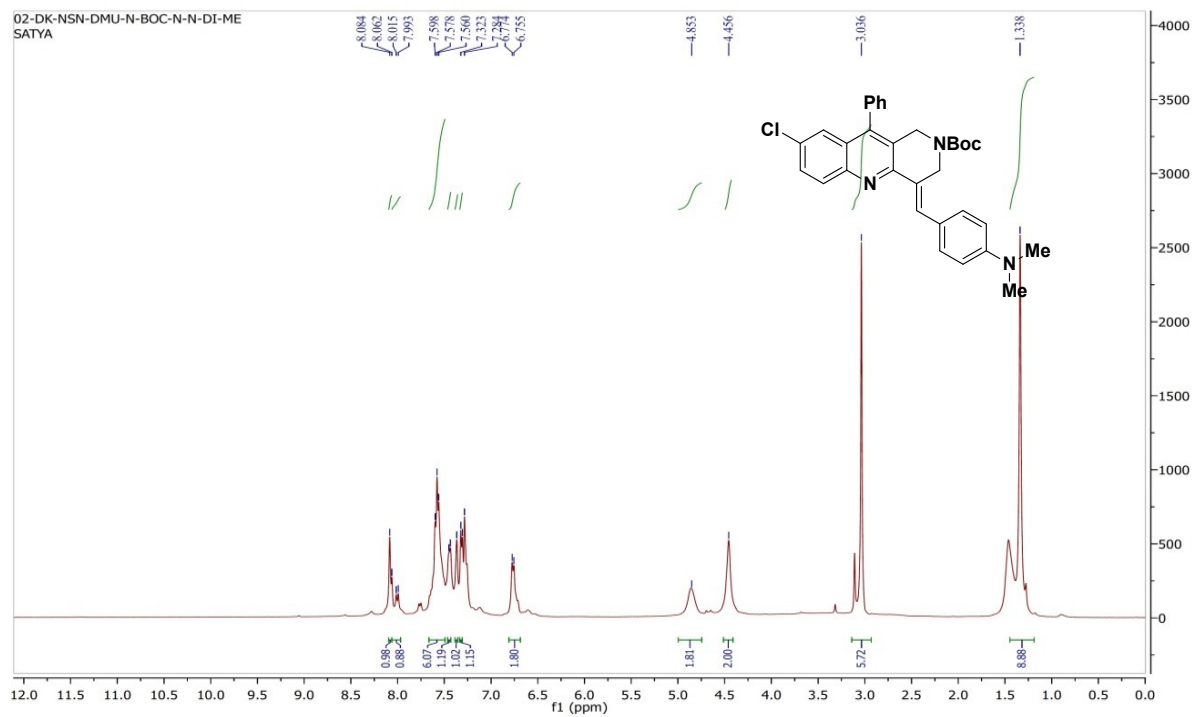


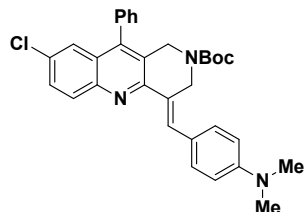
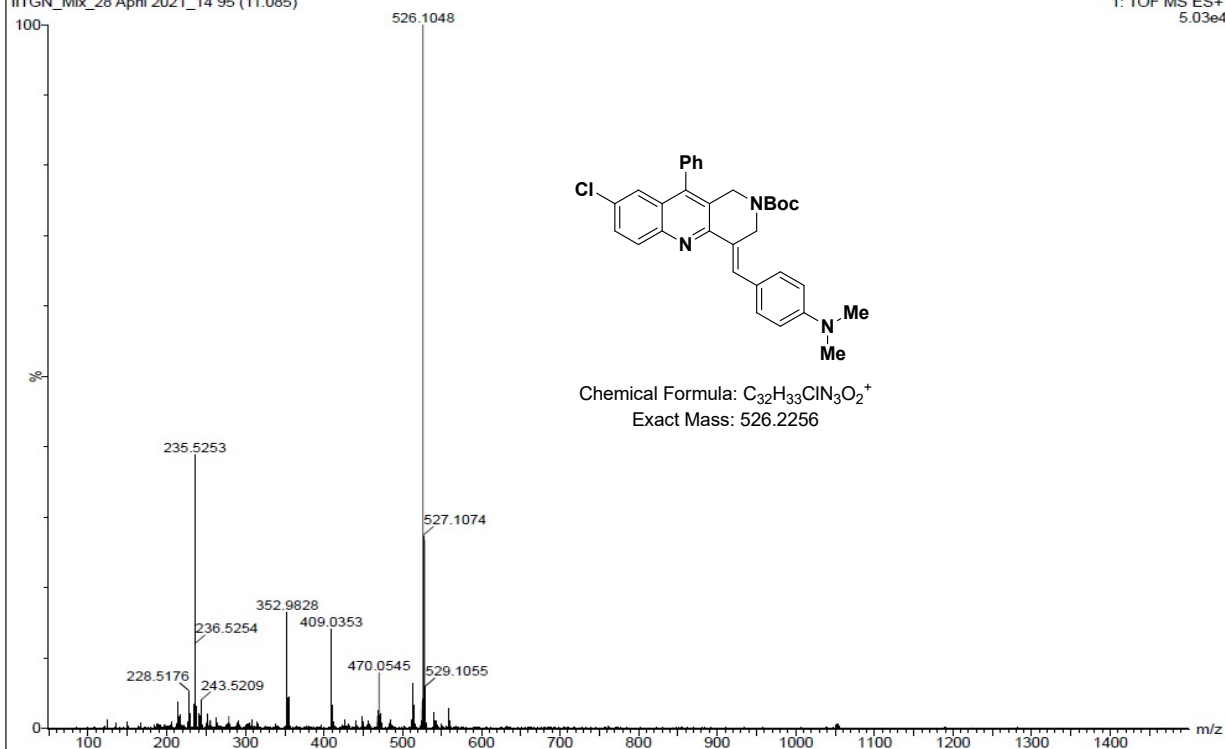
***Tert-butyl-8-chloro-4-(4-nitrobenzylidene)-10-phenyl-3,4-dihydrobenzo[b][1,6]naphthyridine-2(1H)-carboxylate (8f):***





***Tert-butyl-8-chloro-4-(4-(dimethylamino)benzylidene)-10-phenyl-3,4-dihydrobenzo[b][1,6]naphthyridine-2(1H)-carboxylate (8g):***





