

## Supporting Information

### **Metal-free aerobic one-pot synthesis of substituted/annulated quinolines from alcohols via indirect Friedländer annulation**

Namrata Anand, Suvajit Koley, B. Janaki Ramlu and Maya Shankar Singh\*

Department of Chemistry, Faculty of Science, Banaras Hindu University, Varanasi-221005, India

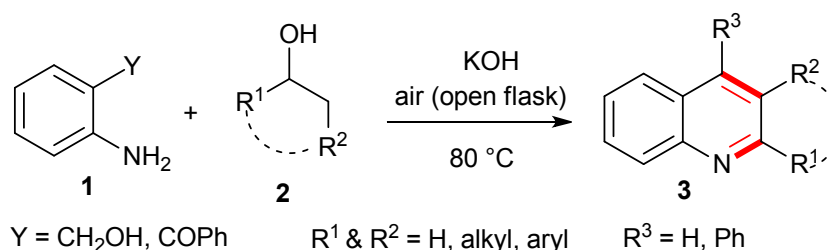
<b>Table of contents</b>	<b>Pages</b>
1. General experimental details	2
2a. General procedure	2
2b. Characterization of compounds <b>3</b>	3-13
3. References	13
4. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra	14-43

## Experimental Section

### 1. General Experimental Details

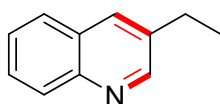
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 300 and 75 MHz, respectively. Chemical shift ( $\delta$ ) values are given in parts per million (ppm) with reference to tetramethylsilane (TMS) as the internal standard. Coupling constant ( $J$ ) values are given in Hertz (Hz). Melting points were determined with Buchi B-540 melting point apparatus and are uncorrected. Commercially obtained reagents were used after further purification when needed. All the reactions were monitored by TLC with silica gel coated plates. Column chromatography was carried out whenever needed, using silica gel of 100/200 mesh. Mixture of hexane/ethyl acetate in appropriate proportion (determined by TLC analysis) was used as eluent.

### 2. a. General experimental procedure for the synthesis of quinolines **3**

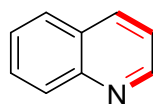


A mixture of 2-aminobenzyl alcohol **1a**/2-aminobenzophenone **1b** or **1c** (1.0 mmol), alcohol **2** (4 mmol) and KOH (5 mmol) was stirred at 80 °C for 6-10 h. After completion of the reaction (monitored by TLC), the mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate, filtered and the solvent was removed under reduced pressure. The crude residue thus obtained was purified over silica gel column chromatography using ethyl acetate-hexane mixture to give the desired quinolines **3** in good to excellent yields.

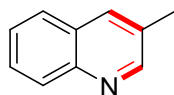
## 2. b. Characterization of Compounds



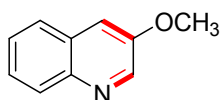
**3-Ethyl quinoline (3aa)**<sup>1</sup>: Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.75 (d, *J* = 1.8 Hz, 1H, ArH), 8.09 (d, *J* = 8.1 Hz, 1H, ArH), 7.79 (s, 1H, ArH), 7.68 (d, *J* = 7.5 Hz, 1H, ArH), 7.61-7.56 (m, 2H, ArH), 7.46-7.41 (m, 1H, ArH), 2.76 (q, *J* = 7.5 Hz, 2H, CH<sub>2</sub>), 1.27 (t, *J* = 7.5 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 151.3, 146.3, 136.2, 133.0, 128.6, 128.1, 127.8, 126.9, 126.1, 25.8, 14.6.



**Quinoline (3ab)**<sup>2</sup>: Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.89 (d, *J* = 2.7 Hz 1H, ArH), 8.13-8.09 (m, 2H, ArH), 7.78-7.75 (m, 1H, ArH), 7.71-7.66 (m, 1H, ArH), 7.53-7.48 (m, 1H, rH), 7.35-7.23 (m, 1H, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 150.2, 148.0, 135.9, 135.8, 129.2, 129.1, 128.1, 127.6, 126.3, 120.8.

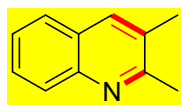


**3-Methyl quinoline (3ac)**<sup>3</sup>: Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.70 (s, 1H, ArH), 8.07 (d, *J* = 8.4 Hz, 1H, ArH), 7.75 (s, 1H, ArH), 7.64 (d, *J* = 8.4 Hz, 1H, ArH), 7.57 (d, *J* = 7.2 Hz, 1H, ArH), 7.45 (m, 2H, ArH), 2.38 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 152.0, 146.1, 134.2, 130.0, 128.7, 128.0, 127.7, 126.8, 126.1, 18.3.

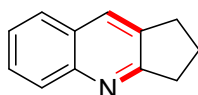


**3-Methoxy quinoline (3ad)**<sup>4</sup>: Colorless oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.63 (d, *J* = 2.4 Hz, 1H, ArH), 8.04 (d, *J* = 8.4 Hz, 1H, ArH), 7.63 (d, *J* = 7.5 Hz, 1H, ArH), 7.49-7.42 (m, 2H, ArH), 7.24 (d, *J* = 1.5 Hz, 1H, ArH), 3.80 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR

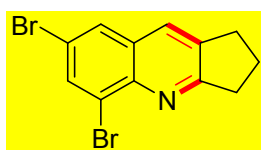
(75 MHz, CDCl<sub>3</sub>)  $\delta$ : 152.6, 144.1, 143.0, 128.6, 128.4, 126.6, 126.3, 126.2, 111.7, 55.0.



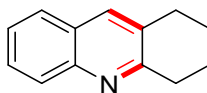
**2,3-Dimethylquinoline (3ag)**<sup>5</sup>: White solid, mp 65-67 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.00 (d,  $J$  = 8.4 Hz, 1H, ArH), 7.77 (s, 1H, ArH), 7.67 (d,  $J$  = 8.1 Hz, 1H, ArH), 7.60-7.55 (m, 1H, ArH), 7.43-7.39 (m, 1H, ArH), 2.65 (s, 3H, CH<sub>3</sub>), 2.39 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 158.8, 146.3, 135.1, 129.9, 128.2, 128.0, 127.3, 126.5, 125.5, 23.3, 19.4.



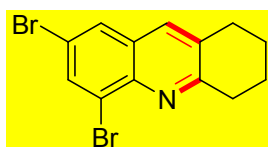
**2,3-Dihydro-1H-cyclopenta[b]quinoline (3ah)**<sup>6</sup>: White solid, mp 55-58 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.02 (d,  $J$  = 8.4 Hz, 1H, ArH), 7.70 (s, 1H, ArH), 7.67-7.64 (m, 1H, ArH), 7.60-7.55 (m, 1H, ArH), 7.43-7.38 (m, 1H, ArH), 3.14 (t,  $J$  = 7.5 Hz, 2H, CH<sub>2</sub>), 3.02 (t,  $J$  = 7.2 Hz, 2H, CH<sub>2</sub>), 2.19-2.09 (dd,  $J_1$  = 7.5 Hz,  $J_2$  = 15.0 Hz, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.6, 147.2, 135.3, 130.0, 128.3, 128.2, 128.0, 127.2, 125.2, 34.3, 30.2, 23.3.



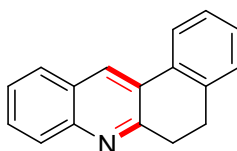
**5,7-Dibromo-2,3-dihydro-1H-cyclopenta[b]quinoline (3bh)**<sup>7</sup>: White solid, mp 140-142 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.97 (d,  $J$  = 1.8 Hz, 1H, ArH), 7.75 (s,  $J$  = 2.1 Hz, 1H, ArH), 7.66 (s, 1H, ArH), 3.20 (t,  $J$  = 7.5 Hz, 2H, CH<sub>2</sub>), 3.08 (t,  $J$  = 7.2 Hz, 2H, CH<sub>2</sub>), 2.24-2.14 (m, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 169.7, 143.2, 137.5, 134.3, 129.4, 129.2 (2C), 124.8, 118.2, 34.7, 30.3, 23.4.



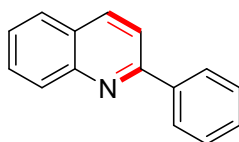
**1,2,3,4- Tetrahydroacridine (3ai)**<sup>6</sup>: White solid, mp 85-87 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.97 (d, *J* = 8.4 Hz, 1H, ArH), 7.75 (s, 1H, ArH), 7.67 (d, *J* = 8.4 Hz, 1H, ArH), 7.60-7.55 (m, 1H, ArH), 7.43-7.37 (m, 1H, ArH), 3.13 (t, 2H, *J* = 6.3 Hz, CH<sub>2</sub>), 2.96 (t, 2H, *J* = 6.3 Hz, CH<sub>2</sub>), 2.01-1.93 (m, 2H, CH<sub>2</sub>), 1.88-1.84 (m, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 159.1, 146.4, 134.8, 130.8, 128.3, 128.1, 127.0, 126.7, 125.3, 33.4, 29.1, 23.0, 22.7.



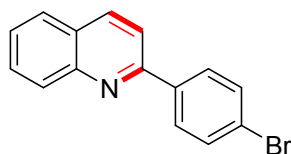
**5,7-Dibromo-1,2,3,4-tetrahydroacridine (3bi)**<sup>7</sup>: White solid, mp 173-175 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.94 (s, 1H, ArH), 7.67 (s, 1H, ArH), 7.54 (s, 1H, ArH), 3.13 (t, 2H, *J* = 6.0 Hz, CH<sub>2</sub>), 2.94 (t, 2H, *J* = 6.6 Hz, CH<sub>2</sub>), 1.97-1.83 (m, 4H, 2 × CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 161.0, 142.0, 134.3, 133.9, 132.8, 128.6, (2C), 124.8, 118.0, 35.5, 28.8, 22.7, 22.4.



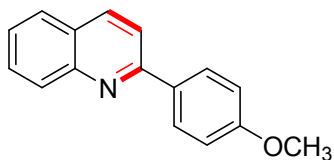
**5,6-Dihydrobenzo[a]acridine (3aj)**<sup>8</sup>: Yellow solid, mp 63-65 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.58 (d, *J* = 7.5 Hz, 1H, ArH), 8.13 (d, *J* = 8.4 Hz, 1H, ArH), 7.84 (s, 1H, ArH), 7.69-7.59 (m, 2H, ArH), 7.45-7.31 (m, 3H, ArH), 7.24 (d, *J* = 7.2 Hz, 1H, ArH), 3.08-3.04 (m, 2H, CH<sub>2</sub>), 2.97-2.93 (m, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 153.2, 147.5, 139.3, 134.6, 133.6, 130.4, 129.5, 129.3, 128.5, 127.8 (2C), 127.2, 126.8, 126.0, 125.9, 28.7, 28.3.



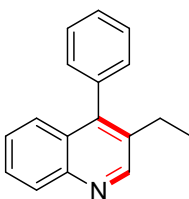
**2-Phenylquinoline (3ak)**<sup>8</sup>: White solid, mp 85-87 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.21-8.14 (m, 3H, ArH), 7.87-7.80 (m, 2H, ArH), 7.71-7.69 (m, 1H, ArH), 7.54-7.45 (m, 5H, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 157.3, 148.2, 139.6, 136.7, 136.6, 129.6, 129.2, 128.9 (2C), 128.8, 127.5 (2C), 127.4, 126.2, 118.9.



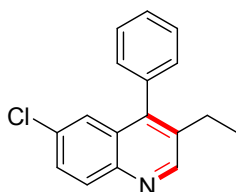
**2-(4-Bromophenyl)quinoline (3al)**<sup>9</sup>: White solid, mp 63-65 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.20-8.08 (m, 4H, ArH), 7.81-7.69 (m, 3H, ArH), 7.54-7.46 (3H, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 155.9, 148.1, 138.0, 136.9, 135.5, 129.8, 129.6, 128.9 (2C), 128.7 (2C), 127.4, 127.1, 126.4, 118.5.



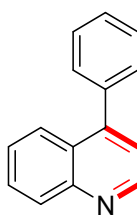
**2-(4-Methoxyphenyl)quinoline (3am)**<sup>8</sup>: White solid, mp 117-120 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.14-8.11 (m, 4H, ArH), 7.80-7.75 (m, 2H, ArH), 7.71-7.65 (m, 1H, ArH), 7.49-7.44 (m, 1H, ArH), 7.03 (d, *J* = 8.7 Hz, 2H, ArH), 3.85 (s, 3H, OCH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 160.7, 156.8, 148.2, 136.5, 132.1, 129.5, 129.4, 128.8, 127.3, 126.8, 125.8, 118.4, 114.1 (2C), 55.3.



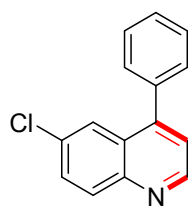
**3-Ethyl-4-phenyl quinoline (3ca):** White solid; mp 97-100 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.87 (s, 1H, ArH), 8.12 (d,  $J = 8.4$  Hz, 1H, ArH), 7.63-7.61 (m, 1H, ArH), 7.50-7.46 (m, 5H, ArH), 7.38-7.37 (m, 2H, ArH), 7.27-7.25 (m, 2H, ArH), 2.64-2.56 (m, 2H,  $\text{CH}_2$ ), 1.36 (t,  $J = 7.5$  Hz, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 152.0, 151.8, 146.6, 145.7, 136.5, 134.0, 129.3, 129.1, 128.3, 128.2, 127.8 (2C), 126.3, 126.0 (2C), 24.3, 15.9; HRMS for  $\text{C}_{17}\text{H}_{16}\text{N}$   $[\text{M}+\text{H}]^+$  calcd 234.1279, found 234.1277.



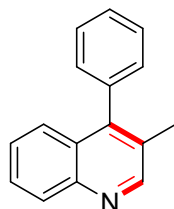
**6-Chloro-3-ethyl-4-phenyl quinoline (3da):** Light yellow solid; mp 95-98 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.85 (s, 1H, ArH), 8.05 (d,  $J = 9.0$  Hz, 1H, ArH), 7.56 (m, 4H, ArH), 7.35 (m,  $J = 1.8$  Hz, 1H, ArH), 7.25-7.23 (m, 2H, ArH), 2.62-2.55 (q,  $J = 7.5$  Hz, 2H,  $\text{CH}_2$ ), 1.15 (t,  $J = 7.5$  Hz, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 152.2, 152.1, 145.0, 144.8, 135.7, 134.9, 132.2, 130.8, 129.1, 129.0, 128.5, 128.4 (2C), 128.1, 124.8, 24.3, 15.6; HRMS for  $\text{C}_{17}\text{H}_{15}\text{NCl}$   $[\text{M}+\text{H}]^+$  calcd 268.0893, found 268.0887.



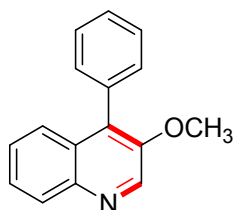
**4-Phenyl quinoline (3cb)<sup>10</sup>:** Colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.93 (d,  $J = 4.5$  Hz, 1H, ArH), 8.18 (d,  $J = 8.4$  Hz, 1H, ArH), 7.91 (d,  $J = 8.4$  Hz, 1H, ArH), 7.72-7.67 (m, 1H, ArH), 7.48-7.44 (m, 5H, ArH), 7.31-7.30 (d,  $J = 4.5$  Hz, 2H, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 149.9, 149.8, 148.5, 148.3, 137.8, 129.7, 129.4, 129.2, 128.4 (2C), 128.3, 126.5 (2C), 125.7, 121.2.



**6-Chloro-4-Phenyl quinoline (3db):** White solid; mp 65-68 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.93 (d,  $J = 4.2$  Hz, 1H, ArH), 8.14 (d,  $J = 9.0$  Hz, 1H, ArH), 7.88 (d,  $J = 2.1$  Hz, 1H, ArH), 7.67-7.63 (m, 1H, ArH), 7.54-7.45 (m, 5H, ArH), 7.35 (d,  $J = 4.5$  Hz, 1H, ArH);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 149.8, 149.6, 148.1, 146.5, 137.1, 132.7, 131.0, 130.9, 130.4, 129.3, 128.7, 127.4, 124.7, 124.6, 122.0; **HRMS for  $\text{C}_{15}\text{H}_{11}\text{NCl}$   $[\text{M}+\text{H}]^+$  calcd 240.0579, found 240.0574.**



**3-Methyl-4-phenyl quinoline (3cc)<sup>11</sup>:** Colorless oil;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.83 (s, 1H, ArH), 8.12 (d,  $J = 5.4$  Hz, 1H, ArH), 7.62-7.57 (m, 1H, ArH), 7.51-7.33 (m, 5H, ArH), 7.23 (d,  $J = 6.0$  Hz, 2H, ArH), 2.23 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 152.4 (2C), 146.6, 146.2, 136.7, 129.0 (2C), 128.4, 128.0 (2C), 127.9, 127.7, 127.4, 126.3, 125.3, 17.4.

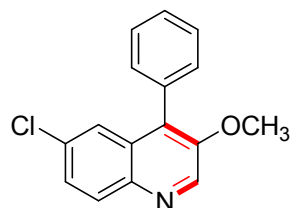


**3-Methoxy-4-phenyl quinoline (3cd):** Yellow solid; mp 121-123 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.86 (s, 1H, ArH), 8.11-8.08 (d,  $J = 9.0$  z, 1H, ArH), 7.55-7.34 (m, 8H, ArH), 3.87 (s, 3H,  $\text{OCH}_3$ );  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$ : 148.9, 144.2, 139.9,

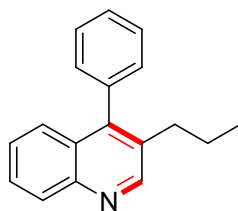


139.7, 133.4, 133.0, 130.1 (2C), 129.2, 129.1, 128.1 (2C), 127.8, 126.7, 125.1, 57.3;

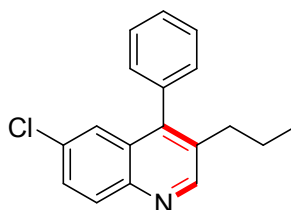
HRMS for  $C_{16}H_{14}ON$   $[M+H]^+$  calcd 236.1073, found 236.1069.



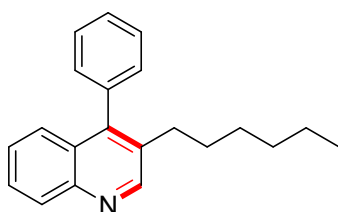
**6-Chloro-3-methoxy-4-phenyl quinoline (3dd):** White solid; mp 115-118 °C;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$ : 8.86 (d,  $J = 5.7$  Hz, 1H, ArH), 8.02 (d,  $J = 8.4$  Hz, 1H, ArH), 7.50 (m, 5H, ArH), 7.35 (m, 2H, ArH), 3.92 (d,  $J = 4.5$  Hz, 3H,  $OCH_3$ );  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$ : 149.4, 142.5, 139.8, 139.7, 132.9, 132.8, 132.1, 130.9, 130.0 (2C), 128.8, 128.3, 128.2, 127.7, 123.8, 57.5; HRMS for  $C_{16}H_{13}ONCl$   $[M+H]^+$  calcd 270.0688, found 270.0680.



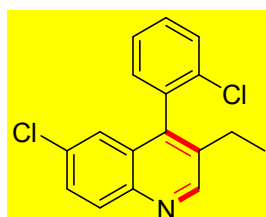
**4-Phenyl-3-propyl quinoline (3ce):** White solid; mp 95-98 °C;  $^1H$  NMR (300 MHz,  $CDCl_3$ )  $\delta$ : 8.85 (s, 1H, ArH), 8.12 (d,  $J = 8.4$  Hz, 1H, ArH), 7.64-7.59 (m, 1H, ArH), 7.50-7.48 (m, 3H, ArH), 7.38-7.37 (m, 2H, ArH), 7.26-7.24 (m, 2H, ArH), 2.54 (t,  $J = 7.8$  Hz, 2H,  $CH_2$ ), 1.58-1.50 (m, 2H,  $CH_2$ ), 0.83 (t,  $J = 7.2$  Hz, 3H,  $CH_3$ );  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$ : 152.3, 152.2, 146.6, 146.0, 136.5, 132.5, 129.4 (2C), 129.1, 128.3, 128.2 (2C), 127.8, 126.3, 126.1, 33.0, 24.4, 13.8; HRMS for  $C_{18}H_{17}N$   $[M+H]^+$  calcd 248.1439, found 248.1426.



**6-Chloro-4-phenyl-3-propyl quinoline (3de):** White solid; mp100-102 ° C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.84 (s, 1H, ArH), 8.05 (d, *J* = 9.0 Hz, 1H, ArH), 7.53-7.47 (m, 4H, ArH), 7.36-7.35 (m, 1, ArH), 7.28-7.20 (m, 2H, ArH), 2.54 (t, *J* = 7.8 Hz, 2H, CH<sub>2</sub>), 1.56-1.49 (m, 2H, CH<sub>2</sub>), 0.87 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 152.3, 144.9 (2C), 135.6, 133.2, 132.0, 130.7, 129.0, 128.8 (2C), 128.3 (2C), 127.9, 124.7, 124.6, 32.8, 24.2, 13.7; **HRMS for C<sub>18</sub>H<sub>17</sub>NCl [M+H]<sup>+</sup> calcd 282.1049, found 282.1044.**

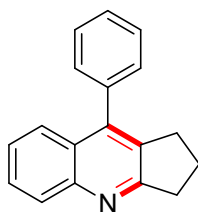


**3-Hexyl-4-phenyl quinoline (3cf)<sup>1</sup>:** Yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.86 (s, 1H, ArH), 8.13 (d, *J* = 8.1 Hz, 1H, ArH), 7.60-7.58 (m, 1H, ArH), 7.49-7.47 (m, 3H, ArH), 7.38-7.32 (m, 2H, ArH), 7.26 (d, *J* = 7.5 Hz, 2H, ArH), 2.59 (t, *J* = 7.5 Hz, 2H, CH<sub>2</sub>), 1.50 (m, 2H, CH<sub>2</sub>), 1.28-1.18 (m, 2H, CH<sub>2</sub>), 1.19-1.18 (m, 2H, CH<sub>2</sub>), 0.87-0.79 (m, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 152.2, 152.0, 146.4, 145.9, 136.4, 132.7, 129.3, 129.1, 129.0, 128.2, 128.1, 127.7, 127.6, 126.2, 126.0, 31.3, 30.8 (2C), 22.0, 13.7, 13.6.

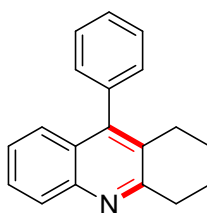


**6-Chloro-4-(2-chlorophenyl)-3-ethylquinoline (3eg):** Light yellow oil; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.05 (m, 1H, ArH), 7.56-7.51 (m, 2H, ArH), 7.42-7.36 (m, 3H, ArH), 7.28-7.21 (m, 2H, ArH), 3.06-3.01 (m, 2H, CH<sub>2</sub>), 1.41-1.39 (m, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 163.5, 146.3, 145.0, 136.0, 133.0, 131.5, 131.0, 130.6,

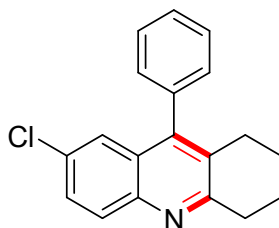
130.0, 129.8 (2C), 126.7, 125.9, 124.1, 122.2, 32.0, 13.5; HRMS for  $C_{17}H_{13}NCl_2$   $[M+Na]^+$  calcd 324.0332, found 324.0364.



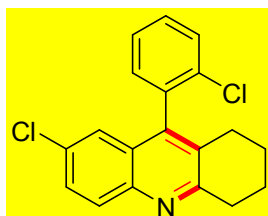
**9-Phenyl-2,3-dihydro-1-cyclopenta[b]quinoline (3bh)<sup>12</sup>:** Yellow solid, mp 133-135 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.09 (d, *J* = 8.4 Hz, 1H, ArH), 7.63 (m, 2H, ArH), 7.51-7.45 (m, 3H, ArH), 7.37-7.34 (m, 3H, ArH), 3.24 (t, *J* = 7.8 Hz, 2H, CH<sub>2</sub>), 2.90 (t, *J* = 7.2 Hz, 2H, CH<sub>2</sub>), 2.21-2.11 (m, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 167.3, 147.7, 142.8, 136.7, 133.6, 129.2 (2C), 128.6, 128.4, 128.2, 127.9 (2C), 126.2, 125.6, 125.4, 35.1, 30.3, 23.5.



