Electronic Supplementary Material (ESI) for Green Chemistry.

Solvent-free Mechanochemical Oxidation and Reduction of Biomass Derived 5-Hydroxymethyl Furfural

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Supporting Information

This document has 34 pages in total.

General Considerations: All glassware was flame dried under argon prior to reaction set up unless otherwise stated. Solids were weighed in open air and added to a septum sealed conical shaped 2 mL microwave vial, which was then purged with argon gas. Liquids were transferred using stainless steel needles and glass or plastic syringes to maintain the inert atmosphere. Flash chromatography was carried out using 40-63µm silica gel (Silicycle).

Materials: All solvents were purchased as ACS grade from Fisher Scientific or JT Baker and were stored under an inert atmosphere with activated 3Å molecular sieves. Distilled water was obtained from an in-house water distillery. All other reagents and chemicals were purchased from Sigma-Aldrich or Alfa Aesar and used without further purification.

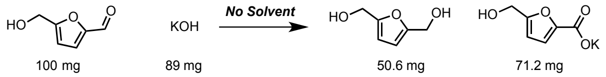
Instrumentation: ^{1}H (500MHz) and ^{13}C (125MHz) NMR spectra were recorded in $CDCl_3$ or *d*^{6}-DMSO using a Varian Inova 500MHz spectrometer. Spectra were referenced to the residual solvent signal or the TMS signal. Spectral features are tabulated in the following order (Note: Spectral features are reported in the following format): chemical shift (δ, ppm); multiplicity (*s*-singlet, *d*-doublet, *t*-triplet, *q*-quartet, *dd*-doublet of doublets, *m*-multiplet), *ddd*-doublet of doublets of doublets; coupling constants (*J*, Hz); number of protons. High resolution mass spectra (HRMS) were obtained using a LTQ Orbitrap Velos ETD (positive and negative mode) mass spectrometer. The reactions were per- formed using a Fritsch Planetary Micro Mill model ‘‘Pulverisette 7’’ housing two stainless steel cups containing eight stainless steel balls each, and sealed by a stainless steel lid fitted with a Teflon gasket.

Synthesis of DHMF and HMFA from HMF under solvent-free mill balling conditions:

100 mg of HMF were placed in a planetary milling jar (approximately 50 mL capacity), 89 mg of finely ground KOH (previously oven dried) are added and the vessel is tightly closed. The reaction is spun at a 60 Hz frequency for 5 min. The reaction mixture is washed with EtOAc (2x2mL), and this organic portion is dried over Na_2SO_4, filtered and the solvent removed under vacuum to afford a pale yellow oil (49.6 mg) of DHMF. The remaining solid (not soluble in EtOAc) can be purified by recrystallization with EtOH:EtOAc (2:98) to obtain the potassium salt of HMFA (66 mg). Crude HNMR analysis shows 100% conversion with >99% yield for the disproportionation using 1,3,5-trimethoxybenzene as internal standard in DMSO-d^6, which suggests that the minor lost in yield comes from the separation/purification step.

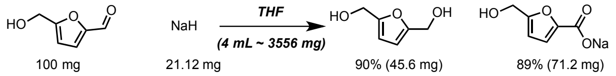
Calculation of the E-factor:

Based on the >99% yield obtained analyzing the crude.



Total mass of reactants: 100 + 89 = 189 mg
Product mass: 50.6 + 71.2 = 121.8 mg
Waste: 189 – 121.8 = 67.2 mg
E-factor = waste/product = 67.2/121.8 = ***0.55***

Calculation of E-factor for previous report: S. Subbiah, S. Simenon, J. Esperanca, L. P. Rebelo and C. Afonso, *Green Chem.*, 2013, **15**, 2849–2853.

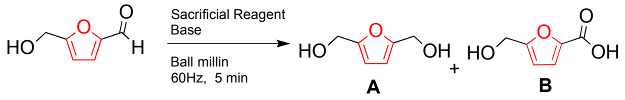


Total mass of reactants: 100 + 21.12 + 355.6 = 476.72 mg (assuming 90% recovery of THF from distillation)
Product mass: 45.6 + 71.2 = 103.4 mg
Waste: 476.72 – 103.4 = 373.32 mg
E-factor = waste/product = 373.32/103.4 = ***3.61***

These calculations were done according to the examples presented in:

1. M. J. Climent, A. Corma, S. Iborra, M. Mifsud and A. Velty, *Green Chem.*, 2010, **12**, 99–107.
2. V. Trombettoni, D. Sciosci, M. P. Bracciale, F. Campana, M. L. Santarelli, A. Marrocchi and L. Vaccaro, *Green Chem.*, 2018, **20**, 3222–3231.

Table S1. Sacrificial reagents tested for the selective cross-Cannizzaro reaction of HMF.



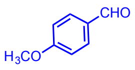
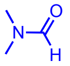
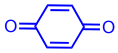
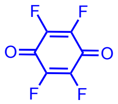
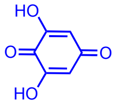
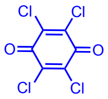
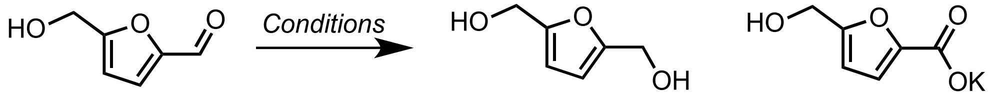
Entry	Sacrifice Reagent (equiv.)		Base (equiv.)	%yield (A:B)
1	$(CH_2O)_n$	1.2 equiv.	KOH (2)	44% (only A)
2	$(CH_2O)_n$	1.2 equiv.	KOH (4)	90% (only A)
3	D-Glucose	1.2 equiv.	KOH (4)	95% (1:1)
4		1.2 equiv.	KOH (4)	88% (1.2:1)
5	Benzaldehyde	1.2 equiv.	KOH (4)	93% (1:1)
6		1.2 equiv.	KOH (4)	87% (1:1)
7		1.2 equiv.	KOH (4)	45% (1:1)
8		1.2 equiv.	KOH (4)	31% (2:1)
9		1.2 equiv.	KOH (4)	52% (4:1)
10		1.2 equiv.	KOH (4)	20% (1:2)
11		1.5 equiv.	KOH (6)	45% (1:2)
12		2.0 equiv.	KOH (4)	20% (1:2.5)
13		2.0 equiv.	KOH (8)	52% (1:2)

Table S2. Effect of milling frequency and reaction time in the disproportionation of HMF.

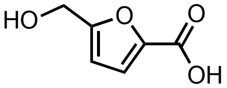


Mass of HMF (g)	Frequency of Milling (Hz)	Reaction Time (min)	Disproportionation % yield (HNMR)
0.100	15	5	88
0.100	30	5	96
0.100	60	5	>99
12.800	60	5	92
12.800	60	7	>99

Conditions: 1 equiv. of HMF, 2.0 equiv. of KOH.

Spectroscopic Data

Compound 1 : 5-hydroxymethylfuran-2-oic acid

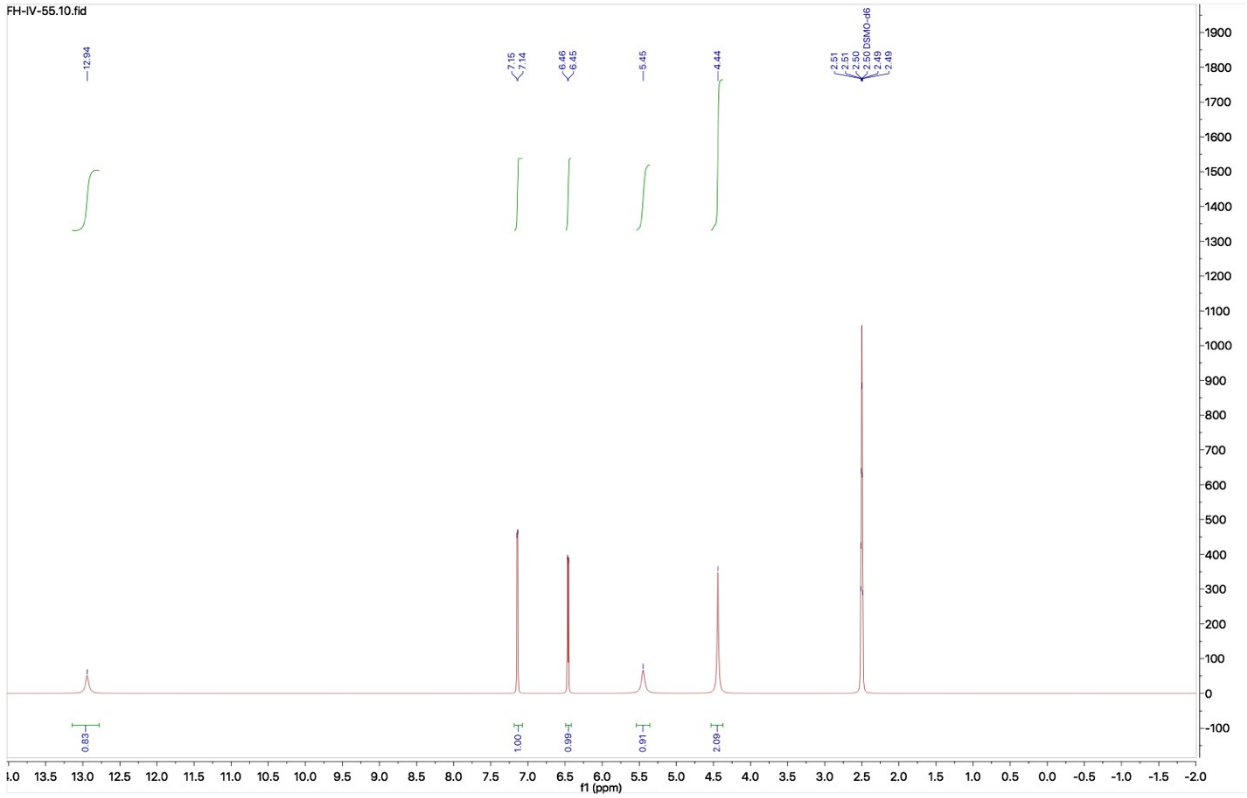


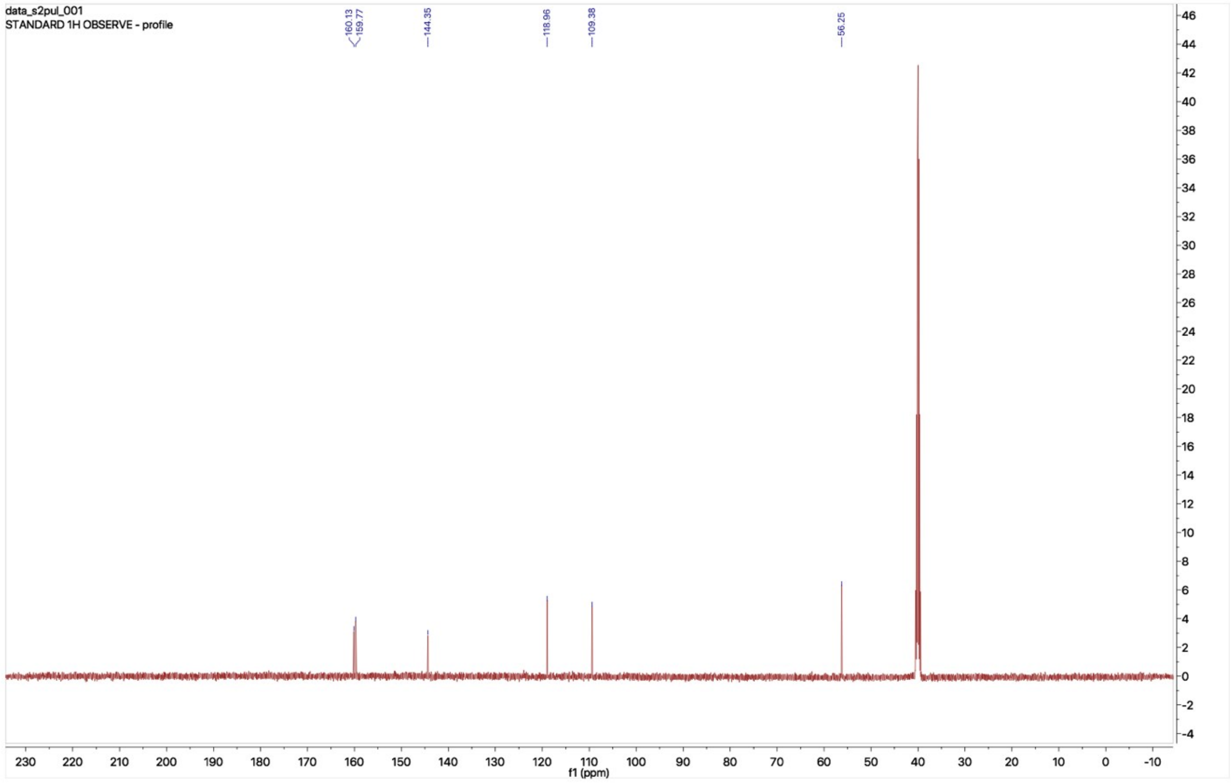
Compound 1 was prepared following the optimized conditions for the Cannizzaro disproportionation of HMF on solvent-free planetary ball milling. It is highly important to use oven dried grinded KOH as humidity could affect the outcome of the reaction greatly. Compound 1 was isolated as described in the experimental section, and converted to the carboxylic with HCl/acid-base extraction treatment, to yield a white solid. This compound has proven to be sensitive to long-term exposure to air and light. So it was properly stored in an amber vial at 4 °C under inert atmosphere.

^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 12.94 (bs, 1H), 7.15 (d, J = 3.4 Hz, 1H), 6.46 (d, J = 3.4 Hz, 1H), 5.45 (bs, 1H), 4.44 (s, 2H).

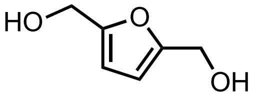
^{13}C NMR (125 MHz, DMSO-d^6) δ ppm 160.1 (1C), 159.8 (1C), 144.4 (1C), 119.0 (1C), 109.4 (1C), 56.2 (1C).

HRMS (EI): Exact mass calculated for $C_5H_3O_3^-$ $[M-1]^{-\cdot}$: 141.1021 found 141.0196 (-1.6 ppm).


FH-IV-55.10.fid
12.94
7.15
7.14
6.46
6.45
5.45
4.44
2.51
2.51
2.50 DSMO-d6
2.49
2.49
0.83
1.00
0.99
0.91
2.09
f1 (ppm)

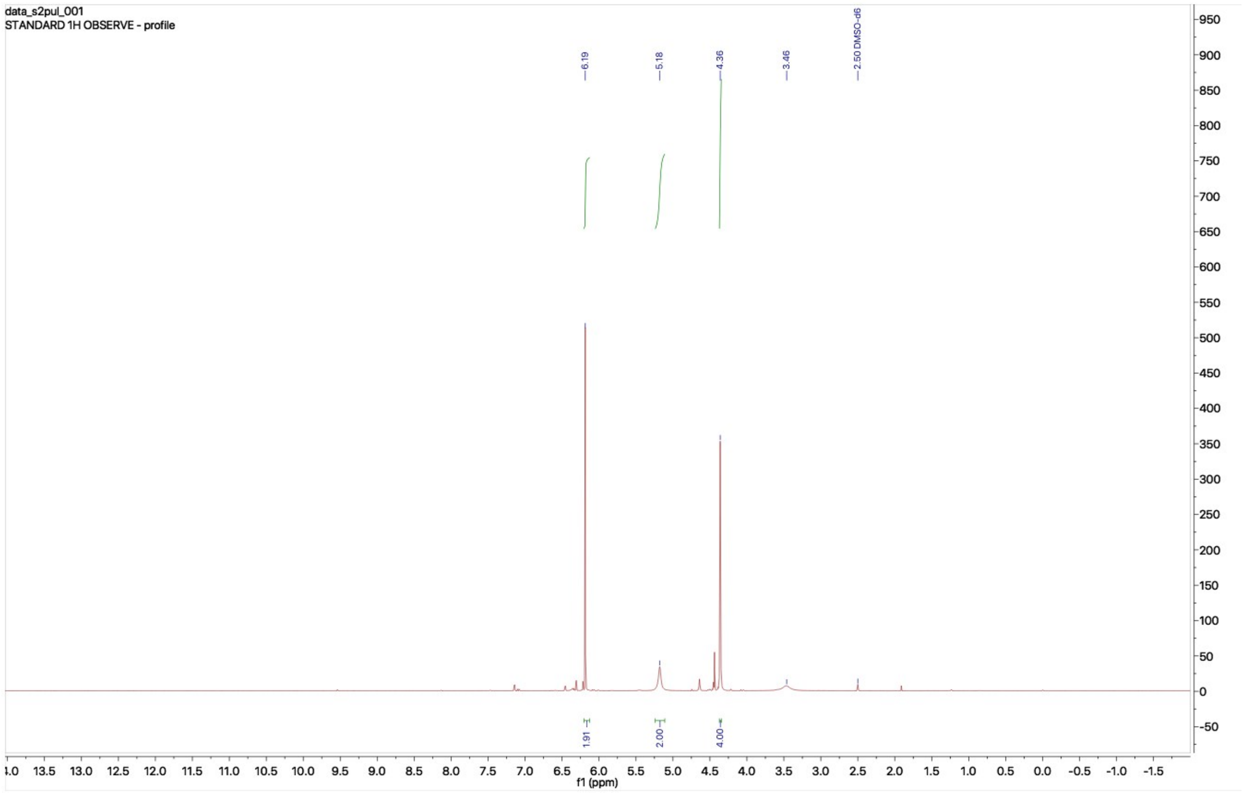

data_s2pul_001
STANDARD 1H OBSERVE - profile
160.13
159.77
144.35
118.96
109.38
56.25
f1 (ppm)

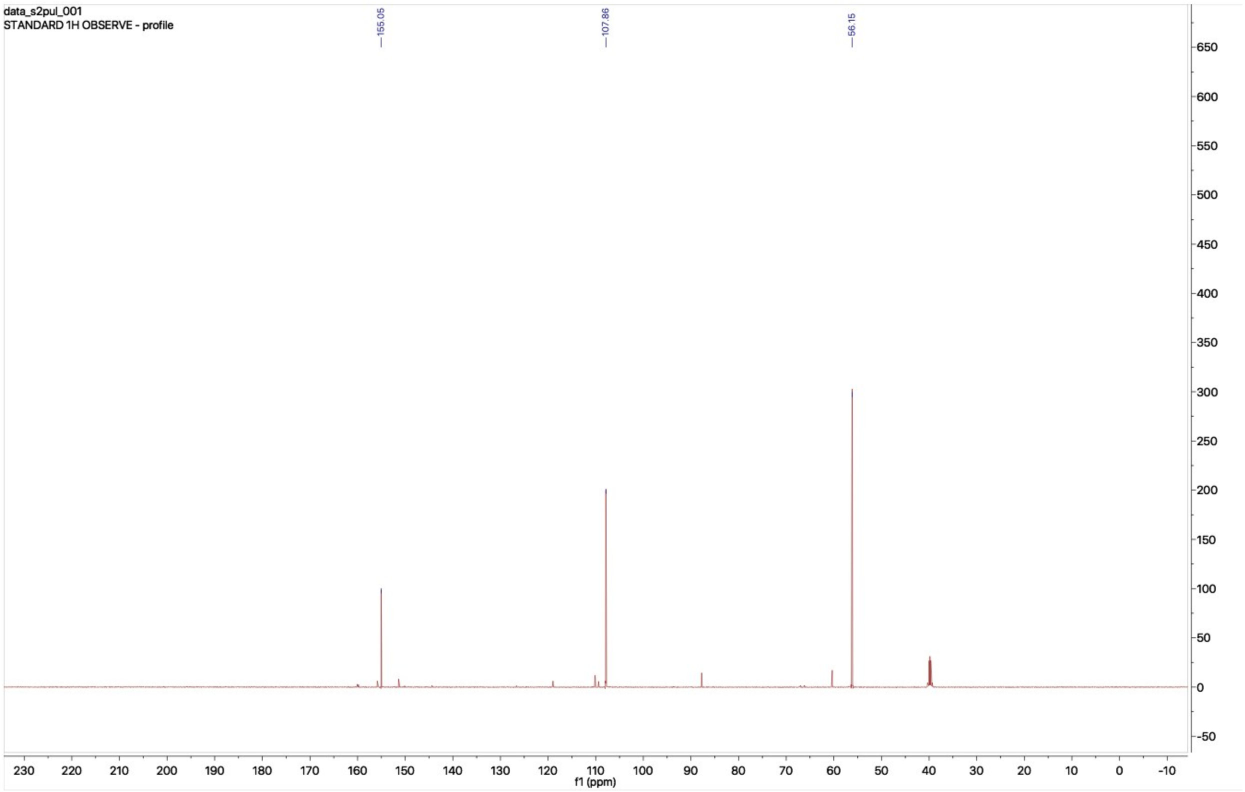
Compound 2 : 2,5-bishydroxymethyl furan



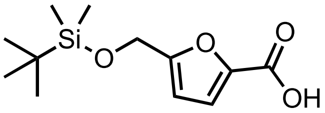
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.19 (s, 2H), 5.18 (bs, 2H), 4.36 (s, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 155.0 (2C), 107.9 (2C), 56.2 (2C).

