Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

A Mild Hydration of Nitriles Catalysed by Copper(II) Acetate

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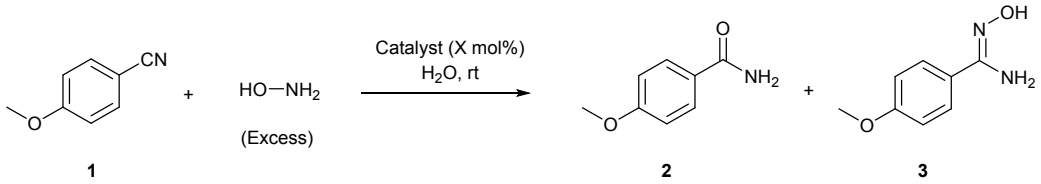
General Remarks

All chemicals and solvents used were reagent grade and used as supplied unless otherwise specified. Analytical thin layer chromatography (TLC) was performed on Merck® silica gel 60 F254 glass or aluminium plates. Organic Compounds were visualized by UV (254 nm) irradiation. Flash column chromatography was carried out using forced flow or by gravity of the indicated solvent on Fluka® silica gel 60 (230 - 400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV 500, Bruker AV 300 or Bruker AV 250 spectrometer in $CDCl_3$ or d^6-DMSO as solvents. Chemical shifts (δ) were referenced internally to residual protic solvent signal for $CDCl_3$ (7.26 ppm) and d^6-dmso (2.5 ppm). Multiplicities are presented as singlet (s), broad singlet (br s), doublet (d), triplet (t), triplet of triplets (tt), quadruplet (q) and, multiplet (m). Coupling constants, (J) were expressed in Hertz (Hz). HRMS-ESI were run on an Agilent® 1200 Series LC/MSD. Uncorrected melting points were determined using Stuart SMP10 melting point equipment using closed end glass capillary.

Influence of the Lewis acid in the formation of amidoxime

4-Methoxybenzonitrile (0.130 g, 1 mmol), hydroxylamine 50% in water solution (1 mL) and the appropriate catalyst were added to a carousel tube (see table S1). The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under vacuum and the crude reaction was analysed by ^{1}H-NMR.



1 **2** **3**

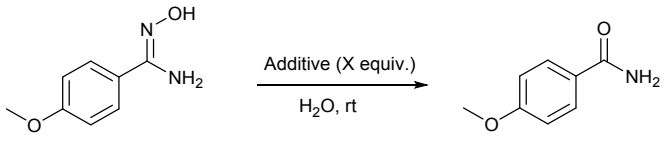
Table S1

Entry	Catalyst	Loading (mol%)	Time h	Conversion[a] (%)	Ratio **2:3**
1	--	--	24	100	50:50
2	$[IrCp^*I_2]_2$	1	24	100	50:50
3	$Cu(OAc)_2$	2	24	100	50:50
4	$Zn(OAc)_2$	5	24	100	50:50
5	$FeCl_2$	5	24	100	50:50
6	$[RuCp^*Cl_2]_2$	1	24	100	50:50

a) Conversions were determined by analysis of the ^{1}H-NMR spectra

Conversion of amidoxime in amide using hydroxylamine and ammonia

N-Hydroxy-4-methoxybenzimidamide (0.170 g, 1 mmol) and water (1 mL) were added in a carousel tube followed by the addition of the corresponding amount of additive. The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under vacuum and the crude reactions were analysed by ^{1}H NMR.



3 **2**

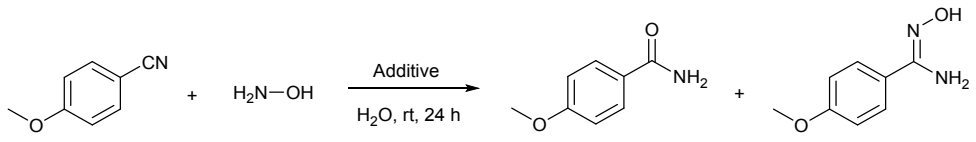
Table S2

Entry	Additive	Conversion (%)[a]
1	NH_2OH (1 equiv.)	0
2	NH_2OH (2 equiv.)	0
3	NH_2OH (3 equiv.)	2
4	NH_2OH (5 equiv.)	3
5	NH_2OH (10 equiv.)	3
6	NH_2OH (20 equiv.)	3
7	NH_4OH (10 equiv.)	0

a) Conversions were determined by analysis of the ^{1}H-NMR spectra

Effect of additives in the formation of amidoxime

4-Methoxybenzonitrile (0.130 g, 1 mmol) and hydroxylamine 50% in water solution (1 mL) were added to a carousel tube. 1 mL of HCl or NaOH 2 M solution was added into the reaction mixture (see table S3). The reaction mixture was stirred at room temperature for 24 hours. The solvent was removed under vacuum and the crude reaction was analysed by ^{1}H-NMR.



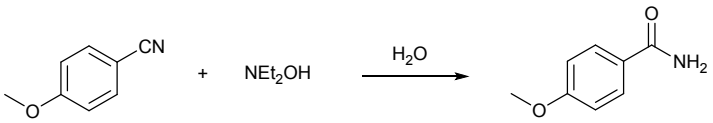
1 **2** **3**

Table S3

Entry	Additive	Notes	Conversion (%)[a]	Ratio **2:3**
1	2 M HCl	Added at the beginning of the reaction	100	50:50
2	2 M HCl	Added after 24 hours	100	55:45
3	2 M NaOH	Added at the beginning of the reaction	100	60:40
4	2 M NaOH	Added after 24 hours	100	100:0

a) Conversions were determined by analysis of the ^{1}H-NMR spectra

Optimization of the reaction conditions using *N*,*N*-diethylhydroxylamine as additive



1 2

4-Methoxybenzonitrile (1 mmol) was added to a carousel tube followed by water (1 mL), the amounts of *N,N*-diethylhydroxylamine and Lewis acid, as well as the temperature and the reaction time were modified according to table S4. The solvent was removed under vacuum and the crude was analysed by ^{1}H-NMR.

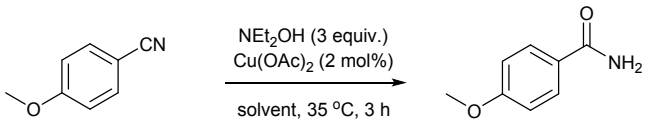
Table S4

Entry	NEt_2OH (x equiv.)	Lewis acid (2 mol%)	Temp (°C)	Time (h)	Conversion (%)[a]
1	10	--	25	24	82
2	10	--	30	24	93
3	10	--	35	24	100
4	10	--	40	24	100
5	1	--	35	24	89
6	2	--	35	24	93
7	3	--	35	24	100
8	3	--	35	3	45
9	3	--	35	5	100
10	3	$Cu(OAc)_2$	35	12	100
11	3	$Zn(OAc)_2$	35	12	95
12	3	$[IrCp^*I_2]_2$	35	12	100
13	3	$Cu(OAc)_2$	35	5	100
14	3	$[IrCp^*I_2]_2$	35	5	100
15	3	$Cu(OAc)_2$	35	3	100
16	3	$[IrCp^*I_2]_2$	35	3	100
17	3	$Cu(OAc)_2$	35	2	92
18	3	$[IrCp^*I_2]_2$	35	2	85

a) Conversions were determined by analysis of the ^{1}H-NMR spectra

Effect of the solvent in the hydration of nitriles

4-Methoxybenzonitrile (1 mmol) was added to carousel tube followed by the addition of solvent (1 mL), *N,N*-diethylhydroxylamine (3 mmol) and copper acetate (2 mol%). The reaction mixture was heated at 35 °C for 3 hours. The solvent was removed under vacuum and the crude reaction was analysed by ^{1}H-NMR using d^6-DMSO as deuterated solvent.



1 **2**

Table S5

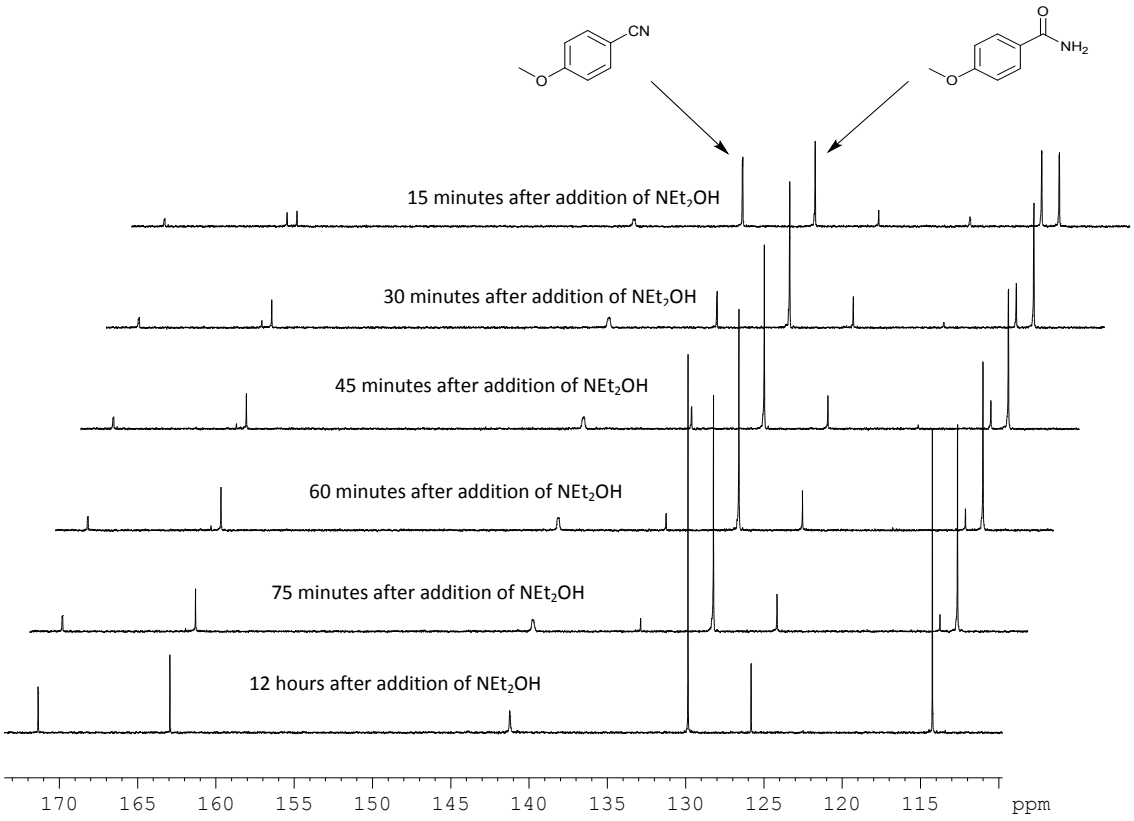
Entry	Solvent	Conversion (%)
1	MeOH	92
2	EtOAc	89
3	DCE	84
4	THF	91
5	Toluene	84
6	Hexane	93

a) Conversions were determined by analysis of the ^{1}H-NMR spectra

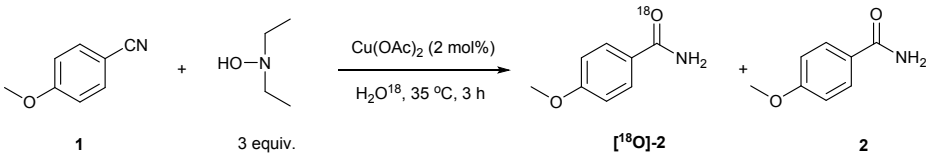
NMR Experiment

4-Methoxybenzonitrile (65 mg, 0.5 mmol) *N,N*-diethylhydroxylamine (133 mg, 1.5 mmol) and D_2O (0.5 mL) were added to a NMR tube. The tube was sealed and heated to 70 °C in a Bruker Avance 500 (500 MHz). ^{13}C NMR spectra were taken every 15 minutes for 12 hours.

Figure S1. ^{13}C-NMR spectra of the reaction progress.

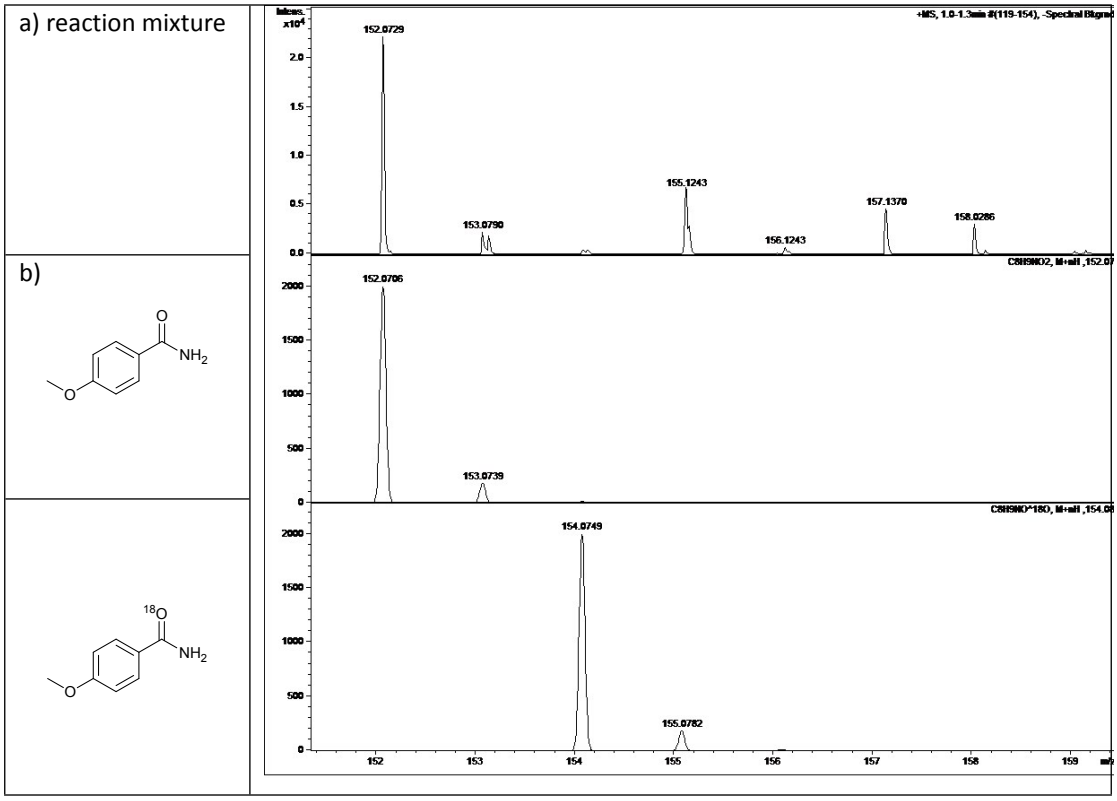


Experiments using ^{18}O-labelled water

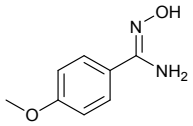


4-Methoxybenzonitrile (13 mg, 0.1 mmol), *N*,*N*-diethylhydroxylamine (27 mg, 0.3 mmol), copper acetate (3.2 mg, 2 mol%) and ^{18}O-labelled water (1 mL) were added in a carousel tube. The reaction mixture was then stirred at room temperature for 24 hours. The final mixture was diluted in methanol and analysed by HRMS-ESI. A peak with *m/z* = 154.0749 was not detected, indicating that incorporation of ^{18}O into the amide product had not occurred. This evidence supports that water does not act as nucleophile.

Figure S2. a) HRMS-ESI of the reaction mixture; b) comparison to the simulated peaks of the ^{18}O-labelled amide



Synthesis of *N*-hydroxy-4-methoxybenzimidamide (3)

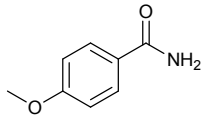


4-Methoxybenzonitrile (1.300 g, 10 mmol) and hydroxylamine (0.600 g, 20 mmol) were dissolved in ethanol (50 mL) and heated at reflux for 3 hours. The reaction mixture was cooled to room temperature and the solvent was removed under vacuum. The resulting residue was dissolved in ethyl acetate (20 mL) and washed with brine (2 x 20 mL). The organic layers were combined, dried over magnesium sulfate and filtered giving N-hydroxy-4-methoxybenzimidamide (1.46 g, 90%) as a white solid. The product obtained was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, 2H, *J* = 7.6 Hz, aromatic), 6.94 (d, 2H, *J* = 7.6 Hz, aromatic), 4.89 (br s, 2H, NH_2), 3.83 (s, 3H, CH_3); HRMS-ESI calcd for $[C_8H_{10}N_2O_2]^+$: 167.0776 $[M+H]^+$. Found 167.0798; m.p. 120 - 122 °C.

General procedure for the synthesis of amides

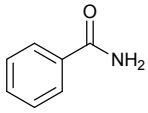
The appropriate nitrile (1 mmol) was added to carousel tube followed by the addition of water (1 mL), *N,N*-diethylhydroxylamine (3 mmol) and copper acetate (2 mol%). The reaction mixture was heated at 35 °C for 3 hours. The solvent was removed under vacuum and the crude reaction was purified over a short pad of silica (eluting with dichloromethane/methanol 95:5).

4-Methoxybenzamide (2)[1]



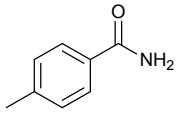
4-Methoxybenzonitrile (0.130 g, 1 mmol) was used as nitrile species. 4-Methoxybenzamide was recovered after purificacion by column chromatography as a white solid (0.147 g, 97%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 ^{o}C) δ 7.91 - 7.71 (m, 3H, aromatic and NH_2), 7.20 (br s, 1H, NH_2), 6.95 (d, *J* = 8.6 Hz, 2H, aromatic), 3.78 (s, 3H, OCH_3); ^{13}C NMR (75.5 MHz, d^6-DMSO, 25 ^{o}C) δ 167.7, 161.9, 129.7, 126.8, 113.7, 55.6; HRMS-ESI calcd for $[C_8H_9NO_2]^+$: 152.0706 $[M+H]^+$. Found 152.0731; FT-IR (neat) ν in cm^{-1}: 3393, 1674; m.p. 207 - 208 °C.