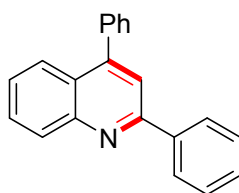
**9-Phenyl tetrahydroacridine (3bh)<sup>13</sup>:** White solid, mp 135-137 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.03 (d, *J* = 8.4 Hz, 1H, ArH), 7.60-7.44 (m, 4H, ArH), 7.31-7.20 (m, 4H, ArH), 3.19 (t, 2H, *J* = 6.6 Hz, CH<sub>2</sub>), 2.59 (t, 2H, *J* = 6.0 Hz, CH<sub>2</sub>), 1.97-1.91 (m, 2H, CH<sub>2</sub>), 1.79-1.73 (m, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 158.9, 146.4, 146.2, 137.0, 129.0 (2C), 128.5 (2C), 128.2 (2C), 127.6 (2C), 126.5, 125.7, 125.2, 34.1, 27.9, 22.9, 22.8.



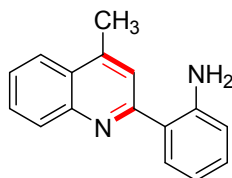
**7-Chloro-9-phenyl-1,2,3,4-tetrahydroacridine (3ch)**<sup>13</sup>: White solid, mp 163-165 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.94 (d, *J* = 9.0 Hz, 1H, ArH), 7.51-7.45 (m, 4H, ArH), 7.28-7.24 (m, 1H, ArH), 7.20-7.18 (m, 2H, ArH), 3.17 (t, 2H, *J* = 6.6 Hz, CH<sub>2</sub>), 2.58 (t, 2H, *J* = 6.6 Hz, CH<sub>2</sub>), 1.96-1.90 (m, 2H, CH<sub>2</sub>), 1.80-1.74 (m, 2H, CH<sub>2</sub>).



**7-Chloro-9-(2-chlorophenyl)-1,2,3,4-tetrahydroacridine (3ei)**<sup>13</sup>: White solid, mp 155-157 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.97-7.94 (m, 1H, ArH), 7.58-7.51 (m, 2H, ArH), 7.43-7.40 (m, 2H, ArH), 7.17-7.13 (m, 2H, ArH), 3.20 (t, 2H, *J* = 6.0 Hz, CH<sub>2</sub>), 2.56-2.50 (m, 2H, CH<sub>2</sub>), 1.96-1.94 (m, 2H, CH<sub>2</sub>), 1.80-1.74 (m, 2H, CH<sub>2</sub>).



**2,4-Diphenylquinoline (3bj)**<sup>14</sup>: White solid, mp 112-115 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.81 (d, *J* = 7.2 Hz, 4H, ArH), 7.64-7.56 (m, 4H, ArH), 7.48-7.40 (m, 4H, ArH), 7.38-7.31 (m, 3H, ArH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 163.1, 140.5, 137.5, 136.2, 136.0, 133.6, 133.0, 132.3, 131.8, 131.0, 130.0, 129.9, 129.0, 128.8, 128.5, 128.2, 128.1, 127.1, 119.4, 118.5, 118.5.



**2-(4-Methylquinolin-2-yl)aniline (4)**<sup>15</sup>: Pale yellow solid; mp 78-80 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.02 (d, *J* = 8.4 Hz, 1H, ArH), 7.91 (d, *J* = 8.1 Hz, 1H, ArH), 7.66-7.60 (m, 2H, ArH), 7.48-7.43 (m, 1H, ArH), 7.18-7.13 (m, 1H, ArH), 6.80-6.73

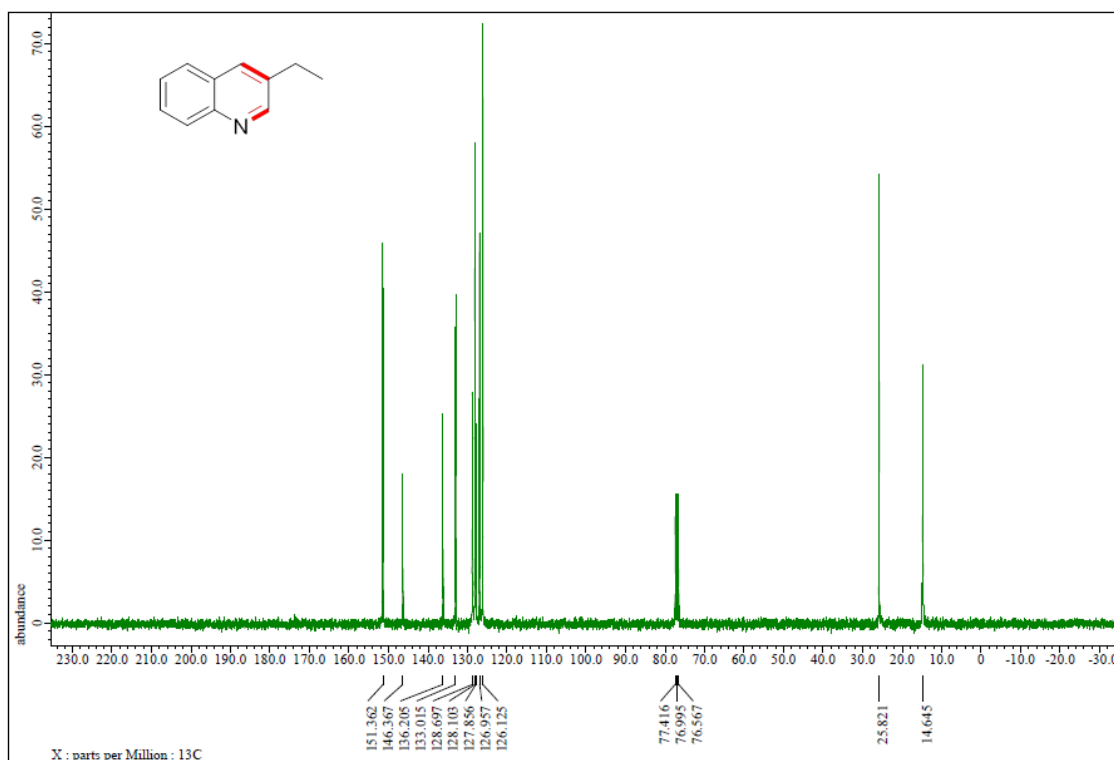
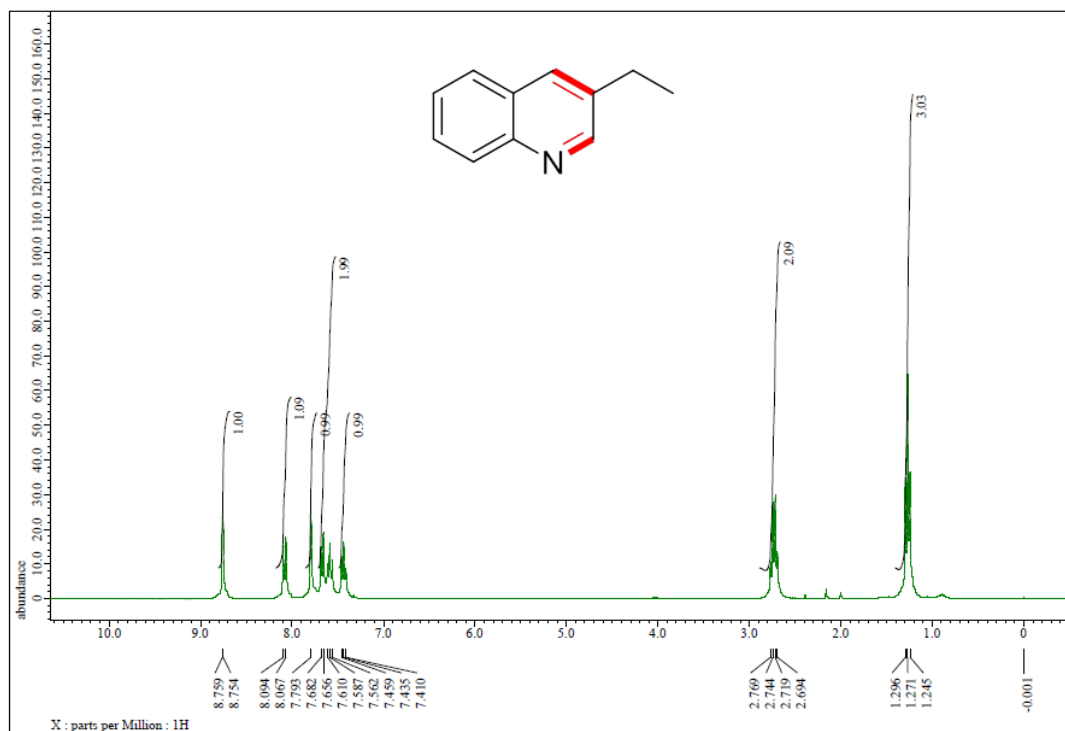
(m, 2H, ArH), 6.12 (bs, 2H, NH<sub>2</sub>), 2.65 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 158.7, 147.3, 146.5, 144.5, 130.0, 129.6, 129.2, 129.1, 126.3, 125.7, 123.4, 121.5, 120.9, 117.2, 117.1, 18.8.

## References

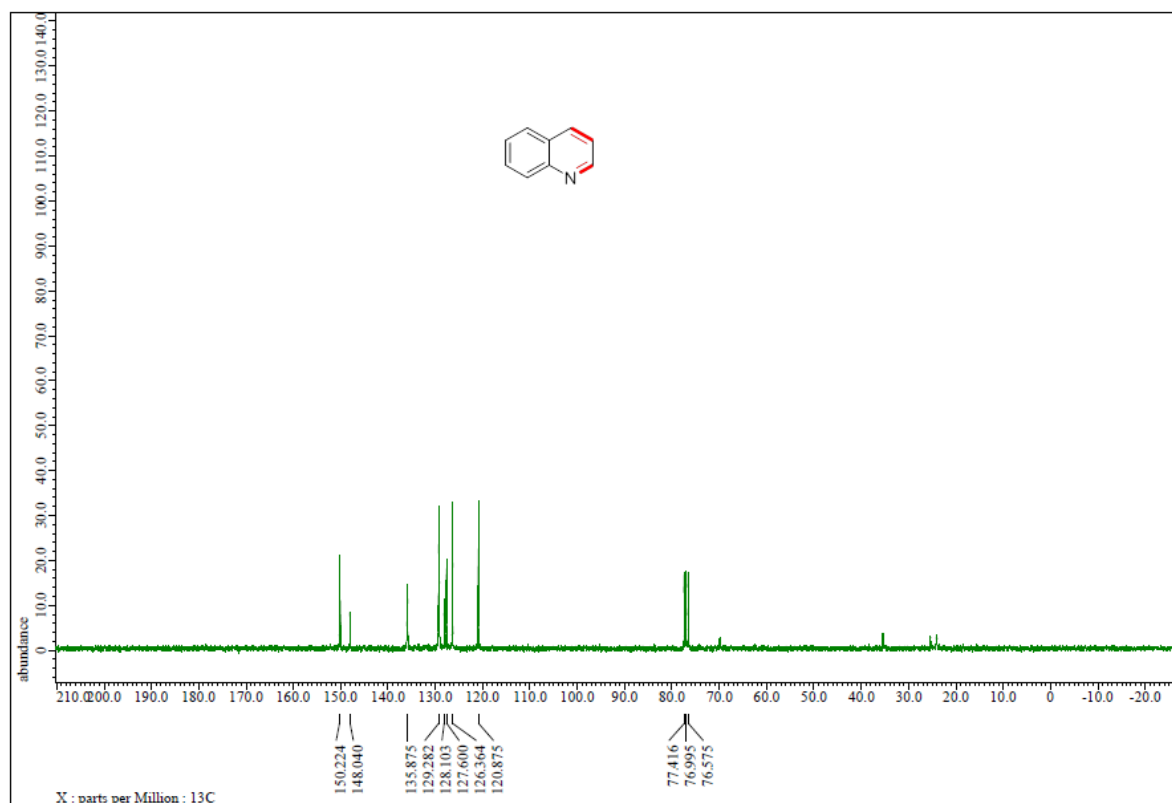
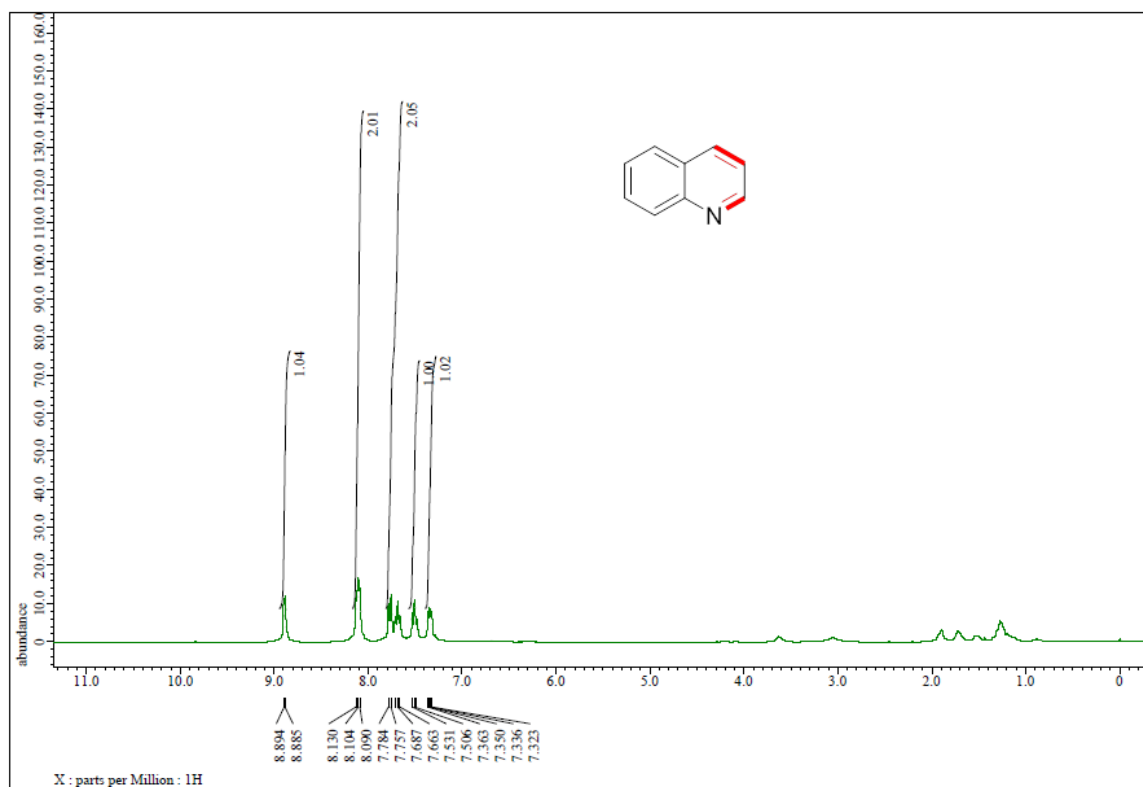
- 1 H. V. Mierde, P.V. D. Voort and F. Verpoor, *Tetrahedron Lett.* 2009, **50**, 201–203.
- 2 S. K. Singh, M. S. Reddy, M. Mangle and K. R. Ganesh, *Tetrahedron*, 2007, **63**, 126–130.
- 3 M. Huiban, A. Huet, L. Barre, F. Sobrio, E. Fouquet and C. Perrio, *Chem. Commun.* 2006, 97–99.
- 4 Y.-J. Cherg, *Tetrahedron* 2002, **58**, 1125-1129.
- 5 P. D. Mayo, L. Sydnes and G. Wenska, *J. Org. Chem.* 1980, **45**, 1549-1556.
- 6 Z.-H. Yu, H. -F. Zheng, W. Yuan, Z.-L. Tang, A.-D. Zhang and D.-Q. Shi, *Tetrahedron*, 2013, **69**, 8137-8141.
- 7 G.-W. Wang, C.-S. Jia and Y.-W. Dong, *Tetrahedron Lett.* 2006, **47**, 1059–1063.
- 8 C. S. Cho, B. T. Kim, H.-J. Choi, T.-J. Kim and S. C. Shim, *Tetrahedron*, 2003, **59**, 7997-8002.
- 9 M. Barbero, S. Bazzi, S. Cadamuro and S. Dughera, *Tetrahedron Lett.*, 2010, **51**, 2342–2344.
- 10 C. Wolf and R. Lerebours, *Org. Lett.*, 2004, **6**, 1147–1150.
- 11 P. Zhao, X. Yan, H. Yin and C. Xi, *Org. Lett.*, 2014, **16**, 1120–1123.
- 12 S. Genovese, F. Epifano, M. C. Marcotullio, C. Pelucchini and M. Curini, *Tetrahedron Lett.*, 2011, **52**, 3474-3477.
- 13 M. Barbero, S. Bazzi, S. Cadamuro and S. Dughera, *Tetrahedron Lett.*, 2010, **51**, 2342–2344.
- 14 R. Martínez, D. J. Ramón and M. Yus, *Eur. J. Org. Chem.*, 2007, 1599-1605.
- 15 N. Sakai, K. Annaka, A. Fujita, A. Sato, and T. Konakahara *J. Org. Chem.* 2008, **73**, 4160–4165.

# Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

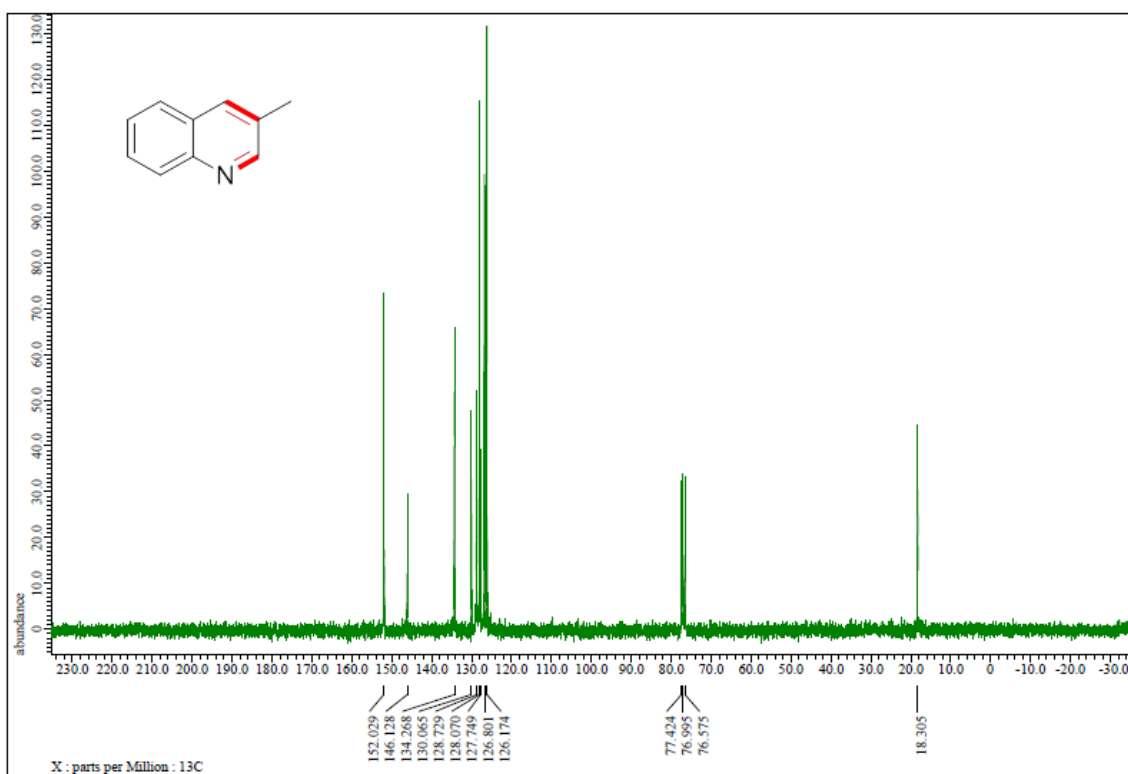
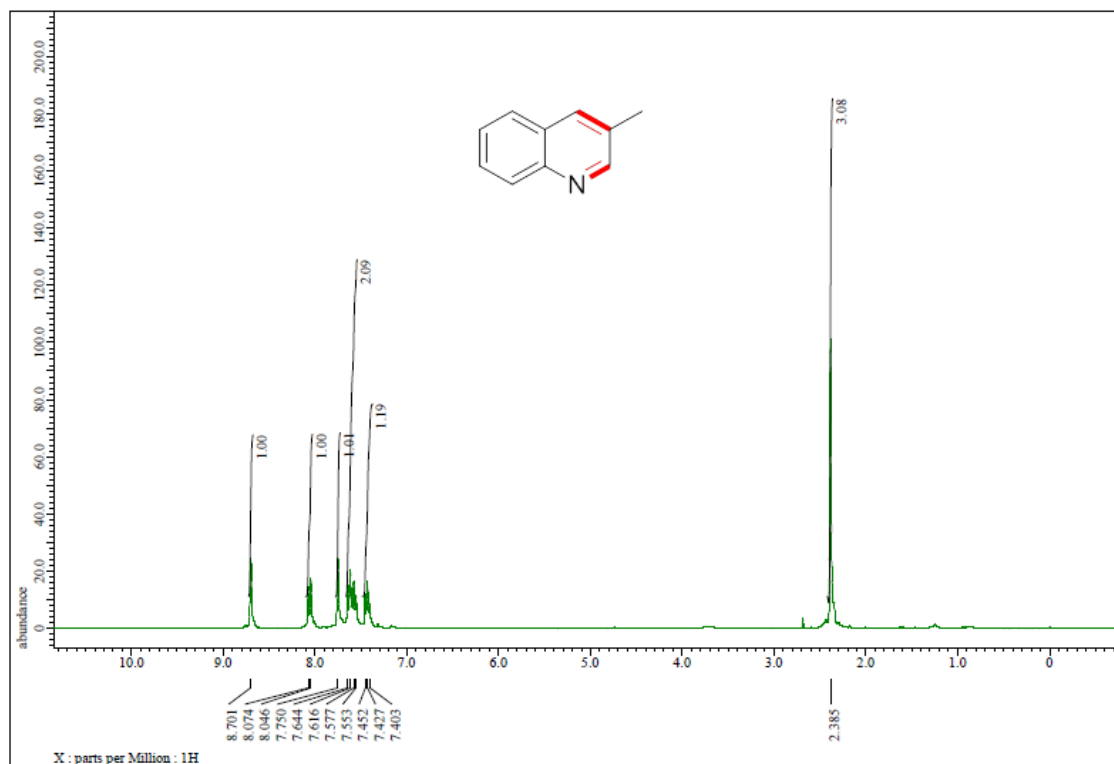
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3aa**