HRMS (EI): Exact mass calculated for $C_6H_7O_3^-$ [M-1]$^{-\cdot}$: 127.1191 found 127.1186 (3.5 ppm).



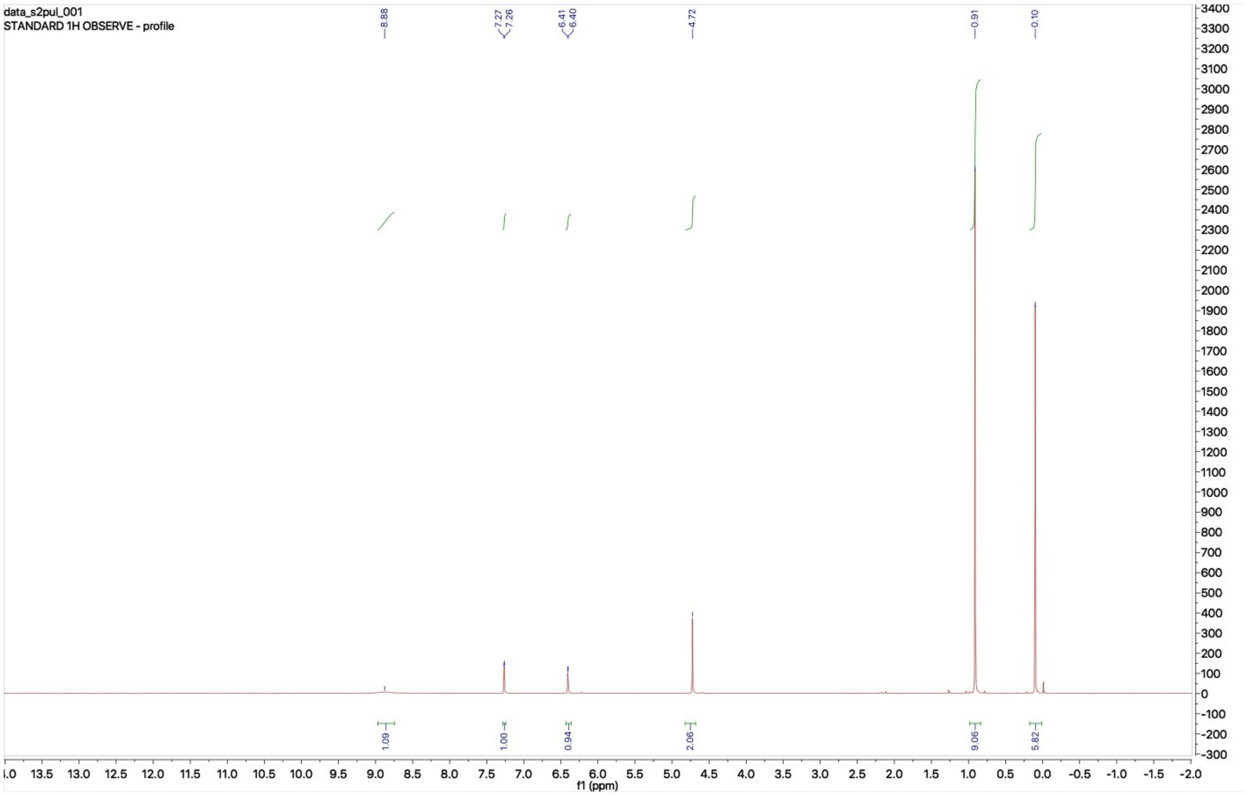


Compound 3.1a : 5-(((*tert*-butyldimethylsilyl)oxy)methyl)furan-2-carboxylic acid



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.88 (bs, 1H), 7.26 (d, J = 3.5 Hz, 1H), 6.40 (d, J = 3.5 Hz, 1H), 4.72 (s, 2H), 0.91 (s, 9H), 0.10 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 163.4 (1C), 160.3 (1C), 121.0 (1C), 109.1 (2C), 58.6 (1C), 25.8 (3C), 18.3 (1C), -5.4 (2C).

HRMS (EI): Exact mass calculated for $C_{12}H_{19}O_4Si^-$ $[M-1]^{-\cdot}$: 255.1059 found 255.1059 (2.4 ppm).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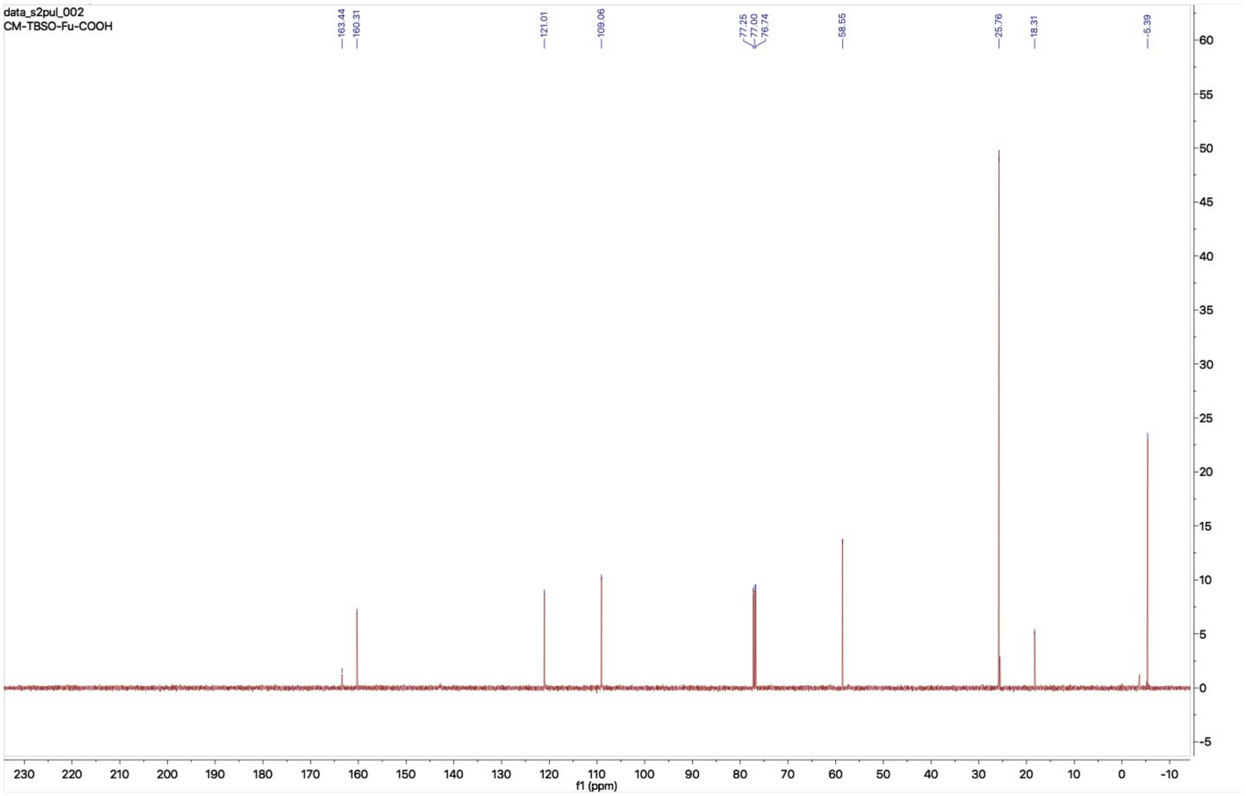
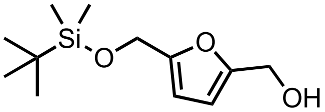
STANDARD 1H OBSERVE - profile
8.88
7.27
7.26
6.41
6.40
4.72
0.91
0.10
1.09
1.00
0.94
2.06
9.06
5.82
f1 (ppm)

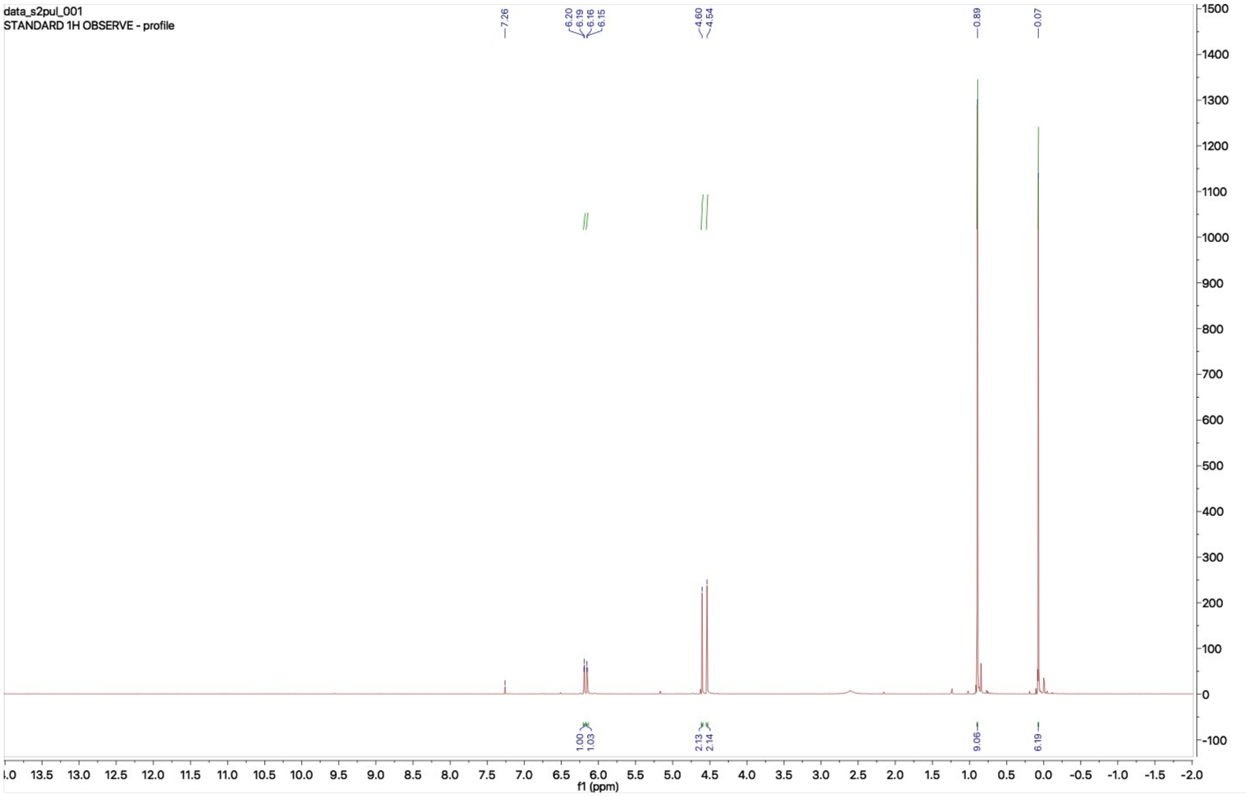

data_s2pul_002
CM-TBSO-Fu-COOH
163.44
160.31
121.01
109.06
77.25
77.00
76.74
58.55
25.76
18.31
-5.39
f1 (ppm)

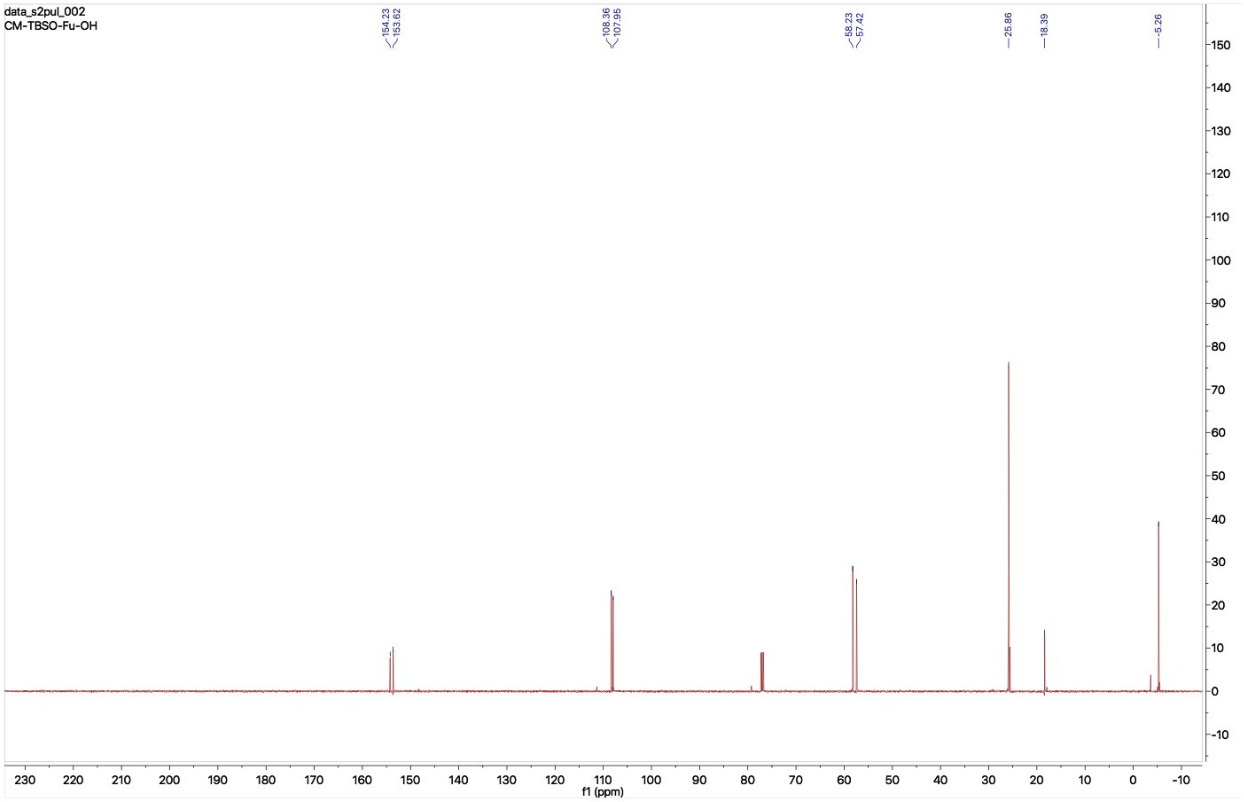
Compound 3.1b : (5-(((*tert*-butyldimethylsilyl)oxy)methyl)furan-2-yl)methanol



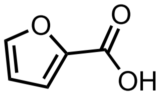
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.20 (d, J = 3.1 Hz, 1H), 6.16 (d, J = 3.1 Hz, 1H), 4.60 (s, 2H), 4.54 (s, 2H), 2.62(bs, 1H), 0.89 (s, 9H), 0.07 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 154.2 (1C), 153.6 (1C), 108.4 (1C), 108.0 (1C), 58.2 (1C), 57.4 (1C), 25.9 (3C), 18.4 (1C), -5.3 (2C).

HRMS (EI): Exact mass calculated for $C_{12}H_{21}O_3Si^-$ $[M-1]^{-\cdot}$: 241.1260 found 241.1267 (2.4 ppm).



