

# **Supporting Information**

## **Synthesis of Diverse Heterocycles via One-Pot Cascade Cross-Dehydrogenative-Coupling (CDC)/Cyclization Reaction**

Chao Zhang<sup>†</sup>, Tianlei Li<sup>†</sup>, Liguang Wang and Yu Rao<sup>\*</sup>

Department of Pharmacology and Pharmaceutical Sciences, School of Medicine and School of Life Sciences,  
Tsinghua University, Beijing 100084, China

[yrao@mail.tsinghua.edu.cn](mailto:yrao@mail.tsinghua.edu.cn)

<b>Table of Contents</b>	<b>Page</b>
<b>Materials and Methods</b>	<b>2</b>
<b>General procedure</b>	<b>2</b>
<b>Date of products</b>	<b>2</b>
<b>Spectra</b>	<b>23-</b>

## Materials and Methods

All commercial materials (Alfa Aesar, Aladdin, J&K Chemical LTD.) were used without further purification. All solvents were analytical grade. The potassium persulfate were ground to powder. The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE<sup>III</sup> 400 MHz spectrometer in  $\text{CDCl}_3$  using TMS or solvent peak as a standard. All  $^{13}\text{C}$  NMR spectra were recorded with complete proton decoupling. Low-resolution mass spectral analyses were performed with a Waters AQUITY UPLC<sup>TM</sup>/MS. All reactions were carried out in sealed tube with Teflon cap. Analytical TLC was performed on Yantai Chemical Industry Research Institute silica gel 60 F254 plates and flash column chromatography was performed on Qingdao Haiyang Chemical Co. Ltd silica gel 60 (200-300mesh). The rotavapor was BUCHI's Rotavapor R-3.

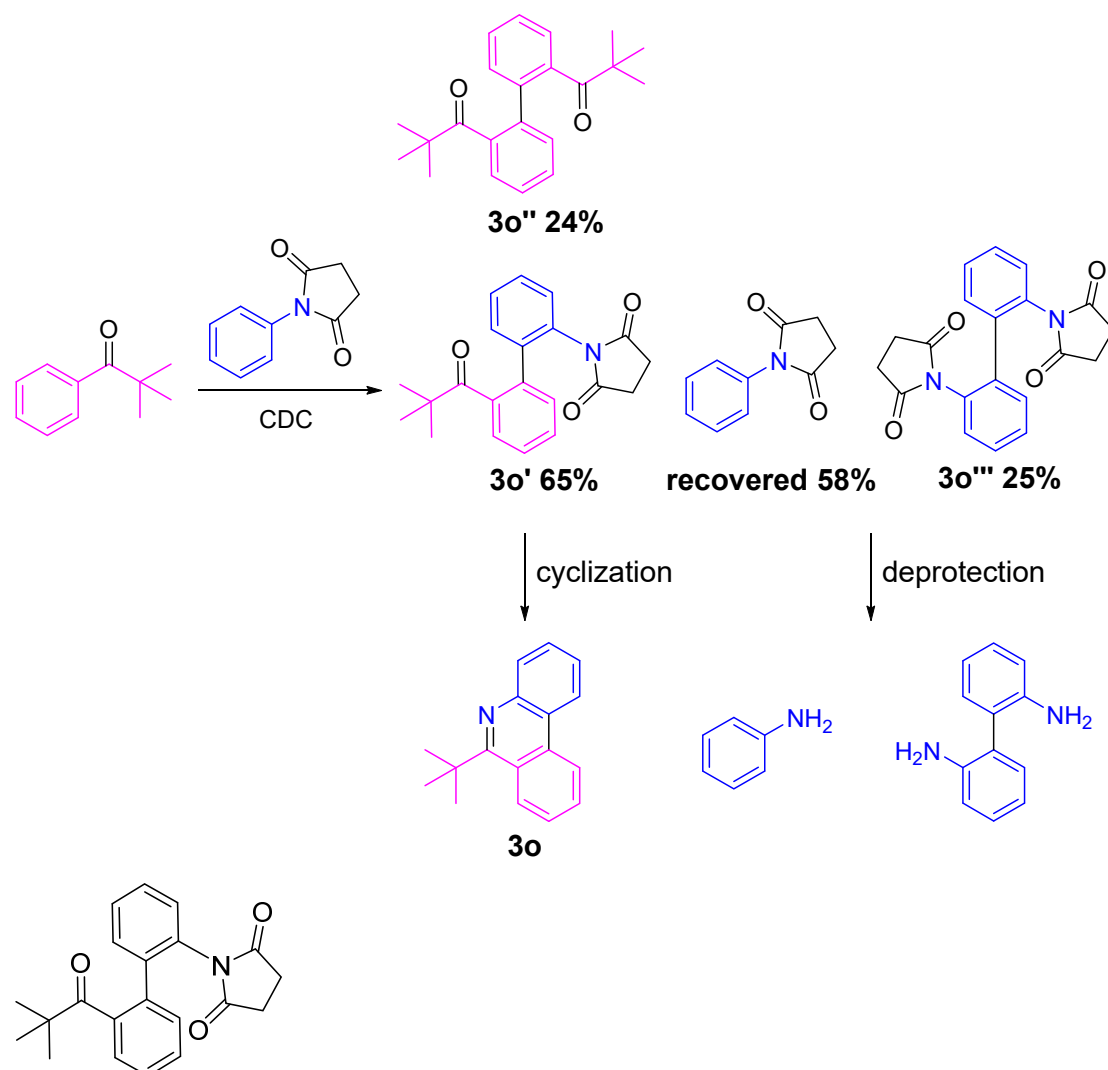
### I. General Procedure for the Heterocycles Synthesis:

The  $\text{Pd}(\text{OAc})_2$  (10%-13%),  $\text{NaIO}_4$  1.0-1.6 equiv,  $\text{K}_2\text{S}_2\text{O}_8$  3.0-4.0 equiv and the starting material (substrate **1** 0.1mmol, substrate **2** 3.0-4.0 equiv) were dissolved in commercial hexafluoroisopropanol (HFIP) 1.5 ml in a 10 mL round bottom flask. Following that, TfOH or TsOH.H<sub>2</sub>O (3.6-4.4 equiv) was added into the reaction solution. The mixture was heated for 5-8 hours at 60 °C. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH 10.0-20.0 equiv in EtOH 1.5 mL or in conc. HCl 1.5 ml was stirred at 80 °C for 2-4 hours. After that, HCl (10%) or saturated  $\text{NaHCO}_3$  was added to neutralize the reaction mixture, and then diluted with DCM. Then organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography.

### II. General Procedure for the Heterocycles Synthesis at a Large Scale Reaction:

Benzophenone (0.2 g, 1.1 mmol), 1-(m-tolyl)pyrrolidine-2,5-dione (0.8 g, 3.8 equiv),  $\text{Pd}(\text{OAc})_2$  (25 mg, 0.10 equiv),  $\text{NaIO}_4$  (263 mg, 1.5 equiv),  $\text{K}_2\text{S}_2\text{O}_8$  (945 mg, 3.2 equiv), HFIP 12 ml and TfOH (3.2 equiv, 330  $\mu\text{L}$ ) were used in a 50 mL round bottom flask. The reaction mixture was stirred at 60 °C for 5 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (0.6 g, 13.6 equiv) in EtOH 15 mL was stirred at 80 °C for 2 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3** (225 mg) in 76% yield.

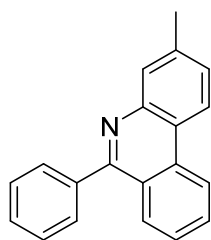
### III. Data of Products



### 1-(2'-pivaloyl-[1,1'-biphenyl]-2-yl)pyrrolidine-2,5-dione (**3o'**)

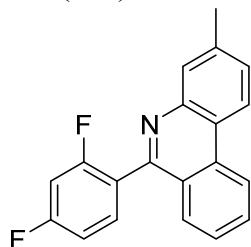
Following the general procedure II, 2,2-dimethyl-1-phenylpropan-1-one (17 mg, 0.10 mmol), 1-phenylpyrrolidine-2,5-dione (105 mg, 0.60 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.010 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (81 mg, 0.30 mmol), HFIP 1.5 ml and TfOH (4.6 equiv, 43  $\mu$ L) were used. The reaction mixture was stirred at 60 °C for 8 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether:Ethyl acetate = 4:1). Finally, compound **3o'** (21 mg, white solid) was isolated in 65% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.49-7.43 (m, 4H), 7.37-7.33 (m, 2H), 7.28-7.25 (m, 1H), 7.00-6.98 (m, 1H), 3.01-2.96 (m, 1H), 2.72-2.68 (m, 1H), 2.60-2.53 (m, 2H), 0.89 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 216.0, 176.3, 175.6, 140.9, 138.9, 134.4, 132.5, 131.8, 130.7, 129.0, 128.8, 128.7, 127.5, 125.5, 44.7, 29.1, 28.3, 27.5; MS (ESI) calcd for C<sub>21</sub>H<sub>21</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 335.15, found 336.14

Besides, we also separated the homo-coupling product of the ketone with a yield of 24%, which could be a reason for some product with unideal yield. Furthermore, though excess succinimide was used in this reaction, only 25% homo-coupling product could be obtained and 58% of the succinimide could be recovered, those would be converted into the deprotected product.



### 3-methyl-6-phenylphenanthridine (3)

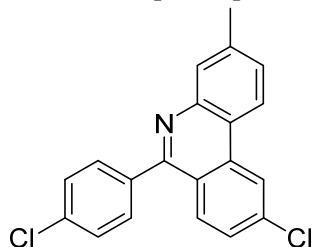
Following the general procedure I, benzophenone (21 mg, 0.115 mmol), 1-(*m*-tolyl)pyrrolidine-2,5-dione (82 mg, 0.4 mmol), Pd(OAc)<sub>2</sub> (2.7 mg, 0.010 mmol), NaIO<sub>4</sub> (35 mg, 0.14 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (100 mg, 0.32 mmol), HFIP 1.5 ml and TfOH (3.5 equiv, 37  $\mu$ L) were used. The reaction mixture was stirred at 60 °C for 6.0 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3** (24.8 mg) in 80% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.65 (d, *J* = 8.4 Hz, 1H), 8.49 (d, *J* = 8.4 Hz, 1H), 8.10-8.06 (m, 2H), 7.82 (t, 1H), 7.84-7.73 (m, 2H), 7.59-7.53 (m, 5H), 7.59-7.53 (m, 5H), 2.61 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 161.3, 144.0, 140.3, 139.1, 133.6, 130.6, 130.1, 129.8, 128.8, 128.7, 128.5, 126.7, 125.0, 122.1, 121.8, 121.5, 21.7; MS (ESI) calcd for C<sub>20</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 269.12, found 270.17.



### 6-(2,4-difluorophenyl)-3-methylphenanthridine (3a)

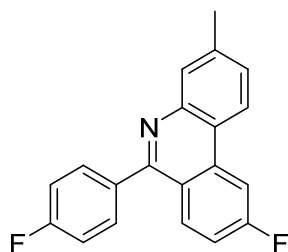
Following the general procedure I, (2,4-difluorophenyl)(phenyl)methanone (22 mg, 0.10 mmol), 1-(*m*-tolyl)pyrrolidine-2,5-dione (80 mg, 0.4 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.013 mmol), NaIO<sub>4</sub> (39 mg, 0.18 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.40 mmol), HFIP 1.5 ml and TfOH (4.2 equiv, 39  $\mu$ L) were used. The reaction mixture was stirred at 60 °C for 6 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 7 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3a** (23 mg) in 75% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.65 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.03 (s, 1H), 7.86-7.79 (m, 1H), 7.64-7.54 (m, 3H), 7.10 (dt, *J* = 9.2 Hz, *J* = 2.4 Hz, 1H), 7.02 (dt, *J* = 9.2 Hz, *J* = 2.4 Hz, 1H), 2.61 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 163.6 (dd, *J*<sub>C-F</sub> = 250 Hz, *J*<sub>C-F</sub> = 12.9 Hz), 160.6 (dd, *J*<sub>C-F</sub> = 248.7

Hz,  $J_{\text{C-F}} = 11.7$  Hz), 156.0, 144.1, 139.3, 133.2, 132.8 (t,  $J_{\text{C-F}} = 4.5$  Hz), 130.9, 130.0, 129.3, 128.23, 128.21, 127.1, 124.1 (dd,  $J_{\text{C-F}} = 16.2$  Hz,  $J_{\text{C-F}} = 3.8$  Hz), 122.1, 122.0, 121.8, 112.0 (dd,  $J_{\text{C-F}} = 21.1$  Hz,  $J_{\text{C-F}} = 3.6$  Hz), 104.4 (t,  $J_{\text{C-F}} = 25.3$  Hz), 21.8;  $^{19}\text{F}$ -NMR (400 MHz,  $\text{CDCl}_3$ ) -108.93 (d, 1F), -108.93 (d, 1F); MS (ESI) calcd for  $\text{C}_{20}\text{H}_{13}\text{F}_2\text{N}$   $[\text{M}+\text{H}]^+$ : 305.10, found 306.51



### 9-chloro-6-(4-chlorophenyl)-3-methylphenanthridine (3b)

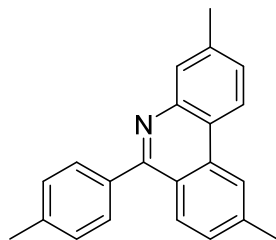
Following the general procedure I, bis(4-chlorophenyl)methanone (26 mg, 0.10 mmol), 1-(m-tolyl)pyrrolidine-2,5-dione (80 mg, 0.4 mmol),  $\text{Pd}(\text{OAc})_2$  (3.0 mg, 0.013 mmol),  $\text{NaIO}_4$  (36 mg, 0.16 mmol),  $\text{K}_2\text{S}_2\text{O}_8$  (108 mg, 0.4 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37  $\mu\text{L}$ ) were used. The reaction mixture was stirred at 60 °C for 7.0 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3b** (25.7 mg) in 76% yield.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.61 (d,  $J = 2$  Hz, 1H), 8.40 (d,  $J = 8.4$  Hz, 1H), 8.01 (s, 1H), 7.97 (d,  $J = 8.8$  Hz, 1H), 7.65 (d,  $J = 8.4$  Hz, 2H), 7.55-7.50 (m, 4H), 2.60 (s, 3H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 159.6, 144.4, 140.1, 138.0, 137.3, 135.2, 135.0, 131.2, 130.2, 130.1, 129.4, 128.9, 127.5, 123.1, 122.0, 121.96, 120.6, 21.8; MS (ESI) calcd for  $\text{C}_{20}\text{H}_{13}\text{Cl}_2\text{N}$   $[\text{M}+\text{H}]^+$ : 337.04, found 338.04



### 9-chloro-6-(4-fluorophenyl)-3-methylphenanthridine (3c)

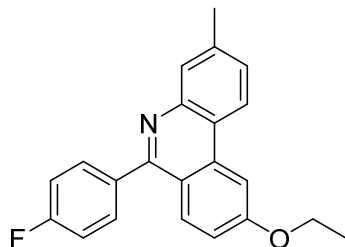
Following the general procedure I, bis(4-fluorophenyl)methanone (21.8 mg, 0.10 mmol), 1-(m-tolyl)pyrrolidine-2,5-dione (94.5 mg, 0.5 mmol),  $\text{Pd}(\text{OAc})_2$  (3.0 mg, 0.013 mmol),  $\text{NaIO}_4$  (36 mg, 0.16 mmol),  $\text{K}_2\text{S}_2\text{O}_8$  (108 mg, 0.4 mmol), HFIP 1.5 ml and TfOH (4.2 equiv, 39  $\mu\text{L}$ ) were used. The reaction mixture was stirred at 60 °C for 10.0 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in THF 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by

silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3c** (19.5 mg) in 64% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.38 (d, *J* = 8.4 Hz, 1H), 8.40 (dd, *J* = 2.4 Hz, 10.4 Hz, 1H), 8.08 (m, 1H), 8.04 (s, 1H), 7.71 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.30 (m, 3H), 2.63 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 163.9 (d, *J*<sub>C-F</sub> = 250 Hz), 163.2 (d, *J*<sub>C-F</sub> = 247 Hz), 159.6, 144.2, 140.0, 135.9 (d, *J*<sub>C-F</sub> = 26 Hz), 135.86 (d, *J*<sub>C-F</sub> = 20 Hz), 131.6, 131.5, 129.9, 128.9, 122.0, 121.9 (d, *J*<sub>C-F</sub> = 8 Hz), 121.0 (d, *J*<sub>C-F</sub> = 4 Hz), 115.9 (d, *J*<sub>C-F</sub> = 24 Hz), 115.5 (d, *J*<sub>C-F</sub> = 22 Hz), 115.5 (d, *J*<sub>C-F</sub> = 22 Hz), 107.3 (d, *J*<sub>C-F</sub> = 22 Hz), 21.6; <sup>19</sup>F-NMR (400 MHz, CDCl<sub>3</sub>) -106.85 (s, 1F), -112.72 (s, 1F); MS (ESI) calcd for C<sub>20</sub>H<sub>13</sub>F<sub>2</sub>N [M+H]<sup>+</sup>: 305.10, found 306.85.



### 3,9-dimethyl-6-(p-tolyl)phenanthridine (**3d**)

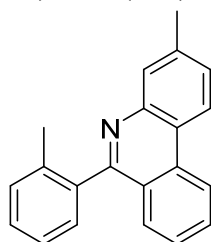
Following the general procedure I, di-p-tolylmethanone (21 mg, 0.10 mmol), 1-(m-tolyl)pyrrolidine-2,5-dione (95 mg, 0.5 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.013 mmol), NaIO<sub>4</sub> (36 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (87 mg, 0.32 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37 uL) were used. The reaction mixture was stirred at 60 °C for 7.0 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3d** (18.4 mg) in 61% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.46 (d, *J* = 8.4 Hz, 1H), 8.42 (s, 1H), 8.01 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.36 (m, 3H), 2.63 (s, 3H), 2.58 (s, 3H), 2.47 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 161.1, 144.2, 140.8, 138.8, 138.4, 137.2, 133.7, 129.8, 129.7, 129.0, 128.9, 128.3, 123.2, 121.7, 121.65, 121.3, 22.3, 21.6, 21.4; MS (ESI) calcd for C<sub>22</sub>H<sub>19</sub>N [M+H]<sup>+</sup>: 297.15, found 298.12.



### 9-chloro-6-(4-fluorophenyl)-3-methylphenanthridine (**3e**)

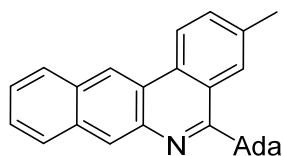
Following the general procedure I, bis(4-fluorophenyl)methanone (21.8 mg, 0.10 mmol), 1-(m-tolyl)pyrrolidine-2,5-dione (100 mg, 0.6 mmol), Pd(OAc)<sub>2</sub> (3.5 mg, 0.015 mmol), NaIO<sub>4</sub> (36 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.4 mmol), HFIP 1.5 ml and TfOH (4.2 equiv, 39 uL) were used. The reaction mixture was stirred at 60 °C for 8.0 h. After that, the reaction mixture was concentrated on rotavapor under reduced

pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C overnight. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3e** (21.2 mg) in 64% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.40 (d, *J* = 8.4 Hz, 1H), 8.01 (s, 1H), 7.96 (m, 2H), 7.71 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.25 (m, 2H), 7.18 (dd, *J* = 2.0, 8.4 Hz, 1H), 4.30 (q, *J* = 6.8 Hz, 2H), 2.61 (s, 3H), 1.56 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 163.2 (d, *J*<sub>C-F</sub> = 246 Hz), 160.9, 159.8, 144.4, 139.3, 135.9 (d, *J*<sub>C-F</sub> = 26 Hz), 131.7 (d, *J*<sub>C-F</sub> = 8 Hz), 130.6, 129.9, 128.4, 121.9, 121.4, 119.9, 117.3, 115.5 (d, *J*<sub>C-F</sub> = 21 Hz), 64.0, 21.7, 14.9; <sup>19</sup>F-NMR (400 MHz, CDCl<sub>3</sub>) -113.24 (s, 1F); MS (ESI) calcd for C<sub>22</sub>H<sub>18</sub>FNO [M+H]<sup>+</sup>: 331.14, found 332.68



### 3-methyl-6-(o-tolyl)phenanthridine (**3f**)

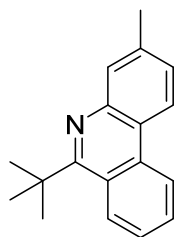
Following the general procedure I, phenyl(o-tolyl)methanone (20 mg, 0.10 mmol), 1-(3-methoxyphenyl)pyrrolidine-2,5-dione (90 mg, 0.4 mmol), Pd(OAc)<sub>2</sub> (3.5 mg, 0.015 mmol), NaIO<sub>4</sub> (36 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.4 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37 uL) were used. The reaction mixture was stirred at 55 °C for 5 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 6 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3f** (18.7 mg) in 66% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.65 (d, *J* = 8.4 Hz, 1H), 8.52 (d, *J* = 8.4 Hz, 1H), 8.06 (s, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.55-7.35 (m, 6H), 2.61 (s, 3H), 2.12 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 162.0, 144.1, 139.4, 139.1, 136.5, 133.2, 130.7, 130.4, 130.0, 129.4, 128.8, 128.7, 128.6, 126.9, 125.9, 122.0, 121.9, 121.6, 21.7, 19.9; MS (ESI) calcd for C<sub>21</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 283.14, found 284.59



### 5-((3r,5r,7r)-adamantan-1-yl)-3-methylbenzo[b]phenanthridine (**3g**)

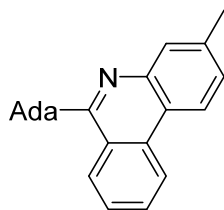
Following the general procedure I, ((3r,5r,7r)-adamantan-1-yl)(naphthalen-2-yl)methanone (30 mg, 0.10 mmol), 1-(m-tolyl)pyrrolidine-2,5-dione (80 mg, 0.4 mmol), Pd(OAc)<sub>2</sub> (3.5 mg, 0.015 mmol), NaIO<sub>4</sub> (36 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.40 mmol), HFIP 1.5 ml and TsOH.H<sub>2</sub>O (4.6 equiv, 90 mg) were used. The reaction mixture was stirred at 60 °C for 6 h. After that, the reaction mixture was concentrated on

rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3g** (16.2 mg) in 43% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 9.37(s, 1H), 9.09(s, 1H), 8.54(d, *J* = 8.4 Hz, 1H), 8.12-8.06(m, 2H), 7.91(s, 1H), 7.64-5.55(m, 2H), 7.45(d, *J* = 8.0 Hz, 1H), 2.58(s, 9H), 2.29(s, 3H), 2.02-1.92(m, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 167.1, 142.6, 138.7, 133.0, 131.2, 130.7, 130.2, 129.4, 128.3, 127.8, 127.6, 126.0, 122.5, 121.8, 121.2, 121.0, 43.5, 42.4, 37.5, 29.5, 21.5; MS (ESI) calcd for C<sub>28</sub>H<sub>27</sub>N [M+H]<sup>+</sup>: 377.21, found 378.20



### 6-(tert-butyl)-3-methylphenanthridine (3h)

Following the general procedure I, 2,2-dimethyl-1-phenylpropan-1-one (17 mg, 0.10 mmol), 1-(m-tolyl)pyrrolidine-2,5-dione (95 mg, 0.5 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.013 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.40 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37 uL) were used. The reaction mixture was stirred at 60 °C for 6 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3h** (17.0 mg) in 67% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.64 (t, *J* = 8.8 Hz, 2H), 8.41 (d, *J* = 8.4 Hz, 1H), 7.96 (s, 1H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 2.60 (s, 3H), 1.75 (s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 143.4, 138.6, 134.3, 129.9, 129.2, 128.3, 128.1, 125.4, 124.3, 123.0, 121.6, 121.1, 43.1, 42.2, 37.4, 29.4, 21.6; MS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>N [M+H]<sup>+</sup>: 249.15, found 250.68.

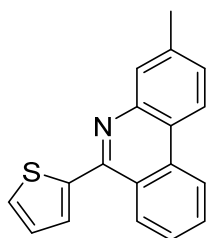


### 6-((3r,5r,7r)-adamantan-1-yl)-3-methylphenanthridine (3i)

Following the general procedure I, ((3r,5r,7r)-adamantan-1-yl)(phenyl)methanone (24 mg, 0.10 mmol), 1-(m-tolyl)pyrrolidine-2,5-dione (95 mg, 0.5 mmol), Pd(OAc)<sub>2</sub> (4.0 mg, 0.017 mmol), NaIO<sub>4</sub> (36 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (98 mg, 0.36 mmol), HFIP 1.5 ml and TsOH.H<sub>2</sub>O (4.6 equiv, 90 mg) were used. The reaction mixture was stirred at 60

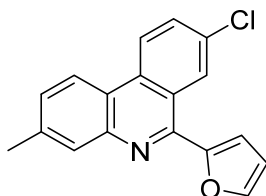


°C for 7.5 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3i** (22 mg) in 67% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.84 (d, *J* = 8.4 Hz, 1H), 8.65 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.60 (m, 1H), 7.43 (dd, *J* = 1.2, 8.0 Hz, 1H), 2.58 (s, 3H), 2.48 (m, 6H), 2.23 (m, 3H), 1.93 (m, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 143.4, 138.6, 134.3, 129.9, 129.2, 128.3, 128.1, 125.4, 124.3, 123.0, 121.6, 121.1, 43.1, 42.2, 37.4, 29.4, 21.6; MS (ESI) calcd for C<sub>24</sub>H<sub>25</sub>N [M+H]<sup>+</sup>: 327.20, found 328.68.



### 3-methyl-6-(thiophen-2-yl)phenanthridine (**3j**)

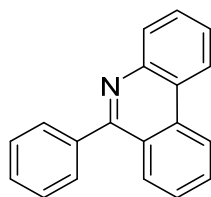
Following the general procedure I, phenyl(thiophen-2-yl)methanone (19 mg, 0.10 mmol), 1-(*m*-tolyl)pyrrolidine-2,5-dione (114 mg, 0.5 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.013 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.40 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37 uL) were used. The reaction mixture was stirred at 60 °C for 6 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 3.5 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3j** (17.5 mg) in 63% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.62 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.43 (d, *J* = 8.4 Hz, 1H), 8.0 (s, 1H), 7.82 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.67-7.62 (m, 2H), 7.55 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1H), 7.47 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 7.25-7.21 (m, 1H), 2.58(s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 154.1, 144.0, 142.8, 139.2, 133.8, 130.7, 129.9, 129.2, 128.9, 128.2, 127.9, 127.4, 127.1, 124.6, 122.3, 121.8, 121.3, 21.7; MS (ESI) calcd for C<sub>18</sub>H<sub>13</sub>NS [M+H]<sup>+</sup>: 275.08, found 276.70



### 8-chloro-6-(furan-2-yl)-3-methylphenanthridine (**3k**)

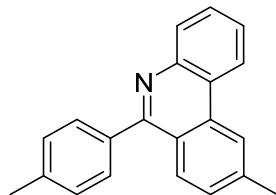
Following the general procedure I, (3-chlorophenyl)(furan-2-yl)methanone (21 mg, 0.10 mmol), 1-(*m*-tolyl)pyrrolidine-2,5-dione (95 mg, 0.5 mmol), Pd(OAc)<sub>2</sub> (4.0 mg, 0.017 mmol), NaIO<sub>4</sub> (36 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.4 mmol), HFIP 1.5 ml

and TfOH (4.0 equiv, 37  $\mu$ L) were used. The reaction mixture was stirred at 60 °C for 7.0 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3k** (13.3 mg) in 45% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.79(d, *J* = 2 Hz, 1H), 8.52(d, *J* = 8.8 Hz, 1H), 8.35(d, *J* = 8.4 Hz, 1H), 7.99(s, 1H), 7.77-7.75(m, 2H), 7.47(dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.27(m, 1H), 2.58(s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 153.4, 148.5, 144.4, 144.0, 139.6, 133.1, 132.2, 131.1, 130.0, 129.4, 127.2, 124.7, 123.9, 121.7, 120.9, 113.6, 112.0, 21.7; MS (ESI) calcd for C<sub>18</sub>H<sub>12</sub>ClNO [M+H]<sup>+</sup>: 361.16, found 362.11



### 6-phenylphenanthridine (**3l**)

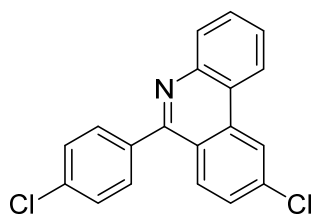
Following the general procedure I, benzophenone (18 mg, 0.10 mmol), 1-phenylpyrrolidine-2,5-dione (80 mg, 0.45 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.013 mmol), NaIO<sub>4</sub> (39 mg, 0.18 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (86 mg, 0.32 mmol), HFIP 1.5 ml and TfOH (4.2 equiv, 39  $\mu$ L) were used. The reaction mixture was stirred at 60 °C for 7.5 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3l** (17 mg) in 64% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.71(d, *J* = 8.4 Hz, 1H), 8.63(d, *J* = 8.0 Hz, 1H), 8.26(d, *J* = 8.4 Hz, 1H), 8.11(d, *J* = 8.0 Hz, 1H), 7.86(t, *J* = 7.8 Hz, 1H), 7.79-7.68(m, 4H), 7.64-7.52(m, 4H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 161.4, 143.9, 139.9, 133.6, 130.7, 130.5, 129.9, 129.1, 129.0, 128.8, 128.6, 127.3, 127.1, 125.4, 123.9, 122.3, 122.1; MS (ESI) calcd for C<sub>19</sub>H<sub>13</sub>N [M+H]<sup>+</sup>: 255.10, found 256.68



### 9-methyl-6-(p-tolyl)phenanthridine (**3m**)

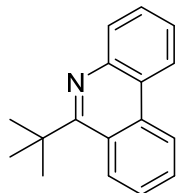
Following the general procedure I, di-p-tolylmethanone (21 mg, 0.10 mmol), 1-phenylpyrrolidine-2,5-dione (80 mg, 0.45 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.013 mmol), NaIO<sub>4</sub> (39 mg, 0.18 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (86 mg, 0.32 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37  $\mu$ L) were used. The reaction mixture was stirred at 60 °C for 7.5 h. After that,

the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 90 °C overnight. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3m** (18 mg) in 63% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.59 (d, *J* = 7.6 Hz, 1H), 8.47 (s, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.75 (t, *J* = 7.6 Hz 1H), 7.67-7.7.63 (m, 3H), 7.42(d, *J* = 8.4 Hz, 1H), 7.37(d, *J* = 8.0 Hz, 2H), 2.65 (s, 3H), 2.48 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm)161.2, 144.2, 141.0, 138.6, 137.2, 133.7, 130.4, 129.8, 129.2, 129.0, 128.9, 128.7, 126.7,123.7, 123.6, 122.0, 121.9, 22.4, 21.5; MS (ESI) calcd for C<sub>21</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 283.14, found 284.20.



#### 9-chloro-6-(4-chlorophenyl)phenanthridine (**3n**)

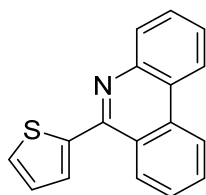
Following the general procedure I, bis(4-chlorophenyl)methanone (26 mg, 0.10 mmol), 1-phenylpyrrolidine-2,5-dione (80 mg, 0.45 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.013 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (94 mg, 0.35 mmol), HFIP 1.5 ml and TfOH (4.2 equiv, 39 uL) were used. The reaction mixture was stirred at 60 °C for 6 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 6 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3n** (16.2 mg) in 50% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.65 (d, *J* = 1.6 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.73-7.66 (m, 3H), 7.58-7.54 (m, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm)159.6, 144.2, 137.9, 137.4, 135.3, 135.0, 131.2, 130.6, 130.3, 129.8, 129.0, 128.0, 127.6, 123.4, 122.9, 122.2, 122.17; MS (ESI) calcd for C<sub>19</sub>H<sub>12</sub>Cl<sub>2</sub>N [M+H]<sup>+</sup>: 323.03, found 324.05



#### 6-(tert-butyl)phenanthridine (**3o**)

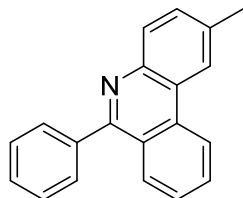
Following the general procedure I, 2,2-dimethyl-1-phenylpropan-1-one (17 mg, 0.10 mmol), 1-phenylpyrrolidine-2,5-dione (110 mg, 0.60 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.013 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.40 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37 uL) were used. The reaction mixture was stirred at 55 °C for 6 h.

After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3o** (14 mg) in 60% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.69(d, *J* = 8.4 Hz, 1H), 8.63(d, *J* = 8.4 Hz, 1H), 8.53(d, *J* = 8.0 Hz, 1H), 8.12(d, *J* = 8.0 Hz, 1H), 7.79(t, *J* = 7.2 Hz, 1H), 7.72-7.59(m, 3H), 1.74(s, 9H), 2.62(s, 3H), 1.73(s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.8, 143.1, 134.2, 130.4, 129.4, 128.5, 128.4, 126.6, 126.1, 124.5, 123.6, 123.1, 121.7, 40.3, 31.3; MS (ESI) calcd for C<sub>17</sub>H<sub>17</sub>N [M+H]<sup>+</sup>: 235.14, found 236.71



### 6-(thiophen-2-yl)phenanthridine (**3p**)

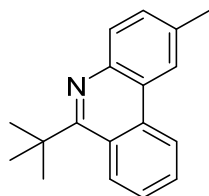
Following the general procedure I, phenyl(thiophen-2-yl)methanone (19 mg, 0.10 mmol), 1-phenylpyrrolidine-2,5-dione (56 mg, 0.30 mmol), Pd(OAc)<sub>2</sub> (4.0 mg, 0.017 mmol), NaIO<sub>4</sub> (30 mg, 0.14 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.35 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37 uL) were used. The reaction mixture was stirred at 60 °C for 9 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3p** (17.0 mg) in 65% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.68 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 2H), 8.20 (dd, *J* = 8.4 Hz, *J* = 1.2 Hz, 1H), 7.86 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.77-7.63 (m, 4H), 7.56 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 1H), 7.25-7.22 (m, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 154.2, 143.7, 142.6, 133.8, 130.8, 130.4, 129.4, 129.0, 128.3, 128.1, 127.6, 127.5, 127.2, 124.9, 123.7, 122.5, 122.0; MS (ESI) calcd for C<sub>17</sub>H<sub>11</sub>NS [M+H]<sup>+</sup>: 261.08, found 262.57



### 2-methyl-6-phenyl-6a,10a-dihydrophenanthridine (**3q**)

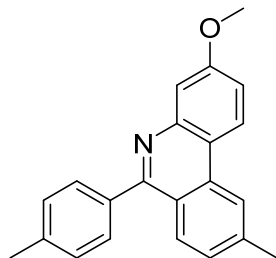
Following the general procedure I, benzophenone (18 mg, 0.10 mmol), 1-(p-tolyl)pyrrolidine-2,5-dione (94.5 mg, 0.5 mmol), Pd(OAc)<sub>2</sub> (3.4 mg, 0.015 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.4 mmol), HFIP 1.5 ml and TfOH (4.2 equiv, 39 uL) were used. The reaction mixture was stirred at 60 °C for 4.0 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue

and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4.5 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3q** (19.1 mg) in 71% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.69 (d, *J* = 8.0 Hz, 1H), 8.40 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.86 (t, *J* = 8.4 Hz, 1H), 7.73 (m, 1H), 7.60 (m, 5H), 2.66 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 160.4, 142.2, 140.0, 136.9, 133.3, 130.7, 130.4, 130.2, 129.9, 129.0, 128.7, 128.5, 127.1, 125.4, 123.7, 122.3, 121.7, 22.1; MS (ESI) calcd for C<sub>20</sub>H<sub>15</sub>N [M+H]<sup>+</sup>: 269.12, found 270.66



### 6-(tert-butyl)-2-methylphenanthridine (**3r**)

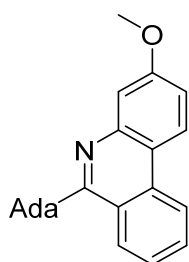
Following the general procedure I, 2,2-dimethyl-1-phenylpropan-1-one (17 mg, 0.10 mmol), 1-(p-tolyl)pyrrolidine-2,5-dione (110 mg, 0.60 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.013 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.40 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37 uL) were used. The reaction mixture was stirred at 55 °C for 6 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3r** (15 mg) in 61% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.67(d, *J* = 8 Hz, 1H), 8.62(d, *J* = 8.4 Hz, 1H), 8.31(s, 1H), 8.02(d, *J* = 8.4 Hz, 1H), 7.76(dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.63(dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.52(dd, *J* = 8 Hz, *J* = 1.2 Hz, 1H), 2.62(s, 3H), 1.73(s, 9H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 165.7, 141.4, 136.3, 133.9, 130.2, 130.1, 129.1, 128.3, 125.9, 124.5, 123.3, 123.1, 121.4, 40.2, 31.3, 22.1; MS (ESI) calcd for C<sub>18</sub>H<sub>19</sub>N [M+H]<sup>+</sup>: 249.15, found 250.15



### 3-methoxy-9-methyl-6-(p-tolyl)phenanthridine (**3s**)

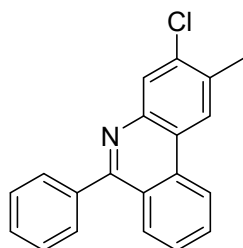
Following the general procedure I, di-p-tolylmethanone (22 mg, 0.10 mmol), 1-(3-methoxyphenyl)pyrrolidine-2,5-dione (90 mg, 0.4 mmol), Pd(OAc)<sub>2</sub> (3.0 mg, 0.013 mmol), NaIO<sub>4</sub> (36 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.4 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37 uL) were used. The reaction mixture was stirred at 60 °C for 6 h. After

that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 6 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3i** (16 mg) in 50% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.47 (d, *J* = 8.8 Hz, 1H), 8.37 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.63-7.60 (m, 3H), 7.37-7.35 (m, 3H), 7.29 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 3.97 (s, 3H), 2.63 (s, 3H), 2.47 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 161.8, 160.3, 145.8, 141.1, 138.6, 137.3, 134.0, 129.7, 129.2, 129.1, 127.9, 123.3, 122.7, 121.4, 117.9, 117.8, 110.0, 55.73, 22.42, 21.54; MS (ESI) calcd for C<sub>22</sub>H<sub>19</sub>NO [M+H]<sup>+</sup>: 313.15, found 314.55



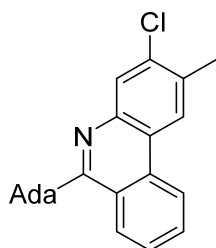
### 6-((3r,5r,7r)-adamantan-1-yl)-3-methylphenanthridine (**3t**)

Following the general procedure I, ((3r,5r,7r)-adamantan-1-yl)(phenyl)methanone (24 mg, 0.10 mmol), 1-(3-methoxyphenyl)pyrrolidine-2,5-dione (123 mg, 0.6 mmol), Pd(OAc)<sub>2</sub> (3.5 mg, 0.015 mmol), NaIO<sub>4</sub> (36 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (98 mg, 0.36 mmol), HFIP 1.5 ml and TsOH.H<sub>2</sub>O (4.6 equiv, 90 mg) were used. The reaction mixture was stirred at 55 °C for 7 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 6 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3t** (22 mg) in 64% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 8.83(d, *J* = 8.4 Hz, 1H), 8.58(d, *J* = 8.0 Hz, 1H), 8.40(d, *J* = 8.8 Hz, 1H), 8.12(s, 1H), 7.73(t, *J* = 7.6 Hz, 1H), 7.58-5.52(m, 2H), 7.24(dd, *J* = 8.8 Hz, *J* = 2.8 Hz, 1H), 4.00(s, 3H), 2.49(s, 6H), 2.24(s, 3H), 1.96-1.88(m, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.9, 160.1, 144.8, 134.4, 129.4, 128.1, 124.7, 123.6, 123.0, 122.8, 117.7, 117.5, 110.0, 55.7, 43.1, 42.2, 37.4, 29.4; MS (ESI) calcd for C<sub>24</sub>H<sub>25</sub>NO [M+H]<sup>+</sup>: 343.19, found 344.23



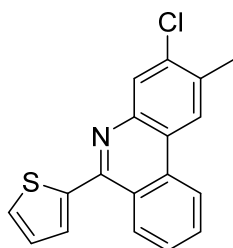
### 3-chloro-2-methyl-6-phenylphenanthridine (**3u**)

Following the general procedure I, benzophenone (18 mg, 0.10 mmol), 1-(3-chloro-4-methylphenyl)pyrrolidine-2,5-dione (132 mg, 0.60 mmol), Pd(OAc)<sub>2</sub> (4.0 mg, 0.017 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (150 mg, 0.56 mmol), HFIP 1.5 ml and TfOH (4.2 equiv, 39  $\mu$ L) were used. The reaction mixture was stirred at 60 °C for 8 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3u** (15.8 mg) in 53% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.63(d, *J* = 8.4 Hz, 1H), 8.43(s, 1H), 8.24(s, 1H), 8.10(d, *J* = 8.4 Hz, 1H), 7.85(dt, *J* = 1.6 Hz, *J* = 7.6 Hz, 1H), 7.73-7.70(m, 2H), 7.64-7.52(m, 2H), 7.63-7.50(m, 4H), 2.66(s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 161.7, 143.2, 139.6, 135.5, 135.2, 132.9, 130.9, 129.9, 129.8, 129.2, 129.0, 128.6, 127.4, 125.3, 123.6, 122.5, 122.2, 20.9; MS (ESI) calcd for C<sub>19</sub>H<sub>13</sub>ClN [M+H]<sup>+</sup>: 303.08, found 304.08.



