

## **Fe(III) – catalysed selective C–N bond cleavage of *N*-phenylamide by electrochemical method**

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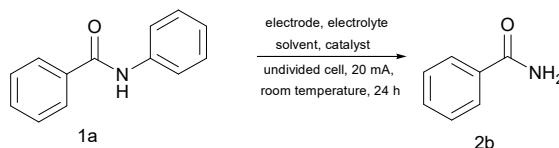
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## General information

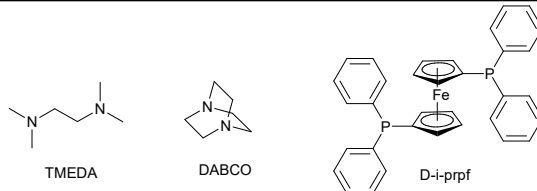
All reagents were purchased from commercial suppliers and used without further purification. Column chromatography was carried out with silica gel (100–200 mesh). Thin layer chromatography was carried out using Merck silica gel GF254 plates. All products were characterised by NMR. <sup>1</sup>H NMR spectra were recorded at 400 MHz and <sup>13</sup>C NMR spectra were recorded at 101 MHz (Bruker DPX) with CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> as solvent. Chemical shifts are reported in ppm using TMS as internal standard. Gas chromatography–mass spectra (GC/Mass) were recorded on an Agilent Technologies 6890 N instrument with an Agilent 5973N mass detector (EI) and a HP5–MS 30 cm\*0.25 mm capillary apolar column (Stationary phase: 5% diphenyldimethylpolysiloxane film, 0.25 μm). GC/Mass method: Initial temperature: 50 °C; Initial time: 3 min; Ramp: about 20°C/min until 280 °C then 10 min. High resolution mass spectra (HR-MS) were obtained with a Shimadzu LCMS–IT–TOF (ESI). Shanghai chenhua CHI600E electrochemical workstation was used in the standard configuration as delivered, including proprietary software. The setup for constant current electrolysis (Shanghai xirui DJS–292B constant potentiometer) consisted of an undivided cell equipped with anode and cathode (Electrodes come from commercial suppliers), if not noted otherwise.

**Table S1: Optimisation of electrochemical dephenylation of secondary phenylamide <sup>a</sup>**



Entry	Solvents	Catalyst	Time	Temperature	Electrolytes	Electrode	Additives	Yields <sup>b</sup>
1	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	room temperature (RT)	<sup>n</sup> Bu <sub>4</sub> NBr	Pt(+)/Pt(-)	-	6
2	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NClO <sub>4</sub>	Pt(+)/Pt(-)	-	18
3	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NF <sub>3</sub> O <sub>3</sub> S	Pt(+)/Pt(-)	-	7
4	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NB	Pt(+)/Pt(-)	-	5
5	<b>MeCN/H<sub>2</sub>O</b>	<b>FeCl<sub>3</sub>·6H<sub>2</sub>O</b>	<b>24 h</b>	<b>RT</b>	<b><sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub></b>	<b>Pt(+)/Pt(-)</b>	-	<b>60</b>
6	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NBF <sub>4</sub>	Pt(+)/Pt(-)	-	Trace
7	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NI	Pt(+)/Pt(-)	-	19
8	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NF <sub>3</sub> ·3H <sub>2</sub> O	Pt(+)/Pt(-)	-	40
9	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Me <sub>4</sub> NBr	Pt(+)/Pt(-)	-	Trace
10	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NBr <sub>3</sub>	Pt(+)/Pt(-)	-	Trace
11	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Pr <sub>4</sub> NBr	Pt(+)/Pt(-)	-	Trace
12	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Et <sub>4</sub> NI	Pt(+)/Pt(-)	-	26
13	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NBH <sub>4</sub>	Pt(+)/Pt(-)	-	Trace
14	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	-	Pt(+)/Pt(-)	-	N.D.
15	MeCN/H <sub>2</sub> O	AlCl <sub>3</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	30
16	MeCN/H <sub>2</sub> O	ZnCl <sub>2</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	58
17	MeCN/H <sub>2</sub> O	Zn(OTf) <sub>2</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	Trace
18	MeCN/H <sub>2</sub> O	SbCl <sub>3</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	Trace
19	MeCN/H <sub>2</sub> O	InCl <sub>3</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	Trace
20	MeCN/H <sub>2</sub> O	Cu(OTf) <sub>2</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	40
21	MeCN/H <sub>2</sub> O	In(OTf) <sub>3</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	Trace
22	MeCN/H <sub>2</sub> O	Ni(OTf) <sub>2</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	8
23	MeCN/H <sub>2</sub> O	RuCl <sub>3</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	42
24	MeCN/H <sub>2</sub> O	AgOTf	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	30
25	MeCN/H <sub>2</sub> O	Ag <sub>2</sub> CO <sub>3</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	Trace
26	MeCN/H <sub>2</sub> O	FeAc <sub>2</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	44
27	MeCN/H <sub>2</sub> O	Fe(acac) <sub>3</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	63
28	MeCN/H <sub>2</sub> O	FeCp <sub>2</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	12
29	MeCN/H <sub>2</sub> O	FeSO <sub>4</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	44
30	MeCN/H <sub>2</sub> O	FeCl <sub>2</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	53
31	MeCN/H <sub>2</sub> O	D-i-prpf	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	30
32	MeCN/H <sub>2</sub> O	-	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	N.D
33 <sup>c</sup>	MeCN	FeCl <sub>3</sub>	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	N.D
34	H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	Trace
35	DMF/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	11
36	MeCN	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	Trace
37	acetone /H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	8

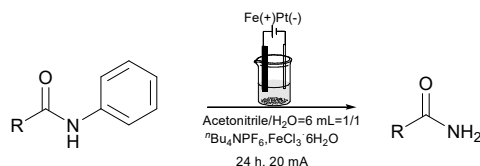
38	ethylene carbonate /H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	18
39	CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	12
40	MeCN/HFiP	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	N.D
41	MeCN/Formic acid	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	20
42	MeCN/HOAc	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	Trace
43	MeCN/ <sup>t</sup> BuOH	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	Trace
44	MeCN/EtOH	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	Trace
45	MeCN/MeOH	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	-	32
46	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	TMEDA <sup>f</sup>	Trace
47	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	TFA Et <sub>3</sub> N <sup>d</sup>	Trace
48	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	Et <sub>3</sub> N <sup>e</sup>	57
49	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Pt(+)/Pt(-)	DABCO <sup>f</sup>	30
<b>50</b>	<b>MeCN/H<sub>2</sub>O</b>	<b>FeCl<sub>3</sub>·6H<sub>2</sub>O</b>	<b>24 h</b>	<b>RT</b>	<b><sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub></b>	<b>Fe(+)/Pt(-)</b>	-	<b>89</b>
<b>51</b>	<b>MeCN/H<sub>2</sub>O</b>	<b>FeCl<sub>3</sub>·6H<sub>2</sub>O</b>	<b>24 h</b>	<b>RT</b>	<b><sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub></b>	<b>Ni(+)/Pt(-)</b>	-	<b>87</b>
52	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Al(+)/Pt(-)	-	20
53	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Cu(+)/Pt(-)	-	79
54	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	14 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Fe(+)/Pt(-)	-	24
55	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	36 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Fe(+)/Pt(-)	-	62
56	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	48 h	RT	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Fe(+)/Pt(-)	-	58
57	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	35	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Fe(+)/Pt(-)	-	88
58	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	45	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Fe(+)/Pt(-)	-	86
59	MeCN/H <sub>2</sub> O	FeCl <sub>3</sub> ·6H <sub>2</sub> O	24 h	60	<sup>n</sup> Bu <sub>4</sub> NPF <sub>6</sub>	Fe(+)/Pt(-)	-	87



<sup>a</sup> Standard conditions: Anode (1.0 \*1.0 cm<sup>2</sup>), Cathode (1.0 \*1.0 cm<sup>2</sup>), **1a** (0.6 mmol), Solvents (6 mL=1/1), Electrolytes (0.05 M), Catalyst (0.2 equiv), 20 mA, Undivided cell, air, 24 h. <sup>b</sup> Yields were determined using GC-Mass analysis with 1H-benzo[d]imidazole as an internal standard. <sup>c</sup> water removal; <sup>d</sup> 2M:2M solution (0.5 mL); <sup>e</sup> 0.5 mL; <sup>f</sup> 1.0 equiv.

Initially, various electrolytes were screened with water and MeCN as solvent and FeCl<sub>3</sub>·6H<sub>2</sub>O as catalyst (Entries 1–12). <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> proved to be the optimal electrolyte giving product in 60% yield (Entry 5). Next, a series of Lewis acid and iron catalyst were tested (Entries 15–32). The results showed that FeCl<sub>3</sub>·6H<sub>2</sub>O exhibited the highest catalytic activity than other catalyst. Water and MeCN were found to be the most suitable solvents for this system (Entries 32–45). H<sub>2</sub>O plays an important role in this reaction system that cannot proceed for the reaction when removal (Entry 33). Electronic transfer media contribute little to the conversion under constant current (Entries 46–49). Further exploration of electrode (Entries 50-53) showed that Fe(+) Pt(-) were the optimal condition with 89% yield. Finally, the time and temperature screening revealed that 24 h and room temperature were the best choice (Entries 54–59).

### Scheme S1: General procedure for the catalytic reactions



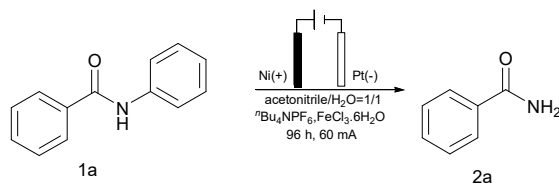
An undivided cell was equipped with a magnet stirrer, Fe plate (1.0 \*1.0 cm<sup>2</sup>), Pt net (1.0\*10 cm<sup>2</sup>), as anode electrode and cathode electrode. The substrate secondary phenylamide (0.6 mmol), <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.05 M), FeCl<sub>3</sub>·6H<sub>2</sub>O (20 %), 3.0 mL of water and 3.0 mL MeCN were placed. The resulting mixture was allowed to stir and electrolyze at constant current conditions (20 mA) at room temperature for 24 hours. Then the reaction mixture was poured into water (10 mL) and extracted with ethyl acetate (10 mL\*3). The residue was purified by silica gel column chromatography to obtain the corresponding product. All products were confirmed by nuclear magnetic resonance and mass spectrometry.

## The setup for constant current electrolysis



Figure S1. Electrolysis setup (A: Shanghai xirui DJS-292B constant potentiometer; B: Fe plate (1.0 \* 1.0 cm<sup>2</sup>), Pt net (1.0 \* 10 cm<sup>2</sup>), An undivided cell of 10 mL flask; C: Series of electrodes; D: Gram scale reaction device).

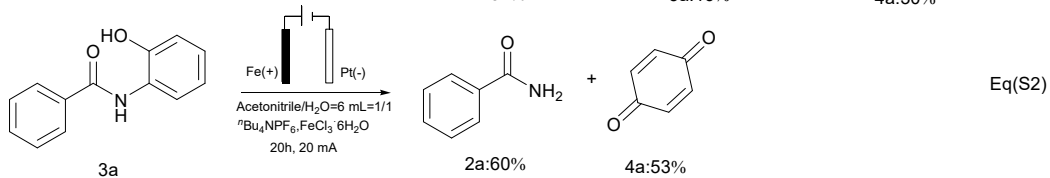
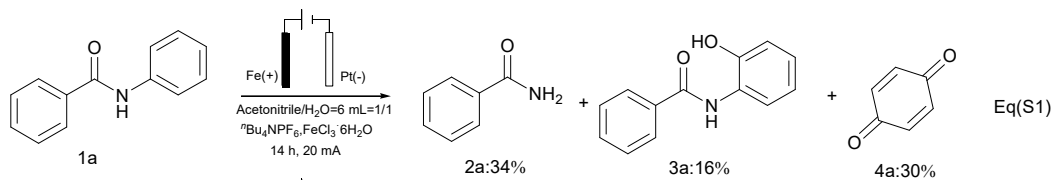
## Scheme S2: General procedure for gram scale reaction



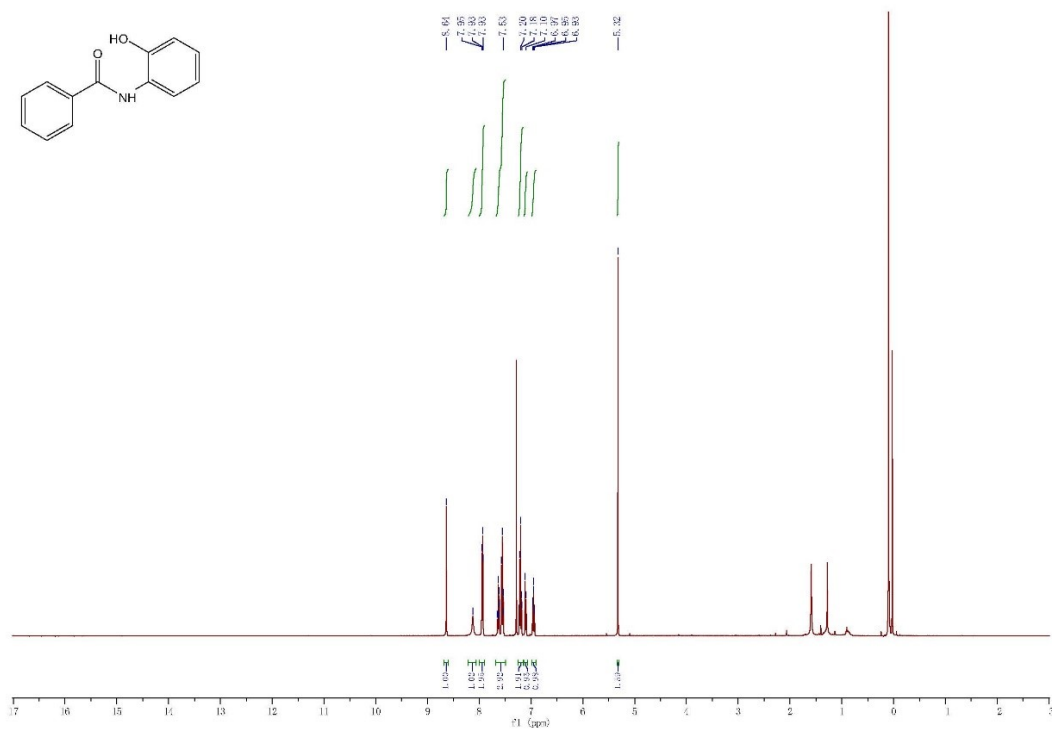
An undivided cell was equipped with a magnet stirrer, Fe plate (25\*4.0 cm<sup>2</sup>), two Pt net (10\*10 cm<sup>2</sup>), as the working electrode and counter electrode. The substrate secondary phenylamide (6.0 mmol), nBu<sub>4</sub>NPF<sub>6</sub> (0.05 M), FeCl<sub>3</sub>·6H<sub>2</sub>O (20 %), 20.0 mL of water and 20.0 mL MeCN were placed. The reaction mixture was stirred at a constant current of 60 mA under room temperature for 96 h. Then the reaction mixture was poured into water (150 mL) and extracted with ethyl acetate (100 mL\*3). The residue was purified by silica gel column chromatography in a yield around 72%.

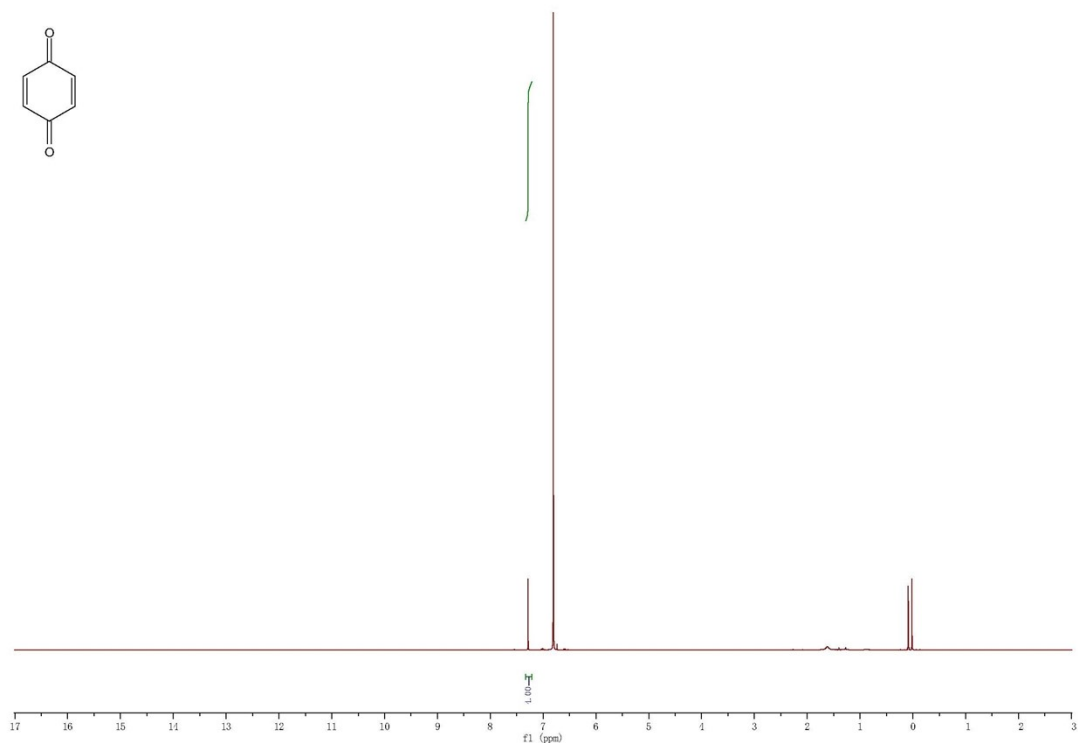
## Mechanism Studies

Scheme S3: Stepwise dephenylation to get intermediate product:

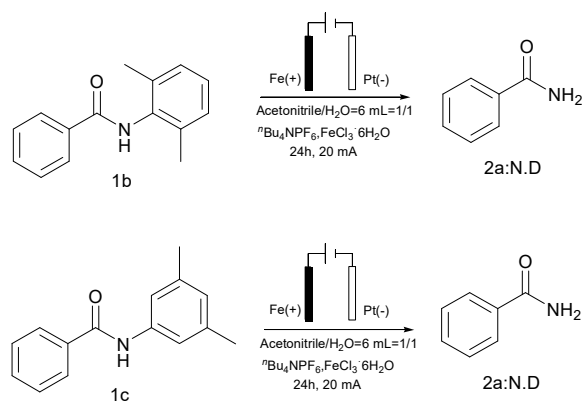


We have tried to collection intermediate product by reduce reaction time, *N*-(2-hydroxyphenyl)benzamide (**3a**) and 1,4-benzoquinone (**4a**) were observed by GC/Mass (Eq S1). And according to optimised condition, product **2a** was obtained in 60 % yield when **3a** was used as starting material (Eq S2). **3a**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64 (s, 1H), 8.12 (s, 1H), 8.00 – 7.90 (m, 2H), 7.68 – 7.50 (m, 3H), 7.20 (dd,  $J = 12.3, 4.6$  Hz, 2H), 7.11 (d,  $J = 8.0$  Hz, 1H), 6.95 (td,  $J = 7.6, 1.4$  Hz, 1H), 5.32 (s, 2H); **4a**:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (s, 4H).



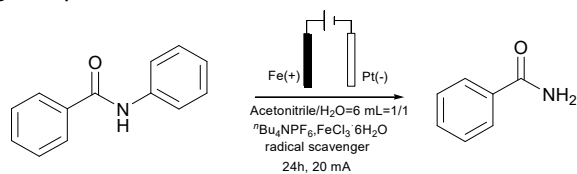


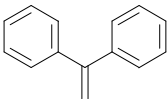
Scheme S4: Steric hindrance effect:



To elucidate the mechanism of this reaction, some reactive site were instead by methyl under the standard conditions. The experiments indicate that Steric hindrance has been shown to affect reaction of ortho C-H activation and electronic attack.

Table S2: Radical scavenger experiments<sup>a</sup>:



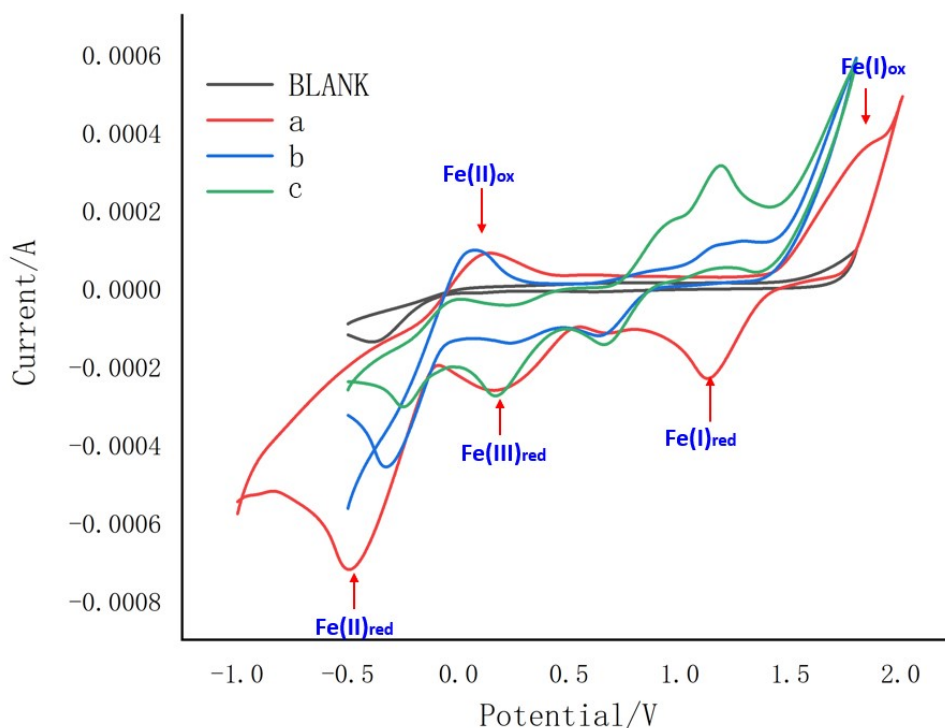
Entry	Scavenger	Equivalent	Yields <sup>b</sup>
1		0.1	66
		0.2	42
		0.5	18
		1.0	Trace
		2.0	Trace

2		0.1	39
		0.2	23
		0.5	Trace
		1.0	n.d
		2.0	n.d
3		0.1	72
		0.2	55
		0.5	30
		1.0	Trace
		2.0	trace

<sup>a</sup> Standard conditions: substrate (0.6 mmol), H<sub>2</sub>O (3 mL), <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.05 M), FeCl<sub>3</sub>·6H<sub>2</sub>O (0.2 equiv), MeCN/H<sub>2</sub>O (6 mL, 1: 1), air, Pt net and Fe plate electrodes (1.0 cm\*1.0 cm<sup>2</sup>), 24 h, room temperature and constant current electrolysis at 20 mA in an undivided cell; <sup>b</sup> Yields were determined using GC/Mass analysis with 1H-benzo[d]imidazole as an internal standard.

### Cyclic voltammetry experiment

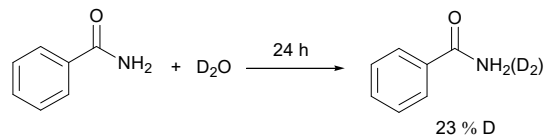
Cyclic voltammograms were measured using Shanghai chenhua CHI600E electrochemical workstation with electrochemical analysis software, using a conventional three-electrode cell. The working electrode was a Pt disk electrode, The counter and reference electrodes consisted of a Pt wire and a calomel electrode, respectively. The Pt disk working electrode was polished with a polishing cloth before each measurement. the concentration of all tested compounds was 0.1M, if not noted otherwise. The scan rate was 0.1 V/s.



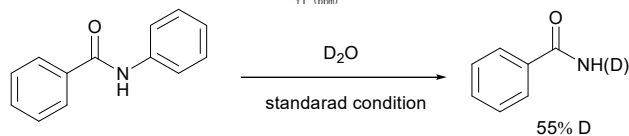
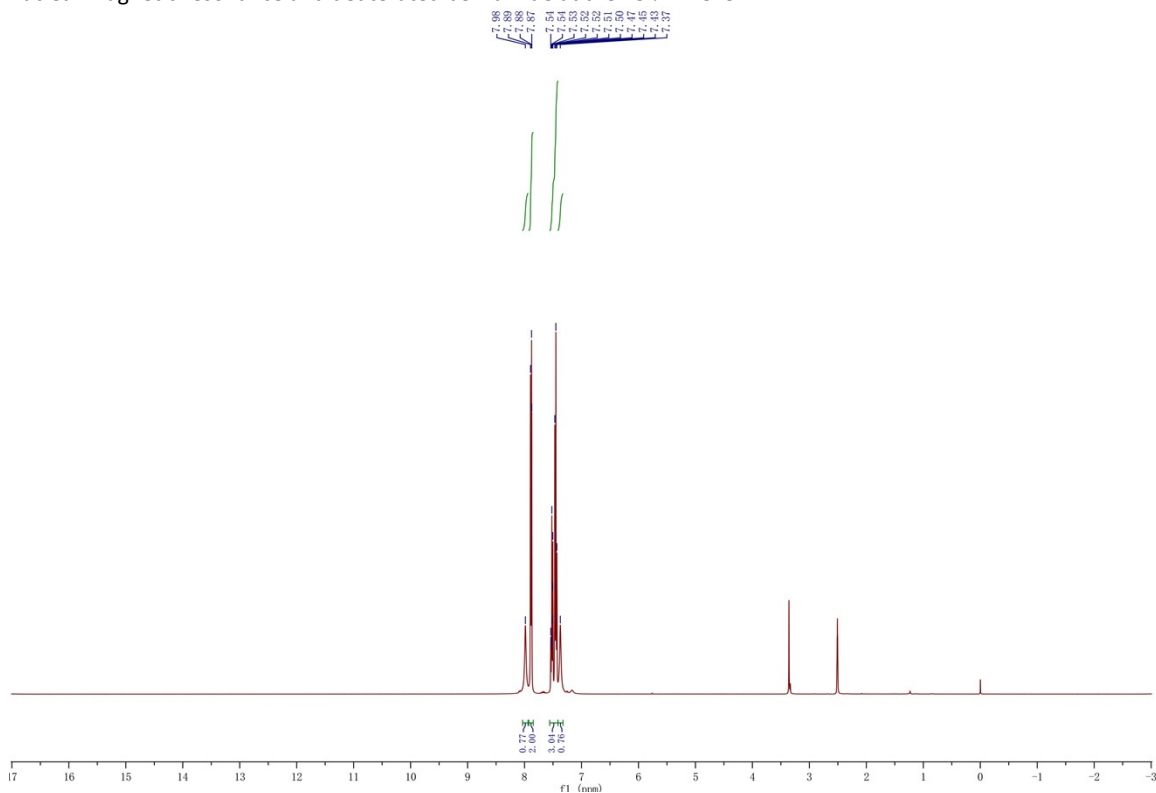
**Figure S2.** Blank: 0.1M nBu<sub>4</sub>NPF<sub>6</sub>, MeCN /H<sub>2</sub>O= 1/1; a: Blank + FeCl<sub>3</sub>·6H<sub>2</sub>O 0.02 mmol; b: Blank + 1a 0.1mmol + FeCl<sub>3</sub>·6H<sub>2</sub>O 0.02 mmol; c: Blank + 3a 0.1 mmol + FeCl<sub>3</sub>·6H<sub>2</sub>O 0.02 mmol

### Scheme S5: Deuterium-labeling experiment

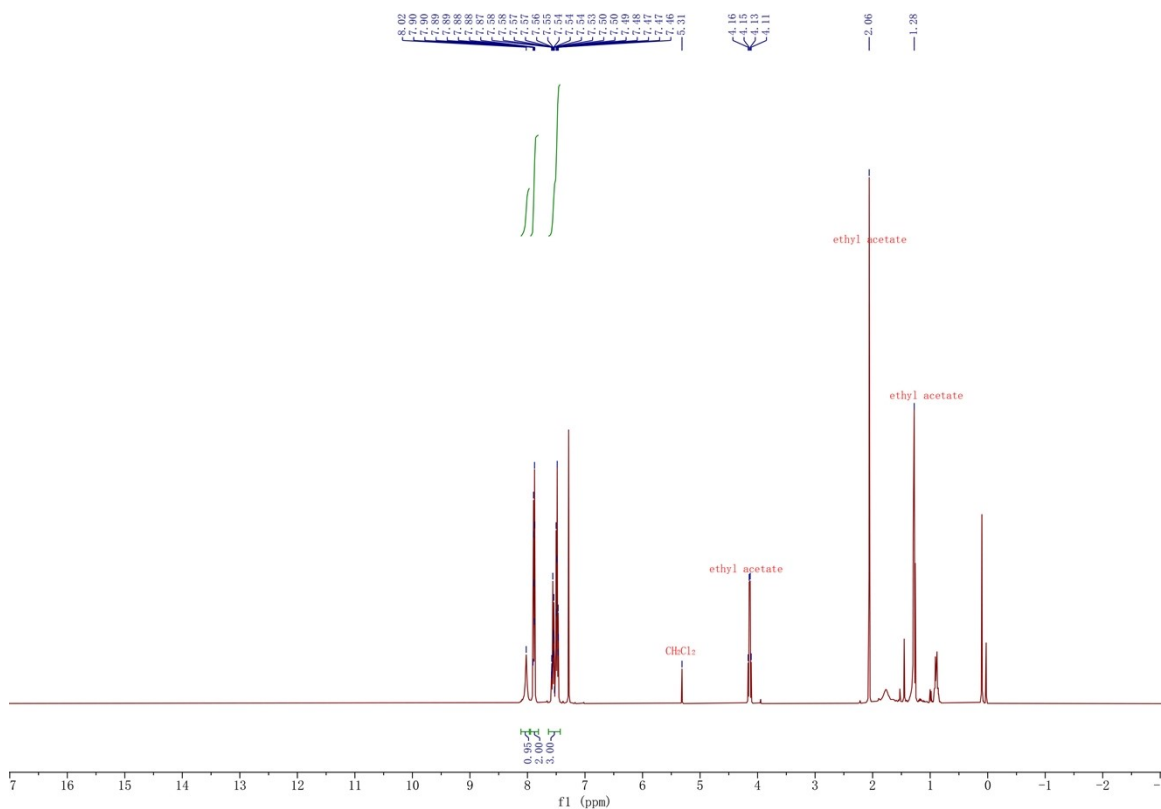




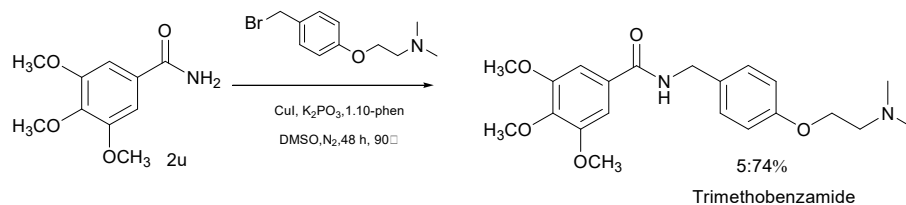
A solution of the benzamide (0.3 mmol) in 3 mL of MeCN was treated with D<sub>2</sub>O (3 mL). The solution was allowed to stir at room temperature for 24 hours. After the solution was evaporated in vacuo. The product was confirmed by nuclear magnetic resonance and deuterated benzamide at the 23 % D level.



