

## Supporting Information

for

### Visible-Light-Promoted $\alpha$ -Methoxymethylation and Aminomethylation of Ketones with Methanol as the C1 Source

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## 1. General Information

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were recorded on an Agilent Technologies DD2 (600 MHz) or a Varian Mercury-400 Plus spectrometer in  $\text{CDCl}_3$ . Chemical shifts ( $\delta$ ) for NMR were quoted in ppm relative to the solvent peak (7.26 ppm for  $^1\text{H}$  and 77.00 ppm for  $^{13}\text{C}$  in  $\text{CDCl}_3$ ). High-resolution mass spectra (HRMS) were performed on a Thermo Orbitrap Elite instrument with an ESI source. Reactions were monitored by thin layer chromatography (TLC) using pre-coated silica gel plates (GF254). Flash column chromatography was performed on silica gel 60 (particle size 200–400 mesh ASTM, purchased from Liangchen, China) and eluted with petroleum ether/ethylacetate or petroleum ether/acetone. The materials obtained from commercial suppliers were used directly without further purification.

The 23 W CFL lamps employed in this work were bought from the supermarket (manufacturer: PHILIPS, type specification: 220 V/23 W/50 Hz). The reaction vessels are borosilicate glass tube. The distance from the light source to the irradiation vessel is about 2.5 cm. The temperature is controlled by a fan and is about 24 °C. The reaction setup is shown below.



## 2. Experimental Procedures

### 1) General procedure for synthesis of 2

Ketones **1** (0.3 mmol), rose bengal (15.3 mg, 0.015 mmol, 5 mol%),  $\text{Cs}_2\text{CO}_3$  (195.2 mg, 0.6 mmol, 2.0 equiv) and MeOH (3 mL) were added into a 10 mL borosilicate glass tube. The reaction mixture was stirred at room temperature under 23 W compact fluorescent lamp (CFL) irradiation and ambient air for 48 h. After completion of the reaction (monitored by TLC), the reaction

solution was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE:EtOAc = 10:1–100:1 or PE:Acetone = 100:1) to afford pure product **2**.

## 2) Procedure for gram-scale synthesis of **2a**

Propiophenone **1a** (1.073 g, 8 mmol), rose bengal (0.529 g, 0.4 mmol, 5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (5.213 g, 16 mmol, 2.0 equiv) and MeOH (50 mL) were added into a 80 mL borosilicate glass tube. The reaction mixture was stirred at room temperature under two 32 W compact fluorescent lamps (CFLs) irradiation and ambient air for 60 h. After completion of the reaction (monitored by TLC), the reaction solution was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE:EtOAc = 10:1) to afford pure product **2a** (62%, 0.887 g). The reaction setup is shown below.

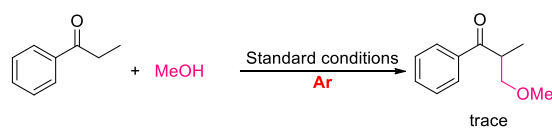


## 2) General procedure for synthesis of **3**.

Ketones **1m** (44.5 mg, 0.3 mmol), rose bengal (15.3 mg, 0.015 mmol, 5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (195.2 mg, 0.6 mmol, 2.0 equiv), N-nucleophiles (0.36 mmol, 1.2 equiv) and MeOH (3 mL) were added into a 10 mL borosilicate glass tube. The reaction mixture was stirred at room temperature under 23 W compact fluorescent lamp (CFL) irradiation and ambient air for 48 h. After completion of the reaction (monitored by TLC), the reaction solution was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE:EtOAc = 5:1–30:1) to afford pure product **3**.

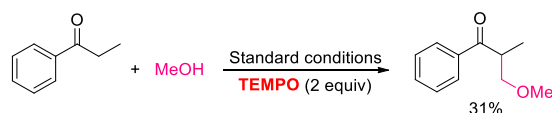
## 3. Mechanistic Studies

### 1) The reaction under argon

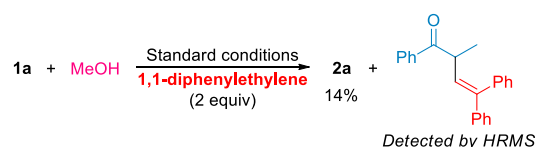


Ketones **1a** (40.3 mg, 0.3 mmol), rose bengal (15.3 mg, 0.015 mmol, 5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (195.2 mg, 0.6 mmol, 2.0 equiv) and degassed MeOH (3 mL) were added into a 10 mL borosilicate glass tube filled with argon. Under argon atmosphere, the reaction mixture was stirred at room temperature under a 23 W compact fluorescent lamp (CFL) irradiation for 48 h. Only a trace amount of product **2a** was detected by TLC.

## 2) Radical-inhibiting experiments



Ketones **1a** (40.3 mg, 0.3 mmol), rose bengal (15.3 mg, 0.015 mmol, 5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (195.2 mg, 0.6 mmol, 2.0 equiv), TEMPO (93.8 mg, 0.6 mmol, 2.0 equiv) and MeOH (3 mL) were added into a 10 mL borosilicate glass tube. The reaction mixture was stirred at room temperature under 23 W compact fluorescent lamp (CFL) irradiation and ambient air for 48 h. The reaction solution was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE:EtOAc = 50:1) to obtain pure product **2a** (31%).



Ketones **1a** (40.3 mg, 0.3 mmol), rose bengal (15.3 mg, 0.015 mmol, 5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (195.2 mg, 0.6 mmol, 2.0 equiv), 1,1-diphenylethylene (108.2 mg, 0.6 mmol, 2.0 equiv), and MeOH (3 mL) were added into a 10 mL borosilicate glass tube. The reaction mixture was stirred at room temperature under 23 W compact fluorescent lamp (CFL) irradiation and ambient air for 48 h. Then, the reaction mixture was analyzed by HRMS, and the carbon radical trapped by 1,1-diphenylethylene was detected (**Figure S1**, data of [M+H]<sup>+</sup> are showed). In addition, after concentration under reduced pressure, **2a** was obtained in 14% yield by column chromatography isolation on silica gel (PE:EtOAc = 30:1).



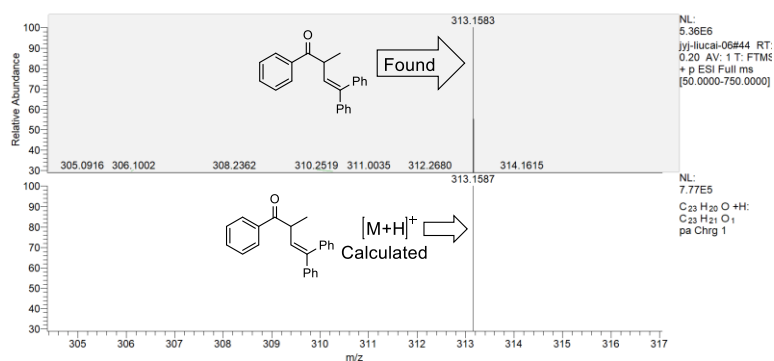
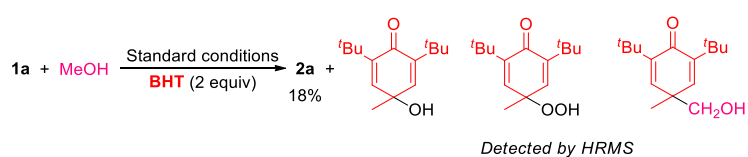


Figure S1



Ketones **1a** (40.3 mg, 0.3 mmol), rose bengal (15.3 mg, 0.015 mmol, 5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (195.2 mg, 0.6 mmol, 2.0 equiv), BHT (132.2 mg, 0.6 mmol, 2.0 equiv), and MeOH (3 mL) were added into a 10 mL borosilicate glass tube. The reaction mixture was stirred at room temperature under 23 W compact fluorescent lamp (CFL) irradiation and ambient air for 48 h. Then, the reaction mixture was analyzed by HRMS, and the oxidation products BHT-OH and BHT-OOH, the hydroxymethyl radical trapped by BHT were detected (**Figures S2–S4**, data of [M+H]<sup>+</sup> or [M+Na]<sup>+</sup> are showed). In addition, after concentration under reduced pressure, **2a** was obtained in 18% yield by column chromatography isolation on silica gel (PE:EtOAc = 30:1).

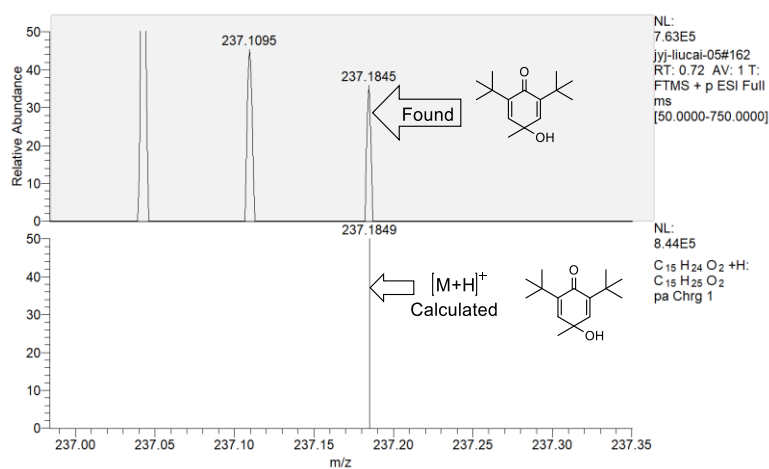


Figure S2

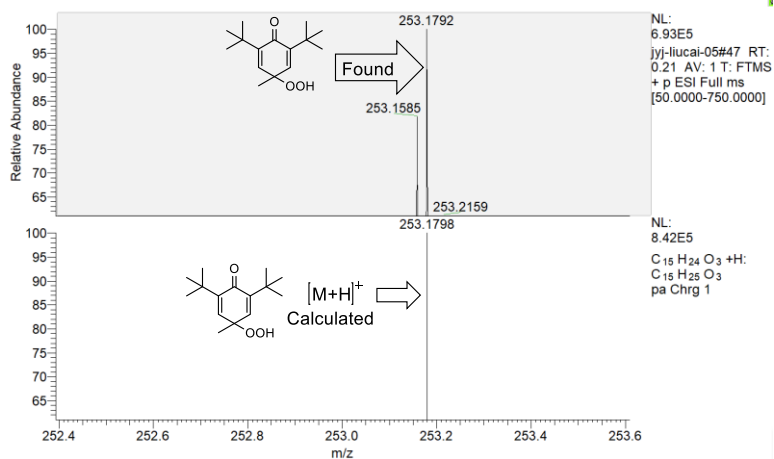


Figure S3

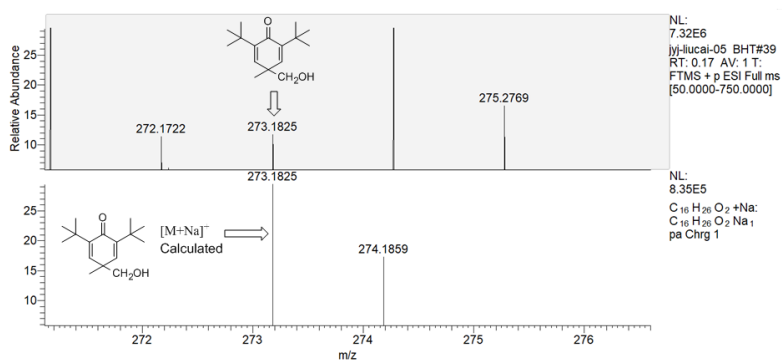
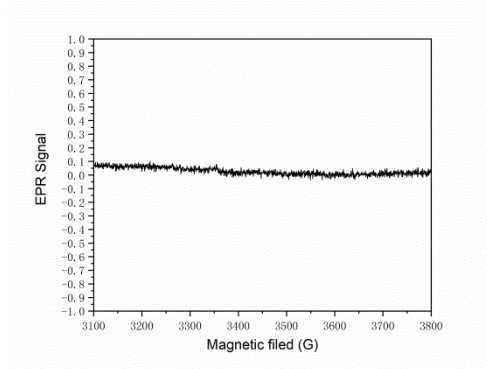


Figure S4

### 3) EPR experiments

#### (a) Reaction of PBN in MeOH

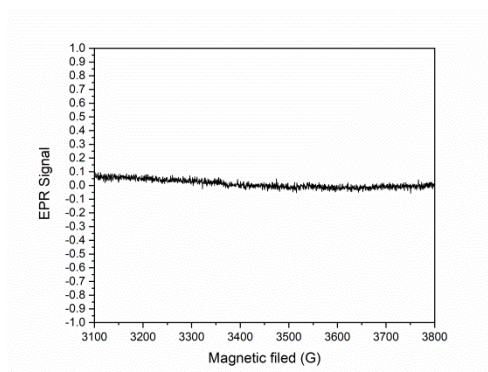
*N-tert-butyl- $\alpha$ -phenylnitrone* (PBN, 35.4 mg, 0.2 mmol) and MeOH (3 mL) were placed into an oven-dried 10 mL borosilicate glass tube. The reaction solution was then irradiated with 23 W CFL under ambient air at room temperature for 3 h. The resulting mixture was transferred to an oven-dried EPR tube, which was sealed with a rubber cap, and then analyzed by EPR (**Figure S5**).



**Figure S5.** The electron paramagnetic resonance (EPR) spectrum of a mixture of PBN in MeOH.

**(b) Reaction of PBN and rose bengal in MeOH**

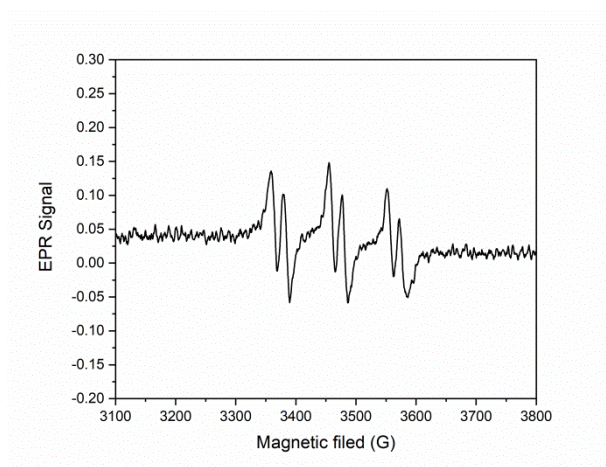
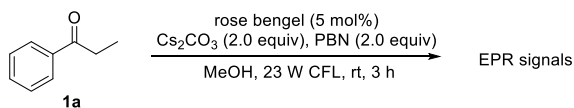
*N-tert-butyl- $\alpha$ -phenylnitrone* (PBN, 35.4 mg, 0.2 mmol), rose bengal (RB, 5.1 mg, 5 mol%) and MeOH (3 mL) were placed into an oven-dried 10 mL borosilicate glass tube. The reaction solution was then irradiated with 23 W CFL under ambient air at room temperature for 3 h. The resulting mixture was transferred to an oven-dried EPR tube, which was sealed with a rubber cap, and then analyzed by EPR (**Figure S6**).



**Figure S6.** The electron paramagnetic resonance (EPR) spectrum of a mixture of PBN and RB in MeOH.

**(c) Reaction of PBN, 1a, Cs<sub>2</sub>CO<sub>3</sub> and rose bengal in MeOH.**

*N-tert-butyl- $\alpha$ -phenylnitrone* (PBN, 35.4 mg, 0.2 mmol), propiophenone (**1a**, 13.4 mg, 0.1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (65.2 mg, 0.2 mmol), rose bengal (RB, 5.1 mg, 5 mol%) and MeOH (3 mL) were placed into an oven-dried 10 mL borosilicate glass tube. The reaction solution was then irradiated with 23 W CFL under ambient air at room temperature for 3 h. The resulting mixture was transferred to an oven-dried EPR tube, which was sealed with a rubber cap, and then analyzed by EPR (**Figure S7**).



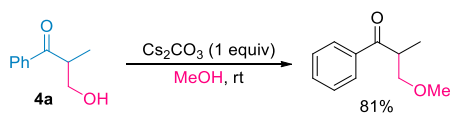
**Figure S7.** The electron paramagnetic resonance (EPR) spectrum of a mixture of PBN, Ketones,  $\text{Cs}_2\text{CO}_3$  and RB in MeOH.

#### 4) Silver mirror reaction

A solution of rose bengal (15.3 mg, 0.015 mmol, 5 mol%),  $\text{Cs}_2\text{CO}_3$  (195.2 mg, 0.6 mmol, 2.0 equiv) in MeOH (3 mL) was stirred at room temperature under 23 W compact fluorescent lamp (CFL) irradiation and ambient air for 24 h. Then, a small amount of the reaction mixture was dropped into a fresh silver ammonia solution in test tube. After shaking, the test tube was warmed in hot water and a layer of metallic silver was found adhering to the inner wall of the test tube. The picture of this phenomenon is shown below.

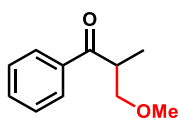


#### 5) The reaction of $\alpha$ -hydroxymethylated propiophenone 4a



$\alpha$ -Hydroxymethylated propiophenone **4a** (49.2 mg, 0.3 mmol), Cs<sub>2</sub>CO<sub>3</sub> (97.6 mg, 0.3 mmol, 1.0 equiv) and MeOH (3 mL) were added into a 10 mL borosilicate glass tube. The reaction mixture was stirred at room temperature for 48 h. The reaction solution was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE:EtOAc = 10:1) to obtain pure product **2a** in 81% yield.

#### 4. Characterization Data of Products



##### 3-Methoxy-2-methyl-1-phenylpropan-1-one (**2a**)<sup>[1]</sup>

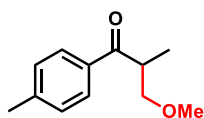
Prepared according to the general procedure from propiophenone **1a** (40.3 mg, 0.3 mmol).

Purified by column chromatography on silica gel (PE:EtOAc = 10:1) to afford the pure product **2a**.

Colorless oil; yield: 39.6 mg (74%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.98–7.96 (m, 2H), 7.56–7.54 (m, 1H), 7.48–7.44 (m, 2H), 3.83–3.73 (m, 2H), 3.49–3.43 (m, 1H), 3.32 (s, 3H), 1.20 (d,  $J$  = 10.2 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 202.7, 136.6, 133.0, 128.6, 128.3, 75.0, 59.1, 41.2, 14.8.



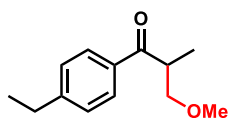
##### 3-Methoxy-2-methyl-1-(*p*-tolyl)propan-1-one (**2b**)<sup>[1]</sup>

Prepared according to the general procedure from 1-(*p*-tolyl)propan-1-one **1b** (44.5 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 20:1) to afford the pure product **2b**.

Colorless oil; yield: 43.3 mg (75%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.88 (d,  $J$  = 8.4 Hz, 2H), 7.27–7.25 (m, 2H), 3.77–3.73 (m, 2H), 3.45–3.43 (m, 1H), 3.32 (s, 3H), 2.41 (s, 3H), 1.19 (d,  $J$  = 6.6 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 202.3, 143.8, 134.1, 129.3, 128.5, 75.0, 59.1, 41.1, 21.6, 14.9.



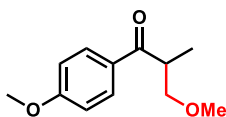
### 1-(4-Ethylphenyl)-3-methoxy-2-methylpropan-1-one (**2c**)<sup>[1]</sup>

Prepared according to the general procedure from 1-(4-ethylphenyl)propan-1-one **1c** (48.7 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 20:1) to afford the pure product **2c**.

Colorless oil; yield: 45.2 mg (73%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.91 (d, *J* = 8.4, Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.79–3.74 (m, 2H), 3.46–3.43 (m, 1H), 3.32 (s, 3H), 2.70 (q, *J* = 7.8 Hz, 2H), 1.26 (t, *J* = 7.8 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 202.3, 150.0, 134.3, 128.6, 128.1, 75.0, 59.1, 41.1, 28.9, 15.2, 14.9.



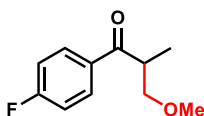
### 3-Methoxy-1-(4-methoxyphenyl)-2-methylpropan-1-one (**2d**)<sup>[1]</sup>

Prepared according to the general procedure from 1-(4-methoxyphenyl)propan-1-one **1d** (49.3 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 20:1) to afford the pure product **2d**.

Colorless oil; yield: 36.3 mg (58%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.96 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 3.76–3.70 (m, 2H), 3.45–3.41 (m, 1H), 3.31 (s, 3H), 1.18 (d, *J* = 6.0 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 201.1, 163.5, 130.7, 129.6, 113.7, 75.1, 59.0, 55.4, 40.8, 15.0.



### 1-(4-Fluorophenyl)-3-methoxy-2-methylpropan-1-one (**2e**)<sup>[1]</sup>

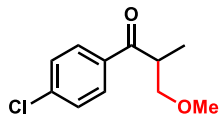
Prepared according to the general procedure from 1-(4-fluorophenyl)propan-1-one **1e** (45.6 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 100:1) to afford the pure product **2e**.

Colorless oil; yield: 24.7 mg (42%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.01–7.99 (m, 2H), 7.14–7.11 (m, 2H), 3.75–3.70 (m, 2H), 3.46–3.43 (m, 1H), 3.31 (s, 3H), 1.19 (d, *J* = 7.2 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 201.2, 165.7 (d,  $J$  = 253.1 Hz), 133.1 (d,  $J$  = 2.9 Hz), 131.0 (d,  $J$  = 9.2 Hz), 115.7 (d,  $J$  = 21.6 Hz), 75.0, 59.1, 41.2, 14.7.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -105.85–105.89



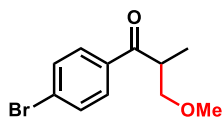
#### 1-(4-Chlorophenyl)-3-methoxy-2-methylpropan-1-one (**2f**)<sup>[1]</sup>

Prepared according to the general procedure from 1-(4-chlorophenyl)propan-1-one **1f** (50.5 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 30:1) to afford the pure product **2f**.

Colorless oil; yield: 50.4 mg (79%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.92–7.90 (m, 2H), 7.45–7.42 (m, 2H), 3.75–3.69 (m, 2H), 3.46–3.42 (m, 1H), 3.31 (s, 3H), 1.19 (d,  $J$  = 6.6 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 201.6, 139.5, 135.1, 129.8, 128.9, 75.0, 59.1, 41.3, 14.7.



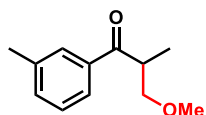
#### 1-(4-Bromophenyl)-3-methoxy-2-methylpropan-1-one (**2g**)<sup>[1]</sup>

Prepared according to the general procedure from 1-(4-bromophenyl)propan-1-one **1g** (63.9 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 30:1) to afford the pure product **2g**.

Colorless oil; yield: 53.2 mg (69%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.84–7.82 (m, 2H), 7.61–7.59 (m, 2H), 3.74–3.68 (m, 2H), 3.46–3.43 (m, 1H), 3.30 (s, 3H), 1.18 (d,  $J$  = 6.6 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 201.8, 135.4, 131.9, 129.9, 128.2, 74.9, 59.1, 41.3, 14.7.



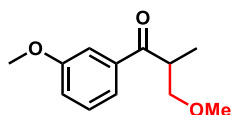
#### 3-Methoxy-2-methyl-1-(*m*-tolyl)propan-1-one (**2h**)<sup>[1]</sup>

Prepared according to the general procedure from 1-(*m*-tolyl)propan-1-one **1h** (44.5 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 90:1) to afford the pure product **2h**.

Colorless oil; yield: 38.2 mg (66%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.78–7.76 (m, 2H), 7.36–7.33 (m, 2H), 3.78–3.73 (m, 2H), 3.46–3.44 (m, 1H), 3.32 (s, 3H), 2.41 (s, 3H), 1.19 (d,  $J$  = 10.2 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 202.9, 138.3, 136.7, 133.7, 128.8, 128.4, 125.5, 75.0, 59.1, 41.2, 21.3, 14.9.



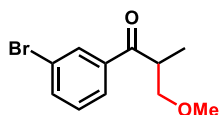
### 3-Methoxy-1-(3-methoxyphenyl)-2-methylpropan-1-one (**2i**)<sup>[1]</sup>

Prepared according to the general procedure from 1-(3-methoxyphenyl)propan-1-one **1i** (49.3 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 50:1) to afford the pure product **2i**.

Colorless oil; yield: 40.6 mg (65%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.56–7.55 (m, 1H), 7.50 (dd,  $J$  = 2.4, 1.8 Hz, 1H), 7.37 (t,  $J$  = 8.2 Hz, 1H), 7.12–7.01 (m, 1H), 3.86 (s, 3H), 3.77–3.73 (m, 2H), 3.47–3.44 (m, 1H), 3.32 (s, 3H), 1.20 (d,  $J$  = 7.2 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 202.5, 159.9, 138.1, 129.6, 121.0, 119.6, 112.6, 75.0, 59.1, 55.4, 41.4, 14.9.



### 1-(3-Bromophenyl)-3-methoxy-2-methylpropan-1-one (**2j**)<sup>[1]</sup>

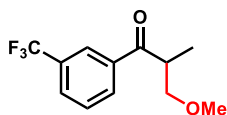
Prepared according to the general procedure from 1-(3-bromophenyl)propan-1-one **1j** (63.9 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:Acetone = 100:1) to afford the pure product **2j**.

Colorless oil; yield: 52.5 mg (68%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.08 (s, 1H), 7.87 (dd,  $J$  = 7.8, 1.0 Hz, 1H), 7.67–7.65 (m, 1H), 7.35–7.31 (m, 1H), 3.73–3.67 (m, 2H), 3.46–3.41 (m, 1H), 3.29 (s, 3H), 1.17 (d,  $J$  = 6.0 Hz, 3H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 201.4, 138.4, 135.8, 131.3, 130.1, 126.8, 122.9, 74.8, 59.0, 41.3, 14.6.





### 3-Methoxy-2-methyl-1-(3-(trifluoromethyl)phenyl)propan-1-one (2k)

Prepared according to the general procedure from 1-(3-(trifluoromethyl)phenyl)propan-1-one **1k** (60.6 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:Acetone = 100:1) to afford the pure product **2k**.

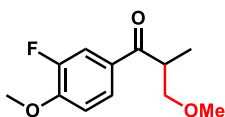
Colorless oil; yield: 29.5 mg (40%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.23 (s, 1H), 8.15 (d,  $J$  = 7.6 Hz, 1H), 7.81 (d,  $J$  = 7.6 Hz, 1H), 7.63–7.59 (m, 1H), 3.80–3.71 (m, 2H), 3.50–3.46 (m, 1H), 3.31 (s, 3H), 1.20 (d,  $J$  = 6.8 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 201.6, 137.3, 131.5, 131.2 (d,  $J$  = 32.6 Hz), 129.3 (q,  $J$  = 3.6 Hz), 129.2, 125.2 (q,  $J$  = 3.8 Hz), 124.7 (d,  $J$  = 271.0 Hz), 74.9, 59.1, 41.5, 14.5.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -143.1 (s).

HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{14}\text{O}_2\text{F}_3^+$ : 247.0946; found: 247.0940.



### 1-(3-Fluoro-4-methoxyphenyl)-3-methoxy-2-methylpropan-1-one (2l)

Prepared according to the general procedure from 1-(3,4-difluorophenyl)propan-1-one **1l** (51.0 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 50:1) to afford the pure product **2l**.

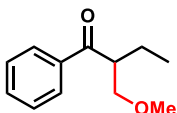
Colorless oil; yield: 46.3 mg (68%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.77–7.75 (m, 1H), 7.71 (dd,  $J$  = 12.0, 1.8 Hz, 1H), 6.99 (t,  $J$  = 8.2 Hz, 1H), 3.94 (s, 3H), 3.72–3.65 (m, 2H), 3.43 (dd,  $J$  = 8.4, 5.4 Hz, 1H), 3.30 (s, 3H), 1.17 (d,  $J$  = 7.2 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 200.4, 152.3 (d,  $J$  = 149.1 Hz), 151.5 (d,  $J$  = 86.2 Hz), 129.9 (d,  $J$  = 4.6 Hz), 125.6 (d,  $J$  = 3.3 Hz), 116.0 (d,  $J$  = 18.7 Hz), 112.3, 75.0, 59.0, 56.2, 40.9, 14.8.

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -134.70–134.76.

HRMS (ESI):  $m/z$   $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{12}\text{H}_{16}\text{FO}_3^+$ : 227.1078; found: 227.1072.



### 2-(Methoxymethyl)-1-phenylbutan-1-one (2m)<sup>[1]</sup>

Prepared according to the general procedure from 1-phenylbutan-1-one **1m** (44.5 mg, 0.3 mmol).

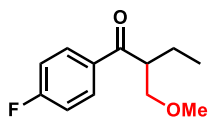
Purified by column chromatography on silica gel (PE:EtOAc = 20:1) to afford the pure product

#### **2m.**

Pale yellow oil; yield: 39.9 mg (69%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.98–7.97 (m, 2H), 7.57–7.54 (m, 1H), 7.48–7.45 (m, 2H), 3.74–3.67 (m, 2H), 3.52 (dd, *J* = 8.7, 5.1 Hz, 1H), 3.30 (s, 3H), 1.81–1.74 (m, 1H), 1.63–1.58 (m, 1H), 0.89 (t, *J* = 7.5 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 202.9, 137.7, 132.9, 128.6, 128.3, 73.8, 59.1, 48.1, 22.9, 11.7.



### 1-(4-Fluorophenyl)-2-(methoxymethyl)butan-1-one (2n)

Prepared according to the general procedure from 1-(4-fluorophenyl)butan-1-one **1n** (49.8 mg,

0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 80:1) to afford the pure product **2n**.

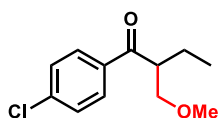
Colorless oil; yield: 39.9 mg (63%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 8.03–7.99 (m, 2H), 7.15–7.11 (m, 2H), 3.70 (t, *J* = 8.4 Hz, 1H), 3.66–3.61 (m, 1H), 3.51 (dd, *J* = 8.7, 5.1 Hz, 1H), 3.29 (s, 3H), 1.80–1.72 (m, 1H), 1.61–1.57 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 201.5, 165.7 (d, *J* = 253.1 Hz), 134.2 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 9.2 Hz), 115.6 (d, *J* = 21.6 Hz), 73.9, 59.1, 48.1, 22.9, 11.7.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ = -106.0–-106.1.

HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>12</sub>H<sub>15</sub>FO<sub>2</sub>Na<sup>+</sup>: 233.0948; found: 233.0943.



### 1-(4-Chlorophenyl)-2-(methoxymethyl)butan-1-one (2o)<sup>[1]</sup>

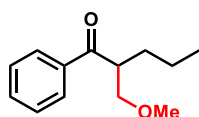
Prepared according to the general procedure from 1-(4-chlorophenyl)butan-1-one **1o** (54.8 mg,

0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 30:1) to afford the pure product **2o**.

Colorless oil; yield: 44.9 mg (66%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.92–7.90 (m, 2H), 7.44–7.42 (m, 2H), 3.70–3.60 (m, 2H), 3.51 (dd,  $J$  = 8.7, 5.1 Hz, 1H), 3.28 (s, 3H), 1.78–1.73 (m, 1H), 1.61–1.56 (m, 1H), 0.88 (t,  $J$  = 7.5 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 201.9, 139.4, 136.1, 129.8, 128.9, 73.8, 59.1, 48.2, 22.8, 11.7.



### 2-(Methoxymethyl)-1-phenylpentan-1-one (**2p**)<sup>[1]</sup>

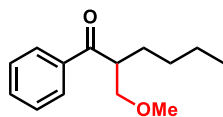
Prepared according to the general procedure from 1-phenylpentan-1-one **1p** (48.7 mg, 0.3 mmol).

Purified by column chromatography on silica gel (PE:EtOAc = 20:1) to afford the pure product **2p**.

Colorless oil; yield: 37.9 mg (61%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.97 (dd,  $J$  = 8.4, 1.2 Hz, 2H), 7.57–7.54 (m, 1H), 7.47–7.45 (m, 2H), 3.79–3.70 (m, 2H), 3.50 (dd,  $J$  = 9.0, 4.8 Hz, 1H), 3.29 (s, 3H), 1.74–1.68 (m, 1H), 1.53–1.50 (m, 1H), 1.33–1.25 (m, 2H), 0.87 (t,  $J$  = 7.5 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 203.1, 137.7, 132.9, 128.5, 128.3, 74.2, 59.1, 46.5, 32.0, 20.6, 14.2.



### 2-(Methoxymethyl)-1-phenylhexan-1-one (**2q**)

Prepared according to the general procedure from 1-phenylhexan-1-one **1q** (48.7 mg, 0.3 mmol).

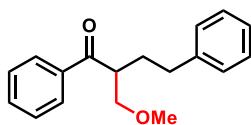
Purified by column chromatography on silica gel (PE:EtOAc = 20:1) to afford the pure product **2q**.

Colorless oil; yield: 39.3 mg (59%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.99–7.97 (m, 2H), 7.57–7.54 (m, 1H), 7.48–7.45 (m, 2H), 3.76–3.70 (m, 2H), 3.52–3.50 (m, 1H), 3.29 (s, 3H), 1.76–1.70 (m, 1H), 1.57–1.51 (m, 1H), 1.29–1.24 (m, 4H), 0.84 (t,  $J$  = 7.2 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 203.1, 137.7, 132.9, 128.5, 128.3, 74.2, 59.1, 46.7, 29.54, 29.53, 22.8, 13.8.

HRMS (ESI):  $m/z$  [ $\text{M}+\text{H}$ ]<sup>+</sup> calcd for  $\text{C}_{14}\text{H}_{21}\text{O}_2$ <sup>+</sup>: 221.1536; found: 221.1532.



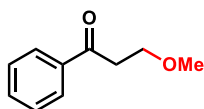
### 2-(Methoxymethyl)-1,4-diphenylbutan-1-one (2r)<sup>[1]</sup>

Prepared according to the general procedure from 1,4-diphenylbutan-1-one **1r** (67.2 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 70:1) to afford the pure product **2r**.

Colorless oil; yield: 48.3 mg (60%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.92–7.90 (m, 2H), 7.58–7.55 (m, 1H), 7.47–7.44 (m, 2H), 7.27–7.25 (m, 2H), 7.20–7.17 (m, 1H), 7.13–7.12 (m, 2H), 3.80–3.73 (m, 2H), 3.55 (dd, *J* = 8.4, 5.4 Hz, 1H), 3.30 (s, 3H), 2.67–2.57 (m, 2H), 2.15–2.10 (m, 1H), 1.92–1.86 (m, 1H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 202.5, 141.4, 137.4, 133.0, 128.5, 128.4, 128.35, 128.34, 126.0, 74.1, 59.1, 46.0, 33.4, 31.3.