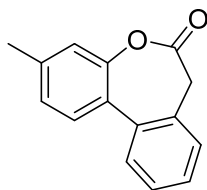
### 6-((3r,5r,7r)-adamantan-1-yl)-3-chloro-2-methylphenanthridine (**3v**)

Following the general procedure I, ((3r,5r,7r)-adamantan-1-yl)(phenyl)methanone (24 mg, 0.10 mmol), 1-(3-chloro-4-methylphenyl)pyrrolidine-2,5-dione (114 mg, 0.50 mmol), Pd(OAc)<sub>2</sub> (4.0 mg, 0.017 mmol), NaIO<sub>4</sub> (36 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.4 mmol), HFIP 1.5 ml and TfOH (4.2 equiv, 39  $\mu$ L) were used. The reaction mixture was stirred at 60 °C for 7.5 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3v** (20.3 mg) in 56% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.83(d, *J* = 8.4 Hz, 1H), 8.60(d, *J* = 8.4 Hz, 1H), 8.33(s, 1H), 8.12(s, 1H), 7.75(t, *J* = 7.6 Hz, 1H), 7.62(t, *J* = 7.6 Hz, 1H), 2.62(s, 3H), 2.46(s, 3H), 2.47(s, 6H), 2.23(s, 3H), 1.91(m, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 166.6, 142.6, 135.0, 134.4, 133.5, 129.8, 129.4, 128.2, 125.9, 124.6, 123.3, 123.1, 122.0, 43.2, 42.2, 37.3, 29.9, 20.8; MS (ESI) calcd for C<sub>24</sub>H<sub>24</sub>ClN [M+H]<sup>+</sup>: 361.16, found 362.11



### 3-chloro-2-methyl-6-(thiophen-2-yl)phenanthridine (3w)

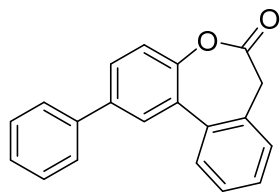
Following the general procedure I, phenyl(thiophen-2-yl)methanone (19 mg, 0.10 mmol), 1-(3-chloro-4-methylphenyl)pyrrolidine-2,5-dione (126 mg, 0.55 mmol), Pd(OAc)<sub>2</sub> (4.0 mg, 0.017 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.40 mmol), HFIP 1.5 ml and TfOH (4.2 equiv, 39  $\mu$ L) were used. The reaction mixture was stirred at 50 °C for 6 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 4 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 40:1) to **3w** (17.6 mg) in 57% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.59 (d, *J* = 8.0 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.37 (s, 1H), 8.19 (s, 1H), 7.85 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.68 (dt, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.62 (d, *J* = 0.4 Hz, 1H), 7.57 (d, *J* = 4.8 Hz, 1H), 7.24 (dd, *J* = 4.8 Hz, *J* = 3.6 Hz, 1H), 2.63 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 154.4, 143.0, 142.5, 135.6, 135.3, 133.1, 130.9, 129.7, 129.5, 128.4, 128.3, 127.7, 127.5, 124.8, 123.5, 122.4, 122.2, 20.9; MS (ESI) calcd for C<sub>18</sub>H<sub>13</sub>NS [M+H]<sup>+</sup>: 309.04, found 310.27



### 3-methyldibenzo[b,d]oxepin-6(7H)-one (4a)

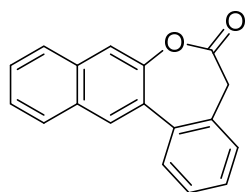
Following the general procedure I, m-tolyl dimethylcarbamate (18 mg, 0.10 mmol), ethyl 2-phenylacetate (96 mg, 0.6 mmol), Pd(OAc)<sub>2</sub> (3.5 mg, 0.015 mmol), NaIO<sub>4</sub> (36 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (81 mg, 0.3 mmol), HFIP 1.5 ml and TfOH (3.6 equiv, 33  $\mu$ L) were used. The reaction mixture was stirred at 35 °C for 11 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 70 °C for 3.0 hours. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then, 10 ml conc. HCl and dichloromethane 3 ml were added and stirred at ambient temperature for 3 h, the reaction mixture was washed once with saturated aqueous NaHCO<sub>3</sub> and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 20:1) to **4a** (12 mg) in 53% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.63-7.61 (m, 1H), 7.51-7.37 (m, 4H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 3.76-3.55 (m, 2H), 2.44 (s, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 169.5, 150.0, 140.1, 135.4, 131.1, 130.0, 129.0, 128.7, 128.6, 128.0, 127.0, 126.8, 121.6, 40.3, 21.2; MS (ESI) calcd for C<sub>15</sub>H<sub>12</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 224.08, found 225.11





#### 2-phenyldibenzo[b,d]oxepin-6(7H)-one (**4b**)

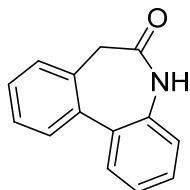
Following the general procedure I, [1,1'-biphenyl]-4-yl dimethylcarbamate (22 mg, 0.10 mmol), ethyl 2-phenylacetate (96 mg, 0.6 mmol), Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.40 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37  $\mu$ L) were used. The reaction mixture was stirred at 35 °C for 14 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80 °C for 2.0 hours. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then, 10 ml conc. HCl and dichloromethane 3 ml were added and stirred at ambient temperature for 3 h, the reaction mixture was washed once with saturated aqueous NaHCO<sub>3</sub> and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 20:1) to **4b** (17.5 mg) in 61% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 7.81 (d, *J* = 2.0 Hz, 1H), 7.72 (d, *J* = 4 Hz, 1H), 7.67-7.62 (m, 3H), 7.52-7.37 (m, 7H), 3.79 (d, *J* = 12.4 Hz, 1H), 3.65 (d, *J* = 12.4 Hz, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 169.4, 149.5, 140.0, 139.1, 135.4, 131.4, 130.2, 129.4, 129.1, 128.9, 128.8, 128.78, 128.3, 128.2, 127.9, 127.3, 121.7, 40.3; MS (ESI) calcd for C<sub>20</sub>H<sub>14</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 286.10, found 287.07



#### benzo[d]naphtho[2,3-b]oxepin-6(5H)-one (**4c**)

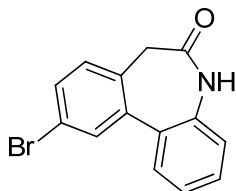
Following the general procedure I, naphthalen-2-yl dimethylcarbamate (22 mg, 0.10 mmol), ethyl 2-phenylacetate (96 mg, 0.6 mmol), Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (108 mg, 0.40 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37  $\mu$ L) were used. The reaction mixture was stirred at 35 °C for 14 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 70 °C for 3.0 hours. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then, 10 ml conc. HCl and dichloromethane 3 ml were added and stirred at ambient temperature for 3 h, the reaction mixture was washed once with saturated aqueous NaHCO<sub>3</sub> and diluted with dichloromethane. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 20:1) to **4c** (8 mg) in 31% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.09 (s, 1H), 7.93-7.88 (m, 2H), 7.80-7.77 (m, 3H), 7.58-7.41 (m, 5H), 3.76-3.68 (m, 2H); <sup>13</sup>C-

NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 169.8, 148.2, 135.8, 133.4, 131.6, 131.2, 129.9, 129.3, 128.9, 128.7, 128.5, 128.1, 127.5, 127.4, 126.6, 40.1; MS (ESI) calcd for C<sub>18</sub>H<sub>12</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 260.08, found 261.01



#### 10-bromo-5H-dibenzo[b,d]azepin-6(7H)-one (**4d**)

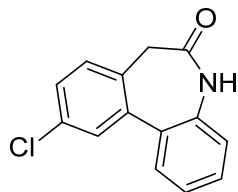
Following the general procedure I, ethyl 2-phenylacetate (17 mg, 0.10 mmol), 1-phenylpyrrolidine-2,5-dione (120 mg, 0.60 mmol), Pd(OAc)<sub>2</sub> (3.5 mg, 0.015 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (81 mg, 0.30 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37  $\mu$ L) were used. The reaction mixture was stirred at 35 °C for 8 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue was stirred in 1.5 ml conc. HCl at 100 °C for 2.0 hours. After that, the reaction mixture was washed once with saturated aqueous NaHCO<sub>3</sub> and diluted with EtOAc. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 4:1) to **4d** (10.5 mg) in 50% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 8.58 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.58-7.55 (m, 1H), 7.43-7.34 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 3.58-3.45 (m, 2H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 173.5, 136.7, 136.0, 134.3, 132.2, 130.2, 129.0, 128.8, 128.6, 127.9, 125.2, 122.1, 41.9; MS (ESI) calcd for C<sub>14</sub>H<sub>11</sub>NO [M+H]<sup>+</sup>: 209.08, found 210.16



#### 10-bromo-5H-dibenzo[b,d]azepin-6(7H)-one (**4e**)

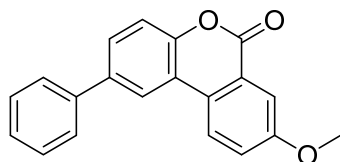
Following the general procedure I, methyl 2-(4-bromophenyl)acetate (23 mg, 0.10 mmol), 1-phenylpyrrolidine-2,5-dione (70 mg, 0.40 mmol), Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol), NaIO<sub>4</sub> (35 mg, 0.16 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (81 mg, 0.30 mmol), HFIP 1.5 ml and TfOH (4.4 equiv, 41  $\mu$ L) were used. The reaction mixture was stirred at 40 °C for 8 h. Then, Pd(OAc)<sub>2</sub> (2.3 mg, 0.01 mmol), NaIO<sub>4</sub> (4 mg, 0.02 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (15 mg, 0.06 mmol), the reaction mixture was stirred at 40 °C for another 2 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue was stirred in 1.5 ml conc. HCl at 100 °C for 2.0 h. After that, the reaction mixture was washed once with saturated aqueous NaHCO<sub>3</sub> and diluted with EtOAc. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 4:1) to **4e** (13.5 mg) in 47% yield. <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>)  $\delta$  (ppm) 10.13 (s, 1H), 7.76 (d, *J* = 1.3 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.60 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 3.47-3.44 (m, 1H), 3.30-3.26 (m, 1H); <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$

(ppm) 171.3, 138.6, 136.9, 133.8, 131.1, 130.9, 130.3, 129.9, 129.7, 129.1, 124.4, 122.1, 120.4, 41.1; MS (ESI) calcd for  $C_{14}H_{10}BrNO$   $[M+H]^+$ : 286.99, found 287.90



#### 10-chloro-5,7-dihydro-6H-dibenzo[b,d]azepin-6-one (4f)

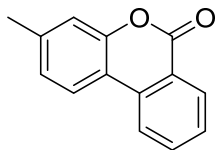
Following the general procedure I, ethyl 2-(4-chlorophenyl)acetate (20 mg, 0.10 mmol), 1-phenylpyrrolidine-2,5-dione (120 mg, 0.60 mmol),  $Pd(OAc)_2$  (3.5 mg, 0.015 mmol),  $NaIO_4$  (35 mg, 0.16 mmol),  $K_2S_2O_8$  (54 mg, 0.20 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37  $\mu$ L) were used. The reaction mixture was stirred at 35 °C for 5 h. Then,  $Pd(OAc)_2$  (1.0 mg, 0.005 mmol),  $K_2S_2O_8$  (27 mg, 0.1 mmol), the reaction mixture was stirred at 40 °C for another 2 h. The reaction mixture was stirred at 35 °C for 5 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue was stirred in 1.5 mL conc. HCl at 100 °C for 2.0 hours. After that, the reaction mixture was washed once with saturated aqueous  $NaHCO_3$  and diluted with EtOAc. Then organic layer was dried over  $Na_2SO_4$  and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 4:1) to **4f** (9.7 mg) in 40% yield.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 8.36 (s, 1H), 7.61 (dd,  $J$  = 8.0 Hz,  $J$  = 1.2 Hz, 1H), 7.55 (d,  $J$  = 2.0 Hz, 1H), 7.42 (dt,  $J$  = 1.6 Hz,  $J$  = 7.6 Hz, 1H), 7.38-7.36 (m, 1H), 7.32-7.29 (m, 2H), 7.14-7.12 (m, 1H), 3.57-3.54 (m, 1H), 3.43-3.40 (m, 1H);  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ )  $\delta$  (ppm) 173.0, 138.3, 136.0, 133.6, 132.7, 131.0, 130.2, 129.9, 129.5, 128.8, 128.7, 125.4, 122.2, 41.3; MS (ESI) calcd for  $C_{14}H_{10}ClNO$   $[M+H]^+$ : 243.05, found 244.11



#### 2-phenyldibenzo[b,d]oxepin-6(7H)-one (4g)

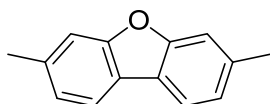
Following the general procedure I, [1,1'-biphenyl]-4-yl dimethylcarbamate (22 mg, 0.10 mmol), ethyl 3-methoxybenzoate (108 mg, 0.6 mmol),  $Pd(OAc)_2$  (4.0 mg, 0.017 mmol),  $NaIO_4$  (35 mg, 0.16 mmol),  $K_2S_2O_8$  (108 mg, 0.40 mmol), HFIP 1.5 ml and  $TsOH \cdot H_2O$  (4.1 equiv, 80 mg) were used. The reaction mixture was stirred at 35 °C for 11 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 ml was stirred at 80 °C for 5.0 hours. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then, 15 ml 6N HCl and dichloromethane were added, shaken vigorously in a funnel (three times), the organic layer was dried over  $Na_2SO_4$  and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 20:1) to **4g** (20 mg) in 66% yield.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  (ppm) 8.16 (d,  $J$  = 2 Hz, 1H), 8.13 (d,  $J$  = 8.8 Hz, 1H), 7.84 (d,  $J$  = 2.8 Hz, 1H), 7.65-7.63 (m, 3H), 7.51-7.47 (m, 2H),

7.45-7.38 (m, 3H), 3.96 (s, 3H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 161.4, 160.3, 150.0, 140.4, 138.1, 129.1, 128.5, 128.2, 127.8, 127.3, 124.5, 123.6, 122.7, 120.1, 118.5, 118.1, 111.5, 56.0; MS (ESI) calcd for  $\text{C}_{26}\text{H}_{18}\text{O}_2$   $[\text{M}+\text{H}]^+$ : 302.09, found 303.10



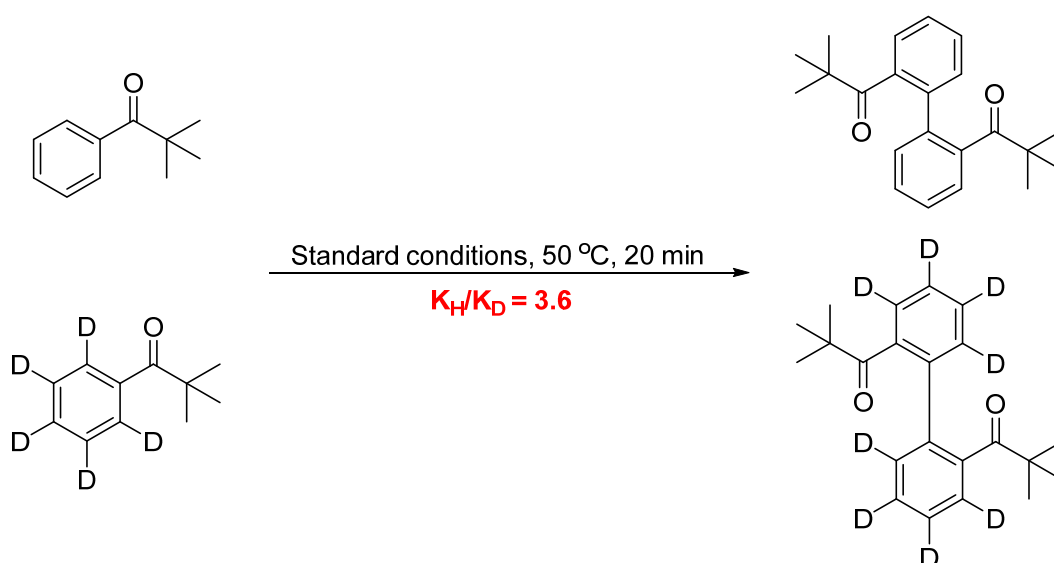
### 3-methyl-6H-benzo[c]chromen-6-one (4h)

Following the general procedure I, *m*-tolyl dimethylcarbamate (18 mg, 0.10 mmol), ethyl benzoate (90 mg, 0.6 mmol),  $\text{Pd}(\text{OAc})_2$  (3.0 mg, 0.013 mmol),  $\text{NaIO}_4$  (35 mg, 0.16 mmol),  $\text{K}_2\text{S}_2\text{O}_8$  (108 mg, 0.40 mmol), HFIP 1.5 ml and TfOH (4.0 equiv, 37  $\mu\text{L}$ ) were used. The reaction mixture was stirred at 35  $^\circ\text{C}$  for 10 h. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (60 mg, 15.0 equiv) in EtOH 1.5 mL was stirred at 80  $^\circ\text{C}$  for 7.0 hours. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then, 15 ml 6N HCl and dichloromethane were added, shaken vigorously in a funnel (three times), the organic layer was dried over  $\text{Na}_2\text{SO}_4$  and concentrated on rotavapor under reduced pressure. Finally, the residue was purified by silica gel column chromatography (Petroleum ether:Ethyl acetate = 20:1) to **4h** (8.5 mg) in 42% yield.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 8.37 (d,  $J$  = 7.6 Hz, 1H), 8.06 (d,  $J$  = 8.0 Hz, 1H), 7.92 (d,  $J$  = 8.0 Hz, 1H), 7.79 (t,  $J$  = 8.0 Hz, 1H), 7.54 (t,  $J$  = 7.6 Hz, 4H), 7.16-7.13 (m, 2H), 2.44 (m, 2H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 161.5, 151.4, 141.4, 135.1, 134.9, 130.6, 128.5, 125.8, 122.6, 121.5, 120.9, 118.0, 115.5; MS (ESI) calcd for  $\text{C}_{14}\text{H}_{10}\text{O}_2$   $[\text{M}+\text{H}]^+$ : 210.07, found 211.58

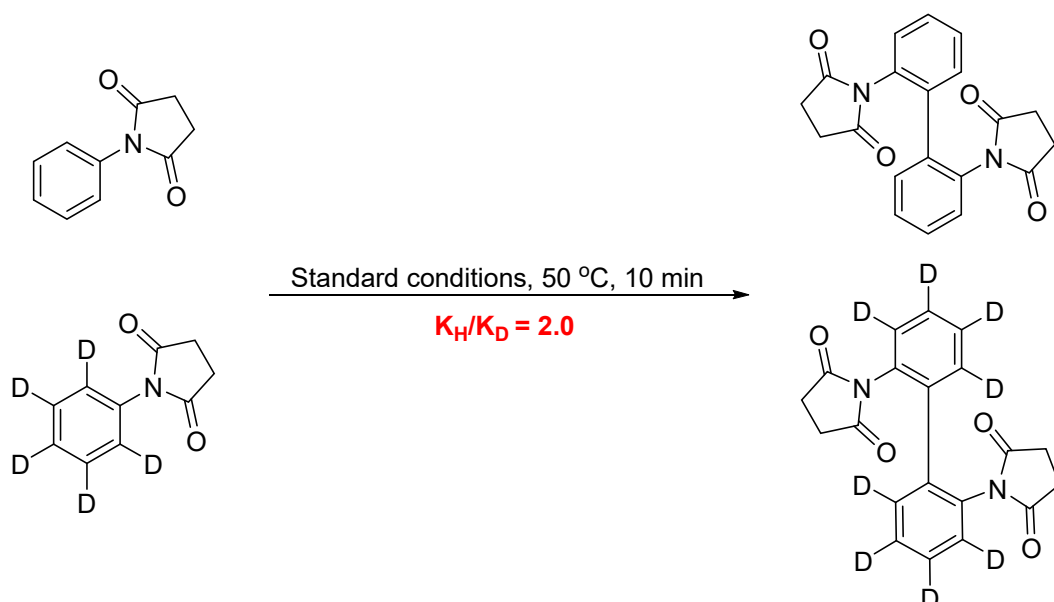


### 3,7-dimethyldibenzo[b,d]furan (4i)

Following the general procedure II, *m*-tolyl dimethylcarbamate (36 mg, 0.20 mmol),  $\text{Pd}(\text{OAc})_2$  (3.0 mg, 0.013 mmol),  $\text{NaIO}_4$  (26 mg, 0.12 mmol),  $\text{K}_2\text{S}_2\text{O}_8$  (43 mg, 0.15 mmol), HFIP 1.5 ml and TsOH·H<sub>2</sub>O (1.3 equiv, 51 mg) were used. The reaction mixture was stirred at 35  $^\circ\text{C}$  overnight. After that, the reaction mixture was concentrated on rotavapor under reduced pressure. The residue and NaOH (80 mg, 20.0 equiv) in EtOH 1.5 ml was stirred at 80  $^\circ\text{C}$  for 7 h. After that, HCl (10%) was added to neutralize the reaction mixture, and diluted with dichloromethane. Then organic layer was concentrated on rotavapor under reduced pressure. The phenol mixture were refluxed in 2 mL toluene in the presence of TfOH (15 equiv, 120  $\mu\text{L}$ ) for 15 h. Finally, the residue was purified by silica gel column chromatography (Petroleum ether) to **4i** (10 mg) in 51% yield.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 7.77 (d,  $J$  = 8.0 Hz, 2H), 7.35 (s,  $J$  = 8.4 Hz, 1H), 7.13 (d,  $J$  = 8.0 Hz, 2H), 8.06 (s, 1H), 2.52 (s, 6H);  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 156.7, 137.1, 123.9, 121.9, 119.9, 112.0, 22.0; MS (ESI) calcd for  $\text{C}_{14}\text{H}_{12}\text{O}$   $[\text{M}+\text{H}]^+$ : 196.09

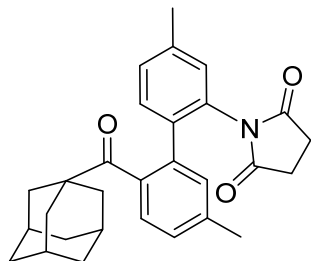


To a 15ml sealed-tube was added 2,2-dimethylpropiophenone (32mg, 0.2 mmol), another was added deuterated 2,2-dimethylpropiophenone (32mg, 0.2 mmol). Each was added Pd(OAc)<sub>2</sub> (1.2 mg, 0.0025 mmol), NaIO<sub>4</sub> (12 mg, 0.06 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (15 mg, 0.056 mmol), HFIP 1.5 ml and TfOH (0.9 equiv, 16 uL) were used. The reaction mixture was stirred at 50 °C for 20 min. After completion of the reaction, the mixture was cooled to room temperature and then saturated NaHCO<sub>3</sub> was added to quench the reaction. The reaction mixture was diluted with EtOAc and washed once with saturated aqueous NaHCO<sub>3</sub>. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. <sup>1</sup>H NMR analysis of the crude reaction mixture with 4-nitrobenzaldehyde as an internal standard showed  $k_H/k_D = 3.6:1$ .



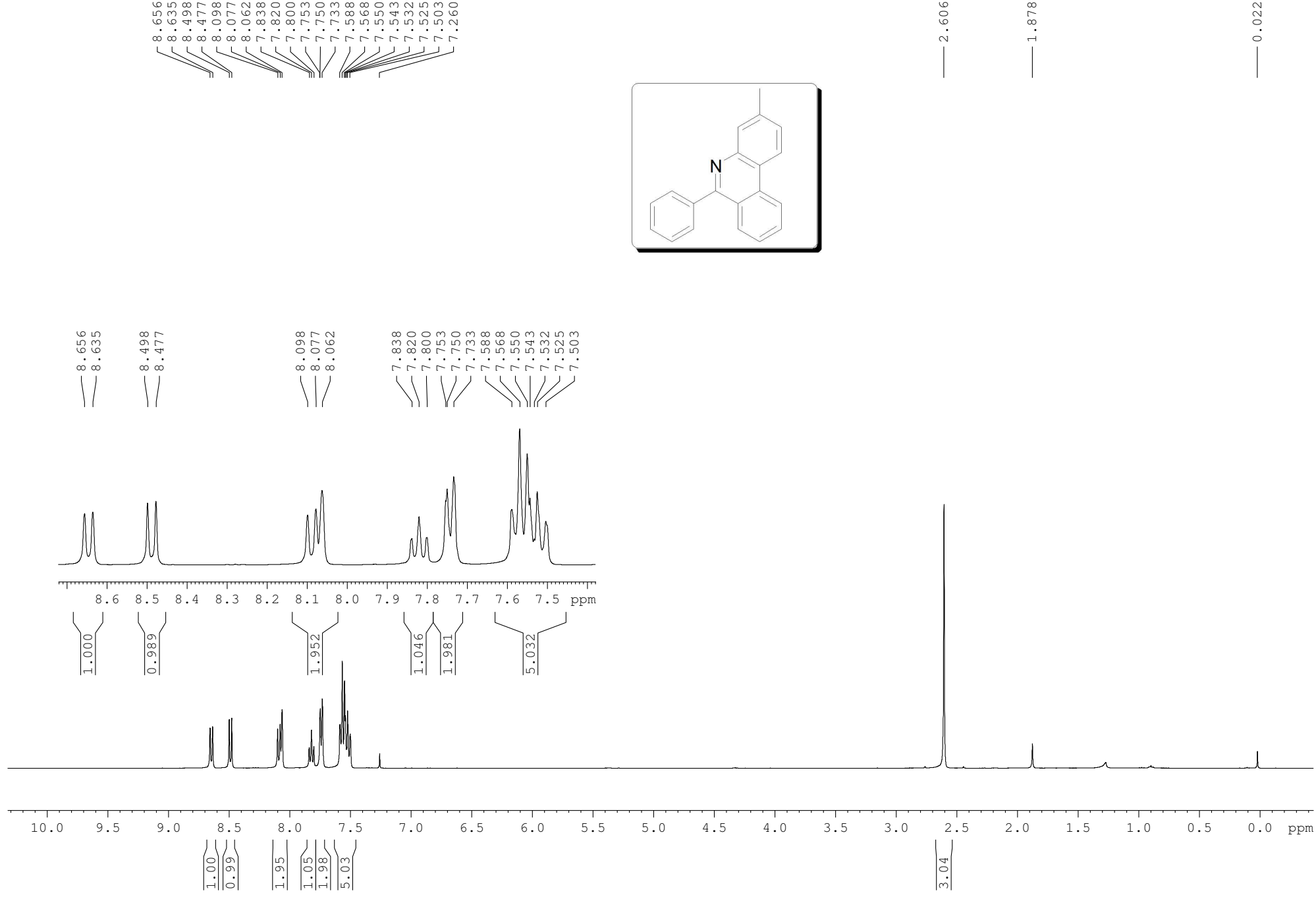
To a 15ml sealed-tube was added 1-phenylpyrrolidine-2,5-dione (36mg, 0.2 mmol), another was added deuterated 1-phenylpyrrolidine-2,5-dione (36mg, 0.2 mmol). Each was added Pd(OAc)<sub>2</sub> (1.2 mg, 0.0025 mmol), NaIO<sub>4</sub> (12 mg, 0.06 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (15 mg, 0.056 mmol), HFIP 1.5 ml and TfOH (0.9 equiv, 16 uL) were used. The reaction mixture was stirred at 50 °C for 10 min. After completion of the reaction, the mixture

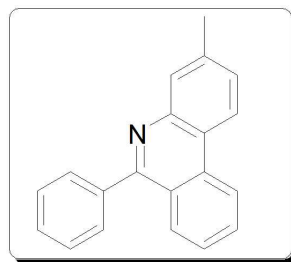
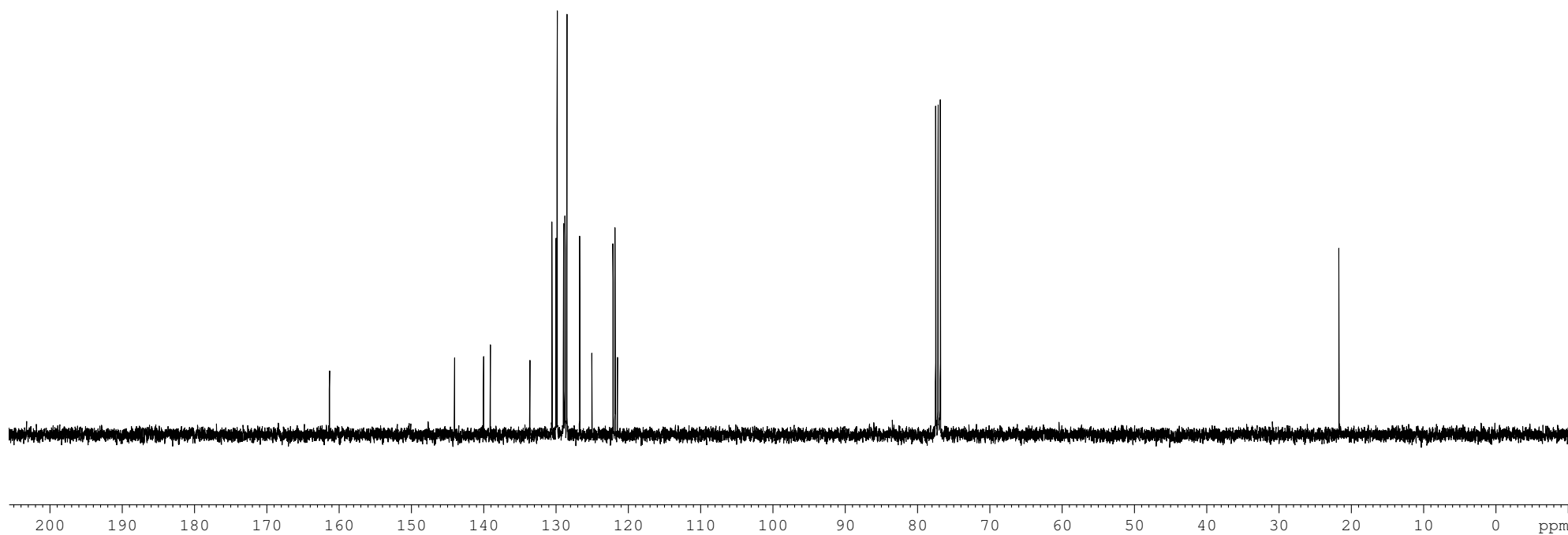
was cooled to room temperature and then saturated NaHCO<sub>3</sub> was added to quench the reaction. The reaction mixture was diluted with EtOAc and washed once with saturated aqueous NaHCO<sub>3</sub>. Then organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated on rotavapor under reduced pressure. <sup>1</sup>H NMR analysis of the crude reaction mixture with 4-nitro-benzaldehyde as an internal standard showed  $k_H/k_D = 2.0:1$ .



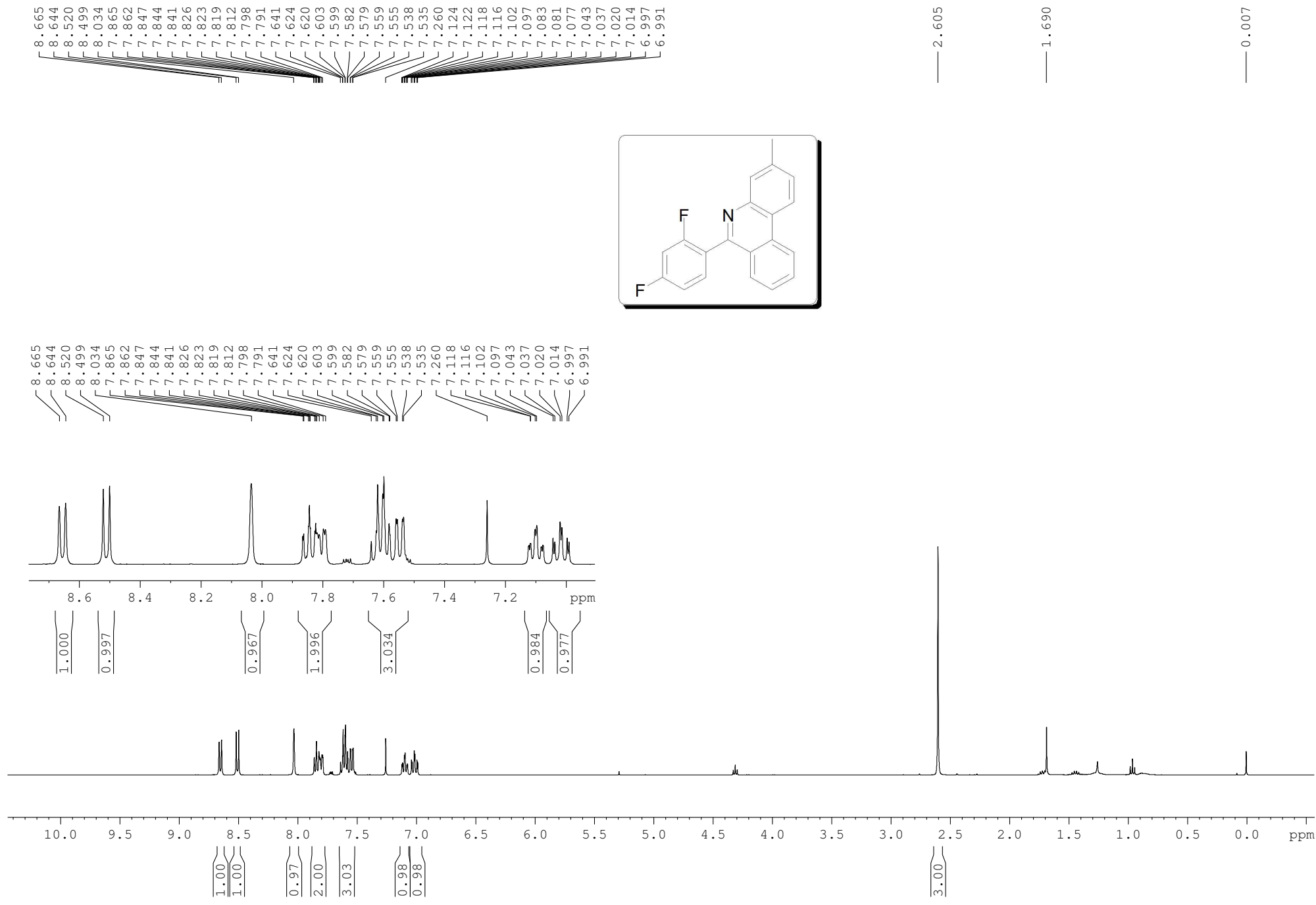
**1-(2'-((3*r*,5*r*,7*r*)-adamantane-1-carbonyl)-4,5'-dimethyl-[1,1'-biphenyl]-2-yl)pyrrolidine-2,5-dione (**5c**)**

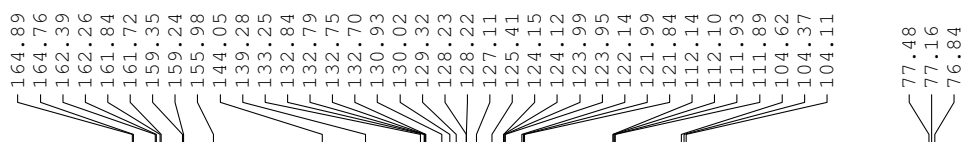
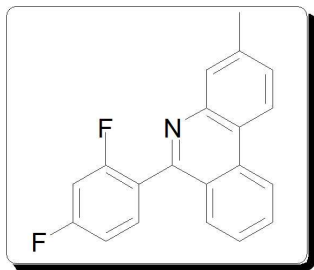
Cyclo-palladium (II) dimeric intermediate (10 mg, 0.02 mmol), NaIO<sub>4</sub> 6 mg, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> 16 mg, HFIP 0.6 ml and TfOH 10 uL were used. The reaction mixture was stirred at 55 °C for 2 h. After completion of the reaction, the residue was purified by silical gel column chromatography (Petroleum ether:Ethyl acetate = 4:1). Finally, compound **5c** (3 mg) was isolated in 35% yield. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.35 (d, *J* = 7.6 Hz, 1H), 7.26-7.25 (m, 1H), 7.12-7.10 (m, 1H), 7.04 (s, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 3.08-2.53 (m, 4H), 2.40 (s, 3H), 2.39 (s, 3H), 1.82 (s, 3H), 1.57-1.42 (m, 9H), 1.36 (s, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 215.7, 176.4, 175.6, 139.0, 138.5, 138.0, 136.3, 134.4, 132.34, 132.32, 130.5, 129.6, 129.0, 127.9, 125.5, 46.8, 38.7, 36.4, 29.1, 28.3, 28.1, 21.4, 21.2; MS (ESI) calcd for C<sub>29</sub>H<sub>31</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 441.23, found 442.19.



