Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

Conversion of Nitroalkanes into Carboxylic Acids *via* Iodide Catalysis in Water

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TABLE OF CONTENTS

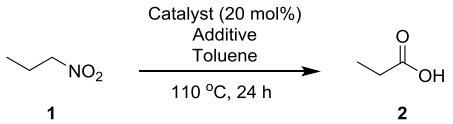
General Remarks

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 300 spectrometer in $CDCl_3$ as solvent. Chemical shifts (δ) were referenced internally to residual protic solvent signal for $CDCl_3$ (7.26 ppm). Multiplicities are presented as singlet (s), doublet (d), triplet (t), quadruplet (q) and, multiplet (m). Coupling constants, (J) were expressed in Hertz (Hz). HRMS-ESI were run on an Agilent® 1200 Series LC/MSD. Infra-red spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer, the relevant absorbances are quoted as ν in cm^{-1}. Uncorrected melting points were determined using Stuart SMP10 melting point equipment using closed end glass capillary.

OPTIMIZATION OF THE REACTION CONDITIONS

General procedure for the optimization of the synthesis of propionic acid.
1-Nitropropane (89 μL, 1 mmol) and toluene (1 mL) were charged into a carousel tube followed by the addition of the corresponding catalyst (20 mol%) and the additive. After heating the reaction at 110 °C for 24 h, the reaction mixture was acidified with 5 mL of 2 M HCl and extracted with ethyl acetate. The organic phase was collected and dried using $MgSO_4$. The organic solvent was removed under vacuum and the crude reaction was analysed by ^{1}H-NMR.

Table S1. Optimization of the catalyst and conditions.



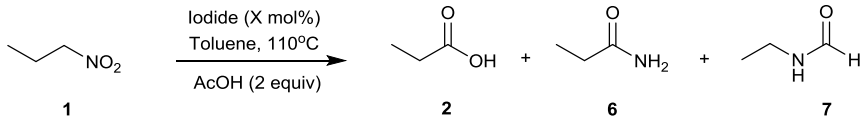
1 2

Entry	Catalyst	Additive[b]	Conversion (%)[a]
1	CuO	AcOH	0
2	$Cu(OAc)_2$	AcOH	2-4
3	$CuCl_2$	AcOH	0
4	$ZnCl_2$	AcOH	0
5	$Zn(OAc)_2$	AcOH	2-4
6	ZnI_2	AcOH	100
7	ZnI_2	--	60
8	ZnI_2	AcOH[c]	50
9	ZnI_2	HCl[d]	44
10	--	AcOH	0

a) Conversions were determined by analysis of the ^{1}H-NMR spectra; b) 2 equiv. of additive were used; c) 4 equiv. of additive were used; d) 1 equiv. of additive was used.

General procedure for the study of the iodide source in the synthesis of propionic acid.
1-Nitropropane (89 μL, 1 mmol) and toluene (1 mL) were charged into a carousel tube followed by the addition of the corresponding iodide source and AcOH (0.12 mL, 2 mmol). After heating the reaction at 110 ^{o}C for 24 h, the reaction mixture was acidified with 5 mL of 2 M HCl and extracted with ethyl acetate. The organic phase was collected and dried using $MgSO_4$. The organic solvent was removed under vacuum and the crude reaction was analysed by ^{1}H-NMR.

Table S2. Screen of different iodide sources.



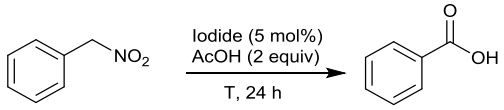
1 **2** **6** **7**

Entry	I^-	mol%	Conversion (%)[a]	**2**	**6**	**7**
1	KI	100	100	70	20	10
2	NaI	100	66	44	22	-
3	MgI_2	100	100	75	25	-
4	LiI	100	75	57	18	-
5	I_2	100	-	-	-	-
6	TBAI	100	100	80	10	10
7	TBAI	5	100	90	5	5
8	KI	5	100	70	20	10
9	LiI	20	60	54	6	-
10	-	-	-	-	-	-

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

General procedure to study the effect of the solvent in the synthesis of benzoic acid.
1-Nitromethylbenzene (137 mg, 1 mmol) and the solvent (1 mL) were charged into a carousel tube followed by the addition of the iodide source (5 mol%) and AcOH (0.12 mL, 2 mmol). The reaction was heated at the temperature detailed in table S3 for 24 h. The reaction mixture was acidified with 5 mL of 2 M HCl and extracted with ethyl acetate. The organic phase was collected and dried using $MgSO_4$. The organic solvent was removed under vacuum and the crude reaction was analysed by ^{1}H-NMR.

Table S3. Solvent screen using KI and TBAI as iodide source.

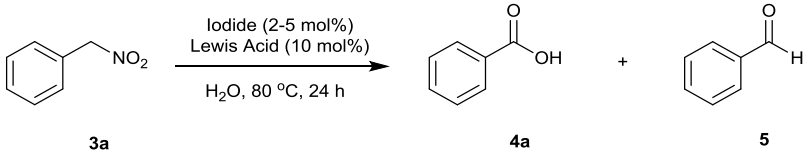


Entry	Iodide	Solvent	Temperature (°C)	Conversion (%)[a]
1	KI	Tol	110	55
2	TBAI	Tol	110	62
3	KI	EtOAc	80	-
4	TBAI	EtOAc	80	-
5	KI	DCM	40	-
6	TBAI	DCM	40	-
7	KI	MeCN	80	30
8	TBAI	MeCN	80	27
9	KI	H_2O	80	40
10	TBAI	H_2O	80	80
11[b]	TBAI	H_2O	80	77
12	KI	Et_2O	40	5
13	TBAI	Et_2O	40	6

a) Conversions were determined by the analysis of the ^{1}H-NMR spectra; b) The reaction was performed in the absence of AcOH

General procedure to study the effect of Lewis acid in the synthesis of benzoic acid.
1-Nitromethylbenzene (137 mg, 1 mmol) and water (1 mL) were charged into a carousel tube followed by the addition of Lewis acid (10 mol%) and TBAI (2 - 5 mol%). After heating the reaction at 80 ^{o}C for 24 h, the reaction mixture was acidified with 5 mL of 2 M HCl and extracted with ethyl acetate. The organic phase was collected and dried using $MgSO_4$. The organic solvent was removed under vacuum and the crude reaction was analysed by ^{1}H-NMR.

Table S4. Lewis acid screening.

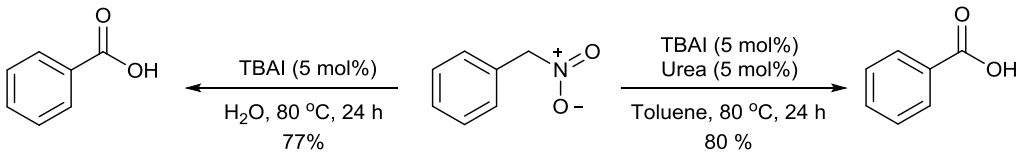


3a **4a** **5**

Entry	TBAI (mol%)	Lewis acid (mol%)	Conversion (%)[a]
1	--	--	0
2	5	-	77
3	2	-	76
4	2	$Zn(OAc)_2$	100 **4a**:**5** 95:5
5	2	Cu(OAc)	100 **4a**:**5** 80:20
6	2	$ZnCl_2$	88
7	2	$CuCl_2$	84

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

Synthesis of benzoic acid in the presence of urea

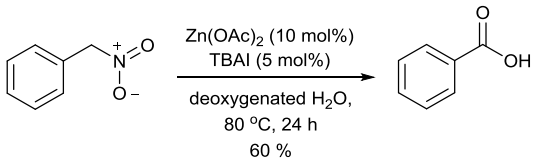


1-Nitromethylbenzene (137 mg, 1 mmol) and toluene (1 mL) were added into a carousel tube, followed by the addition of TBAI (19 mg, 5 mol%) and urea (3 mg, 5 mol%). After heating the reaction at 80 °C for 24 hours, the reaction mixture was acidified with 5 mL of 2 M HCl and extracted with ethyl acetate. The organic phase was collected and dried using $MgSO_4$. The organic solvent was removed under vacuum and the crude reaction was analysed by ^{1}H-NMR. Benzoic acid was afforded in 80% conversion.

When this transformation was carried out using toluene as solvent, benzoic acid was recovered in 60% conversion (Table S3, entry 2). The outcome of the reaction was improved by the addition of urea to the reaction. This result was comparable to the use of water as solvent (Table S4, entry 2).

MECHANISTIC INSIGHTS

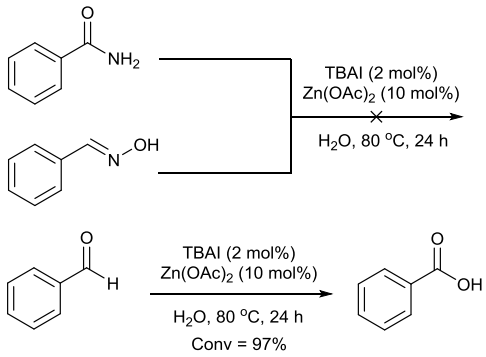
Conversion of nitromethylbenzene into benzoic acid under anaerobic conditions



Following the general procedure for the synthesis of benzoic acid, nitromethylbenzene was converted into benzoic acid under anaerobic conditions. For that purpose, all the glassware was purged with argon and the water was deoxygenated by bubbling argon through for 3 h. After heating the reaction at 80 °C for 24 h, the reaction mixture was acidified with 5 mL of 2 M HCl and extracted with ethyl acetate. The organic phase was collected and dried using $MgSO_4$. The organic solvent was removed under vacuum and the crude reaction was analysed by ^{1}H-NMR affording the benzoic acid in 60% conversion.

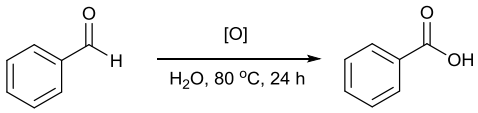
For comparison: standard reaction conditions led to the formation of benzoic acid in 95% conversion (Table S4, entry 4)

Study of the plausible intermediates



Following the general procedure for the synthesis of benzoic acid, benzamide (121 mg, 1 mmol), benzaldehyde (1 mL, 1 mmol), and benzaldehyde oxime (121 mg, 1 mmol) were treated with TBAI and $Zn(OAc)_2$. No reaction took place when benzamide and benzaldehyde oxime were employed. Benzaldehyde gave the benzoic acid in 97% conversion.

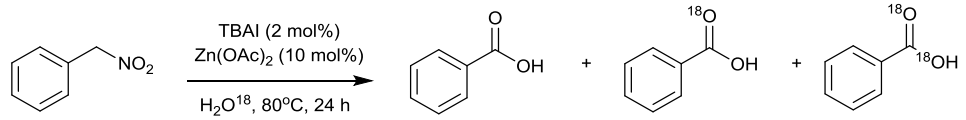
Oxidation of benzaldehyde[a]



Entry	TBAI (mol%)	$Zn(OAc)_2$ (mol%)	Conversion (%)[b]
1	2	--	90
2	--	10	80
3	--	--	96

a) Reactions carried out using 1 mmol of benzaldehyde; b) conversions were determined by the analysis of the ^{1}H-NMR spectra.

Studies with isotopically labelled H_2O^{18}



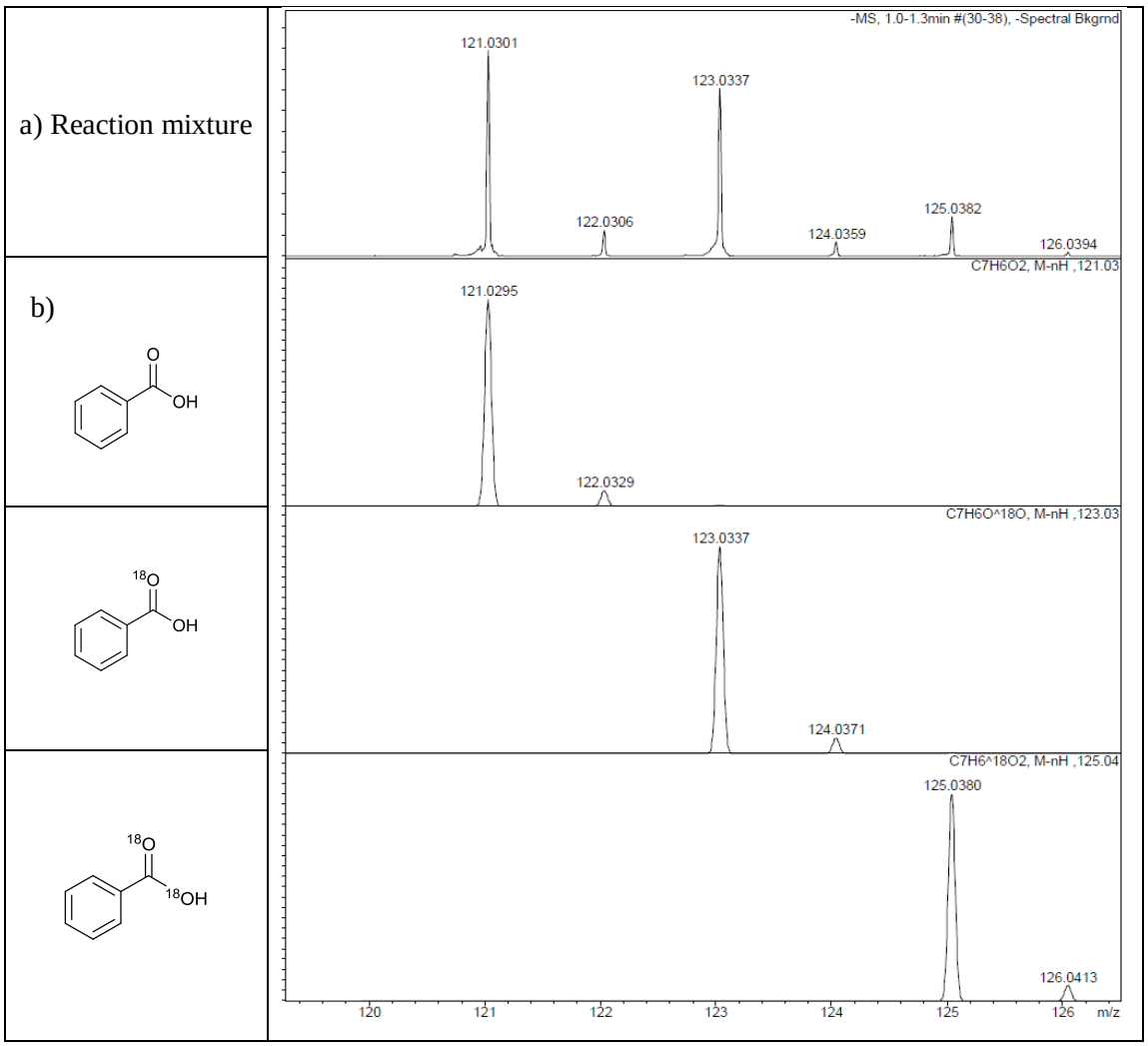


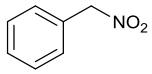
Figure S1. a) ESI-HRMS of the reaction mixture; b) comparison to the simulated peaks of the possible ^{18}O-labelled benzoic acid.

SYNTHESIS OF THE STARTING MATERIALS

General procedure for the synthesis of nitro compounds.[1]

Silver nitrite (2.3 g, 13 mmol) was added to a round bottom flask covered in tin foil containing anhydrous diethyl ether (26 mL). After stirring at room temperature for 15 minutes, the mixture was then cooled at 0 °C. A solution of benzylbromide (10 mmol) in diethyl ether (1.7 mL) was added dropwise *via* addition funnel. The reaction was stirred at 0 °C for 1 h and then heated to reflux for 4 h. The mixture was filtered over Celite using ethyl acetate as eluent. The product was purified by column chromatography on silica gel (eluting with 90:10 hexane/ethyl acetate unless otherwise stated).

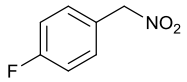
(Nitromethyl)benzene[2]



Benzyl bromide (1.71 g, 10 mmol) was used as alkyl halide. (Nitromethyl)benzene was recovered after purification by column chromatography as clear oil (1.16 g, 85%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.50 - 7.45 (m, 5H, aromatic), 5.44 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 130.1, 130.0, 129.7, 129.1, 80.07; HRMS-ESI calcd for $[C_7H_6NO_2]^-$: 136.0398 $[M-H]^-$. Found 136.0393; FT-IR (neat) ν in cm^{-1}: 1555.

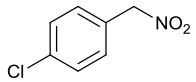
4-Fluoro-(nitromethyl)benzene[3]



4-Fluorobenzyl bromide (1.9 g, 10 mmol) was used as alkyl halide. 4-Fluoro-(nitromethyl)benzene was recovered after purification by column chromatography as clear oil (0.34 g, 87%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.48 – 7.42 (m, 2H, aromatic), 7.18 – 7.09 (m, 2H, aromatic), 5.42 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 163.7 (d, J = 250.7 Hz), 132.1 (d, J = 9.1 Hz), 125.6, 116.2 (d, J = 21.9 Hz), 79.1; HRMS-ESI calcd for $[C_7H_5FNO_2]^-$: 155.0304 $[M-H]^-$. Found 155.0323; FT-IR (neat) ν in cm^{-1}: 1566.

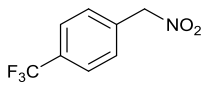
4-Chloro-(nitromethyl)benzene[4]



4-Chlorobenzyl bromide (2.0 g, 10 mmol) was used as alkyl halide. 4-Chloro-(nitromethyl)benzene was recovered after purification by column chromatography as a white solid (1.4 g, 82%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.38 - 7.32 (m, 4H), 5.40 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 136.3, 131.4, 129.4, 128.0, 79.1; HRMS-ESI calcd for $[C_7H_5ClNO_2]^-$: 170.0008 $[M-H]^-$. Found 169.9998; FT-IR (neat) ν in cm^{-1}: 1555; m.p. 30 - 33 °C

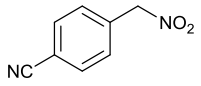
4-Trifluoromethyl-(nitromethyl)benzene[4]



4-(Trifluoromethyl)benzyl bromide (2.4 g, 10 mmol) was used as alkyl halide. 4-Trifluoromethyl-(nitromethyl)benzene was recovered after purification by column chromatography as white solid (1.81 g, 89%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.70 (d, J = 6.2 Hz, 2H, aromatic), 7.61 (d, J = 6.2 Hz, 2H, aromatic), 5.51 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 133.2, 132.2 (q, J = 33.3 Hz), 129.9, 126.4 (q, J = 3.9 Hz), 124.1 (q, J = 272.6 Hz) 79.2; HRMS-ESI calcd for $[C_8H_5F_3NO_3]^-$: 204.0272 $[M-H]^-$. Found 204.0286; FT-IR (neat) ν in cm^{-1}: 1560; m.p. 40 - 42 °C

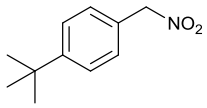
4-Cyano-(nitromethyl)benzene[5]



4-Cyanobenzyl bromide (1.96 g, 10 mmol) was used as alkyl halide. 4-Cyano-(nitromethyl)benzene was recovered after purification by column chromatography as a white solid (1.47 g, 91%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.73 (d, *J* = 6.7 Hz, 2H, aromatic), 7.60 (d, *J* = 6.7 Hz, 2H, aromatic), 5.50 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 134.2, 132.8, 130.9, 117.9, 114.1, 79.0; HRMS-ESI calcd for $[C_8H_5N_2O_2]^-$: 161.0357 $[M-H]^-$. Found 161.0305; FT-IR (neat) ν in cm^{-1}: 1571; m.p. 95 - 98 °C.

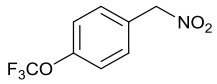
1-*tert*-Butyl-4-(nitromethyl)benzene[6]



4-*tert*-Butylbenzyl bromide (2.27 g, 10 mmol) was used as alkyl halide. 1-*tert*-Butyl-4-(nitromethyl)benzene was recovered after purification by column chromatography as clear solid (1.29 g, 67%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.45 (d, *J* = 9.0 Hz, 2H, aromatic), 7.39 (d, *J* = 9.0 Hz, 2H, aromatic), 5.42 (s, 2H, CH_2), 1.33 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 153.3, 129.7, 126.8, 126.0, 79.8, 34.8, 31.2; HRMS-ESI calcd for $[C_{11}H_{14}NO_2]^-$: 192.1024 $[M-H]^-$. Found 192.1040; FT-IR (neat) ν in cm^{-1}: 1544; m.p. 30 - 31 °C.

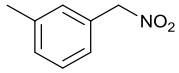
4-Trifluoromethoxy-(nitromethyl)benzene



4-(Trifluoromethoxy)benzyl bromide (2.55 g, 10 mmol) was used as alkyl halide. 4-Trifluoromethoxy-(nitromethyl)benzene was recovered after purification by column chromatography as clear oil (1.98 g, 90%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.43 (d, *J* = 6.2 Hz, 2H, aromatic), 7.23 (d, *J* = 6.2 Hz, 2H, aromatic), 5.37 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 150.4, 131.8, 128.2, 121.4, 120.4 (q, *J* = 258.1 Hz), 79.0; HRMS-ESI calcd for $[C_8H_5F_3NO_3]^-$: 220.0221 $[M-H]^-$. Found 220.0218; FT-IR (neat) ν in cm^{-1}: 1558.

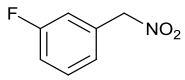
3-Methyl-(nitromethyl)benzene[7]



3-Methylbenzyl bromide (1.85 g, 10 mmol) was used as alkyl halide. 3-Methyl-(nitromethyl)benzene was recovered after purification by column chromatography as clear oil (1.28 g, 85%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.27 – 7.20 (m, 4H, aromatic), 5.43 (s, 2H, CH_2), 2.39 (s, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 135.0, 131.2, 130.4, 130.3, 128.2, 80.1, 21.2; HRMS-ESI calcd for $[C_8H_8NO_2]^-$: 150.0561 $[M-H]^-$. Found 150.0572; FT-IR (neat) ν in cm^{-1}: 1557.

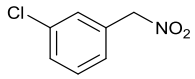
3-Fluoro-(nitromethyl)benzene[7]



3-Fluorobenzyl bromide (1.9 g, 10 mmol) was used as alkyl halide. 3-Fluoro-(nitromethyl)benzene was recovered after purification by column chromatography as clear oil (1.41 g, 91%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.48 - 7.40 (m, 1H, aromatic), 7.30 - 7.12 (m, 3H, aromatic), 5.43 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 162.8 (d, J = 247.6 Hz), 131.6 (d, J = 7.6 Hz), 130.8 (d, J = 7.6 Hz), 125.6 (d, J = 7.6 Hz), 117.3 (d, J = 6 Hz), 79.3; HRMS-ESI calcld for $[C_7H_5FNO_2]^-$: 154.0304 $[M-H]^-$. Found 154.0310; FT-IR (neat) ν in cm^{-1}: 1549.

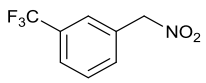
3-Chloro-(nitromethyl)benzene[7]



3-Chlorobenzyl bromide (2.05 g, 10 mmol) was used as alkyl halide. 3-Chloro-(nitromethyl)benzene was recovered after purification by column chromatography as clear oil (1.50 g, 88%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.52 - 7.23 (m, 4H, aromatic), 5.38 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 135.0, 131.3, 130.4, 130.3, 130.2, 128.2, 79.2; HRMS-ESI calcd for $[C_7H_6ClNO_2]^-$: 170.0014 $[M-H]^-$. Found 170.01; FT-IR (neat) ν in cm^{-1}: 1542.

