

*Supporting Information*

**SbCl<sub>3</sub> Initiated Conjunctive C-H Bond Functionalization  
and Carbochlorination between Glycine Esters and  
Methylenecyclopropanes (MCPs)**

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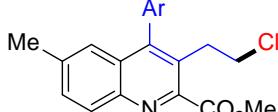
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## General:

Antimony trichloride was purchased from commercial source and used without further purification. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR (400 MHz and 100 MHz, respectively) spectra were recorded in  $\text{CDCl}_3$ . Chemical shifts ( $\delta$ ) are reported in ppm using TMS as internal standard and spin-spin coupling constants ( $J$ ) are given in Hz. The high resolution mass spectra (HRMS) were measured on an electrospray ionization (ESI) apparatus using time of flight (TOF) mass spectrometry.

## Optimization of reaction conditions

### 1. $\text{SbCl}_3/\text{O}_2$ initiated synthesis of chlorinated quinolines

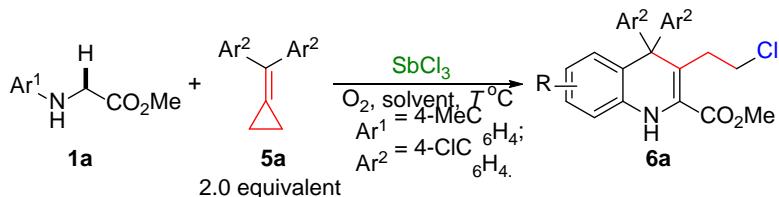
		$\xrightarrow[\text{Ar} = 4\text{-MeC}_6\text{H}_4]{\text{SbCl}_3, \text{O}_2, \text{solvent}, 60^\circ\text{C}}$	
<b>1a</b>	<b>2a</b>		<b>3a</b>
Entry	[Sb]	Solvent	Yield (%) <sup>a</sup>
1	$\text{SbCl}_3$ (1 equiv)	MeCN	41
2	$\text{SbCl}_3$ (2 equiv)	MeCN	76
3	$\text{SbCl}_3$ (2 equiv)	THF	58
4	$\text{SbCl}_3$ (2 equiv)	anisole	66
5	$\text{SbCl}_3$ (2 equiv)	toluene	73
6	$\text{SbCl}_3$ (2 equiv)	DCE	n. r.
7	$\text{SbF}_3$ (2 equiv)	MeCN	n. r.
8	$\text{Sb}_2\text{O}_3$ (2 equiv)	MeCN	n. r.
9	$\text{Sb}_2\text{O}_5$ (2 equiv)	MeCN	n. r.
10	$\text{SbCl}_5$ (2 equiv)	MeCN	25
<b>11</b>	<b><math>\text{SbCl}_3</math> (3 equiv)</b>	<b>MeCN</b>	<b>84 (79) <sup>b</sup></b>

<sup>a</sup> Yields were determined by crude  $^1\text{H}$  NMR using 1,3,5-trimethoxybenzene as an internal standard; <sup>b</sup> The yield in the parentheses is the isolated yield.

The model reaction of glycine **1a** and MCP **2a** was conducted in the presence of one equivalent of  $\text{SbCl}_3$  under dioxygen atmosphere (Table 1), and as our expected, the conjunctive C-H bond oxidation and carbochlorination occurred smoothly, affording the desired chlorinated quinoline **3a** in 41% yield (entry 1). Increasing the amount of  $\text{SbCl}_3$  to 2 equivalent, the reaction efficiency was enhanced to 76% yield (entry 2), and the solvent screen showed that MeCN is still the best solvent (entries 3-6). Other antimony reagents were also evaluated (entries 7-10), however, only  $\text{SbCl}_5$  gave the chlorinated quinolines in 25% yield (entry 10), probably due to that high

concentration of the Sb(V) would cause over-oxidation of the substrates. When the amount of  $\text{SbCl}_3$  was increased to 3 equivalent, the best result was obtained and the desired product **3a** was provided in 84%  $^1\text{H}$  NMR and 79% isolated yields, respectively (entry 11).

## 2. $\text{SbCl}_3/\text{O}_2$ initiated synthesis of chlorinated dihydroquinolines



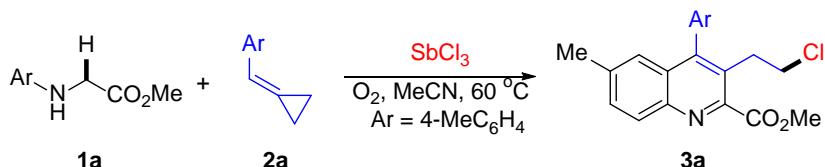
Entry	$\text{SbCl}_3$ (x equiv)	Solvent	Yield (%) <sup>a</sup>
1	2	MeCN	44
2	<b>2.5</b>	<b>MeCN</b>	<b>52</b>
3	3	MeCN	35
4	3	MeCN	30 <sup>b</sup>
5	2.5	THF	18
6	2.5	1,4-dioxane	n. r.
7	2.5	toluene	22
8	2.5	anisole	16
9	2.5	MeCN	21 <sup>c</sup>
10	2.5	MeCN	22 <sup>d</sup>
11	2.5	MeCN	54 <sup>e</sup>
12	2.5	MeCN	23 <sup>f</sup>

<sup>a</sup> The yields in the parentheses are the isolated yields; <sup>b</sup> In the presence of 3 equivalent of **5a**; <sup>c</sup> The reaction was conducted at 50°C; <sup>d</sup> The reaction was conducted at 70°C; <sup>e</sup> 10 mol % CuBr; <sup>f</sup> 10 mol % CuCl.

Using MeCN as the solvent, the desired dihydroquinoline **6a** was isolated in 44% yield (entry 1). Increasing the amount of  $\text{SbCl}_3$  to 2.5 equivalent, the reaction outcome was improved to 52% yield (entry 2). However, further increasing the amount of  $\text{SbCl}_3$  resulted in the decrease of the yields (entries 3-4), and the reaction became complicated with a series of unidentified side-products. Next, a solvent screen was performed, and the results showed that MeCN is still the best solvent (entries 5-8). Evaluation of the reaction temperature revealed that this reaction is sensitive to the reaction temperature (entries 9-10), and at 60°C, the best result was provided. To improve the reaction efficiency, the model reaction was conducted in the presence of CuX (entries 11-12), and the results showed that CuCl decreased the yield of **6a** to 23%. It is believed that in the absence of the terminal aromatization as the driving-force, the efficiency of this *sp*<sup>3</sup> C-H bond oxidation will be greatly reduced, which is consistent with our previous research.

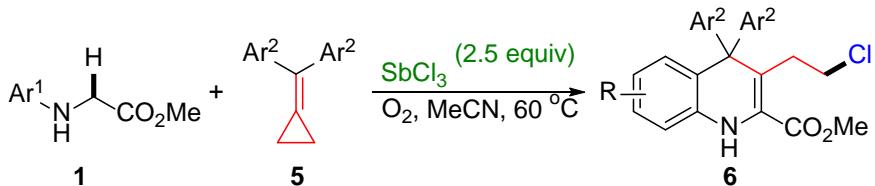
## General Experimental Procedure

### 1. $\text{SbCl}_3/\text{O}_2$ initiated synthesis of chlorinated quinolines



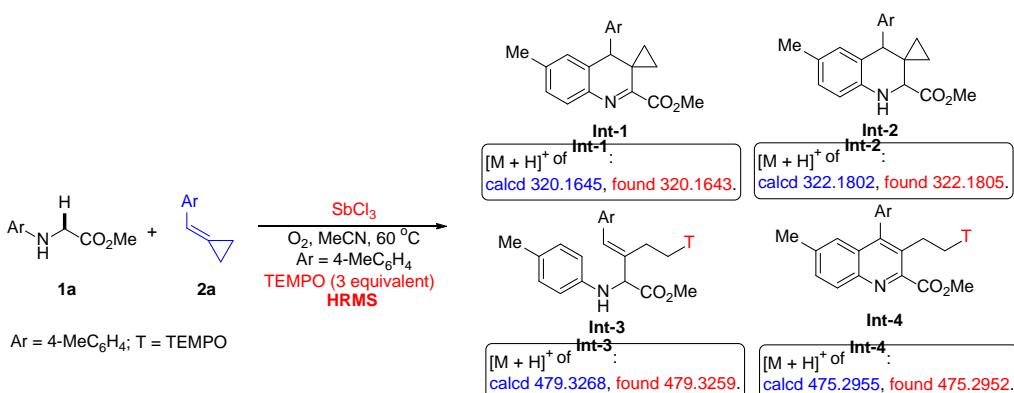
A solution of **1a** (0.3 mmol) and **2a** (0.6 mmol) in MeCN (5 mL) was mixed fully, then SbCl<sub>3</sub> (0.9 mmol) was added dropwise under O<sub>2</sub> atmosphere. The reaction solution was stirred at 60 °C (oil bath). After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/ethyl acetate (v/v 5:1) to afford the product **3a** in 79% yield.

## 2. SbCl<sub>3</sub>/O<sub>2</sub> initiated synthesis of chlorinated dihydroquinolines

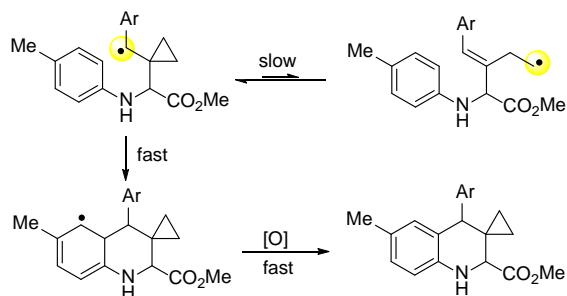


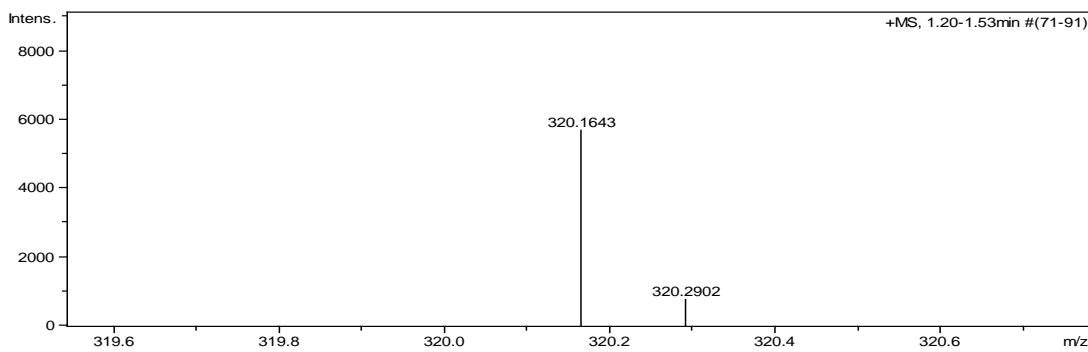
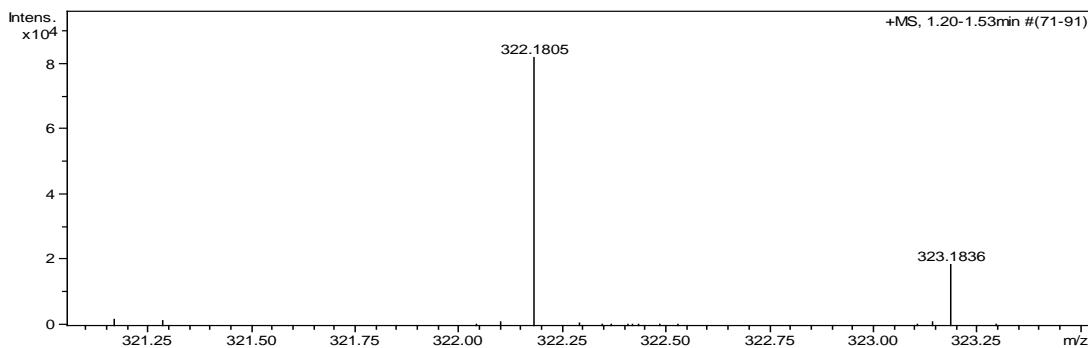
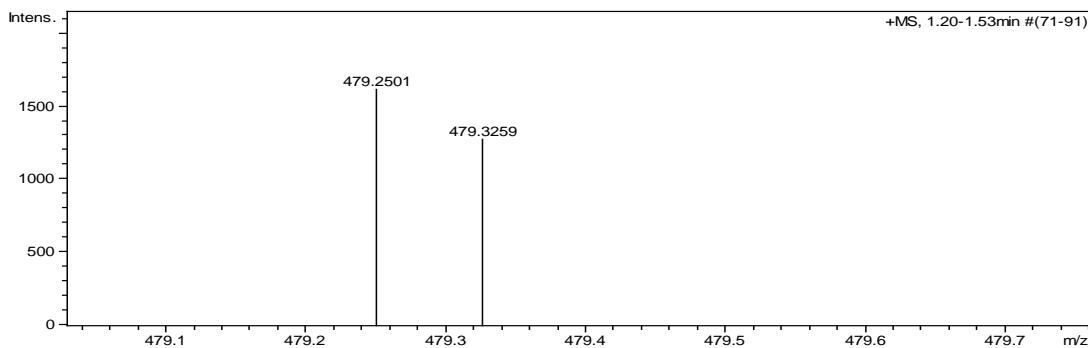
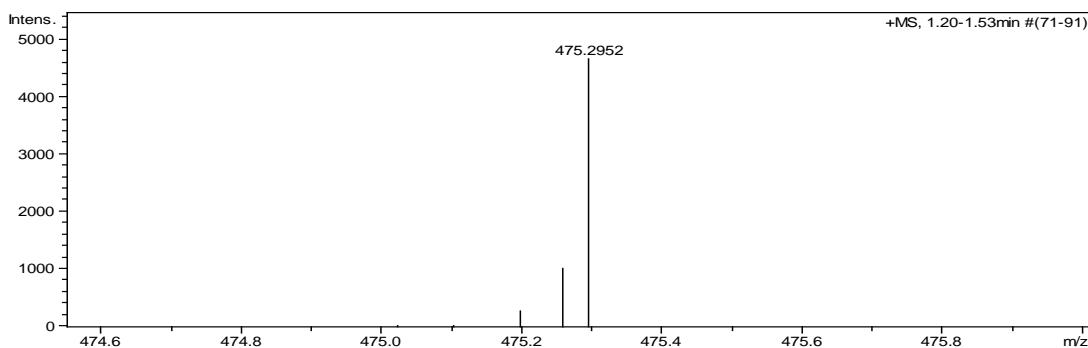
A solution of **1** (0.3 mmol) and **5** (0.6 mmol) in MeCN (5 mL) was mixed fully, then SbCl<sub>3</sub> (0.75 mmol) was added dropwise under O<sub>2</sub> atmosphere. The reaction solution was stirred at 60 °C (oil bath). After completion monitored by TLC (by UV visualization), the solvent was removed under reduced pressure. The products were separated by silica gel column chromatography eluted with petroleum ether/ethyl acetate (v/v 6:1) to afford the product.

## Detection of the intermediate by HRMS



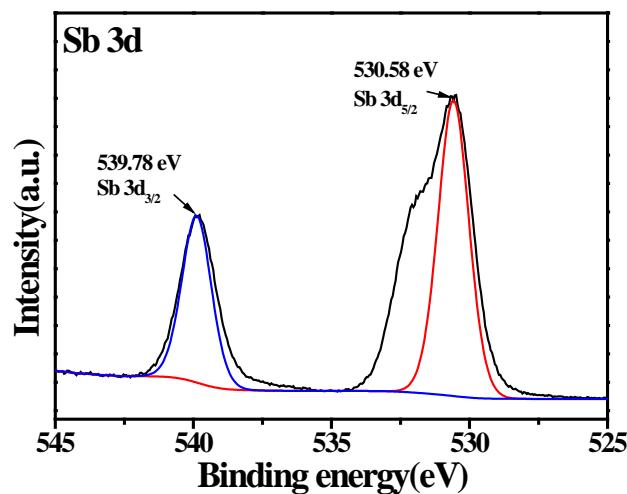
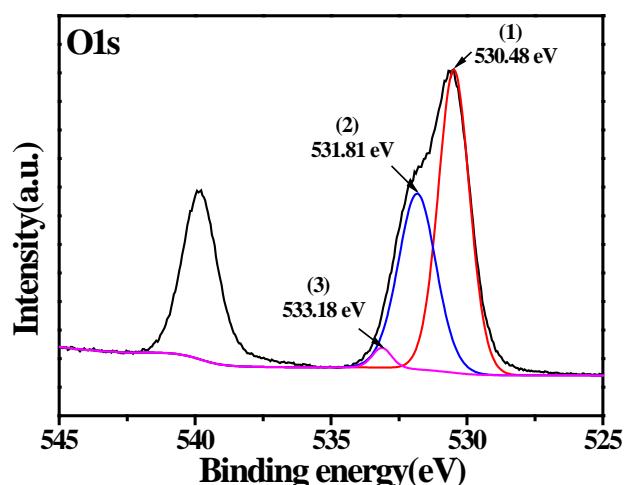
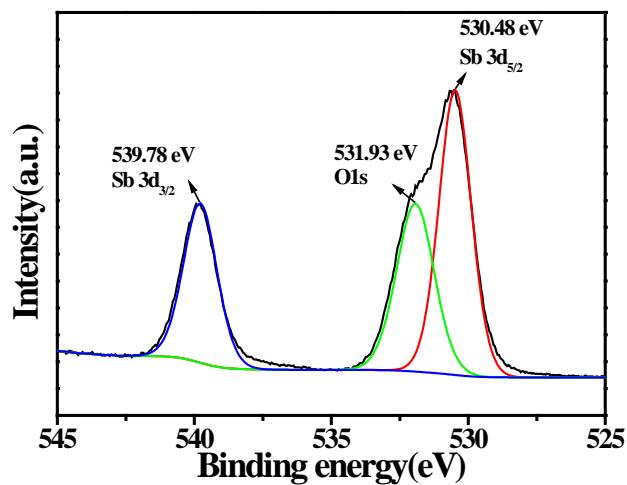
A solution of **1a** (0.3 mmol) and **2a** (0.6 mmol) in MeCN (5 mL) was mixed fully, then SbCl<sub>3</sub> (0.9 mmol) was added dropwise under O<sub>2</sub> atmosphere. The reaction solution was stirred under 60 °C (oil bath). After stirring for 3 hours, 3 equivalent of TEMPO was added and then the reaction mixture was tested by HRMS. Fortunately, several intermediates (**Int-1** to **4**) were detected. These intermediates imply that this reaction is mediated by a radical intermediate and the intramolecular cyclization of the generated radical might be faster than the β-fragmentation of the cyclopropylmethylene radical.



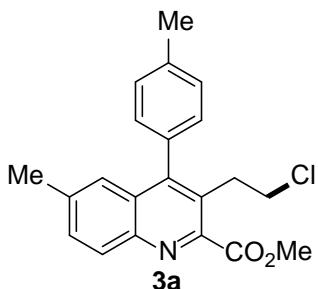
**Int-1:****Int-2:****Int-3:****Int-4:****XPS analysis of the reaction between SbCl<sub>3</sub> and O<sub>2</sub>**

A solution of SbCl<sub>3</sub> (0.3 mmol) in MeCN (5 mL) was mixed stirred at 60 °C (oil bath) under O<sub>2</sub> atmosphere. After stirring for 6 hours, the reaction mixture was tested by XPS, and to our

delight, both peaks of Sb 3d<sub>5/2</sub> (530.58 eV) and Sb 3d<sub>3/2</sub> (539.8 eV) of the Sb<sup>5+</sup> species were detected, suggesting that in the presence of dioxygen, SbCl<sub>3</sub> was oxidized to the Sb(V) species.

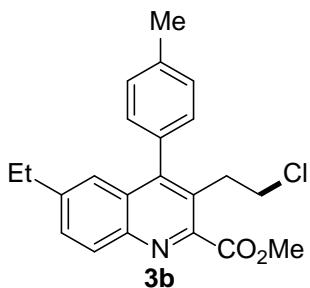


## Analytical data for compounds



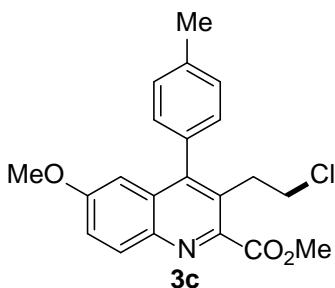
### **Methyl 3-(2-chloroethyl)-6-methyl-4-(p-tolyl)quinoline-2-carboxylate (3a)**

Reddish brown solid, m.p.: 113-116 °C; 84mg (79%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 8.5 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 2H), 7.07 (s, 1H), 4.06 (s, 3H), 3.55 (t, *J* = 7.2 Hz, 2H), 3.23 (t, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 2.38(s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 149.7, 148.9, 144.6, 138.5, 138.2, 132.8, 132.2, 129.6, 129.5, 129.0, 128.7, 127.4, 125.1, 53.2, 43.7, 33.1, 21.9, 21.4; HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>21</sub>ClNO<sub>2</sub>, 354.1255; Found, 354.1251.



### **Methyl 3-(2-chloroethyl)-6-ethyl-4-(p-tolyl)quinoline-2-carboxylate (3b)**

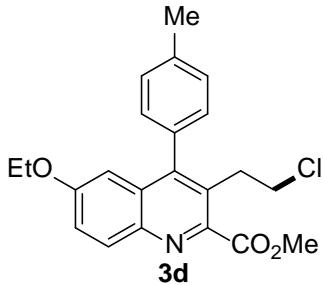
Yellow solid, m.p.: 93-96 °C; 79mg (72%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.7 Hz, 1H), 7.57 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 1.1 Hz, 1H), 4.06 (s, 3H), 3.58 – 3.51 (m, 2H), 3.28 – 3.22 (m, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.48 (s, 3H), 1.17 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 149.9, 149.0, 144.8, 144.7, 138.2, 132.8, 131.0, 129.8, 129.5 (two <sup>13</sup>C), 129.0 (two <sup>13</sup>C), 128.7, 127.4, 124.0, 53.2, 43.8, 33.1, 29.2, 21.4, 15.4; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>ClNO<sub>2</sub>Na, 390.1231; Found, 390.1229.



### **Methyl 3-(2-chloroethyl)-6-methoxy-4-(p-tolyl)quinoline-2-carboxylate (3c)**

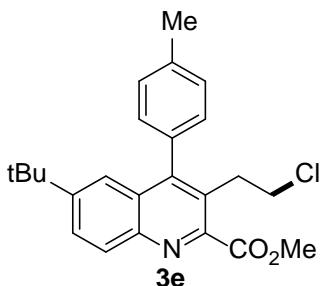
Yellow solid, m.p.: 91-95 °C; 75mg (68%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 9.2 Hz, 1H), 7.41 – 7.28 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.55 (d, *J* =

2.6 Hz, 1H), 4.06 (s, 3H), 3.68 (s, 3H), 3.56 (t,  $J$  = 7.8 Hz, 2H), 3.39 – 3.14 (m, 2H), 2.48 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 159.1, 149.0, 147.0, 142.0, 138.2, 132.9, 131.4, 130.1, 129.6, 128.9, 128.0, 122.6, 104.1, 55.4, 53.2, 43.8, 33.2, 21.4; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for  $\text{C}_{21}\text{H}_{20}\text{ClNO}_3\text{Na}$ , 392.1024; Found, 392.1054.



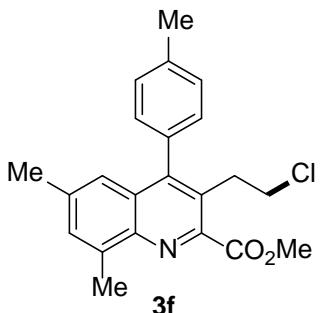
#### **Methyl 3-(2-chloroethyl)-6-ethoxy-4-(p-tolyl)quinoline-2-carboxylate (3d)**

Reddish brown solid, m.p.: 106–108 °C; 82mg (71%); Elution: petroleum ether/ethyl acetate = 6:1 (v : v);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J$  = 9.2 Hz, 1H), 7.40 – 7.27 (m, 3H), 7.10 (d,  $J$  = 8.0 Hz, 2H), 6.52 (d,  $J$  = 2.7 Hz, 1H), 4.04 (s, 3H), 3.85 (q,  $J$  = 7.0 Hz, 2H), 3.59 – 3.51 (m, 2H), 3.31 – 3.19 (m, 2H), 2.46 (s, 3H), 1.36 – 1.29 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 158.5, 148.9, 146.9, 142.0, 138.2, 133.0, 131.5, 130.2, 129.6, 128.9, 127.9, 122.7, 104.9, 63.6, 53.1, 43.8, 33.2, 21.4, 14.5; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for  $\text{C}_{22}\text{H}_{22}\text{ClNO}_3\text{Na}$ , 406.1180; Found, 406.1197.



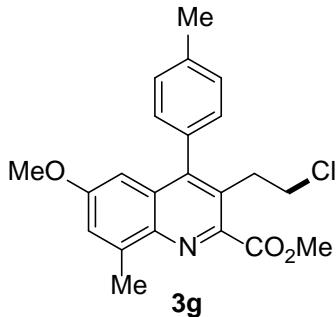
#### **Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(p-tolyl)quinoline-2-carboxylate (3e)**

Yellow solid, m.p.: 132–136 °C; 90mg (76%); Elution: petroleum ether/ethyl acetate = 6:1 (v : v);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J$  = 8.9 Hz, 1H), 7.80 (dd,  $J$  = 8.9, 2.1 Hz, 1H), 7.34 (d,  $J$  = 7.8 Hz, 2H), 7.25 (s, 1H), 7.13 (d,  $J$  = 8.0 Hz, 2H), 4.06 (s, 3H), 3.62 – 3.49 (m, 2H), 3.32 – 3.20 (m, 2H), 2.48 (s, 3H), 1.28 (s, 9H);  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  167.5, 151.3, 150.3, 149.3, 144.6, 138.2, 132.8, 129.4 (two  $^{13}\text{C}$ ), 129.0, 128.9, 128.4, 127.3, 121.3, 53.2, 43.8, 35.2, 33.1, 31.0, 21.4; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for  $\text{C}_{24}\text{H}_{26}\text{ClNO}_2\text{Na}$ , 418.1544; Found, 418.1546.



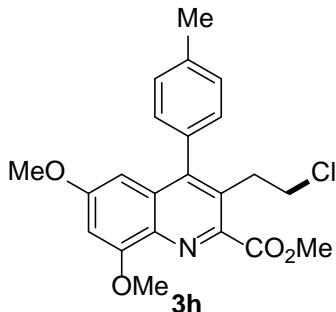
#### **Methyl 3-(2-chloroethyl)-6,8-dimethyl-4-(p-tolyl)quinoline-2-carboxylate (3f)**

Yellow solid, m.p.: 126-128 °C; 47mg (43%); Elution: petroleum ether/ethyl acetate = 6:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 (s, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.90 (s, 1H), 4.06 (s, 3H), 3.59 – 3.48 (m, 2H), 3.24 – 3.14 (m, 2H), 2.80 (s, 3H), 2.48 (s, 3H), 2.33 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.9, 149.4, 148.1, 143.9, 138.0, 137.9, 137.5, 133.3, 132.2, 129.4, 129.0, 128.7, 126.5, 123.1, 52.9, 43.7, 33.2, 21.9, 21.4, 17.8; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>ClNO<sub>2</sub>Na, 390.1231; Found, 390.1236.



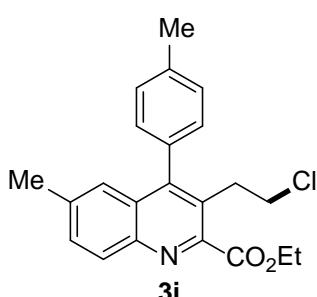
**Methyl 3-(2-chloroethyl)-6-methoxy-8-methyl-4-(p-tolyl)quinoline-2-carboxylate (3g)**

Yellow solid, m.p.: 125-127 °C; 49mg (43%); Elution: petroleum ether/ethyl acetate = 6:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 (d, *J* = 7.7 Hz, 2H), 7.21 – 7.19 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 2.7 Hz, 1H), 4.05 (s, 3H), 3.64 (s, 3H), 3.58 – 3.50 (m, 2H), 3.25 – 3.18 (m, 2H), 2.79 (s, 3H), 2.47 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.8, 158.5, 148.7, 146.2, 141.6, 139.9, 138.0, 133.4, 130.1, 129.5, 128.9, 127.3, 122.2, 102.0, 55.2, 52.8, 43.7, 33.3, 21.4, 17.91; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>ClNO<sub>3</sub>Na, 406.1180; Found, 406.1182.



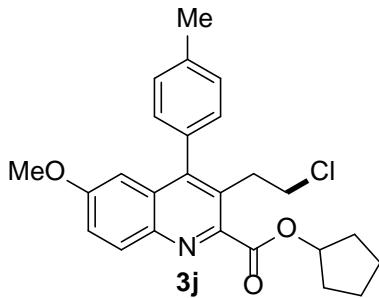
**Methyl 3-(2-chloroethyl)-6,8-dimethoxy-4-(p-tolyl)quinoline-2-carboxylate (3h)**

White solid, m.p.: 161-163 °C; 42mg (35%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.66 (d, *J* = 2.4 Hz, 1H), 6.10 (d, *J* = 2.4 Hz, 1H), 4.04 (s, 3H), 4.02 (s, 3H), 3.64 (s, 3H), 3.61 – 3.50 (m, 2H), 3.35 – 3.24 (m, 2H), 2.46 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.0, 159.8, 156.6, 148.9, 145.1, 138.1, 134.9, 133.3, 131.1, 129.5, 129.3, 128.8, 101.1, 95.9, 56.3, 55.4, 53.0, 43.8, 33.2, 21.4; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>ClNO<sub>4</sub>Na, 422.1130; Found, 422.1128.



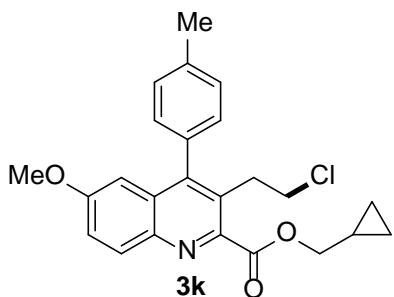
**Ethyl 3-(2-chloroethyl)-6-methyl-4-(p-tolyl)quinoline-2-carboxylate (3i)**

Dark brown solid, m.p.: 88-90 °C; 33mg (30%); Elution: petroleum ether/ethyl acetate = 8:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 8.6 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.08 (s, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 3.64 – 3.36 (m, 2H), 3.30 – 3.03 (m, 2H), 2.49 (s, 2H), 2.39 (s, 2H), 1.49 (t, *J* = 7.1 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 149.9, 149.5, 144.6, 138.3, 138.2, 132.8, 132.1, 129.6, 129.5, 128.9, 128.5, 126.8, 125.1, 62.3, 43.5, 33.3, 21.9, 21.4, 14.2; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>ClNO<sub>2</sub>Na, 390.1231; Found, 390.1257.



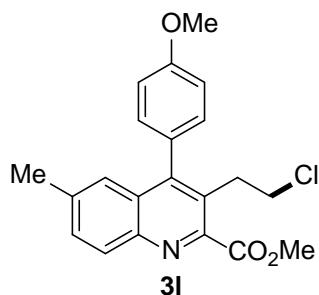
**Cyclopentyl 3-(2-chloroethyl)-6-methoxy-4-(p-tolyl)quinoline-2-carboxylate (3j)**

White solid, m.p.: 130-133 °C; 25mg (20%); Elution: petroleum ether/ethyl acetate = 8:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (d, *J* = 9.2 Hz, 1H), 7.33 (dd, *J* = 8.9, 2.9 Hz, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 2.7 Hz, 1H), 5.55 (tt, *J* = 6.3, 3.3 Hz, 1H), 3.66 (s, 3H), 3.54 – 3.46 (m, 2H), 3.20 – 3.12 (m, 2H), 2.47 (s, 3H), 2.11 – 1.92 (m, 4H), 1.88 – 1.76 (m, 2H), 1.72 – 1.63 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.7, 149.0, 148.5, 142.3, 138.2, 132.9, 131.4, 129.7, 129.6, 128.8, 126.5, 122.3, 104.1, 79.4, 55.4, 43.4, 33.4, 32.7, 23.9, 21.4; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>26</sub>ClNO<sub>3</sub>Na, 446.1493; Found, 446.1486.



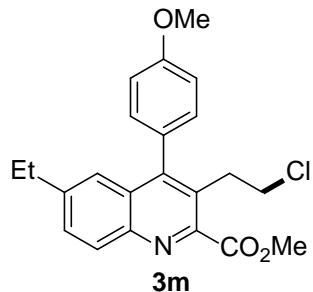
**Cyclopropylmethyl 3-(2-chloroethyl)-6-methoxy-4-(p-tolyl)quinoline-2-carboxylate (3k)**

Yellowish solid, m.p.: 108-110 °C; 22mg (18%); Elution: petroleum ether/ethyl acetate = 6:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 9.2 Hz, 1H), 7.35 (dd, *J* = 9.2, 2.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.56 (d, *J* = 2.7 Hz, 1H), 4.32 (d, *J* = 7.4 Hz, 2H), 3.68 (s, 2H), 3.63 – 3.41 (m, 2H), 3.45 – 3.15 (m, 2H), 2.49 (s, 2H), 1.49 – 1.32 (m, 1H), 0.66 (q, *J* = 6.0 Hz, 1H), 0.43 (q, *J* = 4.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 158.9, 148.7, 148.4, 142.2, 138.2, 132.9, 131.5, 129.9, 129.6, 128.8, 127.1, 122.3, 104.1, 71.1, 55.4, 43.5, 33.4, 21.4, 9.9, 3.6; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>24</sub>ClNO<sub>3</sub>Na, 432.1337; Found, 432.1332.



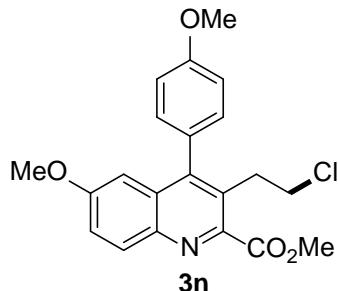
**Methyl 3-(2-chloroethyl)-4-(4-methoxyphenyl)-6-methylquinoline-2-carboxylate  
(3l)**

Yellow solid, m.p.: 144-147 °C; 51mg (46%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 8.6 Hz, 1H), 7.54 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 3H), 4.06 (s, 3H), 3.92 (s, 3H), 3.55 (t, *J* = 7.8 Hz, 2H), 3.29 – 3.23 (m, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 159.5, 149.4, 149.0, 144.6, 138.5, 132.1, 130.3, 129.7, 128.9, 127.9, 127.7, 125.1, 114.2, 55.3, 53.2, 43.7, 33.1, 22.0; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>20</sub>ClNO<sub>3</sub>Na, 392.1024; Found, 392.1024.



**Methyl 3-(2-chloroethyl)-6-ethyl-4-(4-methoxyphenyl)quinoline-2-carboxylate  
(3m)**

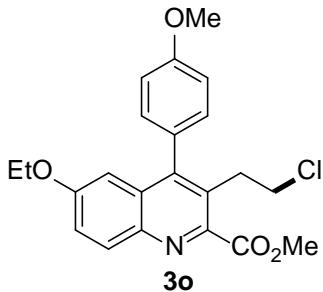
Yellow solid, m.p.: 114-117 °C; 63mg (55%); Elution: petroleum ether/ethyl acetate = 6:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.7 Hz, 1H), 7.58 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.13 – 7.05 (m, 3H), 4.06 (s, 3H), 3.92 (s, 3H), 3.57 – 3.53 (m, 2H), 3.28 – 3.24 (m, 2H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.18 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 159.5, 149.6, 149.1, 144.8, 144.7, 131.0, 130.3, 129.8, 129.0, 127.9, 127.6, 123.9, 114.2, 55.3, 53.2, 43.7, 33.1, 29.2, 15.3; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>ClNO<sub>3</sub>Na, 406.1180; Found, 406.1179.



**Methyl 3-(2-chloroethyl)-6-methoxy-4-(4-methoxyphenyl)quinoline-2-carboxylate (3n)**

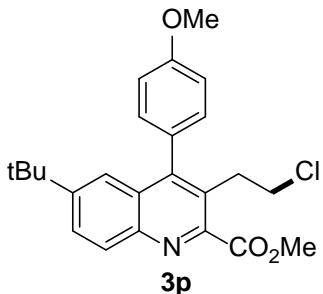
Dark brown solid, m.p.: 114-116 °C; 72mg (62%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 9.2 Hz, 1H), 7.36 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.17 (d, *J* = 8.7

Hz, 2H), 7.08 (d,  $J$  = 8.7 Hz, 2H), 6.57 (d,  $J$  = 2.7 Hz, 1H), 4.07 (s, 2H), 3.92 (s, 3H), 3.69 (s, 2H), 3.57 (t,  $J$  = 7.8 Hz, 2H), 3.38 – 3.01 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 159.5, 159.1, 148.7, 147.1, 142.1, 131.5, 130.4, 130.2, 128.3, 128.0, 122.5, 114.3, 104.0, 55.3, 53.2, 43.7, 33.2, 30.2; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for  $\text{C}_{21}\text{H}_{20}\text{ClNO}_4\text{Na}$ , 408.0973; Found, 408.1005.



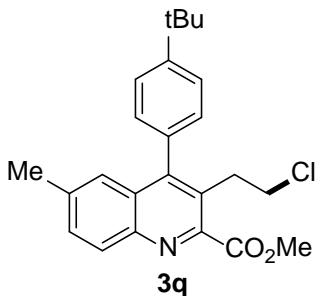
**Methyl 3-(2-chloroethyl)-6-ethoxy-4-(4-methoxyphenyl)quinoline-2-carboxylate (3o)**

Yellow solid, m.p.: 107–110 °C; 83mg (69%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d,  $J$  = 9.2 Hz, 1H), 7.34 (dd,  $J$  = 9.2, 2.7 Hz, 1H), 7.20 – 7.11 (m, 2H), 7.07 (d,  $J$  = 8.7 Hz, 2H), 6.54 (d,  $J$  = 2.7 Hz, 1H), 4.05 (s, 3H), 3.92 (s, 3H), 3.87 (q,  $J$  = 7.0 Hz, 2H), 3.57 – 3.54 (m, 2H), 3.29 – 3.25 (m, 2H), 1.35 (t,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 159.5, 158.5, 148.6, 146.9, 142.0, 131.5, 130.4, 130.2, 128.2, 128.1, 122.7, 114.3, 104.8, 63.7, 55.3, 53.1, 43.7, 33.2, 14.5; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for  $\text{C}_{22}\text{H}_{22}\text{ClNO}_4\text{Na}$ , 422.1130; Found, 422.1124.



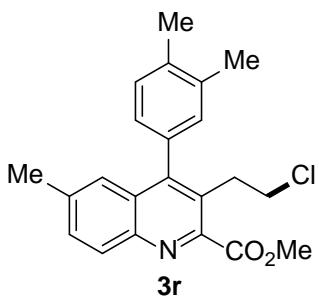
**Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(4-methoxyphenyl)quinoline-2-carboxylate (3p)**

Yellow solid, m.p.: 147–149 °C; 74mg (60%); Elution: petroleum ether/ethyl acetate = 7:1 (v : v);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13 (d,  $J$  = 9.0 Hz, 1H), 7.80 (dd,  $J$  = 8.9, 2.2 Hz, 1H), 7.28 (d,  $J$  = 1.9 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.11 – 7.03 (m, 2H), 4.06 (s, 3H), 3.92 (s, 3H), 3.58 – 3.51 (m, 2H), 3.27 (t,  $J$  = 7.8 Hz, 2H), 1.25 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.4, 159.5, 151.3, 150.0, 149.2, 144.5, 130.3, 129.4, 128.8, 128.6, 127.9, 127.5, 121.3, 114.1, 55.3, 53.2, 43.7, 35.1, 33.1, 30.9; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for  $\text{C}_{24}\text{H}_{26}\text{ClNO}_3\text{Na}$ , 434.1493; Found, 434.1486.



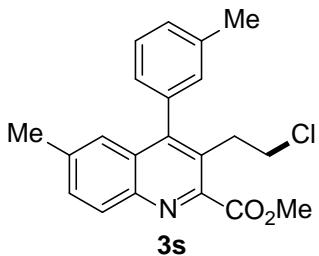
**Methyl 4-(4-(tert-butyl)phenyl)-3-(2-chloroethyl)-6-methylquinoline-2-carboxylate (3q)**

Yellow solid, m.p.: 96–98 °C; 104mg (88%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.07 (s, 1H), 4.06 (s, 3H), 3.54 (t, *J* = 7.8 Hz, 2H), 3.24 (t, *J* = 7.8 Hz, 2H), 2.39 (s, 3H), 1.42 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 151.3, 149.7, 149.0, 144.6, 138.5, 132.8, 132.1, 129.6, 128.8, 128.7, 127.4, 125.6, 125.2, 53.2, 43.8, 34.8, 33.1, 31.4, 22.0; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>26</sub>ClNO<sub>2</sub>Na, 418.1544; Found, 418.1552.



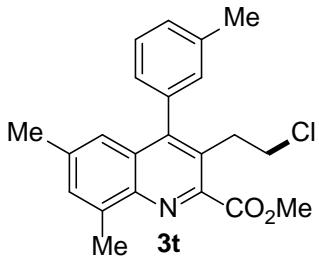
**Methyl 3-(2-chloroethyl)-4-(3,4-dimethylphenyl)-6-methylquinoline-2-carboxylate (3r)**

Yellow liquid; 25mg (23%); Elution: petroleum ether/ethyl acetate = 8:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 8.6 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.10 (s, 1H), 7.03 – 6.81 (m, 2H), 4.07 (s, 2H), 3.64 – 3.44 (m, 2H), 3.44 – 3.13 (m, 2H), 2.40 (s, 3H), 2.40 (s, 3H), 2.35 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.4, 149.9, 149.0, 144.5, 138.4, 137.0, 136.8, 133.2, 132.1, 130.1, 130.0, 129.6, 128.7, 127.3, 126.5, 125.2, 53.2, 43.8, 33.1, 21.9, 19.9, 19.7; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>ClNO<sub>2</sub>Na, 390.1231; Found, 390.1222.



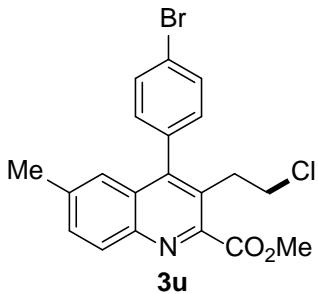
**Methyl 3-(2-chloroethyl)-6-methyl-4-(m-tolyl)quinoline-2-carboxylate (3s)**

Dark brown liquid; 58mg (55%); Elution: petroleum ether/ethyl acetate = 8:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.11 (s, 1H), 7.04 (d, *J* = 6.6 Hz, 2H), 4.10 (s, 3H), 3.61 – 3.49 (m, 2H), 3.39 – 3.22 (m, 2H), 2.45 (s, 3H), 2.41 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.1, 153.3, 146.1, 141.8, 140.0, 138.8, 135.0, 134.2, 129.7, 129.3, 129.1, 128.8, 128.4, 127.5, 125.9, 125.4, 53.9, 43.5, 32.7, 22.1, 21.6; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>20</sub>ClNO<sub>2</sub>Na, 376.1075; Found, 376.1075.



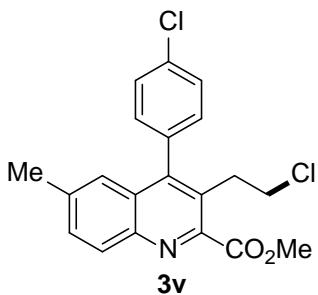
**Methyl 3-(2-chloroethyl)-6,8-dimethyl-4-(m-tolyl)quinoline-2-carboxylate (3t)**

White solid, m.p.: 105-108 °C; 54mg (49%); Elution: petroleum ether/ethyl acetate = 8:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 – 7.39 (m, 2H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 2H), 6.89 (s, 1H), 4.06 (s, 3H), 3.57 – 3.53 (m, 2H), 3.25 – 3.17 (m, 2H), 2.81 (s, 3H), 2.44 (s, 3H), 2.34 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.9, 149.4, 148.1, 143.8, 138.4, 137.9, 137.6, 136.3, 132.2, 129.7, 129.0, 128.5, 126.4, 126.2, 123.1, 52.9, 43.7, 33.2, 21.9, 21.6, 17.8 (one <sup>13</sup>C signal lost for overlap); HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>22</sub>H<sub>22</sub>ClNO<sub>2</sub>Na, 390.1231; Found, 390.1230.



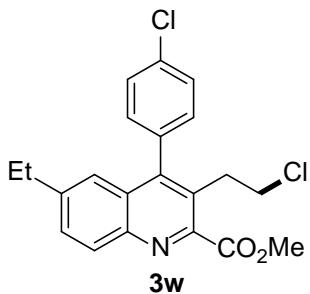
**Methyl 4-(4-bromophenyl)-3-(2-chloroethyl)-6-methylquinoline-2-carboxylate (3u)**

Reddish brown solid, m.p.: 135-138 °C; 67mg (53%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 8.6 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.55 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.00 (s, 1H), 4.06 (s, 3H), 3.55 (t, *J* = 7.6 Hz, 2H), 3.24 (t, *J* = 7.7 Hz, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 148.8, 148.1, 144.5, 139.0, 134.9, 132.4, 132.1, 130.9, 129.8, 128.2, 127.3, 124.7, 122.8, 53.3, 43.6, 32.9, 22.0; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>17</sub>BrClNO<sub>2</sub>Na, 440.0023; Found, 440.0017.



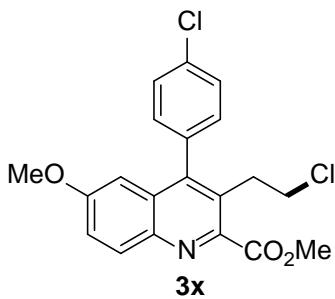
**Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-methylquinoline-2-carboxylate (3v)**

Dark brown solid, m.p.: 91-94 °C; 94mg (84%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 8.6 Hz, 1H), 7.58 – 7.51 (m, 3H), 7.21 – 7.17 (m, 2H), 6.99 (d, *J* = 7.1 Hz, 1H), 4.06 (s, 3H), 3.55 (t, *J* = 7.7 Hz, 2H), 3.24 (t, *J* = 7.7 Hz, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 148.8, 148.2, 144.5, 139.0, 134.6, 134.3, 132.4, 130.6, 129.8, 129.1, 128.3, 127.4, 124.7, 53.2, 43.6, 33.0, 21.9; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>17</sub>Cl<sub>2</sub>NO<sub>2</sub>Na, 396.0529; Found, 396.0538.



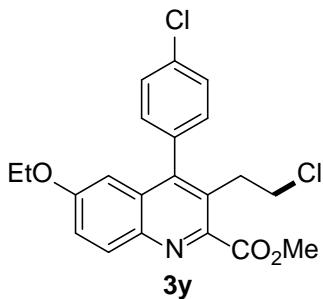
**Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-ethylquinoline-2-carboxylate (3w)**

Yellow solid, m.p.: 98–101 °C; 101mg (87%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 8.7 Hz, 1H), 7.60 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.23 – 7.18 (m, 2H), 7.01 (d, *J* = 1.1 Hz, 1H), 4.06 (s, 3H), 3.57 (t, *J* = 7.6 Hz, 2H), 3.26 (t, *J* = 7.7 Hz, 2H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 148.9, 148.3, 145.1, 144.7, 134.6, 134.4, 131.2, 130.6, 130.0, 129.1, 128.3, 127.4, 123.6, 53.3, 43.6, 33.0, 29.2, 15.4; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>19</sub>Cl<sub>2</sub>NO<sub>2</sub>Na, 410.0685; Found, 410.0681.



**Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-methoxyquinoline-2-carboxylate (3x)**

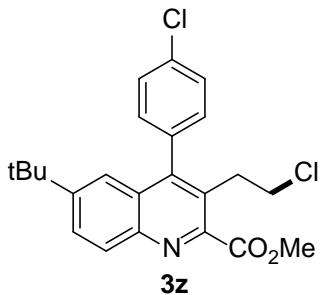
Yellow solid, m.p.: 151–154 °C; 74mg (63%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 9.2 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 2.7 Hz, 1H), 4.06 (s, 3H), 3.69 (s, 3H), 3.56 (t, *J* = 7.6 Hz, 2H), 3.26 (t, *J* = 7.6 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 159.4, 147.4, 146.9, 142.1, 134.7, 134.5, 131.7, 130.6, 129.7, 129.3, 128.0, 122.7, 103.7, 55.4, 53.2, 43.7, 33.0; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>17</sub>Cl<sub>2</sub>NO<sub>3</sub>Na, 412.0478; Found, 412.0472.



**Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-ethoxyquinoline-2-carboxylate (3y)**

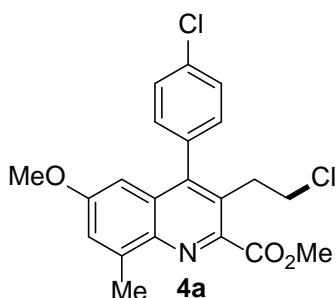
Dark green solid, m.p.: 108–112 °C; 82mg (68%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 9.2 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.37 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.22 – 7.18 (m, 2H), 6.45 (d, *J* = 2.6 Hz, 1H), 4.06 (s, 3H), 3.88 (q, *J* = 7.0 Hz, 2H), 3.56 (t, *J* = 7.7

Hz, 2H), 3.25 (t,  $J$  = 7.7 Hz, 3H), 1.36 (t,  $J$  = 7.0 Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.1, 158.7, 147.3, 146.7, 142.0, 134.6, 134.6, 131.7, 130.6, 129.7, 129.3, 128.0, 122.9, 104.4, 63.8, 53.2, 43.7, 33.1, 14.5; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for  $\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{NO}_3\text{Na}$ , 426.0634; Found, 426.0626.



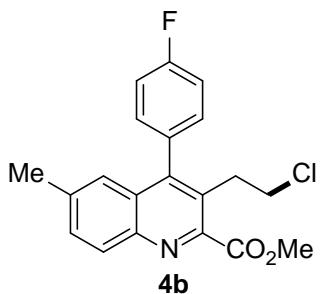
### **Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(4-chlorophenyl)quinoline-2-carboxylate (3z)**

Reddish brown solid, m.p.: 141-143 °C; 83mg (67%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J$  = 8.9 Hz, 1H), 7.82 (dd,  $J$  = 8.9, 1.8 Hz, 1H), 7.54 (d,  $J$  = 8.2 Hz, 2H), 7.22 (d,  $J$  = 8.2 Hz, 2H), 7.18 (s, 1H), 4.06 (s, 3H), 3.54 (t,  $J$  = 7.6 Hz, 2H), 3.25 (t,  $J$  = 7.6 Hz, 2H), 1.24 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.2, 151.7, 149.1, 148.7, 144.5, 134.6, 134.4, 130.6, 129.6, 129.1, 129.0, 127.9, 127.3, 120.8, 53.2, 43.6, 35.2, 32.9, 30.9; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for  $\text{C}_{23}\text{H}_{23}\text{Cl}_2\text{NO}_2\text{Na}$ , 438.0998; Found, 438.1007.



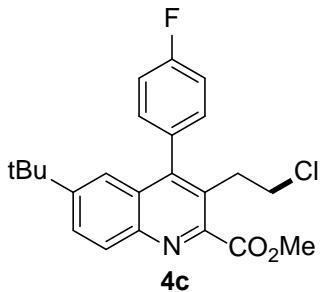
### **Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-methoxy-8-methylquinoline-2-carboxylate (4a)**

Reddish brown solid, m.p.: 134-138 °C; 24mg (20%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J$  = 8.4 Hz, 2H), 7.23 – 7.21 (m, 1H), 7.18 (d,  $J$  = 8.4 Hz, 2H), 6.29 (d,  $J$  = 2.7 Hz, 1H), 4.04 (s, 3H), 3.65 (s, 3H), 3.56 (t,  $J$  = 7.7 Hz, 2H), 3.22 (t,  $J$  = 7.7 Hz, 2H), 2.79 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6, 158.8, 147.1, 146.0, 141.6, 140.1, 135.0, 134.5, 130.6, 129.7, 129.2, 127.3, 122.4, 101.6, 55.2, 52.9, 43.6, 33.1, 17.9; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for  $\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{NO}_3\text{Na}$ , 426.0634; Found, 426.0627.



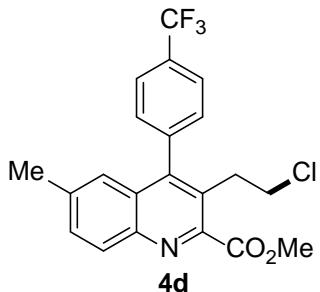
**Methyl 3-(2-chloroethyl)-4-(4-fluorophenyl)-6-methylquinoline-2-carboxylate (4b)**

White solid, m.p.: 170-173 °C; 82mg (77%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 8.6 Hz, 1H), 7.55 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.30 – 7.17 (m, 4H), 6.99 (d, *J* = 9.6 Hz, 1H), 4.06 (s, 3H), 3.55 (t, *J* = 7.7 Hz, 2H), 3.24 (t, *J* = 7.7 Hz, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.2, 162.7 (d, *J*<sub>C-F</sub> = 248.3 Hz), 148.9, 148.4, 144.6, 138.9, 132.3, 131.8 (d, *J*<sub>C-F</sub> = 3.6 Hz), 131.0 (d, *J*<sub>C-F</sub> = 8.1 Hz), 129.8, 128.5, 127.6, 124.8, 116.0 (d, *J*<sub>C-F</sub> = 21.6 Hz), 53.2, 43.6, 33.0, 22.0; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>17</sub>ClFNO<sub>2</sub>Na, 380.0824; Found, 380.0822.



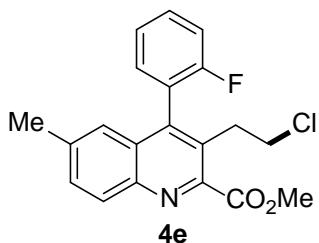
**Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(4-fluorophenyl)quinoline-2-carboxylate (4c)**

Dark brown solid, m.p.: 144-147 °C; 90mg (75%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 8.9 Hz, 1H), 7.82 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.28 – 7.23 (m, 4H), 7.18 (d, *J* = 2.0 Hz, 1H), 4.07 (s, 3H), 3.55 (t, *J* = 7.7 Hz, 2H), 3.27 (t, *J* = 7.7 Hz, 2H), 1.24 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 162.6 (d, *J*<sub>C-F</sub> = 248.3 Hz), 151.6, 149.0 (d, *J*<sub>C-F</sub> = 13.0 Hz), 144.5, 131.8 (d, *J*<sub>C-F</sub> = 3.6 Hz), 131.0, 130.9, 129.6, 129.0, 128.2, 127.4, 120.9, 115.9 (d, *J*<sub>C-F</sub> = 21.6 Hz), 53.2, 43.6, 35.2, 33.0, 30.9; HRMS (ESI) m/z: [M + H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>24</sub>ClFNO<sub>2</sub>, 400.1474; Found, 400.1474.



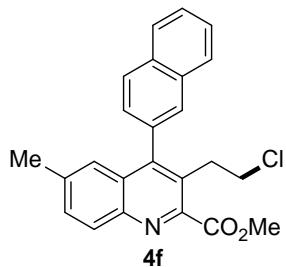
**Methyl 3-(2-chloroethyl)-6-methyl-4-(4-(trifluoromethyl)phenyl)quinoline-2-carboxylate (4d)**

Yellow solid, m.p.: 125-128 °C; 26mg (21%); Elution: petroleum ether/ethyl acetate = 4:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.57 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 6.93 (s, 1H), 4.07 (s, 3H), 3.56 (t, *J* = 7.5 Hz, 2H), 3.24 (t, *J* = 7.6 Hz, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 148.8, 147.8, 144.5, 139.9, 139.2, 132.5, 130.79 (q, *J*<sub>C-F</sub> = 32.8 Hz), 129.8 (two <sup>13</sup>C), 127.9, 127.2, 126.7 (q, *J*<sub>C-F</sub> = 272.3 Hz), 125.8 (q, *J*<sub>C-F</sub> = 3.7 Hz), 124.5, 53.2, 43.6, 32.9, 21.9; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>17</sub>ClF<sub>3</sub>NO<sub>2</sub>Na, 430.0792, Found, 430.0792.



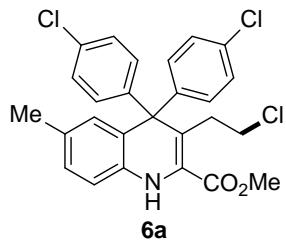
**Methyl 3-(2-chloroethyl)-4-(2-fluorophenyl)-6-methylquinoline-2-carboxylate  
(4e)**

Light yellow solid, m.p.: 101-105 °C; 52mg (49%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v);  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.6 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.38 – 7.32 (m, 1H), 7.29 (t, *J* = 8.9 Hz, 1H), 7.22 (td, *J* = 7.4, 1.6 Hz, 1H), 7.02 (s, 1H), 4.07 (s, 3H), 3.67 – 3.48 (m, 2H), 3.36 – 3.14 (m, 2H), 2.40 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 159.4 (d, *J*<sub>C-F</sub> = 246.5 Hz), 148.7, 144.6, 143.3, 139.1, 132.4, 131.4 (d, *J*<sub>C-F</sub> = 3.1 Hz), 131.0 (d, *J*<sub>C-F</sub> = 7.9 Hz), 129.9, 128.3 (d, *J*<sub>C-F</sub> = 11.4 Hz), 124.6 (d, *J*<sub>C-F</sub> = 3.6 Hz), 124.3, 123.3 (d, *J*<sub>C-F</sub> = 17.2 Hz), 116.3 (d, *J*<sub>C-F</sub> = 21.5 Hz), 53.3, 43.2, 33.6, 22.0; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>17</sub>ClFNO<sub>2</sub>Na, 380.0824; Found, 380.0822.



**Methyl 3-(2-chloroethyl)-6-methyl-4-(naphthalen-2-yl)quinoline-2-carboxylate  
(4f)**

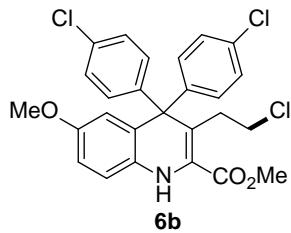
Yellow solid, m.p.: 123-126 °C; 41mg (35%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (t, *J* = 9.4 Hz, 1H), 8.02 (t, *J* = 7.4 Hz, 1H), 8.01 – 7.96 (m, 1H), 7.93 – 7.86 (m, 1H), 7.74 (s, 1H), 7.65 – 7.52 (m, 3H), 7.35 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.05 (s, 1H), 4.08 (s, 3H), 3.58 (t, *J* = 7.7 Hz, 2H), 3.39 – 3.22 (m, 2H), 2.34 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.3, 149.4, 149.0, 144.6, 138.8, 133.4, 133.1, 132.9, 132.3, 129.7, 128.6 (two <sup>13</sup>C), 128.3, 128.2, 128.0, 127.6, 127.0, 126.9, 126.8, 125.1, 53.2, 43.8, 33.1, 21.9; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>20</sub>ClNO<sub>2</sub>Na, 412.1075; Found, 412.1068.



**Methyl 3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-6-methyl-1,4-dihydroquinoline-2-carboxylate (6a)**

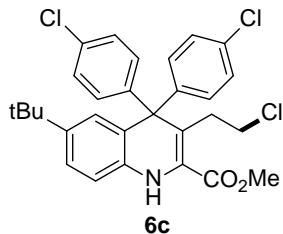
Yellow solid, m.p.: 86-89 °C; 76mg (52%); Elution: petroleum ether/ethyl acetate = 6:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 (d, *J* = 8.7 Hz, 4H), 7.19 (d, *J* = 8.7 Hz, 4H), 6.89 (dd, *J* = 8.1, 1.3 Hz, 1H), 6.79 (s, NH, 1H), 6.64 (s, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 3.95 (s, 3H), 2.76 (s, 4H), 2.15 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.5, 143.7, 134.8, 132.7, 131.3, 131.0, 130.8, 130.1, 128.5, 128.3, 127.5, 125.0,

118.5, 114.0, 57.9, 52.9, 43.3, 35.6, 21.0; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>22</sub>Cl<sub>3</sub>NO<sub>2</sub>Na, 508.0608; Found, 508.0580.



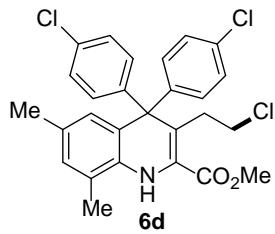
**Methyl 3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-6-methoxy-1,4-dihydroquinoline-2-carboxylate (6b)**

Yellow oil; 41mg (27%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27 (t, J = 8.1 Hz, 4H), 7.18 (d, J = 8.5 Hz, 4H), 6.73 (s, NH, 1H), 6.68 (dd, J = 8.7, 2.1 Hz, 1H), 6.63 (d, J = 8.7 Hz, 1H), 6.39 (d, J = 2.0 Hz, 1H), 3.94 (s, 3H), 3.62 (s, 3H), 2.76 (s, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.5, 154.6, 143.3, 132.8, 131.4, 131.2, 128.3, 127.7, 126.2, 117.2, 115.4, 114.8, 113.5, 58.2, 55.6, 52.9, 43.3, 35.5; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>22</sub>Cl<sub>3</sub>NO<sub>3</sub>Na, 524.0558; Found, 524.0559.



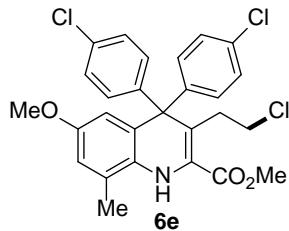
**Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-1,4-dihydroquinoline-2-carboxylate (6c)**

Yellow solid, m.p.: 109-112 °C; 47mg (30%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.22 (m, 4H), 7.16 (d, J = 8.7 Hz, 4H), 7.10 (dd, J = 8.3, 2.1 Hz, 1H), 6.87 (d, J = 1.8 Hz, 1H), 6.78 (s, NH, 1H), 6.62 (d, J = 8.4 Hz, 1H), 3.94 (s, 3H), 2.75 (s, 3H), 1.13 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.5, 144.5, 143.7, 134.8, 132.7, 131.2, 128.2, 127.6, 127.0, 124.6, 124.5, 118.5, 113.5, 58.2, 52.9, 43.2, 35.5, 34.2, 31.3; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>29</sub>H<sub>28</sub>Cl<sub>3</sub>NO<sub>2</sub>Na, 550.1078; Found, 550.1074.



