Electronic Supplementary Information

Clean Synthesis of Primary to Tertiary Carboxamides by CsOH-Catalyzed Aminolysis of Nitriles in Water

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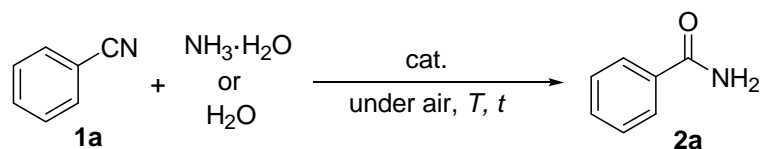[b] School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, P. R. China

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Contents

Table S1. Condition Screening and Optimization for Primary Carboxamide Synthesis by Nitrile Aminolysis with Ammonia.[a]


run	cat. (mol%)	reactant	T, t	2a%[b]
1	CsOH·H$_2$O (10)	H$_2$O	100 ^{o}C, 24 h	61[c]
2	CsOH·H$_2$O (10)	H$_2$O	100 ^{o}C, 2 h	57[d]
3	CsOH·H$_2$O (10)	H$_2$O	100 ^{o}C, 1 h	48[e]
4	CsOH·H$_2$O (10)	NH$_3$·H$_2$O	100 ^{o}C, 1 h	>99 (94)
5	KOH (10)	NH$_3$·H$_2$O	100 ^{o}C, 2 h	64
6	KOH (10)	H$_2$O	100 ^{o}C, 2 h	41
7	NaOH (10)	NH$_3$·H$_2$O	100 ^{o}C, 2 h	80
8	NaOH (10)	H$_2$O	100 ^{o}C, 2 h	11
9	t-BuOK (10)	NH$_3$·H$_2$O	100 ^{o}C, 2 h	60
10	t-BuOK (10)	H$_2$O	100 ^{o}C, 2 h	38
11	t-BuONa (10)	NH$_3$·H$_2$O	100 ^{o}C, 2 h	81
12	t-BuONa (10)	H$_2$O	100 ^{o}C, 2 h	46
13	Cs$_2$CO$_3$ (10)	NH$_3$·H$_2$O	100 ^{o}C, 5 h	0
14	CsF (10)	NH$_3$·H$_2$O	100 ^{o}C, 5 h	0
15	--	NH$_3$·H$_2$O	100 ^{o}C, 24 h	0
16	CsOH·H$_2$O (10)	NH$_3$·H$_2$O	80 ^{o}C, 6 h	96
17	CsOH·H$_2$O (5)	NH$_3$·H$_2$O	100 ^{o}C, 24 h	80

[a] The mixture of **1a** (1.0 mmol) and base catalyst in NH$_3$·H$_2$O or distilled water (0.5 mL) was directly sealed under air in a Schlenk tube and then heated and monitored by GC-MS/TLC. [b] GC yields (isolated yield in parenthesis) based on **1a**. [c] 28% PhCN and 11% PhCOOH were detected. [d] 33% PhCN and 10% PhCOOH were detected. [e] 44% PhCN and 8% PhCOOH were detected.

Control Reactions

1. Reaction progress monitoring of the hydration reaction (runs 1-3 in Table 1 in the manuscript and also in Table S1 of ESI)

run	t	1a/2a/PhCOOH^{GC}
1	1 h	44 / 48 / 8
2	2 h	33 / 57 / 10
3	24 h	28 / 61 / 11
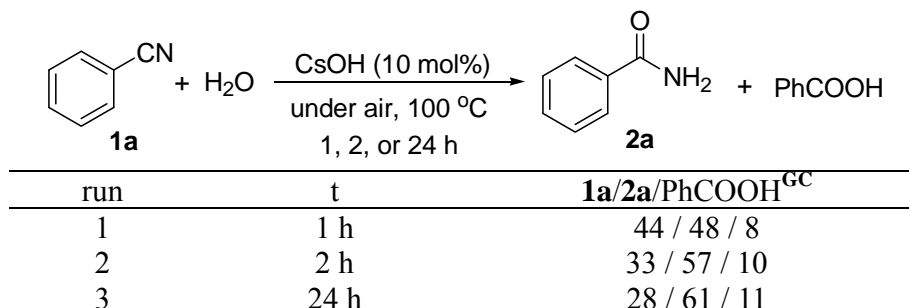
Typical procedure: The mixture of **1a** (0.103 g, 1.0 mmol), CsOH·H$_2$O (0.018 g, 0.1 mmol, 10 mol%), H$_2$O (0.5 mL) in a 20 mL Schlenk tube under air and heated at 100 °C for 1 h. The mixture was then quenched with ethyl acetate and carefully acidified with 0.5 mL HCl (1 M). The organic layer was separated and water layer extracted by ethyl acetate. The combined organic layer was then concentrated, and the crude reaction residues were then subjected to GC-MS analysis (data shown in above table, see also Table 1 in the manuscript and Table S1 in ESI, runs 1-3).

To isolate the generated PhCOOH, the crude reaction residue was again dissolved in ethyl acetate and washed with dilute NaOH for several times to convert PhCOOH to PhCOONa. The separated water layer was also extracted with small amounts of ethyl acetate to remove any organic chemicals. The water layer was then neutralized by HCl to convert PhCOONa back into PhCOOH. However, although we tried several times, the generated low yields of PhCOOH could not be successfully isolated. This is very possibly because the reactions are too small in scale and that the tedious workup procedure involved the use of water. Therefore, GC data were adopted for discussion.
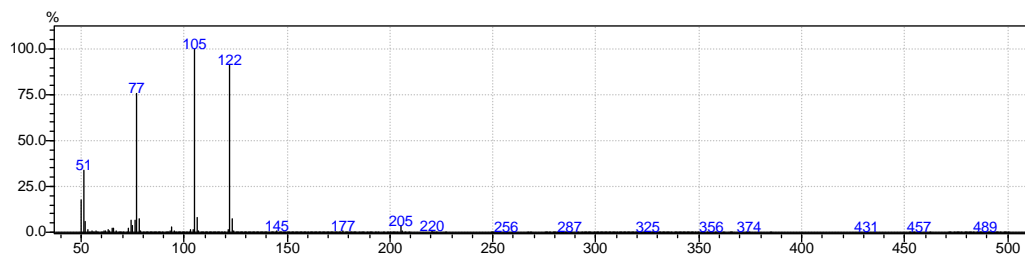
GC spectra of 1 h reaction:
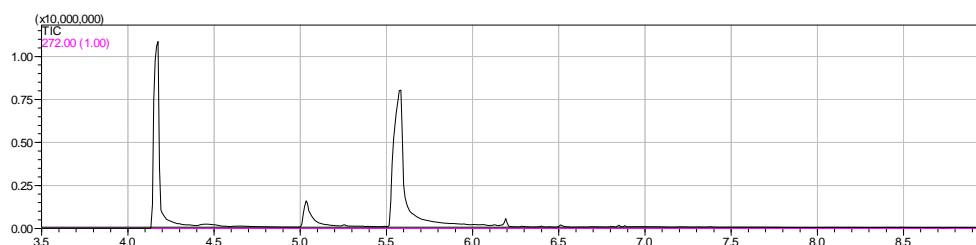
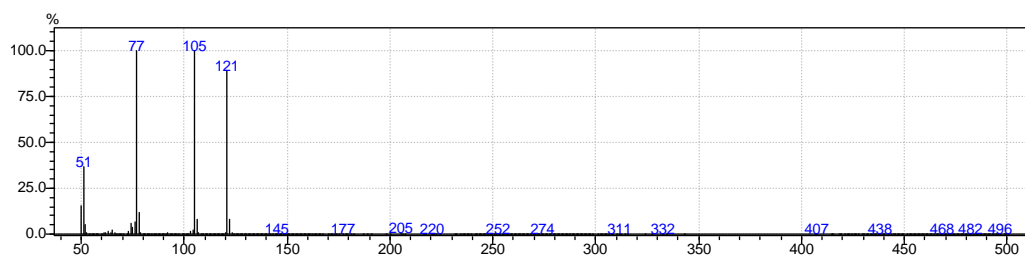| Ret.time	Start TM	End TM	m/z	Area	Area%	Height	Height%	A/H
4.171	4.125	4.833	TIC	30148241	43.55	10859644	53.45	2.78 MI
5.035	4.983	5.258	TIC	5712492	8.25	1534540	7.55	3.72 MI
5.579	5.500	5.767	TIC	33373852	48.20	7925131	39.00	4.21 MI

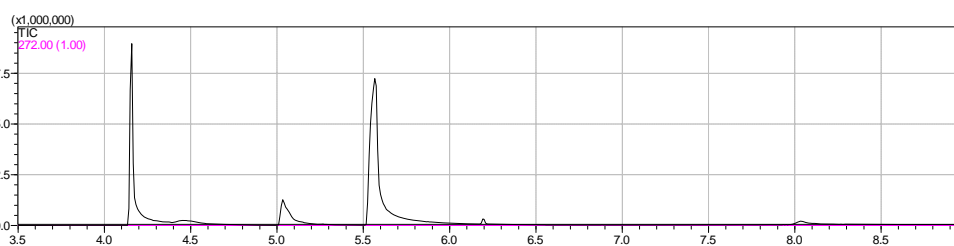**Mass spectra:**

Ret.time: 4.171 min, PhCN (**1a**)
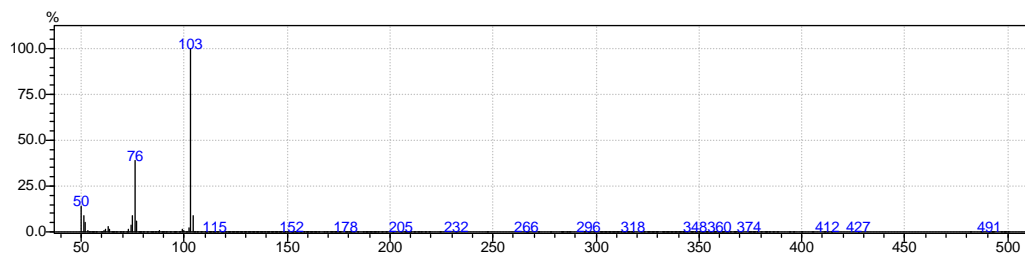
Ret.time: 5.035 min, PhCOOH
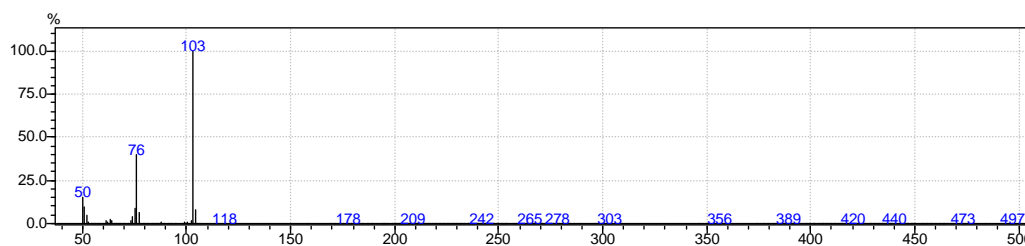

Ret.time: 5.579 min, PhCONH$_2$ (**2a**)

GC spectra of 2 h reaction:

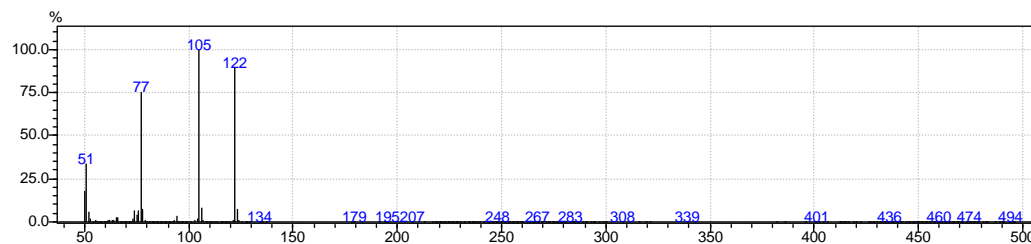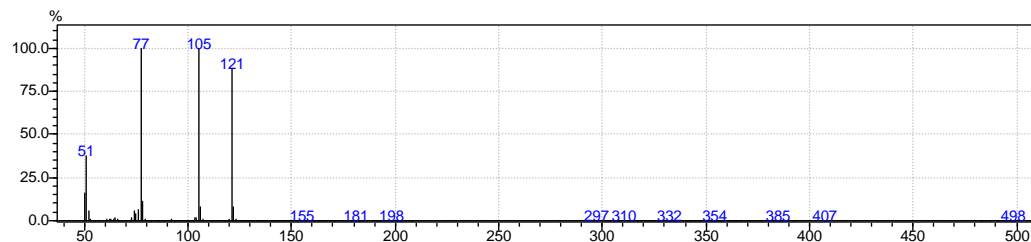| Ret.time	Start TM	End TM	m/z	Area	Area%	Height	Height%	A/H
4.156	4.117	4.642	TIC	17314856	33.31	8955039	51.33	1.93 MI
5.035	4.992	5.325	TIC	5146724	9.90	1263932	7.25	4.07 MI
5.567	5.508	5.967	TIC	29515149	56.79	7225084	41.42	4.09 MI

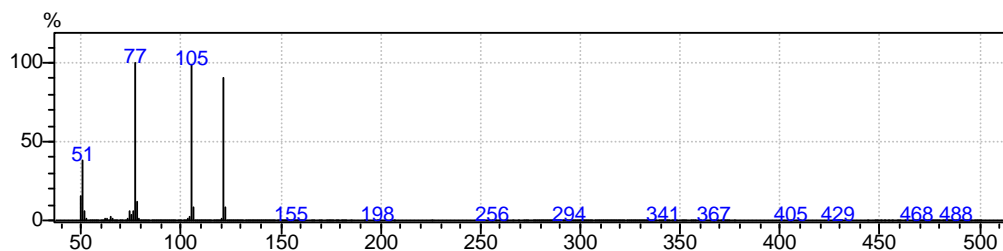**Mass spectra:**

Ret.time: 4.156 min, PhCN (**1a**)

Ret.time: 5.035 min, PhCOOH

Ret.time: 5.567 min, PhCONH$_2$ (**2a**)

GC spectra of 24 h reaction:
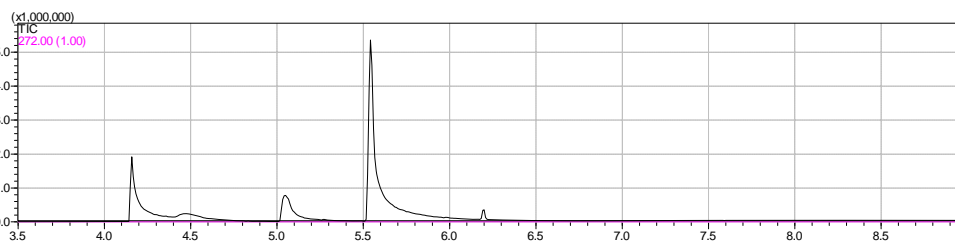
Ret.time	Start TM	End TM	m/z	Area	Area%	Height	Height%	A/H
4.159	4.117	4.700	TIC	8996261	28.28	1905119	23.80	4.72 MI
5.047	4.992	5.200	TIC	3474531	10.92	765860	9.57	4.54 MI
5.543	5.492	6.067	TIC	19340824	60.80	5333476	66.63	3.63 MI

Mass spectra:
Ret.time: 4.159 min, PhCN (**1a**)
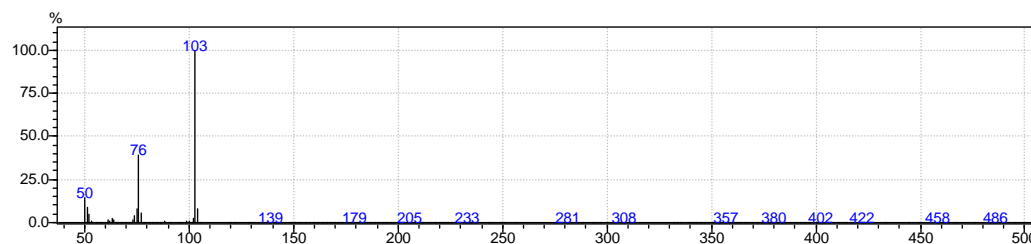
Ret.time: 5.047 min, PhCOOH

S5
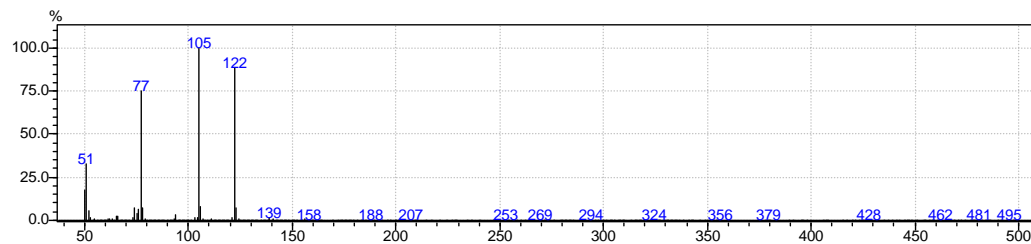
Ret.time: 5.543 min, PhCONH$_2$ (**2a**)
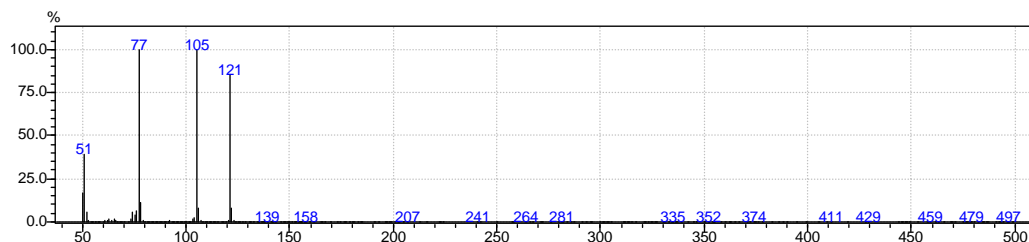

2. Condensation of PhCOOH and ammonia (eq. 1 in the manuscript)

$$\text{PhCOOH} \ + \ \text{NH}_3\cdot\text{H}_2\text{O} \ \xrightarrow[\text{under air, 100 °C, 1 h}]{\text{CsOH (10 mol\%)}} \ \underset{\textbf{2a}}{\text{Ph}\overset{\text{O}}{\diagup}\text{NH}_2}$$
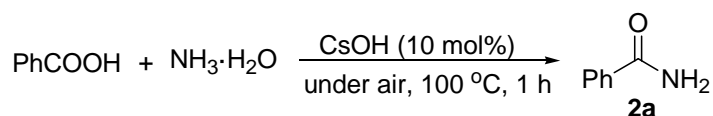
not detected by both TLC and GC

Procedure: The mixture of benzoic acid (0.122 g, 1.0 mmol), NH$_3$·H$_2$O (0.5 mL), CsOH· H$_2$O (0.017 g, 0.1 mmol, 10 mol%) in a 20 mL Schlenk tube was sealed under air and heated at 100 °C for 1 h. The reaction mixture was then quenched with ethyl acetate and monitored by TLC and GC-MS analysis. No **2a** could be detected by TLC analysis by comparison with the authentic sample. No formation of **2a** was also detected by GC-MS analysis.

3. Reaction progress monitoring of the aminolysis reaction with amines (eq. 2 in the manuscript)

$$\underset{\textbf{1a}}{\text{Ph}-\text{CN}} + \underset{\textbf{3a}}{\text{Ph}\diagup\text{NH}_2} \xrightarrow[\substack{\text{H}_2\text{O (0.5 mL)} \\ \text{N}_2\text{, 160 °C}}]{\text{CsOH (10 mol\%)}} \underset{\textbf{2a}}{\text{Ph}\overset{\text{O}}{\diagup}\text{NH}_2} + \underset{\textbf{4aa}}{\text{Ph}\overset{\text{O}}{\diagup}\underset{\text{H}}{\text{N}}\diagup\text{Ph}} + \text{PhCOOH}$$

1) 1 h, **1a**/**2a**/**4aa**/PhCOOH = 4/86/0/10^{GC}
2) 6 h, **1a**/**2a**/**4aa**/PhCOOH = 3/89/5/3^{GC}
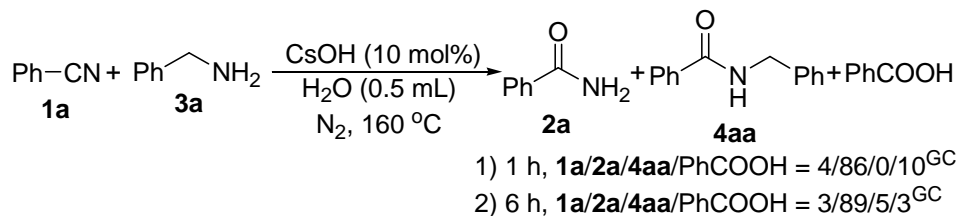
Procedure: The mixture of **1a** (0.103 g, 1.0 mmol), **3a** (0.129 g, 1.2 mmol, 1.2 equiv.), CsOH· H$_2$O (0.017 g, 0.1 mmol, 10 mol%), H$_2$O (0.5 mL) in a 20 mL Schlenk tube was sealed under N$_2$ and heated at 160 °C for 1 h or 6 h. The reaction mixture was then quenched with ethyl acetate and carefully acidified with 0.5 mL HCl (1M). The organic layer was separated and water layer extracted by ethyl acetate. The combined organic layer was then concentrated and the residue subjected to GC-MS analysis.

GC spectra of 1 h reaction:
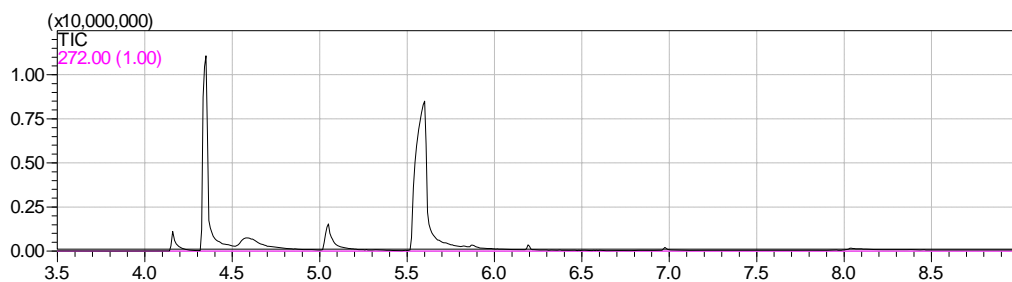
Ret.time	Start TM	End TM	m/z	Area	Area%	Height	Height%	A/H
4.160	4.117	4.275	TIC	2089272	4.27	1106069	9.99	1.89 MI
5.048	4.975	5.300	TIC	4760488	9.73	1493550	13.49	3.19 MI
5.596	5.500	6.075	TIC	42065059	86.00	8469612	76.52	4.97 MI

Mass spectra:

Ret.time: 4.160 min, PhCN (**1a**)
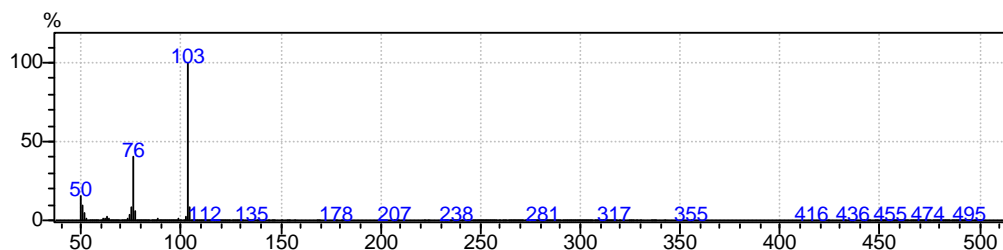
Ret.time: 5.048 min, PhCOOH
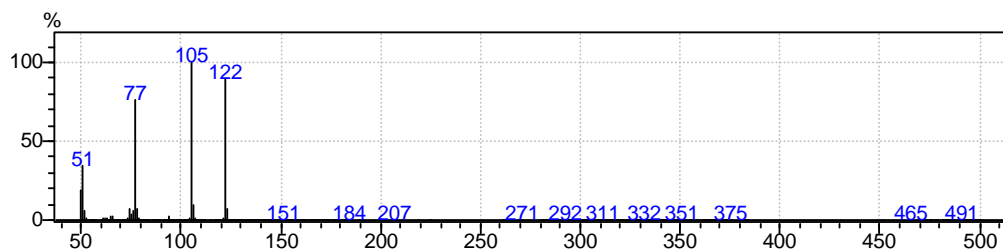
Ret.time: 5.596 min, PhCONH$_2$ (**2a**)

GC spectra of 6 h reaction:
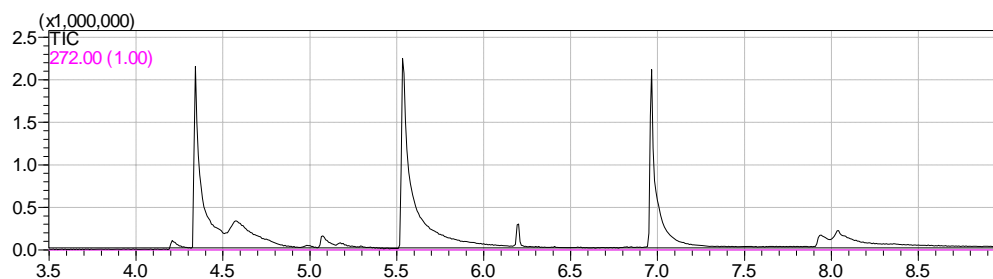
Ret.time	Start TM	End TM	m/z	Area	Area%	Height	Height%	A/H
4.210	4.100	4.300	TIC	319908	2.83	103301	4.00	3.09 MI
5.073	5.017	5.367	TIC	602252	5.33	131869	5.10	4.57 MI
5.537	5.500	6.125	TIC	10038474	88.81	2235666	86.51	4.49 MI
7.940	7.917	7.975	TIC	342722	3.03	113497	4.39	3.05 MI

Mass spectra:

Ret.time: 4.210 min, PhCN (**1a**)
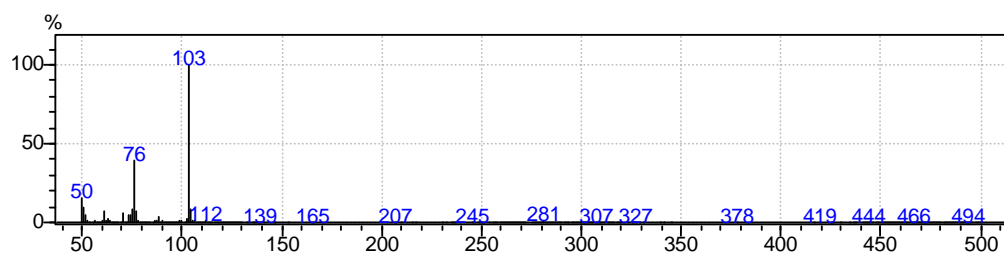
Ret.time: 5.073 min, PhCOOH
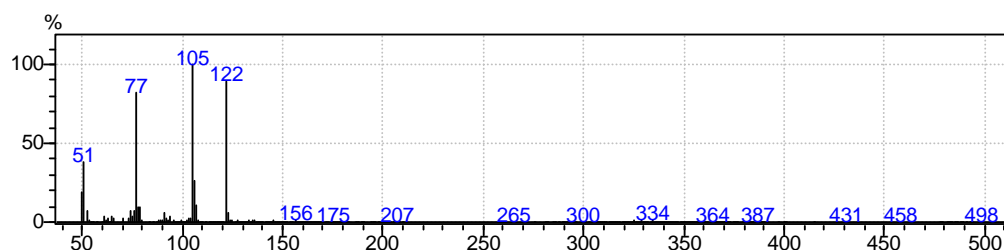
Ret.time: 5.537 min, PhCONH$_2$ (**2a**)
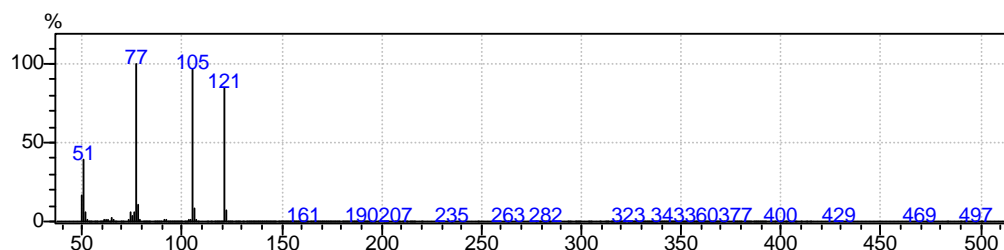
Ret.time: 7.940 min, PhCONHCH$_2$Ph (**4aa**)
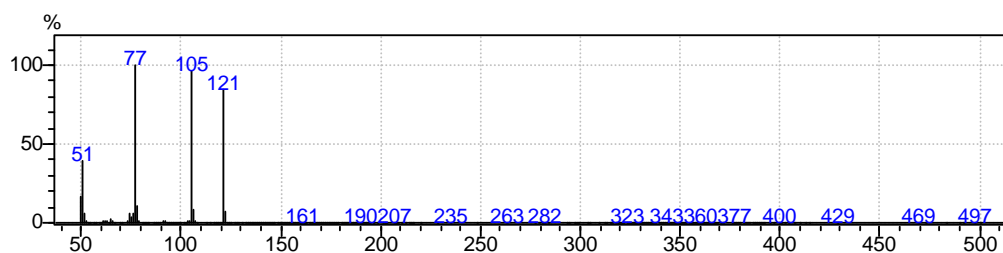
4. Transamidation reaction (eq. 3 in the manuscript)
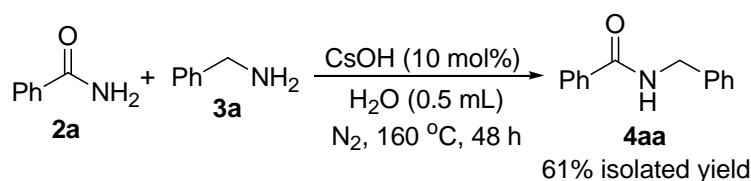
Procedure: The mixture of **2a** (0.242 g, 2.0 mmol), **3a** (0.259 g, 2.4 mmol, 1.2 equiv.), CsOH·H$_2$O (0.040 g, 0.2 mmol, 10 mol%), H$_2$O (0.5 mL) in a 20 mL Schlenk tube was sealed under N$_2$ and heated at 160 °C for 48 h. The mixture was then quenched with ethyl acetate, solvent evaporated under vacuum, and the residue purified by column chromatography using ethyl acetate and petroleum ether (60-90 °C) (v/v 1/5) as the eluent. 61% Isolated yield (0.254 g) of **4aa** was obtained.

5. Condensation of PhCOOH and benzyl amine (eq. 4 in the manuscript)
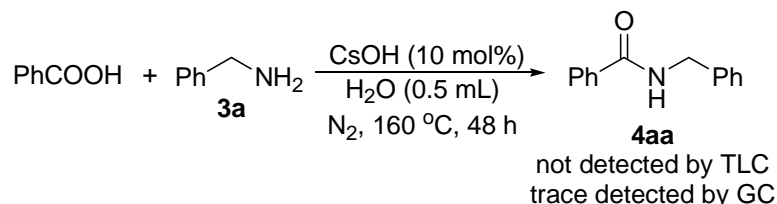
Procedure: The mixture of benzoic acid (0.122 g, 1.0 mmol), **3a** (0.129 g, 1.2 mmol, 1.2 equiv.), CsOH·H$_2$O (0.017 g, 0.1 mmol, 10 mol%), H$_2$O (0.5 mL) in a 20 mL Schlenk tube was sealed under N$_2$ and heated at 160 °C for 48 h. The mixture was then quenched with ethyl acetate and monitored by TLC and GC-MS analysis. No **4aa** could be detected by TLC by comparison with the authentic sample. Only trace amounts of **4aa** was detected by GC-MS analysis.

Experimental

General. Substrates and catalysts were all purchased and used as received. Progresses of the reactions were monitored by TLC and/or GC-MS. Products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-III 500 instrument (500 MHz for ^{1}H and 125.4 MHz for ^{13}C NMR spectroscopy). Unless otherwise noted, d_6-DMSO or CDCl$_3$ was used as the solvent. Chemical shifts for ^{1}H and ^{13}C NMR were referred to internal Me$_4$Si (0 ppm). Mass spectra were measured on a Shimadzu GCMS-QP2010 Plus spectrometer (EI).