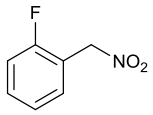
3-Trifluoromethyl-(nitromethyl)benzene[7]



3-(Trifluoromethyl)benzyl bromide (2.4 g, 10 mmol) was used as alkyl halide. 3-Trifluoromethyl-(nitromethyl)benzene was recovered after purification by column chromatography as clear solid (1.88 g, 92%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.70 - 7.40 (m, 4H, aromatic), 5.38 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 133.5, 132.0 (q, J = 32.5 Hz), 130.9 (q, J = 9 Hz), 130.1, 129.0, 127.0, 123.6 (q, J = 272.6 Hz), 79.1; HRMS-ESI calcd for $[C_8H_5F_3NO_2]^-$: 204.0272 $[M-H]^-$. Found 204.0285; FT-IR (neat) ν in cm^{-1}: 1563; m.p. 41-44 °C.

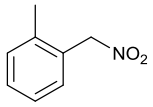
2-Fluoro-(nitromethyl)benzene



2-Fluorobenzyl bromide (1.9 g, 10 mmol) was used as alkyl halide. 2-Fluoro-(nitromethyl)benzene was recovered after purification by column chromatography as clear oil (1.31 g, 85%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.50 - 7.38 (m, 2H, aromatic), 7.60 - 7.12 (m, 2H, aromatic), 5.50 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 161.4 (q, *J* = 250.7 Hz), 132.4 (d, *J* = 8.3 Hz), 132.2 (d, *J* = 3.0 Hz), 124.7 (d, *J* = 3.8 Hz), 117.3 (d, *J* = 15.1 Hz), 115.9 (d, *J* = 19.6 Hz), 73.0; HRMS-ESI calcd for $[C_7H_5FNO_2]^-$: 154.0304 $[M-H]^-$. Found 154.0316; FT-IR (neat) ν in cm^{-1}: 1568.

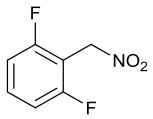
2-Methyl-(nitromethyl)benzene[7]



2-Methylbenzyl bromide (1.85 g, 10 mmol) was used as alkyl halide. 2-Methyl-(nitromethyl)benzene was recovered after purification by column chromatography as clear oil (1.34 g, 89%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.39 - 7.34 (m, 2H, aromatic), 7.32 - 7.25 (m, 2H, aromatic), 5.51 (s, 2H, CH_2), 2.42 (s, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 138.2, 131.5, 130.9, 130.3, 128.3, 126.6, 77.7, 19.1; HRMS-ESI calcd for $[C_8H_8NO_2]^-$: 150.0561 $[M-H]^-$. Found 150.0566; FT-IR (neat) ν in cm^{-1}: 1546.

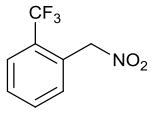
2,6-Difluoro-(nitromethyl)benzene



2,6-Difluorobenzyl bromide (2.05 g, 10 mmol) was used as alkyl halide. 2,6-Difluoro-(nitromethyl)benzene was recovered after purification by column chromatography as clear oil (1.38 g, 80%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.53 - 7.41 (m, 3H, aromatic), 7.00 (t, *J* = 9 Hz, 2H, aromatic), 5.60 - 5.67 (m, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 161.7 (d, *J* = 246.9 Hz,), 132.6 (d, *J* = 10.6 Hz), 111.7 (dd, *J* = 11.3, *J* = 2.3 Hz), 106.6 (t, *J* = 18.9 Hz), 66.3; HRMS-ESI calcd for $[C_7H_4F_2NO_2]^-$: 172.0216 $[M-H]^-$. Found 172.0155; FT-IR (neat) ν in cm^{-1}: 1572.

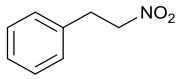
2-Trifluoromethyl-(nitromethyl)benzene[7]



2-(Trifluoromethyl)benzyl bromide (2.4 g, 10 mmol) was used as alkyl halide. 2-Trifluoromethyl-(nitromethyl)benzene was recovered after purification by column chromatography as clear oil (1.74 g, 85%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C) δ 7.83 - 7.52 (m, 4H, aromatic), 5.68 (s, 2H, CH_2); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 133.8, 132.6, 130.2 (q, *J* = 19.6 Hz), 129.5, 129.3 (d, *J* = 10.5 Hz), 126.5 (q, *J* = 5.3 Hz), 123.8 (q, *J* = 273.3 Hz), 75.8; HRMS-ESI calcd for $[C_8H_5F_3NO_2]^-$: 204.0272 $[M-H]^-$. Found 204.0272; FT-IR (neat) ν in cm^{-1}: 1561.

1-Nitro-3-phenylethane



1-Nitro-3-phenylethane was obtained by Henry reaction between benzaldehyde and nitromethane followed by reduction with $NaBH_4$ as reported.[8]

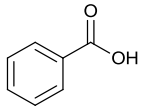
1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H, aromatic), 7.31 – 7.28 (m, 1H, aromatic), 7.24 – 7.22 (m, 2H, aromatic), 4.61 (t, *J* = 7.4 Hz, 1H), 3.32 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.7, 128.9, 128.6, 127.4, 76.25; HRMS-ESI calcd for $[C_8H_8NO_2]^-$: 150.0561 $[M-H]^-$. Found 150.0559.

SYNTHESIS OF CARBOXYLIC ACIDS

General procedure for the synthesis of carboxylic acids

The nitroalkane (1 mmol) and water (1 mL) were added in a carousel tube followed by the addition of TBAI (2 mol%) and zinc acetate (10 mol%). The reaction mixture was heated to 80 °C for 24 hours. The resulting reaction mixture was cooled down and acidified with 2 M HCl. The acidic solution was washed with dichloromethane (2 x 20 mL). The organic phases were collected and washed with a saturated solution of sodium bicarbonate (2 x 20 mL). The aqueous washes were acidified with HCl_{conc} and washed with dichloromethane (2 x 20mL). The organic layers were collected and concentrated under reduced pressure. The carboxylic acids were isolated as pure products and they were analysed by ^{1}H and ^{13}C NMR and mass spectrometry.

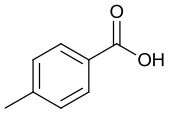
Benzoic acid[9]



Following the general procedure described above, benzoic acid was obtained as a white solid (0.98 g, 81%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 11.43 (br s, 1H, OH), 8.15 (d, *J* = 6.0 Hz, 2H, aromatic), 7.63 (t, *J* = 6.0 Hz, 1H, aromatic), 7.49 (t, *J* = 6.0 Hz, 2H, aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 172.5, 133.8, 130.2, 129.3, 128.5; HRMS-ESI calcd for $[C_7H_5O_2]^-$: 121.0289 [M-H]$^-$. Found 121.0300; FT-IR (neat) ν in cm^{-1}: 1673; m.p. 120 - 121 °C.

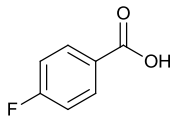
4-Methylbenzoic acid[9]



Following the general procedure described above, 4-methylbenzoic acid was obtained as a white solid (0.125 g, 92%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 7.95 (d, *J* = 9.0 Hz, 2H, aromatic), 7.21 (d, *J* = 9.0 Hz, 2H, aromatic), 2.36 (s, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 172.3, 144.6, 130.3, 129.2, 126.6, 21.8; HRMS-ESI calcd for $[C_8H_7O_2]^-$: 135.0446 [M-H]$^-$. Found 135.0443; FT-IR (neat) ν in cm^{-1}: 1681; m.p. 174 - 177 °C.

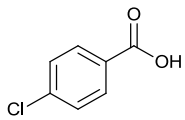
4-Fluorobenzoic acid[10]



Following the general procedure described above, 4-fluorobenzoic acid was obtained as a white solid (0.12 g, 89%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 8.27 - 8.03 (m, 2H, aromatic), 7.23 - 7.03 (m, 2H, aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 171.0, 166.4 (d, *J* = 255.3 Hz), 132.9 (d, *J* = 9.6 Hz), 125.5 (d, *J* = 2.9 Hz), 115.7 (d, *J* = 22.1 Hz); HRMS-ESI calcd for $[C_7H_4FO_2]^-$: 139.0195 [M-H]$^-$. Found 139.0180; FT-IR (neat) ν in cm^{-1}: 1684; m.p. 182 - 183 °C.

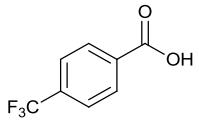
4-Chlorobenzoic acid[9]



Following the general procedure described above, 4-chlorobenzoic acid was obtained as a white solid (0.138 g, 88%).

^{1}H NMR (300 MHz, d_6-DMSO, 25 °C) δ 13.19 (br s, 1H, OH), 7.94 (d, *J* = 6.2 Hz, 2H, aromatic), 7.59 (d, *J* = 6.2 Hz, 2H, aromatic); ^{13}C NMR (75.5 MHz, d_6-DMSO, 25 °C) δ 166.8, 138.1, 131.5, 130.0, 129.1; HRMS-ESI calcd for $[C_7H_4FO_2]^-$: 154.9900 [M-H]$^-$. Found 154.9689; FT-IR (neat) ν in cm^{-1}: 1683; m.p. 236 - 237 °C.

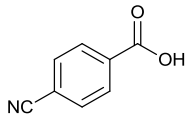
4-(Trifluoromethyl)benzoic acid[11]



Following the general procedure described above, 4-(trifluoromethyl)benzoic acid was obtained as a white solid (0.14 g, 76%).

^{1}H NMR (300 MHz, d_6-DMSO, 25 ^{o}C) δ 13.46 (br s, 1H, OH), 8.13 (d, *J* = 6.2 Hz. 2H, aromatic), 7.89 (d, *J* = 6.2 Hz, 2H, aromatic); ^{13}C NMR (75.5 MHz, d_6-DMSO, 25 ^{o}C) δ 166.5, 135.0, 132.8 (q, *J* = 31.7 Hz), 130.5, 126.0, 122.4; HRMS-ESI calcd for $[C_8H_4F_3O_2]^-$: 189.0163 $[M-H]^-$. Found 189.0111; FT-IR (neat) ν in cm^{-1}: 1699; m.p. 210 - 211 ^{o}C.

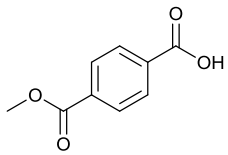
4-Cyanobenzoic acid[11]



Following the general procedure described above, 4-cyano-benzoic acid was obtained as a white solid (0.12 g, 81%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 13.56 (br s, 1H, OH), 8.07 (d, *J* = 9.0 Hz, 2H, aromatic), 8.00 (d, *J* = 9.0 Hz, 2H, aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 166.4, 135.2, 133.0, 130.3, 118.5, 115.4; HRMS-ESI calcd for $[C_8H_4NO_2]^-$: 146.0242 $[M-H]^-$. Found 146.0070; FT-IR (neat) ν in cm^{-1}: 1711; m.p. 217 - 218 ^{o}C.

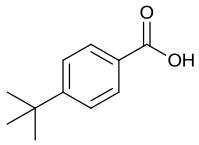
Methyl 4-carboxybenzoate[11]



Following the general procedure described above, methyl 4-carboxybenzoate was recovered as a white solid (0.167 g, 93%).

^{1}H NMR (300 MHz, d_6-DMSO, 25 ^{o}C) δ 8.07 (s, 4H, aromatic), 3.89 (s, 3H, aromatic); ^{13}C NMR (75.5 MHz, d_6-DMSO, 25 ^{o}C) δ 166.9, 166.0, 135.2, 133.5, 129.9, 129.7, 52.8; HRMS-ESI calcd for $[C_9H_7O_4]^-$: 179.0083 $[M-H]^-$. 179.0344; FT-IR (neat) ν in cm^{-1}: 1720, 1689; m.p. 219 - 221 ^{o}C.

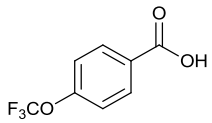
4-*tert*-Butyl benzoic acid[9]



Following the general procedure described above, 4-*tert*-butyl benzoic acid was obtained as a white solid (0.087 g, 50%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 7.99 (d, *J* = 9.0 Hz, 2H, aromatic), 7.44 (d, *J* = 9.0 Hz, 2H, aromatic), 1.28 (s, 9H, $C(CH_3)_3$); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 172.0, 157.6, 130.1, 126.5, 125.5, 35.2, 31.1; HRMS-ESI calcd $[C_{11}H_{13}O_2]^-$: 177.0916 $[M-H]^-$. Found 177.0857; FT-IR (neat) ν in cm^{-1}: 1684; m.p. 163 - 164 °C.

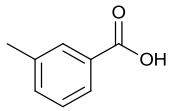
4-(Trifluoromethoxy)benzoic acid[12]



Following the general procedure described above 4-(trifluoromethoxy)benzoic acid was obtained as a white solid (0.159 g, 77%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 8.11 (d, *J* = 9.0 Hz, 2H, aromatic), 7.25 (d, *J* = 9.0 Hz, 2H, aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 173.8, 135.4, 132.3, 127.6, 120.3, 118.6; HRMS-ESI calcd for $[C_8H_4F_3O_3]^-$: 205.0118 $[M-H]^-$. Found 204.9697; FT-IR (neat) ν in cm^{-1}: 1685; m.p. 151 - 153 °C.

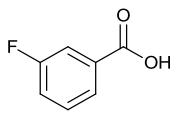
3-Methylbenzoic acid[13]



Following the general procedure described above, 3-methylbenzoic acid was obtained as a white solid (0.114 g, 84%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 7.89 (s, 2H, aromatic), 7.35 - 7.25 (m, 3H, aromatic), 2.34 (s, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 172.2, 138.3, 134.5, 130.7, 128.4, 127.4, 21.3; HRMS-ESI calcd for $[C_8H_7O_2]^-$: 135.0446 $[M-H]^-$. Found 135.0310; FT-IR (neat) ν in cm^{-1}: 1686; m.p. 109 - 111 °C.

3-Fluorobenzoic acid[14]

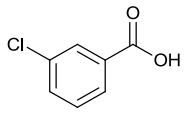


Following the general procedure described above, 3-fluorobenzoic acid was obtained as a white solid (0.126 g, 90%).

^{1}H NMR (300 MHz, CDCl3, 25 °C) δ 7.82 - 7.77 (d, *J* = 6.2 Hz, 1H, aromatic), 7.68 - 7.62 (d, *J* = 6.2 Hz, 1H, aromatic), 7.54 - 7.44 (m, 1H, aromatic), 7.35 - 7.30 (m, 1H, aromatic) ^{13}C NMR (75.5 MHz, CDCl3, 25 °C) δ 171.1, 162.6 (d, *J* = 245.6 Hz), 131.4 (d, *J* = 7.6 Hz), 130.2 (d, *J* = 7.5 Hz), 126.0 (d, *J* = 3.0 Hz), 121.0 (d, *J* = 21.1 Hz), 117.1 (d, *J* = 22.7 Hz); HRMS-

ESI calcd for $[C_7H_4FO_2]^-$: 139.0195 $[M-H]^-$. Found 139.0164; FT-IR (neat) ν in cm^{-1}: 1684; m.p. 122 - 124 °C.

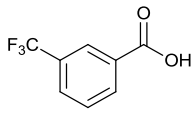
3-Chlorobenzoic acid[15]



Following the general procedure described above, 3-chlorobenzoic acid was obtained as a white solid (0.142 g, 91%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 8.83 (br s, 1H, OH), 8.02 (s, 1H, aromatic), 7.94 (d, *J* = 6.2 Hz, 1H, aromatic), 7.54 (d, *J* = 9.0 Hz, 1H, aromatic), 7.35 (t, *J* = 9.0 Hz, 1H, aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 170.9, 134.7, 133.9, 131.1, 130.3, 129.8, 128.3; HRMS-ESI calcd for $[C_7H_4ClO_2]^-$: 154.9900 $[M-H]^-$. Found 154.9756; FT-IR (neat) ν in cm^{-1}: 1697; m.p. 151 - 152 °C.

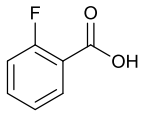
3-(Trifluoromethyl)benzoic acid[13]



Following the general procedure described above, 3-(trifluoromethyl)benzoic acid was obtained as a white solid (0.167 g, 88%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 8.32 (s, 1H, aromatic), 8.26 (d, *J* = 9.0 Hz, 1H, aromatic), 7.83 (d, *J* = 9.0 Hz, 1H, aromatic), 7.57 (t, *J* = 9.0 Hz, 1H, aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 170.5, 133.4, 131.5, 130.4, 129.3 (q, *J* = 34.0 Hz) 127.2, 122.5; HRMS-ESI calcd for $[C_8H_4F_3O_2]^-$: 189.0163 $[M-H]^-$. Found 189.0099; FT-IR (neat) ν in cm^{-1}: 1691; m.p. 102 - 104 °C.

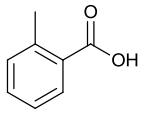
2-Fluorobenzoic acid[10]



Following the general procedure described above, 2-fluorobenzoic acid was obtained as a white solid (0.132 g, 94%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 8.00 - 7.95 (dt, *J* = 9.0 Hz, *J* = 3.2 Hz, 1H, aromatic), 7.56 - 7.48 (m, 1H, aromatic), 7.20 - 7.07 (m, 2H, aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 169.5, 162.7 (d, *J* = 262.0 Hz), 135.6 (d, *J* = 9.1 Hz), 132.8, 124.2 (d, *J* = 3.8 Hz), 117.6 (d, *J* = 9.0 Hz), 117.3 (d, *J* = 21.8 Hz); HRMS-ESI calcd for $[C_7H_4FO_2]^-$: 139.0195 $[M-H]^-$. Found 138.9920; FT-IR (neat) ν in cm^{-1}: 1687; m.p. 122 - 125 °C.

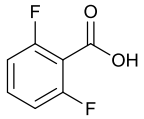
2-Methylbenzoic acid[9]



Following the general procedure described above, 2-methylbenzoic acid was obtained as a white solid (0.122 g, 90%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 7.98 (d, *J* = 9.0 Hz, 1H, aromatic), 7.38 (t, *J* = 9.0 Hz, 1H, aromatic), 7.20 (t, *J* = 9.0 Hz, 2H, aromatic), 2.55 (s, 3H, CH_3); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 173.4, 141.4, 133.0, 131.9, 131.6, 128.4, 125.9, 22.1; HRMS-ESI calcd for $[C_8H_7O_2]^-$: 135.0452 $[M-H]^-$. Found 135.0441; FT-IR (neat) ν in cm^{-1}: 1653; m.p. 104 - 105 °C.

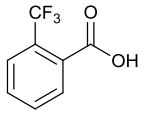
2,6-Difluorobenzoic acid[16]



Following the general procedure described above, 2,6-difluorobenzoic acid was obtained as a white solid (0.141 g, 89%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 7.41 (m, 1H, aromatic), 6.92 (t, *J* = 6.2 Hz, 2H, aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 166.2, 161.3 (dd, *J* = 253.7 Hz, *J* = 6.0 Hz), 133.9 (t, *J* = 11.3 Hz), 112.5, 112.1; HRMS-ESI calcd for $[C_7H_3F_2O_2]^-$: 157.0107 $[M-H]^-$. Found 157.0054; FT-IR (neat) ν in cm^{-1}: 1701; m.p. 159 - 161 °C.

2-(Trifluoromethyl)benzoic acid[16]



Following the general procedure described above, 2-(trifluoromethyl)benzoic acid was obtained as a white solid (0.157 g, 88%).

^{1}H NMR (300MHz, $CDCl_3$, 25 °C) δ 10.0 (br s, 1H, OH), 7.95 - 7.90 (m, 1H, aromatic), 7.72 (m, 1H, aromatic), 7.58 (m, 2H, aromatic); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C) δ 172.0, 132.2, 131.8 (q, *J* = 7.0 Hz), 131.1, 129.7, 129.5 (q, *J* = 32.5 Hz), 127.0 (q, *J* = 6.1 Hz), 123.3 (q, *J* = 273.3 Hz); HRMS-ESI calcd for $[C_8H_4F_3O_2]^-$: 189.0169 $[M-H]^-$. Found 189.0087; FT-IR (neat) ν in cm^{-1}: 1708; m.p. 106 - 107 °C.

