Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information for:

Aerobic Oxidative Decyanation-Amidation of Arylacetonitriles with Urea as Nitrogen Source

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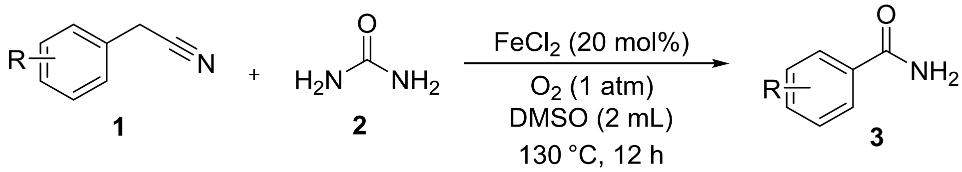
1. General information

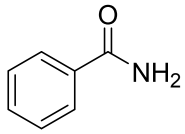
All experiments were conducted with a sealed pressure vessel. Flash column chromatography was performed over silica gel (200-300 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVIII-500MHz spectrometer. Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. GC analyses were performed on an Agilent 7890B gas chromatograph system using dodecane as the internal standard. MS analyses of the products were carried out on a SHIMADZU GCMS-QP2010 gas chromatograph mass spectrometer.

2. Procedure and characterization data for products



A sealed pressure vessel was charged with iron (II) chloride ($FeCl_2$) (12.6mg, 0.10 mmol), phenylacetonitrile (58.5 mg, 0.5 mmol), urea (90 mg, 1.5 mmol), and DMSO (2 mL). The resulting solution was stirred at 130 ^oC under O_2 (monitored by TLC and GC) for 12 hours. Upon completion of the reaction, ethyl acetate (20 mL) was added, the organic layer were washed with brine (20 mL x 2) and the combined aqueous layers was extracted with ethyl acetate (20 mL x 2). The combine organic layers were dried over anhydrous Na_2SO_4. The solvents were removed under reduced pressure and the residue was purified with flash chromatography (silica gel, ethyl acetate: petroleum ether = 4:1) to give 51 mg of the product **3a** in 85% isolated yield as white solid.

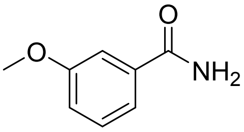
benzamide (**3a**, CAS: 55-21-0)



^{1}H NMR (500 MHz, d_6-DMSO) δ 7.98 (s, 1H), 7.87 (dd, J = 5.2, 3.3 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.44 (dd, J = 10.3, 4.6 Hz, 2H), 7.36 (s, 1H).^{13}C NMR (125 MHz, d_6-DMSO) δ 168.1, 134.4, 131.4, 128.3, 127.6.

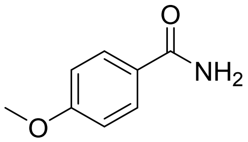
Other amides were synthesized according to similar experimental procedure starting from corresponding nitriles.

3-methoxybenzamide (**3b**, CAS: 5813-86-5)



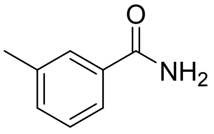
The reaction of 2-(3-methoxyphenyl) acetonitrile with urea gave 57 mg of the product **3b** in 75% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.95 (s, 1H), 7.44 (m, 2H), 7.35 (t, J = 7.9 Hz, 2H), 7.08 (m, 1H), 3.79 (s, 3H).^{13}C NMR (125 MHz, d_6-DMSO) δ 167.7, 159.2, 135.8, 129.4, 119.7, 117.1, 112.7, 55.3.

4-methoxybenzamide (**3c**, CAS: 3424-93-9)



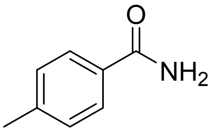
The reaction of 2-(4-methoxyphenyl) acetonitrile with urea gave 59 mg of the product **3c** in 78% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.98 – 7.75 (m, 3H), 7.18 (s, 1H), 7.03 – 6.94 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (125 MHz, d_6-DMSO) δ 167.5, 161.7, 129.4, 126.6, 113.5, 55.4.

3-methylbenzamide (**3d**, CAS: 618-47-3)



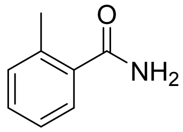
The reaction of 2-(m-tolyl) acetonitrile with urea gave 55 mg of the product **3d** in 81% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.91 (s, 1H), 7.69 (s, 1H), 7.68 – 7.63 (m, 1H), 7.32 (m, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, d_6-DMSO) δ 168.1, 137.5, 134.3, 131.8, 128.1, 128.1, 124.7, 21.0.

4-methylbenzamide (**3e**, CAS: 619-55-6)



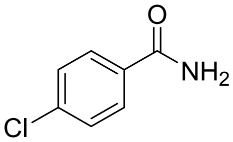
The reaction of 2-(p-tolyl) acetonitrile with urea gave 48 mg of the product **3e** in 71% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.88 (s, 1H), 7.80 – 7.75 (m, 2H), 7.24 (d, J = 7.9 Hz, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, d_6-DMSO) δ 167.9, 141.1, 131.6, 128.8, 127.6, 21.0.

2-methylbenzamide (**3f**, CAS: 527-85-5)



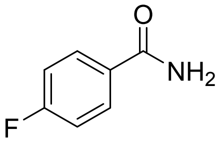
The reaction of 2-(o-tolyl) acetonitrile with urea gave 48 mg of the product **3f** in 71% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.68 (s, 1H), 7.38 – 7.27 (m, 3H), 7.25 – 7.15 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, d_6-DMSO) δ 173.0, 137.0, 136.0, 131.5, 130.5, 127.8, 126.4, 20.3.

4-chlorobenzamide (**3g**, CAS: 619-56-7)



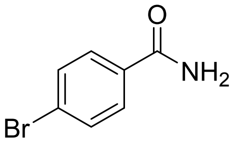
The reaction of 2-(4-chlorophenyl)acetonitrile with urea gave 62 mg of the product **3g** in 80% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 8.04 (s, 1H), 7.90 – 7.87 (m, 2H), 7.54 – 7.51 (m, 2H), 7.45 (s, 1H).^{13}C NMR (125 MHz, d_6-DMSO) δ 166.9, 136.2, 133.1, 129.5, 128.4.

4-fluorobenzamide (**3h**, CAS: 824-75-9)



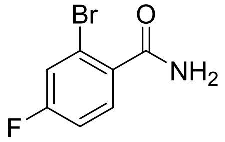
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 51 mg of the product **3h** in 73% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.99 (s, 1H), 7.96 – 7.92 (m, 2H), 7.39 (s, 1H), 7.28 (m, 2H).^{13}C NMR (125 MHz, d_6-DMSO) δ 166.9 (s), 164.0 (d, J = 248.3 Hz), 130.8 (d, J = 2.9 Hz), 130.2 (d, J = 9.0 Hz), 115.2 (d, J = 21.7 Hz).

4-bromobenzamide (**3i**, CAS: 698-67-9)



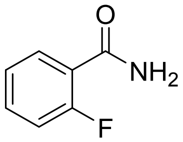
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 79 mg of the product **3i** in 79% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 8.04 (s, 1H), 7.85 – 7.76 (m, 2H), 7.73 – 7.58 (m, 2H), 7.45 (s, 1H).^{13}C NMR (125 MHz, d_6-DMSO) δ 167.0, 133.5, 131.3, 129.7, 125.1.

2-bromo-4-fluorobenzamide (**3j**, CAS: 1006-40-2)



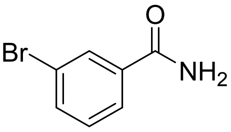
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 56 mg of the product **3j** in 51% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.87 (s, 1H), 7.64 – 7.57 (m, 2H), 7.47 (dd, J = 8.5, 6.1 Hz, 1H), 7.30 (td, J = 8.5, 2.5 Hz, 1H). ^{13}C NMR (126 MHz, d_6-DMSO) δ 168.38 (s), 161.8 (d, J = 249.8 Hz), 136.0 (d, J = 3.5 Hz), 130.3 (d, J = 8.9 Hz), 120.0 (d, J = 24.7 Hz), 119.5 (d, J = 9.9 Hz), 114.7 (d, J = 21.2 Hz).

2-fluorobenzamide (**3k**, CAS: 445-28-3)



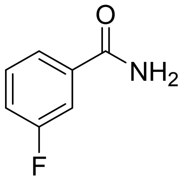
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 51 mg of the product **3k** in 74% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.75 – 7.58 (m, 3H), 7.54 – 7.49 (m, 1H), 7.29 – 7.24 (m, 2H).^{13}C NMR (125 MHz, d_6-DMSO) δ 165.4 (s), 159.4 (d, J = 249.1 Hz), 132.6 (d, J = 8.6 Hz), 130.3 (d, J = 2.9 Hz), 124.5 (d, J = 3.4 Hz), 123.9 (d, J = 14.3 Hz), 116.2 (d, J = 22.6 Hz).

3-bromobenzamide (**3l**, CAS: 22726-00-7)



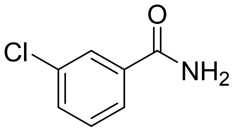
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 75 mg of the product **3l** in 75% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 8.06 (dd, J = 10.6, 8.8 Hz, 2H), 7.88 (m, 1H), 7.73 (m, 1H), 7.52 (s, 1H), 7.43 (t, J = 7.9 Hz, 1H).^{13}C NMR (125 MHz, d_6-DMSO) δ 166.4, 136.6, 134.0, 130.6, 130.3, 126.6, 121.7.

3-fluorobenzamide (**3m**, CAS: 455-37-8)



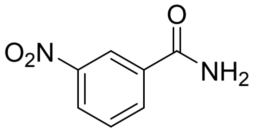
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 52 mg of the product **3m** in 75% isolated yield as a white solid. ^{1}H NMR (500 MHz, DMSO) δ 8.06 (s, 1H), 7.74 – 7.71 (m, 1H), 7.66 (m, 1H), 7.50 (td, J = 8.0, 5.9 Hz, 2H), 7.40 – 7.32 (m, 1H). ^{13}C NMR (126 MHz, d_6-DMSO) δ 166.6 (d, J = 2.4 Hz), 162.0 (d, J = 243.9 Hz), 136.8 (d, *J* = 6.7 Hz), 130.5 (d, *J* = 7.9 Hz), 123.7 (d, *J* = 2.8 Hz), 118.2 (d, *J* = 21.1 Hz), 114.3 (d, *J* = 22.5 Hz).

3-chlorobenzamide (**3n**, CAS: 618-48-4)



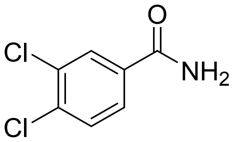
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 65 mg of the product **3n** in 83% isolated yield as a white solid. ^{1}H NMR (500 MHz, *d*$_6$-DMSO) *δ* 8.13 (s, 1H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.56 – 7.41 (m, 2H).^{13}C NMR (125 MHz, *d*$_6$-DMSO) *δ* 167.4, 136.5, 133.7, 131.7, 130.8, 127.7, 126.6.

3-nitrobenzamide (**3o**, CAS: 645-09-0)



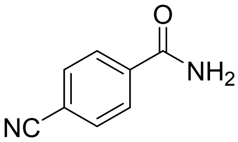
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 64 mg of the product in 77% isolated yield as a white solid. ^{1}H NMR (500 MHz, *d*$_6$-DMSO) *δ* 8.69 (t, *J* = 2.0 Hz, 1H), 8.38 – 8.30 (m, 3H), 7.77 (t, *J* = 8.0 Hz, 1H), 7.71 (s, 1H). ^{13}C NMR (125 MHz, *d*$_6$-DMSO) *δ* 165.8, 147.9, 135.9, 133.9, 130.2, 126.0, 122.3.

3,4-dichlorobenzamide (**3p**, CAS: 2670-38-4**)**



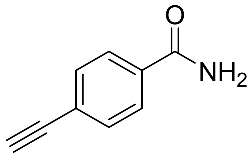
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 66 mg of the product **3p** in 69% isolated yield as a white solid. ^{1}H NMR (500 MHz, *d*$_6$-DMSO) *δ* 8.14 (s, 1H), 8.09 (d, *J* = 1.9 Hz, 1H), 7.84 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.60 (s, 1H).^{13}C NMR (125 MHz, *d*$_6$-DMSO) *δ* 165.7, 134.7, 134.2, 131.3, 130.7, 129.6, 127.8.

4-cyanobenzamide (**3q**, CAS: 3034-34-2**)**



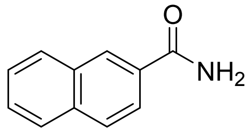
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 55 mg of the product **3q** in 76% isolated yield as a white solid. ^{1}H NMR (500 MHz, *d*$_6$-DMSO) *δ* 8.21 (s, 1H), 8.04 – 8.00 (m, 2H), 7.98 – 7.91 (m, 2H), 7.67 (s, 1H). ^{13}C NMR (125 MHz, *d*$_6$-DMSO) *δ* 166.5, 138.3, 132.4, 128.3, 118.4, 113.6.

4-ethynylbenzamide (**3r**, CAS: 90347-68-7**)**



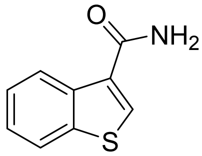
The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 54 mg of the product **3r** in 75% isolated yield as a white solid. ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.02 (d, J = 5.0 Hz, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 8.3 Hz, 2H), 7.43 (s, 1H), 4.34 (s, 1H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 167.1, 134.4, 131.6, 127.8, 124.5, 83.0, 82.7.

2-naphthamide (**3s**, CAS: 2243-82-5**)**



The reaction of 2-(4-fluorophenyl)acetonitrile with urea gave 60 mg of the product **3s** in 70% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 8.49 (s, 1H), 8.13 (s, 1H), 8.02 – 7.94 (m, 4H), 7.59 (m, 2H), 7.46 (s, 1H). ^{13}C NMR (125 MHz, d_6-DMSO) δ 168.1, 134.3, 132.2, 131.7, 129.0, 127.9, 127.9, 127.7, 127.7, 126.7, 124.5.

benzo[b]thiophene-3-carboxamide (**3t**, CAS: 858117-17-6)

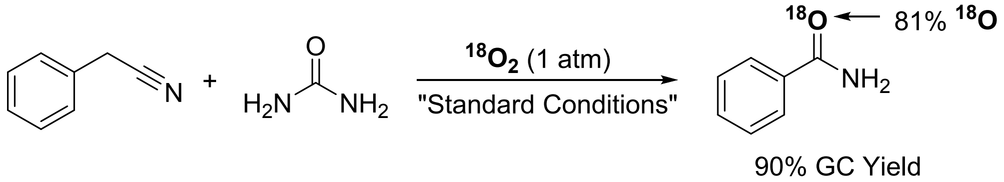


The reaction of 2-(benzo[b]thiophen-3-yl)acetonitrile with urea gave 72 mg of the product **3t** in 81% isolated yield as a white solid. ^{1}H NMR (500 MHz, d_6-DMSO) δ 8.53 – 8.50 (m, 1H), 8.39 (s, 1H), 8.03 – 8.00 (m, 1H), 7.93 (s, 1H), 7.46 – 7.39 (m, 2H), 7.32 (s, 1H).^{13}C NMR (125 MHz, d_6-DMSO) δ 165.0, 139.6, 137.4, 131.3, 130.9, 124.84 124.8, 122.8.

3. Preliminary mechanistic studies

3.1 Isotope labeling experiments

（1） ^{18}O labeling experiment under ^{18}O$_2$



(1)

A sealed pressure vessel was charged with iron (II) chloride ($FeCl_2$) (12.6 mg, 0.05 mmol), phenylacetonitrile (58.5 mg, 0.5 mmol), urea (90 mg, 1.5 mmol), and DMSO (2 mL). The resulting solution was stirred at 130 °C under $^{18}O_2$ (monitored by TLC and GC) for 12 hours. After cooling down to room temperature, the mixture was subjected to GC-MS analysis. The ratio of **3a**-^{18}O : **3a**-^{16}O = 81 : 19 (Figure S1). Also the reaction mixture was analyzed by GC indicating that **3a** was obtained in 90% yield.

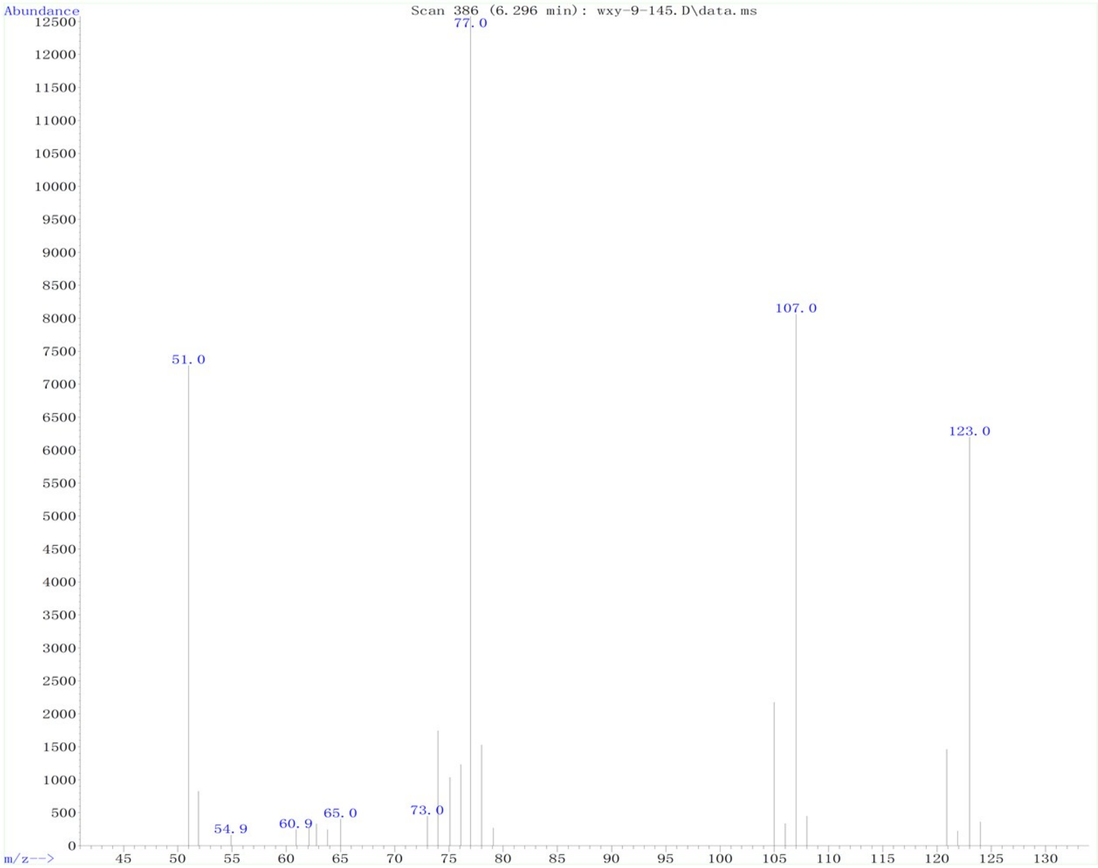
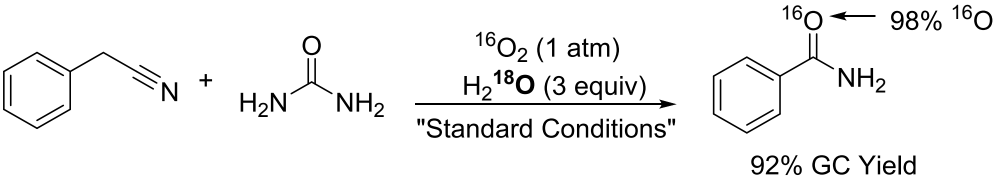


Figure S1

（2） ^{18}O labeling experiment in the present of $H_2{}^{18}O$ under $^{16}O_2$



(2)

A sealed pressure vessel was charged with iron (II) chloride ($FeCl_2$) (12.6 mg, 0.05 mmol), phenylacetonitrile (58.5 mg, 0.5 mmol), urea (90 mg 1.5 mmol), 3.0 equiv of $H_2{}^{18}O$ (27.0 mg), and DMSO (2 mL). The resulting solution was stirred at 130 ^{o}C under $^{16}O_2$ (monitored by TLC and GC) for 12 hours. After cooling down to room temperature, the reaction mixture was subjected to GC-MS analysis. The ratio of **3a-**^{18}O : **3a**-^{16}O = 2 : 98 (Figure S2). Also the reaction mixture was analyzed by GC indicating that **3a** was obtained in 92% yield.