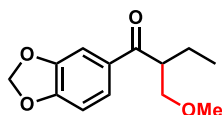
### 3-Methoxy-1-phenylpropan-1-one (2s)<sup>[2]</sup>

Prepared according to the general procedure from 3-chloro-1-phenylpropan-1-one **1s** (50.4 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 100:1) to afford the pure product **2s**.

Colorless oil; yield: 16.5 mg (33%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ = 7.98–7.96 (m, 2H), 7.58–7.55 (m, 1H), 7.48–7.46 (m, 2H), 3.82 (t, *J* = 6.6 Hz, 2H), 3.38 (s, 3H), 3.24 (t, *J* = 6.6 Hz, 2H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 198.3, 137.0, 133.2, 128.6, 128.1, 67.9, 59.0, 38.7.



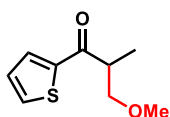
### 1-(Benzo[*d*][1,3]dioxol-5-yl)-2-(methoxymethyl)butan-1-one (2t)<sup>[1]</sup>

Prepared according to the general procedure from 1-(benzo[*d*][1,3]dioxol-5-yl)butan-1-one **1t** (57.7 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 50:1) to afford the pure product **2t**.

Colorless oil; yield: 47.6 mg (67%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.59 (dd,  $J$  = 7.8, 1.8 Hz, 1H), 7.46 (d,  $J$  = 1.2 Hz, 1H), 6.85 (d,  $J$  = 7.8 Hz, 1H), 6.04 (s, 2H), 3.69 (t,  $J$  = 8.4 Hz, 1H), 3.61–3.56 (m, 1H), 3.49 (dd,  $J$  = 8.7, 5.1 Hz, 1H), 3.29 (s, 3H), 1.78–1.70 (m, 1H), 1.61–1.57 (m, 1H), 0.88 (t,  $J$  = 7.5 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 200.9, 151.7, 148.2, 132.6, 124.6, 108.2, 107.8, 101.8, 74.0, 59.1, 47.9, 23.1, 11.7.



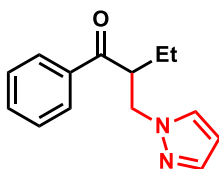
### 3-Methoxy-2-methyl-1-(thiophen-2-yl)propan-1-one (**2u**)<sup>[1]</sup>

Prepared according to the general procedure from 1-(thiophen-2-yl)propan-1-one **1u** (42.0 mg, 0.3 mmol). Purified by column chromatography on silica gel (PE:EtOAc = 20:1) to afford the pure product **2u**.

Colorless oil; yield: 34.8 mg (63%).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.76 (dd,  $J$  = 3.9, 0.9 Hz, 1H), 7.65 (dd,  $J$  = 4.8, 1.2 Hz, 1H), 7.14 (dd,  $J$  = 4.8, 4.2 Hz, 1H), 3.75–3.73 (m, 1H), 3.63–3.57 (m, 1H), 3.45–3.43 (m, 1H), 3.32 (s, 3H), 1.23 (d,  $J$  = 7.2 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 195.4, 144.2, 133.9, 132.1, 128.1, 74.9, 59.1, 43.1, 14.9.



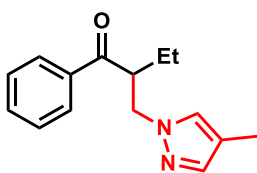
### 2-((1H-Pyrazol-1-yl)methyl)-1-phenylbutan-1-one (**3ma**)<sup>[1]</sup>

Prepared according to the general procedure from 1-phenylbutan-1-one **1m** (44.5 mg, 0.3 mmol) and 1H-pyrazole (24.5 mg, 0.36 mmol, 1.2 equiv). Purified by column chromatography on silica gel (PE:EtOAc = 10:1) to afford the pure product **3ma**.

Colorless oil; yield: 49.9 mg (73%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.85 (d,  $J$  = 8.0 Hz, 2H), 7.53–7.32 (m, 5H), 6.09 (d,  $J$  = 2.0 Hz, 1H), 4.55 (dd,  $J$  = 13.4, 8.6 Hz, 1H), 4.28 (dd,  $J$  = 13.4, 5.4 Hz, 1H), 4.18–4.11 (m, 1H), 1.82–1.71 (m, 1H), 1.66–1.55 (m, 1H), 0.89 (t,  $J$  = 7.4 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 202.3, 139.6, 136.8, 133.2, 130.2, 128.5, 128.1, 52.6, 48.2, 23.8, 11.1.



### 2-((4-Methyl-1H-pyrazol-1-yl)methyl)-1-phenylbutan-1-one (**3mb**)

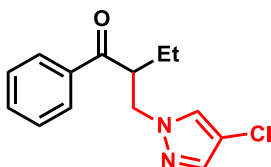
Prepared according to the general procedure from 1-phenylbutan-1-one **1m** (44.5 mg, 0.3 mmol) and 4-methylpyrazole (29.5 mg, 0.36 mmol, 1.2 equiv). Purified by column chromatography on silica gel (PE:EtOAc = 10:1) to afford the pure product **3mb**.

Colorless oil; yield: 45.1 mg (62%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.87 (d,  $J$  = 7.6 Hz, 2H), 7.56–7.52 (m, 1H), 7.42 (t,  $J$  = 7.6 Hz, 2H), 7.25 (s, 1H), 7.10 (s, 1H), 4.48 (dd,  $J$  = 13.6, 8.4 Hz, 1H), 4.22–4.09 (m, 2H), 1.96 (s, 3H), 1.81–1.70 (m, 2H), 1.65–1.54 (m, 1H), 0.89 (t,  $J$  = 7.6 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 202.5, 140.1, 137.0, 133.2, 129.2, 128.6, 128.2, 115.5, 52.5, 48.3, 23.9, 11.2, 8.7.

HRMS (ESI):  $m/z$  [ $\text{M}+\text{H}$ ] $^+$  calcd for  $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}^+$ : 243.1492; found: 243.1494.



### 2-((4-Chloro-1H-pyrazol-1-yl)methyl)-1-phenylbutan-1-one (**3mc**)

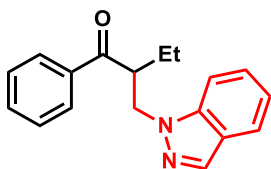
Prepared according to the general procedure from 1-phenylbutan-1-one **1m** (44.5 mg, 0.3 mmol) and 4-chloropyrazole (36.9 mg, 0.36 mmol, 1.2 equiv). Purified by column chromatography on silica gel (PE:EtOAc = 10:1) to afford the pure product **3mc**.

Colorless oil; yield: 50.5 mg (64%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.89–7.86 (m, 2H), 7.57–7.52 (m, 1H), 7.45–7.41 (m, 2H), 7.37–7.35 (m, 2H), 4.56–4.49 (m, 1H), 4.24–4.07 (m, 2H), 1.82–1.71 (m, 1H), 1.66–1.55 (m, 1H), 0.90 (t,  $J$  = 7.4 Hz, 3H).

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 201.8, 138.0, 136.6, 133.4, 128.7, 128.4, 128.2, 109.4, 53.0, 47.9, 23.9, 11.1.

HRMS (ESI):  $m/z$  [ $\text{M}+\text{H}$ ] $^+$  calcd for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}^+$ : 263.0946; found: 263.0941.



### 2-((1*H*-Indazol-1-yl)methyl)-1-phenylbutan-1-one (3md)

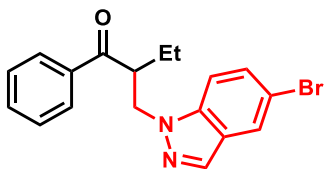
Prepared according to the general procedure from 1-phenylbutan-1-one **1m** (44.5 mg, 0.3 mmol) and 1*H*-indazole (42.5 mg, 0.36 mmol, 1.2 equiv). Purified by column chromatography on silica gel (PE:EtOAc = 20:1) to afford the pure product **3md**.

Colorless oil; yield: 54.3 mg (65%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.95 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.50–7.45 (m, 2H), 7.38–7.35 (m, 3H), 7.10–7.06 (m, 1H), 4.81 (dd, *J* = 14.0, 8.0 Hz, 1H), 4.49 (dd, *J* = 14.0, 6.0 Hz, 1H), 4.34–4.27 (m, 1H), 1.90–1.79 (m, 1H), 1.72–1.61 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 202.4, 139.9, 136.8, 133.4, 133.1, 128.4, 128.1, 126.3, 123.6, 120.8, 120.4, 109.2, 49.3, 47.9, 23.9, 11.2.

HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O<sup>+</sup>: 279.1492; found: 279.1490.



### 2-((5-Bromo-1*H*-indazol-1-yl)methyl)-1-phenylbutan-1-one (3me)

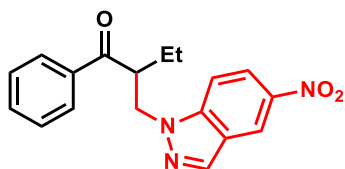
Prepared according to the general procedure from 1-phenylbutan-1-one **1m** (44.5 mg, 0.3 mmol) and 5-bromoindazole (70.9 mg, 0.36 mmol, 1.2 equiv). Purified by column chromatography on silica gel (PE:EtOAc = 10:1) to afford the pure product **3me**.

Colorless oil; yield: 53.4 mg (50%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.88 (s, 1H), 7.83–7.81 (m, 2H), 7.76–7.75 (m, 1H), 7.52–7.48 (m, 1H), 7.44–7.35 (m, 4H), 4.80 (dd, *J* = 14.0, 8.4 Hz, 1H), 4.45 (dd, *J* = 14.0, 5.6 Hz, 1H), 4.31–4.24 (m, 1H), 1.88–1.77 (m, 1H), 1.71–1.60 (m, 1H), 0.92 (t, *J* = 7.6 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 202.3, 138.6, 136.7, 133.3, 132.8, 129.5, 128.6, 128.1, 125.0, 123.2, 113.6, 110.9, 49.5, 47.8, 24.0, 11.3.

HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>18</sub>H<sub>17</sub>BrN<sub>2</sub>ONa<sup>+</sup>: 379.0416; found: 379.0414.



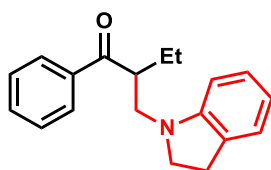
### 2-((5-Nitro-1H-indazol-1-yl)methyl)-1-phenylbutan-1-one (**3mf**)<sup>[1]</sup>

Prepared according to the general procedure from 1-phenylbutan-1-one **1m** (44.5 mg, 0.3 mmol) and 5-nitroindazole (58.7 mg, 0.36 mmol, 1.2 equiv). Purified by column chromatography on silica gel (PE:EtOAc = 10:1) to afford the pure product **3mf**.

Colorless oil; yield: 51.5 mg (53%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.62 (d, *J* = 2.0 Hz, 1H), 8.25 (dd, *J* = 9.6, 2.0 Hz, 1H), 8.15 (s, 1H), 7.82–7.80 (m, 2H), 7.60 (d, *J* = 9.2 Hz, 1H), 7.53–7.48 (m, 1H), 7.40–7.36 (m, 2H), 4.91 (dd, *J* = 13.6, 9.2 Hz, 1H), 4.50 (dd, *J* = 9.8, 5.0 Hz, 1H), 4.35–4.28 (m, 1H), 1.92–1.81 (m, 1H), 1.76–1.65 (m, 1H), 0.97 (t, *J* = 7.6 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 201.9, 142.3, 141.6, 136.5, 136.3, 133.5, 128.6, 128.1, 122.6, 121.5, 118.7, 109.9, 49.7, 47.7, 24.2, 11.3.



### 2-(Indolin-1-ylmethyl)-1-phenylbutan-1-one (**3mg**)

Prepared according to the general procedure from 1-phenylbutan-1-one **1m** (44.5 mg, 0.3 mmol) and indoline (42.9 mg, 0.36 mmol, 1.2 equiv). Purified by column chromatography on silica gel (PE:EtOAc = 20:1) to afford the pure product **3mg**.

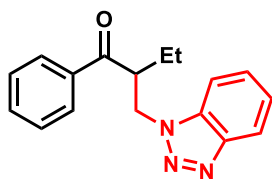
Colorless oil; yield: 38.6 mg (46%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.96 (d, *J* = 8.0 Hz, 2H), 7.58–7.54 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.12–7.00 (m, 2H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 3.85–3.75 (m, 1H), 3.54 (dd, *J* = 13.4, 8.6 Hz, 1H), 3.37–3.21 (m, 3H), 2.86 (t, *J* = 8.2 Hz, 2H), 1.92–1.79 (m, 1H), 1.75–1.64 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 203.6, 152.4, 137.7, 133.0, 129.5, 128.6, 128.2, 127.3, 124.3, 117.3, 106.4, 54.3, 52.0, 46.9, 28.6, 24.2, 11.8.

HRMS (ESI): *m/z* [M+H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>22</sub>NO<sup>+</sup>: 280.1696; found: 280.1693.





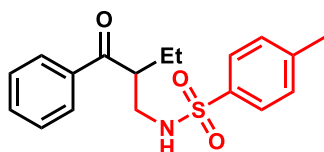
**2-((1H-Benzo[d][1,2,3]triazol-1-yl)methyl)-1-phenylbutan-1-one (3mh)<sup>[3]</sup>**

Prepared according to the general procedure from 1-phenylbutan-1-one **1m** (44.5 mg, 0.3 mmol) and 1H-benzotriazole (42.9 mg, 0.36 mmol, 1.2 equiv). Purified by column chromatography on silica gel (PE:EtOAc = 5:1) to afford the pure product **3mh**.

Colorless oil; yield: 43.5 mg (52%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.98 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.54–7.45 (m, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 5.04 (dd, *J* = 13.6, 8.4 Hz, 1H), 4.77 (dd, *J* = 13.6, 5.6 Hz, 1H), 4.41–4.35 (m, 1H), 1.92–1.83 (m, 1H), 1.77–1.71 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 201.5, 145.6, 136.4, 133.5, 133.4, 128.7, 128.2, 127.4, 123.8, 119.8, 109.8, 48.2, 47.9, 24.2, 11.1.



**N-(2-Benzoylbutyl)-4-methylbenzenesulfonamide (3mi)**

Prepared according to the general procedure from 1-phenylbutan-1-one **1m** (44.5 mg, 0.3 mmol) and *p*-tosylamide (61.6 mg, 0.36 mmol, 1.2 equiv). Purified by column chromatography on silica gel (PE:EtOAc = 30:1) to afford the pure product **3mi**.

Colorless oil; yield: 54.9 mg (55%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.82 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.57–7.53 (m, 1H), 7.44–7.40 (m, 2H), 7.26–7.22 (m, 2H), 5.14 (t, *J* = 6.6 Hz, 1H), 3.60–3.54 (m, 1H), 3.32–3.26 (m, 1H), 3.20–3.13 (m, 1H), 2.38 (s, 3H), 1.75–1.65 (m, 1H), 1.60–1.49 (m, 1H), 0.86 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ = 203.0, 143.2, 137.1, 136.1, 133.4, 129.7, 128.6, 128.2, 126.9, 47.5, 43.0, 23.5, 21.4, 11.2.

HRMS (ESI): *m/z* [M+Na]<sup>+</sup> calcd for C<sub>18</sub>H<sub>21</sub>NO<sub>3</sub>SN<sup>+</sup>: 354.1134; found: 354.1133.

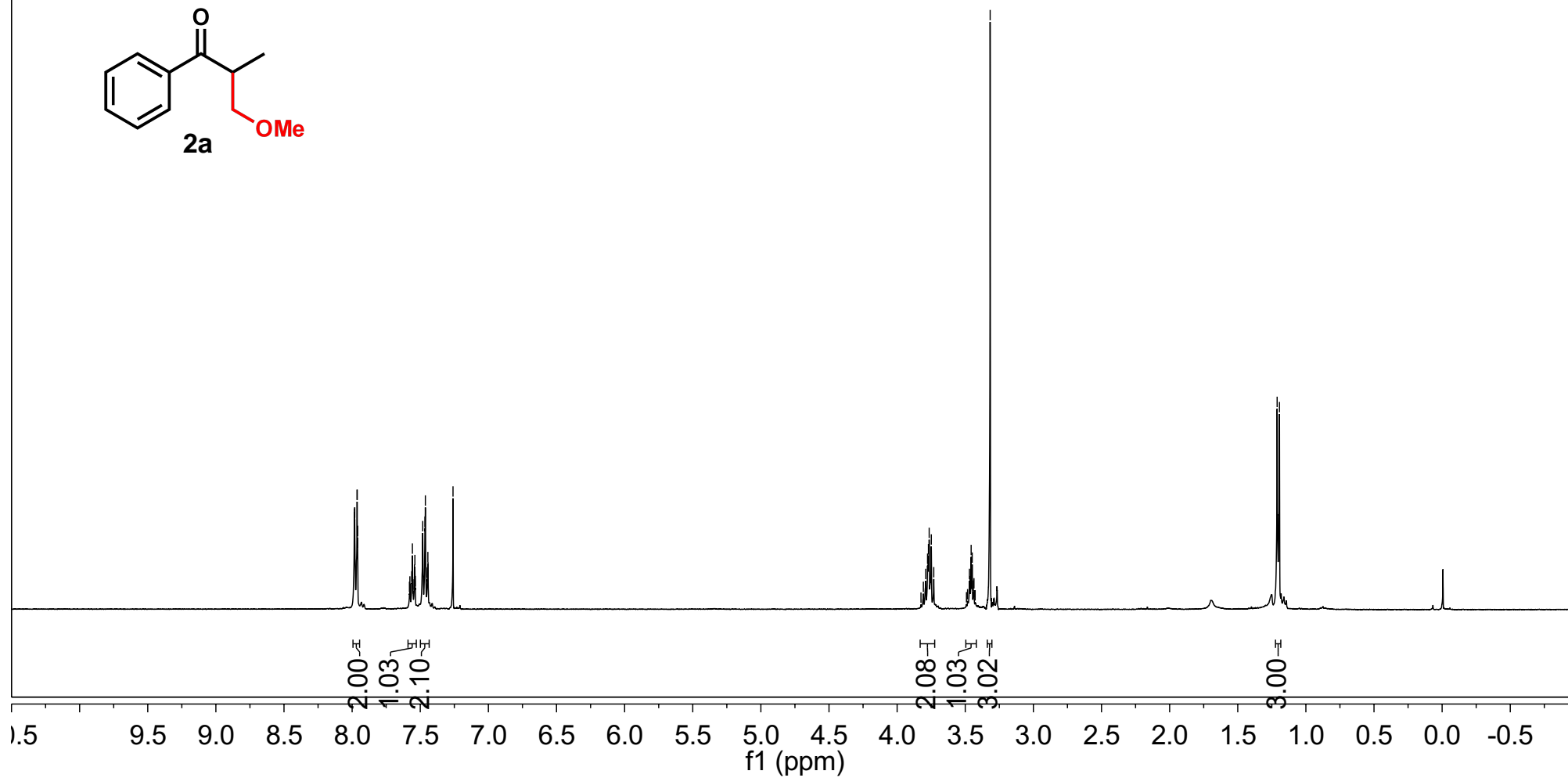
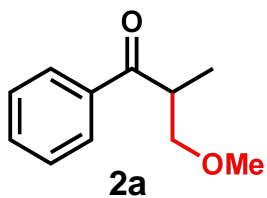
## 5. References

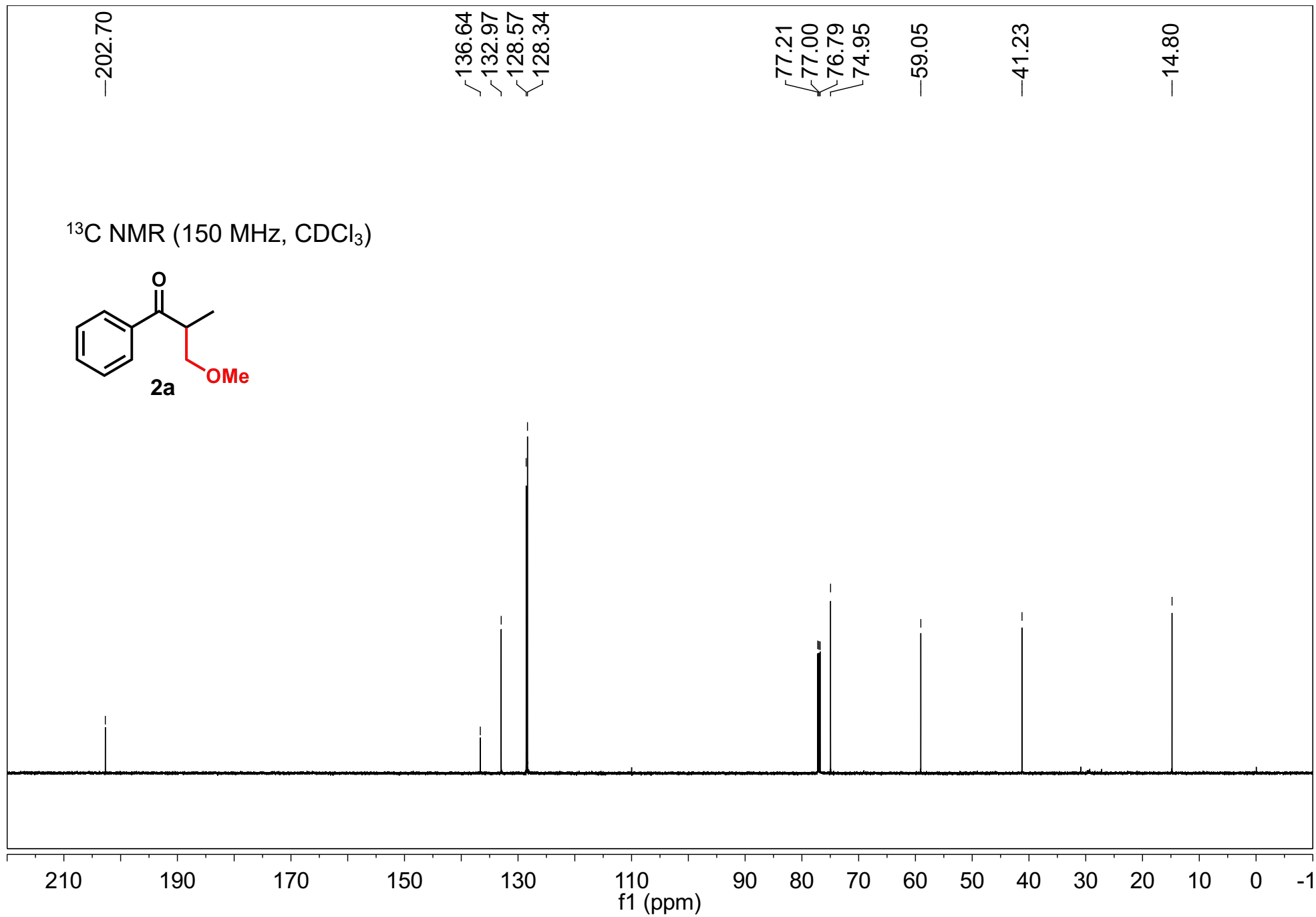
- [1] J. Yang, S. Chen, H. Zhou, C. Wu, B. Ma, J. Xiao, *Org. Lett.* **2018**, *20*, 6774–6779.
- [2] H.-P. Lin, N. Ibrahim, O. Provot, M. Alami, A. Hamaze, *RSC Adv.* **2018**, *8*, 11536–11542.
- [3] N. Fu, L. Zhang, S. Luo, J.-P. Cheng, *Org. Chem. Front.* **2014**, *1*, 68–72.

## 6. Cope of NMR Spectra

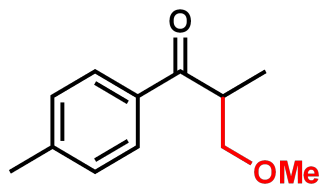
7.984  
7.984  
7.983  
7.981  
7.981  
7.963  
7.963  
7.960  
7.960  
7.563  
7.558  
7.543  
7.539  
7.482  
7.465  
7.462  
7.448  
7.447  
7.444  
7.443  
7.260  
3.825  
3.807  
3.790  
3.777  
3.770  
3.765  
3.749  
3.731  
3.491  
3.483  
3.469  
3.465  
3.457  
3.449  
3.441  
3.436  
3.427  
3.317  
1.211  
1.194

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )

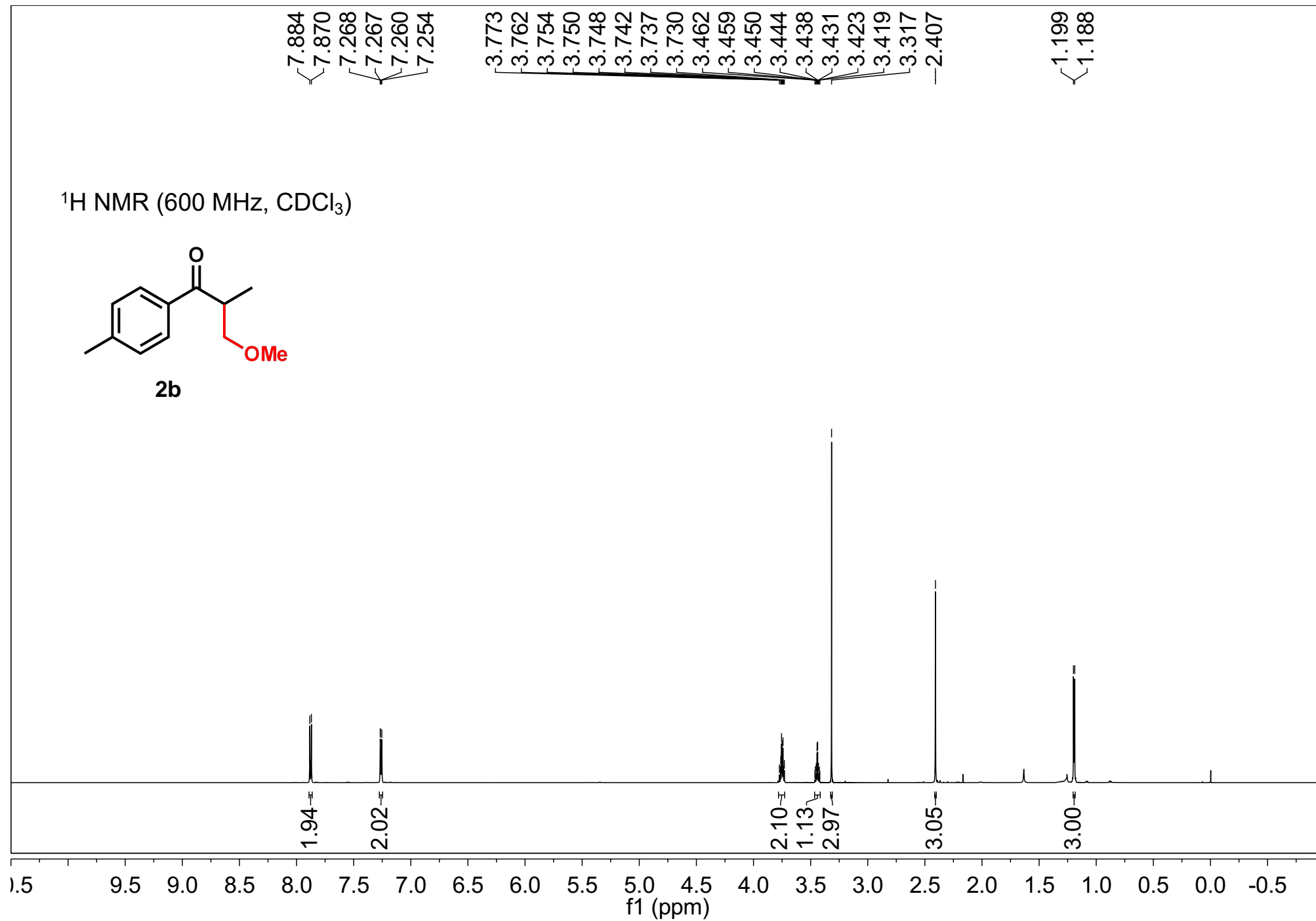




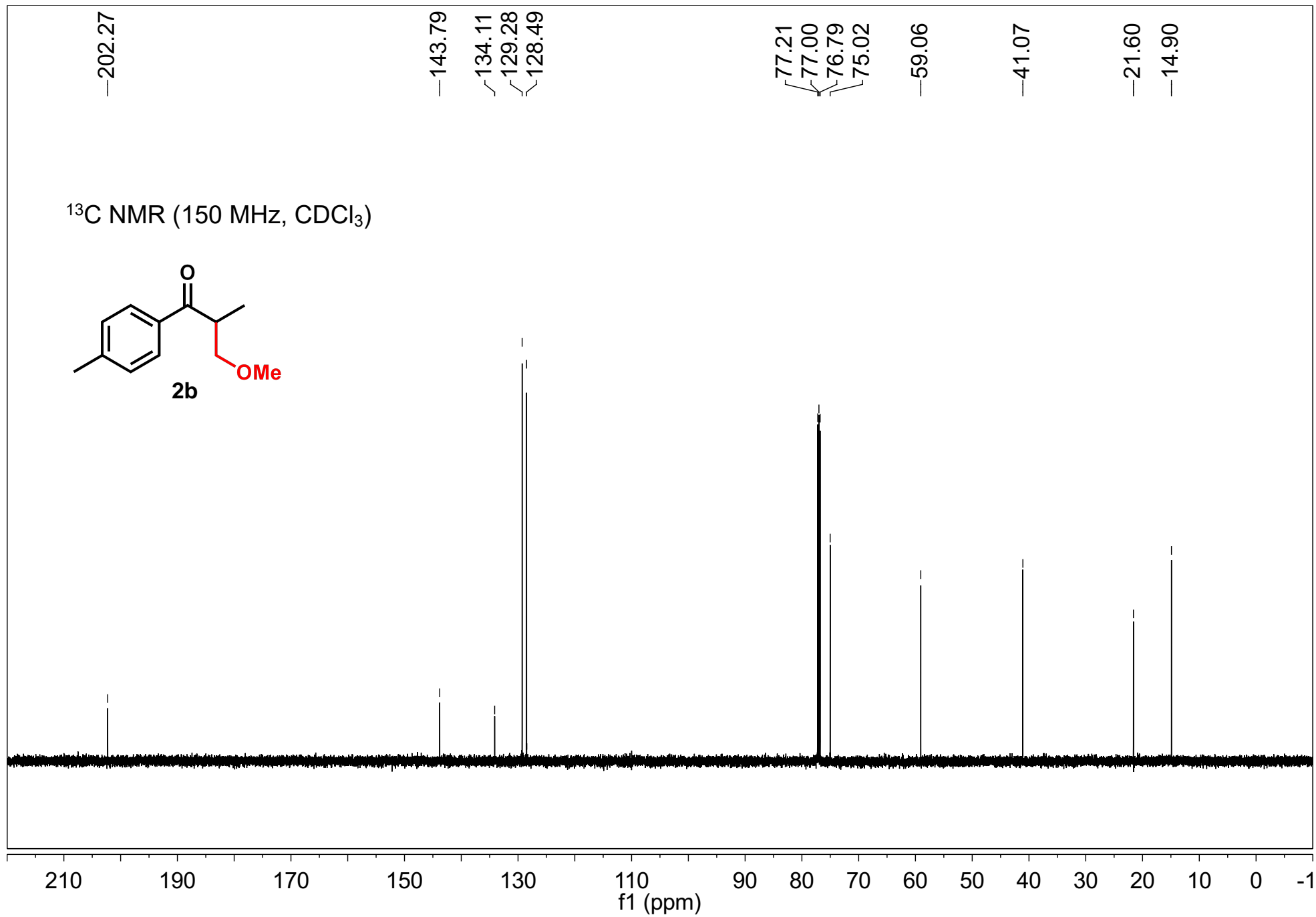
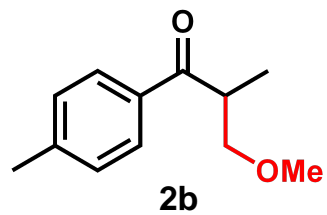
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



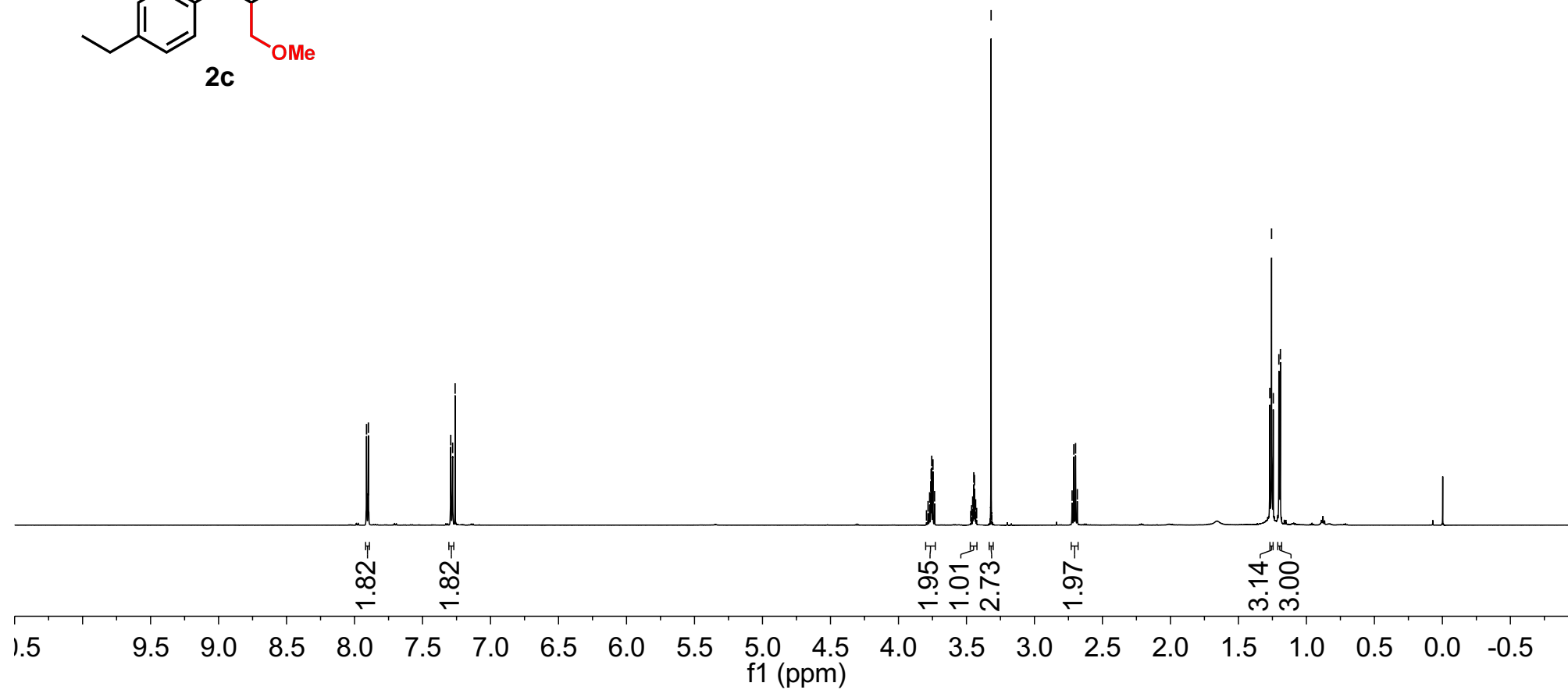
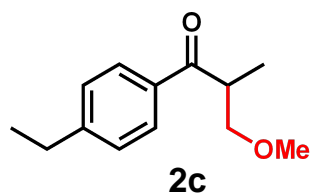
**2b**