Typical Procedure for CsOH-Catalyzed Nitrile Aminolysis with Ammonia for Preparation of Primary Amides. The mixture of benzonitrile **1a** (0.103g, 1.0 mmol) and CsOH·H$_2$O (0.017 g, 0.1 mmol, 10 mol%) in NH$_3$·H$_2$O (0.5 mL) was directly sealed under air in a Schlenk tube and then heated at 100 ^{o}C for 1 h. After completion of the reaction as monitored by GC-MS and/or TLC, the mixture was directly purified, without any workup, through a silica gel column by using ethyl acetate and petroleum ether as the eluent, affording benzamide **2a** in 94% isolated yield.
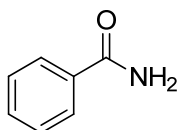
Benzamide (2a). ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.97 (b, 1H), 7.89-7.86 (m, 2H), 7.54-7.51 (m, 1H), 7.47-7.44 (m, 2H), 7.36 (b, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 167.9, 134.2, 131.2, 128.2, 127.4. MS (EI): m/z (%) 122 (6), 121 (86), 106 (8), 105 (100), 78 (12), 77 (83), 76 (6), 75 (4), 74 (6), 65 (2), 52 (6), 51 (35), 50 (20), 44 (8), 39 (6), 38 (4), 37 (3), 27 (4). This compound was known: Li, Z.; Wang, L.; Zhou, X. *Adv. Synth. Catal.* **2012**, *354*, 584-588.
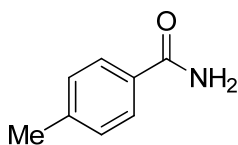

**4-Methylbenzamide (2b).** ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.71 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.01 (b, 2H), 2.40 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 169.4, 142.5, 130.6, 129.3, 127.4, 21.5. MS (EI): m/z (%) 136 (5), 135 (60), 120 (8), 119 (100), 117 (3), 92 (5), 91 (74), 90 (8), 89 (10), 65 (33), 64 (4), 63 (13), 51 (9), 50 (6), 44 (12), 41 (5), 40 (9), 39 (20), 38 (4). This compound was known: Li, Z.; Wang, L.; Zhou, X. *Adv. Synth. Catal*. **2012**, *354*, 584-588.
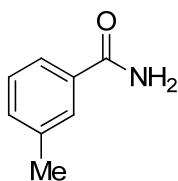
3-Methylbenzamide (2c). ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.92 (b, 1H), 7.71 (s, 1H), 7.68-7.66 (m, 1H), 7.33 (d, J = 5.0 Hz, 2H), 7.30 (b, 1H), 2.35 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 168.0, 137.4, 134.2, 131.7, 128.0, 124.5, 20.9. MS (EI): m/z (%) 136 (6), 135 (63), 120 (9), 119 (100), 117 (4), 116 (2), 92 (6), 91 (77), 90 (5), 89 (7), 65 (18), 63 (6), 62 (2), 51(4), 44 (3), 39 (6). This compound was known: Li, Z.; Wang, L.; Zhou, X. *Adv. Synth. Catal*. **2012**, *354*, 584-588.
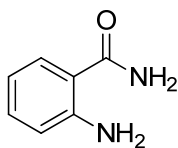
2-Aminobenzamide (2d). ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.70 (b, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.13-7.10 (m, 1H), 7.03 (b, 1H), 6.66 (d, J = 8.0 Hz, 1H), 6.53 (b, 2H), 6.48-6.45 (m, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 171.3, 150.1, 131.8, 128.7, 116.4, 114.4, 113.7. MS (EI): m/z (%) 137(6), 136 (74), 120 (15), 119 (100), 118 (6), 93 (4), 92 (52), 91 (15), 66 (4), 65 (24), 64 (9), 63 (6), 52 (5), 39 (9). This compound was known: Tao, T.; Wang, Z.; Liu, Z.; Feng, X.; Wang, Q. *Green. Chem.* **2012**, *14*, 921-924.
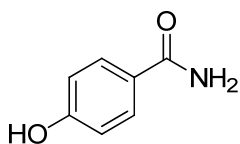

4-Hydroxybenzamide (2e). ^{1}H NMR (500 MHz, d_6-DMSO): δ 9.94 (b, 1H), 7.73 (d, J = 8.5 Hz, 2H), 7.71 (b, 1H), 7.05 (b, 1H), 6.78 (d, J = 9.0 Hz, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 167.6, 160.1, 129.4, 125.0, 114.6. MS (EI): m/z (%) 138 (5), 137 (59), 122 (8), 121 (100), 93 (36), 92 (6), 66 (4), 65 (33), 64 (6), 63 (12), 62 (6), 55 (4), 53 (7), 50 (4), 44 (7), 39 (22), 38 (7), 37 (3). This compound was known: Datta, B.; Pasha, M. A. *Bull. Korean Chem. Soc.* **2012**, *33(7)*, 2129-2130.
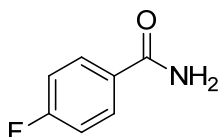
4-Fluorobenzamide (2f). ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.98 (b, 1H), 7.96-7.93 (m, 2H), 7.38 (b, 1H), 7.28-7.25 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 166.8, 163.9 (d, J_{C-F} = 247.7 Hz), 130.7, 130.0, 115.0 (d, J_{C-F} = 21.7 Hz). MS (EI): m/z (%) 140 (6), 139 (62), 124 (8), 123 (100), 122 (2), 121 (5), 96 (10), 95 (80), 94 (8), 93 (3), 83 (3), 76 (4), 75 (35), 74 (10), 70 (4), 69 (8), 68 (6), 63

(4), 62 (3), 61 (3), 57 (4), 51 (7), 50 (14), 44 (11), 39 (3), 38 (3), 37 (4), 31 (3). This compound was known: Tao, T.; Wang, Z.; Liu, Z.; Feng, X.; Wang, Q. *Green. Chem.* **2012**, *14*, 921-924.
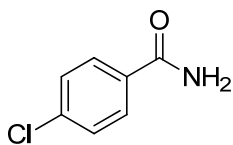
4-Chlorobenzamide (2g). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.04 (b, 1H), 7.89 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.45 (b, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 166.8, 136.0, 133.0, 129.4, 128.2. MS (EI): m/z (%) 157 (16), 155 (50), 141 (29), 140 (8), 139 (100), 137 (8), 113 (16), 112 (5), 111 (51), 85 (4), 77 (5), 76 (8), 75 (35), 74 (15), 73 (5), 51 (10), 50 (21), 44 (10), 38 (5), 28 (4). This compound was known: Li, Z.; Wang, L.; Zhou, X. *Adv. Synth. Catal*. **2012**, *354*, 584-588.
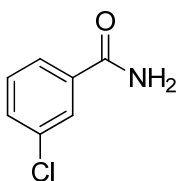
3-Chlorobenzamide (2h). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.09 (b, 1H), 7.92-7.91 (m, 1H), 7.85-7.83 (m, 1H), 7.61-7.59 (m, 1H), 7.52 (b, 1H), 7.51-7.48 (m, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 166.4, 136.3, 133.1, 131.0, 130.2, 127.3, 126.1. MS (EI): m/z (%) 157 (16), 156 (4), 155 (50), 141 (29), 140 (8), 139 (100), 137 (8), 113 (16), 112 (5), 111 (51), 85 (4), 77 (5), 76 (8), 75 (35), 74 (15), 73 (5), 51 (10), 50 (21), 44 (10), 28 (4). This compound was known: Tao, T.; Wang, Z.; Liu, Z.; Feng, X.; Wang, Q. *Green. Chem.* **2012**, *14*, 921-924.
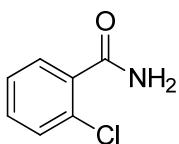
2-Chlorobenzamide (2i). ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.88 (b, 1H), 7.58 (b, 1H), 7.49-7.47 (m, 1H), 7.46-7.42 (m, 2H), 7.40-7.38 (m, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 168.2, 137.1, 130.5, 129.60, 129.57, 128.6, 127.0. MS (EI): m/z (%) 157 (18), 156 (4), 155 (58), 142 (2), 141 (32), 140 (8), 139 (100), 113 (12), 112 (6), 111 (38), 85 (3), 77 (9), 76 (8), 75 (26), 74 (8), 51 (9), 50 (16), 44 (11), 38 (4), 37 (3). This compound was known: Li, Z.; Wang, L.; Zhou, X. *Adv. Synth. Catal*. **2012**, *354*, 584-588.
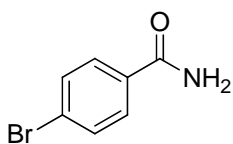

4-Bromobenzamide (2j). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.05 (b, 1H), 7.83-7.81 (m, 2H),

7.67-7.65 (m, 2H), 7.46 (b, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 167.0, 133.4, 131.2, 129.6, 125.0. MS (EI): m/z (%) 201 (51), 199 (53), 185 (94), 184 (7), 183 (100), 157 (37), 155 (38), 77 (20), 76 (46), 75 (45), 74 (26), 73 (6), 65 (6), 51 (22), 50 (67), 49 (6), 44 (25). This compound was known: Tao, T.; Wang, Z.; Liu, Z.; Feng, X.; Wang, Q. *Green. Chem.* **2012**, *14*, 921-924.
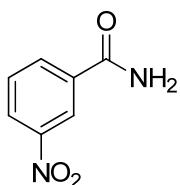
3-Nitrobenzamide (2k). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.69 (s, 1H), 8.39 (b, 1H), 8.36 (d, $J =$ 8.0 Hz, 1H), 8.31 (d, $J =$ 7.5 Hz, 1H), 7.79-7.76 (m, 1H), 7.73 (b, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 165.8, 147.8, 135.7, 133.8, 130.1, 125.9, 122.2. MS (EI): m/z (%) 167 (6), 166 (67), 151 (8), 150 (100), 105 (3), 104 (33), 103 (8), 92 (17), 77 (14), 76 (54), 75 (32), 74 (32), 73 (6), 65 (26), 64 (6), 63 (9), 62 (5), 53 (4), 52 (5), 51 (26), 50 (52), 46 (20), 44 (50), 39 (9), 38 (8), 37 (5), 30 (31). This compound was known: Li, Z.; Wang, L.; Zhou, X. *Adv. Synth. Catal.* **2012**, *354*, 584-588.
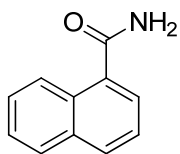
1-Naphthamide (2l). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.31 (d, $J =$ 8.5 Hz, 1H), 8.01-7.96 (m, 3H), 7.64 (d, $J =$ 6.5 Hz, 1H), 7.59-7.52 (m, 4H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 171.4, 135.4, 134.0, 130.53, 130.50, 128.9, 127.4, 126.9, 126.4, 125.9, 125.7. MS (EI): m/z (%) 172 (9), 171 (72), 170 (26), 156 (9), 155 (75), 154 (7), 153 (4), 128 (15), 127 (100), 126 (28), 125.4 (3), 115 (9), 101 (9), 85 (4), 77 (12), 76 (5), 75 (10), 63 (12), 51 (8), 50 (6), 44 (4). This compound was known: Tao, T.; Wang, Z.; Liu, Z.; Feng, X.; Wang, Q. *Green. Chem.* **2012**, *14*, 921-924.
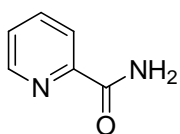
Picolinamide (2m). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.58 (d, $J =$ 4.5 Hz, 1H), 8.22 (d, $J =$ 8.0 Hz, 1H), 7.88-7.85 (m, 2H), 7.47-7.44 (m, 1H), 5.97 (b, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 166.5, 150.8, 149.0, 138.2, 127.0, 122.4. MS (EI): m/z (%) 123 (2), 122 (29), 80 (6), 79 (100), 78 (34), 76 (5), 53 (7), 52 (50), 51 (39), 50 (20), 49 (5), 44 (19), 39 (8), 38 (6), 37 (4), 28 (7), 27 (8), 26 (7), 16 (5). This compound was known: Tamura, M.; Wakasugi, H.; Shimizu, K.; Satsuma, A. *Chem. Eur. J.* **2011**, *17*, 11428-11431.
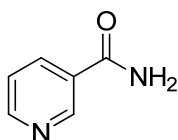
Nicotinamide (2n). ^{1}H NMR (500 MHz, d_6-DMSO): δ 9.02 (s, 1H), 8.69 (dd, J = 1.5, J = 5.0 Hz, 1H), 8.20 (d, J = 7.5 Hz, 1H), 8.14 (b, 1H), 7.58 (b, 1H), 7.48 (dd, J = 8.0, J = 5.0 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 166.4, 151.8, 148.6, 135.1, 129.7, 123.4. MS (EI): m/z (%) 123 (8), 122 (100), 106 (60), 105 (6), 104 (3), 94 (3), 79 (8), 78 (69), 77 (7), 76 (3), 75 (2), 53 (3), 52 (12), 51 (30), 50 (13), 49 (2), 44 (8), 39 (3), 38 (2). This compound was known: Li, Z.; Wang, L.; Zhou, X. *Adv. Synth. Catal*. **2012**, *354*, 584-588.
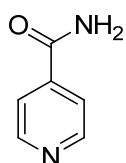
Isonicotinamide (2o). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.72 (d, J = 6.0 Hz, 2H), 8.24 (b, 1H), 7.77 (d, J = 5.5 Hz, 2H), 7.71 (b, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 166.3, 150.2, 141.3, 121.4. MS (EI): m/z (%) 123 (8), 122 (100), 107 (2), 106 (40), 79 (12), 78 (56), 77 (2), 53 (2), 52 (15), 51 (36), 50 (14), 49 (2), 44 (13), 39 (3), 28 (3), 26 (2). This compound was known: Tao, T.; Wang, Z.; Liu, Z.; Feng, X.; Wang, Q. *Green. Chem.* **2012**, *14*, 921-924.
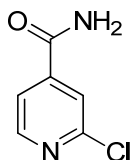
2-Chloroisonicotinamide (2p). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.56 (d, J = 5.0 Hz, 1H), 8.33 (b, 1H), 7.87 (b, 2H), 7.78 (dd, J = 5.0, J = 1.5 Hz, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 164.9, 150.9, 150.7, 144.9, 122.1, 121.0. MS (EI): m/z (%) 158 (25), 157 (7), 156 (78), 142 (32), 141 (8), 140 (100), 114 (16), 112 (48), 85 (14), 78 (8), 76 (19), 75 (4), 51 (10), 50 (16), 44(13), 28 (3). This compound was known: Sahnoun, S.; Messaoudi, S.; Peyrat, J.; Brion, J.; Alami, M. *Tetrahedron Lett.* **2012**, *53*, 2860-2863.
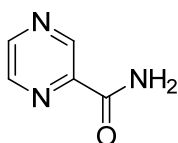
Pyrazine-2-Carboxamide (2q). ^{1}H NMR (500 MHz, d_6-DMSO): δ 9.19 (d, J = 1.5 Hz, 1H), 8.85 (d, J = 2.5 Hz, 1H), 8.71 (dd, J = 2.5, J = 1.5 Hz, 1H), 8.25 (b, 1H), 7.86 (b, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 170.3, 152.6, 150.3, 148.9, 148.8. MS (EI): m/z (%) 124 (7), 123 (100), 81 (4), 80 (80), 79 (18), 54 (2), 53 (51), 52 (32), 51 (9), 44 (18), 40 (2), 28 (12), 26 (15). This compound was known:

Tamura, M.; Wakasugi, H.; Shimizu, K.; Satsuma, A. *Chem. Eur. J.* **2011**, *17*, 11428-11431.
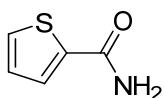
Thiophene-2-Carboxamide (2r). ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.99 (b, 1H), 7.78-7.77 (m, 2H), 7.40 (b, 1H), 7.18-7.16 (m, 1H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 168.1, 145.5, 136.2, 133.9, 133.1. MS (EI): m/z (%) 129 (4), 128 (5), 127(75), 113 (6), 112 (7), 111 (100), 83 (13), 82 (8), 81 (7), 58 (13), 57 (18), 54 (4), 53 (4), 50 (5), 45 (19), 44 (18), 39 (60), 38 (10). This compound was known: Rocío, G.-Á.; Josefina, D.; Pascale, C.; Victorio, C. *Organometallics*. **2011**, *30*, 5442–5451.
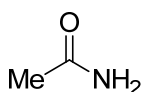
Acetamide (2s). ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.30 (b, 1H), 6.68 (b, 1H), 1.77 (s, 3H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 171.6, 22.4. MS (EI): m/z (%) 59 (M$^+$). This compound was known: Li, Z.; Wang, L.; Zhou, X. *Adv. Synth. Catal*. **2012**, *354*, 584-588.
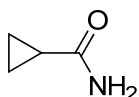
Cyclopropanecarboxamide (2t). ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.49 (b, 1H), 6.72 (b, 1H), 1.52-1.47 (m, 1H), 0.65-0.59 (m, 4H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 175.2, 13.8, 6.7. MS (EI): m/z (%) 85 (8), 84 (61), 69 (25), 68 (8), 54 (5), 44 (100), 43 (8), 42 (41), 41 (72), 40 (16), 39 (90), 38 (20), 37 (12), 28 (26), 27 (20), 26 (12), 16 (10), 15 (7), 14 (6). This compound was known: Jiang, D.; Yuan, F.; Jiang, B.; Li, C. *Chinese Patent Application,* **2011**, CN102249949A (20111123).
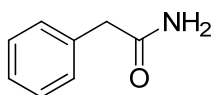
2-Phenylacetamide (2u). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.38-7.35 (m, 2H), 7.32-7.27 (m, 3H), 5.56 (b, 1H), 5.38 (b, 1H), 3.59 (s, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 173.4, 134.9, 129.4, 129.1, 127.5, 43.4. MS (EI): m/z (%) 135 (18), 93 (7), 92 (92), 91 (100), 90 (5), 89 (8), 65 (25), 64 (3), 63 (11), 51 (8), 50 (4), 44 (21), 41 (3), 39 (16), 38 (3). This compound was known: Li, Z.; Wang, L.; Zhou, X. *Adv. Synth. Catal.* **2012**, *354*, 584-588.
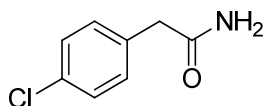
2-(4-Chlorophenyl)acetamide (2v). ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.48 (b, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.90 (b, 1H), 3.38 (s, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 171.8, 135.5, 130.96, 130.91, 128.0, 41.3. MS (EI): m/z (%) 158 (14), 156 (41), 128 (15), 127 (24),

126 (46), 125 (63), 112 (4), 99 (6), 92 (8), 91 (100), 90 (7), 89 (16), 77 (5), 65 (5), 63 (9), 51 (6), 39 (7), 31 (17). This compound was known: Khodaei, M. M.; Nazari, E. *Tetrahedron Lett.* **2012**, *53*, 2881-2884.
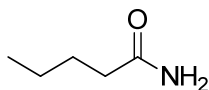
Pentanamide (2w). [^1]H NMR (500 MHz, d_6-DMSO): δ 7.22 (b, 1H), 6.66 (b, 1H), 2.03 (t, J = 7.5 Hz, 2H), 1.49-1.43 (m, 2H), 1.29-1.24 (m, 2H), 0.89-0.85 (m, 3H). [^13]C NMR (125.4 MHz, d_6-DMSO): δ 174.3, 34.8, 27.2, 21.8, 13.7. MS (EI): m/z (%) 86 (3), 85 (2), 73 (3), 72 (18), 60 (3), 59 (100), 57 (11), 55 (5), 44 (39), 43 (9), 42 (4), 41 (16), 39 (6), 29 (19), 28 (4). This compound was known: Das, R.; Chakraborty, D. *Catal. Commun.* **2012**, *26*, 48-53.
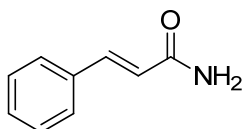
Cinnamamide (2x). [^1]H NMR (500 MHz, d_6-DMSO): δ 7.57-7.54 (m, 3H), 7.44-7.37 (m, 4H), 7.10 (b, 1H), 6.62 (d, J = 16.0 Hz, 1H). [^13]C NMR (125.4 MHz, d_6-DMSO): δ 166.6, 139.1, 134.9, 129.4, 128.9, 127.5, 122.3. MS (EI): m/z (%) 148 (6), 147 (55), 146 (100), 131 (60), 130 (22), 129 (61), 128 (18), 104 (8), 103 (80), 102 (35), 78 (12), 77 (49), 76 (10), 63 (8), 51 (32), 50 (13), 44 (9), 39 (7). This compound was known: Li, Z.; Wang, L.; Zhou, X. *Adv. Synth. Catal*. **2012**, *354*, 584-588.

Typical Procedure for CsOH-Catalyzed Nitrile Aminolysis with Primary and Secondary Amines for Preparation of Secondary and Tertiary Carboxamides. The mixture of benzonitrile **1a** (0.103g, 1.0 mmol), benzylamine **3a** (0.129g, 1.2 mmol, 1.2 equiv.), and CsOH·H$_2$O (0.017 g, 0.1 mmol, 10 mol%) in distilled H$_2$O (0.5 mL) was sealed under nitrogen in a Schlenk tube and then heated at 160 °C for 2 days. After completion of the reaction as monitored by GC-MS and/or TLC, the mixture was directly purified, without any workup, through a silica gel column by using ethyl acetate and petroleum ether as the eluent, affording *N*-benzylbenzamide **4aa** in 68% isolated yield.
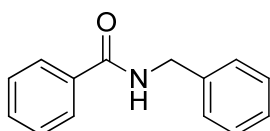
***N*-Benzyl benzamide (4aa)**. [^1]H NMR (500 MHz, d_6-DMSO): δ 9.05 (t, J = 6.0 Hz, 1H), 7.91 (d, J = 7.5 Hz, 2H), 7.56-7.53 (m, 1H), 7.50-7.47 (m, 2H), 7.34-33 (m, 4H), 7.27-7.24 (m, 1H), 4.50 (d, J = 6.0 Hz, 2H). [^13]C NMR (125.4 MHz, d_6-DMSO): δ 166.2, 139.7, 134.3, 131.2, 128.28, 128.24, 127.20, 127.17, 126.7, 42.6. MS (EI): m/z (%) 212 (13), 211 (82), 210 (25), 107 (3), 106 (9), 105

(100), 104 (4), 91 (9), 79 (4), 78 (5), 77 (42), 76 (2), 65 (4), 51 (11), 50 (3). This compound was known: Rattanaburi, P.; Khumraksa, B.; Pattarawarapan, M. *Tetrahedron Lett*. **2012**, *53*, 2689-269.
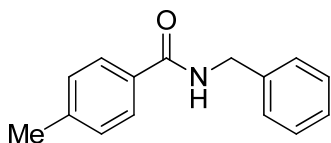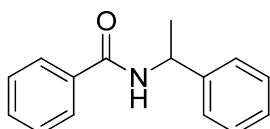
N-Benzyl 4-methylbenzamide (4ba). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.36-7.34 (m, 4H), 7.31-7.28 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.40 (b, 1H), 4.64 (d, *J* = 6.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.3, 142.0, 138.3, 131.6, 129.3, 128.8, 127.9, 127.6, 127.0, 44.1, 21.4. MS (EI): m/z (%) 226 (6), 225 (41), 120 (7), 119 (100), 107 (2), 92 (2), 91 (28), 89 (2), 77 (2), 65 (6). This compound was known: Muthaiah, S.; Ghosh, S. C.; Jee, J.-E.; Chen, C.; Zhang, J.; Hong, S. H. *J. Org. Chem.* **2010**, 75, 3002-3006.
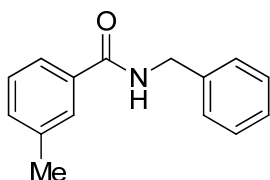
N-Benzyl 3-methylbenzamide (4ca). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.61 (s, 1H), 7.56-7.54 (m, 1H), 7.34-7.33 (m, 4H), 7.29-7.27 (m, 3H), 6.47 (b, 1H), 4.62 (d, *J* = 5.5 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.5, 138.4, 138.2, 134.4, 132.2, 128.7, 128.4, 127.9, 127.7, 127.6, 123.9, 44.1, 21.3. MS (EI): m/z (%) 226 (8), 225 (50), 107 (2), 106 (3), 104 (2), 92 (20), 91 (100), 89 (3), 77 (4), 65 (15), 63 (3), 51 (5), 50 (3), 43 (2), 41 (2). This compound was known: De Sarkar, S.; Studer, A. *Org. Lett.* **2010**, *12*, 1992-1995.
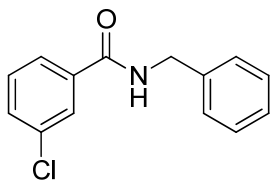
N-Benzyl 3-chlorobenzamide (4ha). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.77 (t, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.48-7.46 (m, 1H), 7.37-7.33 (m, 5H), 7.32-7.30 (m, 1H), 6.42 (b, 1H), 4.63 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 166.0, 137.9, 136.2, 134.8, 131.6, 129.9, 128.9, 128.0, 127.8, 127.4, 125.1, 44.3. MS (EI): m/z (%) 248 (2), 247 (12), 246 (6), 245 (37), 210 (4), 142 (2), 141 (34), 140 (7), 139 (100), 113 (6), 111 (17), 107 (2), 77 (3), 75 (4). This compound was known: De Sarkar, S.; Studer, A. *Org. Lett.* **2010**, *12*, 1992-1995.
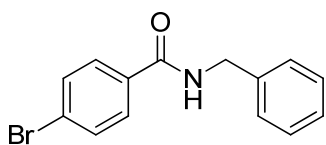
***N*-Benzyl 4-bromobenzamide (4ja)**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.38-7.29 (m, 5H), 6.37 (b, 1H), 4.62 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 166.4, 137.9, 133.2, 131.9, 128.9, 128.6, 128.0, 127.8, 126.3, 44.3. MS (EI): m/z (%) 292 (8), 291 (51), 290 (9), 289 (53), 186 (8), 185 (99), 184 (8), 183 (100), 157 (25), 155 (25), 108 (3), 107 (4), 106 (4), 104 (5), 77 (8), 76 (13), 75 (7), 50 (3). This compound was known: Ren, W.; Yamane, M. *J. Org. Chem*. **2010**, 75, 8410-8415.
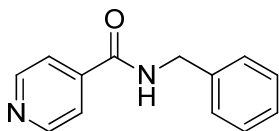
***N*-Benzyl isonicotinamide (4oa)**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.68 (d, *J* = 5.0 Hz, 2H), 7.62-7.61 (m, 2H), 7.37-7.31 (m, 5H), 6.81 (b, 1H), 4.63 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 165.5, 150.5, 141.5, 137.5, 128.9, 128.0, 127.9, 121.0, 44.3. MS (EI): m/z (%) 213 (15), 212 (100), 211 (23), 183 (2), 168 (2), 155 (3), 107 (6), 106 (54), 104 (7), 91 (10), 79 (10), 78 (22), 77 (6), 65 (3), 51 (8), 50 (2), 28 (3). This compound was known: Kim, B. R.; Lee, H.-G.; Kang, S.-B.; Sung, G. H.; Kim, J.-J.; Park, J. K.; Lee, S.-G.; Yoon, Y.-J. *Synthesis*. **2012**, *44*, 42-50.
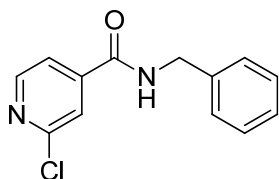
***N*-Benzyl 2-chloroisonicotinamide (4pa)**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.46 (d, *J* = 5.0 Hz, 1H), 7.66 (s, 1H), 7.53 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 1H), 7.38-7.31 (m, 5H), 6.66 (b, 1H), 4.61 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 164.1, 152.5, 150.5, 144.5, 137.2, 129.0, 128.04, 128.00, 122.0, 119.8, 44.4. MS (EI): m/z (%) 249 (5), 248 (28), 247 (21), 246 (100), 245 (27), 211 (42), 210 (12), 182 (7), 169 (7), 139 (10), 135 (11), 111 (11), 107 (27), 106 (8), 85 (9), 80 (12), 79 (7), 69 (19), 53 (9), 52 (9). This compound was known: Ferraccioli, R.; Carenzi, D.; Rombola, O.; Catellani, M. *Org. Lett*. **2004**, *6*, 4759-4762.
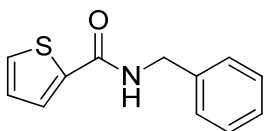
***N*-Benzyl thiophene-2-carboxamide (4ra)**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.51 (dd, *J* = 3.5 Hz, *J* = 1.0 Hz, 1H), 7.47 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 1H), 7.35-7.34 (m, 4H), 7.32-7.28 (m, 1H), 7.06 (dd, *J* = 4.0 Hz, *J* = 5.0 Hz, 1H), 6.31 (b, 1H), 4.61 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 161.8, 138.8, 138.1, 130.0, 128.8, 128.2, 128.0, 127.7, 127.6, 44.0. MS (EI): m/z (%) 219 (4), 218 (11), 217 (72), 216 (4), 113 (8), 112 (13), 111 (100), 106 (42), 105 (12), 104 (7), 91 (20), 84 (10), 83

(11), 79 (8), 77 (11), 65 (10), 51 (8), 39 (24). This compound was known: De Sarkar, S.; Studer, A. *Org. Lett.* **2010**, *12*, 1992-1995.
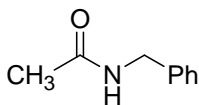
N-Benzyl acetamide (4sa). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.34-7.31 (m, 2H), 7.28-7.26 (m, 3H), 6.03 (b, 1H), 4.40 (d, J = 5.5 Hz, 2H), 2.00 (s, 3H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 169.9, 138.2, 128.7, 127.8, 127.5, 43.7, 23.2. MS (EI): m/z (%) 150 (8), 149 (80), 148 (4), 107 (23), 106 (100), 104 (6), 92 (4), 91 (34), 89 (3), 79 (14), 78 (6), 77 (12), 65 (7), 51 (8), 43 (32), 39 (5), 30 (10), 15 (3). This compound was known: Atkinson, B. N.; Chhatwal, A. R.; Lomax, H. V.; Walton, J. W.; Williams, J. M. J. *Chem. Commun.* **2012**, *48*, 11626-11628.
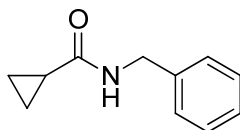
N-Benzyl cyclopropanecarboxamide (4ta). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.35-7.27 (m, 5H), 5.96 (b, 1H), 4.45 (d, J = 6.0 Hz, 2H), 1.38-1.33 (m, 1H), 1.02-0.99 (m, 2H), 0.76-0.73 (m, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 173.4, 138.5, 128.7, 127.9, 127.5, 43.9, 14.8, 7.2. MS (EI): m/z (%) 176 (8), 175 (56), 174 (13), 160 (6), 146 (9), 132 (10), 131 (26), 130 (8), 117 (12), 116 (7), 107 (8), 106 (48), 105 (12), 104 (100), 92 (8), 91 (94), 79 (12), 77 (18), 69 (45), 65 (22), 59 (12), 55 (9), 51 (15), 50 (6), 41 (57), 39 (34), 28 (12), 27 (5). This compound was known: Rolfe, A.; Probst, D. A.; Volp, K. A.; Omar, I.; Flynn, D. L.; Hanson, P. R. *J. Org. Chem.* **2008**, *73*, 8785-8790.
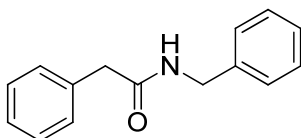
N-Benzyl 2-phenylacetamide (4ua). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36-7.24 (m, 8H), 7.17 (d, J = 7.0 Hz, 2H), 5.73 (b, 1H), 4.41 (d, J = 6.0 Hz, 2H), 3.62 (s, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 170.8, 138.1, 134.8, 129.5, 129.1, 128.7, 127.5, 127.44, 127.42, 43.9, 43.6. MS (EI): m/z (%) 226 (8), 225 (50), 107 (2), 106 (3), 104 (2), 92 (20), 91 (100), 89 (3), 77 (4), 65 (15), 63 (3), 51 (5), 50 (2), 43 (2), 41 (2). This compound was known: Muthaiah, S.; Ghosh, S. C.; Jee, J.-E.; Chen, C.; Zhang, J.; Hong, S. H. *J. Org. Chem.* **2010**, *75*, 3002-3006.
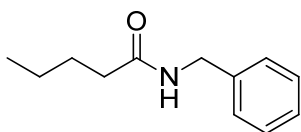
N-Benzyl pentanamide (4wa). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.34-7.26 (m, 5H), 5.82 (b, 1H), 4.42

(d, J = 6.0 Hz, 2H), 2.21 (t, J = 7.5 Hz, 2H), 1.67-1.61 (m, 2H), 1.39-1.33 (m, 2H), 0.92 (t, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 173.0, 138.5, 128.7, 127.8, 127.5, 43.6, 36.5, 27.9, 22.4, 13.8. MS (EI): m/z (%) 192 (6), 191 (42), 148 (18), 130 (3), 107 (33), 106 (100), 105 (13), 104 (4), 103 (3), 92 (3), 91 (29), 85 (2), 79 (10), 77 (4), 65 (4), 58 (5), 43 (10), 42 (3), 28 (2). This compound was known: Sabot, C.; Kumar, K. A.; Meunier, S.; Mioskowski, C. *Tetrahedron Lett*. **2007**, *48*, 3863-3866.
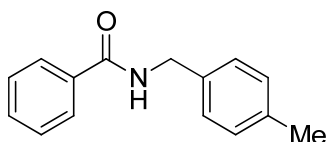
***N*-(4-Methylbenzyl) benzamide (4ab)**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.78 (d, J = 7.0 Hz, 2H), 7.51-7.48 (m, 1H), 7.42-7.40 (m, 2H), 7.26-7.24 (m, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.41 (b, 1H), 4.60 (d, J = 5.5 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.3, 137.4, 135.1, 134.5, 131.5, 129.5, 128.6, 128.0, 126.9, 44.0, 21.1. MS (EI): m/z (%) 226 (8), 225 (44), 210 (10), 156 (22), 120 (8), 113 (6), 106 (10), 105 (100), 104 (28), 79 (6), 78 (10), 77 (58), 56 (8), 51 (17), 50 (5), 42 (7). This compound was known: Maki, T.; Ishihara, K.; Yamamoto, H. *Tetrahedron*. **2007**, *63*, 8645-8657.
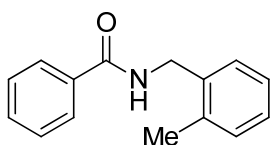
***N*-(2-Methylbenzyl) benzamide (4ac)**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.77 (d, J = 7.0 Hz, 2H), 7.48-7.46 (m, 1H), 7.42-7.39 (m, 2H), 7.28 (d, J = 7.0 Hz, 1H), 7.22-7.18 (m, 3H), 6.35 (b, 1H), 4.61 (d, J = 5.5 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.3, 136.6, 135.8, 134.4, 131.5, 130.6, 128.7, 128.6, 127.9, 127.0, 126.3, 42.3, 19.1. MS (EI): m/z (%) 226 (8), 225 (44), 210 (10), 156 (22), 120 (8), 113 (6), 106 (10), 105 (100), 104 (28), 103 (6), 79 (6), 78 (10), 77 (58), 56 (8), 51 (17), 50 (5), 42(7), 39(4). This compound was known: Molander, G.; Hiebel, M.-A. *Org. Lett*. **2010**, *12*, 4876-4879.
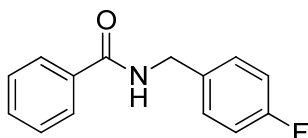
***N*-(4-Fluorobenzyl) benzamide (4ad)**. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.78 (d, J = 7.0 Hz, 2H), 7.52-7.49 (m, 1H), 7.45-7.42 (m, 2H), 7.34-7.31 (m, 2H), 7.05-7.01 (m, 2H), 6.44 (b, 1H), 4.61 (d, J = 6.0 Hz, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.4, 162.3 (d, $J_{C\text{-}F}$ = 245.3 Hz), 134.3, 134.1 (d, $J_{C\text{-}F}$ = 3.3 Hz), 131.7, 129.6 (d, $J_{C\text{-}F}$ = 8.2 Hz), 128.6, 126.9, 115.6 (d, $J_{C\text{-}F}$ = 21.4 Hz), 43.4. MS (EI):

m/z (%) 230 (3), 229 (20), 228 (7), 200 (6), 108 (7), 106 (7), 105 (100), 104 (8), 103 (7), 77 (47), 76 (5), 70 (7), 67 (8), 57 (7), 55 (11), 54 (6), 51 (10), 43 (12), 41 (14), 39 (8). This compound was known: Dube, D.; Scholte, A. A. *Tetrahedron Lett*. **1999**, *40*, 2295-2298.
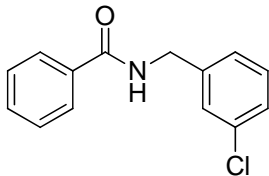
N-(3-Chlorobenzyl) benzamide (4ae). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.79 (d, *J* = 7.5 Hz, 2H), 7.52-7.50 (m, 1H), 7.45-7.42 (m, 2H), 7.33 (s, 1H), 7.27-7.22 (m, 3H), 6.58 (b, 1H), 4.61 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.4, 140.3, 134.6, 134.1, 131.7, 130.0, 128.6, 127.8, 127.7, 126.9, 125.9, 43.4. MS (EI): m/z (%) 247 (5), 246 (2), 245 (14), 211 (10), 210 (63), 106 (8), 105 (100), 78 (4), 77 (46), 76 (2), 51 (8). This compound was known: Julius, V. B.; Kuhn, M.; Weismantel, J. *J. Liebigs. Annalen. der. Chem*. **1926**, *449*, 249-77.
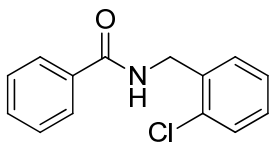
N-(2-Chlorobenzyl) benzamide (4af). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.51-7.37 (m, 5H), 7.25-7.23 (m, 2H), 6.67 (b, 1H), 4.74-4.72 (m, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.4, 135.7, 134.4, 133.8, 131.7, 130.6, 129.7, 129.2, 128.7, 127.3, 127.1, 42.2. MS (EI): m/z (%) 247 (5), 246 (2), 245 (14), 211 (10), 210 (63), 106 (8), 105 (100), 78 (4), 77 (46), 76 (2), 51 (8). This compound was known: Qu, G.-R.; Song, Y.-W.; Niu, H.-Y.; Guo, H.-M.; Fossey, J. S. *RSC. Adv*. **2012**, *2*, 6161-6163.
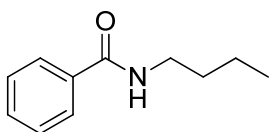
N-Butyl benzamide (4ag). ^{1}H NMR (500 MHz, *d$_6$*-DMSO): δ 8.44 (b, 1H), 7.85-7.83 (m, 2H), 7.53-7.50 (m, 1H), 7.47-7.44 (m, 2H), 3.29-3.25 (m, 2H), 1.54-1.48 (m, 2H), 1.37-1.29 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125.4 MHz, *d$_6$*-DMSO): δ 166.1, 134.7, 130.9, 128.2, 127.1, 38.8, 31.2, 19.6, 13.7. MS (EI): m/z (%) 178 (2), 177 (13), 176 (2), 148 (4), 136 (3), 135 (15), 134 (11), 106 (8), 105 (100), 78 (3), 77 (32), 76 (2), 51 (9), 50 (3). This compound was known: Rattanaburi, P.; Khumraksa, B.; Pattarawarapan, M. *Tetrahedron Lett*. **2012**, *53*, 2689-269.
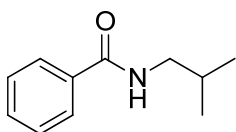
N-Isobutyl benzamide (4ah). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.77 (d, J = 7.5 Hz, 2H), 7.48-7.45 (m, 1H), 7.40-7.37 (m, 2H), 6.61 (b, 1H), 3.25 (t, J = 6.5 Hz, 2H), 1.92-1.86 (m, 1H), 0.95 (d, J = 7.0 Hz, 6H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.8, 134.9, 131.3, 128.5, 126.9, 47.4, 28.6, 20.2. MS (EI): m/z (%) 225 (9), 134 (8), 121 (2), 106 (4), 105 (53), 104 (23), 92 (4), 91 (11), 77 (21), 65 (5), 51 (6), 39 (3), 38 (4), 36 (11), 30 (100), 28 (2). This compound was known: Thomas, G. L.; Boehner, C.; Ladlow, M.; Spring, D. R. *Tetrahedron*. **2005**, *61*, 12153-12159.
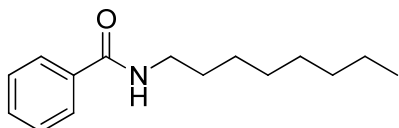
N-Octyl benzamide (4ai). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.75 (d, J = 7.0 Hz, 2H), 7.50-7.46 (m, 1H), 7.43-7.40 (m, 2H), 6.25 (b, 1H), 3.46-3.42 (m, 2H), 1.64-1.58 (m, 2H), 1.31-1.27 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.5, 134.9, 131.3, 128.5, 126.8, 40.1, 31.8, 29.7, 29.3, 29.2, 27.0, 22.6, 14.1. MS (EI): m/z (%) 190 (2), 176 (7), 162 (8), 149 (3), 148 (10), 135 (26), 134 (22), 122 (7), 106 (8), 105 (100), 79 (2), 78 (2), 77 (31), 55 (7), 51 (5), 43 (12), 41 (12). This compound was known: Morcillo, S. P.; Alvarez, L.; Mota, A. J.; Justicia, J.; Robles, R. *J. Org. Chem*. **2011**, *76*, 2277-2281.
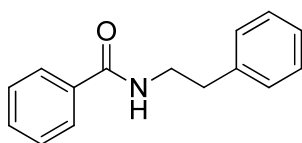
N-(2-Phenethyl) benzamide (4aj). ^{1}H NMR (500 MHz, d_6-DMSO): δ 8.55 (t, J = 5.5 Hz, 1H), 7.81 (d, J = 7.0 Hz, 2H), 7.53-7.50 (m, 1H), 7.47-7.44 (m, 2H), 7.31-7.28 (m, 2H), 7.24 (d, J = 7.0 Hz, 2H), 7.22-7.19 (m, 1H), 3.51-3.47 (m, 2H), 2.85 (t, J = 7.5 Hz, 2H). ^{13}C NMR (125.4 MHz, d_6-DMSO): δ 166.2, 139.5, 134.6, 131.0, 128.6, 128.3, 128.2, 127.1, 126.0, 40.8, 35.1. MS (EI): m/z (%) 225 (9), 134 (8), 121 (2), 106 (4), 105 (53), 104 (23), 92 (4), 91 (11), 77 (21), 65 (5), 51 (6), 39 (3), 38 (4), 36 (11), 30 (100), 28 (2). This compound was known: Arora, J. S.; Kaur, N.; Phanstiel, Otto, IV. *J. Org. Chem*. **2008**, *73*, 6182-6186.