Benzamide (4)[2]



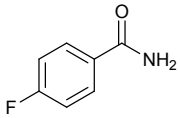
Benzonitrile (0.100 g, 1 mmol) was used as nitrile species. Benzamide was recovered after purification by column chromatography as a white solid (0.119 g, 98%).
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.84 - 7.81 (m, 2H, aromatic), 7.56 - 7.42 (m, 3H, aromatic), 6.33 (br s, 2H, NH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 169.5, 133.2, 132.1, 128.6, 127.01; HRMS-ESI calcd for $[C_7H_6NO]^-$: 120.0455 $[M-H]^-$. Found 120.0458; FT-IR (neat) ν in cm^{-1}: 2268, 1659; m.p. 129 - 130 °C.

4-Methylbenzamide (5)[1]

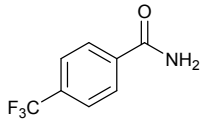


4-Methylbenzonitrile (0.120 g, 1 mmol) was used as nitrile species. 4-Methylbenzamide was recovered after purification by column chromatography as a white solid (0.132 g, 98%).
^{1}H NMR (250 MHz, $CDCl_3$, 25 ^{o}C) δ 7.75 - 7.68 (d, *J* = 8.3 Hz, 2H, aromatic), 7.28 - 7.21 (d, *J* = 8.3 Hz, 2H, aromatic), 6.08 (br s, 2H, NH_2), 2.33 (s, 3H, CH_3); ^{13}C NMR (75.5 MHz, CDCl3, 25 °C) δ 169.5, 142.6, 130.4, 129.3, 127.4, 21.5; HRMS-ESI calcd for $[C_8H_9NONa]^+$: 158.0582 $[M+Na]^+$. Found 158.0590; FT-IR (neat) ν in cm^{-1}: 3303, 1650; m.p. 129 - 130 °C.

4-Fluorobenzamide (6)[1]



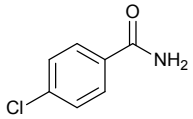
4-Fluorobenzonitrile (0.120 g, 1 mmol) was used as nitrile species. 4-Fluorobenzamide was recovered after purification by column chromatography as a white solid (0.151 g, 92%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 ^{o}C) δ 7.99 (br s, 1H, NH_2), 7.92 (dd, *J* = 5.6 Hz, *J* = 3.3 Hz, 2H, aromatics), 7.40 (s, 1H, NH_2), 7.26 (t, *J* = 9.0 Hz, 2H, aromatic); ^{13}C NMR (75.5 MHz, d^6-DMSO, 25 ^{o}C) δ 167.1, 164.2 (d, *J* = 248.2 Hz), 131.0, 130.5 (d, *J* = 9.0 Hz), 115.5 (d, *J* = 21.1 Hz); HRMS-ESI calcd for $[C_7H_5NOF]^-$: 138.0361 $[M-H]^-$. Found 138.0389; FT-IR (neat) ν in cm^{-1}: 3331, 1674; m.p. 153 - 155 °C**4-(Trifluoromethyl)benzamide (7**



4-(Trifluoromethyl)benzonitrile (0.185 g, 1 mmol) was used as nitrile species. 4-(Trifluoromethyl)benzamide was recovered after purification by column chromatography as a white solid (0.176 g, 93%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 ^{o}C) δ 8.20 (br s, 1H, NH_2), 8.05 (d, *J* = 7.9 Hz, 2H, aromatic), 7.82 (d, *J* = 8.3 Hz, 2H, aromatic), 7.63 (br s, 1H, NH_2); ^{13}C NMR (75.5 MHz, d^6-DMSO, 25 ^{o}C) δ 167.0, 138.4, 131.7

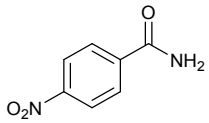
(q, *J* = 31.7 Hz), 124.6, 127.1 (q, *J* = 3.74 Hz), 125.6 (q, *J* = 237.4 Hz); HRMS-ESI calcd for $[C_8H_6F_3NONa]^+$: 212.0299 $[M+Na]^+$. Found 212.0537; FT-IR (neat) ν in cm^{-1}: 3373, 1654; m.p. 183 - 185 °C.

4-Chlorobenzamide (8)[1]



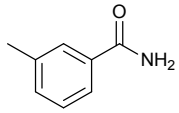
4-Chlorobenzonitrile (0.137 g, 1 mmol) was used as nitrile species. 4-Chlorobenzamide was recovered after purification by column chromatography as a white solid (0.149 g, 96%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 °C) δ 8.07 (br s, 1H, NH_2), 7.88 (d, *J* = 8.6 Hz, 2H, aromatic), 7.45 - 7.54 (m, 3H, aromatic and NH_2); ^{13}C NMR (75.5 MHz, d^6-DMSO, 25 °C) δ 131.3, 138.2, 159.6, 168.3; HRMS-ESI calcd for $[C_7H_5ClNO]^-$: 154.0065 $[M-H]^-$. Found 154.0092; FT-IR (neat) ν in cm^{-1}: 3370, 1653; m.p. 178 - 181 °C.

4-Nitrobenzamide (9)[3]



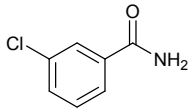
4-Nitrobenzonitrile (0.150 g, 1 mmol) was used as nitrile species. 4-Nitrobenzonitrile was recovered after purification by column chromatography as a white solid (0.134 g, 81%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 °C) δ 8.32 (d, *J* = 8.3 Hz, 3H, aromatic and NH_2), 8.11 (d, *J* = 9.0 Hz, 2H, aromatic), 7.72 (br s, 1H, NH_2); ^{13}C NMR (75 MHz, d^6-DMSO, 25 °C) δ 166.5, 149.4, 140.3, 129.3, 123.8; HRMS-ESI calcd for $[C_7H_6N_2O_3]^-$: 165.0306 $[M-H]^-$. Found 165.0336; FT-IR (neat) ν in cm^{-1}: 3367, 1656; m.p. 197 - 199 °C.

3-Methylbenzamide (10)[3]



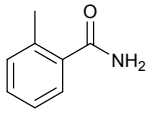
3-Methylbenzonitrile (0.120 g, 1 mmol) was used as nitrile species. 3-Methylbenzamide was recovered after purification by column chromatography as a white solid (0.126 g, 93%).
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.65 (s, 1H, aromatic), 7.62 - 7.55 (m, 1H, aromatic), 7.35 - 7.29 (m, 2H, aromatic), 6.33 (br s, 2H, NH_2), 2.39 (s, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 169.9, 138.5, 133.6, 132.7, 128.5, 128.1, 124.3, 21.3; HRMS-ESI calcd for $[C_8H_9NONa]^+$: 158.0582 $[M+Na]^+$. Found 158.0590; FT-IR (neat) ν in cm^{-1}: 3375, 1649; m.p. 92 - 93 °C.

3-Chlorobenzamide (11)[4]



3-Chlorobenzonitrile (0.140 g, 1 mmol) was used as nitrile species. 3-Chlorobenzamide was recovered after purification by column chromatography as a white solid (0.15 g, 94%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 °C) δ 8.09 (br s, 1H, NH_2), 7.90 (s, 1H, aromatic), 7.81 (d, *J* = 7.9 Hz, 1H, aromatic), 7.52 (m, 3H, aromatic and NH_2); ^{13}C NMR (75.5 MHz, d^6-DMSO, 25 °C) δ 166.7, 136.6, 133.4, 131.4, 130.6, 127.6, 126.5; HRMS-ESI calcd for $[C_7H_5ClNO]^-$: 154.0065 $[M-H]^-$. Found 154.0073; FT-IR (neat) ν in cm^{-1}: 3359, 1659; m.p. 134 - 136 °C.

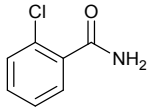
2-Methylbenzamide (12)[4]



2-Methylbenzonitrile (0.120 g, 1 mmol) was used as nitrile species. 2-Methylbenzamide was recovered after purification by column chromatography as a white solid (0.128 g, 95%).

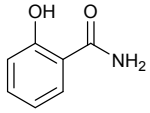
^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ 7.35 (d, *J* = 8.1 Hz, 1H, aromatic), 7.29 - 7.24 (m, 1H, aromatic), 7.15 (m, 2H, aromatic), 2.43 (s, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 ^{o}C) δ 172.3, 136.3, 135.2, 131.2, 130.3, 126.9, 125.7, 19.9; HRMS-ESI calcd for $[C_8H_9NONa]^+$: 158.0582 $[M+Na]^+$. Found 158.0592; FT-IR (neat) ν in cm^{-1}: 3370, 1651; m.p. 139 - 140 °C.

2-Chlorobenzamide (13)[4]



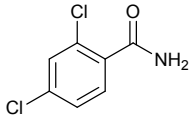
2-Chlorobenzonitrile (0.137 g, 1 mmol) was used as nitrile species. 2-Chlorobenzamide was recovered after purification by column chromatography as a white solid (0.143 g, 92%).
^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ 7.76 (dd, *J* = 8.1 Hz, *J* = 1.2 Hz, 1H, aromatic), 7.40 - 7.25 (m, 3H, aromatic), 6.32 (br s, 2H, NH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 ^{o}C) δ 168.2, 133.8, 131.8, 130.8, 130.7, 130.4 127.2; HRMS-ESI calcd for $[C_7H_6ClNONa]^+$: 178.0036 $[M+Na]^+$. Found 178.0080; FT-IR (neat) ν in cm^{-1}: 3363, 1651; m.p. 139 - 140 °C.

2-Hydroxybenzamide (14)[3]



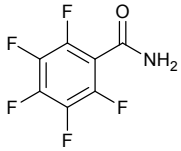
2-Hydroxybenzonitrile (0.120 g, 1 mmol) was used as nitrile species. 2-Hydroxybenzamide was recovered after purification by column chromatography as a white solid (0.137 g, 85%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 ^{o}C) δ 13.01 (s, 1H, OH), 8.40 (br s, 1H, NH_2), 7.80 (br s, 1H, NH_2), 7.85 (d, *J* = 8.2 Hz, 1H, aromatic), 7.42 (t, *J* = 8.2 Hz, 1H, aromatic), 6.88 - 6.81 (m, 2H, aromatic); ^{13}C NMR (75.5 MHz, d^6-DMSO, 25 ^{o}C) δ 172.5, 161.5, 134.4, 128.4, 118.7, 117.8, 114.7; HRMS-ESI calcd for $[C_7H_7NO_2]^-$: 136.0404 $[M-H]^-$. Found 136.0342; FT-IR (neat) ν in cm^{-1}: 3420, 1685; m.p. 140 - 142 °C.

2,4-Dichlorobenzamide (15)[3]



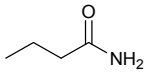
2,4-Dichlorobenzonitrile (0.170 g, 1 mmol) was used as nitrile species. 2,4-Dichlorobenzamide was recovered after purification by column chromatography as a white solid (0.095 g, 50%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 ^{o}C) δ 7.91 (br s, 1H, NH_2), 7.66 - 7.61 (m, 2H, NH_2 and aromatic), 7.47 (d, *J* = 1.2 Hz, 2H, aromatic); ^{13}C NMR (75.5 MHz, d^6-DMSO, 25 ^{o}C) δ 167.6, 136.3, 134.6, 131.2, 130.4, 129.5, 127.6; HRMS-ESI calcd for $[C_7H_4Cl_2NO]^-$: 187.9675 $[M-H]^-$. Found 187.9708; FT-IR (neat) ν in cm^{-1}: 3376, 1651; m.p. 193 - 195 °C.

Pentafluorobenzamide (16)[5]



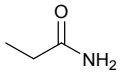
Pentafluorobenzonitrile (0.200 g, 1 mmol) was used as nitrile species. Pentafluorobenzamide was recovered after purification by column chromatography as a white solid (0.201 g, 92%)
^{1}H NMR (500 MHz, d^6-DMSO, 25 °C) δ 8.21 (br s, 1H, NH_2), 8.16 (br s, 1H, NH_2); ^{19}F NMR (470 MHz, d^6-DMSO, 25 °C) δ -139.86 -139.94 (m, 2F), -150.18 (t, *J* = 21 Hz, 1F), -160.12 -160.20 (m, 2F); HRMS-ESI calcd for $[C_7H_1F_5NO]^-$: 209.9984 $[M-H]^-$. Found 209.9978; FT-IR (neat) ν in cm^{-1}: 3391, 1672; m.p. 147 - 149 °C.

Butyramide (17)[1]



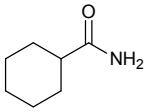
Butyronitrile (70 mg, 1 mmol) was used as nitrile species. Butyramide was recovered after purification by column chromatography as a white solid (70 mg, 79%).
^{1}H NMR (250 MHz, $CDCl_3$, 25 °C) δ 5.35 (br s, 2H, NH_2), 2.14 (t, *J* = 7.5 Hz, 2H, $CH_2\underline{CH_2}C(O)$), 1.60 (sextet, *J* = 7.5 Hz, 2H, $CH_3\underline{CH_2}CH_2$), 0.90 (t, *J* = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 175.5, 37.3, 19.0, 13.7; HRMS-ESI calcd for $[C_4H_{10}NO]^+$: 88.0757 $[M+H]^+$. Found 88.0752; FT-IR (neat) ν in cm^{-1}: 3360, 1632; m.p. 115 - 117 °C.

Propionamide (18)[6]



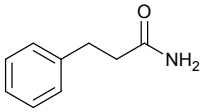
Propionitrile (55 mg, 1 mmol) was used as nitrile species. Propionamide was recovered after purification by column chromatography as a white solid (58 mg, 80%).
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 6.31 (br s, 1H, NH_2), 5.92 (br s, 1H, NH_2), 2.20 (q, *J* = 7.3 Hz, 2H, CH_2), 1.09 (t, *J* = 7.3 Hz, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 177.3, 28.9, 9.5; HRMS-ESI calcd for $[C_3H_6NO]^-$: 72.0455 $[M-H]^-$. Found 72.0523; FT-IR (neat) ν in cm^{-1}: 1626; m.p. 133 - 134 °C.

Cyclohexane amide (19)[2]



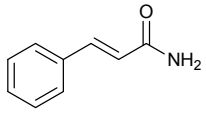
Cyclohexanecarbonitrile (0.110 g, 1 mmol) was used as nitrile species. Cyclohexane amide was recovered after purification by column chromatography as a white solid (0.113 g, 89%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 °C) δ 7.13 (br s, 1H, NH_2), 6.62 (br s, 1H, NH_2), 2.06 - 1.96 (m, 1H, CH), 1.67 - 1.57 (m, 5H, CH_2), 1.35 - 1.03 (m, 5H, CH_2); ^{13}C NMR (75.5 MHz, d^6-DMSO, 25 °C) δ 177.7, 44.0, 28.5 (2C), 25.9, 25.7 (2C); HRMS-ESI calcd for $[C_7H_{13}NONa]^+$: 150.0895 $[M+Na]^+$. Found 150.0968; FT-IR (neat) ν in cm^{-1}: 3340, 1661; m.p. 186 - 188 °C.

Benzenepropanamide (20)[2]



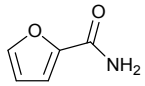
Benzenepropanonitrile (0.130 g, 1 mmol) was used as nitrile species. Benzenepropanamide was recovered after purification by column chromatography as a white solid (0.127 g, 85%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 °C) δ 7.34 - 7.18 (m, 5H, aromatic), 5.98 (br s, 1H, NH_2), 5.60 (br s, 1H, NH_2), 2.95 (t, *J* = 6.2 Hz, 2H, CH_2), 2.51 (t, *J* = 6.2 Hz, 2H, CH_2); ^{13}C NMR (75.5 MHz, d^6-DMSO, 25 °C) δ 174.9, 140,7, 128.5, 128.4, 126.3, 37.5, 31.4; HRMS-ESI calcd for $[C_9H_{11}NONa]^+$: 172.0738 $[M+Na]^+$. Found 172.0827; FT-IR (neat) ν in cm^{-1}: 3389, 1649; m.p. 96 - 98 °C.

Cinnamamide (21)[1]



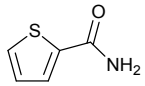
Cinnamonitrile (0.131 g, 1 mmol) was used as nitrile species. Cinnamamide was recovered after purification by column chromatography as an off-white solid (0.127 g, 85%).
^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ 7.66 (d, *J* = 15.9 Hz, 1H, CH=CH), 7.58 - 7.48 (m, 2H, aromatic), 7.41 - 7.33 (m, 3H, aromatic), 6.51 (d, *J* = 15.4 Hz, 1H, CH=CH), 5.86 (br s, 2H, NH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 168.3, 142.7, 134.4, 130.1, 128.9, 128.0, 122.7; HRMS-ESI calcd for $[C_9H_{10}NO]^+$: 148.0762 $[M+H]^+$. Found 148.0797; FT-IR (neat) ν in cm^{-1}: 3382, 1661; m.p. 149 - 151 °C.

Furan-2-carboxylic acid amide (22)[3]



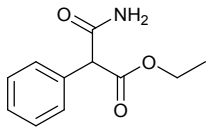
2-Furonitrile (0.090 g, 1 mmol) was used as nitrile species. 2-Furanamide was recovered after purification by column chromatography as a brown solid (0.1 g, 92%).
^{1}H NMR (300 MHz, CDCl3, 25 ^{o}C) δ 7.41 (dd, *J* = 1.5 Hz, *J* = 0.7 Hz, 1H, CH), 7.09 (dd, *J* = 2.6 Hz, 0.7 Hz, 1H, CH), 6.44 (dd, *J* = 3.7 Hz, *J* = 1.5 Hz, 1H, CH), 6.17 (br s, 2H, NH2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 ^{o}C) δ 160.3, 147.4, 144.4, 115.2, 112.3; HRMS-ESI calcd for $[C_5H_6NO_2]^+$: 112.0393 $[M+H]^+$. Found 112.0411; FT-IR (neat) ν in cm^{-1}: 3352, 1625; m.p. 141 - 142 °C.

