

## Supporting Information

for

### **Copper Loaded Nitrogen-Rich Mesoporous Carbon Nitride as a Highly Efficient Photocatalyst for Selective Oxidative Cleavage of C(sp<sup>3</sup>)-C(sp<sup>3</sup>) Bonds at Room Temperature under Visible Light**

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## Supporting Information

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## 1. General information

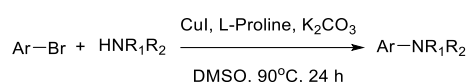
### 1.1 Chemical and materials

Unless otherwise stated, all the materials were purchased from commercial suppliers and were used as received. All the solvents were purchased from local supplier. The tetrahydrofuran (THF) and acetonitrile (MeCN) were redistilled over calcium hydride (CaH), and other solvents were directly used without further purification. Most amines were obtained from commercial sources and used as supplied; others were prepared as detailed below.

Cyclic voltammetry measurement was performed on a Chen Hua electrochemical station (Shanghai) with a three-electrode-cell system: glassy carbon electrode as the working electrode, Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode (SCE) as the reference electrode, platinum sheet as the counter electrode, Bu<sub>4</sub>NBF<sub>4</sub> (0.1 M acetonitrile) with amine (2 mM) as supporting electrolyte with a scan rate of 100 mV s<sup>-1</sup> in the range of -2 to 3 V. For Mott-Schottky plots, 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH = 7.0) was used as the electrolyte with the frequency at 1.0 kHz.<sup>[1]</sup>

Flash chromatography was performed on silica gel. The products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR. All <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker 400 MHz spectrometer. NMR chemical shift values refer to CDCl<sub>3</sub> (δ H, 7.26 ppm; δ C, 77.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = penta, m = multiplet, br = broad), coupling constants (Hz) and integration.

### 1.2 Synthesis of aryl amines<sup>[2]</sup>



General procedure for the synthesis of substrates: A mixture of aryl bromide (10 mmol), amines (20 mmol), K<sub>2</sub>CO<sub>3</sub> (20 mmol), CuI (1.0 mmol) and L-proline (2.0 mmol) in 10 mL of DMSO was heated at 90 °C and for 24 h. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuum. The desired products were isolated by silica gel column chromatography (*n*-hexane/ethyl acetate mixtures).

## 2. Sectional results and figures for materials characterization

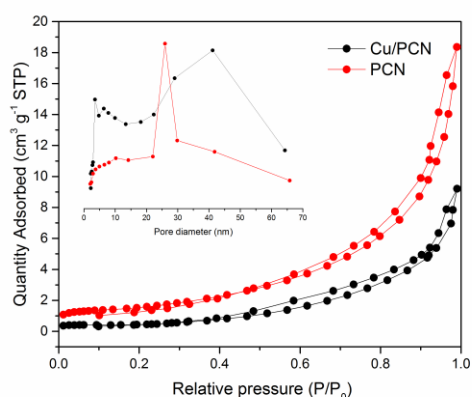


Figure S1. Nitrogen sorption and desorption isotherms and pore size distributions of PCN and Cu/PCN.

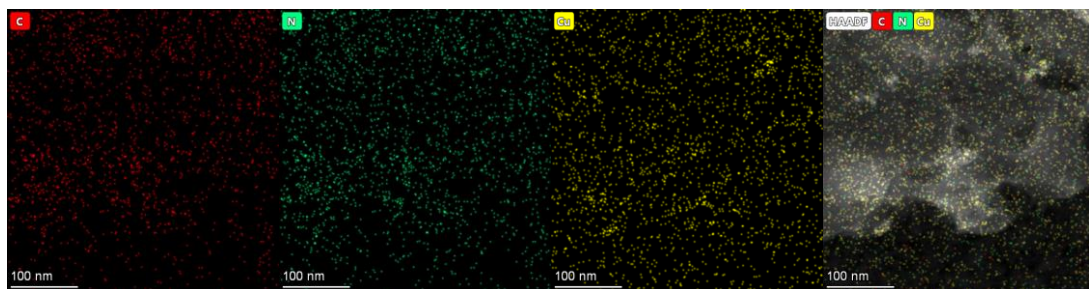


Figure S2. Mapping spectra of Cu/PCN.

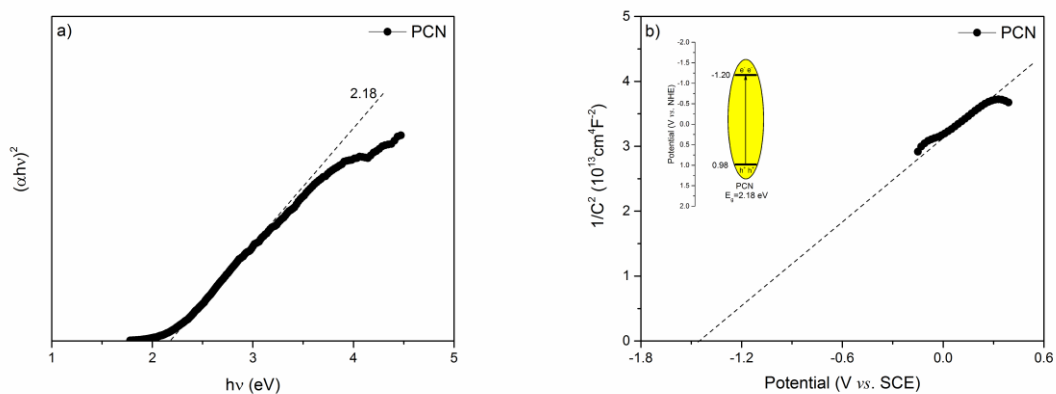


Figure S3. a) Tauc plots of PCN. b) Mott-Schottky plots measured under 1000 Hz of PCN, the inset shows the band structures of PCN.

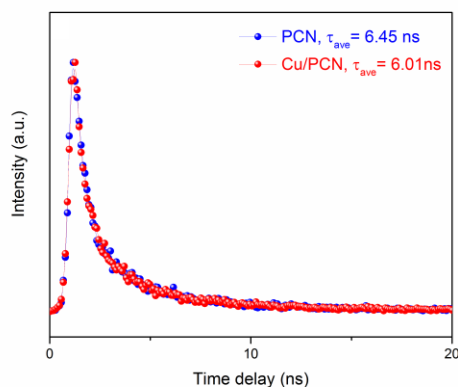


Figure S4. Time-resolved transient PL spectra of PCN and Cu/PCN.

Time-resolved PL decay curves (TRPL) were recorded to obtain the average PL lifetime. As shown in Fig. S4, the average PL lifetime decreased from 6.45 to 6.01 ns after PCN was loaded with Cu NPs. The shorter average PL lifetime of Cu/PCN than that of PCN is indicative of fast PL quenching, which might originate from the improved charge transfer.<sup>[3]</sup>

### 3. Optimization of other conditions

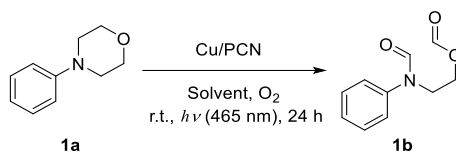
Table S1 Selective cleavage C-C single bond of *N*-phenylmorpholine using different catalysts.<sup>a</sup>

Entry	Catalyst (10 mol%)	Light	Yield (%) <sup>b</sup>
1	mpg-C <sub>3</sub> N <sub>4</sub> <sup>c</sup>	+	0
2	Cu/mpg-C <sub>3</sub> N <sub>4</sub> <sup>d</sup>	+	52
3	Eosin Y	+ <sup>e</sup>	0
4	Benzophenone	+ <sup>f</sup>	0

5	CuI	+	0
6	CuI	-	0
7	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	+	0
8	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	-	0
9	Cu <sub>2</sub> O	+	13
10	CuO	+	0
11	Cu <sub>2</sub> O/PCN <sup>g</sup>	+	35
12	Cu/BiVO <sub>4</sub> <sup>h</sup>	+	0
13	Cu/TiO <sub>2</sub> <sup>i</sup>	+	0

[a] Reaction conditions: **1a** (0.2 mmol), MeCN (2 mL), Catalyst (10 mol%), in the presence of 23 W blue LED light ( $\lambda = 465$  nm) at room temperature under 15 bar O<sub>2</sub> for 24 h. [b] Yield of isolated product. [c] 15 mg mpg-C<sub>3</sub>N<sub>4</sub>. [d] 15 mg Cu/mpg-C<sub>3</sub>N<sub>4</sub> (10 wt%). [e]  $\lambda = 525$  nm. [f]  $\lambda = 365$  nm. [g] 15 mg Cu<sub>2</sub>O/PCN (10 wt%). [h] 15 mg Cu/BiVO<sub>4</sub> (10 wt%). [i] 15 mg Cu/TiO<sub>2</sub> (10 wt%).

**Table S2** Selective cleavage C-C single bond of *N*-phenylmorpholine using different solvents and pressure of O<sub>2</sub>.<sup>a</sup>

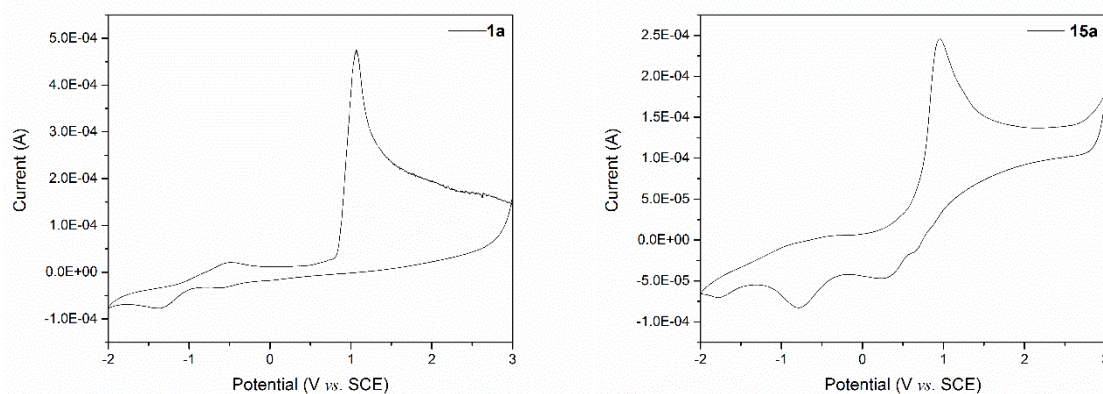


Entry	Solvents	Pressure of O <sub>2</sub> (bar)	Yield (%) <sup>b</sup>
1	H <sub>2</sub> O	15	0
2	alcohol	15	22
3	acetone	15	64
4	toluene	15	10
5	THF	15	50
6	1,4-dioxane	15	42
7	DCM	15	Trace
8	DMF	15	21
9	DMSO	15	Trace
10	acetonitrile	15	83
11	acetonitrile	10	36
12	acetonitrile	5	Trace
13	acetonitrile	1	0
14 <sup>c</sup>	acetonitrile	1	0

[a] Reaction conditions: **1a** (0.2 mmol), Solvent (2 mL), Cu/PCN (15 mg, 10 wt%), in the presence of 23 W blue LED light ( $\lambda = 465$  nm) at room temperature under O<sub>2</sub> for 24 h. [b] Yield of isolated product. [c] 50 °C.

## 4. CV measurement and unsuccessful examples

### 4.1 Cyclic voltammetry of **1a**, **15a** and **16a**



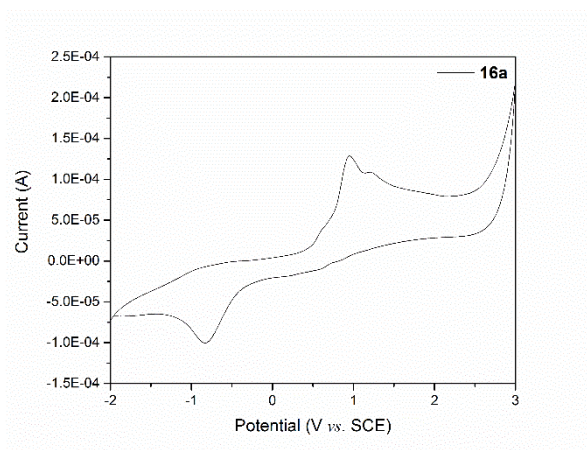
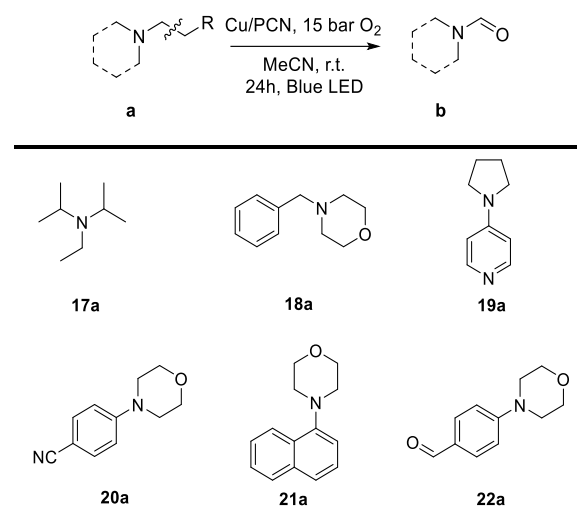


Figure S5. Cyclic voltammetry of **1a** *N*-phenylmorpholine, **15a** 1-phenylpyrrolidine and **16a** 1-phenylpiperidine.

## 4.2 Unsuccessful examples

Table S3 Unsuccessful examples (< 5% yields).<sup>a</sup>



[a] Reaction conditions: 0.2 mmol scale, standard conditions.

## 5. Leaching study and reusability study

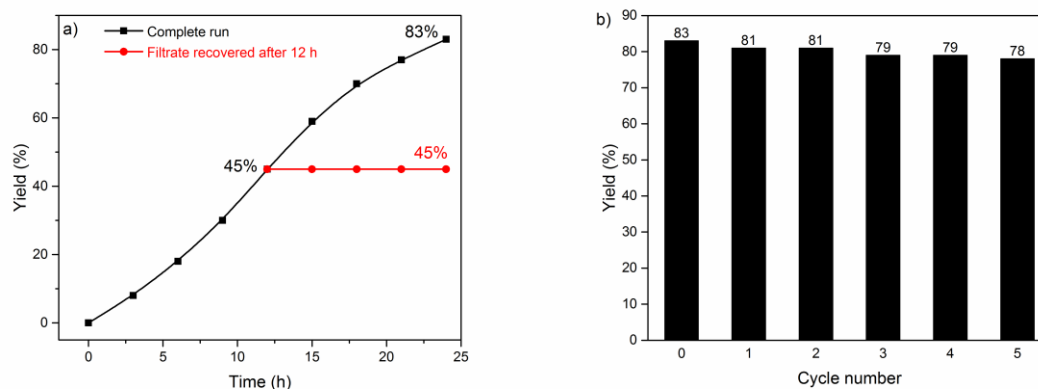


Figure S6. a) Leaching study. b) Reusability study of Cu/PCN catalyst in the reaction of **1a** to **1b**.

To examine the heterogeneity of the studied catalyst, hot filtration test was performed under optimal conditions with **1a** as substrate. The catalyst was separated from reaction mixture after a reaction time of 12 h by filtration. The filtrate was kept for another 12 h under the same reaction conditions. 45% of **1b** was formed after the first 12 h, and no further improvement was observed in the next 12 hours (Fig. S6a).

On the other hand, the recyclability of the photocatalyst was detected. After the fresh reaction, the heterogeneous photocatalyst Cu/PCN was recovered by filtration. After washed with NaBH<sub>4</sub>-ethanol solution and dried overnight, the catalyst was reused for a new experiment. It can be seen from Figure S6b that the Cu/PCN catalyst could be recovered and reused for at least 5 times without appreciable loss in yields for the reaction of **1a** to **1b**. However, if absence of the NaBH<sub>4</sub> solution washing step, a much lower yield around ~30% was observed.