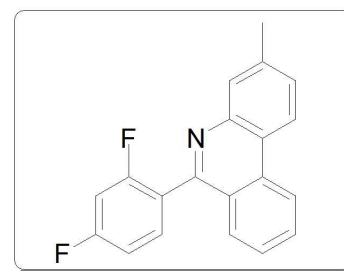




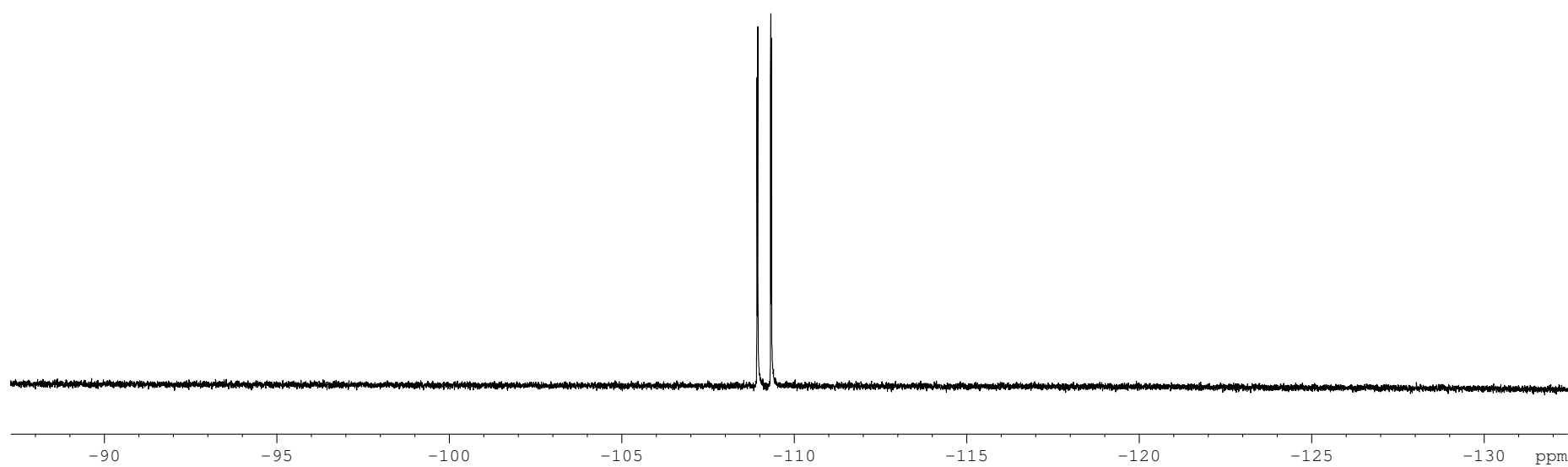


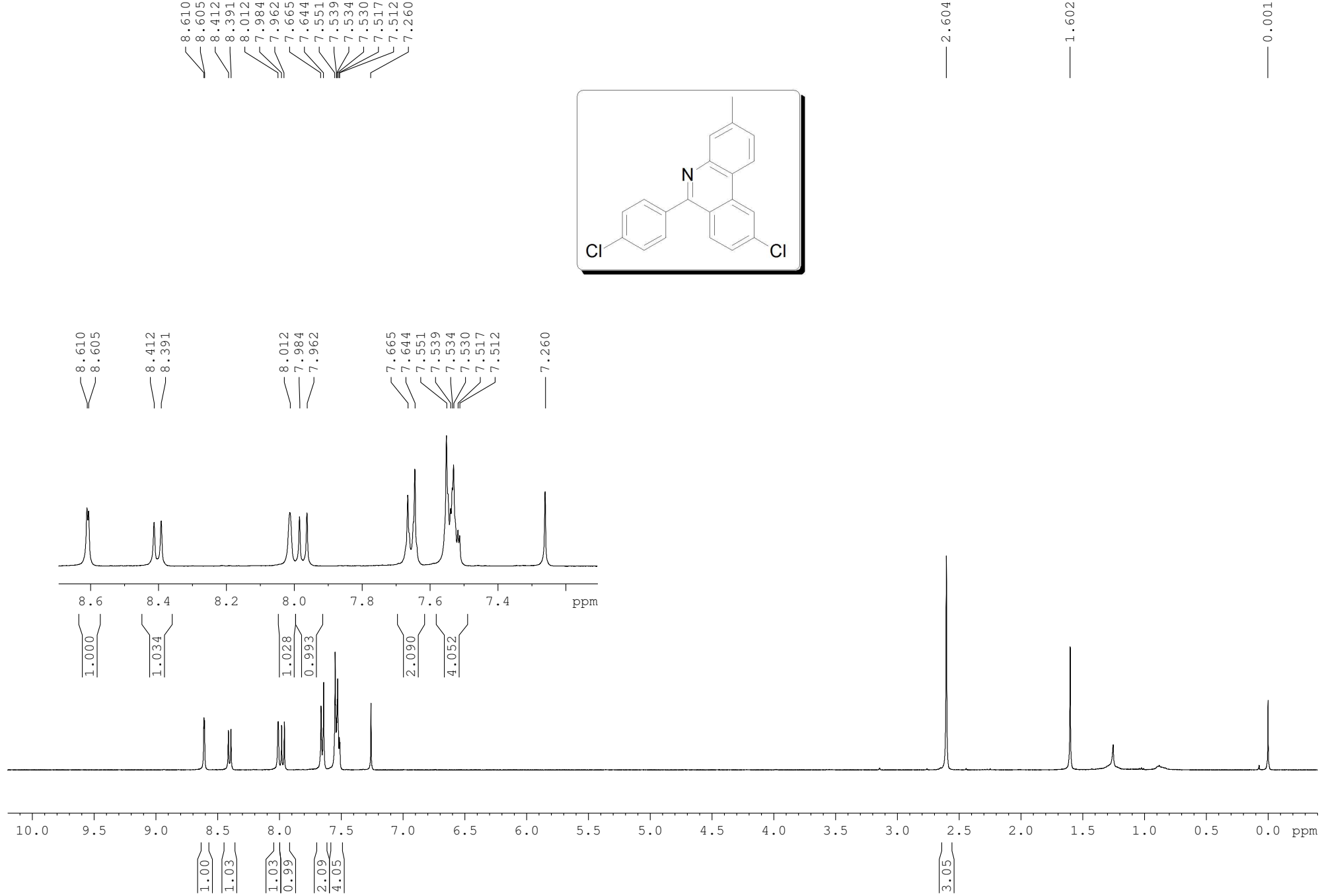


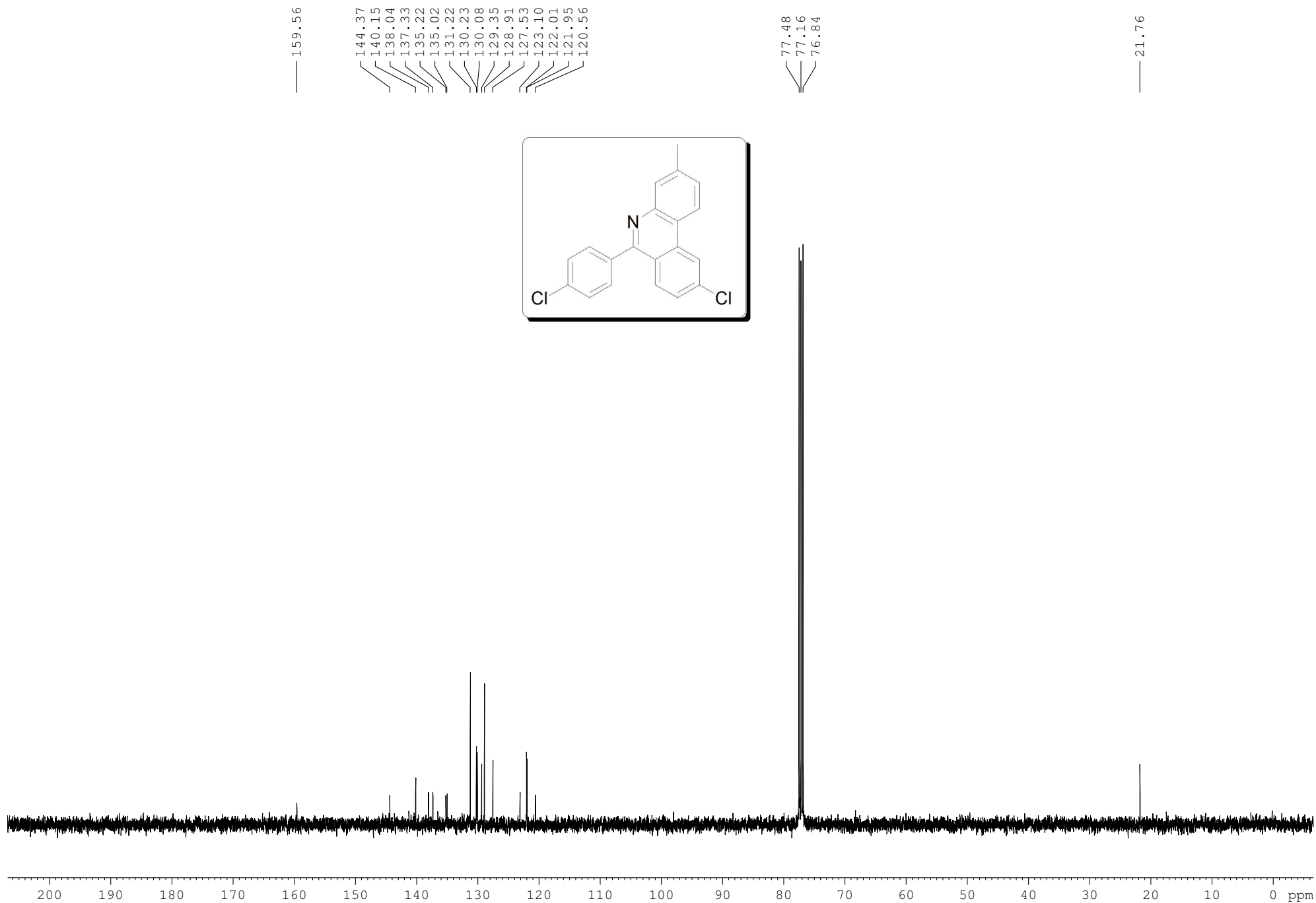
—21.70

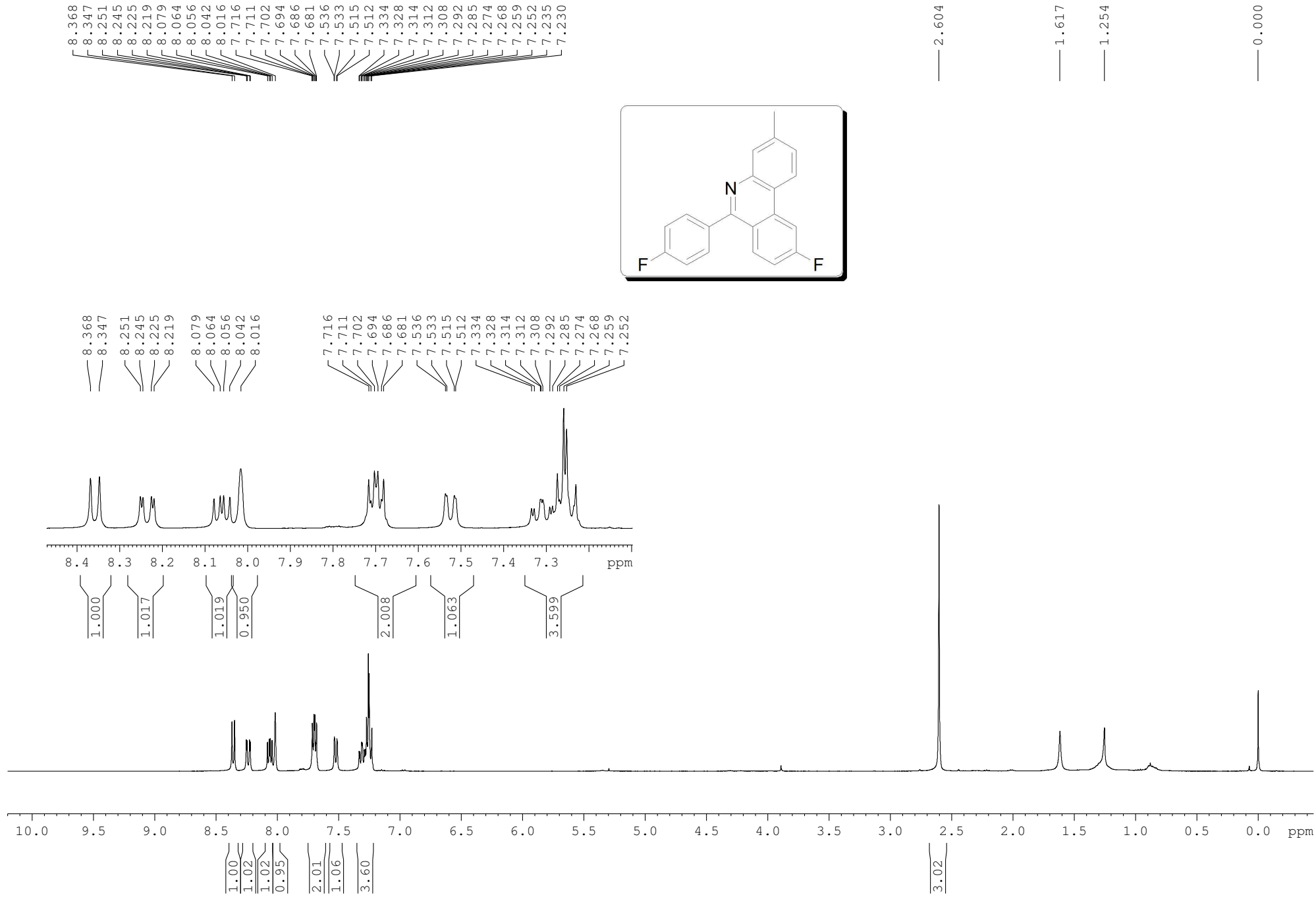


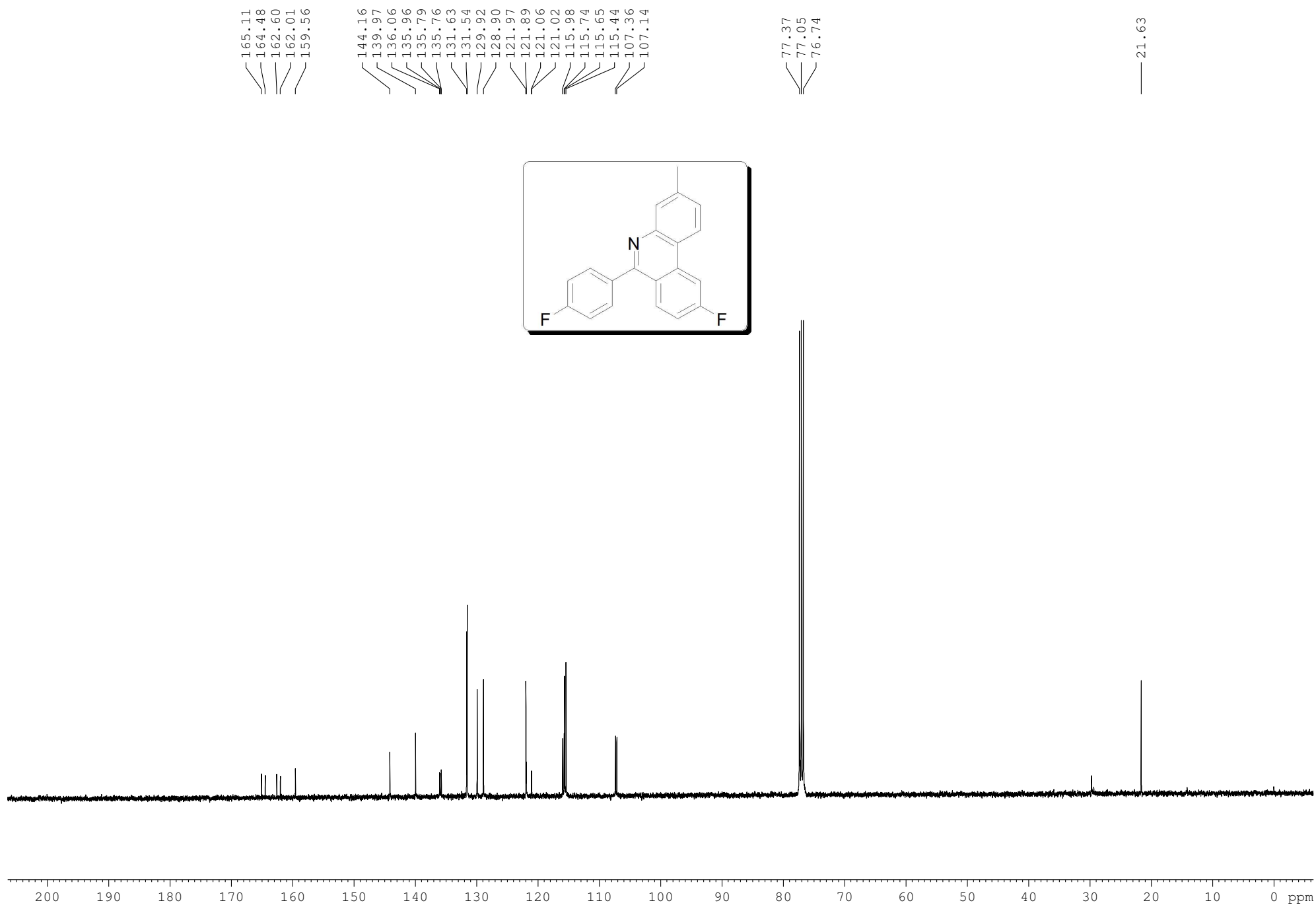
-108.92  
-108.94  
-109.31  
-109.34

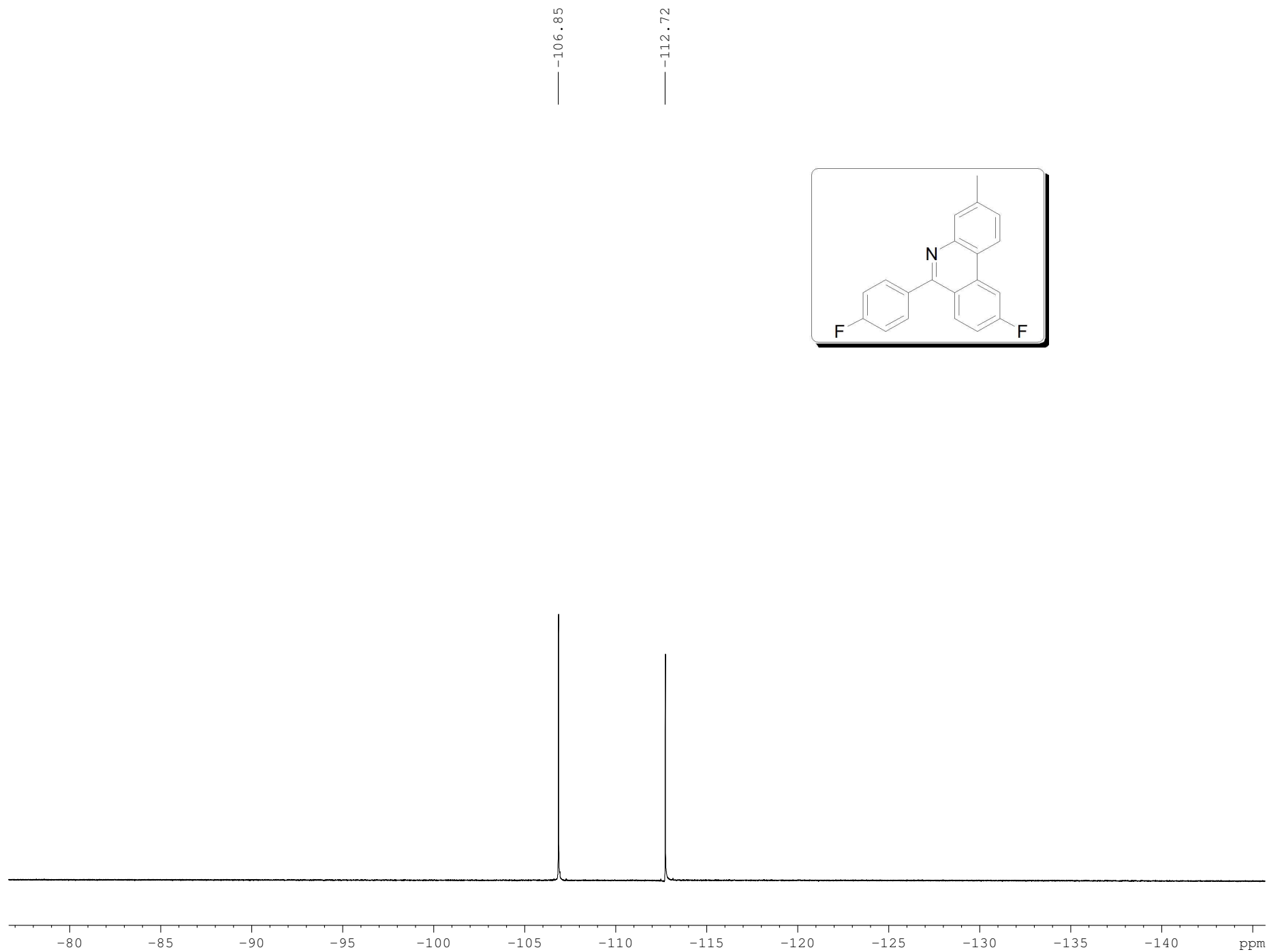
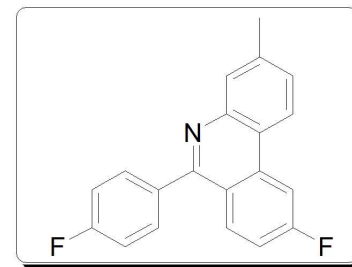




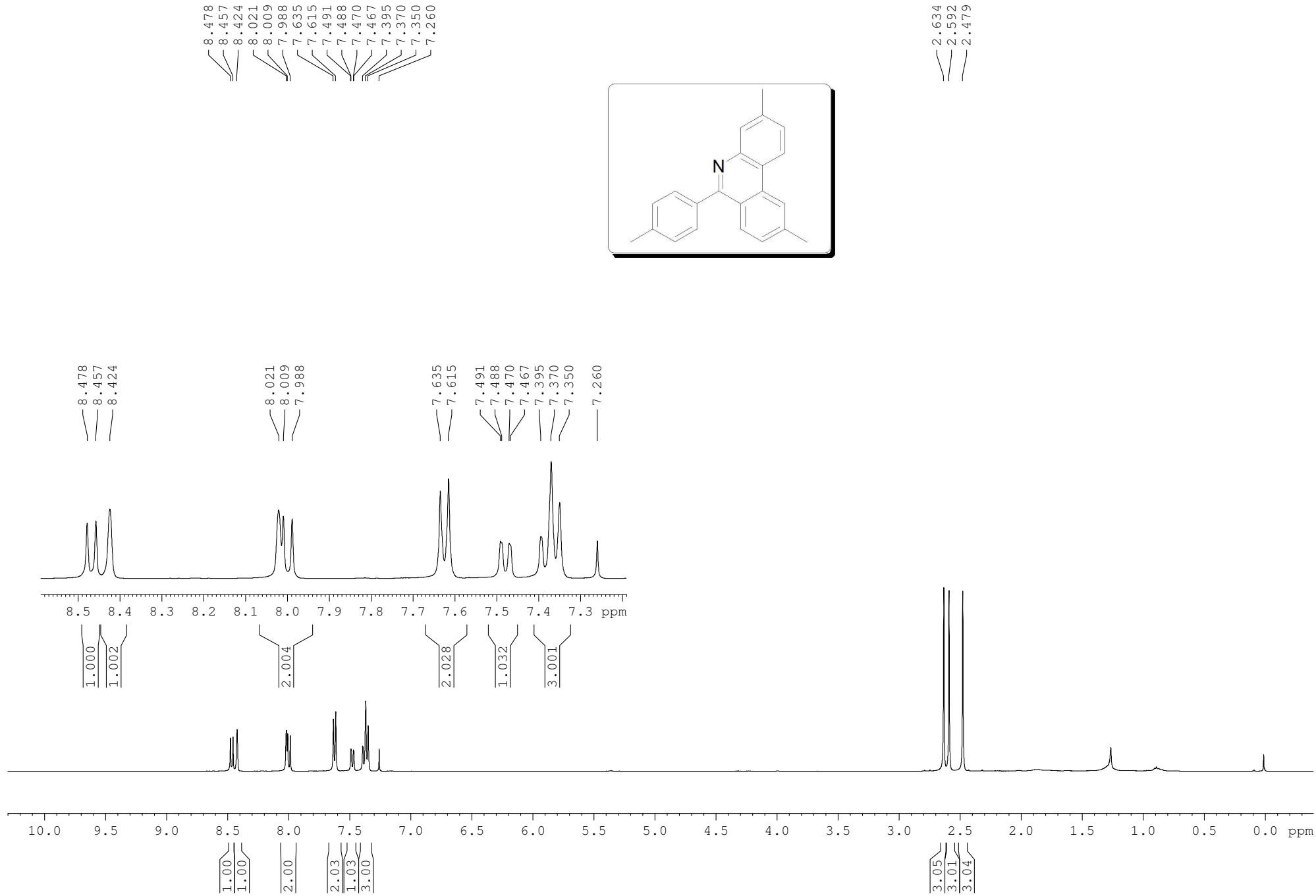


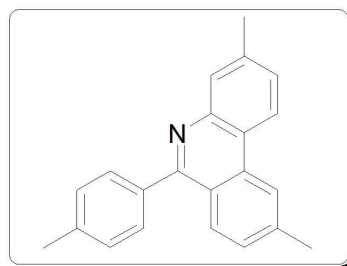
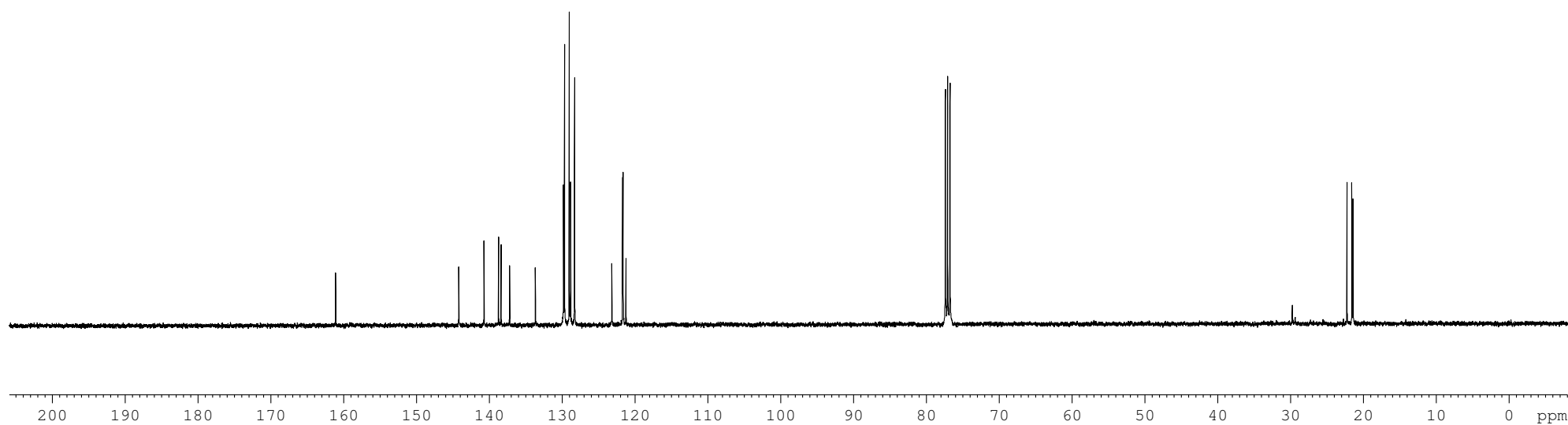










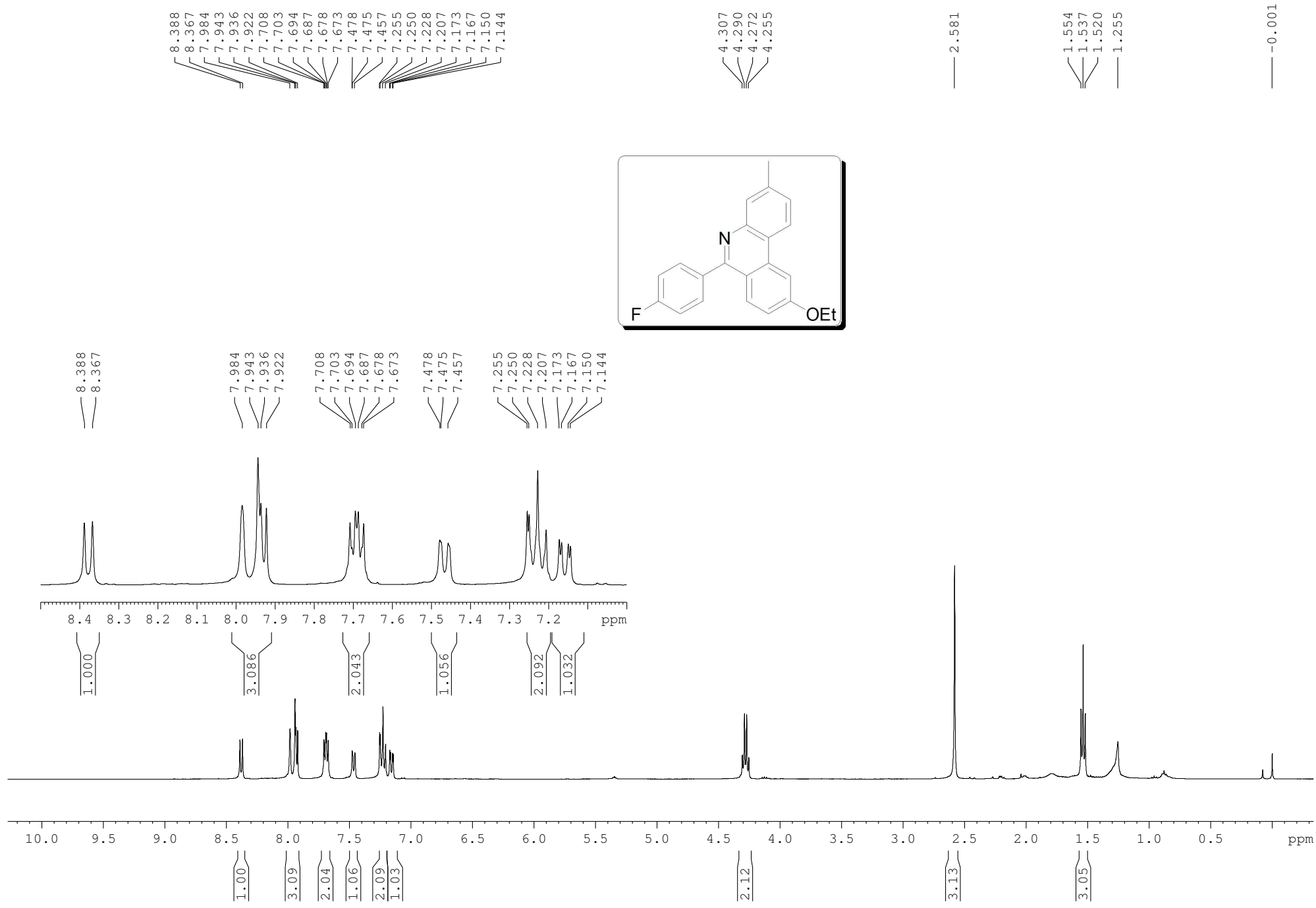


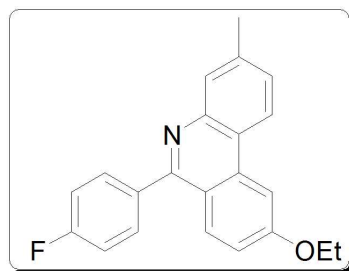
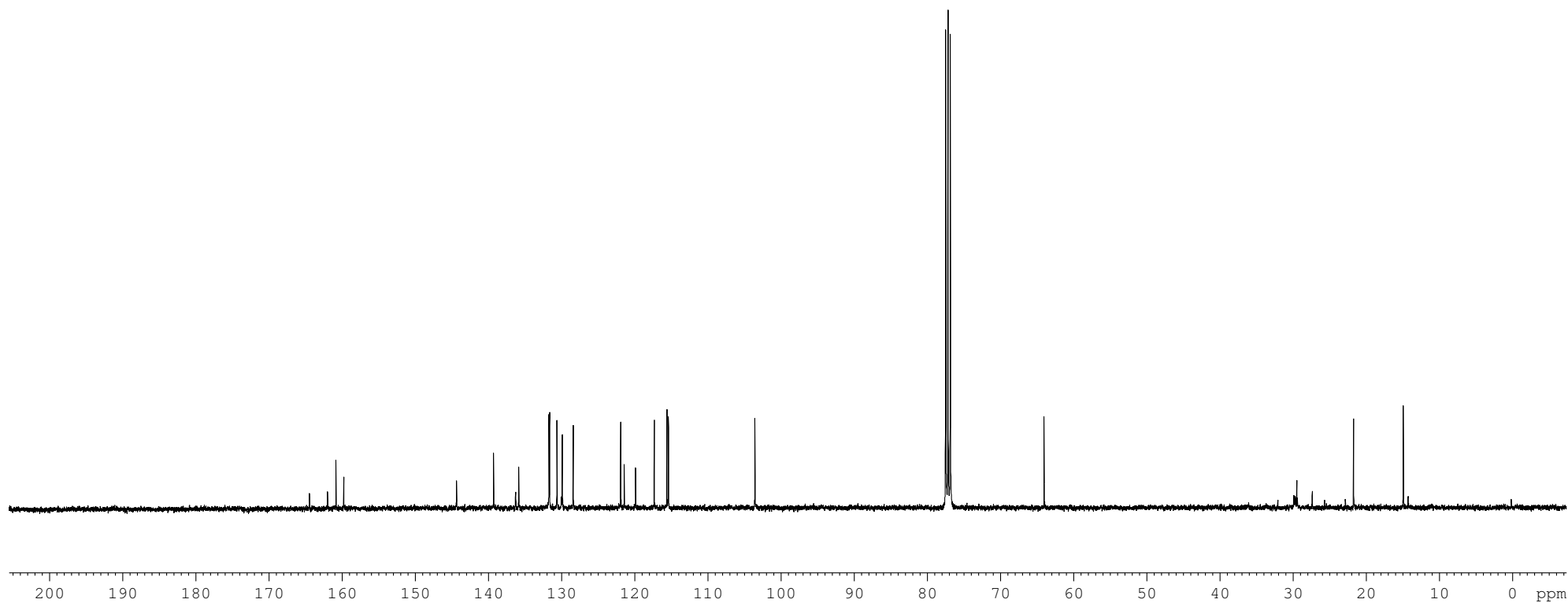
— 161.12

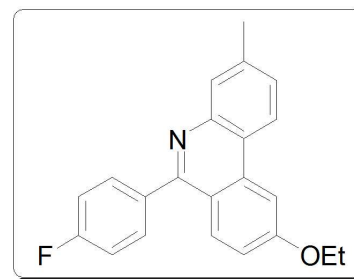
144.22  
140.75  
138.75  
138.41  
137.24  
133.70  
129.84  
129.70  
129.05  
128.86  
128.32  
123.19  
121.72  
121.66  
121.26