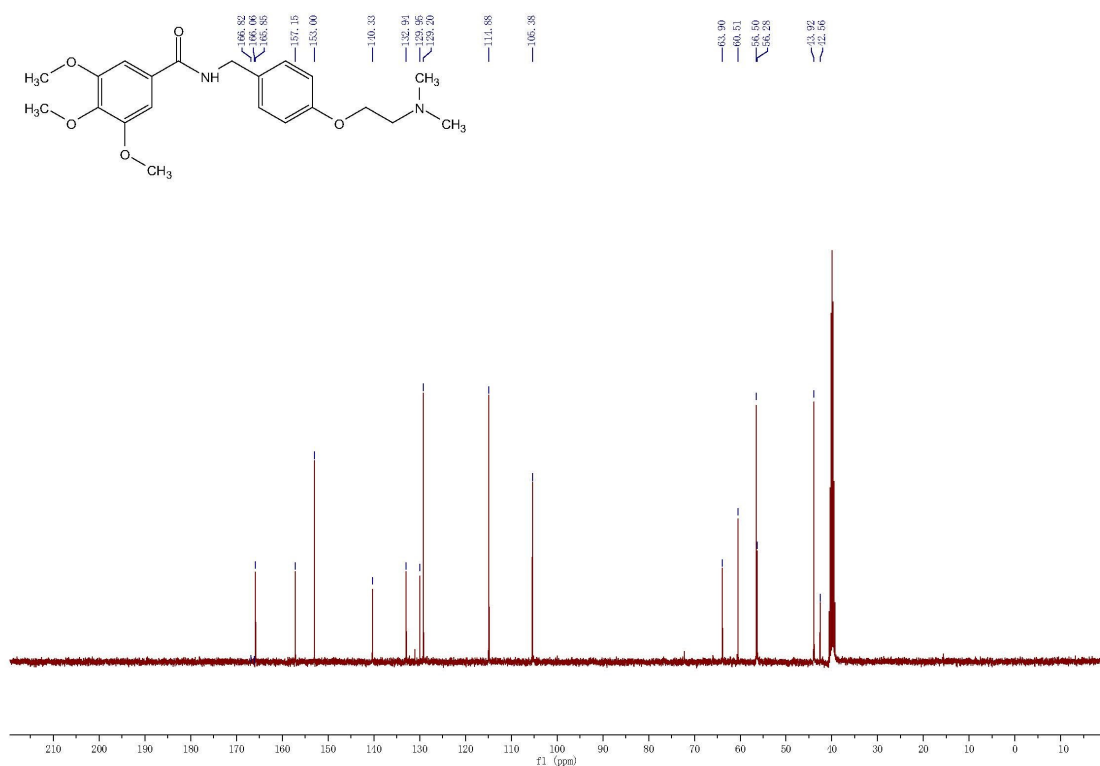
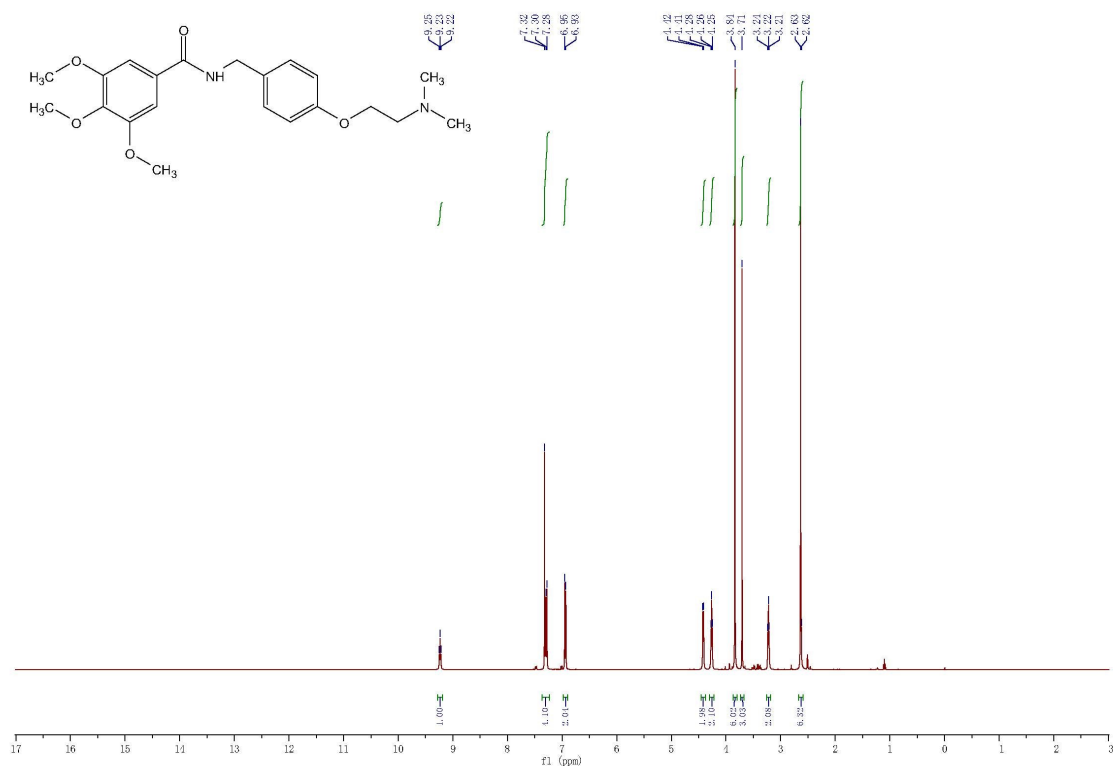
An undivided cell was equipped with a magnet stirrer, Fe plate (1.0 \*1.0 cm<sup>2</sup>), Pt net (1.0\*10 cm<sup>2</sup>), as anode electrode and cathode electrode. The substrate secondary phenylamide (0.6 mmol), <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.05 M), FeCl<sub>3</sub>·6H<sub>2</sub>O (20 %), 3.0 mL D<sub>2</sub>O and 3.0 mL MeCN were placed. The resulting mixture was allowed to stir and electrolyze at constant current conditions (20 mA) at room temperature for 24 hours. Then the reaction mixture was poured into water (10 mL) and extracted with ethyl acetate (10 mL\*3). The residue was purified by silica gel column chromatography to obtain the corresponding product. The product was confirmed by nuclear magnetic resonance and deuterated benzamide at the 55 % D level.



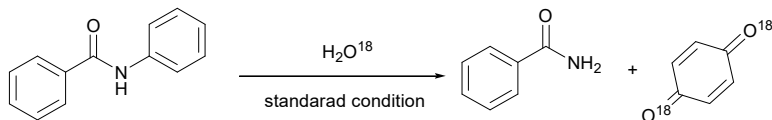
### Scheme S6: Procedure for synthesis of Trimethobenzamide



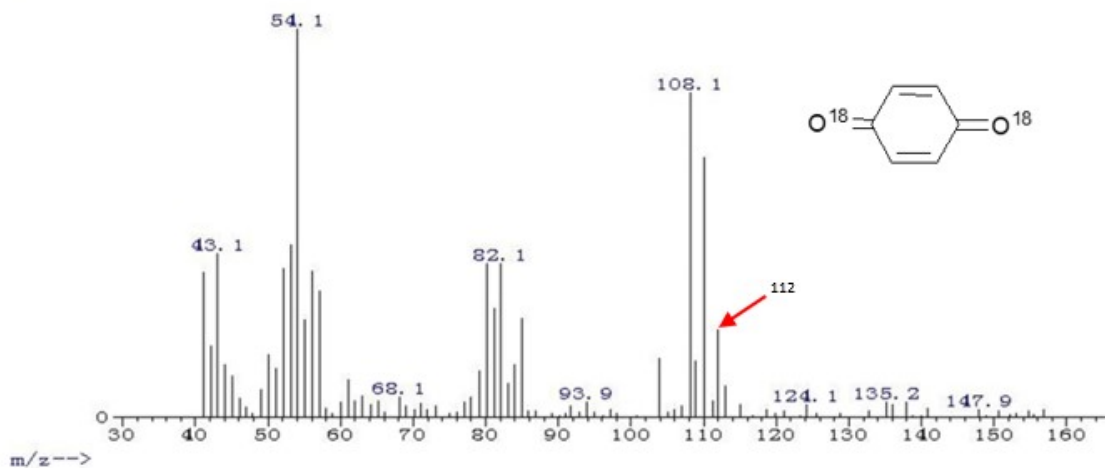
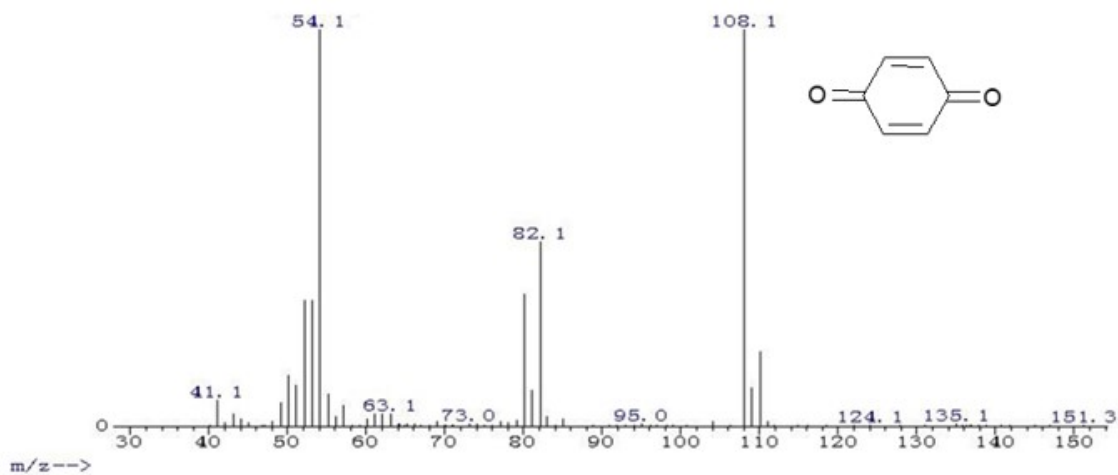
CuI (0.10 equiv), K<sub>2</sub>PO<sub>3</sub> (3.0 equiv), 1,10-phenanthroline (0.2 equiv), DMSO (2.0 mL), 3,4,5-trimethoxybenzamide (1.0 equiv) and 2-(4-(bromomethyl)phenoxy)-N,N-dimethylethanamine (1.1 equiv) were added to a Schlenk flask. The reaction mixture was allowed to stir at 90 °C for 48 h. After allowing the reaction to cool to ambient temperature, the mixture was dissolved in MeOH (10 mL) and concentrated under reduced pressure. The crude residue was directly purified by silica gel column chromatography in 72% yield. **3aa**: <sup>1</sup>H NMR (400 MHz, DMSO) δ 9.23 (t, *J* = 5.9 Hz, 1H), 7.37 – 7.23 (m, 4H), 6.94 (d, *J* = 8.6 Hz, 2H), 4.42 (d, *J* = 5.8 Hz, 2H), 4.26 (t, *J* = 5.3 Hz, 2H), 3.84 (s, 6H), 3.71 (s, 3H), 3.22 (t, *J* = 5.3 Hz, 2H), 2.63 (d, *J* = 5.4 Hz, 6H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 166.82, 166.06, 165.85, 157.15, 153.00, 140.33, 132.94, 129.95, 129.20, 114.88, 105.38, 63.90, 60.51, 56.50, 56.28, 43.92, 42.56; **MS** [EI, *m/z*]: 388.20 [M<sup>+</sup>].



**Scheme S7: H<sub>2</sub>O<sup>18</sup> experiment**

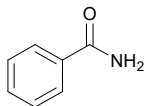


An undivided cell was equipped with a magnet stirrer, Fe plate (1.0 \*1.0 cm<sup>2</sup>), Pt net (1.0\*10 cm<sup>2</sup>), as anode electrode and cathode electrode. The substrate secondary phenylamide (0.6 mmol), <sup>18</sup>Bu<sub>4</sub>NPF<sub>6</sub> (0.05 M), FeCl<sub>3</sub>·6H<sub>2</sub>O (20 %), 3.0 mL of water, 100 μL H<sub>2</sub>O<sup>18</sup> and 3.0 mL MeCN were placed. The resulting mixture was allowed to stir at constant current conditions (20 mA) at room temperature for 24 hours. Then the reaction mixture was poured into water (10 mL) and extracted with ethyl acetate (10 mL\*3). The residue was confirmed by Gas chromatography—mass spectra.



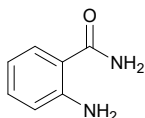
## Experimental procedures and characterisation data

### 2a: benzamide<sup>1</sup>



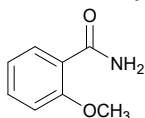
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 6.22 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.62, 133.36, 132.01, 128.63, 127.39; HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>8</sub>NO 122.0606; Found 122.0612.

### 2b: 2-aminobenzamide<sup>2</sup>



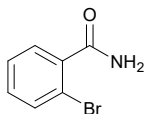
**<sup>1</sup>H NMR** (400 MHz, DMSO)  $\delta$  7.72 (s, 1H), 7.53 (dd,  $J$  = 8.0, 1.4 Hz, 1H), 7.13 (ddd,  $J$  = 8.4, 7.1, 1.5 Hz, 1H), 7.07 (s, 1H), 6.68 (dd,  $J$  = 8.2, 1.0 Hz, 1H), 6.56 (s, 2H), 6.48 (ddd,  $J$  = 8.1, 7.1, 1.2 Hz, 1H); **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  171.76, 150.65, 132.35, 129.20, 116.85, 114.82, 114.12; **HRMS (ESI) m/z**: [M+H]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>9</sub>N<sub>2</sub>O 137.0709; Found 137.0701.

**2c: 2-methoxybenzamide<sup>3</sup>**



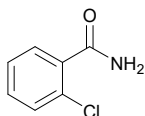
**<sup>1</sup>H NMR** (400 MHz, DMSO)  $\delta$  7.81 (dd,  $J$  = 7.7, 1.8 Hz, 1H), 7.64 (s, 1H), 7.56 – 7.44 (m, 2H), 7.13 (d,  $J$  = 7.9 Hz, 1H), 7.03 (td,  $J$  = 7.6, 1.0 Hz, 1H), 3.89 (s, 3H); **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  166.75, 157.67, 132.89, 131.17, 123.17, 120.83, 112.41, 56.25; **HRMS (ESI) m/z**: [M+H]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>10</sub>NO<sub>2</sub> 152.0706; Found 152.0711.

**2d: 2-bromobenzamide<sup>3</sup>**



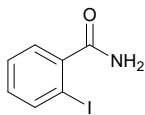
**<sup>1</sup>H NMR** (400 MHz, DMSO)  $\delta$  7.87 (s, 1H), 7.66 – 7.62 (m, 1H), 7.57 (s, 1H), 7.45 – 7.39 (m, 2H), 7.34 (ddd,  $J$  = 8.0, 6.1, 3.1 Hz, 1H); **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  169.51, 139.82, 133.15, 131.09, 129.00, 127.94, 119.06; **HRMS (ESI) m/z**: [M+H]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>7</sub>BrNO 199.9711; Found 199.9719.

**2e: 2-chlorobenzamide<sup>2</sup>**



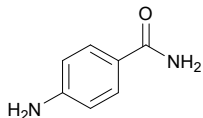
**<sup>1</sup>H NMR** (400 MHz, DMSO)  $\delta$  7.87 (s, 1H), 7.58 (s, 1H), 7.50 – 7.35 (m, 4H); **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  168.61, 137.62, 131.00, 130.08, 130.05, 129.11, 127.47; **HRMS (ESI) m/z**: [M+H]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>7</sub>ClNO 156.0211; Found 156.0209.

**2f: 2-iodobenzamide<sup>4</sup>**



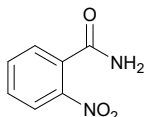
**<sup>1</sup>H NMR** (400 MHz, DMSO)  $\delta$  7.87 (dd,  $J$  = 7.9, 0.9 Hz, 1H), 7.82 (s, 1H), 7.51 (s, 1H), 7.43 (td,  $J$  = 7.5, 1.1 Hz, 1H), 7.34 (dd,  $J$  = 7.6, 1.7 Hz, 1H), 7.18 – 7.12 (m, 1H); **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  171.15, 143.60, 139.61, 131.04, 128.38, 128.23, 93.59; **HRMS (ESI) m/z**: [M+H]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>7</sub>INO 247.9572; Found 247.9573.

**2g: 4-aminobenzamide<sup>2</sup>**



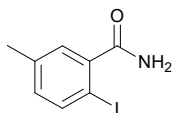
**<sup>1</sup>H NMR** (400 MHz, DMSO)  $\delta$  7.62 – 7.55 (m, 2H), 7.50 (s, 1H), 6.82 (s, 1H), 6.58 – 6.46 (m, 2H), 5.59 (s, 2H); **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  168.47, 152.11, 129.57, 121.43, 112.90; **HRMS (ESI) m/z**: [M+H]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O 137.0709; Found 137.0707.

**2h: 2-nitrobenzamide<sup>3</sup>**



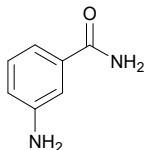
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  8.14 (s, 1H), 8.00 (dd,  $J = 8.0, 1.1$  Hz, 1H), 7.77 (td,  $J = 7.5, 1.2$  Hz, 1H), 7.73 – 7.59 (m, 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  167.60, 147.70, 133.78, 133.04, 131.07, 129.30, 124.40; **HRMS (ESI) m/z:**  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_7\text{H}_6\text{N}_2\text{O}_3\text{Na}$  189.0271; Found 189.0270.

**2i: 2-iodo-5-methylbenzamide<sup>5</sup>**



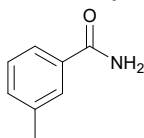
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.77 (s, 1H), 7.72 (d,  $J = 8.0$  Hz, 1H), 7.47 (s, 1H), 7.18 (d,  $J = 1.7$  Hz, 1H), 7.01 – 6.94 (m, 1H), 2.28 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  171.15, 143.40, 139.39, 138.00, 131.81, 128.98, 89.50, 20.79; **HRMS (ESI) m/z:**  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_8\text{H}_8\text{INa}$  283.9548; Found 283.9550.

**2j: 3-aminobenzamide<sup>6</sup>**



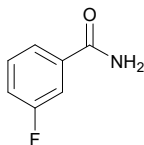
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.71 (s, 1H), 7.23 – 6.95 (m, 4H), 6.68 (ddd,  $J = 8.0, 2.3, 1.0$  Hz, 1H), 5.18 (s, 2H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  169.16, 149.03, 135.67, 128.97, 116.91, 115.11, 113.56; **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_7\text{H}_8\text{N}_2\text{O}$  137.0709; Found 137.0715.

**2k: 3-methylbenzamide<sup>3</sup>**



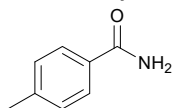
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.92 (s, 1H), 7.74 – 7.62 (m, 2H), 7.33 (d,  $J = 4.6$  Hz, 3H), 2.35 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  168.45, 137.87, 134.71, 132.20, 128.53, 128.52, 125.03, 21.41; **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_8\text{H}_{10}\text{NO}$  136.0757; Found 136.0755.

**2l: 3-fluorobenzamide<sup>3</sup>**



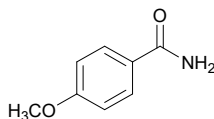
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  8.07 (s, 1H), 7.76 – 7.70 (m, 1H), 7.67 (ddd,  $J = 10.1, 2.5, 1.6$  Hz, 1H), 7.58 – 7.46 (m, 2H), 7.42 – 7.33 (m, 1H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  166.94 (d,  $J = 2.4$  Hz), 162.42 (d,  $J = 244.42$  Hz), 137.16 (d,  $J = 6.6$  Hz), 130.84 (d,  $J = 8.0$  Hz), 124.06 (d,  $J = 2.8$  Hz), 118.57 (d,  $J = 21.2$  Hz), 114.65 (d,  $J = 22.4$  Hz); **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_7\text{H}_7\text{FNO}$  140.0506; Found 140.0505.

**2m: 4-methylbenzamide<sup>3</sup>**



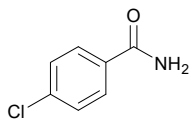
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.89 (s, 1H), 7.77 (d,  $J = 8.2$  Hz, 2H), 7.25 (d,  $J = 7.9$  Hz, 3H), 2.35 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  168.21, 141.49, 131.94, 129.18, 127.95, 21.41; **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_8\text{H}_{10}\text{NO}$  136.0762; Found 136.0760.

**2n: 4-methoxybenzamide<sup>3</sup>**



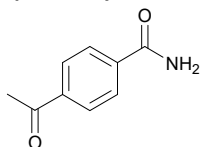
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.90 – 7.79 (m, 3H), 7.18 (s, 1H), 7.00 – 6.95 (m, 2H), 3.81 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  167.86, 162.02, 129.79, 126.97, 113.83, 55.77; **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_8\text{H}_{10}\text{NO}_2$  152.0711; Found 152.0722.

**2o: 4-chlorobenzamide<sup>2</sup>**



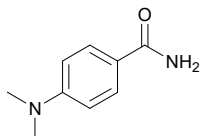
<sup>1</sup>H NMR (400 MHz, DMSO) δ 8.05 (s, 1H), 7.92 – 7.86 (m, 2H), 7.56 – 7.51 (m, 2H), 7.47 (s, 1H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 167.24, 136.53, 133.48, 129.86, 128.76; HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>7</sub>ClNO 156.0211; Found 156.0201.

**2p: 4-acetylbenzamide<sup>2</sup>**



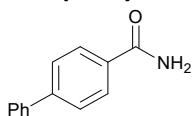
<sup>1</sup>H NMR (400 MHz, DMSO) δ 8.15 (s, 1H), 8.04 – 7.97 (m, 4H), 7.57 (s, 1H), 2.62 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 198.20, 167.53, 139.10, 138.56, 128.55, 128.21, 27.44; HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>10</sub>NO<sub>2</sub> 164.0706; Found 164.0701.

**2q: 4-(dimethylamino)benzamide<sup>6</sup>**



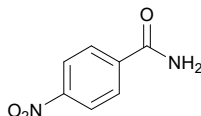
<sup>1</sup>H NMR (400 MHz, DMSO) δ 7.76 – 7.71 (m, 2H), 7.63 (s, 1H), 6.92 (s, 1H), 6.70 – 6.66 (m, 2H), 2.96 (s, 6H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 168.36, 152.57, 129.36, 121.41, 111.16, 40.19; HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>O 165.1022; Found 165.1019.

**2r: 4-phenyl benzamide<sup>6</sup>**



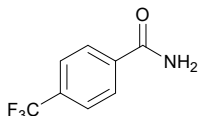
<sup>1</sup>H NMR (400 MHz, DMSO) δ 7.96 (d, J = 8.3 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 169.29, 140.36, 130.14, 129.40, 128.04, 127.27, 127.20, 126.37, 126.32; HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>12</sub>NO 198.0919; Found 198.0922.

**2s: 4-nitrobenzamide<sup>3</sup>**



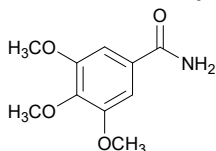
<sup>1</sup>H NMR (400 MHz, DMSO) δ 8.34 – 8.26 (m, 3H), 8.12 – 8.06 (m, 2H), 7.74 (s, 1H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 166.66, 149.50, 140.43, 129.37, 123.91; HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd for C<sub>7</sub>H<sub>7</sub>N<sub>2</sub>O<sub>3</sub> 167.0451; Found 167.0458.

**2t: 4-(trifluoromethyl)benzamide<sup>3</sup>**



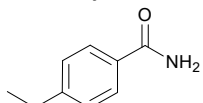
<sup>1</sup>H NMR (400 MHz, DMSO) δ 8.20 (s, 1H), 8.07 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.63 (s, 1H); <sup>13</sup>C NMR (101 MHz, DMSO) δ 167.13, 138.55, 131.61 (q, J = 31.8 Hz), 128.78, 125.73 (q, J = 3.8 Hz), 123.07; HRMS (ESI) m/z: [M+Na]<sup>+</sup> Calcd for C<sub>8</sub>H<sub>7</sub>F<sub>3</sub>NONa 212.0299; Found 212.0297.

**2u: 3,4,5-trimethoxybenzamide<sup>7</sup>**



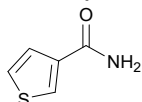
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.95 (s, 1H), 7.33 (s, 1H), 7.22 (s, 2H), 3.82 (s, 6H), 3.70 (s, 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  167.75, 152.95, 140.40, 129.90, 105.51, 60.50, 56.42; **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{10}\text{H}_{13}\text{NO}_4$  212.0928; Found 212.0929.

**2v: 4-ethylbenzamide<sup>15</sup>**



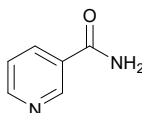
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.90 (s, 1H), 7.81 (d,  $J = 8.2$  Hz, 2H), 7.28 (d,  $J = 8.2$  Hz, 3H), 2.64 (q,  $J = 7.6$  Hz, 2H), 1.19 (t,  $J = 7.6$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  168.28, 147.66, 132.23, 128.04, 128.00, 28.48, 15.82; **HRMS (ESI) m/z:**  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_9\text{H}_{11}\text{NONa}$  172.0738; Found 172.0733.

**2w: thiophene-3-carboxamide<sup>8</sup>**



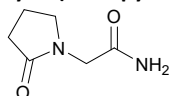
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  8.13 (dd,  $J = 3.0, 1.3$  Hz, 1H), 7.78 (s, 1H), 7.56 (dd,  $J = 5.0, 3.0$  Hz, 1H), 7.48 (dd,  $J = 5.0, 1.3$  Hz, 1H), 7.23 (s, 1H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  164.12, 138.47, 129.45, 127.61, 127.00; **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_5\text{H}_5\text{NOS}$  128.0165; Found 125.0168.

**2x: nicotinamide<sup>2</sup>**



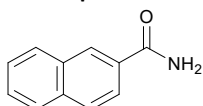
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  9.04 (dd,  $J = 2.2, 0.7$  Hz, 1H), 8.70 (dd,  $J = 4.8, 1.7$  Hz, 1H), 8.24 – 8.13 (m, 2H), 7.61 (s, 1H), 7.50 (ddd,  $J = 7.9, 4.8, 0.8$  Hz, 1H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  166.90, 152.35, 149.13, 135.60, 130.11, 123.86; **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_6\text{H}_7\text{N}_2\text{O}$  123.0558; Found 123.0555.

**2y: 2-(2-oxopyrrolidin-1-yl)acetamide<sup>13</sup>**



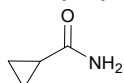
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.39 (s, 1H), 7.09 (s, 1H), 3.75 (s, 2H), 3.36 (t,  $J = 7.1$  Hz, 2H), 2.27 – 2.18 (m, 2H), 1.98 – 1.88 (m, 2H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  174.86, 170.16, 47.73, 45.27, 30.43, 17.80; **HRMS (ESI) m/z:**  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_6\text{H}_{10}\text{N}_2\text{O}_2\text{Na}$  165.0634; Found 165.0634.

**2z: 2-naphthamide<sup>2</sup>**



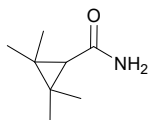
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  8.50 (s, 1H), 8.16 (s, 1H), 8.06 – 7.93 (m, 4H), 7.66 – 7.55 (m, 2H), 7.49 (s, 1H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  168.43, 134.62, 132.61, 132.10, 129.32, 128.27, 128.22, 128.04, 128.02, 127.10, 124.86; **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{11}\text{H}_9\text{NO}$  172.0757; Found 172.0756.

**2aa: cyclopropanecarboxamide<sup>2</sup>**



$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.51 (s, 1H), 6.75 (s, 1H), 1.51 (tt,  $J = 7.3, 5.2$  Hz, 1H), 1.20 (dd,  $J = 17.1, 9.9$  Hz, 1H), 0.63 (dd,  $J = 6.0, 4.6$  Hz, 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  175.09, 13.69, 6.66; **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_4\text{H}_8\text{NO}$  86.0605; Found 86.0599.

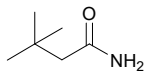
**2bb: 2,2,3,3-tetramethylcyclopropanecarboxamide<sup>9</sup>**



$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.21 (s, 1H), 6.48 (s, 1H), 1.18 (s, 6H), 1.14 (s, 6H), 1.12 (s, 1H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  173.36, 35.30, 23.72, 16.90; **HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_8\text{H}_{16}\text{NO}$  142.1226; Found 142.1223.

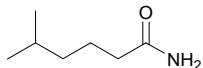
**2cc: 3,3-dimethylbutanamide<sup>10</sup>**





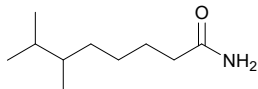
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.31 – 7.06 (m, 1H), 6.61 (d,  $J$  = 42.5 Hz, 1H), 1.92 (s, 2H), 0.96 (s, 9H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  173.49, 48.98, 30.63, 30.16; **HRMS (ESI) m/z**:  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_6\text{H}_{13}\text{NONa}$  138.0895; Found 138.0891.

**2dd: 5-methylhexanamide**<sup>11</sup>



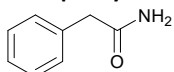
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.61 (s, 1H), 7.12 (s, 1H), 3.32 – 3.19 (m, 1H), 2.46 (t,  $J$  = 7.2 Hz, 2H), 1.75 – 1.37 (m, 4H), 0.81 (dt,  $J$  = 11.2, 7.4 Hz, 6H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  170.99, 42.78, 21.44, 16.97, 13.93, 12.21; **HRMS (ESI) m/z**:  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_7\text{H}_{16}\text{NO}$  130.1226; Found 130.1223.

**2ee: 6,7-dimethyloctanamide**<sup>12</sup>



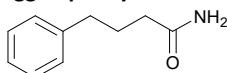
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.67 (s, 1H), 7.13 (s, 1H), 3.46 (dd,  $J$  = 8.7, 5.5 Hz, 1H), 2.53 – 2.50 (m, 3H), 1.69 – 1.08 (m, 6H), 0.86 – 0.82 (m, 9H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  171.08, 38.66, 37.04, 27.46, 26.04, 23.34, 22.78, 22.67, 22.45; **HRMS (ESI) m/z**:  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{10}\text{H}_{21}\text{NONa}$  194.1521; Found 194.1518.

**2ff: 2-phenylacetamide**<sup>6</sup>



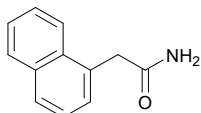
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.47 (s, 1H), 7.32 – 7.19 (m, 5H), 6.89 (s, 1H), 3.37 (s, 2H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  172.67, 136.96, 129.51, 128.60, 126.71, 42.72; **HRMS (ESI) m/z**:  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_8\text{H}_9\text{NONa}$  158.0582; Found 158.0576.

**2gg: 4-phenylbutanamide**<sup>3</sup>



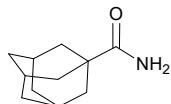
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.32 – 7.23 (m, 3H), 7.21 – 7.15 (m, 3H), 6.74 (s, 1H), 2.61 – 2.53 (m, 2H), 2.07 (t,  $J$  = 7.5 Hz, 2H), 1.85 – 1.73 (m, 2H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  174.48, 142.29, 128.76, 128.72, 126.18, 35.17, 35.01, 27.35; **HRMS (ESI) m/z**:  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{10}\text{H}_{13}\text{NONa}$  186.0895; Found 186.0890.

**2hh: 2-(naphthalen-1-yl)acetamide**<sup>6</sup>



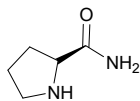
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  8.13 – 8.05 (m, 1H), 7.93 (dd,  $J$  = 7.1, 2.3 Hz, 1H), 7.82 (dd,  $J$  = 7.4, 1.8 Hz, 1H), 7.60 – 7.41 (m, 5H), 6.99 (s, 1H), 3.87 (s, 2H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  172.59, 133.79, 133.41, 132.48, 128.80, 128.29, 127.43, 126.36, 126.05, 125.96, 125.94, 124.76, 40.62; **HRMS (ESI) m/z**:  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{12}\text{H}_{12}\text{NO}$  186.0913; Found 186.0916.

**2ii: adamantane-1-carboxamide**<sup>6</sup>



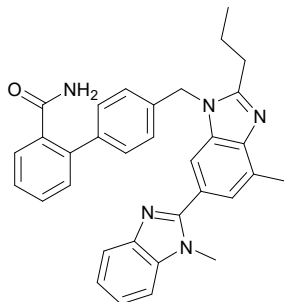
$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  6.80 (d,  $J$  = 111.4 Hz, 2H), 1.94 (s, 3H), 1.74 (d,  $J$  = 2.7 Hz, 6H), 1.70 – 1.59 (m, 6H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  179.80, 39.30, 39.21, 36.62, 28.14; **HRMS (ESI) m/z**:  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{11}\text{H}_{18}\text{NO}$  180.1388; Found 180.1366.

**2jj: (R)-pyrrolidine-2-carboxamide**<sup>14</sup> (from (R)-N-phenylpyrrolidine-2-carboxamide)



$^1\text{H NMR}$  (400 MHz, DMSO)  $\delta$  7.17 (d,  $J$  = 144.4 Hz, 2H), 3.42 (dd,  $J$  = 8.7, 5.5 Hz, 1H), 3.07 – 2.69 (m, 3H), 2.02 – 1.83 (m, 1H), 1.70 – 1.52 (m, 3H);  $^{13}\text{C NMR}$  (101 MHz, DMSO)  $\delta$  177.46, 60.67, 47.22, 30.96, 26.29; **HRMS (ESI) m/z**:  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_5\text{H}_{11}\text{N}_2\text{O}$  115.0866; Found 115.0862.