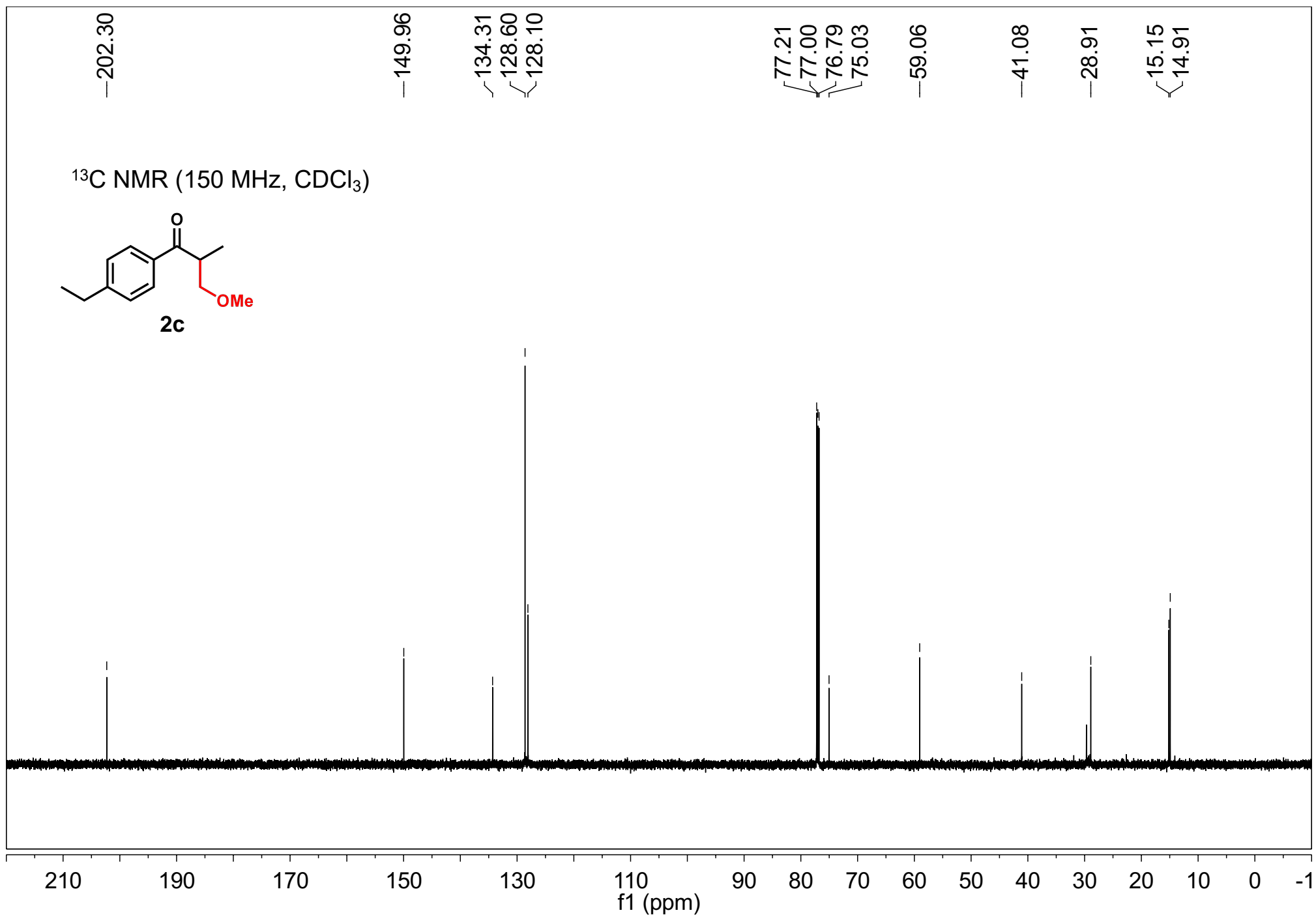
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)

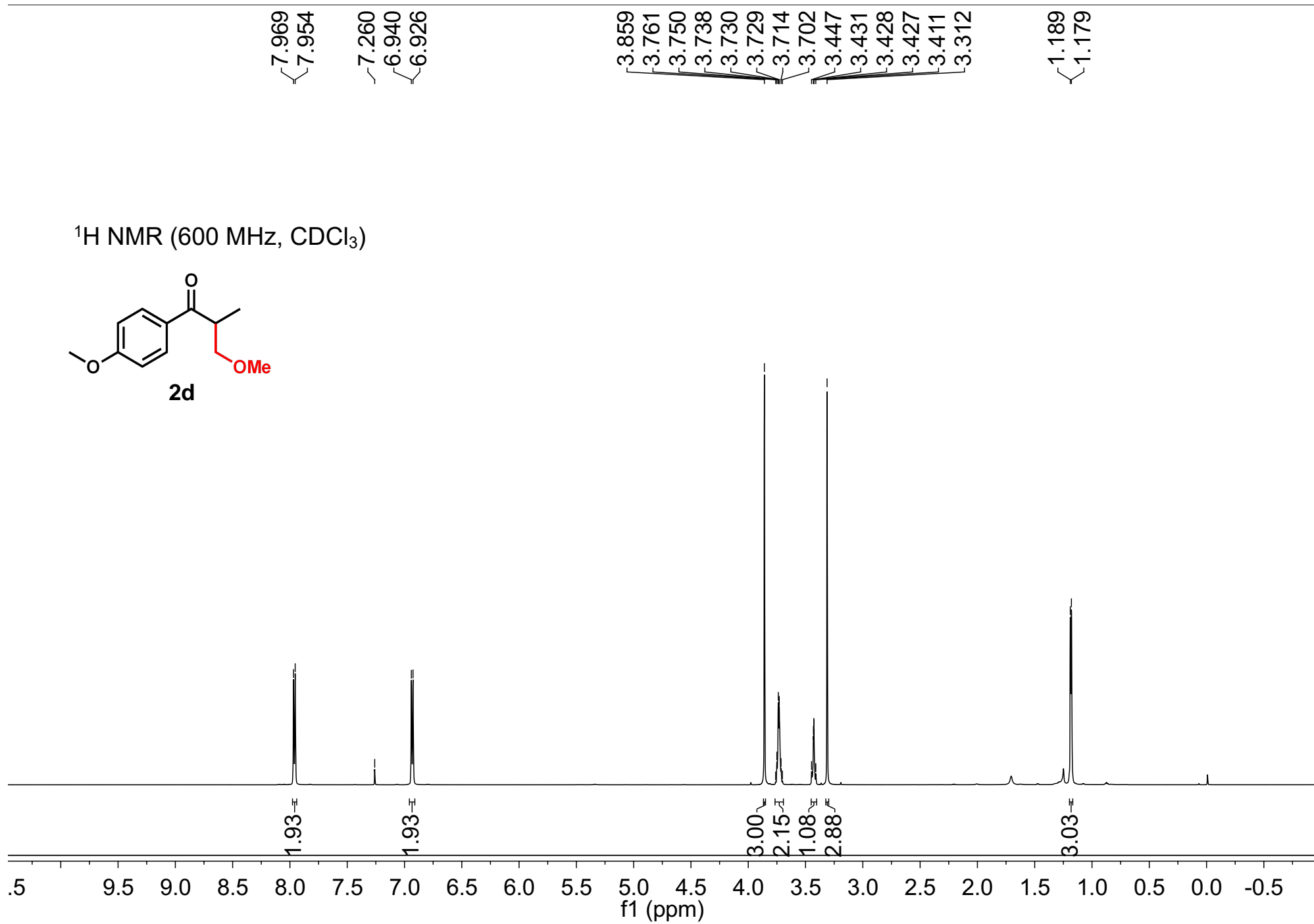
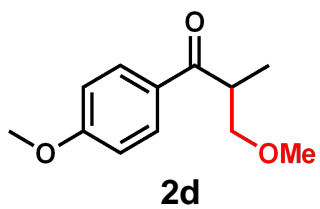


7.912  
7.898  
7.293  
7.279  
7.260  
3.794  
3.782  
3.771  
3.762  
3.760  
3.755  
3.746  
3.735  
3.462  
3.454  
3.450  
3.446  
3.441  
3.437  
3.433  
3.425  
3.319  
2.723  
2.710  
2.698  
2.685  
1.269  
1.256  
1.244  
1.202  
1.191





<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



—201.13

—163.46

{ 130.65  
129.63

—113.73

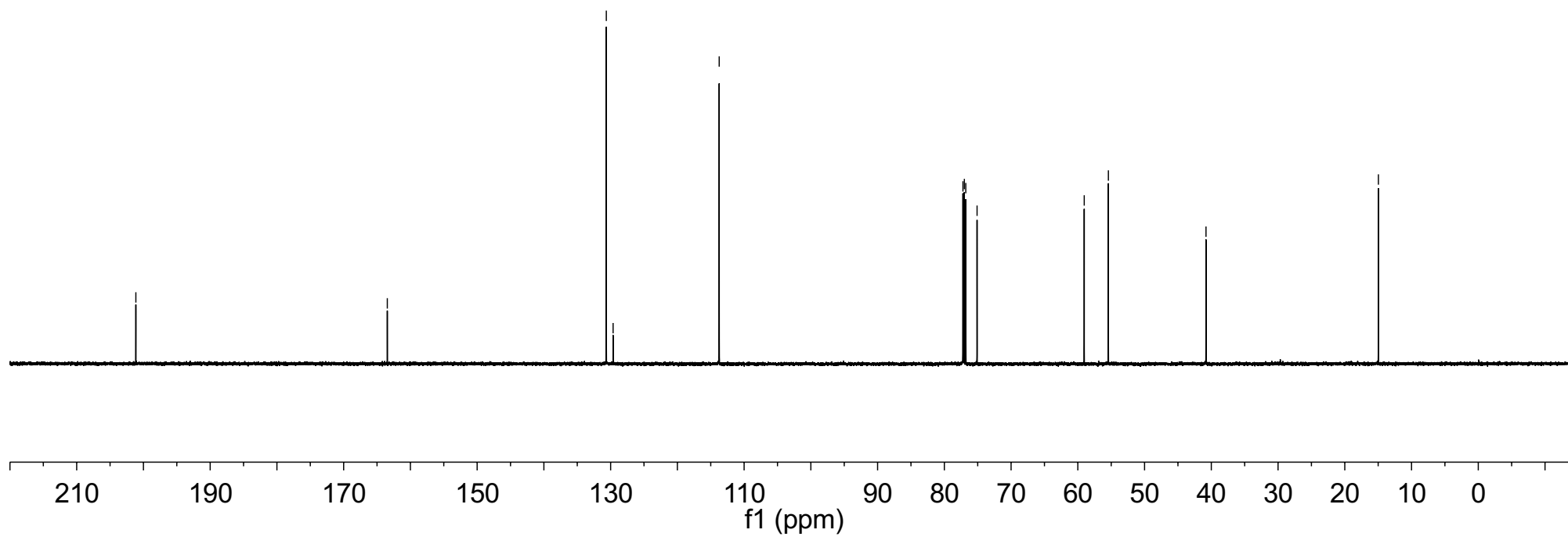
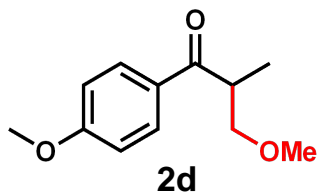
{ 77.21  
77.00  
76.79  
75.10

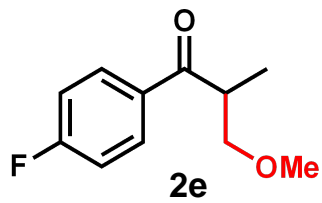
~59.04  
~55.42

—40.80

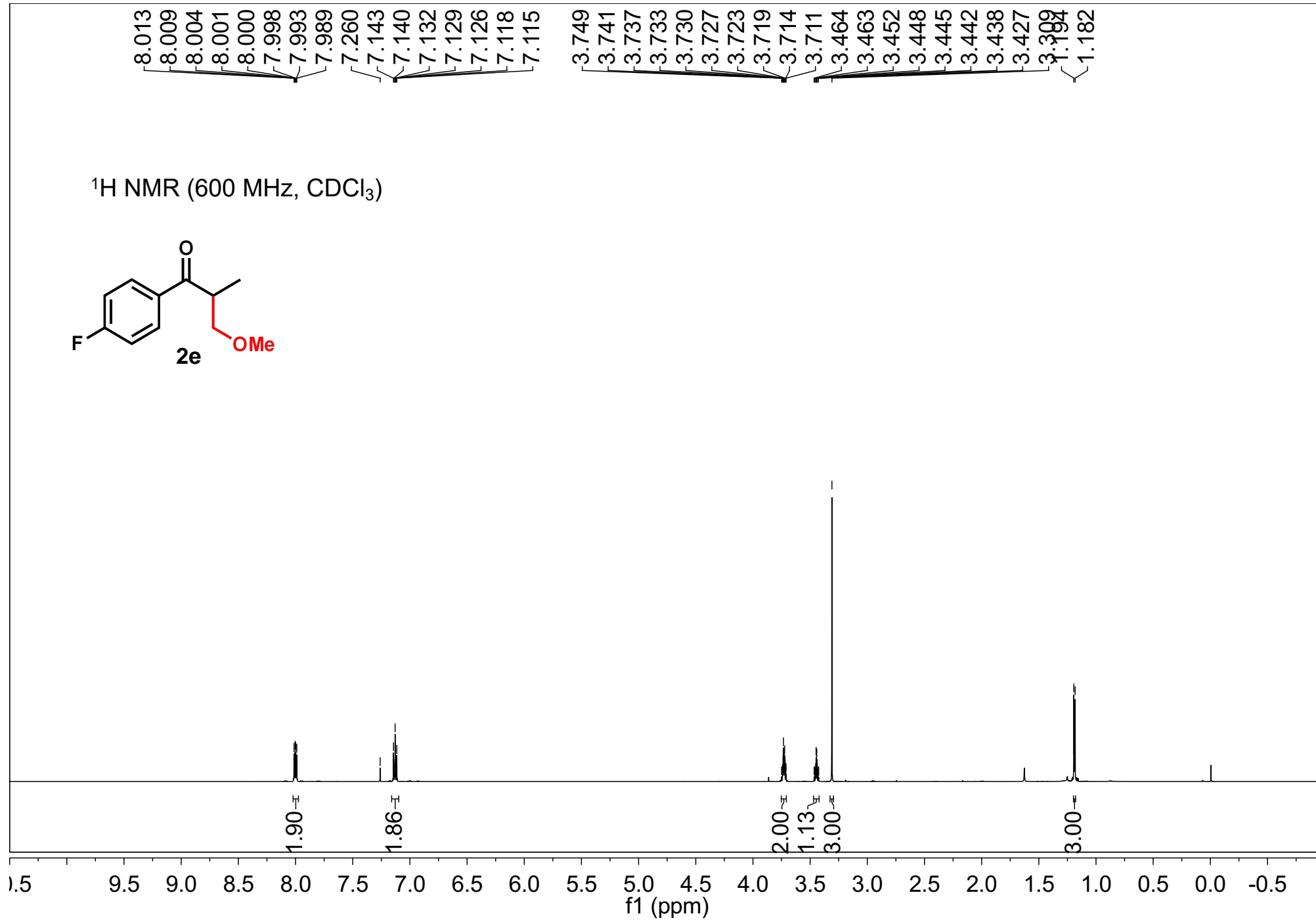
—14.96

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)





$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )



-201.177

166.561  
164.874

133.147  
133.128  
131.044  
130.983  
115.721  
115.577

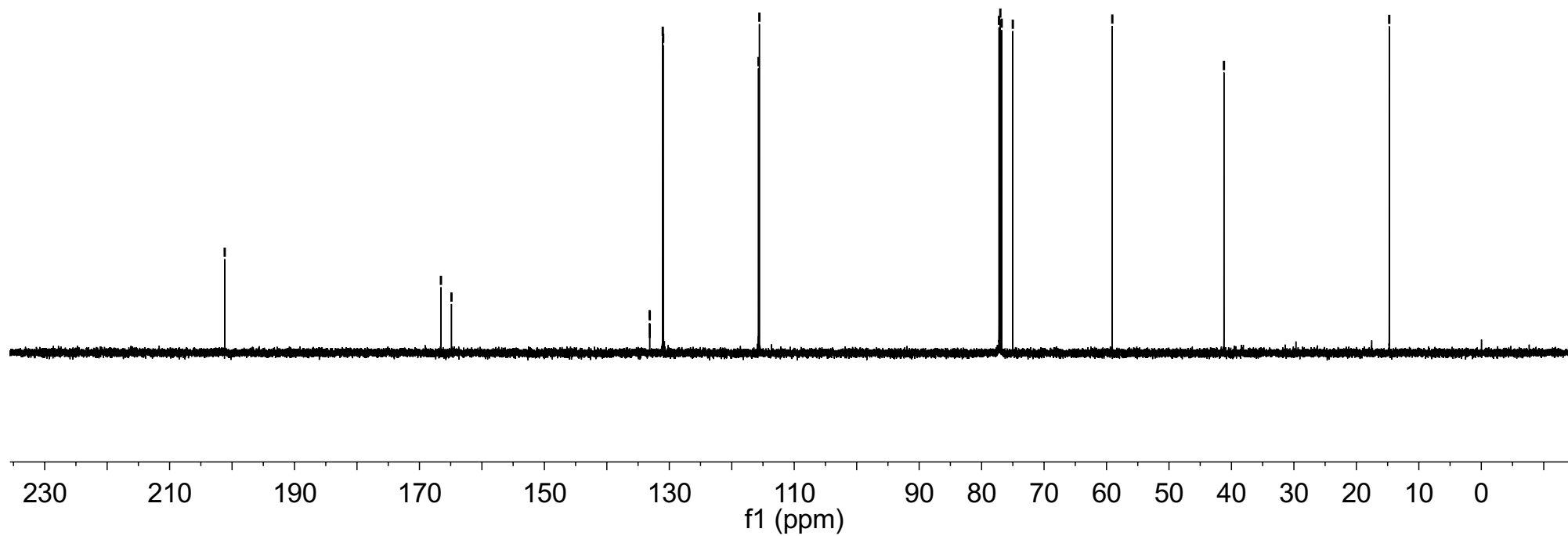
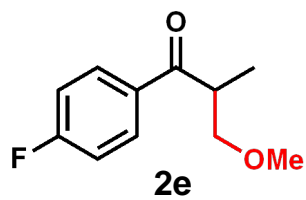
77.212  
77.000  
76.789  
75.005

-59.076

-41.202

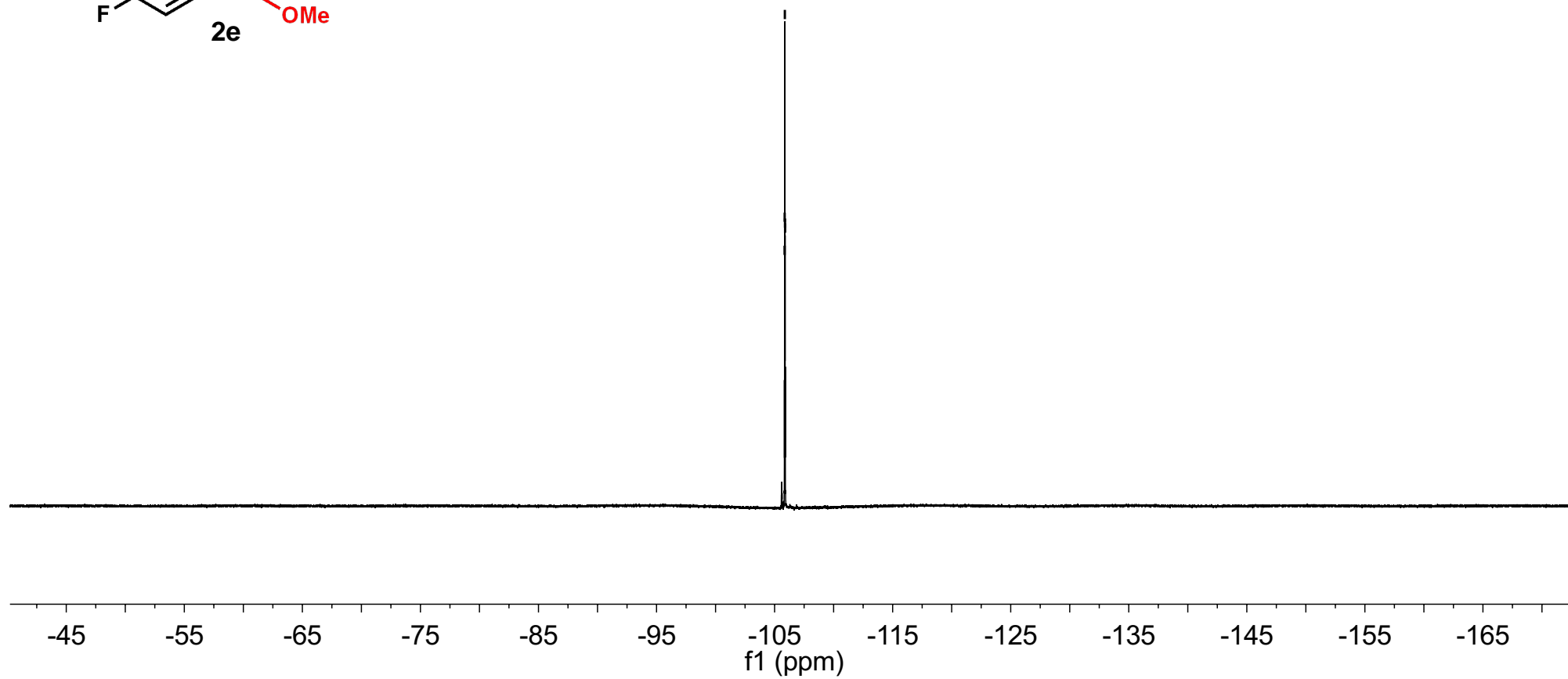
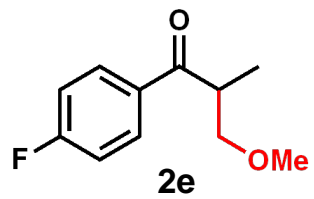
-14.739

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )

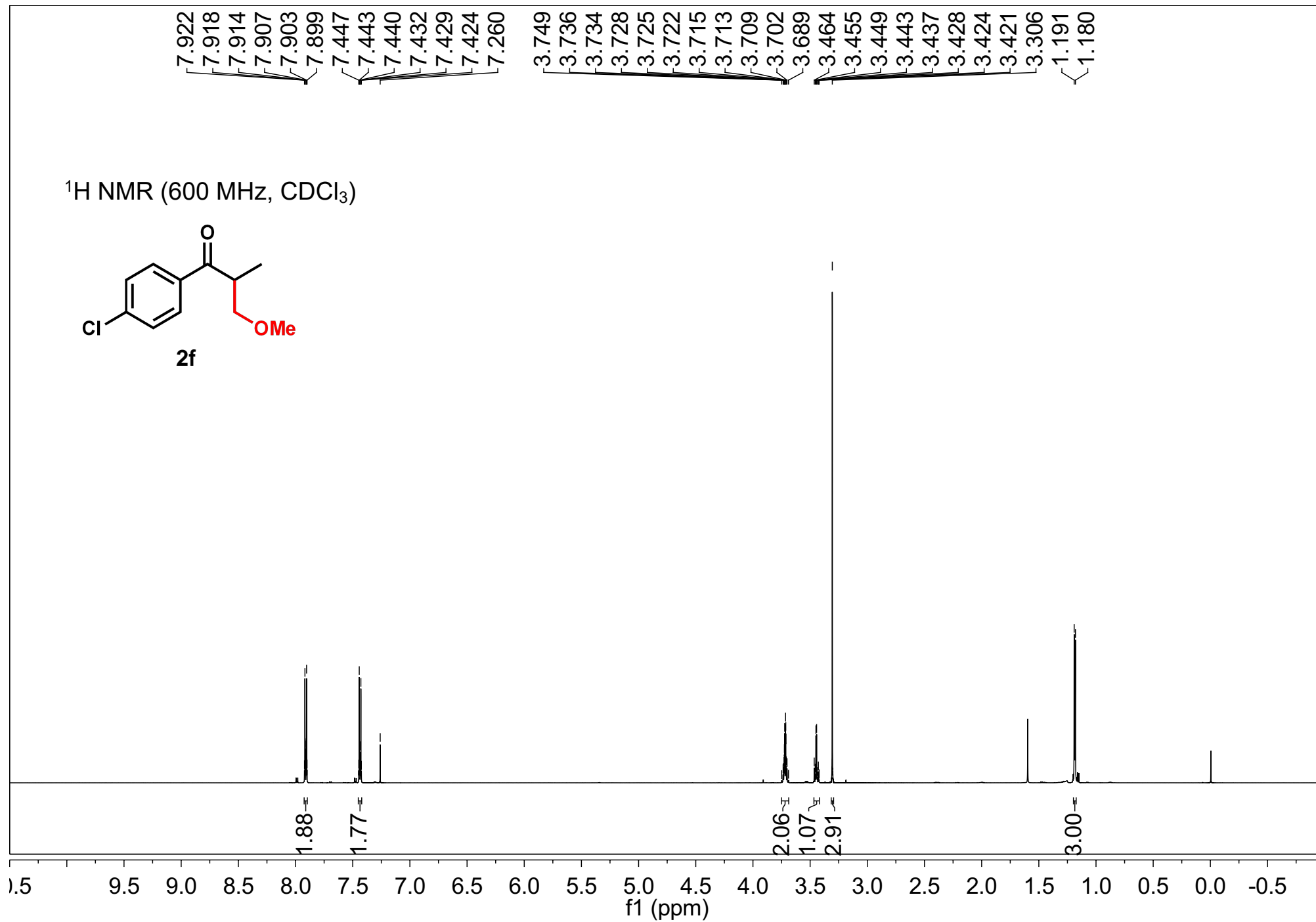
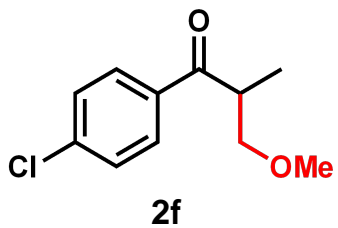


105.85  
105.85  
105.87  
105.88  
105.89

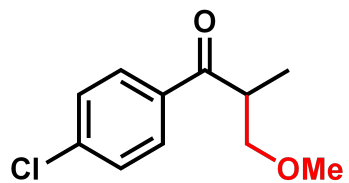
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



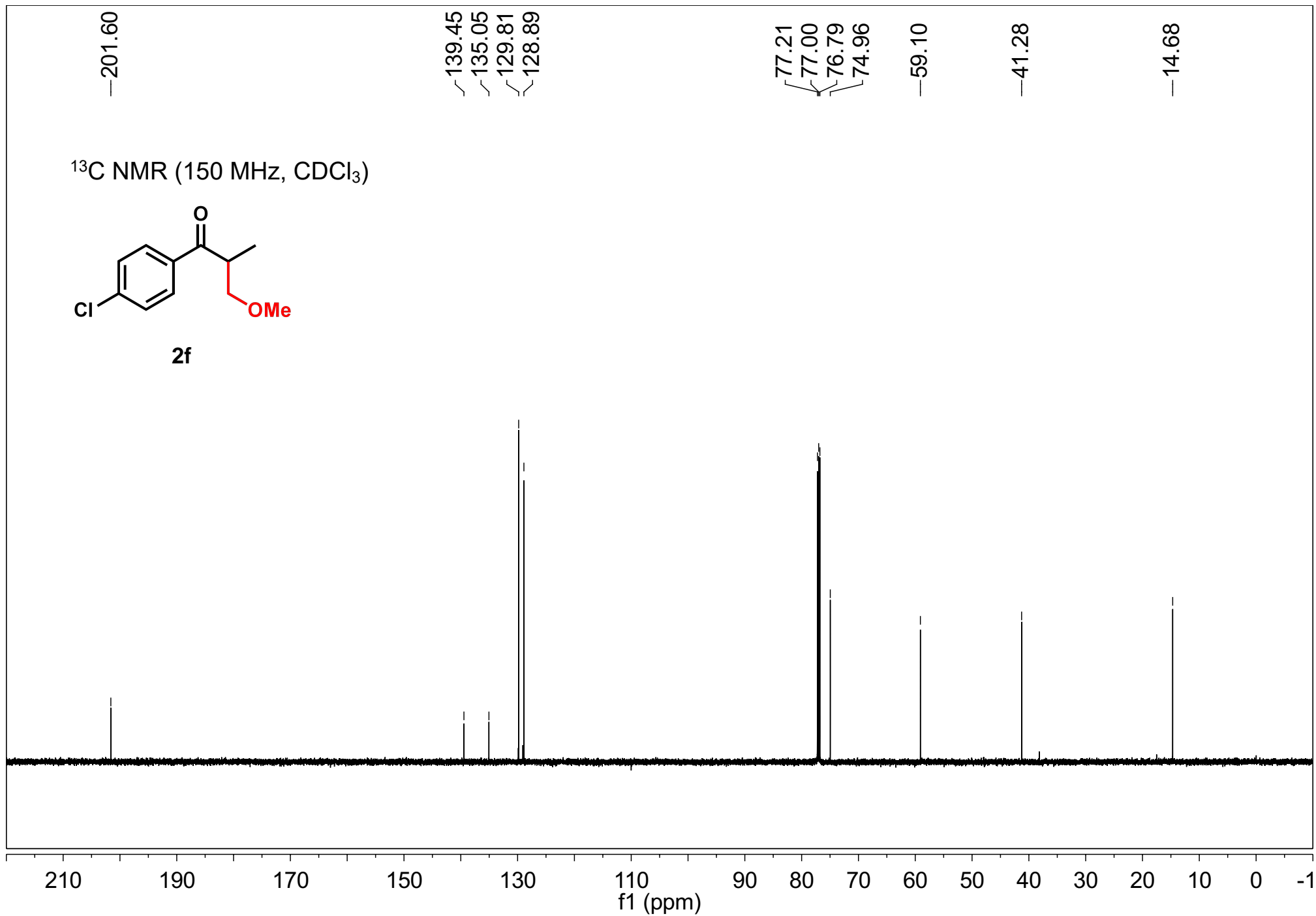
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



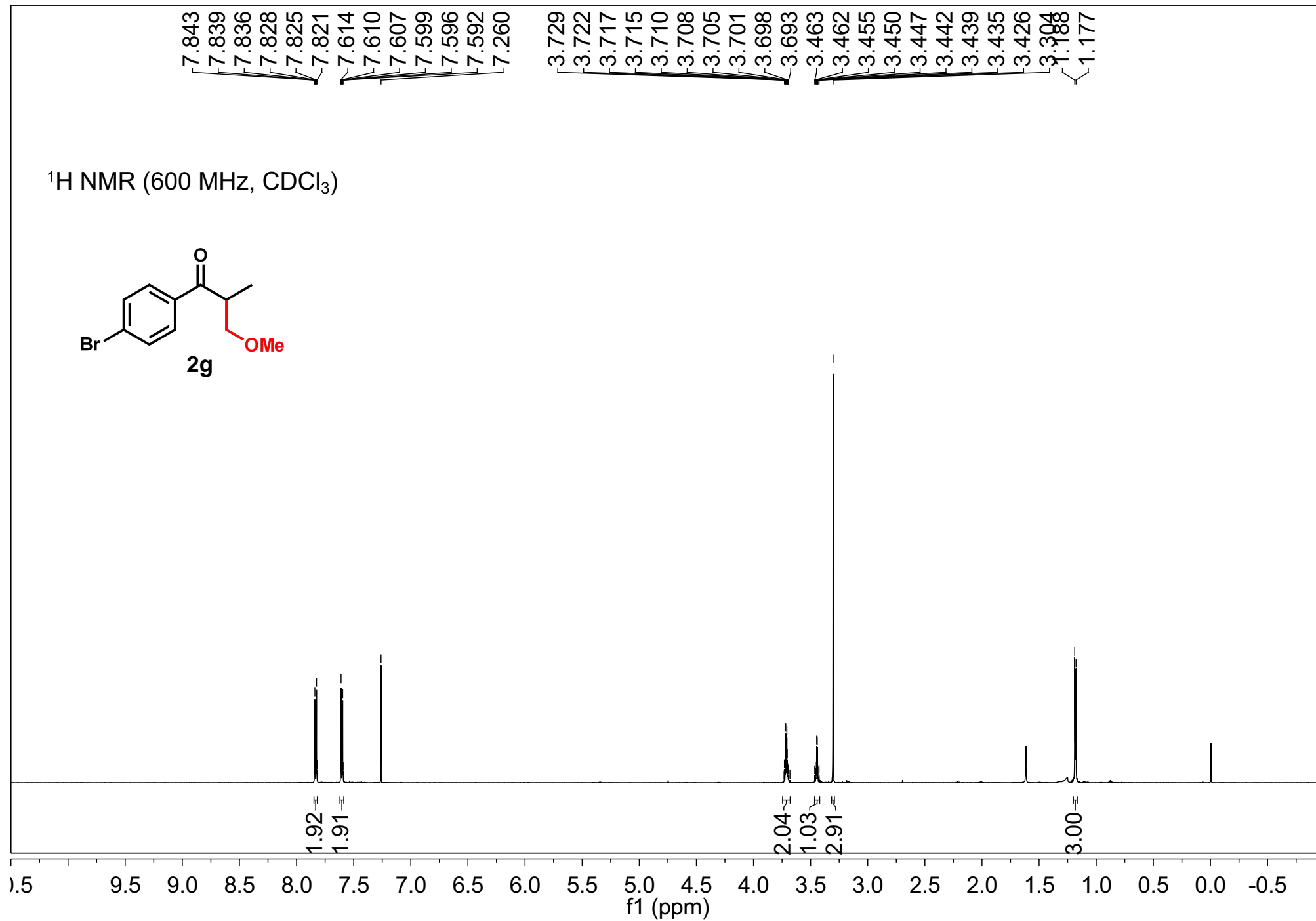
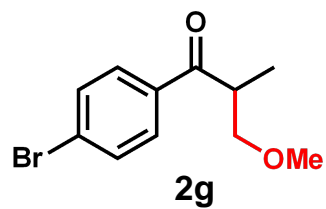
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