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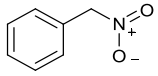
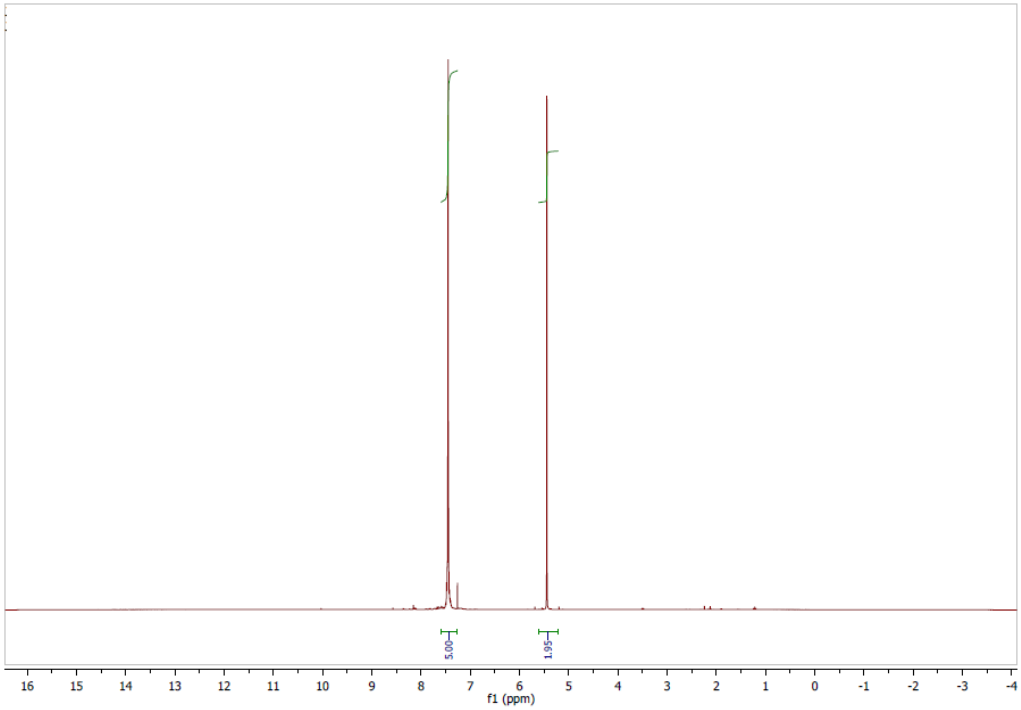
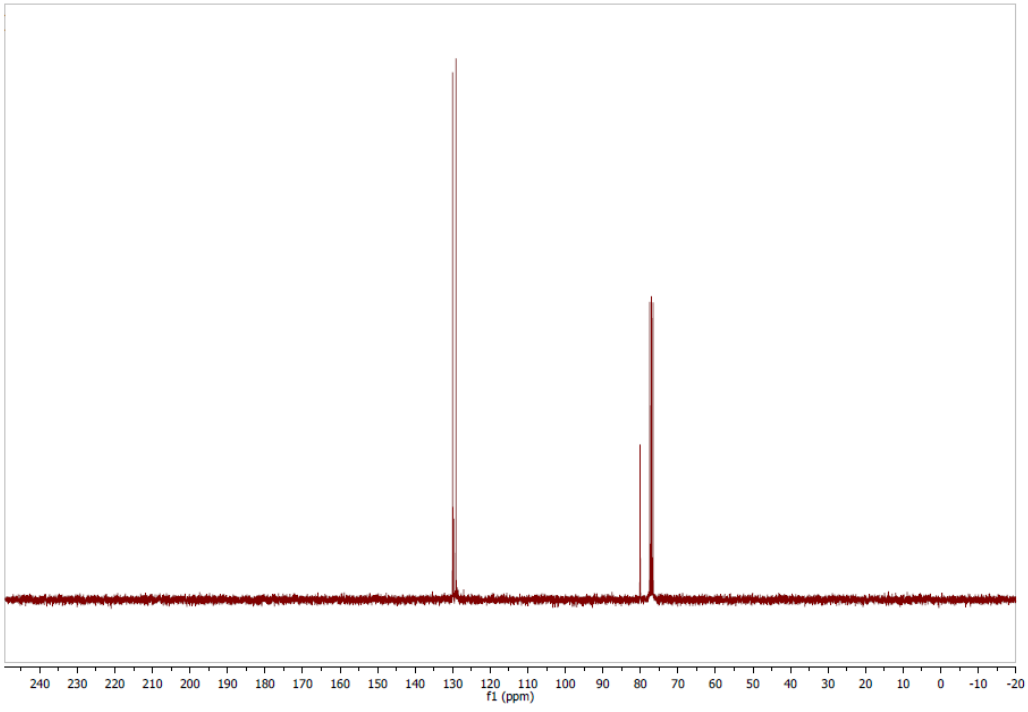
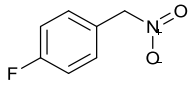
^{1}H-NMR and ^{13}C-NMR spectroscopic data





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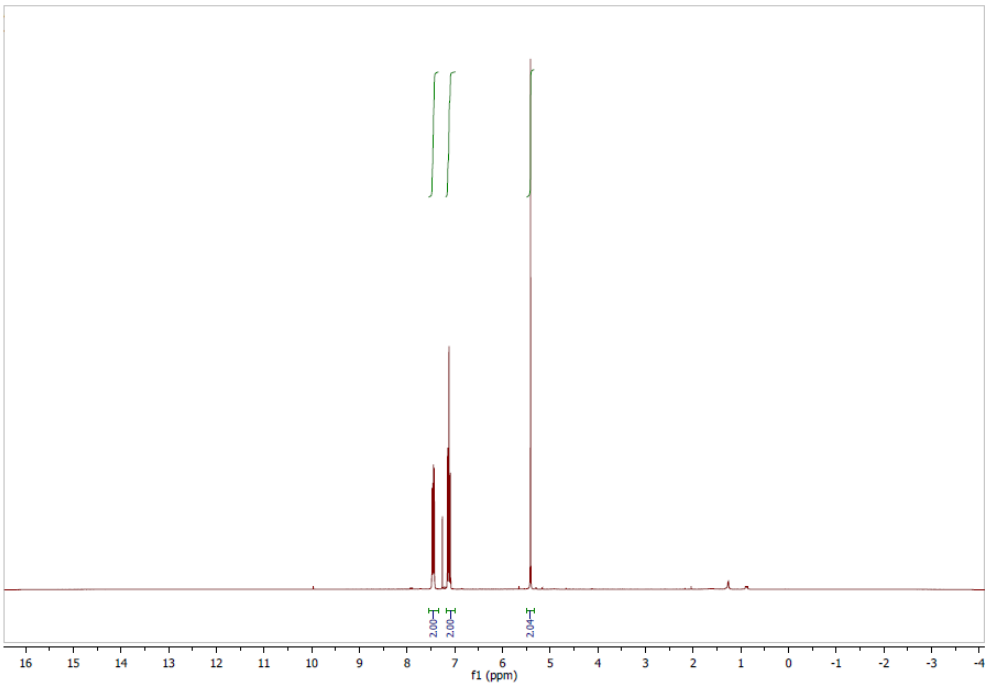
O
O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2.00
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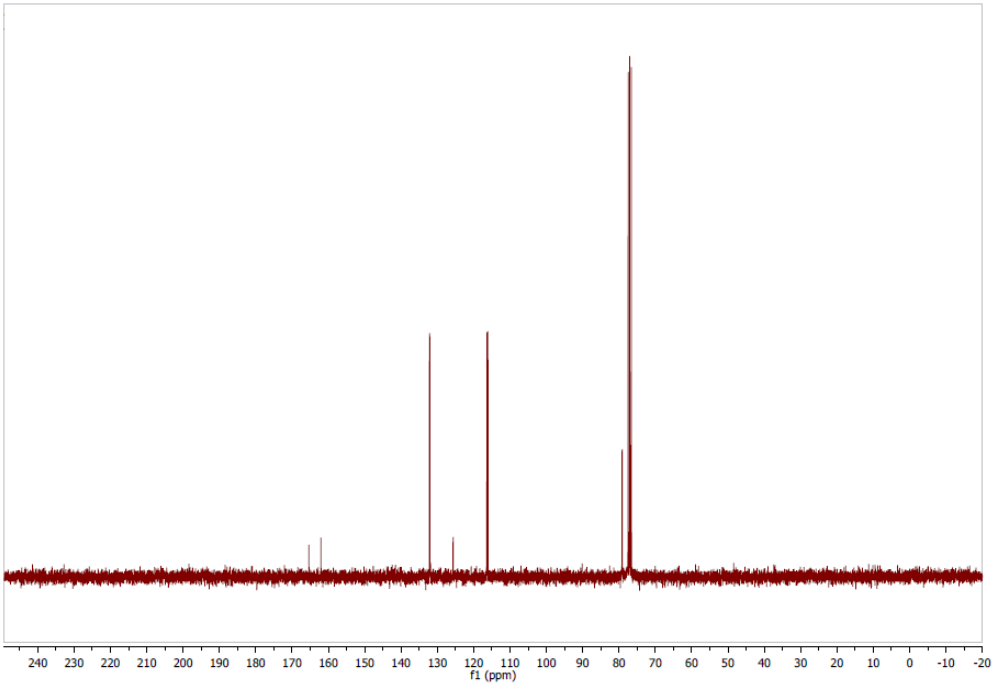
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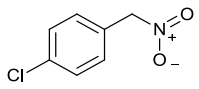
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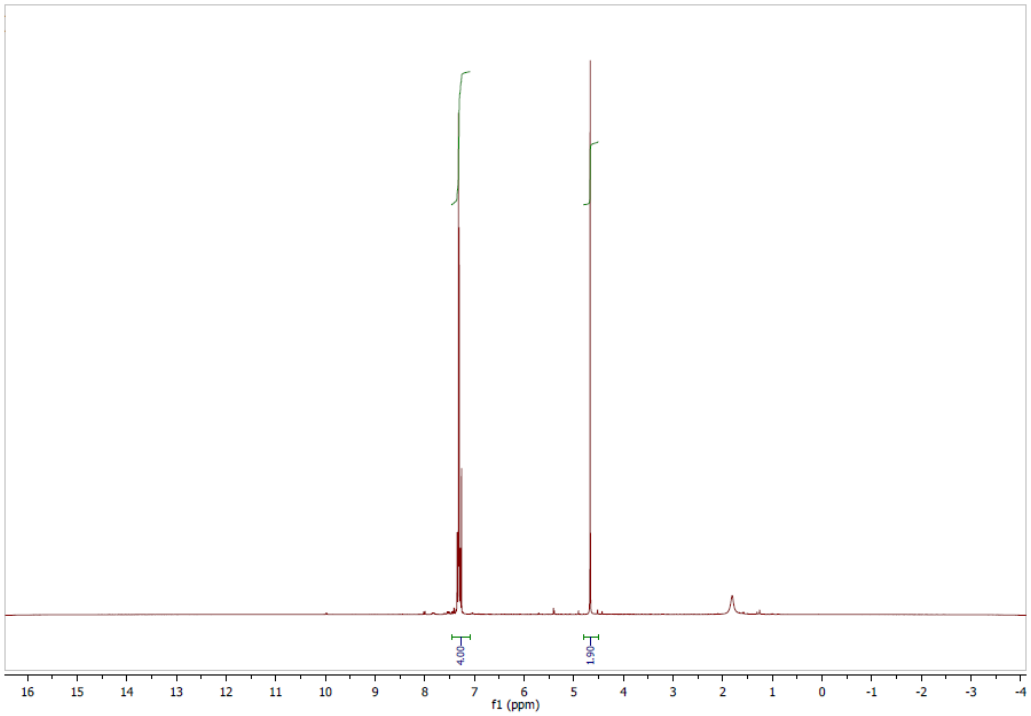
O
O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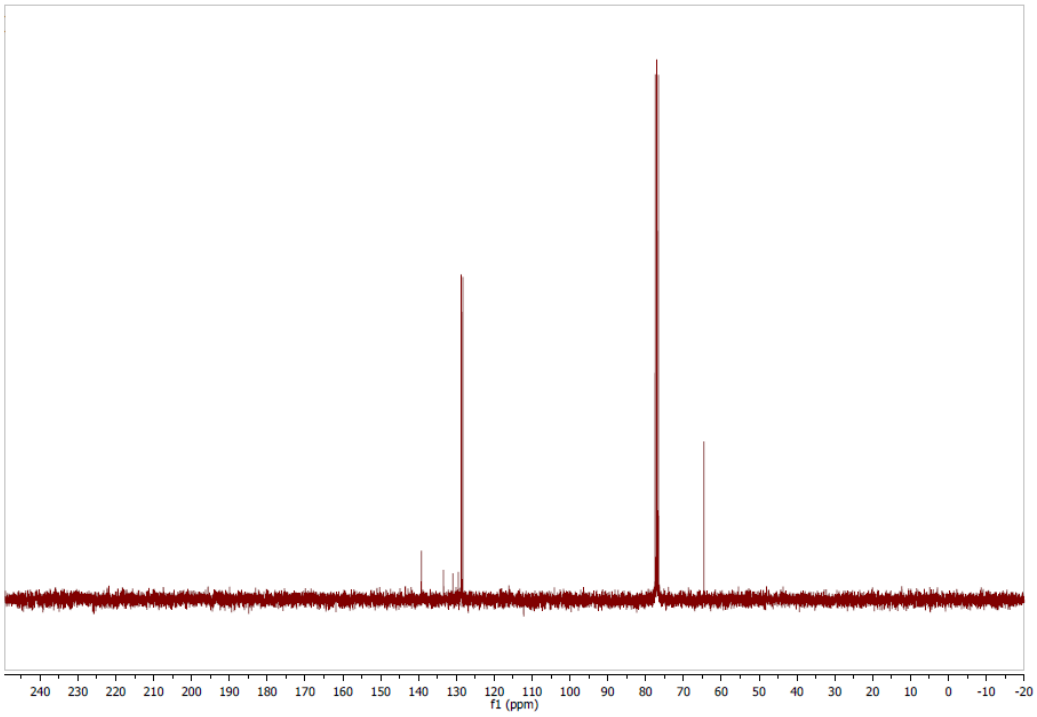
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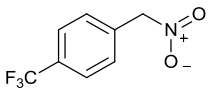
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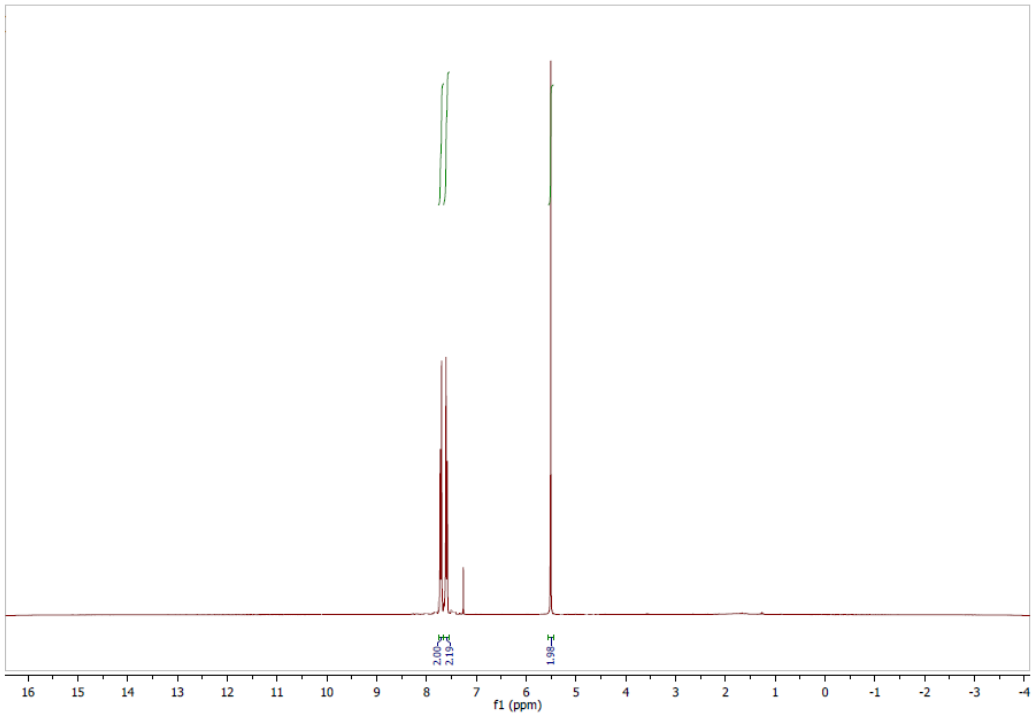
O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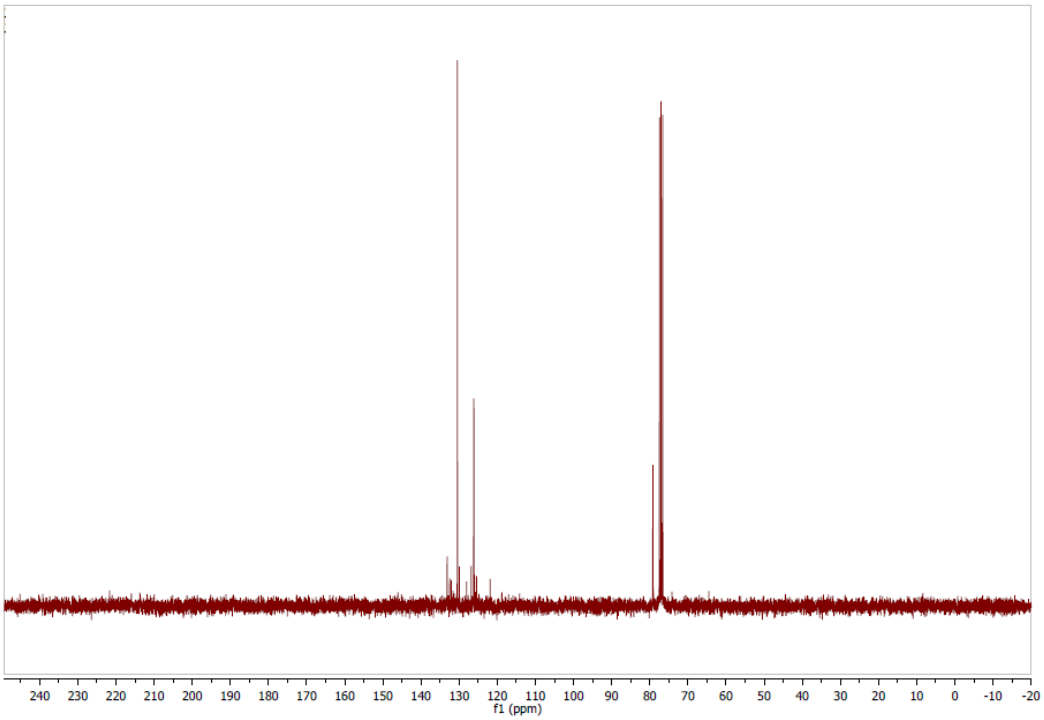
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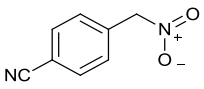
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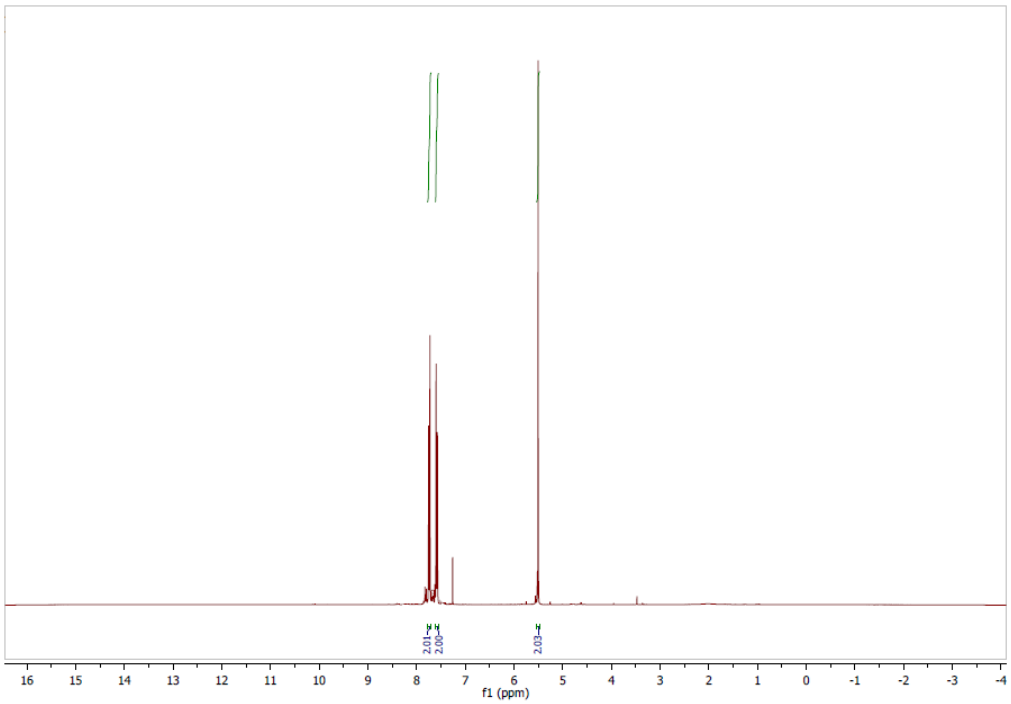
O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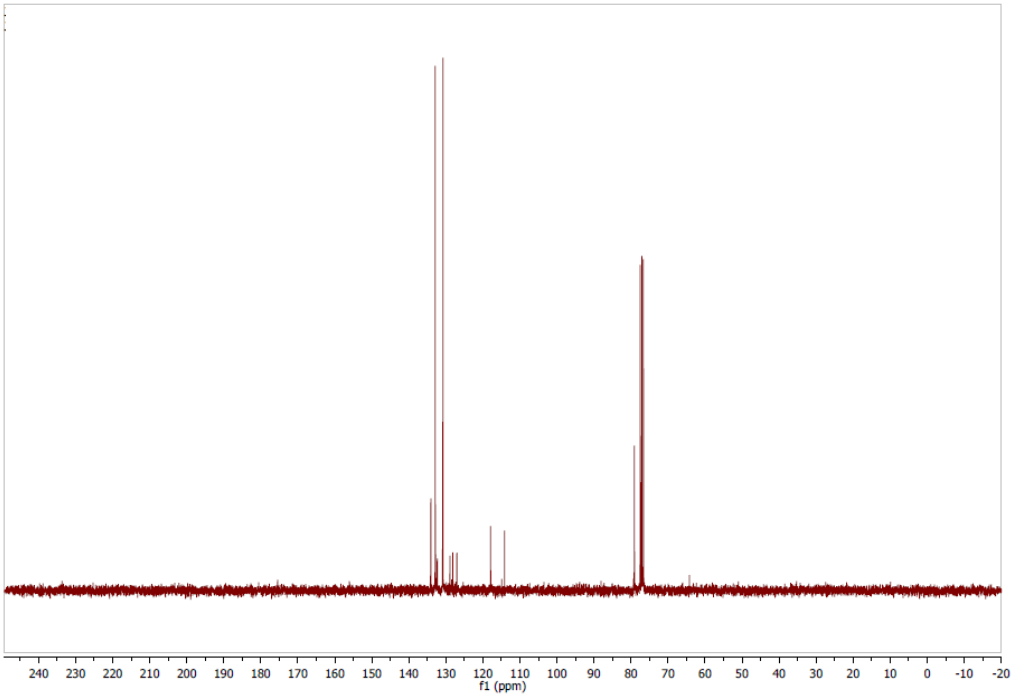
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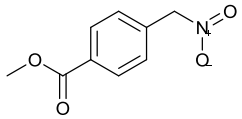

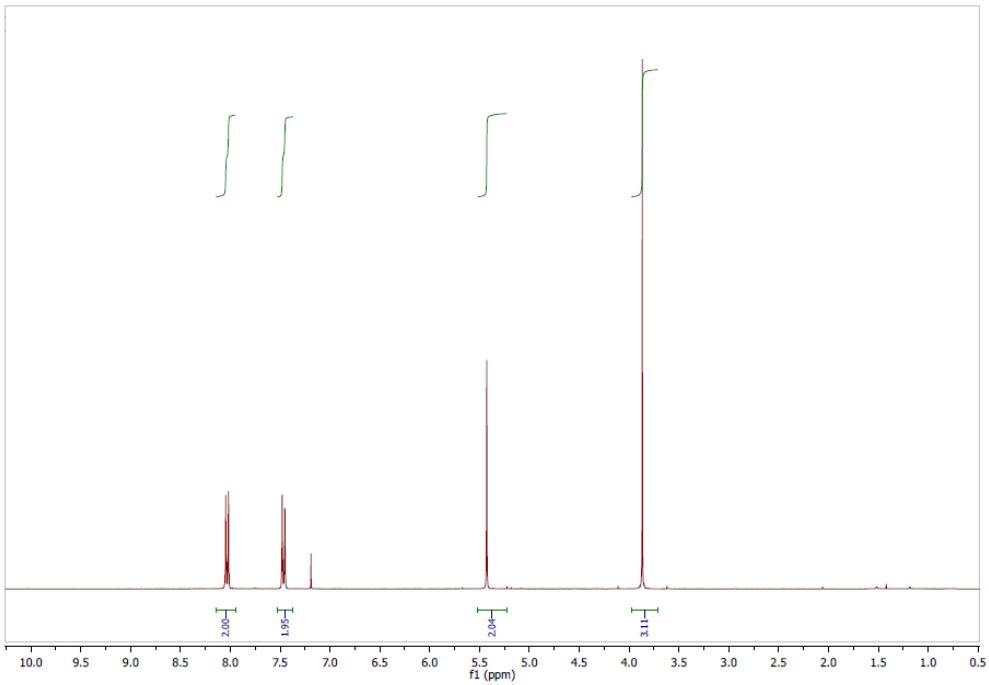
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3.11
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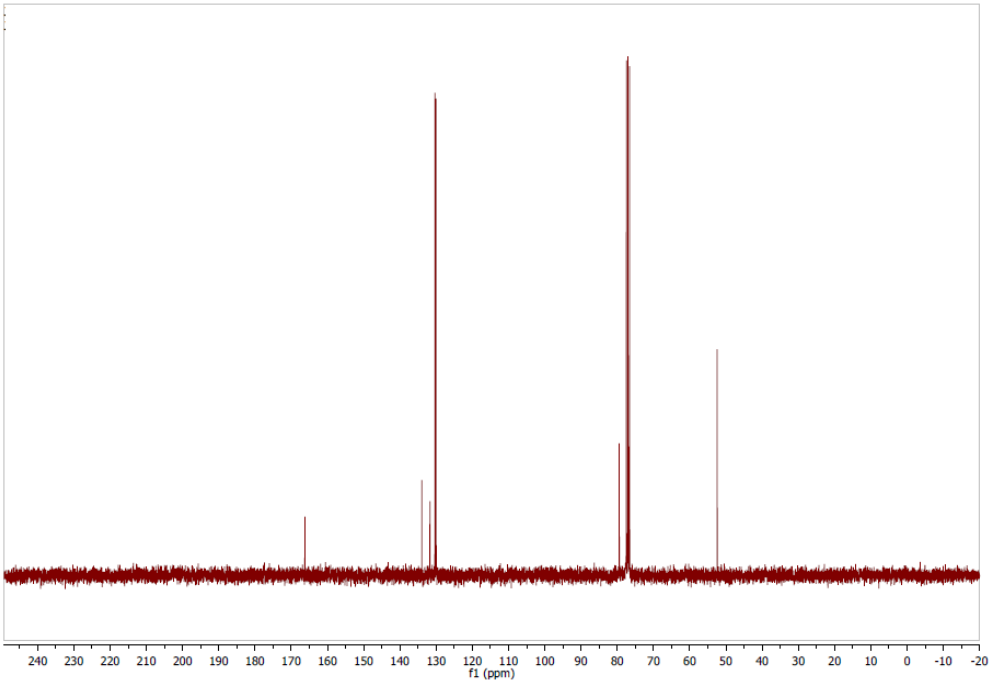
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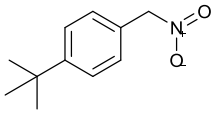

