

## Supporting Information

# Synthesis of Carbonylated Heteroaromatic Compounds via Visible-Light-Driven Intramolecular Decarboxylative Cyclization of *o*-Alkynylated Carboxylic Acids

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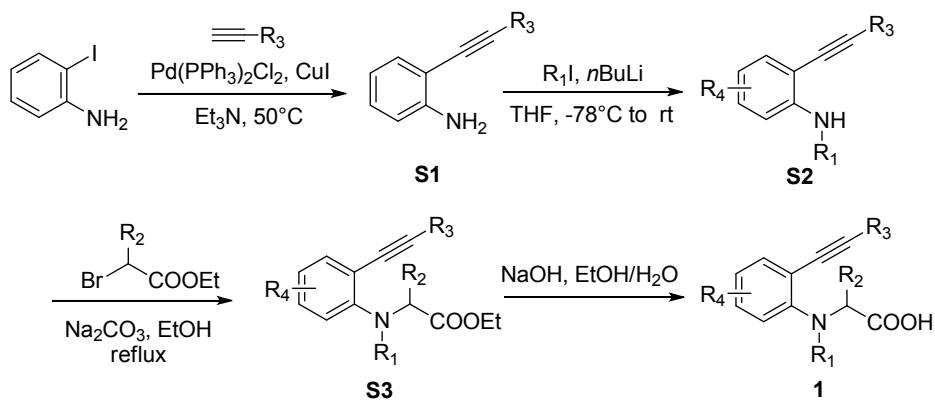
## 1. General Information

All starting materials were purchased from commercial sources without further purification. Glassware was dried in oven and cooled before use. All reactions were monitored by TLC and visualized by UV lamp (254nm). The solvents were distilled from the appropriate drying reagents. Yields generally referred to chromatographically isolated yields, unless otherwise noted.

<sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were obtained on Bruker AV-400 instrument in CDCl<sub>3</sub> or DMSO-d<sub>6</sub>. For <sup>1</sup>H NMR (400MHz), CDCl<sub>3</sub> ( $\delta$  = 7.26 ppm) and DMSO-d<sub>6</sub> ( $\delta$  = 2.5 ppm) served as internal standard and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet), coupling constant (in Hz), and integration. HRMS (ESI) spectra were recorded on a Bruker Esquire LC mass spectrometer using electrospray ionization. GC-MS analysis was performed on a 7890A-5975C/Agilent. Flash column chromatography was performed using 200-300 mesh silica gel.

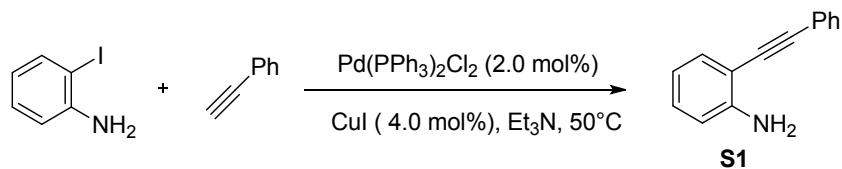
## 2. Typical Procedures for Preparation of Substrates

### 2.1 Synthesis of *o*-alkynylated $\alpha$ -amino acids 1



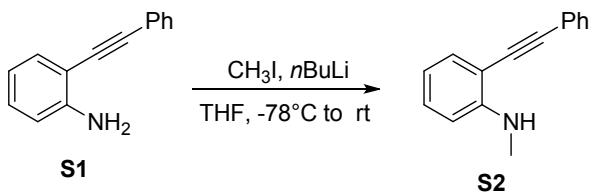
For substrates **1a-1c**, **1e-1r** were synthesized according to the procedure described in the literature.<sup>1</sup> Synthesis of **1a** is representative.

#### Synthesis of S1



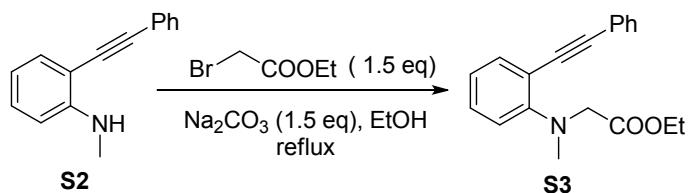
To a stirred solution of 2-iodoaniline (1.0 equiv), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 equiv), and CuI (0.04 equiv) at room temperature in degassed Et<sub>3</sub>N (0.2 M) was added dropwise phenylacetylene (1.5 equiv). The mixture was heated to 50 °C for 5-8 h. When the consumption of the corresponding 2-iodoaniline completed (monitored by TLC), the reaction was cooled to room temperature. Subsequent filtration through a pad of celite rinsing with ethyl acetate, followed by purification of the remaining crude material via flash chromatography afforded the compound S1.

#### Synthesis of S2



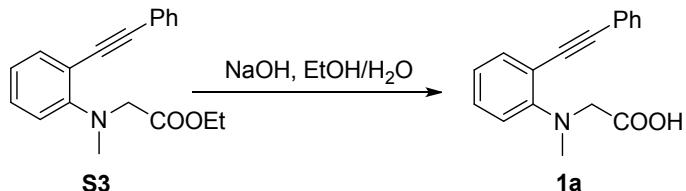
Compound **S1** (1.0 equiv) was dissolved in THF (0.2 M) under N<sub>2</sub> atmosphere and cooled to -78 °C. nBuLi solution (2.5 M in hexanes, 1.1 equiv) was added dropwise and the mixture was stirred for 1 h. CH<sub>3</sub>I (1.5 equiv) was added and the mixture was stirred at room temperature for 2 h. Upon reaction completion, the reaction was carefully quenched by dropwise addition of NH<sub>4</sub>Cl aq. solution at 0 °C. Then the solution was added to saturated NaHCO<sub>3</sub> aq. solution and extracted with EtOAc (3 x). The combined organic phases were dried with MgSO<sub>4</sub>, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography using the indicated eluent.

#### Synthesis of S3



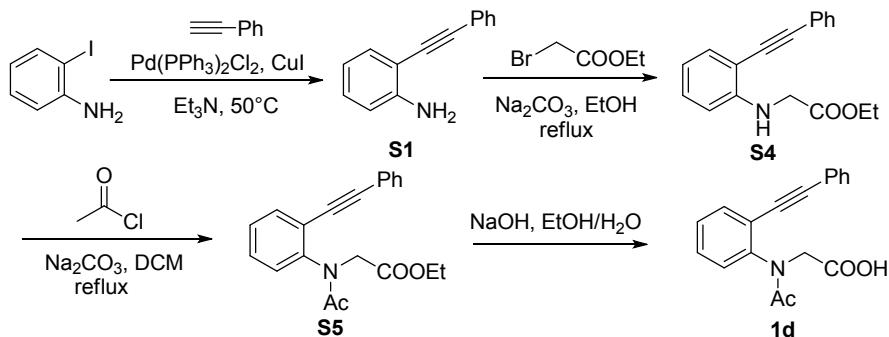
To a solution of **S2** (1.0 equiv) in ethanol (0.5 M) was added Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) and ethyl bromoacetate (1.5 equiv). Then the suspension was stirred at reflux for 14 h. Upon reaction completion, the reaction was quenched with water and extracted with ethyl acetate (4 x). The combined organics were washed with water (1 x), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The crude material was purified by flash chromatography using the indicated eluent.

#### Synthesis of 1a



To a solution of **S3** (1.0 equiv) in EtOH (0.2 M) at 0°C was slowly added a 15% m/v NaOH<sub>(aq)</sub> solution (5.0 equiv). The reaction mixture was allowed to room temperature overnight with stirring. Ethanol and water was removed *in vacuo* and the residue redissolved in the minimal amount of H<sub>2</sub>O possible. Concentrated hydrochloric acid was added dropwise until the pH was acidic. The solid formed was filtered off and washed with cold H<sub>2</sub>O (5 mL). The solid was dried under high vacuum and pure **1a** was obtained.

#### 2.2 Synthesis of N-acetyl-N-(2-(phenylethynyl)phenyl)glycine **1d**



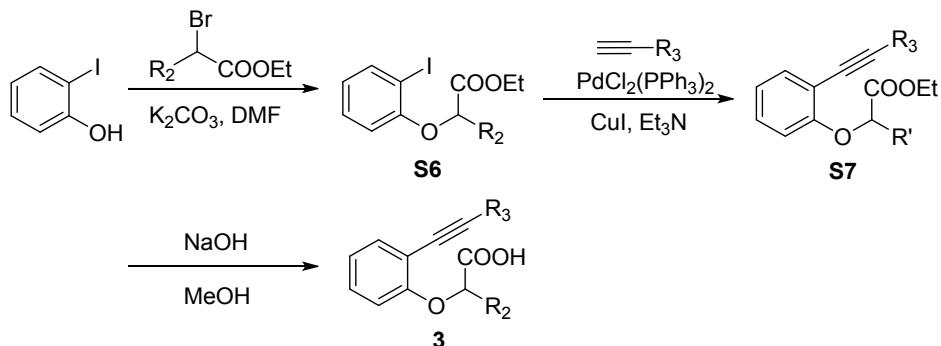
**Step 1:** To a stirred solution of 2-iodoaniline (1.0 equiv), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.02 equiv), and CuI (0.04 equiv) at room temperature in degassed Et<sub>3</sub>N (0.2 M) was added dropwise phenylacetylene (1.5 equiv). The mixture was heated to 50 °C for 5-8 h. When the consumption of the corresponding 2-iodoaniline completed (monitored by TLC), the reaction was cooled to room temperature. Subsequent filtration through a pad of celite rinsing with ethyl acetate, followed by purification of the remaining crude material via flash chromatography afforded the compound **S1**.

**Step 2:** To a solution of **S1** (1.0 equiv) in ethanol (0.5 M) was added Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) and ethyl bromoacetate (1.5 equiv). Then the suspension was stirred at reflux for 14 h. The reaction was quenched with water and extracted with ethyl acetate (4 x). The combined organics were washed with water (1 x), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The crude material was purified by flash chromatography using the indicated eluent.

**Step 3:** To a solution of **S4** (1.0 equiv.) in anhydrous dichloromethane, were added Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv.) and acetyl chloride (2.5 equiv.). The mixture was refluxed overnight and cooled to rt. The reaction was quenched with water and extracted with dichloromethane (3 x). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvent was removed *in vacuo*. The crude material was purified by flash chromatography using the indicated eluent.

**Step 4:** To a solution of **S5** (1.0 equiv) in EtOH (0.2 M) at 0°C was slowly added a 15% m/v NaOH<sub>(aq)</sub> solution (5.0 equiv). The reaction mixture was allowed to room temperature overnight with stirring. Ethanol and water was removed *in vacuo* and the residue redissolved in the minimal amount of H<sub>2</sub>O possible. Concentrated hydrochloric acid was added dropwise until the pH was acidic. The solid formed was filtered off and washed with cold H<sub>2</sub>O (5 mL). The solid was dried under high vacuum and pure **1d** was obtained.

### 2.3 Synthesis of *o*-alkynylated phenoxyacetic acids **3**



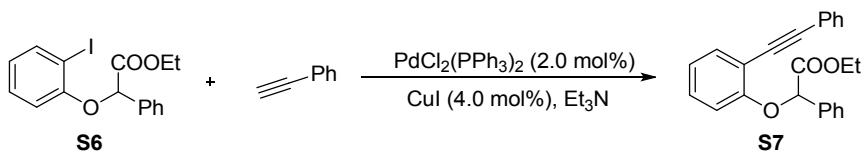
Phenoxyacetic acids **3a-3q** were synthesized according to the procedure described in the literature.<sup>2</sup> Synthesis of **3b** is representative.

#### *Synthesis of S6*



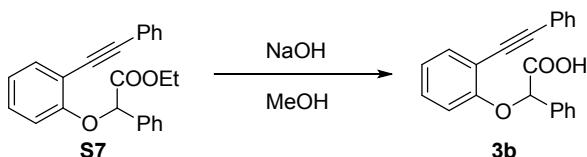
To a 0.3 M solution of 2-iodophenol (1.0 equiv.) in N, N-dimethylformamide (DMF), was added K<sub>2</sub>CO<sub>3</sub> (1.5 equiv.), and the resulting solution was stirred at ambient temperature for 30 min. Then was added ethyl *a*-bromophenylacetate (1.5 equiv) in one portion and the resulting solution was stirred at ambient temperature for 18 h. The solvent was added H<sub>2</sub>O (a volume equivalent to the amount of DMF initially used), and dichloromethane was used to extract (3 x half the volume of DMF initially used). The combined organics were washed with brine (1 x), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated *in vacuo*. The crude material was purified by flash chromatography using the indicated eluent.

### Synthesis of S7



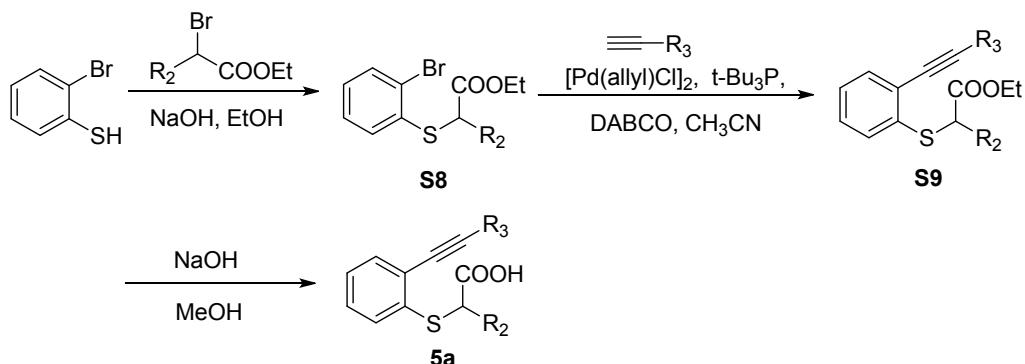
To solution of **S6** (1.0 equiv),  $\text{PdCl}_2(\text{PPh}_3)_2$  (0.02 equiv) and  $\text{CuI}$  (0.04 equiv) in anhydrous  $\text{NEt}_3$  (0.2 M) was added phenylacetylene (1.5 equiv) under  $\text{N}_2$ . The reaction mixture was stirred at ambient temperature. Upon full consumption of the starting material, the reaction mixture was filtered through a pad of celite, eluting with  $\text{EtOAc}$  (3 x). The combined organics were concentrated *in vacuo*. The resulting crude mixture was purified by flash chromatography using the indicated eluent.

### Synthesis of 3b



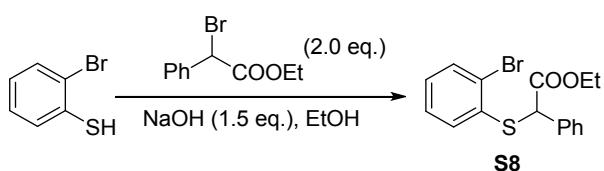
The corresponding ester **S7** (1.0 equiv) was dissolved in methanol. To the resulting 0.5 M solution was added a 15% m/v  $\text{NaOH}_{(\text{aq})}$  solution (5.0 equiv). The reaction mixture was stirred at ambient temperature for 18 h. The solvent was removed *in vacuo* and the residue redissolved in the minimal amount of  $\text{H}_2\text{O}$  possible. Concentrated hydrochloric acid was added drop wise until the pH was acidic. The white solid formed was filtered off and washed with cold  $\text{H}_2\text{O}$  (5 mL). The solid was dried under high vacuum and pure *o*-alkynylated phenoxyacetic acids **3b** was obtained.

## 2.4 Synthesis of *o*-alkynylated carboxylic acids 5



Carboxylic acids **5a-5h** were synthesized according to the procedure described in the literature.<sup>3</sup> Synthesis of **5a** is representative.

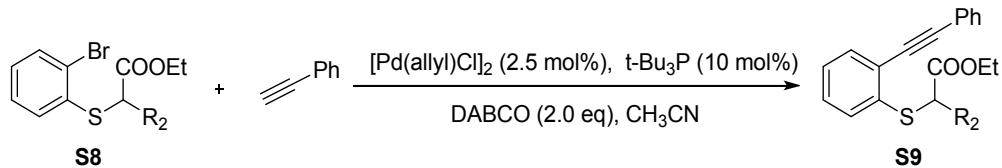
### Synthesis of S8



To a 0.2 M solution of 2-bromothiophenol (1.0 equiv) in  $\text{EtOH}$  was added  $\text{NaOH}$  (1.5 equiv), and the resulting solution was stirred at ambient temperature for 30 min. Then was added ethyl *a*-bromophenylacetate (2.0 equiv) in one portion and the resulting solution was stirred overnight at room temperature. The reaction mixture was filtered through a pad of celite, eluting with  $\text{EtOAc}$  (3 x). The combined organics were concentrated *in vacuo*. The resulting crude mixture was

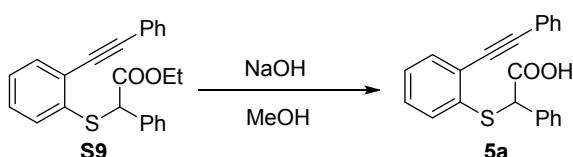
purified by flash chromatography using the indicated eluent.

### Synthesis of S9



To a solution of **S8** (1.0 equiv.), 1,4-diazabicyclo[2.2.2]octane (2.0 equiv),  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  (0.025 equiv),  $t\text{-Bu}_3\text{P}$  (0.1 equiv) in acetonitrile (1.0 M) was added phenylacetylene (1.6 equiv) under  $\text{N}_2$  atmosphere. The reaction mixture was stirred overnight at room temperature. The mixture was diluted with ether, filtered celite pad and concentrated *in vacuo*. The resulting crude mixture was purified by flash chromatography using the indicated eluent.

### Synthesis of 5a



The corresponding ester **S9** (1.0 equiv.) was dissolved in methanol. To the resulting 0.5 M solution was added a 15% m/v  $\text{NaOH}_{(\text{aq})}$  solution (5.0 equiv). The reaction mixture was stirred overnight at ambient temperature. The solvent was removed *in vacuo* and the residue redissolved in the minimal amount of  $\text{H}_2\text{O}$  possible. Concentrated hydrochloric acid was added dropwise until the pH was acidic. The pale yellow solid formed was filtered off and washed with cold  $\text{H}_2\text{O}$  (5 mL). The solid was dried under high vacuum and pure *o*-alkynylated carboxylic acids **5a** was obtained.

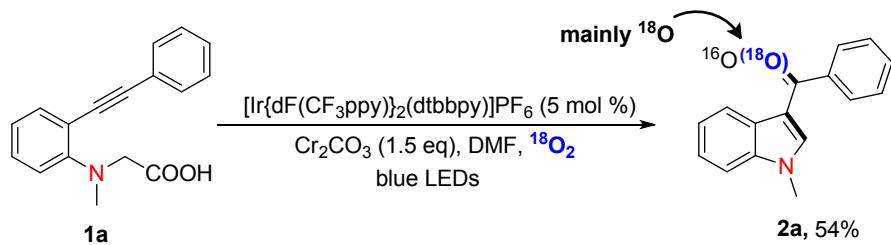
### Reference:

- [1] (a) J. E. Perea-Buceta, T. Wirtanen, O.-V. Laukkanen, M. K. Mäkelä, M. Nieger, M. Melchionna, N. Huittinen, J. A. Lopez-Sanchez, J. Helaja, *Angew. Chem., Int. Ed.*, 2013, **52**, 11835; (b) O. Ghashghaei, M. Revés, N. Kielland, R. Lavilla, *Eur. J. Org. Chem.*, 2015, 4383; (c) S. O'Sullivan, E. Doni, T. Tuttle, J. A. Murphy, *Angew. Chem., Int. Ed.*, 2014, **53**, 474; (d) V. Pace, W. Holzer, G. Verniest, A. R. Alcántara, N. De Kimpe, *Adv. Synth. Catal.*, 2013, **355**, 919.
- [2] (a) M. Rueda-Becerril, O. Mahe, M. Drouin, M. B. Majewski, J. G. West, M. O. Wolf, G. M. Sammis, J.-F. Paquin, *J. Am. Chem. Soc.*, 2014, **136**, 2637; (b) A. Kondoh, H. T. Q. Tran, K. Kimura, M. Terada, *Chem. Commun.*, 2016, **52**, 5726.
- [3] (a) T. Yamauchi, F. Shibahara, T. Murai, *Tetrahedron Lett.*, 2016, **57**, 2945.

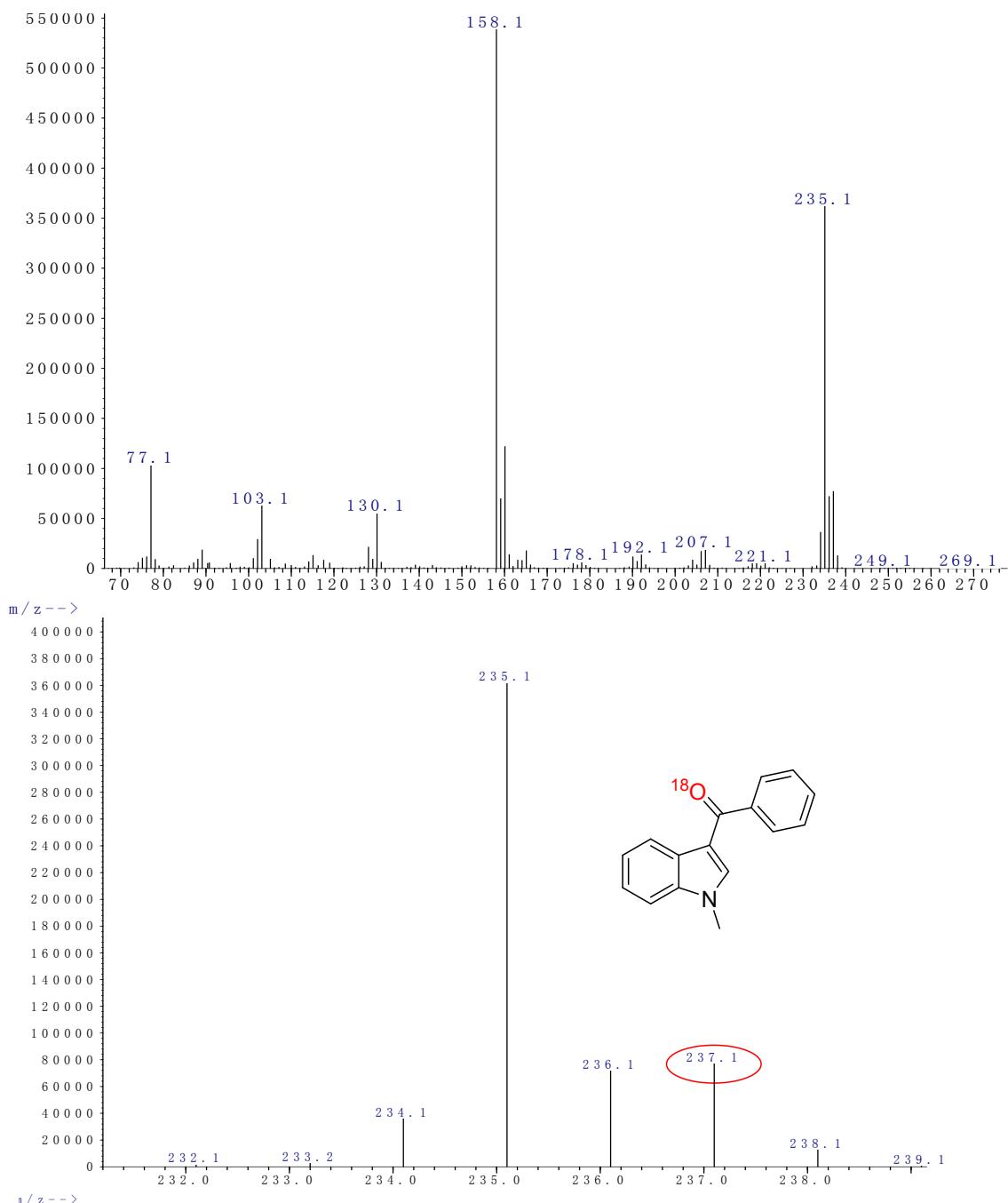
## 3. Study of Mechanism

### 3.1 Controlled Experiment

**Typical procedure for  $^{18}\text{O}_2$  labeling experiments:** We have performed an  $^{18}\text{O}_2$  labeling experiment under the standard conditions ( $^{18}\text{O}_2$  gas instead of  $^{16}\text{O}_2$  air, was filled in the reaction system). Isolated yield: 54%. From GC-MS (EI) the final product which was determined to contain an  $^{18}\text{O}$  was obtained exclusively, indicating that the oxygen atom of the ketonic carbonyl group in the 3-Acyliindoles products is originated from  $\text{O}_2$  in the air.

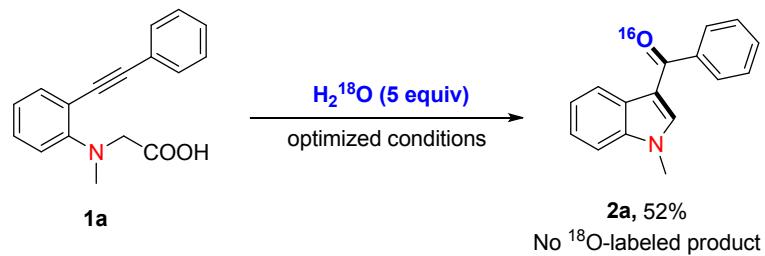


## The GC-MS spectra

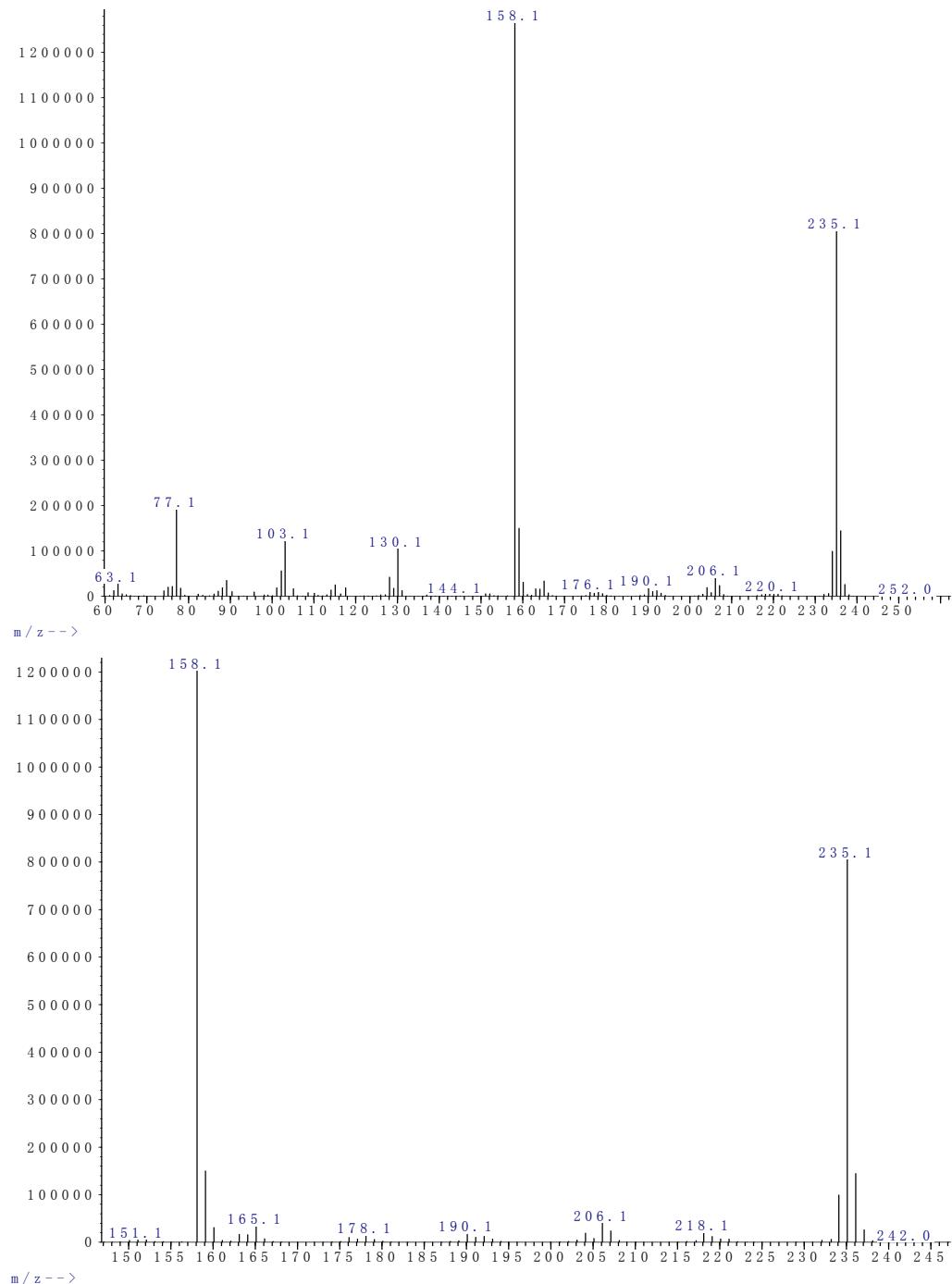


**Typical procedure for H<sub>2</sub><sup>18</sup>O labeling experiment:** To a 10 mL bottom flask were added compound **1a** (0.1 mmol), Ir[dpF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub> (5 mol %, 5.6 mg), Cs<sub>2</sub>CO<sub>3</sub> (1.5 equiv, 48.8 mg), anhydrous DMF (4 mL). Then, H<sub>2</sub><sup>18</sup>O (5.0 equiv) was added into the system. The reaction mixture was stirred under air atmosphere with the irradiation of blue LEDs (30 W) at room temperature for about 24 h. After the reaction was completed, as monitored by TLC, water

(12 mL) was added, the resulting mixture was extracted with ethyl acetate ( $15\text{ mL} \times 5$ ). The organic layer was combined, dried over  $\text{Na}_2\text{SO}_4$ . The filtrate was concentrated for purification by chromatography on silica gel with petroleum ether/EtOAc to afford the desired products **2a**. Isolated yield: 52%.

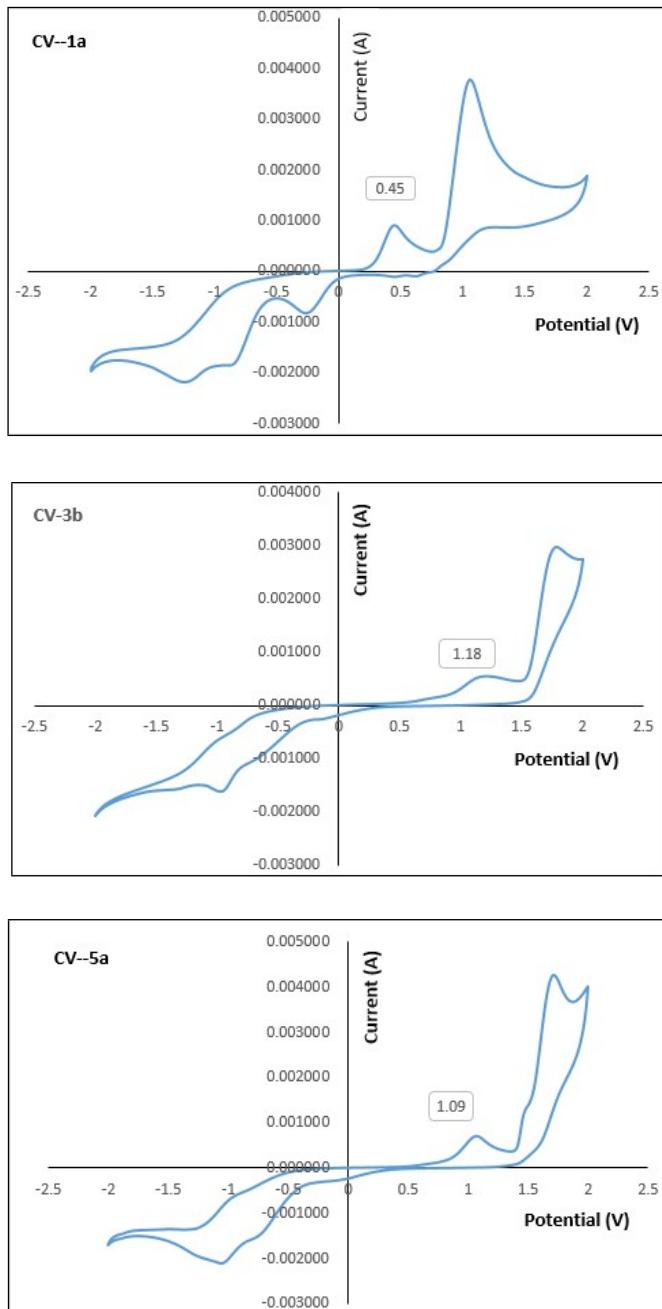


## The GC-MS spectra

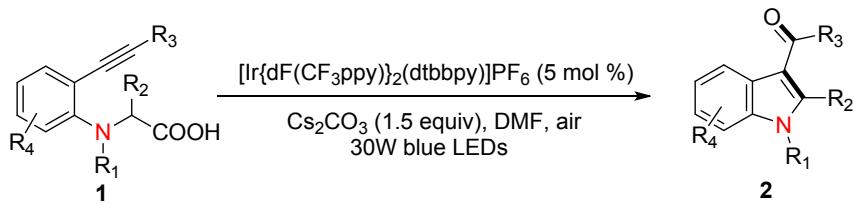


### 3.2 Cyclic voltammogram experiment

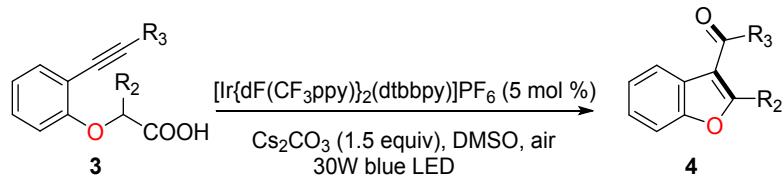
Cyclic voltammogram **1a**, **3b** and **5a** in 0.1 M TBAP/MeCN at a Pt working electrode with a Pt counter electrode and saturated calomel electrode (SCE). Potential sweep rate was 100 mV/s.



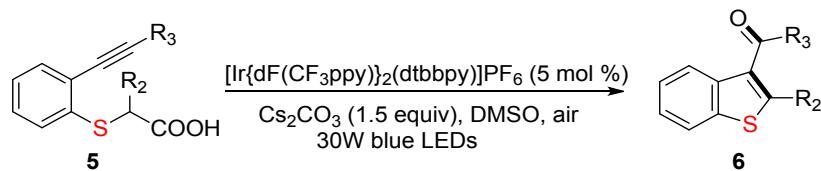
### 4. General Procedures for Decarboxylative Cyclization



**General procedure 1:** To a 10 mL bottom flask were added substrate **1** (0.1 mmol),  $\text{Cr}_2\text{CO}_3$  (0.15 mmol), DMF (anhydrous, 4.0 mL),  $[\text{Ir}\{\text{dF}(\text{CF}_3\text{ppy})\}_2(\text{dtbbpy})]\text{PF}_6$  (0.005 mmol). The reaction mixture was stirred under air atmosphere with the irradiation of blue LEDs (30 W) at room temperature. After the reaction was completed, as monitored by TLC, water (12 mL) was added, the resulting mixture was extracted with ethyl acetate (15 mL  $\times$  5). The organic layer was combined and dried over  $\text{Na}_2\text{SO}_4$ . Then the filtrate was concentrated for purification by chromatography on silica gel with petroleum ether/EtOAc to afford the desired products **2**.

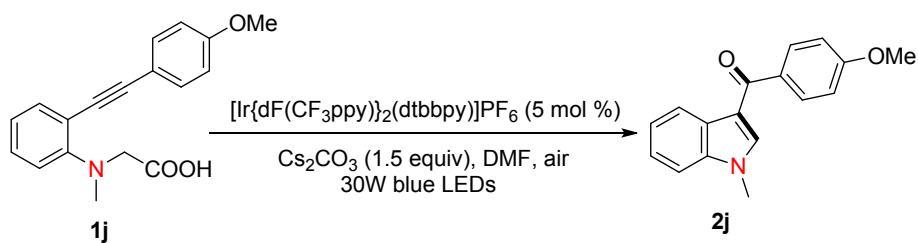


**General procedure 2:** To a 10 mL bottom flask were added substrate **3** (0.1 mmol),  $\text{Cr}_2\text{CO}_3$  (0.15 mmol), DMSO (anhydrous, 4.0 mL),  $[\text{Ir}\{\text{dF}(\text{CF}_3\text{ppy})\}_2(\text{dtbbpy})]\text{PF}_6$  (0.005 mmol). The mixture was carried out under air atmosphere with blue LEDs (30 W) irradiation at room temperature. After the substrate was consumed (monitored by TLC), the reaction mixture was quenched with water (12 mL) and extracted with EtOAc (15 mL  $\times$  5). The organic layer was combined, dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc) to afford the desired product **4**.



**General procedure 3:** To a 10 mL bottom flask were added substrate **5** (0.1 mmol),  $\text{Cr}_2\text{CO}_3 (0.15 mmol), DMSO (anhydrous, 4.0 mL),  $[\text{Ir}\{\text{dF}(\text{CF}_3\text{ppy})\}_2(\text{dtbbpy})]\text{PF}_6$  (0.005 mmol). The mixture was carried out under air atmosphere with blue LEDs (30 W) irradiation at room temperature. After the substrate was consumed (monitored by TLC), the reaction mixture was quenched with water (12 mL) and extracted with EtOAc (15 mL  $\times$  5). The organic layer was combined, dried ( $\text{Na}_2\text{SO}_4$ ), filtered, and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (petroleum ether/EtOAc) to afford the desired product **6**.$

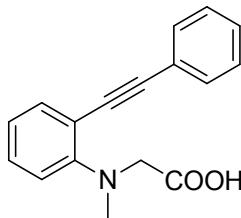
### Gram Scale Reaction



To a 250 mL flask unsealed under air atmosphere was charged with compound **1j** (0.885 g, 3 mmol),  $[\text{Ir}\{\text{dF}(\text{CF}_3\text{ppy})\}_2(\text{dtbbpy})]\text{PF}_6$  (5 mol %, 168 mg),  $\text{Cs}_2\text{CO}_3$  (1.5 equiv, 1.46 g), anhydrous DMF (120 mL). The reaction mixture was stirred at room temperature with the irradiation of a 30 W blue LEDs for about 36 h. After the reaction was completed, as monitored by TLC, water (150 mL) was added. The resulting mixture was extracted with ethyl acetate (70 mL  $\times$  5). The combined organic layers were washed with brine and dried over  $\text{Na}_2\text{SO}_4$ . Then the filtrate was concentrated for purification by chromatography on silica gel with petroleum ether /ethylacetate to afford the desired products **2j** (574 mg, 72%).

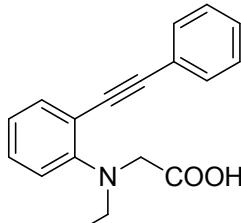
## 5. Characterization of new substrates

### N-methyl-N-(2-(phenylethynyl)phenyl)glycine (1a)



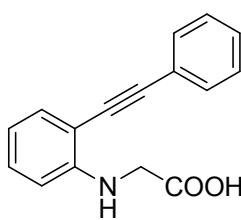
White solid, mp = 103.7-104.8 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 12.54 (s, 1H), 7.55-7.50 (m, 2H), 7.45-7.39 (m, 4H), 7.28 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 4.27 (s, 2H), 2.98 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 171.9, 152.4, 134.2, 130.9, 129.6, 128.7, 128.4, 122.8, 119.7, 117.5, 111.8, 94.3, 88.9, 55.7, 40.0. **IR** (cm<sup>-1</sup>): 754, 948, 1198, 1496, 1592, 1719. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>15</sub>NNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 288.1000, found: 288.1003.

### N-ethyl-N-(2-(phenylethynyl)phenyl)glycine (1b)



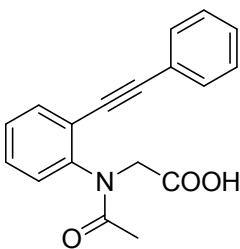
Yellow oil. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.89 (s, 1H), 7.62-7.47 (m, 3H), 7.40-7.29 (m, 4H), 7.13 (t, *J* = 7.5 Hz, 2H), 3.92 (s, 2H), 3.26 (q, *J* = 6.8 Hz, 2H), 1.15 (t, *J* = 7.0 Hz, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 172.5, 150.7, 134.0, 131.6, 129.5, 128.7, 128.5, 124.7, 122.7, 122.3, 119.7, 95.2, 86.8, 56.9, 49.5, 12.6. **IR** (cm<sup>-1</sup>): 755, 1222, 1386, 1495, 1593, 1722, 2975, 3059. **HRMS** m/z (ESI) calcd for C<sub>18</sub>H<sub>17</sub>NNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 302.1157, found: 302.1163.

### N-methyl-N-(2-(phenylethynyl)phenyl)glycine (1c)



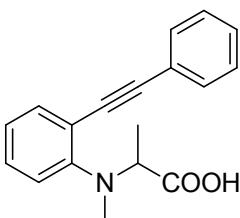
White solid, mp = 124.6-125.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.62-7.57 (m, 2H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.41-7.35 (m, 3H), 7.29-7.23 (m, 1H), 6.78 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 4.11 (s, 2H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 176.5, 147.4, 132.2, 131.5, 130.1, 128.5, 128.3, 123.2, 117.8, 109.7, 108.5, 95.7, 85.5, 45.3. **IR** (cm<sup>-1</sup>): 744, 895, 1257, 1284, 1435, 1511, 1595, 1726, 2922, 2953, 3393. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>13</sub>NNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 274.0844, found: 274.0846.

### N-acetyl-N-(2-(phenylethynyl)phenyl)glycine (1d)



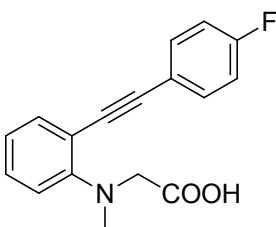
White solid, mp = 134.0-134.8 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.58 (s, 1H), 7.67-7.62 (m, 1H), 7.60-7.56 (m, 1H), 7.52 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.44-7.36 (m, 5H), 5.14 (d, *J* = 17.5 Hz, 1H), 3.90 (d, *J* = 17.5 Hz, 1H), 1.99 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 173.8, 172.0, 144.0, 133.0, 131.8, 129.7, 129.4, 129.0, 128.7, 128.5, 122.5, 122.3, 95.5, 84.7, 50.3, 21.8. **IR** (cm<sup>-1</sup>): 757, 1023, 1200, 1315, 1391, 1496, 1622, 1739, 2926, 2955. **HRMS** m/z (ESI) calcd for C<sub>18</sub>H<sub>15</sub>NNaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup>: 316.0950, found: 316.0947.

### N-methyl-N-(2-(phenylethynyl)phenyl)alanine (1e)



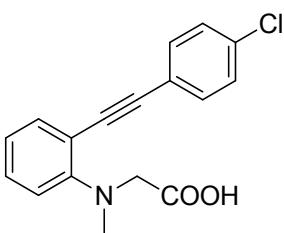
White solid, mp = 122.3-123.1 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.99 (s, 1H), 7.62-7.55 (m, 3H), 7.41-7.32 (m, 4H), 7.18-7.10 (m, 2H), 4.57 (q, *J* = 7.1 Hz, 1H), 2.81 (s, 3H), 1.43 (d, *J* = 7.1 Hz, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 175.1, 152.0, 134.3, 131.6, 129.4, 128.6, 128.5, 123.6, 122.7, 120.6, 117.8, 95.9, 86.9, 62.4, 35.0, 11.5. **IR** (cm<sup>-1</sup>): 755, 1097, 1205, 1374, 1445, 1495, 1591, 1710, 2986, 3061. **HRMS** m/z (ESI) calcd for C<sub>18</sub>H<sub>17</sub>NNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 302.1157, found: 302.1154.

### N-(2-((4-fluorophenyl)ethynyl)phenyl)-N-methylglycine (1f)



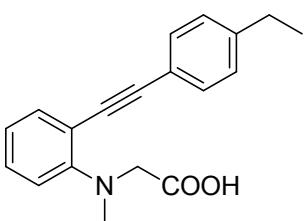
White solid, mp = 113.0-113.8 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 9.57 (s, 1H), 7.53-7.47 (m, 3H), 7.29 (t, *J* = 7.8, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 7.04-6.99 (m, 3H), 4.11 (s, 2H), 2.95 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 174.7, 162.6 (d, *J* = 249.9 Hz), 152.2, 134.3, 133.4 (d, *J* = 8.1 Hz), 129.5, 122.5, 119.1 (d, *J* = 3.4 Hz), 118.5, 115.7 (d, *J* = 22.0 Hz), 115.5, 94.5, 87.0, 58.4, 40.9. **IR** (cm<sup>-1</sup>): 758, 836, 948, 1231, 1356, 1508, 1599, 1724, 2882. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>14</sub>FNNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 306.0906, found: 306.0903.

### N-(2-((4-chlorophenyl)ethynyl)phenyl)-N-methylglycine (1g)



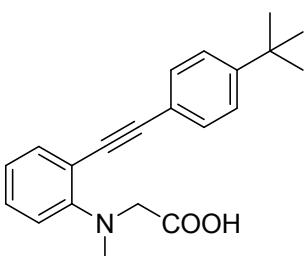
White solid, mp = 128.7-129.4 °C. **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  10.49 (s, 1H), 7.54 (dd,  $J$  = 7.7, 1.6 Hz, 1H), 7.47 (d,  $J$  = 8.5 Hz, 2H), 7.36-7.30 (m, 3H), 7.10 (d,  $J$  = 8.2 Hz, 1H), 7.05 (td,  $J$  = 7.5, 1.1 Hz, 1H), 4.11 (s, 2H), 2.98 (s, 3H). **<sup>13</sup>C NMR** (151 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  174.0, 152.3, 134.5, 134.4, 132.7, 129.7, 128.8, 122.7, 121.5, 118.6, 115.5, 94.5, 88.2, 58.7, 41.0. **IR** ( $\text{cm}^{-1}$ ): 760, 830, 949, 1093, 1495, 1592, 1726, 2962. **HRMS** m/z (ESI) calcd for  $\text{C}_{17}\text{H}_{14}\text{ClNNaO}_2^+$  [M+Na]<sup>+</sup>: 322.0611, found: 322.0608.

#### N-(2-((4-ethylphenyl)ethynyl)phenyl)-N-methylglycine (1h)



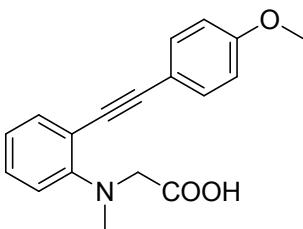
Yellow oil. **<sup>1</sup>H NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  9.22 (s, 1H), 7.51 (d,  $J$  = 7.6 Hz, 1H), 7.44 (d,  $J$  = 7.4 Hz, 2H), 7.28 (t,  $J$  = 7.7 Hz, 1H), 7.16 (d,  $J$  = 7.5 Hz, 2H), 7.07 (d,  $J$  = 8.2 Hz, 1H), 7.02 (t,  $J$  = 7.4 Hz, 1H), 4.10 (s, 2H), 2.93 (s, 3H), 2.64 (q,  $J$  = 7.5 Hz, 2H), 1.22 (t,  $J$  = 7.6 Hz, 3H). **<sup>13</sup>C NMR** (151 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  173.7, 152.1, 145.0, 134.2, 131.5, 129.2, 128.0, 122.8, 120.1, 118.9, 116.4, 96.0, 86.5, 58.7, 41.1, 28.9, 15.4. **IR** ( $\text{cm}^{-1}$ ): 750, 833, 948, 1198, 1370, 1487, 1593, 1720, 2931, 2965, 3027. **HRMS** m/z (ESI) calcd for  $\text{C}_{19}\text{H}_{19}\text{NNaO}_2^+$  [M+Na]<sup>+</sup>: 316.1313, found: 316.1311.

#### N-(2-((4-(tert-butyl)phenyl)ethynyl)phenyl)-N-methylglycine (1i)



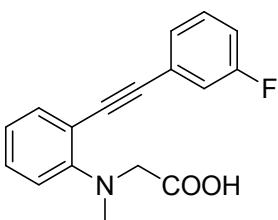
Brown oil. **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  9.42 (s, 1H), 7.52 (d,  $J$  = 7.6 Hz, 1H), 7.47 (d,  $J$  = 7.5 Hz, 2H), 7.36 (d,  $J$  = 7.7 Hz, 2H), 7.29 (t,  $J$  = 7.7 Hz, 1H), 7.08 (d,  $J$  = 8.2 Hz, 1H), 7.03 (t,  $J$  = 7.5 Hz, 1H), 4.08 (s, 2H), 2.94 (s, 3H), 1.31 (s, 9H). **<sup>13</sup>C NMR** (151 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  173.3, 152.0, 151.8, 134.3, 131.3, 129.3, 125.5, 123.0, 119.8, 119.0, 116.6, 96.1, 86.4, 58.9, 41.2, 34.8, 31.2. **IR** ( $\text{cm}^{-1}$ ): 754, 948, 1199, 1268, 1363, 1487, 1593, 1721, 2962, 3034. **HRMS** m/z (ESI) calcd for  $\text{C}_{21}\text{H}_{23}\text{NNaO}_2^+$  [M+Na]<sup>+</sup>: 344.1626, found: 344.1629.

#### N-(2-((4-methoxyphenyl)ethynyl)phenyl)-N-methylglycine (1j)



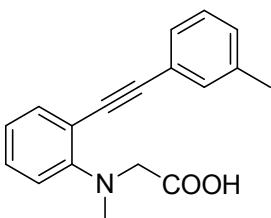
Yellow solid, mp = 103.2-104.4 °C. **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 9.53 (s, 1H), 7.54 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.51-7.47 (m, 2H), 7.34-7.29 (m, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.91-6.87 (m, 2H), 4.09 (s, 2H), 3.84 (s, 3H), 2.96 (s, 3H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 173.4, 159.8, 152.0, 134.1, 133.0, 129.1, 123.0, 118.8, 116.7, 115.0, 114.1, 95.9, 85.7, 58.9, 55.3, 41.1. **IR** (cm<sup>-1</sup>): 754, 948, 1029, 1176, 1248, 1487, 1512, 1605, 1721, 2837, 2957. **HRMS** m/z (ESI) calcd for C<sub>18</sub>H<sub>17</sub>NNaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup>: 318.1106, found: 318.1100.

### N-(2-((3-fluorophenyl)ethynyl)phenyl)-N-methylglycine (1k)



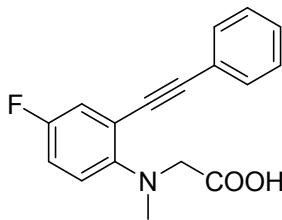
Yellow solid, mp = 82.3-87.6 °C. **1H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.45 (s, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.32-7.24 (m, 3H), 7.20 (d, *J* = 9.4 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 7.02-6.97 (m, 2H), 4.14 (s, 2H), 2.97 (s, 3H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 175.3, 162.4 (d, *J* = 246.4 Hz), 152.5, 134.4, 130.0 (d, *J* = 8.7 Hz), 129.8, 127.4 (d, *J* = 2.8 Hz), 124.9 (d, *J* = 9.2 Hz), 122.1, 118.4, 118.1 (d, *J* = 22.5 Hz), 115.7 (d, *J* = 21.1 Hz), 114.8, 94.1 (d, *J* = 3.2 Hz), 88.4, 58.1, 40.7. **IR** (cm<sup>-1</sup>): 752, 784, 948, 1202, 1231, 1494, 1578, 1721, 2884, 3068. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>14</sub>FNNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 306.0906, found: 306.0903.

### N-methyl-N-(2-(m-tolylethynyl)phenyl)glycine (1l)



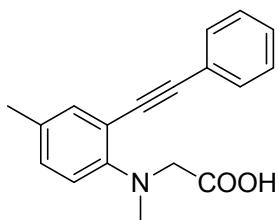
Brown oil. **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.36 (s, 1H), 7.55 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.39-7.29 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 4.15 (s, 2H), 2.99 (s, 3H), 2.37 (s, 3H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 174.4, 152.2, 138.1, 134.3, 132.0, 129.4, 129.3, 128.6, 128.3, 122.8, 122.5, 118.8, 116.0, 95.9, 87.0, 58.3, 41.0, 21.3. **IR** (cm<sup>-1</sup>): 750, 948, 1047, 1358, 1493, 1593, 1715, 2920. **HRMS** m/z (ESI) calcd for C<sub>18</sub>H<sub>17</sub>NNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 302.1157, found: 302.1157.

### N-(4-fluoro-2-(phenylethynyl)phenyl)-N-methylglycine (1m)



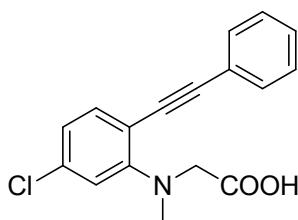
Yellow oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.04 (s, 1H), 7.55 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.38-7.33 (m, 3H), 7.24 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.10-6.98 (m, 2H), 4.10 (s, 2H), 2.96 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 173.5, 158.2 (d, *J* = 242.9 Hz), 148.6 (d, *J* = 2.5 Hz), 131.6, 128.9, 128.5, 122.4, 120.7 (d, *J* = 8.6 Hz), 120.2 (d, *J* = 23.6 Hz), 118.2 (d, *J* = 9.3 Hz), 116.3 (d, *J* = 22.5 Hz), 96.4, 85.9, 58.7, 41.6. **IR** (cm<sup>-1</sup>): 756, 871, 944, 1120, 1195, 1413, 1488, 1723, 2886, 3059. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>14</sub>FNNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 306.0906, found: 306.0907.

### N-methyl-N-(4-methyl-2-(phenylethynyl)phenyl)glycine (1n)



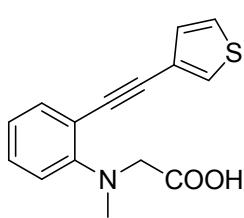
Yellow solid, mp = 97.0-98.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 9.30 (s, 1H), 7.55 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.41-7.33 (m, 4H), 7.14 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 4.04 (s, 2H), 2.94 (s, 3H), 2.33 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 173.5, 149.9, 134.5, 132.8, 131.5, 130.2, 128.5, 128.4, 122.9, 119.1, 116.5, 95.4, 87.1, 59.1, 41.4, 20.5. **IR** (cm<sup>-1</sup>): 756, 950, 1094, 1192, 1353, 1502, 1722, 2920. **HRMS** m/z (ESI) calcd for C<sub>18</sub>H<sub>17</sub>NNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 302.1157, found: 302.1159.

### N-(5-chloro-2-(phenylethynyl)phenyl)-N-methylglycine (1o)



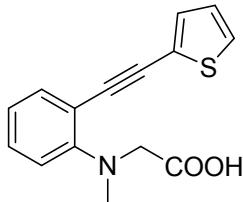
Purple solid, mp = 111.4-112.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 9.56 (s, 1H), 7.51-7.47 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.33-7.29 (m, 3H), 7.00 (d, *J* = 1.9 Hz, 1H), 6.95 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.22 (s, 2H), 2.97 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 174.8, 153.1, 135.2, 135.1, 131.4, 128.6, 128.4, 122.8, 122.0, 118.7, 113.3, 96.3, 86.6, 57.4, 40.6. **IR** (cm<sup>-1</sup>): 755, 953, 1201, 1236, 1406, 1496, 1585, 1721, 2961, 3061. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>14</sub>ClNNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 322.0611, found: 322.0610.

### N-methyl-N-(2-(thiophen-3-ylethynyl)phenyl)glycine (1p)



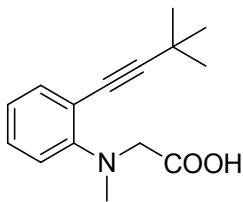
Yellow oil. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.84 (s, 1H), 7.55 (d, *J* = 2.1 Hz, 1H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.27-7.25 (m, 1H), 7.19 (d, *J* = 4.8 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 4.07 (s, 2H), 2.94 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 174.0, 152.2, 134.1, 129.8, 129.3, 129.0, 125.5, 122.8, 121.9, 118.6, 116.0, 91.0, 86.6, 58.9, 41.0. **IR** (cm<sup>-1</sup>): 747, 841, 1076, 1238, 1373, 1465, 1524, 1609, 1720, 2931, 3105. **HRMS** m/z (ESI) calcd for C<sub>15</sub>H<sub>13</sub>NNaO<sub>2</sub>S<sup>+</sup> [M+Na]<sup>+</sup>: 294.0565, found: 294.0561.

#### N-methyl-N-(2-(thiophen-2-ylethynyl)phenyl)glycine (1q)



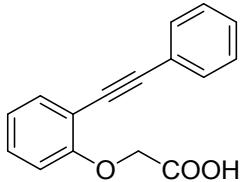
Brown solid, mp = 110.4-111.2 °C. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.51 (s, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.31-7.24 (m, 3H), 7.05 (d, *J* = 8.2 Hz, 1H), 7.02-6.94 (m, 2H), 4.11 (s, 2H), 2.96 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 174.6, 152.2, 134.0, 132.2, 129.6, 127.6, 127.2, 122.9, 122.4, 118.6, 115.3, 90.9, 88.9, 58.3, 40.8. **IR** (cm<sup>-1</sup>): 749, 853, 951, 1039, 1119, 1246, 1405, 1489, 1593, 1694, 2883. **HRMS** m/z (ESI) calcd for C<sub>15</sub>H<sub>13</sub>NNaO<sub>2</sub>S<sup>+</sup> [M+Na]<sup>+</sup>: 294.0565, found: 294.0559.

#### N-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)-N-methylglycine (1r)



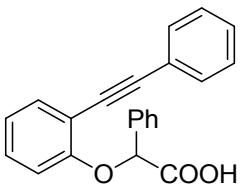
Yellow oil. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.91 (s, 1H), 7.37 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.21 (td, *J* = 8.2, 1.6 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 4.07 (s, 2H), 2.89 (s, 3H), 1.31 (s, 9H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 174.4, 151.7, 134.4, 128.6, 122.6, 118.8, 116.8, 105.0, 77.0, 58.2, 41.0, 30.8, 28.3. **IR** (cm<sup>-1</sup>): 750, 949, 1097, 1198, 1283, 1361, 1490, 1594, 1723, 2868, 2967. **HRMS** m/z (ESI) calcd for C<sub>15</sub>H<sub>19</sub>NNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 268.1313, found: 268.1311.

#### 2-(2-(phenylethynyl)phenoxy)acetic acid (3a)



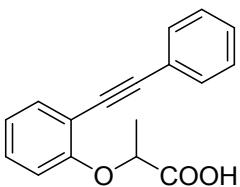
Pale yellow soild, mp = 94.2-97.0 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 13.13 (s, 1H), 7.59-7.53 (m, 2H), 7.51 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.47-7.40 (m, 3H), 7.36 (t, *J* = 8.6 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 4.82 (s, 2H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 167.0, 158.2, 133.1, 131.2, 130.1, 128.7, 128.6, 122.7, 121.0, 112.2, 111.5, 93.1, 86.1, 64.8. **IR** (cm<sup>-1</sup>): 1705, 1593, 1574, 1497, 1482, 1447, 1218, 1163, 1114, 1071, 920, 783, 755, 689. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>13</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 253.0865, found: 253.0860.

#### 2-phenyl-2-(2-(phenylethynyl)phenoxy)acetic acid (3b)



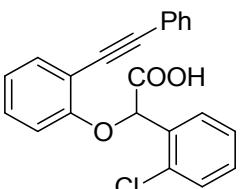
Pale yellow soild, mp = 162.3-164.3 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 13.33 (s, 1H), 7.68 (d, *J* = 7.1 Hz, 2H), 7.55-7.49 (m, 3H), 7.47-7.35 (m, 7H), 7.05-6.98 (m, 2H), 5.97 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 170.6, 157.7, 136.1, 132.8, 131.1, 130.1, 128.8, 128.7, 128.6, 128.5, 127.0, 122.7, 121.4, 113.2, 112.3, 93.5, 86.0, 77.4. **IR** (cm<sup>-1</sup>): 1697, 1593, 1496, 1241, 1227, 955, 752, 718, 688. **HRMS** m/z (ESI) calcd for C<sub>22</sub>H<sub>16</sub>NaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup>: 351.0997, found: 351.0994.

### 2-(2-(phenylethynyl)phenoxy)propanoic acid (3c)



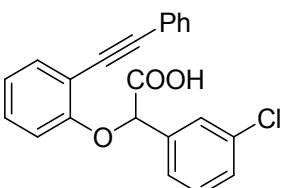
Pale yellow soild, mp = 107.2-110.7 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 13.23 (s, 1H), 7.56-7.47 (m, 3H), 7.47-7.39 (m, 3H), 7.34 (t, *J* = 7.9 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 4.90 (q, *J* = 6.7 Hz, 1H), 1.58 (d, *J* = 6.7 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 173.4, 158.6, 133.5, 131.7, 130.6, 129.2, 129.0, 123.3, 121.5, 113.7, 112.5, 93.6, 86.7, 73.0, 18.8. **IR** (cm<sup>-1</sup>): 1699, 1498, 1482, 1446, 1285, 1275, 1240, 1134, 1044, 757, 692. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>14</sub>NaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup>: 289.0841, found: 289.0841.

### 2-(2-chlorophenyl)-2-(2-(phenylethynyl)phenoxy)acetic acid (3d)



Pale yellow soild, mp = 107.0-110.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 11.01 (s, 1H), 7.82-7.74 (m, 1H), 7.53-7.47 (m, 3H), 7.41-7.36 (m, 1H), 7.33-7.25 (m, 5H), 7.19 (t, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.24 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 173.5, 157.2, 133.5, 133.4, 133.1, 131.6, 130.5, 129.9, 129.7, 129.0, 128.4, 127.5, 123.3, 122.7, 114.7, 114.4, 94.7, 85.2, 75.9. **IR** (cm<sup>-1</sup>): 1720, 1594, 1574, 1498, 1484, 1447, 1233, 1198, 1109, 931, 746, 723, 687. **HRMS** m/z (ESI) calcd for C<sub>22</sub>H<sub>16</sub>ClO<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 363.0788, found: 363.0781.

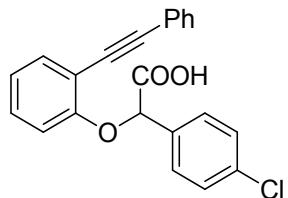
### 2-(3-chlorophenyl)-2-(2-(phenylethynyl)phenoxy)acetic acid (3e)



White soild, mp = 169.3-170.6 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 13.54 (s, 1H), 7.78 (s, 1H), 7.66-7.60 (m, 1H), 7.59-7.52 (m, 3H), 7.51-7.42 (m, 5H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 8.3 Hz, 2H), 6.07 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 170.2, 157.4, 138.4, 133.2, 132.8, 131.1, 130.5, 130.2, 128.8, 128.7, 128.6, 126.4, 125.7, 122.6, 121.5, 113.0,

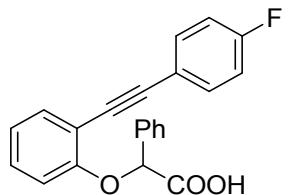
112.3, 93.6, 85.9, 76.5. **IR** ( $\text{cm}^{-1}$ ): 1698, 1593, 1575, 1497, 1481, 1286, 1277, 1237, 1226, 1115, 1070, 766, 751, 715, 688. **HRMS** m/z (ESI) calcd for  $\text{C}_{22}\text{H}_{15}\text{ClNaO}_3^+ [\text{M}+\text{Na}]^+$ : 385.0607, found: 385.0603.

### **2-(4-chlorophenyl)-2-(phenylethynyl)phenoxyacetic acid (3f)**



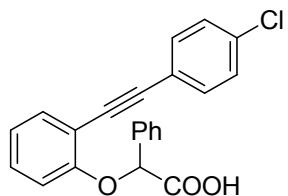
White soild, mp = 150.6-153.1 °C. **1H NMR** (400 MHz, DMSO)  $\delta_{\text{H}}$  13.43 (s, 1H), 7.69 (d,  $J$  = 8.5 Hz, 2H), 7.58-7.50 (m, 5H), 7.49-7.41 (m, 3H), 7.37 (td,  $J$  = 8.3, 1.6 Hz, 1H), 7.07-6.97 (m, 2H), 6.03 (s, 1H). **13C NMR** (100 MHz, DMSO)  $\delta_{\text{C}}$  170.3, 157.4, 135.1, 133.4, 132.9, 131.1, 130.1, 128.9, 128.8, 128.7, 128.6, 122.7, 121.5, 113.3, 112.4, 93.6, 85.9, 76.7. **IR** ( $\text{cm}^{-1}$ ): 1703, 1595, 1574, 1498, 1451, 1287, 1243, 1093, 1016, 934, 753, 686. **HRMS** m/z (ESI) calcd for  $\text{C}_{22}\text{H}_{15}\text{ClNaO}_3^+ [\text{M}+\text{Na}]^+$ : 385.0607, found: 385.0607.

### **2-(2-((4-fluorophenyl)ethynyl)phenoxy)-2-phenylacetic acid (3g)**



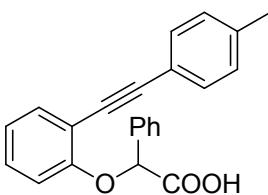
Pale yellow soild, mp = 177.4-181.6 °C. **1H NMR** (400 MHz, DMSO)  $\delta_{\text{H}}$  13.34 (s, 1H), 7.68 (d,  $J$  = 7.2 Hz, 2H), 7.57 (dd,  $J$  = 8.6, 5.6 Hz, 2H), 7.52 (dd,  $J$  = 7.7, 1.3 Hz, 1H), 7.49-7.43 (m, 2H), 7.42-7.34 (m, 2H), 7.31 (t,  $J$  = 8.8 Hz, 2H), 7.07-6.96 (m, 2H), 5.97 (s, 1H). **13C NMR** (100 MHz, DMSO)  $\delta_{\text{C}}$  170.6, 161.9 (d,  $J$  = 247.6 Hz), 157.7, 136.1, 133.3 (d,  $J$  = 8.6 Hz), 132.7, 130.2, 128.7, 128.5, 127.0, 121.4, 119.2 (d,  $J$  = 3.2 Hz), 116.1 (d,  $J$  = 22.1 Hz), 113.2, 112.2, 92.4, 85.8, 77.4. **IR** ( $\text{cm}^{-1}$ ): 1698, 1593, 1509, 1485, 1447, 1285, 1228, 1115, 831, 752, 718, 689. **HRMS** m/z (ESI) calcd for  $\text{C}_{22}\text{H}_{15}\text{FNaO}_3^+ [\text{M}+\text{Na}]^+$ : 369.0903, found: 369.0901.

### **2-(2-((4-chlorophenyl)ethynyl)phenoxy)-2-phenylacetic acid (3h)**



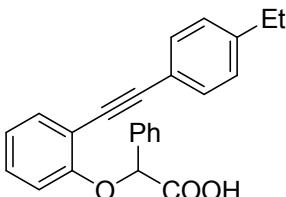
White soild, mp = 180.2-185.9 °C. **1H NMR** (400 MHz, DMSO)  $\delta_{\text{H}}$  13.35 (s, 1H), 7.68 (d,  $J$  = 7.6 Hz, 2H), 7.56-7.51 (m, 5H), 7.46 (t,  $J$  = 7.3 Hz, 2H), 7.41 (d,  $J$  = 6.9, 7.4 Hz, 1H), 7.37 (d,  $J$  = 7.8 Hz, 1H), 7.07-7.00 (m, 2H), 5.98 (s, 1H). **13C NMR** (100 MHz, DMSO)  $\delta_{\text{C}}$  171.1, 158.3, 136.6, 133.8, 133.3, 133.2, 130.8, 129.5, 129.2, 129.0, 127.5, 122.1, 121.9, 113.7, 112.6, 92.8, 87.7, 78.0. **IR** ( $\text{cm}^{-1}$ ): 1699, 1495, 1480, 1447, 1278, 1088, 823, 752, 717, 688. **HRMS** m/z (ESI) calcd for  $\text{C}_{22}\text{H}_{15}\text{ClNaO}_3^+ [\text{M}+\text{Na}]^+$ : 385.0607, found: 385.0597.

### **2-phenyl-2-(2-(p-tolylethynyl)phenoxy)acetic acid (3i)**



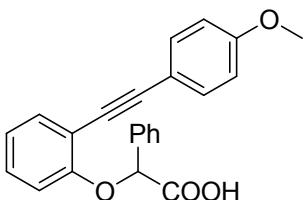
Pale yellow soild, mp = 175.9-178.0 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 13.34 (s, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.51 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.48-7.33 (m, 6H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.02 (dd, *J* = 7.9, 4.9 Hz, 2H), 5.96 (s, 1H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 171.1, 158.1, 138.9, 136.6, 133.2, 131.5, 130.4, 129.9, 129.2, 129.0, 127.5, 121.9, 120.3, 113.7, 113.1, 94.2, 85.9, 78.0, 21.5. **IR** (cm<sup>-1</sup>): 1699, 1596, 1513, 1497, 1485, 1450, 1277, 1243, 1190, 1114, 1065, 951, 812, 750, 717, 688. **HRMS** m/z (ESI) calcd for C<sub>23</sub>H<sub>18</sub>NaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup>: 365.1154, found: 365.1150.

### 2-(2-((4-ethylphenyl)ethynyl)phenoxy)-2-phenylacetic acid (3j)



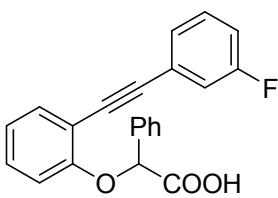
White soild, mp = 153.6-156.6 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 13.34 (s, 1H), 7.69 (d, *J* = 7.0 Hz, 2H), 7.50 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.48-7.33 (m, 6H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.05-6.96 (m, 2H), 5.96 (s, 1H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 170.7, 157.6, 144.6, 136.1, 132.7, 131.1, 129.9, 128.7, 128.5, 128.2, 127.0, 121.3, 120.0, 113.1, 112.5, 93.7, 85.4, 77.4, 28.1, 15.3. **IR** (cm<sup>-1</sup>): 1699, 1595, 1514, 1485, 1448, 1276, 1240, 1224, 1114, 1063, 828, 752, 717, 688. **HRMS** m/z (ESI) calcd for C<sub>24</sub>H<sub>21</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 357.1491, found: 357.1496.

### 2-(2-((4-methoxyphenyl)ethynyl)phenoxy)-2-phenylacetic acid (3k)



Pale yellow soild, mp = 157.6-158.0 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 13.33 (s, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.51-7.38 (m, 6H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 4H), 5.96 (s, 1H), 3.81 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 171.2, 159.9, 158.0, 136.6, 133.1, 133.0, 130.1, 129.2, 129.0, 127.5, 121.8, 115.2, 115.0, 113.7, 113.3, 94.2, 85.1, 78.0, 55.8. **IR** (cm<sup>-1</sup>): 1698, 1608, 1513, 1485, 1289, 1247, 1222, 752, 720, 692. **HRMS** m/z (ESI) calcd for C<sub>23</sub>H<sub>19</sub>O<sub>4</sub><sup>+</sup> [M+H]<sup>+</sup>: 359.1283, found: 359.1286.

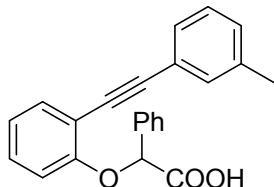
### 2-(2-((3-fluorophenyl)ethynyl)phenoxy)-2-phenylacetic acid (3l)



Pale yellow soild, mp = 168.7-172.0 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 13.35 (s, 1H), 7.67 (d, *J* = 6.9 Hz, 2H), 7.55-7.26 (m, 9H), 7.03 (dd, *J* = 7.8, 5.6 Hz, 2H), 5.98 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 170.6, 161.9 (d, *J* = 244.8 Hz), 157.8, 136.1, 132.8, 131.0 (d, *J* = 8.9 Hz), 130.5, 128.7, 128.5, 127.4 (d, *J* = 2.3 Hz), 127.0, 124.7 (d, *J* = 9.7 Hz),

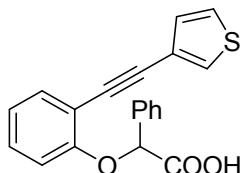
121.4, 117.6 (d,  $J = 22.9$  Hz), 115.9 (d,  $J = 21.0$  Hz), 113.3, 111.9, 92.2 (d,  $J = 2.8$  Hz), 87.1, 77.4. **IR** ( $\text{cm}^{-1}$ ): 1698, 1577, 1495, 1448, 1279, 1247, 1229, 943, 788, 751, 718, 680. **HRMS** m/z (ESI) calcd for  $\text{C}_{22}\text{H}_{16}\text{FO}_3^+ [\text{M}+\text{H}]^+$ : 347.1083, found: 347.1082.

### **2-phenyl-2-(2-(m-tolylethynyl)phenoxy)acetic acid (3m)**



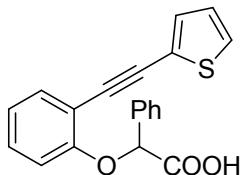
Pale yellow soild, mp = 168.7-172.6 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO)  $\delta_{\text{H}}$  13.34 (s, 1H), 7.70 (d,  $J = 7.0$  Hz, 2H), 7.51 (d,  $J = 6.6$  Hz, 1H), 7.49-7.29 (m, 7H), 7.24 (d,  $J = 6.5$  Hz, 1H), 7.02 (t,  $J = 7.2$  Hz, 2H), 5.97 (s, 1H), 2.34 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO)  $\delta_{\text{C}}$  170.7, 157.7, 138.1, 136.1, 132.7, 131.6, 130.0, 129.4, 128.7, 128.6, 128.5, 128.1, 127.0, 122.6, 121.4, 113.1, 112.4, 93.7, 85.7, 77.4, 20.8. **IR** ( $\text{cm}^{-1}$ ): 1698, 1593, 1574, 1494, 1446, 1277, 1228, 1115, 1065, 955, 768, 752, 716, 689. **HRMS** m/z (ESI) calcd for  $\text{C}_{23}\text{H}_{18}\text{NaO}_3^+ [\text{M}+\text{Na}]^+$ : 365.1154, found: 365.1152.

