Supporting Information File for:

Lithium Triethylborohydride as Catalyst for Solvent-Free Hydroboration of Aldehydes and Ketones

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Experimental Details

General Information. All reactions were carried out under air atmosphere and at ambient temperature. Dry solvent was used throughout in case of solid substrates. Tetrahydrofuran (THF) was pre-dried over calcium hydride (CaH_2) and finally dried by adding sodium and benzophenone. THF was mixed at reflux under argon atmosphere until a deep-blue solution was appeared. Pinacolborane, lithium triethylborohydride ($LiHBEt_3$), aldehydes and ketones were purchased from Sigma-Aldrich and were used as received. The structure of products was determined by NMR spectroscopy. The ^1H NMR (400 or 600 MHz) and ^{13}C NMR (101 or 151 MHz) spectra were recorded on a Bruker Avance III HD NanoBay spectrometer, using chloroform-d ($CDCl_3$) as the solvent. Deuterated solvent was purchased from Sigma-Aldrich (99.8 atom% D) and used as received.

General procedure for the synthesis of compounds 3a-3z. To a 10 mL one-necked flask equipped with a stirring bar, carbonyl compound (ketone or aldehyde; 1.0 equiv.), pinacolborane (1.15 equiv., 0.12 g), lithium triethylborohydride (1M solution in THF; 1-3 µL, 0.001-0.003 equiv.), and 0.5 mL of THF (only in case of solid substrates) were added under air atmosphere (molar ratio carbonyl:pinacolborane 1:1.15). Subsequently, the reaction mixture was stirred at rt for definite time. Next, 1 mL of diethyl ether and 1 mL of 1M aqueous solution of NaOH were added and stirred at rt for 30 minutes. After this time, the reaction mixture was transferred to a separation funnel, diluted with dietyl ether (5 mL) and washed with H_2O (2 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated. Then, the remaining residue was purified and isolated by flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10) as eluents. Lastly, all volatiles were evaporated under reduced pressure to give the corresponding alcohols **3a**-**3z**. The pure products were characterized by ^1H and ^{13}C NMR spectroscopies. All products are known in the literature.

Gram-scale synthesis of 1-phenylethanol. To a 50 mL one-neck round-bottom flask acetophenone (1.5 g, 12.5 mmol, 1.0 eq.), pinacolborane (1.84 g, 14.4 mmol, 1.15 eq.), 5 mL of THF and lithium triethylborohydride (1M solution in THF; 12.5 µL, 0.0125 mmol, 0.001 eq.)were added under an air atmosphere, and the flask was closed with a stopper. Subsequently, the reaction mixture was stirred at rt for 0.5 h. Next, 15 mL of diethyl ether and 15 mL of 1M aqueous solution of NaOH were added and stirred at rt for 30 minutes. After this time, the reaction mixture was transferred to a separation funnel, diluted with dietyl ether (10 mL) and washed with H_2O (2 x 5 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was evaporated. Then, the remaining residue was purified and isolated by flash column chromatography with SiO_2 using ethyl acetate/hexane (1:10) as eluents. Lastly, all volatiles were evaporated under reduced pressure to give 1-phenylethanol (**3a**) in 97% (1.46 g).

Determination of the by-product formation via ^{1}H NMR

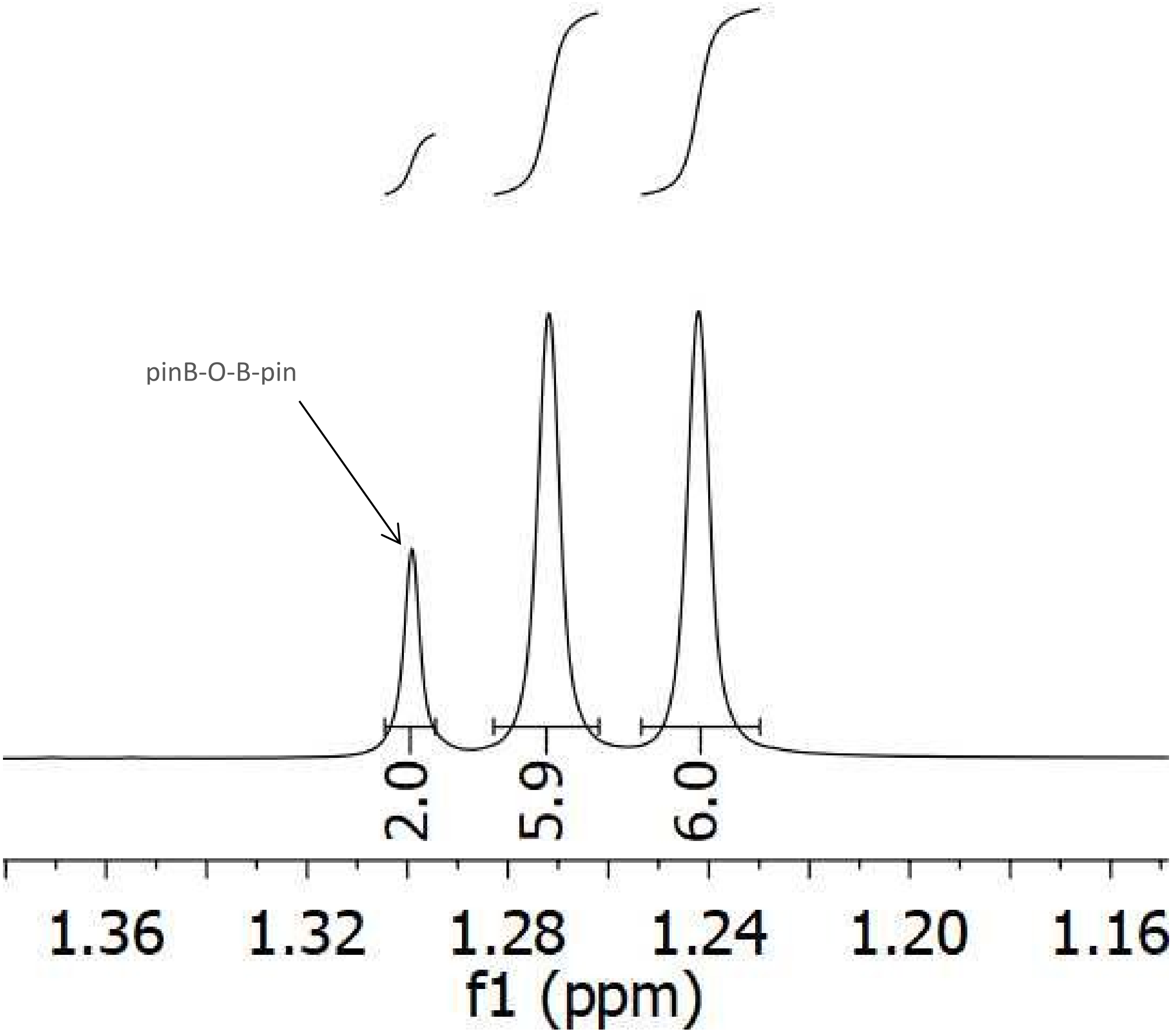
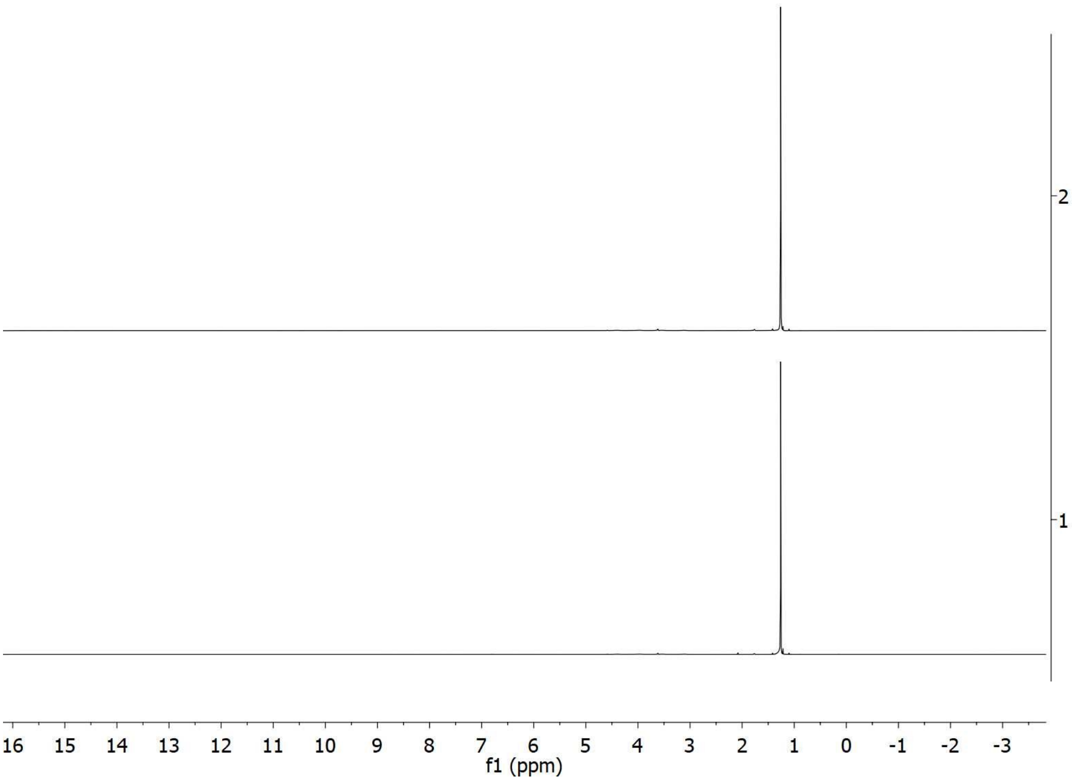


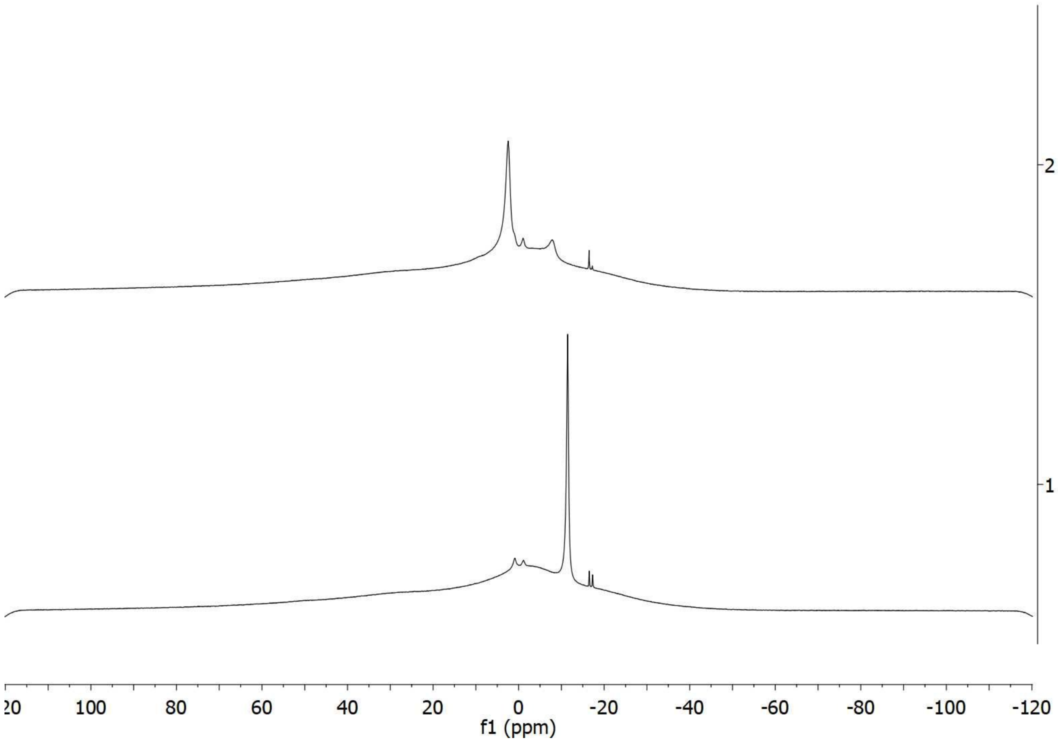
Figure 1. Determination of the diboraxane formation.

^{1}H and ^{11}B NMR spectra – Mechanistic Studies

(1) HBPin in THF-D8; **(2)** The 1:4 mixture of $LiHBEt_3$ and HBPin (both ^{1}H NMR)



(1) $LiHBEt_3$ in THF-D8; **(2)** The equimolar mixture of $LiHBEt_3$ and Acetophenone (both ^{11}B NMR)



Characterization data

1-Phenylethanol (**3a**) was obtained as colorless oil in 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.52 (d, *J* = 6.6 Hz, 3H), 2.20 (s, 1H), 4.91 (q, *J* = 6.5 Hz, 1H), 7.26-7.34 (m, 1H), 7.35-7.43 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 25.2, 70.4, 125.4, 127.5, 128.5, 145.8.

1-(4-Fluorophenyl)ethanol (**3b**) was obtained as colorless oil in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.48 (d, *J* = 6.4 Hz, 3H), 2.24 (s, 1H), 4.88 (q, *J* = 6.4 Hz, 1H), 6.91-7.14 (m, 2H), 7.32-7.39 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 25.3, 69.7, 115.23 (d, *J* = 21.3 Hz), 127.05 (d, *J* = 8 Hz), 141.51 (d, *J* = 3.1 Hz), 162.09 (d, *J* = 245.1 Hz).

1-(4-Bromophenyl)ethanol (**3c**) was obtained as white solid in 90% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.49 (d, *J* = 6.5 Hz, 3H), 1.90 (s, 1H), 4.88 (q, *J* = 6.5 Hz, 1H), 7.17-7.36 (m, 2H), 7.45-7.59 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 25.3, 69.8, 121.2, 127.2, 131.6, 144.8.

1-(4-Methylphenyl)ethanol (**3d**) was obtained as colorless oil in 91% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 1.51 (d, *J* = 6.5 Hz, 3H), 2.12 (s, 1H), 2.38 (s, 3H), 4.88 (q, *J* = 6.5 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 21.1, 25.1, 70.2, 125.4, 129.2, 137.1, 142.9.

1-(4-Methoxyphenyl)ethanol (**3e**) was obtained as colorless oil in 93% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 1.48 (d, *J* = 6.6 Hz, 3H), 2.28 (s, 1H), 3.81 (s, 3H), 4.84 (qd, *J* = 6.4, 2.5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 25.0, 55.3, 69.9, 113.8, 126.7, 138.1, 158.9.

1-(4-Trifluorophenyl)ethanol (**3f**) was obtained as colorless oil in 82% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 1.49 (d, *J* = 6.5 Hz, 3H), 2.58 (s, 1H), 4.93 (q, *J* = 6.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 25.3, 69.8, 124.2 (d, *J* = 271.8 Hz), 125.4 (d, *J* = 3.8 Hz), 129.6 (d, *J* = 32.4 Hz), 149.7 (d, *J* = 1.4 Hz).

4-(1-Hydroxyethyl)benzonitrile (**3g**) was obtained as colorless oil in 90% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 1.46 (d, *J* = 6.9 Hz, 3H), 2.96 (s, 1H), 4.91 (q, *J* = 6.6 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 25.1, 68.5, 120.6, 149.4, 155.5.

1-(Pyridin-4-yl)ethan-1-ol (**3h**) was obtained as white solid in 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.49 (d, *J* = 6.5 Hz, 3H), 4.14 (s, 1H), 4.89 (q, *J* = 6.5 Hz, 1H), 7.16-7.48 (m, 2H), 8.25-8.78 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 25.3, 69.4, 110.7, 118.9, 126.1, 132.3, 151.4.

2-Decanol **(3i)** was obtained as colorless oil in 84% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.89 (t, *J* = 6.7 Hz, 3H), 1.16-1.22 (m, 3H), 1.25-1.40 (m, 12H), 1.40-1.52 (m, 3H), 3.80 (q, *J* = 6.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 14.1, 22.7, 23.5, 25.8, 29.3, 29.6, 29.7, 31.9, 39.4, 68.2.

Diphenylmethanol **(3j)** was obtained as white solid in 91% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 2.36 (d, *J* = 3.4 Hz, 1H), 5.86 (d, *J* = 3.4 Hz, 1H), 7.29-7.34 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 4H), 7.42 (d, *J* = 8.2 Hz, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 76.3, 126.6, 127.6, 128.5, 143.8.

(4-Methoxyphenyl)(phenyl)methanol **(3k)** was obtained as white solid in 93% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 2.29 (d, *J* = 3.6 Hz, 1H), 3.82 (s, 3H), 5.83 (d, *J* = 3.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 3H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 55.3, 75.8, 113.9, 126.4, 127.4, 127.9, 128.4, 136.2, 144.0, 159.0.

2-Bromo-1-(2-methoxyphenyl)ethan-1-ol **(3l)** was obtained as colorless oil in 88% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 2.96 (d, *J* = 5.3 Hz, 1H), 3.50-3.64 (m, 1H), 3.74-3.83 (m, 1H), 3.88 (s, 3H), 5.09-5.25 (m, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 7.28-7.36 (m, 1H), 7.43-7.50 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 39.1, 55.3, 70.1, 110.4, 120.9, 127.1, 128.2, 129.2, 156.2.

Cyclohexanol **(3m)** was obtained as colorless oil in 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.15-1.34 (m, 5H), 1.47-1.63 (m, 2H), 1.68-1.81 (m, 2H), 1.86-1.96 (m, 2H), 3.58-3.75 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 24.1, 25.5, 35.6, 70.3.

1-Phenylpropan-1-ol **(3n)** was obtained as colorless oil in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.94 (t, *J* = 7.4 Hz, 3H), 1.70-1.91 (m, 2H), 2.01-2.14 (m, 1H), 4.61 (t, *J* = 6.6 Hz, 1H), 7.27-7.34 (m, 1H), 7.35-7.41 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 10.2, 31.9, 76.0, 126.0, 127.5, 128.4, 144.6.

1-(4-Fluorophenyl)propan-1-ol **(3o)** was obtained as colorless oil in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 0.91 (t, *J* = 7.4 Hz, 3H), 1.64-1.88 (m, 2H), 2.11-2.26 (m, 1H), 4.58 (t, *J* = 6.7 Hz, 1H), 6.95-7.12 (m, H), 7.23-7.36 (m, H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 10.0, 32.0, 75.3, 115.2 (d, *J* = 21.3 Hz), 127.6 (d, *J* = 8.1 Hz), 140.3 (d, *J* = 3.0 Hz), 162.1 (d, *J* = 245.1 Hz).

Benzyl Alcohol **(3p)** was obtained as colorless oil in 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.10-2.57 (m, 1H), 4.60-4.75 (m, 2H), 7.29-7.36 (m, 1H), 7.34-7.49 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 65.2, 127.0, 127.6, 128.6, 140.9.

4-Methylbenzyl Alcohol (**3r**) was obtained as colorless oil in 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.94 (d, *J* = 4.5 Hz, 1H), 2.39 (s, 3H), 4.57-4.74 (m, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 21.2, 65.2, 127.1, 129.2, 137.4, 137.9.

3-Methoxybenzyl Alcohol (**3s**) was obtained as white solid in 90% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 2.12 (d, *J* = 5.3 Hz, 1H), 3.82 (s, 3H), 4.60 (s, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H)

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 55.3, 64.9, 113.9, 128.6, 133.2, 159.2.

3-Methylbenzyl Alcohol (**3t**) was obtained as colorless oil in 98% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 2.41 (s, 3H), 2.65 (s, 1H), 4.63 (s, 2H), 7.12-7.20 (m, 2H), 7.20 (s, 1H), 7.29 (t, *J* = 7.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 21.4, 65.2, 124.1, 127.8, 128.3, 128.5, 138.2, 140.9.

2-Bromobenzyl Alcohol (**3u**) was obtained as white solid in 91% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 2.73 (s, 1H), 4.73 (s, 2H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 64.9, 122.5, 127.6, 128.8, 129.1, 132.6, 139.7.

4-Fluorobenzyl Alcohol (**3v)** was obtained as colorless oil in 90% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 2.59 (s, 1H), 4.60 (s, 2H), 7.04 (t, *J* = 8.5 Hz, 2H), 7.20-7.38 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 64.4, 115.33 (d, *J* = 21.4 Hz), 128.74 (d, *J* = 8.1 Hz), 136.56 (d, *J* = 3.3 Hz), 162.27 (d, *J* = 245.5 Hz).

2-Fluorobenzyl Alcohol (**3w)** was obtained as colorless oil in 86% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 2.34 (s, 1H), 4.76 (s, 2H), 7.03-7.11 (m, 1H), 7.16 (t, J = 7.5 Hz, 1H), 7.26-7.34 (m, 1H), 7.40-7.49 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 59.2, 115.24 (d, *J* = 21.1 Hz), 124.22 (d, *J* = 3.7 Hz), 127.80 (d, *J* = 14.5 Hz), 129.29 (d, *J* = 4.8 Hz), 129.34 (d, *J* = 8.1 Hz), 160.60 (d, *J* = 246.1 Hz).

Thiophen-2-ylmethanol (**3x**) was obtained as colorless oil in 99% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 2.83 (s, 1H), 4.78 (s, 2H), 6.74-7.19 (m, 2H), 729 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 59.8, 125.5, 125.5, 126.9, 144.0.

(E)-non-2-en-1-ol (**3y**) was obtained as colorless oil in 91% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 20.90 (t, *J* = 7.0 Hz, 3H), 1.20-1.26 (m, 2H), 1.28-1.36 (m, 4H), 1.37-1.43 (m, 2H), 1.55 (s, 1H), 1.99-2.11 (m, 2H), 4.09 (d, *J* = 5.7 Hz, 2H), 5.61-5.67 (m, 1H), 5.68-5.74 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 14.0, 22.5, 24.8, 28.8, 31.4, 32.2, 63.8, 128.8, 133.5.

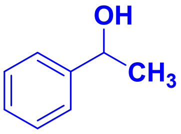
1-(4-(Hydroxymethyl)phenyl)ethan-1-one (**3z**) was obtained as white solid in 95% yield.