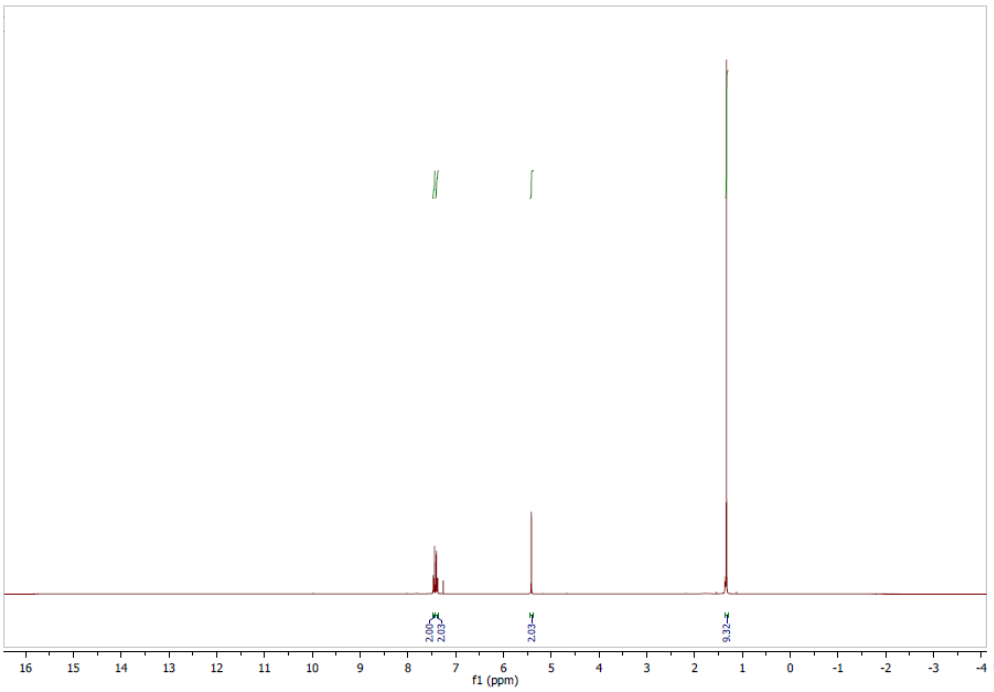
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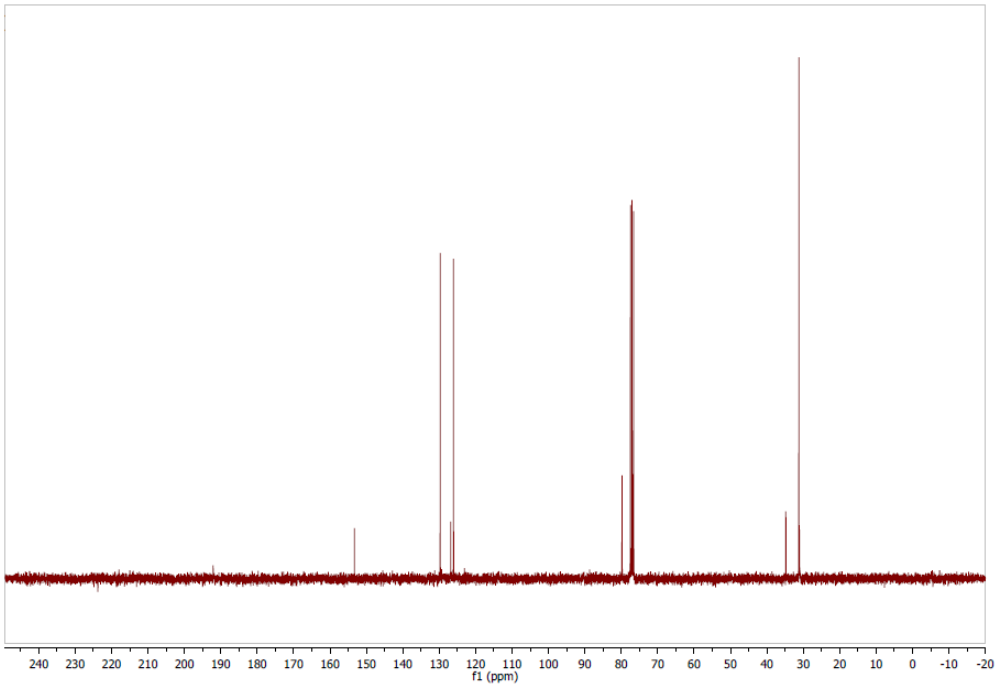
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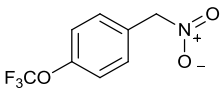
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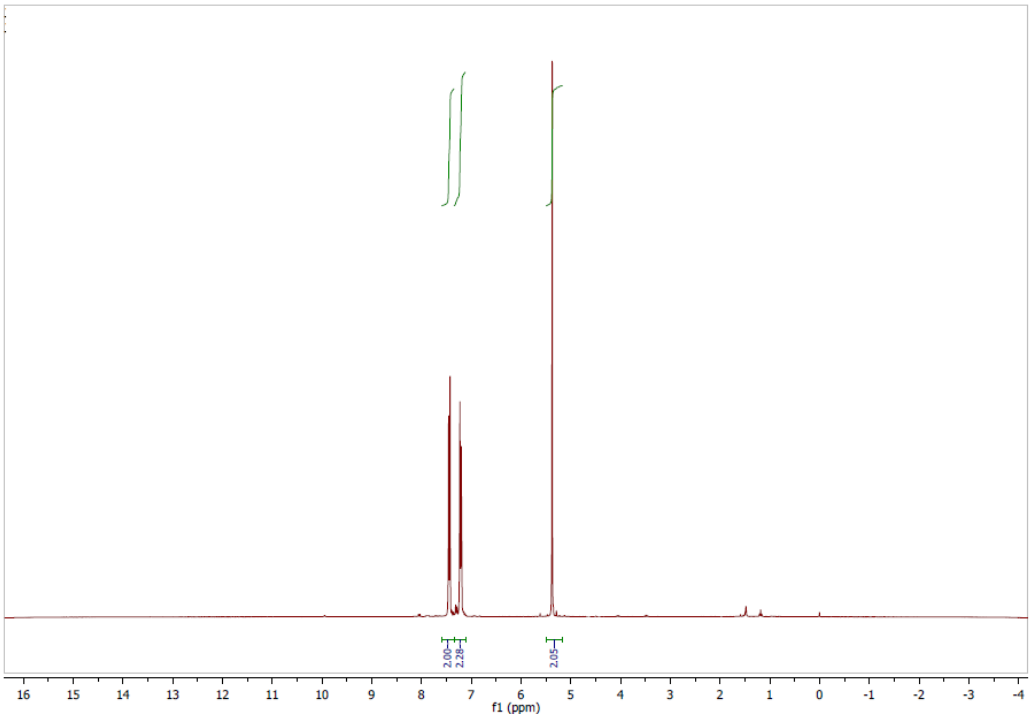
O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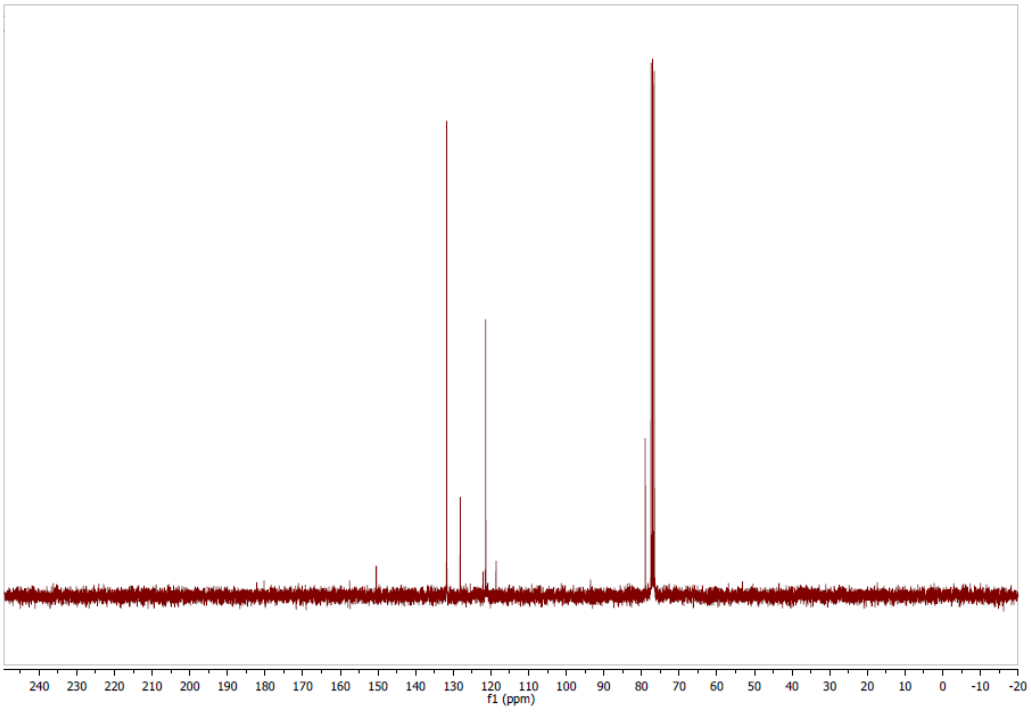
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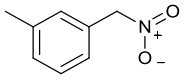
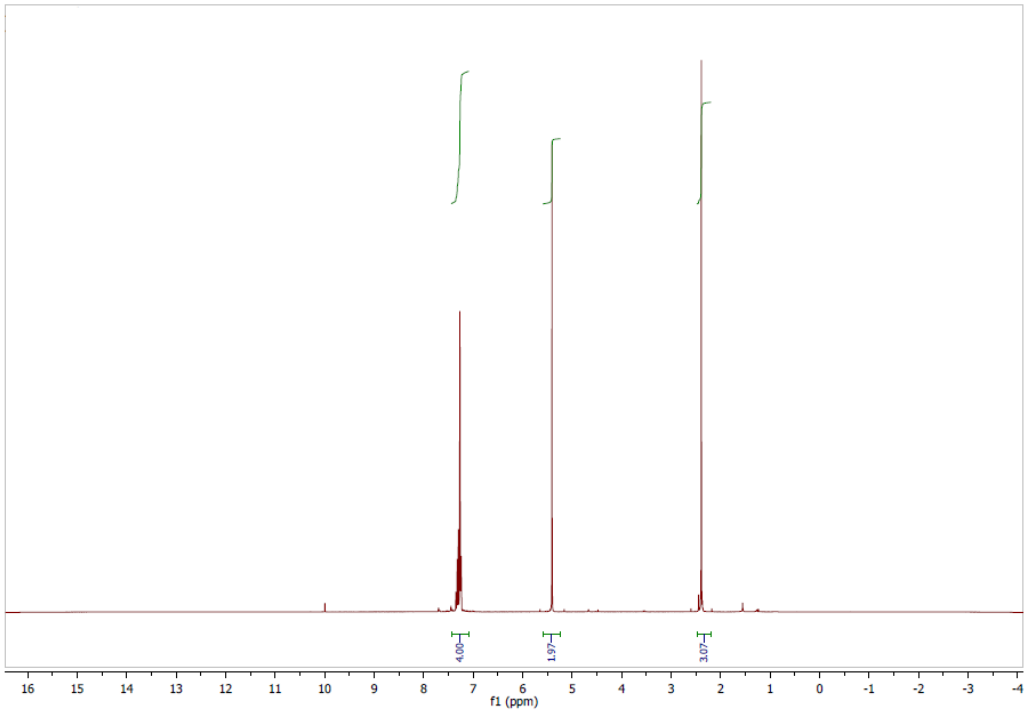
f1 (ppm)

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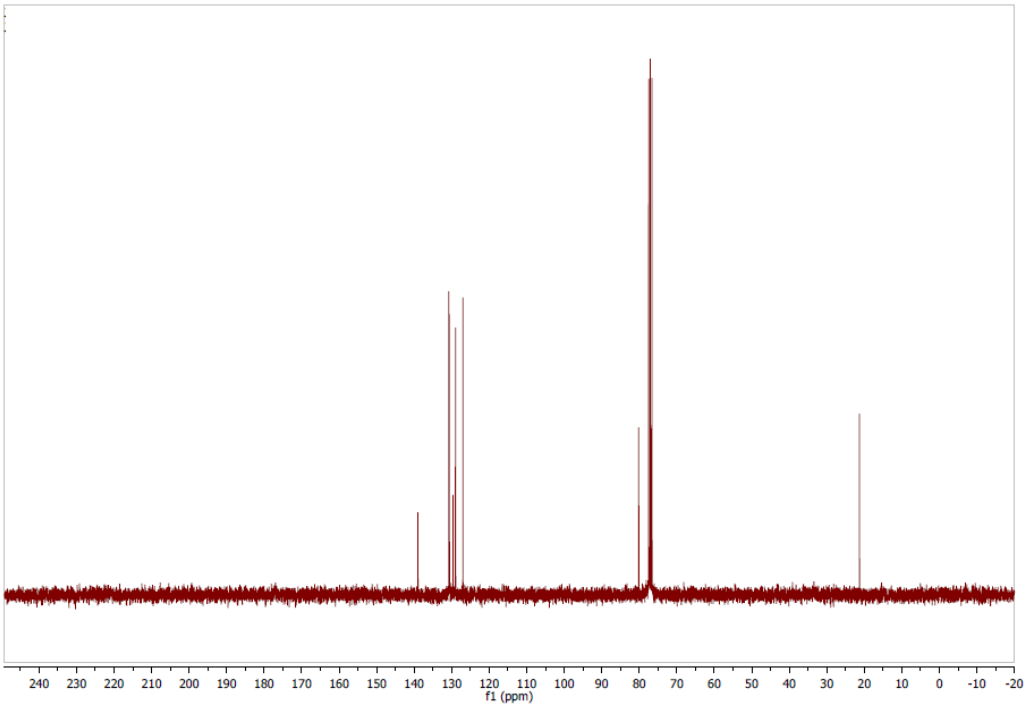
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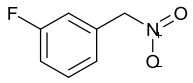
F
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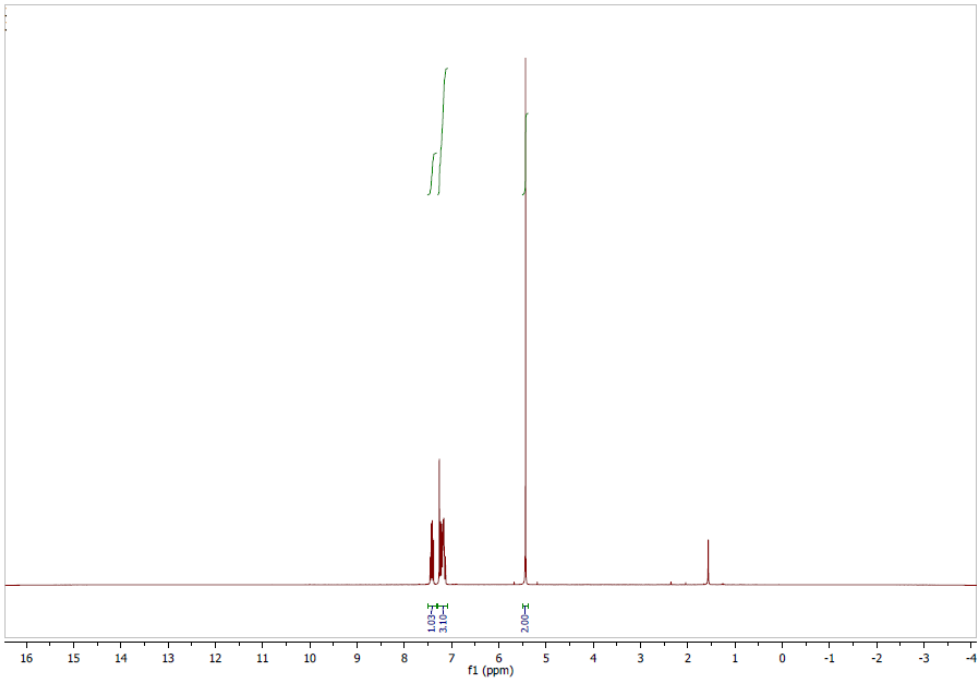
O
O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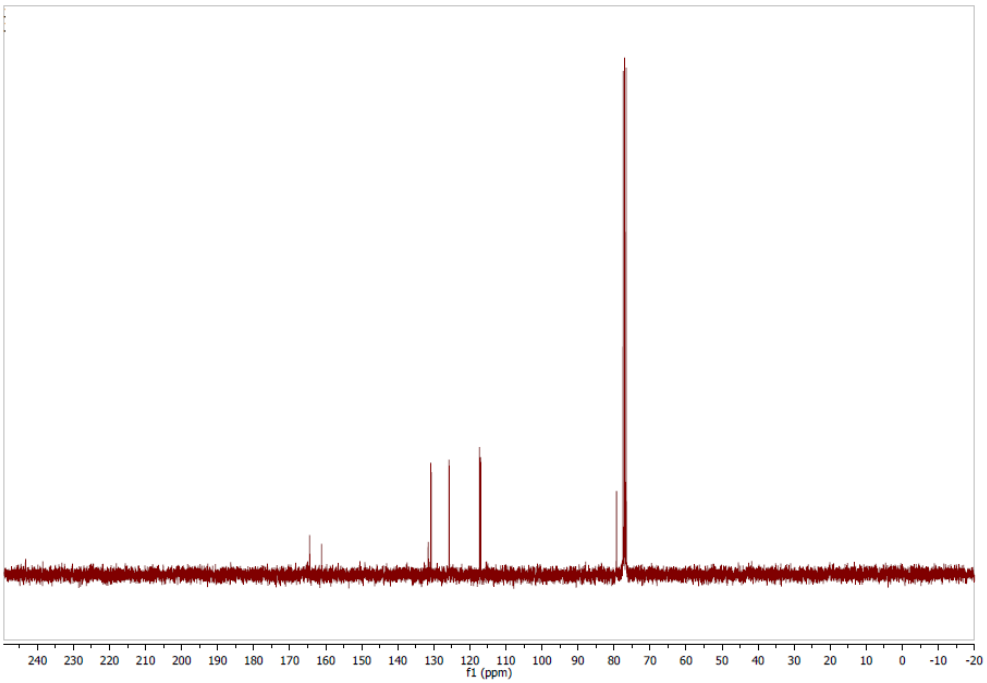
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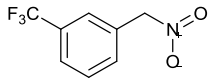