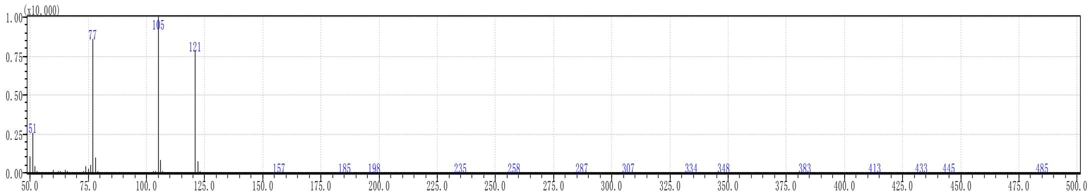
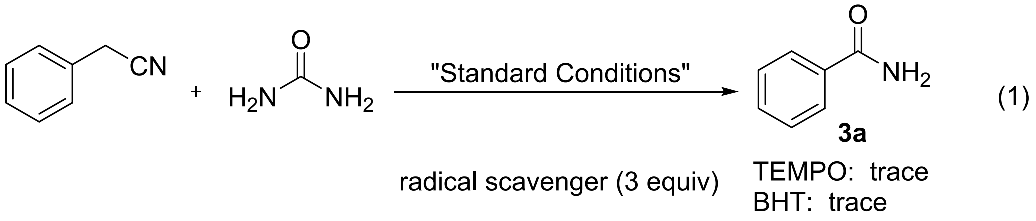


Figure S2

3.2 Radical capture experiments

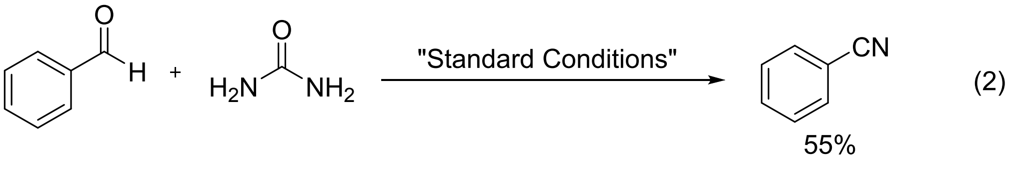


The experimental procedures for radical capture experiments with TEMPO and BHP:

(1) A sealed pressure vessel was charged with iron (II) chloride ($FeCl_2$) (12.6 mg, 0.10 mmol), phenylacetonitrile (58.5 mg, 0.5 mmol), urea (90 mg, 1.5 mmol), TEMPO (234.4 mg, 1.5 mmol), and DMSO (2 mL). The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 12 hours. The resulting solution was detected by GC and no product **3a** was formed.

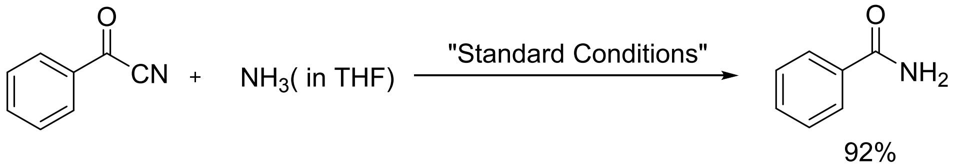
(2) A sealed pressure vessel was charged with iron (II) chloride ($FeCl_2$) (12.6 mg, 0.10 mmol), phenylacetonitrile (58.5 mg, 0.5 mmol), urea (90 mg, 1.5 mmol), BHP (330.5 mg, 1.5 mmol), and DMSO (2 mL). The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 12 hours. The resulting solution was detected by GC and no product **3a** was formed.

3.3 Intermediate experiments



A sealed pressure vessel was charged with iron (II) chloride ($FeCl_2$) (12.6 mg, 0.10 mmol), benzaldehyde (53 mg, 0.5 mmol), urea (90 mg 1.5 mmol), and DMSO (2 mL). The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 12 hours. The resulting solution was detected by GC and GC-MS. Benzonitrile was obtained in 55% yield and no product **3a** was formed.

A sealed pressure vessel was charged with iron (II) chloride ($FeCl_2$) (12.6 mg, 0.10 mmol), benzoyl cyanide (65.5 mg, 0.5 mmol), urea (90 mg, 1.5 mmol), and DMSO (2 mL). The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 12 hours. The resulting solution was detected by GC showing that benzamide **3a** was obtained in 24% yield.

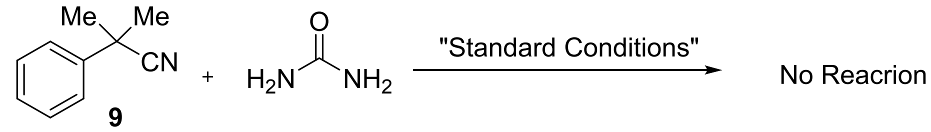


(4)

A sealed pressure vessel was charged with iron (II) chloride ($FeCl_2$) (12.6 mg, 0.10 mmol), benzoyl cyanide (65.5 mg, 0.5 mmol), NH_3 (in THF) (1.5 mmol), and DMSO (2 mL). The resulting solution was stirred at 130 °C under O_2 (monitored by TLC and GC) for 12 hours. The resulting solution was detected by GC showing that benzamide **3a** was obtained in 92% yield.

(5)

A sealed pressure vessel was charged with iron (II) chloride ($FeCl_2$) (12.6 mg, 0.10 mmol), 2-phenylpropanenitrile **8** (65 mg, 0.5 mmol, commercially available), urea (90 mg 1.5 mmol), and DMSO (2 mL). The resulting solution was stirred at 130 °C under O_2 for 12 hours. The resulting solution was detected GC-MS. Acetophenone and phenol were obtained in 23% and 7% yield determined by GC. About 60% of **8** were recovered.



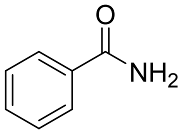
(6)

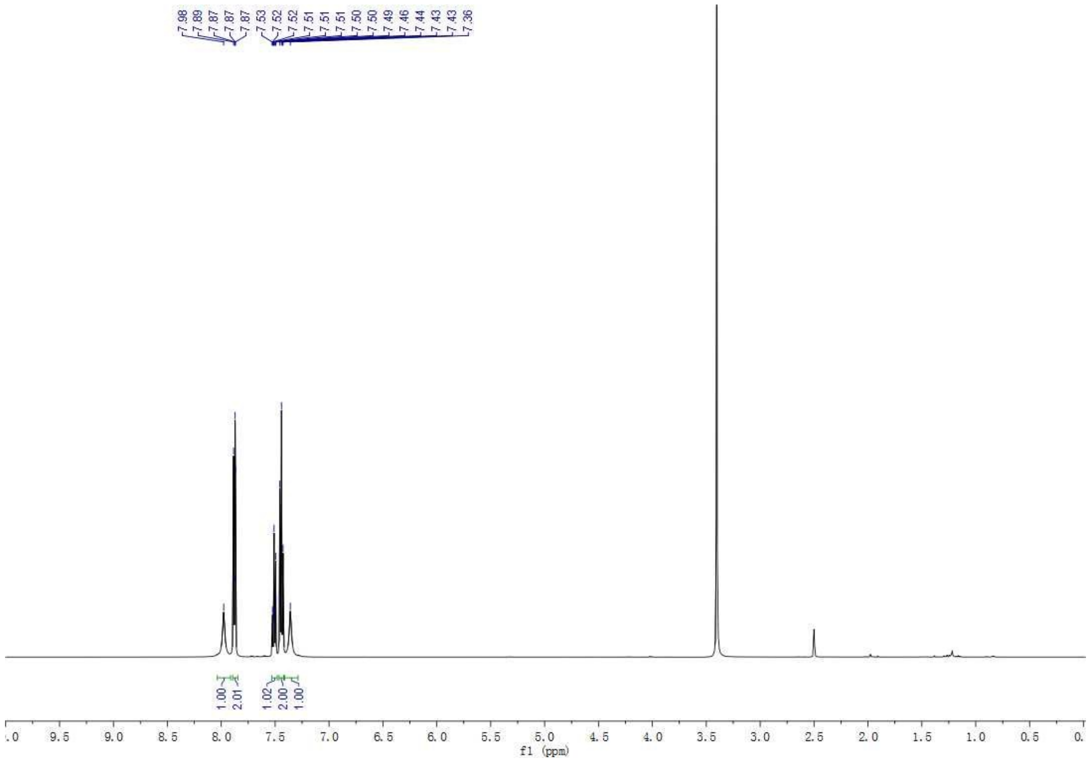
2-Methyl-2-phenylpropanenitrile (**9**) was synthesized according to literature (R. Shang, D.-S. Ji, L. Chu, Y. Fu and L. Liu, *Angew. Chem. Int. Ed.*, 2011, **50**, 4470-4474). Light yellow oil liquid. ^1H NMR: (500 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.40-7.36 (m, 2H), 7.32-7.29 (m, 1H), 1.72 (s, 6H).

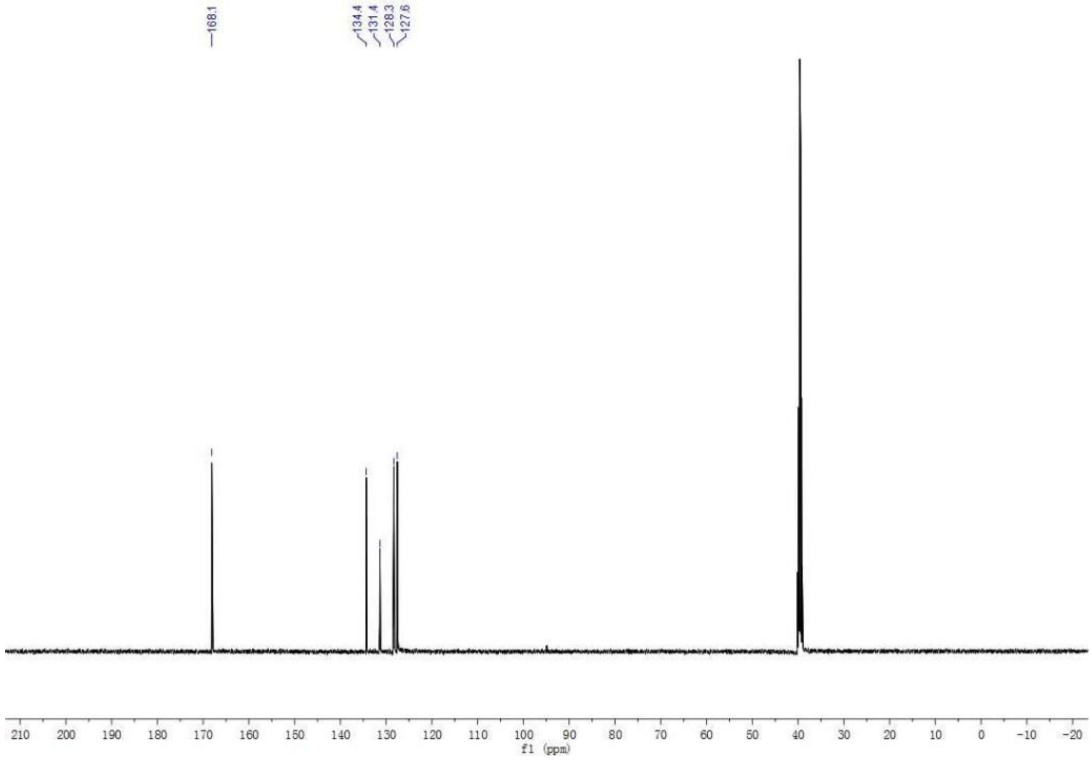
A sealed pressure vessel was charged with iron (II) chloride ($FeCl_2$) (12.6 mg, 0.10 mmol), 2-methyl-2-phenylpropanenitrile **9** (73 mg, 0.5 mmol), urea (90 mg 1.5 mmol), and DMSO (2 mL). The resulting solution was stirred at 130 °C under O_2 for 12 hours. The resulting solution was detected GC-MS. No reaction occurred and **9** were recovered.

4. Spectroscopic data

3a







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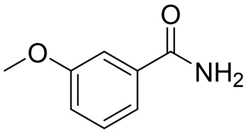
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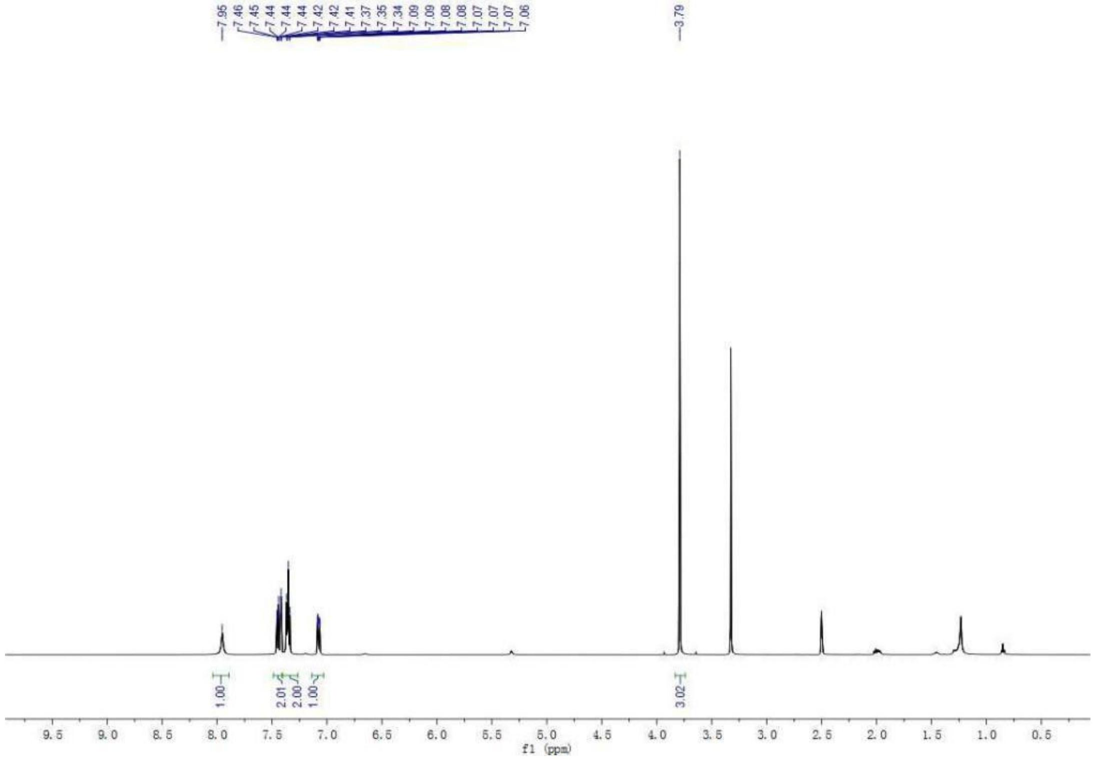
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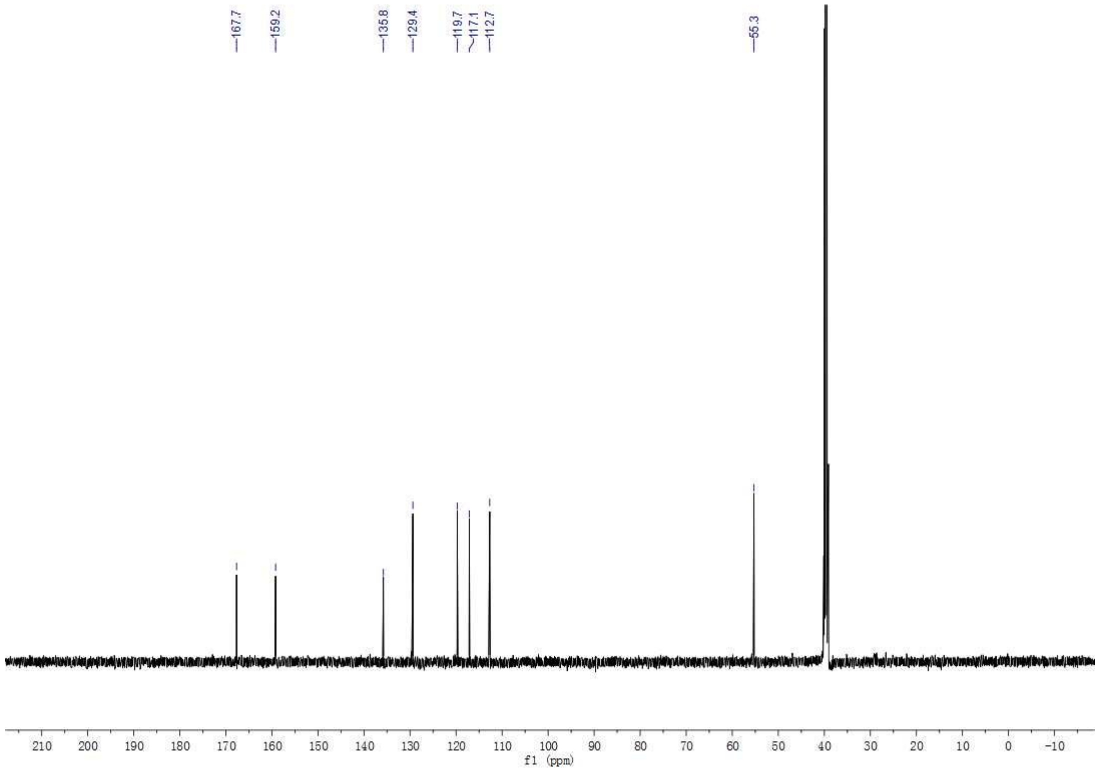
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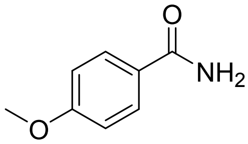
f1 (ppm)