We can rationalize that inactive Cu(I) species were generated under the oxygen atmosphere.<sup>[4]</sup> The powder XRD analysis (Fig. S7) of recovered catalyst was also confirmed the explanation. Thus, the catalyst Cu/PCN can be considered as a quasi-recyclable catalyst.<sup>[5]</sup>

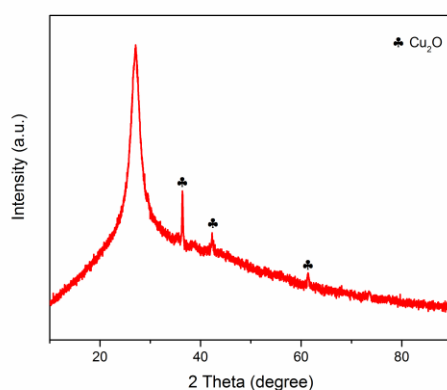


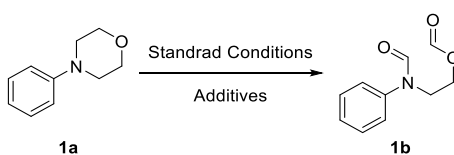
Figure S7. XRD pattern of recovered catalyst Cu/PCN.

## 6. Mechanism study

### 6.1. Control experiments

In order to better understand the catalytic mechanism of the catalyst, control experiments were carried out.<sup>[6]</sup>

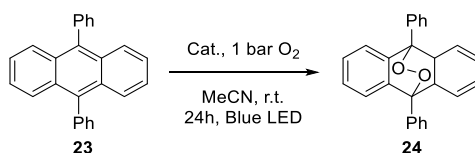
Table S4 Control experiments.<sup>a</sup>



Entry	Additives	Conversion (%)	Yield (%) <sup>b</sup>
1 <sup>c</sup>	TEMPO	8	Trace
2 <sup>d</sup>	BHT	10	Trace
3	<i>i</i> -PrOH as a hydroxyl radical scavenger	76	73
4 <sup>e</sup>	BQ as a superoxide scavenger	1	0
5	KI as a hole scavenger	2	0

[a] Reaction conditions: standard conditions, 2 e.q. additives. [b] Yield of isolated product. [c] TEMPO: 2,2,6,6-tetramethyl-1-piperidinyloxy. [d] BHT: 2,6-di-tert-butyl-4-methylphenol. [e] BQ: benzoquinone.

Table S5 Reaction of the photosensitized <sup>1</sup>O<sub>2</sub> with 9,10-diphenylanthracene.<sup>a</sup>



Catalyst	Yield (%) <sup>b</sup>
PCN	47
Cu/PCN	63
mpg-C <sub>3</sub> N <sub>4</sub>	35

[a] Reaction conditions: 9,10-diphenylanthracene 50  $\mu$ mol; 10 mg catalyst, MeCN (3 mL); O<sub>2</sub> 1 bar; Blue LED (23 W); r.t.; 24 h. [b] Yield of isolated product.

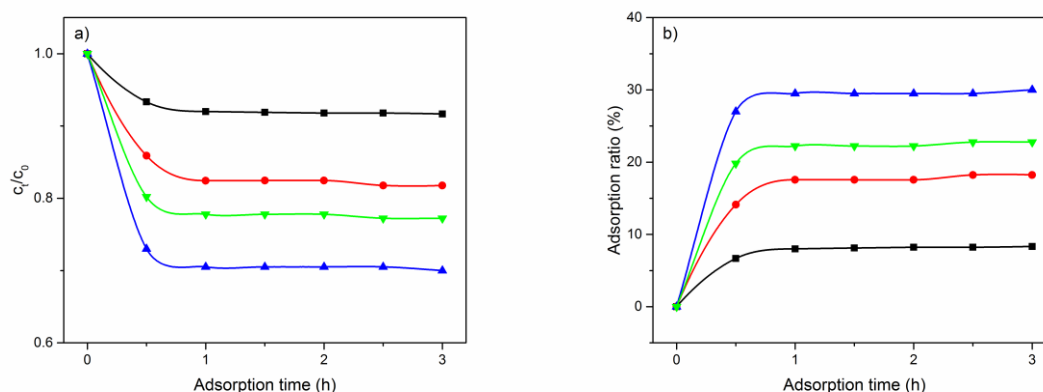
A glass tube was charged with 9,10-diphenylanthracene (**23**) (50  $\mu$ mol), MeCN (3 mL) and catalyst. The following amount of the catalyst was used: PCN 10 mg, Cu/PCN 10 mg, mpg-C<sub>3</sub>N<sub>4</sub> 10 mg. Magnetic stir bar was placed in the tube. The tube was closed with the rubber septum and a balloon filled with O<sub>2</sub> was connected to the reaction mixture head space via needle. The reaction mixture was vigorously stirred under blue LED irradiation for 24 h. Then it was separated by centrifugation, washed with MeCN (3  $\times$  2 mL). MeCN solutions were combined and concentrated in vacuum. Column chromatography of the product mixture on silica using CH<sub>2</sub>Cl<sub>2</sub> as eluent.<sup>[7]</sup>

9,10-Diphenyl-9,10-dihydro-9,10-epidioxyanthracene, **24**<sup>[7]</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.70 (d, *J* = 7.5 Hz, 4H), 7.61 (t, *J* = 7.5 Hz, 4H), 7.52 (t, *J* = 7.0 Hz, 2H), 7.19 (m, 8H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.3, 133.1, 128.4, 128.3, 127.7, 127.6, 123.6, 84.2.

## 6.2 Dark adsorption.

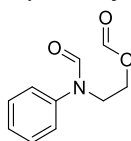


**Figure S8.** a) Relative concentration ( $c_i/c_0$ ) and b) adsorption ratio of **1a** solution vs. adsorption time. Initial **1a** concentration: green triangles 10 mg/L, blue triangles 10 mg/L, circles 20 mg/L, and squares 20 mg/L; blue triangles and circles: 1 g/L PCN as catalyst, green triangles and squares: 1 g/L Cu/PCN as catalyst.

Fig. S8 shows the adsorption ratio in the dark of the as-prepared catalysts, with magnetic stirring throughout the process. The adsorption processes for every system with different initial **1a** concentration and catalysts get its equilibrium after  $\sim$ 1 h. Under the same initial concentration of **1a**, the PCN sample exhibited the higher adsorption ratio than that of Cu/PCN (squares vs. circles or green triangles vs. blue triangles). It is also found that the adsorption ratio is related to the initial **1a** solution concentration, and the adsorption ratio increases with the initial concentration of **1a** decreases.<sup>[8]</sup> Although Cu/PCN exhibits lower adsorption capacity and smaller specific surface area than that of PCN, the enhanced photogenerated charge separation and transport efficiency may be responsible for the higher reaction efficiency of Cu/PCN.

## 7. NMR spectra

2-(*N*-Phenylformamido)ethyl formate, **1b**<sup>[9]</sup>



**1b**

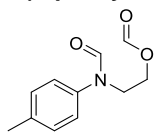
Light yellow oil (32 mg, 83%)



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.40 (s, 1H), 7.97 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 4.34 (t, *J* = 5.6 Hz, 2H), 4.10 (t, *J* = 5.6 Hz, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.8, 160.7, 140.6, 129.9, 127.4, 124.5, 60.7, 44.2.

**2-(*N*-*p*-Tolylformamido)ethyl formate, 2b<sup>[9]</sup>**



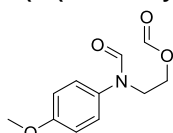
**2b**

Light yellow oil (36 mg, 88%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.34 (s, 1H), 7.97 (s, 1H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.31 (t, *J* = 5.6 Hz, 2H), 4.07 (t, *J* = 5.6 Hz, 2H), 2.37 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.8, 160.6, 138.0, 137.4, 130.4, 124.6, 60.6, 44.2, 21.0.

**2-(*N*-(4-Methoxyphenyl)formamido)ethyl formate, 3b<sup>[9]</sup>**



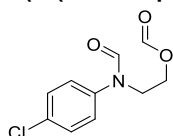
**3b**

Yellow oil (38 mg, 86%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.29 (s, 1H), 7.99 (s, 1H), 7.17-7.08 (m, 2H), 6.98-6.91 (m, 2H), 4.31 (t, *J* = 5.6 Hz, 2H), 4.04 (t, *J* = 5.6 Hz, 2H), 3.83 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.9, 160.7, 158.9, 133.3, 127.9, 126.7, 114.9, 60.6, 55.6, 44.5.

**2-(*N*-(4-Chlorophenyl)formamido)ethyl formate, 4b<sup>[9]</sup>**



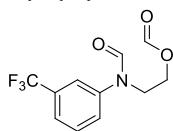
**4b**

Yellow oil (34 mg, 75%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.37 (s, 1H), 7.97 (s, 1H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 4.34 (t, *J* = 5.5 Hz, 2H), 4.08 (t, *J* = 5.5 Hz, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.4, 160.5, 139.3, 133.2, 130.0, 125.8, 60.6, 44.4.

**2-(*N*-(3-(Trifluoromethyl)phenyl)formamido)ethyl formate, 5b**



**5b**

Light yellow oil (38 mg, 72%)

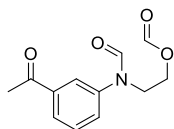
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.45 (s, 1H), 7.98 (s, 1H), 7.59 (t, *J* = 6.8 Hz, 2H), 7.53 (s, 1H), 7.47-7.34 (m, 1H), 4.38 (t, *J* = 5.5 Hz, 2H), 4.15 (t, *J* = 5.5 Hz, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.3, 160.5, 141.6, 132.4 (q, *J* = 32.9 Hz), 130.6, 130.1, 127.5, 124.9, 124.0 (q, *J* = 3.7 Hz), 122.2, 121.0 (q, *J* = 3.8 Hz), 60.7, 44.5.

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -62.80.

HRMS (ESI) ([*M* + *H*]<sup>+</sup>) Calcd. for C<sub>11</sub>H<sub>11</sub>F<sub>3</sub>NO<sub>3</sub>: 262.0686, found: 262.0687.

**2-(*N*-(3-Acetylphenyl)formamido)ethyl formate, 6b<sup>[9]</sup>**



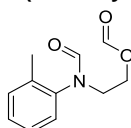
**6b**

Light yellow oil (32 mg, 68%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.44 (s, 1H), 7.97 (s, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 1.7 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.42 (dd, *J* = 1.4, 7.9 Hz, 1H), 4.36 (t, *J* = 5.5 Hz, 2H), 4.14 (t, *J* = 5.5 Hz, 2H), 2.63 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 196.9, 162.4, 160.5, 141.3, 138.7, 130.2, 128.6, 127.2, 123.6, 60.7, 44.3, 26.7.

**2-(*N*-*o*-Tolylformamido)ethyl formate, 7b<sup>[9]</sup>**



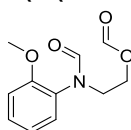
**7b**

Light yellow oil (22 mg, 53%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.15 (s, 1H), 7.98 (s, 1H), 7.40-7.22 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 1H), 4.31 (t, *J* = 5.6 Hz, 2H), 3.98 (t, *J* = 5.3 Hz, 2H), 2.27 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.4, 160.6, 138.9, 135.9, 131.7, 128.8, 127.9, 127.3, 60.7, 44.2, 17.8.

**2-(*N*-(2-Methoxyphenyl)formamido)ethyl formate, 8b<sup>[9]</sup>**



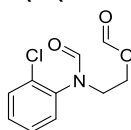
**8b**

Yellow oil (30 mg, 67%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H), 7.95 (s, 1H), 7.40-7.30 (m, 1H), 7.17 (dd, *J* = 1.5, 7.6 Hz, 1H), 7.05-6.92 (m, 2H), 4.26 (t, *J* = 5.7 Hz, 2H), 4.01 (t, *J* = 5.7 Hz, 2H), 3.84 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.6, 160.7, 155.3, 130.0, 129.6, 129.0, 128.7, 120.9, 112.2, 112.0, 60.8, 55.6, 43.6.

**2-(*N*-(2-Chlorophenyl)formamido)ethyl formate, 9b<sup>[9]</sup>**



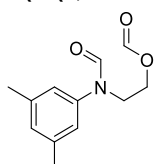
**9b**

Light yellow oil (23 mg, 51%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.08 (s, 1H), 7.89 (s, 1H), 7.50-7.39 (m, 1H), 7.33-7.16 (m, 3H), 4.23 (t, *J* = 5.5 Hz, 2H), 3.97 (t, *J* = 5.5 Hz, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.1, 160.6, 137.7, 132.9, 130.8, 130.3, 130.0, 128.1, 60.8, 44.2.

**2-(*N*-(3,5-Dimethylphenyl)formamido)ethyl formate, 10b<sup>[9]</sup>**



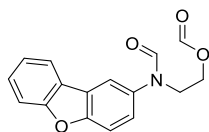
**10b**

Light yellow oil (32 mg, 73%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.38 (d, *J* = 12.1 Hz, 1H), 7.99 (s, 1H), 6.98 (d, *J* = 15.1 Hz, 1H), 6.88-6.76 (m, 2H), 4.32 (t, *J* = 5.7 Hz, 2H), 4.07 (t, *J* = 5.7 Hz, 2H), 3.95 (t, *J* = 5.3 Hz, 1H), 3.81 (t, *J* = 5.2 Hz, 1H), 2.34 (s, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.8, 160.7, 140.4, 139.7, 129.1, 122.3, 60.6, 44.0, 21.3.

**2-(*N*-(Dibenzo[*b,d*]furan-2-yl)formamido)ethyl formate, 11b<sup>[9]</sup>**



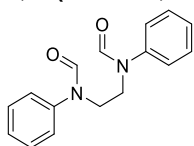
**11b**

Light yellow oil (52 mg, 92%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.43 (s, 1H), 7.99 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.51 (dd, *J* = 4.1, 11.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.28 (dd, *J* = 2.2, 8.7 Hz, 1H), 4.38 (t, *J* = 5.5 Hz, 2H), 4.17 (t, *J* = 5.6 Hz, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.1, 160.7, 157.0, 154.9, 135.8, 128.2, 125.5, 124.5, 123.4, 123.2, 120.9, 117.8, 112.7, 112.0, 60.7, 45.0.

***N,N'*-(Ethane-1,2-diyl)bis(*N*-phenylformamide), 12b<sup>[9]</sup>**



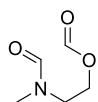
**12b**

Yellow solid (21 mg, 40%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.31 (s, 2H), 7.37 (t, *J* = 7.7 Hz, 4H), 7.29 (d, *J* = 7.3 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 4H), 4.05 (s, 4H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.7, 140.7, 129.7, 126.9, 125.3, 123.6, 43.3.

**2-(*N*-Methylformamido)ethyl formate, 13b<sup>[9]</sup>**



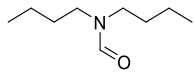
**13b**

Colorless liquid (23 mg, 87%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.07 (s, 2H), 4.45-3.71 (m, 2H), 3.57 (ddd, *J* = 26.8, 34.3, 63.3 Hz, 2H), 3.00 (d, *J* = 50.5 Hz, 3H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 163.3, 163.0, 160.7, 160.5, 60.9, 59.9, 48.3, 43.3, 35.6, 29.9.

***N,N*-Dibutylformamide, 14b<sup>[9]</sup>**



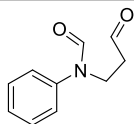
**14b**

Colorless liquid (23 mg, 73%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.04 (s, 1H), 3.37-3.15 (m, 4H), 1.60-1.46 (m, 4H), 1.32 (dt, *J* = 7.2, 14.1 Hz, 4H), 0.94 (td, *J* = 2.8, 7.3 Hz, 6H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 162.8, 47.2, 41.9, 30.8, 29.4, 20.2, 19.7, 13.8, 13.7.

***N*-(3-Oxopropyl)-*N*-phenylformamide, 15b**



**15b**

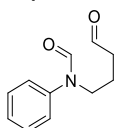
Light yellow oil (30 mg, 85%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.75 (s, 1H), 8.35 (s, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 4.15 (t, *J* = 7.0 Hz, 2H), 2.76 (td, *J* = 1.1, 7.0 Hz, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 199.9, 162.5, 140.4, 129.9, 127.4, 124.5, 42.1, 39.4.

HRMS (ESI) ([M + H]<sup>+</sup>) Calcd. for C<sub>10</sub>H<sub>12</sub>NO<sub>2</sub>: 178.0863, found: 178.0859.