**2kk: 4'-((1,7'-dimethyl-2'-propyl-1H,3'H-[2,5'-bibenzo[d]imidazol]-3'-yl)methyl)-[1,1'-biphenyl]-2-carboxamide**<sup>16</sup>



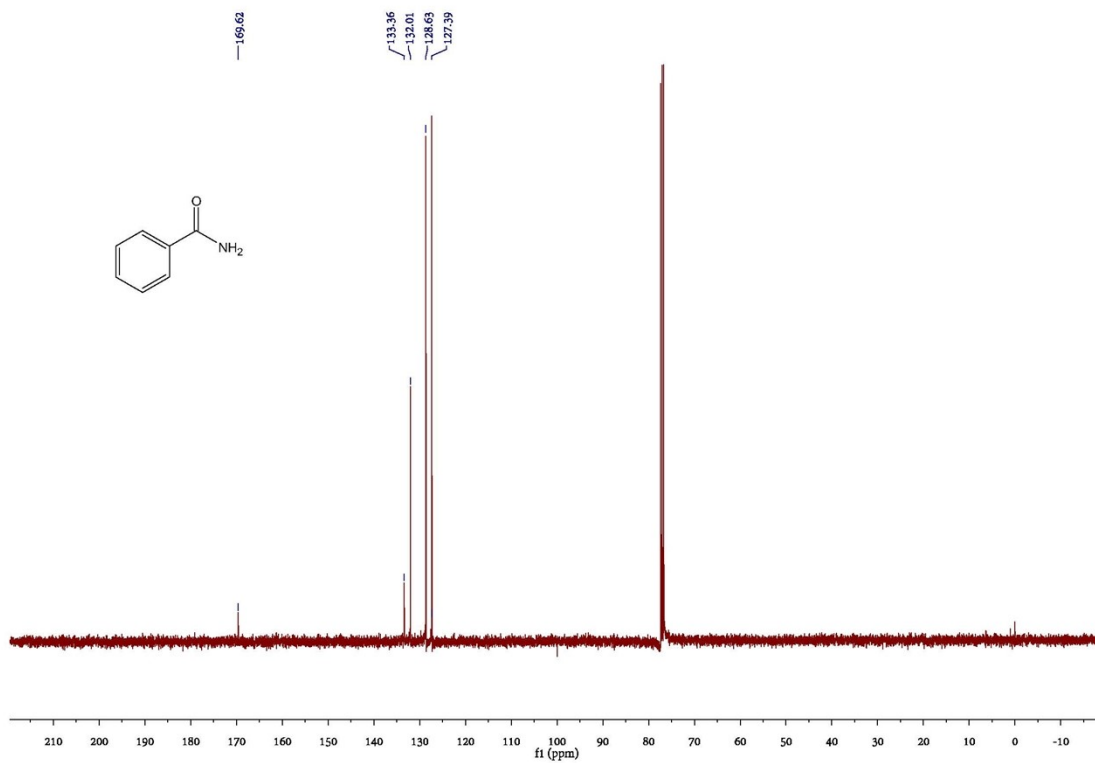
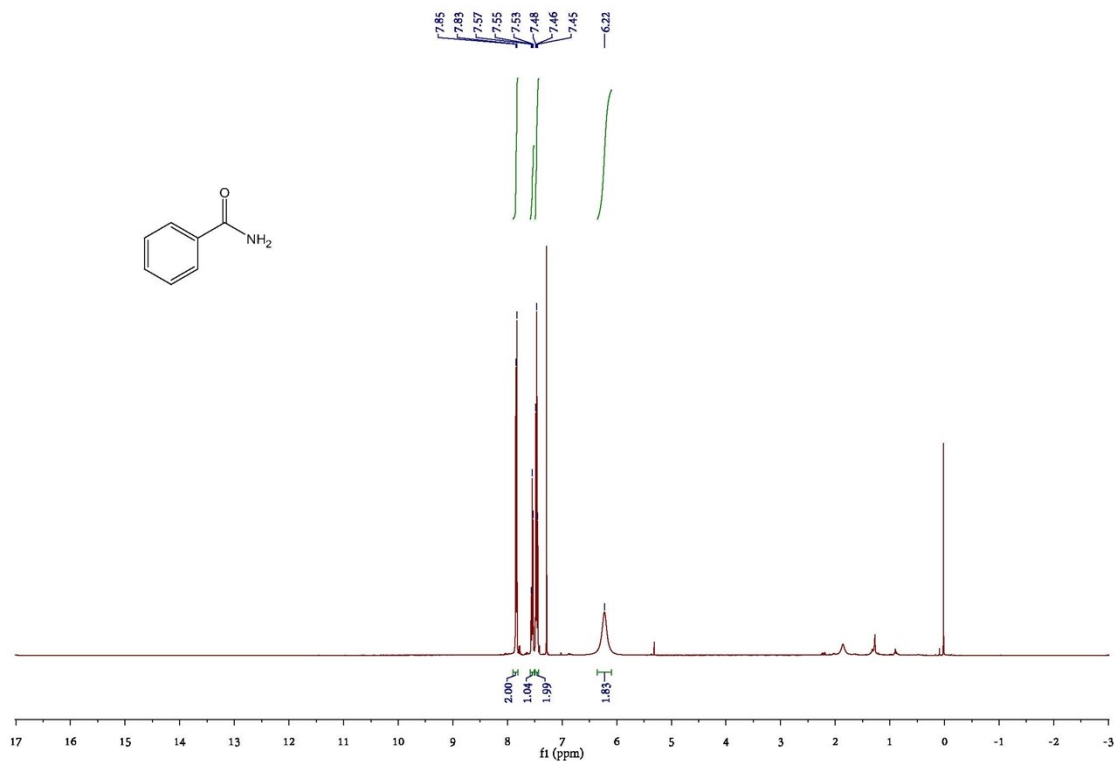
**<sup>1</sup>H NMR** (400 MHz, DMSO)  $\delta$  7.76 (s, 1H), 7.68 – 7.56 (m, 3H), 7.51 – 7.15 (m, 11H), 5.62 (s, 1H), 3.83 (s, 1H), 2.94 (t,  $J$  = 7.6 Hz, 1H), 2.64 (s, 1H), 1.91 – 1.76 (m, 1H), 1.02 (t,  $J$  = 7.4 Hz, 3H); **<sup>13</sup>C NMR** (101 MHz, DMSO)  $\delta$  171.50, 156.63, 154.50, 143.14, 142.96, 140.18, 138.77, 137.81, 137.13, 136.41, 135.17, 130.28, 129.63, 129.19, 128.71, 127.93, 127.50, 126.83, 123.76, 123.68, 122.49, 122.24, 119.15, 110.86, 109.72, 46.49, 32.23, 29.20, 21.21, 16.93, 14.33. **HRMS (ESI) m/z:** [M+Na]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>31</sub>N<sub>5</sub>ONa 536.2421; Found 536.2392.

## References

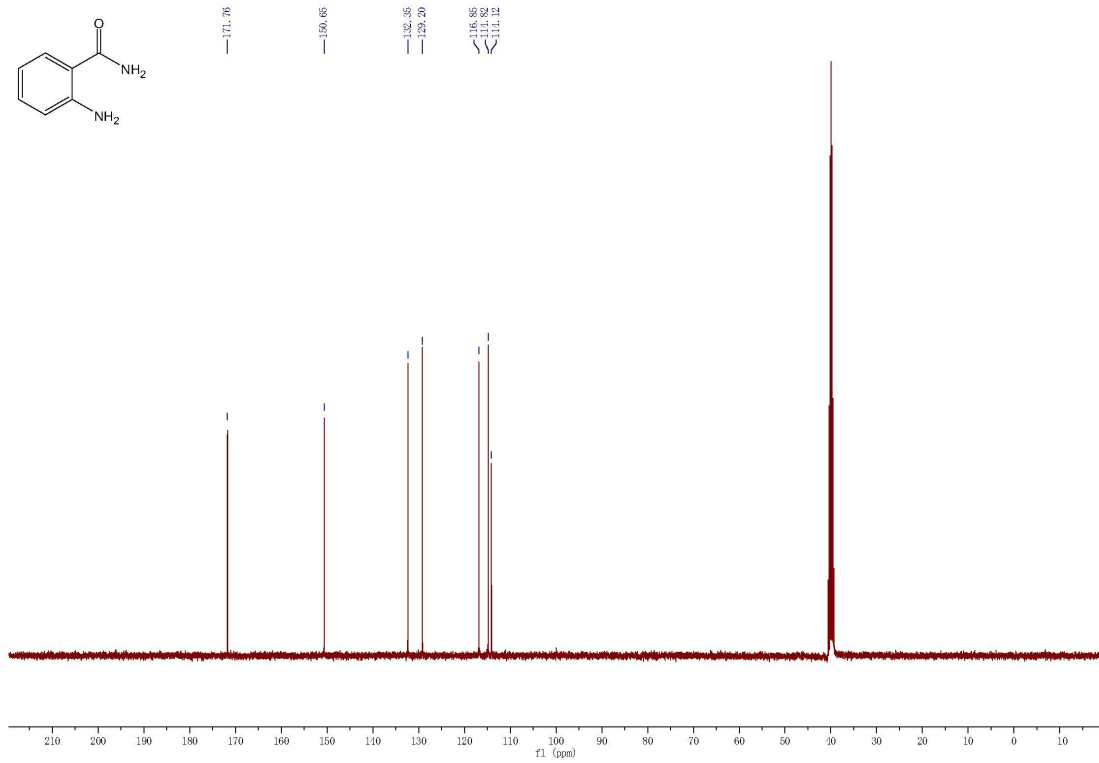
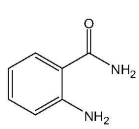
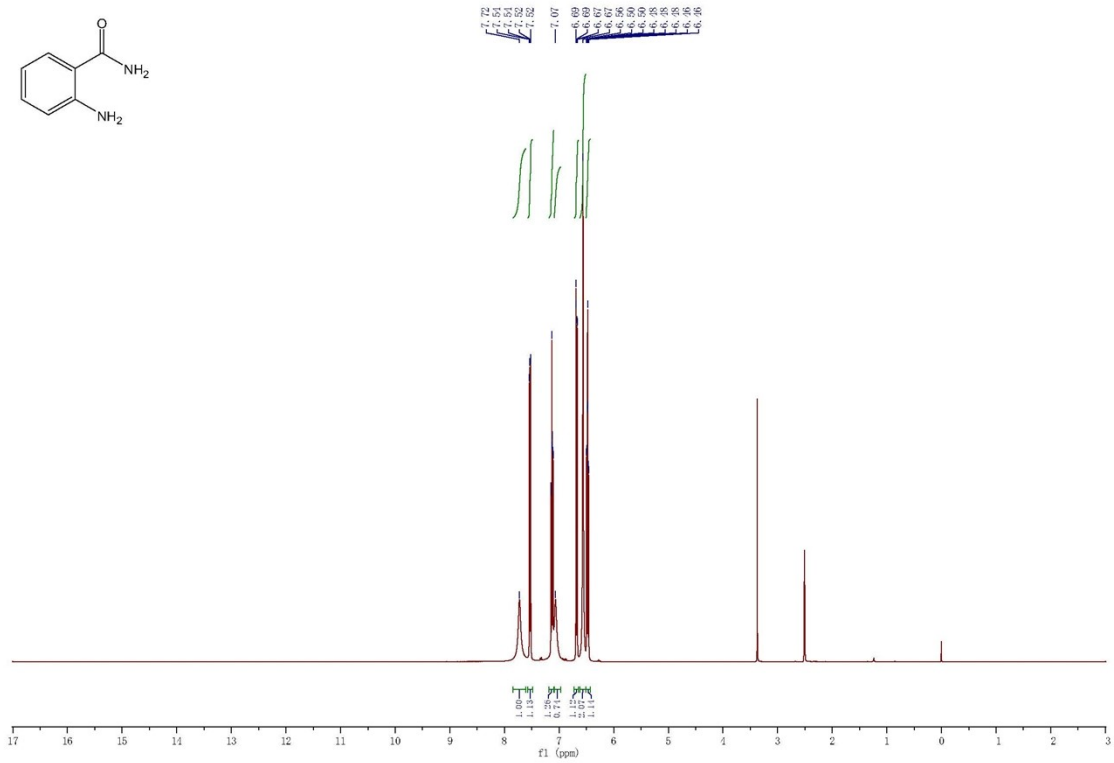
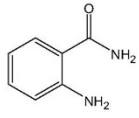
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# $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra for the products

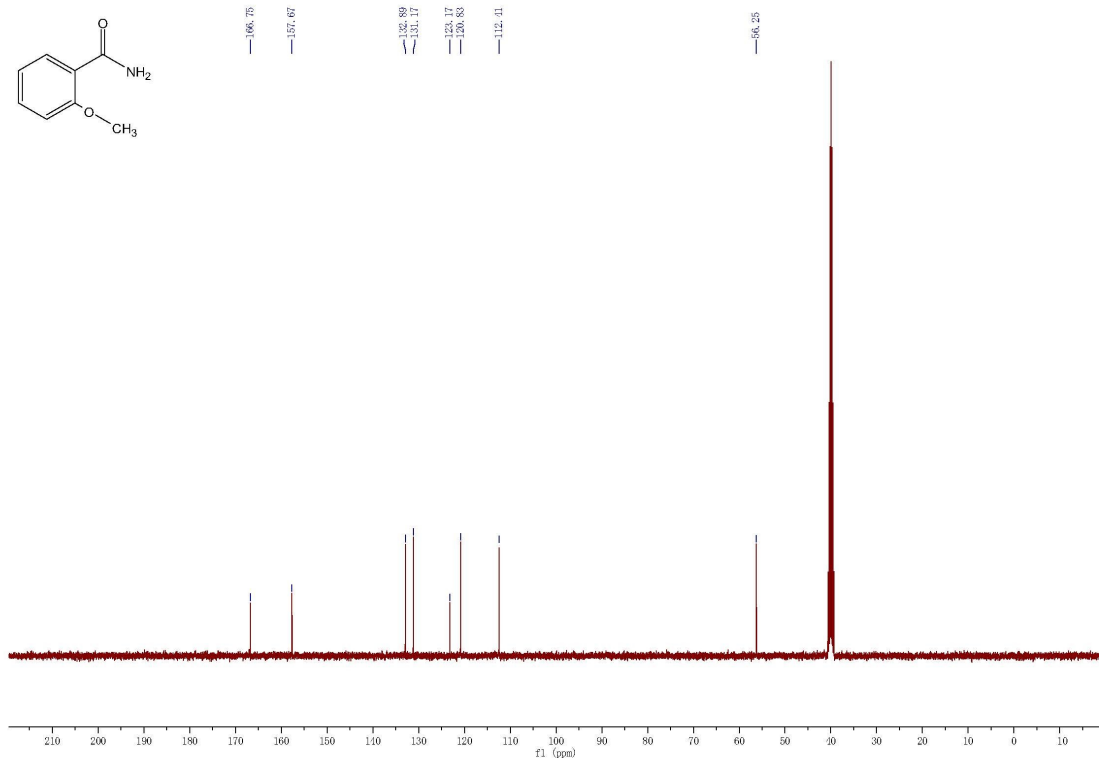
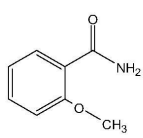
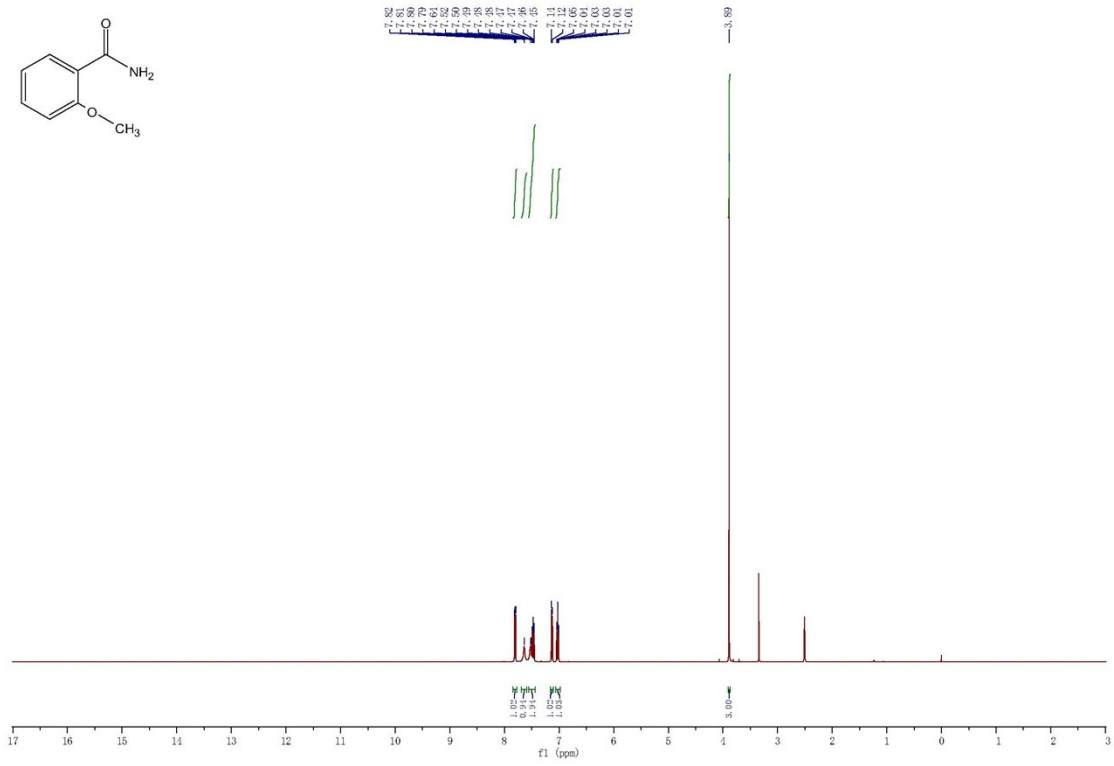
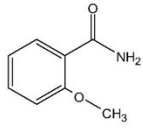
2a: benzamide



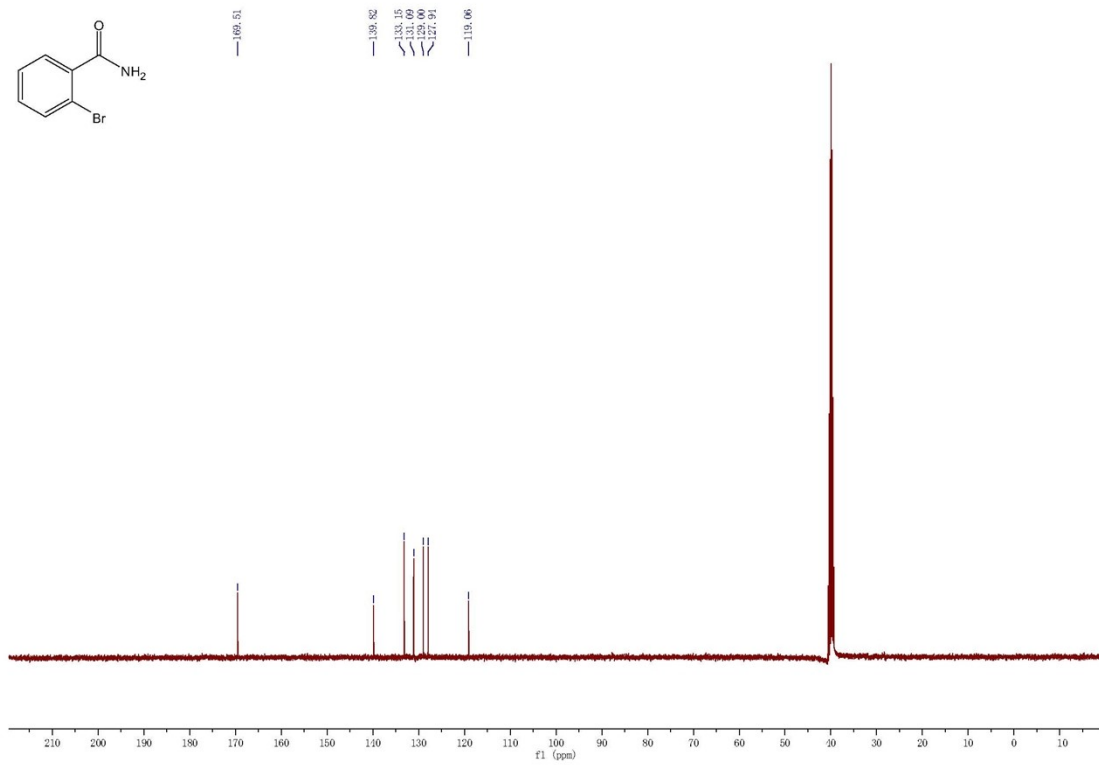
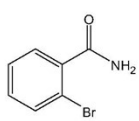
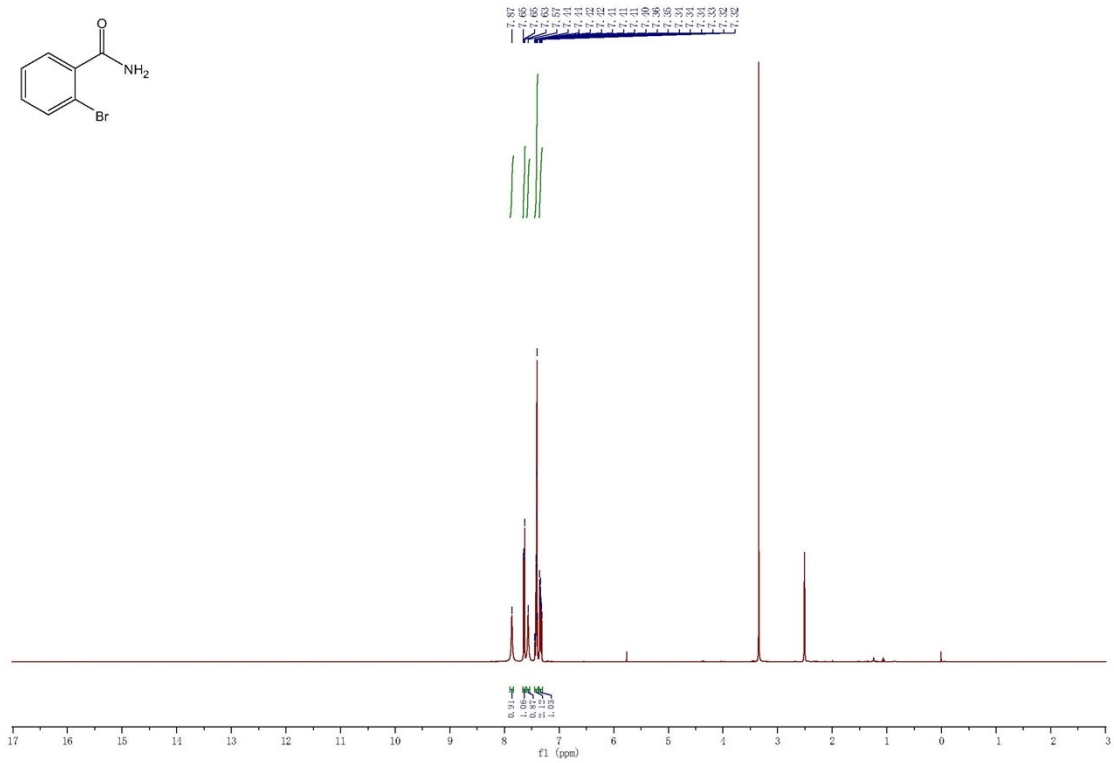
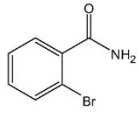
**2b: 2-aminobenzamide**



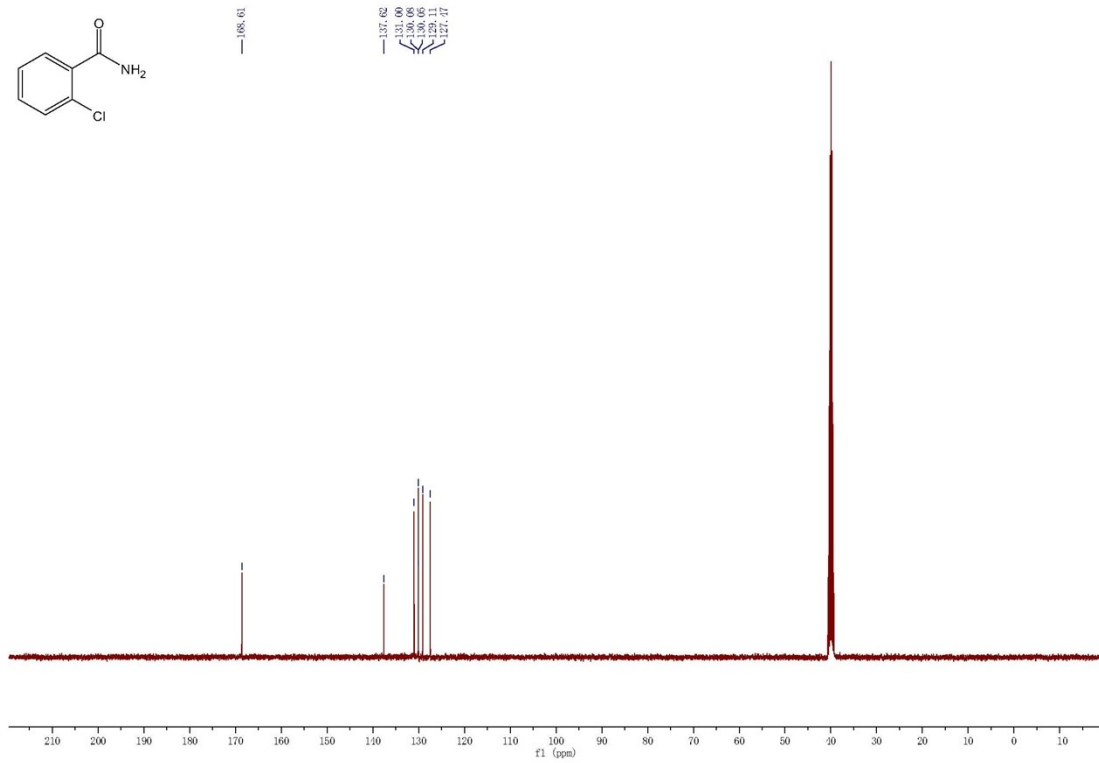
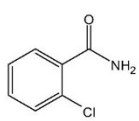
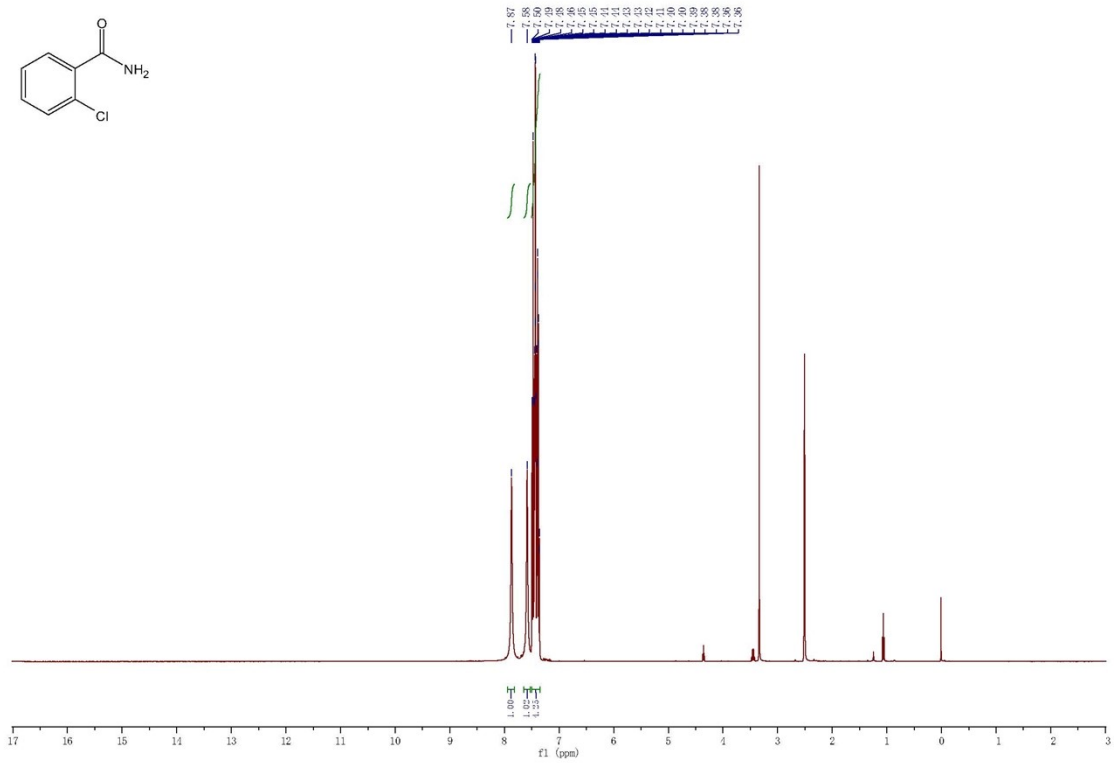
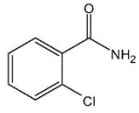
2c: 2-methoxybenzamide



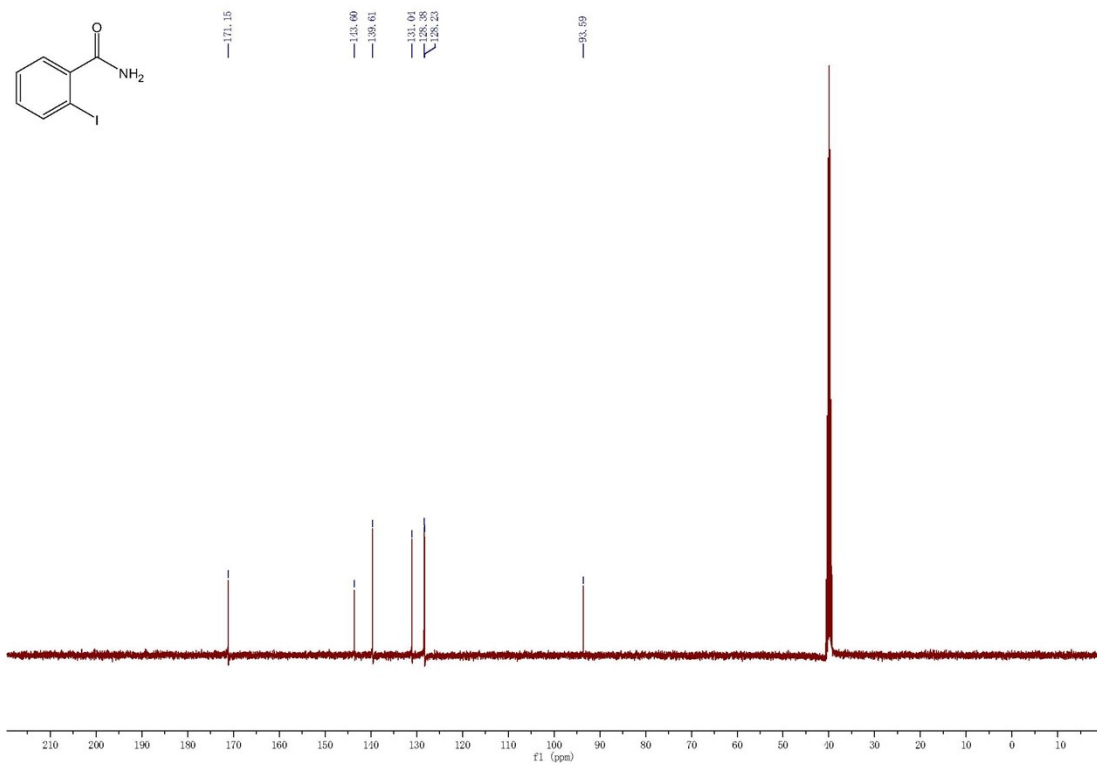
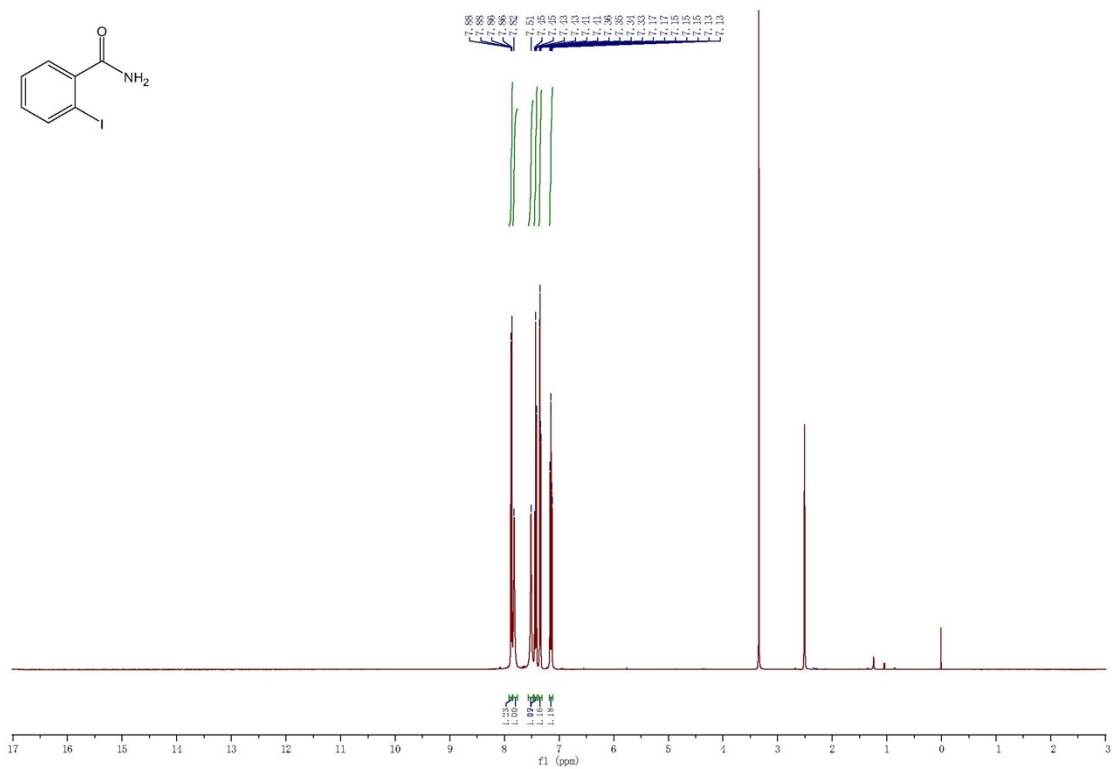
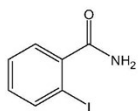
2d: 2-bromobenzamide