### **2-phenyl-2-(2-(thiophen-3-ylethynyl)phenoxy)acetic acid (3n)**



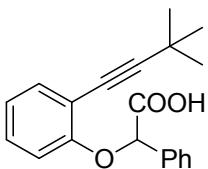
Yellow soild, mp = 177.9-182.8 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO)  $\delta_{\text{H}}$  13.33 (s, 1H), 7.82 (d,  $J = 2.0$  Hz, 1H), 7.74-7.66 (m, 3H), 7.52 -7.34 (m, 5H), 7.22 (d,  $J = 4.8$  Hz, 1H), 7.05-6.98 (m, 2H), 5.96 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, DMSO)  $\delta_{\text{C}}$  171.1, 158.1, 136.6, 133.2, 130.4, 129.9, 129.8, 129.2, 129.0, 127.5, 127.4, 122.1, 121.9, 113.7, 113.0, 89.5, 85.8, 78.0. **IR** ( $\text{cm}^{-1}$ ): 1699, 1597, 1485, 1448, 1273, 1239, 1223, 1190, 1113, 773, 750, 717, 689, 623. **HRMS** m/z (ESI) calcd for  $\text{C}_{20}\text{H}_{15}\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$ : 335.0742, found: 335.0739.

### **2-phenyl-2-(2-(thiophen-2-ylethynyl)phenoxy)acetic acid (3o)**



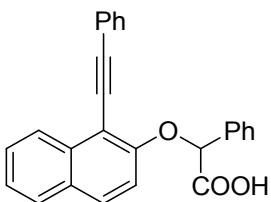
Yellow soild, mp = 168.5-174.0 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO)  $\delta_{\text{H}}$  13.37 (s, 1H), 7.74-7.66 (m, 3H), 7.52 (d,  $J = 6.5$  Hz, 1H), 7.46 (t,  $J = 7.3$  Hz, 2H), 7.44-7.36 (m, 3H), 7.15 (dd,  $J = 5.0, 3.8$  Hz, 1H), 7.06- 6.99 (m, 2H), 5.98 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, DMSO)  $\delta_{\text{C}}$  171.1, 158.0, 136.5, 132.9, 132.6, 130.7, 129.3, 129.1, 129.0, 128.3, 127.4, 122.9, 121.9, 113.5, 112.5, 90.2, 87.2, 77.9. **IR** ( $\text{cm}^{-1}$ ): 1699, 1484, 1450, 1274, 1241, 1224, 1214, 952, 751, 719, 690. **HRMS** m/z (ESI) calcd for  $\text{C}_{20}\text{H}_{15}\text{O}_3\text{S}^+ [\text{M}+\text{H}]^+$ : 335.0742, found: 335.0741.

### **2-(2-(3,3-dimethylbut-1-yn-1-yl)phenoxy)-2-phenylacetic acid (3p)**



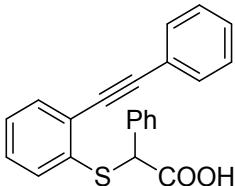
White soild, mp = 90.1-93.5 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 13.27 (s, 1H), 7.66 (d, *J* = 6.6 Hz, 2H), 7.44-7.37 (m, 3H), 7.32 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 6.95-6.88 (m, 2H), 5.84 (s, 1H), 1.29 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 170.8, 157.5, 136.2, 132.6, 129.0, 128.5, 128.3, 126.8, 121.1, 113.2, 113.0, 102.6, 77.3, 75.2, 30.8, 27.8. **IR** (cm<sup>-1</sup>): 2968, 1703, 1490, 1450, 1276, 1240, 1222, 1122, 752, 719, 692. **HRMS** m/z (ESI) calcd for C<sub>20</sub>H<sub>20</sub>NaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup>: 331.1310, found: 331.1308.

### 2-phenyl-2-((1-(phenylethynyl)naphthalen-2-yl)oxy)acetic acid (3q)



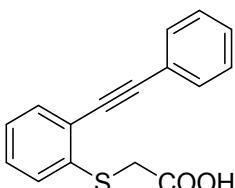
Pale yellow soild, mp = 151.9-154.7 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 8.30 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 9.1 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.75 (d, *J* = 7.2 Hz, 2H), 7.70-7.62 (m, 3H), 7.54-7.40 (m, 8H), 6.21 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 170.7, 156.9, 136.2, 133.4, 131.1, 130.4, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 127.8, 127.2, 124.7, 124.6, 123.0, 115.0, 106.4, 98.9, 84.2, 78.0. **IR** (cm<sup>-1</sup>): 1702, 1589, 1509, 1491, 1267, 1227, 803, 754, 719, 690. **HRMS** m/z (ESI) calcd for C<sub>26</sub>H<sub>18</sub>NaO<sub>3</sub><sup>+</sup> [M+Na]<sup>+</sup>: 401.1154, found: 401.1150.

### 2-phenyl-2-((2-(phenylethynyl)phenyl)thio)acetic acid (5a)



Yellow soild, mp = 90.8-93.6 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 9.88 (s, 1H), 7.57-7.50 (m, 3H), 7.46 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.35-7.32 (m, 3H), 7.31-7.27 (m, 3H), 7.25-7.16 (m, 2H), 5.19 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 175.9, 135.7, 134.8, 133.0, 132.4, 131.8, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 127.9, 126.2, 122.9, 95.5, 87.3, 54.5. **IR** (cm<sup>-1</sup>): 1710, 1598, 1492, 756, 720, 691. **HRMS** m/z (ESI) calcd for C<sub>22</sub>H<sub>17</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 345.0949, found: 345.0953.

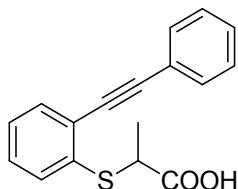
### 2-((2-(phenylethynyl)phenyl)thio)acetic acid (5b)



Pale yellow soild, mp = 117.7-120.2 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.78 (s, 1H), 7.60 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.56 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.41-7.35 (m, 3H), 7.32 (td, *J* = 7.7, 1.3 Hz, 1H), 7.25 (t, *J* = 7.2

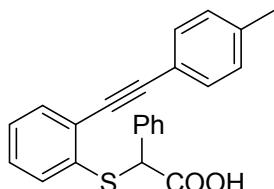
Hz, 1H), 3.80 (s, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 175.6, 137.2, 132.8, 131.7, 129.0, 128.7, 128.5, 128.4, 126.6, 123.8, 122.9, 96.0, 86.8, 35.1. **IR** (cm<sup>-1</sup>): 1710, 1598, 1491, 1295, 755, 719, 690. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 269.0636, found: 269.0635.

### 2-((2-(phenylethynyl)phenyl)thio)propanoic acid (**5c**)



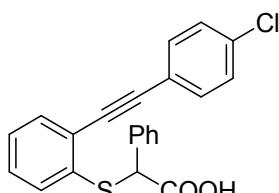
Yellow oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.65 (s, 1H), 7.62-7.57 (m, 3H), 7.54 (dd, *J* = 5.8, 3.3 Hz, 1H), 7.41-7.36 (m, 3H), 7.31-7.26 (m, 2H), 4.05 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 178.8, 135.8, 133.0, 132.3, 131.7, 128.8, 128.6, 128.4, 127.7, 126.1, 123.0, 95.3, 87.4, 44.1, 17.1. **IR** (cm<sup>-1</sup>): 3449, 1726, 1598, 1492, 1014, 757, 720, 691. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>15</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 283.0793, found: 283.0794.

### 2-phenyl-2-((2-(p-tolylethynyl)phenyl)thio)acetic acid (**5d**)



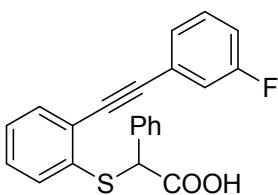
Pale yellow soild, mp = 113.5-115.3 °C. **<sup>1</sup>H NMR** (400 MHz, DMSO) δ<sub>H</sub> 13.24 (s, 1H), 7.56-7.49 (m, 3H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.40-7.30 (m, 5H), 7.29-7.21 (m, 3H), 5.41 (s, 1H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, DMSO) δ<sub>C</sub> 171.1, 138.9, 137.4, 135.9, 132.4, 131.2, 129.4, 129.1, 128.7, 128.5, 128.4, 128.2, 126.3, 122.3, 119.0, 95.5, 86.4, 53.0, 21.1. **IR** (cm<sup>-1</sup>): 1708, 1599, 1495, 816, 749, 700. **HRMS** m/z (ESI) calcd for C<sub>23</sub>H<sub>19</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 359.1106, found: 359.1103.

### 2-((2-((4-chlorophenyl)ethynyl)phenyl)thio)-2-phenylacetic acid (**5e**)



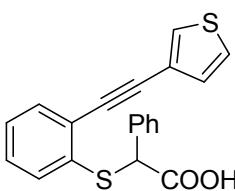
Yellow soild, mp = 124.7-128.9 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.38 (s, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.48-7.40 (m, 4H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.33-7.27 (m, 5H), 7.25-7.18 (m, 2H), 5.13 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 176.3, 135.8, 134.7, 134.6, 133.0, 132.9, 132.4, 129.0, 128.9, 128.8, 128.7, 128.6, 127.9, 125.9, 121.4, 94.3, 88.3, 54.7. **IR** (cm<sup>-1</sup>): 1709, 1583, 1491, 1092, 1014, 828, 755, 720, 696. **HRMS** m/z (ESI) calcd for C<sub>22</sub>H<sub>16</sub>ClO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 379.0560, found: 379.0560.

### 2-((2-((3-fluorophenyl)ethynyl)phenyl)thio)-2-phenylacetic acid (**5f**)



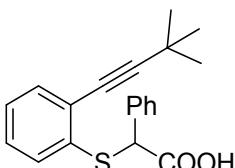
Yellow oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 11.80 (s, 1H), 7.61 (dd, J = 7.3, 1.5 Hz, 1H), 7.55 (dd, J = 6.5, 2.8 Hz, 2H), 7.47 (d, J = 8.6 Hz, 1H), 7.40-7.32 (m, 5H), 7.30-7.23 (m, 3H), 7.10 (t, J = 8.0 Hz, 1H), 5.23 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 177.0, 162.4 (d, J = 246.9 Hz), 136.1, 134.8, 133.2, 132.3, 130.1 (d, J = 8.6 Hz), 129.2, 128.9, 128.8, 128.7, 128.0, 127.7 (d, J = 2.5 Hz), 125.7, 124.8 (d, J = 9.6 Hz), 118.5 (d, J = 22.6 Hz), 116.0 (d, J = 21.1 Hz), 94.2, 88.3, 54.8. **IR** (cm<sup>-1</sup>): 1709, 1608, 1579, 1489, 1455, 1435, 1287, 1208, 943, 872, 785, 755, 681. **HRMS** m/z (ESI) calcd for C<sub>22</sub>H<sub>16</sub>FO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 363.0855, found: 363.0850.

### 2-phenyl-2-((2-(thiophen-3-ylethynyl)phenyl)thio)acetic acid (5g)



Pale yellow solid, mp = 126.3-128.6 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 9.78 (s, 1H), 7.56-7.49 (m, 2H), 7.45 (dd, J = 6.1, 2.4 Hz, 2H), 7.37 (d, J = 7.7 Hz, 1H), 7.32-7.27 (m, 4H), 7.22 (d, J = 7.4 Hz, 1H), 7.20-7.15 (m, 2H), 5.18 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 176.1, 135.5, 134.8, 132.9, 132.5, 129.9, 129.3, 128.8, 128.7, 128.6, 128.5, 127.9, 126.3, 125.5, 122.0, 90.7, 86.9, 54.5. **IR** (cm<sup>-1</sup>): 3434, 1708, 1583, 1495, 756, 720, 696. **HRMS** m/z (ESI) calcd for C<sub>20</sub>H<sub>15</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 351.0513, found: 351.0511.

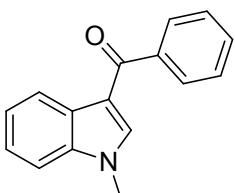
### 2-((2-(3,3-dimethylbut-1-yn-1-yl)phenyl)thio)-2-phenylacetic acid (5h)



White oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 10.35 (s, 1H), 7.44 (d, J = 6.5 Hz, 2H), 7.37 (d, J = 7.5 Hz, 1H), 7.31-7.22 (m, 4H), 7.12 (t, J = 7.4 Hz, 1H), 7.06 (t, J = 7.4 Hz, 1H), 5.16 (s, 1H), 1.33 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 176.5, 135.3, 135.1, 132.9, 131.9, 128.7, 128.6, 128.4, 128.0, 127.5, 126.6, 105.0, 54.3, 30.9, 28.3. **IR** (cm<sup>-1</sup>): 2969, 1708, 1599, 1583, 1462, 1385, 1292, 751, 736, 697. **HRMS** m/z (ESI) calcd for C<sub>20</sub>H<sub>21</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 325.1262, found: 325.1259.

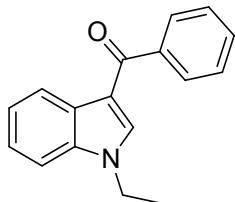
## 6. Characterization of products

### (1-methyl-1H-indol-3-yl)(phenyl)methanone (2a)



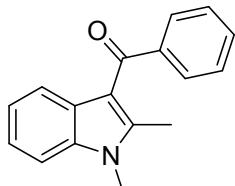
Yellow solid (13.7 mg, 58%), mp = 110.5-111.6 °C. **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.46-8.39 (m, 1H), 7.81 (d, *J* = 7.4 Hz, 2H), 7.56-7.45 (m, 4H), 7.39-7.32 (m, 3H), 3.83 (s, 3H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 190.9, 141.0, 138.0, 137.6, 131.1, 128.7, 128.3, 127.2, 123.7, 122.8, 122.7, 115.6, 109.7, 33.6. **IR** (cm<sup>-1</sup>): 746, 874, 1073, 1125, 1232, 1368, 1465, 1524, 1616, 2933, 3054, 3110. **GC-MS** (EI): 235.2, 158.1, 130.1, 103.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>13</sub>NNaO<sup>+</sup> [M+Na]<sup>+</sup>: 258.0895, found: 258.0887.

**(1-ethyl-1H-indol-3-yl)(phenyl)methanone (2b)**



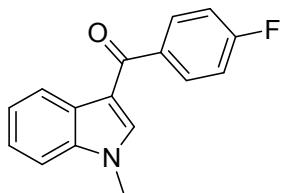
Yellow oil (14.0 mg, 56%). **1H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.40-8.31 (m, 1H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.51 (s, 1H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.36-7.31 (m, 1H), 7.30-7.25 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.3 Hz, 3H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 190.9, 141.0, 136.6, 136.3, 131.1, 128.7, 128.3, 127.4, 123.6, 122.9, 122.7, 115.7, 109.8, 41.8, 15.3. **IR** (cm<sup>-1</sup>): 716, 746, 874, 1221, 1384, 1520, 1622, 2933, 2978. **GC-MS** (EI): 249.1, 234.1, 220.1, 192.0, 172.1, 144.0, 116.1, 105.0, 89.0, 77.1. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>15</sub>NNaO<sup>+</sup> [M+Na]<sup>+</sup>: 272.1051, found: 272.1048.

**(1,2-dimethyl-1H-indol-3-yl)(phenyl)methanone (2e)**



Yellow solid (14.3 mg, 57%), mp = 134.3-135.8 °C. **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.79 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.34 (dd, *J* = 7.9, 4.7 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 3.76 (s, 3H), 2.62 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 192.9, 144.8, 141.5, 136.6, 131.5, 129.1, 128.3, 127.1, 122.1, 121.4, 121.0, 113.6, 109.2, 29.7, 12.6. **IR** (cm<sup>-1</sup>): 728, 754, 1057, 1227, 1382, 1403, 1446, 1471, 1520, 1614, 2938, 3051. **GC-MS** (EI): 249.2, 248.2, 232.2, 172.1, 143.1, 115.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>15</sub>NNaO<sup>+</sup> [M+Na]<sup>+</sup>: 272.1051, found: 272.1051.

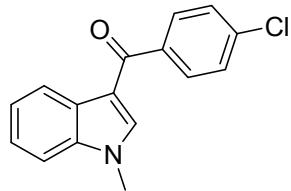
**(4-fluorophenyl)(1-methyl-1H-indol-3-yl)methanone (2f)**



Yellow solid (15.2 mg, 60%), mp = 138.1-138.6 °C. **1H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.33-8.28 (m, 1H), 7.79-7.71 (m, 2H), 7.43 (s, 1H), 7.32-7.25 (m, 3H), 7.08 (t, *J* = 8.6 Hz, 2H), 3.77 (s, 3H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 189.4, 164.6 (d, *J* = 251.6 Hz), 137.6, 137.5, 137.1 (d, *J* = 2.5 Hz), 131.0 (d, *J* = 8.8 Hz), 127.2, 123.8, 122.8, 122.7, 115.5, 115.3 (d, *J* = 21.4 Hz), 109.7, 33.6. **IR** (cm<sup>-1</sup>): 750, 773, 844, 881, 1079, 1128, 1237, 1372, 1523, 1619, 2927, 3046. **GC-MS** (EI): 253.1, 183.1, 158.1, 130.1, 112.6, 95.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>12</sub>FNNaO<sup>+</sup> [M+Na]<sup>+</sup>:

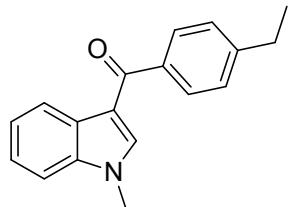
276.0801, found: 276.0793.

**(4-chlorophenyl)(1-methyl-1H-indol-3-yl)methanone (2g)**



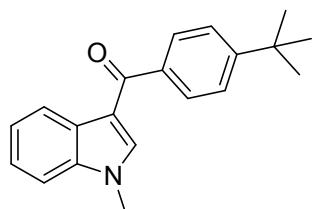
White solid (16.9 mg, 63%), mp = 144.0-144.7 °C. **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.49-8.35 (m, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.53 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.42-7.34 (m, 3H), 3.88 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 189.4, 139.2, 137.7, 137.6, 137.3, 130.1, 128.6, 127.1, 123.8, 122.9, 122.7, 115.4, 109.7, 33.7. **IR** (cm<sup>-1</sup>): 754, 879, 1086, 1234, 1371, 1389, 1470, 1522, 1589, 1624, 2934, 3053, 3086, 3112. **GC-MS** (EI): 269.1, 234.1, 158.1, 130.1, 103.0, 77.1. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>12</sub>CINaO<sup>+</sup> [M+Na]<sup>+</sup>: 292.0505, found: 292.0504.

**(4-ethylphenyl)(1-methyl-1H-indol-3-yl)methanone (2h)**



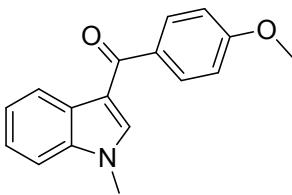
Yellow oil (12.6 mg, 48%). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.50-8.43 (m, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.57 (s, 1H), 7.41-7.30 (m, 5H), 3.86 (s, 3H), 2.77 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 190.7, 147.8, 138.4, 137.7, 137.5, 129.0, 127.8, 127.3, 123.6, 122.8, 122.6, 115.7, 109.6, 33.6, 28.9, 15.5. **IR** (cm<sup>-1</sup>): 748, 879, 1234, 1369, 1464, 1524, 1620, 1695, 2874, 2932, 2965, 3051. **GC-MS** (EI): 263.1, 246.1, 234.1, 158.1, 130.1, 103.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>18</sub>H<sub>17</sub>NNaO<sup>+</sup>[M+Na]<sup>+</sup>: 286.1208, found: 286.1207.

**(4-(tert-butyl)phenyl)(1-methyl-1H-indol-3-yl)methanone (2i)**



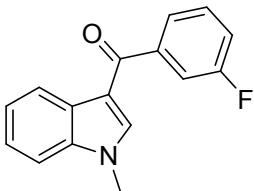
Yellow oil (15.9 mg, 55%). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.51-8.46 (m, 1H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.59 (s, 1H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.40-7.35 (m, 3H), 3.86 (s, 3H), 1.41 (s, 9H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 189.6, 153.5, 137.1, 136.7, 136.4, 127.6, 126.2, 124.2, 122.5, 121.7, 121.6, 114.6, 108.5, 33.9, 32.5, 30.2. **IR** (cm<sup>-1</sup>): 745, 836, 881, 1235, 1370, 1464, 1523, 1614, 2962. **GC-MS** (EI): 291.1, 276.1, 248.1, 234.1, 220.1, 158.0, 145.1, 130.1, 115.1, 103.0, 77.1. **HRMS** m/z (ESI) calcd for C<sub>20</sub>H<sub>21</sub>NNaO<sup>+</sup>[M+Na]<sup>+</sup>: 314.1521, found: 314.1517.

**(4-methoxyphenyl)(1-methyl-1H-indol-3-yl)methanone (2j)**



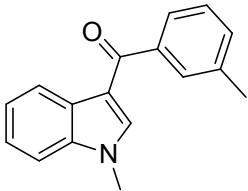
Yellow solid (20.6 mg, 78%), mp = 135.7-137.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.42-8.38 (m, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.57 (s, 1H), 7.42-7.32 (m, 3H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H), 3.87 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 189.8, 162.2, 137.5, 137.1, 133.5, 130.9, 127.3, 123.5, 122.7, 122.5, 115.7, 113.5, 109.6, 55.5, 33.6. **IR** (cm<sup>-1</sup>): 754, 832, 1029, 1176, 1248, 1487, 1512, 1605, 1721, 2837, 2957. **GC-MS** (EI): 265.1, 250.1, 234.1, 222.1, 158.0, 130.1, 118.6, 103.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>15</sub>NNaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 288.1000, found: 288.1002.

### (3-fluorophenyl)(1-methyl-1H-indol-3-yl)methanone (2k)



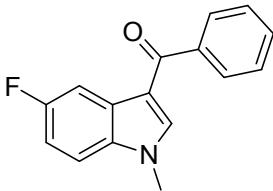
Yellow solid (17.0 mg, 67%), mp = 121.2-122.0 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.50-8.40 (m, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.56-7.44 (m, 3H), 7.42-7.35 (m, 3H), 7.29-7.23 (m, 1H), 3.87 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 189.1 (d, *J* = 1.5 Hz), 162.5 (d, *J* = 247.4 Hz), 143.0 (d, *J* = 6.0 Hz), 138.0, 137.6, 130.0 (d, *J* = 7.9 Hz), 127.1, 124.4 (d, *J* = 2.4 Hz), 123.9, 122.9, 122.7, 118.0 (d, *J* = 21.5 Hz), 115.6 (d, *J* = 22.2 Hz), 115.2, 109.8, 33.7. **IR** (cm<sup>-1</sup>): 748, 769, 829, 1208, 1245, 1371, 1525, 1578, 1623, 2936, 3066. **GC-MS** (EI): 253.1, 158.1, 130.1, 103.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>12</sub>FNNaO<sup>+</sup> [M+Na]<sup>+</sup>: 276.0801, found: 276.0798.

### (1-methyl-1H-indol-3-yl)(m-tolyl)methanone (2l)



Yellow oil (14.1 mg, 57%). **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.49-8.43 (m, 1H), 7.65 (s, 1H), 7.64-7.59 (m, 1H), 7.54 (s, 1H), 7.41-7.35 (m, 5H), 3.86 (s, 3H), 2.46 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ 190.0, 139.9, 137.1, 136.9, 136.5, 130.8, 128.1, 127.0, 126.2, 124.8, 122.6, 121.7, 121.6, 114.6, 108.6, 32.5, 20.4. **IR** (cm<sup>-1</sup>): 747, 1243, 1368, 1464, 1522, 1621, 2917. **GC-MS** (EI): 249.1, 234.1, 158.0, 130.1, 103.1, 91.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>15</sub>NNaO<sup>+</sup> [M+Na]<sup>+</sup>: 272.1051, found: 272.1041.

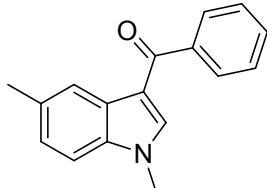
### (5-fluoro-1-methyl-1H-indol-3-yl)(phenyl)methanone (2m)



Yellow oil (15.1 mg, 60%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.13 (dd, *J* = 9.7, 2.5 Hz, 1H), 7.80 (d, *J* = 7.0 Hz, 2H), 7.60-7.54 (m, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.28 (dd, *J* = 9.0, 4.1 Hz 1H), 7.08 (td, *J* = 9.0, 2.5 Hz 1H), 3.83 (s, 3H). **<sup>13</sup>C NMR**

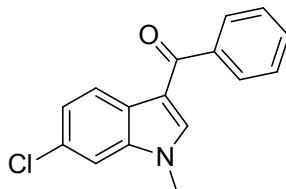
**NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 189.5, 158.8 (d, *J* = 237.9 Hz), 139.5, 137.9, 133.0, 131.2, 127.5, 127.3, 126.8 (d, *J* = 11.1 Hz), 114.3 (d, *J* = 4.4 Hz), 110.9 (d, *J* = 26.5 Hz), 109.5 (d, *J* = 9.8 Hz), 106.9 (d, *J* = 25.0 Hz), 32.8. **IR** (cm<sup>-1</sup>): 717, 842, 1111, 1197, 1259, 1368, 1479, 1524, 1615, 1681, 2926, 3060, 3112. **GC-MS** (EI): 253.1, 224.1, 176.0, 148.1, 101.0, 77.1. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>12</sub>NFNaO<sup>+</sup>[M+Na]<sup>+</sup>: 276.0801, found: 276.0793.

### (1,5-dimethyl-1H-indol-3-yl)(phenyl)methanone (2n)



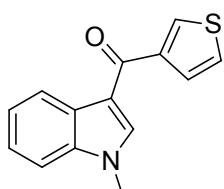
Yellow oil (14.0 mg, 56%). **1H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.27 (s, 1H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.48-7.44 (m, 3H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 3.80 (s, 3H), 2.51 (s, 3H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 190.9, 141.1, 138.1, 136.0, 132.5, 131.0, 128.7, 128.3, 127.4, 125.2, 122.5, 115.1, 109.3, 33.6, 21.6. **IR** (cm<sup>-1</sup>): 718, 837, 1237, 1364, 1524, 1616, 2917, 3056. **GC-MS** (EI): 249.2, 234.1, 220.2, 204.1, 190.1, 172.2, 143.2, 115.1, 77.2. **HRMS** m/z (ESI) calcd for C<sub>17</sub>H<sub>15</sub>NNaO<sup>+</sup>[M+Na]<sup>+</sup>: 272.1051, found: 272.1053.

### (6-chloro-1-methyl-1H-indol-3-yl)(phenyl)methanone (2o)



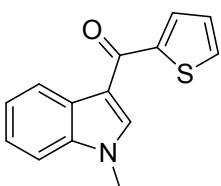
Yellow solid (13.8 mg, 51%), mp = 126.6-127.5 °C. **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.36 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 7.0 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.54-7.48 (m, 3H), 7.38 (d, *J* = 1.6 Hz, 1H), 7.32 (dd, *J* = 8.5, 1.7 Hz, 1H), 3.83 (s, 3H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 190.7, 140.5, 138.2, 138.0, 131.3, 129.6, 128.7, 128.4, 125.7, 123.7, 123.3, 115.7, 109.8, 33.7. **IR** (cm<sup>-1</sup>): 719, 814, 886, 1072, 1227, 1365, 1464, 1525, 1624, 2933, 3054. **GC-MS** (EI): 269.1, 252.1, 192.1, 164.1, 128.1, 102.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>12</sub>NClNaO<sup>+</sup>[M+Na]<sup>+</sup>: 292.0505, found: 292.0494.

### (1-methyl-1H-indol-3-yl)(thiophen-3-yl)methanone (2p)



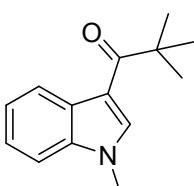
Yellow oil (13.3 mg, 55%). **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.48-8.42 (m, 1H), 7.91 (d, *J* = 2.7 Hz, 1H), 7.69 (s, 1H), 7.61 (d, *J* = 5.0 Hz, 1H), 7.42-7.33 (m, 4H), 3.87 (s, 3H). **13C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 184.2, 143.7, 137.5, 136.8, 129.7, 128.2, 127.1, 126.0, 123.7, 122.7, 122.6, 116.3, 109.7, 33.6. **IR** (cm<sup>-1</sup>): 747, 768, 841, 1238, 1465, 1524, 1609, 2931, 3105. **GC-MS** (EI): 241.0, 213.1, 198.0, 171.0, 158.0, 130.1, 103.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>14</sub>H<sub>11</sub>NNaOS<sup>+</sup>[M+Na]<sup>+</sup>: 264.0459, found: 264.0451.

### (1-methyl-1H-indol-3-yl)(thiophen-2-yl)methanone (2q)



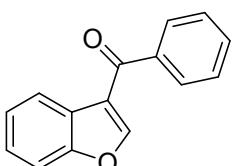
Brown solid (15.1 mg, 63%), mp = 136.1-137.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.49-8.42 (m, 1H), 7.82 (s, 1H), 7.76 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.63 (d, *J* = 4.9 Hz, 1H), 7.40-7.34 (m, 3H), 7.18 (dd, *J* = 4.8, 3.8 Hz, 1H), 3.89 (s, 3H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 181.4, 145.4, 137.4, 136.1, 131.3, 131.0, 127.6, 127.3, 123.7, 122.6, 115.4, 109.7, 33.6. **IR** (cm<sup>-1</sup>): 734, 747, 811, 1237, 1370, 1464, 1521, 1572, 1586, 2931, 3046, 3077, 3109. **GC-MS** (EI): 241.1, 224.1, 213.1, 158.1, 130.1, 103.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>14</sub>H<sub>11</sub>NNaOS<sup>+</sup>[M+Na]<sup>+</sup>: 264.0459, found: 264.0459.

### 2,2-dimethyl-1-(1-methyl-1H-indol-3-yl)propan-1-one (2r)



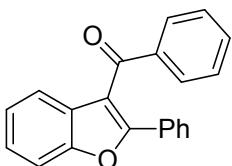
Yellow solid (6.2 mg, 29%), mp = 126.0-127.2 °C. **<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.52 (d, *J* = 6.9 Hz, 1H), 7.79 (s, 1H), 7.34-7.28 (m, 3H), 3.85 (s, 3H), 1.42 (s, 9H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 202.1, 136.5, 134.4, 128.3, 123.4, 123.2, 122.5, 112.7, 109.2, 44.1, 33.5, 29.0. **IR** (cm<sup>-1</sup>): 749, 899, 1083, 1360, 1469, 1523, 1624, 2967. **GC-MS** (EI): 215.1, 172.1, 158.1, 130.1, 103.1, 77.1. **HRMS** m/z (ESI) calcd for C<sub>14</sub>H<sub>17</sub>NNaO<sup>+</sup>[M+Na]<sup>+</sup>: 238.1208, found: 238.1207.

### Benzofuran-3-yl(phenyl)methanone (4a)



Pale yellow soild (5.8 mg, 26%), mp = 58.2-60.9 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.27-8.22 (m, 1H), 8.09 (s, 1H), 7.89 (d, *J* = 7.0 Hz, 2H), 7.64-7.50 (m, 4H), 7.44-7.38 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 190.3, 155.6, 152.3, 139.3, 132.5, 128.8, 128.7, 125.9, 125.2, 124.6, 122.9, 121.3, 111.6. **IR** (cm<sup>-1</sup>): 1646, 1547, 1479, 1449, 1286, 1132, 886, 749, 715, 698. **GC-MS** (EI): 77.1, 89.1, 145.1, 165.1, 194.1, 222.1. **HRMS** m/z (ESI) calcd for C<sub>15</sub>H<sub>11</sub>O<sub>2</sub><sup>+</sup>[M+H]<sup>+</sup>: 223.0759, found: 223.0760.

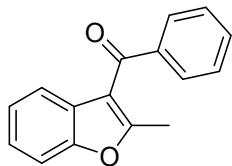
### Phenyl(2-phenylbenzofuran-3-yl)methanone (4b)



Pale yellow soild (16.3 mg, 55%), mp = 90.5-93.9 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.88 (d, *J* = 7.1 Hz, 2H), 7.76-7.67 (m, 2H), 7.61 (t, *J* = 9.0 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.43-7.28 (m, 7H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 192.4, 157.7, 153.9, 137.8, 133.2, 129.9, 129.7, 129.5, 128.5, 128.4, 125.4, 123.9, 121.5, 116.2, 111.3. **IR** (cm<sup>-1</sup>): 1658,

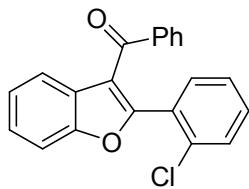
1454, 1235, 884, 747, 718, 693. **GC-MS** (EI): 51.2, 77.2, 105.1, 165.1, 221.1, 298.1. **HRMS** m/z (ESI) calcd for C<sub>21</sub>H<sub>15</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 299.1072, found: 299.1073.

**(2-methylbenzofuran-3-yl)(phenyl)methanone (4c)**



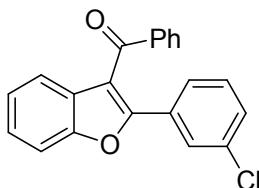
Yellow oil (2.3 mg, 10%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.86-7.79 (m, 2H), 7.62-7.57 (m, 1H), 7.52-7.45 (m, 3H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.30-7.26 (m, 1H), 7.19 (td, *J* = 7.8, 1.0 Hz, 1H), 2.54 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 192.0, 162.0, 153.7, 139.4, 132.7, 129.1, 128.5, 127.0, 124.1, 123.6, 121.4, 117.0, 110.9, 14.7. **IR** (cm<sup>-1</sup>): 3462, 1740, 1648, 1578, 1454, 1386, 1242, 1179, 899, 749, 699. **GC-MS** (EI): 77.1, 105.1, 159.1, 236.1. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>13</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 237.0916, found: 237.0915.

**(2-(2-chlorophenyl)benzofuran-3-yl)(phenyl)methanone (4d)**



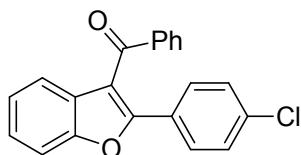
Pale yellow soild (14.9 mg, 45%), mp = 104.9-107.1 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.84 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.1 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.44-7.29 (m, 5H), 7.26-7.21 (m, 3H), 7.17 (td, *J* = 7.5, 1.3 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 191.7, 156.9, 154.4, 138.1, 133.8, 132.6, 132.4, 131.1, 129.9, 129.5, 129.4, 128.0, 127.2, 126.6, 125.7, 124.2, 122.1, 118.9, 111.5. **IR** (cm<sup>-1</sup>): 1647, 1574, 1449, 1378, 1043, 884, 750, 697. **GC-MS** (EI): 77.1, 105.2, 148.7, 163.1, 220.1, 297.1, 332.1. **HRMS** m/z (ESI) calcd for C<sub>21</sub>H<sub>14</sub>ClO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 333.0682, found: 333.0686.

**(2-(3-chlorophenyl)benzofuran-3-yl)(phenyl)methanone (4e)**



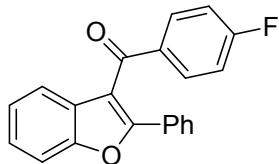
Pale yellow soild (17.9 mg, 54%), mp = 90.2-91.4 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.84 (d, *J* = 7.7 Hz, 2H), 7.74 (s, 1H), 7.60-7.50 (m, 4H), 7.37 (q, *J* = 7.6 Hz, 3H), 7.30-7.24 (m, 2H), 7.20 (t, *J* = 7.9 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 192.1, 155.7, 153.8, 137.7, 134.5, 133.5, 131.1, 129.8, 129.7, 129.6, 128.6, 128.2, 128.1, 126.5, 125.8, 124.0, 121.7, 117.1, 111.4. **IR** (cm<sup>-1</sup>): 3437, 1656, 1450, 1234, 888, 748, 696. **GC-MS** (EI): 77.2, 105.2, 163.1, 199.1, 200.1, 255.1, 332.1. **HRMS** m/z (ESI) calcd for C<sub>21</sub>H<sub>14</sub>ClO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 333.0682, found: 333.0687.

**(2-(4-chlorophenyl)benzofuran-3-yl)(phenyl)methanone (4f)**



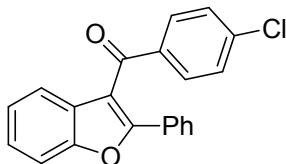
Pale yellow soild (18.4 mg, 55%), mp = 105.0-110.3 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.84 (d, *J* = 7.1 Hz, 2H), 7.64 (m, 2H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.40-7.34 (m, 3H), 7.30-7.23 (m, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 192.2, 156.2, 153.8, 137.7, 135.9, 133.5, 129.8, 129.5, 128.8, 128.6, 128.3, 127.9, 125.6, 124.0, 121.6, 116.6, 111.3. **IR** (cm<sup>-1</sup>): 1656, 1598, 1578, 1488, 1450, 1094, 884, 748, 695. **GC-MS** (EI): 77.2, 105.2, 163.1, 255.1, 332.1. **HRMS** m/z (ESI) calcd for C<sub>21</sub>H<sub>14</sub>ClO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 333.0682, found: 333.0690.

#### (4-fluorophenyl)(2-phenylbenzofuran-3-yl)methanone (4g)



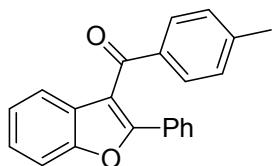
Pale yellow soild (15.8 mg, 50%), mp = 132.0-136.8°C (uncorrected). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.86 (dd, *J* = 8.8, 5.5 Hz, 2H), 7.66 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 2H), 7.40-7.35 (m, 1H), 7.34-7.26 (m, 4H), 6.99 (t, *J* = 8.6 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 190.7, 165.8 (d, *J* = 255.3 Hz), 157.7, 153.9, 134.1 (d, *J* = 2.5 Hz), 132.5 (d, *J* = 9.5 Hz), 129.9, 129.3, 128.5, 128.4, 128.3, 125.5, 124.0, 121.4, 115.9, 115.6 (d, *J* = 22.0 Hz), 111.3. **IR** (cm<sup>-1</sup>): 3467, 1646, 1598, 1236, 1154, 888, 764, 749, 693, 603. **GC-MS** (EI): 95.1, 123.1, 165.1, 221.1, 316.1. **HRMS** m/z (ESI) calcd for C<sub>21</sub>H<sub>14</sub>FO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 317.0978, found: 317.0980.

#### (4-chlorophenyl)(2-phenylbenzofuran-3-yl)methanone (4h)



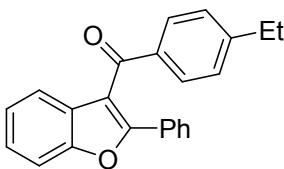
White soild (18.1 mg, 55%), mp = 115.3-117.9 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.80 (d, *J* = 8.5 Hz, 2H), 7.69 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.61 (t, *J* = 8.1 Hz, 2H), 7.43-7.29 (m, 7H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 191.0, 157.9, 153.9, 139.6, 136.2, 131.2, 130.0, 129.3, 128.8, 128.6, 128.5, 128.3, 125.5, 124.0, 121.4, 115.8, 111.4. **IR** (cm<sup>-1</sup>): 1654, 1588, 1454, 1372, 1239, 1088, 885, 749, 694. **GC-MS** (EI): 111.1, 139.1, 165.1, 221.1, 332.1. **HRMS** m/z (ESI) calcd for C<sub>21</sub>H<sub>14</sub>ClO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 333.0682, found: 333.0675.

#### (2-phenylbenzofuran-3-yl)(p-tolyl)methanone (4i)



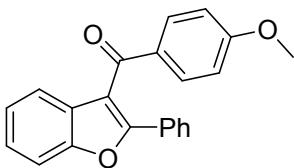
Pale yellow soild (16.5 mg, 53%), mp = 98.9-102.1 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.77 (d, *J* = 8.2 Hz, 2H), 7.73-7.67 (m, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.37-7.29 (m, 4H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 192.1, 156.9, 153.8, 144.3, 135.2, 130.1, 129.7, 129.5, 129.2, 128.6, 128.5, 128.2, 125.3, 123.8, 121.4, 116.4, 111.3, 21.8. **IR** (cm<sup>-1</sup>): 1655, 1605, 1454, 887, 747, 693. **GC-MS** (EI): 91.2, 119.2, 221.1, 297.1, 312.2. **HRMS** m/z (ESI) calcd for C<sub>22</sub>H<sub>17</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 313.1229, found: 313.1231.

#### (4-ethylphenyl)(2-phenylbenzofuran-3-yl)methanone (4j)



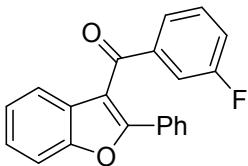
Pale yellow oil (16.0 mg, 49%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.82 (d, *J* = 8.2 Hz, 2H), 7.74 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.41-7.36 (m, 1H), 7.36-7.31 (m, 3H), 7.31-7.26 (m, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 192.1, 157.0, 153.8, 150.4, 135.4, 130.2, 129.6, 129.5, 128.6, 128.4, 128.2, 128.0, 125.3, 123.7, 121.5, 116.4, 111.2, 29.0, 15.2. **IR** (cm<sup>-1</sup>): 3467, 1655, 1605, 1454, 1257, 1237, 888, 748, 707, 693. **GC-MS** (EI): 133.2, 165.1, 222.1, 297.1, 326.2. **HRMS** m/z (ESI) calcd for C<sub>23</sub>H<sub>19</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 327.1385, found: 327.1389.

#### (4-methoxyphenyl)(2-phenylbenzofuran-3-yl)methanone (4k)



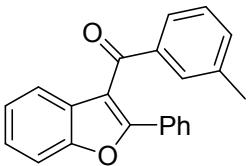
Pale yellow oil (16.7 mg, 51%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.87 (d, *J* = 8.9 Hz, 2H), 7.75-7.70 (m, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.37-7.30 (m, 4H), 7.26-7.22 (m, 1H), 6.82 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 190.9, 163.9, 156.3, 153.8, 132.4, 130.6, 129.6, 128.7, 128.5, 128.1, 125.3, 123.7, 121.3, 116.4, 113.8, 111.2, 55.5. **IR** (cm<sup>-1</sup>): 3462, 1650, 1599, 1258, 1246, 1169, 888, 750. **GC-MS** (EI): 77.2, 135.2, 222.1, 328.2. **HRMS** m/z (ESI) calcd for C<sub>22</sub>H<sub>17</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 329.1178, found: 329.1172.

#### (3-fluorophenyl)(2-phenylbenzofuran-3-yl)methanone (4l)



Pale yellow oil (16.7 mg, 53%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.69-7.50 (m, 6H), 7.41-7.36 (m, 1H), 7.34-7.23 (m, 5H), 7.16 (tdd, *J* = 8.2, 2.5, 0.8 Hz, 1H). **<sup>13</sup>C NMR** (151 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 191.0 (d, *J* = 1.9 Hz), 162.7 (d, *J* = 248.3 Hz), 158.4, 153.9, 140.0 (d, *J* = 6.5 Hz), 130.0 (d, *J* = 9 Hz), 129.9, 129.3, 128.6, 128.5, 128.2, 125.7 (d, *J* = 2.5 Hz), 125.6, 124.1, 121.5, 120.0 (d, *J* = 21.7 Hz), 116.3 (d, *J* = 22.7 Hz), 115.8, 111.3. **IR** (cm<sup>-1</sup>): 3444, 1649, 1587, 1442, 1376, 1258, 1200, 1110, 1070, 816, 748, 693. **GC-MS** (EI): 95.2, 123.1, 165.1, 222.1, 316.2. **HRMS** m/z (ESI) calcd for C<sub>21</sub>H<sub>14</sub>FO<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 317.0978, found: 317.0981.

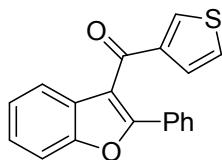
#### (2-phenylbenzofuran-3-yl)(m-tolyl)methanone (4m)



Pale yellow oil (15.2 mg, 49%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.71-7.65 (m, 3H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* =

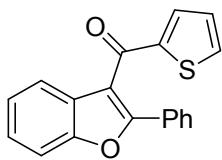
8.1 Hz, 2H), 7.38-7.33 (m, 1H), 7.32-7.24 (m, 5H), 7.20 (t,  $J$  = 7.6 Hz, 1H), 2.27 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  192.6, 157.6, 153.8, 138.3, 137.8, 134.0, 130.3, 129.7, 129.6, 128.5, 128.4, 128.3, 127.2, 125.3, 123.8, 121.5, 116.3, 111.2, 21.2. **IR** ( $\text{cm}^{-1}$ ): 3061, 1658, 1584, 1560, 1454, 1374, 1257, 748, 693. **GC-MS** (EI): 65.2, 91.2, 119.2, 165.1, 221.1, 312.2. **HRMS** m/z (ESI) calcd for  $\text{C}_{22}\text{H}_{17}\text{O}_2^+$  [M+H] $^+$ : 313.1229, found: 313.1227.

#### (2-phenylbenzofuran-3-yl)(thiophen-3-yl)methanone (4n)



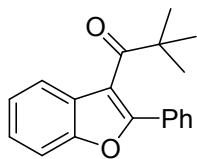
Pale yellow oil (14.5 mg, 48%).  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.83 (dd,  $J$  = 2.9, 1.2 Hz, 1H), 7.74-7.69 (m, 2H), 7.65 (d,  $J$  = 7.8 Hz, 1H), 7.57 (d,  $J$  = 8.2 Hz, 1H), 7.52 (dd,  $J$  = 5.1, 1.1 Hz, 1H), 7.38-7.24 (m, 5H), 7.22 (dd,  $J$  = 5.1, 2.9 Hz, 1H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  185.6, 156.9, 153.8, 142.3, 135.0, 129.8, 129.5, 128.6, 128.4, 128.3, 127.8, 126.3, 125.5, 123.9, 121.4, 117.1, 111.3. **IR** ( $\text{cm}^{-1}$ ): 3104, 1641, 1561, 1510, 1454, 1413, 1242, 1070, 848, 748, 694. **GC-MS** (EI): 39.2, 83.1, 111.1, 165.1, 221.1, 275.1, 304.2. **HRMS** m/z (ESI) calcd for  $\text{C}_{19}\text{H}_{13}\text{O}_2\text{S}^+$  [M+H] $^+$ : 305.0636, found: 305.0633.

#### (2-phenylbenzofuran-3-yl)(thiophen-2-yl)methanone (4o)



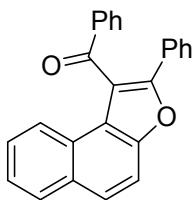
Pale yellow soild (16.4 mg, 54%), mp = 79.4-82.9 °C.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.76 (dd,  $J$  = 6.5, 3.2 Hz, 2H), 7.66-7.61 (m, 2H), 7.58 (d,  $J$  = 8.2 Hz, 1H), 7.45 (dd,  $J$  = 3.8, 1.0 Hz, 1H), 7.39-7.32 (m, 4H), 7.28 (t,  $J$  = 7.9 Hz, 1H), 6.93 (dd,  $J$  = 4.8, 3.9 Hz, 1H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  184.0, 156.4, 153.8, 144.4, 135.2, 134.8, 129.8, 129.5, 128.6, 128.3, 128.2, 128.1, 125.5, 123.8, 121.2, 116.3, 111.3. **IR** ( $\text{cm}^{-1}$ ): 1630, 1454, 1411, 1244, 815, 747, 728, 690. **GC-MS** (EI): 39.2, 111.1, 165.1, 221.1, 271.1, 304.1. **HRMS** m/z (ESI) calcd for  $\text{C}_{19}\text{H}_{13}\text{O}_2\text{S}^+$  [M+H] $^+$ : 305.0636, found: 305.0634.

#### 2,2-dimethyl-1-(2-phenylbenzofuran-3-yl)propan-1-one (4p)



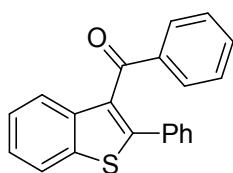
White soild (6.2 mg, 22%), mp = 93.9-96.8 °C.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{H}}$  7.68 (dd,  $J$  = 8.2, 1.5 Hz, 2H), 7.53 (d,  $J$  = 8.2 Hz, 1H), 7.46-7.39 (m, 4H), 7.35-7.30 (m, 1H), 7.28-7.23 (m, 1H), 1.17 (s, 9H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta_{\text{C}}$  211.2, 153.7, 151.2, 130.5, 129.4, 128.8, 128.6, 127.1, 125.1, 123.4, 120.5, 116.9, 111.3, 46.5, 26.9. **IR** ( $\text{cm}^{-1}$ ): 3437, 2969, 1687, 1589, 1455, 1259, 1065, 922, 746, 696. **GC-MS** (EI): 28.2, 165.1, 221.1, 278.1. **HRMS** m/z (ESI) calcd for  $\text{C}_{19}\text{H}_{19}\text{O}_2^+$  [M+H] $^+$ : 279.1385, found: 279.1378.

#### Phenyl(2-phenylnaphtho[2,1-b]furan-1-yl)methanone (4q)



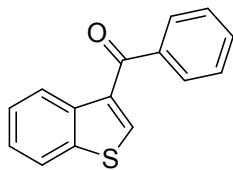
Yellow oil (11.1 mg, 32%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.04 (d, *J* = 7.3 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.84-7.79 (m, 2H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.44-7.41 (m, 1H), 7.41-7.35 (m, 3H), 7.34-7.26 (m, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 195.2, 152.9, 151.7, 137.3, 134.2, 131.0, 130.1, 129.6, 129.1, 129.0, 128.9, 128.7, 127.3, 127.0, 126.9, 126.7, 124.8, 123.9, 122.6, 117.5, 112.1. **IR** (cm<sup>-1</sup>): 2968, 1724, 1594, 1491, 1362, 1284, 1198, 950, 750. **HRMS** m/z (ESI) calcd for C<sub>25</sub>H<sub>16</sub>NaO<sub>2</sub><sup>+</sup> [M+Na]<sup>+</sup>: 371.1048, found: 371.1050.

### Phenyl(2-phenylbenzo[b]thiophen-3-yl)methanone (6a)



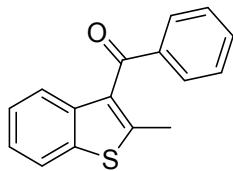
Pale yellow soild (15.4 mg, 49%), mp = 110.8-113.3°C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.95-7.89 (m, 1H), 7.83-7.74 (m, 3H), 7.487.38 (m, 5H), 7.32-7.21 (m, 5H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 194.3, 146.5, 139.7, 138.9, 137.5, 133.3, 131.5, 129.9, 129.4, 128.8, 128.6, 128.3, 125.2, 125.1, 123.7, 122.1. **IR** (cm<sup>-1</sup>): 3455, 1650, 1596, 1348, 1232, 753, 727, 694. **GC-MS** (EI): 77.1, 105.1, 165.1, 208.1, 237.1, 314.1. **HRMS** m/z (ESI) calcd for C<sub>21</sub>H<sub>15</sub>OS<sup>+</sup> [M+H]<sup>+</sup>: 315.0844, found: 315.0840.

### Benzob[**b**]thiophen-3-yl(phenyl)methanone (6b)



Yellow oil (12.4 mg, 52%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 8.57 (d, *J* = 7.9 Hz, 1H), 8.00 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.89-7.85 (m, 2H), 7.63-7.57 (m, 1H), 7.54-7.43 (m, 4H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 190.9, 140.1, 139.3, 138.3, 137.5, 134.8, 132.4, 129.5, 128.5, 125.7, 125.6, 125.2, 122.4. **IR** (cm<sup>-1</sup>): 1644, 1597, 1494, 1459, 1364, 1237, 1050, 841, 765, 713, 665. **GC-MS** (EI): 77.1, 89.1, 105.1, 133.0, 161.1, 238.1. **HRMS** m/z (ESI) calcd for C<sub>15</sub>H<sub>11</sub>OS<sup>+</sup> [M+H]<sup>+</sup>: 239.0531, found: 239.0532.

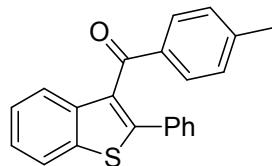
### (2-methylbenzo[b]thiophen-3-yl)(phenyl)methanone (6c)



Pale yellow oil (12.6 mg, 50%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.84 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.78 (dd, *J* = 6.7, 1.3 Hz, 1H), 7.62-7.57 (m, 1H), 7.52-7.44 (m, 3H), 7.32-7.24 (m, 2H), 2.50 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 193.5, 145.9, 139.1, 138.7, 138.0, 133.3, 132.3, 129.7, 128.7, 124.8, 124.3, 123.3, 121.8, 15.8. **IR** (cm<sup>-1</sup>): 3444, 1651, 1433,

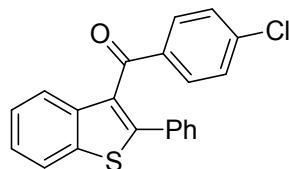
1353, 1274, 1231, 754, 726, 694. **GC-MS** (EI): 77.1, 105.1, 147.1, 175.1, 235.1, 251.1. **HRMS** m/z (ESI) calcd for C<sub>16</sub>H<sub>13</sub>OS<sup>+</sup> [M+H]<sup>+</sup>: 253.0687, found: 253.0686.

**(2-phenylbenzo[b]thiophen-3-yl)(p-tolyl)methanone (6d)**



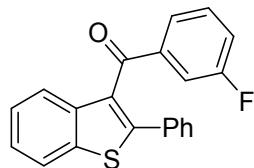
Pale yellow oil (14.4 mg, 44%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.88 (dd, *J* = 6.6, 2.0 Hz, 1H), 7.72-7.65 (m, 3H), 7.47-7.42 (m, 2H), 7.40-7.32 (m, 2H), 7.26-7.21 (m, 3H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 194.1, 145.5, 144.4, 139.8, 138.9, 134.9, 133.3, 131.8, 130.1, 129.2, 129.1, 128.7, 128.6, 125.1, 125.0, 123.6, 122.0, 21.7. **IR** (cm<sup>-1</sup>): 1651, 1604, 1457, 1433, 1346, 1277, 1235, 1176, 755, 728, 695. **GC-MS** (EI): 91.1, 119.1, 165.1, 179.1, 208.1, 237.1, 328.1. **HRMS** m/z (ESI) calcd for C<sub>22</sub>H<sub>17</sub>OS<sup>+</sup> [M+H]<sup>+</sup>: 329.1000, found: 329.1001.

**(4-chlorophenyl)(2-phenylbenzo[b]thiophen-3-yl)methanone (6e)**



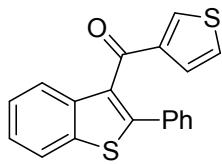
Pale yellow oil (17.7 mg, 51%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.92-7.86 (m, 1H), 7.80-7.73 (m, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.42-7.36 (m, 4H), 7.26 -7.19 (m, 5H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 192.9, 146.9, 139.6, 139.5, 139.0, 135.8, 133.1, 131.3, 131.0, 129.4, 129.1, 128.7, 128.6, 125.4, 125.3, 123.6, 122.1. **IR** (cm<sup>-1</sup>): 3467, 1651, 1586, 1347, 1232, 1217, 1089, 1013, 845, 755, 734, 695. **GC-MS** (EI): 75.1, 111.1, 139.1, 165.1, 208.1, 237.1, 348.1. **HRMS** m/z (ESI) calcd for C<sub>21</sub>H<sub>14</sub>ClOS<sup>+</sup> [M+H]<sup>+</sup>: 349.0454, found: 349.0448.

**(3-fluorophenyl)(2-phenylbenzo[b]thiophen-3-yl)methanone (6f)**



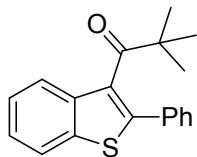
Pale yellow oil (13.3 mg, 40%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.89 (dd, *J* = 6.3, 2.7 Hz, 1H), 7.80 (dd, *J* = 6.4, 2.8 Hz, 1H), 7.50-7.43 (m, 2H), 7.43-7.36 (m, 4H), 7.25-7.16 (m, 4H), 7.08 (td, *J* = 8.2, 1.8 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 192.8, 162.5 (d, *J* = 248.2 Hz), 147.5, 139.6 (d, *J* = 6.5 Hz), 139.5, 139.0, 133.1, 130.9, 129.9 (d, *J* = 7.5 Hz), 129.4, 129.0, 128.7, 125.8 (d, *J* = 2.9 Hz), 125.4, 125.3, 123.6, 122.1, 120.1 (d, *J* = 21.7 Hz), 116.3 (d, *J* = 22.4 Hz). **IR** (cm<sup>-1</sup>): 3449, 1655, 1587, 1442, 1349, 1250, 755, 724, 696. **GC-MS** (EI): 95.1, 165.1, 208.1, 237.1, 332.1. **HRMS** m/z (ESI) calcd for C<sub>21</sub>H<sub>14</sub>FOS<sup>+</sup> [M+H]<sup>+</sup>: 333.0749, found: 333.0757.

**(2-phenylbenzo[b]thiophen-3-yl)(thiophen-3-yl)methanone (6g)**



Pale yellow oil (10.1 mg, 32%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.90-7.85 (m, 1H), 7.83-7.78 (m, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.4-7.43 (m, 3H), 7.42-7.36 (m, 2H), 7.30-7.24 (m, 3H), 7.14 (dd, *J* = 5.0, 3.0 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 187.6, 146.0, 142.5, 139.5, 138.9, 135.5, 133.4, 132.4, 129.3, 128.9, 128.7, 127.6, 126.1, 125.2, 125.1, 123.6, 122.0. **IR** (cm<sup>-1</sup>): 3457, 1646, 1509, 1238, 756, 723, 695. **GC-MS (EI)**: 39.2, 83.1, 111.1, 165.1, 208.1, 237.1, 291.1, 303.1, 320.1. **HRMS m/z (ESI)** calcd for C<sub>19</sub>H<sub>13</sub>OS<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 321.0408, found: 321.0411.

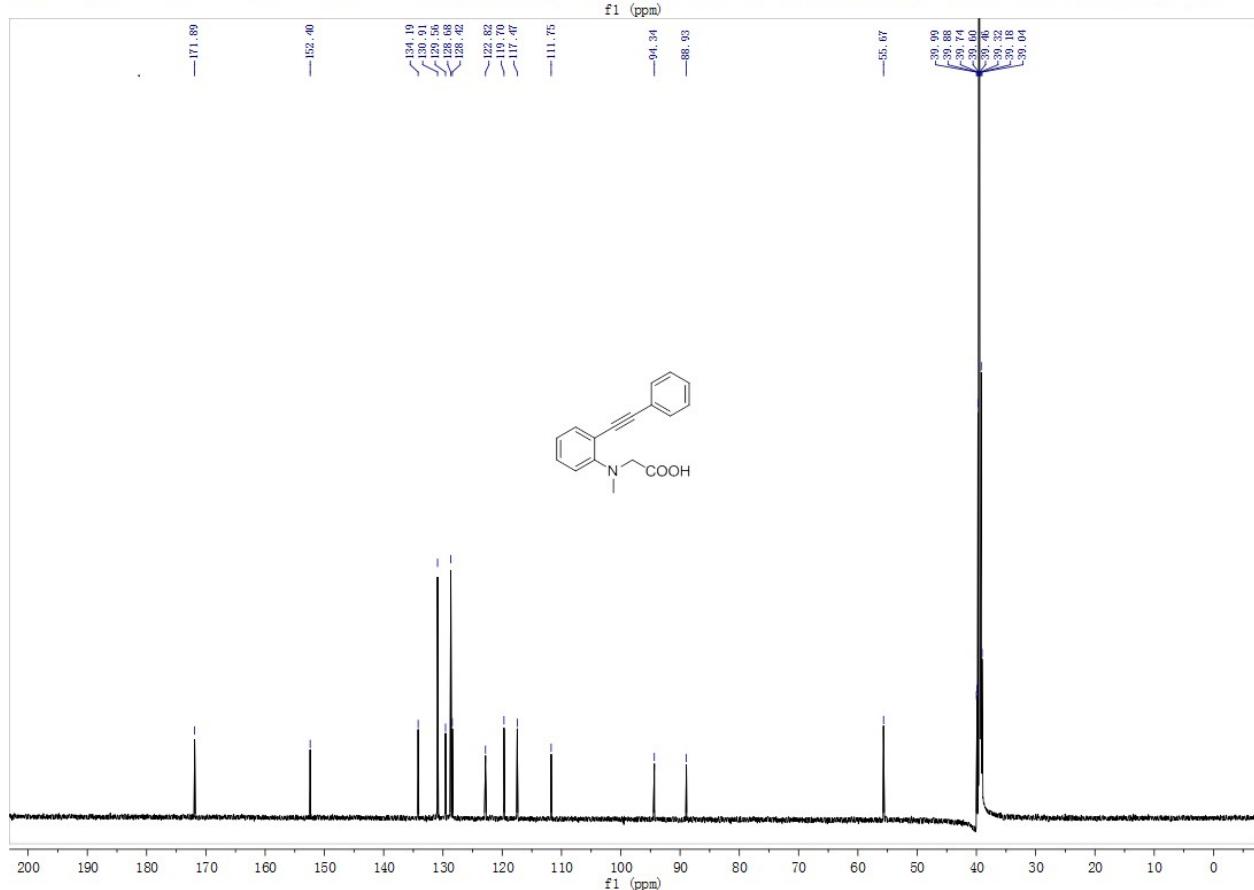
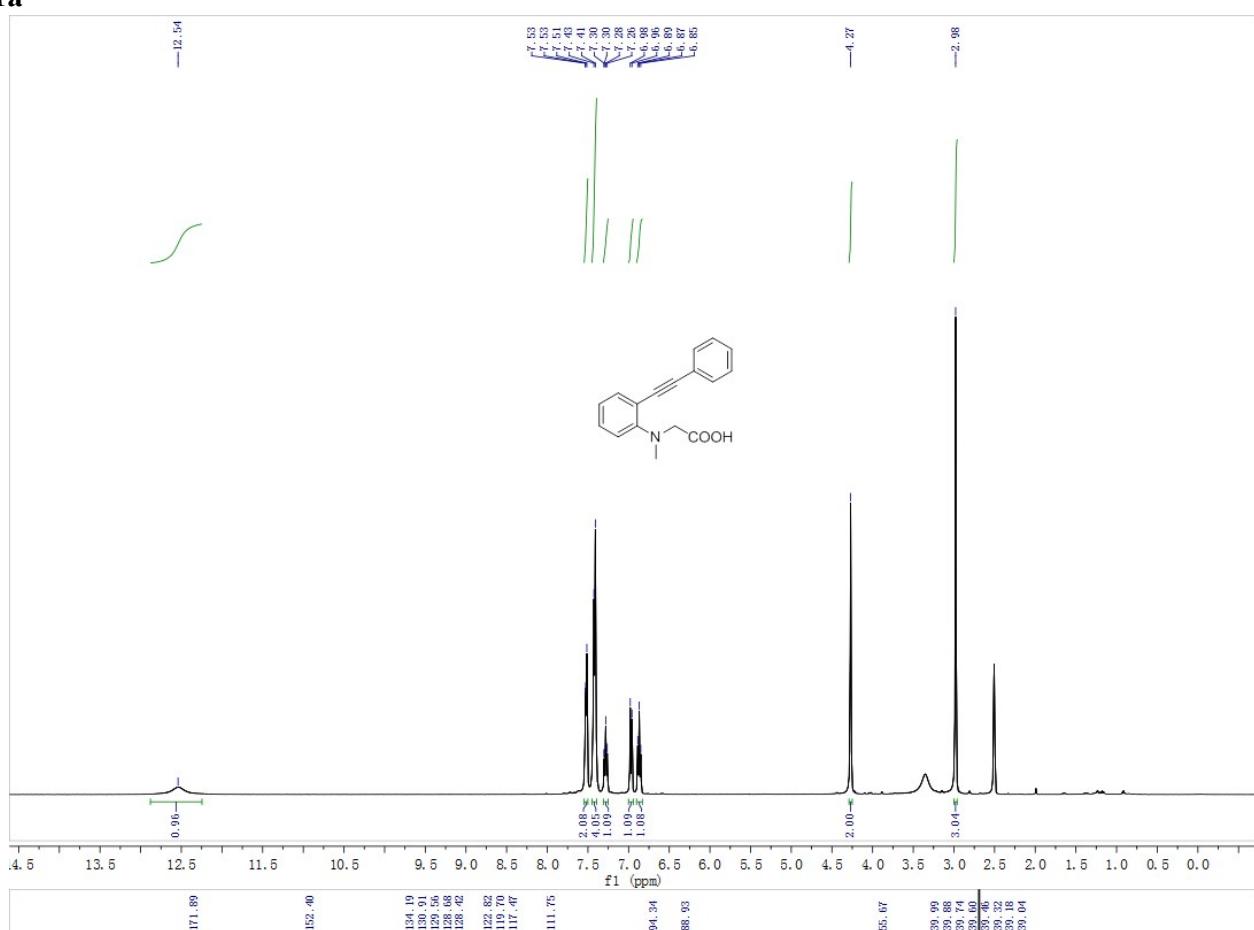
### 2,2-dimethyl-1-(2-phenylbenzo[b]thiophen-3-yl)propan-1-one (6h)

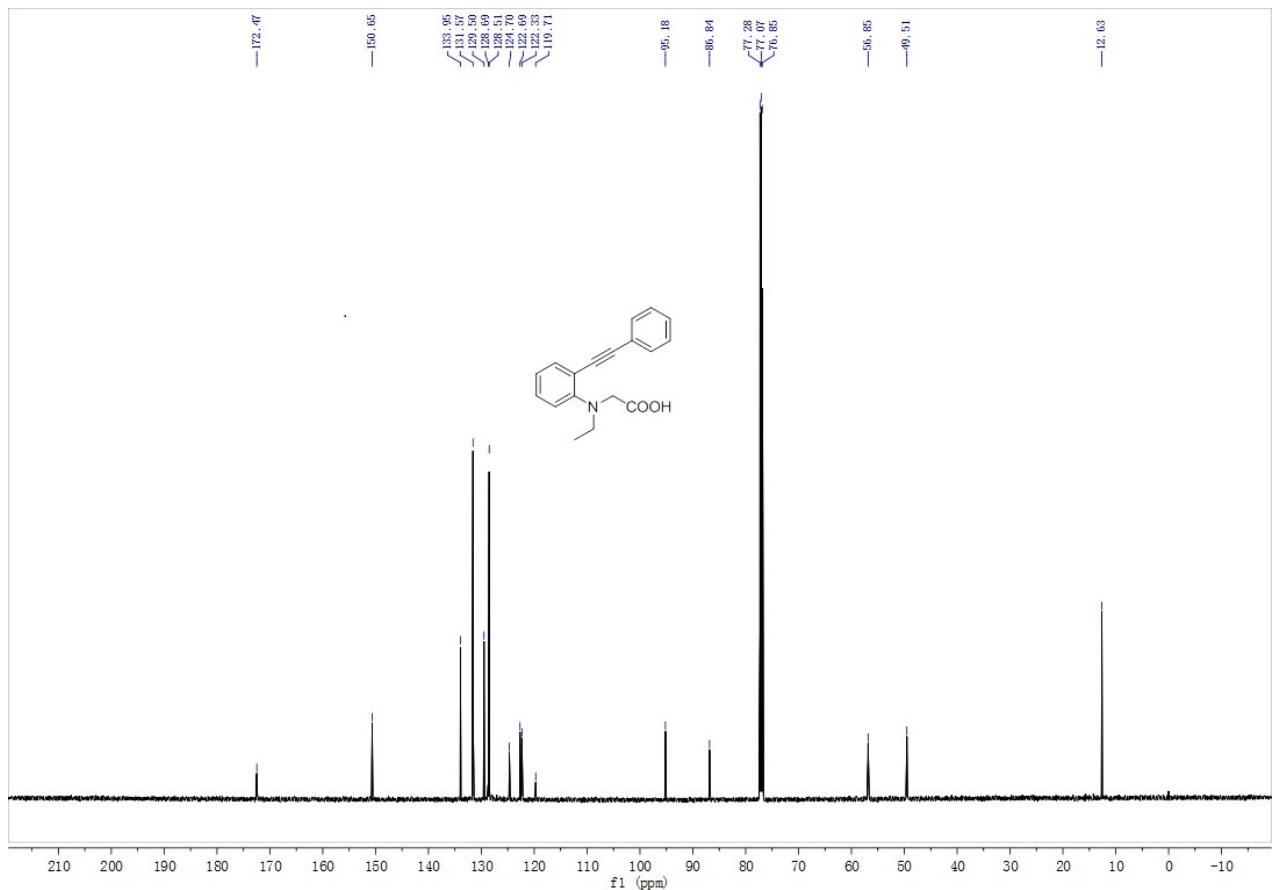
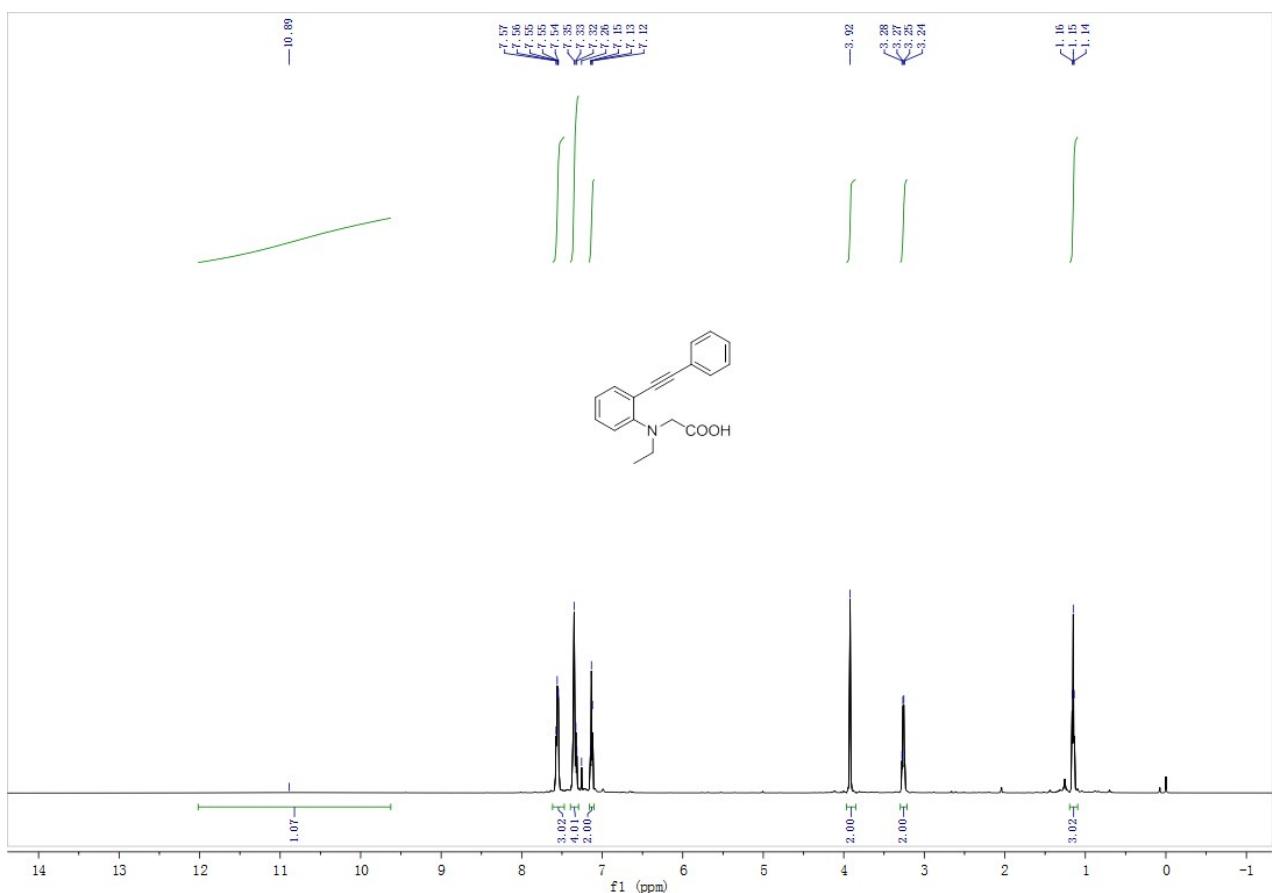


Pale yellow oil (7.3 mg, 25%). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ<sub>H</sub> 7.76 (d, *J* = 6.8 Hz, 1H), 7.46-7.39 (m, 3H), 7.37-7.25 (m, 5H), 0.92 (s, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ<sub>C</sub> 212.6, 138.8, 138.3, 138.2, 133.5, 132.4, 128.0, 127.9, 127.8, 123.8, 123.7, 122.0, 121.1, 45.0, 26.0. **IR** (cm<sup>-1</sup>): 1681, 1261, 1099, 755, 696. **GC-MS (EI)**: 165.1, 208.1, 237.1, 294.1. **HRMS m/z (ESI)** calcd for C<sub>19</sub>H<sub>19</sub>OS<sup>+</sup> [M+H]<sup>+</sup>: 295.1157, found: 295.1156.