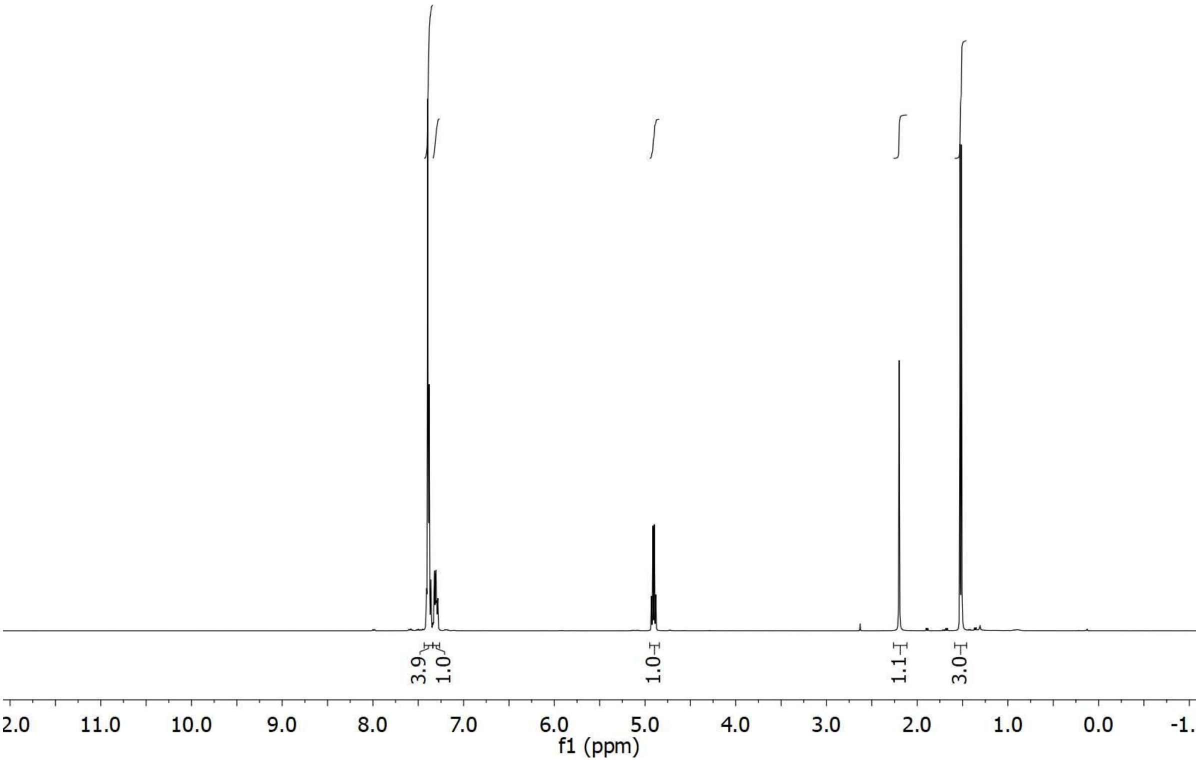
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 2.44-2.61 (m, 3H), 3.55 (s, 1H), 4.70 (s, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.1 Hz, 2H).

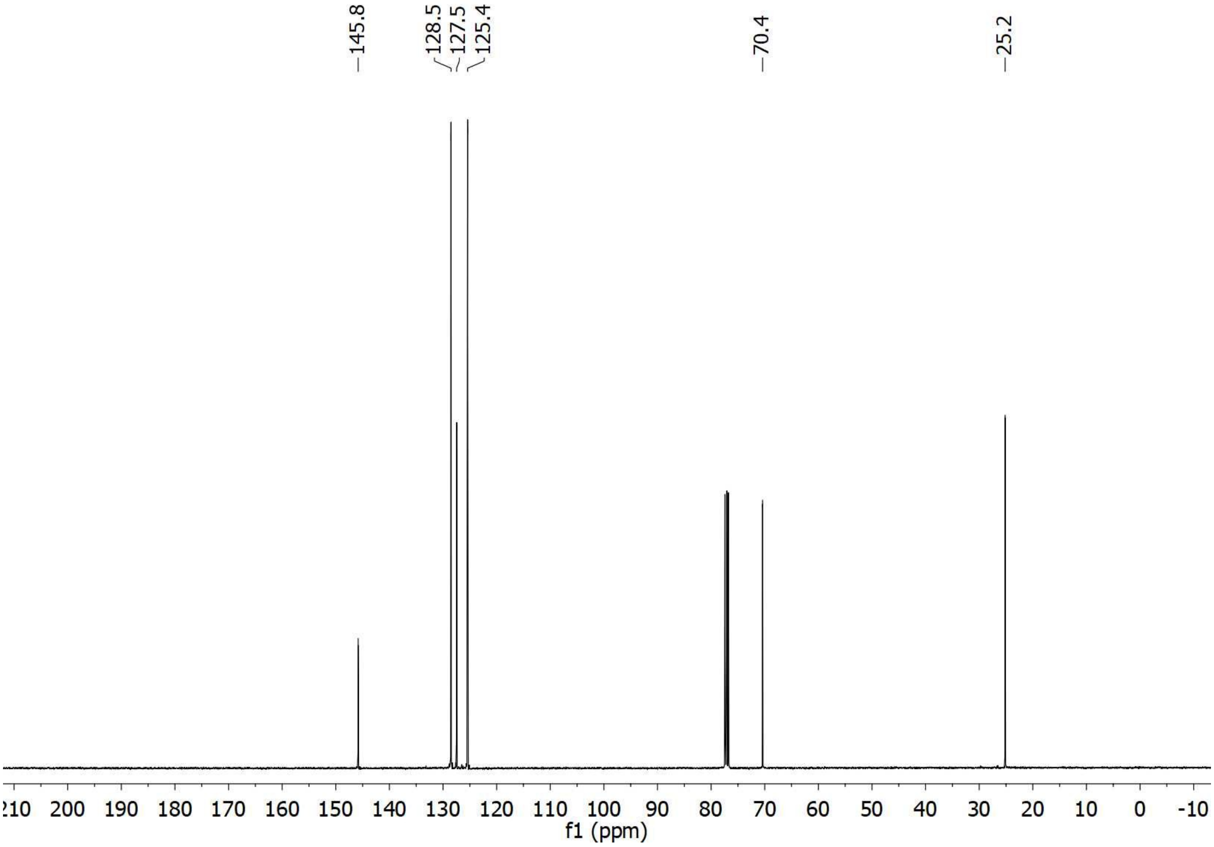
^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) = 26.6, 64.2, 126.6, 128.5, 136.0, 146.7, 198.5.

^{1}H and ^{13}C NMR spectra

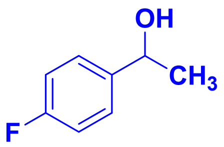
1-Phenylethanol (**3a**)

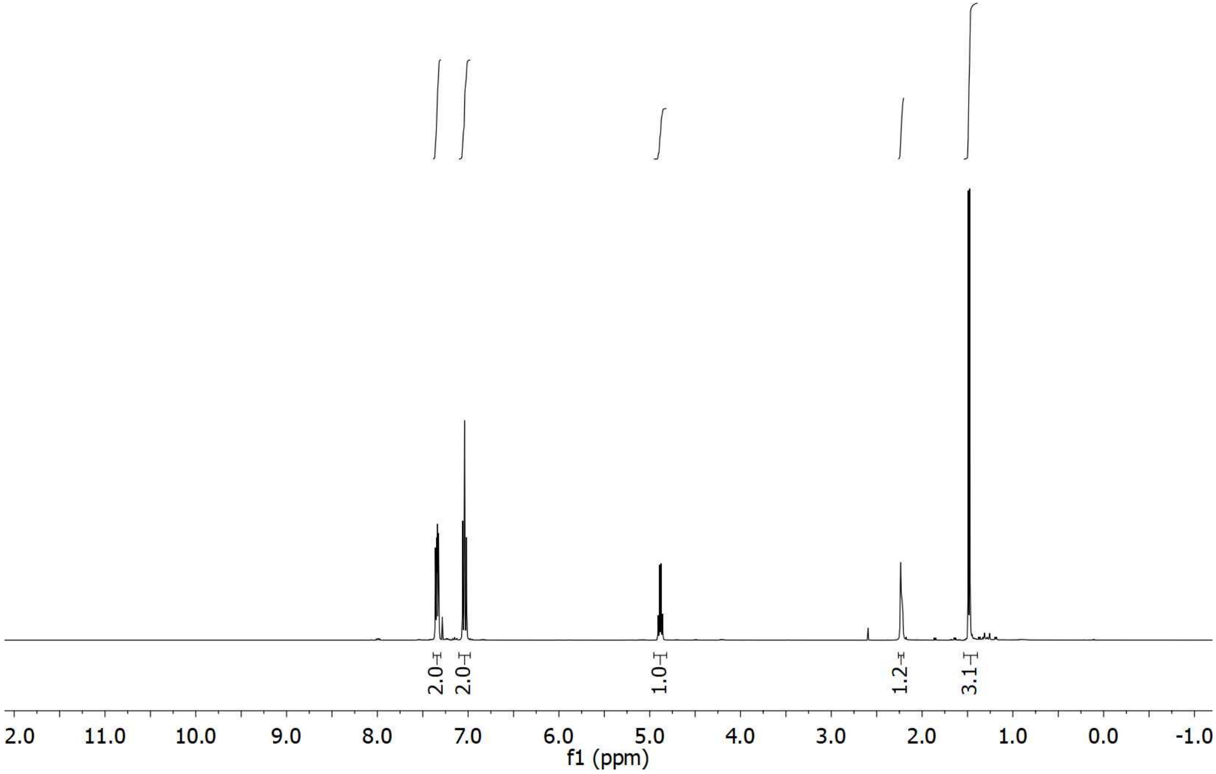


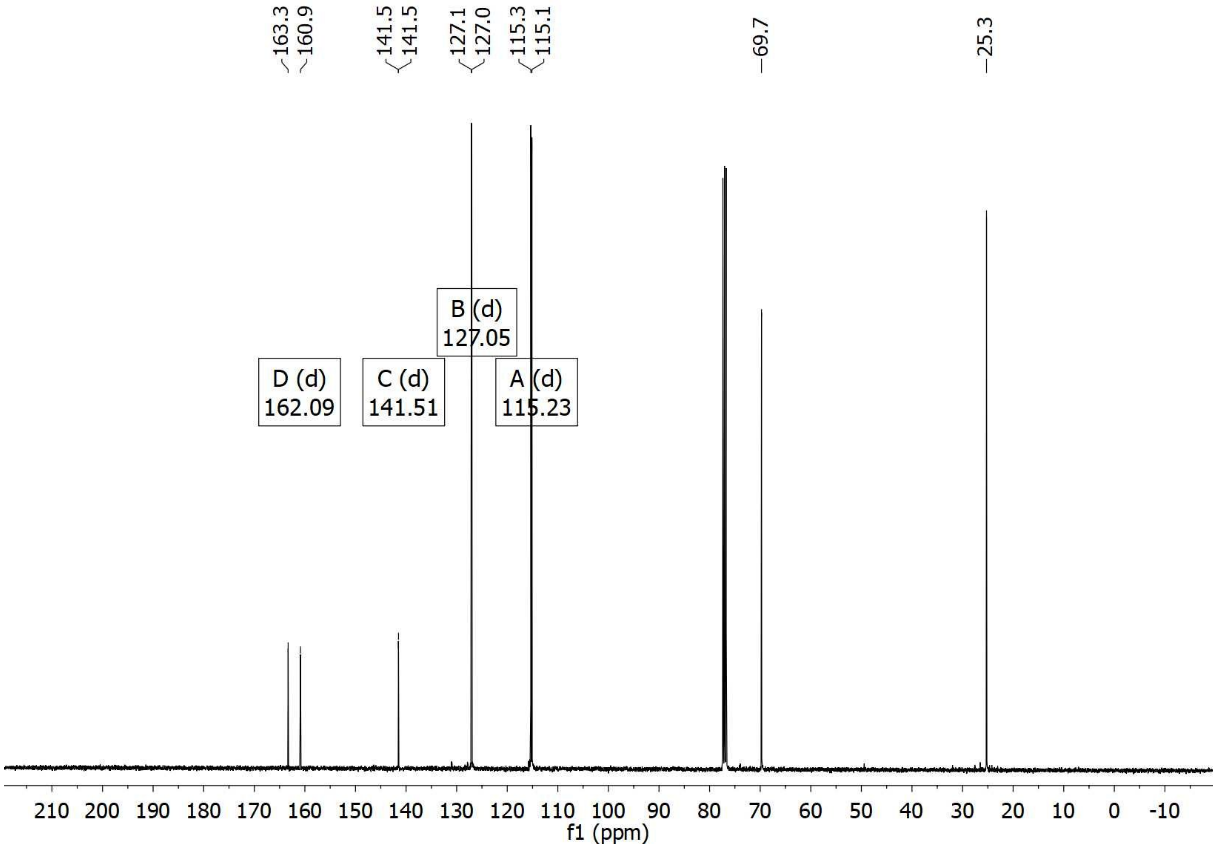




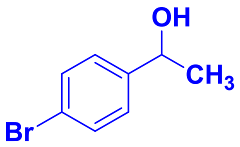
1-(4-Fluorophenyl)ethanol (**3b**)

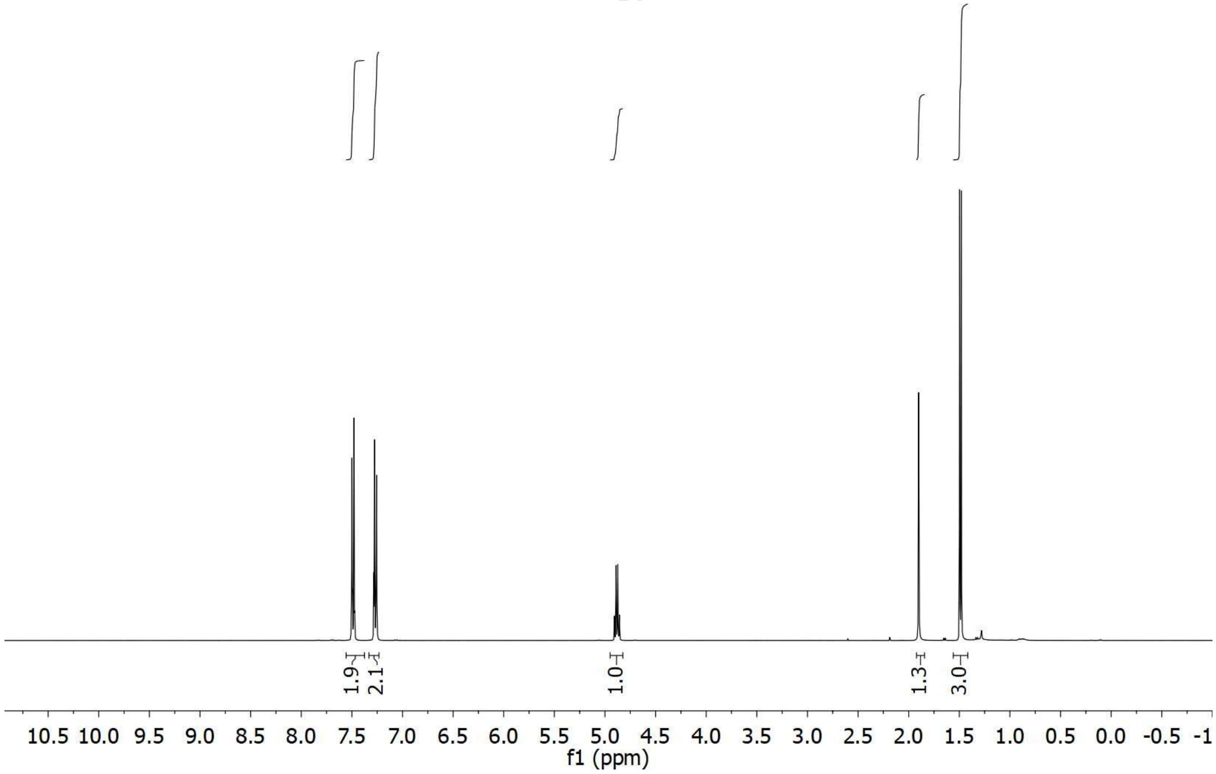


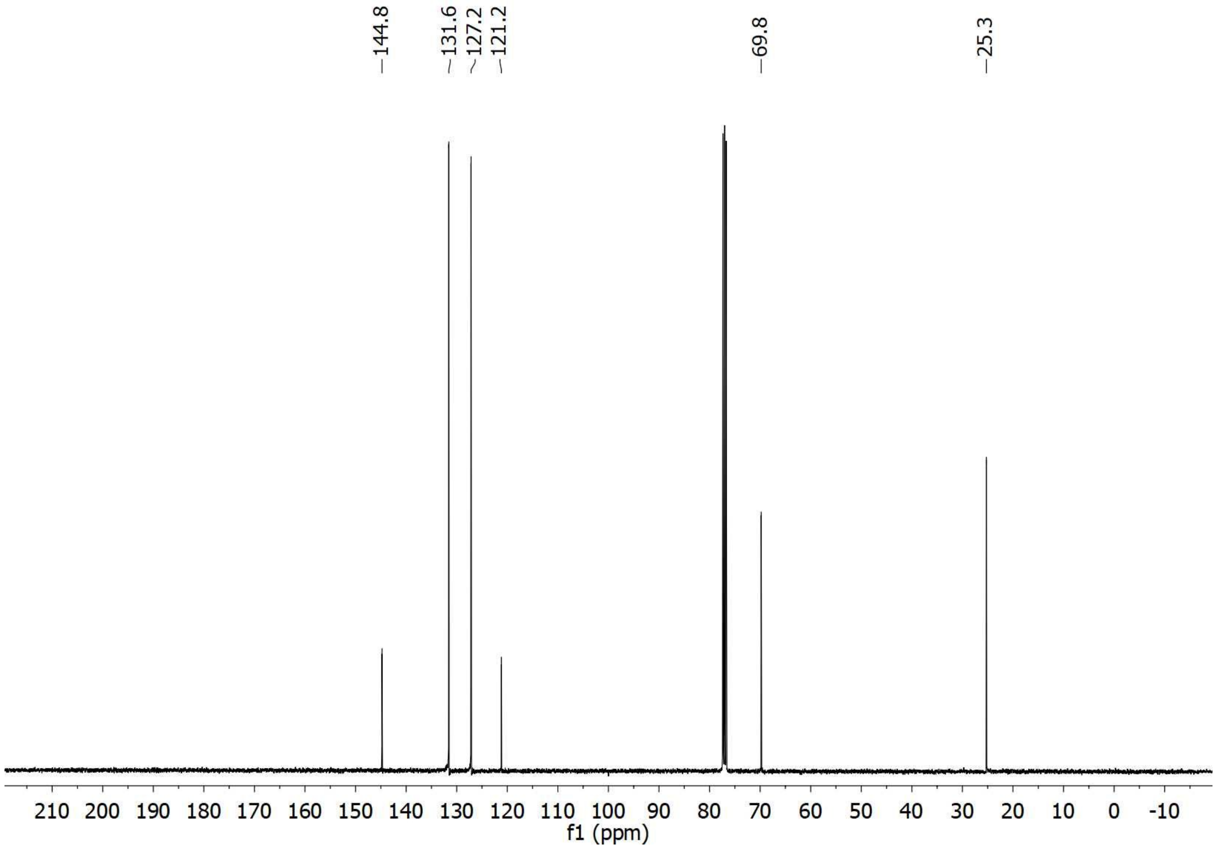




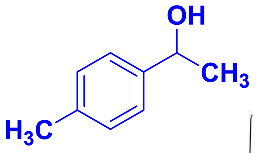
1-(4-Bromophenyl)ethanol (**3c**)