$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ab**

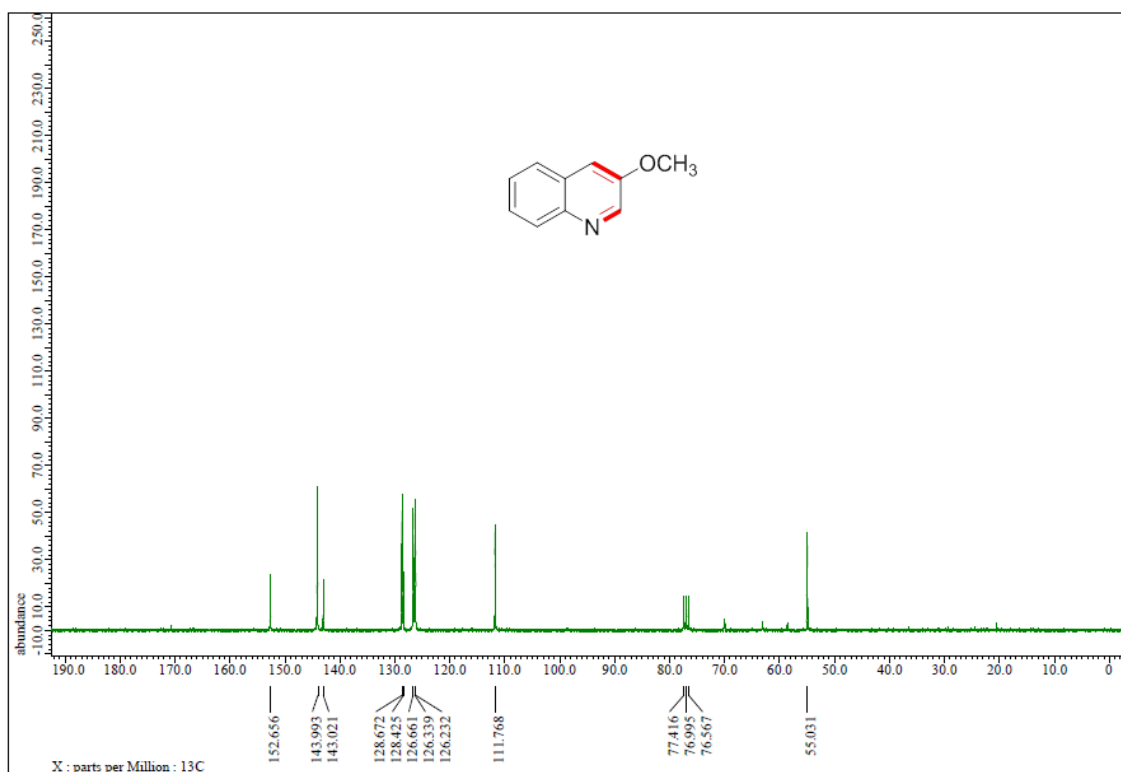
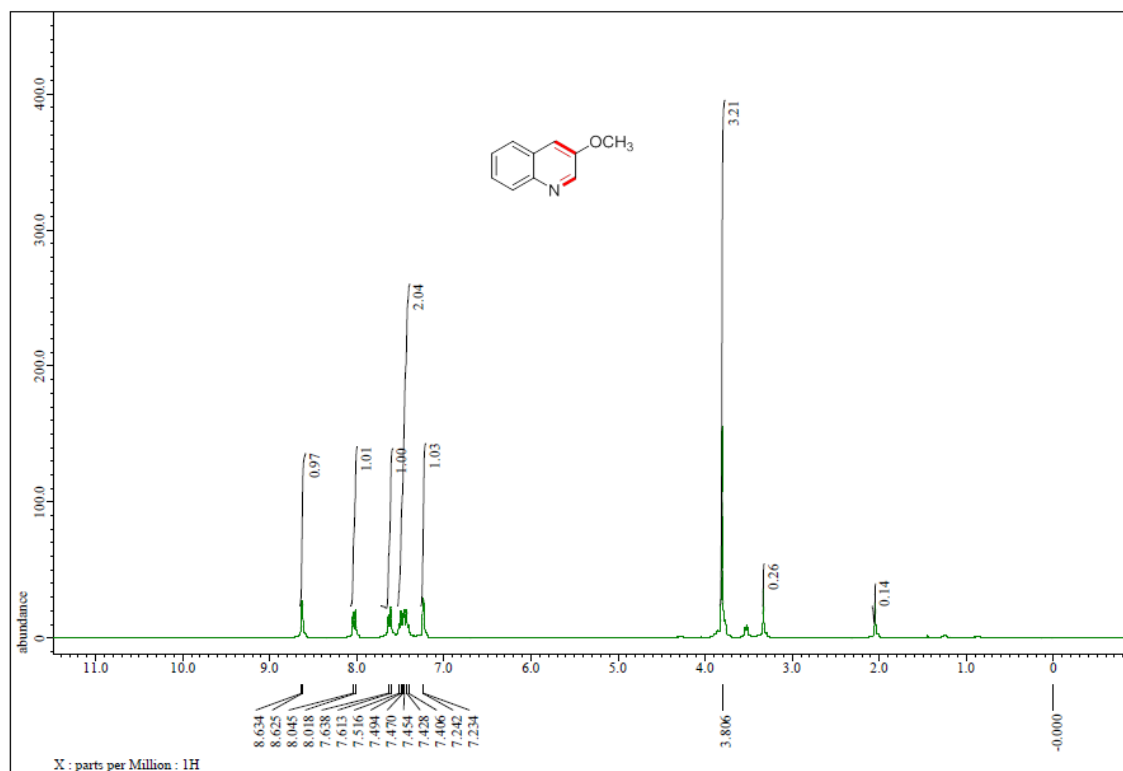


$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ac**

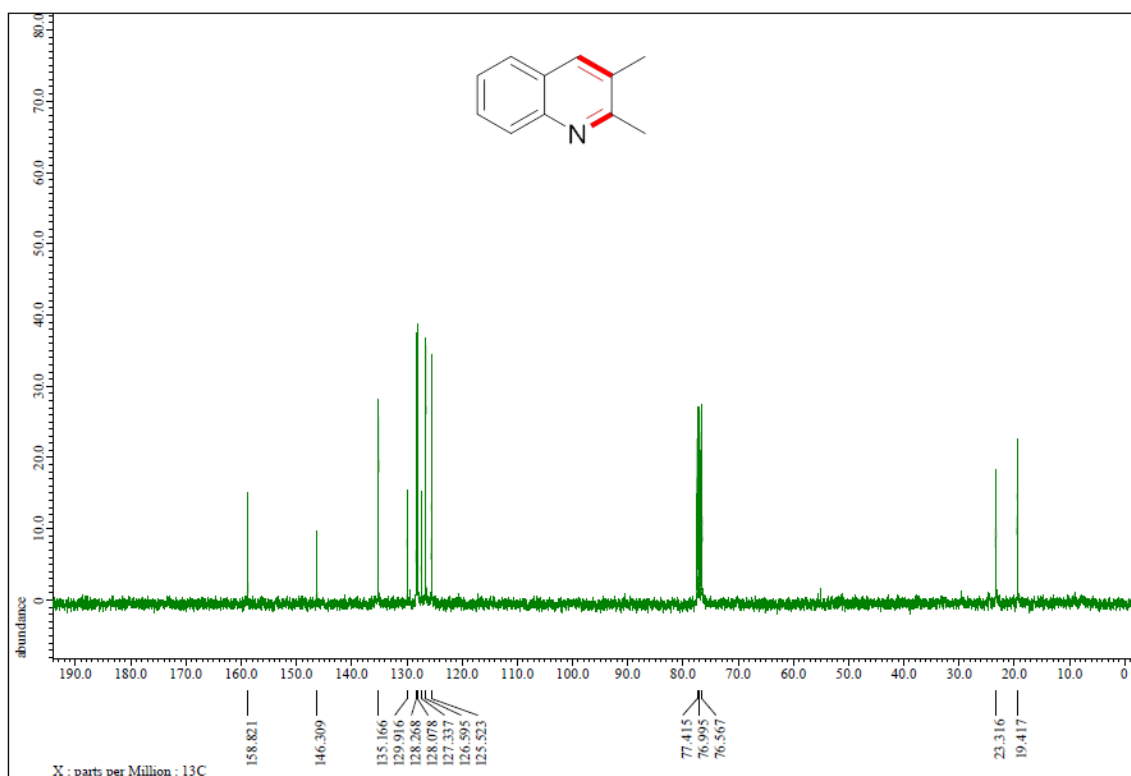
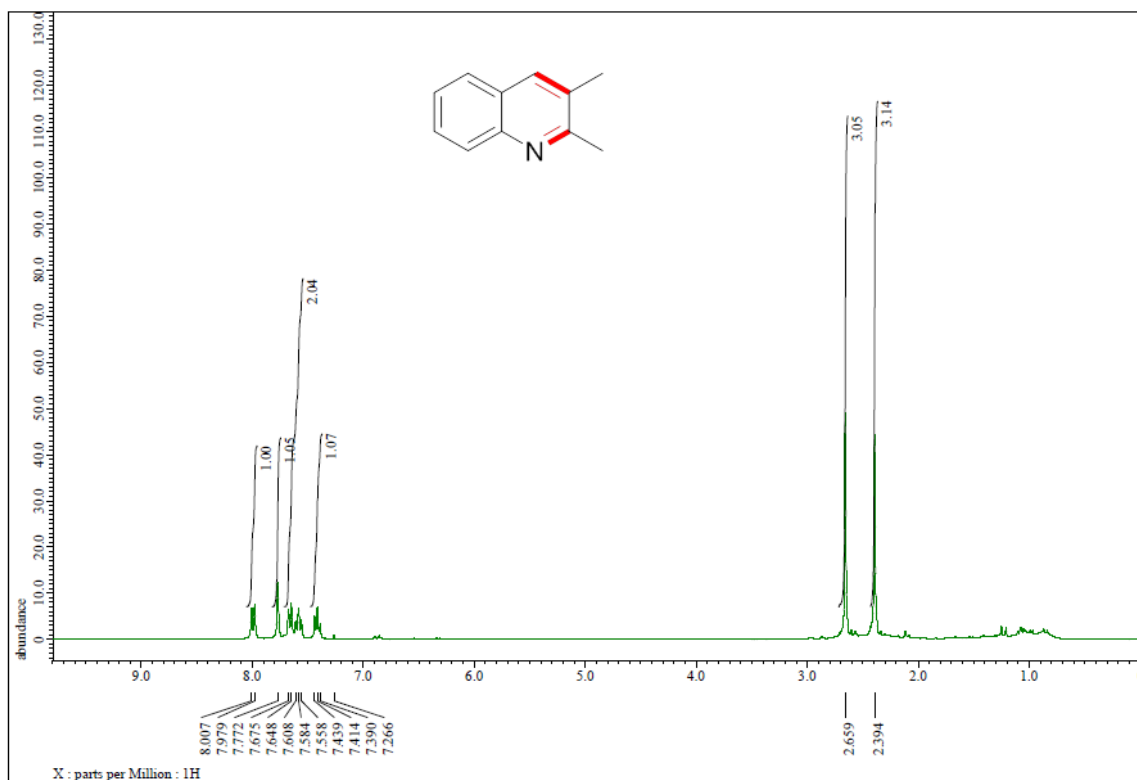




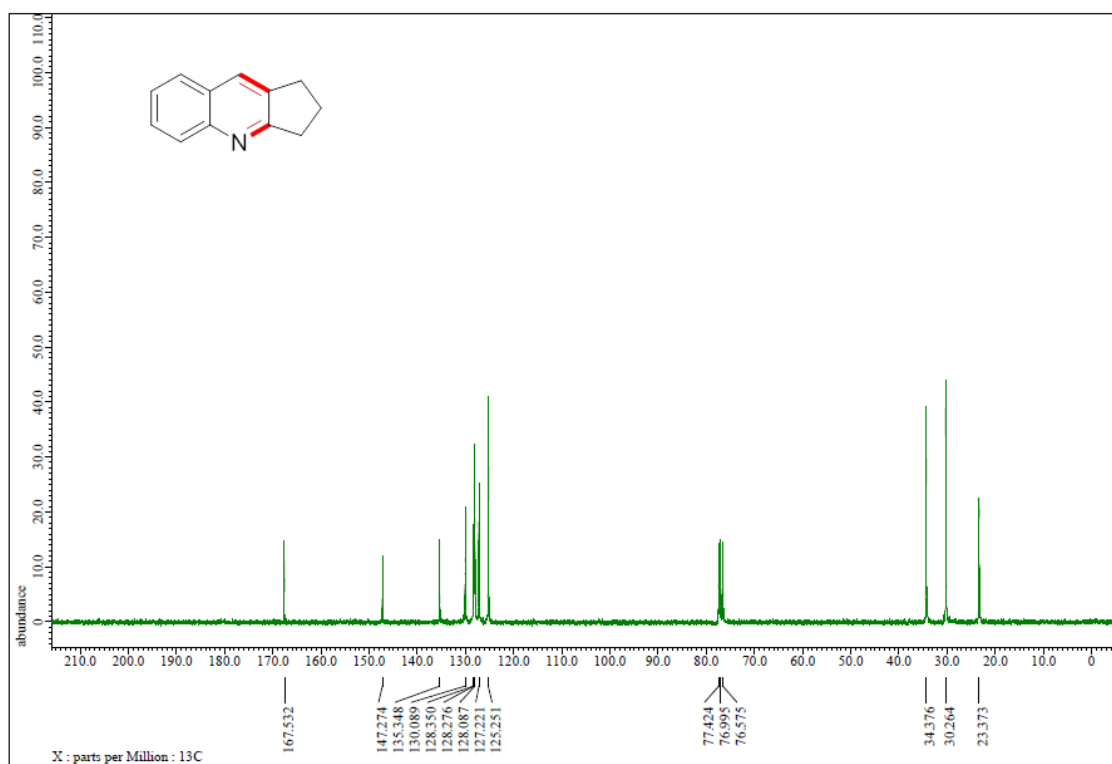
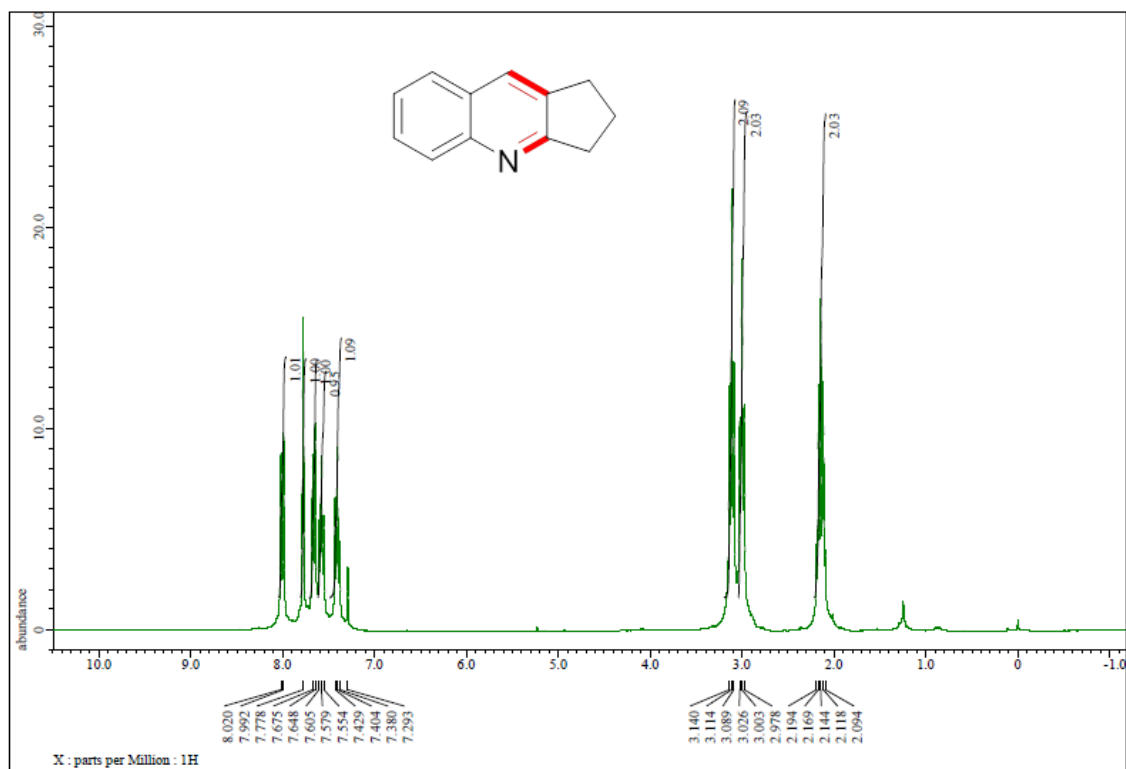
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ad**



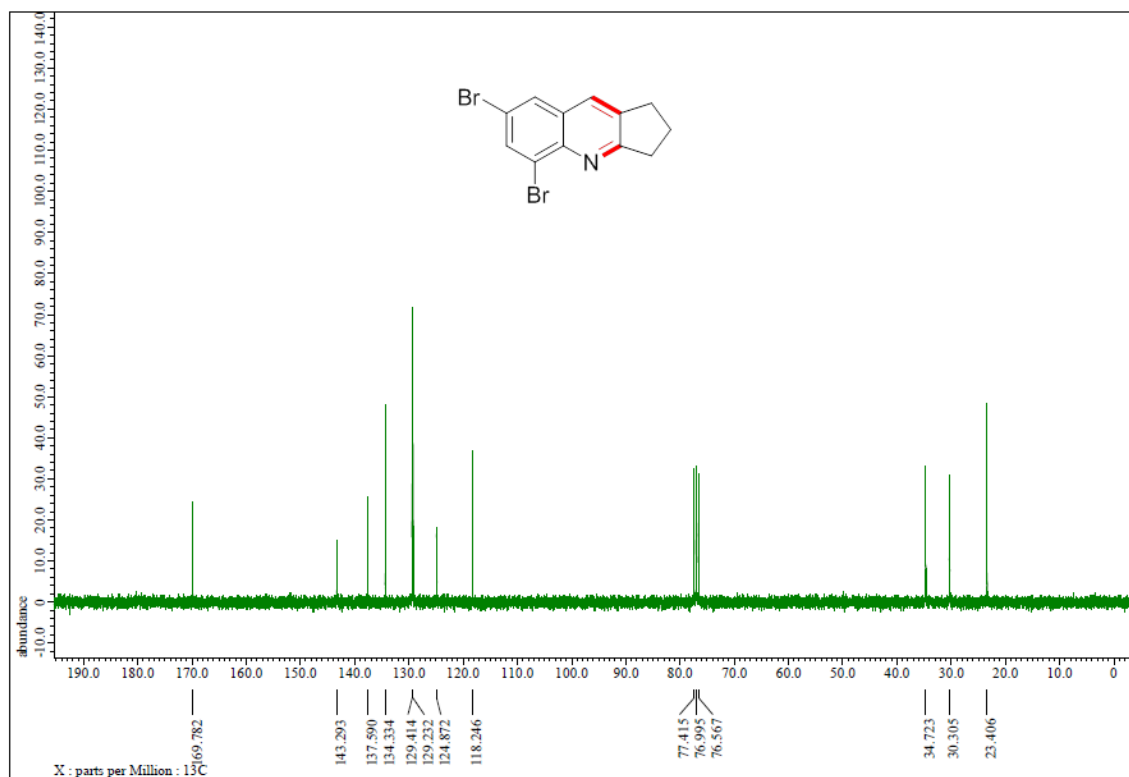
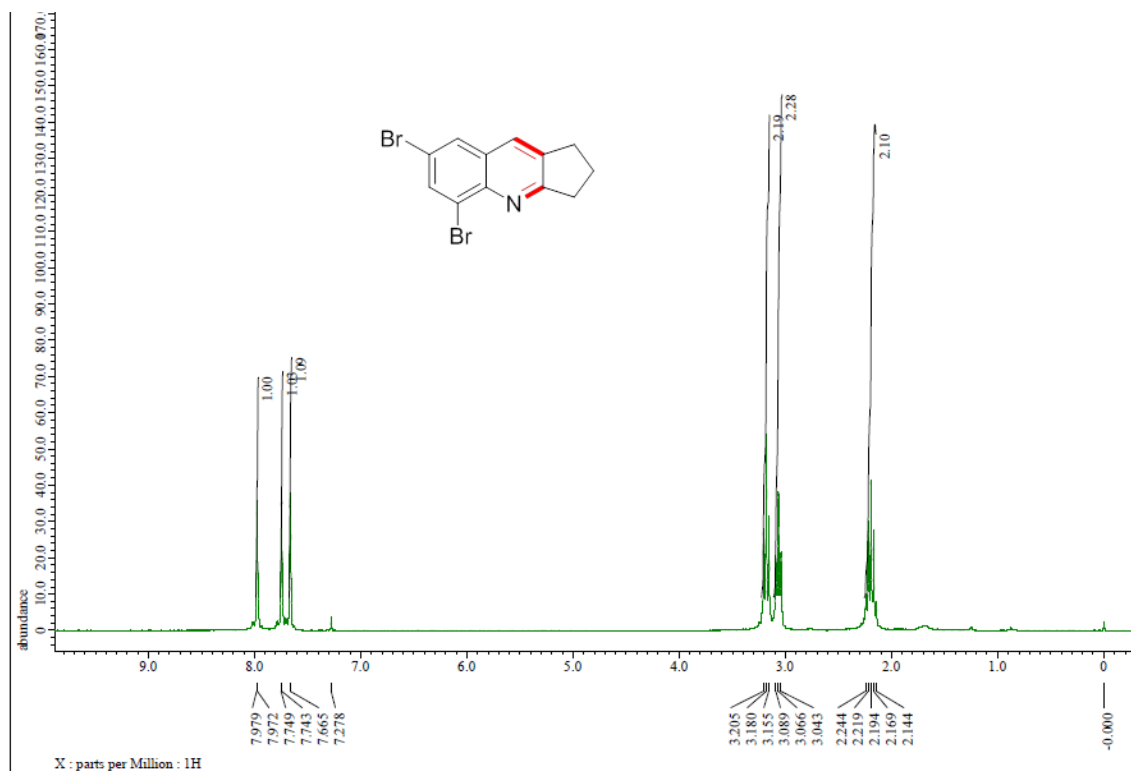
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ag**



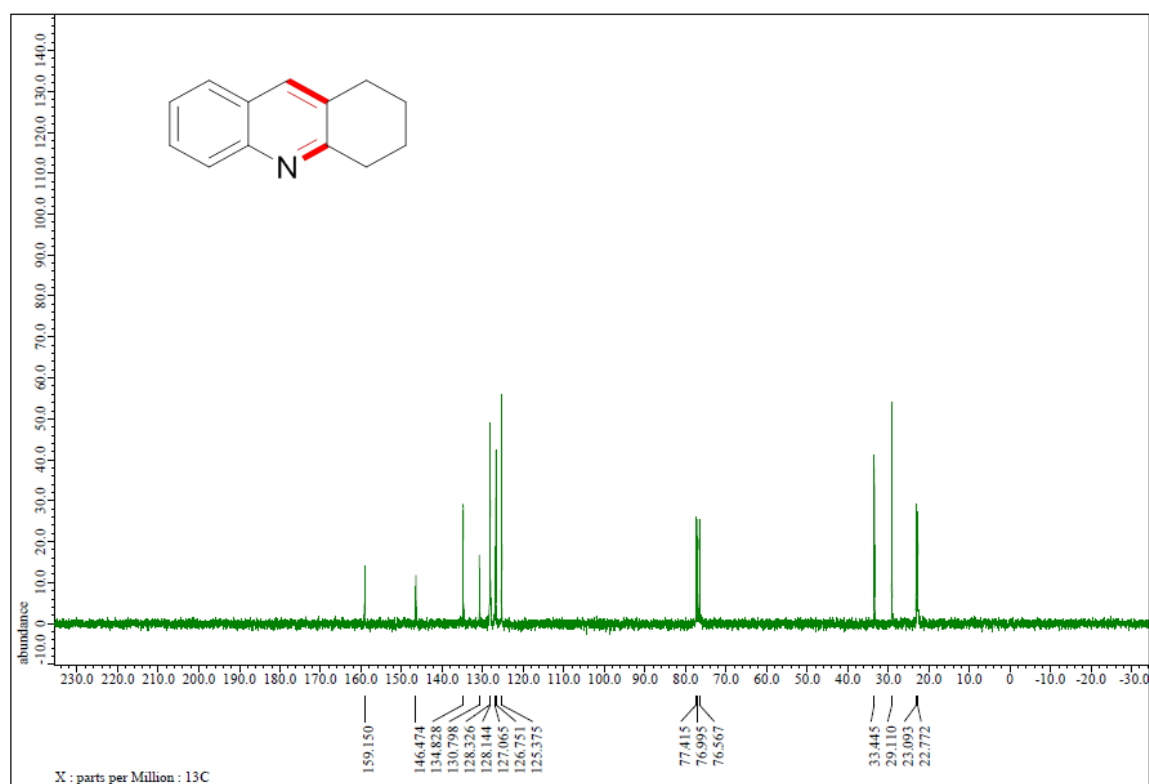
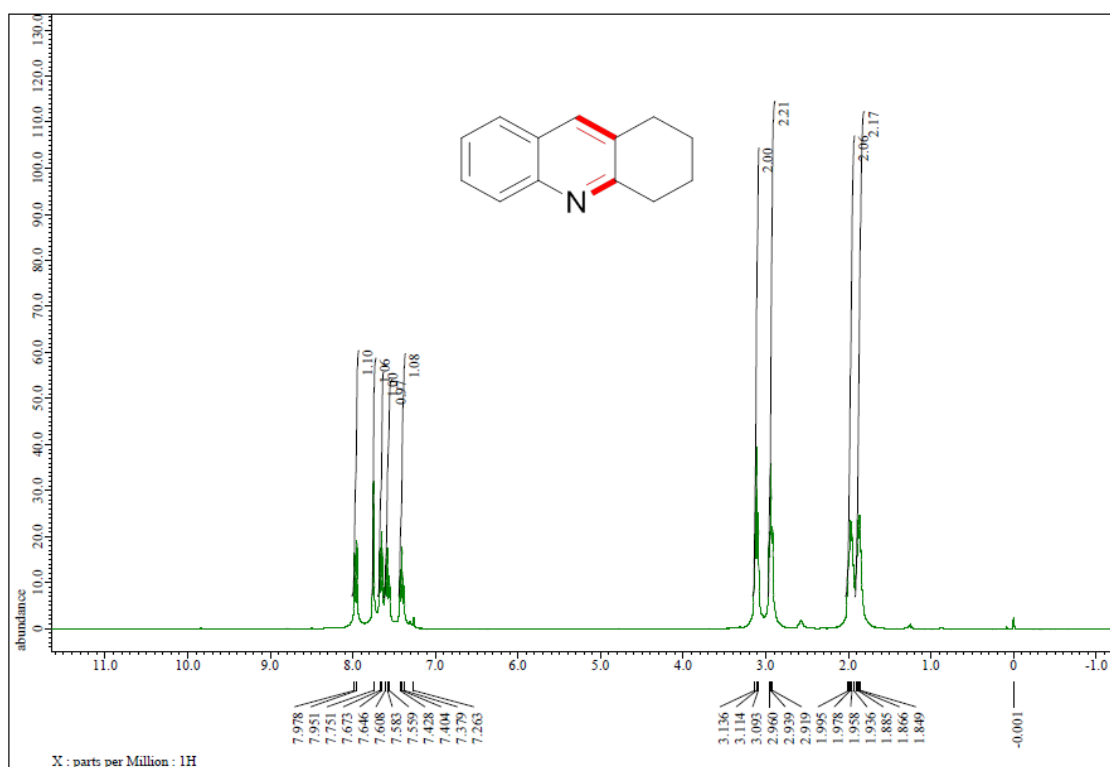
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ah**