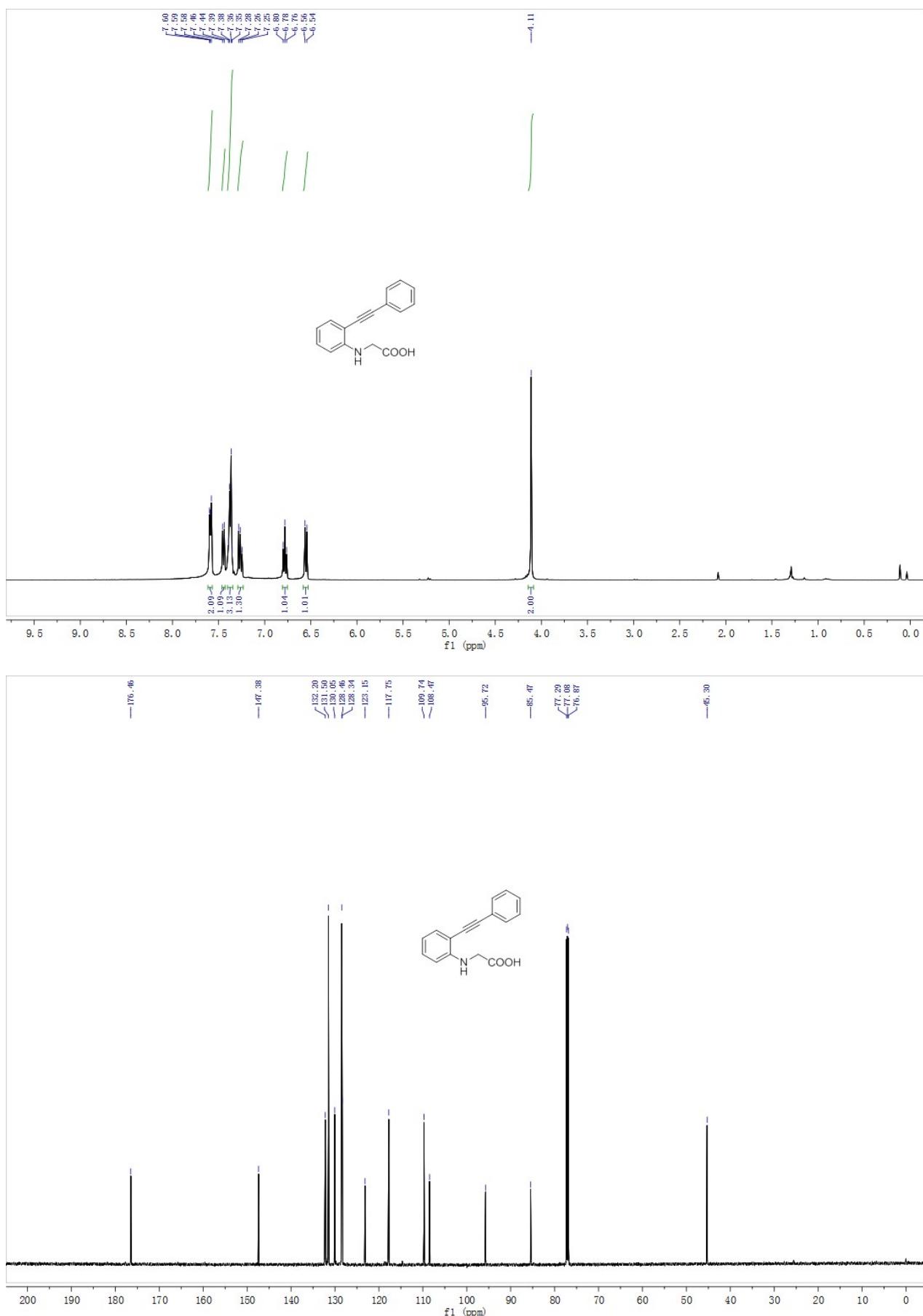
## 7. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra for new substrates

**1a**

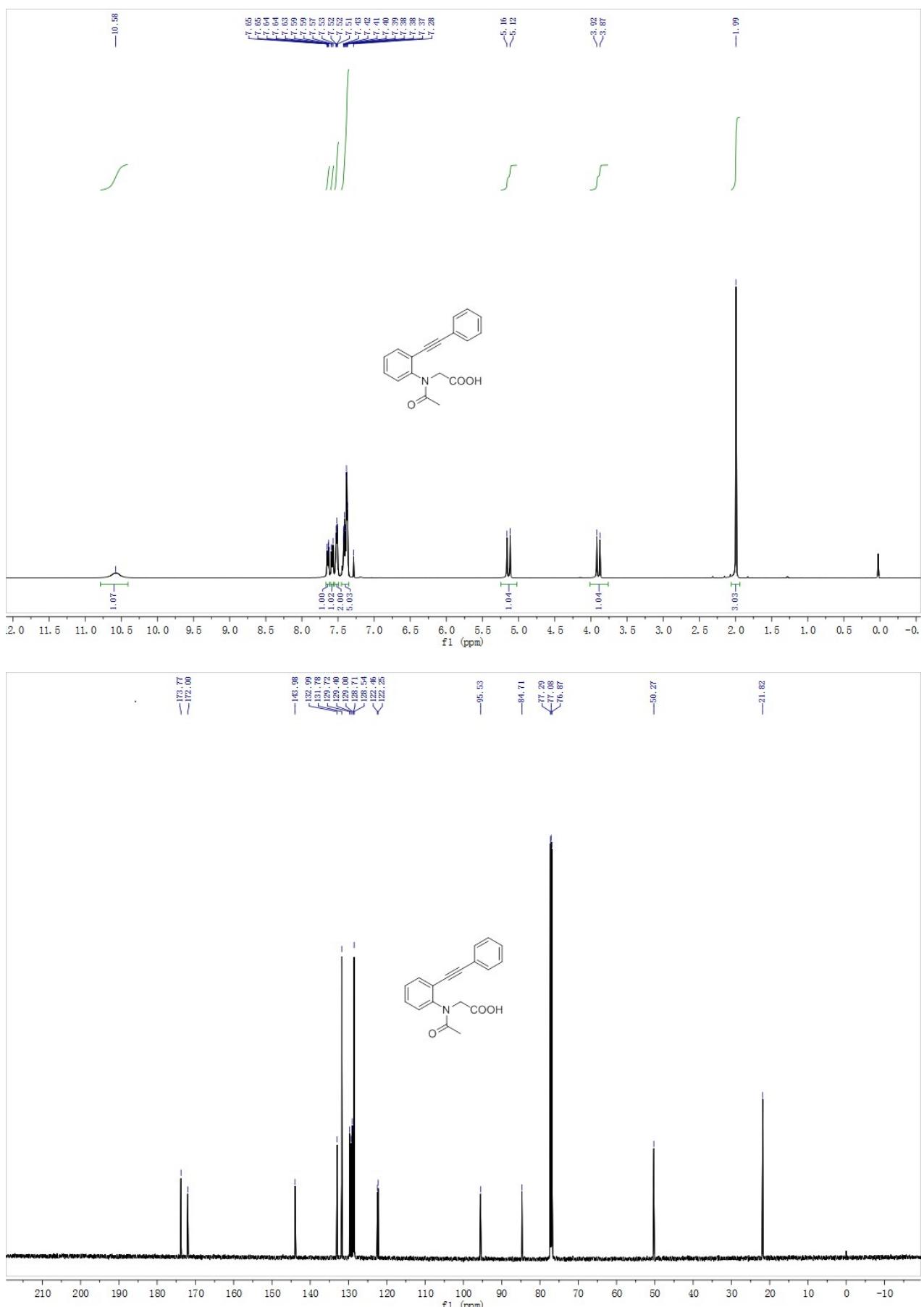


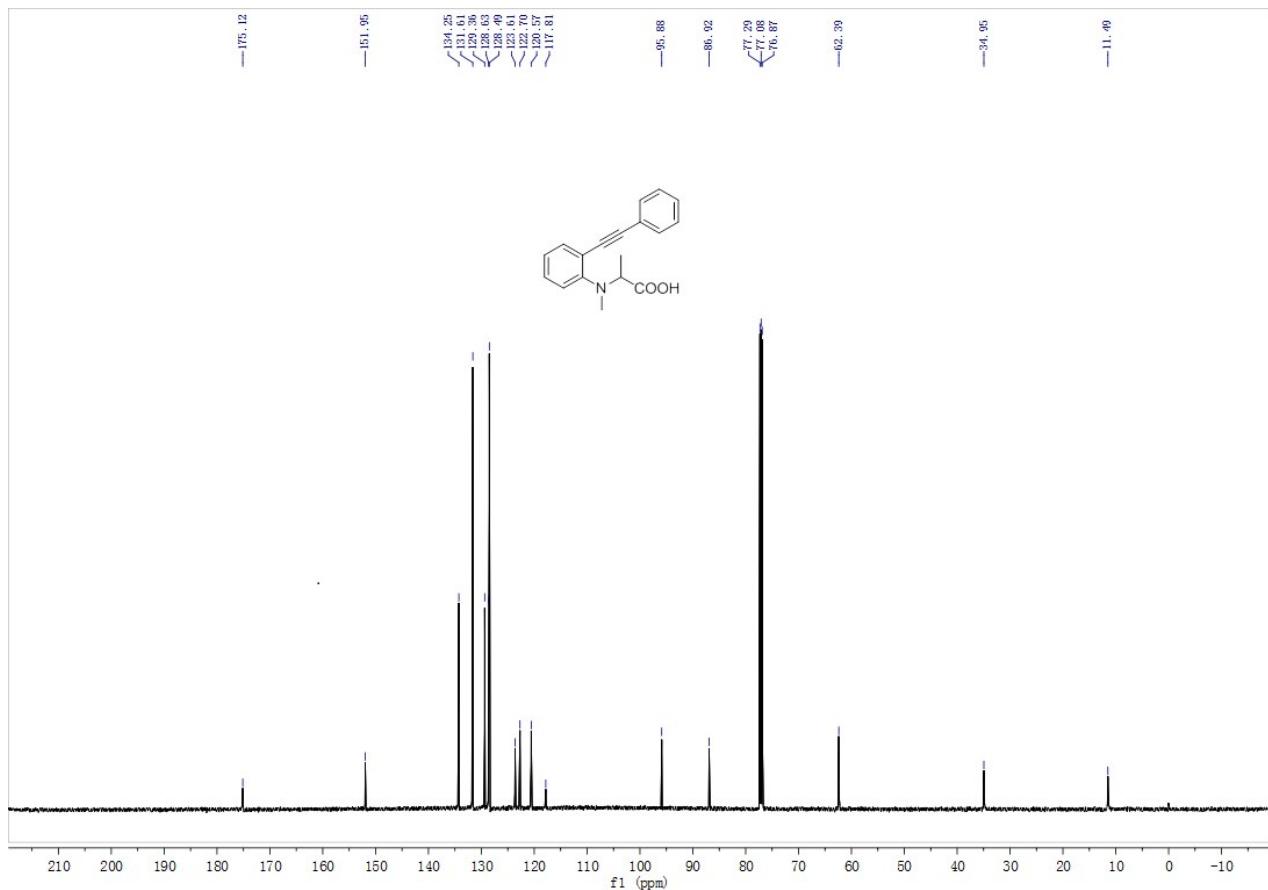
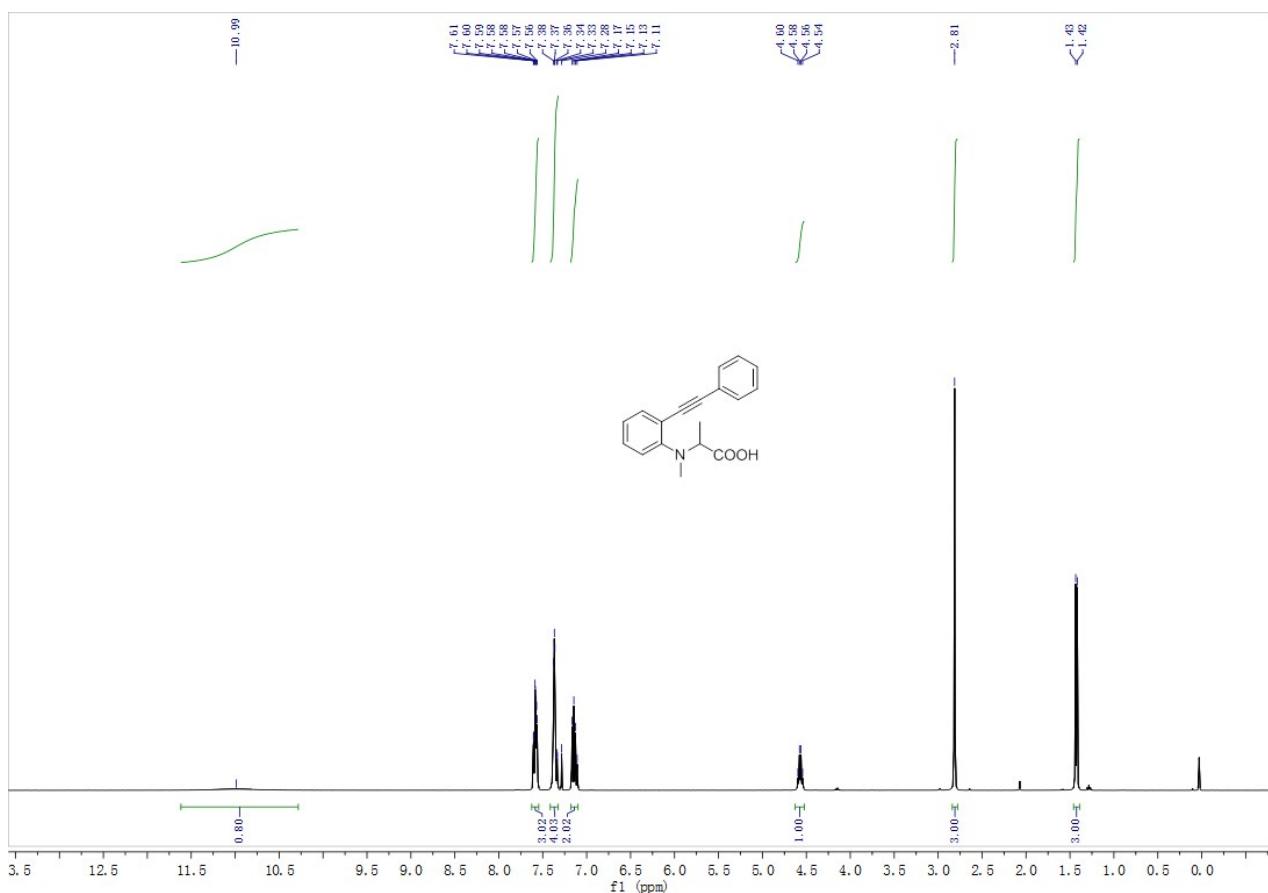
**1b**

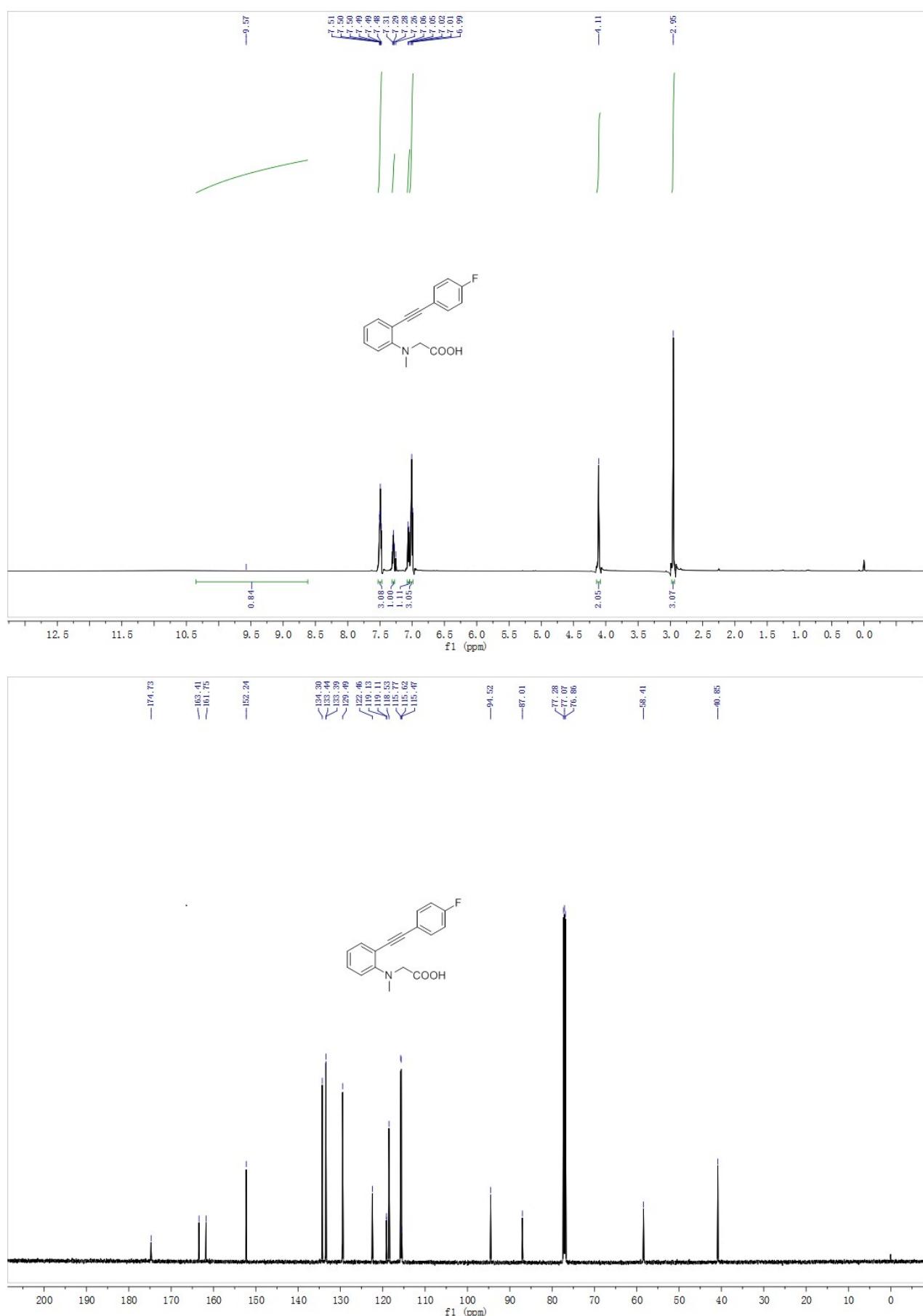
**1c**

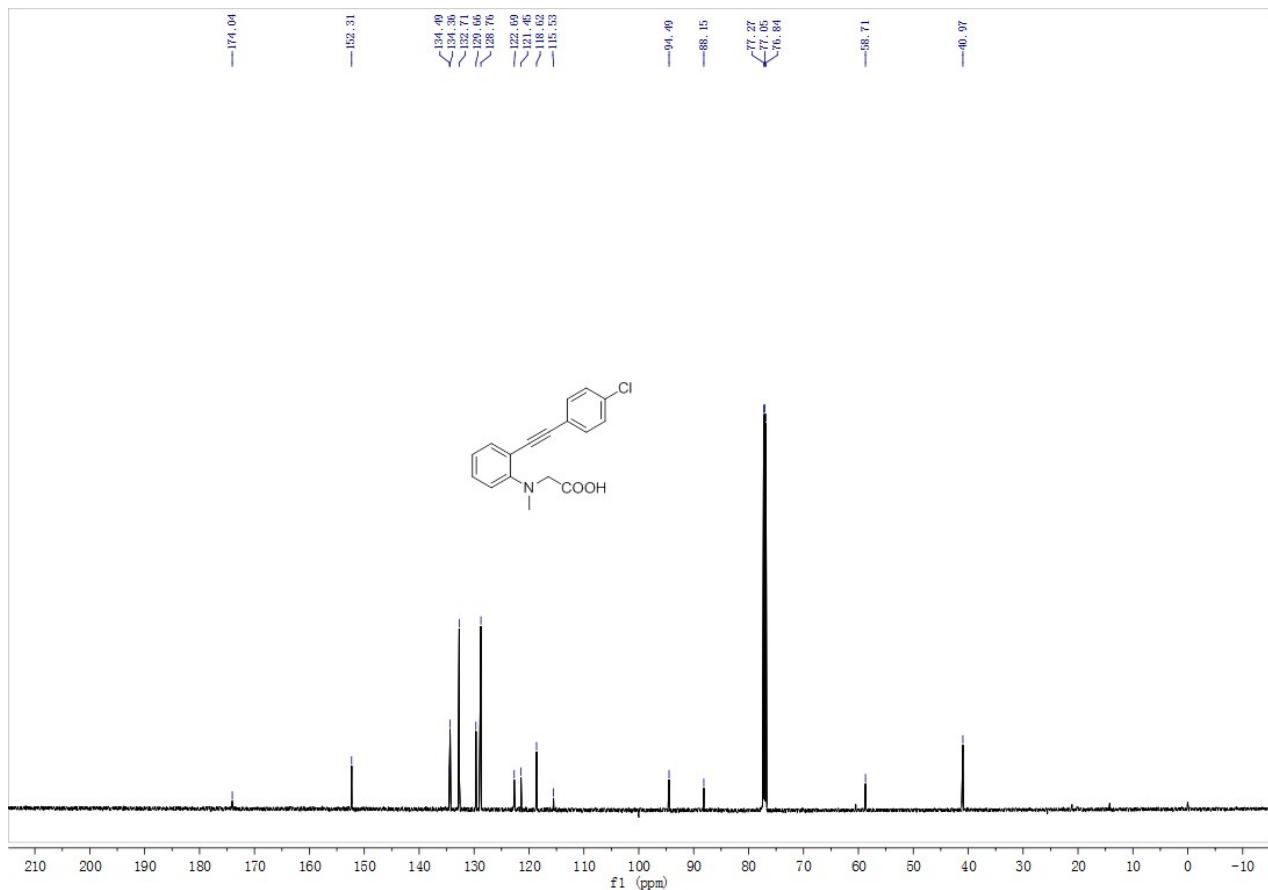
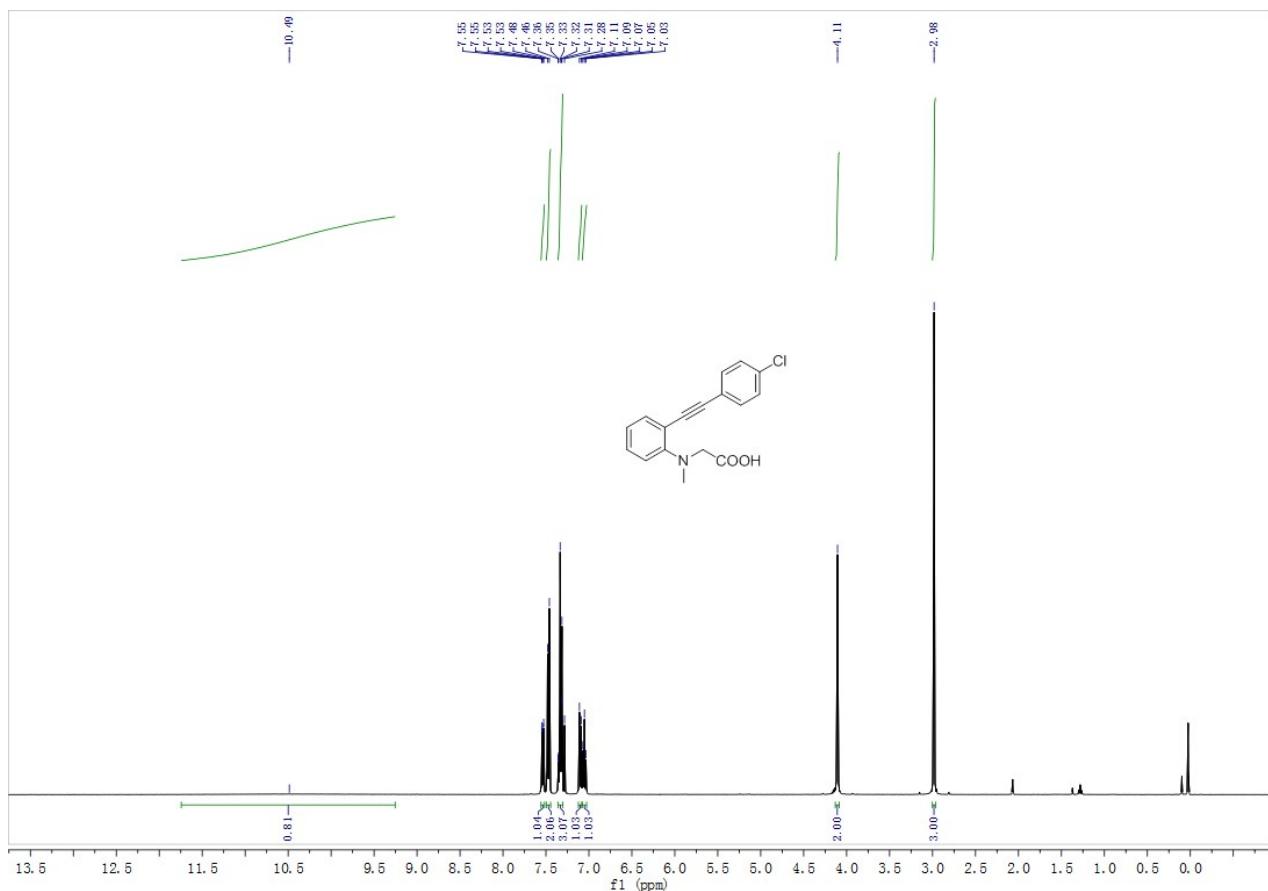


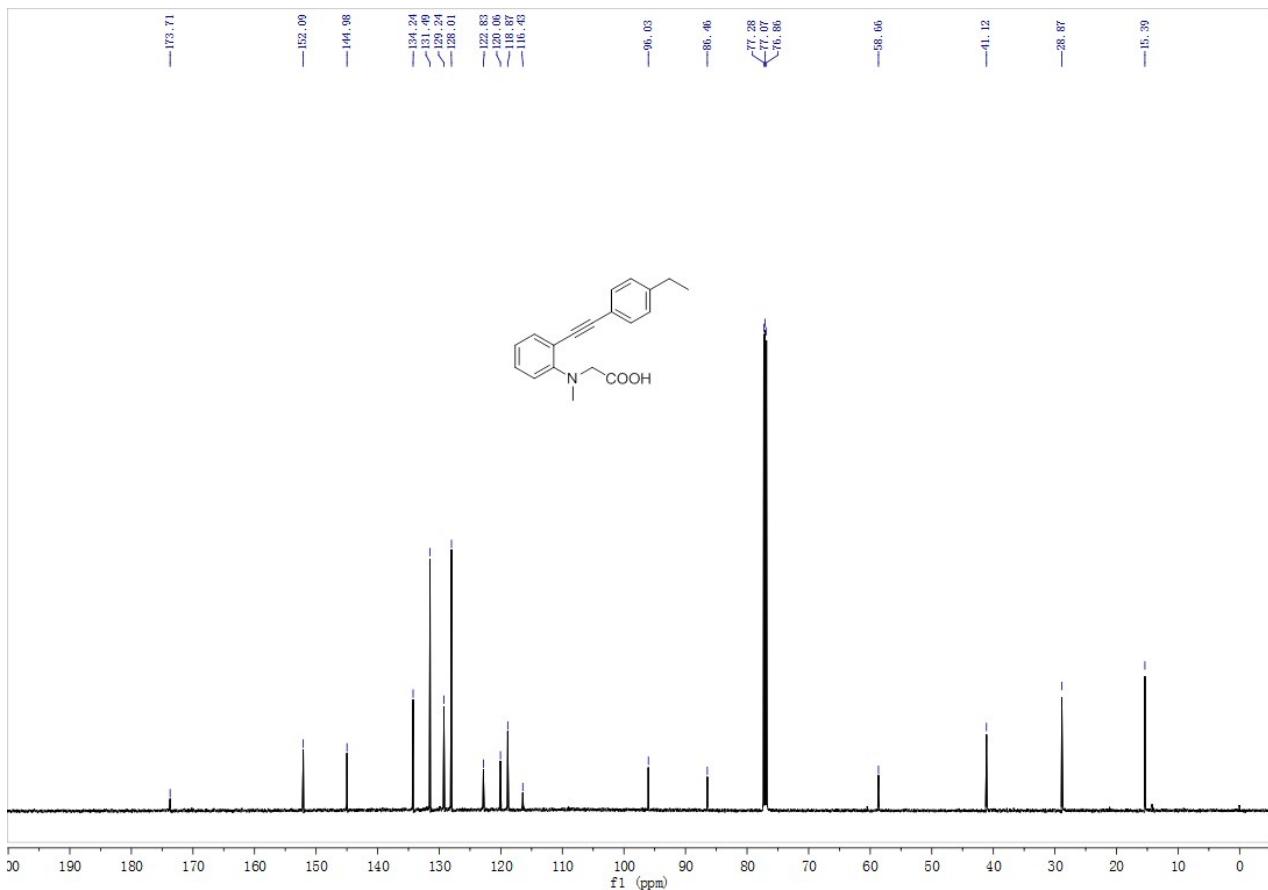
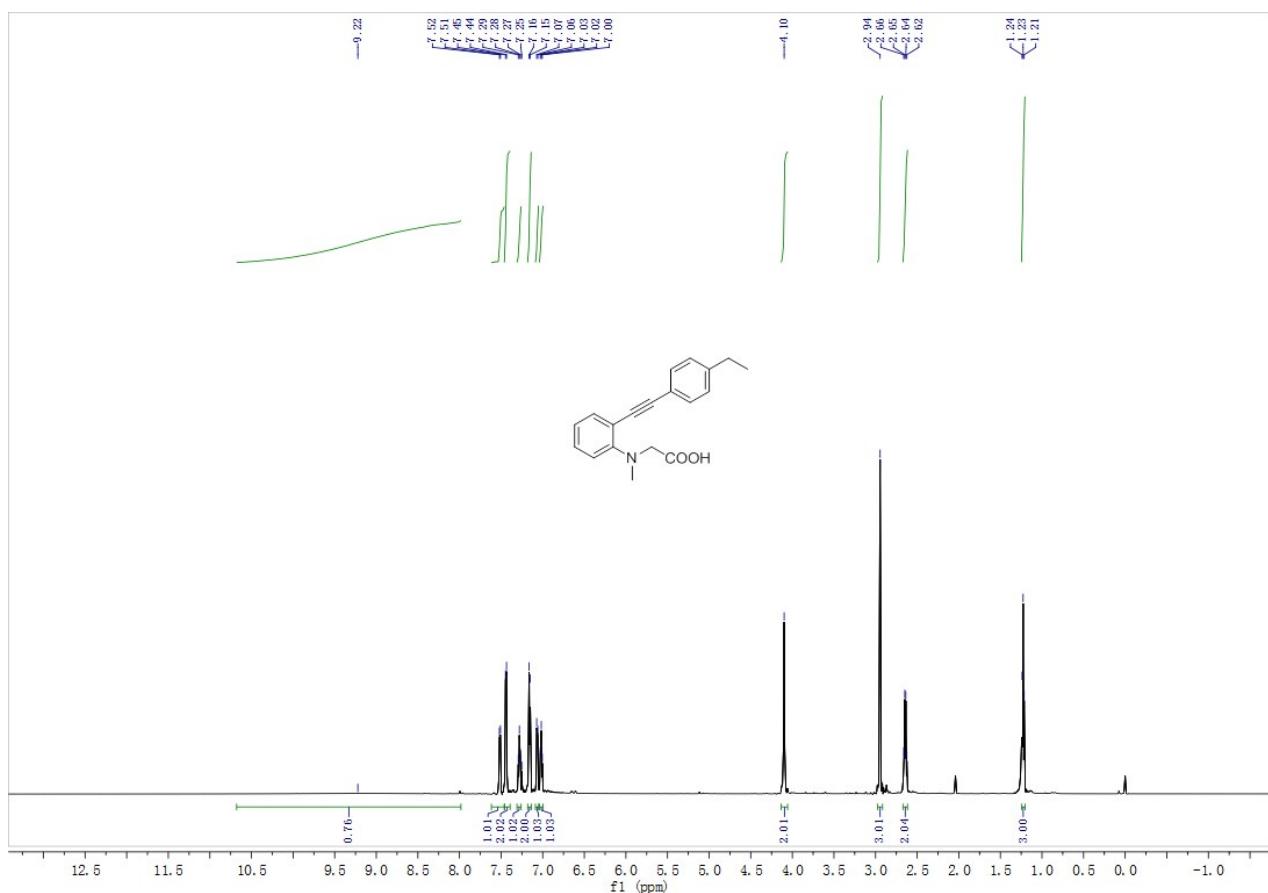
**1d**



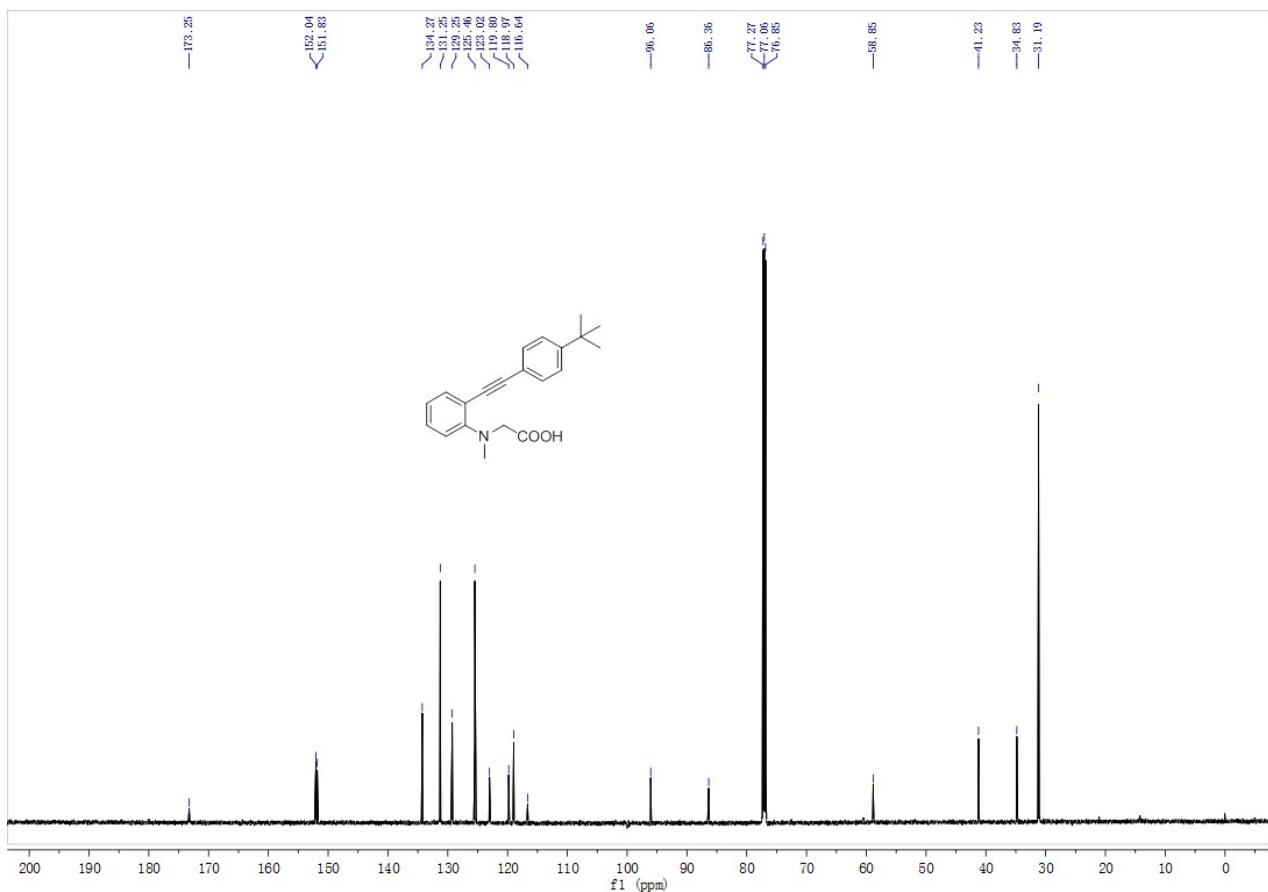
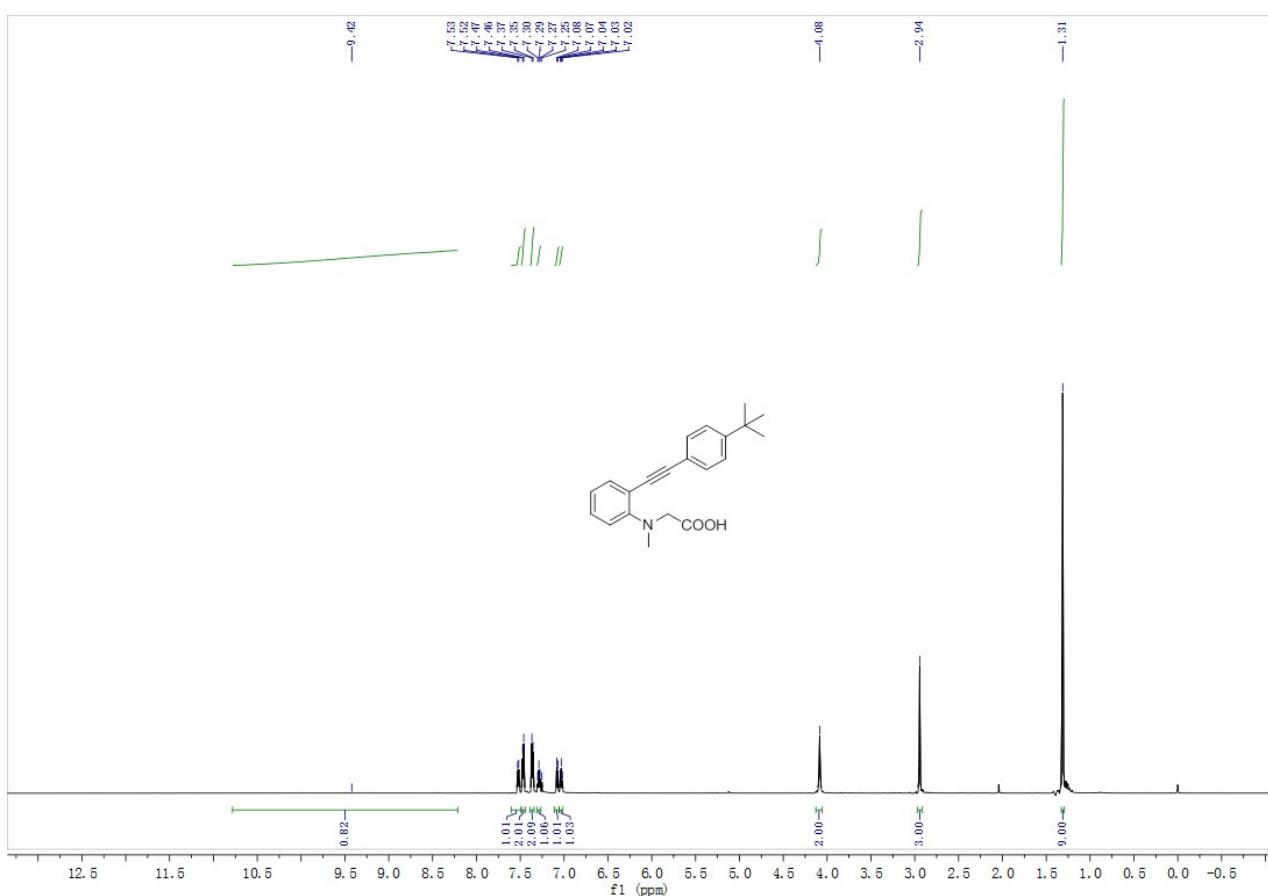
**1e**

**1f**

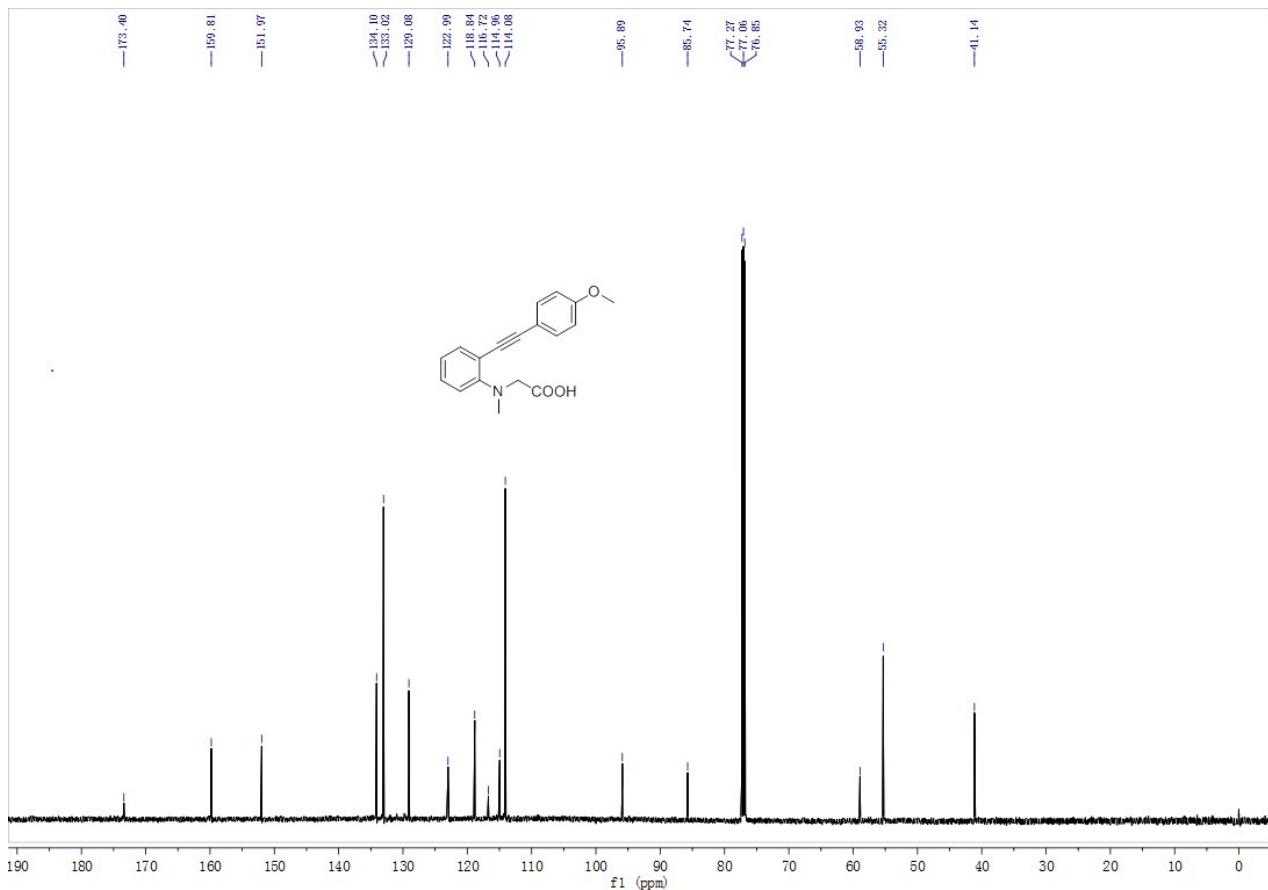
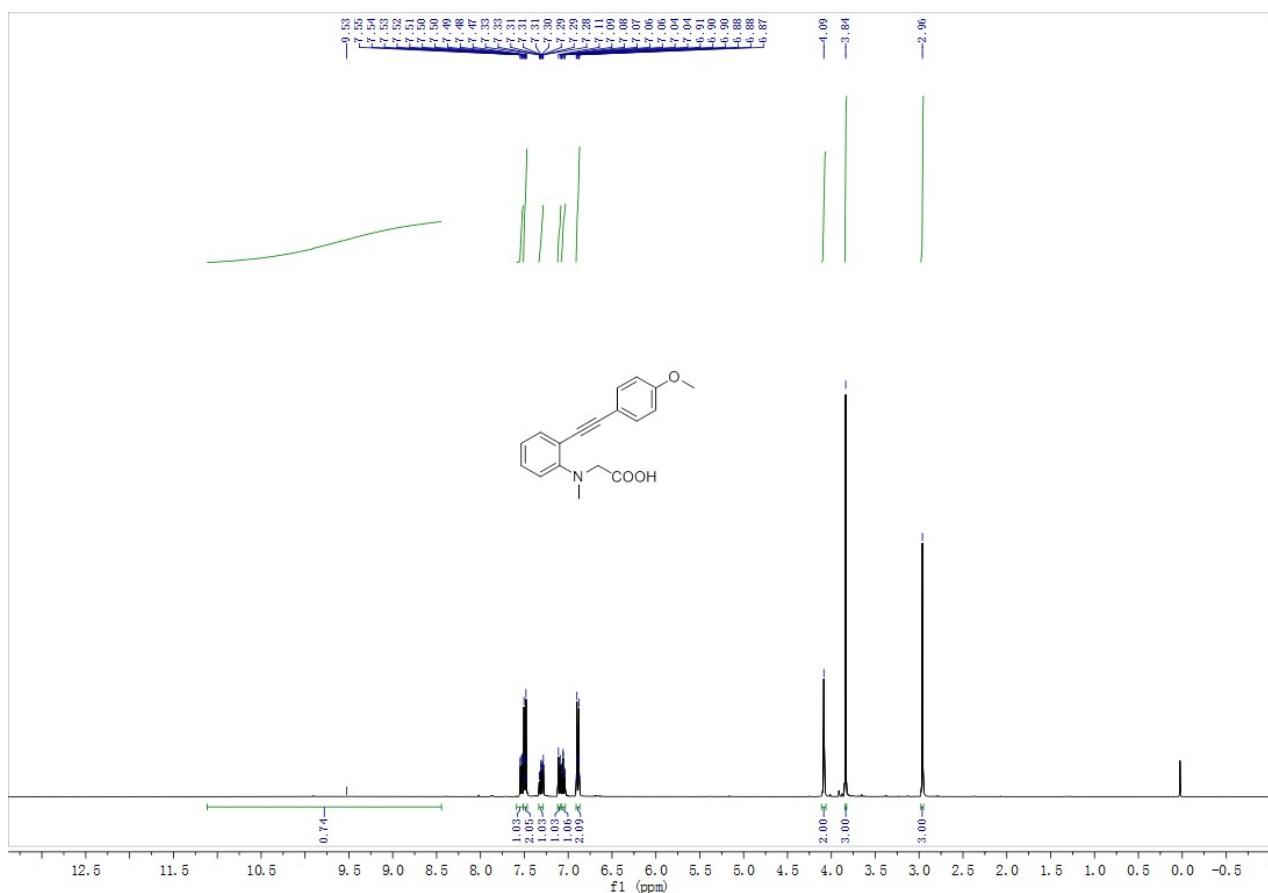
**1g**

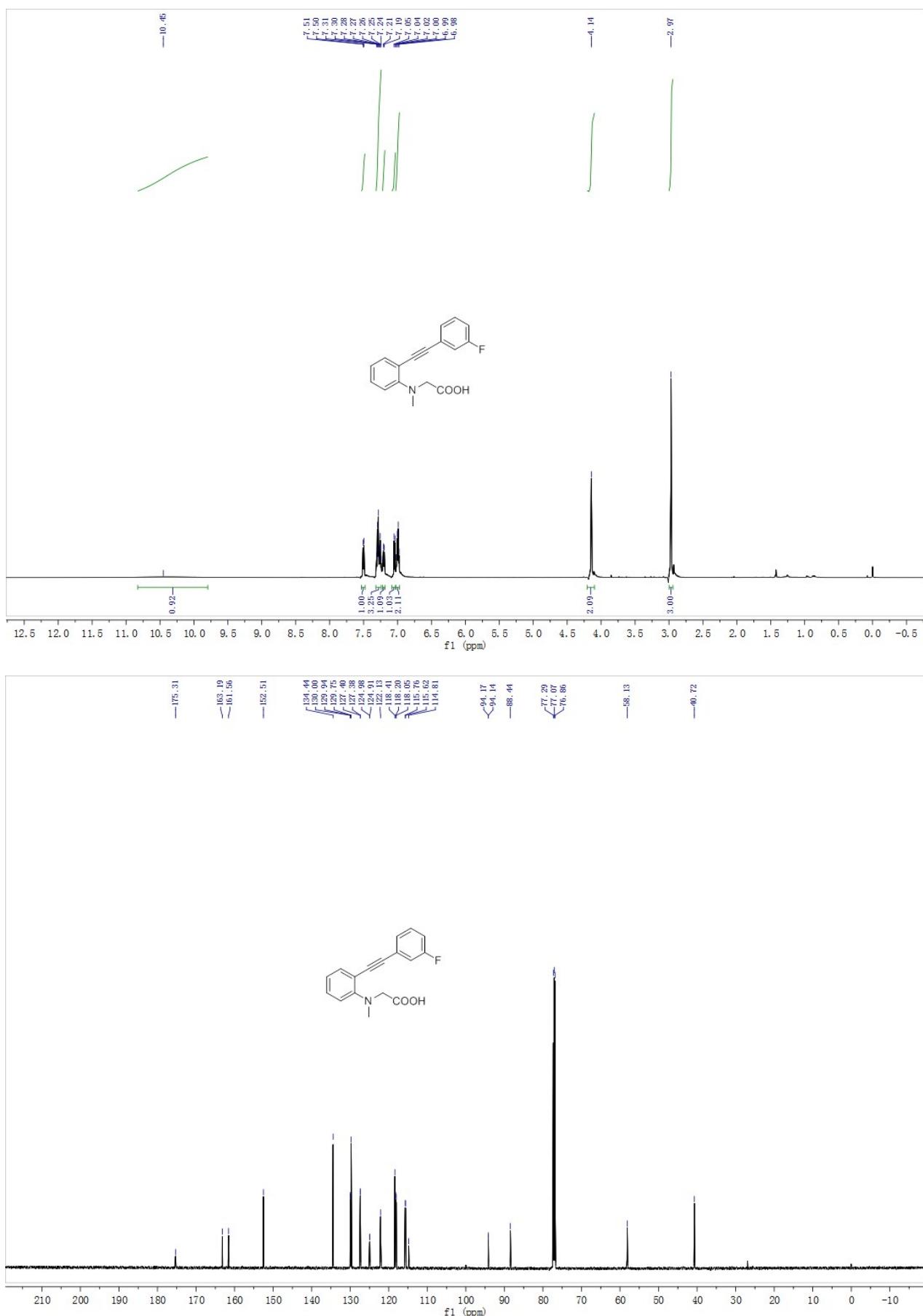
**1h**

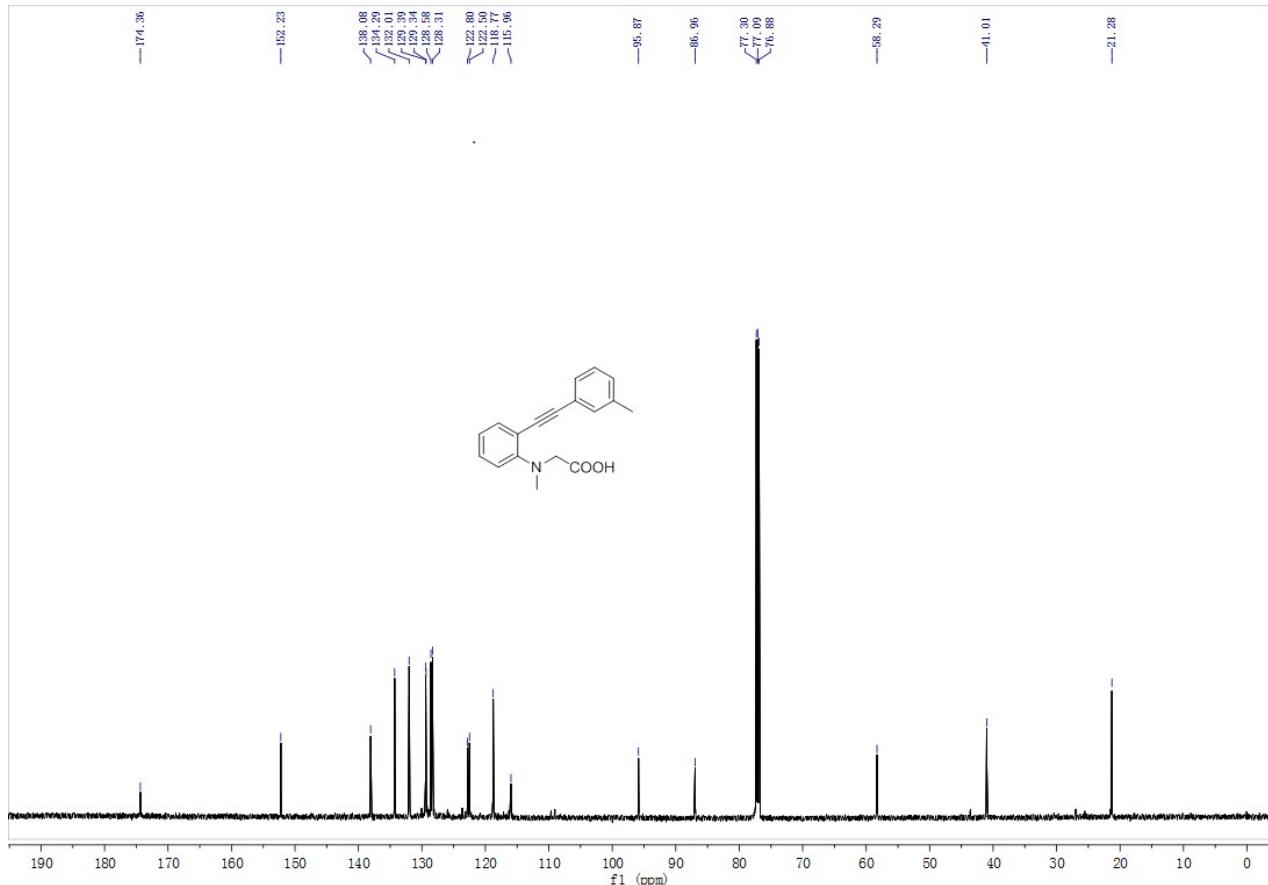
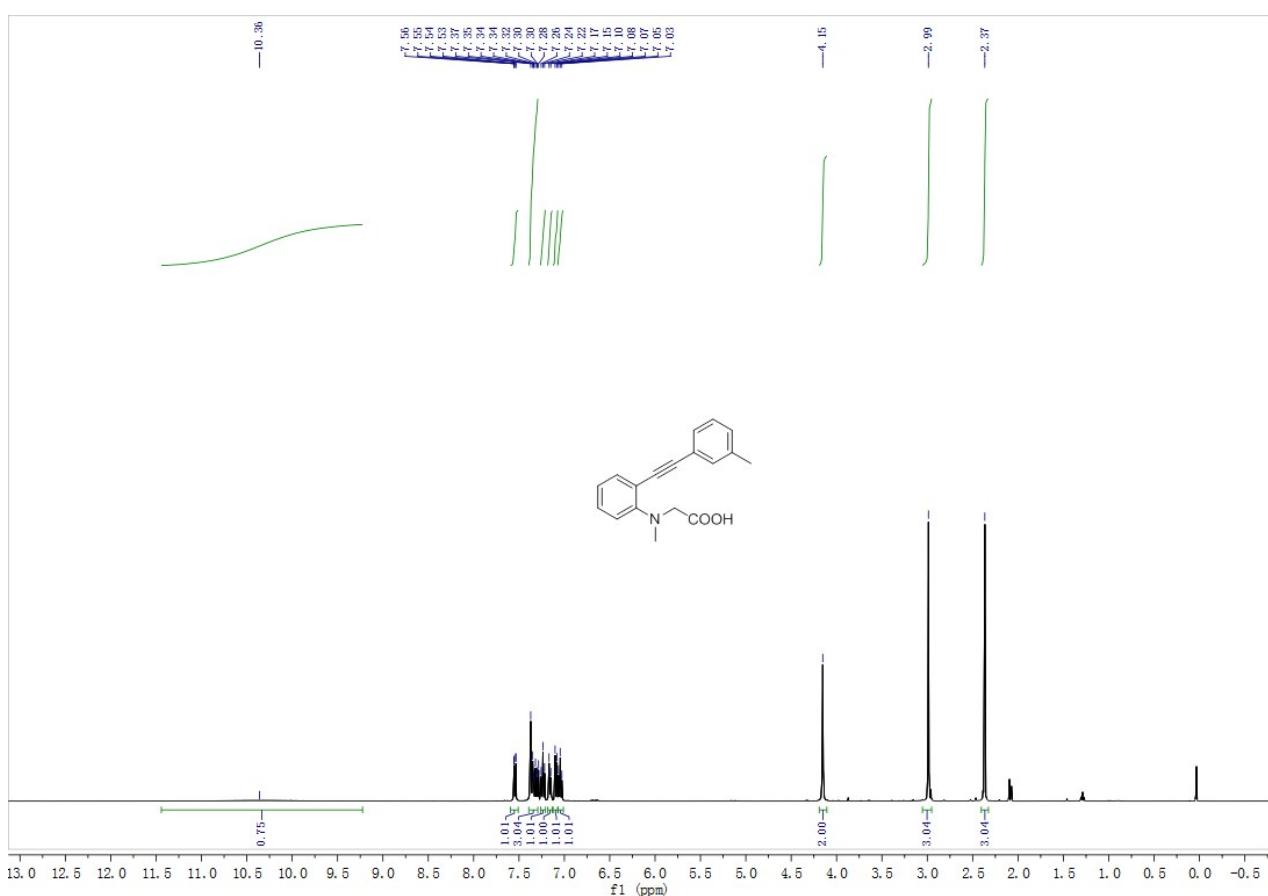
**1i**

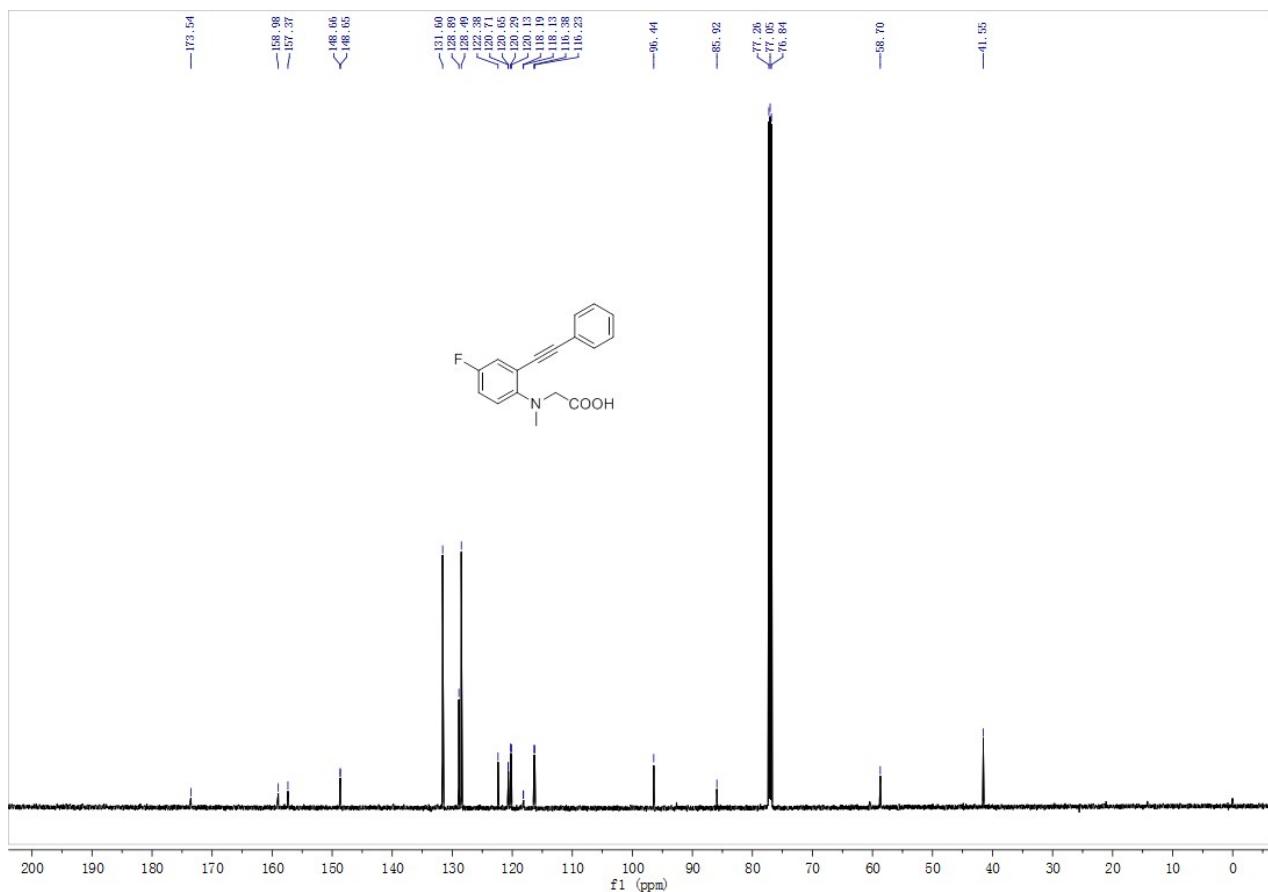
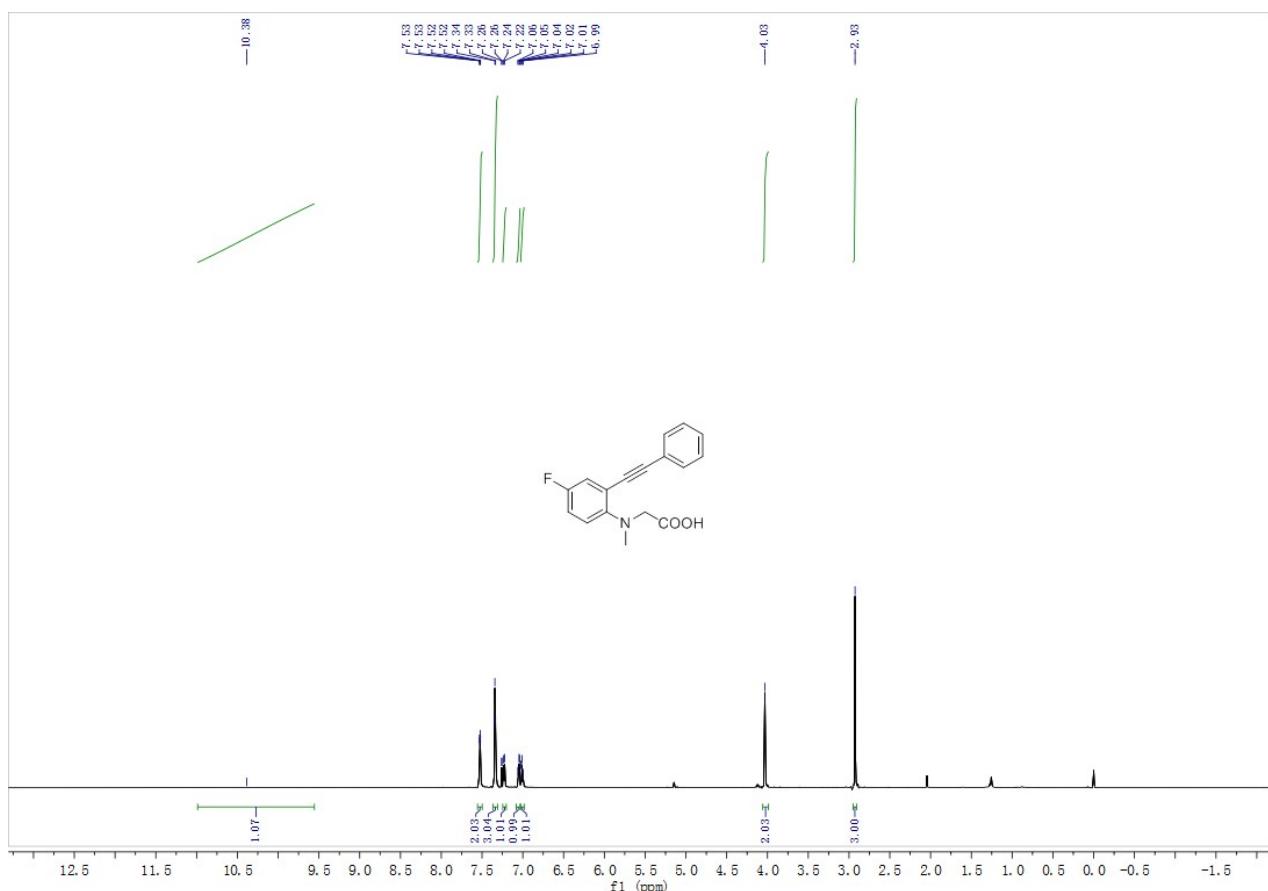


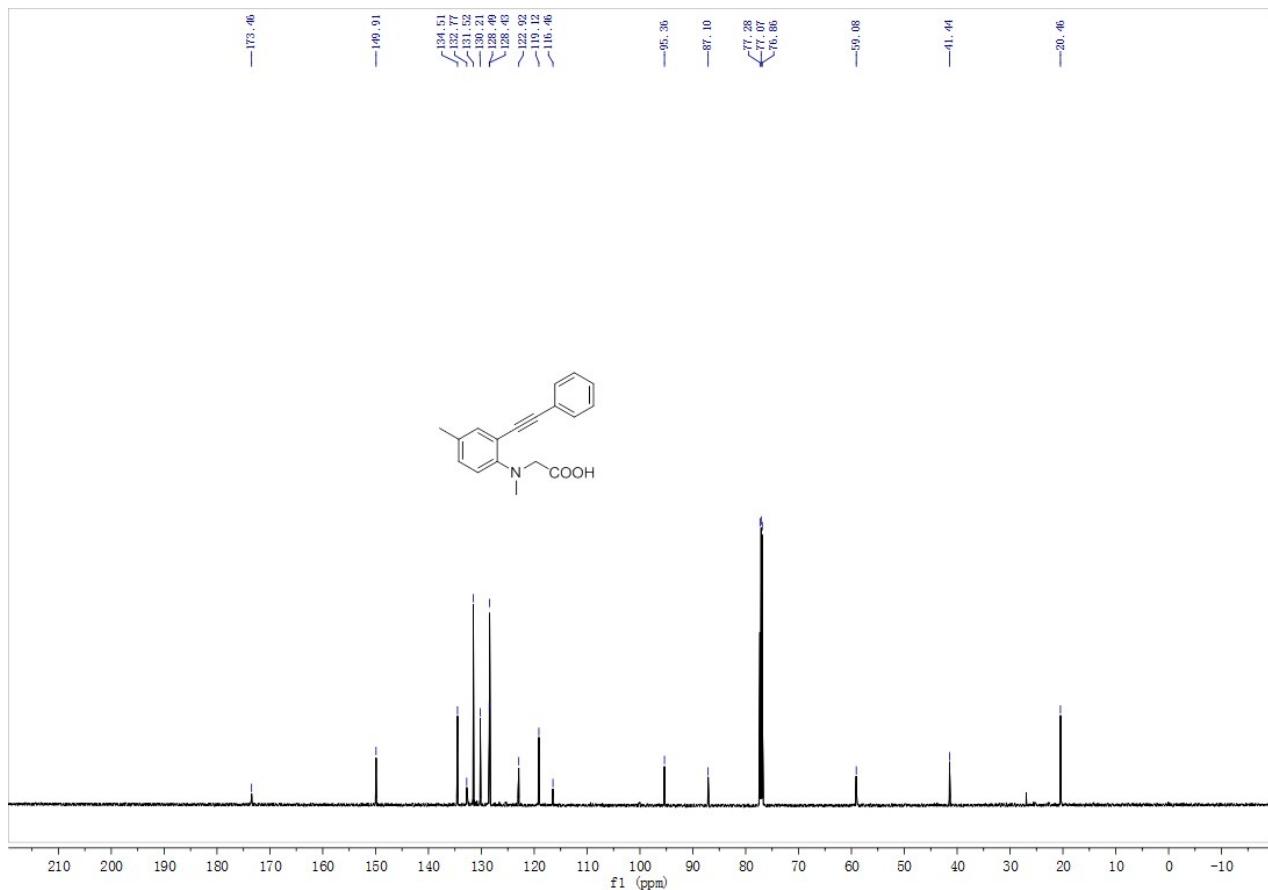
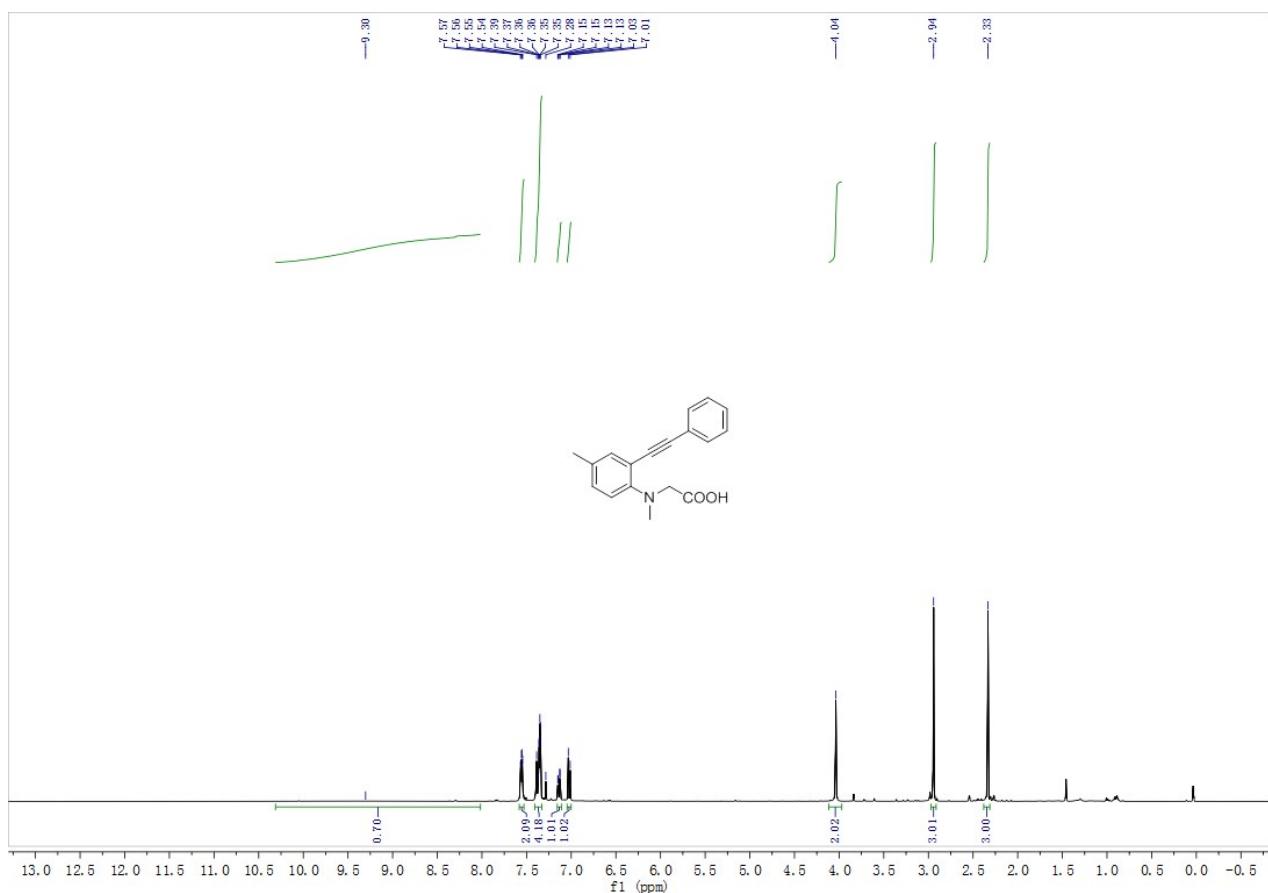
**1j**