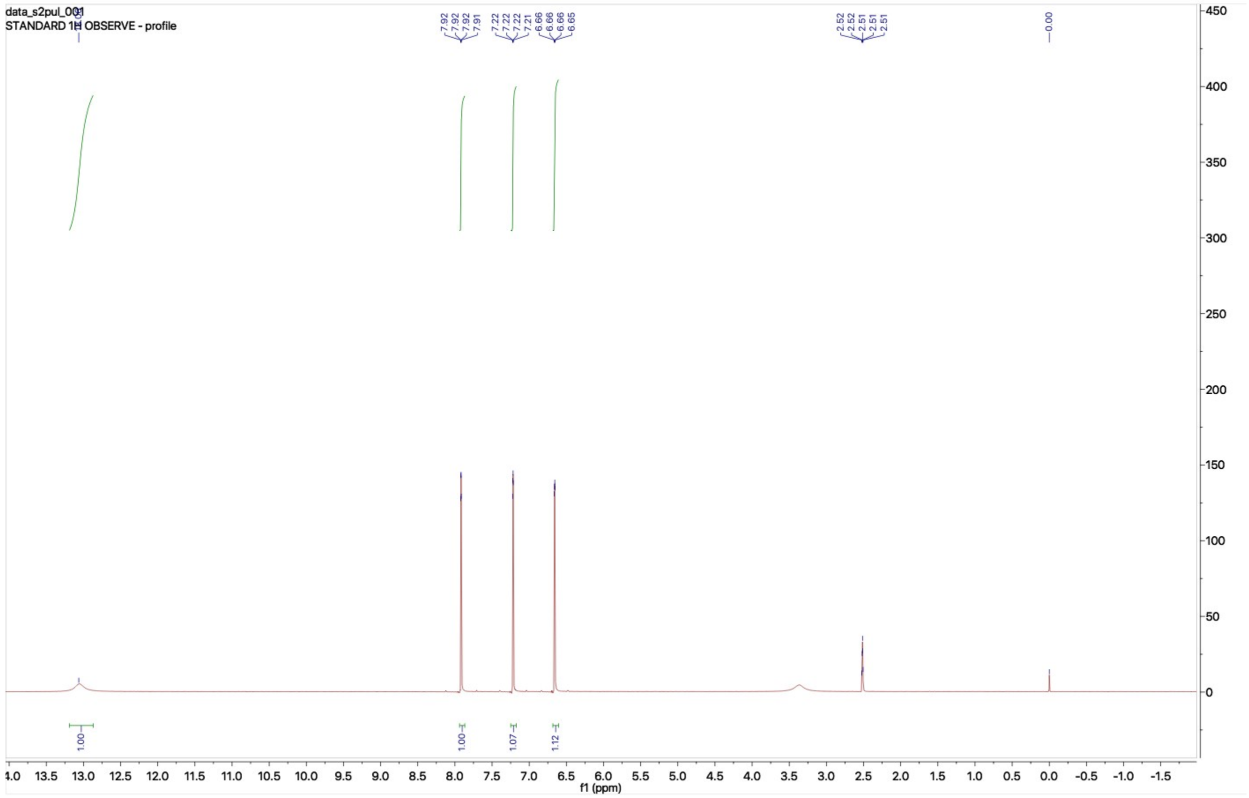


Compound 3.2a : furan-2-carboxylic acid



^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 13.06 (bs, 1H), 7.92 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.22 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.66 (dd, *J* = 3.5, 1.7 Hz, 1H).
^{13}C NMR (125 MHz, DMSO-d^6) δ ppm 159.7 (1C), 147.5 (1C), 145.3 (1C), 118.1 (1C), 112.5 (1C).

HRMS (EI): Exact mass calculated for $C_5H_3O_3^-$ [M-1]$^{-\cdot}$: 111.0082found 111.0085 (2.6 ppm).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7.92
7.92
7.91
7.22
7.22
7.22
7.21
6.66
6.66
6.66
6.65
2.52
2.52
2.51
2.51
2.51
0.00
1.00
1.00
1.07
1.12
4.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)
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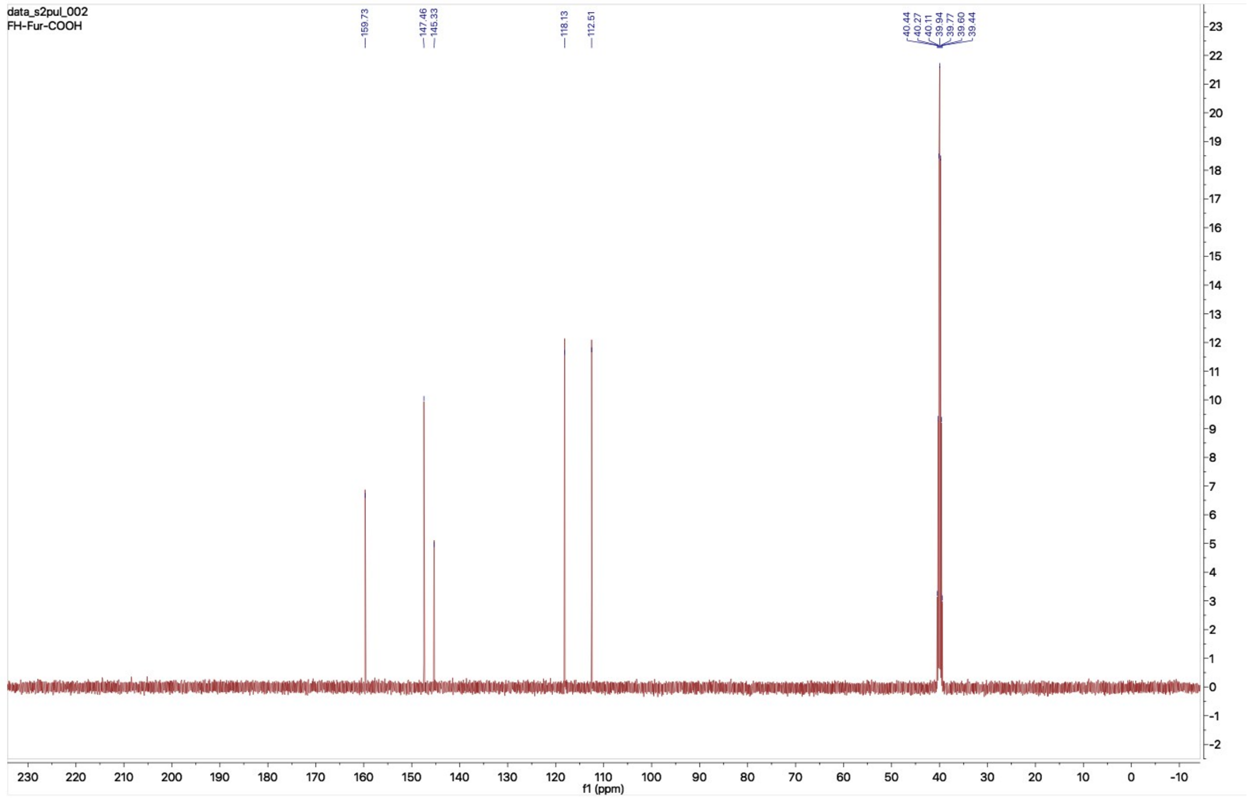
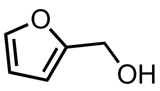
400
350
300
250
200
150
100
50
0


data_s2pul_002
FH-Fur-COOH
159.73
147.46
145.33
118.13
112.51
40.44
40.27
40.11
39.94
39.77
39.60
39.44
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
f1 (ppm)
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2

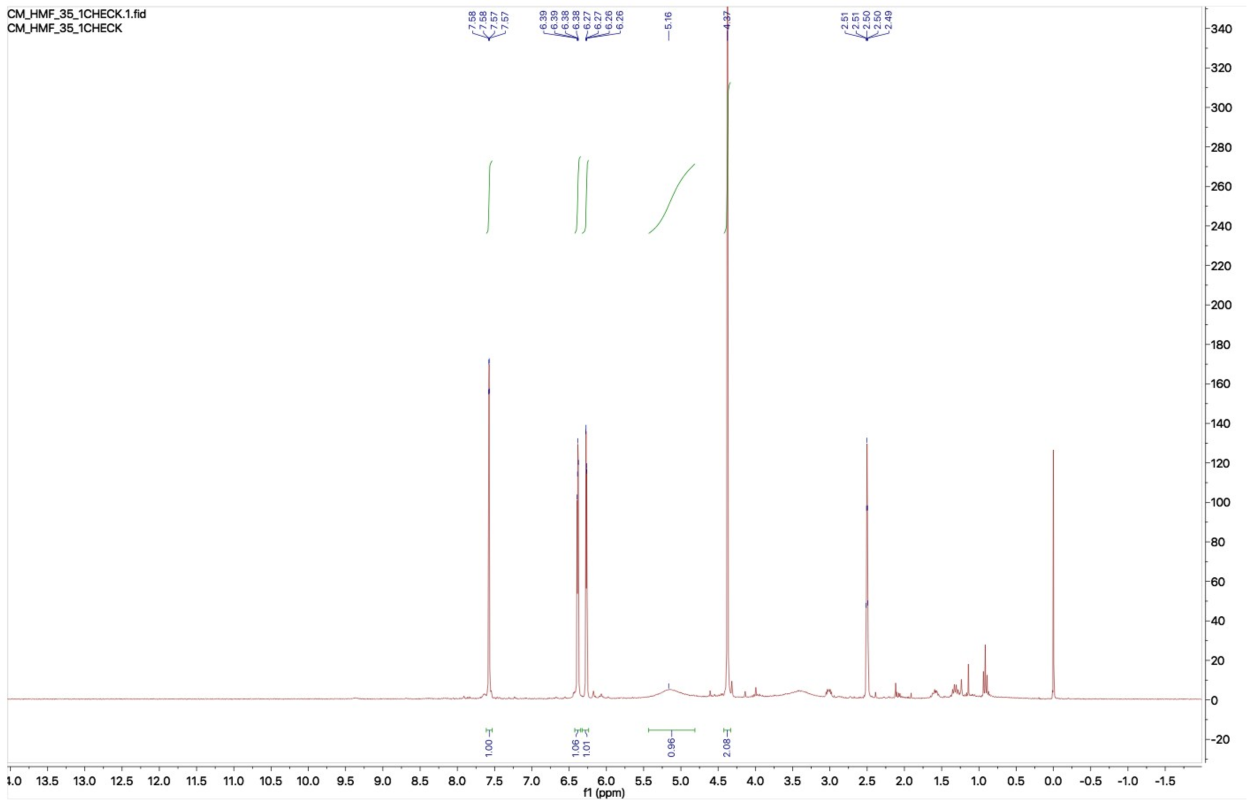
Compound 3.2b : furan-2-ylmethanol



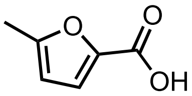
^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 7.57 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.38 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.27 (dd, *J* =3.1, 0.8, 1H), 5.16 (bs, 1H), 4.37 (s, 2H).

HRMS (EI): Exact mass calculated for $C_5H_5O_2^-$ [M-1]$^{-\cdot}$: 97.0931 found 97.0927 (3.7 ppm).

Spectral data in agreement with reported data from R. Ambre, C. Y. Yu, S. B. Mane, C. F. Yao and C. H. Hung, *Tetrahedron*, 2011, **67**, 4680–4688.

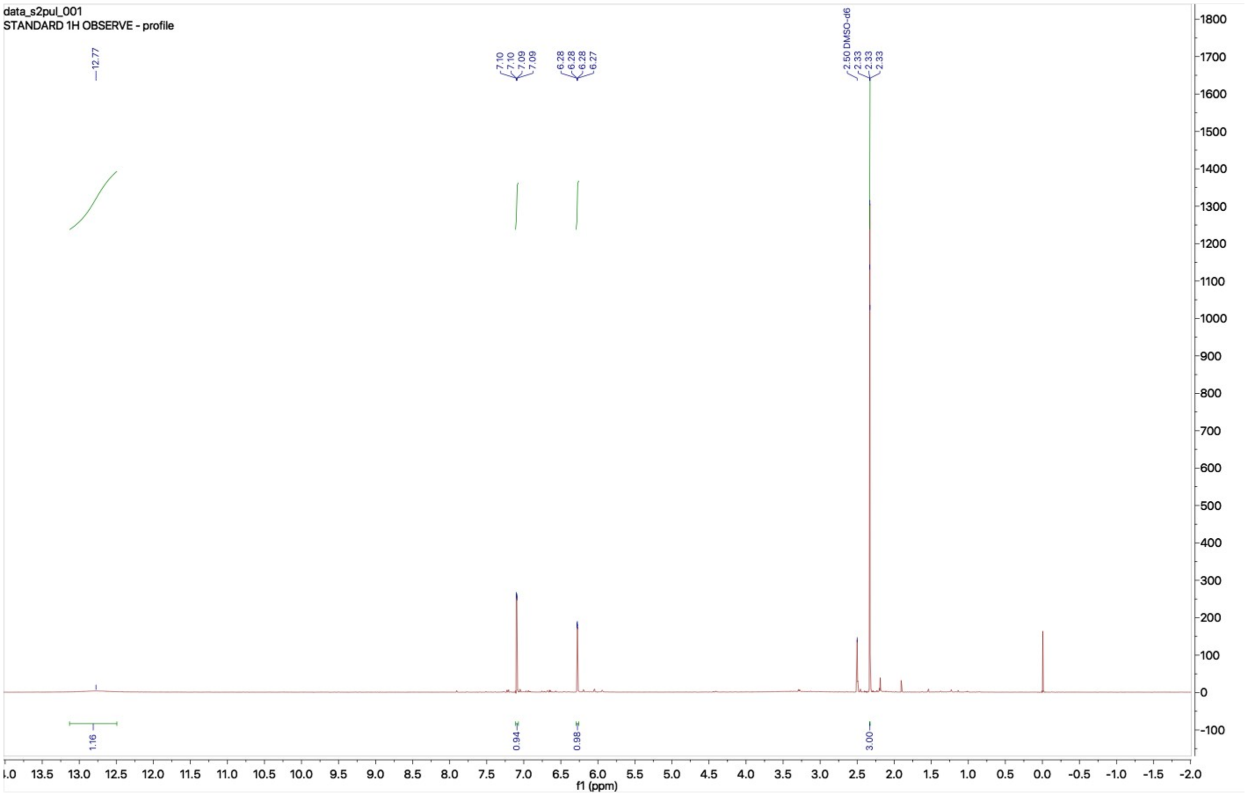


Compound 3.3a : 5-methylfuran-2-carboxylic acid

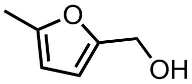


^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 12.77 (bs, 1H), 7.10 (dd, J = 3.3, 0.5 Hz, 1H), 6.28 (dd, J = 3.3, 0.9 Hz, 1H), 2.33 (dd, J = 0.9, 0.5 Hz, 3H).

HRMS (EI): Exact mass calculated for $C_6H_6O_3^-$ $[M-1]^{-\cdot}$: 125.0239 found 125.0245 (4.7 ppm). Spectral data in agreement with reported data from E. Grovenstein and P. C. Lu, *J. Org. Chem*., 1982, **47**, 2928–2939.



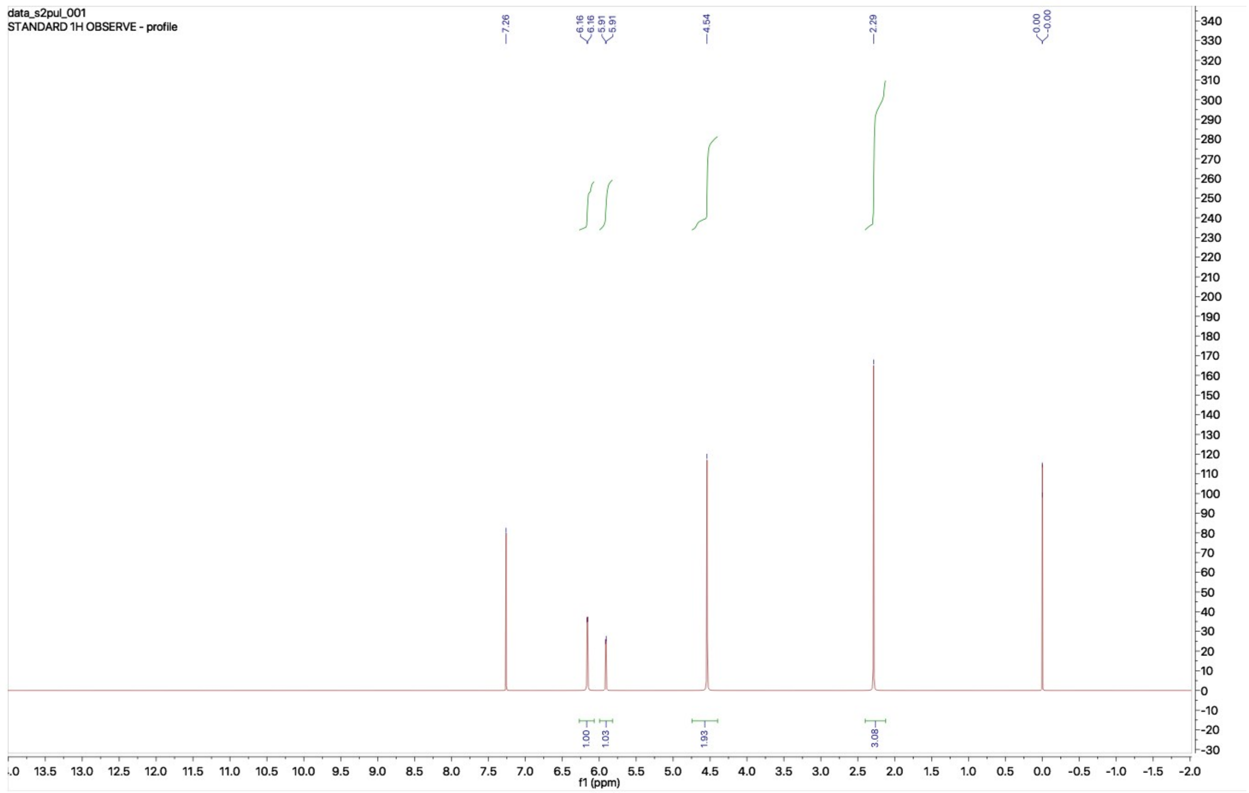
Compound 3.3b : (5-methylfuran-2-yl)methanol



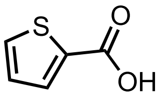
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.16 (d, J = 3.1 Hz, 1H), 5.91 (d, J = 3.1 Hz, 1H), 4.54 (s, 2H), 2.29 (s, 3H).

HRMS (EI): Exact mass calculated for $C_6H_7O_2^-$ $[M-1]^{-\cdot}$: 111.1201 found 111.1205 (3.9 ppm).

Spectral data in agreement with reported data from B. Martín-Matute, C. Nevado, D. J. Cárdenas and A. M. Echavarren, *J. Am. Chem. Soc*., 2003, **125**, 5757–5766.