N-(1-Phenylethyl) benzamide (4ak). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.77 (d, J = 7.0 Hz, 2H), 7.51-7.48 (m, 1H), 7.44-7.35 (m, 6H), 7.30-7.28 (m, 1H), 6.31 (b, 1H), 5.38-5.32 (m, 1H), 1.61 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 166.6, 143.1, 134.6, 131.5, 128.8, 128.6, 127.5, 126.9, 126.3, 49.2, 21.7. MS (EI): m/z (%) 225 (9), 134 (8), 121 (2), 106 (4), 105 (53), 104 (23), 92

(4), 91 (11), 77 (21), 65 (5), 51 (6), 39 (3), 38 (4), 36 (11), 30 (100), 28 (2). This compound was known: Liu, X.; Zhang, Y.; Wang, L.; Fu, H.; Jiang, Y.; Zhao, Y. *J. Org. Chem*. **2008**, *73*, 6207-6212.
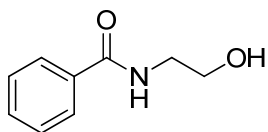
N-(2-Hydroxyethyl) benzamide (4al). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.45-7.42 (m, 1H), 7.34-7.31 (m, 2H), 4.38 (b, 1H), 3.72 (t, *J* = 5.0 Hz, 2H), 3.53-3.50 (m, 2H), 3.15 (b, 1H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 168.9, 134.0, 131.6, 128.5, 127.0, 61.5, 42.7. MS (EI): m/z (%) 165 (2), 147 (14), 135 (4), 134 (9), 122 (20), 117 (8), 106 (9), 105 (100), 104 (3), 78 (6), 77 (67), 76 (5), 51 (28), 50 (10), 40 (4), 33 (9), 32 (4), 31 (3). This compound was known: Denton, R. M.; An, J.; Adeniran, B.; Blake, A. J.; Lewis, W.; Poulton, A. M. *J. Org. Chem*. **2011**, *76*, 6749-6767.
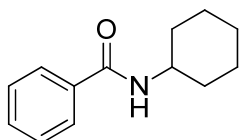
N-Cyclohexyl benzamide (4am). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.50-7.40 (m, 3H), 5.99 (b, 1H), 4.01-3.95 (m, 1H), 2.05-2.02 (m, 2H), 1.90-1.74 (m, 2H), 1.67-1.64 (m, 1H), 1.48-1.39 (m, 2H), 1.28-1.20 (m, 3H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 166.6, 135.2, 131.2, 128.5, 126.8, 48.7, 33.2, 25.6, 24.9. MS (EI): m/z (%) 176 (4), 175 (36), 174 (28), 146 (8), 106 (7), 105 (100), 78 (4), 77 (49), 70 (9), 68 (4), 55 (4), 51 (16), 50 (6), 44 (4), 43 (6), 41 (16). This compound was known: Rattanaburi, P.; Khumraksa, B.; Pattarawarapan, M. *Tetrahedron Lett*. **2012**, *53*, 2689-269.
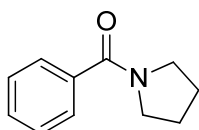
N-Benzoyl pyrrolidine (4an). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.48-7.46 (m, 2H), 7.35-7.34 (m, 3H), 3.60 (t, *J* = 7.0 Hz, 2H), 3.37 (t, *J* = 6.5 Hz, 2H), 1.94-1.88 (m, 2H), 1.85-1.79 (m, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 169.7, 137.2, 129.7, 128.2, 127.0, 49.6, 46.1, 26.3, 24.4. MS (EI): m/z (%) 176 (5), 175 (34), 174 (23), 147 (3), 146 (17), 106 (9), 105 (100), 104 (13), 78 (5), 77 (55), 76 (2), 70 (4), 56 (2), 51 (12), 50 (3). This compound was known: Rolfe, A.; Probst, D. A.; Volp, K. A.; Omar, I.; Flynn, D. L.; Hanson, P. R. *J. Org. Chem*. **2008**, *73*, 8785-8790.
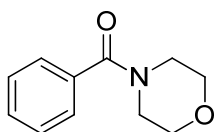
N-Benzoyl morpholine (4ao). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.44-7.41 (m, 5H), 3.79-3.46 (m, 8H).

^{13}C NMR (125.4 MHz, CDCl$_3$): δ 170.5, 135.3, 129.9, 128.6, 127.1, 66.9, 48.2, 42.6. MS (EI): m/z (%) 191 (4), 176 (13), 148 (4), 134 (7), 106 (7), 105 (100), 78 (3), 77 (29), 57 (5), 56 (5), 51 (9), 41 (8), 39 (4), 29 (5), 27 (3). This compound was known: Luo, Q.-L.; Lu, L.; Li, Y.; Tan, J.-P.; Nan, W.; Hui, Q. *Eur. J. Org. Chem.* **2011**, *34*, 6916–6922.
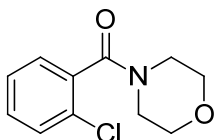
N-(2-Chlorobenzoyl) morpholine (4io). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.15 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.51-7.47 (m, 1H), 7.27-7.21 (m, 2H), 3.88 (t, *J* = 4.5 Hz, 4H), 3.04 (t, *J* = 4.5 Hz, 4H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 168.7, 151.2, 132.6, 131.9, 127.5, 124.9, 120.1, 67.4, 53.6. MS (EI): m/z (%) 226 (4), 225 (6), 224 (10), 210 (4), 190 (5), 162 (3), 141 (34), 140 (7), 139 (100), 113 (8), 111 (23), 86 (23), 77 (3), 76 (3), 75 (10), 56 (16), 42 (3). This compound was known: Lysén, M.; Kelleher, S.; Begtrup, M.; Kristensen, J. L. *J. Org. Chem.* **2005**, *70*, 5342-5343.
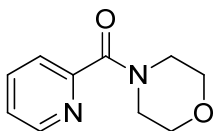
N-(2-Pyridinzoyl) morpholine (4mo). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.57-8.56 (m, 1H), 7.82-7.78 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.36-7.33 (m, 1H), 3.80 (b, 4H), 3.69-3.63 (m, 4H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.5, 153.6, 148.3, 137.2, 124.7, 124.2, 67.0, 66.8, 47.8, 42.8. MS (EI): m/z (%) 149 (3), 107 (3), 106 (19), 94 (5), 93 (4), 87 (7), 86 (100), 79 (3), 78 (6), 72 (3), 65 (3), 58 (12), 56 (5), 51 (3), 42 (6), 30 (9), 29 (5), 27 (3). This compound was known: Wang, X.; Wang, D. Z. *Tetrahedron*. **2011**, *67*, 3406-3411.
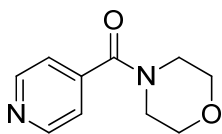
N-(4-Pyridinzoyl) morpholine (4oo). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.71 (dd, *J* = 4.0 Hz, *J* = 1.5 Hz, 2H), 7.30 (dd, *J* = 4.0 Hz, *J* = 1.5 Hz, 2H), 3.80 (b, 4H), 3.63 (b, 2H), 3.39 (b, 2H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 167.7, 150.3, 142.9, 121.2, 66.7, 47.8, 42.4. MS (EI): m/z (%) 192 (34), 191 (55), 177 (52), 161 (14), 149 (7), 135 (6), 107 (10), 106 (100), 93 (7), 86 (39), 79 (8), 78 (68), 56 (70), 51 (41), 50 (9), 42 (10), 29 (7), 28 (12). This compound was known: Wang, X.; Wang, D. Z. *Tetrahedron*. **2011**, *67*, 3406-3411.
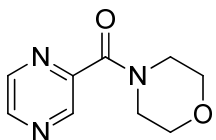
N-(2-Pyrazinzoyl) morpholine (4qo). ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.92 (d, J = 1.0 Hz, 1H), 8.60 (d, J = 2.5 Hz, 1H), 8.50 (dd, J = 2.0 Hz, J = 1.5 Hz, 1H), 3.77 (b, 4H), 3.67-3.63 (m, 4H). ^{13}C NMR (125.4 MHz, CDCl$_3$): δ 165.0, 148.8, 145.9, 145.4, 142.4, 66.9, 66.7, 47.6, 42.8. MS (EI): m/z (%) 193 (9), 175 (5), 109 (5), 108 (46), 86 (100), 81 (18), 80 (44), 79 (29), 77 (9), 56 (7), 55 (7), 53 (10), 41 (19), 39 (12), 27 (11). This compound was known: Takács, A.; Jakab, B.; Petz, A.; Kollár, L. *Tetrahedron.* **2007**, *63*, 10372-10378.

^{1}H NMR and ^{13}C NMR Spectra of the Products

2a

^{1}H NMR

^{13}C NMR

2b

¹H NMR

¹³C NMR

S27

2c

¹H NMR

¹³C NMR

S28

2d

¹H NMR

¹³C NMR

2e

¹H NMR

¹³C NMR

2f
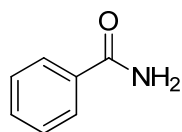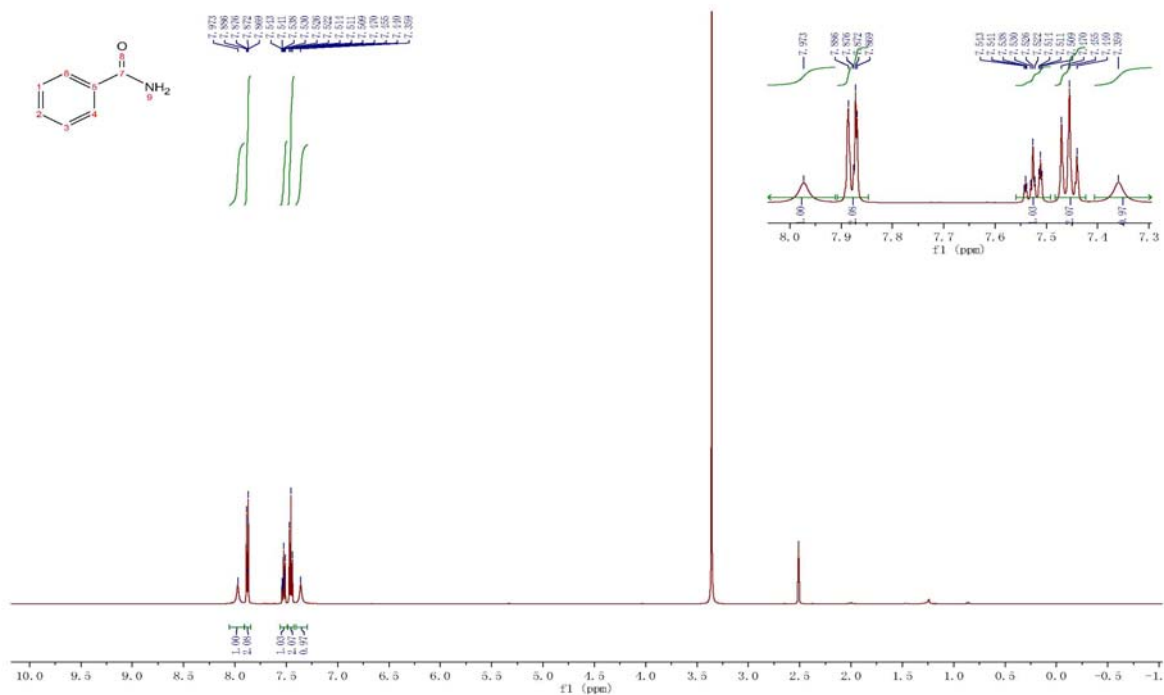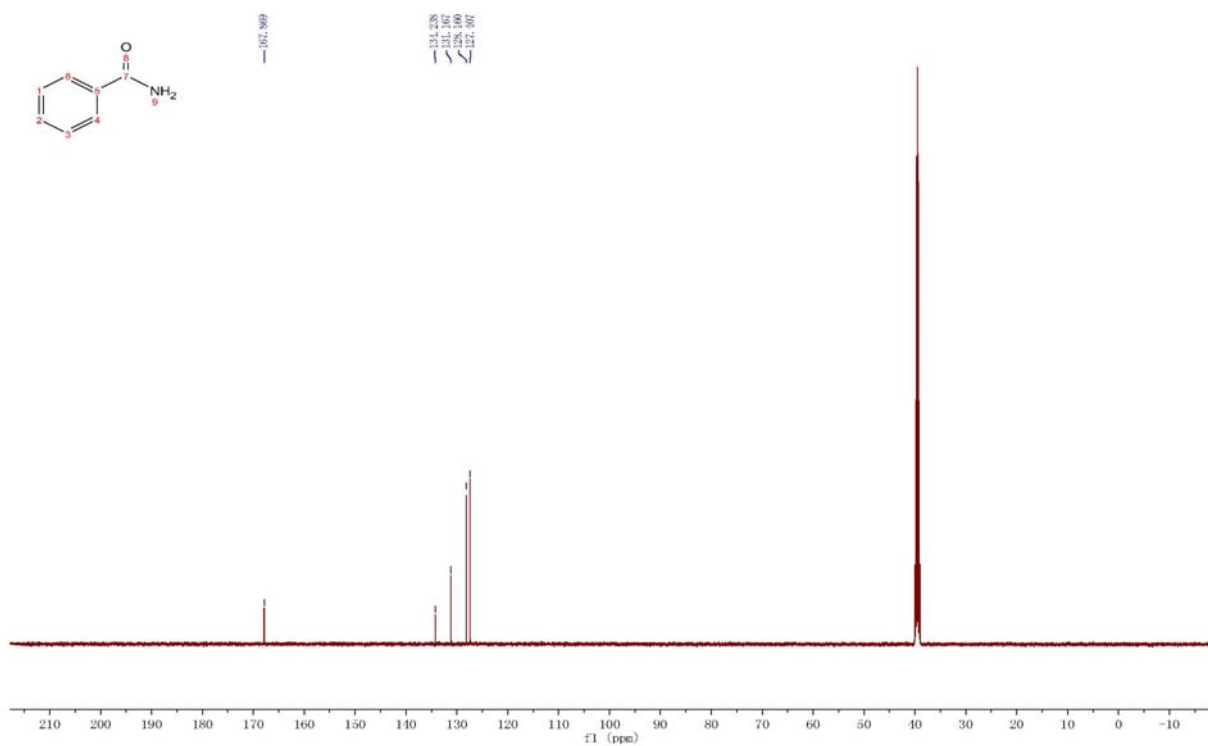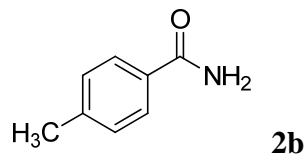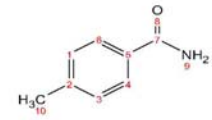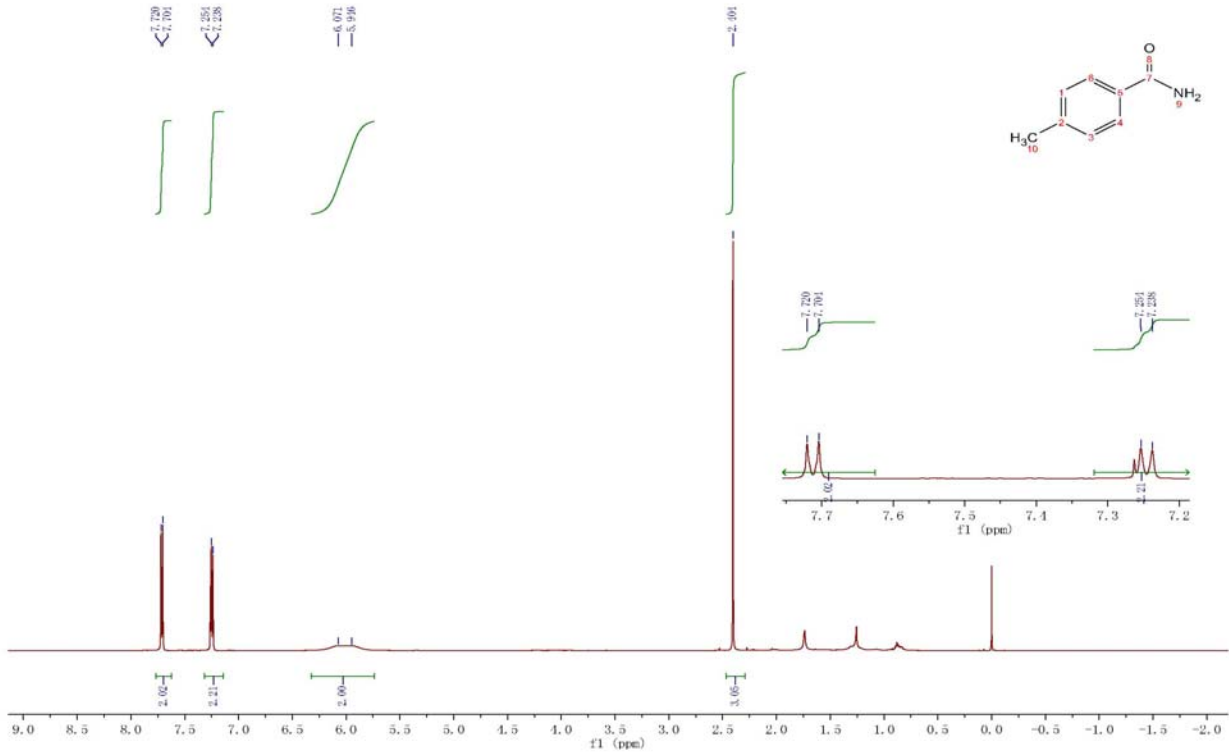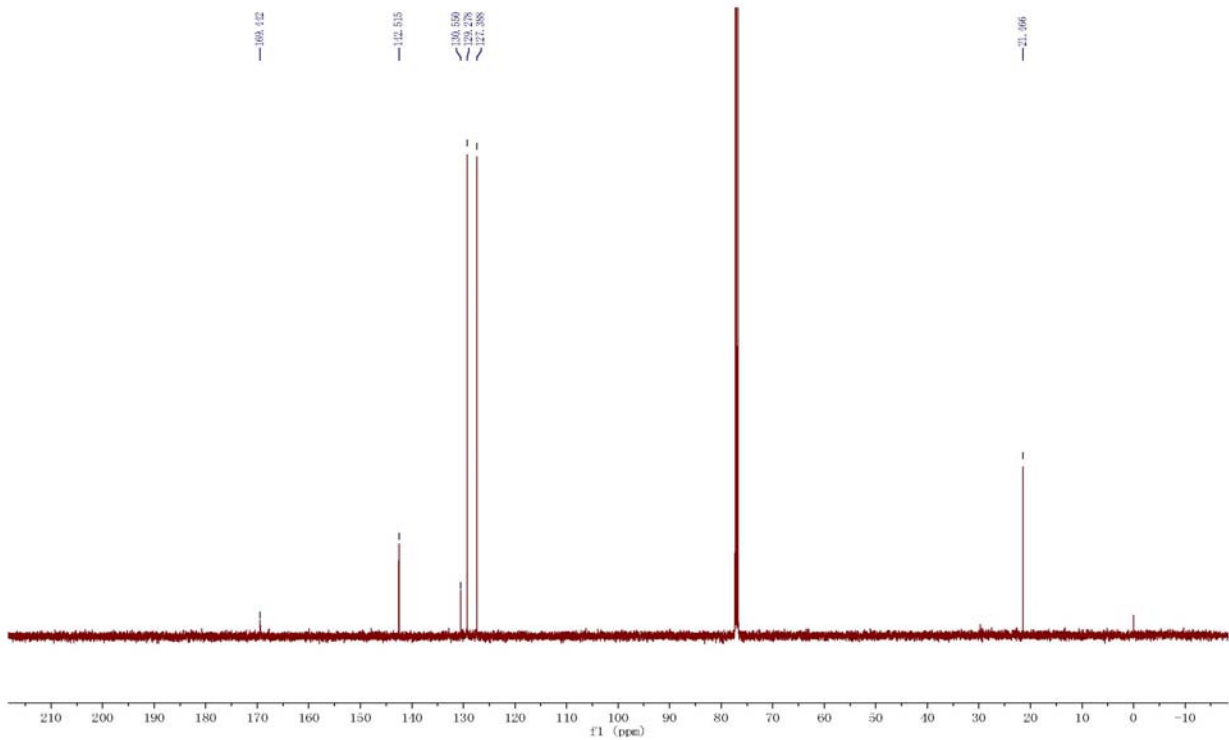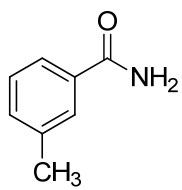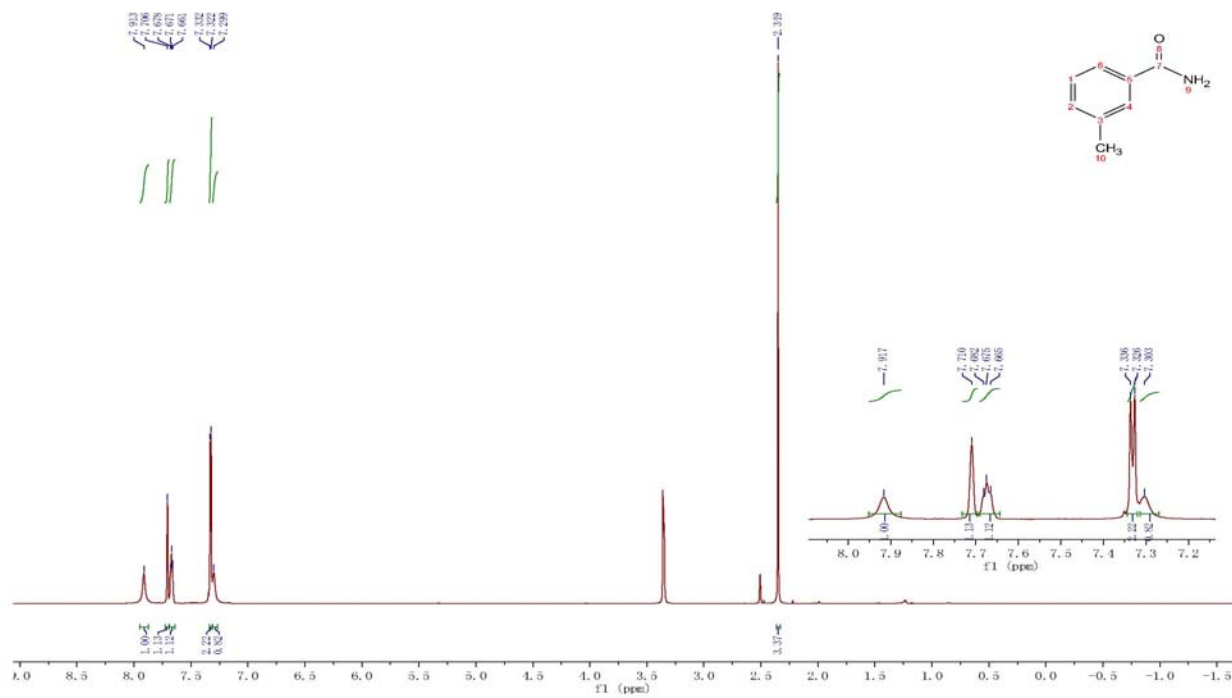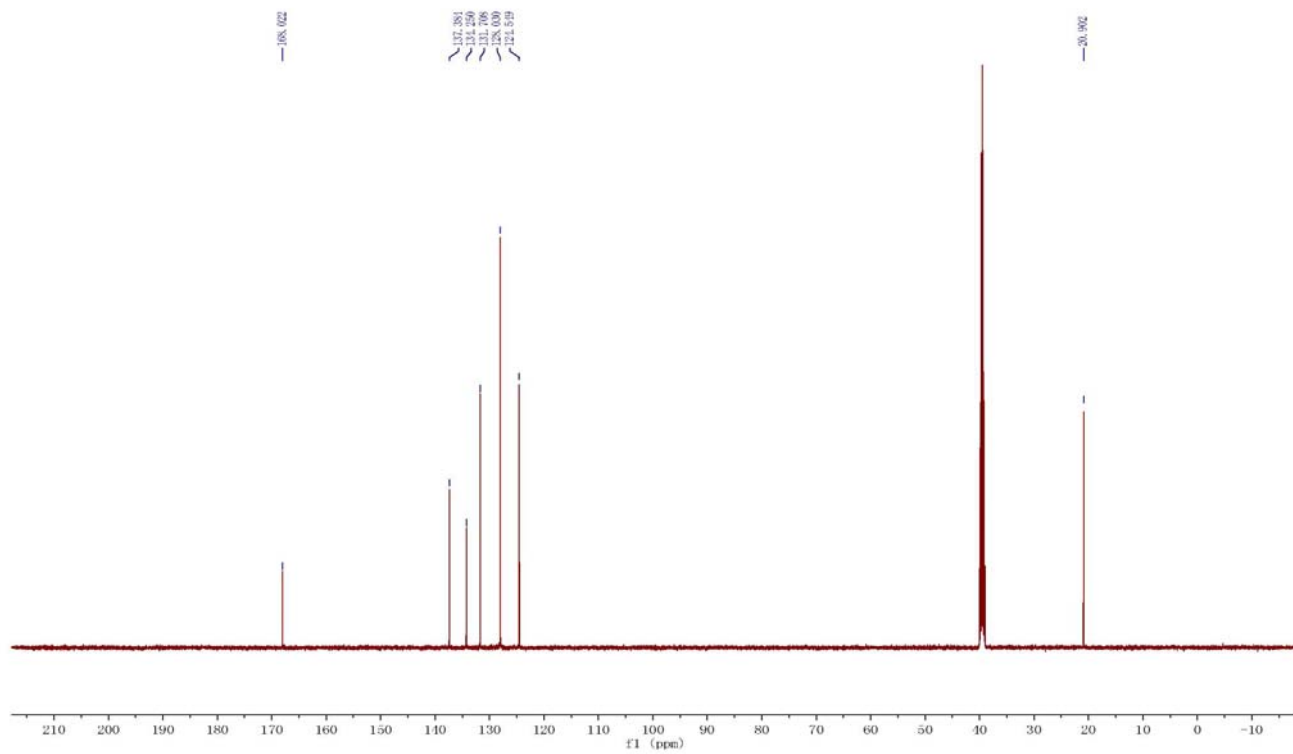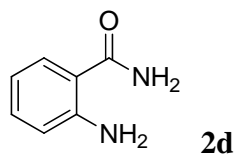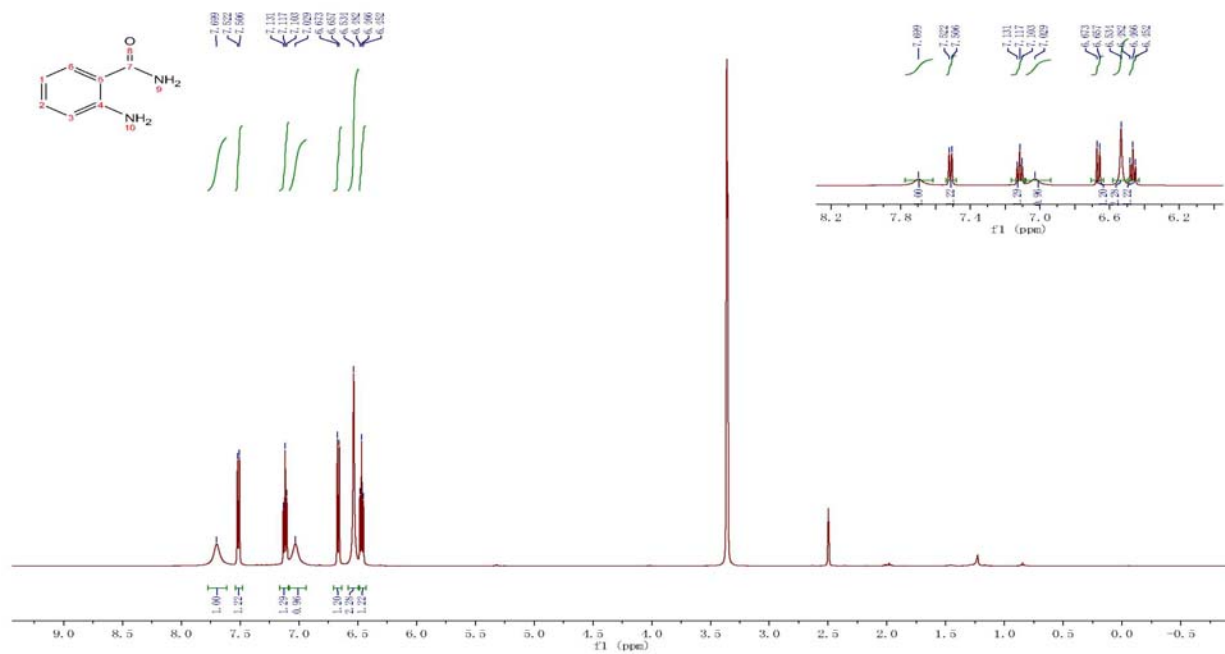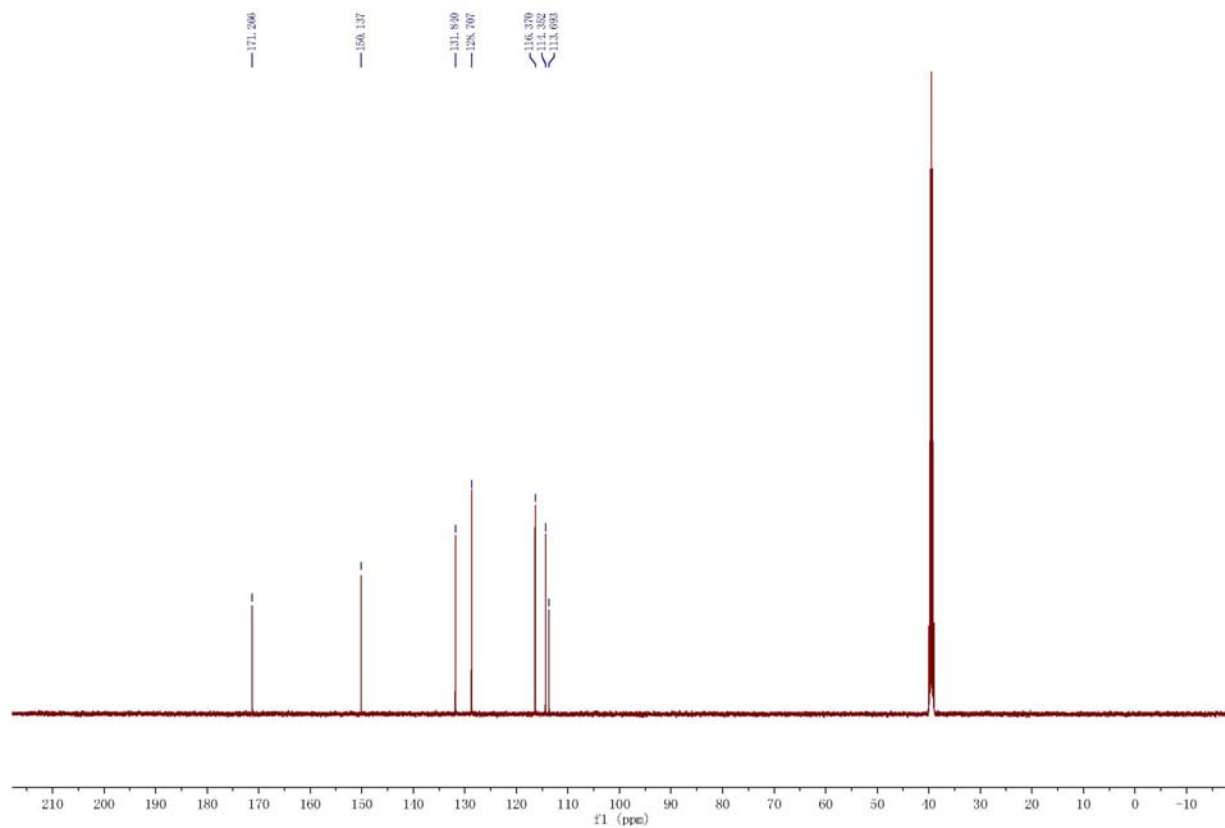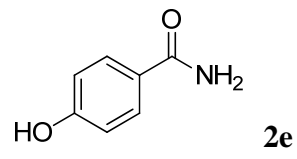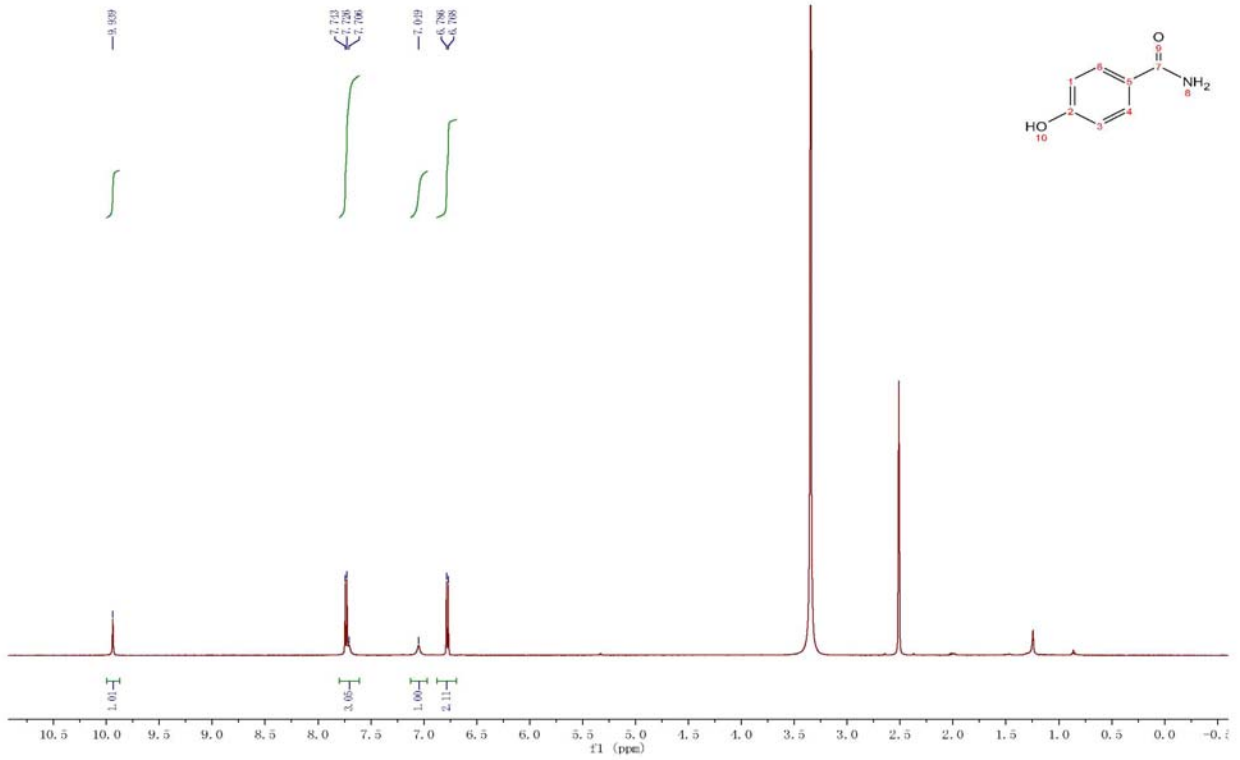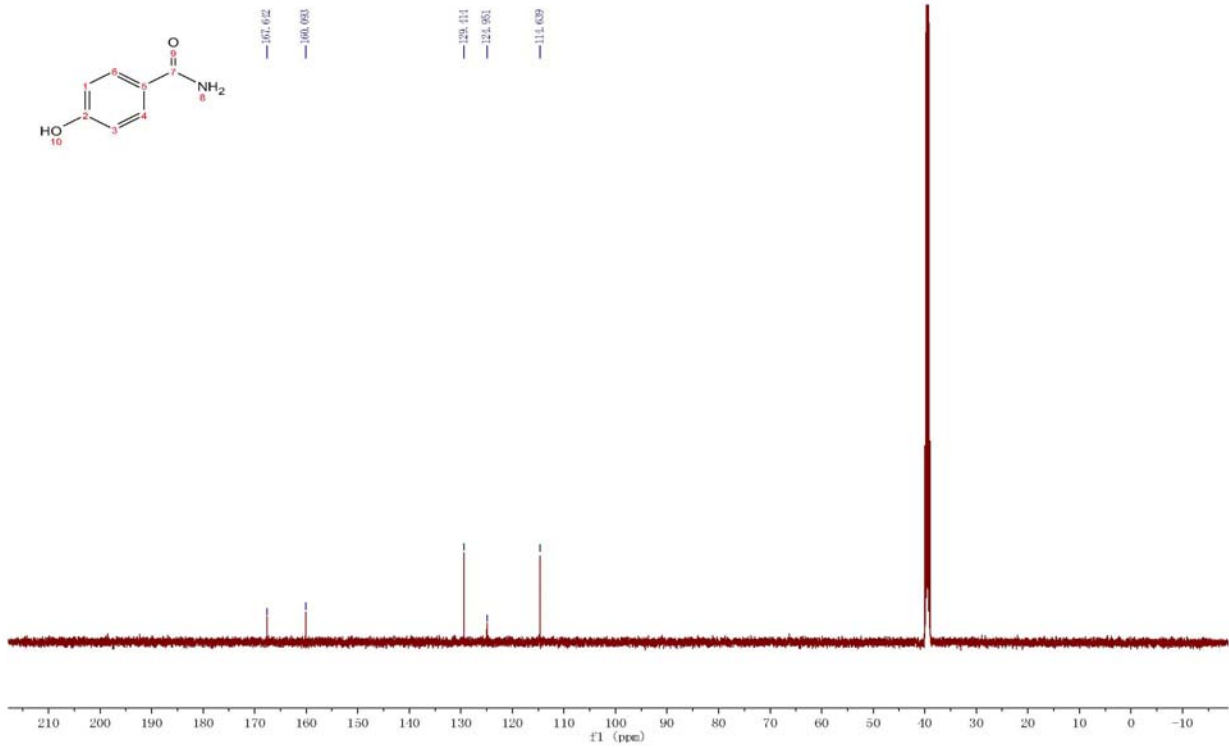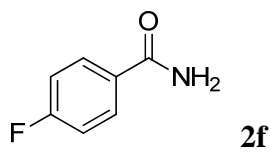
¹H NMR