### ***N*-(4-Oxobutyl)-*N*-phenylformamide, 16b**



**16b**

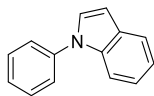
Light yellow oil (30 mg, 78%)

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.75 (s, 1H), 8.39 (s, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 3.87 (t, *J* = 7.3 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 1.92-1.84 (m, 2H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 201.2, 162.6, 140.6, 129.9, 127.1, 124.1, 44.1, 41.0, 20.2.

HRMS (ESI) ([M + H]<sup>+</sup>) Calcd. for C<sub>11</sub>H<sub>14</sub>NO<sub>2</sub>: 192.1019, found: 192.1015.

### **1-Phenyl-1*H*-indole, 1d<sup>[10]</sup>**



**1d**

Light yellow solid (37 mg, 96%)

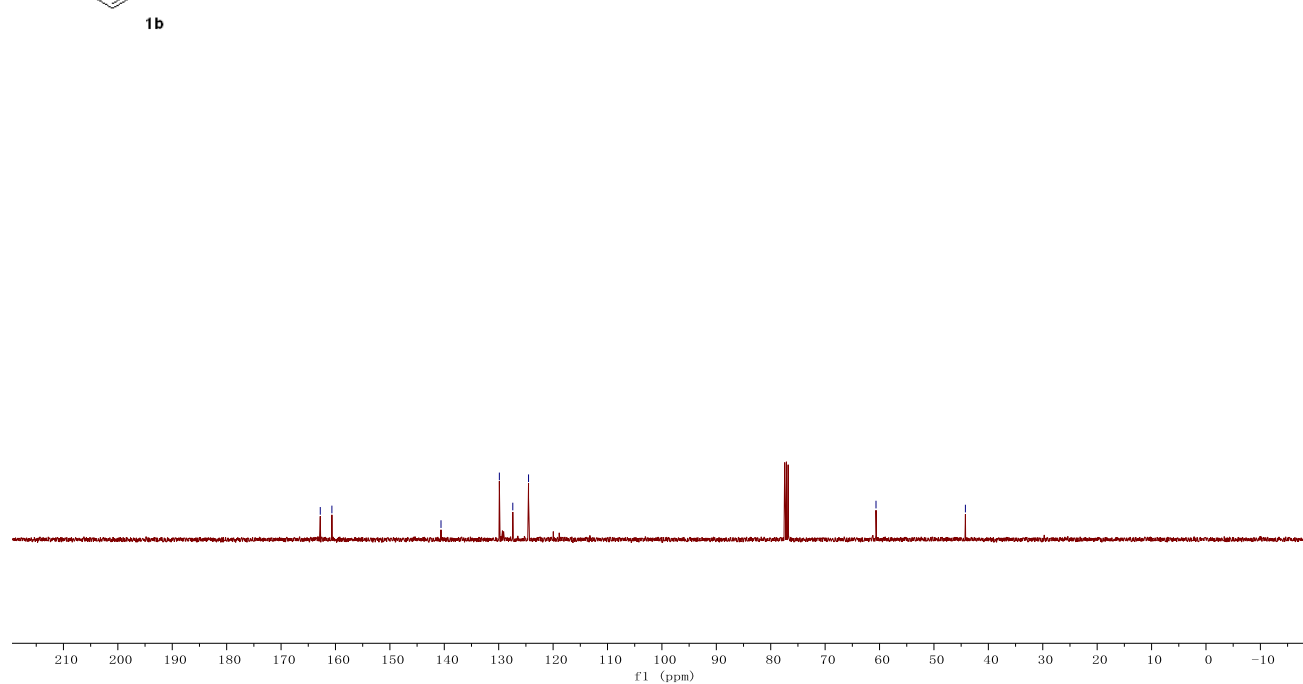
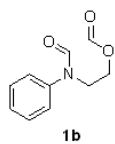
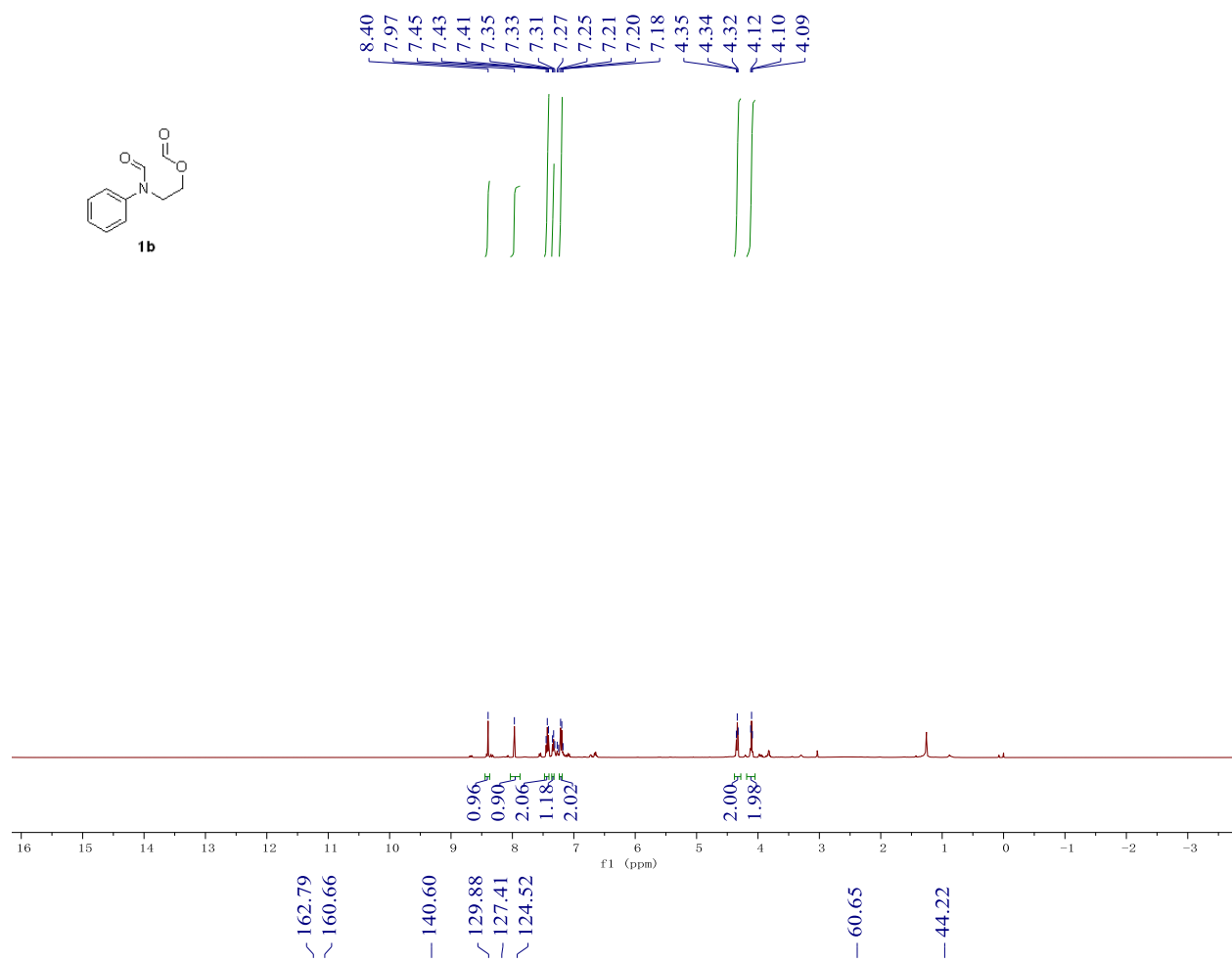
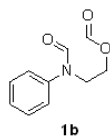
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.71-7.62 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.41-7.34 (m, 4H), 7.27-7.20 (m, 2H), 7.15 (tt, *J* = 3.6, 13.2 Hz, 2H), 6.62 (d, *J* = 3.2 Hz, 1H).

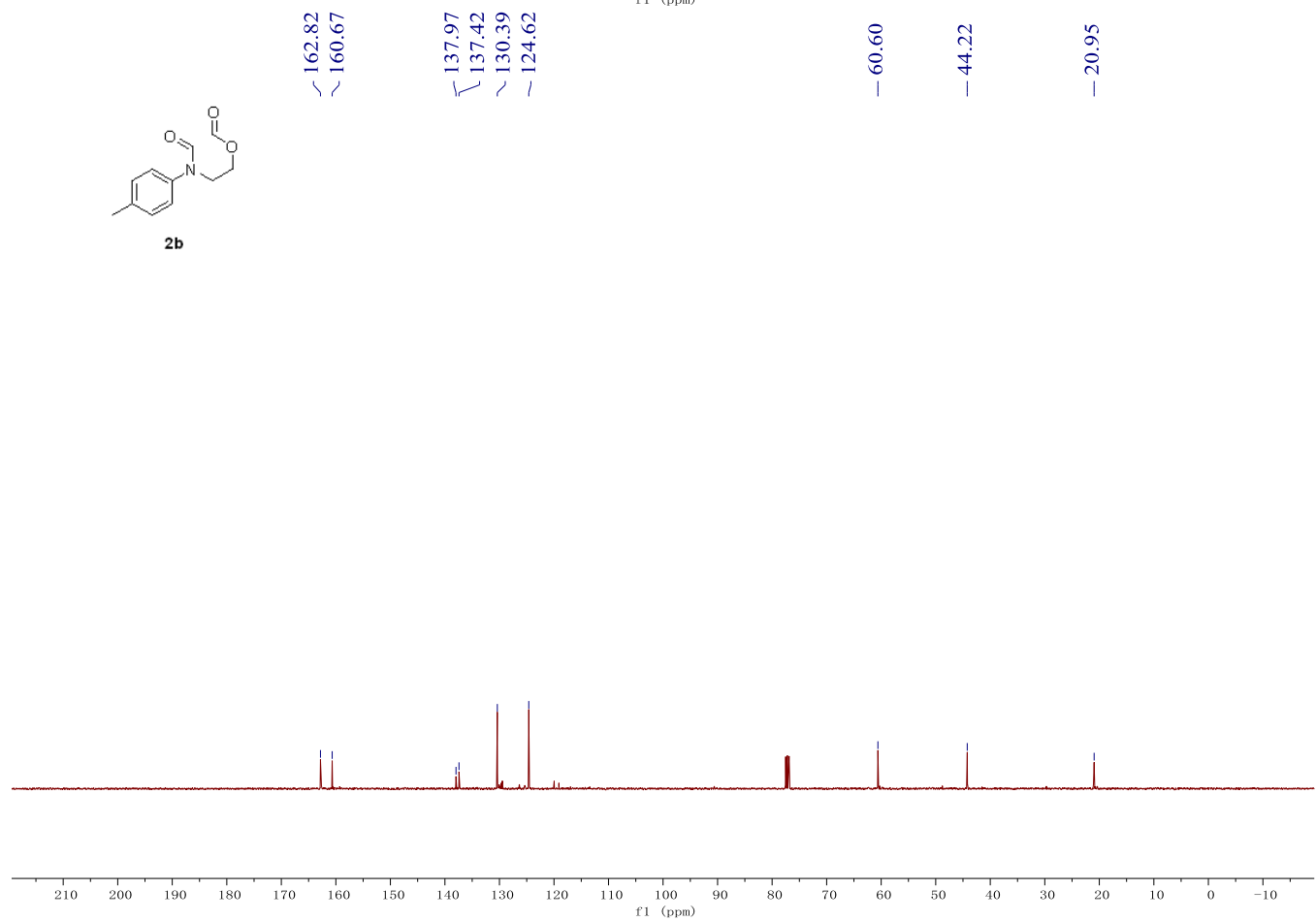
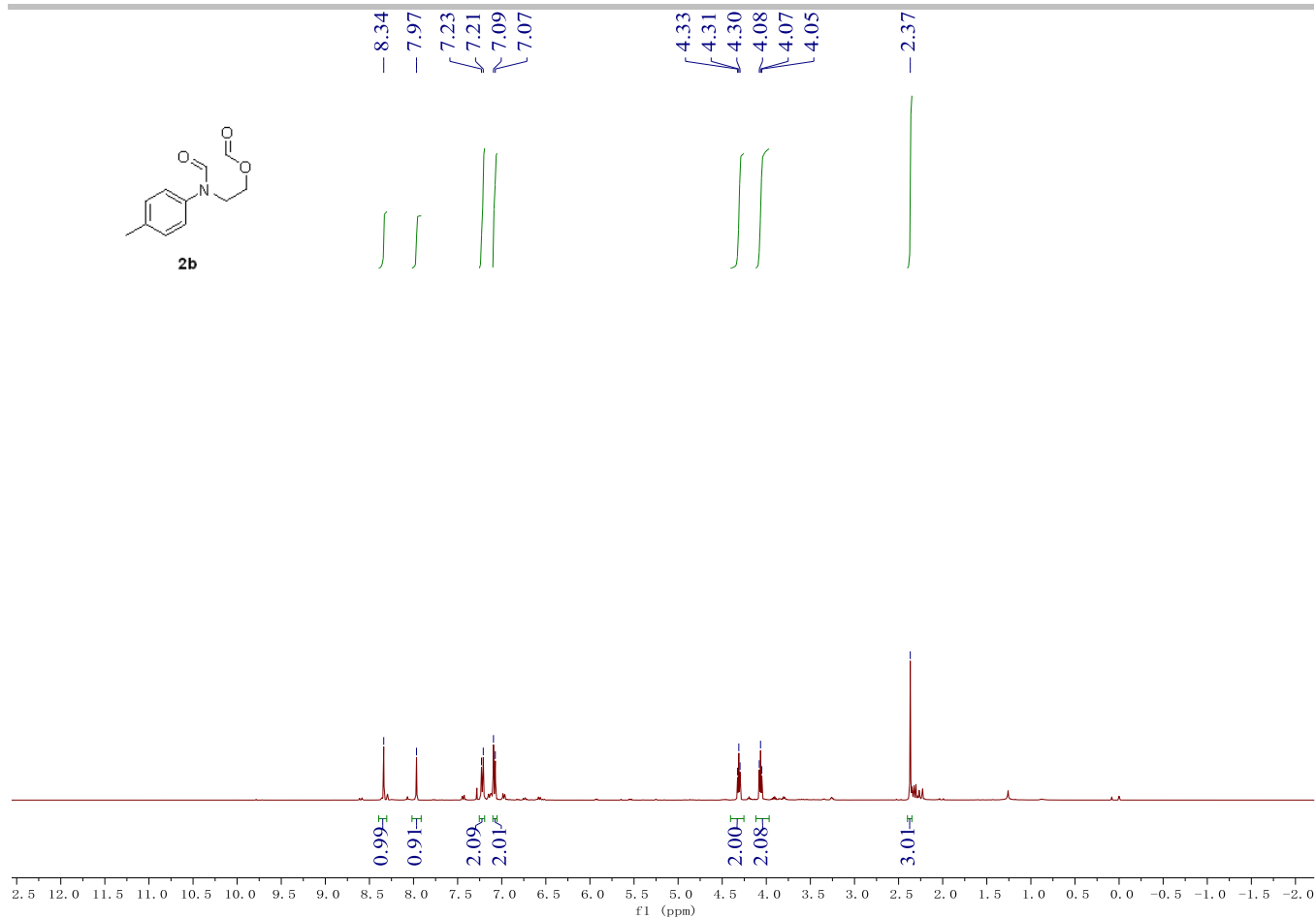
**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 139.9, 135.9, 129.6, 129.4, 128.0, 126.4, 124.4, 122.5, 121.2, 120.5, 110.6, 103.7.