77.41  
77.09  
76.77

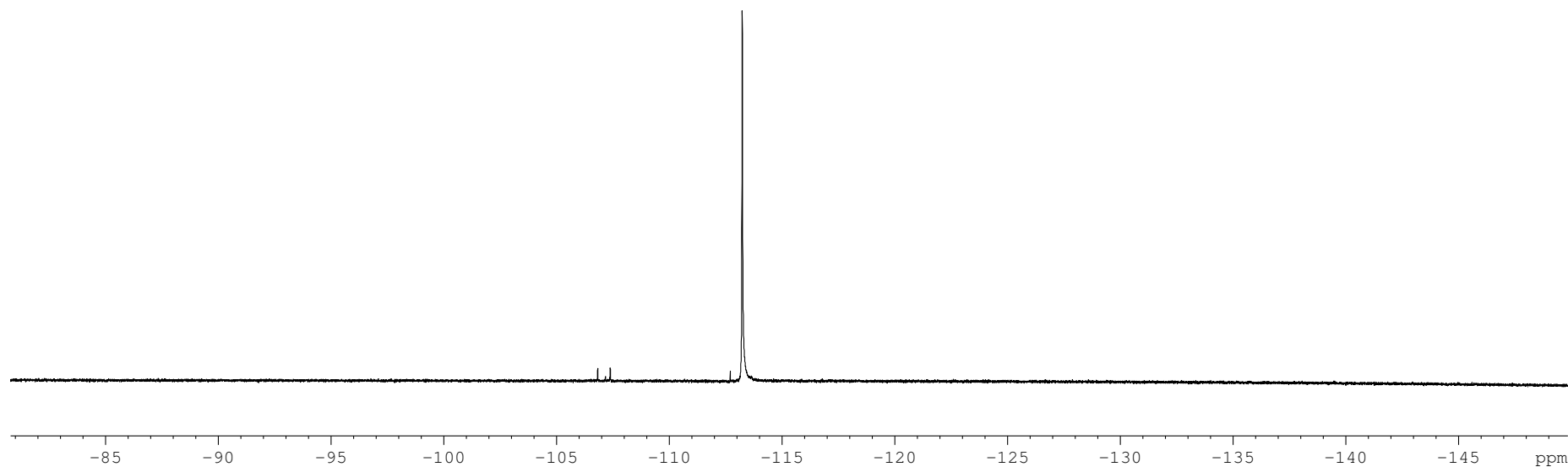
22.26  
21.59  
21.43

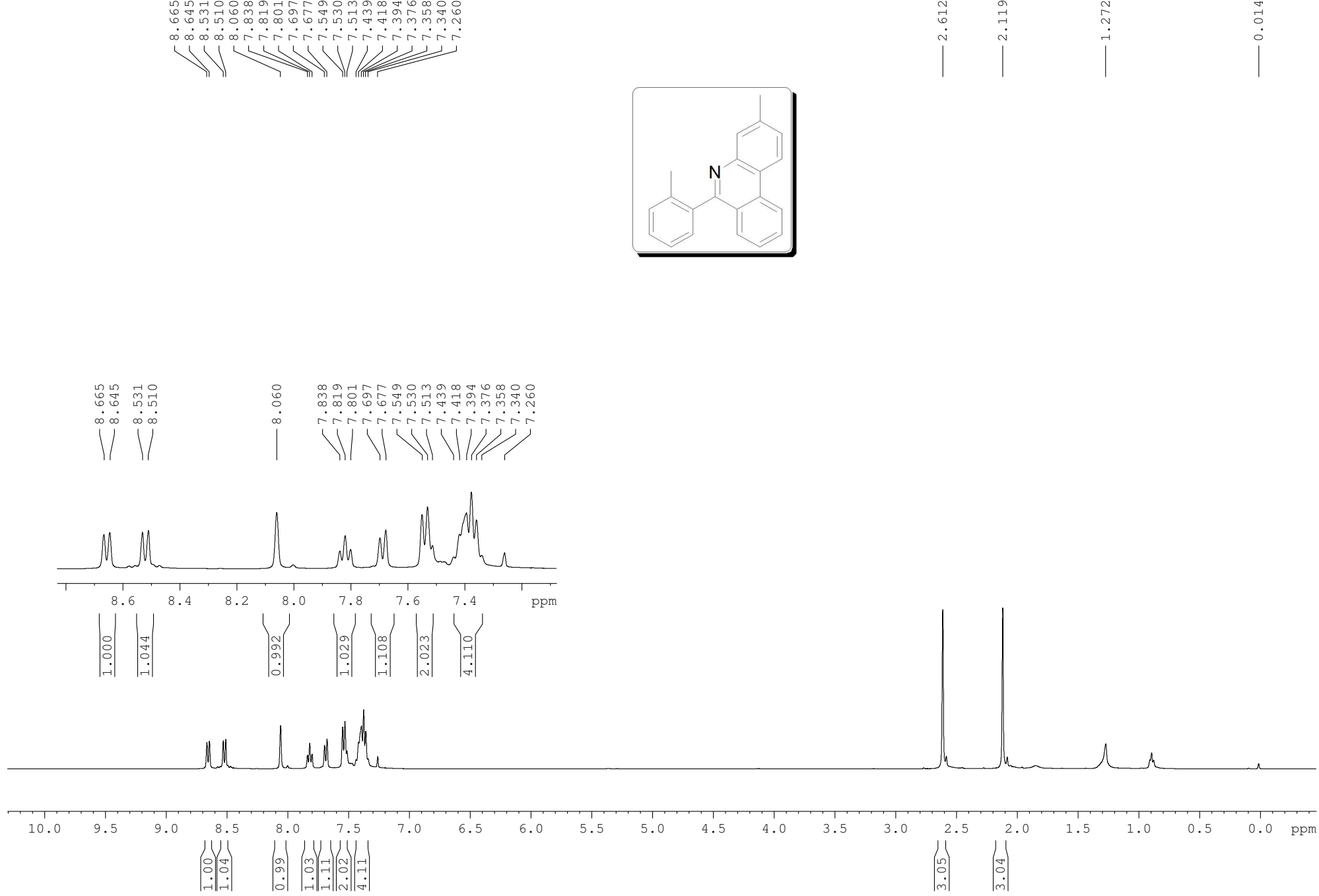


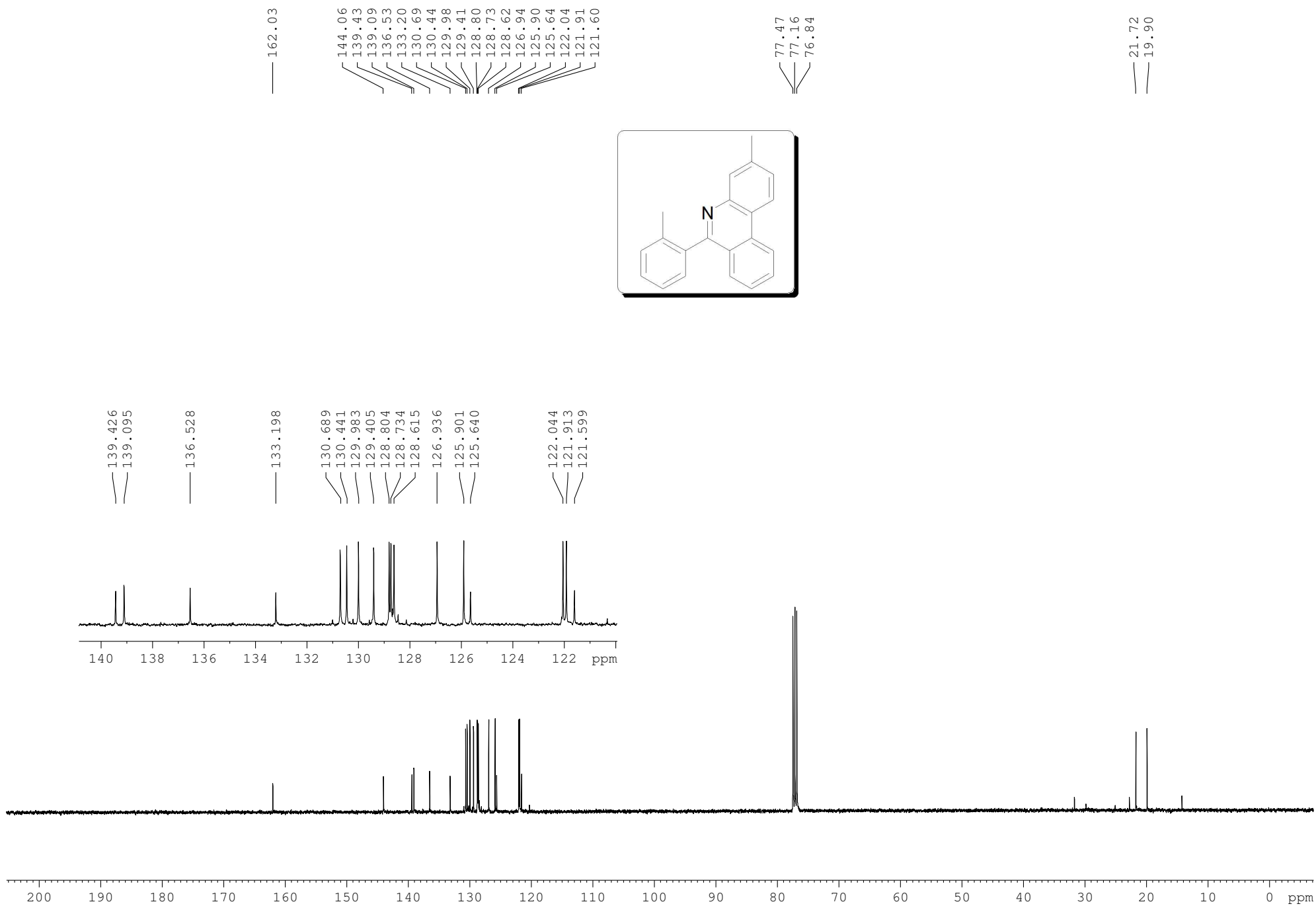


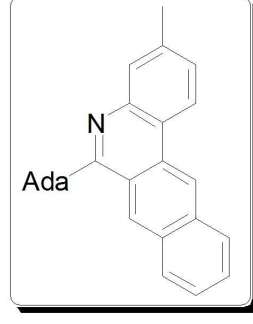
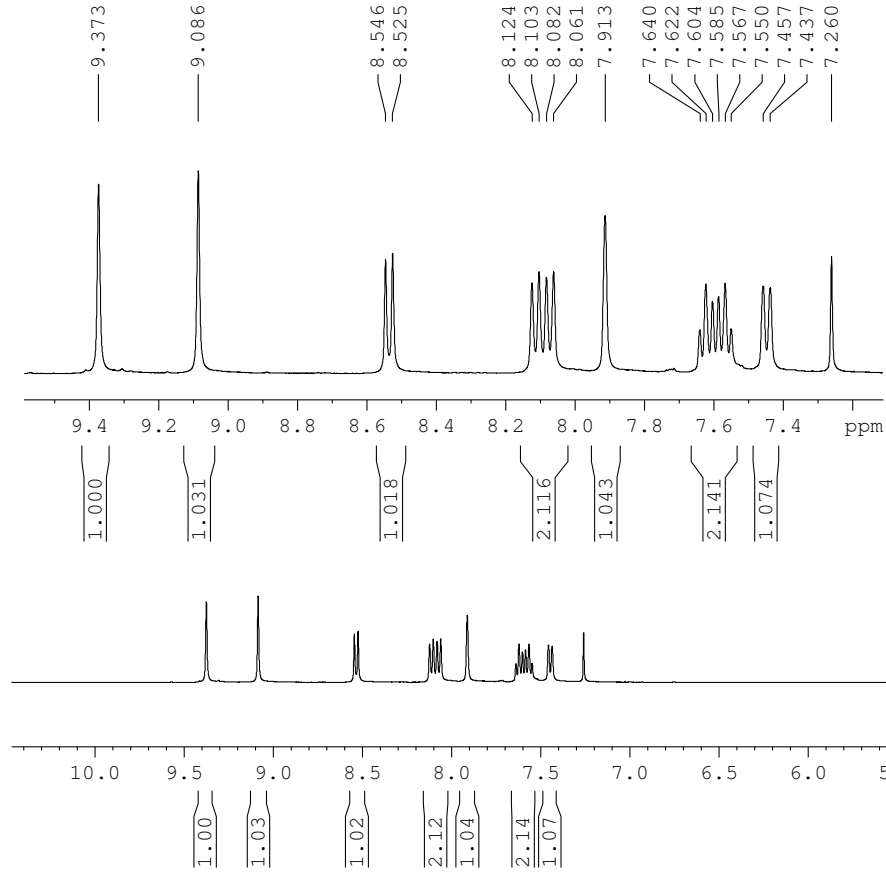


— -113.24

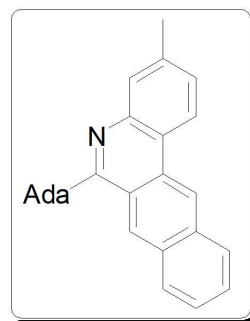
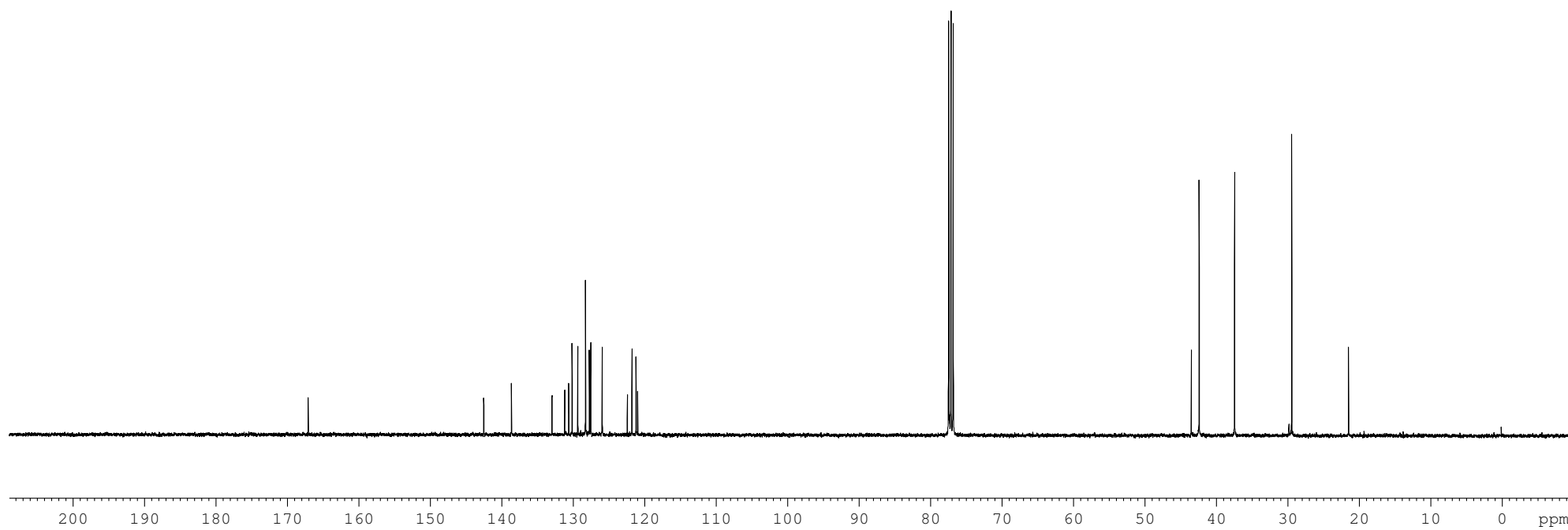


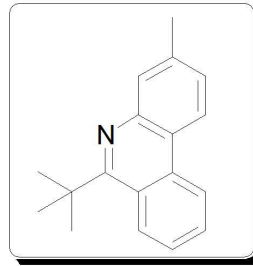
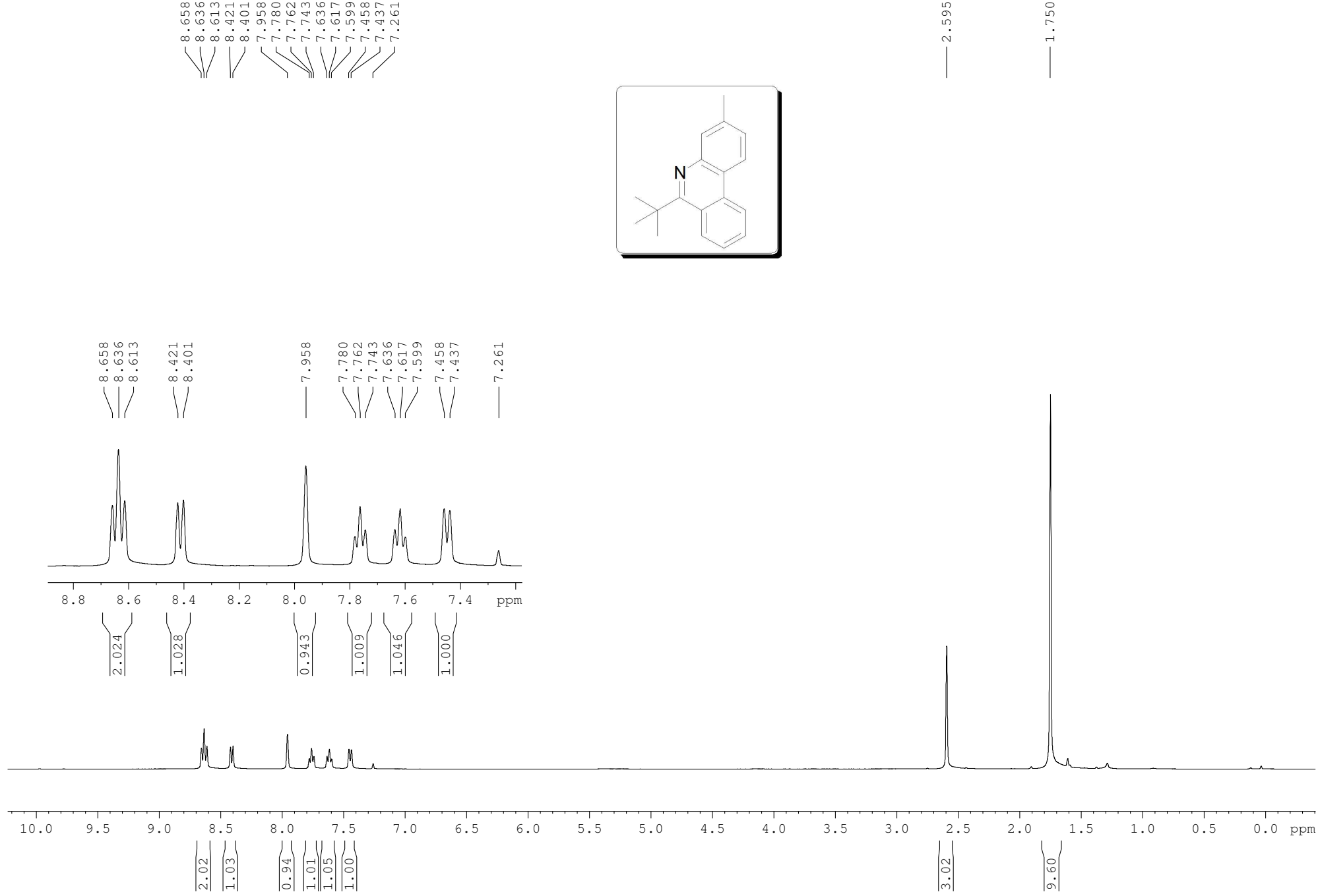


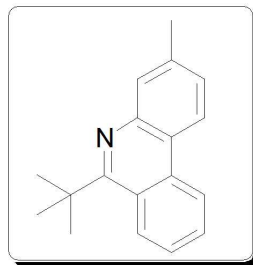
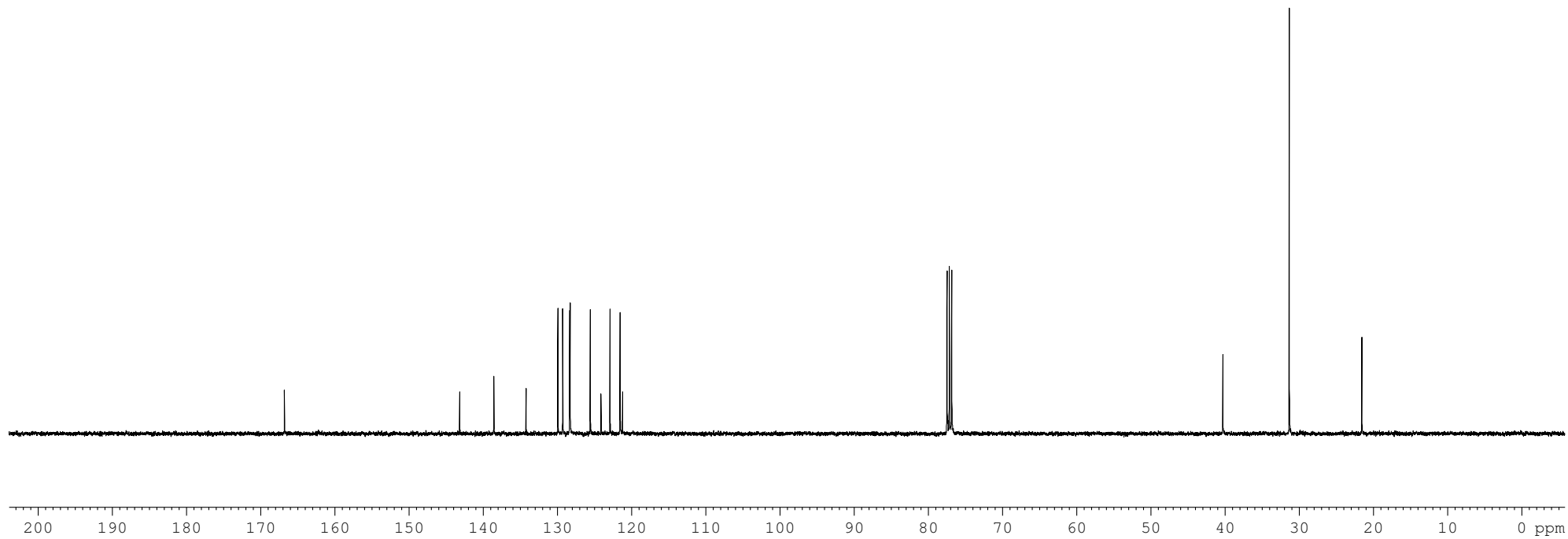


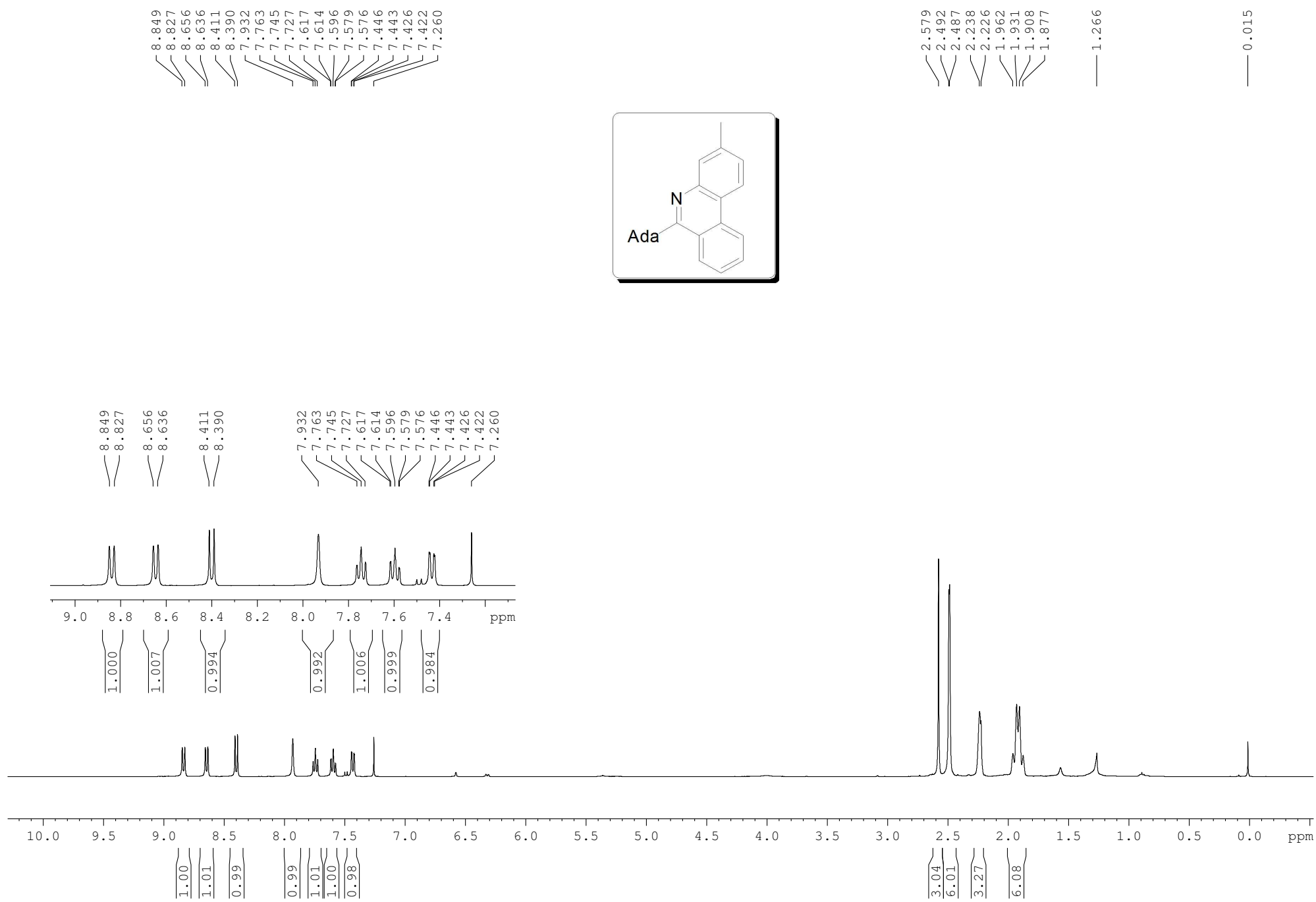


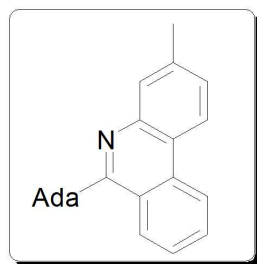
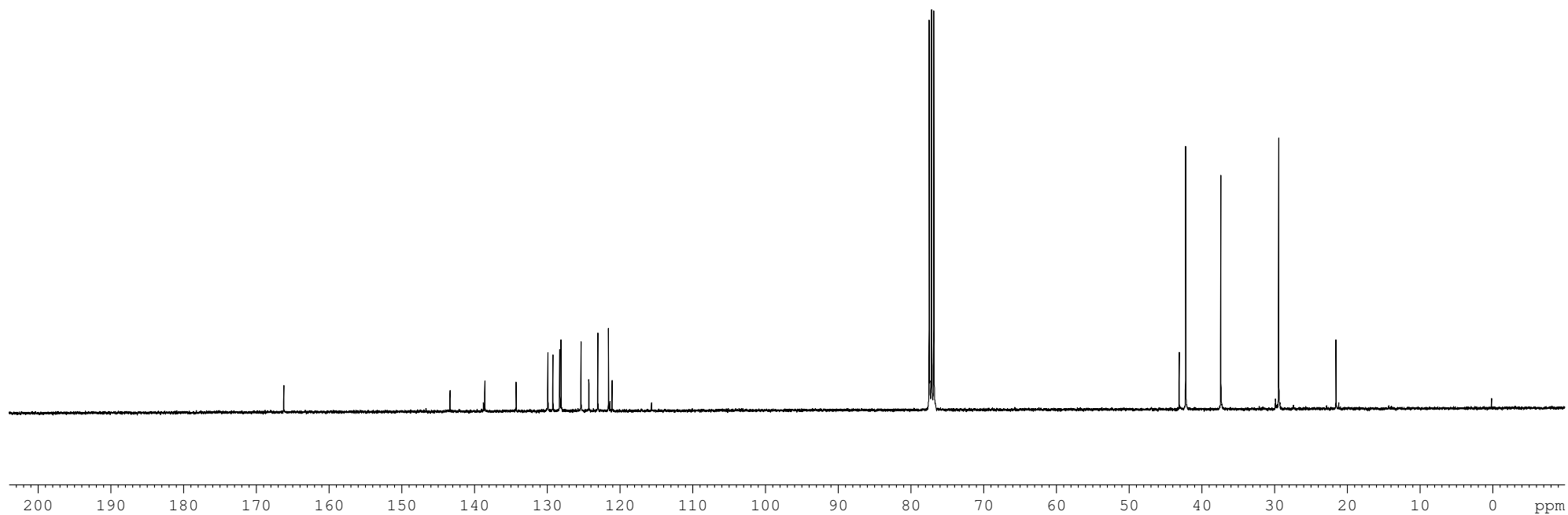


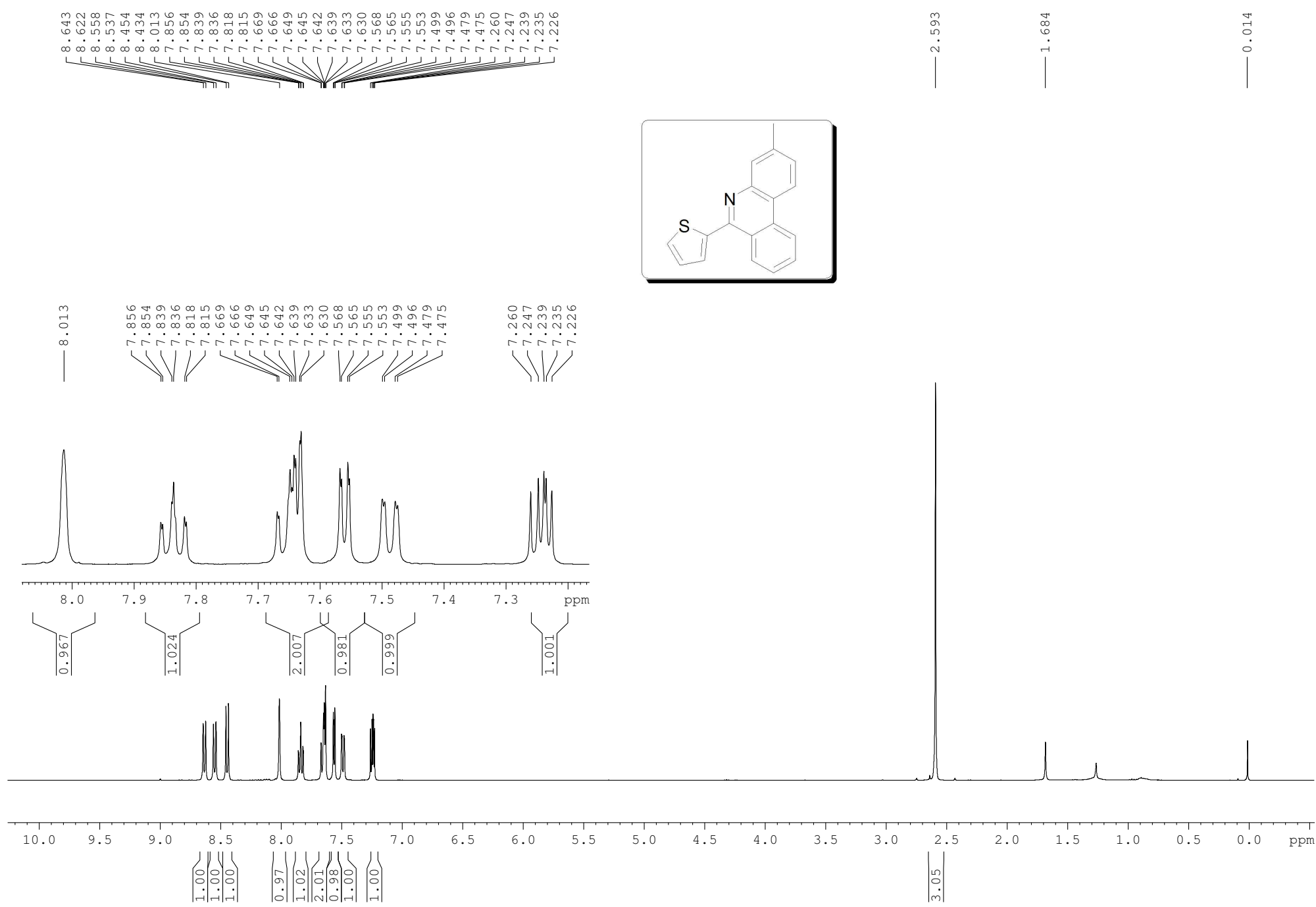


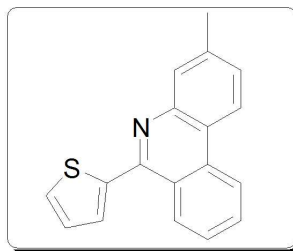
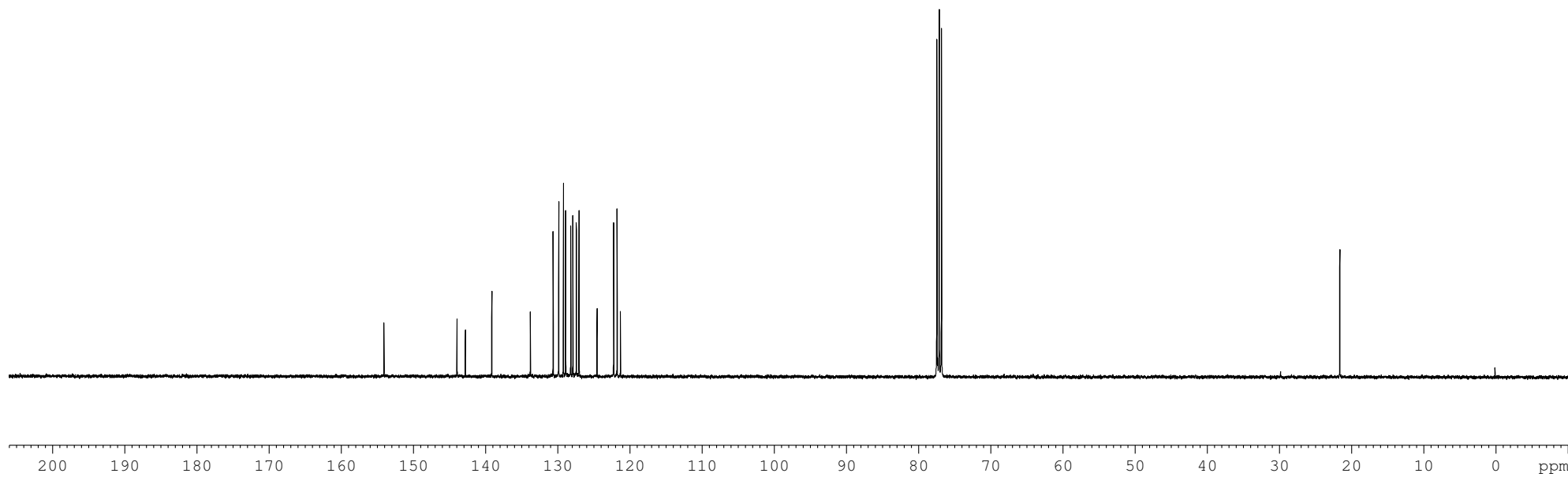








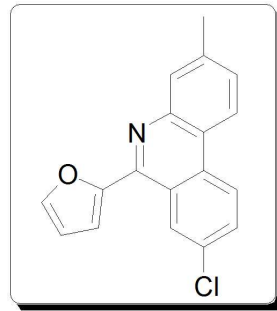
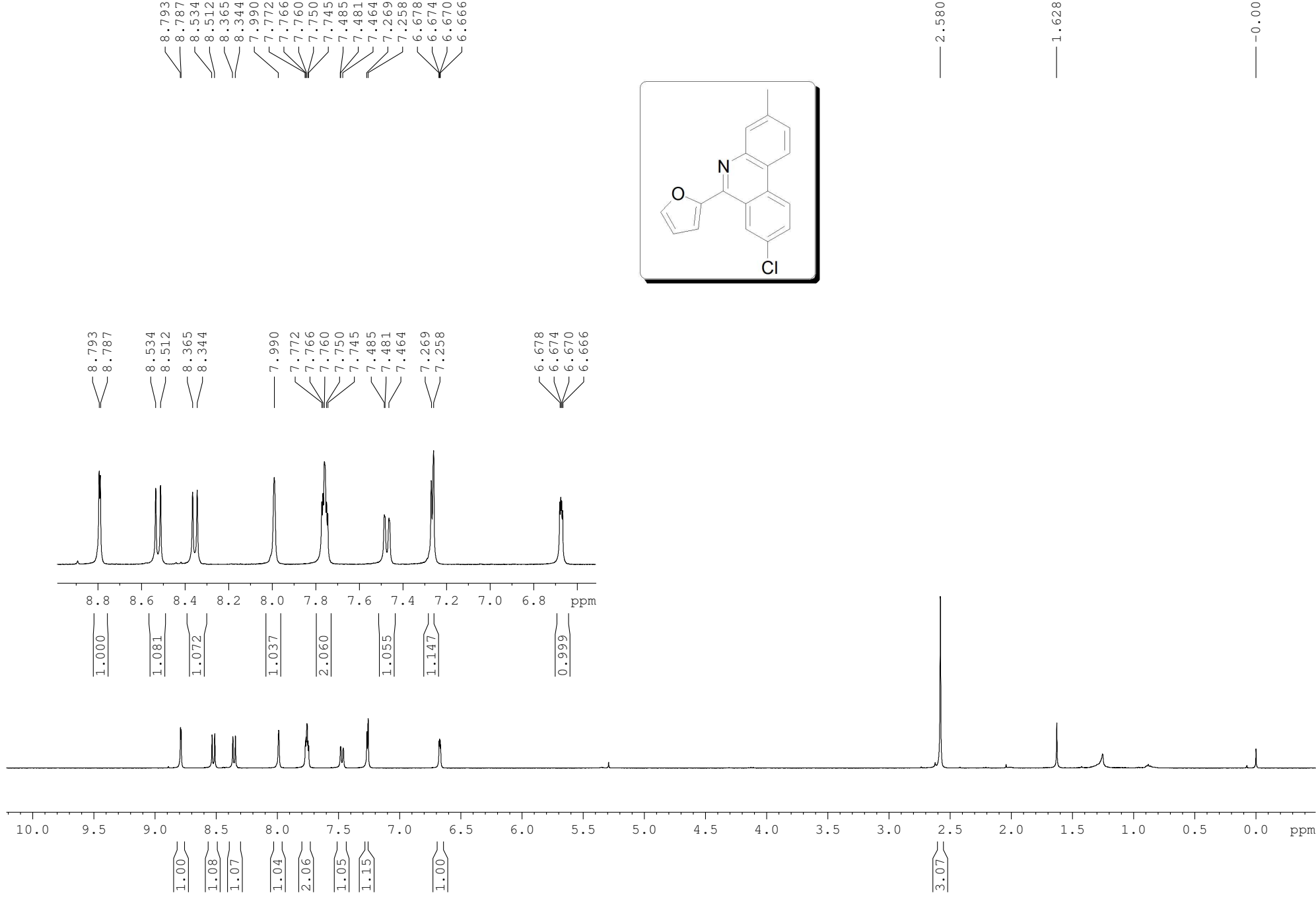