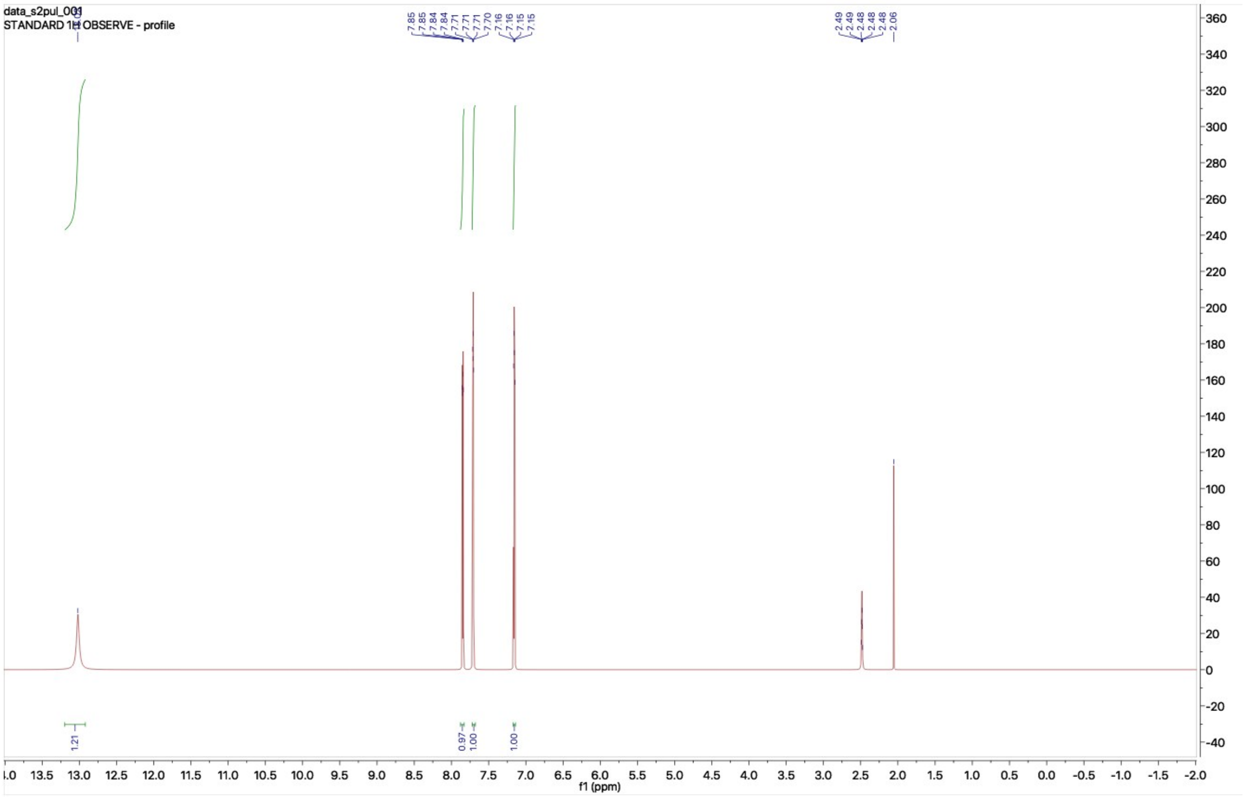


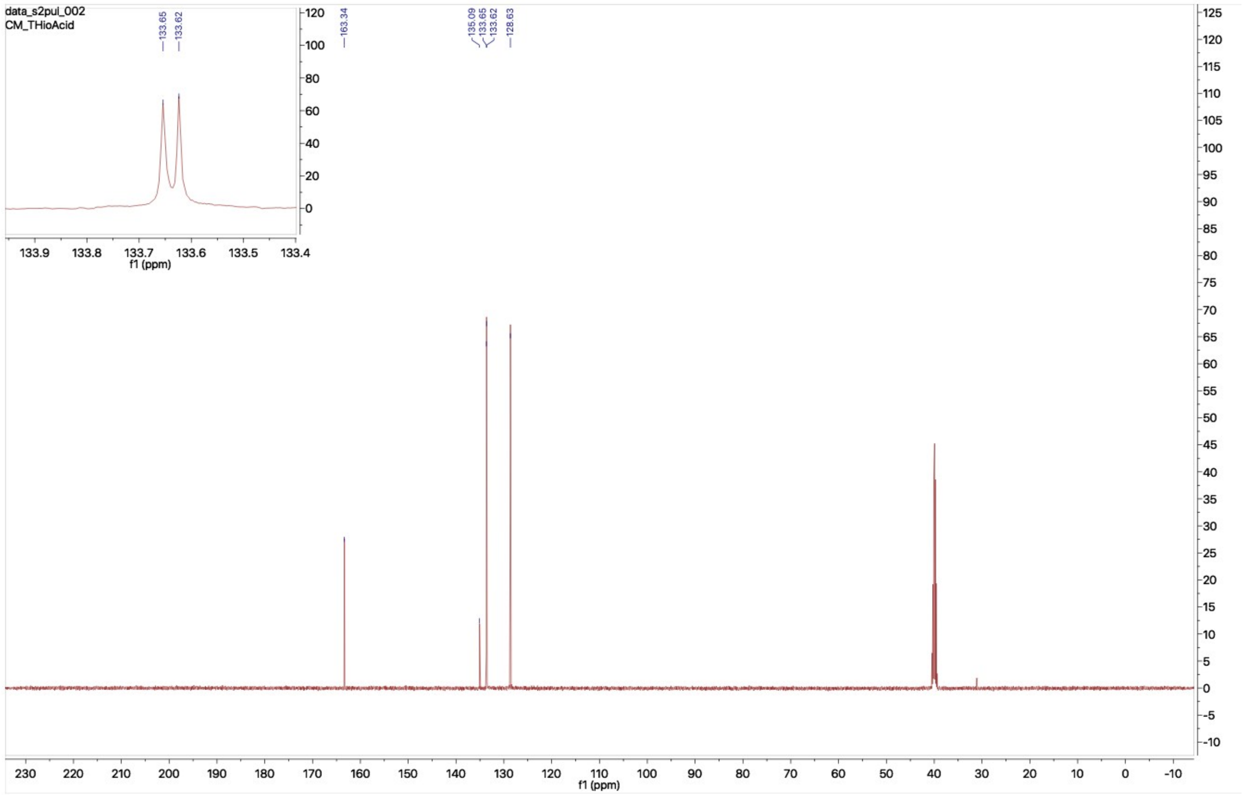
Compound 3.4a : Thiophene-2-carboxylic acid



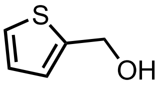
^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 13.02 (bs, 1H), 7.85 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.71 (dd, *J* = 3.7, 1.3 Hz, 1H), 7.16 (dd, *J* = 5.0, 3.7 Hz, 1H).
^{13}C NMR (125 MHz, DMSO-d^6) δ ppm 163.3 (1C), 135.1 (1C), 133.7 (1C), 133.6 (1C), 128.6 (1C).

HRMS (EI): Exact mass calculated for $C_5H_3O_2S^-$ [M-1]$^{-\cdot}$: 126.9853 found 128.9847 (4.4 ppm).


data_s2pul_001
STANDARD 1H OBSERVE - profile
7.85
7.85
7.84
7.84
7.71
7.71
7.71
7.70
7.16
7.16
7.15
7.15
2.49
2.49
2.48
2.48
2.48
2.06
1.21
0.97
1.00
1.00
f1 (ppm)

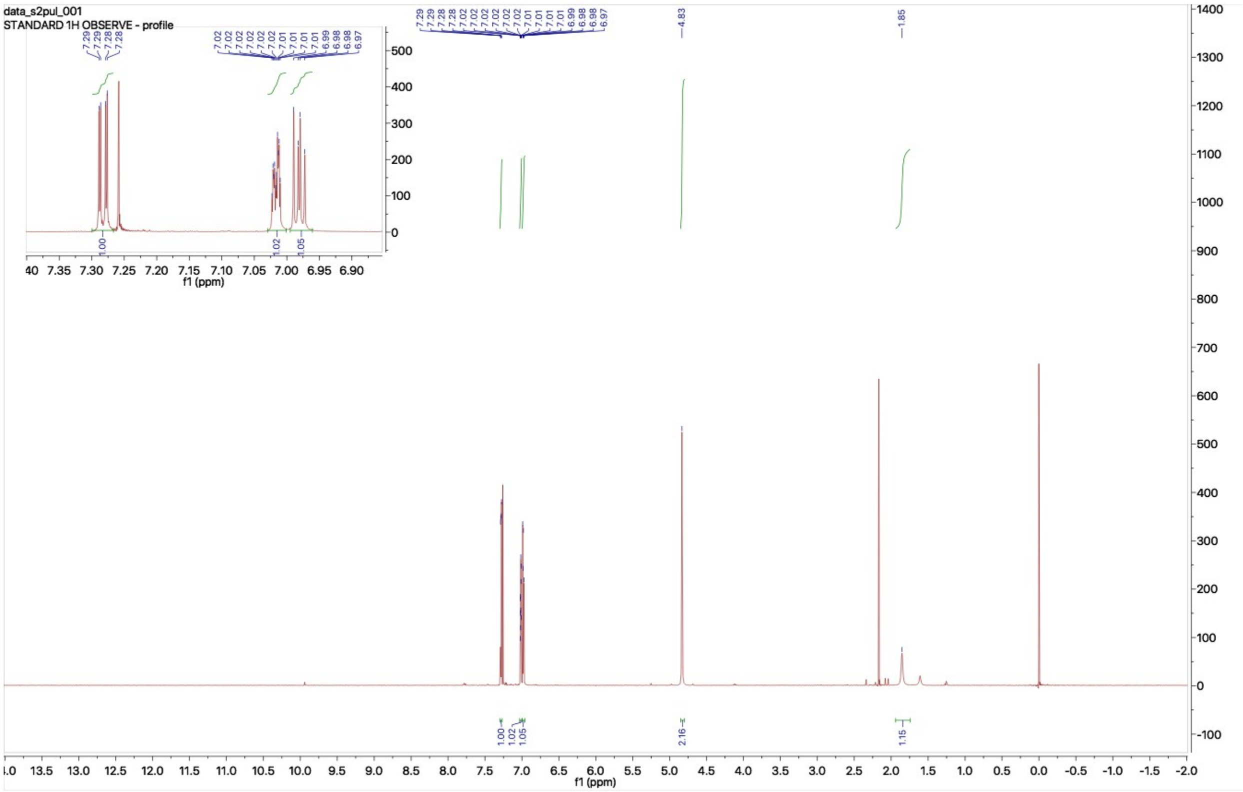

data_s2pul_002
CM_THioAcid
133.65
133.62
163.34
135.09
133.65
133.62
128.63
f1 (ppm)
f1 (ppm)

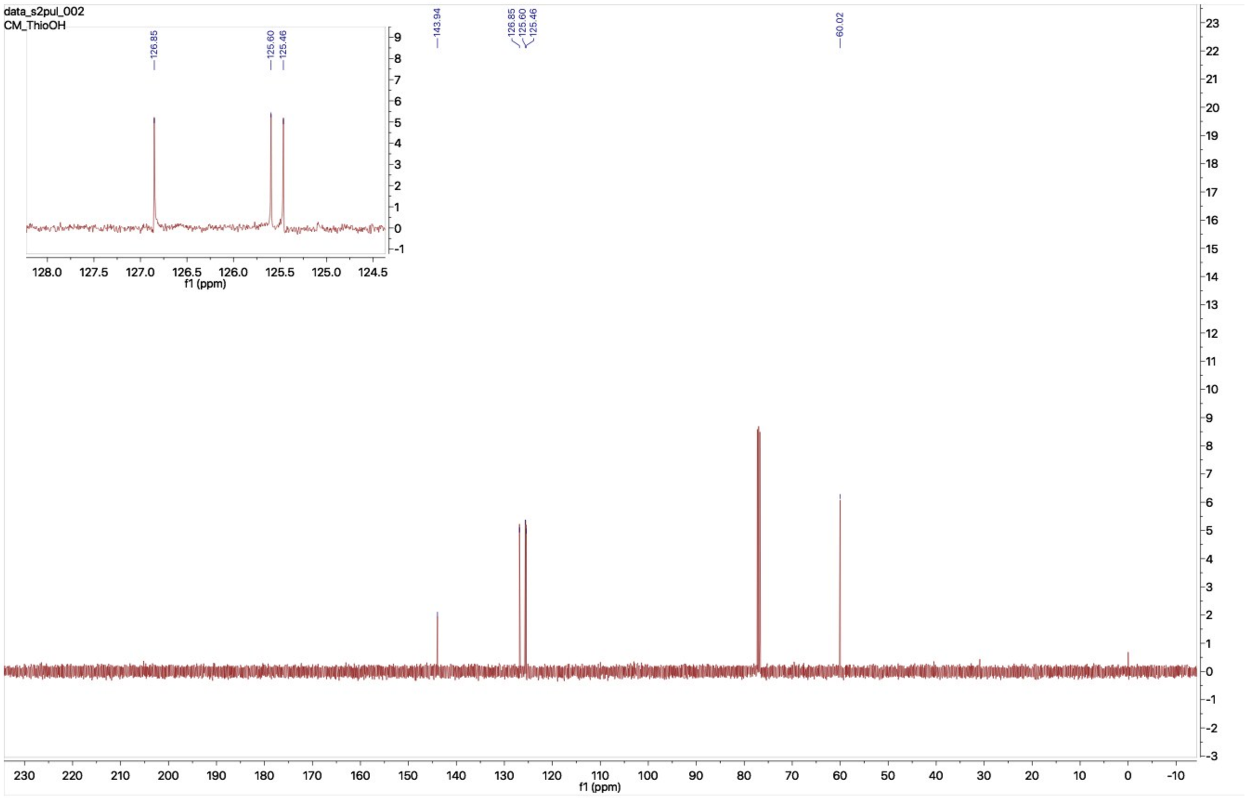
Compound 3.4b : Thiophene-2-ylmethanol



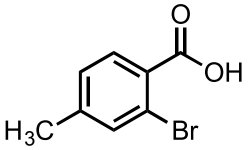
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.28 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.02 (ddt, *J* = 3.5, 1.3, 0.8 Hz, 1H), 6.98 (dd, *J* = 5.0, 3.5 Hz, 1H), 4.83 (s, 2H), 1.85 (bs, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 143.9 (1C), 126.8 (1C), 125.6 (1C), 125.5 (1C), 60.0 (1C).

HRMS (EI): Exact mass calculated for $C_5H_5OS^-$ $[M-1]^{-\cdot}$: 113.0060 found 113.0063 (3.0 ppm).

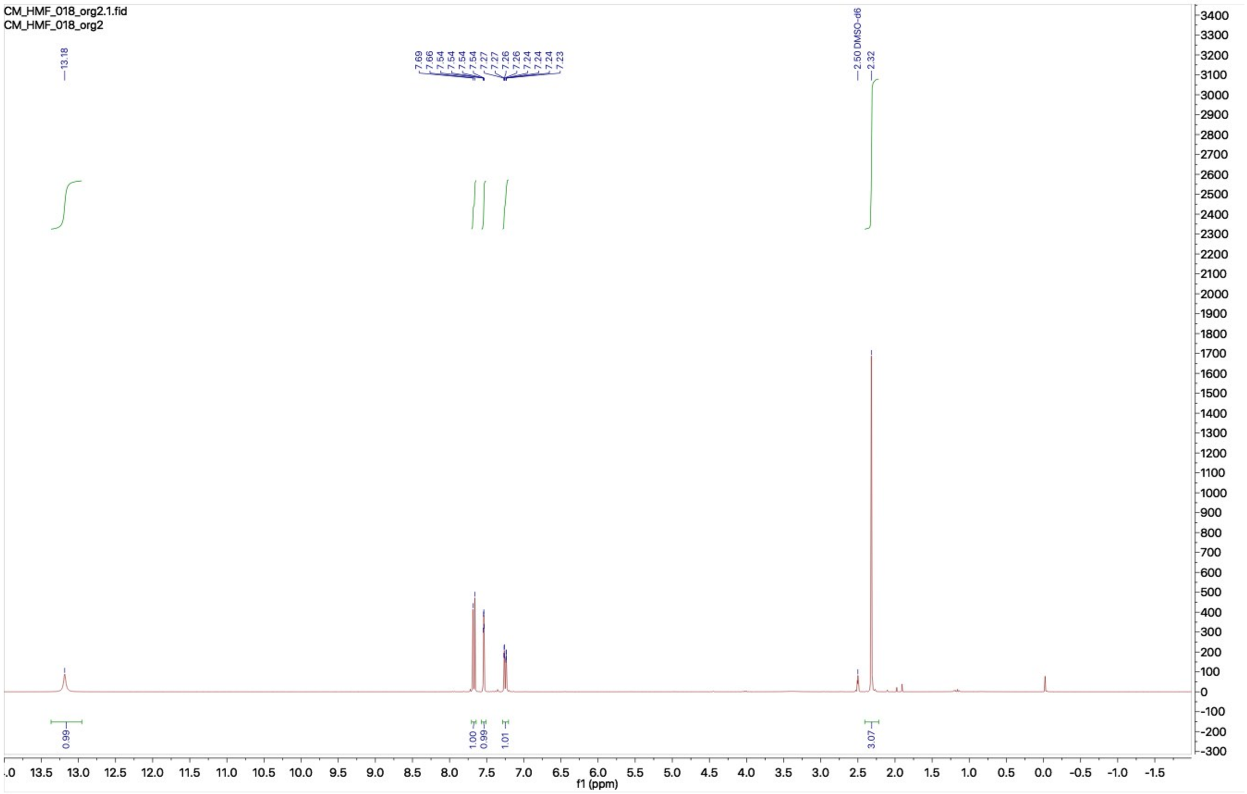




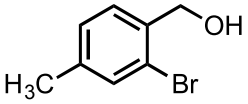
Compound 3.5a : 2-bromo-4-methylbenzoic acid



^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 13.18 (bs, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.54 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.25 (ddd, *J* = 7.8, 1.7, 0.8 Hz, 1H), 2.32 (s, 3H).
HRMS (EI): Exact mass calculated for C8H6O2Br- [M-1]-·: 212.9550 found 212.9544 (-2.6ppm). Spectral data in agreement with reported data from T. S. Mei, R. Giri, N. Maugel and J. Q. Yu, *Angew. Chemie - Int. Ed.*, 2008, **47**, 5215–5219.