Thiophene-2-carboxylic acid amide (23)[1]



2-Thiophenecarbonitrile (0.110 g, 1 mmol) was used as nitrile species. 2-Thiophenecarboxamide was recovered after purification by column chromatography as a white solid (0.10 g, 79%).
^{1}H NMR (300 MHz, d^6-DMSO, 25 ^{o}C) δ 7.98 (br s, 1H, NH_2), 7.76 - 7.69 (m, 2H, CH), 7.40 (br. s, 1H, NH_2), 7.11 (t, *J* = 4.2 Hz, 1H, CH); ^{13}C NMR (75.5 MHz, d^6-DMSO, 25 ^{o}C) δ 163.2, 140.4, 131.2, 128.8, 128.1; HRMS-ESI calcd for $[C_5H_4NOSNa]^+$: 149.9990 $[M+Na]^+$. Found 149.9969; FT-IR (neat) ν in cm^{-1}: 3366, 1654; m.p. 177 - 179 °C.

2-Phenyl-malonamic acid ethyl ester (24)[7]



Cyano-phenylacetic acid ethyl ester (0.190 g, 1 mmol) was used the nitrile species. 2-Phenyl-malonamic acid ethyl ester was recovered after purification by column chromatography as a white solid (0.166 g, 80%).
^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ 7.40 - 7.20 (m, 5H, aromatic), 6.81 (br s, 1H, NH_2), 5.71 (br s, 1H, NH_2), 4.44 (s, 1H, CH), 4.21 - 4.06 (m, 2H, CH_2), 1.21 (t, *J* = 6 Hz, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 ^{o}C) δ 170.6, 169.6, 133.9, 129.1, 128.3, 128.2, 62.0, 58.4, 13.9; HRMS-ESI calcd for $[C_{11}H_{13}NO_3Na]^+$: 230.0793 $[M+Na]^+$. Found 230.0859; FT-IR (neat) ν in cm^{-1}: 3394, 1655; m.p. 133 - 134 °C.

[1] R. Ohmura, M. Takahata and H. Togo, *Tetrahedron Lett.,* 2010, **51**, 4378

[2] S. K. Sharma, S. D. Bishopp, C. L. Allen, R. Lawerence, M. J. Bamford, A. A. Lapkin, P. Plucinski, R. J. Watson and J. M. J Williams, *Tetrahedron Lett*., 2011, **52**, 4252
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[4] C. C. Hughes and D. Trauner, *Angew. Chem. Int. Ed*., 2002, **41**, 4556
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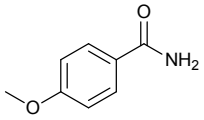
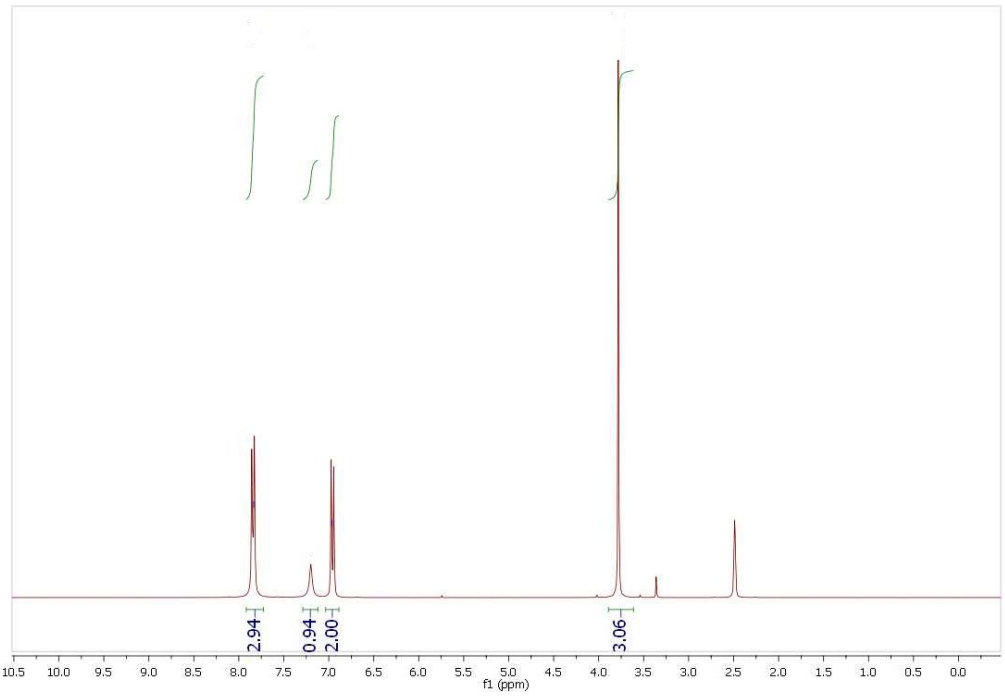
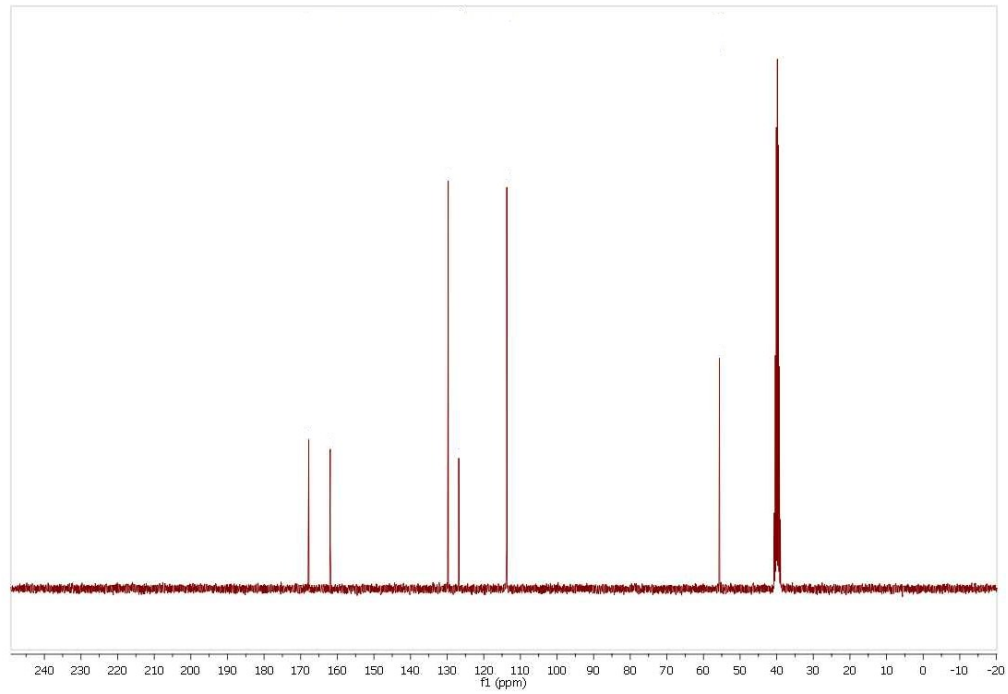
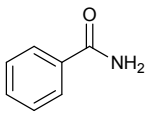
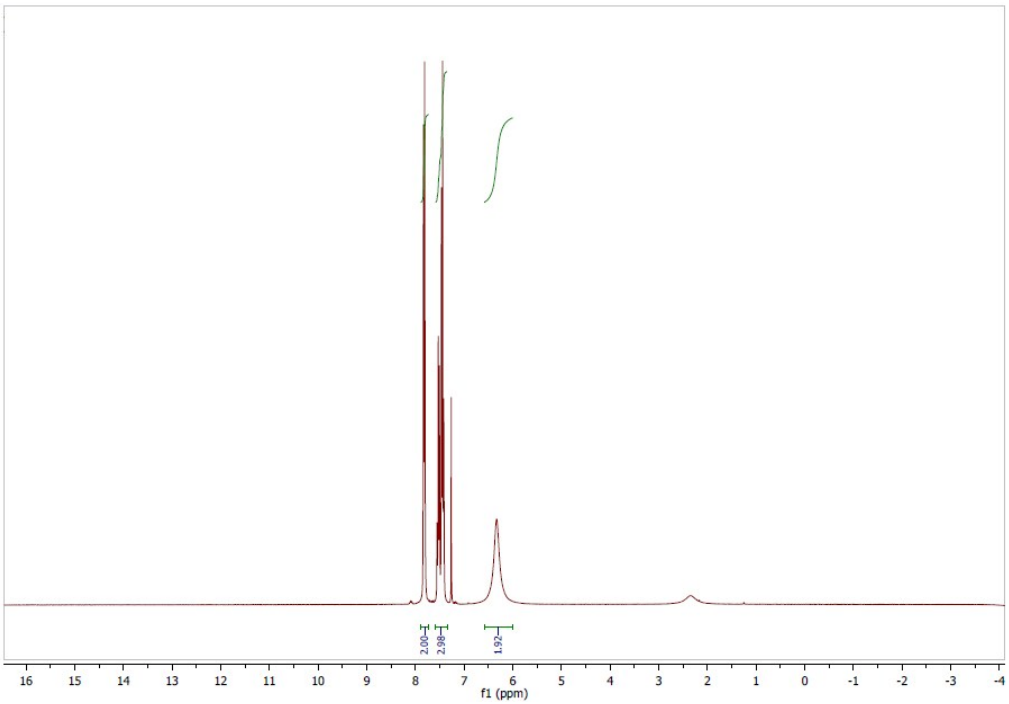
^{1}H-NMR and ^{13}C-NMR spectroscopic data