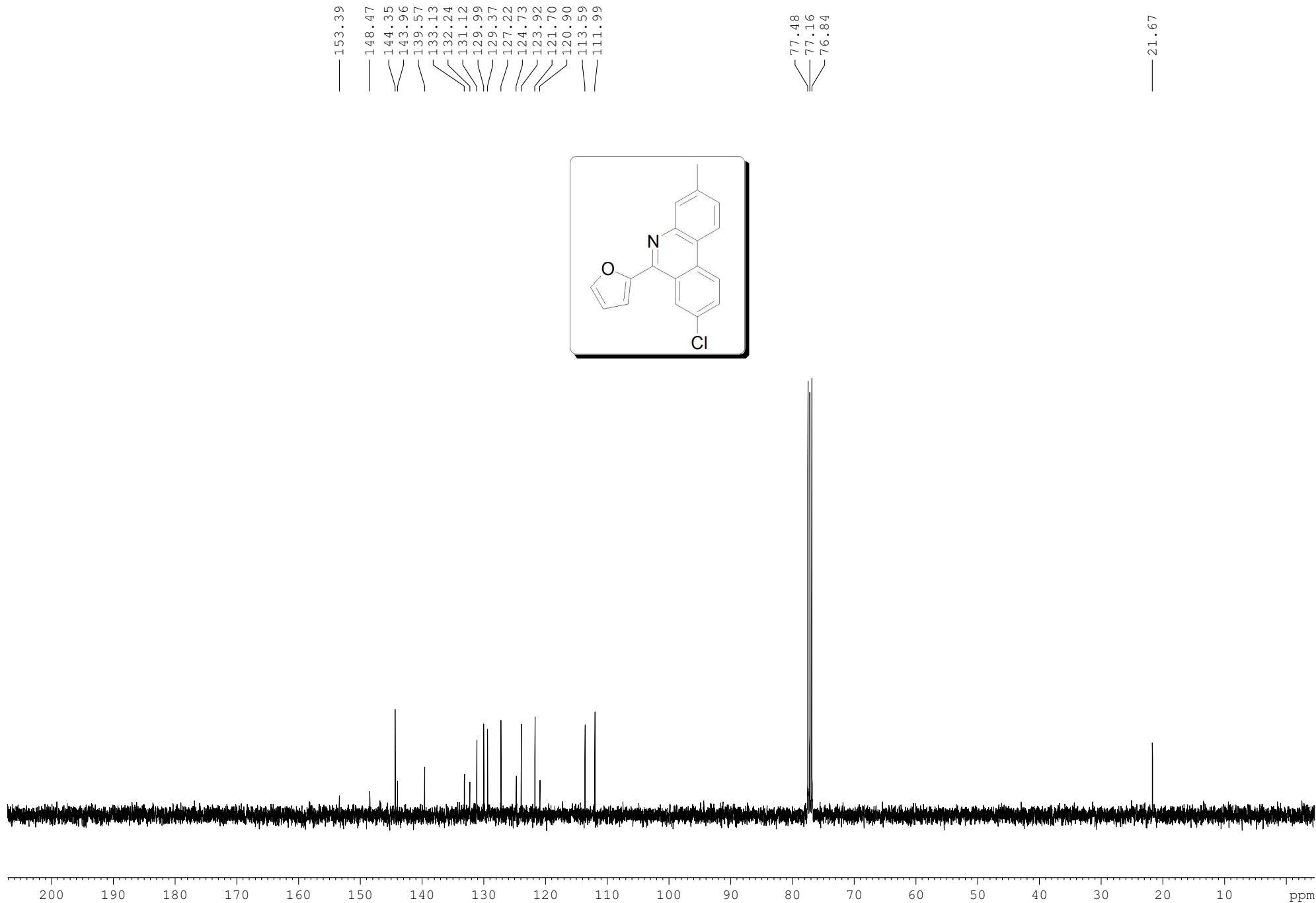
154.11  
143.98  
142.84  
139.17  
133.82  
130.66  
129.89  
129.24  
128.93  
128.21  
127.93  
127.44  
127.07  
124.59  
122.28  
121.80  
121.34

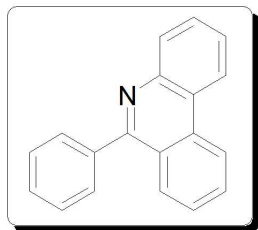
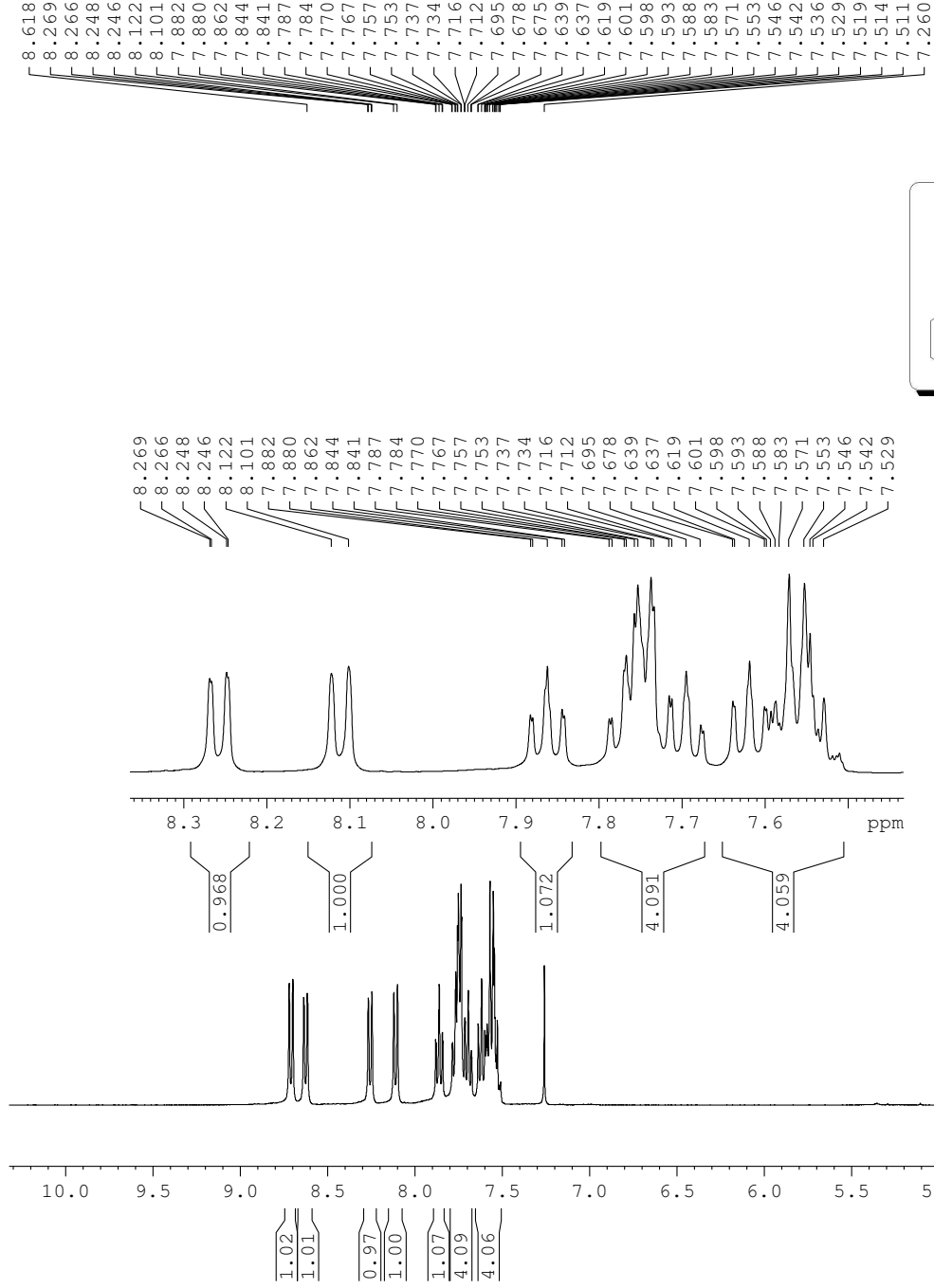
77.48  
77.16  
76.84

21.65





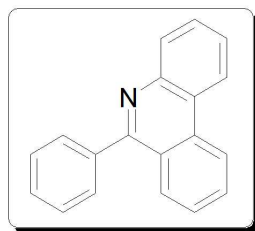
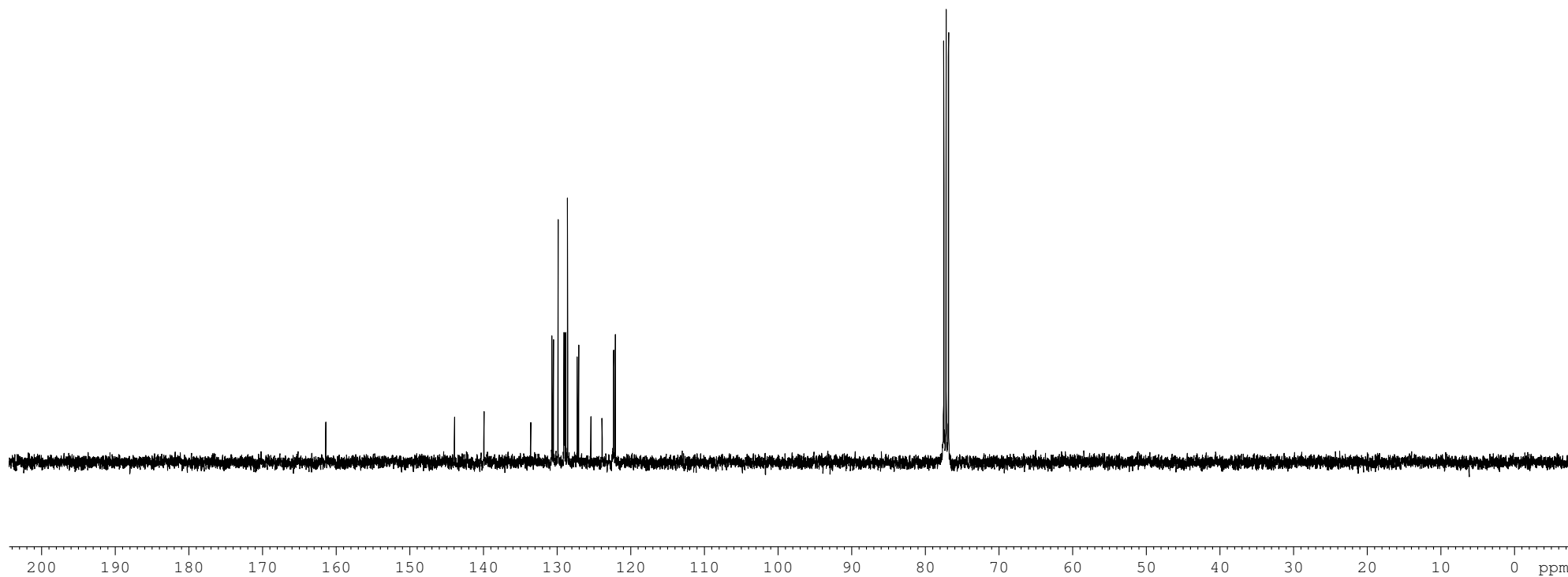


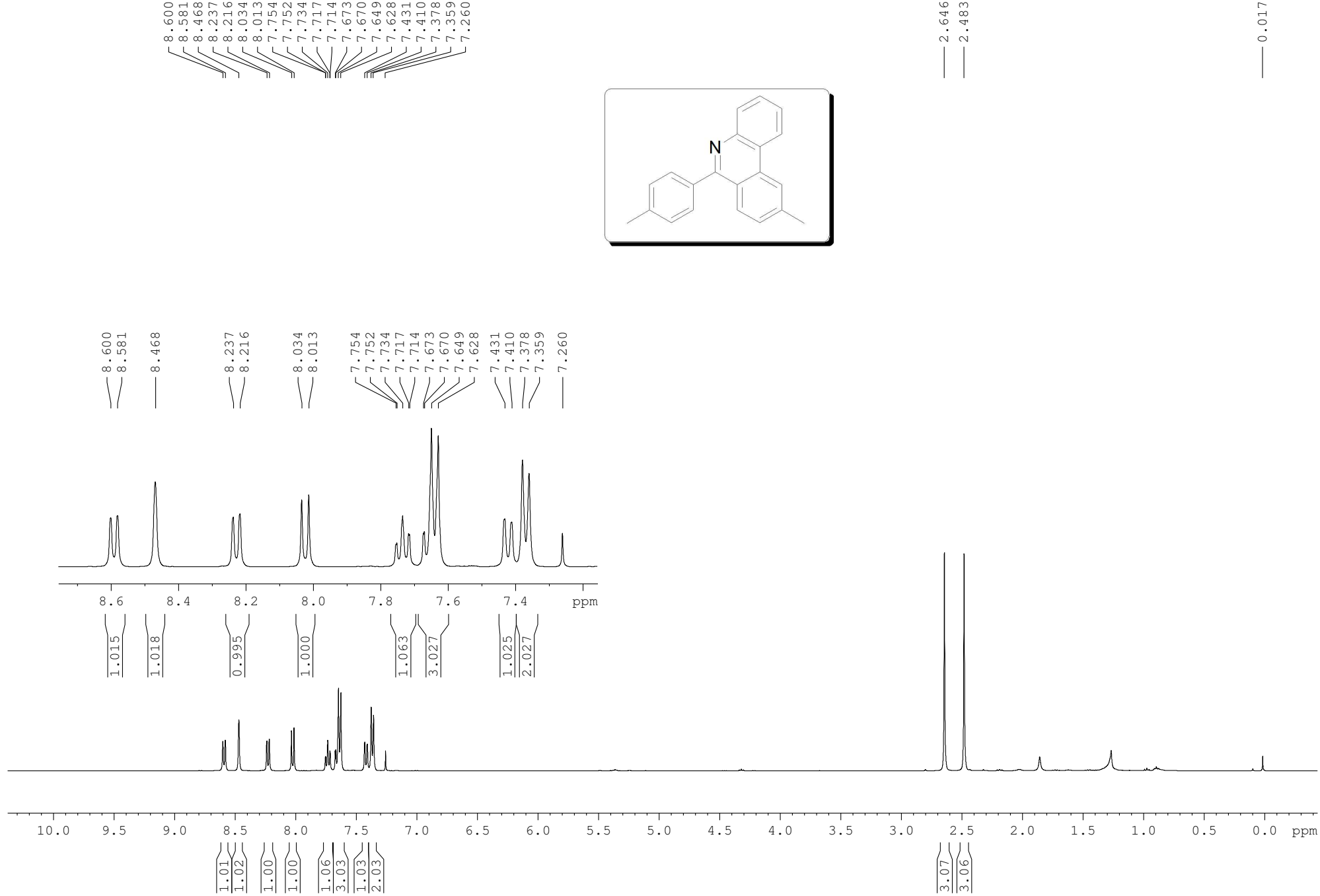


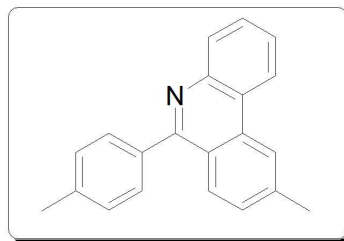
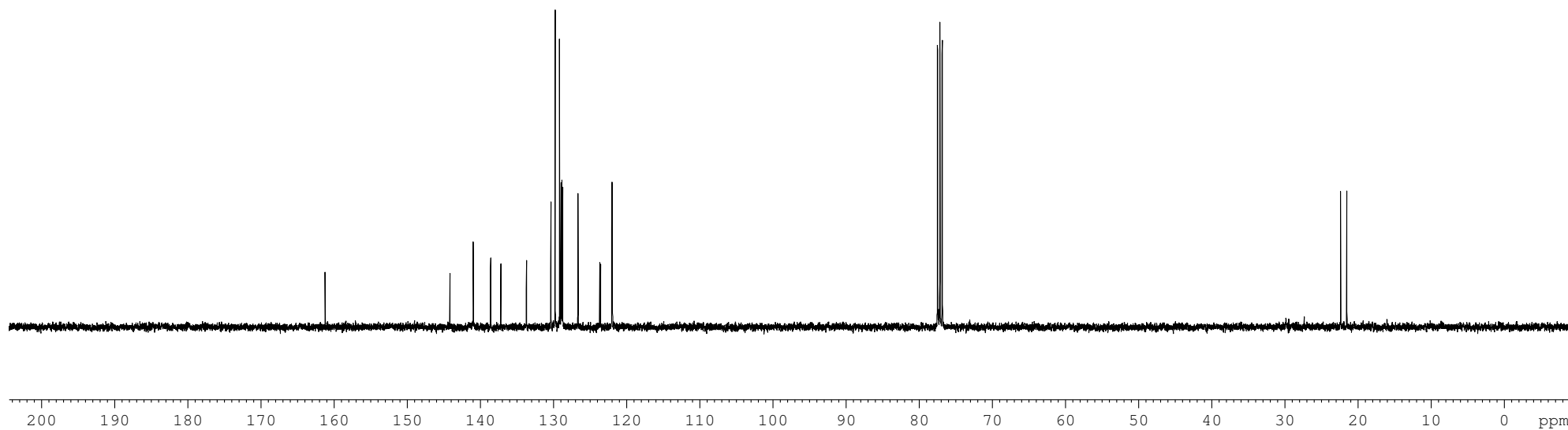
— 1.685

— 1.261

— 0.008





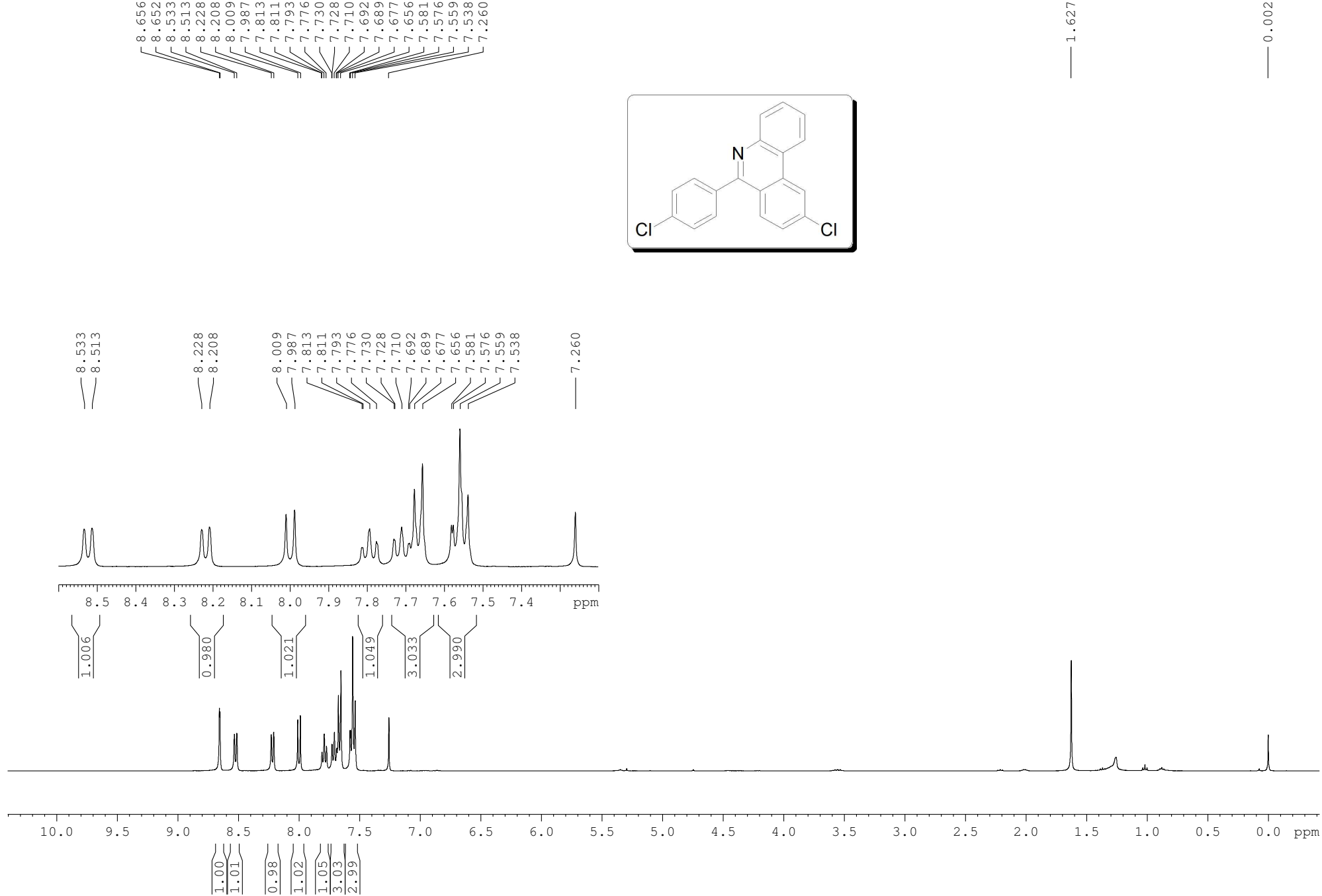


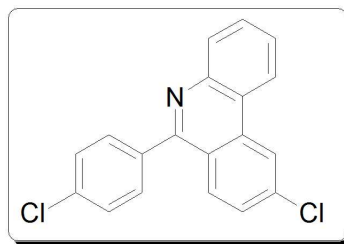
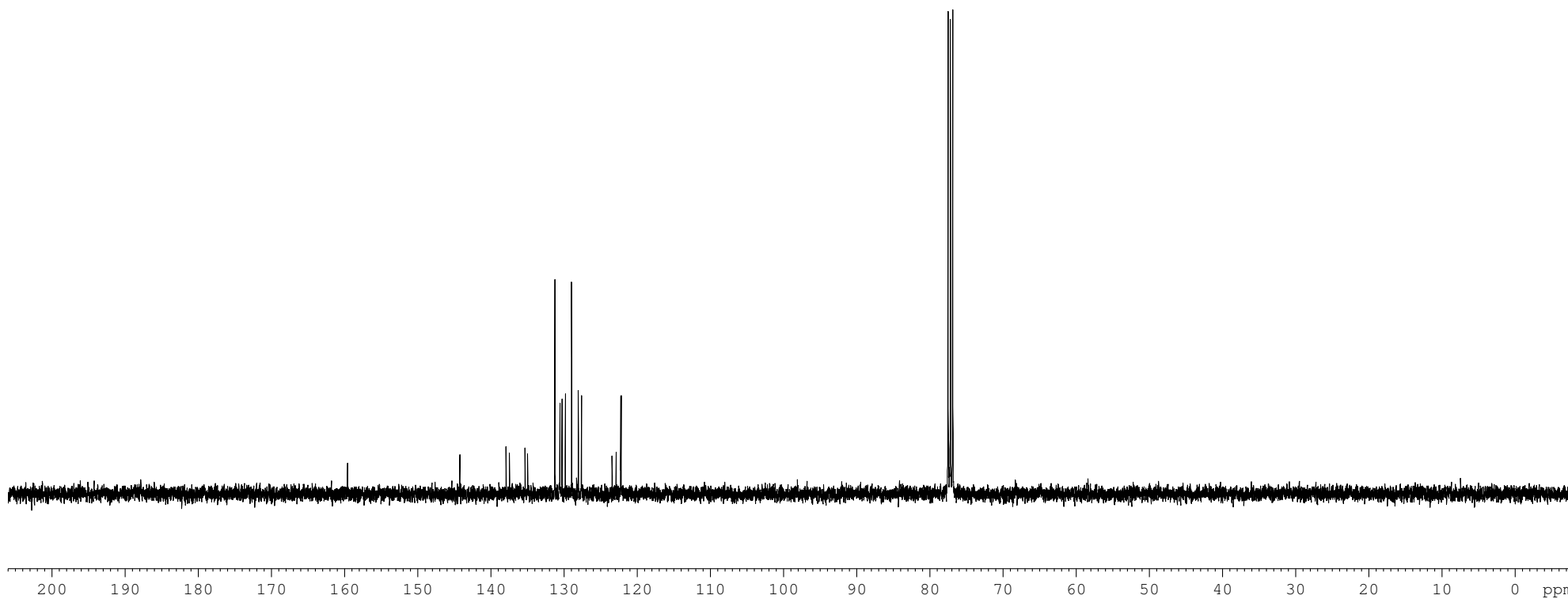
161.24

144.16  
140.97  
138.60  
137.19  
133.71  
130.36  
129.78  
129.17  
128.98  
128.87  
128.75  
126.66  
123.67  
123.57  
122.02  
121.95

77.48  
77.16  
76.85

22.37  
21.52

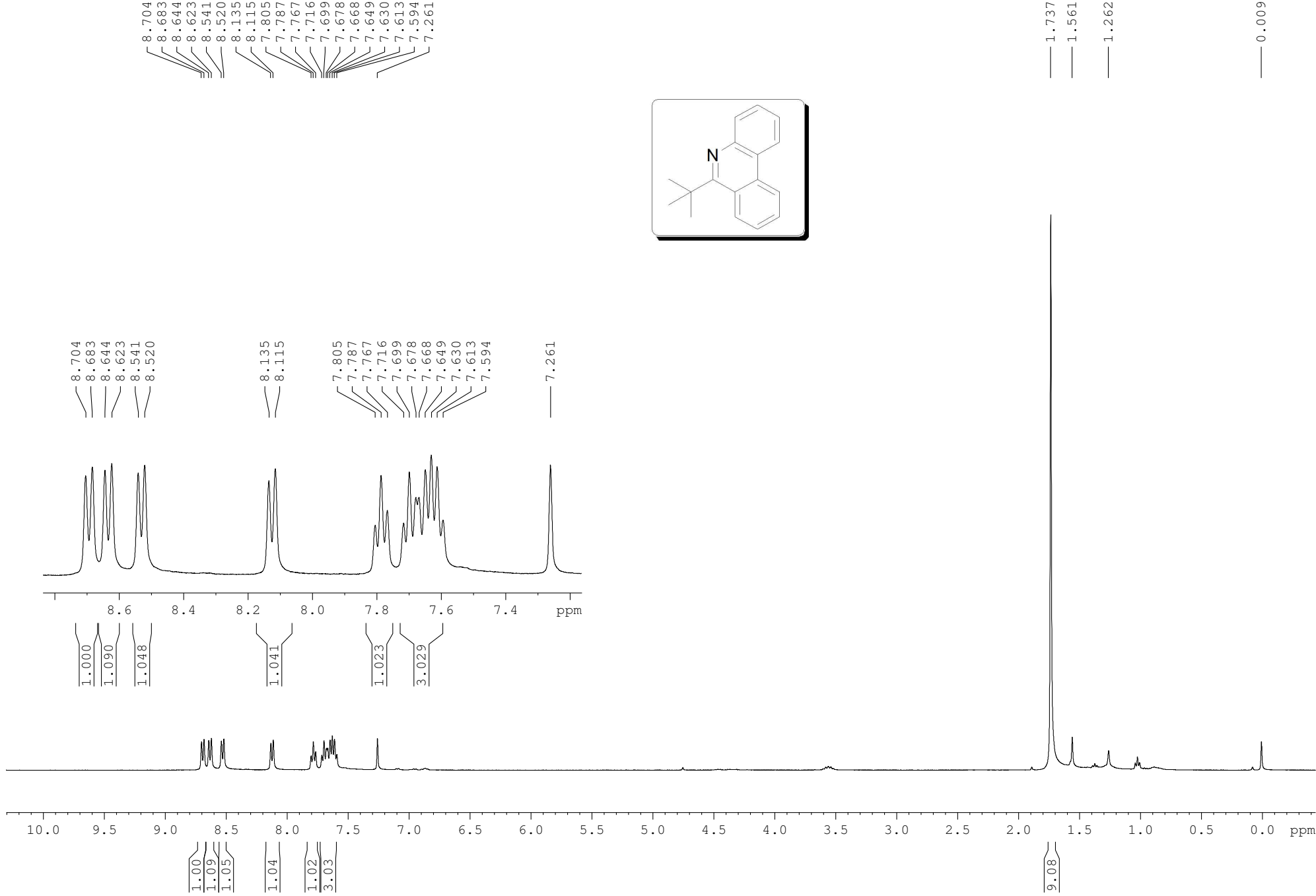




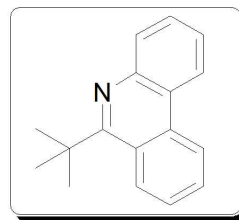
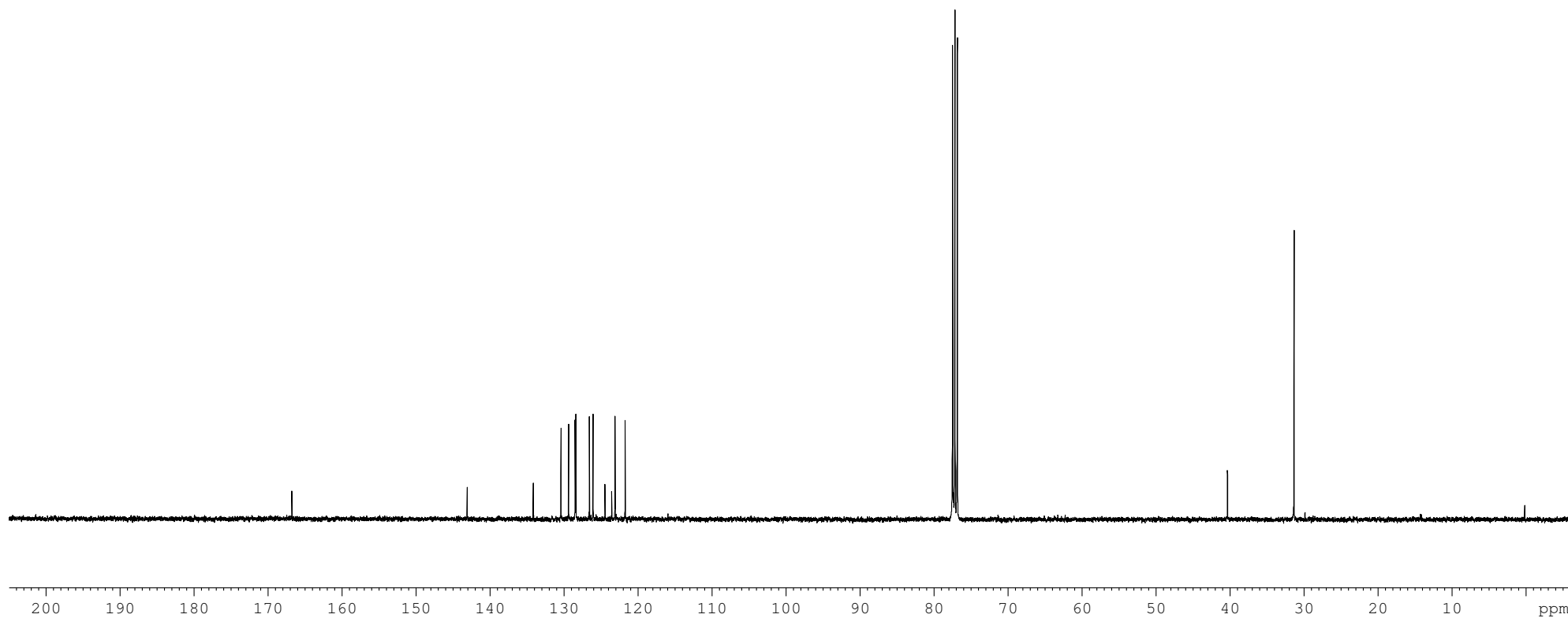
159.57

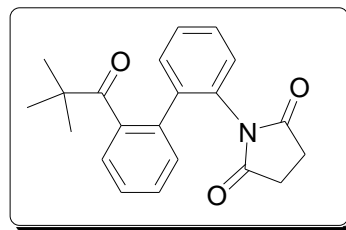
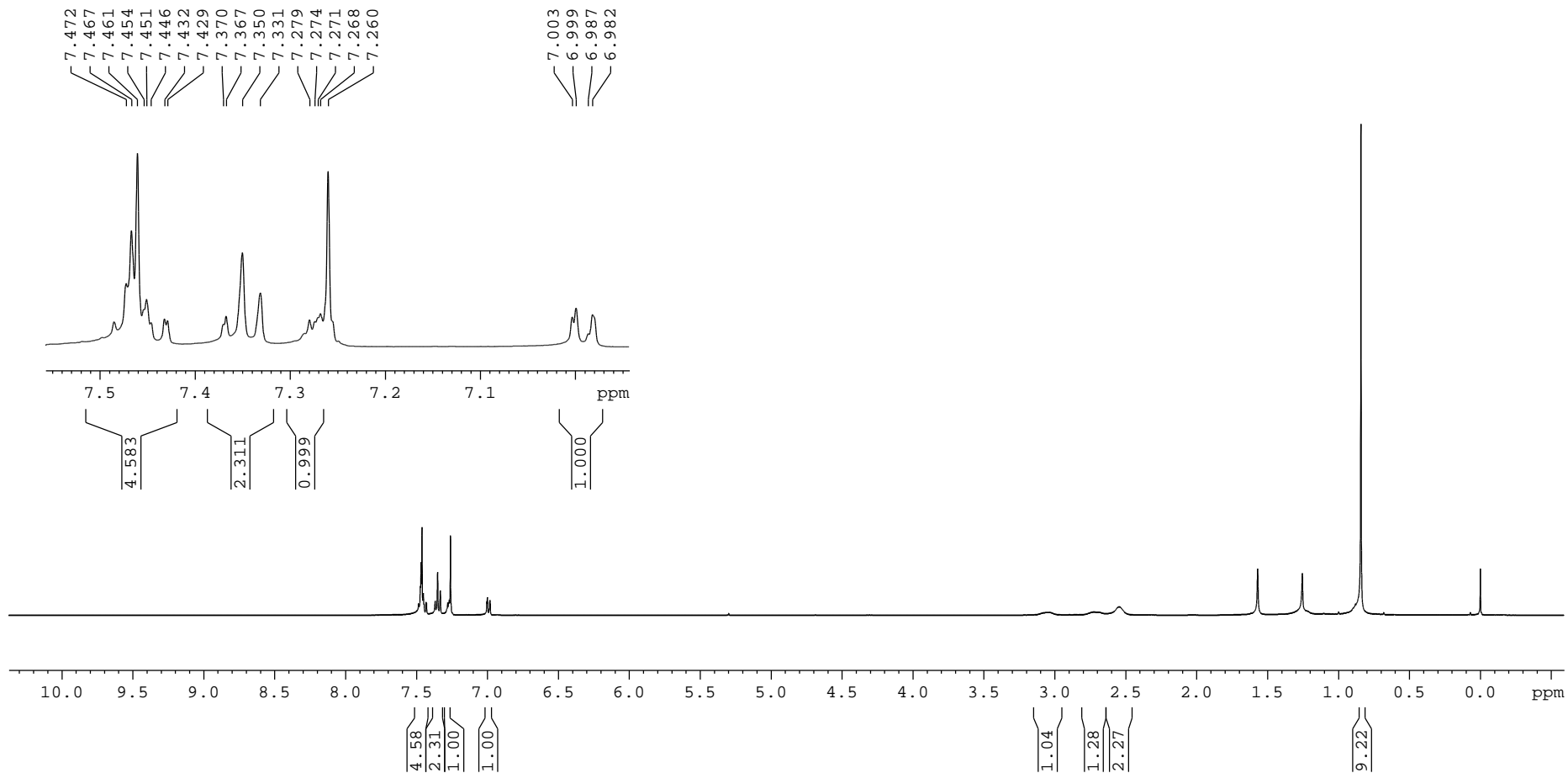
144.22  
137.90  
137.44  
135.31  
134.96  
131.22  
130.55  
130.25  
129.80  
128.95  
128.02  
127.58  
123.41  
122.86  
122.23  
122.17

77.48  
77.16  
76.84

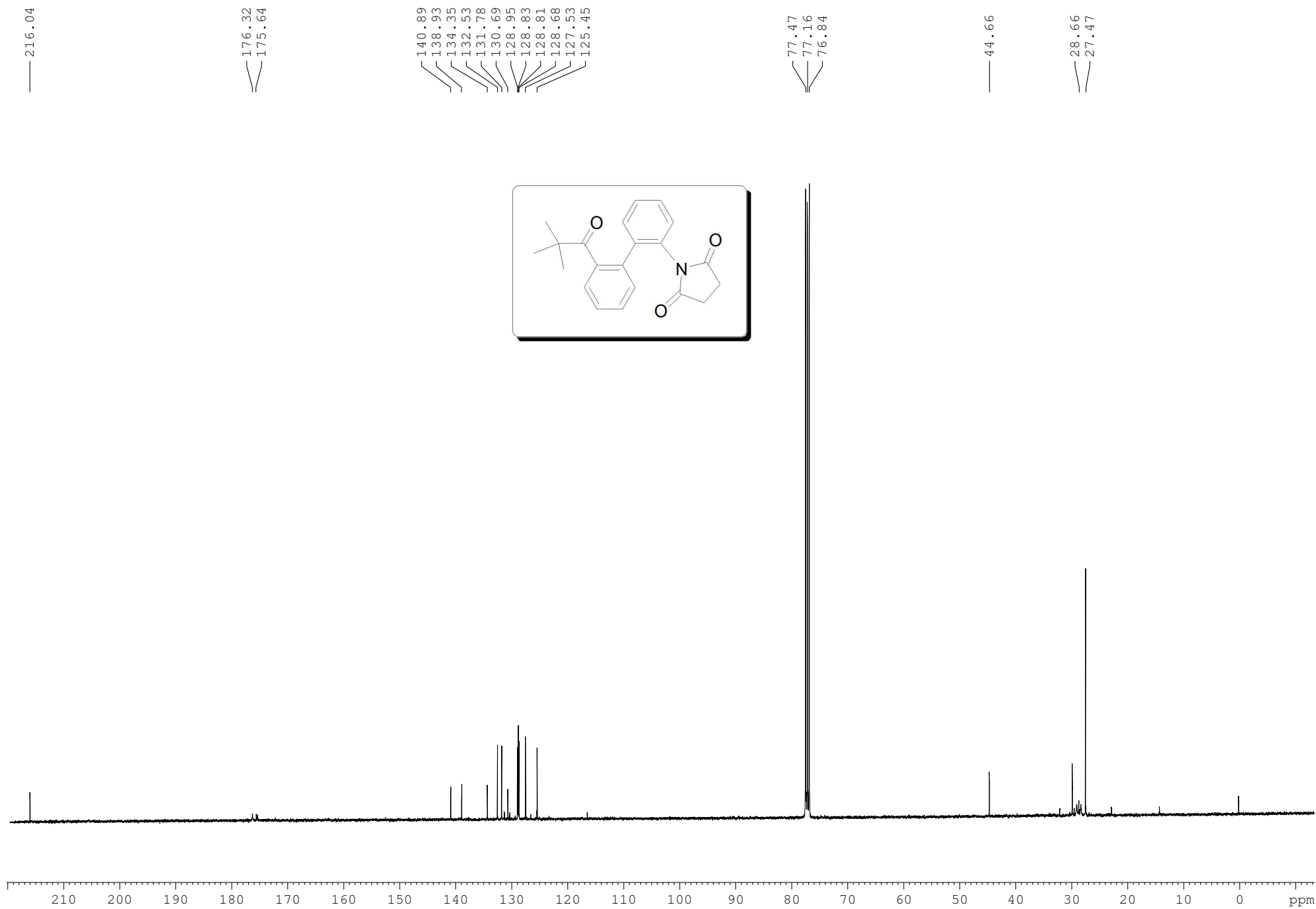








— 3.0361  
 — 2.7199  
 — 2.6970  
 — 2.5436  
 — 0.8402

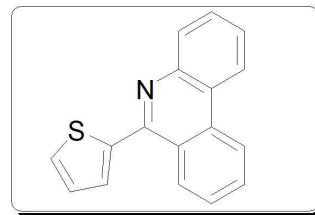


8.678  
8.584  
8.563  
8.227  
8.224  
8.206  
8.204  
7.891  
7.888  
7.874  
7.871  
7.868  
7.853  
7.850  
7.767  
7.764  
7.750  
7.747  
7.729  
7.726  
7.715  
7.712  
7.710  
7.694  
7.691  
7.688  
7.684  
7.676  
7.673  
7.670  
7.667  
7.664  
7.653  
7.650  
7.644  
7.642  
7.579  
7.576  
7.566  
7.564  
7.260  
7.255  
7.246  
7.242  
7.233