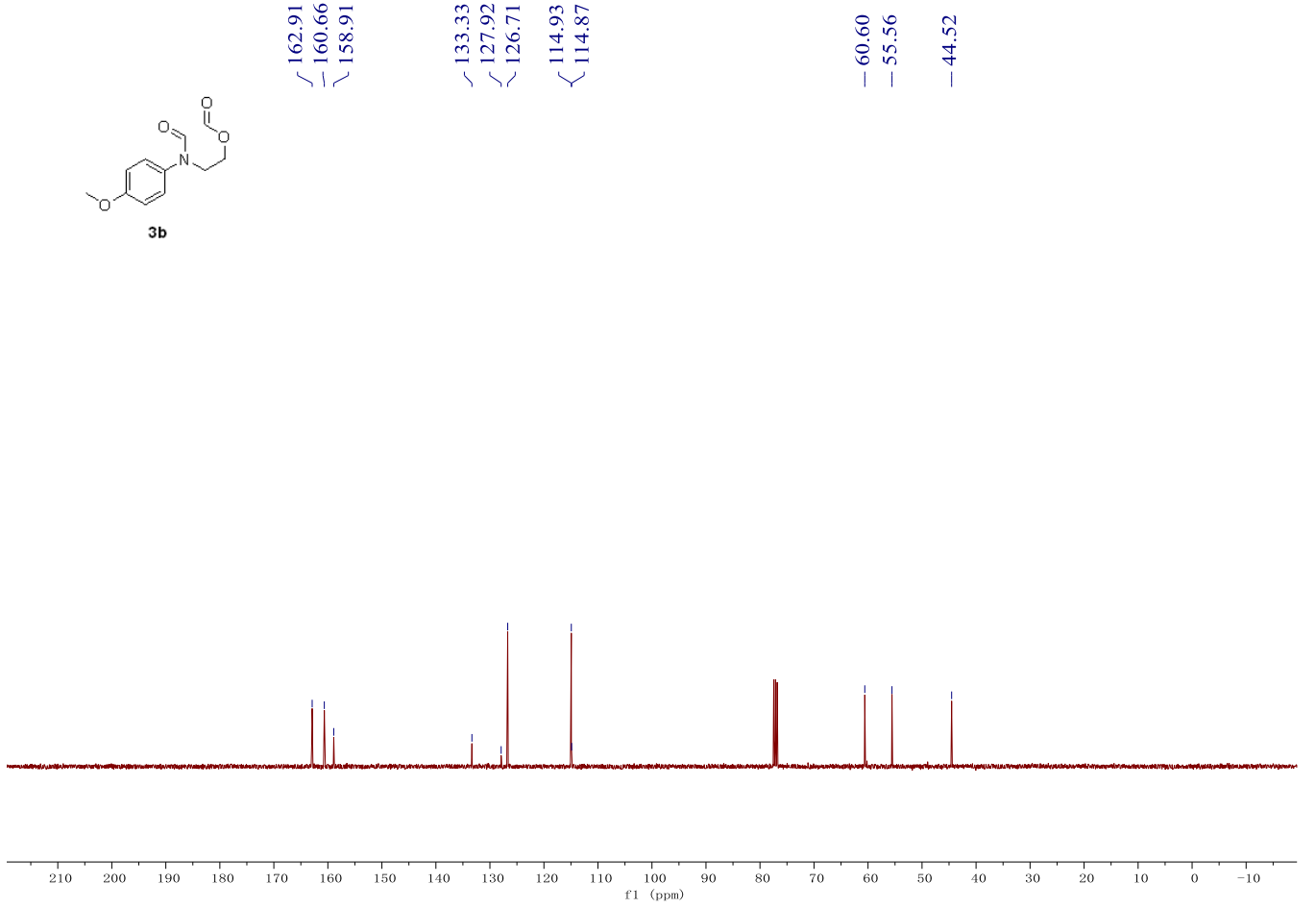
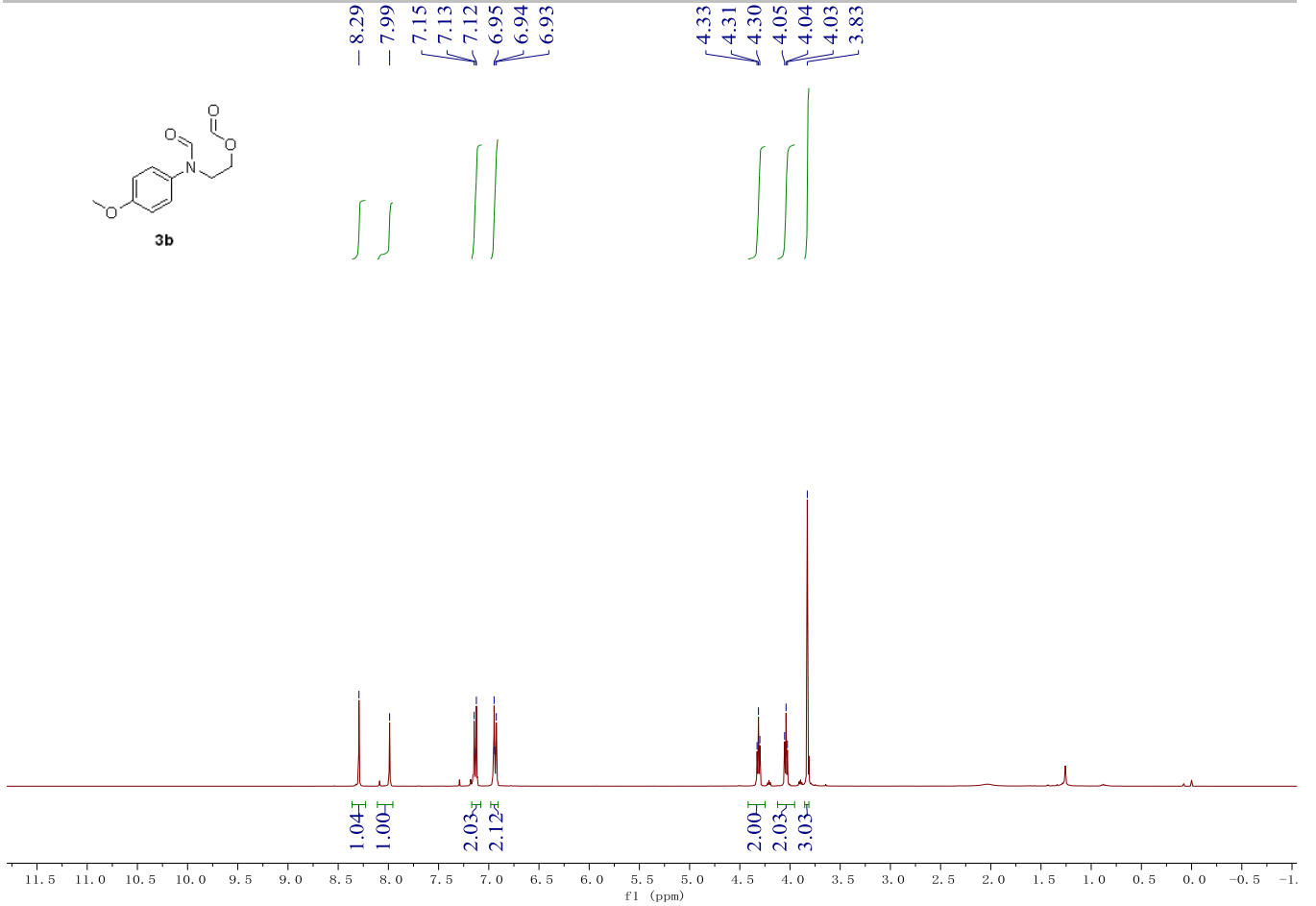
## **8. References**

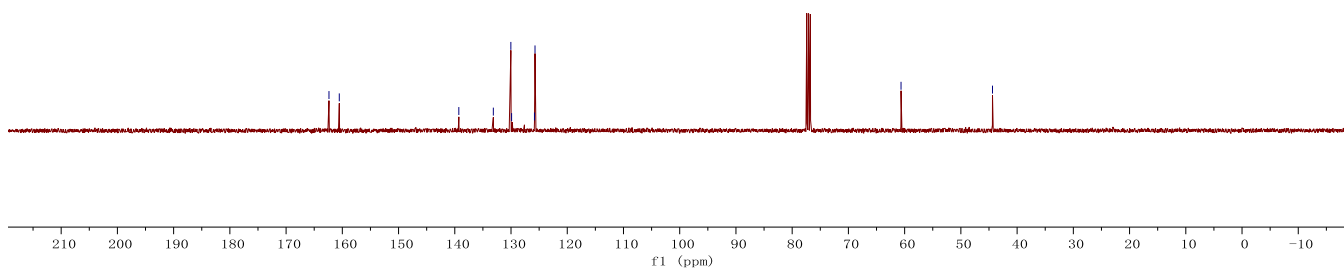
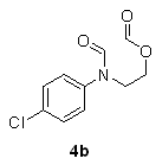
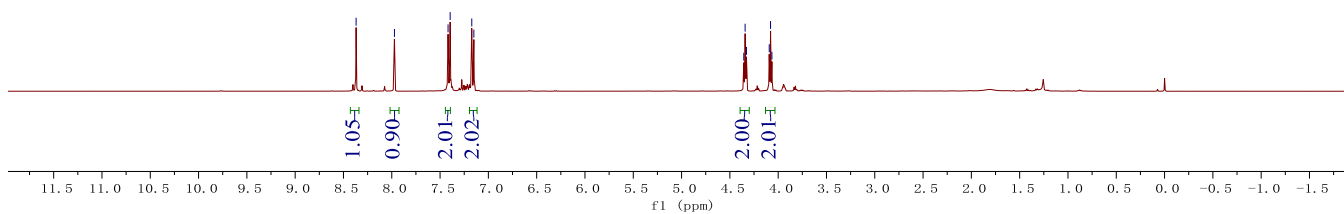
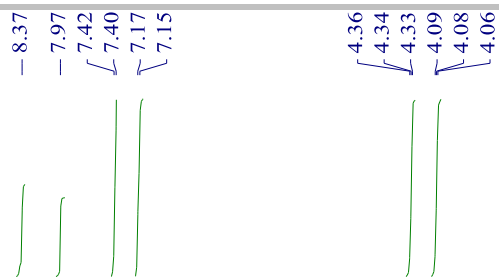
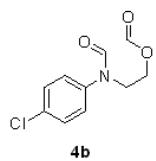
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## 9. Copies of spectra

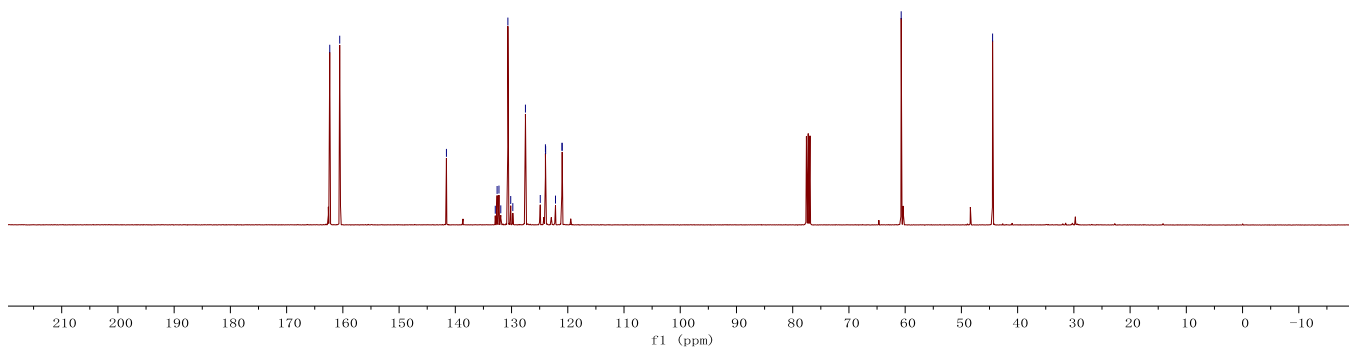
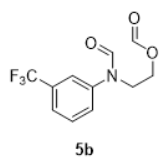
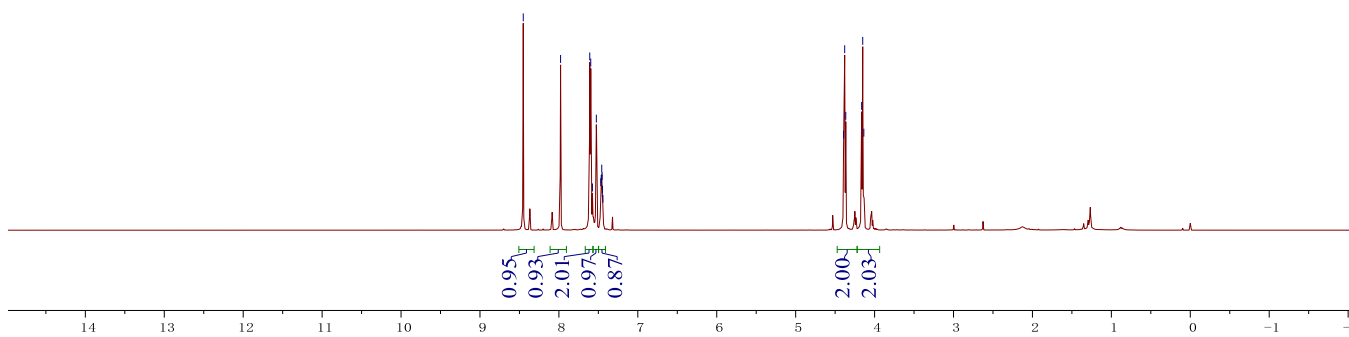
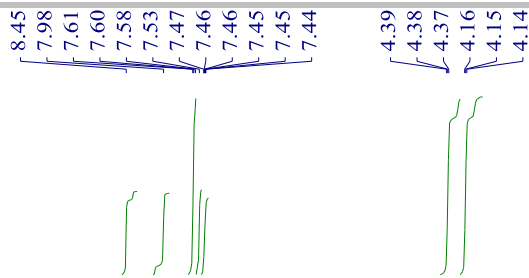
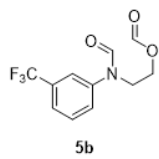