7.984
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7.955
7.950
7.941
7.934
7.930
7.927
7.378
7.285
7.269
7.252
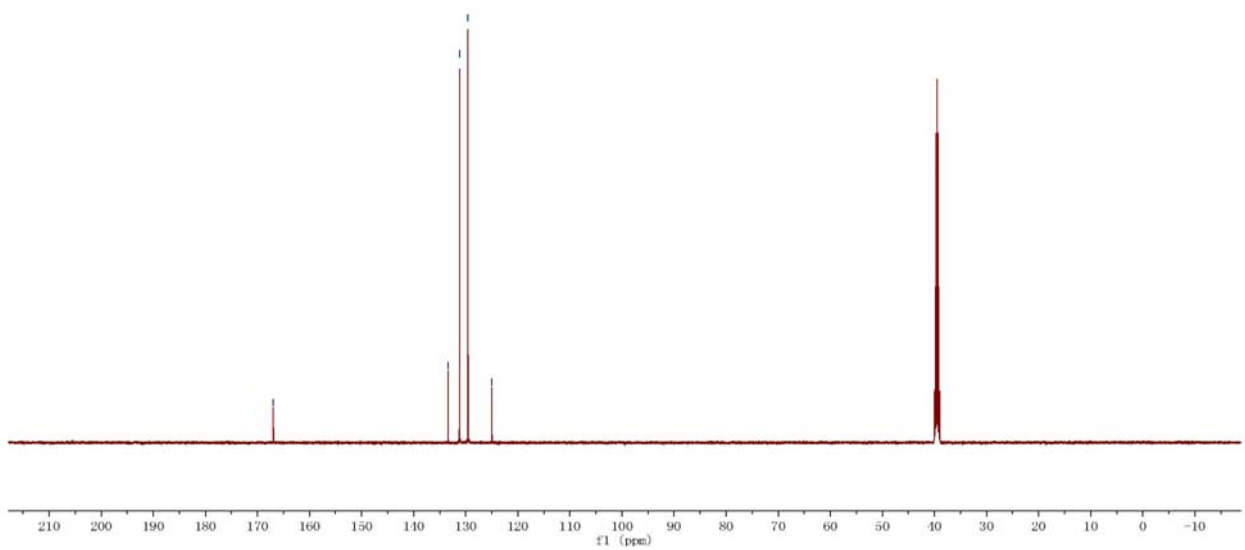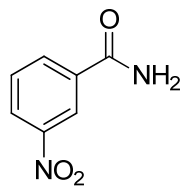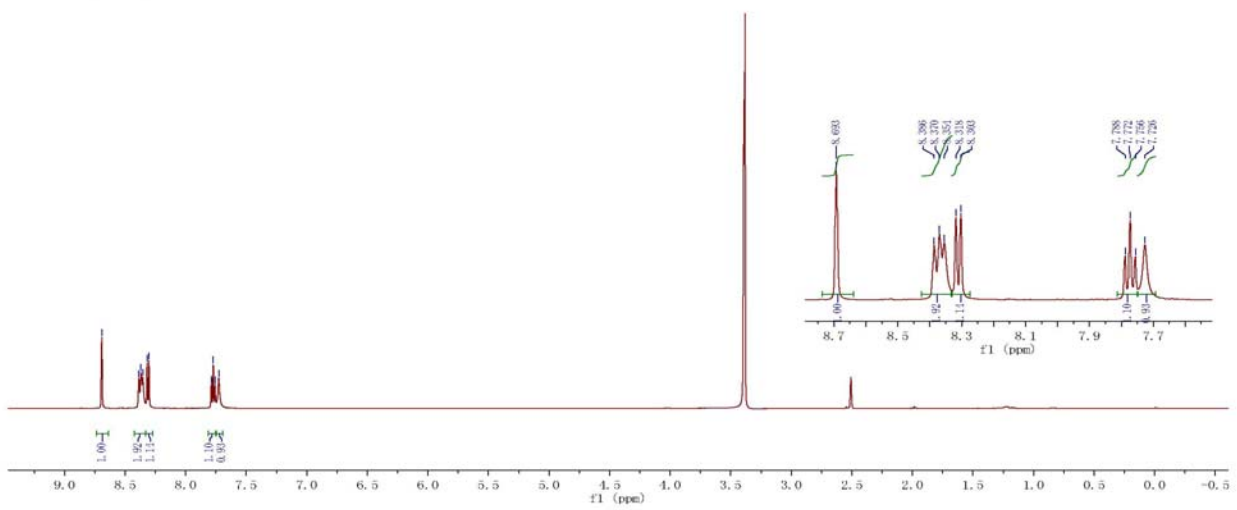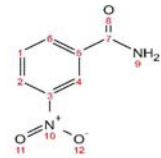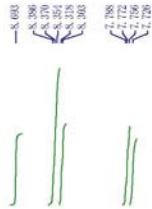
0.71
2.20
0.88
2.00

¹³C NMR

166.814
164.879
162.904
130.727
130.109
130.038
115.127
114.954
130.727
130.109
130.038
39.856
39.689
39.522
39.355
39.188

166.814
164.879
162.904

A (d)
163.89

C (d)
130.07

B (d)
115.04

130.5
129.5
f1 (ppm)

115.127
114.954

116   115   114   113
f1 (ppm)

170   168   166   164   162   160
f1 (ppm)

¹³C NMR (125.4 MHz, DMSO) δ 163.89 (d, *J* = 248.3 Hz), 130.07 (d, *J* = 8.9 Hz), 115.04 (d, *J* = 22.6 Hz).

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S31

2g

¹H NMR

¹³C NMR

2h

¹H NMR

¹³C NMR

S33

2i

^{1}H NMR

^{13}C NMR

2j

¹H NMR

¹³C NMR

2k

¹H NMR

¹³C NMR
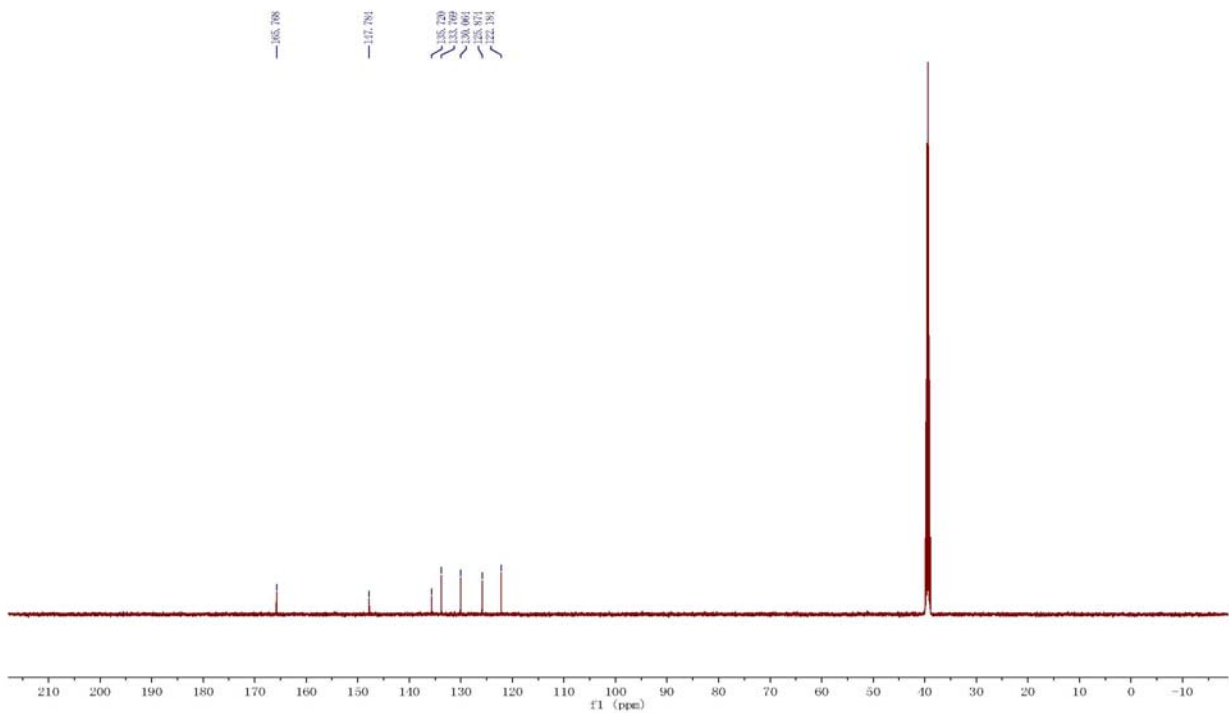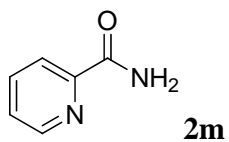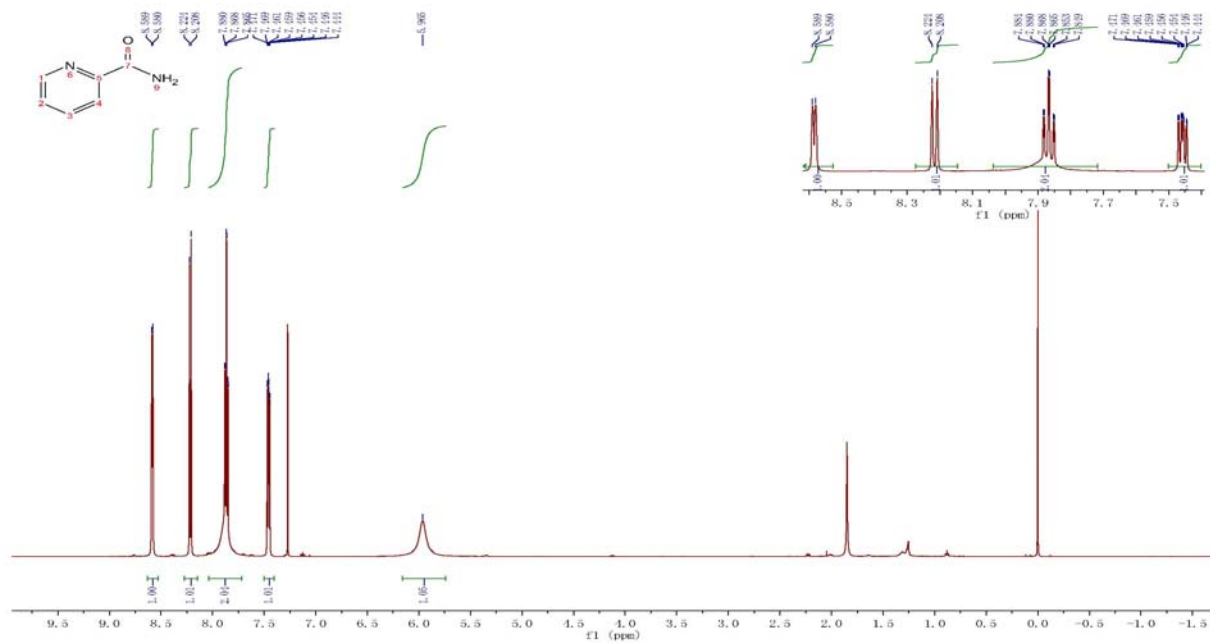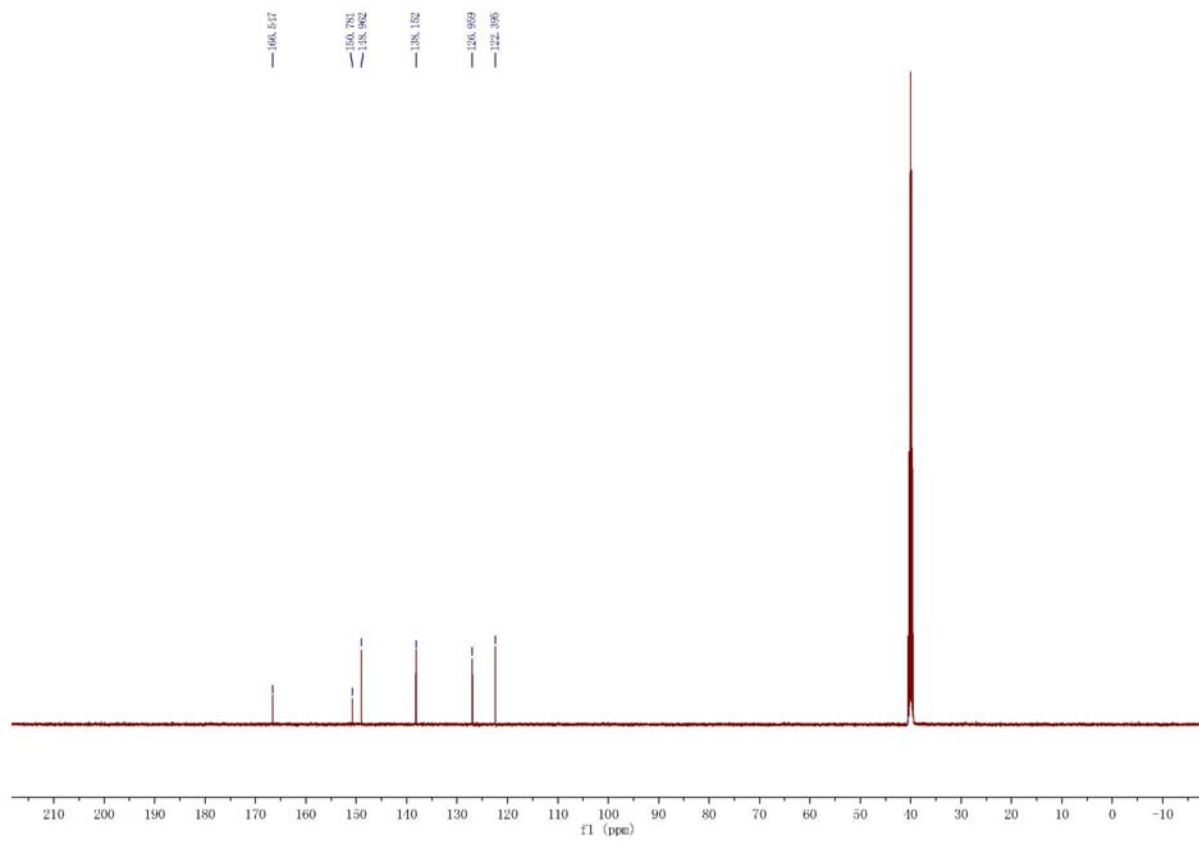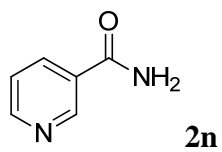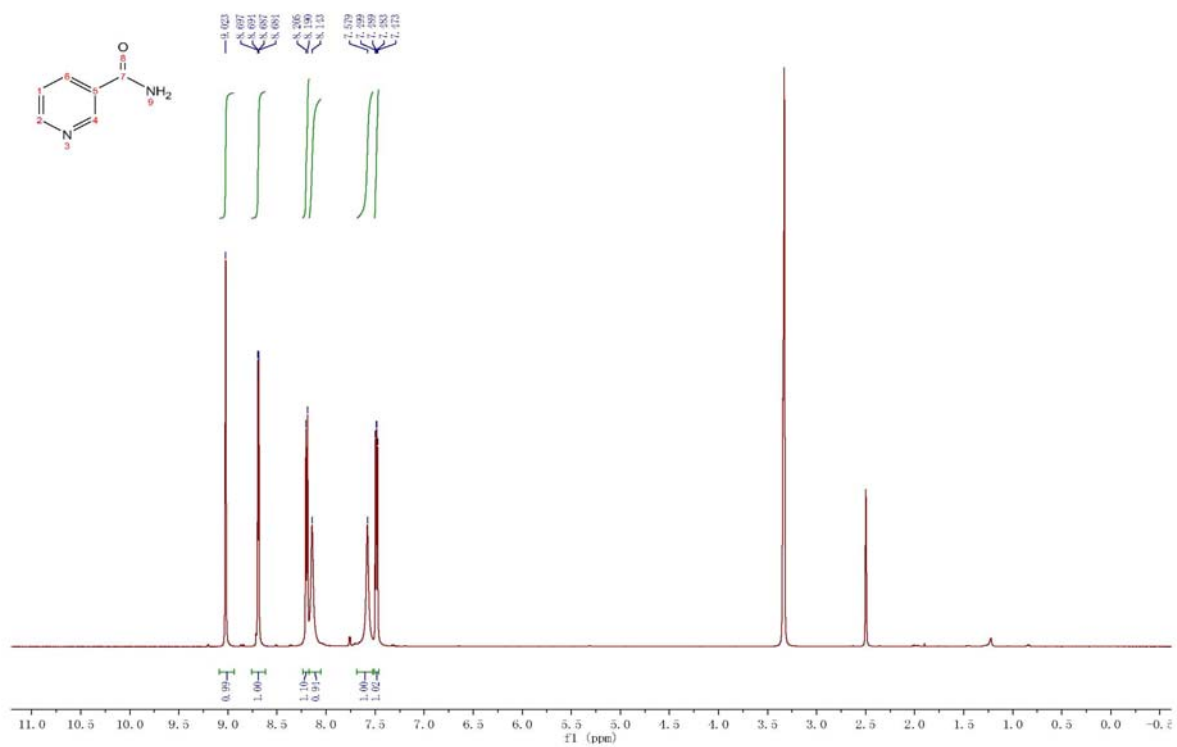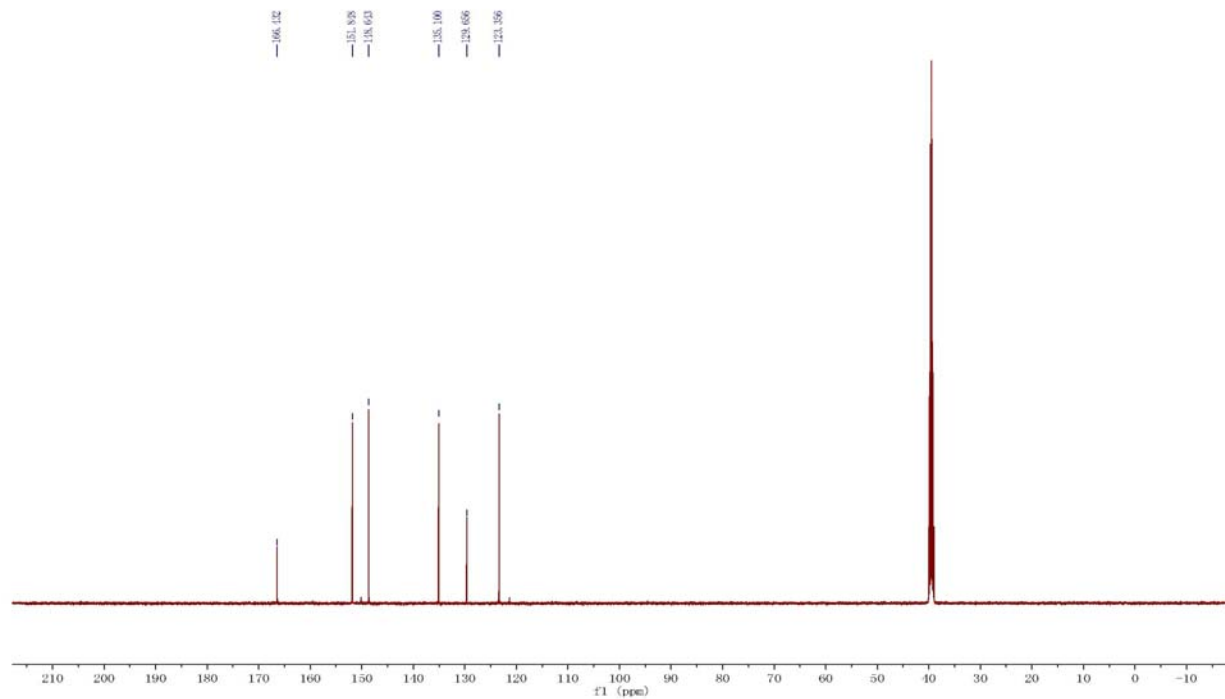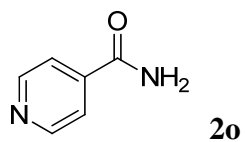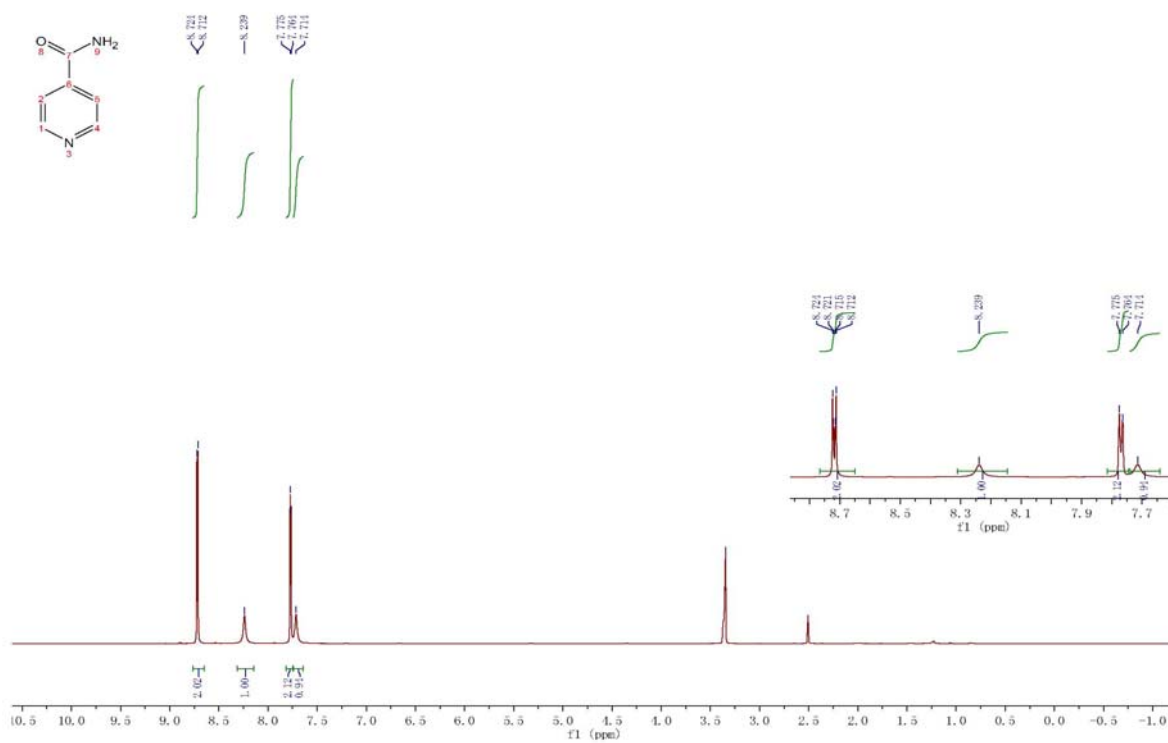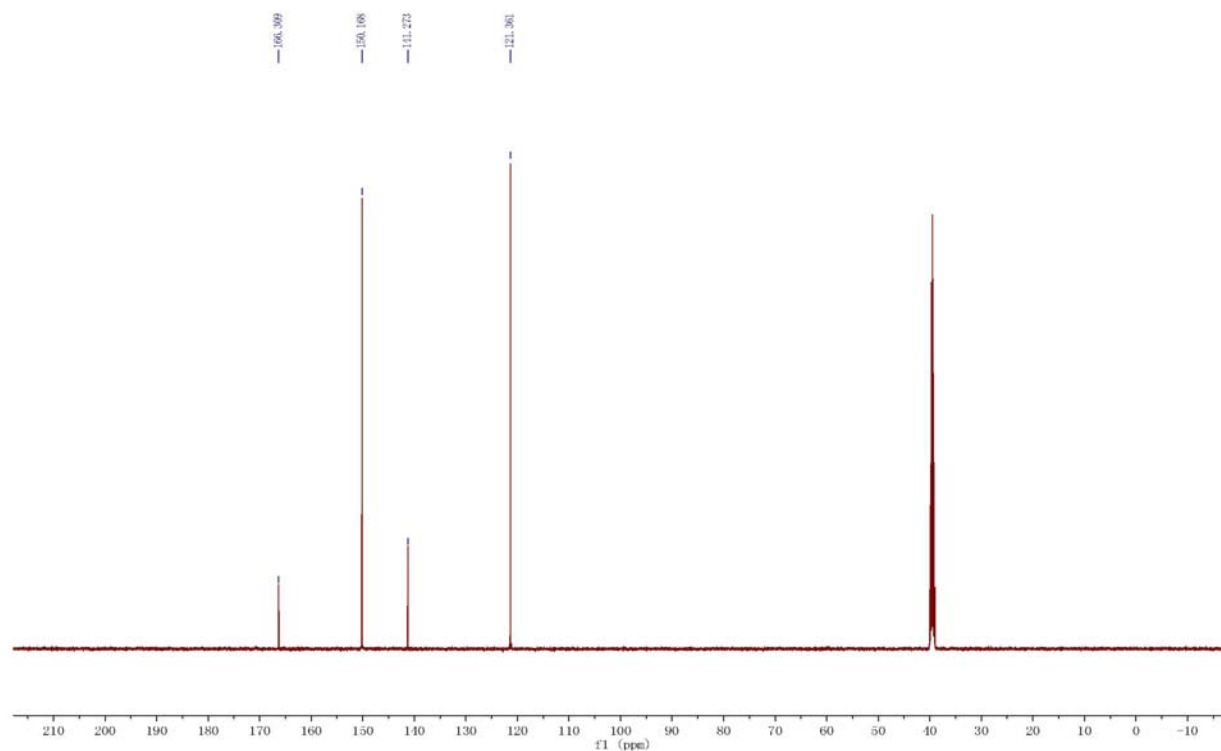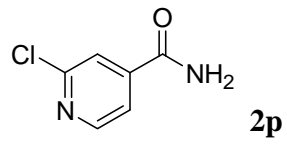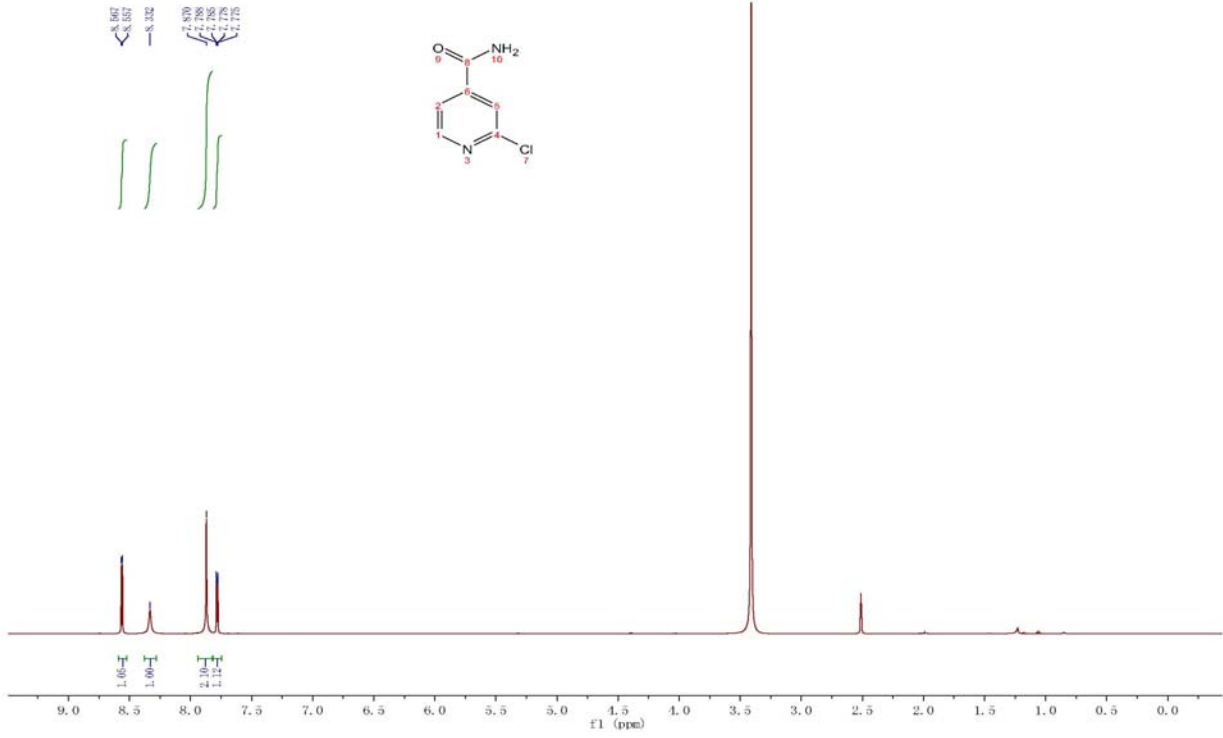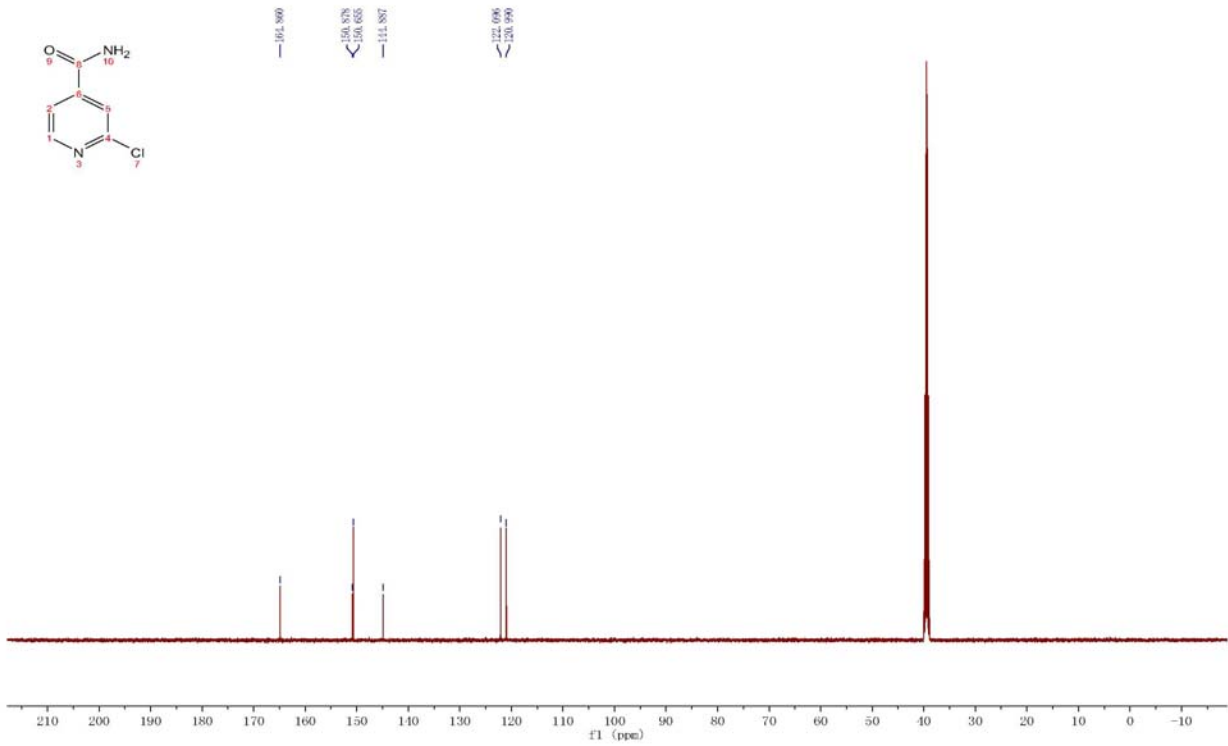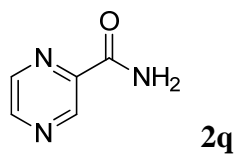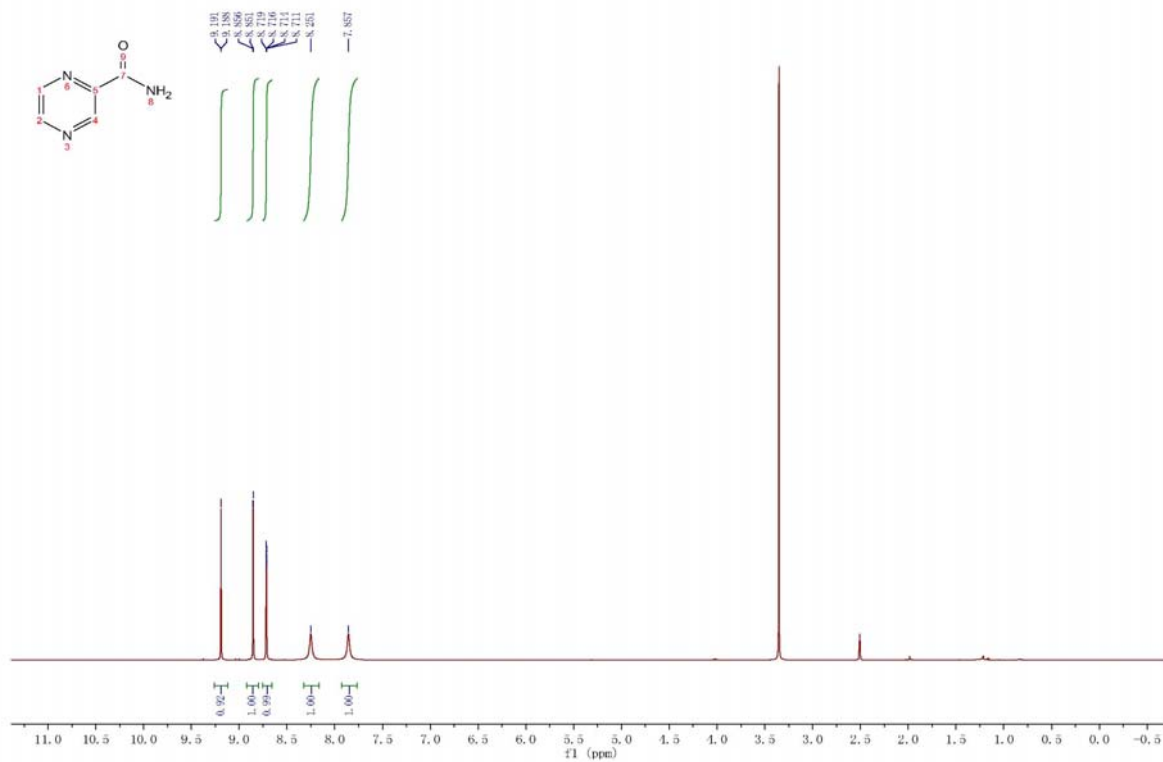
2l