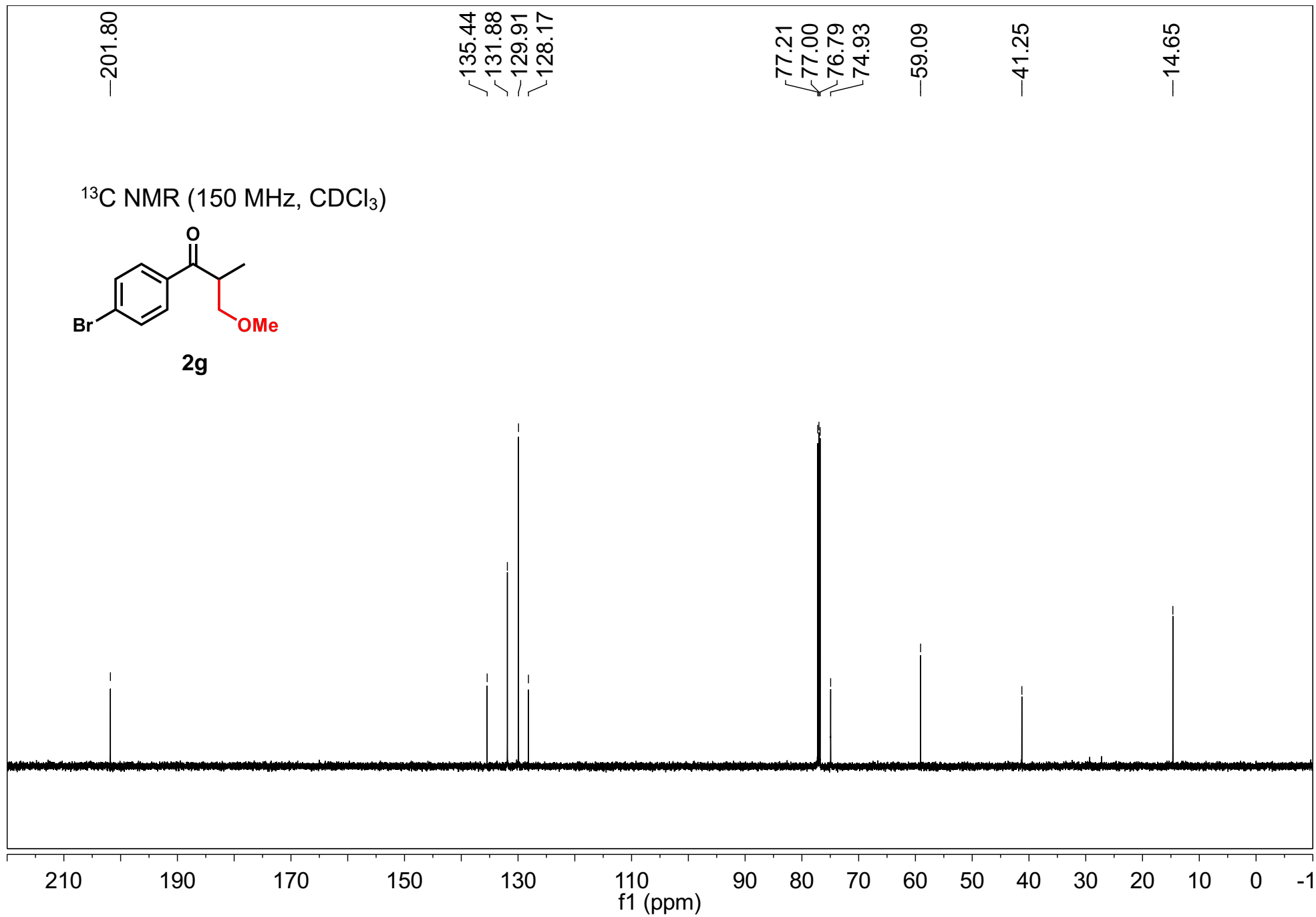
2f



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)





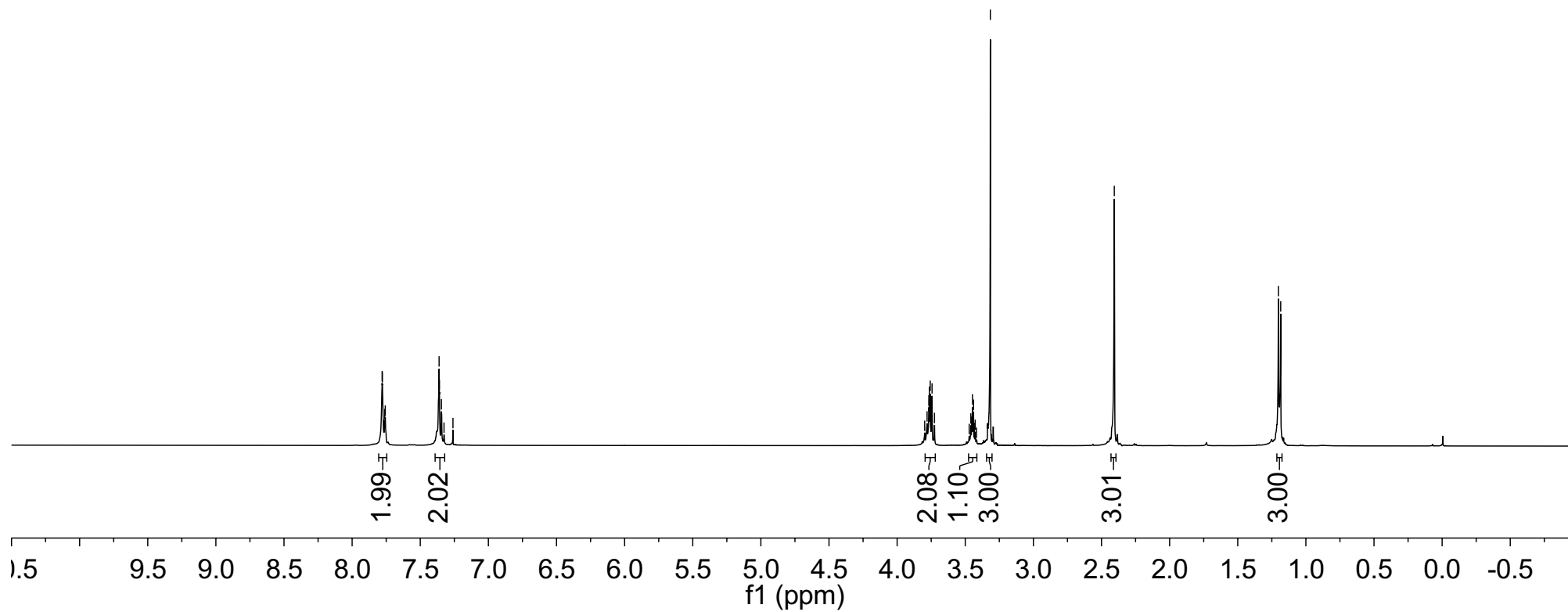
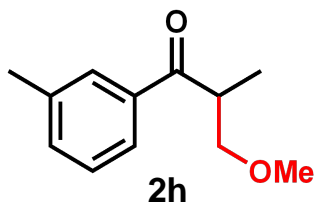


7.780  
7.778  
7.767  
7.761  
7.757  
7.362  
7.359  
7.345  
7.326  
7.260

3.798  
3.780  
3.767  
3.764  
3.757  
3.744  
3.726  
3.471  
3.459  
3.453  
3.447  
3.439  
3.434  
3.427  
3.418  
3.316  
2.406

1.202  
1.185

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



-202.88

138.34  
136.68  
133.73  
128.83  
128.43  
125.54

77.21  
77.00  
76.79  
74.97

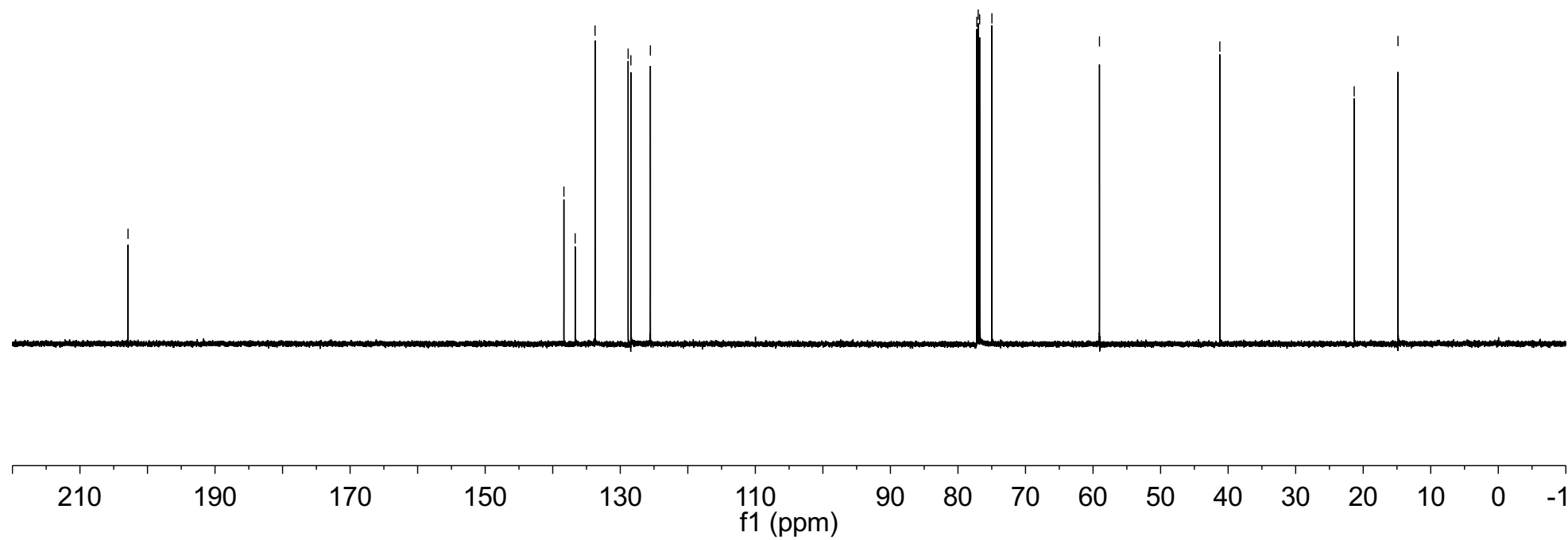
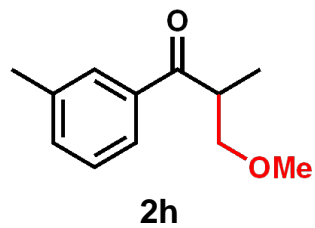
-59.05

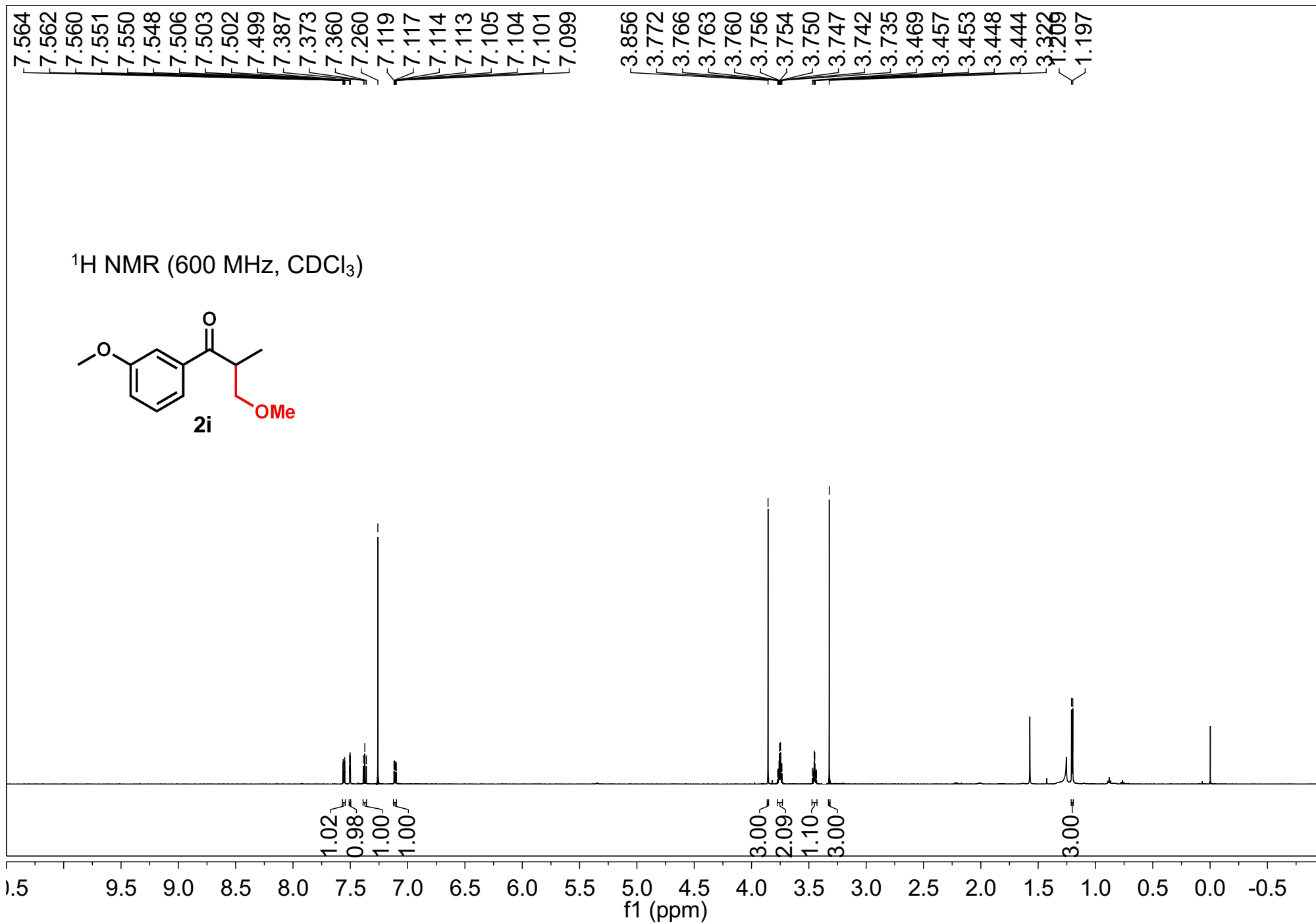
-41.23

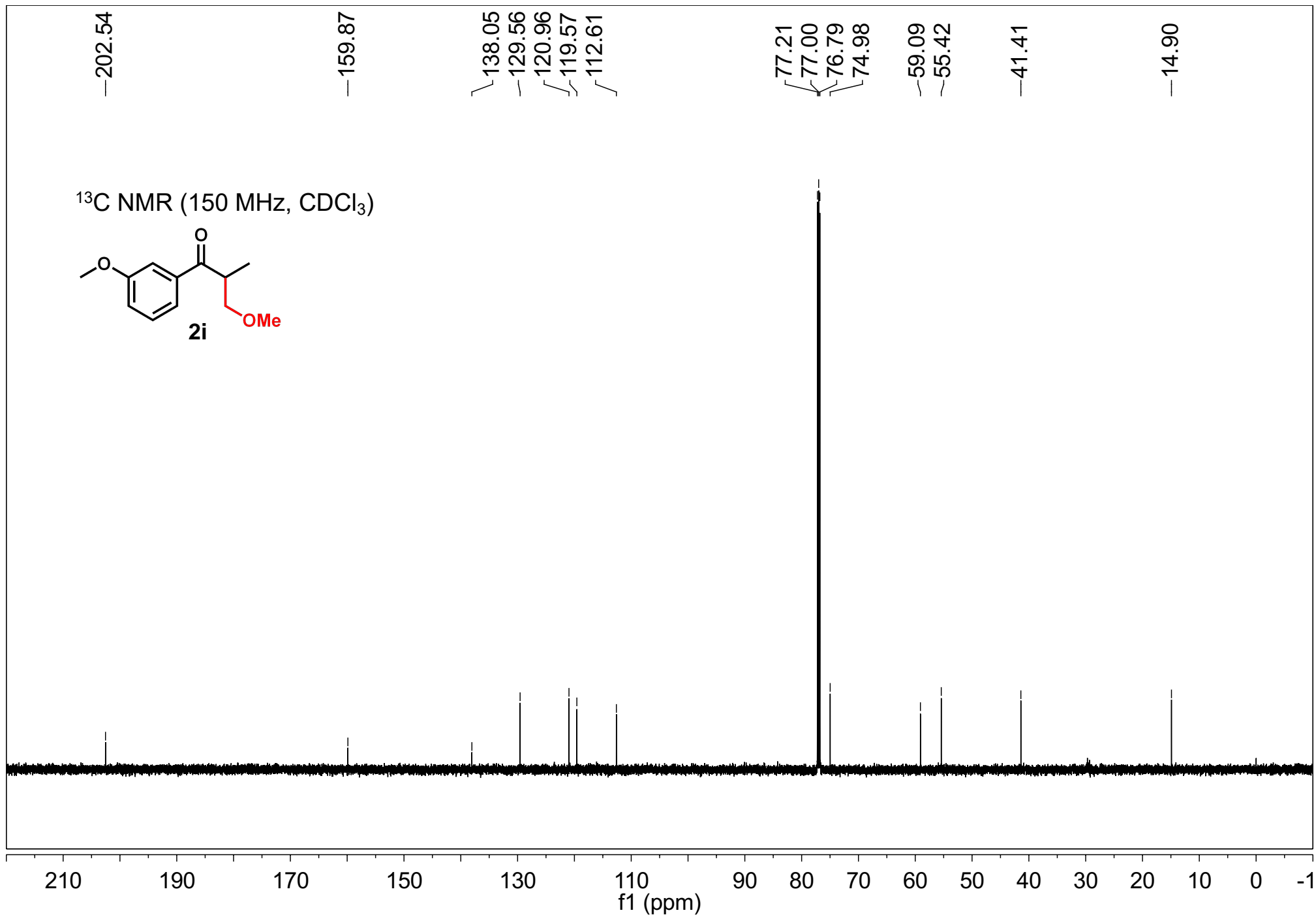
-21.33

-14.85

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )





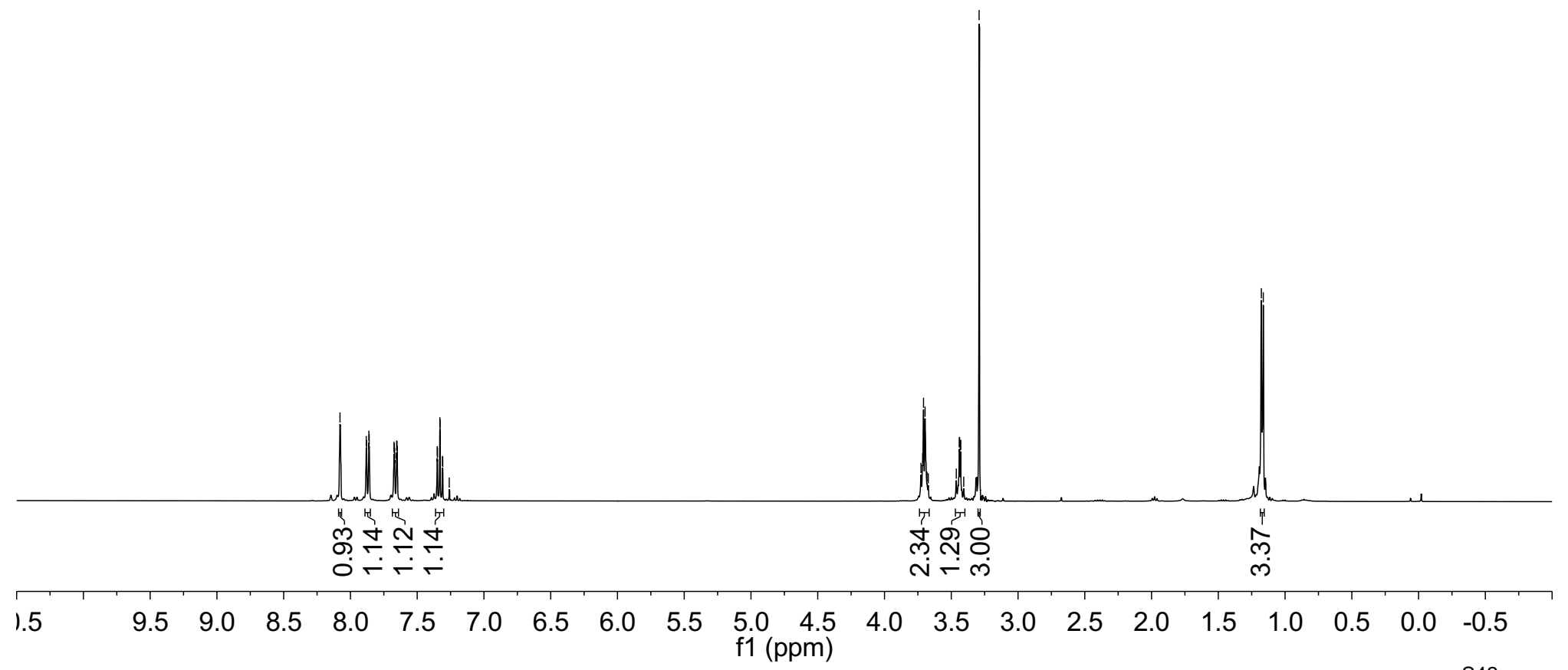
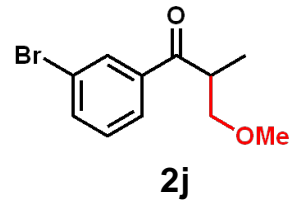


8.078  
7.881  
7.879  
7.862  
7.859  
7.674  
7.671  
7.669  
7.654  
7.651  
7.649  
7.350  
7.348  
7.330  
7.328  
7.311  
7.309  
7.260

3.727  
3.714  
3.708  
3.696  
3.682  
3.672  
3.462  
3.440  
3.437  
3.432  
3.429  
3.407  
3.292

1.178  
1.163

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



-201.42

138.42  
135.75  
131.34  
130.12  
126.83  
122.91

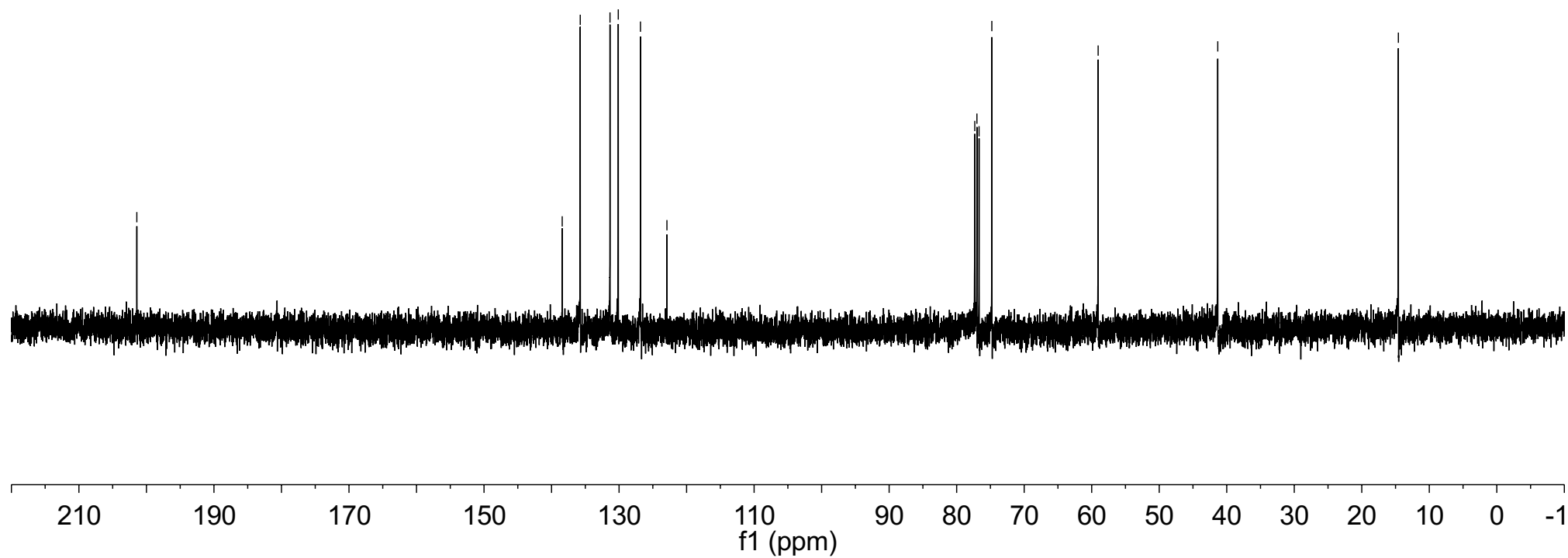
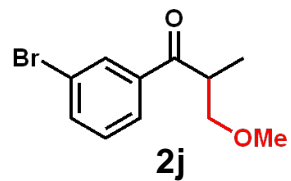
77.32  
77.00  
76.68  
74.79

-59.04

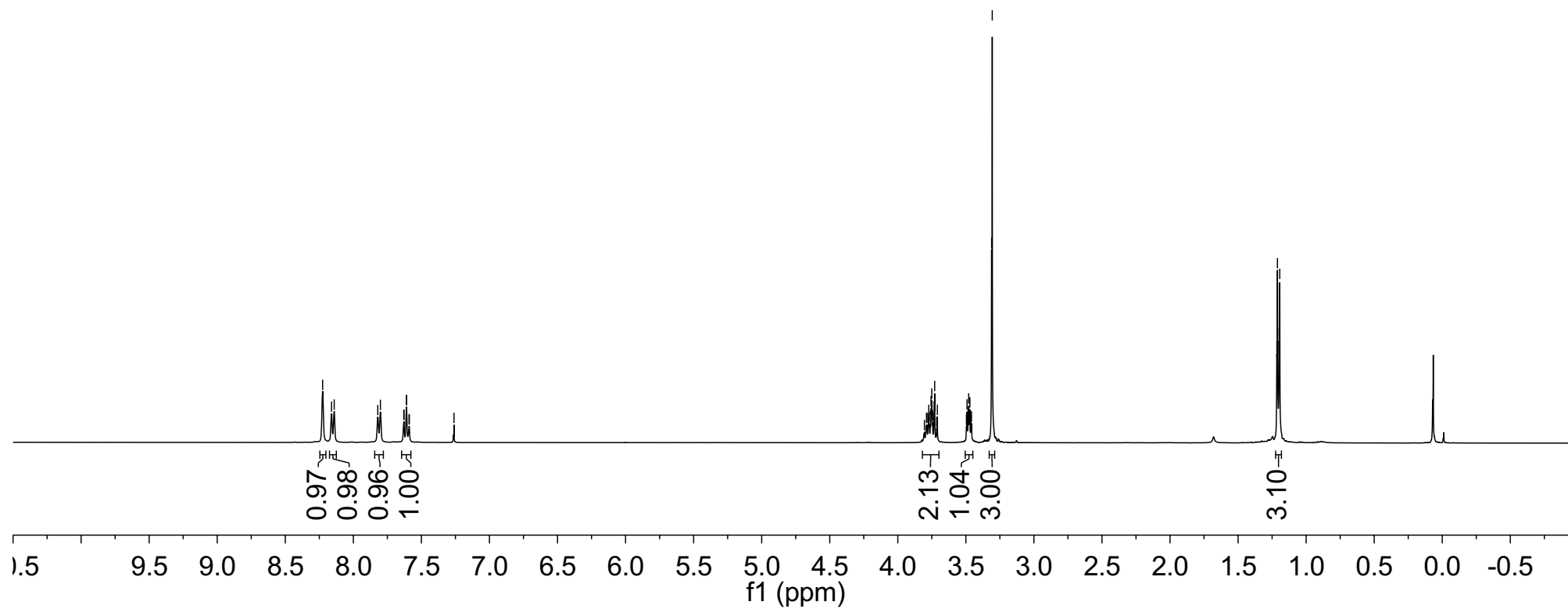
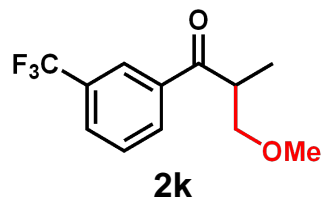
-41.33

-14.58

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

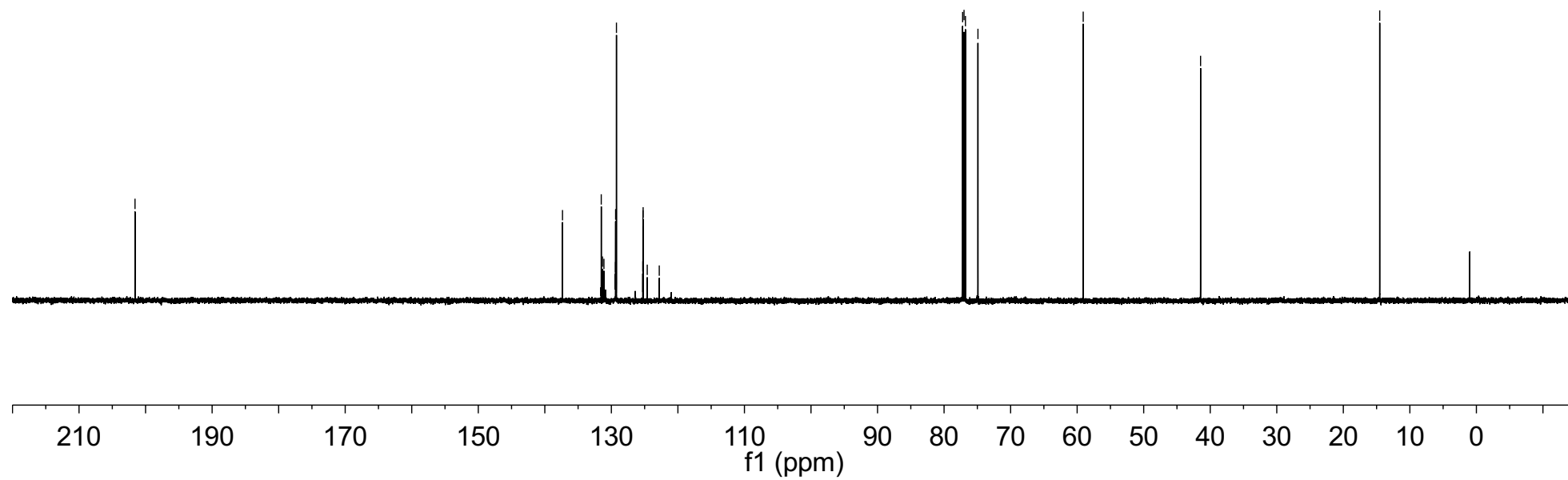
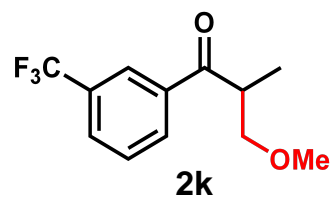


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

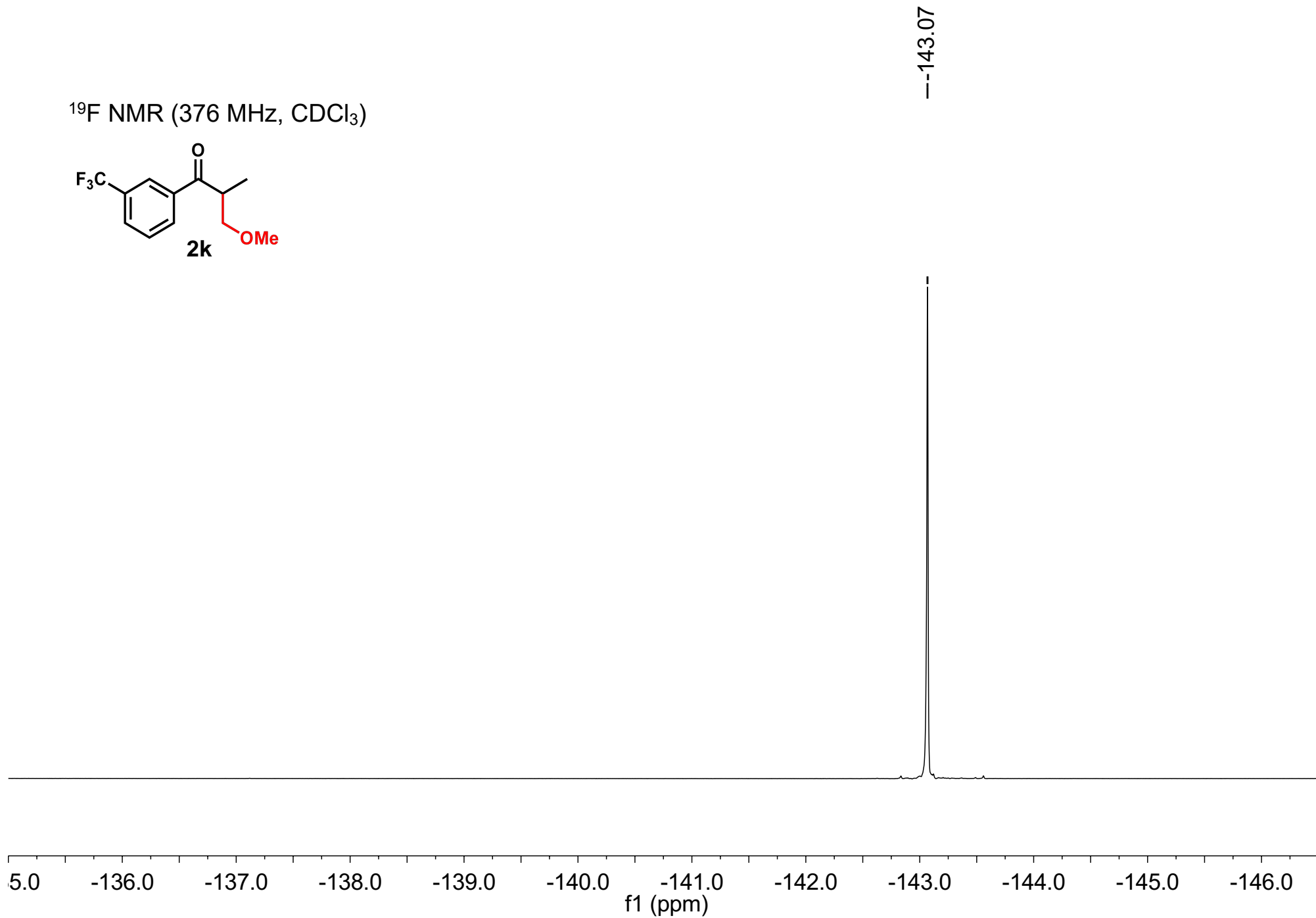
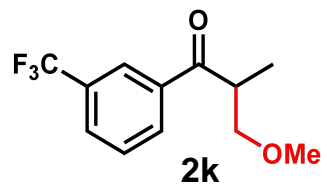