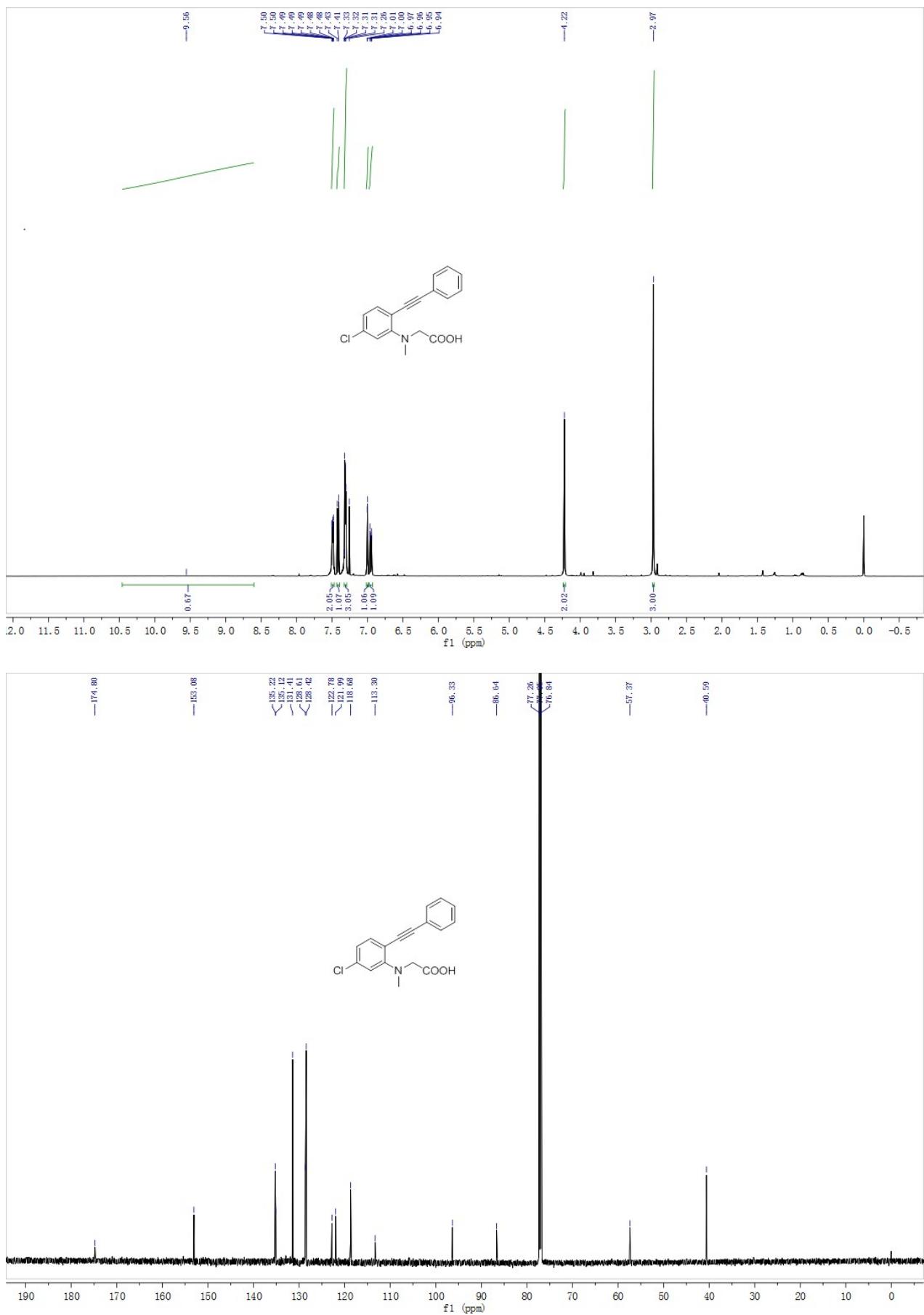


**1k**

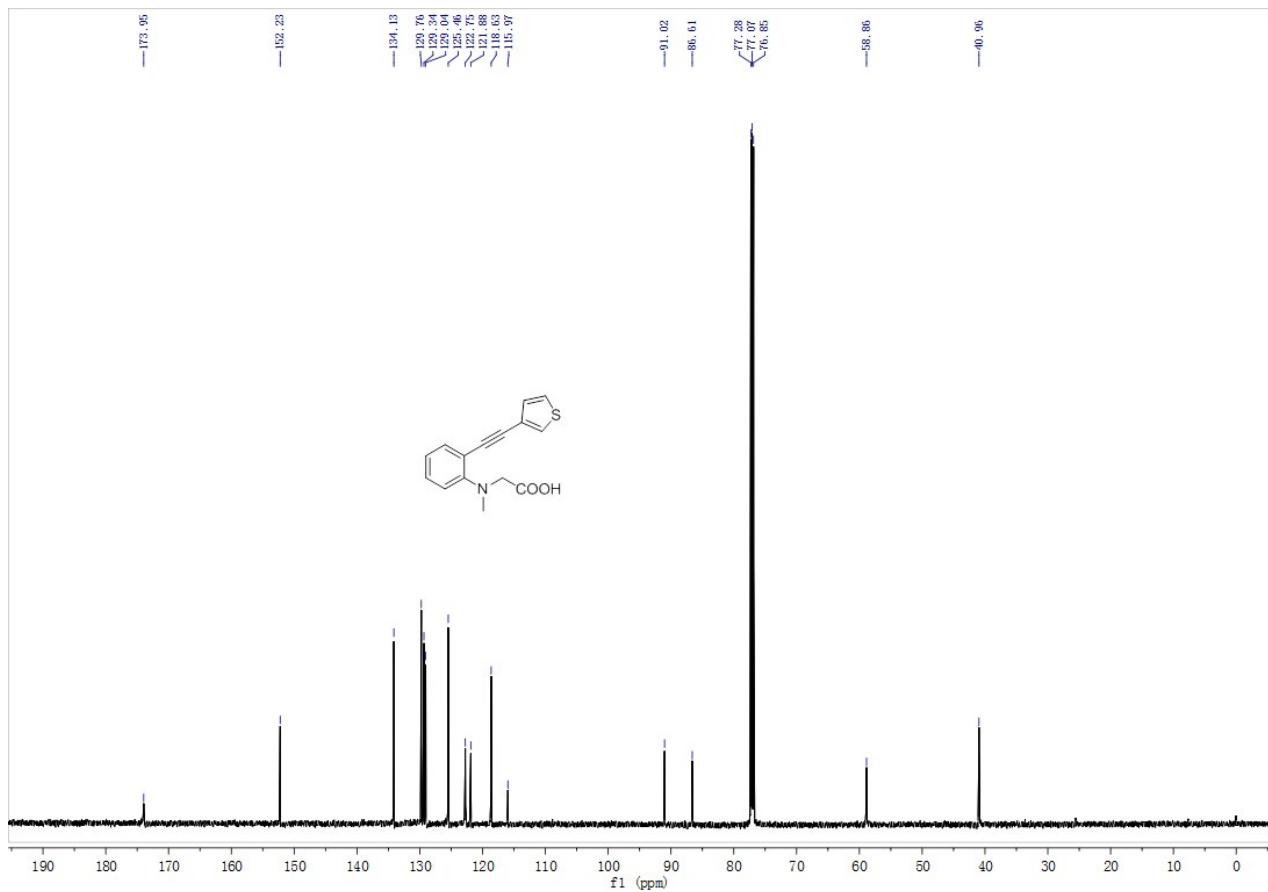
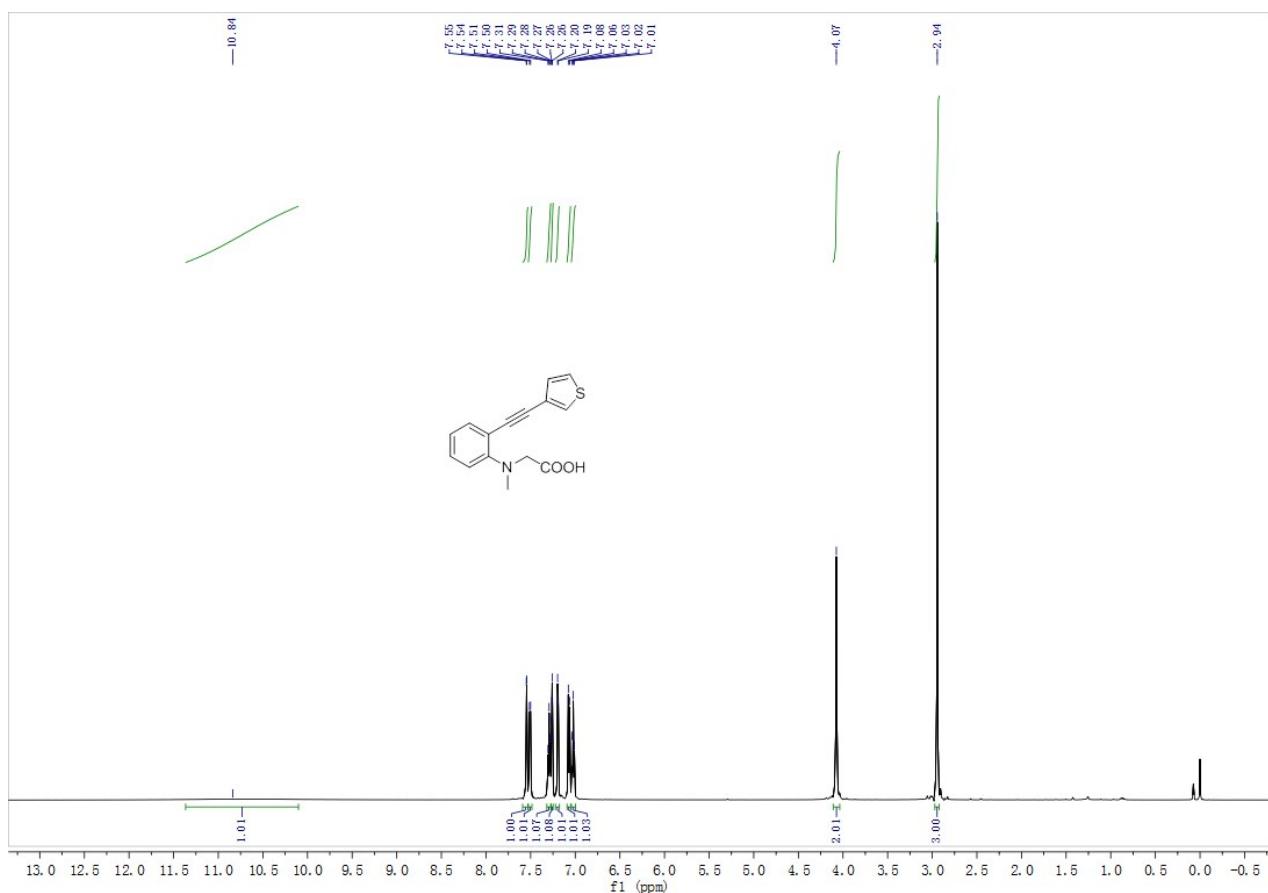


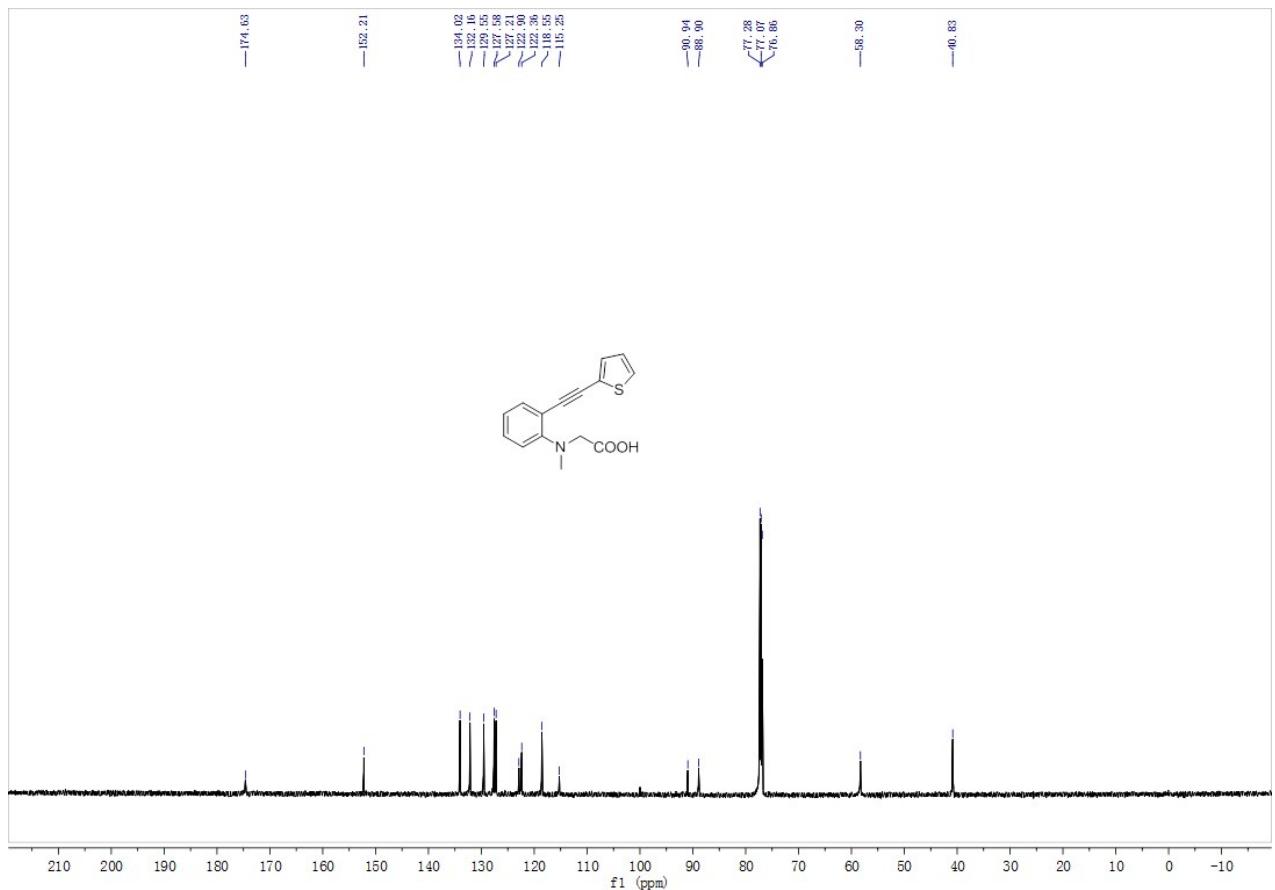
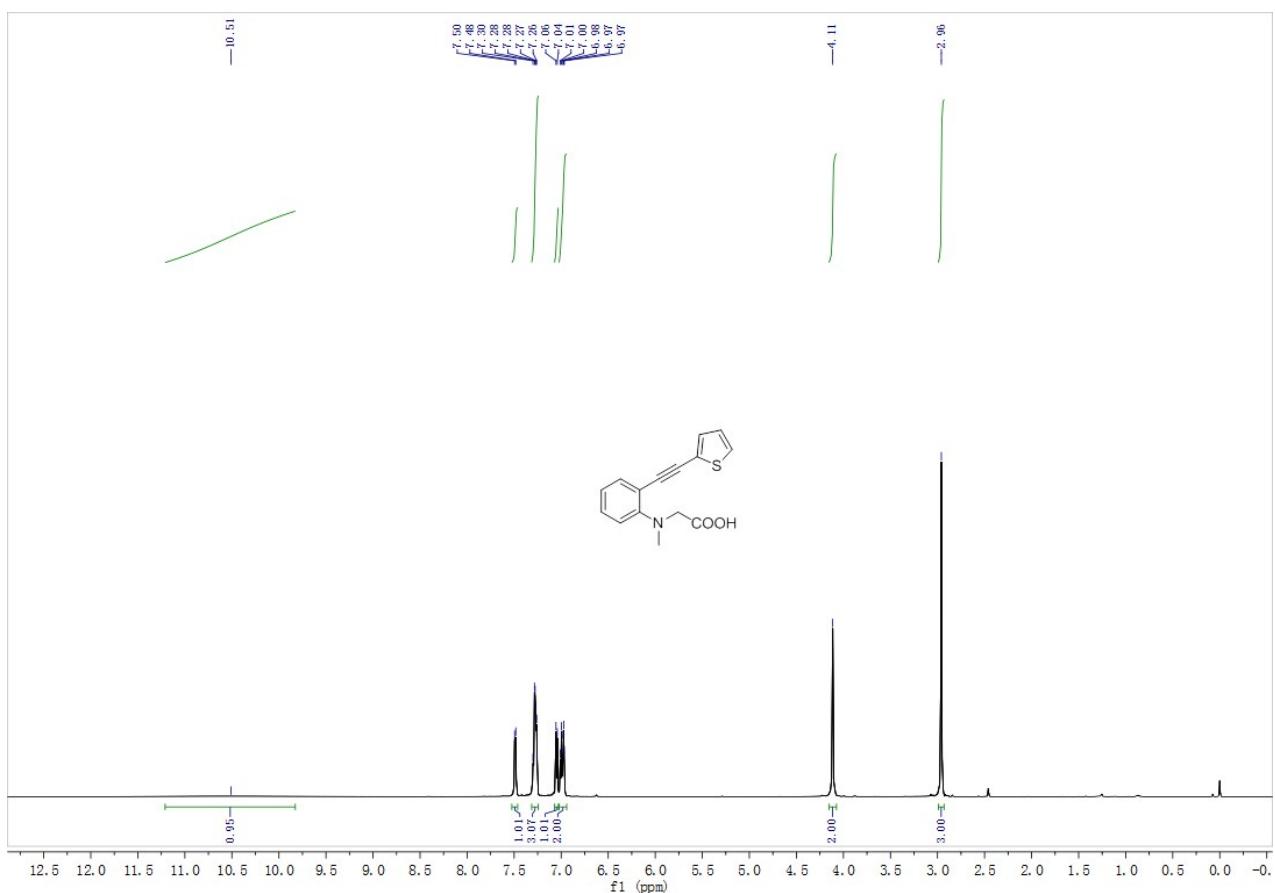
**1m**

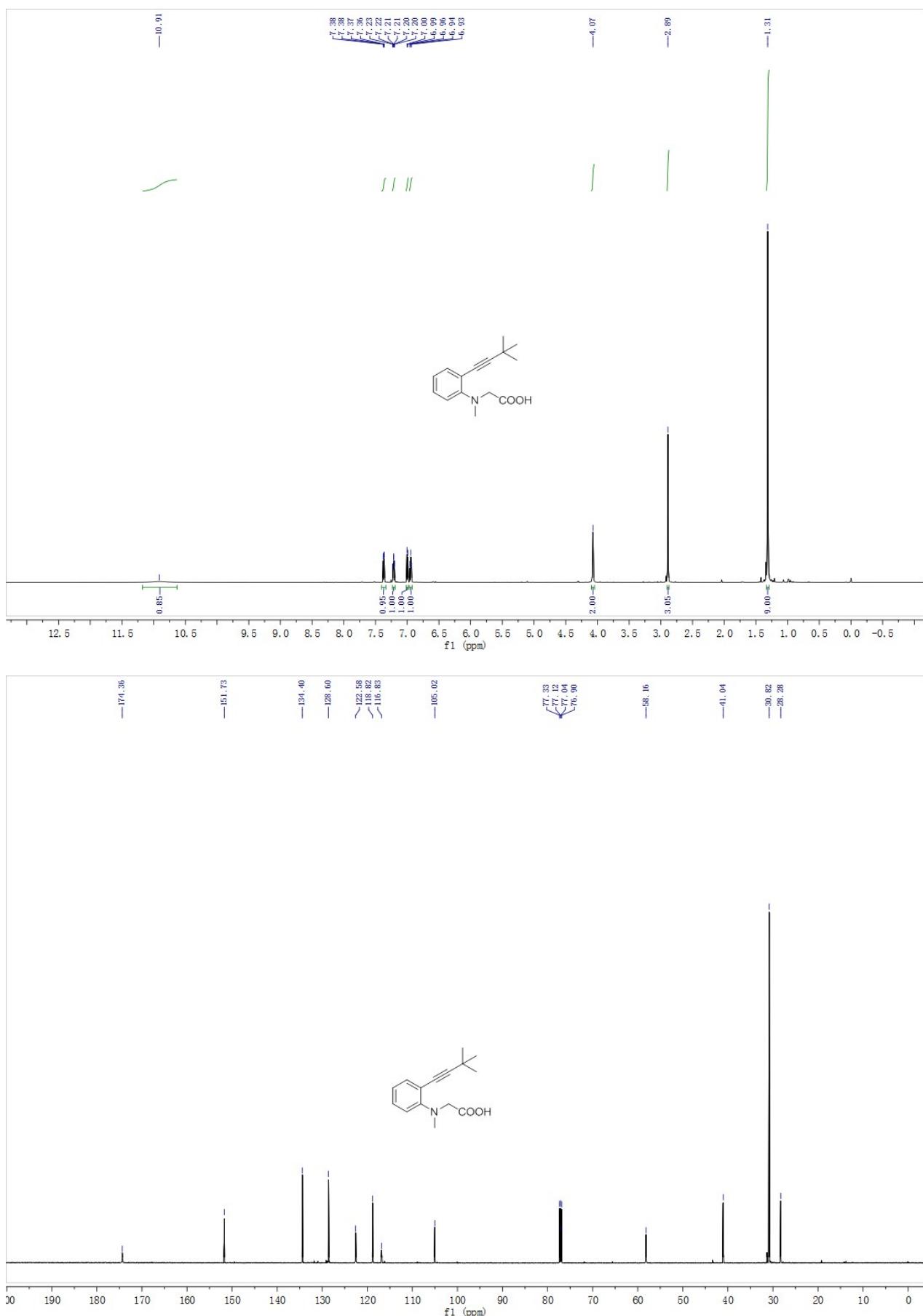
**1n**

**10**

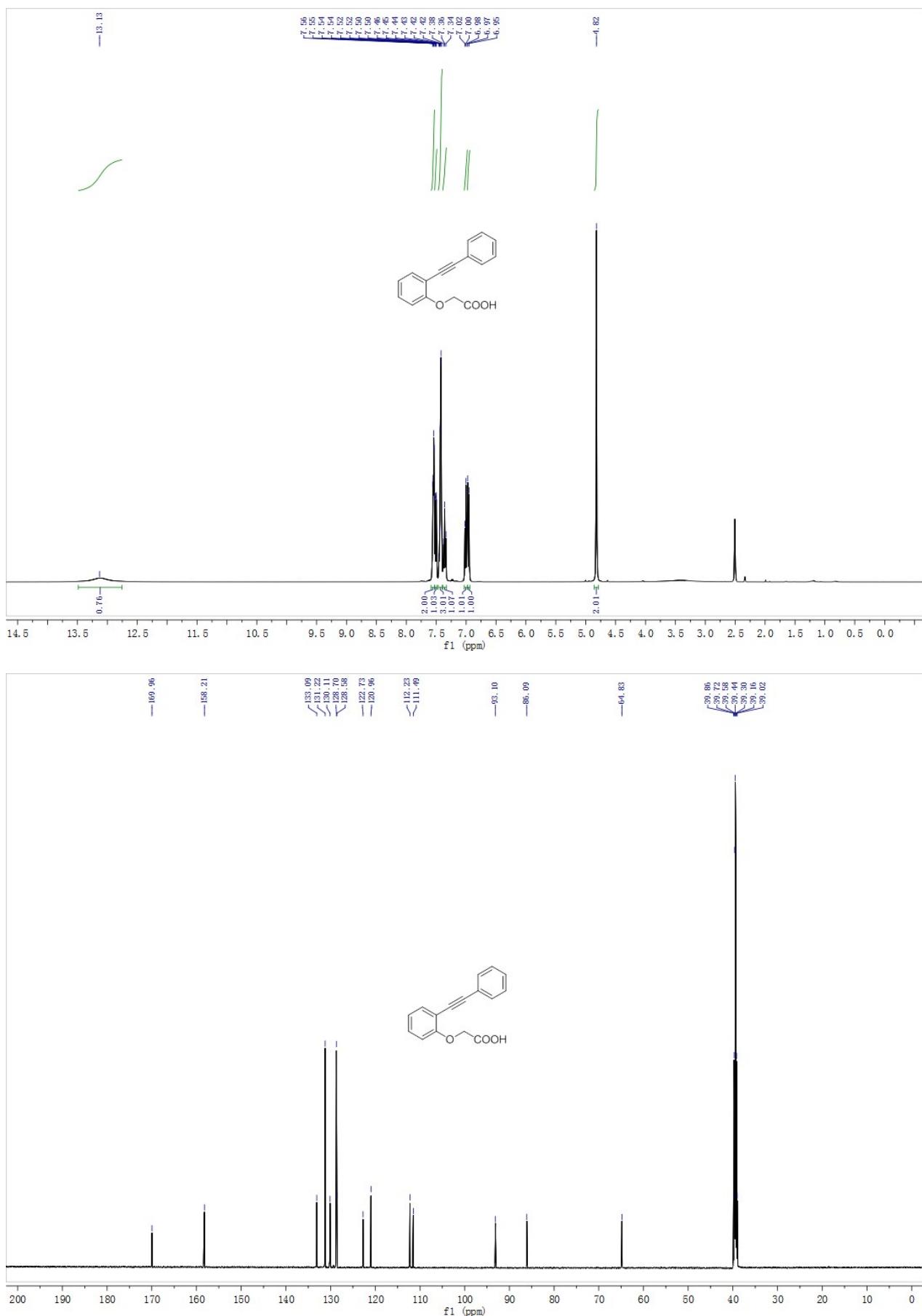
**1p**



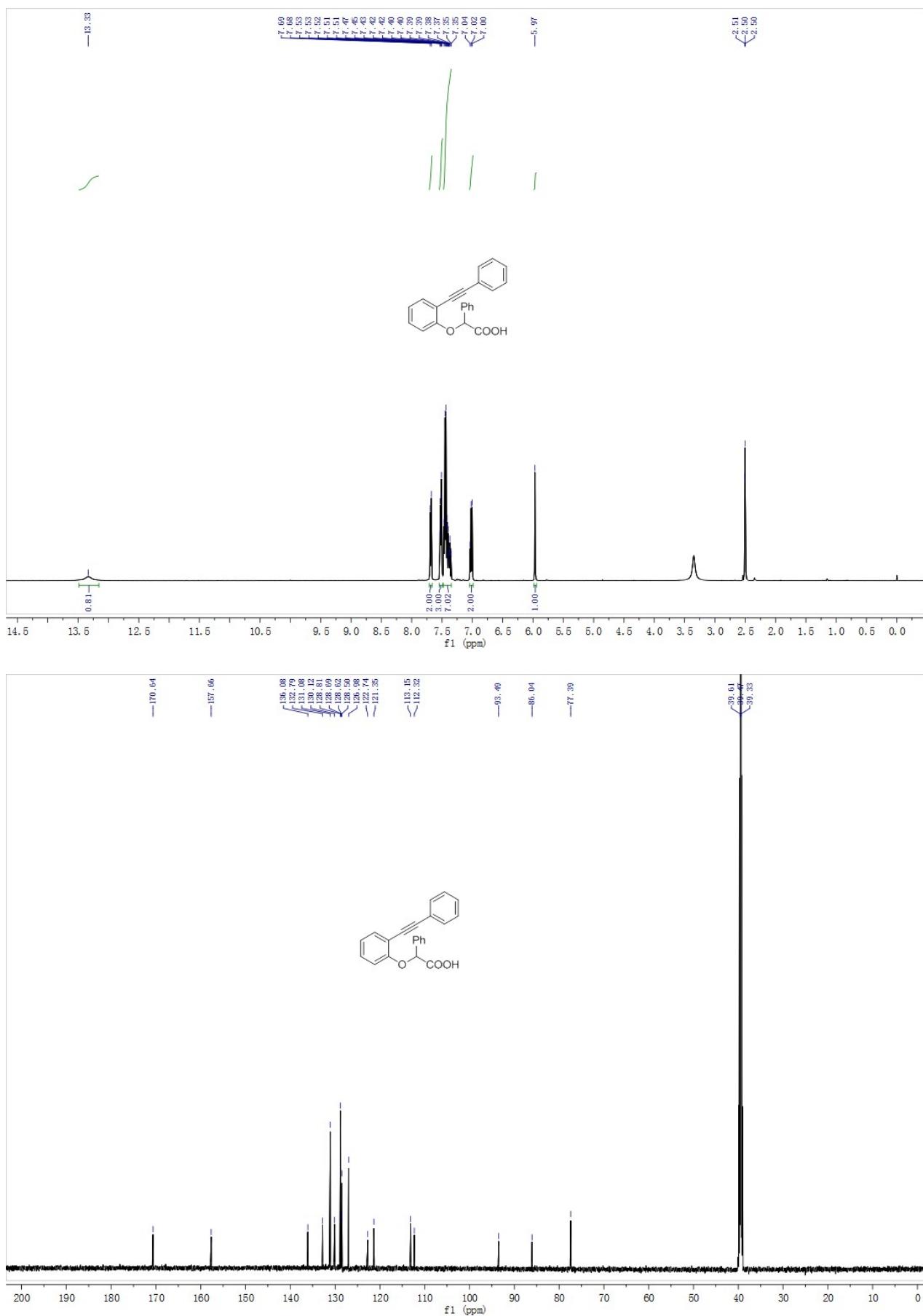
**1q**

**1r**

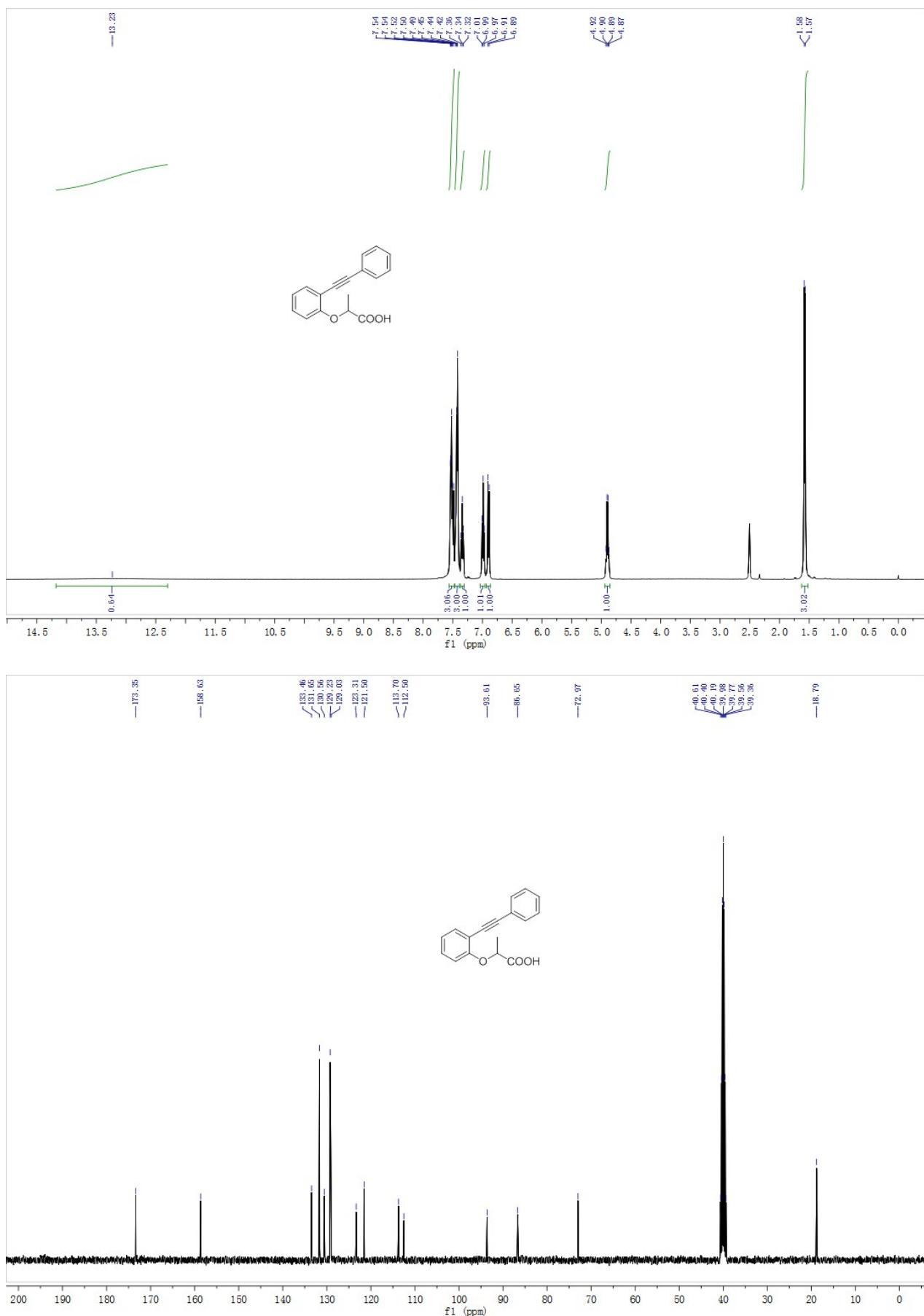
**3a**

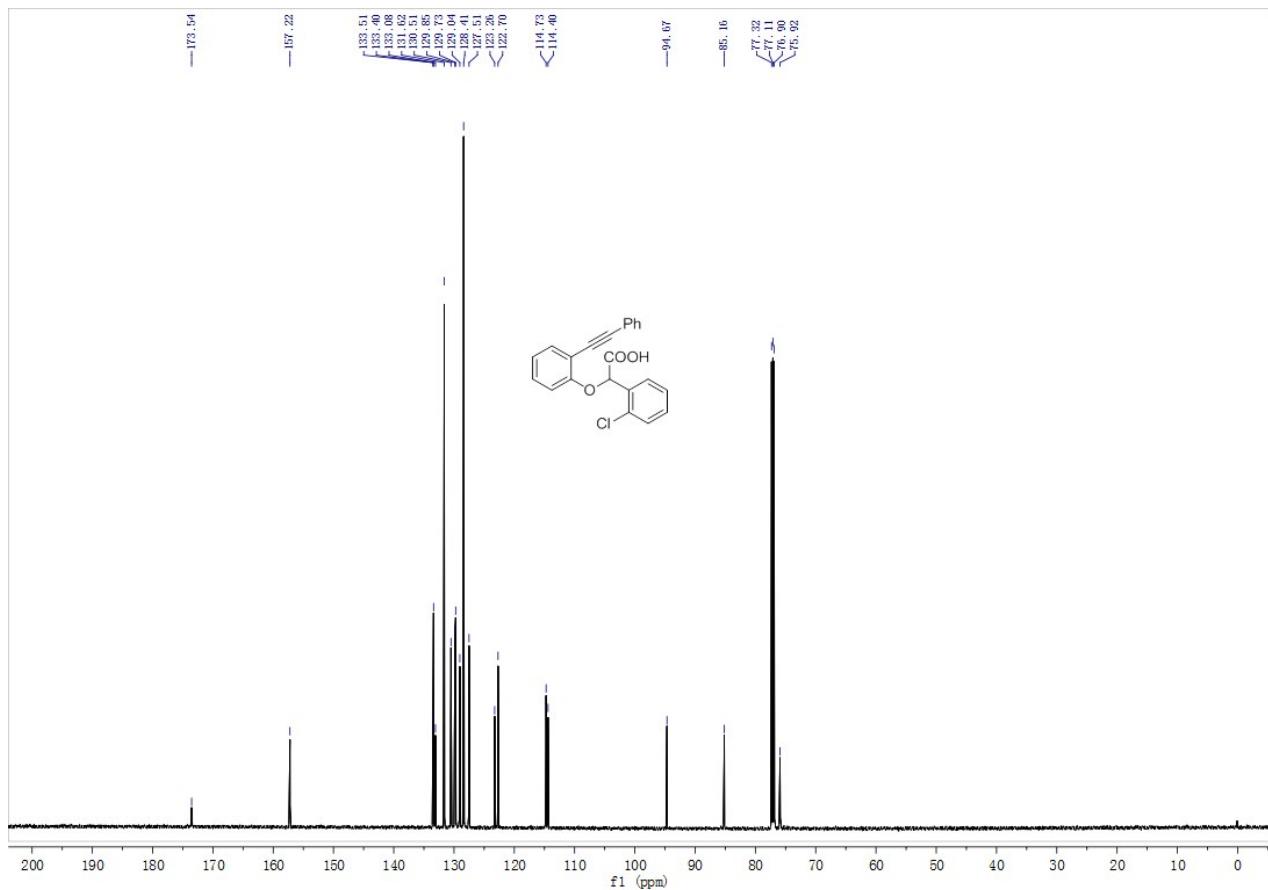
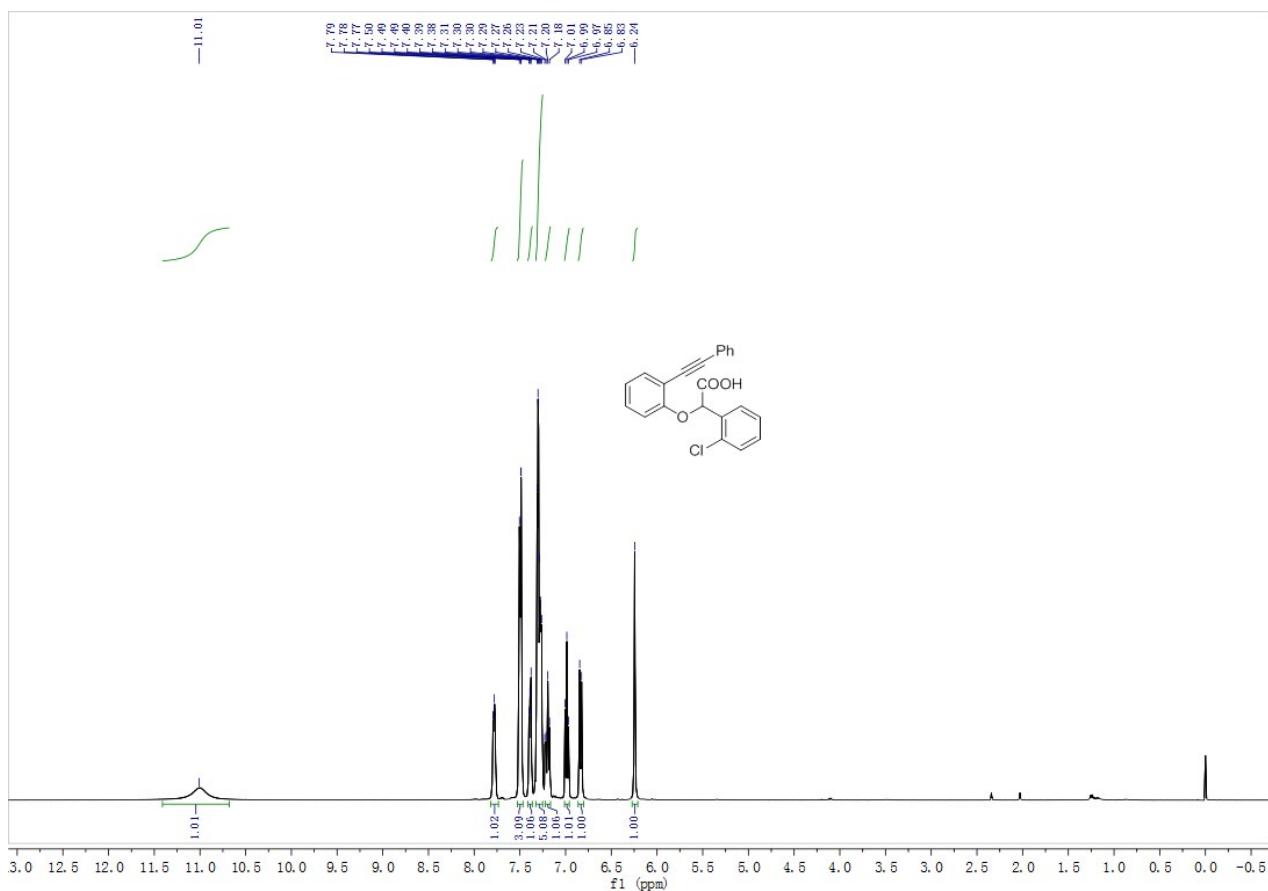


**3b**

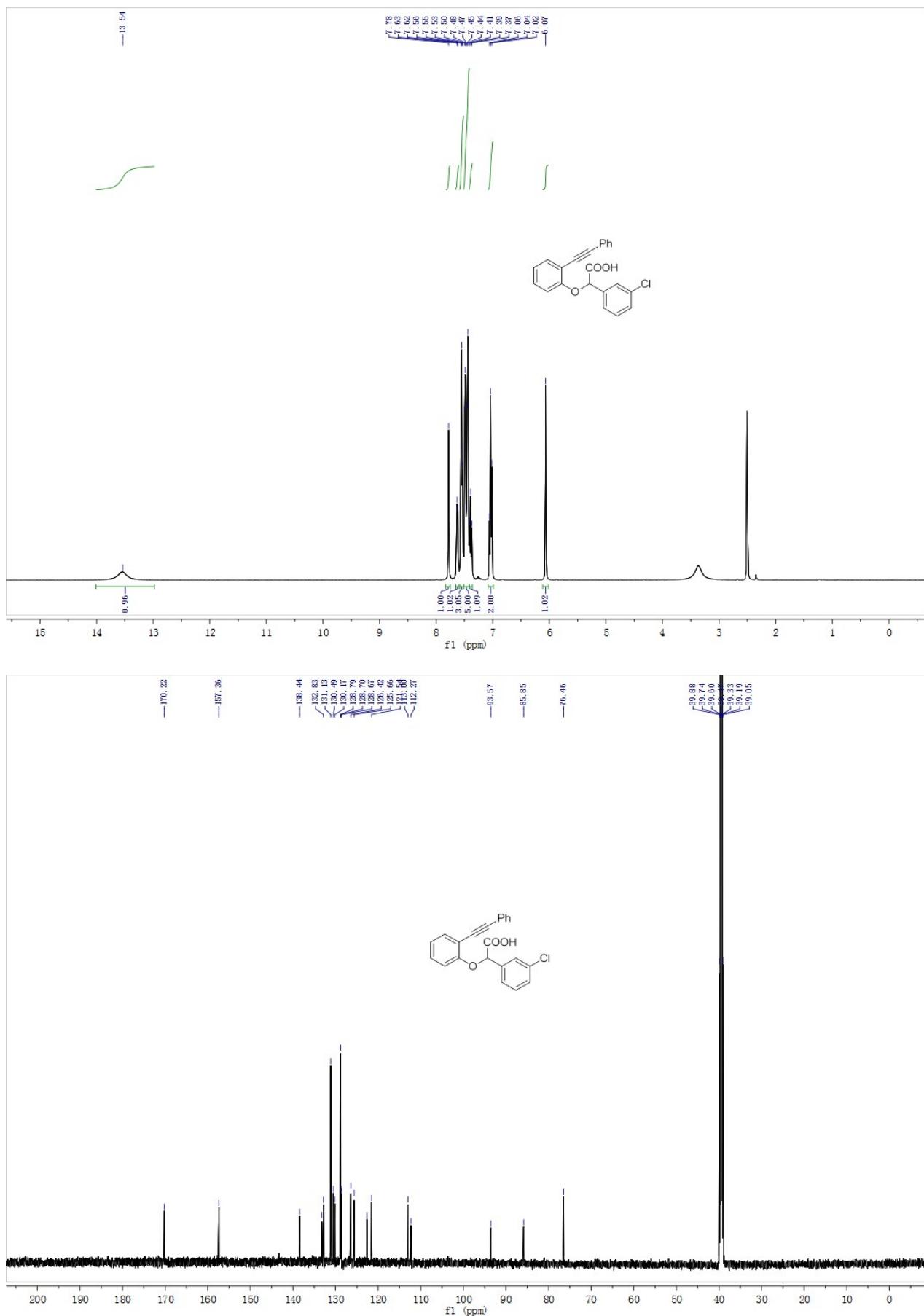


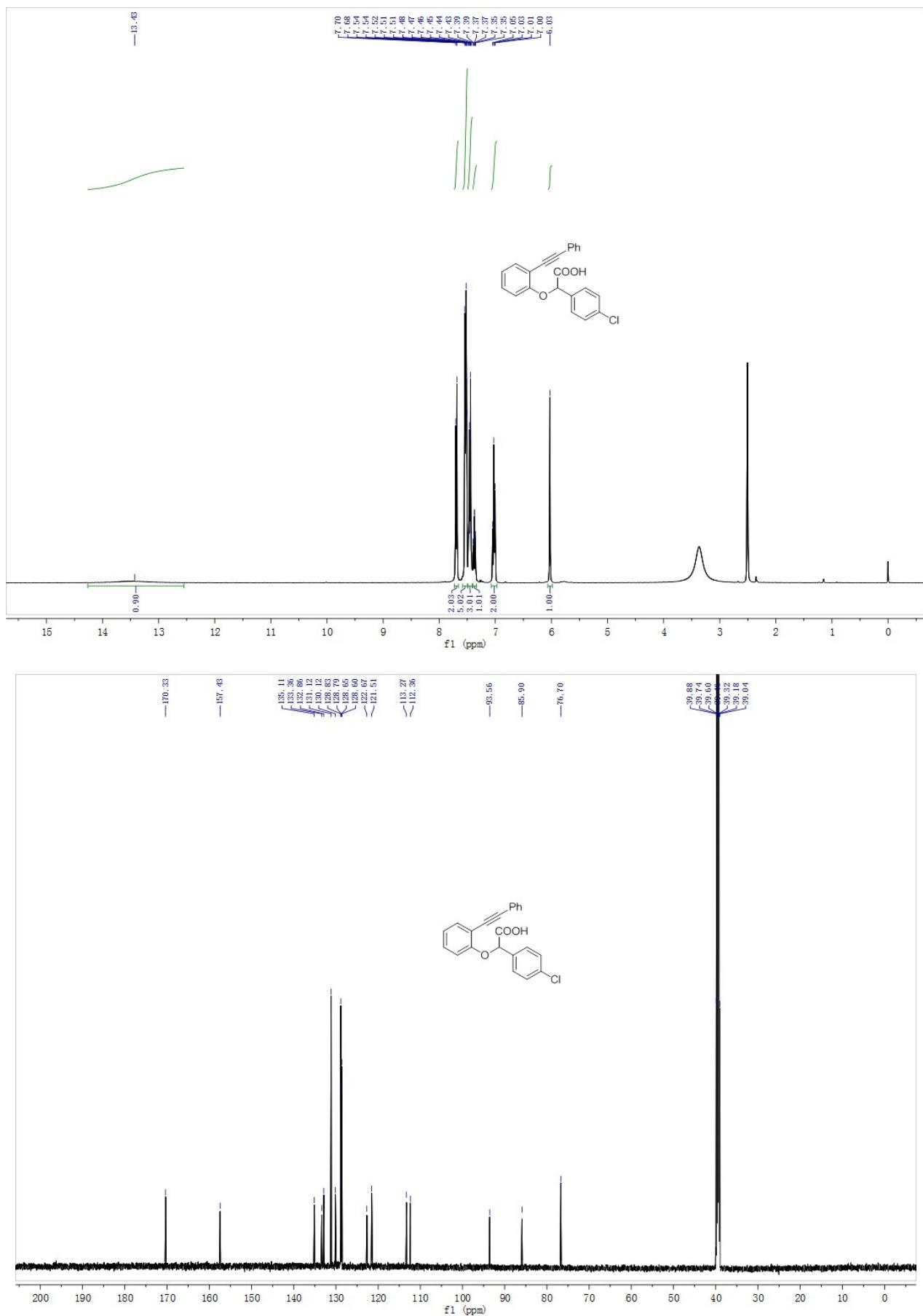
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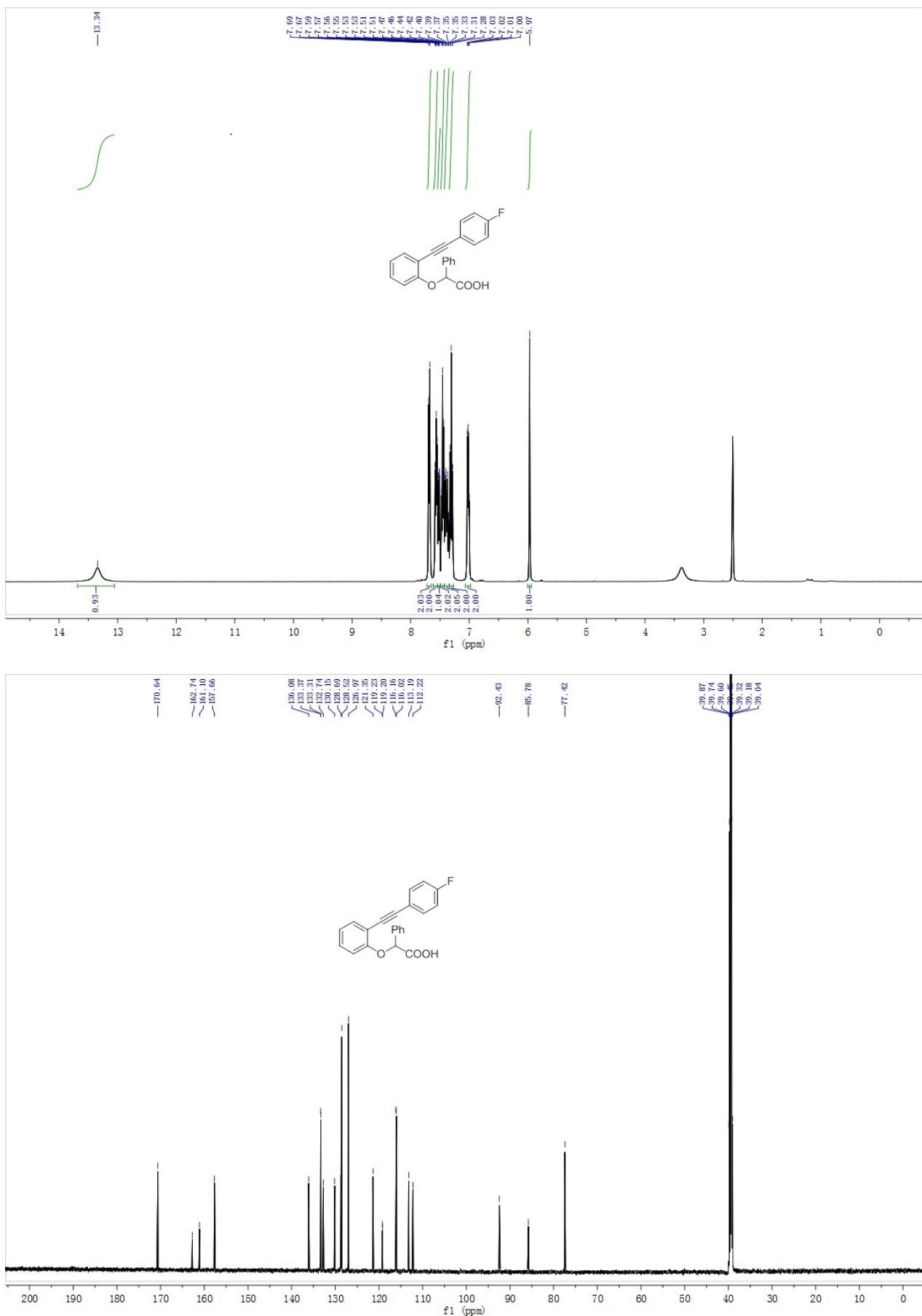


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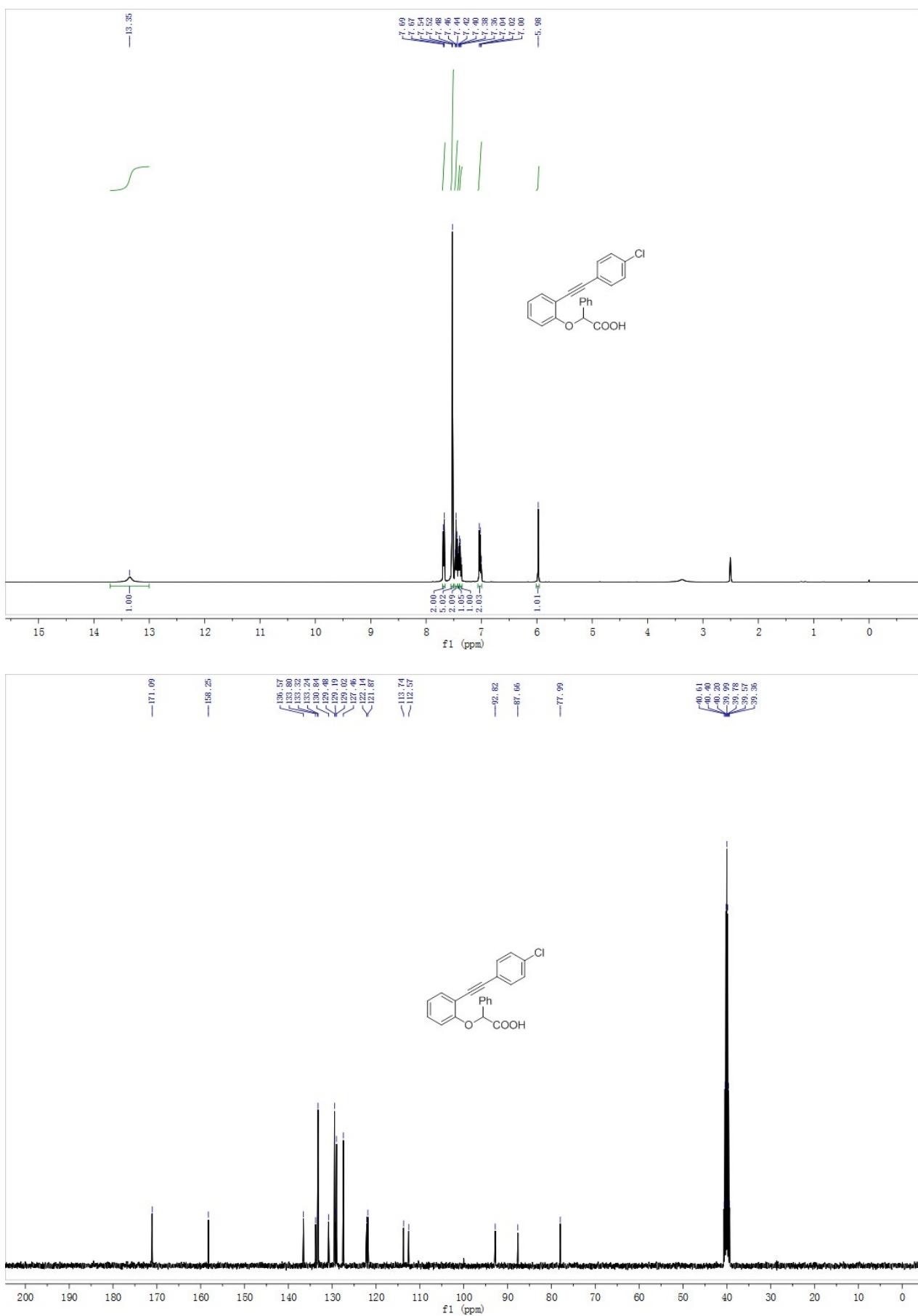
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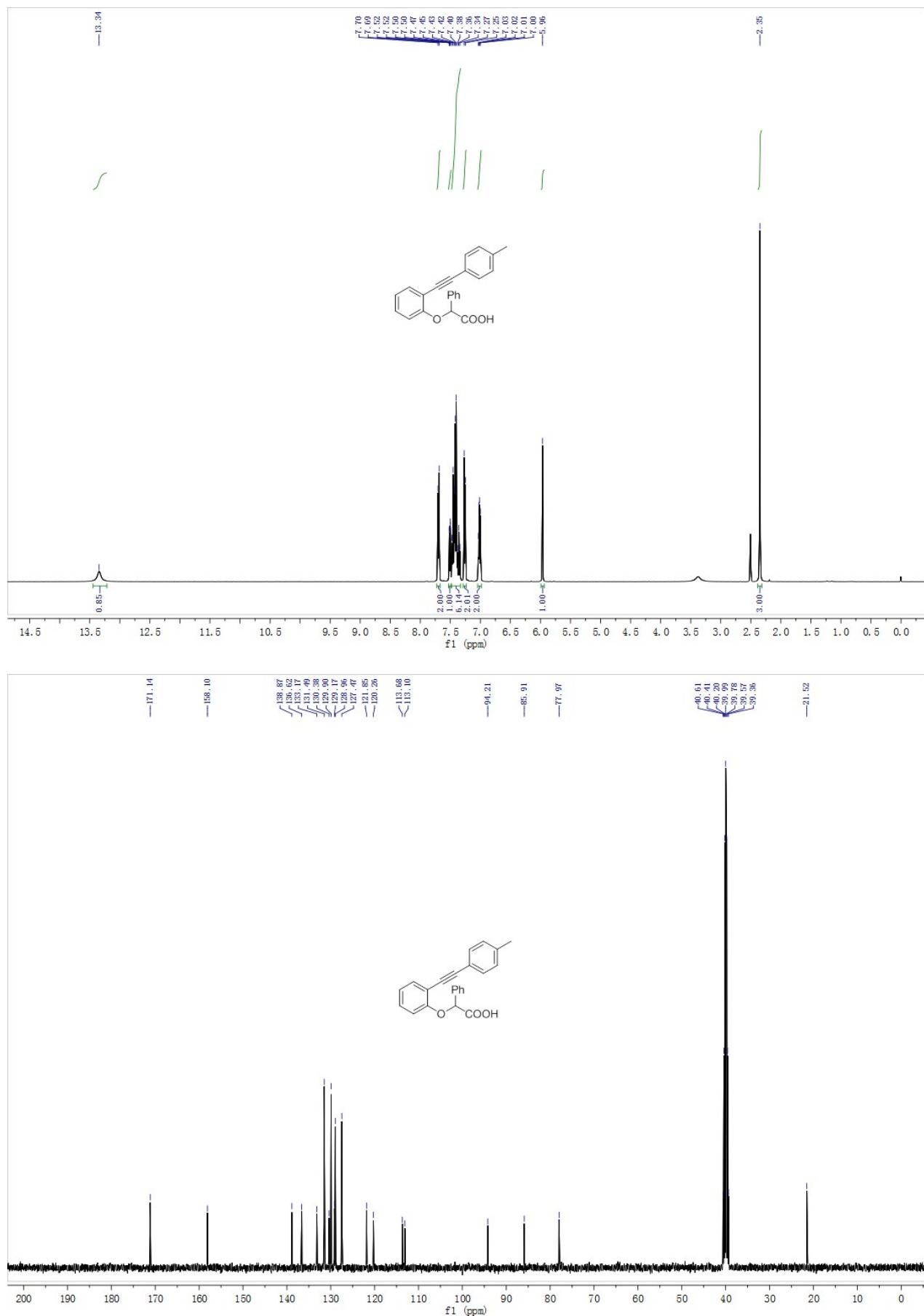


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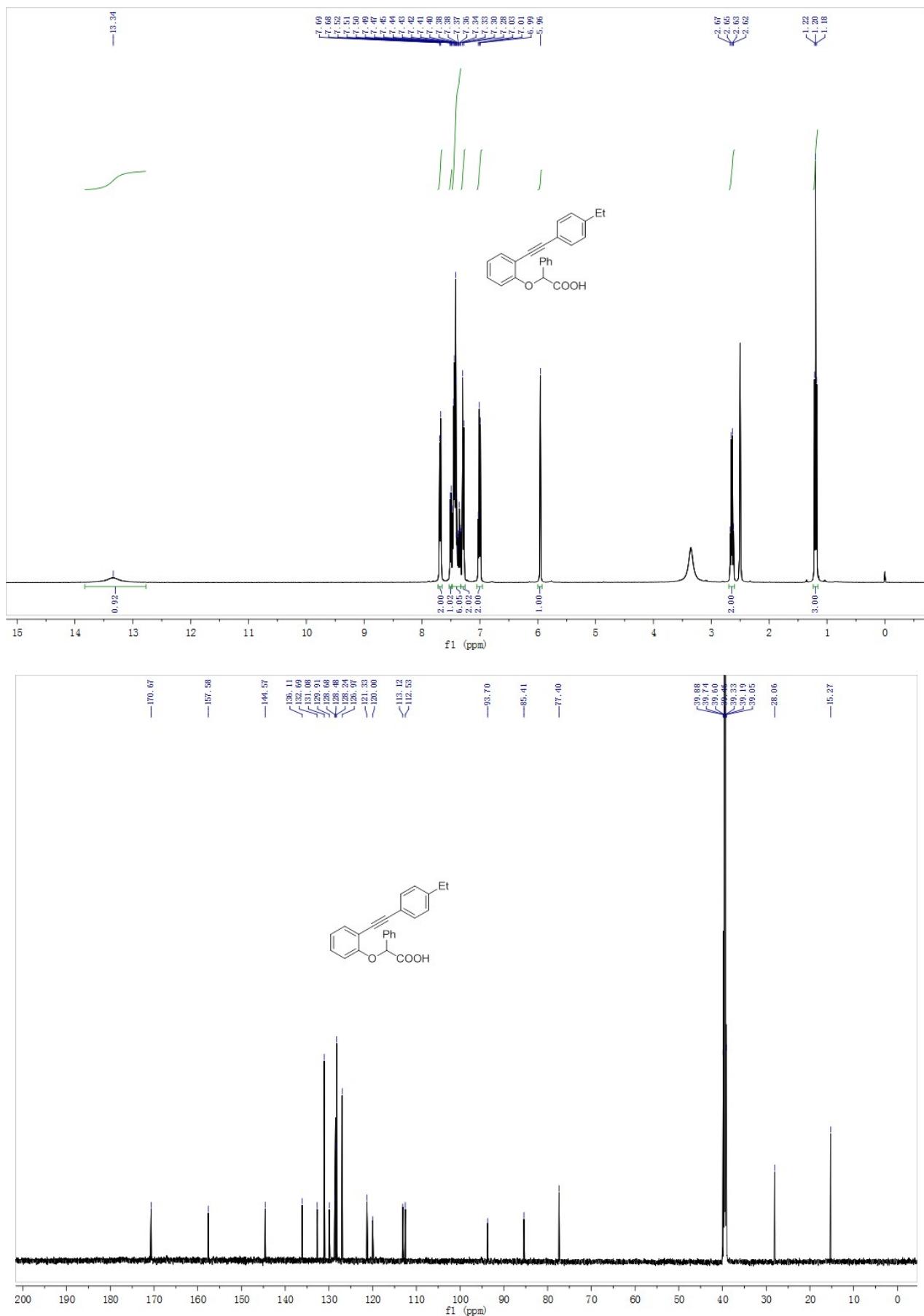
**3g**

3h

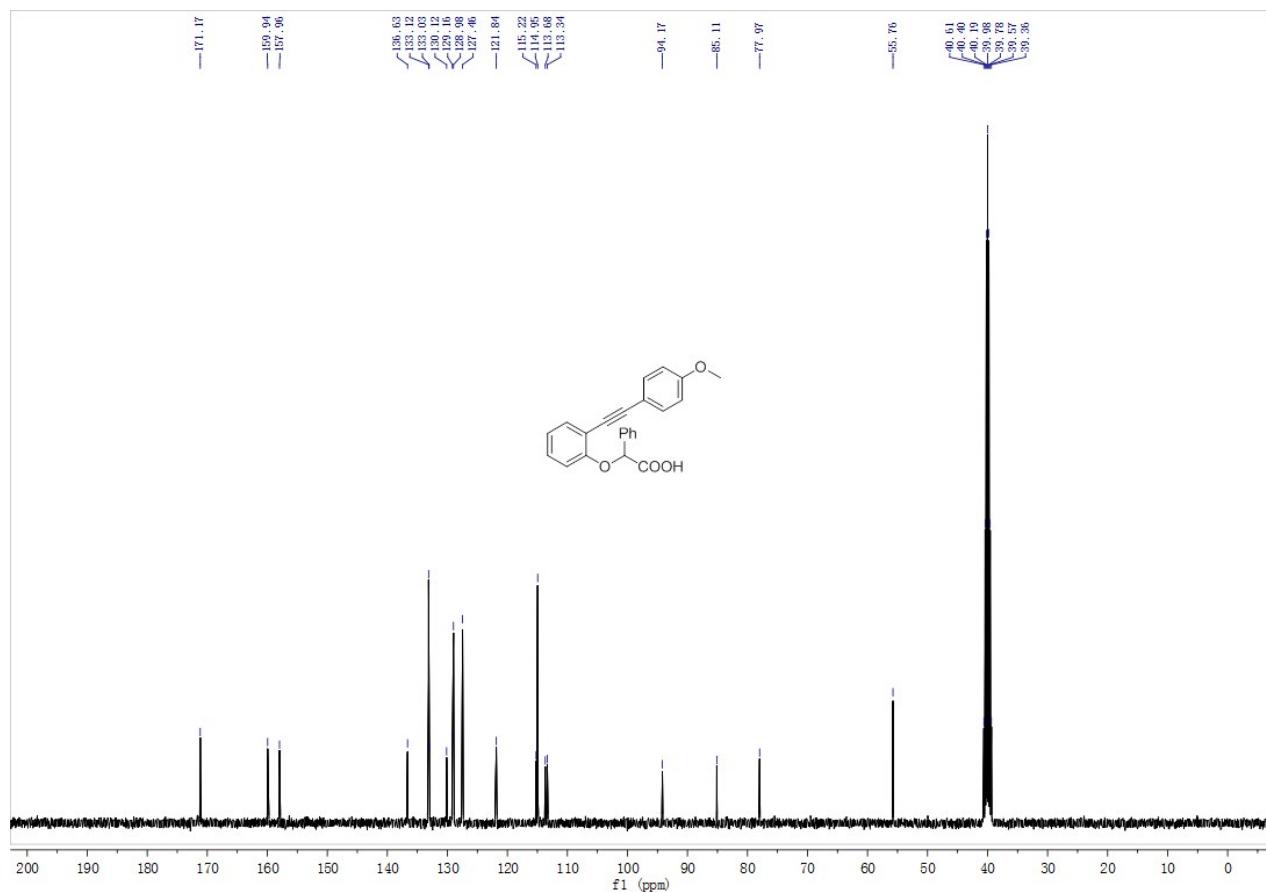
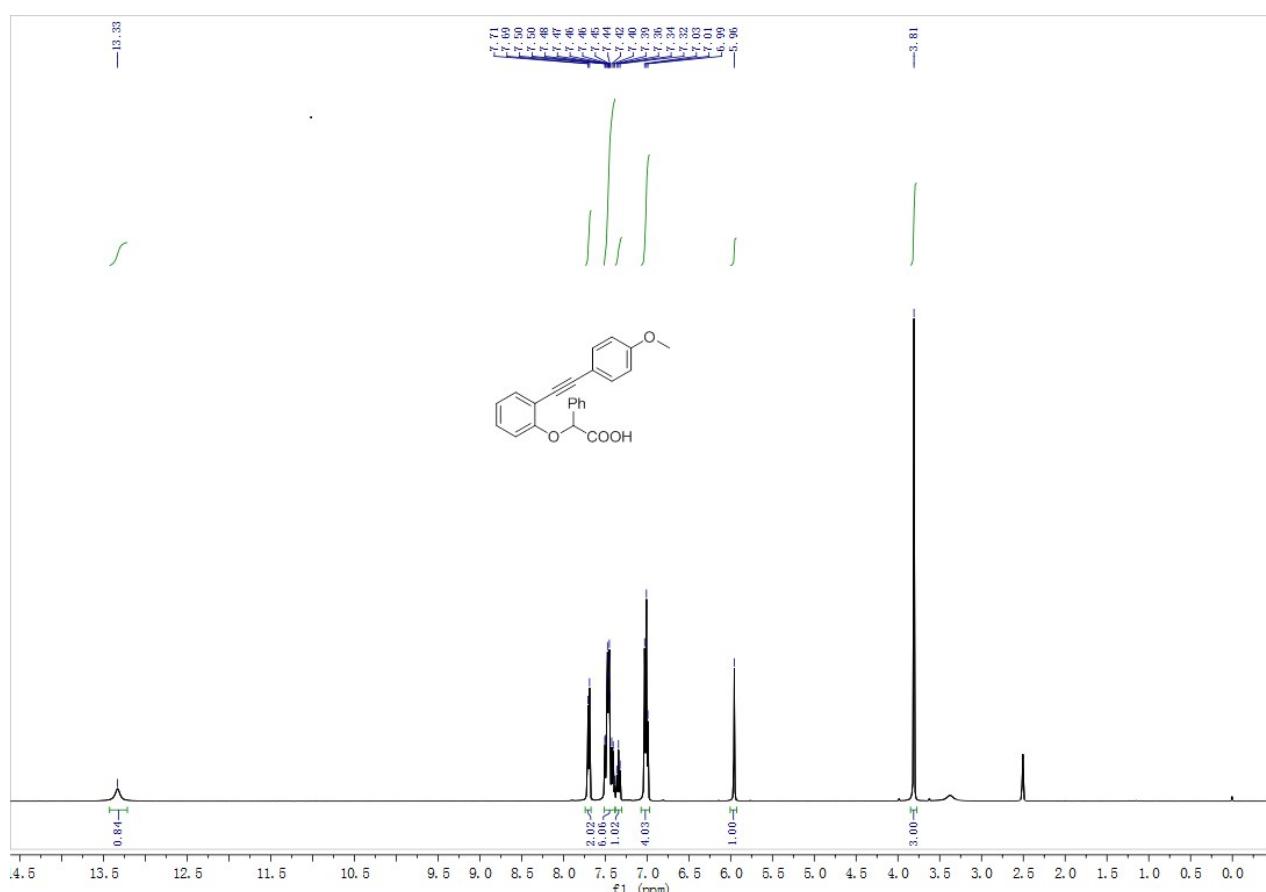