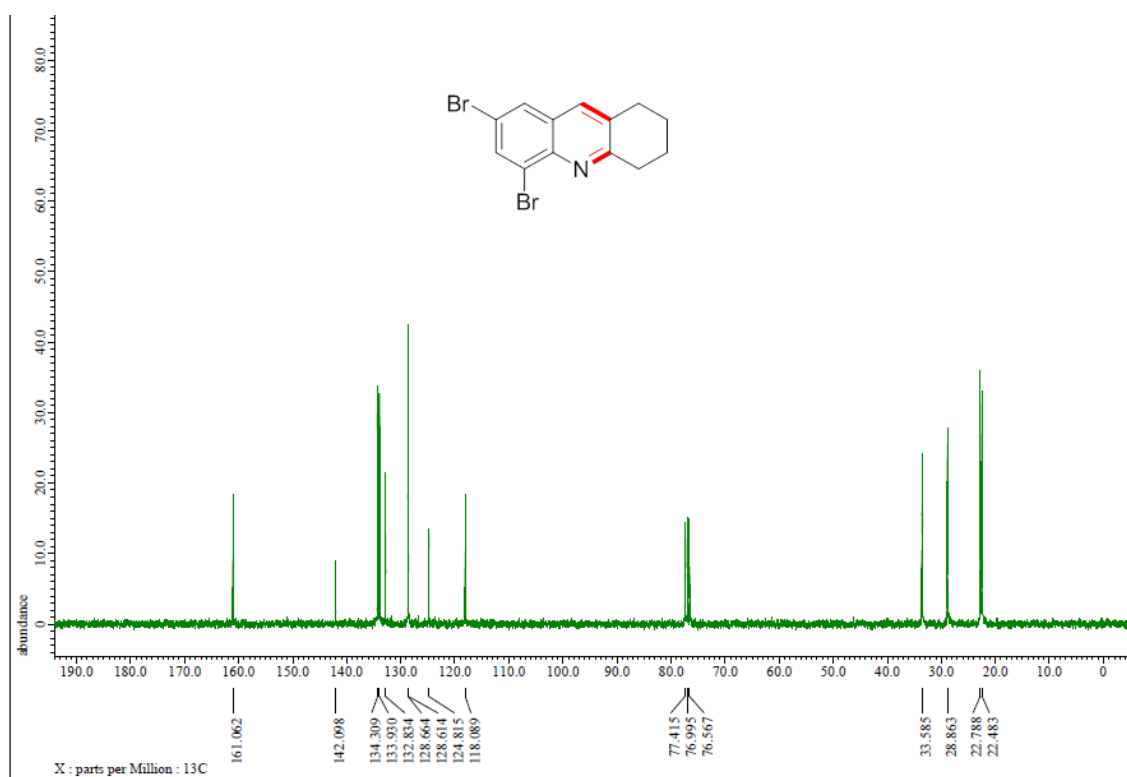
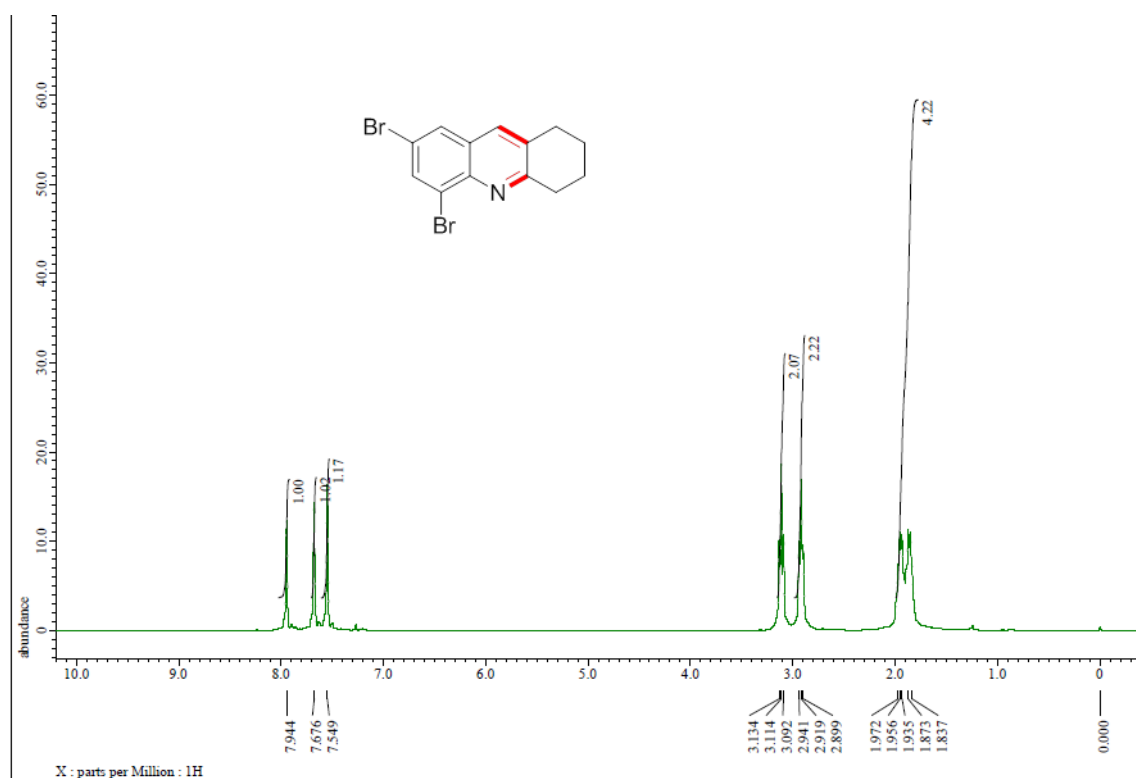
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3bh**



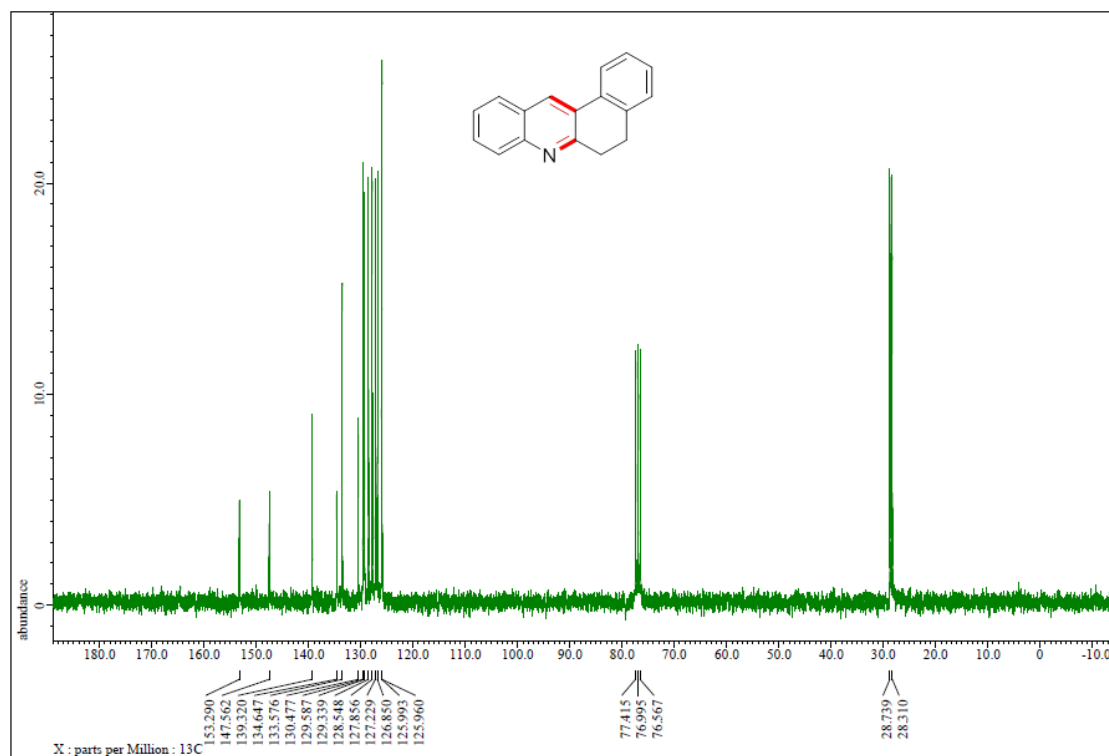
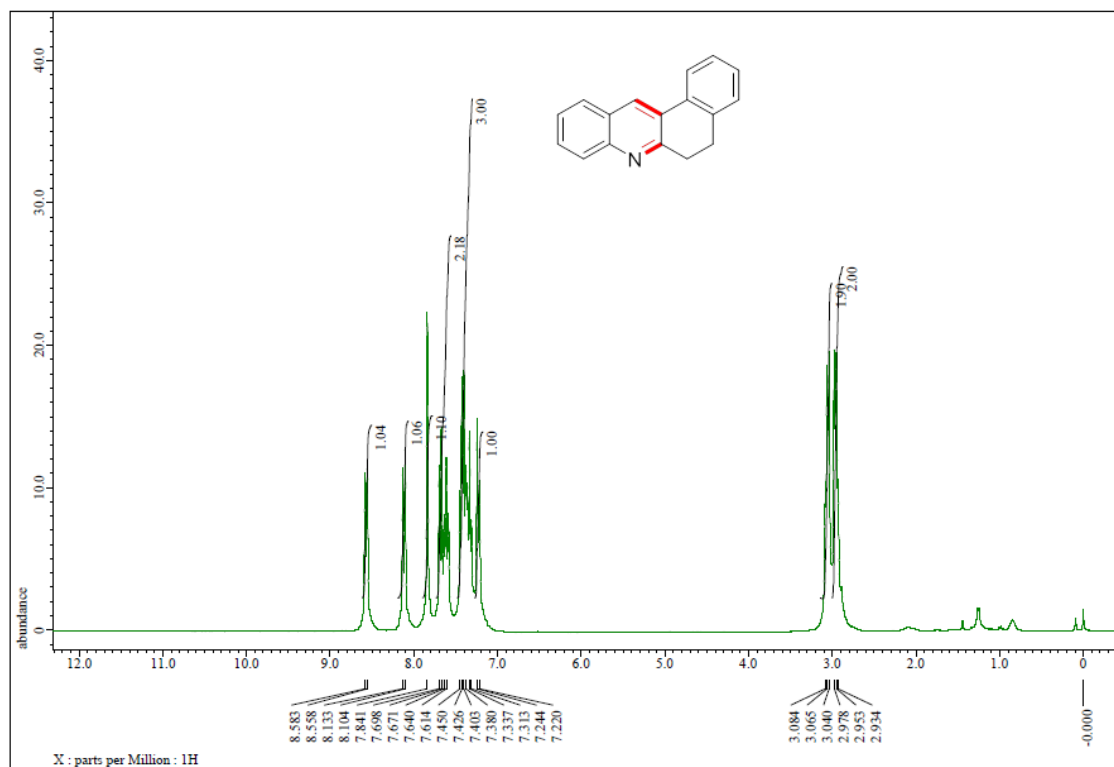
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ai**



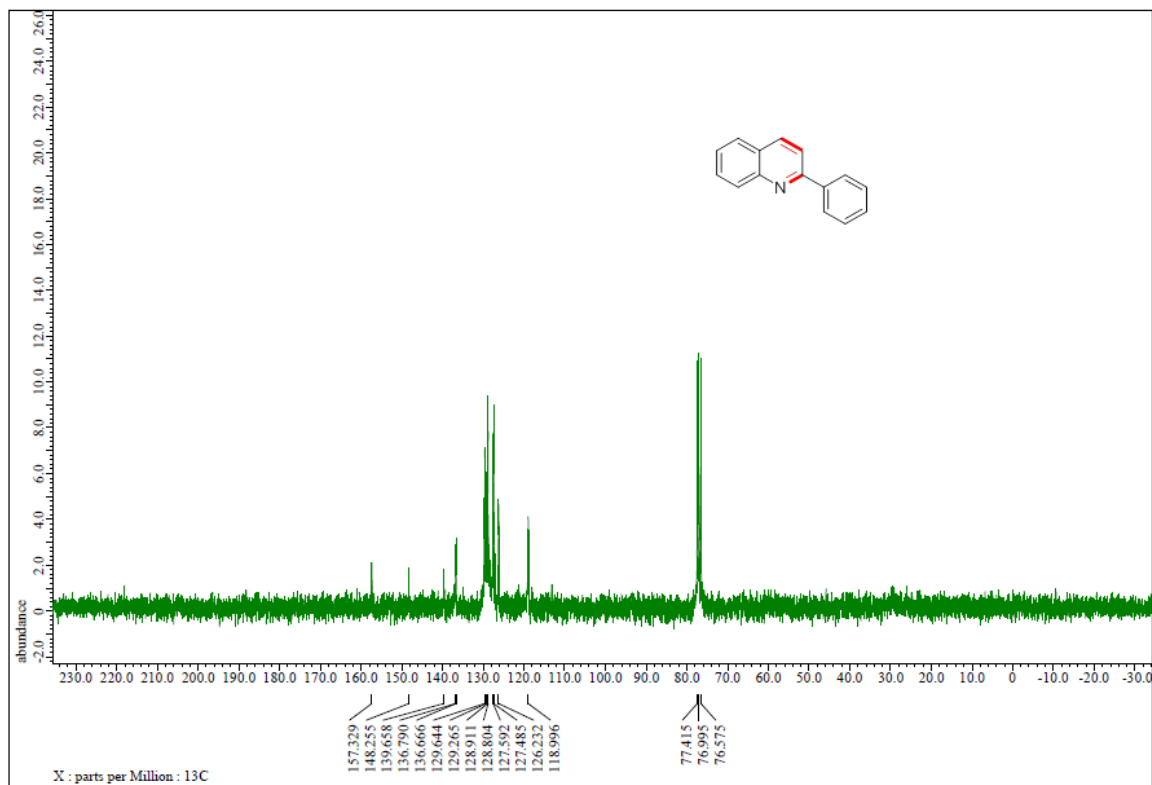
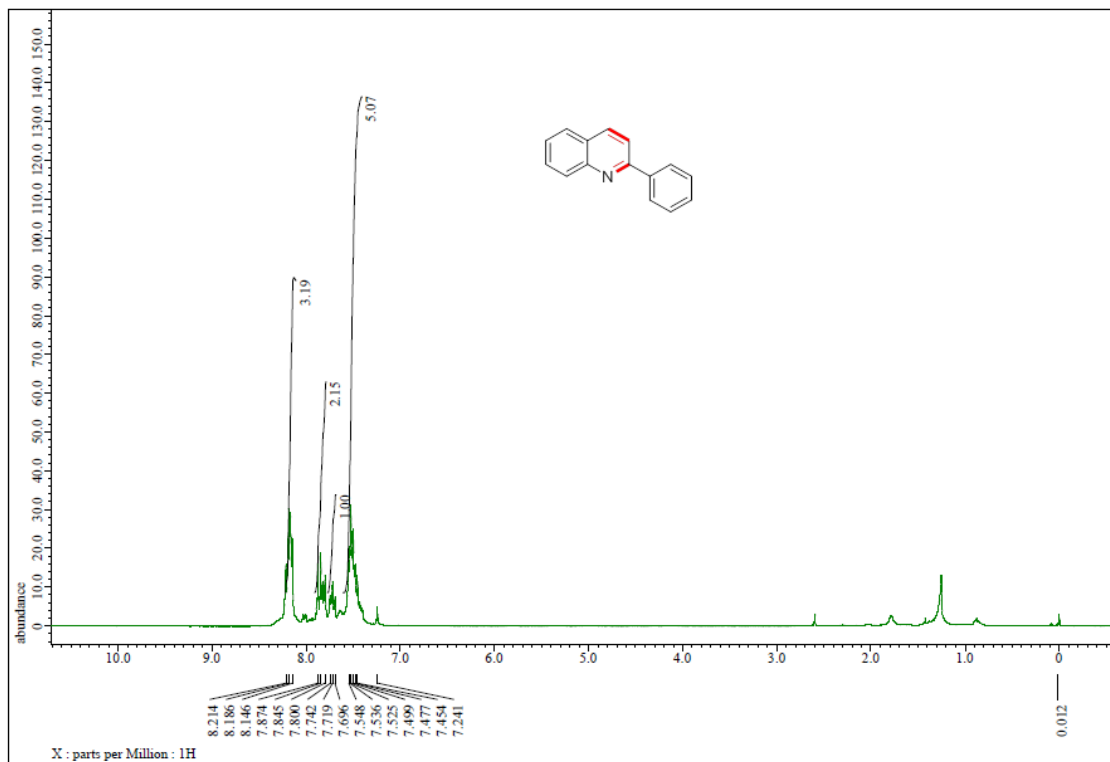
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3bi**



$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3aj**

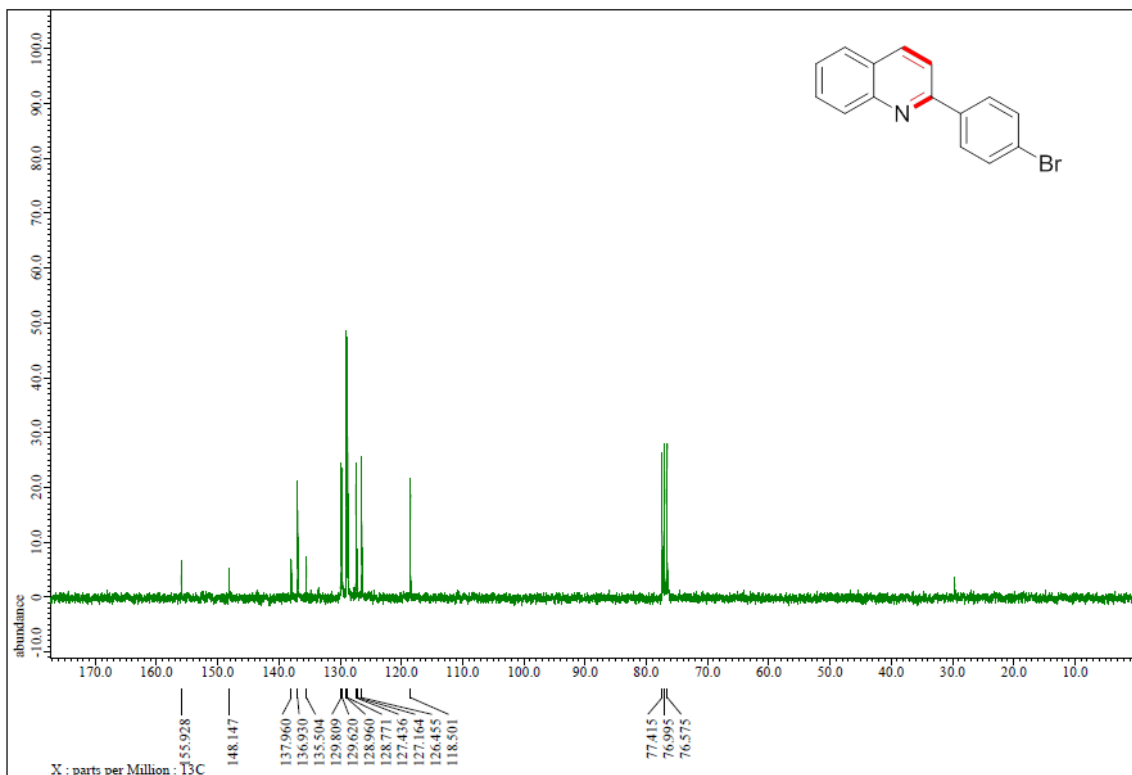
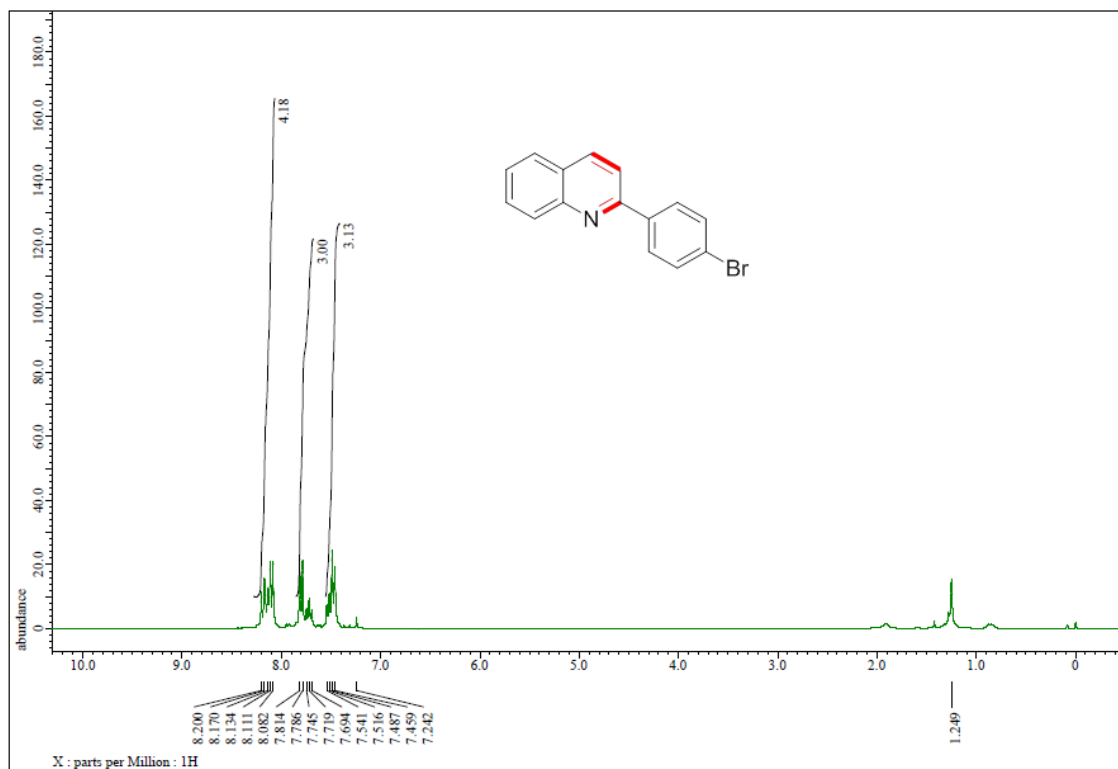