2e: 2-chlorobenzamide

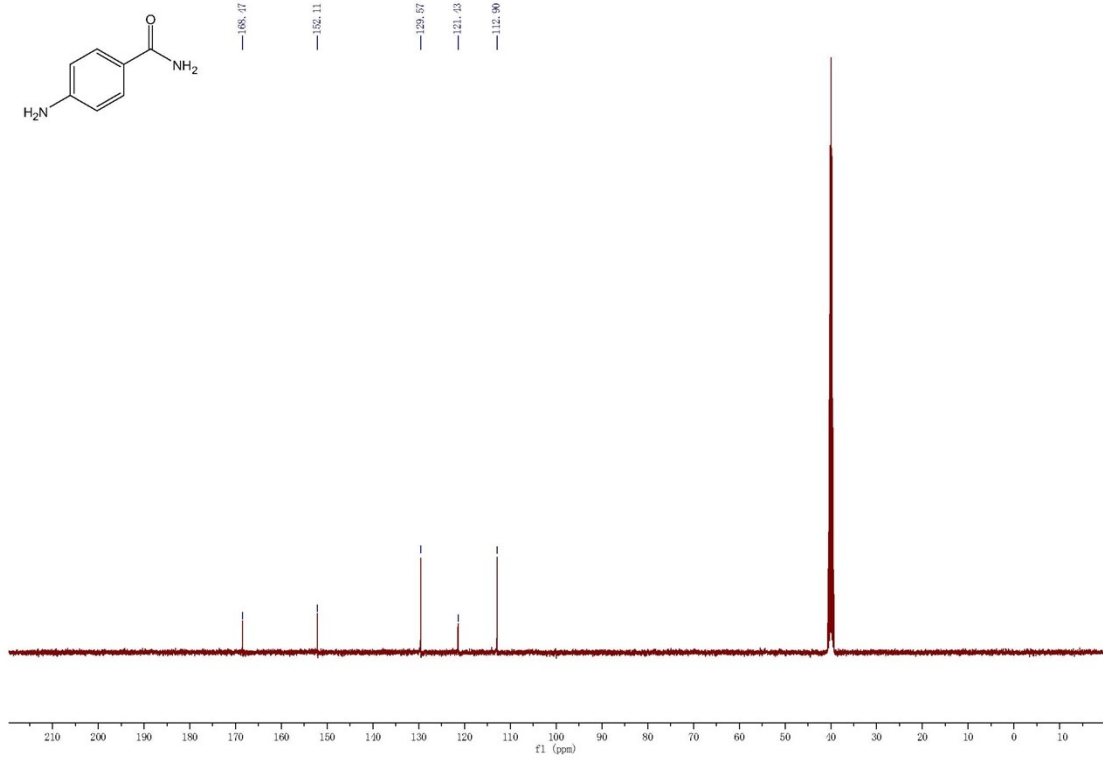
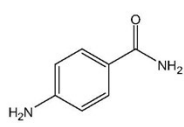
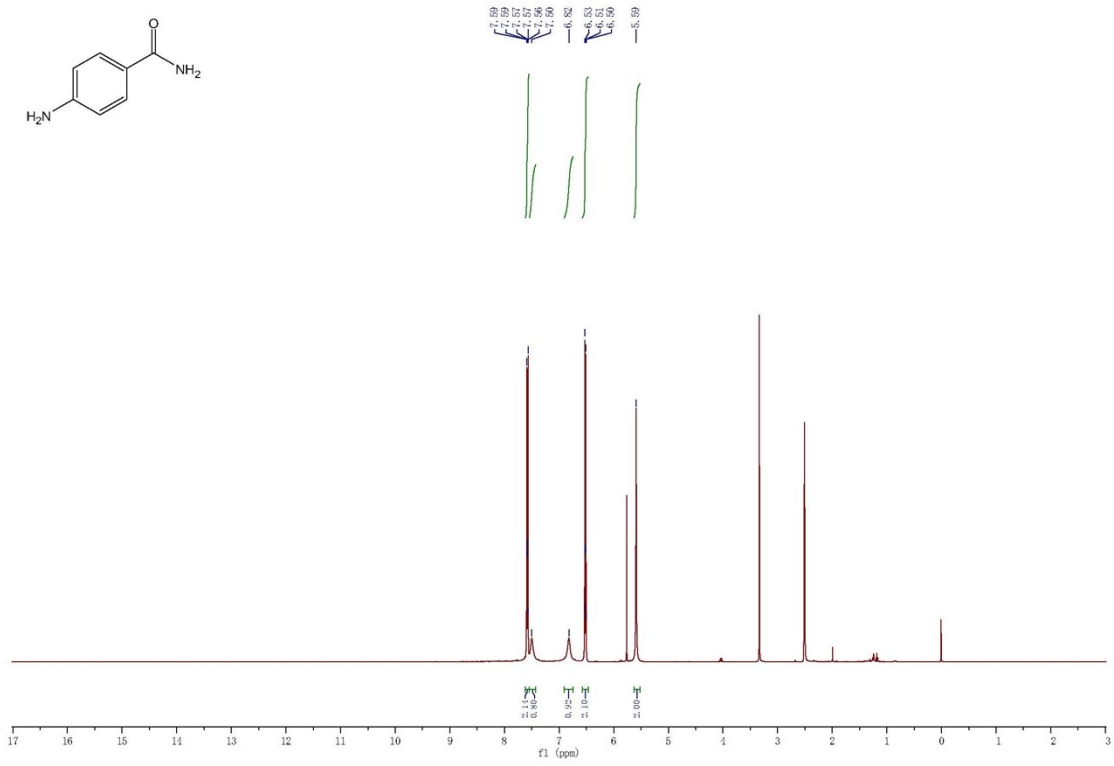
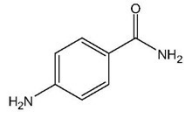


2f: 2-iodobenzamide

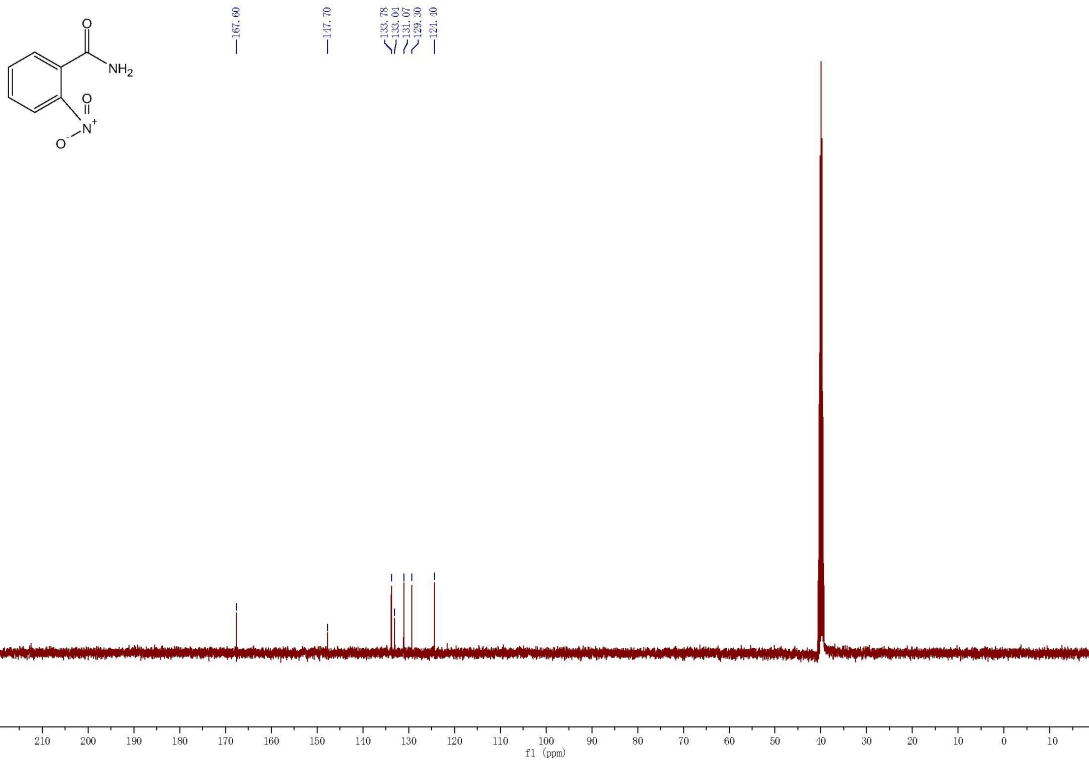
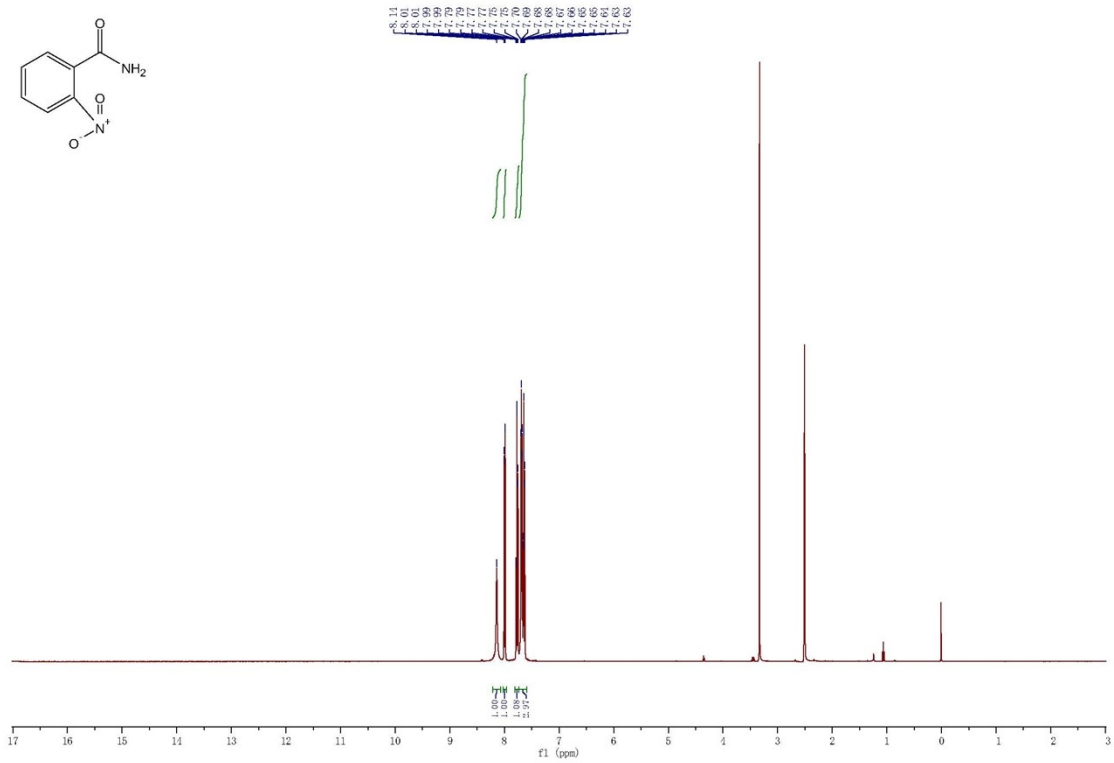
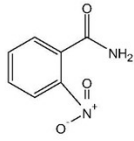




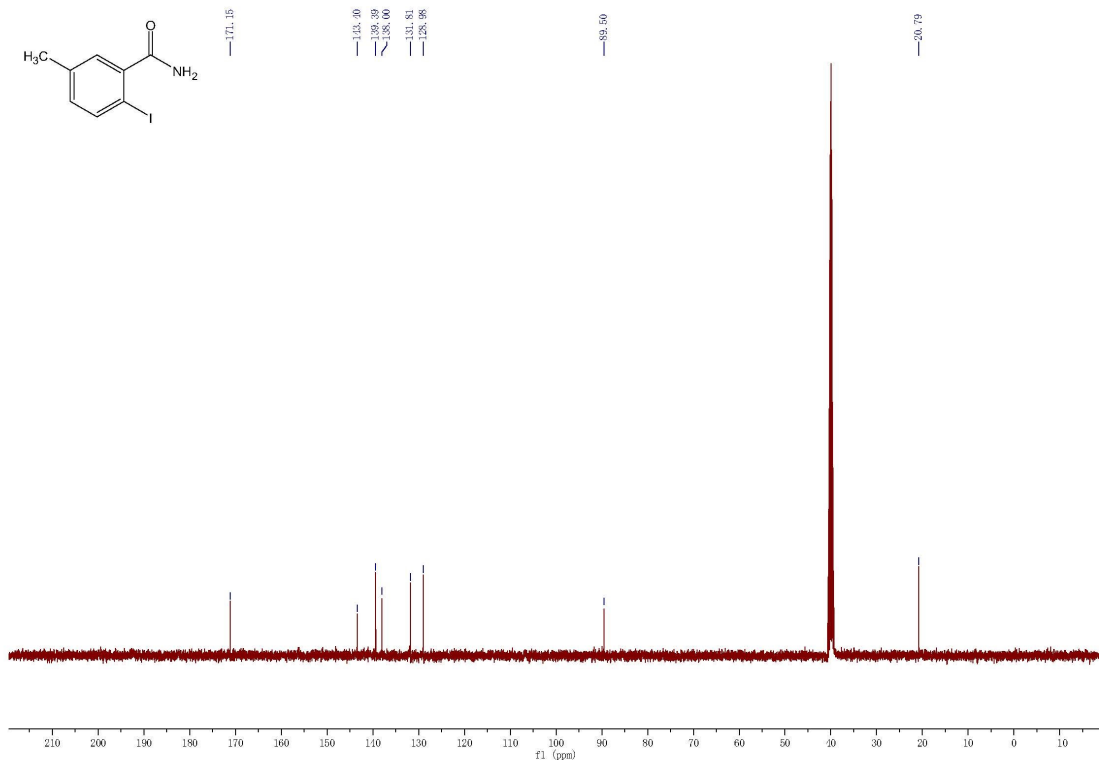
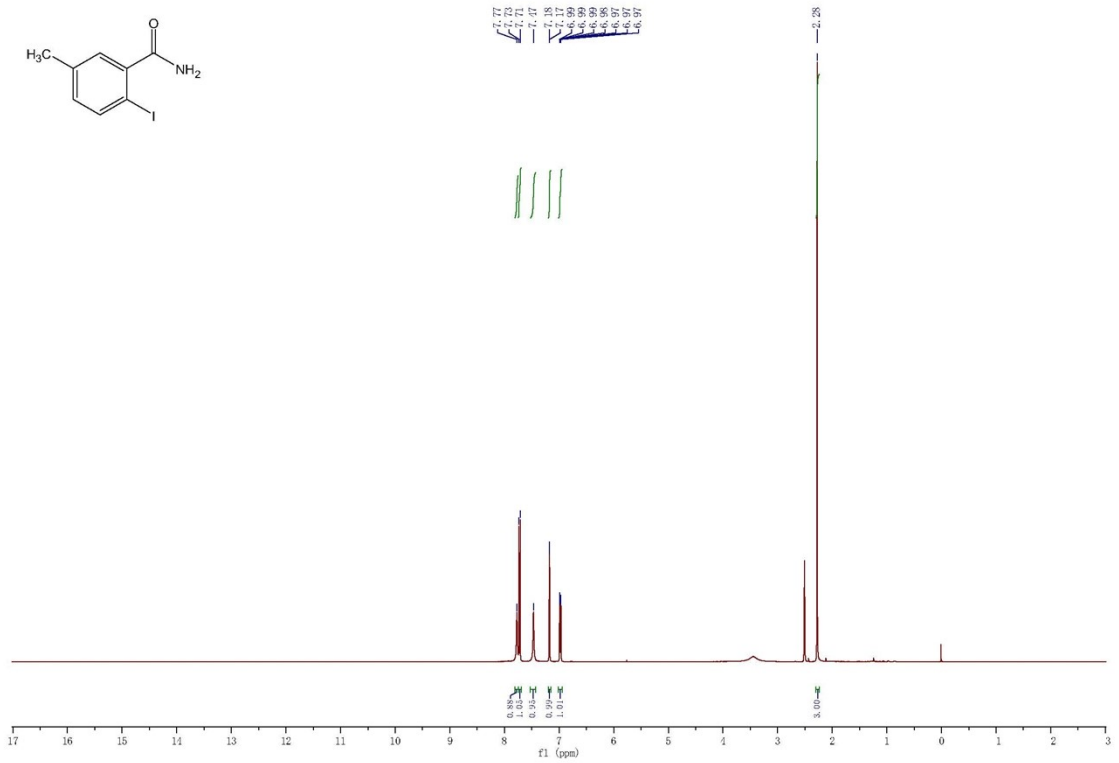
2g: 4-aminobenzamide



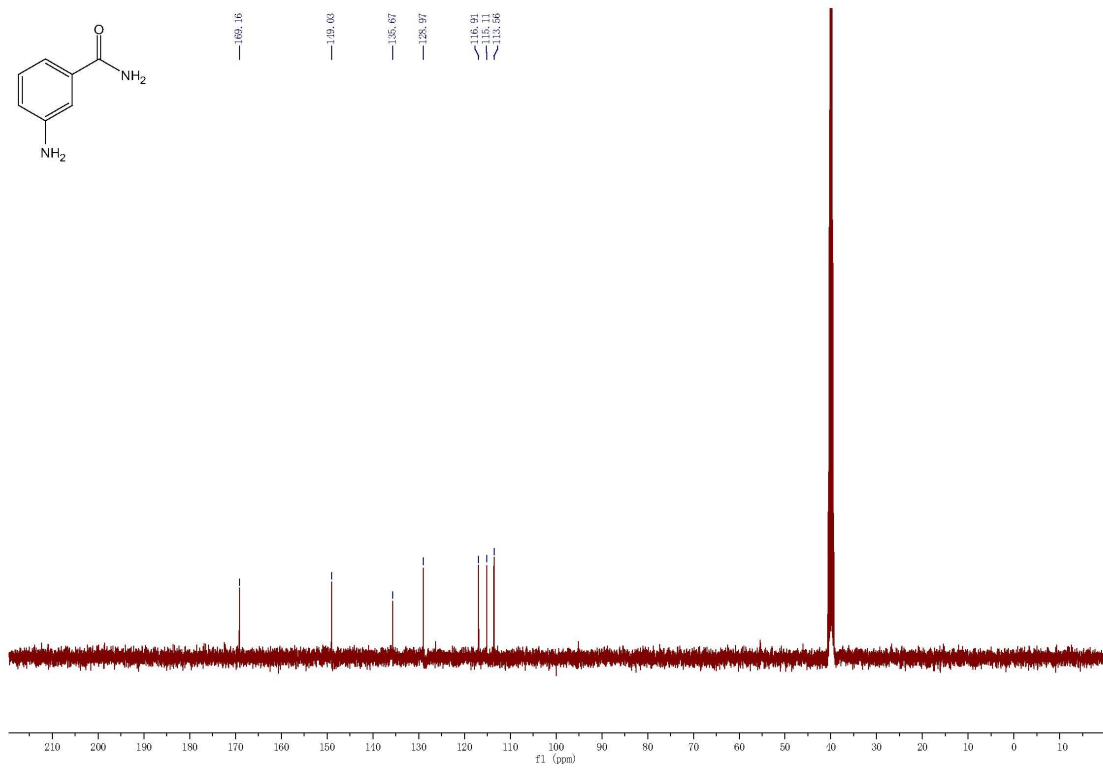
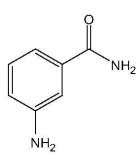
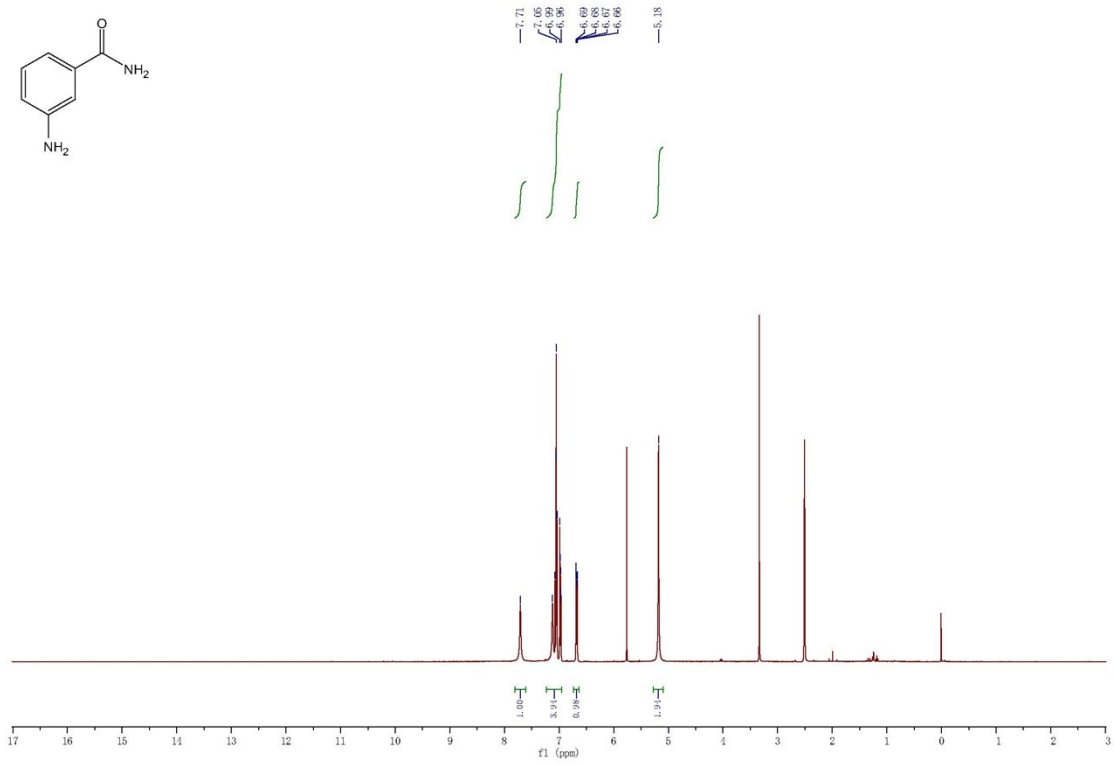
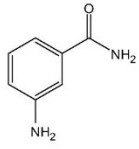
2h: 2-nitrobenzamide



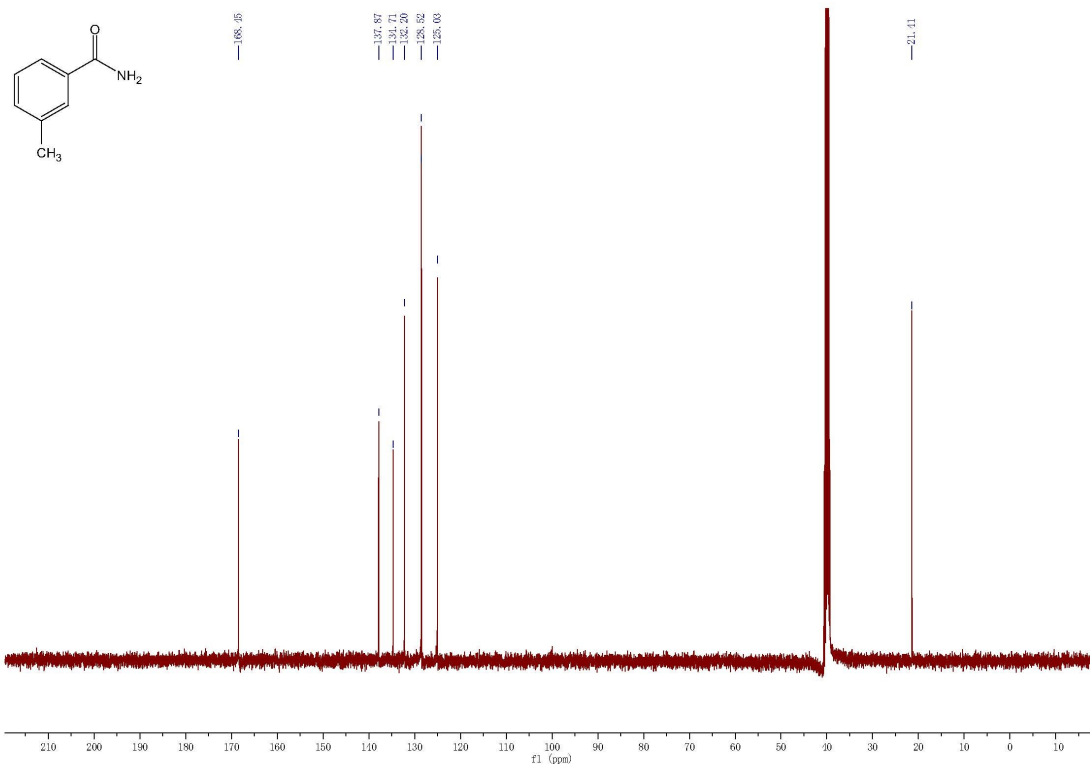
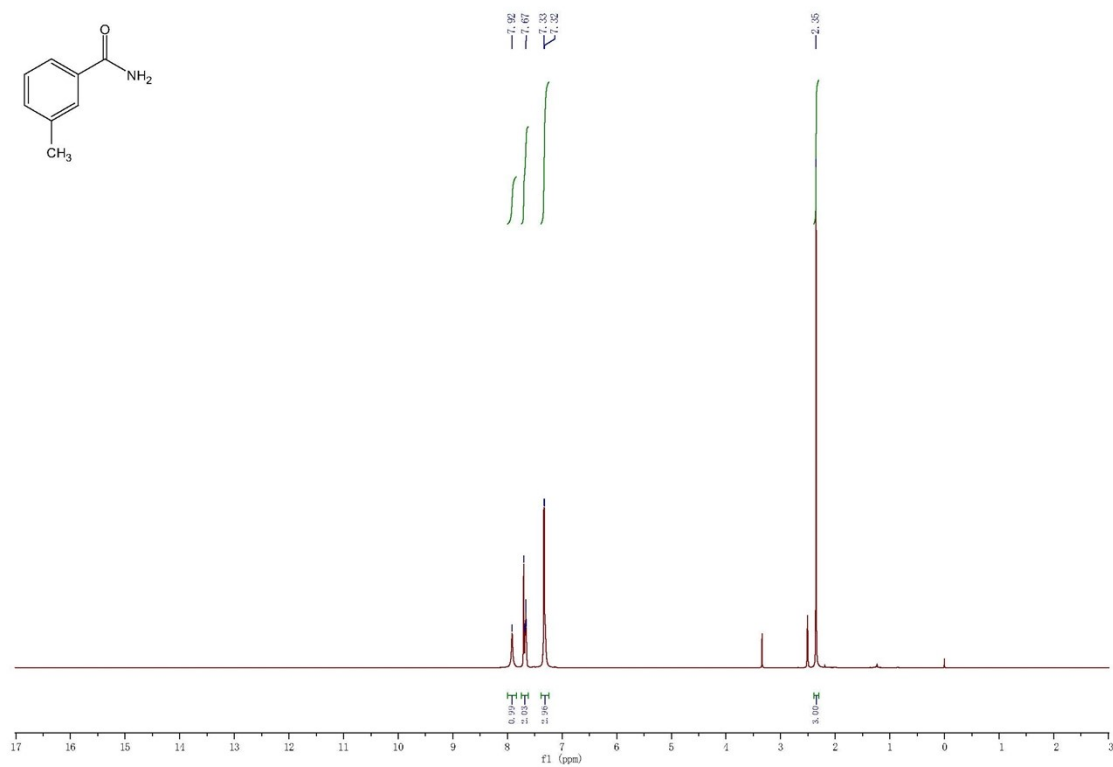
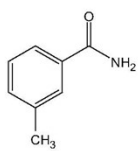
2i: 2-iodo-5-methylbenzamide



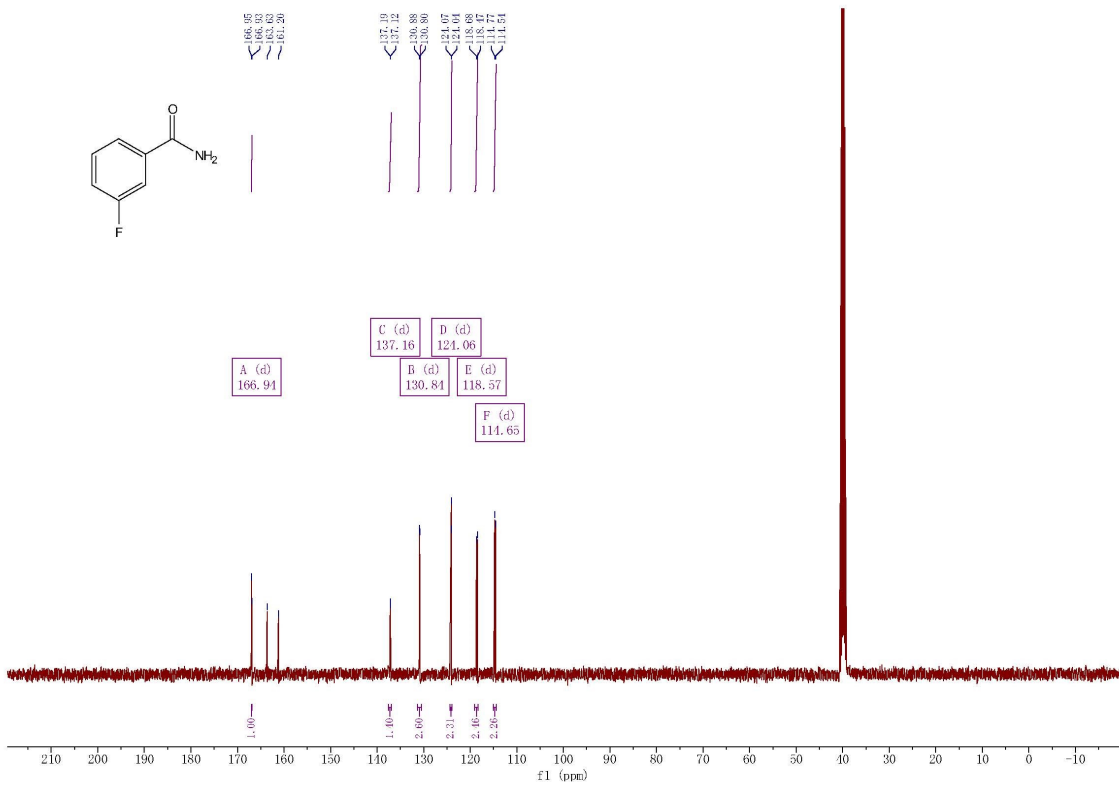
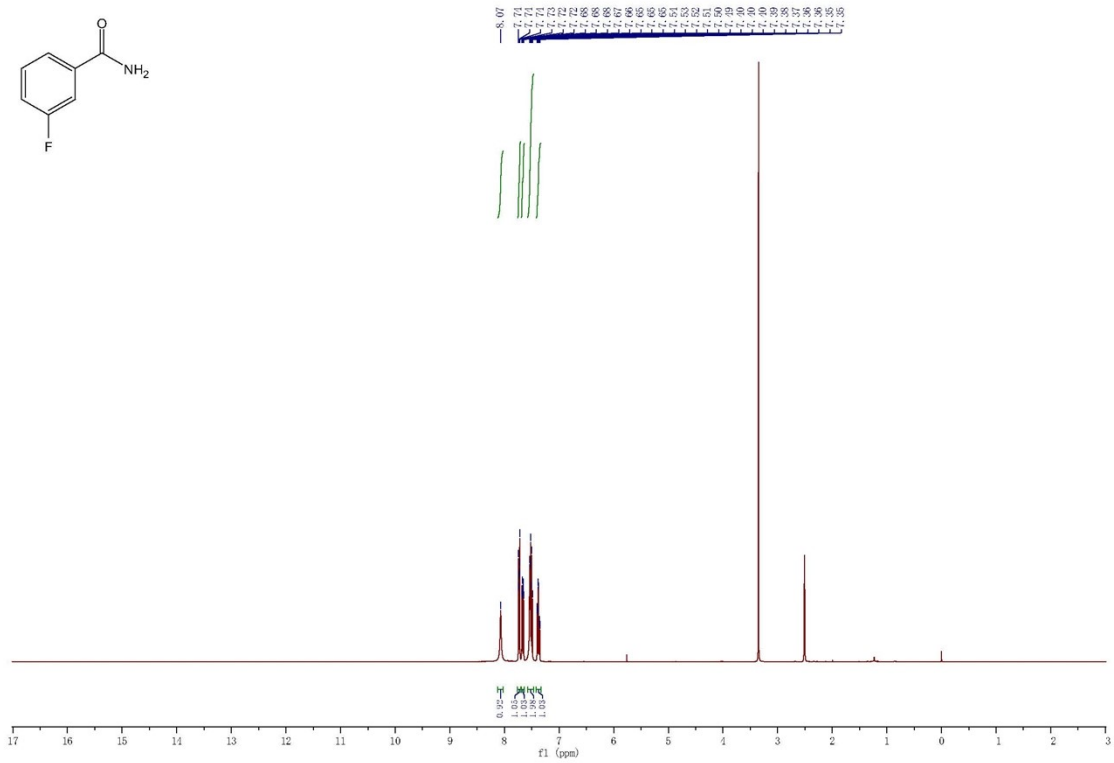
2j: 3-aminobenzamide