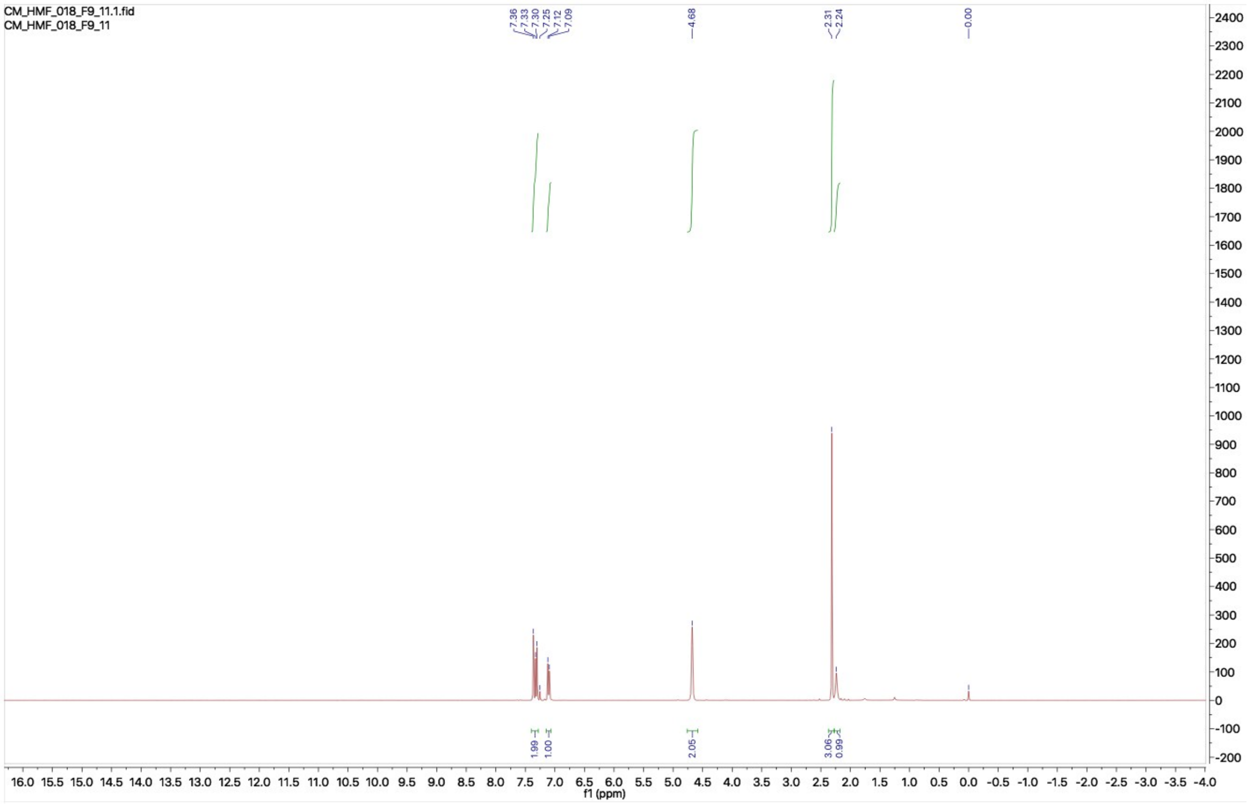


Compound 3.5b : 2-bromo-4-methylbenzoic acid

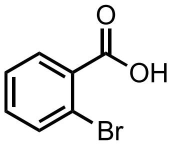


^{1}H NMR (500 MHz,$CDCl_3$) δ ppm 7.33 (m, 2H), 7.10 (d, J = 7.8Hz, 1), 4.68 (s, 2H), 2.31 (s, 3H), 2.24 (bs, 1H).

HRMS (EI): Exact mass calculated for $C_8H_8OBr^-$ $[M-1]^{-\cdot}$: 198.9758 found 198.9764 (3.2 ppm). Spectral data in agreement with reported data from Spectral data in agreement with reported data from G. Giorgi, S. Maiti, P. López-Alvarado and J. C. Menéndez, *Org. Biomol. Chem*., 2011, **9**, 2722–2730.

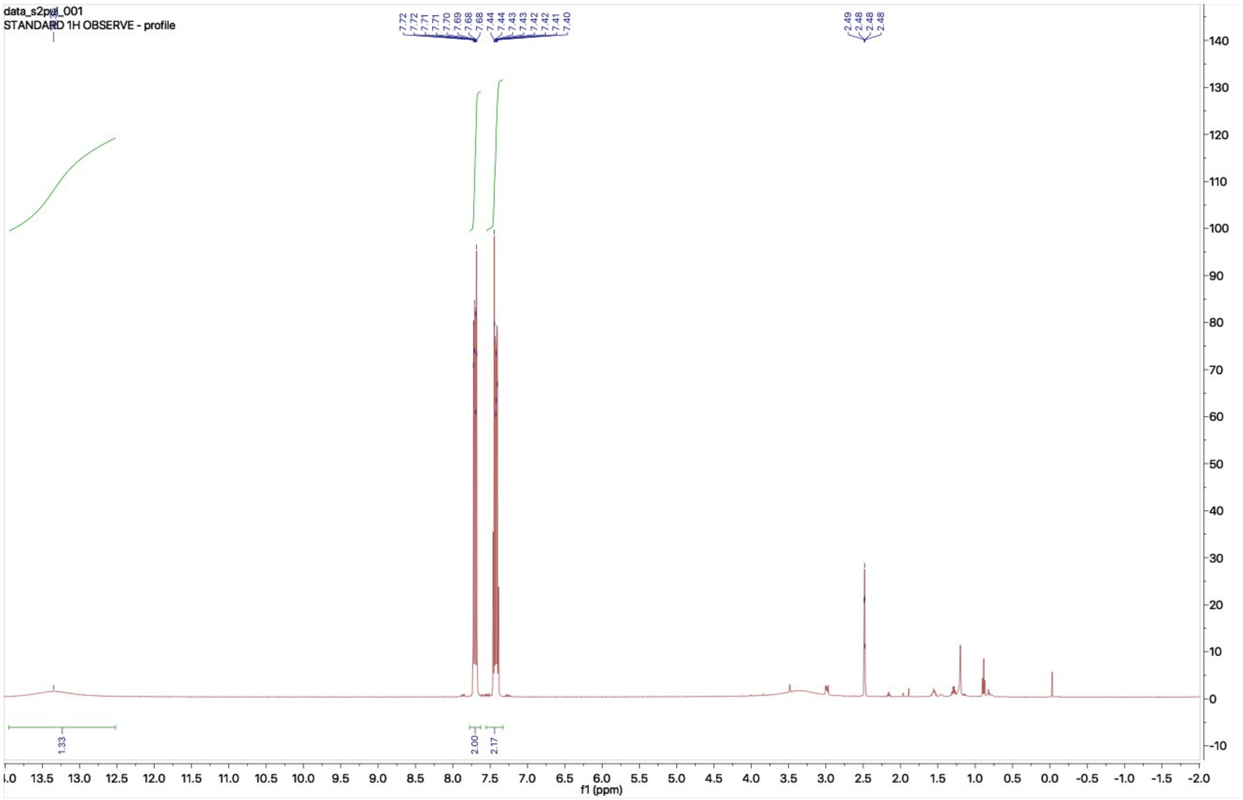


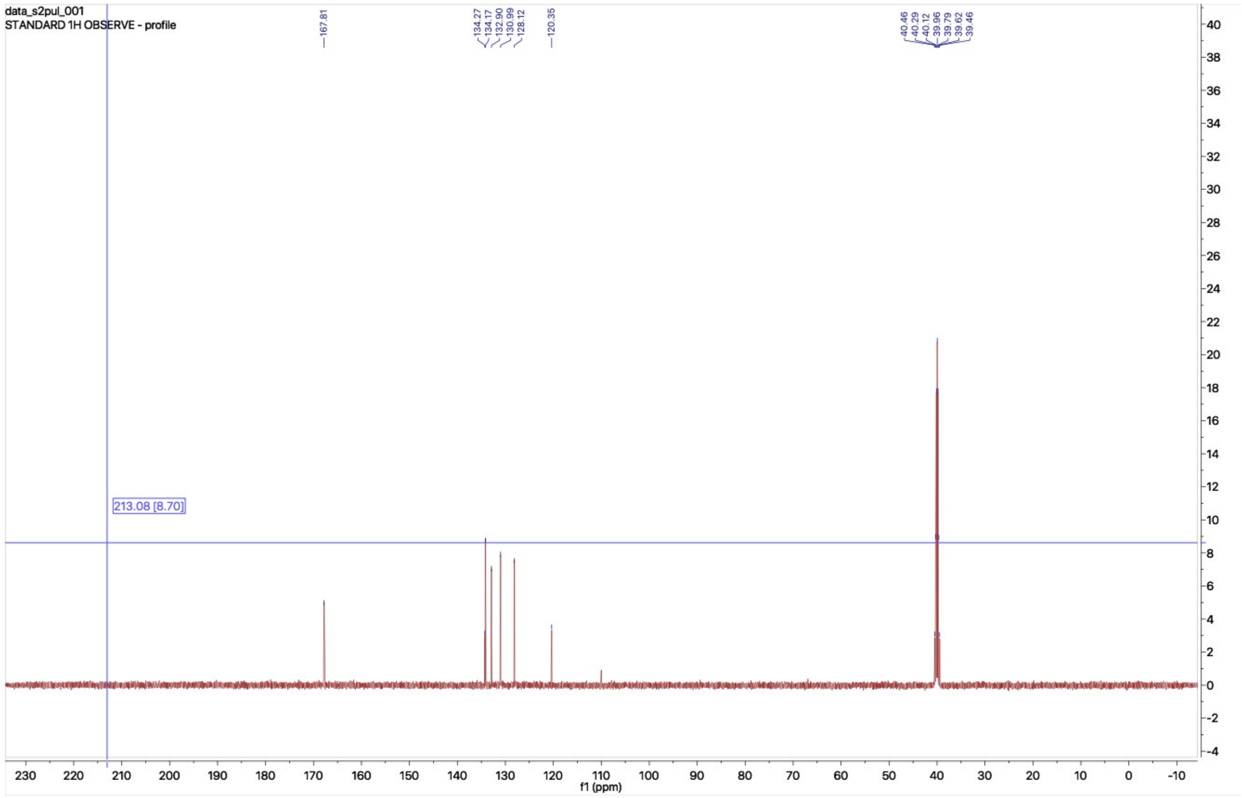
Compound 3.6a : 2-bromobenzoic acid



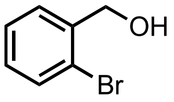
^{1}H NMR (500 MHz, DMSO-d^{6}) δ ppm 13.37 (bs, 1H), 7.70 (ddd, *J* = 12.9, 7.6, 1.7 Hz, 2H), 7.42 (ddd, *J* = 12.9, 7.6, 1.7 Hz, 2H).
^{13}C NMR (125 MHz, DMSO-d^{6}) δ ppm 167.8 (1C), 134.3 (1C), 134.2 (1C), 132.9 (1C), 131.0 (1C), 128.1 (1C), 120.4 (1C).

HRMS (EI): Exact mass calculated for $C_7H_4O_2Br^-$ [M-1]$^{-\cdot}$: 198.9394 found 198.9389 (-2.3 ppm).


data_s2pul_001
STANDARD 1H OBSERVE - profile
7.72
7.72
7.71
7.70
7.69
7.68
7.68
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.40
2.49
2.48
2.48
2.48
1.33
2.00
2.17
f1 (ppm)

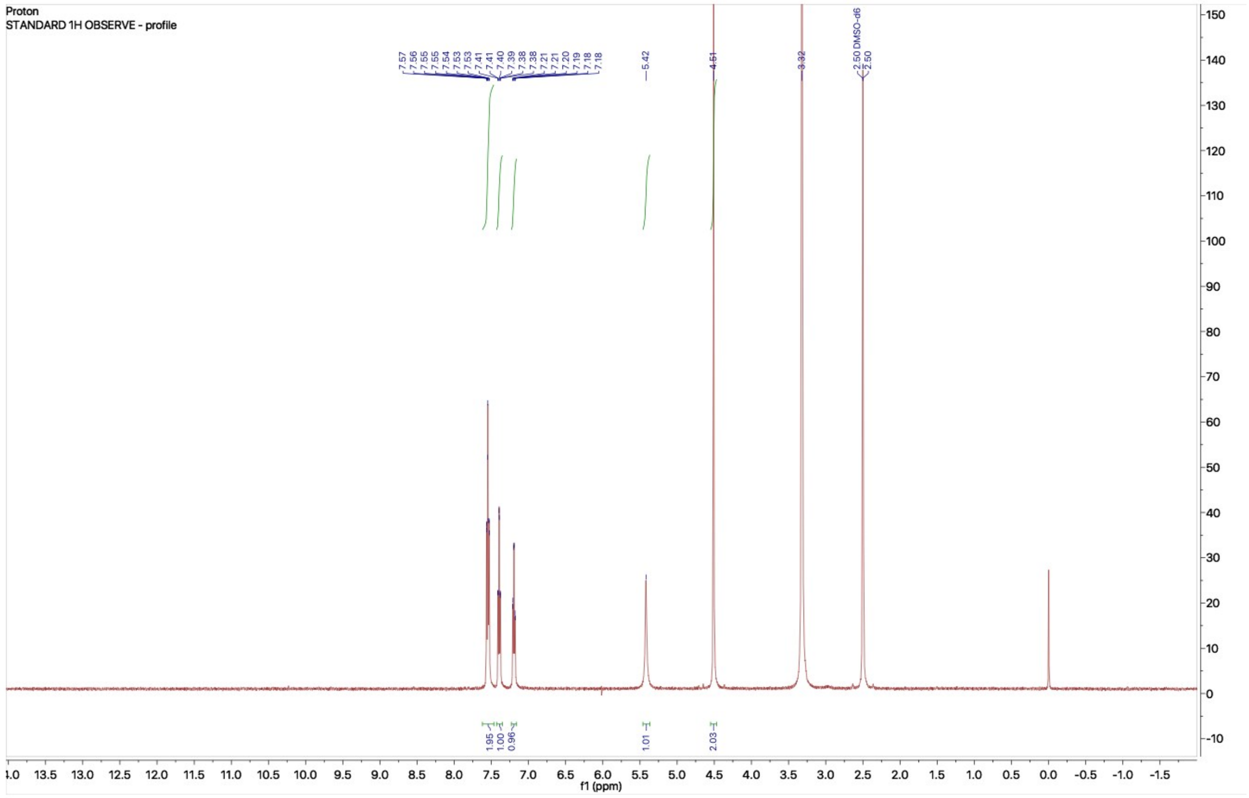

data_s2pul_001
STANDARD 1H OBSERVE - profile
167.81
134.27
134.17
132.90
130.99
128.12
120.35
40.46
40.29
40.12
39.96
39.79
39.62
39.46
213.08 [8.70]
f1 (ppm)

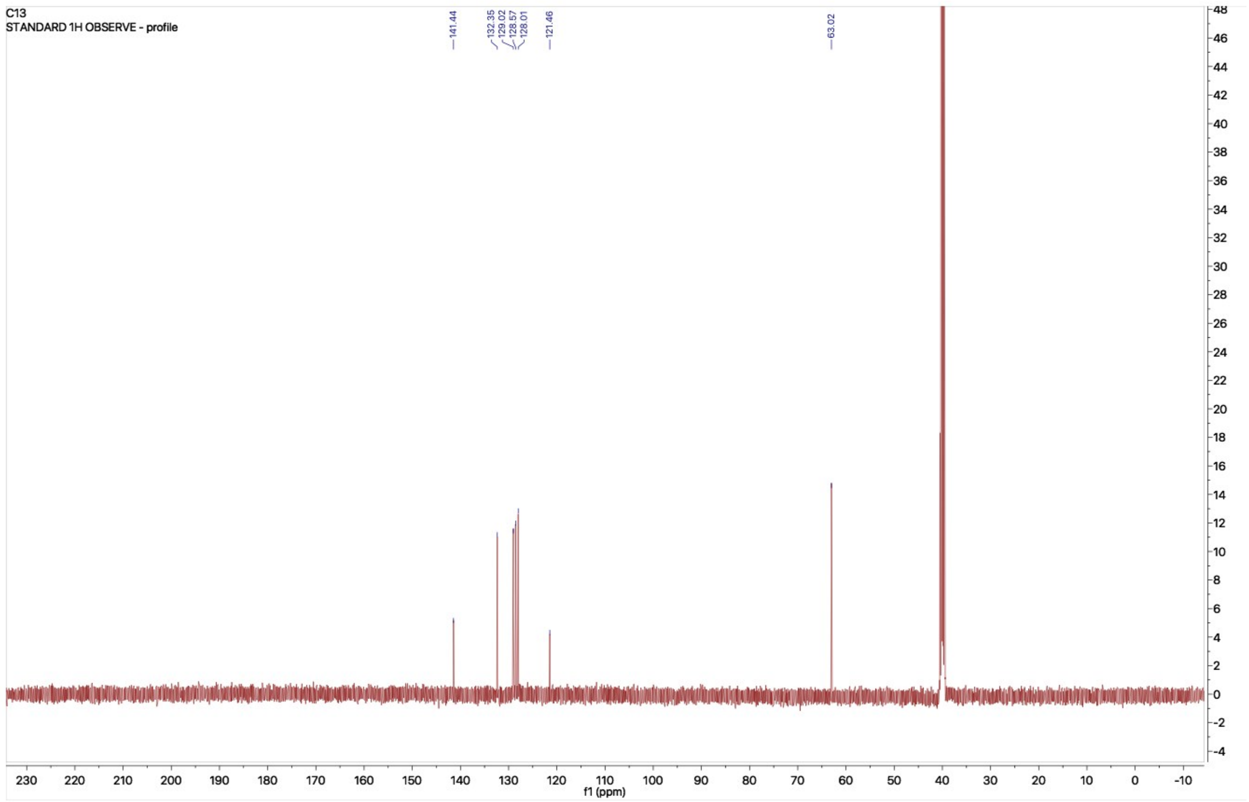
Compound 3.6b : 2-bromobenzyl alcohol



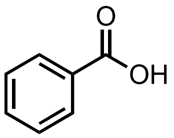
^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 7.55 (dd, *J* = 7.6, 1.3 Hz, 2H), 7.40 (td, *J* = 7.6, 1.3 Hz, 1H), 7.20 (td, *J* = 7.5, 1.3 Hz, 1H), 5.41 (bs, 1H), 4.51, (s, 2H).
^{13}C NMR (125 MHz, DMSO-d^6) δ ppm 141.4 (1C), 132.4 (1C), 129.0 (1C), 128.6 (1C), 128.0 (1C), 121.5 (1C), 63.0 (1C).

HRMS (EI): Exact mass calculated for $C_7H_6OBr^-$ $[M-1]^{-\cdot}$: 184.9601 found 184.9594 (-3.6 ppm).