$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ak**

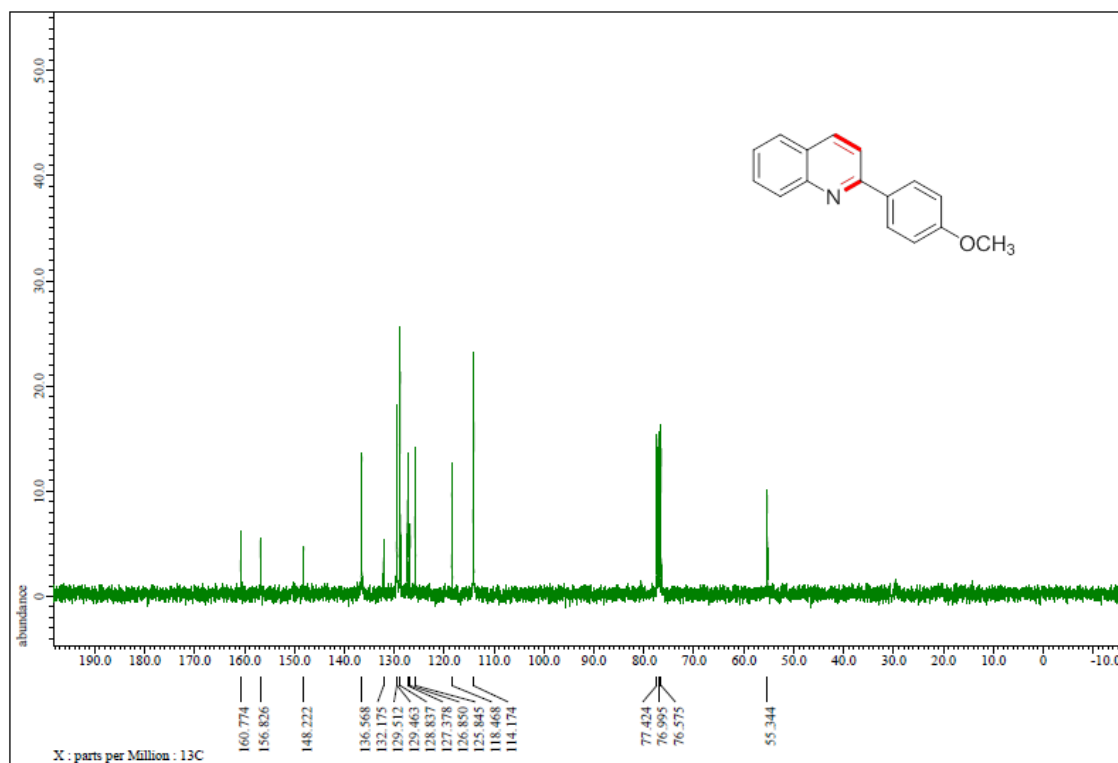
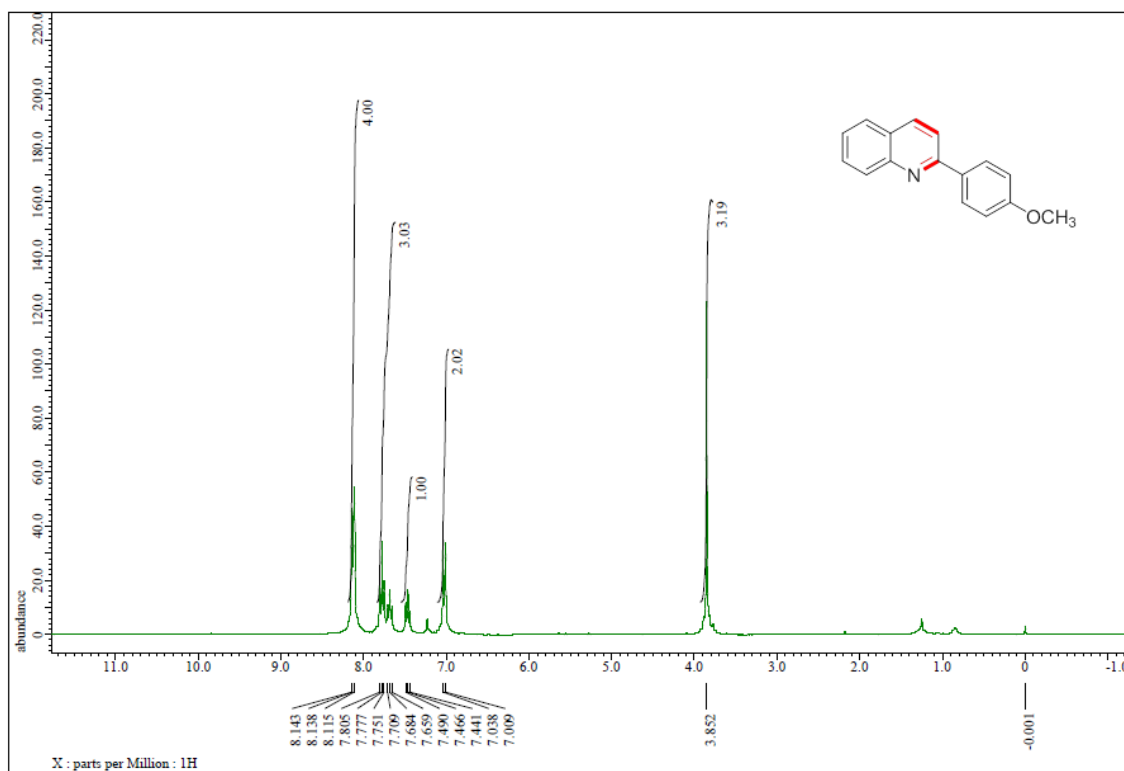




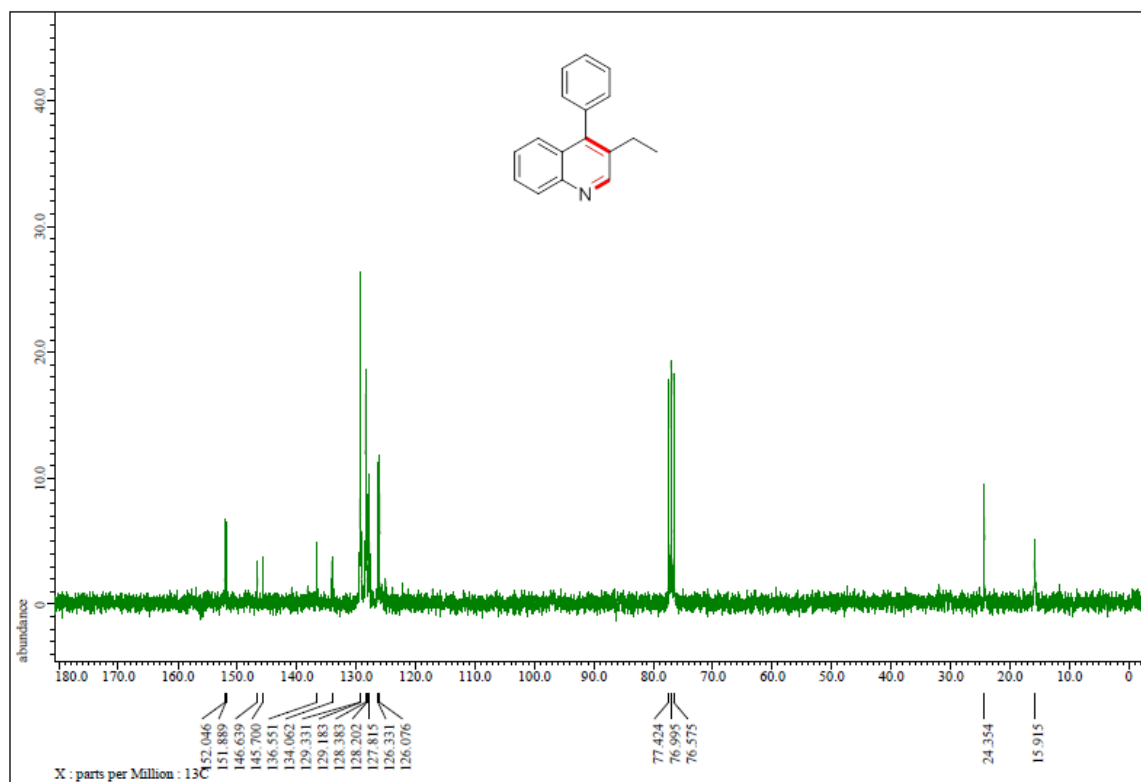
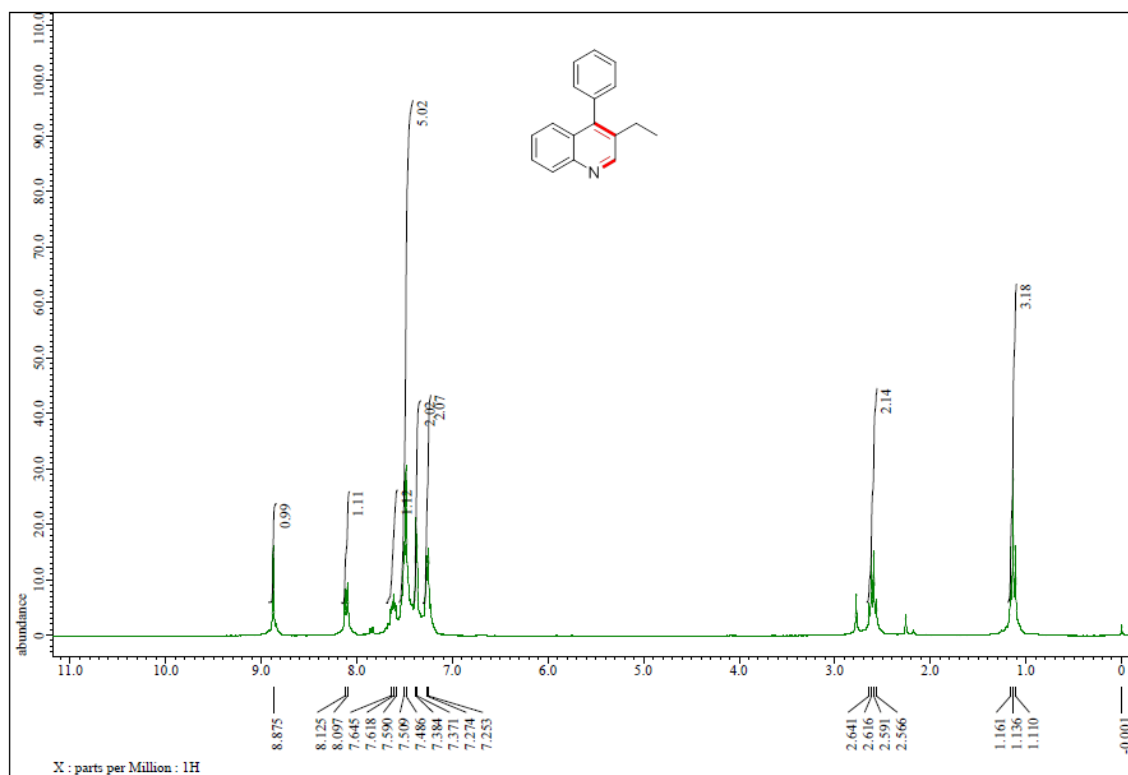
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3a**



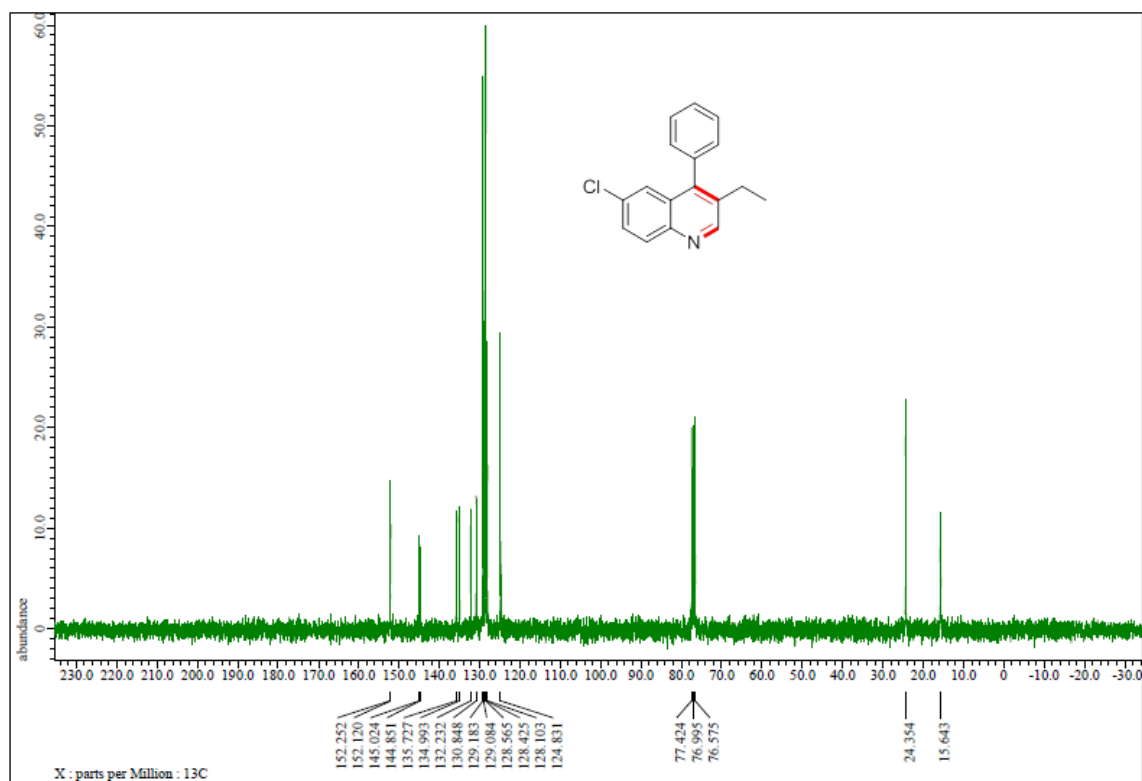
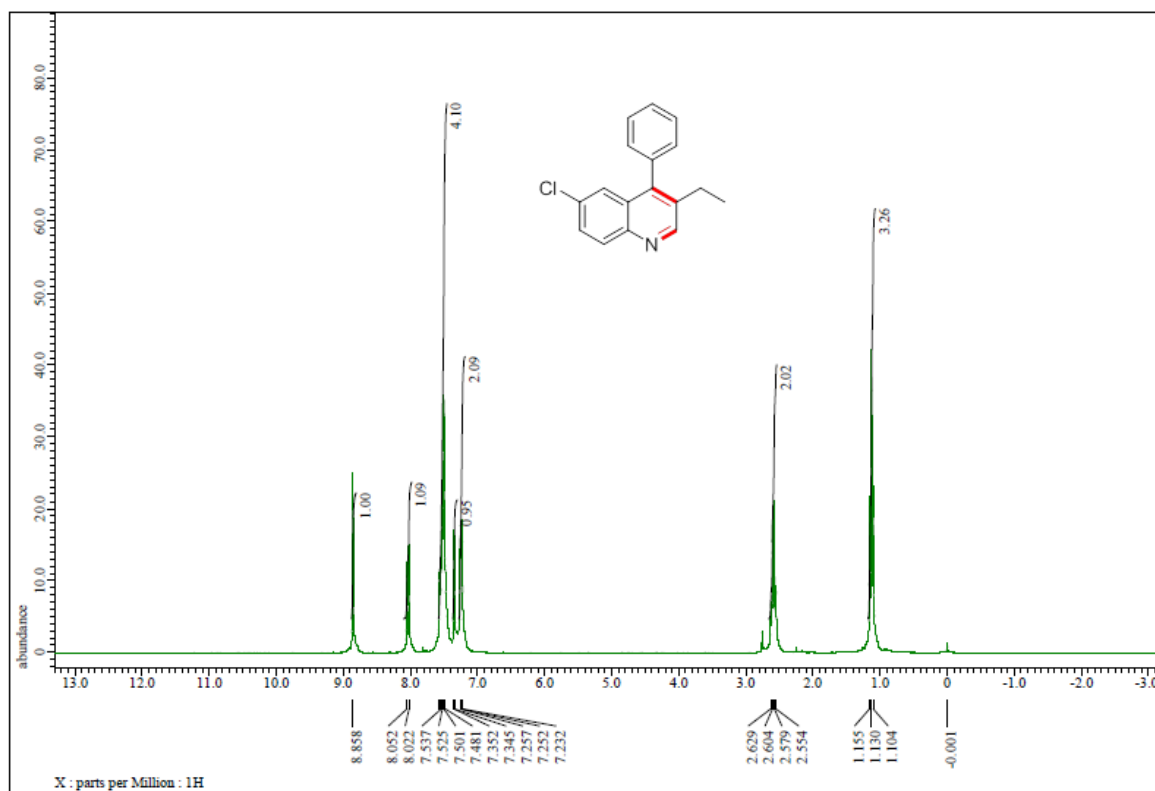
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3am**



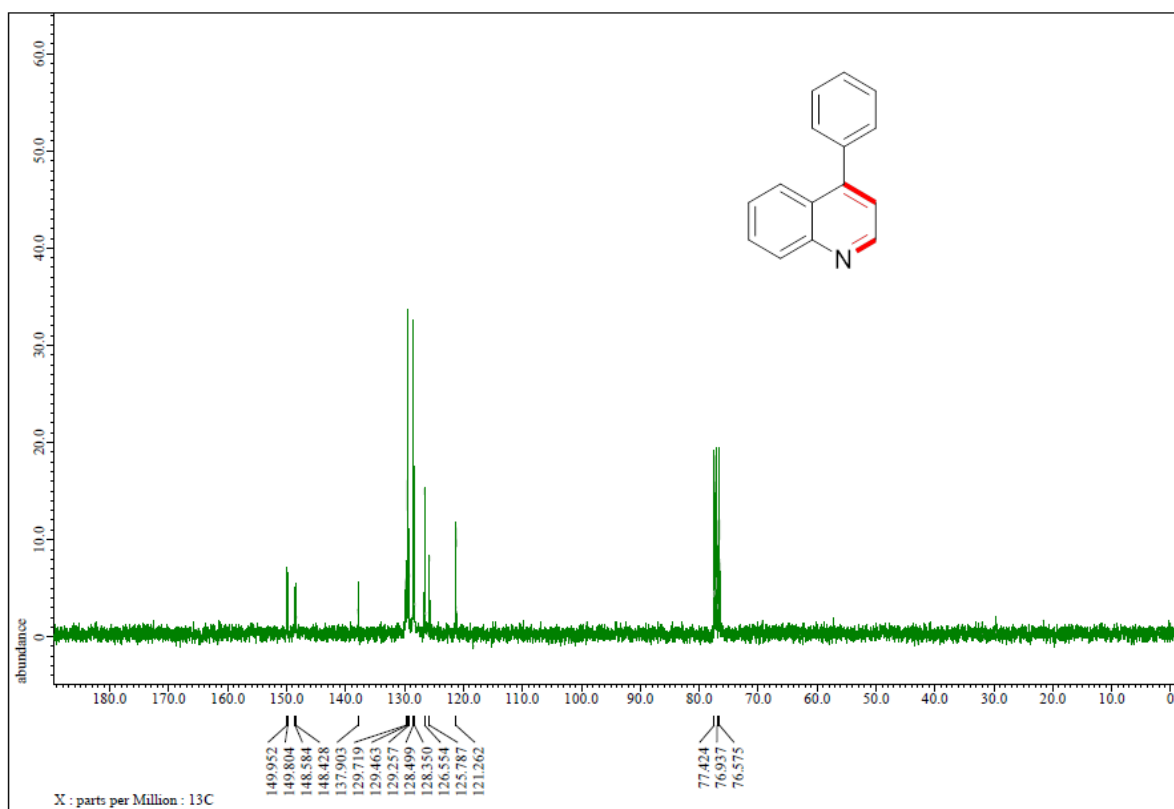
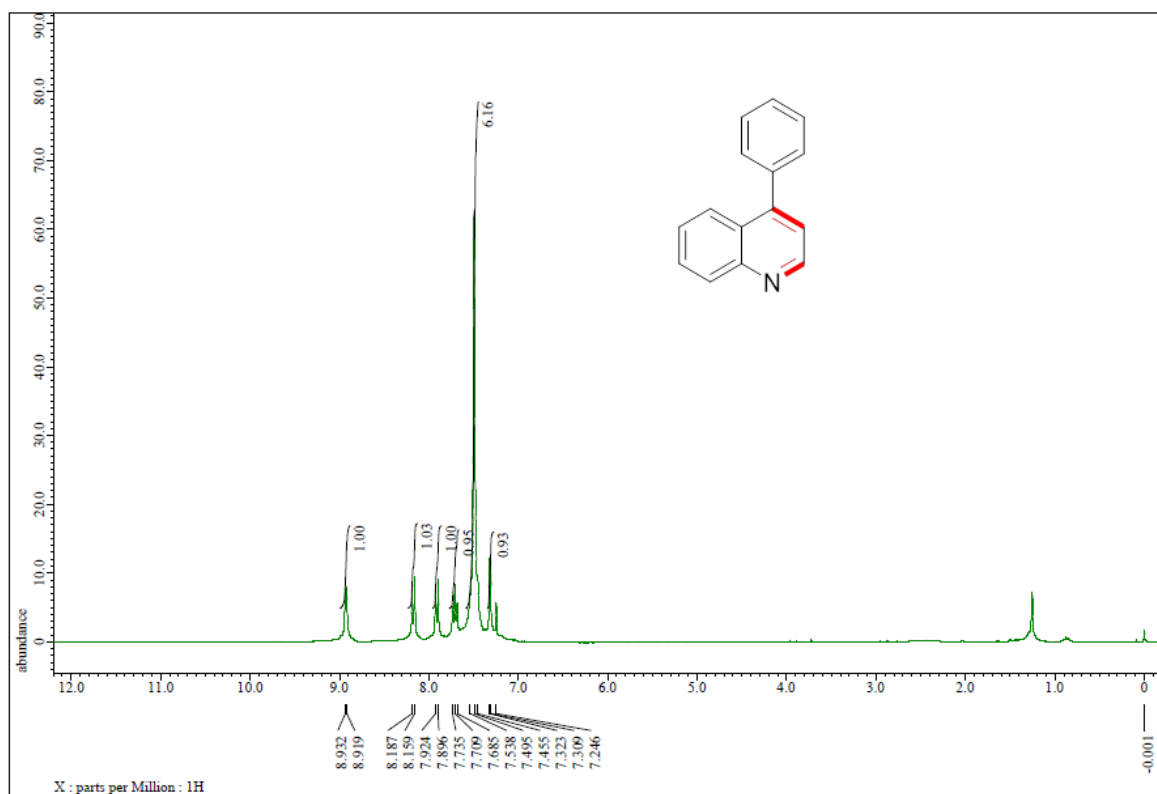
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ca**