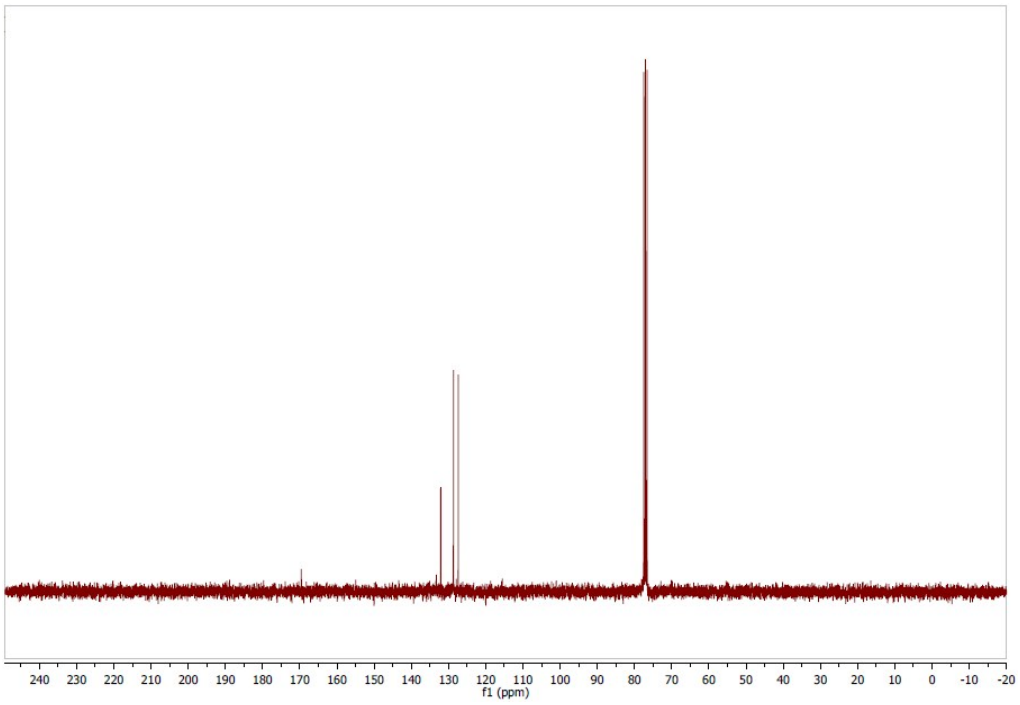


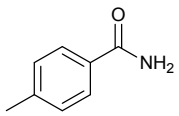


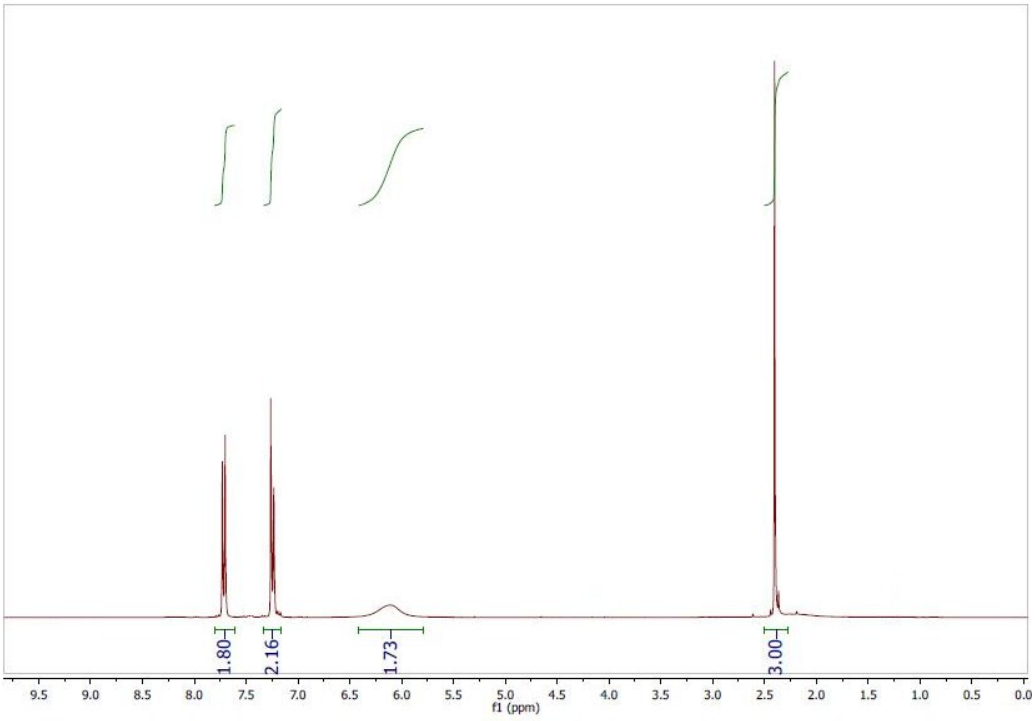


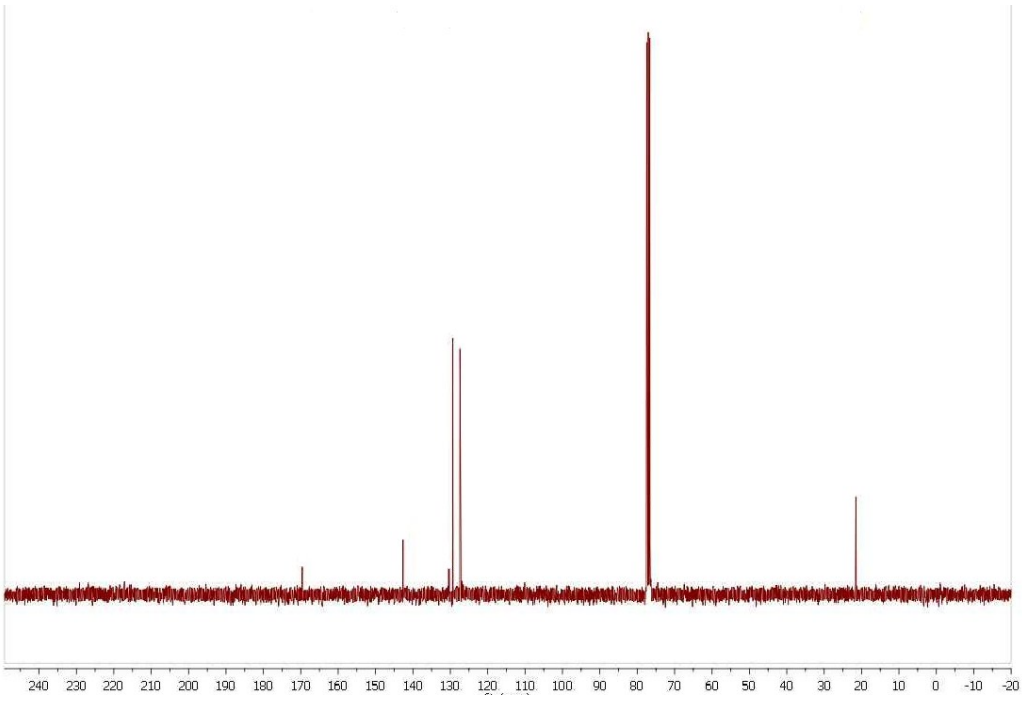



2.00
2.98
1.92
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O
NH2


1.80
2.16
1.73
3.00
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 0.0
f1 (ppm)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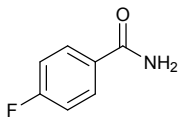
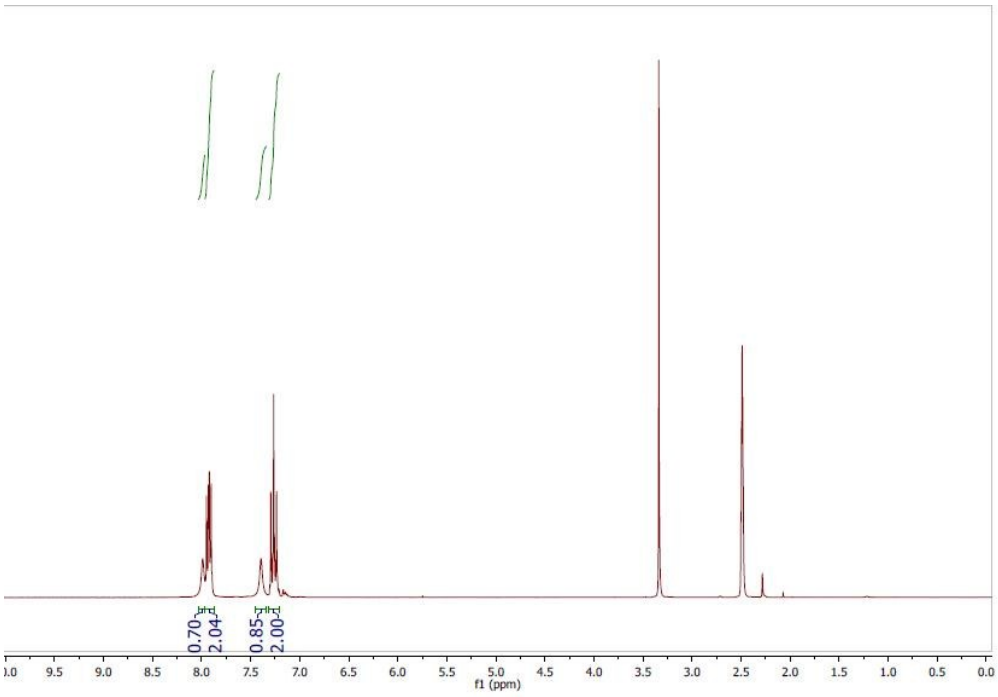
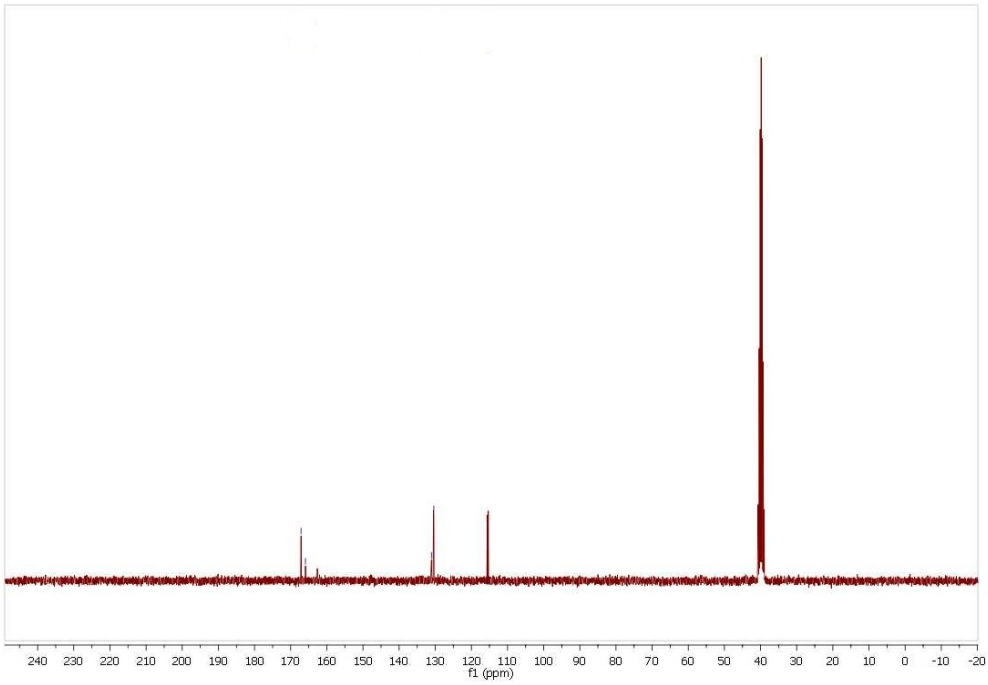
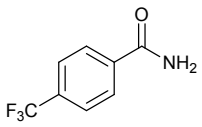
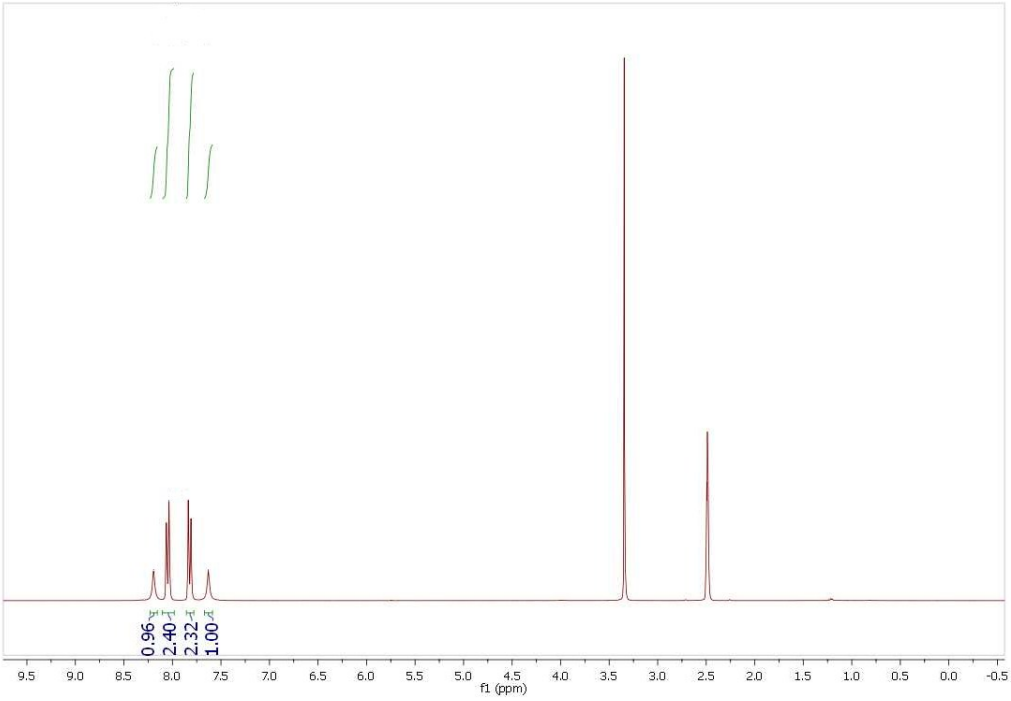
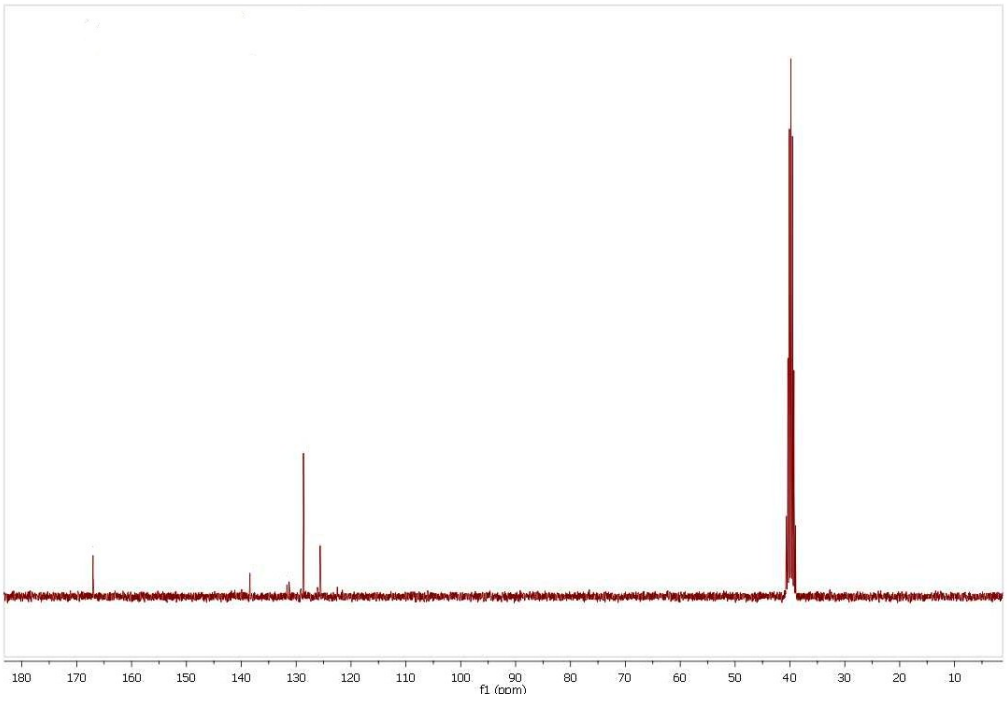

O
NH2
F

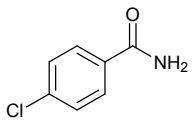

0.70
2.04
0.85
2.00
f1 (ppm)

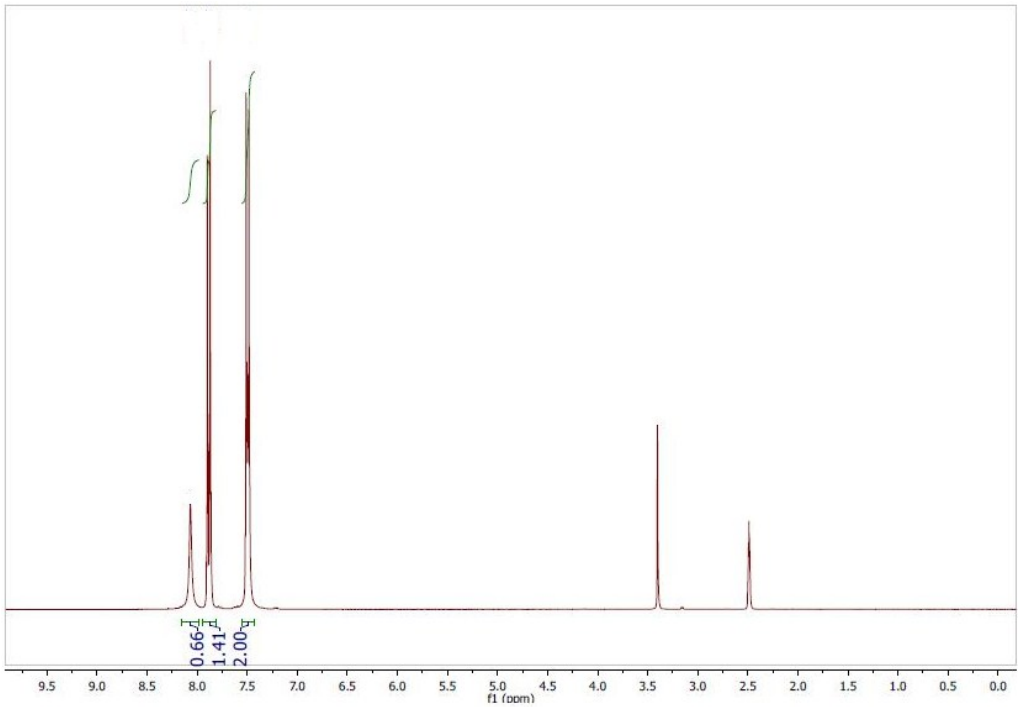

f1 (ppm)

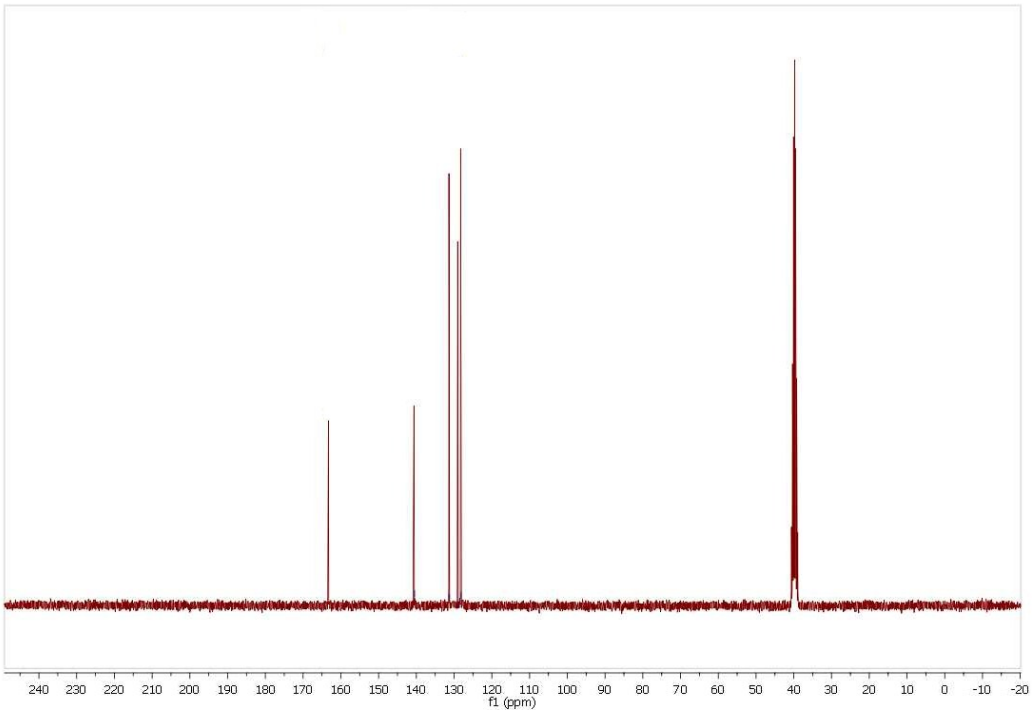

O
NH2
F3C

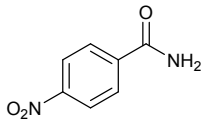

0.96
2.40
2.32
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

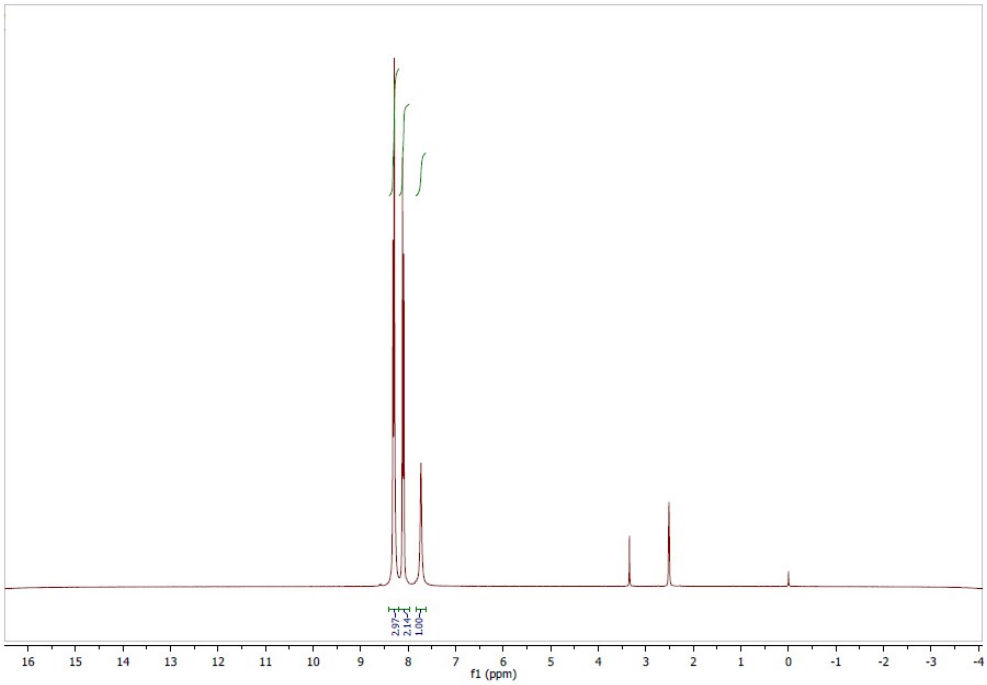

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


O
NH2
Cl


0.66
1.41
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 0.0
f1 (ppm)