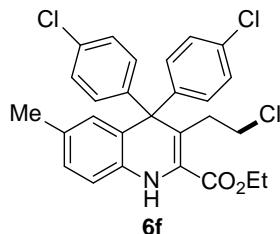
**Methyl 3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-6,8-dimethyl-1,4-dihydroquinoline-2-carboxylate (6d)**

Yellow solid, m.p.: 75-78°C; 69mg (46%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 (d, J = 8.7 Hz, 4H), 7.18 (d, J = 8.7 Hz, 4H), 6.79 – 6.80 (m, 2H), 6.51 (s, 1H), 3.97 (s, 3H), 2.78 (s, 4H), 2.21 (s, 3H), 2.13 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.7, 143.8, 133.3, 132.6, 131.3, 130.2, 129.7, 128.2, 128.0, 127.5, 124.7, 120.8, 118.8, 58.1, 53.0, 43.3, 35.6, 20.9, 16.7; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>24</sub>Cl<sub>3</sub>NO<sub>2</sub>Na, 522.0765; Found, 522.0764.



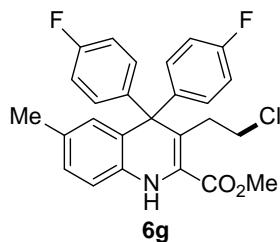
**Methyl 3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-6-methoxy-8-methyl-1,4-dihydroquinoline-2-carboxylate (6e)**

Yellow oil; 26mg (17%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 (d, *J* = 8.6 Hz, 4H), 7.18 (d, *J* = 8.5 Hz, 4H), 6.72 (s, NH, 1H), 6.59 (d, *J* = 2.2 Hz, 1H), 6.26 (d, *J* = 2.2 Hz, 1H), 3.96 (s, 3H), 3.61 (s, 3H), 2.82 – 2.74 (m, 4H), 2.23 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.8, 154.0, 143.4, 132.7, 131.2, 130.0, 128.2, 127.7, 125.7, 122.2, 117.6, 115.0, 113.1, 58.4, 55.6, 52.9, 43.3, 35.5, 17.1; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>24</sub>Cl<sub>3</sub>NO<sub>3</sub>Na, 538.0714; Found, 538.0719.



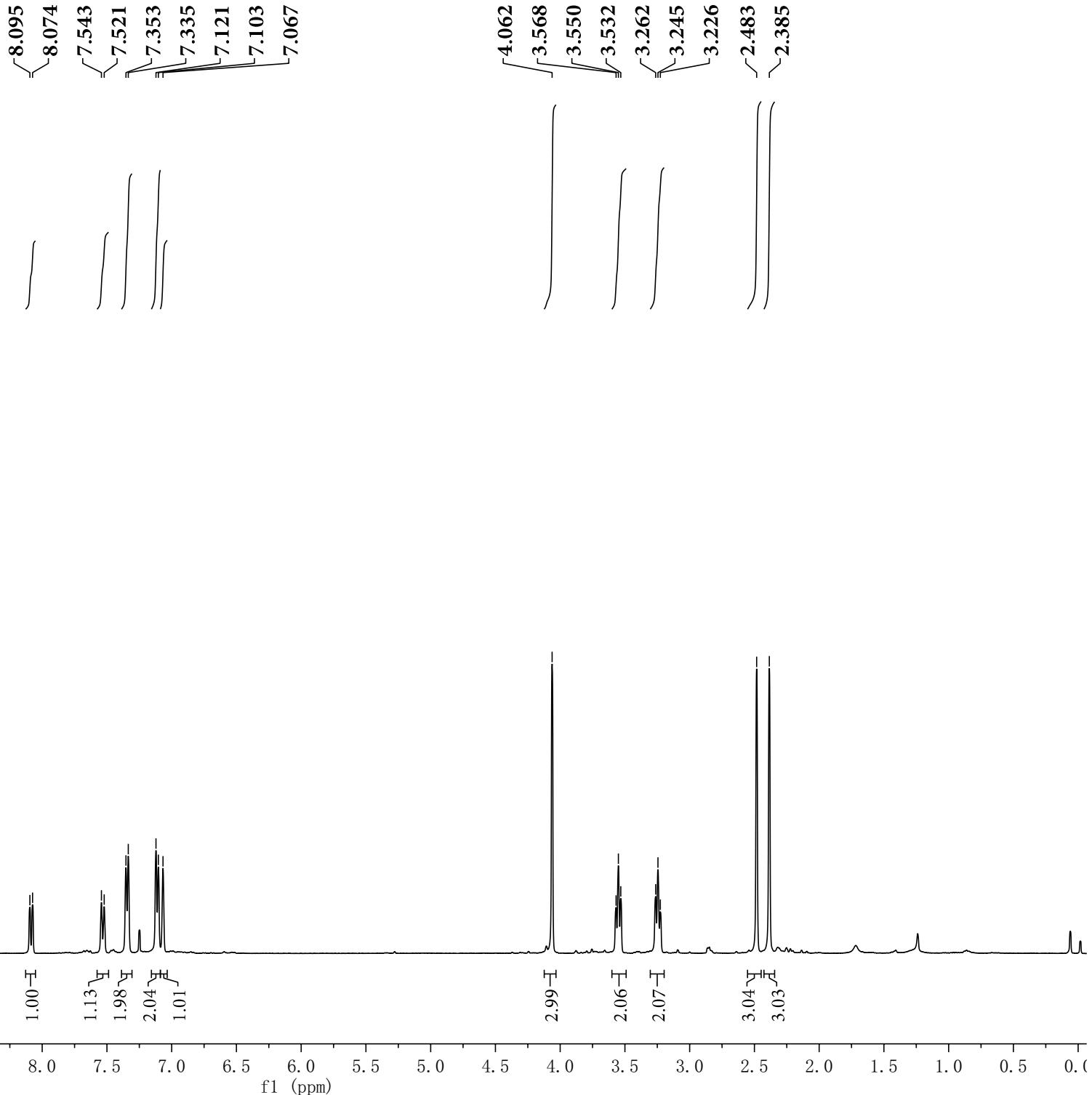
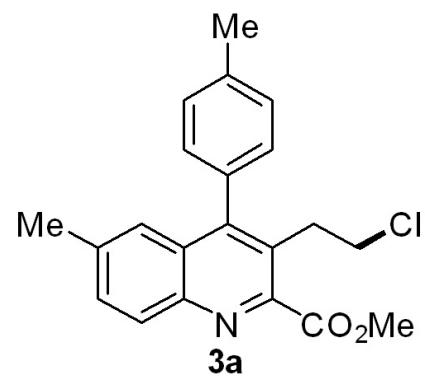
**Ethyl 3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-6-methyl-1,4-dihydroquinoline-2-carboxylate (6f)**

Yellow oil; 22mg (15%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 (d, *J* = 8.6 Hz, 3H), 7.19 (d, *J* = 8.6 Hz, 4H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.81 (s, NH, 1H), 6.63 (s, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 4H), 2.14 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.4, 143.7, 134.8, 132.7, 131.3, 130.9, 130.1, 128.4, 128.2, 127.7, 125.0, 117.8, 114.0, 62.4, 58.0, 43.2, 35.6, 20.9, 14.1; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>24</sub>Cl<sub>3</sub>NO<sub>2</sub>Na, 522.0765; Found, 522.0738.

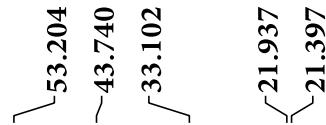
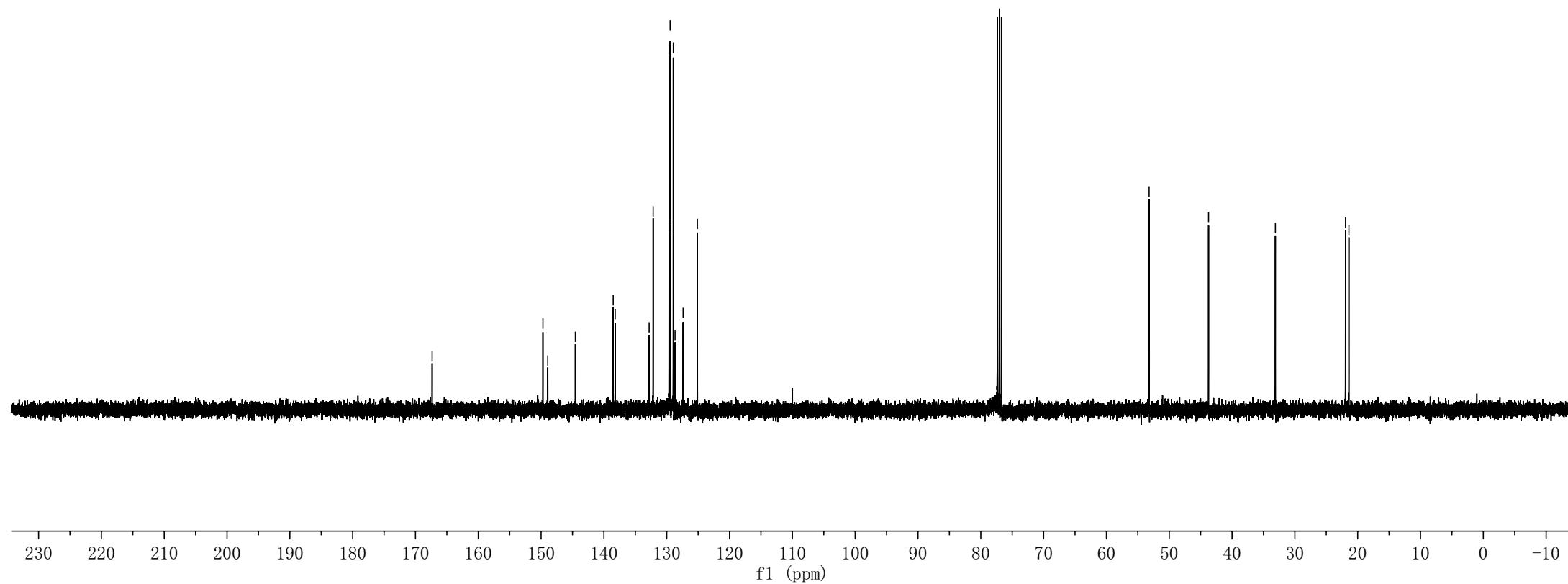
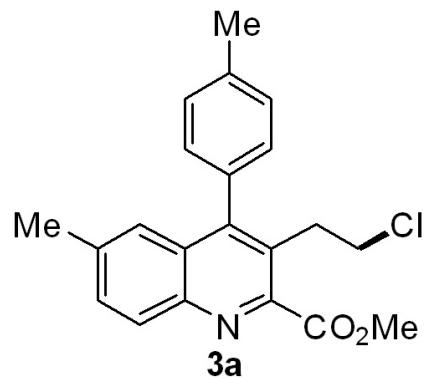


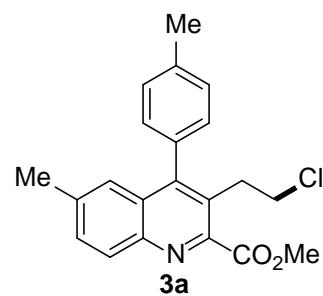
**Methyl 3-(2-chloroethyl)-4,4-bis(4-fluorophenyl)-6-methyl-1,4-dihydroquinoline-2-carboxylate (6g)**

Yellow oil; 31mg (23%); Elution: petroleum ether/ethyl acetate = 5:1 (v : v); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.6 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 4H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.77 (s, NH, 1H), 6.67 (s, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 3.95 (s, 3H), 2.76 (s, 4H), 2.16 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.5, 161.3 (d, *J*<sub>C-F</sub> = 247.1 Hz), 141.2 (d, *J*<sub>C-F</sub> = 3.3 Hz), 134.8, 131.5 (d, *J*<sub>C-F</sub> = 7.8 Hz), 130.8, 130.2, 128.3, 127.3, 125.5, 119.2, 114.9 (d, *J*<sub>C-F</sub> = 21.2 Hz), 113.9, 57.7, 52.8, 43.3, 35.7, 20.9; HRMS (ESI) m/z: [M + Na]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>22</sub>ClF<sub>2</sub>NO<sub>2</sub>Na, 476.1199; Found, 476.1198.

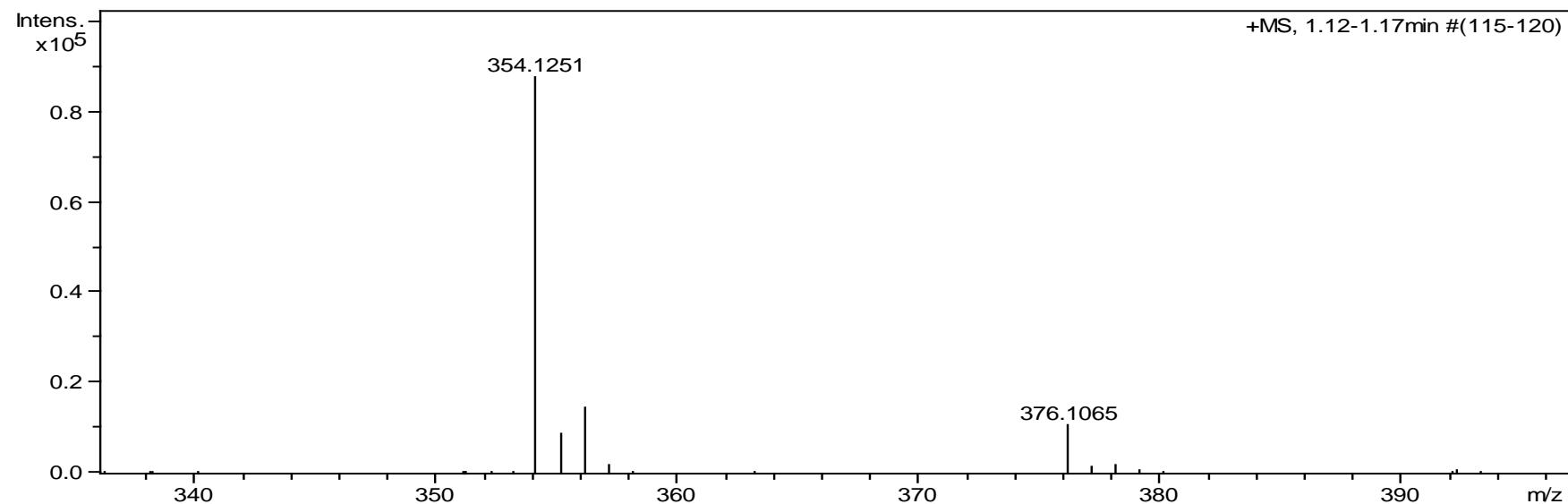
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

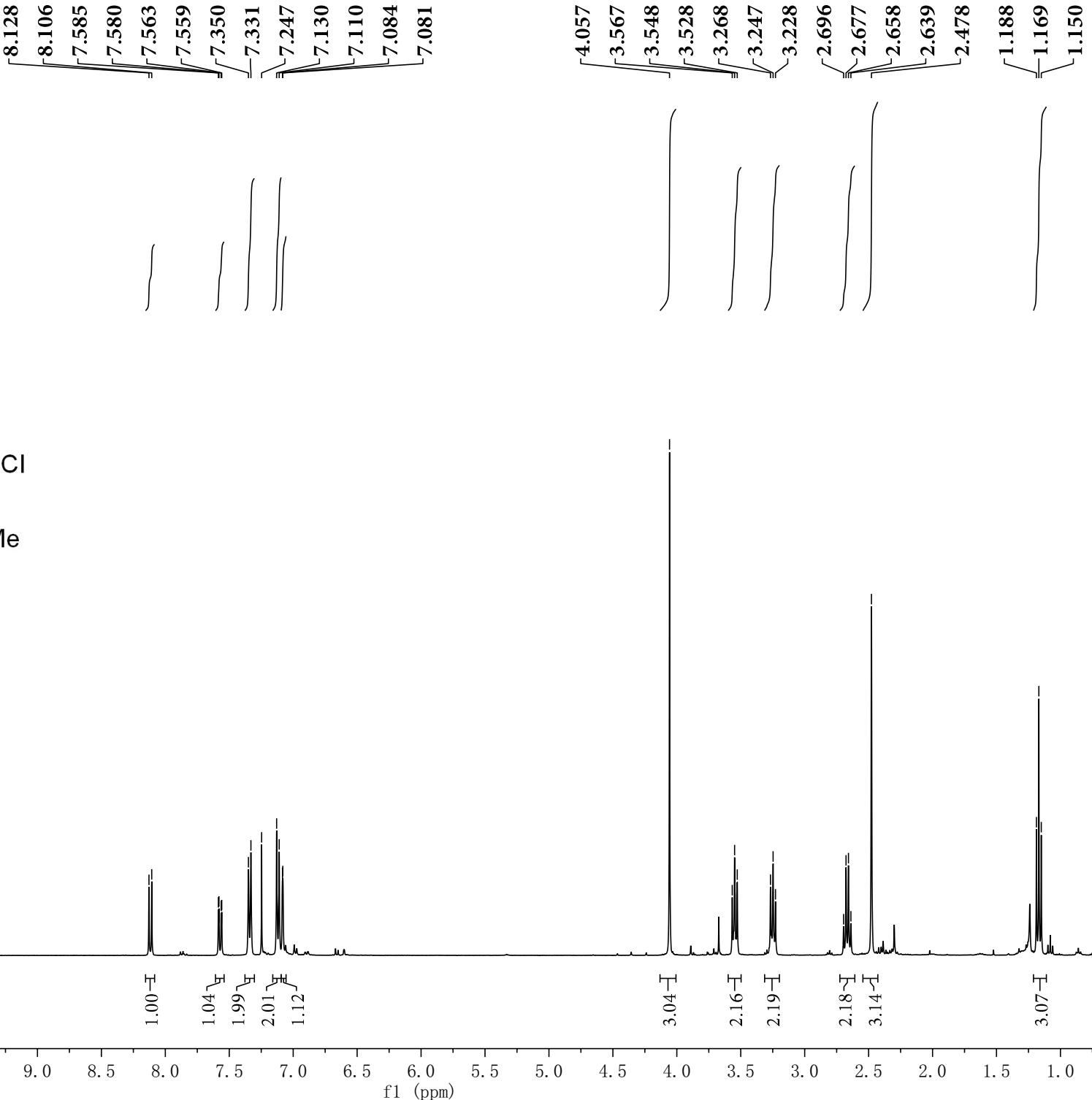
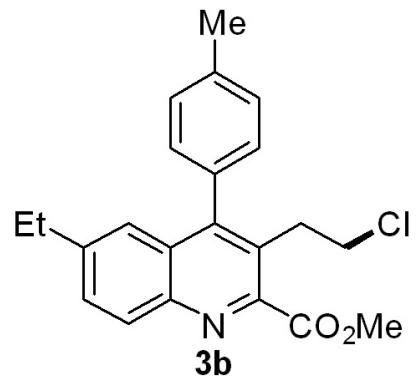
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



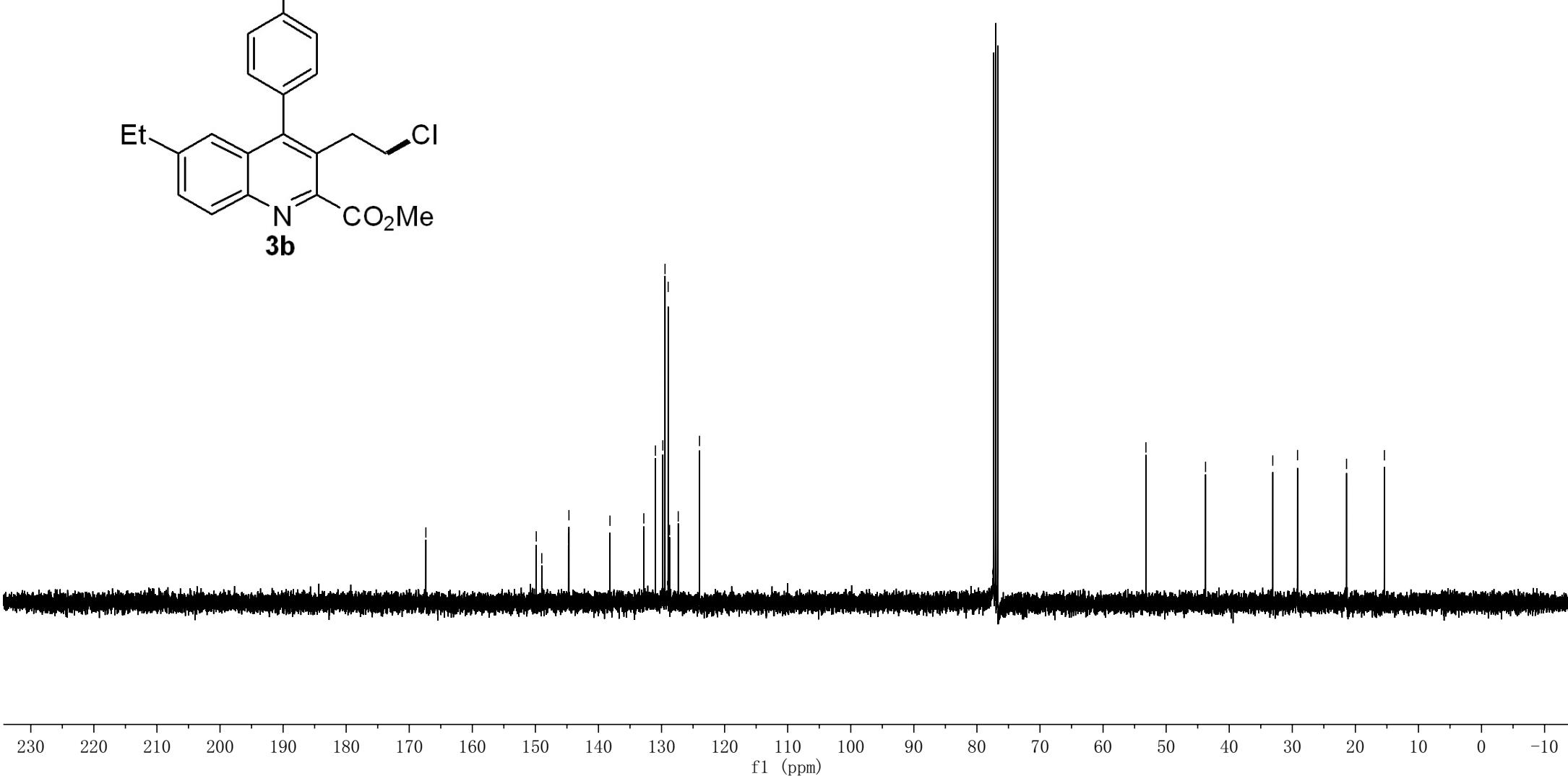
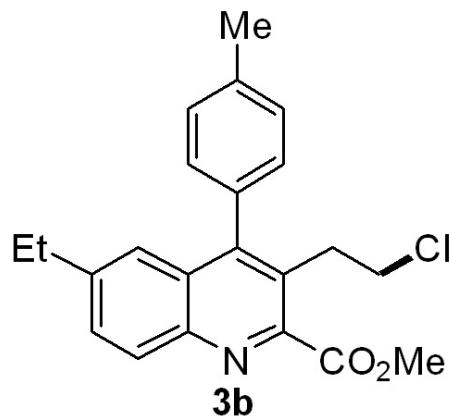


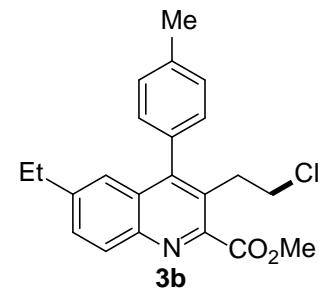
Methyl 3-(2-chloroethyl)-6-methyl-4-(p-tolyl)quinoline-2-carboxylate (3a)



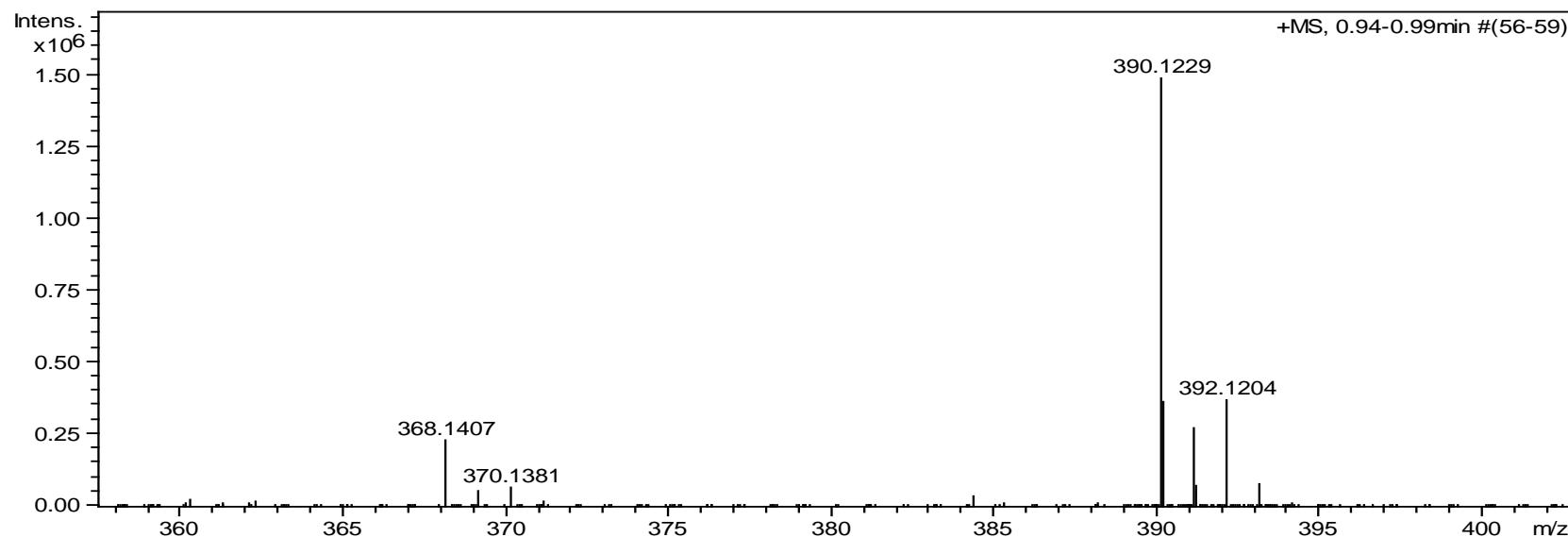
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

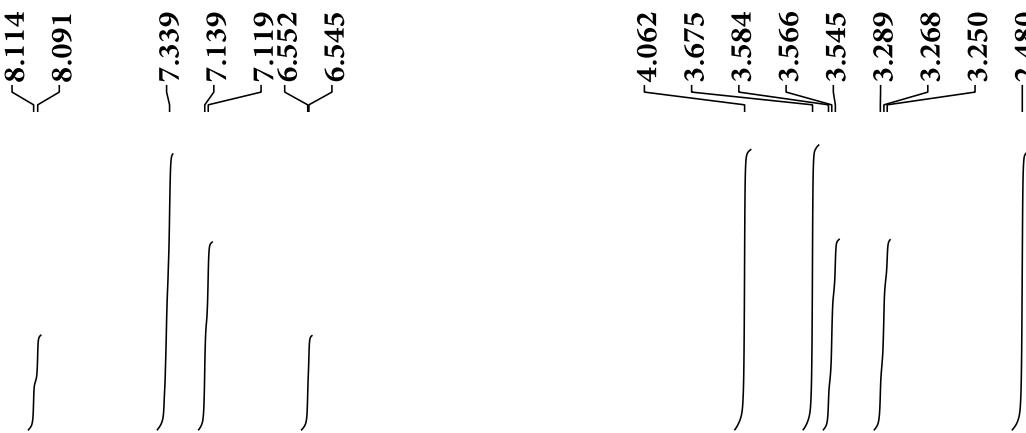
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



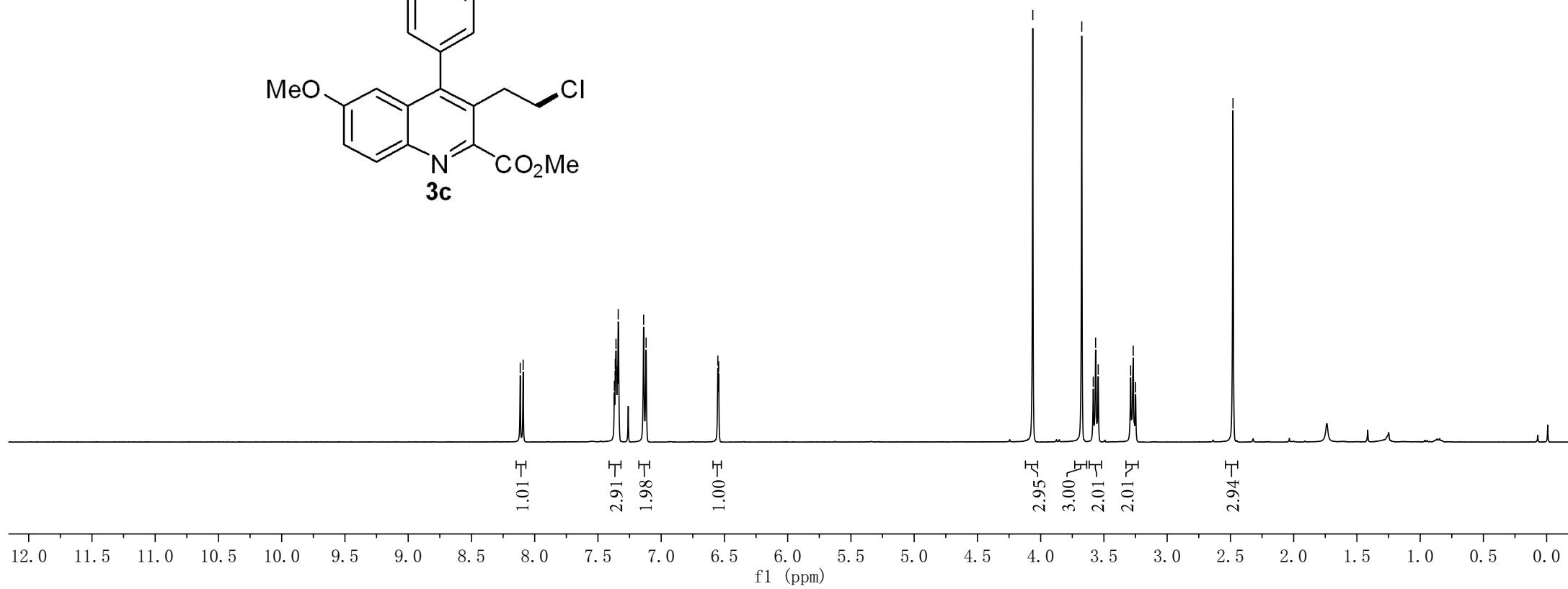
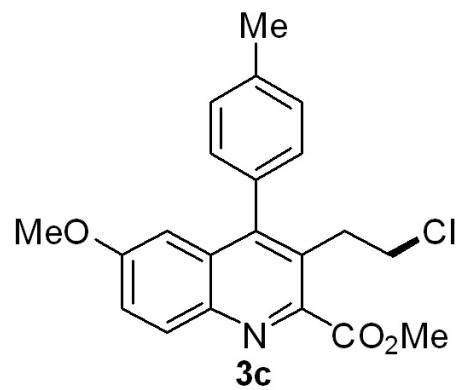


**Methyl 3-(2-chloroethyl)-6-ethyl-4-(p-tolyl)quinoline-2-carboxylate (3b)**

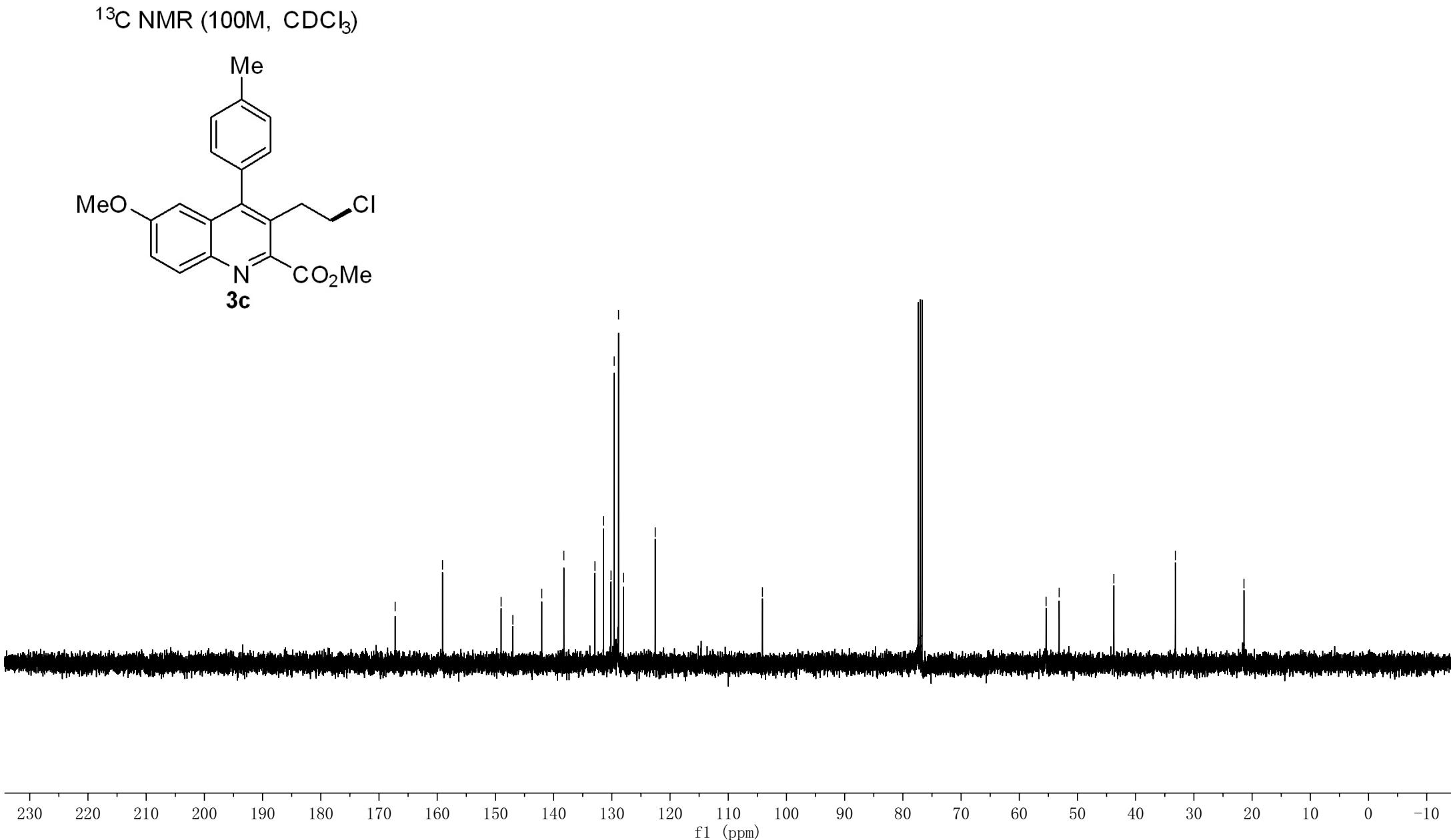
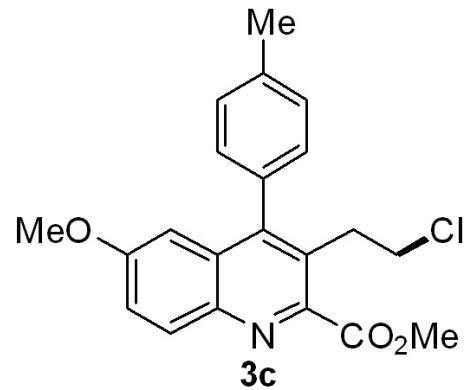


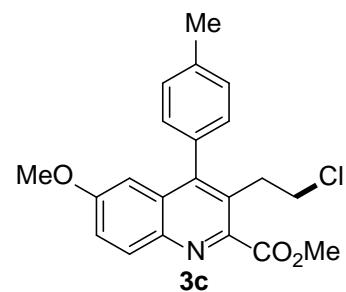


<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

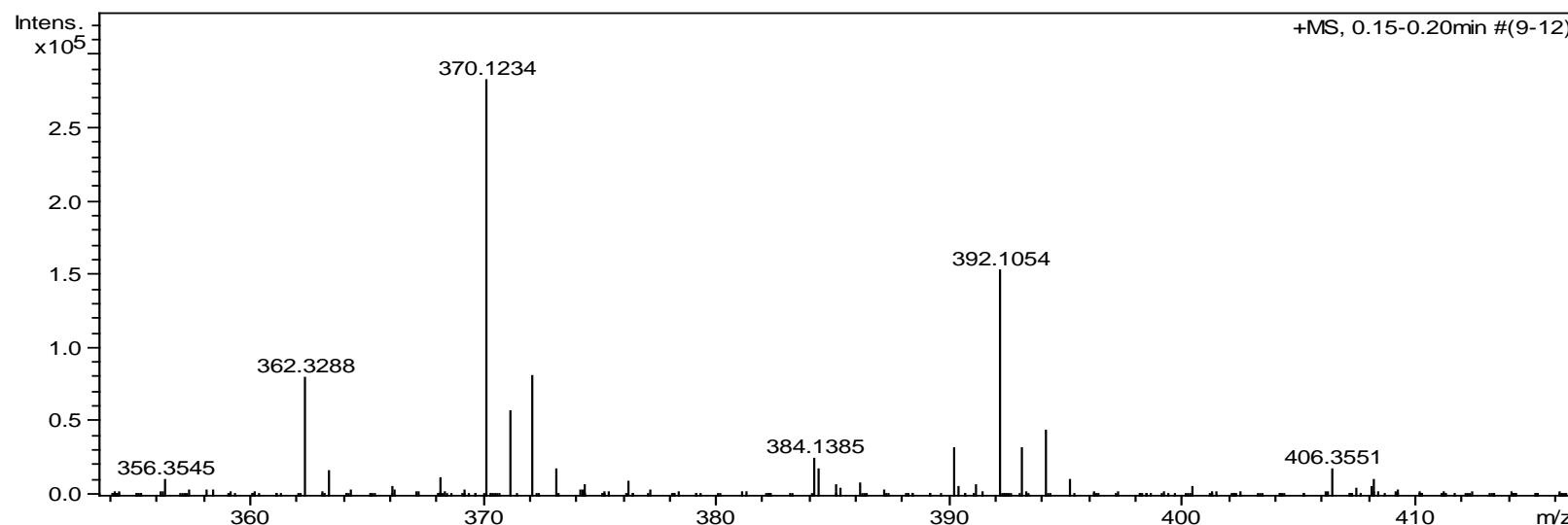


$^{13}\text{C}$  NMR (100M,  $\text{CDCl}_3$ )

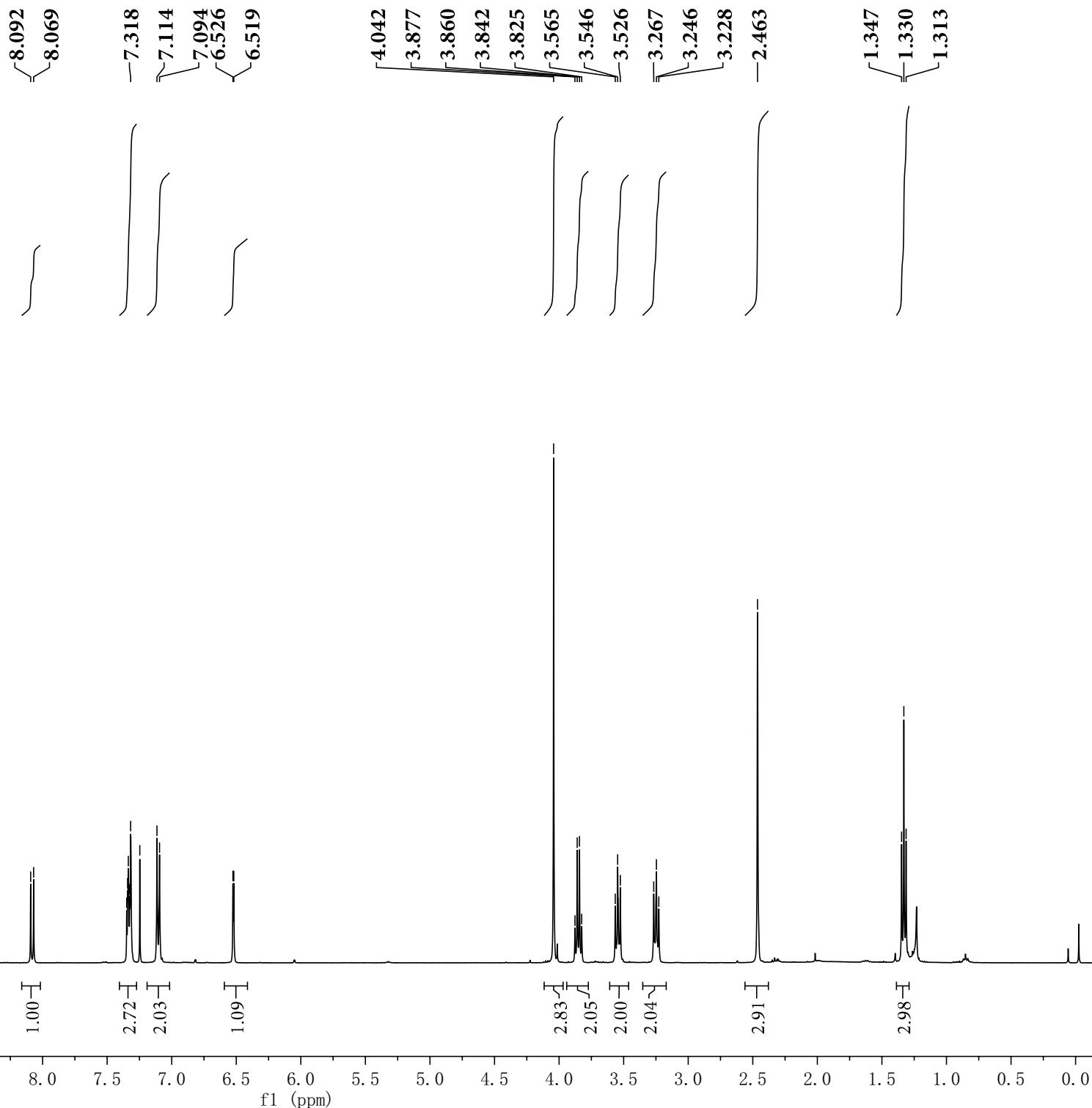
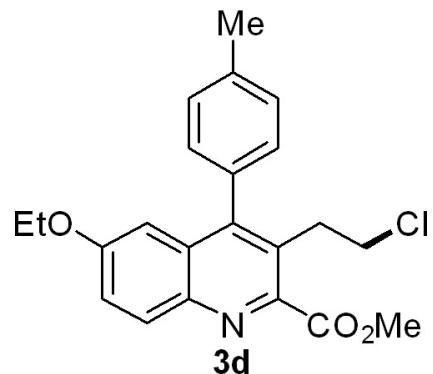




Methyl 3-(2-chloroethyl)-6-methoxy-4-(p-tolyl)quinoline-2-carboxylate (3c)

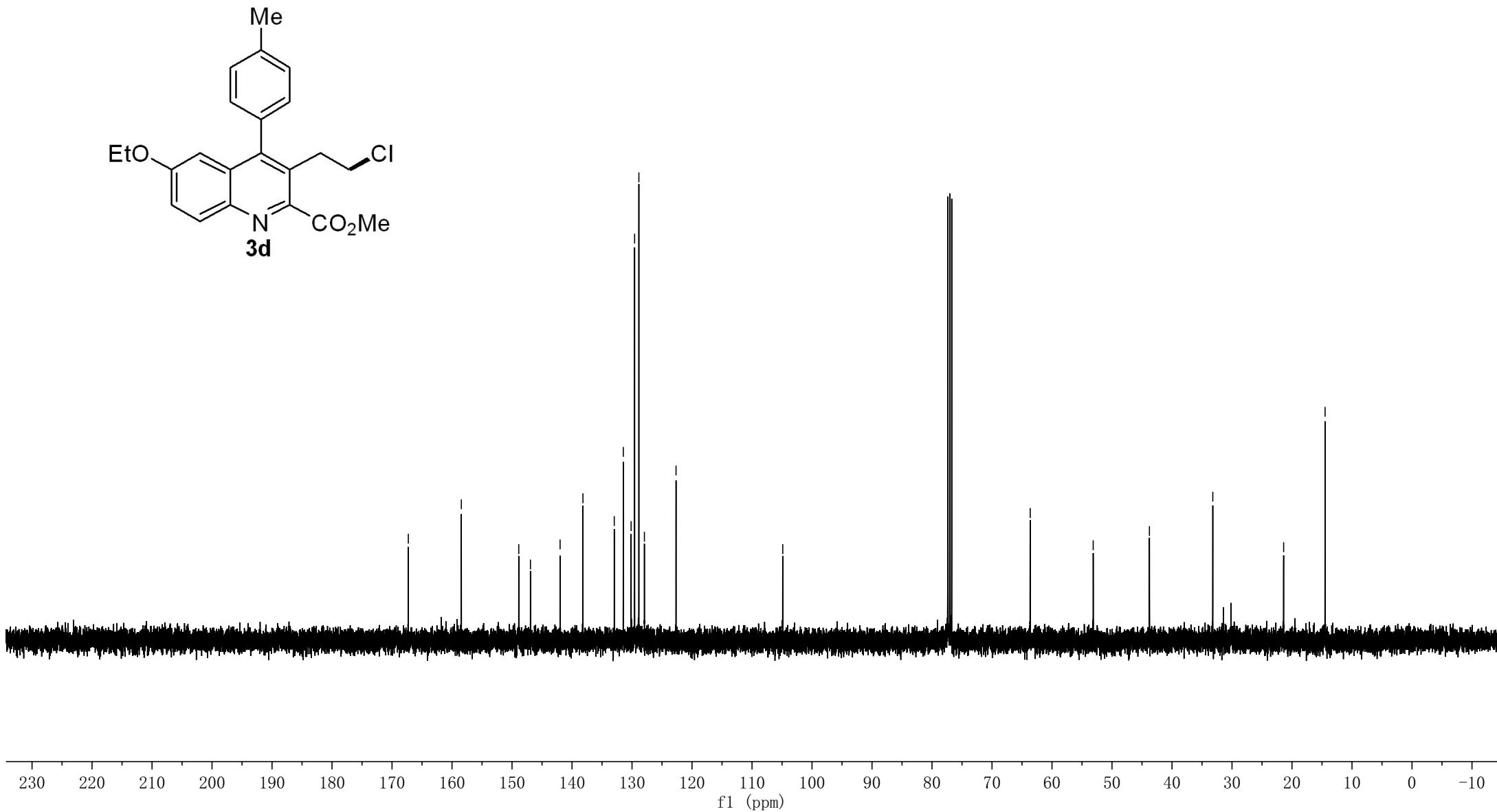
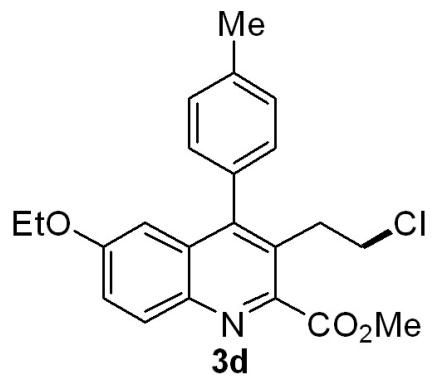


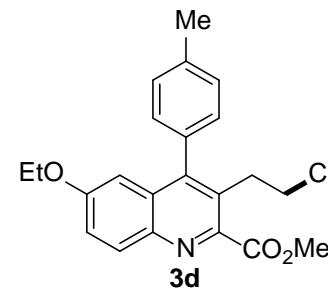
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)



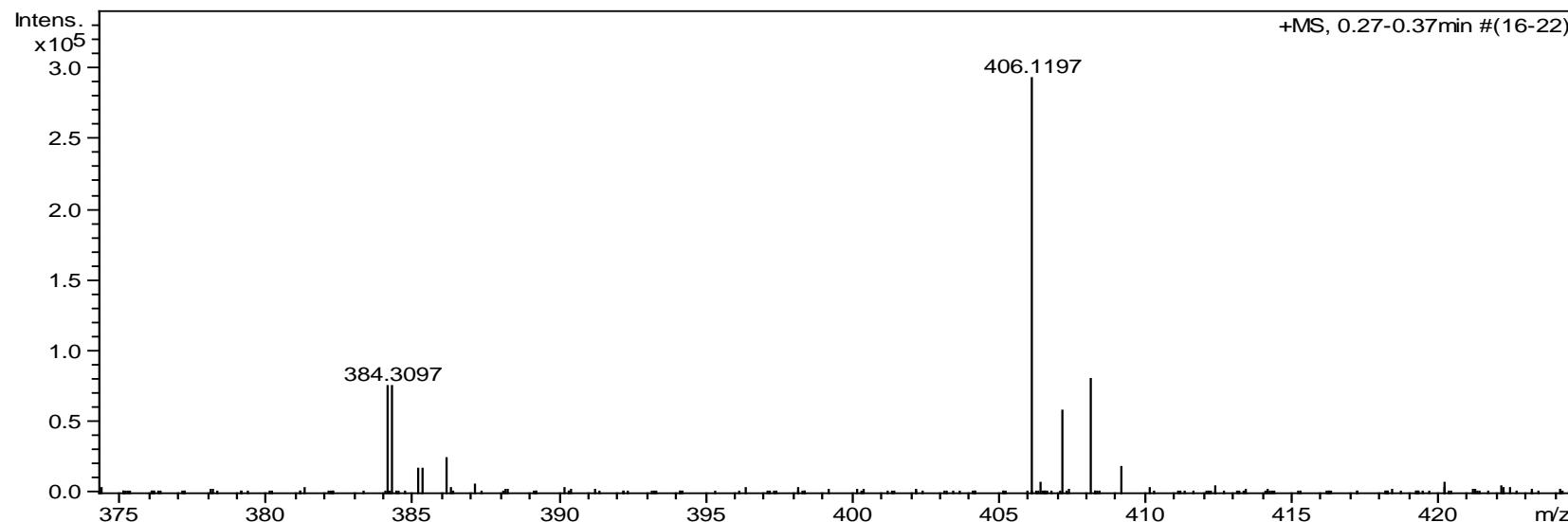


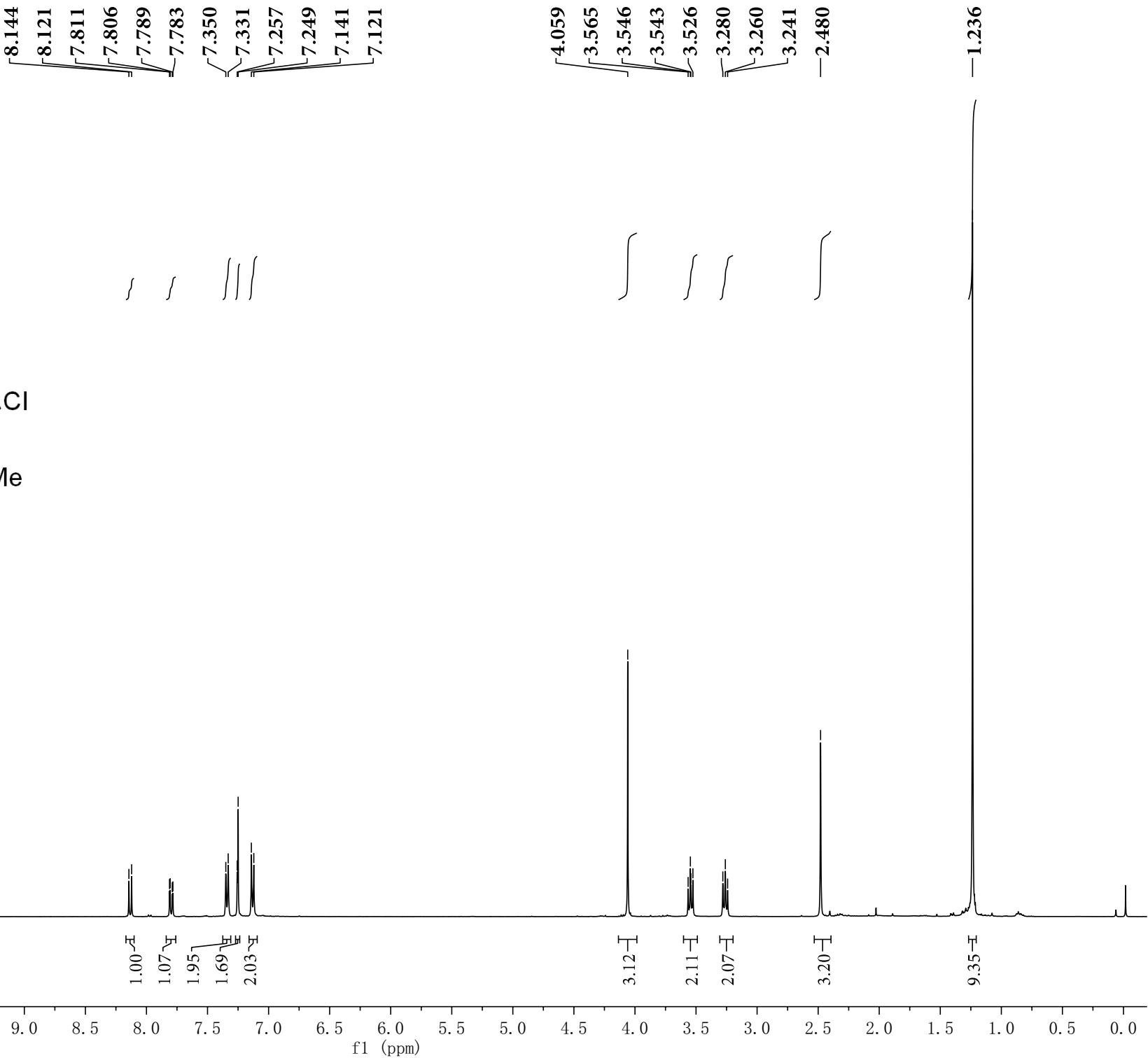
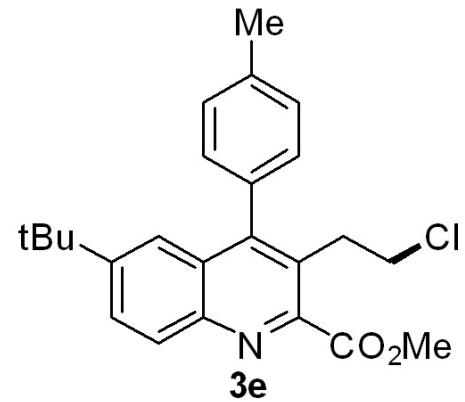
$^{13}\text{C}$  NMR (100M,  $\text{CDCl}_3$ )



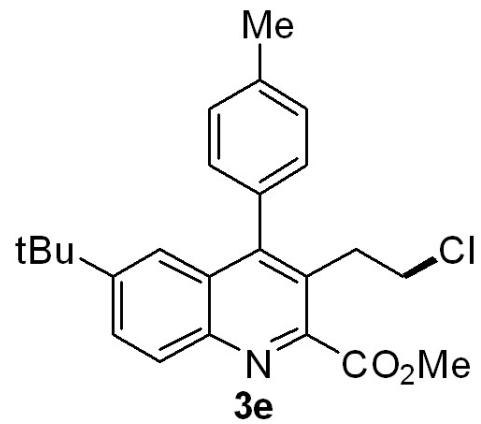


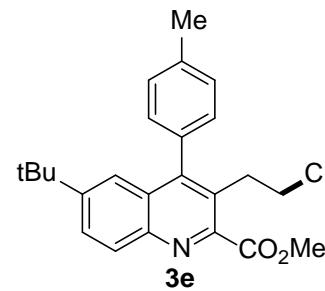
**Methyl 3-(2-chloroethyl)-6-ethoxy-4-(p-tolyl)quinoline-2-carboxylate (3d)**



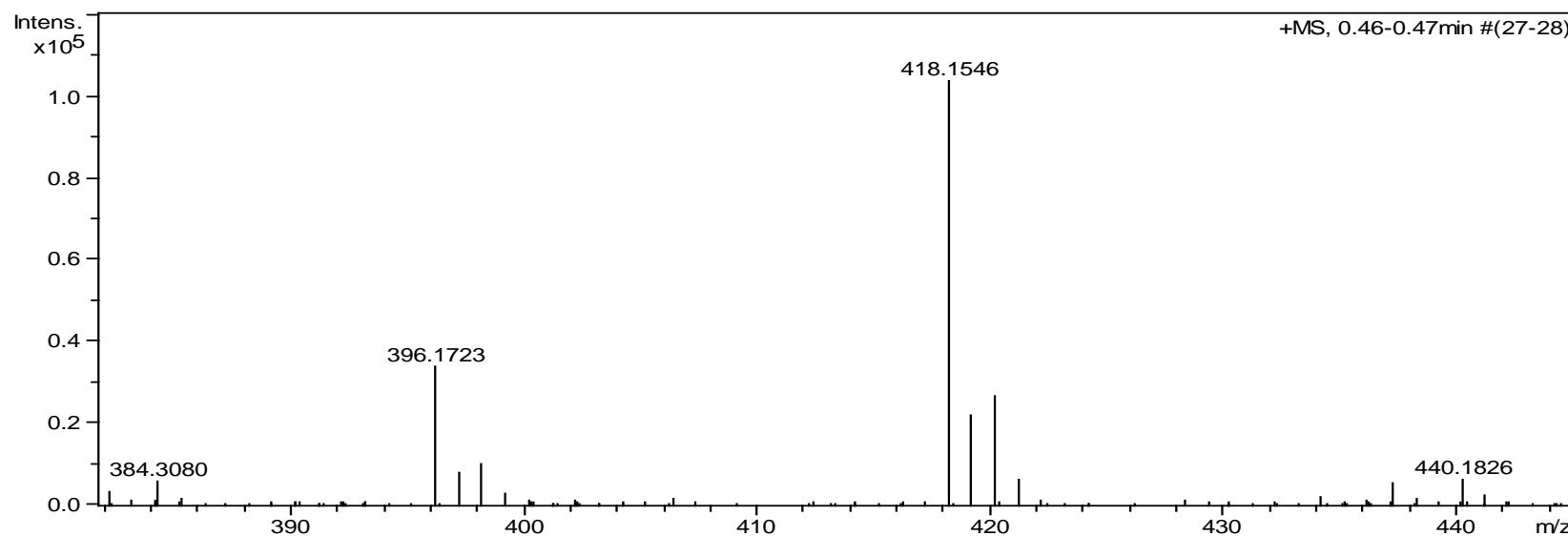
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

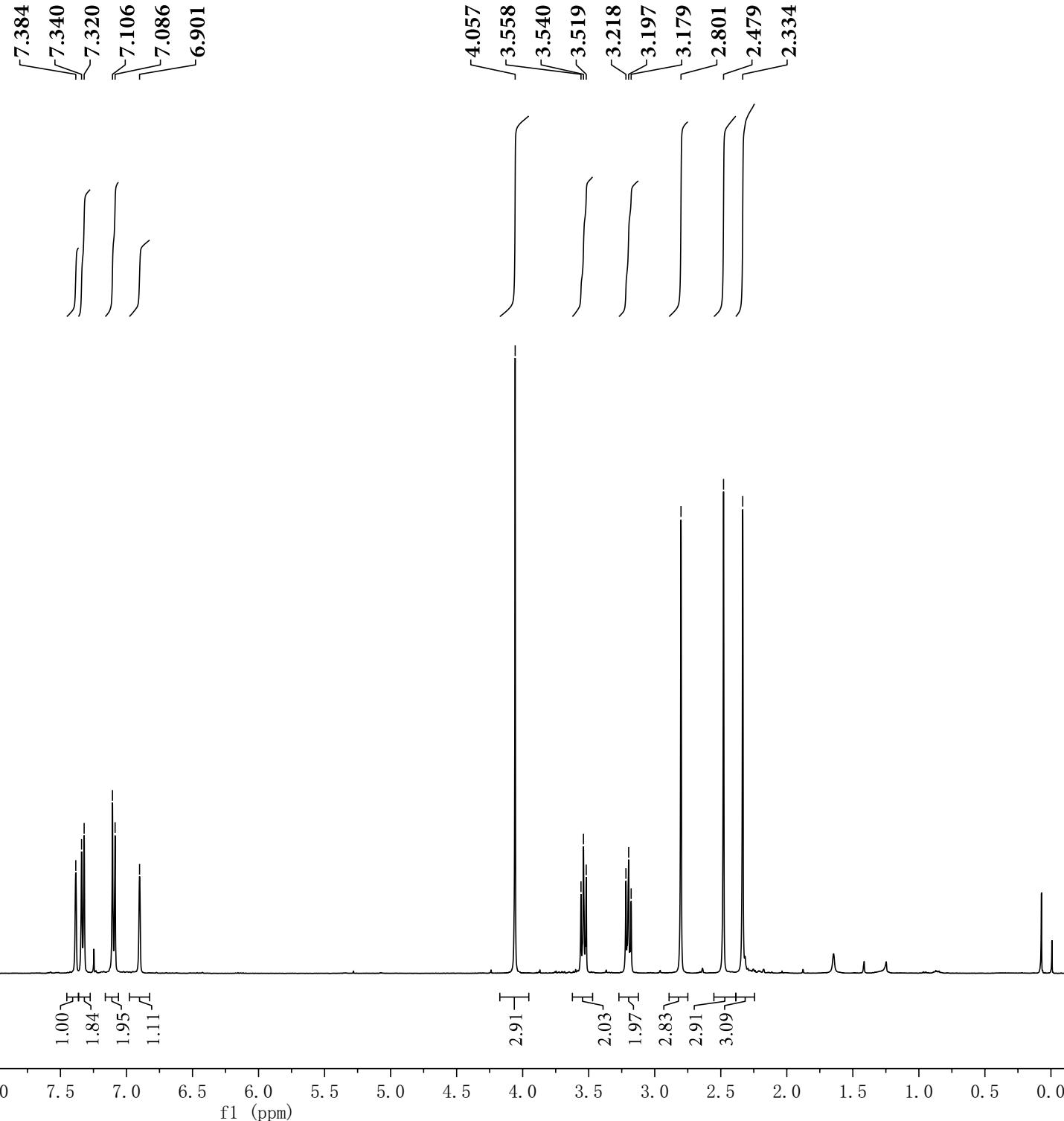
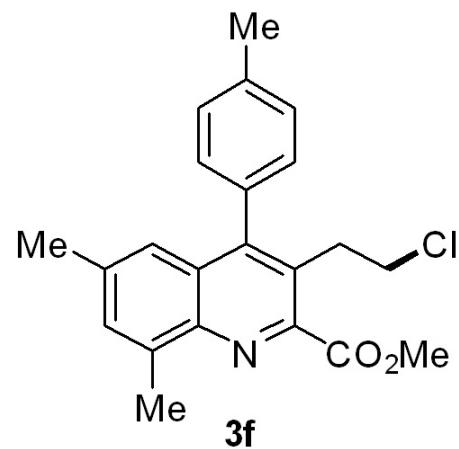
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