— 1.649

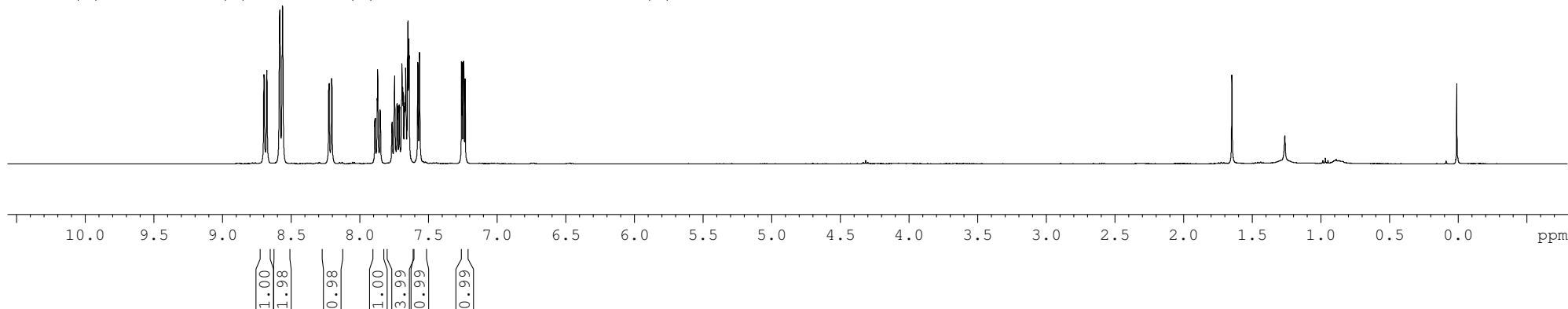
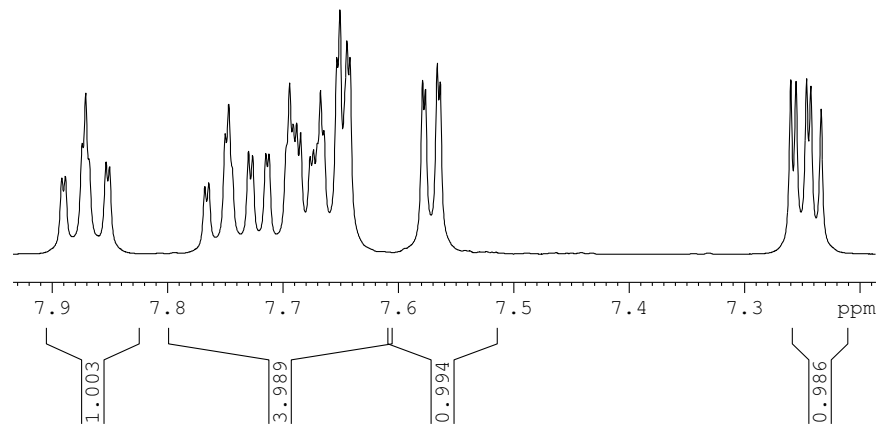
— 1.263

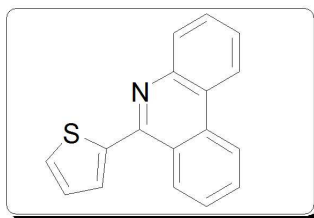
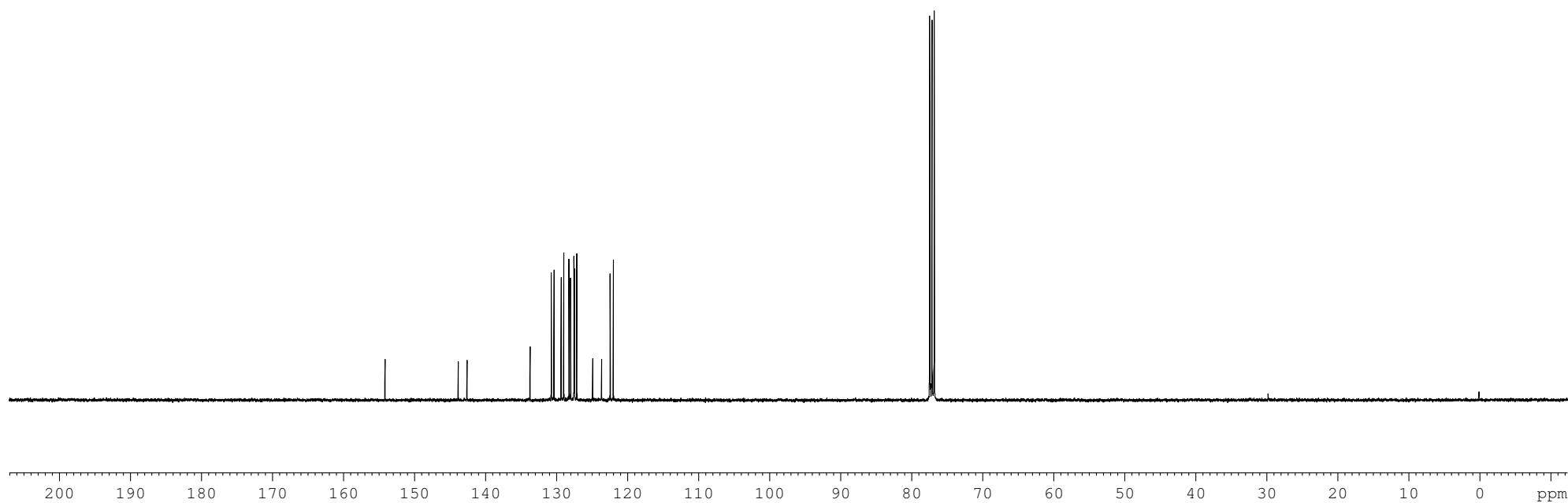
— 0.011



7.850  
7.767  
7.764  
7.750  
7.747  
7.729  
7.726  
7.715  
7.712  
7.694  
7.691  
7.688  
7.684  
7.676  
7.673  
7.670  
7.667  
7.664  
7.653  
7.650  
7.644  
7.642  
7.579  
7.576  
7.566  
7.564

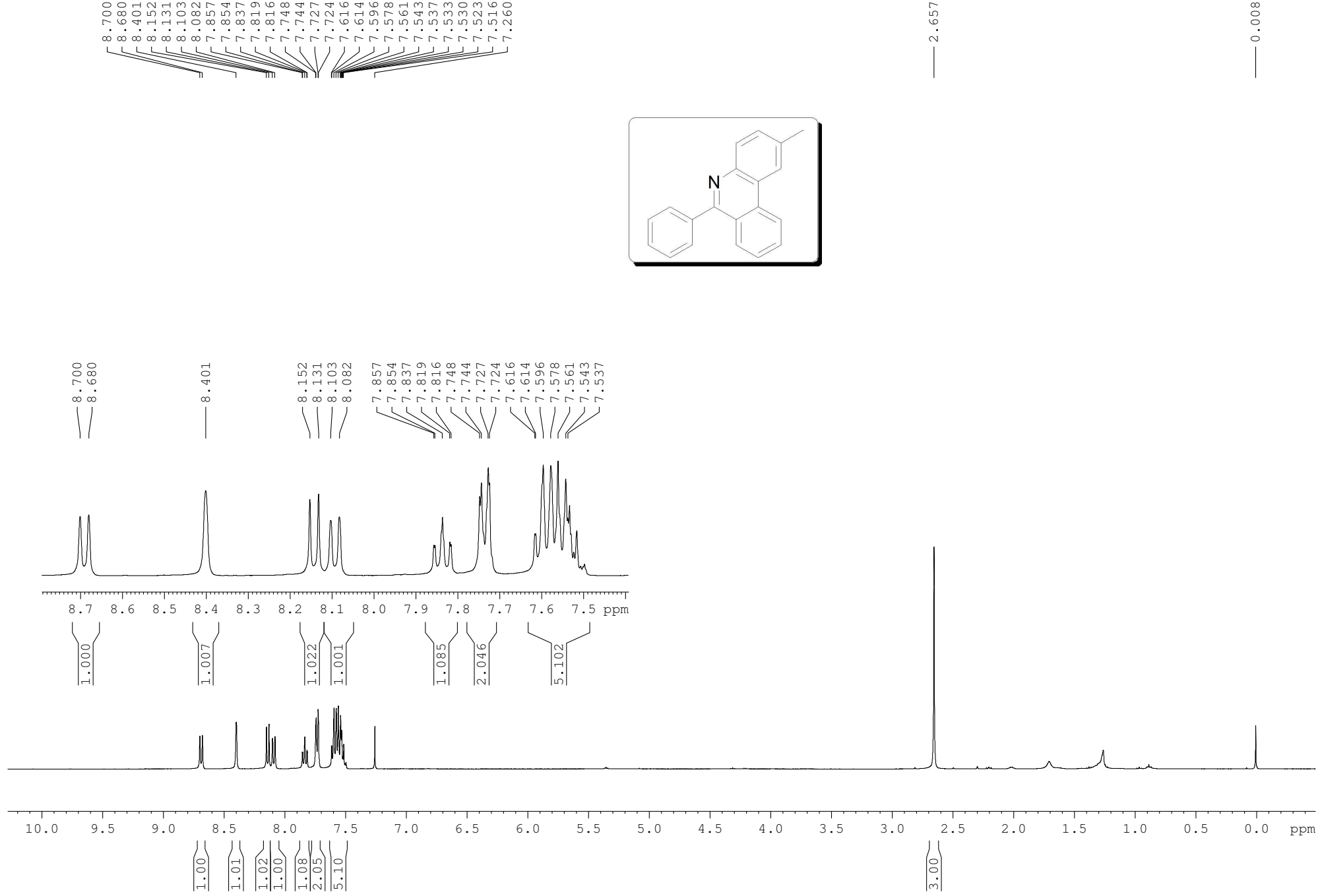
7.260  
7.255  
7.246  
7.242  
7.233

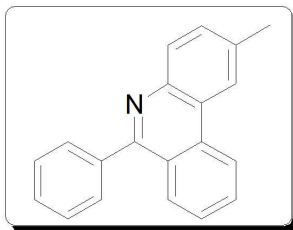
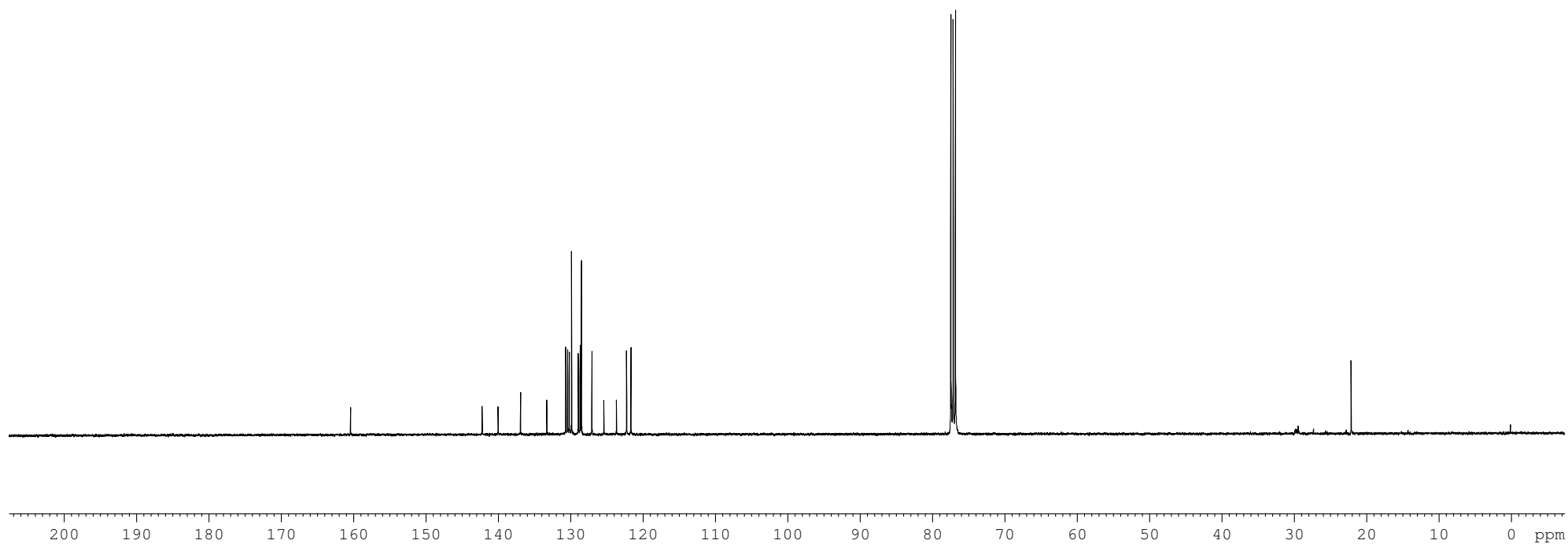




154.19  
143.86  
142.64  
133.77  
130.39  
129.38  
129.02  
128.28  
128.05  
127.58  
127.49  
127.17  
124.93  
123.68  
122.48  
122.03

77.48  
77.16  
76.84



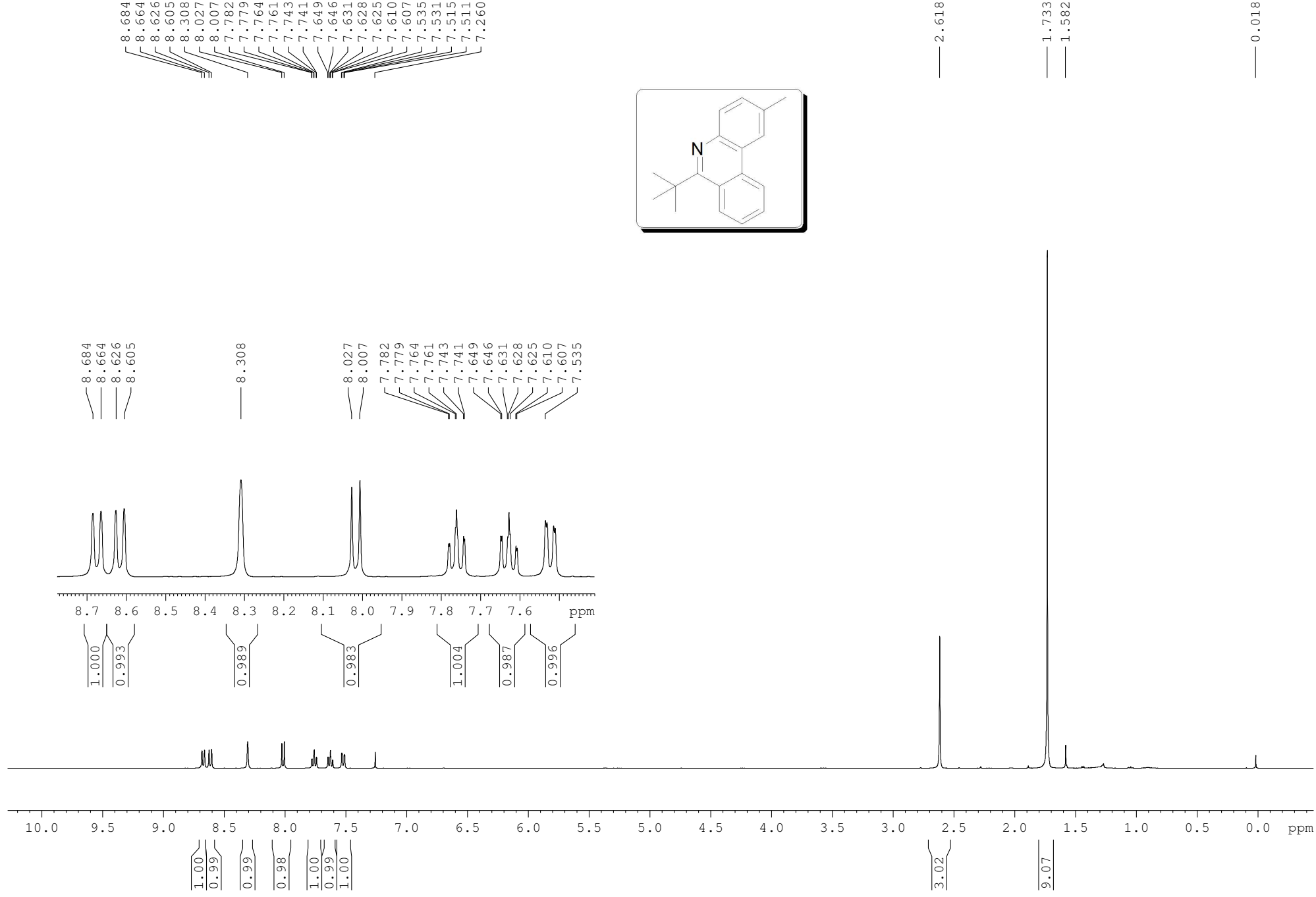


160.43

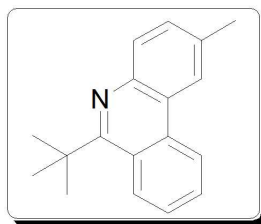
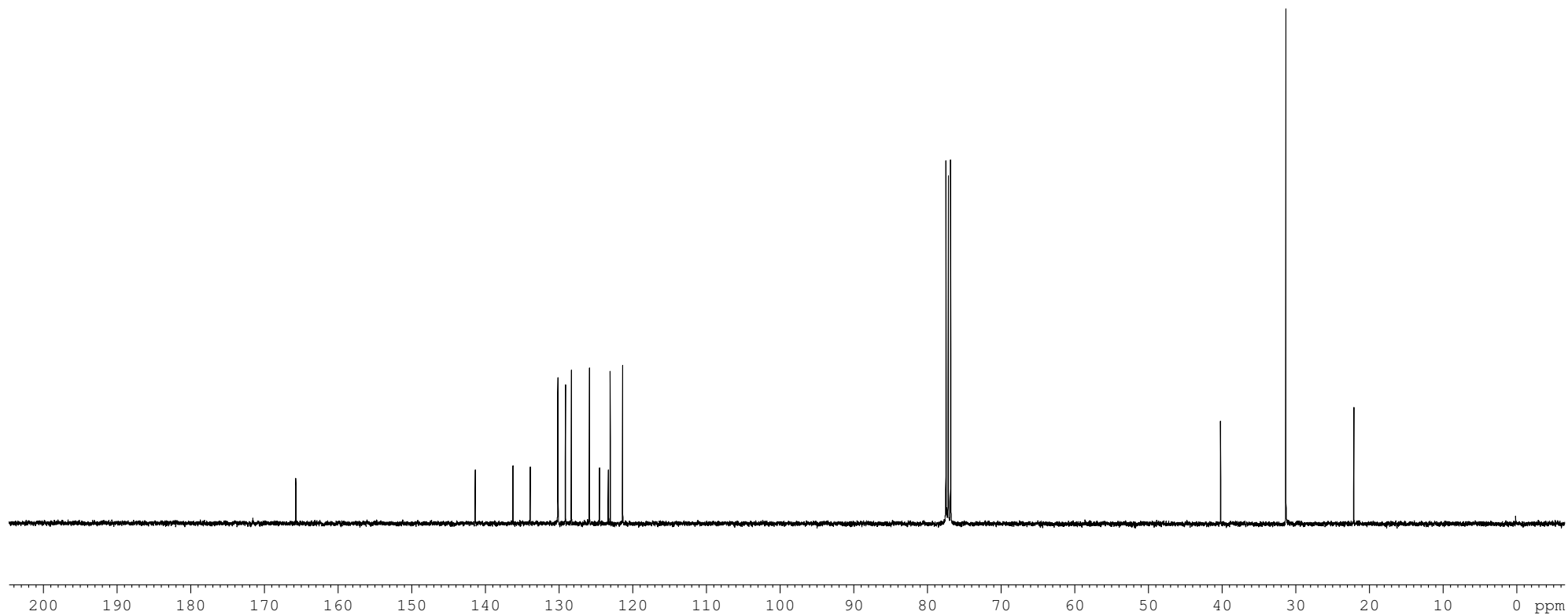
142.25  
140.04  
136.93  
133.31  
130.68  
130.43  
130.21  
129.88  
128.96  
128.70  
128.52  
127.07  
125.43  
123.69  
122.28  
121.67

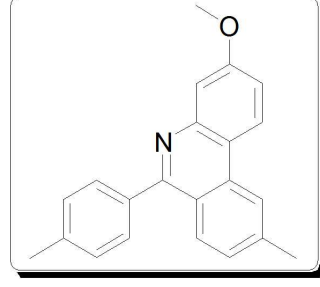
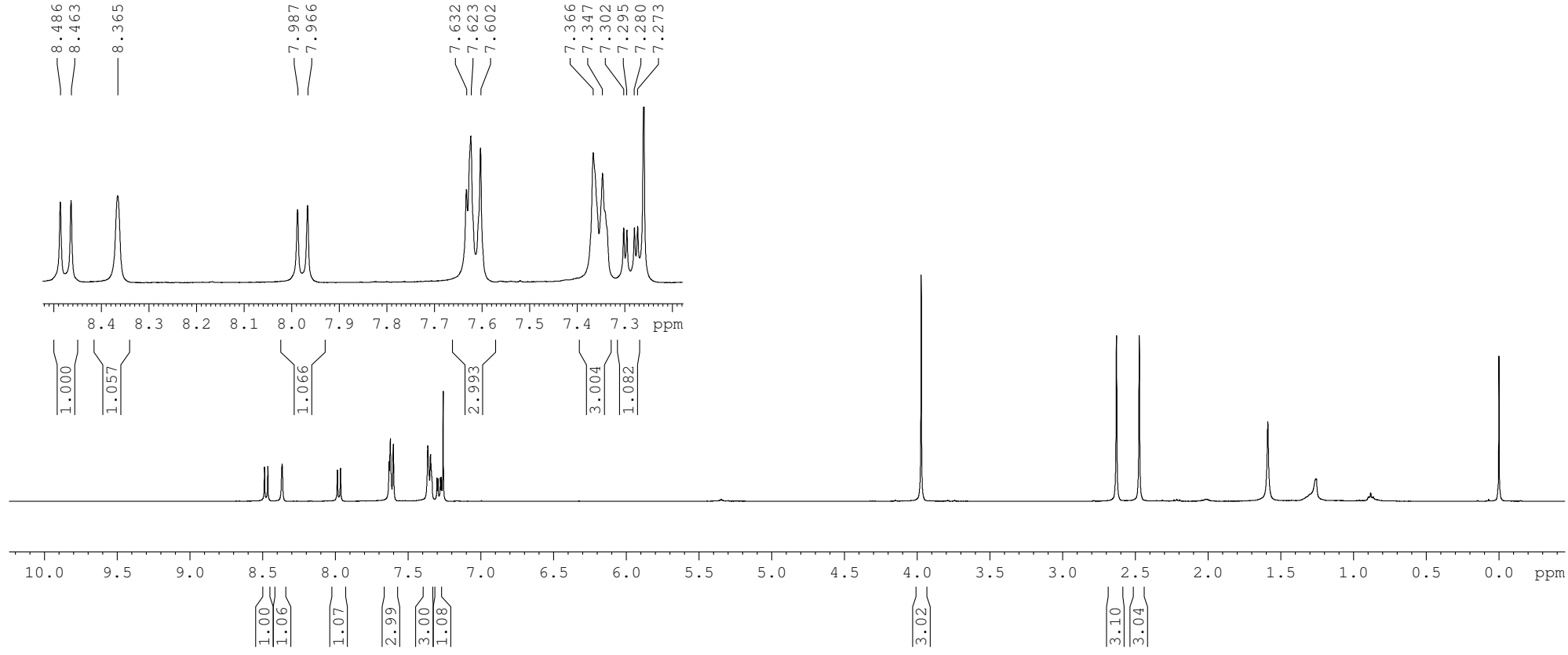
77.46  
77.14  
76.82

22.14









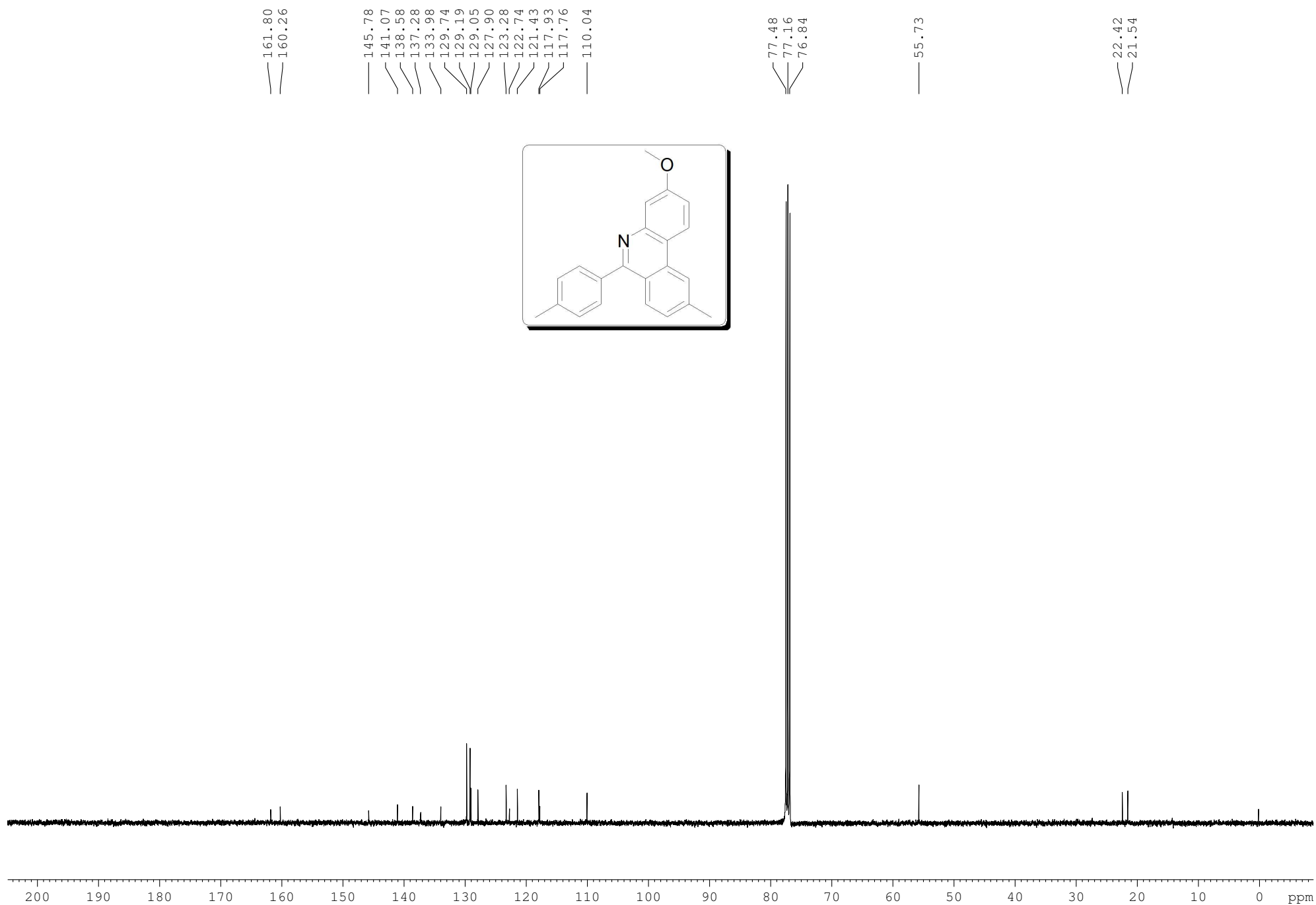
8.486  
8.463  
8.365  
7.987  
7.966  
7.632  
7.623  
7.602  
7.366  
7.347  
7.302  
7.295  
7.280  
7.273  
7.260

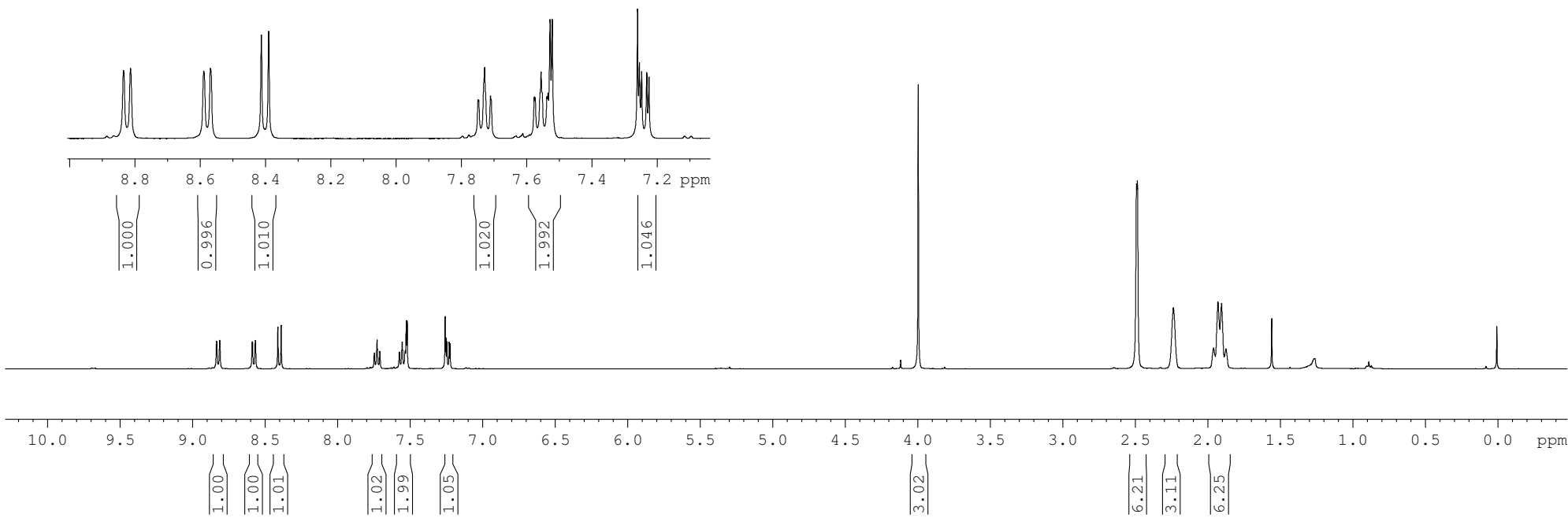
3.973

2.630  
2.474

1.590

0.001





8.835  
8.814

8.589  
8.569

8.413  
8.390

7.749  
7.747  
7.729  
7.711  
7.708  
7.576  
7.574  
7.556  
7.538  
7.535  
7.528  
7.521  
7.260  
7.254  
7.247  
7.232  
7.225

1.000

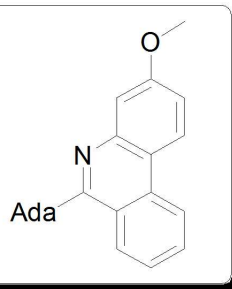
0.996

1.010

1.020

1.992

1.046



3.997

2.492  
2.487

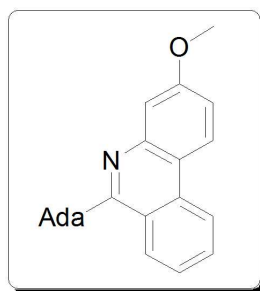
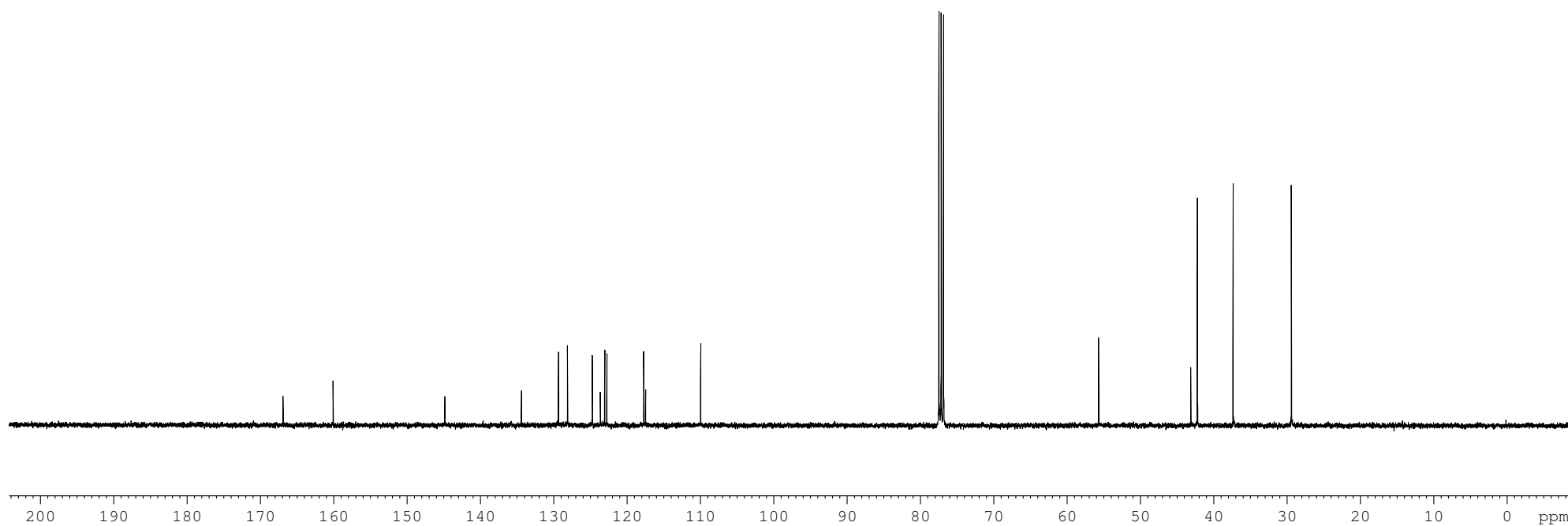
2.238

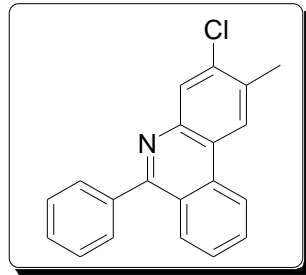
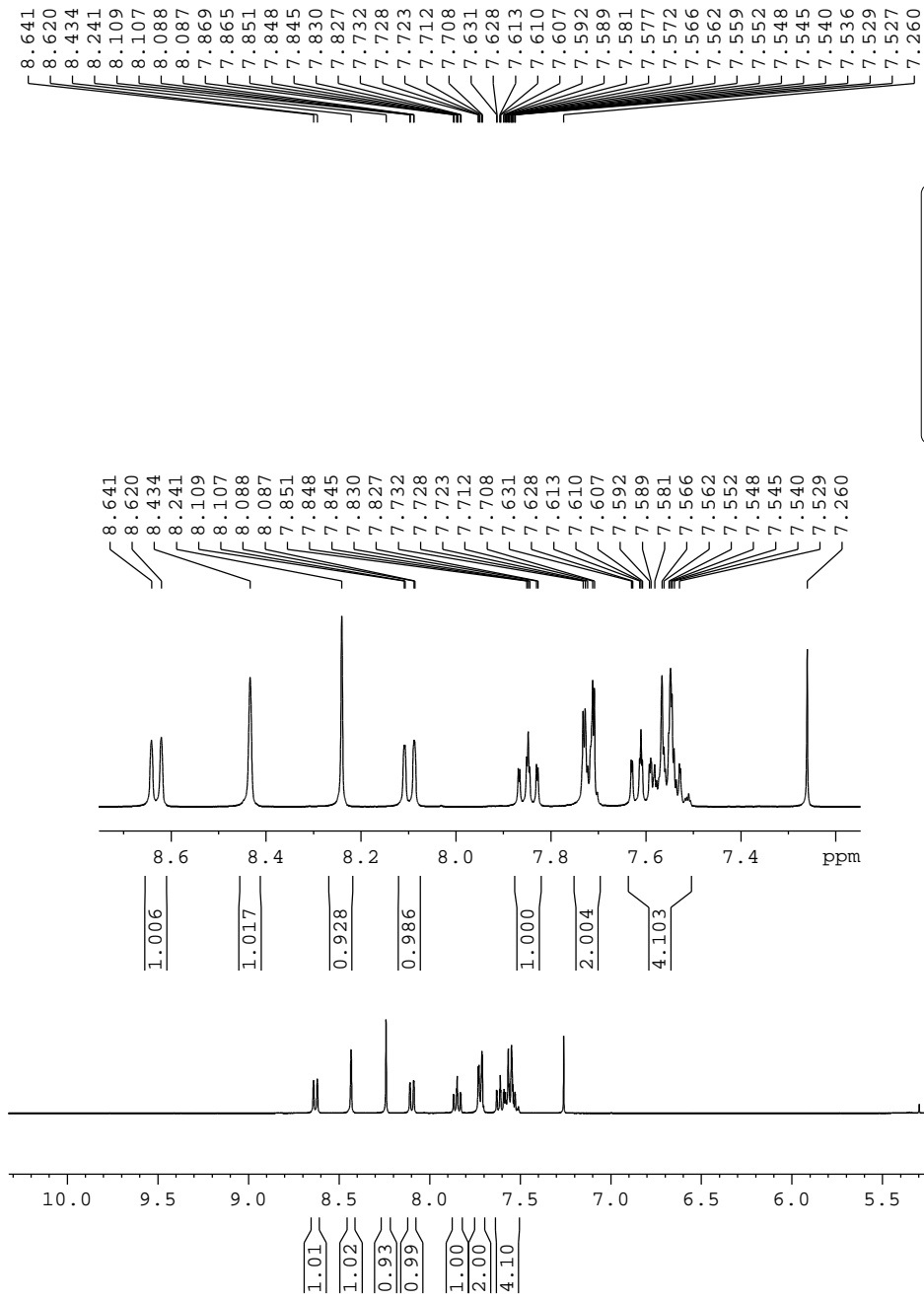
1.961  
1.931  
1.906