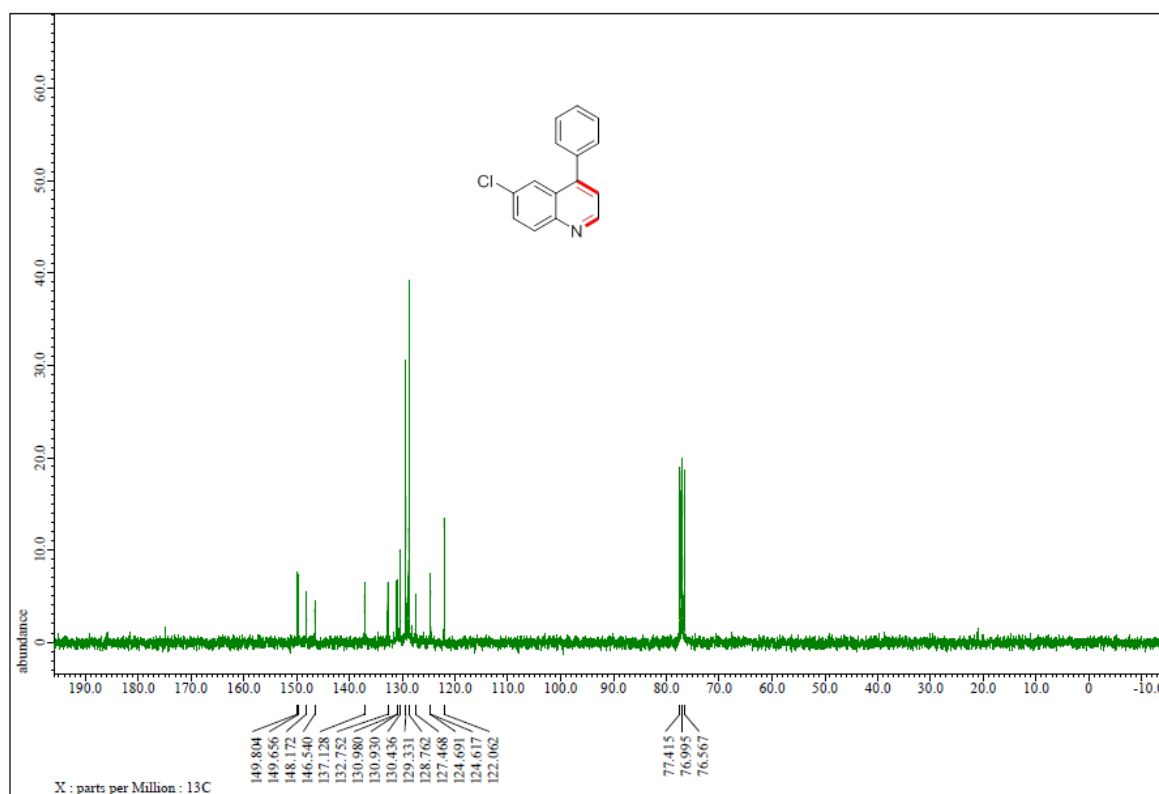
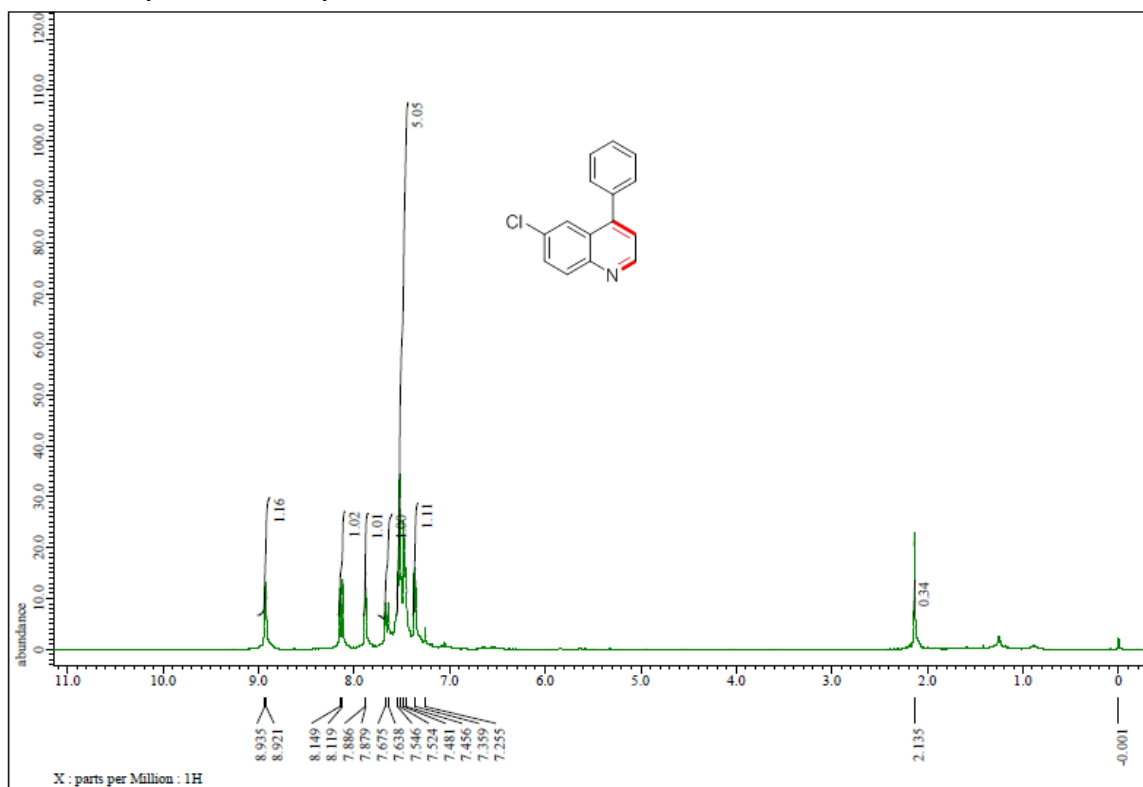
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3da**



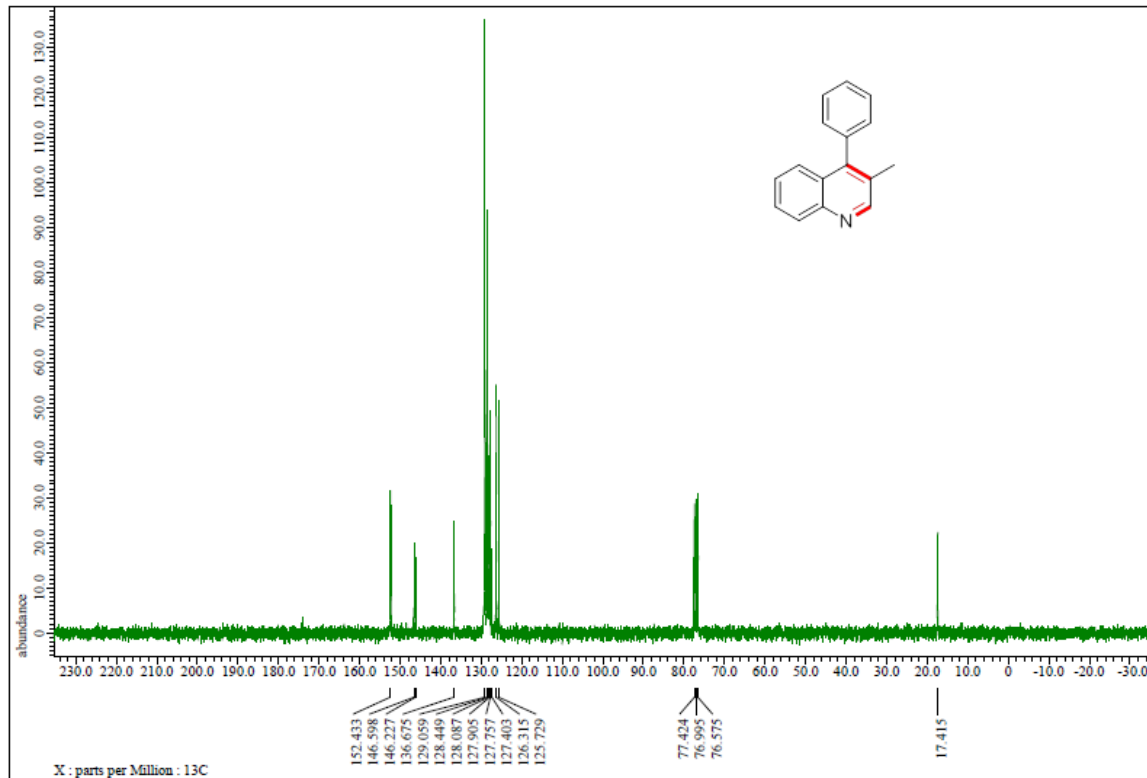
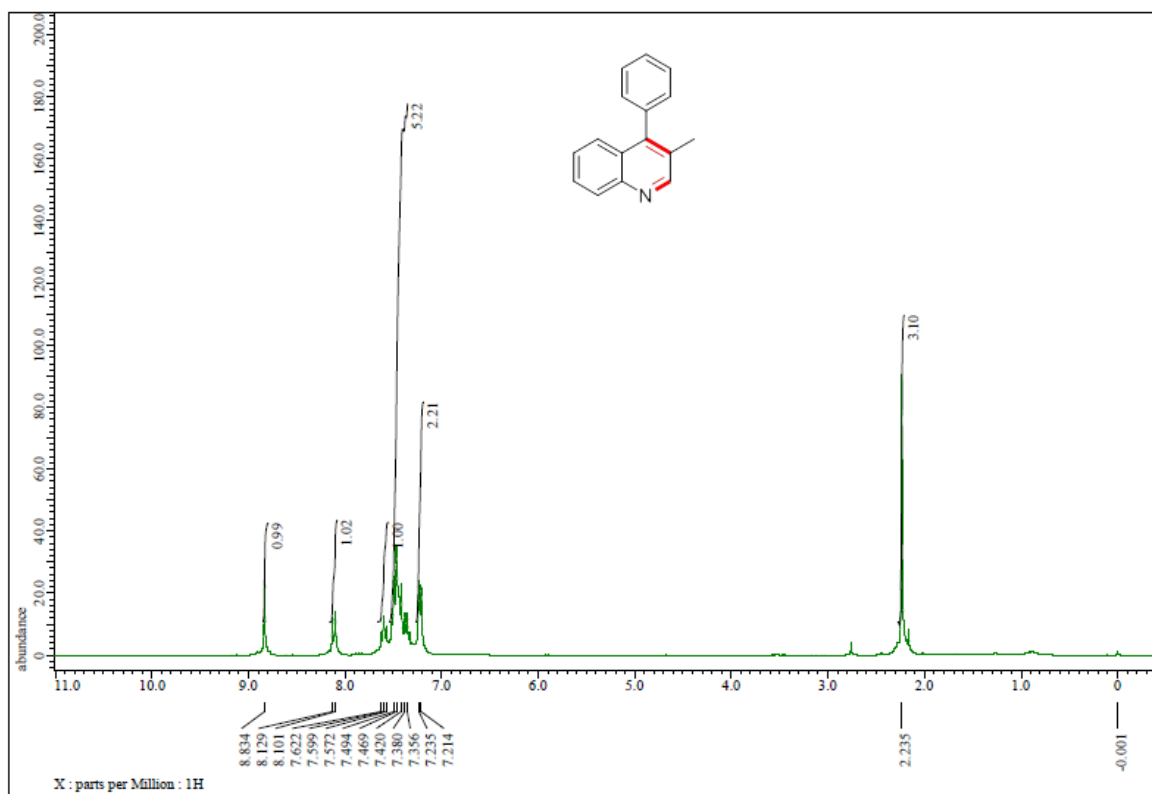
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3cb**



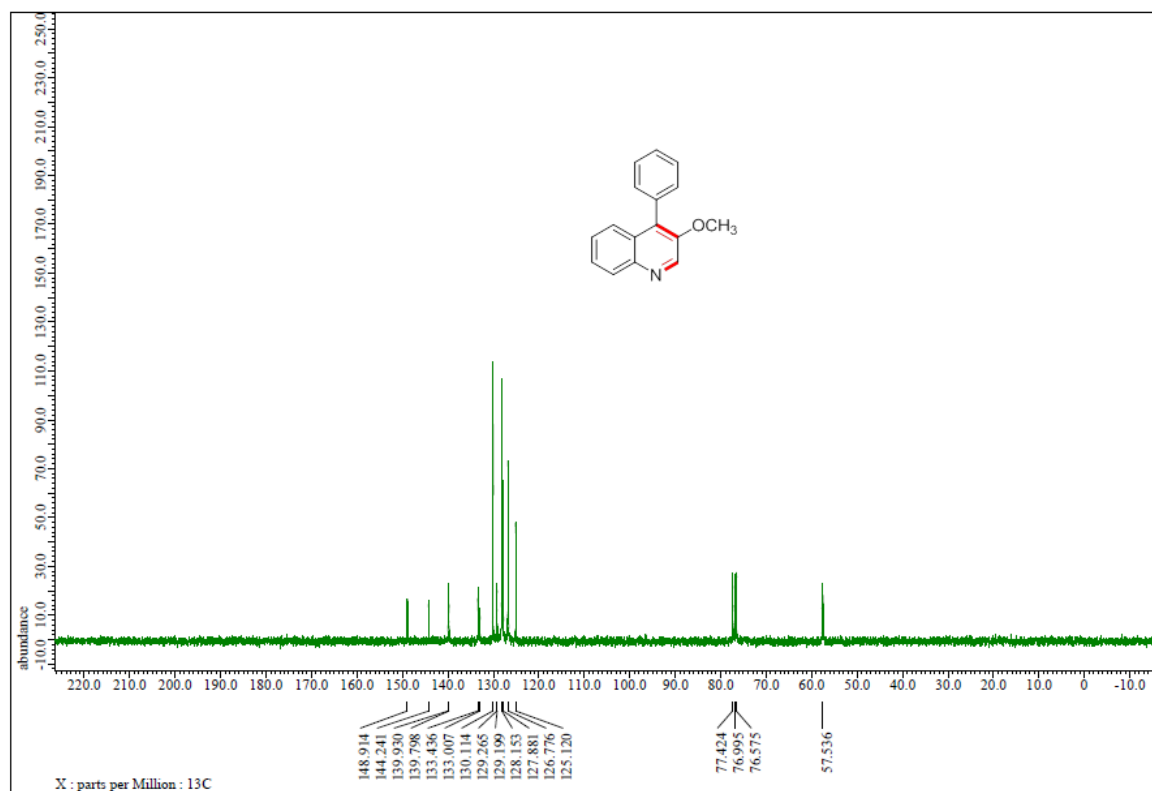
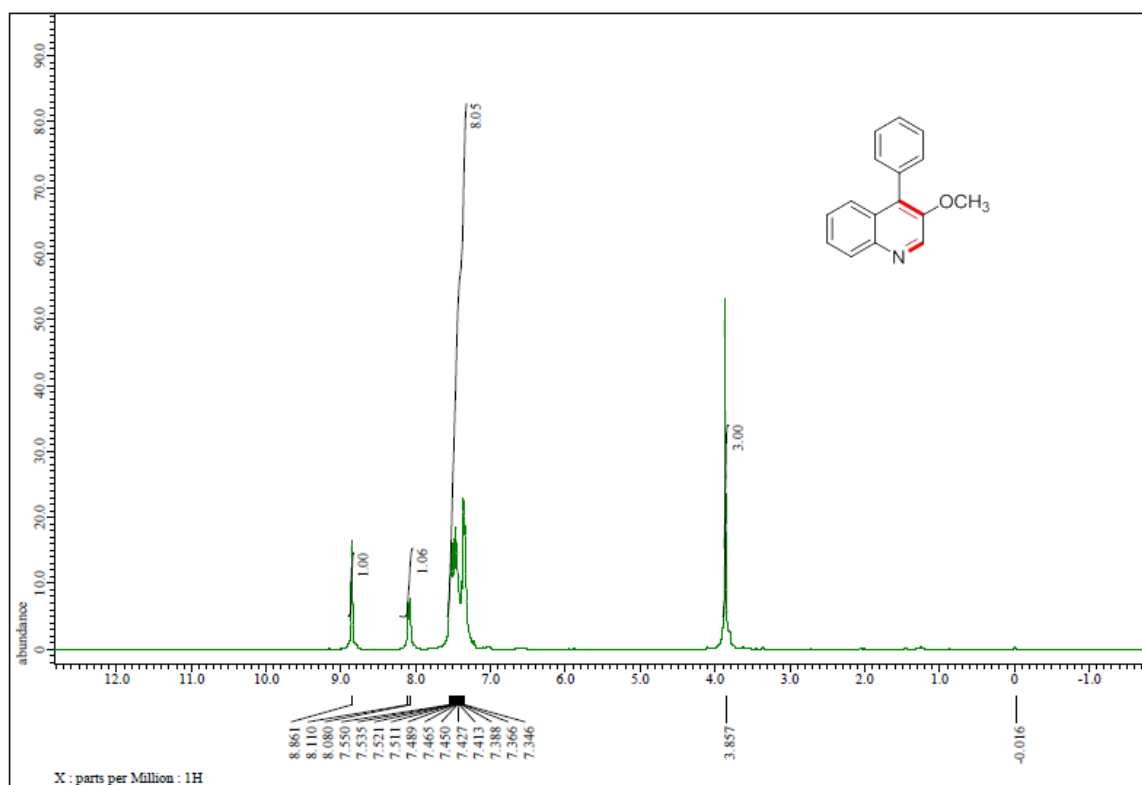
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3db**



$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3cc**

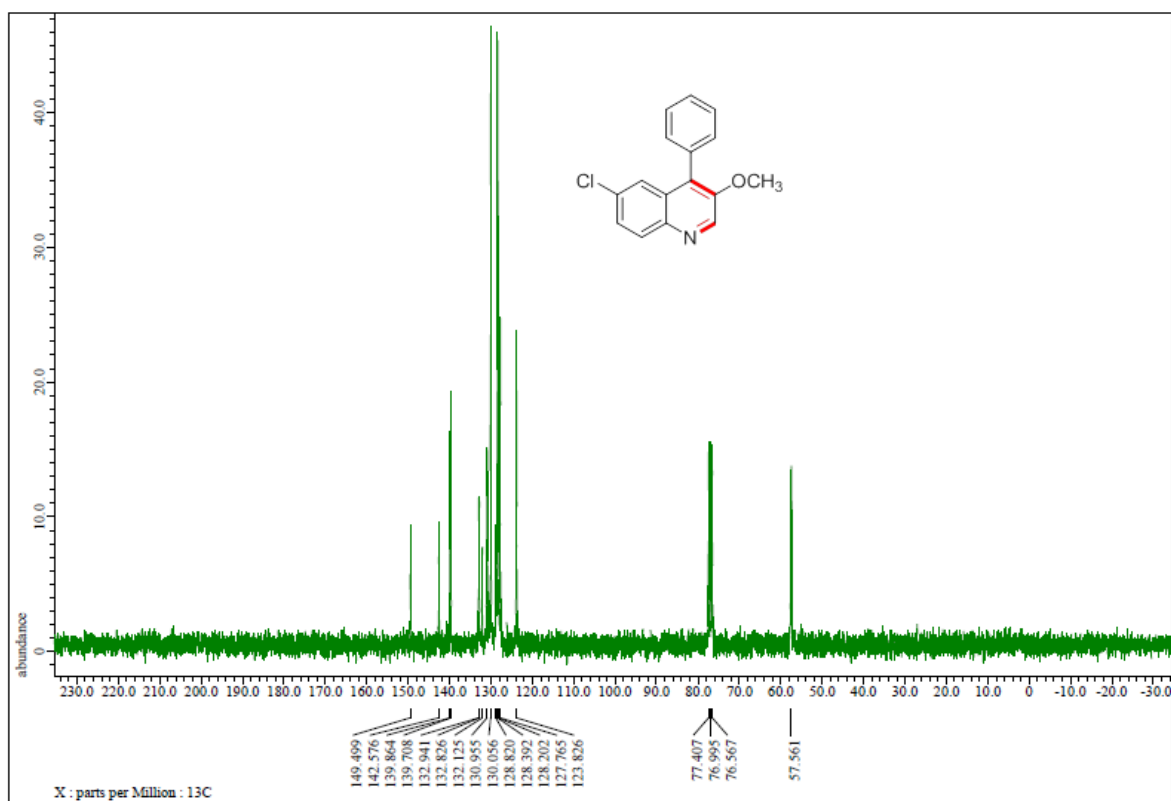
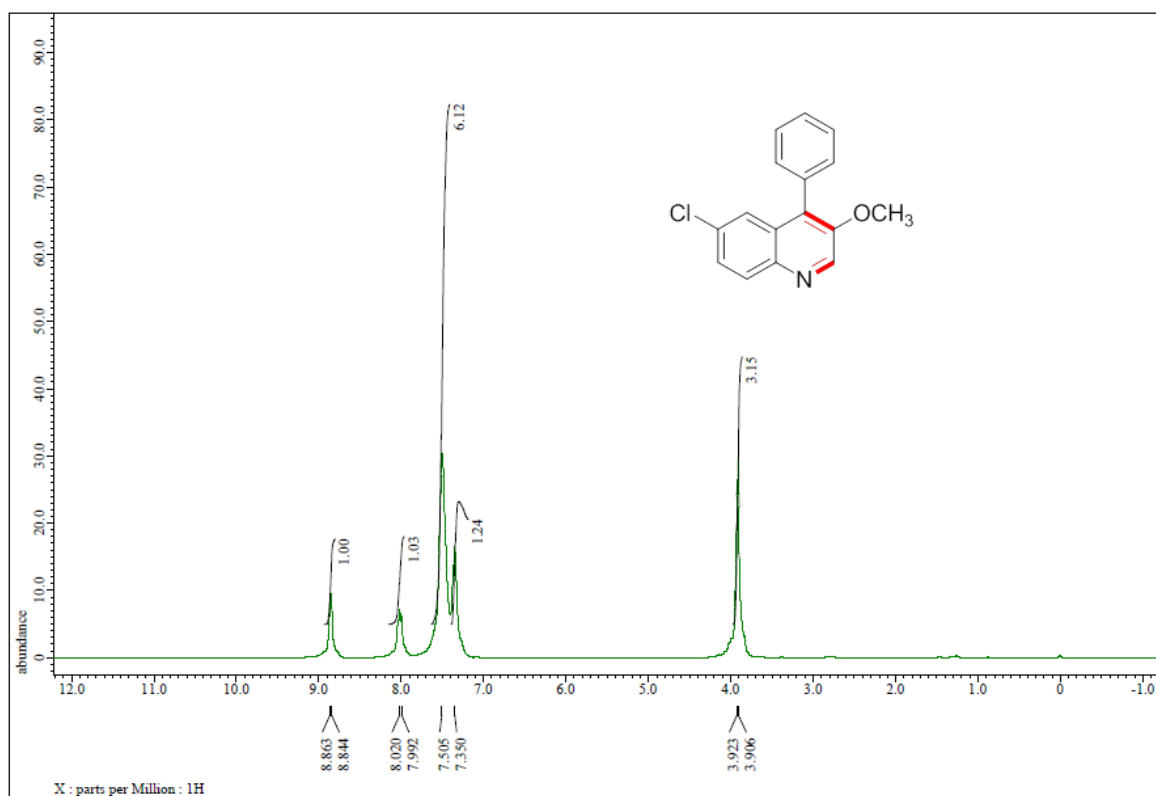


$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3cd**

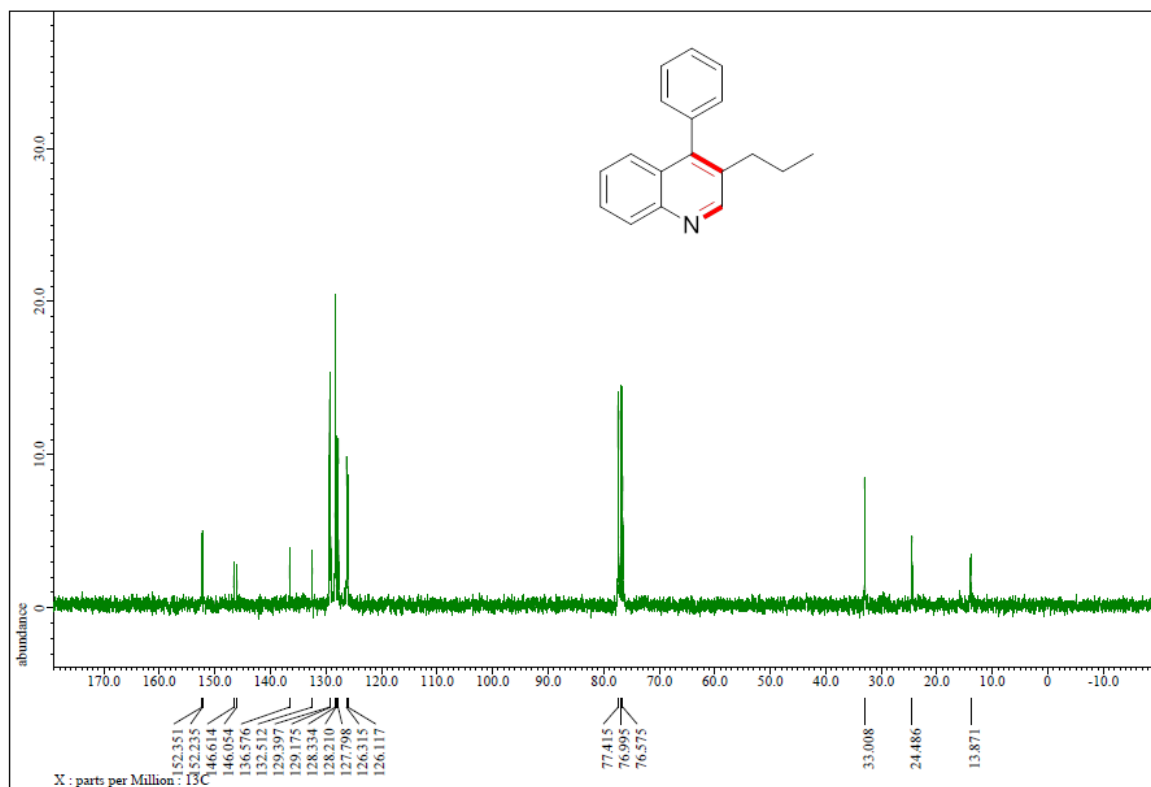
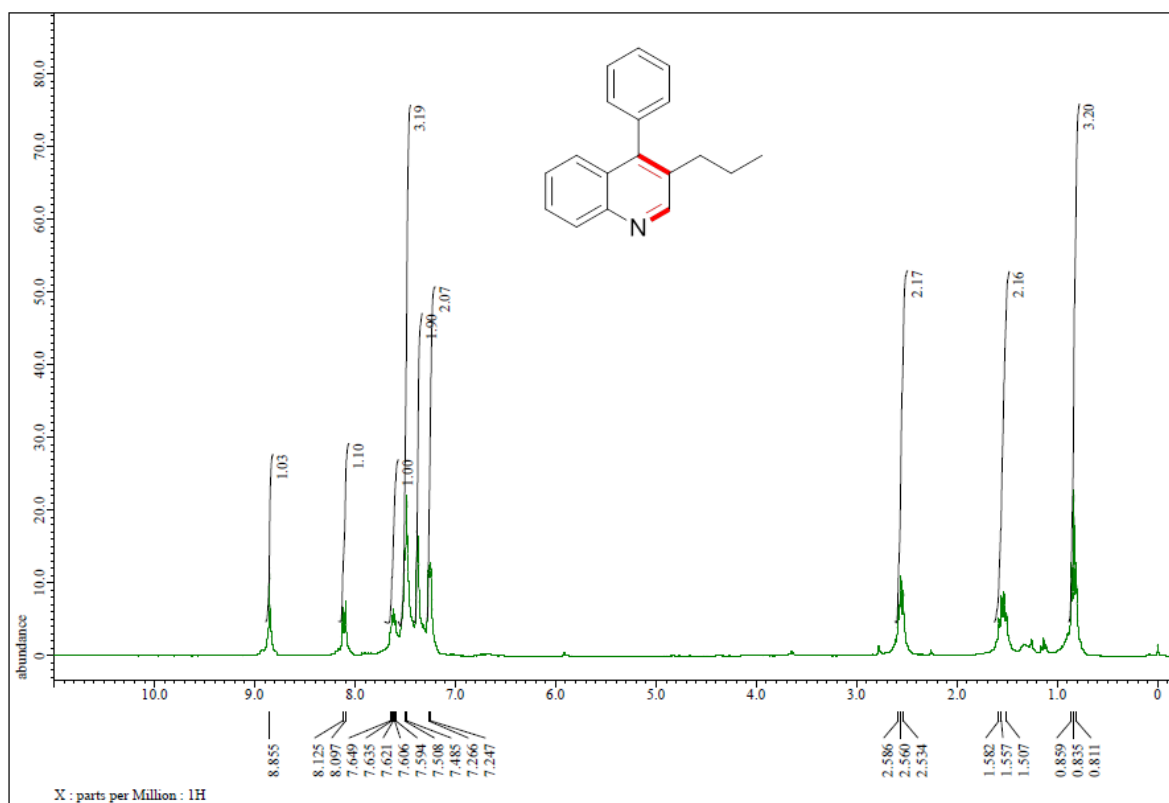