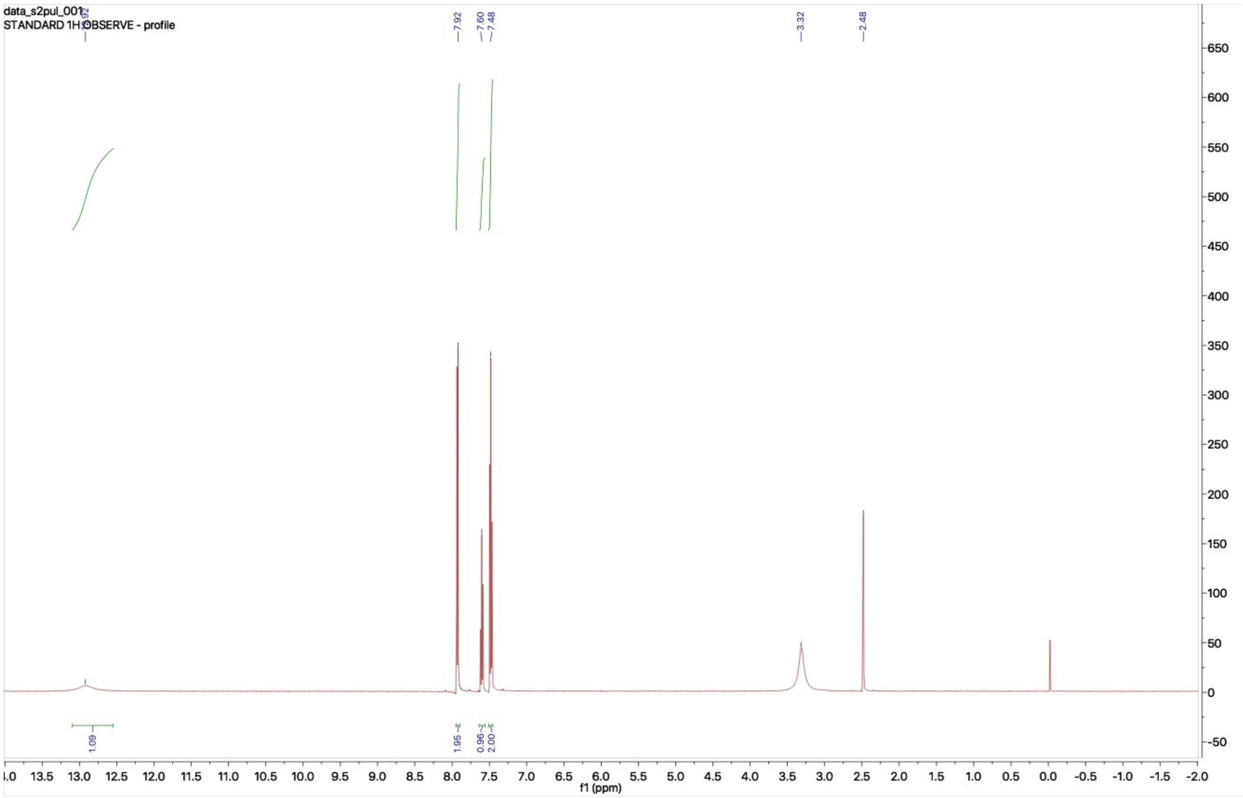


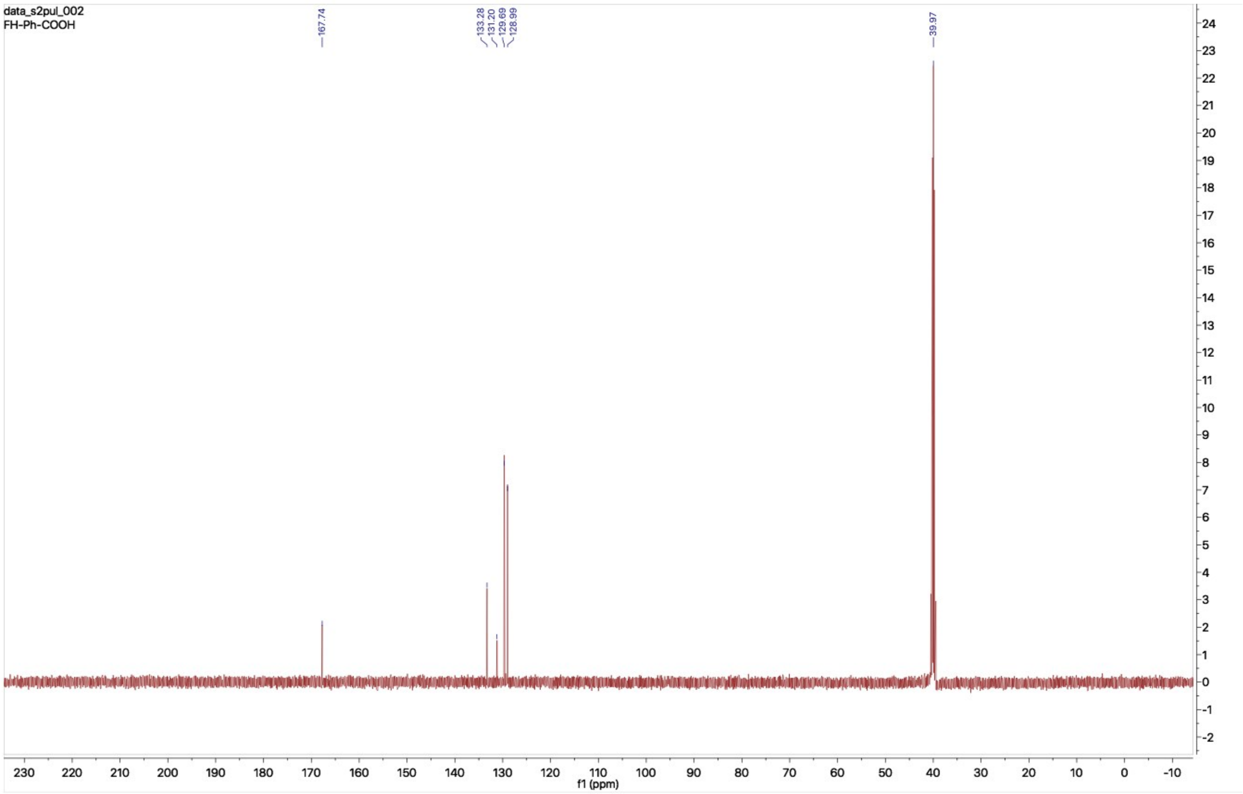
Compound 3.7a : Benzoic acid



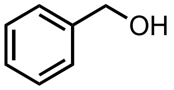
^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 12.92 (bs, 1H), 7.92 (m, 2H), 7.60 (m, 1H), 7.48 (m, 2H).
^{13}C NMR (125 MHz, DMSO-d^6) δ ppm 167.7 (1C), 133.3 (1C), 131.2 (1C), 129.7 (2C), 129.0 (2C)

HRMS (EI): Exact mass calculated for $C_7H_5O_2^-$ [M-1]$^{-\cdot}$: 121.0290 found 121.0293 (2.9 ppm).


data_s2pul_001
STANDARD 1H OBSERVE - profile
12.92
7.92
7.60
7.48
3.32
2.48
1.09
1.95
0.96
2.00
f1 (ppm)

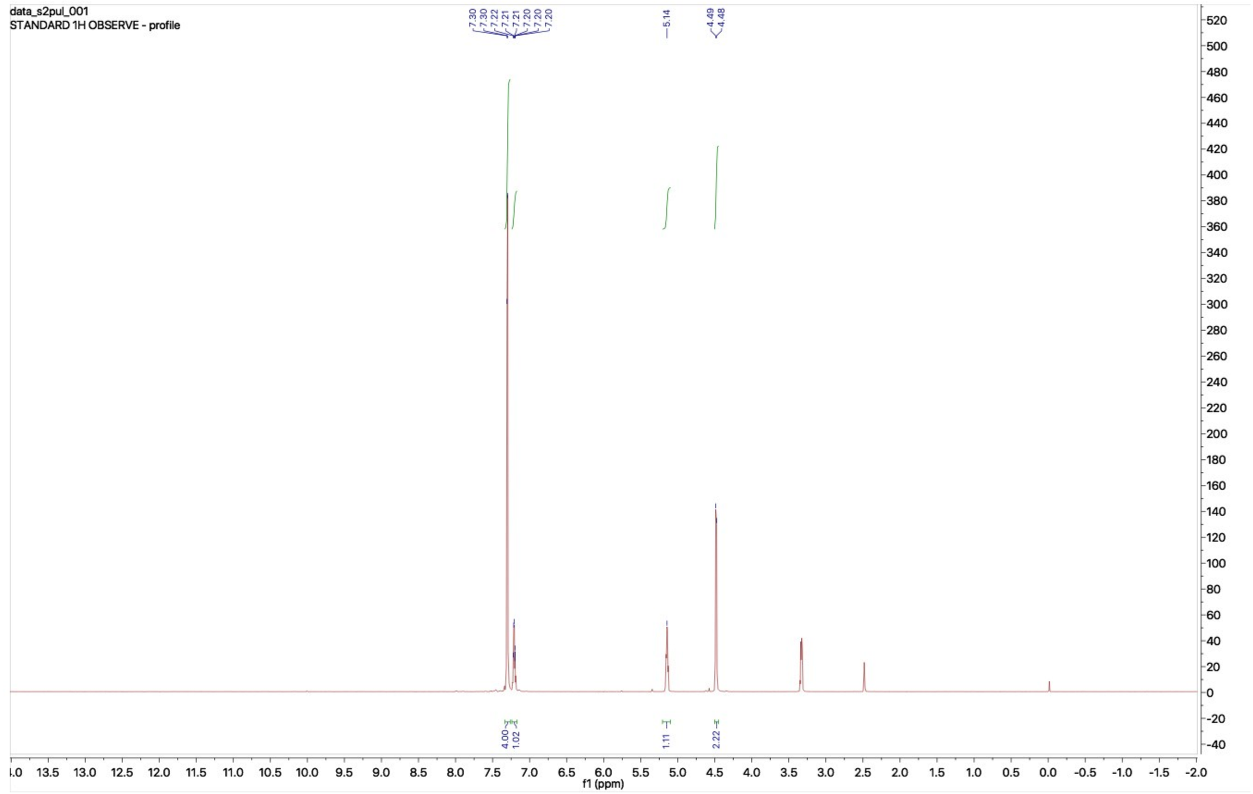

data_s2pul_002
FH-Ph-COOH
167.74
133.28
131.20
129.69
128.99
39.97
f1 (ppm)

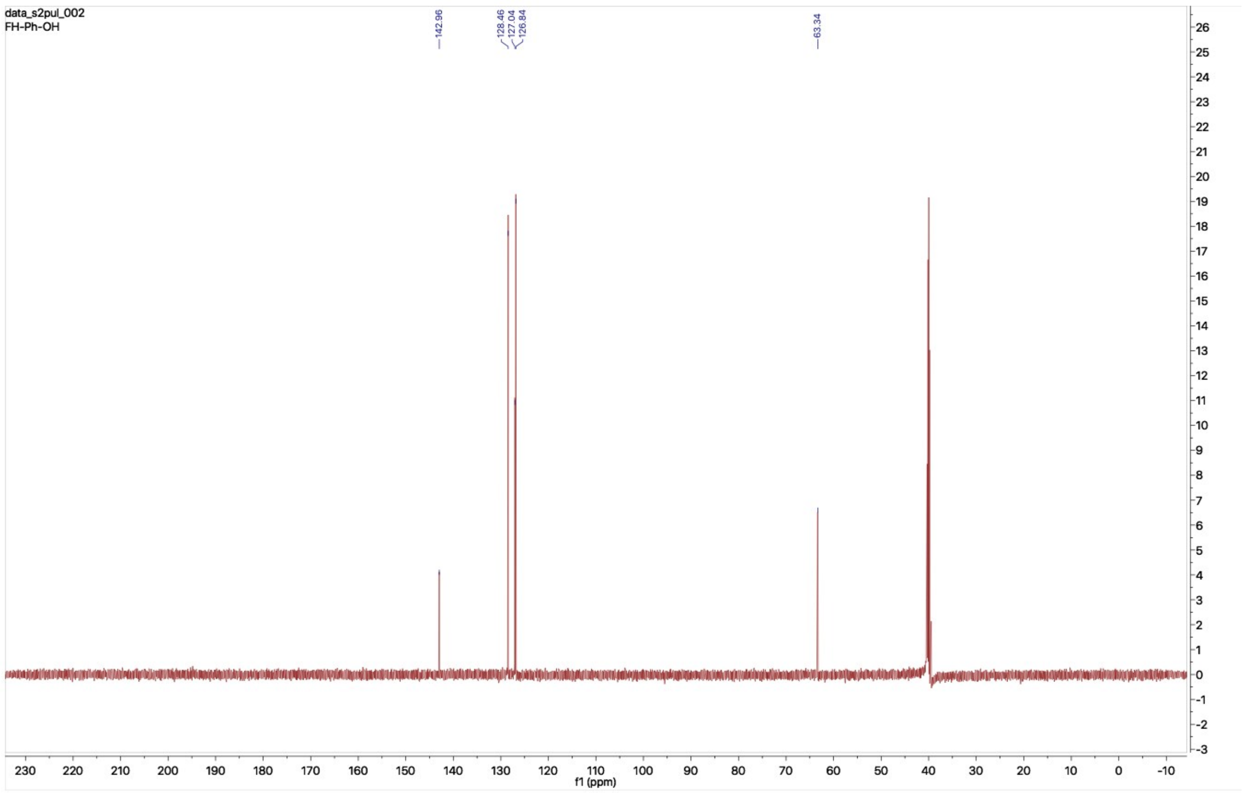
Compound 3.7b : Benzyl alcohol



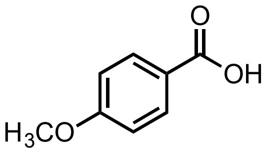
^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 7.30 (d, *J* = 4.4 Hz, 4H), 7.21 (m, 1H), 5.14 (m, 1H), 4.49 (d, J = 5.7 Hz, 1H)
^{13}C NMR (125 MHz, DMSO-d^6) δ ppm 143.0 (1C), 128.5 (2C), 127.0 (1C), 126.8 (2C), 63.3 (1C).

HRMS (EI): Exact mass calculated for Tropylium $C_7H_7^+$ $[M\text{-}OH]^{+\cdot}$: 91.0542 found 91.0541 (1.4 ppm).



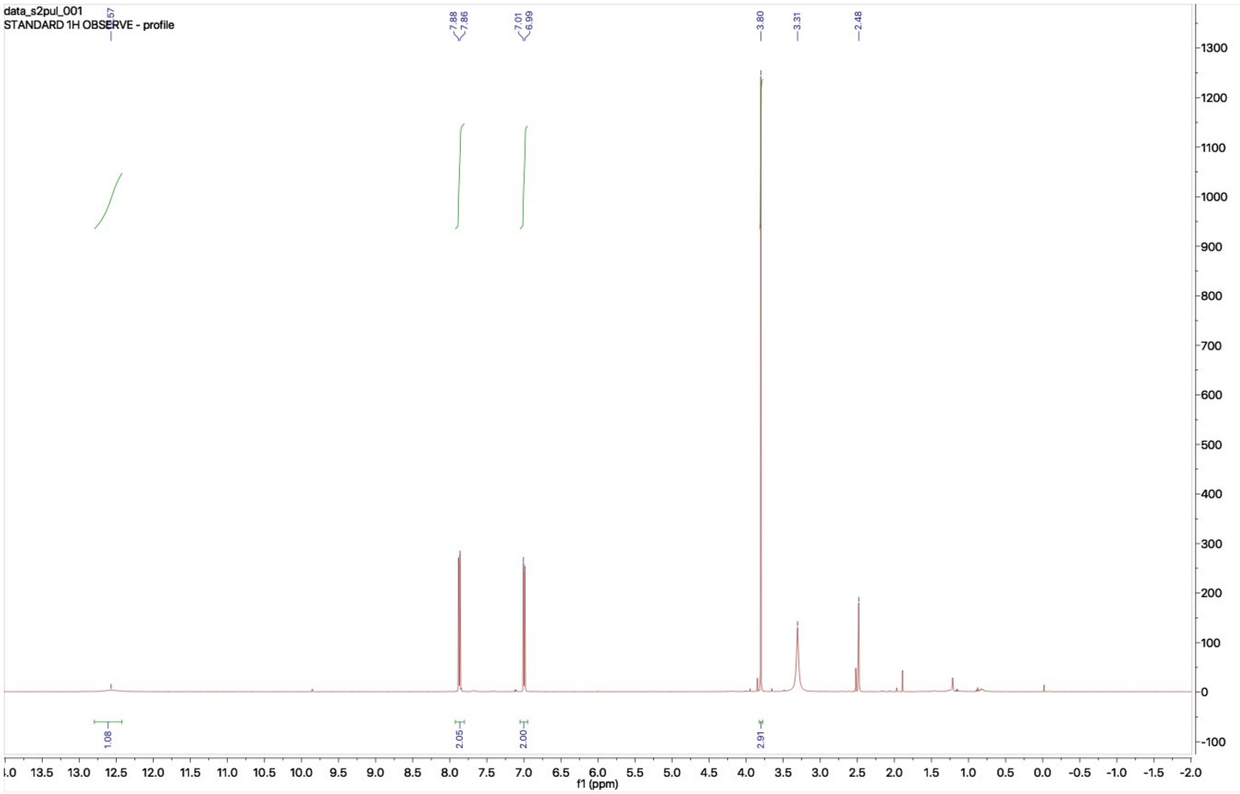


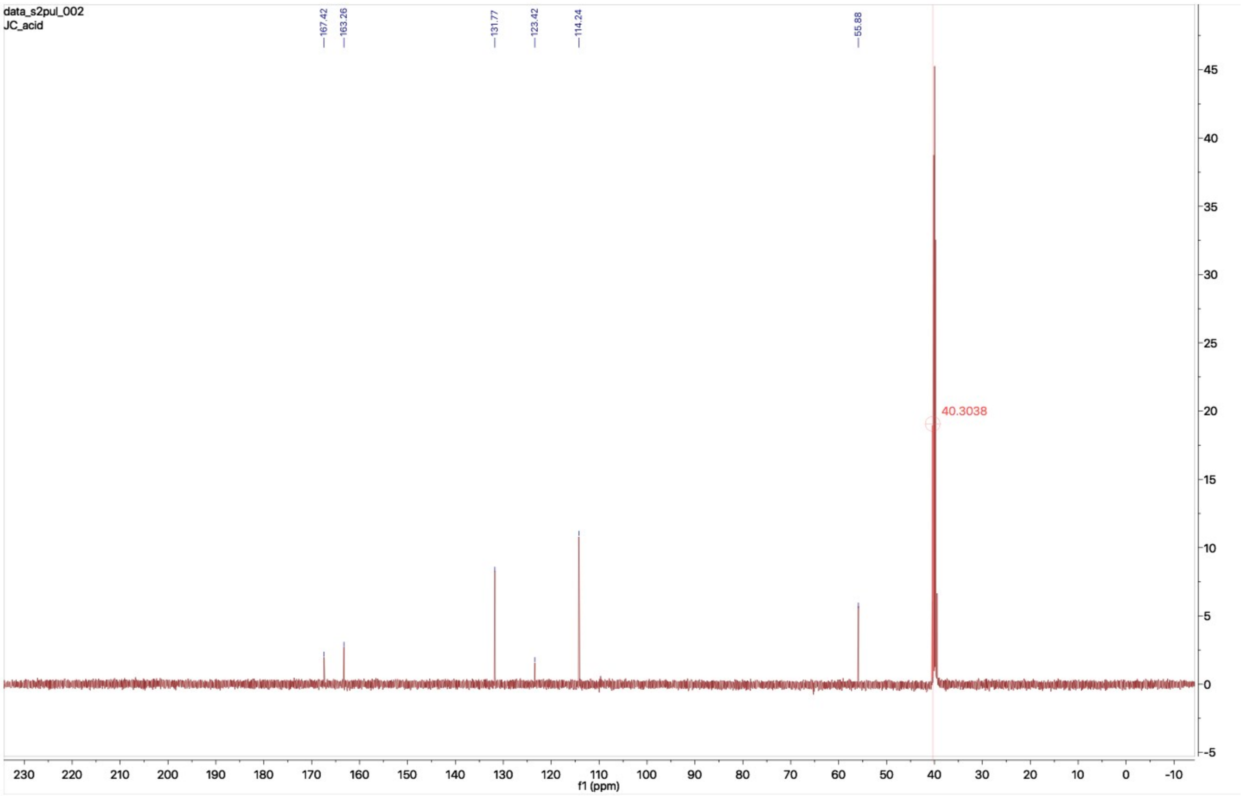
Compound 3.8a : 4-methoxy benzoic acid



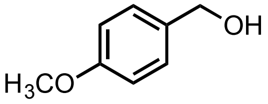
^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 12.57 (bs, 1H), 7.87 (d, J = 8.9Hz, 2H), 7.00 (d, J = 8.9Hz, 2H), 3.80 (s, 3H).
^{13}C NMR (125 MHz, DMSO-d^6) δ ppm 167.4 (1C), 163.3 (1C), 131.8 (2C), 123.4 (1C), 114.2 (2C), 55.9 (1C).