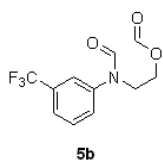




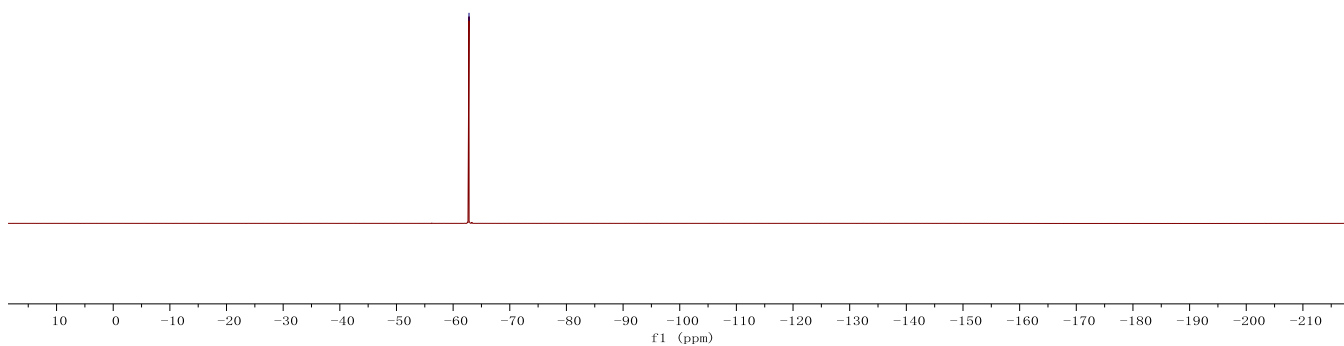


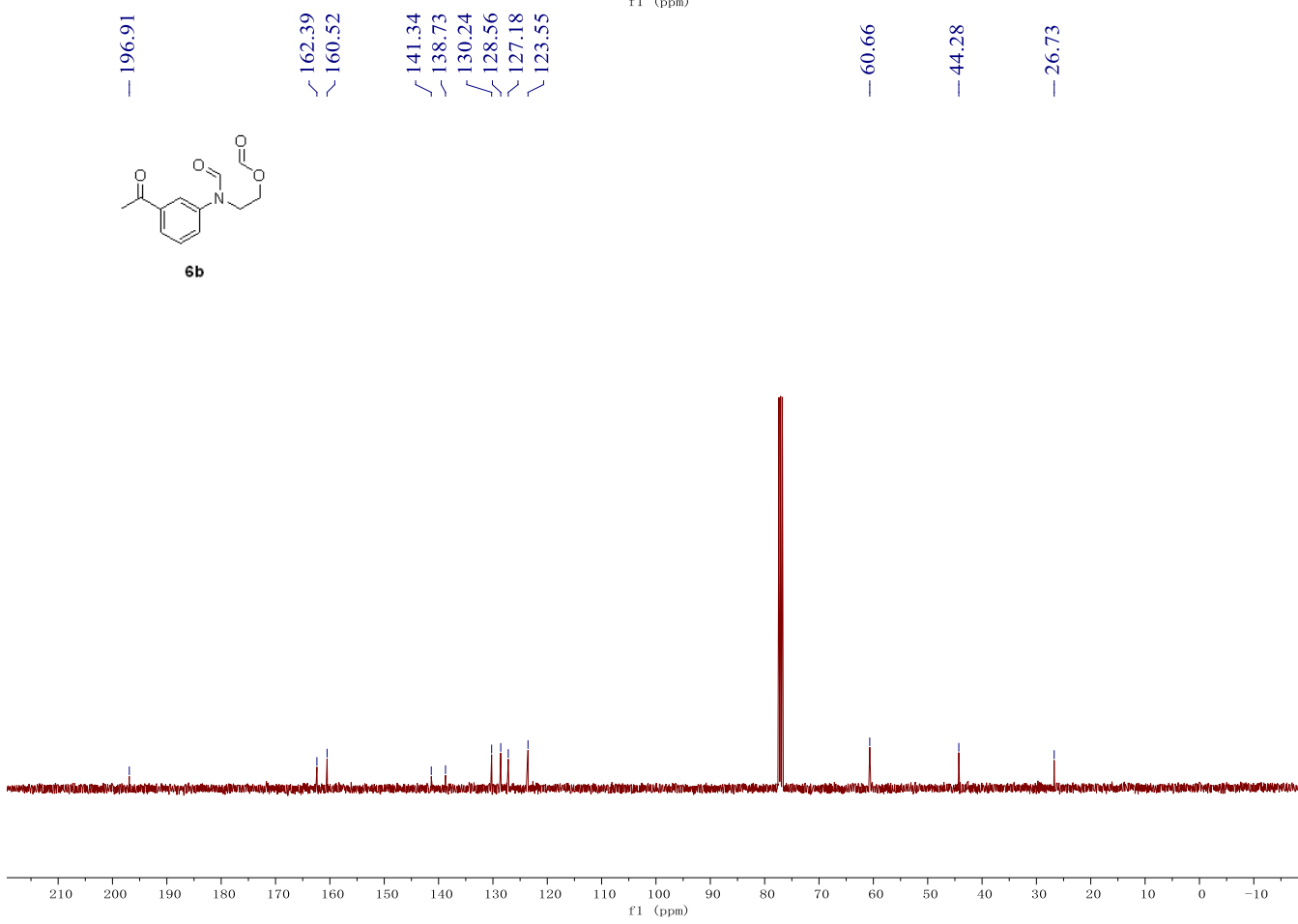
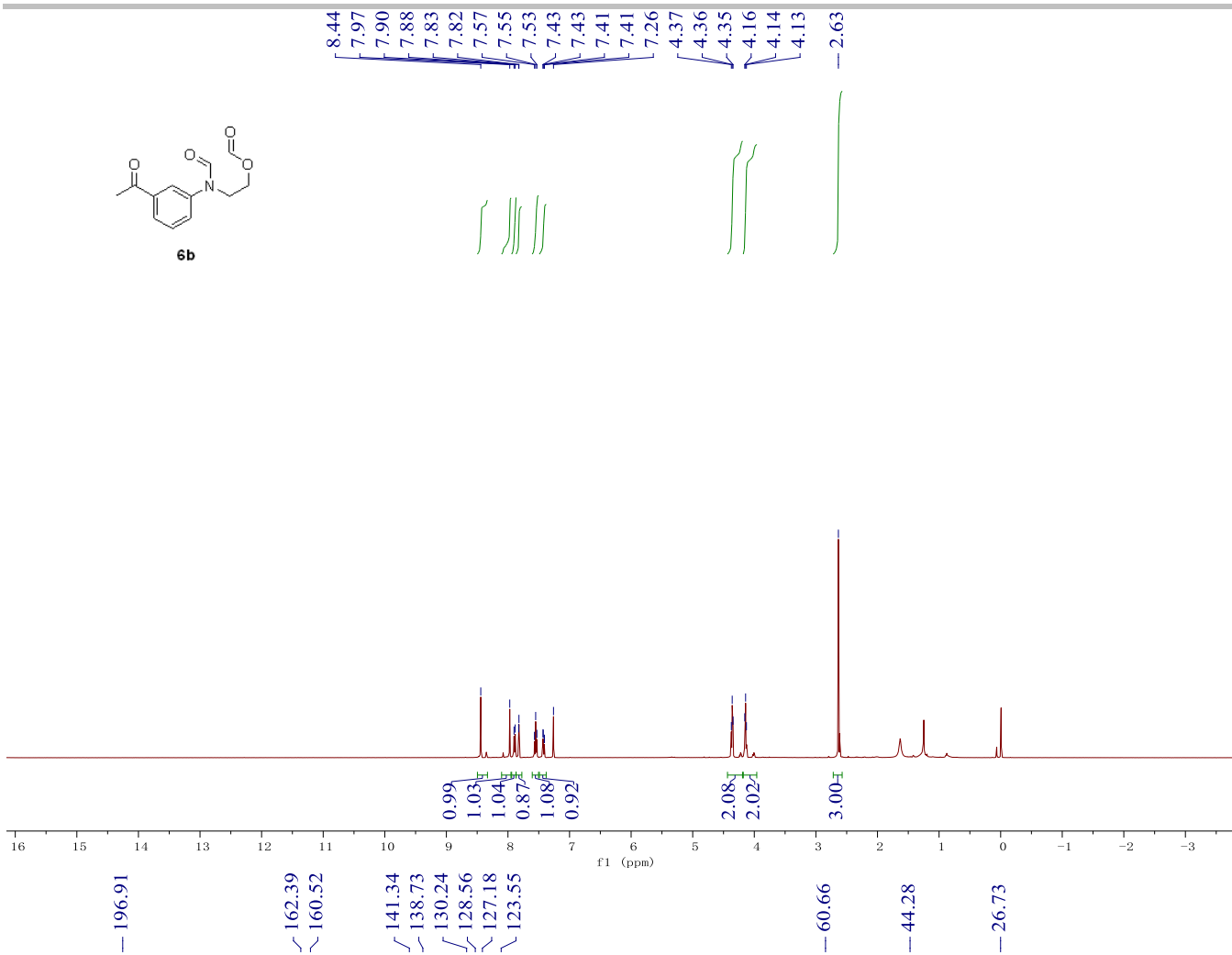


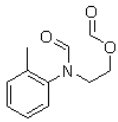




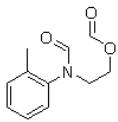
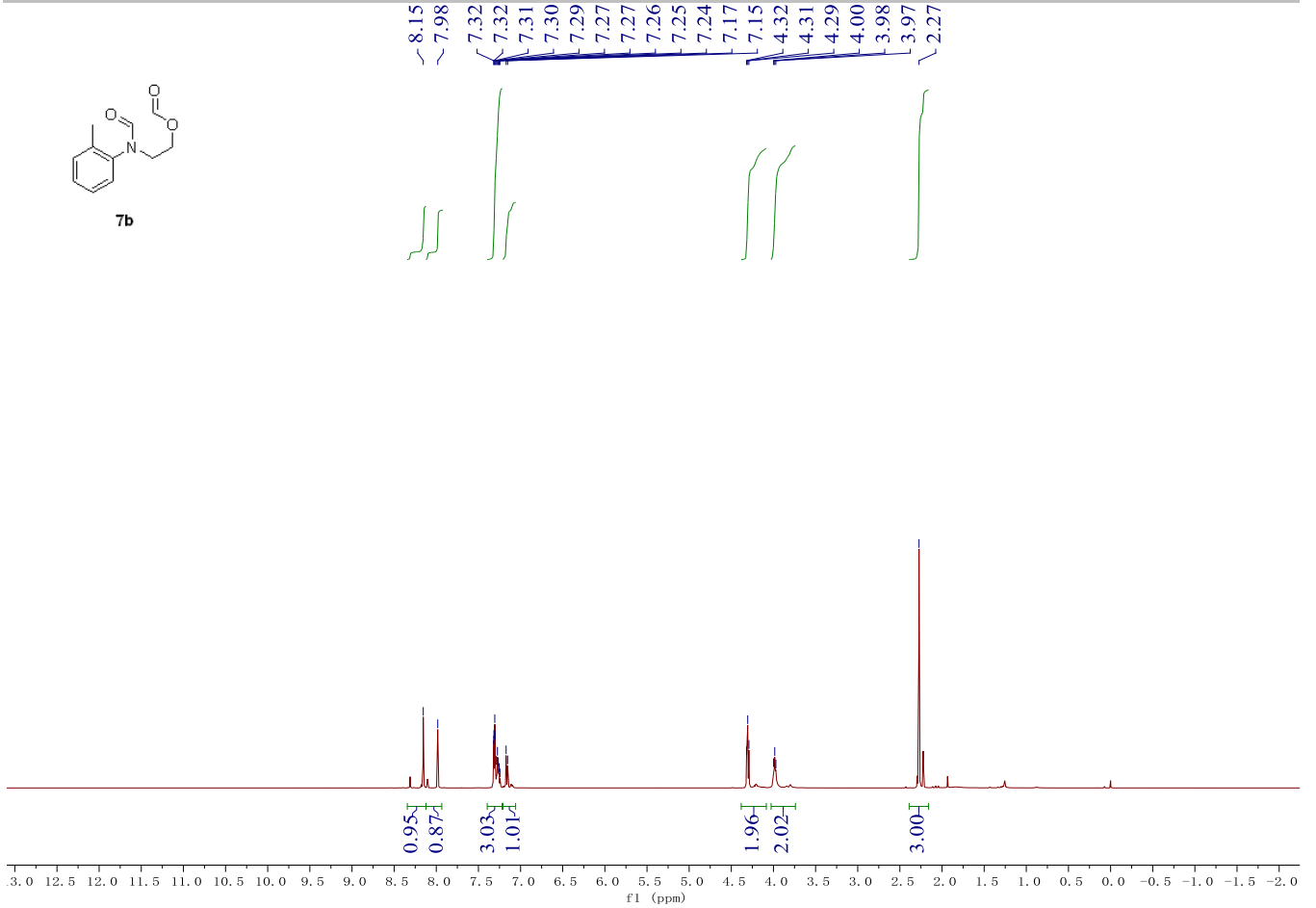
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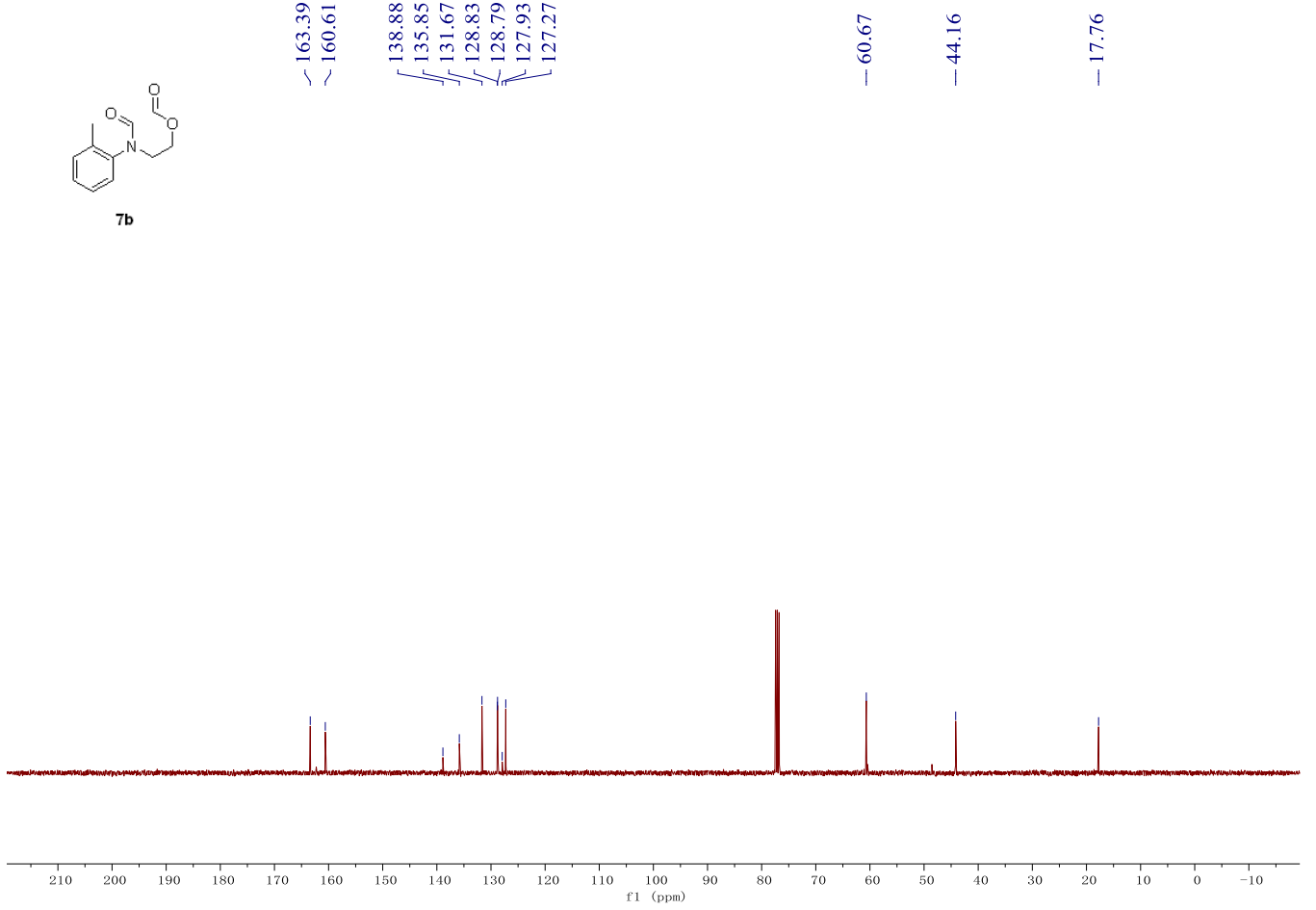


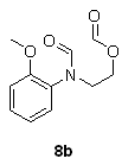


7b



7b

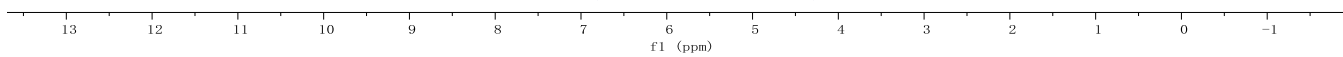




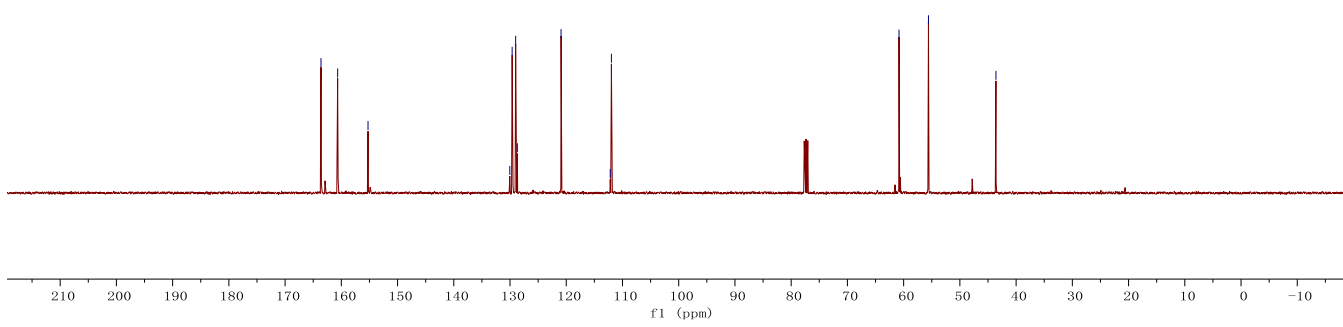
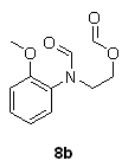
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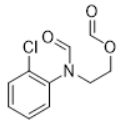