3c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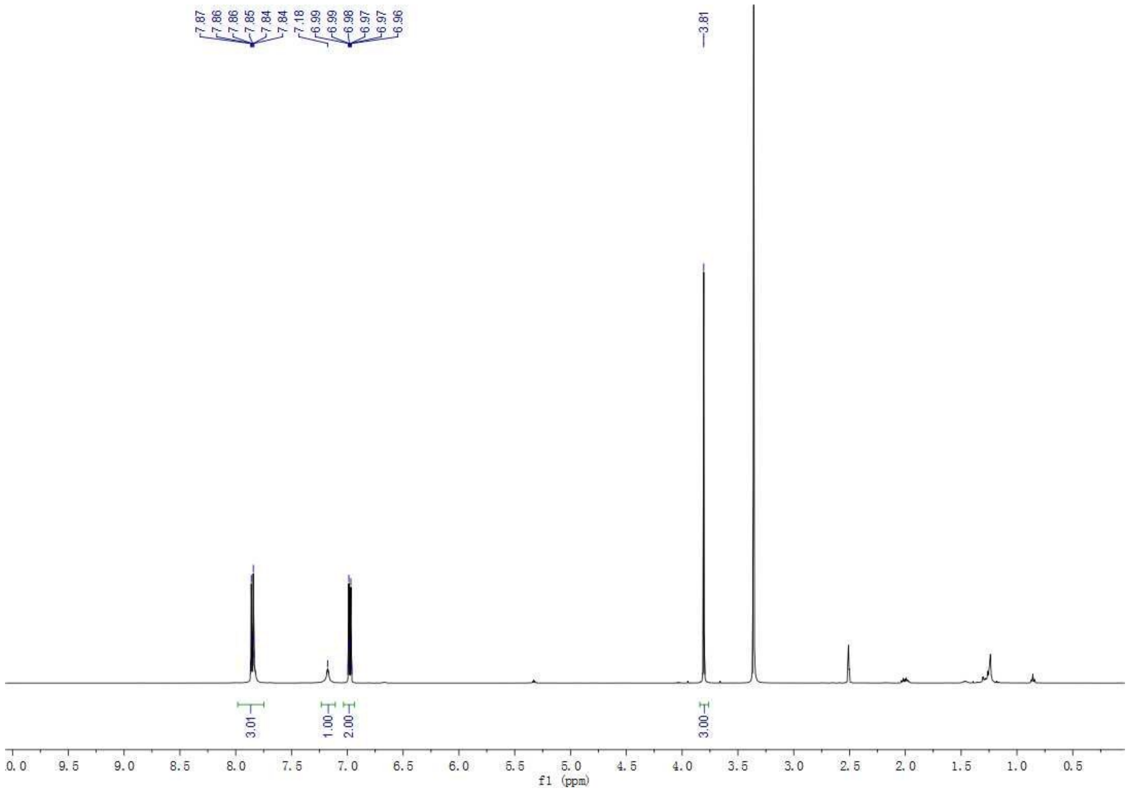
NH2
O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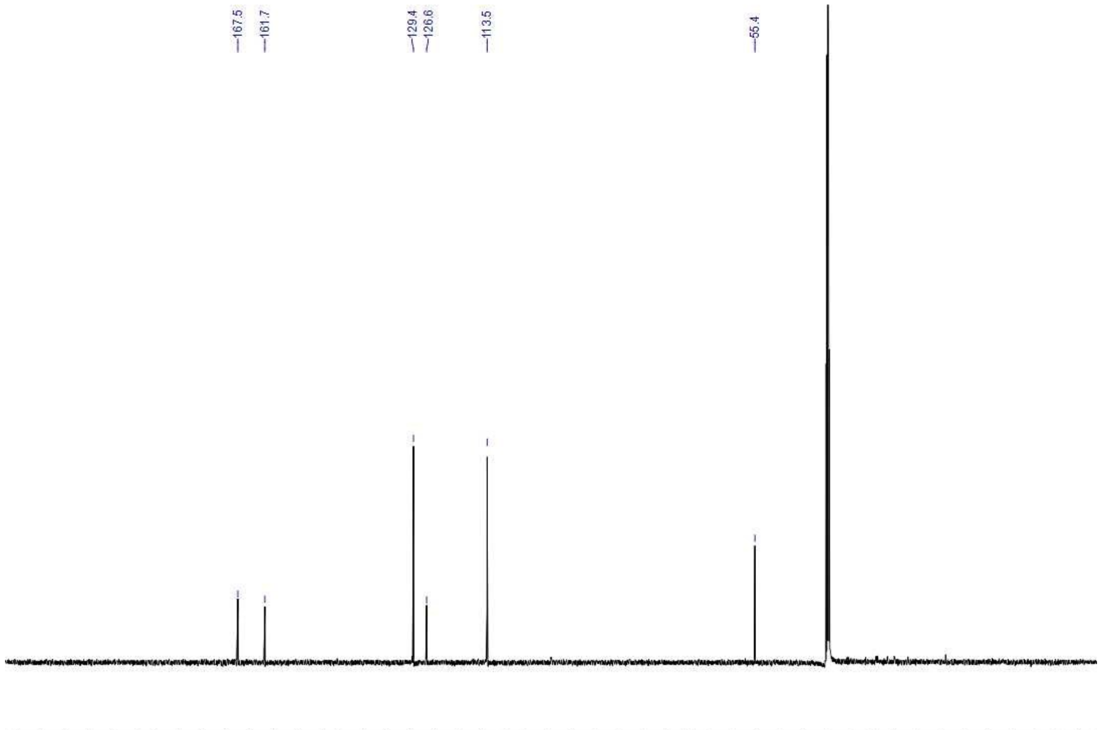
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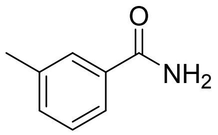
f1 (ppm)