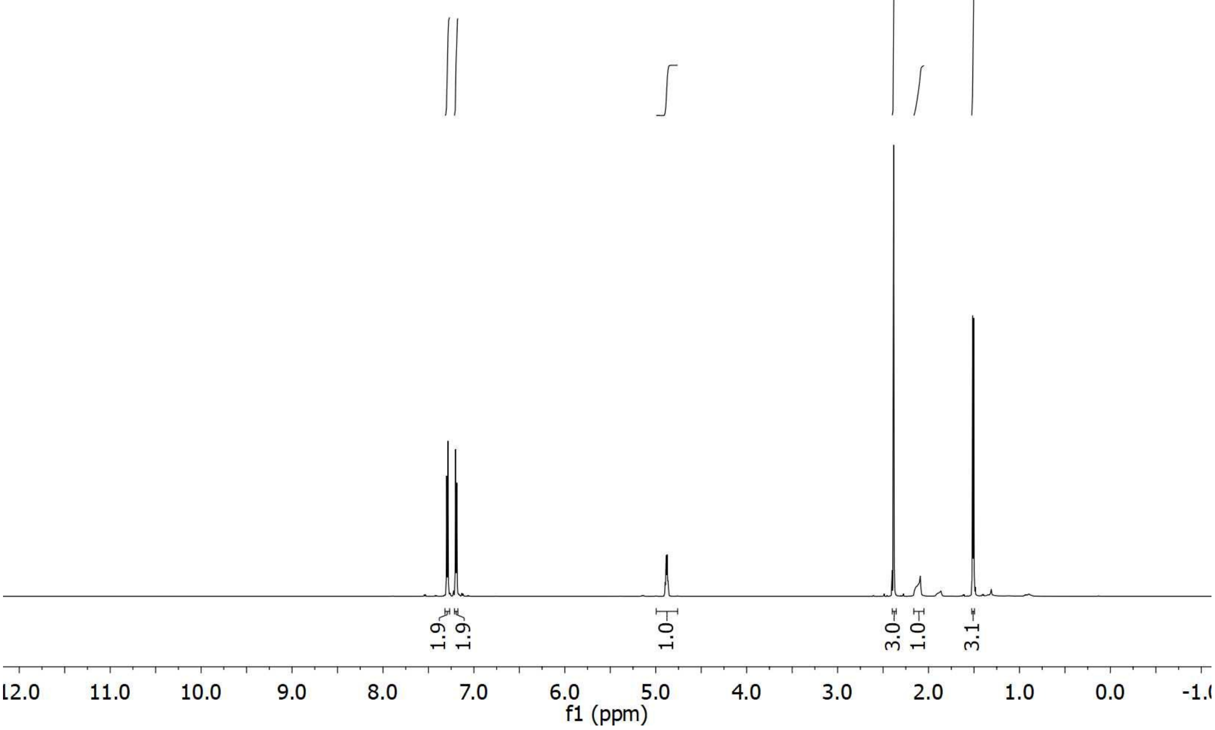


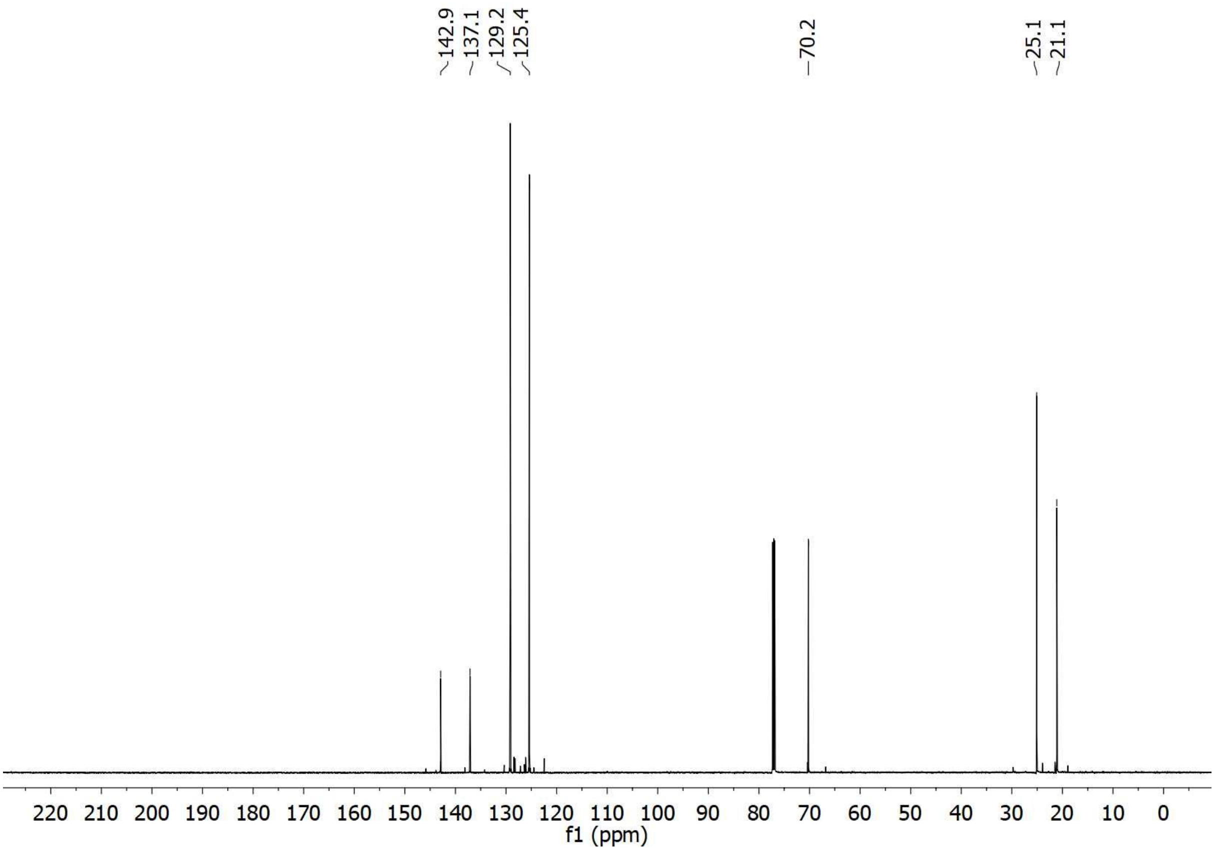




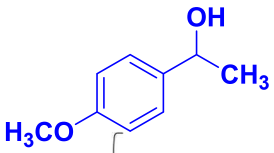
1-(4-Methylphenyl)ethanol (**3d**)

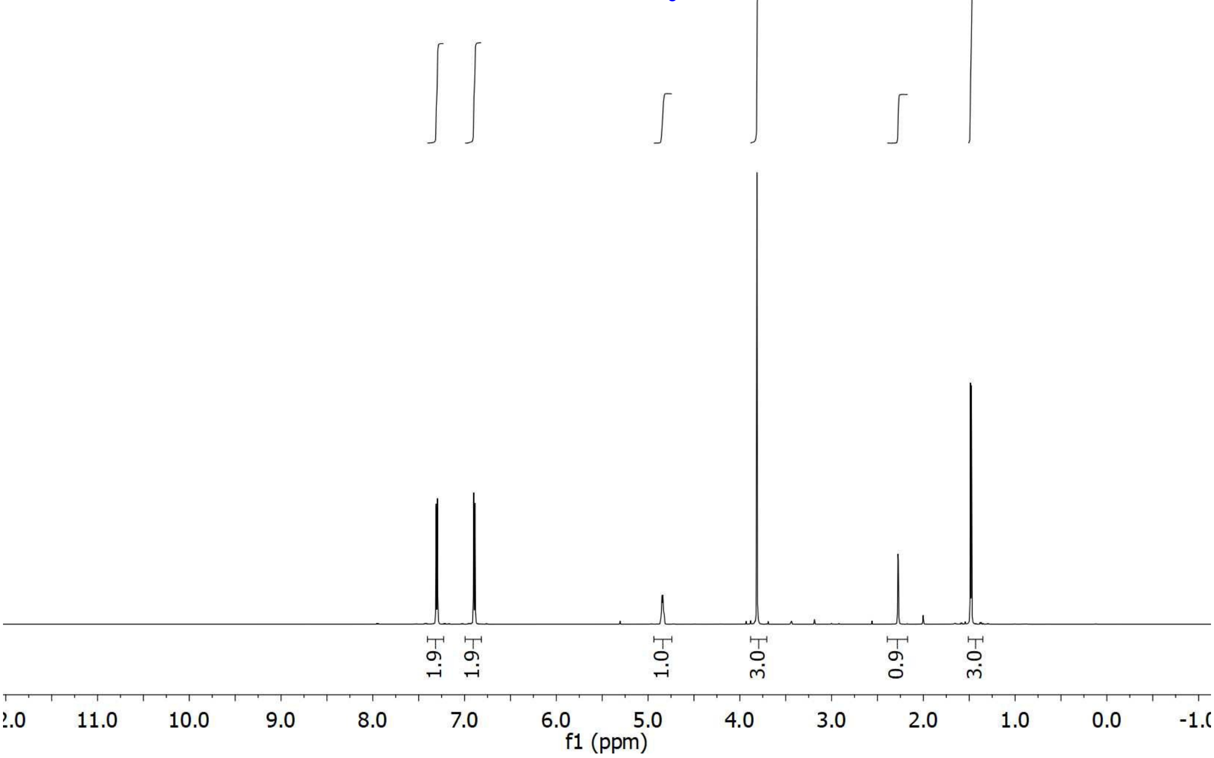


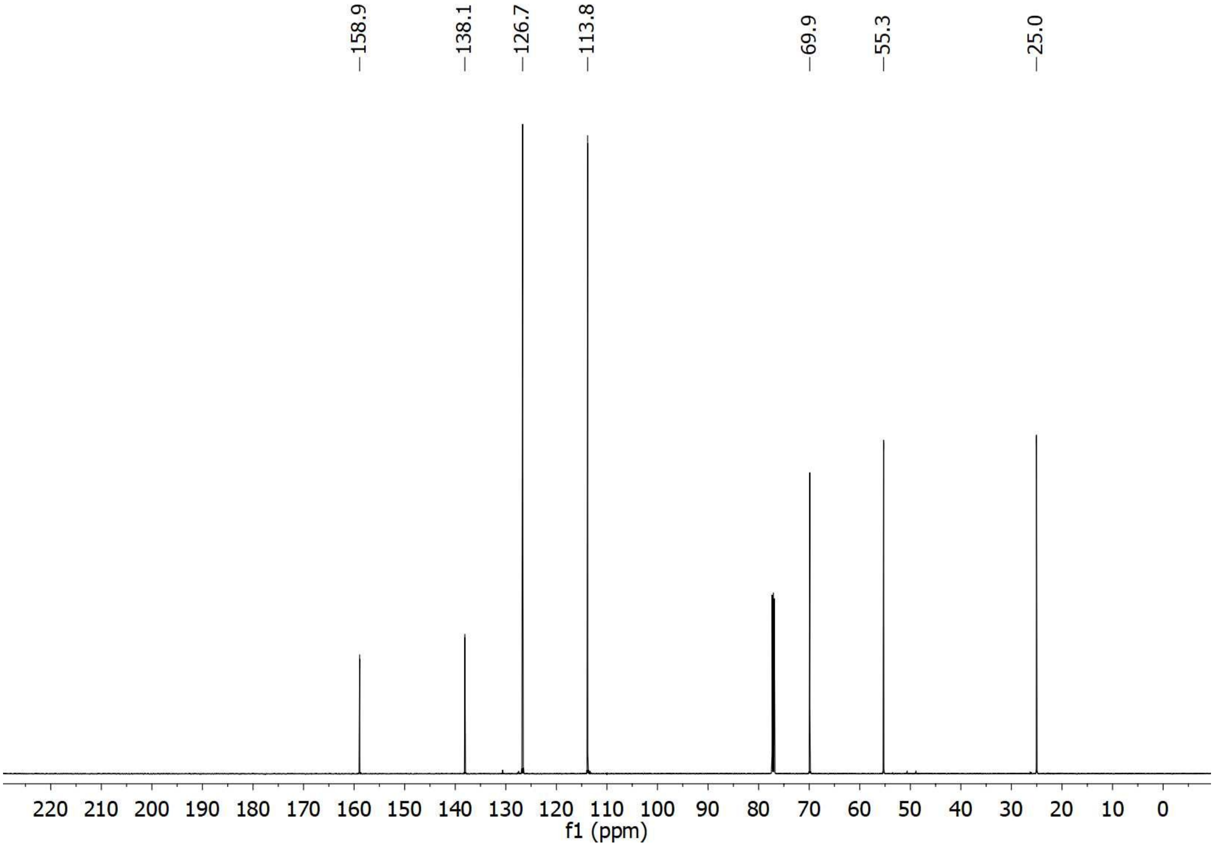




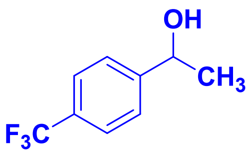
1-(4-Methoxyphenyl)ethanol (**3e**)

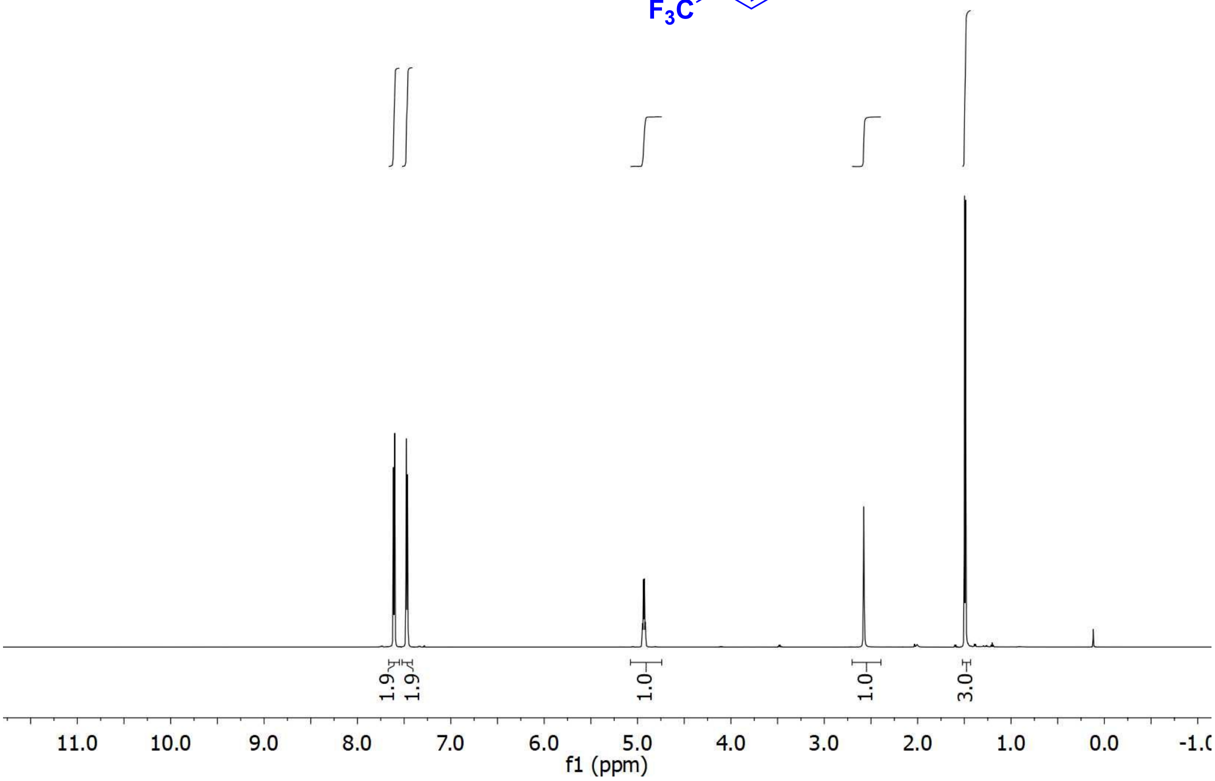


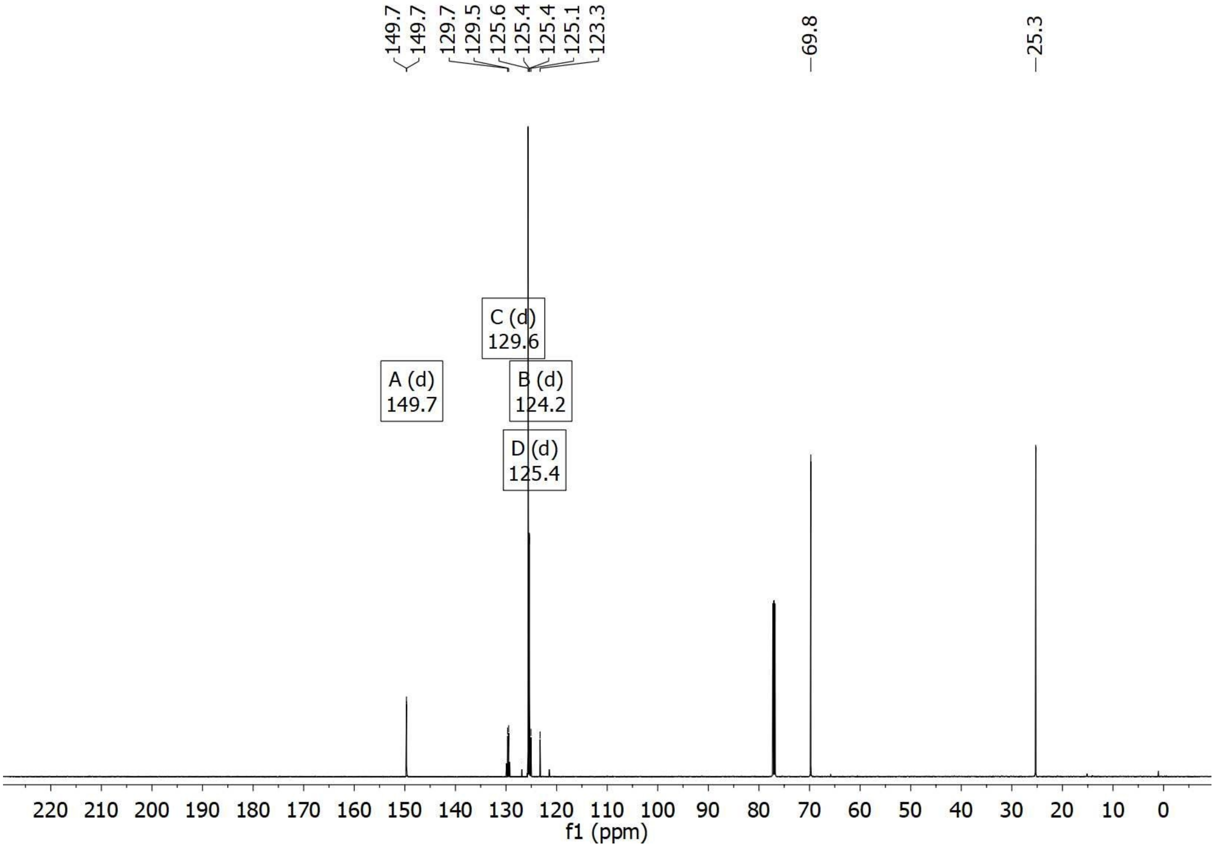




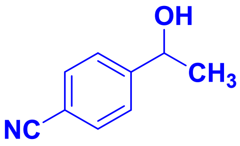
1-(4-Trifluoromethylphenyl)ethanol (**3f**)

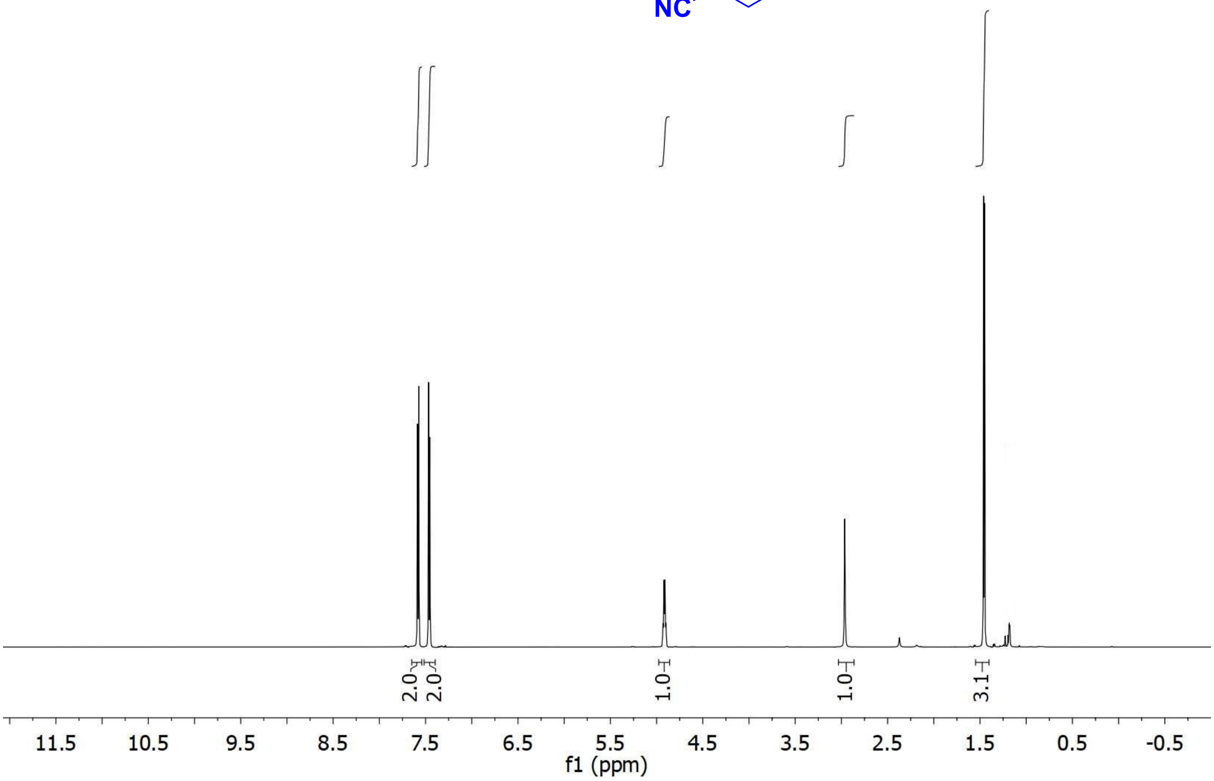


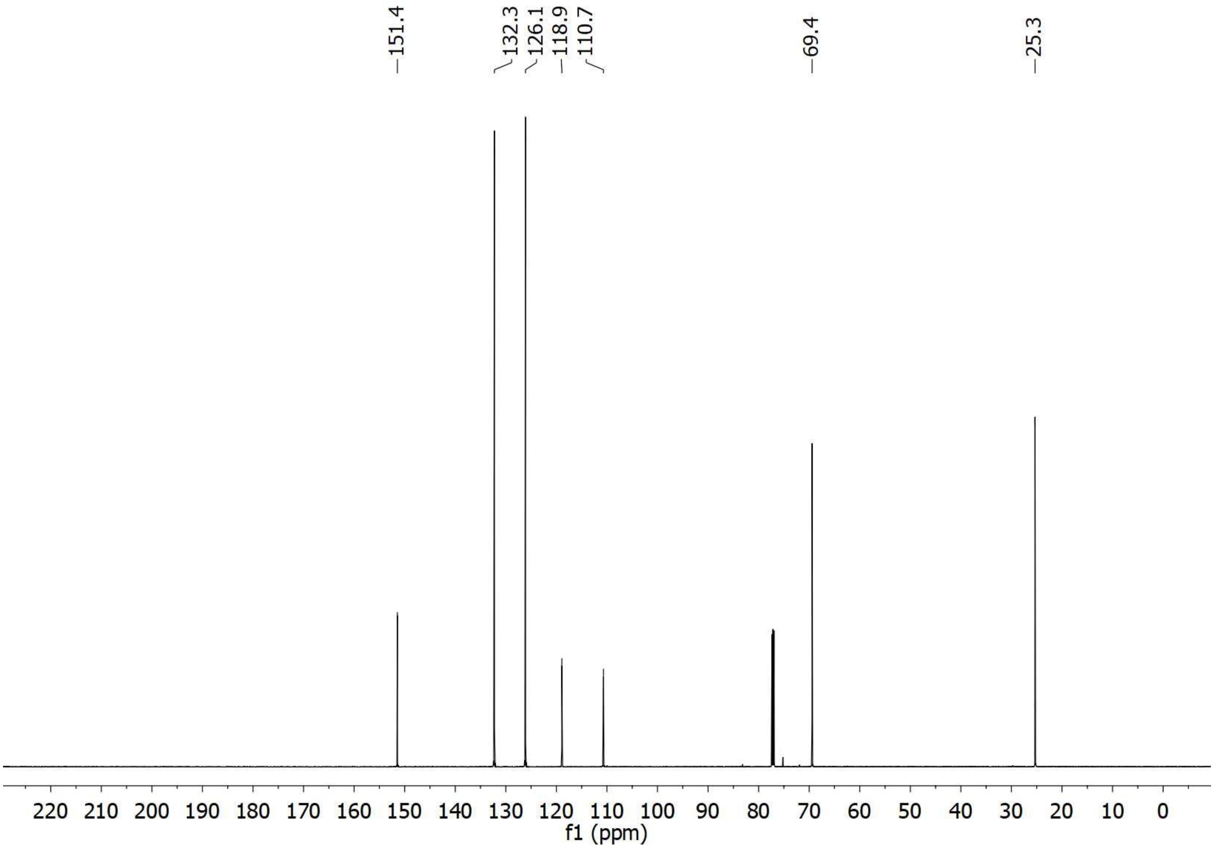




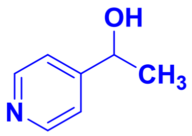
4-(1-Hydroxyethyl)benzonitrile (**3g**)