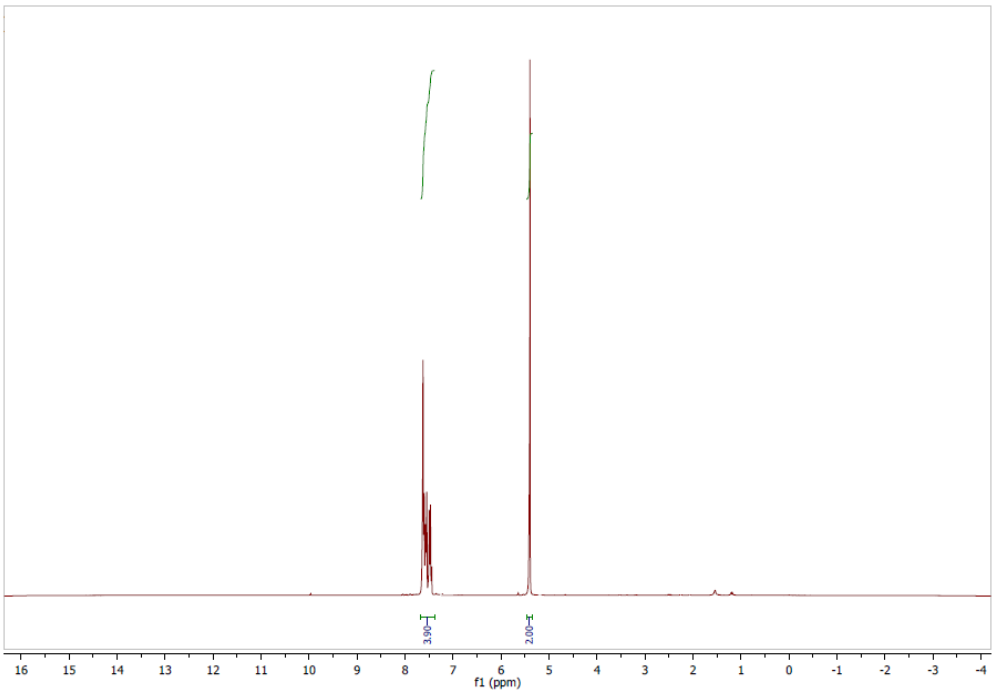
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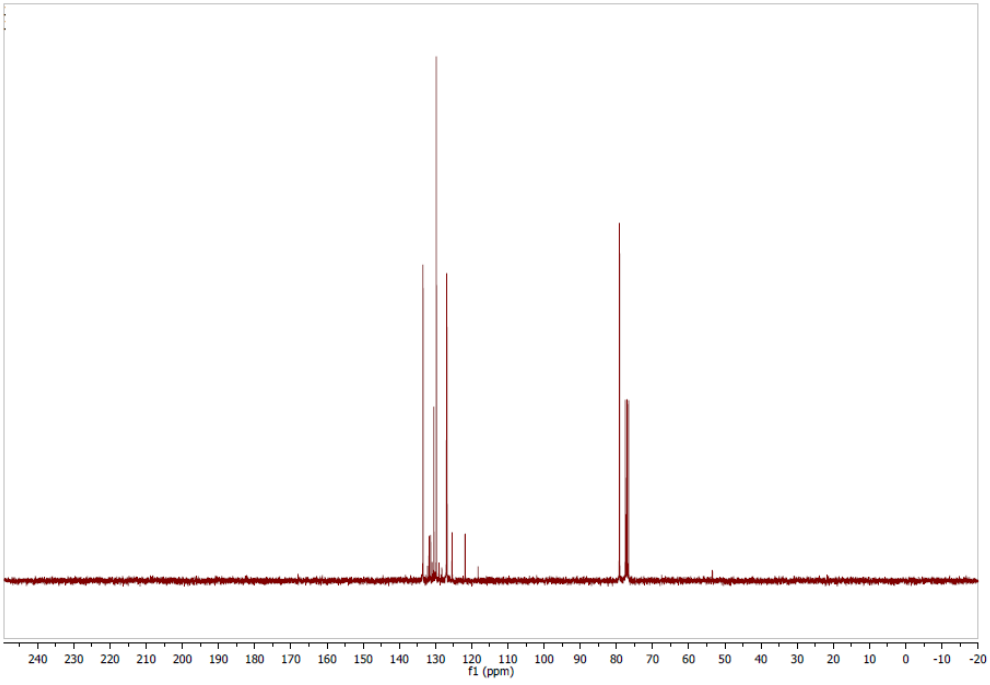
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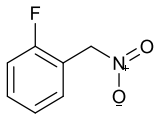
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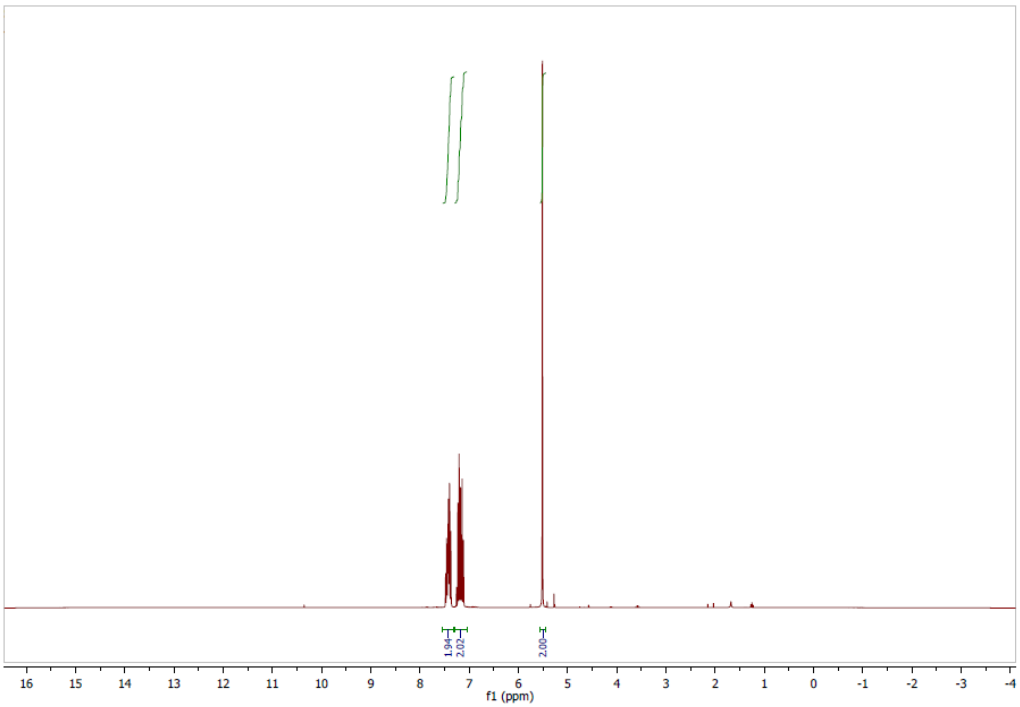
O
O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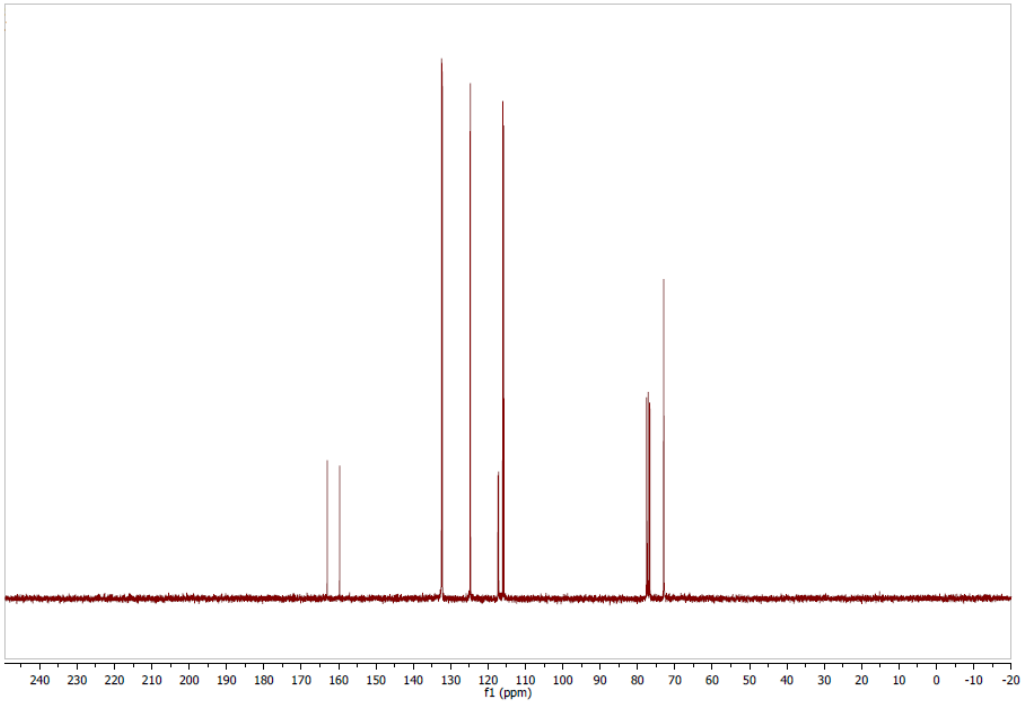
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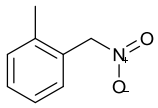

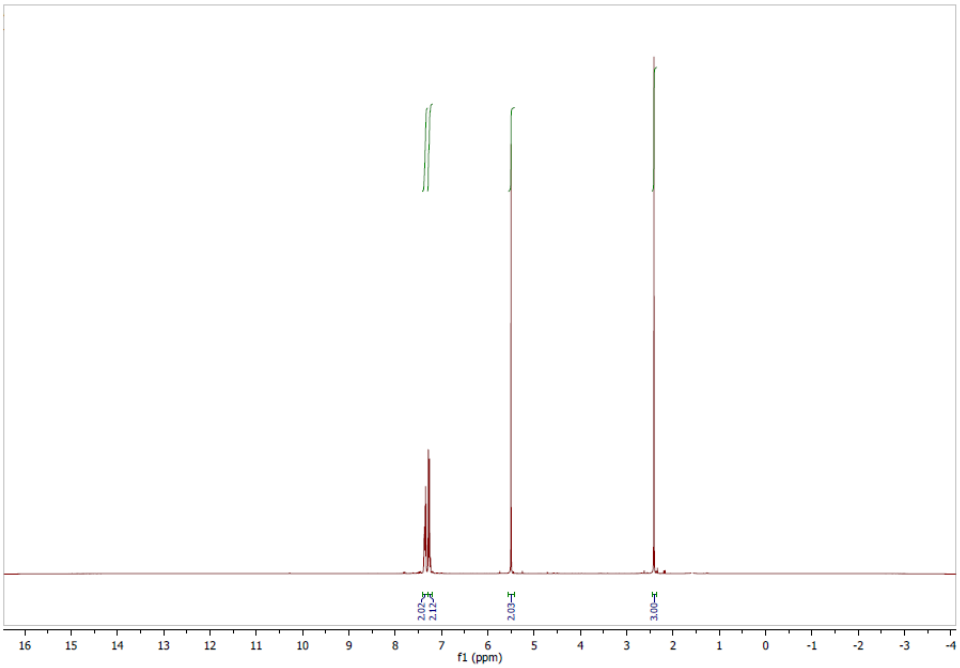
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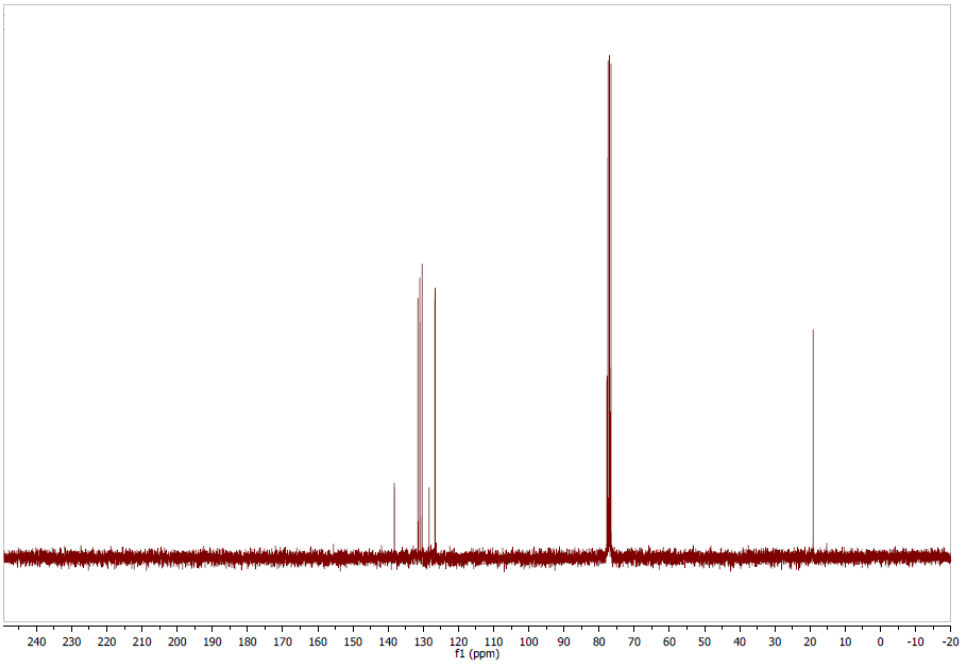
f1 (ppm)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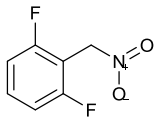
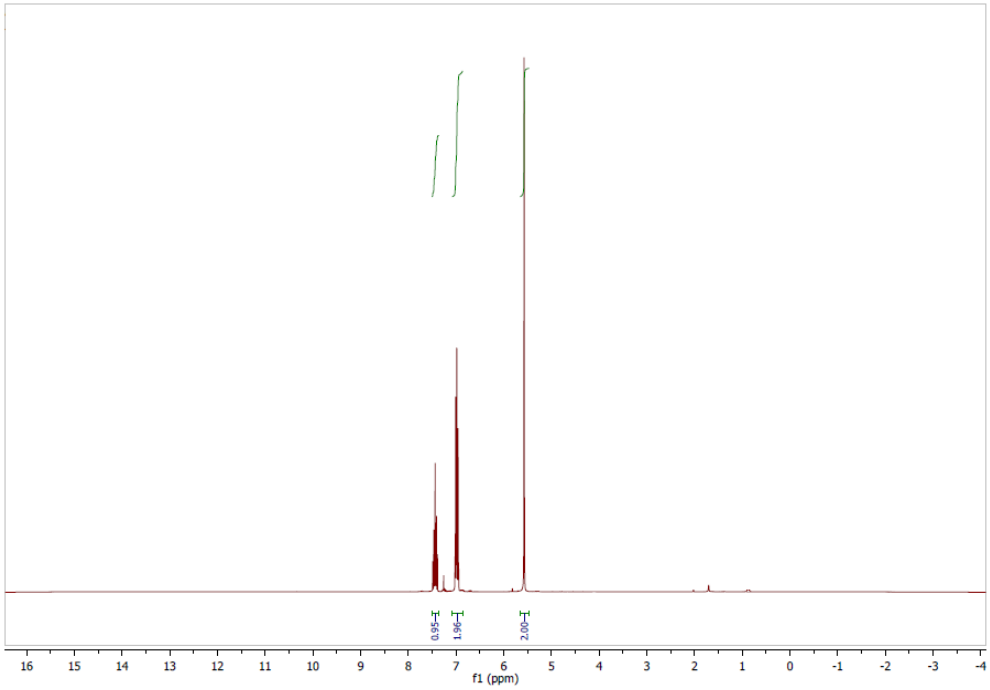
f1 (ppm)