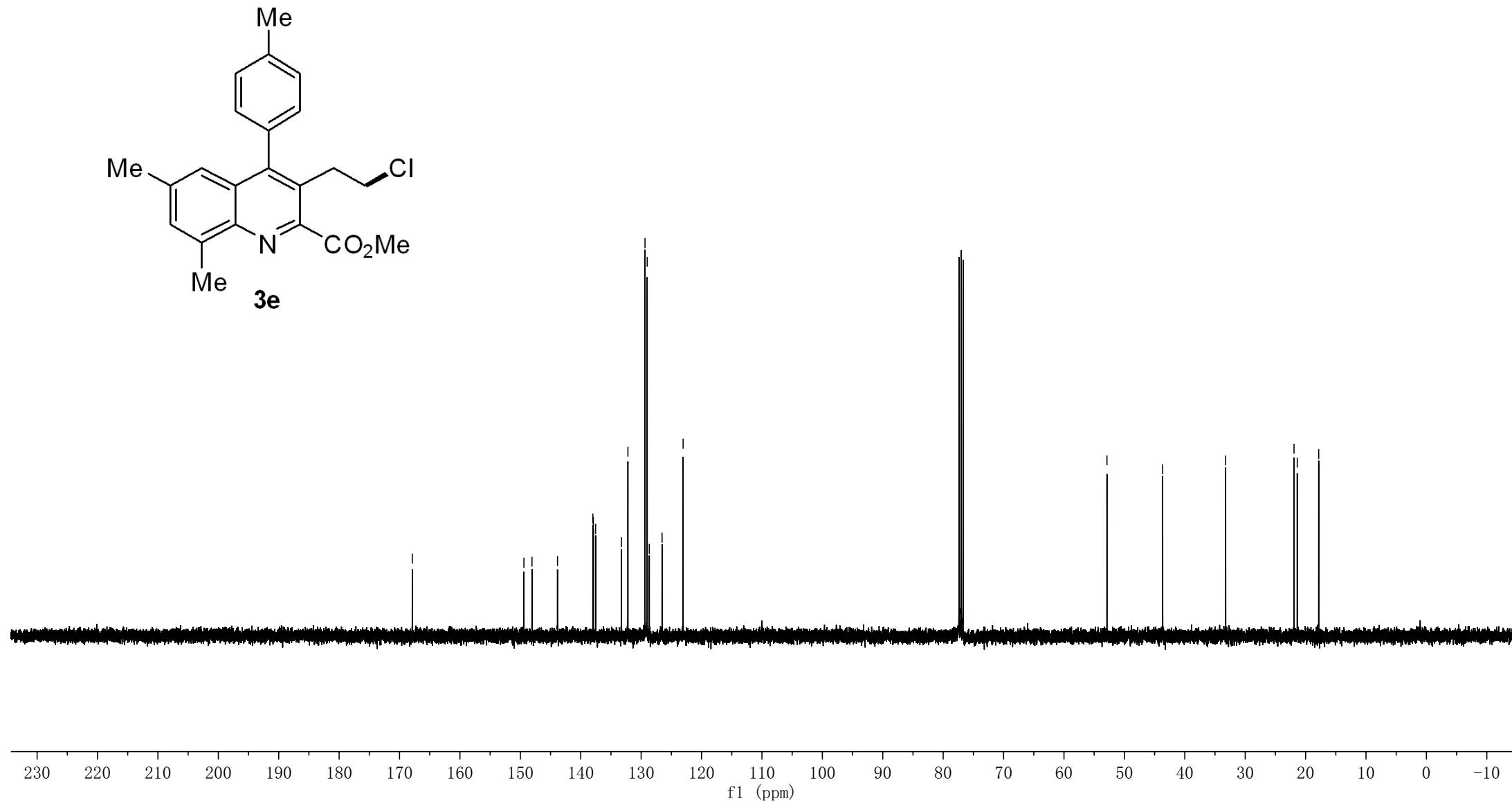
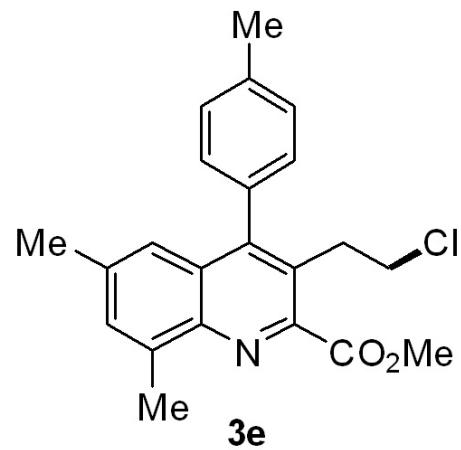


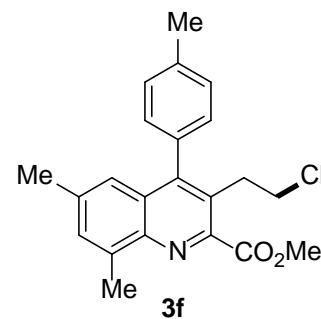
Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(p-tolyl)quinoline-2-carboxylate (3e)



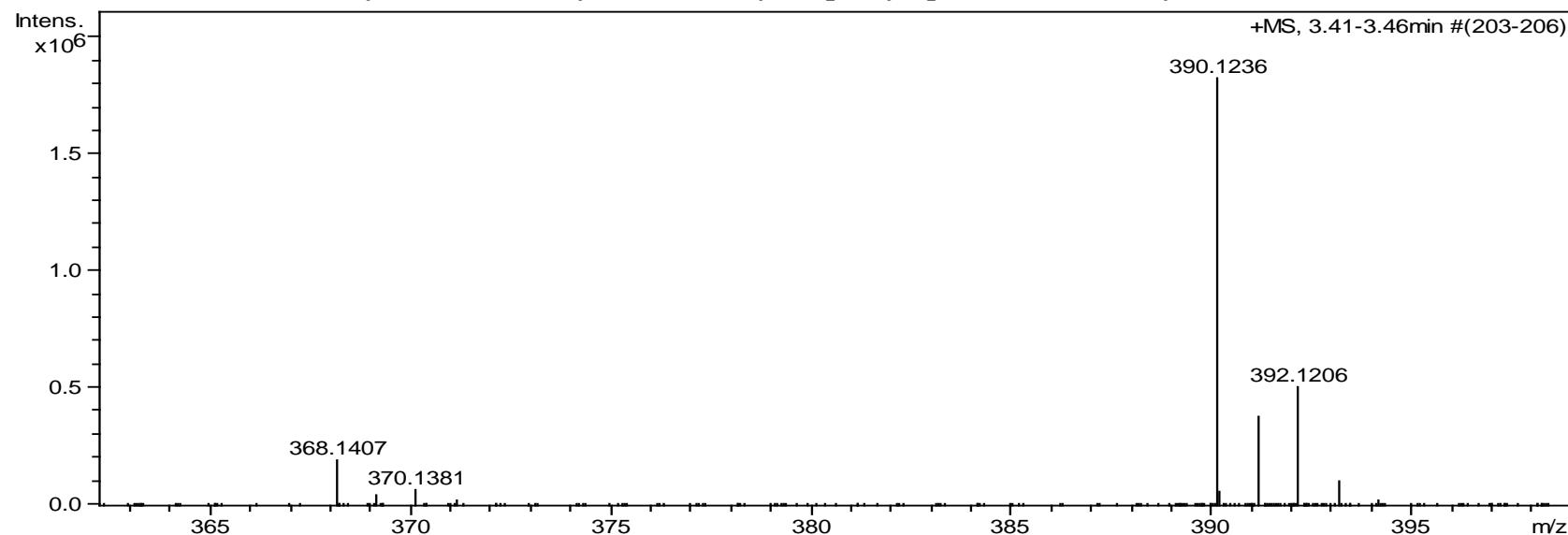
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

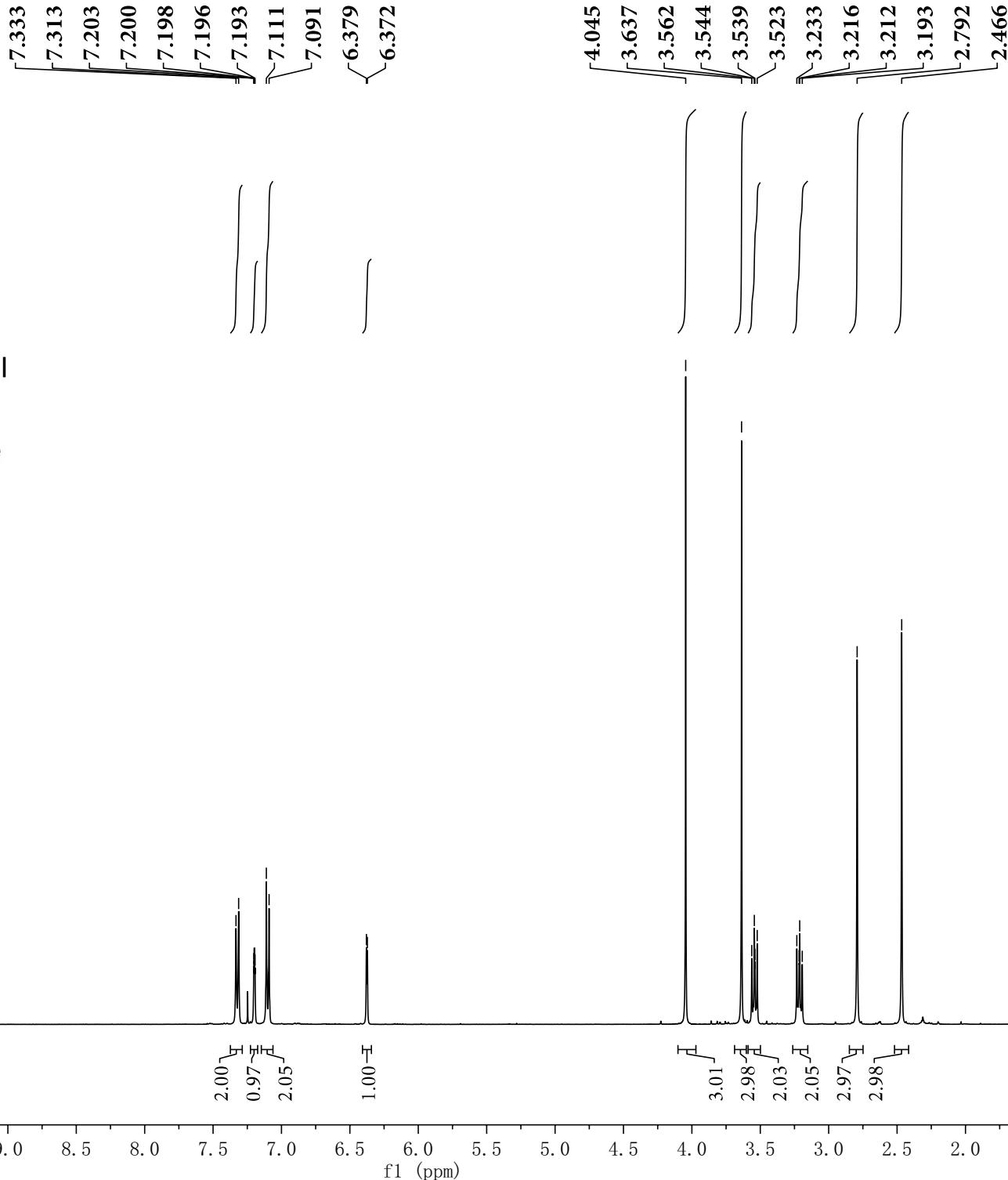
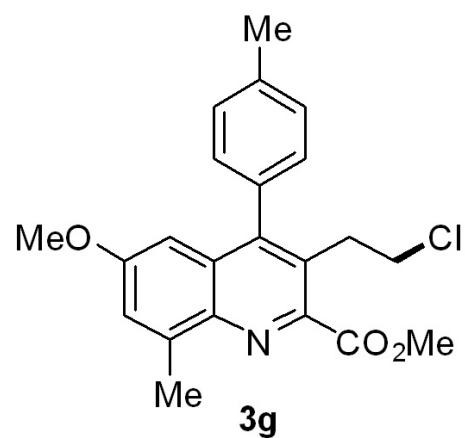
$^{13}\text{C}$  NMR (100M,  $\text{CDCl}_3$ )

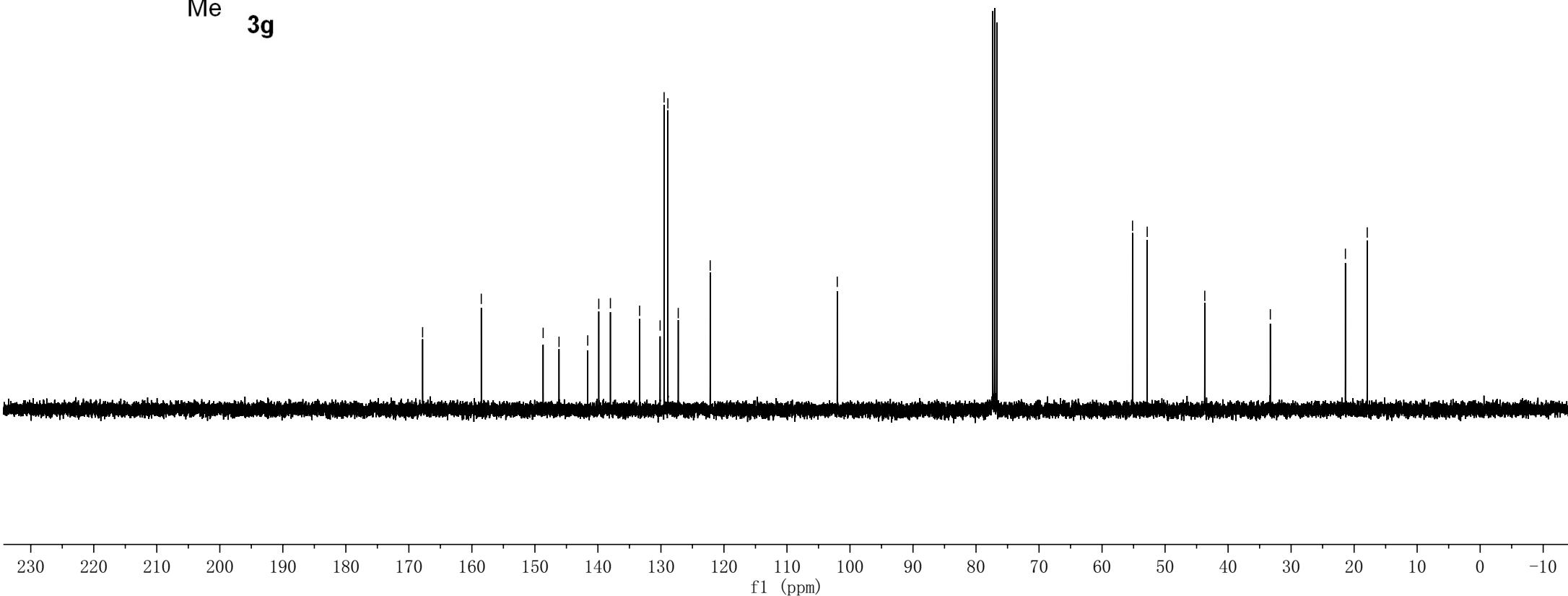
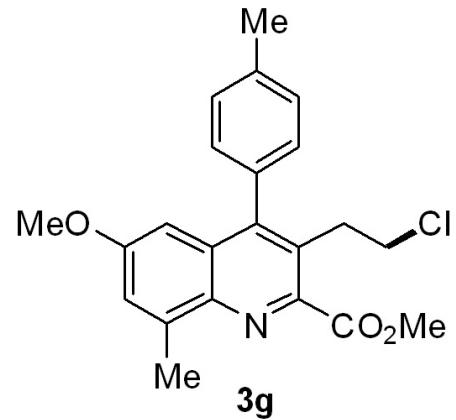


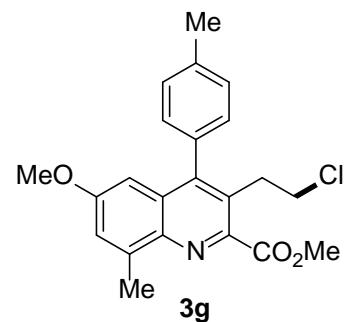


Methyl 3-(2-chloroethyl)-6,8-dimethyl-4-(p-tolyl)quinoline-2-carboxylate (**3f**)

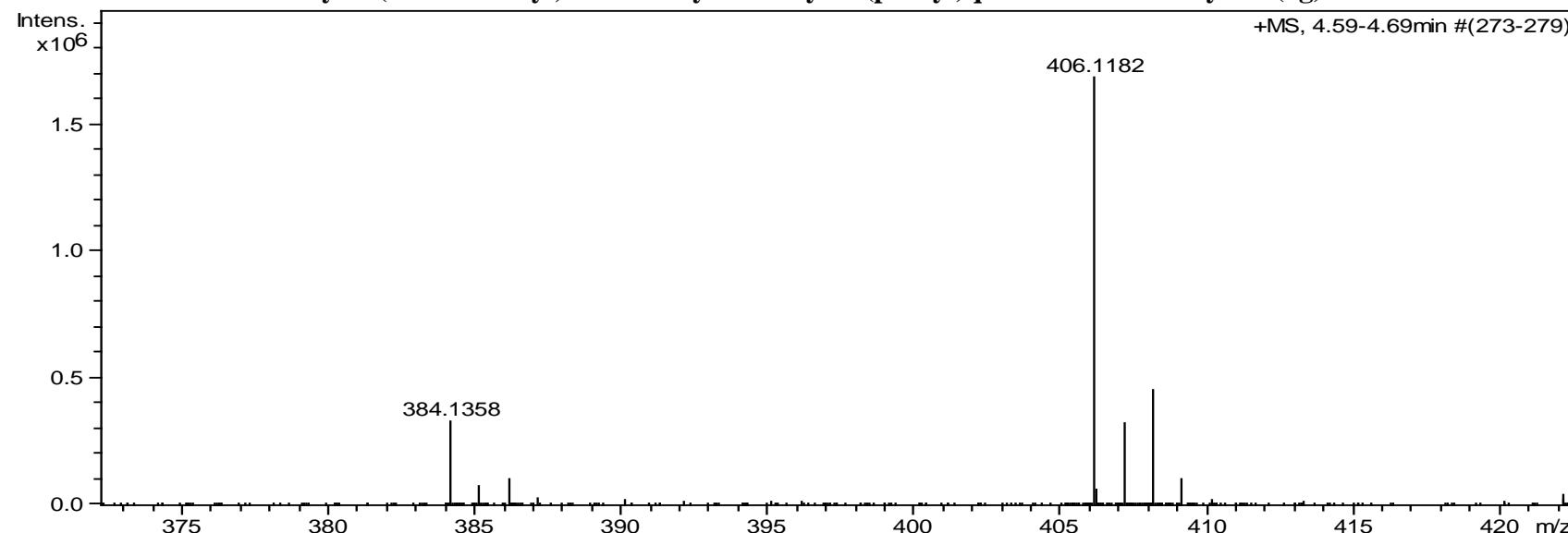


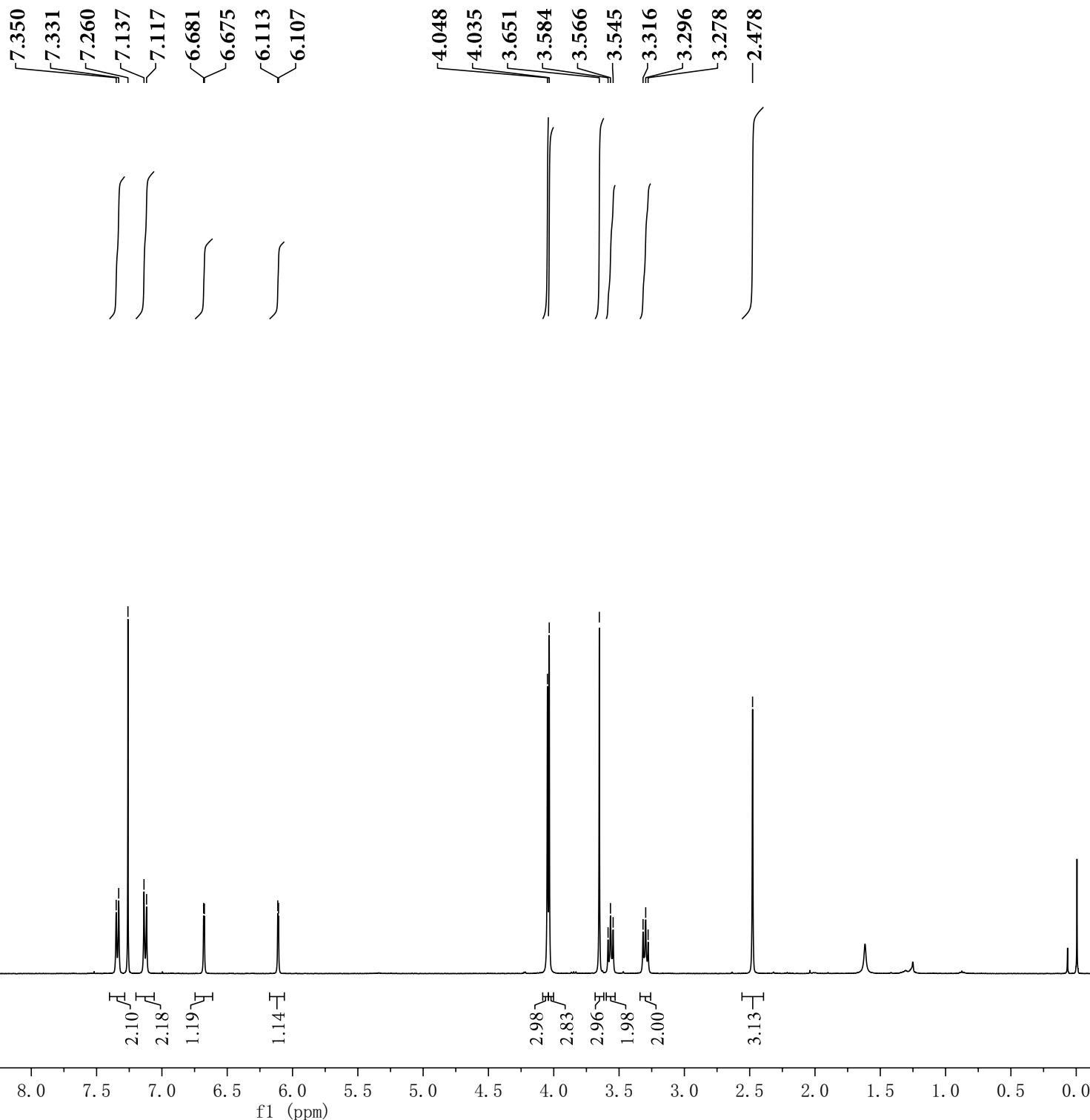
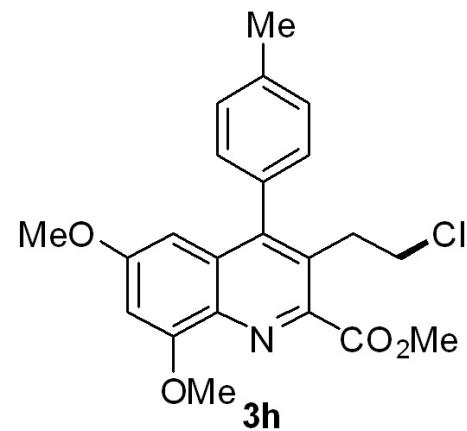
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)

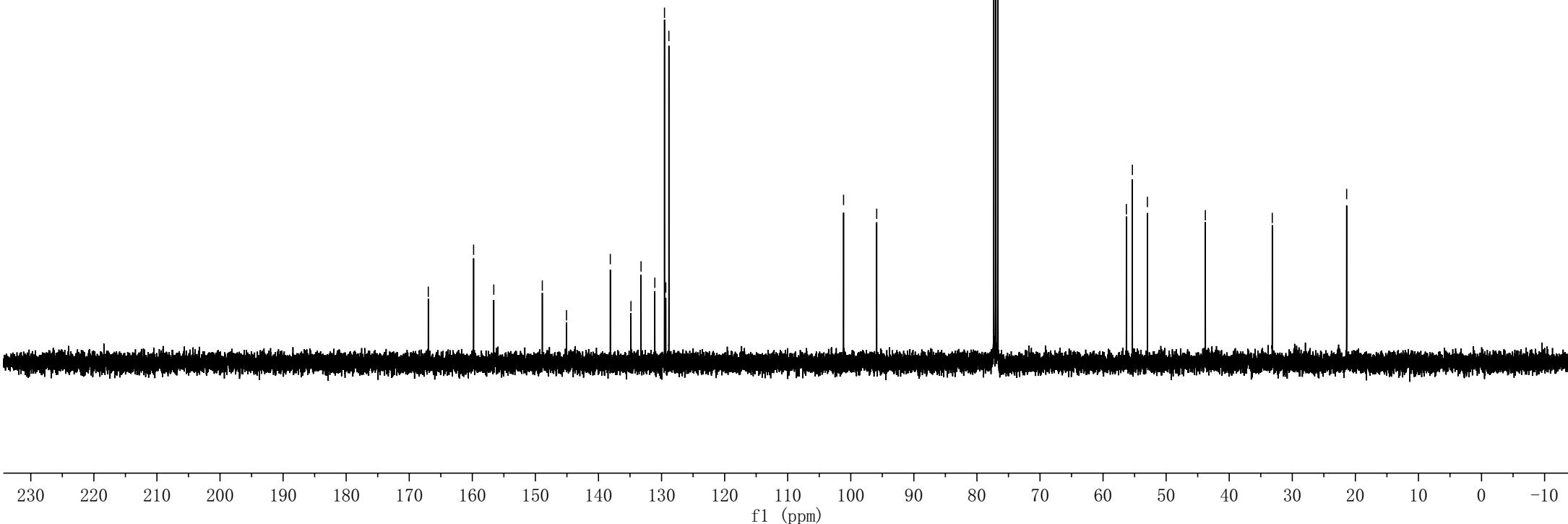
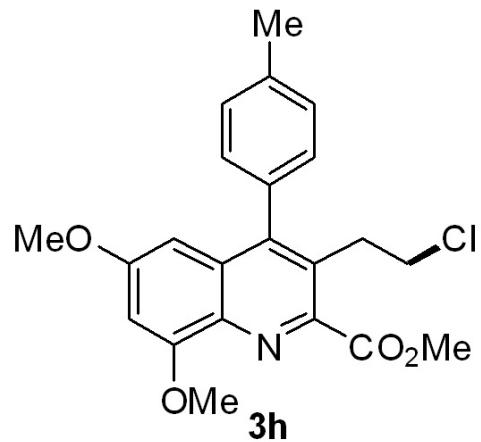


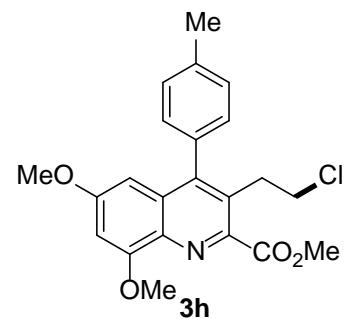
Methyl 3-(2-chloroethyl)-6-methoxy-8-methyl-4-(p-tolyl)quinoline-2-carboxylate (**3g**)



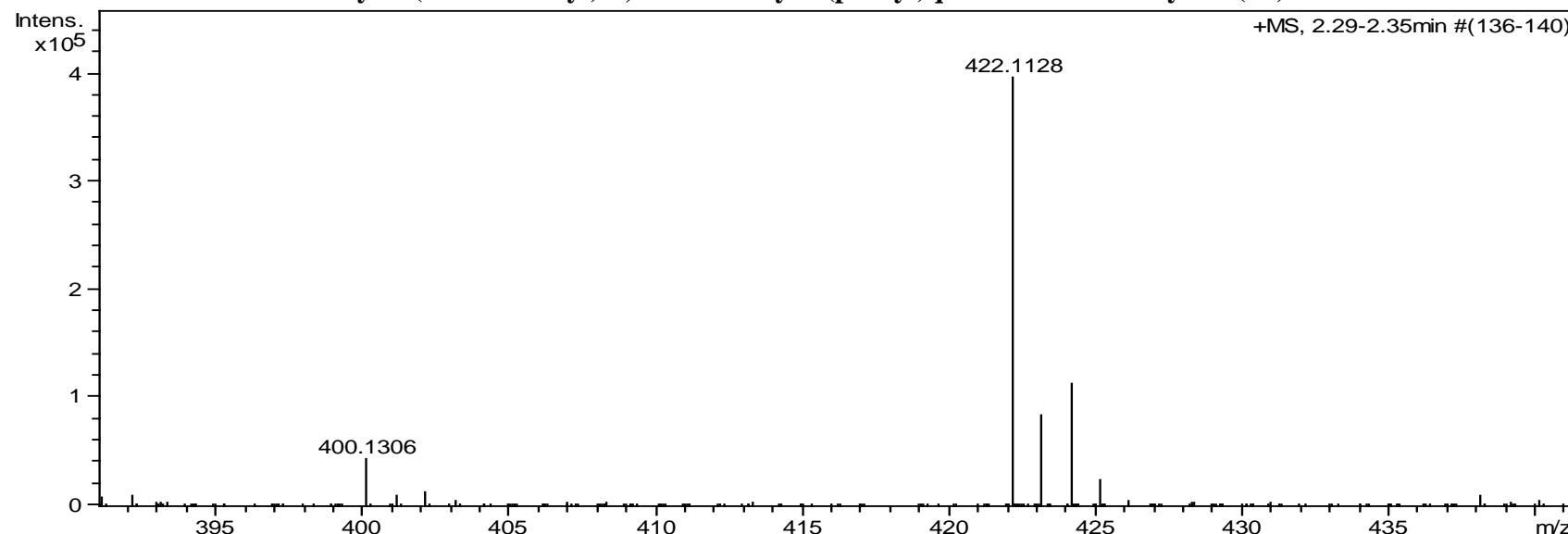
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

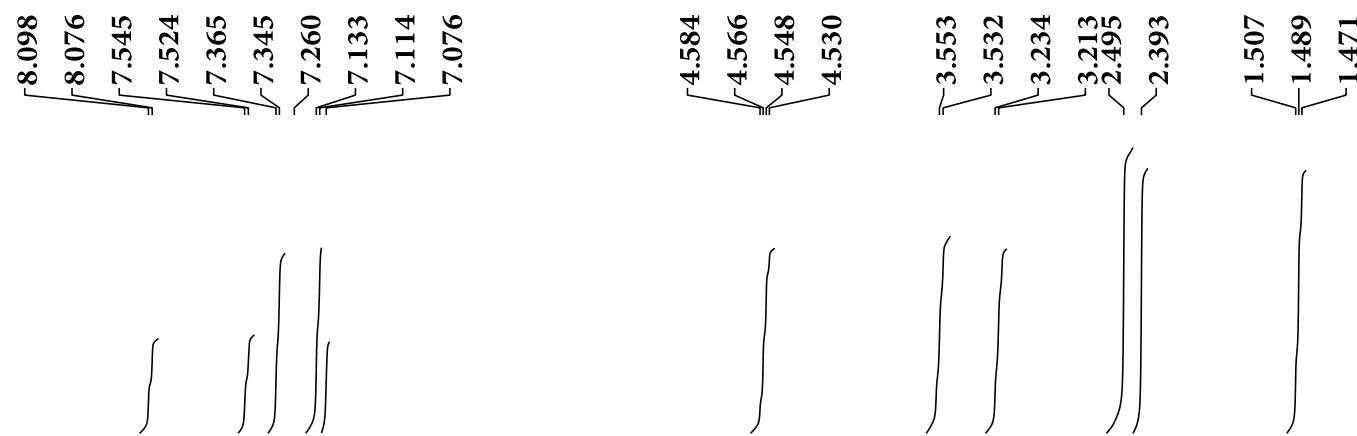
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



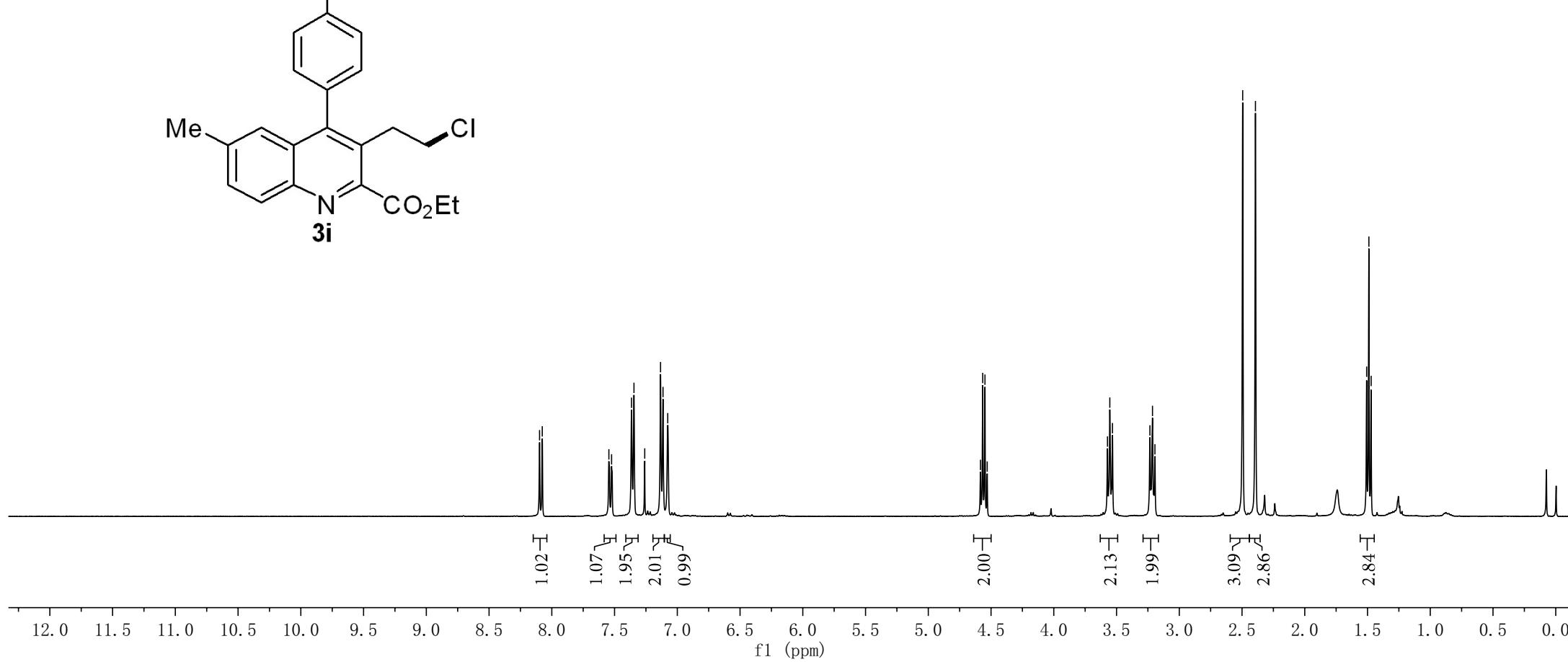
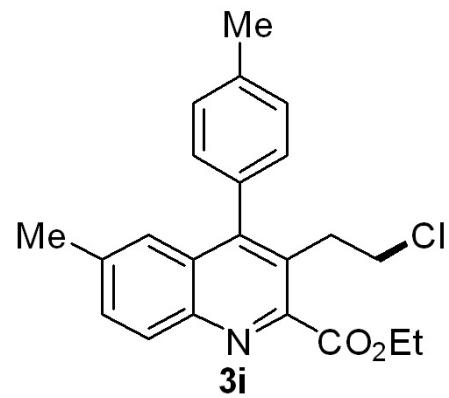


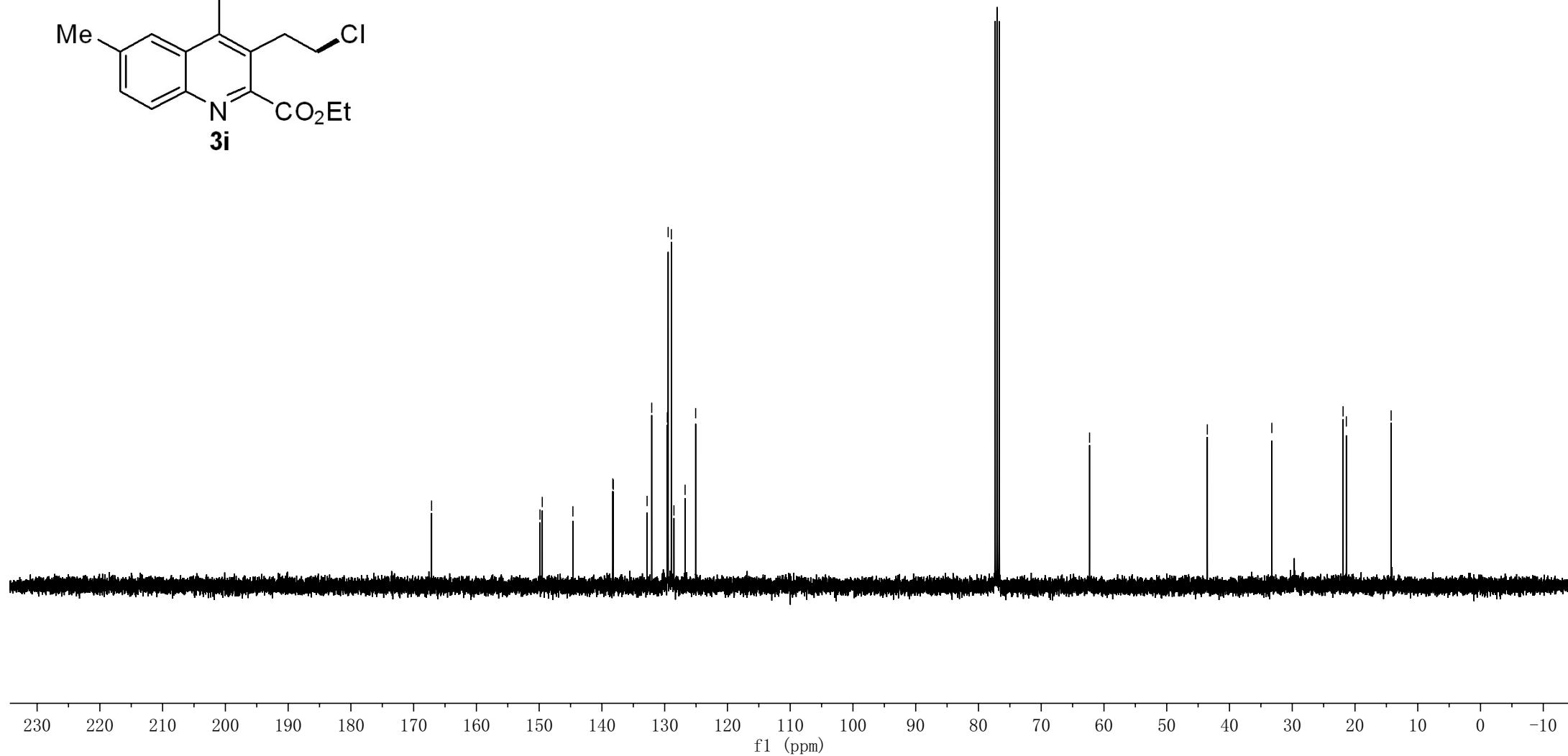
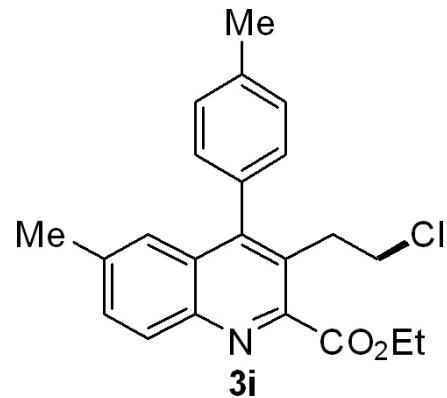
Methyl 3-(2-chloroethyl)-6,8-dimethoxy-4-(p-tolyl)quinoline-2-carboxylate (**3h**)

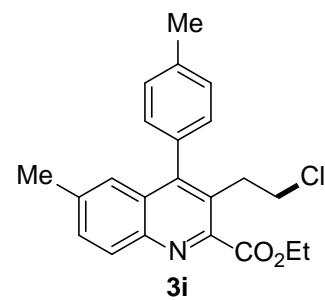




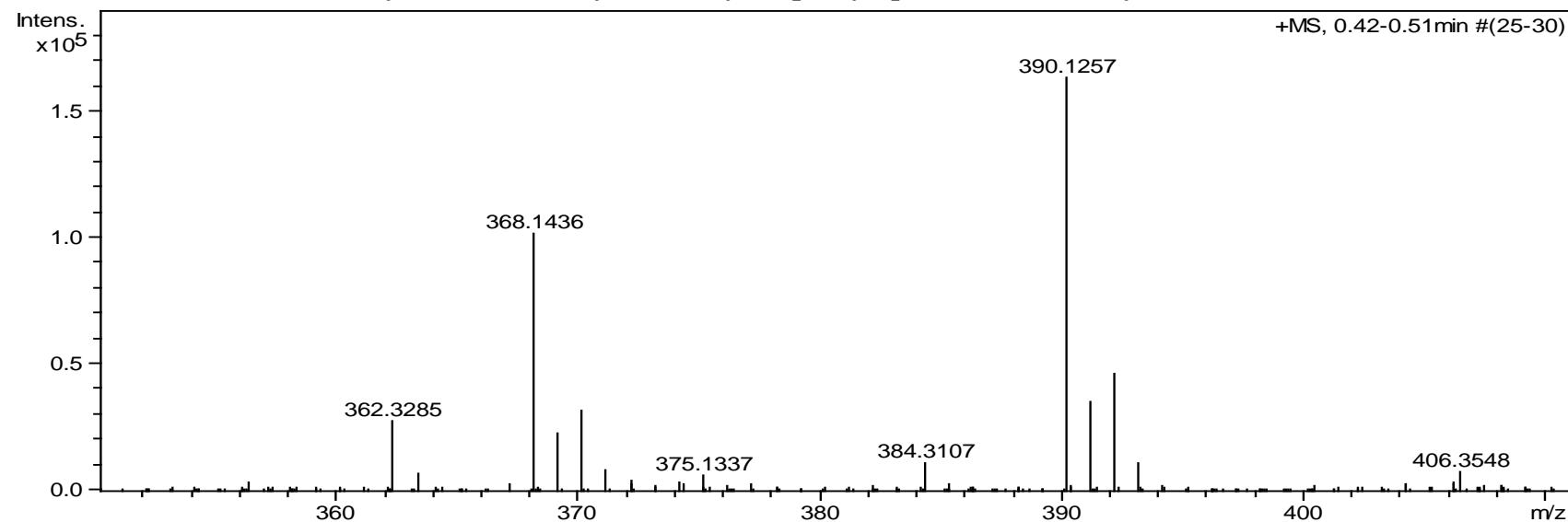
$^1\text{H}$  NMR (400M,  $\text{CDCl}_3$ )

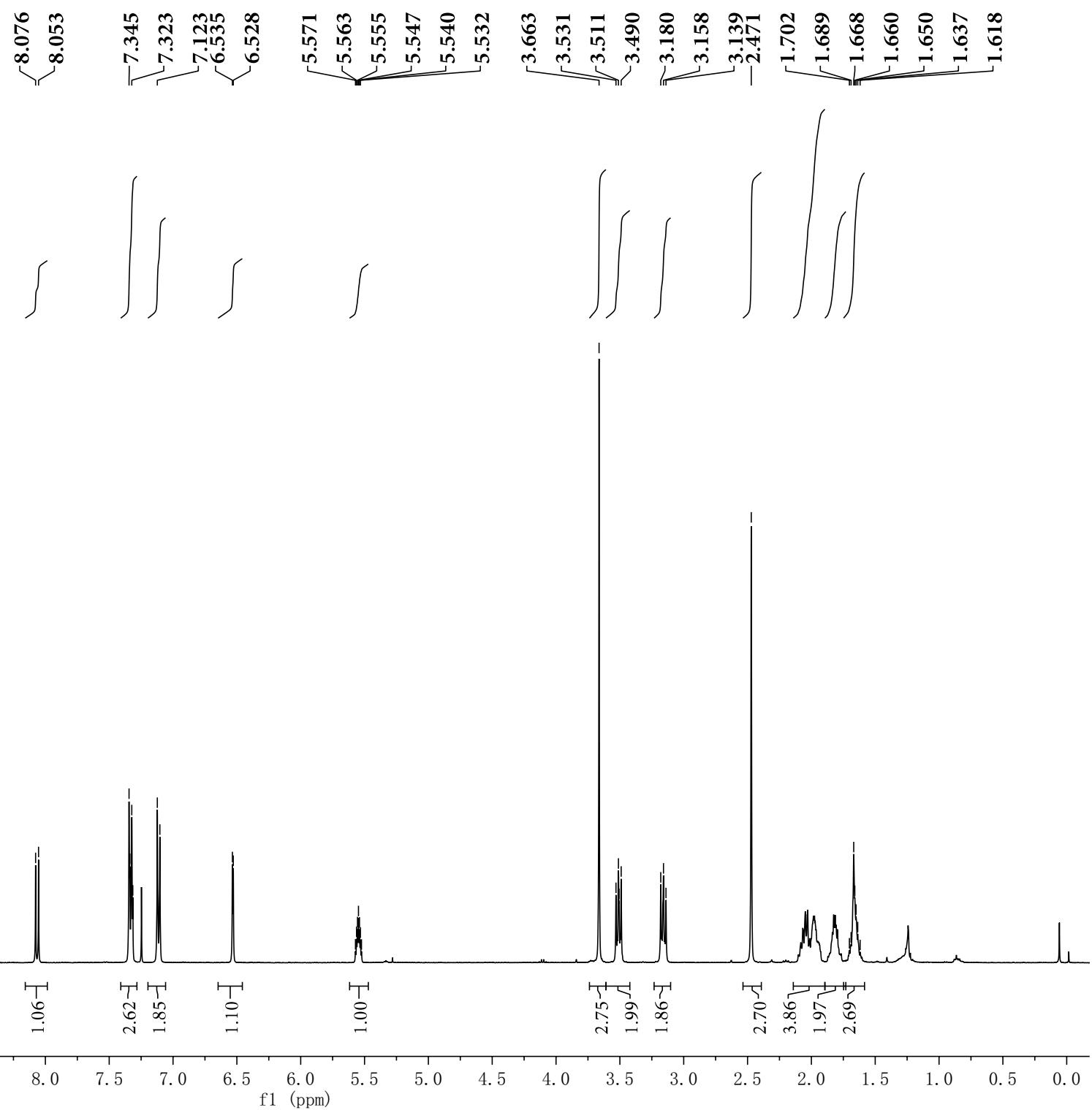
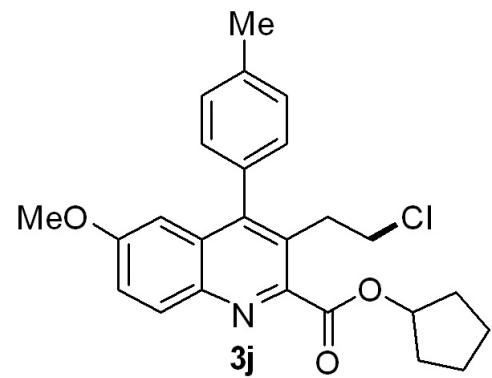


$^{13}\text{C}$  NMR (100M,  $\text{CDCl}_3$ )

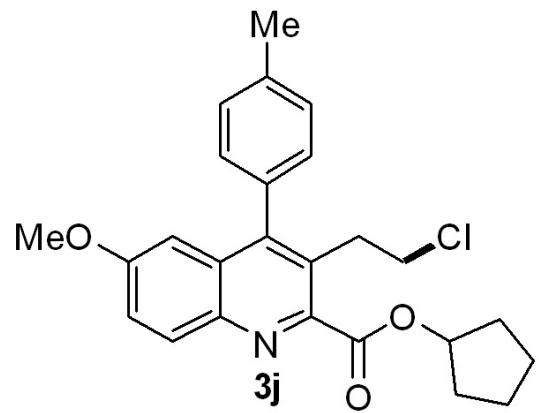


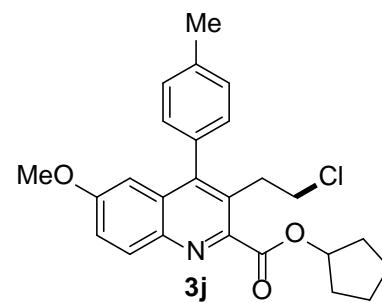
**Ethyl 3-(2-chloroethyl)-6-methyl-4-(p-tolyl)quinoline-2-carboxylate (3i)**



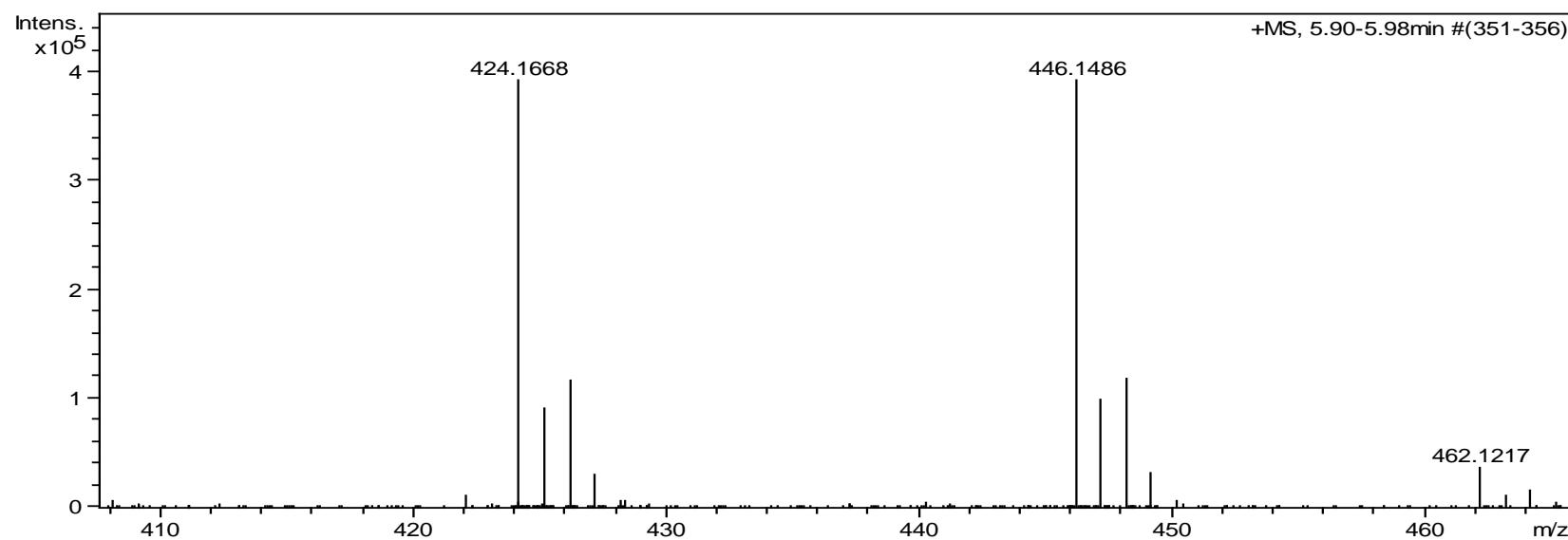
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

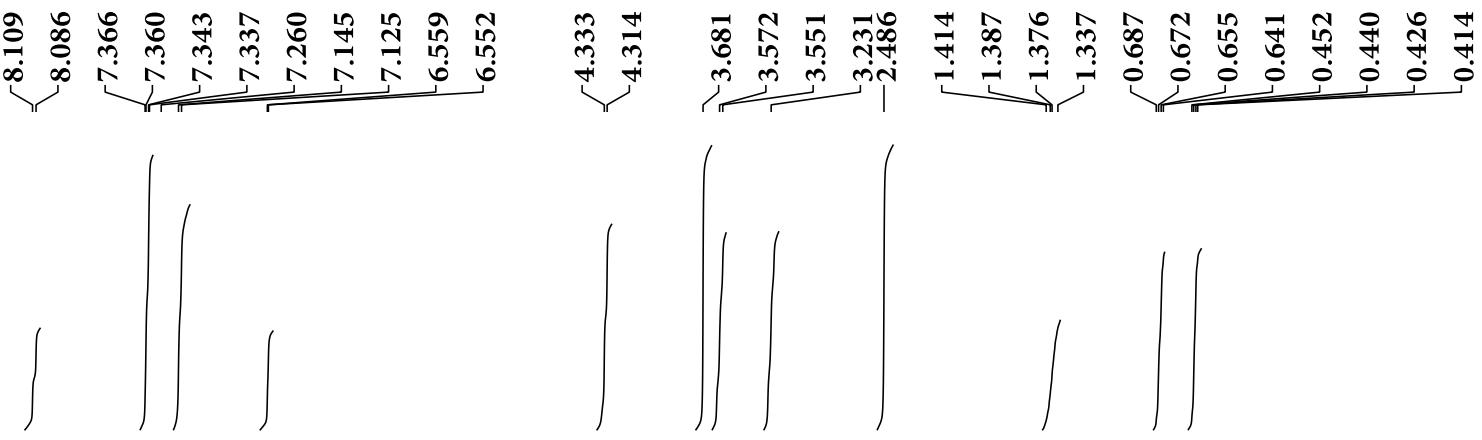
$^{13}\text{C}$  NMR (100M,  $\text{CDCl}_3$ )



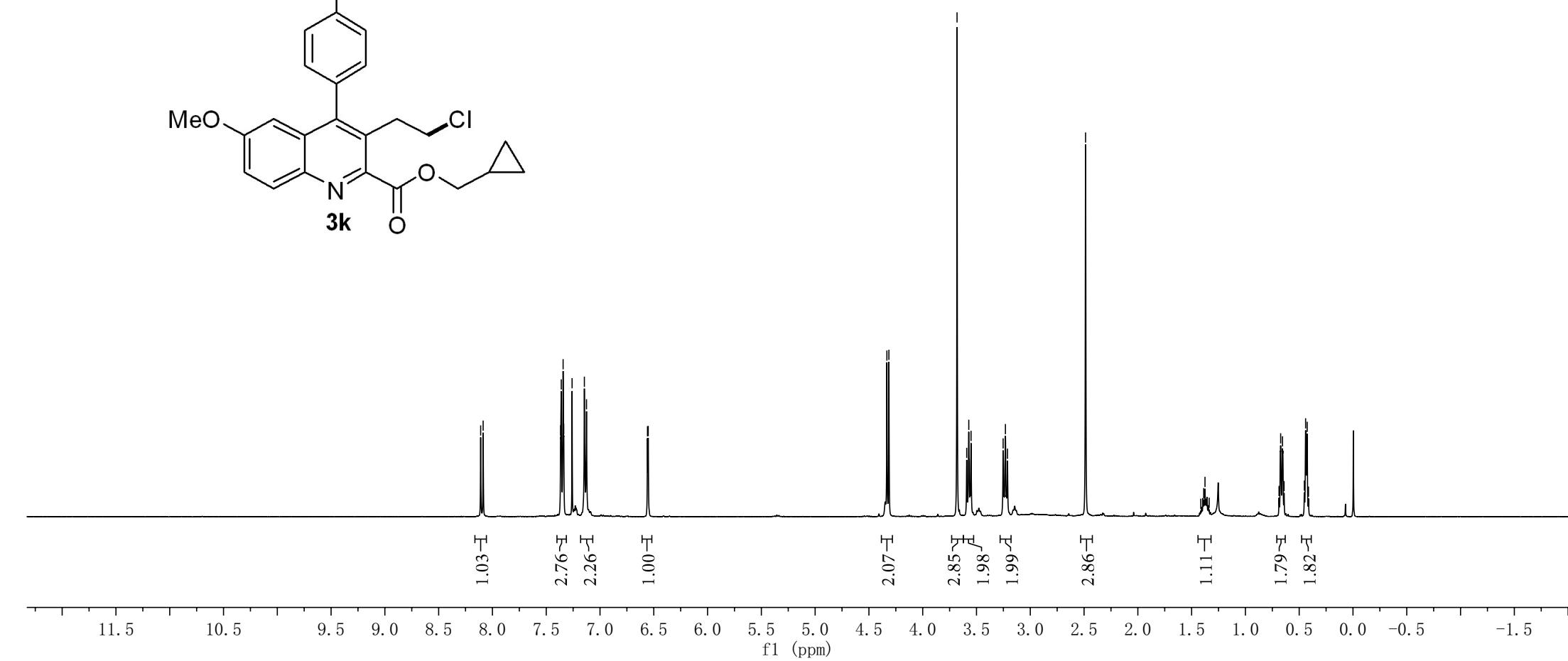
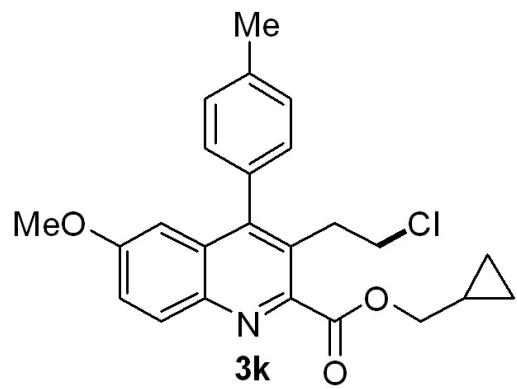


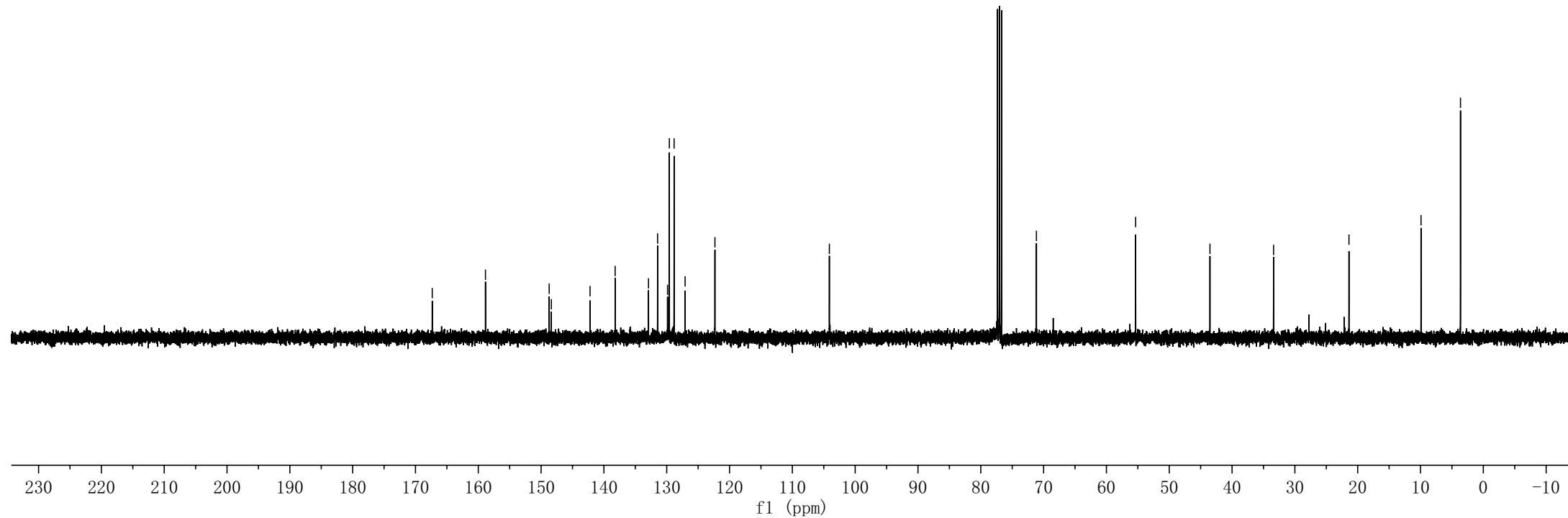
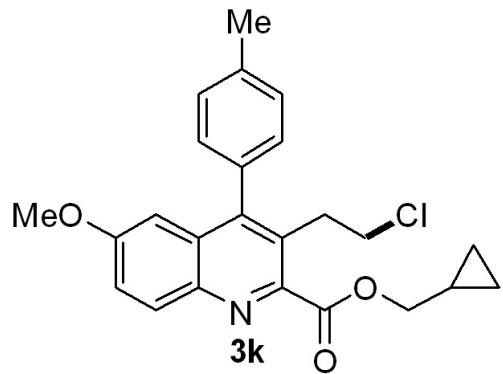
**Cyclopentyl 3-(2-chloroethyl)-6-methoxy-4-(p-tolyl)quinoline-2-carboxylate (3j)**