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O
NH2
O2N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2.14
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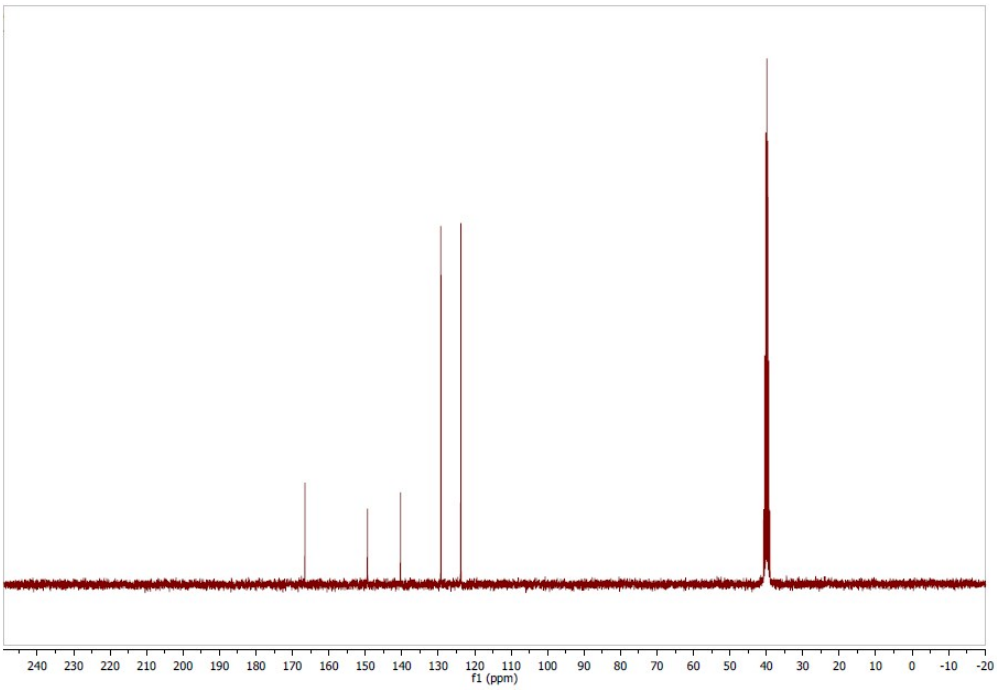
f1 (ppm)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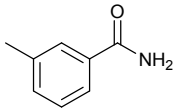
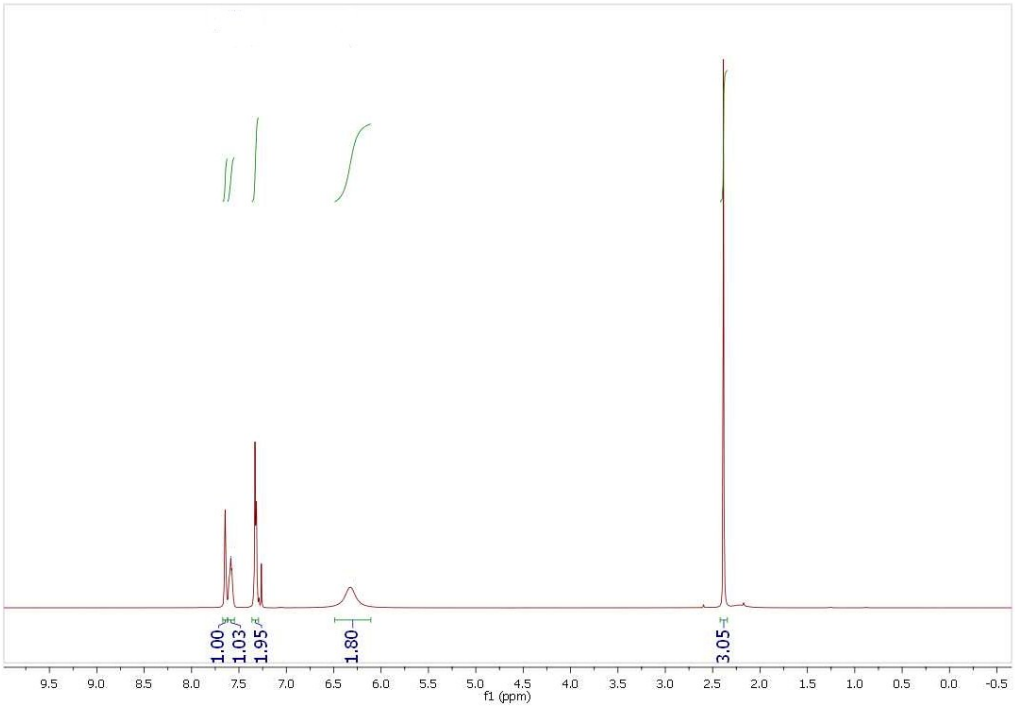
f1 (ppm)


O
NH2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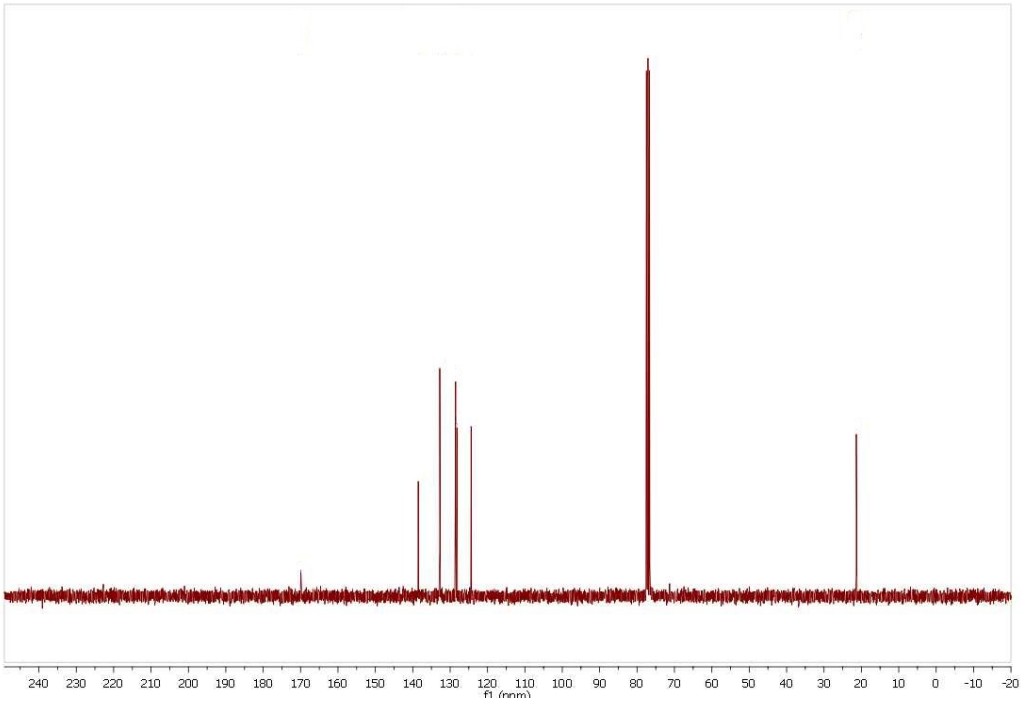
1.03
1.95
1.80
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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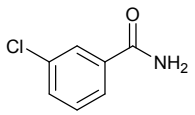
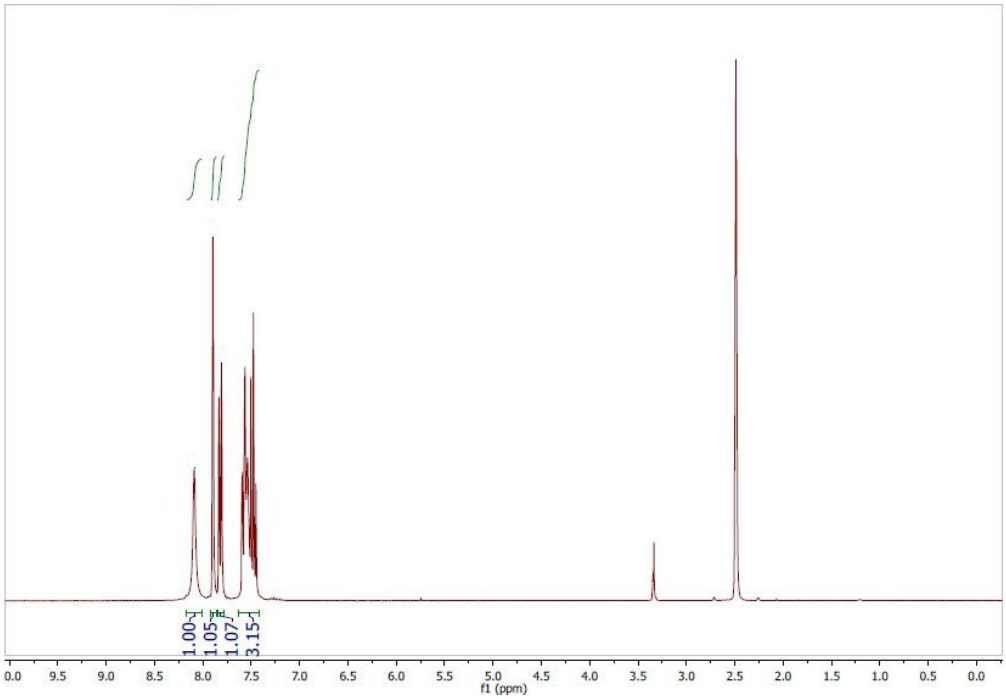
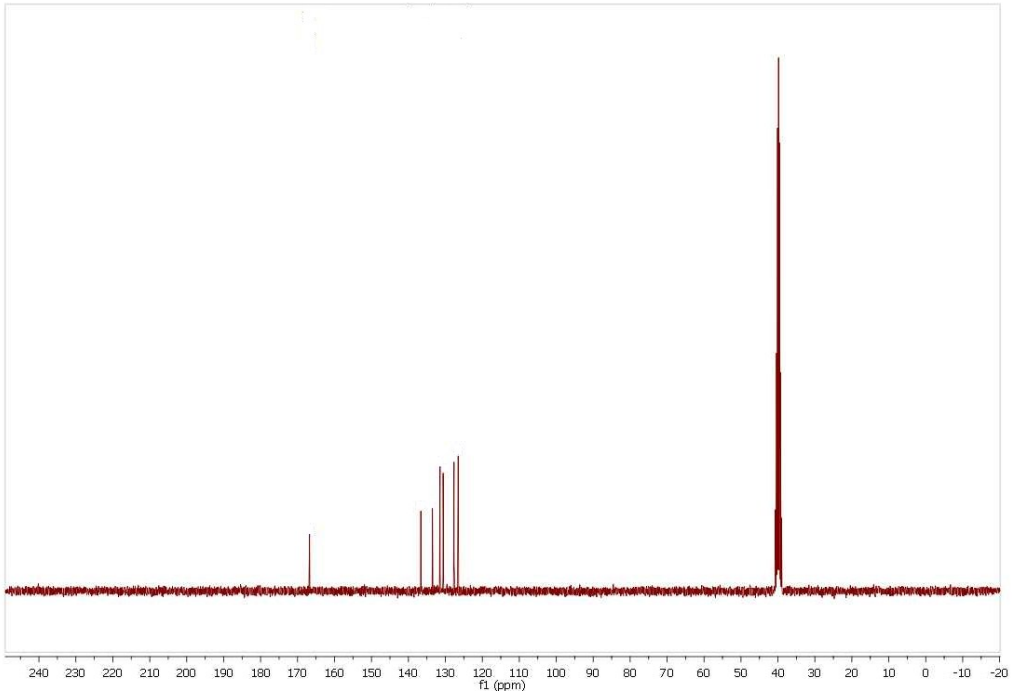

O
Cl
NH2


1.00
1.05
1.07
3.15
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 0.0
f1 (ppm)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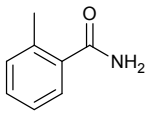
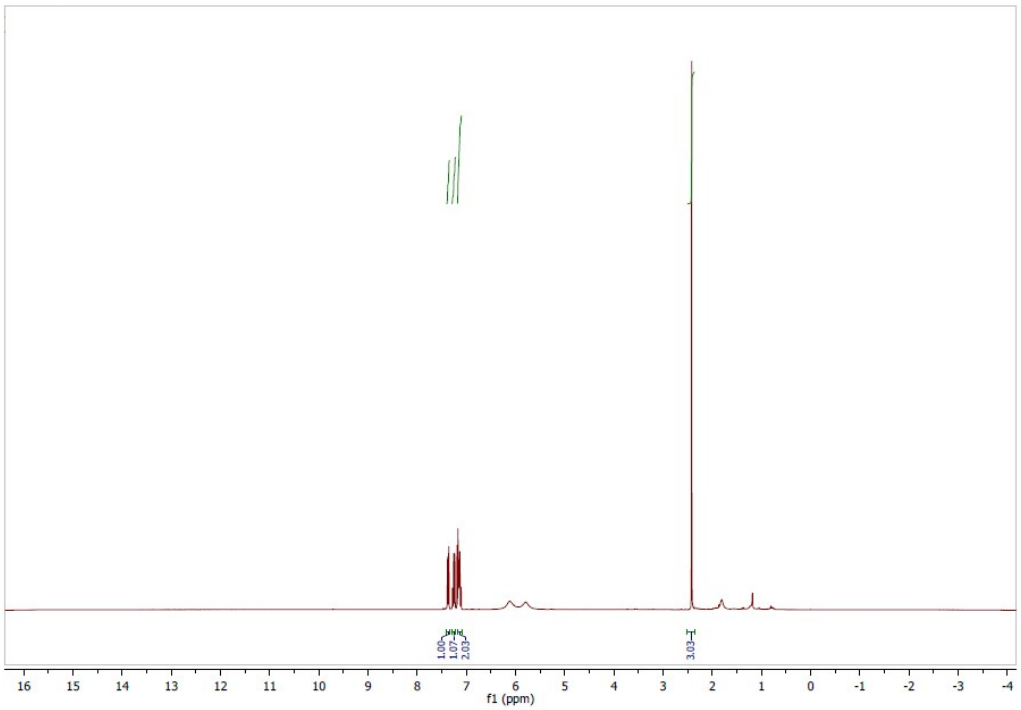
f1 (ppm)


O
NH2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1.07
2.03
3.03
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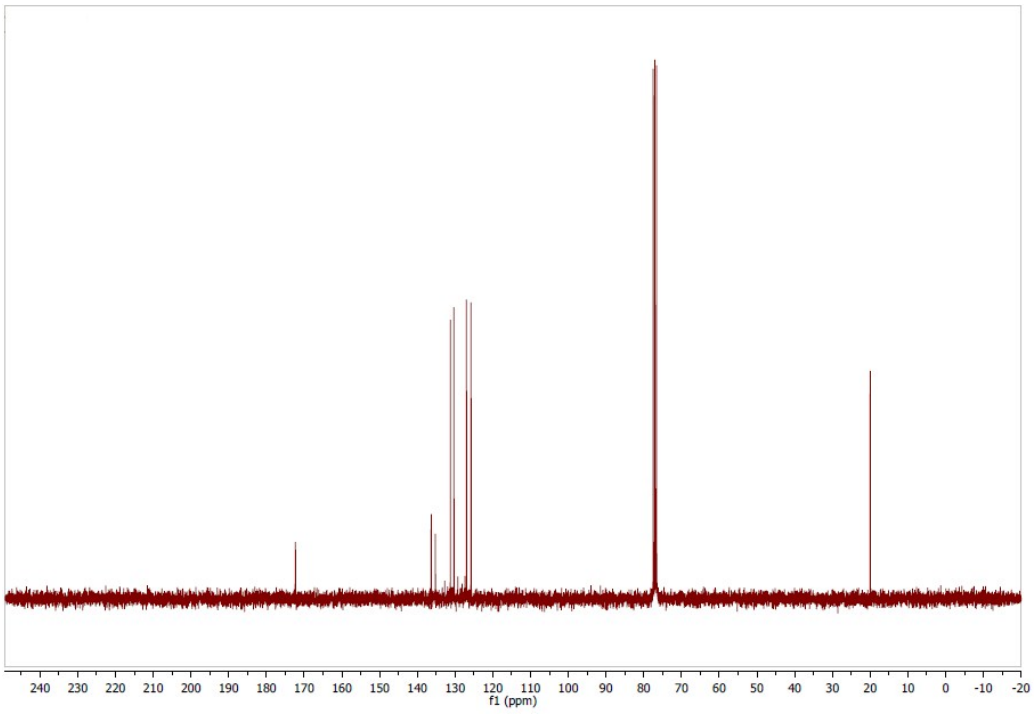
f1 (ppm)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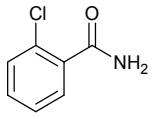
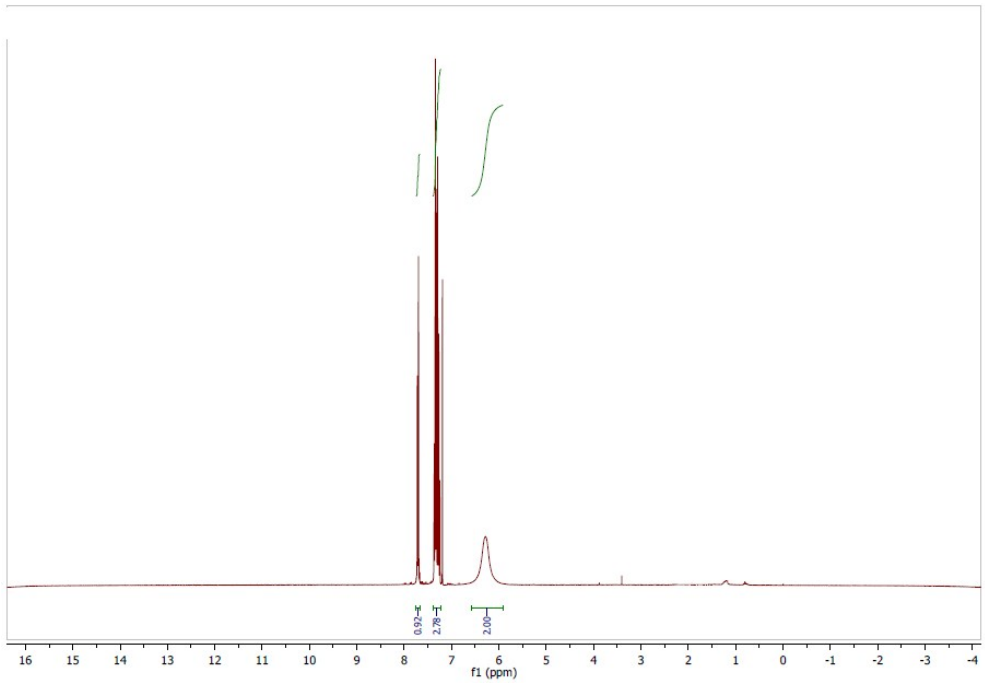
f1 (ppm)