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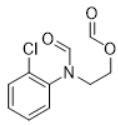
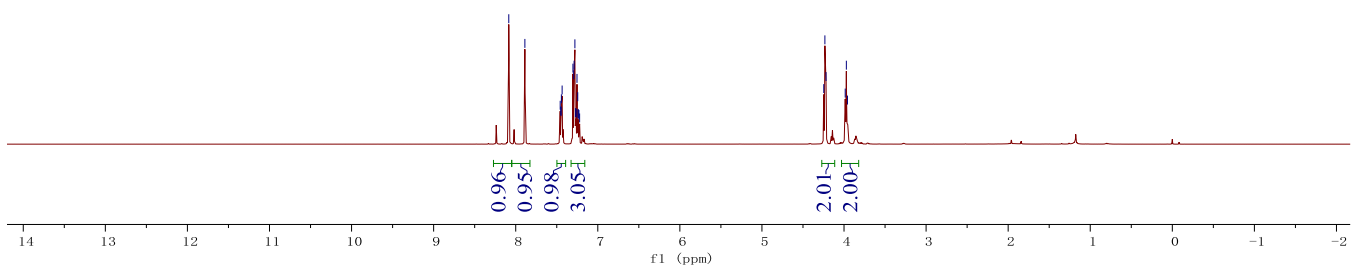
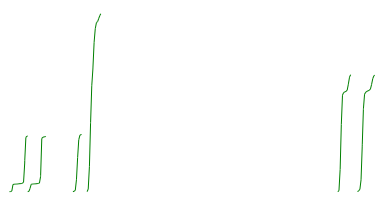
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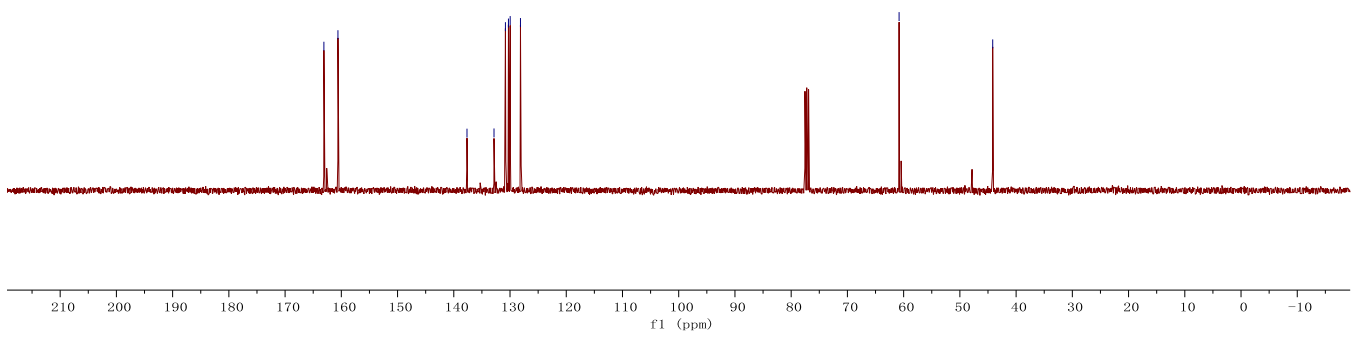
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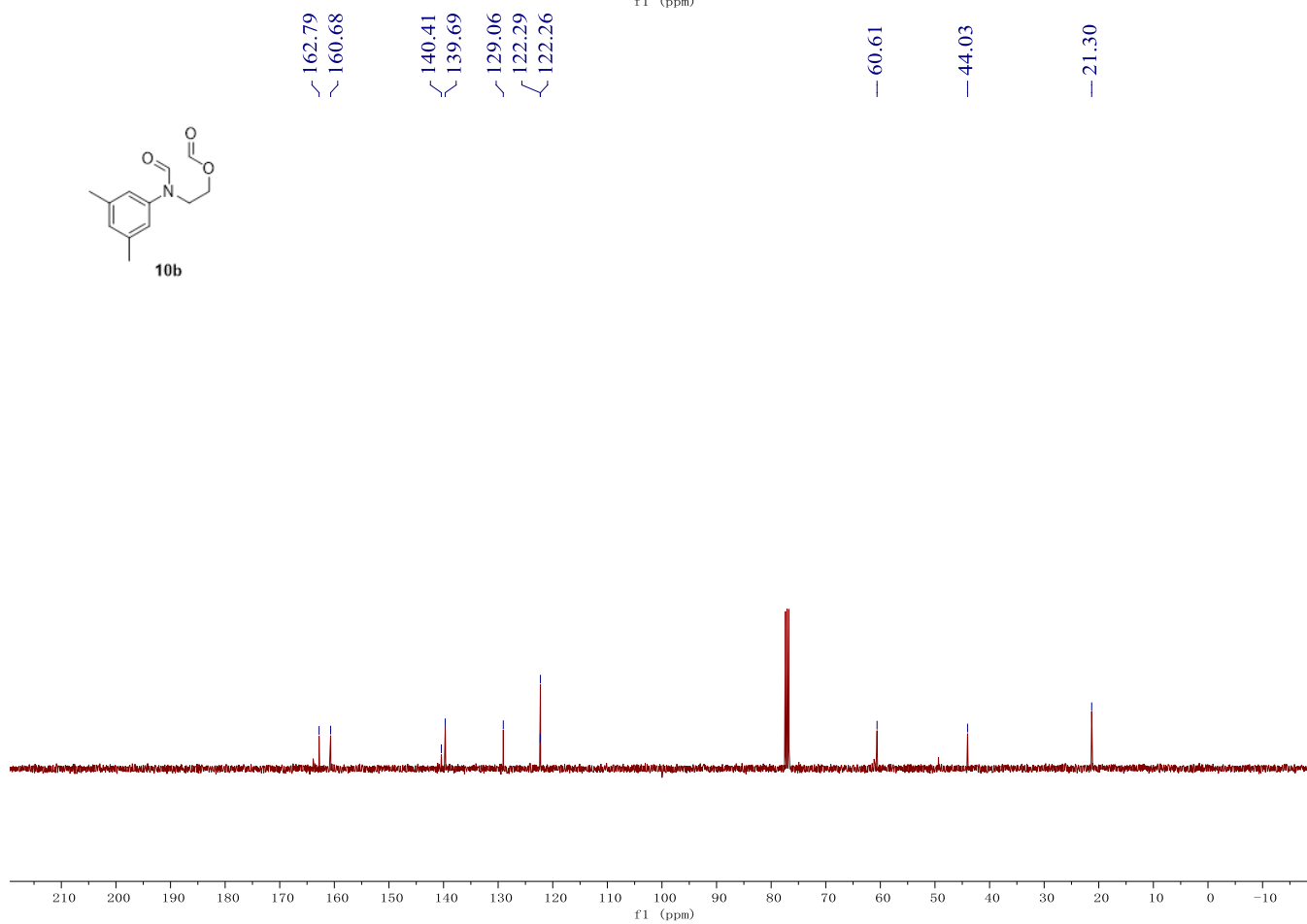
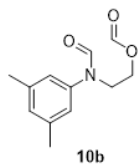
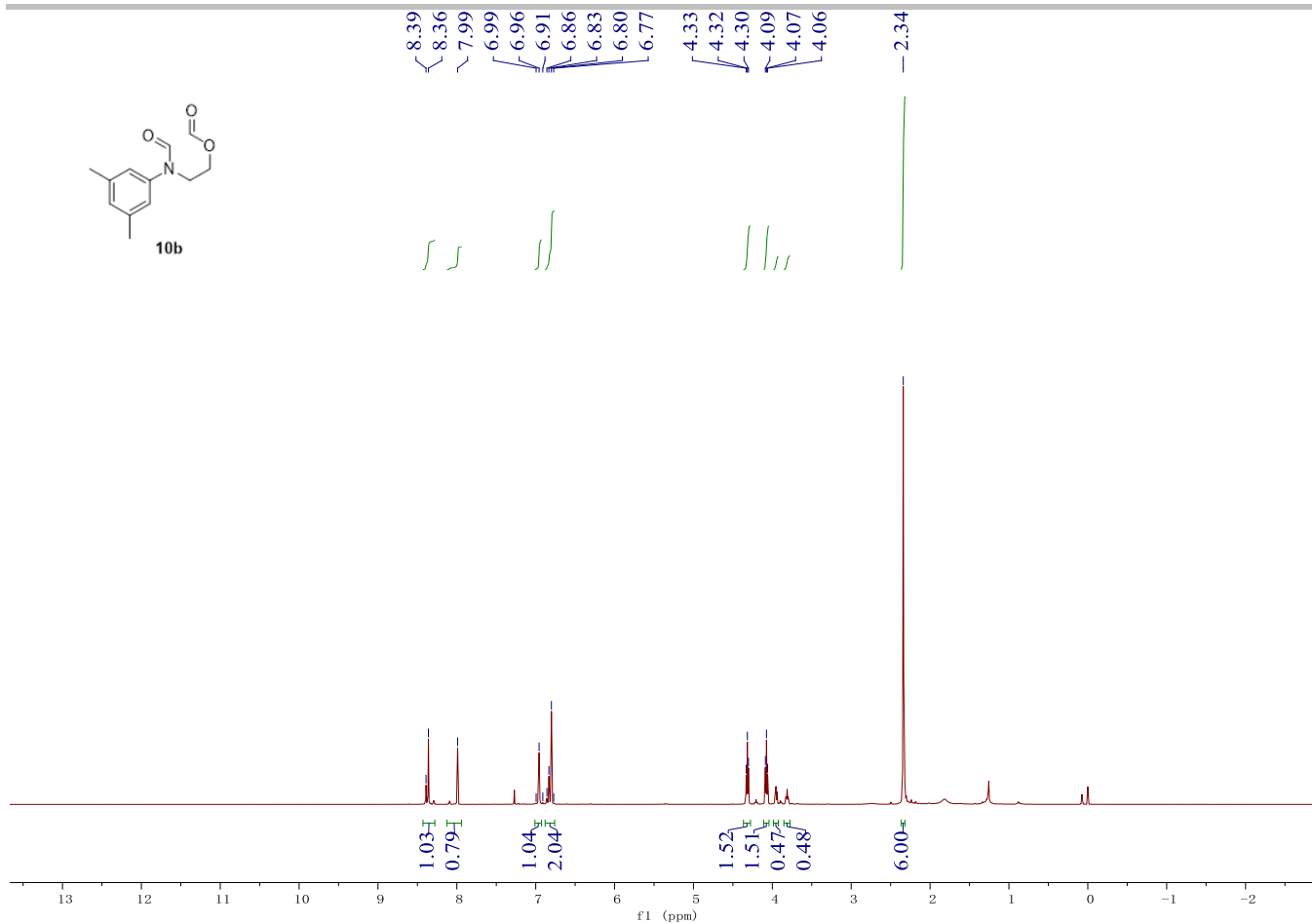
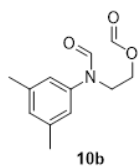
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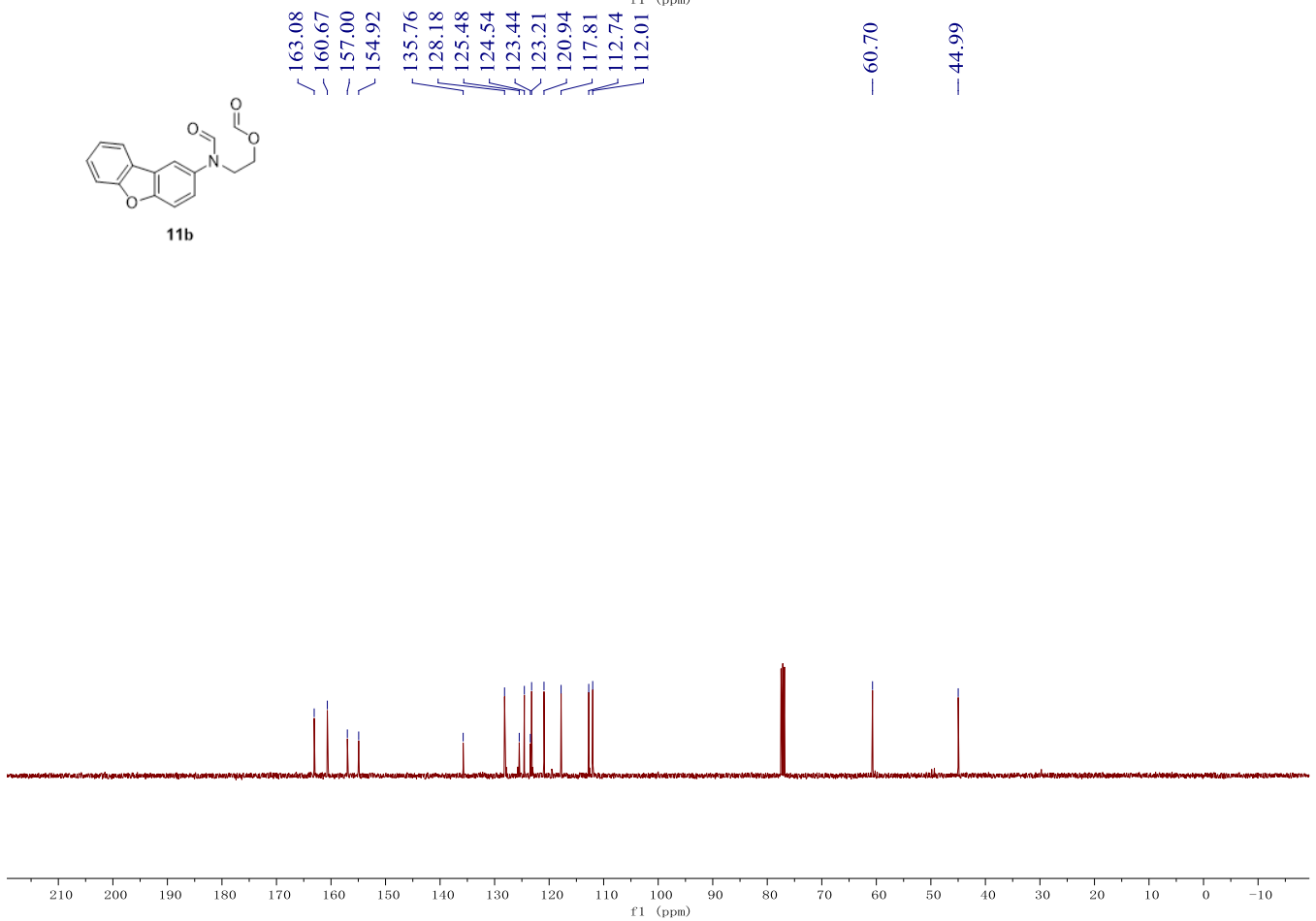
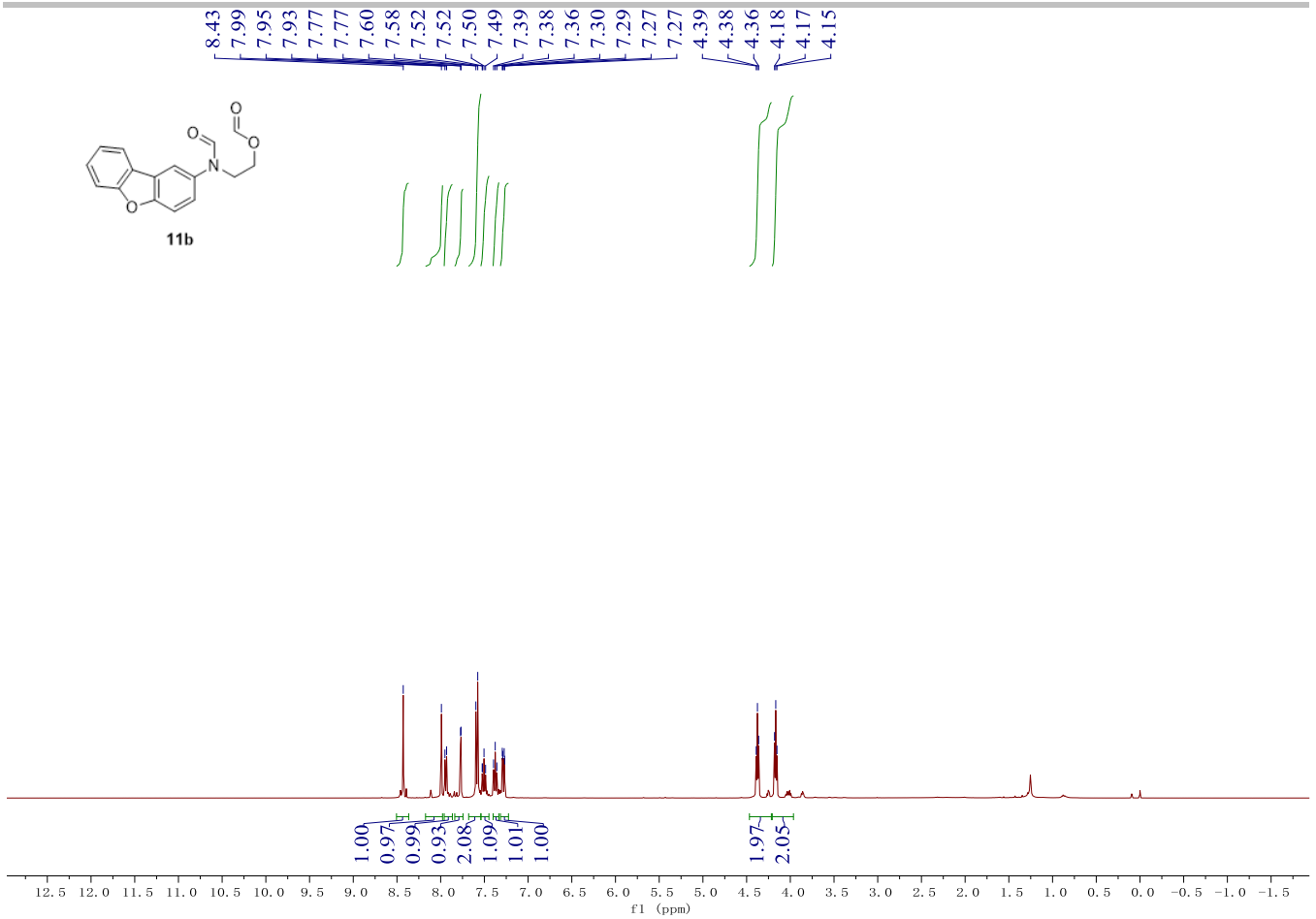