F
N
O
O
F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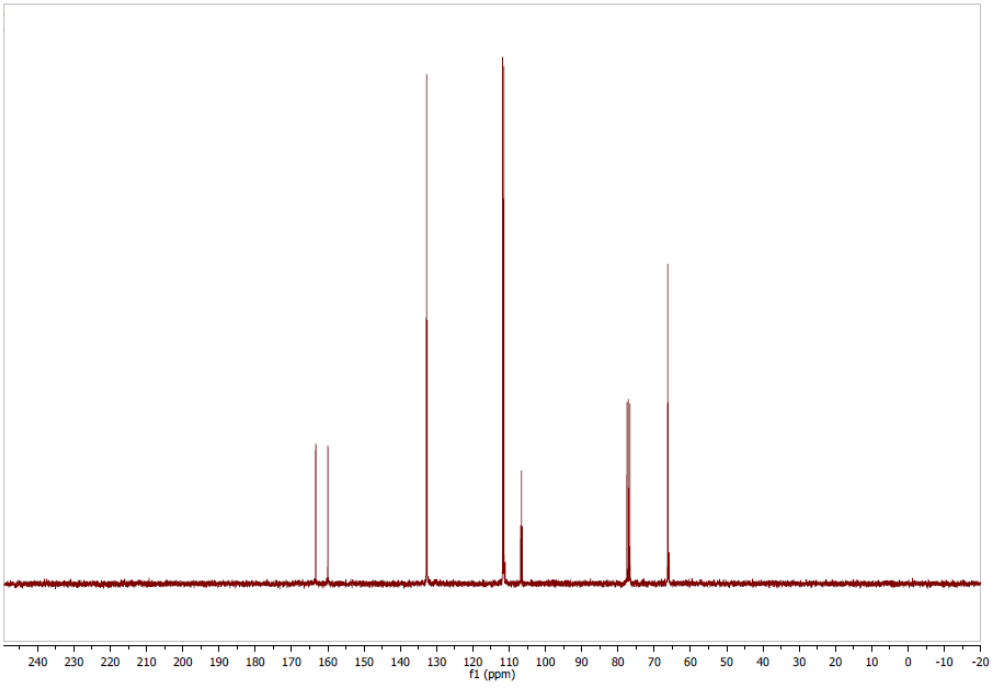
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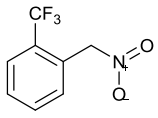
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O
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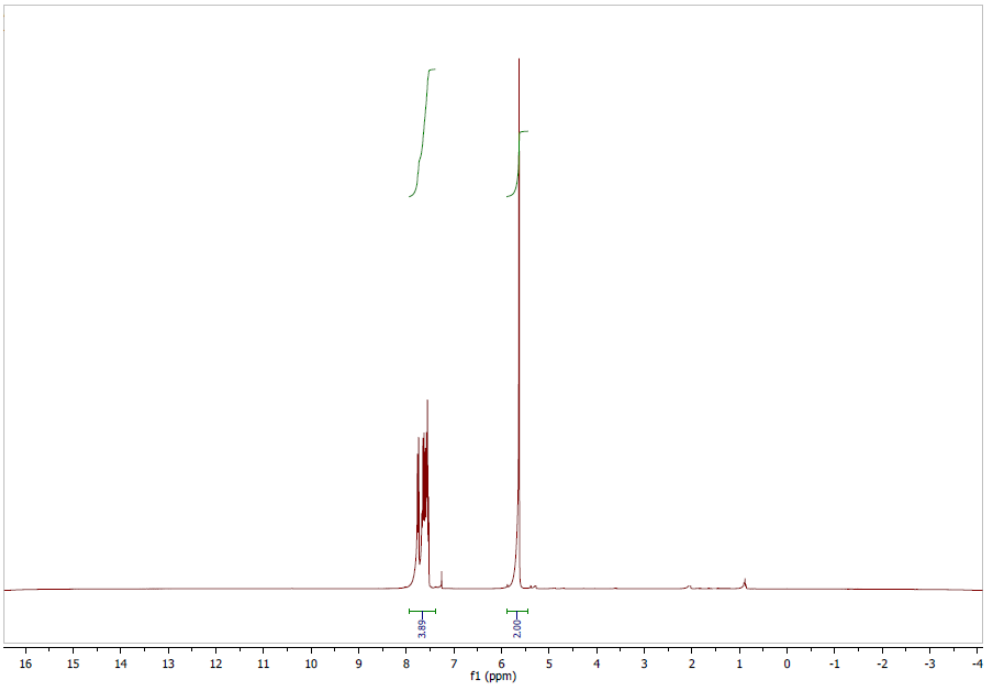
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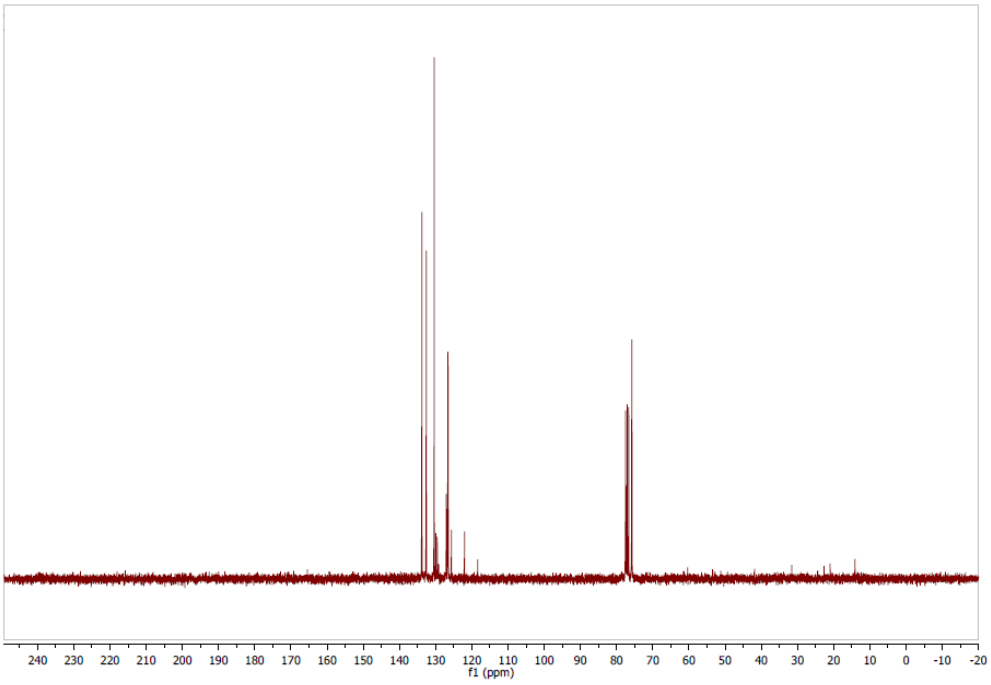
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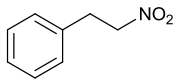
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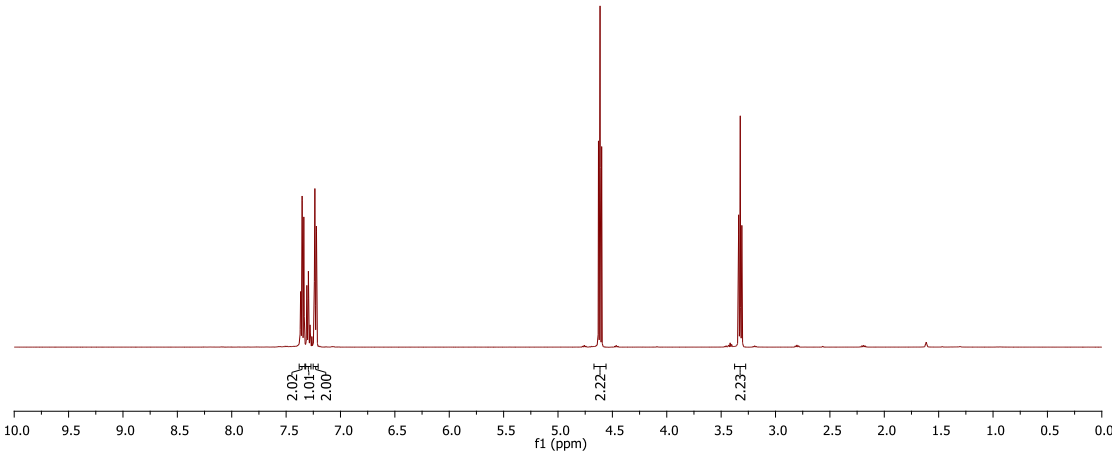
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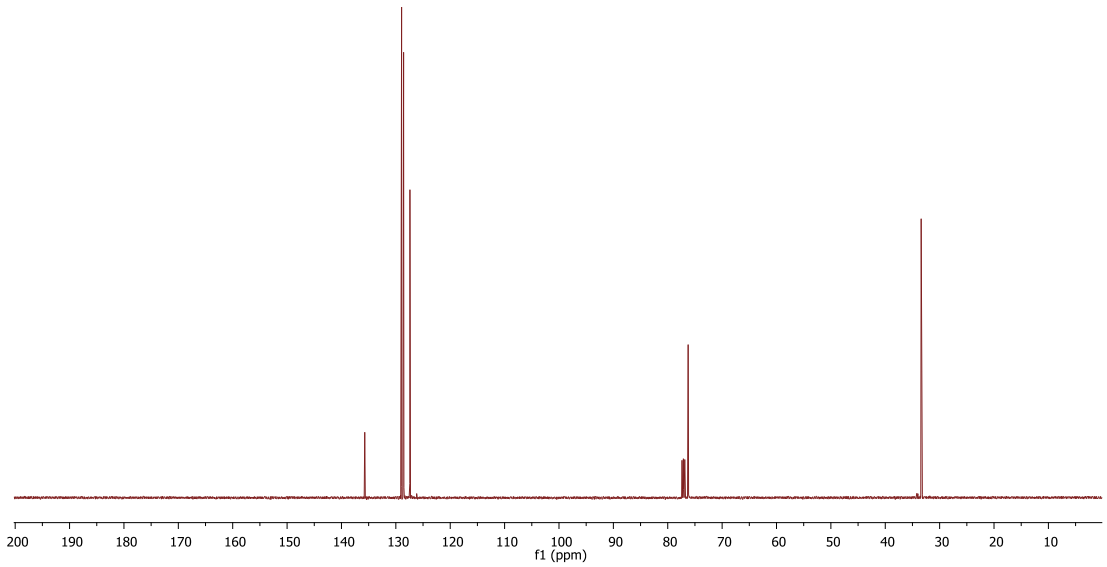
1.01
2.00
2.22
2.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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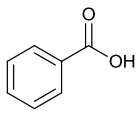
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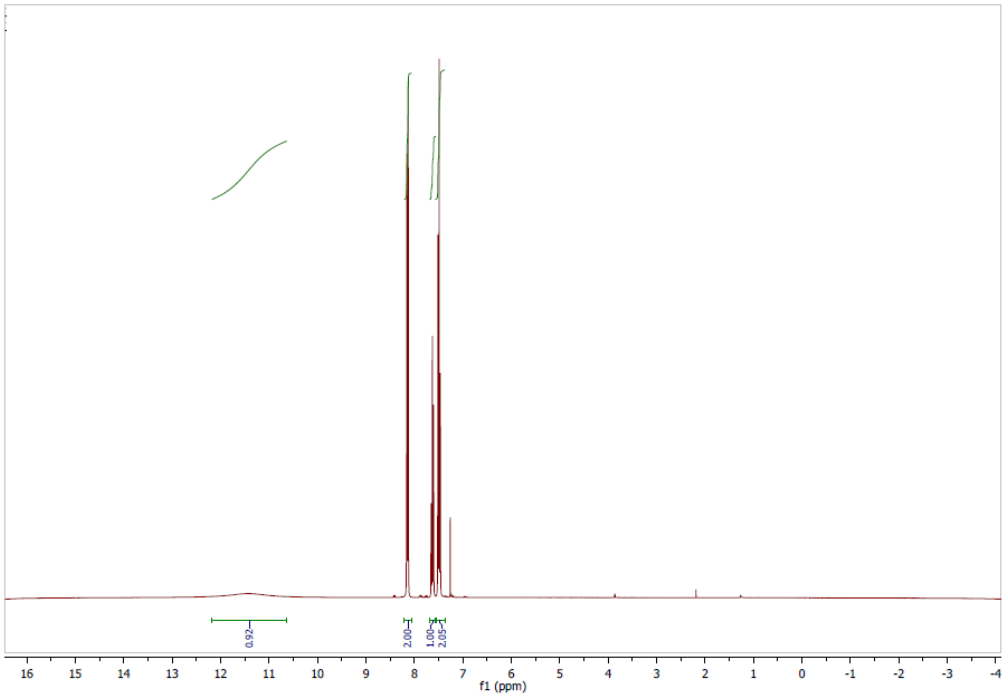
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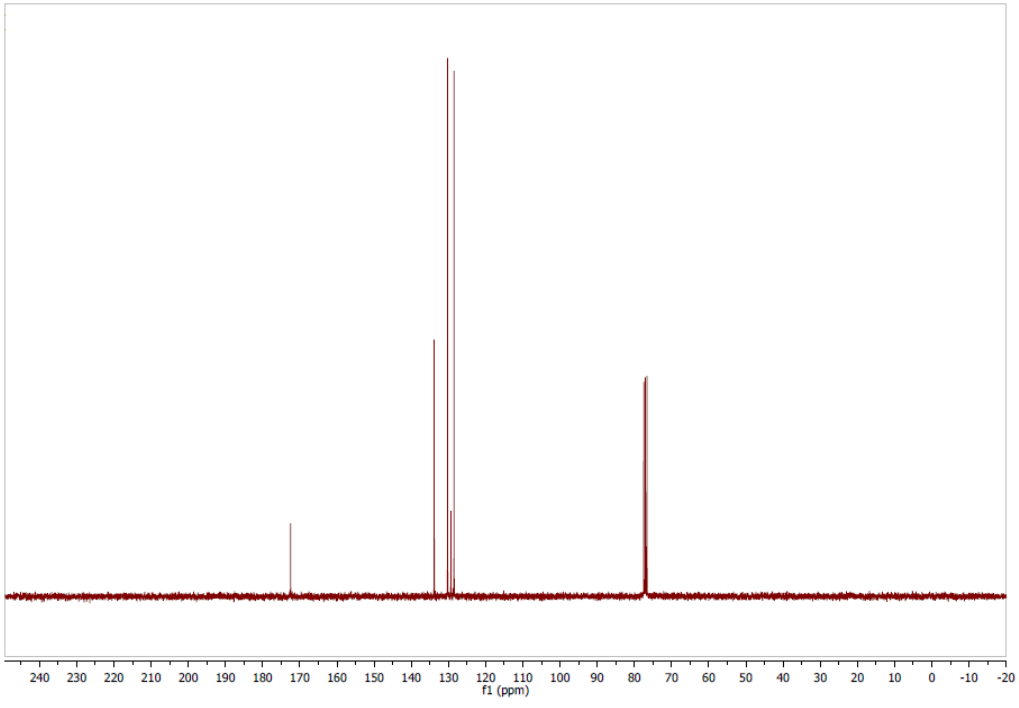
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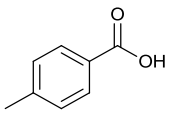
f1 (ppm)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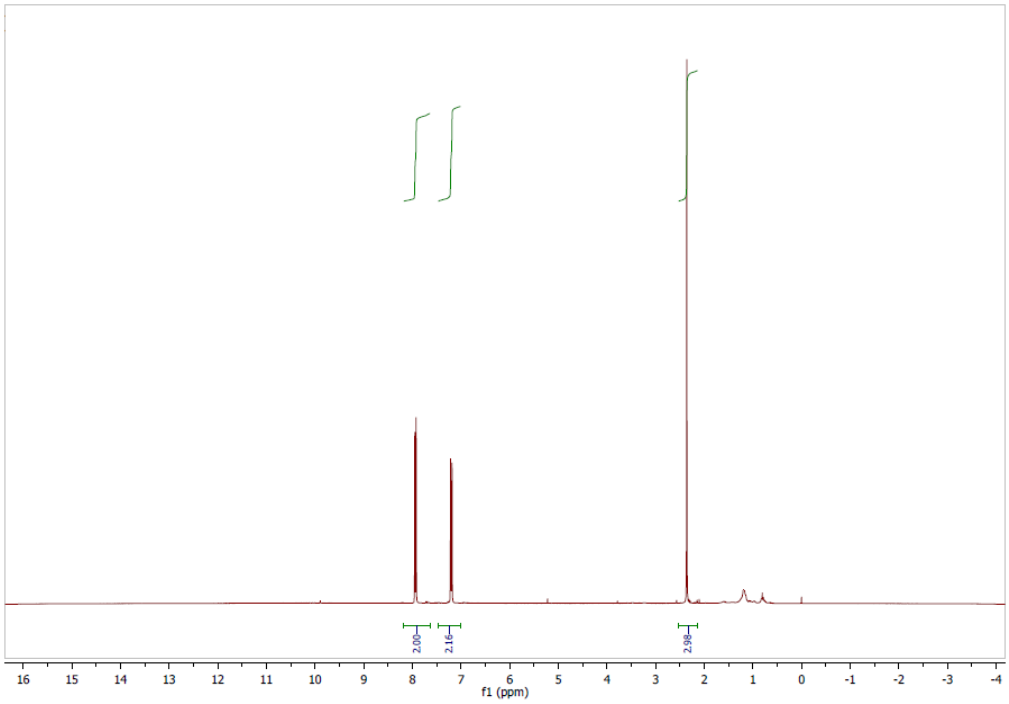
OH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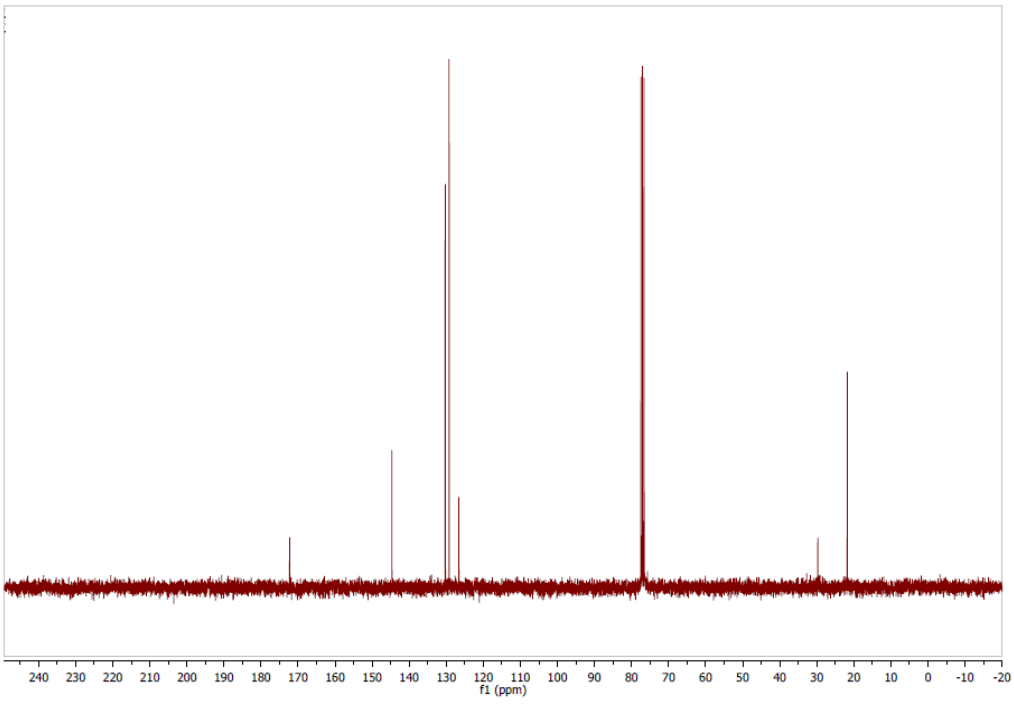
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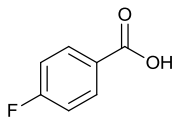
f1 (ppm)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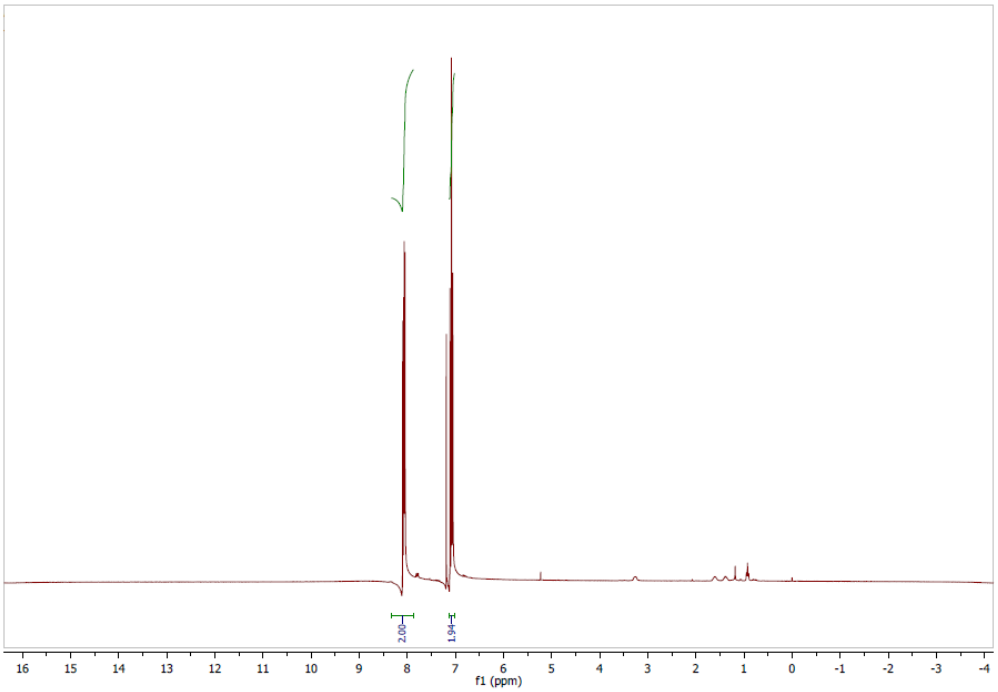
OH
F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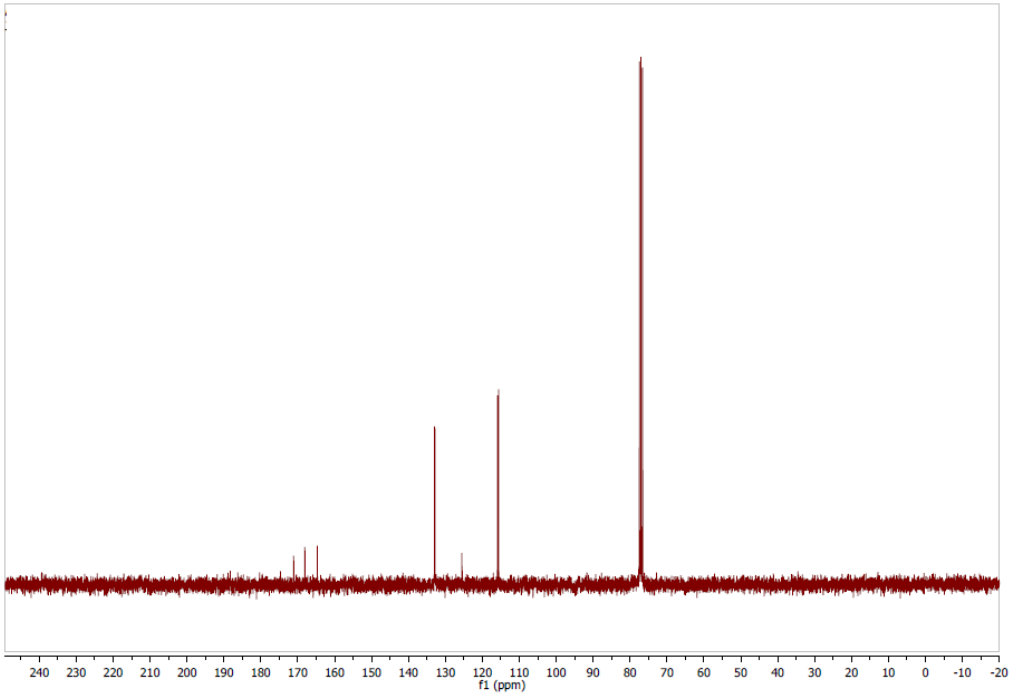
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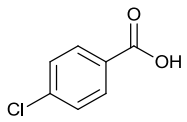
f1 (ppm)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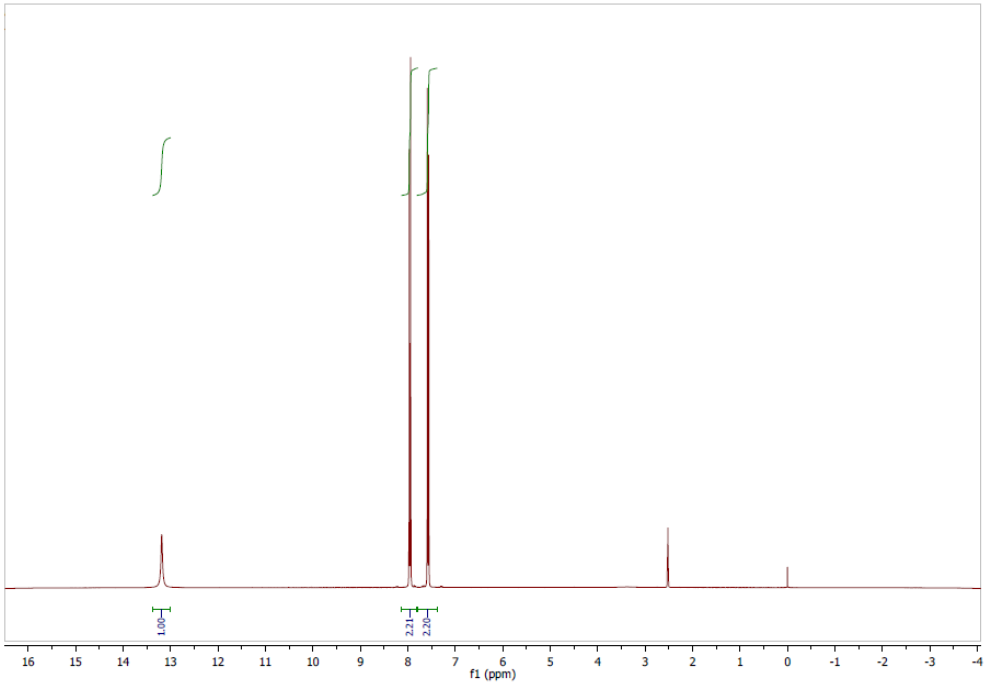
OH
Cl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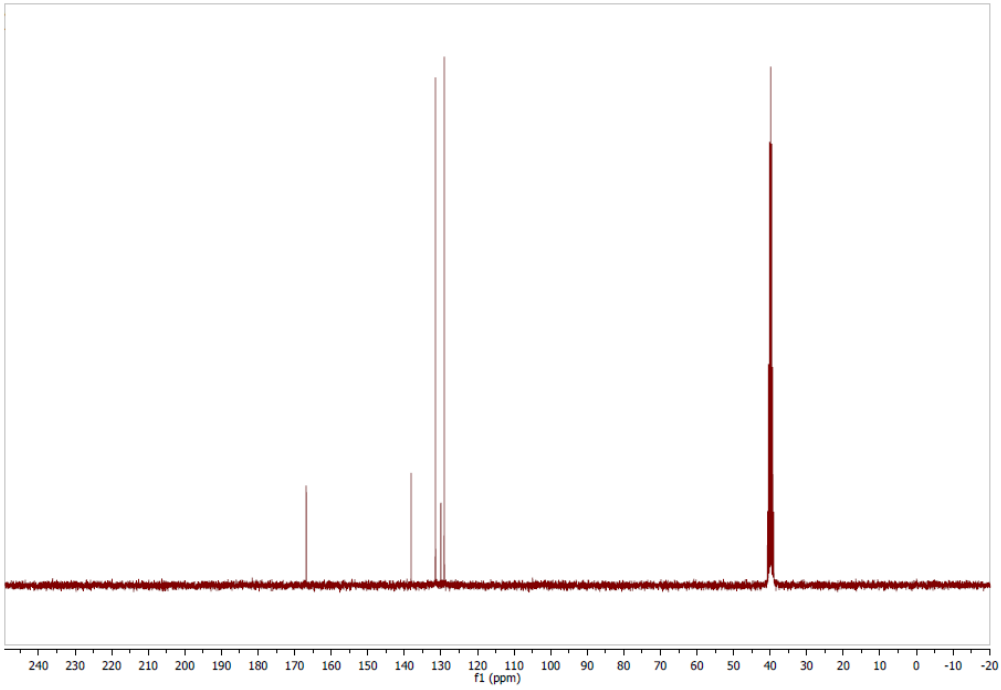
f1 (ppm)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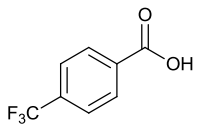
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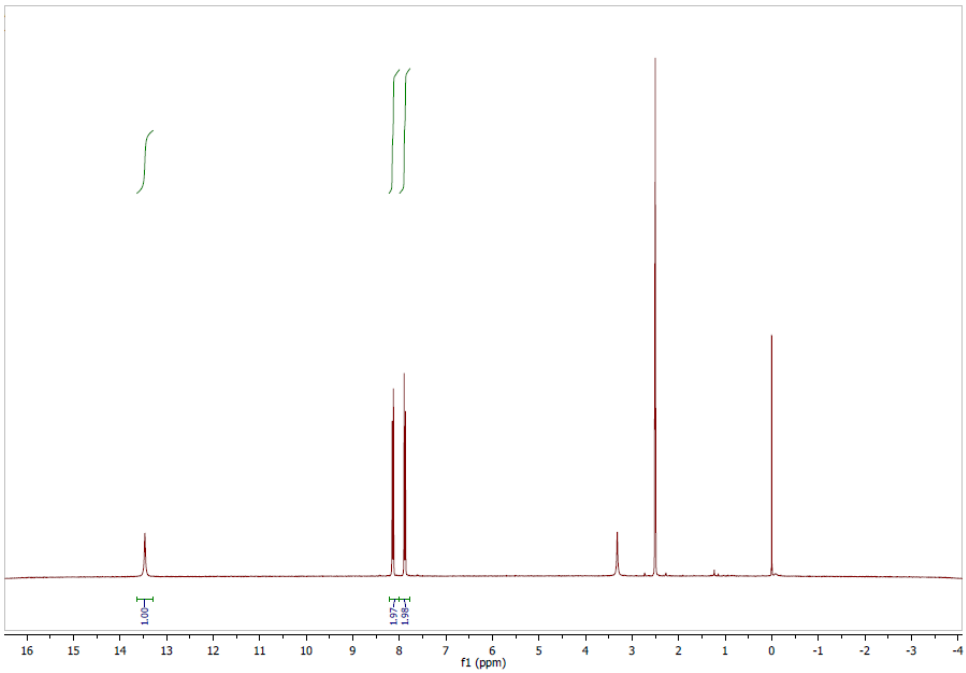
OH
F3C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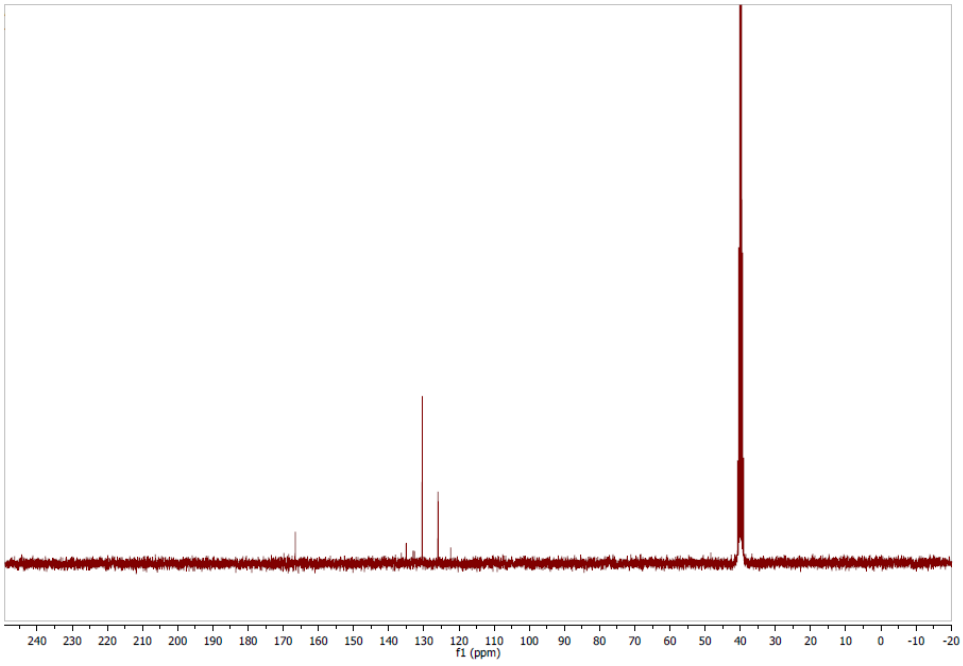
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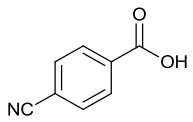
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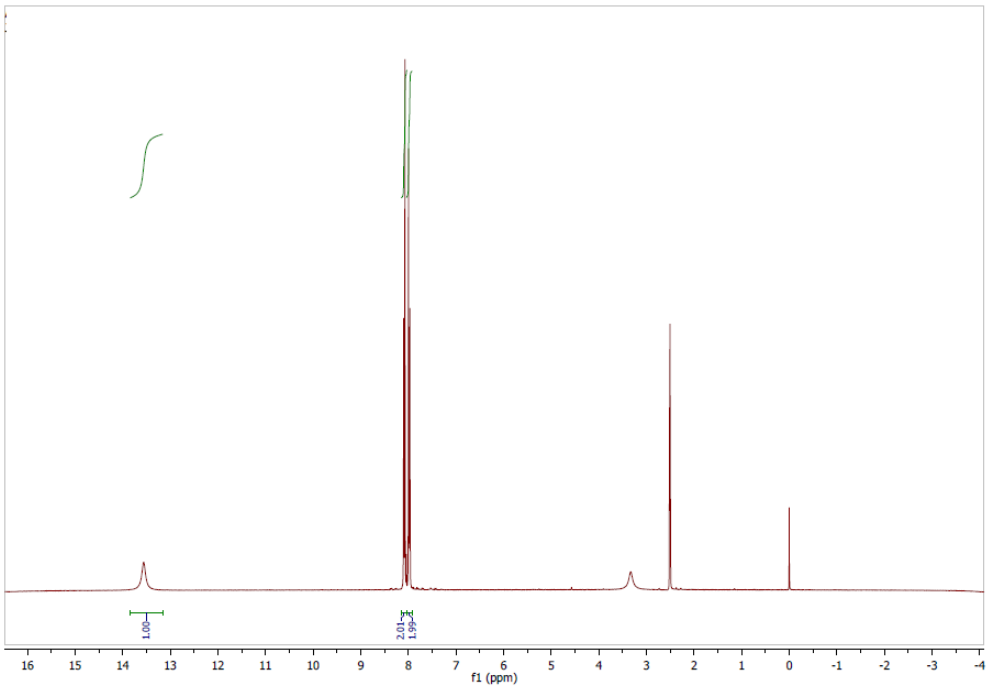
OH
NC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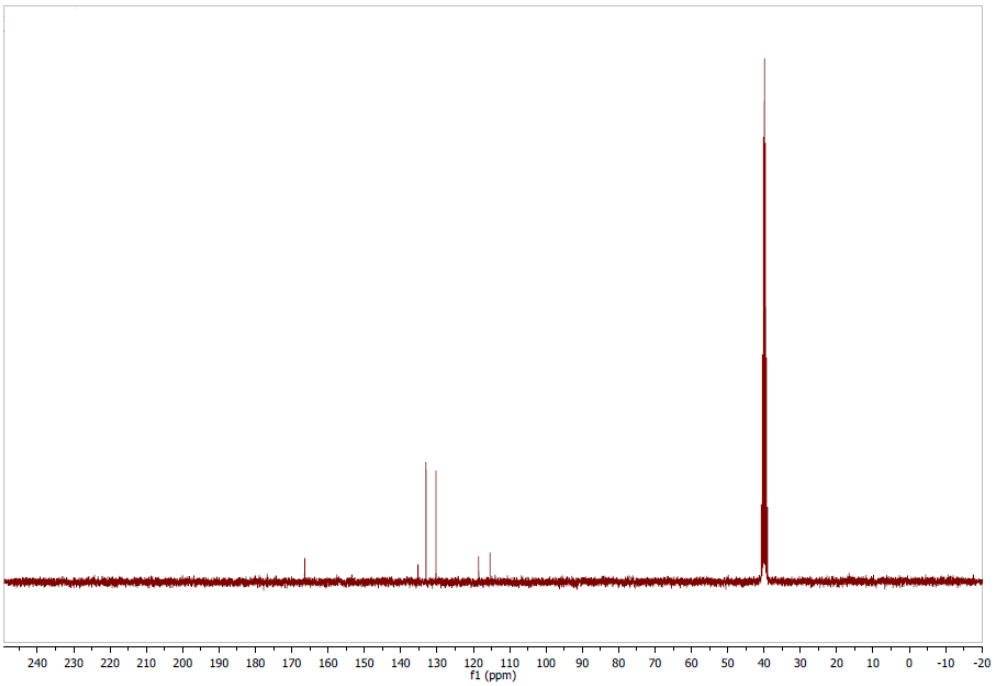
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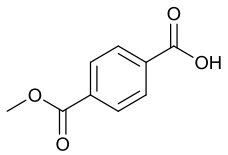
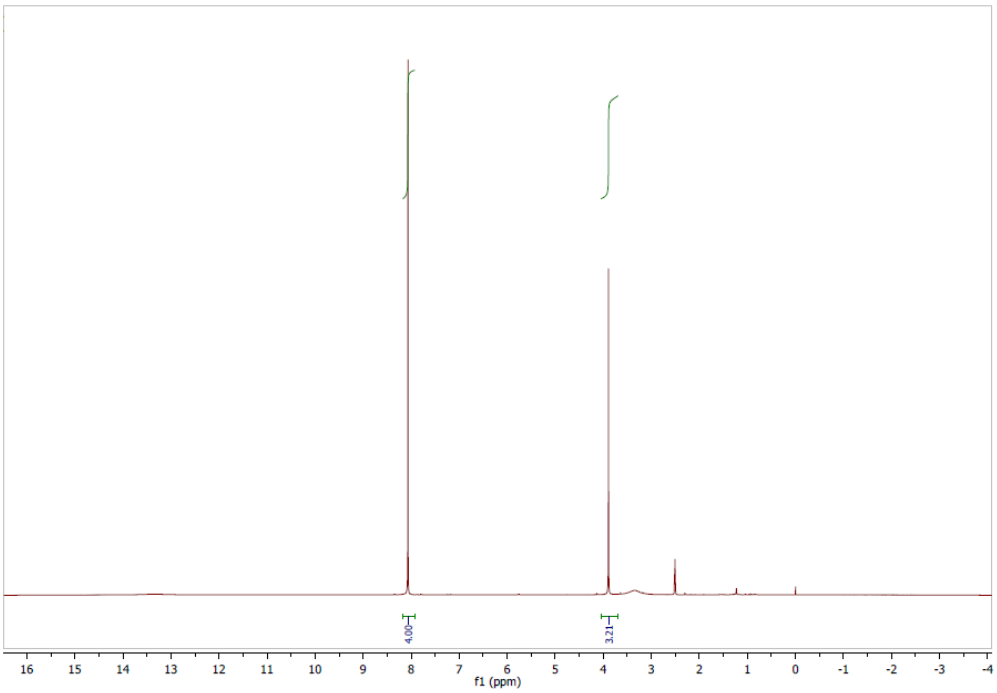