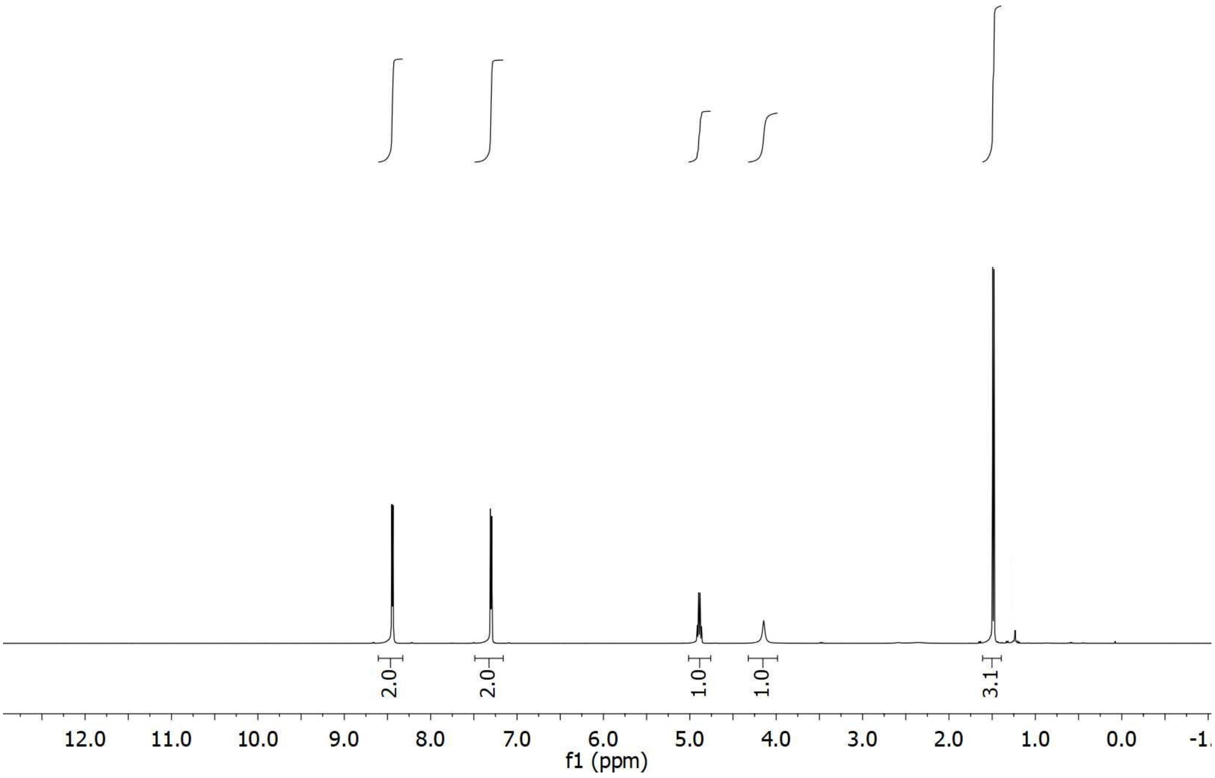


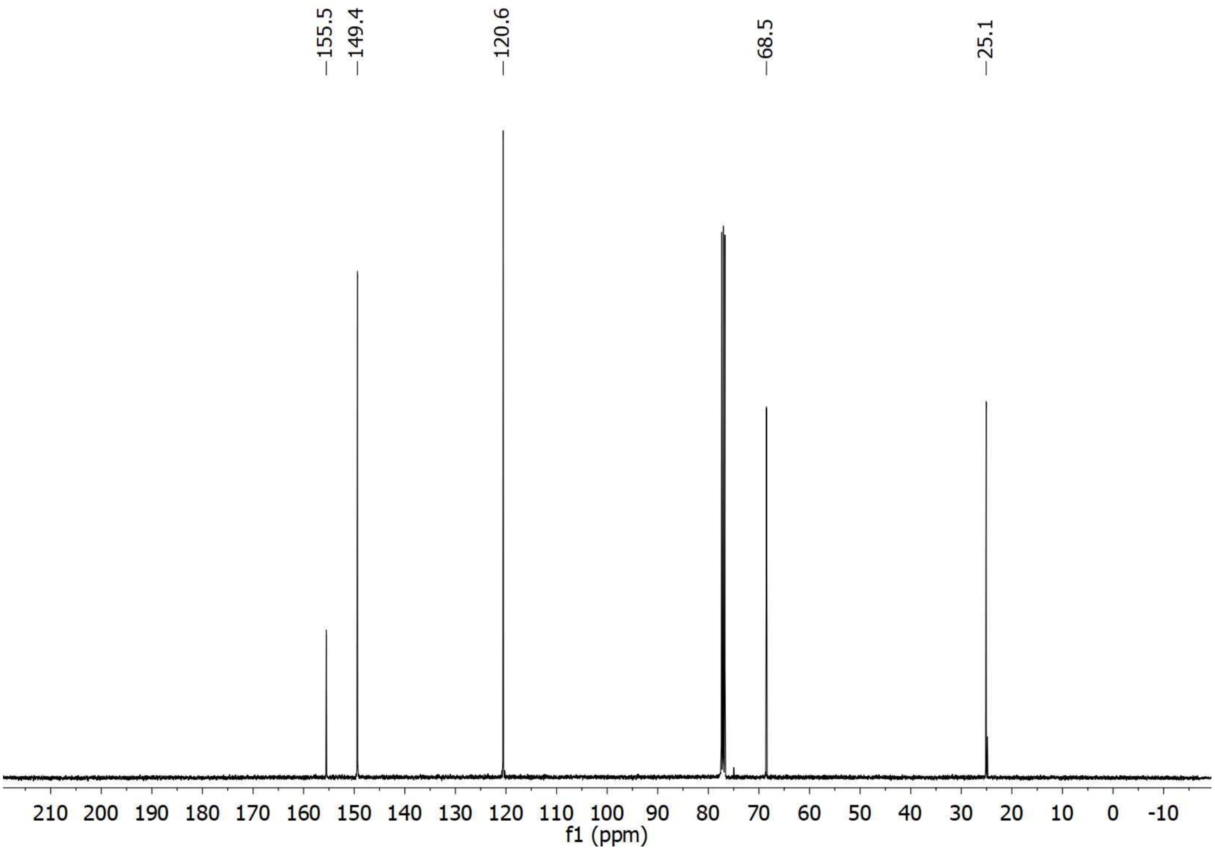




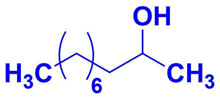
1-(Pyridin-4-yl)ethan-1-ol **(3h)**

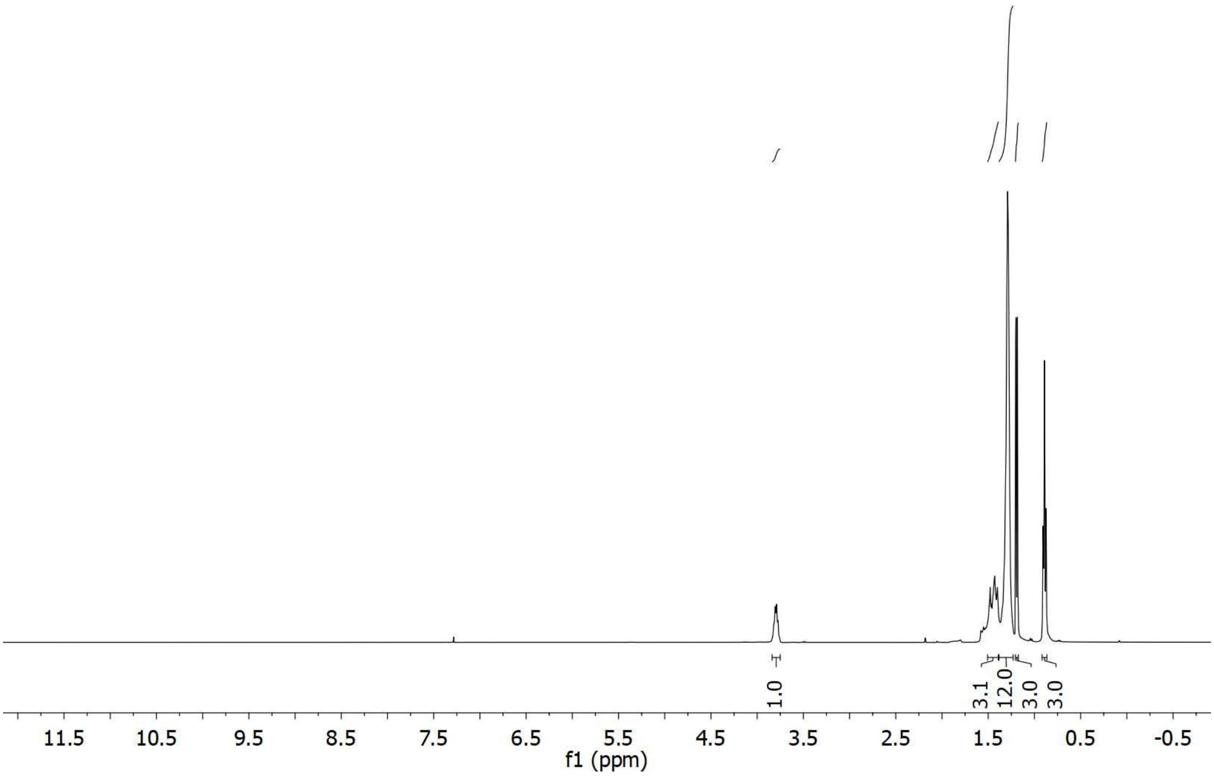


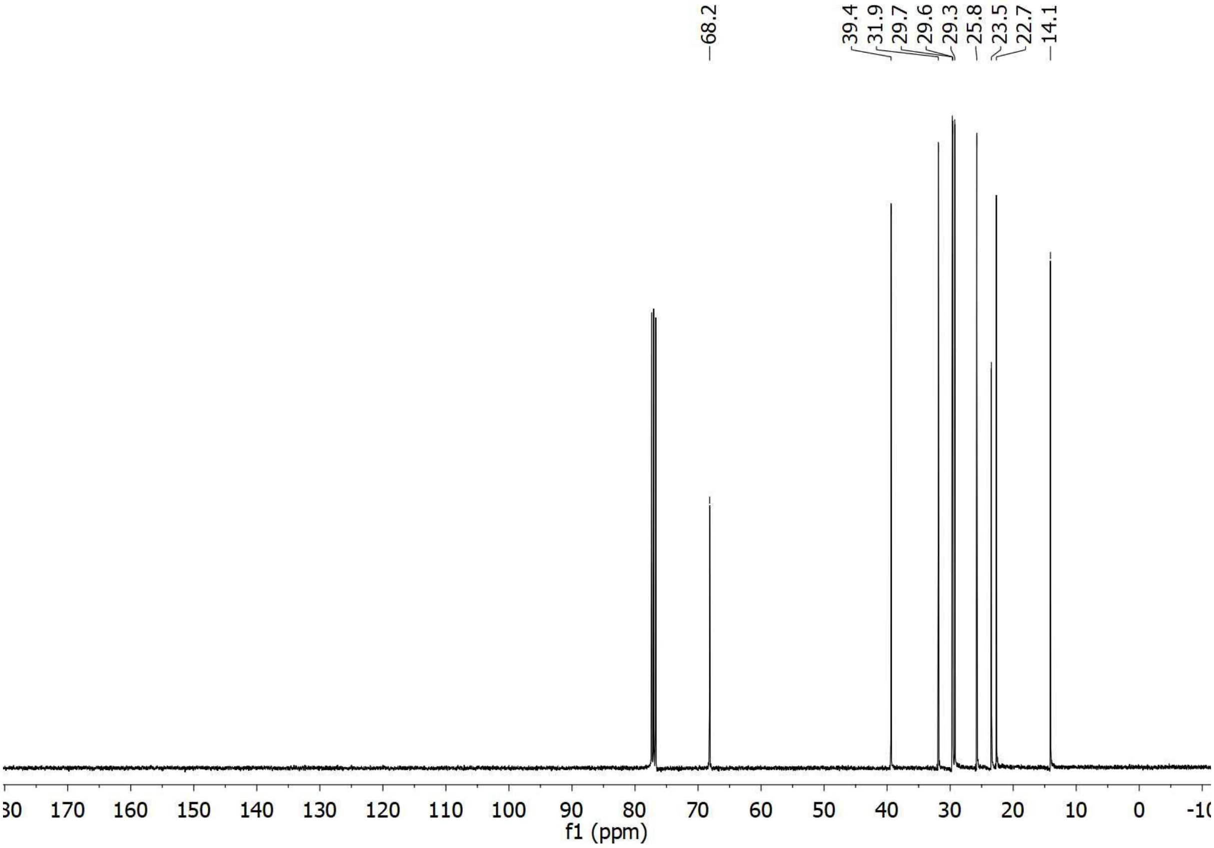




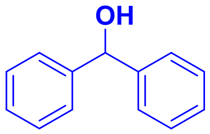
2-Decanol **(3i)**

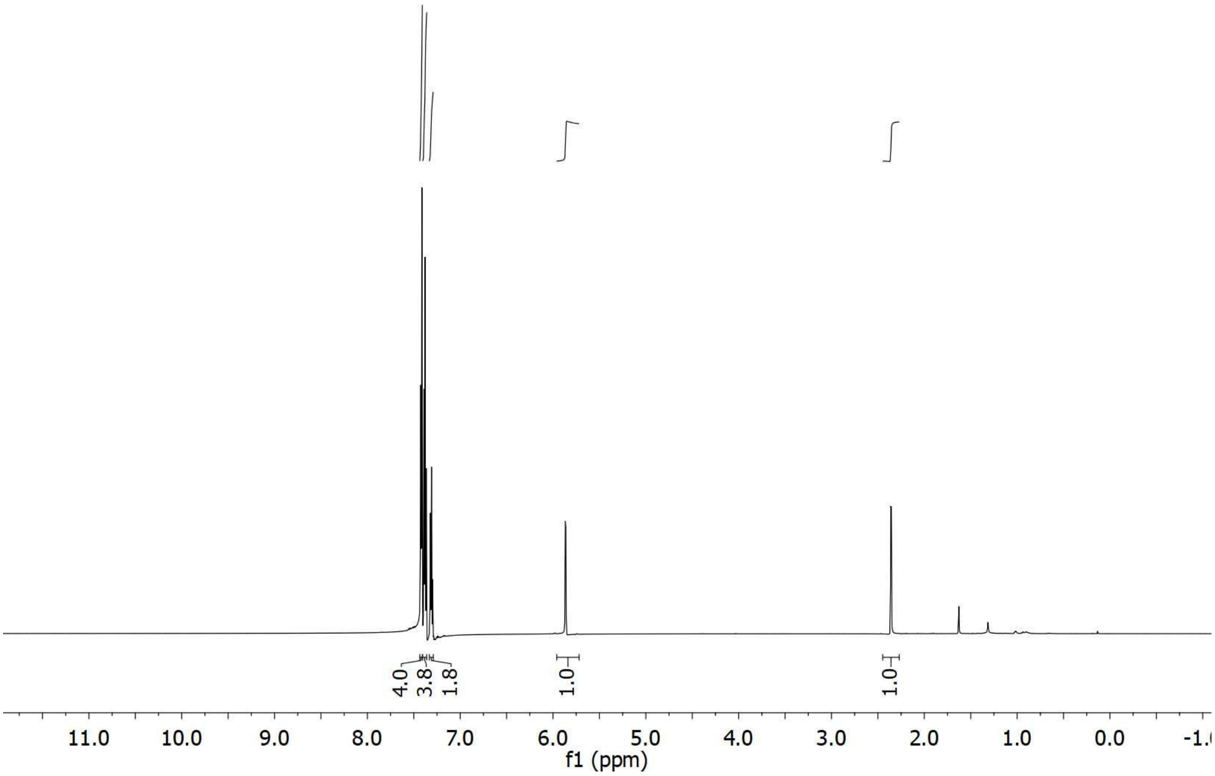

OH
H3C
6
CH3

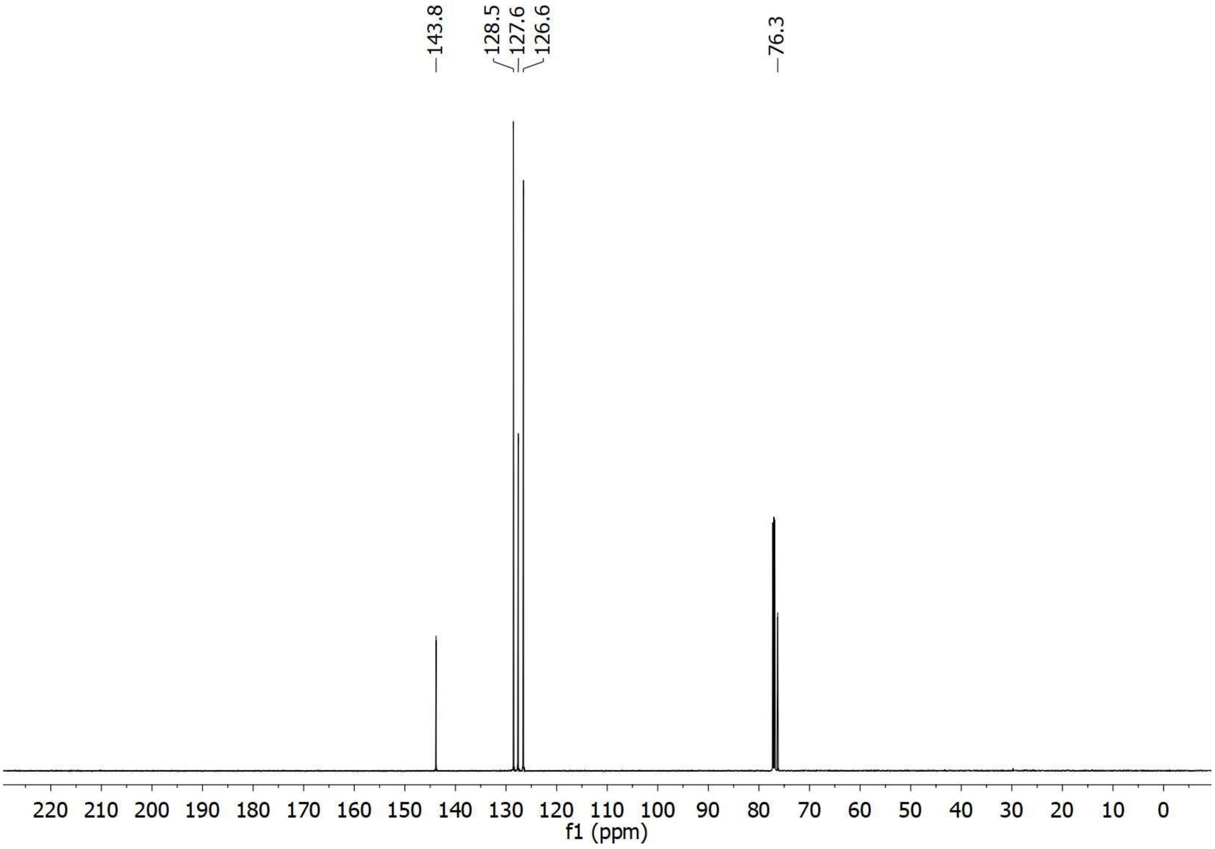

1.0
3.1
12.0
3.0
3.0
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


68.2
39.4
31.9
29.7
29.6
29.3
25.8
23.5
22.7
14.1
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