HRMS (EI): Exact mass calculated for $C_8H_7O_3^-$ [M-H]$^{-\cdot}$: 151.0395 found 151.0401 (3.9 ppm).


data_s2pul_001
STANDARD 1H OBSERVE - profile
12.57
7.88
7.86
7.01
6.99
3.80
3.31
2.48
1.08
2.05
2.00
2.91
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
.0
13.5
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)

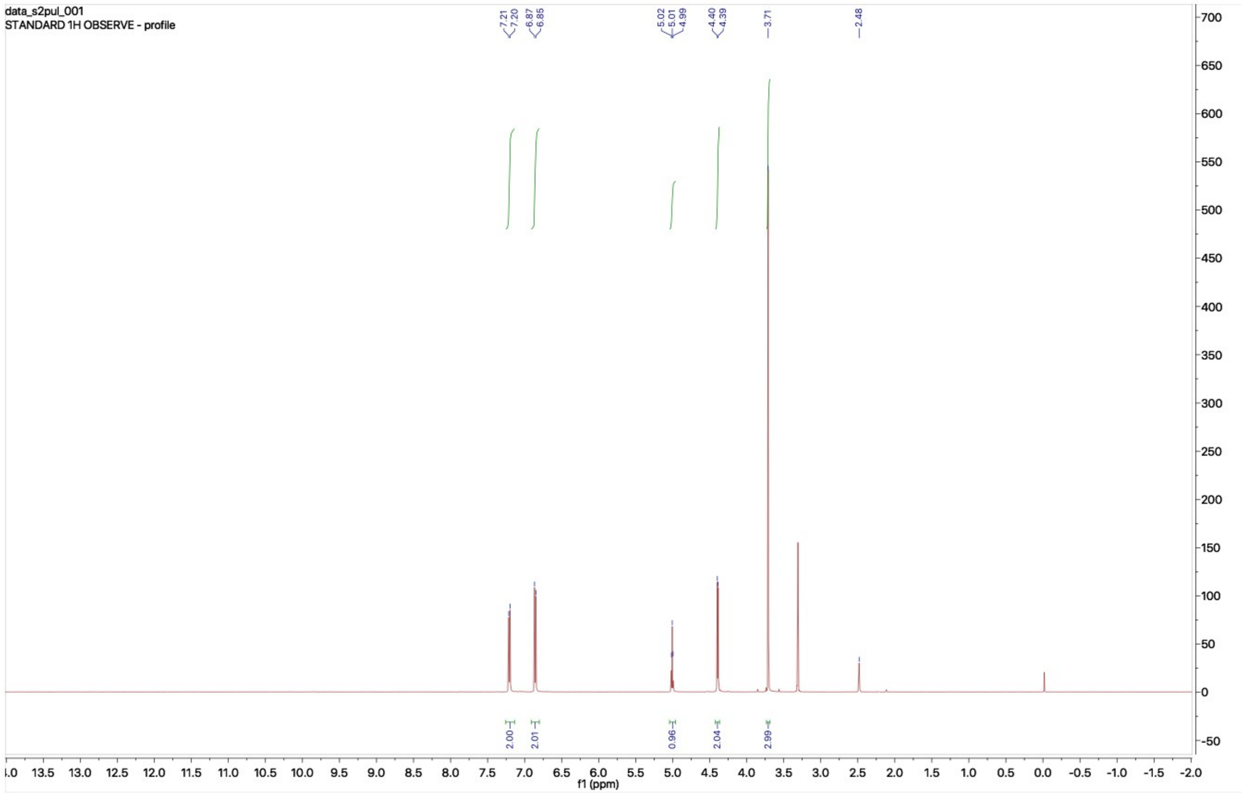

data_s2pul_002
JC_acid
167.42
163.26
131.77
123.42
114.24
55.88
40.3038
45
40
35
30
25
20
15
10
5
0
-5
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

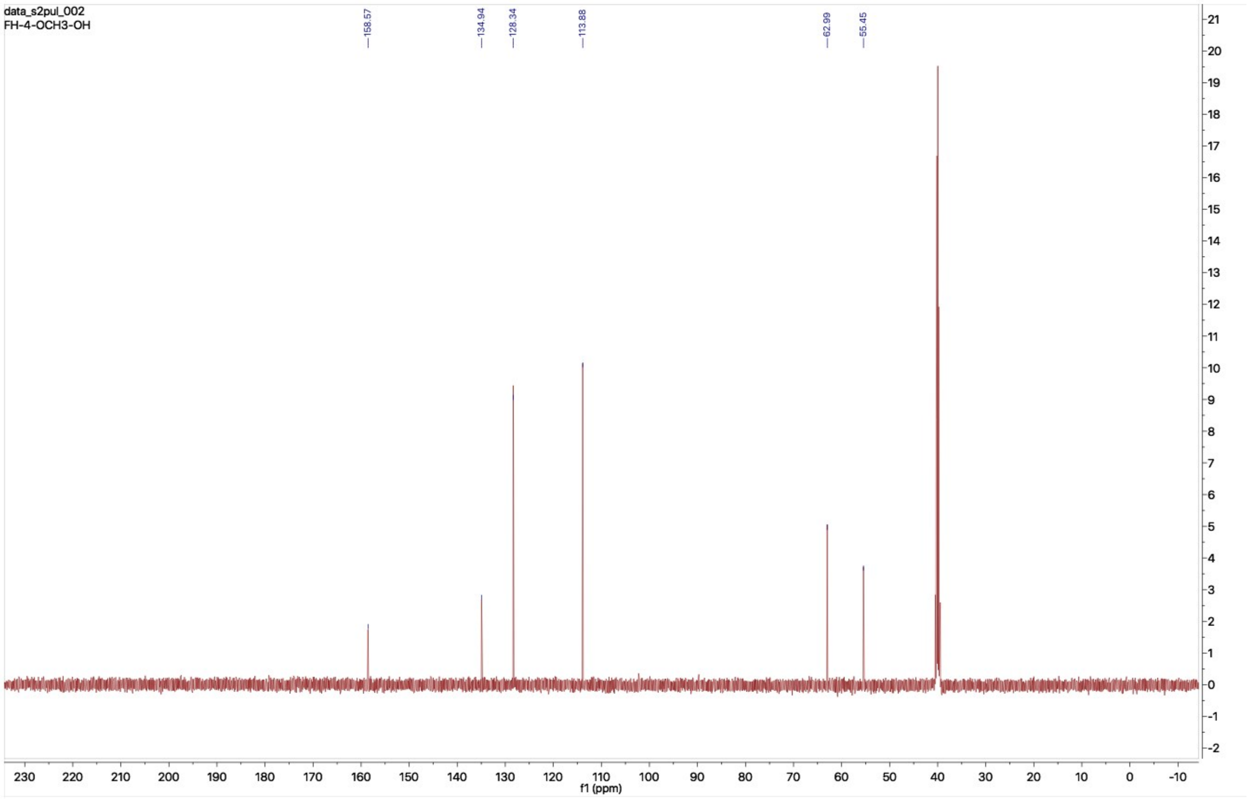
Compound 3.8b : 4-methoxy benzoic acid



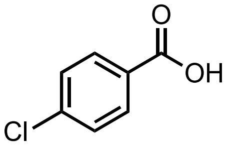
^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 7.20 (d, J = 8.5Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 5.01 (t, J = 5.7Hz, 1H), 4.40 (d, J = 5.7Hz, 2H), 3.71 (s, 3H).
^{13}C NMR (125 MHz, DMSO-d^6) δ ppm 158.6 (1C), 134.9 (1C), 128.3 (2C), 113.9 (2C), 63.0 (1C), 55.5 (1C).

HRMS (EI): Exact mass calculated for $C_8H_9O_2^-$ $[M-H]^{-\cdot}$: 137.0602 found 137.0606 (3.2 ppm).



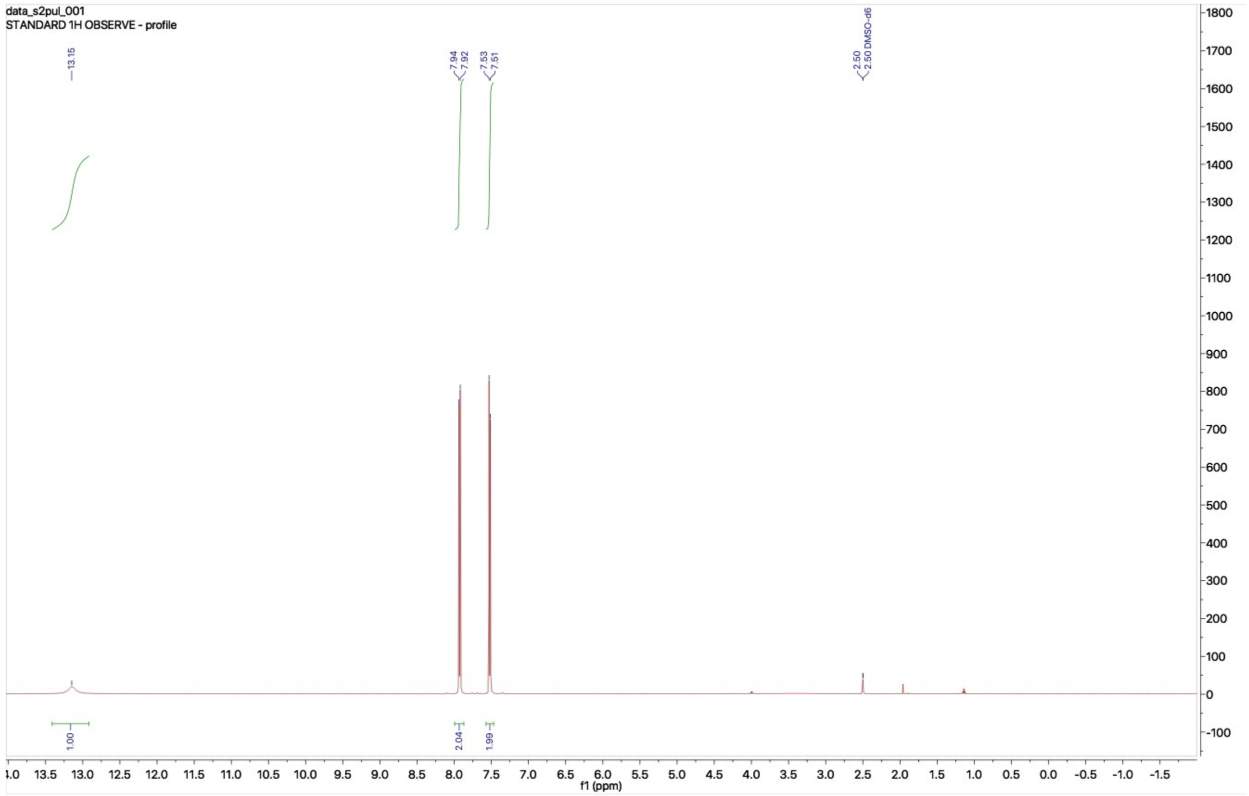


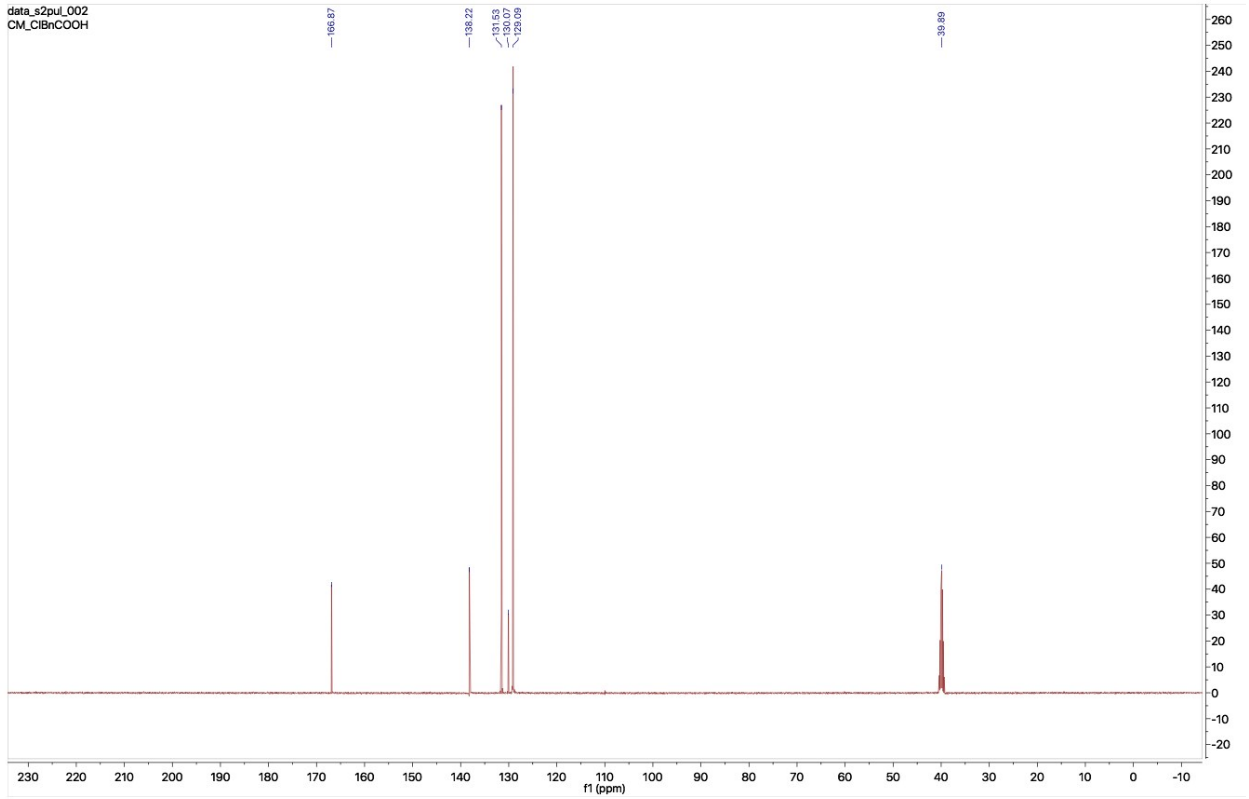
Compound 3.9a : 4-chlorobenzoic acid



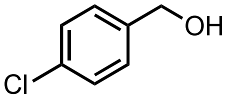
^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 13.5 (bs, 1H), 7.93 (d, J = 8.7Hz, 2H), 7.52 (d, J = 8.7Hz, 2H).
^{13}C NMR (125 MHz, DMSO-d^6) δ ppm 166.9 (1C), 138.2 (1C), 131.5 (2C), 130.1 (1C), 129.1 (2C).

HRMS (EI): Exact mass calculated for $C_7H_4O_2Cl^-$ [M-H]$^{-\cdot}$: 154.9899 found 154.9903 (2.8 ppm).


data_s2pul_001
STANDARD 1H OBSERVE - profile
13.15
7.94
7.92
7.53
7.51
2.50
2.50 DMSO-d6
1.00
2.04
1.99
f1 (ppm)

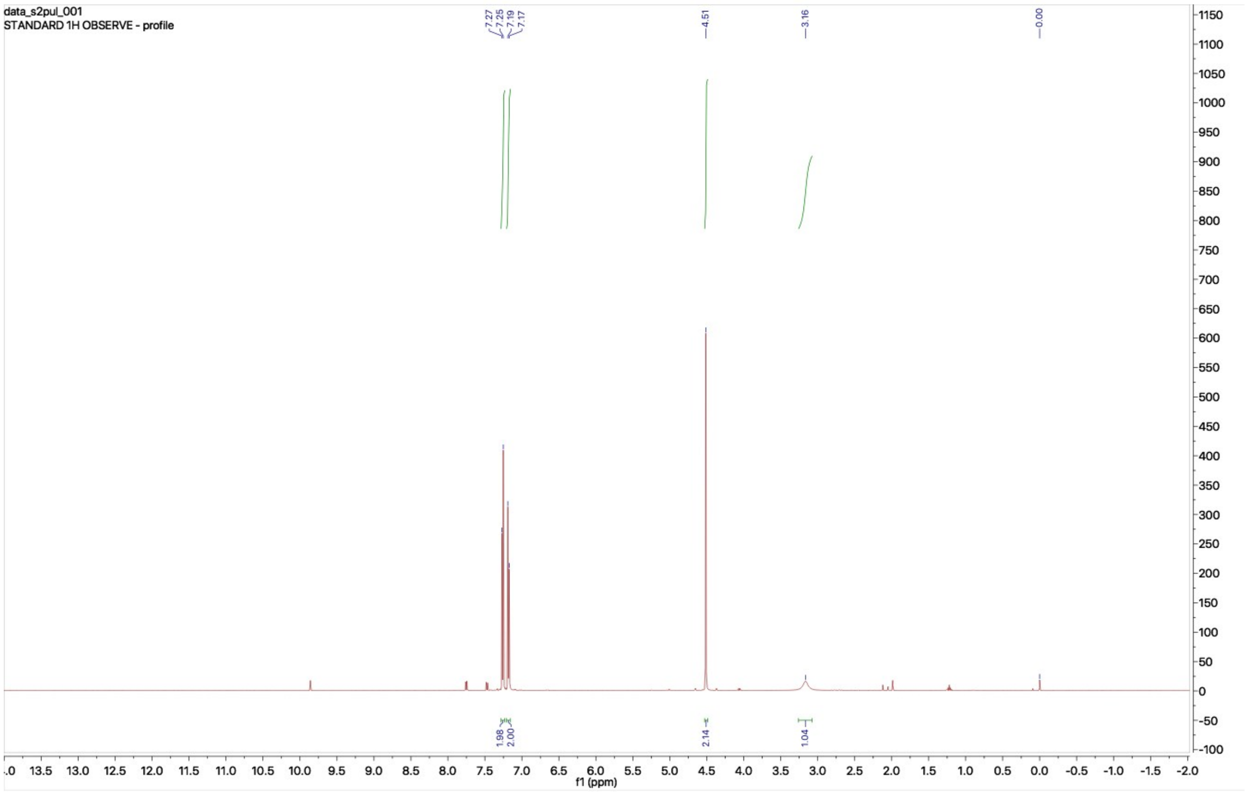

data_s2pul_002
CM_ClBnCOOH
166.87
138.22
131.53
130.07
129.09
39.89
f1 (ppm)