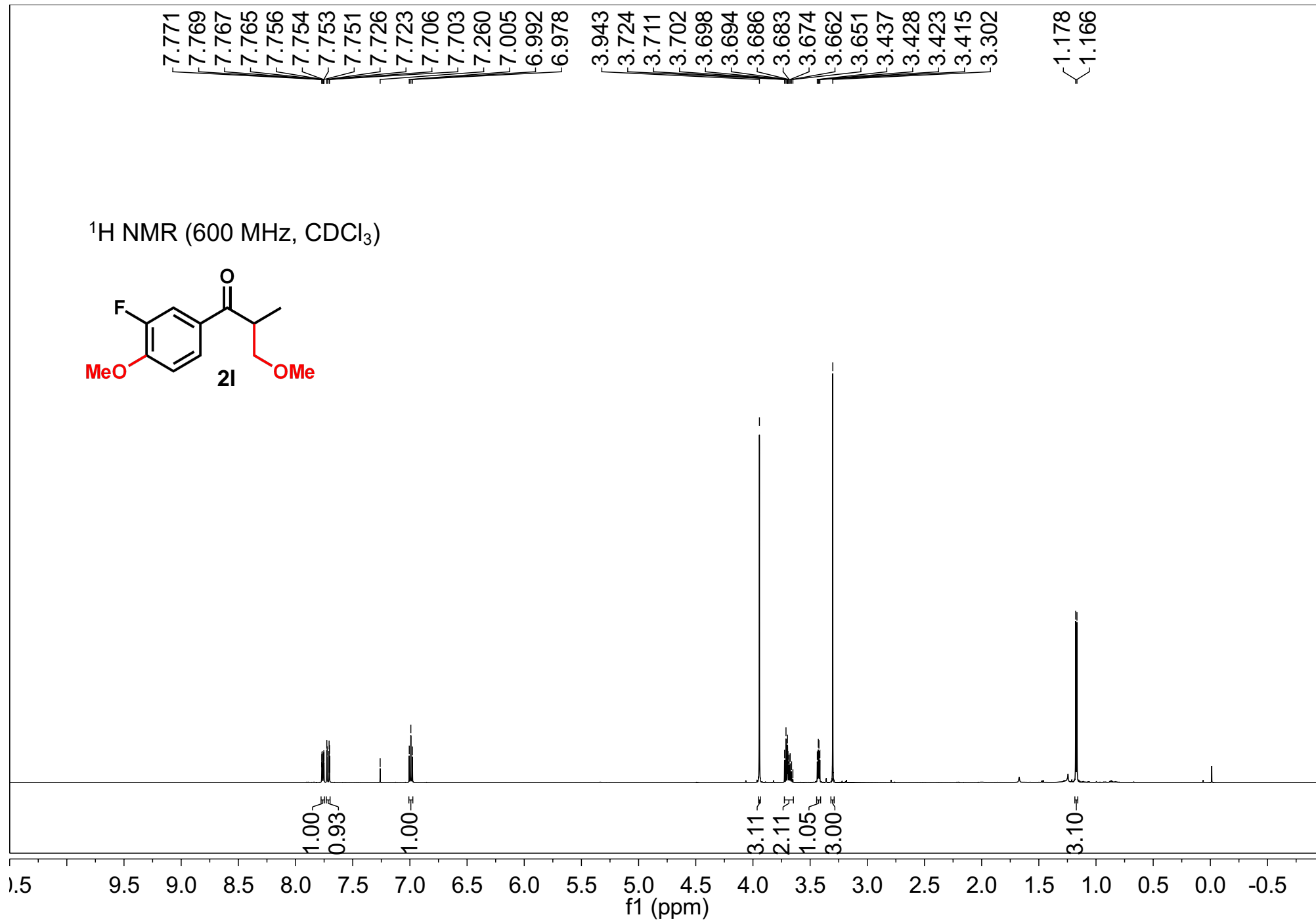
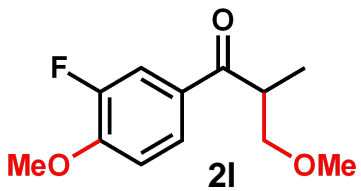
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



-200.391

152.841  
151.847  
151.774  
151.199

129.960  
129.929  
125.635  
125.613  
116.092  
115.967  
112.287

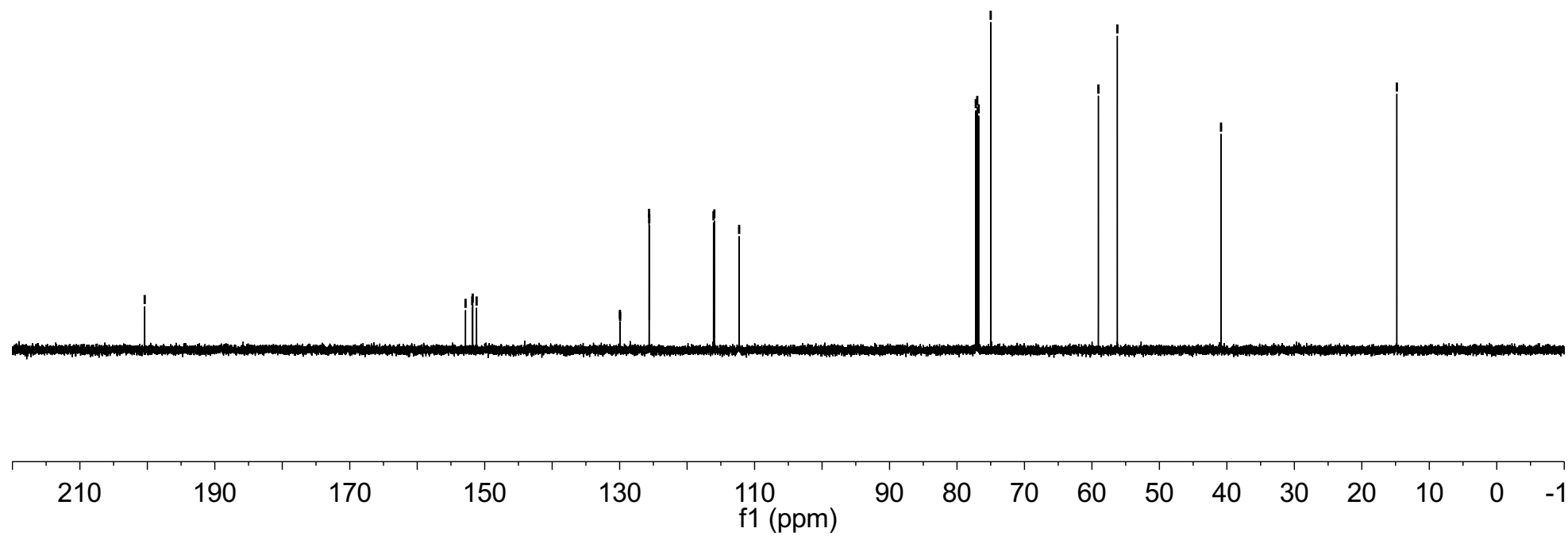
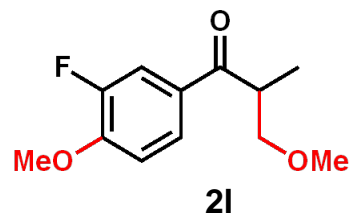
77.212  
77.000  
76.788  
75.008

~59.042  
~56.232

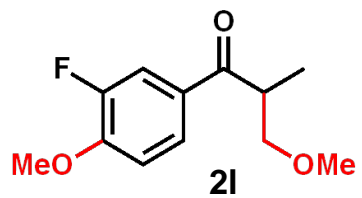
-40.867

-14.808

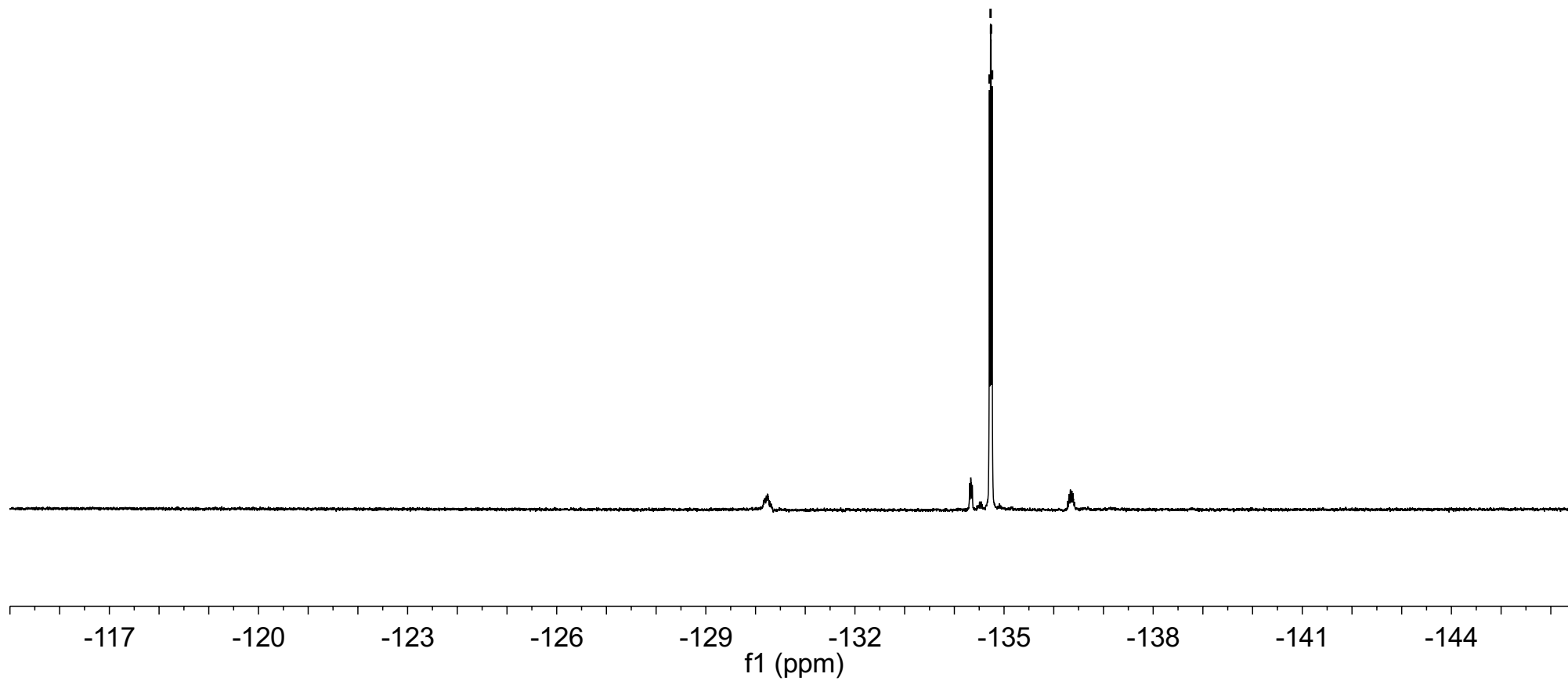
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



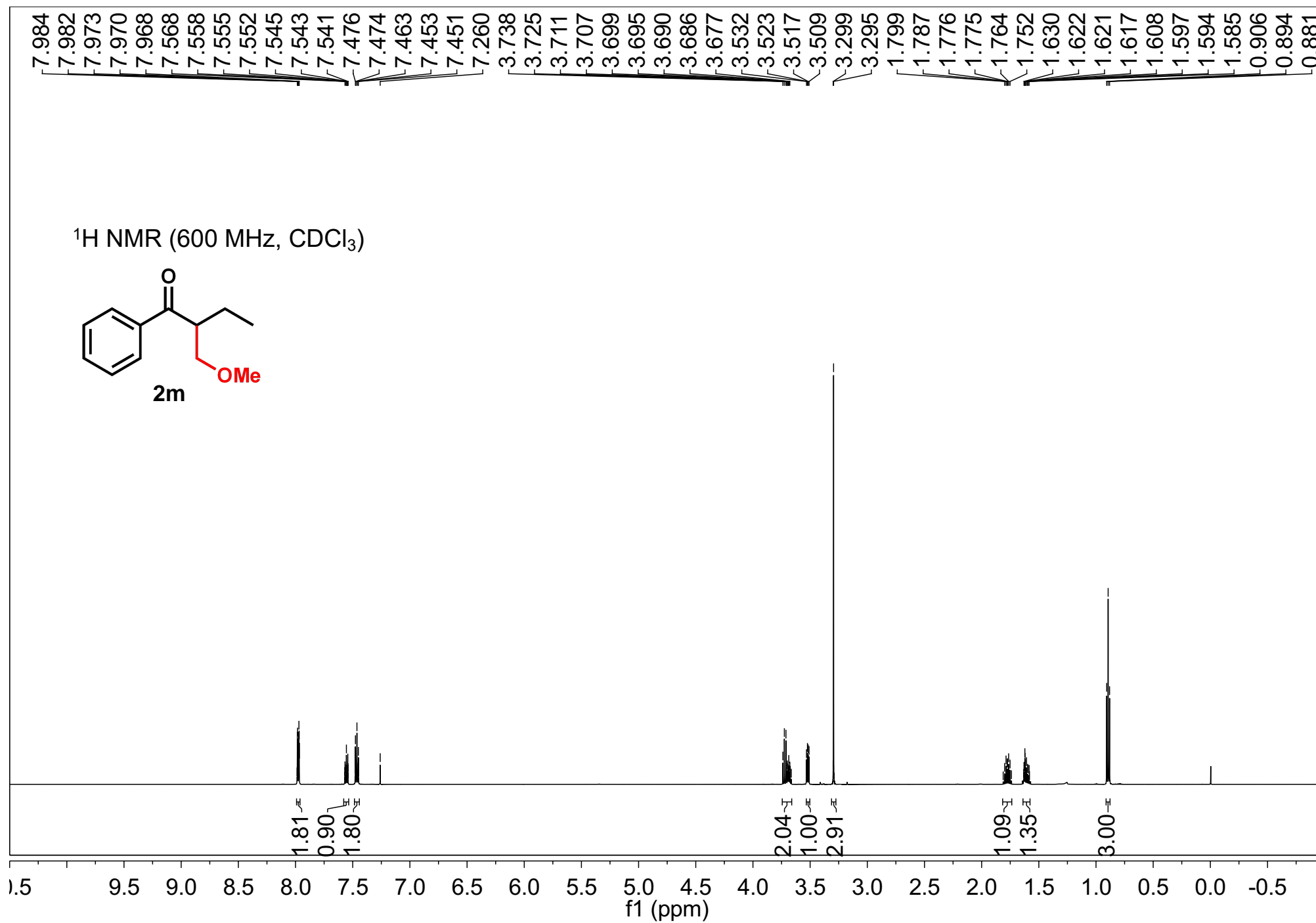
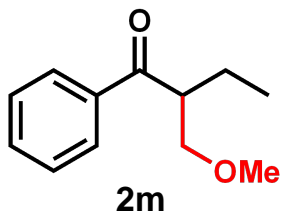
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



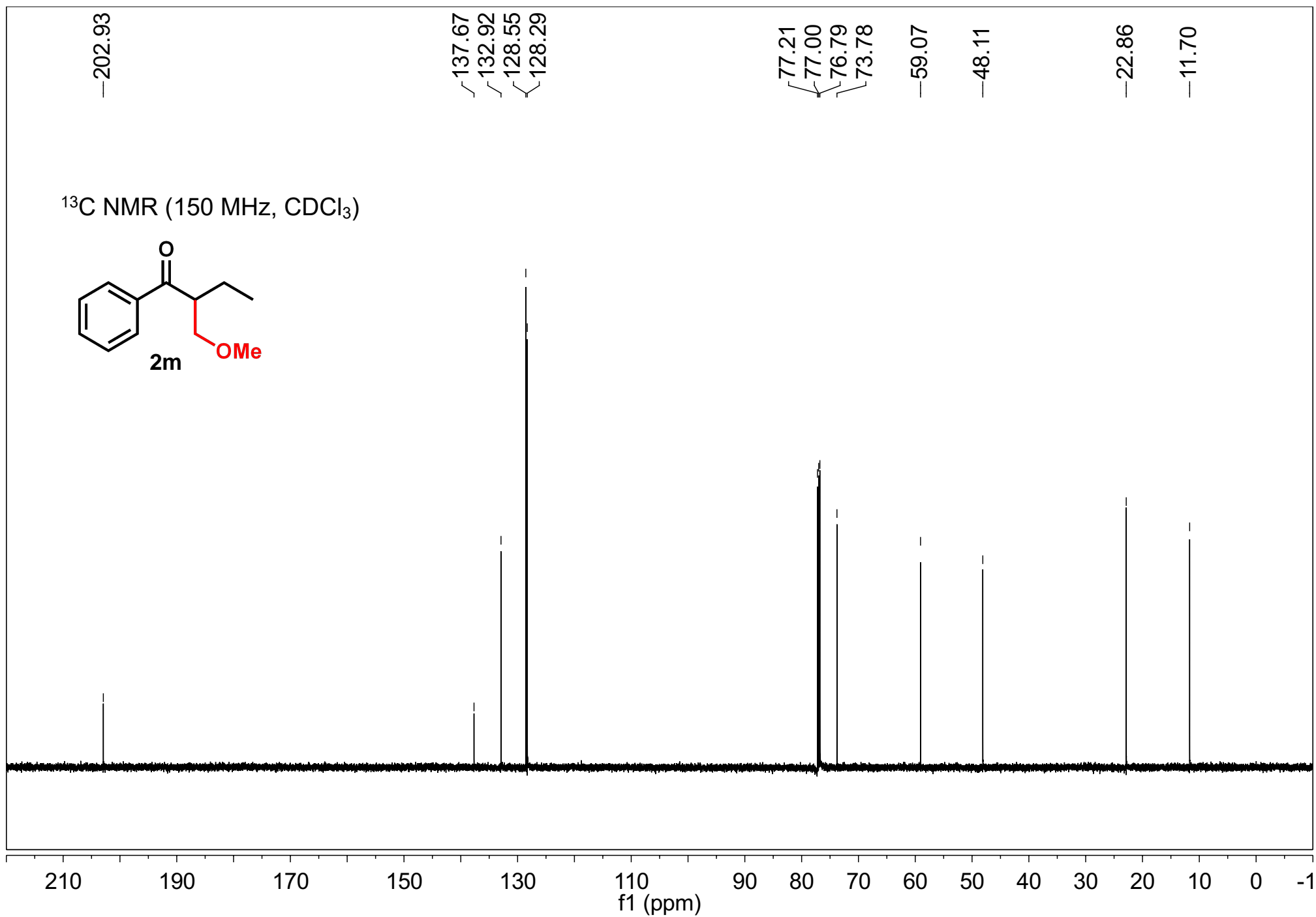
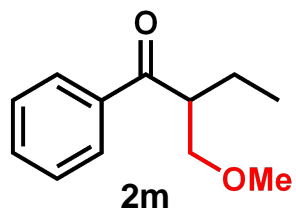
-134.706  
-134.728  
-134.738  
-134.760

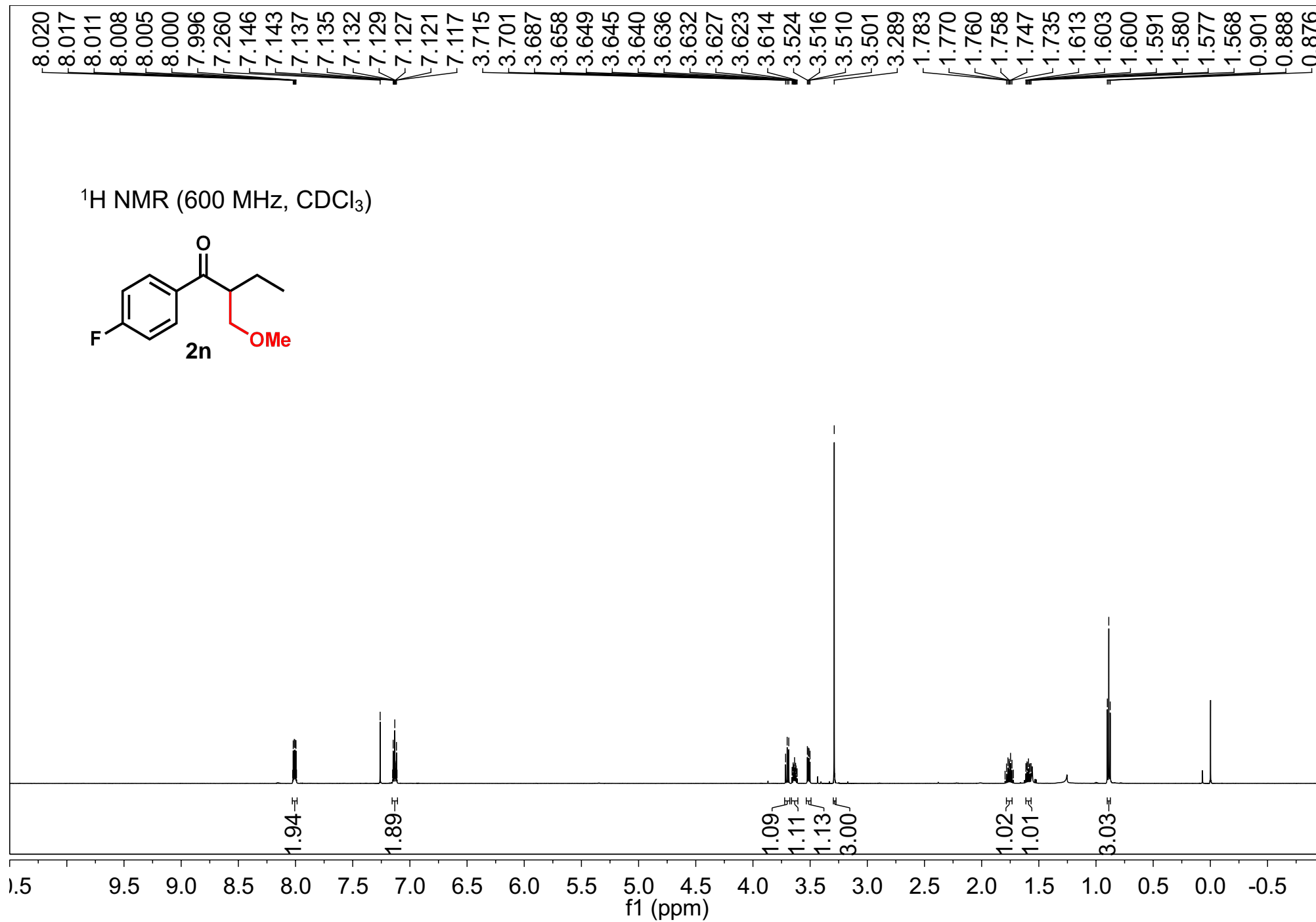


<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



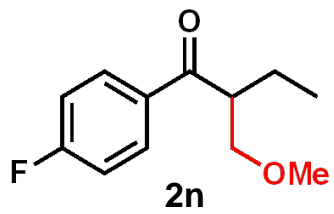
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)







$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )



—201.452

—166.562  
—164.875

—134.180  
—134.161  
—130.992  
—130.931

—115.695  
—115.551

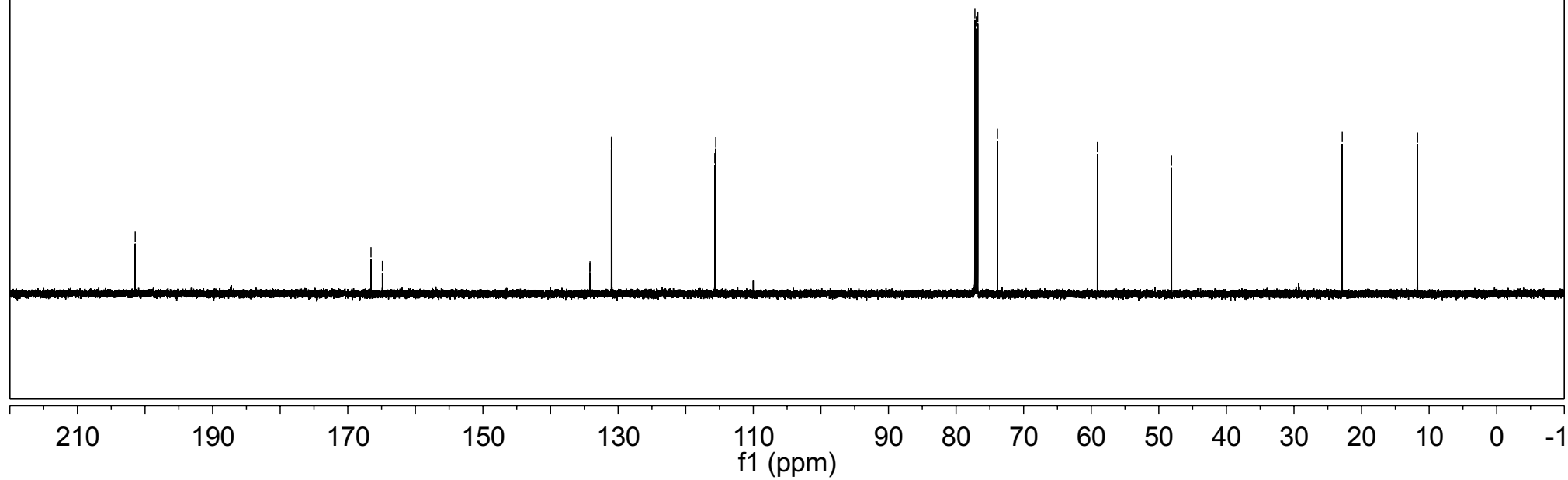
—77.211  
—77.000  
—76.787  
—73.876

—59.085

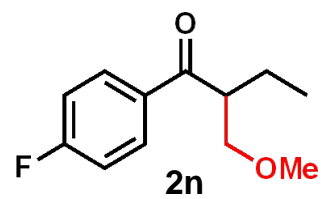
—48.121

—22.858

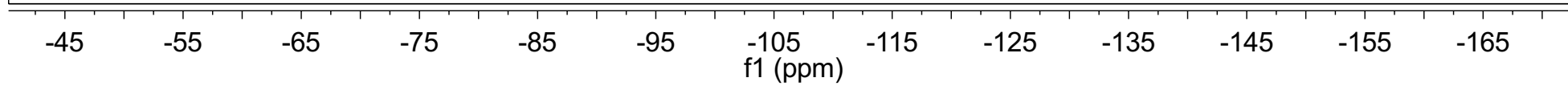
—11.714



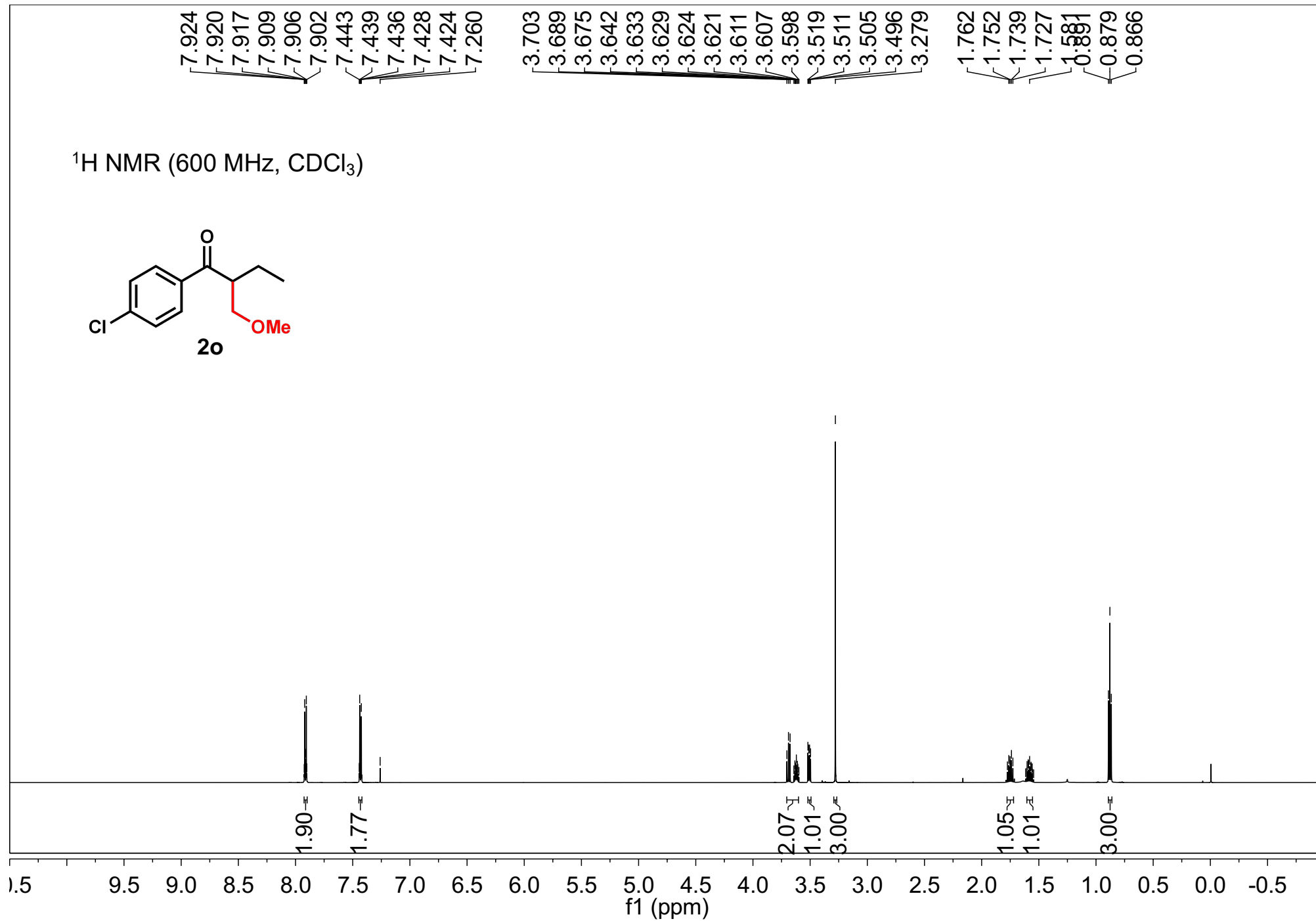
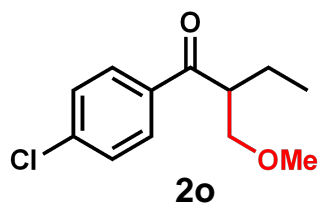
$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )



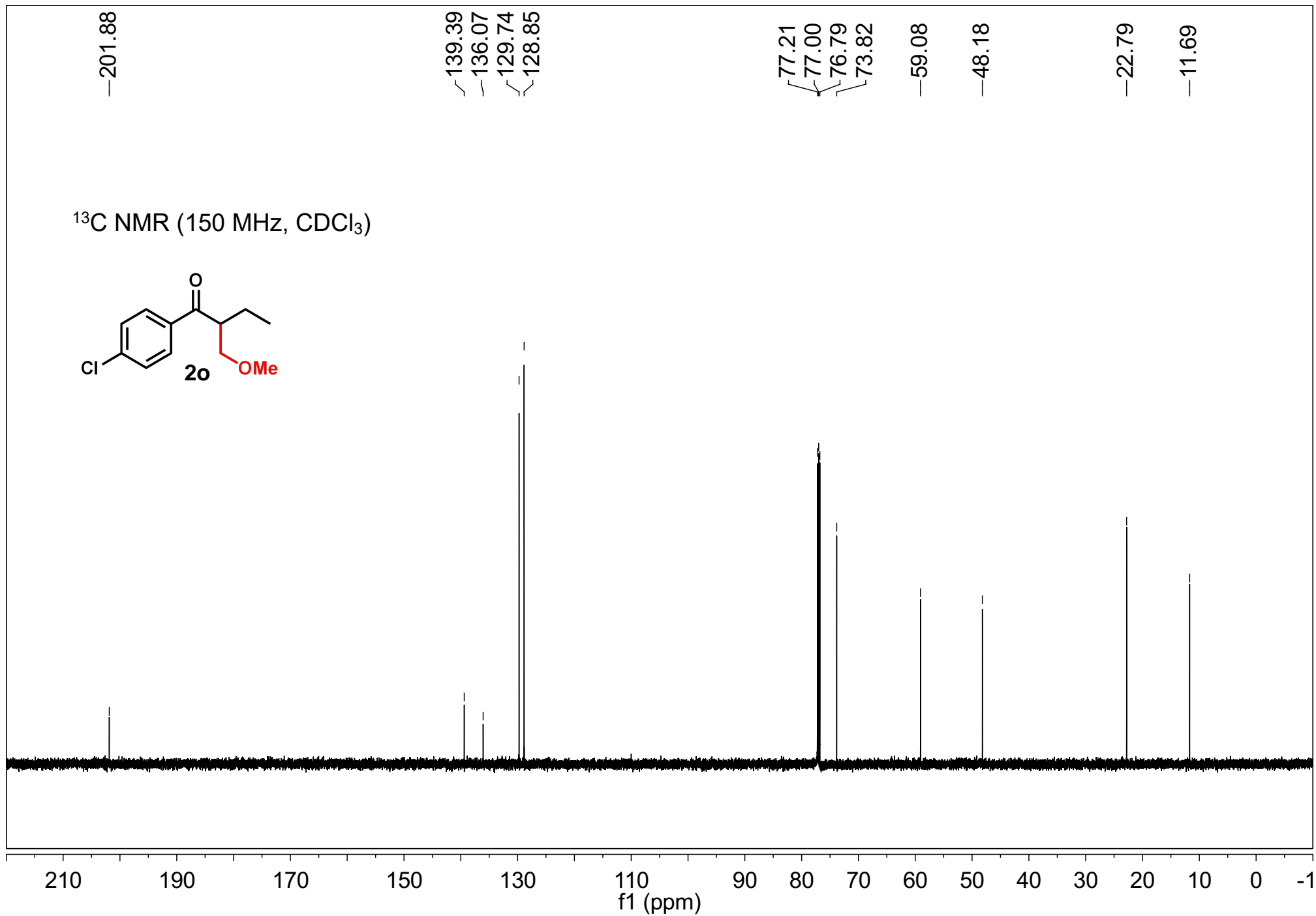
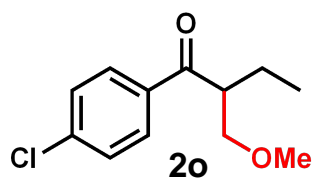
106.010  
106.018  
106.032  
106.047  
106.055