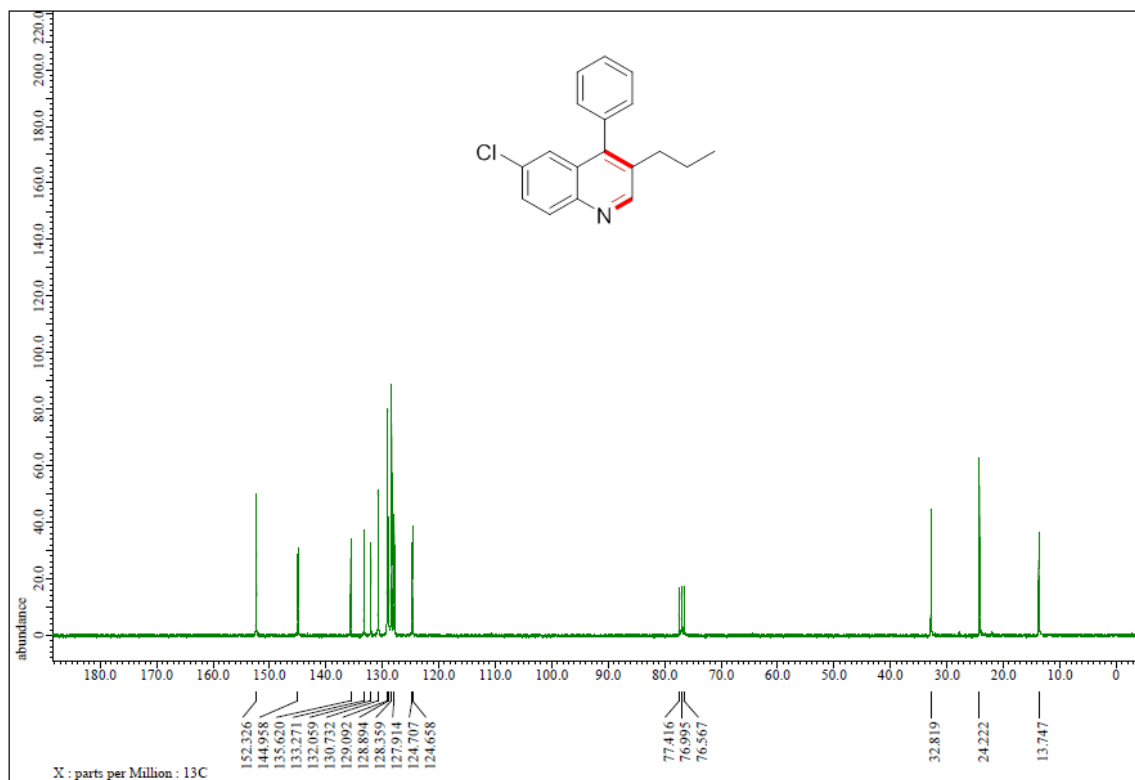
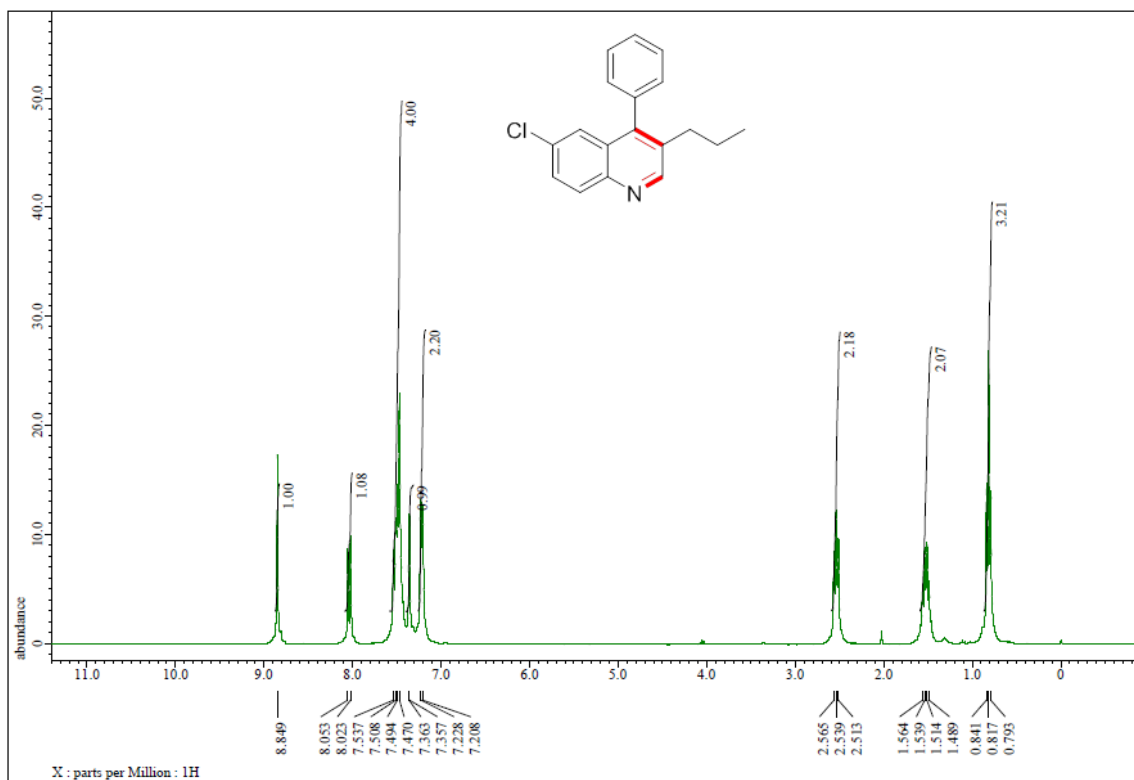
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3dd**



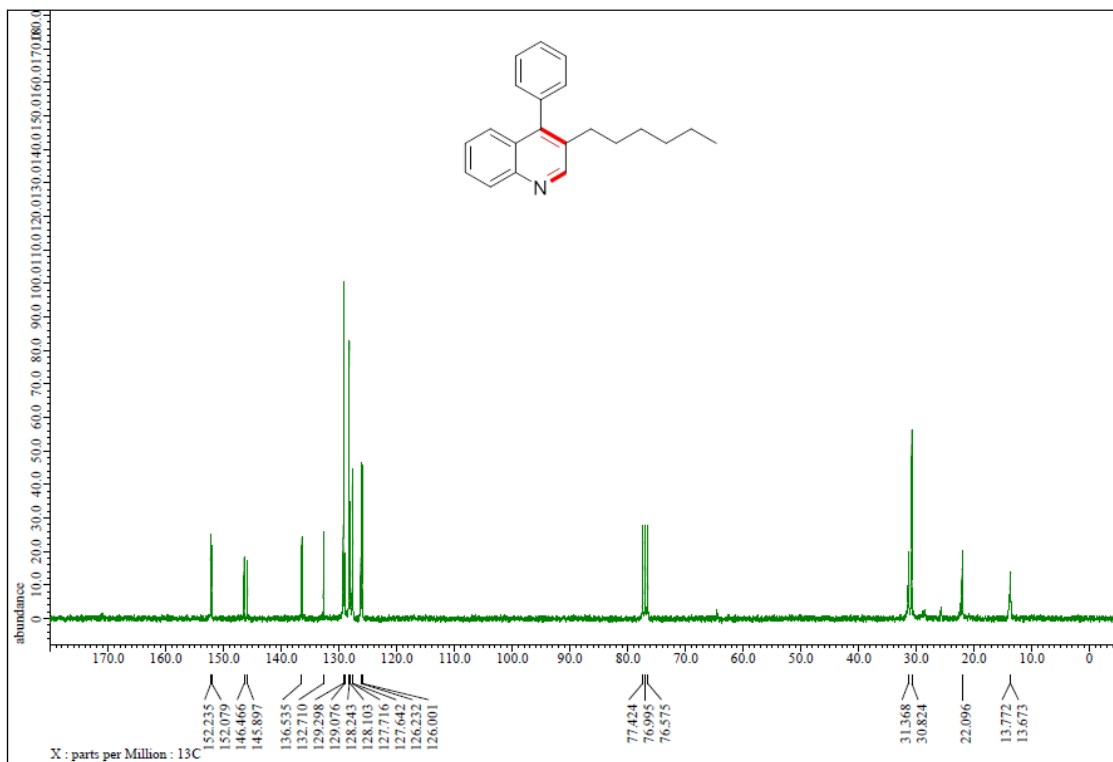
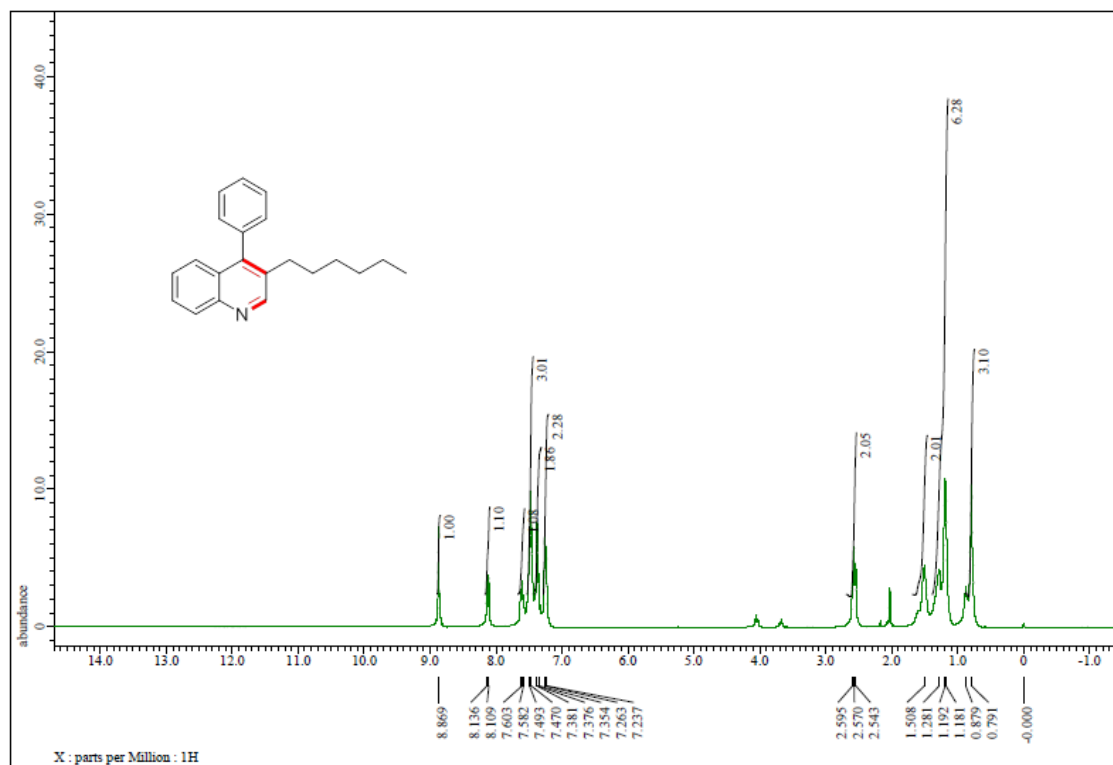
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ce**



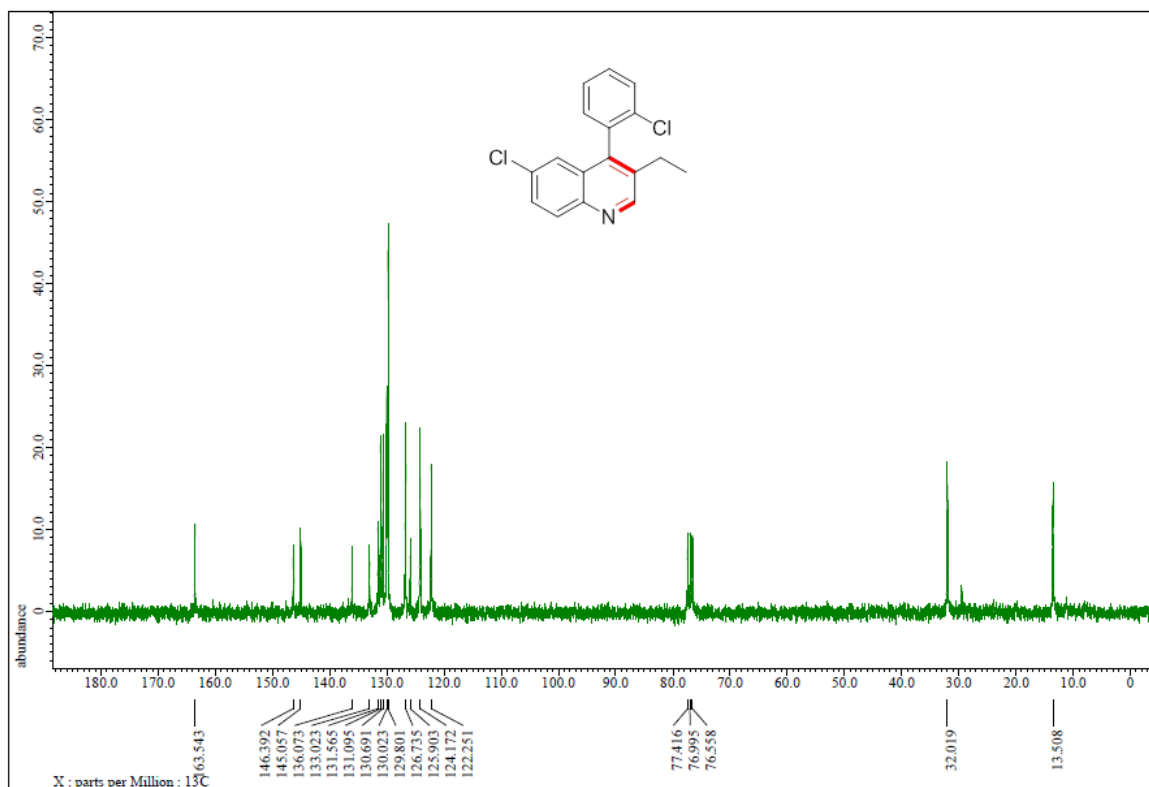
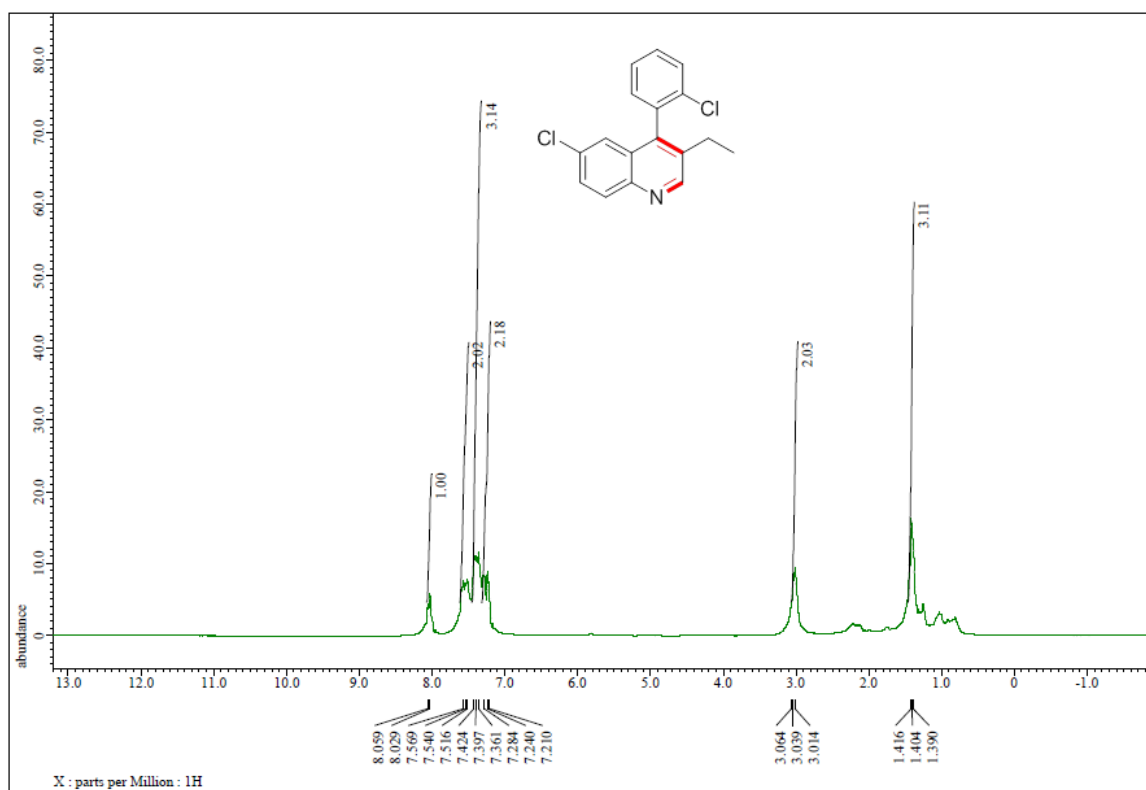
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3de**



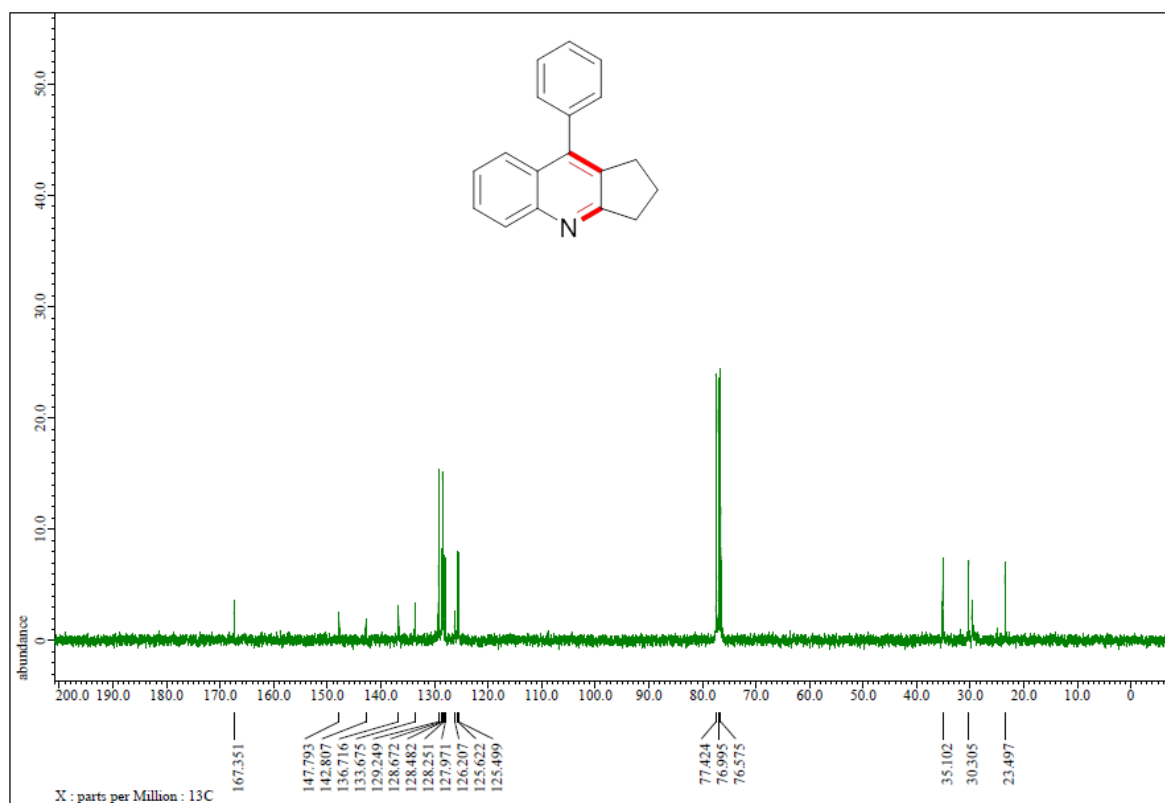
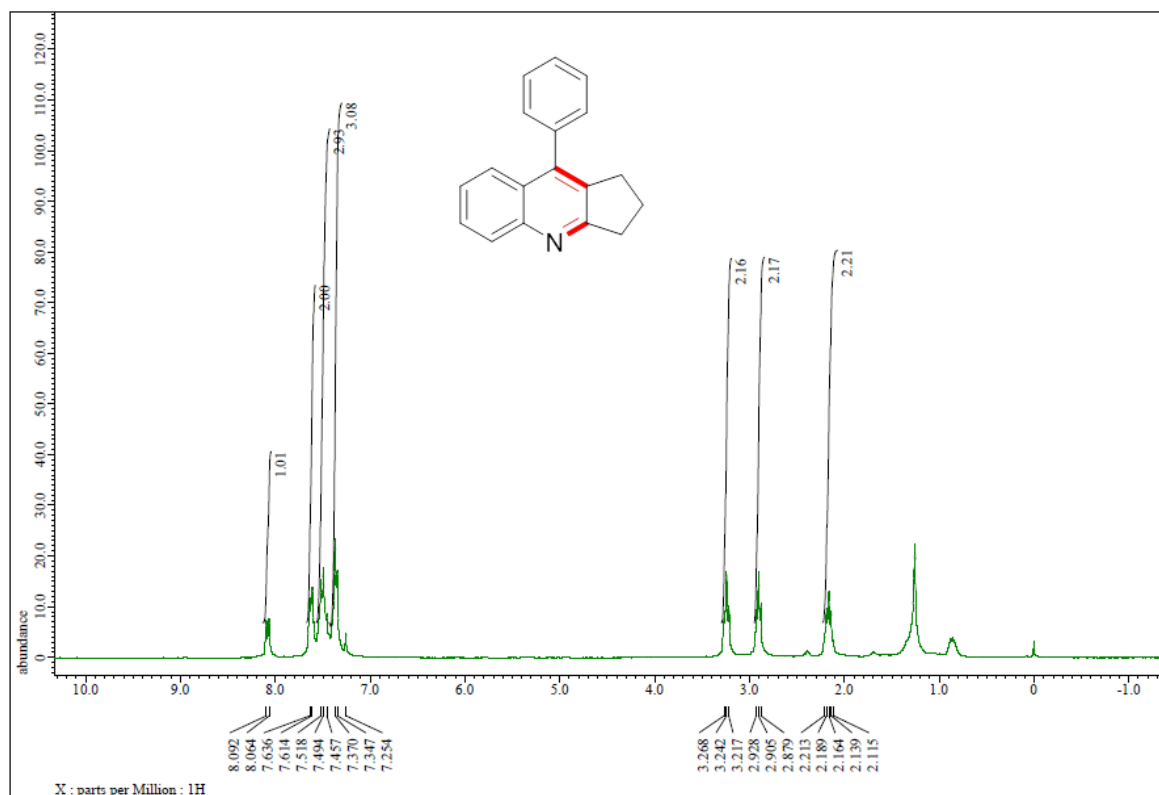
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3cf**