¹H NMR

¹³C NMR

S37

2m

¹H NMR

¹³C NMR

S38

2n

¹H NMR

¹³C NMR

S39

2o

¹H NMR

¹³C NMR

S40

2p

¹H NMR

¹³C NMR

S41

2q

¹H NMR

¹³C NMR

S42

2r

¹H NMR

¹³C NMR

S43

2s

¹H NMR

¹³C NMR

S44

2t

¹H NMR

¹³C NMR

2u

^{1}H NMR

^{13}C NMR

S46

2v

¹H NMR

¹³C NMR

S47

2w
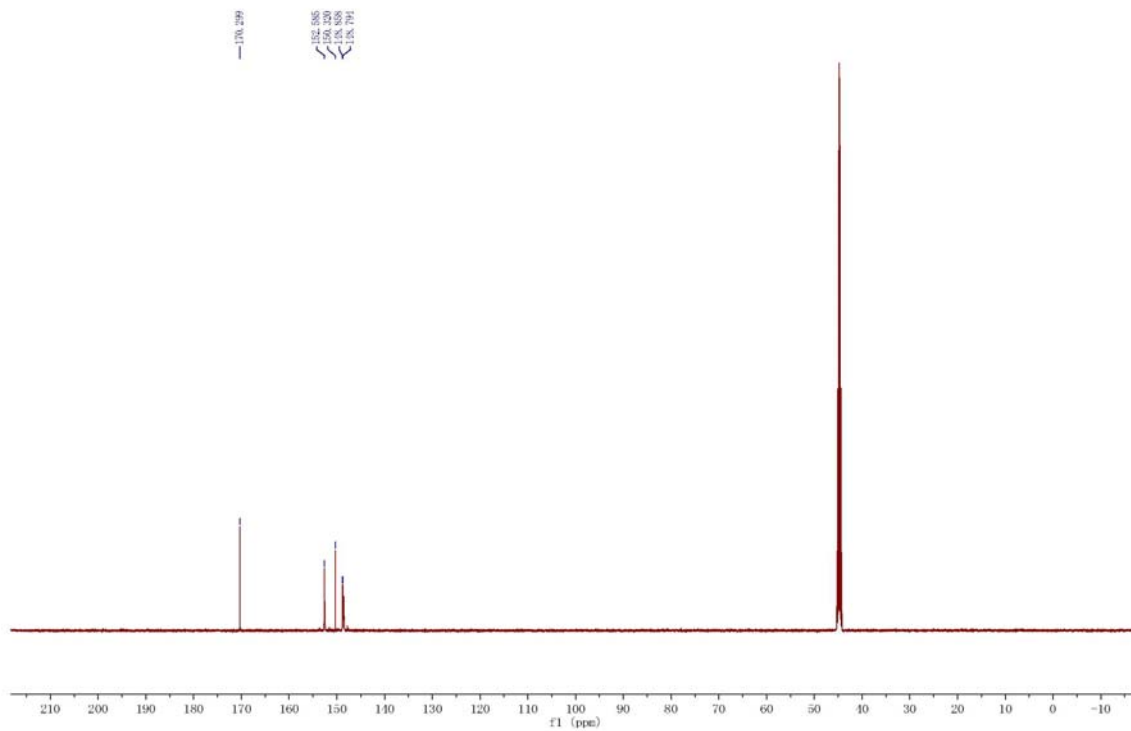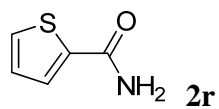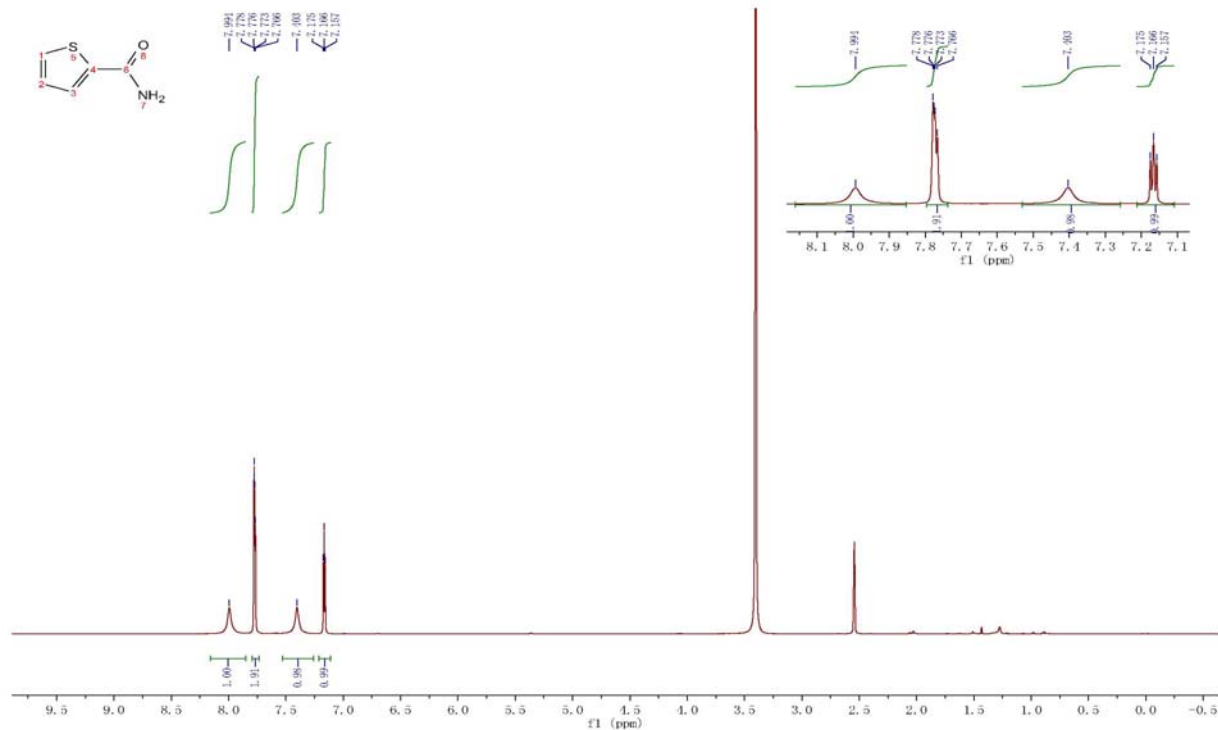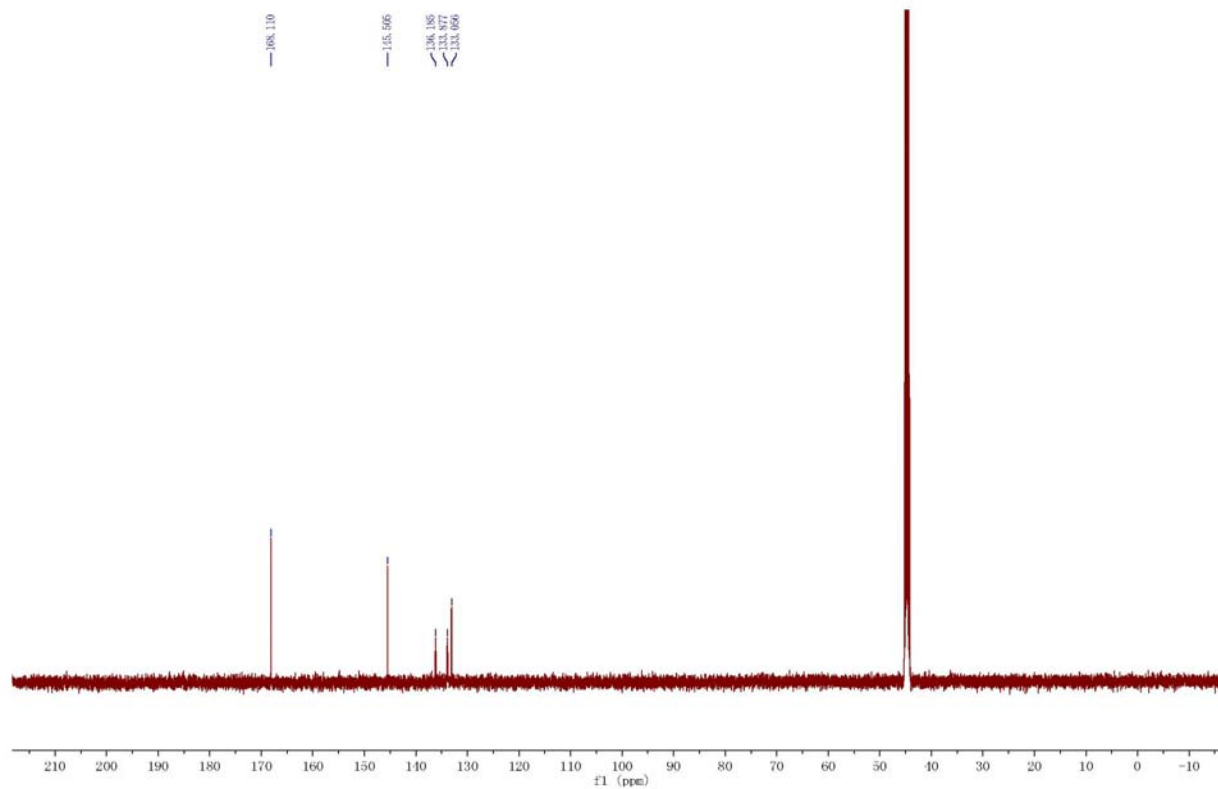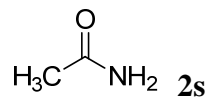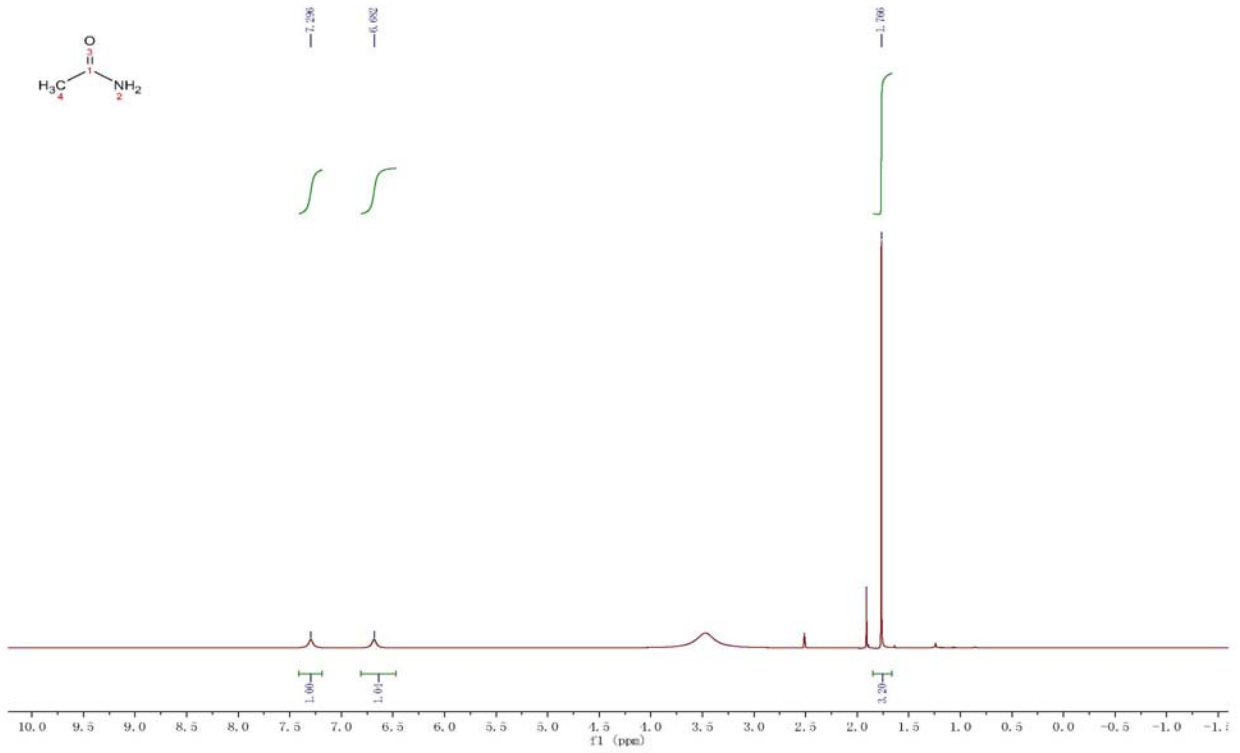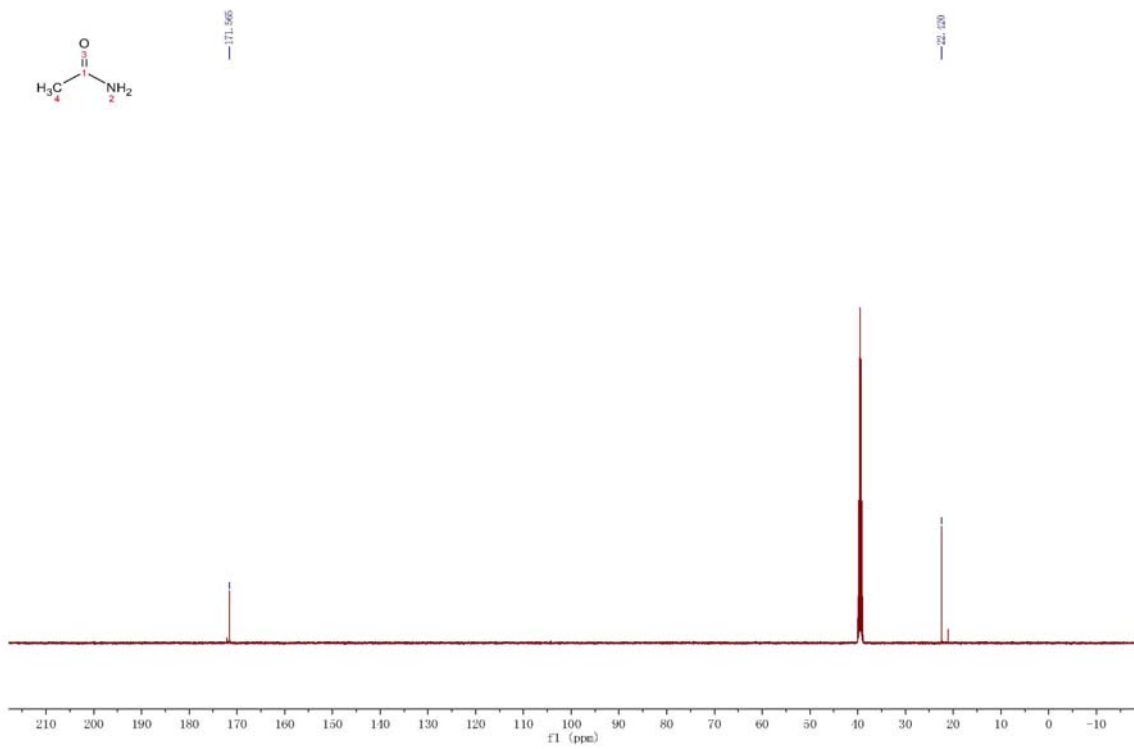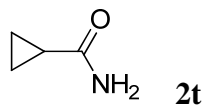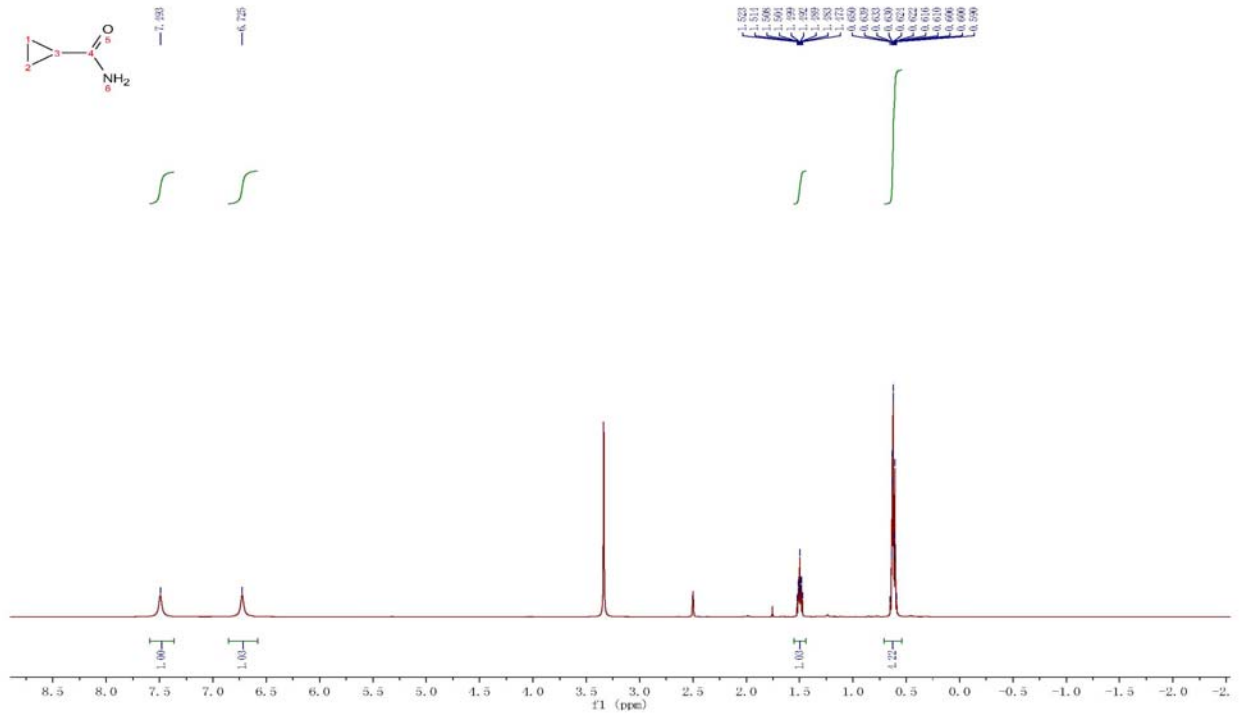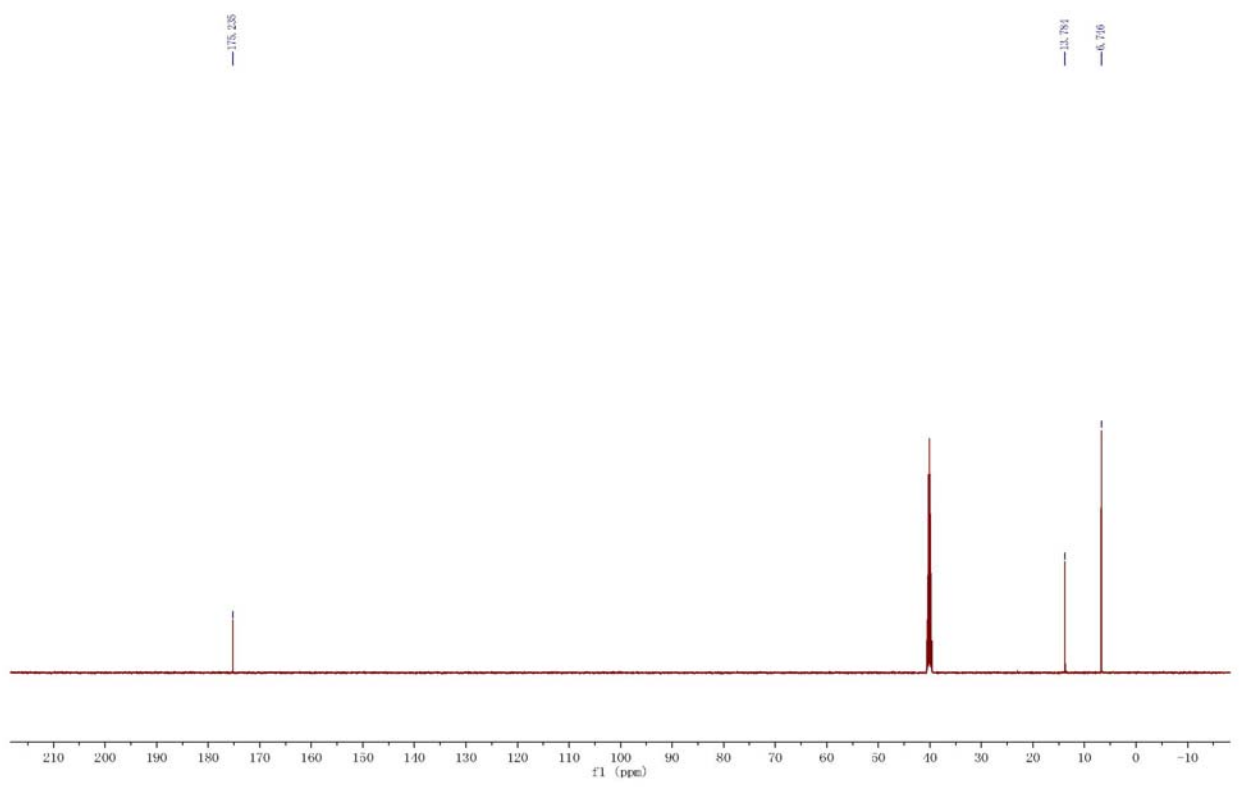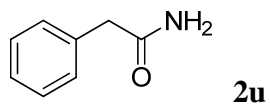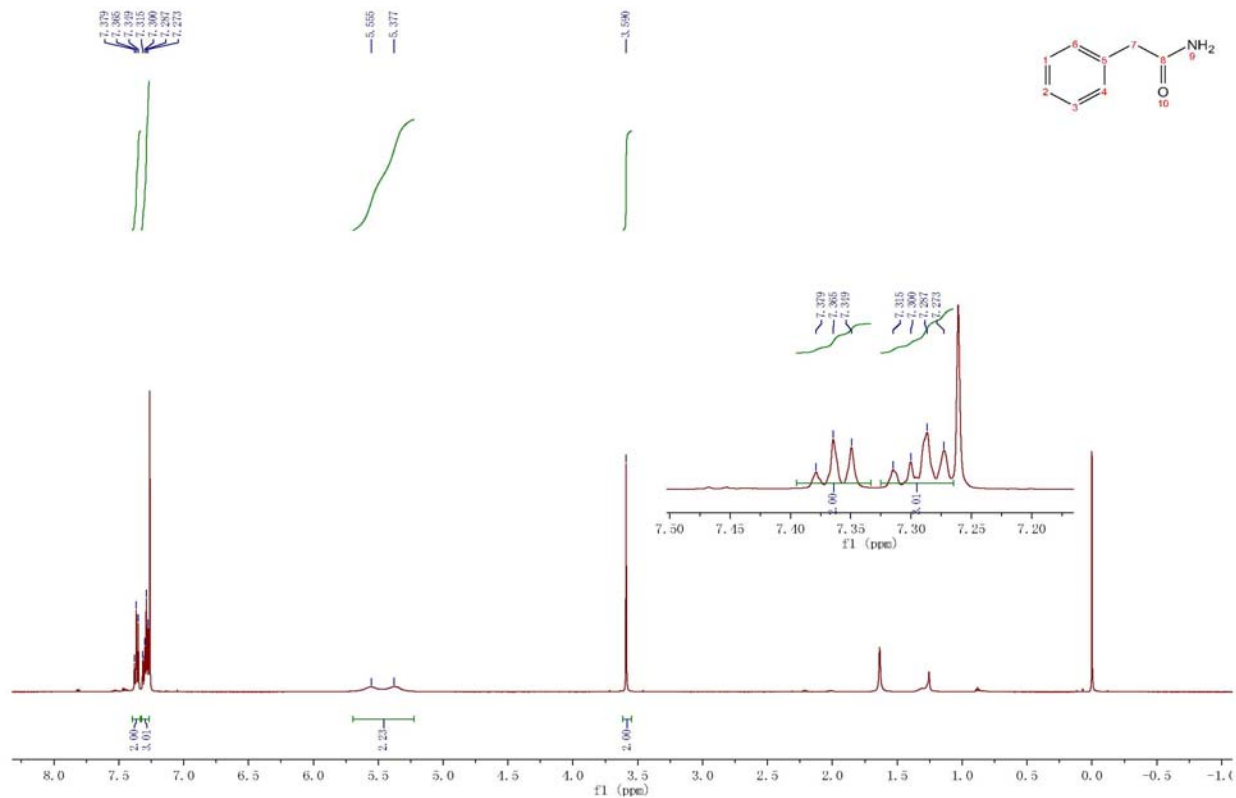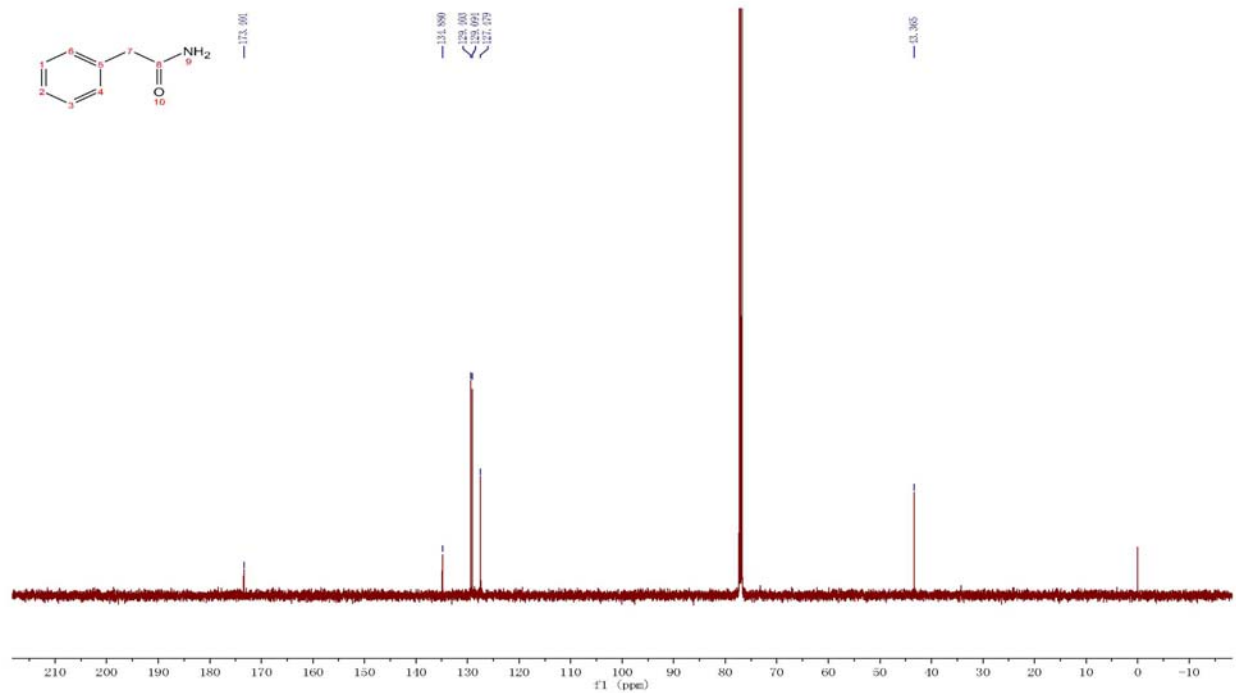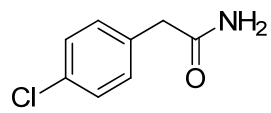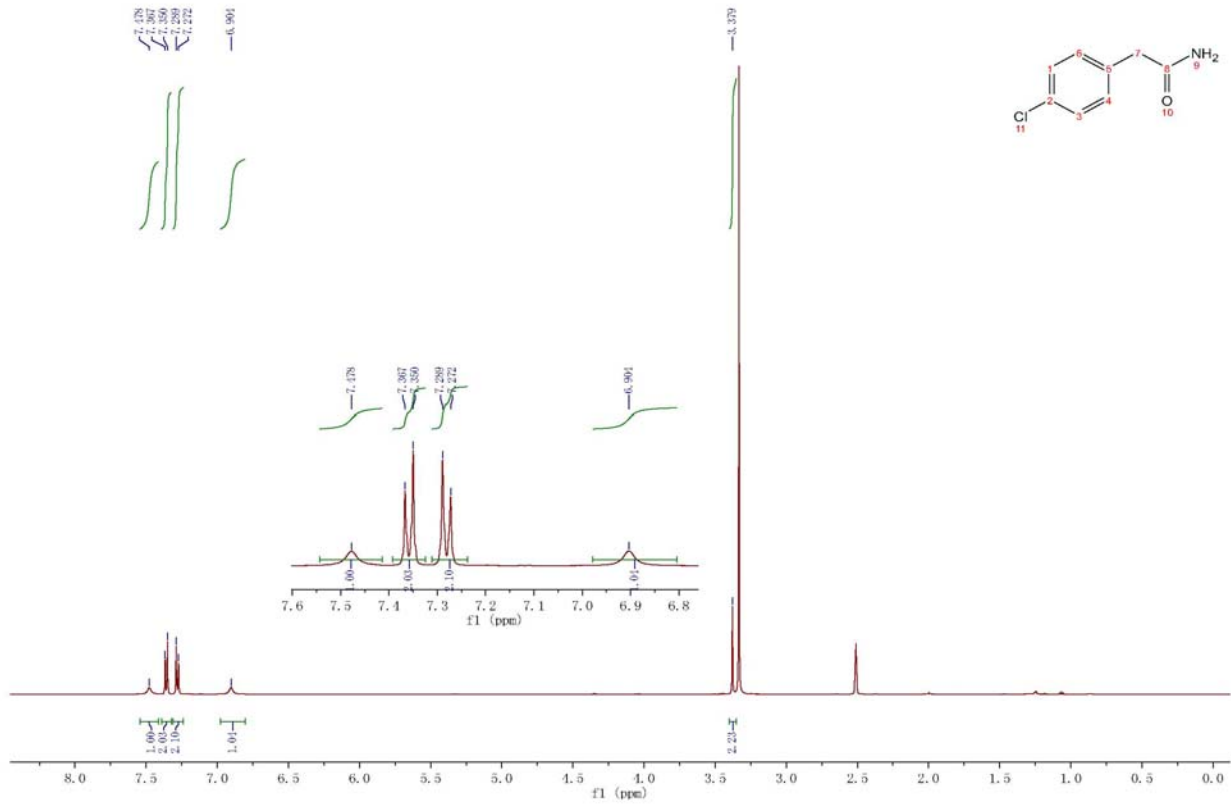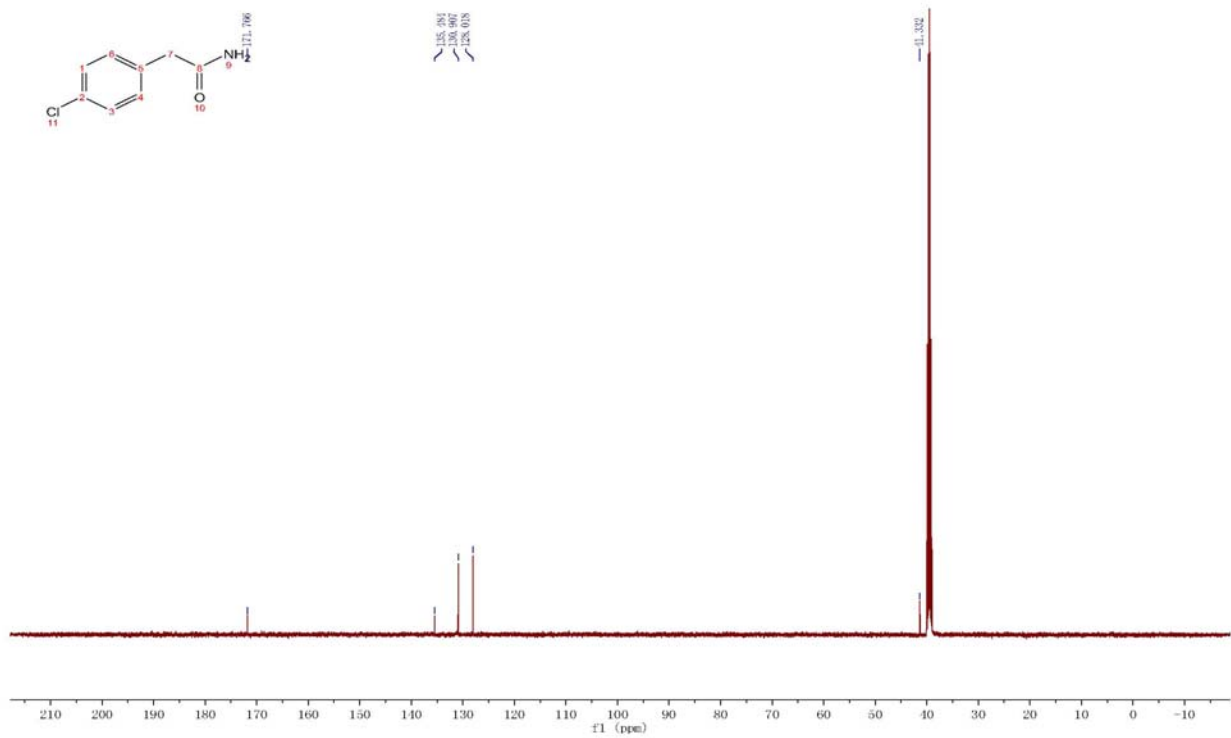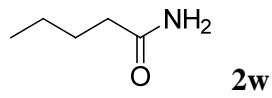
¹H NMR