1.876

1.560

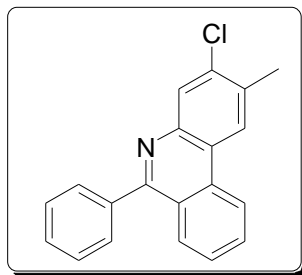
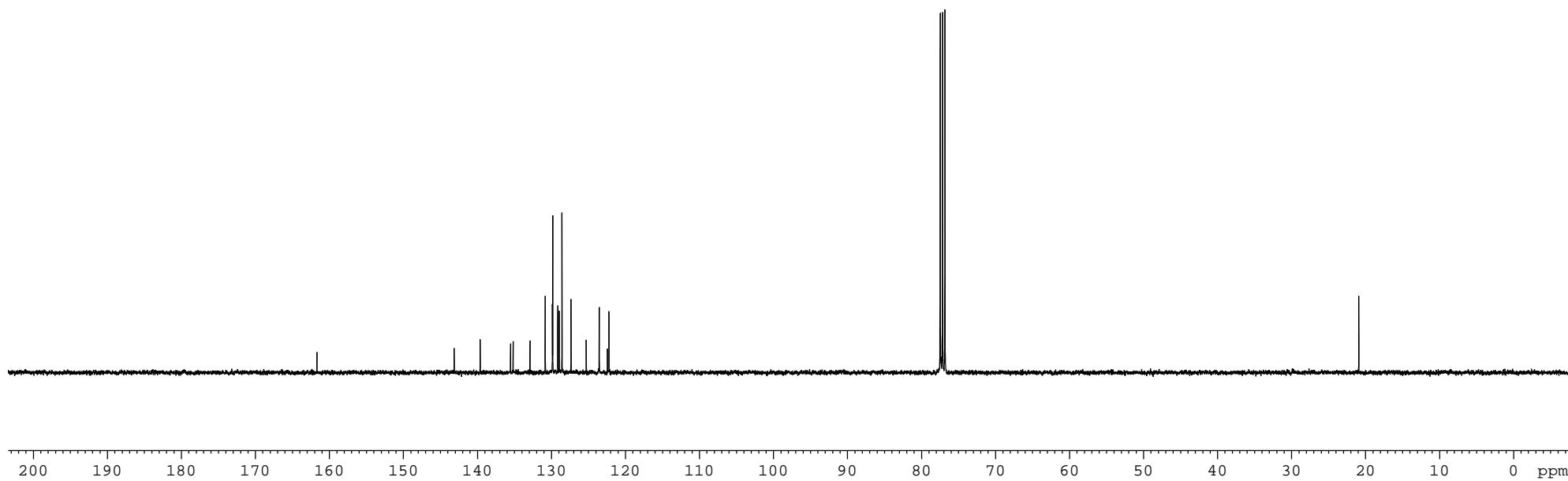
0.008





— 2.661

— 0.003

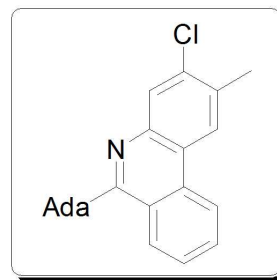
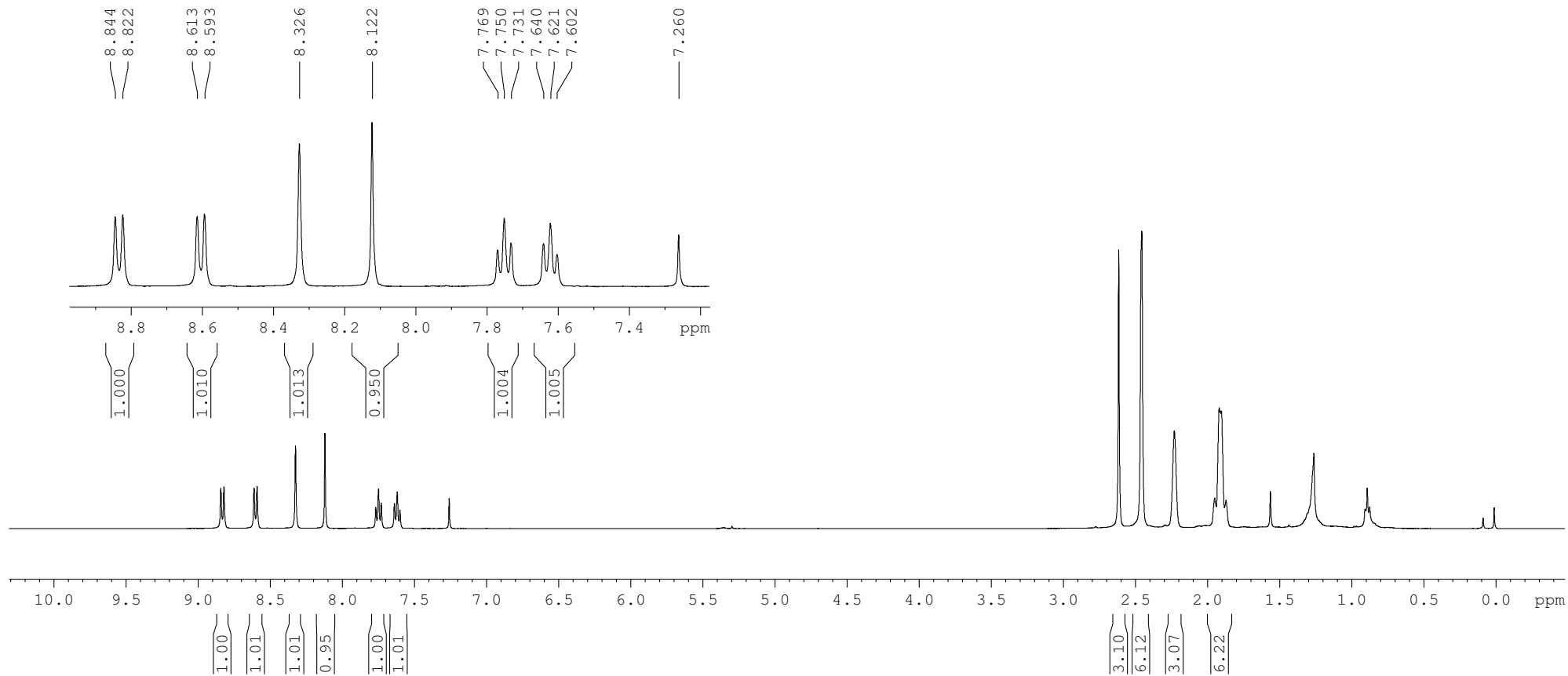


— 161.66

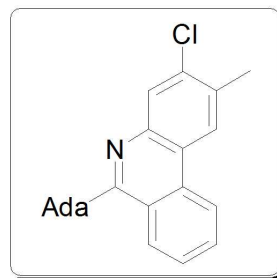
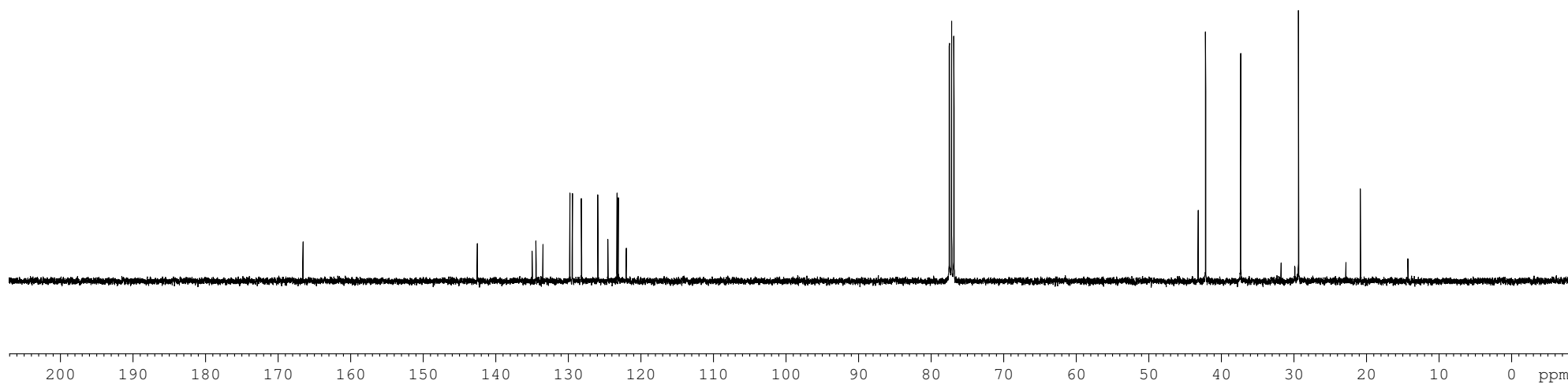
143.15  
139.64  
135.54  
135.18  
132.91  
130.85  
129.89  
129.84  
129.16  
128.96  
128.59  
127.36  
125.31  
123.55  
122.45  
122.23

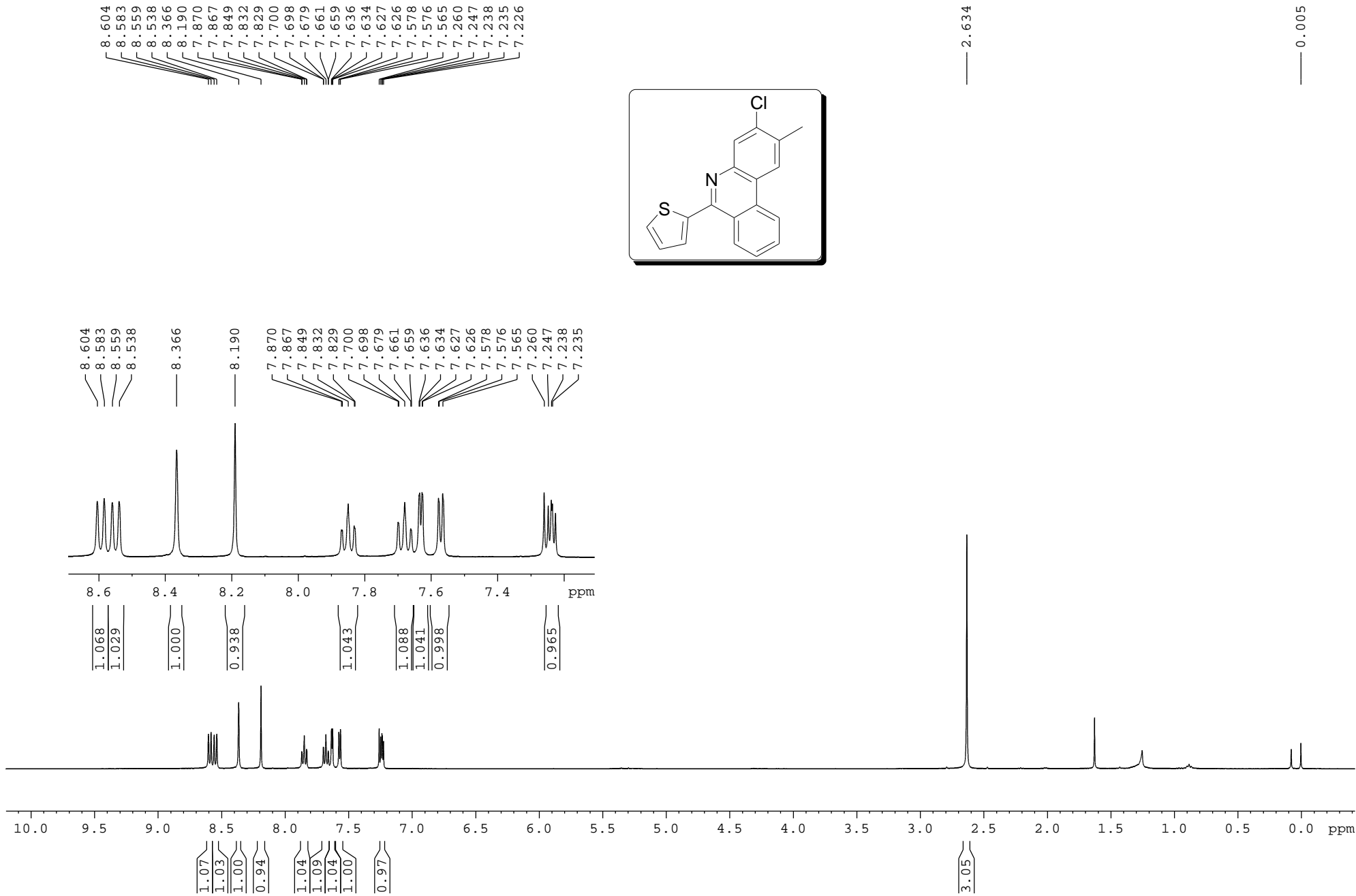
77.48  
77.16  
76.84

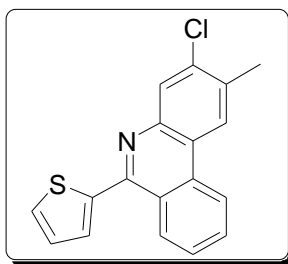
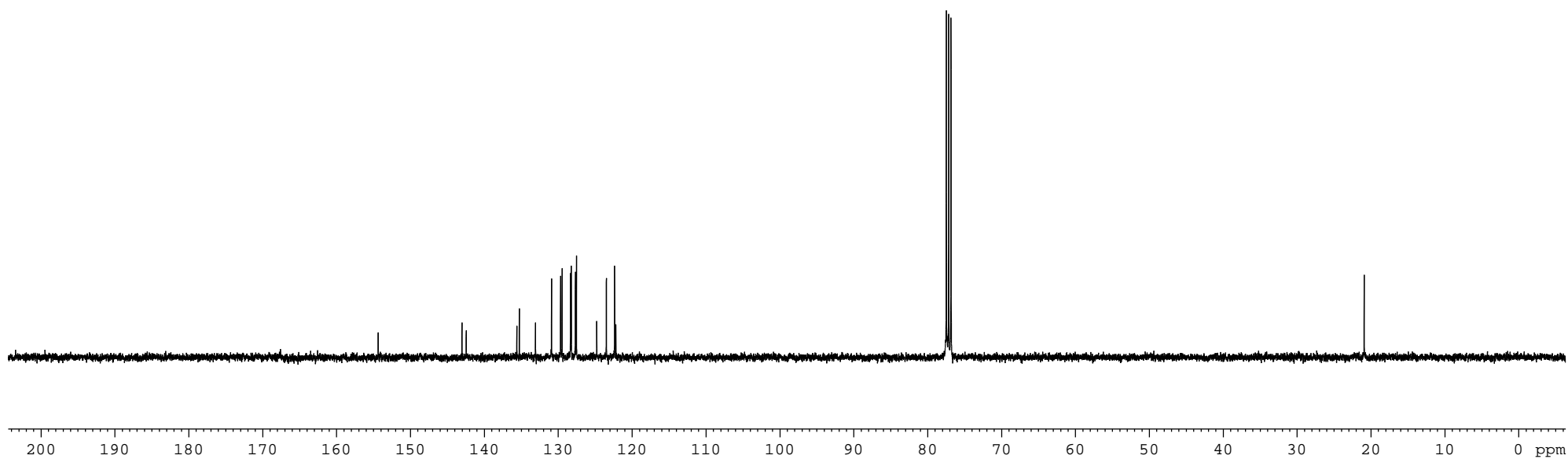
— 20.92







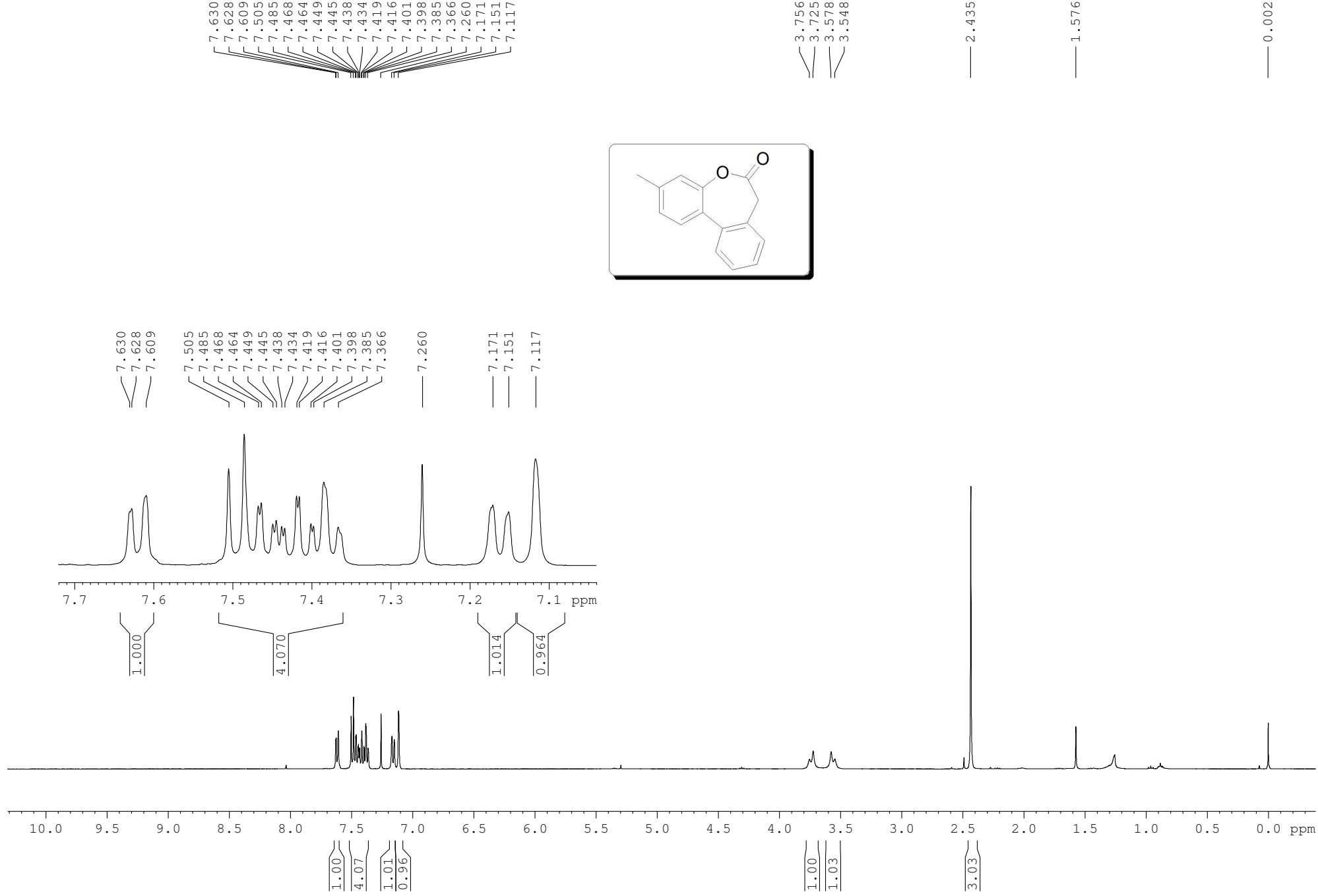


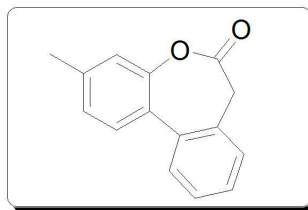
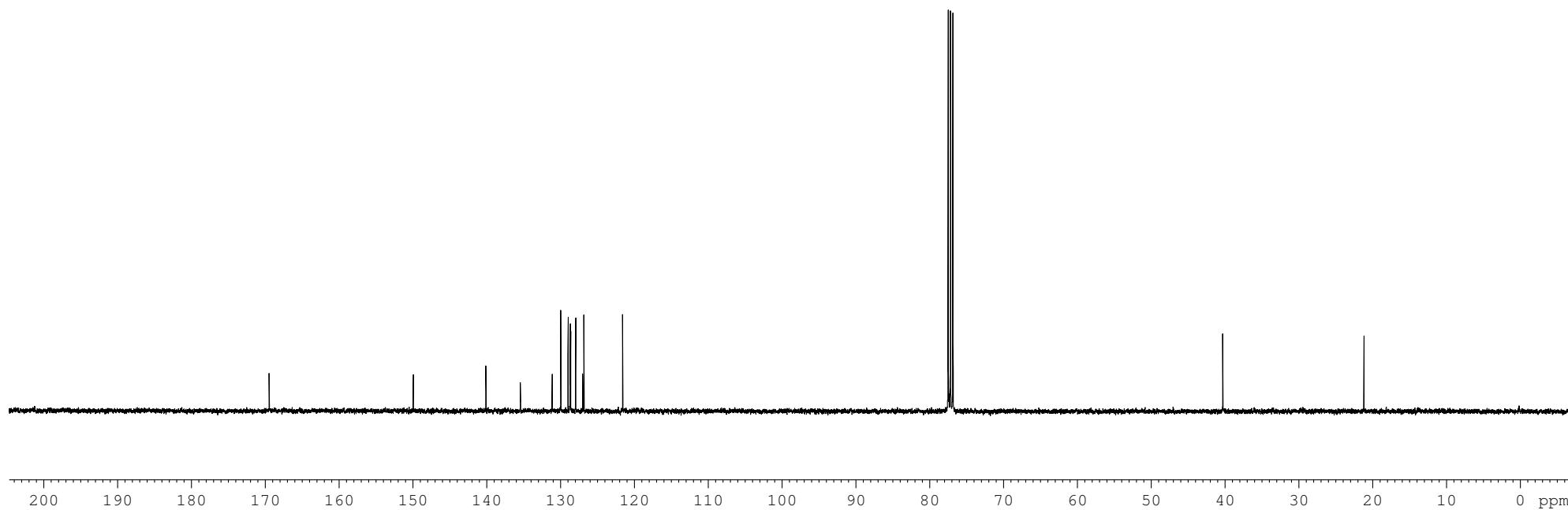


154.38  
143.03  
142.46  
135.61  
135.28  
133.08  
130.91  
129.69  
129.48  
128.35  
128.25  
127.68  
127.54  
124.80  
123.50  
122.38  
122.21

77.48  
77.16  
76.84

20.92





— 169.48

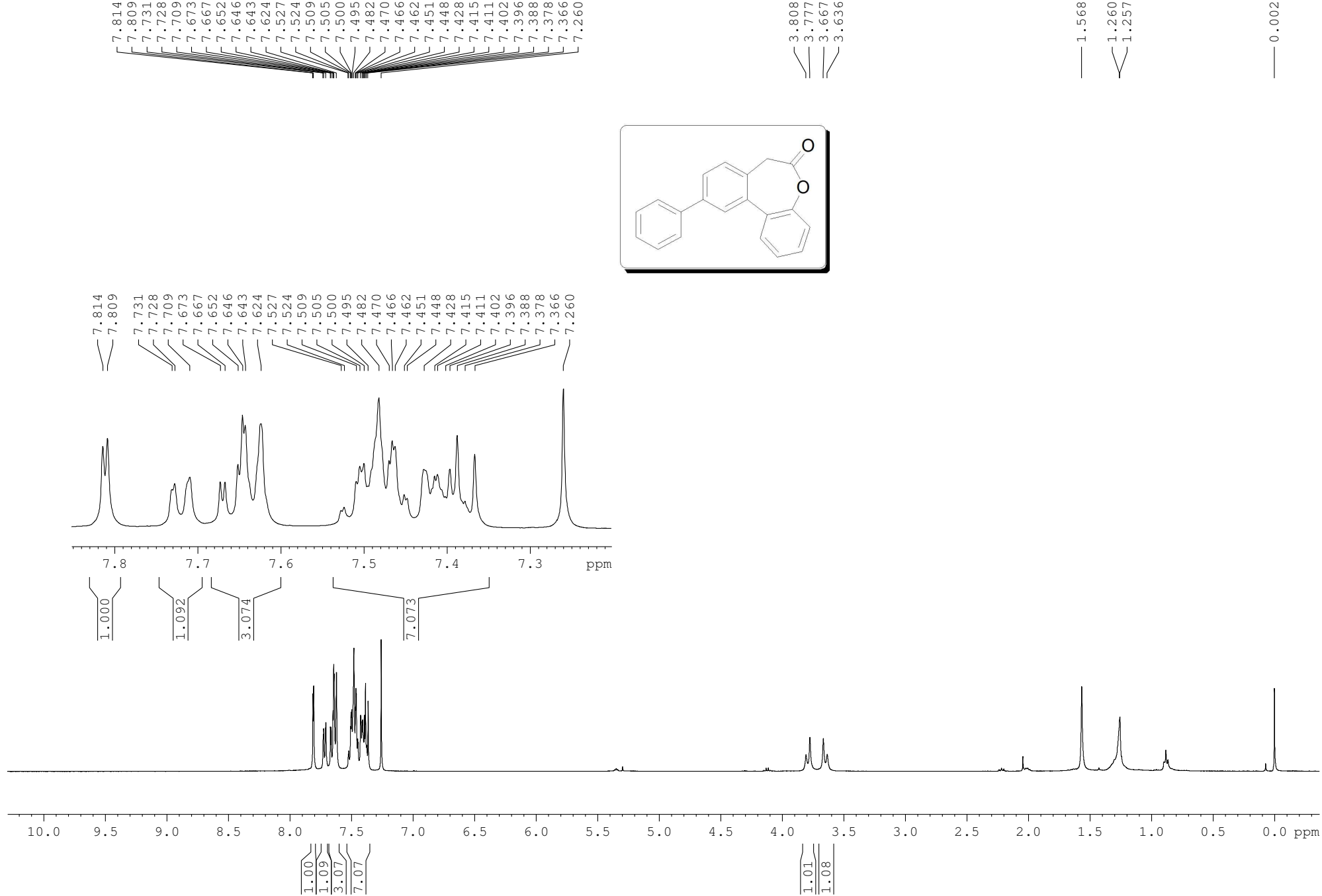
— 149.95

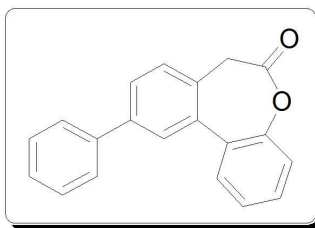
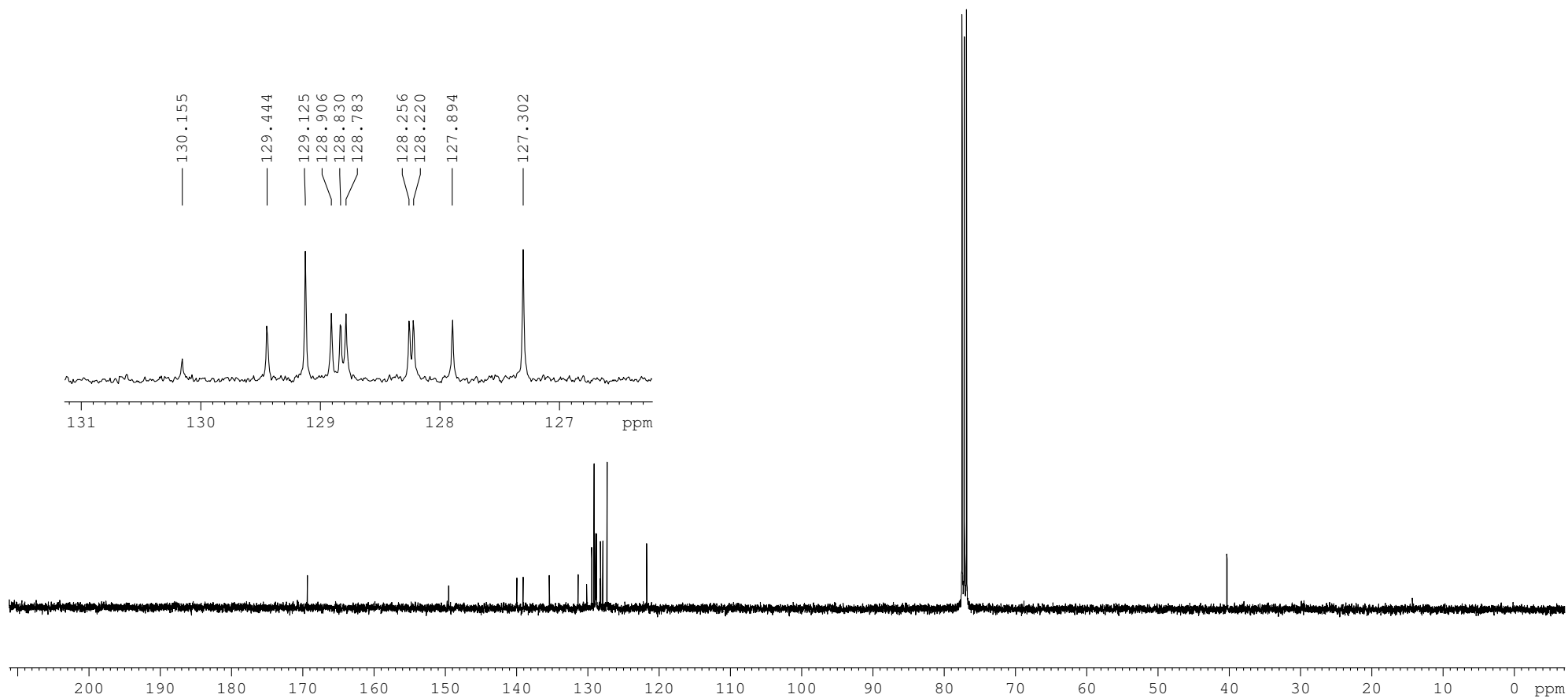
140.10  
135.43  
131.13  
129.98  
128.98  
128.68  
128.65  
127.95  
126.99  
126.83  
121.59

77.48  
77.17  
76.85

— 40.30

— 21.16



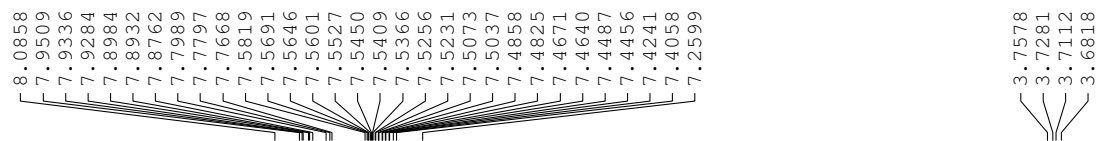
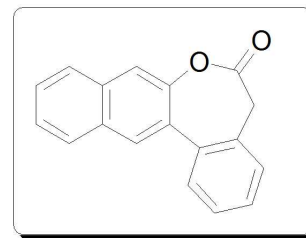
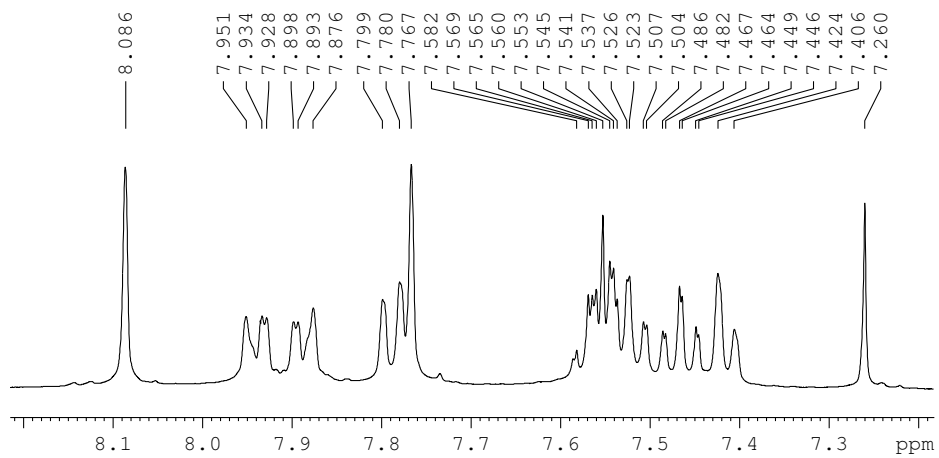


169.35

149.53  
139.96  
139.09  
135.40  
131.36  
130.15  
129.44  
129.12  
128.91  
128.83  
128.78  
128.26  
128.22  
127.89  
127.30  
121.74

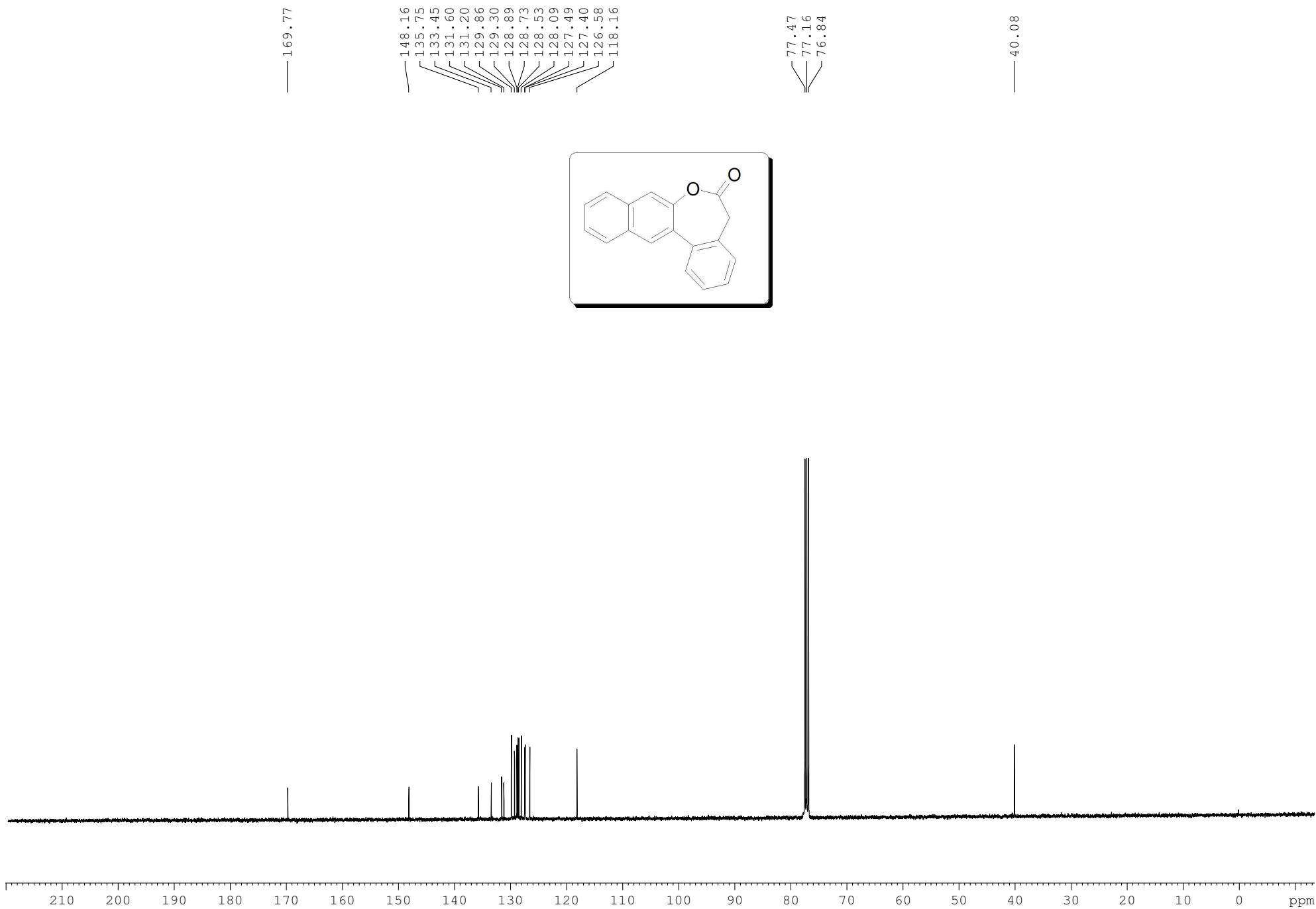
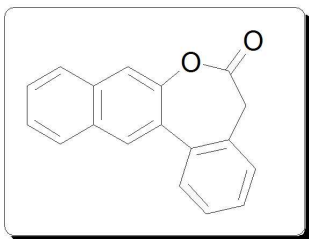
77.48  
77.16  
76.85

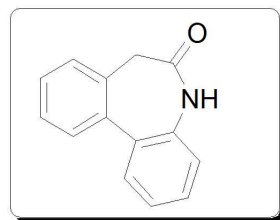
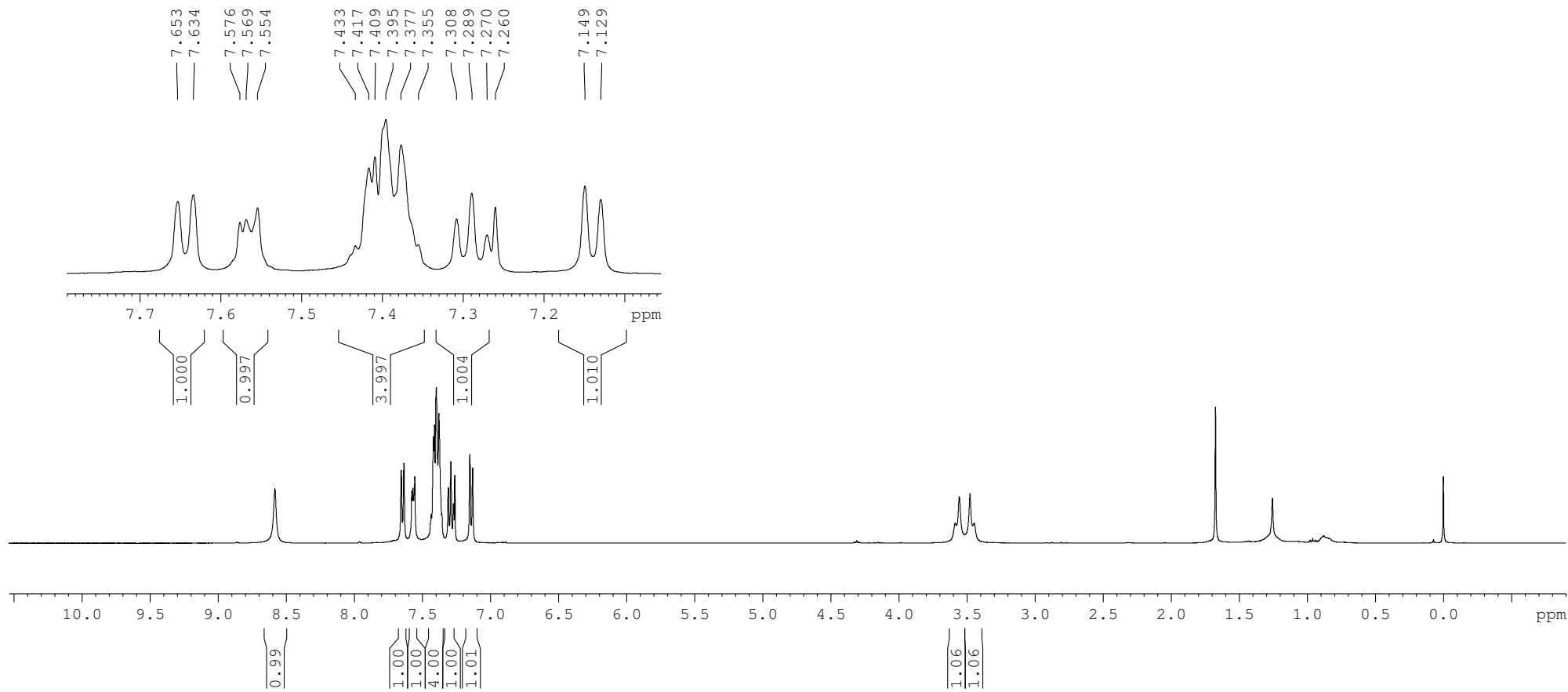
40.31