3d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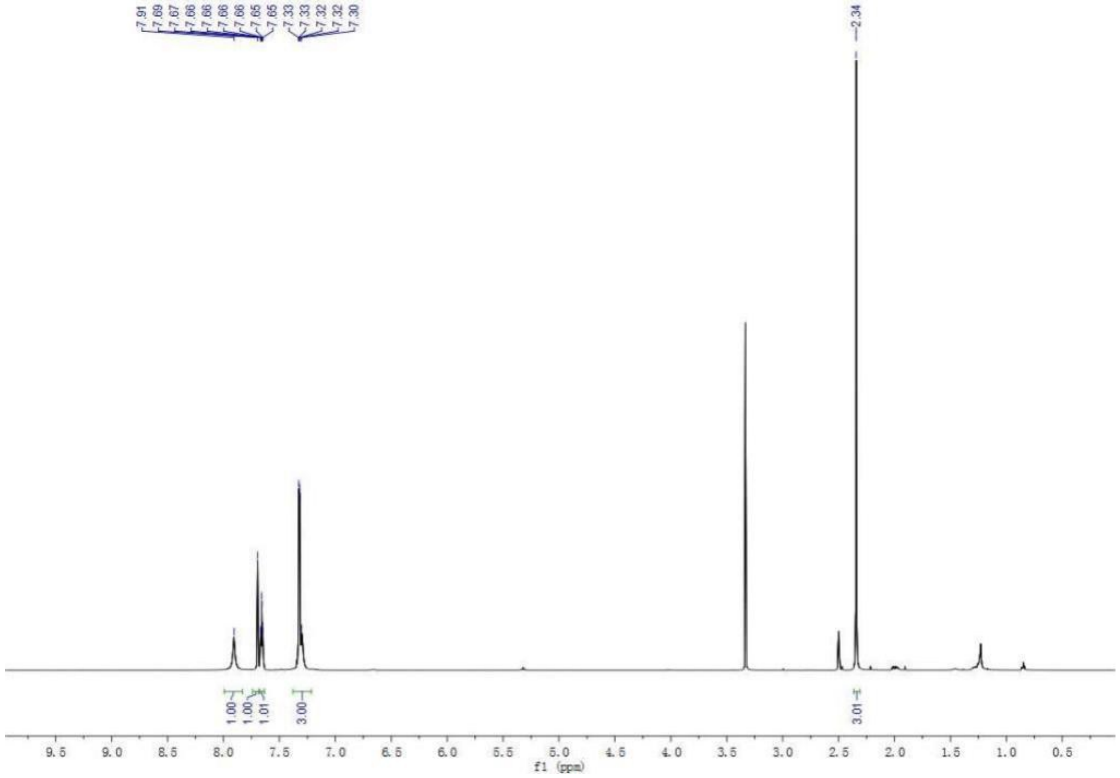
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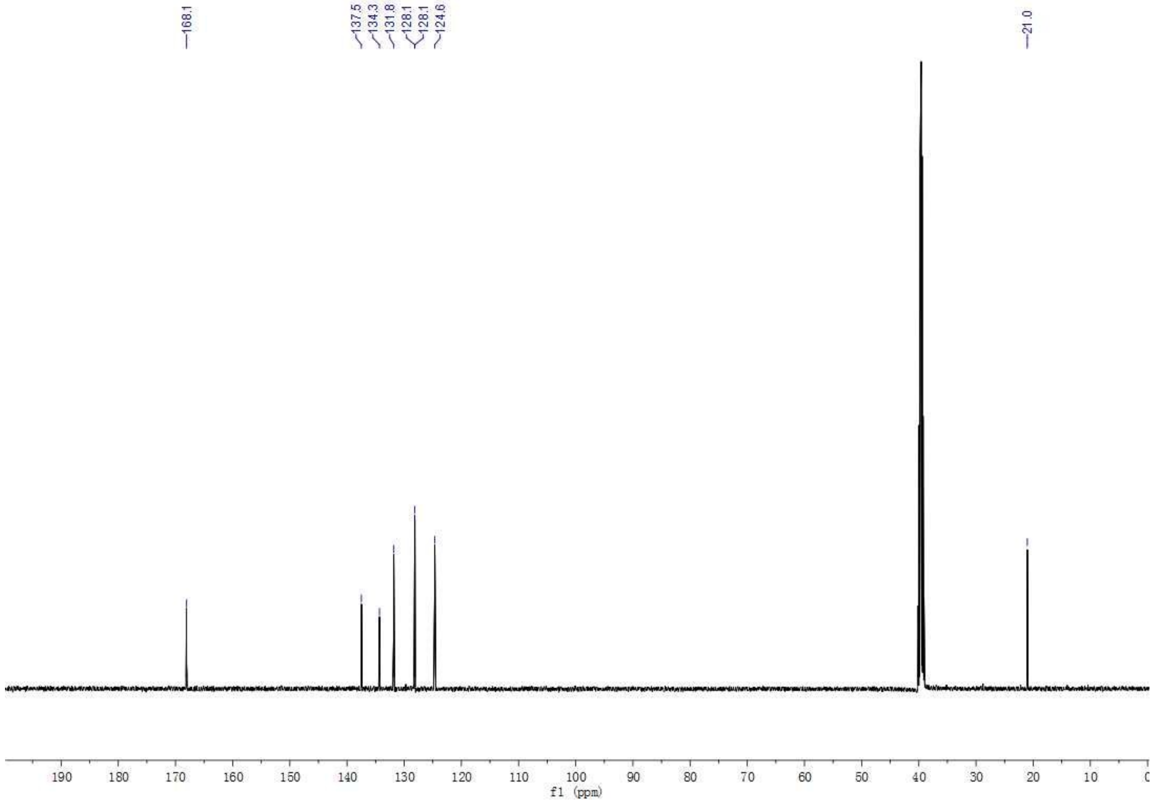
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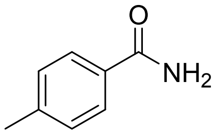
3e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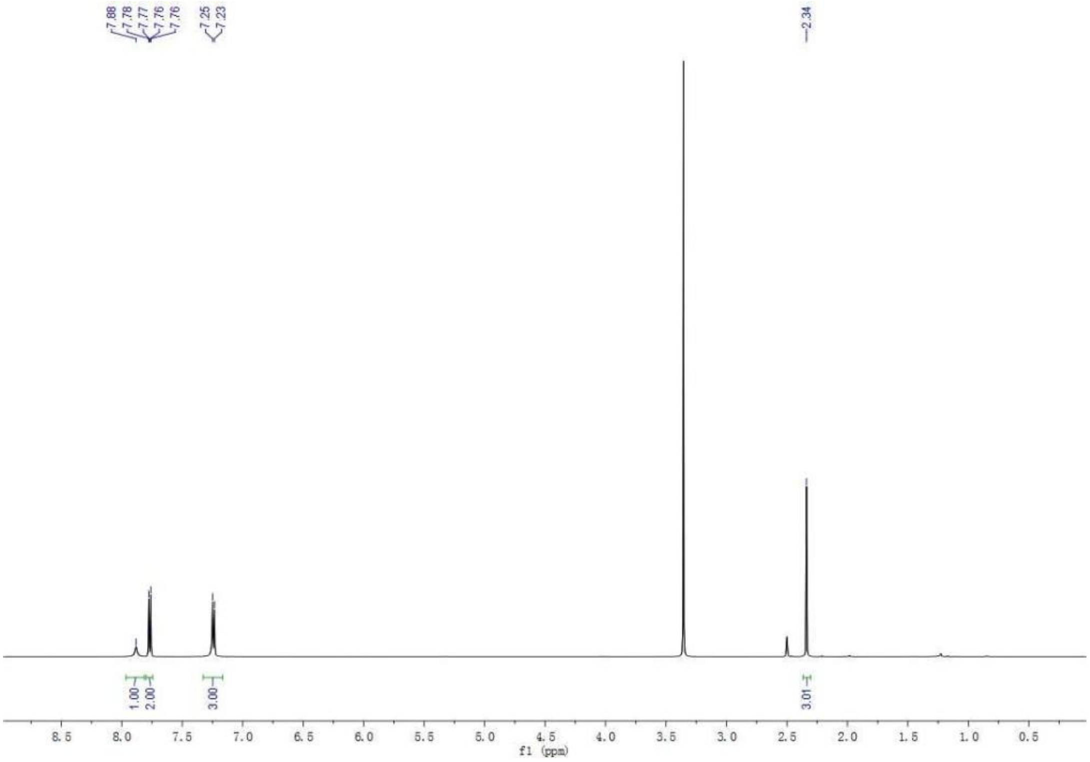
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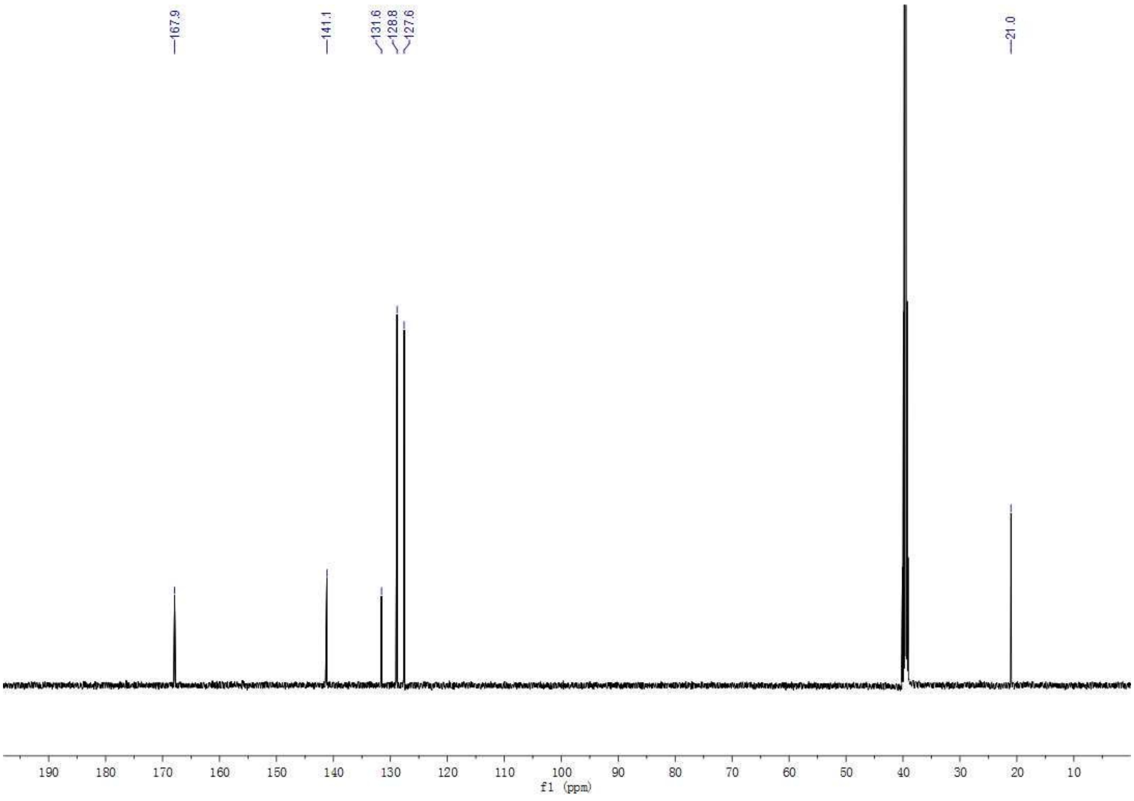
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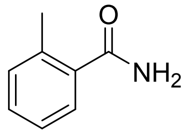
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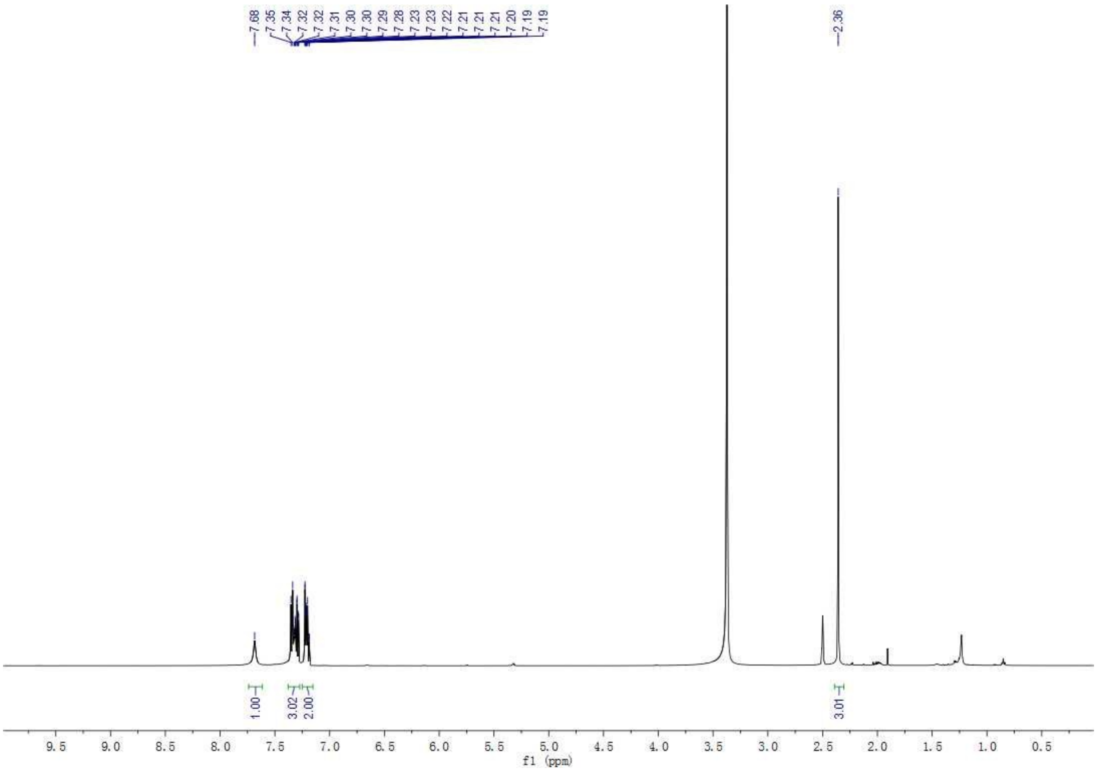
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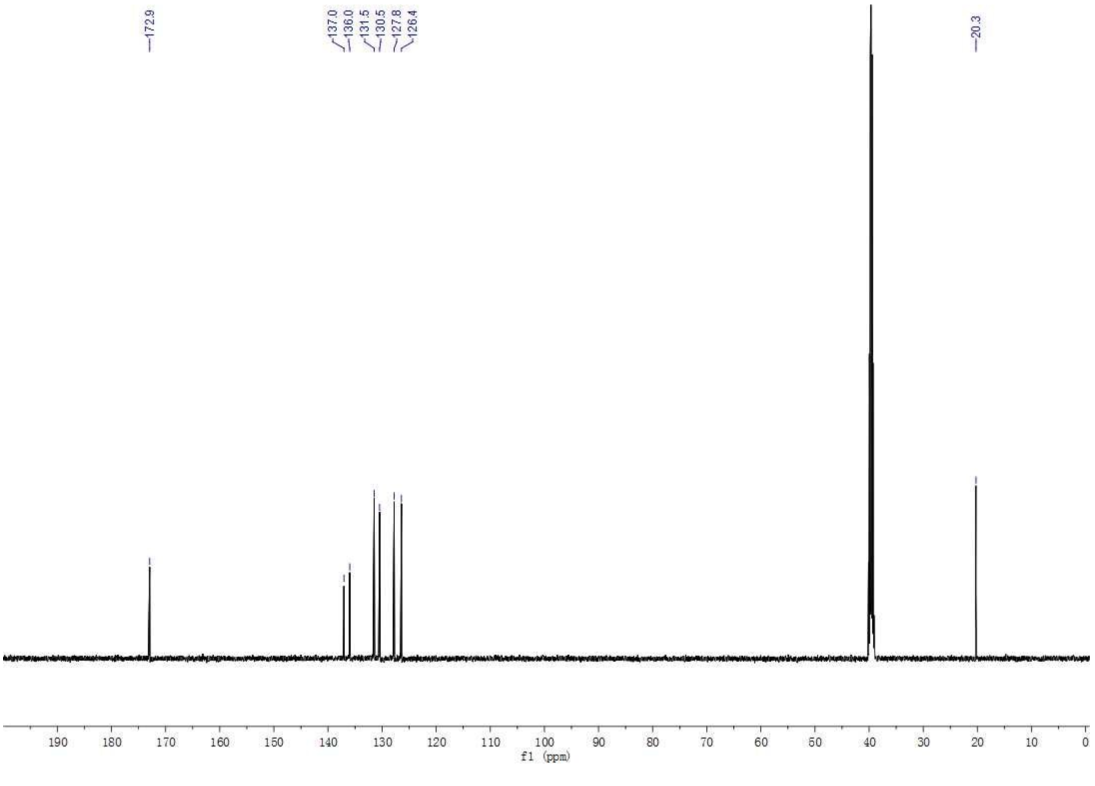
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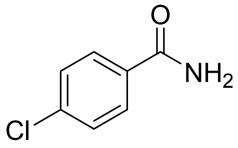
3g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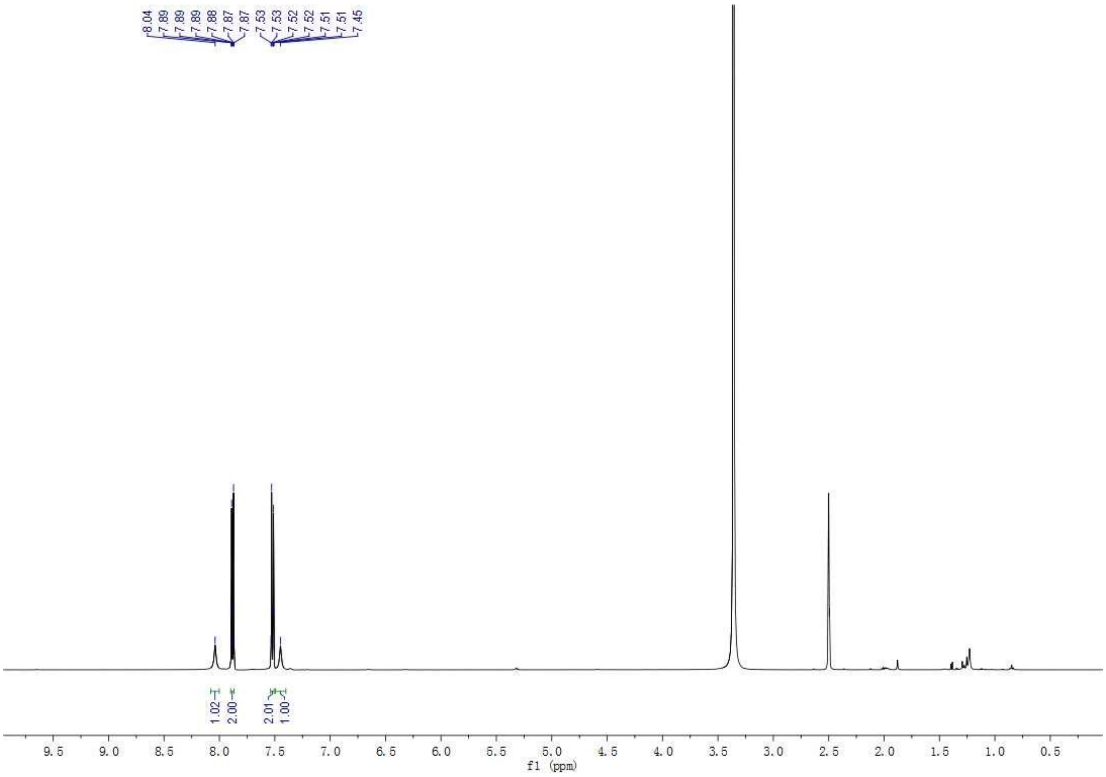
NH$_2$
Cl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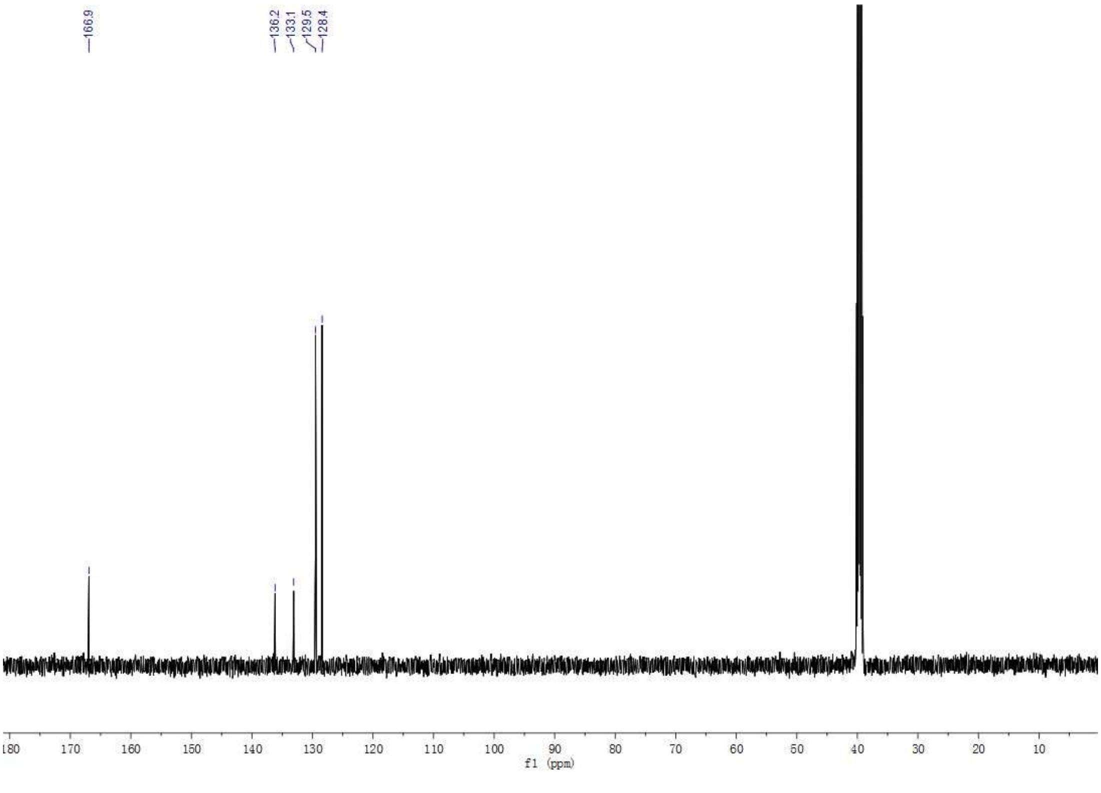
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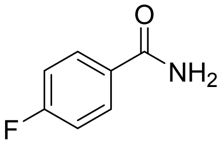
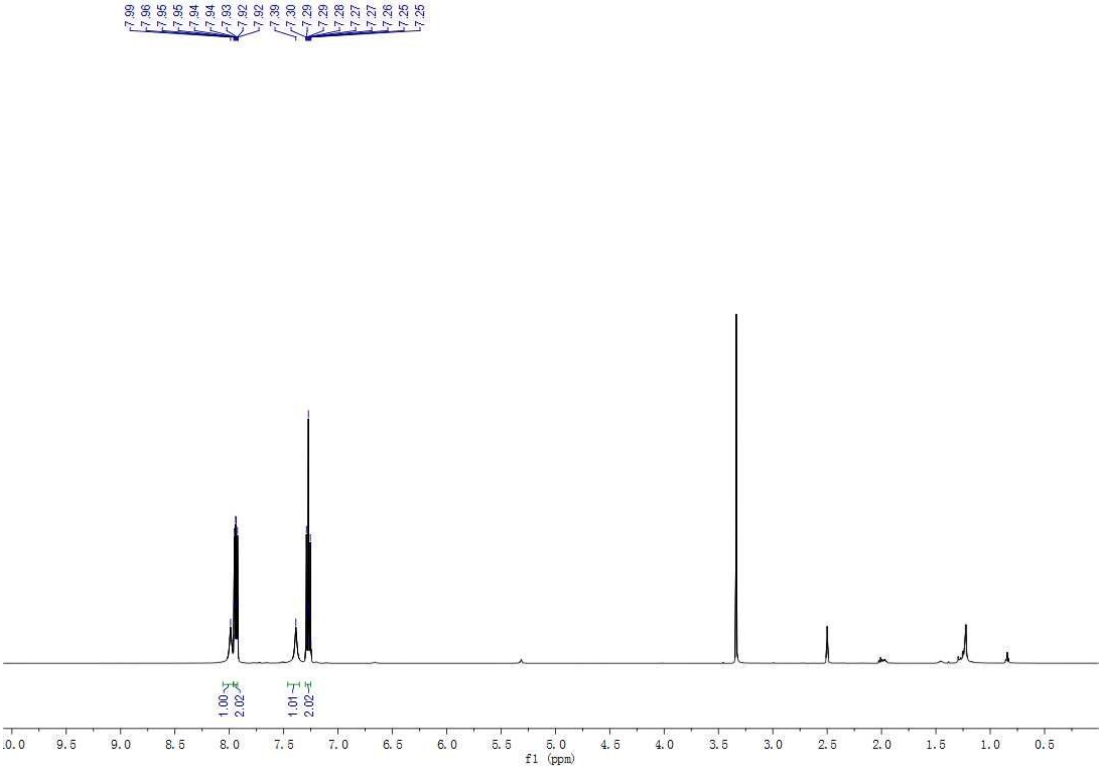
f1 (ppm)