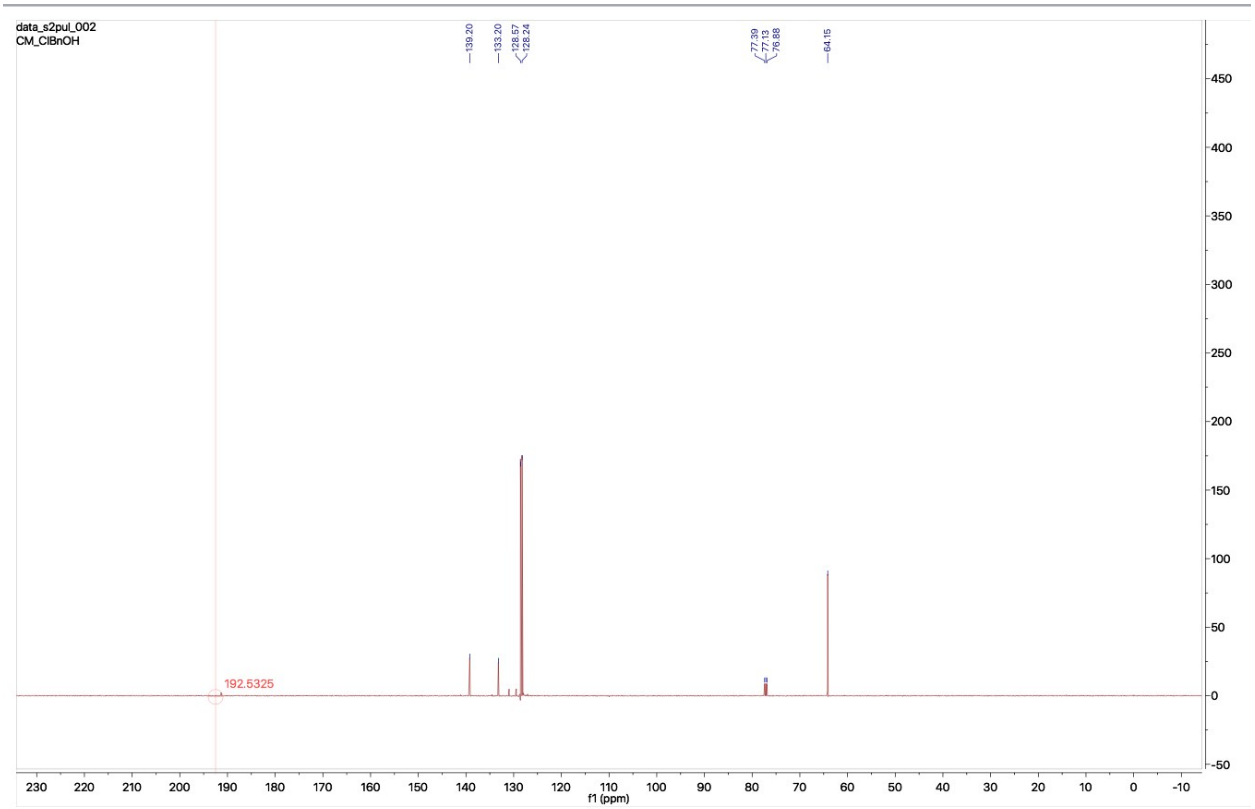
Compound 3.9a : 4-chlorobenzyl alcohol



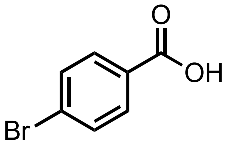
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.26 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 4.51 (s, 2H), 3.16 (bs, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 139.2 (1C), 133.2 (1C), 128.6 (2C), 128.2 (2C), 64.2 (1C).

HRMS (EI): Exact mass calculated for $C_7H_6OCl^-$ $[M-H]^{-\cdot}$: 141.0206 found 141.0210 (3.1 ppm).





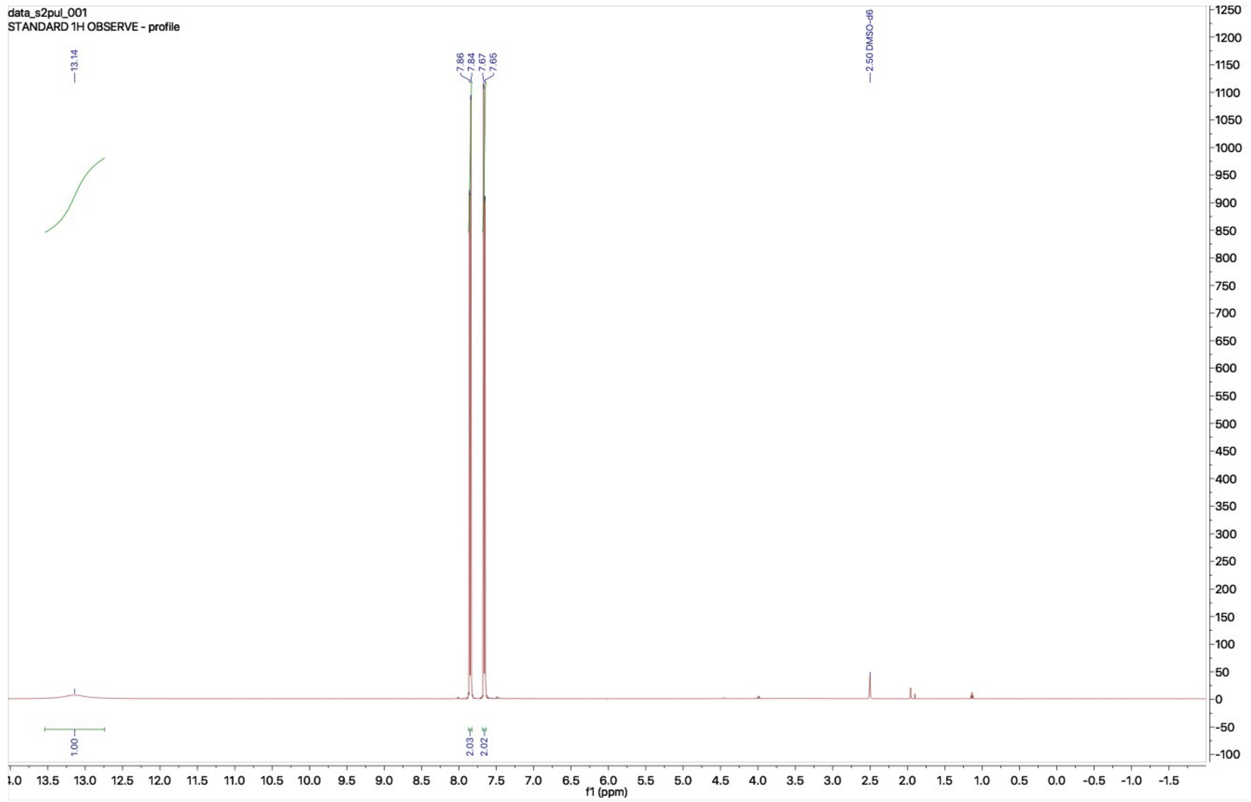
Compound 3.10a : 4-bromobenzoic acid

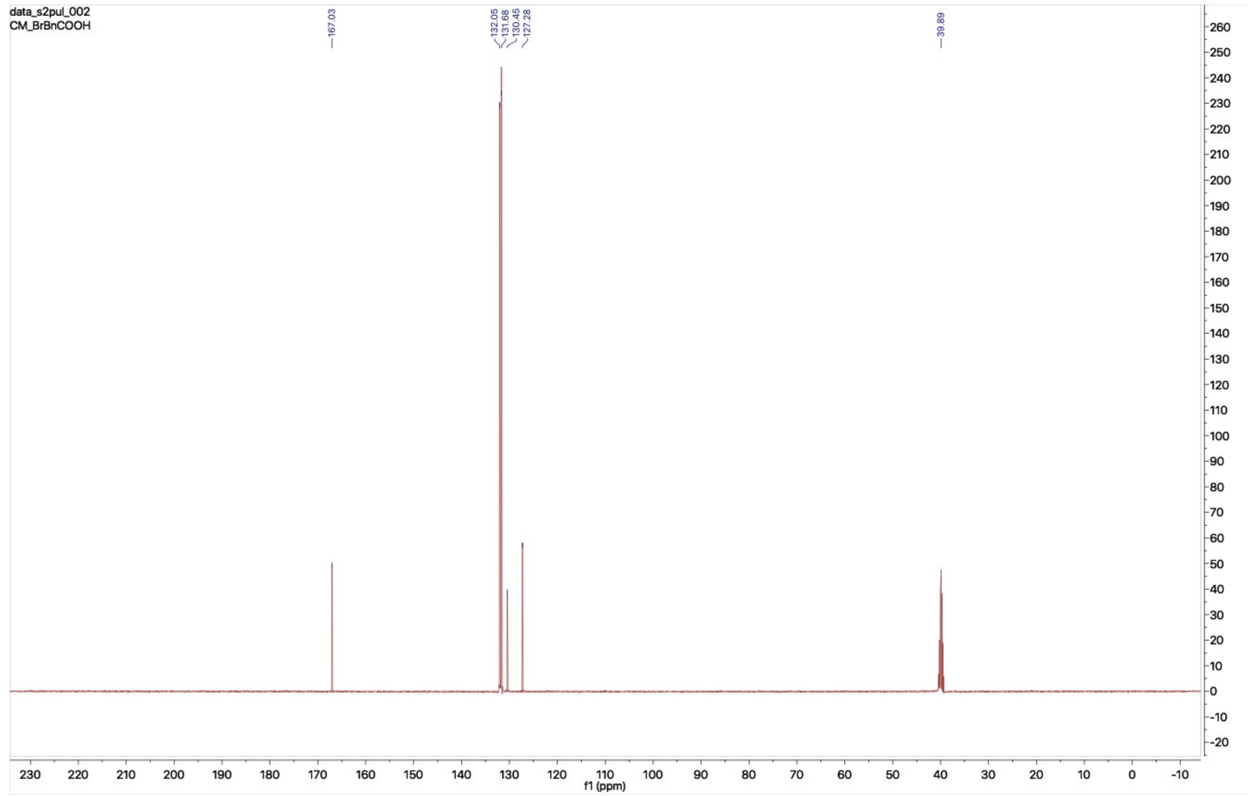


^{1}H NMR (500 MHz, DMSO-d^6) δ ppm 13.14 (bs, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.66 (d, J = 8.7 Hz, 2H).

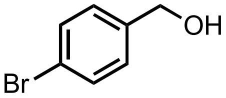
^{13}C NMR (125 MHz, DMSO-d^6) δ ppm 167.0 (1C), 132.0 (2C), 131.7 (2C), 130.4 (1C), 127.8 (1C).

HRMS (EI): Exact mass calculated for $C_7H_4O_2Br^-$ $[M-H]^{-\cdot}$: 198.9394 found 198.9399 (2.7 ppm).


data_s2pul_001
STANDARD 1H OBSERVE - profile
13.14
7.86
7.84
7.67
7.65
2.50 DMSO-d6
1.00
2.03
2.02
f1 (ppm)


data_s2pul_002
CM_BrBnCOOH
167.03
132.05
131.68
130.45
127.28
39.89
f1 (ppm)

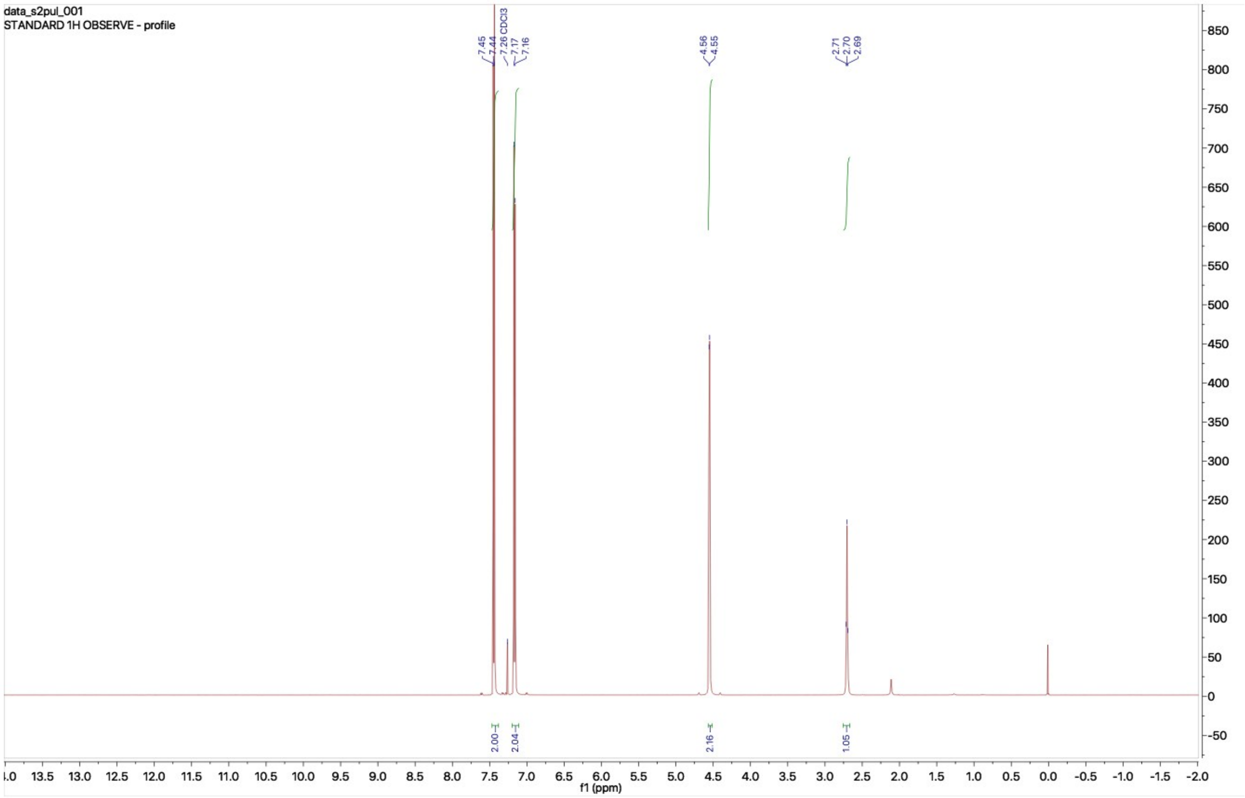
Compound 3.10b : 4-bromobenzyl alcohol

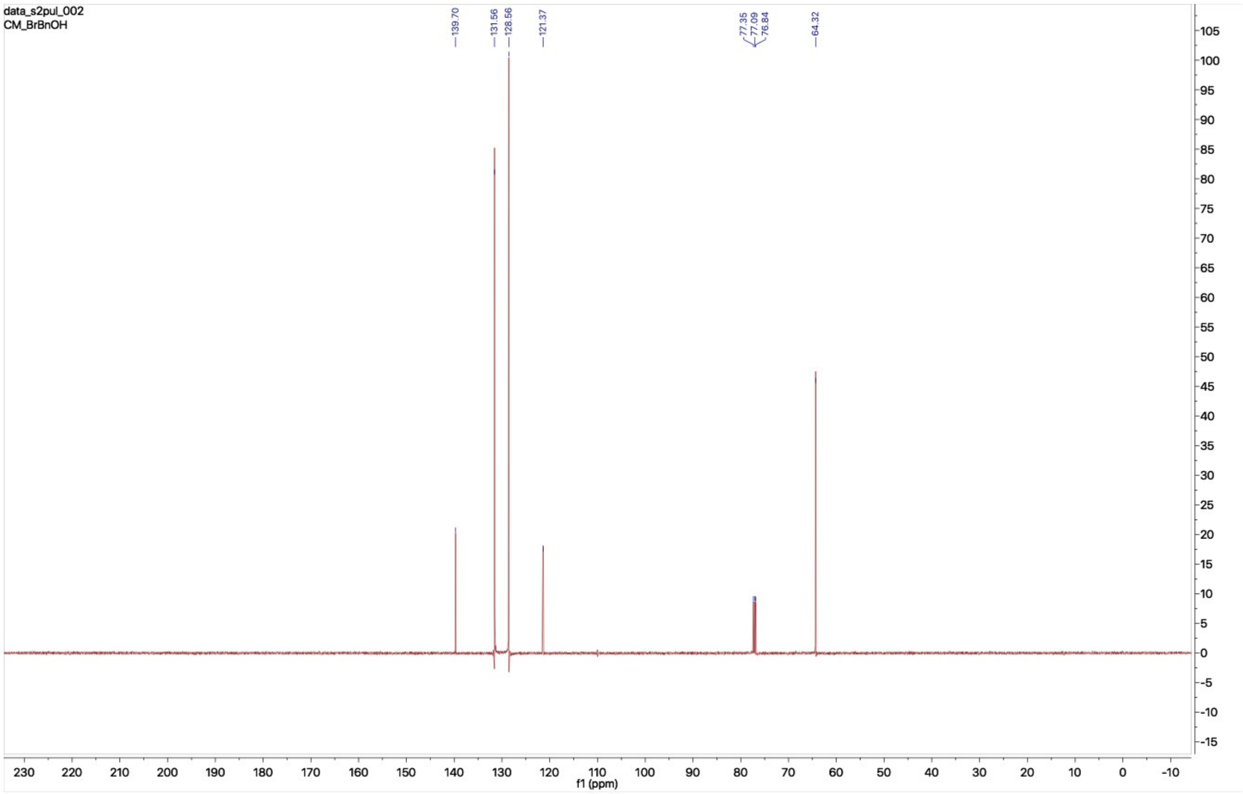


^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.45 (d, J = 8.5 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 4.56 (d, J = 3.9Hz, 2H), 2.70 (t, J = 3.9 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 139.7 (1C), 131.6 (2C), 128.6 (2C), 121.4 (1C), 64.3 (1C).

HRMS (EI): Exact mass calculated for $C_7H_6OBr^-$ $[M\text{-}H]^{-\cdot}$: 184.9601 found 184.9596 (-2.5 ppm).




data_s2pul_002
CM_BrBnOH
139.70
131.56
128.56
121.37
77.35
77.09
76.84
64.32
f1 (ppm)
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
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
-15