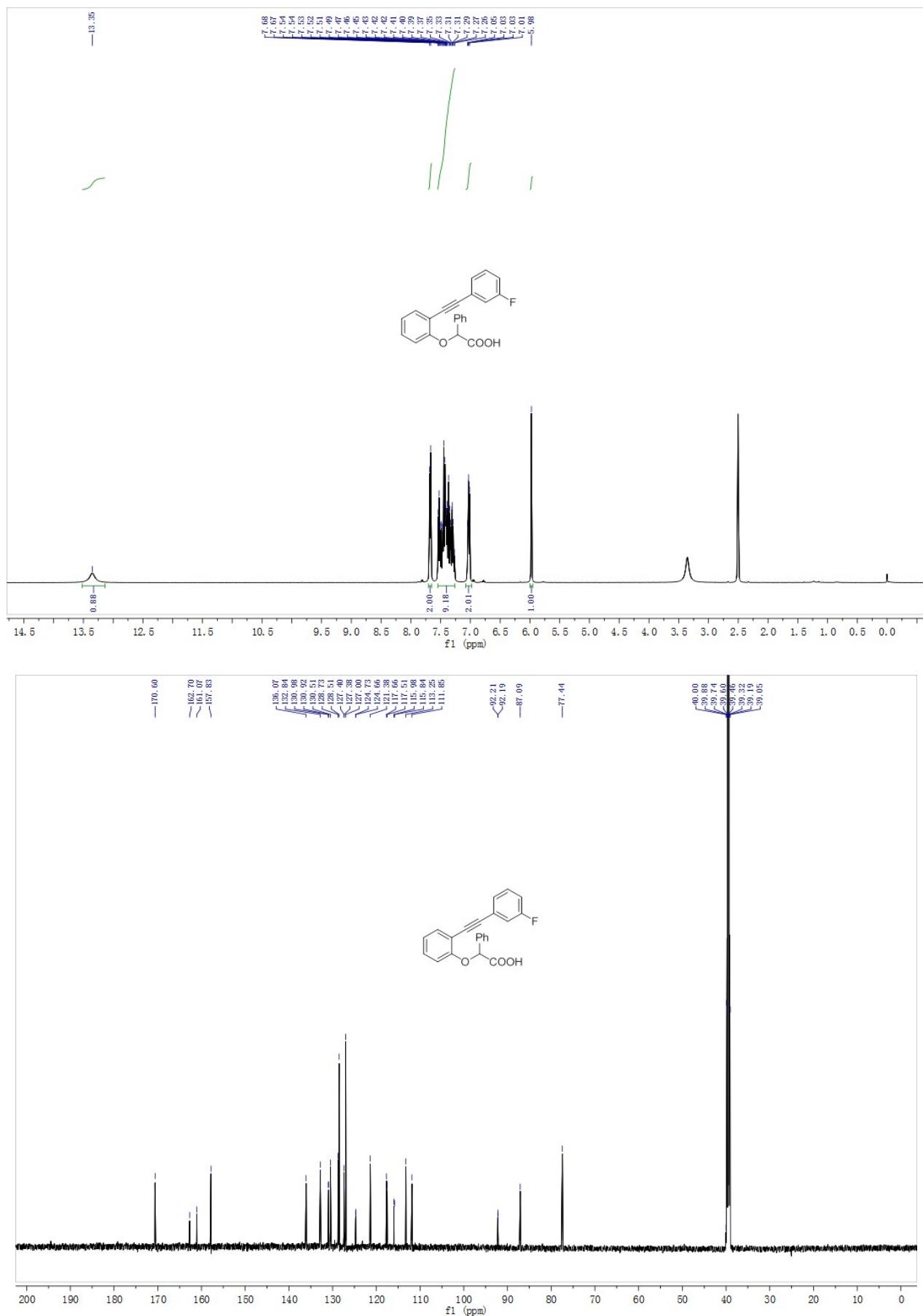
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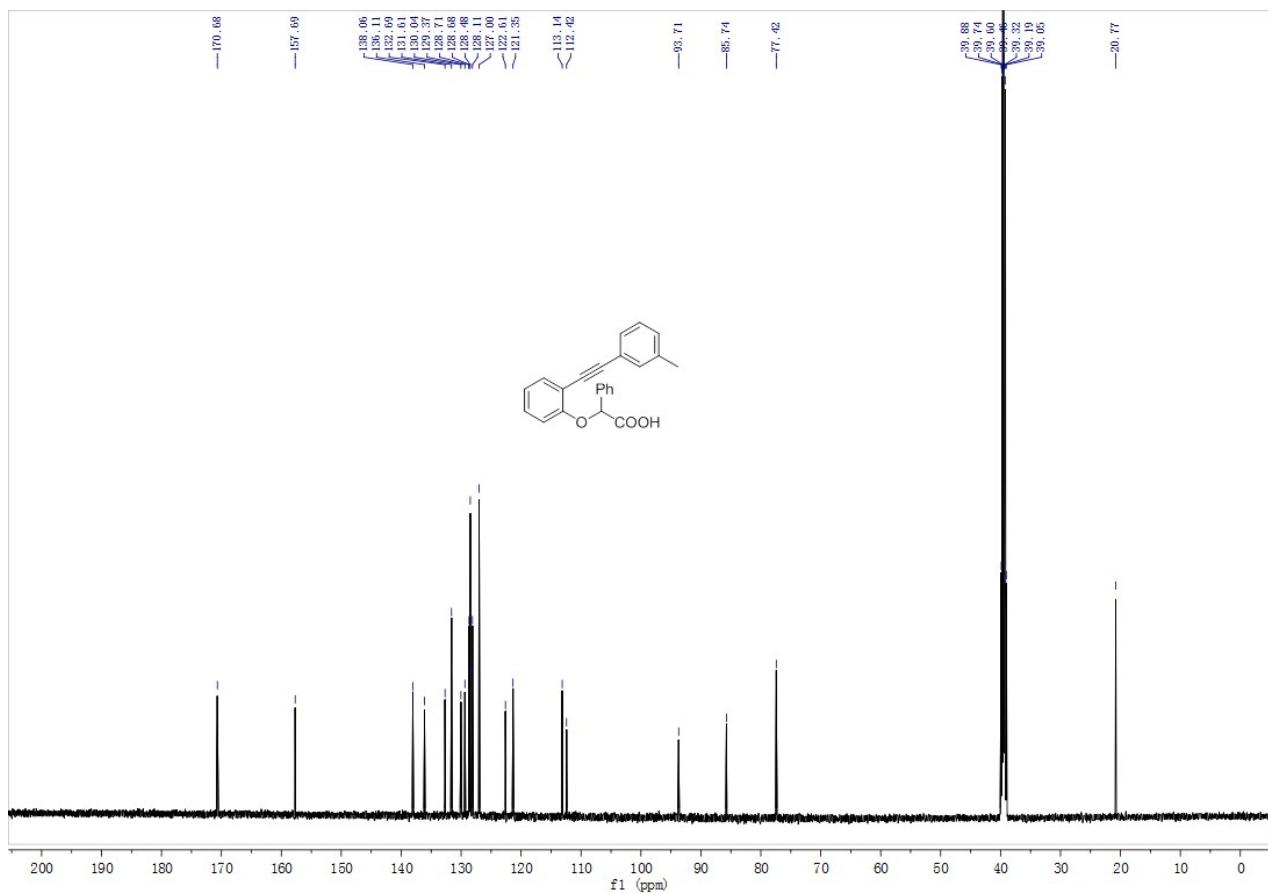
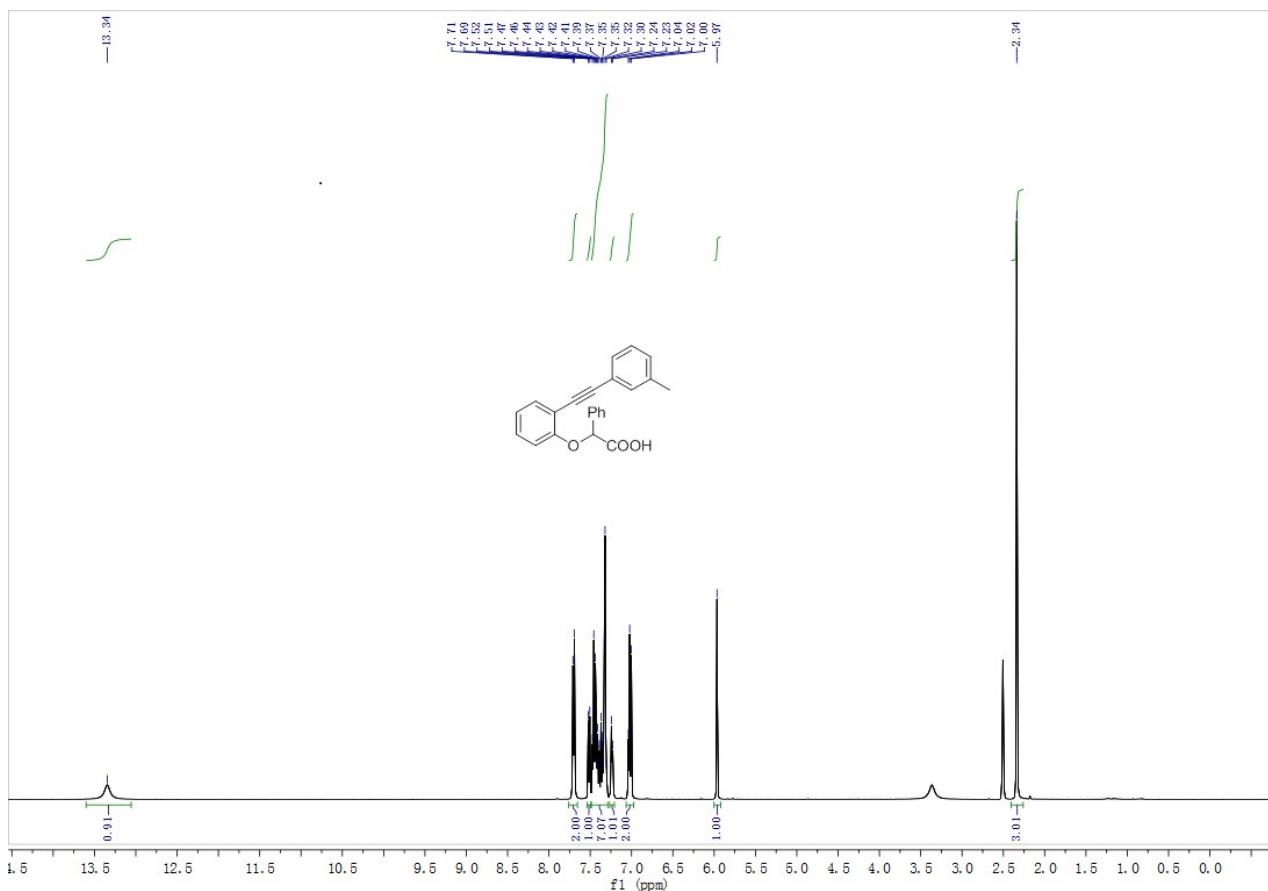
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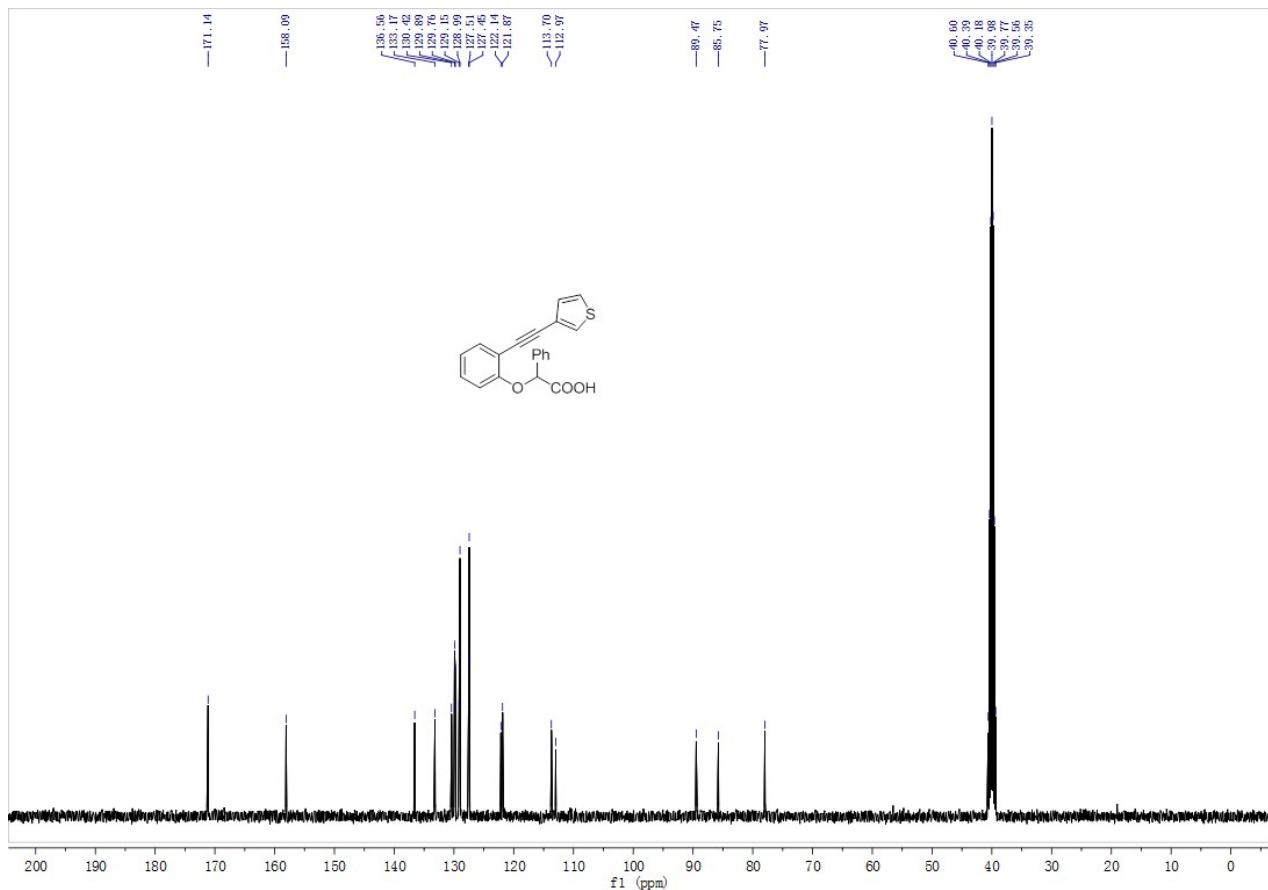
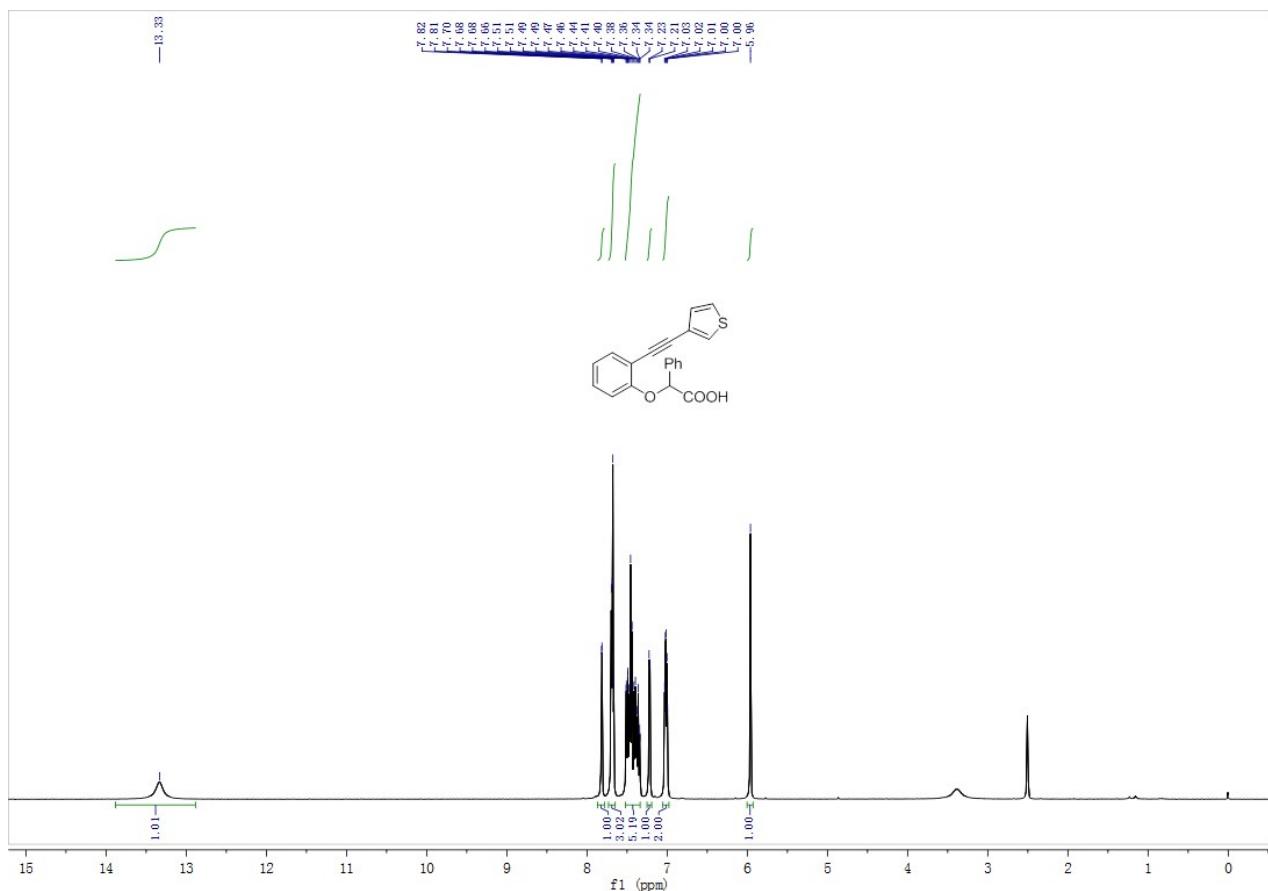


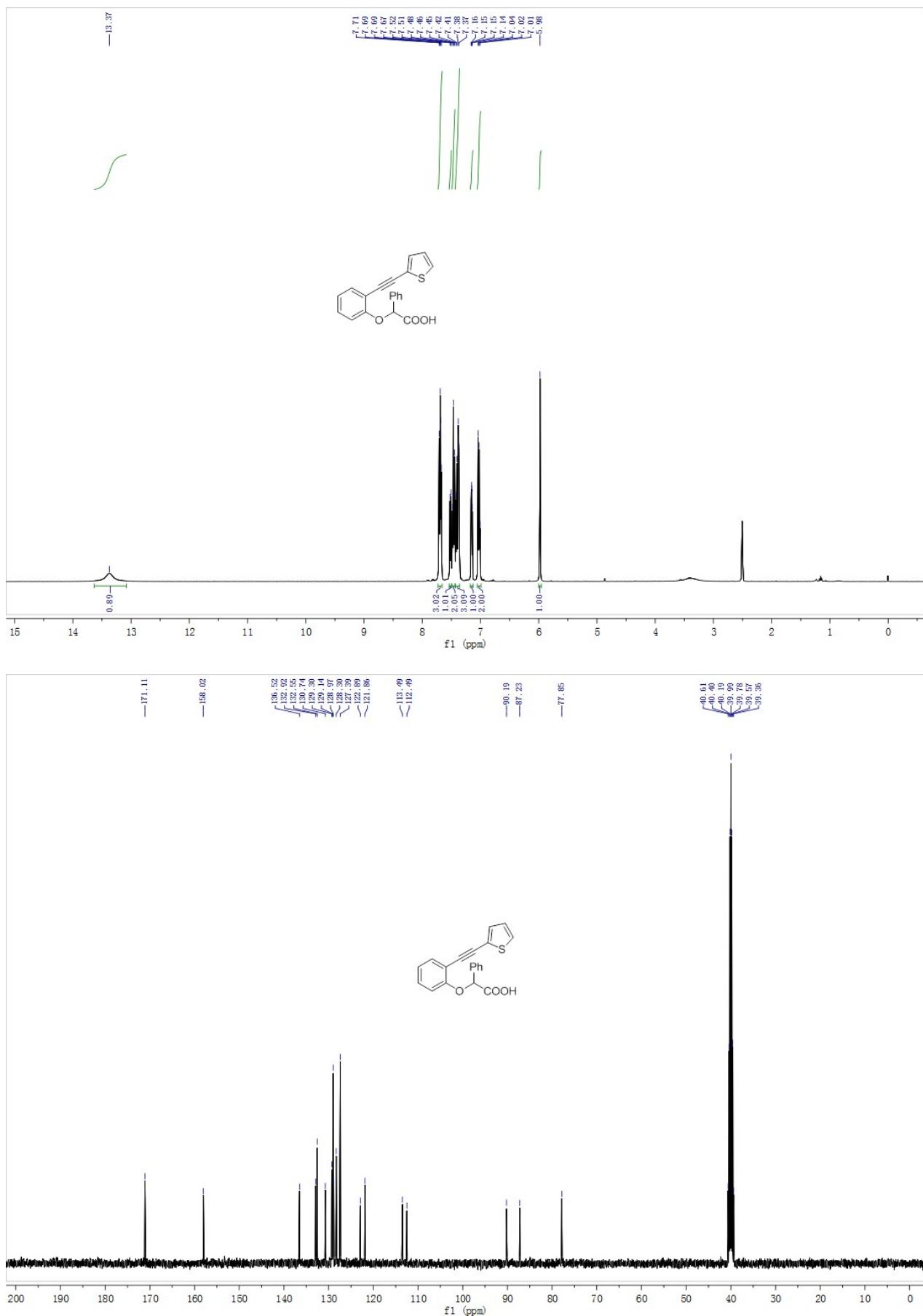
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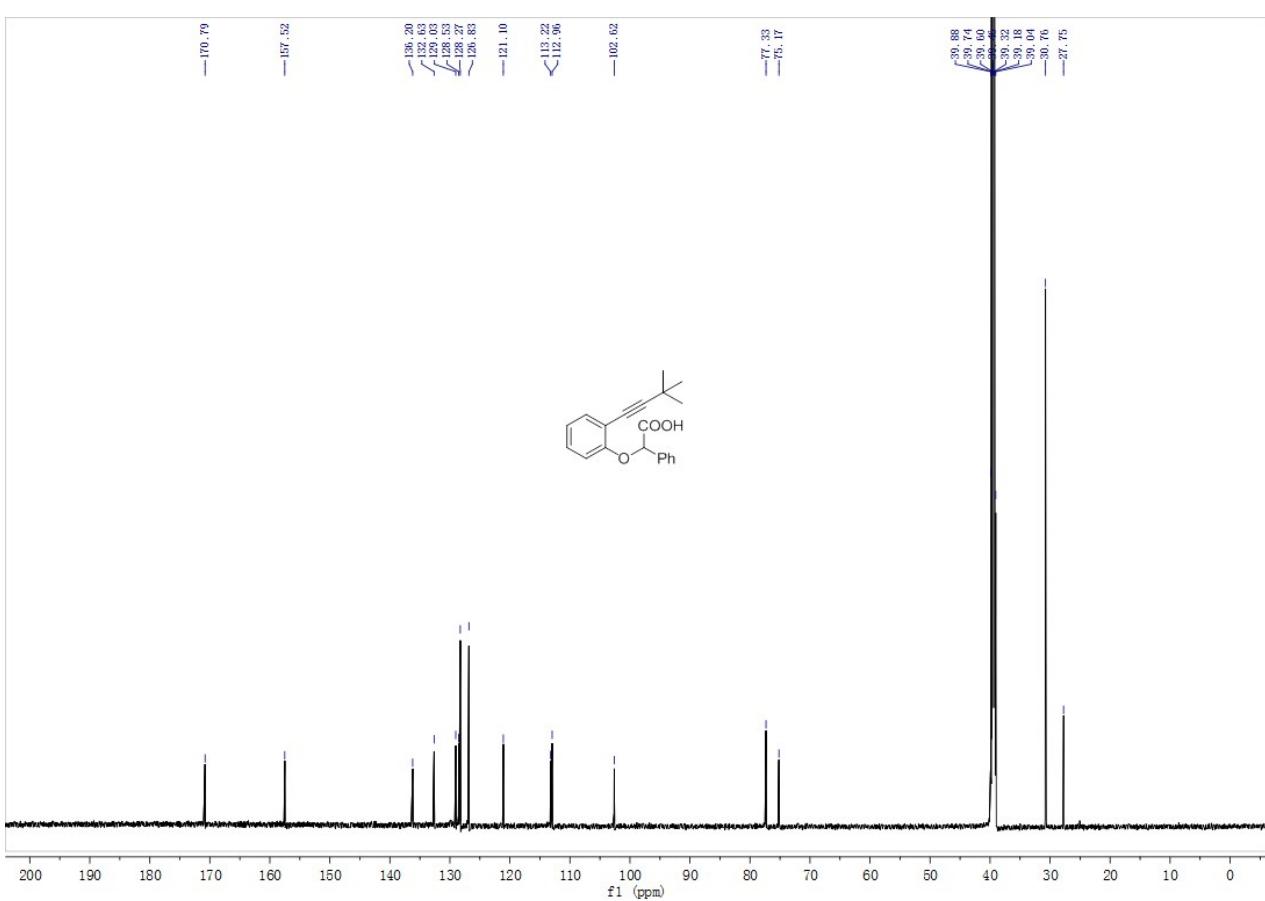
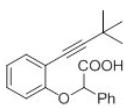
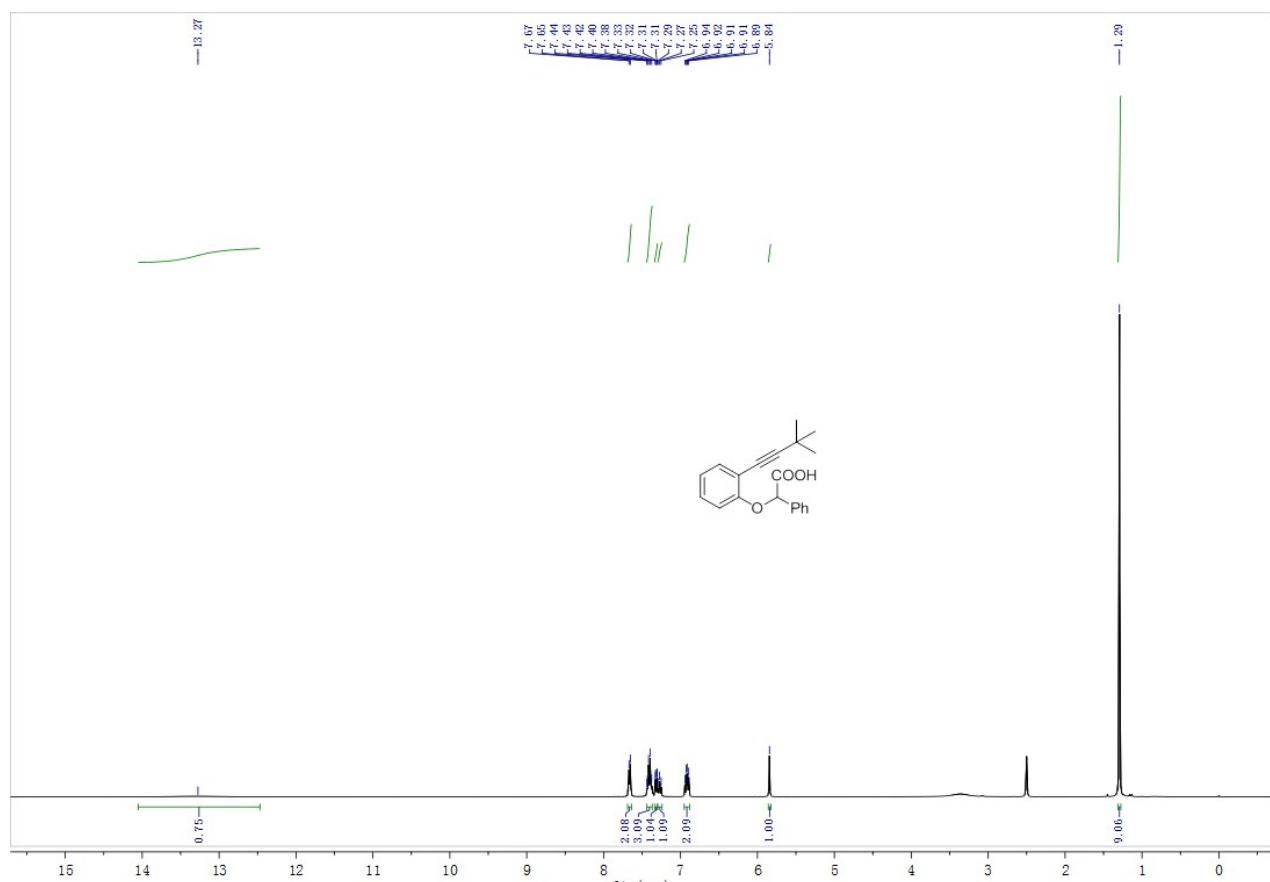


**3m**

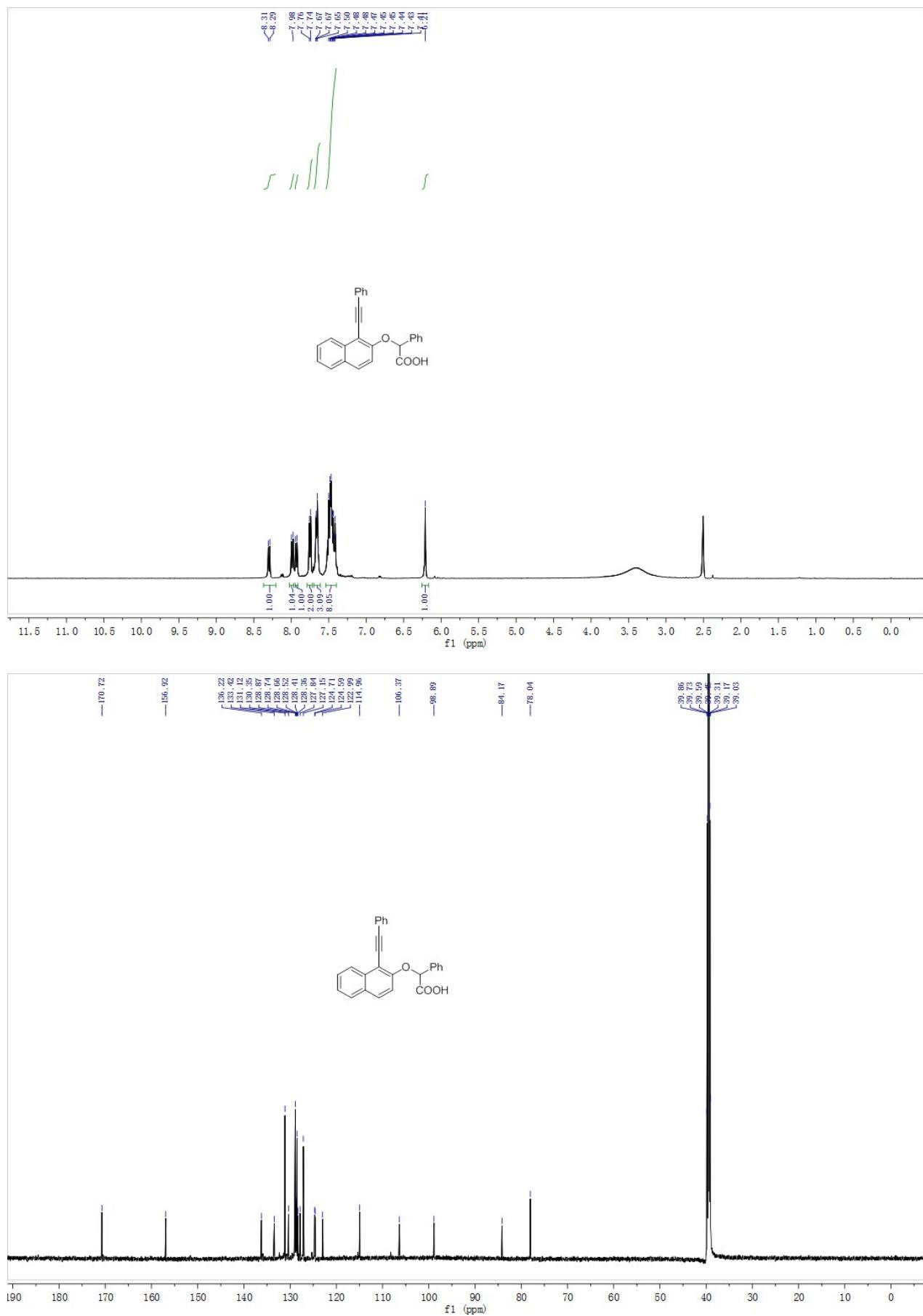
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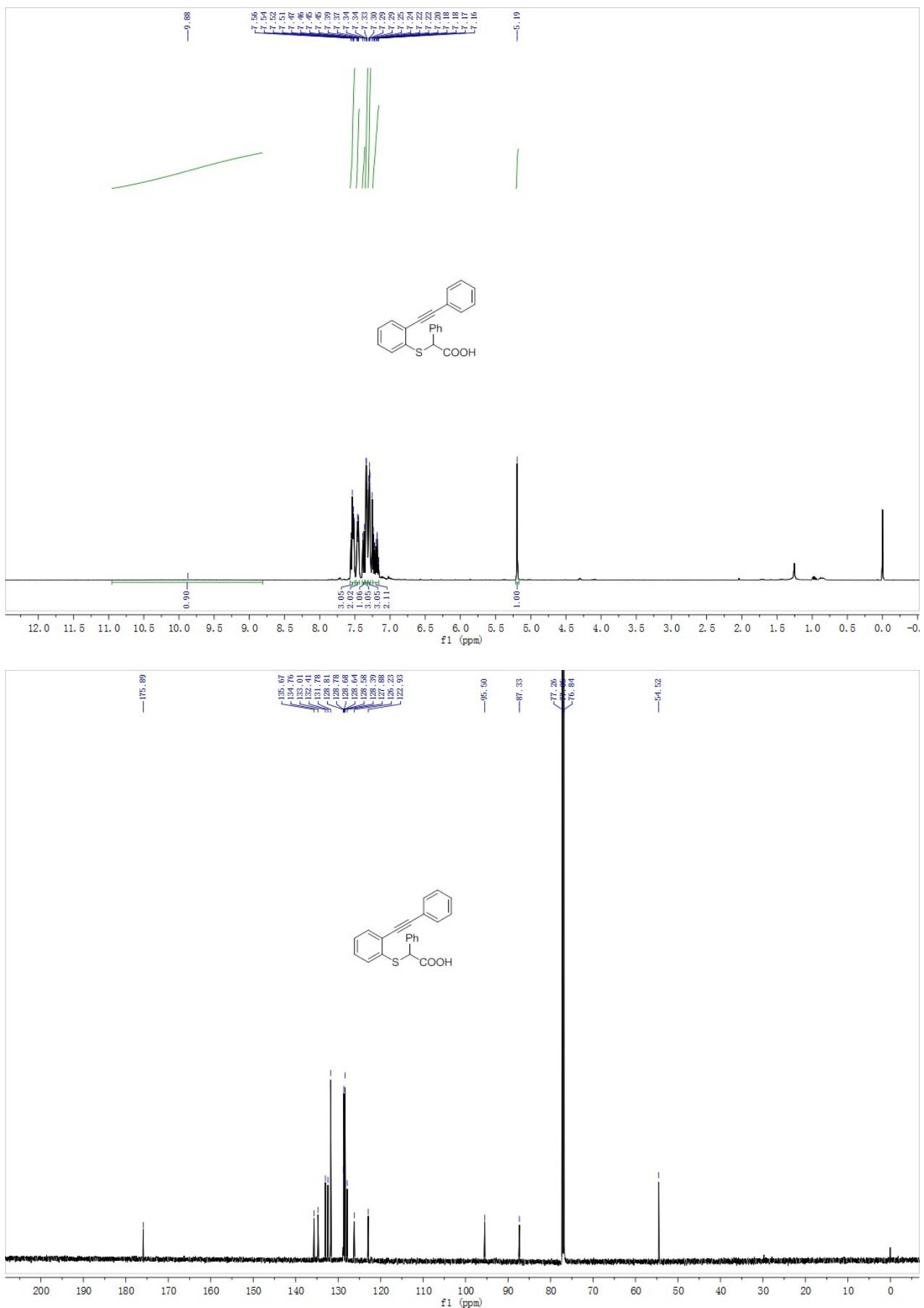
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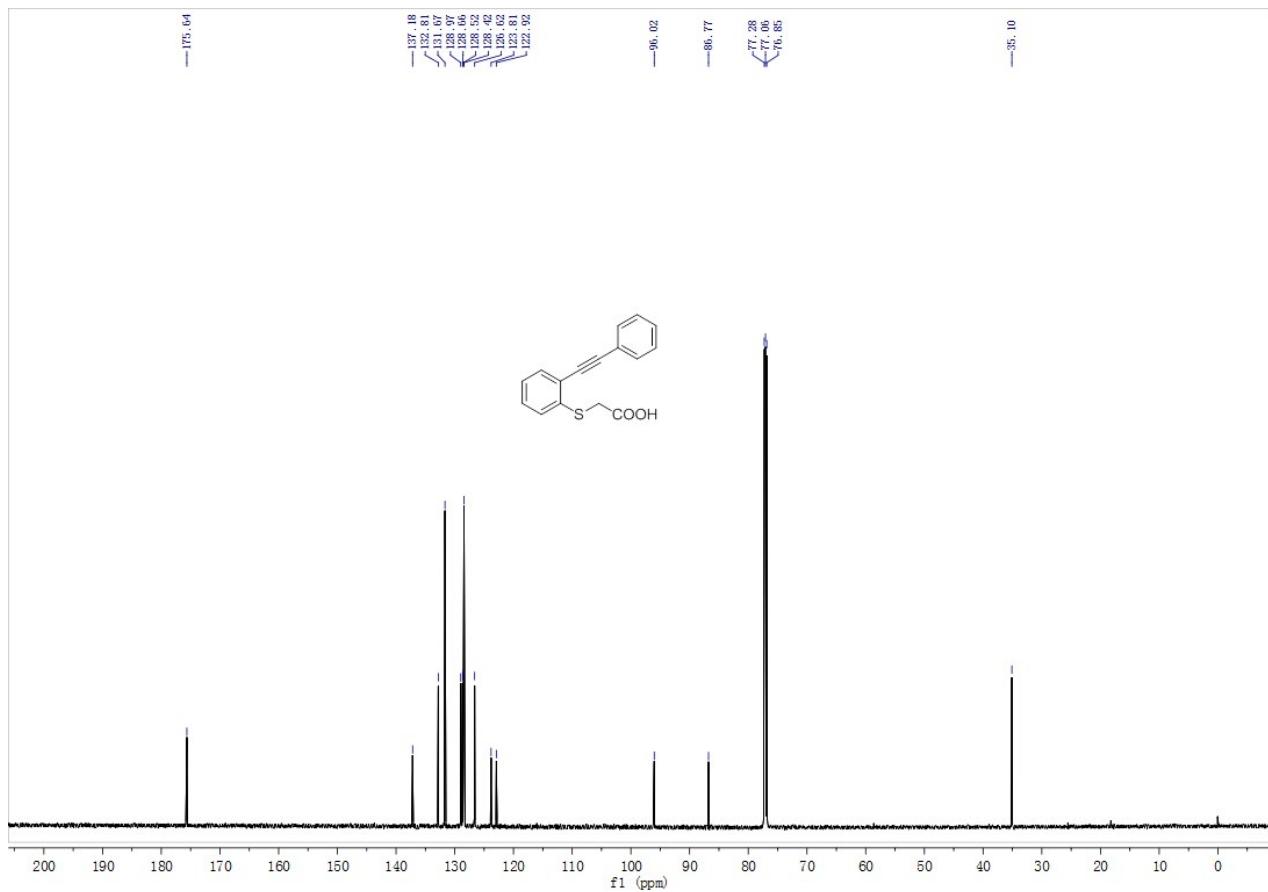
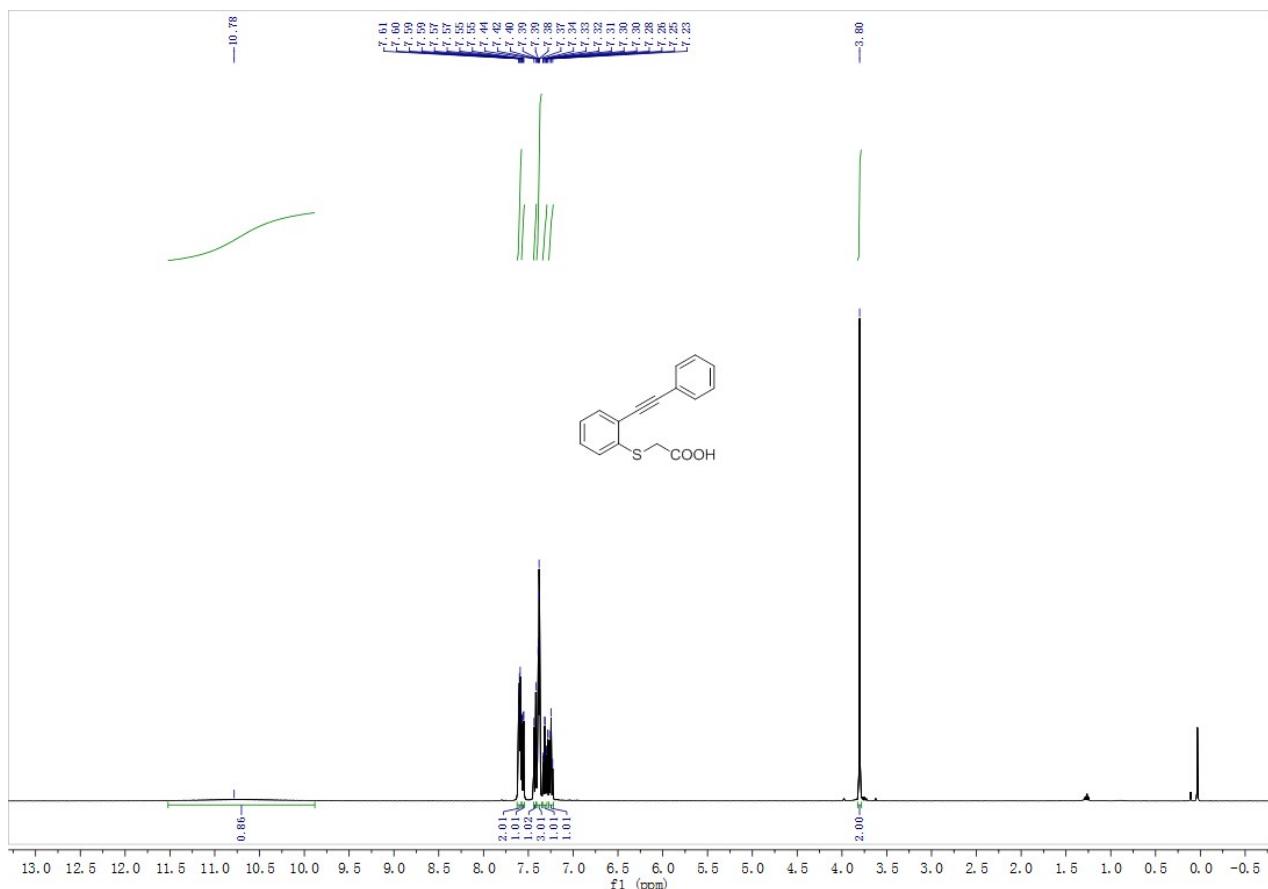
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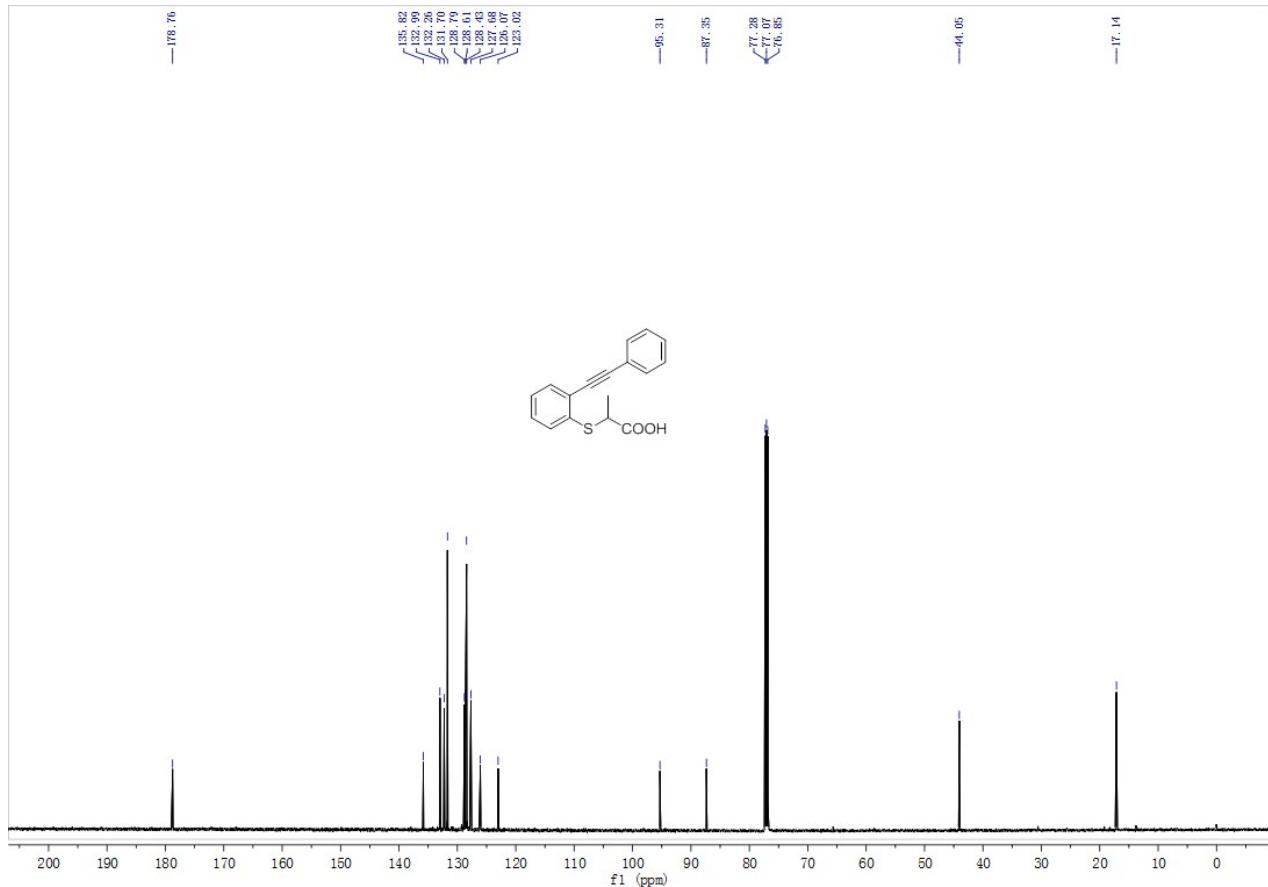
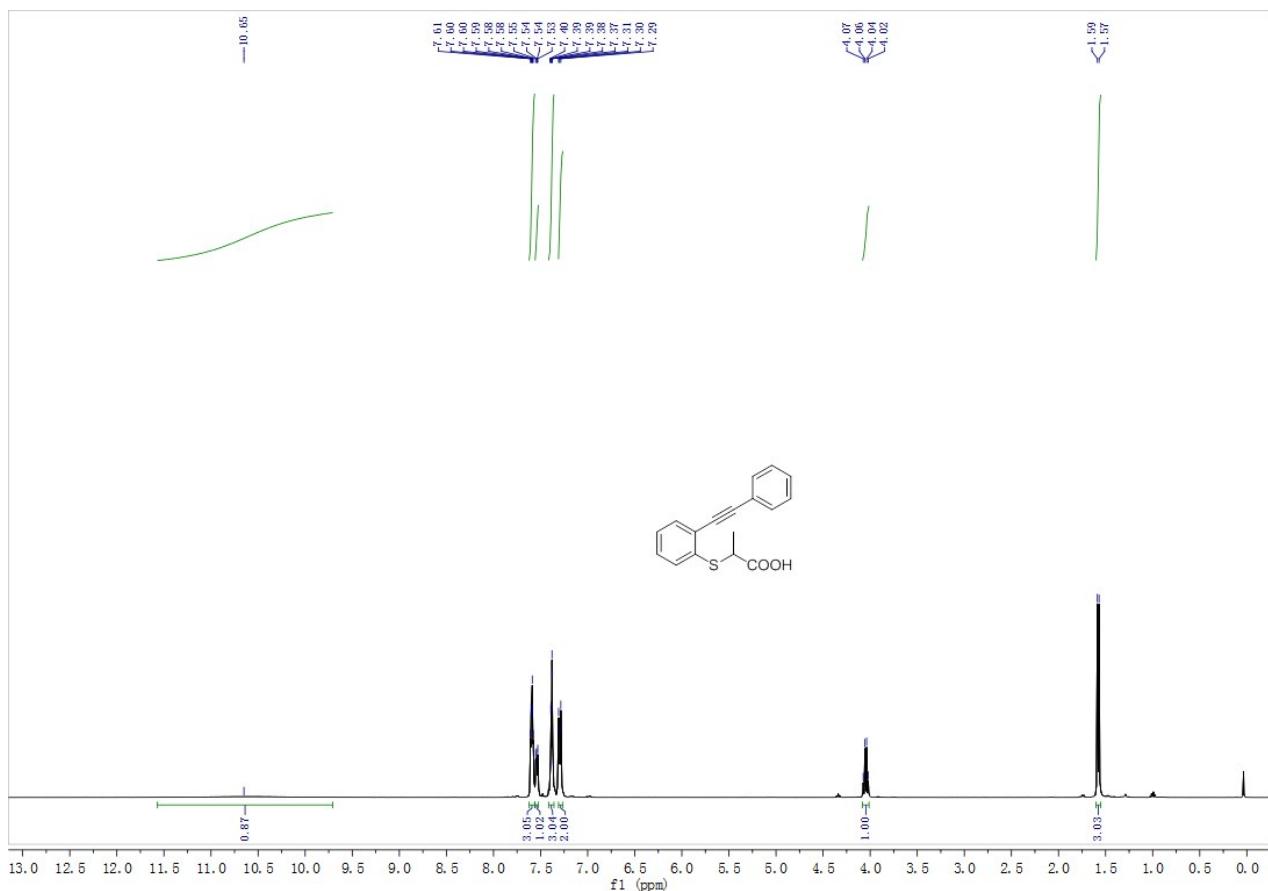
5a

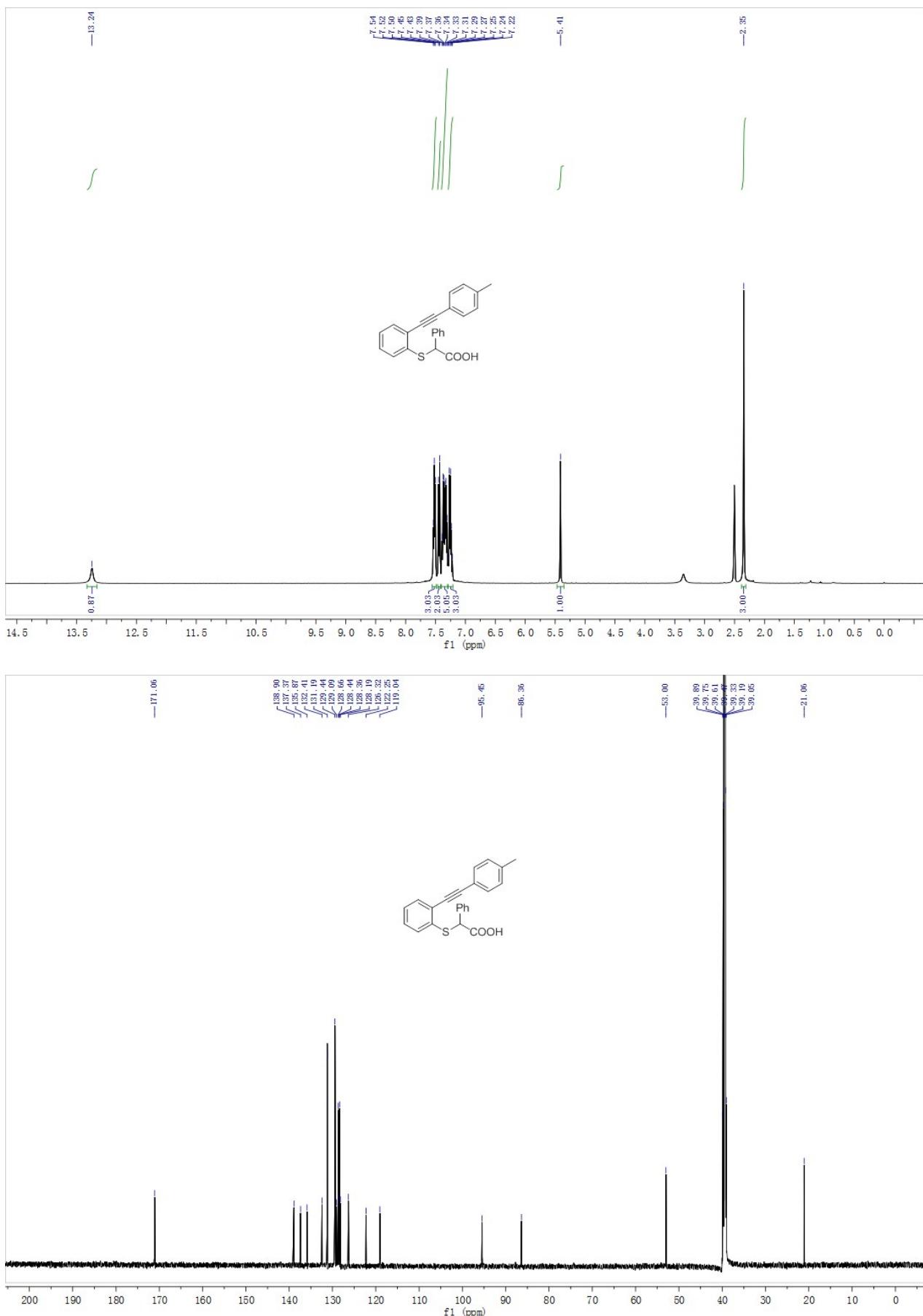


**5b**

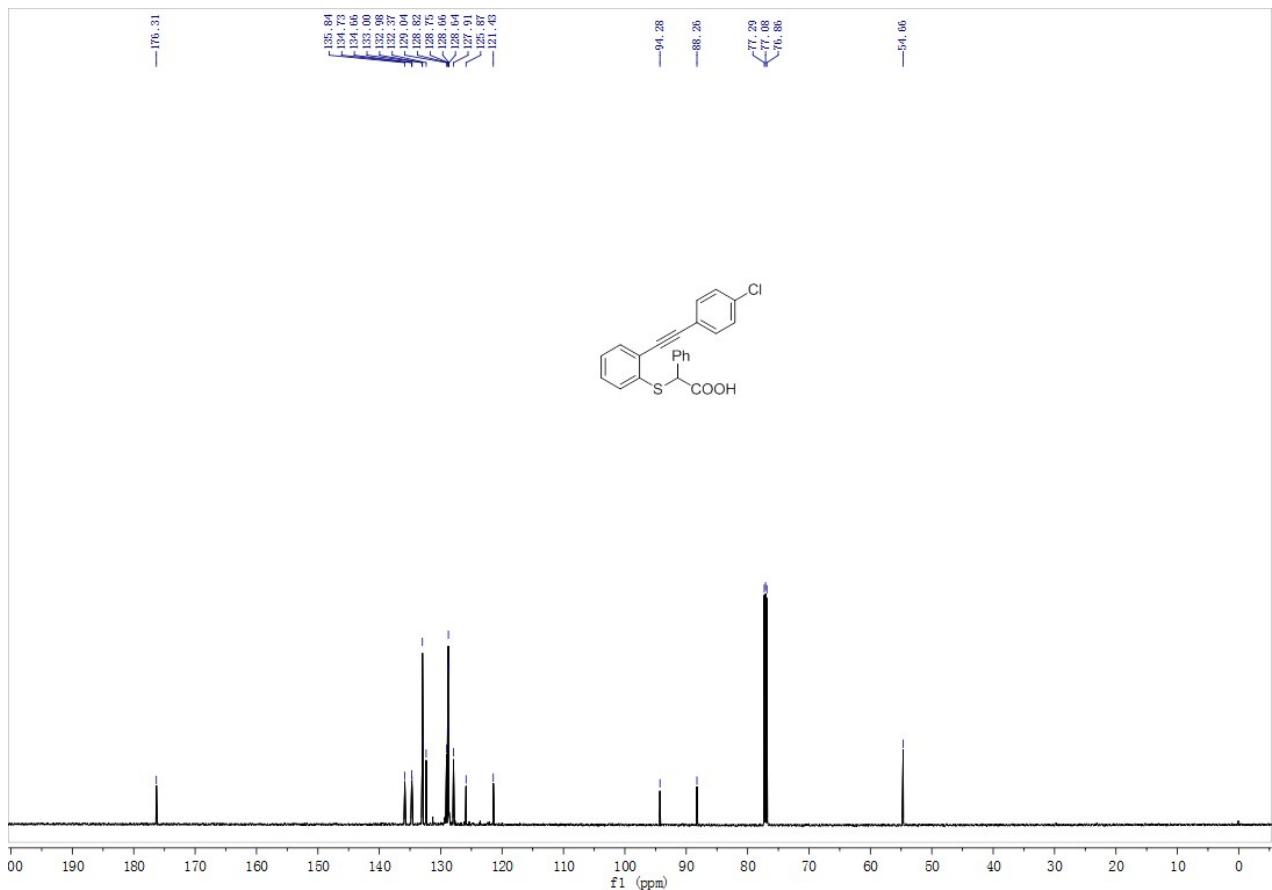
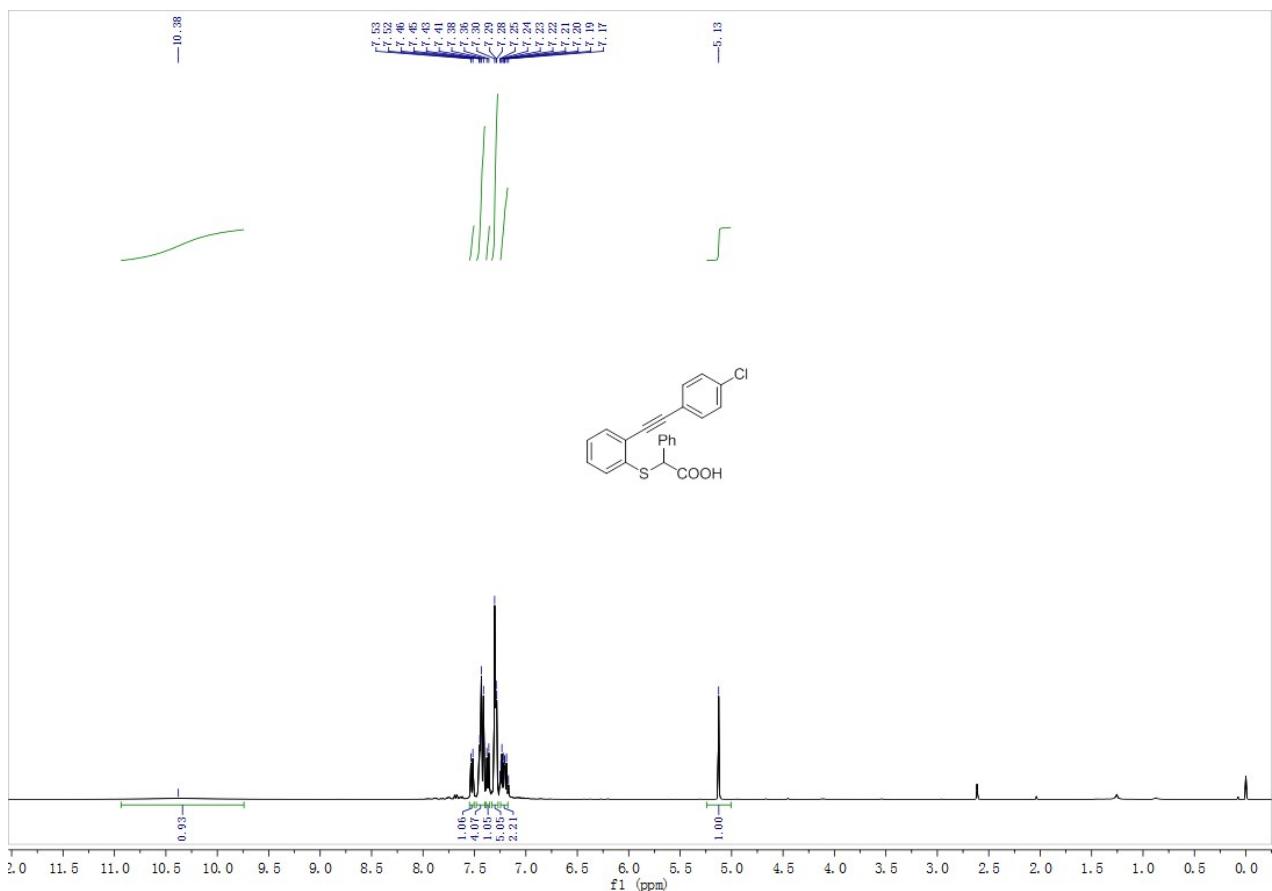


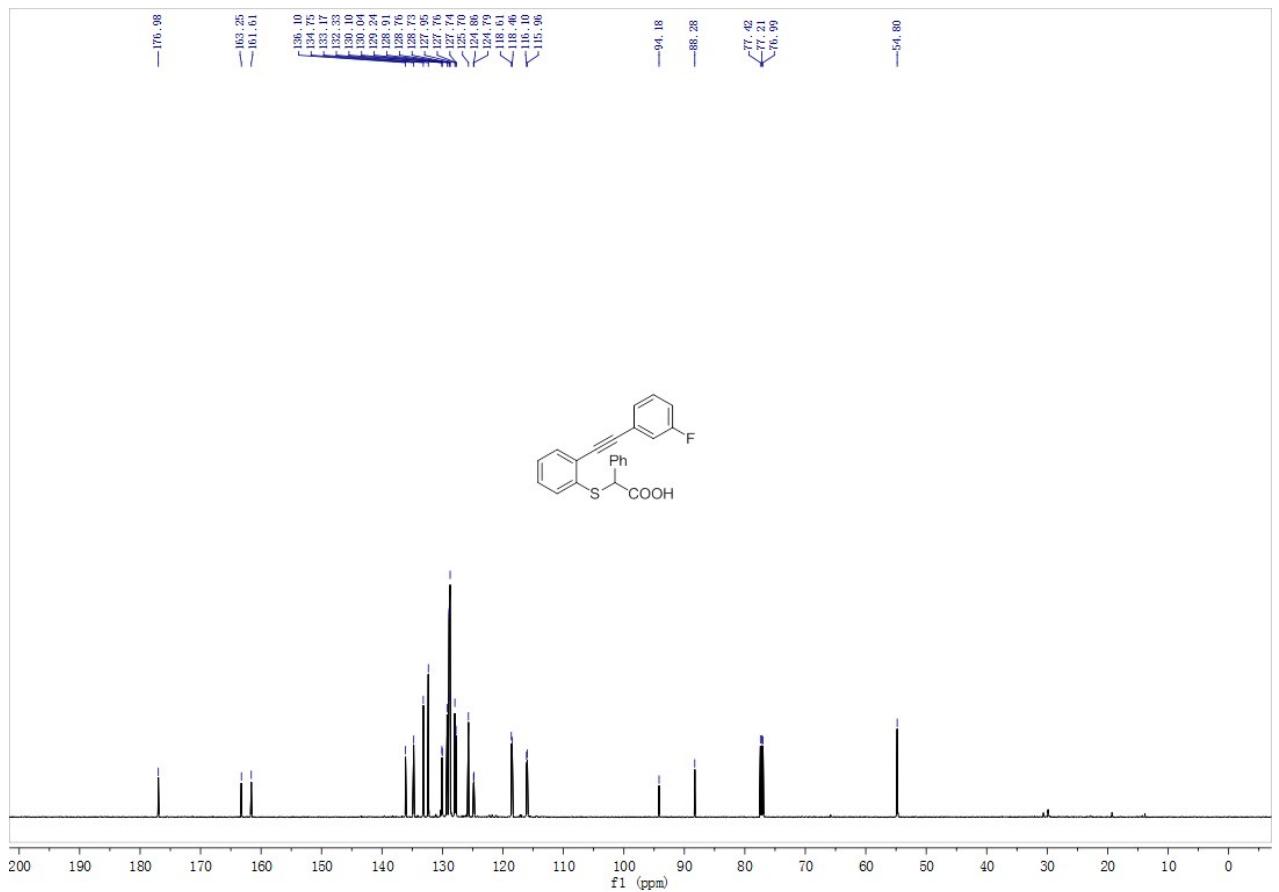
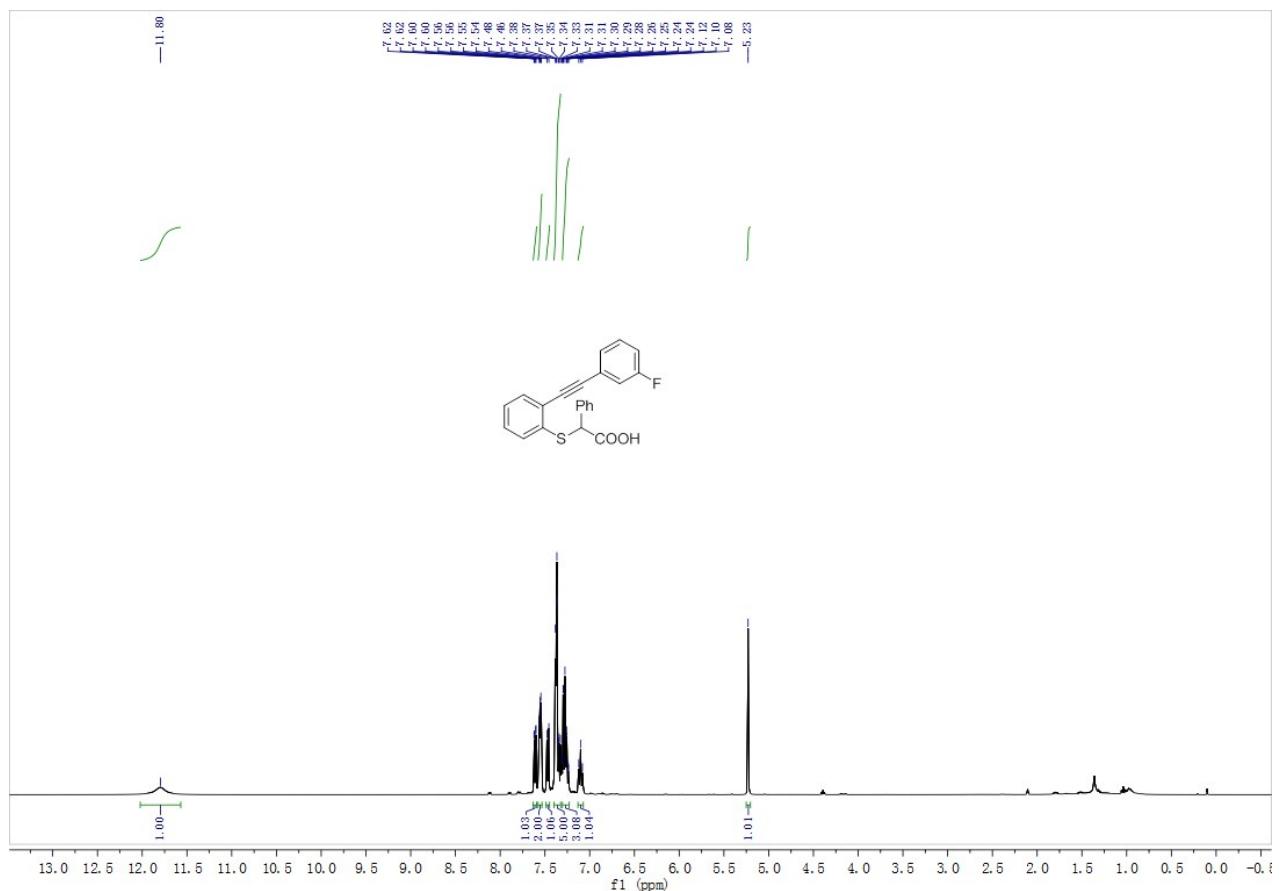
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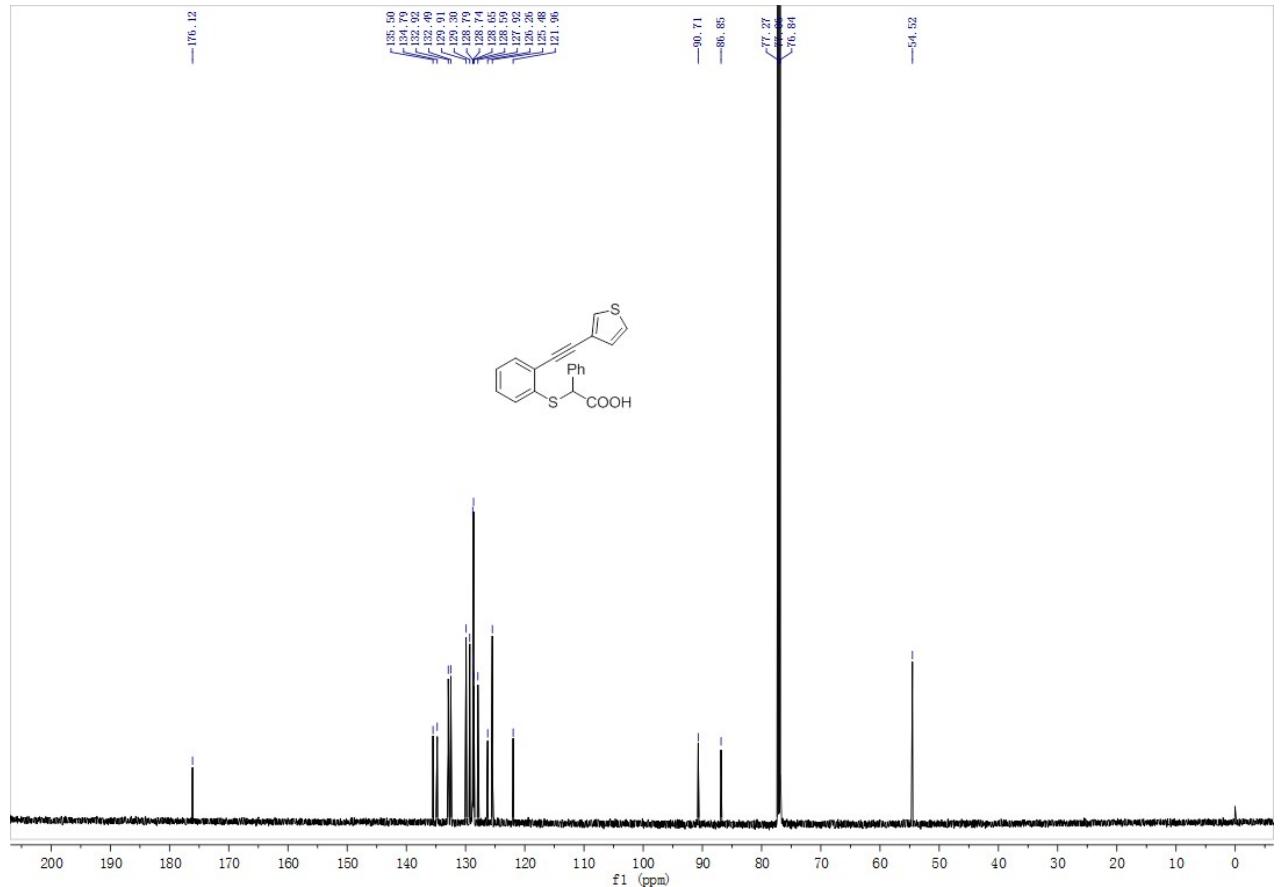
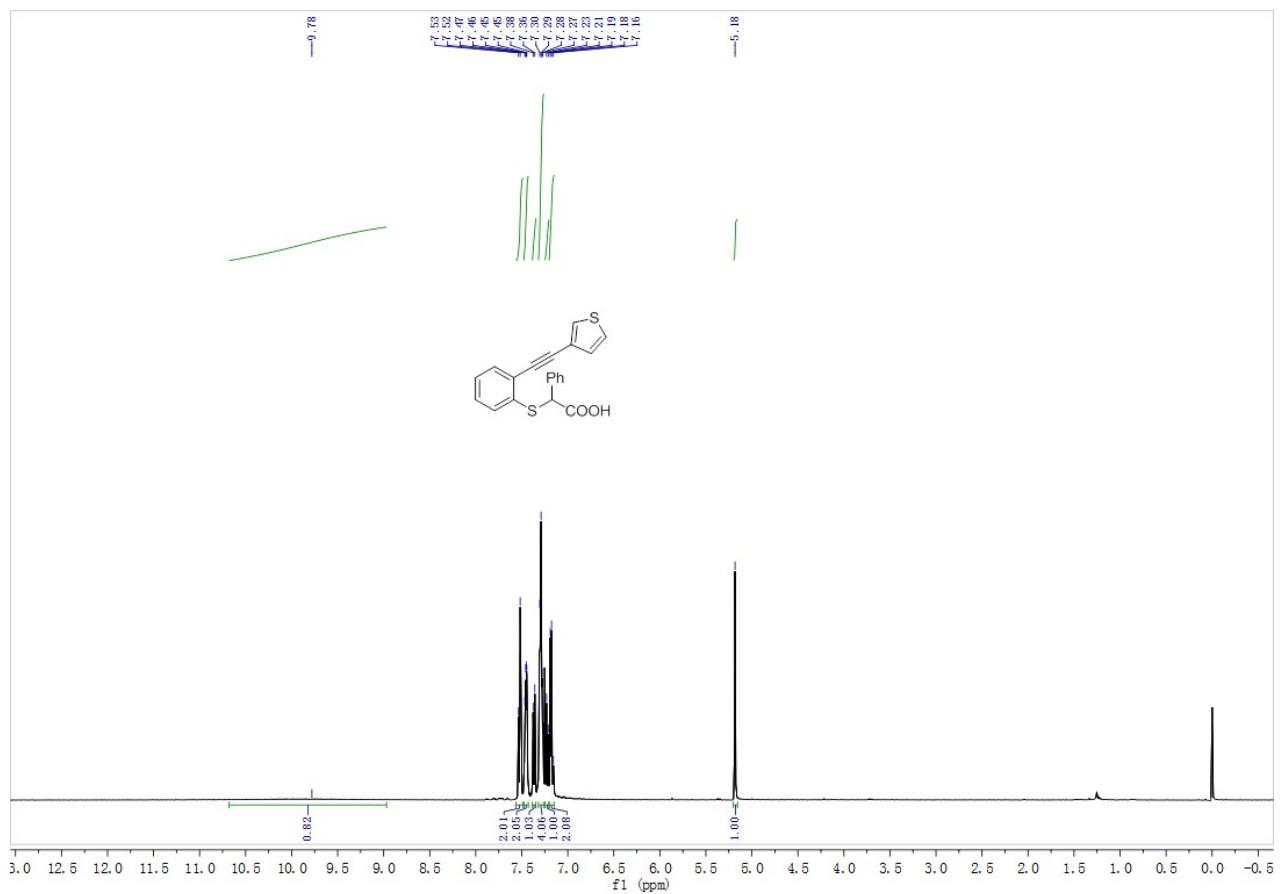
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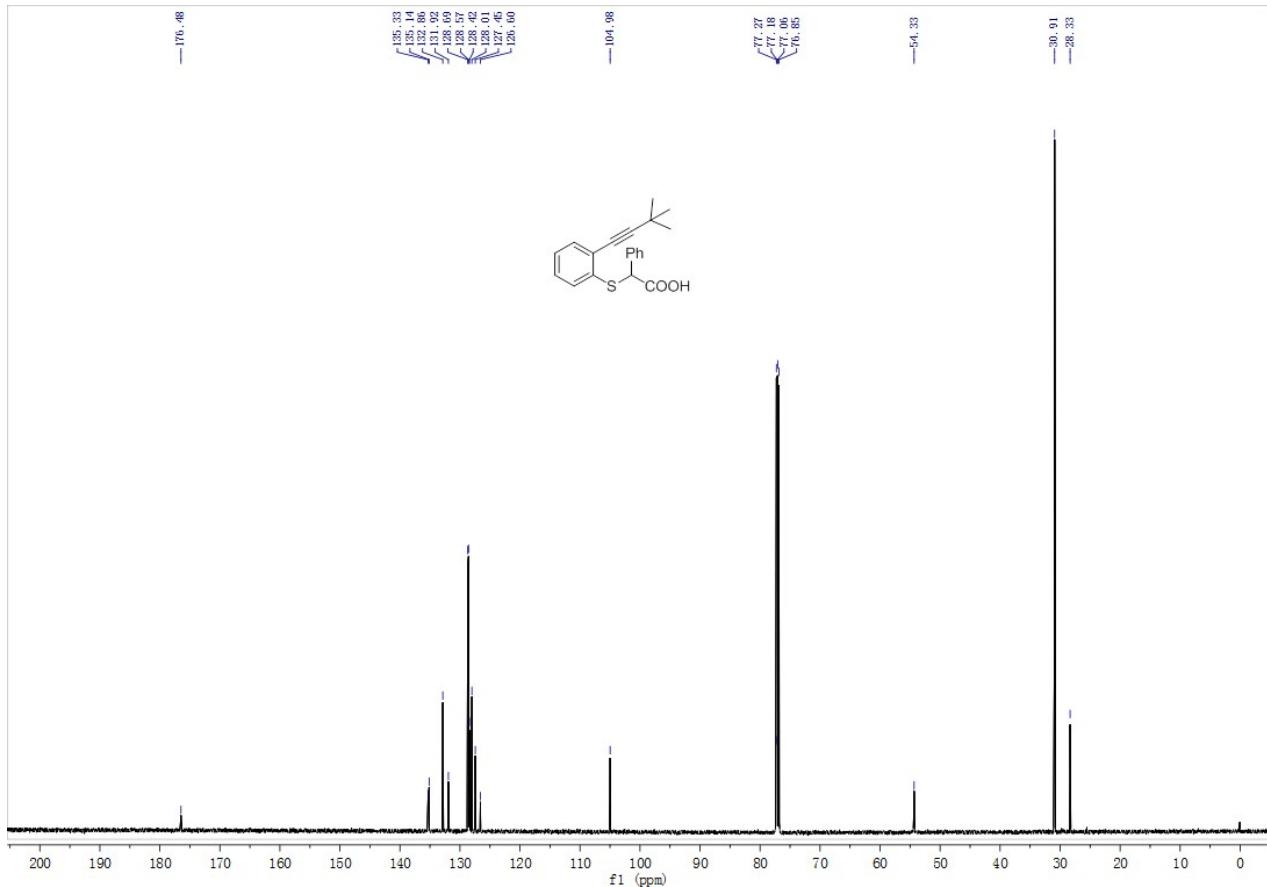
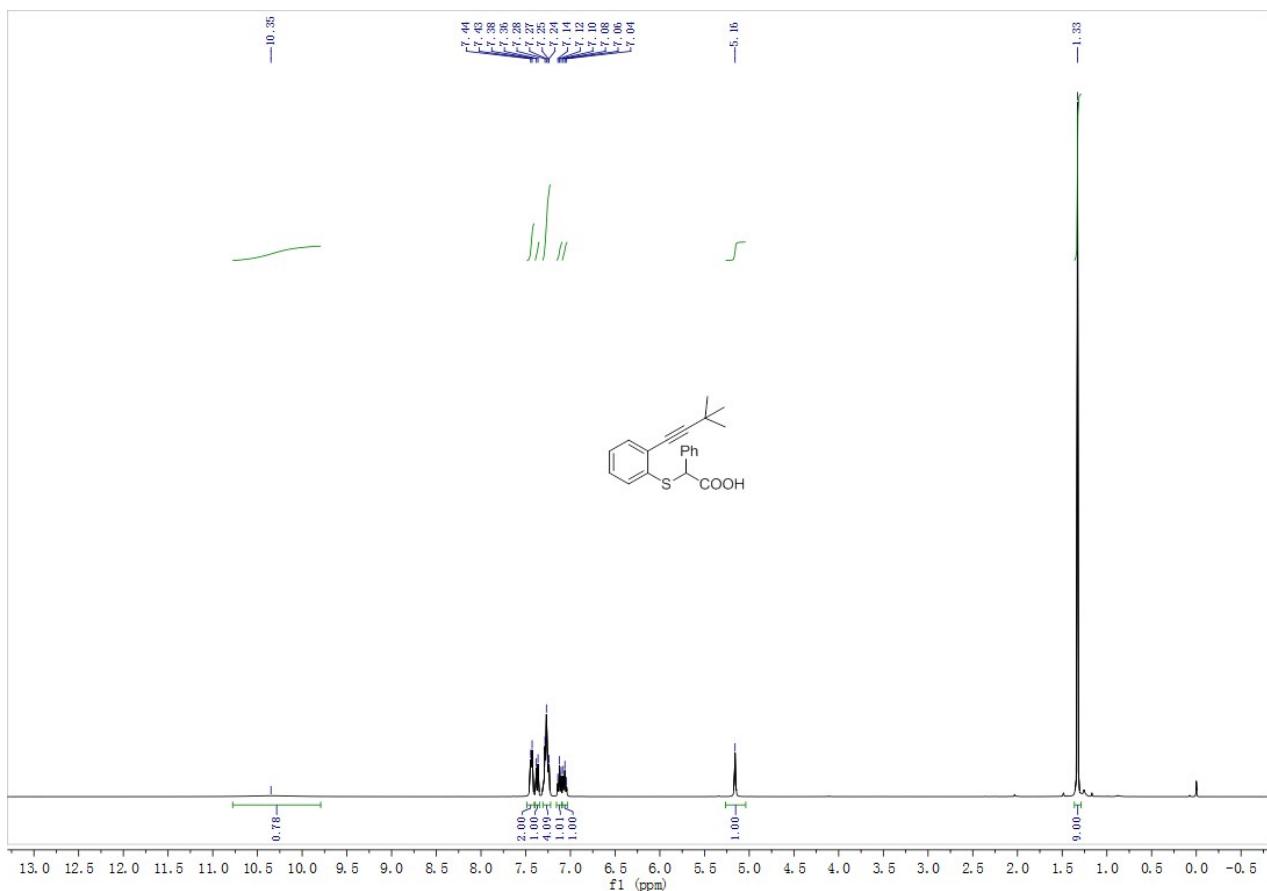
**5e**