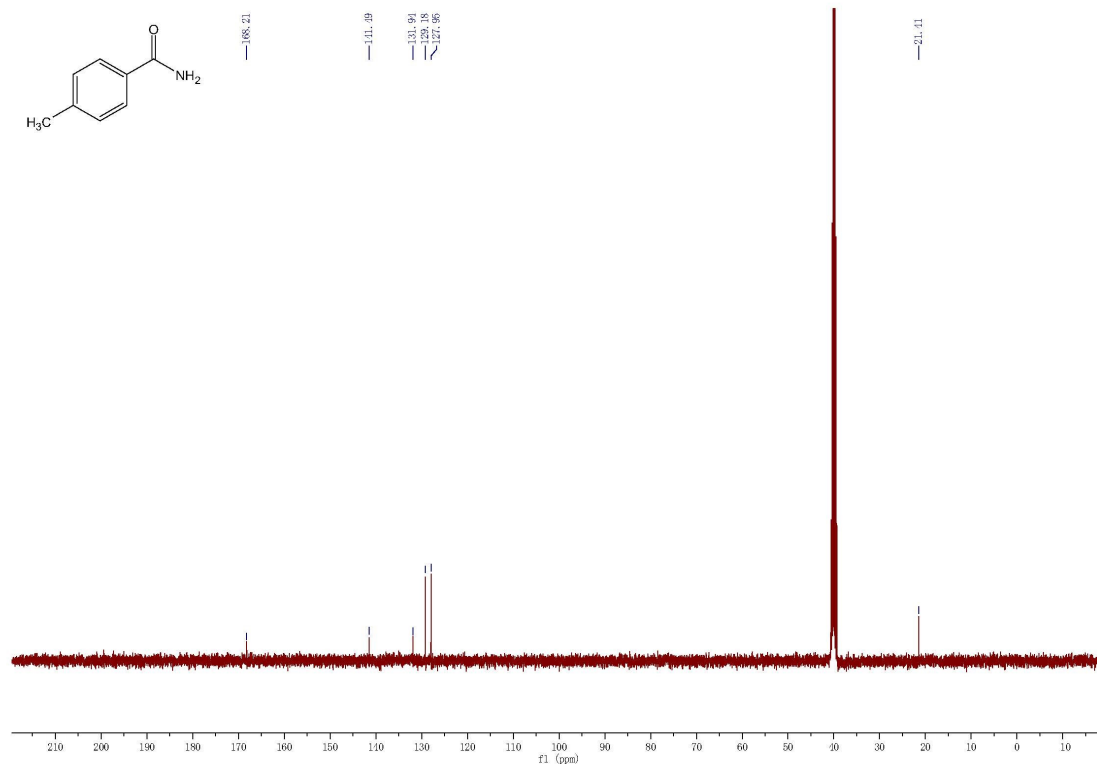
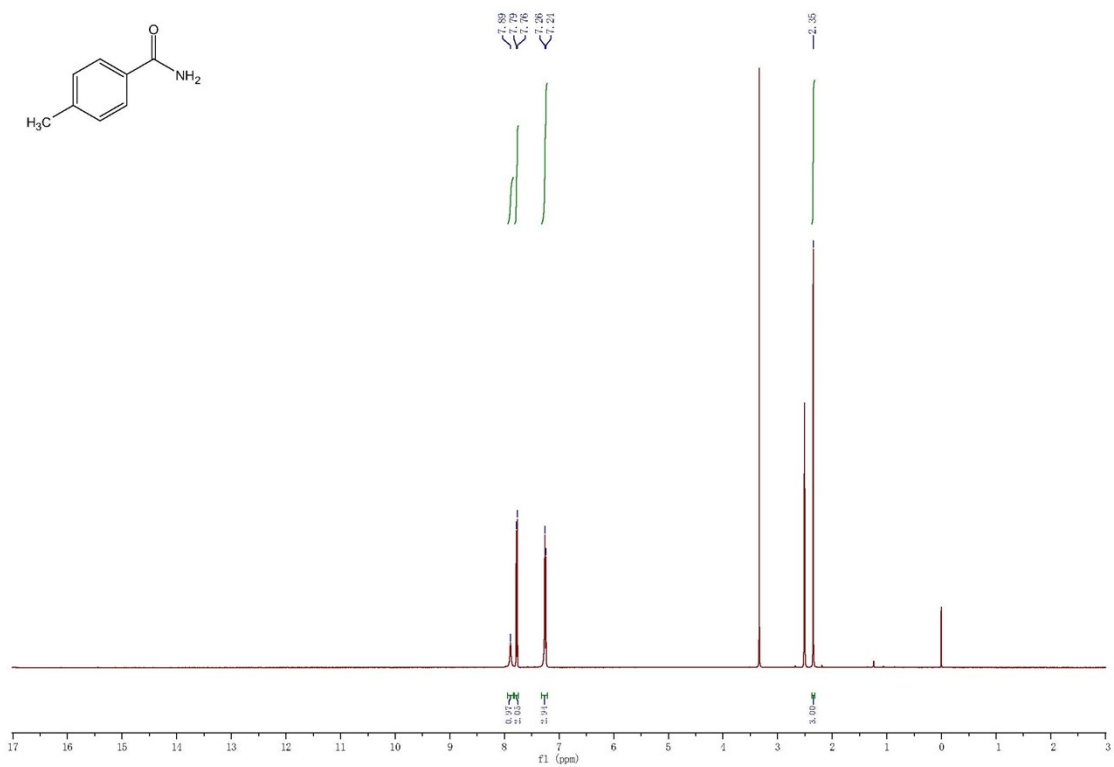
**2k: 3-methylbenzamide**



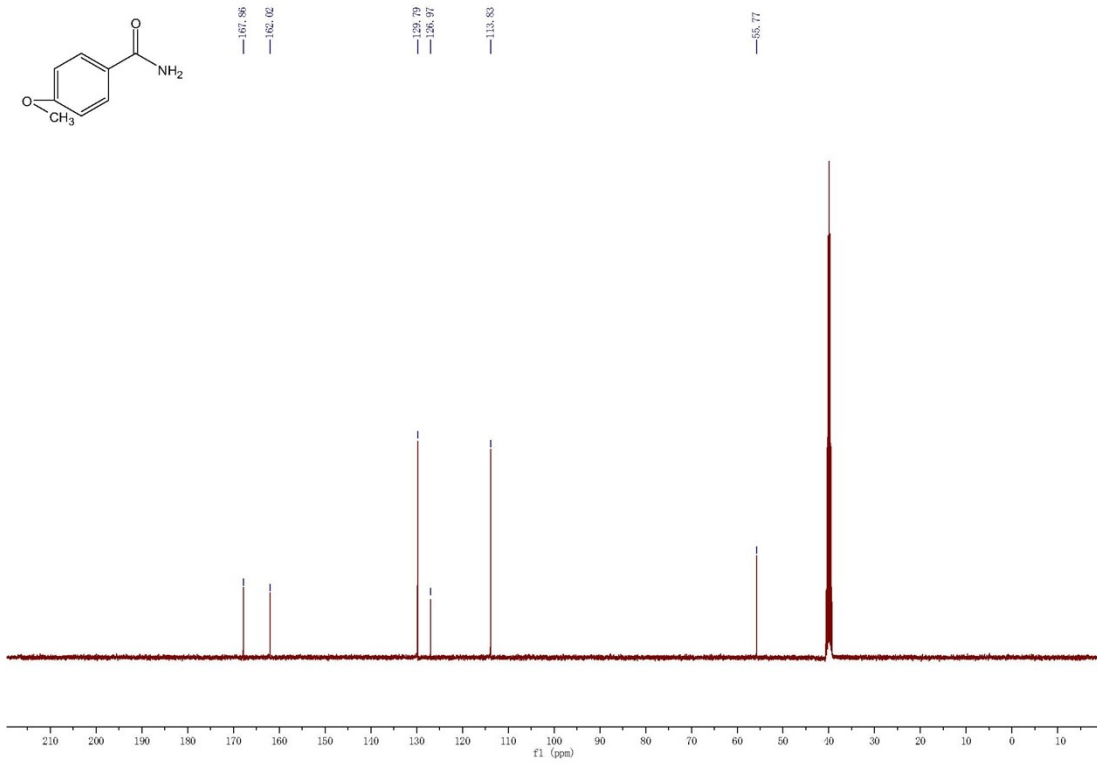
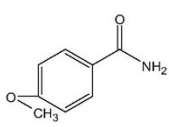
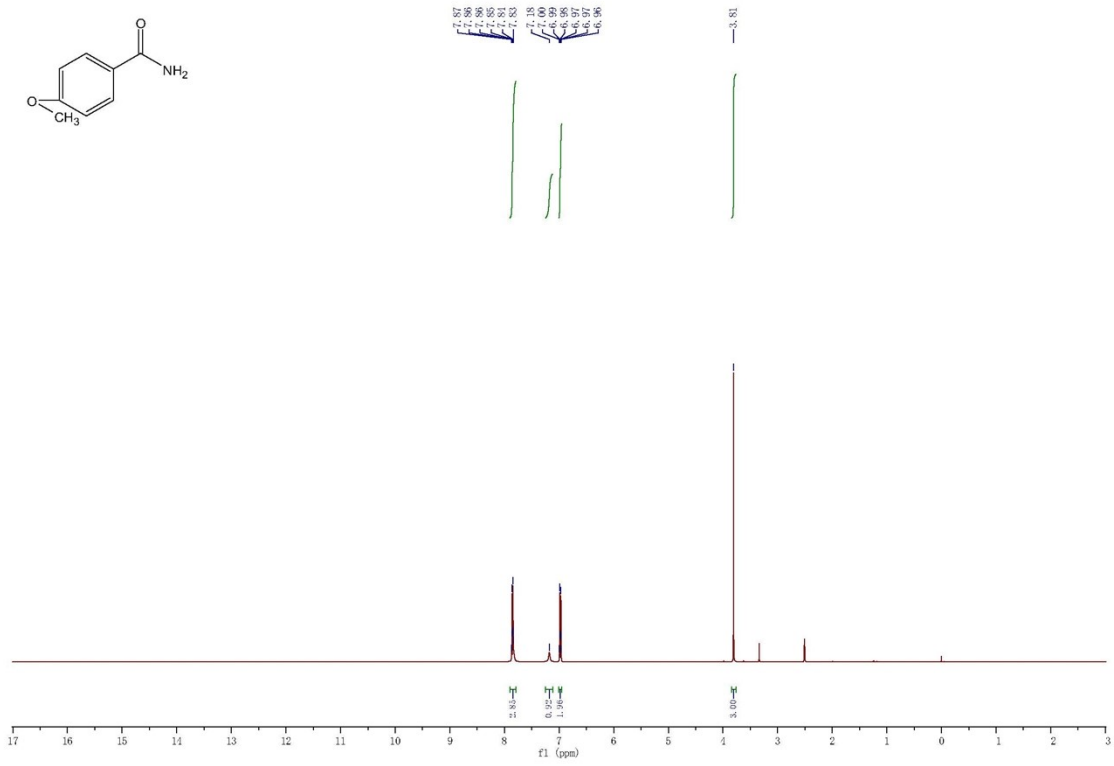
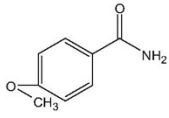
2l: 3-fluorobenzamide



2m: 4-methylbenzamide

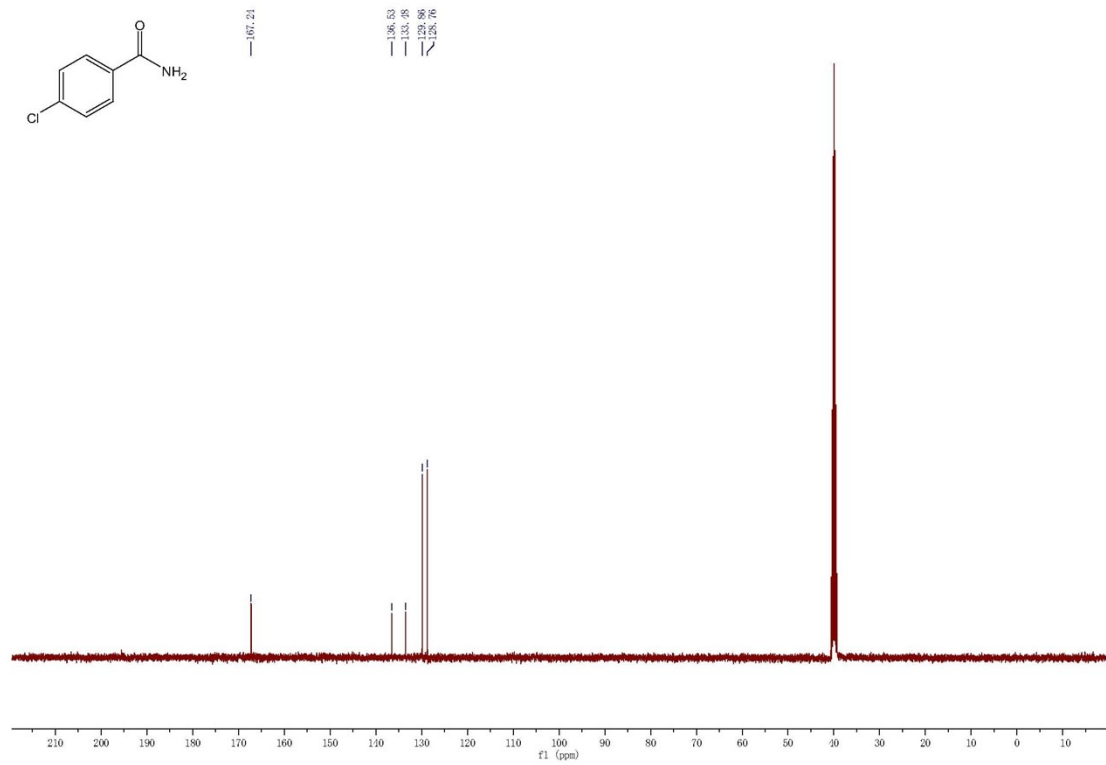
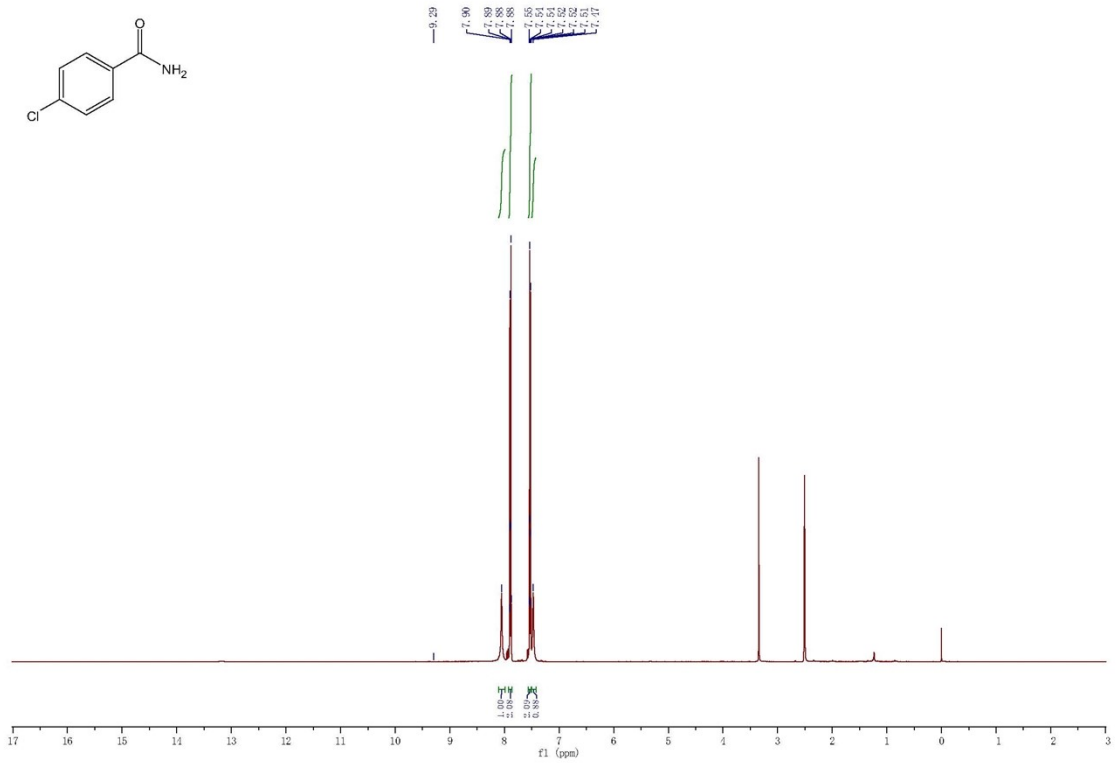


2n: 4-methoxybenzamide

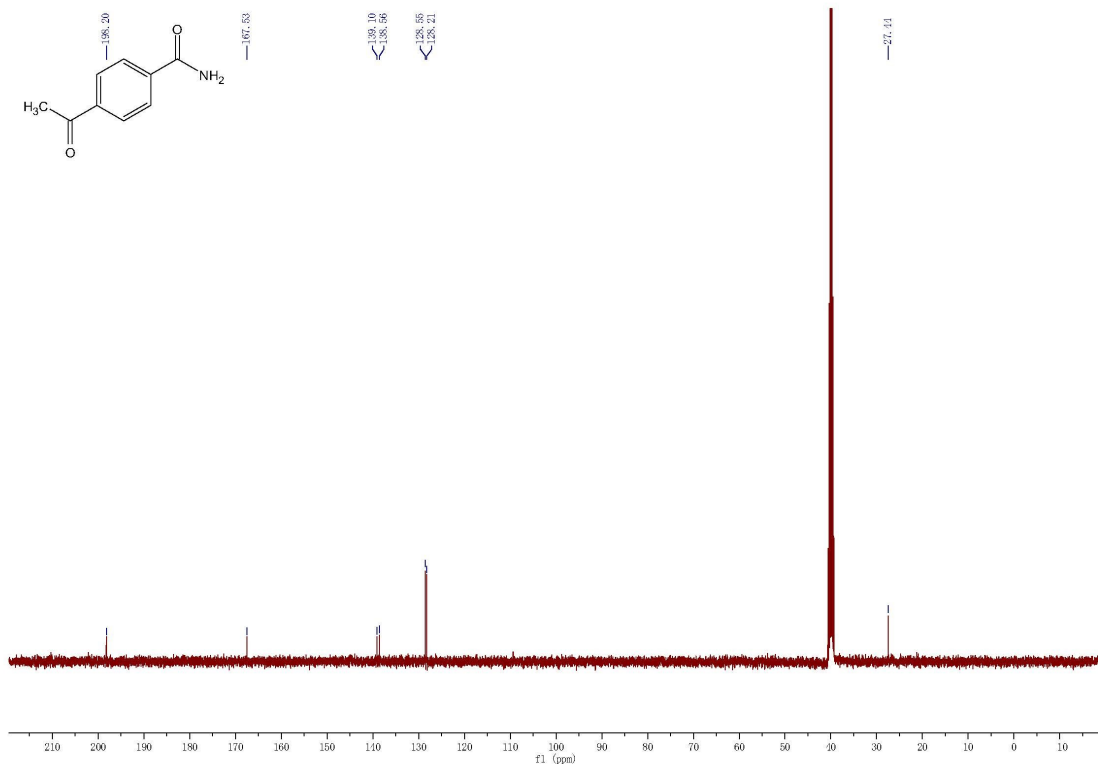
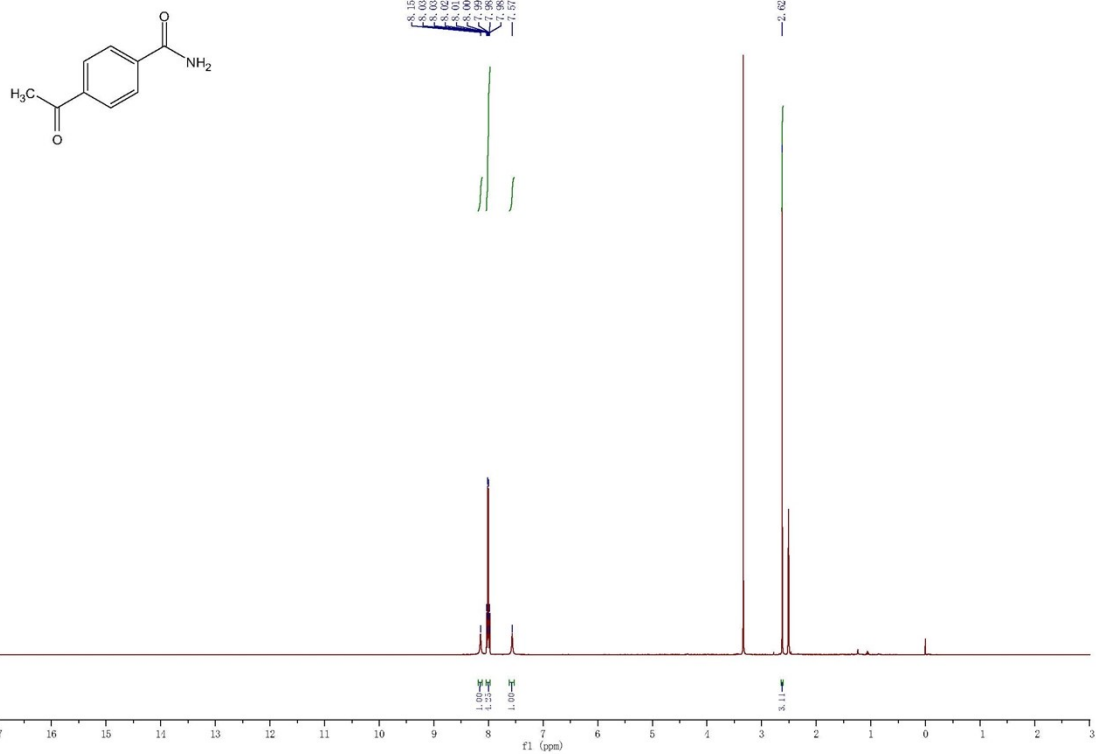




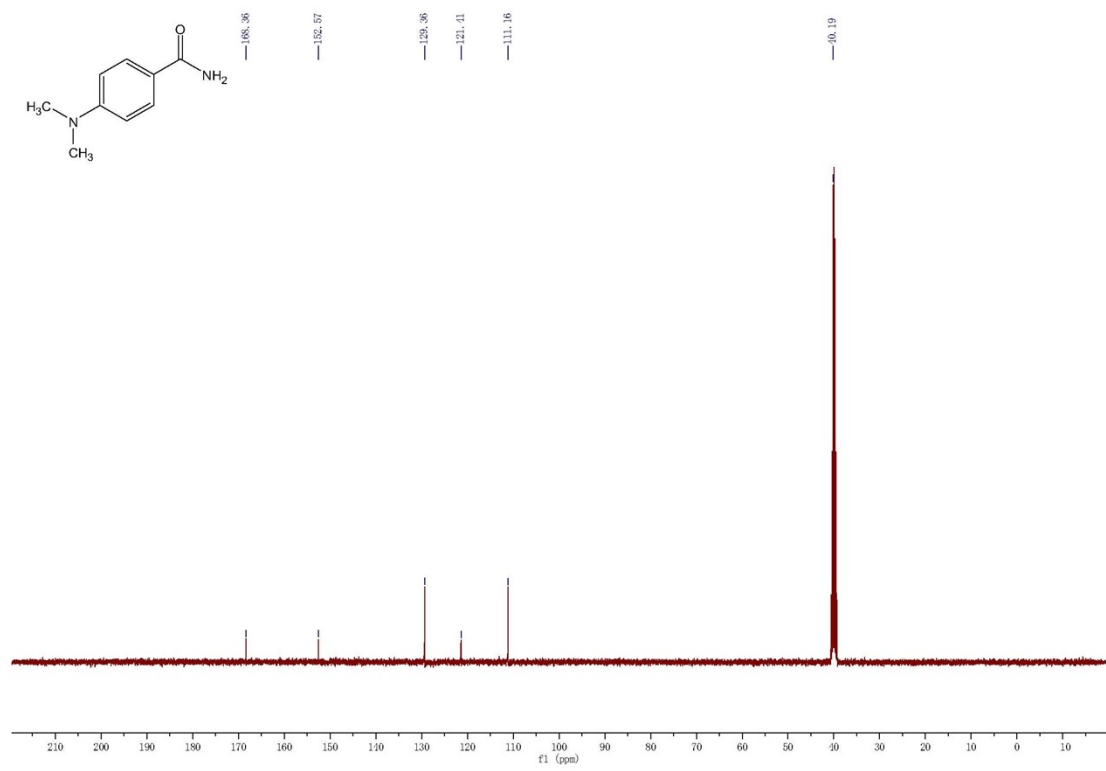
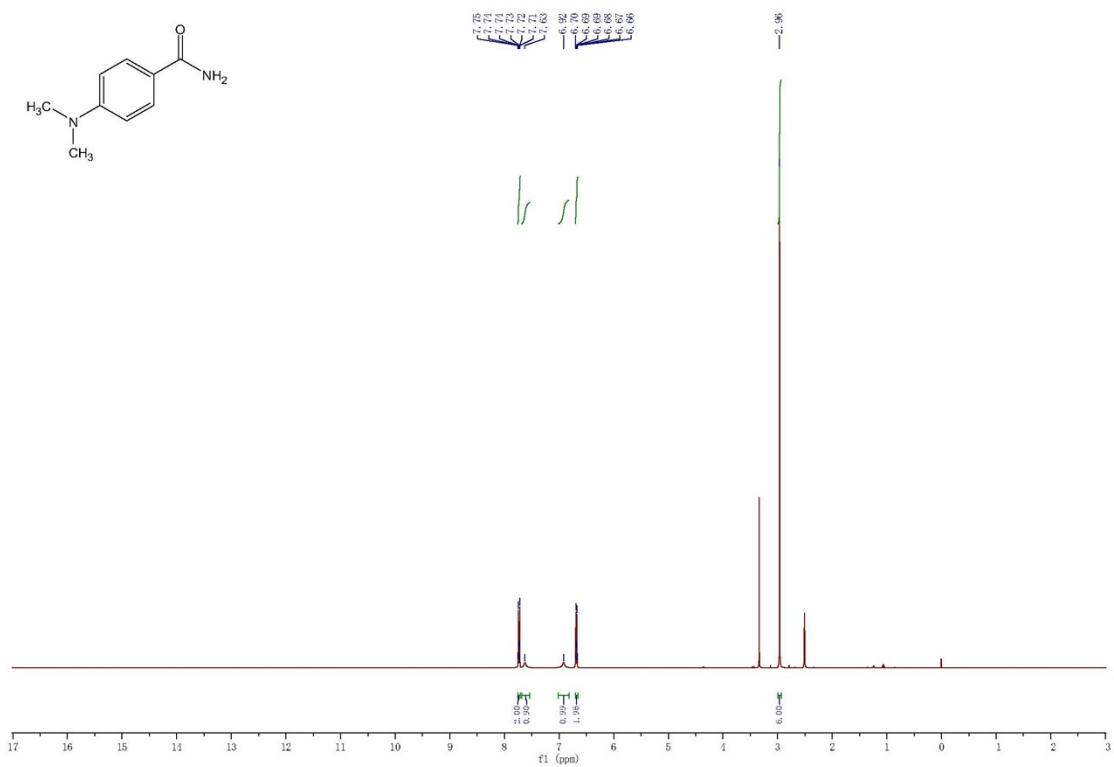
2o: 4-chlorobenzamide



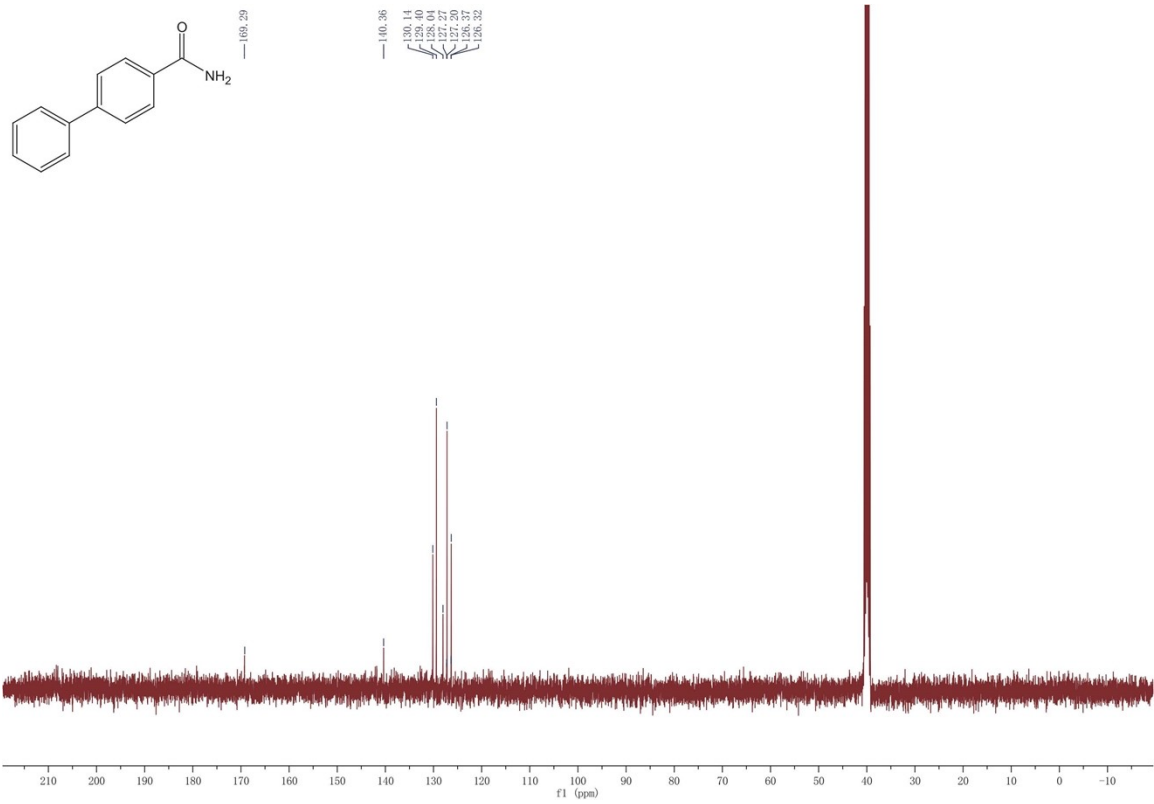
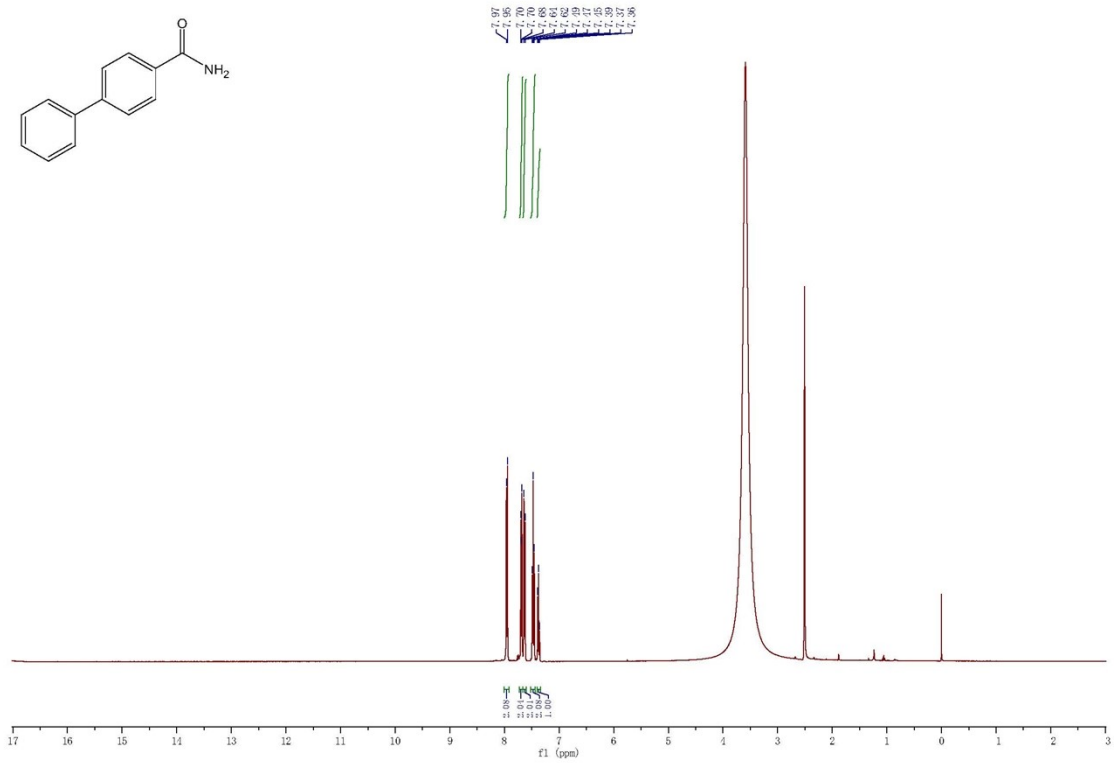
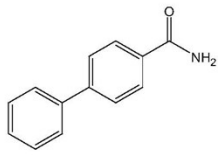
**2p: 4-acetylbenzamide**