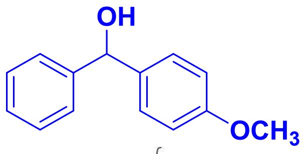
Diphenylmethanol **(3j)**

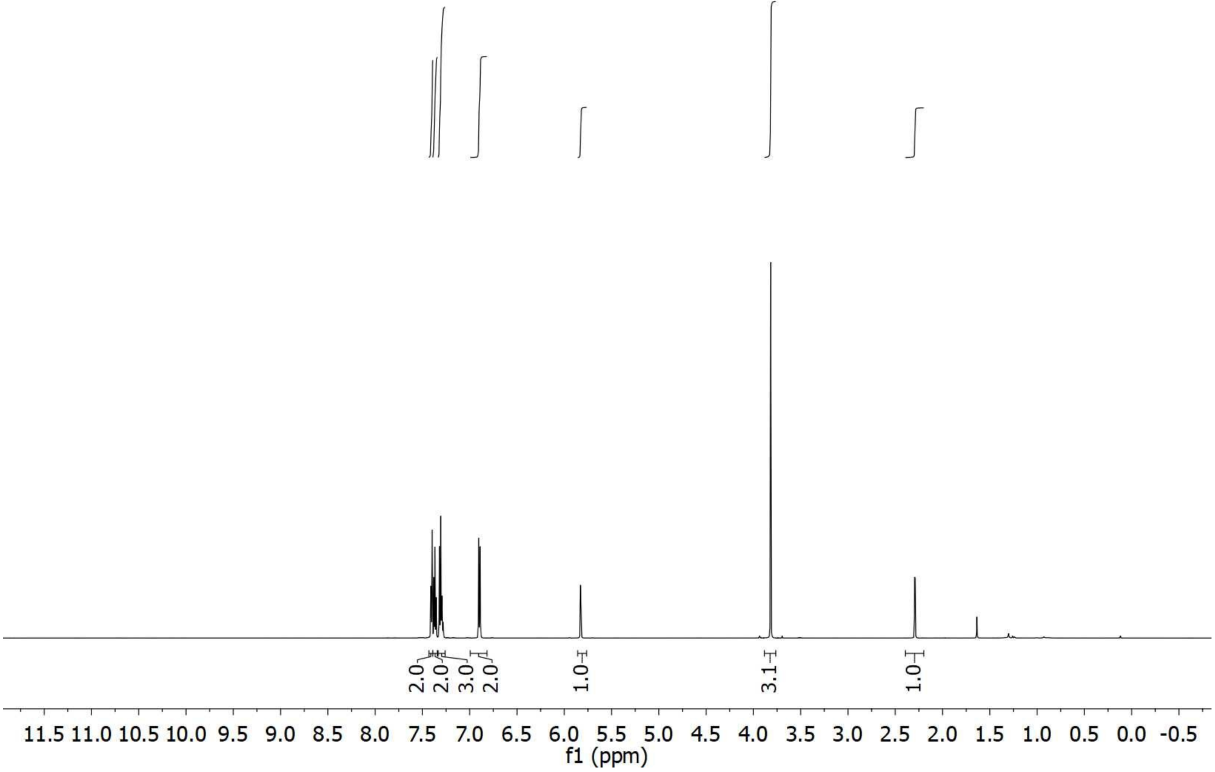


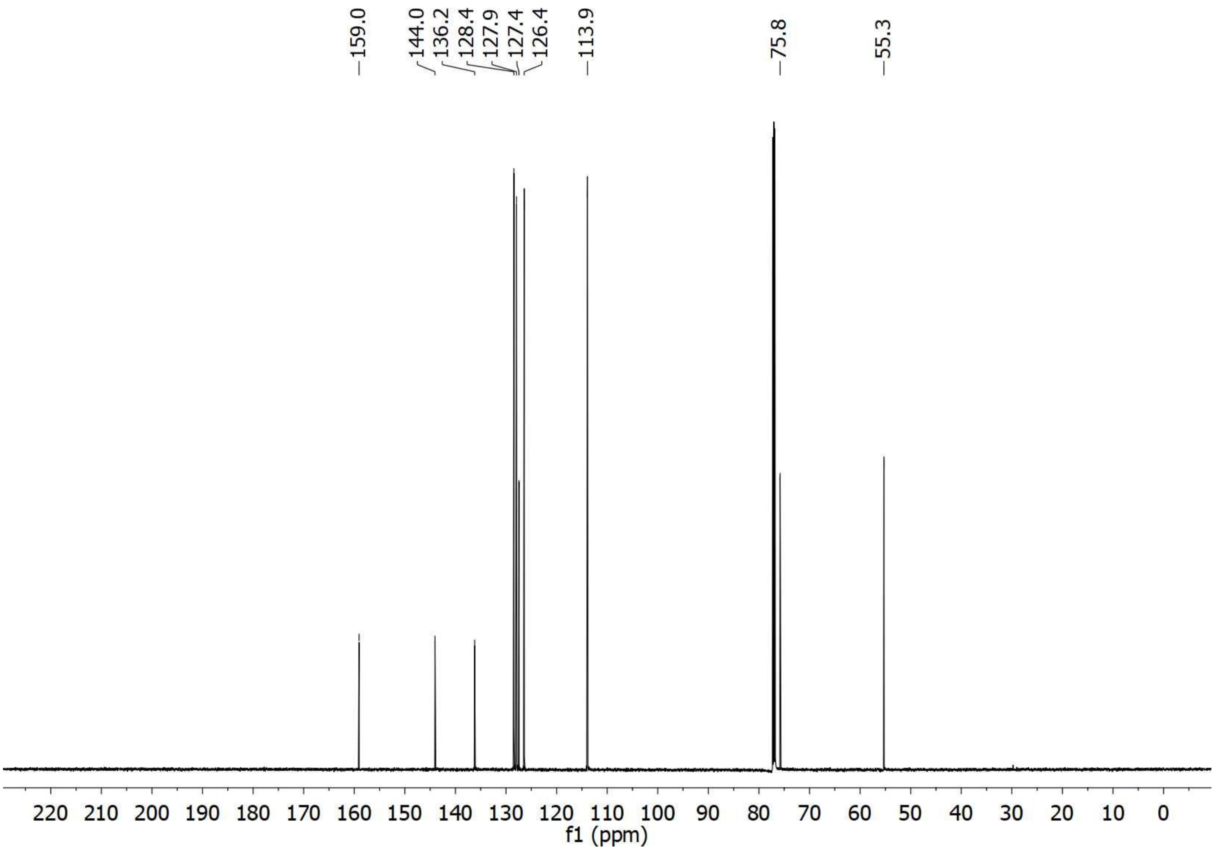




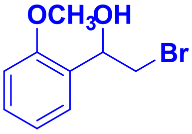
(4-Methoxyphenyl)(phenyl)methanol **(3k)**

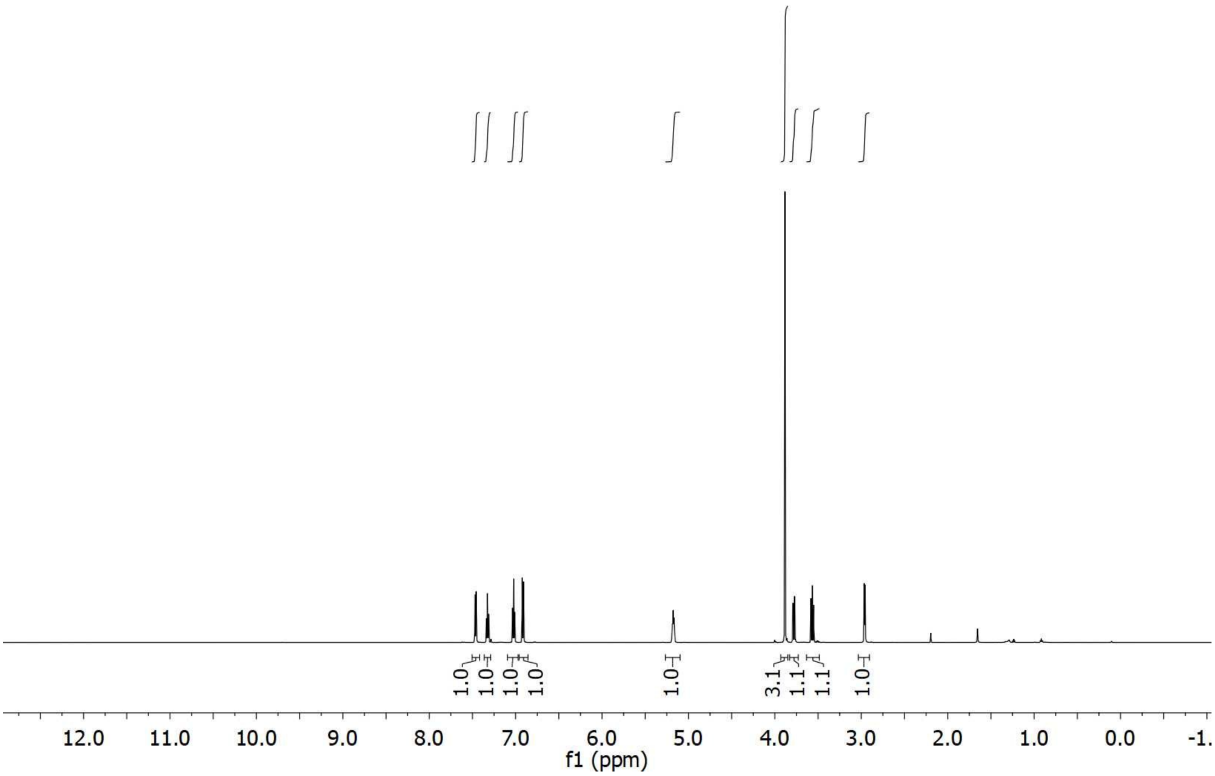


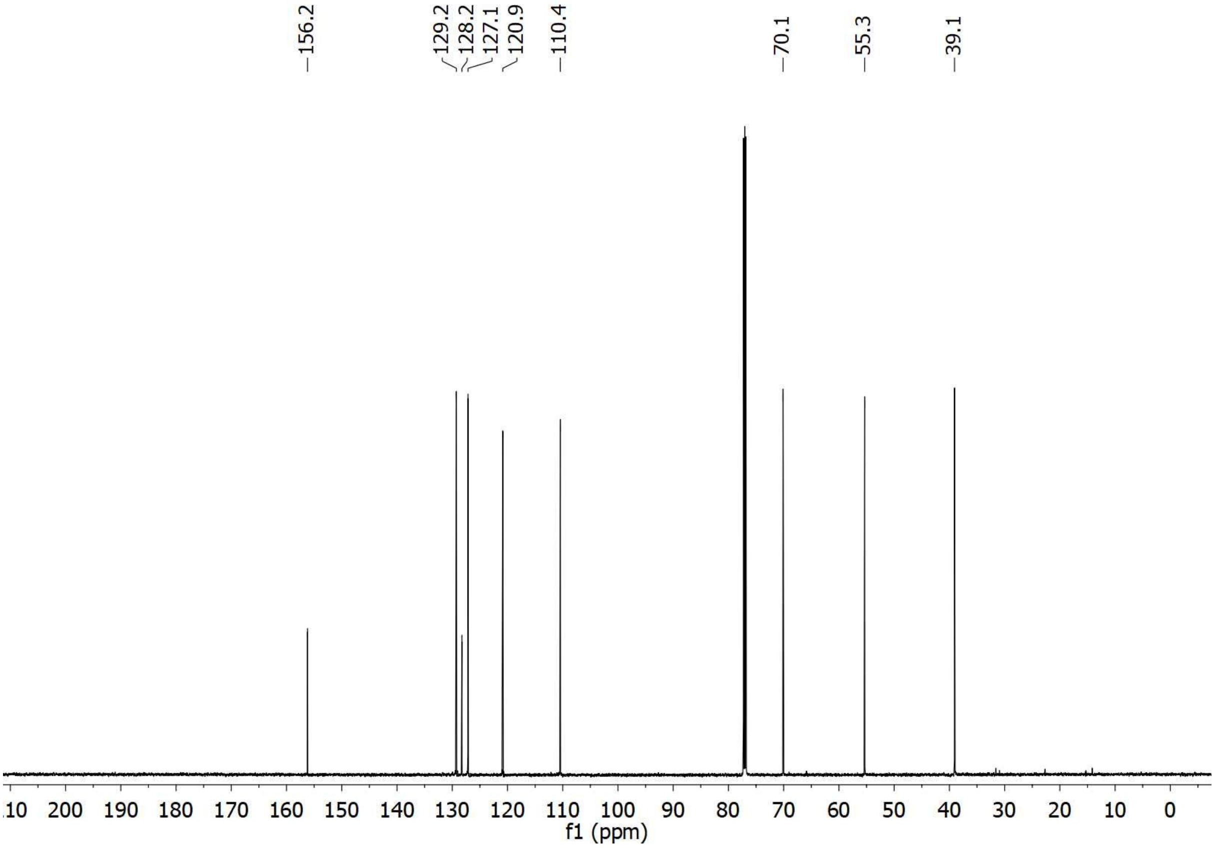




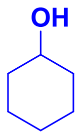
2-Bromo-1-(2-methoxyphenyl)ethan-1-ol **(3l)**