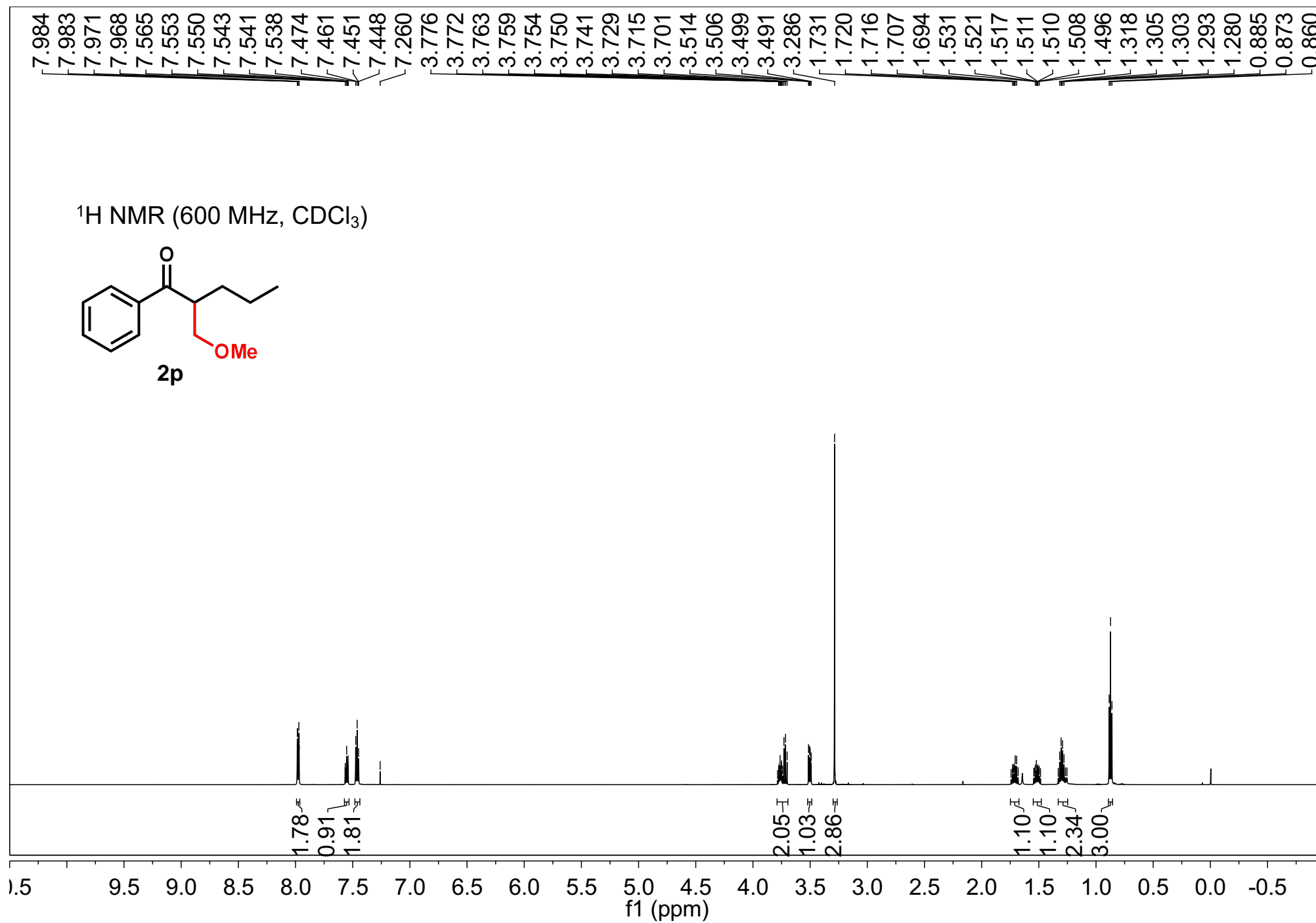
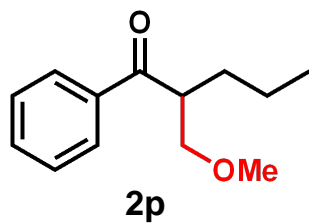
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



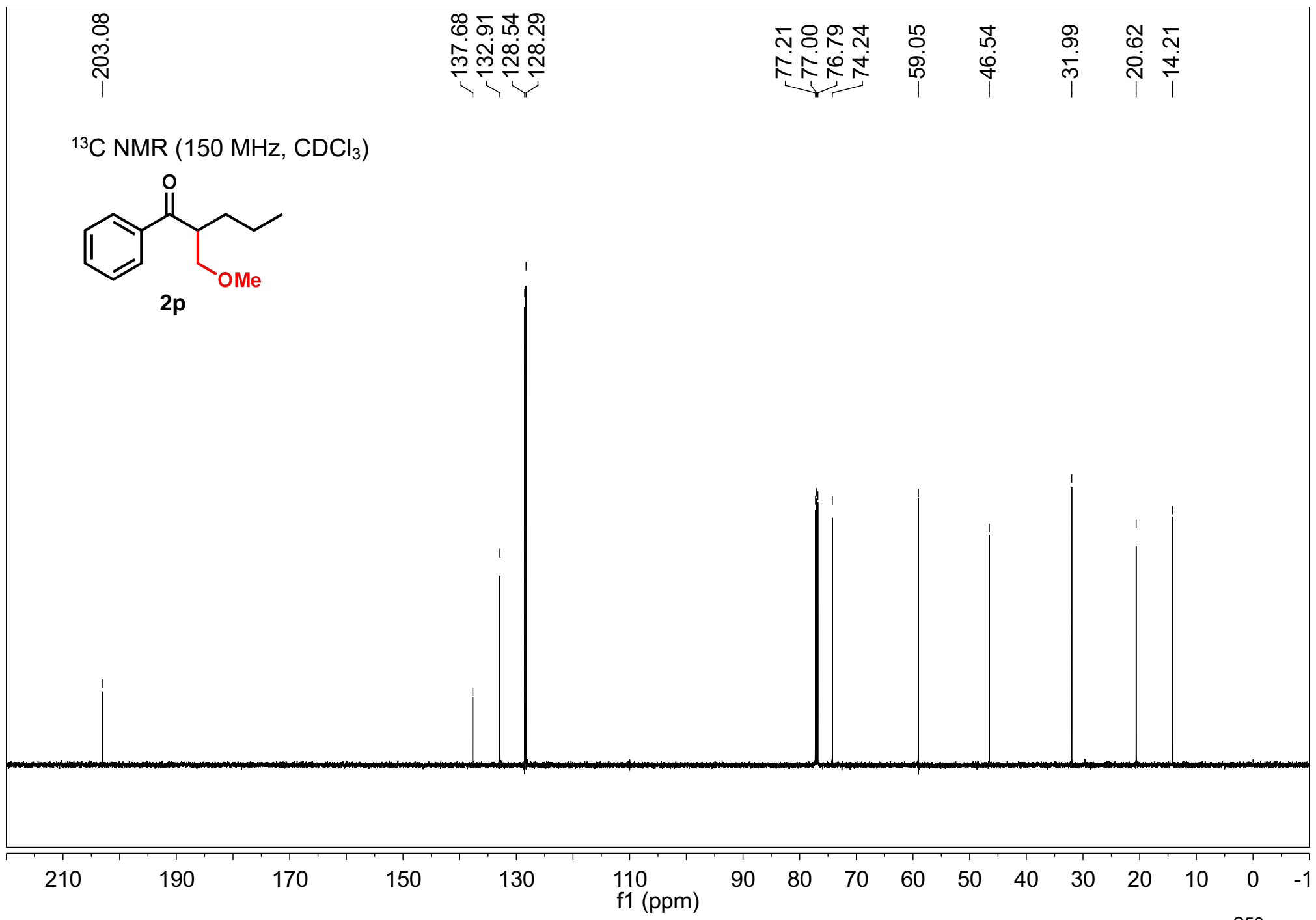
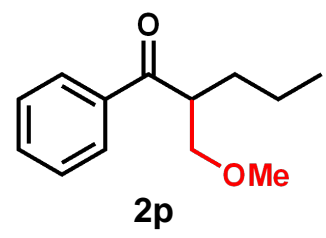
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)

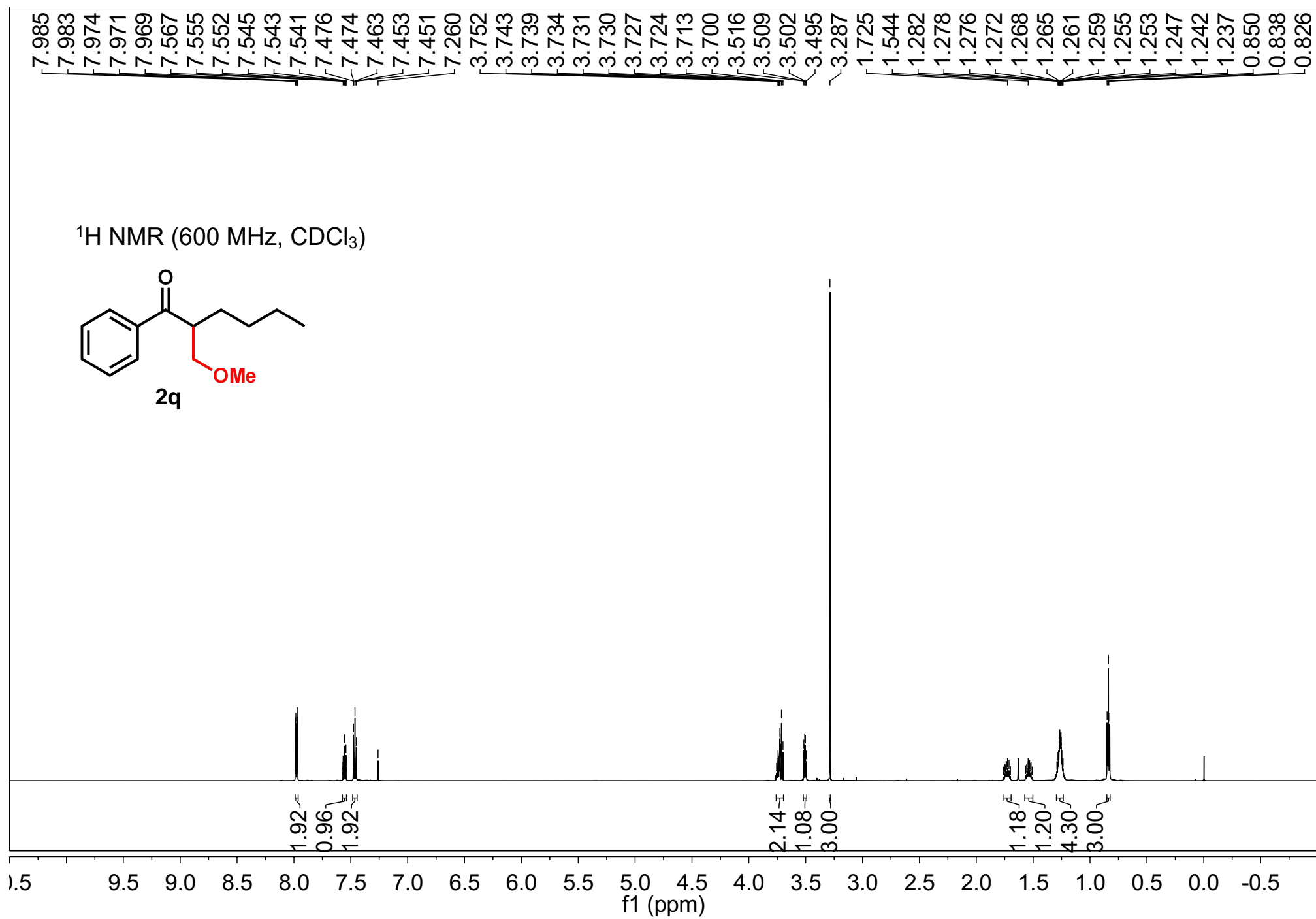


<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)

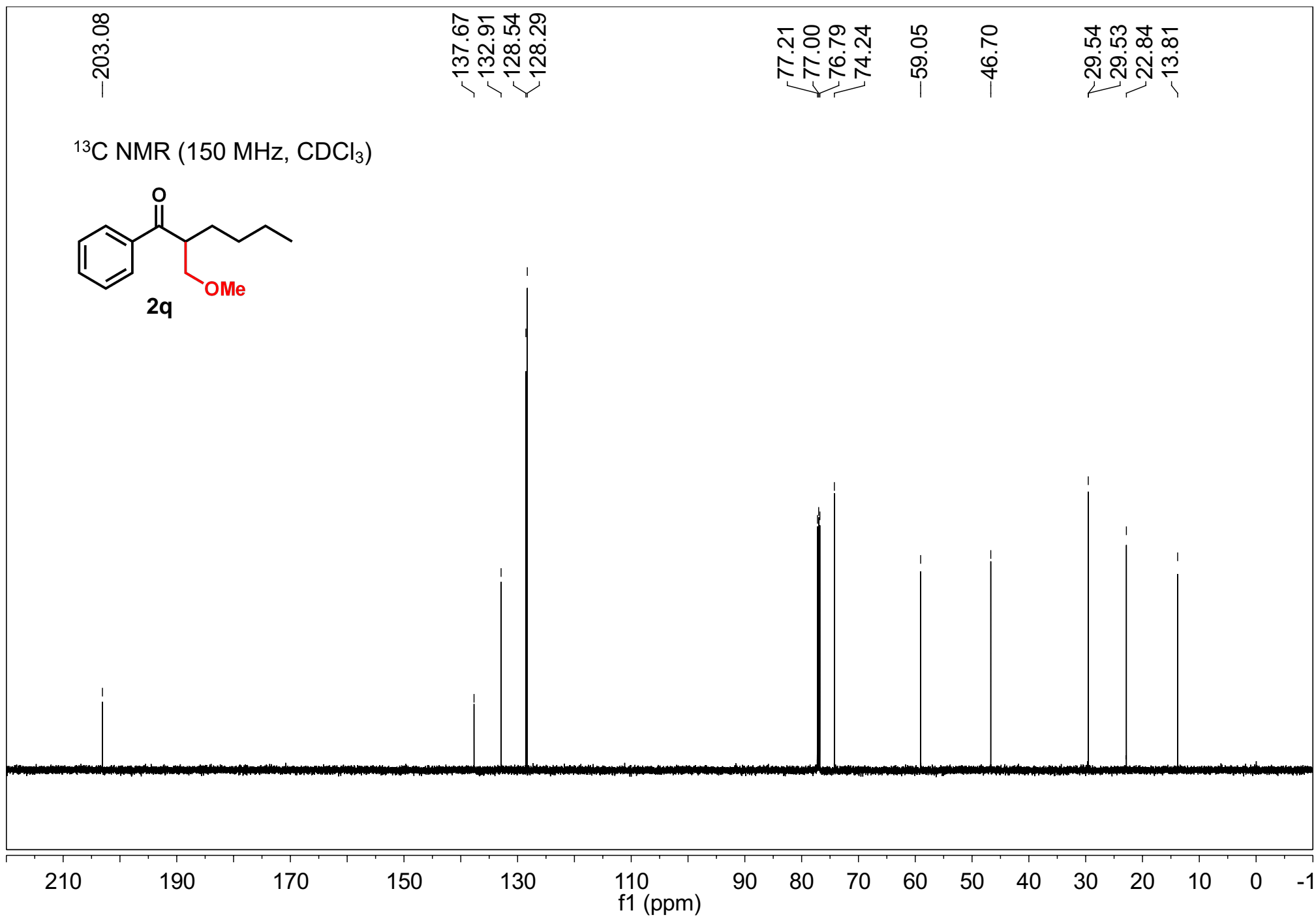
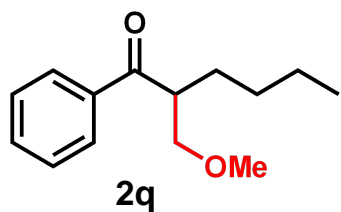


<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)

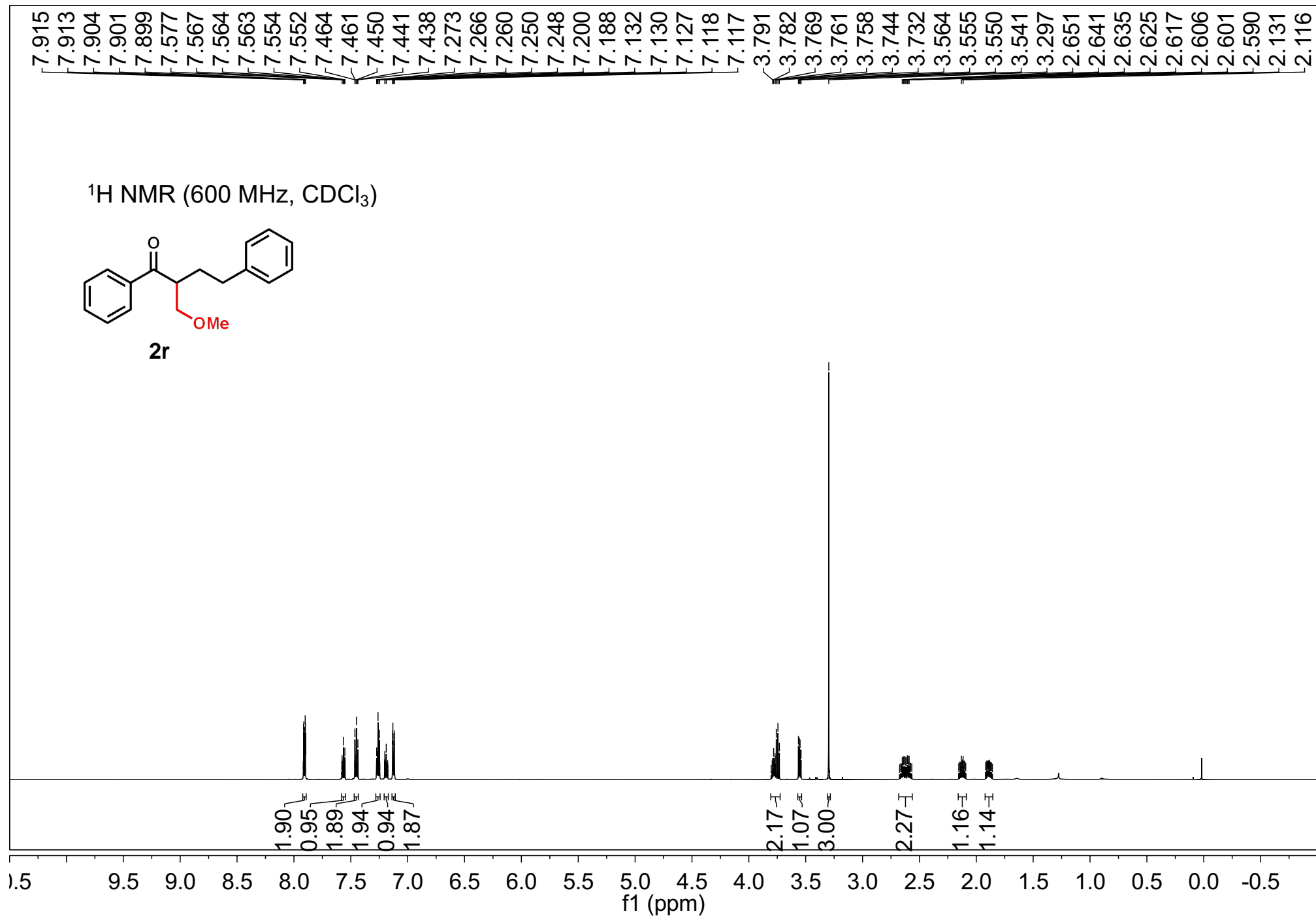




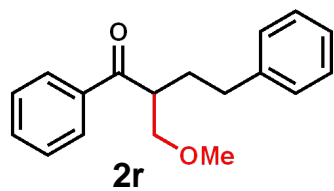
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)







<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



—202.54

141.40  
137.41  
133.00  
128.54  
128.42  
128.35  
128.34  
125.98

77.21  
77.00  
76.79  
74.09

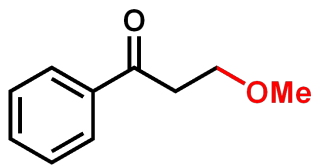
—59.07

—45.98

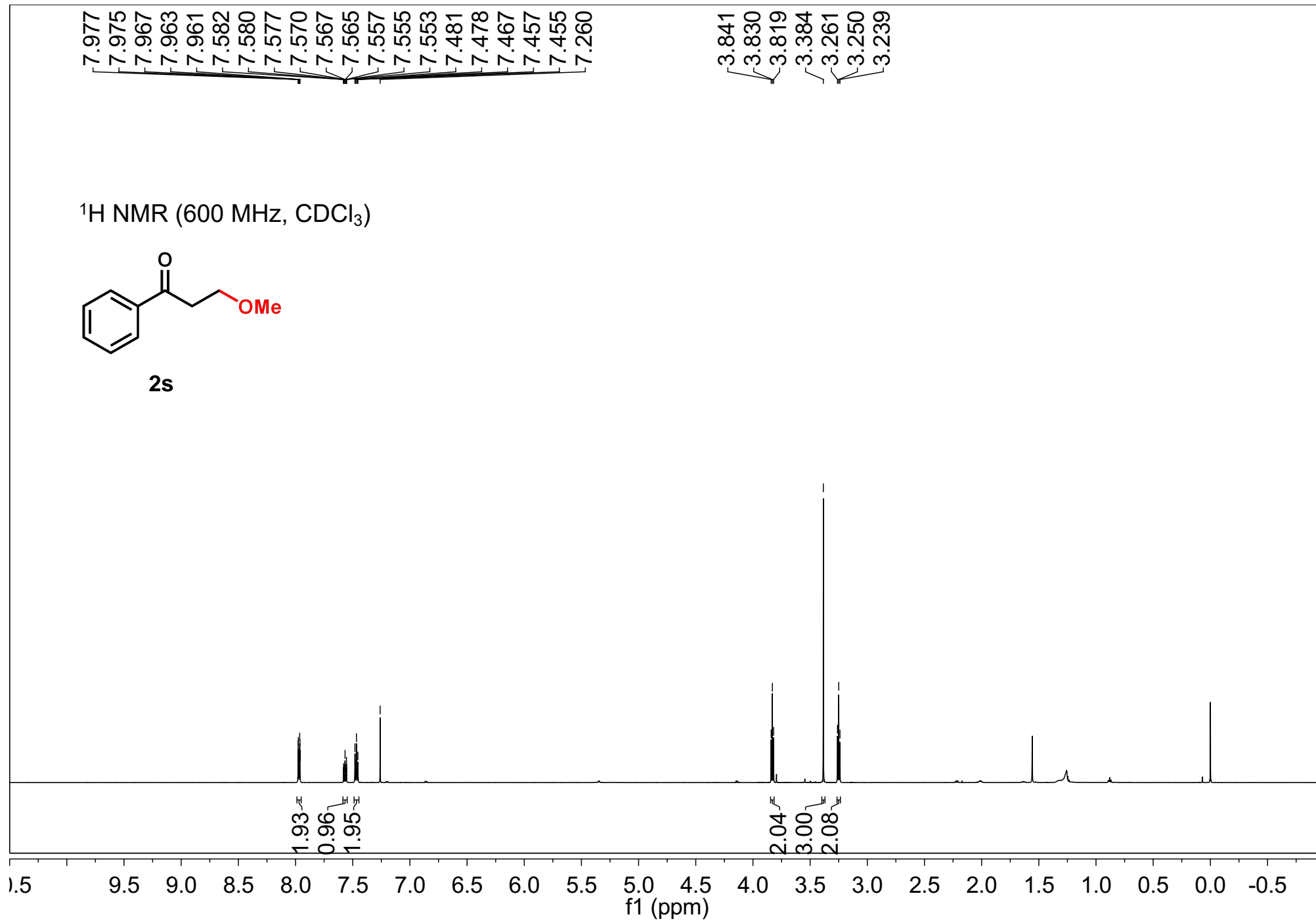
~33.39  
~31.26

210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1  
f1 (ppm)

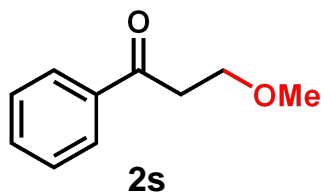
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



2s



<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



198.29

136.98

133.15

128.59

128.12

77.21

77.00

76.79

67.88

58.94

38.68

210

190

170

150

130

110

90

80

70

60

50

40

30

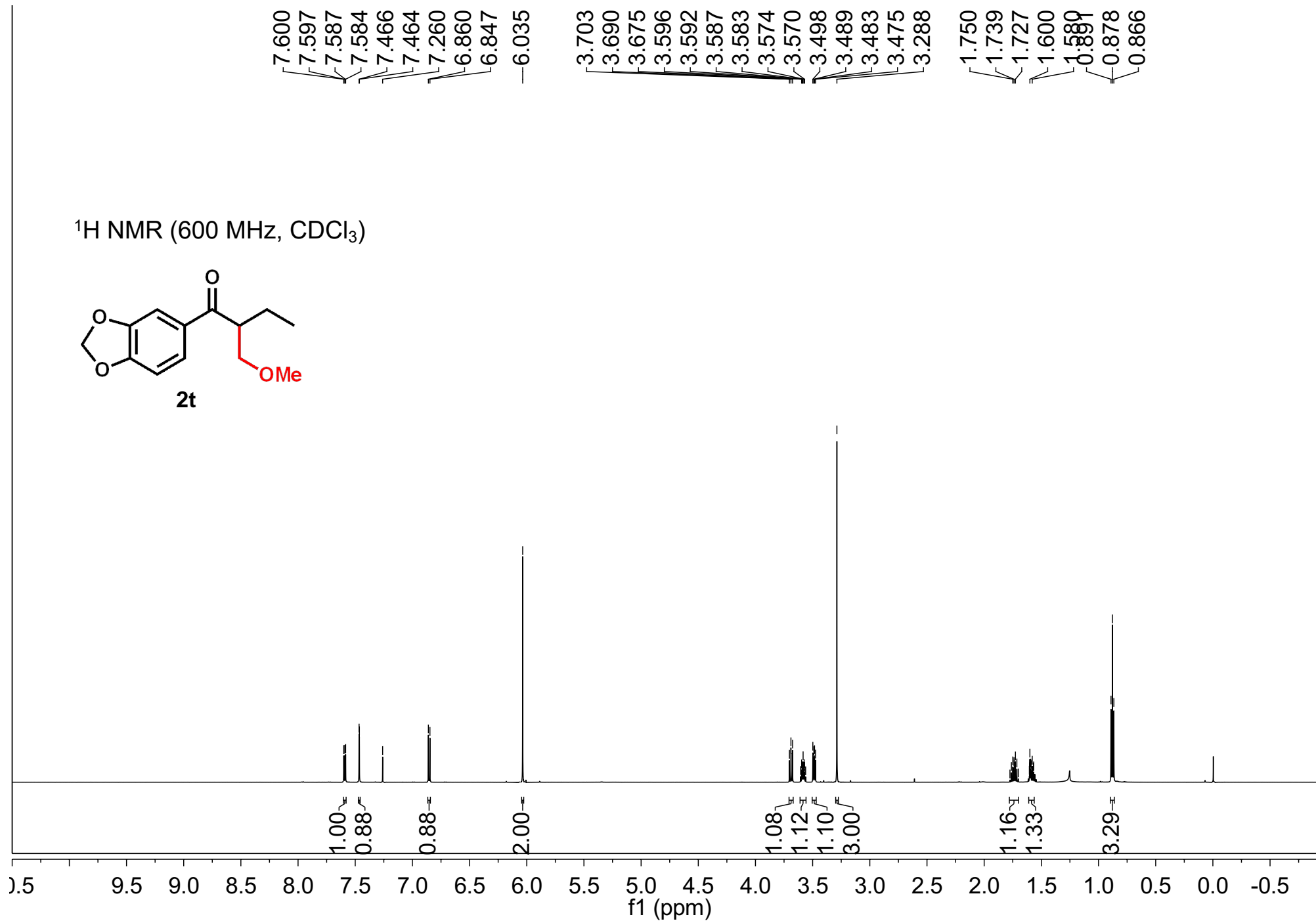
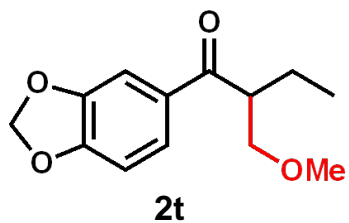
20

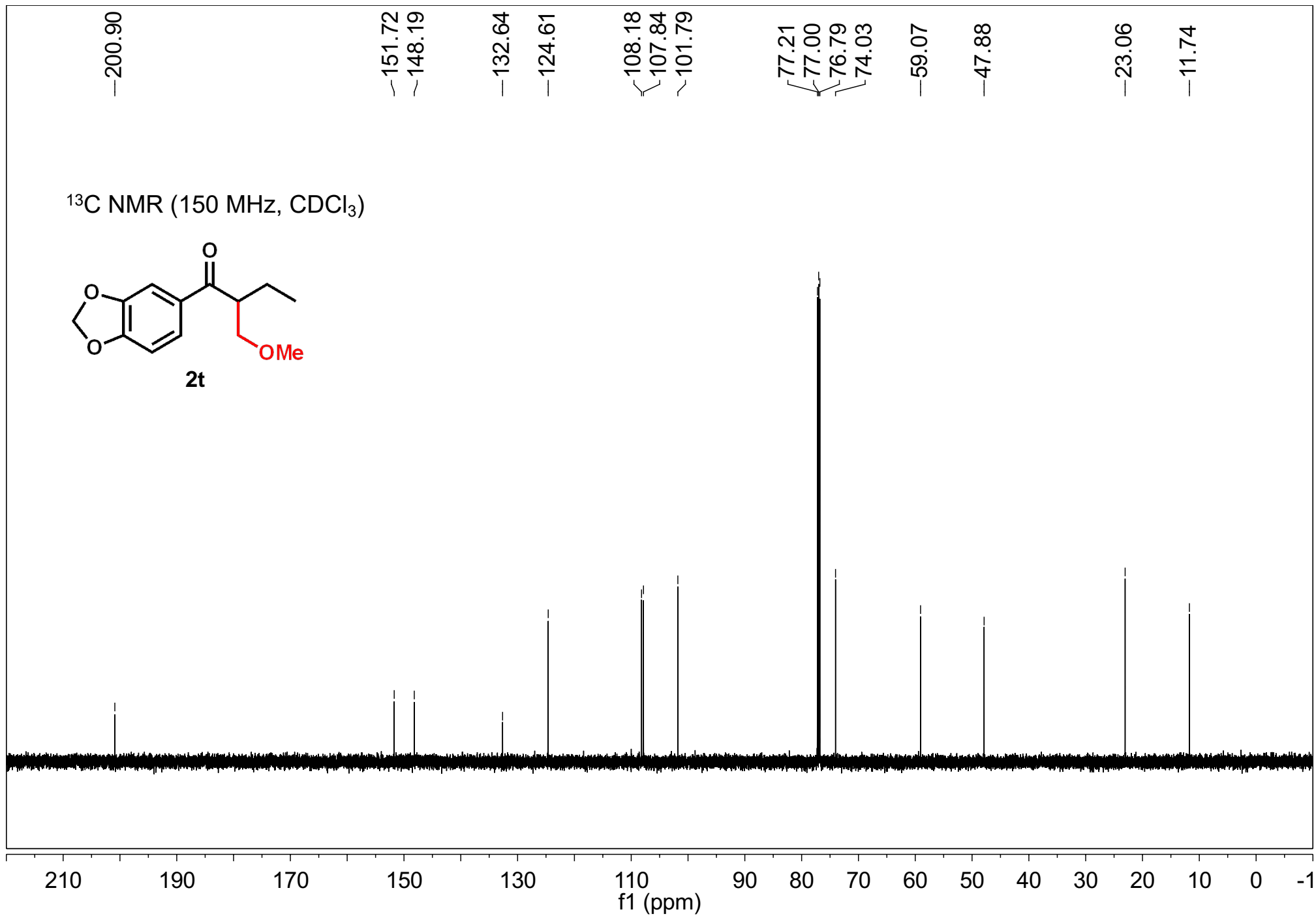
10

0

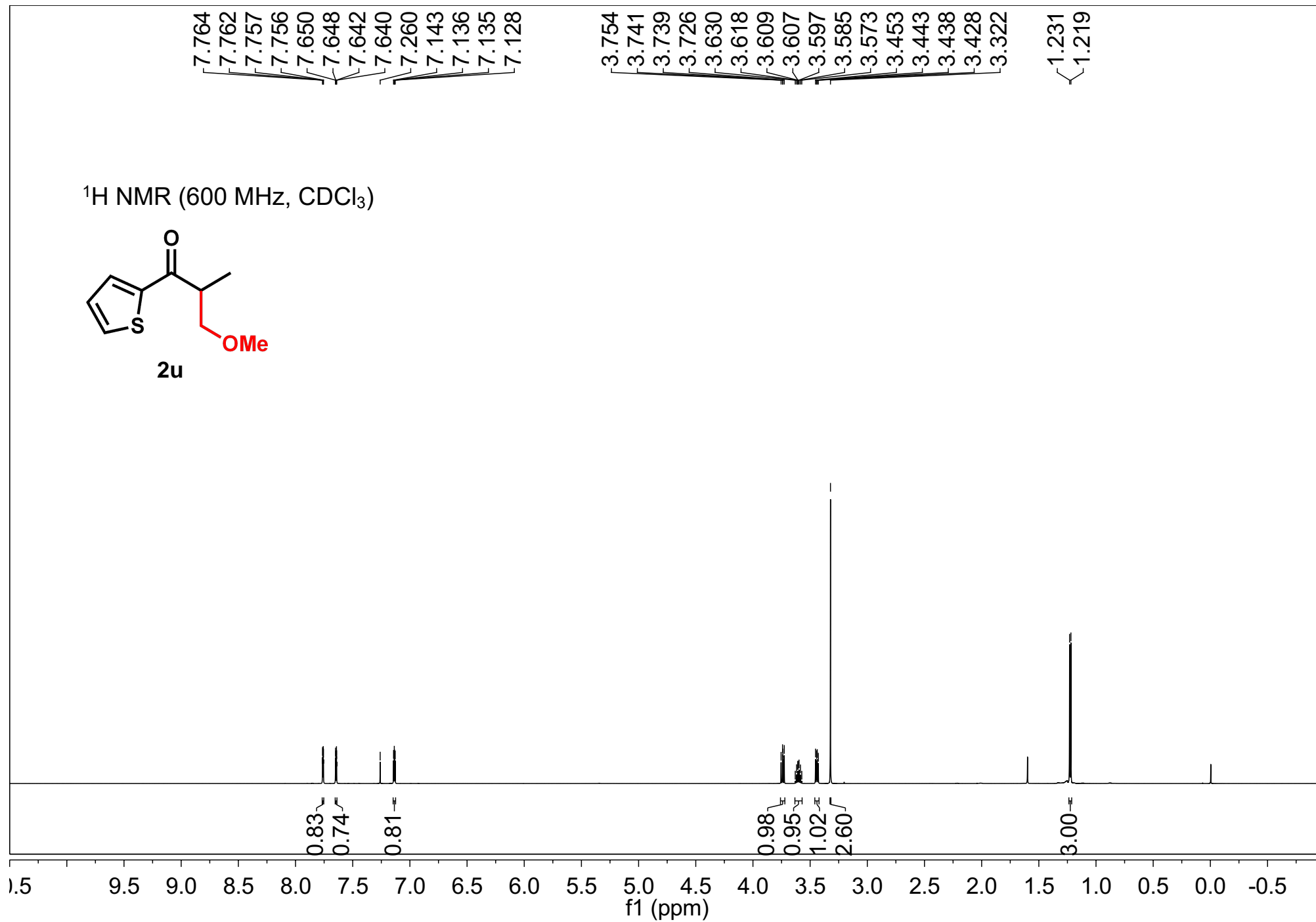
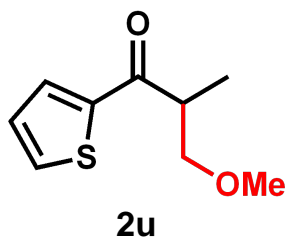
f1 (ppm)