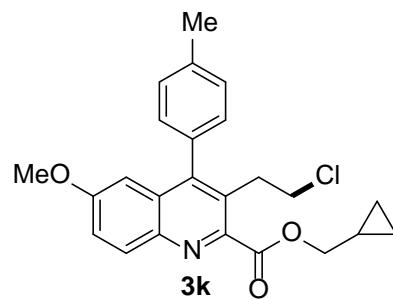




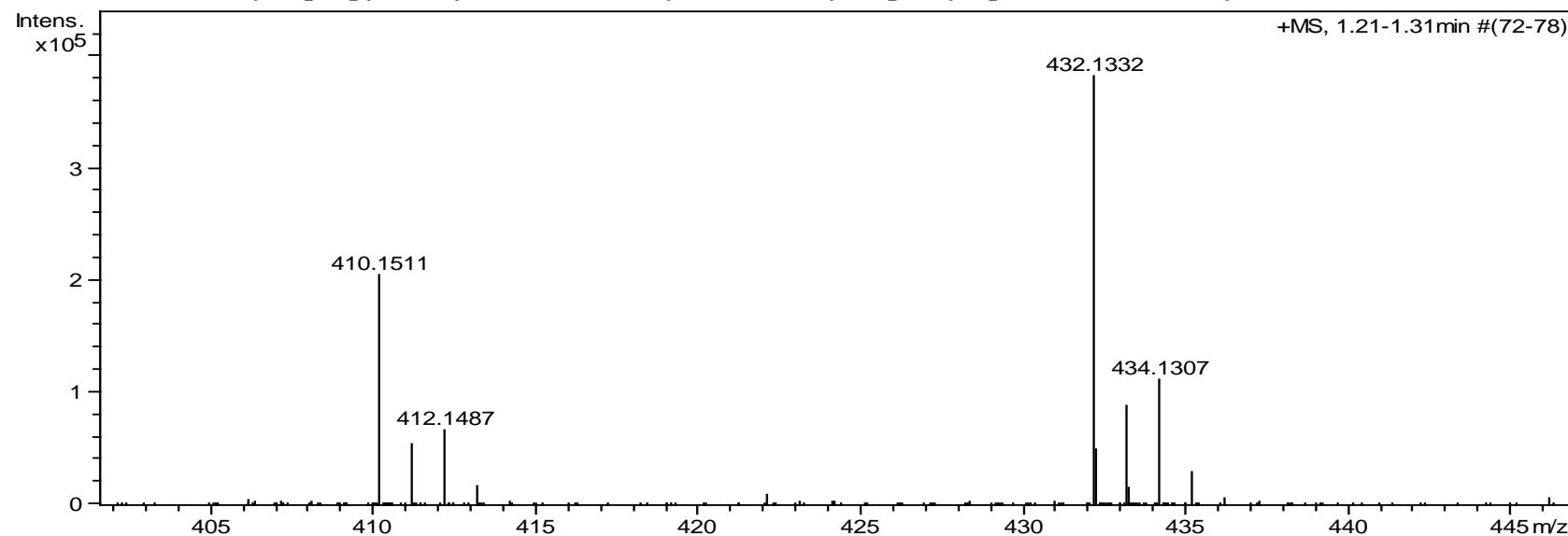
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

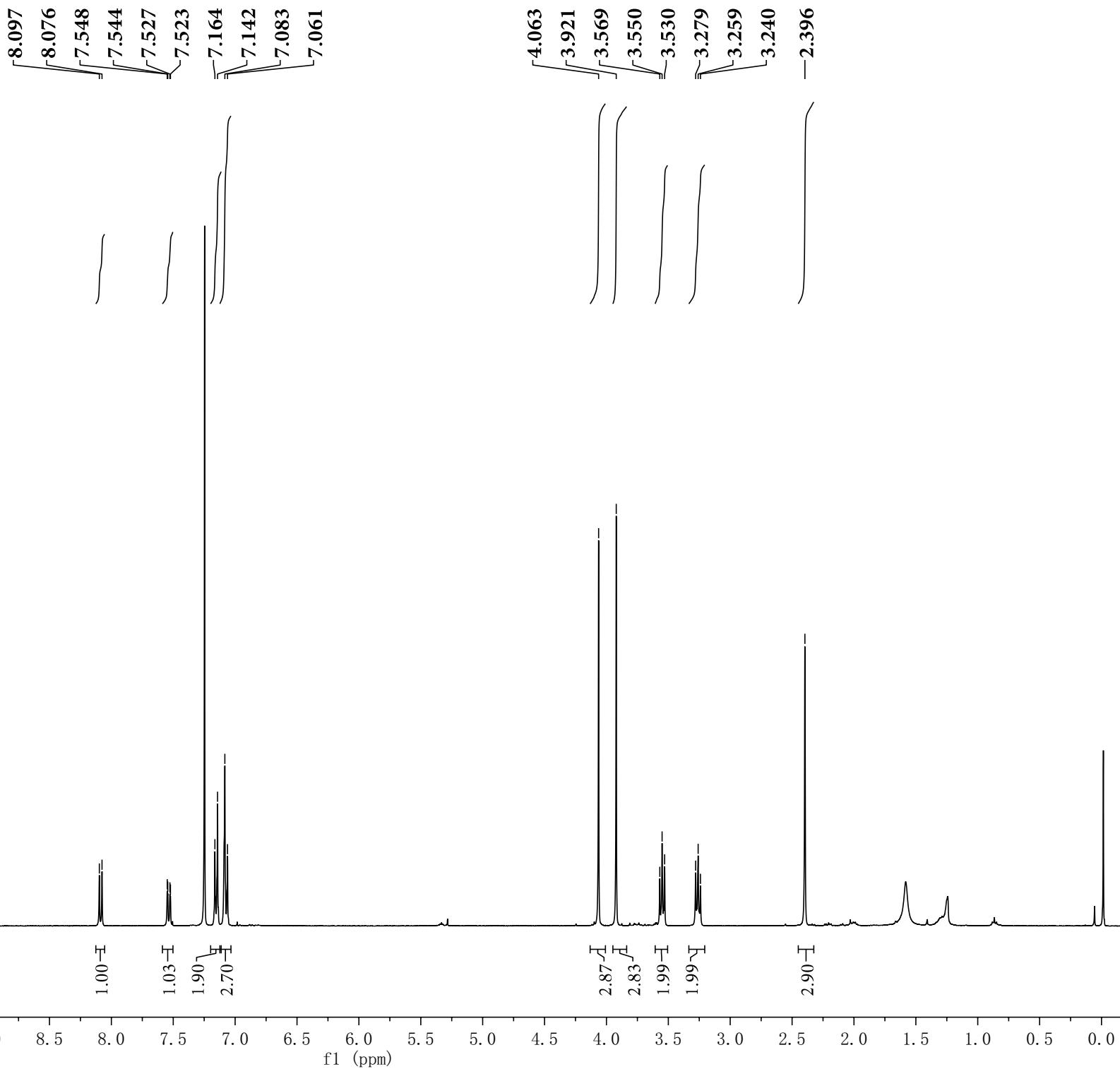
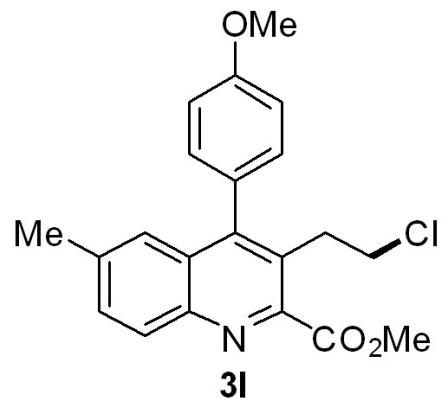


<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)

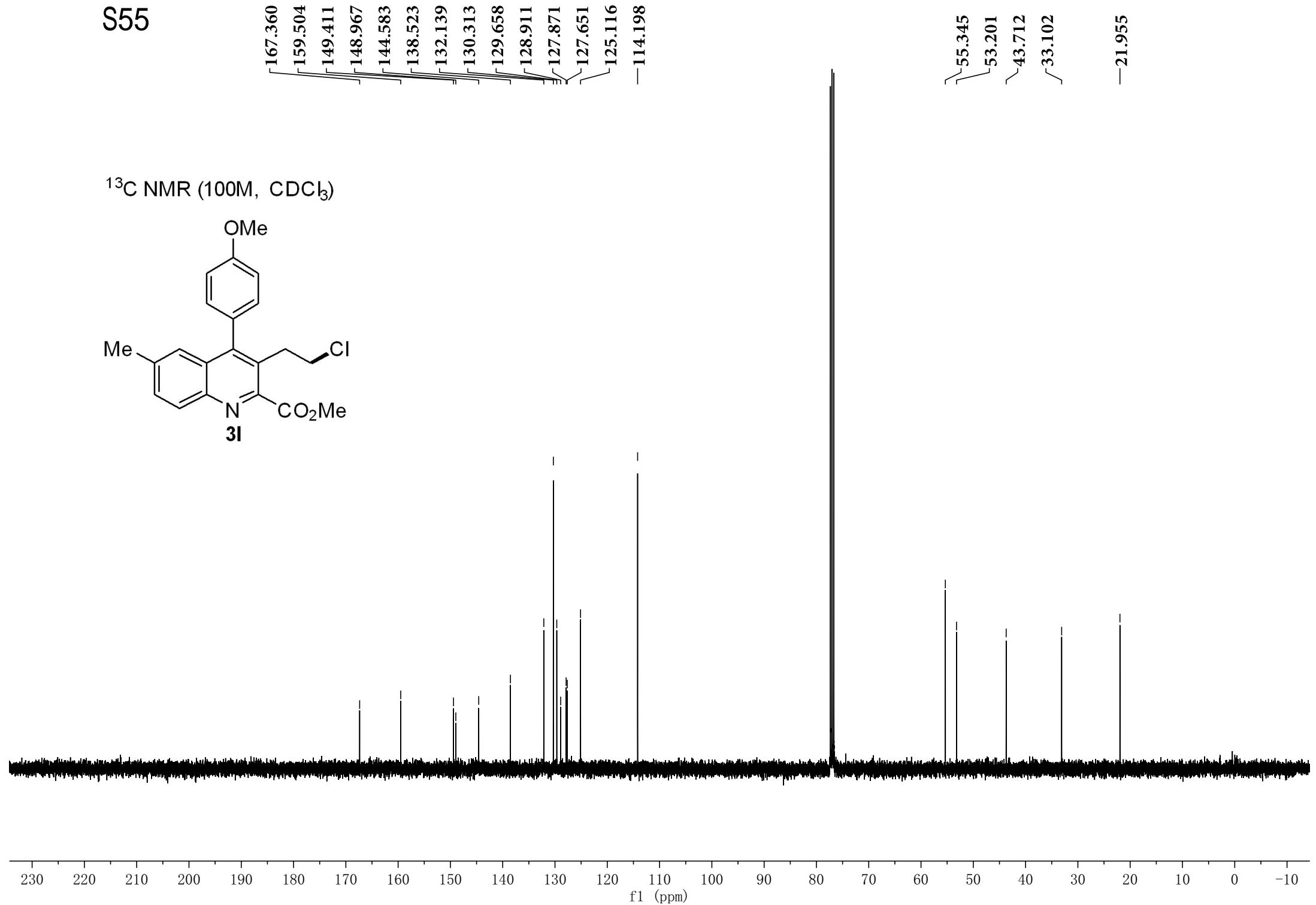
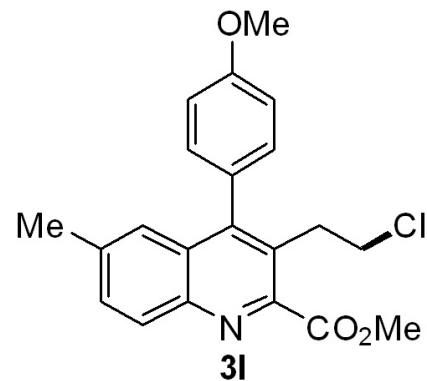


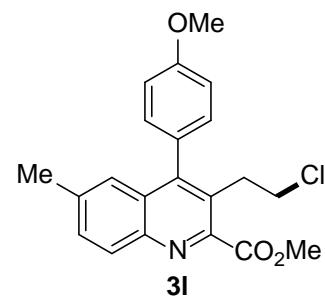
**Cyclopropylmethyl 3-(2-chloroethyl)-6-methoxy-4-(p-tolyl)quinoline-2-carboxylate (3k)**



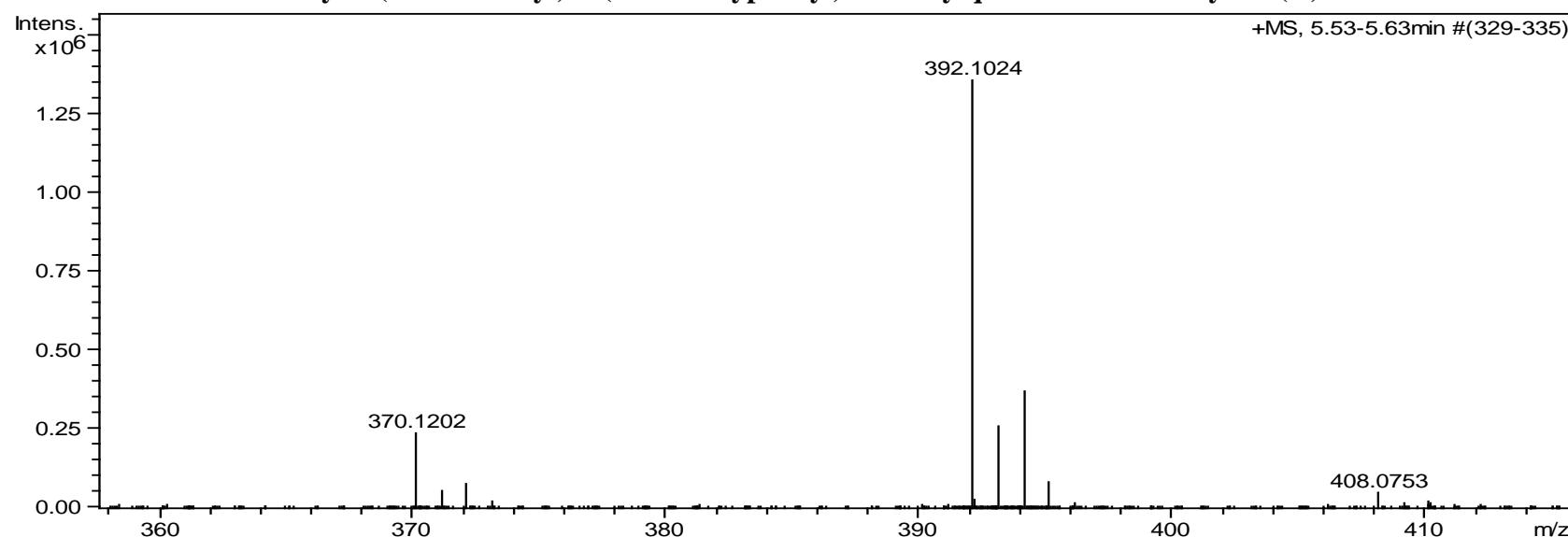
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

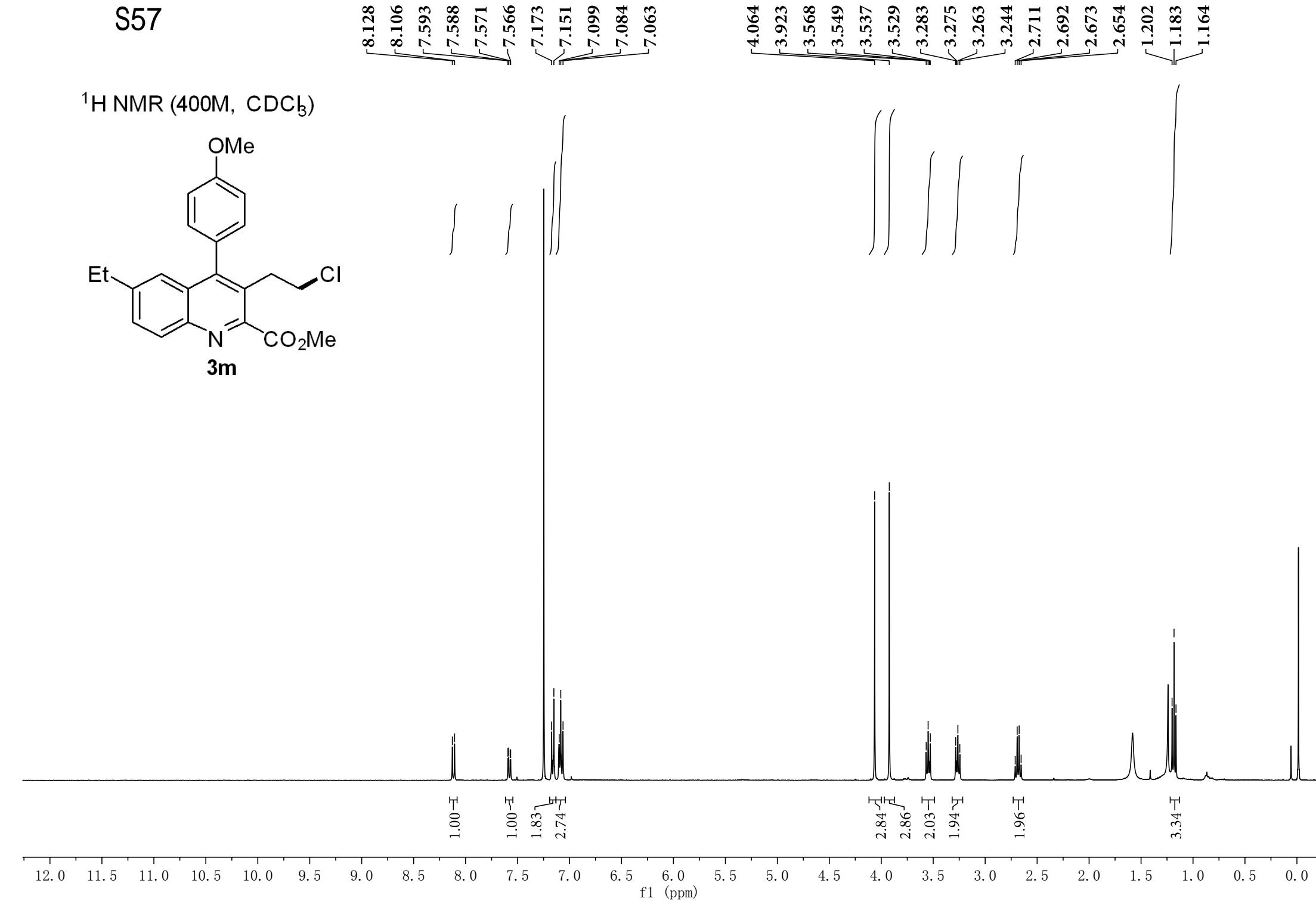
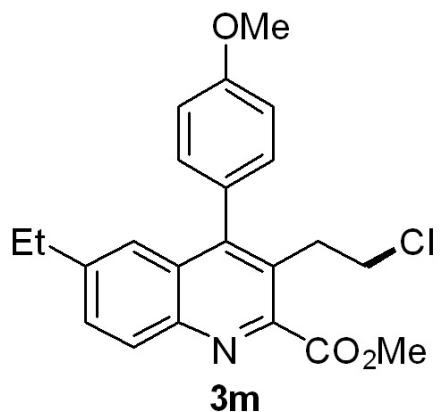
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



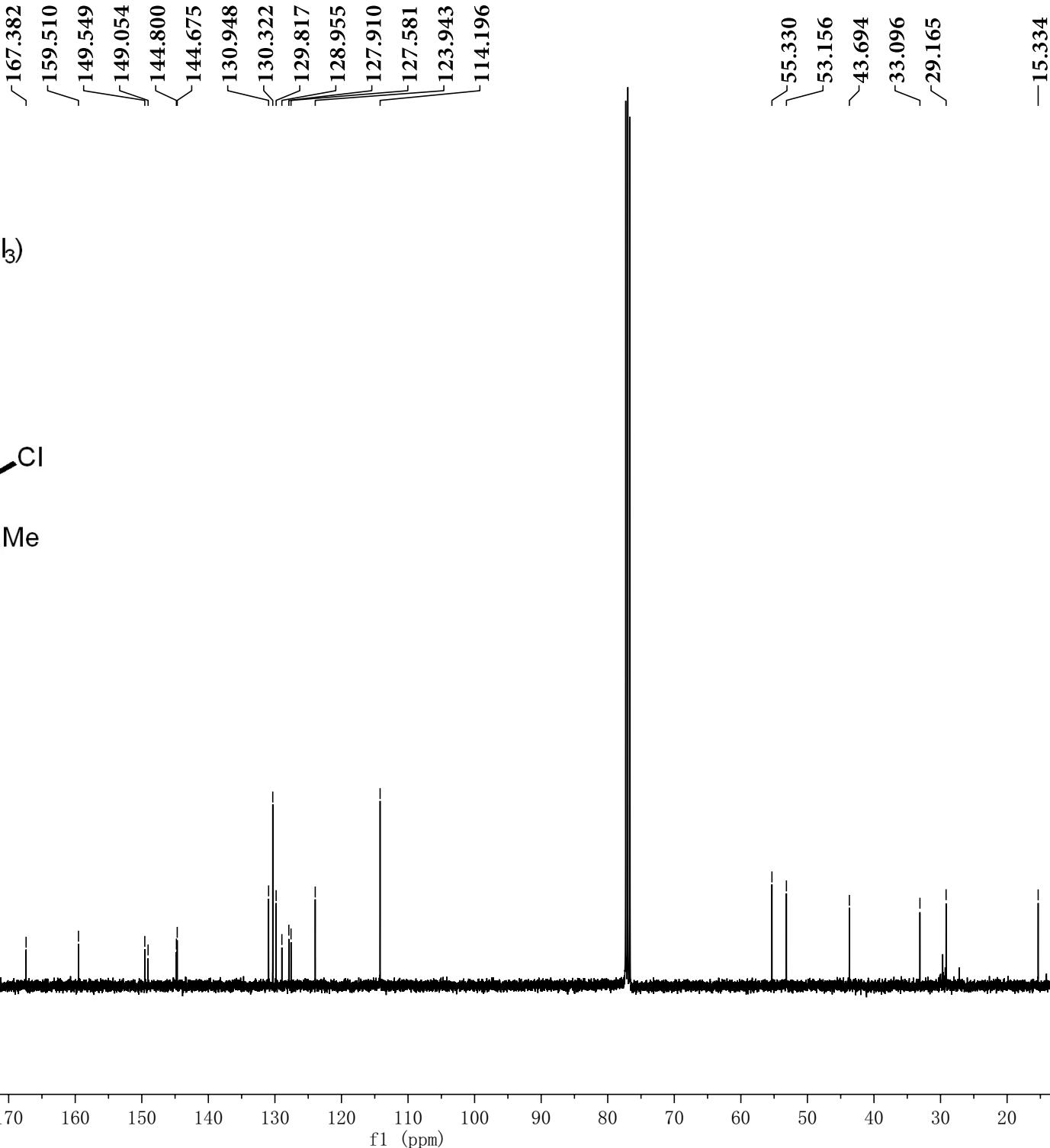
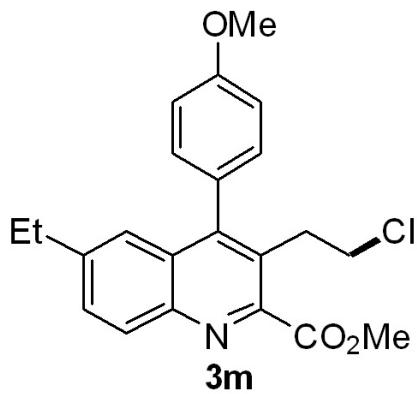


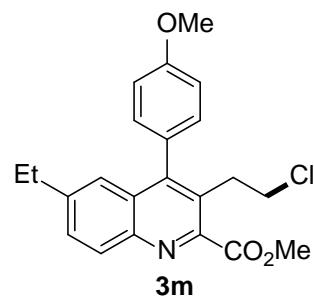
Methyl 3-(2-chloroethyl)-4-(4-methoxyphenyl)-6-methylquinoline-2-carboxylate (**3l**)



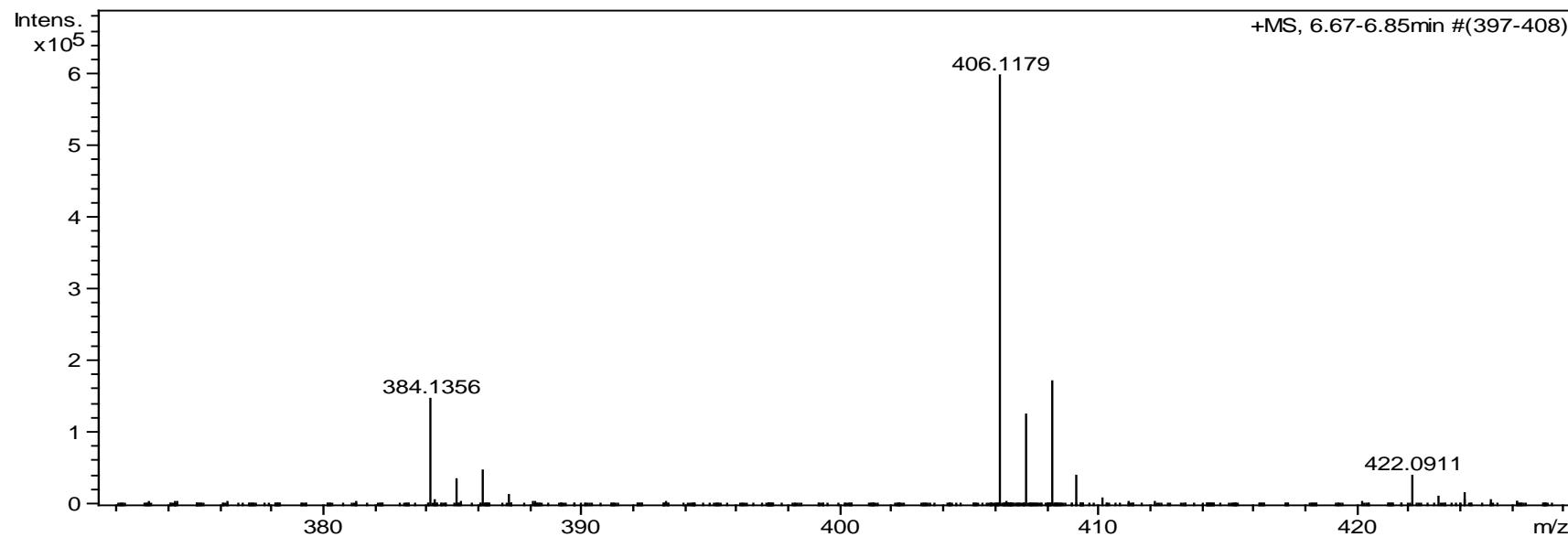


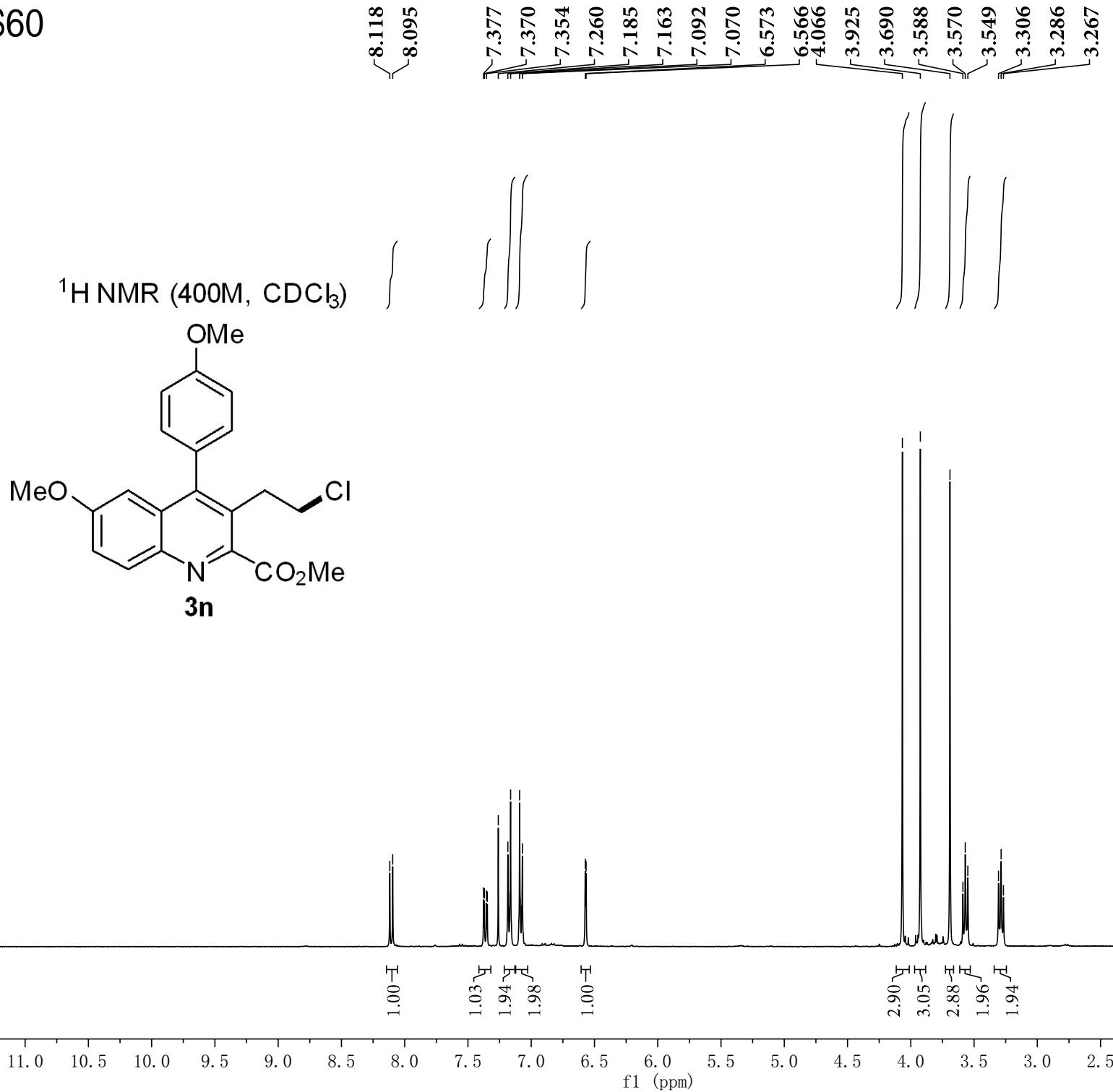
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



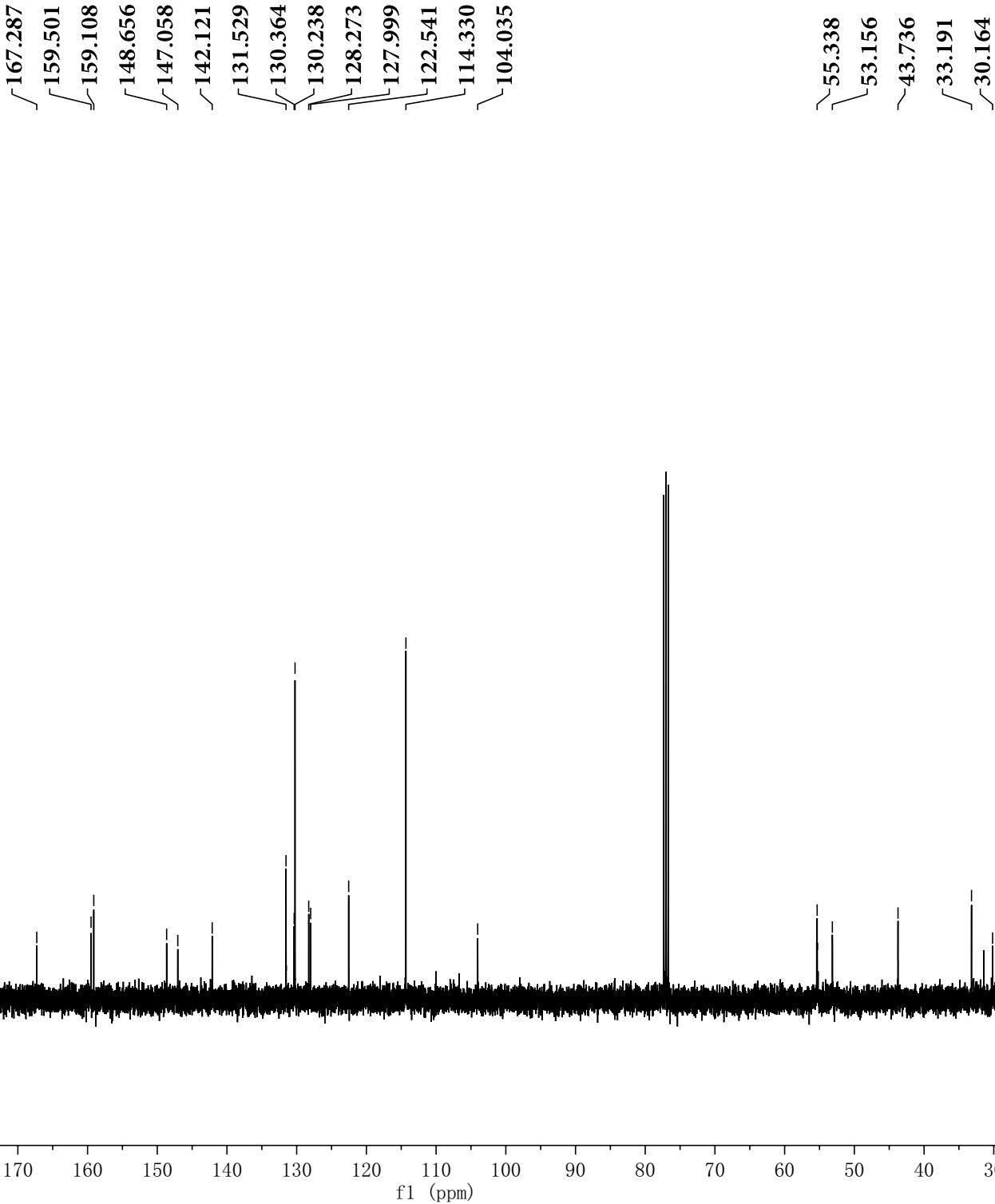
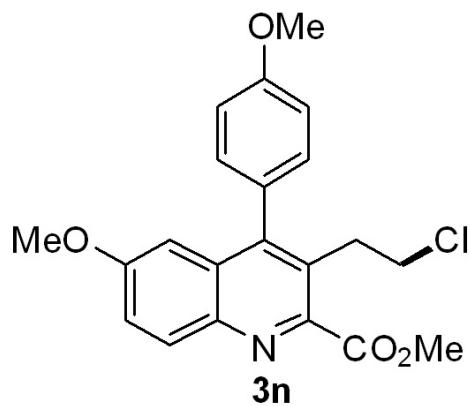


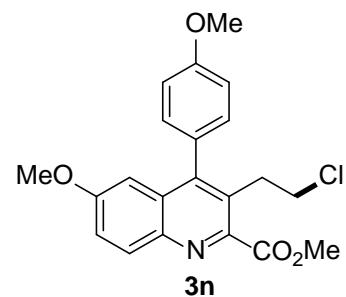
**Methyl 3-(2-chloroethyl)-6-ethyl-4-(4-methoxyphenyl)quinoline-2-carboxylate (3m)**



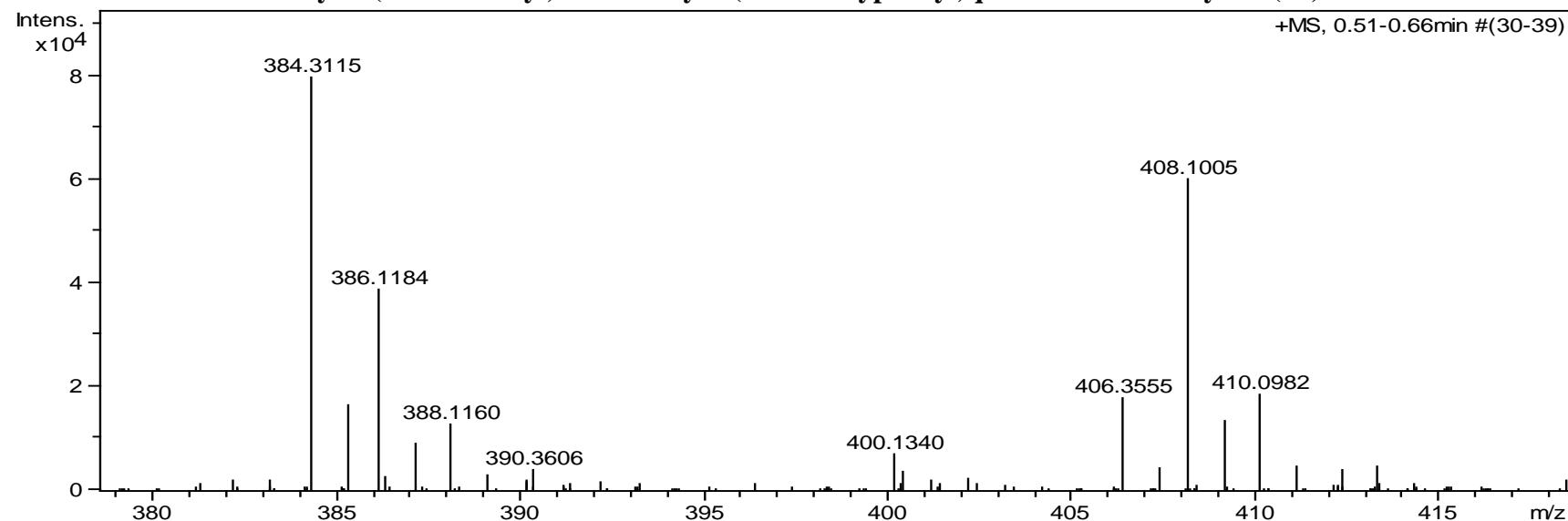


S61  
 $^{13}\text{C}$  NMR (100M,  $\text{CDCl}_3$ )

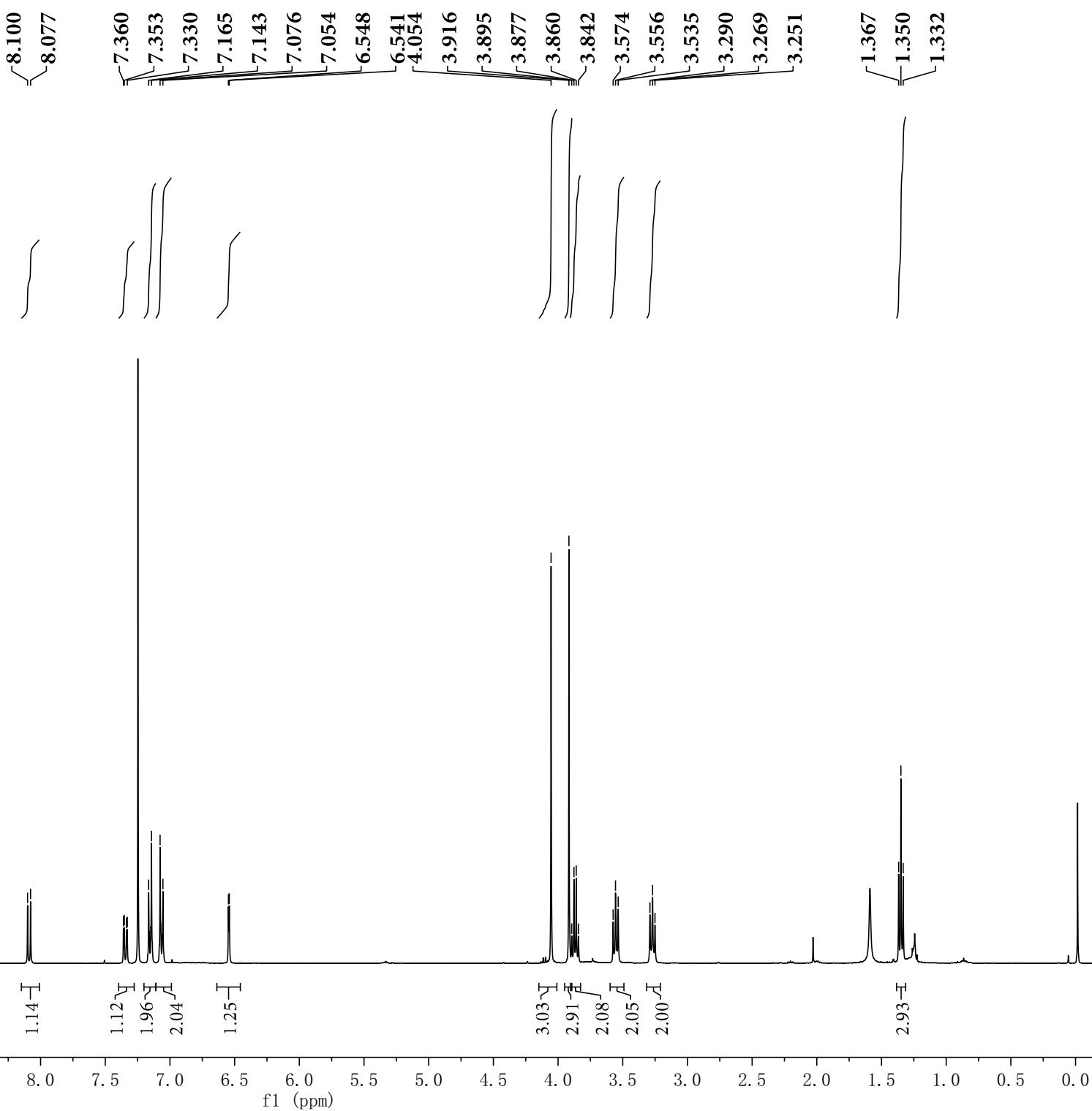
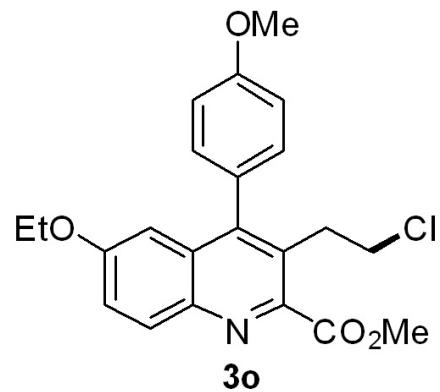




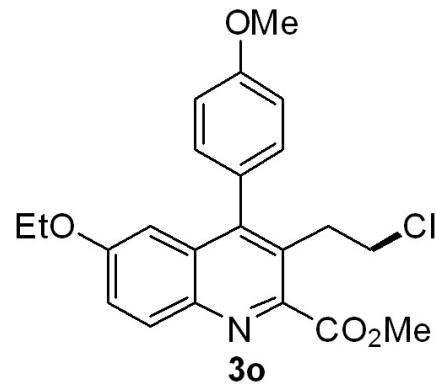
Methyl 3-(2-chloroethyl)-6-methoxy-4-(4-methoxyphenyl)quinoline-2-carboxylate (**3n**)

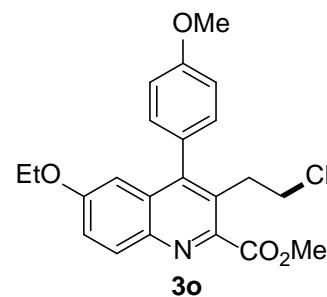


S63  
 $^1\text{H}$  NMR (400M,  $\text{CDCl}_3$ )

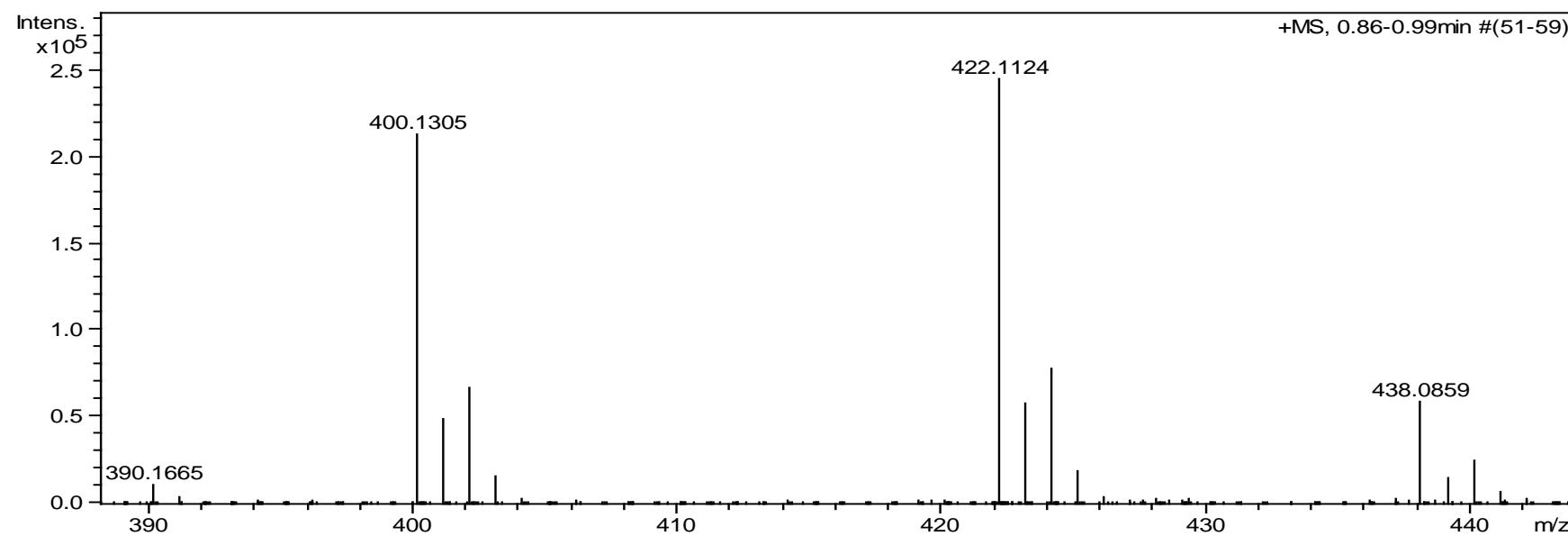


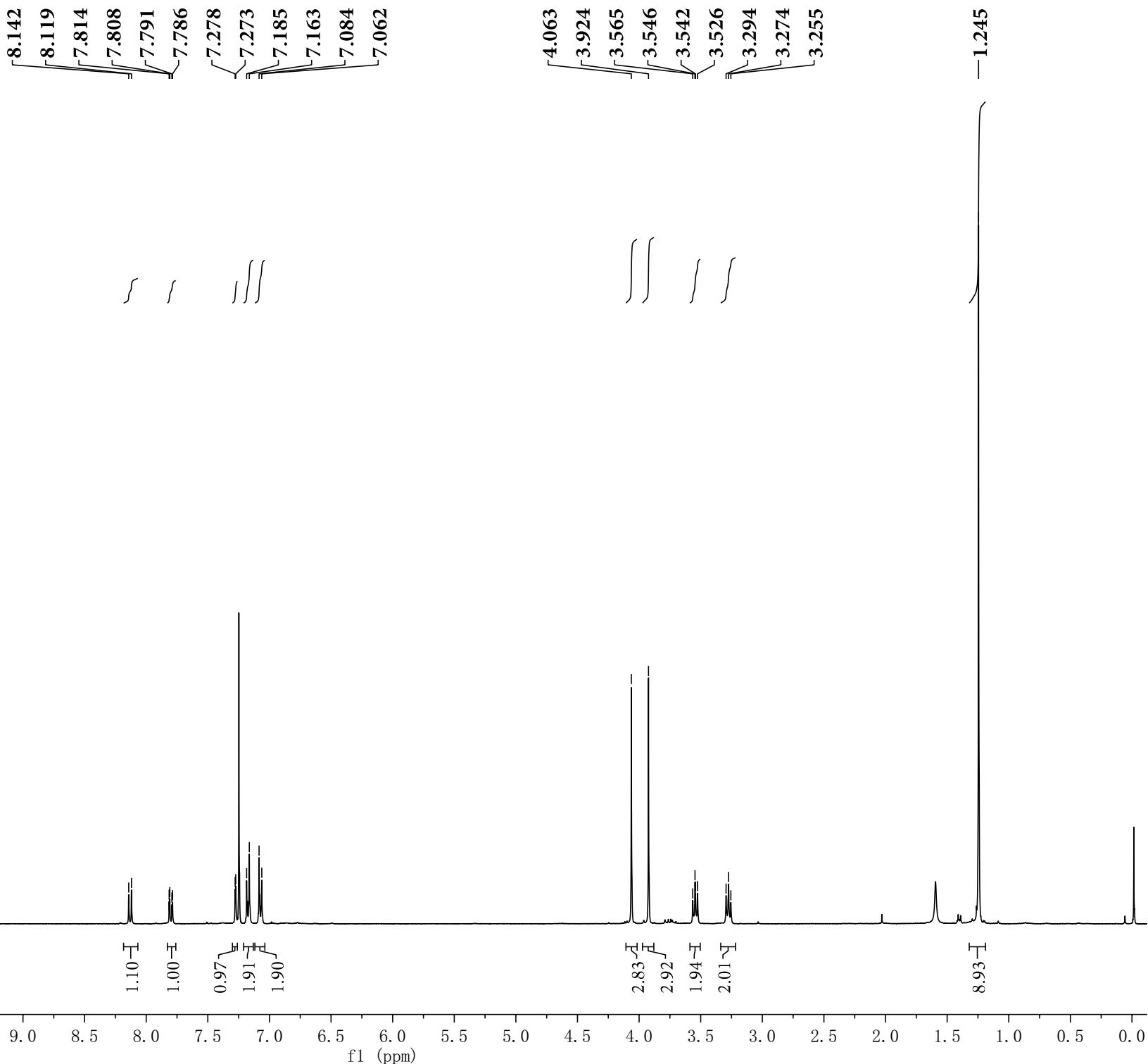
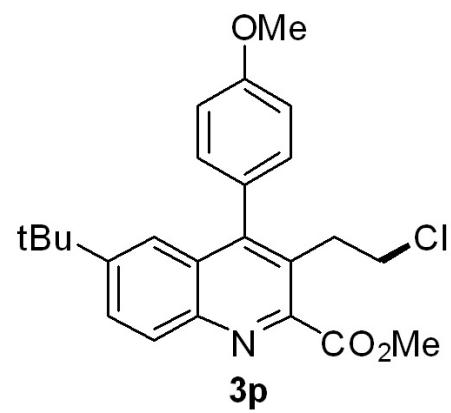
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



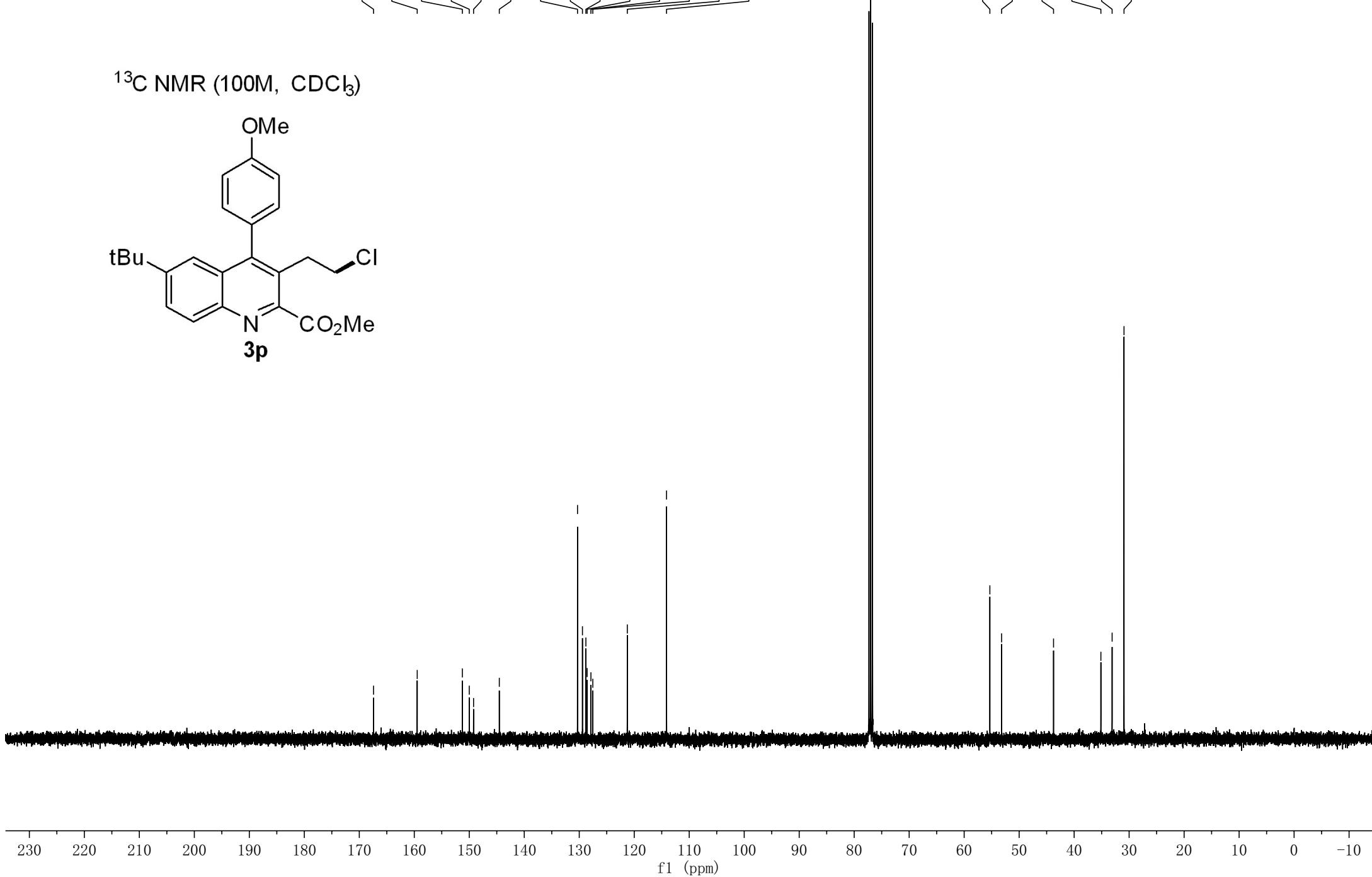
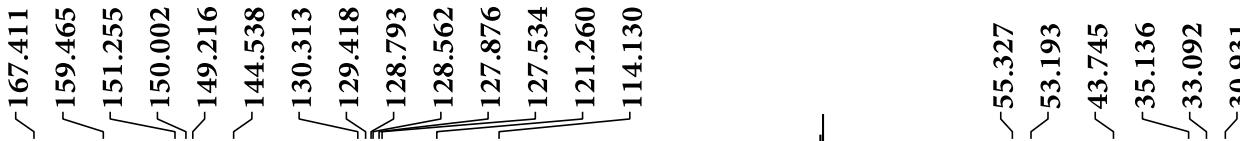
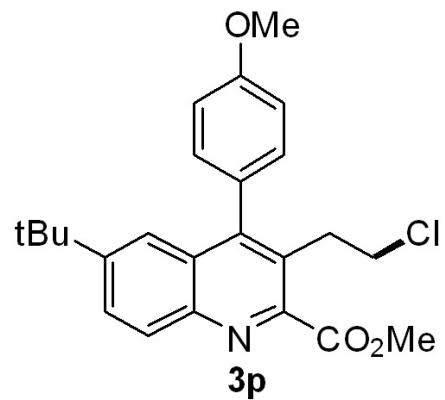


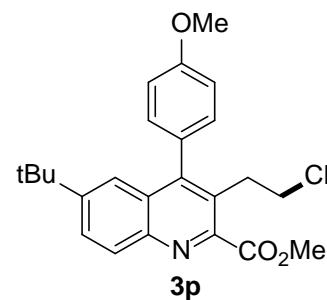
Methyl 3-(2-chloroethyl)-6-ethoxy-4-(4-methoxyphenyl)quinoline-2-carboxylate (**3o**)



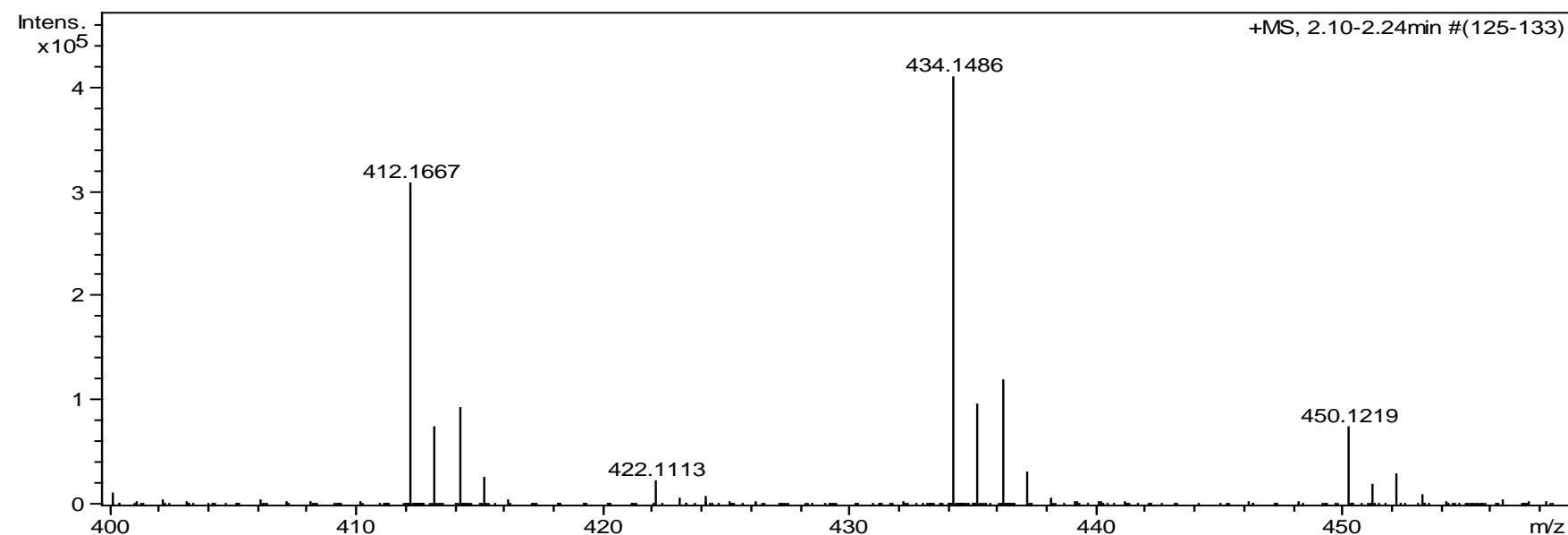
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

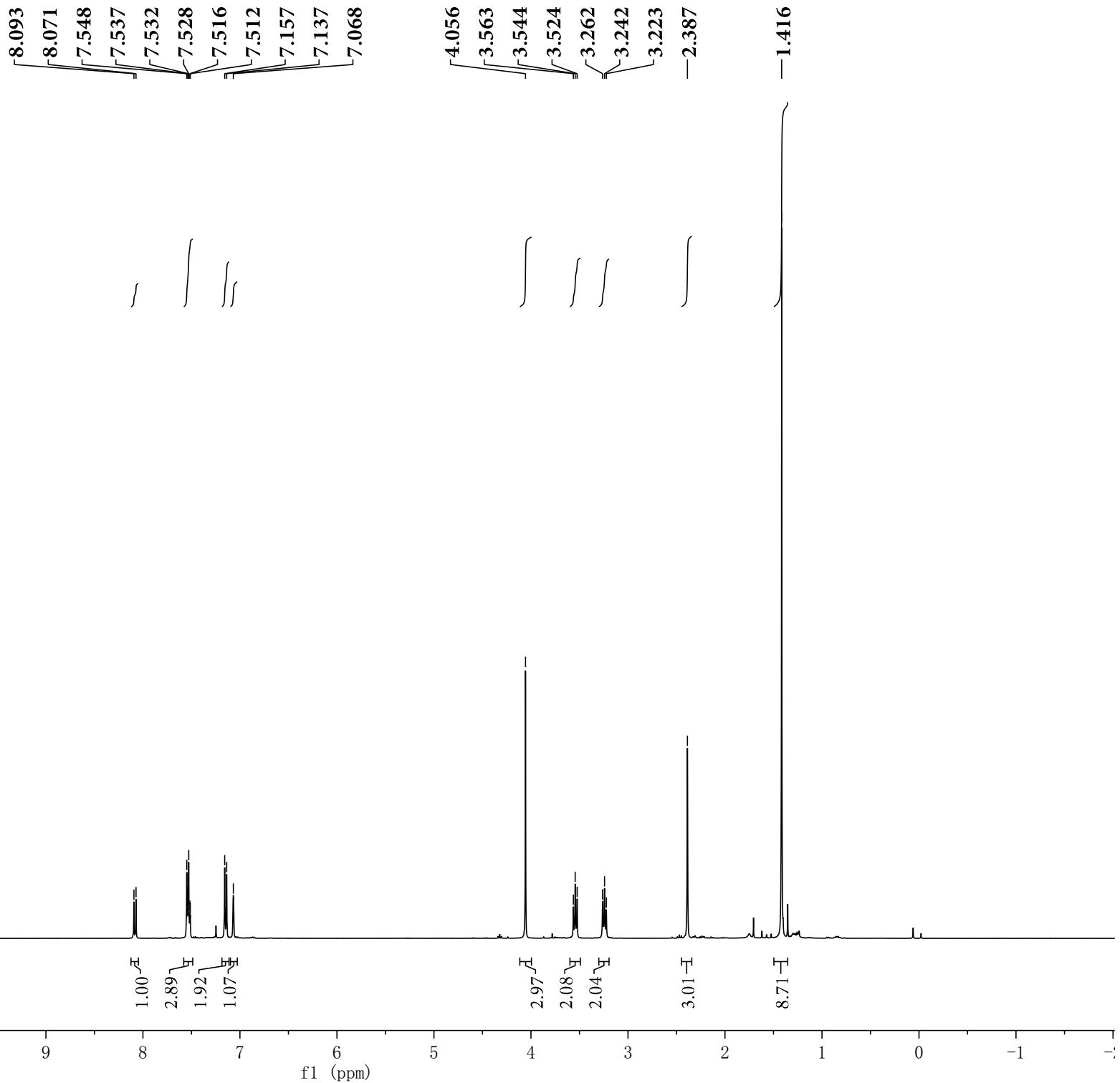
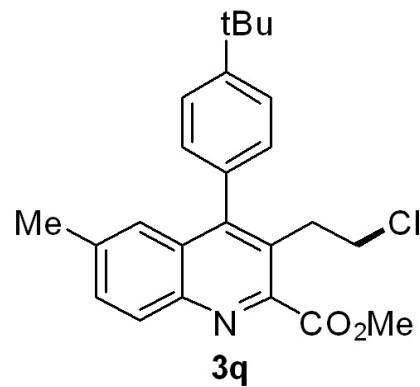
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