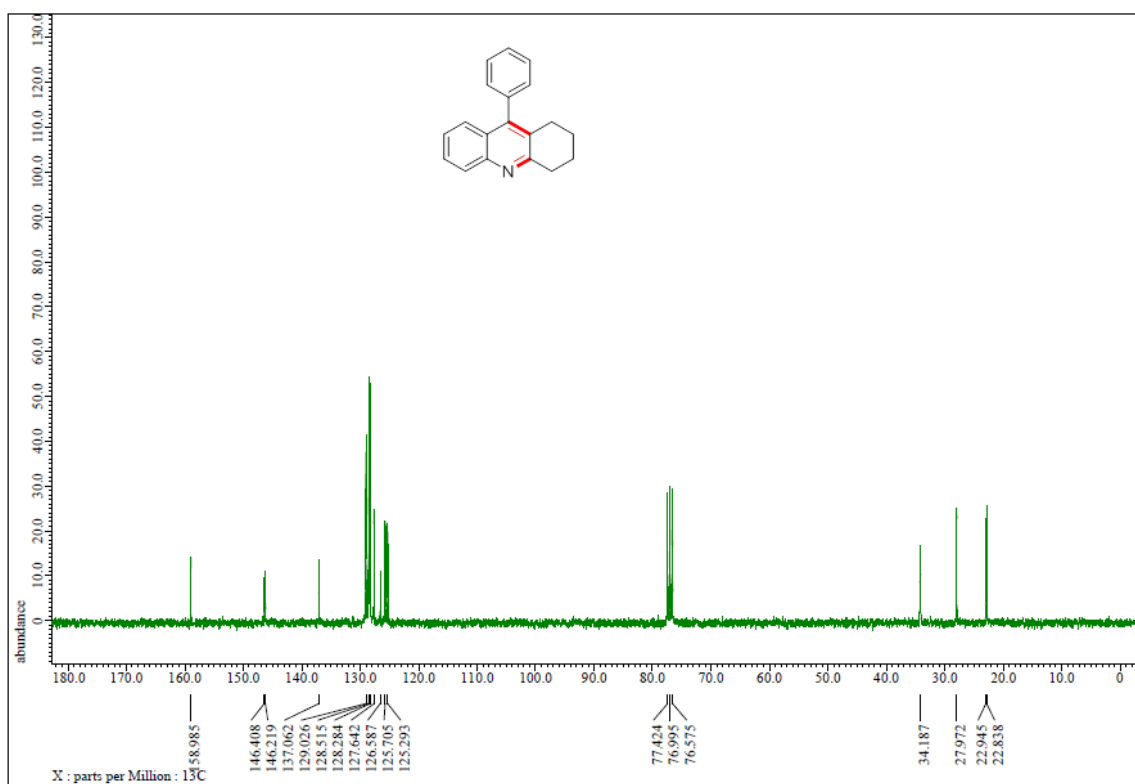
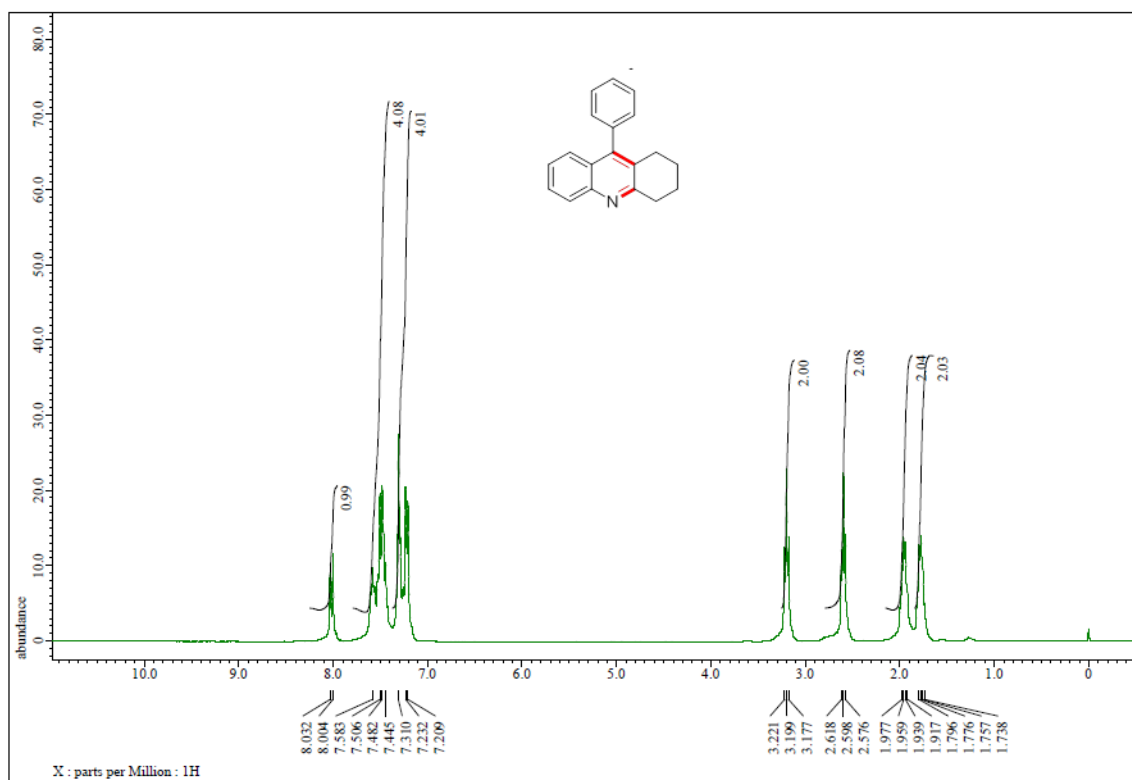
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3eg**



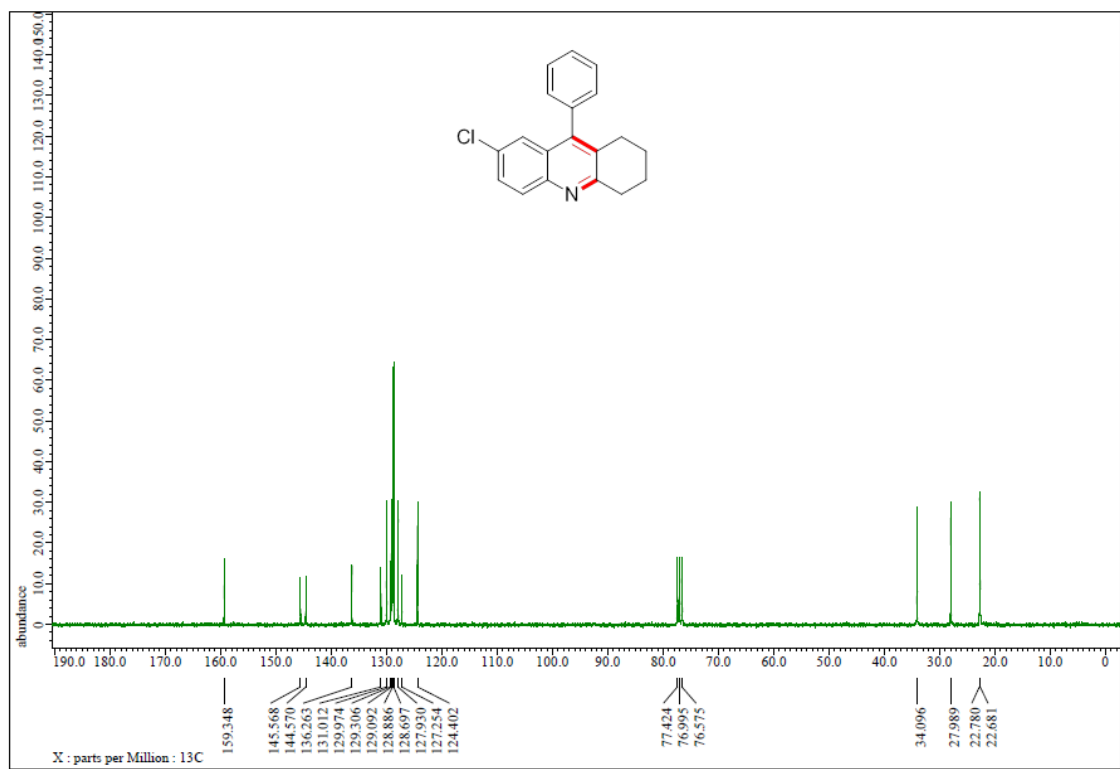
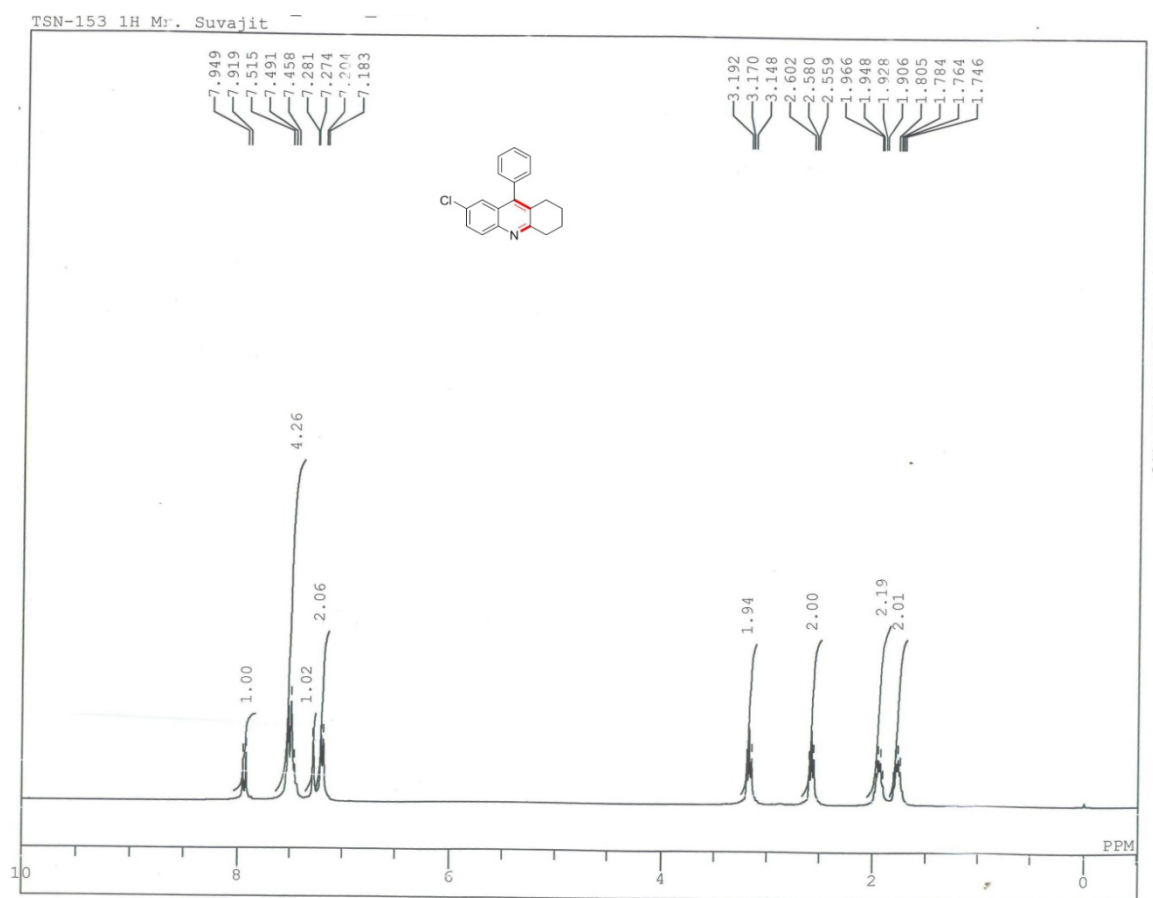
$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ch**



$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ci**

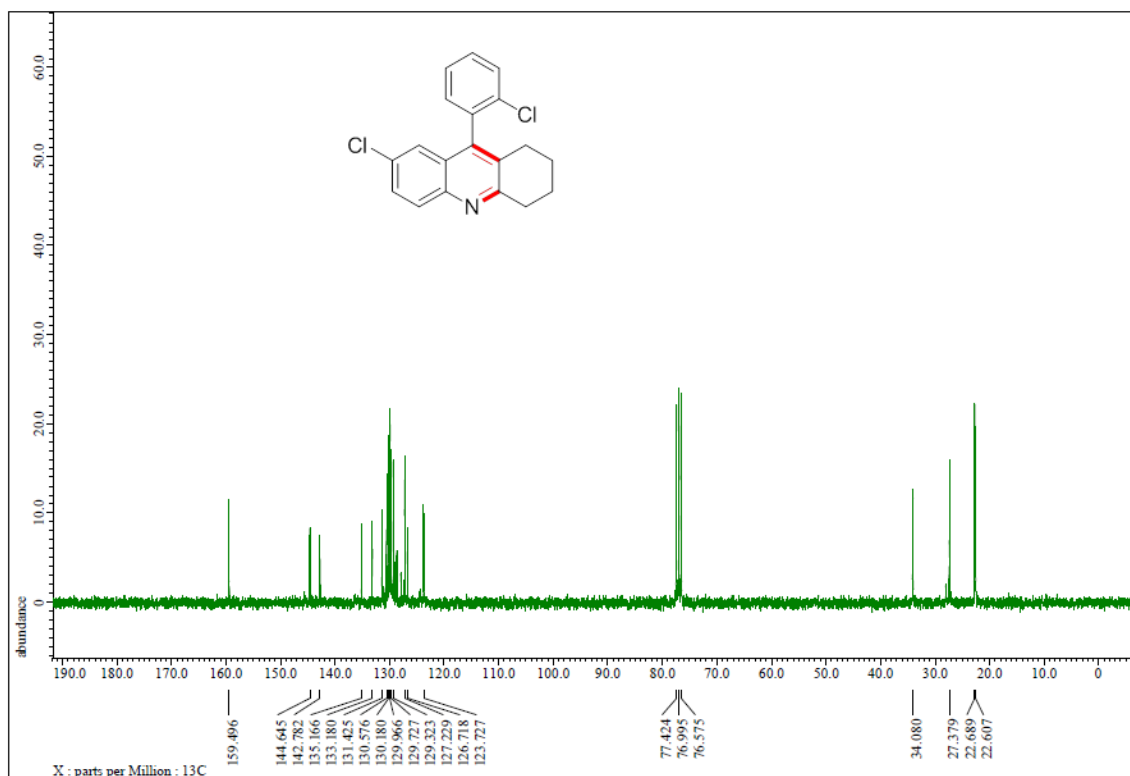
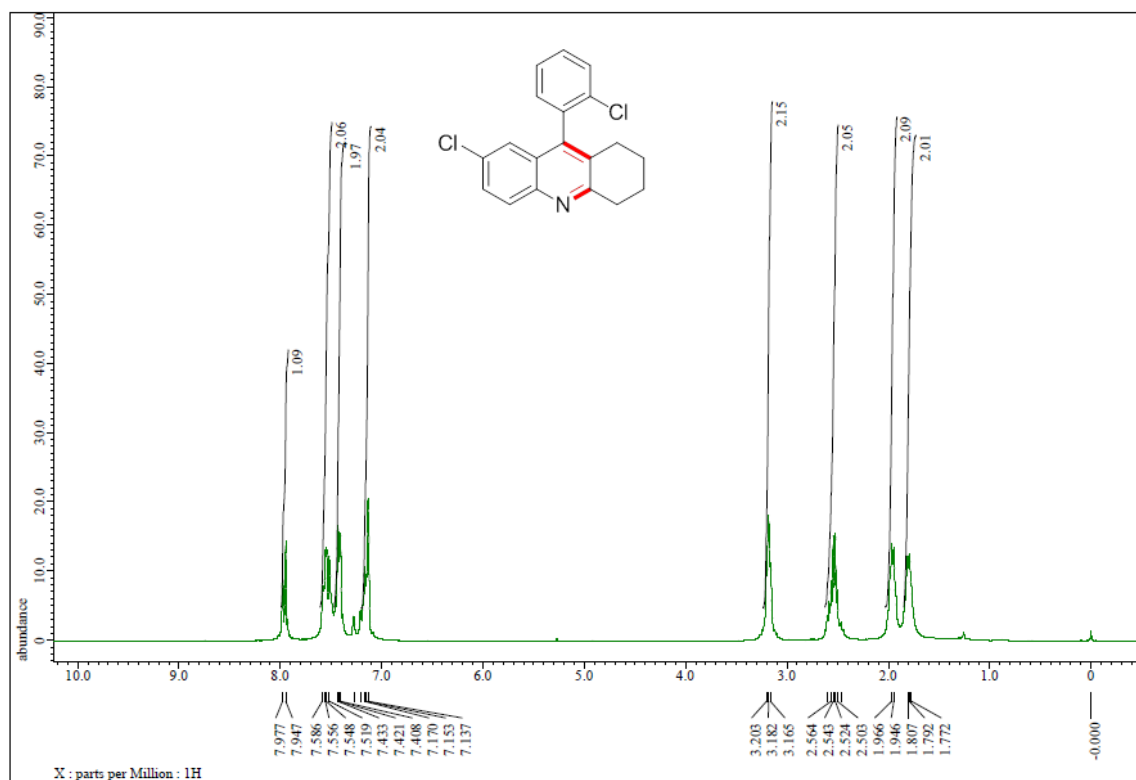


$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3di**

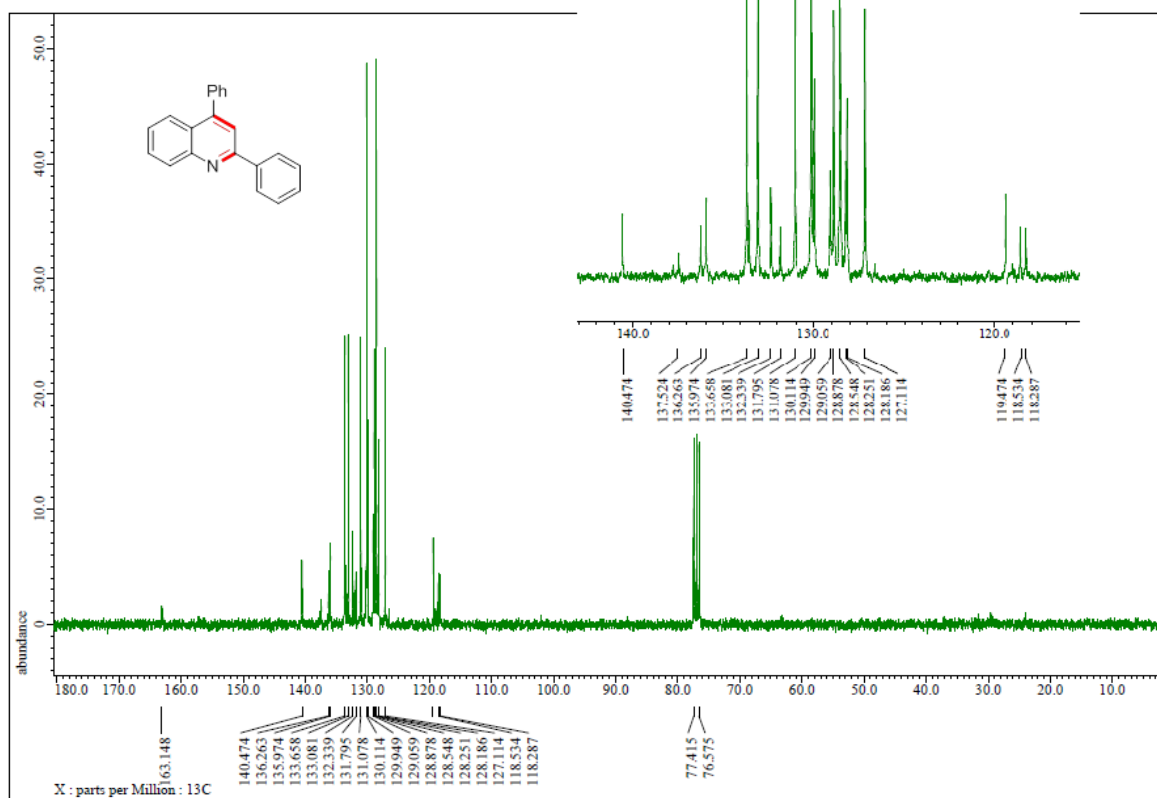
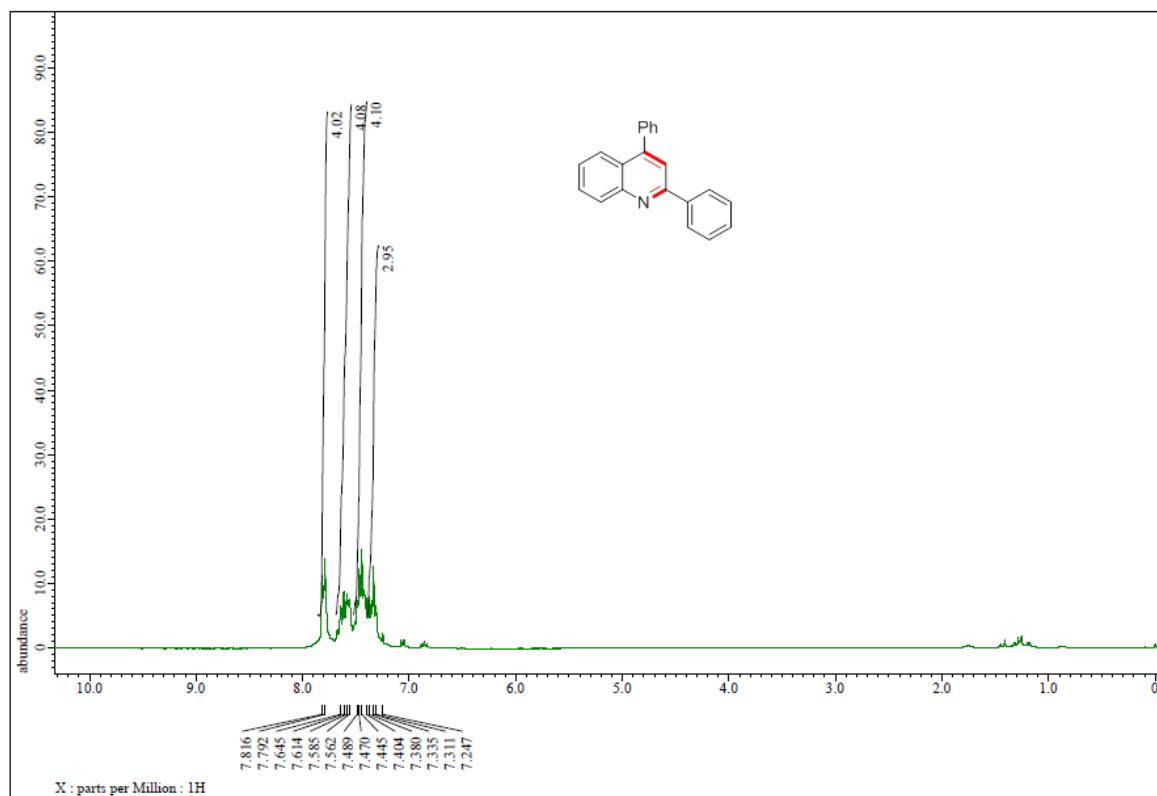




$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ei**



$^1\text{H}$  and  $^{13}\text{C}$  spectra of compound **3ck**



# $^1\text{H}$ and $^{13}\text{C}$ spectra of compound 4