Cl
O
NH2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2.00
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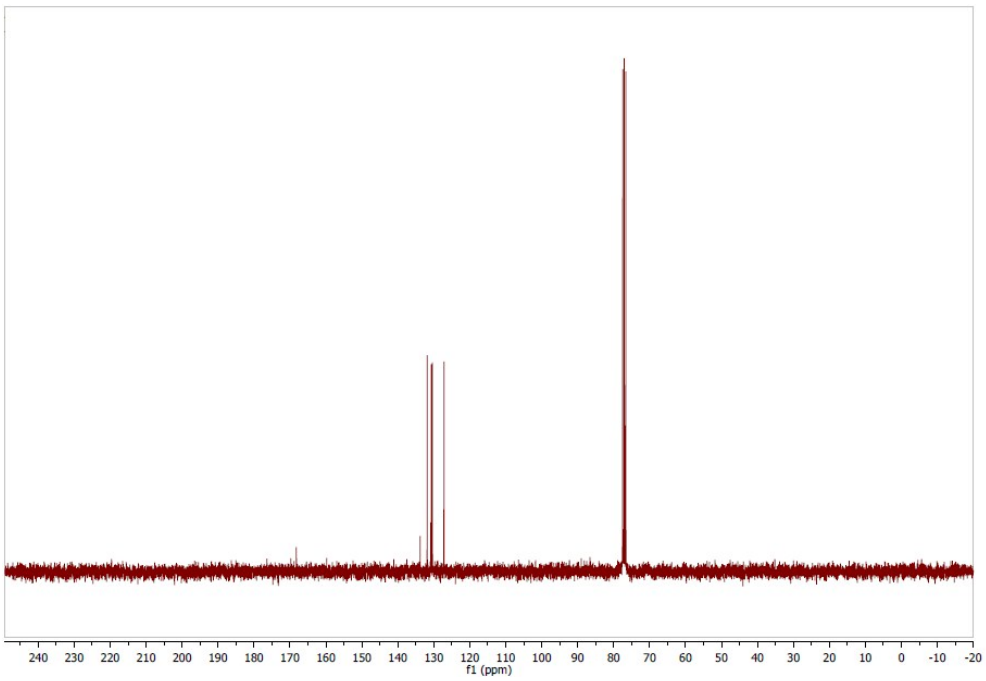
f1 (ppm)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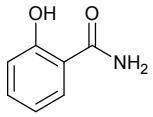
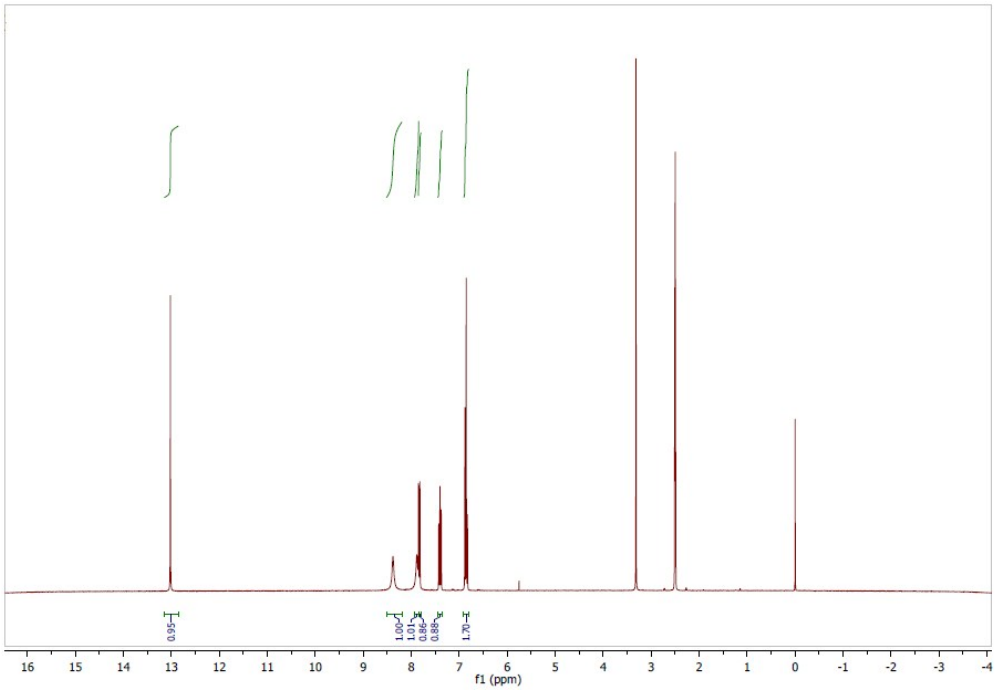
f1 (ppm)


OH
O
NH2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0.86
1.70
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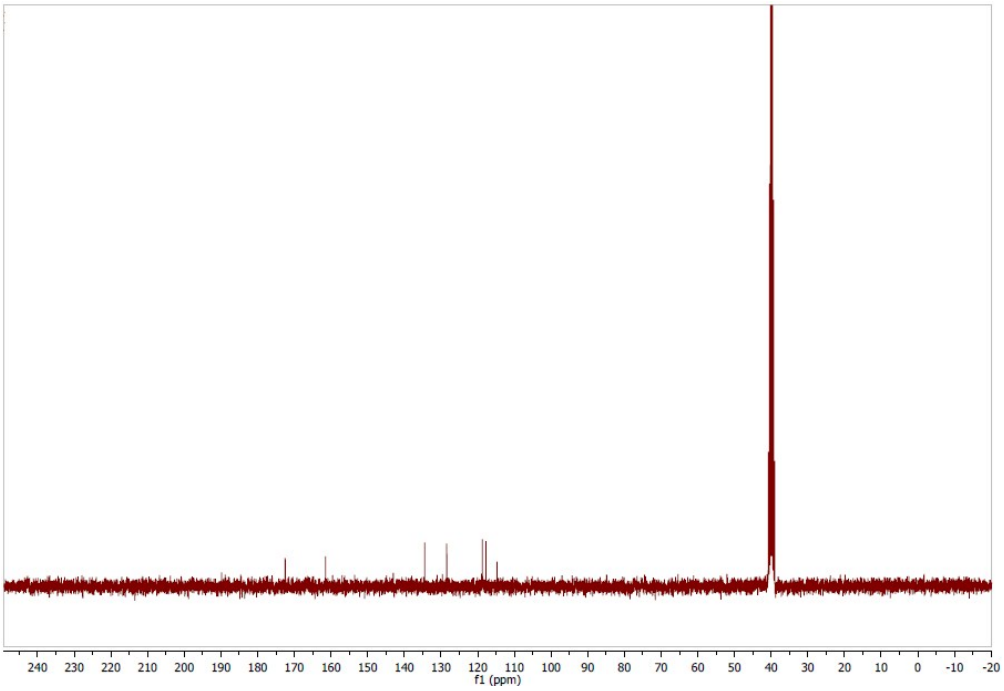
f1 (ppm)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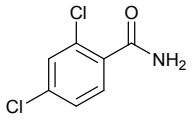
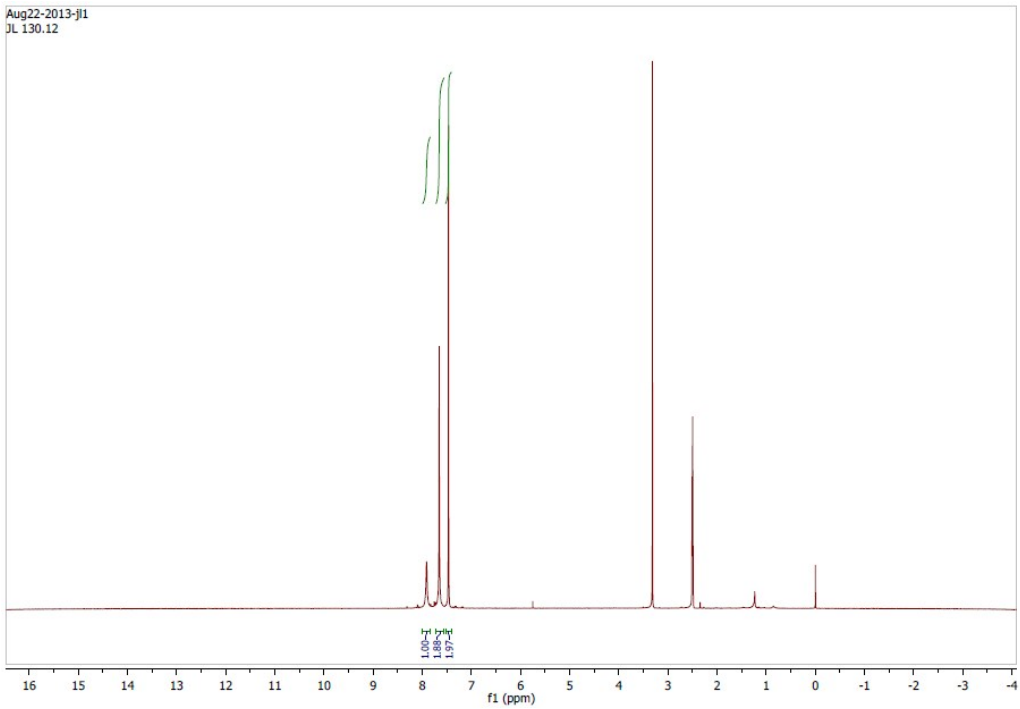
f1 (ppm)


Cl
O
NH2
Cl


Aug22-2013-jl1
JL 130.12
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1.88
1.97
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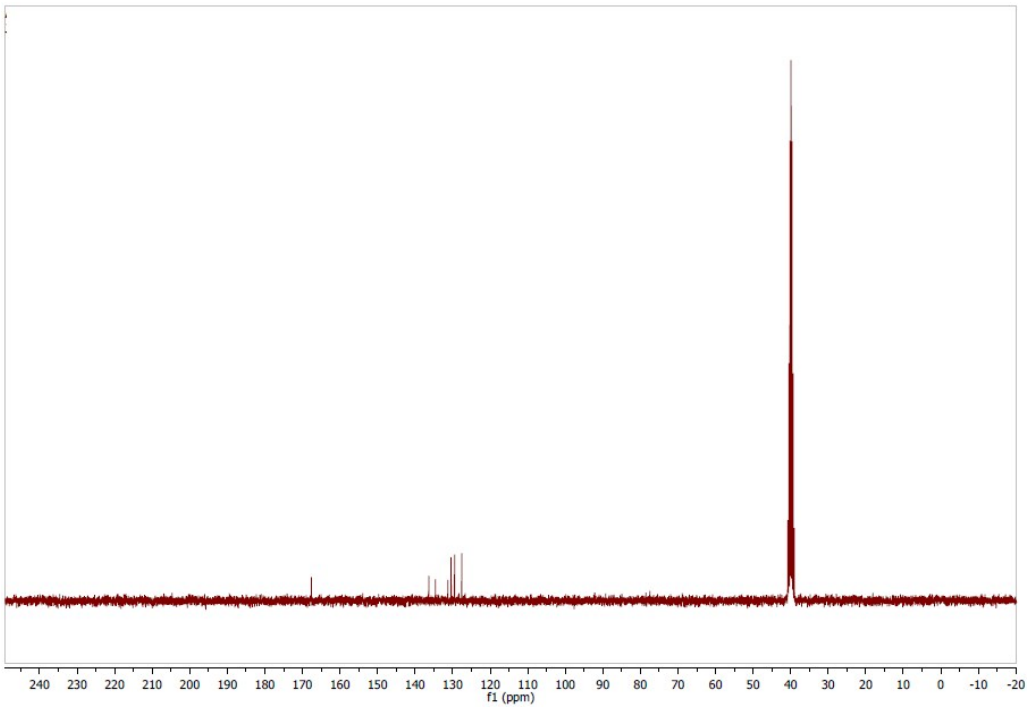
f1 (ppm)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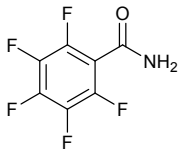
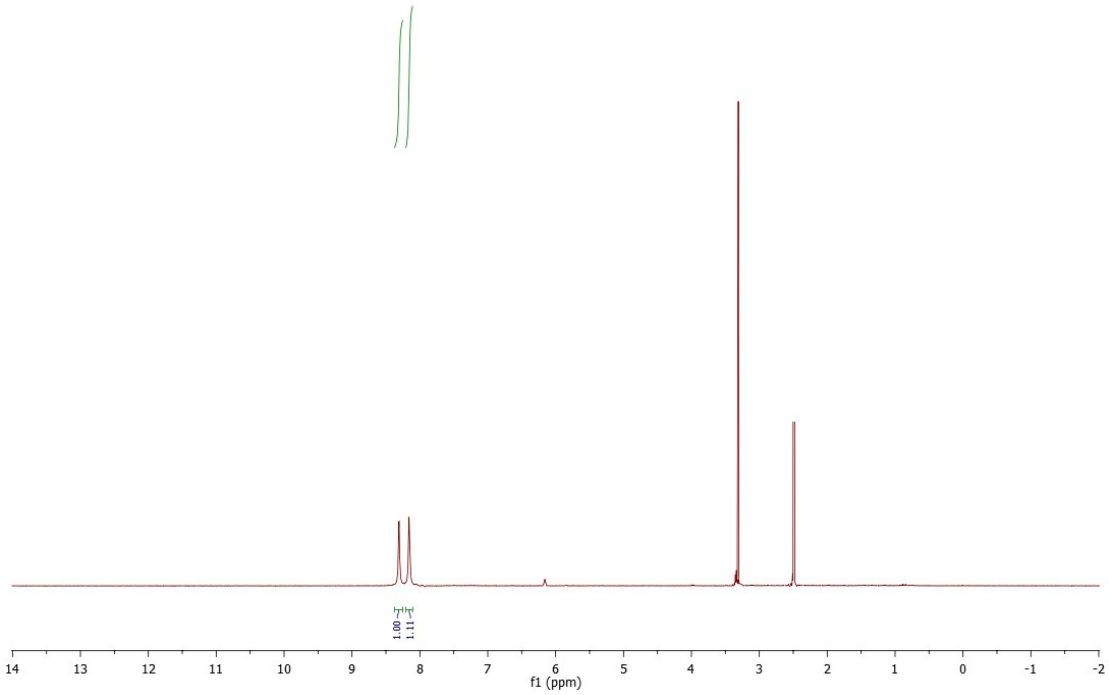
f1 (ppm)