3h


O
NH2
F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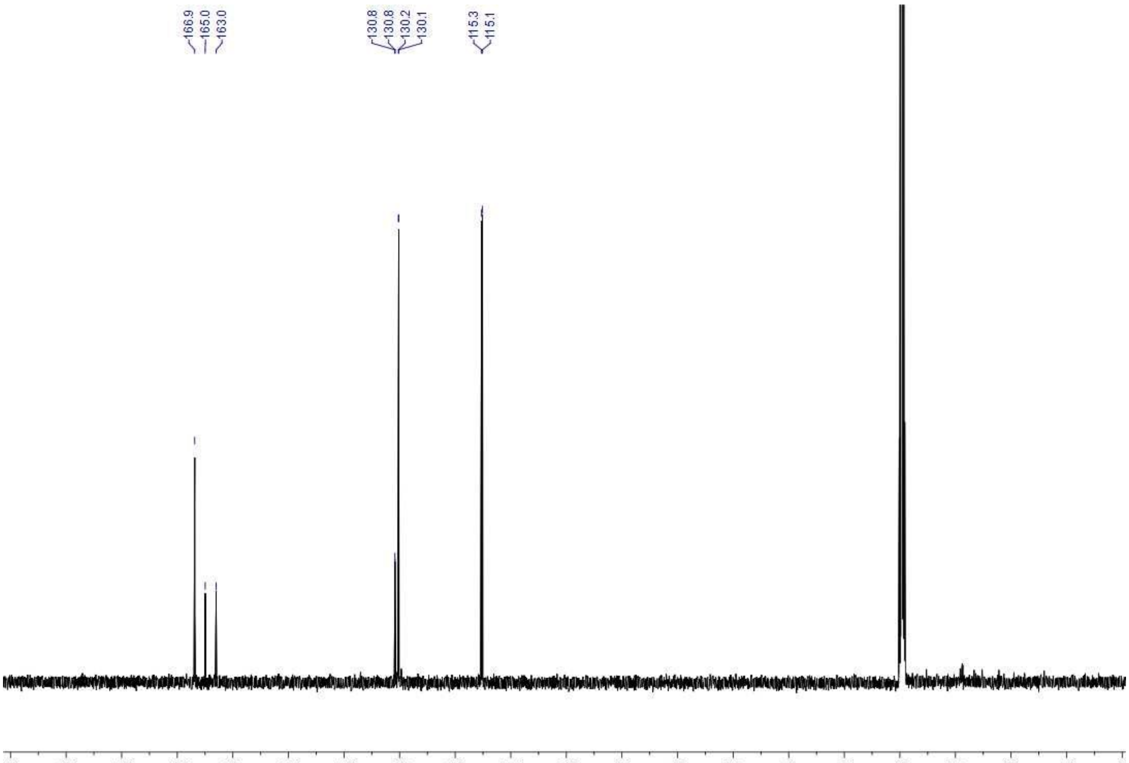
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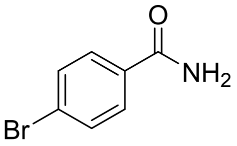
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NH2
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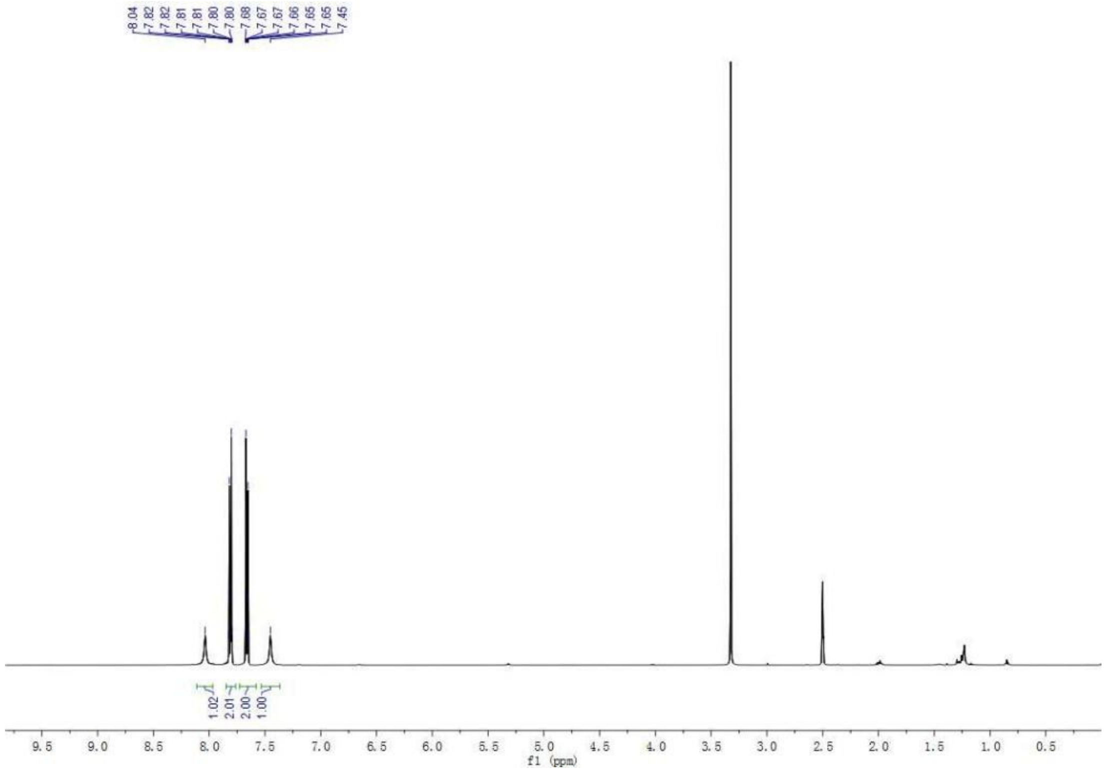
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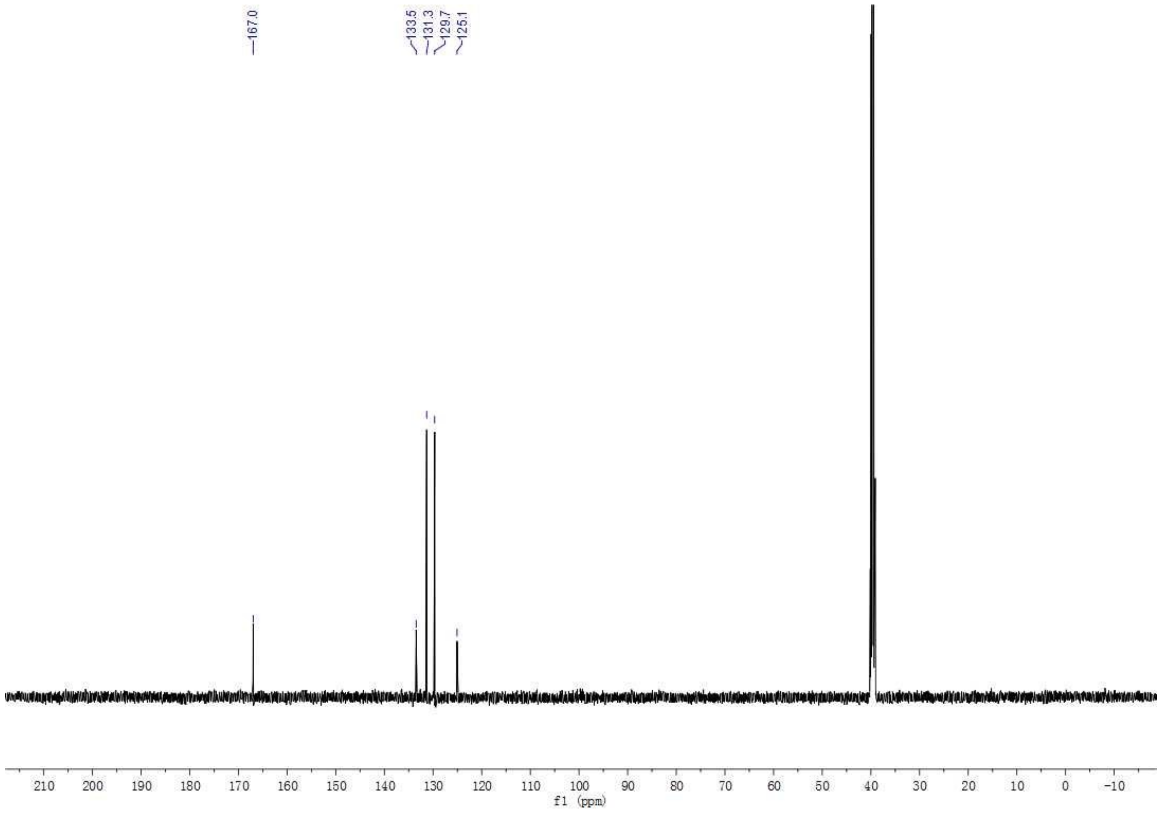
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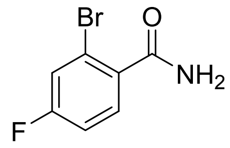
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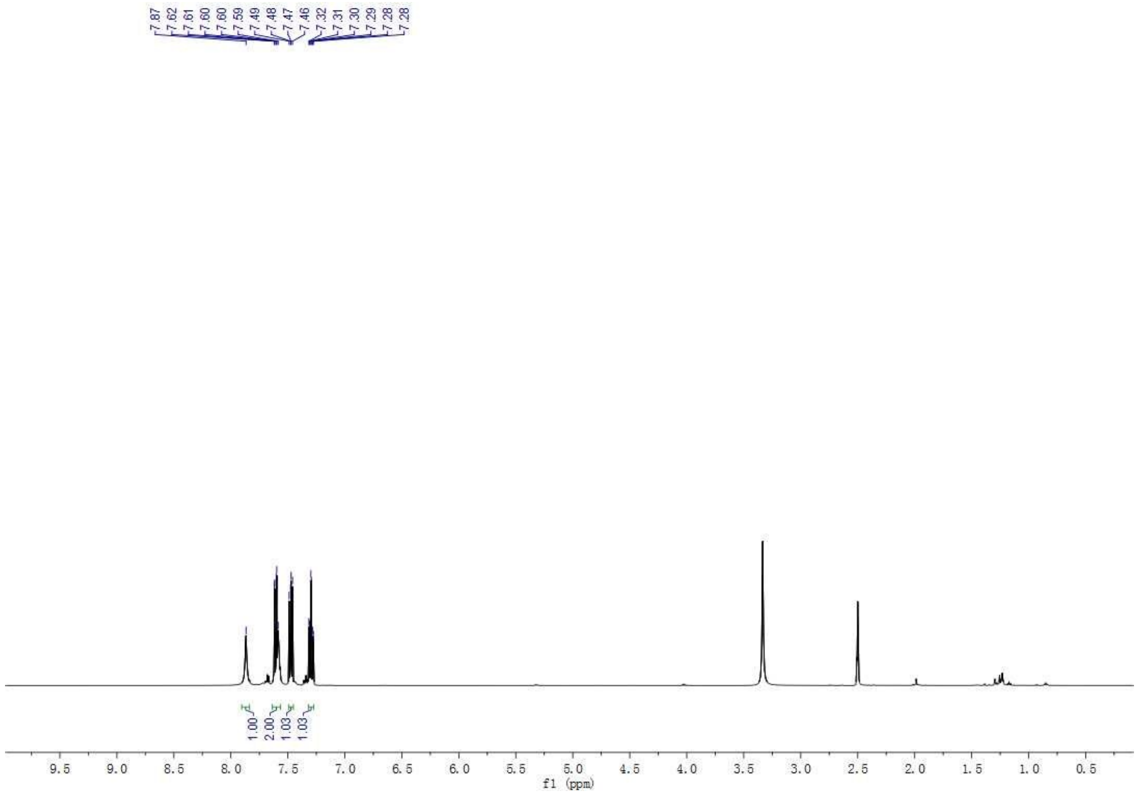
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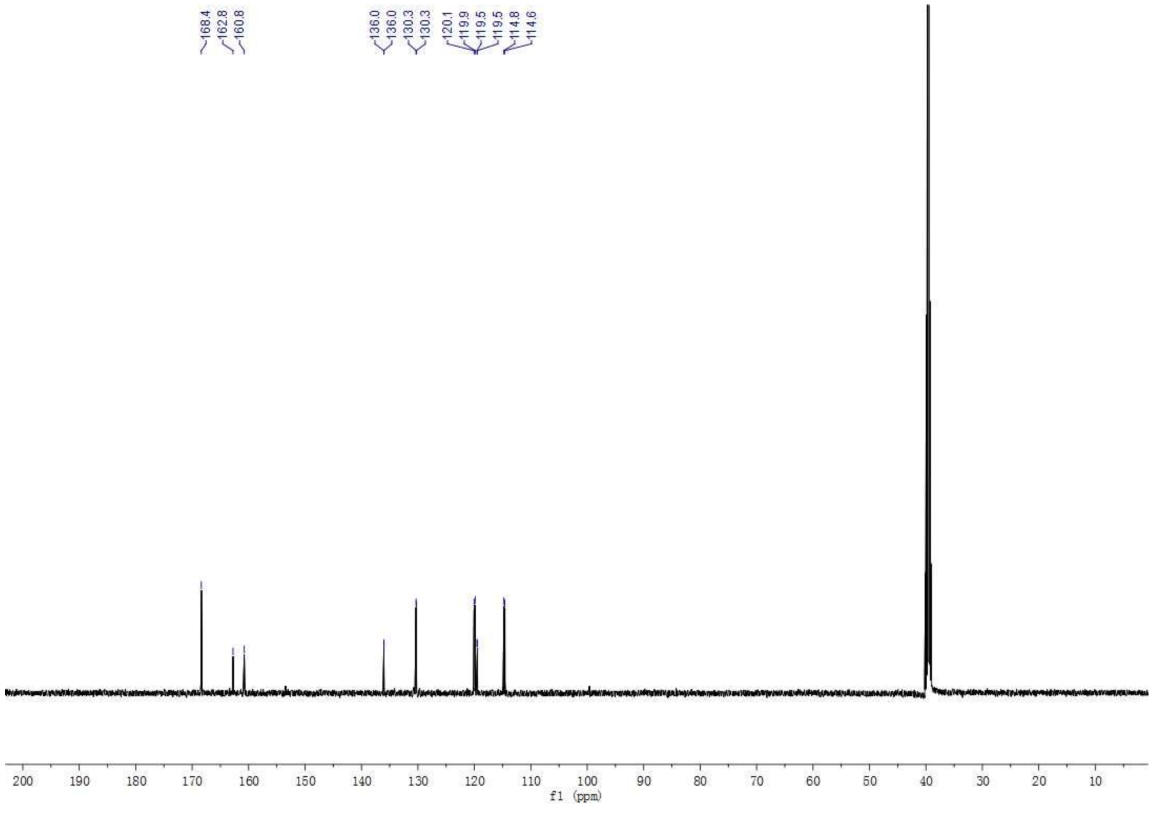
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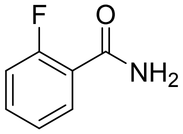
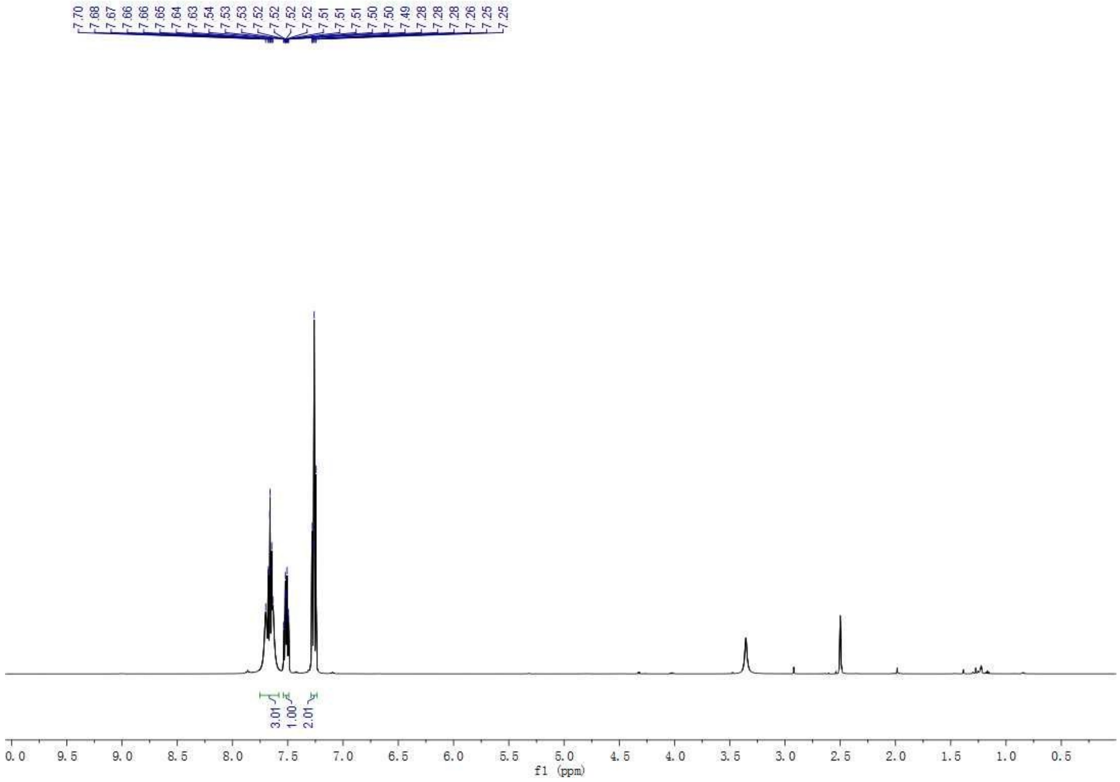
f1 (ppm)

3k


F
O
NH2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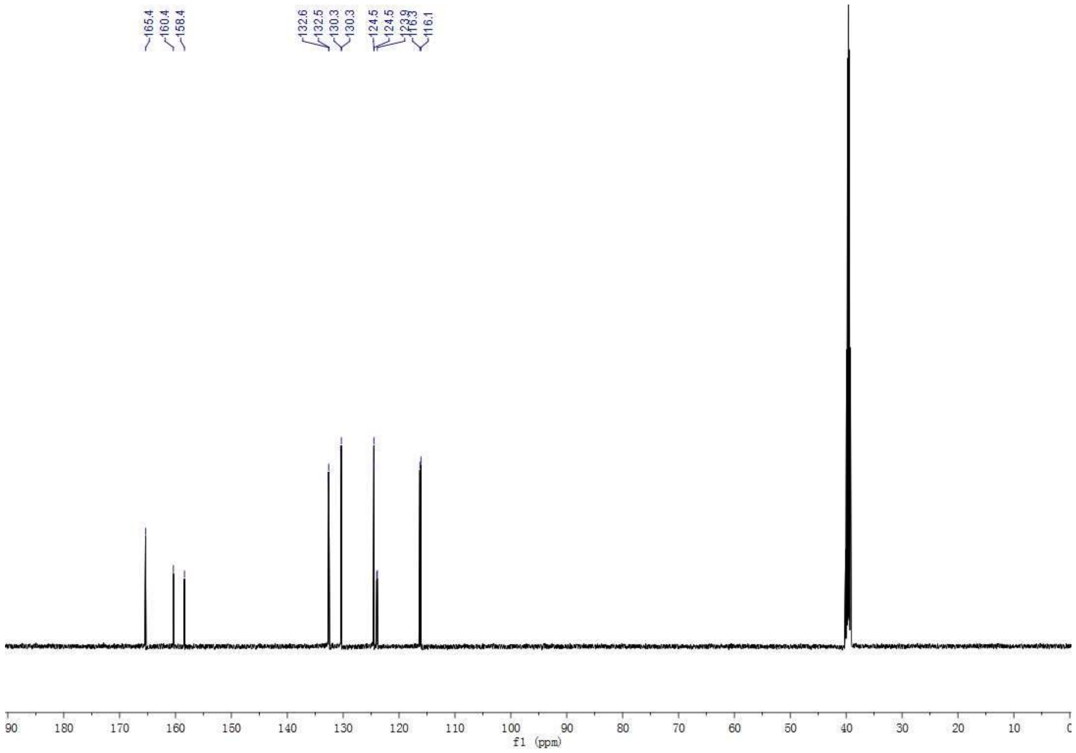
f1 (ppm)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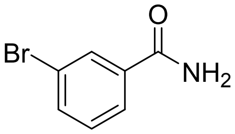
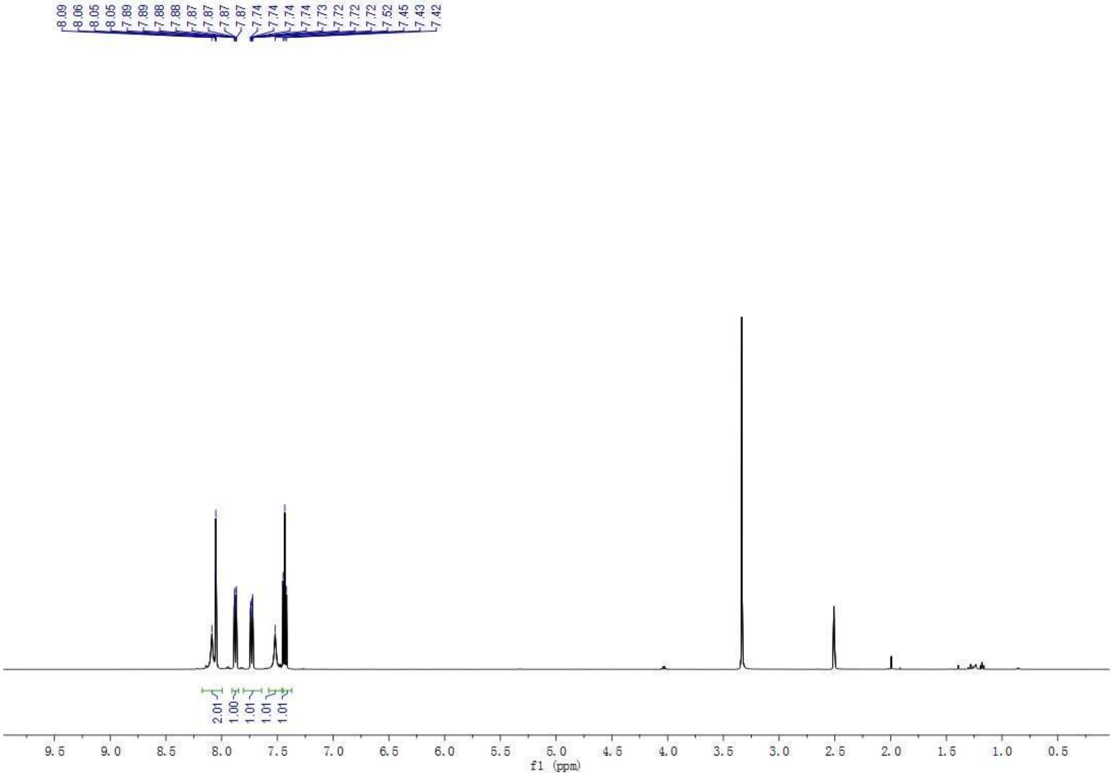
f1 (ppm)