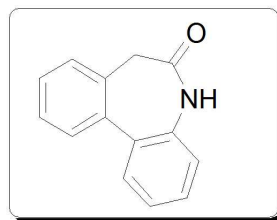
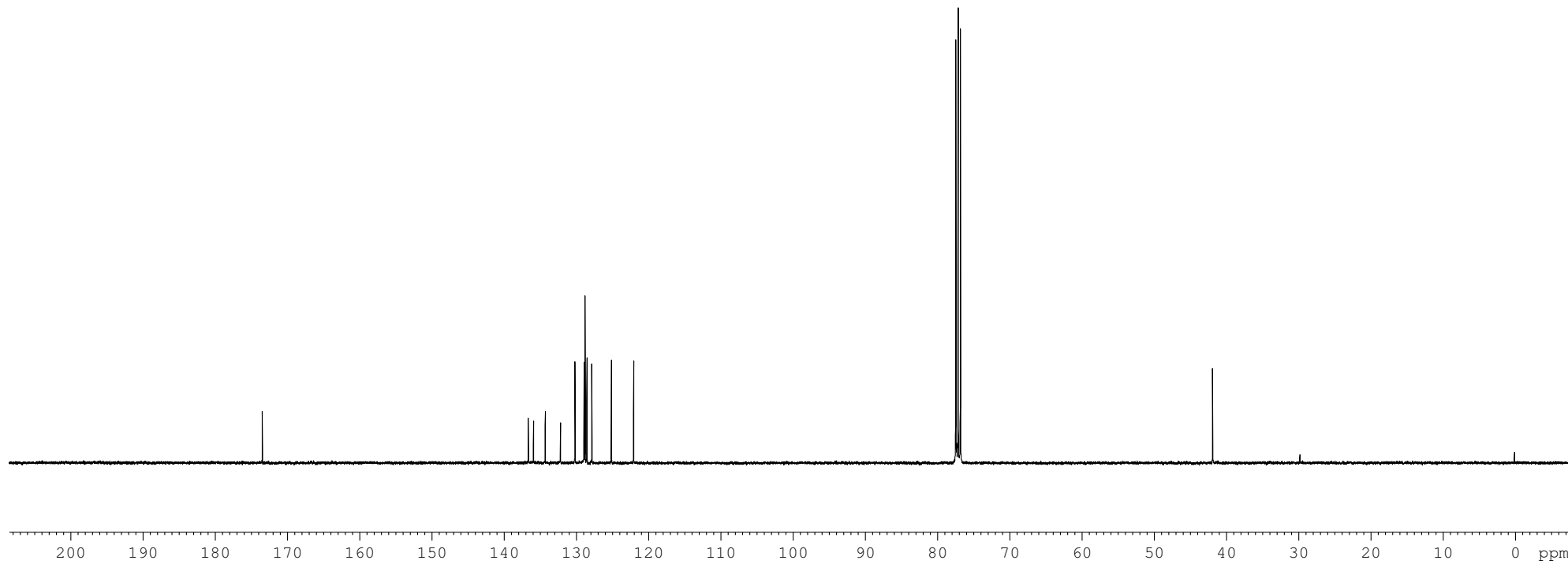


— 0.0050







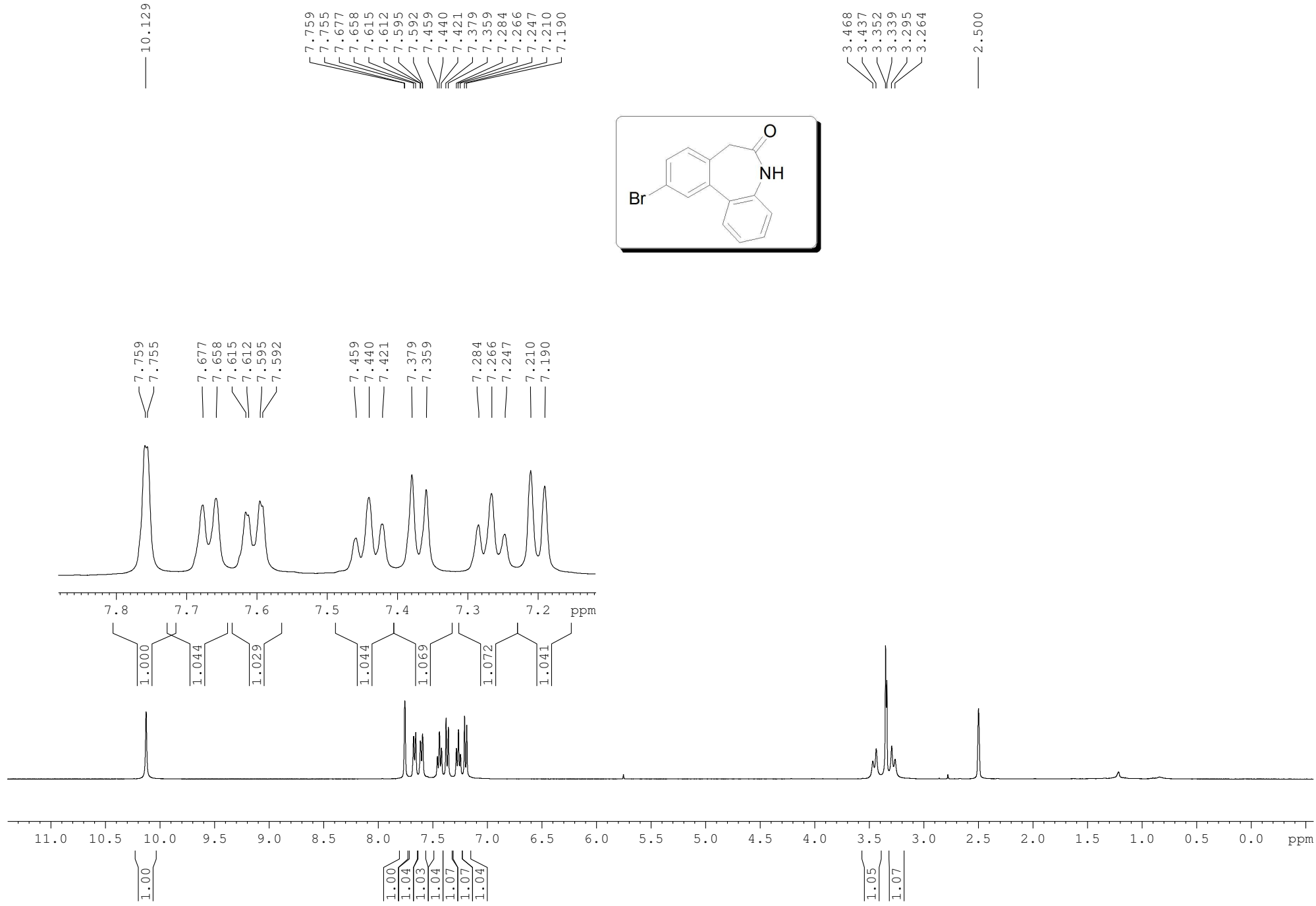


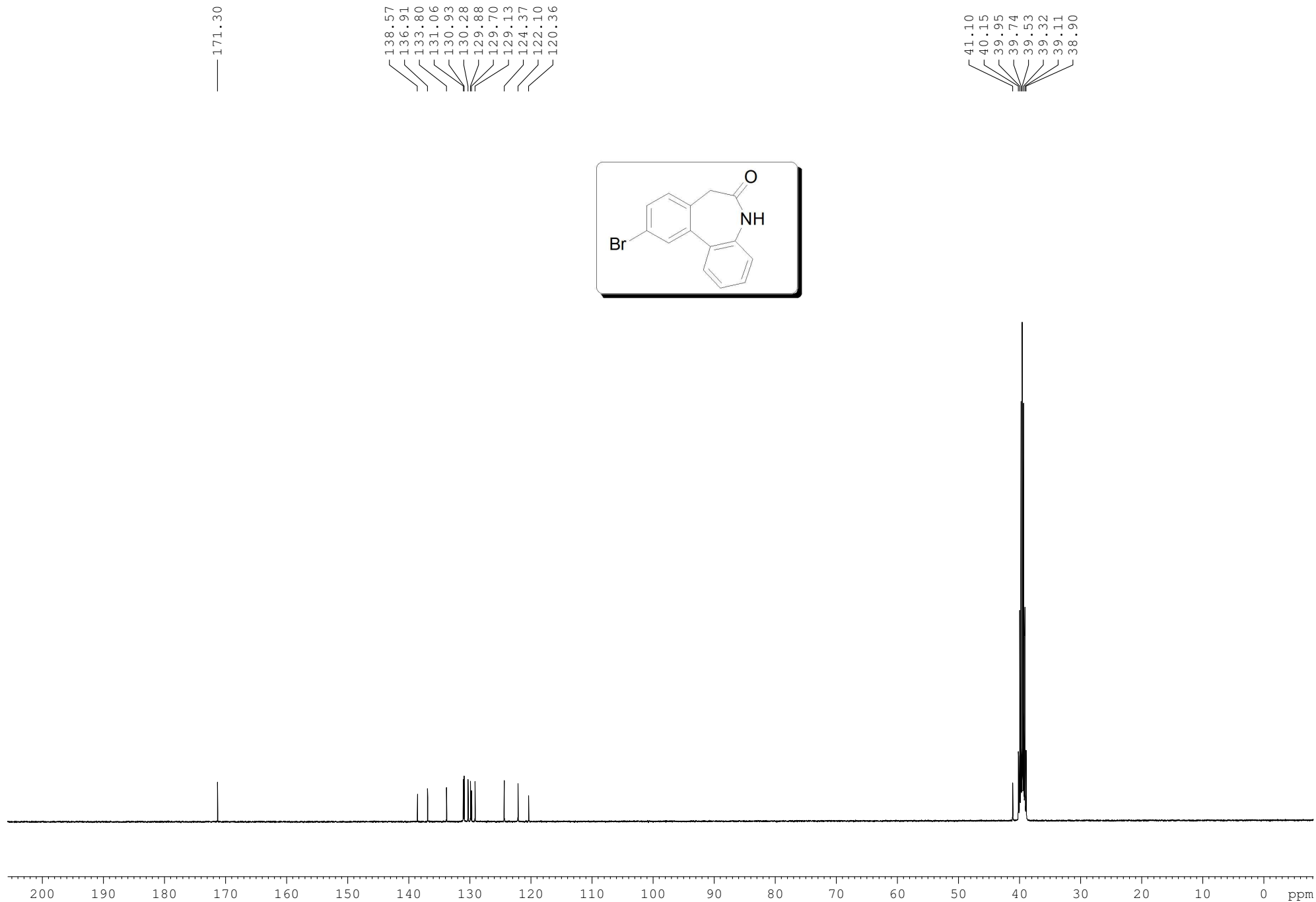
— 173.51

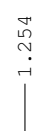
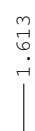
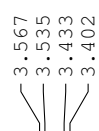
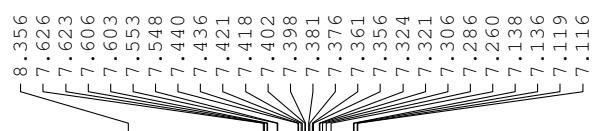
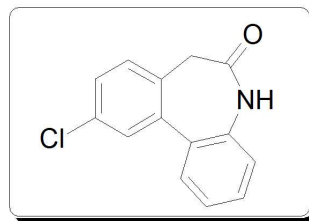
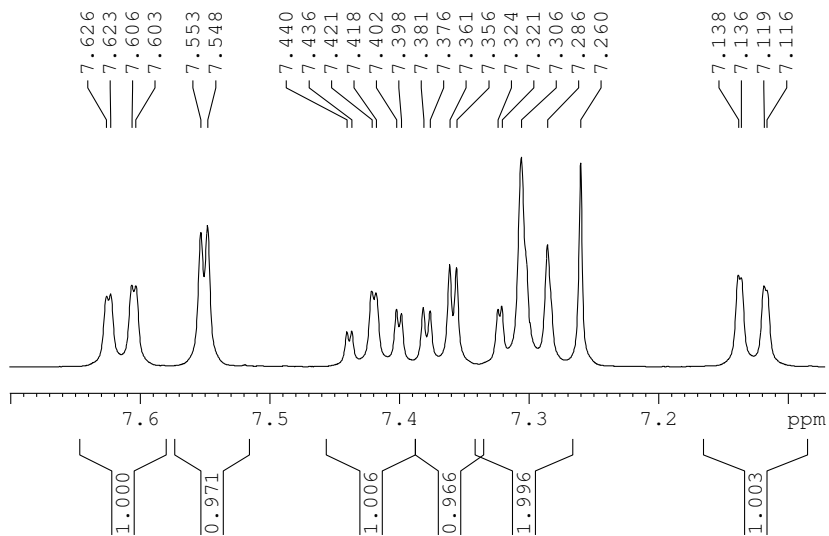
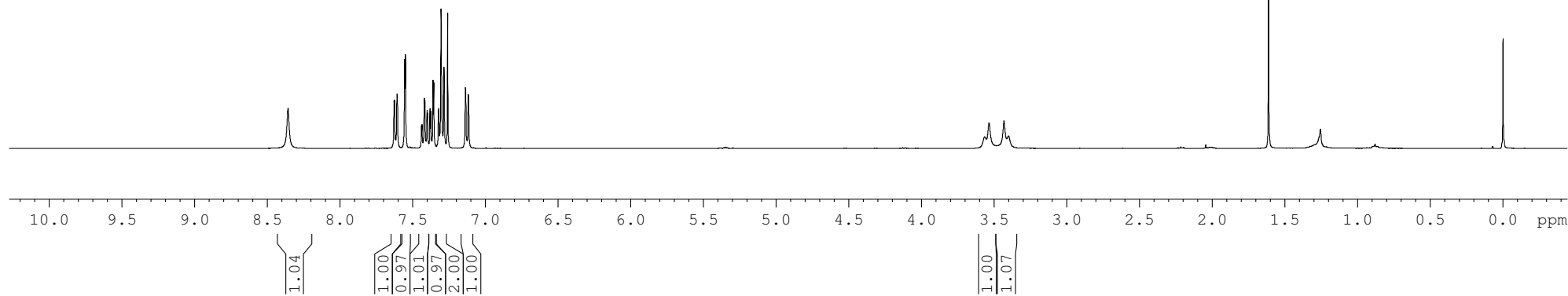
136.68  
135.96  
134.34  
132.23  
130.21  
128.96  
128.81  
128.57  
127.88  
125.17  
122.10

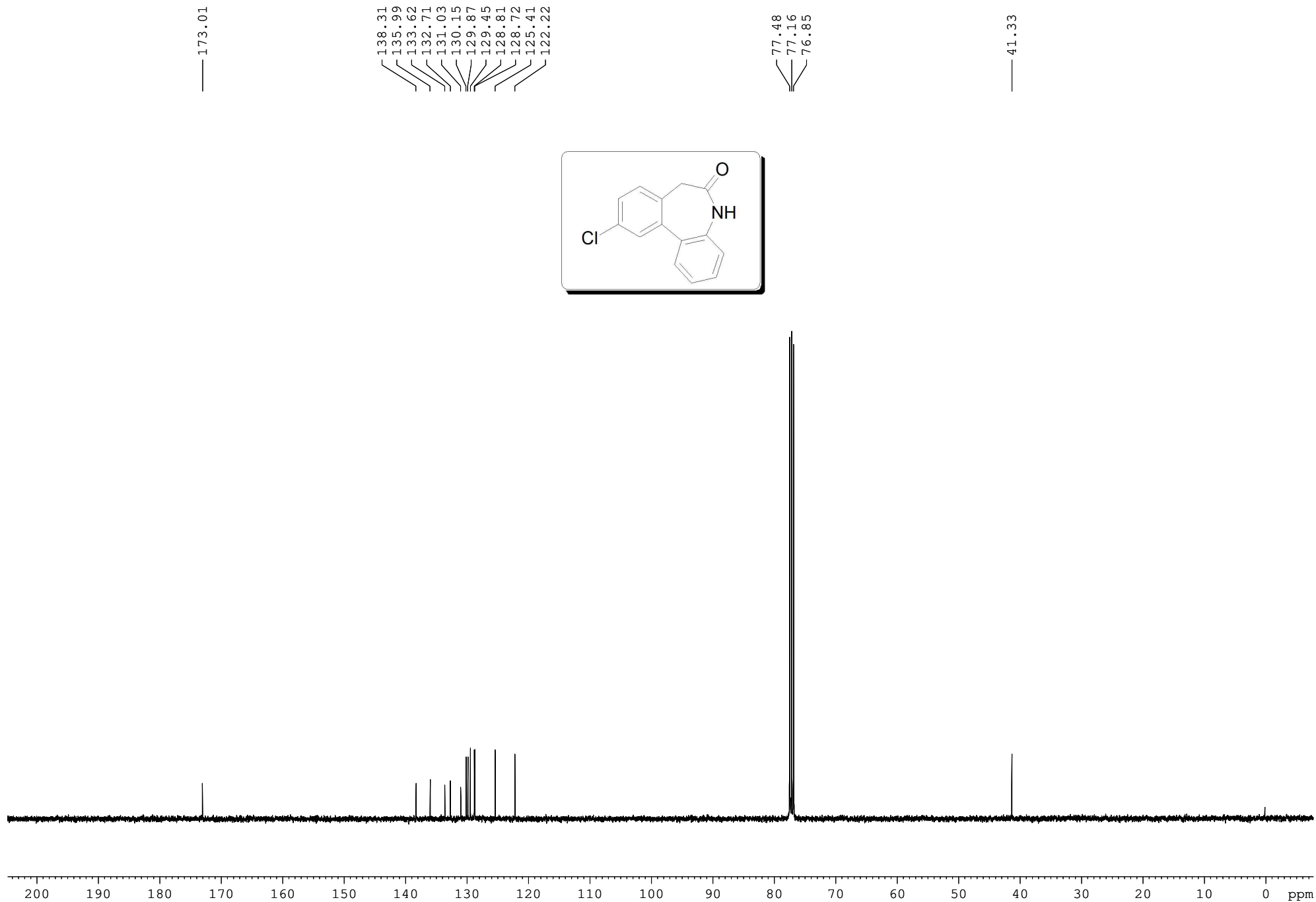
77.48  
77.16  
76.84

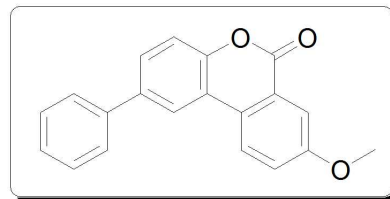
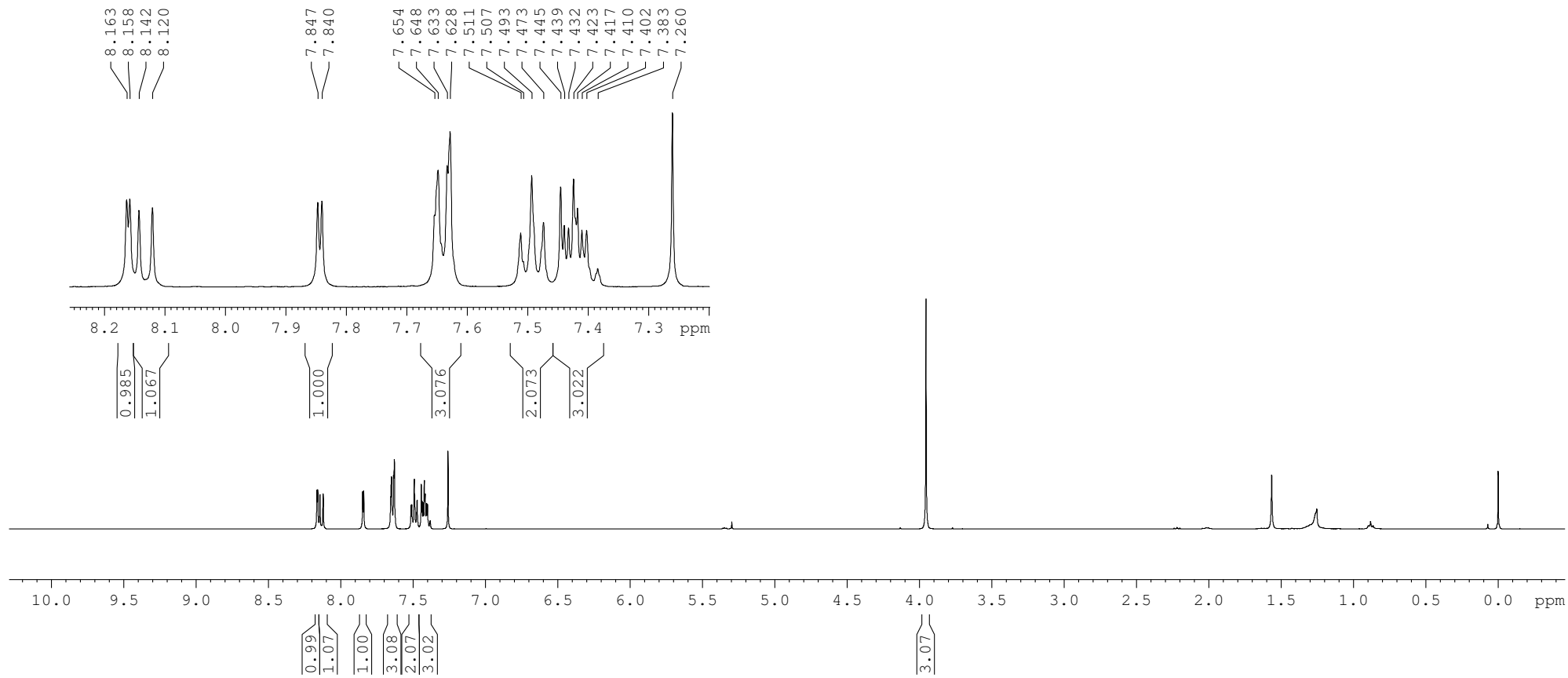
— 41.94











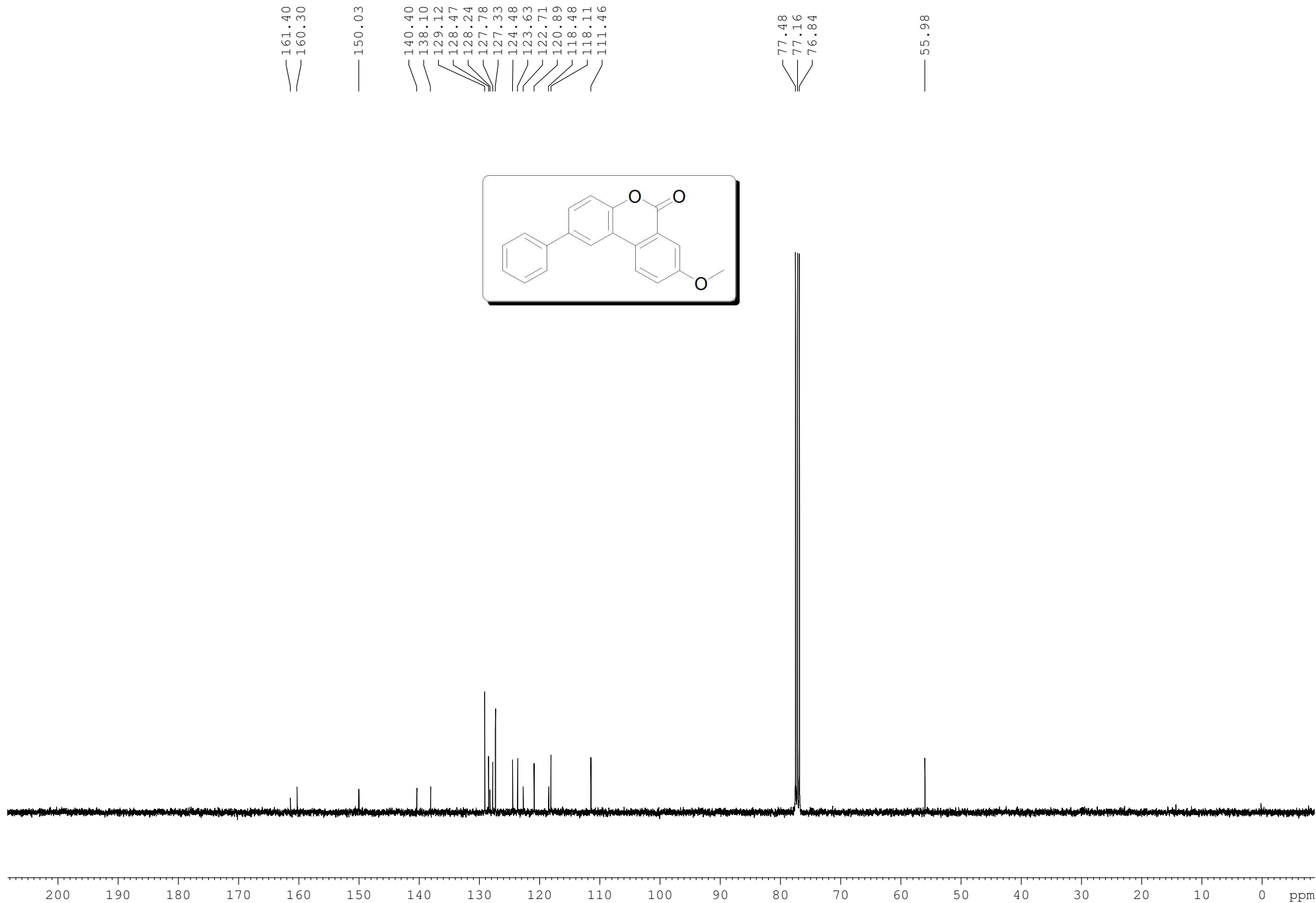
8.163  
8.158  
8.142  
8.120  
7.847  
7.840  
7.654  
7.648  
7.633  
7.628  
7.511  
7.507  
7.493  
7.473  
7.445  
7.439  
7.432  
7.423  
7.417  
7.410  
7.402  
7.383  
7.260

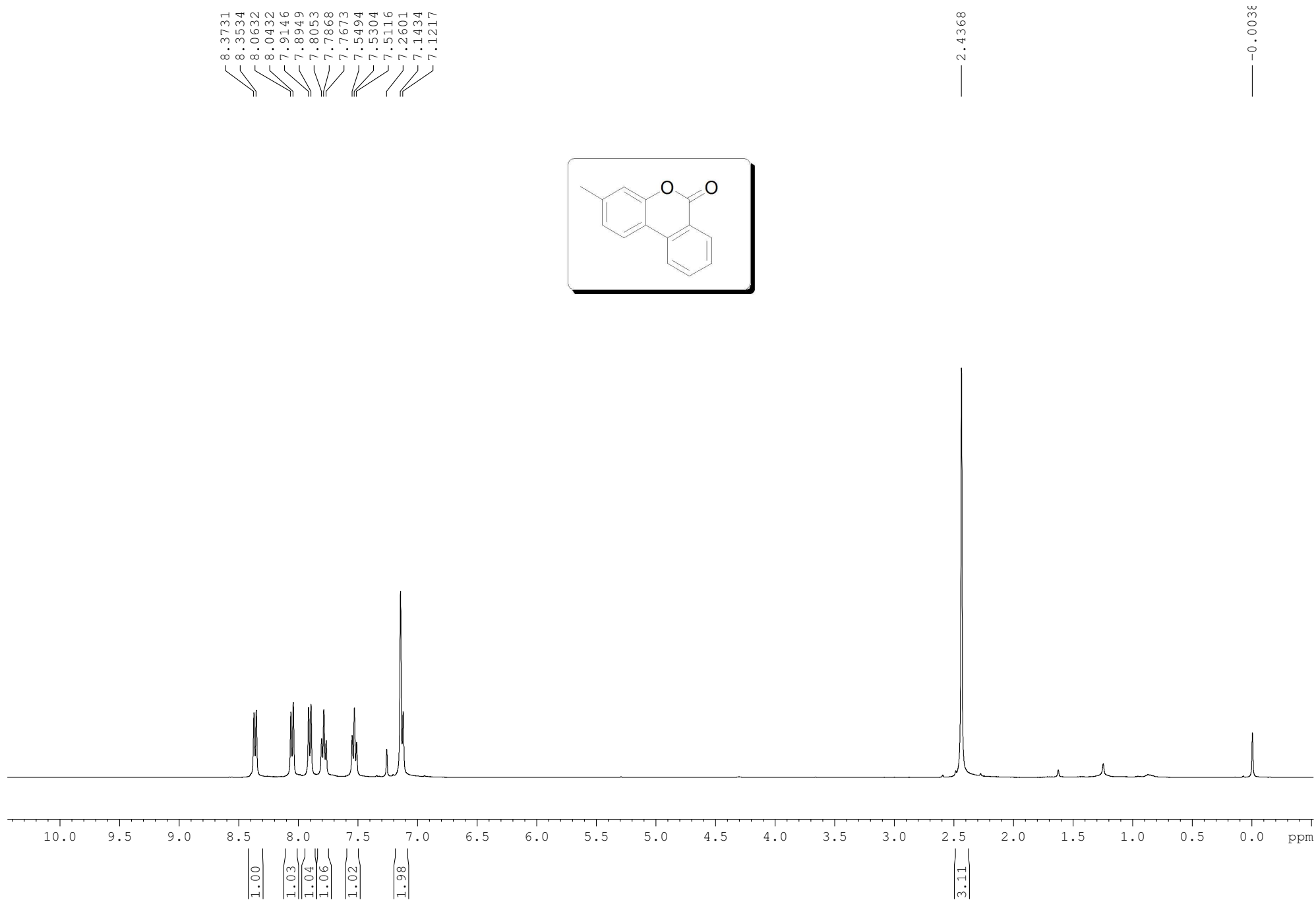
3.956

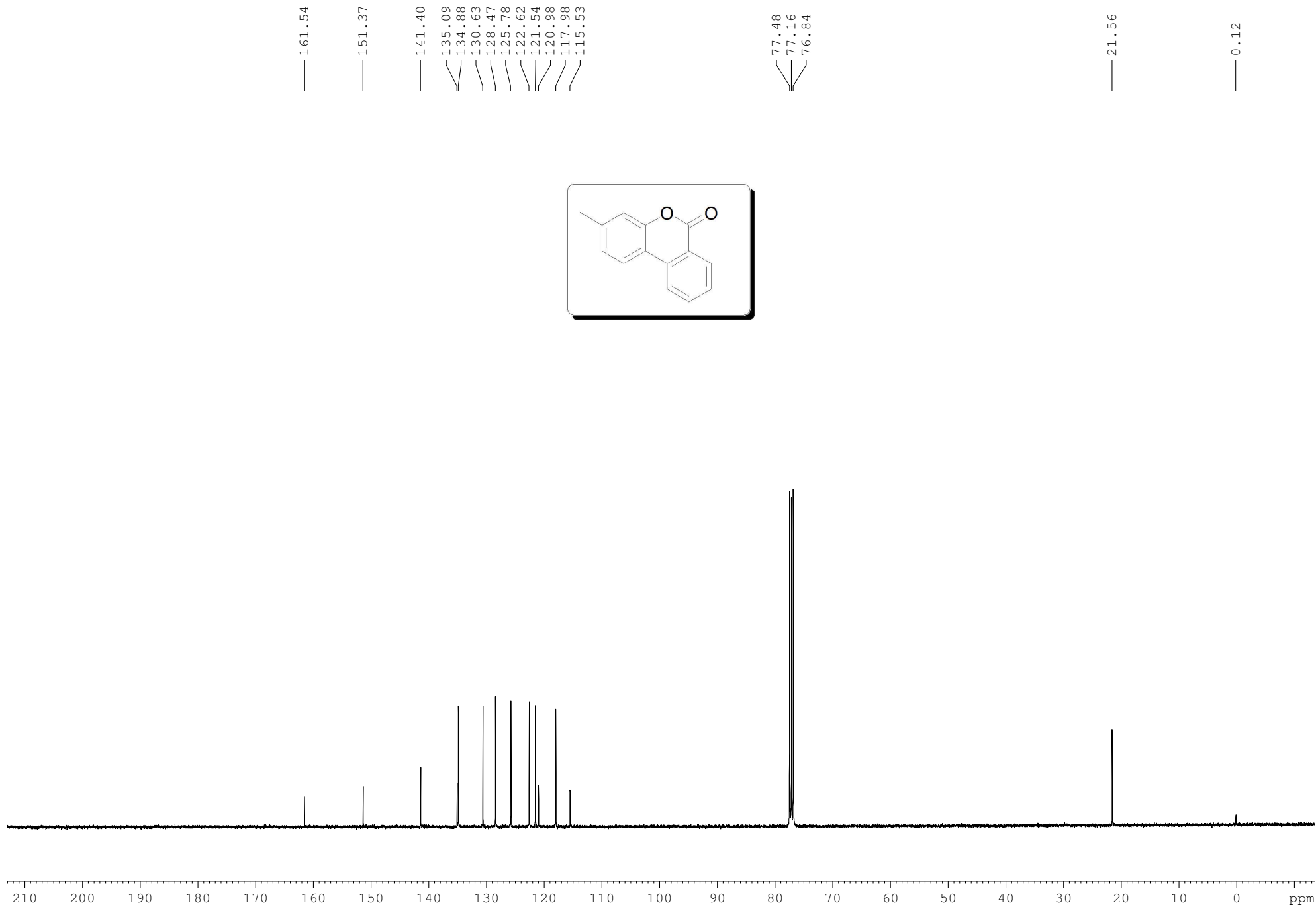
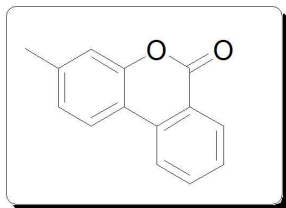
1.566

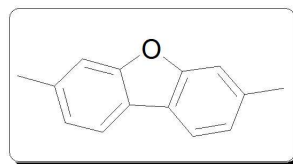
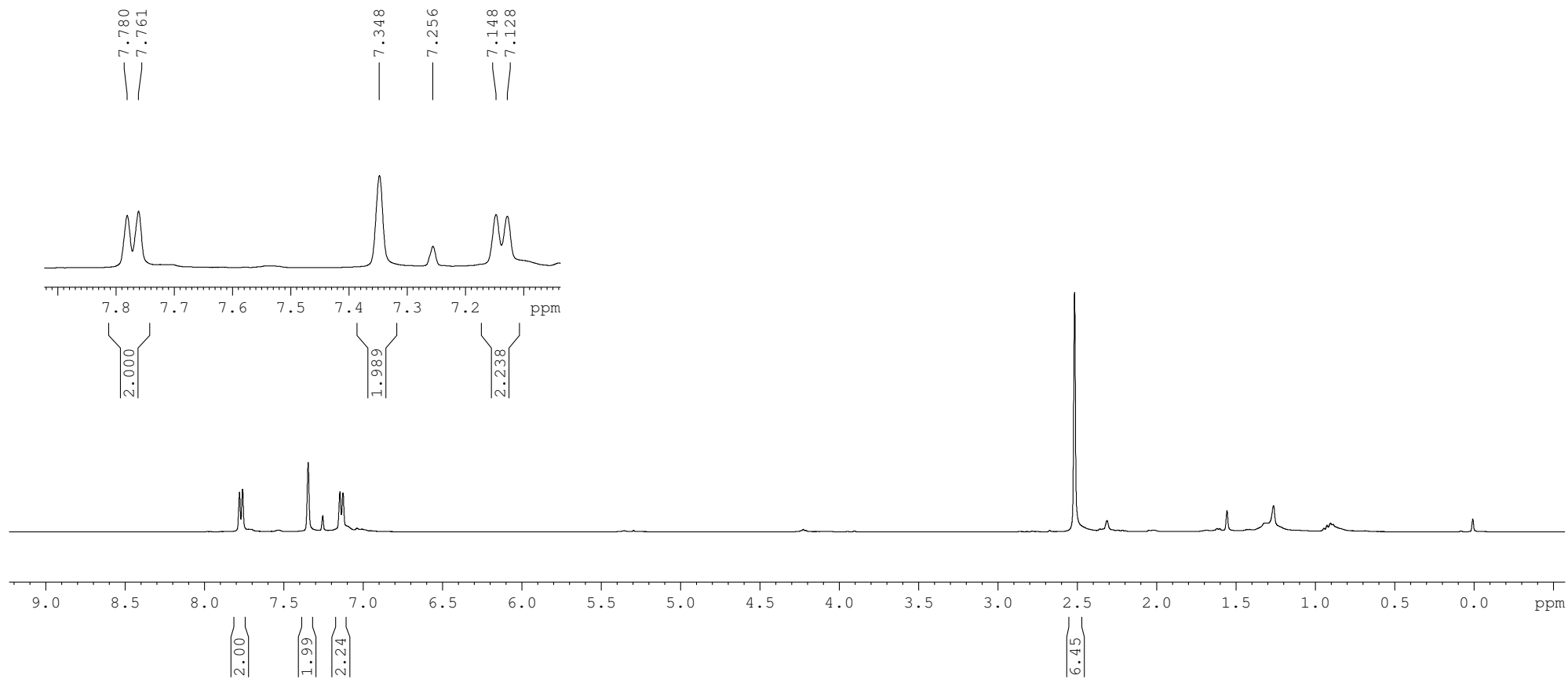
0.000











7.780  
7.761

7.348  
7.256  
7.148  
7.128

2.518