**5f**

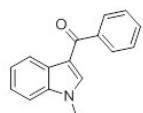
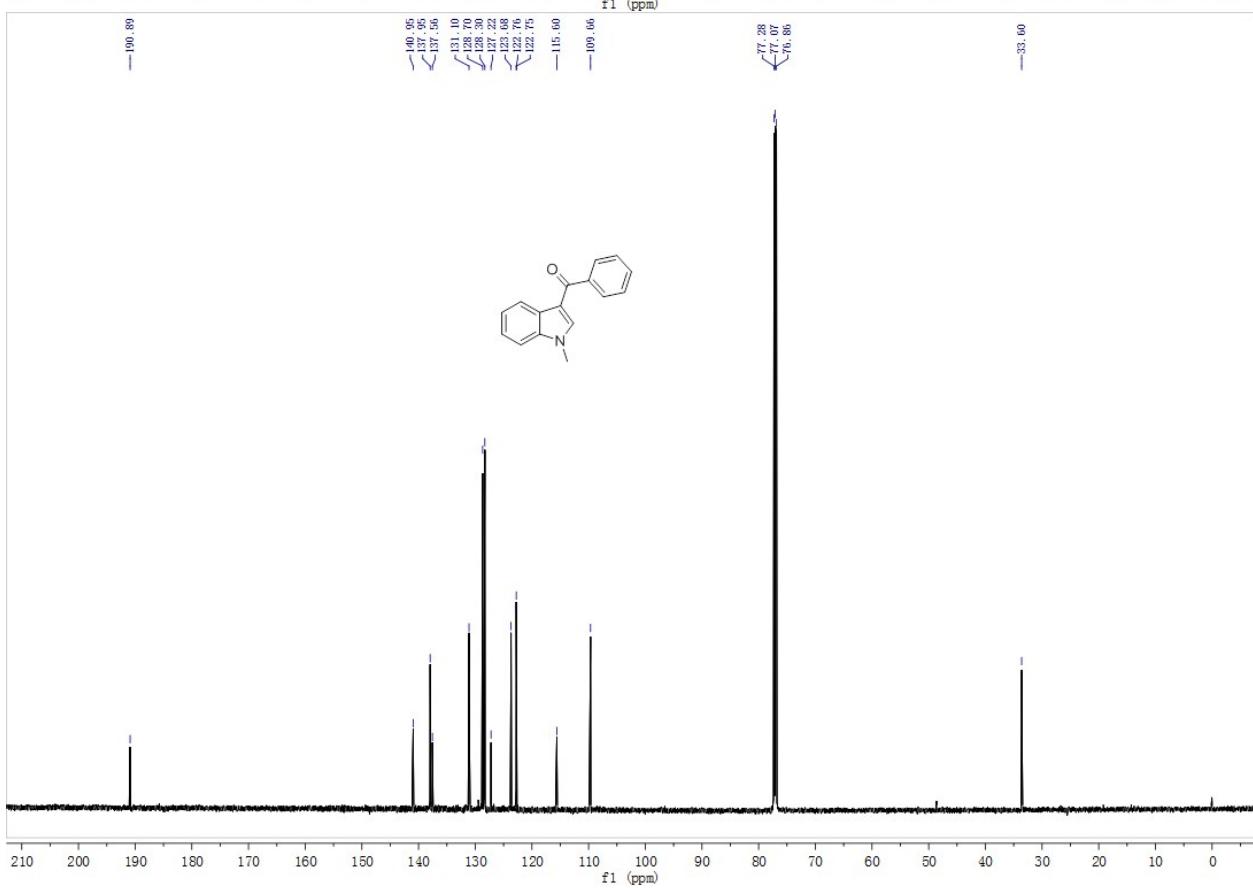
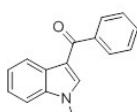
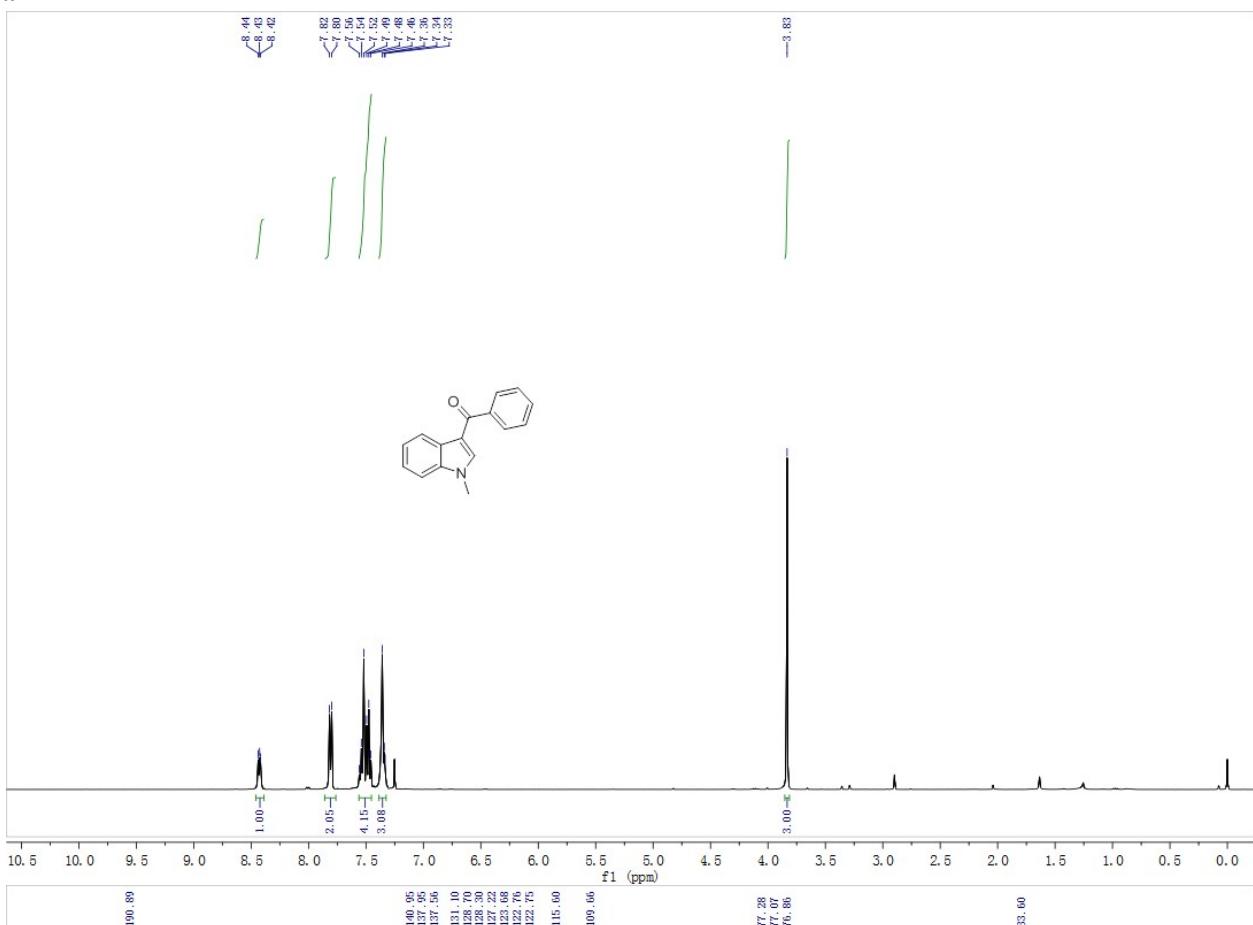
**5g**

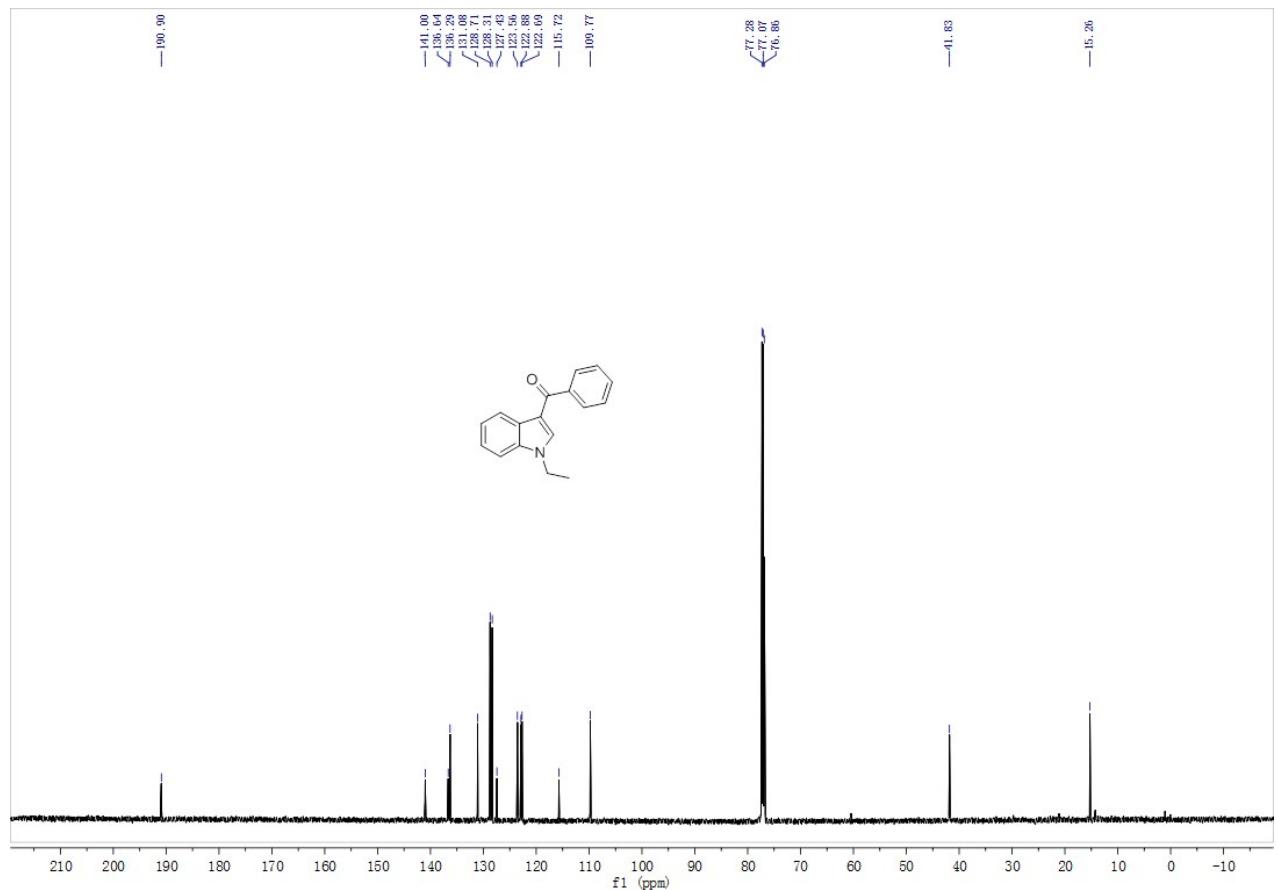
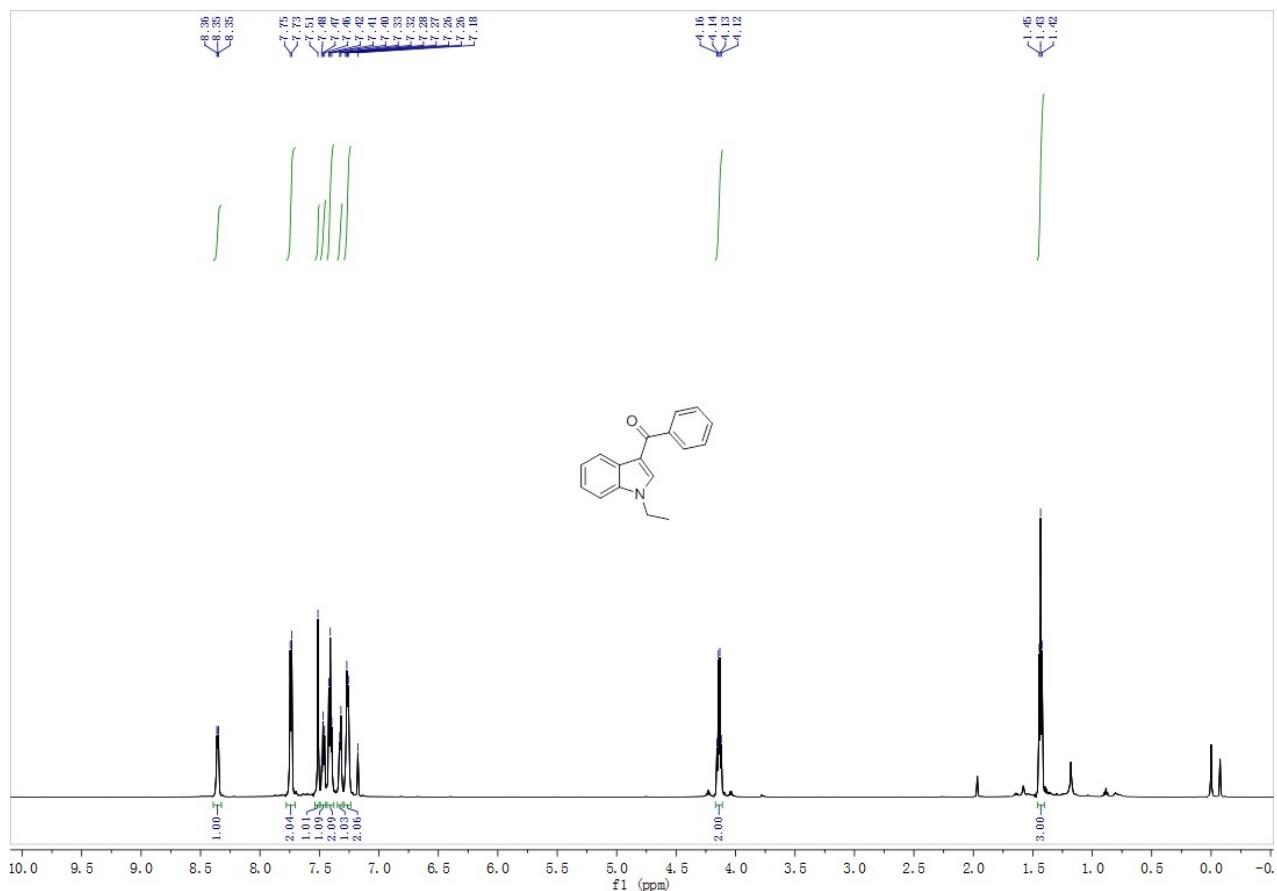


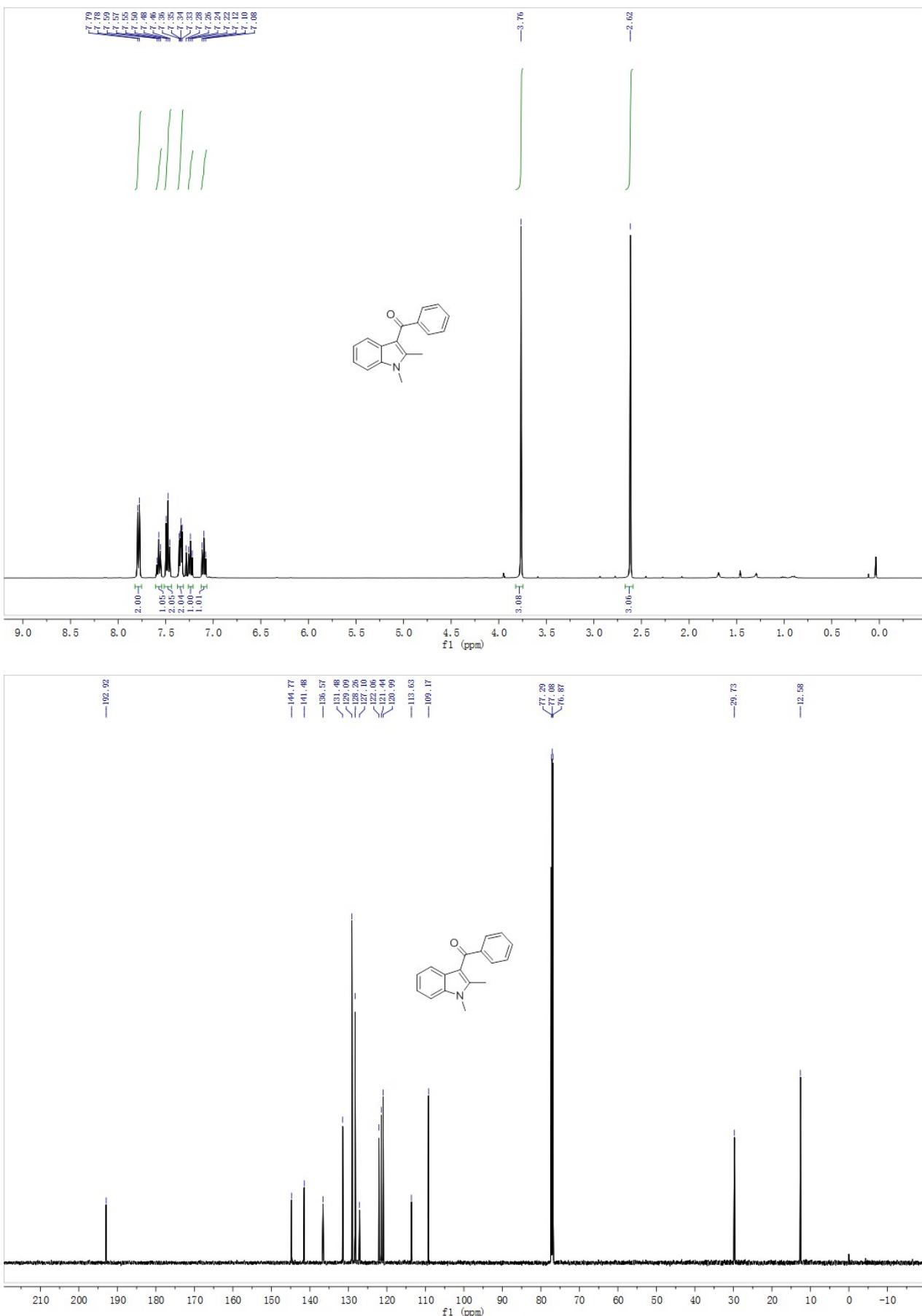
**5h**

## 8. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra for products

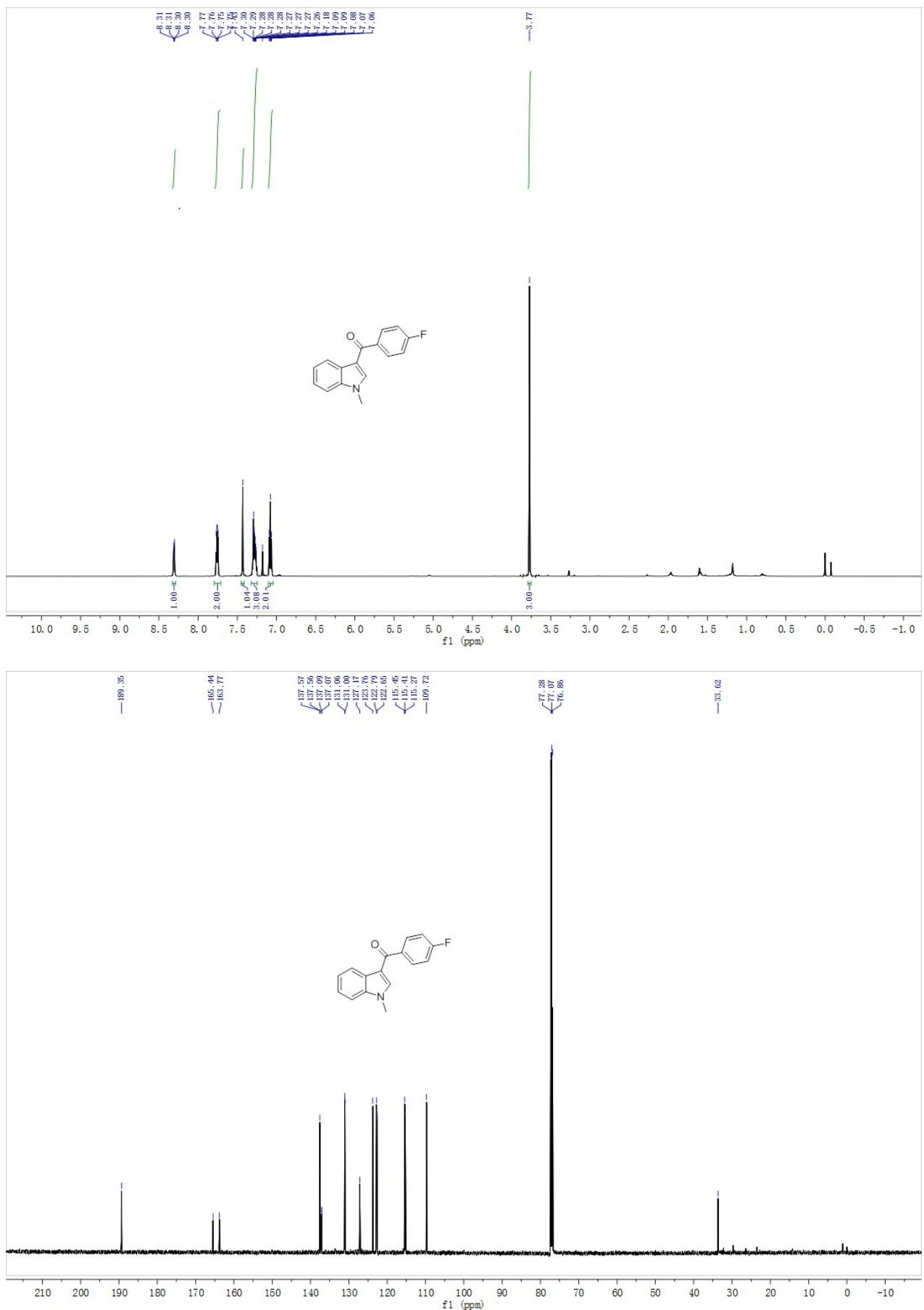
2a



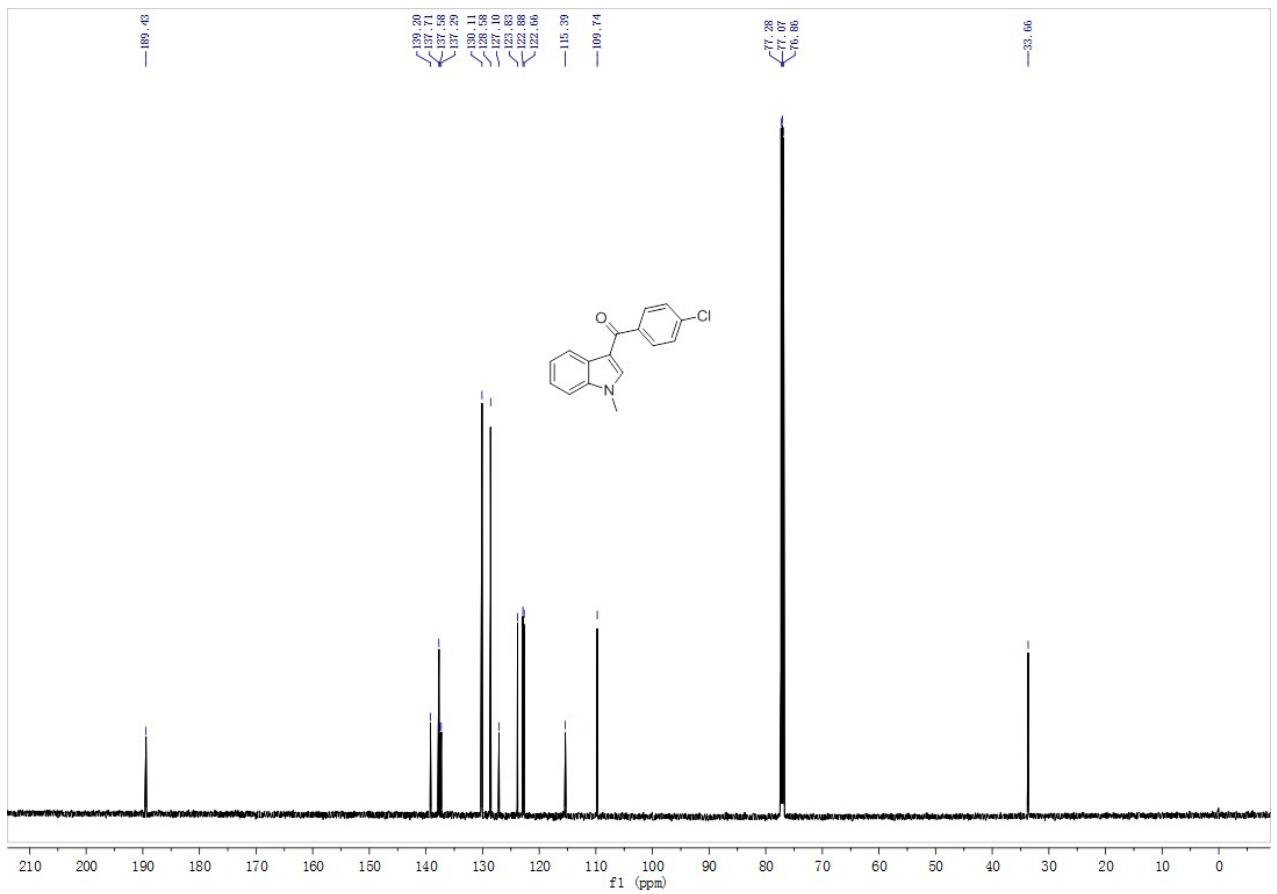
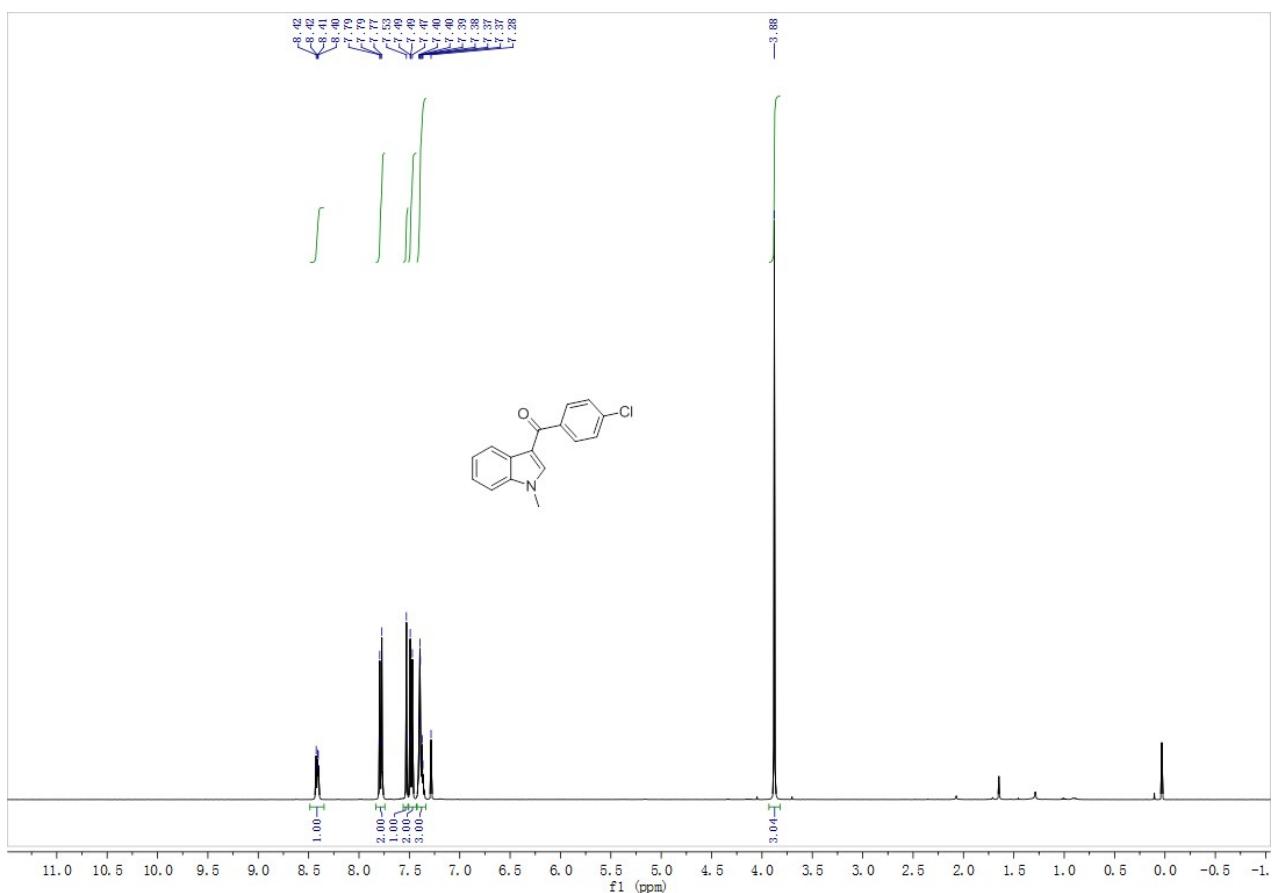
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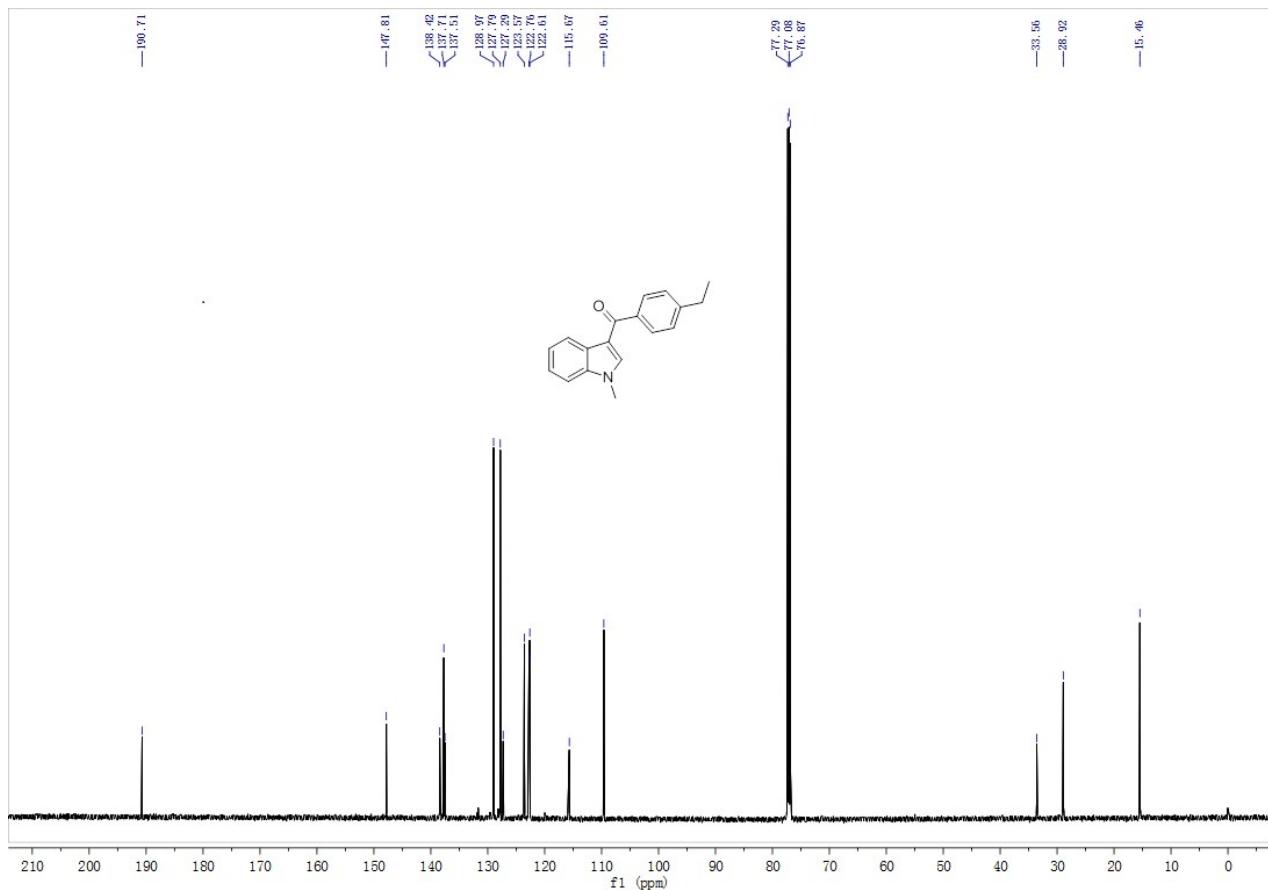
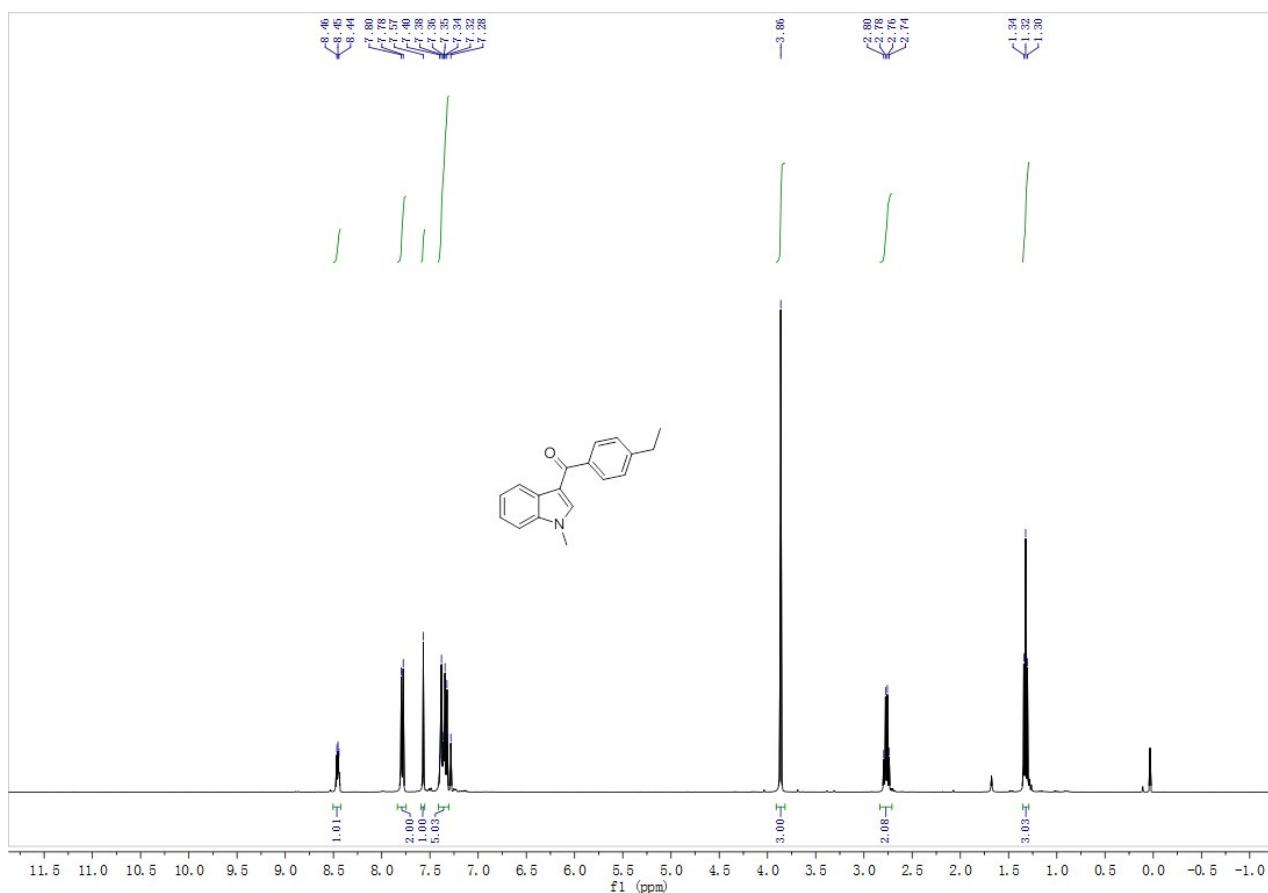
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2f

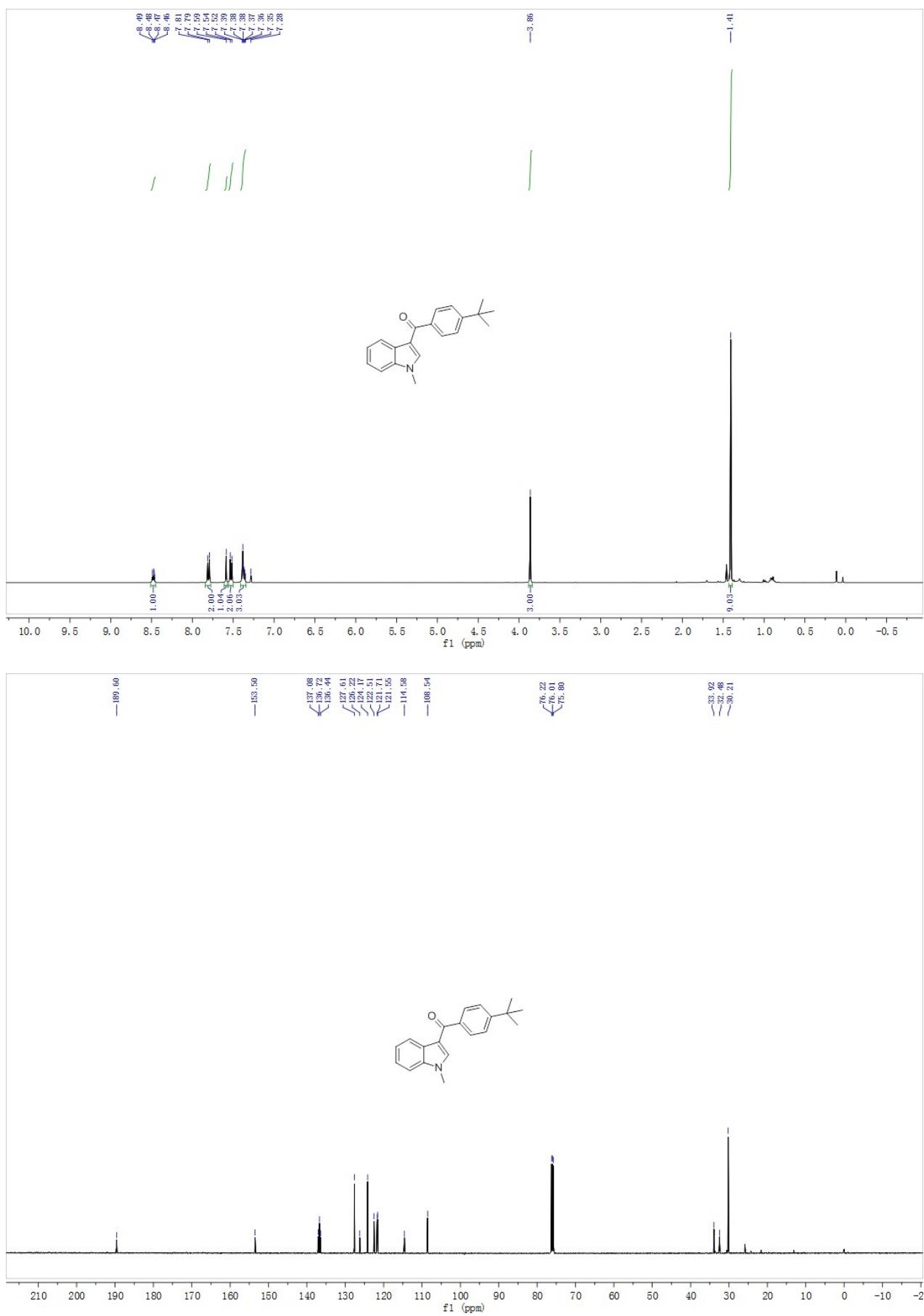


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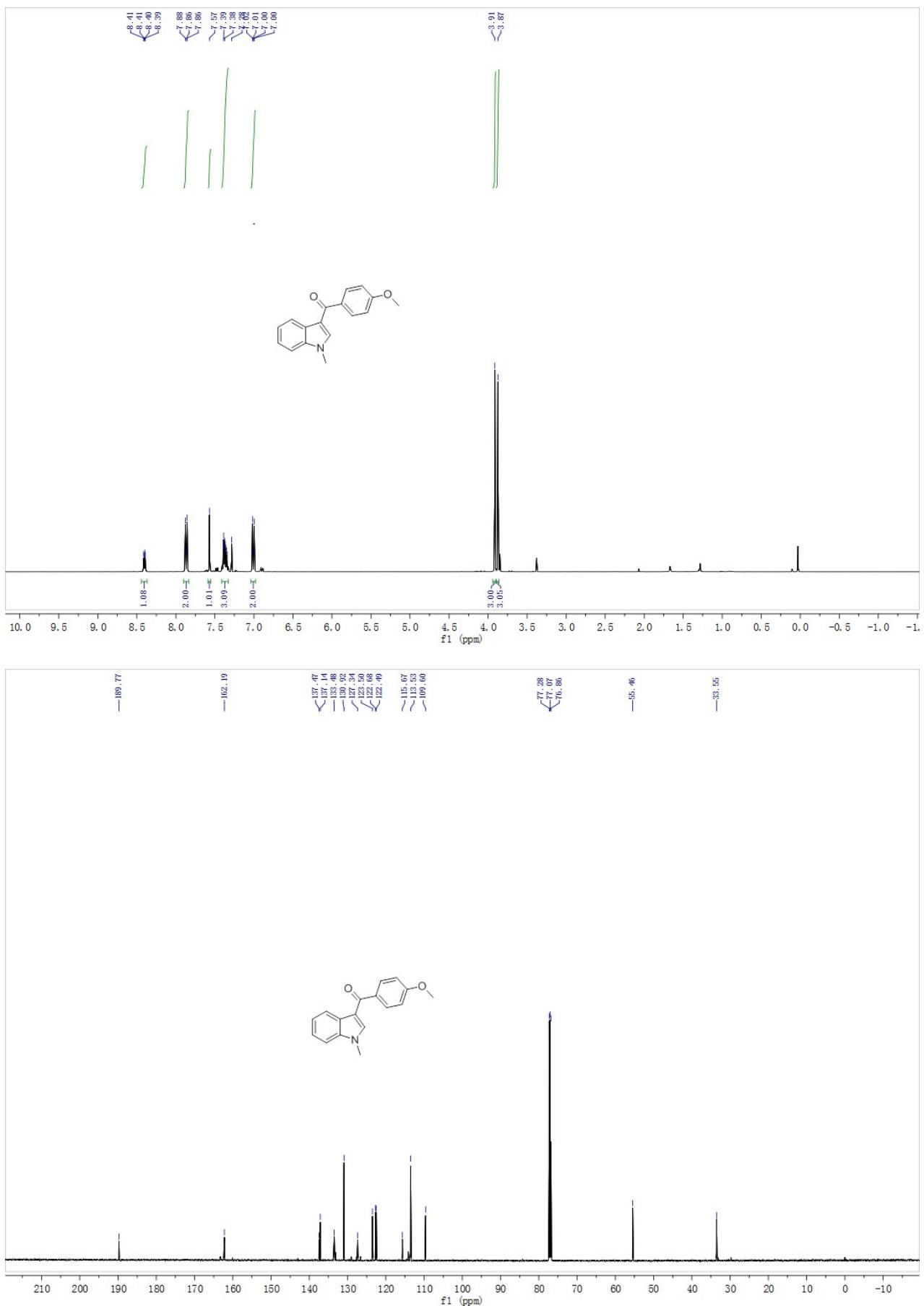


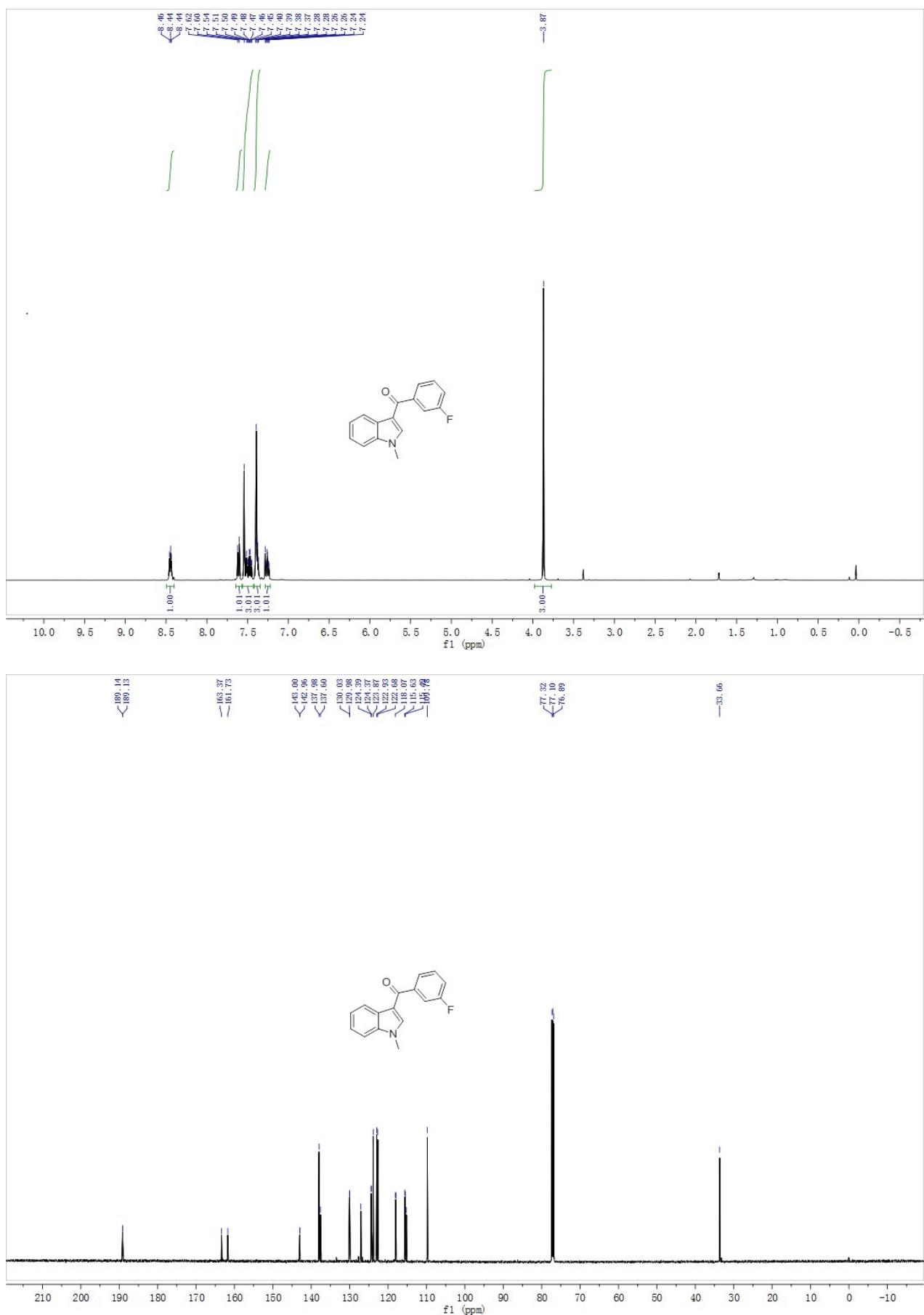
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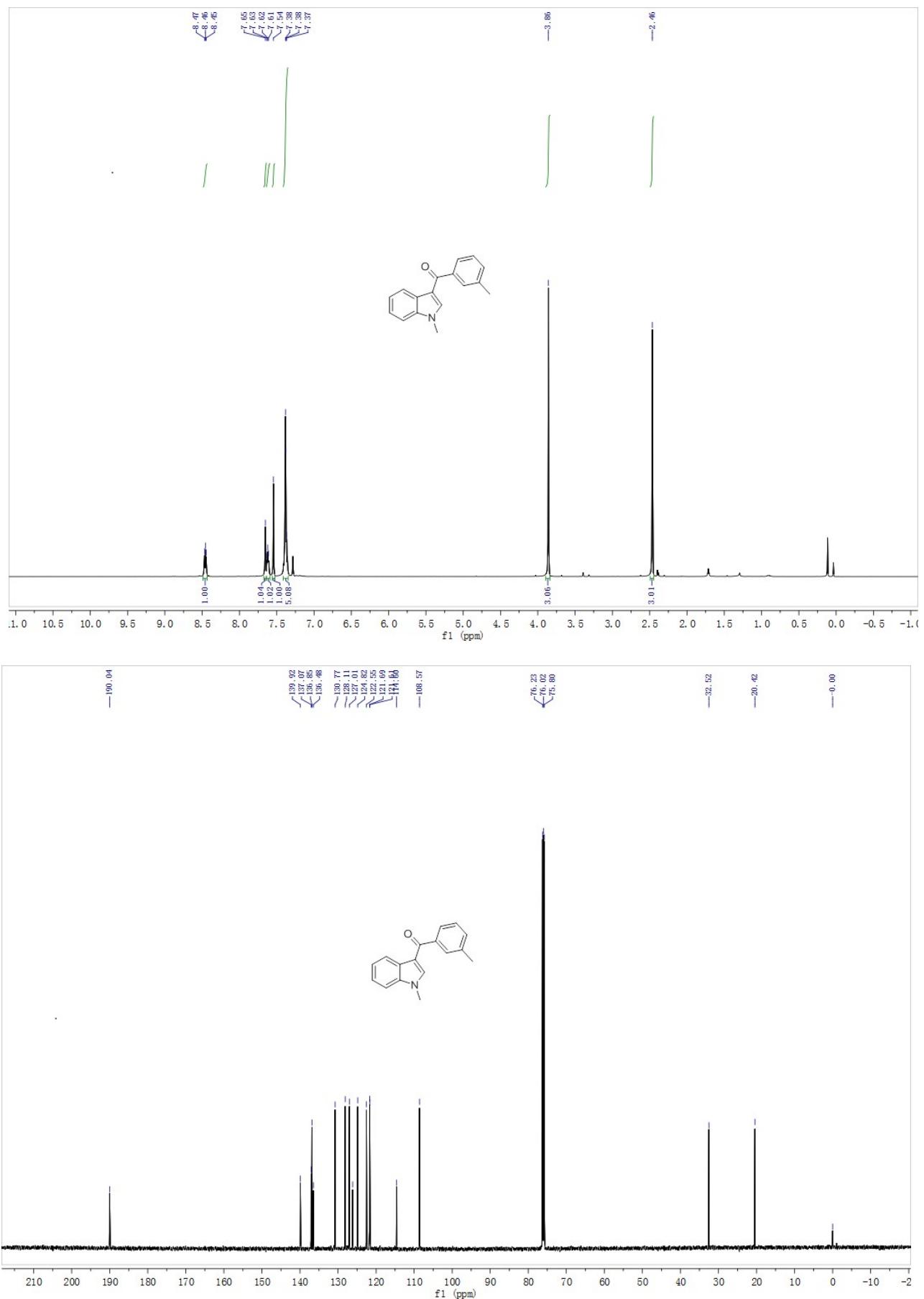
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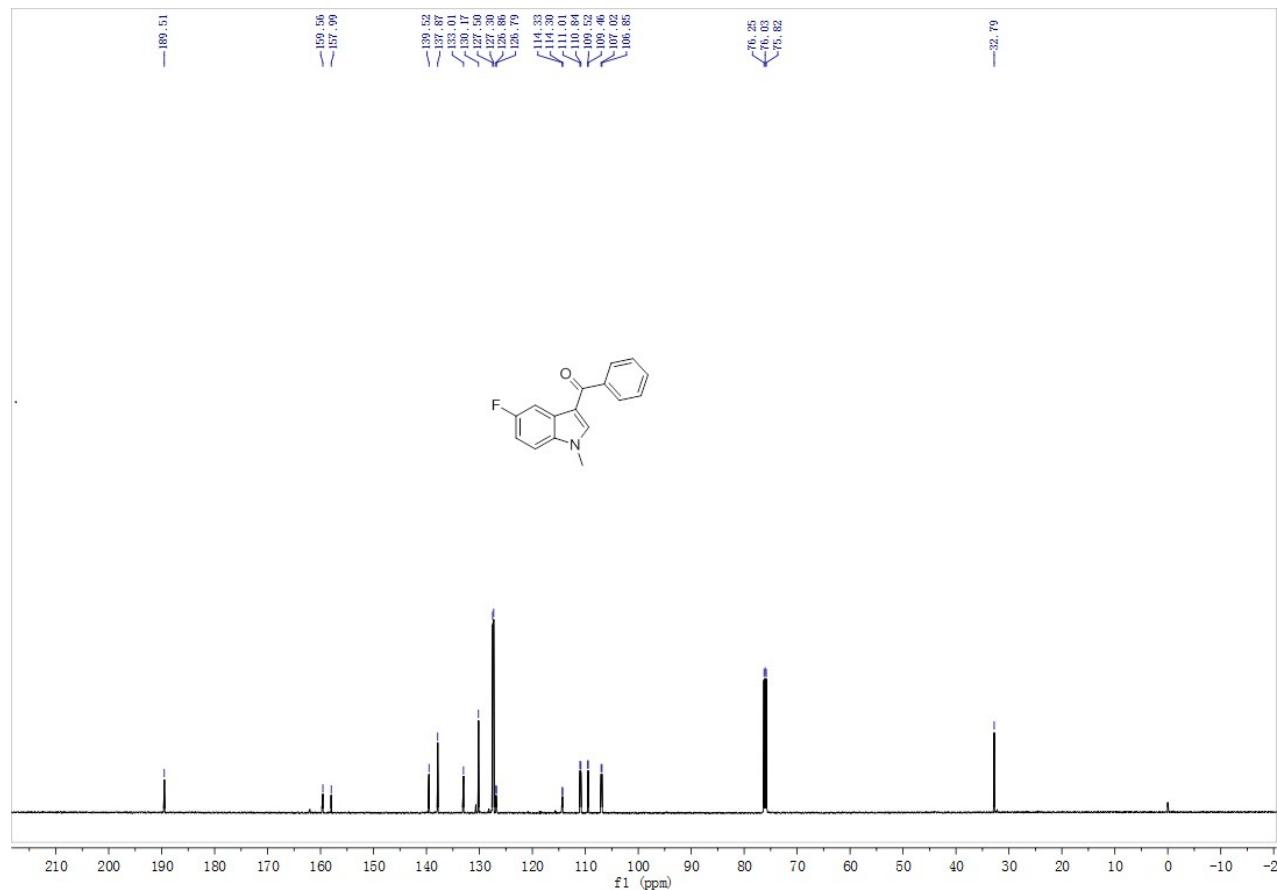
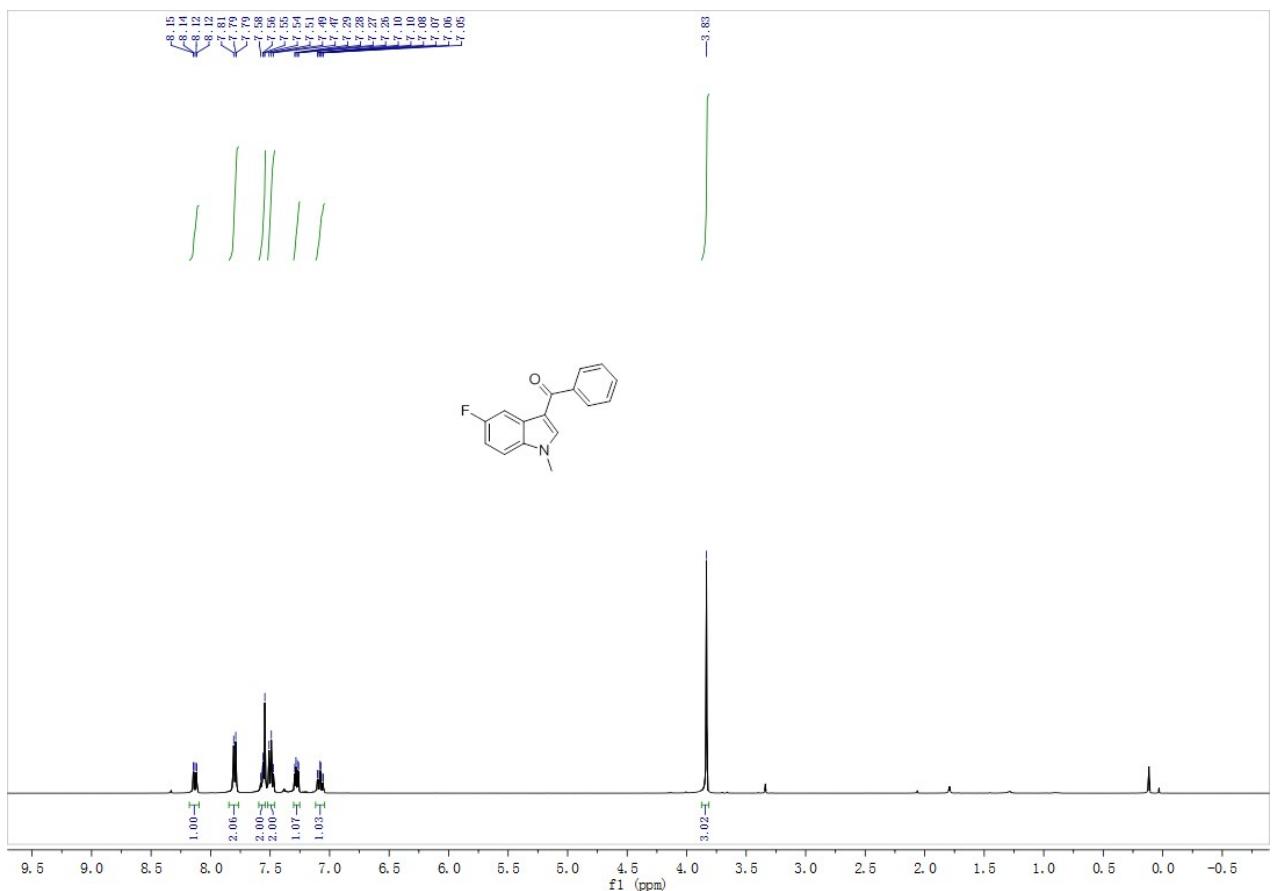


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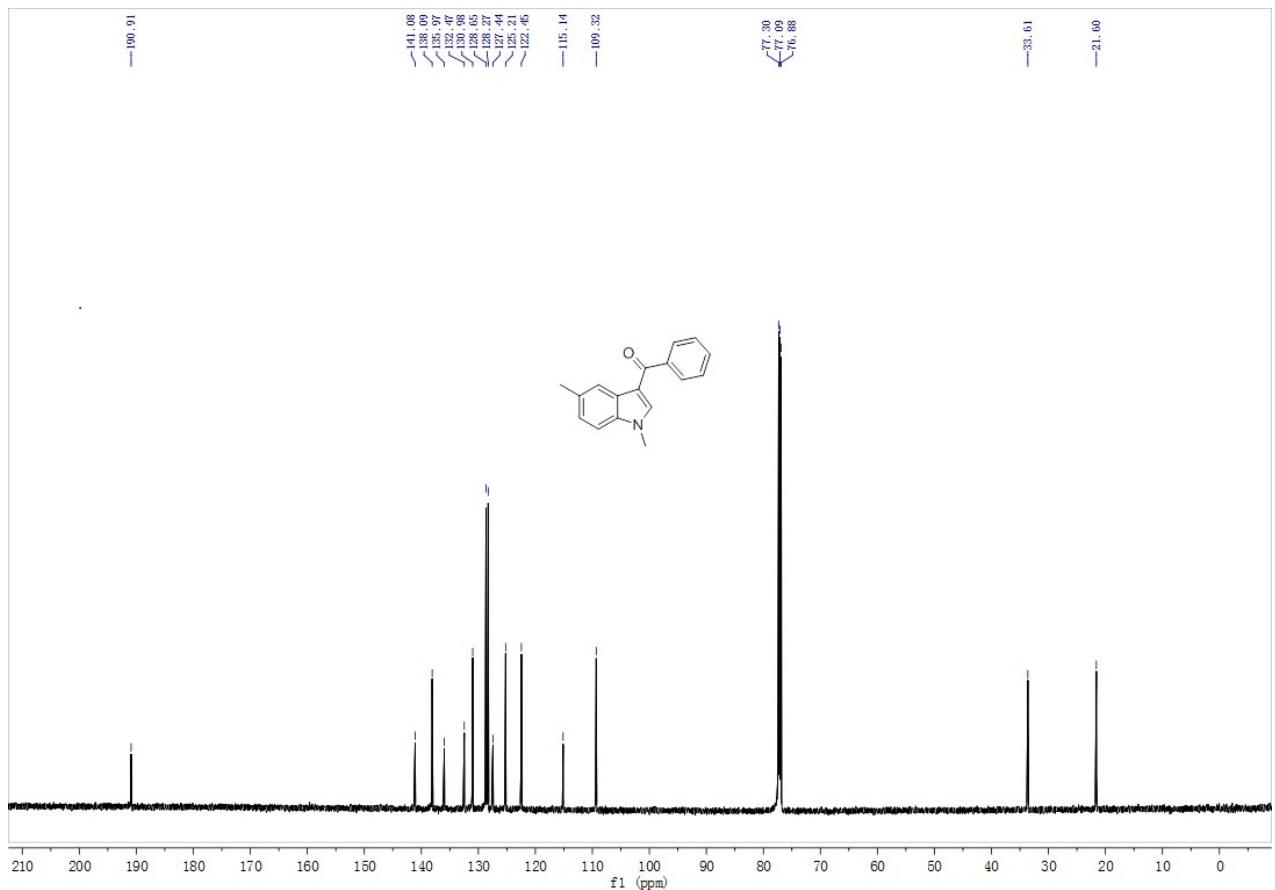
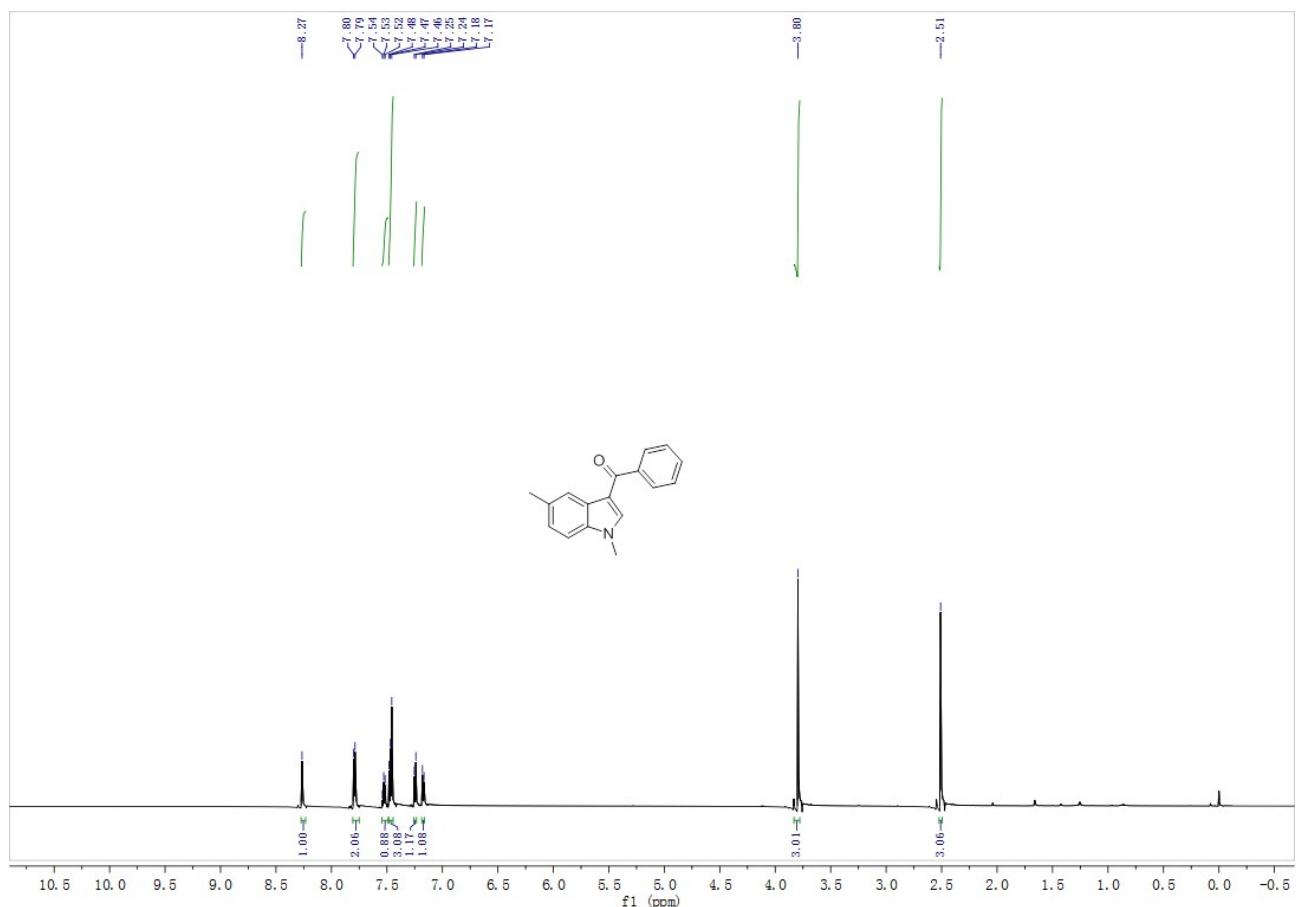