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)

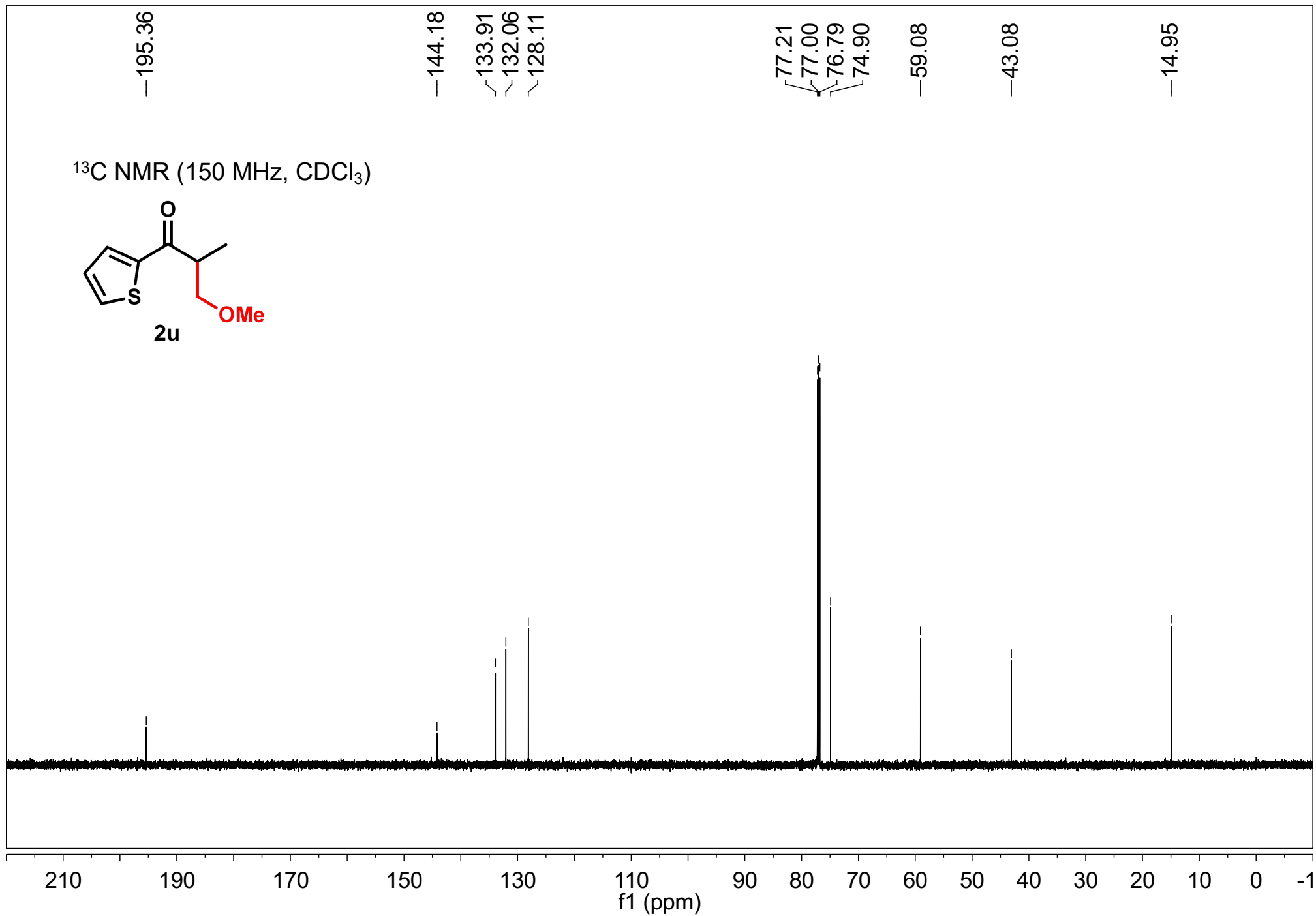
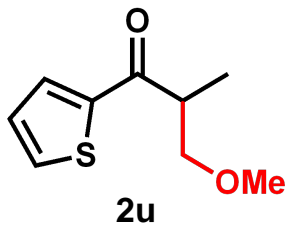




<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)



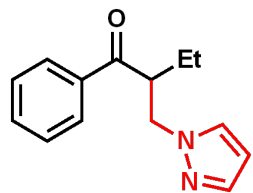
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



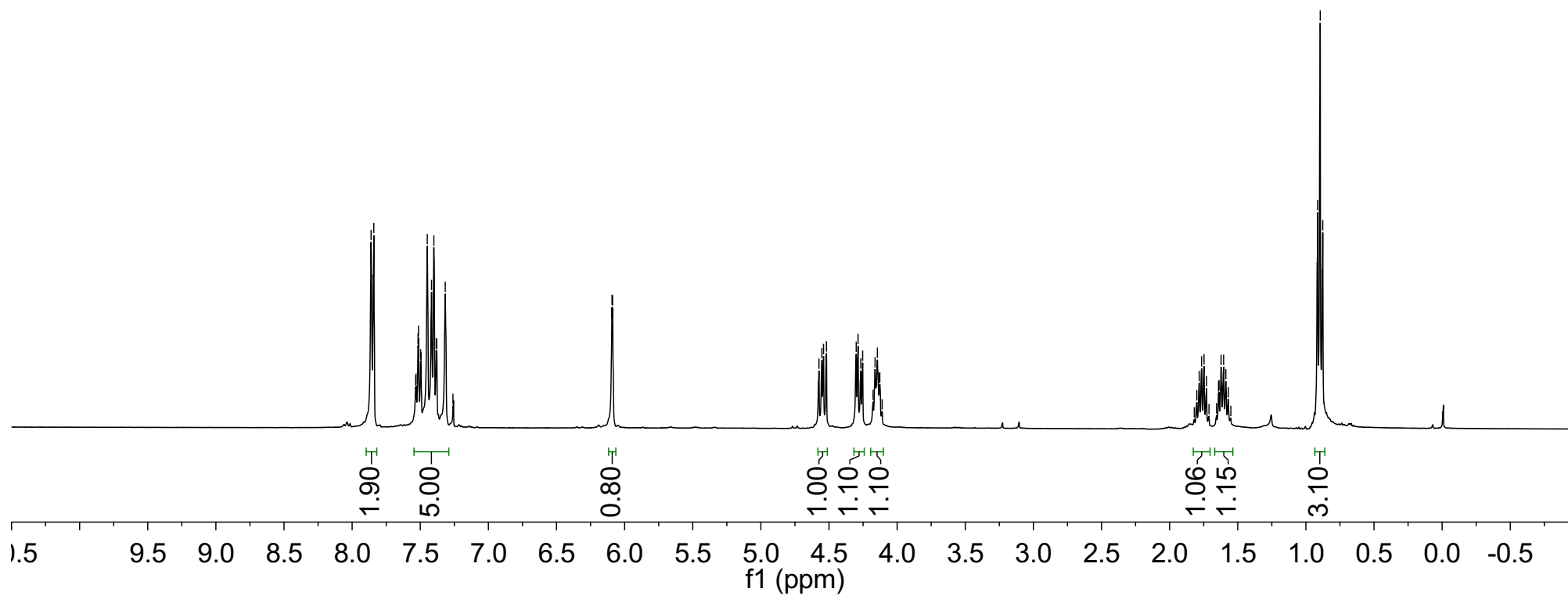


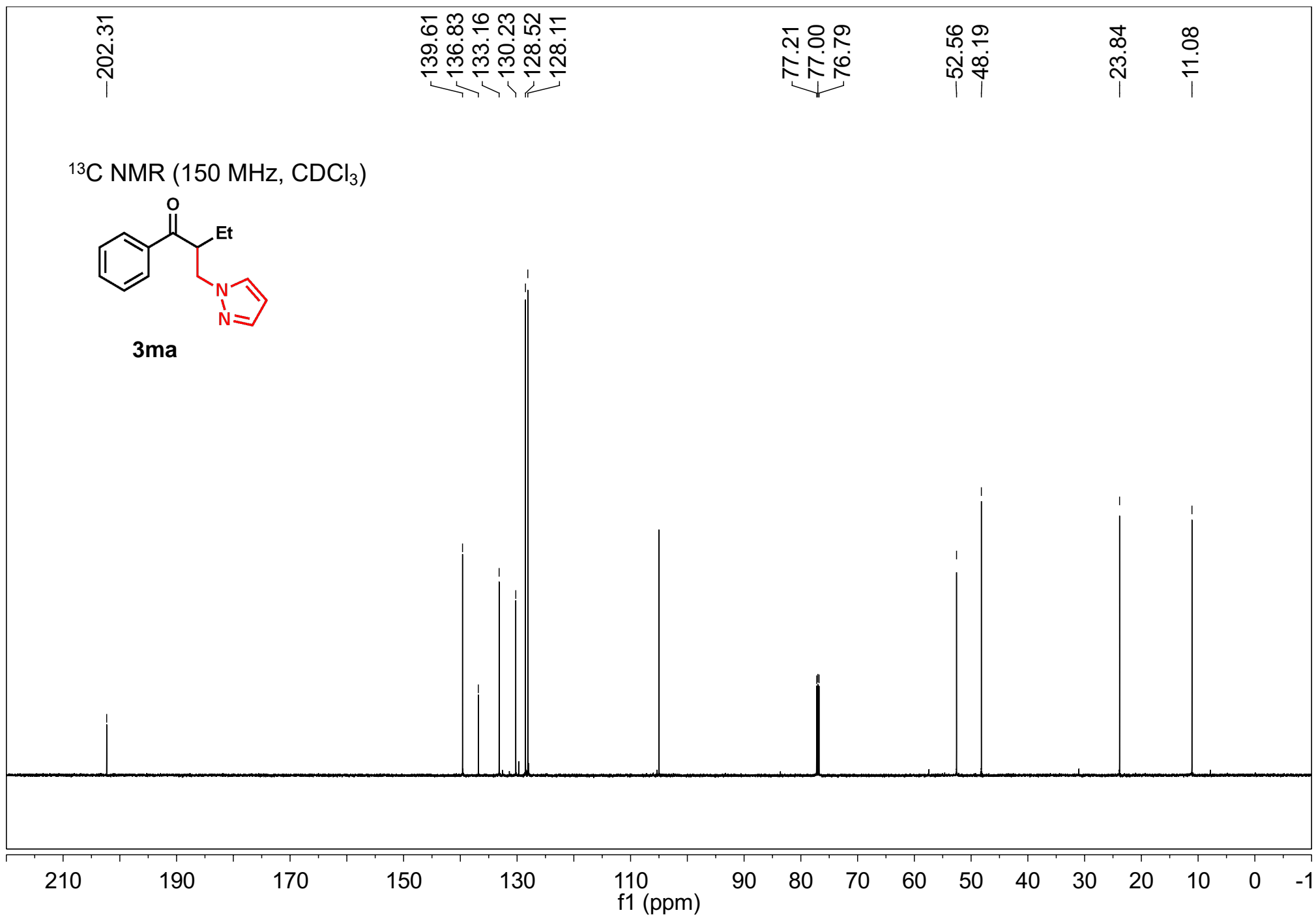
7.861 7.841 7.534 7.531 7.516 7.513 7.497 7.494 7.449 7.417 7.400 7.382 7.379 7.317 7.260 6.093 6.088 4.574 4.552 4.540 4.519 4.300 4.287 4.267 4.253 4.162 4.145 4.130 4.127 1.783 1.766 1.748 1.729 1.622 1.604 1.588 1.573 0.895 0.876

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



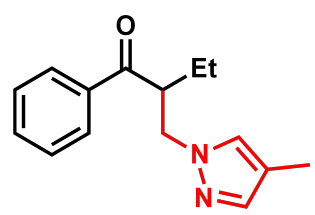
**3ma**



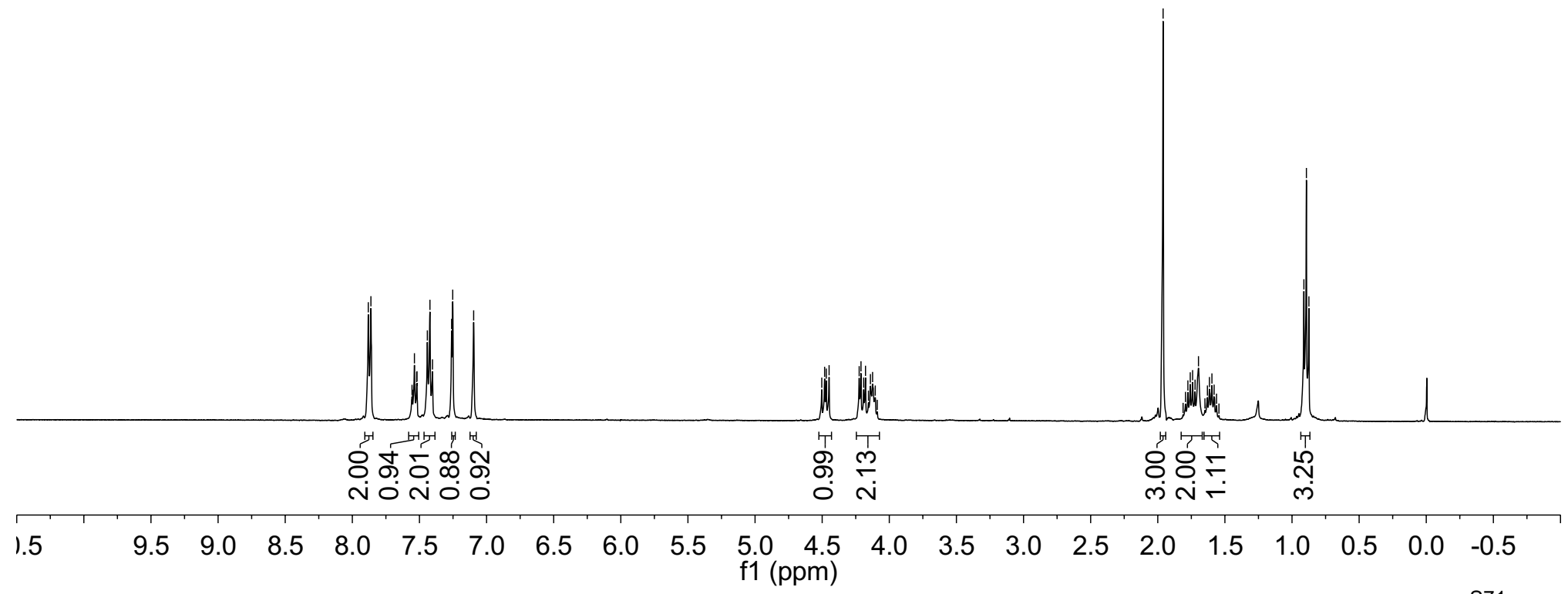


7.881  
7.862  
7.555  
7.552  
7.537  
7.521  
7.519  
7.441  
7.422  
7.403  
7.260  
7.252  
7.096  
4.503  
4.482  
4.469  
4.448  
4.224  
4.211  
4.191  
4.177  
4.155  
4.140  
4.124  
4.105  
4.090  
1.960  
1.758  
1.741  
1.722  
1.697  
1.615  
1.597  
0.912  
0.893  
0.874

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



**3mb**



-202.54

140.06  
136.95  
133.21  
129.19  
128.59  
128.22  
-115.51

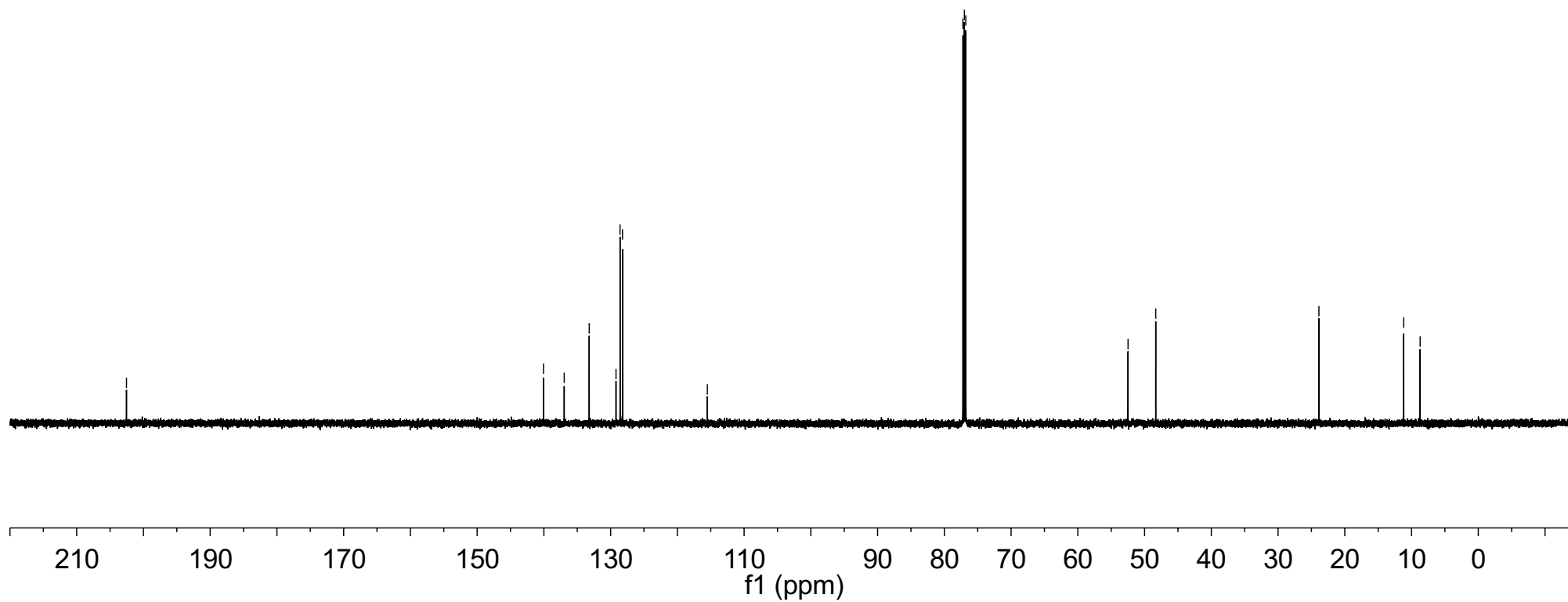
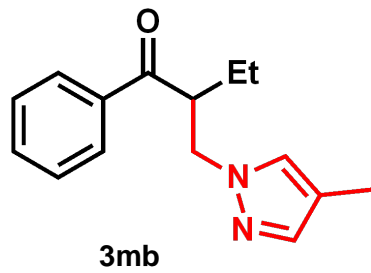
77.21  
77.00  
76.79

-52.47  
-48.32

-23.88

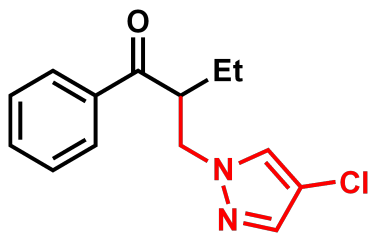
11.17  
8.71

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)

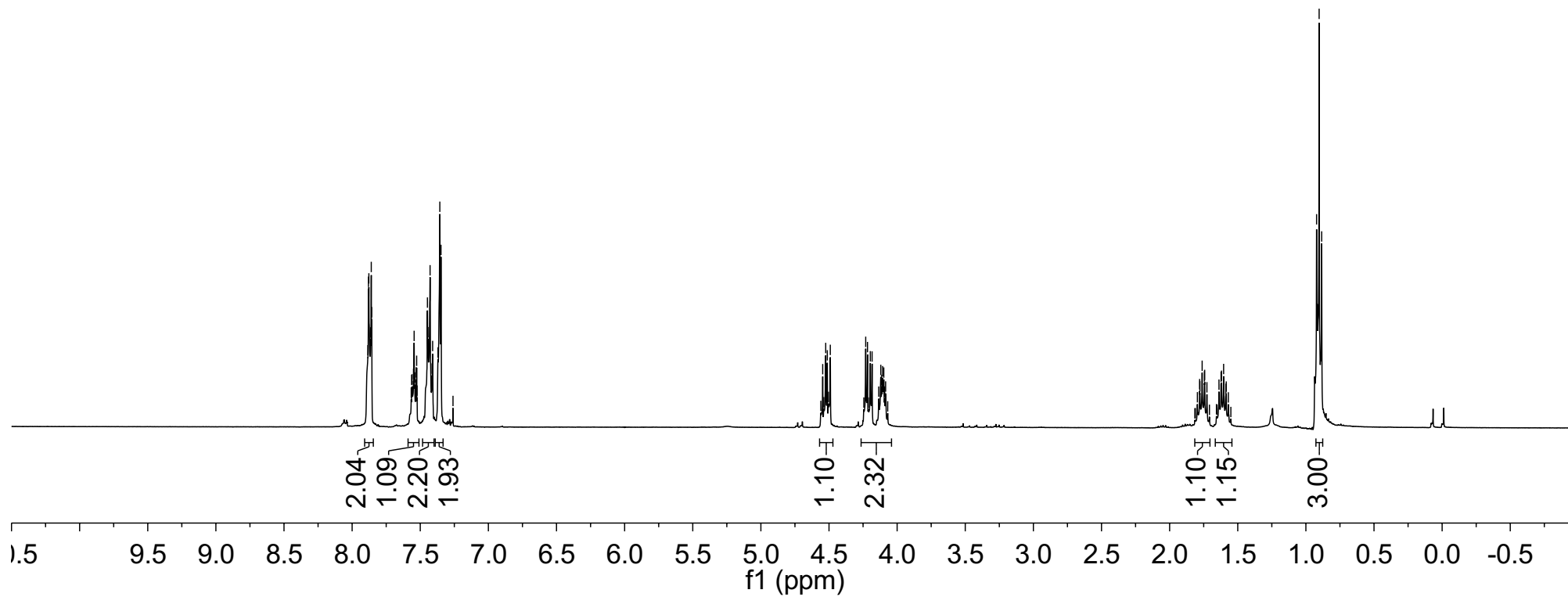


7.885  
7.880  
7.877  
7.864  
7.860  
7.856  
7.563  
7.560  
7.550  
7.545  
7.540  
7.530  
7.526  
7.523  
7.447  
7.443  
7.428  
7.413  
7.409  
7.370  
7.356  
7.348  
4.546  
4.524  
4.512  
4.490  
4.231  
4.218  
4.197  
4.184  
4.120  
4.113  
4.106  
4.098  
4.084  
1.780  
1.778  
1.761  
1.745  
1.743  
1.726  
1.638  
1.623  
1.619  
1.604  
1.588  
1.585  
0.921  
0.903  
0.884

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



3mc



-201.75

138.00  
136.56  
133.40  
128.67  
128.37  
128.19

-109.37

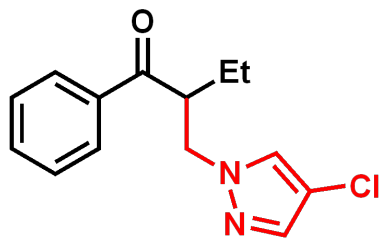
77.21  
77.00  
76.79

-52.96  
-47.91

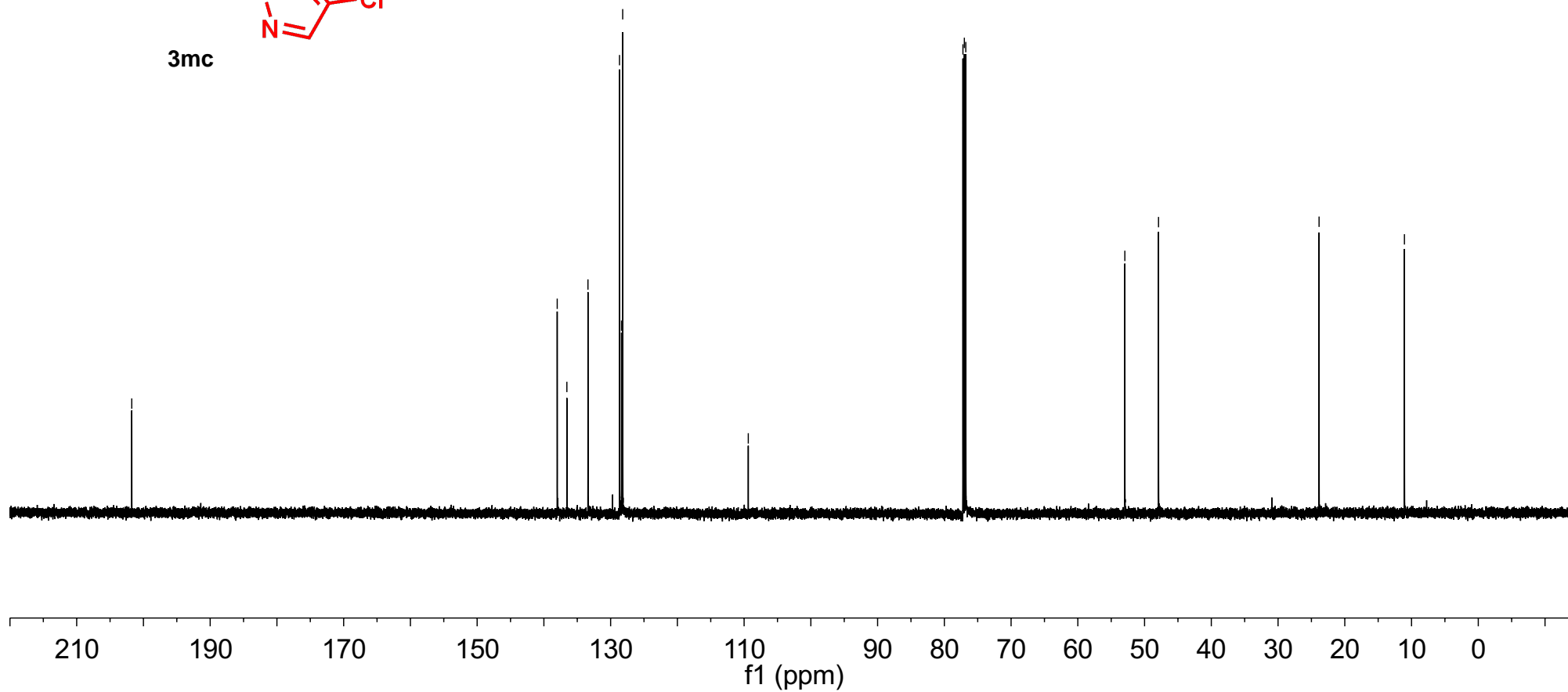
-23.85

-11.06

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )

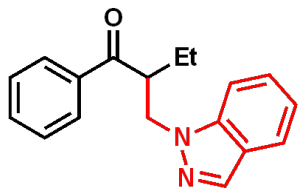


3mc

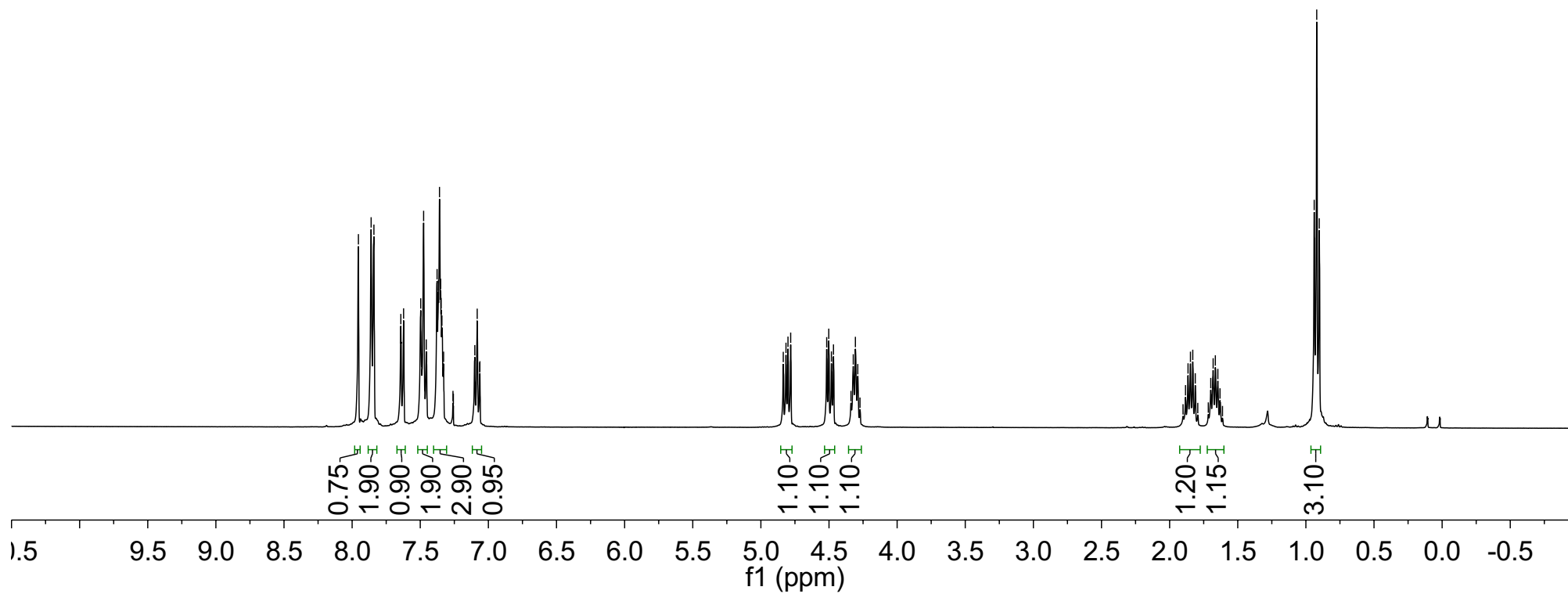


7.954  
7.860  
7.840  
7.642  
7.622  
7.497  
7.490  
7.475  
7.456  
7.453  
7.377  
7.367  
7.359  
7.350  
7.347  
7.341  
7.329  
7.260  
7.257  
7.100  
7.082  
7.064  
7.062  
4.836  
4.816  
4.801  
4.781  
4.517  
4.502  
4.482  
4.467  
4.339  
4.322  
4.306  
4.289  
4.272  
1.883  
1.865  
1.847  
1.830  
1.812  
1.716  
1.698  
1.681  
1.664  
1.646  
1.630  
0.939  
0.920  
0.902

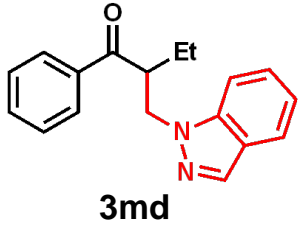
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



3md



<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)



—202.39

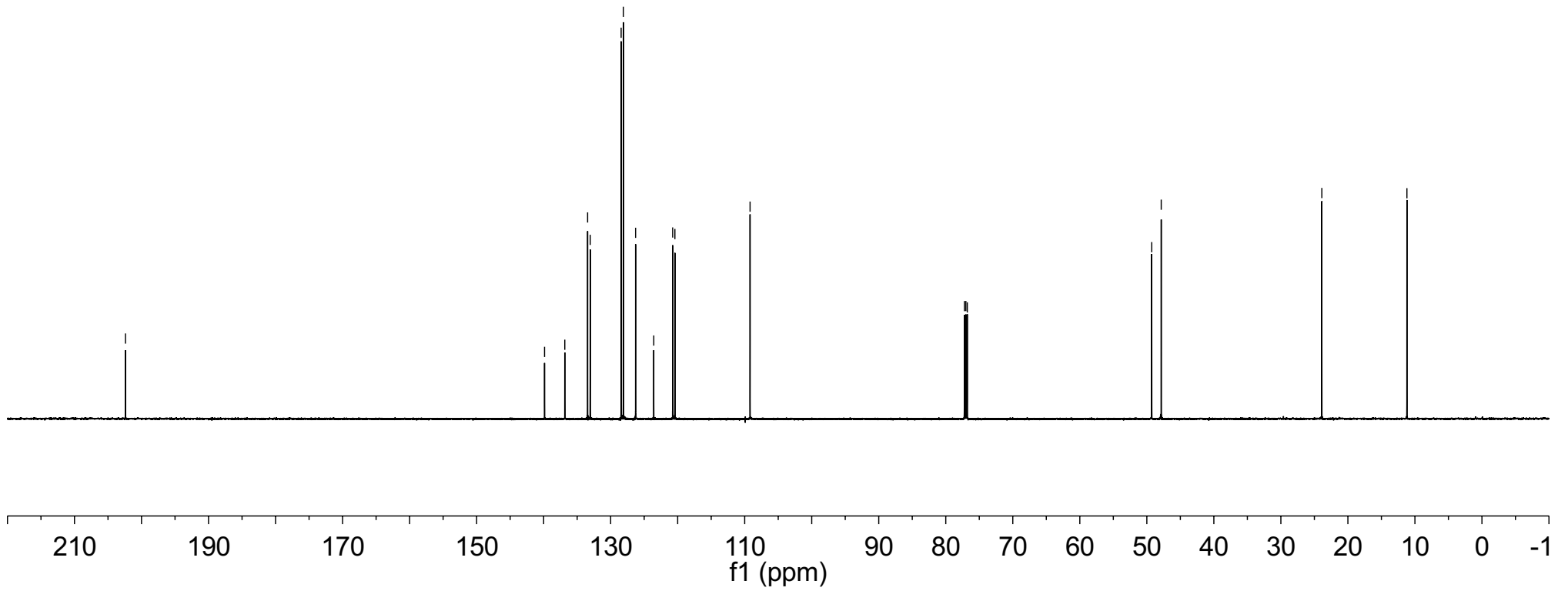
139.86  
136.84  
133.44  
133.05  
128.44  
128.11  
126.28  
123.57  
120.75  
120.42  
—109.20