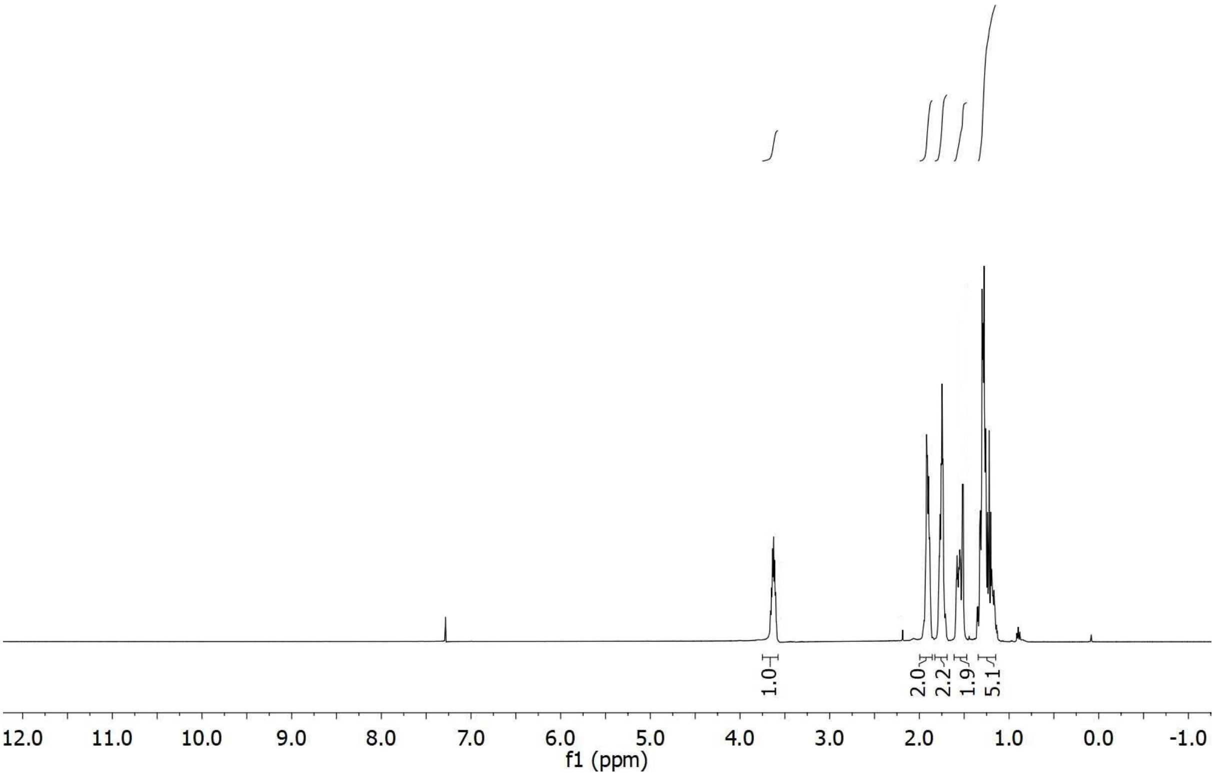


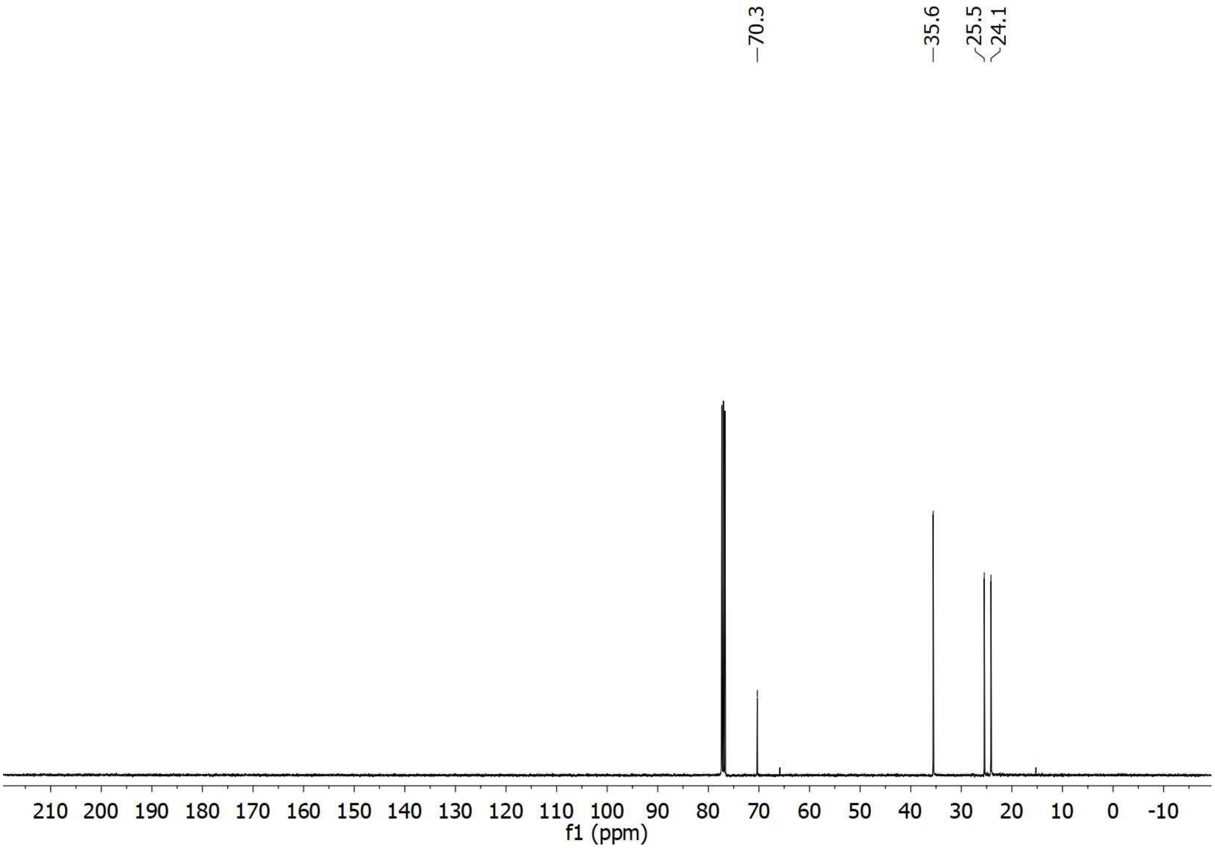




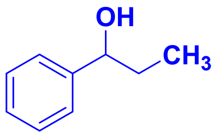
Cyclohexanol **(3m)**

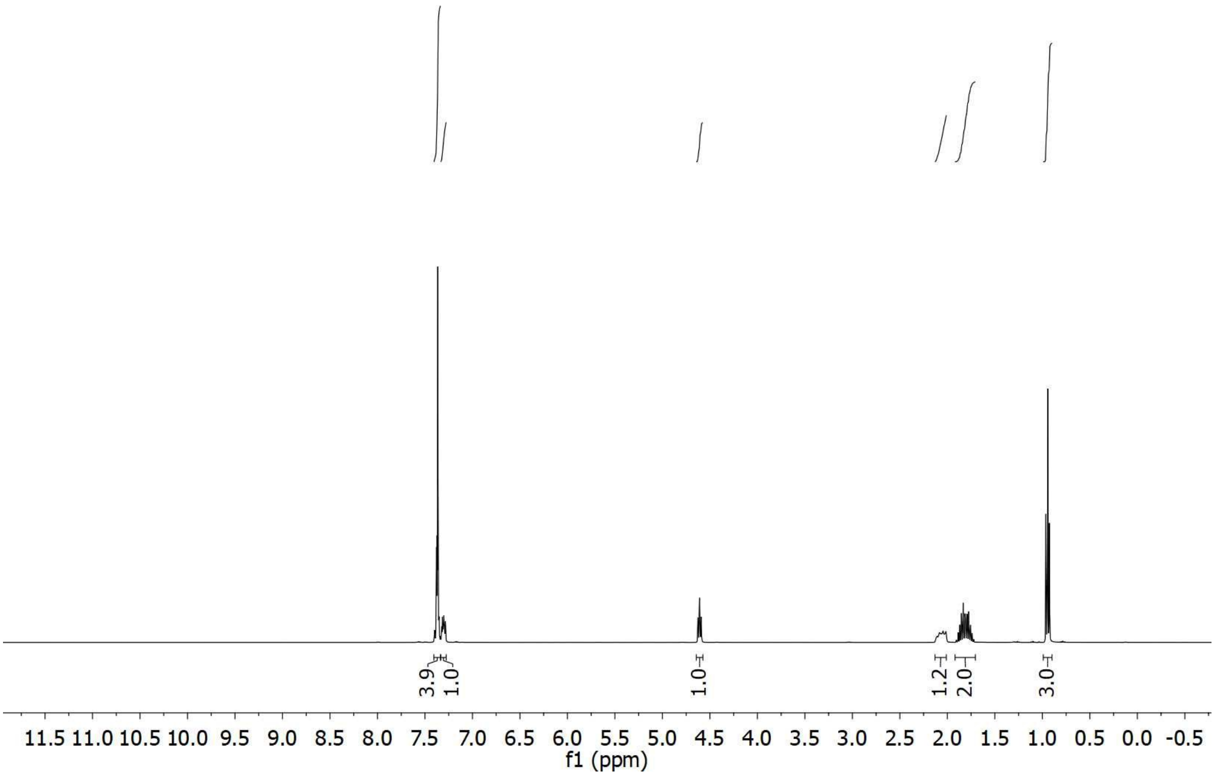


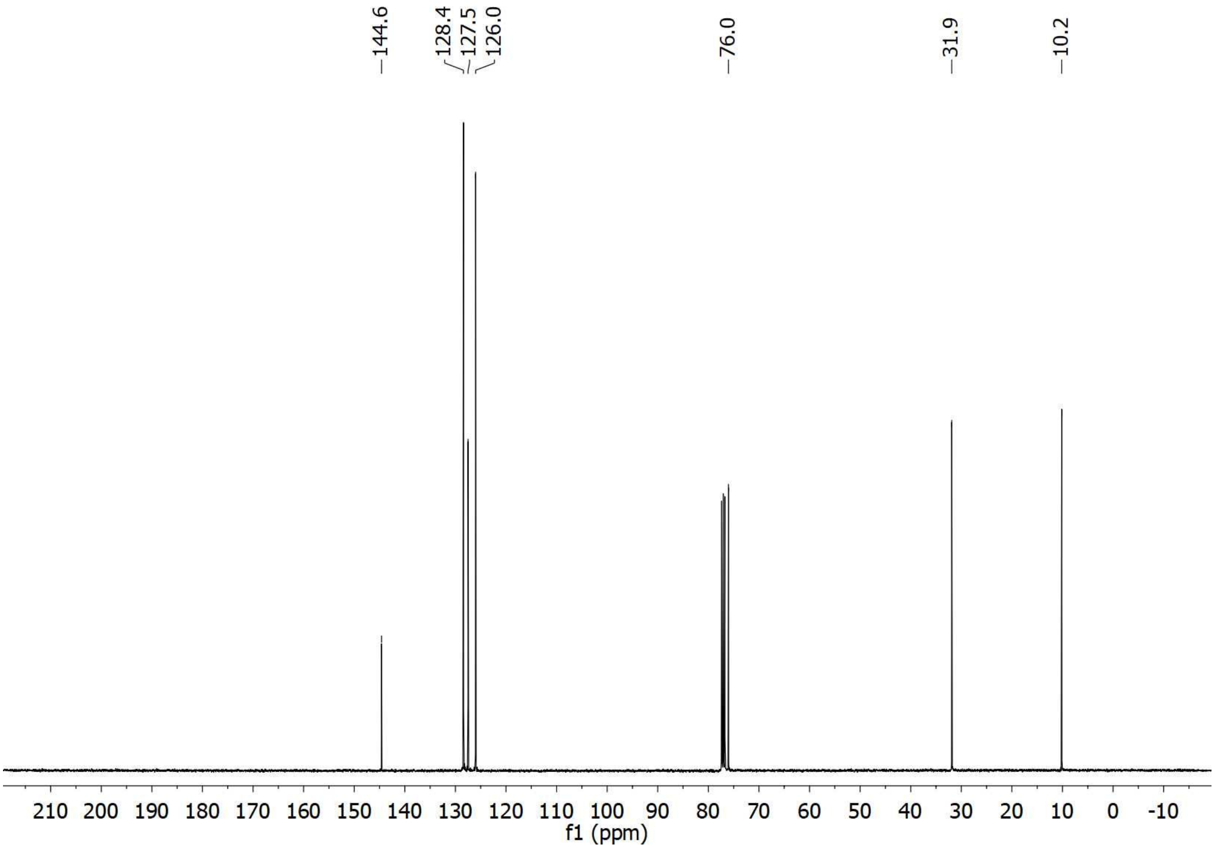




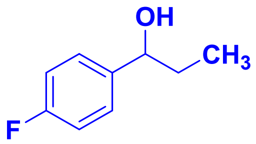
1-Phenylpropan-1-ol **(3n)**

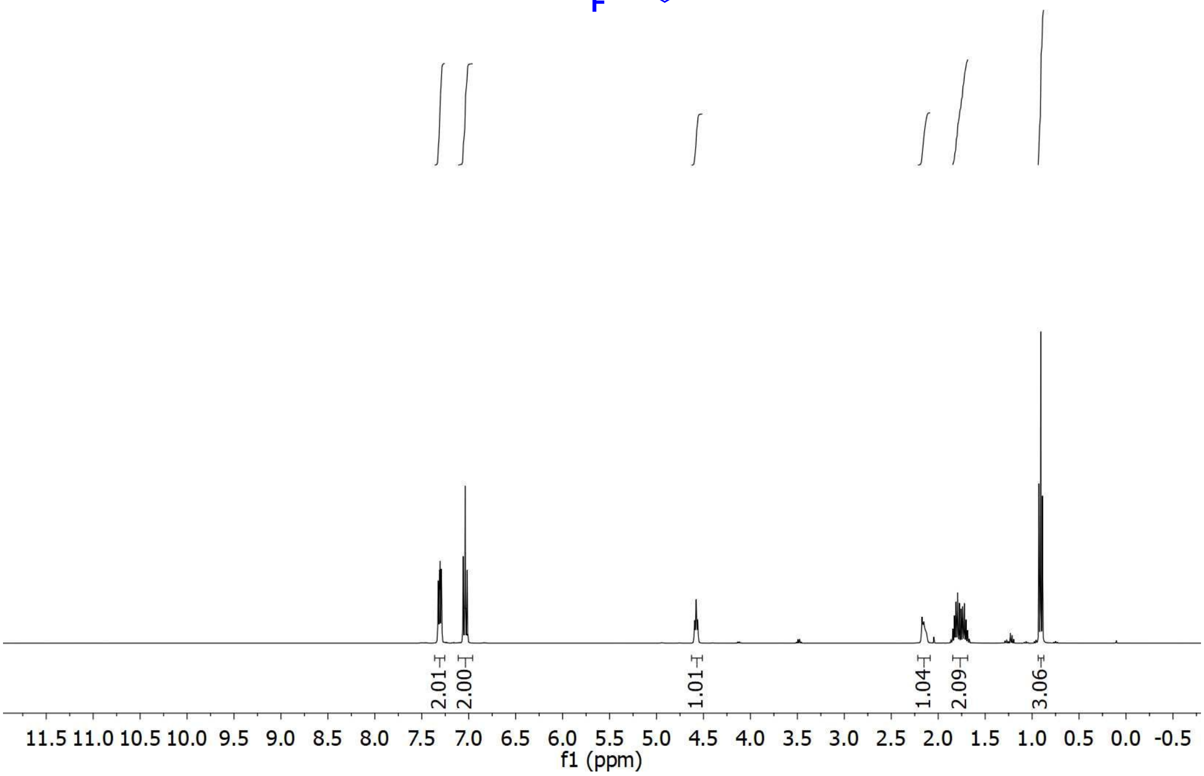


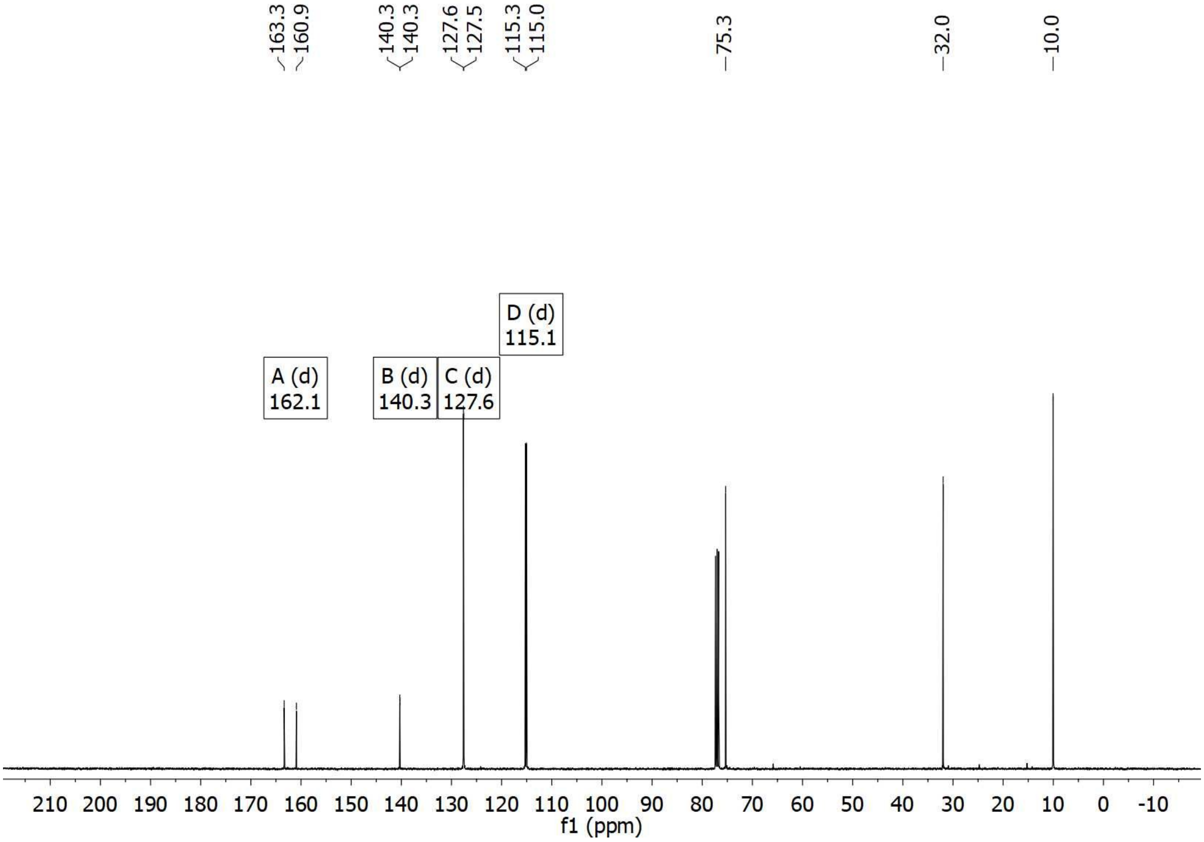




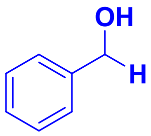
1-(4-Fluorophenyl)propan-1-ol **(3n)**

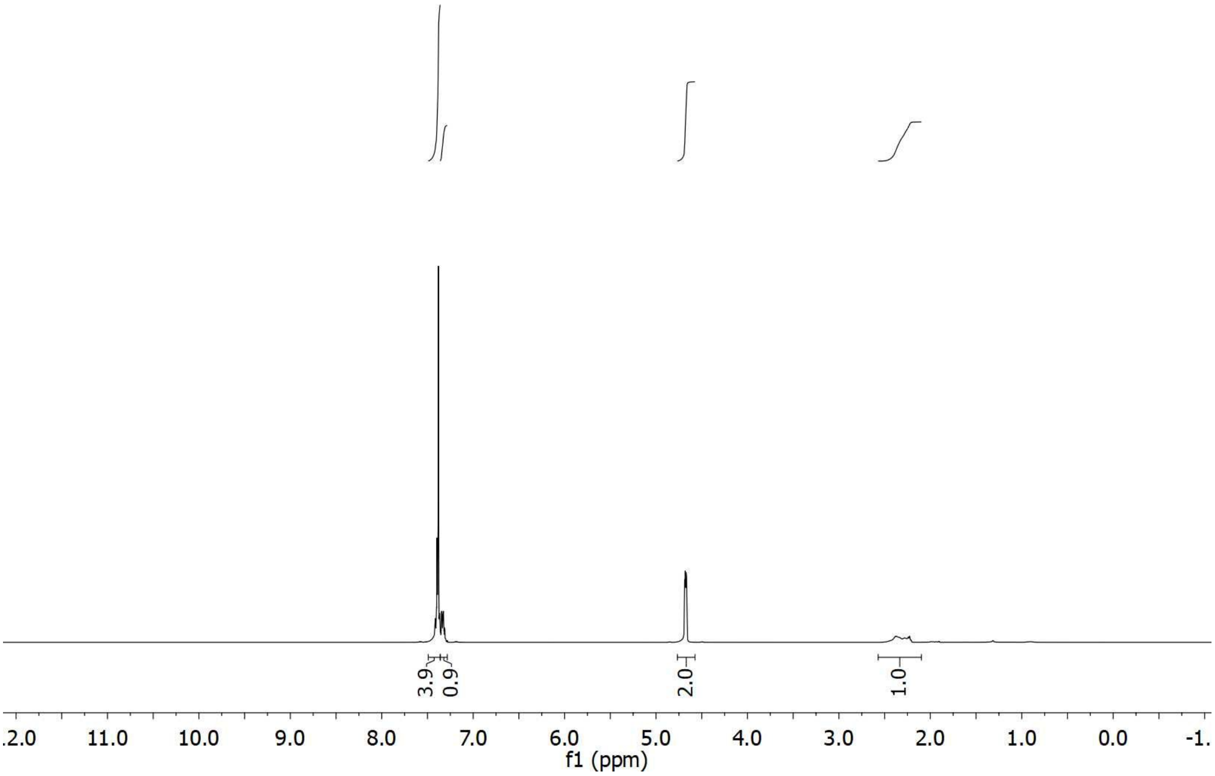


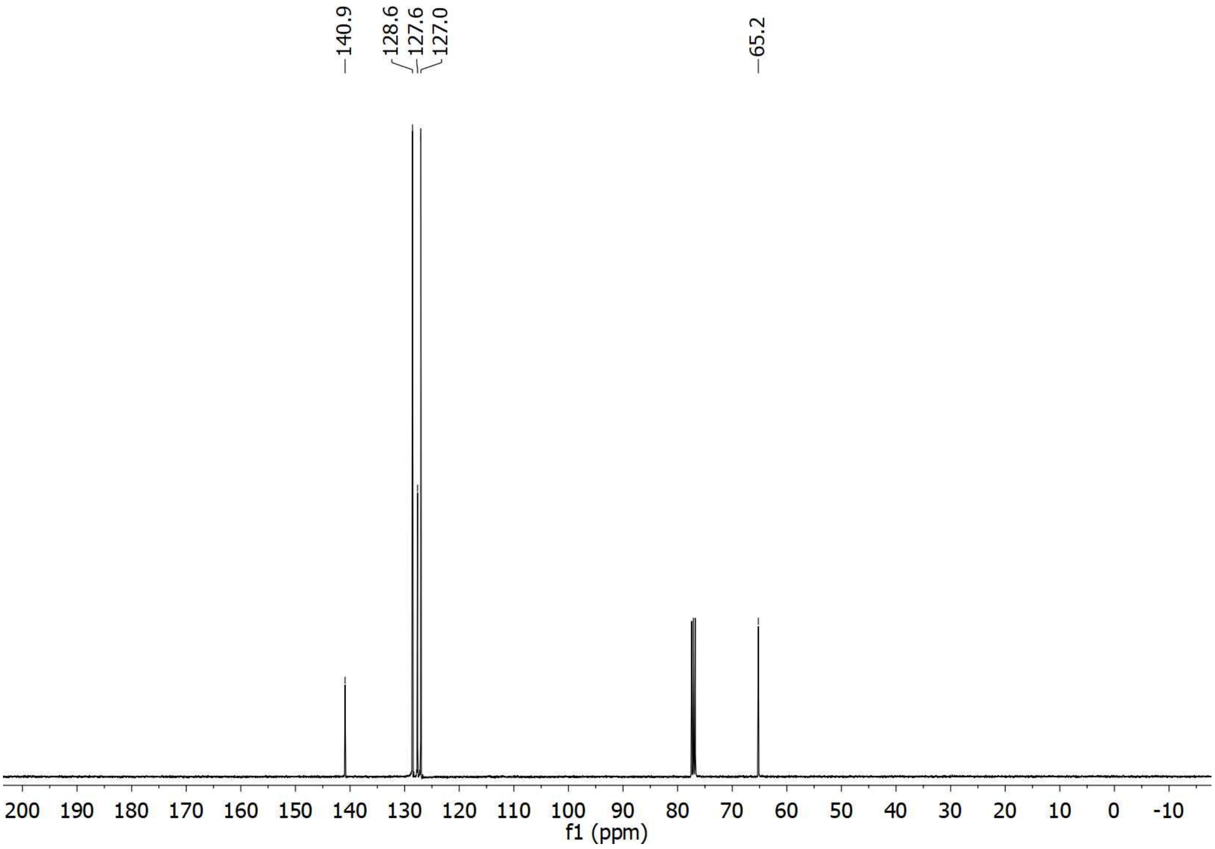




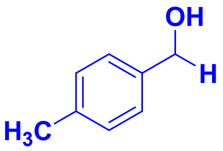
Benzyl Alcohol **(3p)**

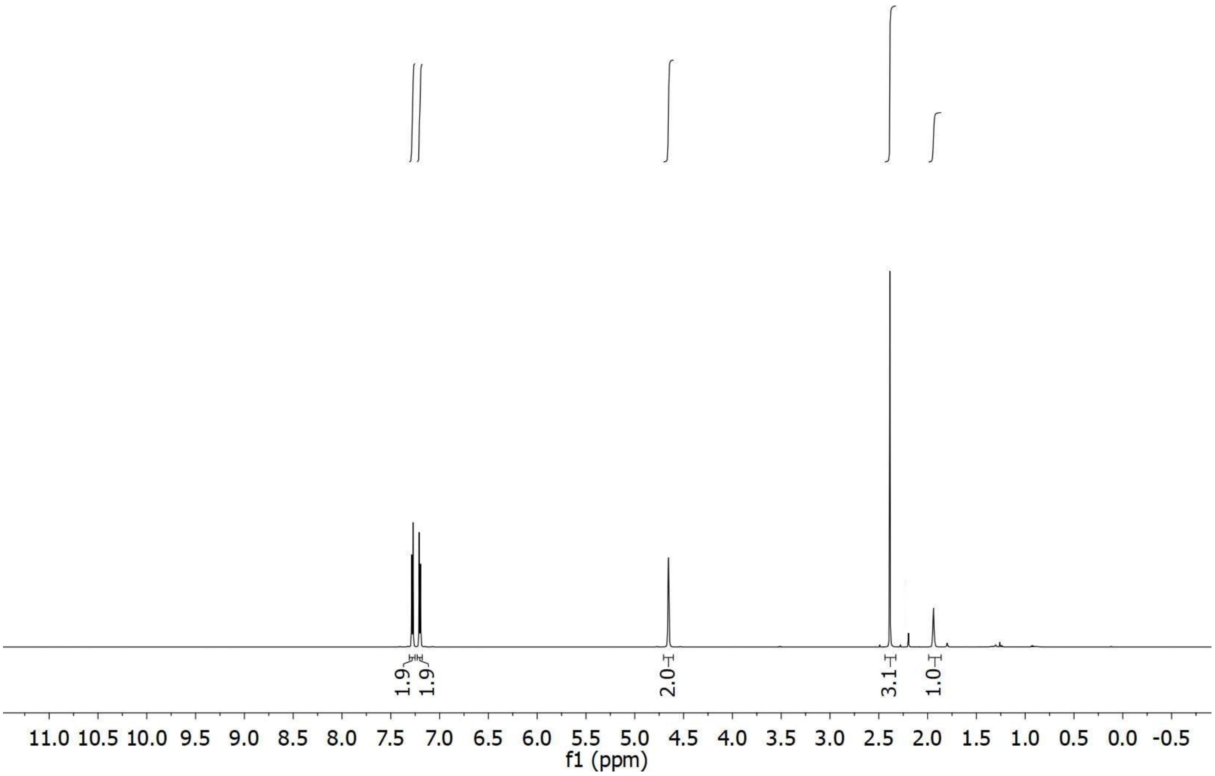


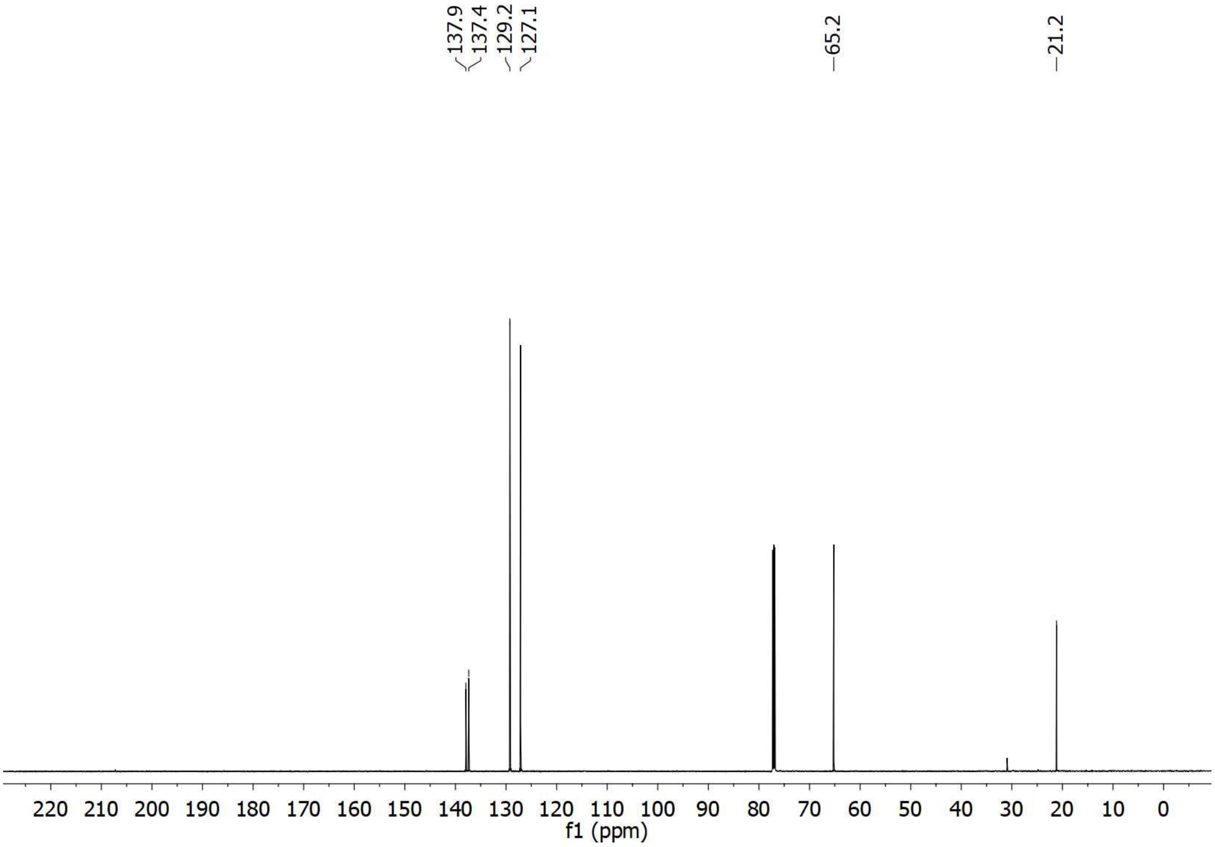




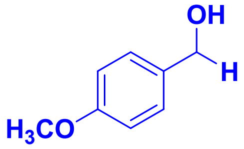
4-Methylbenzyl Alcohol (**3r**)