O
OH
O
O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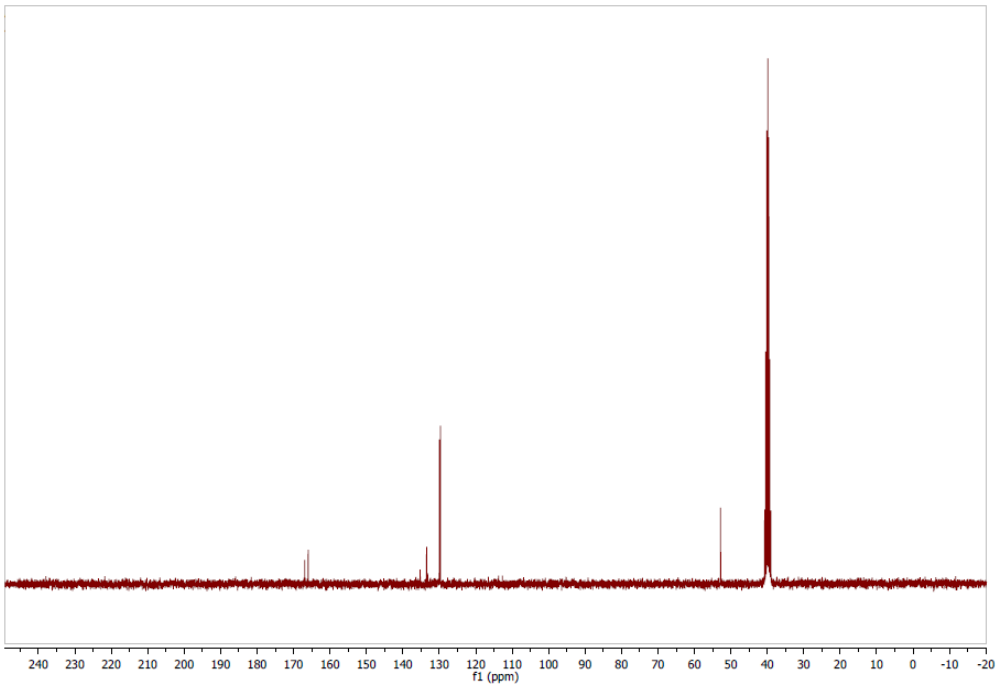
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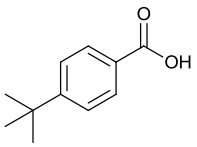
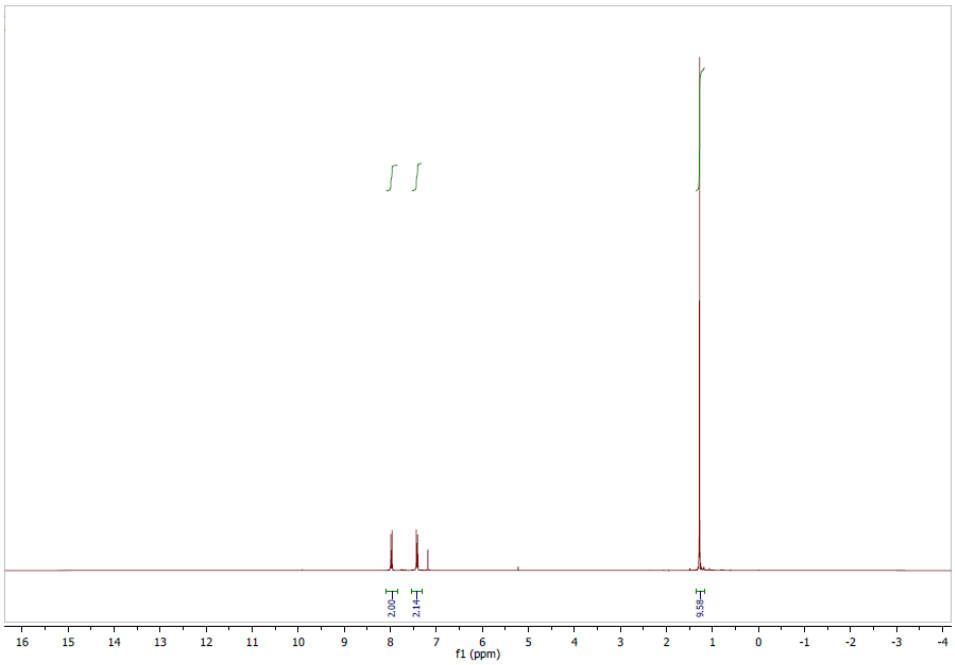

O
OH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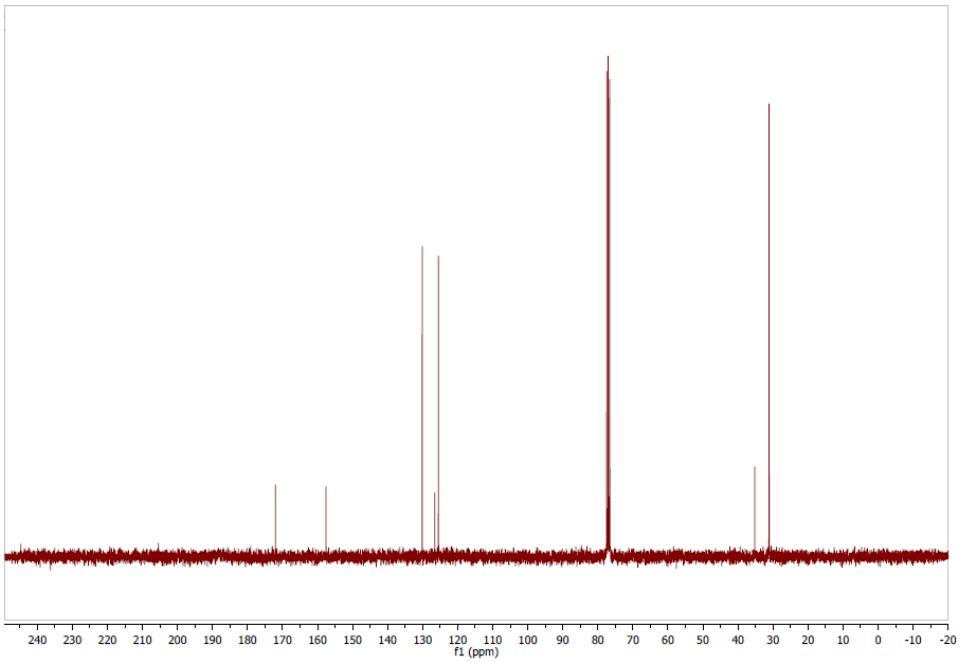
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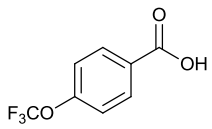
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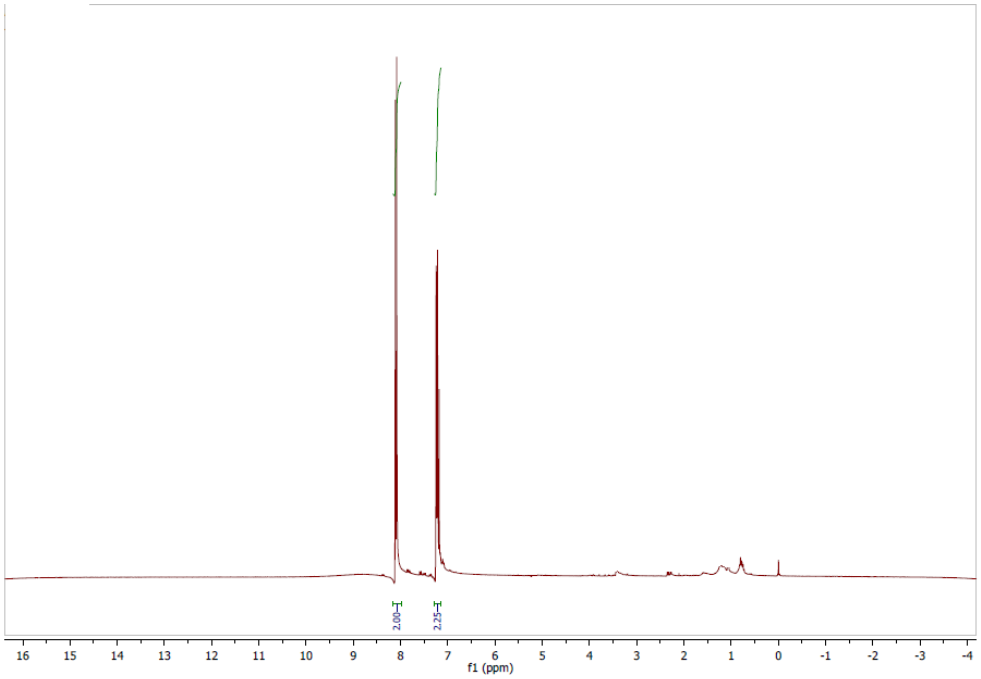
OH
F3CO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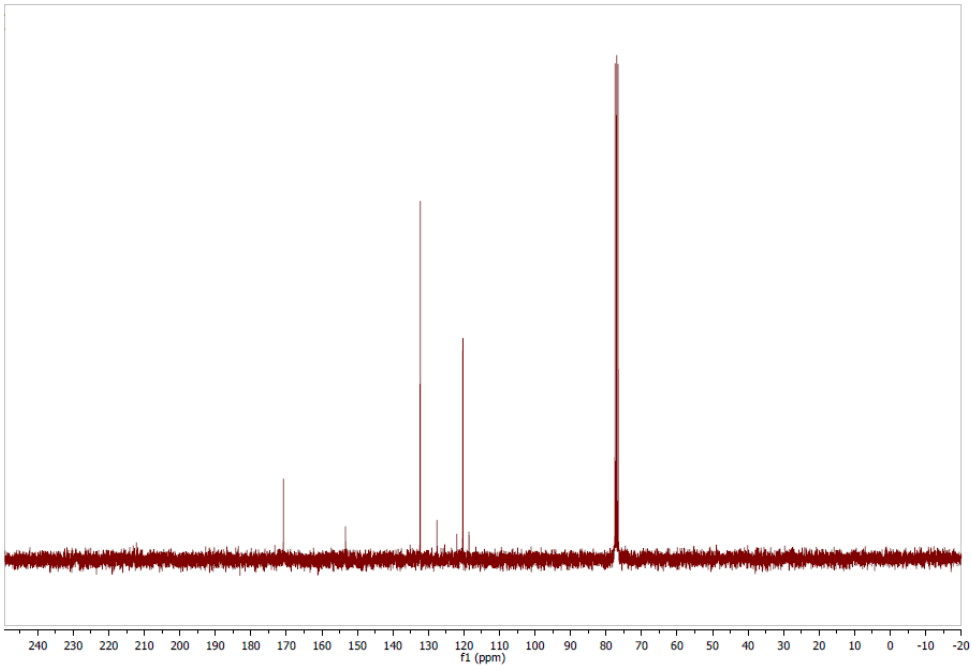
f1 (ppm)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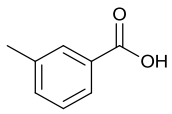
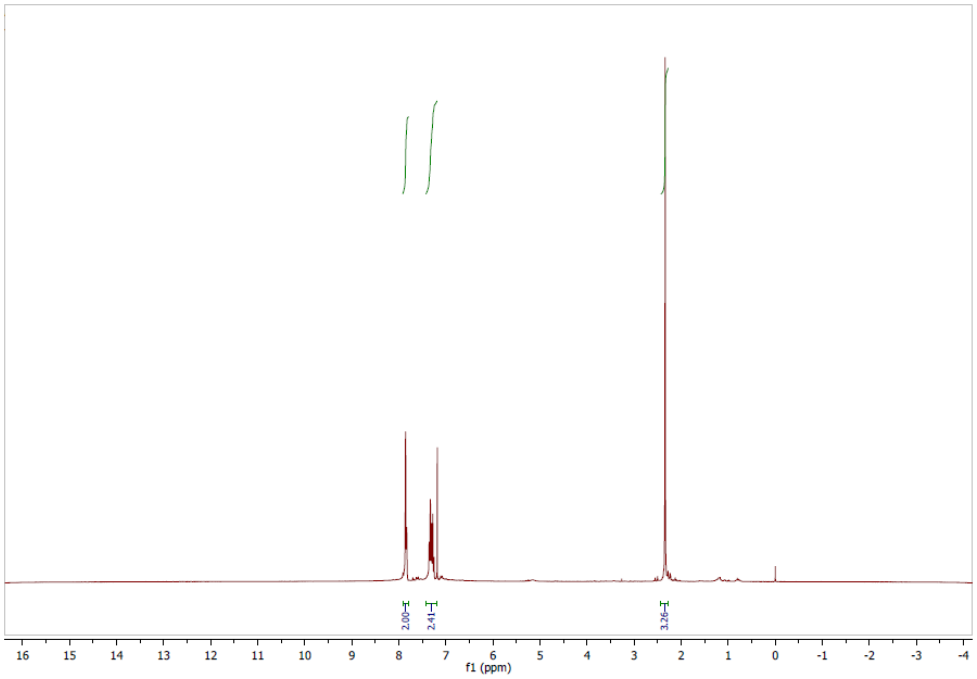
f1 (ppm)


O
OH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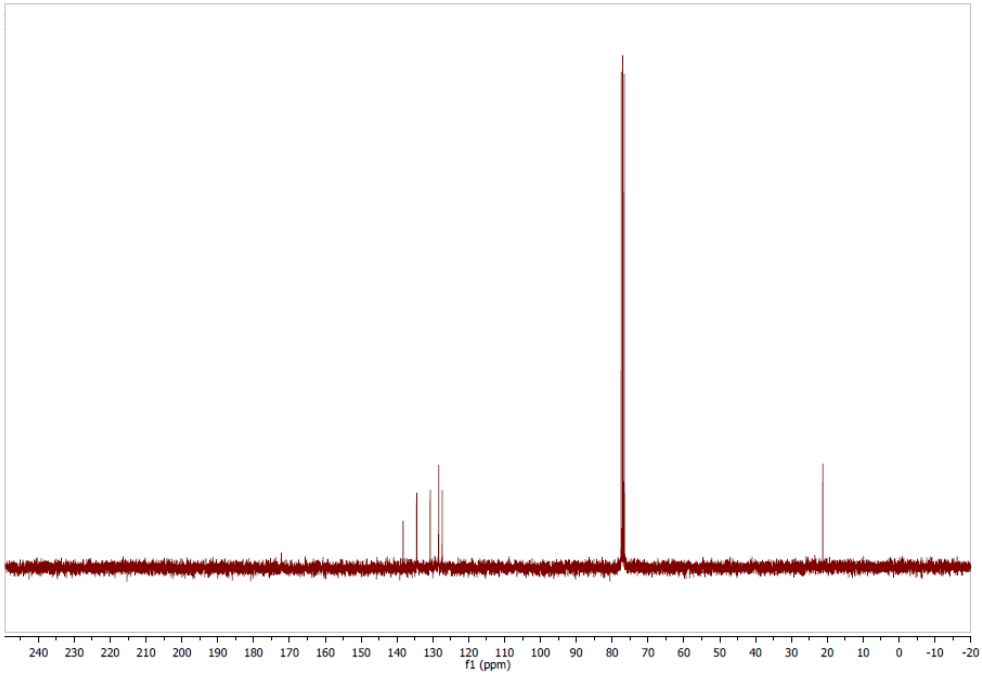
f1 (ppm)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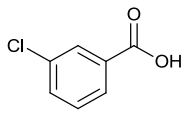
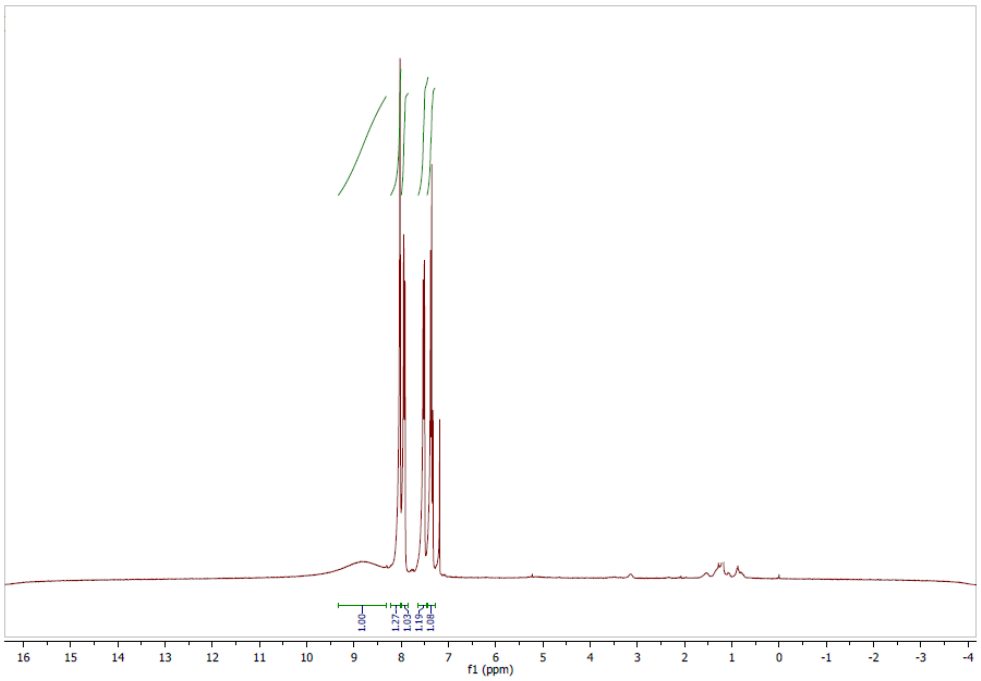