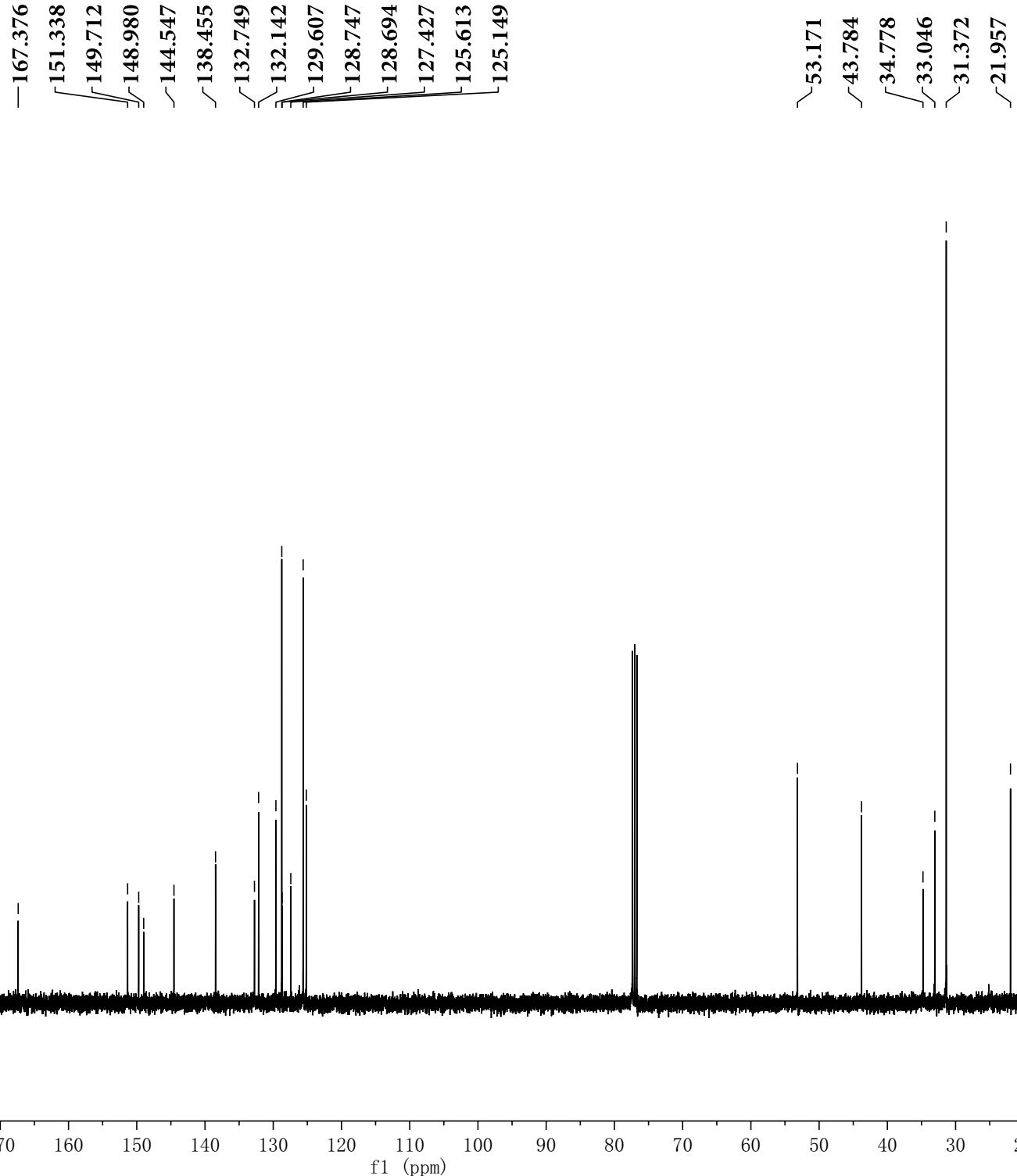
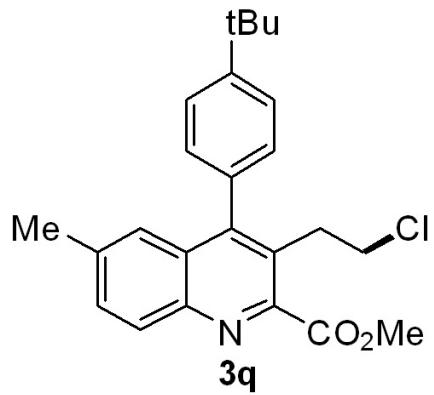


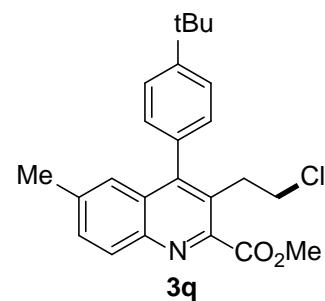
**Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(4-methoxyphenyl)quinoline-2-carboxylate (3p)**



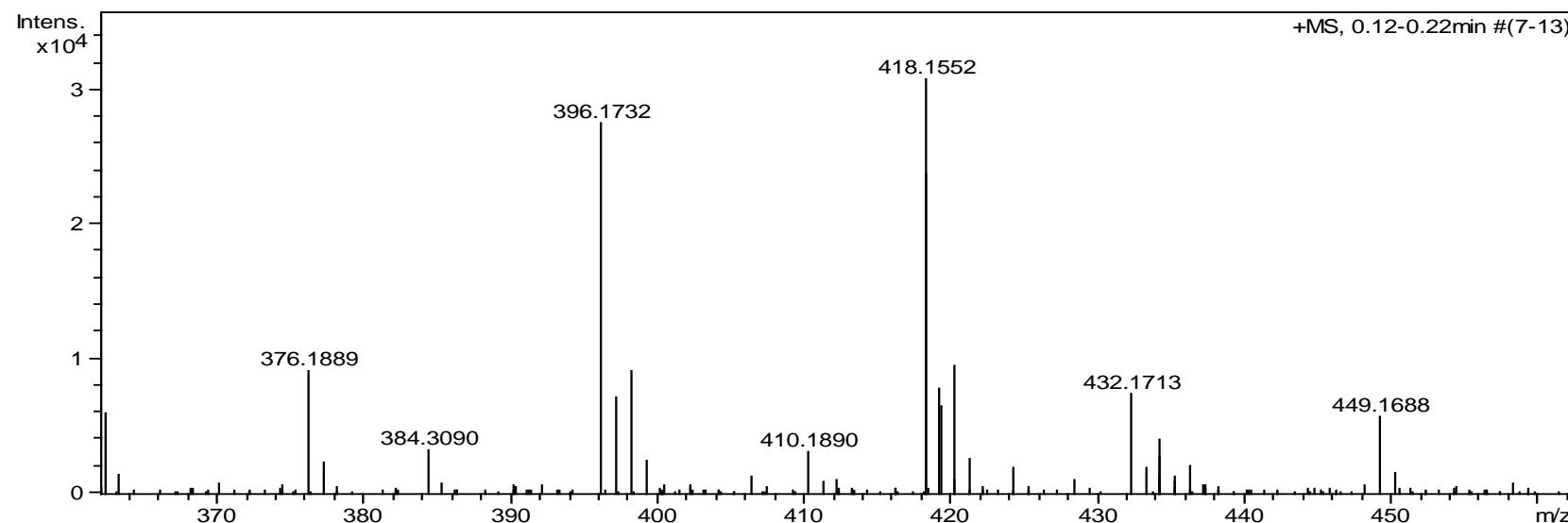
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

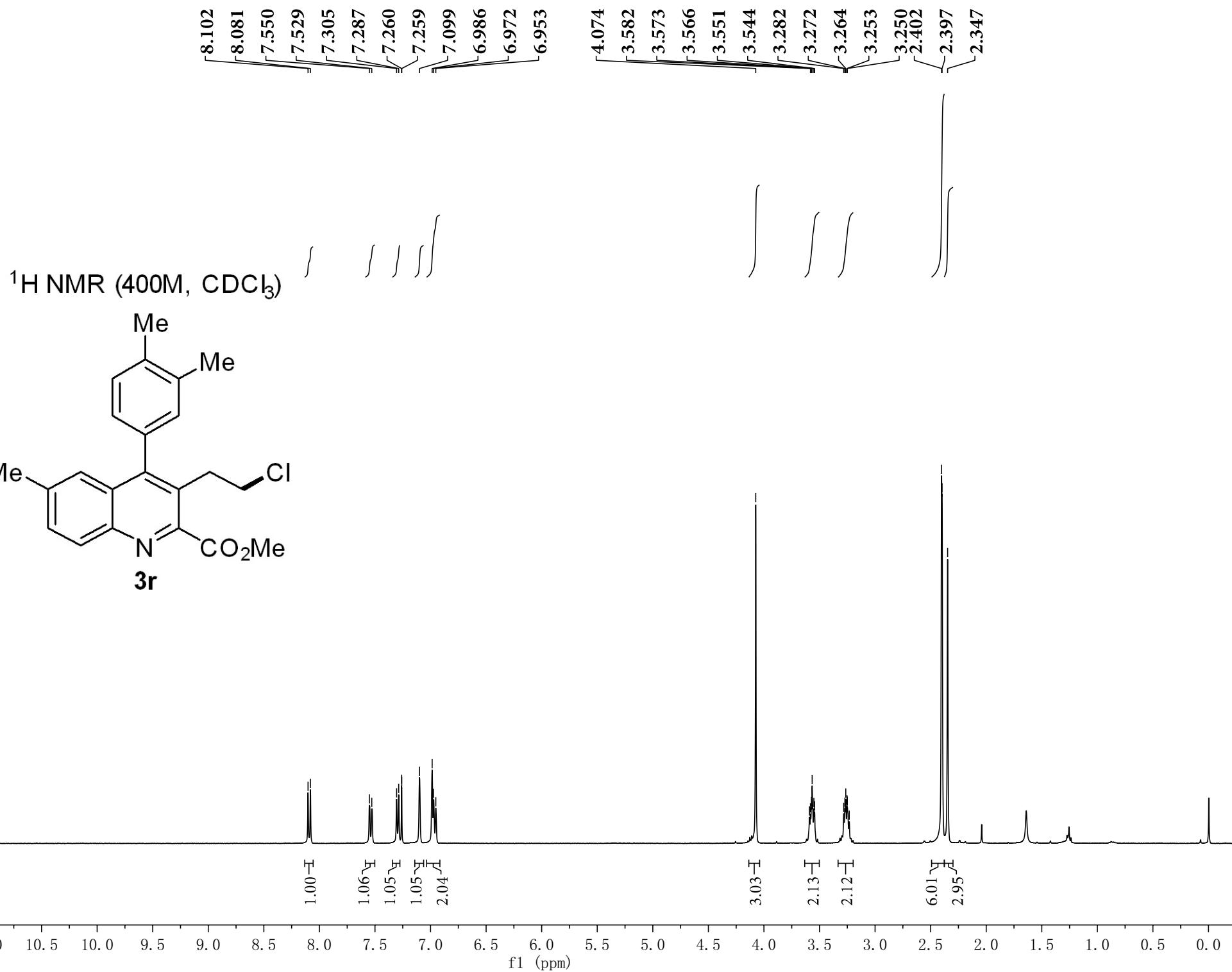
S70  
 $^{13}\text{C}$  NMR (100M,  $\text{CDCl}_3$ )



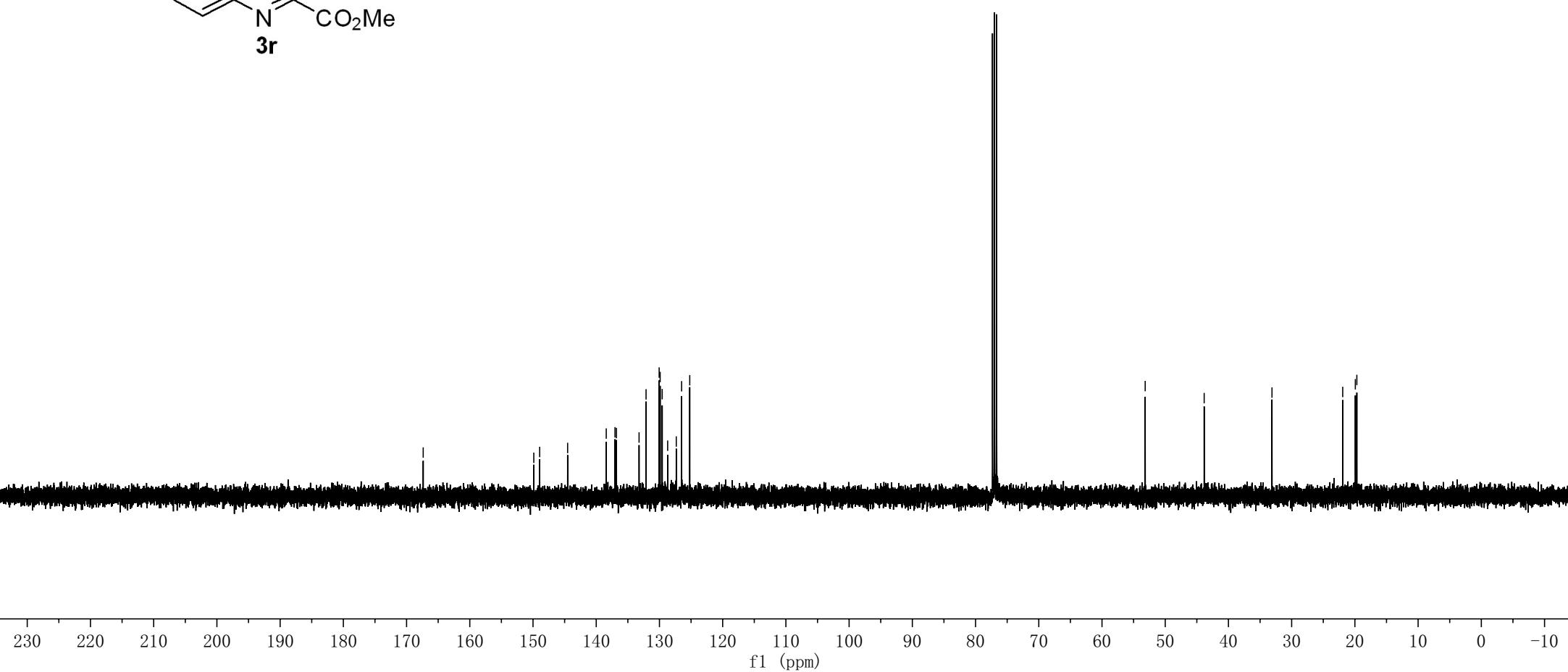
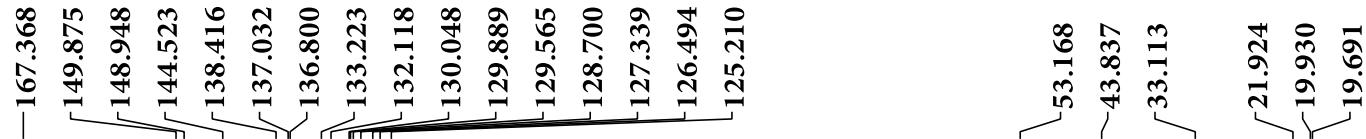
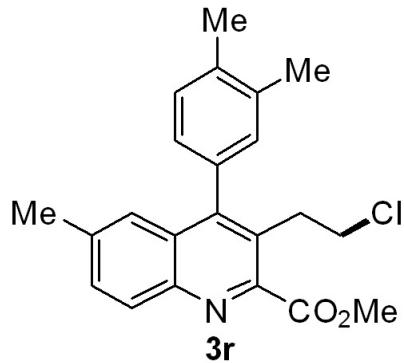


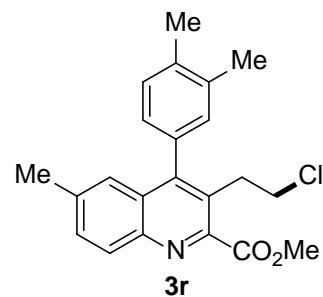
Methyl 4-(4-(tert-butyl)phenyl)-3-(2-chloroethyl)-6-methylquinoline-2-carboxylate (**3q**)



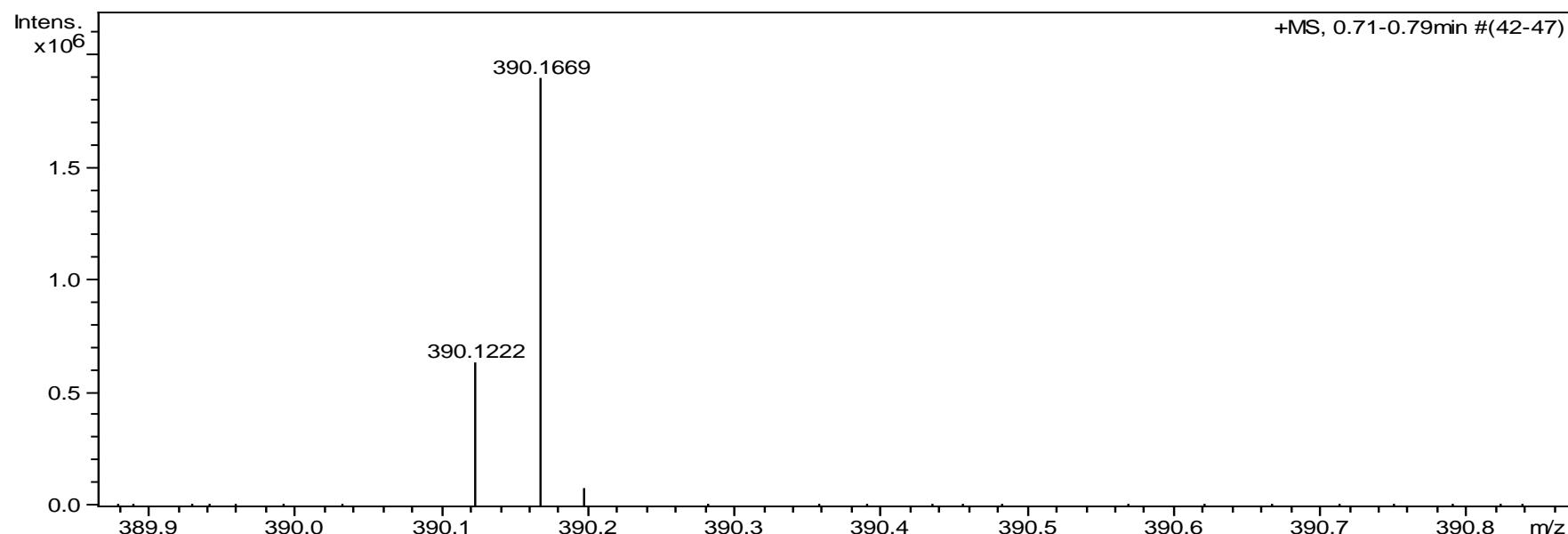


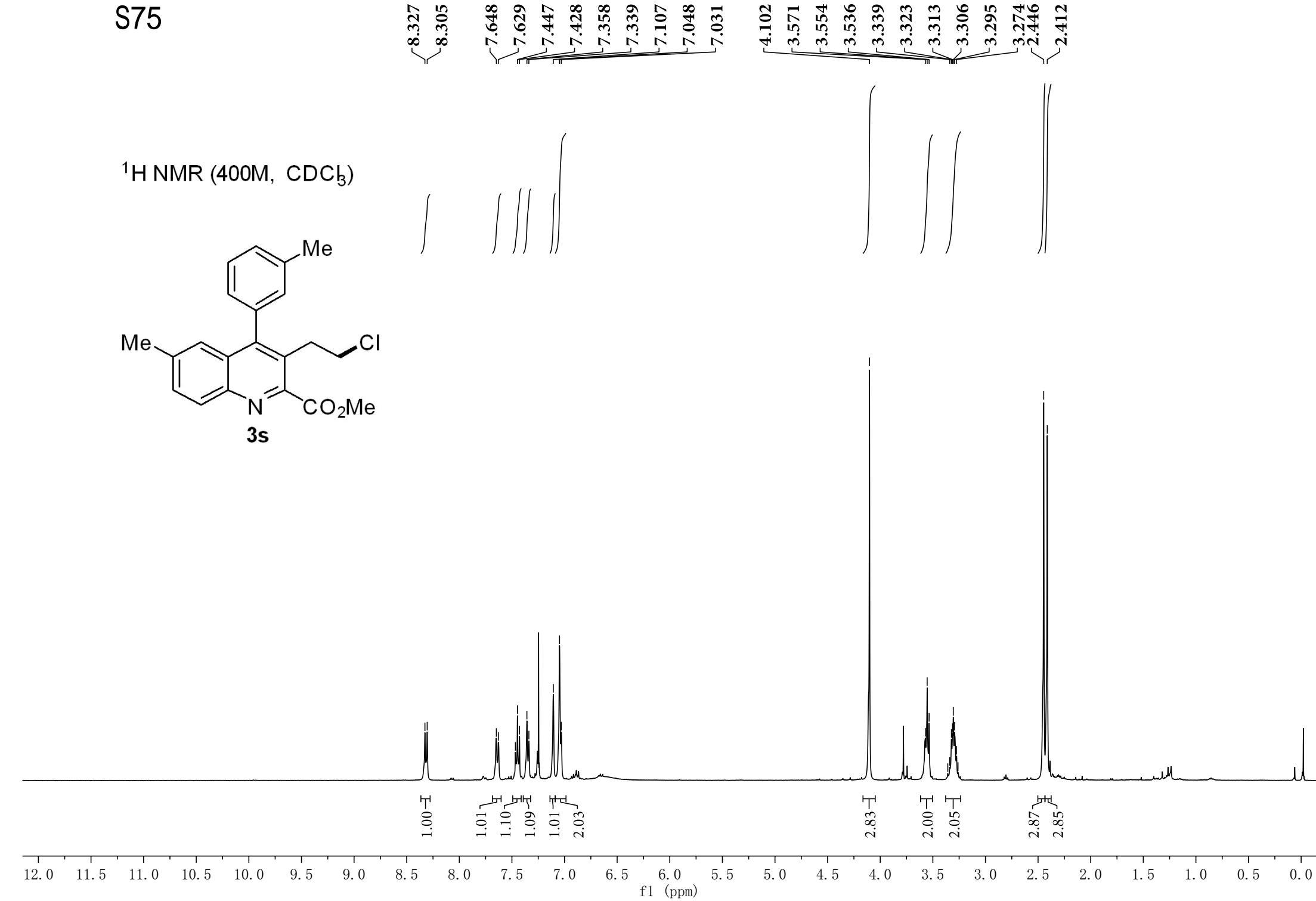
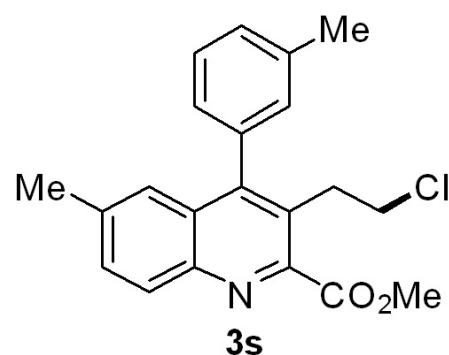
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



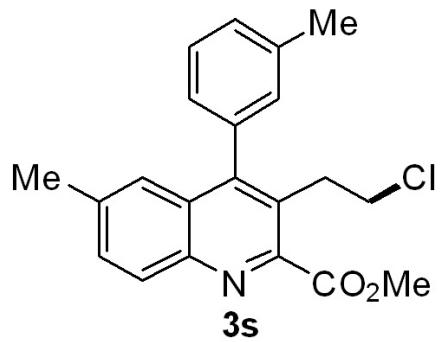


Methyl 3-(2-chloroethyl)-4-(3,4-dimethylphenyl)-6-methylquinoline-2-carboxylate (**3r**)



<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

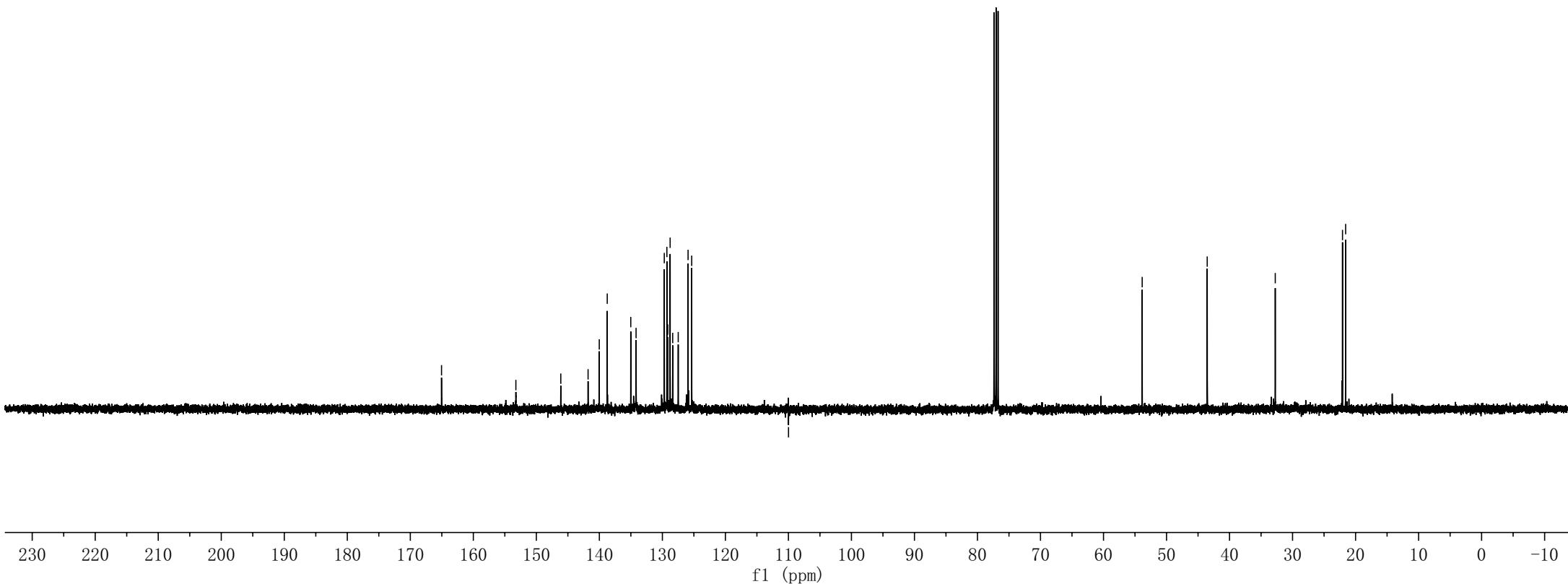
S76

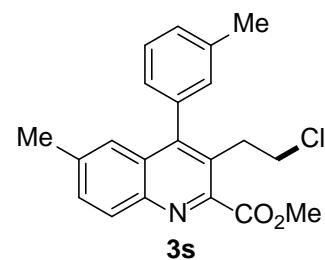
 $^{13}\text{C}$  NMR (100M,  $\text{CDCl}_3$ )

-165.047

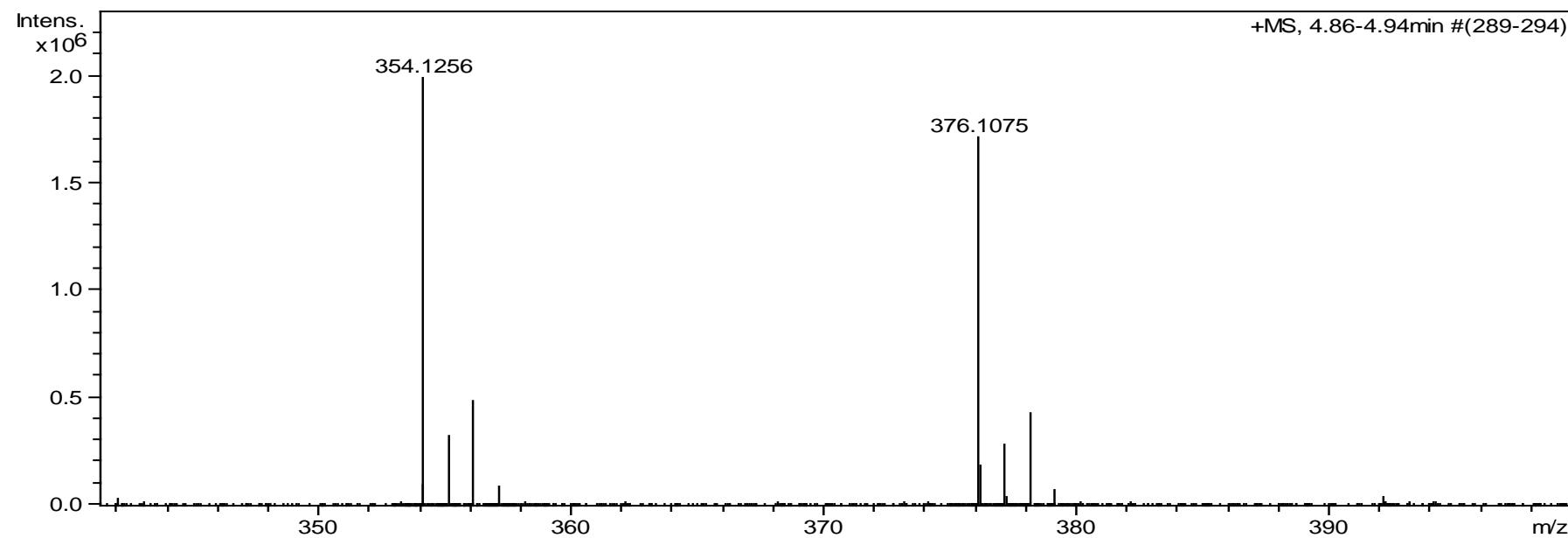
138.750  
135.015  
134.175  
129.698  
129.287  
129.139  
128.769  
125.923  
125.347  
109.983

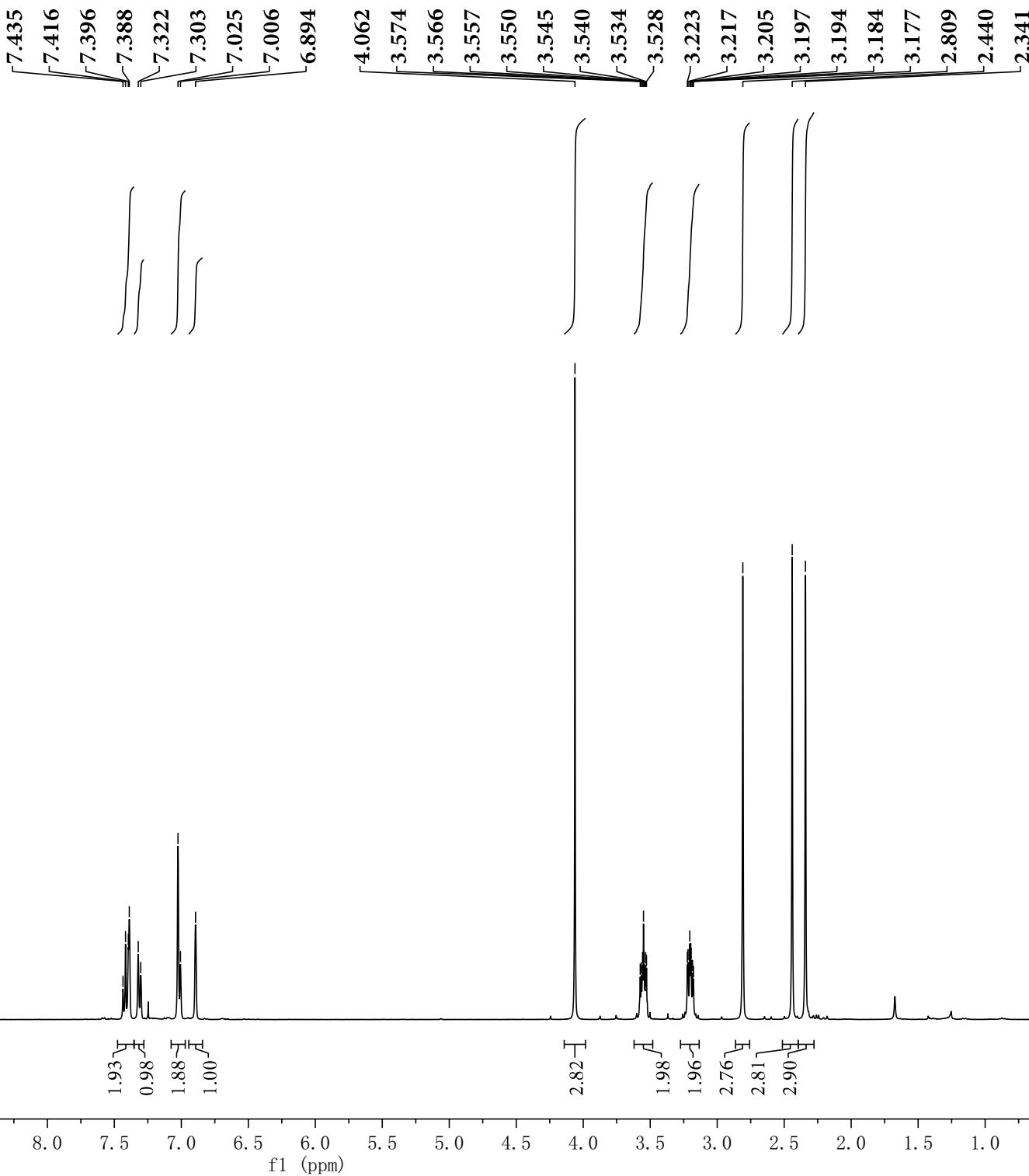
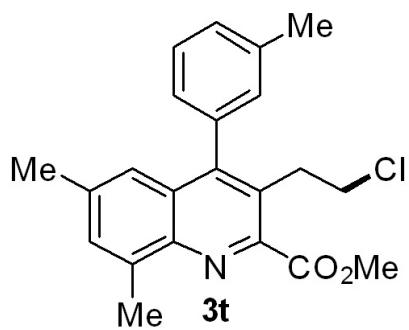
53.860  
~43.542  
32.743  
22.073  
21.575



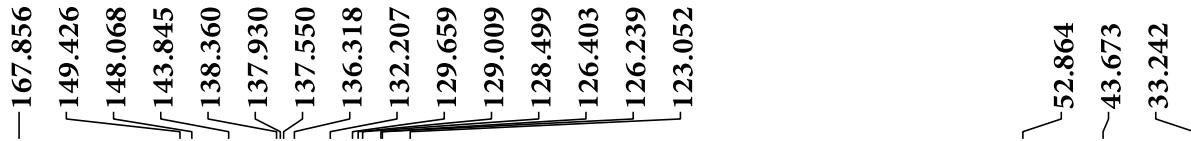
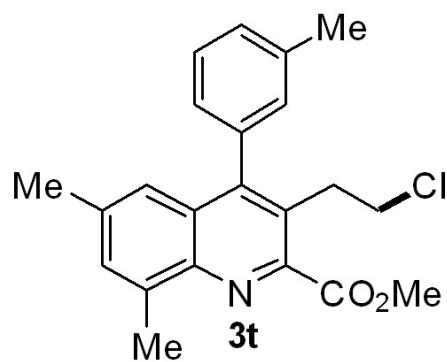


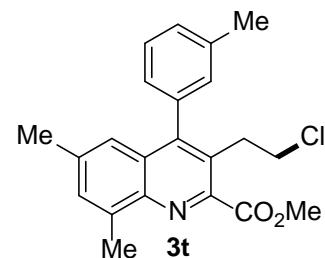
Methyl 3-(2-chloroethyl)-6-methyl-4-(m-tolyl)quinoline-2-carboxylate (**3s**)



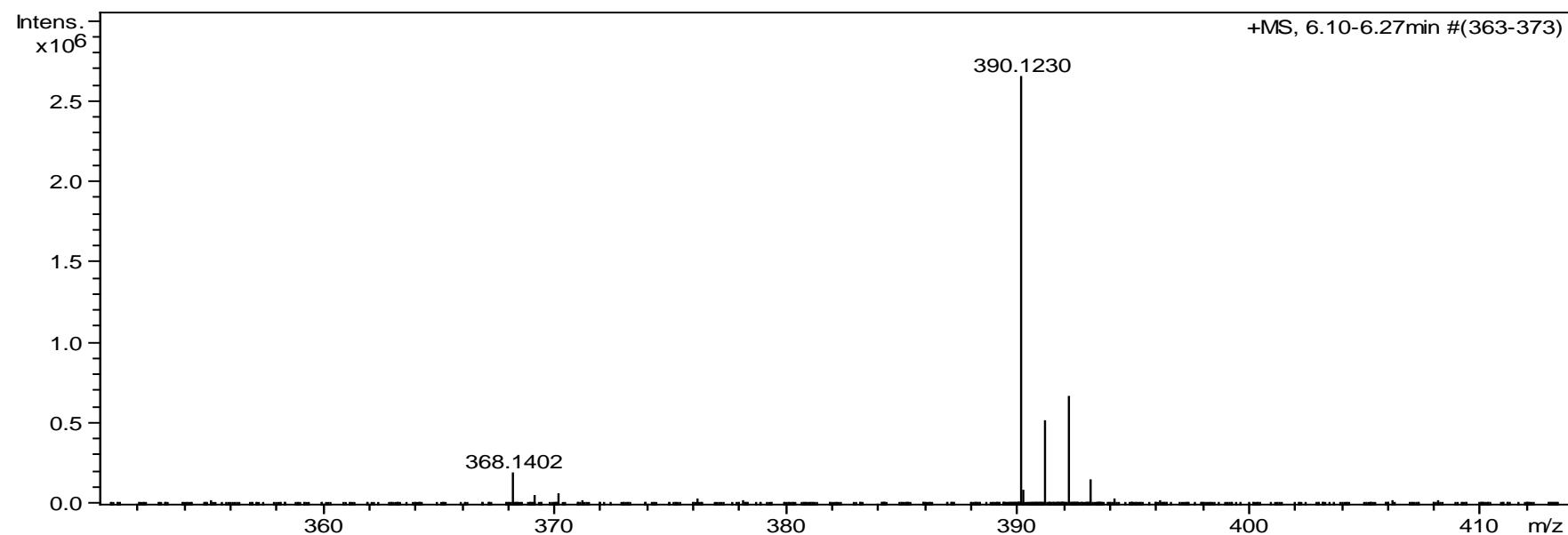
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

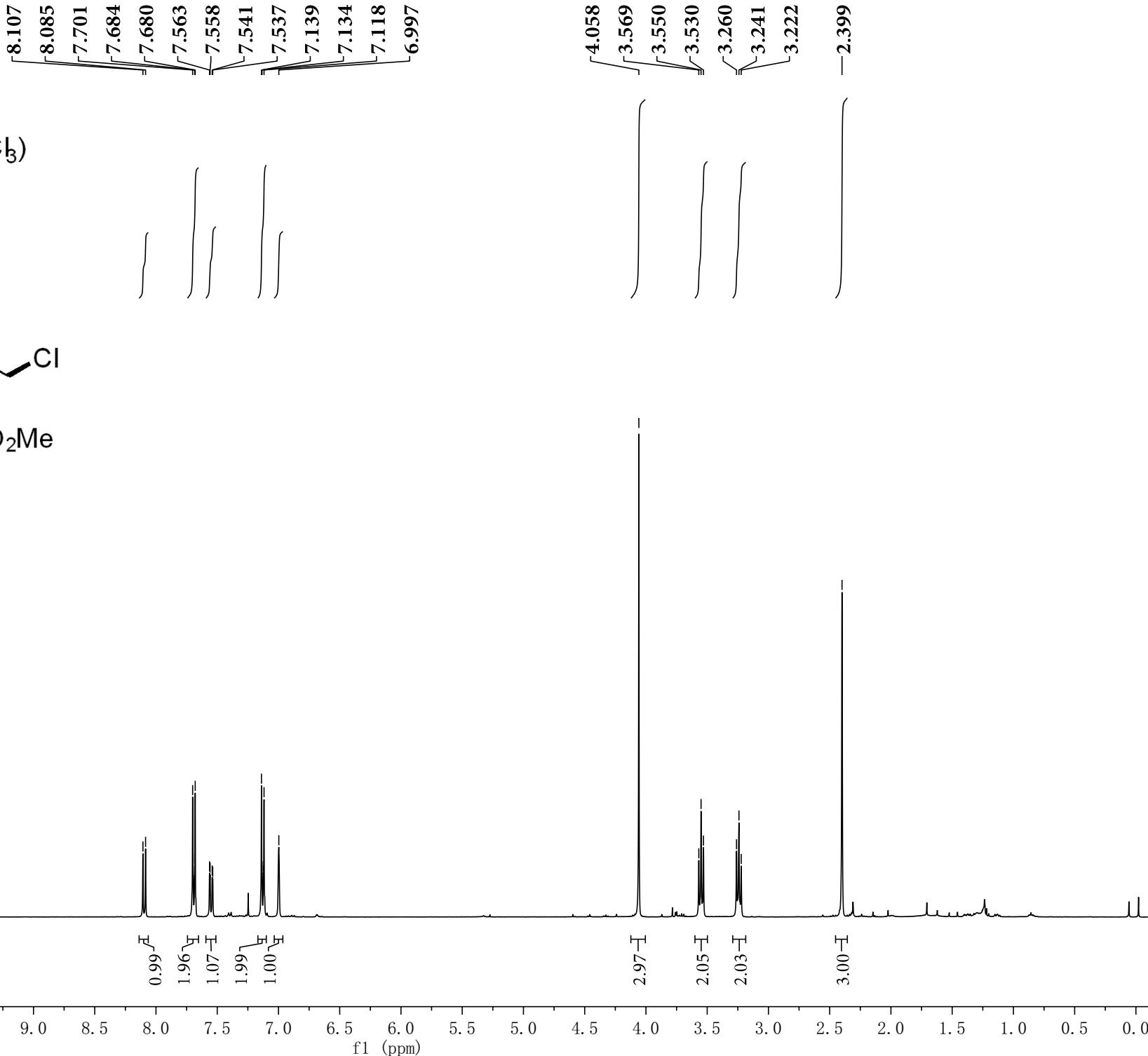
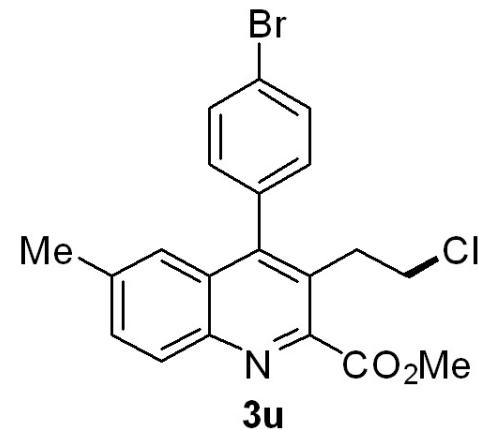
$^{13}\text{C}$  NMR (100M,  $\text{CDCl}_3$ )

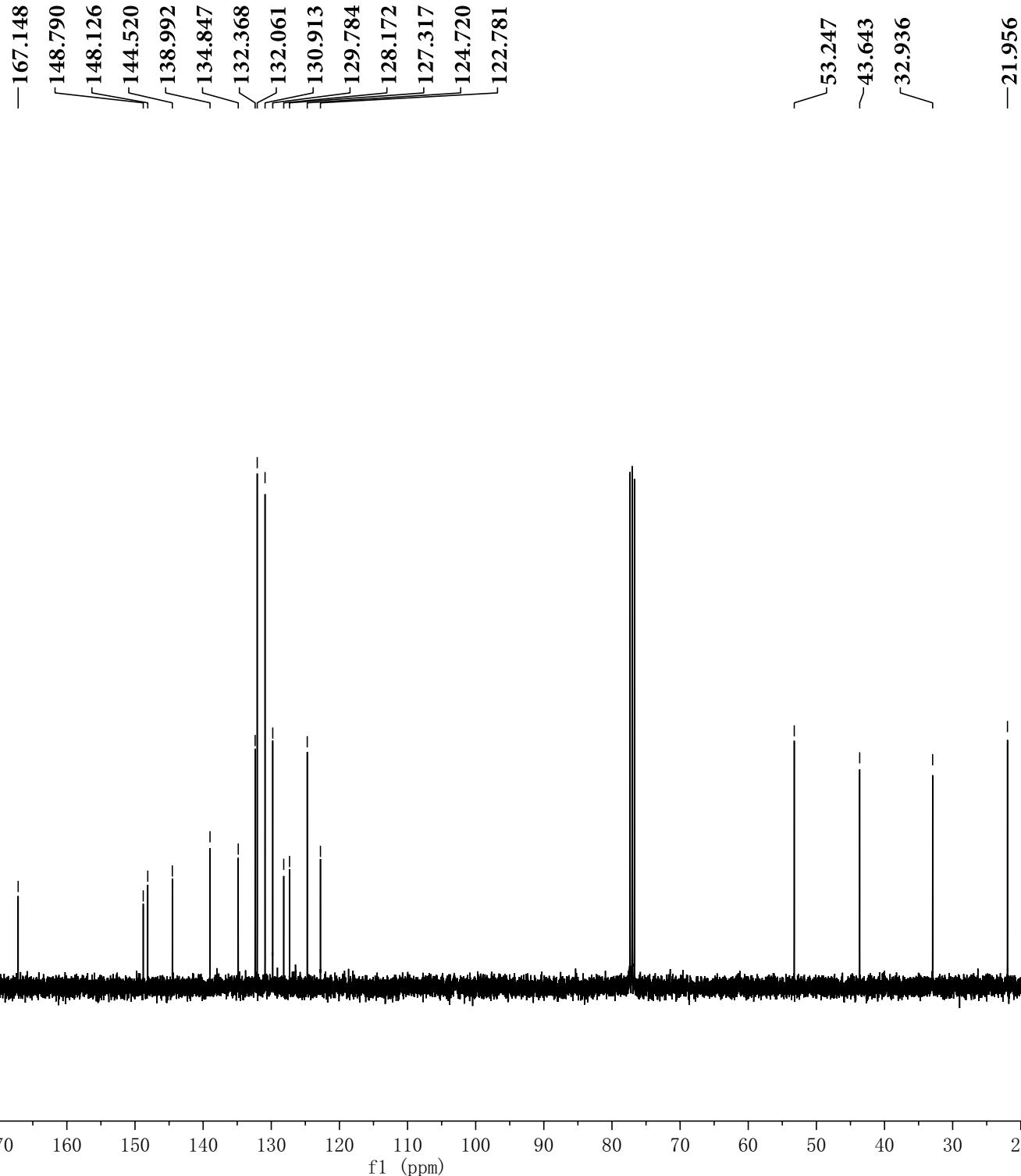
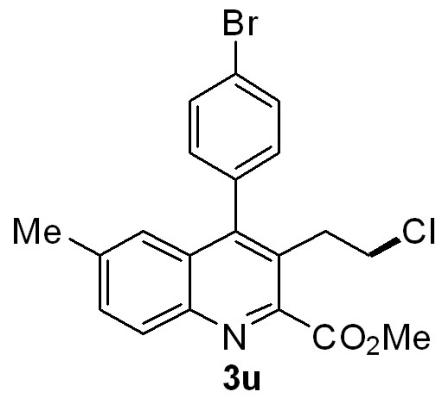


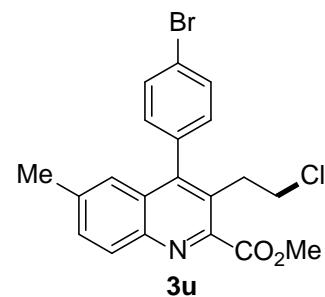


**Methyl 3-(2-chloroethyl)-6,8-dimethyl-4-(m-tolyl)quinoline-2-carboxylate (3t)**

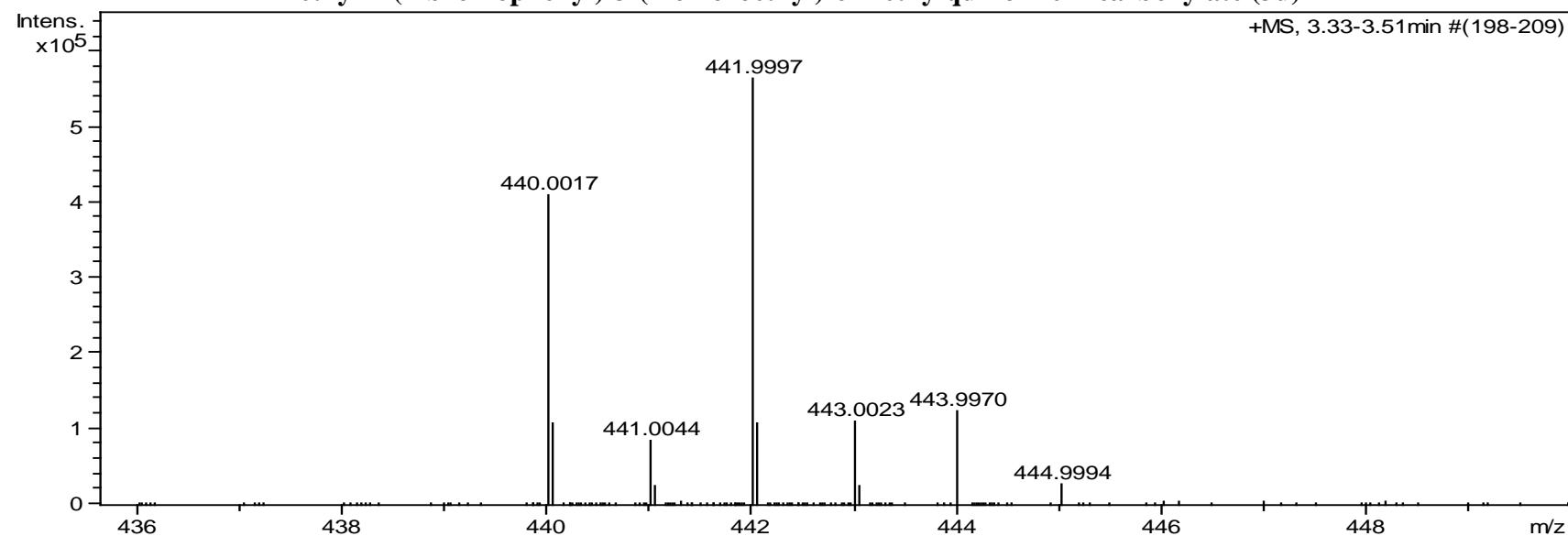


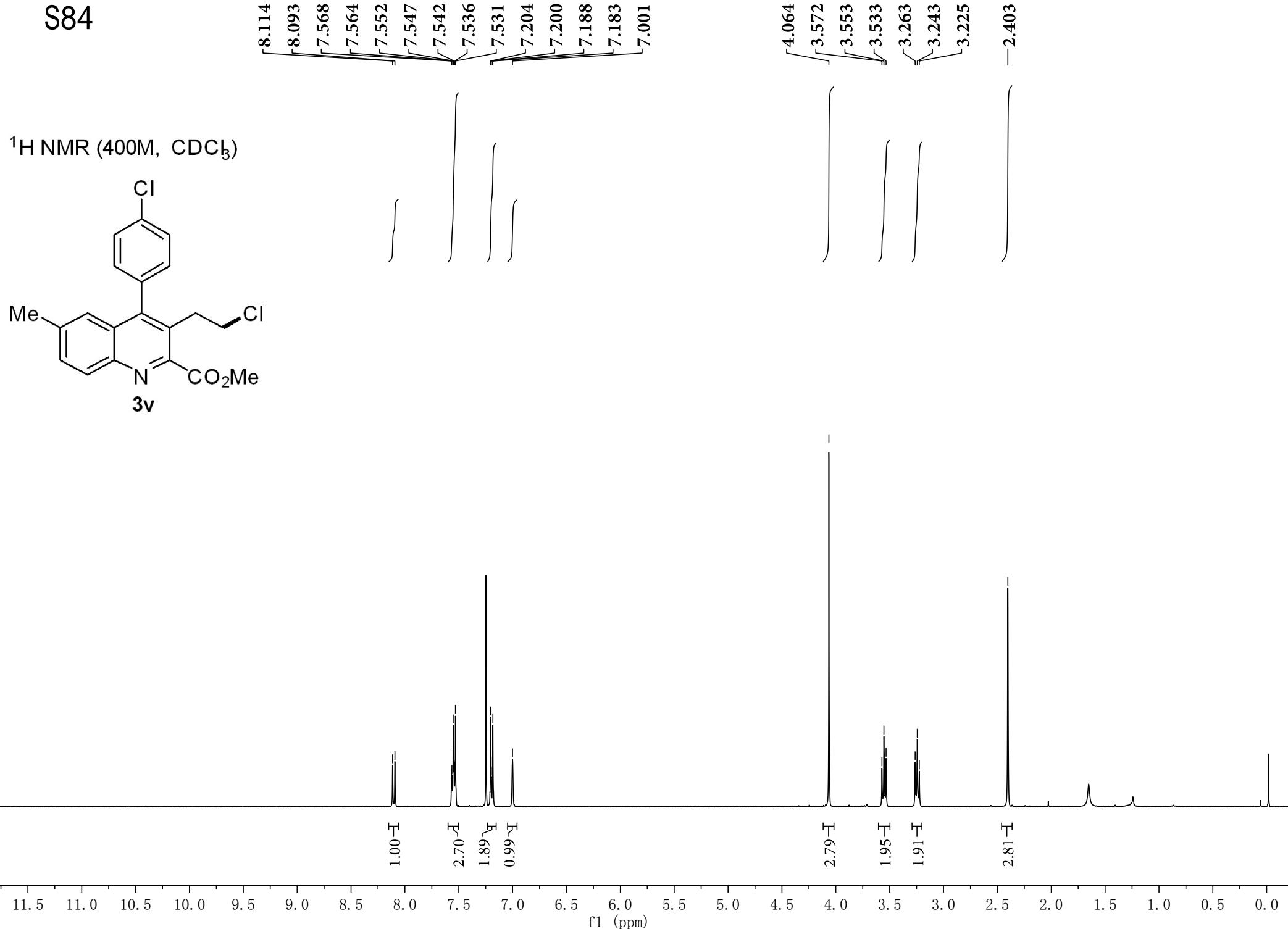
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

$^{13}\text{C}$  NMR (100M,  $\text{CDCl}_3$ )

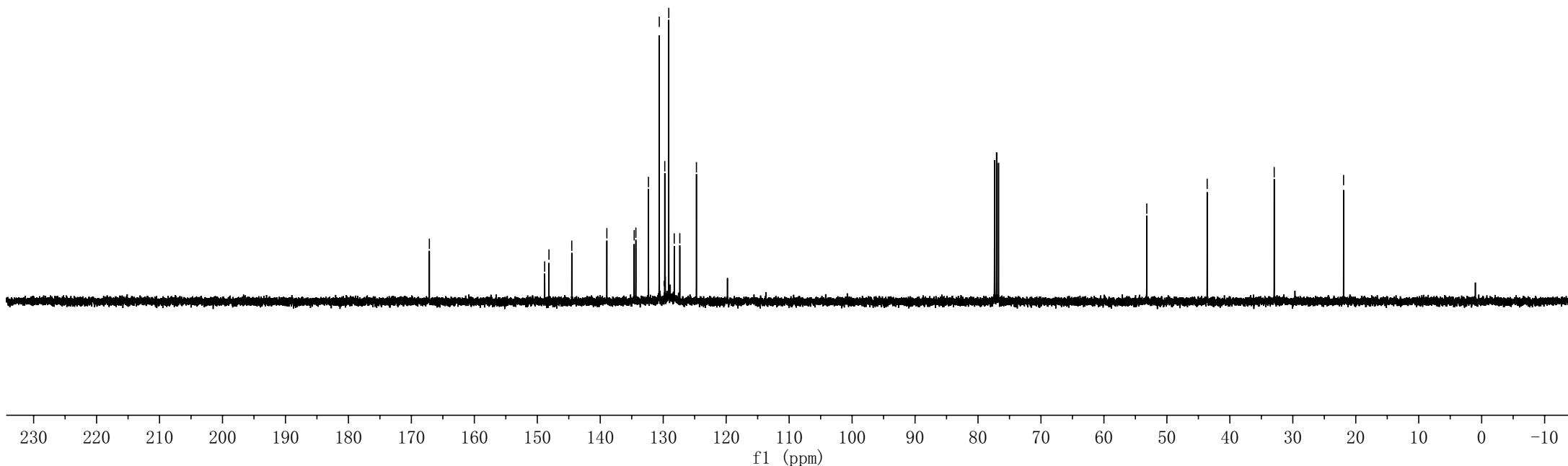
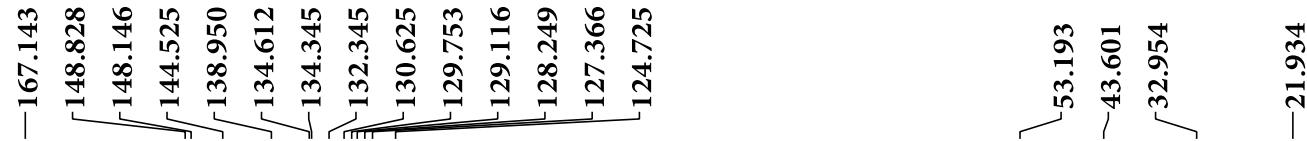
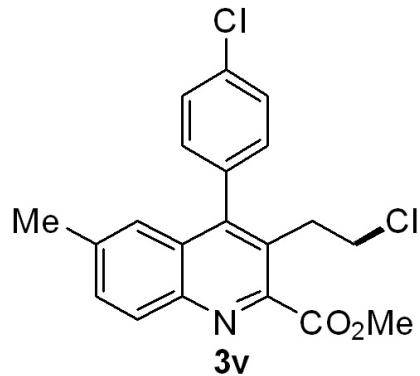


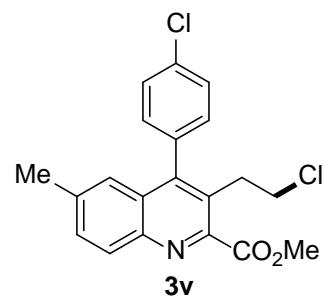
Methyl 4-(4-bromophenyl)-3-(2-chloroethyl)-6-methylquinoline-2-carboxylate (**3u**)



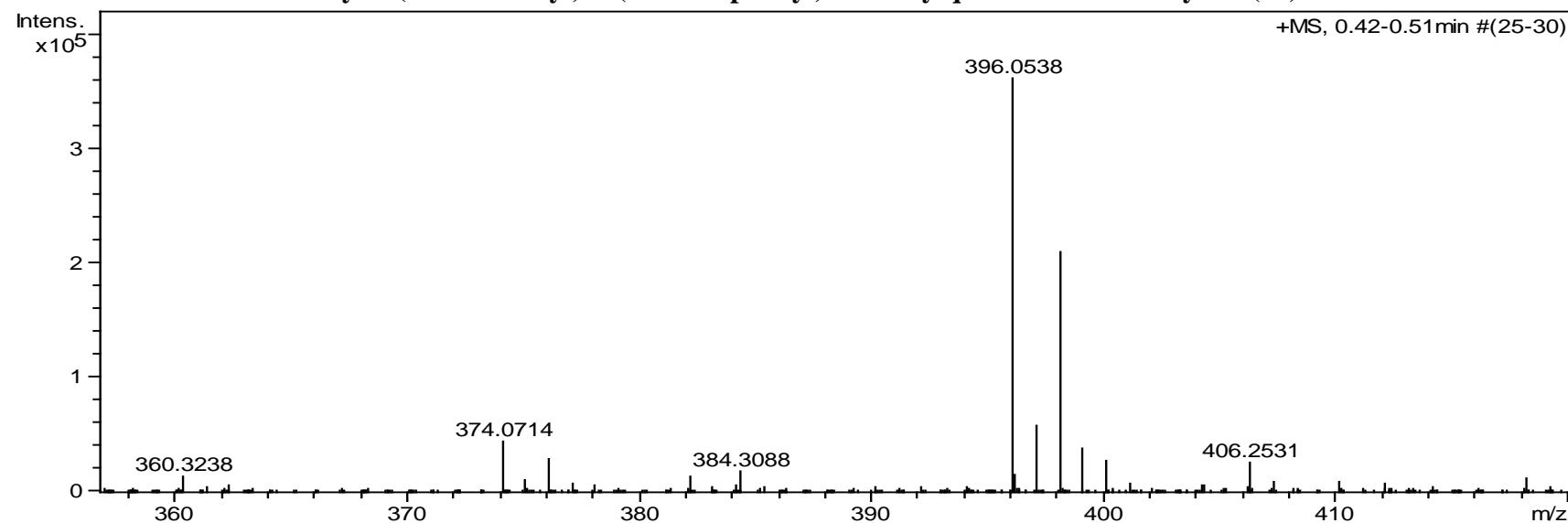


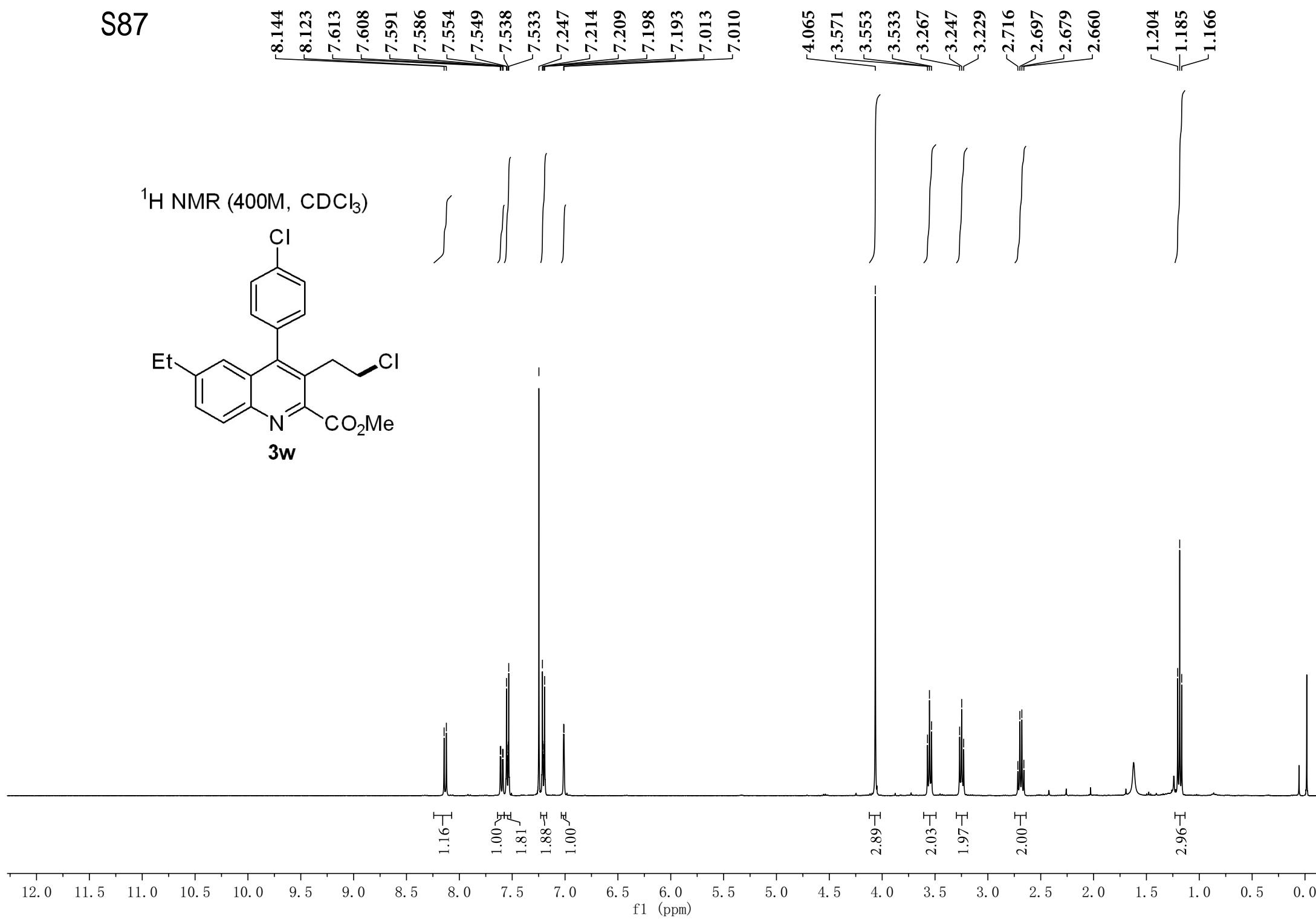
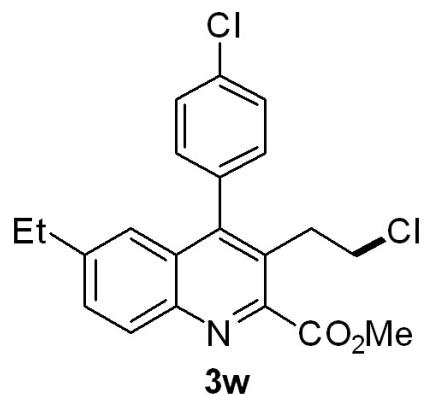
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