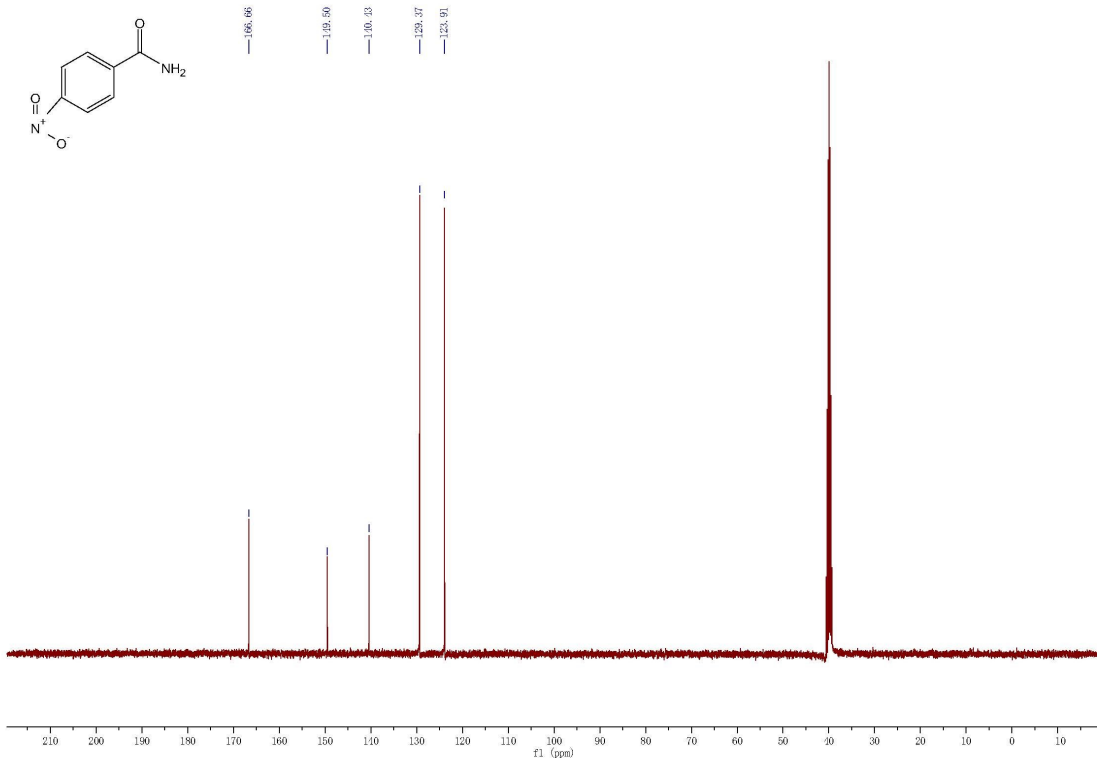
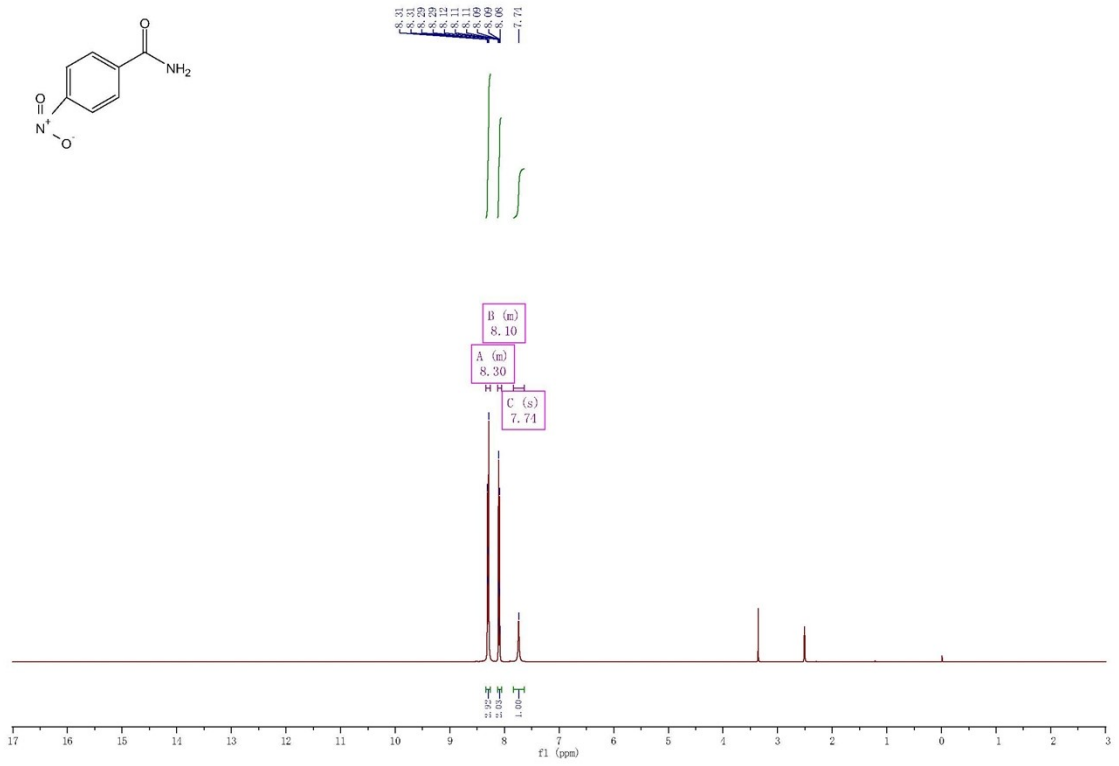
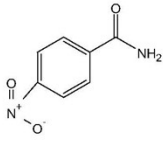
2q: 4-(dimethylamino)benzamide



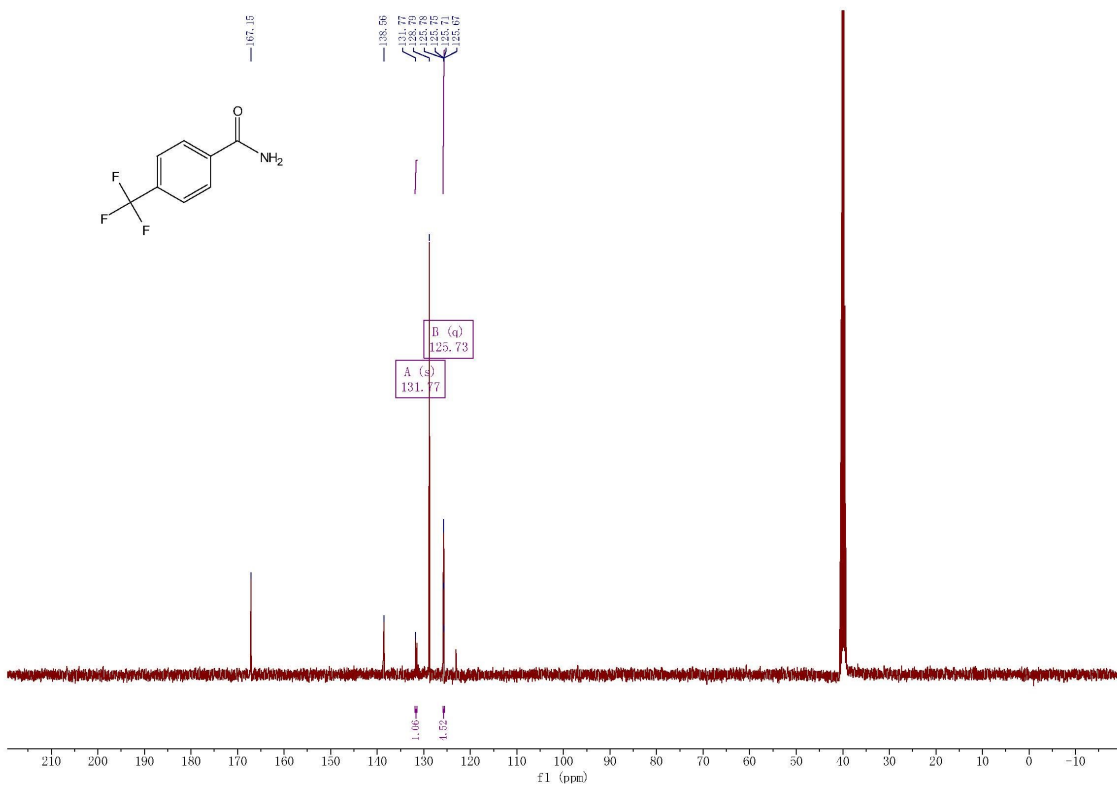
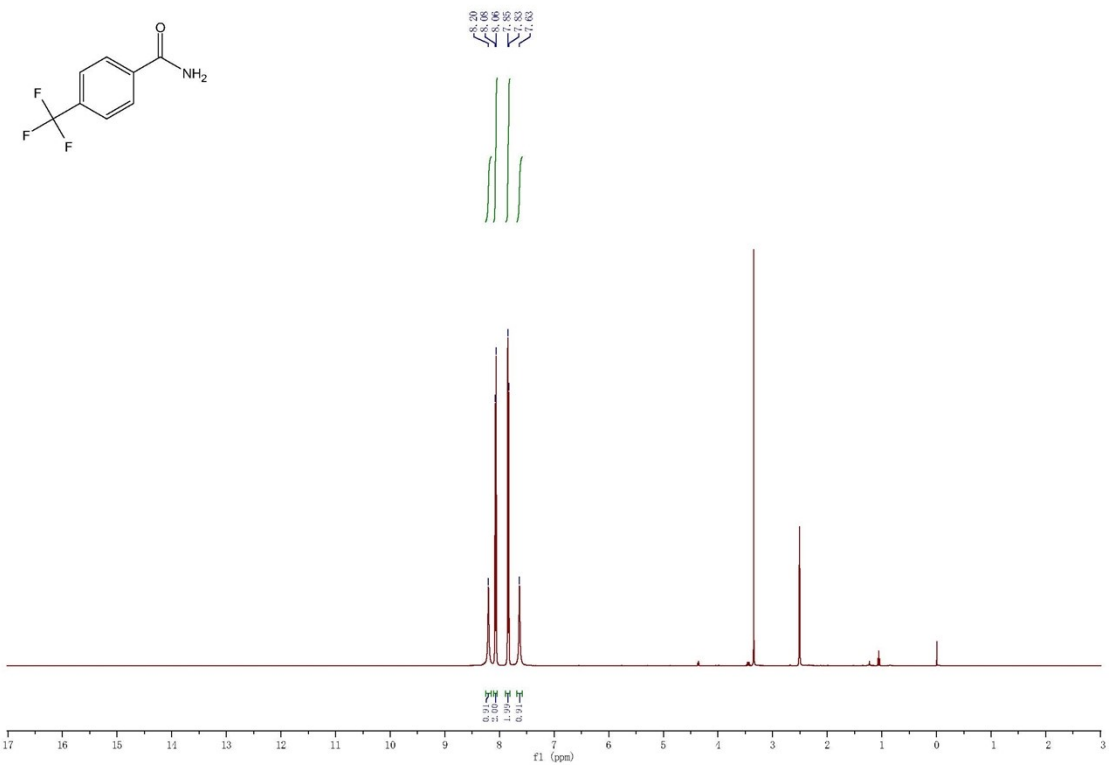
**2r: 4-phenyl benzamide**



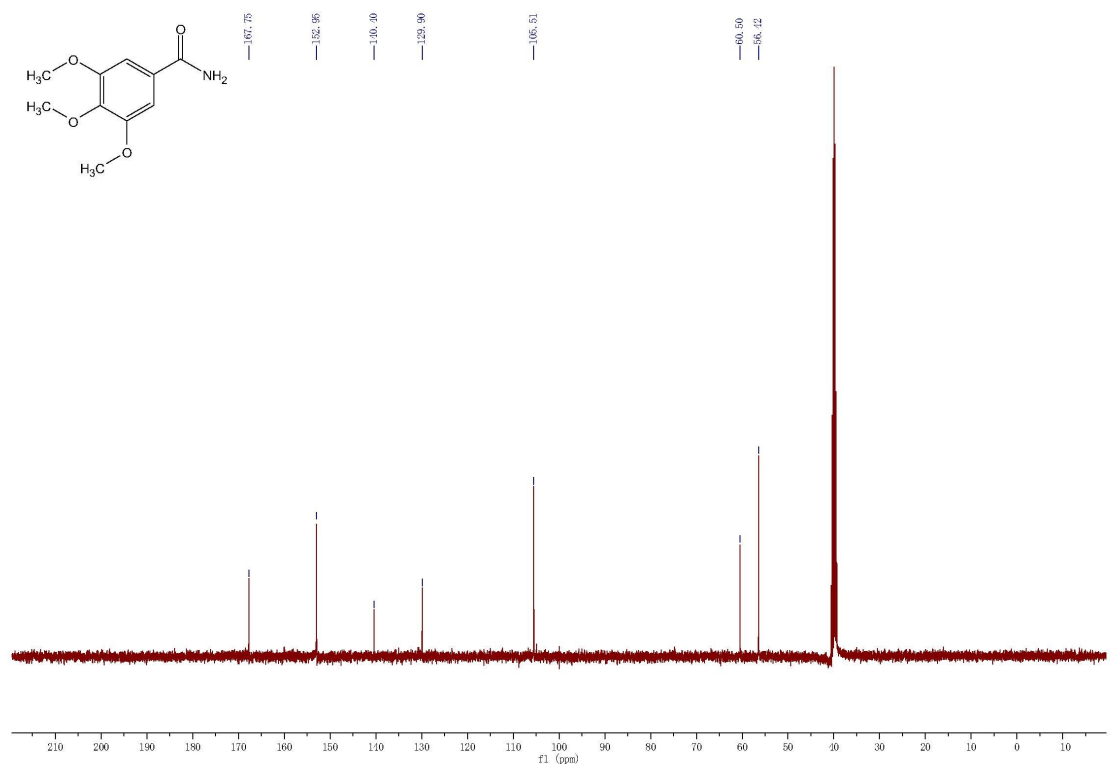
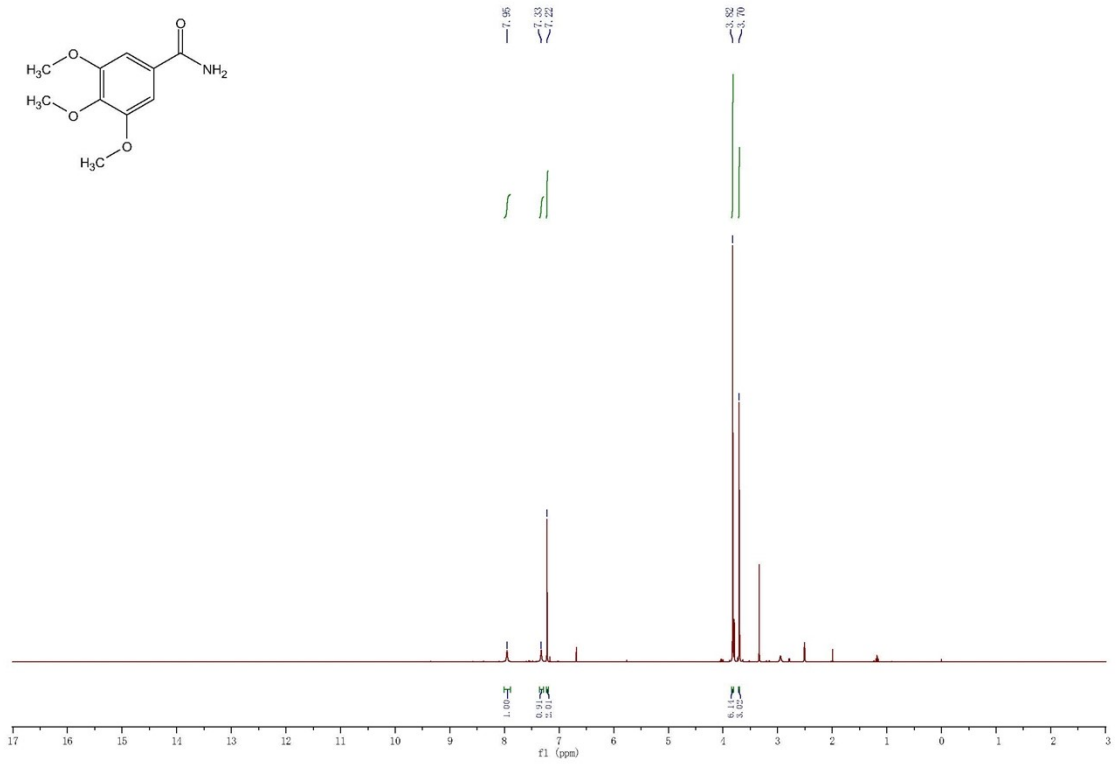
**2s: 4-nitrobenzamide**



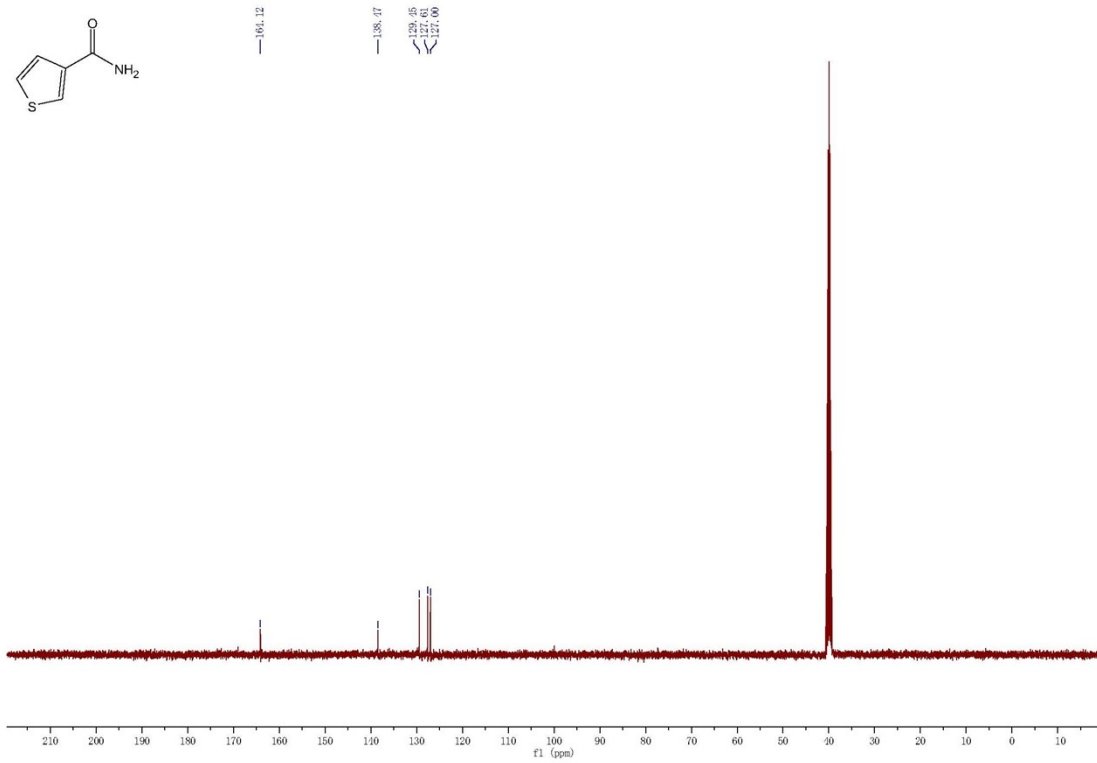
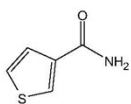
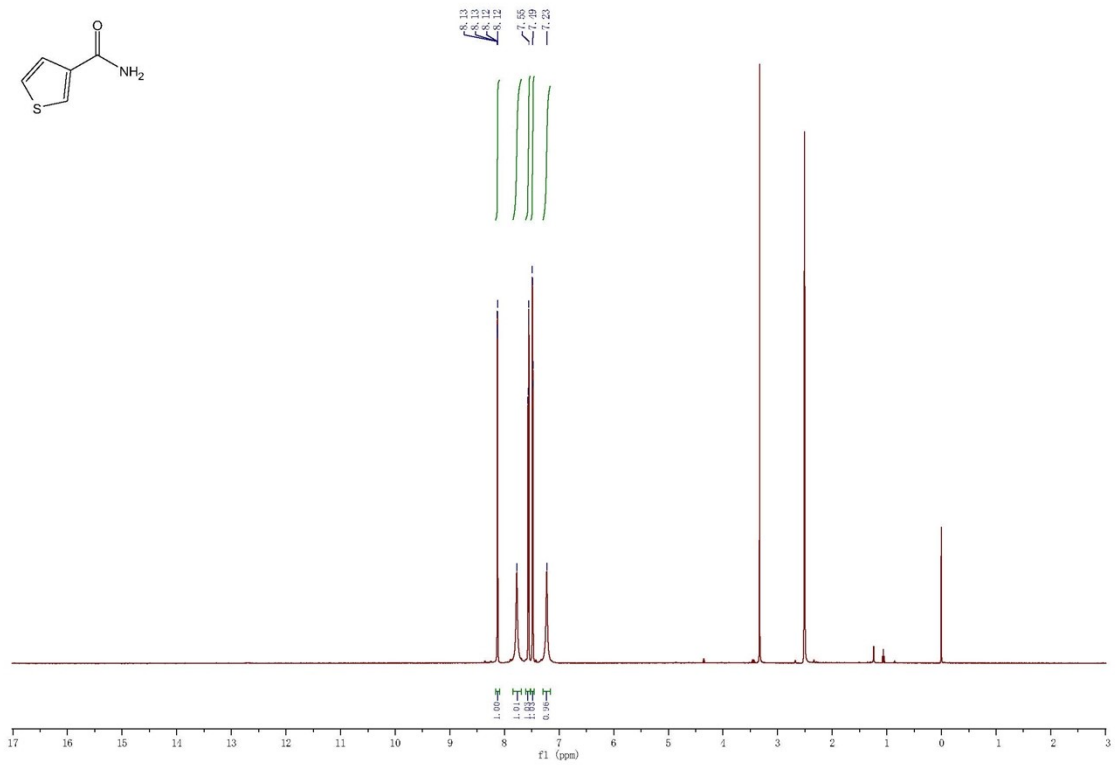
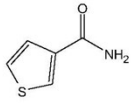
2t: 4-(trifluoromethyl)benzamide



2u: 3,4,5-trimethoxybenzamide

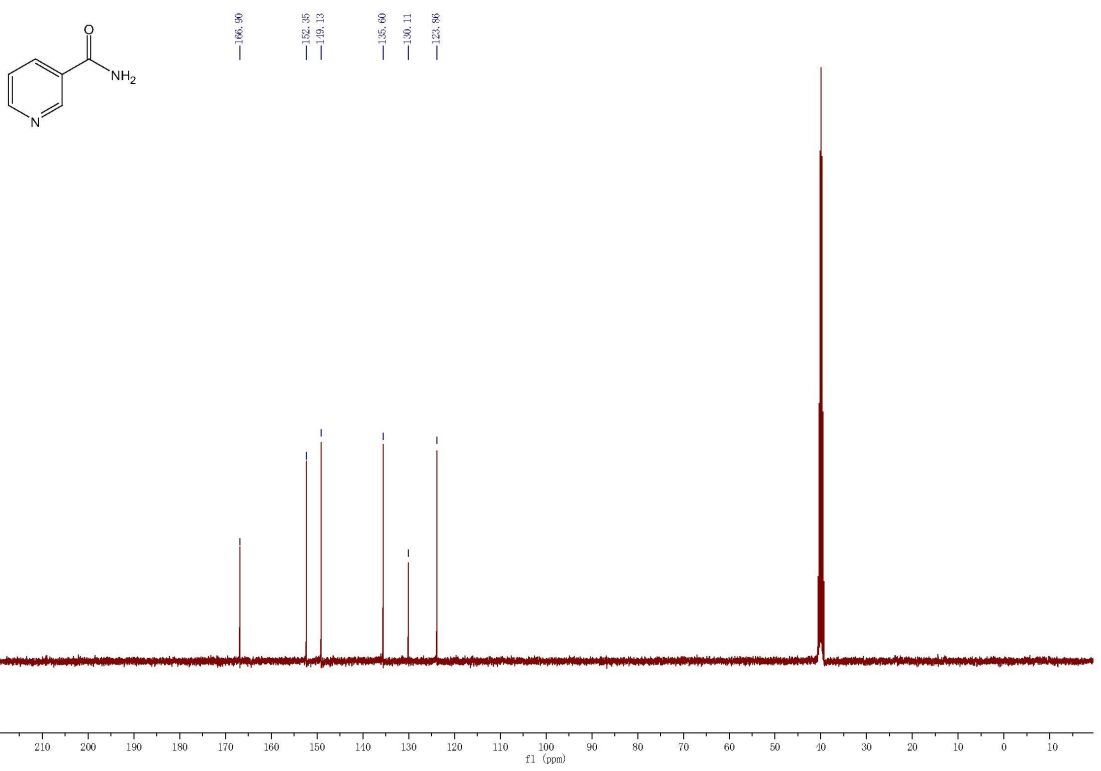
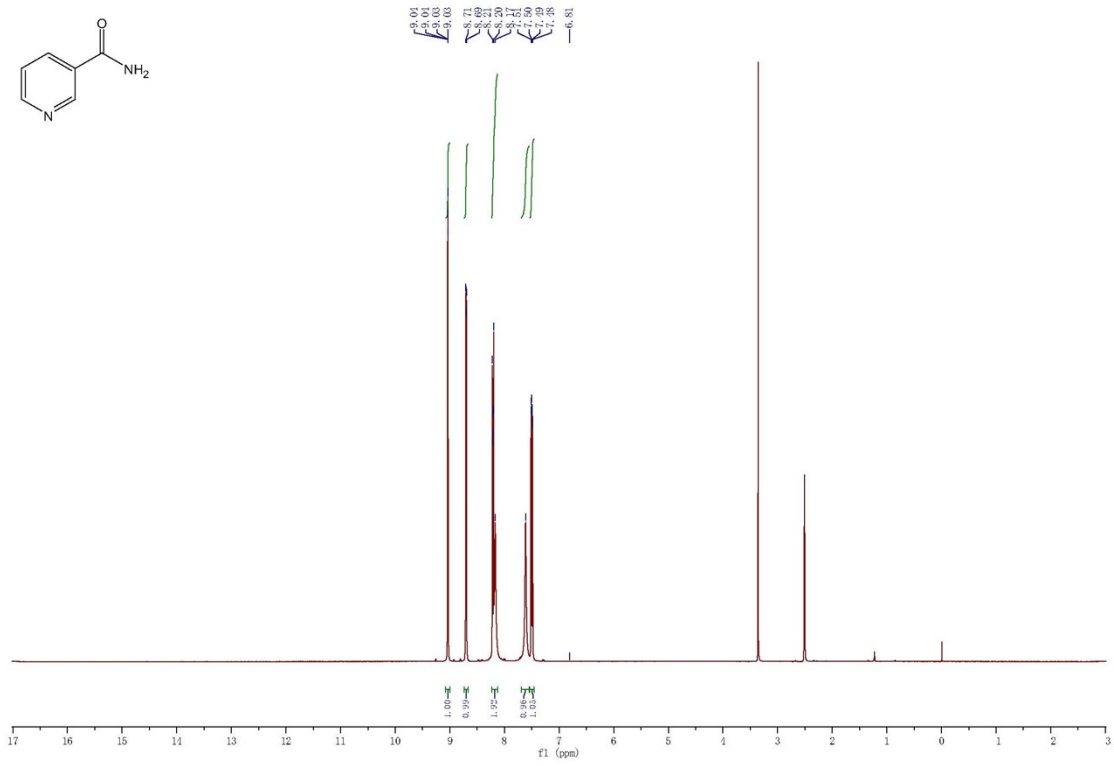
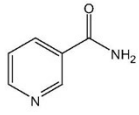