F
O
F
NH2
F
F
F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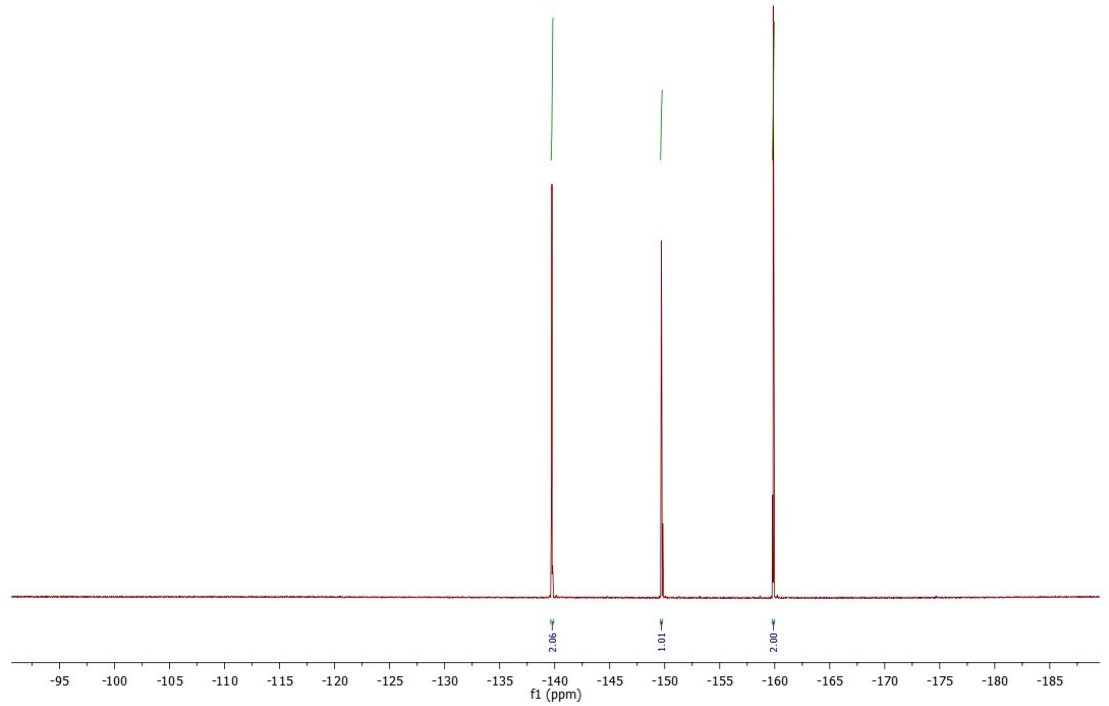
f1 (ppm)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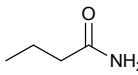
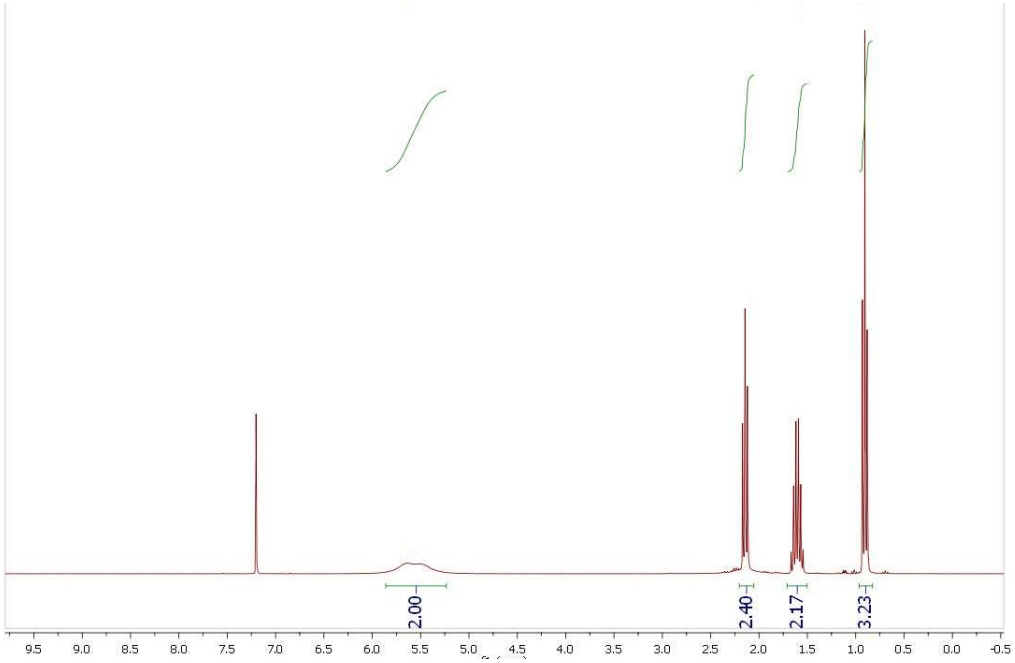
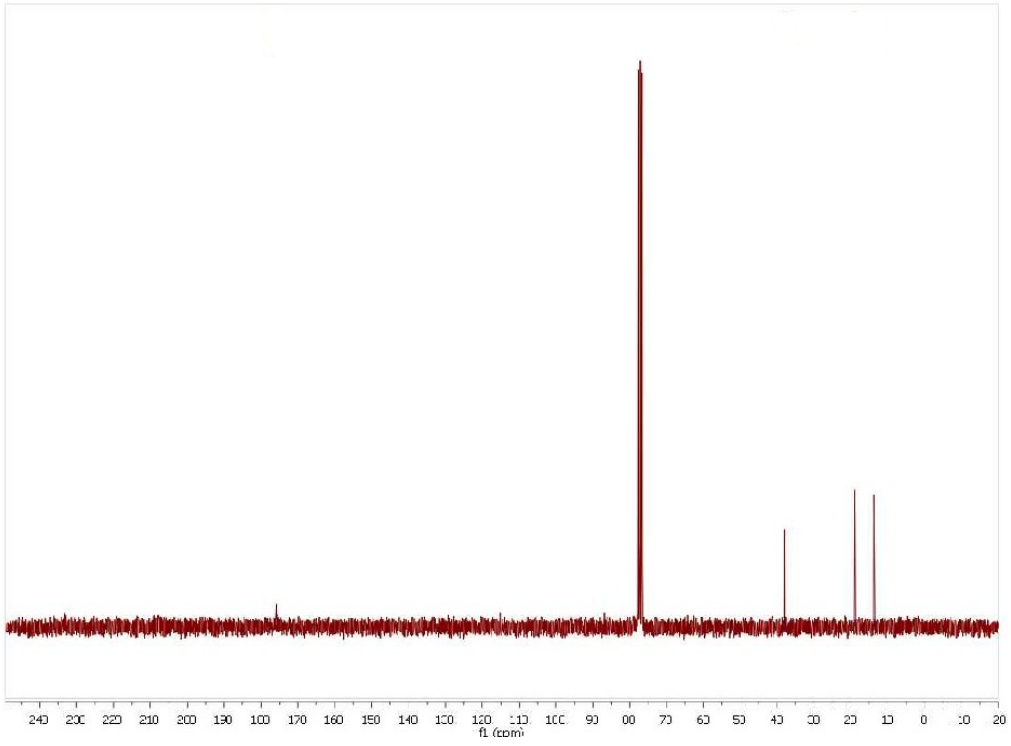
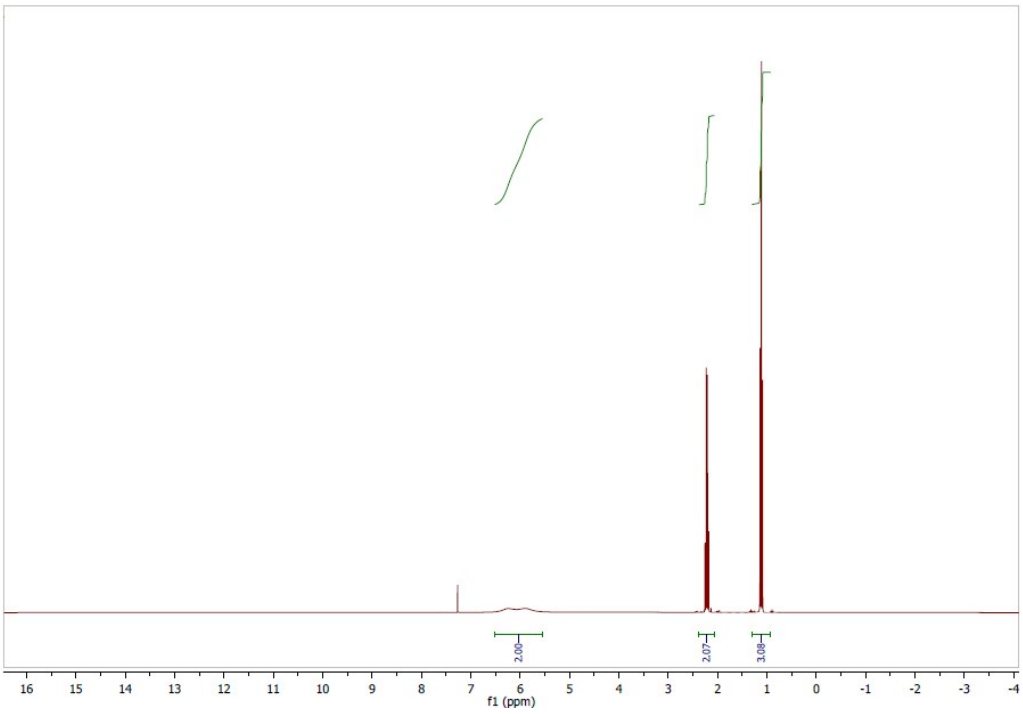
1.01
2.00
-95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185
f1 (ppm)


O
NH2


2.00
2.40
2.17
3.23
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)

O
NH2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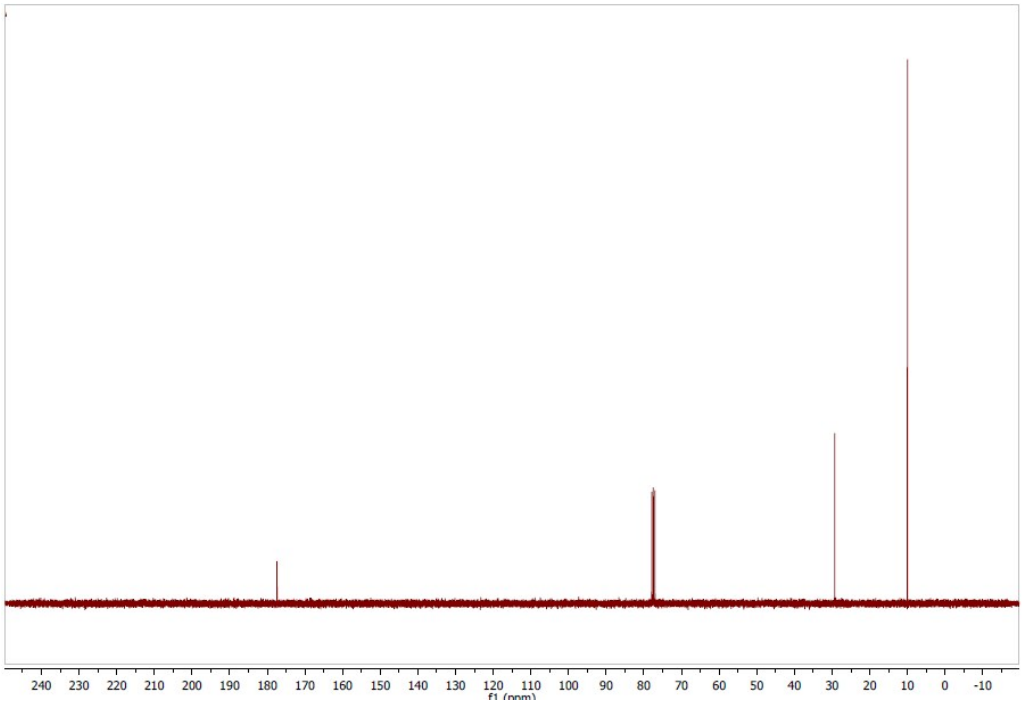
2.07
3.08
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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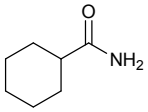
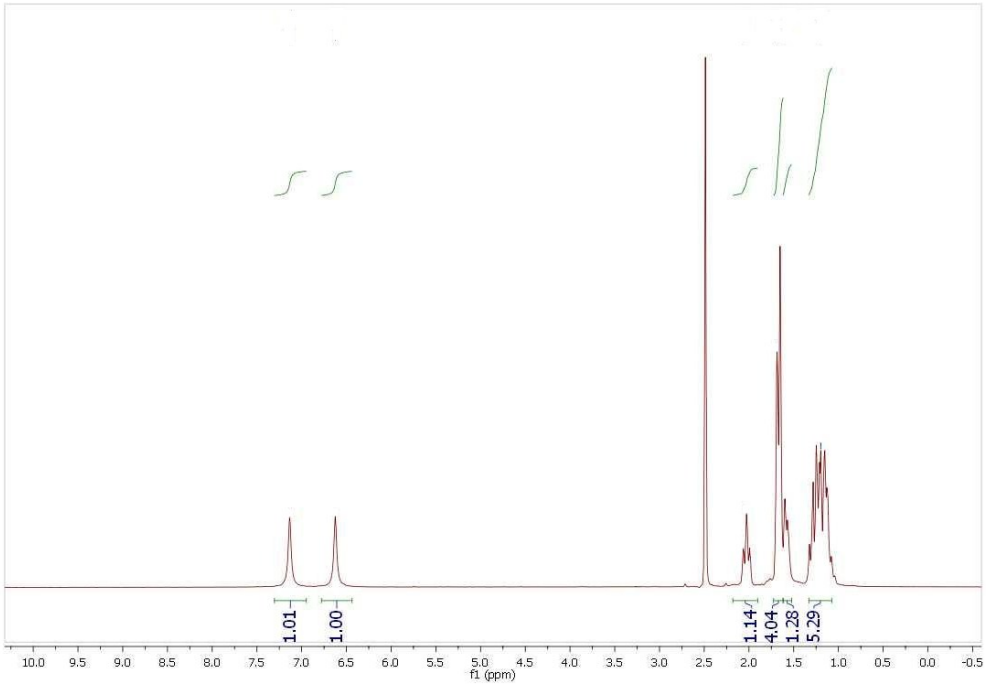
f1 (ppm)


O
NH2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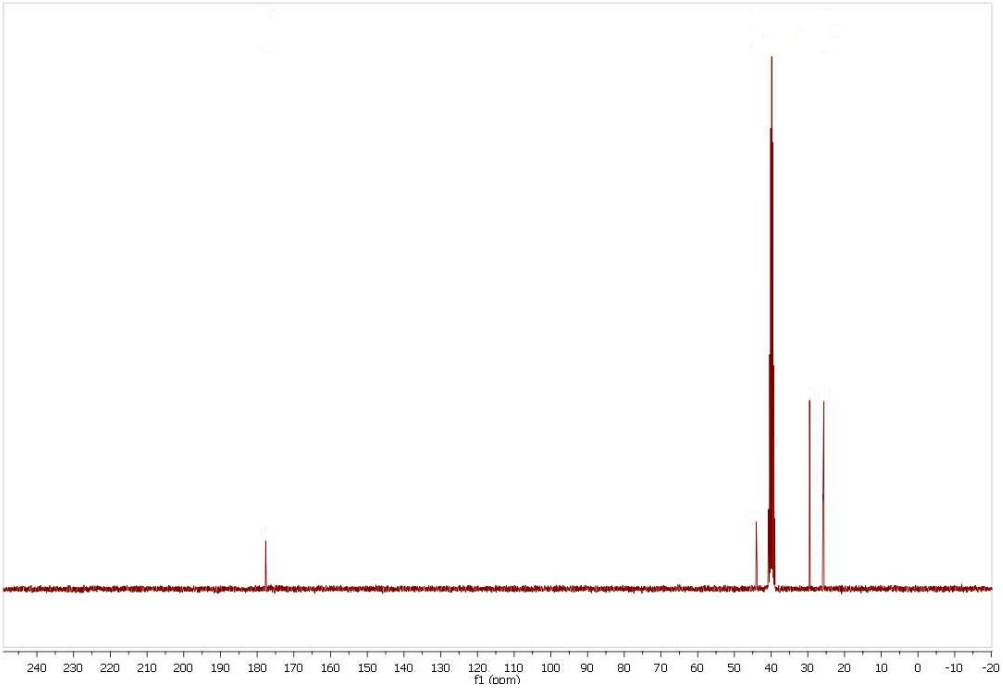
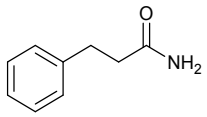
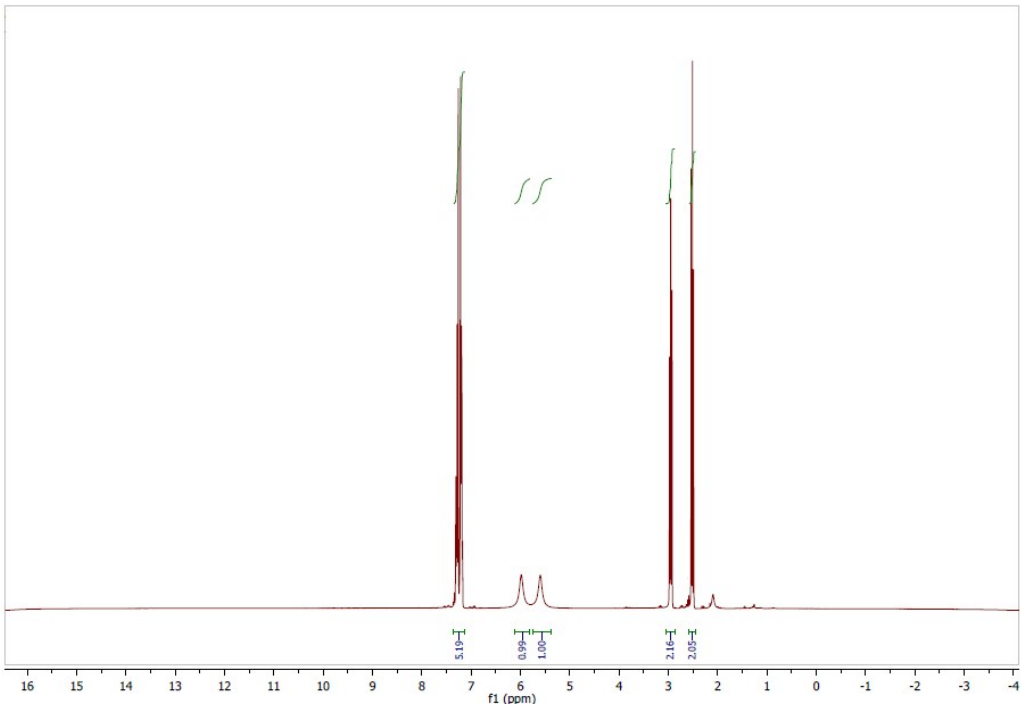
1.00
1.14
4.04
1.28
5.29
f1 (ppm)


f1 (ppm)


O
NH2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2.16
2.05
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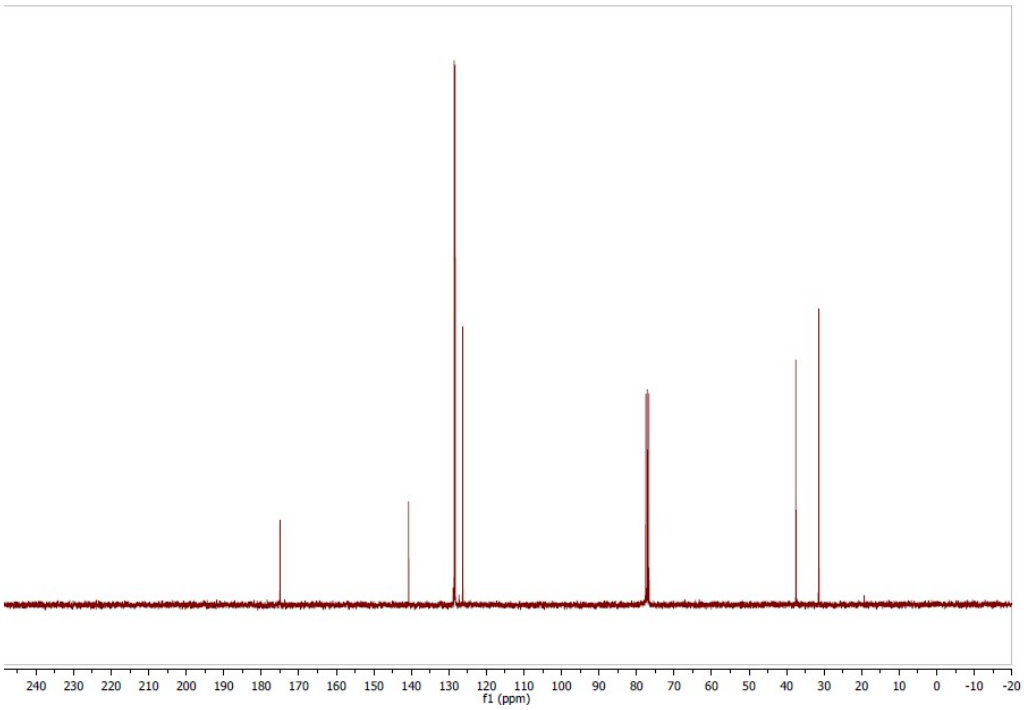
f1 (ppm)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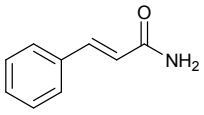
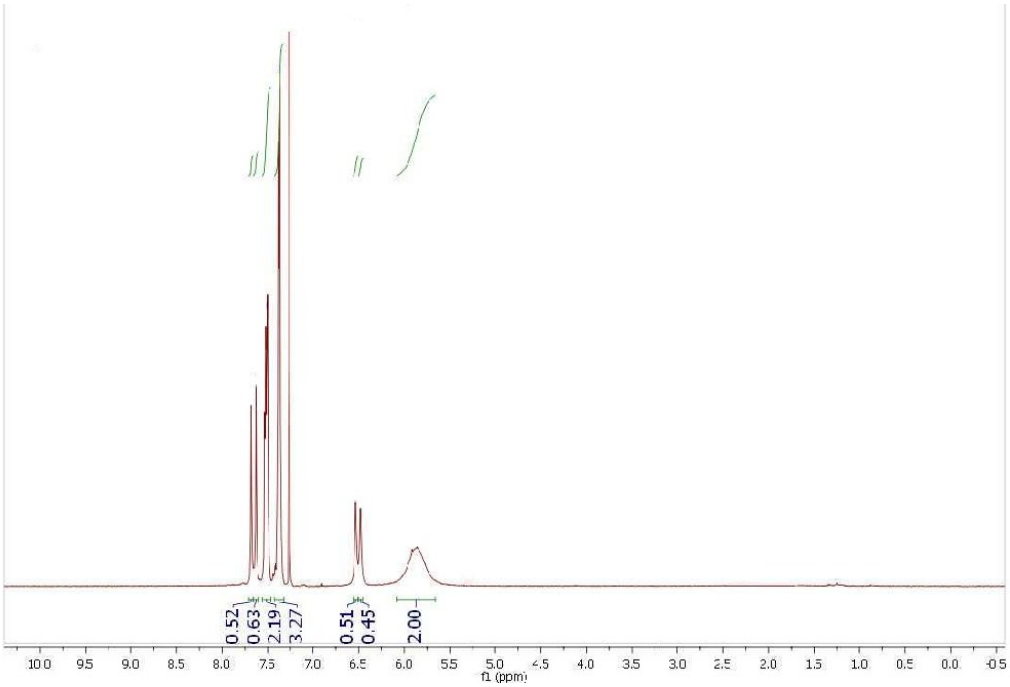
f1 (ppm)