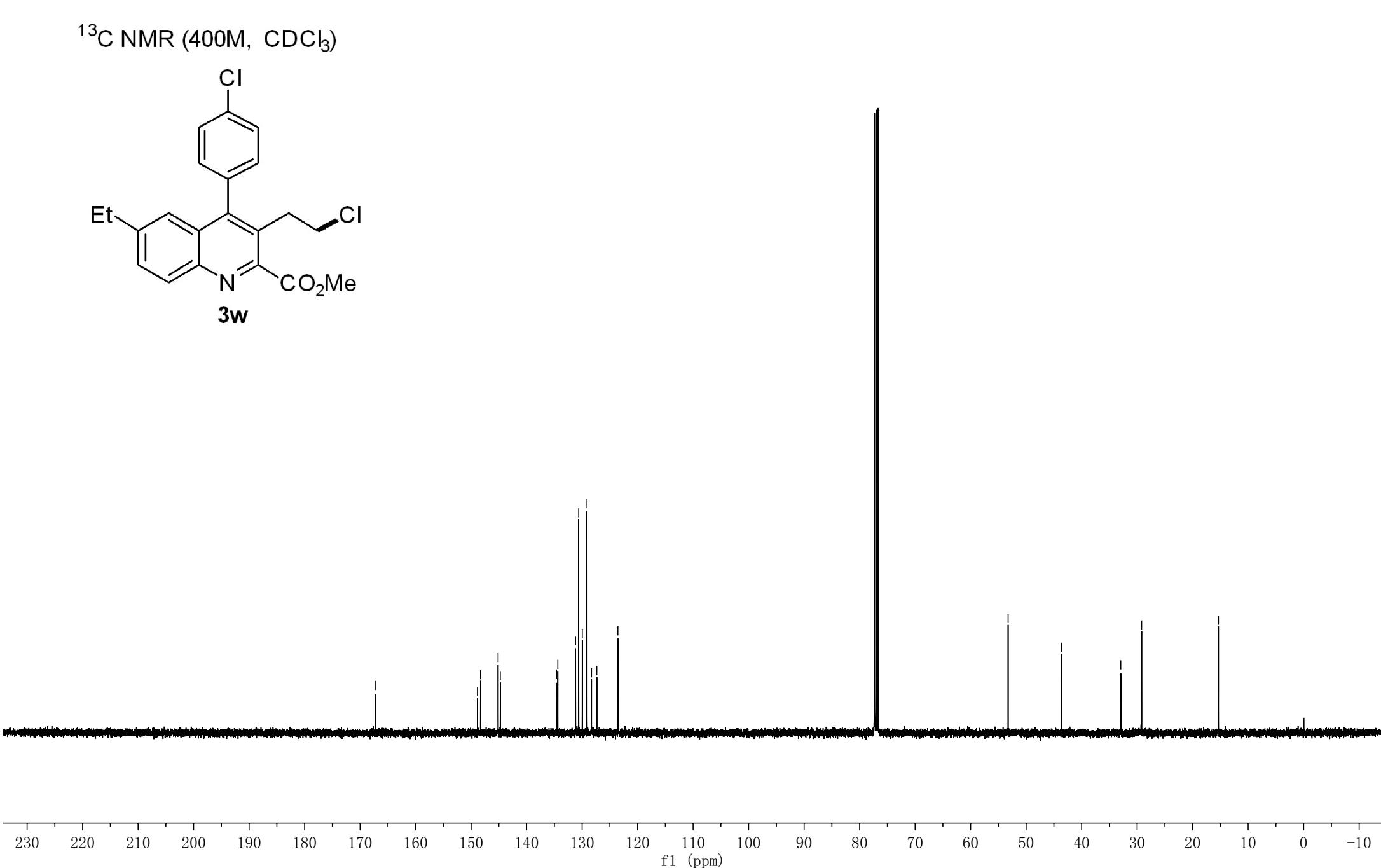
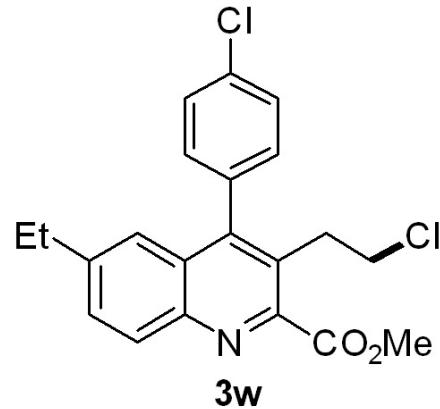


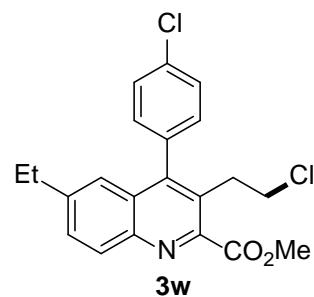
Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-methylquinoline-2-carboxylate (**3v**)



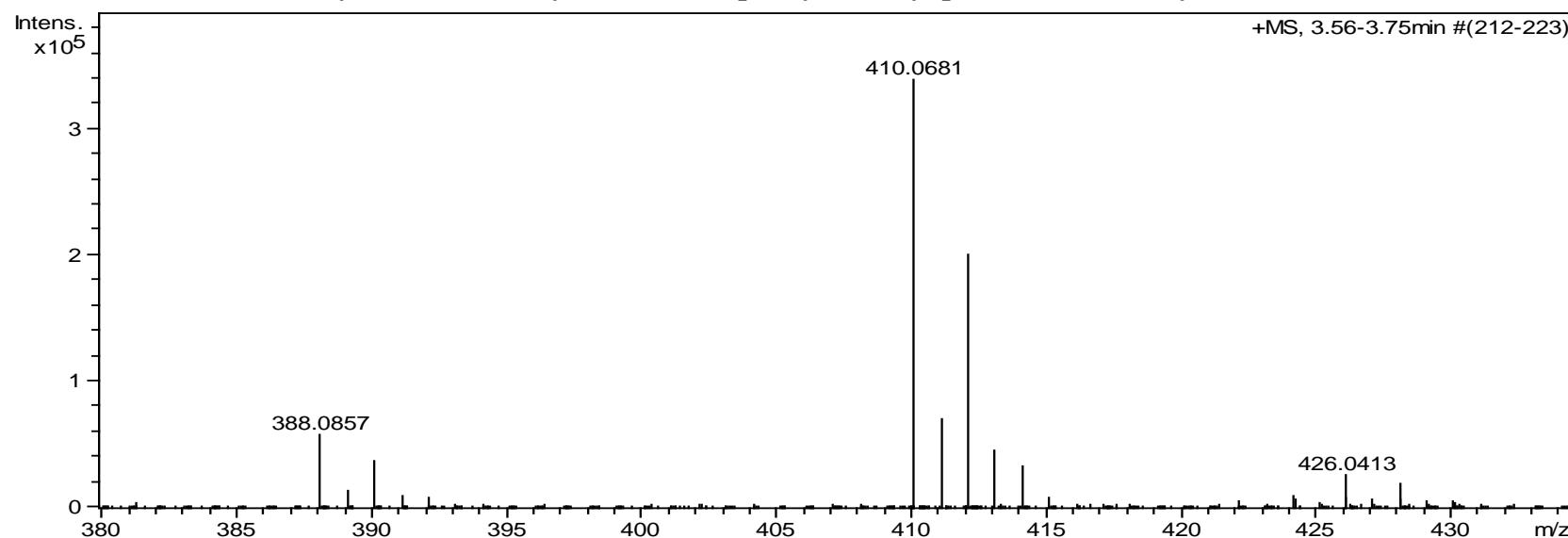
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

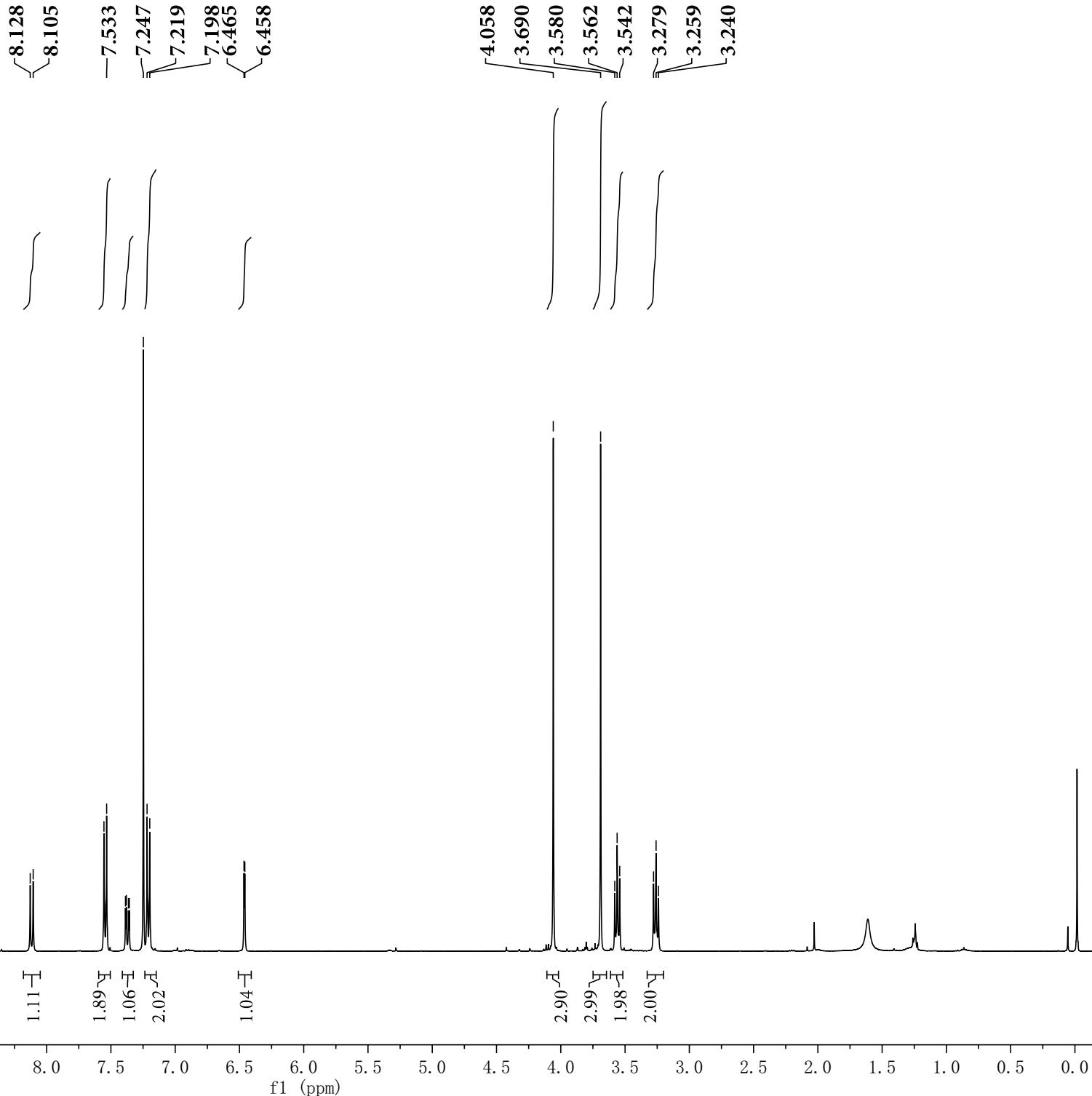
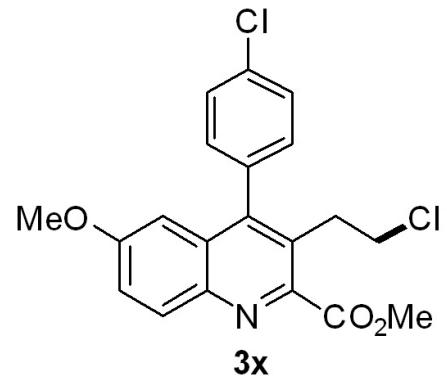
<sup>13</sup>C NMR (400M, CDCl<sub>3</sub>)



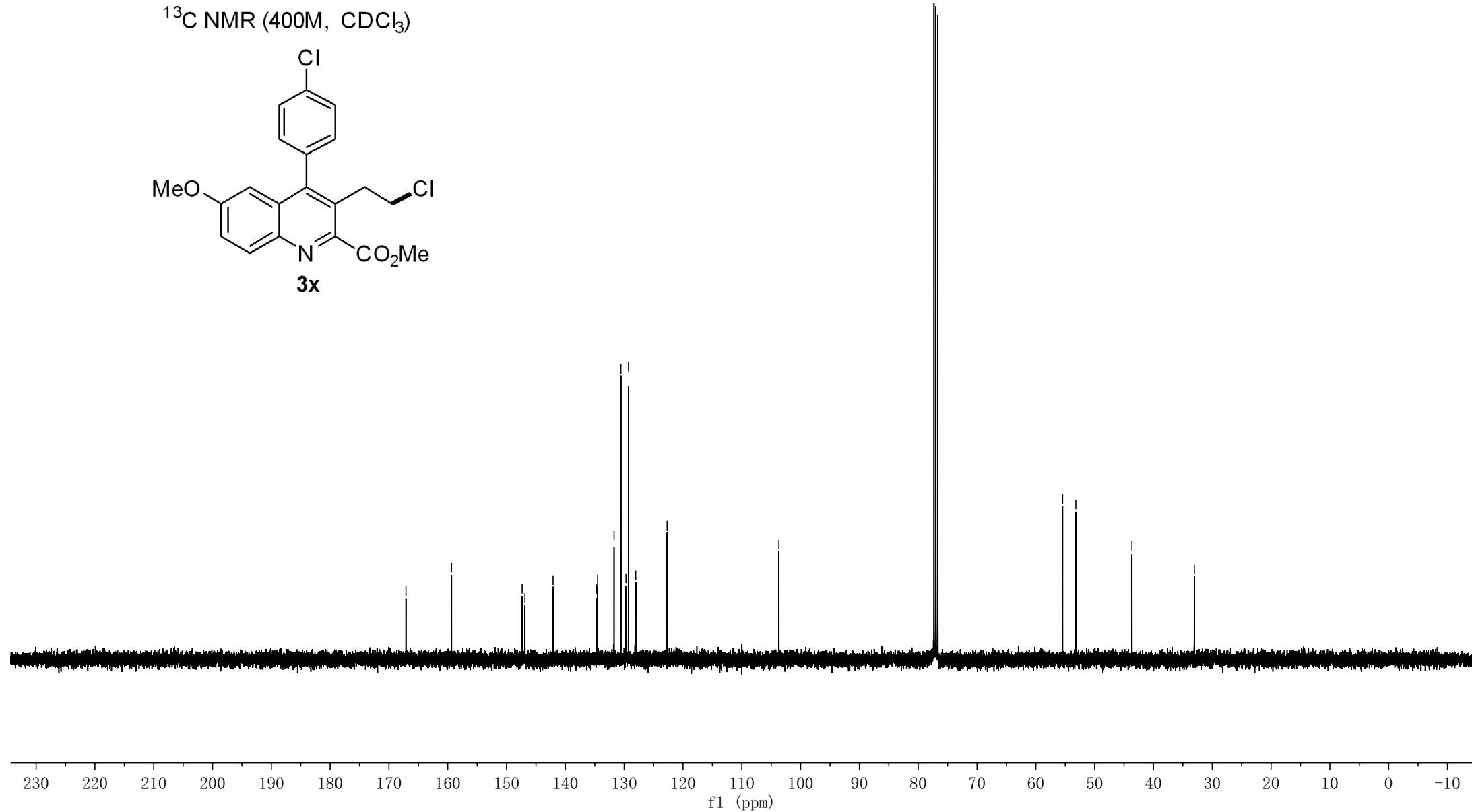
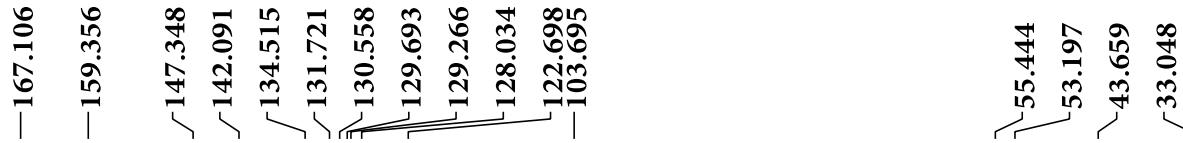
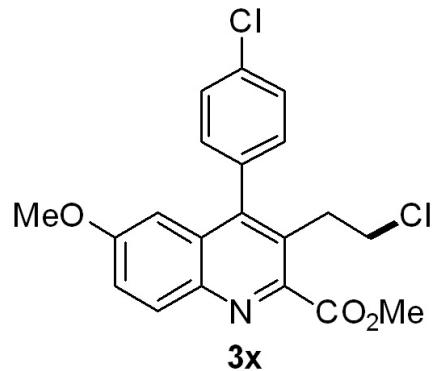


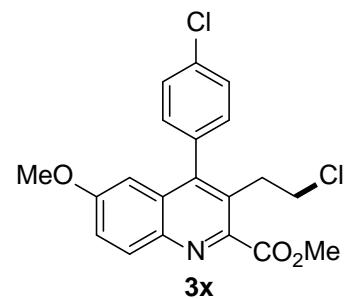
Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-ethylquinoline-2-carboxylate (**3w**)



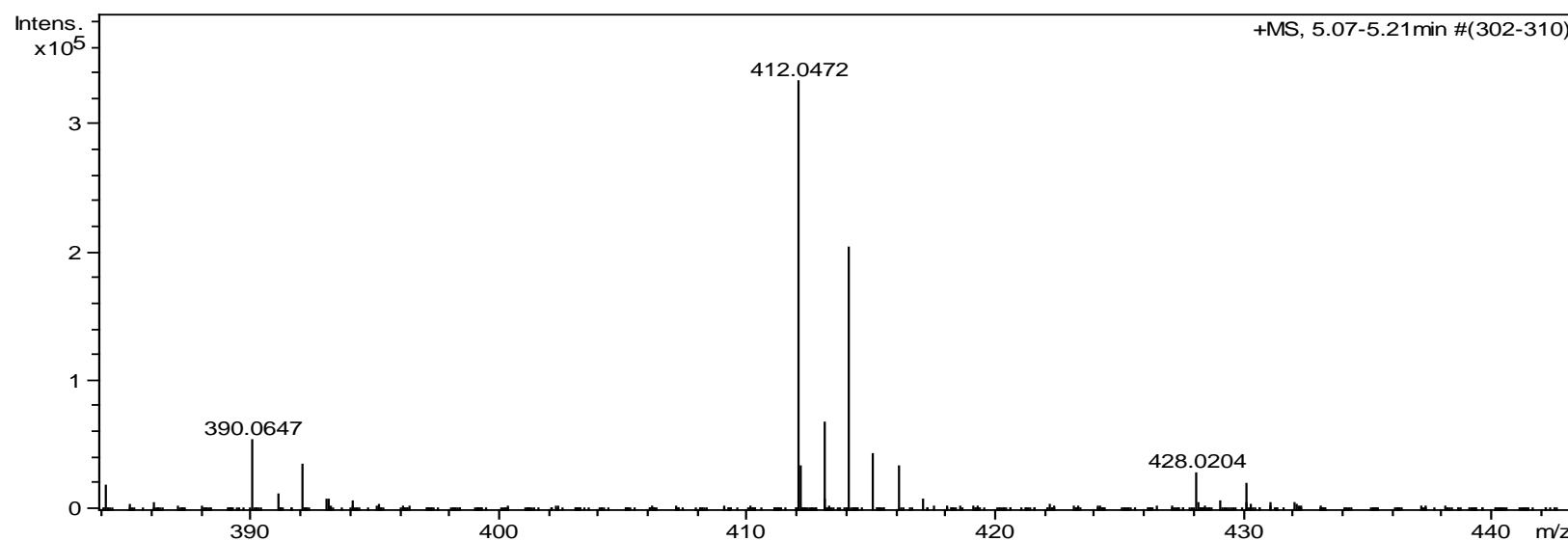
$^1\text{H}$  NMR (400M,  $\text{CDCl}_3$ )

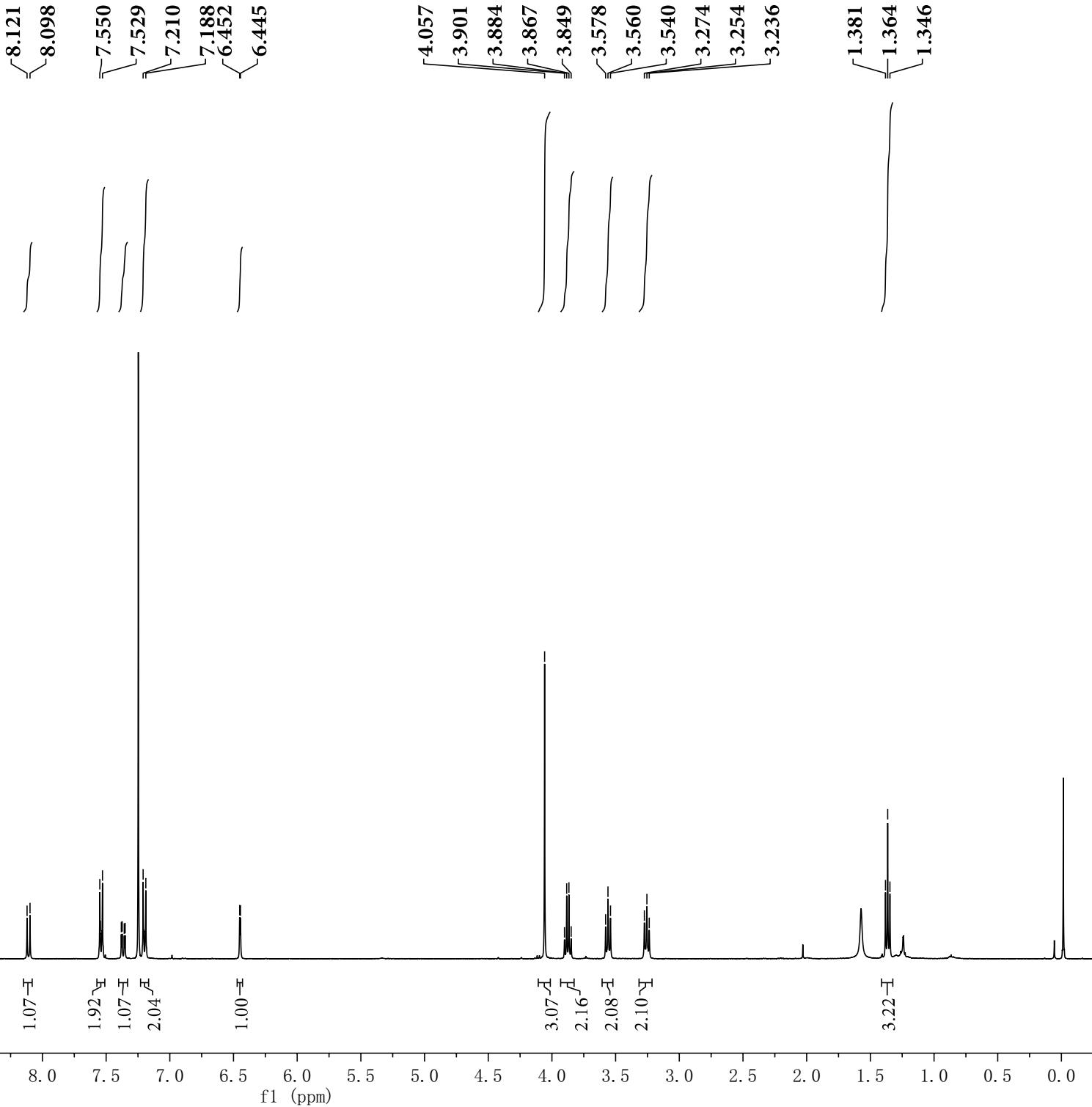
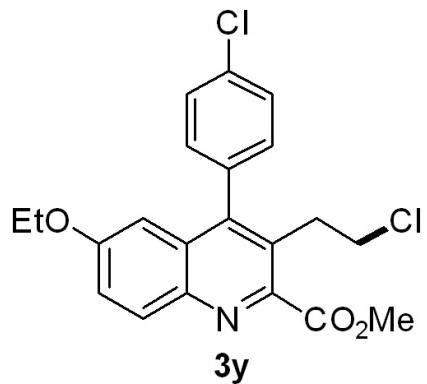
<sup>13</sup>C NMR (400M, CDCl<sub>3</sub>)



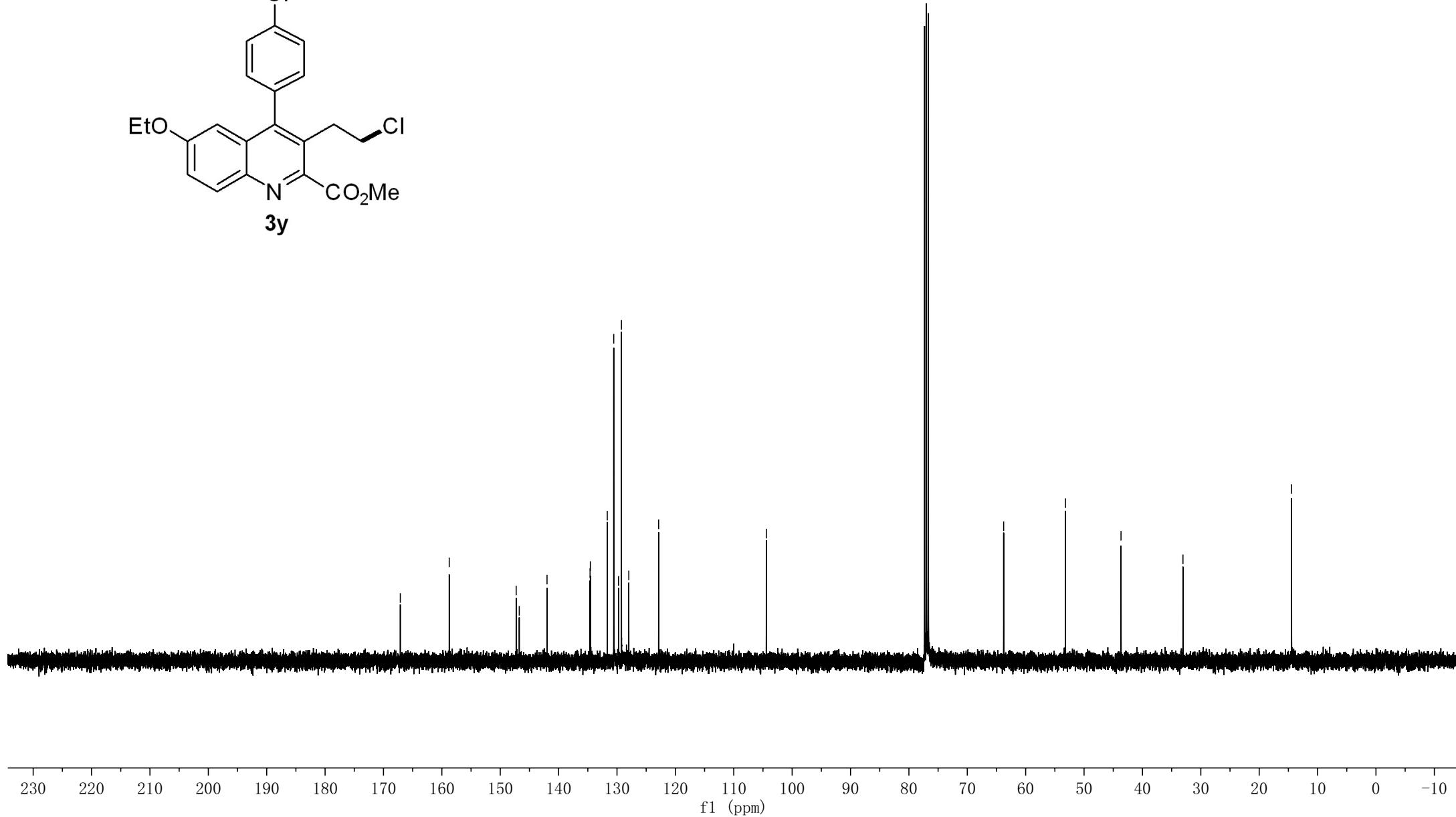
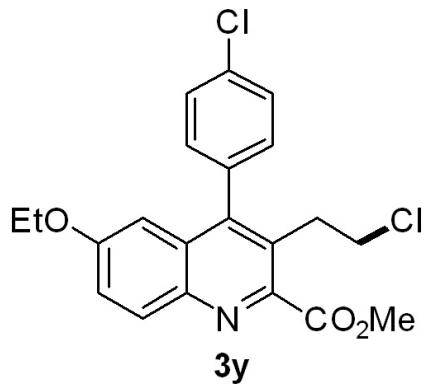


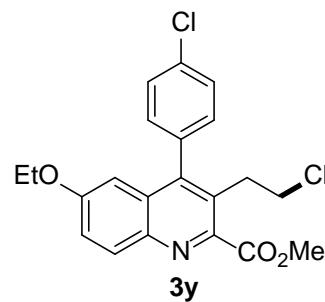
**Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-methoxyquinoline-2-carboxylate (3x)**



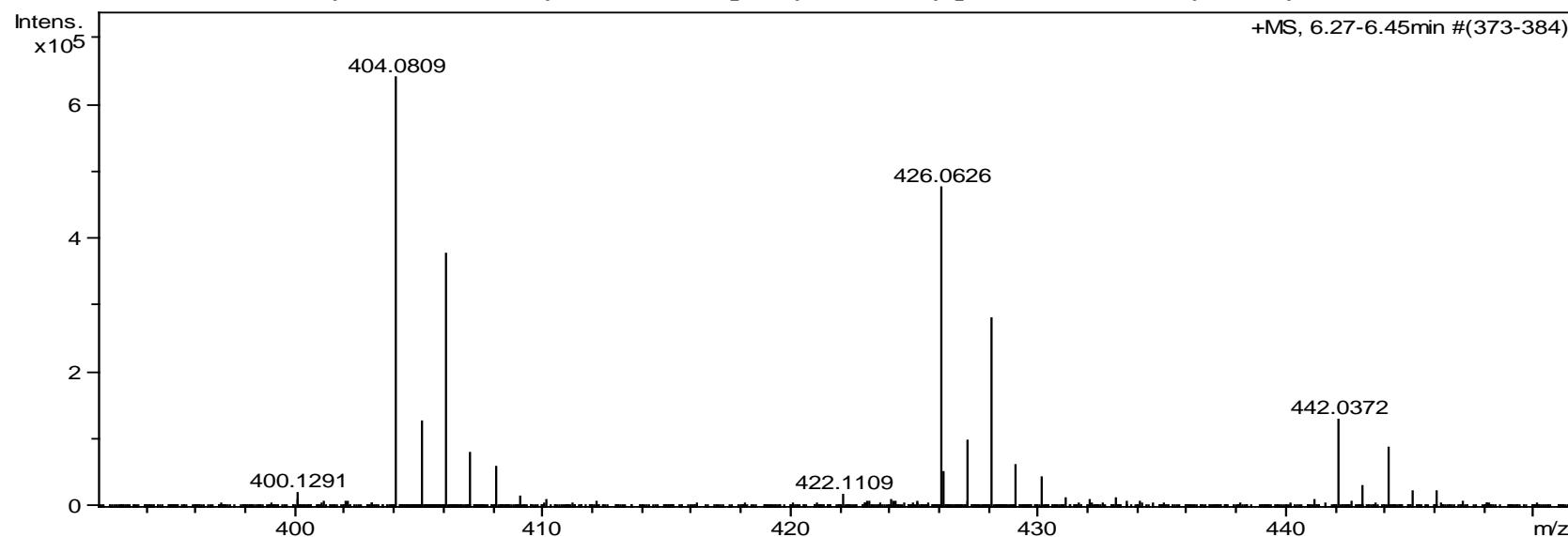
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

<sup>13</sup>C NMR (400M, CDCl<sub>3</sub>)

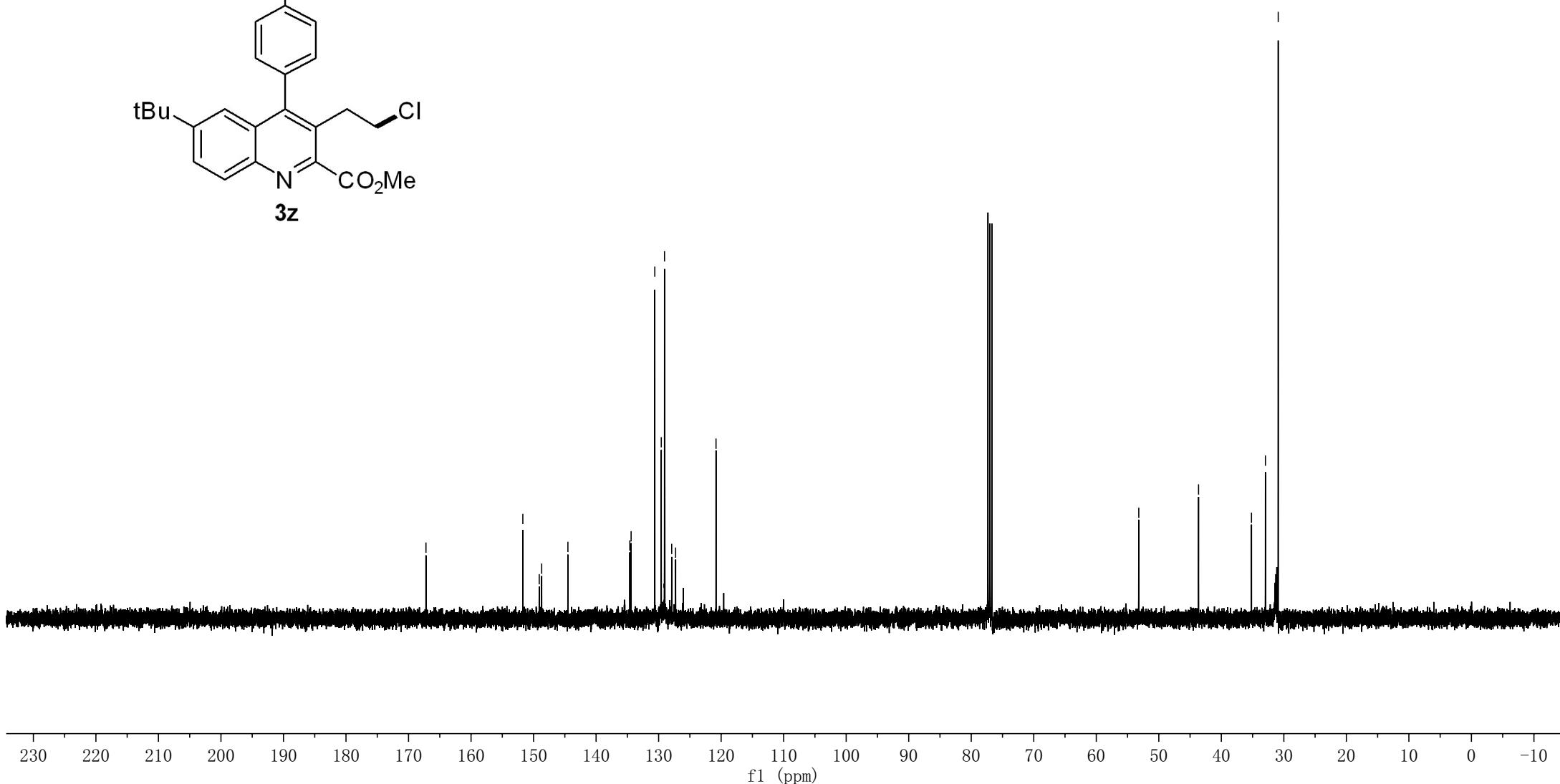
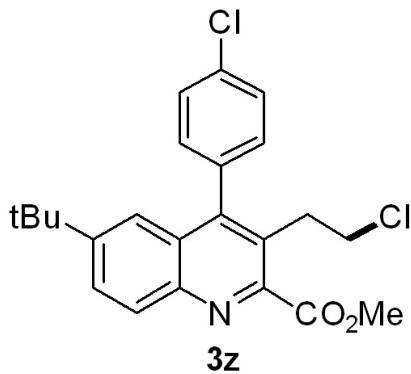


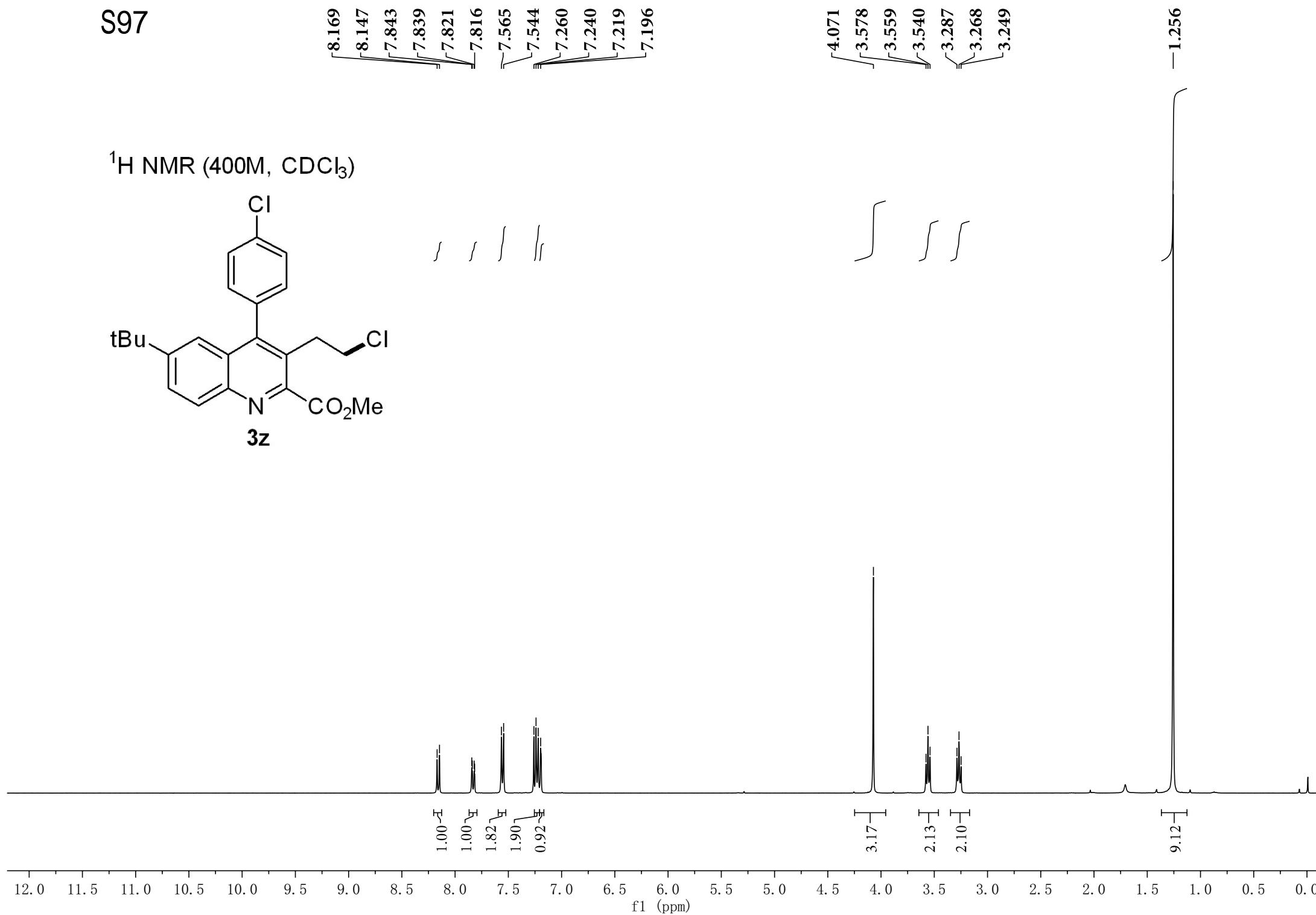
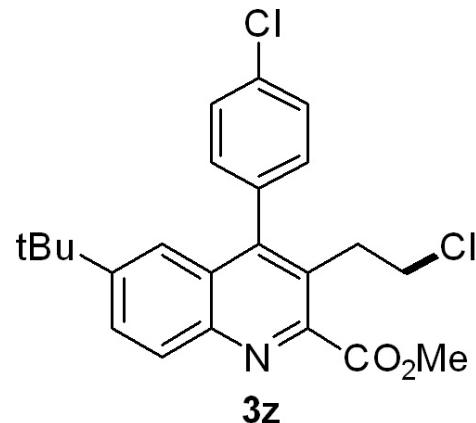


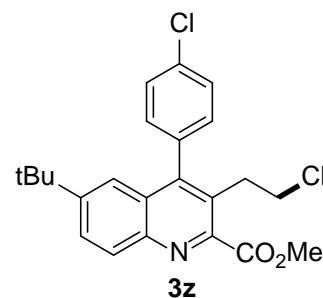
Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-ethoxyquinoline-2-carboxylate (**3y**)



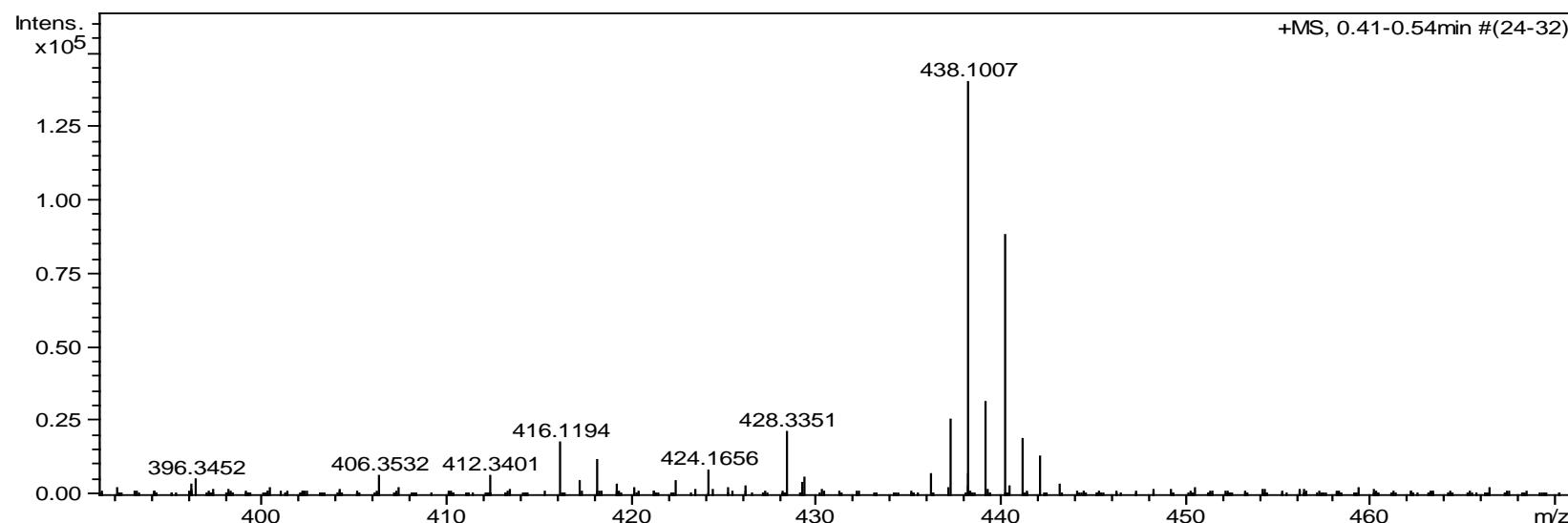
<sup>13</sup>C NMR (400M, CDCl<sub>3</sub>)



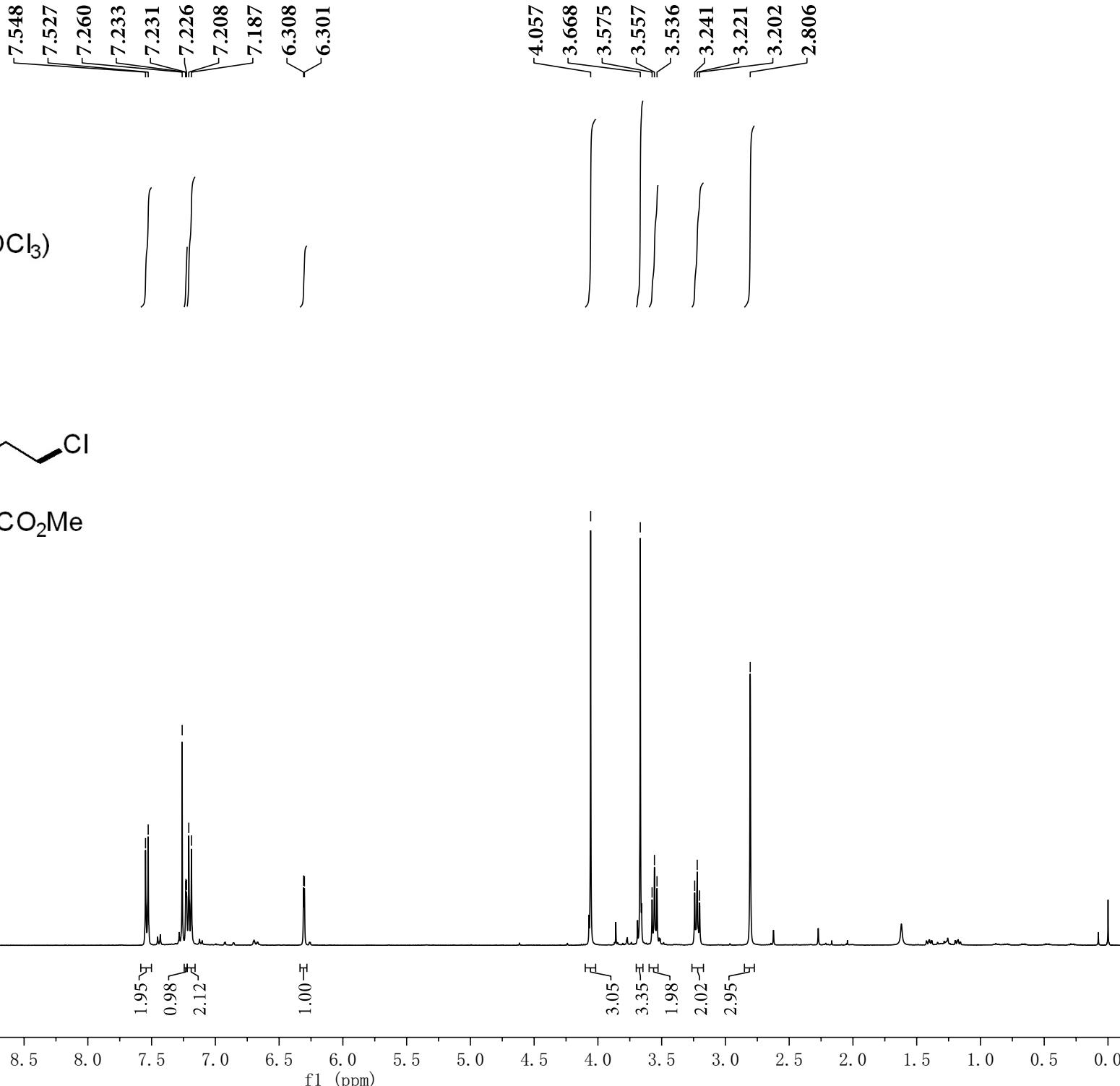
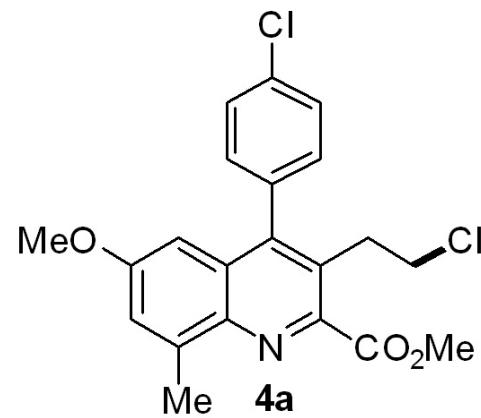
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

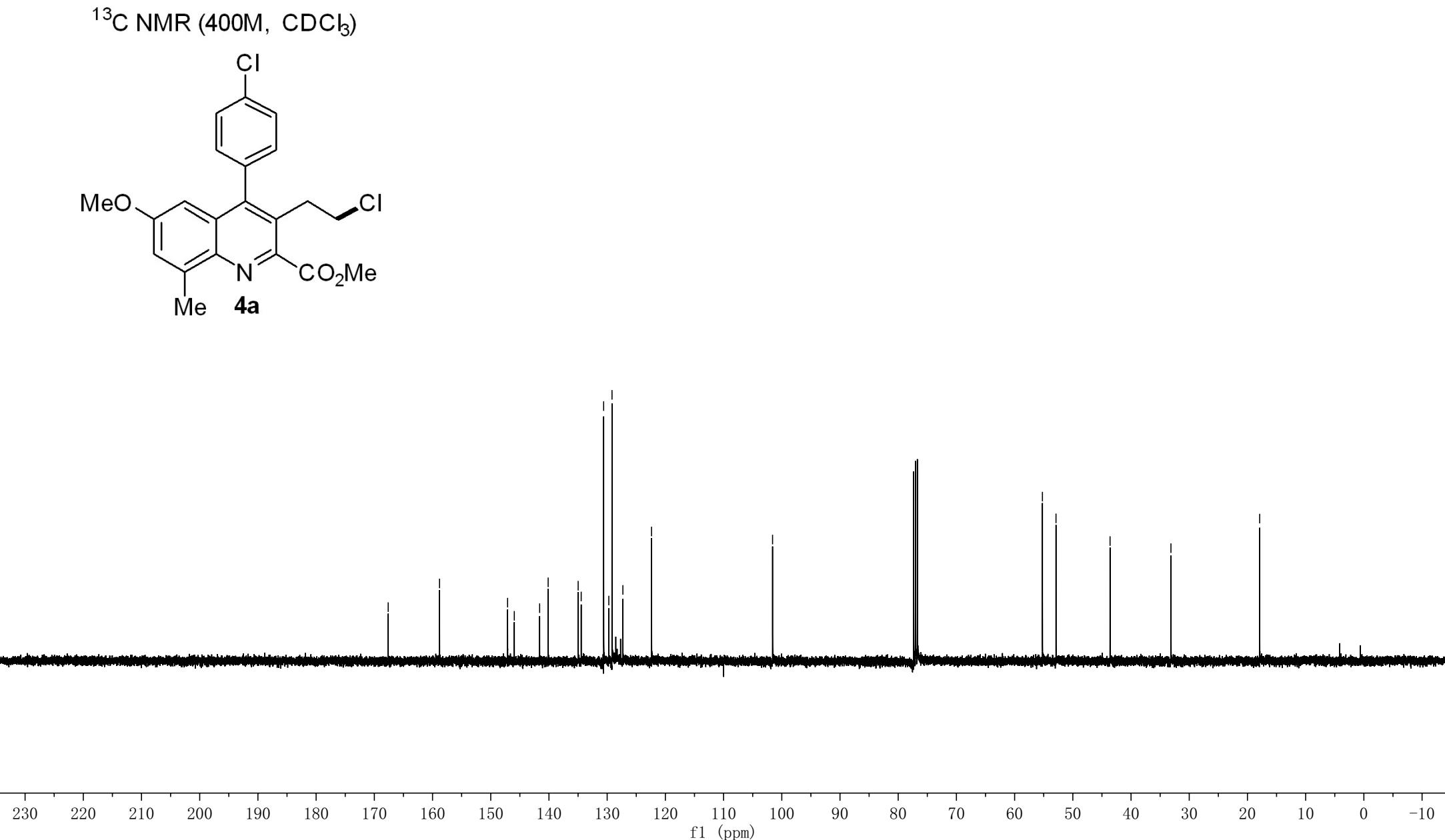
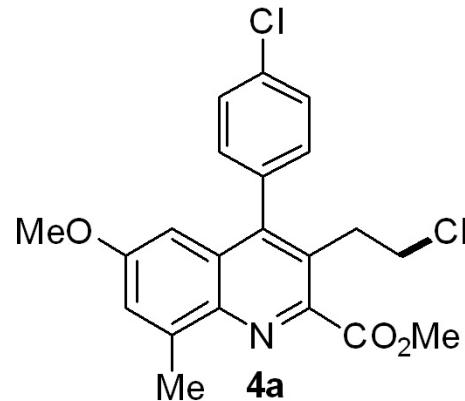


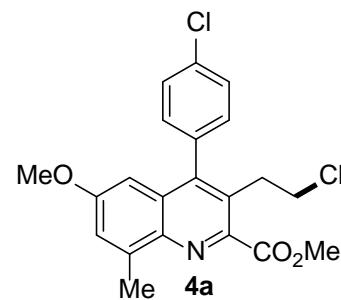
Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(4-chlorophenyl)quinoline-2-carboxylate (**3z**)



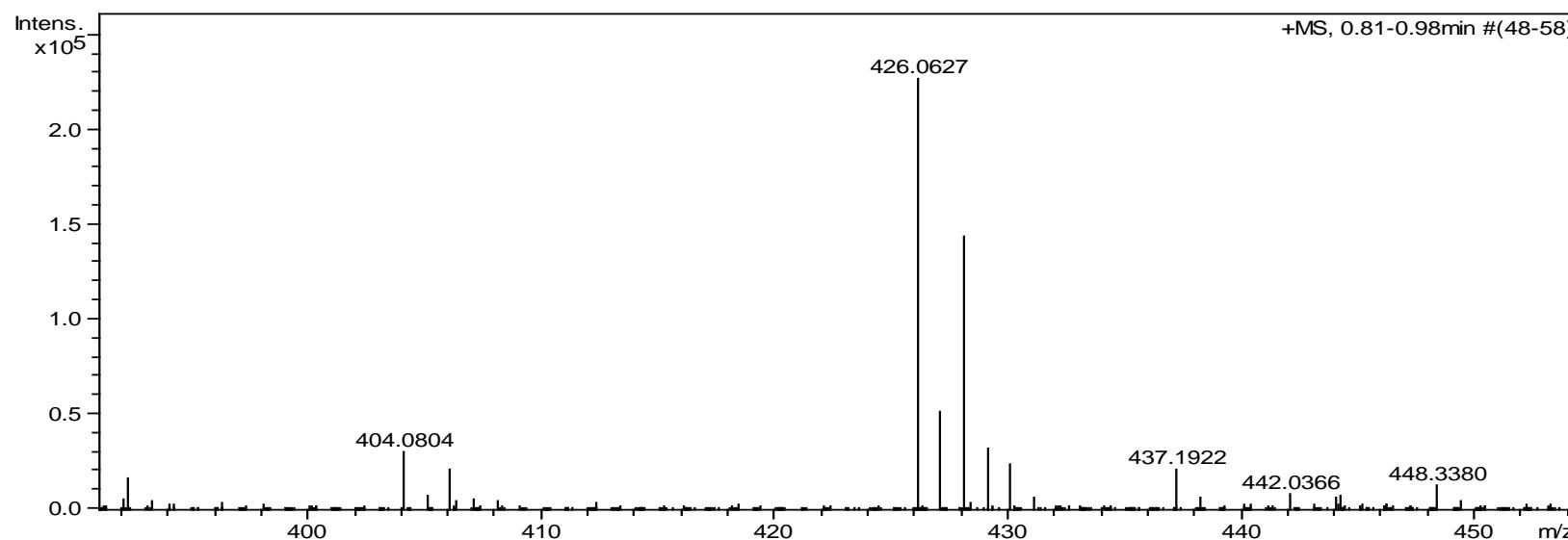
$^1\text{H}$  NMR (400M,  $\text{CDCl}_3$ )

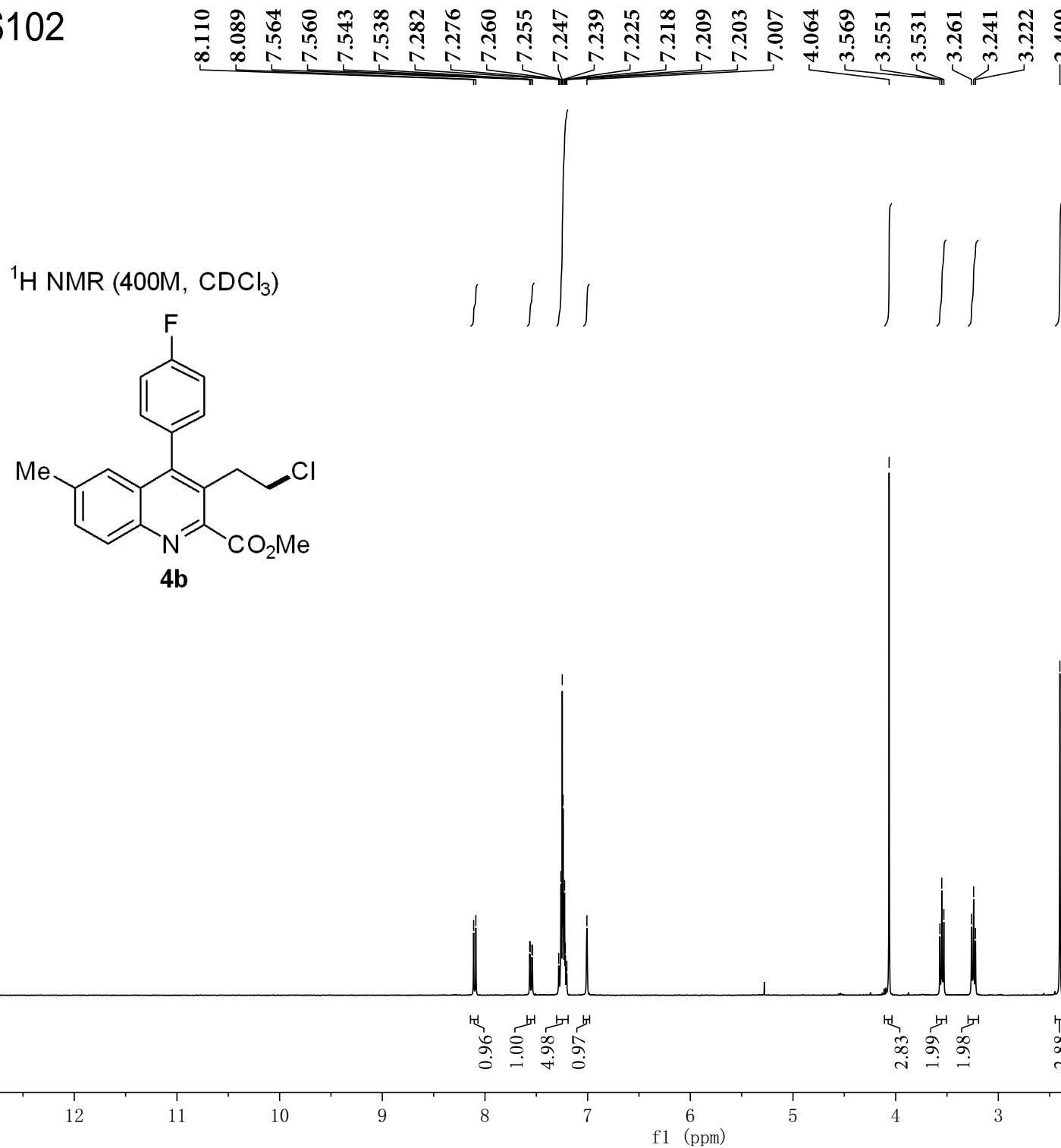


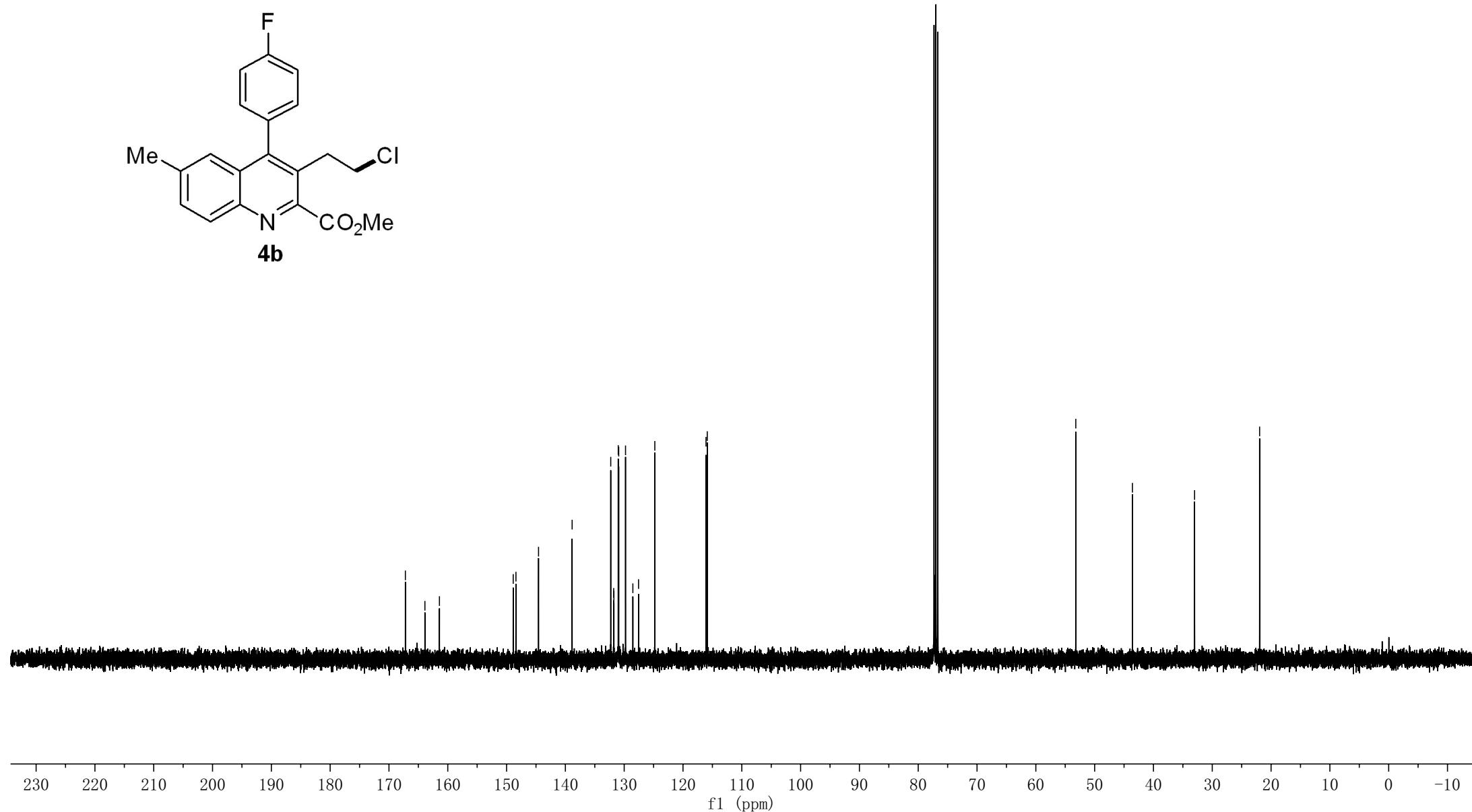
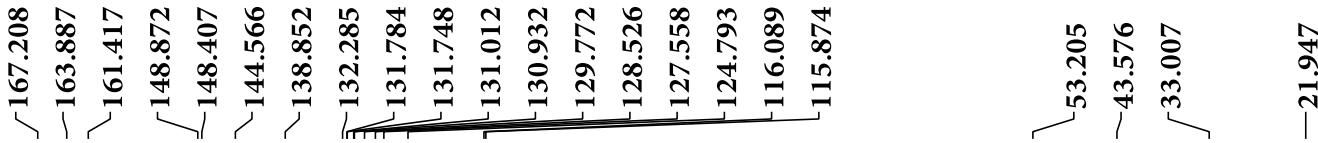
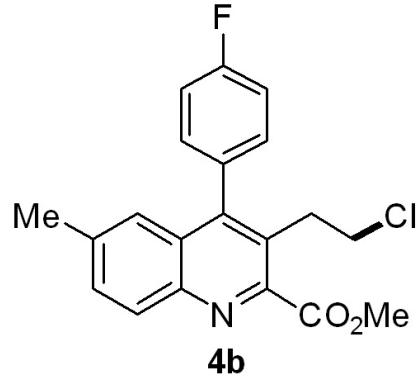
<sup>13</sup>C NMR (400M, CDCl<sub>3</sub>)