¹³C NMR

2x

¹H NMR

¹³C NMR
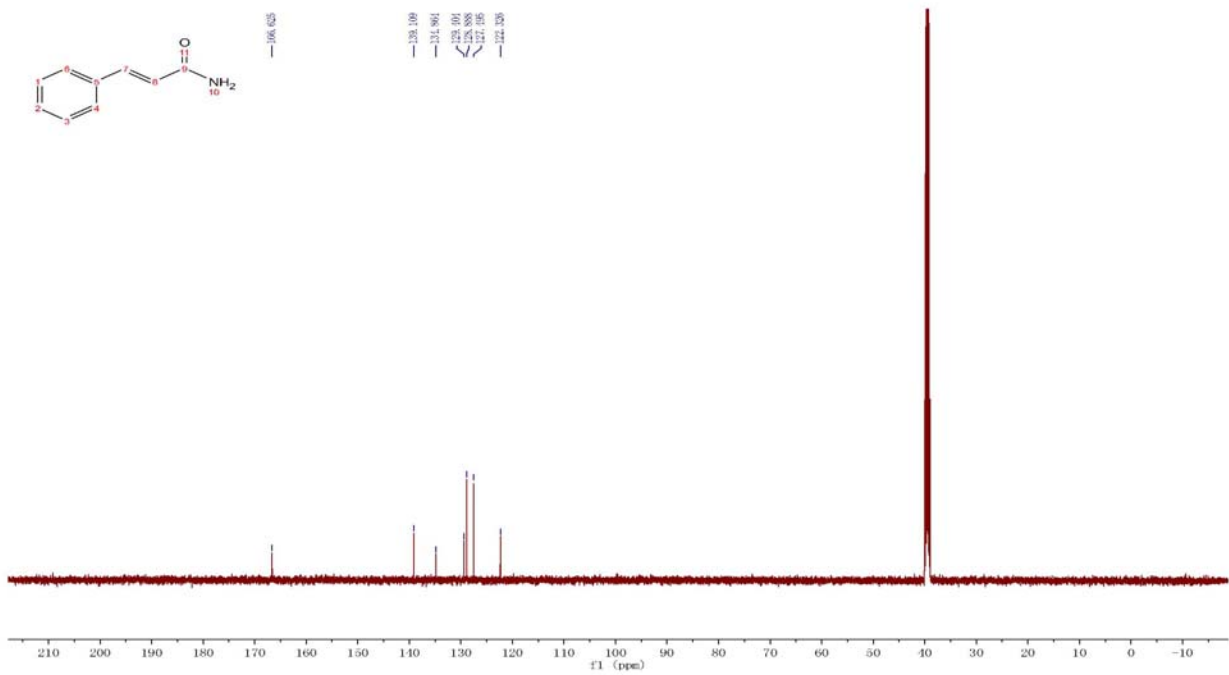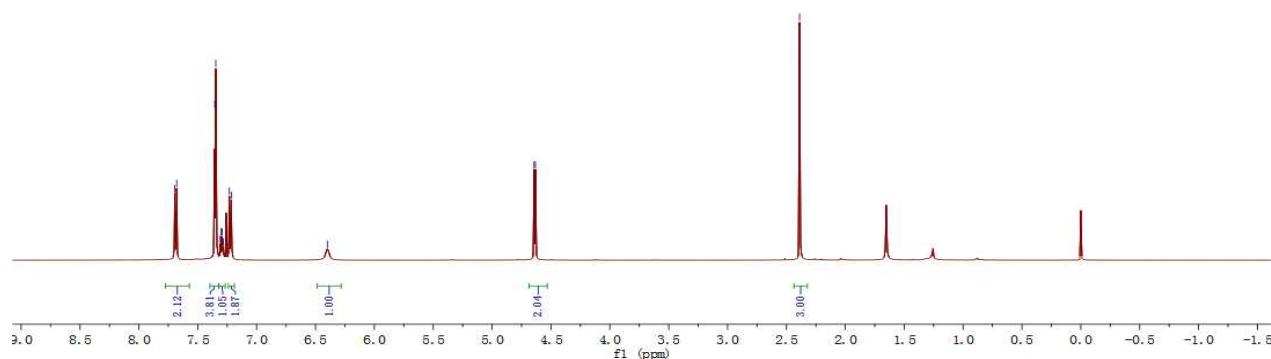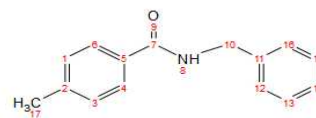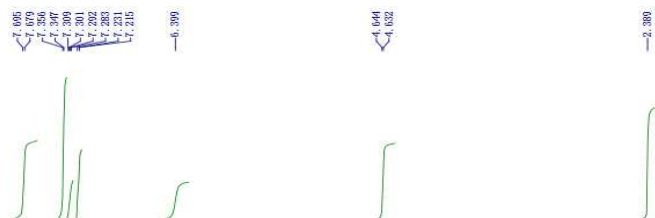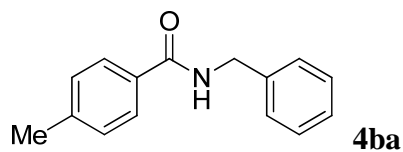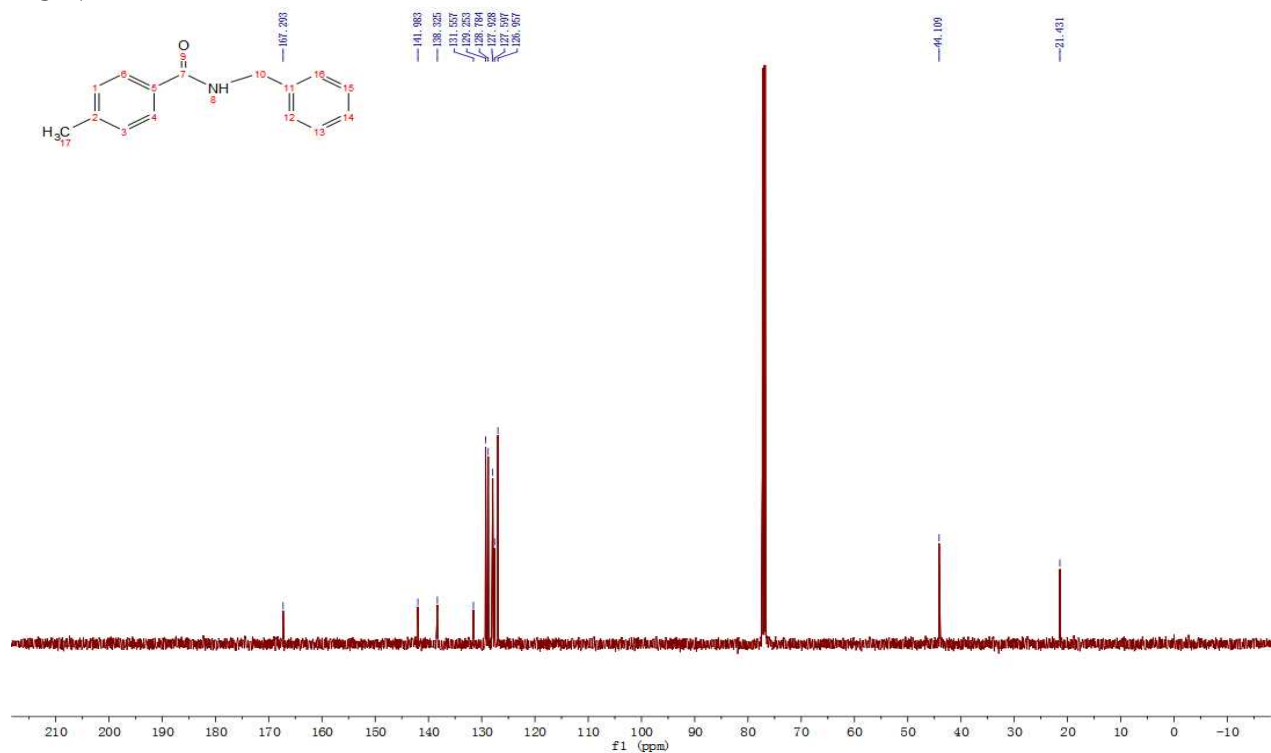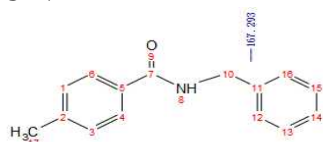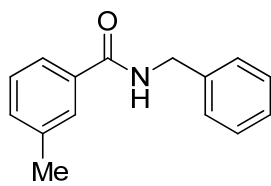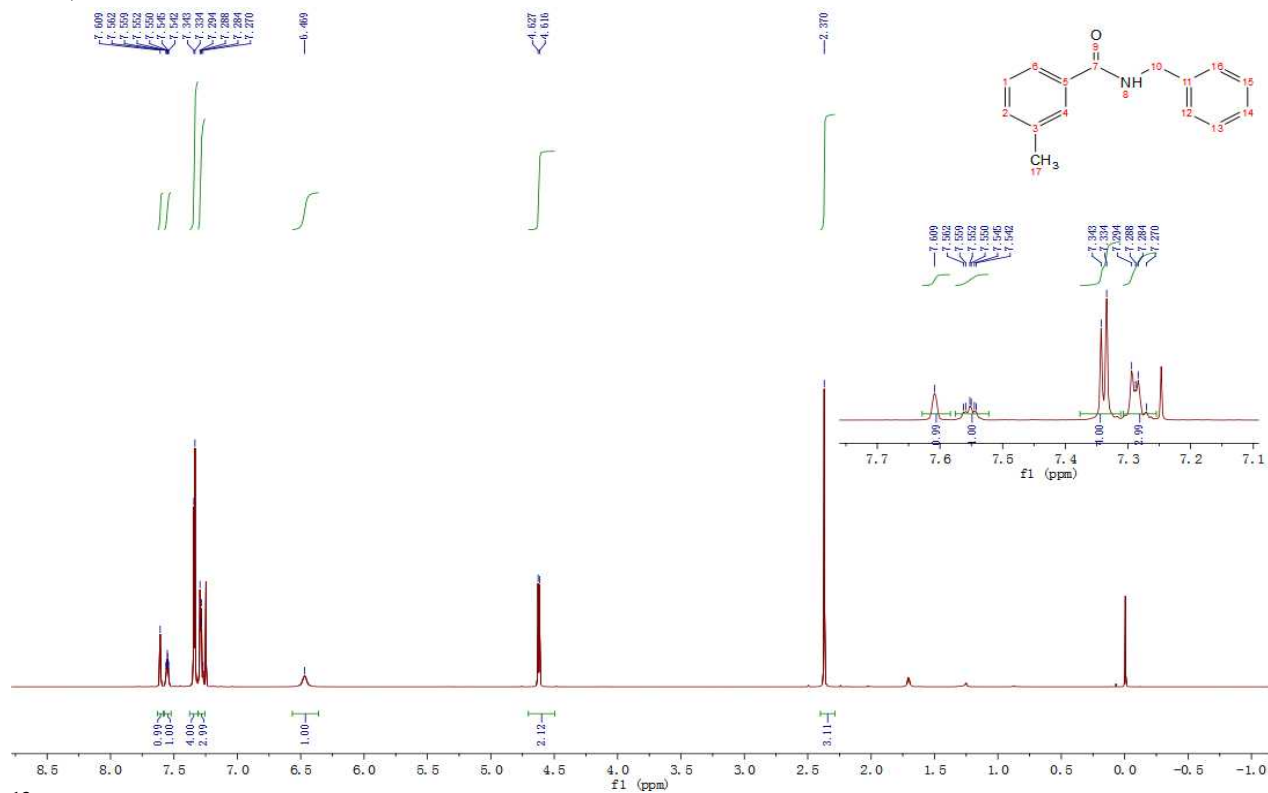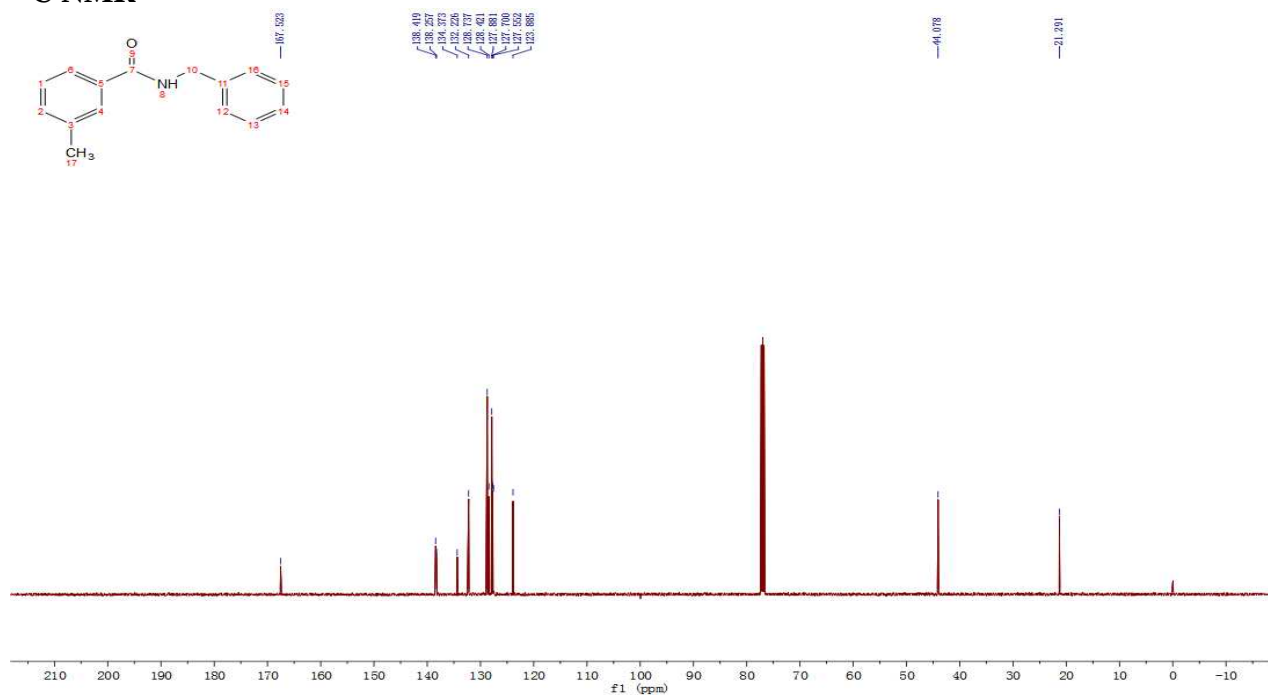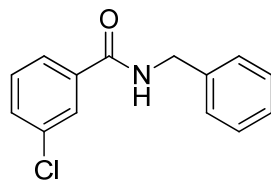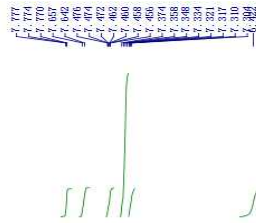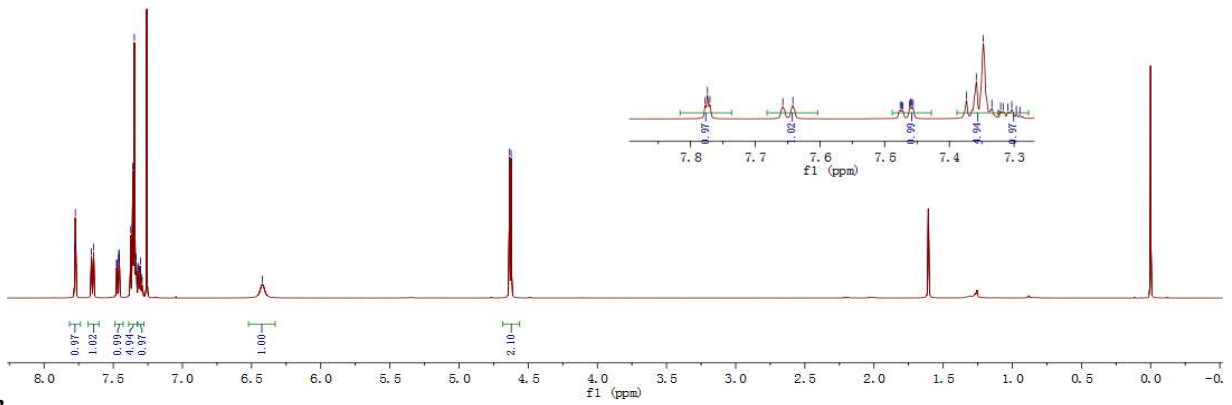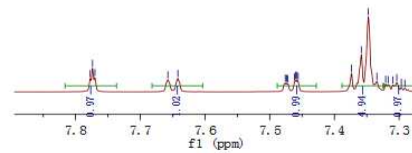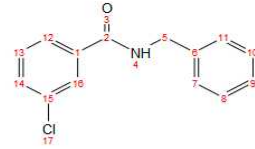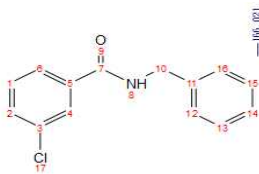
4aa

¹H NMR

¹³C NMR

S50

4ba

^{1}H NMR

7.695
7.679
7.356
7.347
7.309
7.301
7.292
7.283
7.231
7.215
6.399
4.644
4.632
2.389

2.12
3.81
1.05
1.87
1.00
2.04
3.00

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

^{13}C NMR

167.293
141.983
138.325
131.557
129.253
128.784
127.928
127.597
126.957
44.109
21.431

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S51

4ca

¹H NMR

¹³C NMR

¹**H NMR**

¹³**C NMR**

S53

4ja

¹H NMR

¹³C NMR

S54

4oa
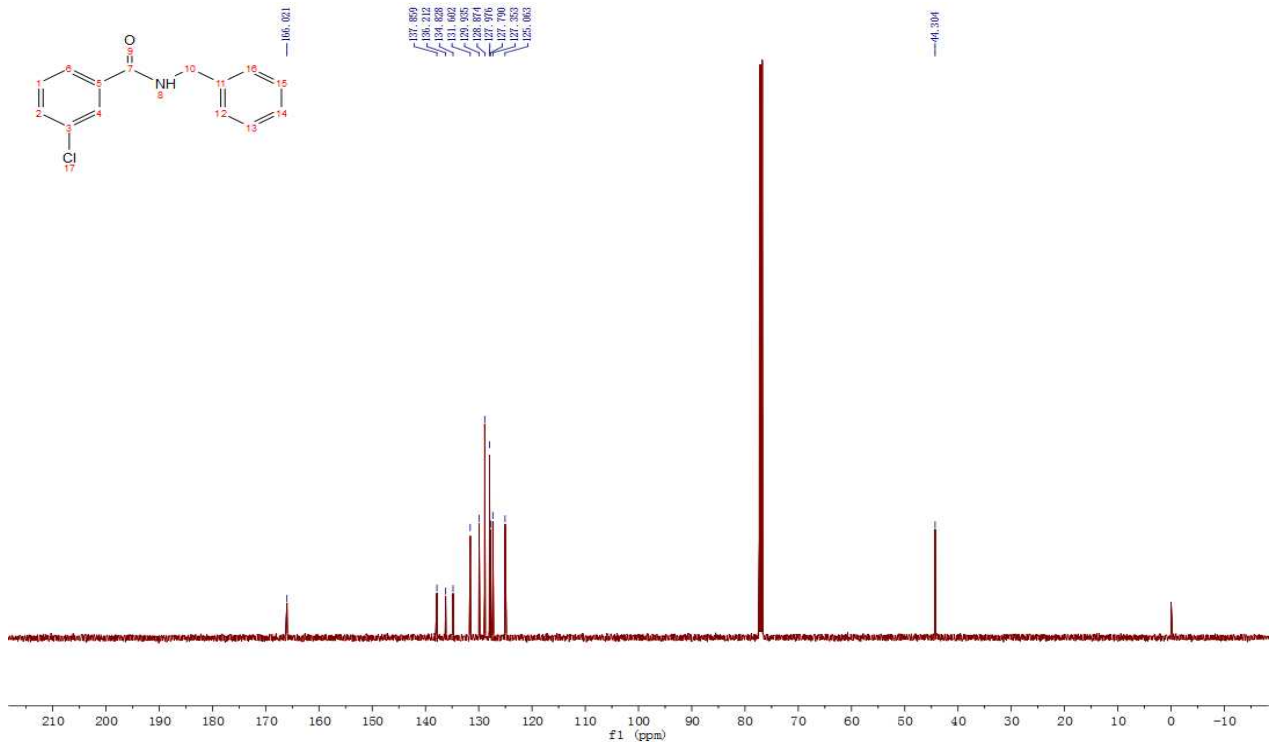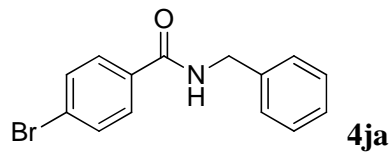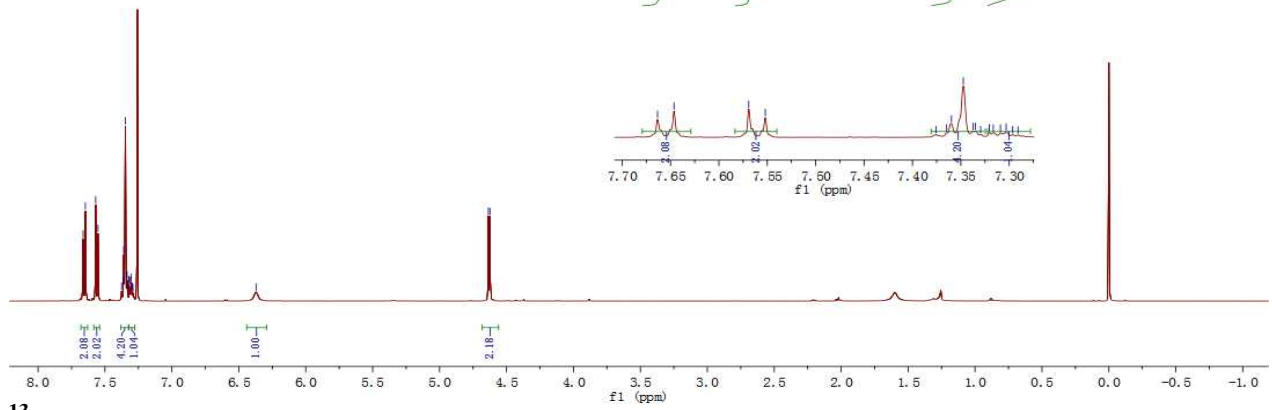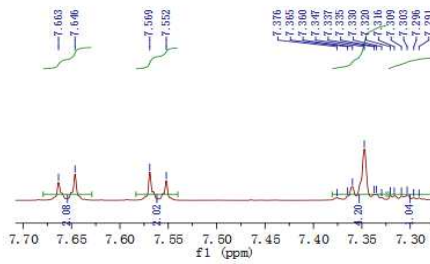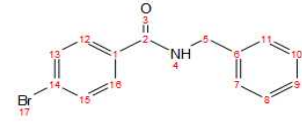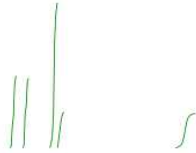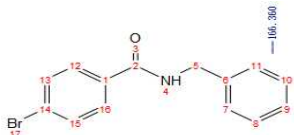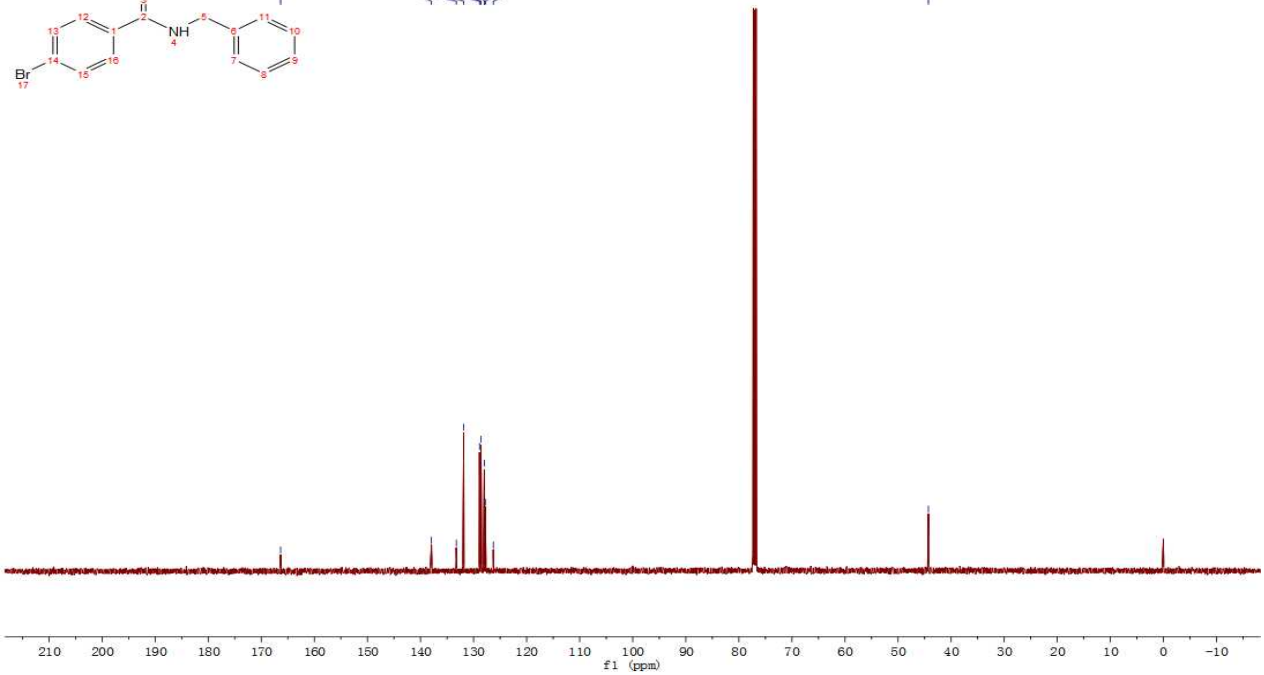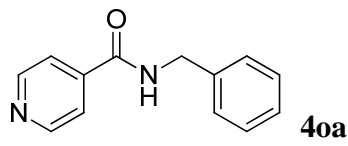
¹H NMR

¹³C NMR

4pa

¹H NMR

¹³C NMR
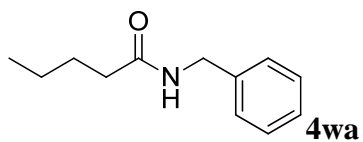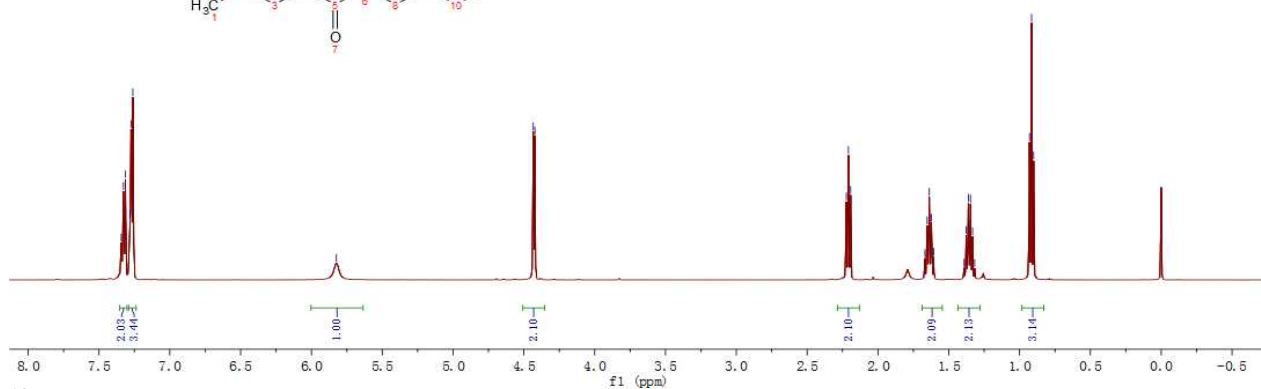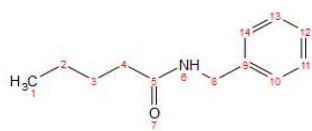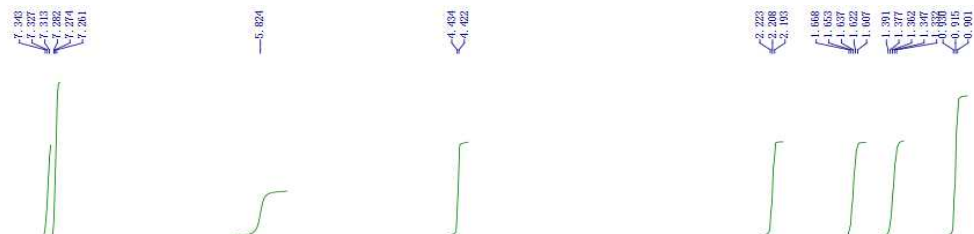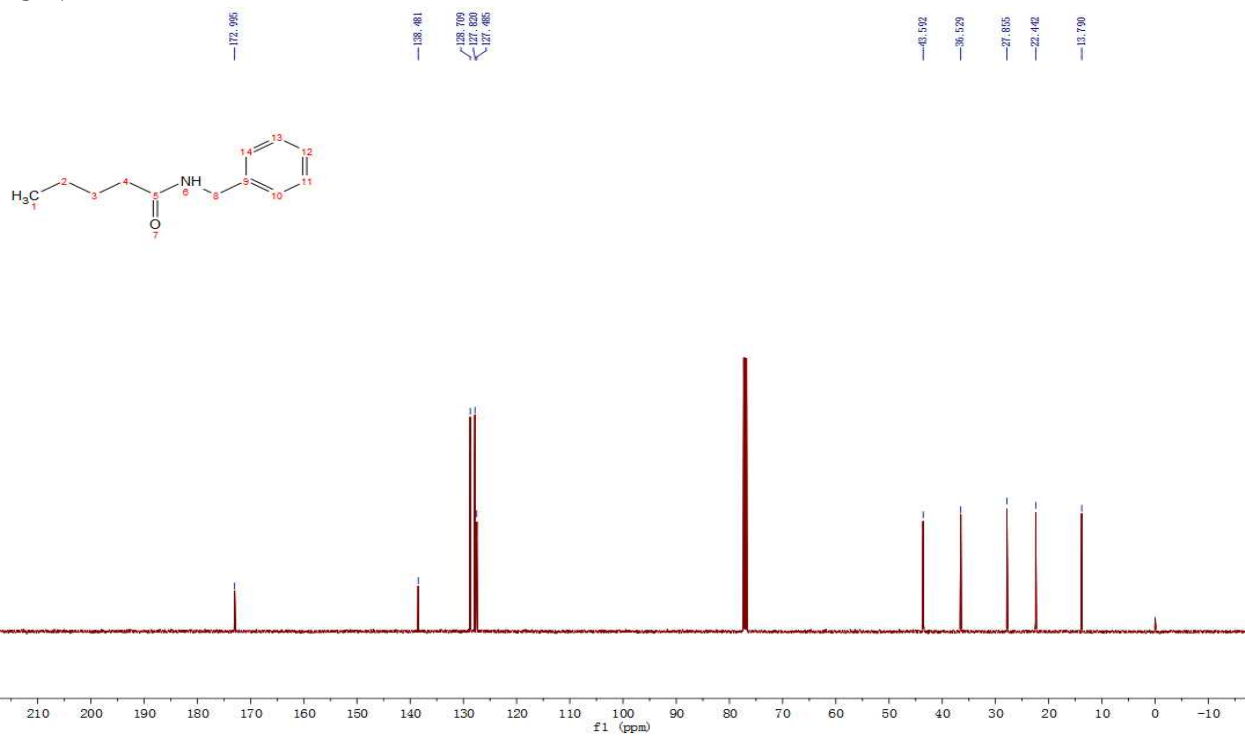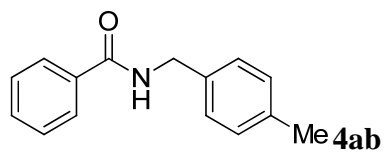
S56