3l



Br
O
NH2



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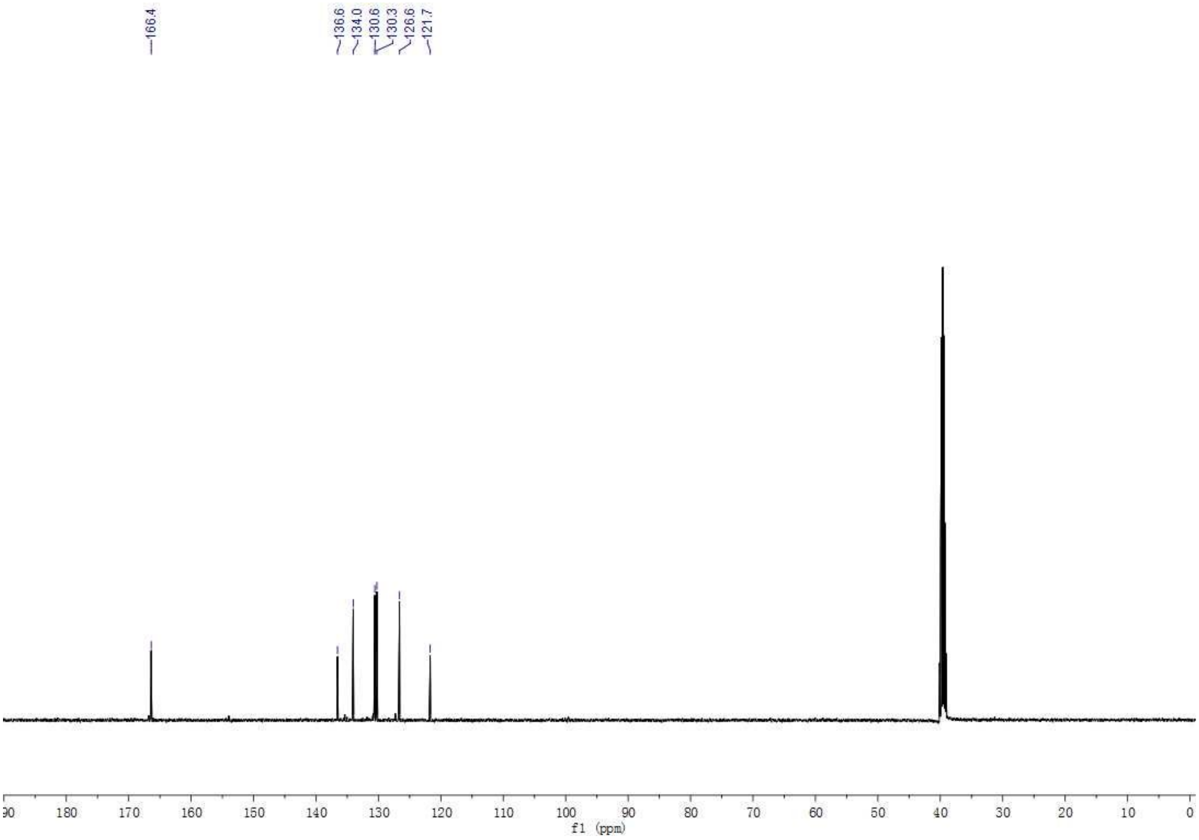

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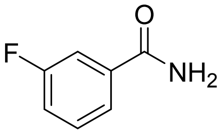
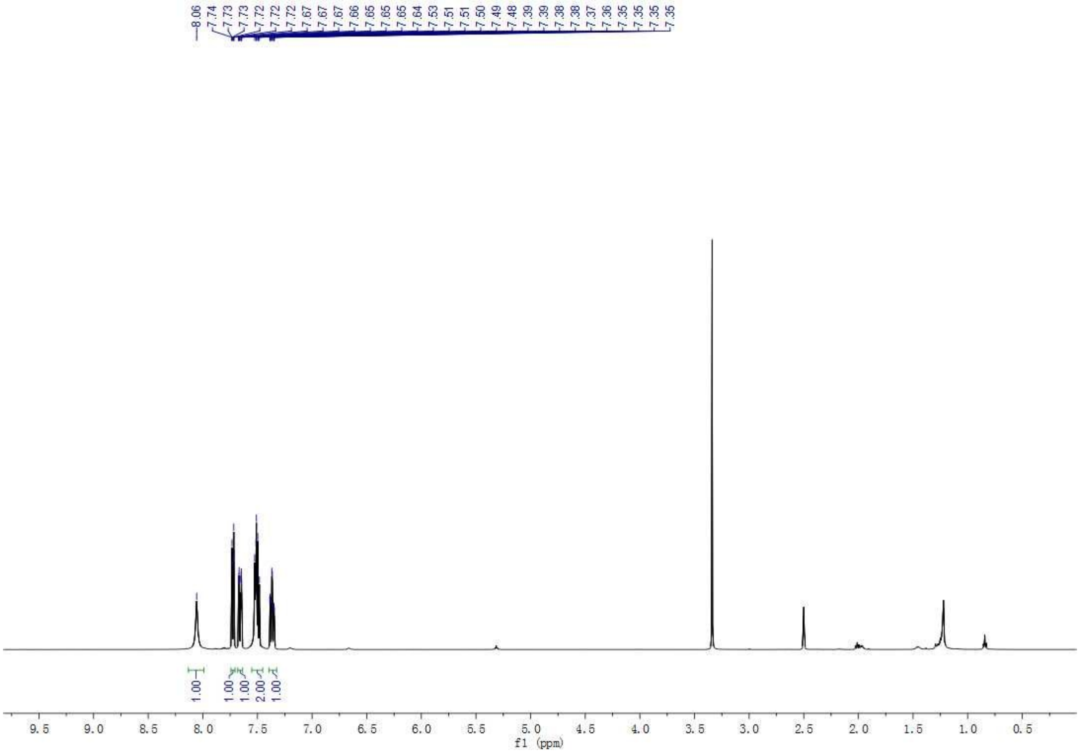
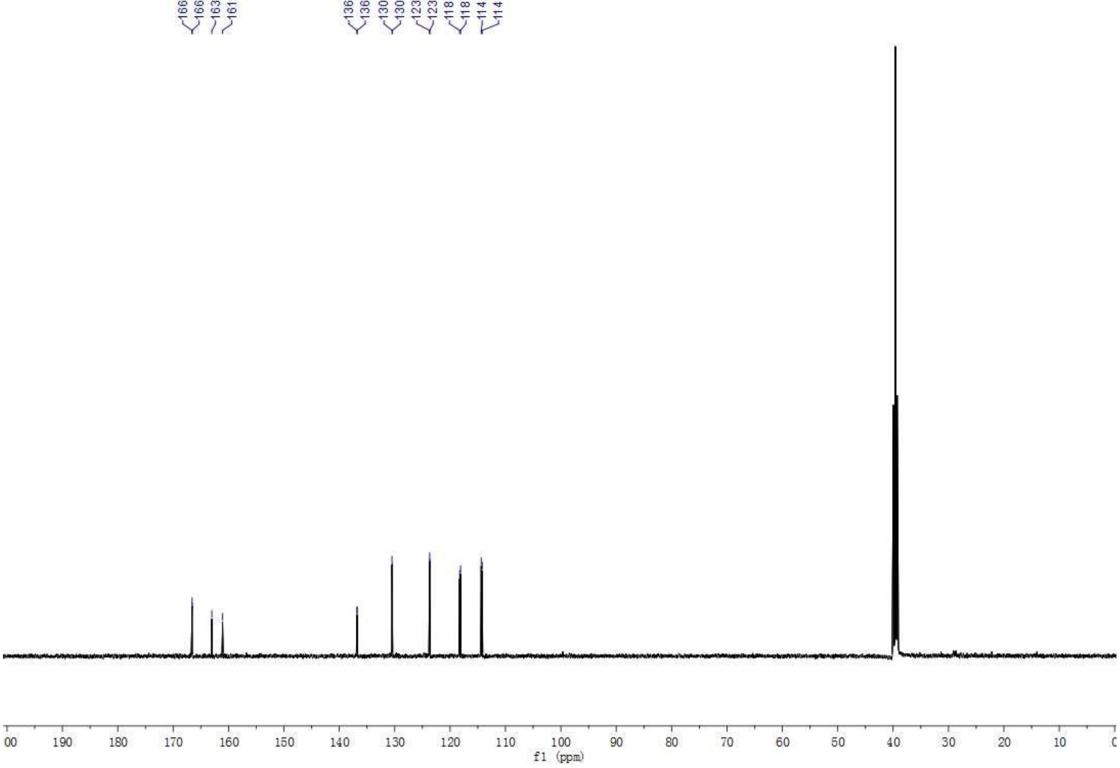
f1 (ppm)

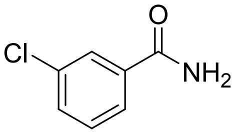
3m


F
O
NH2

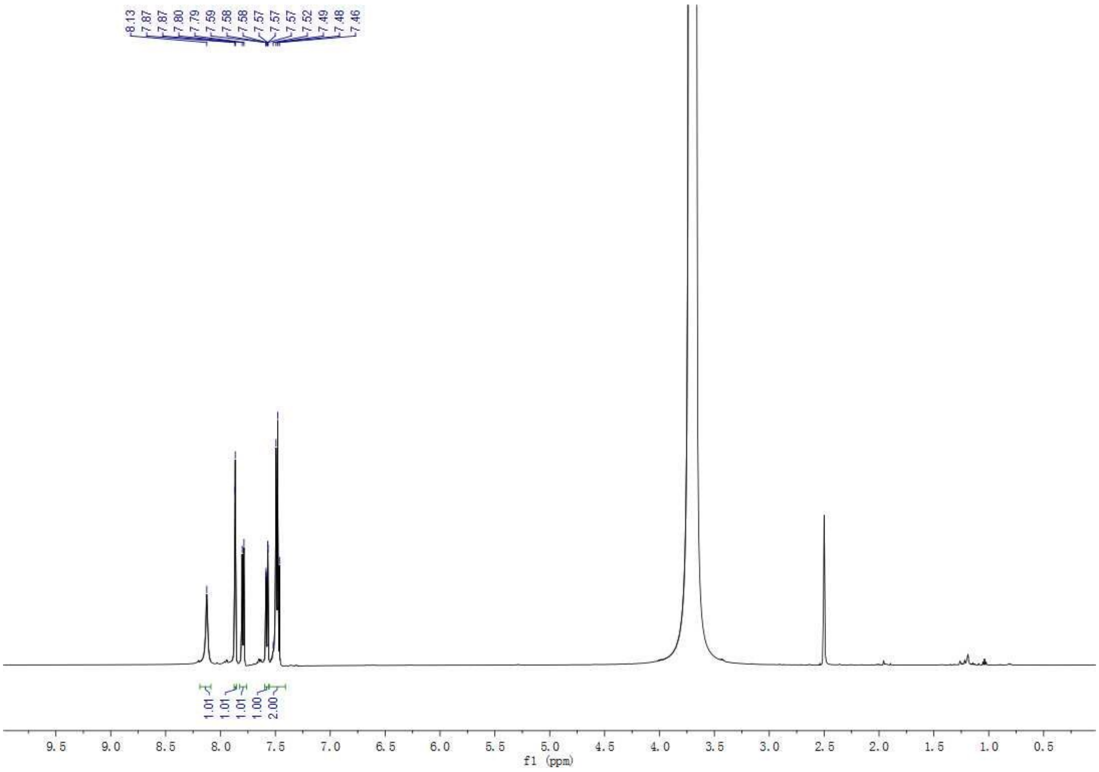

8.06
7.74
7.73
7.73
7.72
7.72
7.72
7.67
7.67
7.67
7.66
7.65
7.65
7.65
7.64
7.53
7.51
7.51
7.50
7.49
7.48
7.39
7.39
7.38
7.38
7.37
7.36
7.35
7.35
7.35
7.35
1.00
1.00
1.00
2.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


166.6
166.6
163.0
161.1
136.8
136.8
130.5
130.4
123.7
118.3
118.1
114.4
114.2
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

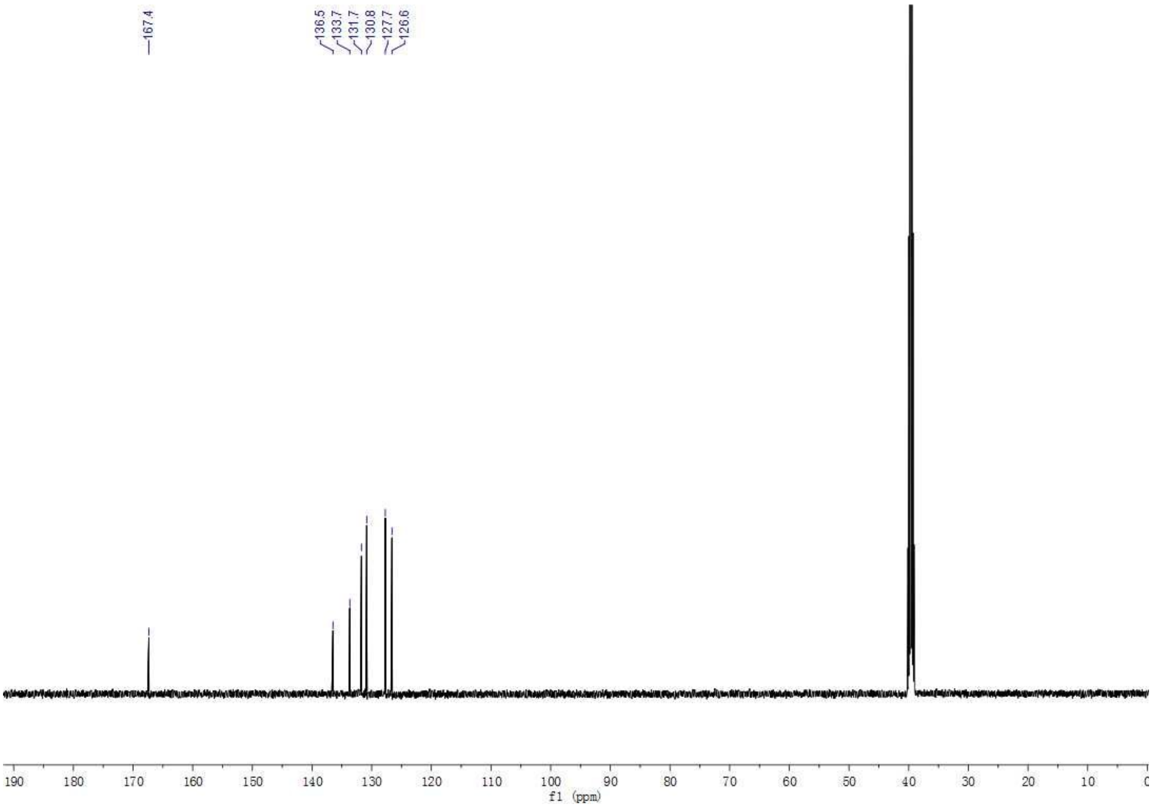
3n



O
Cl
NH$_2$

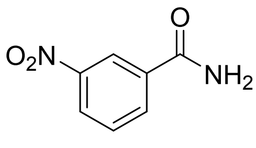


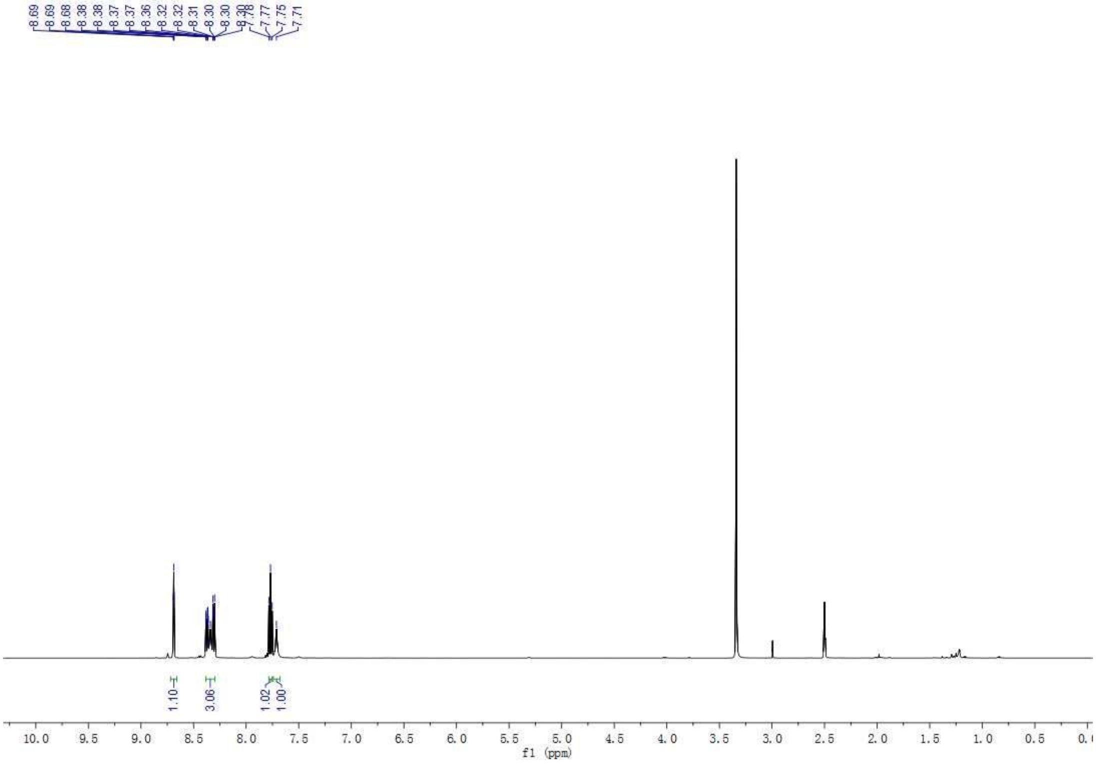
8.13
7.87
7.87
7.80
7.79
7.59
7.58
7.58
7.57
7.57
7.57
7.52
7.49
7.48
7.46
1.01
1.01
1.01
1.00
2.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