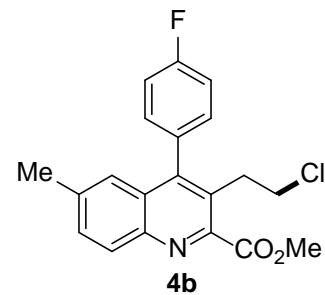


Methyl 3-(2-chloroethyl)-4-(4-chlorophenyl)-6-methoxy-8-methylquinoline-2-carboxylate (**4a**)

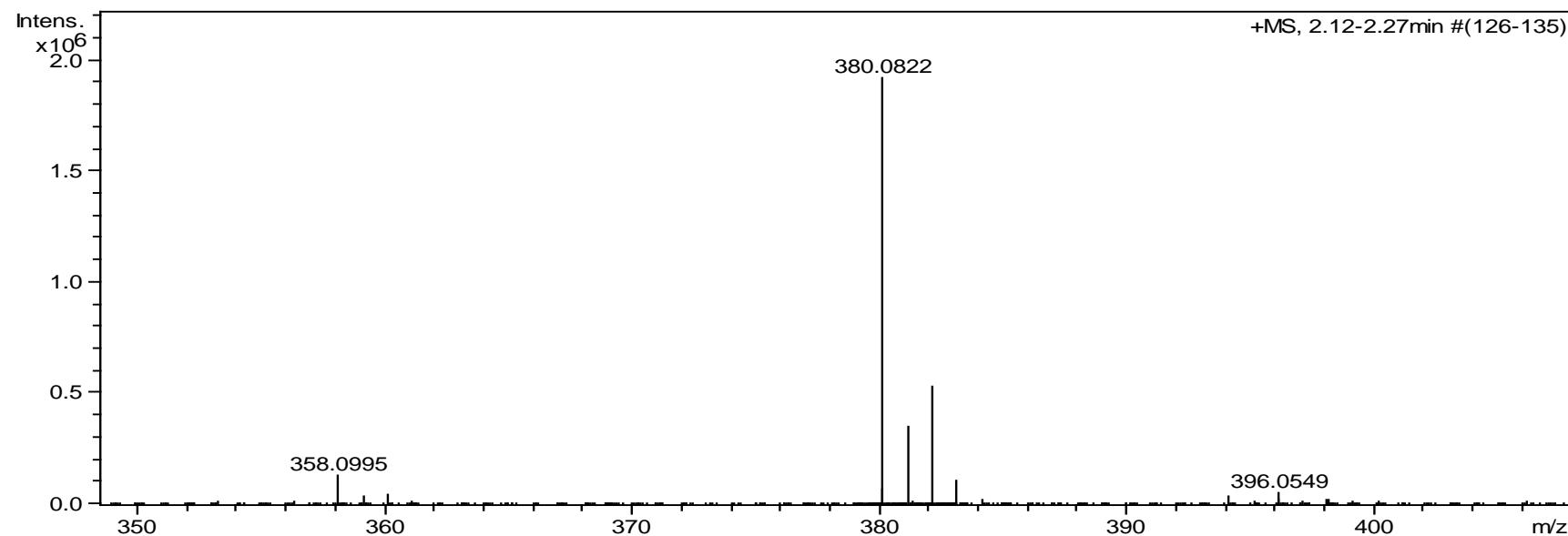


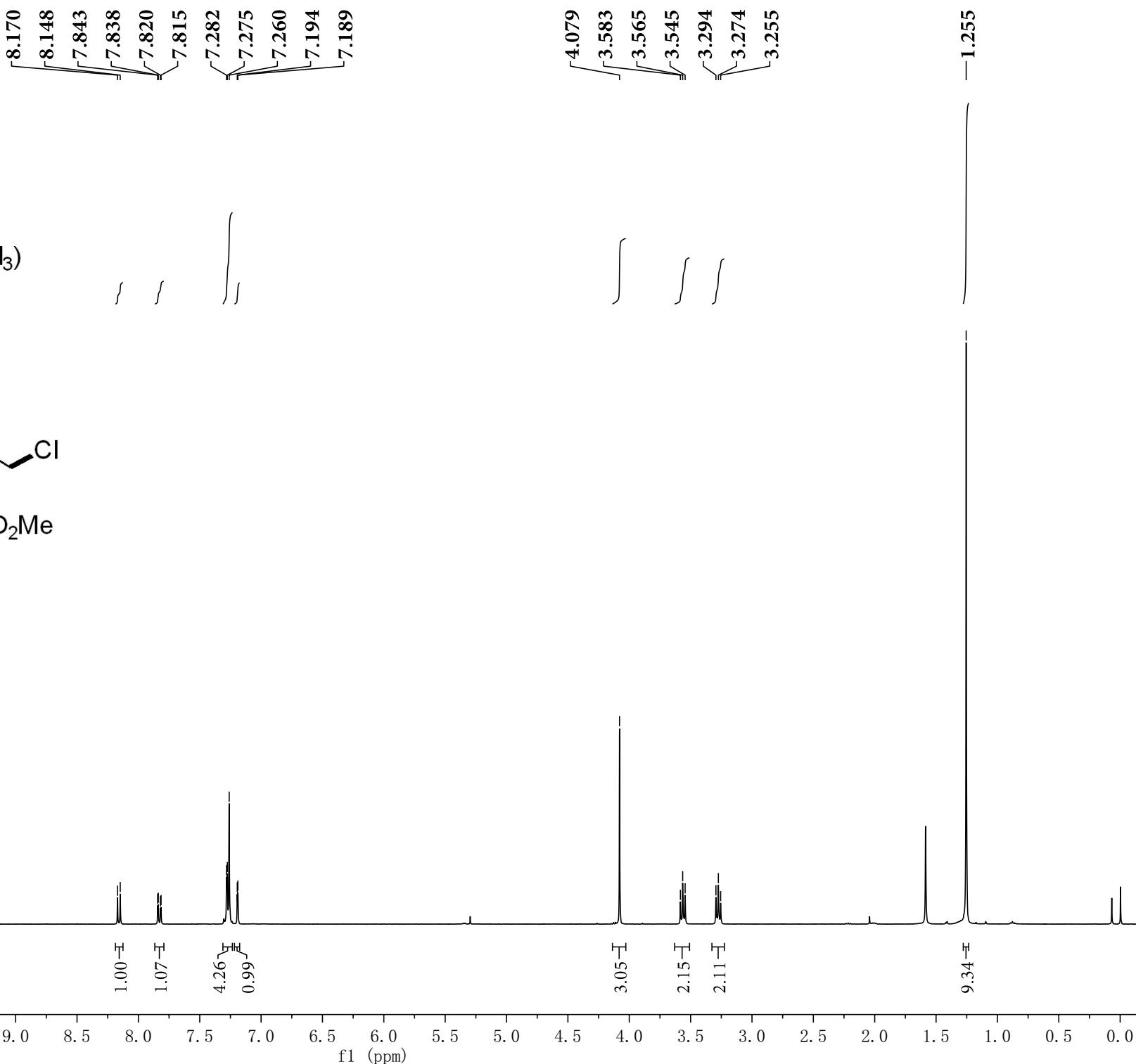
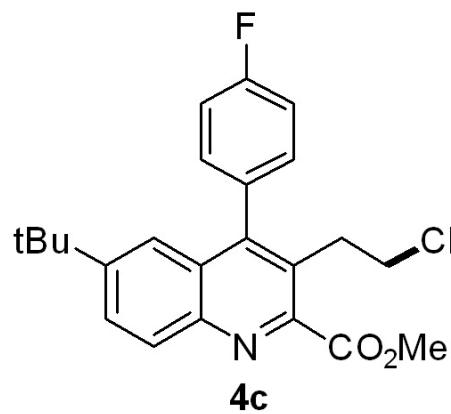


<sup>13</sup>C NMR (400M, CDCl<sub>3</sub>)

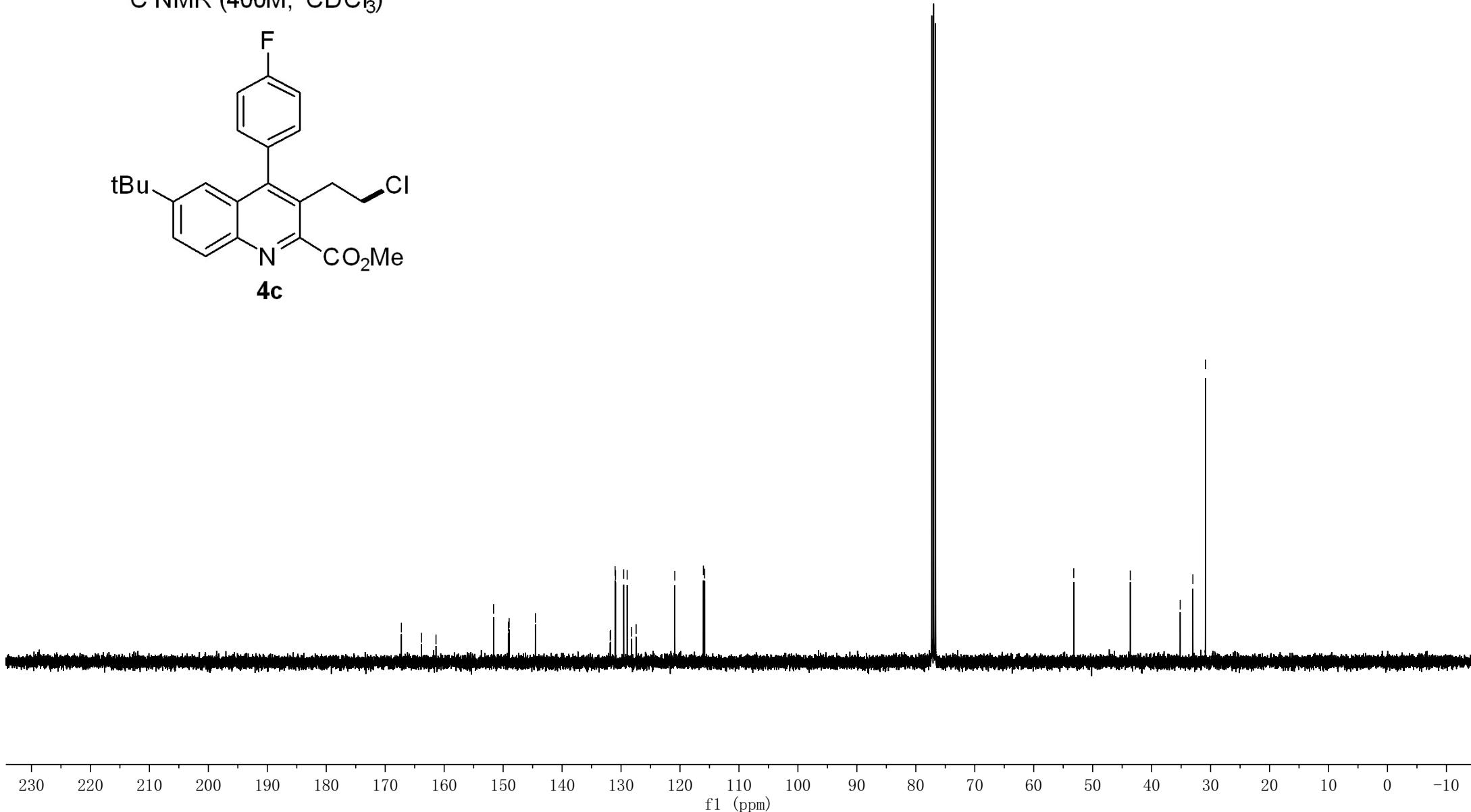
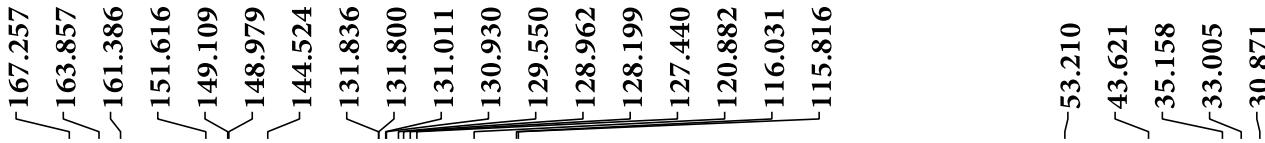
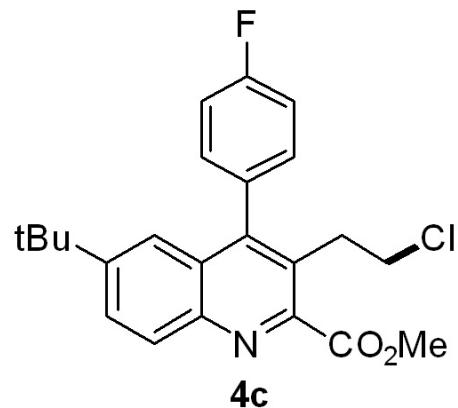


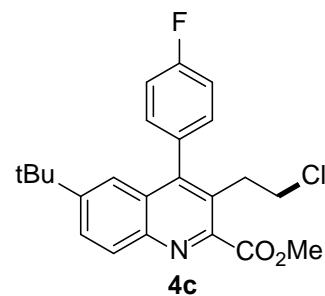
**Methyl 3-(2-chloroethyl)-4-(4-fluorophenyl)-6-methylquinoline-2-carboxylate (4b)**



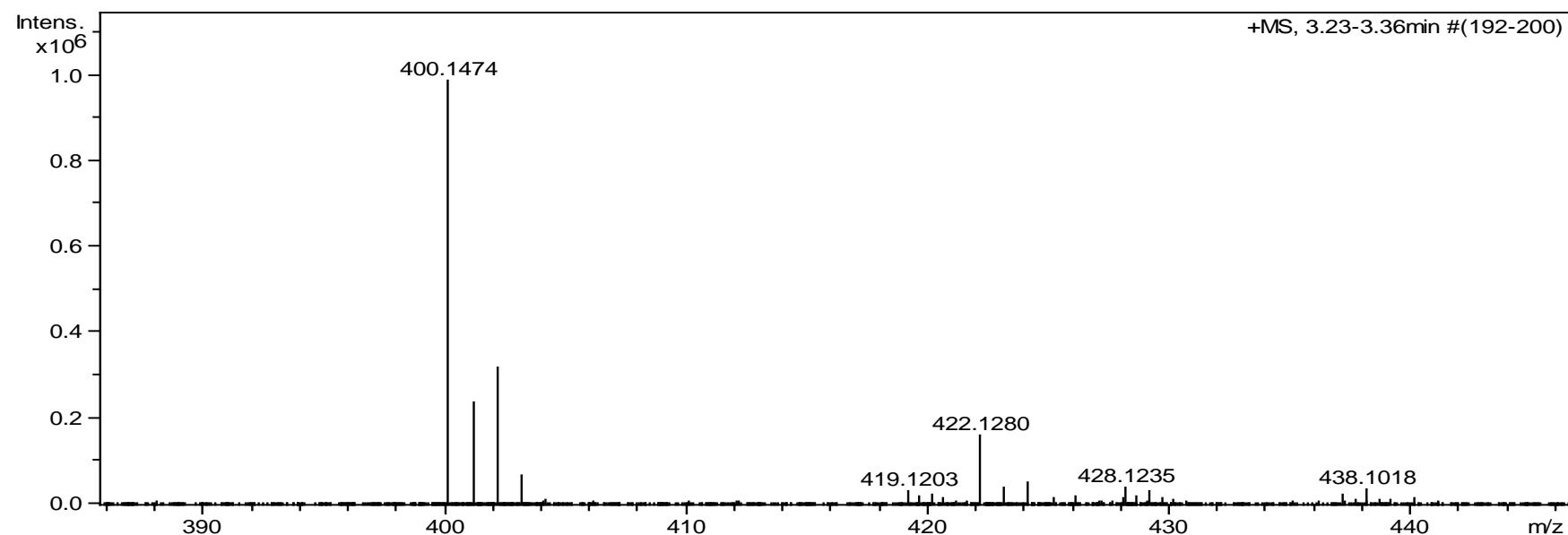
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

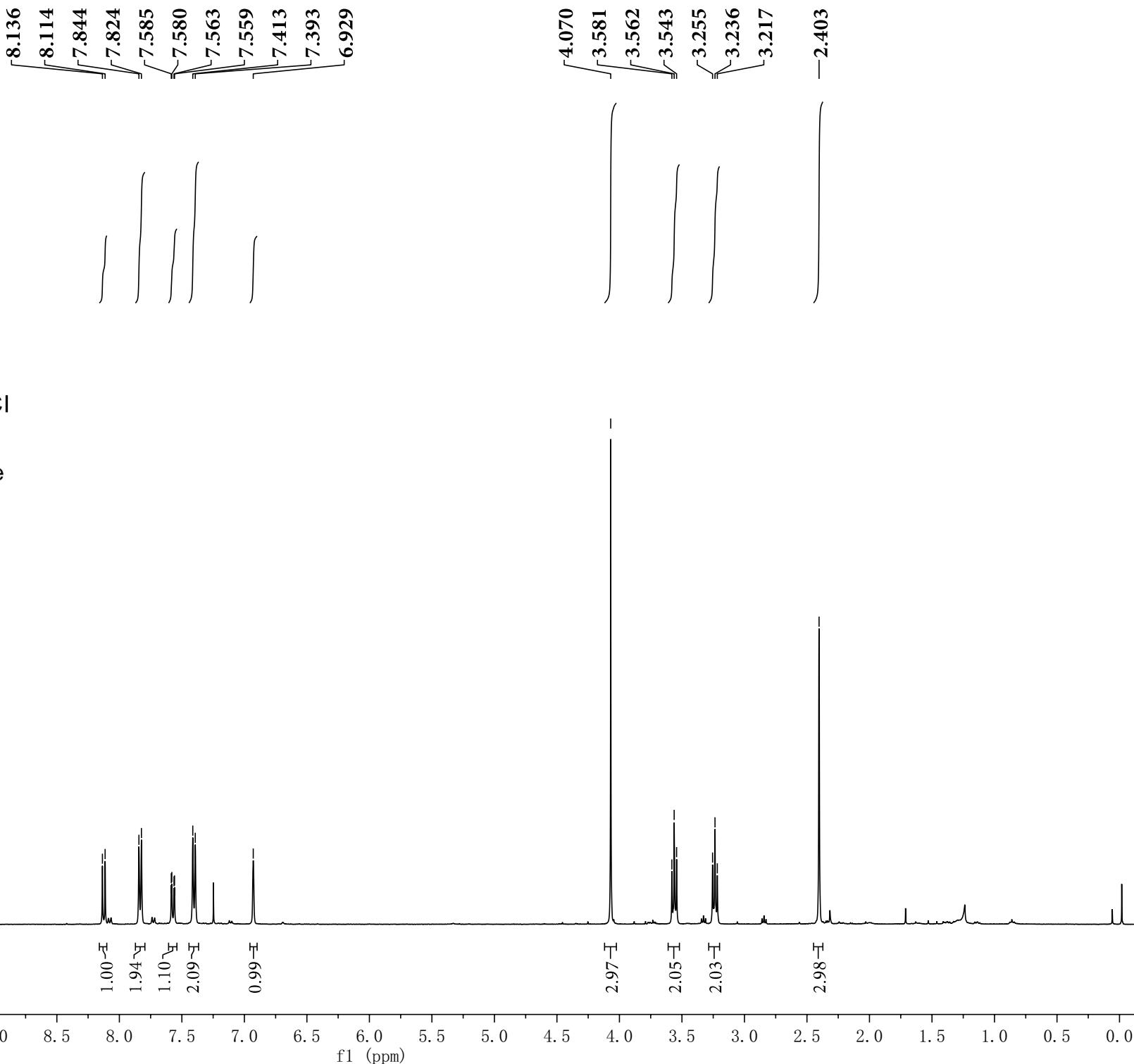
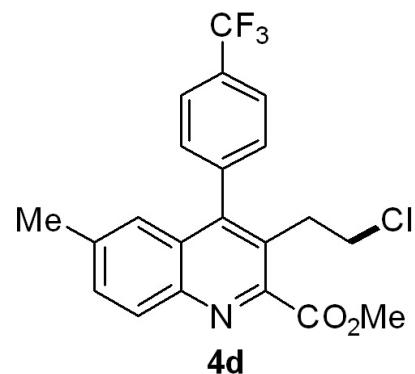
<sup>13</sup>C NMR (400M, CDCl<sub>3</sub>)



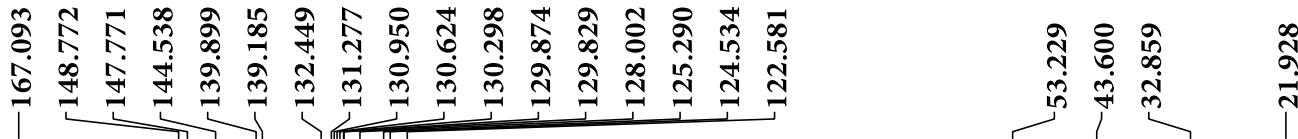
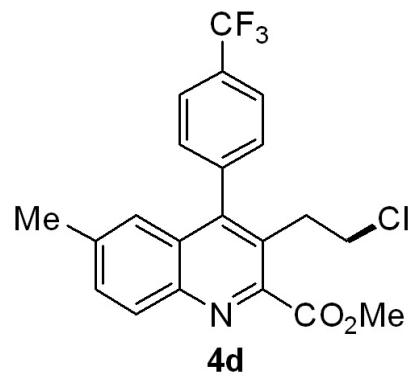


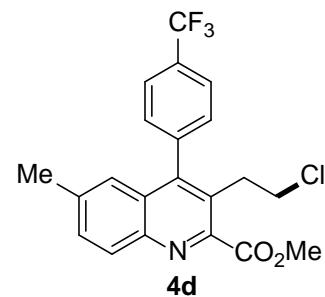
Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4-(4-fluorophenyl)quinoline-2-carboxylate (**4c**)



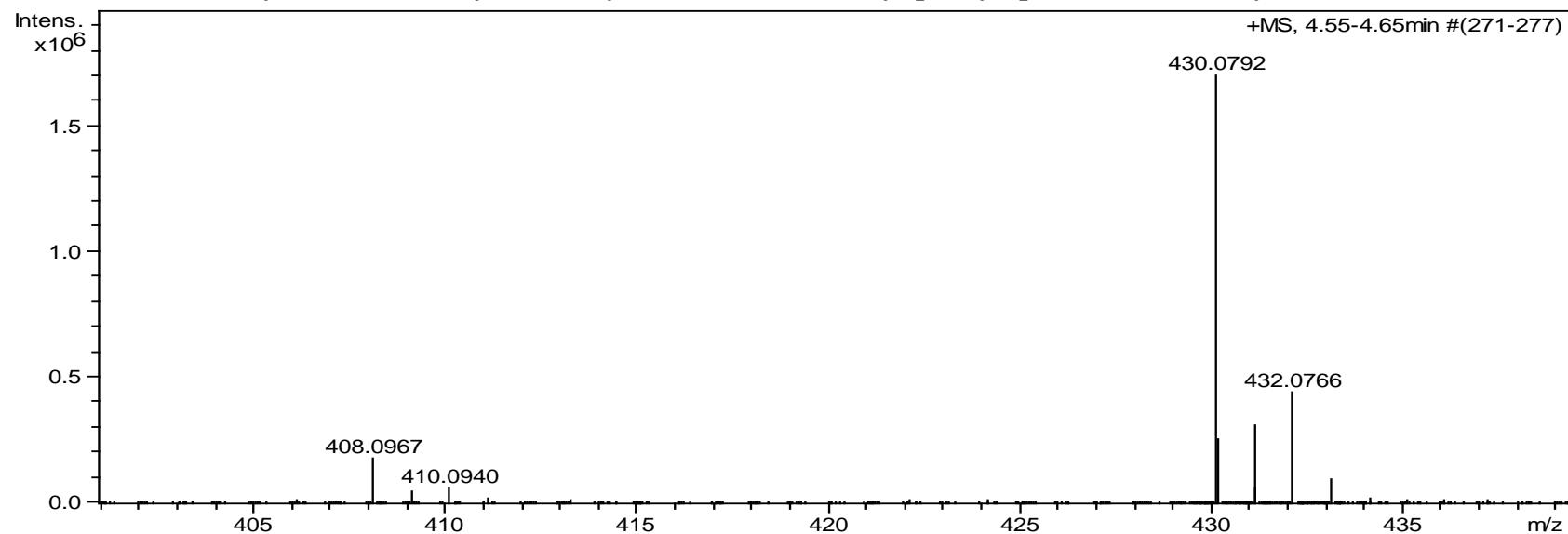
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



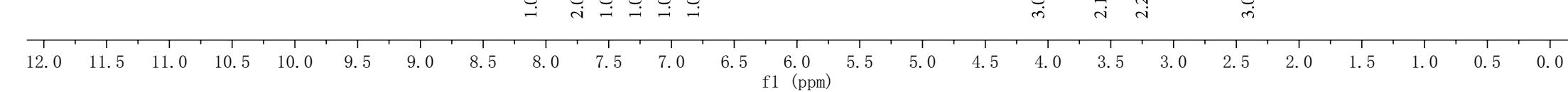
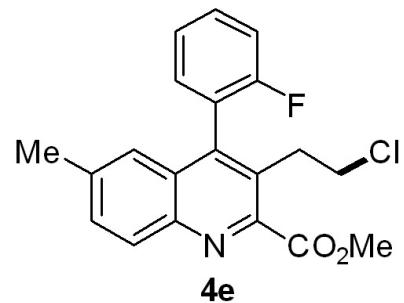


Methyl 3-(2-chloroethyl)-6-methyl-4-(4-(trifluoromethyl)phenyl)quinoline-2-carboxylate (**4d**)



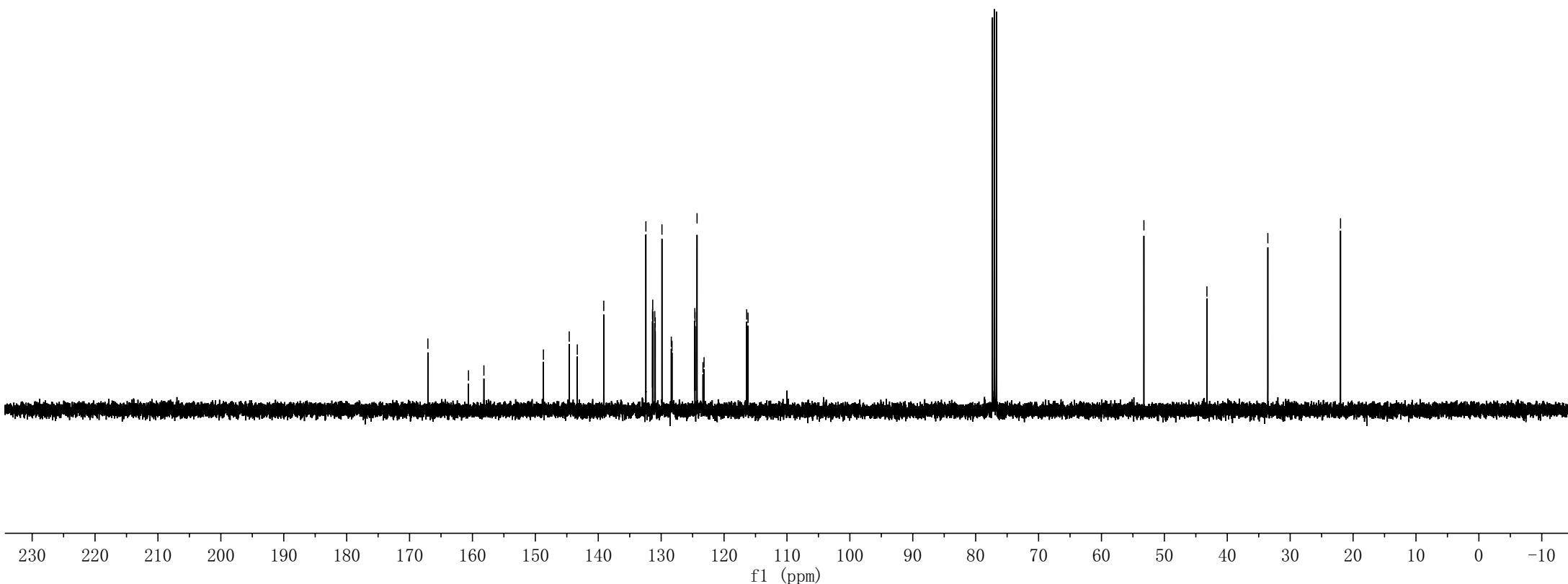
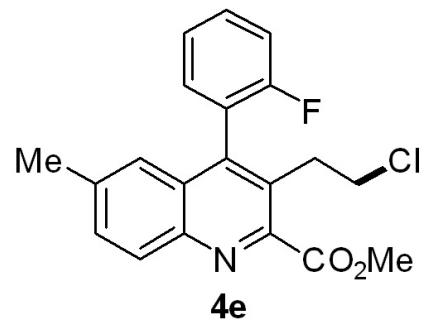
S 8.148  
8.119  
7.586  
7.582  
7.561  
7.541  
7.536  
7.382  
7.363  
7.345  
7.326  
7.304  
7.281  
7.260  
7.250  
7.246  
7.232  
7.228  
7.214  
7.209  
7.030

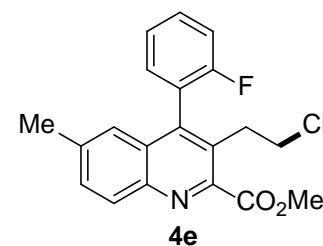
$^1\text{H}$  NMR (400M,  $\text{CDCl}_3$ )



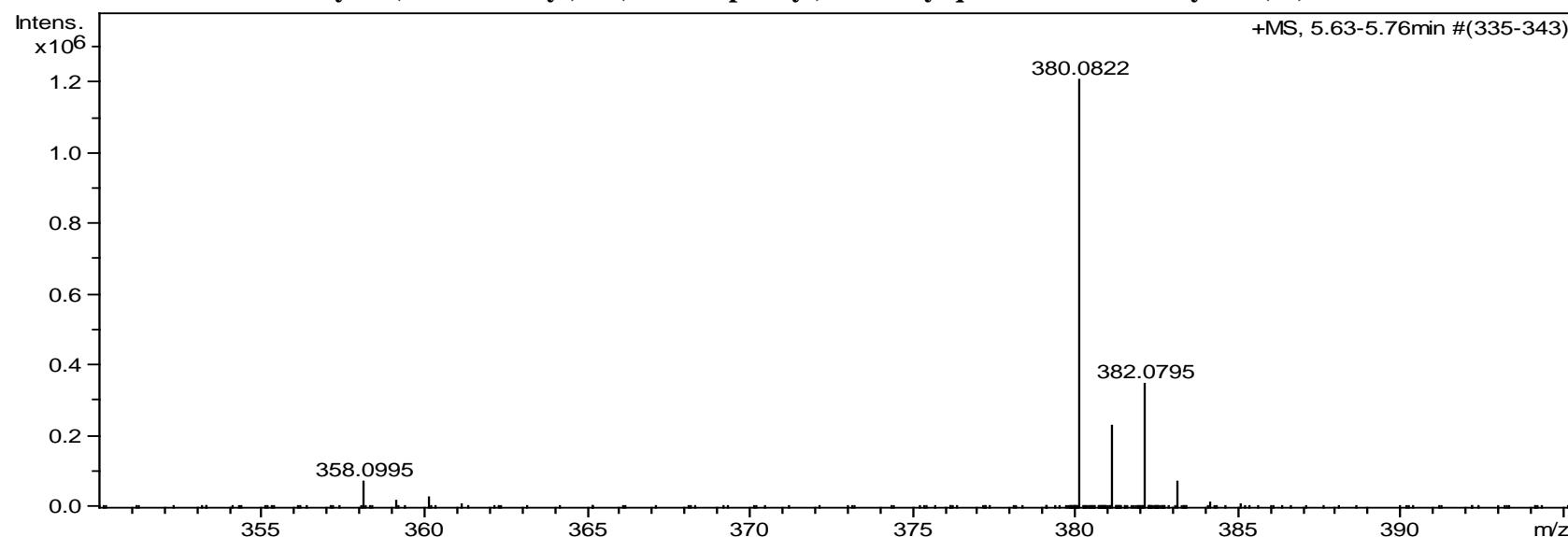
S112

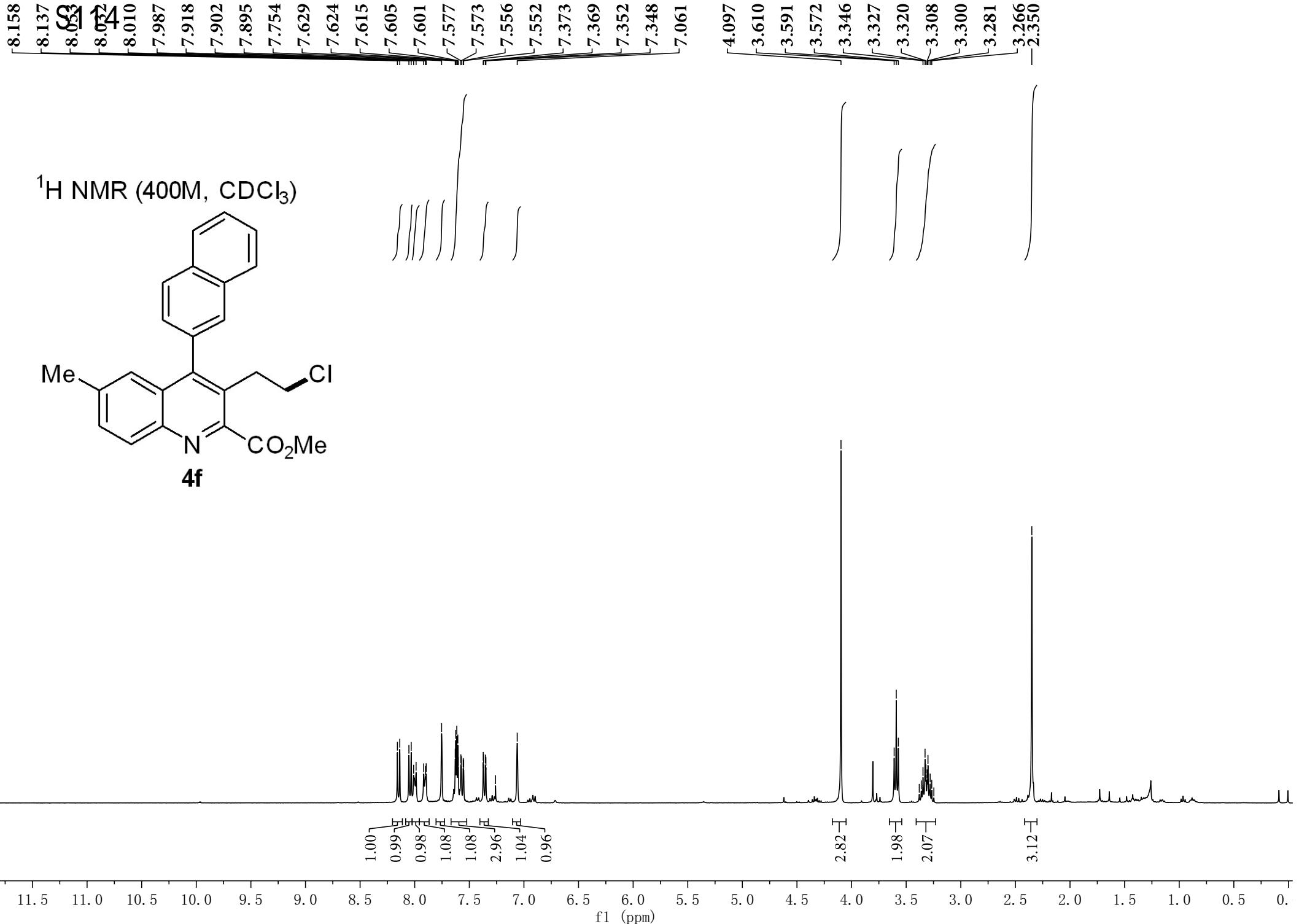
$^{13}\text{C}$  NMR (400M,  $\text{CDCl}_3$ )



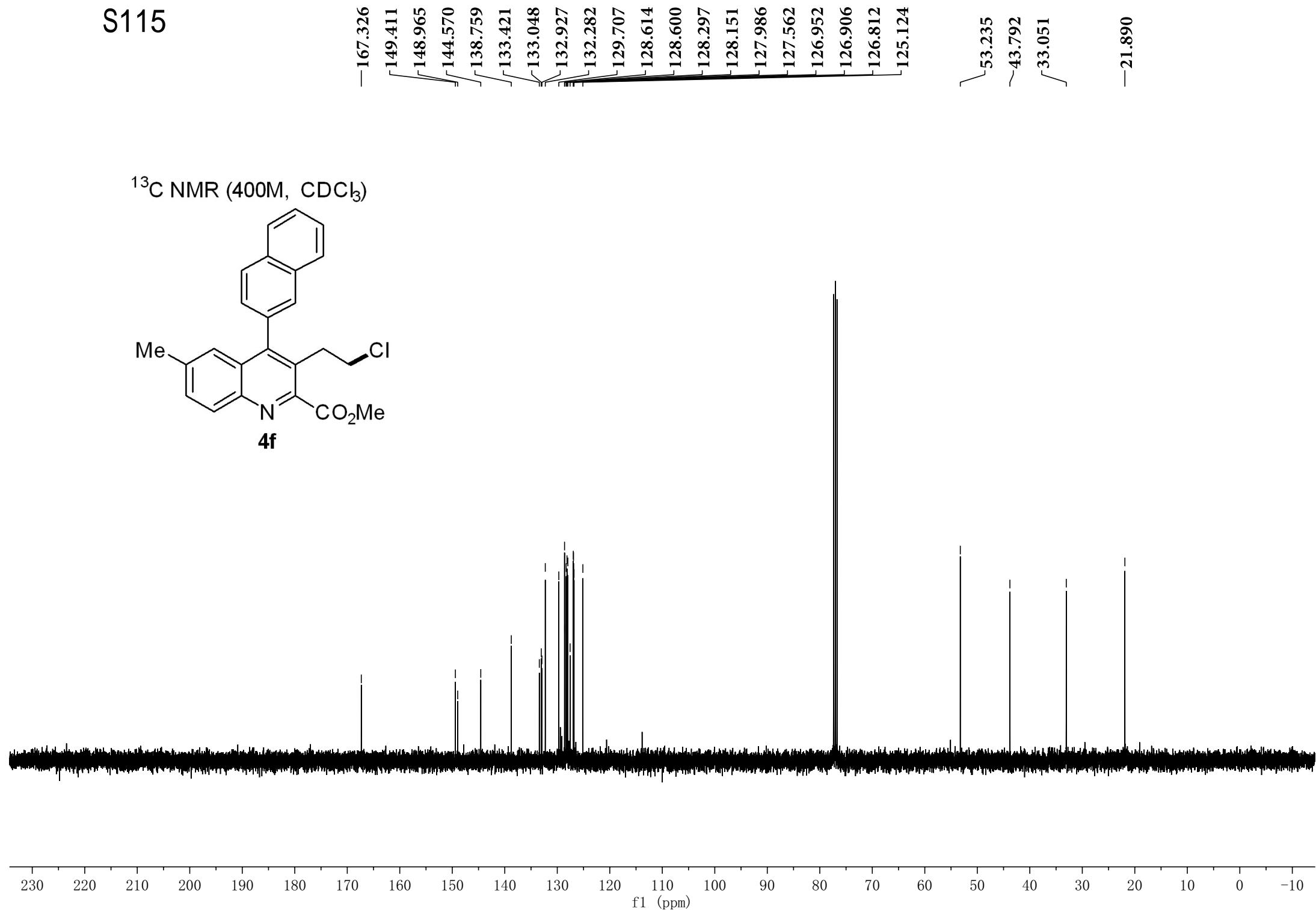
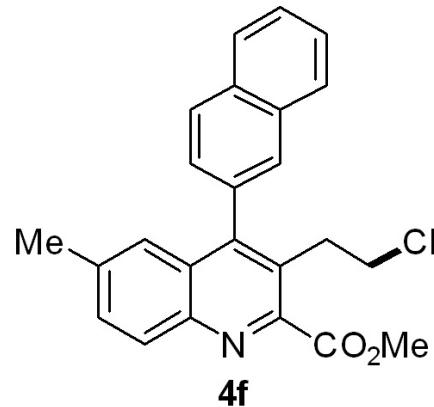


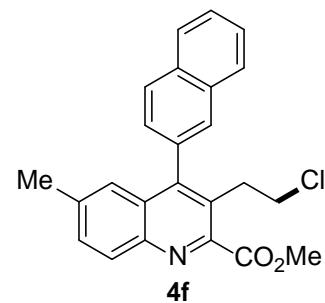
**Methyl 3-(2-chloroethyl)-4-(2-fluorophenyl)-6-methylquinoline-2-carboxylate (4e)**



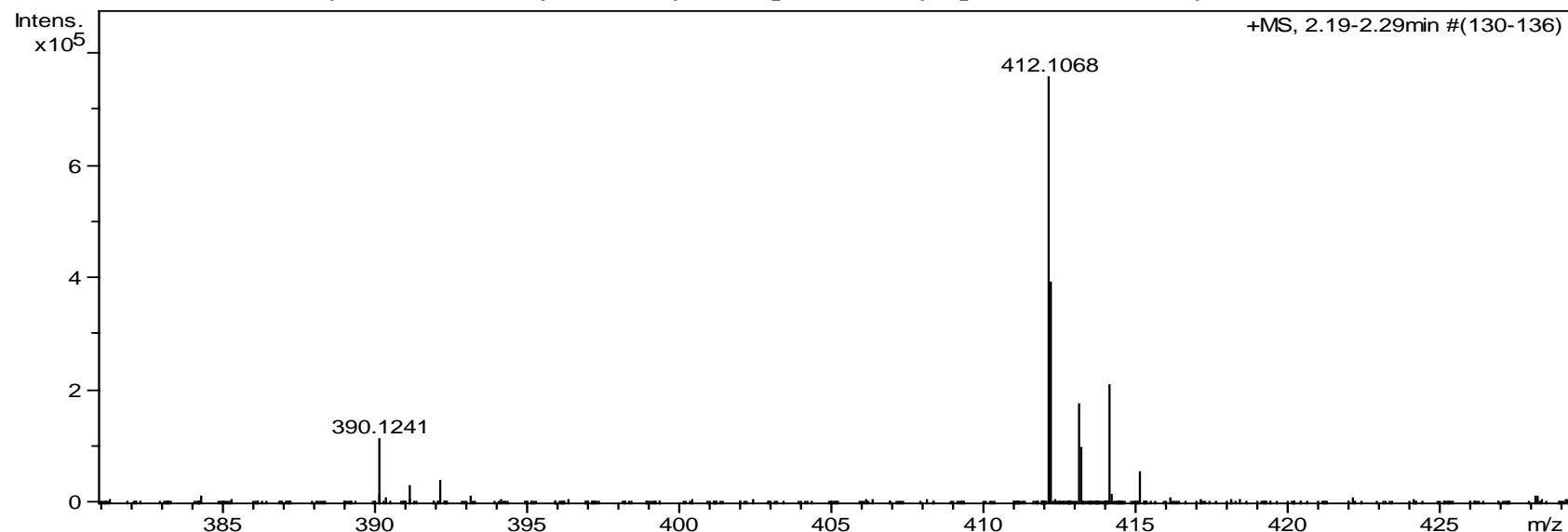


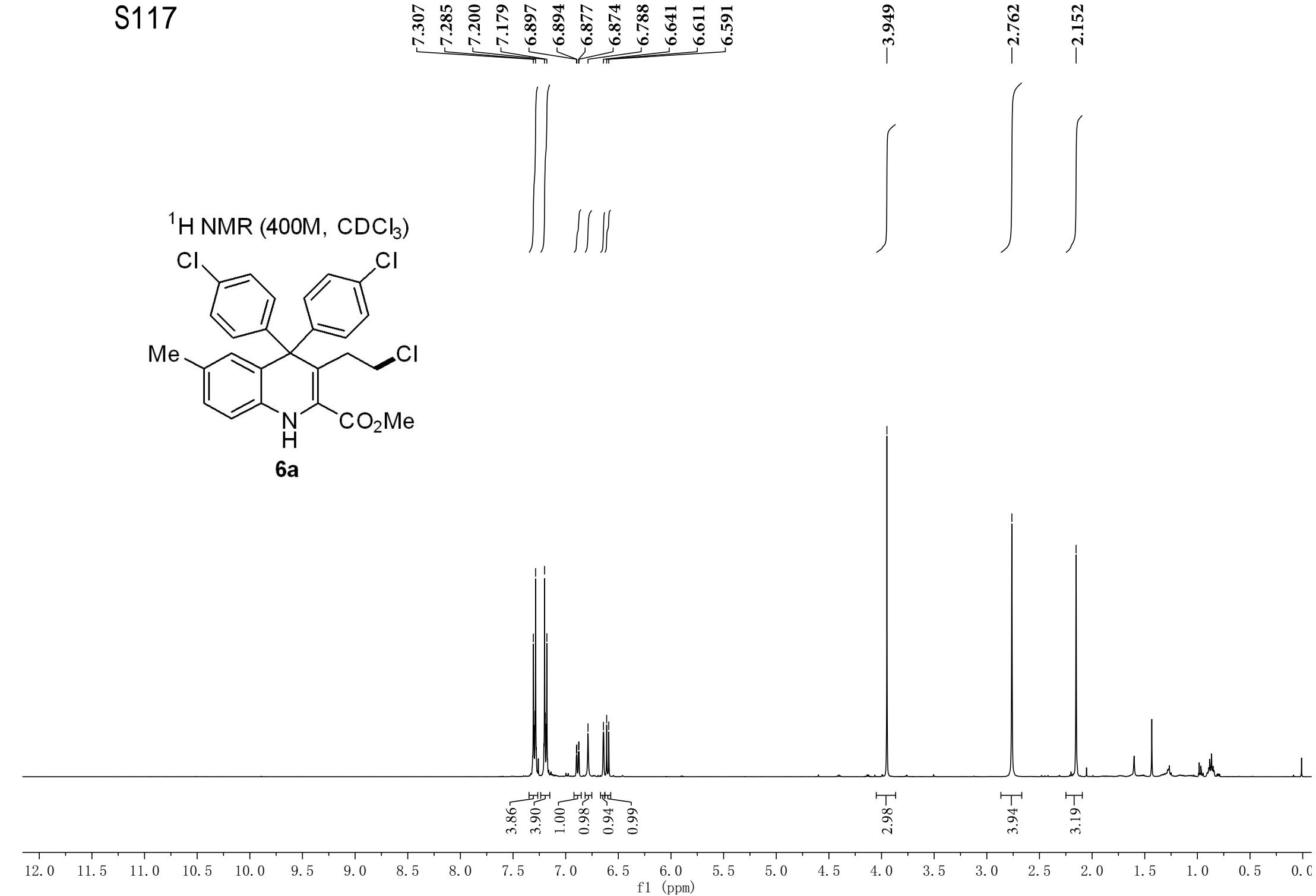
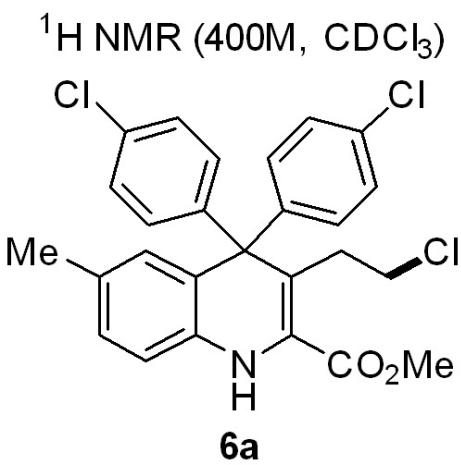
<sup>13</sup>C NMR (400M, CDCl<sub>3</sub>)



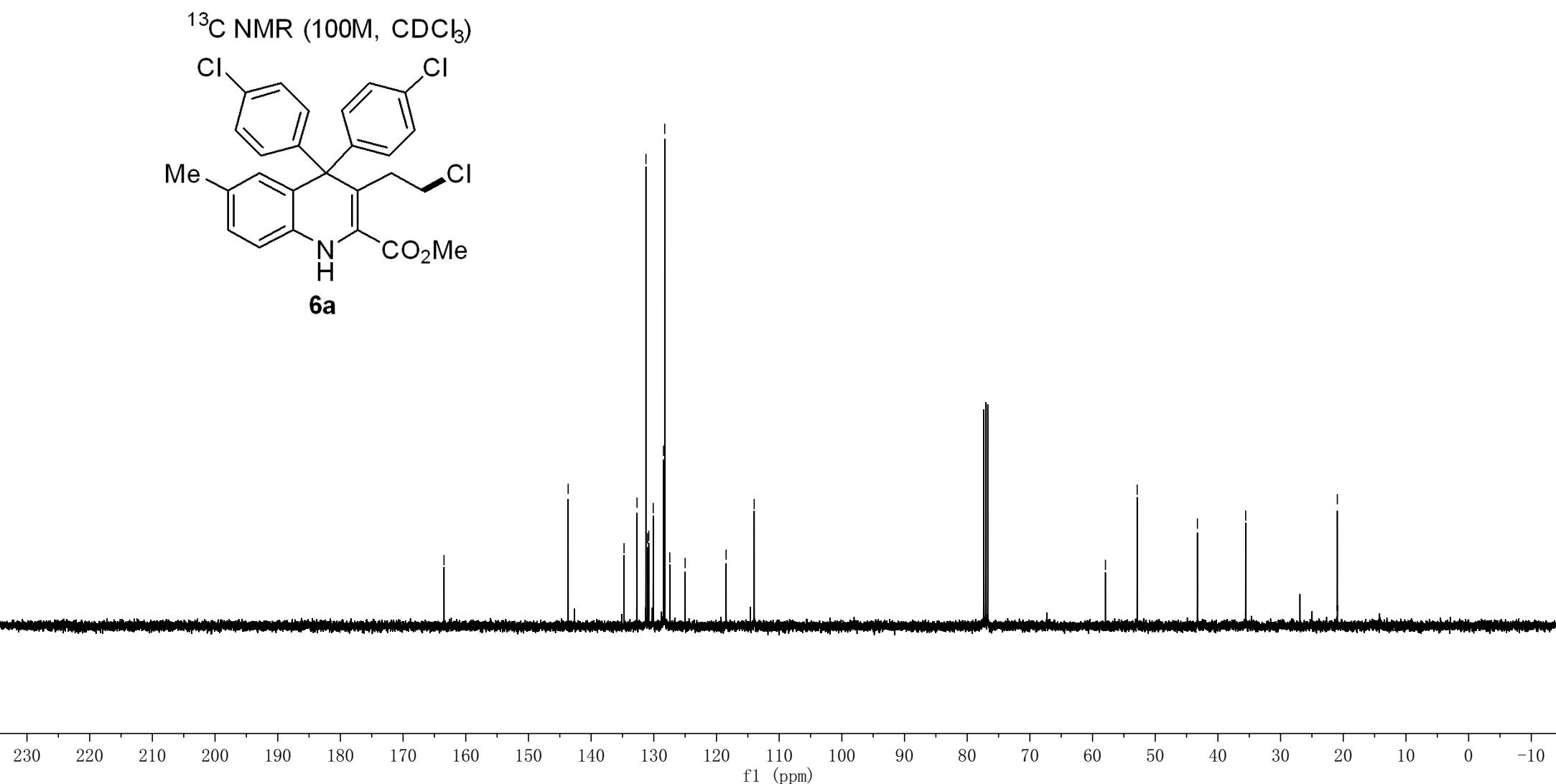
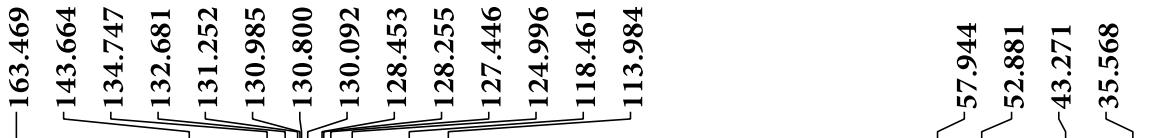
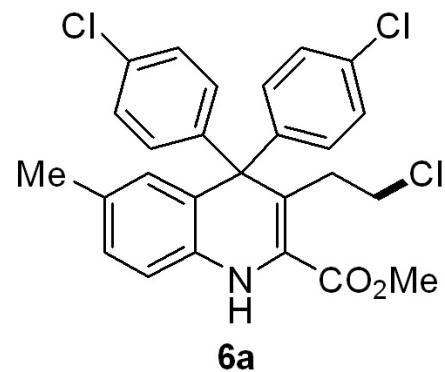


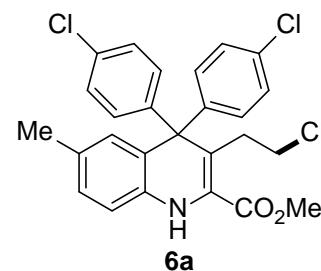
Methyl 3-(2-chloroethyl)-6-methyl-4-(naphthalen-2-yl)quinoline-2-carboxylate (**4f**)



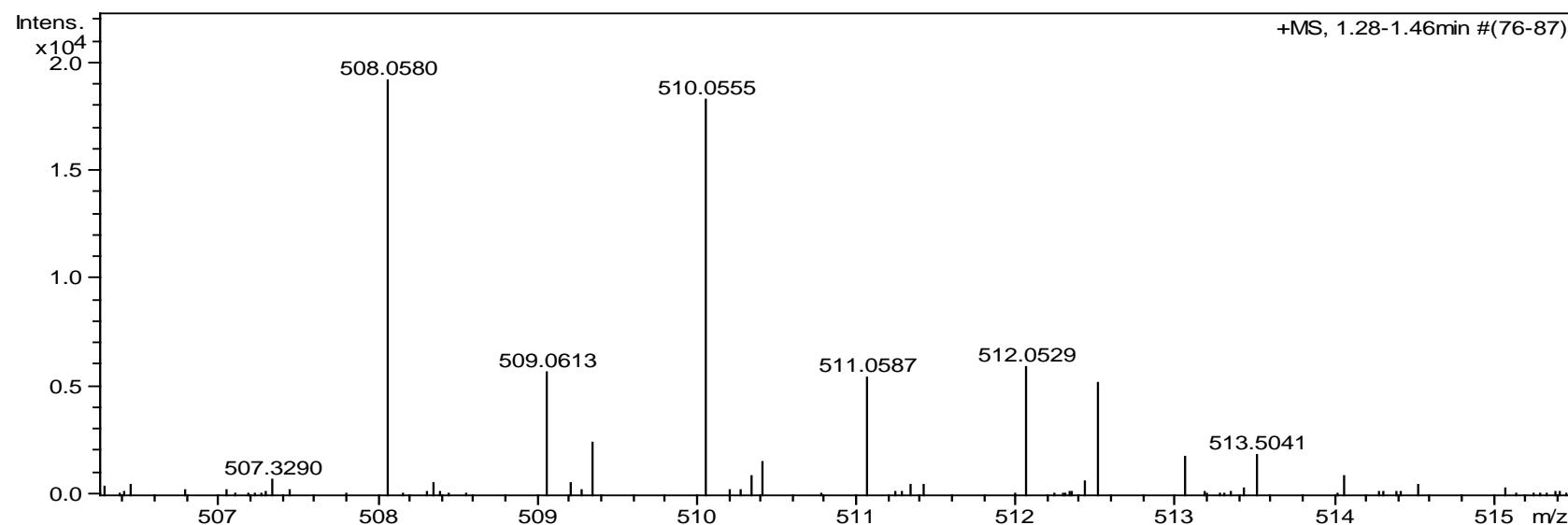


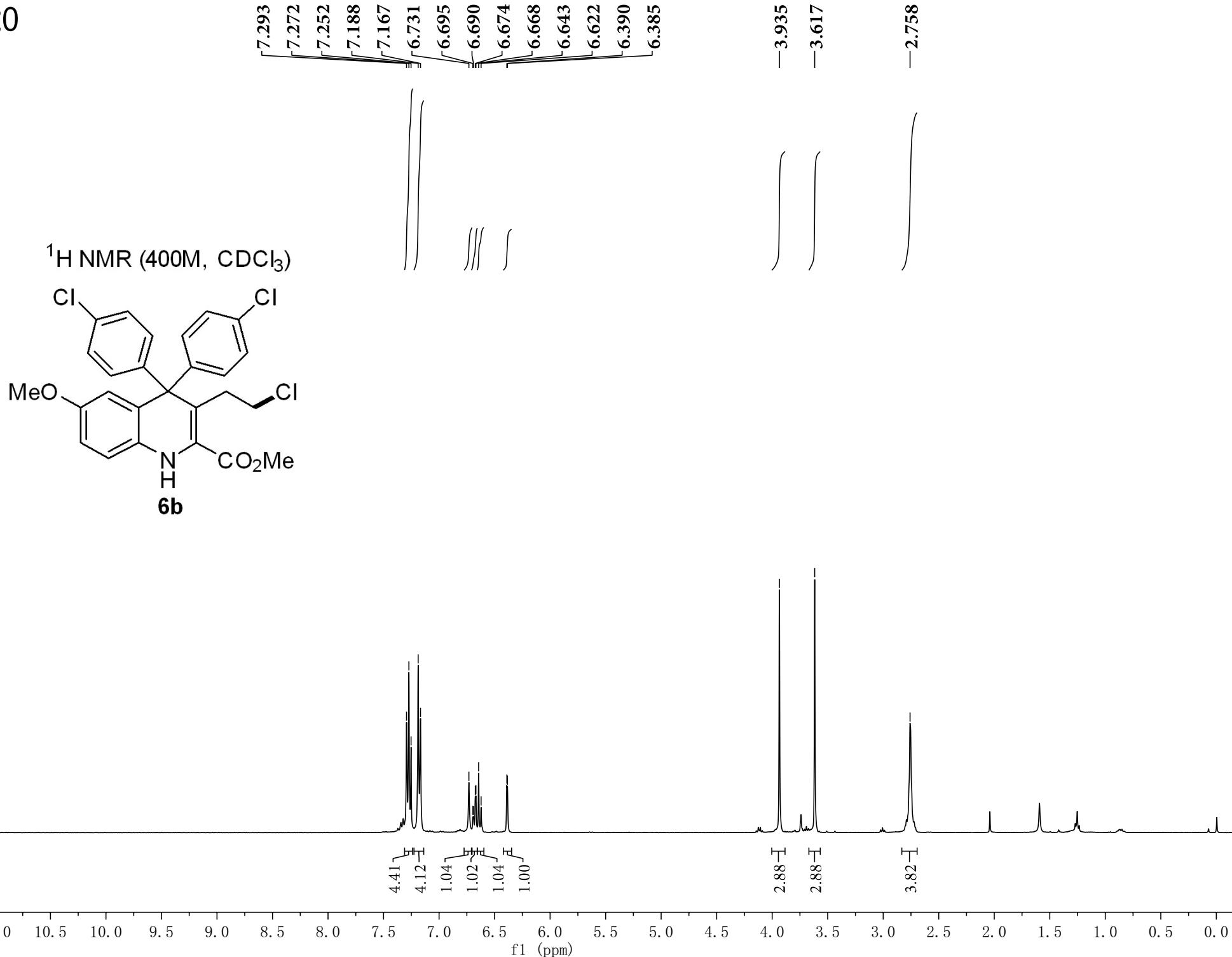
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