4ra

¹H NMR

¹³C NMR

S57

4sa

¹H NMR

¹³C NMR

S58

¹H NMR

¹³C NMR

S59

4ua

^{1}H NMR

^{13}C NMR

4wa

¹H NMR

¹³C NMR

¹H NMR

¹³C NMR

S62

¹H NMR

¹³C NMR

4ad

^{1}H NMR

^{13}C NMR

S64

¹H NMR

¹³C NMR

S65

¹H NMR

¹³C NMR

4ag

8.437

7.851
7.841
7.837
7.834
7.527
7.512
7.508
7.500
7.498
7.495
7.468
7.453
7.442
7.439
7.437

3.286
3.272
3.261
3.246

1.542
1.528
1.513
1.499
1.484
1.369
1.354
1.339
1.323
1.309
1.294
0.920
0.905
0.890

7.851
7.841
7.837
7.834

7.527
7.512
7.508
7.500
7.498
7.495
7.468
7.453
7.442
7.439
7.437

7.8   7.7   7.6   7.5   7.4
f1 (ppm)

2.06   1.04   2.02

1.00   2.06   1.04   2.02   2.11   2.11   2.11   3.14

9.0   8.5   8.0   7.5   7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0   0.5   0.0
f1 (ppm)

¹³C NMR

166.070

134.724
130.901
128.158
127.674

38.829

31.228

19.631

13.676

210   200   190   180   170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20   10   0   -10
f1 (ppm)

S67

4ah

¹H NMR

7.783
7.768
7.478
7.464
7.449
7.404
7.389
7.374

6.009

3.266
3.253
3.240

1.919
1.906
1.892
1.879
1.865

0.959
0.945

2.04
1.02
2.05
1.00
2.12
1.03
6.34

f1 (ppm)

¹³C NMR

167.788

134.923
131.254
128.480
126.914

47.393

28.694

20.171

f1 (ppm)
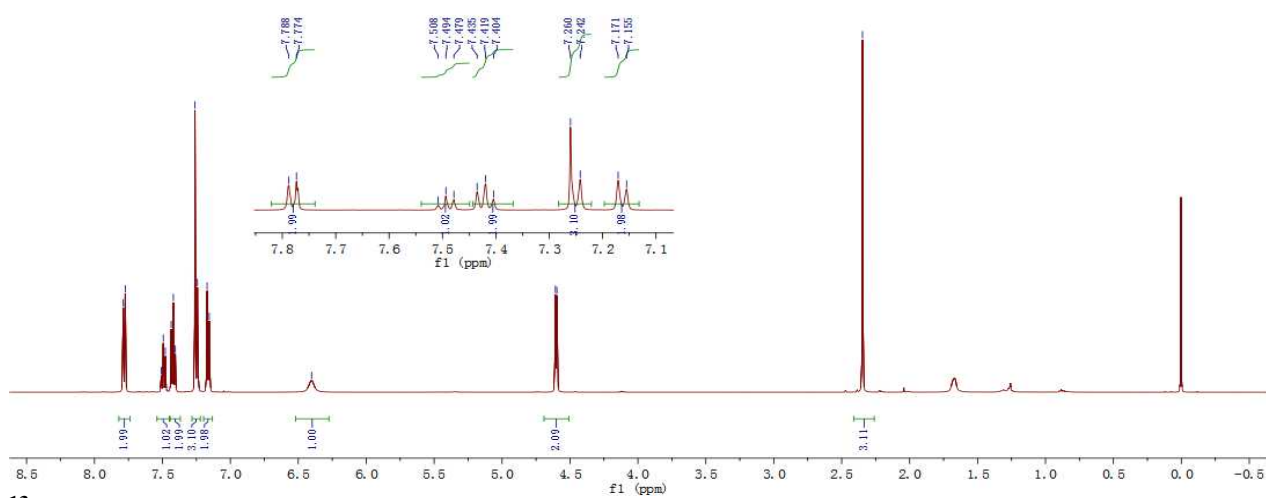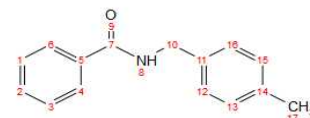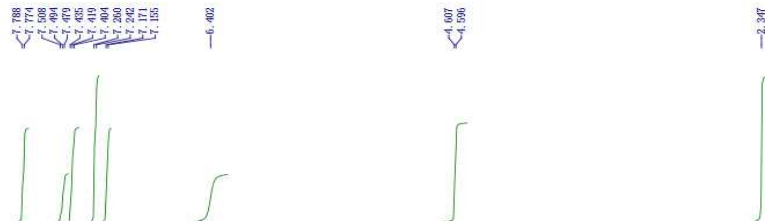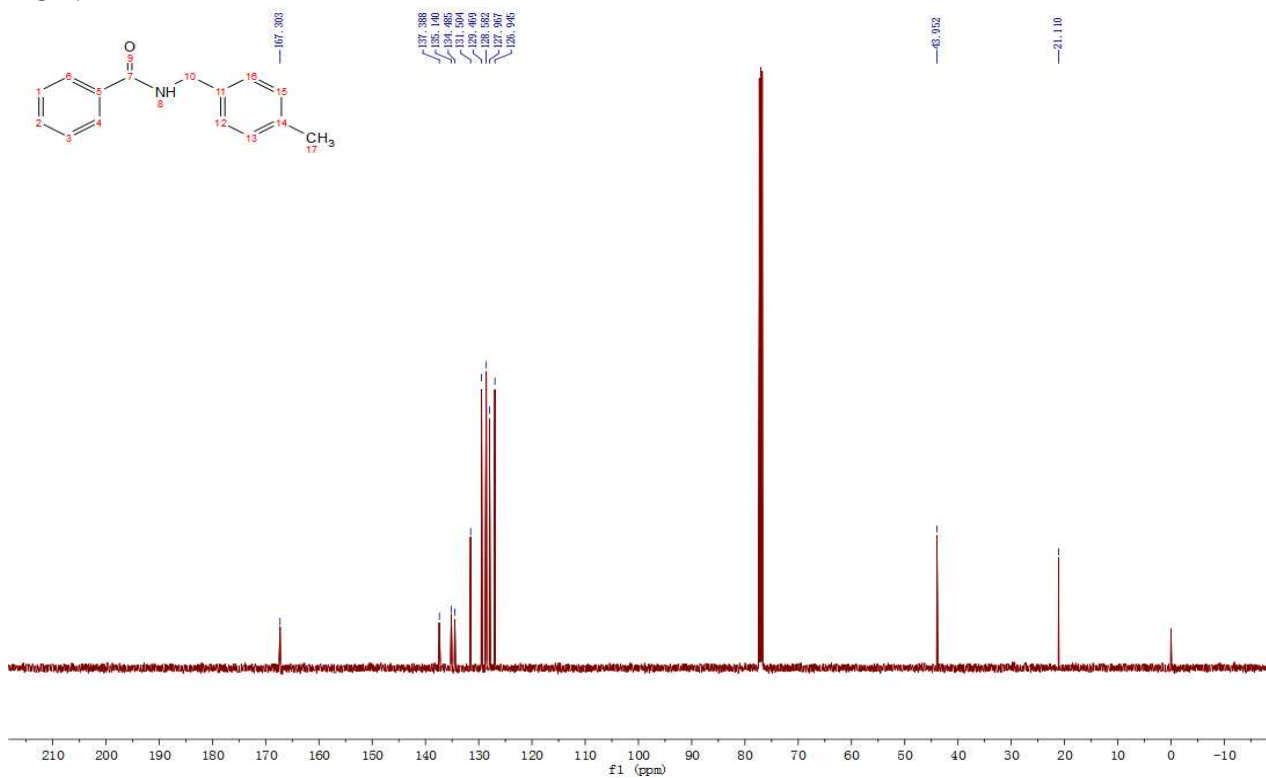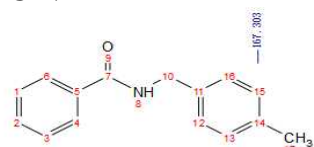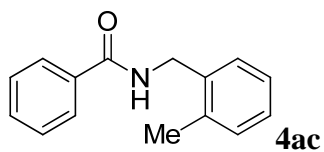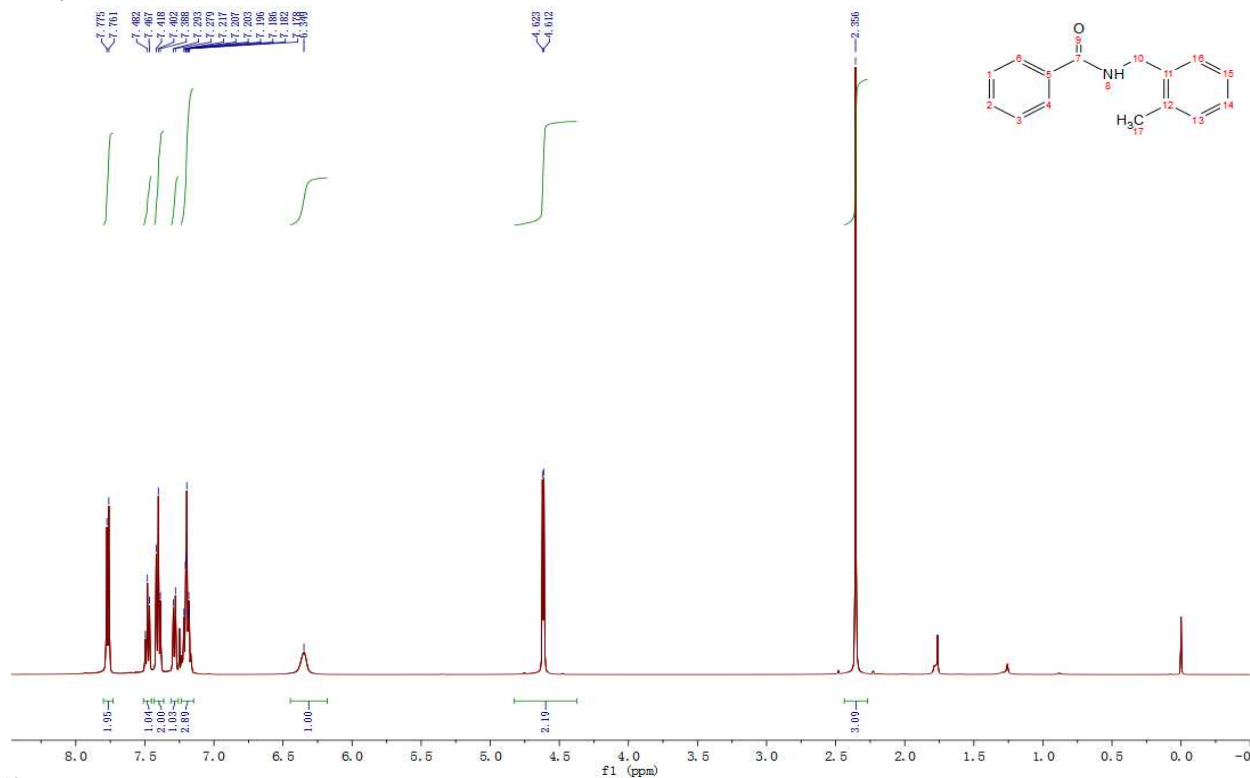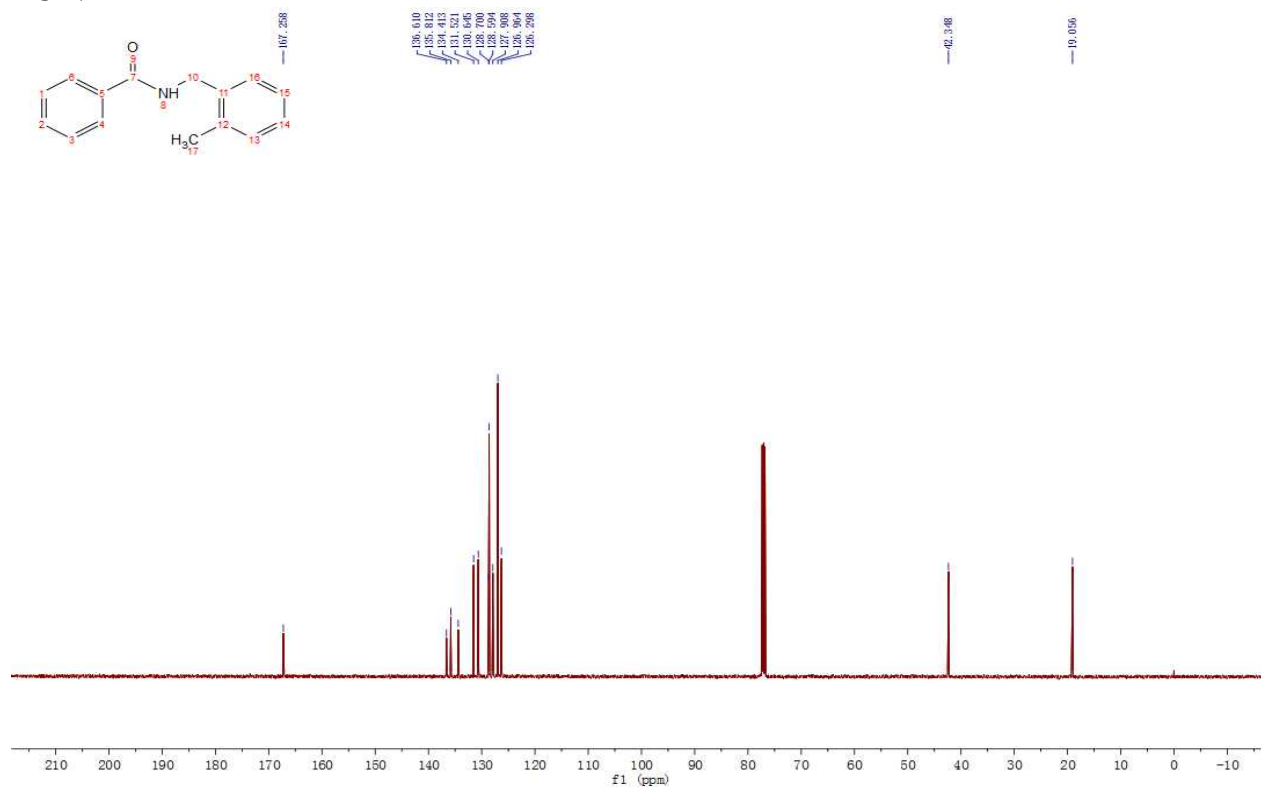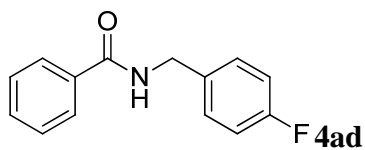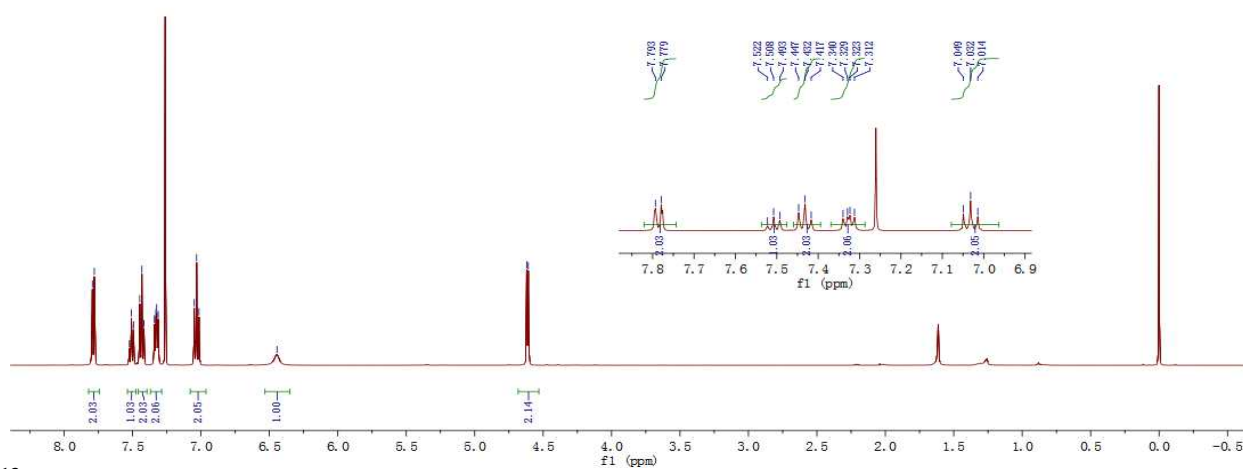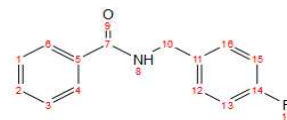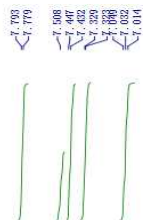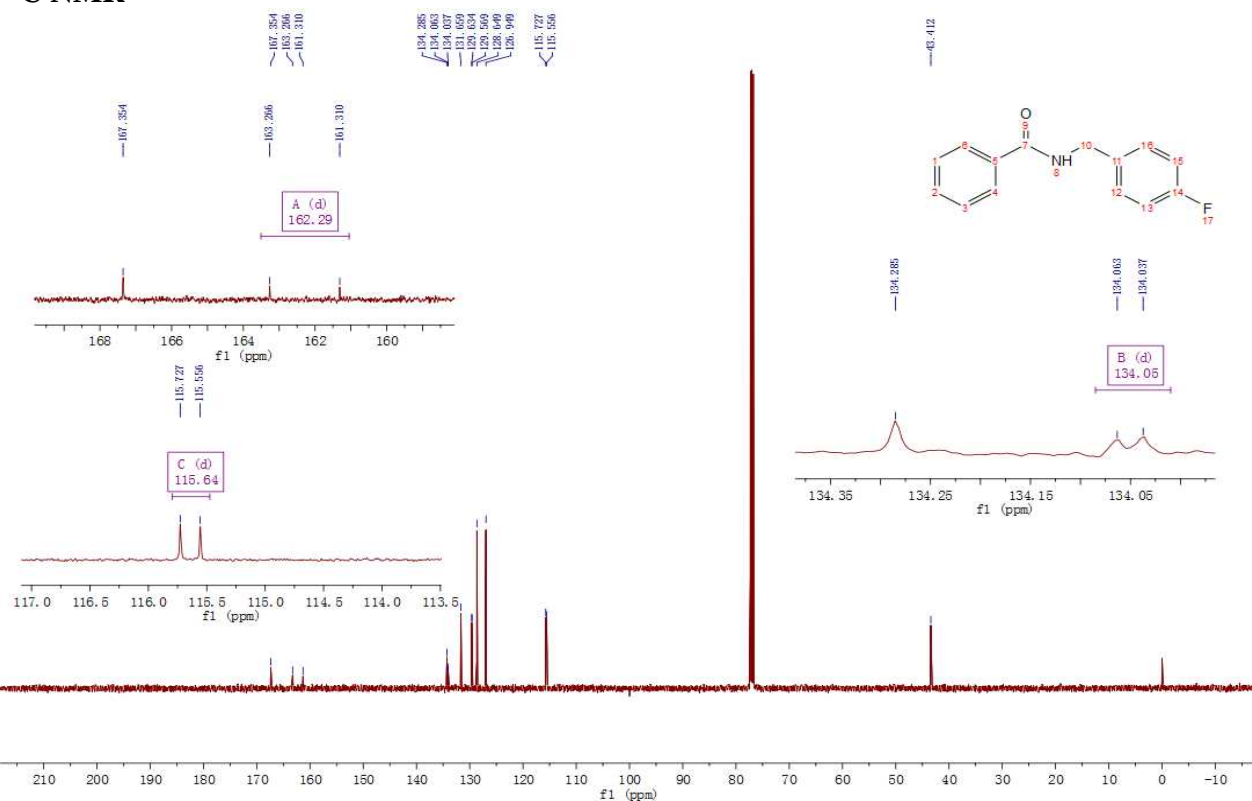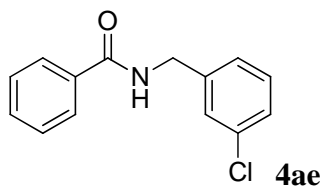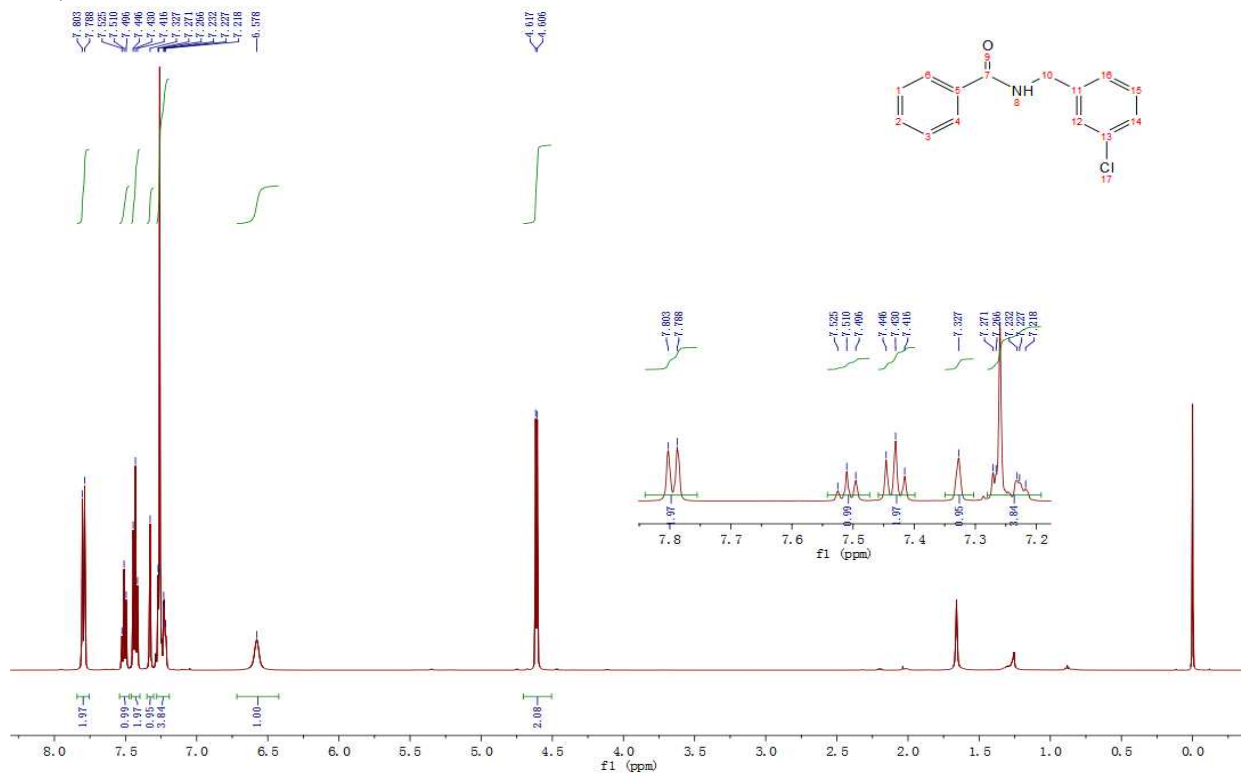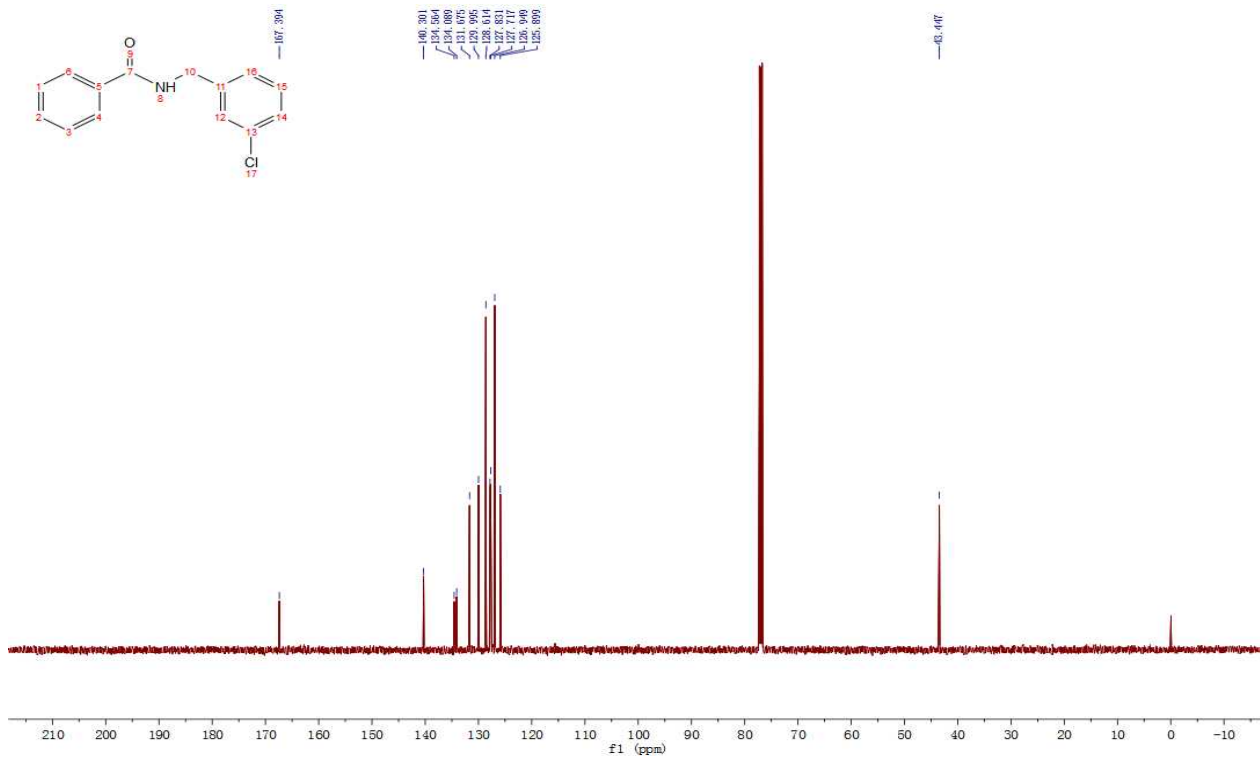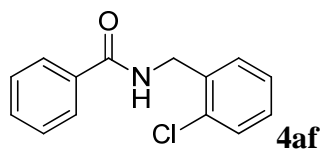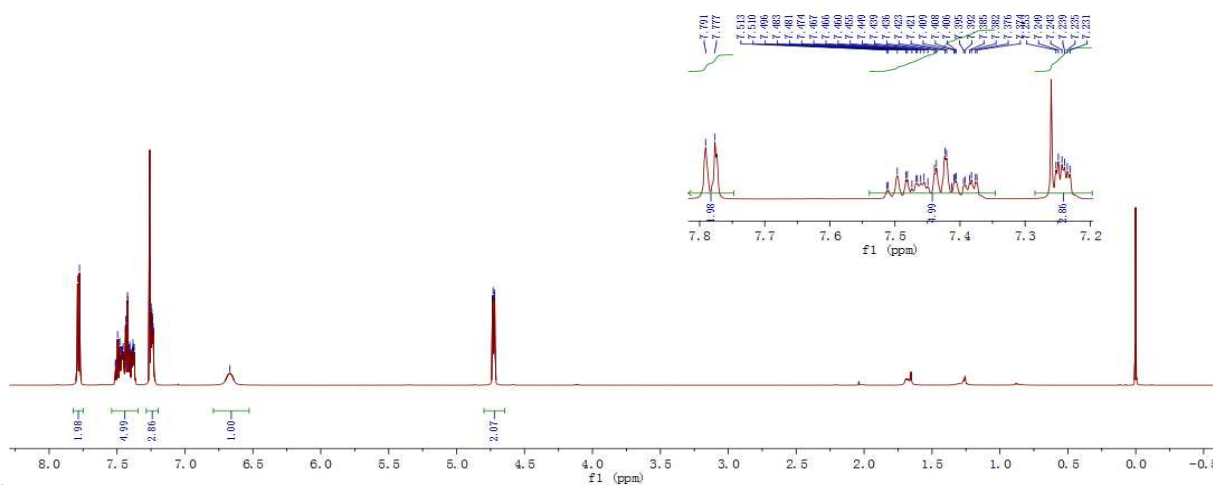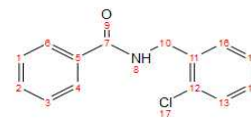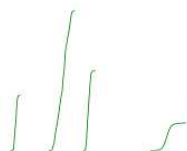
4ai

¹H NMR

7.767
7.753
7.498
7.495
7.493
7.485
7.481
7.477
7.468
7.466
7.464
7.429
7.414
7.399

6.247

3.458
3.444
3.432
3.430
3.418

1.635
1.621
1.606
1.592
1.577

1.314
1.298
1.286
1.275

0.880
0.865

2.03
1.00
2.04

1.00

2.12

2.14
10.51

3.28

f1 (ppm)

¹³C NMR

167.538

134.920
131.268
128.519
126.841

40.136
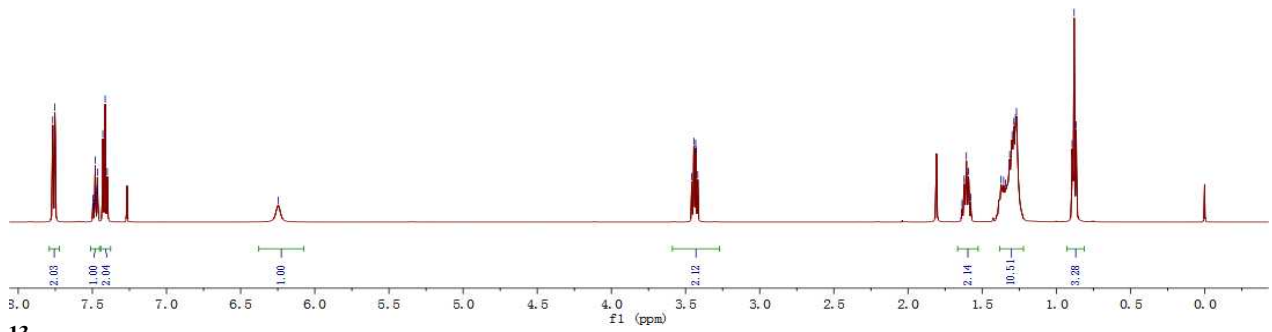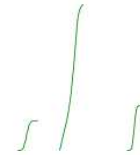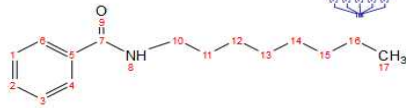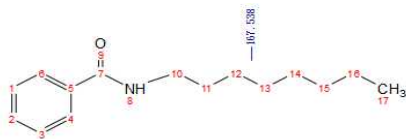
31.794
29.687
29.394
29.208
27.019
22.632

14.069

f1 (ppm)