77.21  
77.00  
76.79

49.27  
47.85

—23.89

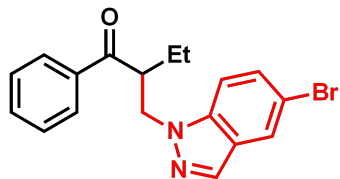
—11.19



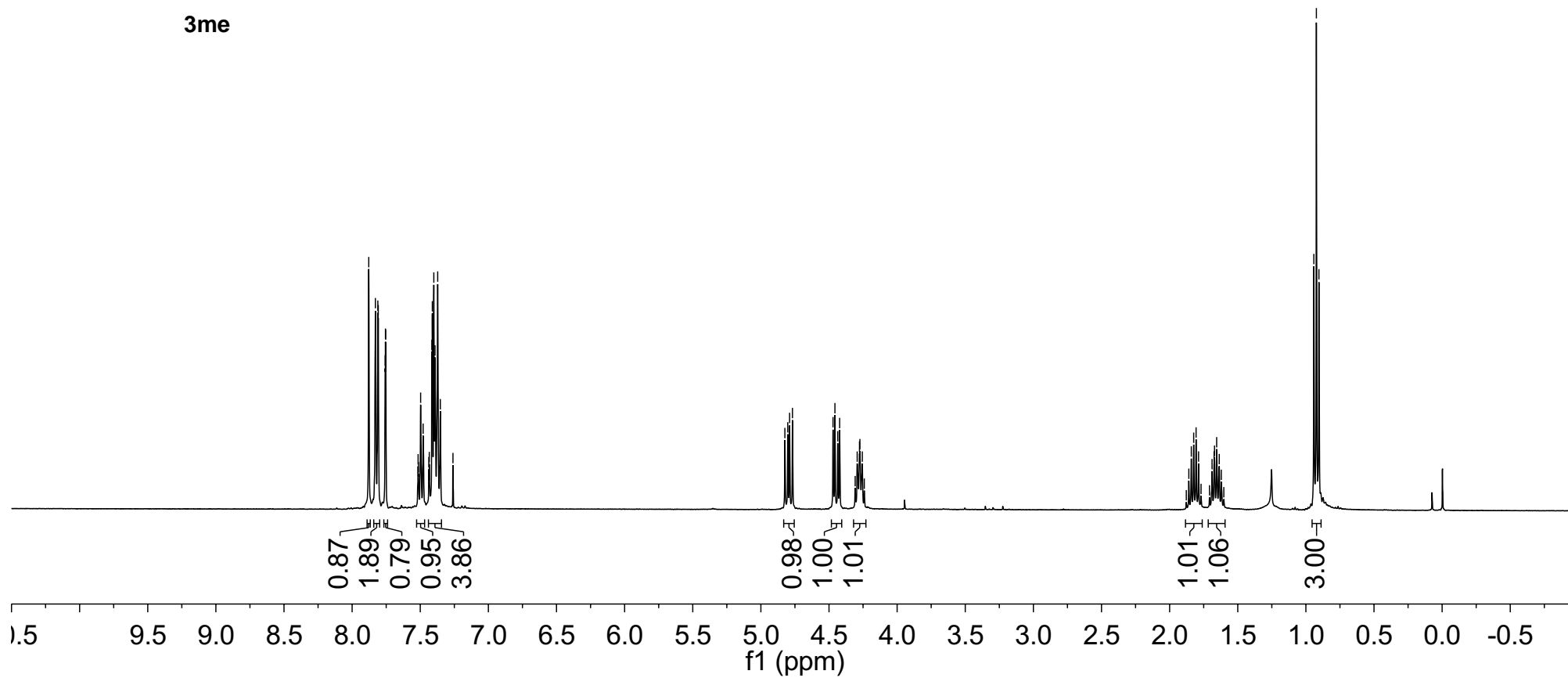


7.878  
7.829  
7.811  
7.808  
7.757  
7.755  
7.754  
7.516  
7.513  
7.497  
7.479  
7.476  
7.437  
7.434  
7.415  
7.411  
7.400  
7.392  
7.372  
7.353  
7.260  
4.824  
4.803  
4.789  
4.768  
4.470  
4.456  
4.436  
4.422  
4.308  
4.293  
4.276  
4.273  
4.256  
4.241  
1.859  
1.841  
1.823  
1.806  
1.788  
1.769  
1.689  
1.674  
1.670  
1.655  
1.636  
1.621  
0.942  
0.923  
0.904

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



3me



-202.30

138.62  
136.73  
133.25  
132.76  
129.47  
128.55  
128.14  
125.04  
123.17  
113.60  
110.88

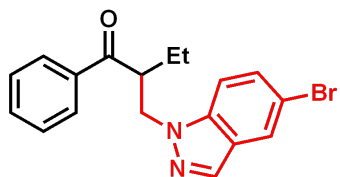
77.21  
77.00  
76.79

49.49  
47.83

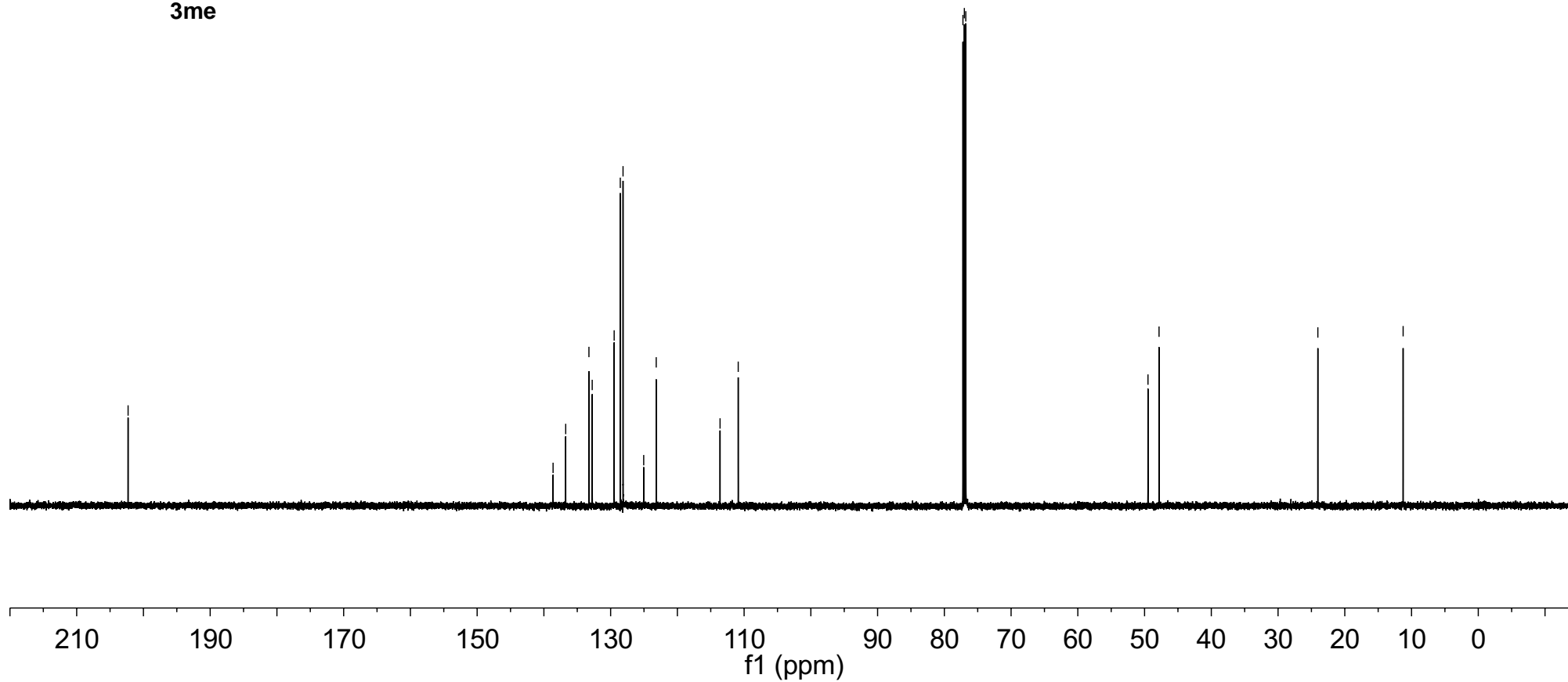
-24.04

-11.26

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)

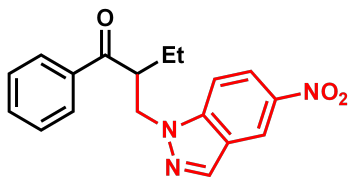


3me

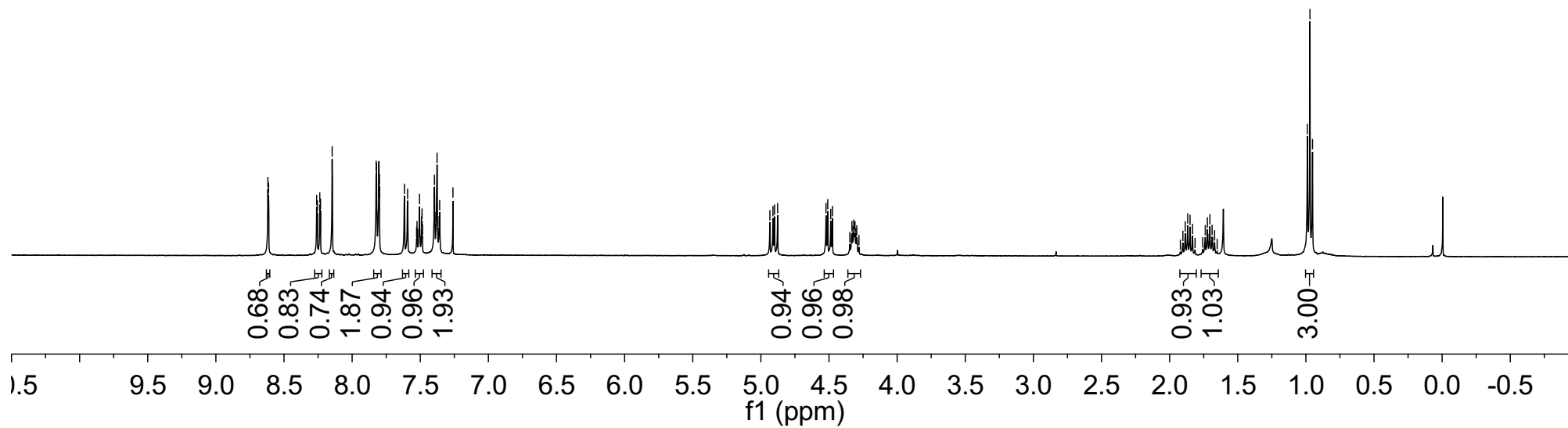


8.618  
8.613  
8.260  
8.255  
8.237  
8.232  
8.147  
7.824  
7.821  
7.800  
7.616  
7.593  
7.527  
7.524  
7.521  
7.506  
7.490  
7.487  
7.484  
7.396  
7.392  
7.377  
7.361  
7.357  
7.260  
4.934  
4.911  
4.900  
4.877  
4.522  
4.509  
4.487  
4.475  
4.332  
4.324  
4.318  
4.309  
4.303  
4.296  
1.886  
1.867  
1.850  
1.832  
1.738  
1.723  
1.704  
1.688  
0.989  
0.970  
0.951

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



**3mf**



-201.94

142.30  
141.64  
136.49  
136.29  
133.45  
128.64  
128.14  
122.62  
121.53  
118.67  
109.92

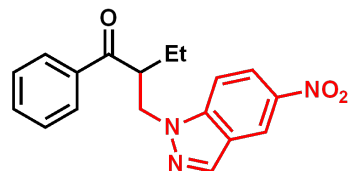
77.21  
77.00  
76.79

49.71  
47.66

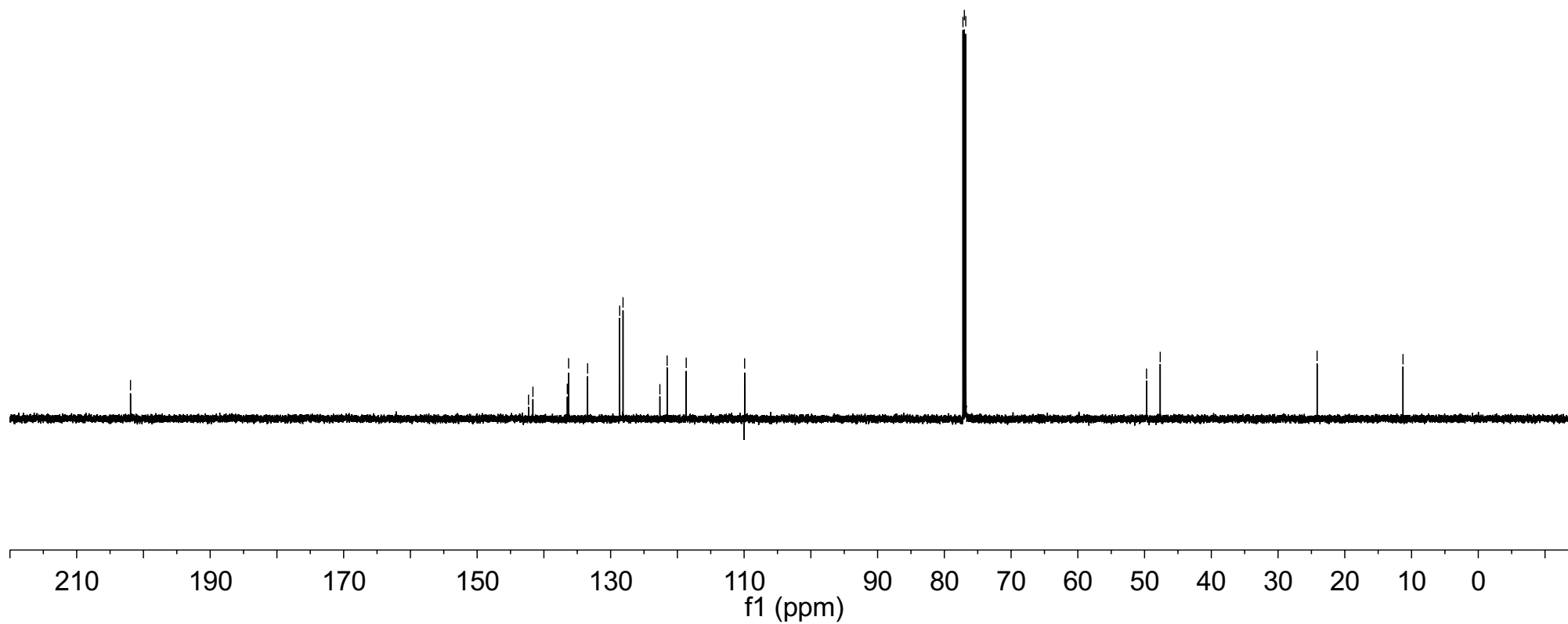
-24.15

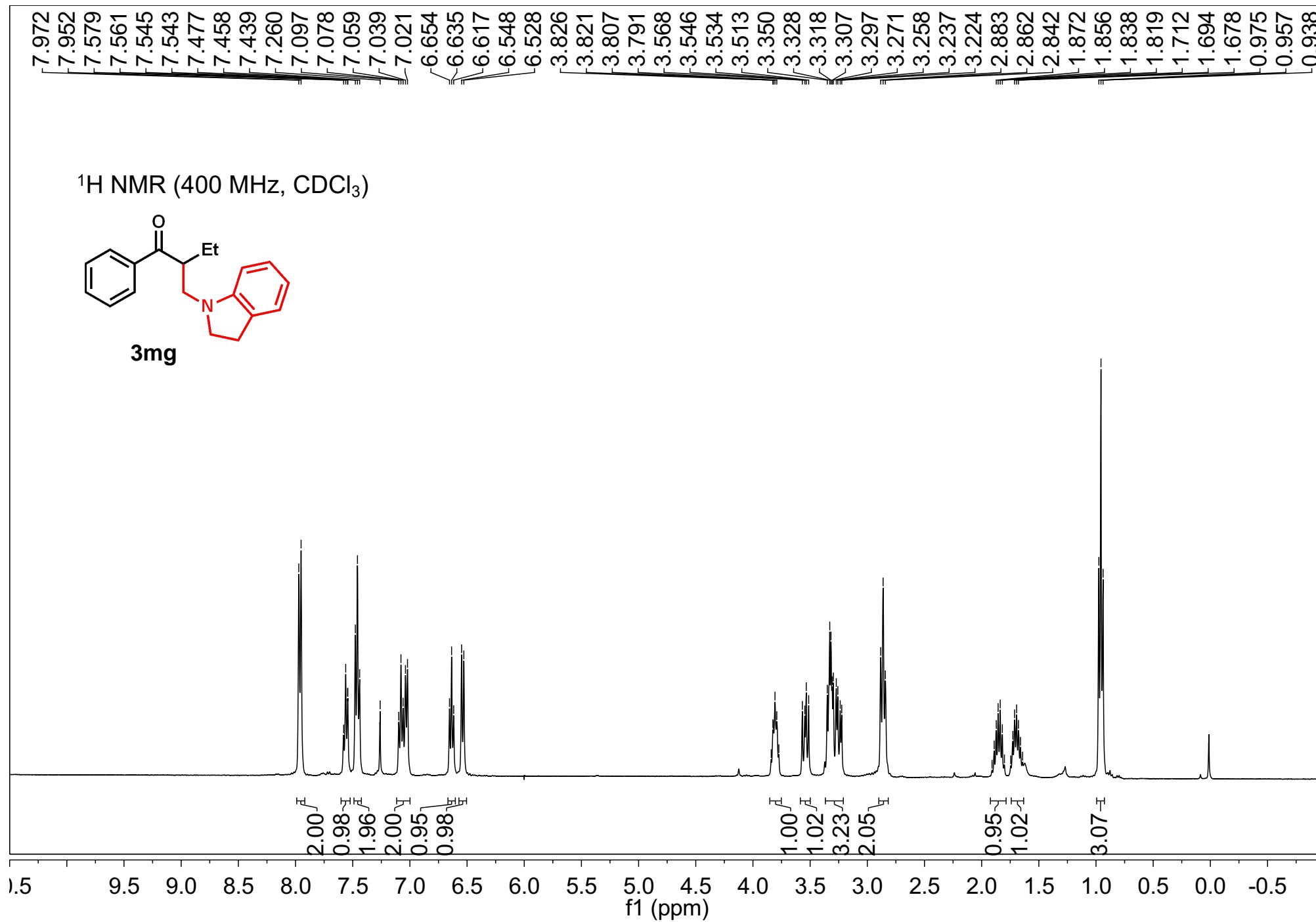
-11.28

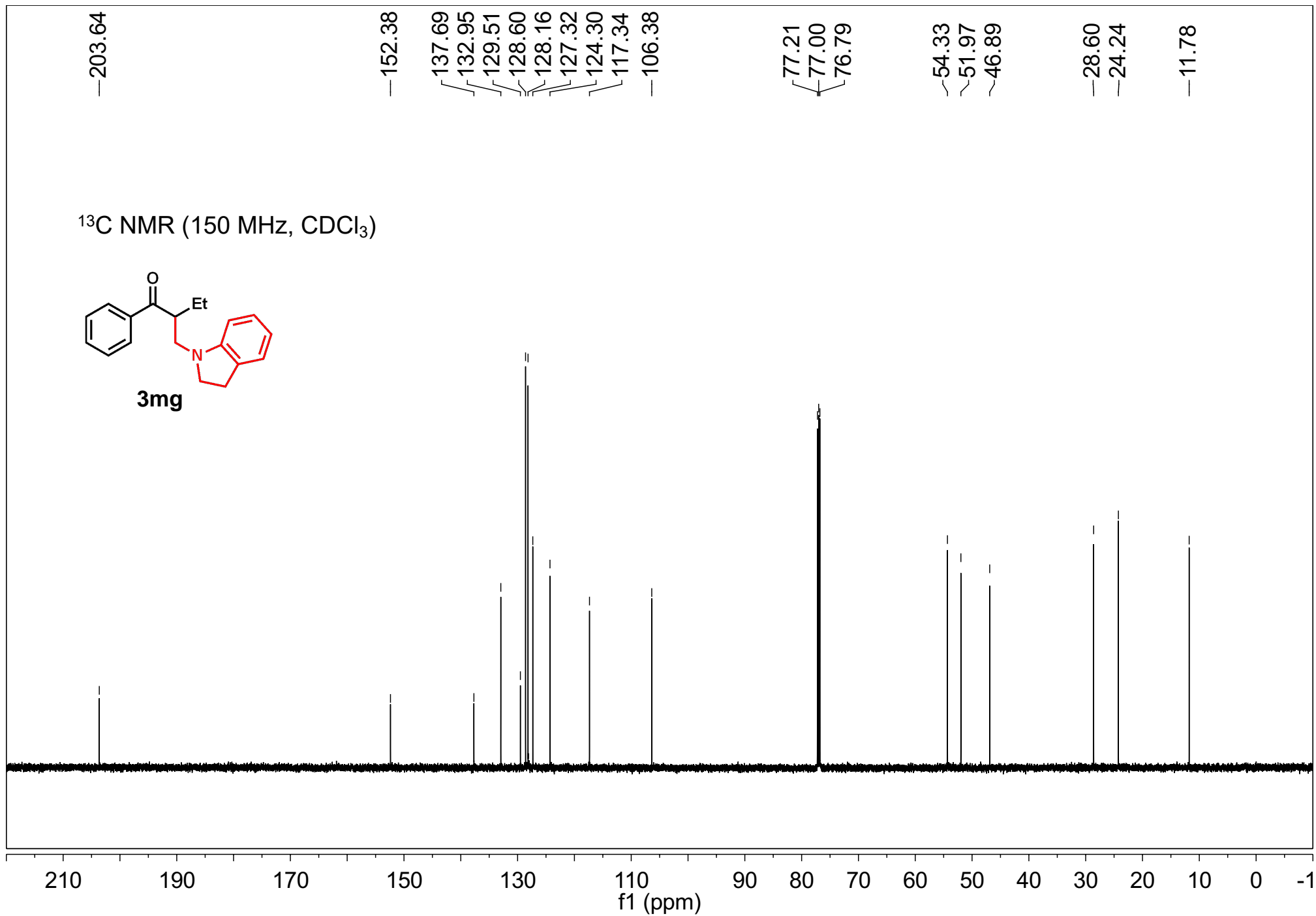
$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )

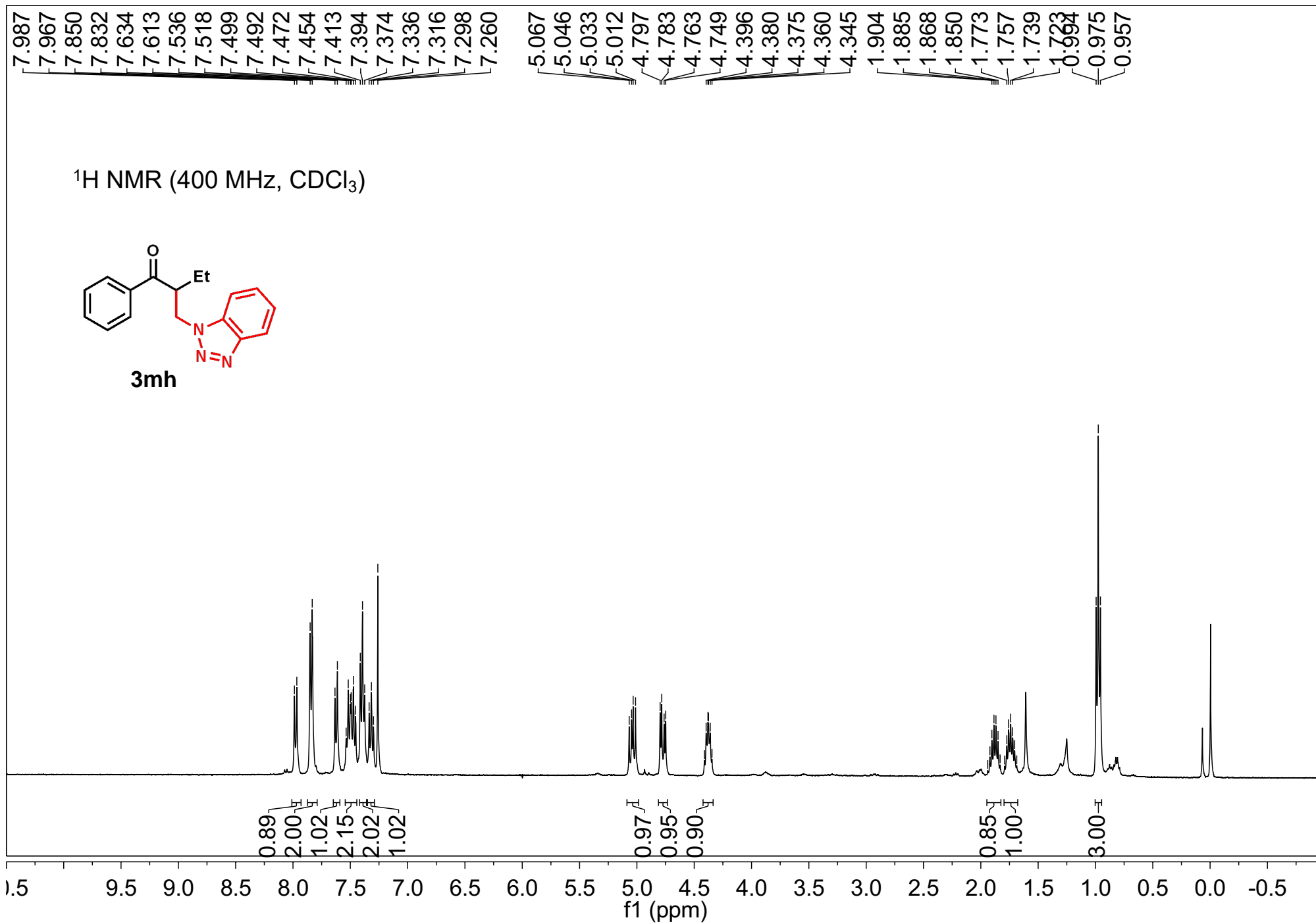


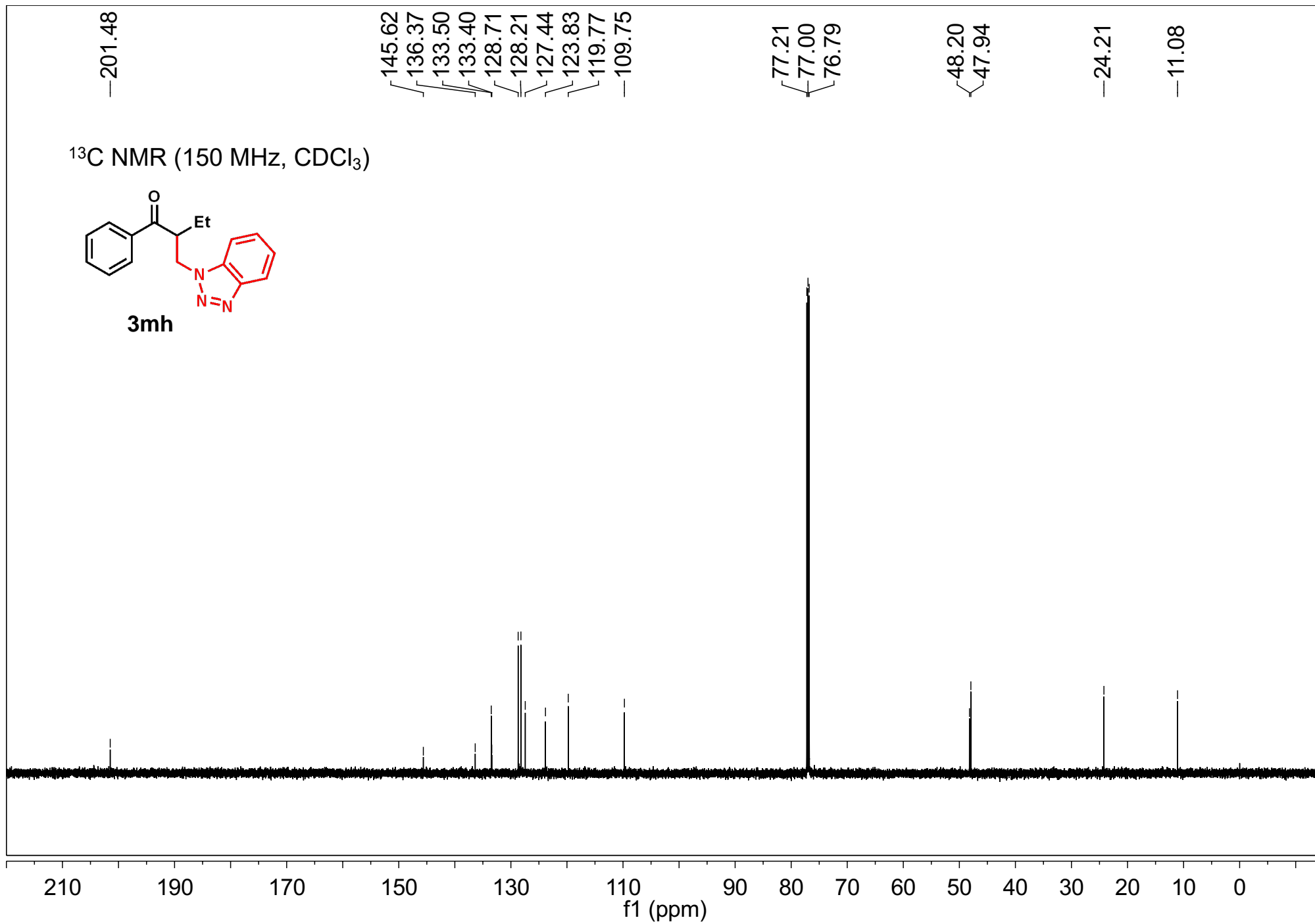
**3mf**







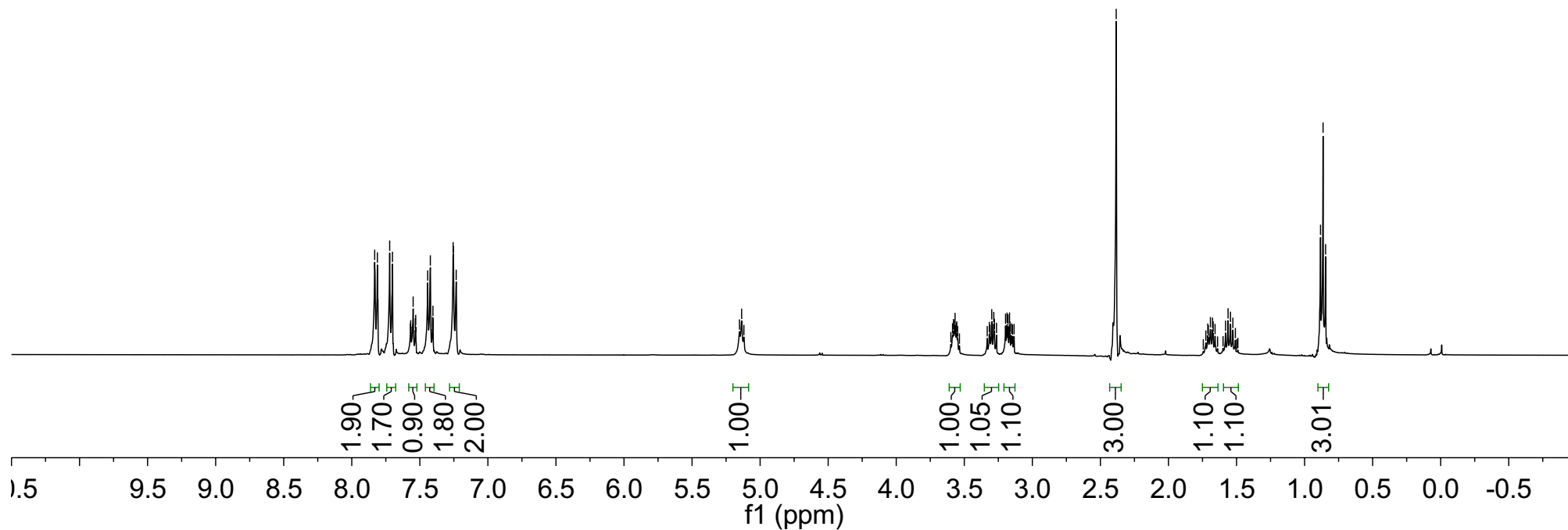
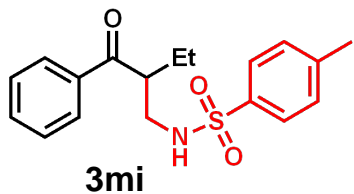






7.832  
7.812  
7.722  
7.701  
7.570  
7.567  
7.549  
7.533  
7.530  
7.442  
7.423  
7.407  
7.404  
7.255  
7.253  
7.233  
5.152  
5.136  
3.586  
3.580  
3.573  
3.568  
3.560  
3.555  
3.316  
3.298  
3.283  
3.279  
3.263  
3.197  
3.186  
3.179  
3.168  
3.164  
3.153  
3.146  
3.134  
2.384  
1.711  
1.692  
1.676  
1.672  
1.658  
1.581  
1.562  
1.544  
1.527  
0.883  
0.864  
0.846

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



-202.97

143.23  
137.09  
136.14  
133.38  
129.66  
128.63  
128.26  
126.90

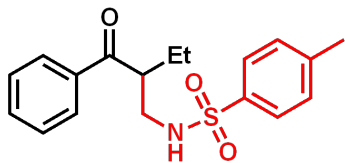
77.21  
77.00  
76.79

47.50  
43.04

23.46  
21.42

-11.20

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )



**3mi**