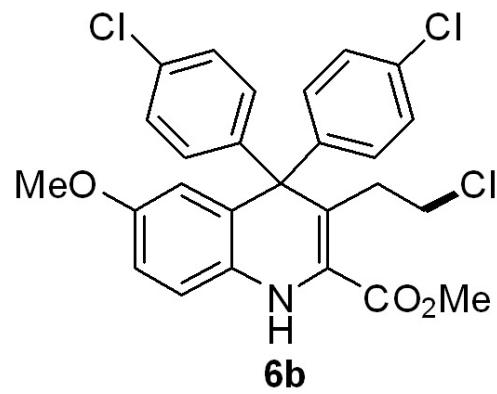


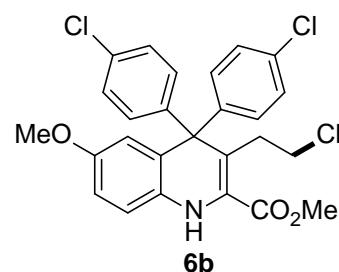
**methyl 3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-6-methyl-1,4-dihydroquinoline-2-carboxylate (6a)**



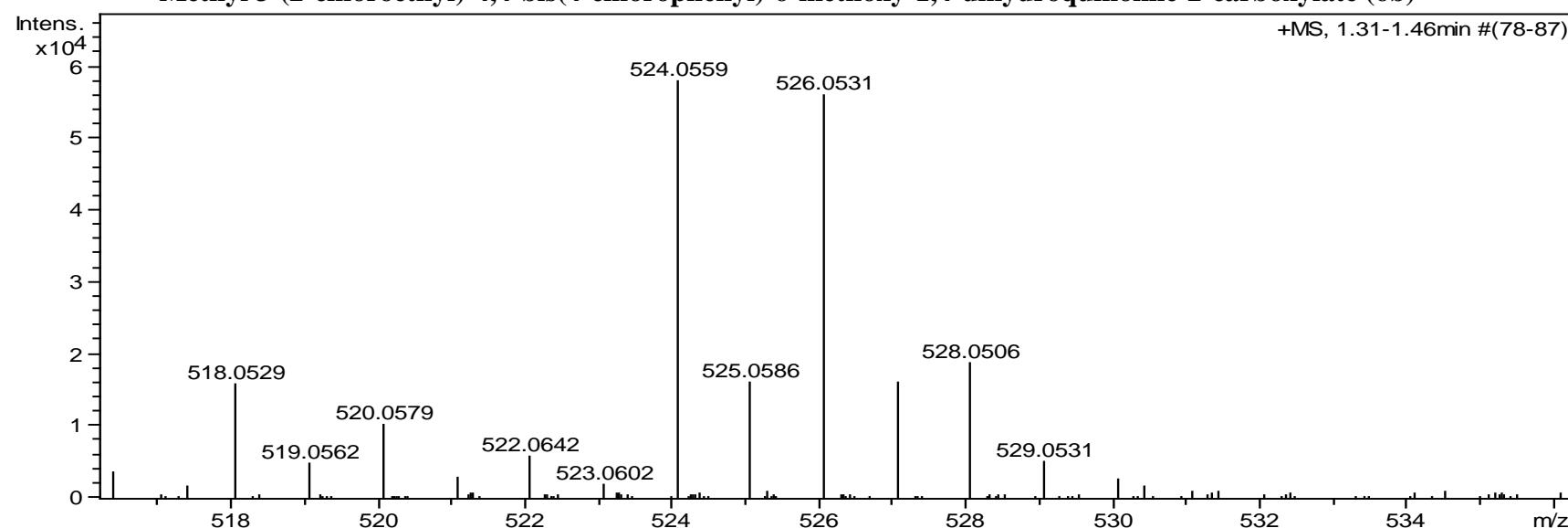


<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)

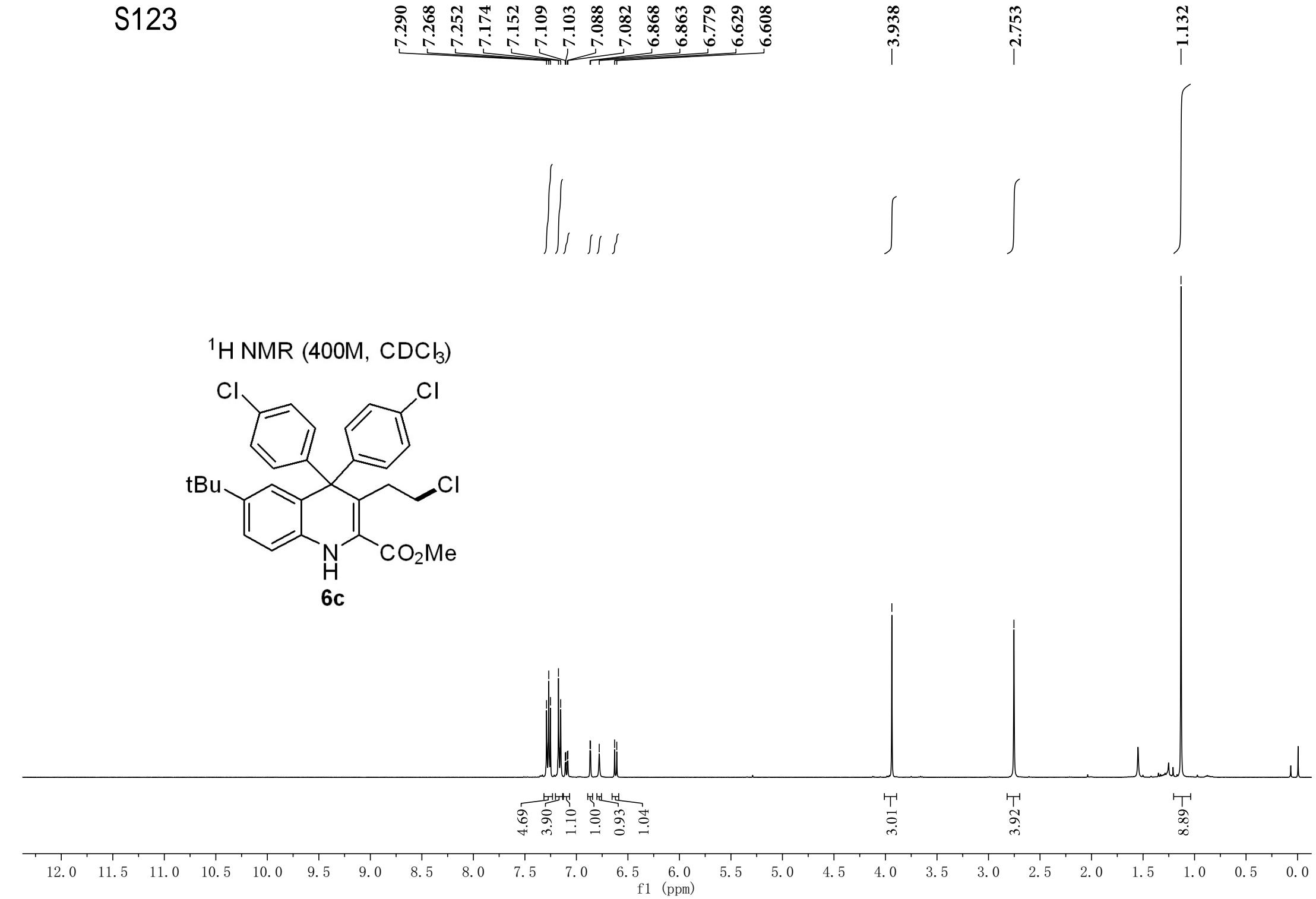
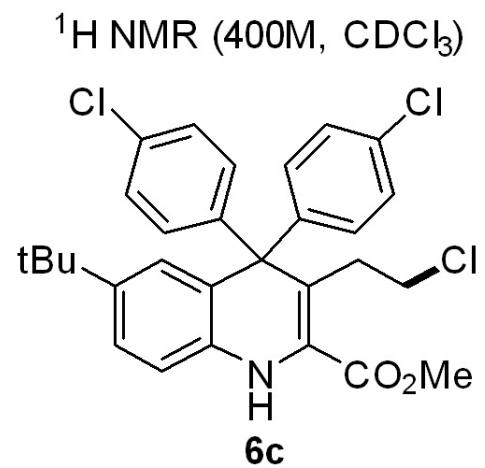




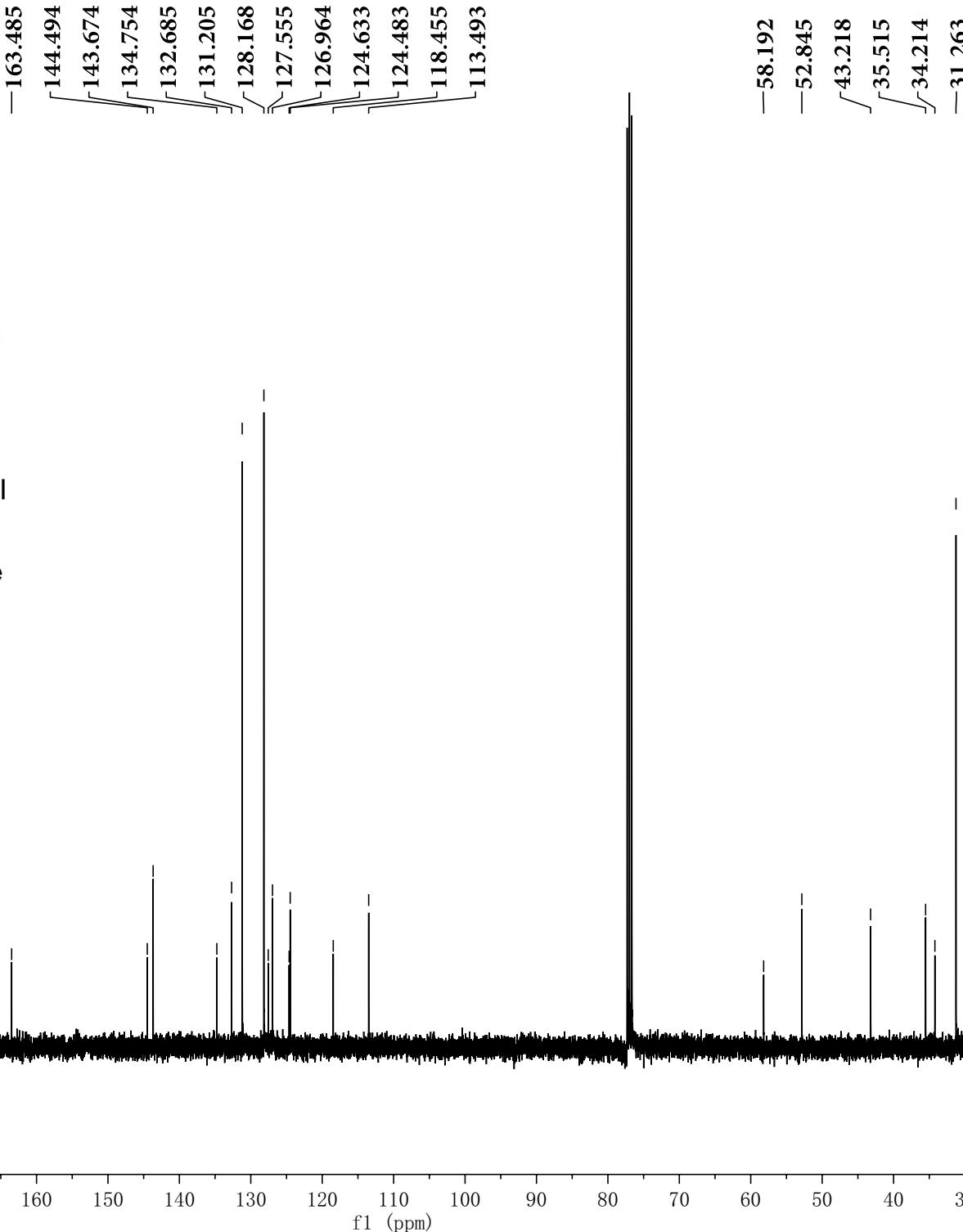
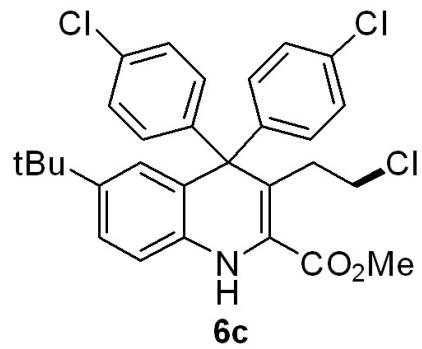
Methyl 3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-6-methoxy-1,4-dihydroquinoline-2-carboxylate (**6b**)

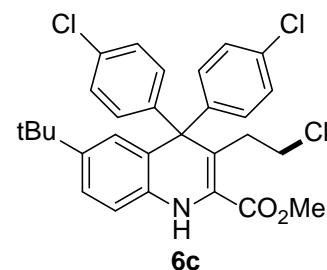


S123

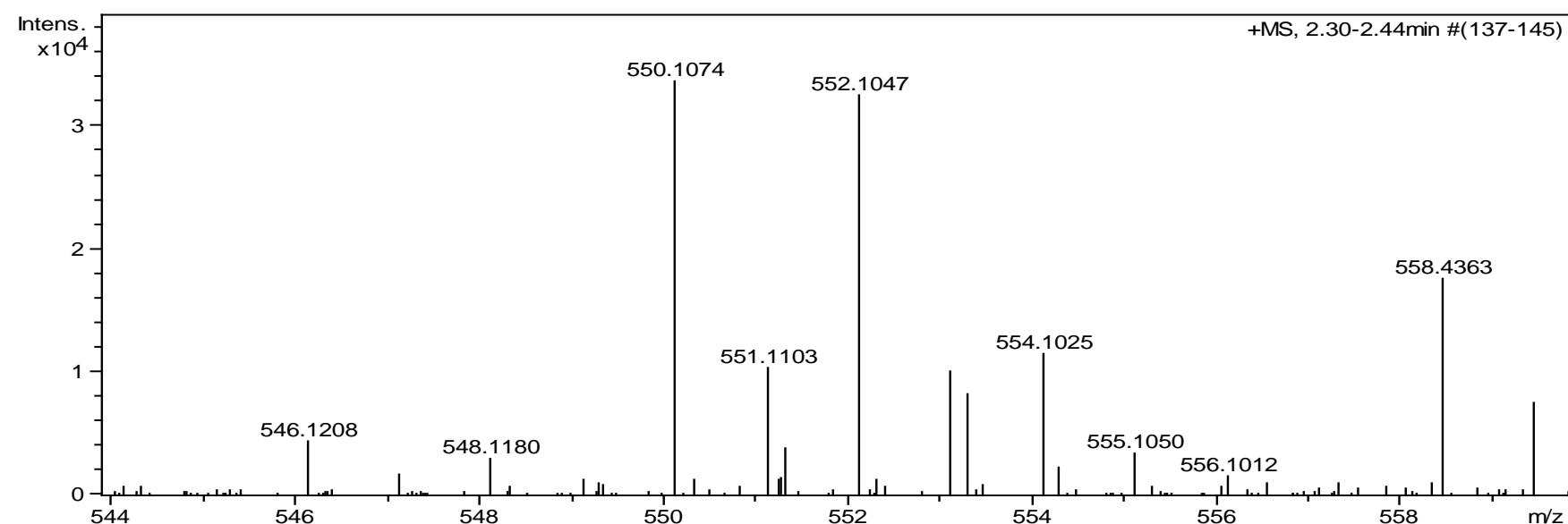


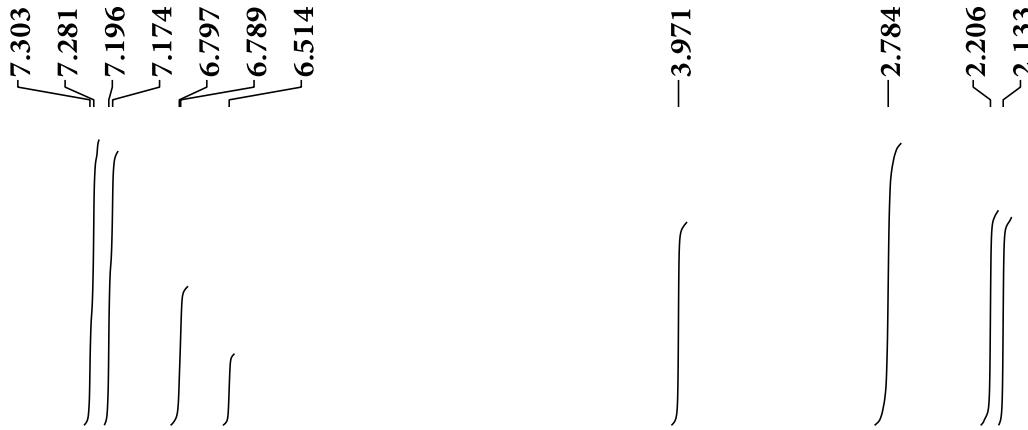
<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)



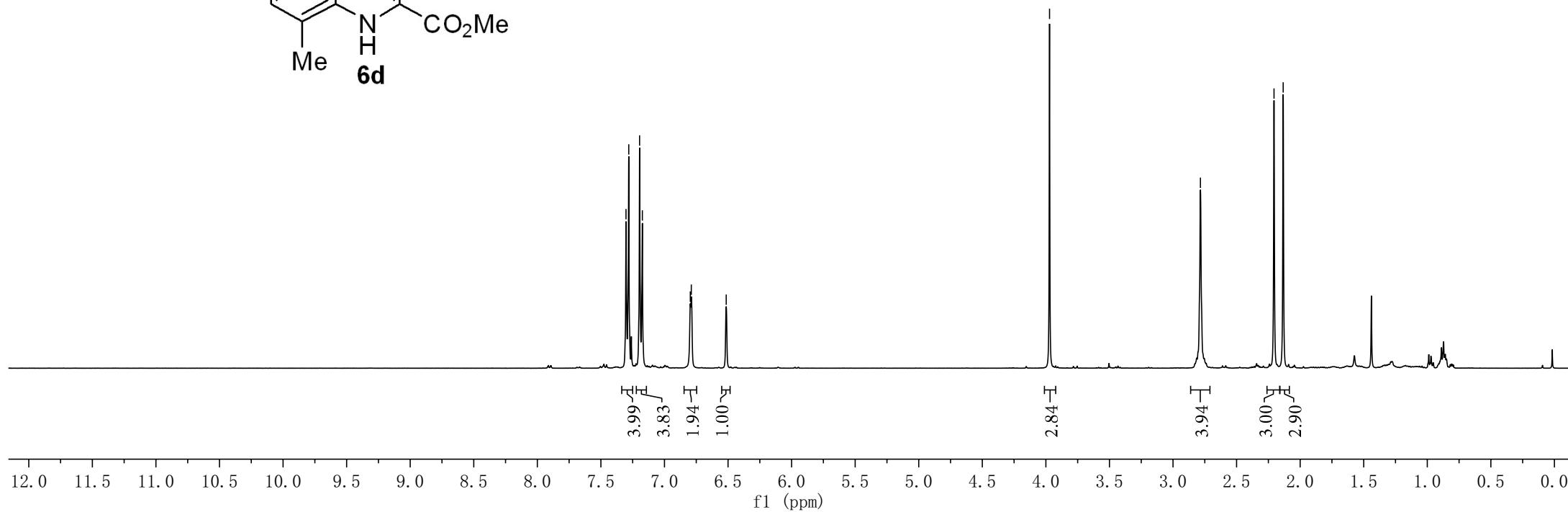
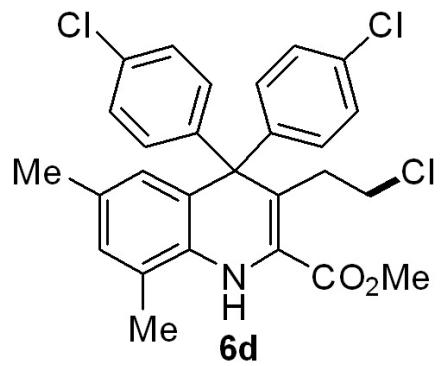


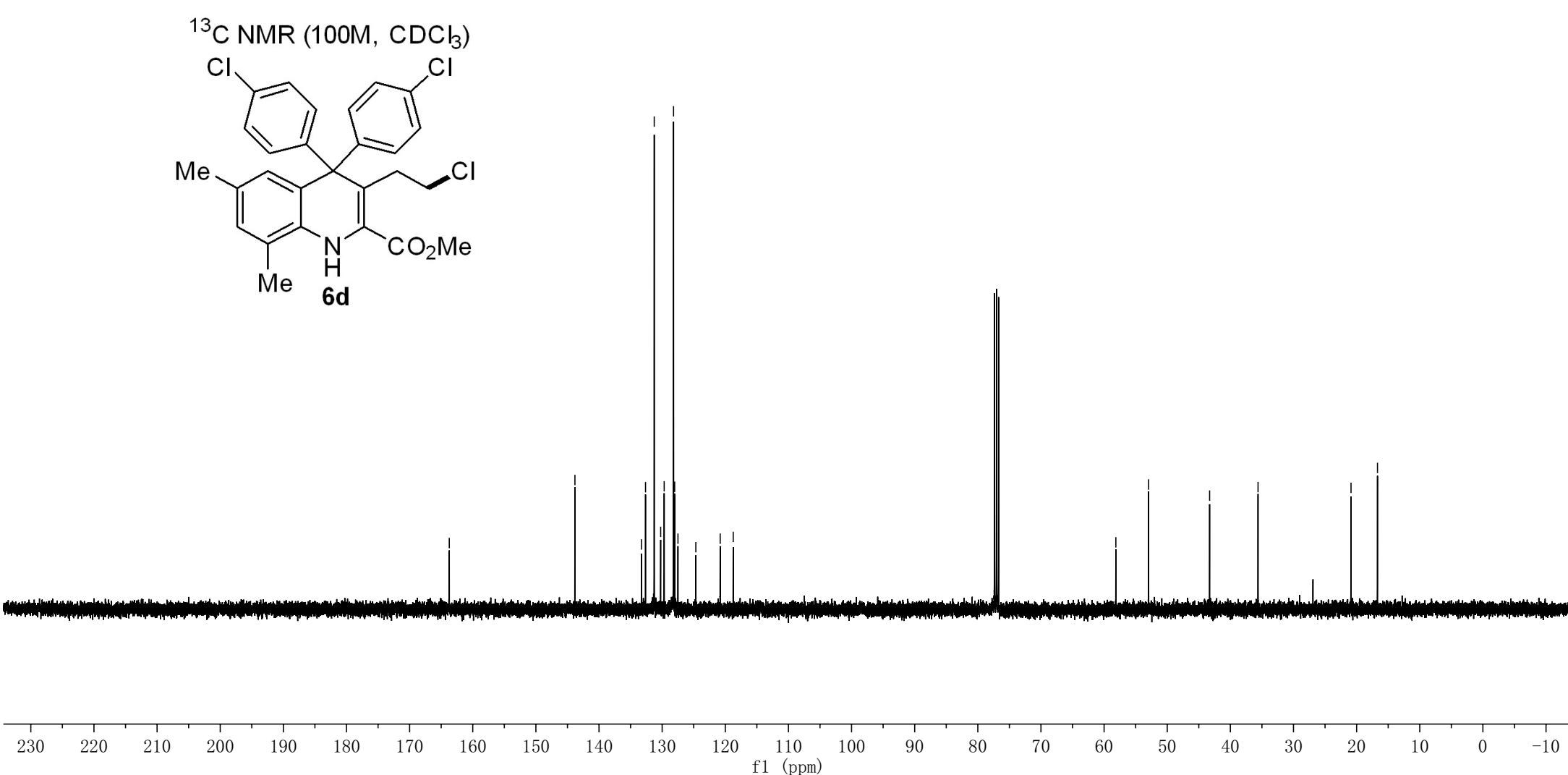
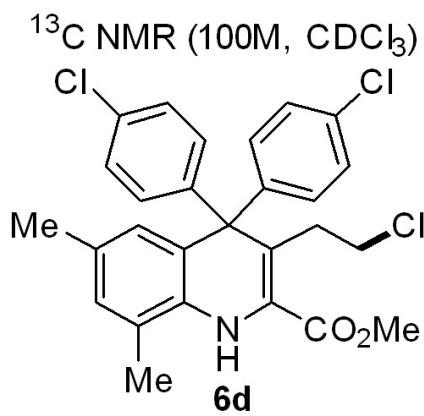
**Methyl 6-(tert-butyl)-3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-1,4-dihydroquinoline-2-carboxylate (6c)**

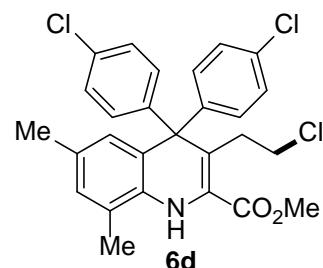




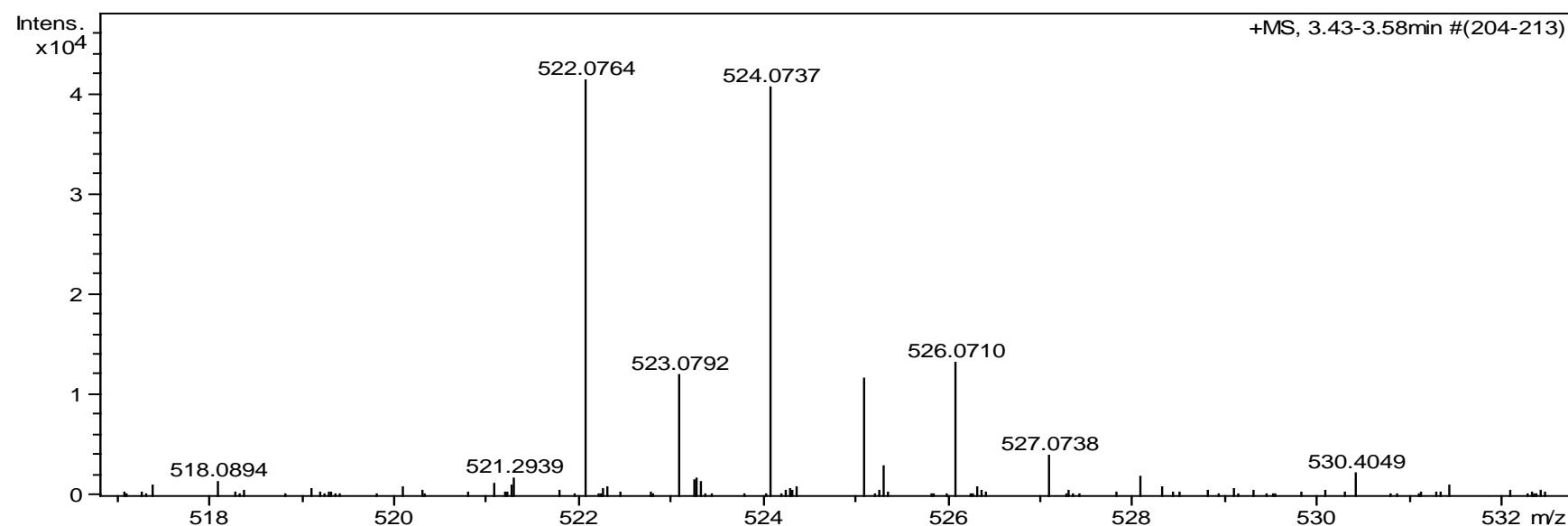
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

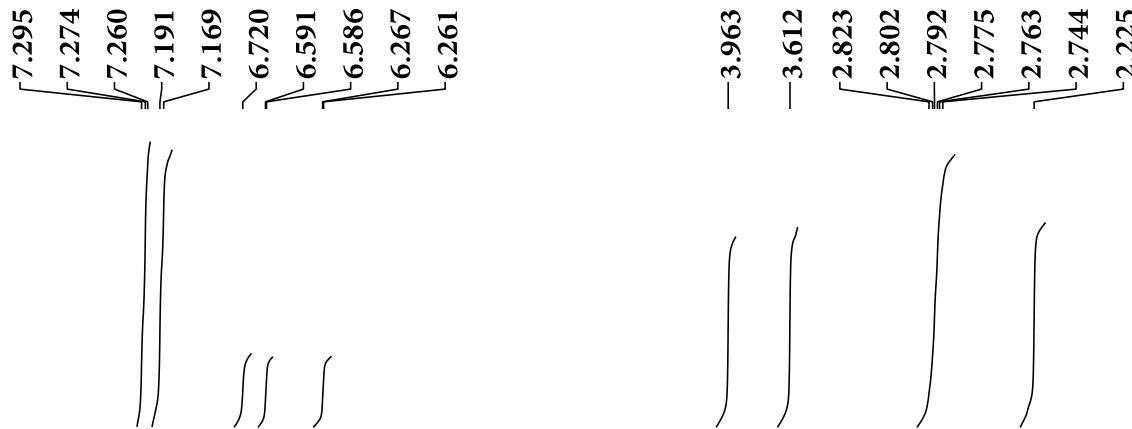




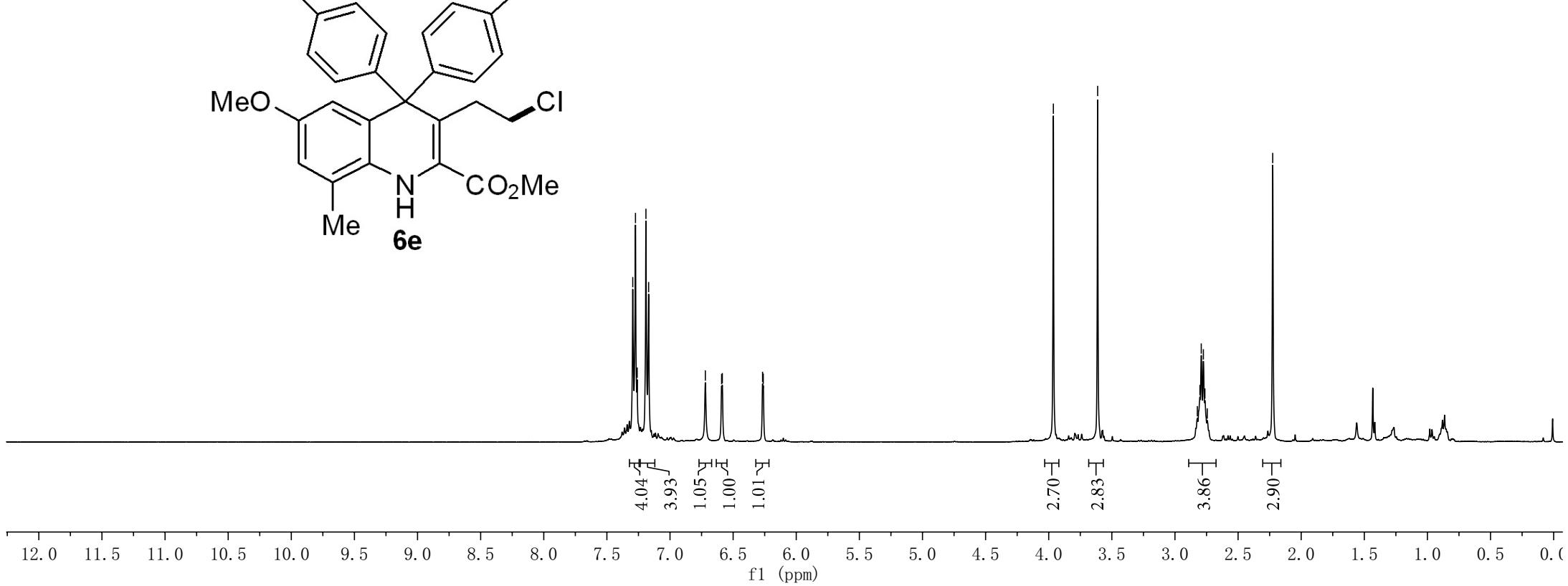
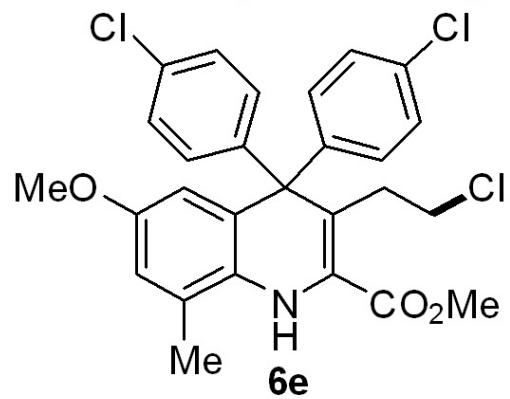


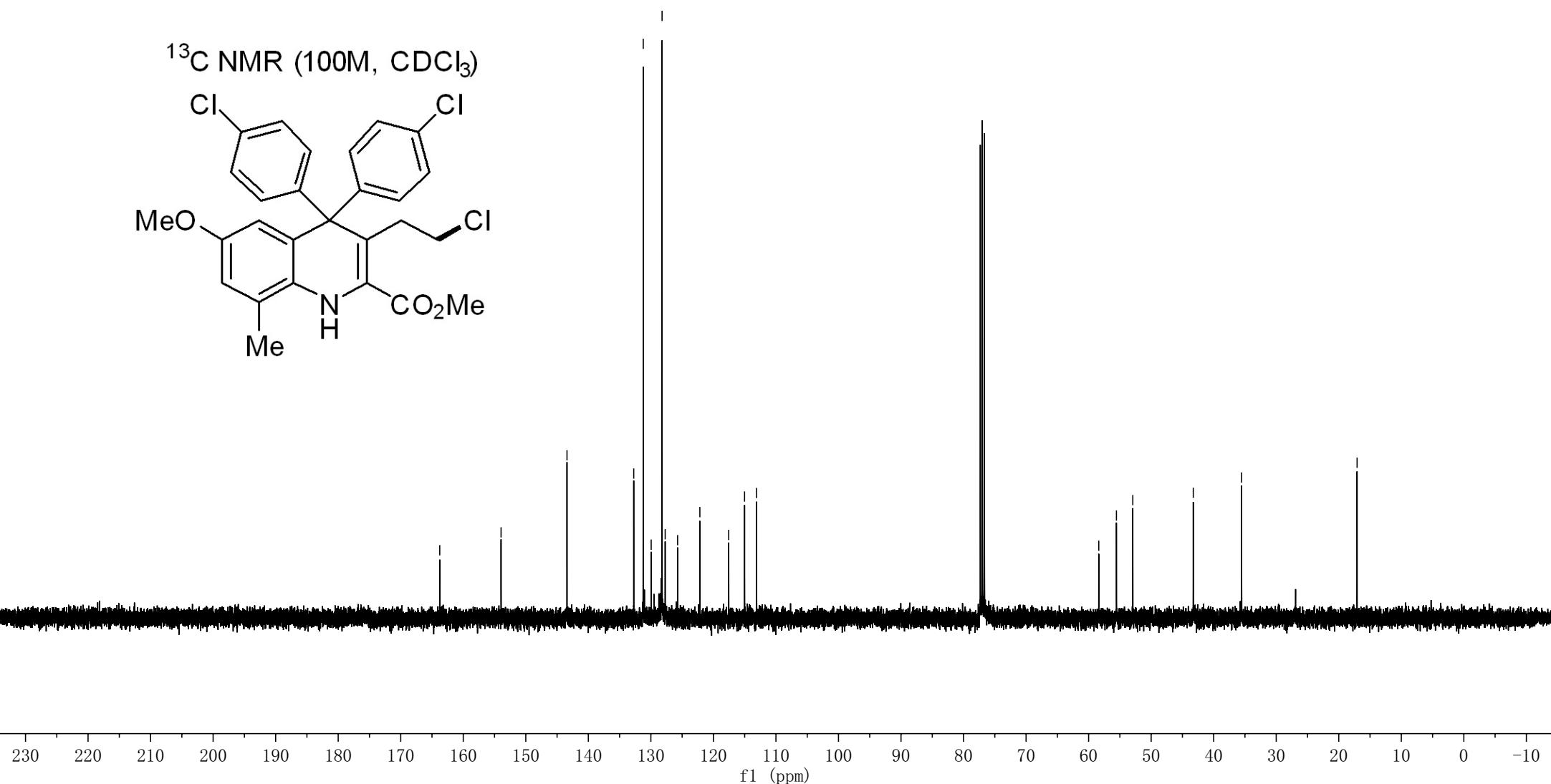
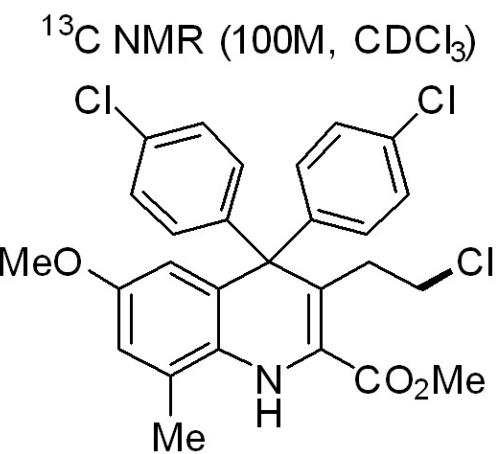
Methyl 3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-6,8-dimethyl-1,4-dihydroquinoline-2-carboxylate (**6d**)

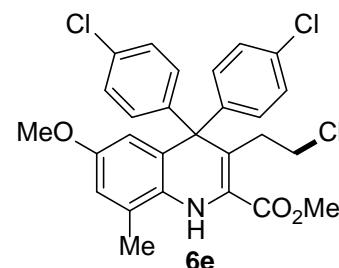




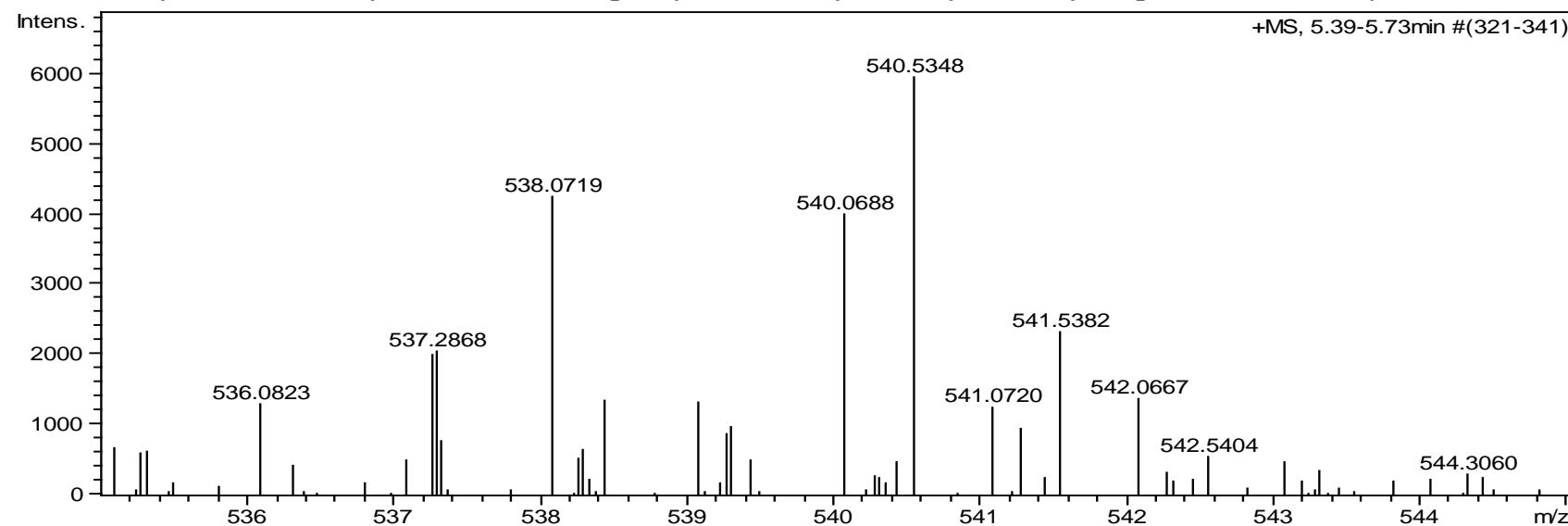
<sup>1</sup>H NMR (400M, CDCl<sub>3</sub>)

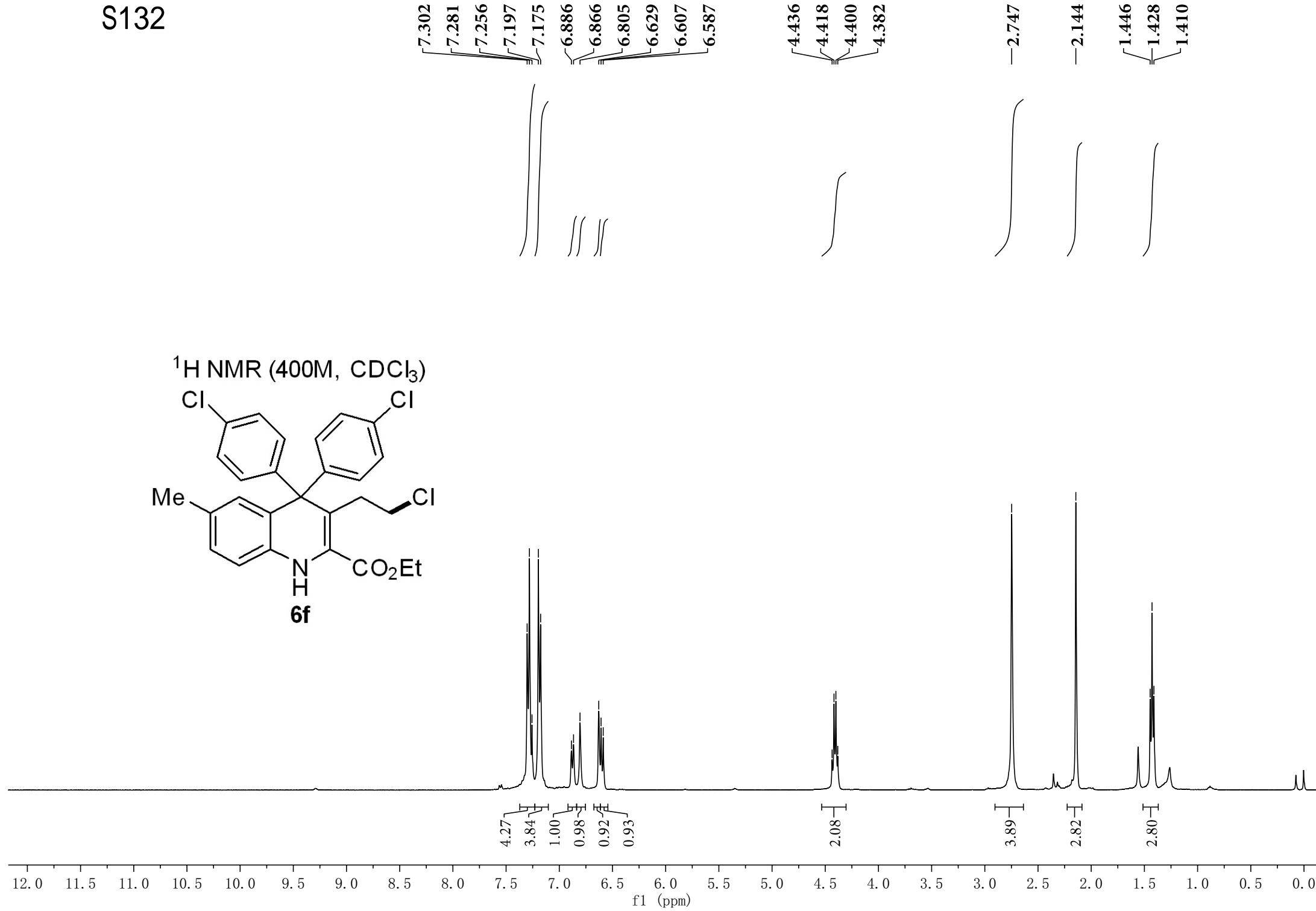
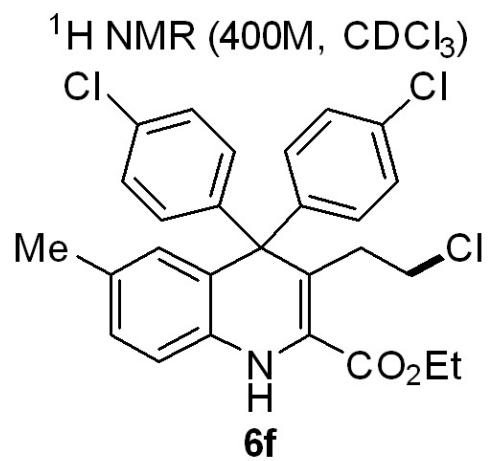


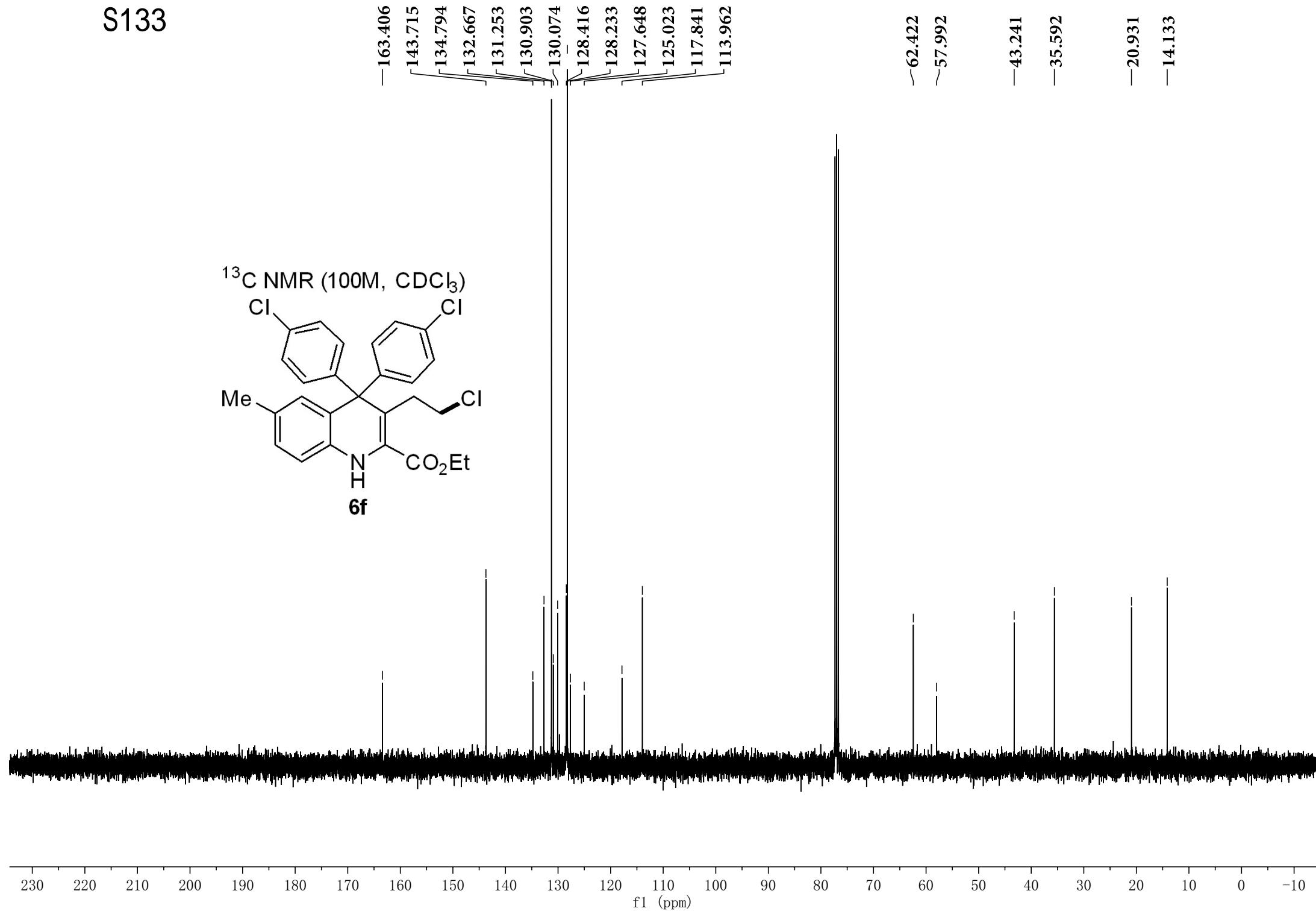
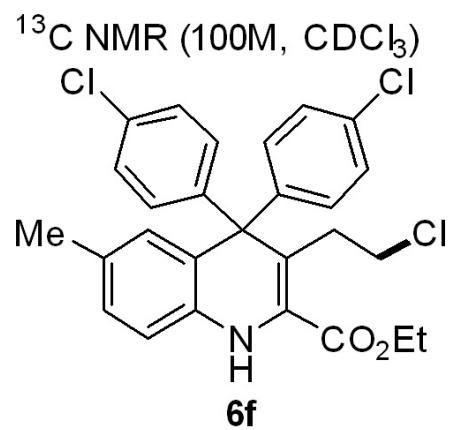


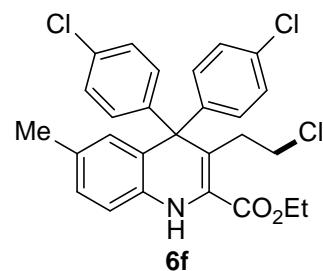


Methyl 3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-6-methoxy-8-methyl-1,4-dihydroquinoline-2-carboxylate (**6e**)

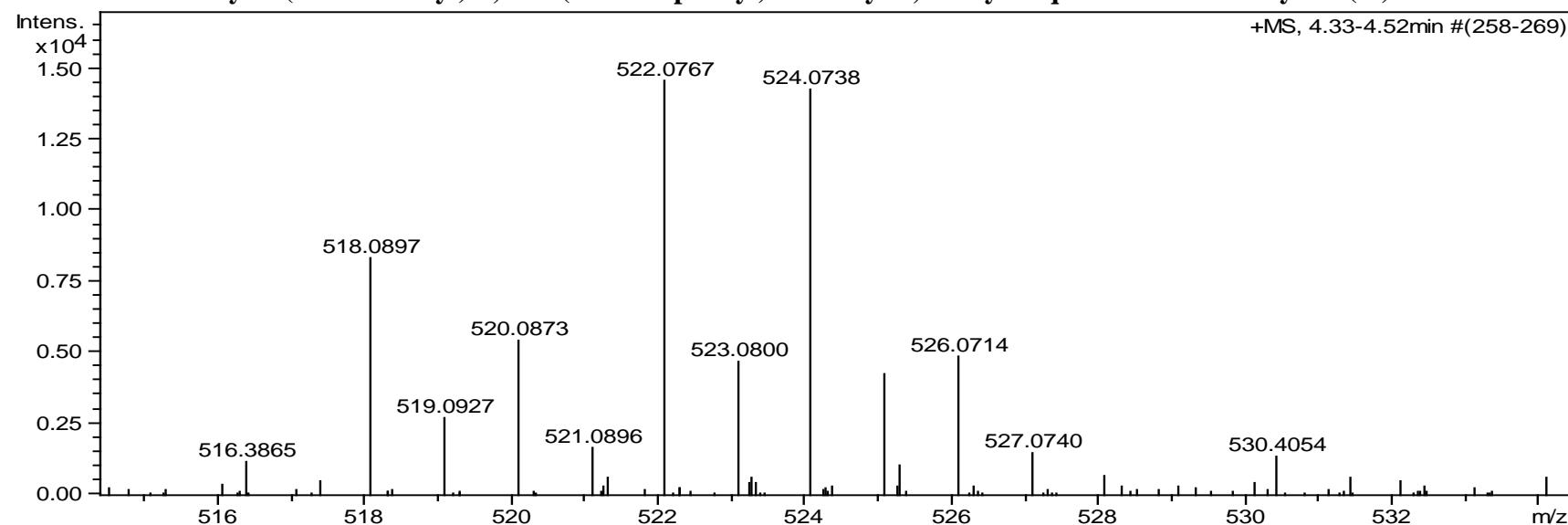


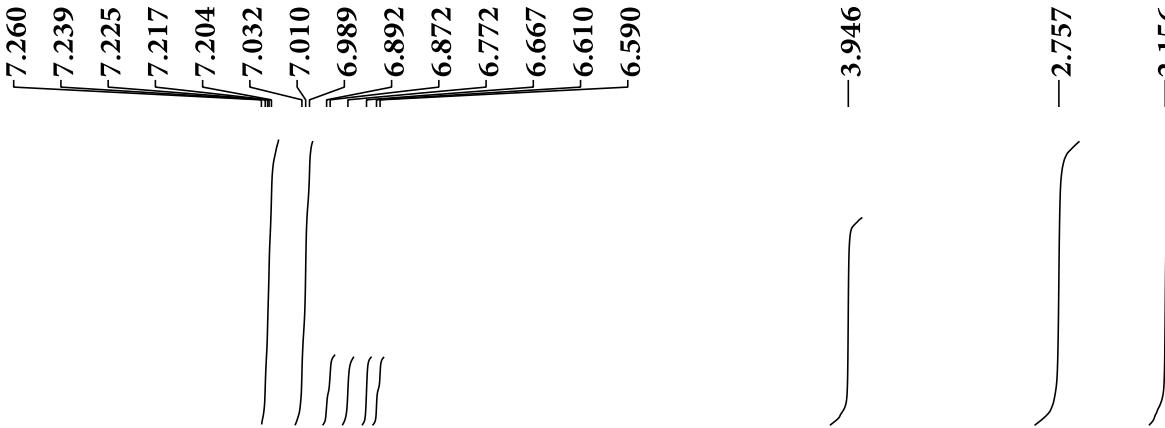




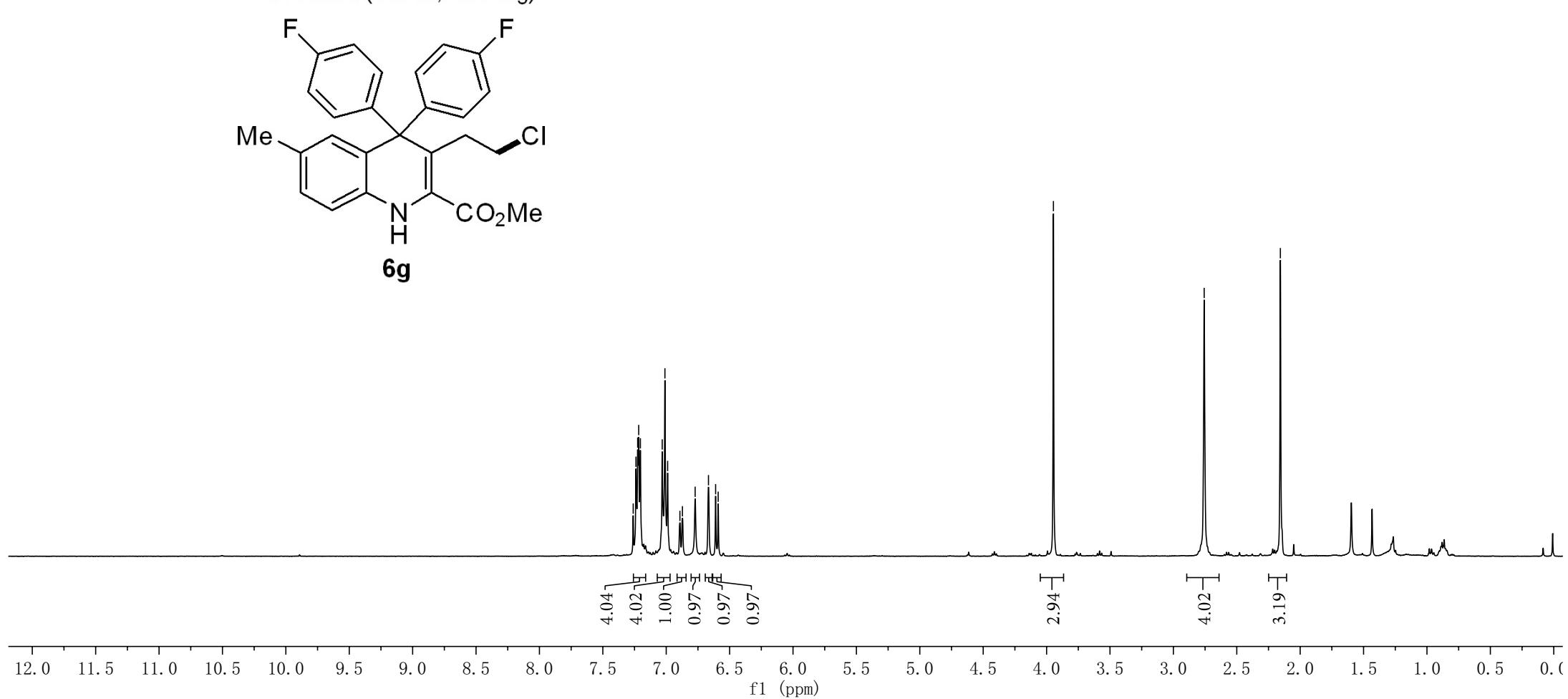
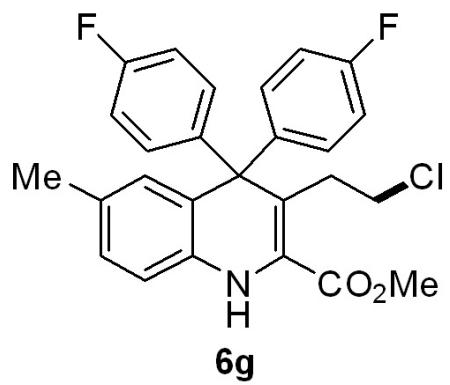


**Ethyl 3-(2-chloroethyl)-4,4-bis(4-chlorophenyl)-6-methyl-1,4-dihydroquinoline-2-carboxylate (6f)**

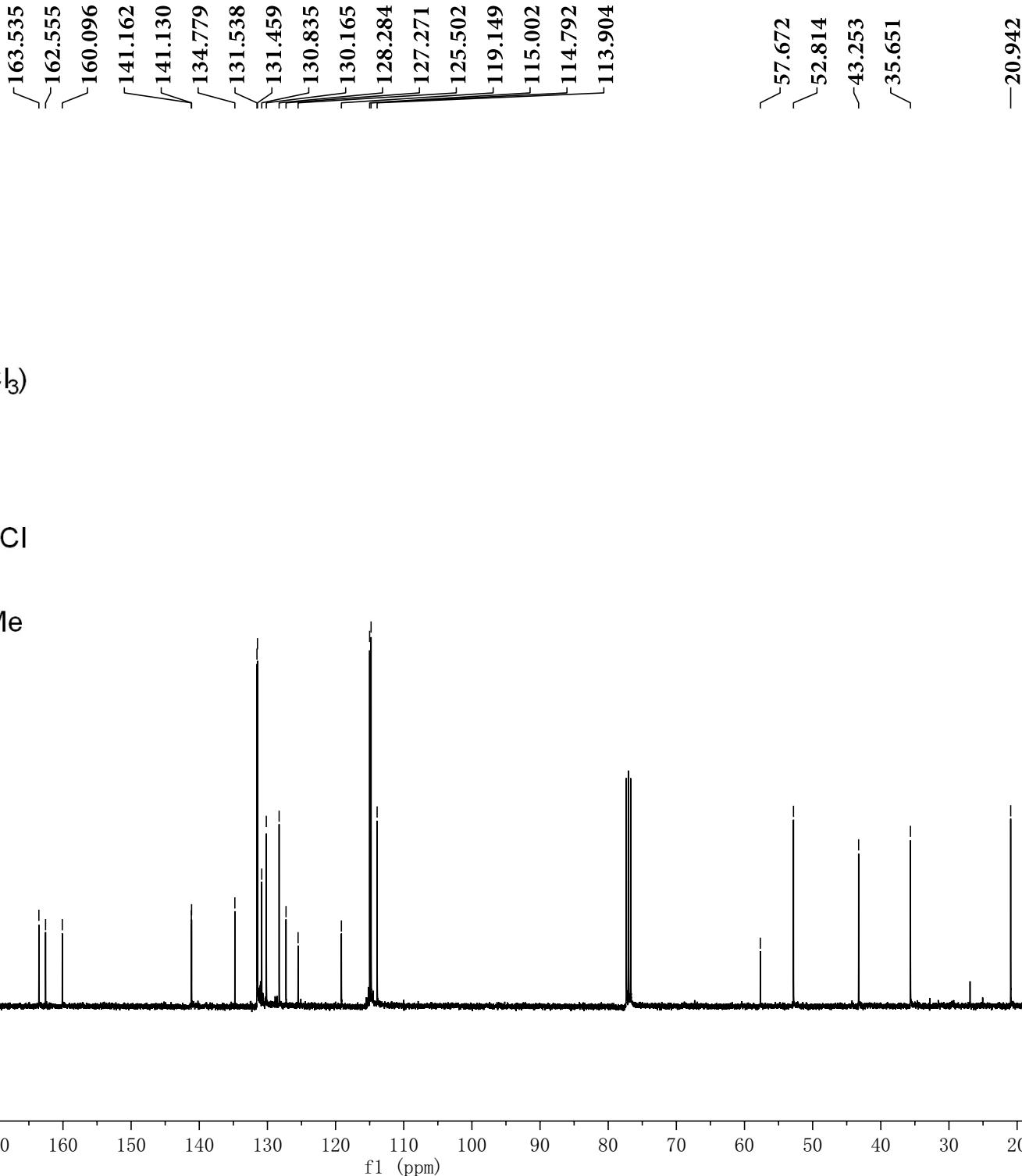
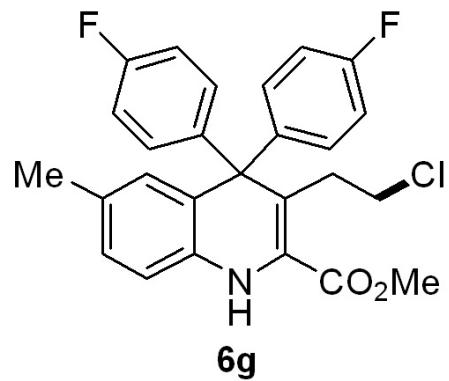


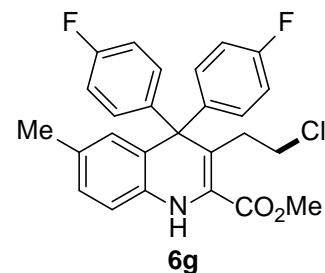


$^1\text{H}$  NMR (400M,  $\text{CDCl}_3$ )



<sup>13</sup>C NMR (100M, CDCl<sub>3</sub>)





Methyl 3-(2-chloroethyl)-4,4-bis(4-fluorophenyl)-6-methyl-1,4-dihydroquinoline-2-carboxylate (**6g**)