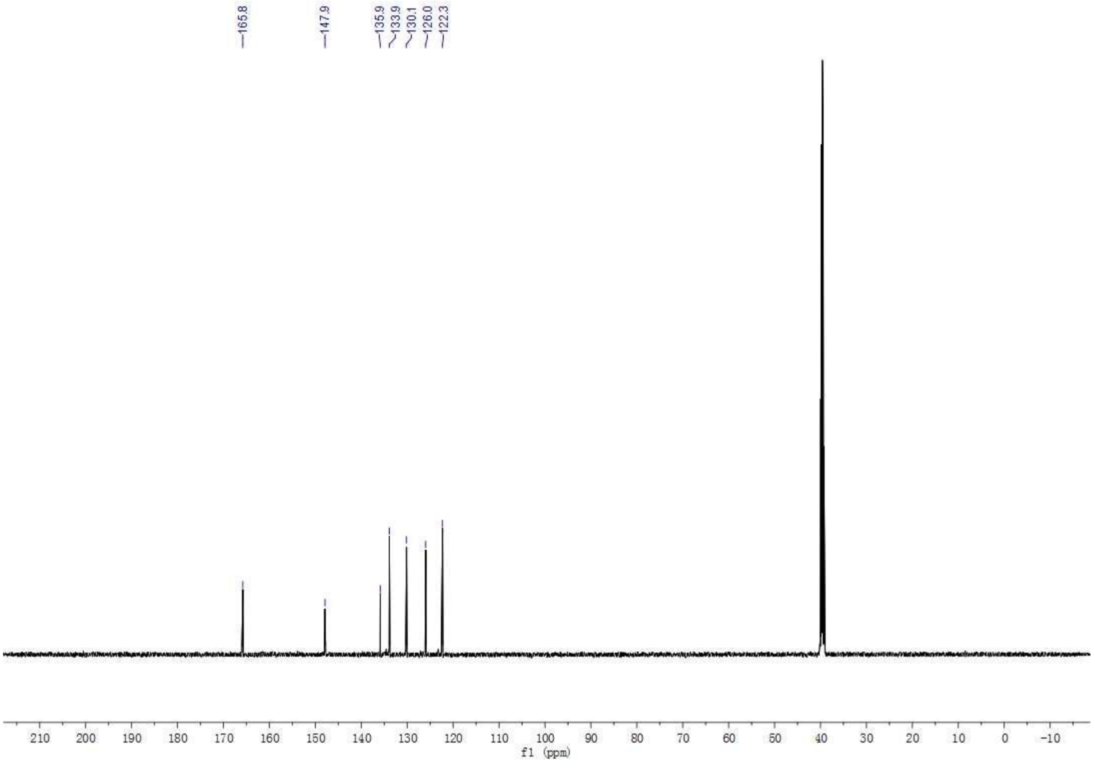


167.4
136.5
133.7
131.7
130.8
127.7
126.6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

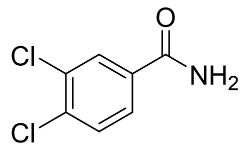
3o

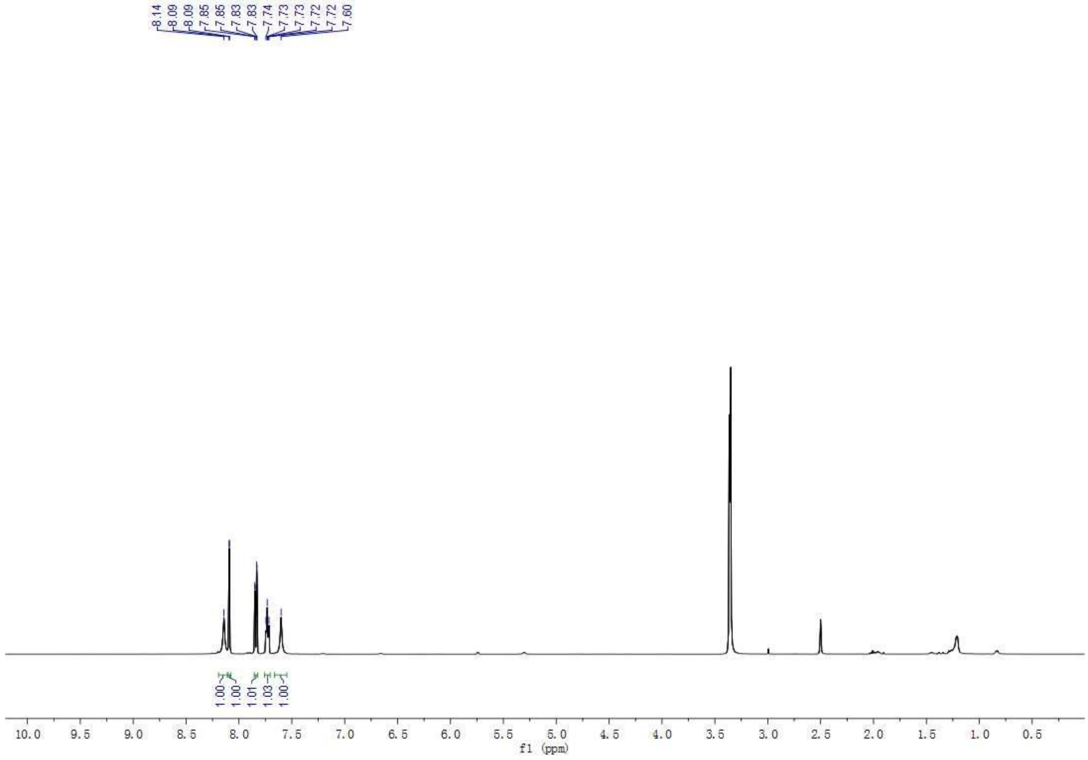

O
O2N
NH2

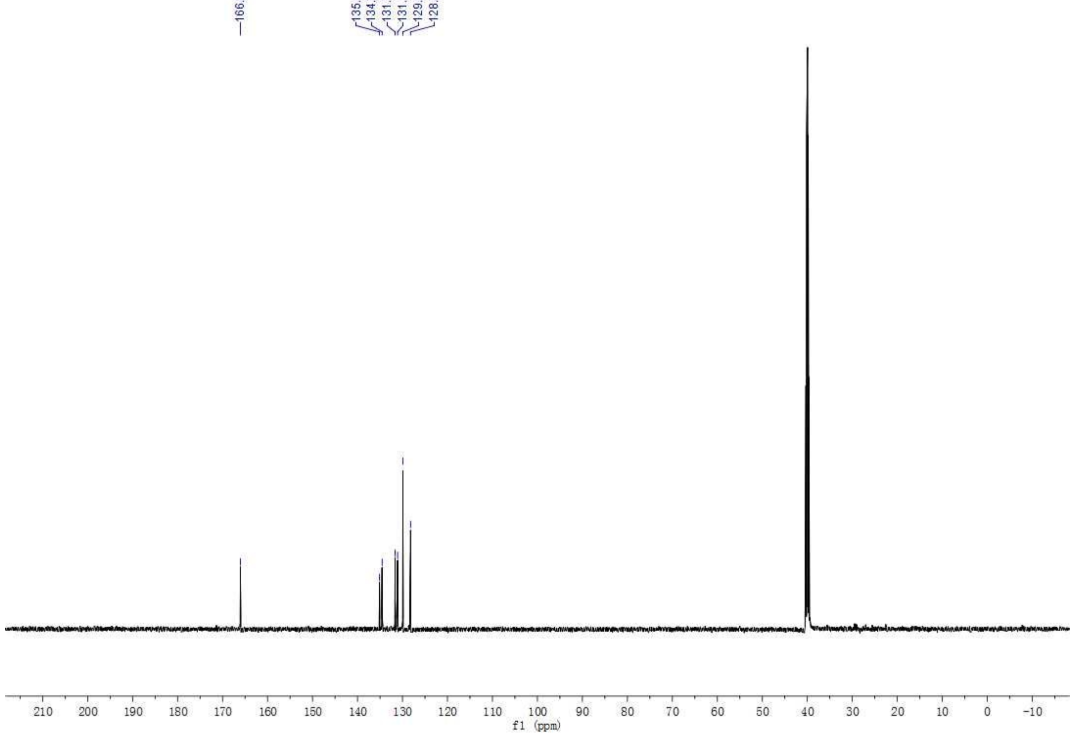

8.69
8.69
8.68
8.38
8.38
8.37
8.37
8.36
8.32
8.32
8.31
8.30
8.30
8.30
7.78
7.77
7.75
7.71
1.10
3.06
1.02
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


165.8
147.9
135.9
133.9
130.1
126.0
122.3
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)

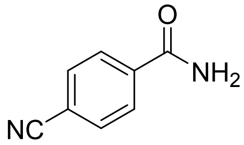
3p

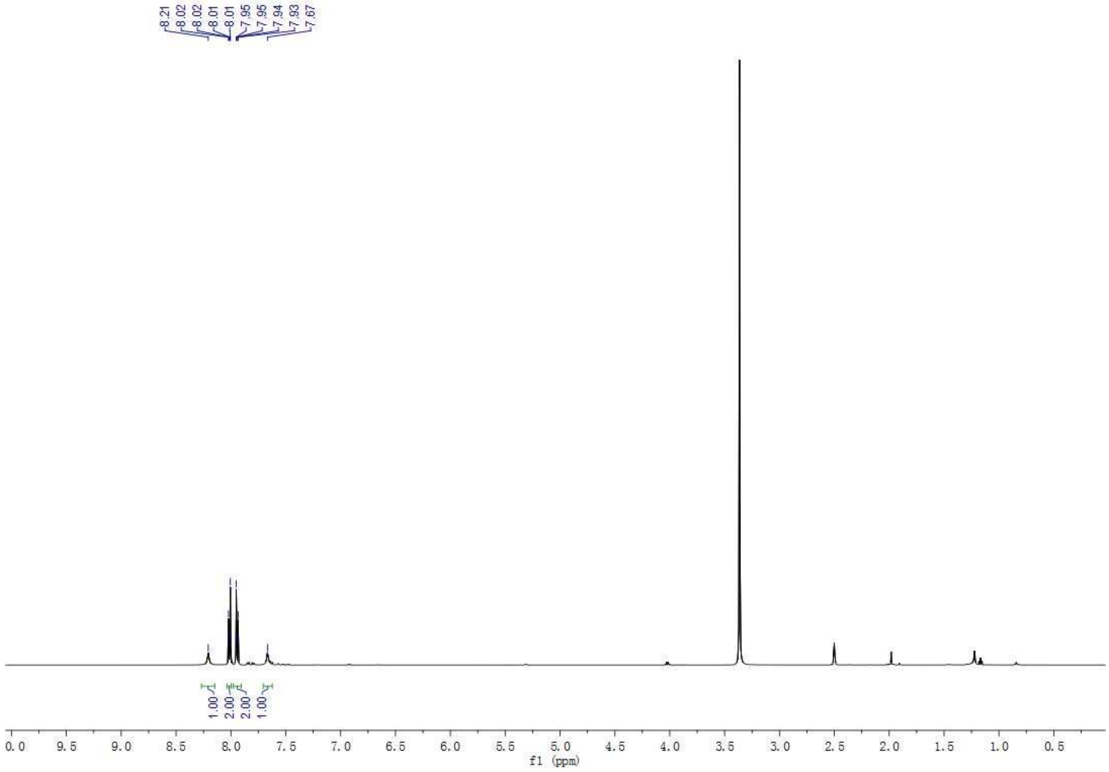

Cl
Cl
O
NH2

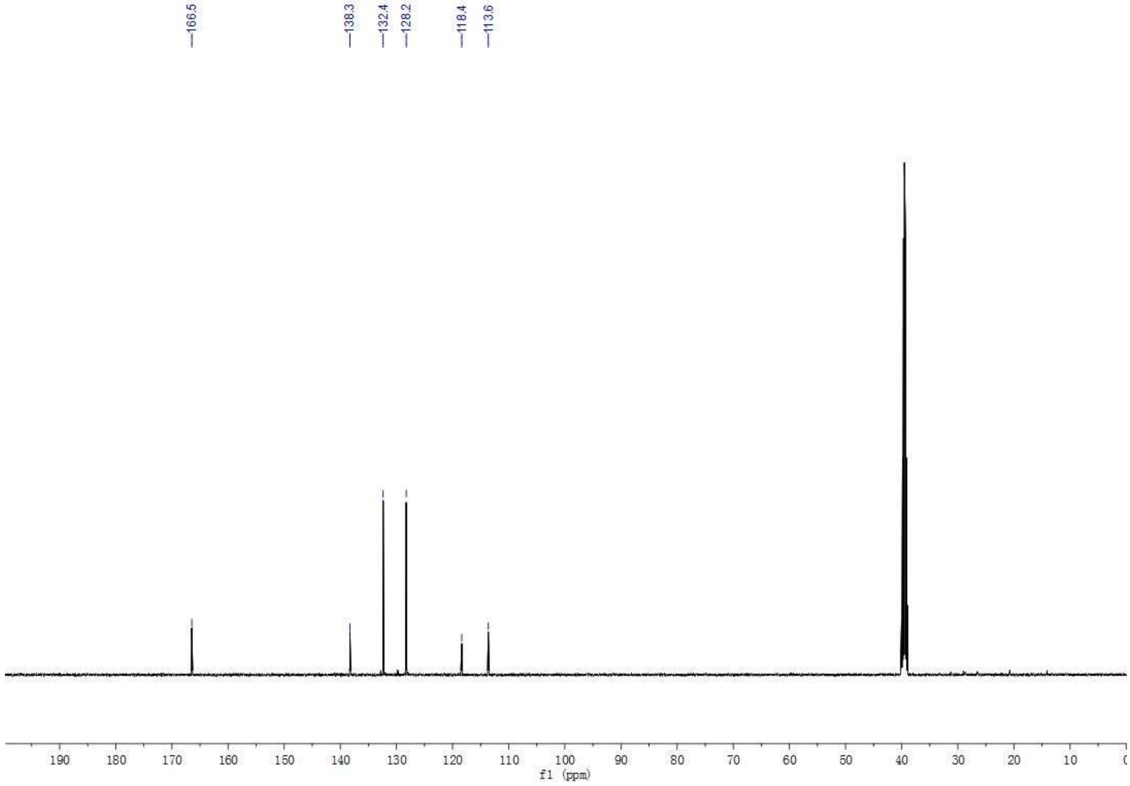

8.14
8.09
8.09
7.85
7.83
7.83
7.74
7.73
7.73
7.72
7.72
7.60
1.00
1.00
1.01
1.03
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


166.0
135.1
134.5
131.7
131.1
129.9
128.2
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)

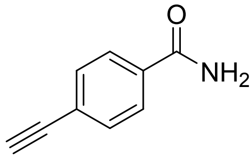
3q

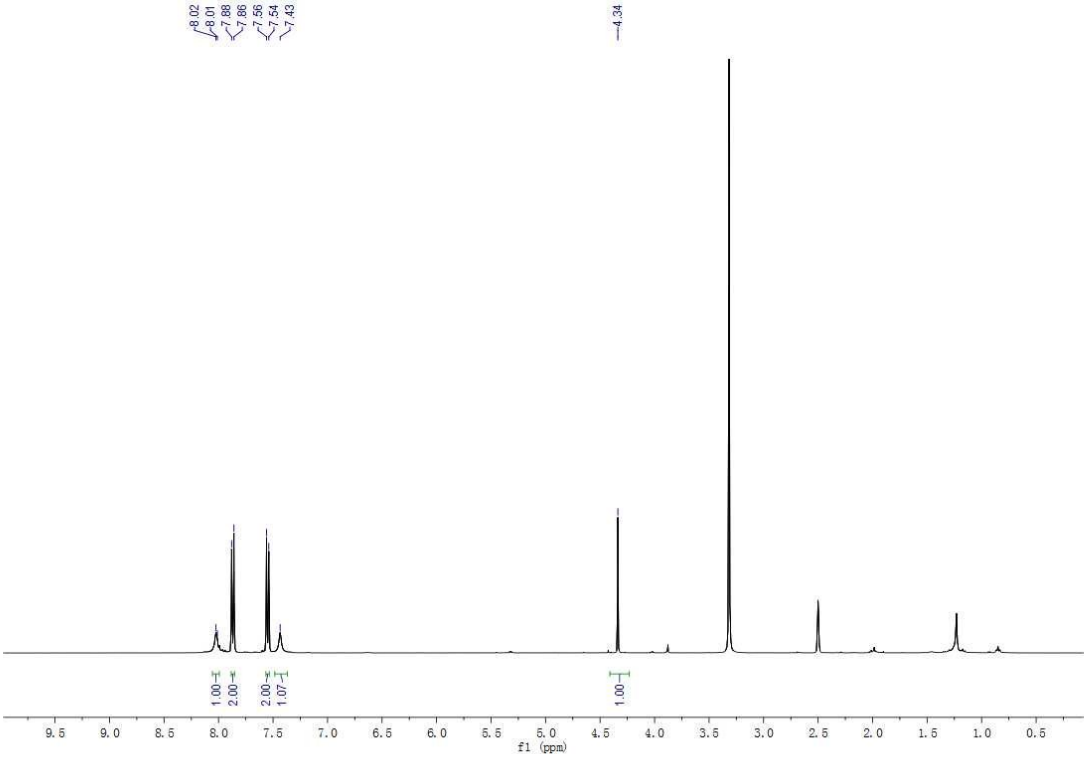

O
NH2
NC

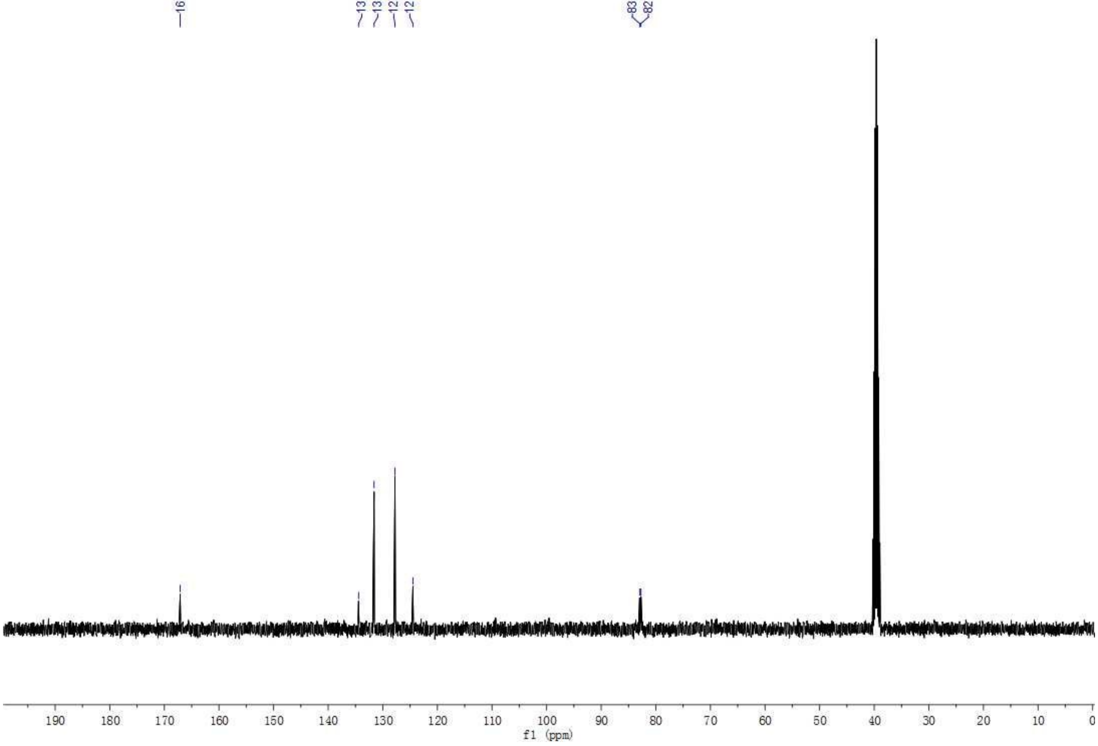

8.21
8.02
8.02
8.01
8.01
7.95
7.95
7.94
7.93
7.67
1.00
2.00
2.00
1.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