**2w: thiophene-3-carboxamide**

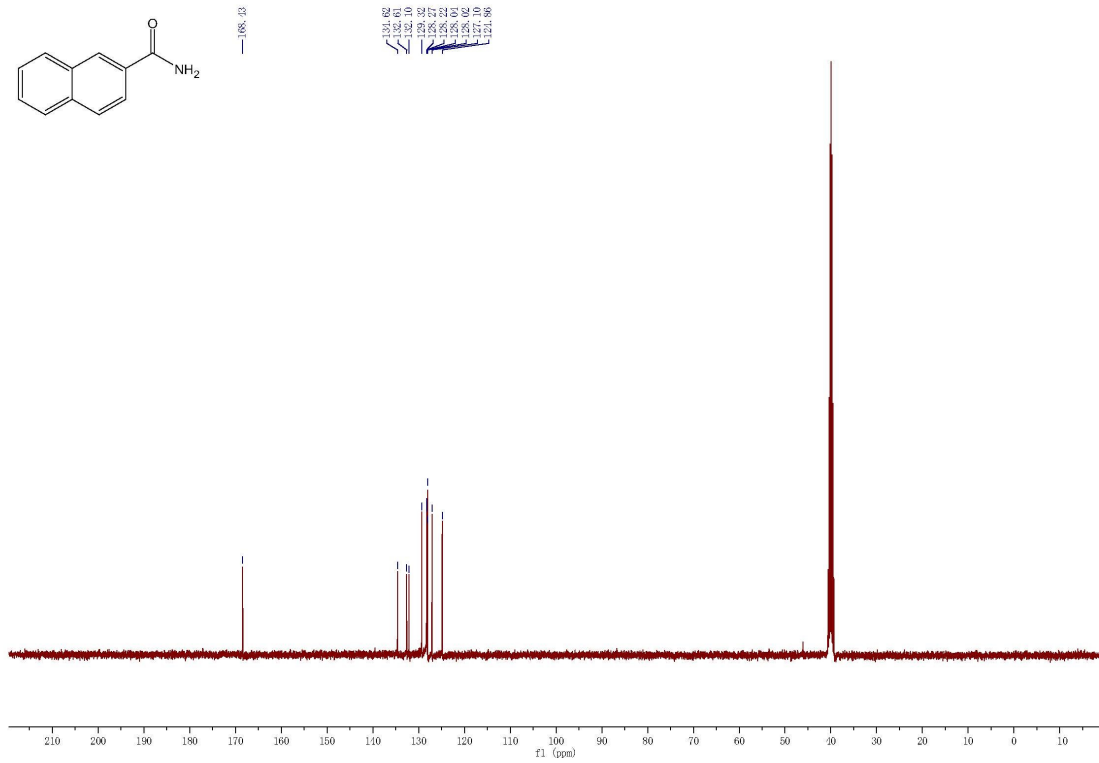
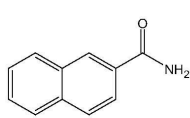
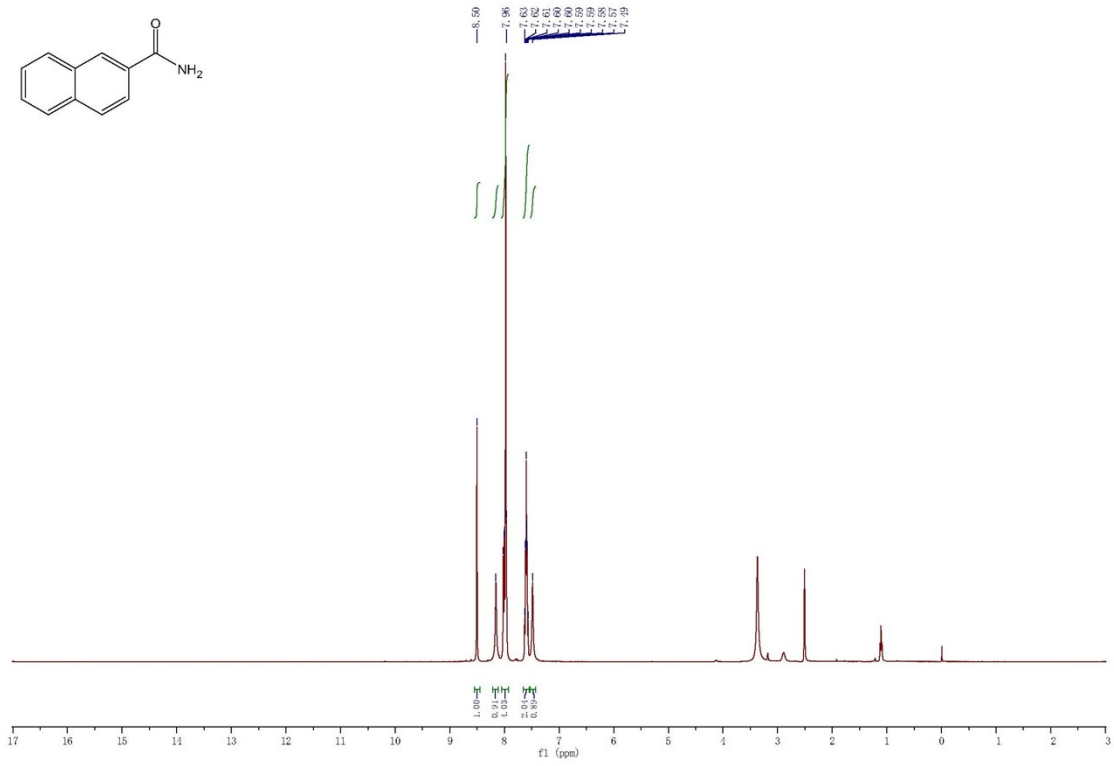
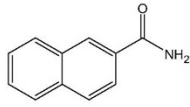




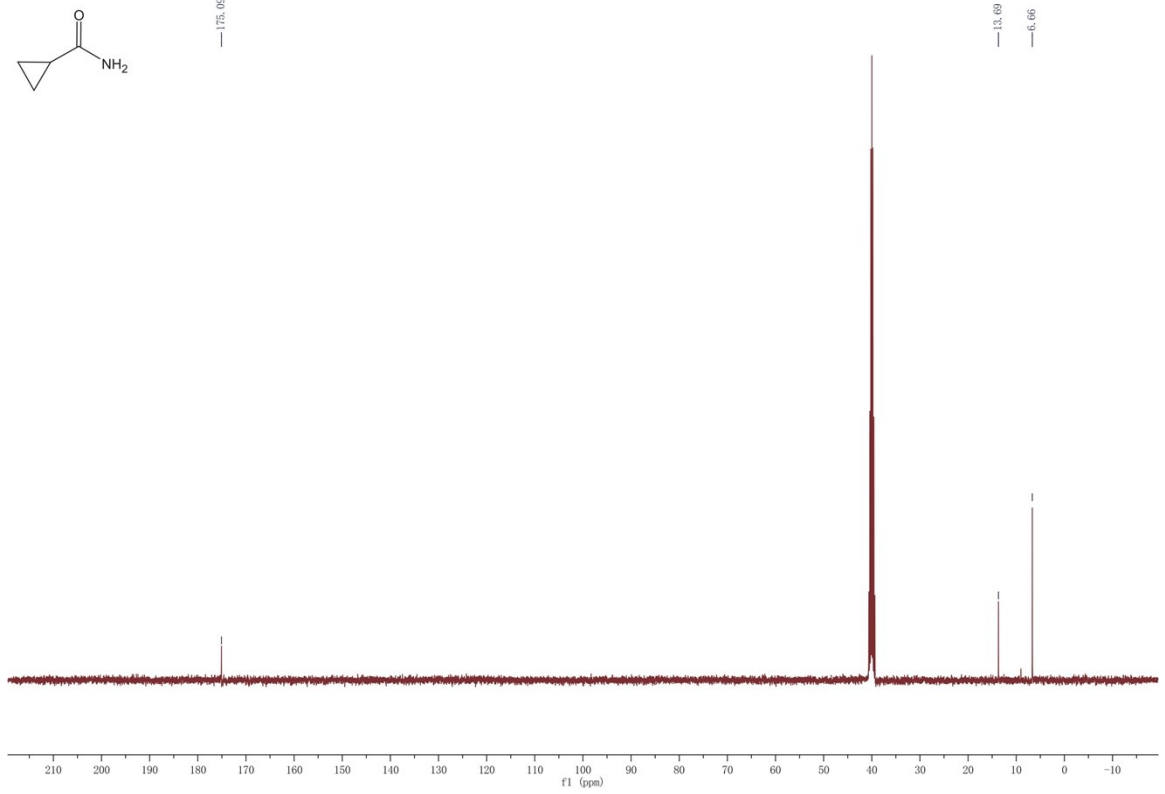
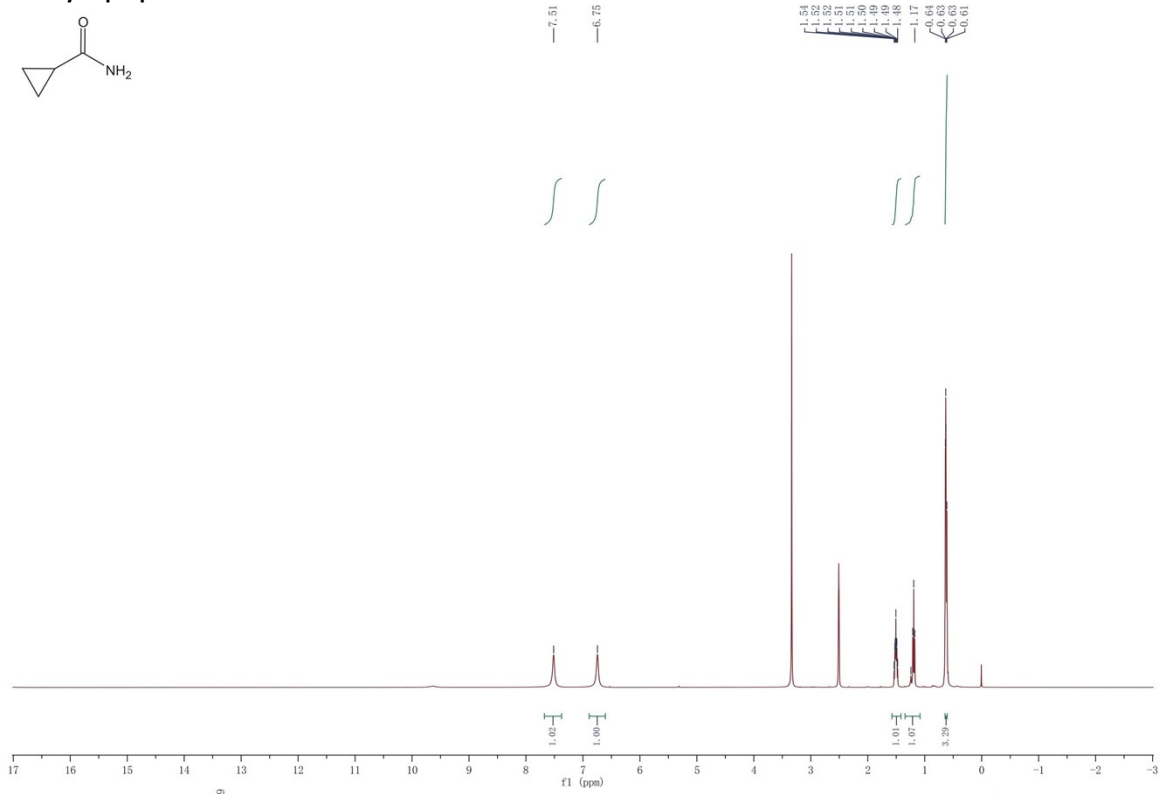
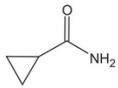
2x: nicotinamide



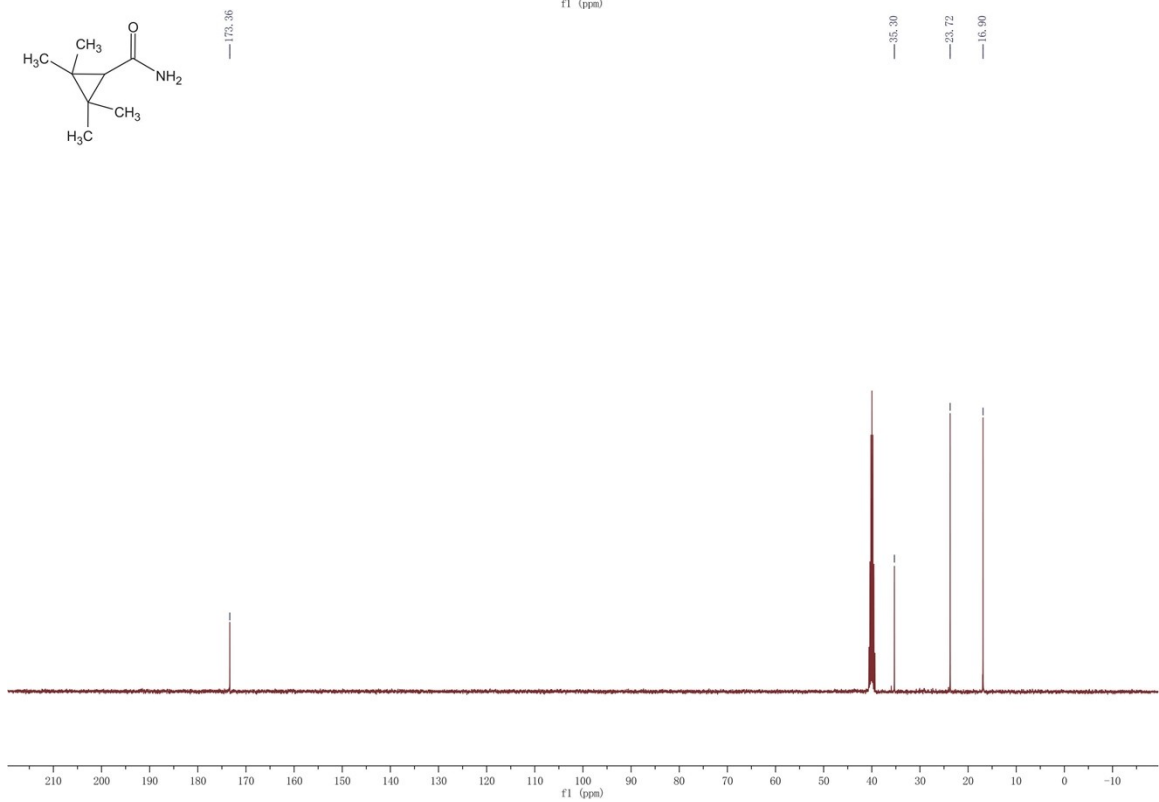
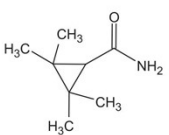
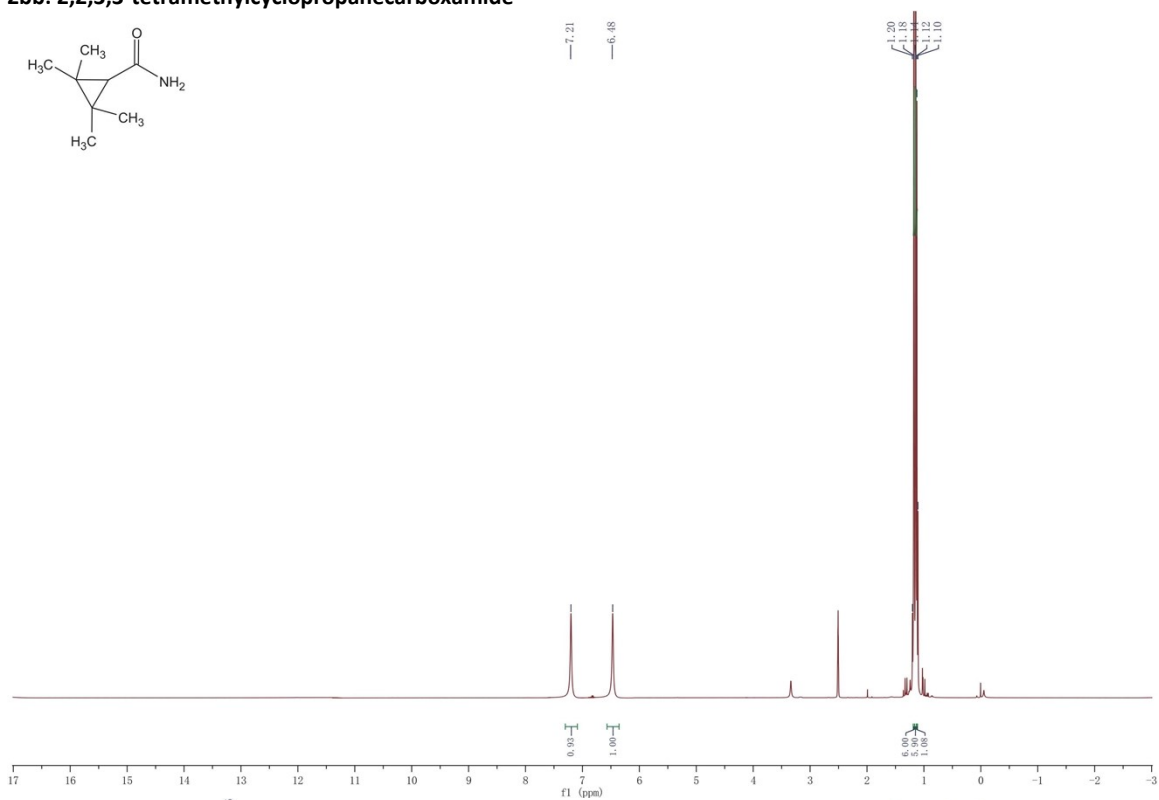
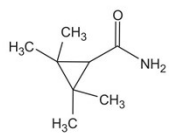
2z: 2-naphthamide



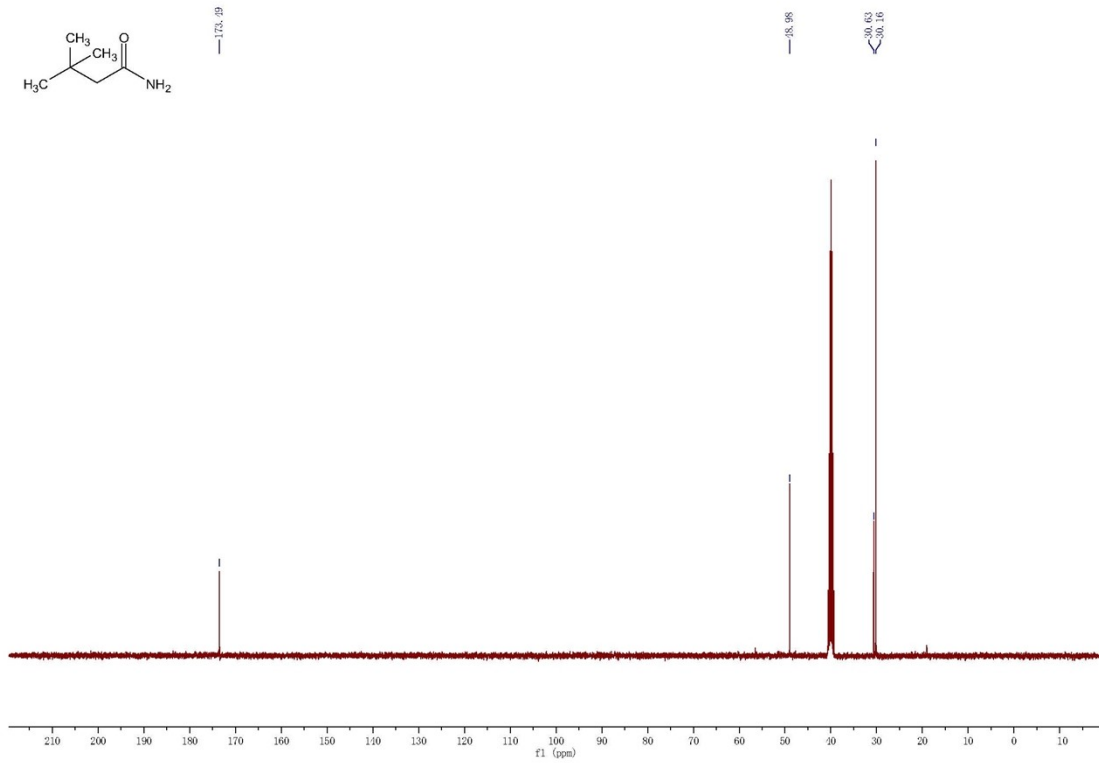
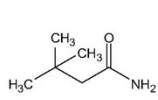
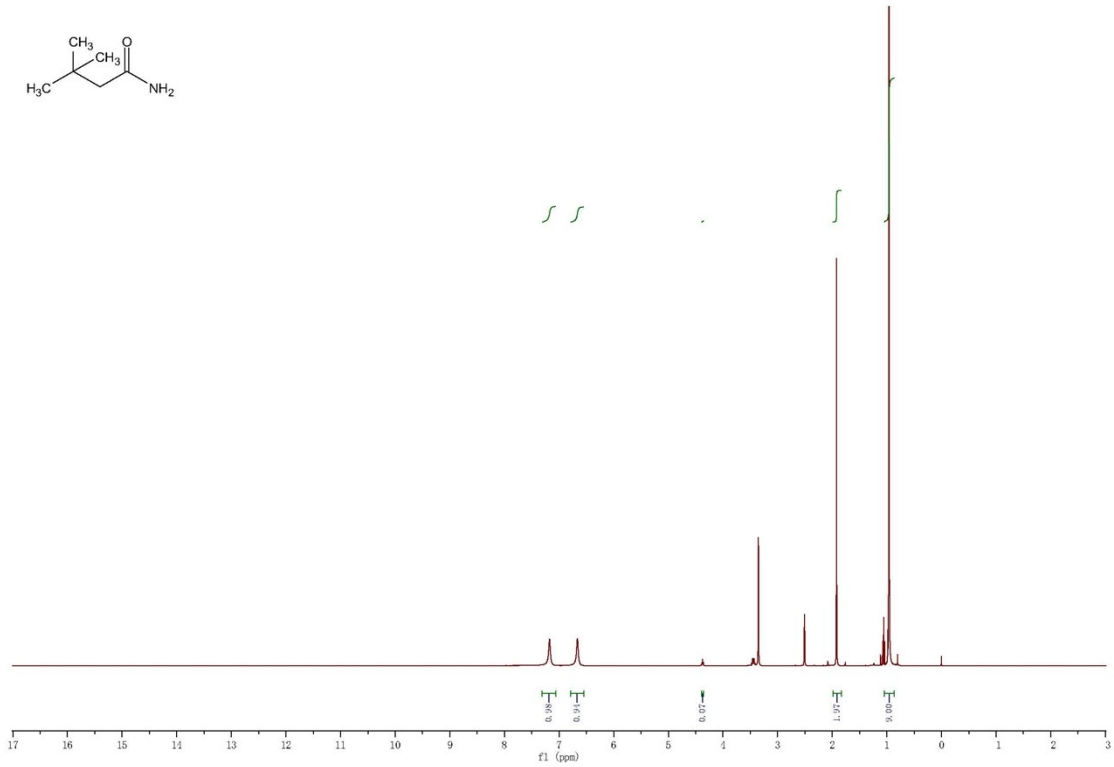
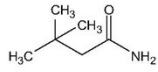
2aa: cyclopropanecarboxamide



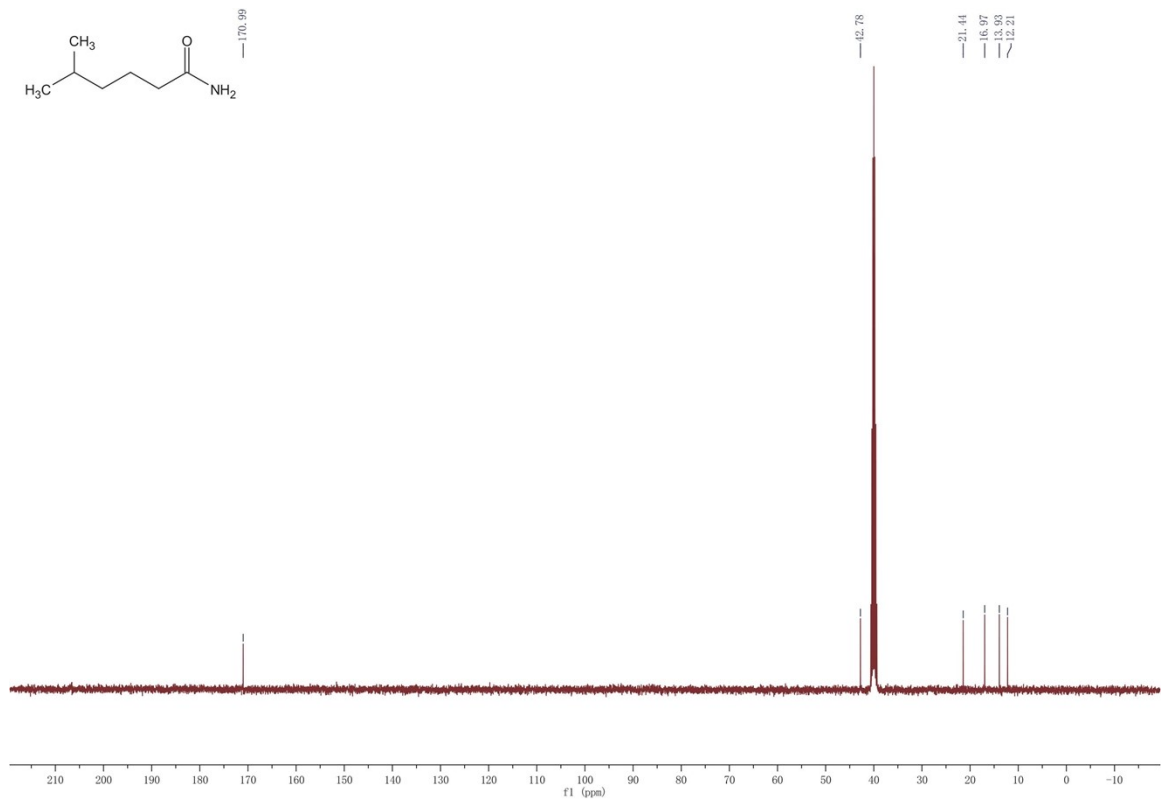
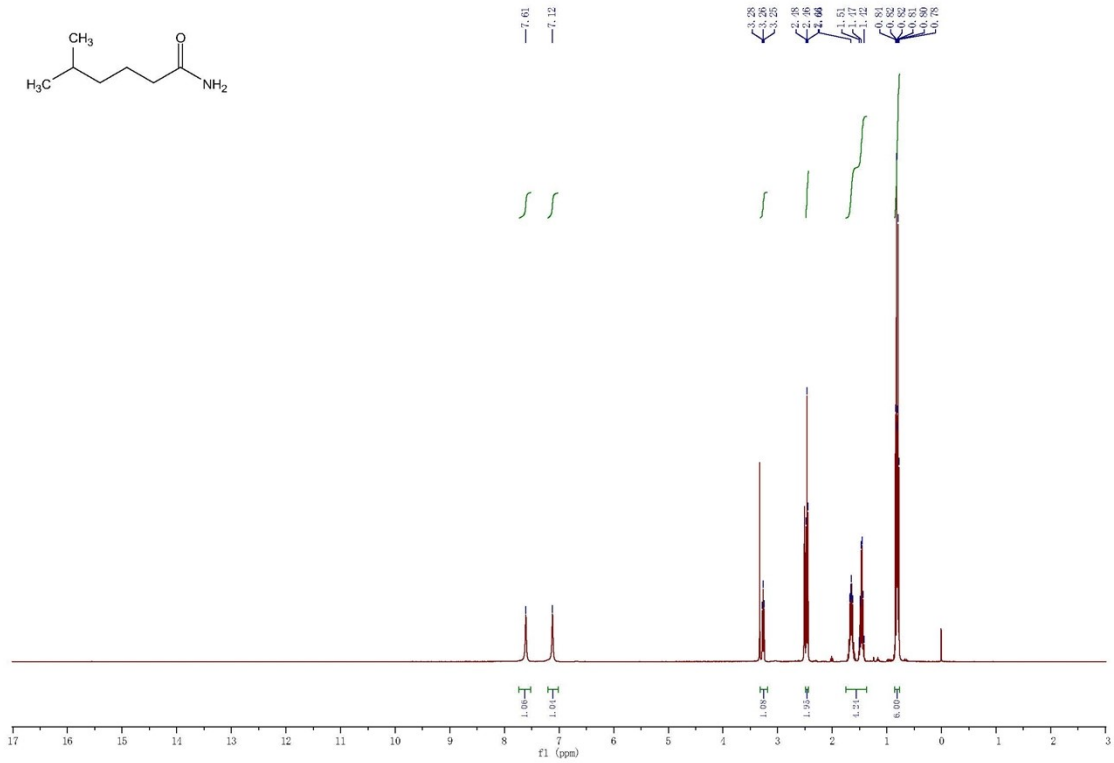
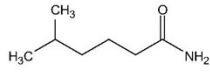
**2bb: 2,2,3,3-tetramethylcyclopropanecarboxamide**



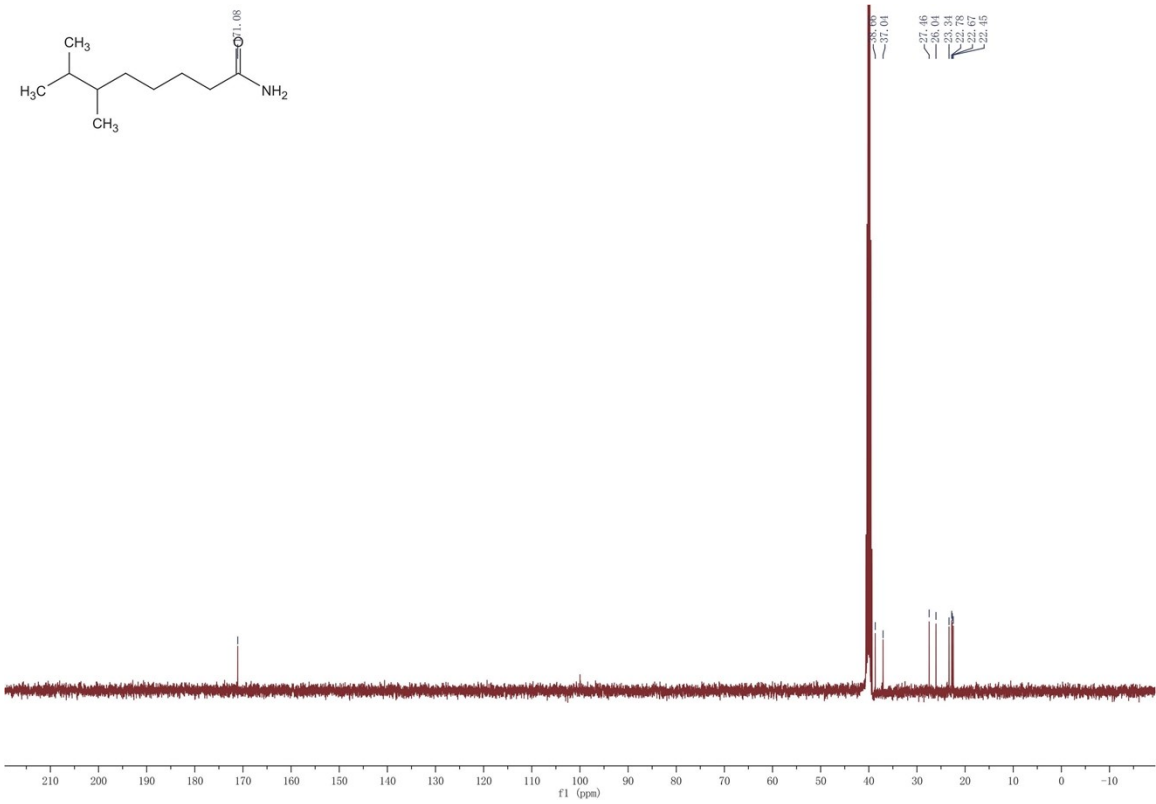
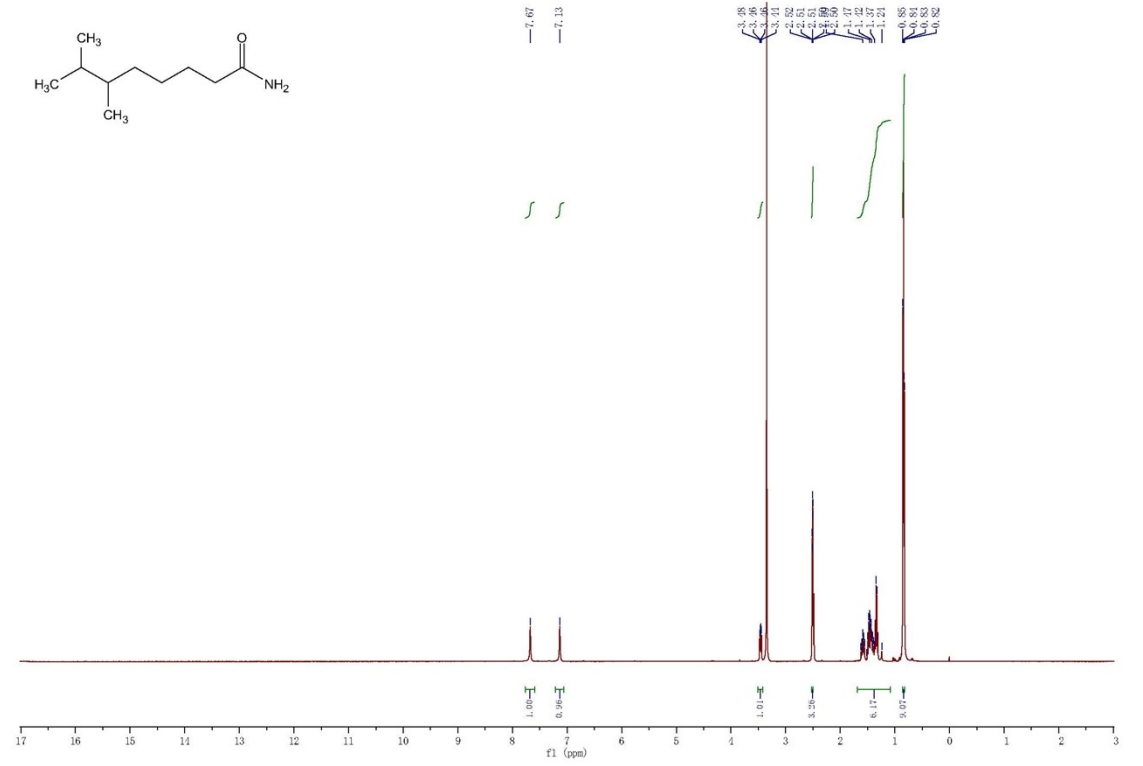
2cc: 3,3-dimethylbutanamide