9b

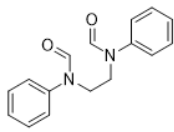
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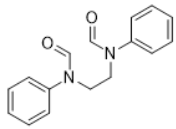
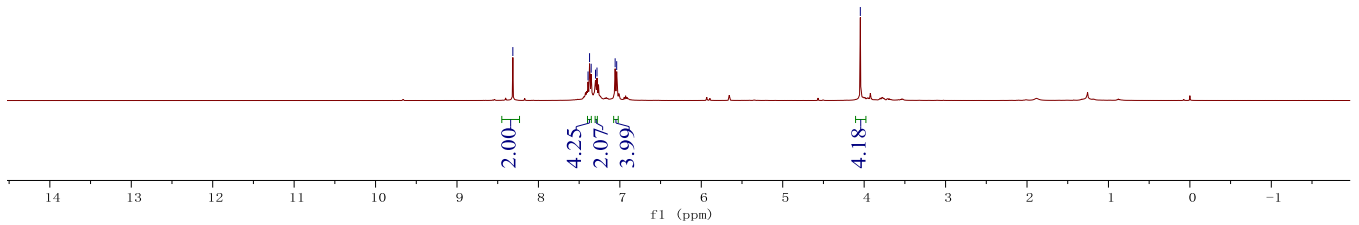
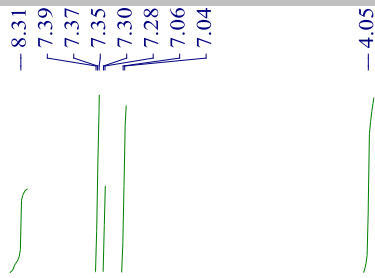




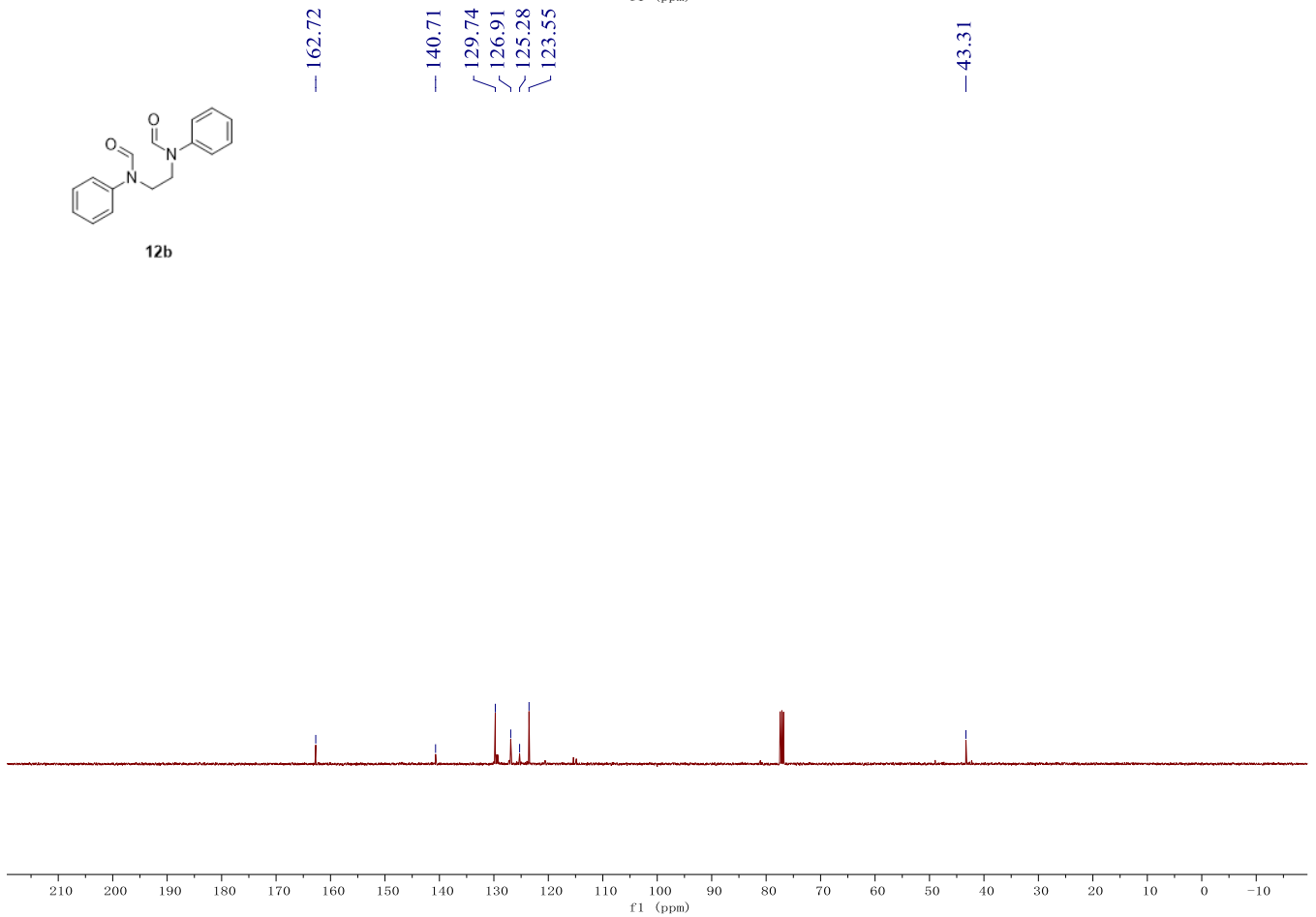


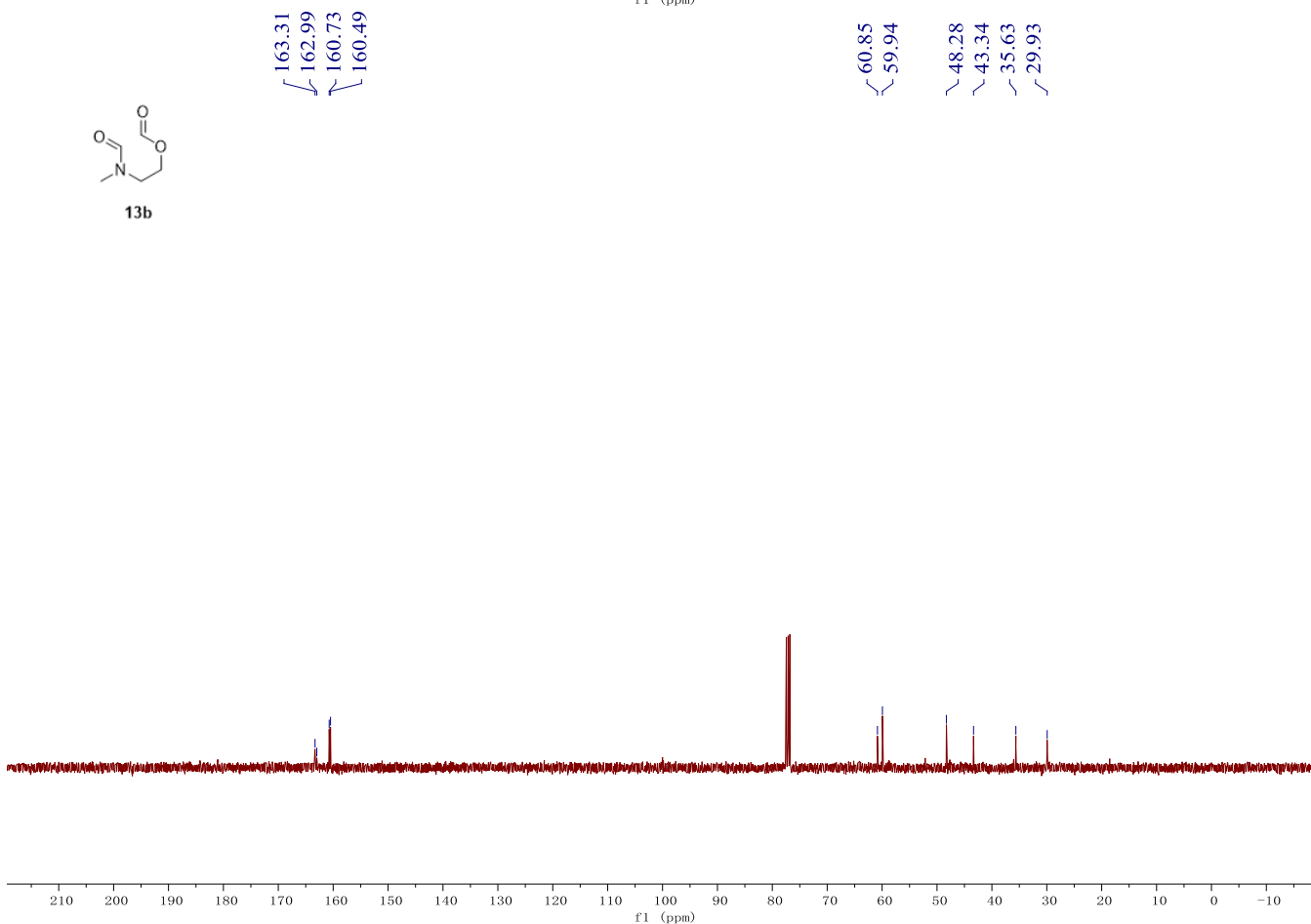
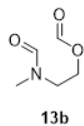
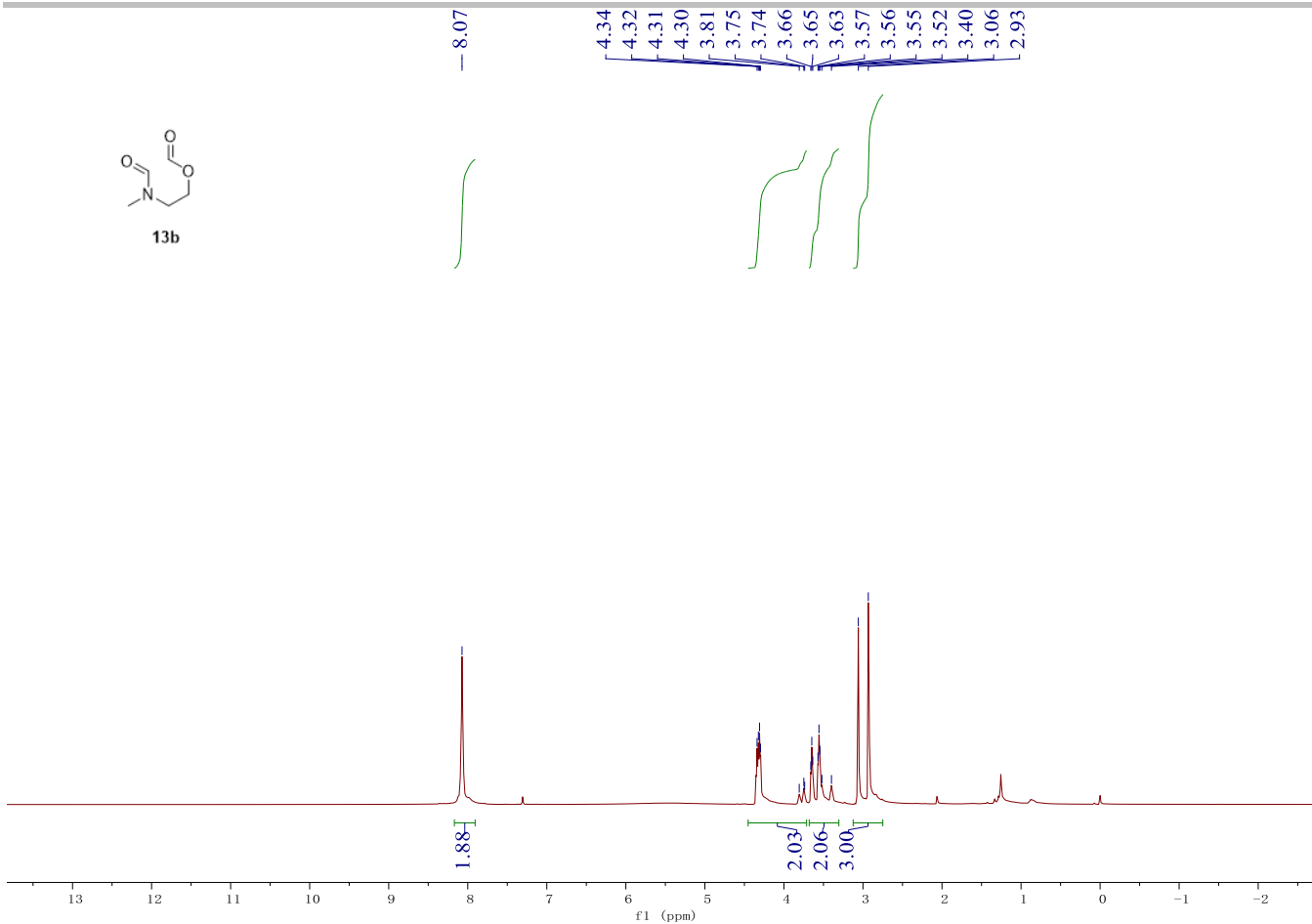
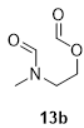