166.5
138.3
132.4
128.2
118.4
113.6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

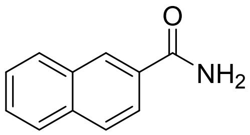
3r

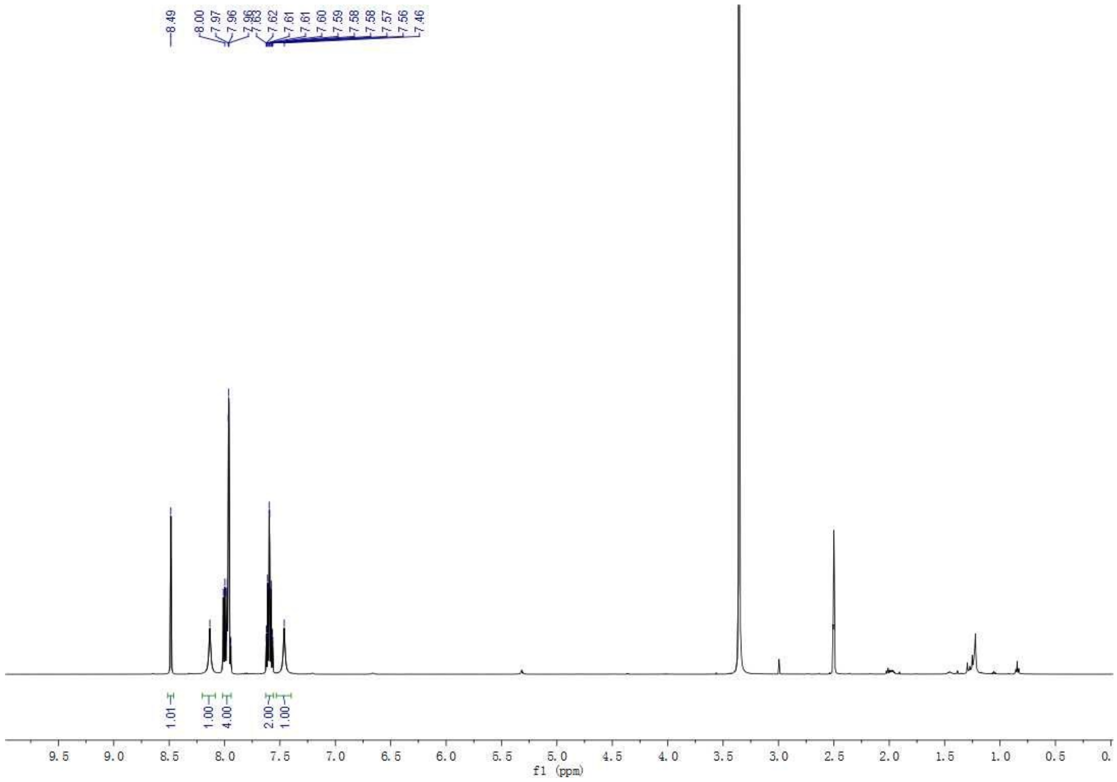

O
NH2

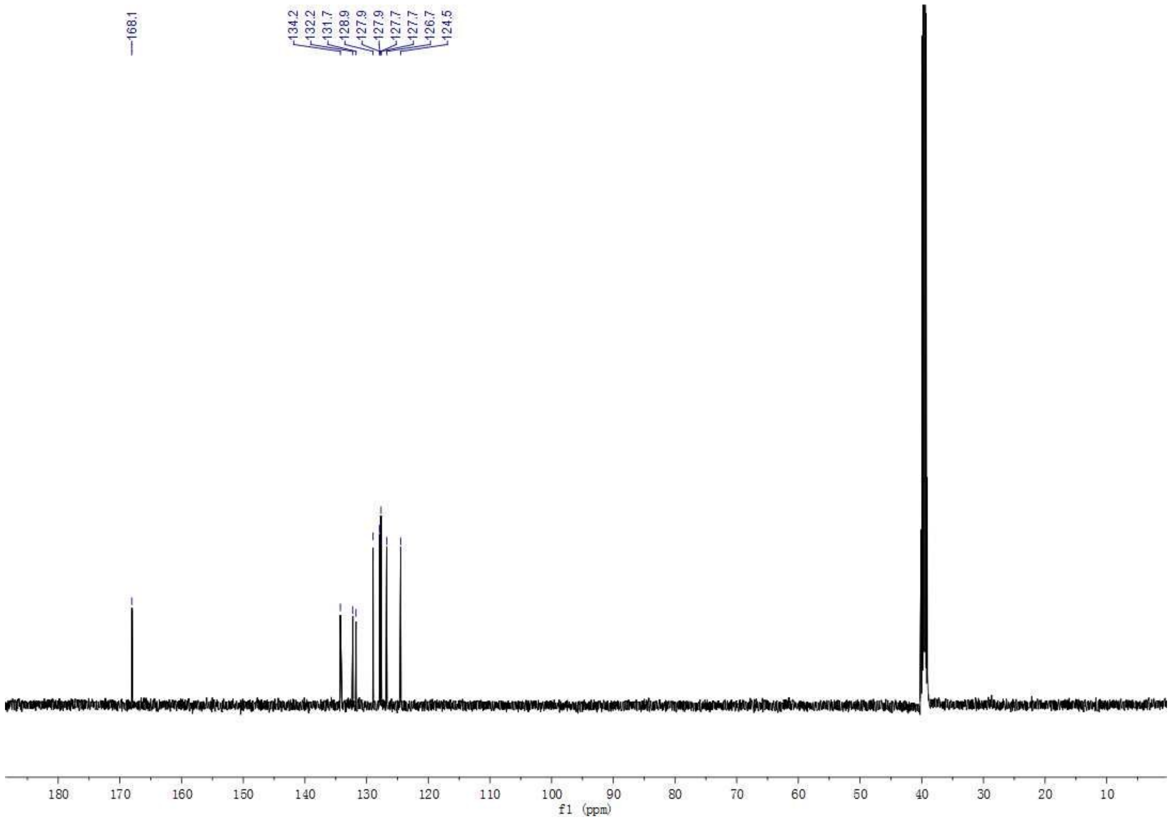

8.02
8.01
7.88
7.86
7.56
7.54
7.43
4.34
1.00
2.00
2.00
1.07
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


167.1
134.4
131.6
127.8
124.5
83.0
82.7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

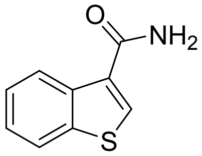
3s

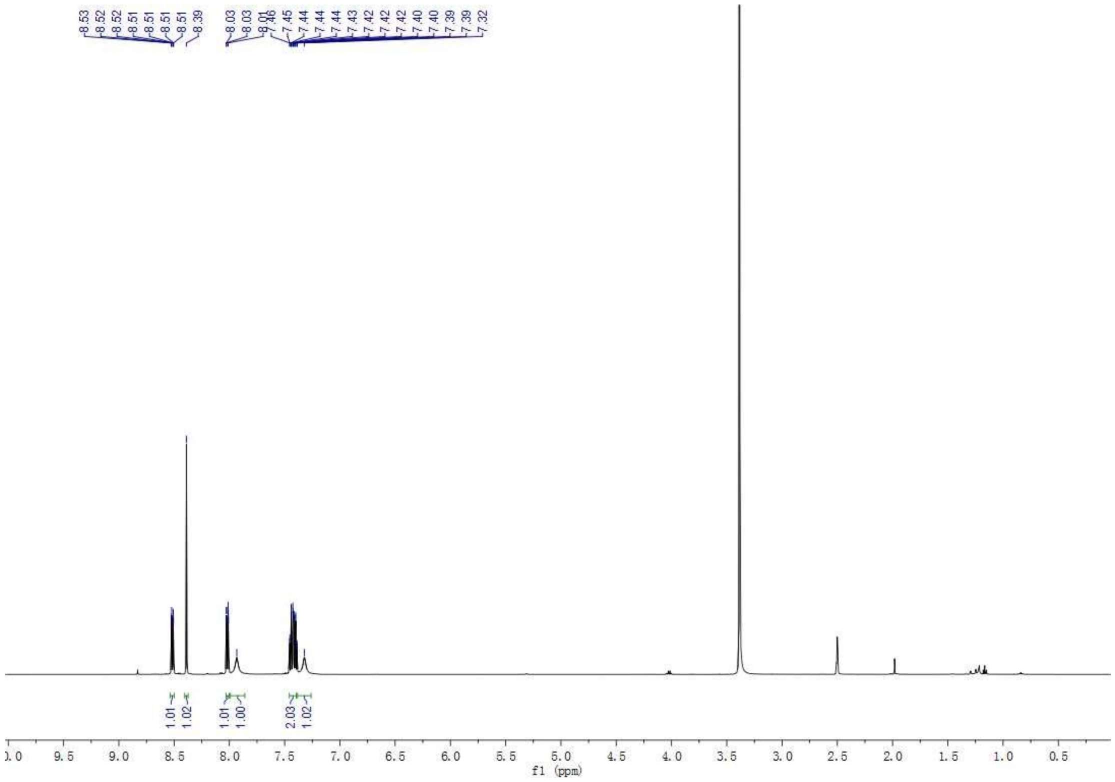

O
NH2

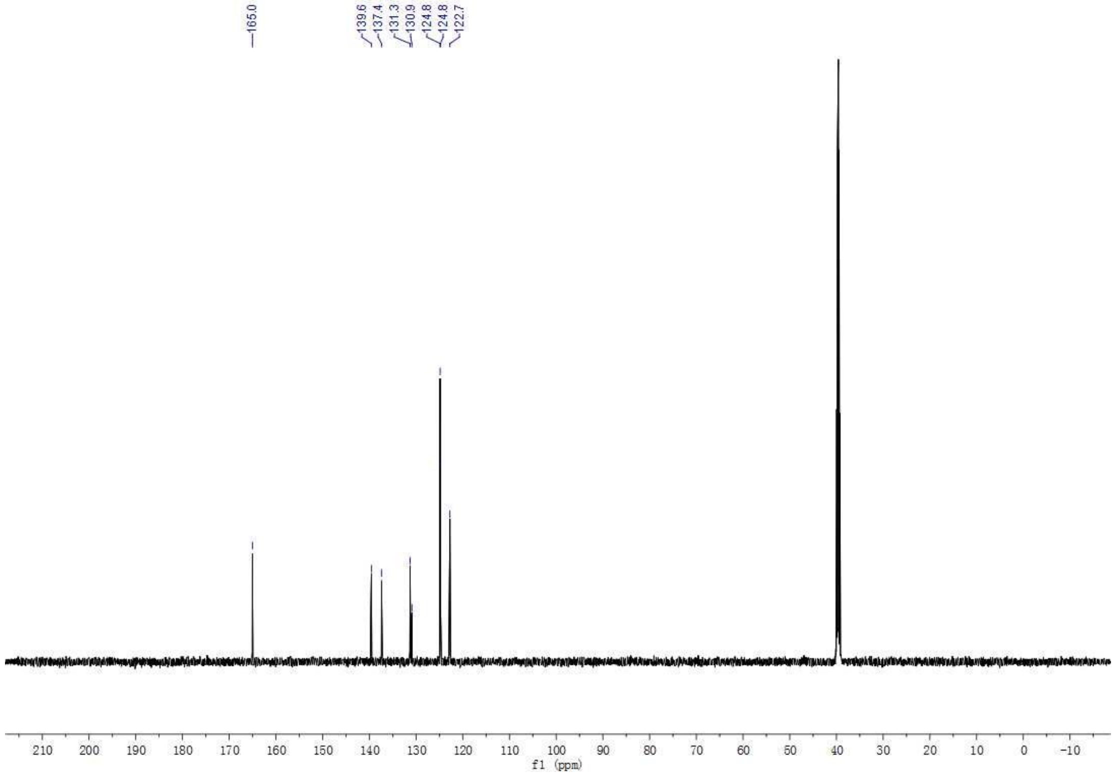

8.49
8.00
7.97
7.96
7.96
7.63
7.62
7.61
7.61
7.60
7.59
7.58
7.58
7.57
7.56
7.46
1.01
1.00
4.00
2.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

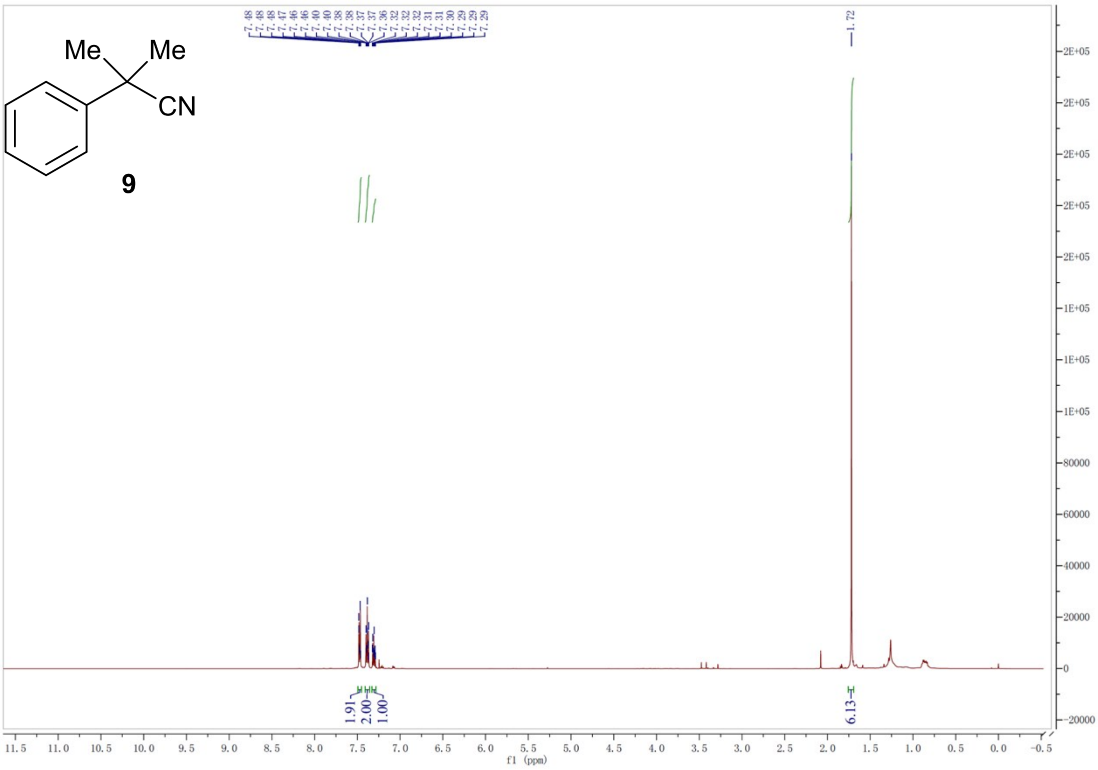

168.1
134.2
132.2
131.7
128.9
127.9
127.7
127.7
126.7
124.5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3t


O
NH2
S


8.53
8.52
8.52
8.51
8.51
8.51
8.51
8.51
8.39
8.03
8.03
8.01
7.46
7.45
7.44
7.44
7.44
7.43
7.42
7.42
7.42
7.40
7.40
7.39
7.39
7.32
1.01
1.02
1.01
1.00
2.03
1.02
9.5
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
f1 (ppm)


165.0
139.6
137.4
131.3
130.9
124.8
124.8
122.7
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)


Me
Me
CN
7.48
7.48
7.48
7.47
7.46
7.46
7.40
7.40
7.38
7.38
7.37
7.37
7.36
7.32
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.29
1.72
1.91
2.00
1.00
6.13
2E+05
2E+05
2E+05
2E+05
2E+05
1E+05
1E+05
1E+05
80000
60000
40000
20000
0
-20000
11.5
11.0
10.5
10.0
9.5
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
f1 (ppm)

9