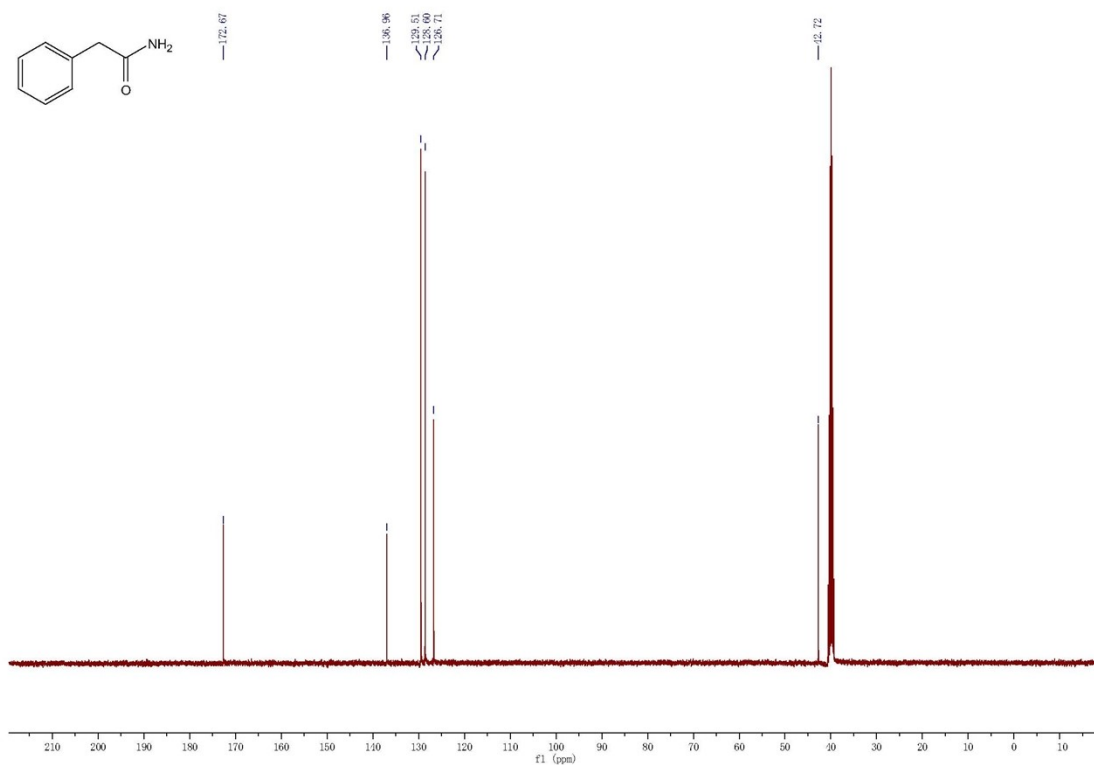
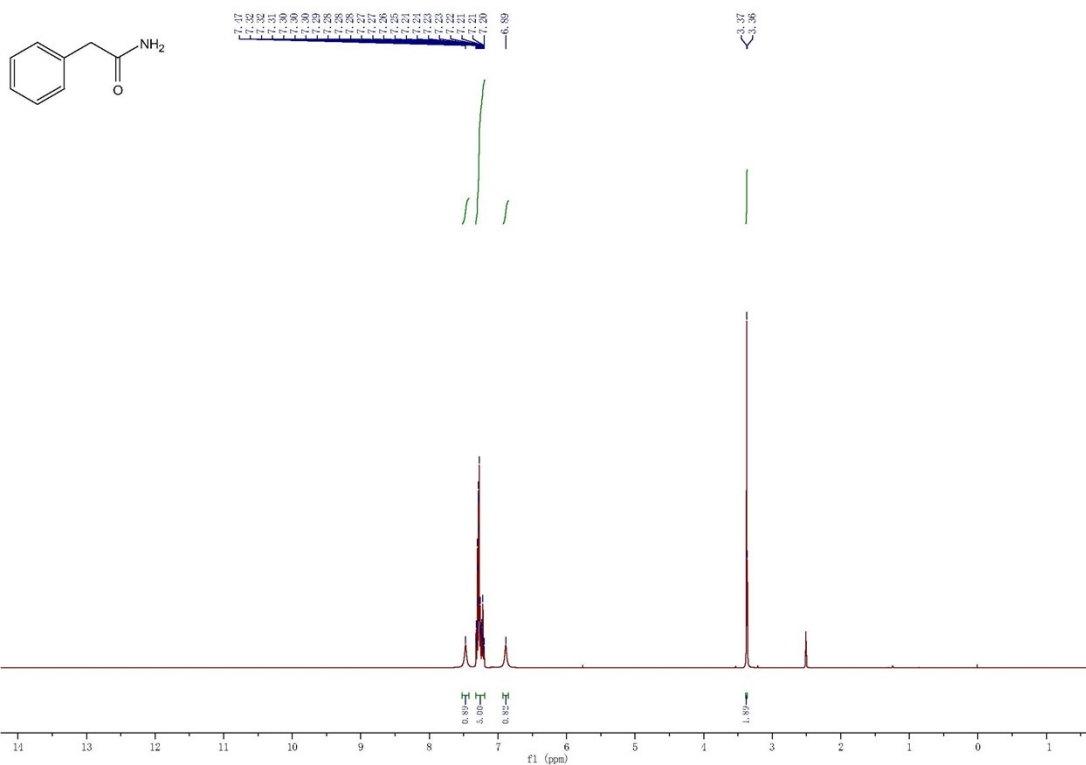
2dd: 5-methylhexanamide



**2ee: 6,7-dimethyloctanamide**

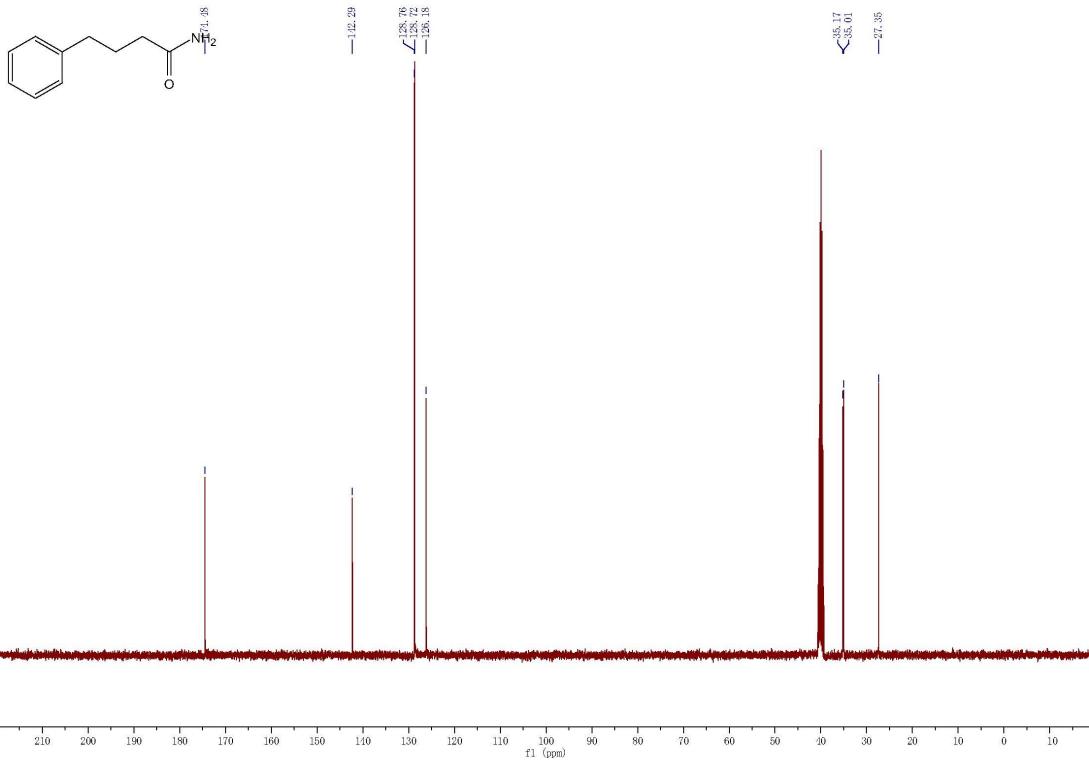
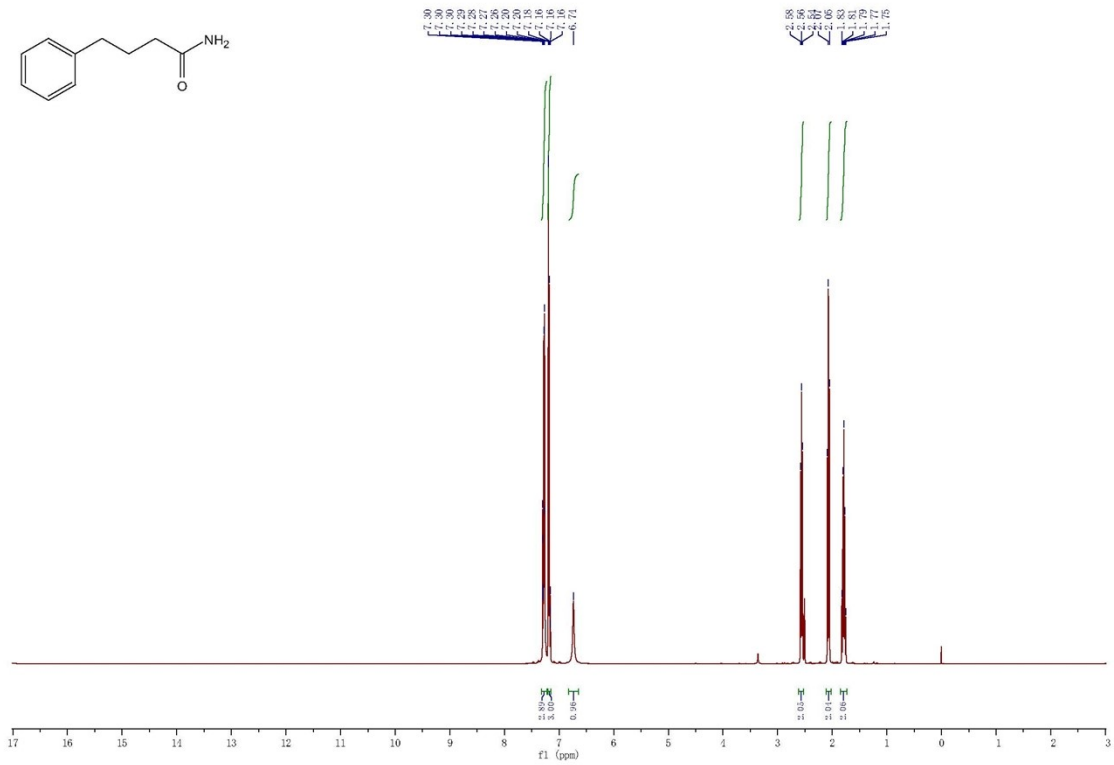
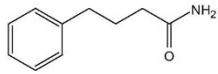


**2ff: 2-phenylacetamide**



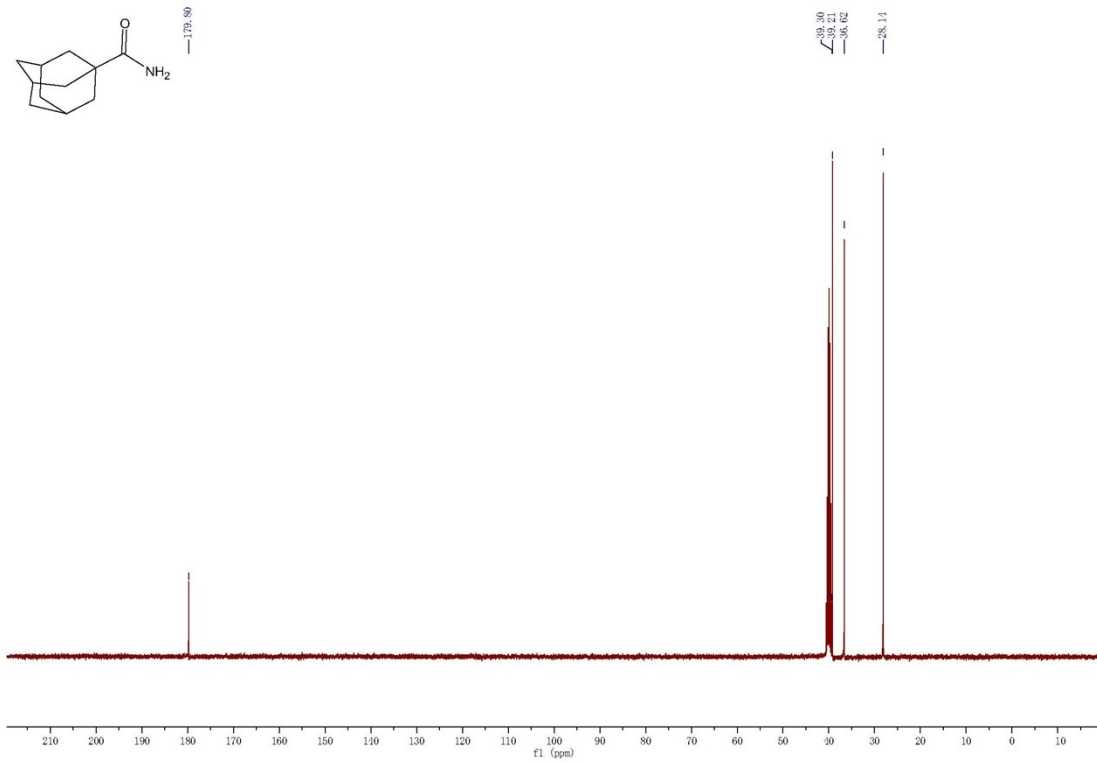
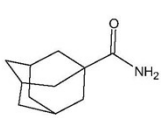
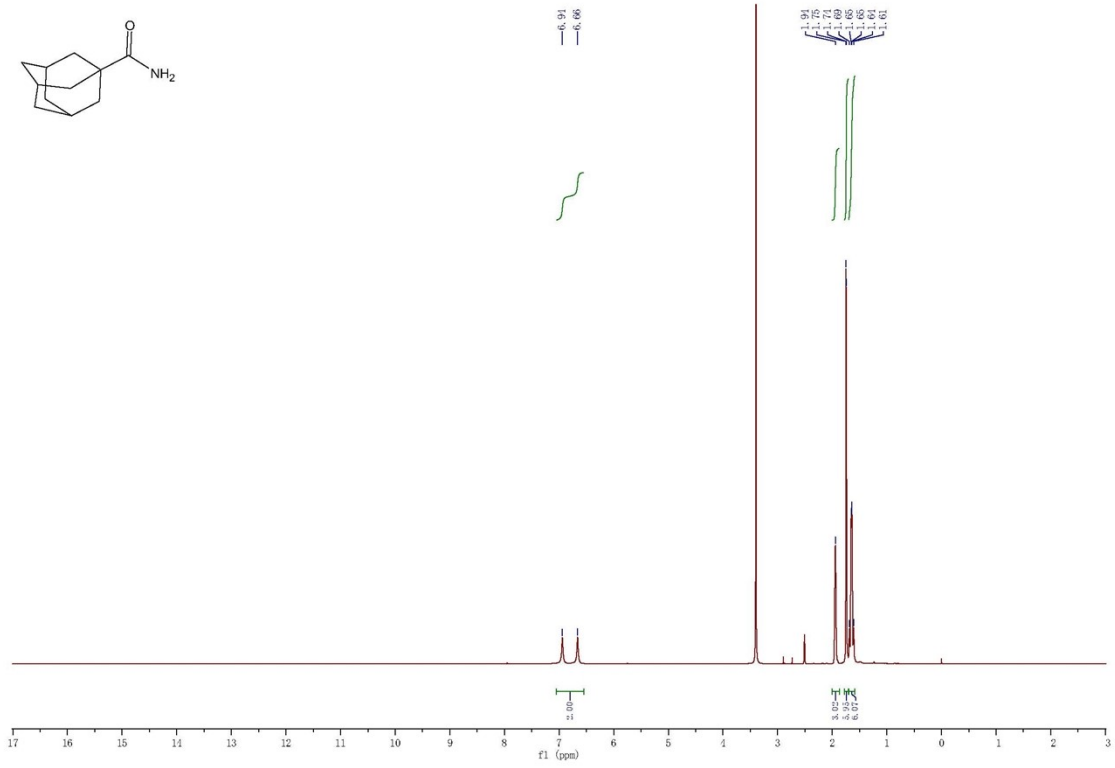
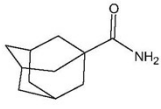


2gg: 4-phenylbutanamide

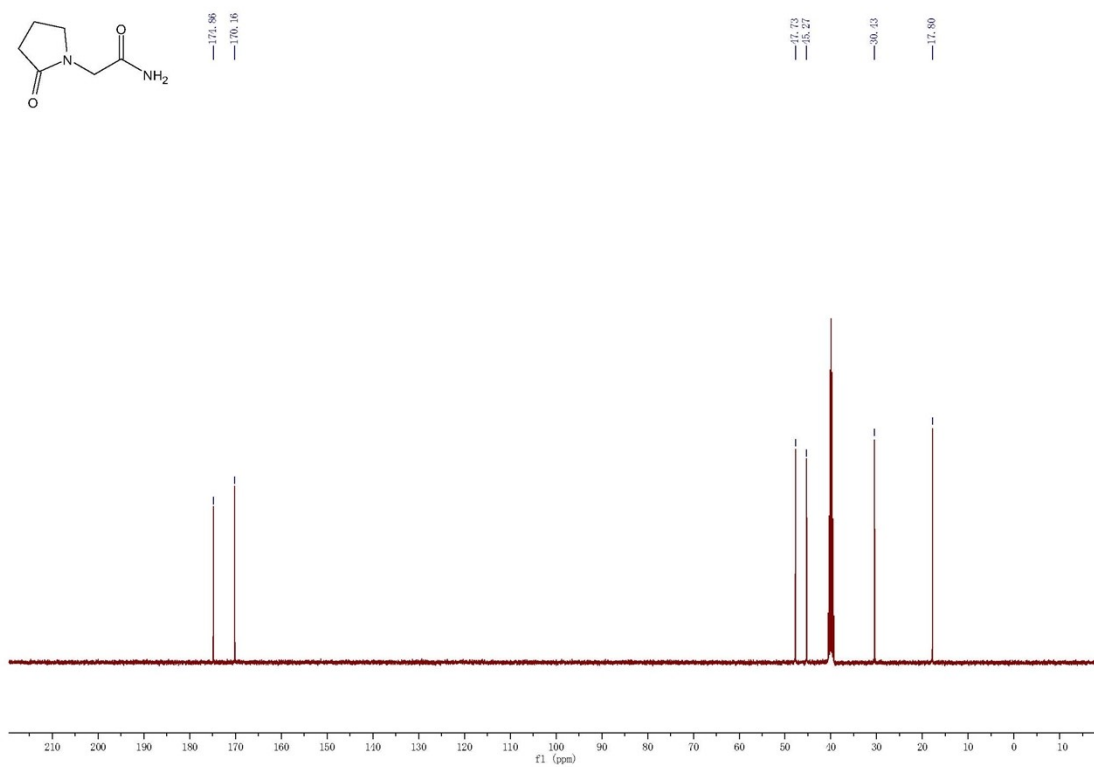
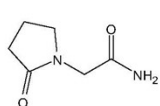
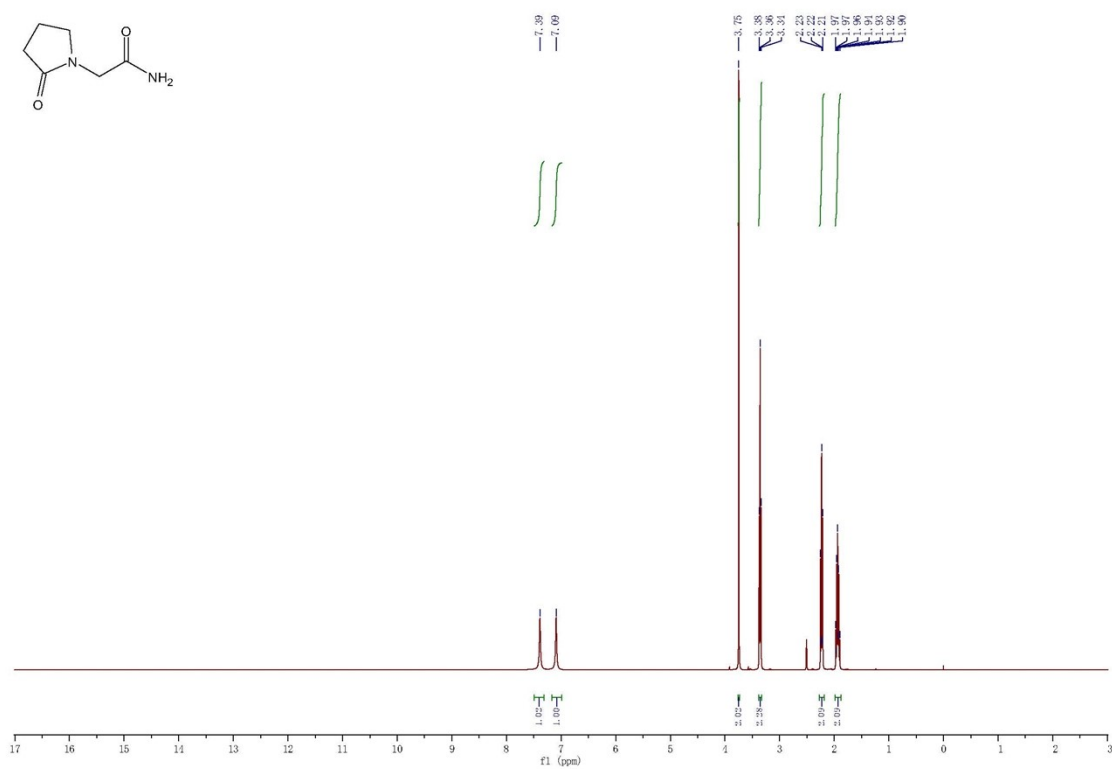
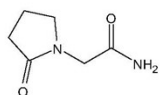




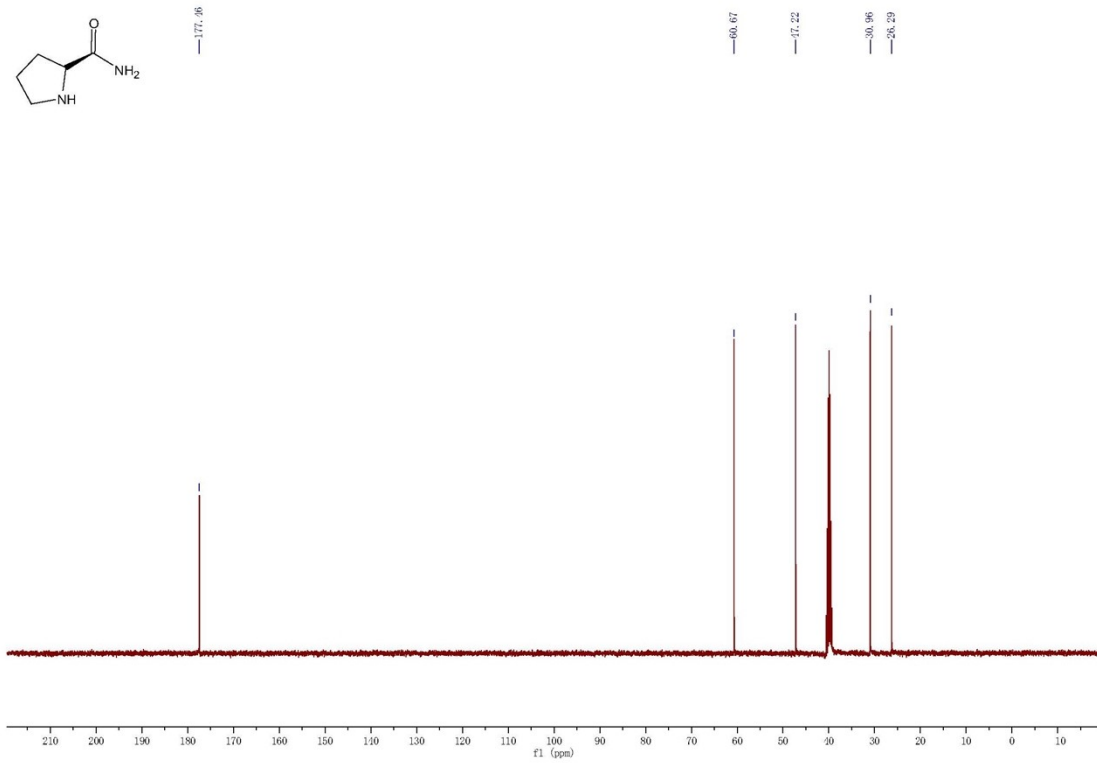
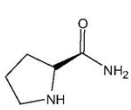
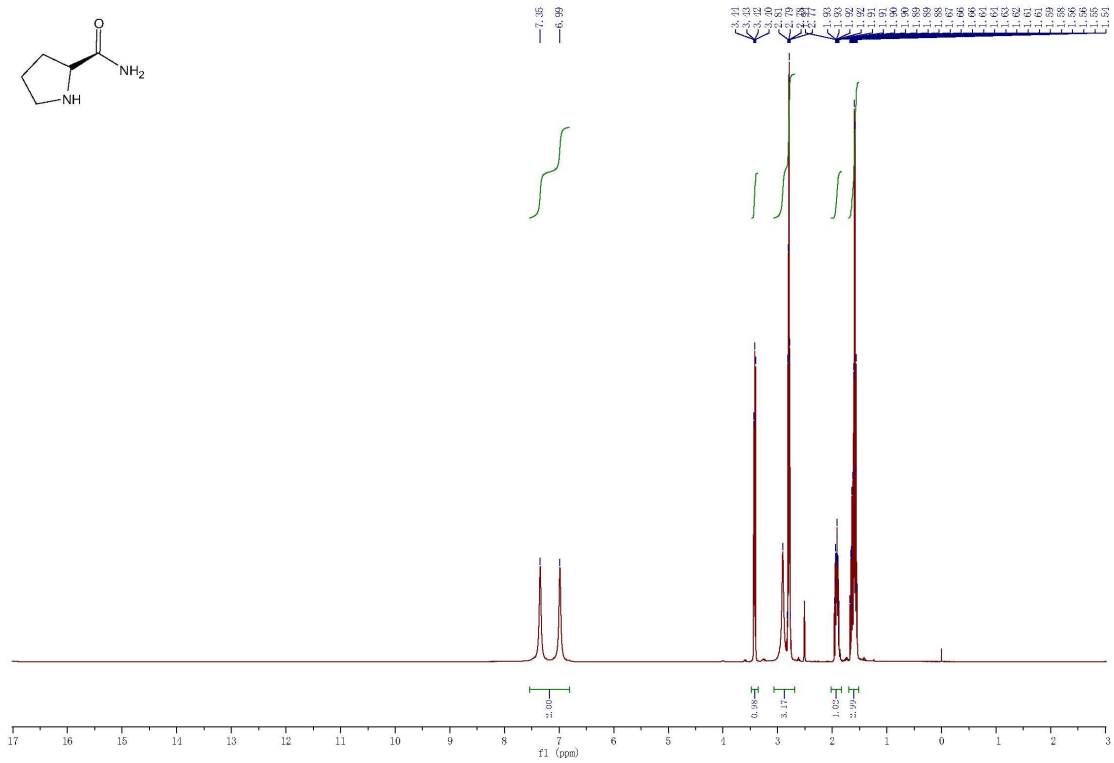
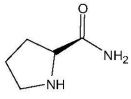
2ii: adamantane-1-carboxamide



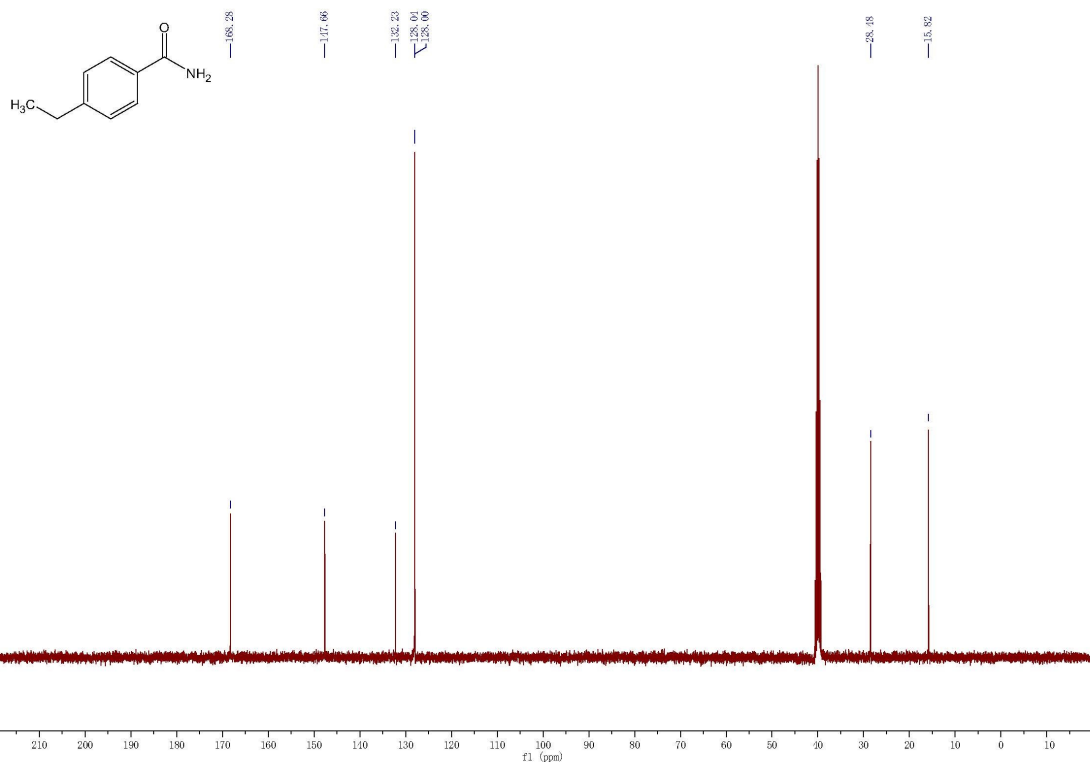
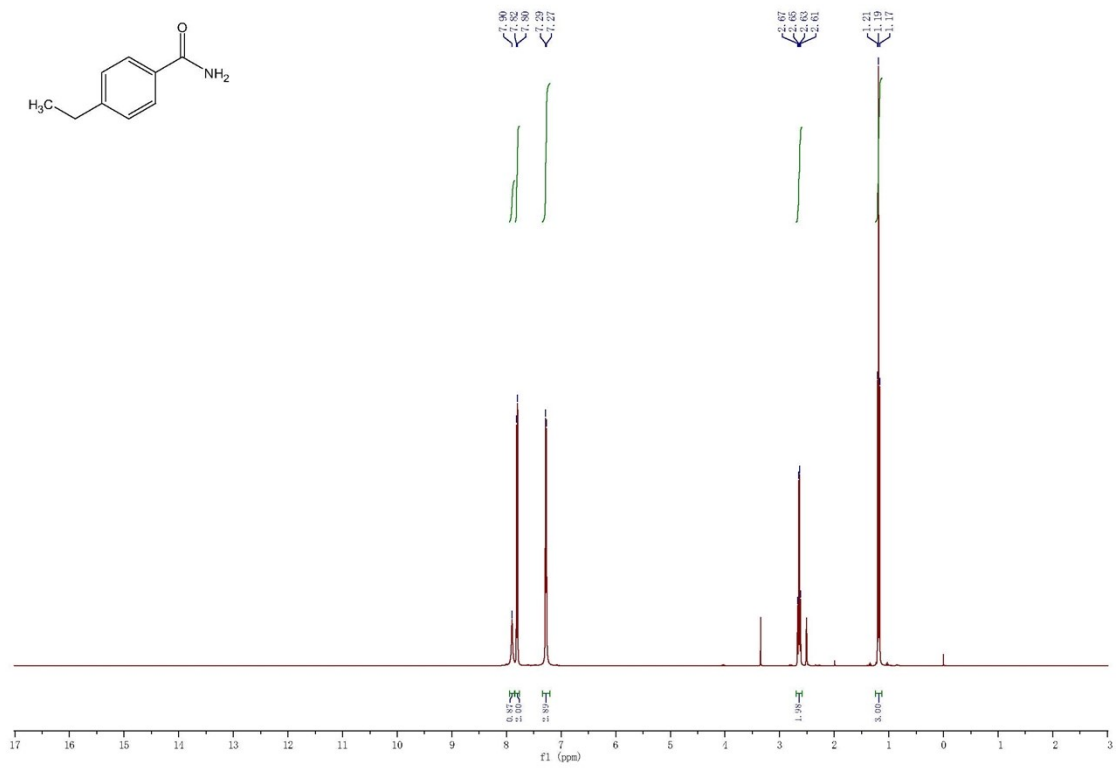
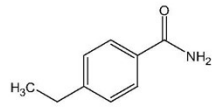
2y: 2-(2-oxopyrrolidin-1-yl)acetamide



2jj: (R)-pyrrolidine-2-carboxamide



**2v: 4-ethylbenzamide**



2kk: 4'-((1,7-dimethyl-2'-propyl-1H,3'H-[2,5'-bibenzo[d]imidazol]-3'-yl)methyl)-[1,1'-biphenyl]-2-carboxamide