O
NH2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0.45
2.00
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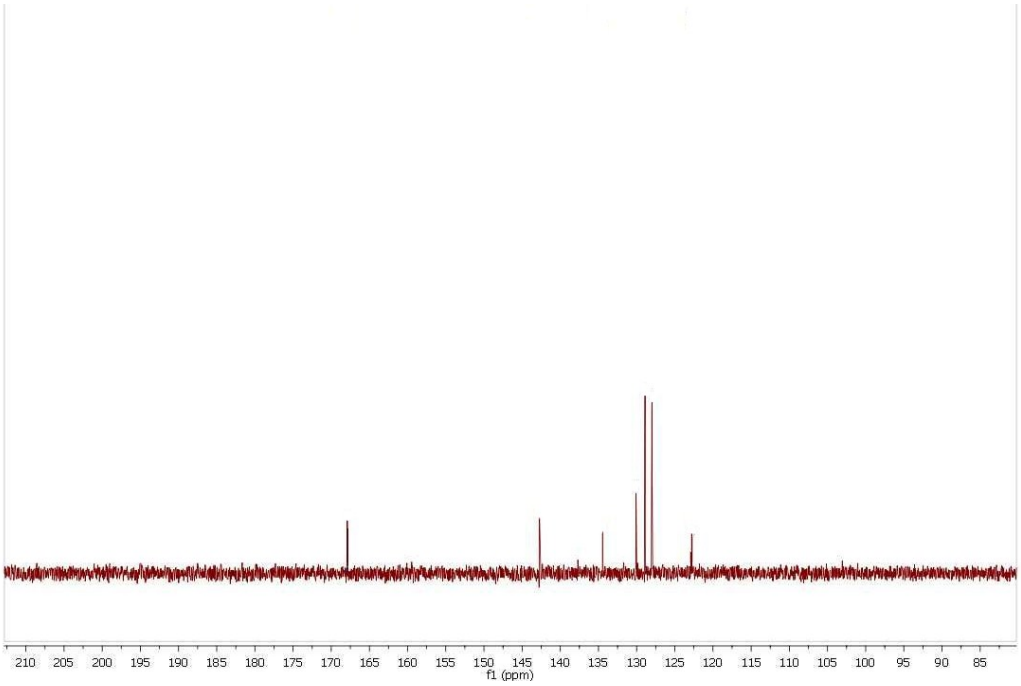
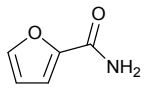
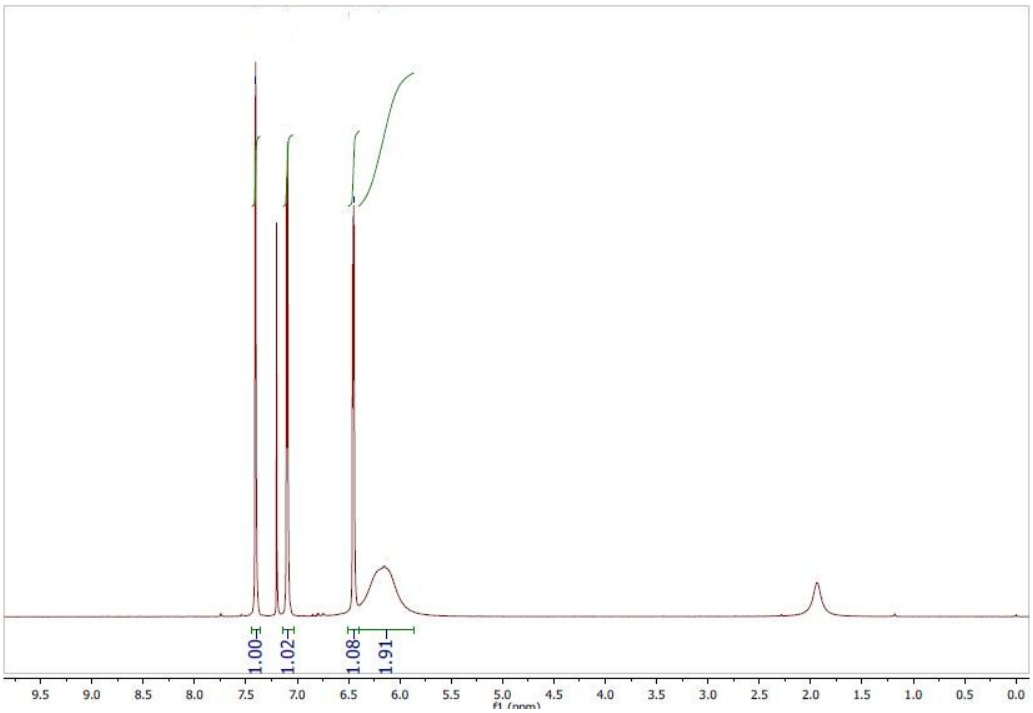
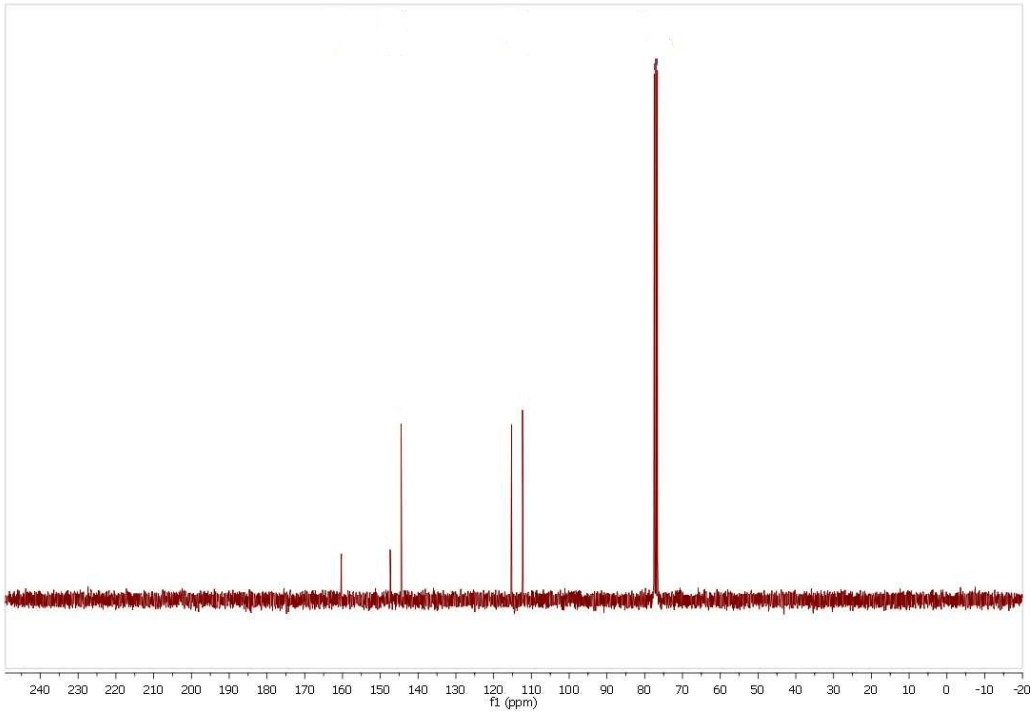

f1 (ppm)


O
O
NH2


1.00
1.02
1.08
1.91
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
f1 (ppm)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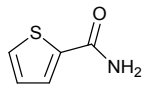
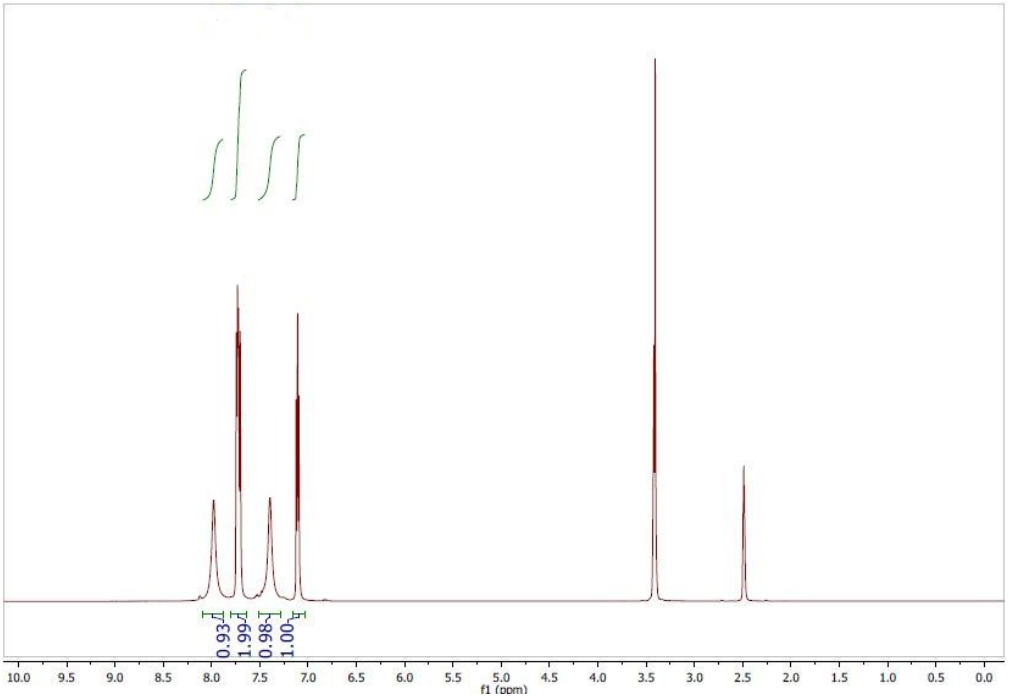
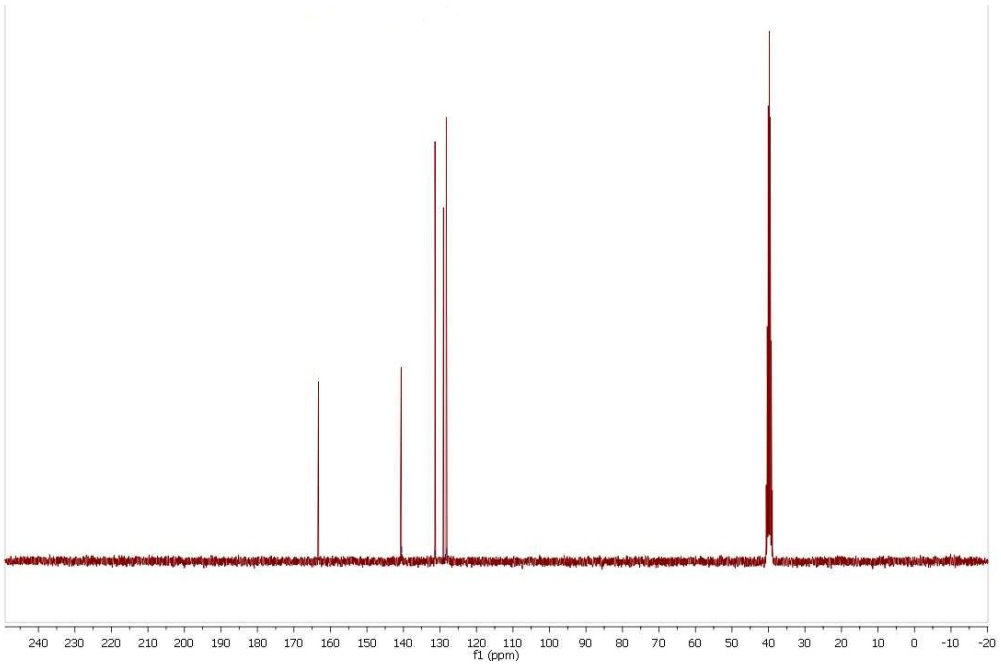
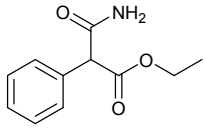
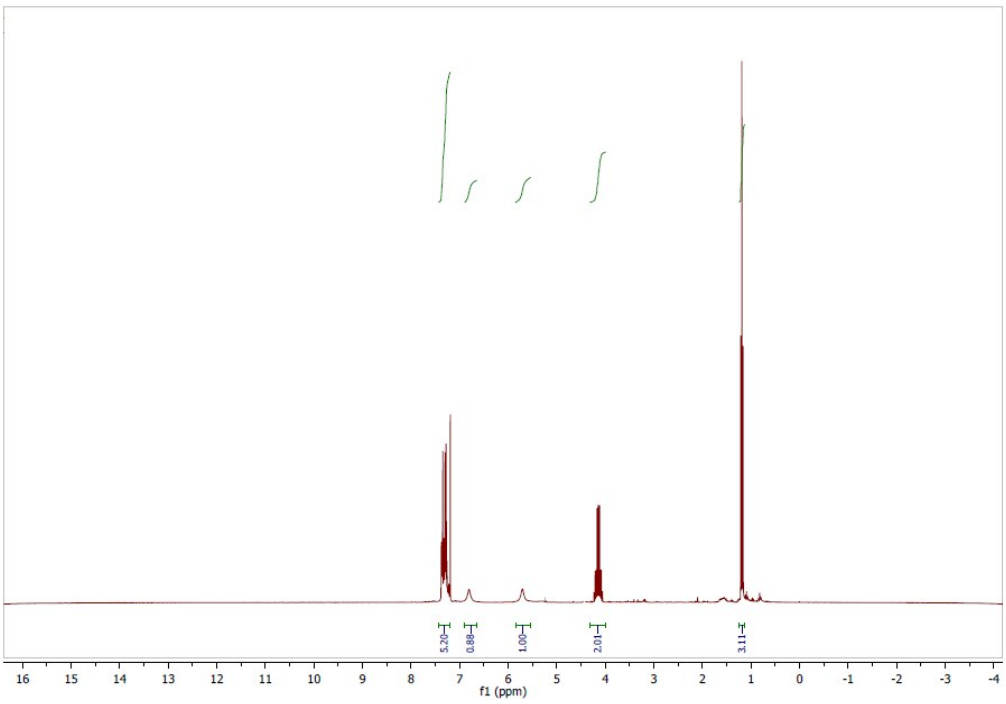
f1 (ppm)

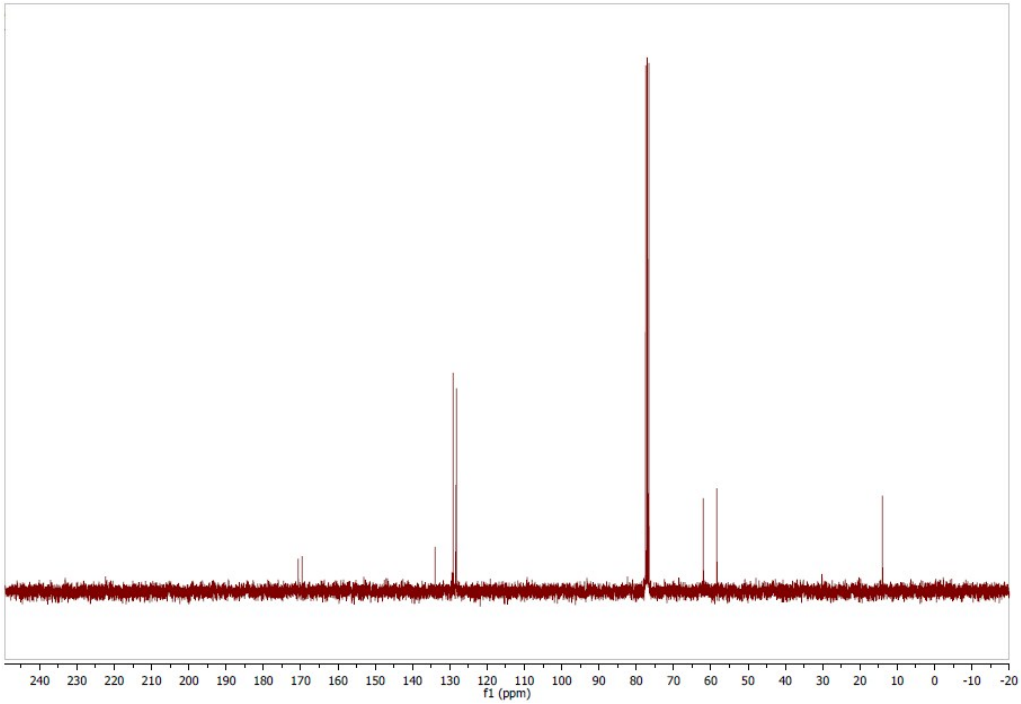

O
S
NH2


0.93
1.99
0.98
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 0.0
f1 (ppm)


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O
NH2
O
O
O


5.20
0.88
1.00
2.01
3.11
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)