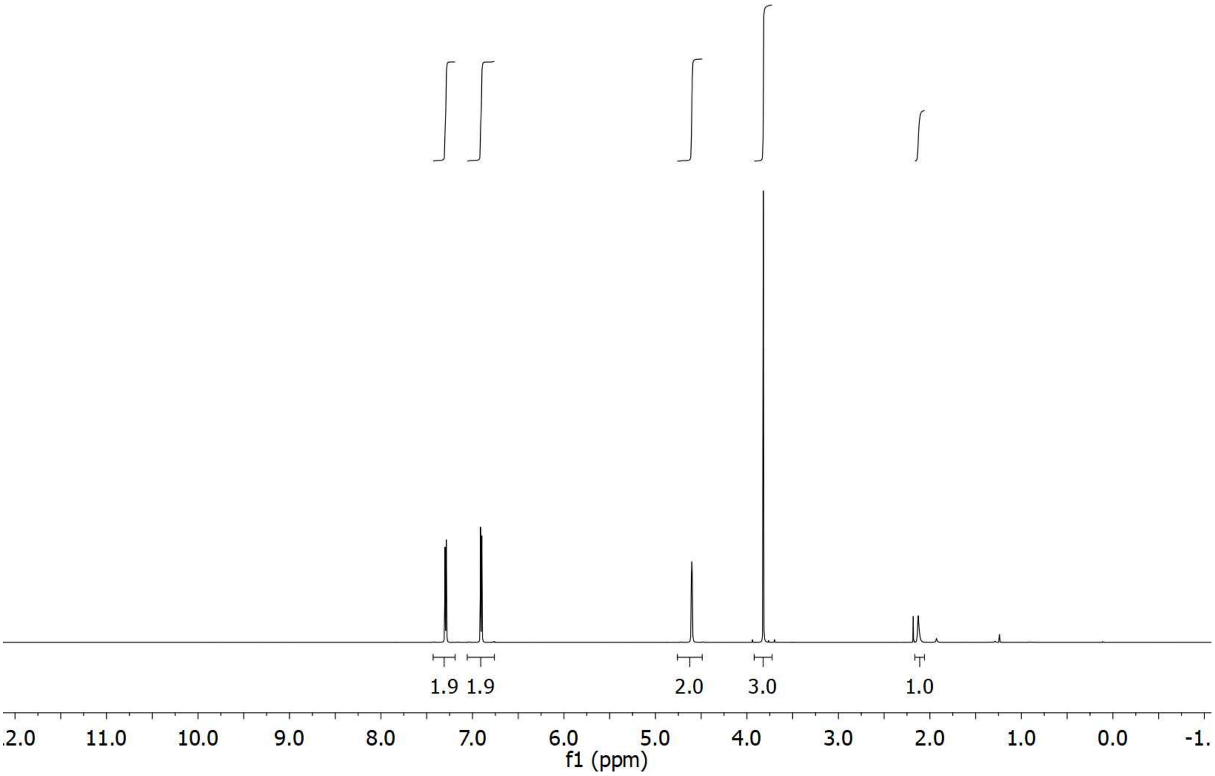


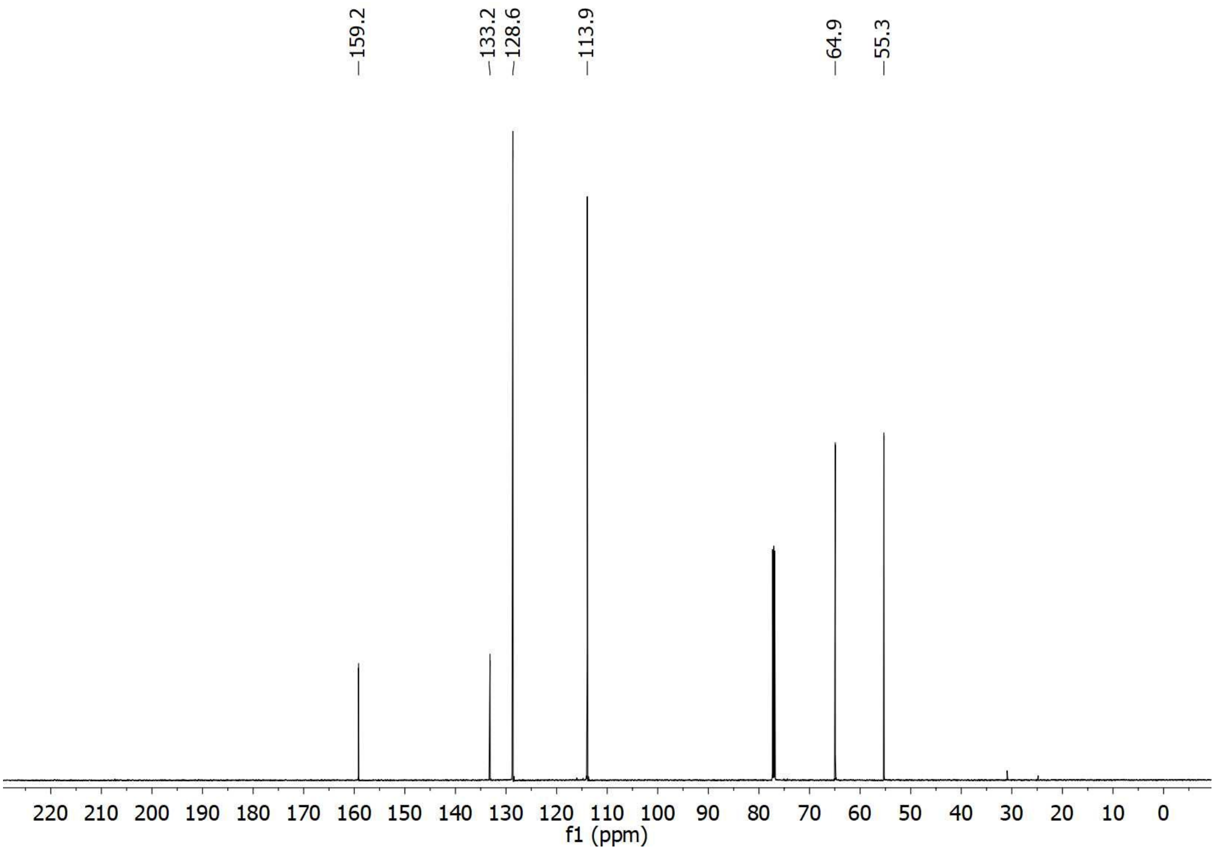




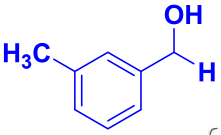
4-Methoxybenzyl Alcohol (**3s**)

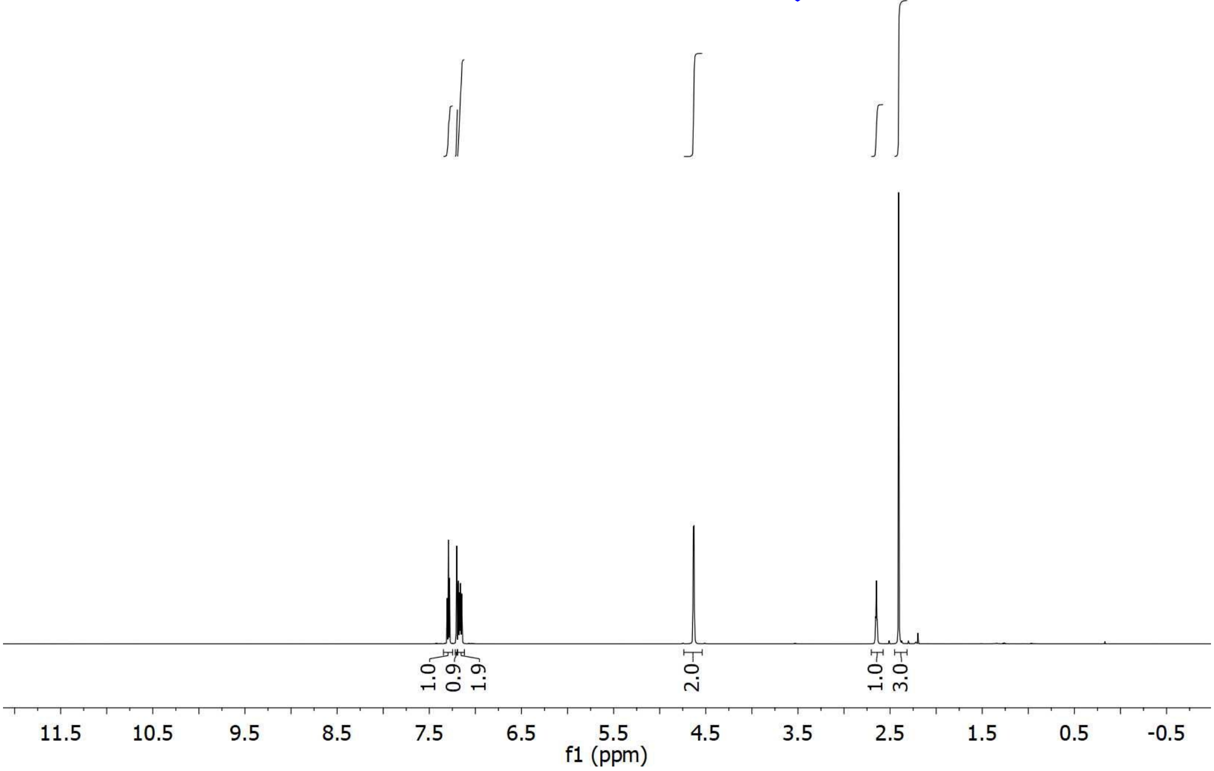


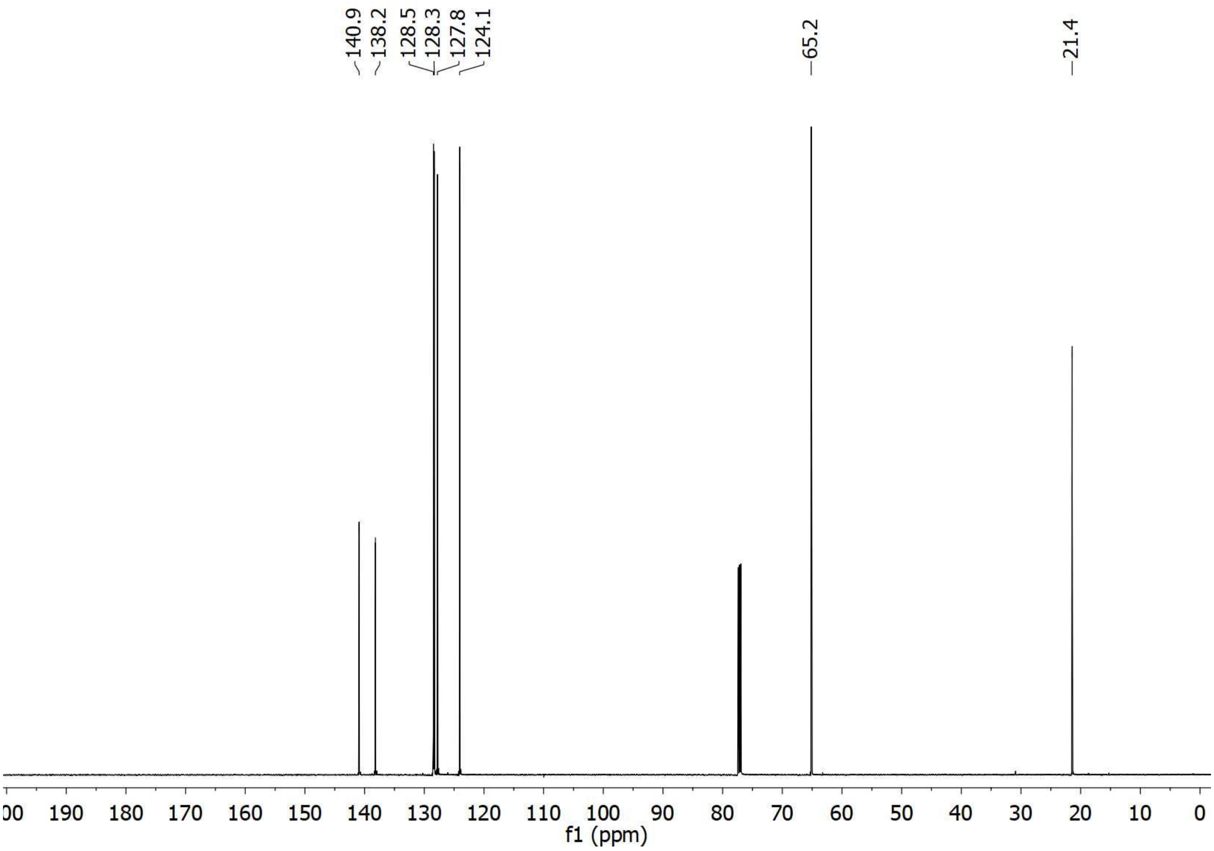




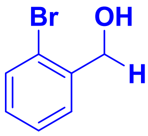
3-Methylbenzyl Alcohol (**3t**)