Chemical Formula: C<sub>32</sub>H<sub>33</sub>ClN<sub>3</sub>O<sub>2</sub><sup>+</sup>  
Exact Mass: 526.2256

**NOESY of the compound 7h:**

**7-chloro-4-(4-chlorobenzylidene)-9-phenyl-1,2,3,4-tetrahydroacridine (7h):**

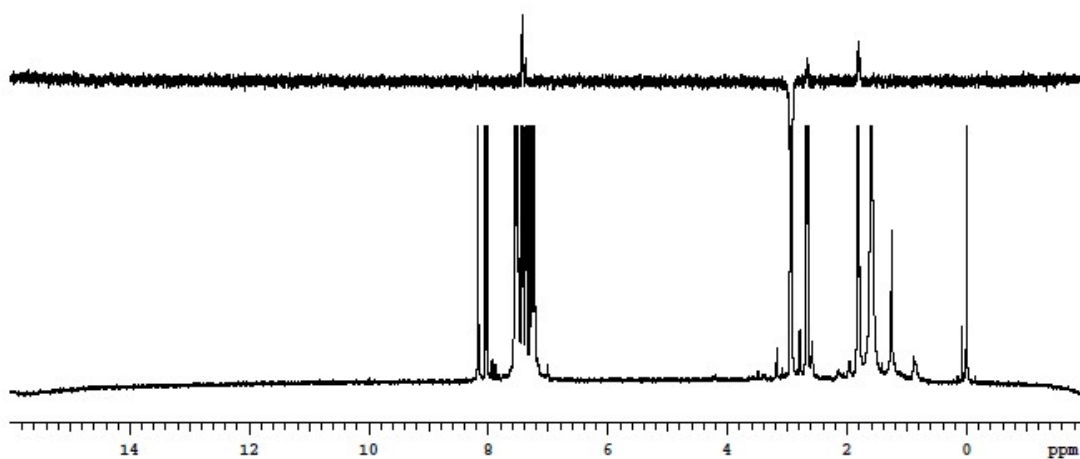
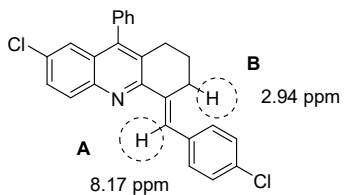
sample code: nx-7h-hex

selective band center: 2.94 (ppm); width: 30.7 (Hz)