S69

4aj

¹H NMR

¹³C NMR

¹H NMR

¹³C NMR

4al

^{1}H NMR

7.752, 7.737, 7.445, 7.431, 7.416, 7.344, 7.329, 7.313

4.384

3.729, 3.719, 3.709, 3.533, 3.523, 3.512, 3.501

3.149
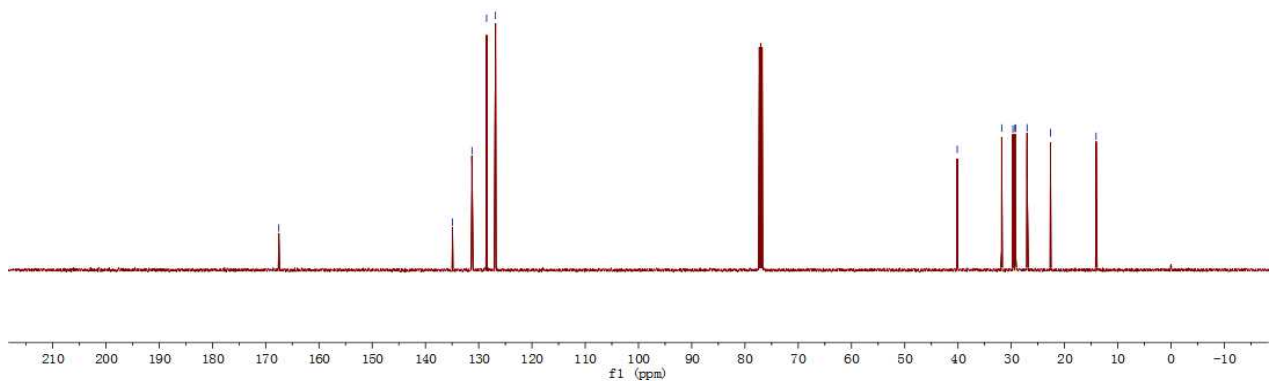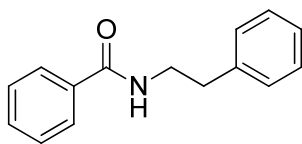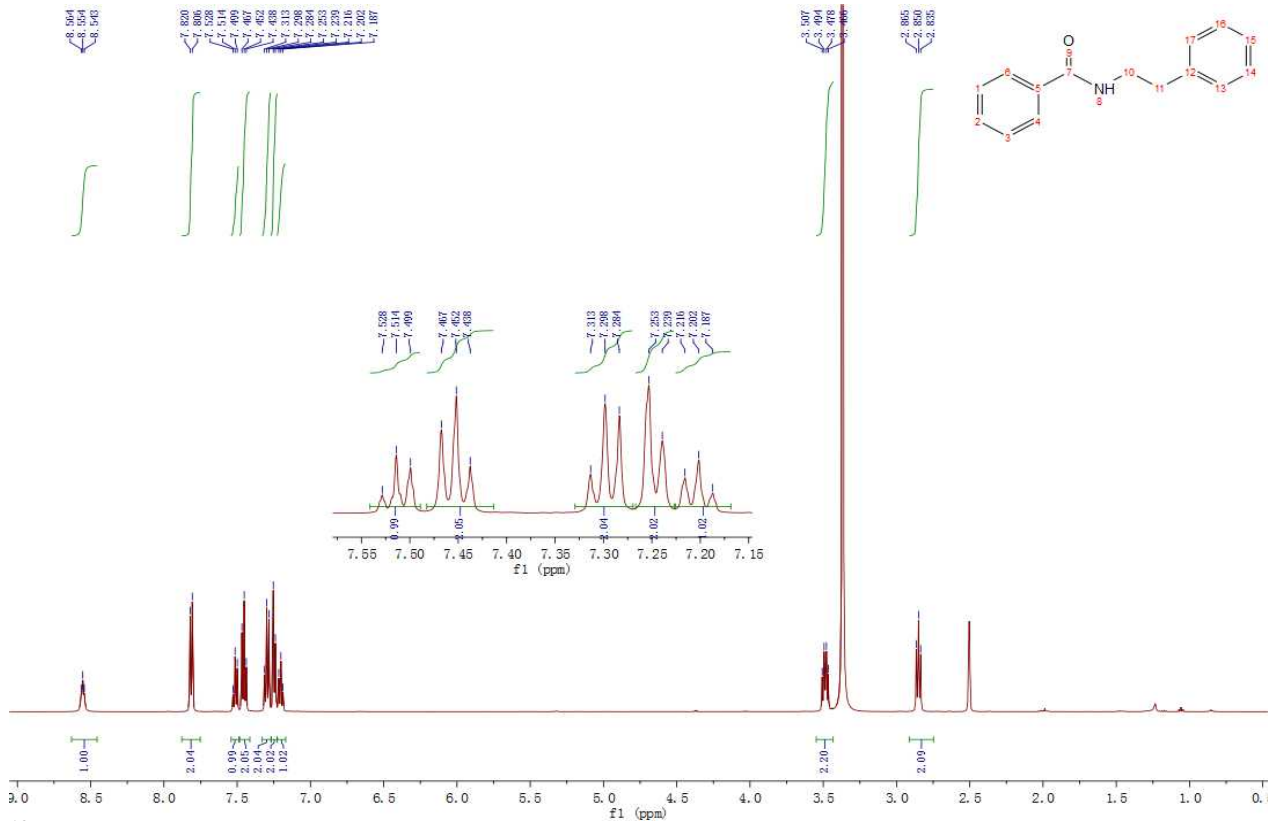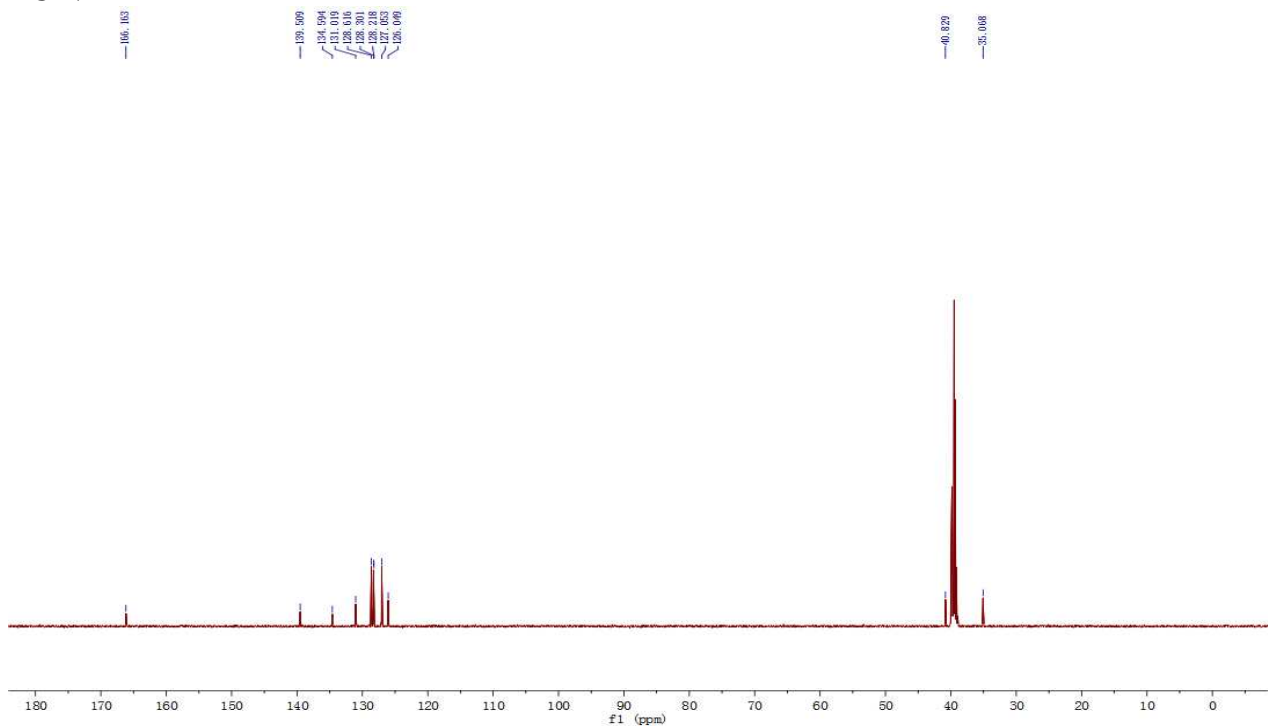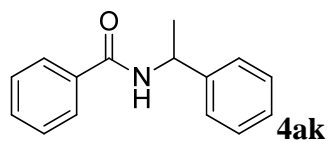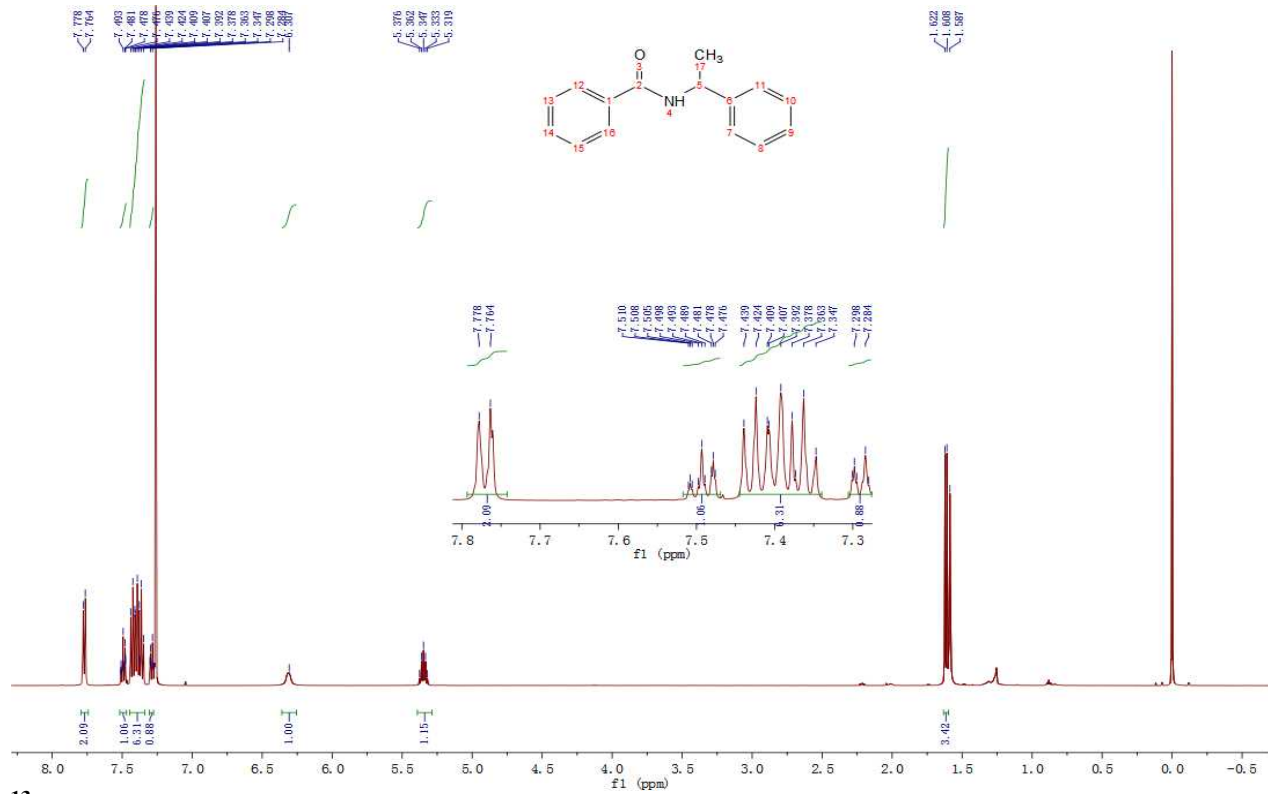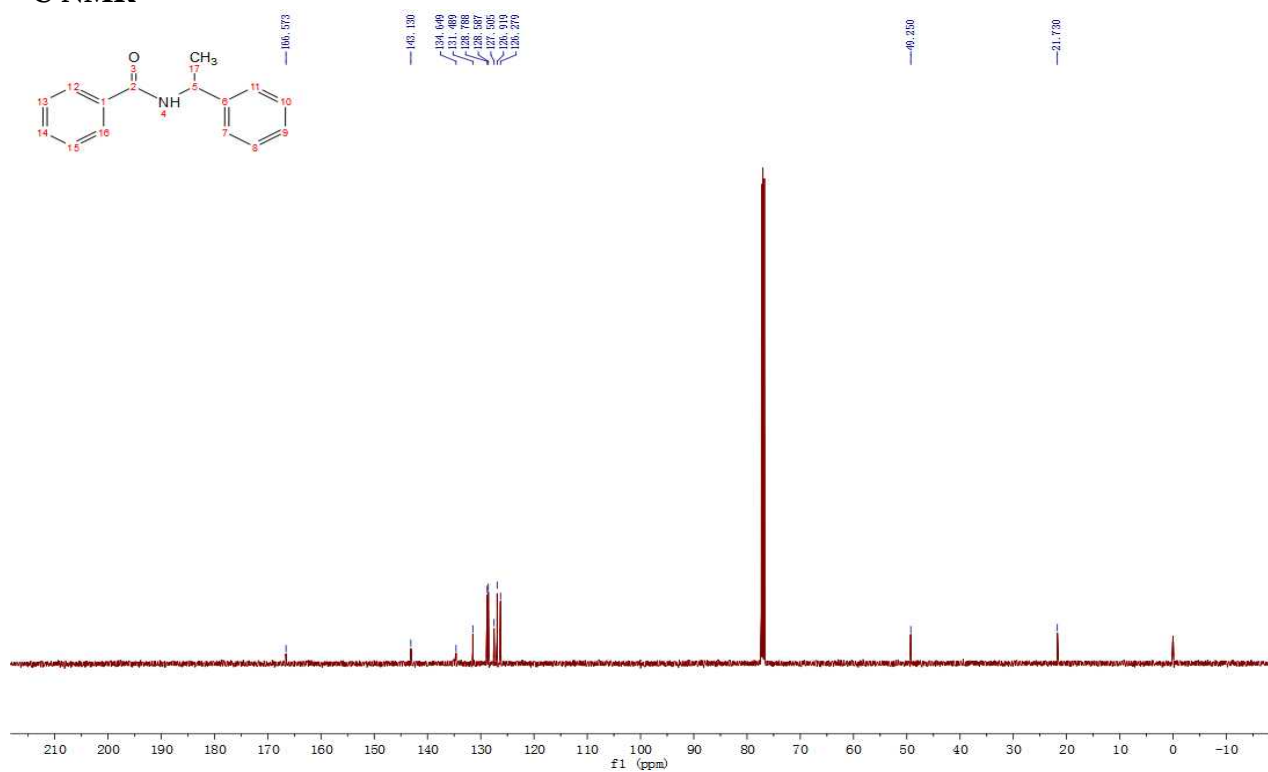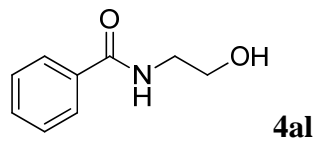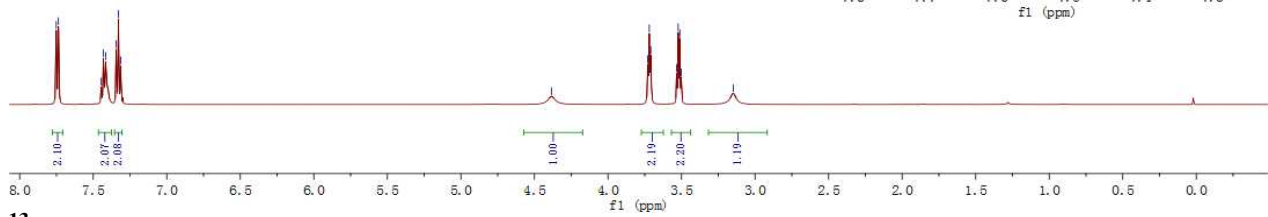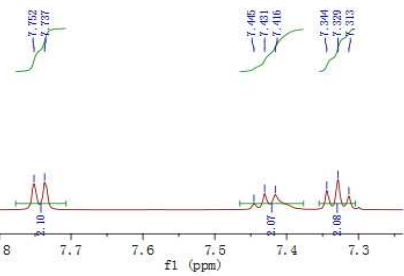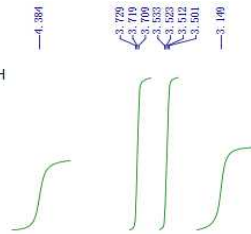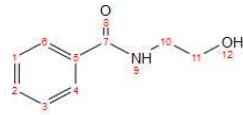
^{13}C NMR

168.862

134.040, 131.604, 128.500, 127.043

61.505

42.735

4am

¹H NMR

¹³C NMR

S73

4an

¹H NMR

7.475, 7.472, 7.461, 7.456, 7.353, 7.341

3.615, 3.601, 3.587, 3.386, 3.373, 3.360

1.938, 1.925, 1.911, 1.897, 1.884, 1.846, 1.833, 1.820, 1.806, 1.794

¹³C NMR

169.738

137.204

129.746, 128.210, 127.037

49.573, 46.145

26.347, 24.418

S74

4ao

¹H NMR

¹³C NMR

4io

¹H NMR

8.162
8.159
8.146
8.143
7.505
7.502
7.490
7.487
7.474
7.471
7.274
7.261
7.260
7.245
7.227
7.211

3.888
3.879
3.870

3.046
3.037
3.027

0.94 0.99 2.23 4.00 3.96

f1 (ppm)

¹³C NMR

168.656
151.227
132.645
131.921
127.496
124.878
120.080
67.359
53.581

f1 (ppm)

S76

4mo
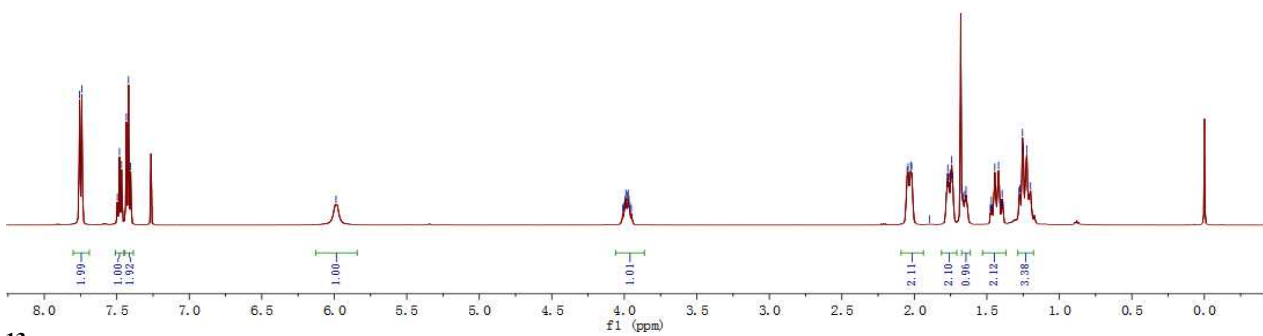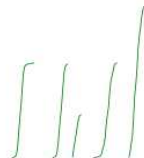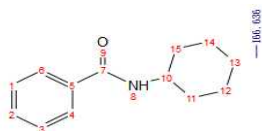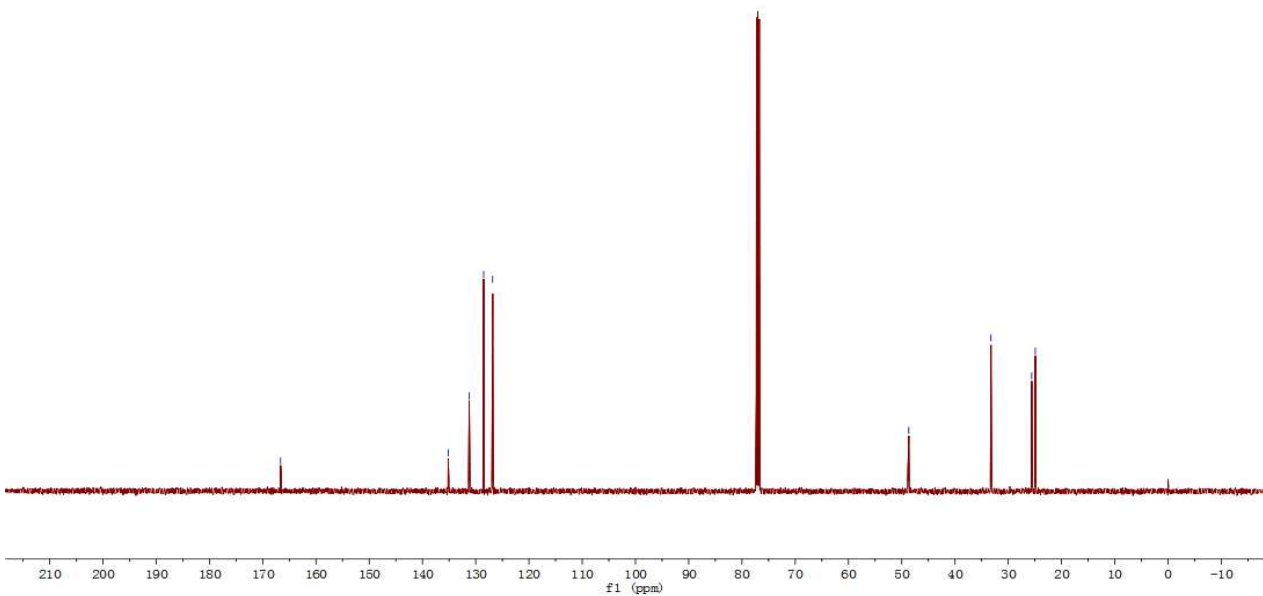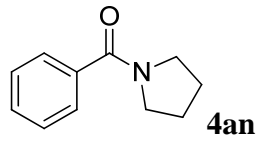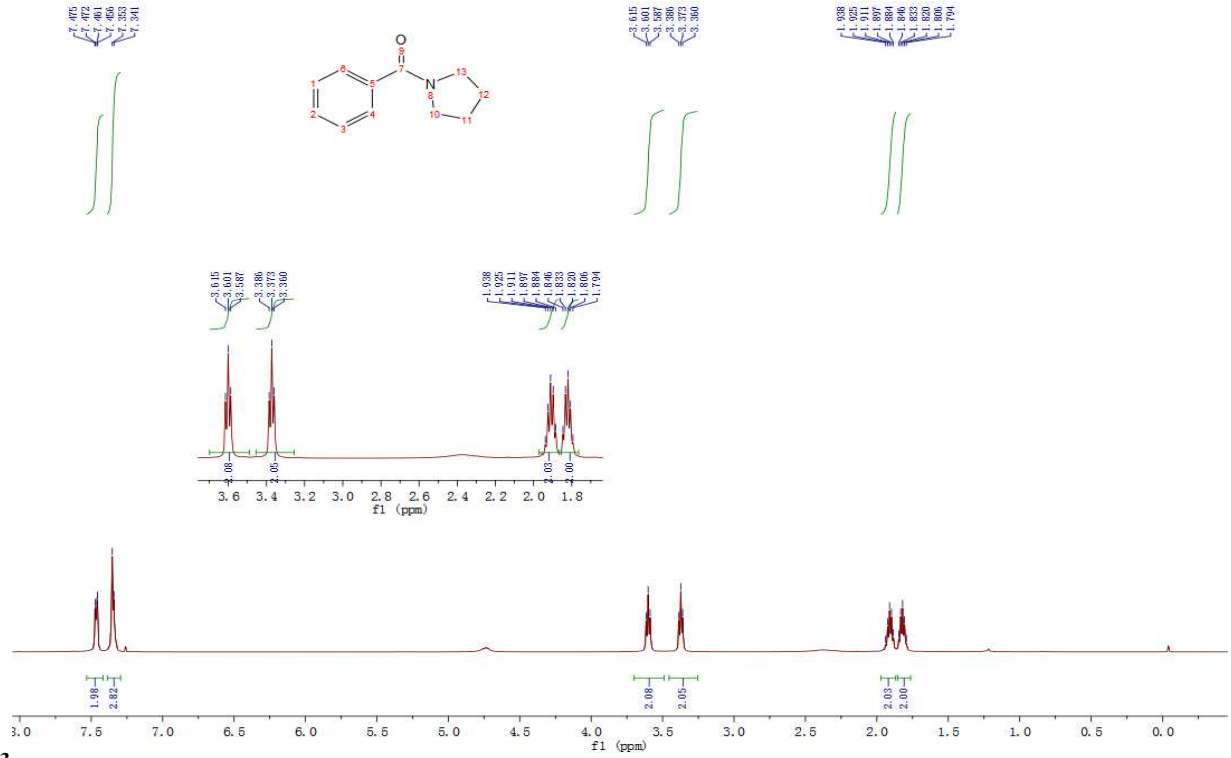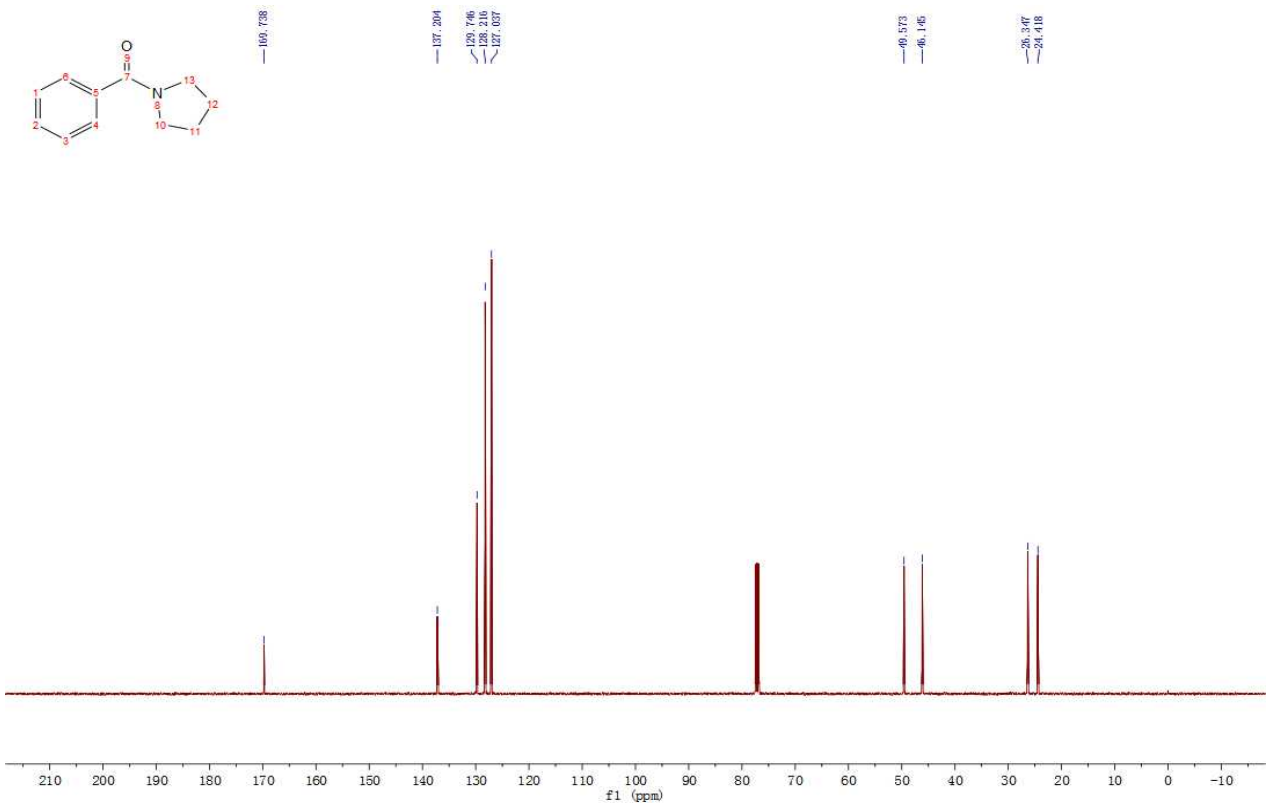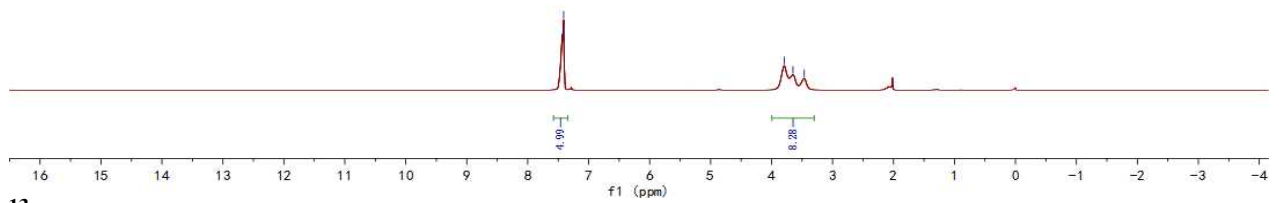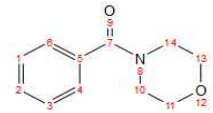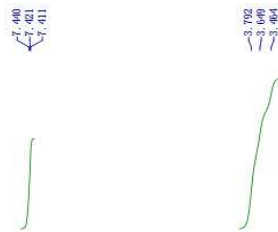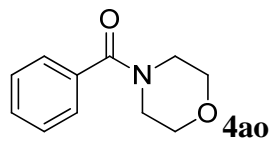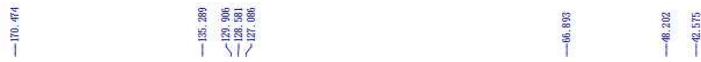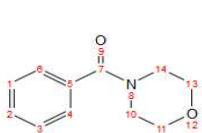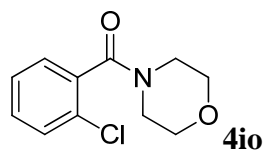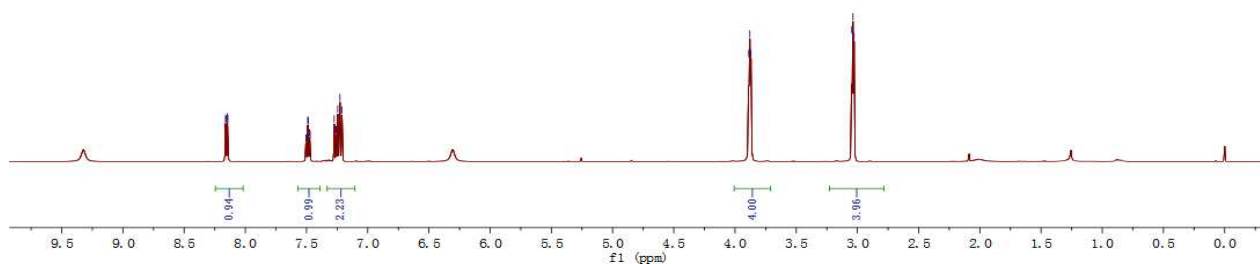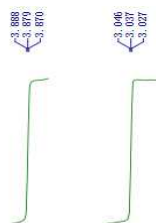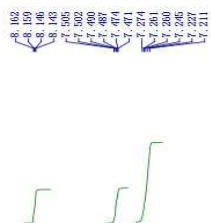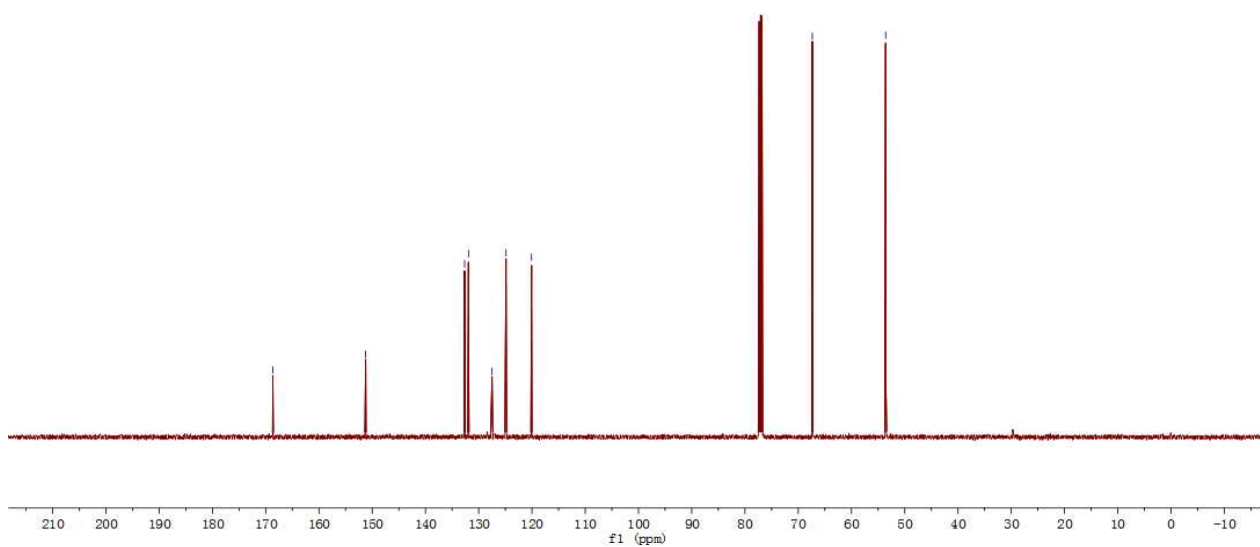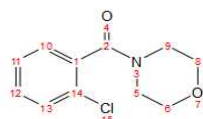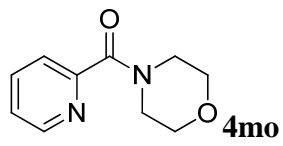
¹H NMR

8.574, 8.573, 8.571, 8.566, 8.565, 8.564, 7.818, 7.814, 7.802, 7.799, 7.787, 7.783, 7.672, 7.656, 7.356, 7.354, 7.347, 7.344, 7.341, 7.339, 7.331, 7.329

3.801, 3.686, 3.679, 3.669, 3.646, 3.637, 3.629

1.856, 1.844

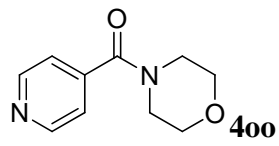1.00 0.98 0.96 0.99 4.13 4.34 1.59
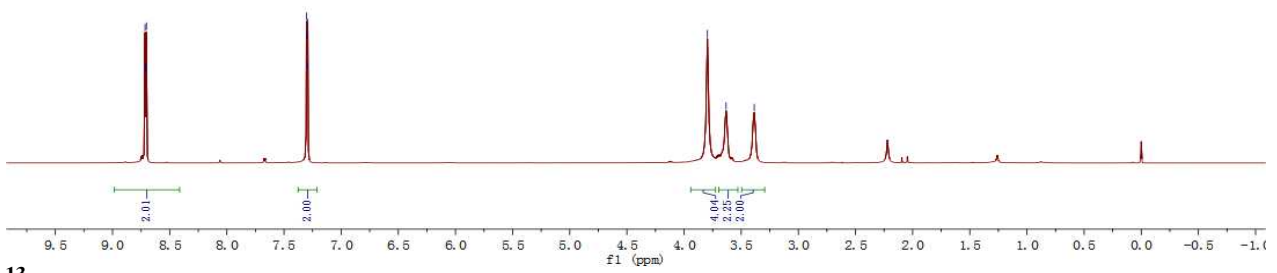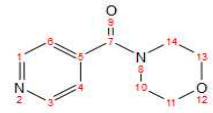
f1 (ppm)

¹³C NMR

167.496

153.627

148.285
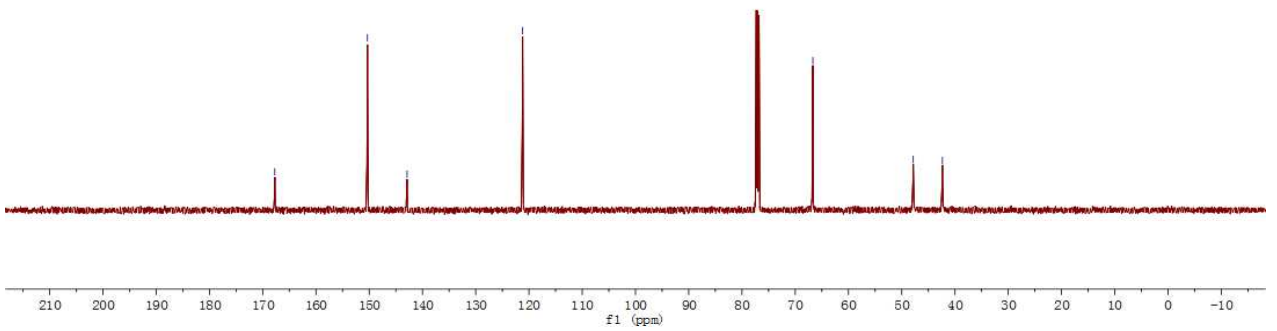
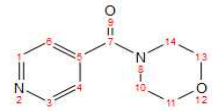137.206

124.691, 124.174

67.037, 66.822

47.750

42.798

f1 (ppm)

S77

4oo

¹H NMR

8.715
8.713
8.707
8.704

7.303
7.300
7.295
7.292

3.795
3.632
3.386

2.01
2.00
4.04
2.25
2.00

f1 (ppm)

¹³C NMR

167.729

150.330
142.895

121.184

66.691

47.834
42.363

f1 (ppm)

4qo

¹H NMR

¹³C NMR