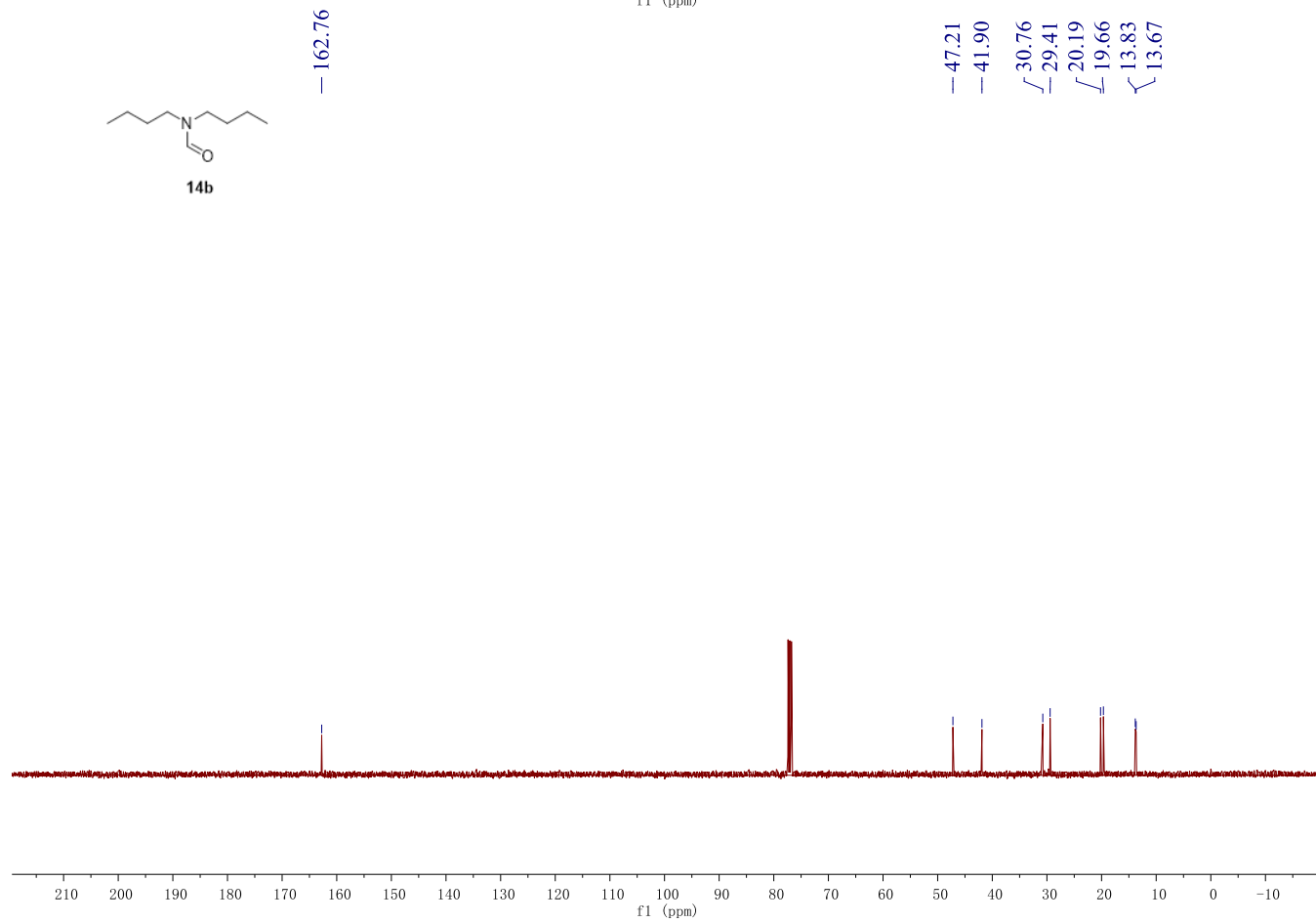
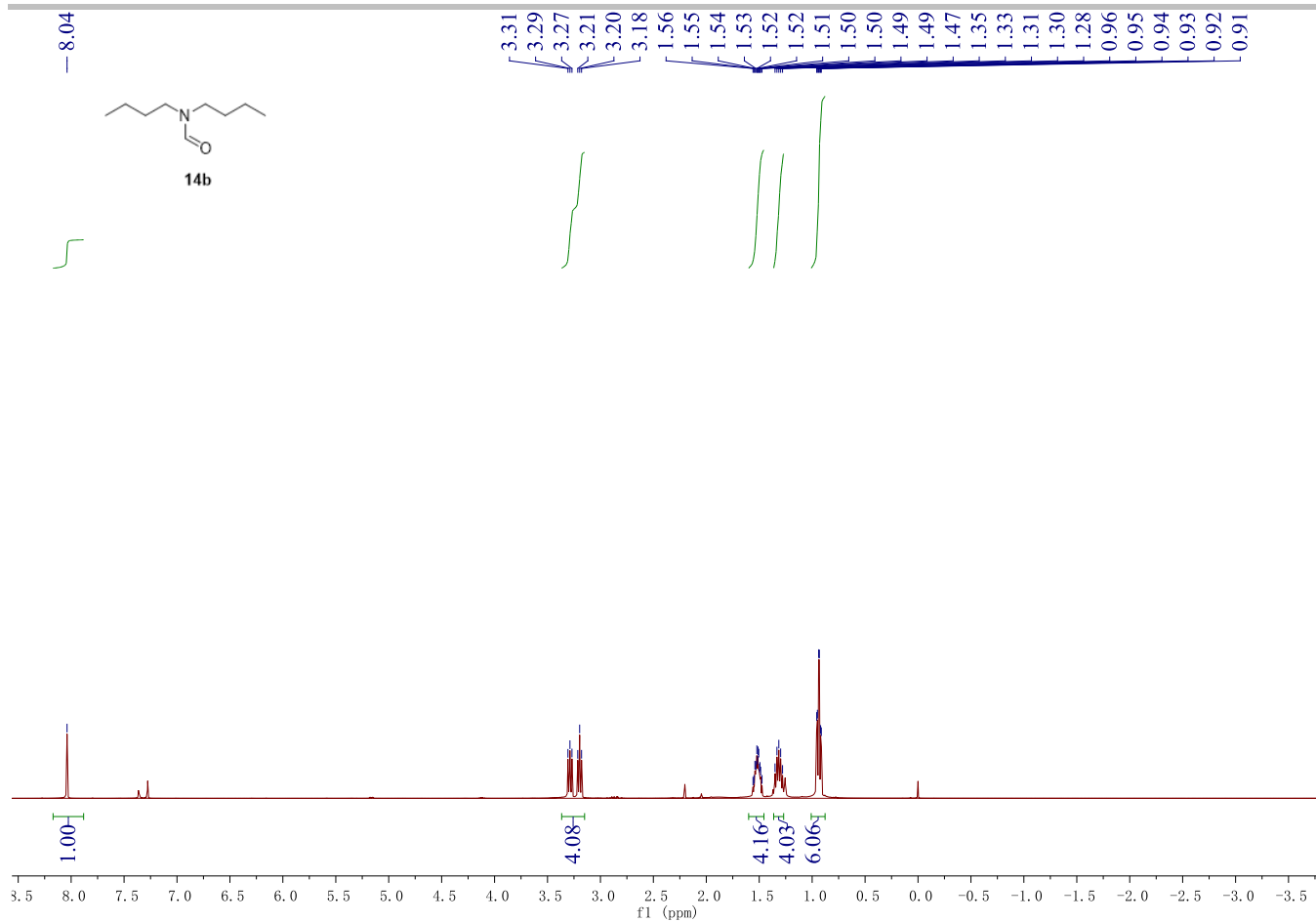
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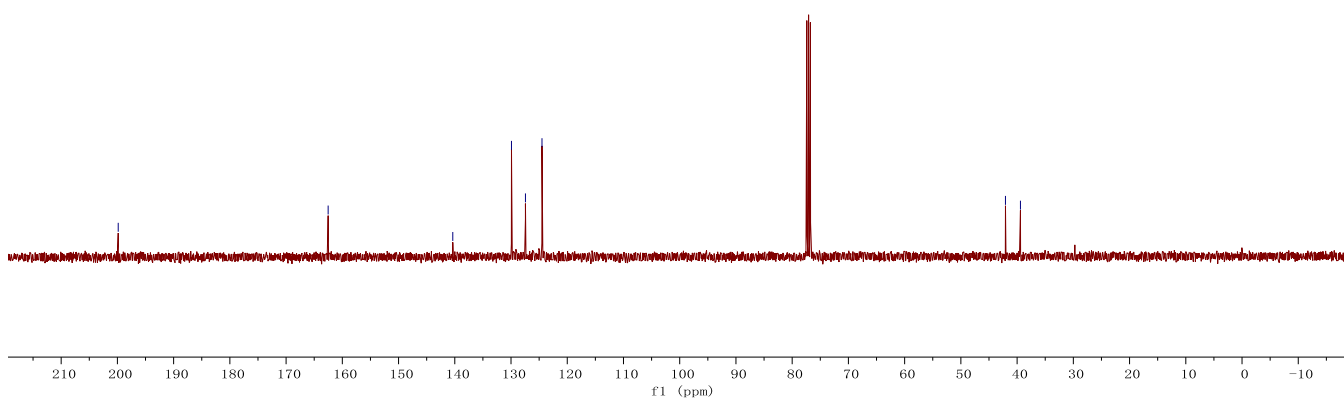
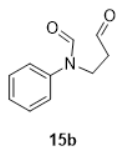
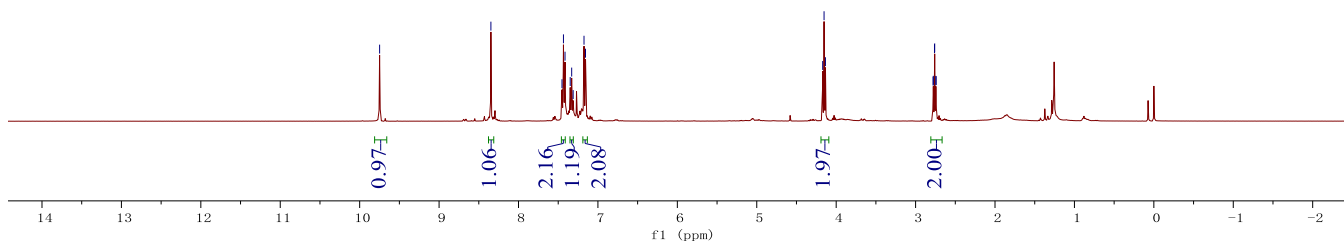
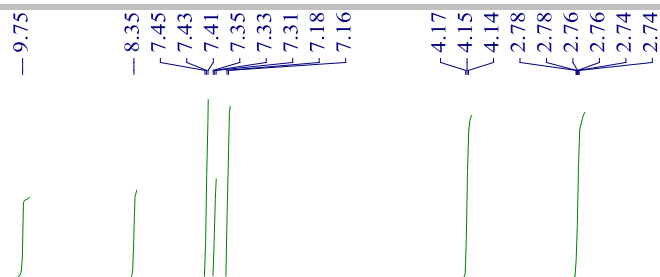
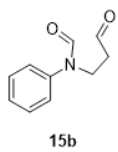


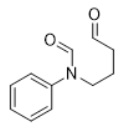
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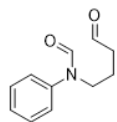
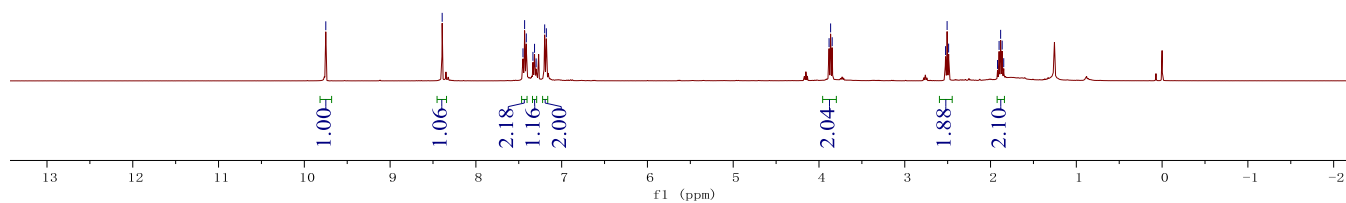
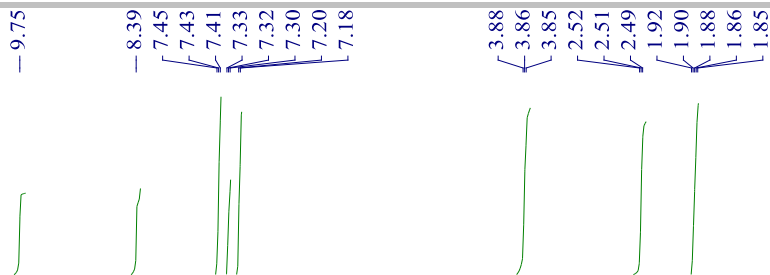




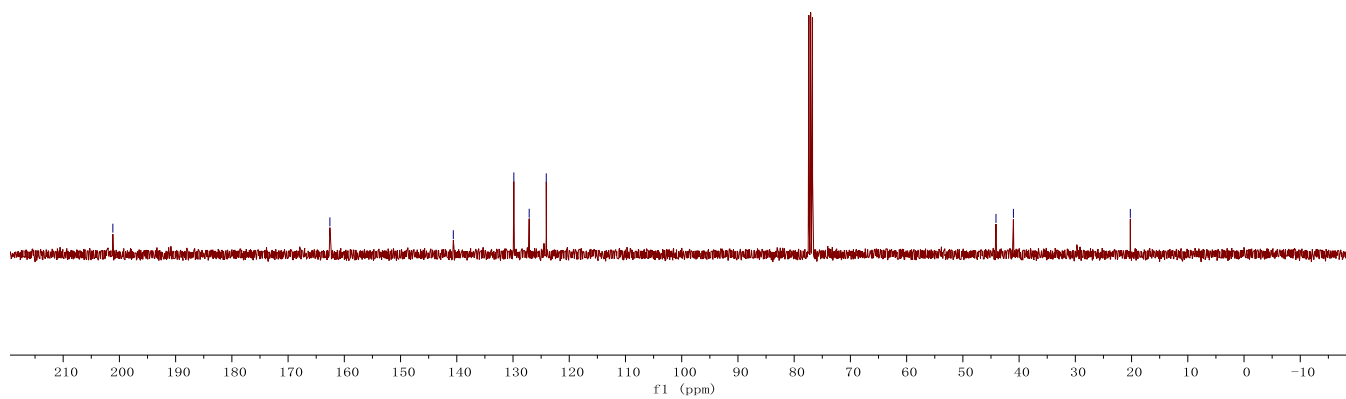


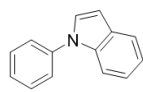


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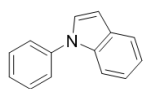
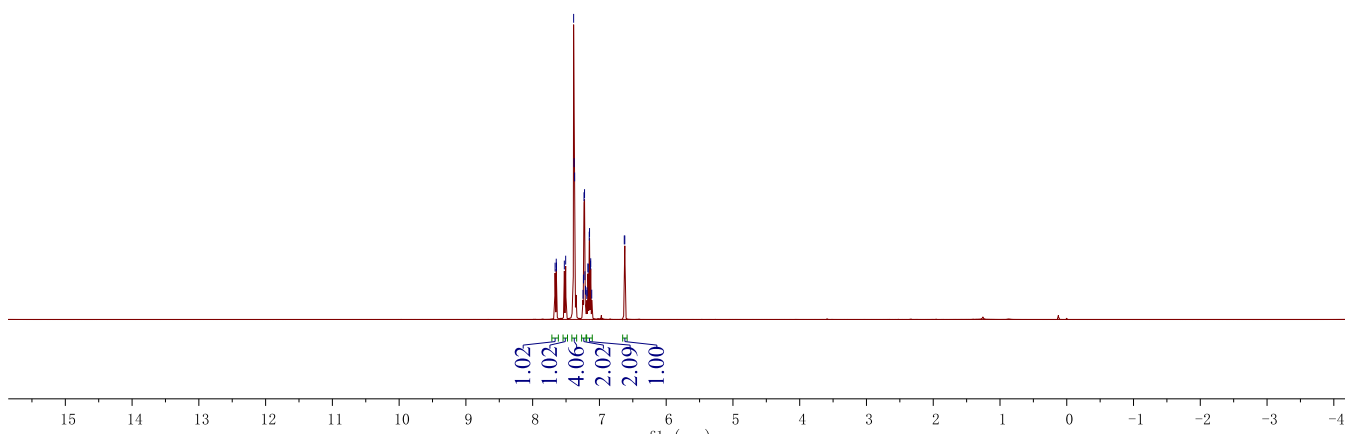
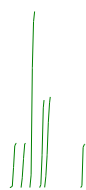
16b





1d

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