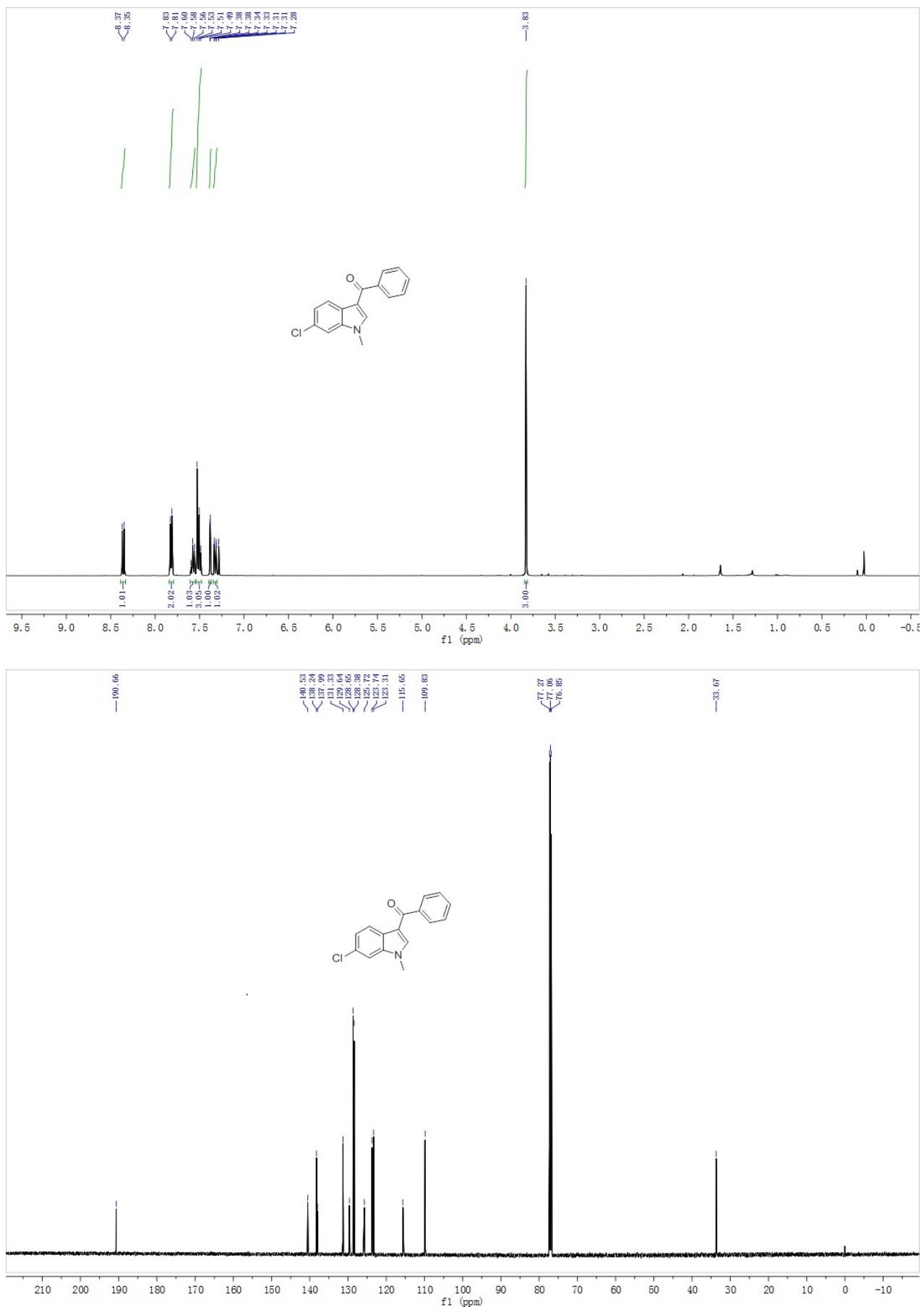
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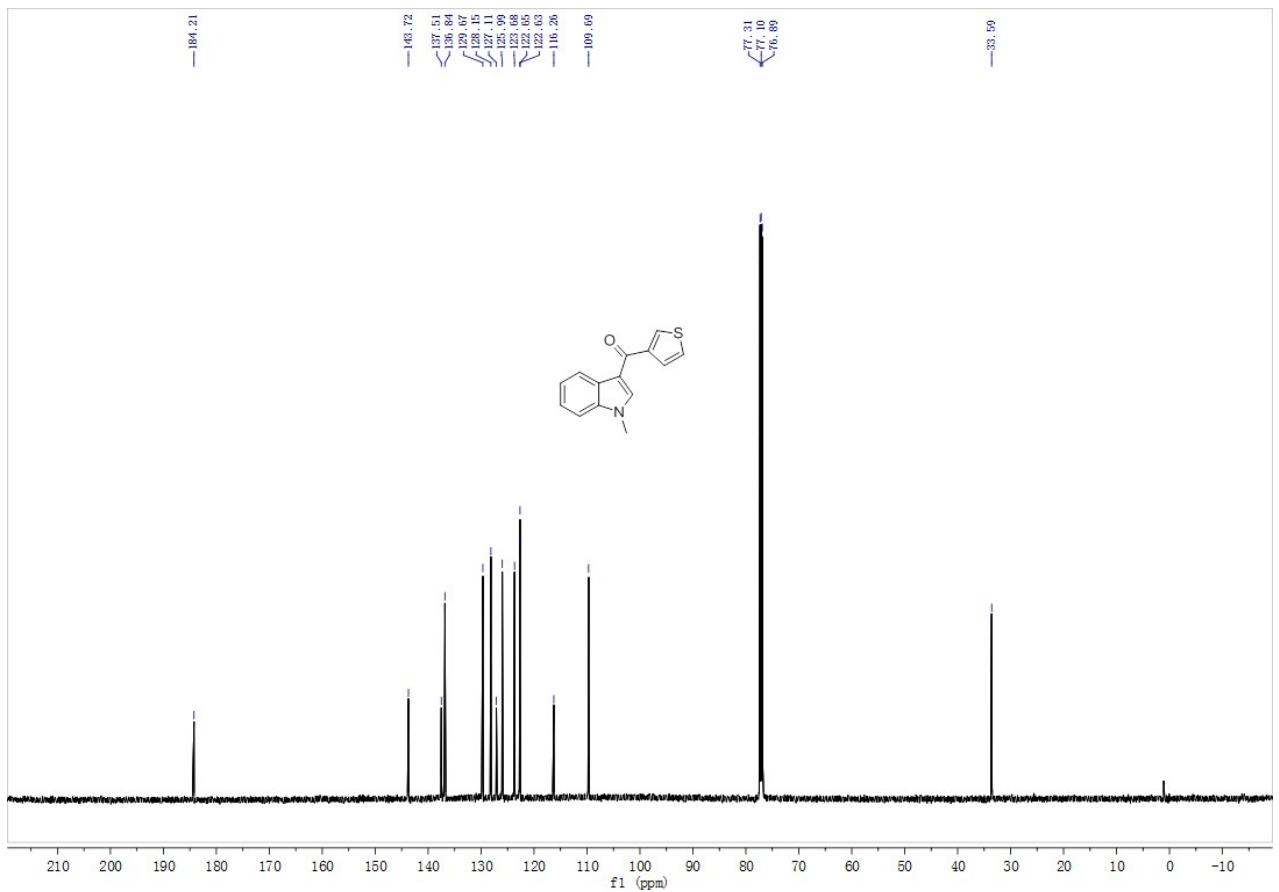
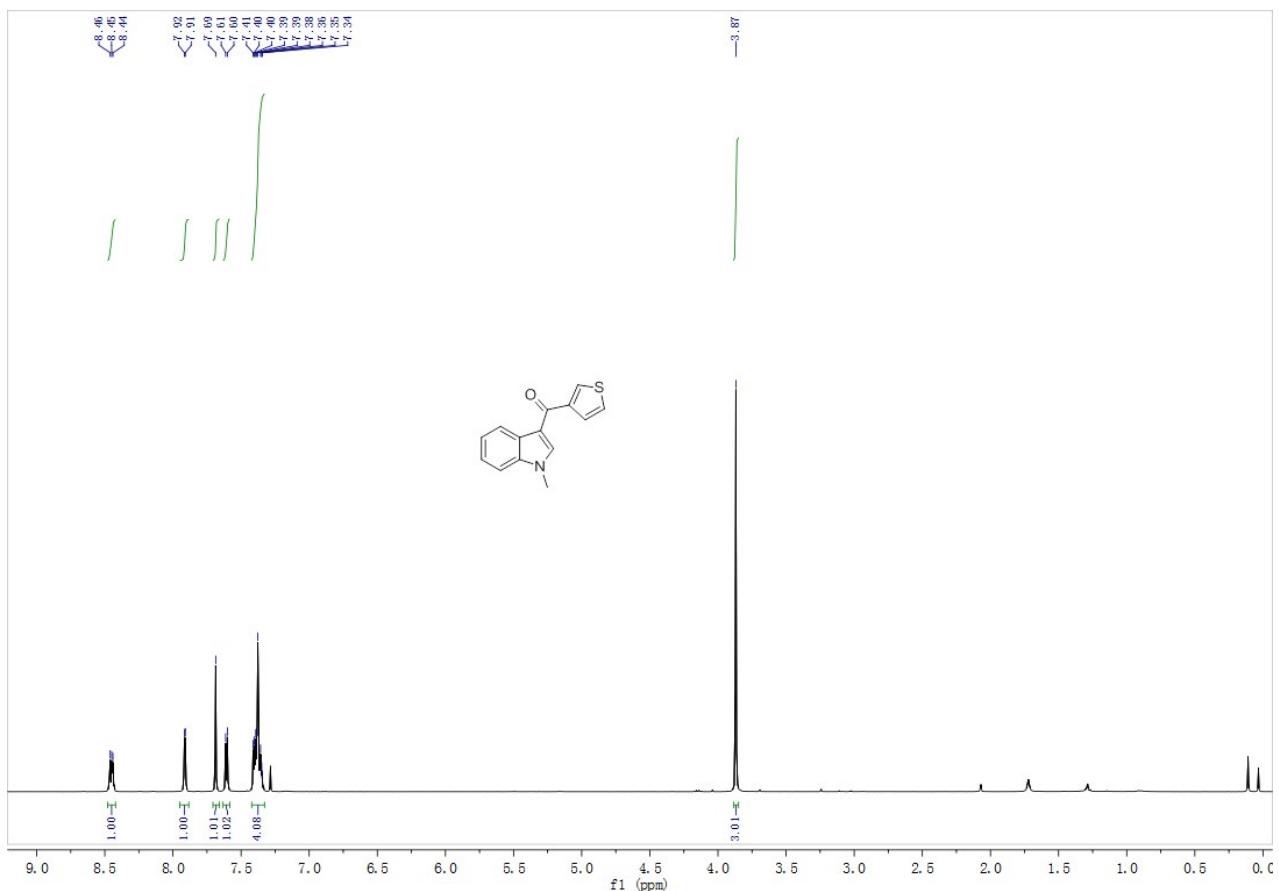
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**2n**

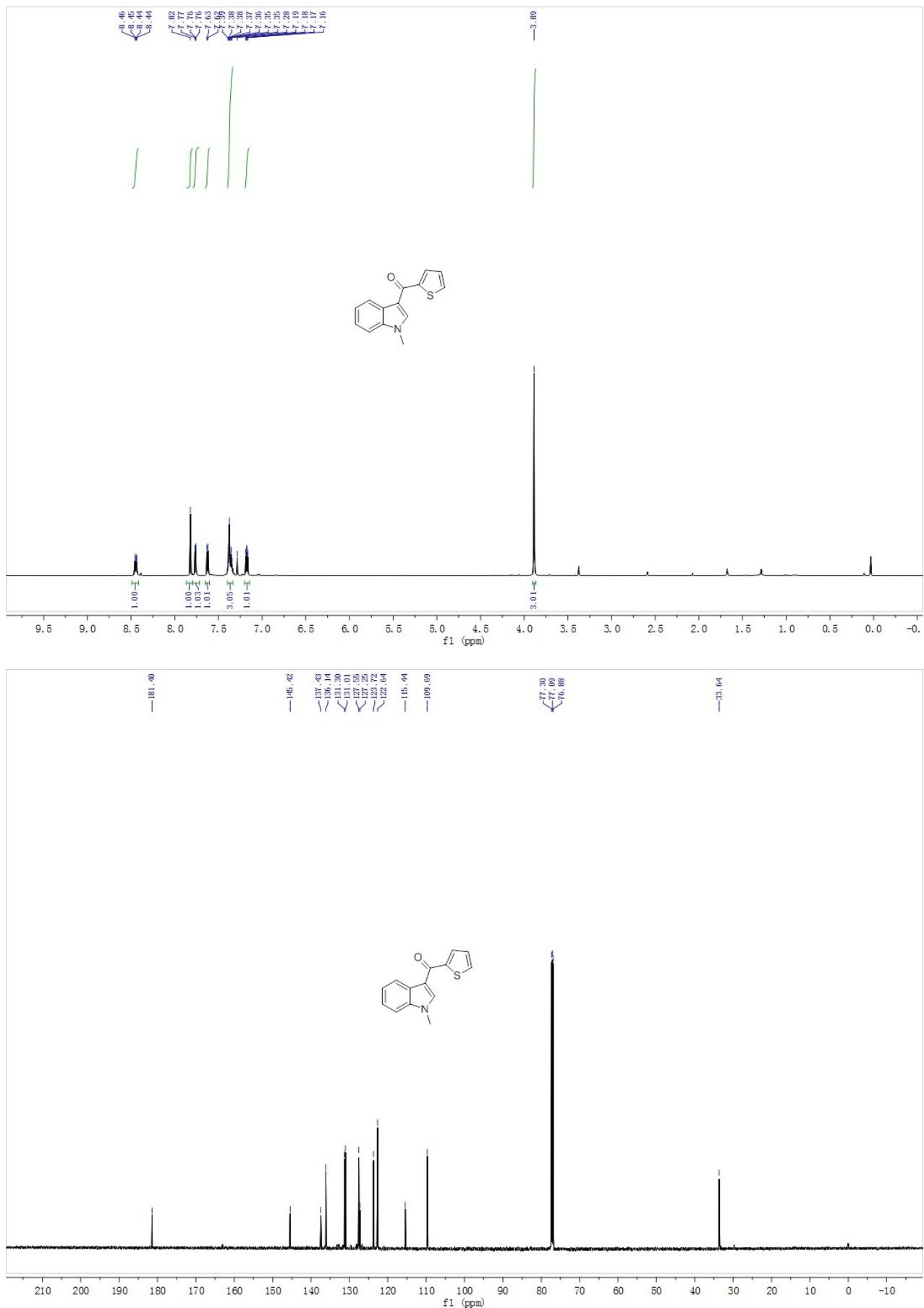


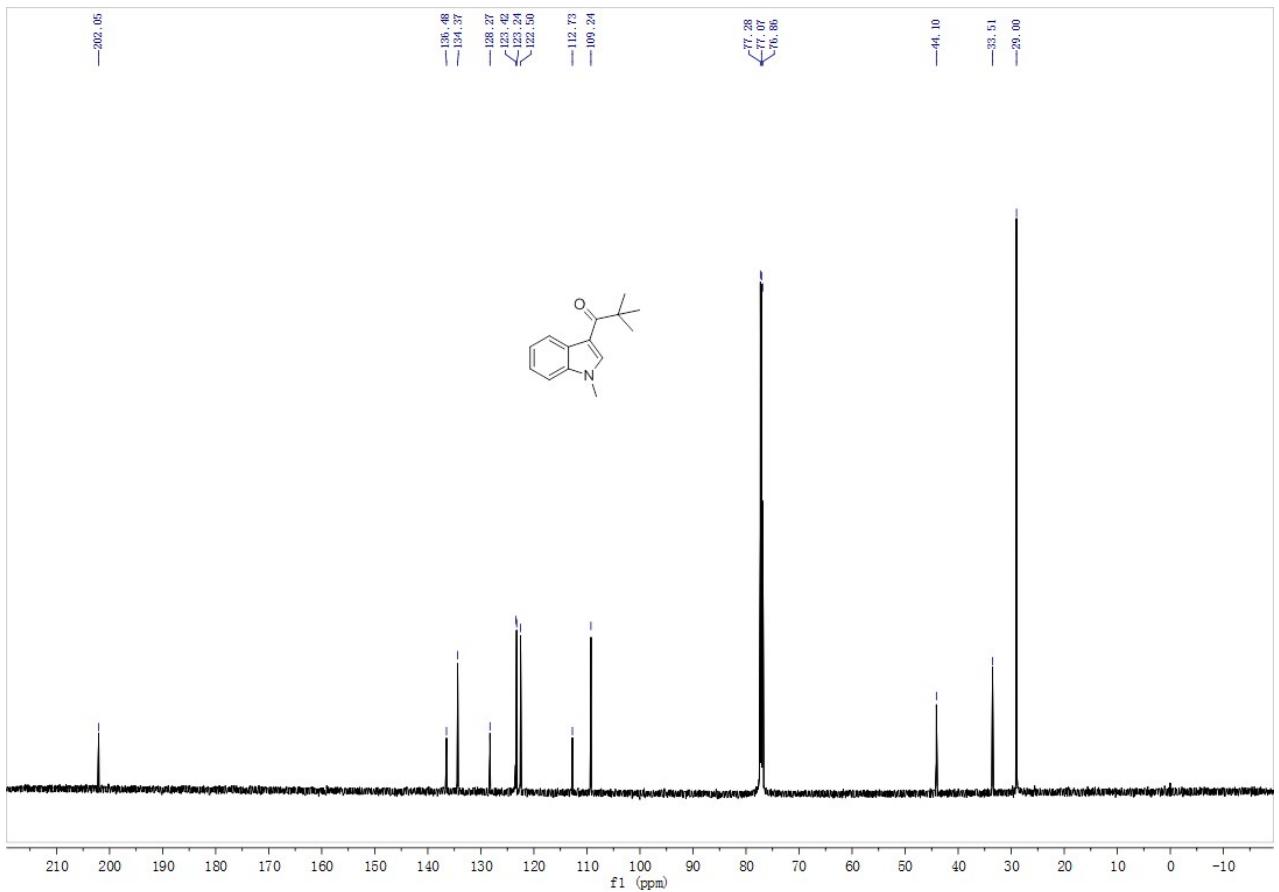
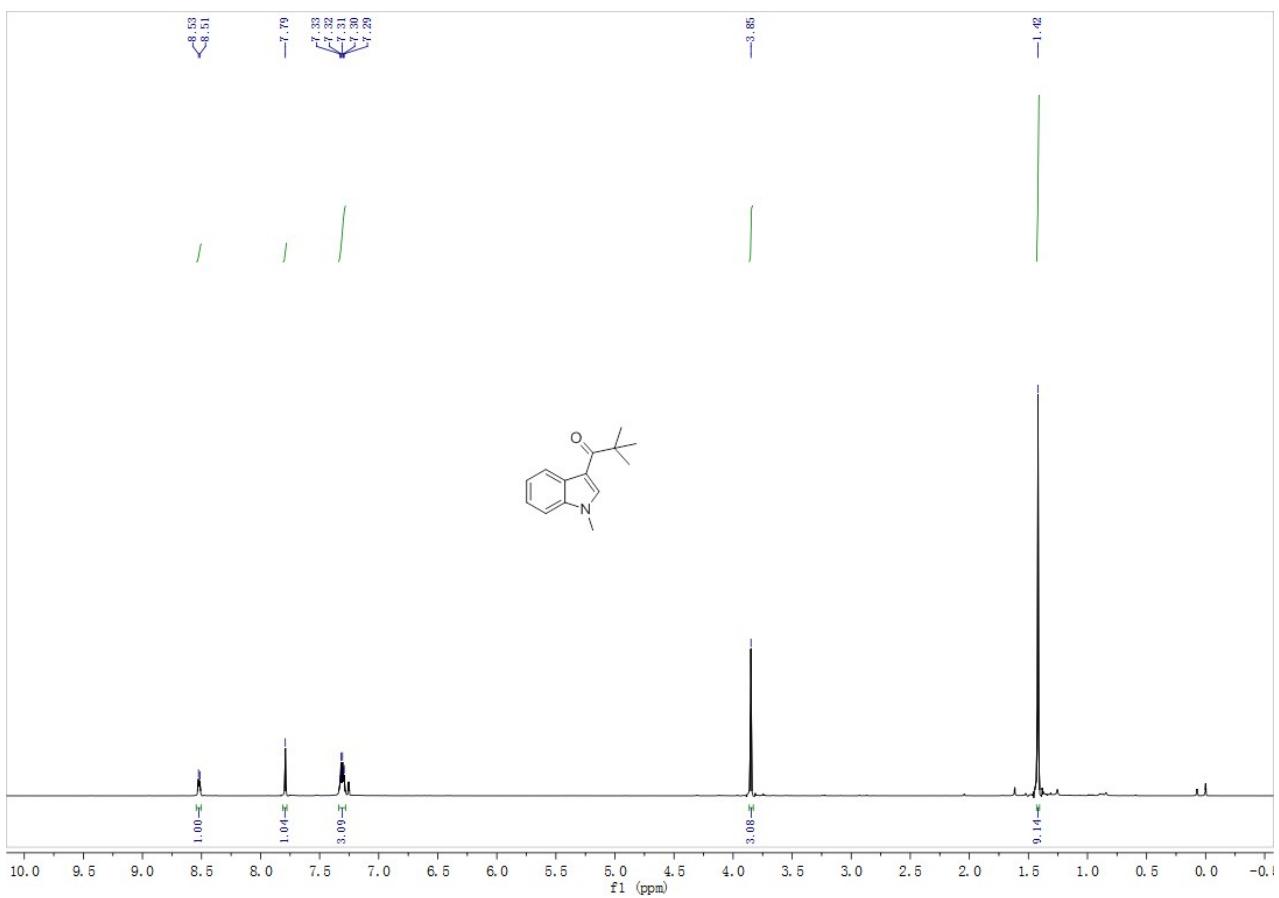


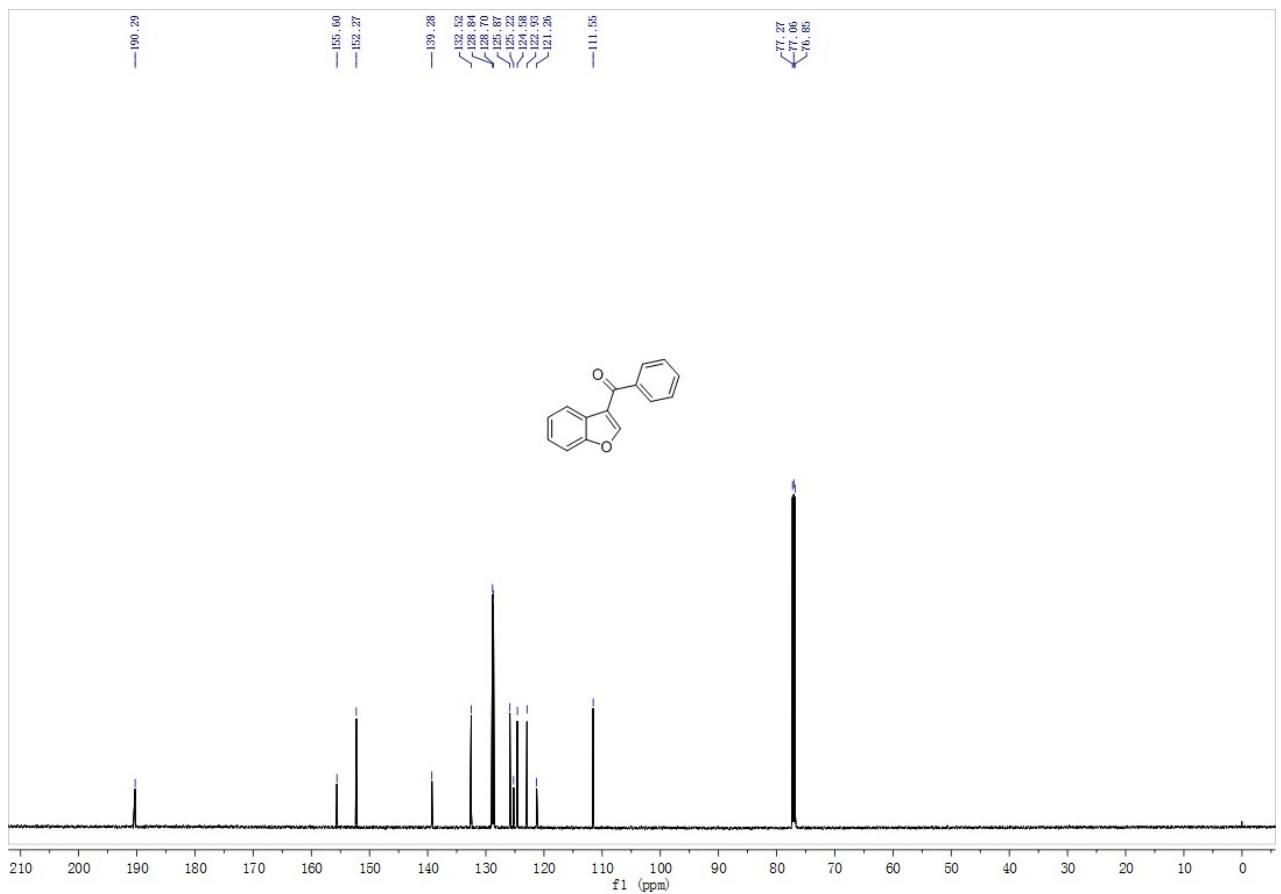
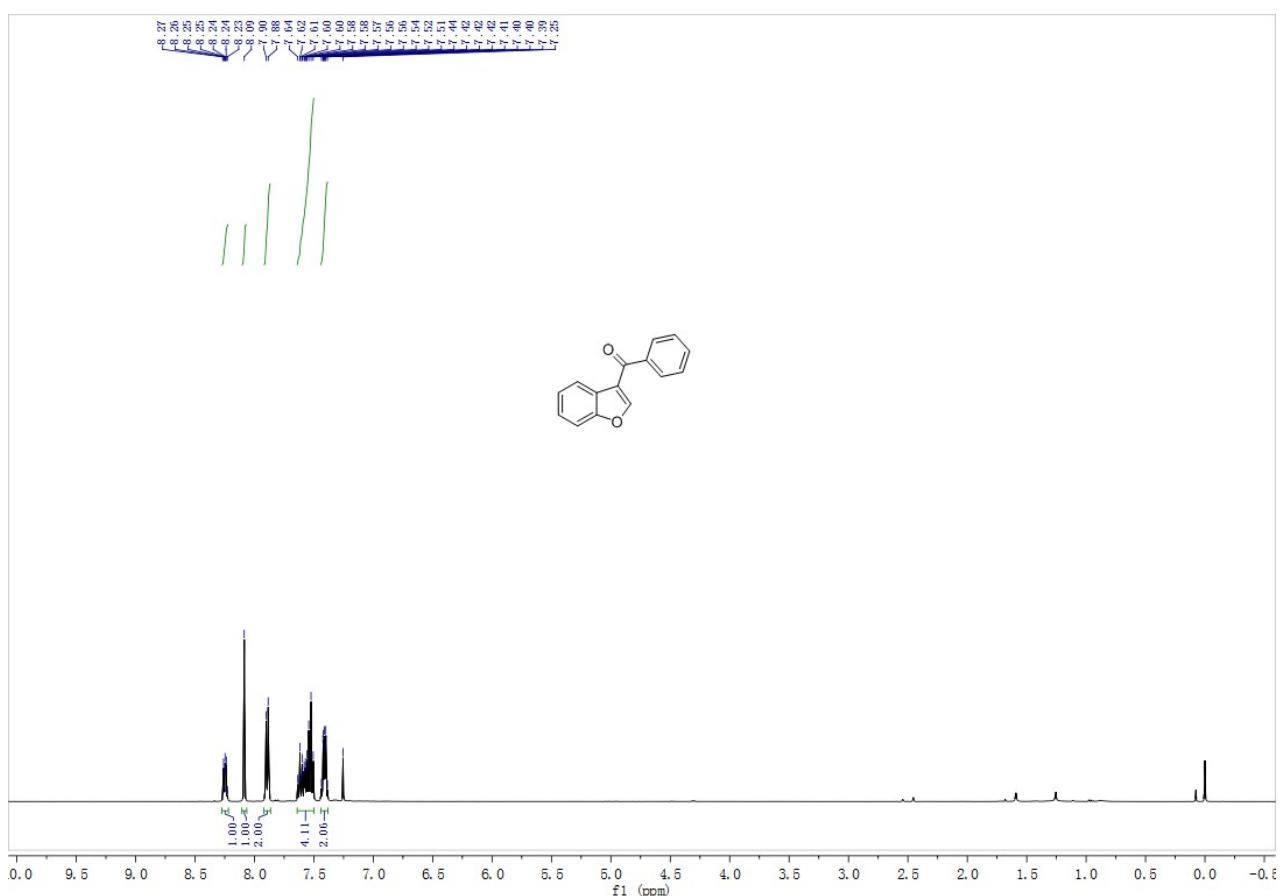
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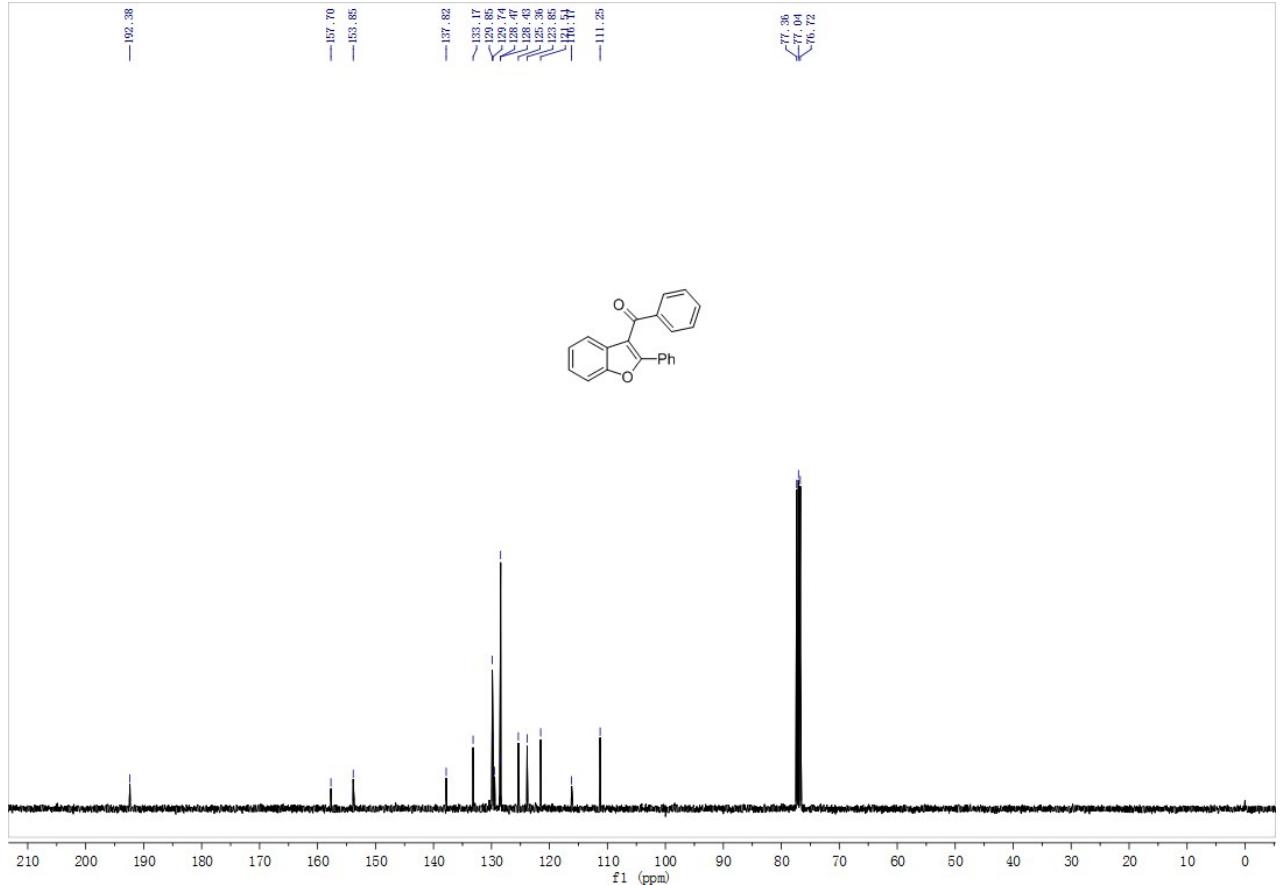
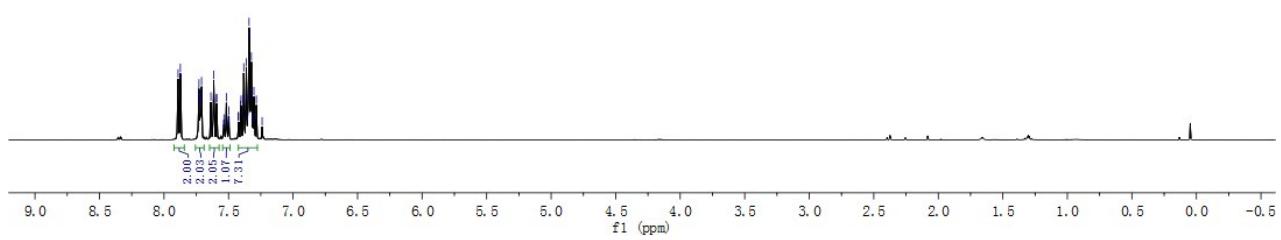
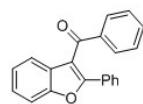


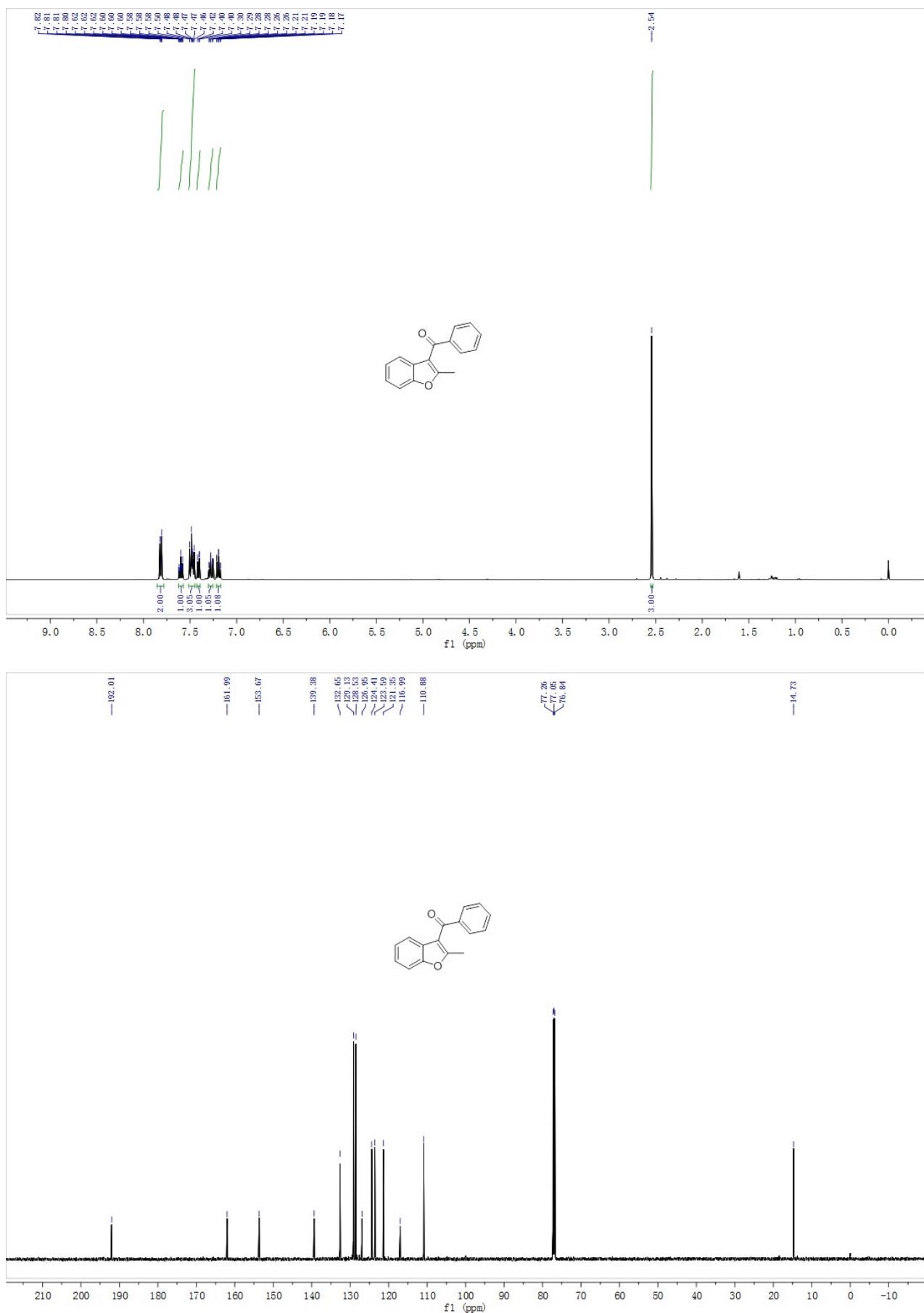
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**4a**

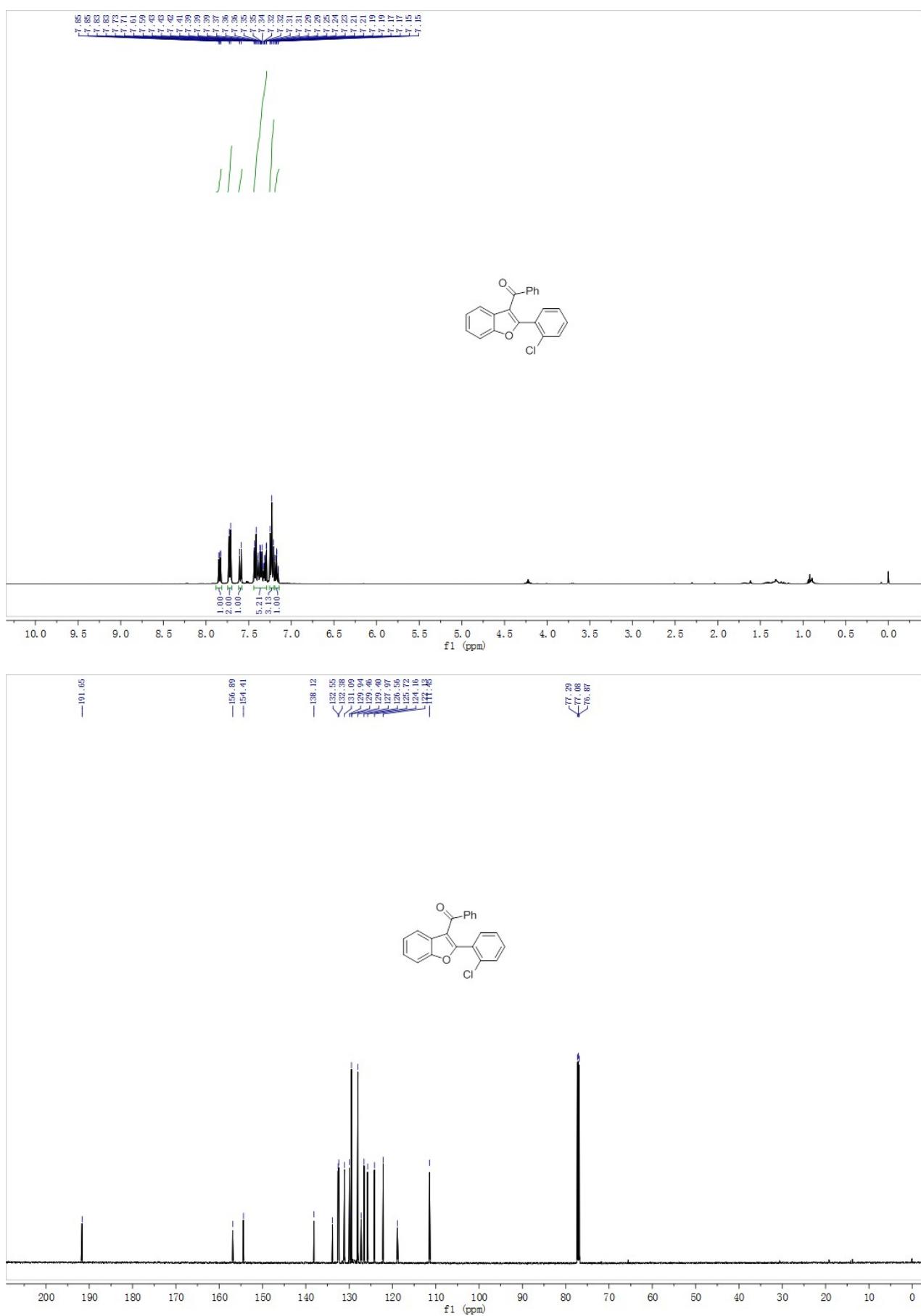
**4b**

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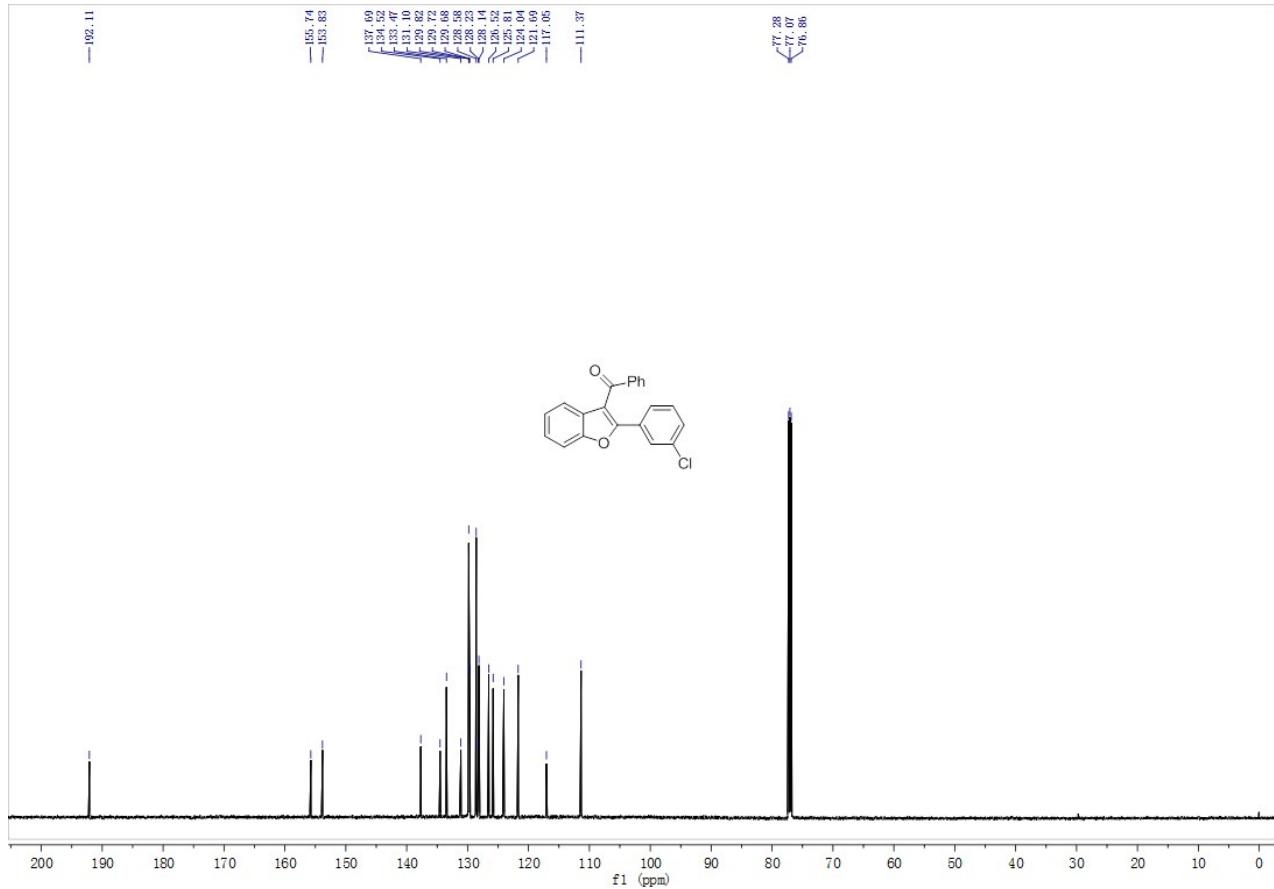
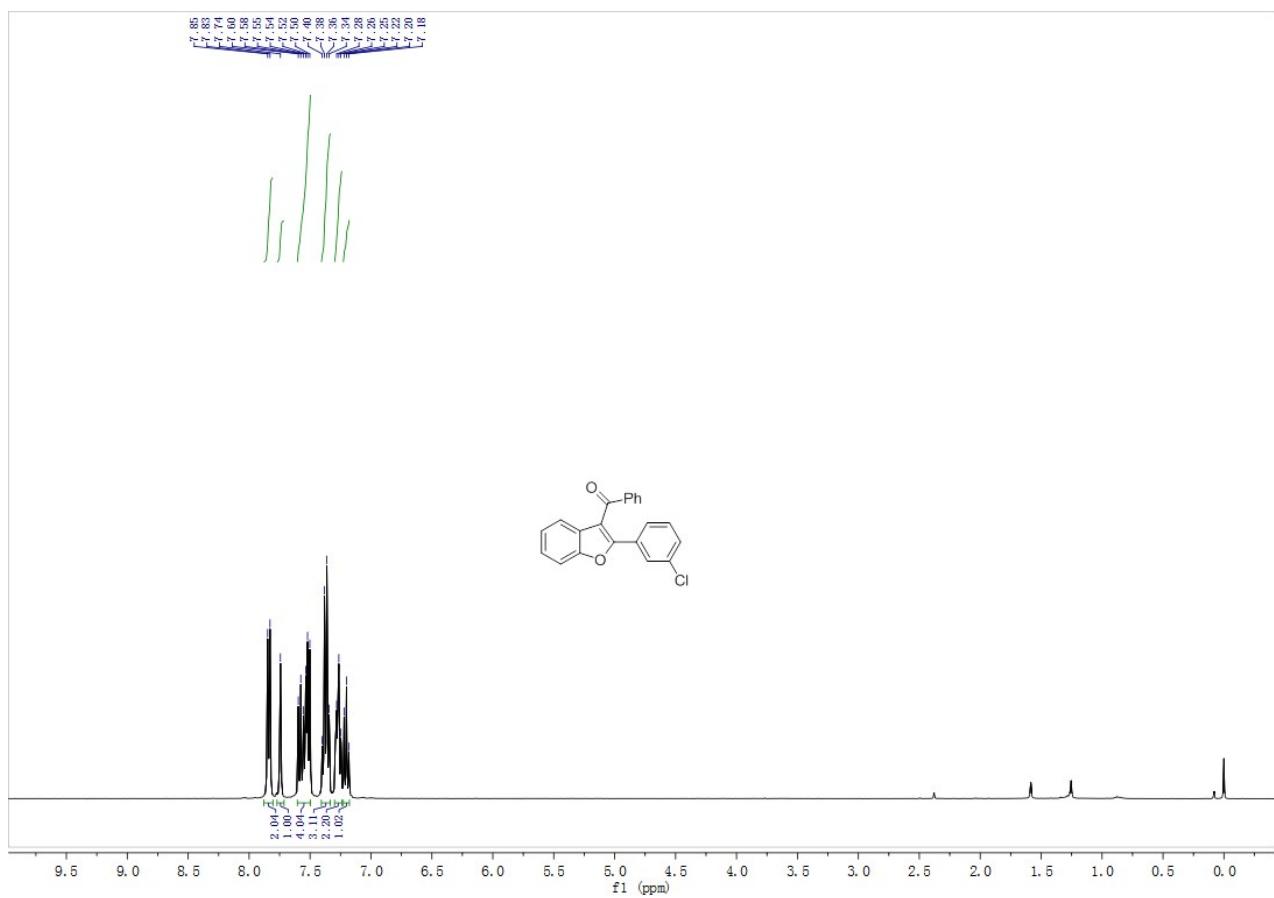


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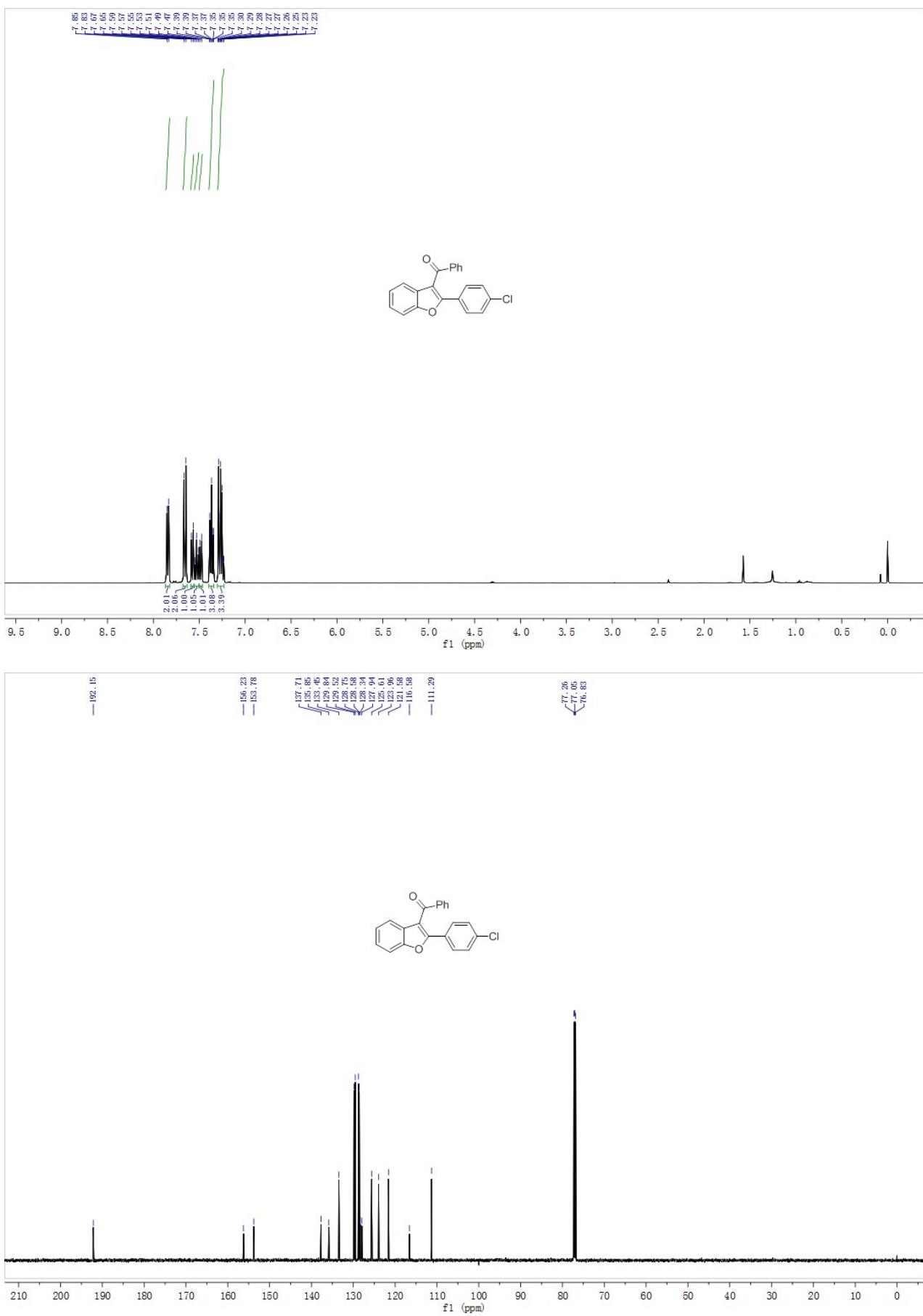
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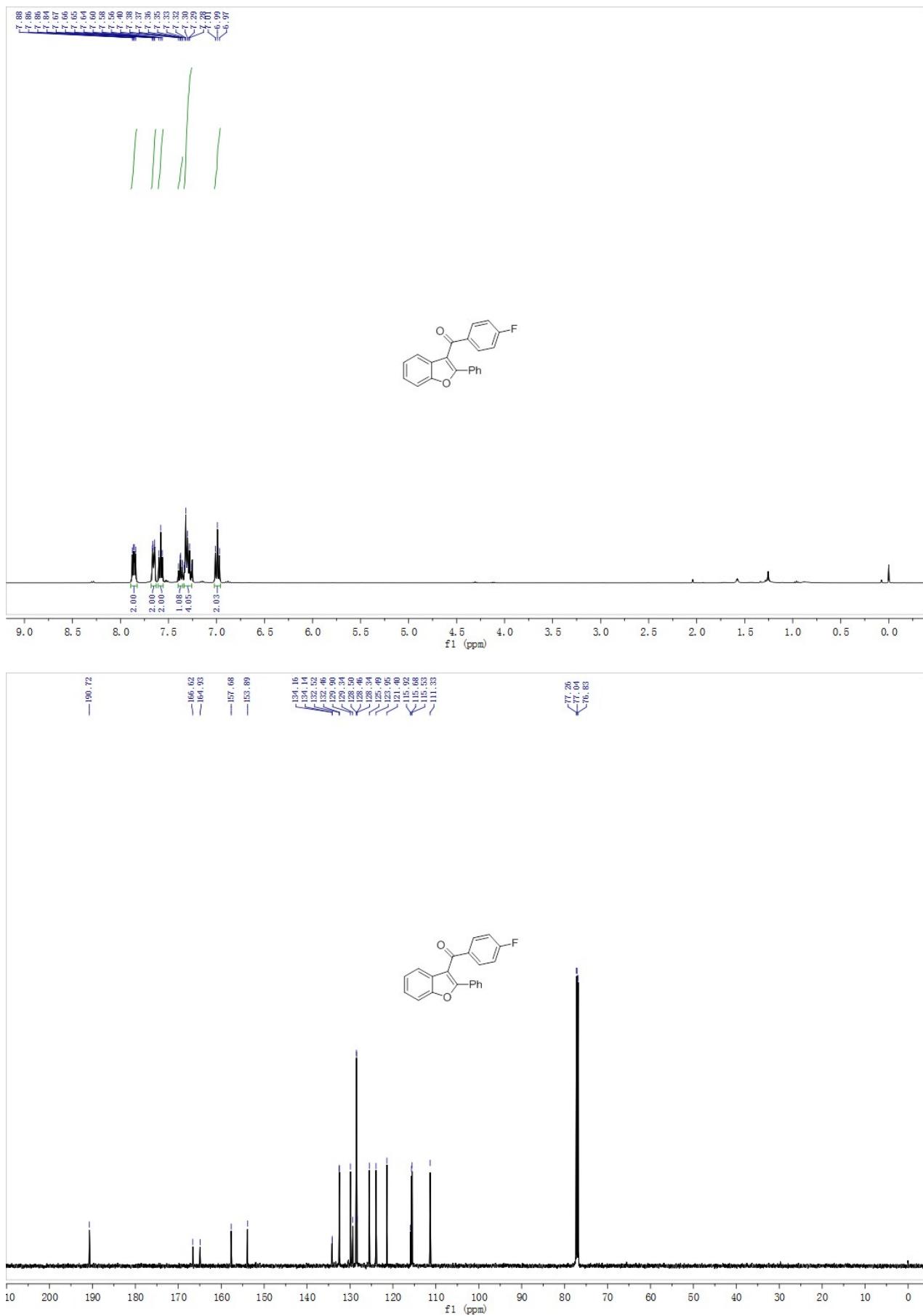
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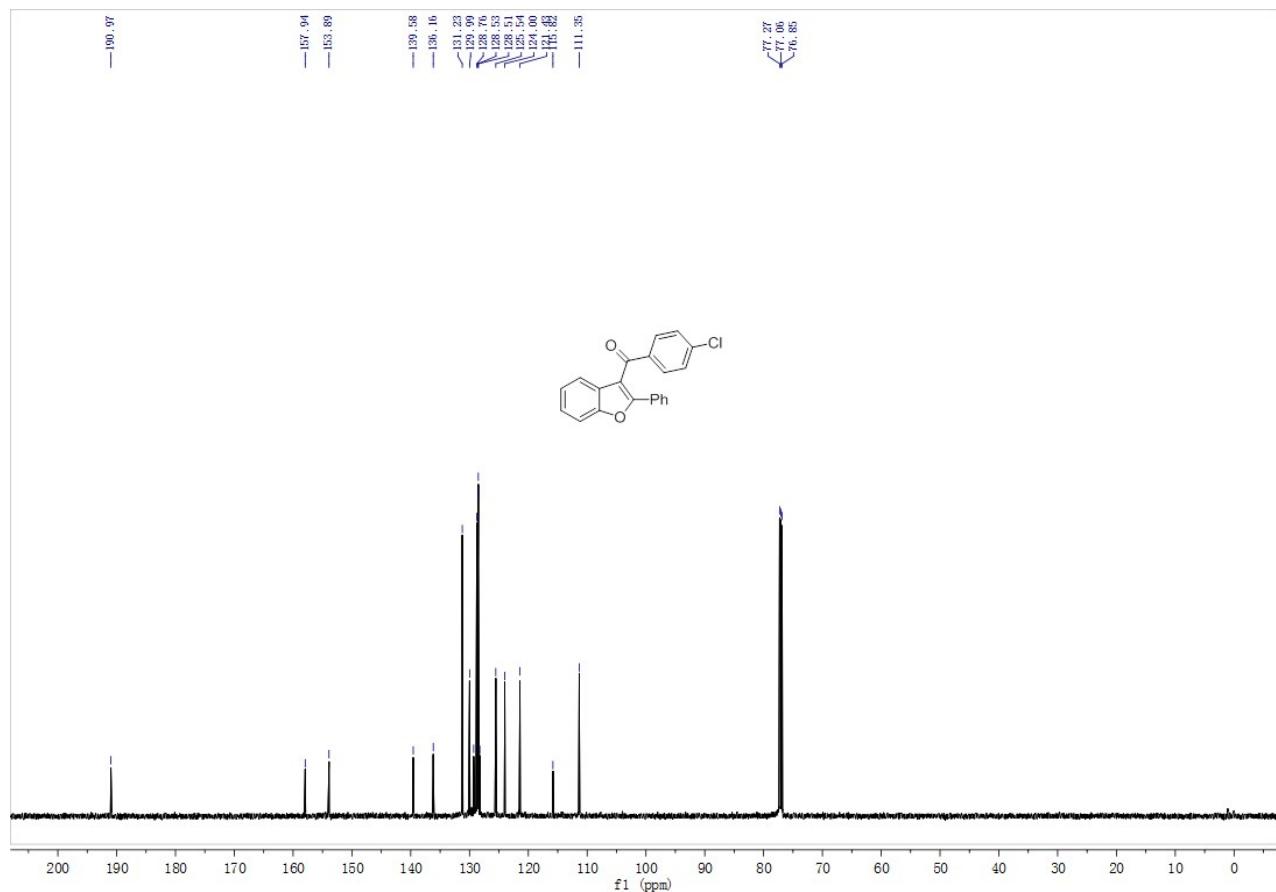
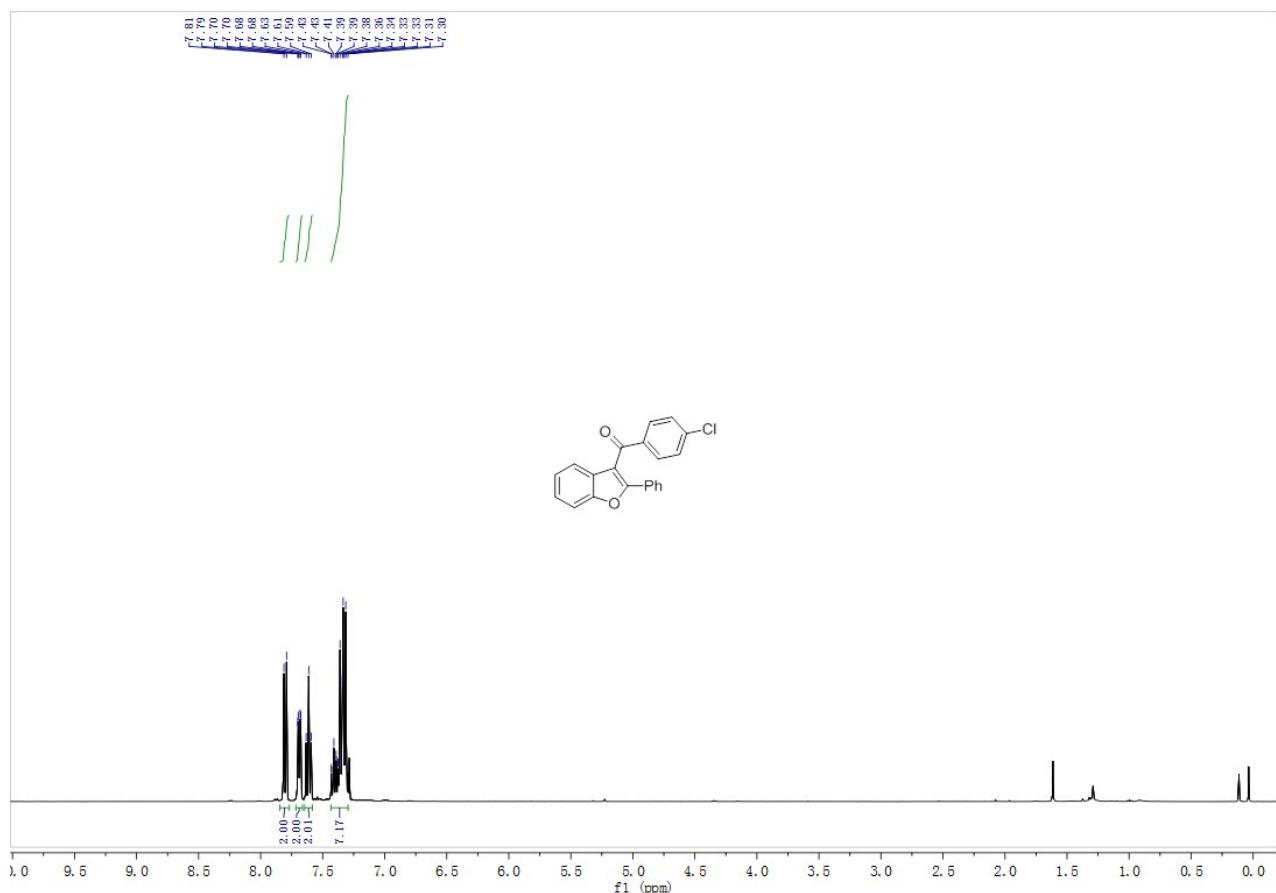
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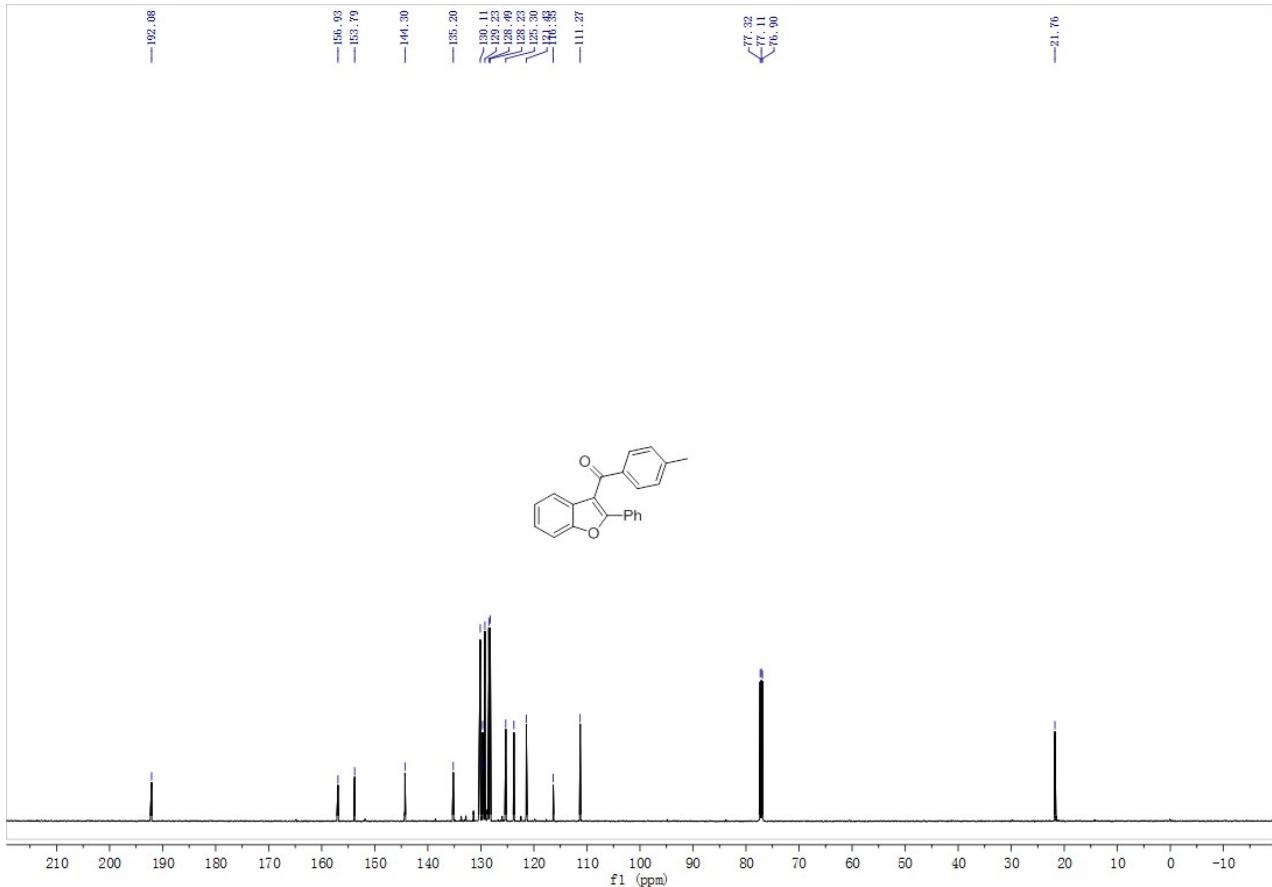
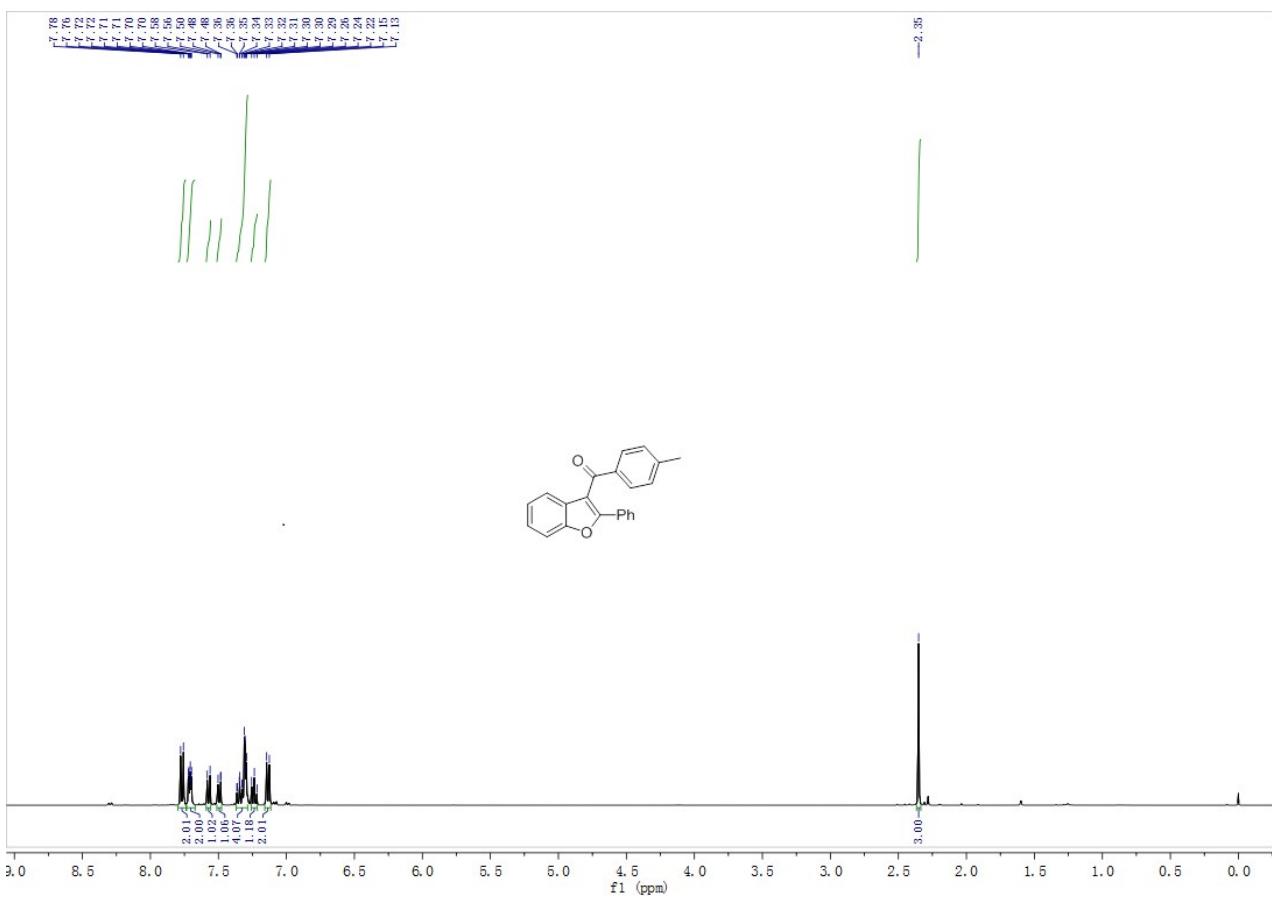
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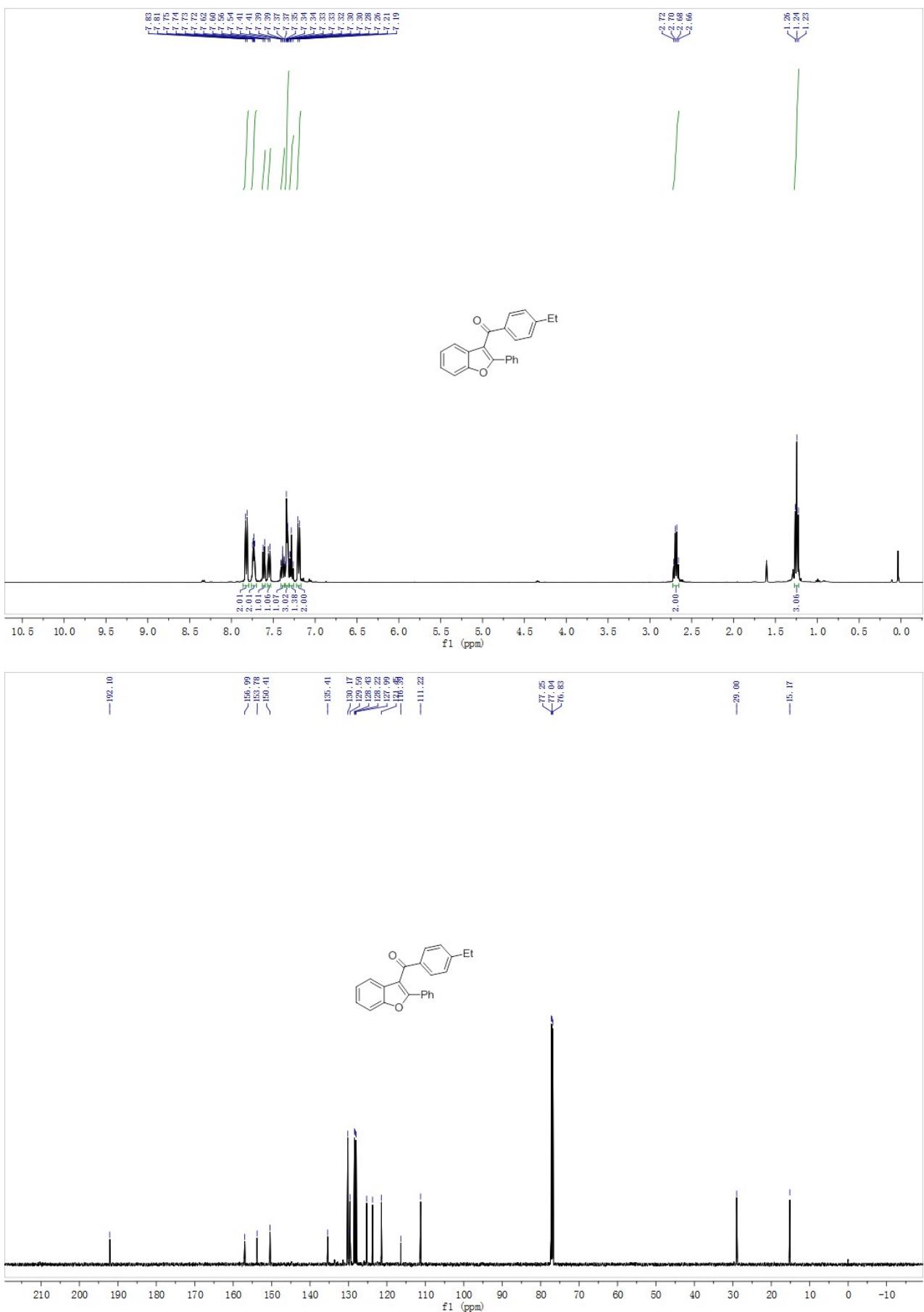
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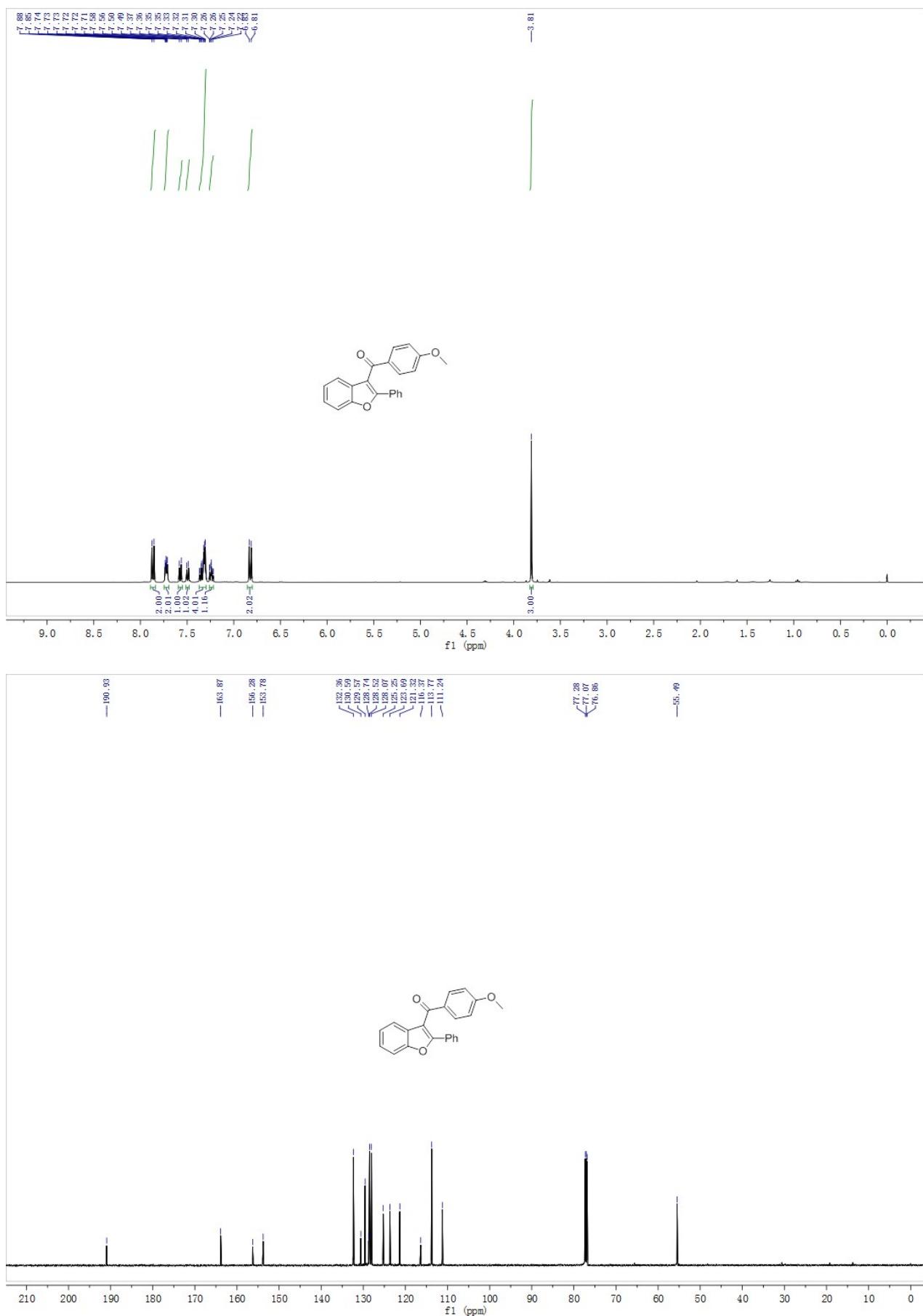