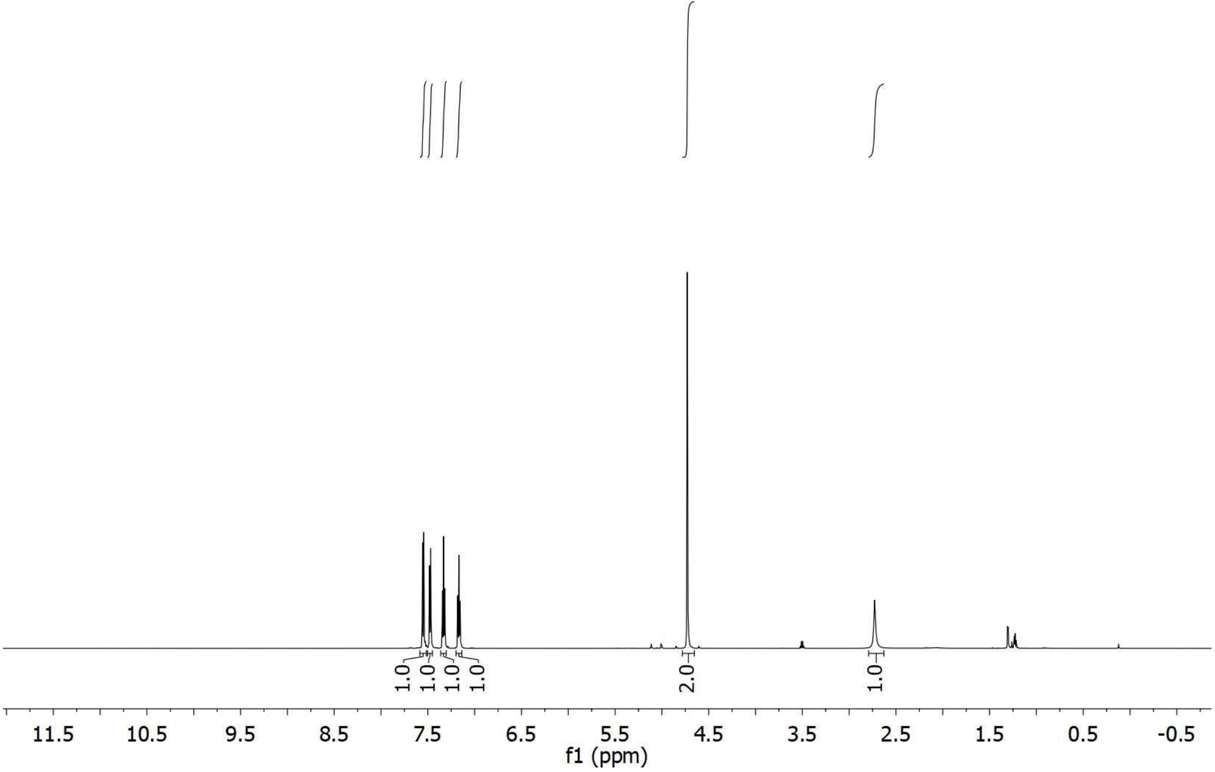


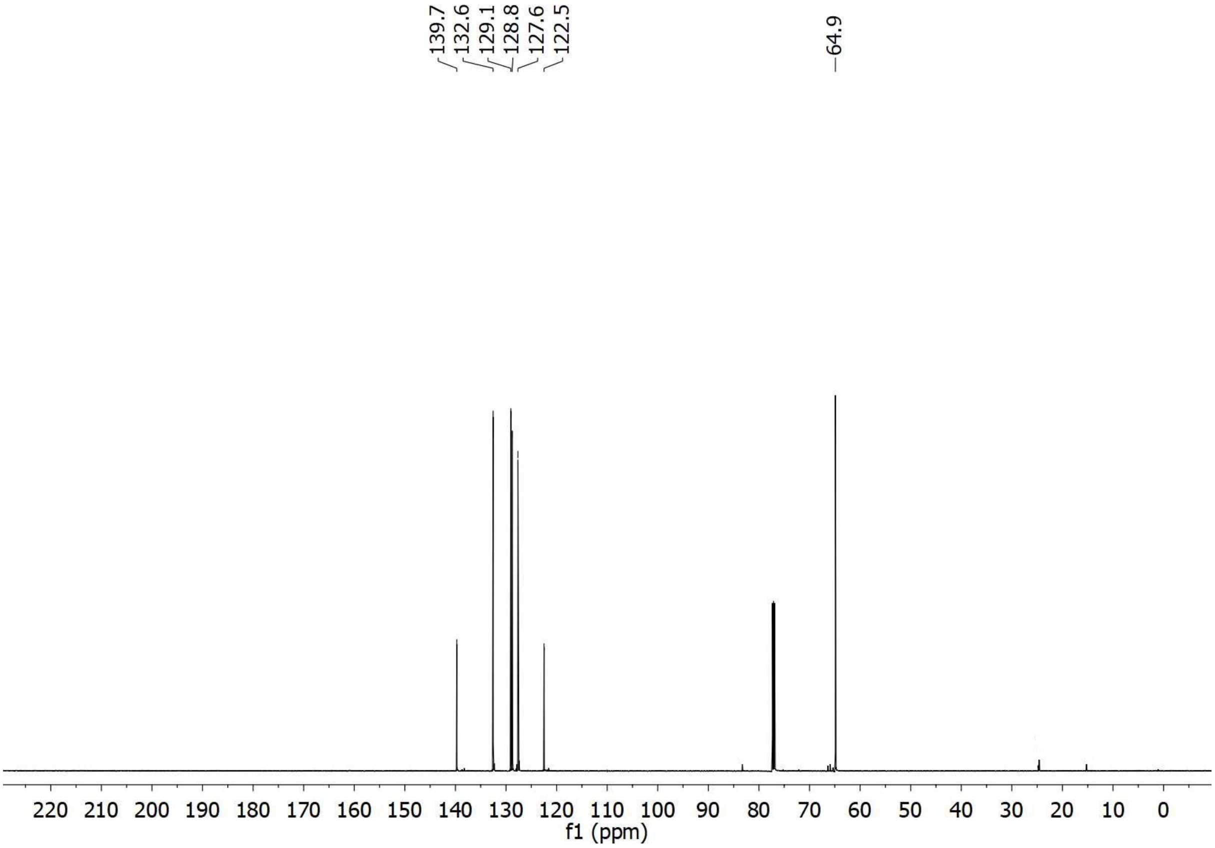




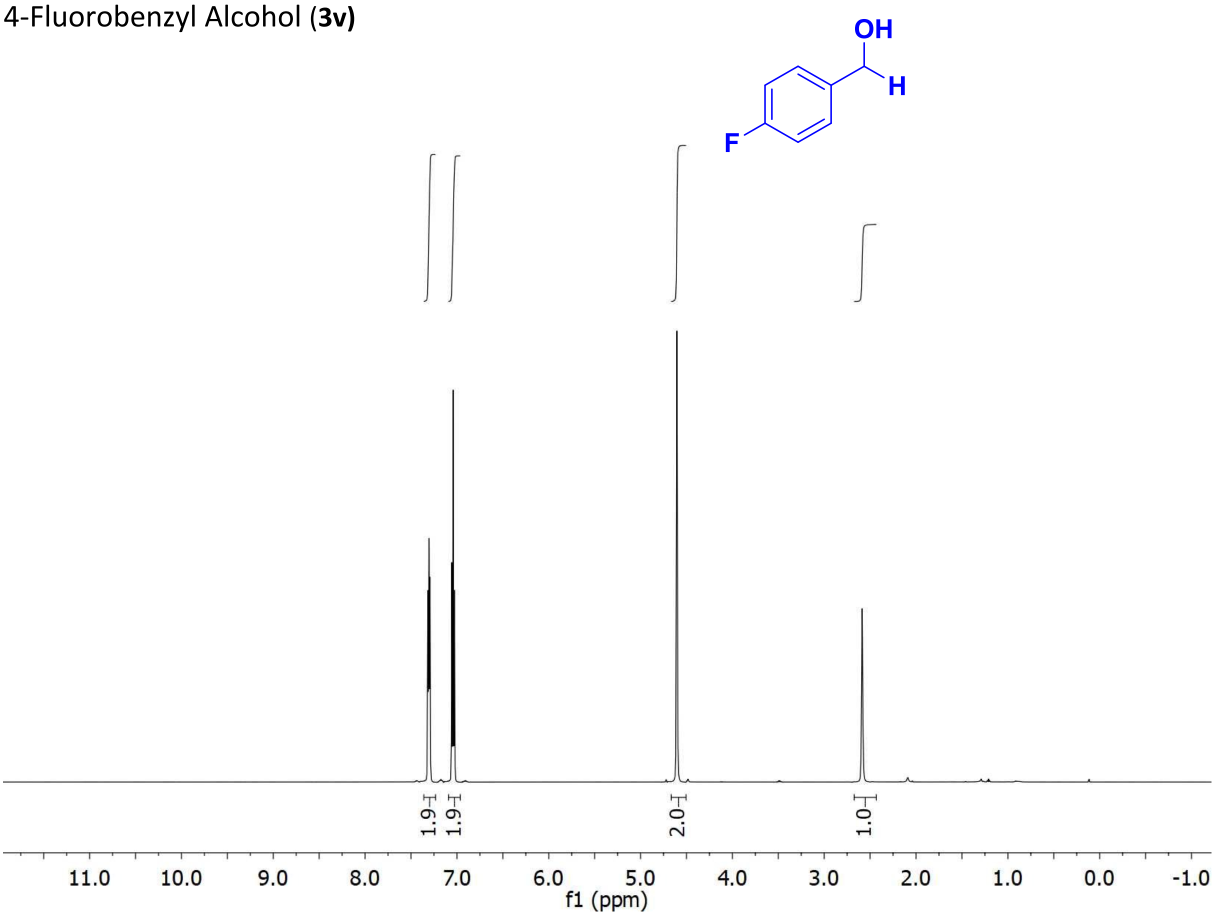
2-Bromobenzyl Alcohol (**3u)**

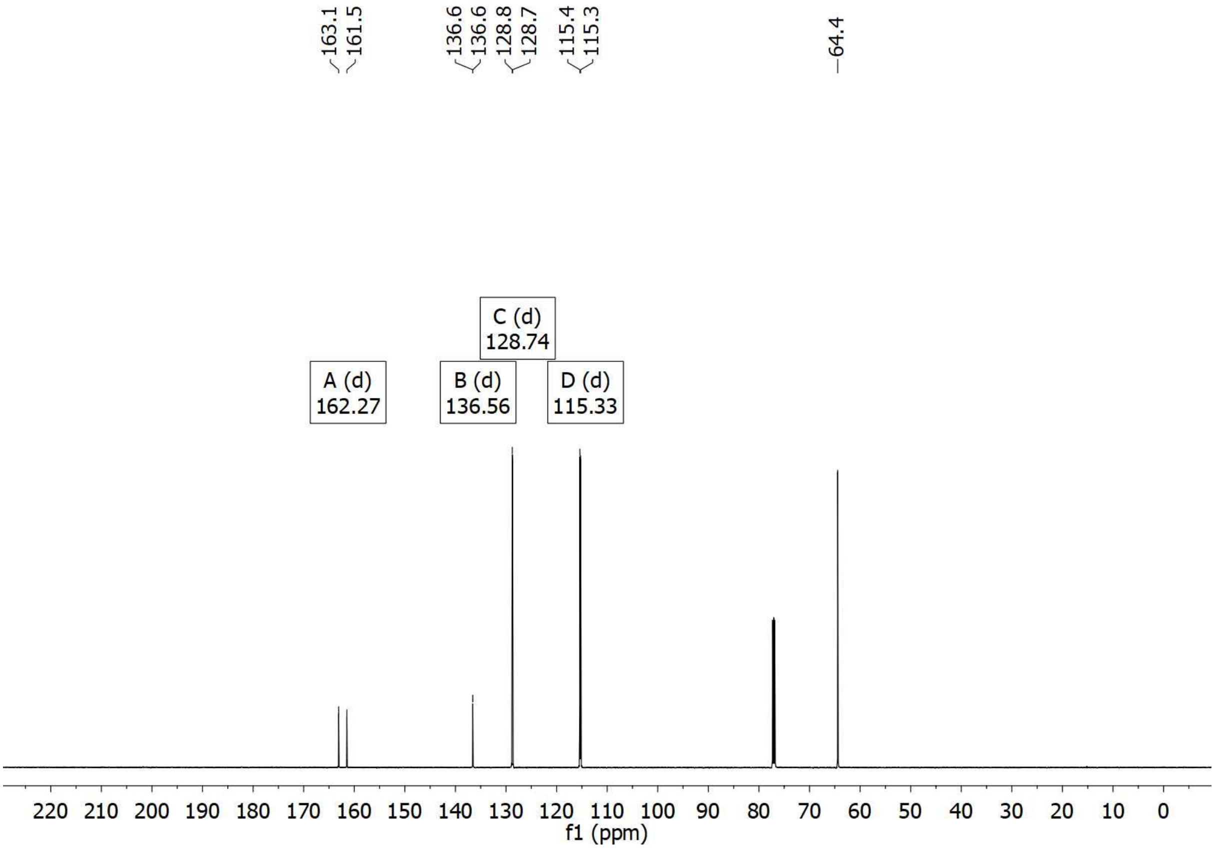




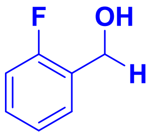


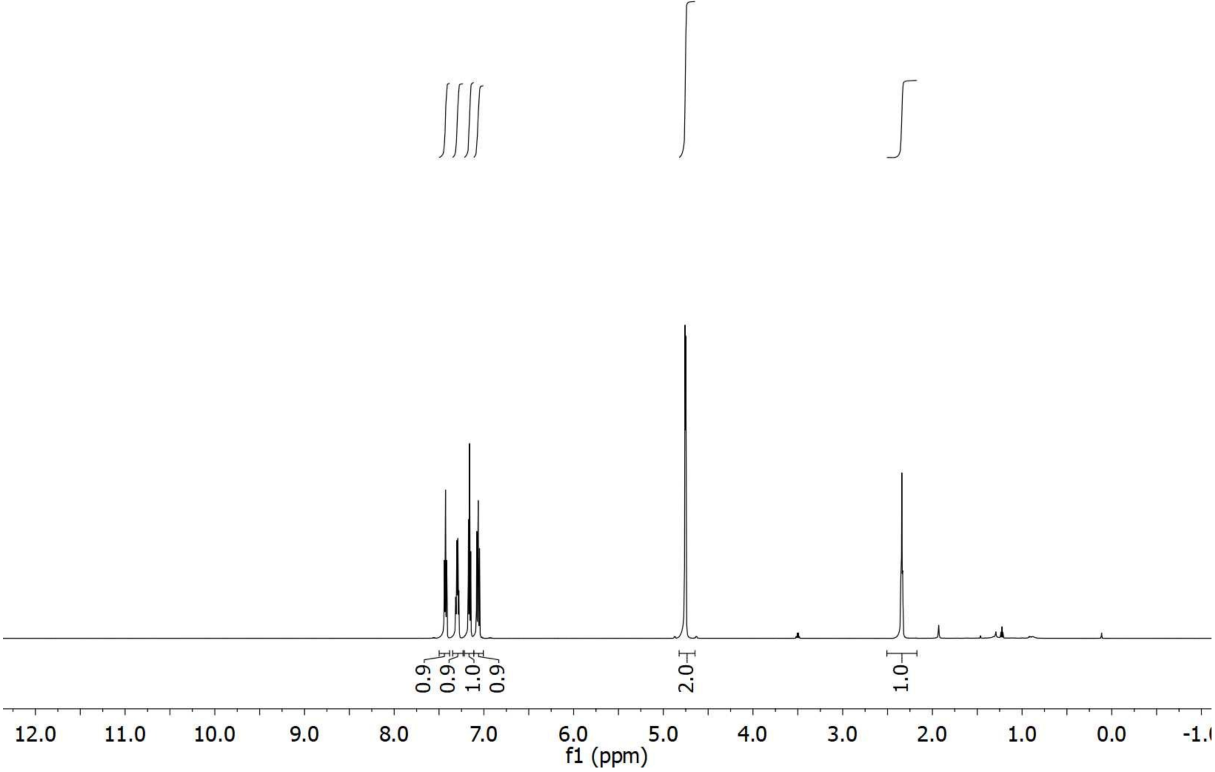
4-Fluorobenzyl Alcohol (**3v**)

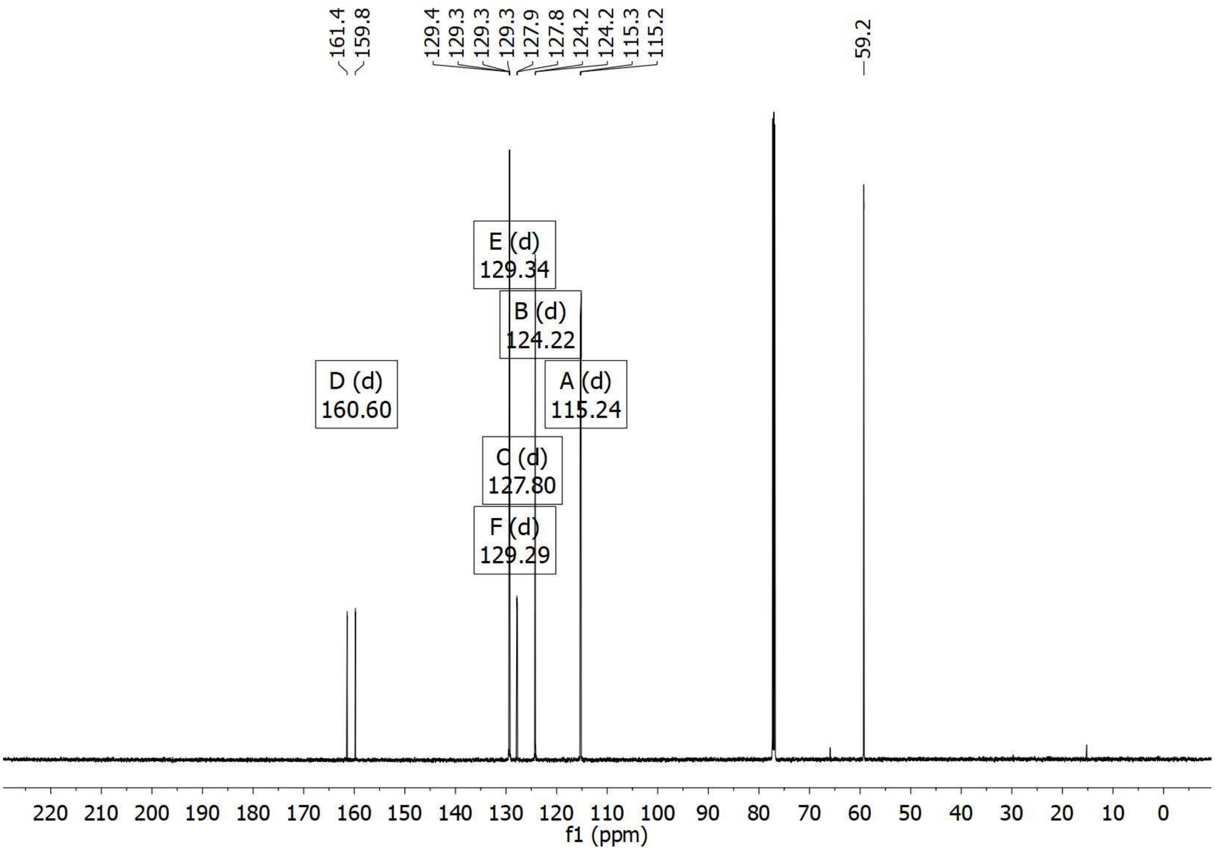




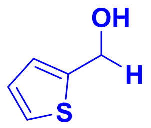
2-Fluorobenzyl Alcohol (**3w)**

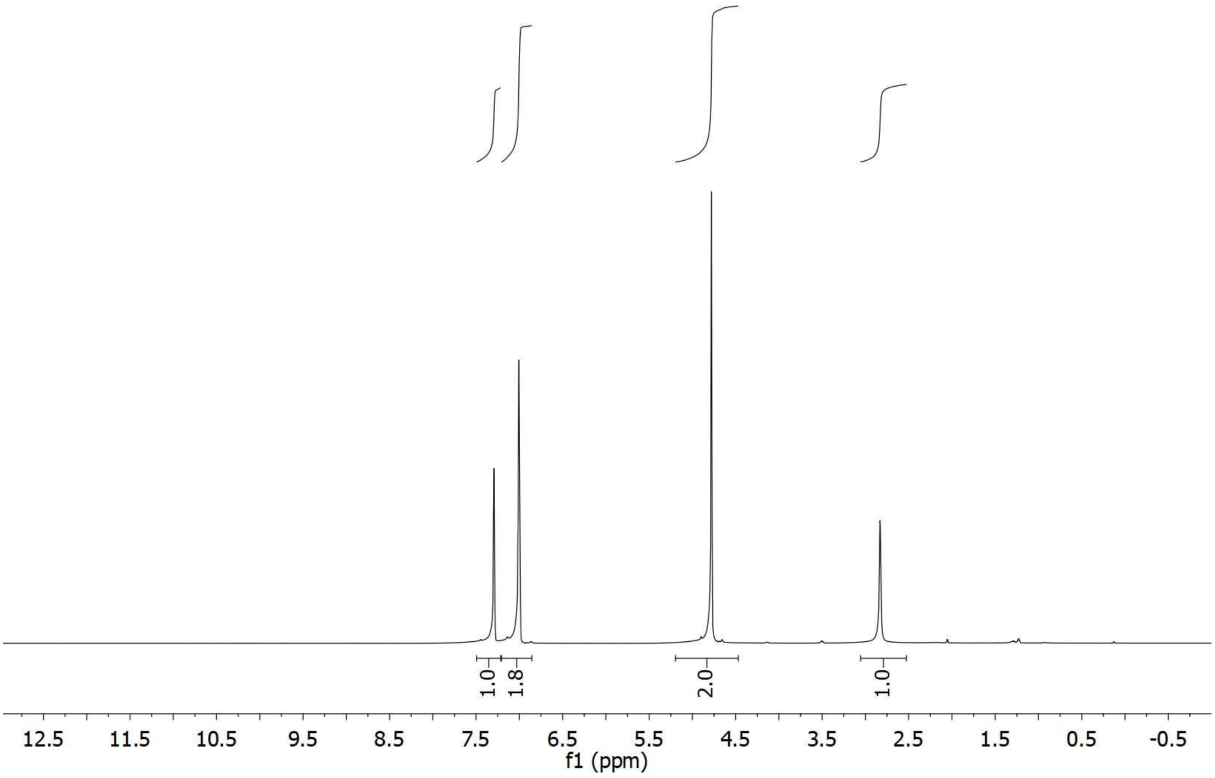


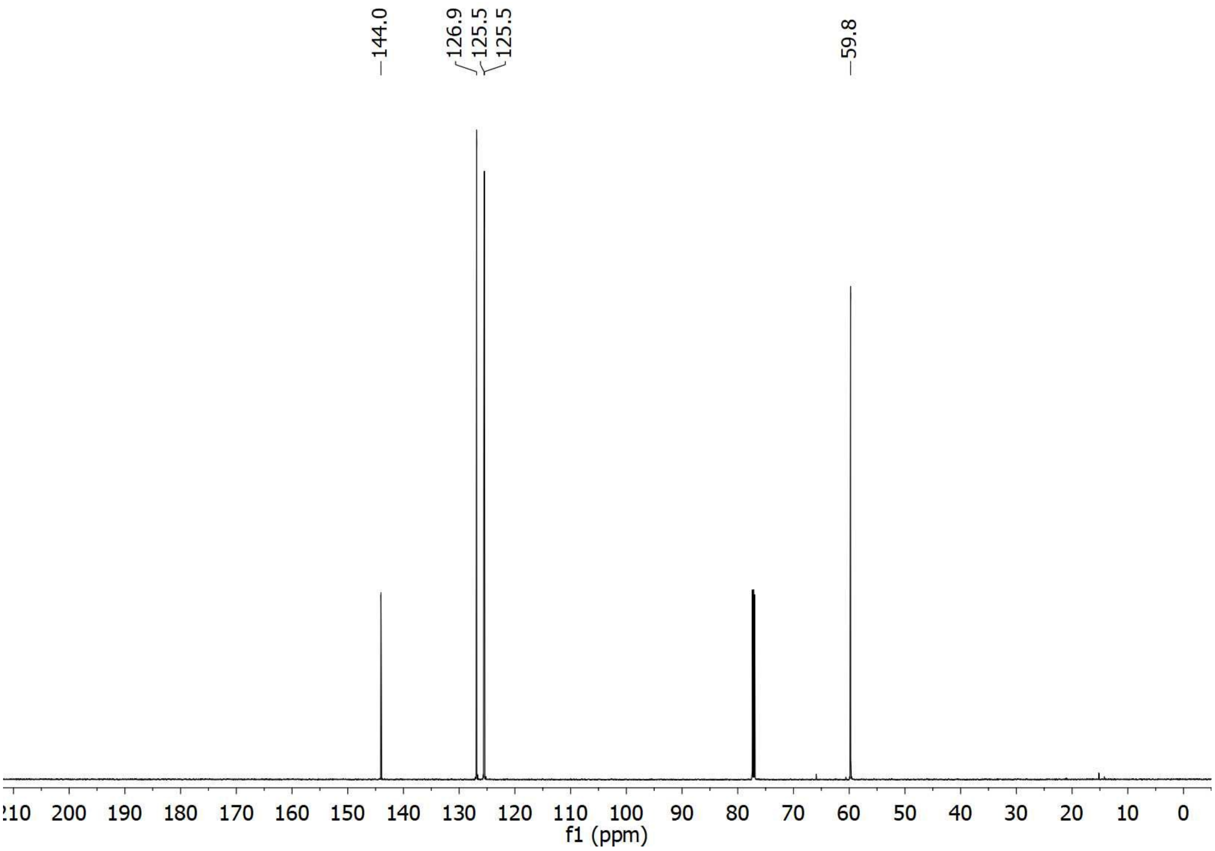




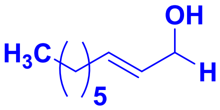
Thiophen-2-ylmethanol (**3x**)

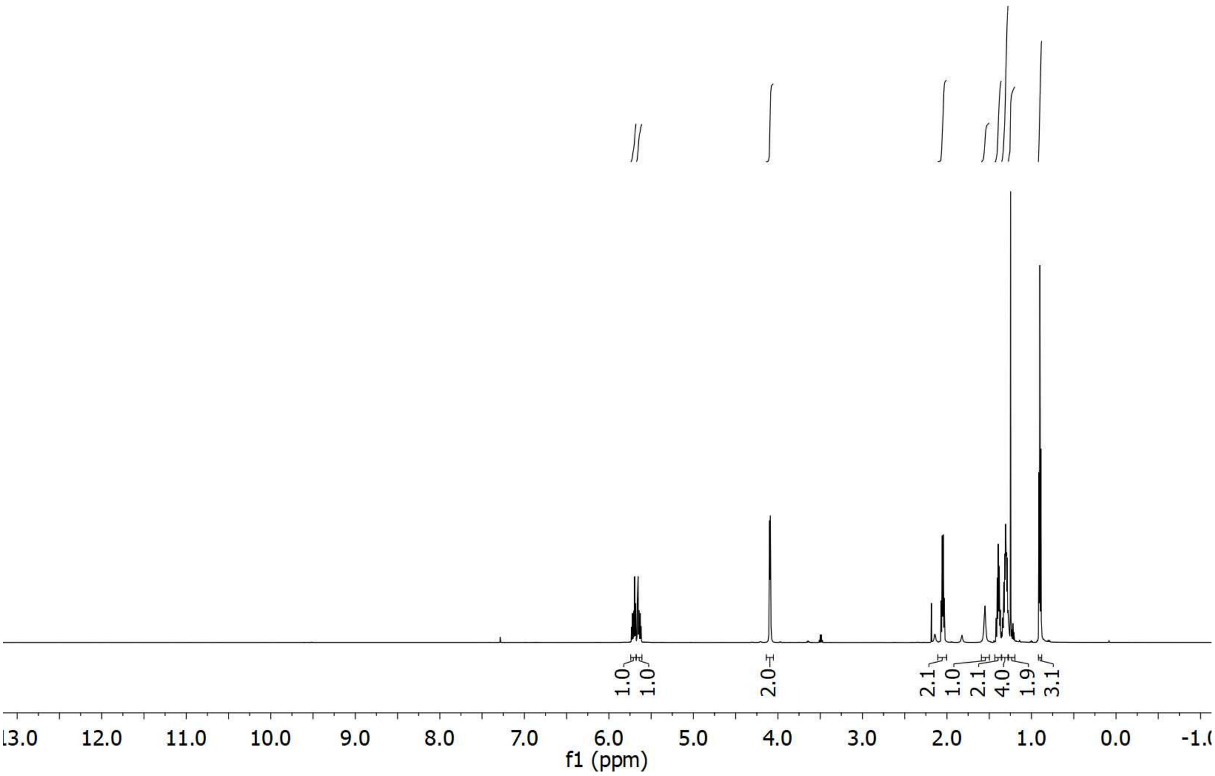


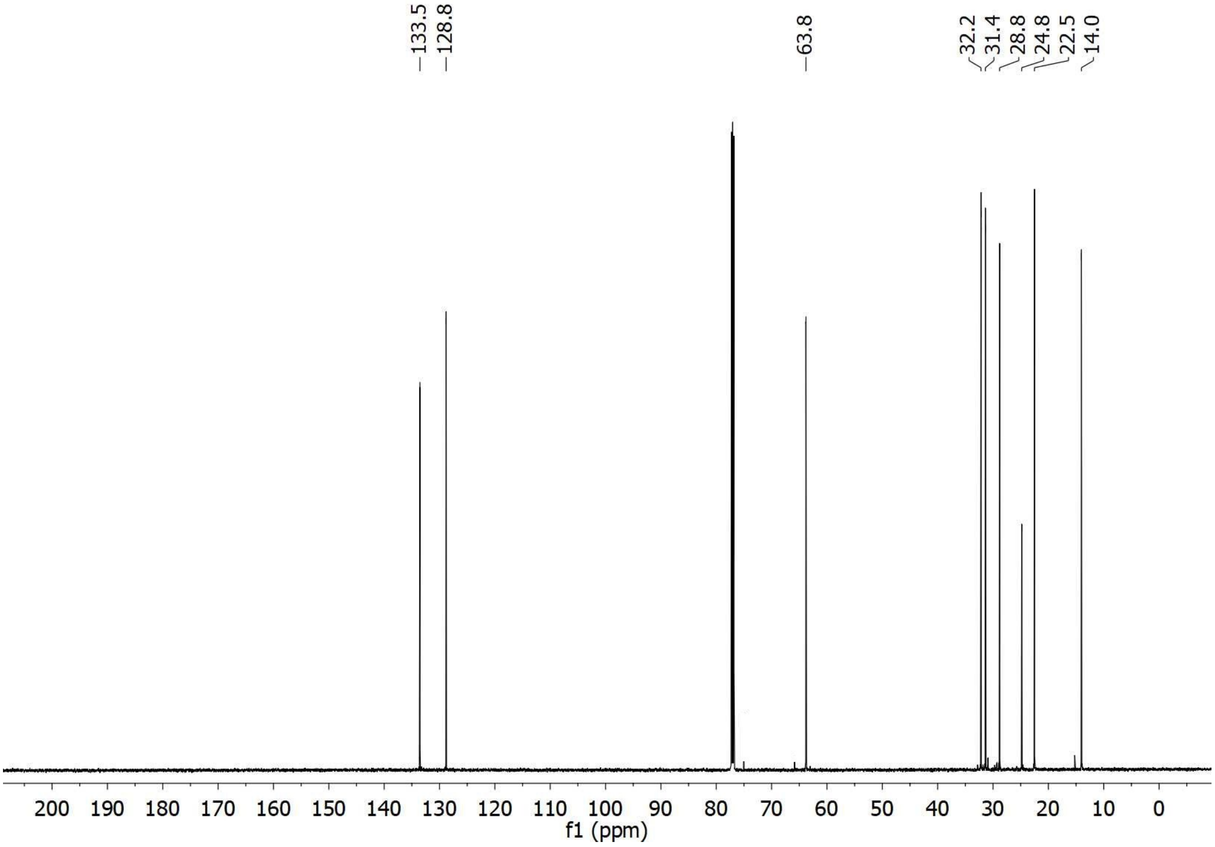




(E)-non-2-en-1-ol (**3y**)







1-(4-(Hydroxymethyl)phenyl)ethan-1-one (**3z**)