Cl
O
OH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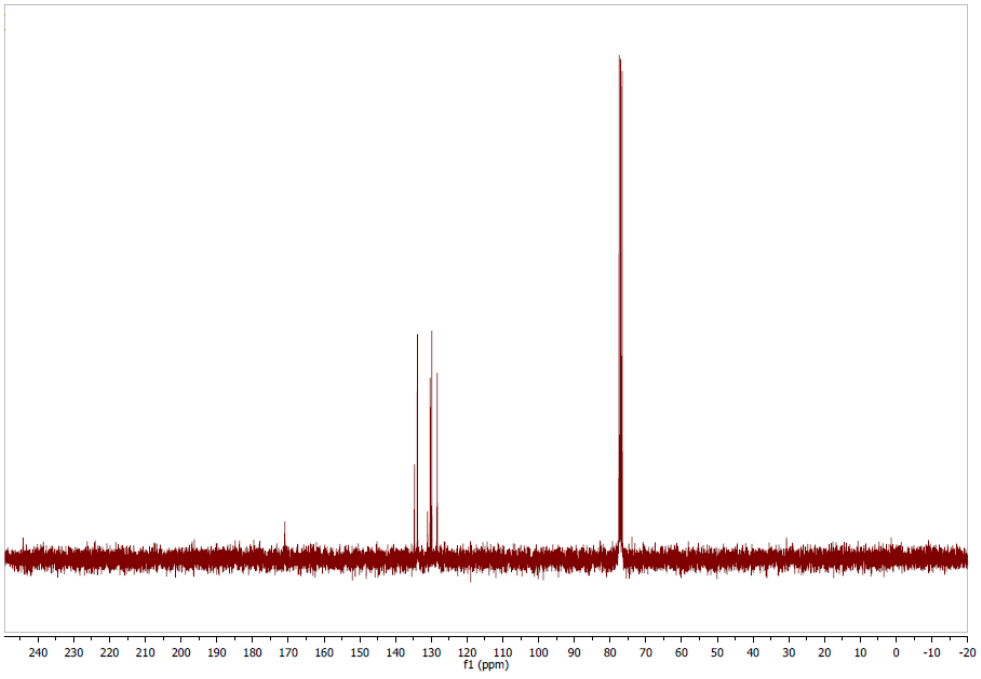
f1 (ppm)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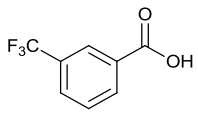
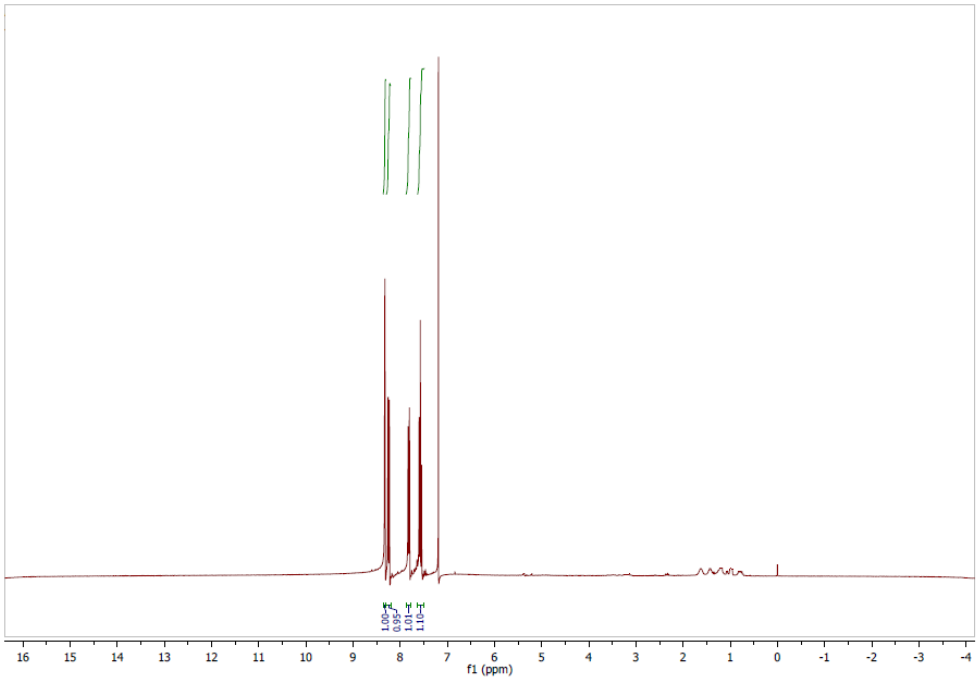

O
F3C
OH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0.95
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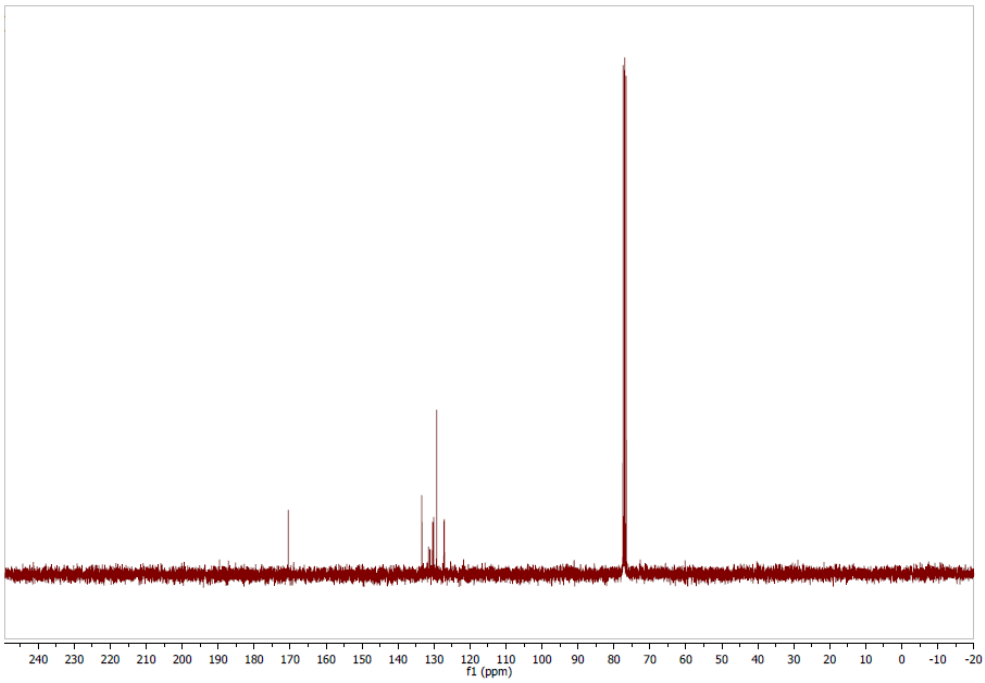
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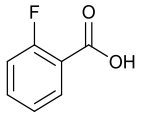
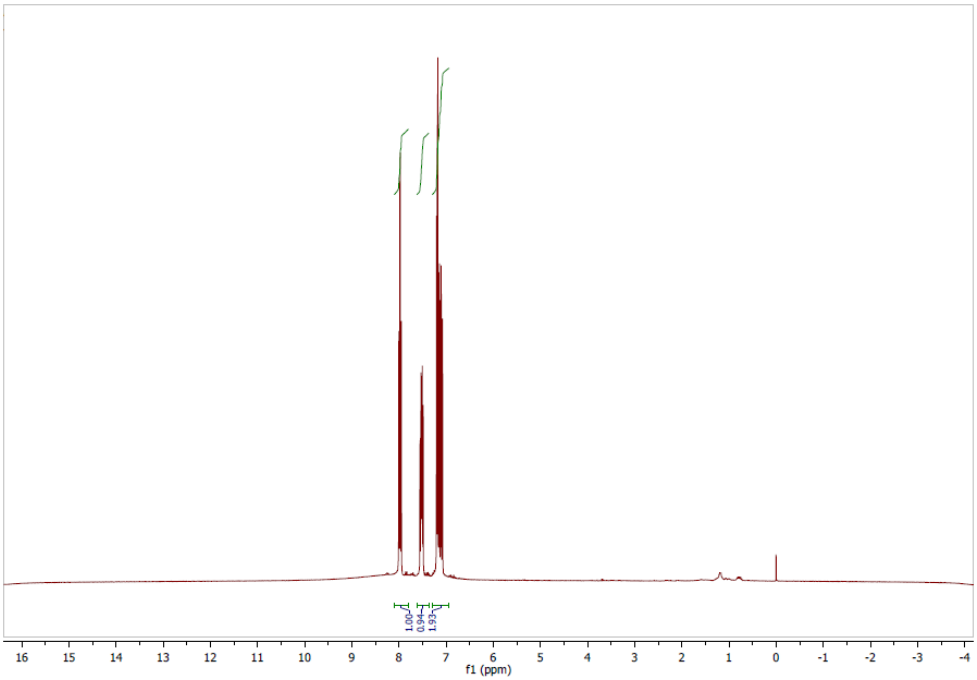
f1 (ppm)


F
O
OH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0.94
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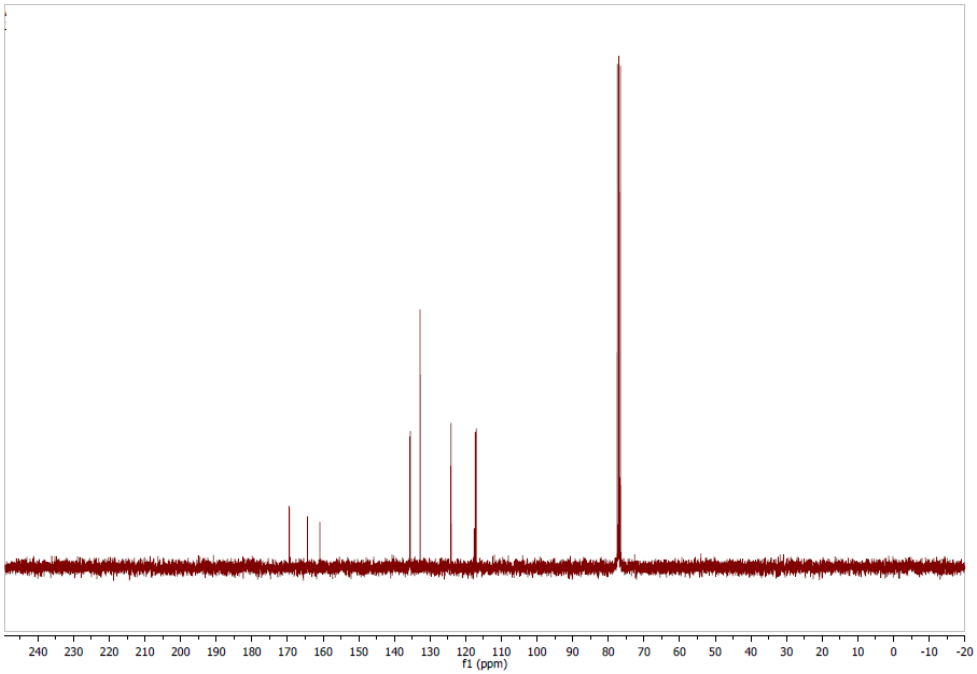
f1 (ppm)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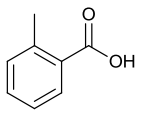
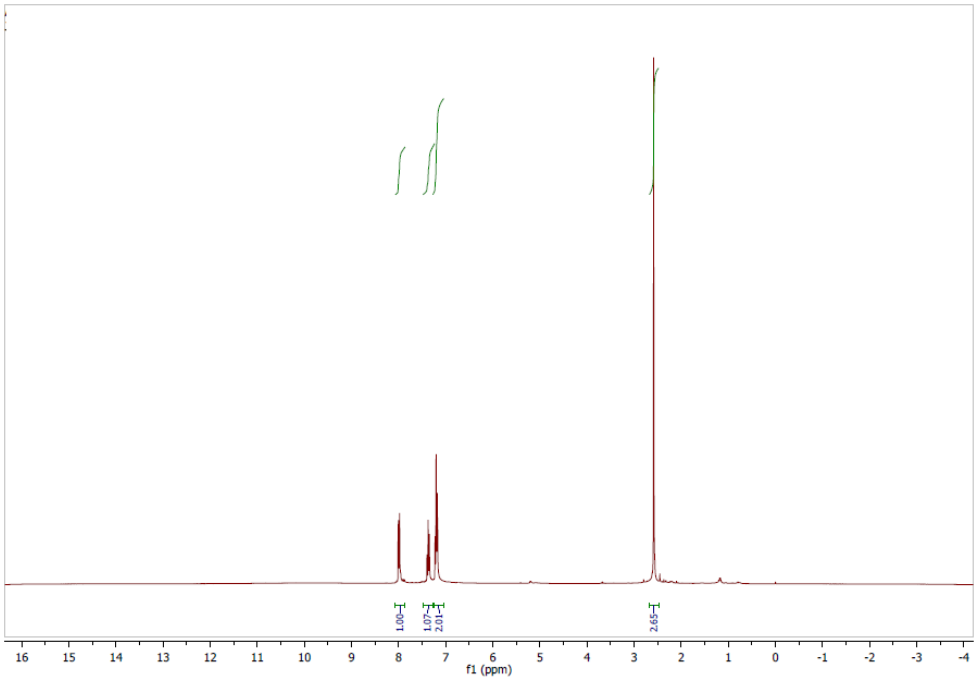
f1 (ppm)


O
OH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1.07
2.01
2.65
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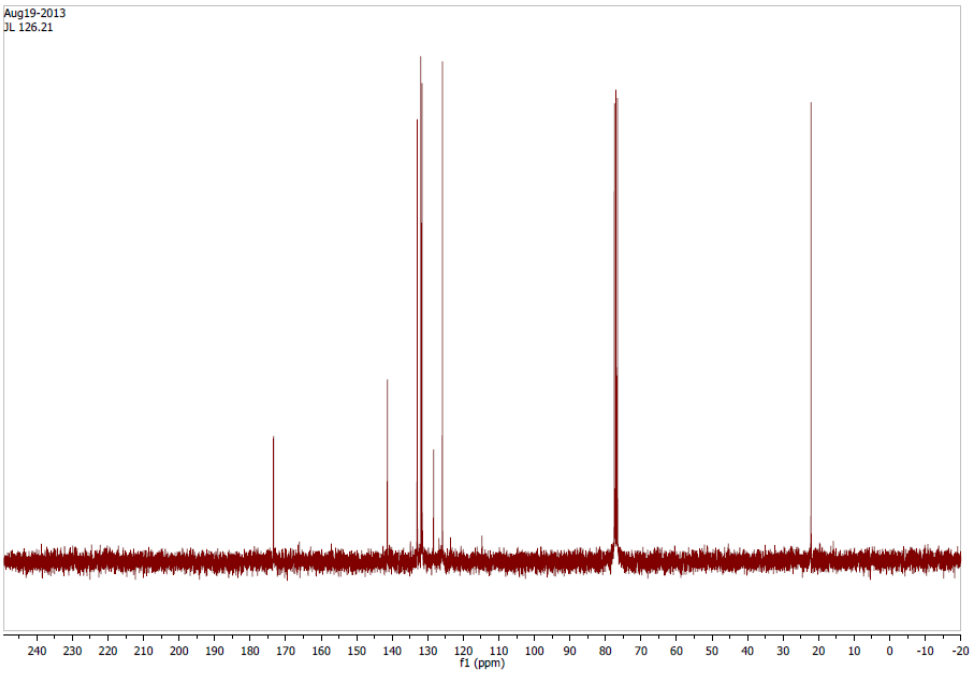
Aug19-2013
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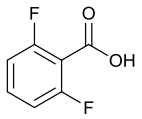
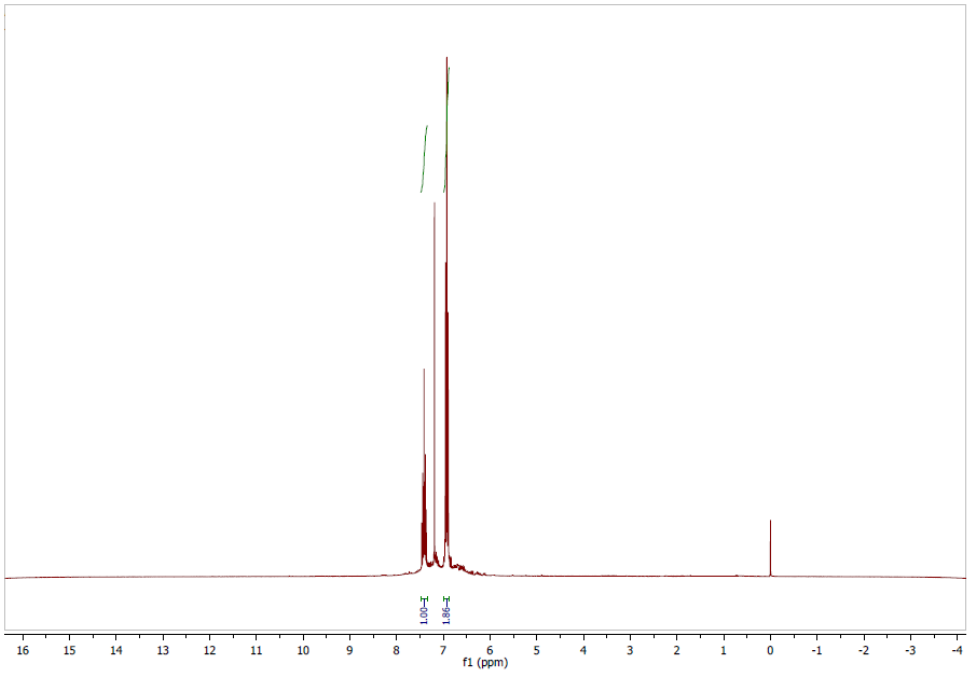

F
O
OH
F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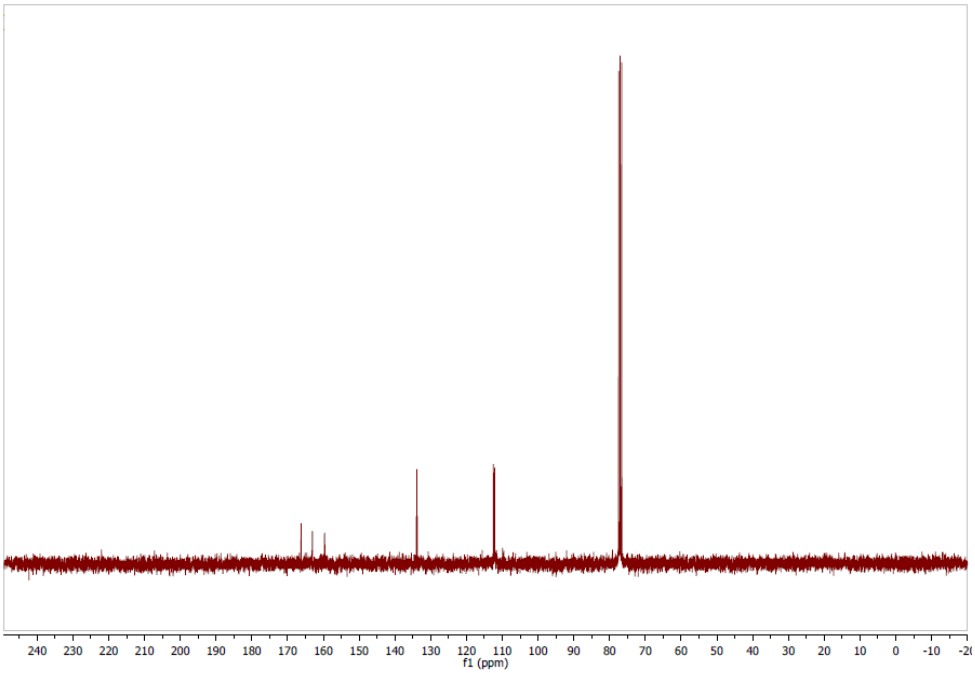
f1 (ppm)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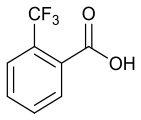
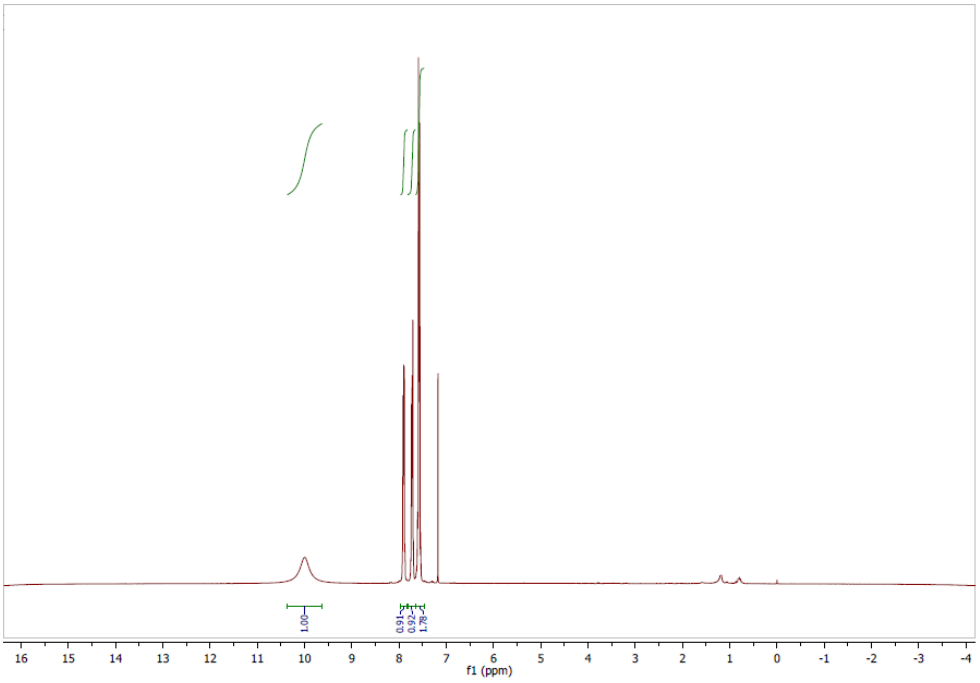

CF3
O
OH


1.00
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0.92
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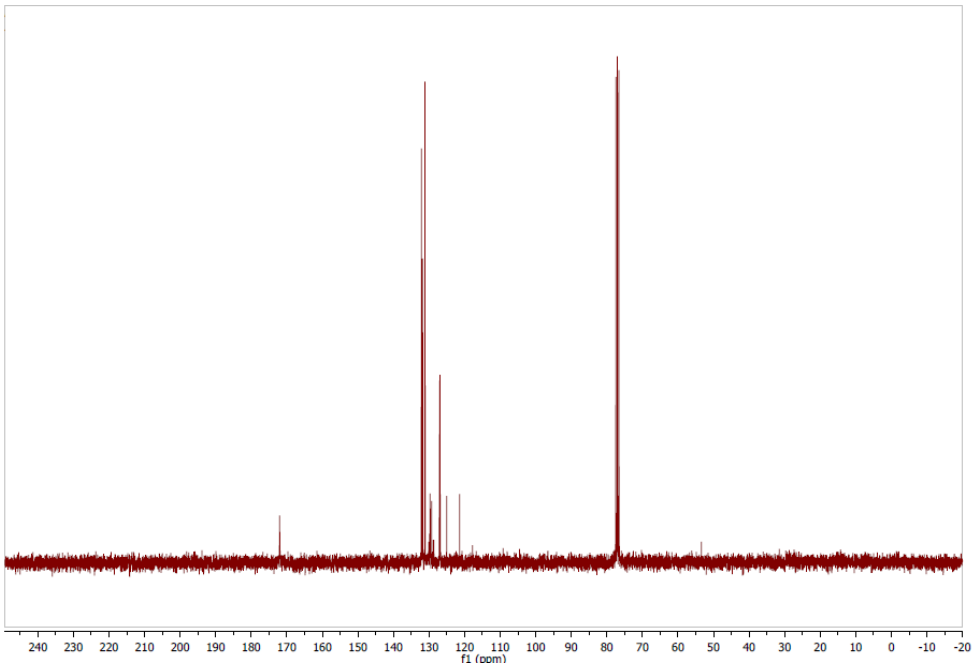
f1 (ppm)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f1 (ppm)