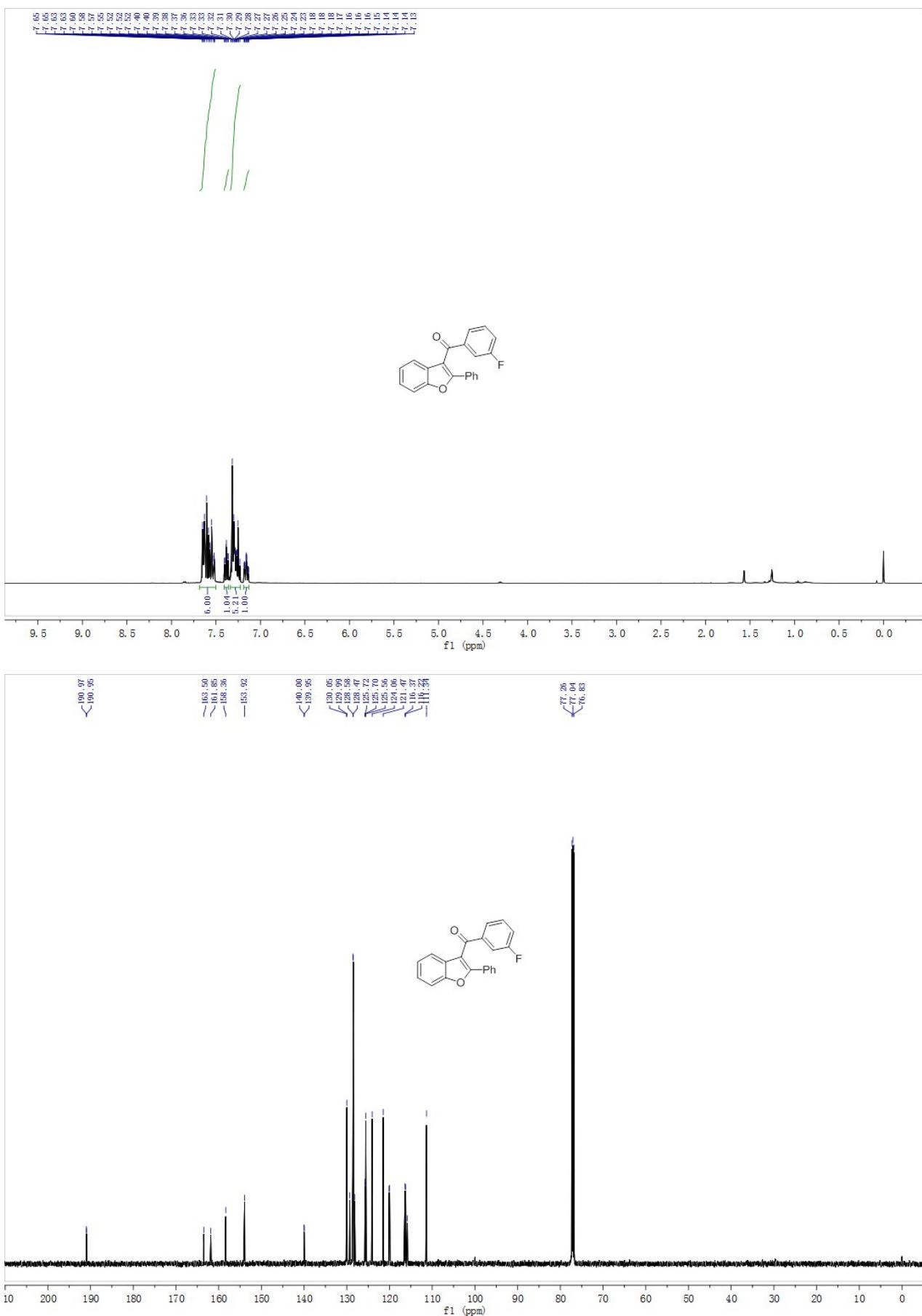
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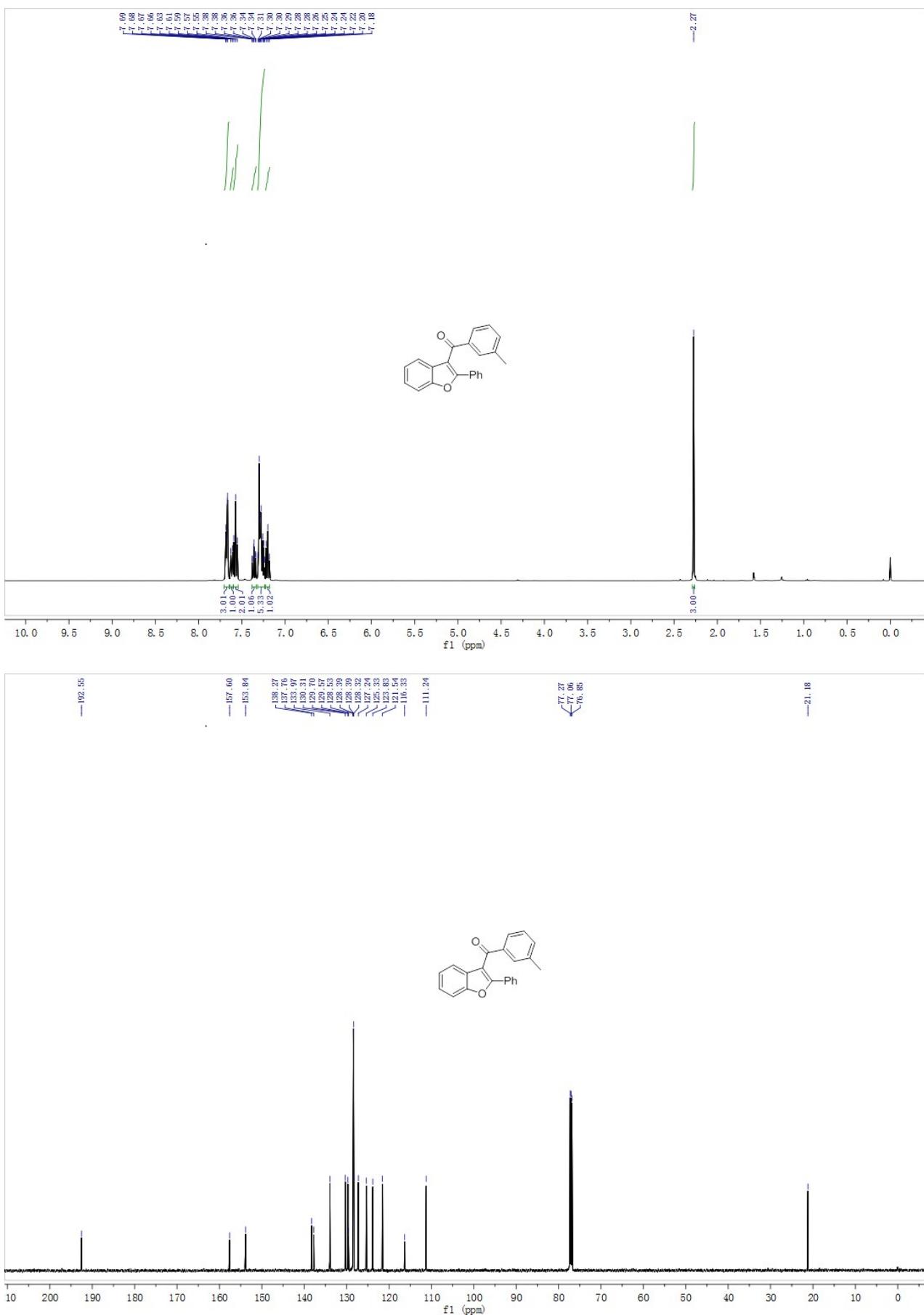


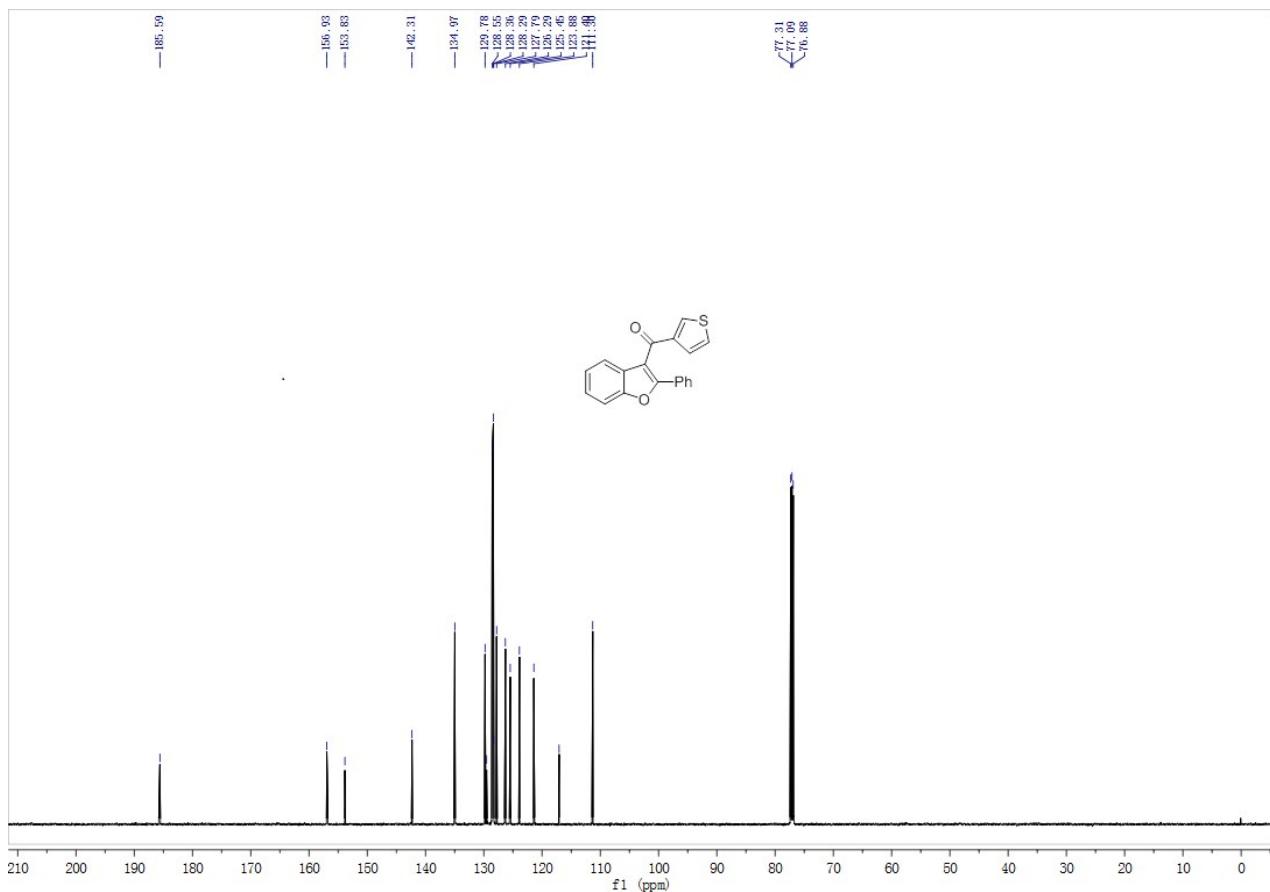
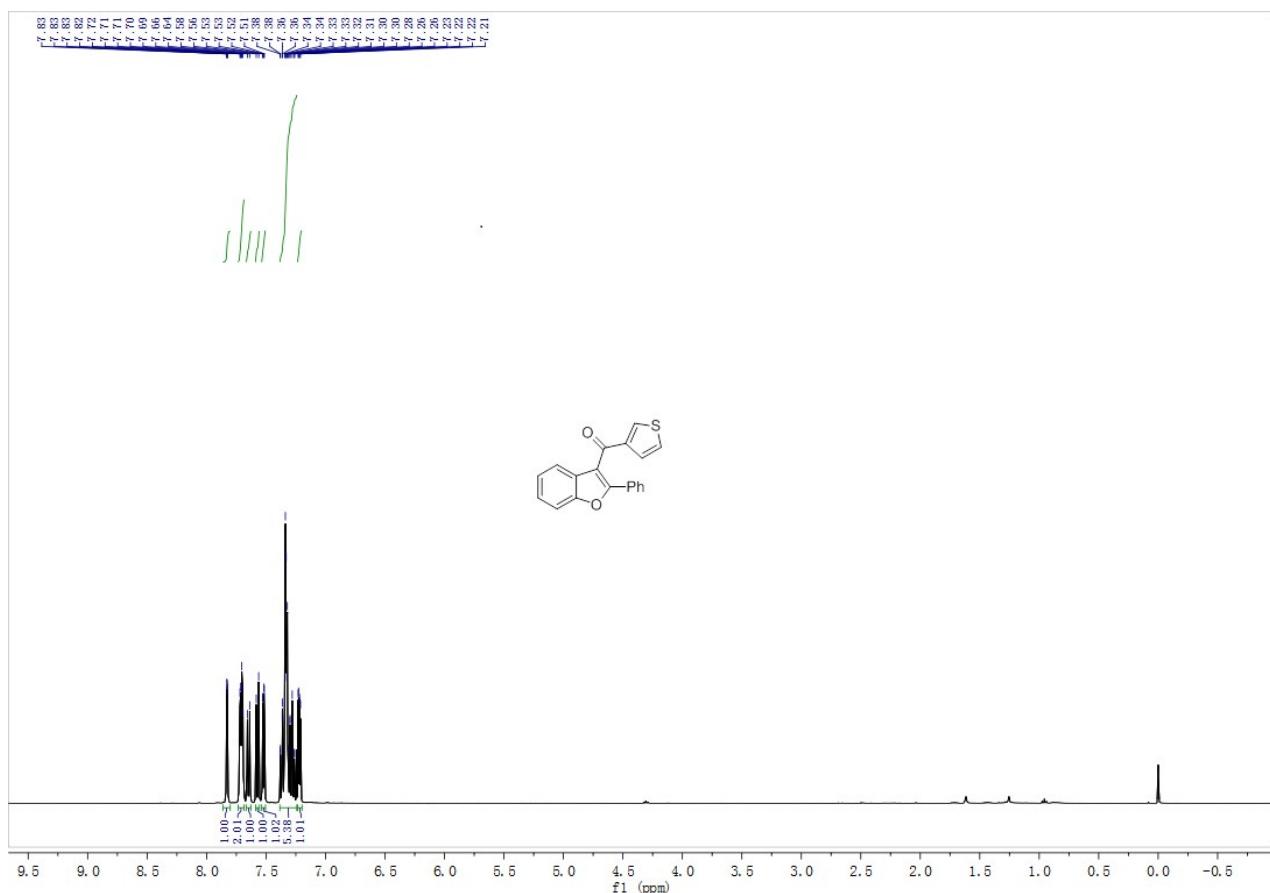
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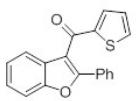
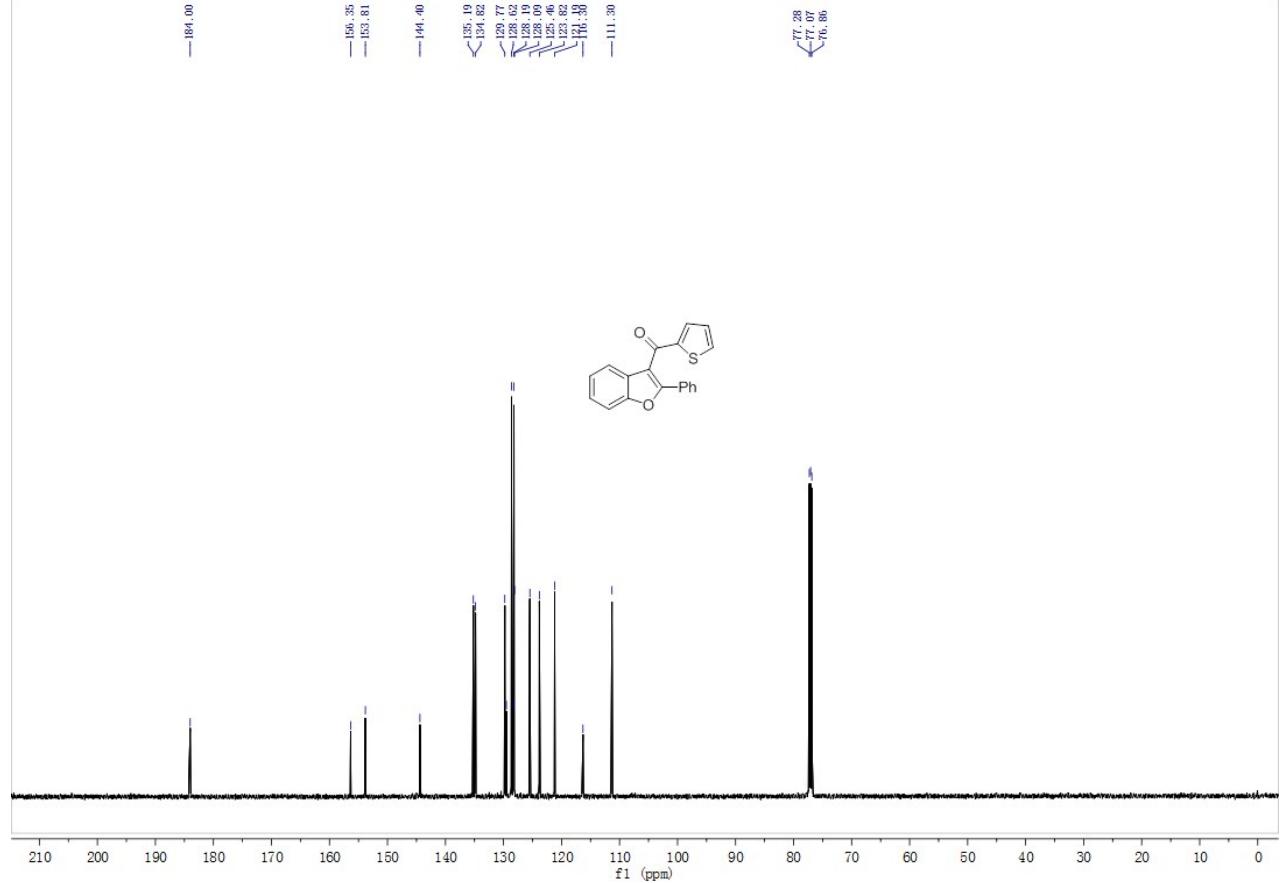
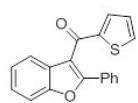
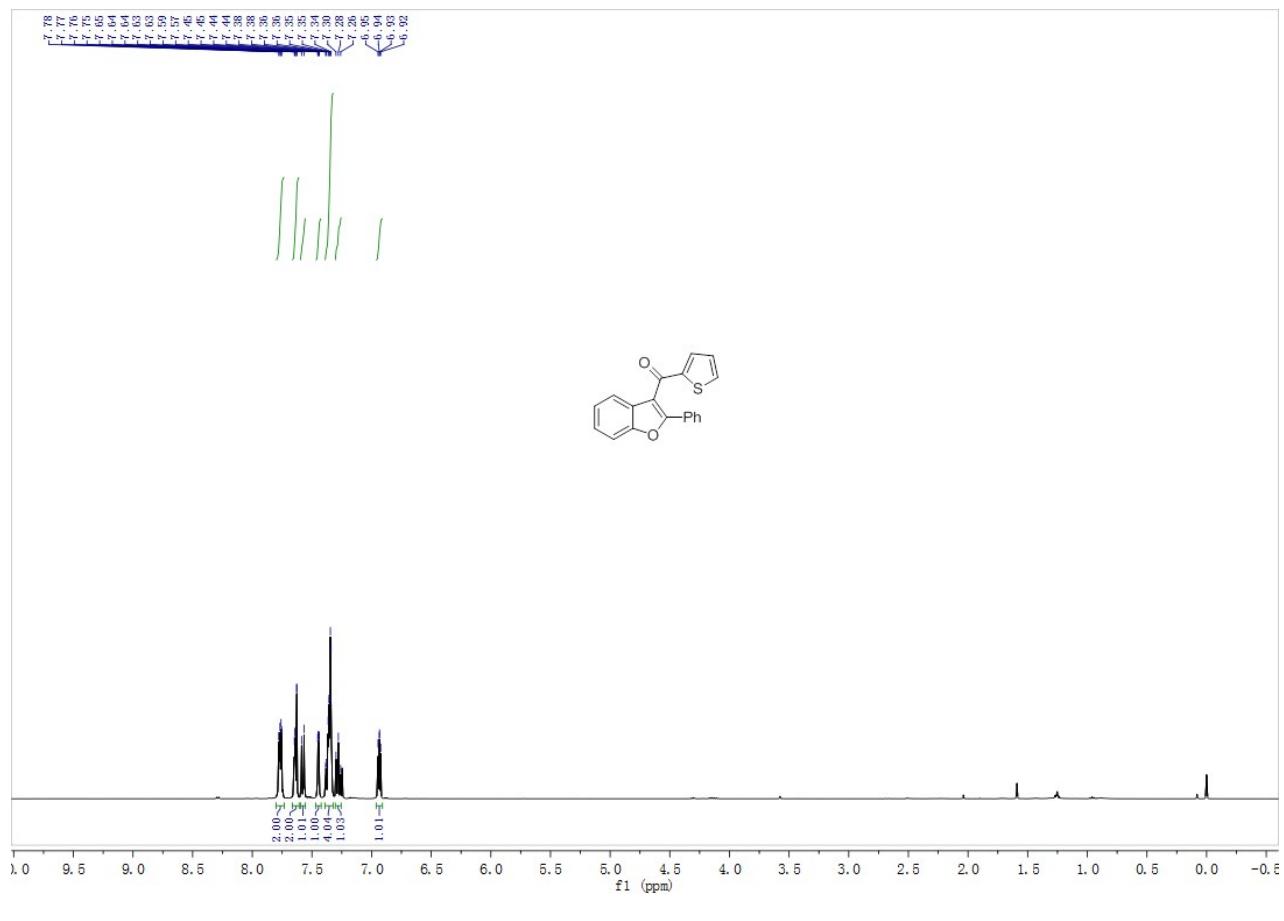


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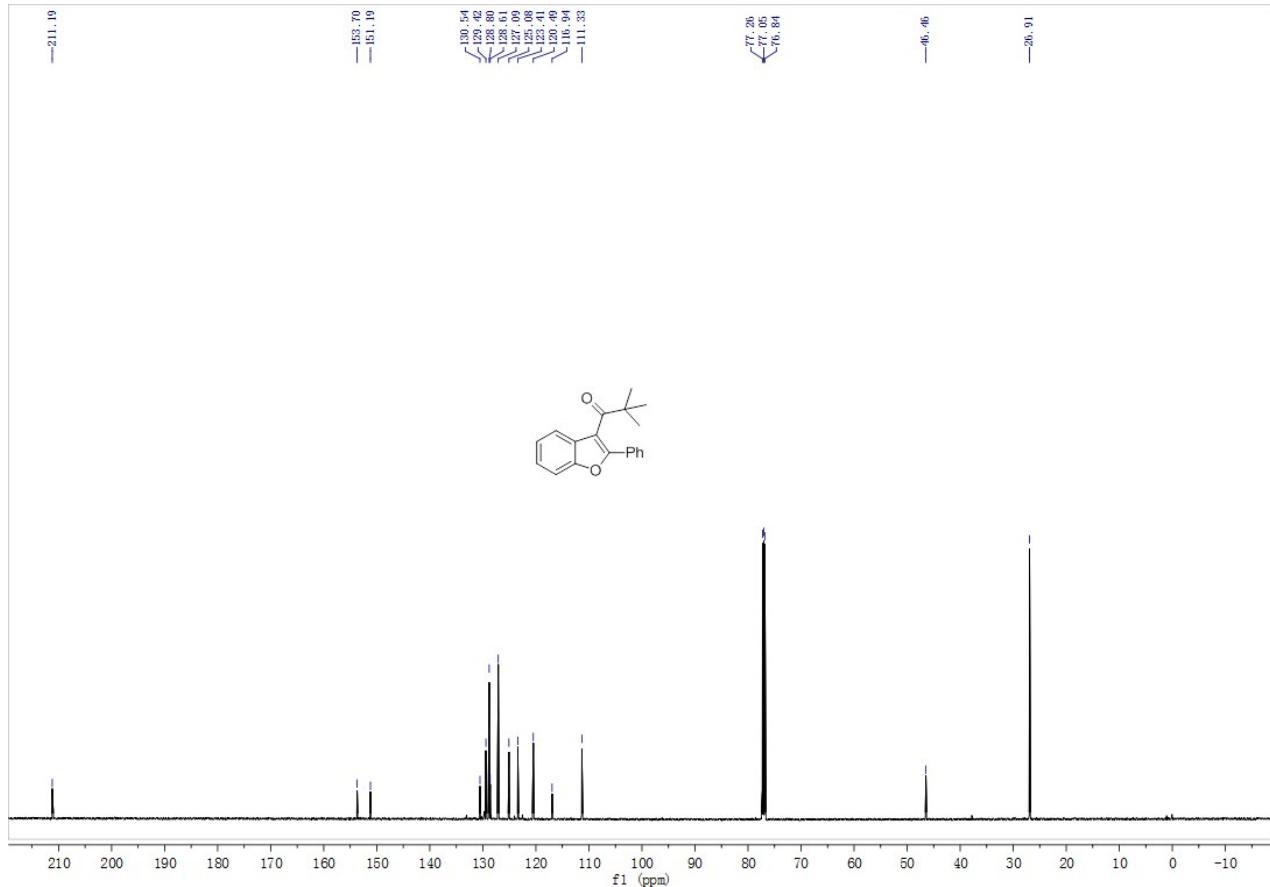
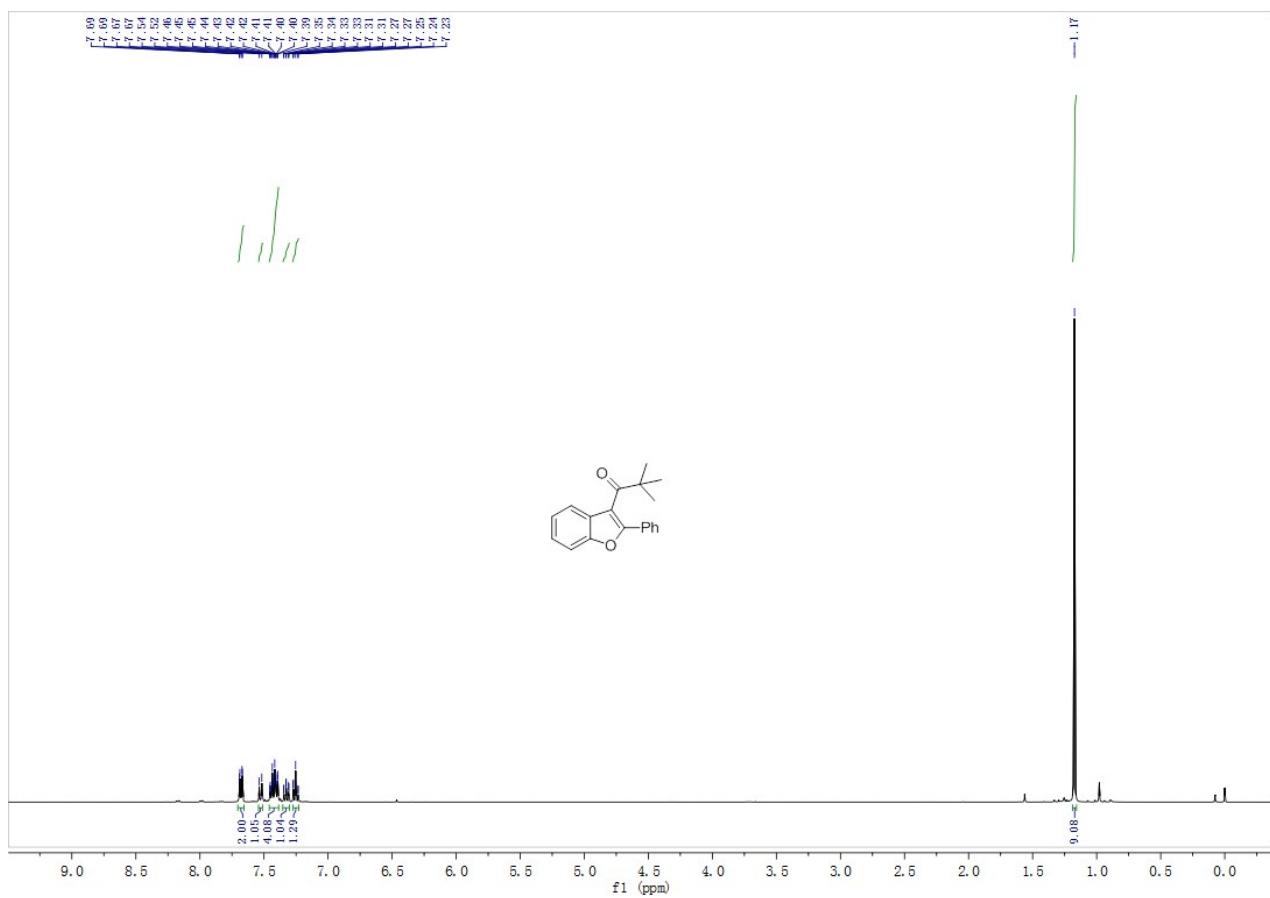


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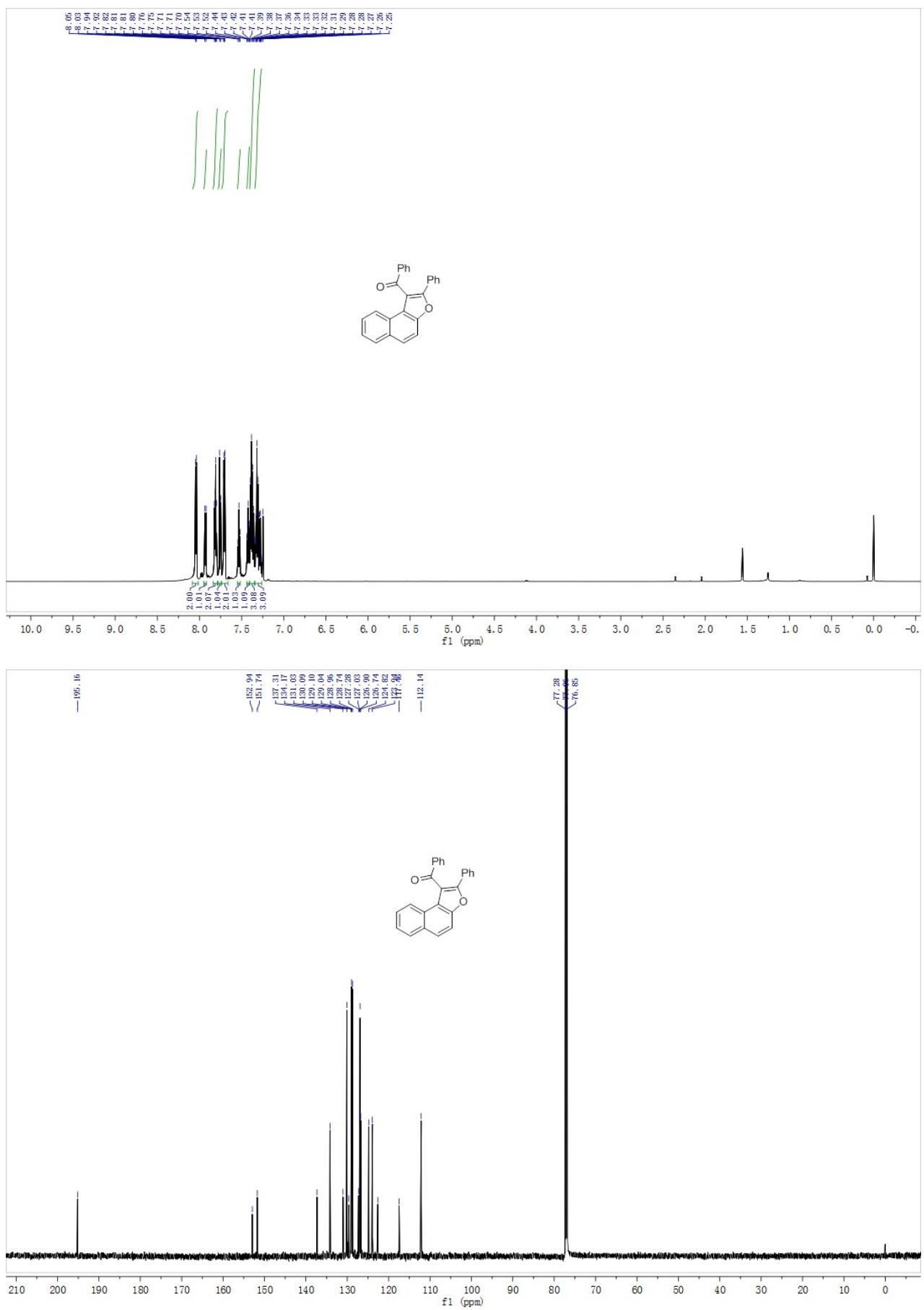
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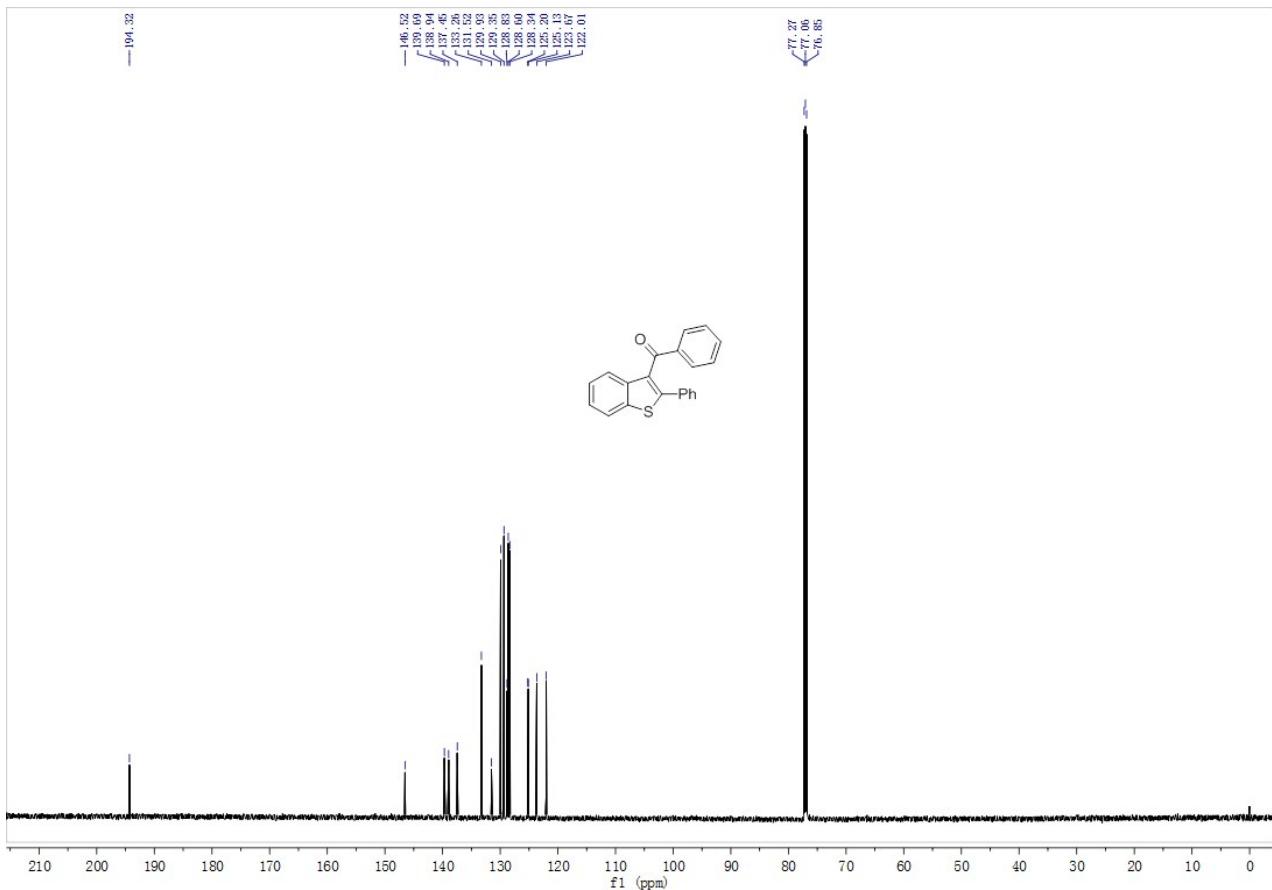
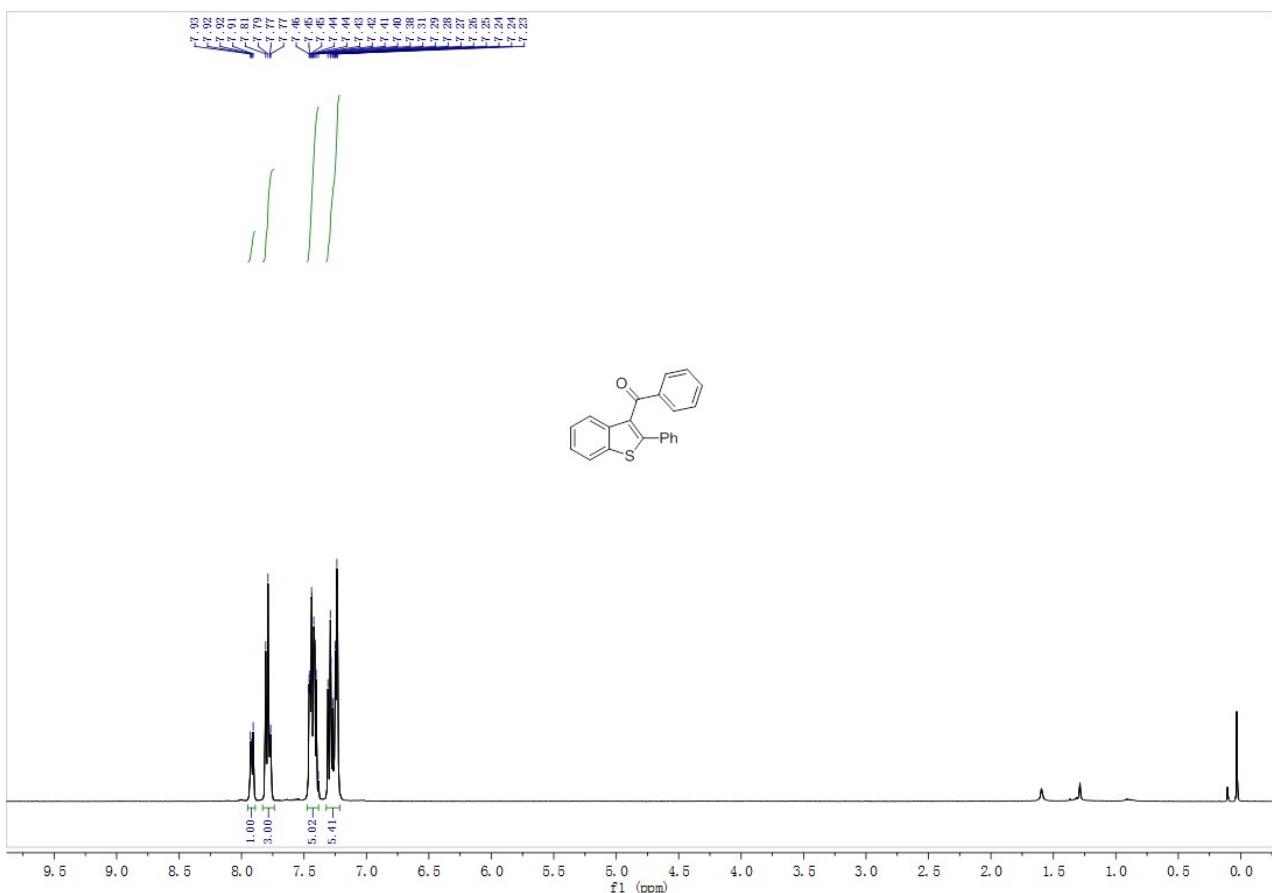
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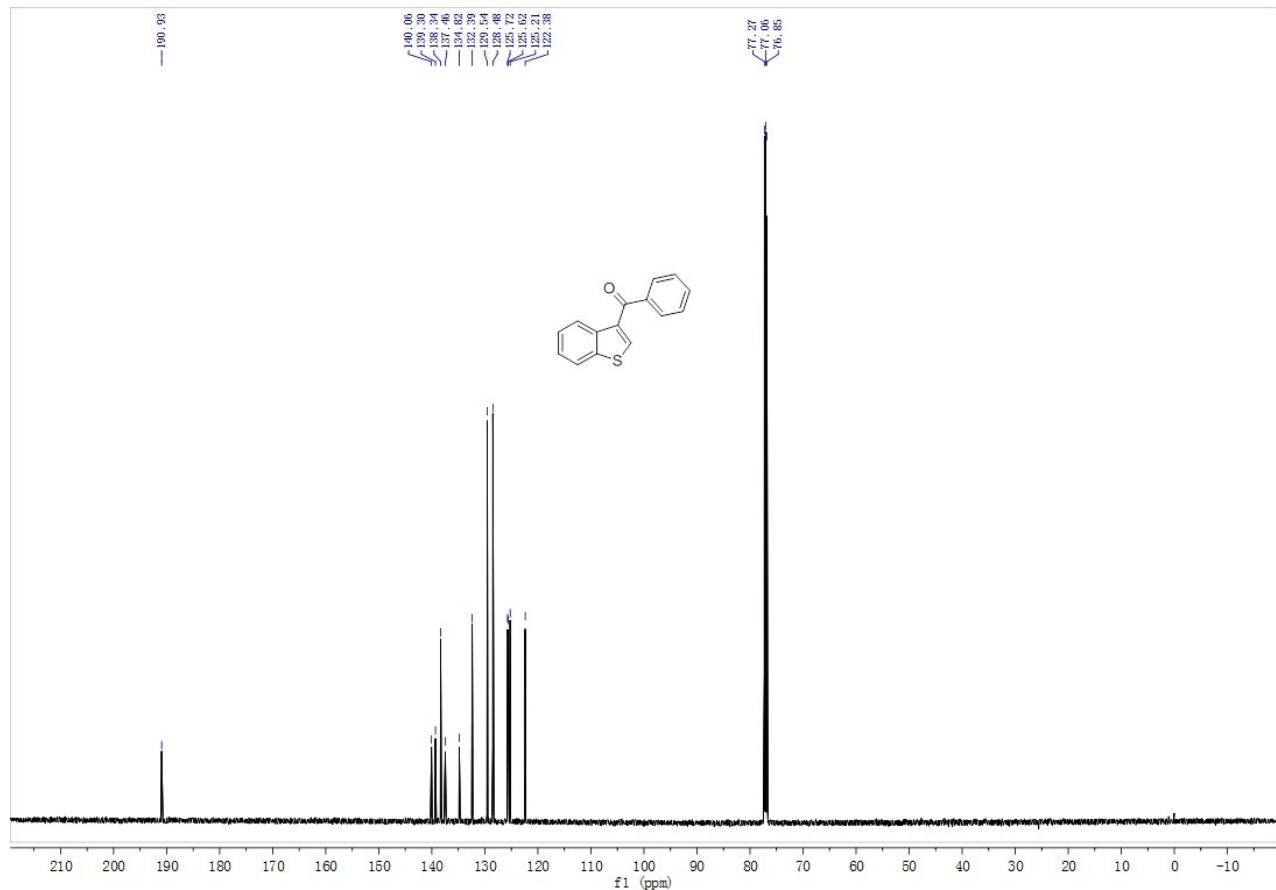
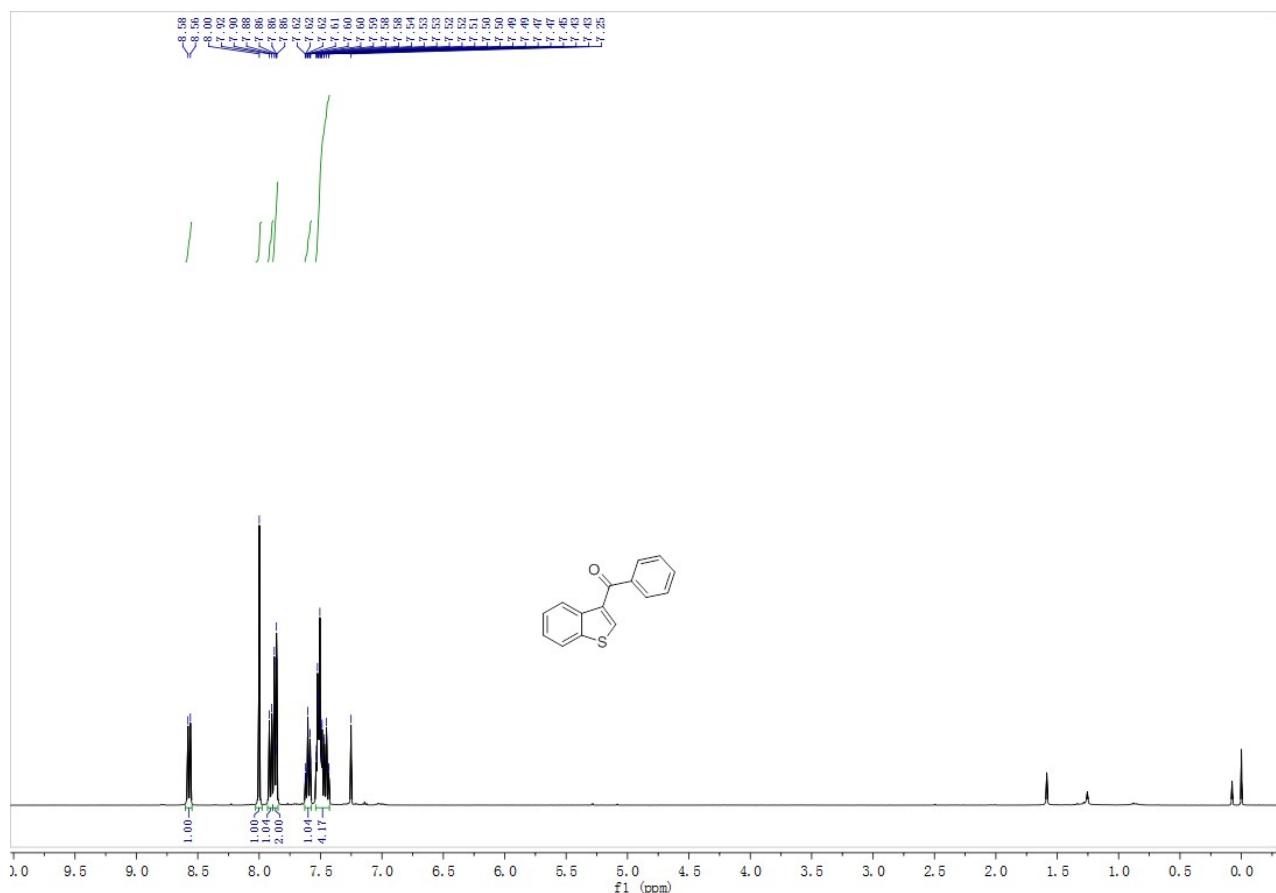


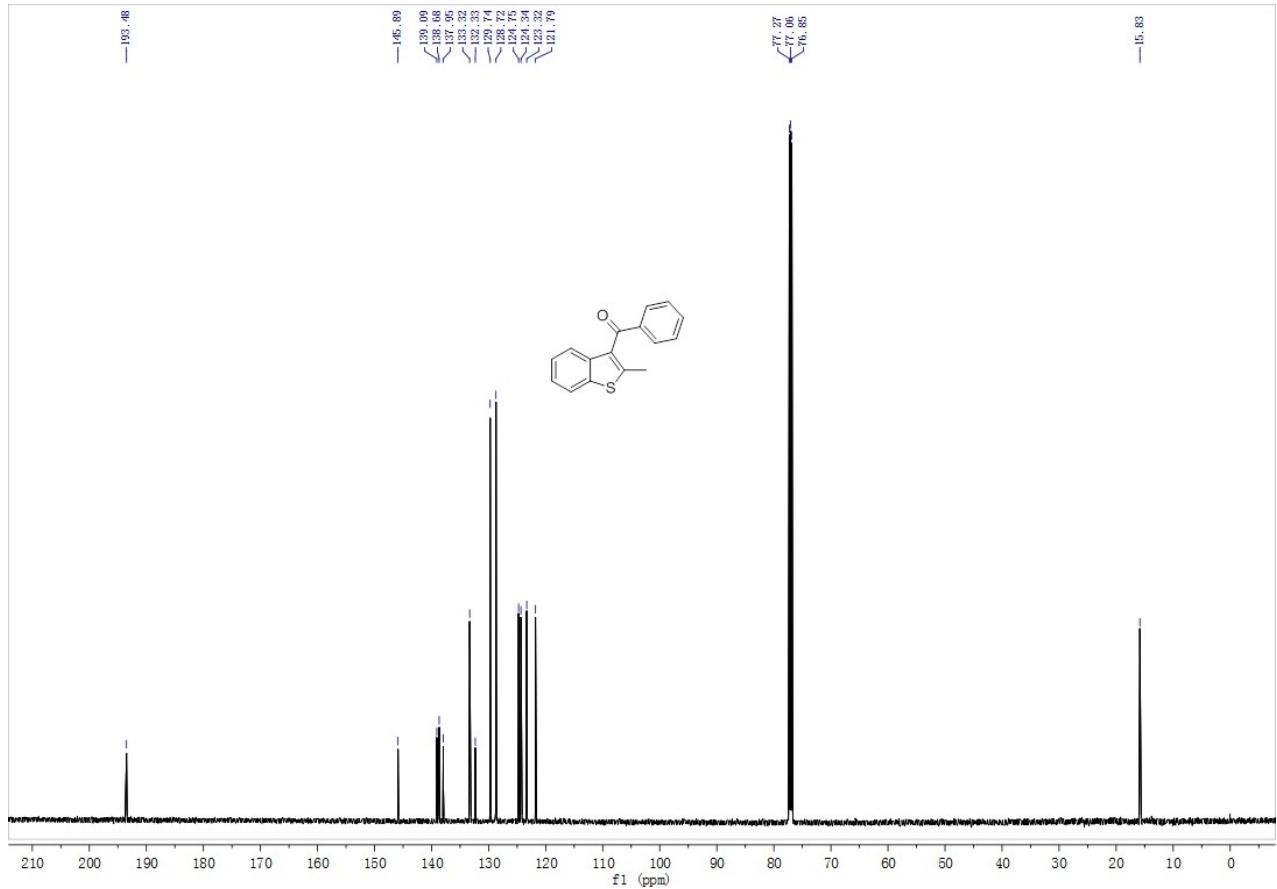
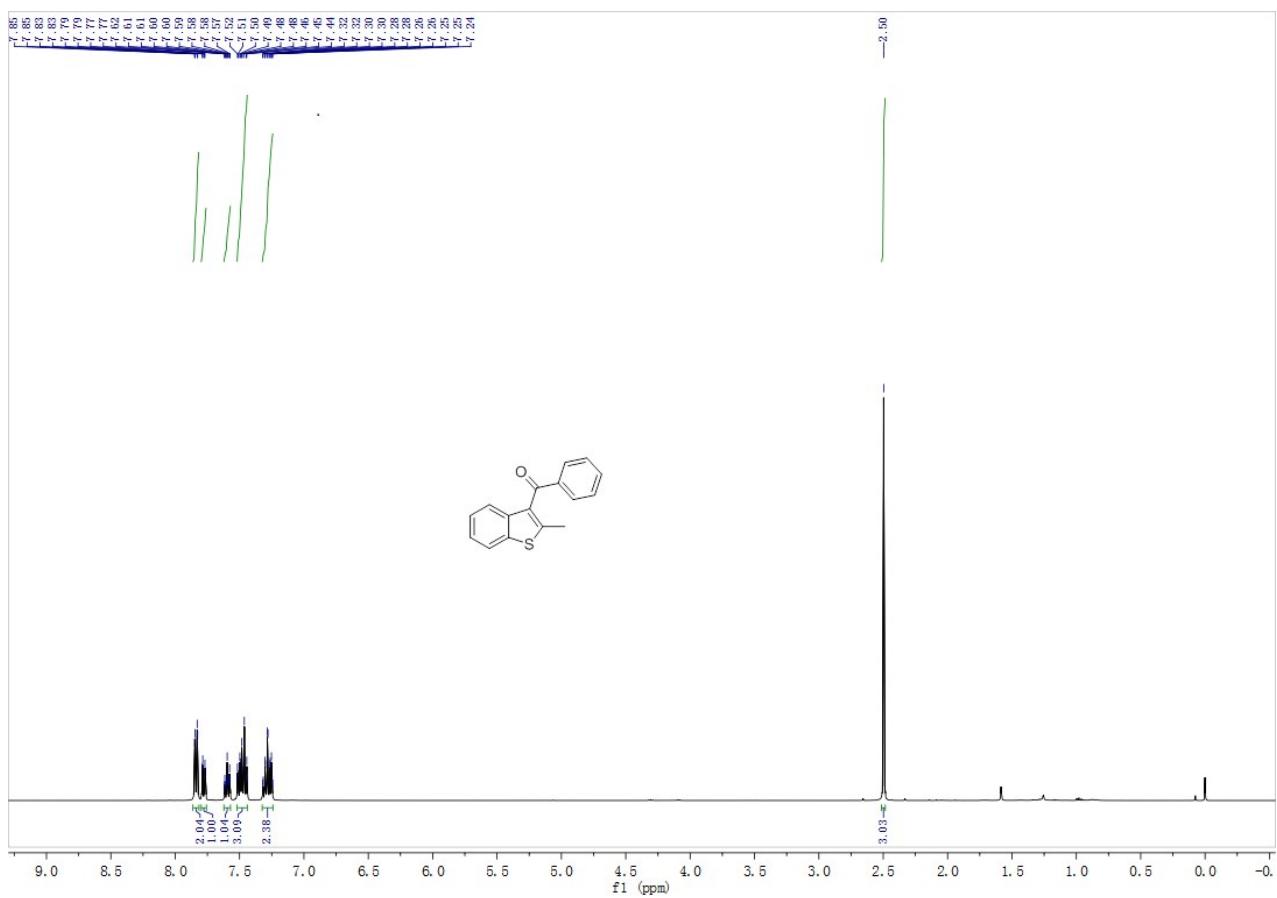
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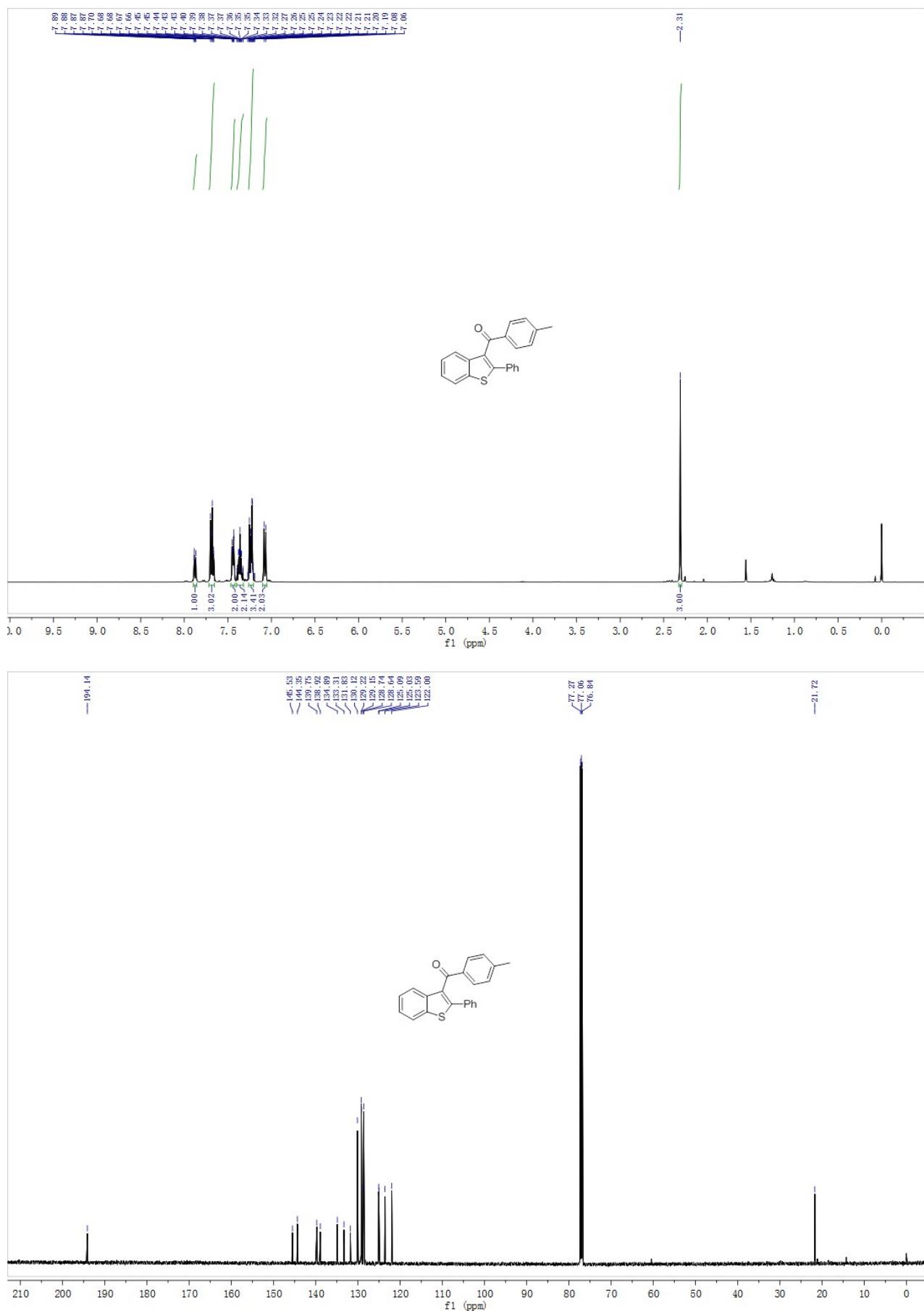


**6a**

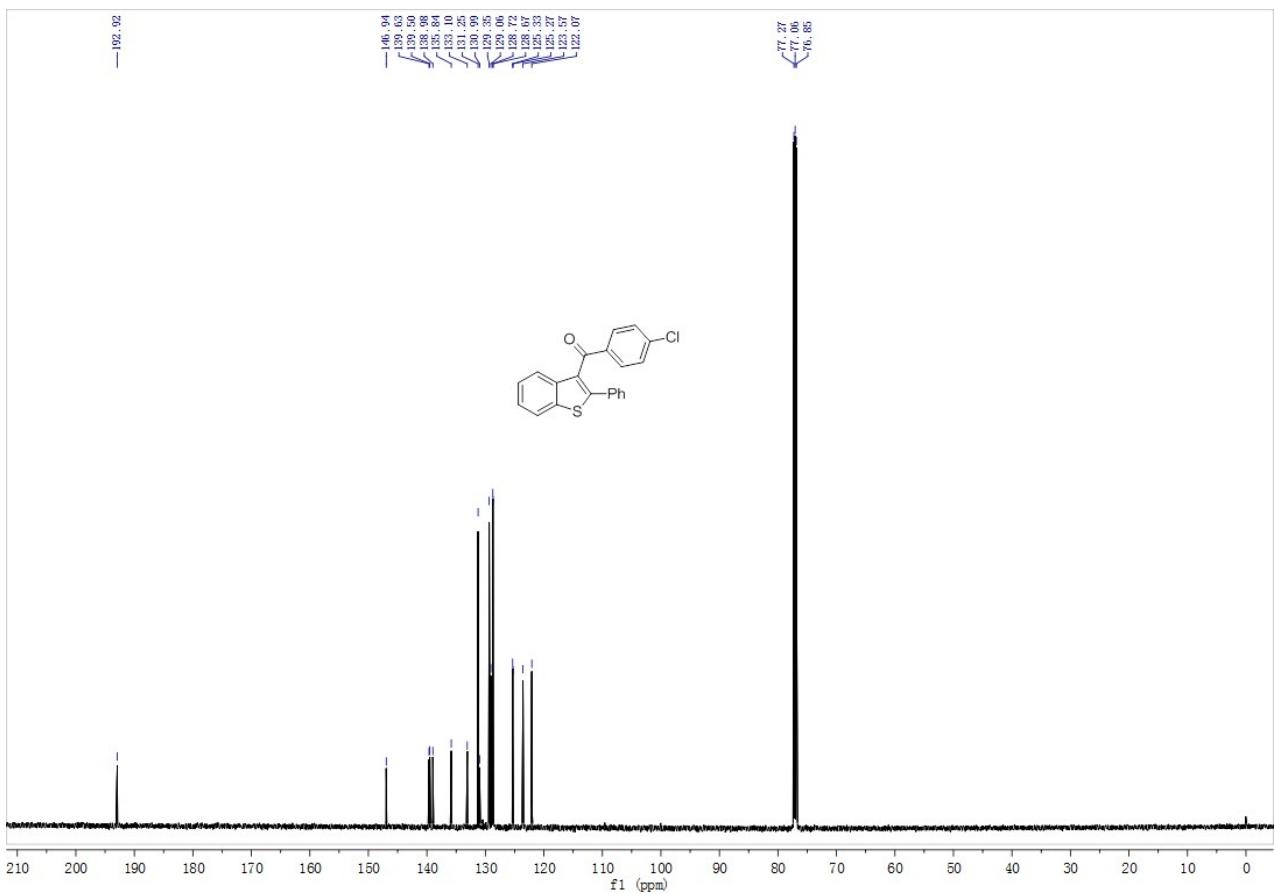
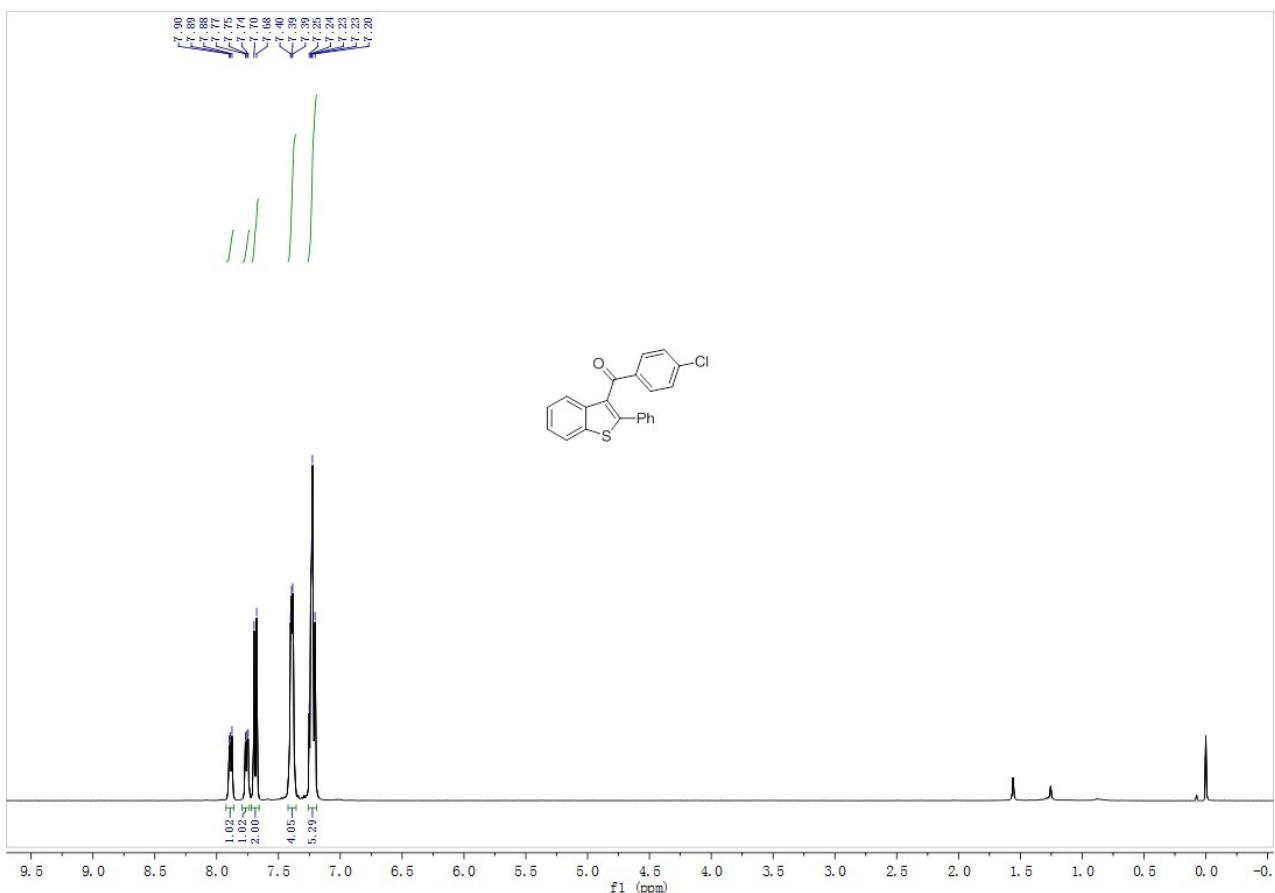


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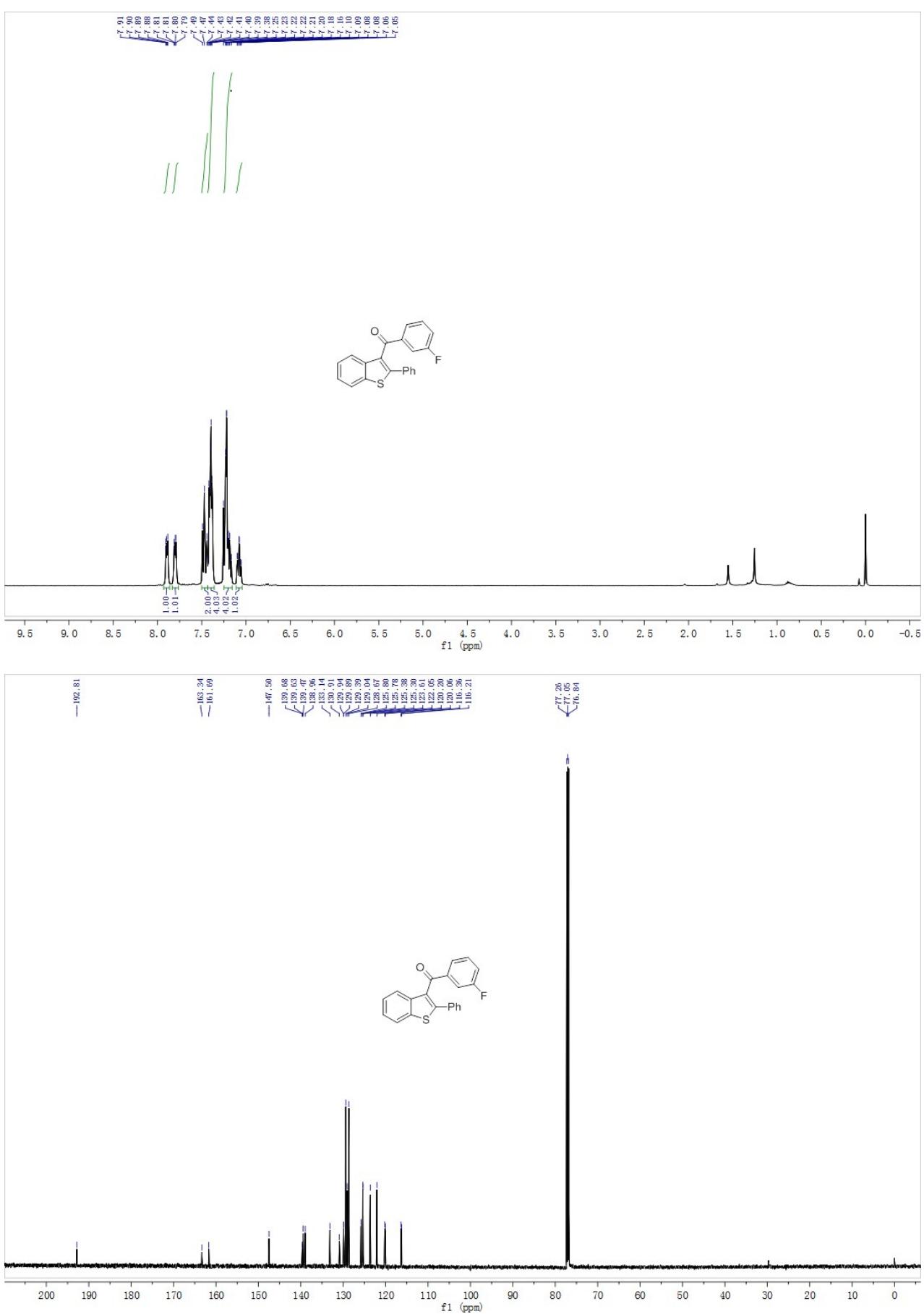
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**6d**

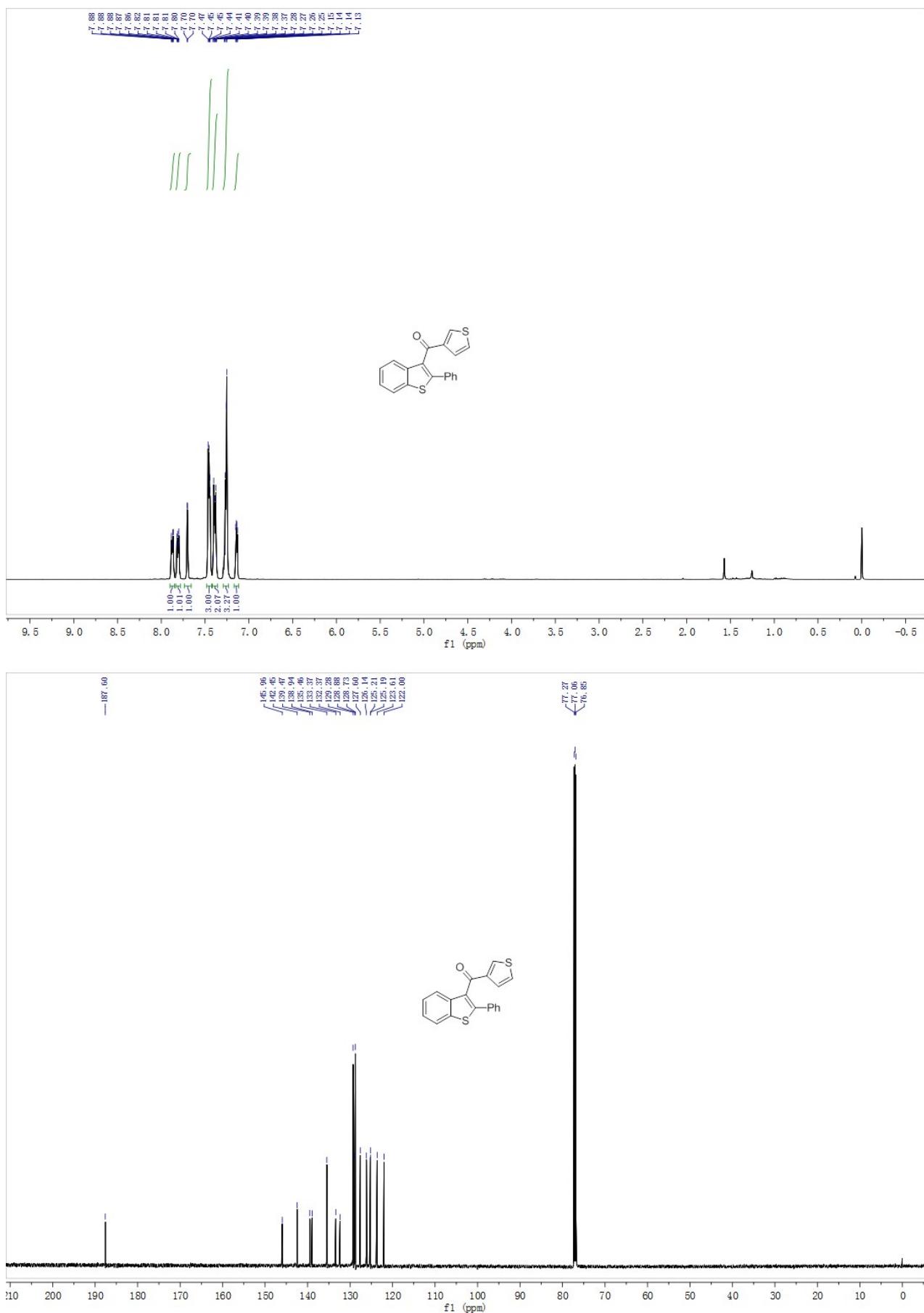
**6e**



6f



**6g**



**6h**