VARIAN 400MHz NMR

solvent: cdcl3

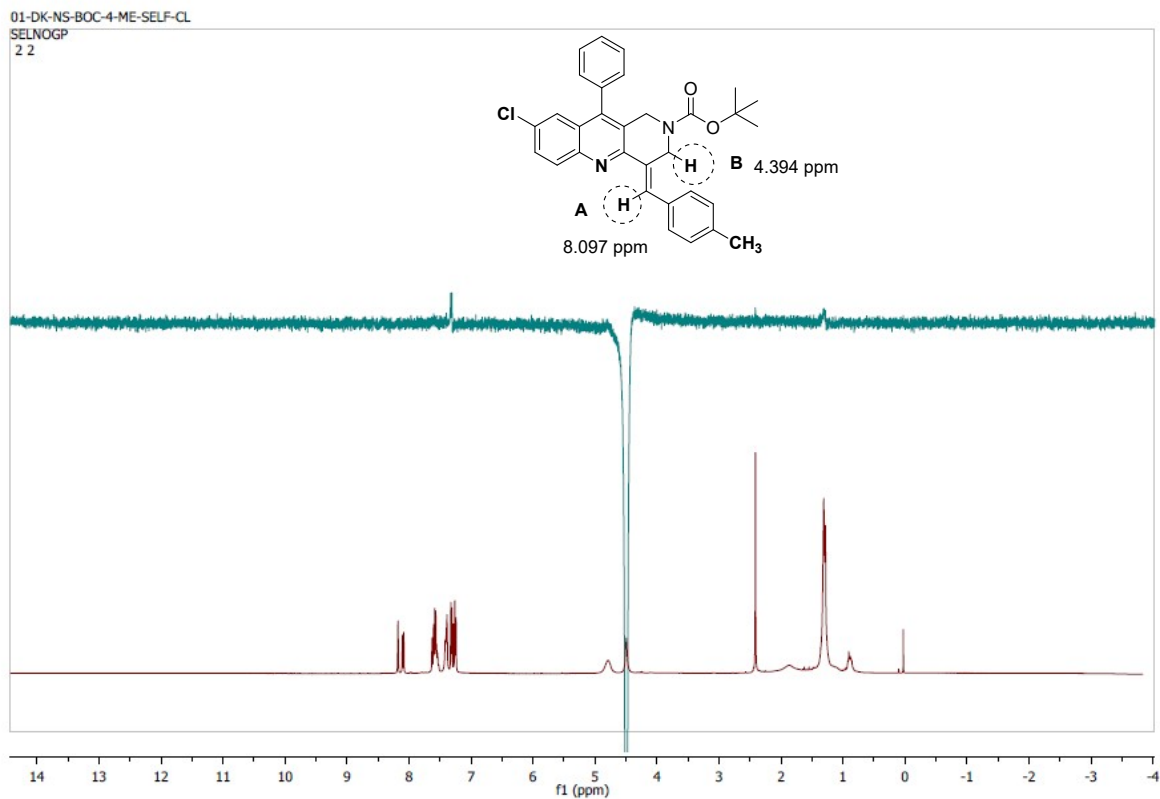
date: sep 30 2021



plotname: nx-7h-hex\_nmrvid\_01\_plot01

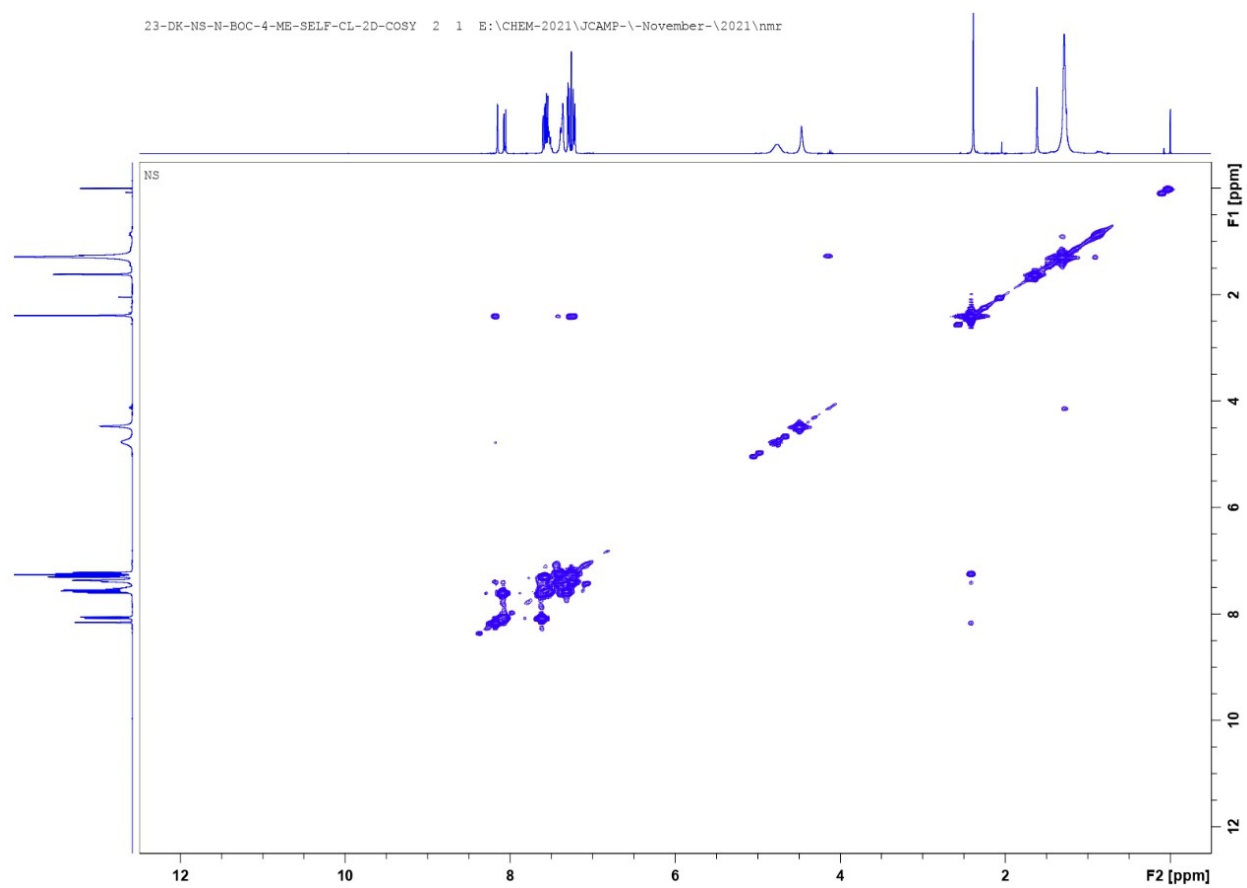
**NOESY of the compound 8a:**

**Tert-butyl-8-chloro-4-(4-methylbenzylidene)-10-phenyl-3,4-dihydrobenzo[b][1,6] naphthyridin-2(1H)-carboxylate (8a):**



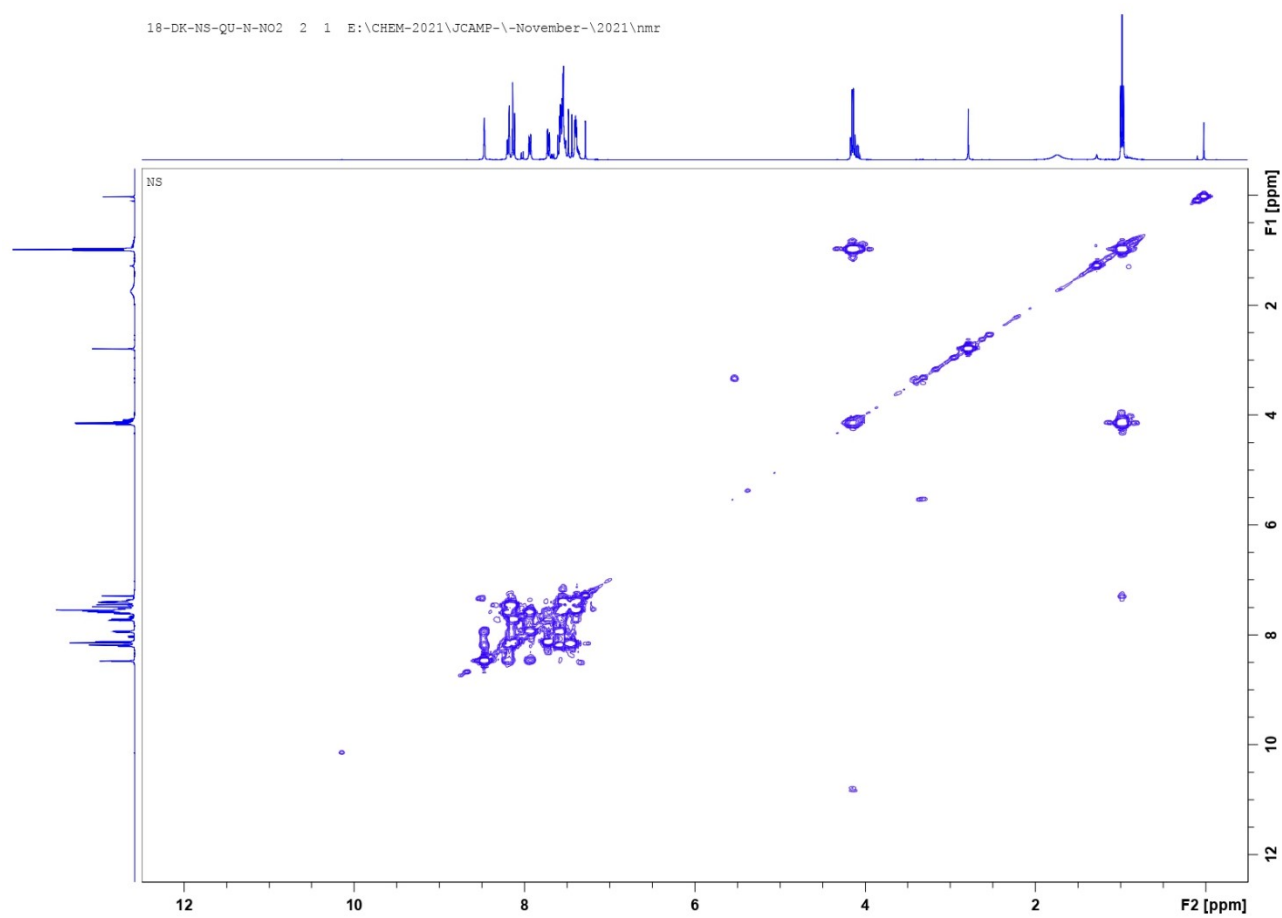


***COSY of the compound 8a:***



***COSY of the compound 5m:***

***Ethyl-6-chloro-2-(3-nitrostyryl)-4-phenylquinoline-3-carboxylate (5m):***



**Table-S1:** Photo physical properties data of the resulting acyclic/aliphatic compounds (**5a-6h**):

Compounds	$\lambda_{\text{Abs}}$ (nm)	$\lambda_{\text{em}}$ (nm)	Stokes shift ( $\Delta\lambda$ nm)
5n	375	557	182
5o	426	488	65
5p	425	525	100
6b	394	502	108
6f	458	548	90
6h	400	484	84

**Table-S2:** Photo physical properties data of the resulting cyclic compounds (**7a-8d**):

Compounds	$\lambda_{\text{Abs}}$ (nm)	$\lambda_{\text{em}}$ (nm)	Stokes shift ( $\Delta\lambda$ nm)
7a	441	494	53
7b	420	551	131
7c	536	644	108
7d	411	464	53
8a	400	464	64
8c	390	449	59
8d	420	558	138

**Table-S3:** Data of the solvatochromic effect of compound **7e** in various solvents.

solvent	$\lambda_{\text{Abs}}$ (nm)	$\lambda_{\text{em}}$ (nm)	Stokes shift ( $\Delta\lambda$ nm)
<i>n</i> -Hexane	456	543	87
DCM	498	568	70
CHCl <sub>3</sub>	488	553	65
Acetone	485	585	100
MeOH	496	597	101
MeCN	470	618	148
DMF	514	601	87
DMSO	511	605	94